Optimization and Basis-Set Dependence of a Restricted Open-Shell Form of B2–PLYP Double-Hybrid Density Functional Theory

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SUPPORTING INFORMATION

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Table S5.1a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 45% and a_C = 15%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05837596	-0.04961776	-8.065819	144.142685	144.1426852	4.8	4.8
2	BERYLLIUM HYDRIDE	-15.2355244	-0.05832729	-15.244273	316.879780	316.8797796	-25.0	-25.0
3	DOUBLET CH	-38.44444815	-0.15337579	-38.467455	597.283680	597.6512503	1.1	1.4
4	CH2 3-B1	-39.10886064	-0.172433	-39.134726	395.518396	395.8859657	3.5	3.8
5	Singlet methylene,	-39.08868708	-0.19545645	-39.118006	437.804810	438.1723803	7.7	8.1
6	Methyl radical,	-39.78668975	-0.21963087	-39.819634	151.367777	151.7353468	4.9	5.3
7	ch4 //b3lyp/6-31G*	-40.45577582	-0.2641577	-40.495399	-63.472558	-63.10498824	11.4	11.8
8	NH,TRIPLET, //b3lyp/6-31G*	-55.18048793	-0.19718801	-55.210066	353.965295	353.9652946	-2.5	-2.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.82805975	-0.25425057	-55.866197	183.550758	183.5507576	-5.1	-5.1
10	AMMONIA, //b3lyp/6-31G*	-56.49884042	-0.31171981	-56.545598	-39.281498	-39.28149839	6.7	6.7
11	OH RADICAL	-75.68688155	-0.271411	-75.727593	40.961389	41.9065686	1.6	2.6
12	Water //b3lyp/6-31G*	-76.37037772	-0.34490248	-76.422113	-226.832124	-225.8869443	15.0	15.9
13	HYDROGEN FLUORIDE,	-100.3924619	-0.35437705	-100.445618	-262.664896	-261.063341	9.7	11.3
14	SIH2 singlet	-290.5269867	-0.32066045	-290.575086	271.808975	273.5943151	-1.0	0.8
15	SIH2 3B1	-290.4976428	-0.29629502	-290.542087	359.457996	361.2433363	-1.2	0.6
16	SIH3 c3v	-291.1426267	-0.32565695	-291.191475	199.406241	201.1915808	-1.0	0.8
17	SIH4 //b3lyp/6-31G*	-291.788494	-0.35430593	-291.841640	39.259029	41.04436873	5.0	6.7
18	ph2 doublet	-342.4148266	-0.36102315	-342.468980	133.465100	133.4650996	-5.0	-5.0
19	PH3 c3v	-343.0459658	-0.39479045	-343.105184	11.469690	11.4696896	6.0	6.0
20	SH2 //b3lyp/6-31G*	-399.2965904	-0.41666736	-399.359090	-11.305666	-8.968971494	9.2	11.5
21	HCL //b3lyp/6-31G*	-460.7091645	-0.3532817	-460.762157	-87.725045	-84.20687463	4.7	8.3
22	DILITHIUM //b3lyp/6-31G*	-14.97764894	-0.06248431	-14.987022	229.931465	229.9314646	14.0	14.0
23	Lithium Fluoride,	-107.3631241	-0.38674373	-107.421136	-332.986586	-331.3850313	2.2	3.8
24	ACETYLENE //b3lyp/6-31g*	-77.24226039	-0.44656455	-77.309245	240.849141	241.5842814	14.1	14.8
25	ETHYLENE //b3lyp/6-31g*	-78.48781461	-0.46604186	-78.557721	68.468449	69.20358938	16.2	16.9
26	ETHANE //b3lyp/6-31g*	-79.71461777	-0.49943541	-79.789533	-61.469397	-60.73425688	22.6	23.4
27	CYANO RADICAL,	-92.62205838	-0.49495552	-92.696302	454.156377	454.523947	15.3	15.6
28	HYDROGEN CYANIDE	-93.33467263	-0.49465012	-93.408870	134.242625	134.6101948	2.4	2.8
29	CARBON MONOXIDE	-113.2299162	-0.50470952	-113.305623	-102.162674	-100.8499236	8.3	9.6
30	HCO BENT	-113.7593682	-0.52784758	-113.838545	41.341839	42.65458896	-0.5	0.8
31	H2CO //b3lyp/6-31g*	-114.4039789	-0.54746302	-114.486098	-102.486286	-101.1735364	6.3	7.6

32	METHANOL //b3lyp/6-31g*	-115.6141045	-0.57564792	-115.700452	-183.655844	-182.3430943	17.2	18.5
33	Nitrogen N2,	-109.4378312	-0.5301903	-109.517360	4.047247	4.047247032	4.0	4.0
34	H2NNH2 //b3lyp/6-31g*	-111.7560005	-0.59179986	-111.844770	103.683005	103.683005	8.3	8.3
35	NO radical,	-129.79432	-0.57325781	-129.880309	91.343092	92.28827185	1.0	1.9
36	O2 //b3lyp/6-31g*	-150.2146491	-0.6371394	-150.310220	3.603830	5.494190247	3.6	5.5
37	HYDROGEN PEROXIDE	-151.4360113	-0.67023168	-151.536546	-112.712579	-110.8222194	23.3	25.2
38	F2 //b3lyp/6-31g*	-199.4007415	-0.69956873	-199.505677	20.200584	23.40369378	20.2	23.4
39	CO2 D*H	-188.4493233	-0.84791853	-188.576511	-395.382894	-393.1249639	-2.1	0.2
40	na2 //b3lyp/6-31G*	-324.4265747	-0.38851239	-324.484852	142.318537	142.3185366	0.1	0.1
41	SI2 3-SGG	-578.7021144	-0.58608829	-578.790028	589.427744	592.9984244	4.1	7.7
42	P2 //b3lyp/6-31g*	-682.5227046	-0.74946497	-682.635124	154.615837	154.6158374	11.1	11.1
43	S2 //b3lyp/6-31g*	-796.1912412	-0.79258286	-796.310129	131.816072	136.4894622	3.4	8.0
44	CL2 //b3lyp/6-31g*	-920.1769158	-0.68611852	-920.279834	10.811662	17.848002	10.8	17.8
45	Sodium Chloride	-622.3964206	-0.53297999	-622.476368	-170.384246	-166.866076	12.0	15.6
46	SIO //b3lyp/6-31g*	-364.5985152	-0.65422341	-364.696649	-87.242901	-84.51238063	15.7	18.4
47	Carbon monosulfide,	-436.0857898	-0.61287434	-436.177721	294.793866	297.4981306	14.9	17.6
48	OS //b3lyp/6-31g*	-473.2232516	-0.72391738	-473.331839	10.660718	13.94259272	5.6	8.9
49	CLO 2-PI	-535.1587793	-0.64722722	-535.255863	108.550565	113.0139153	7.3	11.8
50	CLF 1-SG	-559.8136374	-0.68953856	-559.917068	-48.511260	-43.39153548	6.7	11.8
51	si2h6 //b3lyp/6-31g*	-582.399758	-0.68897817	-582.503105	95.650826	99.22150626	15.7	19.3
52	Methyl chloride,	-499.9631078	-0.59010381	-500.051623	-70.302348	-66.41660803	11.7	15.6
53	H3C-SH METHANETHIOL	-438.5534642	-0.65596437	-438.651859	-2.604238	0.100027357	20.4	23.1
54	HOCl //b3lyp/6-31g*	-535.8094925	-0.68170836	-535.911749	-61.995659	-57.53230889	12.5	16.9
55	SO2 //b3lyp/6-31G*	-548.4289925	-1.09864338	-548.593789	-264.242094	-260.015039	32.8	37.0
56	BF3 PLANAR	-324.4002754	-1.12466096	-324.568975	-1129.439683	-1124.503743	6.1	11.0
57	bcl3 B3LYP	-1405.269164	-1.16833544	-1405.444414	-399.722747	-389.0369619	3.2	13.9
58	ALf3 B3LYP	-541.9818453	-1.26901615	-542.172198	-1174.637993	-1168.940658	34.5	40.2
59	alcl3 B3LYP	-1622.906937	-1.27087592	-1623.097568	-570.667025	-559.2198453	13.8	25.3
60	cf4 B3LYP	-437.2634516	-1.53764371	-437.494098	-921.717048	-914.9432578	11.3	18.1
61	ccl4 B3LYP	-1878.461626	-1.62236224	-1878.704981	-64.793137	-50.35288686	31.0	45.5
62	O=C=S. Singlet	-511.362208	-0.9410577	-511.503367	-142.766532	-139.1170869	-4.3	-0.6
63	CS2 B3LYP	-834.2719622	-1.04172876	-834.428222	115.682973	120.723933	-1.1	4.0
64	COF2 B3LYP	-312.834612	-1.19381631	-313.013684	-602.393974	-597.8781145	21.4	26.0
65	sif4 B3LYP	-688.8838616	-1.63935546	-689.129765	-1552.204535	-1544.012975	62.8	71.0
66	sicl4, td	-2130.062267	-1.68075797	-2130.314381	-620.542030	-604.6840102	42.2	58.1
67	nno B3LYP	-184.5113994	-0.91501655	-184.648652	74.533115	75.47829513	-7.5	-6.5
68	clno B3LYP	-589.8888645	-0.98639612	-590.036824	54.982685	59.44603545	3.1	7.6

69	nf3 c3v	-353.8817315	-1.31975604	-354.079695	-127.676961	-122.8722958	4.5	9.3
70	pf3 c3v	-640.765969	-1.3710326	-640.971624	-925.345669	-920.5410043	33.2	38.0
71	ozone 1-a1	-225.2352986	-1.1062888	-225.401242	175.356093	178.1916332	32.7	35.5
72	f2o B3LYP	-274.4971298	-1.03663293	-274.652625	44.297142	48.44543219	19.6	23.8
73	CLF3, C2V	-759.2493876	-1.46653796	-759.469368	-147.690483	-139.3676477	11.3	19.6
74	CF2=CF2 D2H	-475.2465647	-1.75442336	-475.509728	-668.526810	-661.3854499	-10.0	-2.8
75	cl2c=ccl2 B3LYP	-1916.514521	-1.83389257	-1916.789605	9.592590	24.40041049	22.1	37.0
76	cf3cn B3LYP	-430.1884032	-1.69753999	-430.443034	-488.084903	-482.5450983	7.3	12.8
77	PROPYNE C3V	-116.5146683	-0.68293961	-116.617109	205.188160	206.2908697	20.3	21.4
78	ALLENE D2D	-116.5157407	-0.67604696	-116.617148	203.430328	204.5330384	13.1	14.2
79	CYCLOPROPENE C2V	-116.4755618	-0.68484348	-116.578288	306.392966	307.4956756	29.4	30.5
80	PROPENE CS	-117.7539277	-0.70532431	-117.859726	47.551334	48.65404443	27.5	28.6
81	CYCLOPROPANE D3H	-117.7399243	-0.71032174	-117.846473	84.830325	85.93303452	31.7	32.8
82	PROPANE C2V	-118.9755018	-0.73833769	-119.086252	-68.190261	-67.08755136	36.4	37.5
83	TRANS-1,3-BUTADIENE C2H	-155.7987976	-0.91391198	-155.935884	142.019509	143.4897887	32.0	33.5
84	Dimethyl acetylene	-155.7849727	-0.92004545	-155.922980	176.053654	177.5239338	30.5	31.9
85	Methylene cyclopropane.	-155.7660646	-0.91942929	-155.903979	224.534966	226.0052458	24.1	25.6
86	Bicyclo[1.1.0]butane. C2v	-155.7496025	-0.93056286	-155.889187	265.303794	266.7740742	48.2	49.6
87	CYCLOBUTENE b3lyp	-155.7749949	-0.92214164	-155.913316	202.383169	203.8534494	45.9	47.4
88	CYCLOBUTANE b3lyp/6-31G*	-157.0015842	-0.95077921	-157.144201	76.570553	78.04083341	48.1	49.6
89	Isobutene. Single	-157.0197158	-0.94753823	-157.161847	25.453452	26.92373205	42.2	43.7
90	Trans butane	-158.2362514	-0.97780716	-158.382922	-74.789115	-73.31883492	50.7	52.2
91	isobutane B3LYP/6-31G*	-158.2372646	-0.98125841	-158.384453	-80.102910	-78.63263032	54.2	55.7
92	Spiropentane. D2d	-195.0204524	-1.16396775	-195.195048	234.577480	236.4153304	49.2	51.1
93	Benzene B3LYP	-231.9699047	-1.34053429	-232.170985	121.561059	123.7664793	39.1	41.3
94	DIFLUOROMETHANE C2V	-238.8427183	-0.90048467	-238.977791	-443.650651	-440.0799714	7.0	10.5
95	HCF3 TRI-FLUOROMETHANE	-338.0550817	-1.22065467	-338.238180	-687.758592	-682.5863569	9.3	14.5
96	CH2CL2 C2V	-959.4684055	-0.92606539	-959.607315	-78.416350	-71.01243995	17.0	24.4
97	chcl3 B3LYP/6-31G*	-1418.968747	-1.27047565	-1419.159319	-78.966948	-68.04486799	24.4	35.3
98	METHYLAMINE b3lyp	-95.74628953	-0.54529916	-95.828084	-7.440595	-7.073025488	15.6	15.9
99	Acetonitrile. CH3-CN.	-132.6129909	-0.72856073	-132.722275	84.535842	85.27098169	9.2	10.0
100	NITRO METHANE	-244.8006484	-1.20554536	-244.981480	-61.083764	-58.82583426	13.4	15.6
101	Methyl-nitrite. CH3-O-N=O.	-244.7960426	-1.19784602	-244.975719	-49.687306	-47.4293763	16.8	19.1
102	Methylsilane. CH3-SiH3.	-331.0647219	-0.59510509	-331.153988	-5.280488	-3.127578178	24.0	26.2
103	Formic Acid.	-189.6161715	-0.86841676	-189.746434	-366.385473	-364.1275428	12.3	14.5
104	Methyl formate.	-228.8645171	-1.10512532	-229.030286	-339.931627	-337.3061272	15.7	18.3
105	acetamide ch3cohn2	-209.0171292	-1.07190907	-209.177916	-218.216314	-216.5359944	20.3	22.0

106	Aziridine. (cyclic	-133.7667018	-0.75879615	-133.880521	149.249886	149.9850261	22.9	23.6
107	Cyanogen. NCCN.	-185.4797937	-0.98018245	-185.626821	305.401752	306.1368917	-1.3	-0.6
108	DIMETHYLAMINE b3lyp	-134.9984433	-0.78323073	-135.115928	7.842663	8.577802556	26.3	27.0
109	TRANS ETHYLAMINE	-135.0099598	-0.78438475	-135.127618	-21.911165	-21.17602539	25.4	26.1
110	KETENE B3LYP	-152.4623015	-0.7622262	-152.576635	-46.886031	-45.20571128	0.4	2.1
111	OXIRANE B3LYP	-153.6352086	-0.79165453	-153.753957	-30.092919	-28.41259874	22.6	24.3
112	Acetaldehyde B3LYP	-153.6804273	-0.78473642	-153.798138	-149.209316	-147.5289962	16.9	18.6
113	Glyoxal, O=CH-CH=O.	-227.6325454	-1.07256511	-227.793430	-200.259664	-197.6341636	11.9	14.5
114	ETHANOL TRANS	-154.8801818	-0.81388976	-155.002265	-204.053264	-202.3729439	31.1	32.8
115	DIMETHYL ETHER,	-154.8634753	-0.8111809	-154.985152	-159.966343	-158.2860231	24.1	25.8
116	Thiooxirane. (cyclic	-476.5931498	-0.87776052	-476.724814	107.556466	110.6283011	25.6	28.6
117	Dimethylsulfoxide. (CH3)2SO.	-552.9556057	-1.24323587	-553.142091	-103.113292	-99.09627655	48.3	52.4
118	Thioethanol. CH3-CH2-SH.	-477.8149261	-0.89643969	-477.949392	-11.075723	-8.003887513	35.4	38.4
119	ch3sch3 B3LYP	-477.8132156	-0.89874162	-477.948027	-4.965789	-1.893953875	32.3	35.3
120	Vinyl fluoride,	-177.6831367	-0.78863168	-177.801431	-130.495602	-128.1589068	8.4	10.7
121	Ethyl chloride.	-539.2277179	-0.82989465	-539.352202	-86.935299	-82.68198942	25.2	29.4
122	Vinyl chloride,	-538.0011475	-0.80166866	-538.121398	39.300870	43.55418014	16.3	20.5
123	h2c=chcn B3LYP	-170.6490719	-0.93816098	-170.789796	201.554653	202.6573633	20.8	21.9
124	ACETONE B3LYP	-192.9530059	-1.02352292	-193.106534	-187.042784	-184.9948936	30.1	32.2
125	CH3COOH ACETIC	-228.8900405	-1.10357148	-229.055576	-406.785689	-404.1601894	25.8	28.5
126	CH3CFO HCCO	-252.905007	-1.11126621	-253.071697	-424.849954	-421.5680791	17.4	20.7
127	ch3c(o)cl hcco	-613.2104203	-1.12978921	-613.379889	-224.546467	-219.3479765	18.1	23.3
128	ch3ch2ch2cl B3LYP	-578.4885639	-1.06964962	-578.649011	-93.805380	-89.18450025	38.0	42.6
129	Isopropyl alcohol,	-194.1459109	-1.05584321	-194.304287	-226.395159	-224.3472689	46.4	48.4
130	Methyl ethyl	-194.1294518	-1.05007702	-194.286963	-180.362324	-178.3144339	36.0	38.0
131	Trimethyl Amine.	-174.253005	-1.02646348	-174.406975	13.411185	14.51389465	37.3	38.4
132	FURAN B3LYP	-229.7862729	-1.21898148	-229.969120	-3.339695	-0.924235351	31.4	33.8
133	Thiophene b3lyp	-552.7340546	-1.31337	-552.931060	155.374655	159.1816299	40.3	44.1
134	PYROLE PLANAR	-209.9324888	-1.18868093	-210.110791	135.669353	137.1396328	27.3	28.8
135	C2v Pyridine	-248.0040001	-1.38801348	-248.212202	165.429107	167.2669574	24.8	26.7
136	H2 B3LYP/6-31G*	-1.16425189	-0.03682199	-1.169775	4.899968	4.899967743	4.9	4.9
137	SH b3lyp/6-31G*	-398.6545555	-0.37482899	-398.710780	145.457403	147.7940984	2.4	4.7
138	CCH B3LYP	-76.52462933	-0.40786503	-76.585809	587.090221	587.8253609	21.8	22.6
139	C2H3 CS,2-A'	-77.80907455	-0.42818074	-77.873302	306.702340	307.4374799	7.1	7.9
140	ch3co hcco	-153.036412	-0.76260727	-153.150803	-2.276074	-0.595753626	7.8	9.4
141	H2COH C1	-114.9589055	-0.54224133	-115.040242	-7.531516	-6.218765629	9.6	10.9
142	ch3o CS,	-114.9502998	-0.51515725	-115.027573	22.156042	23.46879207	5.0	6.3

143	ch3ch2o 2A"	-154.2162743	-0.75402572	-154.329378	1.198618	2.878937813	16.7	18.4
144	ch3s 2-A'	-437.9173142	-0.61767196	-438.009965	133.467808	136.1720726	8.8	11.5
145	c2h5 staggered	-79.05165236	-0.45843036	-79.120417	135.628001	136.3631408	14.7	15.4
146	(ch3)2ch Cs	-118.3175511	-0.69917644	-118.422428	115.127830	116.2305397	25.2	26.3
147	TERT-BUTYL RADICAL	-157.5834187	-0.94213602	-157.724739	93.575266	95.0455463	42.1	43.6
148	NO2 RADICAL	-204.9163565	-0.96741279	-205.061468	28.229107	30.11946727	-4.8	-2.9

MAD	**17.8**	**20.2**
LD	**62.8**	**71.0**

Table S5.1b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 45% and a_C = 15%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498434	0.000000	-0.498434
2	li	-7.474504	-0.015040	-7.476760
3	be	-14.647886	-0.058119	-14.656604
4	b	-24.631473	-0.082598	-24.643863
5	c	-37.819101	-0.109763	-37.835565
6	n	-54.556197	-0.140825	-54.577321
7	o	-75.029946	-0.200044	-75.059953
8	f	-99.686293	-0.265101	-99.726058
9	na	-162.202142	-0.178365	-162.228897
10	al	-242.293001	-0.229094	-242.327365
11	si	-289.297244	-0.260138	-289.336265
12	p	-341.182710	-0.290262	-341.226249
13	s	-398.024722	-0.333179	-398.074699
14	cl	-460.050094	-0.304776	-460.095810

Table S5.2a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 45% and a_C = 40%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0361869	-0.04966228	-8.056052	144.381570	144.3815703	5.1	5.1
2	BERYLLIUM HYDRIDE	-15.20846995	-0.05811822	-15.231717	325.523537	325.5235373	-16.3	-16.3
3	DOUBLET CH	-38.39500739	-0.15346992	-38.456395	593.620385	593.9879545	-2.6	-2.2
4	CH2 3-B1	-39.05503849	-0.17238761	-39.123994	390.996287	391.363857	-1.0	-0.7
5	Singlet methylene,	-39.03049482	-0.19535995	-39.108639	429.698084	430.0656541	-0.4	0.0
6	Methyl radical,	-39.7220486	-0.21972381	-39.809938	144.126177	144.4937465	-2.3	-1.9
7	ch4 //b3lyp/6-31G*	-40.38212085	-0.2640128	-40.487726	-76.024893	-75.65732258	-1.1	-0.8
8	NH,TRIPLET, //b3lyp/6-31G*	-55.12098223	-0.19744737	-55.199961	346.500923	346.5009233	-10.0	-10.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.75816458	-0.25443587	-55.859939	165.987280	165.9872797	-22.7	-22.7
10	AMMONIA, //b3lyp/6-31G*	-56.4193717	-0.3117694	-56.544079	-69.288470	-69.28847048	-23.3	-23.3
11	OH RADICAL	-75.61163698	-0.27168582	-75.720311	22.065112	23.01029244	-17.3	-16.3
12	Water //b3lyp/6-31G*	-76.28529724	-0.34509848	-76.423337	-268.059412	-267.1142322	-26.2	-25.3
13	HYDROGEN FLUORIDE,	-100.3019022	-0.35463372	-100.443756	-294.770937	-293.169382	-22.4	-20.8
14	SIH2 singlet	-290.3776094	-0.32045408	-290.505791	275.595118	277.3804581	2.8	4.6
15	SIH2 3B1	-290.3530784	-0.29557825	-290.471310	367.136804	368.922144	6.5	8.3
16	SIH3 c3v	-290.988701	-0.32526058	-291.118805	212.054168	213.8395083	11.6	13.4
17	SIH4 //b3lyp/6-31G*	-291.6261567	-0.35406879	-291.767784	55.019914	56.80525442	20.7	22.5
18	ph2 doublet	-342.2540191	-0.36100504	-342.398421	136.828956	136.8289558	-1.7	-1.7
19	PH3 c3v	-342.8769633	-0.39455604	-343.034786	14.412954	14.41295386	9.0	9.0
20	SH2 //b3lyp/6-31G*	-399.1211213	-0.41652552	-399.287731	-19.188881	-16.85218621	1.3	3.6
21	HCL //b3lyp/6-31G*	-460.5273825	-0.35323086	-460.668675	-96.425948	-92.90777769	-4.0	-0.4
22	DILITHIUM //b3lyp/6-31G*	-14.94419492	-0.06237077	-14.969143	226.063335	226.0633351	10.2	10.2
23	Lithium Fluoride,	-107.2587449	-0.38719534	-107.413623	-375.662632	-374.0610766	-40.5	-38.9
24	ACETYLENE //b3lyp/6-31g*	-77.13101744	-0.44605963	-77.309441	174.935724	175.6708637	-51.8	-51.1
25	ETHYLENE //b3lyp/6-31g*	-78.36315581	-0.46567251	-78.549425	24.851551	25.58669085	-27.4	-26.7
26	ETHANE //b3lyp/6-31g*	-79.57656464	-0.49914568	-79.776223	-91.921790	-91.18665029	-7.8	-7.1
27	CYANO RADICAL,	-92.51519124	-0.49229579	-92.712110	345.958824	346.3263936	-92.9	-92.6
28	HYDROGEN CYANIDE	-93.21848582	-0.49423935	-93.416182	48.352464	48.72003418	-83.4	-83.1
29	CARBON MONOXIDE	-113.1086728	-0.50454301	-113.310490	-185.655922	-184.3431721	-75.2	-73.9
30	HCO BENT	-113.6322663	-0.52756375	-113.843292	-41.833769	-40.52101868	-83.7	-82.4
31	H2CO //b3lyp/6-31g*	-114.2687918	-0.54734337	-114.487729	-177.481865	-176.1691153	-68.7	-67.4

32	METHANOL //b3lyp/6-31g*	-115.4650653	-0.57559865	-115.695305	-240.856459	-239.5437089	-40.0	-38.7
33	Nitrogen N2,	-109.3168538	-0.52977354	-109.528763	-93.882393	-93.8823933	-93.9	-93.9
34	H2NNH2 //b3lyp/6-31g*	-111.6067899	-0.59181106	-111.843514	38.991108	38.99110768	-56.4	-56.4
35	NO radical,	-129.6622771	-0.57301152	-129.891482	-10.001395	-9.05621456	-100.4	-99.4
36	O2 //b3lyp/6-31g*	-150.0715625	-0.63708704	-150.326397	-114.899296	-113.0089364	-114.9	-113.0
37	HYDROGEN PEROXIDE	-151.2769449	-0.67039639	-151.545103	-211.209706	-209.3193458	-75.2	-73.3
38	F2 //b3lyp/6-31g*	-199.2318251	-0.6996889	-199.511701	-69.608258	-66.40514772	-69.6	-66.4
39	CO2 D*H	-188.2514943	-0.8475591	-188.590518	-540.886716	-538.6287863	-147.6	-145.3
40	na2 //b3lyp/6-31G*	-324.2158633	-0.38837081	-324.371212	137.519738	137.5197383	-4.7	-4.7
41	SI2 3-SGG	-578.4274921	-0.58556532	-578.661718	570.009561	573.5802408	-15.3	-11.8
42	P2 //b3lyp/6-31g*	-682.2190565	-0.74881736	-682.518583	96.817079	96.81707874	-46.7	-46.7
43	S2 //b3lyp/6-31g*	-795.8644551	-0.79231047	-796.181379	79.375265	84.04865464	-49.1	-44.4
44	CL2 //b3lyp/6-31g*	-919.8236481	-0.68592061	-920.098016	-20.102406	-13.0660659	-20.1	-13.1
45	Sodium Chloride	-622.1131903	-0.53307257	-622.326419	-182.412932	-178.8947622	0.0	3.5
46	SIO //b3lyp/6-31g*	-364.3853727	-0.65450858	-364.647176	-173.514554	-170.7840343	-70.6	-67.9
47	Carbon monosulfide,	-435.8736641	-0.61231514	-436.118590	222.106387	224.8106524	-57.8	-55.1
48	OS //b3lyp/6-31g*	-472.9880692	-0.72373486	-473.277563	-80.088359	-76.80648365	-85.1	-81.8
49	CLO 2-PI	-534.910745	-0.64604396	-535.169163	44.031048	48.49439788	-57.2	-52.8
50	CLF 1-SG	-559.5520599	-0.68953929	-559.827876	-105.470628	-100.3509034	-50.2	-45.1
51	si2h6 //b3lyp/6-31g*	-582.0842701	-0.68853417	-582.359684	115.908127	119.4788075	36.0	39.6
52	Methyl chloride,	-499.7174485	-0.58987741	-499.953399	-99.252419	-95.36667853	-17.2	-13.4
53	H3C-SH METHANETHIOL	-438.3138003	-0.6556685	-438.576068	-31.549966	-28.84570056	-8.5	-5.8
54	HOCl //b3lyp/6-31g*	-535.5531708	-0.6816707	-535.825839	-128.592511	-124.1291613	-54.1	-49.7
55	SO2 //b3lyp/6-31G*	-548.1152916	-1.09838428	-548.554645	-432.736165	-428.50911	-135.7	-131.4
56	BF3 PLANAR	-324.1018822	-1.12470684	-324.551765	-1223.959351	-1219.023411	-88.4	-83.5
57	bcl3 B3LYP	-1404.696884	-1.16784314	-1405.164021	-454.676518	-443.9907326	-51.8	-41.1
58	ALf3 B3LYP	-541.5936253	-1.26928298	-542.101338	-1274.546555	-1268.84922	-65.4	-59.7
59	alcl3 B3LYP	-1622.244912	-1.27046858	-1622.753099	-603.635640	-592.1884601	-19.1	-7.7
60	cf4 B3LYP	-436.86553	-1.53745829	-437.480513	-1066.735982	-1059.962192	-133.7	-126.9
61	ccl4 B3LYP	-1877.698531	-1.62169307	-1878.347208	-174.710892	-160.2706416	-78.9	-64.5
62	O=C=S. Singlet	-511.0734397	-0.94046471	-511.449626	-267.619535	-263.9700903	-129.1	-125.5
63	CS2 B3LYP	-833.8919885	-1.04089154	-834.308345	7.246948	12.28790807	-109.5	-104.4
64	COF2 B3LYP	-312.5368884	-1.19357292	-313.014318	-748.763541	-744.2476811	-124.9	-120.4
65	sif4 B3LYP	-688.3951335	-1.63928493	-689.050847	-1671.140722	-1662.949162	-56.1	-47.9
66	sicl4, td	-2129.208361	-1.68007979	-2129.880393	-675.804548	-659.946528	-13.1	2.8
67	nno B3LYP	-184.3144761	-0.91438665	-184.680231	-114.381781	-113.4366011	-196.4	-195.4
68	clno B3LYP	-589.578108	-0.98584817	-589.972447	-102.143864	-97.68051446	-154.0	-149.6

69	nf3 c3v	-353.5622328	-1.3196041	-354.090074	-299.913213	-295.1085483	-167.7	-162.9
70	pf3 c3v	-640.3529508	-1.37098042	-640.901343	-1033.701442	-1028.896777	-75.1	-70.3
71	ozone 1-a1	-225.0158128	-1.10564365	-225.458070	-87.891391	-85.05585056	-230.6	-227.7
72	f2o B3LYP	-274.2539487	-1.03659257	-274.668586	-109.616512	-105.4682225	-134.3	-130.2
73	CLF3, C2V	-758.8136275	-1.46651103	-759.400232	-331.300458	-322.9776227	-172.3	-164.0
74	CF2=CF2 D2H	-474.7976799	-1.75419156	-475.499357	-854.680967	-847.5396066	-196.1	-189.0
75	cl2c=ccl2 B3LYP	-1915.699285	-1.8330737	-1916.432514	-134.815986	-120.0081662	-122.3	-107.5
76	cf3cn B3LYP	-429.7648542	-1.69691612	-430.443621	-700.007761	-694.467956	-204.6	-199.1
77	PROPYNE C3V	-116.3387929	-0.68230391	-116.611714	121.254757	122.3574667	-63.7	-62.6
78	ALLENE D2D	-116.3397723	-0.6754671	-116.609959	124.206459	125.3091693	-66.2	-65.1
79	CYCLOPROPENE C2V	-116.2982966	-0.68438294	-116.572050	224.674929	225.7776392	-52.3	-51.2
80	PROPENE CS	-117.5645967	-0.70481677	-117.846523	-15.881532	-14.77882191	-36.0	-34.9
81	CYCLOPROPANE D3H	-117.548879	-0.70994003	-117.832855	22.485756	23.5884655	-30.7	-29.5
82	PROPANE C2V	-118.7728212	-0.73789464	-119.067979	-118.310611	-117.2079013	-13.7	-12.6
83	TRANS-1,3-BUTADIENE C2H	-155.558196	-0.9131852	-155.923470	43.816890	45.28716983	-66.2	-64.8
84	Dimethyl acetylene	-155.5444725	-0.91927724	-155.912183	73.602253	75.07253266	-72.0	-70.5
85	Methylene cyclopropane.	-155.5239118	-0.91882897	-155.891443	126.650632	128.1209124	-73.8	-72.3
86	Bicyclo[1.1.0]butane. C2v	-155.5057488	-0.93005613	-155.877771	164.479272	165.9495523	-52.7	-51.2
87	CYCLOBUTENE b3lyp	-155.5322287	-0.92153605	-155.900843	104.334691	105.8049711	-52.1	-50.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.745474	-0.95023519	-157.125568	-5.304951	-3.834671269	-33.8	-32.3
89	Isobutene. Single	-156.7655178	-0.94688662	-157.144272	-59.202192	-57.73191196	-42.5	-41.0
90	Trans butane	-157.9689211	-0.97720291	-158.359802	-144.883700	-143.4134205	-19.4	-17.9
91	isobutane B3LYP/6-31G*	-157.9697055	-0.98065634	-158.361968	-151.864070	-150.3937901	-17.6	-16.1
92	Spiropentane. D2d	-194.7119417	-1.16333673	-195.177276	117.740132	119.5779825	-67.6	-65.8
93	Benzene B3LYP	-231.6225239	-1.33953663	-232.158339	-41.430859	-39.22543893	-123.9	-121.7
94	DIFLUOROMETHANE C2V	-238.607504	-0.90051498	-238.967710	-523.875465	-520.3047849	-73.3	-69.7
95	HCF3 TRI-FLUOROMETHANE	-337.7385612	-1.220617	-338.226808	-801.590648	-796.4184132	-104.5	-99.4
96	CH2CL2 C2V	-959.0504688	-0.92571967	-959.420757	-129.581056	-122.1771456	-34.2	-26.8
97	chcl3 B3LYP/6-31G*	-1418.378307	-1.26997899	-1418.886298	-157.264958	-146.3428782	-53.9	-43.0
98	METHYLAMINE b3lyp	-95.60258511	-0.54515442	-95.820647	-54.607419	-54.23984943	-31.6	-31.2
99	Acetonitrile. CH3-CN.	-132.4321736	-0.72800388	-132.723375	-17.745648	-17.01050761	-93.1	-92.3
100	NITRO METHANE	-244.5199931	-1.20501351	-245.001998	-257.678403	-255.4204729	-183.2	-180.9
101	Methyl-nitrite. CH3-O-N=O.	-244.5163029	-1.19726762	-244.995210	-243.583207	-241.3252766	-177.1	-174.8
102	Methylsilane. CH3-SiH3.	-330.8377875	-0.59474271	-331.075685	-10.542033	-8.389123499	18.7	20.9
103	Formic Acid.	-189.4047082	-0.86828094	-189.752021	-489.781644	-487.523714	-111.1	-108.9
104	Methyl formate.	-228.5887578	-1.10473106	-229.030650	-482.316228	-479.6907283	-126.7	-124.1
105	acetamide ch3cohn2	-208.7460464	-1.07155928	-209.174670	-347.103601	-345.4232807	-108.6	-106.9

106	Aziridine. (cyclic	-133.5705067	-0.75848409	-133.873900	67.239958	67.97509845	-59.1	-58.4
107	Cyanogen. NCCN.	-185.2566223	-0.97928449	-185.648336	115.526052	116.2611925	-191.2	-190.4
108	DIMETHYLAMINE b3lyp	-134.7901894	-0.78290046	-135.103350	-58.526062	-57.79092151	-40.1	-39.4
109	TRANS ETHYLAMINE	-134.8016188	-0.78407697	-135.115250	-88.832297	-88.09715728	-41.6	-40.8
110	KETENE B3LYP	-152.2754516	-0.76181795	-152.580179	-159.602198	-157.9218775	-112.3	-110.6
111	OXIRANE B3LYP	-153.4339674	-0.79140903	-153.750531	-124.511824	-122.8315045	-71.8	-70.1
112	Acetaldehyde B3LYP	-153.4805204	-0.78445199	-153.794301	-242.549379	-240.8690591	-76.4	-74.8
113	Glyoxal, O=CH-CH=O.	-227.3712123	-1.07222239	-227.800101	-359.202515	-356.5770147	-147.1	-144.4
114	ETHANOL TRANS	-154.6664941	-0.81367601	-154.991964	-280.421772	-278.7414518	-45.3	-43.6
115	DIMETHYL ETHER,	-154.6501085	-0.8109126	-154.974474	-235.342136	-233.6618163	-51.2	-49.6
116	Thiooxirane. (cyclic	-476.3007105	-0.8773157	-476.651637	39.048619	42.12045351	-43.0	-39.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.5753793	-1.242778	-553.072490	-219.026143	-215.0091282	-67.6	-63.5
118	Thioethanol. CH3-CH2-SH.	-477.5106445	-0.89598556	-477.869039	-60.742558	-57.67072306	-14.3	-11.2
119	ch3sch3 B3LYP	-477.5091146	-0.8982861	-477.868429	-56.616180	-53.54434548	-19.4	-16.3
120	Vinyl fluoride,	-177.4774582	-0.78837643	-177.792809	-210.251662	-207.9149674	-71.3	-69.0
121	Ethyl chloride.	-538.9174446	-0.82950763	-539.249248	-136.164359	-131.9110491	-24.0	-19.8
122	Vinyl chloride,	-537.70406	-0.8012178	-538.024547	-25.953602	-21.70029223	-49.0	-44.7
123	h2c=chcn B3LYP	-170.4171601	-0.93739203	-170.792117	63.368957	64.47166664	-117.4	-116.3
124	ACETONE B3LYP	-192.6882745	-1.02305616	-193.097497	-299.427354	-297.3794644	-82.3	-80.2
125	CH3COOH ACETIC	-228.6137952	-1.10325686	-229.055098	-546.957929	-544.3324287	-114.3	-111.7
126	CH3CFO HCCO	-252.6238261	-1.11093449	-253.068200	-556.078435	-552.7965605	-113.8	-110.5
127	ch3c(o)cl hcco	-612.838184	-1.12929204	-613.289901	-345.834166	-340.6356756	-103.2	-98.0
128	ch3ch2ch2cl B3LYP	-578.1136632	-1.06910396	-578.541305	-163.257045	-158.6361652	-31.5	-26.8
129	Isopropyl alcohol,	-193.8673608	-1.05545195	-194.289542	-323.792437	-321.7445471	-51.0	-48.9
130	Methyl ethyl	-193.8514283	-1.04963556	-194.271282	-275.304372	-273.2564823	-59.0	-56.9
131	Trimethyl Amine.	-173.9798777	-1.02596514	-174.390264	-74.806939	-73.7042286	-51.0	-49.9
132	FURAN B3LYP	-229.4798362	-1.21829841	-229.967156	-166.993066	-164.5776063	-132.3	-129.9
133	Thiophene b3lyp	-552.3364988	-1.31250292	-552.861500	11.972220	15.77919464	-103.1	-99.3
134	PYROLE PLANAR	-209.6308326	-1.18795664	-210.106015	-16.583530	-15.11325007	-124.9	-123.5
135	C2v Pyridine	-247.6514538	-1.38706899	-248.206281	-16.516588	-14.67873804	-157.1	-155.3
136	H2 B3LYP/6-31G*	-1.15469131	-0.0368311	-1.169424	5.822670	5.822669525	5.8	5.8
137	SH b3lyp/6-31G*	-398.487582	-0.37486734	-398.637529	142.541337	144.8780317	-0.6	1.8
138	CCH B3LYP	-76.42321788	-0.40727838	-76.586129	520.851430	521.5865702	-44.4	-43.7
139	C2H3 CS,2-A'	-77.69336777	-0.42757776	-77.864399	264.678364	265.4135038	-34.9	-34.2
140	ch3co hcco	-152.8447386	-0.76210363	-153.149580	-102.477982	-100.7976618	-92.4	-90.8
141	H2COH C1	-114.8181453	-0.5420106	-115.034950	-64.350877	-63.03812743	-47.2	-45.9
142	ch3o CS,	-114.8103419	-0.51466365	-115.016207	-18.716537	-17.40378683	-35.9	-34.6

143	ch3ch2o 2A"	-154.0116861	-0.75327986	-154.312998	-59.208336	-57.52801615	-43.7	-42.0
144	ch3s 2-A'	-437.685869	-0.61743744	-437.932844	108.013660	110.717925	-16.7	-14.0
145	c2h5 staggered	-78.92225447	-0.45822044	-79.105543	109.282148	110.017288	-11.6	-10.9
146	(ch3)2ch Cs	-118.1233343	-0.69870409	-118.402816	68.520983	69.6236929	-21.4	-20.3
147	TERT-BUTYL RADICAL	-157.3243182	-0.94139821	-157.700878	25.427381	26.89766135	-26.0	-24.6
148	NO2 RADICAL	-204.7082978	-0.96684174	-205.095034	-169.923349	-168.0329894	-203.0	-201.1

MAD	**65.1**	**62.7**
LD	**-230.6**	**-227.7**

Table S5.2b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 45% and a_C = 40%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498434	0.000000	-0.498434
2	li	-7.461075	-0.015024	-7.467084
3	be	-14.624149	-0.057979	-14.647340
4	b	-24.599852	-0.082687	-24.632926
5	c	-37.779143	-0.109919	-37.823111
6	n	-54.508001	-0.140929	-54.564373
7	o	-74.965346	-0.200318	-75.045474
8	f	-99.605820	-0.265368	-99.711967
9	na	-162.099838	-0.178312	-162.171163
10	al	-242.169078	-0.229120	-242.260726
11	si	-289.164344	-0.260170	-289.268412
12	p	-341.040923	-0.290121	-341.156971
13	s	-397.867045	-0.333233	-398.000338
14	cl	-459.877073	-0.304853	-459.999014

Table S5.3a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 46% and a_C = 20%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05398057	-0.0493901	-8.063859	144.381534	144.3815335	5.1	5.1
2	BERYLLIUM HYDRIDE	-15.23023072	-0.05802827	-15.241836	318.479032	318.479032	-23.4	-23.4
3	DOUBLET CH	-38.43451912	-0.15268537	-38.465056	596.872250	597.23982	0.7	1.0
4	CH2 3-B1	-39.09813355	-0.17173055	-39.132480	394.765008	395.1325785	2.7	3.1
5	Singlet methylene,	-39.07701961	-0.19451653	-39.115923	436.622683	436.9902528	6.5	6.9
6	Methyl radical,	-39.77380675	-0.21876462	-39.817560	150.222997	150.5905671	3.8	4.2
7	ch4 //b3lyp/6-31G*	-40.44110963	-0.26303605	-40.493717	-65.588567	-65.22099684	9.3	9.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.16844308	-0.19647629	-55.207738	353.137116	353.1371161	-3.3	-3.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.8138578	-0.25325106	-55.864508	181.104431	181.1044309	-7.6	-7.6
10	AMMONIA, //b3lyp/6-31G*	-56.48270059	-0.31043104	-56.544787	-43.974150	-43.97415037	2.0	2.0
11	OH RADICAL	-75.67145485	-0.27043883	-75.725543	37.971652	38.91683168	-1.4	-0.4
12	Water //b3lyp/6-31G*	-76.35286595	-0.34354599	-76.421575	-233.735143	-232.7899627	8.1	9.0
13	HYDROGEN FLUORIDE,	-100.3737691	-0.35312689	-100.444395	-268.128881	-266.5273255	4.2	5.9
14	SIH2 singlet	-290.4971616	-0.31945731	-290.561053	272.665244	274.4505839	-0.1	1.7
15	SIH2 3B1	-290.4688341	-0.29515721	-290.527866	360.810000	362.5953402	0.1	1.9
16	SIH3 c3v	-291.1120345	-0.32446303	-291.176927	201.674007	203.4593473	1.3	3.0
17	SIH4 //b3lyp/6-31G*	-291.7563191	-0.35302374	-291.826924	42.025732	43.81107206	7.7	9.5
18	ph2 doublet	-342.3827312	-0.35977927	-342.454687	134.506864	134.5068638	-4.0	-4.0
19	PH3 c3v	-343.0122819	-0.39331026	-343.090944	12.431394	12.4313945	7.0	7.0
20	SH2 //b3lyp/6-31G*	-399.2615602	-0.41516535	-399.344593	-12.494056	-10.15736075	8.0	10.3
21	HCL //b3lyp/6-31G*	-460.672899	-0.3519286	-460.743285	-89.220252	-85.70208244	3.2	6.8
22	DILITHIUM //b3lyp/6-31G*	-14.97104925	-0.06209157	-14.983468	229.331799	229.3317991	13.4	13.4
23	Lithium Fluoride,	-107.3416272	-0.38525109	-107.418677	-340.233284	-338.6317289	-5.1	-3.5
24	ACETYLENE //b3lyp/6-31g*	-77.2196251	-0.44423899	-77.308473	229.460023	230.1951631	2.7	3.4
25	ETHYLENE //b3lyp/6-31g*	-78.46273989	-0.46387499	-78.555515	60.960152	61.69529212	8.7	9.4
26	ETHANE //b3lyp/6-31g*	-79.68711252	-0.49729685	-79.786572	-66.878632	-66.14349183	17.2	18.0
27	CYANO RADICAL,	-92.59975388	-0.49116549	-92.697987	435.967359	436.3349293	-2.9	-2.6
28	HYDROGEN CYANIDE	-93.31074767	-0.49205578	-93.409159	119.778514	120.1460843	-12.0	-11.6
29	CARBON MONOXIDE	-113.2048606	-0.50221686	-113.305304	-116.524155	-115.2114047	-6.1	-4.8
30	HCO BENT	-113.733068	-0.52528626	-113.838125	27.304972	28.6177221	-14.5	-13.2
31	H2CO //b3lyp/6-31g*	-114.3762098	-0.54492343	-114.485195	-115.195039	-113.8822889	-6.4	-5.1

32	METHANOL //b3lyp/6-31g*	-115.583821	-0.57324831	-115.698471	-193.419996	-192.1072461	7.4	8.7
33	Nitrogen N2,	-109.4127298	-0.52745564	-109.518221	-12.209621	-12.20962055	-12.2	-12.2
34	H2NNH2 //b3lyp/6-31g*	-111.7255847	-0.58929489	-111.843444	93.403256	93.40325617	-2.0	-2.0
35	NO radical,	-129.7667332	-0.57046333	-129.880826	74.555726	75.50090624	-15.8	-14.9
36	O2 //b3lyp/6-31g*	-150.1844806	-0.63439776	-150.311360	-16.252934	-14.3625739	-16.3	-14.4
37	HYDROGEN PEROXIDE	-151.4029028	-0.66729766	-151.536362	-128.977287	-127.0869267	7.0	8.9
38	F2 //b3lyp/6-31g*	-199.3653041	-0.69657033	-199.504618	5.509209	8.71231864	5.5	8.7
39	CO2 D*H	-188.4082487	-0.84376742	-188.577002	-420.301996	-418.0440662	-27.0	-24.7
40	na2 //b3lyp/6-31G*	-324.3839594	-0.3871249	-324.461384	141.642960	141.64296	-0.6	-0.6
41	SI2 3-SGG	-578.646979	-0.58381289	-578.763742	586.236017	589.8066972	0.9	4.5
42	P2 //b3lyp/6-31g*	-682.4616204	-0.74612917	-682.610846	145.156341	145.1563407	1.6	1.6
43	S2 //b3lyp/6-31g*	-796.125547	-0.78965456	-796.283478	123.053734	127.7271238	-5.4	-0.7
44	CL2 //b3lyp/6-31g*	-920.1062195	-0.6833114	-920.242882	5.625063	12.66140289	5.6	12.7
45	Sodium Chloride	-622.3397055	-0.53106265	-622.445918	-172.685108	-169.1669382	9.7	13.3
46	SIO //b3lyp/6-31g*	-364.5550296	-0.65119827	-364.685269	-101.900508	-99.1699879	1.0	3.8
47	Carbon monosulfide,	-436.042921	-0.60978928	-436.164879	282.377397	285.0816619	2.5	5.2
48	OS //b3lyp/6-31g*	-473.1752679	-0.72091732	-473.319451	-4.613625	-1.331749751	-9.6	-6.4
49	CLO 2-PI	-535.1084241	-0.6436027	-535.237145	98.163245	102.6265946	-3.1	1.4
50	CLF 1-SG	-559.7605328	-0.68668212	-559.897869	-57.941664	-52.82193897	-2.7	2.4
51	si2h6 //b3lyp/6-31g*	-582.3371594	-0.68645424	-582.474450	99.026399	102.5970788	19.1	22.7
52	Methyl chloride,	-499.9140617	-0.58767684	-500.031597	-75.416995	-71.53125531	6.6	10.5
53	H3C-SH METHANETHIOL	-438.5056009	-0.65339443	-438.636280	-7.602187	-4.897921702	15.4	18.1
54	HOCl //b3lyp/6-31g*	-535.7575638	-0.67878782	-535.893321	-73.089956	-68.62660594	1.4	5.8
55	SO2 //b3lyp/6-31G*	-548.36459	-1.09333728	-548.583257	-292.821910	-288.594855	4.2	8.5
56	BF3 PLANAR	-324.3390821	-1.12039773	-324.563162	-1146.263072	-1141.327132	-10.7	-5.8
57	bcl3 B3LYP	-1405.155039	-1.16353994	-1405.387747	-410.126146	-399.4403612	-7.2	3.5
58	ALf3 B3LYP	-541.9025562	-1.26435094	-542.155426	-1192.412387	-1186.715052	16.8	22.5
59	alcl3 B3LYP	-1622.774986	-1.26607268	-1623.028200	-577.447921	-566.0007412	7.1	18.5
60	cf4 B3LYP	-437.1815555	-1.53169243	-437.487894	-947.136282	-940.3624916	-14.1	-7.3
61	ccl4 B3LYP	-1878.308999	-1.61553406	-1878.632106	-84.633289	-70.19303947	11.2	25.6
62	O=C=S. Singlet	-511.3033873	-0.93665541	-511.490718	-164.123528	-160.4740828	-25.6	-22.0
63	CS2 B3LYP	-834.1953276	-1.03703846	-834.402735	97.096736	102.1376956	-19.6	-14.6
64	COF2 B3LYP	-312.7730941	-1.18874813	-313.010844	-627.604803	-623.0889426	-3.8	0.7
65	sif4 B3LYP	-688.7841733	-1.63337081	-689.110847	-1573.581584	-1565.390024	41.4	49.6
66	sicl4, td	-2129.892091	-1.67425857	-2130.226942	-631.482033	-615.6240132	31.3	47.1
67	nno B3LYP	-184.4700678	-0.91008031	-184.652084	43.094948	44.04012755	-38.9	-38.0
68	clno B3LYP	-589.8250893	-0.98116626	-590.021323	29.150029	33.61337864	-22.7	-18.3

69	nf3 c3v	-353.8150782	-1.31383779	-354.077846	-156.026519	-151.221854	-23.8	-19.0
70	pf3 c3v	-640.681597	-1.36574656	-640.954746	-943.840759	-939.0360936	14.7	19.5
71	ozone 1-a1	-225.1884208	-1.09973557	-225.408368	131.351617	134.1871571	-11.3	-8.5
72	f2o B3LYP	-274.4459788	-1.03176081	-274.652331	19.165911	23.31420133	-5.5	-1.4
73	CLF3, C2V	-759.159486	-1.45982859	-759.451452	-177.958734	-169.635899	-19.0	-10.6
74	CF2=CF2 D2H	-475.1540365	-1.74728866	-475.503494	-700.634449	-693.4930885	-42.1	-34.9
75	cl2c=ccl2 B3LYP	-1916.35126	-1.82603585	-1916.716467	-16.324514	-1.516694219	-3.8	11.0
76	cf3cn B3LYP	-430.1011506	-1.69013391	-430.439177	-524.695916	-519.1561113	-29.3	-23.8
77	PROPYNE C3V	-116.4791371	-0.67961831	-116.615061	190.499877	191.6025874	5.6	6.7
78	ALLENE D2D	-116.4801196	-0.67278881	-116.614677	189.849594	190.9523036	-0.5	0.6
79	CYCLOPROPENE C2V	-116.4397699	-0.68165721	-116.576101	292.068290	293.1710001	15.1	16.2
80	PROPENE CS	-117.7159527	-0.70212185	-117.856377	36.394631	37.49734056	16.3	17.4
81	CYCLOPROPANE D3H	-117.7016958	-0.70724545	-117.843145	73.616869	74.71957916	20.5	21.6
82	PROPANE C2V	-118.935118	-0.73515988	-119.082150	-77.252943	-76.15023257	27.3	28.4
83	TRANS-1,3-BUTADIENE C2H	-155.7503294	-0.90961145	-155.932252	124.840776	126.3110555	14.8	16.3
84	Dimethyl acetylene	-155.7365485	-0.9157176	-155.919692	157.968311	159.4385906	12.4	13.8
85	Methylene cyclopropane.	-155.7173446	-0.91525526	-155.900396	207.226309	208.6965885	6.8	8.3
86	Bicyclo[1.1.0]butane. C2v	-155.7006396	-0.92645808	-155.885931	247.135027	248.605307	30.0	31.5
87	CYCLOBUTENE b3lyp	-155.7262164	-0.91792961	-155.909802	184.892020	186.3623002	28.4	29.9
88	CYCLOBUTANE b3lyp/6-31G*	-156.950414	-0.94663088	-157.139740	61.682434	63.1527138	33.2	34.7
89	Isobutene. Single	-156.9688154	-0.94328428	-157.157472	10.337946	11.80822576	27.1	28.5
90	Trans butane	-158.1829856	-0.97358581	-158.377703	-87.568941	-86.09866096	38.0	39.4
91	isobutane B3LYP/6-31G*	-158.1839607	-0.97701791	-158.379364	-93.225476	-91.75519569	41.1	42.6
92	Spiropentane. D2d	-194.9586109	-1.15888064	-195.190387	213.447048	215.2848981	28.1	29.9
93	Benzene B3LYP	-231.8998536	-1.33437632	-232.166729	92.485588	94.69100836	10.1	12.3
94	DIFLUOROMETHANE C2V	-238.7944894	-0.89694789	-238.973879	-457.500688	-453.9300077	-6.9	-3.3
95	HCF3 TRI-FLUOROMETHANE	-337.9900115	-1.21588297	-338.233188	-707.567324	-702.3950889	-10.5	-5.3
96	CH2CL2 C2V	-959.3848889	-0.9222395	-959.569337	-87.557345	-80.15343457	7.8	15.2
97	chcl3 B3LYP/6-31G*	-1418.850696	-1.26517692	-1419.103731	-93.035572	-82.1134916	10.3	21.2
98	METHYLAMINE b3lyp	-95.71733506	-0.54298531	-95.825932	-15.263346	-14.89577625	7.7	8.1
99	Acetonitrile. CH3-CN.	-132.5761813	-0.72498655	-132.721179	67.058359	67.79349946	-8.3	-7.5
100	NITRO METHANE	-244.7425305	-1.19964806	-244.982460	-94.109921	-91.85199088	-19.6	-17.4
101	Methyl-nitrite. CH3-O-N=O.	-244.738116	-1.191706	-244.976457	-82.077512	-79.81958168	-15.6	-13.3
102	Methylsilane. CH3-SiH3.	-331.019653	-0.59278264	-331.138210	-6.375465	-4.222554768	22.9	25.1
103	Formic Acid.	-189.5726103	-0.8644534	-189.745501	-387.449216	-385.191286	-8.8	-6.5
104	Methyl formate.	-228.808121	-1.10006447	-229.028134	-364.444989	-361.8194887	-8.8	-6.2
105	acetamide ch3cohn2	-208.961967	-1.06708366	-209.175384	-240.240731	-238.5604107	-1.8	-0.1

106	Aziridine. (cyclic	-133.7270815	-0.75546026	-133.878174	135.173742	135.9088818	8.8	9.6
107	Cyanogen. NCCN.	-185.4335954	-0.97488289	-185.628572	273.276132	274.0112724	-33.4	-32.7
108	DIMETHYLAMINE b3lyp	-134.9566157	-0.77986315	-135.112588	-3.513020	-2.777880082	14.9	15.6
109	TRANS ETHYLAMINE	-134.9681206	-0.78102127	-135.124325	-33.389987	-32.6548466	13.9	14.6
110	KETENE B3LYP	-152.4239329	-0.75852293	-152.575637	-66.113987	-64.43366687	-18.8	-17.2
111	OXIRANE B3LYP	-153.5942783	-0.78815272	-153.751909	-46.448101	-44.76778079	6.3	8.0
112	Acetaldehyde B3LYP	-153.6397486	-0.78115561	-153.795980	-165.275127	-163.5948074	0.8	2.5
113	Glyoxal, O=CH-CH=O.	-227.5787564	-1.06749848	-227.792256	-227.456978	-224.8314779	-15.3	-12.7
114	ETHANOL TRANS	-154.8370151	-0.81044768	-154.999105	-217.370552	-215.6902321	17.8	19.5
115	DIMETHYL ETHER,	-154.8203536	-0.80770785	-154.981895	-173.030068	-171.3497484	11.1	12.7
116	Thiooxirane. (cyclic	-476.5345516	-0.87411532	-476.709375	95.425045	98.49688033	13.4	16.5
117	Dimethylsulfoxide. (CH3)2SO.	-552.8789447	-1.23778651	-553.126502	-123.166712	-119.1496972	28.3	32.3
118	Thioethanol. CH3-CH2-SH.	-477.7541815	-0.89281421	-477.932744	-19.918002	-16.84616719	26.5	29.6
119	ch3sch3 B3LYP	-477.7524768	-0.89508218	-477.931493	-14.107466	-11.03563113	23.1	26.2
120	Vinyl fluoride,	-177.6411954	-0.78521964	-177.798239	-144.208370	-141.8716754	-5.3	-3.0
121	Ethyl chloride.	-539.1657895	-0.8264135	-539.331072	-95.802563	-91.54925335	16.3	20.6
122	Vinyl chloride,	-537.9415748	-0.7981245	-538.101200	27.870781	32.12409084	4.9	9.1
123	h2c=chcn B3LYP	-170.6017889	-0.93346875	-170.788483	177.880223	178.9829332	-2.9	-1.8
124	ACETONE B3LYP	-192.8994162	-1.01890557	-193.103197	-206.663409	-204.615519	10.5	12.5
125	CH3COOH ACETIC	-228.8335899	-1.09861511	-229.053313	-431.006764	-428.3812645	1.6	4.2
126	CH3CFO HCCO	-252.8474368	-1.10636943	-253.068711	-447.535140	-444.2532655	-5.3	-2.0
127	ch3c(o)cl hcco	-613.1352052	-1.12466225	-613.360138	-245.581769	-240.383279	-2.9	2.3
128	ch3ch2ch2cl B3LYP	-578.4137587	-1.06512282	-578.626783	-106.439524	-101.8186439	25.4	30.0
129	Isopropyl alcohol,	-194.0898246	-1.05133344	-194.300091	-243.644066	-241.5961764	29.2	31.2
130	Methyl ethyl	-194.0734464	-1.04555664	-194.282558	-197.060818	-195.0129276	19.3	21.3
131	Trimethyl Amine.	-174.1982461	-1.0220065	-174.402647	-2.001729	-0.899019083	21.8	22.9
132	FURAN B3LYP	-229.7239488	-1.21337806	-229.966624	-32.051703	-29.63624258	2.7	5.1
133	Thiophene b3lyp	-552.6540495	-1.30752007	-552.915553	129.887373	133.6943484	14.8	18.6
134	PYROLE PLANAR	-209.8714206	-1.18329036	-210.108079	109.017659	110.4879394	0.7	2.1
135	C2v Pyridine	-247.9325728	-1.38158515	-248.208890	133.586445	135.4242948	-7.0	-5.2
136	H2 B3LYP/6-31G*	-1.16235501	-0.03666316	-1.169688	5.246131	5.246130729	5.2	5.2
137	SH b3lyp/6-31G*	-398.6212125	-0.3735948	-398.695931	145.132868	147.469563	2.0	4.4
138	CCH B3LYP	-76.50389354	-0.40561186	-76.585016	575.698078	576.4332179	10.4	11.2
139	C2H3 CS,2-A'	-77.7857099	-0.42605506	-77.870921	299.594689	300.3298287	0.0	0.8
140	ch3co hcco	-152.9972348	-0.75899191	-153.149033	-19.419160	-17.73884035	-9.4	-7.7
141	H2COH C1	-114.9301898	-0.53988413	-115.038167	-17.106822	-15.79407177	0.0	1.4
142	ch3o CS,	-114.9218529	-0.51275375	-115.024404	15.454592	16.76734247	-1.7	-0.4

143	ch3ch2o 2A"	-154.1749344	-0.75051681	-154.325038	-9.079187	-7.398866804	6.4	8.1
144	ch3s 2-A'	-437.8710543	-0.61529511	-437.994113	129.127422	131.8316866	4.4	7.1
145	c2h5 staggered	-79.02582413	-0.45647183	-79.117118	131.045999	131.7811392	10.1	10.9
146	(ch3)2ch Cs	-118.2787779	-0.69613237	-118.418004	106.848846	107.9515558	16.9	18.0
147	TERT-BUTYL RADICAL	-157.5317021	-0.93799221	-157.719301	81.311952	82.78223225	29.8	31.3
148	NO2 RADICAL	-204.8724776	-0.96231519	-205.064941	-4.748587	-2.858226561	-37.8	-35.9

MAD	**12.2**	**13.0**
LD	**-42.1**	**49.6**

Table S5.3b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 46% and a_C = 20%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498456	0.000000	-0.498456
2	li	-7.471868	-0.015002	-7.474869
3	be	-14.643215	-0.057698	-14.654754
4	b	-24.625190	-0.082170	-24.641624
5	c	-37.811124	-0.109320	-37.832988
6	n	-54.546585	-0.140355	-54.574656
7	o	-75.016853	-0.199439	-75.056741
8	f	-99.669866	-0.264325	-99.722731
9	na	-162.181471	-0.177816	-162.217035
10	al	-242.268130	-0.228373	-242.313805
11	si	-289.270647	-0.259334	-289.322514
12	p	-341.154439	-0.289347	-341.212309
13	s	-397.993273	-0.332159	-398.059705
14	cl	-460.015606	-0.303703	-460.076347

Table S5.4a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 50% and a_C = 23%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05149828	-0.04847797	-8.062648	145.202655	145.2026552	5.9	5.9
2	BERYLLIUM HYDRIDE	-15.22747517	-0.05700767	-15.240587	318.960891	318.9608914	-22.9	-22.9
3	DOUBLET CH	-38.42844339	-0.14994978	-38.462932	597.800997	598.1685673	1.6	1.9
4	CH2 3-B1	-39.09186106	-0.16902148	-39.130736	394.929801	395.2973708	2.9	3.3
5	Singlet methylene,	-39.06994591	-0.19093268	-39.113860	437.624563	437.9921334	7.5	7.9
6	Methyl radical,	-39.76625722	-0.21532131	-39.815781	150.714961	151.0825312	4.3	4.6
7	ch4 //b3lyp/6-31G*	-40.43256088	-0.2587452	-40.492072	-65.212830	-64.84526022	9.7	10.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.16075042	-0.19353107	-55.205263	354.910650	354.9106502	-1.6	-1.6
9	NH2,2-B-1, //b3lyp/6-31G*	-55.80460626	-0.24922805	-55.861929	183.385339	183.3853392	-5.3	-5.3
10	AMMONIA, //b3lyp/6-31G*	-56.47221147	-0.30536129	-56.542445	-42.080107	-42.08010732	3.9	3.9
11	OH RADICAL	-75.66094119	-0.26645853	-75.722227	38.969517	39.91469653	-0.4	0.6
12	Water //b3lyp/6-31G*	-76.34070532	-0.33811359	-76.418471	-233.059011	-232.1138313	8.8	9.7
13	HYDROGEN FLUORIDE,	-100.3606098	-0.34806227	-100.440664	-268.006535	-266.4049796	4.4	6.0
14	SIH2 singlet	-290.4794827	-0.31490165	-290.551910	273.702310	275.4876501	0.9	2.7
15	SIH2 3B1	-290.4519758	-0.29118993	-290.518949	361.251066	363.0364063	0.6	2.4
16	SIH3 c3v	-291.0943946	-0.32005751	-291.168008	202.359115	204.1444552	1.9	3.7
17	SIH4 //b3lyp/6-31G*	-291.7380602	-0.34816413	-291.818138	42.596183	44.38152285	8.3	10.1
18	ph2 doublet	-342.3637431	-0.35493476	-342.445378	136.428577	136.4285765	-2.1	-2.1
19	PH3 c3v	-342.992518	-0.38768009	-343.081684	14.459157	14.45915663	9.0	9.0
20	SH2 //b3lyp/6-31G*	-399.2408029	-0.40938658	-399.334962	-11.678972	-9.342276899	8.8	11.2
21	HCL //b3lyp/6-31G*	-460.6514835	-0.34667114	-460.731218	-89.154626	-85.63645571	3.3	6.8
22	DILITHIUM //b3lyp/6-31G*	-14.96741963	-0.06066029	-14.981371	229.650458	229.6504584	13.8	13.8
23	Lithium Fluoride,	-107.3266608	-0.37913204	-107.413861	-340.087848	-338.4862925	-4.9	-3.3
24	ACETYLENE //b3lyp/6-31g*	-77.20477758	-0.43553404	-77.304950	229.410826	230.1459659	2.6	3.4
25	ETHYLENE //b3lyp/6-31g*	-78.44726305	-0.45566909	-78.552067	61.186366	61.92150599	8.9	9.6
26	ETHANE //b3lyp/6-31g*	-79.67102518	-0.48912569	-79.783524	-67.231882	-66.49674156	16.9	17.6
27	CYANO RADICAL,	-92.58330048	-0.47830688	-92.693311	438.397505	438.7650753	-0.5	-0.1
28	HYDROGEN CYANIDE	-93.29410509	-0.48224949	-93.405022	121.027599	121.3951693	-10.8	-10.4
29	CARBON MONOXIDE	-113.1871358	-0.492634	-113.300442	-116.586166	-115.2734163	-6.1	-4.8
30	HCO BENT	-113.7143594	-0.51550009	-113.832924	28.367276	29.68002644	-13.5	-12.2
31	H2CO //b3lyp/6-31g*	-114.357122	-0.53510975	-114.480197	-114.431537	-113.1187869	-5.6	-4.3

32	METHANOL //b3lyp/6-31g*	-115.5640953	-0.5639023	-115.693793	-193.024407	-191.7116568	7.8	9.1
33	Nitrogen N2,	-109.3946371	-0.51710283	-109.513571	-9.924936	-9.924936441	-9.9	-9.9
34	H2NNH2 //b3lyp/6-31g*	-111.7054457	-0.57950093	-111.838731	96.794423	96.79442312	1.4	1.4
35	NO radical,	-129.7462304	-0.55976026	-129.874975	77.010464	77.95564425	-13.4	-12.4
36	O2 //b3lyp/6-31g*	-150.1611504	-0.62378127	-150.304620	-14.444582	-12.55422165	-14.4	-12.6
37	HYDROGEN PEROXIDE	-151.3787002	-0.65574929	-151.529523	-126.435749	-124.5453894	9.5	11.4
38	F2 //b3lyp/6-31g*	-199.3384821	-0.68481168	-199.495989	8.350462	11.55357173	8.4	11.6
39	CO2 D*H	-188.3785705	-0.82785579	-188.568977	-420.004596	-417.7466658	-26.7	-24.5
40	na2 //b3lyp/6-31G*	-324.3568532	-0.38179071	-324.444665	142.267890	142.2678897	0.0	0.0
41	SI2 3-SGG	-578.6132632	-0.5753075	-578.745584	587.030449	590.6011294	1.7	5.3
42	P2 //b3lyp/6-31g*	-682.4238451	-0.7336138	-682.592576	147.144146	147.1441456	3.6	3.6
43	S2 //b3lyp/6-31g*	-796.0850555	-0.77843458	-796.264095	124.055187	128.7285772	-4.4	0.3
44	CL2 //b3lyp/6-31g*	-920.0637273	-0.67248653	-920.218399	6.201083	13.23742262	6.2	13.2
45	Sodium Chloride	-622.3055032	-0.52350033	-622.425908	-173.636667	-170.1184971	8.8	12.3
46	SIO //b3lyp/6-31g*	-364.5261013	-0.63927486	-364.673135	-101.423838	-98.69331839	1.5	4.2
47	Carbon monosulfide,	-436.0157592	-0.59820393	-436.153346	282.828670	285.5329355	2.9	5.6
48	OS //b3lyp/6-31g*	-473.1433261	-0.70935593	-473.306478	-3.439199	-0.157324218	-8.5	-5.2
49	CLO 2-PI	-535.0757782	-0.63030325	-535.220748	101.417376	105.8807262	0.2	4.6
50	CLF 1-SG	-559.7260591	-0.6755408	-559.881433	-56.548623	-51.42889777	-1.3	3.8
51	si2h6 //b3lyp/6-31g*	-582.3013934	-0.67687759	-582.457075	99.179367	102.750047	19.3	22.8
52	Methyl chloride,	-499.8849888	-0.57834186	-500.018007	-75.766752	-71.88101182	6.2	10.1
53	H3C-SH METHANETHIOL	-438.477191	-0.64354573	-438.625207	-7.415049	-4.710783938	15.6	18.3
54	HOCl //b3lyp/6-31g*	-535.7242182	-0.66742349	-535.877726	-71.703057	-67.23970683	2.8	7.2
55	SO2 //b3lyp/6-31G*	-548.3204187	-1.07290186	-548.567186	-291.457712	-287.2306567	5.6	9.8
56	BF3 PLANAR	-324.2973304	-1.10369869	-324.551181	-1148.587620	-1143.65168	-13.1	-8.1
57	bcl3 B3LYP	-1405.087811	-1.14514421	-1405.351194	-413.769018	-403.083233	-10.8	-0.2
58	ALf3 B3LYP	-541.8495187	-1.24594081	-542.136085	-1194.931172	-1189.233837	14.2	19.9
59	alcl3 B3LYP	-1622.697489	-1.24756703	-1622.984429	-581.658546	-570.2113658	2.8	14.3
60	cf4 B3LYP	-437.1247146	-1.5085486	-437.471681	-949.082729	-942.3089394	-16.1	-9.3
61	ccl4 B3LYP	-1878.217562	-1.58933028	-1878.583108	-88.280118	-73.83986816	7.5	22.0
62	O=C=S. Singlet	-511.2645714	-0.91992677	-511.476155	-163.657800	-160.008355	-25.2	-21.5
63	CS2 B3LYP	-834.1472811	-1.01935765	-834.381733	97.465865	102.5068246	-19.3	-14.2
64	COF2 B3LYP	-312.7296041	-1.16913682	-312.998506	-627.853981	-623.3381215	-4.0	0.5
65	sif4 B3LYP	-688.7179157	-1.61000701	-689.088217	-1577.235394	-1569.043834	37.8	46.0
66	sicl4, td	-2129.79221	-1.64930767	-2130.171551	-636.896372	-621.0383524	25.8	41.7
67	nno B3LYP	-184.4387498	-0.89133579	-184.643757	47.088873	48.03405338	-34.9	-34.0
68	clno B3LYP	-589.7814216	-0.96128753	-590.002518	33.764666	38.22801572	-18.1	-13.7

69	nf3 c3v	-353.7658772	-1.29091616	-354.062788	-151.176506	-146.3718406	-19.0	-14.2
70	pf3 c3v	-640.6251105	-1.34513894	-640.934492	-943.376655	-938.5719897	15.2	20.0
71	ozone 1-a1	-225.1502735	-1.07484903	-225.397489	136.083594	138.919134	-6.6	-3.8
72	f2o B3LYP	-274.4068516	-1.01287146	-274.639812	24.275489	28.42377903	-0.4	3.7
73	CLF3, C2V	-759.0963699	-1.4337764	-759.426138	-173.072616	-164.7497813	-14.1	-5.8
74	CF2=CF2 D2H	-475.0893526	-1.71958407	-475.484857	-701.100759	-693.9593991	-42.5	-35.4
75	cl2c=ccl2 B3LYP	-1916.252768	-1.79592414	-1916.665830	-20.552060	-5.744239662	-8.0	6.8
76	cf3cn B3LYP	-430.0403303	-1.66167431	-430.422515	-525.403187	-519.8633822	-30.0	-24.5
77	PROPYNE C3V	-116.4566839	-0.66710234	-116.610117	189.767765	190.8704754	4.8	5.9
78	ALLENE D2D	-116.4573738	-0.66047852	-116.609284	190.299714	191.4024243	-0.1	1.0
79	CYCLOPROPENE C2V	-116.4172178	-0.66953642	-116.571211	291.196716	292.2994258	14.2	15.3
80	PROPENE CS	-117.6928794	-0.68995818	-117.851570	35.776767	36.87947665	15.7	16.8
81	CYCLOPROPANE D3H	-117.6787702	-0.69547363	-117.838729	71.970955	73.07366528	18.8	19.9
82	PROPANE C2V	-118.9114898	-0.72302726	-119.077786	-78.564102	-77.46139231	26.0	27.1
83	TRANS-1,3-BUTADIENE C2H	-155.7201722	-0.89332711	-155.925637	124.082428	125.5527079	14.0	15.5
84	Dimethyl acetylene	-155.7064956	-0.8993504	-155.913346	156.505340	157.97562	10.9	12.4
85	Methylene cyclopropane.	-155.687232	-0.89936052	-155.894085	205.671299	207.1415794	5.3	6.7
86	Bicyclo[1.1.0]butane. C2v	-155.6707082	-0.91075795	-155.880183	244.104395	245.5746753	27.0	28.4
87	CYCLOBUTENE b3lyp	-155.6962883	-0.90189157	-155.903723	182.728495	184.198775	26.2	27.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.9199948	-0.9307761	-157.134073	58.908118	60.37839784	30.5	31.9
89	Isobutene. Single	-156.9381768	-0.92710461	-157.151411	8.599475	10.0697554	25.3	26.8
90	Trans butane	-158.1518186	-0.95748014	-158.372039	-89.880468	-88.41018844	35.6	37.1
91	isobutane B3LYP/6-31G*	-158.1527966	-0.9608365	-158.373789	-95.769236	-94.298956	38.5	40.0
92	Spiropentane. D2d	-194.9211584	-1.13941834	-195.183225	209.714722	211.5525721	24.4	26.2
93	Benzene B3LYP	-231.8560074	-1.31101238	-232.157540	88.717906	90.92332554	6.3	8.5
94	DIFLUOROMETHANE C2V	-238.7616157	-0.88310382	-238.964730	-457.707099	-454.1364185	-7.1	-3.5
95	HCF3 TRI-FLUOROMETHANE	-337.9450932	-1.19725879	-338.220463	-708.527894	-703.3556585	-11.5	-6.3
96	CH2CL2 C2V	-959.3351171	-0.90752622	-959.543848	-88.753071	-81.34916052	6.6	14.0
97	chcl3 B3LYP/6-31G*	-1418.780122	-1.24482138	-1419.066431	-95.307371	-84.38529106	8.0	19.0
98	METHYLAMINE b3lyp	-95.69929605	-0.5340365	-95.822124	-13.934961	-13.5673914	9.1	9.4
99	Acetonitrile. CH3-CN.	-132.5519767	-0.71144047	-132.715608	67.659668	68.39480828	-7.7	-6.9
100	NITRO METHANE	-244.7010407	-1.17704921	-244.971762	-91.049384	-88.7914542	-16.6	-14.3
101	Methyl-nitrite. CH3-O-N=O.	-244.6967829	-1.16823832	-244.965478	-78.278205	-76.02027472	-11.8	-9.5
102	Methylsilane. CH3-SiH3.	-330.9937692	-0.58393952	-331.128075	-6.677975	-4.525064878	22.6	24.8
103	Formic Acid.	-189.5422603	-0.84910156	-189.737554	-386.884280	-384.6263501	-8.2	-6.0
104	Methyl formate.	-228.7701828	-1.08059656	-229.018720	-364.442959	-361.8174586	-8.8	-6.2
105	acetamide ch3cohn2	-208.9257776	-1.04849216	-209.166931	-239.544154	-237.8638336	-1.1	0.6

106	Aziridine. (cyclic	-133.7020954	-0.7426368	-133.872902	135.461661	136.1968007	9.1	9.8
107	Cyanogen. NCCN.	-185.4006607	-0.95491064	-185.620290	275.327007	276.0621471	-31.4	-30.6
108	DIMETHYLAMINE b3lyp	-134.9310071	-0.76691898	-135.107398	-2.968888	-2.23374757	15.4	16.2
109	TRANS ETHYLAMINE	-134.9425232	-0.76807832	-135.119181	-32.967032	-32.23189194	14.3	15.0
110	KETENE B3LYP	-152.3976055	-0.74437653	-152.568812	-65.435427	-63.75510744	-18.2	-16.5
111	OXIRANE B3LYP	-153.5674887	-0.77464452	-153.745657	-46.803804	-45.12348379	5.9	7.6
112	Acetaldehyde B3LYP	-153.6130606	-0.76738158	-153.789558	-165.186060	-163.5057397	0.9	2.6
113	Glyoxal, O=CH-CH=O.	-227.5414263	-1.04799799	-227.782466	-226.937742	-224.3122424	-14.8	-12.2
114	ETHANOL TRANS	-154.809745	-0.79713578	-154.993086	-217.868446	-216.1881264	17.3	19.0
115	DIMETHYL ETHER,	-154.7930493	-0.79431421	-154.975742	-173.172745	-171.4924254	10.9	12.6
116	Thiooxirane. (cyclic	-476.4991111	-0.86017649	-476.696952	94.271707	97.34354202	12.3	15.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.8310024	-1.21684115	-553.110876	-123.382698	-119.3656829	28.1	32.1
118	Thioethanol. CH3-CH2-SH.	-477.7182137	-0.87894449	-477.920371	-20.730425	-17.65858957	25.7	28.8
119	ch3sch3 B3LYP	-477.7164098	-0.88108356	-477.919059	-14.760264	-11.68842862	22.5	25.5
120	Vinyl fluoride,	-177.6133801	-0.7720759	-177.790958	-144.059538	-141.7228431	-5.2	-2.8
121	Ethyl chloride.	-539.1291527	-0.81306466	-539.316158	-97.086618	-92.83330847	15.0	19.3
122	Vinyl chloride,	-537.9053923	-0.78459782	-538.085850	27.258600	31.51190956	4.2	8.5
123	h2c=chcn B3LYP	-170.5704606	-0.91572134	-170.781076	178.416751	179.5194614	-2.3	-1.2
124	ACETONE B3LYP	-192.8651918	-1.00119818	-193.095467	-207.551761	-205.5038711	9.6	11.6
125	CH3COOH ACETIC	-228.7957595	-1.07949373	-229.044043	-431.382652	-428.7571518	1.2	3.9
126	CH3CFO HCCO	-252.8084844	-1.08749044	-253.058607	-447.921526	-444.6396511	-5.7	-2.4
127	ch3c(o)cl hcco	-613.0875943	-1.10500937	-613.341746	-246.152924	-240.9544342	-3.5	1.7
128	ch3ch2ch2cl B3LYP	-578.3695882	-1.04779125	-578.610580	-108.753813	-104.1329326	23.0	27.7
129	Isopropyl alcohol,	-194.0550102	-1.03396668	-194.292823	-245.272103	-243.2242133	27.5	29.6
130	Methyl ethyl	-194.0386005	-1.0281837	-194.275083	-198.147620	-196.0997297	18.2	20.2
131	Trimethyl Amine.	-174.1650556	-1.00491774	-174.396187	-2.534047	-1.431337108	21.3	22.4
132	FURAN B3LYP	-229.6831597	-1.19197032	-229.957313	-34.143132	-31.72767151	0.6	3.0
133	Thiophene b3lyp	-552.6045053	-1.28527857	-552.900119	126.871150	130.6781249	11.8	15.6
134	PYROLE PLANAR	-209.832397	-1.1627314	-210.099825	107.365504	108.8357845	-1.0	0.5
135	C2v Pyridine	-247.8867397	-1.35713931	-248.198882	131.656919	133.4947694	-8.9	-7.1
136	H2 B3LYP/6-31G*	-1.16127204	-0.03603653	-1.169560	6.051214	6.051214312	6.1	6.1
137	SH b3lyp/6-31G*	-398.6014221	-0.36874809	-398.686234	145.885262	148.221957	2.8	5.1
138	CCH B3LYP	-76.48996254	-0.3972694	-76.581335	575.830569	576.5657085	10.6	11.3
139	C2H3 CS,2-A'	-77.77099458	-0.41818714	-77.867178	300.360764	301.0959045	0.8	1.5
140	ch3co hcco	-152.9709581	-0.74523307	-153.142362	-18.908786	-17.22846573	-8.9	-7.2
141	H2COH C1	-114.9111121	-0.53083662	-115.033204	-16.200178	-14.88742781	1.0	2.3
142	ch3o CS,	-114.9033162	-0.50374497	-115.019178	17.054220	18.36697009	-0.1	1.2

143	ch3ch2o 2A"	-154.1488051	-0.73736962	-154.318400	-8.186609	-6.506288959	7.3	9.0
144	ch3s 2-A'	-437.8434689	-0.6061739	-437.982889	129.476072	132.180337	4.8	7.5
145	c2h5 staggered	-79.01055997	-0.44896519	-79.113822	131.110233	131.8453729	10.2	10.9
146	(ch3)2ch Cs	-118.2558405	-0.68455825	-118.413289	106.225279	107.3279891	16.3	17.4
147	TERT-BUTYL RADICAL	-157.5011424	-0.92229584	-157.713270	79.726872	81.19715174	28.3	29.7
148	NO2 RADICAL	-204.8385469	-0.94290487	-205.055415	-0.588838	1.301522171	-33.6	-31.8

MAD	**11.5**	**12.3**
LD	**-42.5**	**46.0**

Table S5.4b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 50% and a_C = 23%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498546	0.000000	-0.498546
2	li	-7.470464	-0.014860	-7.473881
3	be	-14.640678	-0.056177	-14.653599
4	b	-24.621571	-0.080467	-24.640078
5	c	-37.806402	-0.107501	-37.831128
6	n	-54.540922	-0.138451	-54.572766
7	o	-75.008430	-0.196892	-75.053716
8	f	-99.658904	-0.261104	-99.718958
9	na	-162.168385	-0.175692	-162.208794
10	al	-242.252950	-0.225544	-242.304825
11	si	-289.254666	-0.256179	-289.313587
12	p	-341.137804	-0.285861	-341.203552
13	s	-397.974732	-0.328141	-398.050205
14	cl	-459.995339	-0.299461	-460.064215

Table S5.5a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 23%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05159256	-0.04803572	-8.062641	145.573951	145.5739506	6.2	6.2
2	BERYLLIUM HYDRIDE	-15.22772523	-0.05652599	-15.240726	318.697141	318.6971413	-23.1	-23.1
3	DOUBLET CH	-38.42838005	-0.14862575	-38.462564	598.461045	598.8286154	2.2	2.6
4	CH2 3-B1	-39.0919636	-0.1677071	-39.130536	395.267990	395.6355602	3.2	3.6
5	Singlet methylene,	-39.0699112	-0.18920873	-39.113429	438.570428	438.9379976	8.5	8.8
6	Methyl radical,	-39.76637146	-0.21364102	-39.815509	151.362879	151.7304489	4.9	5.3
7	ch4 //b3lyp/6-31G*	-40.43271882	-0.25666493	-40.491752	-64.318626	-63.9510564	10.6	10.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.16048404	-0.19208525	-55.204664	356.214824	356.214824	-0.3	-0.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.80418632	-0.24726258	-55.861057	185.525970	185.5259698	-3.2	-3.2
10	AMMONIA, //b3lyp/6-31G*	-56.47174927	-0.30289296	-56.541415	-39.405377	-39.4053771	6.6	6.6
11	OH RADICAL	-75.66021181	-0.26450655	-75.721048	40.566538	41.51171808	1.2	2.2
12	Water //b3lyp/6-31G*	-76.33974536	-0.33546007	-76.416901	-230.313480	-229.3683	11.5	12.5
13	HYDROGEN FLUORIDE,	-100.3594797	-0.34557976	-100.438963	-266.063114	-264.461559	6.3	7.9
14	SIH2 singlet	-290.479625	-0.3127028	-290.551547	273.956776	275.7421159	1.2	2.9
15	SIH2 3B1	-290.4522401	-0.2893	-290.518779	360.998911	362.7842514	0.3	2.1
16	SIH3 c3v	-291.0948314	-0.31793467	-291.167956	201.914011	203.6993505	1.5	3.3
17	SIH4 //b3lyp/6-31G*	-291.7386941	-0.34581064	-291.818231	41.892491	43.67783135	7.6	9.4
18	ph2 doublet	-342.3639163	-0.35257935	-342.445010	137.144780	137.1447803	-1.3	-1.3
19	PH3 c3v	-342.9927984	-0.38495469	-343.081338	15.236634	15.2366336	9.8	9.8
20	SH2 //b3lyp/6-31G*	-399.2409719	-0.40658252	-399.334486	-10.839328	-8.502632547	9.7	12.0
21	HCL //b3lyp/6-31G*	-460.6516974	-0.34411495	-460.730844	-88.620035	-85.10186453	3.8	7.4
22	DILITHIUM //b3lyp/6-31G*	-14.967616	-0.05998626	-14.981413	230.006475	230.0064754	14.1	14.1
23	Lithium Fluoride,	-107.3254631	-0.37613805	-107.411975	-337.545152	-335.9435969	-2.4	-0.8
24	ACETYLENE //b3lyp/6-31g*	-77.20404938	-0.43135612	-77.303261	233.234042	233.9691817	6.5	7.2
25	ETHYLENE //b3lyp/6-31g*	-78.44702793	-0.45170903	-78.550921	63.822415	64.55755525	11.5	12.3
26	ETHANE //b3lyp/6-31g*	-79.67129005	-0.48516539	-79.782878	-65.669438	-64.93429811	18.4	19.2
27	CYANO RADICAL,	-92.5815221	-0.47231091	-92.690154	445.874352	446.241922	7.0	7.3
28	HYDROGEN CYANIDE	-93.29277827	-0.47753707	-93.402612	126.663271	127.0308408	-5.1	-4.8
29	CARBON MONOXIDE	-113.1855737	-0.48800956	-113.297816	-111.733635	-110.4208853	-1.3	0.0
30	HCO BENT	-113.7126599	-0.51077916	-113.830139	33.758095	35.07084455	-8.1	-6.8
31	H2CO //b3lyp/6-31g*	-114.3557193	-0.53036167	-114.477702	-109.684165	-108.3714145	-0.9	0.4

32	METHANOL //b3lyp/6-31g*	-115.5632044	-0.55935963	-115.691857	-189.505675	-188.1929247	11.3	12.6
33	Nitrogen N2,	-109.3928725	-0.51212368	-109.510661	-3.060818	-3.060817952	-3.1	-3.1
34	H2NNH2 //b3lyp/6-31g*	-111.7043578	-0.57473912	-111.836548	102.228647	102.2286465	6.8	6.8
35	NO radical,	-129.7439289	-0.5545991	-129.871487	84.165791	85.11097086	-6.2	-5.3
36	O2 //b3lyp/6-31g*	-150.1580926	-0.61865502	-150.300383	-6.553003	-4.662642619	-6.6	-4.7
37	HYDROGEN PEROXIDE	-151.3761769	-0.65013894	-151.525709	-119.416196	-117.5258361	16.6	18.5
38	F2 //b3lyp/6-31g*	-199.3352411	-0.67910751	-199.491436	15.020371	18.22348093	15.0	18.2
39	CO2 D*H	-188.3756513	-0.82017809	-188.564292	-411.361636	-409.1037065	-18.1	-15.8
40	na2 //b3lyp/6-31G*	-324.3559692	-0.37920175	-324.443186	142.830263	142.8302628	0.6	0.6
41	SI2 3-SGG	-578.6129145	-0.57121761	-578.744295	588.538656	592.1093361	3.2	6.8
42	P2 //b3lyp/6-31g*	-682.4232118	-0.72761372	-682.590563	151.449191	151.4491911	7.9	7.9
43	S2 //b3lyp/6-31g*	-796.0844477	-0.7730152	-796.262241	127.625518	132.298908	-0.8	3.9
44	CL2 //b3lyp/6-31g*	-920.0637099	-0.66724073	-920.217175	8.281021	15.31736105	8.3	15.3
45	Sodium Chloride	-622.305424	-0.51981228	-622.424981	-173.429343	-169.9111726	9.0	12.5
46	SIO //b3lyp/6-31g*	-364.5244634	-0.63350962	-364.670171	-96.196918	-93.46639817	6.7	9.5
47	Carbon monosulfide,	-436.014937	-0.59265628	-436.151248	287.263275	289.9675399	7.4	10.1
48	OS //b3lyp/6-31g*	-473.1414977	-0.70376687	-473.303364	2.471120	5.75299528	-2.5	0.7
49	CLO 2-PI	-535.0743915	-0.62395503	-535.217901	106.708572	111.171922	5.5	9.9
50	CLF 1-SG	-559.724553	-0.67013449	-559.878684	-52.538605	-47.41887973	2.7	7.8
51	si2h6 //b3lyp/6-31g*	-582.3024843	-0.67224075	-582.457100	97.955028	101.5257081	18.0	21.6
52	Methyl chloride,	-499.8852203	-0.57381452	-500.017198	-74.274151	-70.38841087	7.7	11.6
53	H3C-SH METHANETHIOL	-438.4773984	-0.63877195	-438.624316	-5.672948	-2.96868251	17.3	20.0
54	HOCl //b3lyp/6-31g*	-535.722959	-0.66191236	-535.875199	-67.132274	-62.66892373	7.3	11.8
55	SO2 //b3lyp/6-31G*	-548.3172183	-1.0630498	-548.561720	-280.987088	-276.760033	16.1	20.3
56	BF3 PLANAR	-324.2944185	-1.09556987	-324.546400	-1144.214990	-1139.27905	-8.7	-3.7
57	bcl3 B3LYP	-1405.08859	-1.13623547	-1405.349924	-412.390591	-401.7048061	-9.5	1.2
58	ALf3 B3LYP	-541.846361	-1.23697121	-542.130864	-1190.357908	-1184.660573	18.8	24.5
59	alcl3 B3LYP	-1622.698521	-1.23858696	-1622.983396	-581.852916	-570.4057355	2.7	14.1
60	cf4 B3LYP	-437.1202535	-1.49729737	-437.464632	-941.569166	-934.7953764	-8.5	-1.8
61	ccl4 B3LYP	-1878.217709	-1.57664425	-1878.580337	-83.697454	-69.25720441	12.1	26.6
62	O=C=S. Singlet	-511.2625404	-0.91186987	-511.472270	-156.150559	-152.5011138	-17.7	-14.0
63	CS2 B3LYP	-834.146107	-1.01085746	-834.378604	103.958084	108.9990439	-12.8	-7.7
64	COF2 B3LYP	-312.7257913	-1.15963127	-312.992506	-619.428775	-614.9129148	4.4	8.9
65	sif4 B3LYP	-688.7141951	-1.59863493	-689.081881	-1572.106339	-1563.914779	42.9	51.1
66	sicl4, td	-2129.793582	-1.63721016	-2130.170141	-636.400080	-620.5420596	26.3	42.2
67	nno B3LYP	-184.4349582	-0.88232659	-184.637893	60.092328	61.03750822	-21.9	-21.0
68	clno B3LYP	-589.7782928	-0.95175676	-589.997197	45.163881	49.62723099	-6.7	-2.3

69	nf3 c3v	-353.7605293	-1.27983539	-354.054891	-138.758234	-133.953569	-6.5	-1.7
70	pf3 c3v	-640.6217264	-1.33512826	-640.928806	-936.863244	-932.0585787	21.7	26.5
71	ozone 1-a1	-225.1444289	-1.06294363	-225.388906	153.769135	156.6046745	11.1	13.9
72	f2o B3LYP	-274.4019406	-1.00375513	-274.632804	35.774230	39.92252018	11.1	15.2
73	CLF3, C2V	-759.091051	-1.42119068	-759.417925	-160.000687	-151.6778524	-1.0	7.3
74	CF2=CF2 D2H	-475.0840434	-1.70613631	-475.476455	-690.459375	-683.318015	-31.9	-24.8
75	cl2c=ccl2 B3LYP	-1916.252527	-1.78135295	-1916.662238	-14.237724	0.570095977	-1.7	13.1
76	cf3cn B3LYP	-430.0354254	-1.64790688	-430.414444	-513.375889	-507.8360843	-18.0	-12.5
77	PROPYNE C3V	-116.456044	-0.66107504	-116.608091	194.289757	195.3924668	9.4	10.5
78	ALLENE D2D	-116.4565951	-0.65454572	-116.607141	195.128902	196.2316123	4.8	5.9
79	CYCLOPROPENE C2V	-116.4166121	-0.66368221	-116.569259	295.524261	296.6269707	18.5	19.6
80	PROPENE CS	-117.6927392	-0.68408	-117.850078	39.135379	40.23808898	19.1	20.2
81	CYCLOPROPANE D3H	-117.6788055	-0.68976893	-117.837452	74.764244	75.8669539	21.6	22.7
82	PROPANE C2V	-118.9118744	-0.71714824	-119.076819	-76.343662	-75.24095208	28.3	29.4
83	TRANS-1,3-BUTADIENE C2H	-155.7195786	-0.88547128	-155.923237	129.400718	130.8709977	19.4	20.8
84	Dimethyl acetylene	-155.7059463	-0.8914548	-155.910981	161.731388	163.2016683	16.1	17.6
85	Methylene cyclopropane.	-155.6867526	-0.89167536	-155.891838	210.586564	212.0568441	10.2	11.6
86	Bicyclo[1.1.0]butane. C2v	-155.67042	-0.90315423	-155.878145	248.468512	249.9387919	31.3	32.8
87	CYCLOBUTENE b3lyp	-155.6959389	-0.89413806	-155.901591	187.343640	188.8139201	30.9	32.3
88	CYCLOBUTANE b3lyp/6-31G*	-156.9202012	-0.92309458	-157.132513	62.259642	63.7299221	33.8	35.3
89	Isobutene. Single	-156.9381587	-0.91928034	-157.149593	12.626416	14.0966961	29.4	30.8
90	Trans butane	-158.1523252	-0.9496772	-158.370751	-87.004825	-85.53454498	38.5	40.0
91	isobutane B3LYP/6-31G*	-158.1533185	-0.95299684	-158.372508	-92.911536	-91.44125625	41.4	42.9
92	Spiropentane. D2d	-194.9210018	-1.12998903	-195.180899	214.649433	216.4872829	29.3	31.1
93	Benzene B3LYP	-231.8549911	-1.29972856	-232.153929	96.365360	98.57078008	13.9	16.1
94	DIFLUOROMETHANE C2V	-238.7593415	-0.87636798	-238.960906	-453.139017	-449.5683371	-2.5	1.0
95	HCF3 TRI-FLUOROMETHANE	-337.9416932	-1.18820217	-338.214980	-702.364186	-697.191951	-5.3	-0.1
96	CH2CL2 C2V	-959.3353523	-0.90039504	-959.542443	-86.384197	-78.98028713	9.0	16.4
97	chcl3 B3LYP/6-31G*	-1418.780324	-1.23496198	-1419.064365	-91.889422	-80.96734165	11.5	22.4
98	METHYLAMINE b3lyp	-95.6989262	-0.52969174	-95.820755	-10.555886	-10.18831566	12.5	12.8
99	Acetonitrile. CH3-CN.	-132.55076	-0.70491355	-132.712890	73.915817	74.65095653	-1.4	-0.7
100	NITRO METHANE	-244.6972047	-1.16614134	-244.965417	-78.077884	-75.81995379	-3.6	-1.3
101	Methyl-nitrite. CH3-O-N=O.	-244.6929783	-1.15693818	-244.959074	-65.152267	-62.89433689	1.4	3.6
102	Methylsilane. CH3-SiH3.	-330.9944778	-0.57965531	-331.127798	-6.598249	-4.44533947	22.7	24.8
103	Formic Acid.	-189.5398242	-0.84166941	-189.733408	-379.418927	-377.1609971	-0.8	1.5
104	Methyl formate.	-228.7678248	-1.07117824	-229.014196	-356.169395	-353.5438948	-0.5	2.1
105	acetamide ch3cohn2	-208.9240083	-1.03948958	-209.163091	-231.719716	-230.0393962	6.8	8.4

106	Aziridine. (cyclic	-133.7014128	-0.73642172	-133.870790	140.365931	141.1010706	14.0	14.7
107	Cyanogen. NCCN.	-185.397633	-0.94532773	-185.615058	287.436951	288.1720907	-19.3	-18.5
108	DIMETHYLAMINE b3lyp	-134.9307391	-0.76064155	-135.105687	1.123737	1.858876579	19.5	20.3
109	TRANS ETHYLAMINE	-134.942265	-0.76180026	-135.117479	-28.900046	-28.16490606	18.4	19.1
110	KETENE B3LYP	-152.3956965	-0.73755051	-152.565333	-58.528901	-56.84858083	-11.2	-9.6
111	OXIRANE B3LYP	-153.5662109	-0.7680971	-153.742873	-41.483940	-39.80362034	11.2	12.9
112	Acetaldehyde B3LYP	-153.6117548	-0.76071654	-153.786720	-159.721524	-158.0412044	6.4	8.1
113	Glyoxal, O=CH-CH=O.	-227.5385015	-1.03857423	-227.777374	-217.411759	-214.7862595	-5.3	-2.7
114	ETHANOL TRANS	-154.8089735	-0.79067328	-154.990828	-213.690023	-212.0097033	21.5	23.1
115	DIMETHYL ETHER,	-154.7922433	-0.78781675	-154.973441	-168.882841	-167.2025215	15.2	16.9
116	Thiooxirane. (cyclic	-476.4989804	-0.8534292	-476.695269	97.667846	100.7396806	15.7	18.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.829917	-1.20670715	-553.107460	-116.812248	-112.7952329	34.6	38.7
118	Thioethanol. CH3-CH2-SH.	-477.7185318	-0.87222375	-477.919143	-18.289775	-15.21793999	28.2	31.2
119	ch3sch3 B3LYP	-477.7166679	-0.87430177	-477.917757	-12.125218	-9.053383091	25.1	28.2
120	Vinyl fluoride,	-177.6118566	-0.76571007	-177.787970	-139.349581	-137.0128865	-0.4	1.9
121	Ethyl chloride.	-539.1294919	-0.80659416	-539.315009	-94.889835	-90.63652505	17.2	21.5
122	Vinyl chloride,	-537.9051668	-0.77805864	-538.084120	30.740425	34.9937345	7.7	12.0
123	h2c=chcn B3LYP	-170.5687597	-0.90717825	-170.777411	186.736205	187.8389145	6.0	7.1
124	ACETONE B3LYP	-192.8640197	-0.9926287	-193.092324	-201.474609	-199.4267192	15.7	17.7
125	CH3COOH ACETIC	-228.7934819	-1.07023443	-229.039636	-423.416441	-420.7909411	9.2	11.8
126	CH3CFO HCCO	-252.8059427	-1.07834876	-253.053963	-440.478258	-437.1963825	1.8	5.1
127	ch3c(o)cl hcco	-613.0861859	-1.09550948	-613.338153	-239.393527	-234.195037	3.3	8.5
128	ch3ch2ch2cl B3LYP	-578.3700506	-1.03939211	-578.609111	-105.902100	-101.28122	25.9	30.5
129	Isopropyl alcohol,	-194.0543709	-1.02554231	-194.290246	-240.442524	-238.3946341	32.4	34.4
130	Methyl ethyl	-194.0379157	-1.01976034	-194.272461	-193.199190	-191.1513002	23.1	25.2
131	Trimethyl Amine.	-174.1649029	-0.99663499	-174.394129	2.280263	3.382973192	26.1	27.2
132	FURAN B3LYP	-229.6812144	-1.18161867	-229.952987	-25.623999	-23.2085389	9.1	11.5
133	Thiophene b3lyp	-552.6036514	-1.27453583	-552.896795	133.728112	137.5350865	18.7	22.5
134	PYROLE PLANAR	-209.8310421	-1.15278911	-210.096184	115.435215	116.905495	7.1	8.5
135	C2v Pyridine	-247.8850438	-1.34533168	-248.194470	141.322830	143.1606798	0.7	2.6
136	H2 B3LYP/6-31G*	-1.16130598	-0.03573137	-1.169524	6.385353	6.385353295	6.4	6.4
137	SH b3lyp/6-31G*	-398.6015617	-0.36638743	-398.685831	146.414698	148.7513933	3.3	5.7
138	CCH B3LYP	-76.48910192	-0.39328072	-76.579556	579.767691	580.5028311	14.5	15.2
139	C2H3 CS,2-A'	-77.77060364	-0.41441312	-77.865919	303.174090	303.9092296	3.6	4.3
140	ch3co hcco	-152.9693632	-0.73859308	-153.139240	-12.820068	-11.13974797	-2.8	-1.1
141	H2COH C1	-114.9100494	-0.52645492	-115.031134	-12.447154	-11.13440421	4.7	6.0
142	ch3o CS,	-114.9024822	-0.49941839	-115.017348	20.173559	21.48630931	3.0	4.3

143	ch3ch2o 2A"	-154.1480667	-0.73105137	-154.316209	-4.302078	-2.621757739	11.2	12.9
144	ch3s 2-A'	-437.8435939	-0.60175469	-437.981998	131.100522	133.8047869	6.4	9.1
145	c2h5 staggered	-79.0107162	-0.44532771	-79.113142	132.643484	133.3786244	11.7	12.5
146	(ch3)2ch Cs	-118.2560627	-0.67895812	-118.412223	108.584307	109.6870171	18.6	19.7
147	TERT-BUTYL RADICAL	-157.5014599	-0.91470641	-157.711842	82.850580	84.32085953	31.4	32.9
148	NO2 RADICAL	-204.8341194	-0.93357067	-205.048841	13.052018	14.94237752	-20.0	-18.1

MAD	**11.9**	**13.4**
LD	**42.9**	**51.1**

Table S5.5b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 23%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498591	0.000000	-0.498591
2	li	-7.470568	-0.014791	-7.473970
3	be	-14.640835	-0.055464	-14.653592
4	b	-24.621662	-0.079648	-24.639981
5	c	-37.806444	-0.106615	-37.830966
6	n	-54.540989	-0.137518	-54.572618
7	o	-75.008104	-0.195635	-75.053100
8	f	-99.658263	-0.259516	-99.717951
9	na	-162.167991	-0.174653	-162.208161
10	al	-242.252807	-0.224167	-242.304365
11	si	-289.254661	-0.254643	-289.313229
12	p	-341.138006	-0.284170	-341.203365
13	s	-397.974936	-0.326181	-398.049958
14	cl	-459.995599	-0.297393	-460.063999

Table S5.6a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 24%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0507045	-0.04803715	-8.062233	145.621272	145.6212715	6.3	6.3
2	BERYLLIUM HYDRIDE	-15.22664334	-0.05651807	-15.240208	319.018671	319.018671	-22.8	-22.8
3	DOUBLET CH	-38.4264023	-0.14862959	-38.462073	598.354958	598.7225281	2.1	2.5
4	CH2 3-B1	-39.08981073	-0.16770535	-39.130060	395.124222	395.491792	3.1	3.5
5	Singlet methylene,	-39.06758338	-0.18920498	-39.112993	438.322726	438.6902956	8.2	8.6
6	Methyl radical,	-39.76378561	-0.21364459	-39.815060	151.146552	151.5141224	4.7	5.1
7	ch4 //b3lyp/6-31G*	-40.42977249	-0.25665908	-40.491371	-64.712170	-64.34459968	10.2	10.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15810353	-0.19209544	-55.204206	355.965982	355.965982	-0.5	-0.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.80139012	-0.24726964	-55.860735	184.921813	184.9218134	-3.8	-3.8
10	AMMONIA, //b3lyp/6-31G*	-56.46856997	-0.30289437	-56.541265	-40.460720	-40.46071993	5.6	5.6
11	OH RADICAL	-75.65720147	-0.26451699	-75.720686	39.876788	40.82196799	0.5	1.5
12	Water //b3lyp/6-31G*	-76.3363414	-0.33546704	-76.416853	-231.830479	-230.885299	10.0	10.9
13	HYDROGEN FLUORIDE,	-100.3558566	-0.34558913	-100.438798	-267.262109	-265.6605545	5.1	6.7
14	SIH2 singlet	-290.4736502	-0.31269481	-290.548697	274.167782	275.9531218	1.4	3.2
15	SIH2 3B1	-290.4464588	-0.28927245	-290.515884	361.328491	363.1138312	0.7	2.5
16	SIH3 c3v	-291.0886753	-0.31791933	-291.164976	202.468262	204.253602	2.1	3.8
17	SIH4 //b3lyp/6-31G*	-291.7322009	-0.34580147	-291.815193	42.595817	44.38115738	8.3	10.1
18	ph2 doublet	-342.3574842	-0.35257882	-342.442103	137.342811	137.3428113	-1.1	-1.1
19	PH3 c3v	-342.9860385	-0.38494551	-343.078425	15.450713	15.45071319	10.0	10.0
20	SH2 //b3lyp/6-31G*	-399.2339531	-0.40657685	-399.331532	-11.076472	-8.739776633	9.4	11.8
21	HCL //b3lyp/6-31G*	-460.6444261	-0.34411289	-460.727013	-88.922903	-85.40473302	3.5	7.1
22	DILITHIUM //b3lyp/6-31G*	-14.96627767	-0.05998199	-14.980673	229.903609	229.9036088	14.0	14.0
23	Lithium Fluoride,	-107.3212868	-0.3761541	-107.411564	-339.120728	-337.5191733	-4.0	-2.4
24	ACETYLENE //b3lyp/6-31g*	-77.19960024	-0.43133689	-77.303121	230.813959	231.5490988	4.0	4.8
25	ETHYLENE //b3lyp/6-31g*	-78.44204195	-0.45169467	-78.550449	62.274371	63.00951135	10.0	10.7
26	ETHANE //b3lyp/6-31g*	-79.66576796	-0.48515381	-79.782205	-66.690074	-65.95493367	17.4	18.1
27	CYANO RADICAL,	-92.57725085	-0.47221383	-92.690582	441.905835	442.2734049	3.0	3.4
28	HYDROGEN CYANIDE	-93.2881313	-0.47752134	-93.402736	123.492734	123.8603035	-8.3	-7.9
29	CARBON MONOXIDE	-113.1807241	-0.48800316	-113.297845	-114.846160	-113.5334098	-4.4	-3.1
30	HCO BENT	-113.7075764	-0.51076734	-113.830161	30.665484	31.97823397	-11.2	-9.9
31	H2CO //b3lyp/6-31g*	-114.3503119	-0.53035674	-114.477597	-112.444725	-111.1319747	-3.7	-2.3

32	METHANOL //b3lyp/6-31g*	-115.5572426	-0.55935715	-115.691488	-191.573490	-190.2607404	9.3	10.6
33	Nitrogen N2,	-109.388034	-0.51210775	-109.510940	-6.691636	-6.691635554	-6.7	-6.7
34	H2NNH2 //b3lyp/6-31g*	-111.6983889	-0.57473882	-111.836326	99.911982	99.91198199	4.5	4.5
35	NO radical,	-129.7386476	-0.55458942	-129.871749	80.385440	81.33062	-10.0	-9.0
36	O2 //b3lyp/6-31g*	-150.1523694	-0.61865348	-150.300846	-11.052853	-9.162492845	-11.1	-9.2
37	HYDROGEN PEROXIDE	-151.3698136	-0.65014458	-151.525848	-123.066782	-121.1764221	12.9	14.8
38	F2 //b3lyp/6-31g*	-199.3284842	-0.67911173	-199.491471	11.662878	14.86598759	11.7	14.9
39	CO2 D*H	-188.3677389	-0.82016432	-188.564578	-416.791184	-414.5332539	-23.5	-21.2
40	na2 //b3lyp/6-31G*	-324.3475408	-0.37919623	-324.438548	142.688075	142.6880749	0.4	0.4
41	SI2 3-SGG	-578.6019312	-0.57119811	-578.739019	587.848545	591.4192247	2.5	6.1
42	P2 //b3lyp/6-31g*	-682.4110671	-0.72758921	-682.585688	149.381583	149.3815831	5.9	5.9
43	S2 //b3lyp/6-31g*	-796.0713772	-0.77300523	-796.256898	125.665695	130.3390846	-2.8	1.9
44	CL2 //b3lyp/6-31g*	-920.0495798	-0.66723297	-920.209716	7.145315	14.18165456	7.1	14.2
45	Sodium Chloride	-622.2940944	-0.51981521	-622.418850	-173.852834	-170.334664	8.6	12.1
46	SIO //b3lyp/6-31g*	-364.5159373	-0.63351936	-364.667982	-99.363655	-96.63313528	3.6	6.3
47	Carbon monosulfide,	-436.0064529	-0.59263523	-436.148685	284.603572	287.307837	4.7	7.4
48	OS //b3lyp/6-31g*	-473.1320911	-0.70375917	-473.300993	-0.940141	2.341734327	-6.0	-2.7
49	CLO 2-PI	-535.0644725	-0.62391012	-535.214211	104.394892	108.8582419	3.1	7.6
50	CLF 1-SG	-559.7140899	-0.6701342	-559.874922	-54.654977	-49.53525195	0.6	5.7
51	si2h6 //b3lyp/6-31g*	-582.2898657	-0.67222359	-582.451199	98.904507	102.4751873	19.0	22.6
52	Methyl chloride,	-499.8753942	-0.57380554	-500.013108	-75.290085	-71.40434494	6.7	10.6
53	H3C-SH METHANETHIOL	-438.4678121	-0.63876024	-438.621115	-6.655477	-3.95121156	16.4	19.1
54	HOCl //b3lyp/6-31g*	-535.7127061	-0.66191052	-535.871565	-69.593323	-65.12997344	4.9	9.3
55	SO2 //b3lyp/6-31G*	-548.3046709	-1.06303952	-548.559800	-287.225884	-282.9988286	9.8	14.1
56	BF3 PLANAR	-324.2824829	-1.09557109	-324.545420	-1147.768550	-1142.83261	-12.2	-7.3
57	bcl3 B3LYP	-1405.065701	-1.13621653	-1405.338392	-414.422888	-403.7371033	-11.5	-0.8
58	ALf3 B3LYP	-541.8308318	-1.23698037	-542.127707	-1194.094630	-1188.397295	15.1	20.8
59	alcl3 B3LYP	-1622.672041	-1.23857102	-1622.969298	-583.049328	-571.6021478	1.5	12.9
60	cf4 B3LYP	-437.1043373	-1.49728989	-437.463687	-947.012545	-940.2387549	-14.0	-7.2
61	ccl4 B3LYP	-1878.187187	-1.57661848	-1878.565576	-87.777116	-73.33686568	8.0	22.5
62	O=C=S. Singlet	-511.2509909	-0.91184736	-511.469834	-160.784287	-157.1348416	-22.3	-18.6
63	CS2 B3LYP	-834.1309099	-1.01082575	-834.373508	99.956823	104.9977829	-16.8	-11.7
64	COF2 B3LYP	-312.713883	-1.15962167	-312.992192	-624.904992	-620.3891315	-1.1	3.4
65	sif4 B3LYP	-688.6946466	-1.59863159	-689.078318	-1576.552982	-1568.361422	38.5	46.7
66	sicl4, td	-2129.759429	-1.63718397	-2130.152353	-638.410224	-622.5522036	24.3	40.2
67	nno B3LYP	-184.4270824	-0.88230287	-184.638835	53.079104	54.02428443	-28.9	-28.0
68	clno B3LYP	-589.7658637	-0.9517367	-589.994281	39.368914	43.83226362	-12.5	-8.0

69	nf3 c3v	-353.7477498	-1.2798295	-354.054909	-145.151015	-140.3463504	-12.9	-8.1
70	pf3 c3v	-640.6052061	-1.33512551	-640.925636	-940.871728	-936.0670626	17.7	22.5
71	ozone 1-a1	-225.1356504	-1.06291954	-225.390751	143.998108	146.8336476	1.3	4.2
72	f2o B3LYP	-274.3922135	-1.00375346	-274.633114	30.052833	34.20112273	5.4	9.5
73	CLF3, C2V	-759.073621	-1.42118915	-759.414706	-166.808744	-158.4859088	-7.8	0.5
74	CF2=CF2 D2H	-475.066089	-1.70612688	-475.475559	-697.427194	-690.2858344	-38.9	-31.7
75	cl2c=ccl2 B3LYP	-1916.21992	-1.7813214	-1916.647437	-19.607942	-4.800122464	-7.1	7.8
76	cf3cn B3LYP	-430.0184849	-1.6478828	-430.413977	-521.284409	-515.7446038	-25.9	-20.4
77	PROPYNE C3V	-116.4490097	-0.66105058	-116.607662	191.234745	192.3374554	6.3	7.4
78	ALLENE D2D	-116.4495573	-0.65452333	-116.606643	192.253439	193.3561494	1.9	3.0
79	CYCLOPROPENE C2V	-116.4095222	-0.6636643	-116.568802	292.542885	293.645595	15.6	16.7
80	PROPENE CS	-117.6851666	-0.68406015	-117.849341	36.887194	37.98990431	16.8	17.9
81	CYCLOPROPANE D3H	-117.6711641	-0.6897538	-117.836705	72.544173	73.64688282	19.4	20.5
82	PROPANE C2V	-118.9037674	-0.71713061	-119.075879	-78.058543	-76.95583259	26.5	27.6
83	TRANS-1,3-BUTADIENE C2H	-155.7099557	-0.88544311	-155.922462	125.859098	127.3293777	15.8	17.3
84	Dimethyl acetylene	-155.6963273	-0.89142505	-155.910269	158.023270	159.4935496	12.4	13.9
85	Methylene cyclopropane.	-155.6770674	-0.89165188	-155.891064	207.042486	208.5127657	6.6	8.1
86	Bicyclo[1.1.0]butane. C2v	-155.6606666	-0.9031343	-155.877419	244.799904	246.2701841	27.7	29.1
87	CYCLOBUTENE b3lyp	-155.6862292	-0.89411438	-155.900817	183.799538	185.2698181	27.3	28.8
88	CYCLOBUTANE b3lyp/6-31G*	-156.9099573	-0.92307302	-157.131495	59.356204	60.82648405	30.9	32.4
89	Isobutene. Single	-156.9279916	-0.91925478	-157.148613	9.624371	11.09465057	26.4	27.8
90	Trans butane	-158.1416324	-0.94965322	-158.369549	-89.425894	-87.9556141	36.1	37.6
91	isobutane B3LYP/6-31G*	-158.1426165	-0.95297294	-158.371330	-95.395737	-93.92545709	38.9	40.4
92	Spiropentane. D2d	-194.9086624	-1.1299641	-195.179854	210.424126	212.2619762	25.1	26.9
93	Benzene B3LYP	-231.841098	-1.29968992	-232.153024	90.377313	92.58273291	8.0	10.2
94	DIFLUOROMETHANE C2V	-238.7499328	-0.87636855	-238.960261	-456.105012	-452.5343318	-5.5	-1.9
95	HCF3 TRI-FLUOROMETHANE	-337.9290326	-1.1882002	-338.214201	-706.610477	-701.4382422	-9.6	-4.4
96	CH2CL2 C2V	-959.3186357	-0.90038152	-959.534727	-88.240887	-80.8369772	7.2	14.6
97	chcl3 B3LYP/6-31G*	-1418.756708	-1.23494274	-1419.053094	-94.772309	-83.85022939	8.6	19.5
98	METHYLAMINE b3lyp	-95.6931778	-0.5296856	-95.820302	-12.209982	-11.84241217	10.8	11.2
99	Acetonitrile. CH3-CN.	-132.543528	-0.70489206	-132.712702	70.171923	70.90706311	-5.1	-4.4
100	NITRO METHANE	-244.6859793	-1.16612071	-244.965848	-85.337554	-83.07962408	-10.9	-8.6
101	Methyl-nitrite. CH3-O-N=O.	-244.6817896	-1.15691614	-244.959450	-72.265749	-70.00781933	-5.7	-3.5
102	Methylsilane. CH3-SiH3.	-330.9854009	-0.57964112	-331.124515	-6.641693	-4.488782568	22.6	24.8
103	Formic Acid.	-189.5313658	-0.84166371	-189.733365	-383.984186	-381.7262562	-5.3	-3.1
104	Methyl formate.	-228.756795	-1.07116267	-229.013874	-361.397243	-358.7717432	-5.8	-3.1
105	acetamide ch3cohn2	-208.9131654	-1.03947546	-209.162640	-236.414172	-234.7338516	2.1	3.8

106	Aziridine. (cyclic	-133.6935653	-0.73640924	-133.870304	137.405266	138.1404055	11.0	11.8
107	Cyanogen. NCCN.	-185.3887078	-0.94529348	-185.615578	280.385452	281.1205918	-26.3	-25.6
108	DIMETHYLAMINE b3lyp	-134.922409	-0.76062814	-135.104960	-1.205194	-0.47005403	17.2	17.9
109	TRANS ETHYLAMINE	-134.9339313	-0.76178769	-135.116760	-31.250581	-30.51544112	16.0	16.8
110	KETENE B3LYP	-152.3882232	-0.73753473	-152.565232	-62.692612	-61.0122917	-15.4	-13.7
111	OXIRANE B3LYP	-153.5581616	-0.76808716	-153.742502	-44.940834	-43.2605138	7.8	9.5
112	Acetaldehyde B3LYP	-153.6037587	-0.76070509	-153.786328	-163.123760	-161.4434402	3.0	4.7
113	Glyoxal, O=CH-CH=O.	-227.5280488	-1.03856061	-227.777303	-223.299942	-220.6744418	-11.2	-8.5
114	ETHANOL TRANS	-154.8004259	-0.79066433	-154.990185	-216.432175	-214.7518553	18.7	20.4
115	DIMETHYL ETHER,	-154.7837087	-0.78780574	-154.972782	-171.582829	-169.9025087	12.5	14.2
116	Thiooxirane. (cyclic	-476.4872835	-0.85341181	-476.692102	95.200211	98.27204616	13.2	16.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.8147086	-1.2066889	-553.104314	-120.977226	-116.9602108	30.5	34.5
118	Thioethanol. CH3-CH2-SH.	-477.706361	-0.8722058	-477.915690	-20.006126	-16.93429052	26.4	29.5
119	ch3sch3 B3LYP	-477.7045044	-0.8742838	-477.914332	-13.915228	-10.84339307	23.3	26.4
120	Vinyl fluoride,	-177.6036297	-0.76569986	-177.787398	-142.268014	-139.9313185	-3.4	-1.0
121	Ethyl chloride.	-539.1170815	-0.80657885	-539.310660	-96.622306	-92.36899641	15.5	19.8
122	Vinyl chloride,	-537.8932842	-0.77804113	-538.080014	28.372853	32.6261631	5.4	9.6
123	h2c=chcn B3LYP	-170.5594845	-0.9071487	-170.777200	181.657297	182.7600069	0.9	2.0
124	ACETONE B3LYP	-192.853431	-0.99261015	-193.091657	-205.548172	-203.5002822	11.6	13.6
125	CH3COOH ACETIC	-228.7824325	-1.07022174	-229.039286	-428.569733	-425.9442333	4.1	6.7
126	CH3CFO HCCO	-252.794696	-1.07833557	-253.053497	-445.316698	-442.034823	-3.1	0.2
127	ch3c(o)cl hcco	-613.0712974	-1.09549013	-613.334215	-243.845109	-238.646619	-1.2	4.0
128	ch3ch2ch2cl B3LYP	-578.3550553	-1.03937057	-578.604504	-108.350182	-103.7293021	23.4	28.1
129	Isopropyl alcohol,	-194.0432291	-1.02552639	-194.289355	-243.929596	-241.8817059	28.9	30.9
130	Methyl ethyl	-194.0267951	-1.01974254	-194.271533	-196.588985	-194.5410948	19.7	21.8
131	Trimethyl Amine.	-174.1539781	-0.99661493	-174.393166	-0.822234	0.28047629	23.0	24.1
132	FURAN B3LYP	-229.6689583	-1.18159209	-229.952540	-31.670887	-29.25542745	3.1	5.5
133	Thiophene b3lyp	-552.5877511	-1.27450232	-552.893632	128.462607	132.269582	13.4	17.2
134	PYROLE PLANAR	-209.8189773	-1.15276091	-210.095640	109.837220	111.3074997	1.5	2.9
135	C2v Pyridine	-247.870944	-1.34529504	-248.193815	134.623654	136.4615038	-6.0	-4.1
136	H2 B3LYP/6-31G*	-1.16092343	-0.03573169	-1.169499	6.451410	6.451409562	6.5	6.5
137	SH b3lyp/6-31G*	-398.5948828	-0.36638908	-398.682816	146.335883	148.6725776	3.2	5.6
138	CCH B3LYP	-76.48504648	-0.39325902	-76.579429	577.315175	578.0503148	12.1	12.8
139	C2H3 CS,2-A'	-77.76597637	-0.41439064	-77.865430	301.668573	302.4037133	2.1	2.8
140	ch3co hcco	-152.9616972	-0.73857263	-153.138955	-16.502196	-14.82187625	-6.5	-4.8
141	H2COH C1	-114.9044194	-0.52644587	-115.030766	-14.518268	-13.20551781	2.6	3.9
142	ch3o CS,	-114.8968849	-0.49940101	-115.016741	18.731842	20.04459239	1.6	2.9

143	ch3ch2o 2A"	-154.1398845	-0.73102462	-154.315330	-6.426972	-4.746651816	9.1	10.7
144	ch3s 2-A'	-437.8343367	-0.60174607	-437.978756	130.223987	132.9282519	5.5	8.2
145	c2h5 staggered	-79.00554062	-0.44531978	-79.112417	131.756725	132.4918652	10.8	11.6
146	(ch3)2ch Cs	-118.2482948	-0.67894004	-118.411240	106.982085	108.0847947	17.0	18.1
147	TERT-BUTYL RADICAL	-157.491097	-0.91467794	-157.710620	80.484345	81.95462529	29.0	30.5
148	NO2 RADICAL	-204.8257982	-0.9335486	-205.049850	5.668738	7.559097913	-27.4	-25.5

MAD	**11.4**	**12.4**
LD	**38.9**	**46.7**

Table S5.6b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 24%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498591	0.000000	-0.498591
2	li	-7.470031	-0.014791	-7.473581
3	be	-14.639886	-0.055459	-14.653196
4	b	-24.620397	-0.079652	-24.639514
5	c	-37.804846	-0.106622	-37.830435
6	n	-54.539061	-0.137522	-54.572066
7	o	-75.005520	-0.195646	-75.052474
8	f	-99.655043	-0.259527	-99.717330
9	na	-162.163899	-0.174651	-162.205815
10	al	-242.247850	-0.224168	-242.301650
11	si	-289.249345	-0.254644	-289.310460
12	p	-341.132335	-0.284165	-341.200534
13	s	-397.968629	-0.326183	-398.046913
14	cl	-459.988678	-0.297396	-460.060053

Table S5.7a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04981647	-0.04803858	-8.061826	145.668483	145.6684827	6.3	6.3
2	BERYLLIUM HYDRIDE	-15.22556152	-0.05651018	-15.239689	319.340250	319.3402499	-22.5	-22.5
3	DOUBLET CH	-38.4244246	-0.14863345	-38.461583	598.248993	598.6165627	2.0	2.4
4	CH2 3-B1	-39.08765797	-0.16770364	-39.129584	394.980699	395.3482685	2.9	3.3
5	Singlet methylene,	-39.06525561	-0.18920124	-39.112556	438.075551	438.4431205	8.0	8.3
6	Methyl radical,	-39.76119982	-0.21364819	-39.814612	150.930329	151.2978991	4.5	4.9
7	ch4 //b3lyp/6-31G*	-40.4268262	-0.25665323	-40.490990	-65.105043	-64.73747294	9.8	10.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15572307	-0.19210566	-55.203749	355.716743	355.7167433	-0.8	-0.8
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79859397	-0.24727672	-55.860413	184.317431	184.3174311	-4.4	-4.4
10	AMMONIA, //b3lyp/6-31G*	-56.46539072	-0.30289579	-56.541115	-41.515985	-41.5159853	4.5	4.5
11	OH RADICAL	-75.65419117	-0.26452746	-75.720323	39.187036	40.13221632	-0.1	0.8
12	Water //b3lyp/6-31G*	-76.33293747	-0.335474	-76.416806	-233.347245	-232.4020648	8.5	9.4
13	HYDROGEN FLUORIDE,	-100.3522334	-0.3455985	-100.438633	-268.461052	-266.8594972	3.9	5.5
14	SIH2 singlet	-290.4676754	-0.31268682	-290.545847	274.379283	276.1646232	1.6	3.4
15	SIH2 3B1	-290.4406777	-0.28924493	-290.512989	361.659233	363.4445726	1.0	2.8
16	SIH3 c3v	-291.0825193	-0.31790401	-291.161995	203.023277	204.8086167	2.6	4.4
17	SIH4 //b3lyp/6-31G*	-291.7257079	-0.3457923	-291.812156	43.299701	45.0850408	9.0	10.8
18	ph2 doublet	-342.3510521	-0.35257832	-342.439197	137.540563	137.5405634	-0.9	-0.9
19	PH3 c3v	-342.9792787	-0.38493634	-343.075513	15.664981	15.6649813	10.2	10.2
20	SH2 //b3lyp/6-31G*	-399.2269344	-0.40657118	-399.328577	-11.313143	-8.976447605	9.2	11.5
21	HCL //b3lyp/6-31G*	-460.6371548	-0.34411078	-460.723182	-89.225422	-85.70725205	3.2	6.8
22	DILITHIUM //b3lyp/6-31G*	-14.96493943	-0.05997771	-14.979934	229.800825	229.8008249	13.9	13.9
23	Lithium Fluoride,	-107.3171106	-0.37617018	-107.411153	-340.696578	-339.0950234	-5.6	-4.0
24	ACETYLENE //b3lyp/6-31g*	-77.19515118	-0.43131767	-77.302981	228.395605	229.1307447	1.6	2.4
25	ETHYLENE //b3lyp/6-31g*	-78.43705605	-0.45168031	-78.549976	60.727807	61.46294719	8.4	9.2
26	ETHANE //b3lyp/6-31g*	-79.66024595	-0.48514223	-79.781532	-67.709375	-66.97423547	16.4	17.1
27	CYANO RADICAL,	-92.57297974	-0.47211682	-92.691009	437.942759	438.3103293	-1.0	-0.6
28	HYDROGEN CYANIDE	-93.28348438	-0.47750561	-93.402861	120.323648	120.6912182	-11.5	-11.1
29	CARBON MONOXIDE	-113.1758747	-0.48799675	-113.297874	-117.957334	-116.6445837	-7.5	-6.2
30	HCO BENT	-113.702493	-0.51075551	-113.830182	27.574456	28.88720604	-14.3	-13.0
31	H2CO //b3lyp/6-31g*	-114.3449045	-0.5303518	-114.477492	-115.204064	-113.891314	-6.4	-5.1

32	METHANOL //b3lyp/6-31g*	-115.5512808	-0.55935467	-115.691119	-193.640247	-192.3274967	7.2	8.5
33	Nitrogen N2,	-109.3831956	-0.51209183	-109.511219	-10.321202	-10.32120211	-10.3	-10.3
34	H2NNH2 //b3lyp/6-31g*	-111.69242	-0.57473854	-111.836105	97.595715	97.59571496	2.2	2.2
35	NO radical,	-129.7333664	-0.55457975	-129.872011	76.606420	77.55160027	-13.8	-12.8
36	O2 //b3lyp/6-31g*	-150.1466462	-0.61865196	-150.301309	-15.551424	-13.66106393	-15.6	-13.7
37	HYDROGEN PEROXIDE	-151.3634504	-0.65015023	-151.525988	-126.716486	-124.8261257	9.3	11.2
38	F2 //b3lyp/6-31g*	-199.3217273	-0.67911595	-199.491506	8.306357	11.50946727	8.3	11.5
39	CO2 D*H	-188.3598266	-0.82015055	-188.564864	-422.218329	-419.9603989	-28.9	-26.7
40	na2 //b3lyp/6-31G*	-324.3391125	-0.37919069	-324.433910	142.545829	142.5458288	0.3	0.3
41	SI2 3-SGG	-578.590948	-0.57117865	-578.733743	587.159557	590.7302366	1.8	5.4
42	P2 //b3lyp/6-31g*	-682.3989224	-0.72756471	-682.580814	147.314734	147.3147341	3.8	3.8
43	S2 //b3lyp/6-31g*	-796.0583067	-0.77299527	-796.251556	123.706818	128.3802077	-4.7	-0.1
44	CL2 //b3lyp/6-31g*	-920.0354498	-0.66722522	-920.202256	6.010452	13.04679216	6.0	13.0
45	Sodium Chloride	-622.2827649	-0.51981815	-622.412719	-174.276340	-170.7581697	8.1	11.7
46	SIO //b3lyp/6-31g*	-364.5074113	-0.63352911	-364.665794	-102.530189	-99.79966944	0.4	3.1
47	Carbon monosulfide,	-435.9979689	-0.59261419	-436.146122	281.945585	284.6498499	2.0	4.7
48	OS //b3lyp/6-31g*	-473.1226845	-0.70375147	-473.298622	-4.350203	-1.068328085	-9.4	-6.1
49	CLO 2-PI	-535.0545534	-0.62386522	-535.210520	102.084364	106.5477145	0.8	5.3
50	CLF 1-SG	-559.7036269	-0.6701339	-559.871160	-56.770522	-51.65079663	-1.5	3.6
51	si2h6 //b3lyp/6-31g*	-582.2772472	-0.67220642	-582.445299	99.855125	103.4258047	19.9	23.5
52	Methyl chloride,	-499.8655682	-0.57379656	-500.009017	-76.304976	-72.41923617	5.7	9.6
53	H3C-SH METHANETHIOL	-438.4582259	-0.63874853	-438.617913	-7.636826	-4.932561236	15.4	18.1
54	HOCl //b3lyp/6-31g*	-535.7024533	-0.66190868	-535.867930	-72.053449	-67.59009923	2.4	6.9
55	SO2 //b3lyp/6-31G*	-548.2921236	-1.06302925	-548.557881	-293.462680	-289.2356253	3.6	7.8
56	BF3 PLANAR	-324.2705474	-1.09557231	-324.544440	-1151.320105	-1146.384165	-15.8	-10.8
57	bcl3 B3LYP	-1405.042811	-1.13619761	-1405.326860	-416.453248	-405.7674631	-13.5	-2.8
58	ALf3 B3LYP	-541.8153028	-1.23698954	-542.124550	-1197.829906	-1192.132571	11.3	17.0
59	alcl3 B3LYP	-1622.645562	-1.23855508	-1622.955201	-584.244057	-572.7968768	0.3	11.7
60	cf4 B3LYP	-437.0884212	-1.49728241	-437.462742	-952.452674	-945.6788836	-19.4	-12.6
61	ccl4 B3LYP	-1878.156666	-1.5765927	-1878.550814	-91.854037	-77.41378671	4.0	18.4
62	O=C=S. Singlet	-511.2394415	-0.91182486	-511.467398	-165.415630	-161.7661845	-26.9	-23.3
63	CS2 B3LYP	-834.1157128	-1.01079404	-834.368411	95.958046	100.9990057	-20.8	-15.7
64	COF2 B3LYP	-312.7019747	-1.15961208	-312.991878	-630.378482	-625.8626219	-6.5	-2.0
65	sif4 B3LYP	-688.6750982	-1.59862826	-689.074755	-1580.996860	-1572.8053	34.0	42.2
66	sicl4, td	-2129.725275	-1.63715779	-2130.134564	-640.417853	-624.5598329	22.3	38.2
67	nno B3LYP	-184.4192066	-0.88227915	-184.639776	46.068219	47.01339866	-35.9	-35.0
68	clno B3LYP	-589.7534347	-0.95171664	-589.991364	33.576064	38.03941372	-18.3	-13.8

69	nf3 c3v	-353.7349704	-1.27982361	-354.054926	-151.541433	-146.7367675	-19.3	-14.5
70	pf3 c3v	-640.5886859	-1.33512277	-640.922467	-944.878516	-940.0738513	13.7	18.5
71	ozone 1-a1	-225.126872	-1.06289547	-225.392596	134.230189	137.065729	-8.4	-5.6
72	f2o B3LYP	-274.3824864	-1.0037518	-274.633424	24.333356	28.4816461	-0.4	3.8
73	CLF3, C2V	-759.0561911	-1.42118764	-759.411488	-173.614680	-165.2918452	-14.6	-6.3
74	CF2=CF2 D2H	-475.0481347	-1.70611746	-475.474664	-704.391227	-697.2498666	-45.8	-38.7
75	cl2c=ccl2 B3LYP	-1916.187313	-1.78128986	-1916.632636	-24.974689	-10.16686868	-12.4	2.4
76	cf3cn B3LYP	-430.0015445	-1.64785872	-430.413509	-529.188778	-523.6489733	-33.8	-28.3
77	PROPYNE C3V	-116.4419756	-0.66102613	-116.607232	188.182179	189.2848892	3.2	4.4
78	ALLENE D2D	-116.4425196	-0.65450093	-116.606145	189.380326	190.4830362	-1.0	0.1
79	CYCLOPROPENE C2V	-116.4024324	-0.6636464	-116.568344	289.563610	290.6663204	12.6	13.7
80	PROPENE CS	-117.677594	-0.6840403	-117.848604	34.641167	35.74387675	14.6	15.7
81	CYCLOPROPANE D3H	-117.6635227	-0.68973867	-117.835957	70.326064	71.42877352	17.2	18.3
82	PROPANE C2V	-118.8956605	-0.71711298	-119.074939	-79.771409	-78.66869881	24.8	25.9
83	TRANS-1,3-BUTADIENE C2H	-155.7003329	-0.88541495	-155.921687	122.320507	123.7907869	12.3	13.8
84	Dimethyl acetylene	-155.6867085	-0.89139529	-155.909557	154.318276	155.7885561	8.7	10.2
85	Methylene cyclopropane.	-155.6673824	-0.89162841	-155.890289	203.501216	204.9714963	3.1	4.6
86	Bicyclo[1.1.0]butane. C2v	-155.6509134	-0.90311437	-155.876692	241.133952	242.6042318	24.0	25.5
87	CYCLOBUTENE b3lyp	-155.6765196	-0.89409071	-155.900042	180.258229	181.7285093	23.8	25.2
88	CYCLOBUTANE b3lyp/6-31G*	-156.8997136	-0.92305147	-157.130477	56.455448	57.92572794	28.0	29.5
89	Isobutene. Single	-156.9178246	-0.91922922	-157.147632	6.625171	8.095451078	23.4	24.8
90	Trans butane	-158.1309398	-0.94962925	-158.368347	-91.844207	-90.3739267	33.7	35.1
91	isobutane B3LYP/6-31G*	-158.1319147	-0.95294905	-158.370152	-97.877212	-96.40693188	36.4	37.9
92	Spiropentane. D2d	-194.8963231	-1.12993918	-195.178808	206.202094	208.0399438	20.9	22.7
93	Benzene B3LYP	-231.827205	-1.29965128	-232.152118	84.393708	86.5991281	2.0	4.2
94	DIFLUOROMETHANE C2V	-238.7405241	-0.87636912	-238.959616	-459.069453	-455.4987729	-8.5	-4.9
95	HCF3 TRI-FLUOROMETHANE	-337.916372	-1.18819824	-338.213422	-710.854438	-705.6822031	-13.8	-8.6
96	CH2CL2 C2V	-959.3019191	-0.90036799	-959.527011	-90.096002	-82.69209222	5.3	12.7
97	chcl3 B3LYP/6-31G*	-1418.733092	-1.23492351	-1419.041822	-97.653074	-86.73099389	5.7	16.6
98	METHYLAMINE b3lyp	-95.68742948	-0.52967946	-95.819849	-13.863209	-13.49563911	9.1	9.5
99	Acetonitrile. CH3-CN.	-132.5362962	-0.70487056	-132.712514	66.430153	67.16529345	-8.9	-8.1
100	NITRO METHANE	-244.6747541	-1.16610007	-244.966279	-92.594271	-90.33634093	-18.1	-15.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6706011	-1.1568941	-244.959825	-79.376211	-77.11828087	-12.9	-10.6
102	Methylsilane. CH3-SiH3.	-330.976324	-0.57962693	-331.121231	-6.683899	-4.530989319	22.6	24.8
103	Formic Acid.	-189.5229074	-0.84165801	-189.733322	-388.547545	-386.2896154	-9.9	-7.6
104	Methyl formate.	-228.7457653	-1.07114709	-229.013552	-366.622252	-363.9967515	-11.0	-8.4
105	acetamide ch3cohn2	-208.9023226	-1.03946135	-209.162188	-241.106285	-239.4259646	-2.6	-0.9

106	Aziridine. (cyclic	-133.6857179	-0.73639676	-133.869817	134.446245	135.1813846	8.1	8.8
107	Cyanogen. NCCN.	-185.3797826	-0.94525924	-185.616097	273.337049	274.0721892	-33.4	-32.6
108	DIMETHYLAMINE b3lyp	-134.914079	-0.76061473	-135.104233	-3.532510	-2.797370481	14.9	15.6
109	TRANS ETHYLAMINE	-134.9255978	-0.76177512	-135.116042	-33.599520	-32.86437988	13.7	14.4
110	KETENE B3LYP	-152.38075	-0.73751896	-152.565130	-66.854130	-65.17380976	-19.6	-17.9
111	OXIRANE B3LYP	-153.5501123	-0.76807723	-153.742132	-48.395815	-46.71549484	4.3	6.0
112	Acetaldehyde B3LYP	-153.5957628	-0.76069363	-153.785936	-166.523991	-164.8436712	-0.4	1.3
113	Glyoxal, O=CH-CH=O.	-227.5175961	-1.03854699	-227.777233	-229.185341	-226.5598406	-17.1	-14.4
114	ETHANOL TRANS	-154.7918784	-0.79065538	-154.989542	-219.172513	-217.4921928	16.0	17.6
115	DIMETHYL ETHER,	-154.7751742	-0.78779473	-154.972123	-174.280893	-172.6005733	9.8	11.5
116	Thiooxirane. (cyclic	-476.4755868	-0.85339442	-476.688935	92.734496	95.80633094	10.7	13.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.7995004	-1.20667066	-553.101168	-125.139706	-121.1226909	26.3	30.3
118	Thioethanol. CH3-CH2-SH.	-477.6941903	-0.87218786	-477.912237	-21.720586	-18.64875147	24.7	27.8
119	ch3sch3 B3LYP	-477.692341	-0.87426583	-477.910907	-15.703367	-12.63153211	21.5	24.6
120	Vinyl fluoride,	-177.595403	-0.76568965	-177.786825	-145.184560	-142.8478652	-6.3	-3.9
121	Ethyl chloride.	-539.1046712	-0.80656354	-539.306312	-98.352987	-94.09967718	13.8	18.0
122	Vinyl chloride,	-537.8814016	-0.77802363	-538.075908	26.007207	30.2605175	3.0	7.2
123	h2c=chcn B3LYP	-170.5502095	-0.90711915	-170.776989	176.581345	177.684055	-4.2	-3.1
124	ACETONE B3LYP	-192.8428424	-0.9925916	-193.090990	-209.619001	-207.5711113	7.5	9.6
125	CH3COOH ACETIC	-228.7713831	-1.07020905	-229.038935	-433.720370	-431.0948697	-1.1	1.5
126	CH3CFO HCCO	-252.7834494	-1.07832239	-253.053030	-450.152458	-446.8705831	-7.9	-4.6
127	ch3c(o)cl hcco	-613.0564091	-1.09547079	-613.330277	-248.294023	-243.0955334	-5.6	-0.4
128	ch3ch2ch2cl B3LYP	-578.3400601	-1.03934902	-578.599897	-110.795777	-106.1748971	21.0	25.6
129	Isopropyl alcohol,	-194.0320873	-1.02551047	-194.288465	-247.414124	-245.3662343	25.4	27.4
130	Methyl ethyl	-194.0156746	-1.01972474	-194.270606	-199.976164	-197.9282736	16.3	18.4
131	Trimethyl Amine.	-174.1430535	-0.99659487	-174.392202	-3.922352	-2.819641909	19.9	21.0
132	FURAN B3LYP	-229.6567024	-1.18156552	-229.952094	-37.714133	-35.29867287	-3.0	-0.6
133	Thiophene b3lyp	-552.5718509	-1.27446881	-552.890468	123.200699	127.0076738	8.1	11.9
134	PYROLE PLANAR	-209.8069125	-1.15273271	-210.095096	104.242498	105.7127785	-4.1	-2.7
135	C2v Pyridine	-247.8568443	-1.3452584	-248.193159	127.928663	129.766513	-12.7	-10.8
136	H2 B3LYP/6-31G*	-1.16054088	-0.03573202	-1.169474	6.517442	6.517442462	6.5	6.5
137	SH b3lyp/6-31G*	-398.588204	-0.36639076	-398.679802	146.257136	148.593831	3.2	5.5
138	CCH B3LYP	-76.48099114	-0.39323736	-76.579300	574.864445	575.5995849	9.6	10.3
139	C2H3 CS,2-A'	-77.76134921	-0.41436819	-77.864941	300.164865	300.9000046	0.6	1.3
140	ch3co hcco	-152.9540313	-0.73855216	-153.138669	-20.181919	-18.5015993	-10.1	-8.5
141	H2COH C1	-114.8987895	-0.52643684	-115.030399	-16.587990	-15.27524016	0.6	1.9
142	ch3o CS,	-114.8912876	-0.49938366	-115.016133	17.291974	18.60472382	0.1	1.5

143	ch3ch2o 2A"	-154.1317024	-0.73099791	-154.314452	-8.549143	-6.868822987	6.9	8.6
144	ch3s 2-A'	-437.8250796	-0.60173748	-437.975514	129.348397	132.0526618	4.7	7.4
145	c2h5 staggered	-79.00036512	-0.44531187	-79.111693	130.871095	131.606235	10.0	10.7
146	(ch3)2ch Cs	-118.240527	-0.67892199	-118.410257	105.381880	106.4845905	15.4	16.5
147	TERT-BUTYL RADICAL	-157.4807343	-0.9146495	-157.709397	78.121011	79.59129144	26.7	28.1
148	NO2 RADICAL	-204.817477	-0.93352653	-205.050859	-1.711908	0.178451681	-34.8	-32.9

MAD	**11.4**	**12.0**
LD	**-45.8**	**42.2**

Table S5.7b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498591	0.000000	-0.498591
2	li	-7.469494	-0.014790	-7.473191
3	be	-14.638936	-0.055454	-14.652800
4	b	-24.619132	-0.079656	-24.639046
5	c	-37.803247	-0.106628	-37.829904
6	n	-54.537133	-0.137526	-54.571514
7	o	-75.002935	-0.195656	-75.051849
8	f	-99.651824	-0.259537	-99.716708
9	na	-162.159807	-0.174649	-162.203470
10	al	-242.242893	-0.224169	-242.298935
11	si	-289.244029	-0.254646	-289.307691
12	p	-341.126663	-0.284159	-341.197703
13	s	-397.962322	-0.326186	-398.043868
14	cl	-459.981757	-0.297399	-460.056107

Table S5.8a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04892847	-0.04804001	-8.061419	145.715558	145.715558	6.4	6.4
2	BERYLLIUM HYDRIDE	-15.22447978	-0.0565023	-15.239170	319.661843	319.6618434	-22.2	-22.2
3	DOUBLET CH	-38.42244694	-0.14863732	-38.461093	598.143090	598.5106597	1.9	2.3
4	CH2 3-B1	-39.08550534	-0.16770195	-39.129108	394.837287	395.2048569	2.8	3.2
5	Singlet methylene,	-39.06292788	-0.18919749	-39.112119	437.828851	438.1964207	7.7	8.1
6	Methyl radical,	-39.75861408	-0.21365181	-39.814164	150.714149	151.0817189	4.3	4.6
7	ch4 //b3lyp/6-31G*	-40.42387996	-0.25664738	-40.490608	-65.497363	-65.12979327	9.4	9.8
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15334265	-0.19211591	-55.203293	355.467112	355.4671124	-1.0	-1.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79579786	-0.24728381	-55.860092	183.712835	183.7128352	-5.0	-5.0
10	AMMONIA, //b3lyp/6-31G*	-56.46221152	-0.3028972	-56.540965	-42.571180	-42.57117979	3.5	3.5
11	OH RADICAL	-75.65118091	-0.26453793	-75.719961	38.497276	39.44245573	-0.8	0.1
12	Water //b3lyp/6-31G*	-76.32953359	-0.33548098	-76.416759	-234.863875	-233.9186951	7.0	7.9
13	HYDROGEN FLUORIDE,	-100.3486103	-0.34560787	-100.438468	-269.659948	-268.0583932	2.7	4.3
14	SIH2 singlet	-290.4617008	-0.31267883	-290.542997	274.591333	276.3766733	1.8	3.6
15	SIH2 3B1	-290.4348969	-0.28921745	-290.510093	361.991153	363.7764933	1.3	3.1
16	SIH3 c3v	-291.0763635	-0.3178887	-291.159015	203.579061	205.3644006	3.2	5.0
17	SIH4 //b3lyp/6-31G*	-291.7192149	-0.34578314	-291.809118	44.004214	45.78955434	9.7	11.5
18	ph2 doublet	-342.3446202	-0.35257784	-342.436290	137.738009	137.7380089	-0.8	-0.8
19	PH3 c3v	-342.972519	-0.38492716	-343.072600	15.879418	15.87941849	10.4	10.4
20	SH2 //b3lyp/6-31G*	-399.2199158	-0.40656552	-399.325623	-11.549384	-9.212689045	9.0	11.3
21	HCL //b3lyp/6-31G*	-460.6298835	-0.34410863	-460.719352	-89.527626	-86.00945603	2.9	6.5
22	DILITHIUM //b3lyp/6-31G*	-14.96360126	-0.05997344	-14.979194	229.698111	229.6981109	13.8	13.8
23	Lithium Fluoride,	-107.3129344	-0.37618626	-107.410743	-342.272769	-340.6712137	-7.1	-5.5
24	ACETYLENE //b3lyp/6-31g*	-77.19070218	-0.43129844	-77.302840	225.978863	226.7140032	-0.8	-0.1
25	ETHYLENE //b3lyp/6-31g*	-78.43207023	-0.45166595	-78.549503	59.182541	59.91768107	6.9	7.6
26	ETHANE //b3lyp/6-31g*	-79.65472402	-0.48513065	-79.780858	-68.727525	-67.99238521	15.4	16.1
27	CYANO RADICAL,	-92.56870878	-0.47201986	-92.691434	433.984997	434.3525665	-4.9	-4.5
28	HYDROGEN CYANIDE	-93.27883753	-0.47748988	-93.402985	117.155852	117.5234219	-14.6	-14.3
29	CARBON MONOXIDE	-113.1710252	-0.48799035	-113.297903	-121.067260	-119.75451	-10.6	-9.3
30	HCO BENT	-113.6974096	-0.51074365	-113.830203	24.484856	25.79760638	-17.4	-16.0
31	H2CO //b3lyp/6-31g*	-114.3394972	-0.53034686	-114.477387	-117.962252	-116.6495024	-9.2	-7.9

32	METHANOL //b3lyp/6-31g*	-115.5453191	-0.55935219	-115.690751	-195.706034	-194.3932837	5.1	6.4
33	Nitrogen N2,	-109.3783572	-0.51207591	-109.511497	-13.949498	-13.94949792	-13.9	-13.9
34	H2NNH2 //b3lyp/6-31g*	-111.6864512	-0.57473825	-111.835883	95.279773	95.27977296	-0.1	-0.1
35	NO radical,	-129.7280852	-0.55457008	-129.872273	72.828693	73.77387282	-17.5	-16.6
36	O2 //b3lyp/6-31g*	-150.140923	-0.61865044	-150.301772	-20.048702	-18.15834221	-20.0	-18.2
37	HYDROGEN PEROXIDE	-151.3570872	-0.65015588	-151.526128	-130.365352	-128.4749918	5.6	7.5
38	F2 //b3lyp/6-31g*	-199.3149705	-0.67912018	-199.491542	4.950660	8.15376977	5.0	8.2
39	CO2 D*H	-188.3519143	-0.82013678	-188.565150	-427.643266	-425.385336	-34.3	-32.1
40	na2 //b3lyp/6-31G*	-324.3306843	-0.37918513	-324.429272	142.403592	142.403592	0.1	0.1
41	SI2 3-SGG	-578.5799649	-0.57115922	-578.728466	586.471828	590.0425081	1.1	4.7
42	P2 //b3lyp/6-31g*	-682.3867778	-0.7275402	-682.575938	145.248671	145.2486712	1.7	1.7
43	S2 //b3lyp/6-31g*	-796.0452364	-0.77298531	-796.246213	121.748794	126.4221836	-6.7	-2.0
44	CL2 //b3lyp/6-31g*	-920.0213198	-0.66721747	-920.194796	4.876403	11.91274314	4.9	11.9
45	Sodium Chloride	-622.2714356	-0.51982109	-622.406589	-174.699879	-171.1817085	7.7	11.2
46	SIO //b3lyp/6-31g*	-364.4988854	-0.63353887	-364.663605	-105.696494	-102.9659736	-2.8	0.0
47	Carbon monosulfide,	-435.9894849	-0.59259314	-436.143559	279.289173	281.9934375	-0.6	2.1
48	OS //b3lyp/6-31g*	-473.113278	-0.70374376	-473.296251	-7.759149	-4.477273609	-12.8	-9.5
49	CLO 2-PI	-535.0446345	-0.62382033	-535.206828	99.776906	104.2402557	-1.5	3.0
50	CLF 1-SG	-559.693164	-0.67013361	-559.867399	-58.885342	-53.76561666	-3.7	1.5
51	si2h6 //b3lyp/6-31g*	-582.2646288	-0.67218925	-582.439398	100.806981	104.3776609	20.9	24.5
52	Methyl chloride,	-499.8557423	-0.57378758	-500.004927	-77.318921	-73.43318064	4.7	8.6
53	H3C-SH METHANETHIOL	-438.4486398	-0.63873682	-438.614711	-8.617124	-5.912859137	14.4	17.1
54	HOCl //b3lyp/6-31g*	-535.6922006	-0.66190684	-535.864296	-74.512734	-70.04938434	0.0	4.4
55	SO2 //b3lyp/6-31G*	-548.2795764	-1.06301898	-548.555961	-299.697586	-295.4705312	-2.6	1.6
56	BF3 PLANAR	-324.2586119	-1.09557353	-324.543461	-1154.869769	-1149.933829	-19.3	-14.4
57	bcl3 B3LYP	-1405.019922	-1.13617868	-1405.315328	-418.481712	-407.7959273	-15.6	-4.9
58	ALf3 B3LYP	-541.7997738	-1.23699871	-542.121393	-1201.563818	-1195.866483	7.6	13.3
59	alcl3 B3LYP	-1622.619083	-1.23853914	-1622.941103	-585.437137	-573.9899571	-0.9	10.5
60	cf4 B3LYP	-437.0725053	-1.49727494	-437.461797	-957.889911	-951.1161206	-24.9	-18.1
61	ccl4 B3LYP	-1878.126144	-1.57656693	-1878.536052	-95.928421	-81.48817099	-0.1	14.3
62	O=C=S. Singlet	-511.2278922	-0.91180236	-511.464961	-170.044682	-166.3952369	-31.6	-27.9
63	CS2 B3LYP	-834.1005158	-1.01076234	-834.363314	91.961634	97.00259352	-24.8	-19.7
64	COF2 B3LYP	-312.6900665	-1.15960249	-312.991563	-635.849447	-631.3335871	-12.0	-7.5
65	sif4 B3LYP	-688.6555499	-1.59862493	-689.071192	-1585.438121	-1577.246561	29.6	37.8
66	sicl4, td	-2129.691121	-1.6371316	-2130.116776	-642.423027	-626.5650073	20.3	36.2
67	nno B3LYP	-184.4113309	-0.88225544	-184.640717	39.059600	40.00477974	-42.9	-42.0
68	clno B3LYP	-589.7410058	-0.9516966	-589.988447	27.785267	32.24861748	-24.1	-19.6

69	nf3 c3v	-353.722191	-1.27981773	-354.054944	-157.929687	-153.1250223	-25.7	-20.9
70	pf3 c3v	-640.5721657	-1.33512003	-640.919297	-948.883759	-944.0790941	9.7	14.5
71	ozone 1-a1	-225.1180936	-1.0628714	-225.394440	124.465314	127.3008544	-18.2	-15.4
72	f2o B3LYP	-274.3727594	-1.00375014	-274.633734	18.615638	22.76392751	-6.1	-1.9
73	CLF3, C2V	-759.0387612	-1.42118613	-759.408270	-180.418665	-172.0958303	-21.4	-13.1
74	CF2=CF2 D2H	-475.0301805	-1.70610804	-475.473769	-711.351908	-704.2105475	-52.8	-45.6
75	cl2c=ccl2 B3LYP	-1916.154707	-1.78125832	-1916.617834	-30.338238	-15.53041809	-17.8	-3.0
76	cf3cn B3LYP	-429.9846042	-1.64783464	-430.413041	-537.089348	-531.5495431	-41.7	-36.2
77	PROPYNE C3V	-116.4349416	-0.66100168	-116.606802	185.131739	186.2344492	0.2	1.3
78	ALLENE D2D	-116.435482	-0.65447853	-116.605646	186.509231	187.6119414	-3.9	-2.8
79	CYCLOPROPENE C2V	-116.3953427	-0.6636285	-116.567886	286.586197	287.6889068	9.6	10.7
80	PROPENE CS	-117.6700215	-0.68402045	-117.847867	32.397050	33.49976003	12.3	13.4
81	CYCLOPROPANE D3H	-117.6558815	-0.68972354	-117.835210	68.109617	69.21232721	15.0	16.1
82	PROPANE C2V	-118.8875537	-0.71709534	-119.073999	-81.482526	-80.37981645	23.1	24.2
83	TRANS-1,3-BUTADIENE C2H	-155.6907102	-0.88538678	-155.920911	118.784568	120.2548483	8.7	10.2
84	Dimethyl acetylene	-155.6770897	-0.89136554	-155.908845	150.616005	152.0862853	5.0	6.5
85	Methylene cyclopropane.	-155.6576975	-0.89160493	-155.889515	199.962353	201.4326329	-0.5	1.0
86	Bicyclo[1.1.0]butane. C2v	-155.6411602	-0.90309444	-155.875965	237.470213	238.9404928	20.3	21.8
87	CYCLOBUTENE b3lyp	-155.6668101	-0.89406703	-155.899268	176.719389	178.1896695	20.2	21.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8894701	-0.92302991	-157.129458	53.556971	55.02725077	25.1	26.6
89	Isobutene. Single	-156.9076577	-0.91920367	-157.146651	3.628474	5.098753687	20.4	21.8
90	Trans butane	-158.1202473	-0.94960527	-158.367145	-94.260140	-92.78985956	31.3	32.7
91	isobutane B3LYP/6-31G*	-158.121213	-0.95292516	-158.368974	-100.356318	-98.88603794	34.0	35.4
92	Spiropentane. D2d	-194.8839839	-1.12991426	-195.177762	201.982887	203.8207374	16.6	18.5
93	Benzene B3LYP	-231.8133121	-1.29961264	-232.151211	78.414027	80.61944683	-4.0	-1.8
94	DIFLUOROMETHANE C2V	-238.7311155	-0.8763697	-238.958972	-462.032581	-458.4619011	-11.4	-7.8
95	HCF3 TRI-FLUOROMETHANE	-337.9037115	-1.18819627	-338.212643	-715.096322	-709.9240871	-18.0	-12.9
96	CH2CL2 C2V	-959.2852027	-0.90035447	-959.519295	-91.949735	-84.54582518	3.4	10.8
97	chcl3 B3LYP/6-31G*	-1418.709476	-1.23490427	-1419.030551	-100.531888	-89.60980764	2.8	13.7
98	METHYLAMINE b3lyp	-95.68168125	-0.52967332	-95.819396	-15.515703	-15.14813301	7.5	7.9
99	Acetonitrile. CH3-CN.	-132.5290644	-0.70484906	-132.712325	62.690300	63.42544041	-12.6	-11.9
100	NITRO METHANE	-244.6635289	-1.16607945	-244.966710	-99.848242	-97.59031151	-25.4	-23.1
101	Methyl-nitrite. CH3-O-N=O.	-244.6594126	-1.15687207	-244.960199	-86.483872	-84.22594205	-20.0	-17.7
102	Methylsilane. CH3-SiH3.	-330.9672473	-0.57961274	-331.117947	-6.724934	-4.572023521	22.6	24.7
103	Formic Acid.	-189.5144491	-0.84165233	-189.733279	-393.109160	-390.8512303	-14.5	-12.2
104	Methyl formate.	-228.7347357	-1.07113153	-229.013230	-371.844725	-369.2192247	-16.2	-13.6
105	acetamide ch3cohn2	-208.8914799	-1.03944723	-209.161736	-245.796295	-244.115975	-7.3	-5.6

106	Aziridine. (cyclic	-133.6778706	-0.73638428	-133.869330	131.488640	132.2237804	5.1	5.9
107	Cyanogen. NCCN.	-185.3708576	-0.94522499	-185.616616	266.291509	267.026649	-40.4	-39.7
108	DIMETHYLAMINE b3lyp	-134.9057491	-0.76060133	-135.103505	-5.858394	-5.12325446	12.6	13.3
109	TRANS ETHYLAMINE	-134.9172644	-0.76176255	-135.115323	-35.947090	-35.2119497	11.3	12.1
110	KETENE B3LYP	-152.3732769	-0.7375032	-152.565028	-71.013637	-69.33331668	-23.7	-22.1
111	OXIRANE B3LYP	-153.5420631	-0.7680673	-153.741761	-51.849111	-50.16879083	0.9	2.5
112	Acetaldehyde B3LYP	-153.587767	-0.76068218	-153.785544	-169.922490	-168.2421698	-3.8	-2.1
113	Glyoxal, O=CH-CH=O.	-227.5071436	-1.03853338	-227.777162	-235.068248	-232.4427477	-22.9	-20.3
114	ETHANOL TRANS	-154.783331	-0.79064644	-154.988899	-221.911276	-220.2309561	13.2	14.9
115	DIMETHYL ETHER,	-154.7666399	-0.78778372	-154.971464	-176.977269	-175.2969487	7.1	8.8
116	Thiooxirane. (cyclic	-476.4638902	-0.85337703	-476.685768	90.270455	93.34229026	8.3	11.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.7842922	-1.20665242	-553.098022	-129.299873	-125.2828584	22.2	26.2
118	Thioethanol. CH3-CH2-SH.	-477.6820198	-0.87216991	-477.908784	-23.433390	-20.36155468	23.0	26.1
119	ch3sch3 B3LYP	-477.6801778	-0.87424787	-477.907482	-17.489834	-14.41799924	19.7	22.8
120	Vinyl fluoride,	-177.5871763	-0.76567944	-177.786253	-148.099462	-145.7627667	-9.2	-6.9
121	Ethyl chloride.	-539.092261	-0.80654824	-539.301964	-100.082124	-95.82881362	12.0	16.3
122	Vinyl chloride,	-537.8695192	-0.77800613	-538.071801	23.643281	27.89659055	0.6	4.9
123	h2c=chcn B3LYP	-170.5409345	-0.9070896	-170.776778	171.508083	172.6107932	-9.2	-8.1
124	ACETONE B3LYP	-192.8322539	-0.99257305	-193.090323	-213.687421	-211.6395307	3.5	5.5
125	CH3COOH ACETIC	-228.7603339	-1.07019637	-229.038585	-438.868563	-436.2430632	-6.2	-3.6
126	CH3CFO HCCO	-252.7722029	-1.07830921	-253.052563	-454.985798	-451.7039225	-12.7	-9.5
127	ch3c(o)cl hcco	-613.0415209	-1.09545145	-613.326338	-252.740556	-247.5420655	-10.1	-4.9
128	ch3ch2ch2cl B3LYP	-578.3250651	-1.03932747	-578.595290	-113.239195	-108.618315	18.6	23.2
129	Isopropyl alcohol,	-194.0209457	-1.02549456	-194.287574	-250.896388	-248.8484979	21.9	23.9
130	Methyl ethyl	-194.0045542	-1.01970694	-194.269678	-203.360946	-201.3130559	13.0	15.0
131	Trimethyl Amine.	-174.132129	-0.99657481	-174.391238	-7.020383	-5.91767336	16.8	17.9
132	FURAN B3LYP	-229.6444466	-1.18153894	-229.951647	-43.754164	-41.33870362	-9.0	-6.6
133	Thiophene b3lyp	-552.5559509	-1.2744353	-552.887304	117.941961	121.7489357	2.9	6.7
134	PYROLE PLANAR	-209.7948479	-1.1527045	-210.094551	98.650701	100.1209815	-9.7	-8.2
135	C2v Pyridine	-247.8427448	-1.34522176	-248.192502	121.237357	123.0752073	-19.3	-17.5
136	H2 B3LYP/6-31G*	-1.16015834	-0.03573234	-1.169449	6.583439	6.583438606	6.6	6.6
137	SH b3lyp/6-31G*	-398.5815253	-0.36639245	-398.676787	146.178433	148.5151279	3.1	5.4
138	CCH B3LYP	-76.47693588	-0.39321574	-76.579172	572.415369	573.1505091	7.2	7.9
139	C2H3 CS,2-A'	-77.75672216	-0.41434576	-77.864452	298.662786	299.3979264	-0.9	-0.2
140	ch3co hcco	-152.9463655	-0.73853167	-153.138384	-23.859469	-22.17914897	-13.8	-12.1
141	H2COH C1	-114.8931597	-0.52642782	-115.030031	-18.656459	-17.34370856	-1.5	-0.2
142	ch3o CS,	-114.8856904	-0.49936634	-115.015526	15.853809	17.16655867	-1.3	0.0

143	ch3ch2o 2A"	-154.1235205	-0.73097124	-154.313573	-10.668854	-8.988534065	4.8	6.5
144	ch3s 2-A'	-437.8158226	-0.60172891	-437.972272	128.473681	131.177946	3.8	6.5
145	c2h5 staggered	-78.99518972	-0.445304	-79.110969	129.986344	130.7214843	9.1	9.8
146	(ch3)2ch Cs	-118.2327593	-0.67890397	-118.409274	103.783393	104.8861034	13.8	14.9
147	TERT-BUTYL RADICAL	-157.4703717	-0.91462109	-157.708173	75.760239	77.23051851	24.3	25.8
148	NO2 RADICAL	-204.8091559	-0.93350446	-205.051867	-9.089992	-7.199631538	-42.1	-40.3

MAD	**12.0**	**12.3**
LD	**-52.8**	**-45.6**

Table S5.8b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498591	0.000000	-0.498591
2	li	-7.468957	-0.014789	-7.472802
3	be	-14.637987	-0.055449	-14.652403
4	b	-24.617867	-0.079659	-24.638579
5	c	-37.801648	-0.106634	-37.829373
6	n	-54.535205	-0.137530	-54.570962
7	o	-75.000351	-0.195667	-75.051224
8	f	-99.648604	-0.259547	-99.716087
9	na	-162.155715	-0.174647	-162.201124
10	al	-242.237936	-0.224170	-242.296220
11	si	-289.238713	-0.254647	-289.304922
12	p	-341.120992	-0.284154	-341.194872
13	s	-397.956015	-0.326188	-398.040824
14	cl	-459.974837	-0.297402	-460.052161

Table S5.9a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04537675	-0.04804579	-8.059790	145.902441	145.902441	6.6	6.6
2	BERYLLIUM HYDRIDE	-15.22015358	-0.05647102	-15.237095	320.948346	320.9483463	-20.9	-20.9
3	DOUBLET CH	-38.4145367	-0.14865298	-38.459133	597.720641	598.088211	1.5	1.9
4	CH2 3-B1	-39.07689597	-0.16769546	-39.127205	394.265683	394.633253	2.2	2.6
5	Singlet methylene,	-39.05361742	-0.18918253	-39.110372	436.847168	437.2147383	6.7	7.1
6	Methyl radical,	-39.74827166	-0.21366652	-39.812372	149.850315	150.2178852	3.4	3.8
7	ch4 //b3lyp/6-31G*	-40.41209554	-0.25662398	-40.489083	-67.060603	-66.6930333	7.8	8.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1438214	-0.19215719	-55.201469	354.464753	354.4647526	-2.0	-2.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.7846139	-0.24731237	-55.858808	181.292207	181.2922066	-7.4	-7.4
10	AMMONIA, //b3lyp/6-31G*	-56.44949523	-0.30290289	-56.540366	-46.791181	-46.7911806	-0.8	-0.8
11	OH RADICAL	-75.63914025	-0.26457995	-75.718514	35.738223	36.68340284	-3.6	-2.6
12	Water //b3lyp/6-31G*	-76.31591849	-0.3355089	-76.416571	-240.928569	-239.983389	0.9	1.9
13	HYDROGEN FLUORIDE,	-100.3341181	-0.34564538	-100.437812	-274.455214	-272.8536594	-2.1	-0.5
14	SIH2 singlet	-290.4378027	-0.31264685	-290.531597	275.444787	277.2301272	2.6	4.4
15	SIH2 3B1	-290.4117756	-0.28910788	-290.498508	363.330357	365.1156968	2.7	4.5
16	SIH3 c3v	-291.0517412	-0.31782759	-291.147089	205.809758	207.5950979	5.4	7.2
17	SIH4 //b3lyp/6-31G*	-291.6932435	-0.34574647	-291.796967	46.828144	48.61348438	12.5	14.3
18	ph2 doublet	-342.3188931	-0.35257617	-342.424666	138.524787	138.5247873	0.0	0.0
19	PH3 c3v	-342.9454806	-0.38489045	-343.060948	16.739105	16.73910486	11.3	11.3
20	SH2 //b3lyp/6-31G*	-399.1918419	-0.40654285	-399.313805	-12.489847	-10.15315207	8.0	10.3
21	HCL //b3lyp/6-31G*	-460.600799	-0.34410019	-460.704029	-90.733738	-87.21556767	1.7	5.3
22	DILITHIUM //b3lyp/6-31G*	-14.9582494	-0.0599563	-14.976236	229.287622	229.2876224	13.4	13.4
23	Lithium Fluoride,	-107.2962301	-0.37625076	-107.409105	-348.580975	-346.9794196	-13.4	-11.8
24	ACETYLENE //b3lyp/6-31g*	-77.17290684	-0.43122153	-77.302273	216.329029	217.0641685	-10.4	-9.7
25	ETHYLENE //b3lyp/6-31g*	-78.41212767	-0.4516085	-78.547610	53.015909	53.75104897	0.7	1.5
26	ETHANE //b3lyp/6-31g*	-79.63263717	-0.48508432	-79.778162	-72.787545	-72.05240537	11.3	12.0
27	CYANO RADICAL,	-92.55162631	-0.47163269	-92.693116	418.208018	418.5755879	-20.7	-20.3
28	HYDROGEN CYANIDE	-93.26025065	-0.47742697	-93.403479	104.498837	104.8664068	-27.3	-26.9
29	CARBON MONOXIDE	-113.151628	-0.48796476	-113.298017	-133.493943	-132.1811926	-23.0	-21.7
30	HCO BENT	-113.677077	-0.51069603	-113.830286	12.141788	13.45453805	-29.7	-28.4
31	H2CO //b3lyp/6-31g*	-114.3178684	-0.53032714	-114.476967	-128.983062	-127.6703122	-20.2	-18.9

32	METHANOL //b3lyp/6-31g*	-115.5214729	-0.5593423	-115.689276	-203.958890	-202.6461397	-3.1	-1.8
33	Nitrogen N2,	-109.3590041	-0.51201224	-109.512608	-28.449745	-28.44974532	-28.4	-28.4
34	H2NNH2 //b3lyp/6-31g*	-111.6625769	-0.57473717	-111.834998	86.019864	86.01986445	-9.4	-9.4
35	NO radical,	-129.706961	-0.55453142	-129.873320	57.731023	58.6762034	-32.6	-31.7
36	O2 //b3lyp/6-31g*	-150.1180308	-0.61864445	-150.303624	-38.025079	-36.13471906	-38.0	-36.1
37	HYDROGEN PEROXIDE	-151.3316352	-0.65017854	-151.526689	-144.952267	-143.0619075	-9.0	-7.1
38	F2 //b3lyp/6-31g*	-199.2879435	-0.67913712	-199.491685	-8.462794	-5.259683937	-8.5	-5.3
39	CO2 D*H	-188.3202657	-0.82008175	-188.566290	-449.319715	-447.0617853	-56.0	-53.8
40	na2 //b3lyp/6-31G*	-324.2969732	-0.37916281	-324.410722	141.834409	141.8344088	-0.4	-0.4
41	SI2 3-SGG	-578.5360342	-0.57108192	-578.707359	583.732634	587.3033145	-1.6	2.0
42	P2 //b3lyp/6-31g*	-682.3382007	-0.72744216	-682.556433	136.992144	136.9921437	-6.5	-6.5
43	S2 //b3lyp/6-31g*	-795.9929559	-0.77294559	-796.224840	113.925844	118.5992343	-14.5	-9.8
44	CL2 //b3lyp/6-31g*	-919.9648008	-0.66718649	-920.164957	0.348661	7.385001177	0.3	7.4
45	Sodium Chloride	-622.2261188	-0.51983295	-622.382069	-176.394029	-172.8758586	6.0	9.5
46	SIO //b3lyp/6-31g*	-364.4647825	-0.63357797	-364.654856	-118.359849	-115.6293288	-15.4	-12.7
47	Carbon monosulfide,	-435.95555	-0.59250897	-436.133303	268.680211	271.3844757	-11.2	-8.5
48	OS //b3lyp/6-31g*	-473.075653	-0.70371288	-473.286767	-21.383116	-18.10124096	-26.4	-23.1
49	CLO 2-PI	-535.0049597	-0.62364078	-535.192052	90.578222	95.04157232	-10.7	-6.2
50	CLF 1-SG	-559.6513128	-0.67013248	-559.852353	-67.336559	-62.21683388	-12.1	-7.0
51	si2h6 //b3lyp/6-31g*	-582.2141564	-0.67212056	-582.415793	104.626118	108.1967977	24.7	28.3
52	Methyl chloride,	-499.8164395	-0.57375167	-499.988565	-81.364585	-77.4788451	0.6	4.5
53	H3C-SH METHANETHIOL	-438.4102964	-0.63868997	-438.601903	-12.527052	-9.822787343	10.5	13.2
54	HOCl //b3lyp/6-31g*	-535.6511904	-0.66189951	-535.849760	-84.340898	-79.87754819	-9.9	-5.4
55	SO2 //b3lyp/6-31G*	-548.2293884	-1.06297797	-548.548282	-324.617463	-320.3904082	-27.6	-23.3
56	BF3 PLANAR	-324.2108706	-1.09557848	-324.539544	-1169.049314	-1164.113374	-33.5	-28.6
57	bcl3 B3LYP	-1404.928366	-1.13610299	-1405.269197	-426.576287	-415.8905023	-23.7	-13.0
58	ALf3 B3LYP	-541.7376588	-1.23703547	-542.108769	-1216.485185	-1210.78785	-7.3	-1.6
59	alcl3 B3LYP	-1622.513167	-1.2384754	-1622.884710	-590.192518	-578.7453383	-5.7	5.8
60	cf4 B3LYP	-437.0088421	-1.4972451	-437.458016	-979.607618	-972.8338276	-46.6	-39.8
61	ccl4 B3LYP	-1878.004061	-1.57646388	-1878.477000	-112.199157	-97.75890699	-16.4	-1.9
62	O=C=S. Singlet	-511.181696	-0.91171236	-511.455210	-188.537270	-184.8878249	-50.0	-46.4
63	CS2 B3LYP	-834.0397292	-1.0106355	-834.342920	76.000483	81.04144336	-40.7	-35.7
64	COF2 B3LYP	-312.6424345	-1.15956419	-312.990304	-657.706656	-653.1907963	-33.9	-29.4
65	sif4 B3LYP	-688.5773575	-1.59861165	-689.056941	-1603.176288	-1594.984728	11.8	20.0
66	sicl4, td	-2129.554509	-1.63702686	-2130.045617	-650.418701	-634.5606814	12.3	28.2
67	nno B3LYP	-184.3798286	-0.88216062	-184.644477	11.048344	11.99352398	-71.0	-70.0
68	clno B3LYP	-589.6912909	-0.95161645	-589.976776	4.643108	9.106457539	-47.2	-42.8

69	nf3 c3v	-353.6710742	-1.27979428	-354.055013	-183.459838	-178.6551732	-51.2	-46.4
70	pf3 c3v	-640.5060862	-1.33510912	-640.906619	-964.888295	-960.0836296	-6.3	-1.5
71	ozone 1-a1	-225.0829806	-1.06277519	-225.401813	85.436663	88.27220302	-57.2	-54.4
72	f2o B3LYP	-274.333852	-1.00374357	-274.634975	-4.236724	-0.08843447	-28.9	-24.8
73	CLF3, C2V	-758.9690427	-1.42118015	-759.395397	-207.614037	-199.2912025	-48.6	-40.3
74	CF2=CF2 D2H	-474.9583645	-1.70607041	-475.470186	-739.158486	-732.0171262	-80.6	-73.5
75	cl2c=ccl2 B3LYP	-1916.024283	-1.78113218	-1916.558622	-51.758735	-36.95091481	-39.2	-24.4
76	cf3cn B3LYP	-429.9168441	-1.64773839	-430.411166	-568.651399	-563.1115943	-73.3	-67.7
77	PROPYNE C3V	-116.4068065	-0.66090386	-116.605078	172.953527	174.056237	-12.0	-10.9
78	ALLENE D2D	-116.4073324	-0.65438896	-116.603649	175.047363	176.1500733	-15.3	-14.2
79	CYCLOPROPENE C2V	-116.3669846	-0.66355689	-116.566052	274.696722	275.7994319	-2.3	-1.2
80	PROPENE CS	-117.6397327	-0.68394104	-117.844915	23.441445	24.54415538	3.4	4.5
81	CYCLOPROPANE D3H	-117.6253176	-0.68966304	-117.832217	59.262350	60.36505961	6.1	7.2
82	PROPANE C2V	-118.8551278	-0.71702482	-119.070235	-88.307650	-87.2049397	16.3	17.4
83	TRANS-1,3-BUTADIENE C2H	-155.6522207	-0.88527412	-155.917803	104.669910	106.1401897	-5.4	-3.9
84	Dimethyl acetylene	-155.6386161	-0.89124652	-155.905990	135.836800	137.3070801	-9.8	-8.3
85	Methylene cyclopropane.	-155.618959	-0.89151104	-155.886412	185.833708	187.3039883	-14.6	-13.1
86	Bicyclo[1.1.0]butane. C2v	-155.6021487	-0.90301476	-155.873053	222.840378	224.3106576	5.7	7.2
87	CYCLOBUTENE b3lyp	-155.6279733	-0.89397234	-155.896165	162.590892	164.0611719	6.1	7.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8484971	-0.92294371	-157.125380	41.988619	43.45889869	13.5	15.0
89	Isobutene. Single	-156.8669914	-0.91910145	-157.142722	-8.330853	-6.860573147	8.4	9.9
90	Trans butane	-158.0774788	-0.94950937	-158.362332	-103.897605	-102.4273255	21.6	23.1
91	isobutane B3LYP/6-31G*	-158.0784079	-0.95282959	-158.364257	-110.246474	-108.776194	24.1	25.5
92	Spiropentane. D2d	-194.8346286	-1.12981461	-195.173573	185.137332	186.9751818	-0.2	1.6
93	Benzene B3LYP	-231.7577422	-1.2994581	-232.147580	54.537856	56.74327585	-27.9	-25.7
94	DIFLUOROMETHANE C2V	-238.6934818	-0.87637204	-238.956393	-473.870426	-470.2997456	-23.3	-19.7
95	HCF3 TRI-FLUOROMETHANE	-337.8530703	-1.18818846	-338.209527	-732.041920	-726.8696848	-35.0	-29.8
96	CH2CL2 C2V	-959.2183382	-0.9003004	-959.488428	-99.349576	-91.94566566	-4.0	3.4
97	chcl3 B3LYP/6-31G*	-1418.615014	-1.23482736	-1418.985462	-112.026538	-101.1044577	-8.7	2.2
98	METHYLAMINE b3lyp	-95.65868913	-0.52964878	-95.817584	-22.117288	-21.74971752	0.9	1.3
99	Acetonitrile. CH3-CN.	-132.5001382	-0.70476308	-132.711567	47.751601	48.48674081	-27.6	-26.8
100	NITRO METHANE	-244.6186294	-1.16599698	-244.968428	-128.835430	-126.5774998	-54.4	-52.1
101	Methyl-nitrite. CH3-O-N=O.	-244.6146599	-1.15678399	-244.961695	-114.885053	-112.6271234	-48.4	-46.1
102	Methylsilane. CH3-SiH3.	-330.9309413	-0.57955599	-331.104808	-6.876959	-4.724048897	22.4	24.6
103	Formic Acid.	-189.4806167	-0.84162962	-189.733106	-411.337036	-409.0791064	-32.7	-30.4
104	Methyl formate.	-228.6906185	-1.07106929	-229.011939	-392.707160	-390.0816598	-37.1	-34.4
105	acetamide ch3cohn2	-208.8481104	-1.03939086	-209.159928	-264.533789	-262.8534691	-26.0	-24.4

106	Aziridine. (cyclic	-133.6464822	-0.73633439	-133.867383	119.673982	120.4091217	-6.7	-5.9
107	Cyanogen. NCCN.	-185.3351583	-0.94508805	-185.618685	238.139594	238.8747336	-68.5	-67.8
108	DIMETHYLAMINE b3lyp	-134.8724308	-0.76054774	-135.100595	-15.146198	-14.41105838	3.3	4.0
109	TRANS ETHYLAMINE	-134.8839318	-0.76171231	-135.112445	-45.322044	-44.58690394	2.0	2.7
110	KETENE B3LYP	-152.3433853	-0.73744016	-152.564617	-87.630146	-85.94982578	-40.4	-38.7
111	OXIRANE B3LYP	-153.5098672	-0.76802759	-153.740275	-65.644003	-63.96368296	-12.9	-11.2
112	Acetaldehyde B3LYP	-153.5557846	-0.76063641	-153.783975	-183.497515	-181.8171952	-17.4	-15.7
113	Glyoxal, O=CH-CH=O.	-227.4653345	-1.03847899	-227.776878	-258.573325	-255.9478248	-46.4	-43.8
114	ETHANOL TRANS	-154.7491425	-0.79061067	-154.986326	-232.848988	-231.1686678	2.3	4.0
115	DIMETHYL ETHER,	-154.7325034	-0.78773972	-154.968825	-187.744407	-186.0640875	-3.6	-2.0
116	Thiooxirane. (cyclic	-476.4171049	-0.85330747	-476.673097	80.432550	83.50438528	-1.6	1.5
117	Dimethylsulfoxide. (CH3)2SO.	-552.7234612	-1.20657951	-553.085435	-145.916019	-141.8990036	5.5	9.6
118	Thioethanol. CH3-CH2-SH.	-477.6333389	-0.87209811	-477.894968	-30.266418	-27.19458331	16.2	19.2
119	ch3sch3 B3LYP	-477.631526	-0.87417601	-477.893779	-24.617498	-21.54566253	12.6	15.7
120	Vinyl fluoride,	-177.5542704	-0.76563863	-177.783962	-159.740876	-157.4041806	-20.8	-18.5
121	Ethyl chloride.	-539.0426214	-0.80648702	-539.284567	-106.981588	-102.7282779	5.1	9.4
122	Vinyl chloride,	-537.8219904	-0.77793615	-538.055371	14.206041	18.45935052	-8.8	-4.6
123	h2c=chcn B3LYP	-170.5038358	-0.90697142	-170.775927	151.243812	152.3465215	-29.5	-28.4
124	ACETONE B3LYP	-192.7899013	-0.99249889	-193.087651	-229.934678	-227.8867879	-12.8	-10.7
125	CH3COOH ACETIC	-228.7161381	-1.07014569	-229.037182	-459.435581	-456.8100813	-26.8	-24.2
126	CH3CFO HCCO	-252.7272178	-1.07825653	-253.050695	-474.293131	-471.0112562	-32.0	-28.8
127	ch3c(o)cl hcco	-612.9819693	-1.09537411	-613.310582	-270.500917	-265.3024273	-27.8	-22.6
128	ch3ch2ch2cl B3LYP	-578.2650864	-1.03924129	-578.576859	-122.988935	-118.3680552	8.8	13.4
129	Isopropyl alcohol,	-193.9763808	-1.02543091	-194.284010	-264.800947	-262.7530567	8.0	10.0
130	Methyl ethyl	-193.9600741	-1.01963577	-194.265965	-216.874644	-214.8267543	-0.6	1.5
131	Trimethyl Amine.	-174.0884324	-0.99649462	-174.387381	-19.389764	-18.28705446	4.5	5.6
132	FURAN B3LYP	-229.5954245	-1.18143265	-229.949854	-67.879412	-65.4639521	-33.2	-30.7
133	Thiophene b3lyp	-552.4923521	-1.27430128	-552.874642	96.941806	100.7487815	-18.1	-14.3
134	PYROLE PLANAR	-209.7465909	-1.15259172	-210.092368	76.315337	77.78561721	-32.1	-30.6
135	C2v Pyridine	-247.7863481	-1.34507525	-248.189871	94.512412	96.35026219	-46.1	-44.2
136	H2 B3LYP/6-31G*	-1.15862821	-0.03573364	-1.169348	6.847161	6.847160629	6.8	6.8
137	SH b3lyp/6-31G*	-398.554811	-0.36639945	-398.664731	145.864025	148.2007201	2.8	5.1
138	CCH B3LYP	-76.46071575	-0.39312976	-76.578655	562.636410	563.3715497	-2.6	-1.9
139	C2H3 CS,2-A'	-77.73821505	-0.41425634	-77.862492	292.671928	293.4070678	-6.9	-6.2
140	ch3co hcco	-152.9157035	-0.73844954	-153.137238	-38.546293	-36.8659728	-28.5	-26.8
141	H2COH C1	-114.8706413	-0.5263919	-115.028559	-26.917207	-25.60445731	-9.8	-8.5
142	ch3o CS,	-114.8633024	-0.49929734	-115.013092	10.118799	11.43154932	-7.0	-5.7

143	ch3ch2o 2A"	-154.0907937	-0.73086488	-154.310053	-19.121622	-17.44130191	-3.6	-2.0
144	ch3s 2-A'	-437.7787955	-0.60169486	-437.959304	124.984138	127.6884034	0.3	3.0
145	c2h5 staggered	-78.97448903	-0.44527277	-79.108071	126.457662	127.1928023	5.5	6.3
146	(ch3)2ch Cs	-118.2016899	-0.67883215	-118.405340	97.408556	98.511266	7.5	8.6
147	TERT-BUTYL RADICAL	-157.4289231	-0.91450765	-157.703275	66.345098	67.81537784	14.9	16.4
148	NO2 RADICAL	-204.7758722	-0.9334162	-205.055897	-38.576424	-36.68606386	-71.6	-69.7

MAD	**18.0**	**17.1**
LD	**-80.6**	**-73.5**

Table S5.9b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 52% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498591	0.000000	-0.498591
2	li	-7.466809	-0.014787	-7.471245
3	be	-14.634189	-0.055428	-14.650818
4	b	-24.612808	-0.079674	-24.636710
5	c	-37.795255	-0.106659	-37.827252
6	n	-54.527493	-0.137546	-54.568756
7	o	-74.990014	-0.195710	-75.048727
8	f	-99.635727	-0.259588	-99.713604
9	na	-162.139349	-0.174638	-162.191740
10	al	-242.218109	-0.224175	-242.285362
11	si	-289.217450	-0.254653	-289.293846
12	p	-341.098308	-0.284131	-341.183547
13	s	-397.930788	-0.326198	-398.028648
14	cl	-459.947155	-0.297415	-460.036379

Table S5.10a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 24%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0507525	-0.04781987	-8.062229	145.808342	145.8083415	6.5	6.5
2	BERYLLIUM HYDRIDE	-15.22676944	-0.05628113	-15.240277	318.885545	318.8855445	-22.9	-22.9
3	DOUBLET CH	-38.42637256	-0.1479793	-38.461888	598.686676	599.0542464	2.5	2.8
4	CH2 3-B1	-39.08986418	-0.16705717	-39.129958	395.296372	395.6639418	3.3	3.6
5	Singlet methylene,	-39.06756856	-0.18835775	-39.112774	438.799544	439.1671137	8.7	9.1
6	Methyl radical,	-39.76384523	-0.21281572	-39.814921	151.476536	151.8441058	5.0	5.4
7	ch4 //b3lyp/6-31G*	-40.4298546	-0.25563258	-40.491206	-64.256527	-63.88895676	10.6	11.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15797261	-0.19138266	-55.203904	356.620700	356.6206998	0.1	0.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.80118302	-0.24630059	-55.860295	185.998199	185.998199	-2.7	-2.7
10	AMMONIA, //b3lyp/6-31G*	-56.46834223	-0.30167688	-56.540745	-39.113420	-39.11342045	6.9	6.9
11	OH RADICAL	-75.65683978	-0.26355408	-75.720093	40.679290	41.62446992	1.3	2.3
12	Water //b3lyp/6-31G*	-76.33586507	-0.33415807	-76.416063	-230.448754	-229.5035739	11.4	12.3
13	HYDROGEN FLUORIDE,	-100.3552953	-0.34436346	-100.437943	-266.284860	-264.6833045	6.1	7.7
14	SIH2 singlet	-290.4737261	-0.31161135	-290.548513	274.296638	276.0819782	1.5	3.3
15	SIH2 3B1	-290.4465958	-0.28833985	-290.515797	361.202001	362.987341	0.5	2.3
16	SIH3 c3v	-291.088899	-0.31687153	-291.164948	202.246802	204.0321421	1.8	3.6
17	SIH4 //b3lyp/6-31G*	-291.7325236	-0.34463977	-291.815237	42.246459	44.0317989	7.9	9.7
18	ph2 doublet	-342.3575753	-0.35141694	-342.441915	137.703006	137.7030058	-0.8	-0.8
19	PH3 c3v	-342.9861842	-0.38360107	-343.078248	15.842977	15.84297655	10.4	10.4
20	SH2 //b3lyp/6-31G*	-399.2340424	-0.40519332	-399.331289	-10.652293	-8.315597703	9.8	12.2
21	HCL //b3lyp/6-31G*	-460.6445366	-0.3428515	-460.726821	-88.652235	-85.13406497	3.8	7.3
22	DILITHIUM //b3lyp/6-31G*	-14.96637668	-0.05965314	-14.980693	230.082883	230.0828832	14.2	14.2
23	Lithium Fluoride,	-107.3206934	-0.37467896	-107.410616	-337.845755	-336.2442001	-2.7	-1.1
24	ACETYLENE //b3lyp/6-31g*	-77.19924138	-0.42928262	-77.302269	232.738333	233.4734726	6.0	6.7
25	ETHYLENE //b3lyp/6-31g*	-78.44193027	-0.44974374	-78.549869	63.605010	64.34015046	11.3	12.0
26	ETHANE //b3lyp/6-31g*	-79.66590658	-0.48319975	-79.781875	-65.894272	-65.15913202	18.2	18.9
27	CYANO RADICAL,	-92.57637107	-0.46928339	-92.688999	445.647599	446.0151688	6.7	7.1
28	HYDROGEN CYANIDE	-93.28747369	-0.47520496	-93.401523	126.324435	126.6920051	-5.5	-5.1
29	CARBON MONOXIDE	-113.1799494	-0.48572857	-113.296524	-112.409183	-111.0964333	-2.0	-0.6
30	HCO BENT	-113.7067338	-0.50844392	-113.828760	33.371546	34.68429586	-8.5	-7.2
31	H2CO //b3lyp/6-31g*	-114.3496179	-0.52801905	-114.476343	-110.059775	-108.7470251	-1.3	0.0

32	METHANOL //b3lyp/6-31g*	-115.5568043	-0.55711647	-115.690512	-189.800551	-188.4878012	11.0	12.3
33	Nitrogen N2,	-109.3871575	-0.50965952	-109.509476	-3.244358	-3.244358255	-3.2	-3.2
34	H2NNH2 //b3lyp/6-31g*	-111.6978519	-0.57239054	-111.835226	102.645601	102.6456011	7.3	7.3
35	NO radical,	-129.7375037	-0.55205085	-129.869996	83.976118	84.92129791	-6.4	-5.5
36	O2 //b3lyp/6-31g*	-150.1508459	-0.61613329	-150.298718	-7.093041	-5.202681189	-7.1	-5.2
37	HYDROGEN PEROXIDE	-151.3685601	-0.64738097	-151.523932	-119.542171	-117.6518112	16.4	18.3
38	F2 //b3lyp/6-31g*	-199.3268722	-0.67630321	-199.489185	15.007352	18.21046187	15.0	18.2
39	CO2 D*H	-188.3662918	-0.81638708	-188.562225	-412.456169	-410.1982394	-19.2	-16.9
40	na2 //b3lyp/6-31G*	-324.3471051	-0.37791848	-324.437806	142.969529	142.9695285	0.7	0.7
41	SI2 3-SGG	-578.6017648	-0.56918473	-578.738369	588.604132	592.1748121	3.3	6.8
42	P2 //b3lyp/6-31g*	-682.4107593	-0.72464139	-682.584673	151.541283	151.5412826	8.0	8.0
43	S2 //b3lyp/6-31g*	-796.071081	-0.7703374	-796.255962	127.457118	132.1305084	-1.0	3.7
44	CL2 //b3lyp/6-31g*	-920.0495792	-0.66464732	-920.209095	8.187987	15.22432672	8.2	15.2
45	Sodium Chloride	-622.2940616	-0.51799483	-622.418380	-173.747474	-170.2293037	8.7	12.2
46	SIO //b3lyp/6-31g*	-364.5151276	-0.63068726	-364.666492	-96.741986	-94.01146641	6.2	8.9
47	Carbon monosulfide,	-436.0060496	-0.58991194	-436.147628	286.828575	289.5328401	6.9	9.6
48	OS //b3lyp/6-31g*	-473.1311848	-0.70100764	-473.299427	2.025413	5.307288037	-3.0	0.3
49	CLO 2-PI	-535.0637929	-0.62079303	-535.212783	107.035064	111.4984143	5.8	10.2
50	CLF 1-SG	-559.7133458	-0.66747047	-559.873539	-52.645609	-47.52588434	2.6	7.7
51	si2h6 //b3lyp/6-31g*	-582.2904222	-0.6699354	-582.451207	98.296369	101.8670491	18.4	22.0
52	Methyl chloride,	-499.875517	-0.57157243	-500.012694	-74.535017	-70.6492774	7.5	11.4
53	H3C-SH METHANETHIOL	-438.4679237	-0.6364054	-438.620661	-5.773989	-3.06972409	17.2	19.9
54	HOCl //b3lyp/6-31g*	-535.7120848	-0.65919543	-535.870292	-67.299350	-62.83599952	7.2	11.6
55	SO2 //b3lyp/6-31G*	-548.3030865	-1.05819709	-548.557054	-281.976238	-277.7491833	15.1	19.3
56	BF3 PLANAR	-324.2810419	-1.0915605	-324.543016	-1145.574870	-1140.63893	-10.0	-5.1
57	bcl3 B3LYP	-1405.066104	-1.13182484	-1405.337742	-413.728534	-403.0427488	-10.8	-0.1
58	ALf3 B3LYP	-541.8292696	-1.23255583	-542.125083	-1191.799882	-1186.102547	17.4	23.1
59	alcl3 B3LYP	-1622.672572	-1.23414093	-1622.968766	-583.141881	-571.6947009	1.4	12.8
60	cf4 B3LYP	-437.1021276	-1.49173899	-437.460145	-943.244356	-936.4705659	-10.2	-3.4
61	ccl4 B3LYP	-1878.187281	-1.57036606	-1878.564168	-85.475183	-71.03493335	10.3	24.8
62	O=C=S. Singlet	-511.2499882	-0.90788418	-511.467880	-157.018294	-153.3688486	-18.5	-14.9
63	CS2 B3LYP	-834.1303357	-1.00664523	-834.371931	103.215063	108.2560232	-13.5	-8.5
64	COF2 B3LYP	-312.7119936	-1.15493762	-312.989179	-620.680736	-616.1648763	3.2	7.7
65	sif4 B3LYP	-688.6928072	-1.59301924	-689.075132	-1573.976977	-1565.785417	41.0	49.2
66	sicl4, td	-2129.760134	-1.63121673	-2130.151626	-638.154764	-622.2967435	24.6	40.4
67	nno B3LYP	-184.4251996	-0.87787623	-184.635890	59.600886	60.54606634	-22.4	-21.5
68	clno B3LYP	-589.7643142	-0.94706058	-589.991609	45.077268	49.54061837	-6.8	-2.3

69	nf3 c3v	-353.7450963	-1.27437789	-354.050947	-138.933595	-134.1289301	-6.7	-1.9
70	pf3 c3v	-640.6035334	-1.33018986	-640.922779	-937.608946	-932.8042813	20.9	25.8
71	ozone 1-a1	-225.1327431	-1.05708501	-225.386444	152.865478	155.7010176	10.2	13.0
72	f2o B3LYP	-274.3897732	-0.9992729	-274.629599	35.811764	39.96005406	11.1	15.3
73	CLF3, C2V	-759.0709847	-1.41500084	-759.410585	-160.267981	-151.9451456	-1.3	7.0
74	CF2=CF2 D2H	-475.0634592	-1.69949704	-475.471338	-692.092341	-684.9509812	-33.5	-26.4
75	cl2c=ccl2 B3LYP	-1916.219822	-1.77414081	-1916.645616	-16.435720	-1.627899897	-3.9	10.9
76	cf3cn B3LYP	-430.0160554	-1.64110132	-430.409920	-515.249699	-509.7098942	-19.9	-14.3
77	PROPYNE C3V	-116.4486983	-0.65808332	-116.606638	193.514094	194.6168043	8.6	9.7
78	ALLENE D2D	-116.449177	-0.65160211	-116.605561	194.684517	195.787227	4.3	5.4
79	CYCLOPROPENE C2V	-116.4092279	-0.66078023	-116.567815	294.724629	295.8273392	17.7	18.8
80	PROPENE CS	-117.6851056	-0.68116286	-117.848585	38.585093	39.68780256	18.5	19.6
81	CYCLOPROPANE D3H	-117.6711905	-0.68693971	-117.836056	73.960255	75.06296515	20.8	21.9
82	PROPANE C2V	-118.903969	-0.71422996	-119.075384	-76.927525	-75.8248155	27.7	28.8
83	TRANS-1,3-BUTADIENE C2H	-155.709671	-0.88157368	-155.921249	128.540531	130.0108114	18.5	20.0
84	Dimethyl acetylene	-155.6960643	-0.8875356	-155.909073	160.660371	162.1306512	15.1	16.5
85	Methylene cyclopropane.	-155.6768396	-0.88786389	-155.889927	209.523369	210.993649	9.1	10.6
86	Bicyclo[1.1.0]butane. C2v	-155.660534	-0.89938461	-155.876386	247.006680	248.4769599	29.9	31.3
87	CYCLOBUTENE b3lyp	-155.6860667	-0.89029293	-155.899737	186.130165	187.600445	29.6	31.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.9100727	-0.91928381	-157.130701	61.057085	62.52736486	32.6	34.1
89	Isobutene. Single	-156.9279948	-0.91539733	-157.147690	11.662779	13.13305936	28.4	29.9
90	Trans butane	-158.1418981	-0.94580342	-158.368891	-87.960989	-86.49070902	37.6	39.0
91	isobutane B3LYP/6-31G*	-158.1428898	-0.94910509	-158.370675	-93.939570	-92.46928968	40.4	41.8
92	Spiropentane. D2d	-194.9085987	-1.12531325	-195.178674	212.921738	214.7595881	27.6	29.4
93	Benzene B3LYP	-231.8406059	-1.29412966	-232.151197	94.236098	96.44151848	11.8	14.0
94	DIFLUOROMETHANE C2V	-238.7488079	-0.87304587	-238.958339	-453.811332	-450.240652	-3.2	0.4
95	HCF3 TRI-FLUOROMETHANE	-337.9273494	-1.18373289	-338.211445	-703.518553	-698.3463179	-6.5	-1.3
96	CH2CL2 C2V	-959.3187645	-0.89686532	-959.534012	-87.047440	-79.64352992	8.3	15.8
97	chcl3 B3LYP/6-31G*	-1418.756824	-1.23008264	-1419.052044	-93.053829	-82.13174932	10.3	21.2
98	METHYLAMINE b3lyp	-95.69299951	-0.52754237	-95.819610	-10.505135	-10.13756475	12.5	12.9
99	Acetonitrile. CH3-CN.	-132.5429287	-0.70167975	-132.711332	73.319153	74.05429302	-2.0	-1.3
100	NITRO METHANE	-244.6840786	-1.16075301	-244.962659	-78.827098	-76.56916752	-4.4	-2.1
101	Methyl-nitrite. CH3-O-N=O.	-244.6799066	-1.15136174	-244.956233	-65.683963	-63.4260332	0.8	3.1
102	Methylsilane. CH3-SiH3.	-330.9857637	-0.57752699	-331.124370	-6.592268	-4.439358056	22.7	24.8
103	Formic Acid.	-189.5301603	-0.83800416	-189.731281	-380.237272	-377.9793421	-1.6	0.7
104	Methyl formate.	-228.7556321	-1.06652374	-229.011598	-357.241102	-354.6156019	-1.6	1.0
105	acetamide ch3cohn2	-208.9122957	-1.03503962	-209.160705	-232.479776	-230.7994558	6.0	7.7

106	Aziridine. (cyclic	-133.6932336	-0.73334462	-133.869236	139.877202	140.6123421	13.5	14.3
107	Cyanogen. NCCN.	-185.3872064	-0.94058569	-185.612947	286.464648	287.199788	-20.2	-19.5
108	DIMETHYLAMINE b3lyp	-134.922285	-0.75753161	-135.104093	0.861834	1.596973765	19.3	20.0
109	TRANS ETHYLAMINE	-134.9338121	-0.75869086	-135.115898	-29.195757	-28.46061665	18.1	18.8
110	KETENE B3LYP	-152.3872795	-0.73417525	-152.563482	-59.224368	-57.54404821	-11.9	-10.3
111	OXIRANE B3LYP	-153.5575332	-0.76485969	-153.741099	-42.263213	-40.58289342	10.5	12.1
112	Acetaldehyde B3LYP	-153.6031166	-0.75742181	-153.784898	-160.374846	-158.6945259	5.7	7.4
113	Glyoxal, O=CH-CH=O.	-227.5266012	-1.03392209	-227.774743	-218.517011	-215.8915107	-6.4	-3.8
114	ETHANOL TRANS	-154.8000504	-0.78747662	-154.989045	-214.323297	-212.642977	20.8	22.5
115	DIMETHYL ETHER,	-154.7833166	-0.78460119	-154.971621	-169.419520	-167.7391997	14.7	16.4
116	Thiooxirane. (cyclic	-476.4872289	-0.85008532	-476.691249	96.914274	99.98610909	14.9	18.0
117	Dimethylsulfoxide. (CH3)2SO.	-552.8141838	-1.20169674	-553.102591	-117.672821	-113.6558059	33.8	37.8
118	Thioethanol. CH3-CH2-SH.	-477.7065312	-0.86889057	-477.915065	-18.769096	-15.69726099	27.7	30.7
119	ch3sch3 B3LYP	-477.7046447	-0.87093883	-477.913670	-12.581009	-9.50917383	24.7	27.7
120	Vinyl fluoride,	-177.6028787	-0.76256281	-177.785894	-139.900242	-137.563547	-1.0	1.3
121	Ethyl chloride.	-539.1172613	-0.80338725	-539.310074	-95.509035	-91.25572455	16.6	20.9
122	Vinyl chloride,	-537.8931816	-0.77481905	-538.079138	30.126446	34.37975555	7.1	11.4
123	h2c=chcn B3LYP	-170.5586462	-0.90294553	-170.775353	185.840002	186.9427119	5.1	6.2
124	ACETONE B3LYP	-192.8528588	-0.9883871	-193.090072	-202.486797	-200.4389072	14.7	16.7
125	CH3COOH ACETIC	-228.7813092	-1.06566002	-229.037068	-424.566135	-421.9406347	8.1	10.7
126	CH3CFO HCCO	-252.7934409	-1.07383159	-253.051160	-441.578228	-438.2963526	0.7	4.0
127	ch3c(o)cl hcco	-613.0706089	-1.09081156	-613.332404	-240.449356	-235.2508655	2.2	7.4
128	ch3ch2ch2cl B3LYP	-578.3552997	-1.03522753	-578.603754	-106.903155	-102.2822746	24.9	29.5
129	Isopropyl alcohol,	-194.0429229	-1.02137103	-194.288052	-241.488851	-239.4409612	31.3	33.4
130	Methyl ethyl	-194.0264666	-1.01558796	-194.270208	-194.090288	-192.0423981	22.2	24.3
131	Trimethyl Amine.	-174.1539153	-0.99252949	-174.392122	1.611428	2.714138356	25.5	26.6
132	FURAN B3LYP	-229.6680014	-1.17649131	-229.950359	-27.382983	-24.96752282	7.3	9.8
133	Thiophene b3lyp	-552.5873404	-1.26920954	-552.891951	131.917744	135.724719	16.9	20.7
134	PYROLE PLANAR	-209.8183142	-1.14786063	-210.093801	113.903226	115.3735055	5.5	7.0
135	C2v Pyridine	-247.8701132	-1.33947767	-248.191588	139.491715	141.3295652	-1.1	0.7
136	H2 B3LYP/6-31G*	-1.16094081	-0.0355812	-1.169480	6.620958	6.620958051	6.6	6.6
137	SH b3lyp/6-31G*	-398.5949567	-0.36522441	-398.682611	146.602488	148.9391835	3.5	5.8
138	CCH B3LYP	-76.48462126	-0.39130007	-76.578533	579.293537	580.0286774	14.0	14.8
139	C2H3 CS,2-A'	-77.76578696	-0.41253356	-77.864795	303.083979	303.8191193	3.5	4.2
140	ch3co hcco	-152.9609105	-0.73530279	-153.137383	-13.442490	-11.76217001	-3.4	-1.7
141	H2COH C1	-114.9038956	-0.52428597	-115.029724	-12.631847	-11.31909711	4.5	5.8
142	ch3o CS,	-114.896477	-0.49727359	-115.015823	20.293423	21.60617257	3.1	4.5

143	ch3ch2o 2A"	-154.139528	-0.72791645	-154.314228	-4.478195	-2.797875492	11.0	12.7
144	ch3s 2-A'	-437.834407	-0.59956723	-437.978303	131.043145	133.74741	6.4	9.1
145	c2h5 staggered	-79.00562473	-0.44352601	-79.112071	132.534464	133.2696045	11.6	12.4
146	(ch3)2ch Cs	-118.2484152	-0.67617836	-118.410698	108.178417	109.2811269	18.2	19.3
147	TERT-BUTYL RADICAL	-157.4912685	-0.91093517	-157.709893	82.068954	83.53923426	30.6	32.1
148	NO2 RADICAL	-204.8235981	-0.92896188	-205.046549	12.508851	14.39921119	-20.5	-18.7

MAD	**11.7**	**13.0**
LD	**41.0**	**49.2**

Table S5.10b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 24%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498614	0.000000	-0.498614
2	li	-7.470083	-0.014756	-7.473625
3	be	-14.639965	-0.055111	-14.653191
4	b	-24.620443	-0.079251	-24.639464
5	c	-37.804868	-0.106187	-37.830352
6	n	-54.539096	-0.137061	-54.571990
7	o	-75.005358	-0.195025	-75.052164
8	f	-99.654725	-0.258742	-99.716823
9	na	-162.163705	-0.174137	-162.205498
10	al	-242.247781	-0.223489	-242.301418
11	si	-289.249346	-0.253887	-289.310279
12	p	-341.132439	-0.283330	-341.200438
13	s	-397.968734	-0.325216	-398.046786
14	cl	-459.988811	-0.296375	-460.059941

Table S5.11a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04986442	-0.04782126	-8.061820	145.860545	145.8605446	6.5	6.5
2	BERYLLIUM HYDRIDE	-15.22568771	-0.05627331	-15.239756	319.204026	319.2040258	-22.6	-22.6
3	DOUBLET CH	-38.42439486	-0.14798318	-38.461391	598.586291	598.9538606	2.4	2.7
4	CH2 3-B1	-39.0877115	-0.16705548	-39.129475	395.158163	395.5257326	3.1	3.5
5	Singlet methylene,	-39.0652408	-0.18835402	-39.112329	438.563099	438.9306693	8.4	8.8
6	Methyl radical,	-39.76125944	-0.21281931	-39.814464	151.270600	151.6381705	4.8	5.2
7	ch4 //b3lyp/6-31G*	-40.42690832	-0.25562673	-40.490815	-64.633956	-64.26638604	10.3	10.6
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15559213	-0.19139288	-55.203440	356.378048	356.3780477	-0.1	-0.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79838684	-0.24630764	-55.859964	185.407178	185.4071777	-3.3	-3.3
10	AMMONIA, //b3lyp/6-31G*	-56.46516294	-0.30167821	-56.540582	-40.148736	-40.14873649	5.9	5.9
11	OH RADICAL	-75.65382943	-0.26356447	-75.719721	39.998559	40.94373868	0.7	1.6
12	Water //b3lyp/6-31G*	-76.33246107	-0.33416493	-76.416002	-231.947348	-231.0021678	9.9	10.8
13	HYDROGEN FLUORIDE,	-100.3516721	-0.34437271	-100.437765	-267.472079	-265.8705239	4.9	6.5
14	SIH2 singlet	-290.4677514	-0.3116034	-290.545652	274.516571	276.3019106	1.7	3.5
15	SIH2 3B1	-290.440815	-0.28831251	-290.512893	361.536543	363.321883	0.9	2.7
16	SIH3 c3v	-291.0827432	-0.31685629	-291.161957	202.808944	204.594284	2.4	4.2
17	SIH4 //b3lyp/6-31G*	-291.7260306	-0.34463065	-291.812188	42.960821	44.74616095	8.7	10.4
18	ph2 doublet	-342.3511434	-0.35141648	-342.438998	137.909282	137.9092821	-0.6	-0.6
19	PH3 c3v	-342.9794245	-0.38359192	-343.075322	16.070601	16.07060136	10.6	10.6
20	SH2 //b3lyp/6-31G*	-399.2270237	-0.40518766	-399.328321	-10.877959	-8.541264416	9.6	12.0
21	HCL //b3lyp/6-31G*	-460.6372653	-0.34284943	-460.722978	-88.948392	-85.43022242	3.5	7.0
22	DILITHIUM //b3lyp/6-31G*	-14.96503846	-0.0596489	-14.979951	229.986914	229.9869138	14.1	14.1
23	Lithium Fluoride,	-107.316517	-0.37469477	-107.410191	-339.404051	-337.8024963	-4.3	-2.7
24	ACETYLENE //b3lyp/6-31g*	-77.19479244	-0.42926352	-77.302108	230.350559	231.0856985	3.6	4.3
25	ETHYLENE //b3lyp/6-31g*	-78.43694447	-0.44972943	-78.549377	62.086412	62.82155155	9.8	10.5
26	ETHANE //b3lyp/6-31g*	-79.66038462	-0.48318817	-79.781182	-66.885362	-66.1502223	17.2	17.9
27	CYANO RADICAL,	-92.57210053	-0.46918782	-92.689397	441.735360	442.1029297	2.8	3.2
28	HYDROGEN CYANIDE	-93.28282688	-0.47518932	-93.401624	123.192158	123.5597279	-8.6	-8.2
29	CARBON MONOXIDE	-113.1751	-0.4857222	-113.296531	-115.488747	-114.1759967	-5.0	-3.7
30	HCO BENT	-113.7016505	-0.50843201	-113.828759	30.313279	31.62602919	-11.5	-10.2
31	H2CO //b3lyp/6-31g*	-114.3442106	-0.52801409	-114.476214	-112.785729	-111.4729791	-4.0	-2.7

32	METHANOL //b3lyp/6-31g*	-115.5508425	-0.55711393	-115.690121	-191.836364	-190.5236141	9.0	10.3
33	Nitrogen N2,	-109.3823192	-0.5096437	-109.509730	-6.834361	-6.834360885	-6.8	-6.8
34	H2NNH2 //b3lyp/6-31g*	-111.691883	-0.57239016	-111.834981	100.366746	100.3667464	5.0	5.0
35	NO radical,	-129.7322225	-0.5520412	-129.870233	80.234874	81.1800544	-10.1	-9.2
36	O2 //b3lyp/6-31g*	-150.1451227	-0.61613184	-150.299156	-11.558511	-9.668151017	-11.6	-9.7
37	HYDROGEN PEROXIDE	-151.3621969	-0.6473865	-151.524043	-123.151995	-121.2616353	12.8	14.7
38	F2 //b3lyp/6-31g*	-199.3201153	-0.67630736	-199.489192	11.683072	14.88618189	11.7	14.9
39	CO2 D*H	-188.3583796	-0.81637339	-188.562473	-417.828933	-415.5710027	-24.5	-22.3
40	na2 //b3lyp/6-31G*	-324.3386769	-0.37791295	-324.433155	142.833885	142.8338855	0.6	0.6
41	SI2 3-SGG	-578.5907819	-0.56916548	-578.733073	587.927522	591.4982019	2.6	6.2
42	P2 //b3lyp/6-31g*	-682.3986149	-0.72461707	-682.579769	149.507617	149.5076173	6.0	6.0
43	S2 //b3lyp/6-31g*	-796.0580108	-0.77032758	-796.250593	125.517225	130.1906147	-2.9	1.7
44	CL2 //b3lyp/6-31g*	-920.0354493	-0.6646396	-920.201609	7.067268	14.10360842	7.1	14.1
45	Sodium Chloride	-622.2827322	-0.51799767	-622.412232	-174.163148	-170.6449778	8.3	11.8
46	SIO //b3lyp/6-31g*	-364.5066015	-0.63069679	-364.664276	-99.870217	-97.13969662	3.1	5.8
47	Carbon monosulfide,	-435.9975657	-0.58989106	-436.145039	284.204769	286.9090336	4.3	7.0
48	OS //b3lyp/6-31g*	-473.1217784	-0.70099987	-473.297028	-1.354435	1.927439616	-6.4	-3.1
49	CLO 2-PI	-535.0538743	-0.62074857	-535.209061	104.761968	109.2253175	3.5	8.0
50	CLF 1-SG	-559.7028829	-0.66747014	-559.869750	-54.738778	-49.61905345	0.5	5.6
51	si2h6 //b3lyp/6-31g*	-582.2778039	-0.66991831	-582.445283	99.266954	102.8376337	19.4	22.9
52	Methyl chloride,	-499.8656911	-0.57156347	-500.008582	-75.529686	-71.64394571	6.5	10.4
53	H3C-SH METHANETHIOL	-438.4583376	-0.6363937	-438.617436	-6.730471	-4.026205817	16.3	19.0
54	HOCl //b3lyp/6-31g*	-535.7018321	-0.65919355	-535.866630	-69.731391	-65.26804139	4.7	9.2
55	SO2 //b3lyp/6-31G*	-548.2905393	-1.05818684	-548.555086	-288.144402	-283.9173469	8.9	13.1
56	BF3 PLANAR	-324.2691064	-1.09156164	-324.541997	-1149.094127	-1144.158187	-13.6	-8.6
57	bcl3 B3LYP	-1405.043215	-1.13180601	-1405.326167	-415.734997	-405.0492116	-12.8	-2.1
58	ALf3 B3LYP	-541.8137406	-1.2325648	-542.121882	-1195.498967	-1189.801632	13.7	19.4
59	alcl3 B3LYP	-1622.646093	-1.23412504	-1622.954624	-584.318838	-572.8716576	0.2	11.6
60	cf4 B3LYP	-437.0862117	-1.49173151	-437.459145	-948.633812	-941.8600217	-15.6	-8.8
61	ccl4 B3LYP	-1878.156759	-1.57034043	-1878.549345	-89.507260	-75.06700979	6.3	20.7
62	O=C=S. Singlet	-511.238439	-0.90786184	-511.465404	-161.599426	-157.9499809	-23.1	-19.5
63	CS2 B3LYP	-834.1151389	-1.00661376	-834.366792	99.263124	104.3040836	-17.5	-12.4
64	COF2 B3LYP	-312.7000855	-1.15492804	-312.988818	-626.101116	-621.5852557	-2.3	2.2
65	sif4 B3LYP	-688.673259	-1.59301584	-689.071513	-1578.376795	-1570.185235	36.6	44.8
66	sicl4, td	-2129.725981	-1.63119067	-2130.133779	-640.133472	-624.2754518	22.6	38.5
67	nno B3LYP	-184.4173241	-0.87785271	-184.636787	52.664787	53.60996741	-29.3	-28.4
68	clno B3LYP	-589.7518854	-0.94704076	-589.988646	39.351179	43.81452915	-12.5	-8.1

69	nf3 c3v	-353.732317	-1.27437203	-354.050910	-145.255762	-140.4510973	-13.0	-8.2
70	pf3 c3v	-640.5870133	-1.33018704	-640.919560	-941.570550	-936.7658854	17.0	21.8
71	ozone 1-a1	-225.1239649	-1.05706116	-225.388230	143.200820	146.0363602	0.5	3.4
72	f2o B3LYP	-274.3800462	-0.99927124	-274.629864	30.151727	34.30001665	5.5	9.6
73	CLF3, C2V	-759.0535549	-1.41499927	-759.407305	-167.000737	-158.6779022	-8.0	0.3
74	CF2=CF2 D2H	-475.045505	-1.69948759	-475.470377	-698.988939	-691.8475787	-40.4	-33.3
75	cl2c=ccl2 B3LYP	-1916.187216	-1.77410943	-1916.630743	-21.744976	-6.937155803	-9.2	5.6
76	cf3cn B3LYP	-429.9991153	-1.64107736	-430.409385	-523.074343	-517.5345382	-27.7	-22.1
77	PROPYNE C3V	-116.4416643	-0.658059	-116.606179	190.504460	191.6071703	5.6	6.7
78	ALLENE D2D	-116.4421394	-0.65157982	-116.605034	191.853088	192.9557977	1.5	2.6
79	CYCLOPROPENE C2V	-116.4021383	-0.6607624	-116.567329	291.786195	292.8889046	14.8	15.9
80	PROPENE CS	-117.6775331	-0.68114307	-117.847819	36.380311	37.48302108	16.3	17.4
81	CYCLOPROPANE D3H	-117.6635493	-0.6869246	-117.835280	71.781260	72.88397002	18.6	19.7
82	PROPANE C2V	-118.8958622	-0.71421234	-119.074415	-78.598946	-77.49623584	26.0	27.1
83	TRANS-1,3-BUTADIENE C2H	-155.7000484	-0.88154564	-155.920435	125.056901	126.5271814	15.0	16.5
84	Dimethyl acetylene	-155.6864457	-0.88750598	-155.908322	157.010877	158.4811574	11.4	12.9
85	Methylene cyclopropane.	-155.6671548	-0.88784049	-155.889115	206.035034	207.5053138	5.6	7.1
86	Bicyclo[1.1.0]butane. C2v	-155.6507809	-0.89936473	-155.875622	243.392722	244.863002	26.2	27.7
87	CYCLOBUTENE b3lyp	-155.6763572	-0.89026933	-155.898925	182.642695	184.1129752	26.2	27.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8998292	-0.91926228	-157.129645	58.209433	59.67971291	29.8	31.2
89	Isobutene. Single	-156.917828	-0.91537184	-157.146671	8.718417	10.18869659	25.5	26.9
90	Trans butane	-158.1312056	-0.94577948	-158.367650	-90.324561	-88.85428074	35.2	36.7
91	isobutane B3LYP/6-31G*	-158.1321882	-0.94908122	-158.369458	-96.365823	-94.89554311	37.9	39.4
92	Spiropentane. D2d	-194.8962596	-1.12528838	-195.177582	208.763801	210.6016507	23.4	25.3
93	Benzene B3LYP	-231.8267133	-1.29409119	-232.150236	88.328486	90.53390587	5.9	8.1
94	DIFLUOROMETHANE C2V	-238.7393992	-0.87304636	-238.957661	-456.741612	-453.1709324	-6.1	-2.6
95	HCF3 TRI-FLUOROMETHANE	-337.9146889	-1.18373086	-338.210622	-707.719237	-702.5470016	-10.7	-5.5
96	CH2CL2 C2V	-959.3020481	-0.89685184	-959.526261	-88.875578	-81.47166793	6.5	13.9
97	chcl3 B3LYP/6-31G*	-1418.733208	-1.23006349	-1419.040724	-95.899319	-84.97723866	7.4	18.4
98	METHYLAMINE b3lyp	-95.68725121	-0.52753618	-95.819135	-12.125771	-11.75820136	10.9	11.3
99	Acetonitrile. CH3-CN.	-132.535697	-0.70165836	-132.711112	69.626089	70.36122927	-5.7	-5.0
100	NITRO METHANE	-244.6728536	-1.16073247	-244.963037	-85.999999	-83.74206949	-11.5	-9.3
101	Methyl-nitrite. CH3-O-N=O.	-244.6687182	-1.15133985	-244.956553	-72.705767	-70.44783712	-6.2	-3.9
102	Methylsilane. CH3-SiH3.	-330.976687	-0.57751284	-331.121065	-6.610569	-4.457659104	22.7	24.8
103	Formic Acid.	-189.521702	-0.83799843	-189.731202	-384.749057	-382.4911273	-6.1	-3.8
104	Methyl formate.	-228.7446026	-1.0665082	-229.011230	-362.400585	-359.7750853	-6.8	-4.1
105	acetamide ch3cohn2	-208.901453	-1.0350255	-209.160209	-237.107346	-235.4270261	1.4	3.1

106	Aziridine. (cyclic	-133.6853863	-0.73333215	-133.868719	136.963233	137.6983727	10.6	11.3
107	Cyanogen. NCCN.	-185.3782815	-0.94055167	-185.613419	279.491622	280.2267616	-27.2	-26.5
108	DIMETHYLAMINE b3lyp	-134.9139551	-0.75751818	-135.103335	-1.419495	-0.684354954	17.0	17.7
109	TRANS ETHYLAMINE	-134.9254786	-0.75867826	-135.115148	-31.498667	-30.76352698	15.8	16.5
110	KETENE B3LYP	-152.3798065	-0.73415956	-152.563346	-63.337535	-61.65721506	-16.1	-14.4
111	OXIRANE B3LYP	-153.549484	-0.76484975	-153.740696	-45.673093	-43.99277257	7.0	8.7
112	Acetaldehyde B3LYP	-153.5951208	-0.75741035	-153.784473	-163.728543	-162.0482225	2.4	4.1
113	Glyoxal, O=CH-CH=O.	-227.5161488	-1.0339085	-227.774626	-224.336889	-221.7113888	-12.2	-9.6
114	ETHANOL TRANS	-154.791503	-0.78746762	-154.988370	-217.019445	-215.3391253	18.1	19.8
115	DIMETHYL ETHER,	-154.7747821	-0.78459015	-154.970930	-172.073045	-170.3927248	12.0	13.7
116	Thiooxirane. (cyclic	-476.4755323	-0.85006798	-476.688049	94.487194	97.55902941	12.5	15.6
117	Dimethylsulfoxide. (CH3)2SO.	-552.7989757	-1.20167851	-553.099395	-121.769325	-117.7523103	29.7	33.7
118	Thioethanol. CH3-CH2-SH.	-477.6943607	-0.86887265	-477.911579	-20.445119	-17.37328357	26.0	29.1
119	ch3sch3 B3LYP	-477.6924815	-0.8709209	-477.910212	-14.329942	-11.25810681	22.9	26.0
120	Vinyl fluoride,	-177.594652	-0.76255261	-177.785290	-142.778427	-140.4417322	-3.9	-1.5
121	Ethyl chloride.	-539.1048511	-0.80337197	-539.305694	-97.205946	-92.95263561	14.9	19.2
122	Vinyl chloride,	-537.8812992	-0.77480162	-538.075000	27.795239	32.04854864	4.8	9.0
123	h2c=chcn B3LYP	-170.5493714	-0.90291614	-170.775100	180.827048	181.9297576	0.1	1.2
124	ACETONE B3LYP	-192.8422704	-0.98836857	-193.089363	-206.498043	-204.4501532	10.7	12.7
125	CH3COOH ACETIC	-228.77026	-1.06564733	-229.036672	-429.653168	-427.0276682	3.0	5.6
126	CH3CFO HCCO	-252.7821944	-1.07381842	-253.050649	-446.356287	-443.0744121	-4.1	-0.8
127	ch3c(o)cl hcco	-613.0557208	-1.09079229	-613.328419	-244.842141	-239.6436507	-2.2	3.0
128	ch3ch2ch2cl B3LYP	-578.3403047	-1.03520602	-578.599106	-109.301592	-104.6807119	22.5	27.1
129	Isopropyl alcohol,	-194.0317812	-1.02135508	-194.287120	-244.915410	-242.8675197	27.9	29.9
130	Methyl ethyl	-194.0153463	-1.01557015	-194.269239	-197.419583	-195.371693	18.9	20.9
131	Trimethyl Amine.	-174.1429908	-0.99250942	-174.391118	-1.428383	-0.325672895	22.4	23.5
132	FURAN B3LYP	-229.6557458	-1.17646483	-229.949862	-33.355468	-30.94000811	1.4	3.8
133	Thiophene b3lyp	-552.5714406	-1.26917619	-552.888735	126.722590	130.5295654	11.7	15.5
134	PYROLE PLANAR	-209.8062497	-1.14783254	-210.093208	108.378278	109.848558	0.0	1.5
135	C2v Pyridine	-247.8560139	-1.33944119	-248.190874	132.878774	134.7166241	-7.7	-5.9
136	H2 B3LYP/6-31G*	-1.16055825	-0.03558152	-1.169454	6.690975	6.690974885	6.7	6.7
137	SH b3lyp/6-31G*	-398.5882779	-0.36522611	-398.679584	146.528941	148.8656359	3.4	5.8
138	CCH B3LYP	-76.48056611	-0.39127867	-76.578386	576.870609	577.6057491	11.6	12.3
139	C2H3 CS,2-A'	-77.76116001	-0.41251134	-77.864288	301.605365	302.3405049	2.0	2.8
140	ch3co hcco	-152.9532448	-0.73528226	-153.137065	-17.076255	-15.39593473	-7.0	-5.4
141	H2COH C1	-114.8982658	-0.52427698	-115.029335	-14.673101	-13.36035142	2.5	3.8
142	ch3o CS,	-114.8908799	-0.49725657	-115.015194	18.880795	20.19354514	1.7	3.0

143	ch3ch2o 2A"	-154.1313462	-0.72789016	-154.313319	-6.559126	-4.878805571	8.9	10.6
144	ch3s 2-A'	-437.82515	-0.59955875	-437.975040	130.187605	132.8918701	5.5	8.2
145	c2h5 staggered	-79.00044933	-0.44351818	-79.111329	131.672654	132.4077936	10.8	11.5
146	(ch3)2ch Cs	-118.2406476	-0.67616044	-118.409688	106.615721	107.7184311	16.7	17.8
147	TERT-BUTYL RADICAL	-157.480906	-0.91090689	-157.708633	79.757203	81.22748335	28.3	29.8
148	NO2 RADICAL	-204.8152771	-0.92893991	-205.047512	5.202943	7.093303232	-27.9	-26.0

MAD	**11.3**	**12.2**
LD	**-40.4**	**44.8**

Table S5.11b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498614	0.000000	-0.498614
2	li	-7.469546	-0.014756	-7.473235
3	be	-14.639015	-0.055106	-14.652792
4	b	-24.619178	-0.079255	-24.638992
5	c	-37.803269	-0.106193	-37.829817
6	n	-54.537168	-0.137065	-54.571434
7	o	-75.002774	-0.195036	-75.051533
8	f	-99.651506	-0.258752	-99.716194
9	na	-162.159613	-0.174134	-162.203147
10	al	-242.242824	-0.223490	-242.298696
11	si	-289.244030	-0.253888	-289.307502
12	p	-341.126767	-0.283325	-341.197599
13	s	-397.962427	-0.325219	-398.043732
14	cl	-459.981890	-0.296378	-460.055985

Table S5.12a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04897637	-0.04782265	-8.061410	145.912640	145.9126401	6.6	6.6
2	BERYLLIUM HYDRIDE	-15.22460605	-0.0562655	-15.239235	319.522548	319.5225475	-22.3	-22.3
3	DOUBLET CH	-38.42241721	-0.14798707	-38.460894	598.485946	598.8535164	2.3	2.6
4	CH2 3-B1	-39.08555893	-0.16705381	-39.128993	395.020123	395.387693	3.0	3.3
5	Singlet methylene,	-39.06291308	-0.18835029	-39.111884	438.327129	438.6946991	8.2	8.6
6	Methyl radical,	-39.75867371	-0.21282293	-39.814008	151.064682	151.432252	4.6	5.0
7	ch4 //b3lyp/6-31G*	-40.4239621	-0.25562087	-40.490424	-65.010846	-64.64327551	9.9	10.3
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1532117	-0.19140312	-55.202977	356.134996	356.134996	-0.3	-0.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79559071	-0.24631469	-55.859633	184.815937	184.8159369	-3.9	-3.9
10	AMMONIA, //b3lyp/6-31G*	-56.46198369	-0.30167956	-56.540420	-41.183959	-41.18395906	4.8	4.8
11	OH RADICAL	-75.65081911	-0.26357488	-75.719349	39.317854	40.2630337	0.0	0.9
12	Water //b3lyp/6-31G*	-76.3290571	-0.33417179	-76.415942	-233.445716	-232.5005365	8.4	9.3
13	HYDROGEN FLUORIDE,	-100.3480489	-0.34438196	-100.437588	-268.659267	-267.0577122	3.7	5.3
14	SIH2 singlet	-290.4617768	-0.31159545	-290.542792	274.737004	276.5223444	1.9	3.7
15	SIH2 3B1	-290.4350345	-0.2882852	-290.509989	361.872190	363.6575303	1.2	3.0
16	SIH3 c3v	-291.0765876	-0.31684105	-291.158966	203.371839	205.1571788	3.0	4.7
17	SIH4 //b3lyp/6-31G*	-291.7195377	-0.34462152	-291.809139	43.675726	45.46106649	9.4	11.2
18	ph2 doublet	-342.3447115	-0.35141604	-342.436080	138.115224	138.115224	-0.4	-0.4
19	PH3 c3v	-342.9726648	-0.38358277	-343.072396	16.298335	16.29833539	10.9	10.9
20	SH2 //b3lyp/6-31G*	-399.2200051	-0.405182	-399.325352	-11.103214	-8.766519451	9.4	11.7
21	HCL //b3lyp/6-31G*	-460.6299941	-0.34284733	-460.719134	-89.244236	-85.72606586	3.2	6.7
22	DILITHIUM //b3lyp/6-31G*	-14.96370031	-0.05964466	-14.979208	229.891072	229.8910715	14.0	14.0
23	Lithium Fluoride,	-107.3123407	-0.3747106	-107.409765	-340.962604	-339.3610493	-5.8	-4.2
24	ACETYLENE //b3lyp/6-31g*	-77.19034356	-0.42924443	-77.301947	227.964390	228.6995297	1.2	1.9
25	ETHYLENE //b3lyp/6-31g*	-78.43195874	-0.44971513	-78.548885	60.569140	61.30428008	8.3	9.0
26	ETHANE //b3lyp/6-31g*	-79.65486275	-0.48317659	-79.780489	-67.875314	-67.14017416	16.2	17.0
27	CYANO RADICAL,	-92.56783012	-0.46909231	-92.689794	437.828422	438.1959919	-1.1	-0.7
28	HYDROGEN CYANIDE	-93.27818012	-0.47517369	-93.401725	120.061229	120.4287992	-11.7	-11.4
29	CARBON MONOXIDE	-113.1702506	-0.48571583	-113.296537	-118.567033	-117.2542831	-8.1	-6.8
30	HCO BENT	-113.6965673	-0.50842007	-113.828757	27.256522	28.56927217	-14.6	-13.3
31	H2CO //b3lyp/6-31g*	-114.3388033	-0.52800914	-114.476086	-115.510566	-114.1978157	-6.7	-5.4

32	METHANOL //b3lyp/6-31g*	-115.5448808	-0.55711138	-115.689730	-193.871173	-192.5584231	7.0	8.3
33	Nitrogen N2,	-109.3774809	-0.50962788	-109.509984	-10.423074	-10.42307387	-10.4	-10.4
34	H2NNH2 //b3lyp/6-31g*	-111.6859142	-0.57238978	-111.834736	98.088239	98.08823933	2.7	2.7
35	NO radical,	-129.7269414	-0.55203155	-129.870470	76.494926	77.44010632	-13.9	-12.9
36	O2 //b3lyp/6-31g*	-150.1393997	-0.6161304	-150.299594	-16.022714	-14.1323543	-16.0	-14.1
37	HYDROGEN PEROXIDE	-151.3558337	-0.64739203	-151.524156	-126.760965	-124.8706051	9.2	11.1
38	F2 //b3lyp/6-31g*	-199.3133585	-0.67631151	-199.489199	8.359686	11.56279616	8.4	11.6
39	CO2 D*H	-188.3504675	-0.81635971	-188.562721	-423.199456	-420.941526	-29.9	-27.6
40	na2 //b3lyp/6-31G*	-324.3302488	-0.37790741	-324.428505	142.698245	142.6982445	0.4	0.4
41	SI2 3-SGG	-578.5797992	-0.56914627	-578.727777	587.252063	590.8227432	1.9	5.5
42	P2 //b3lyp/6-31g*	-682.3864705	-0.72459275	-682.574865	147.474618	147.4746178	4.0	4.0
43	S2 //b3lyp/6-31g*	-796.0449406	-0.77031776	-796.245223	123.578259	128.2516493	-4.9	-0.2
44	CL2 //b3lyp/6-31g*	-920.0213195	-0.66463187	-920.194124	5.947463	12.98380326	5.9	13.0
45	Sodium Chloride	-622.2714028	-0.51800052	-622.406083	-174.578823	-171.0606525	7.8	11.4
46	SIO //b3lyp/6-31g*	-364.4980756	-0.63070634	-364.662059	-102.998265	-100.2677452	-0.1	2.7
47	Carbon monosulfide,	-435.989082	-0.5898702	-436.142448	281.582569	284.2868338	1.7	4.4
48	OS //b3lyp/6-31g*	-473.112372	-0.70099208	-473.294630	-4.733083	-1.451208426	-9.8	-6.5
49	CLO 2-PI	-535.0439557	-0.62070412	-535.205339	102.491969	106.9553189	1.2	5.7
50	CLF 1-SG	-559.69242	-0.66746981	-559.865962	-56.831124	-51.71139868	-1.6	3.5
51	si2h6 //b3lyp/6-31g*	-582.2651857	-0.66990122	-582.439360	100.238682	103.8093625	20.3	23.9
52	Methyl chloride,	-499.8558652	-0.5715545	-500.004469	-76.523361	-72.63762106	5.5	9.4
53	H3C-SH METHANETHIOL	-438.4487516	-0.63638201	-438.614211	-7.685900	-4.981634719	15.3	18.0
54	HOCl //b3lyp/6-31g*	-535.6915794	-0.65919167	-535.862969	-72.162538	-67.69918797	2.3	6.8
55	SO2 //b3lyp/6-31G*	-548.2779922	-1.05817659	-548.553118	-294.310610	-290.0835555	2.8	7.0
56	BF3 PLANAR	-324.257171	-1.09156278	-324.540977	-1152.611430	-1147.67549	-17.1	-12.1
57	bcl3 B3LYP	-1405.020326	-1.13178719	-1405.314591	-417.739485	-407.0537	-14.8	-4.1
58	ALf3 B3LYP	-541.7982116	-1.23257378	-542.118681	-1199.196619	-1193.499284	10.0	15.7
59	alcl3 B3LYP	-1622.619614	-1.23410915	-1622.940482	-585.494071	-574.046891	-1.0	10.5
60	cf4 B3LYP	-437.0702958	-1.49172403	-437.458144	-954.020214	-947.2464245	-21.0	-14.2
61	ccl4 B3LYP	-1878.126239	-1.57031479	-1878.534520	-93.536703	-79.09645338	2.3	16.7
62	O=C=S. Singlet	-511.22689	-0.9078395	-511.462928	-166.178276	-162.5288306	-27.7	-24.0
63	CS2 B3LYP	-834.0999423	-1.00658229	-834.361654	95.313580	100.35454	-21.4	-16.4
64	COF2 B3LYP	-312.6881775	-1.15491848	-312.988456	-631.518899	-627.0030385	-7.7	-3.2
65	sif4 B3LYP	-688.6537108	-1.59301245	-689.067894	-1582.773949	-1574.582389	32.3	40.4
66	sicl4, td	-2129.691828	-1.63116461	-2130.115931	-642.109647	-626.2516271	20.6	36.5
67	nno B3LYP	-184.4094485	-0.8778292	-184.637684	45.730987	46.67616736	-36.3	-35.3
68	clno B3LYP	-589.7394567	-0.94702094	-589.985682	33.627183	38.09053299	-18.3	-13.8

69	nf3 c3v	-353.7195378	-1.27436617	-354.050873	-151.575632	-146.7709673	-19.4	-14.6
70	pf3 c3v	-640.5704932	-1.33018422	-640.916341	-945.530539	-940.7258738	13.0	17.8
71	ozone 1-a1	-225.1151866	-1.05703732	-225.390016	133.539244	136.3747835	-9.1	-6.3
72	f2o B3LYP	-274.3703192	-0.99926957	-274.630129	24.493560	28.64184965	-0.2	4.0
73	CLF3, C2V	-759.0361252	-1.41499771	-759.404025	-173.731421	-165.4085857	-14.7	-6.4
74	CF2=CF2 D2H	-475.027551	-1.69947816	-475.469415	-705.882063	-698.7407027	-47.3	-40.2
75	cl2c=ccl2 B3LYP	-1916.15461	-1.77407806	-1916.615870	-27.050927	-12.24310726	-14.5	0.3
76	cf3cn B3LYP	-429.9821753	-1.64105341	-430.408849	-530.895085	-525.3552797	-35.5	-30.0
77	PROPYNE C3V	-116.4346304	-0.65803468	-116.605719	187.496964	188.5996744	2.6	3.7
78	ALLENE D2D	-116.435102	-0.65155753	-116.604507	189.023716	190.1264263	-1.3	-0.2
79	CYCLOPROPENE C2V	-116.3950487	-0.66074457	-116.566842	288.849610	289.9523199	11.9	13.0
80	PROPENE CS	-117.6699608	-0.68112328	-117.847053	34.177430	35.28013994	14.1	15.2
81	CYCLOPROPANE D3H	-117.6559082	-0.6869095	-117.834505	69.603939	70.70664891	16.5	17.6
82	PROPANE C2V	-118.8877555	-0.71419472	-119.073446	-80.268606	-79.16589605	24.3	25.4
83	TRANS-1,3-BUTADIENE C2H	-155.690426	-0.8815176	-155.919621	121.575962	123.0462421	11.5	13.0
84	Dimethyl acetylene	-155.6768272	-0.88747636	-155.907571	153.364157	154.8344371	7.8	9.2
85	Methylene cyclopropane.	-155.6574701	-0.88781709	-155.888303	202.549146	204.0194257	2.1	3.6
86	Bicyclo[1.1.0]butane. C2v	-155.641028	-0.89934485	-155.874858	239.781052	241.2513324	22.6	24.1
87	CYCLOBUTENE b3lyp	-155.6666479	-0.89024573	-155.898112	179.157709	180.6279892	22.7	24.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.8895858	-0.91924076	-157.128588	55.364123	56.83440289	26.9	28.4
89	Isobutene. Single	-156.9076613	-0.91534635	-157.145651	5.776558	7.246838018	22.5	24.0
90	Trans butane	-158.1205133	-0.94575553	-158.366410	-92.685729	-91.21544908	32.8	34.3
91	isobutane B3LYP/6-31G*	-158.1214866	-0.94905736	-158.368242	-98.789664	-97.31938423	35.5	37.0
92	Spiropentane. D2d	-194.8839207	-1.1252635	-195.176489	204.608699	206.4465488	19.3	21.1
93	Benzene B3LYP	-231.8128208	-1.29405273	-232.149275	82.424793	84.63021261	0.0	2.2
94	DIFLUOROMETHANE C2V	-238.7299907	-0.87304685	-238.956983	-459.670476	-456.0997955	-9.1	-5.5
95	HCF3 TRI-FLUOROMETHANE	-337.9020284	-1.18372884	-338.209798	-711.917756	-706.7455208	-14.9	-9.7
96	CH2CL2 C2V	-959.2853319	-0.89683836	-959.518510	-90.702255	-83.29834511	4.7	12.1
97	chcl3 B3LYP/6-31G*	-1418.709593	-1.23004434	-1419.029404	-98.742760	-87.82067957	4.6	15.5
98	METHYLAMINE b3lyp	-95.68150299	-0.52753	-95.818661	-13.745634	-13.37806449	9.3	9.6
99	Acetonitrile. CH3-CN.	-132.5284654	-0.70163697	-132.710891	65.934987	66.6701273	-9.4	-8.6
100	NITRO METHANE	-244.6616286	-1.16071193	-244.963414	-93.170065	-90.9121354	-18.7	-16.4
101	Methyl-nitrite. CH3-O-N=O.	-244.65753	-1.15131797	-244.956873	-79.724697	-77.46676716	-13.2	-10.9
102	Methylsilane. CH3-SiH3.	-330.9676103	-0.5774987	-331.117760	-6.627745	-4.474835387	22.7	24.8
103	Formic Acid.	-189.5132438	-0.83799271	-189.731122	-389.259020	-387.0010905	-10.6	-8.3
104	Methyl formate.	-228.7335732	-1.06649266	-229.010861	-367.557446	-364.9319465	-11.9	-9.3
105	acetamide ch3cohn2	-208.8906105	-1.03501138	-209.159713	-241.732751	-240.0524309	-3.2	-1.6

106	Aziridine. (cyclic	-133.6775391	-0.73331967	-133.868202	134.050737	134.7858772	7.7	8.4
107	Cyanogen. NCCN.	-185.3693567	-0.94051765	-185.613891	272.521502	273.2566423	-34.2	-33.4
108	DIMETHYLAMINE b3lyp	-134.9056253	-0.75750476	-135.102576	-3.699365	-2.96422547	14.7	15.4
109	TRANS ETHYLAMINE	-134.9171452	-0.75866566	-135.114398	-33.800182	-33.06504212	13.5	14.2
110	KETENE B3LYP	-152.3723335	-0.73414387	-152.563211	-67.448657	-65.76833717	-20.2	-18.5
111	OXIRANE B3LYP	-153.5414349	-0.7648398	-153.740293	-49.081248	-47.40092835	3.6	5.3
112	Acetaldehyde B3LYP	-153.587125	-0.7573989	-153.784049	-167.080450	-165.4001296	-1.0	0.7
113	Glyoxal, O=CH-CH=O.	-227.5056964	-1.0338949	-227.774509	-230.154214	-227.5287139	-18.0	-15.4
114	ETHANOL TRANS	-154.7829556	-0.78745863	-154.987695	-219.713986	-218.0336657	15.4	17.1
115	DIMETHYL ETHER,	-154.7662478	-0.78457911	-154.970238	-174.724848	-173.0445281	9.4	11.1
116	Thiooxirane. (cyclic	-476.4638359	-0.85005065	-476.684849	92.061847	95.13368204	10.1	13.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.7837678	-1.20166028	-553.096199	-125.863485	-121.8464696	25.6	29.6
118	Thioethanol. CH3-CH2-SH.	-477.6821903	-0.86885474	-477.908093	-22.119431	-19.0475959	24.3	27.4
119	ch3sch3 B3LYP	-477.6803184	-0.87090297	-477.906753	-16.077157	-13.00532219	21.2	24.2
120	Vinyl fluoride,	-177.5864254	-0.7625424	-177.784686	-145.654892	-143.3181967	-6.7	-4.4
121	Ethyl chloride.	-539.0924411	-0.80335669	-539.301314	-98.901260	-94.64795037	13.2	17.5
122	Vinyl chloride,	-537.8694169	-0.77478419	-538.070861	25.465767	29.71907717	2.5	6.7
123	h2c=chcn B3LYP	-170.5400967	-0.90288675	-170.774847	175.816780	176.9194897	-4.9	-3.8
124	ACETONE B3LYP	-192.8316821	-0.98835004	-193.088653	-210.506791	-208.4589007	6.6	8.7
125	CH3COOH ACETIC	-228.7592109	-1.06563464	-229.036276	-434.737703	-432.1122029	-2.1	0.5
126	CH3CFO HCCO	-252.770948	-1.07380525	-253.050137	-451.131865	-447.8499899	-8.9	-5.6
127	ch3c(o)cl hcco	-613.0408328	-1.09077303	-613.324434	-249.232436	-244.0339465	-6.6	-1.4
128	ch3ch2ch2cl B3LYP	-578.3253099	-1.03518452	-578.594458	-111.697834	-107.0769543	20.1	24.7
129	Isopropyl alcohol,	-194.0206398	-1.02133913	-194.286188	-248.339684	-246.2917939	24.5	26.5
130	Methyl ethyl	-194.004226	-1.01555233	-194.268270	-200.746463	-198.698573	15.6	17.6
131	Trimethyl Amine.	-174.1320664	-0.99248935	-174.390114	-4.466102	-3.363392148	19.4	20.5
132	FURAN B3LYP	-229.6434902	-1.17643836	-229.949364	-39.324687	-36.90922729	-4.6	-2.2
133	Thiophene b3lyp	-552.5555409	-1.26914284	-552.885518	121.530678	125.3376534	6.5	10.3
134	PYROLE PLANAR	-209.7941854	-1.14780444	-210.092615	102.856260	104.3265399	-5.5	-4.0
135	C2v Pyridine	-247.8419147	-1.33940471	-248.190160	126.269580	128.1074296	-14.3	-12.5
136	H2 B3LYP/6-31G*	-1.16017569	-0.03558184	-1.169427	6.760975	6.760974916	6.8	6.8
137	SH b3lyp/6-31G*	-398.5815992	-0.36522783	-398.676558	146.455457	148.7921523	3.4	5.7
138	CCH B3LYP	-76.47651105	-0.39125731	-76.578238	574.449308	575.1844477	9.2	9.9
139	C2H3 CS,2-A'	-77.75653316	-0.41248915	-77.863780	300.128401	300.8635409	0.6	1.3
140	ch3co hcco	-152.9455793	-0.73526172	-153.136747	-20.707819	-19.02749877	-10.7	-9.0
141	H2COH C1	-114.8926361	-0.524268	-115.028946	-16.713105	-15.40035547	0.4	1.8
142	ch3o CS,	-114.8852829	-0.49723958	-115.014565	17.469852	18.78260223	0.3	1.6

143	ch3ch2o 2A"	-154.1231644	-0.72786391	-154.312409	-8.637534	-6.957214121	6.8	8.5
144	ch3s 2-A'	-437.8158931	-0.59955029	-437.971776	129.332968	132.0372333	4.6	7.4
145	c2h5 staggered	-78.99527403	-0.44351038	-79.110587	130.811737	131.5468774	9.9	10.6
146	(ch3)2ch Cs	-118.2328801	-0.67614254	-118.408677	105.054788	106.1574976	15.1	16.2
147	TERT-BUTYL RADICAL	-157.4705437	-0.91087863	-157.707372	77.448011	78.91829073	26.0	27.5
148	NO2 RADICAL	-204.8069563	-0.92891794	-205.048475	-2.100358	-0.209998133	-35.2	-33.3

MAD	**11.4**	**12.0**
LD	**-47.3**	**40.4**

Table S5.12b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498614	0.000000	-0.498614
2	li	-7.469009	-0.014755	-7.472846
3	be	-14.638066	-0.055101	-14.652392
4	b	-24.617914	-0.079259	-24.638521
5	c	-37.801670	-0.106199	-37.829282
6	n	-54.535240	-0.137069	-54.570878
7	o	-75.000190	-0.195046	-75.050902
8	f	-99.648287	-0.258762	-99.715565
9	na	-162.155521	-0.174132	-162.200796
10	al	-242.237867	-0.223491	-242.295975
11	si	-289.238714	-0.253890	-289.304726
12	p	-341.121096	-0.283319	-341.194759
13	s	-397.956120	-0.325221	-398.040678
14	cl	-459.974970	-0.296382	-460.052029

Table S5.13a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04808834	-0.04782405	-8.061001	145.964621	145.9646208	6.6	6.6
2	BERYLLIUM HYDRIDE	-15.22352447	-0.05625772	-15.238714	319.841081	319.8410813	-22.0	-22.0
3	DOUBLET CH	-38.42043959	-0.14799097	-38.460397	598.385756	598.7533257	2.2	2.5
4	CH2 3-B1	-39.08340648	-0.16705217	-39.128511	394.882279	395.2498485	2.8	3.2
5	Singlet methylene,	-39.06058541	-0.18834656	-39.111439	438.091667	438.4592371	8.0	8.3
6	Methyl radical,	-39.75608803	-0.21282656	-39.813551	150.858879	151.2264488	4.4	4.8
7	ch4 //b3lyp/6-31G*	-40.42101592	-0.25561502	-40.490032	-65.387096	-65.01952568	9.5	9.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15083131	-0.19141339	-55.202513	355.891556	355.8915565	-0.6	-0.6
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79279462	-0.24632177	-55.859301	184.224476	184.2244758	-4.5	-4.5
10	AMMONIA, //b3lyp/6-31G*	-56.45880449	-0.3016809	-56.540258	-42.219101	-42.2191005	3.8	3.8
11	OH RADICAL	-75.64780884	-0.2635853	-75.718977	38.637123	39.58230298	-0.7	0.3
12	Water //b3lyp/6-31G*	-76.32565318	-0.33417865	-76.415881	-234.943917	-233.9987374	6.9	7.8
13	HYDROGEN FLUORIDE,	-100.3444257	-0.34439122	-100.437411	-269.846405	-268.2448496	2.5	4.1
14	SIH2 singlet	-290.4558023	-0.31158749	-290.539931	274.957975	276.7433146	2.2	3.9
15	SIH2 3B1	-290.4292541	-0.28825793	-290.507084	362.209014	363.9943538	1.5	3.3
16	SIH3 c3v	-291.070432	-0.31682583	-291.155975	203.935500	205.7208403	3.5	5.3
17	SIH4 //b3lyp/6-31G*	-291.7130449	-0.3446124	-291.806090	44.391269	46.17660871	10.1	11.9
18	ph2 doublet	-342.3382797	-0.35141563	-342.433162	138.320909	138.3209085	-0.2	-0.2
19	PH3 c3v	-342.9659052	-0.38357362	-343.069470	16.526317	16.52631701	11.1	11.1
20	SH2 //b3lyp/6-31G*	-399.2129866	-0.40517633	-399.322384	-11.327963	-8.99126829	9.2	11.5
21	HCL //b3lyp/6-31G*	-460.6227229	-0.3428452	-460.715291	-89.539795	-86.0216247	2.9	6.4
22	DILITHIUM //b3lyp/6-31G*	-14.96236225	-0.05964041	-14.978465	229.795258	229.7952584	13.9	13.9
23	Lithium Fluoride,	-107.3081644	-0.37472645	-107.409341	-342.521520	-340.9199648	-7.4	-5.8
24	ACETYLENE //b3lyp/6-31g*	-77.18589475	-0.42922533	-77.301786	225.579934	226.3150739	-1.2	-0.5
25	ETHYLENE //b3lyp/6-31g*	-78.42697309	-0.44970082	-78.548392	59.053304	59.78844398	6.8	7.5
26	ETHANE //b3lyp/6-31g*	-79.64934097	-0.48316501	-79.779796	-68.864007	-68.12886683	15.2	16.0
27	CYANO RADICAL,	-92.56355985	-0.46899688	-92.690189	433.926795	434.294365	-5.0	-4.6
28	HYDROGEN CYANIDE	-93.27353342	-0.47515805	-93.401826	116.931691	117.2992607	-14.9	-14.5
29	CARBON MONOXIDE	-113.1654013	-0.48570947	-113.296543	-121.644020	-120.3312704	-11.2	-9.9
30	HCO BENT	-113.6914842	-0.50840812	-113.828754	24.201266	25.51401589	-17.6	-16.3
31	H2CO //b3lyp/6-31g*	-114.3333961	-0.52800419	-114.475957	-118.234171	-116.9214207	-9.5	-8.1

32	METHANOL //b3lyp/6-31g*	-115.5389191	-0.55710884	-115.689339	-195.904962	-194.5922123	4.9	6.2
33	Nitrogen N2,	-109.3726427	-0.50961207	-109.510238	-14.010542	-14.0105421	-14.0	-14.0
34	H2NNH2 //b3lyp/6-31g*	-111.6799455	-0.57238941	-111.834491	95.810140	95.81013998	0.4	0.4
35	NO radical,	-129.7216604	-0.5520219	-129.870706	72.756315	73.7014954	-17.6	-16.7
36	O2 //b3lyp/6-31g*	-150.1336766	-0.61612897	-150.300031	-20.485609	-18.59524931	-20.5	-18.6
37	HYDROGEN PEROXIDE	-151.3494705	-0.64739756	-151.524268	-130.369038	-128.478678	5.6	7.5
38	F2 //b3lyp/6-31g*	-199.3066017	-0.67631566	-199.489207	5.037170	8.240279995	5.0	8.2
39	CO2 D*H	-188.3425554	-0.81634603	-188.562969	-428.567630	-426.3096999	-35.3	-33.0
40	na2 //b3lyp/6-31G*	-324.3218209	-0.37790186	-324.423854	142.562541	142.5625414	0.3	0.3
41	SI2 3-SGG	-578.5688166	-0.56912709	-578.722481	586.577789	590.1484693	1.2	4.8
42	P2 //b3lyp/6-31g*	-682.3743263	-0.72456843	-682.569960	145.442482	145.4424821	1.9	1.9
43	S2 //b3lyp/6-31g*	-796.0318705	-0.77030795	-796.239854	121.640206	126.3135963	-6.8	-2.1
44	CL2 //b3lyp/6-31g*	-920.0071898	-0.66462414	-920.186638	4.828449	11.86478891	4.8	11.9
45	Sodium Chloride	-622.2600735	-0.51800337	-622.399934	-174.994529	-171.4763595	7.4	10.9
46	SIO //b3lyp/6-31g*	-364.4895497	-0.63071589	-364.659843	-106.126097	-103.3955766	-3.2	-0.5
47	Carbon monosulfide,	-435.9805983	-0.58984933	-436.139858	278.962065	281.6663296	-0.9	1.8
48	OS //b3lyp/6-31g*	-473.1029658	-0.7009843	-473.292232	-8.110547	-4.828672104	-13.1	-9.8
49	CLO 2-PI	-535.0340373	-0.62065967	-535.201615	100.225038	104.6883879	-1.0	3.4
50	CLF 1-SG	-559.6819571	-0.66746948	-559.862174	-58.922729	-53.80300352	-3.7	1.4
51	si2h6 //b3lyp/6-31g*	-582.2525676	-0.66988413	-582.433436	101.211611	104.7822911	21.3	24.9
52	Methyl chloride,	-499.8460395	-0.57154553	-500.000357	-77.516047	-73.63030738	4.5	8.4
53	H3C-SH METHANETHIOL	-438.4391657	-0.63637032	-438.610986	-8.640174	-5.935909189	14.4	17.1
54	HOCl //b3lyp/6-31g*	-535.6813268	-0.6591898	-535.859308	-74.592807	-70.12945684	-0.1	4.3
55	SO2 //b3lyp/6-31G*	-548.2654452	-1.05816635	-548.551150	-300.474820	-296.247765	-3.4	0.8
56	BF3 PLANAR	-324.2452356	-1.09156393	-324.539958	-1156.126887	-1151.190947	-20.6	-15.7
57	bcl3 B3LYP	-1404.997437	-1.13176837	-1405.303015	-419.742113	-409.0563285	-16.8	-6.1
58	ALf3 B3LYP	-541.7826827	-1.23258277	-542.115480	-1202.892940	-1197.195605	6.3	12.0
59	alcl3 B3LYP	-1622.593135	-1.23409326	-1622.926340	-586.667675	-575.2204948	-2.2	9.3
60	cf4 B3LYP	-437.0543801	-1.49171656	-437.457144	-959.403613	-952.6298229	-26.4	-19.6
61	ccl4 B3LYP	-1878.095718	-1.57028916	-1878.519696	-97.563515	-83.12326544	-1.7	12.7
62	O=C=S. Singlet	-511.215341	-0.90781716	-511.460452	-170.754726	-167.1052811	-32.3	-28.6
63	CS2 B3LYP	-834.0847458	-1.00655082	-834.356514	91.366484	96.40744387	-25.4	-20.3
64	COF2 B3LYP	-312.6762695	-1.15490892	-312.988095	-636.934068	-632.4182076	-13.1	-8.6
65	sif4 B3LYP	-688.6341627	-1.59300905	-689.064275	-1587.168473	-1578.976913	27.9	36.0
66	sicl4, td	-2129.657675	-1.63113855	-2130.098083	-644.083389	-628.2253685	18.7	34.5
67	nno B3LYP	-184.4015731	-0.87780569	-184.638581	38.799476	39.74465596	-43.2	-42.3
68	clno B3LYP	-589.727028	-0.94700114	-589.982718	27.905249	32.36859942	-24.0	-19.5

69	nf3 c3v	-353.7067586	-1.27436033	-354.050836	-157.893328	-153.0886625	-25.7	-20.9
70	pf3 c3v	-640.5539733	-1.3301814	-640.913122	-949.488928	-944.6842632	9.1	13.9
71	ozone 1-a1	-225.1064085	-1.05701348	-225.391802	123.880765	126.7163052	-18.8	-16.0
72	f2o B3LYP	-274.3605923	-0.99926791	-274.630395	18.837194	22.98548374	-5.8	-1.7
73	CLF3, C2V	-759.0186955	-1.41499615	-759.400744	-180.460159	-172.1373242	-21.5	-13.1
74	CF2=CF2 D2H	-475.009597	-1.69946873	-475.468454	-712.771682	-705.6303216	-54.2	-47.1
75	cl2c=ccl2 B3LYP	-1916.122004	-1.77404669	-1916.600997	-32.353574	-17.54575425	-19.8	-5.0
76	cf3cn B3LYP	-429.9652354	-1.64102945	-430.408313	-538.711898	-533.1720929	-43.3	-37.8
77	PROPYNE C3V	-116.4275967	-0.65801035	-116.605259	184.491848	185.5945576	-0.4	0.7
78	ALLENE D2D	-116.4280647	-0.65153525	-116.603979	186.196577	187.2992869	-4.2	-3.1
79	CYCLOPROPENE C2V	-116.3879592	-0.66072674	-116.566355	285.915082	287.0177925	8.9	10.0
80	PROPENE CS	-117.6623886	-0.68110349	-117.846287	31.976630	33.07934029	11.9	13.0
81	CYCLOPROPANE D3H	-117.6482671	-0.68689439	-117.833729	67.428513	68.53122262	14.3	15.4
82	PROPANE C2V	-118.8796489	-0.71417711	-119.072477	-81.936306	-80.8335958	22.7	23.8
83	TRANS-1,3-BUTADIENE C2H	-155.6808037	-0.88148955	-155.918806	118.097936	119.5682157	8.1	9.5
84	Dimethyl acetylene	-155.6672088	-0.88744673	-155.906819	149.720459	151.1907391	4.1	5.6
85	Methylene cyclopropane.	-155.6477855	-0.88779369	-155.887490	199.065946	200.536226	-1.3	0.1
86	Bicyclo[1.1.0]butane. C2v	-155.6312751	-0.89932497	-155.874093	236.171913	237.6421928	19.0	20.5
87	CYCLOBUTENE b3lyp	-155.6569388	-0.89022213	-155.897299	175.675422	177.1457022	19.2	20.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8793425	-0.91921924	-157.127532	52.521376	53.99165642	24.1	25.5
89	Isobutene. Single	-156.8974947	-0.91532087	-157.144631	2.837464	4.30774436	19.6	21.0
90	Trans butane	-158.109821	-0.94573159	-158.365169	-95.044240	-93.57395962	30.5	31.9
91	isobutane B3LYP/6-31G*	-158.1107853	-0.94903349	-158.367024	-101.210864	-99.74058436	33.1	34.6
92	Spiropentane. D2d	-194.8715819	-1.12523864	-195.175396	200.456766	202.2946165	15.1	16.9
93	Benzene B3LYP	-231.7989285	-1.29401426	-232.148312	76.525368	78.73078815	-5.9	-3.7
94	DIFLUOROMETHANE C2V	-238.7205822	-0.87304735	-238.956305	-462.597945	-459.0272653	-12.0	-8.4
95	HCF3 TRI-FLUOROMETHANE	-337.8893681	-1.18372682	-338.208974	-716.114173	-710.9419378	-19.1	-13.9
96	CH2CL2 C2V	-959.2686157	-0.89682489	-959.510758	-92.527482	-85.12357171	2.9	10.3
97	chcl3 B3LYP/6-31G*	-1418.685977	-1.2300252	-1419.018084	-101.584220	-90.66214034	1.8	12.7
98	METHYLAMINE b3lyp	-95.67575486	-0.52752382	-95.818186	-15.364690	-14.9971195	7.6	8.0
99	Acetonitrile. CH3-CN.	-132.5212339	-0.70161558	-132.710670	62.245936	62.98107585	-13.1	-12.3
100	NITRO METHANE	-244.6504037	-1.1606914	-244.963790	-100.337310	-98.0793802	-25.9	-23.6
101	Methyl-nitrite. CH3-O-N=O.	-244.6463418	-1.15129609	-244.957192	-86.740702	-84.4827724	-20.2	-18.0
102	Methylsilane. CH3-SiH3.	-330.9585338	-0.57748455	-331.114455	-6.643695	-4.4907853	22.6	24.8
103	Formic Acid.	-189.5047856	-0.837987	-189.731042	-393.767138	-391.5092081	-15.1	-12.9
104	Methyl formate.	-228.7225439	-1.06647713	-229.010493	-372.711555	-370.0860553	-17.1	-14.4
105	acetamide ch3cohn2	-208.879768	-1.03499727	-209.159217	-246.355914	-244.6755935	-7.9	-6.2

106	Aziridine. (cyclic	-133.6696919	-0.7333072	-133.867685	131.139791	131.874931	4.8	5.5
107	Cyanogen. NCCN.	-185.3604321	-0.94048364	-185.614363	265.554366	266.2895057	-41.1	-40.4
108	DIMETHYLAMINE b3lyp	-134.8972956	-0.75749133	-135.101818	-5.977676	-5.242535651	12.4	13.2
109	TRANS ETHYLAMINE	-134.908812	-0.75865307	-135.113648	-36.100168	-35.3650279	11.2	11.9
110	KETENE B3LYP	-152.3648606	-0.73412818	-152.563075	-71.557619	-69.87729875	-24.3	-22.6
111	OXIRANE B3LYP	-153.5333859	-0.76482986	-153.739890	-52.487578	-50.80725835	0.2	1.9
112	Acetaldehyde B3LYP	-153.5791294	-0.75738744	-153.783624	-170.430438	-168.750118	-4.3	-2.6
113	Glyoxal, O=CH-CH=O.	-227.4952441	-1.03388131	-227.774392	-235.968862	-233.3433622	-23.8	-21.2
114	ETHANOL TRANS	-154.7744084	-0.78744963	-154.987020	-222.406763	-220.7264428	12.7	14.4
115	DIMETHYL ETHER,	-154.7577136	-0.78456808	-154.969547	-177.374768	-175.6944484	6.7	8.4
116	Thiooxirane. (cyclic	-476.4521396	-0.85003331	-476.681649	89.638322	92.71015729	7.6	10.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.76856	-1.20164206	-553.093003	-129.955181	-125.9381664	21.5	25.5
118	Thioethanol. CH3-CH2-SH.	-477.67002	-0.86883682	-477.904606	-23.791890	-20.72005515	22.7	25.7
119	ch3sch3 B3LYP	-477.6681554	-0.87088504	-477.903294	-17.822552	-14.75071678	19.4	22.5
120	Vinyl fluoride,	-177.5781989	-0.7625322	-177.784083	-148.529606	-146.192911	-9.6	-7.3
121	Ethyl chloride.	-539.0800311	-0.80334141	-539.296933	-100.594890	-96.34157981	11.5	15.8
122	Vinyl chloride,	-537.8575348	-0.77476676	-538.066722	23.138146	27.39145643	0.1	4.4
123	h2c=chcn B3LYP	-170.5308221	-0.90285737	-170.774594	170.809366	171.9120765	-9.9	-8.8
124	ACETONE B3LYP	-192.8210939	-0.98833152	-193.087943	-214.512923	-212.4650333	2.6	4.7
125	CH3COOH ACETIC	-228.7481619	-1.06562195	-229.035880	-439.819654	-437.194154	-7.2	-4.6
126	CH3CFO HCCO	-252.7597017	-1.07379209	-253.049626	-455.904852	-452.6229767	-13.7	-10.4
127	ch3c(o)cl hcco	-613.0259449	-1.09075377	-613.320448	-253.620205	-248.4217149	-10.9	-5.7
128	ch3ch2ch2cl B3LYP	-578.3103152	-1.03516301	-578.589809	-114.091666	-109.4707865	17.7	22.3
129	Isopropyl alcohol,	-194.0094984	-1.02132318	-194.285256	-251.761472	-249.7135815	21.0	23.1
130	Methyl ethyl	-193.9931059	-1.01553452	-194.267300	-204.070765	-202.0228753	12.2	14.3
131	Trimethyl Amine.	-174.1211422	-0.99246929	-174.389109	-7.501509	-6.398798598	16.3	17.5
132	FURAN B3LYP	-229.6312348	-1.17641189	-229.948866	-45.290397	-42.87493749	-10.6	-8.1
133	Thiophene b3lyp	-552.5396414	-1.26910949	-552.882301	116.342284	120.1492592	1.3	5.1
134	PYROLE PLANAR	-209.7821212	-1.14777635	-210.092021	97.337446	98.80772633	-11.0	-9.6
135	C2v Pyridine	-247.8278157	-1.33936824	-248.189445	119.664394	121.5022445	-20.9	-19.1
136	H2 B3LYP/6-31G*	-1.15979314	-0.03558216	-1.169400	6.830932	6.830931888	6.8	6.8
137	SH b3lyp/6-31G*	-398.5749206	-0.36522957	-398.673533	146.382019	148.7187137	3.3	5.6
138	CCH B3LYP	-76.47245608	-0.391236	-76.578090	572.029743	572.7648835	6.8	7.5
139	C2H3 CS,2-A'	-77.75190643	-0.41246698	-77.863273	298.653160	299.3883003	-0.9	-0.2
140	ch3co hcco	-152.9379138	-0.73524116	-153.136429	-24.337006	-22.65668593	-14.3	-12.6
141	H2COH C1	-114.8870065	-0.52425904	-115.028556	-18.751785	-17.43903548	-1.6	-0.3
142	ch3o CS,	-114.8796859	-0.49722261	-115.013936	16.060706	17.37345647	-1.1	0.2

143	ch3ch2o 2A"	-154.1149828	-0.7278377	-154.311499	-10.713387	-9.033067271	4.8	6.4
144	ch3s 2-A'	-437.8066363	-0.59954186	-437.968513	128.479269	131.1835339	3.8	6.5
145	c2h5 staggered	-78.99009882	-0.44350261	-79.109845	129.951861	130.6870007	9.0	9.8
146	(ch3)2ch Cs	-118.2251127	-0.67612467	-118.407666	103.495736	104.5984463	13.5	14.6
147	TERT-BUTYL RADICAL	-157.4601816	-0.91085039	-157.706111	75.141616	76.61189636	23.7	25.1
148	NO2 RADICAL	-204.7986354	-0.92889597	-205.049437	-9.401069	-7.510708654	-42.5	-40.6
						MD	**-1.4**	
						MAD	**12.1**	**12.3**
						LD	**-54.2**	**-47.1**

Table S5.13b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 53% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498614	0.000000	-0.498614
2	li	-7.468472	-0.014754	-7.472456
3	be	-14.637117	-0.055096	-14.651992
4	b	-24.616649	-0.079262	-24.638049
5	c	-37.800072	-0.106205	-37.828747
6	n	-54.533311	-0.137073	-54.570321
7	o	-74.997605	-0.195057	-75.050271
8	f	-99.645067	-0.258772	-99.714936
9	na	-162.151430	-0.174130	-162.198445
10	al	-242.232910	-0.223492	-242.293253
11	si	-289.233398	-0.253891	-289.301949
12	p	-341.115425	-0.283314	-341.191920
13	s	-397.949814	-0.325223	-398.037624
14	cl	-459.968049	-0.296385	-460.048073

Table S5.14a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04991298	-0.04760647	-8.061815	146.050106	146.0501057	6.7	6.7
2	BERYLLIUM HYDRIDE	-15.22581456	-0.05603892	-15.239824	319.069095	319.0690948	-22.8	-22.8
3	DOUBLET CH	-38.42436639	-0.14734048	-38.461202	598.920943	599.2885134	2.7	3.1
4	CH2 3-B1	-39.08776642	-0.16641318	-39.129370	395.334078	395.7016477	3.3	3.7
5	Singlet methylene,	-39.06522768	-0.18751633	-39.112107	439.045902	439.4134725	8.9	9.3
6	Methyl radical,	-39.76132073	-0.21199782	-39.814320	151.607872	151.9754422	5.2	5.5
7	ch4 //b3lyp/6-31G*	-40.42699252	-0.25460915	-40.490645	-64.167661	-63.80009068	10.7	11.1
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15546271	-0.19068672	-55.203134	357.036602	357.0366019	0.6	0.6
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79818164	-0.24534753	-55.859519	186.491844	186.491844	-2.2	-2.2
10	AMMONIA, //b3lyp/6-31G*	-56.46493742	-0.30047159	-56.540055	-38.788452	-38.78845181	7.2	7.2
11	OH RADICAL	-75.65346972	-0.26261008	-75.719122	40.806589	41.75176912	1.5	2.4
12	Water //b3lyp/6-31G*	-76.33198714	-0.33286757	-76.415204	-230.553851	-229.6086706	11.3	12.2
13	HYDROGEN FLUORIDE,	-100.3511134	-0.34315721	-100.436903	-266.487405	-264.8858498	5.9	7.5
14	SIH2 singlet	-290.4678305	-0.31053034	-290.545463	274.649198	276.4345377	1.9	3.6
15	SIH2 3B1	-290.4409552	-0.28738805	-290.512802	361.411005	363.1963447	0.8	2.5
16	SIH3 c3v	-291.0829705	-0.3158174	-291.161925	202.590509	204.3758489	2.2	4.0
17	SIH4 //b3lyp/6-31G*	-291.7263571	-0.3434788	-291.812227	42.616519	44.40185945	8.3	10.1
18	ph2 doublet	-342.3512376	-0.35026494	-342.438804	138.273583	138.2735834	-0.2	-0.2
19	PH3 c3v	-342.9795738	-0.3822594	-343.075139	16.469494	16.46949357	11.0	11.0
20	SH2 //b3lyp/6-31G*	-399.2271161	-0.40381622	-399.328070	-10.447345	-8.110649598	10.1	12.4
21	HCL //b3lyp/6-31G*	-460.6373783	-0.34159907	-460.722778	-88.673522	-85.15535226	3.8	7.3
22	DILITHIUM //b3lyp/6-31G*	-14.96513801	-0.0593253	-14.979969	230.169163	230.1691629	14.3	14.3
23	Lithium Fluoride,	-107.3159271	-0.37323379	-107.409236	-338.121114	-336.5195588	-3.0	-1.4
24	ACETYLENE //b3lyp/6-31g*	-77.19443709	-0.42723185	-77.301245	232.293173	233.0283126	5.5	6.3
25	ETHYLENE //b3lyp/6-31g*	-78.43683672	-0.4477975	-78.548786	63.434415	64.16955545	11.1	11.9
26	ETHANE //b3lyp/6-31g*	-79.66052738	-0.48125118	-79.780840	-66.070821	-65.33568061	18.0	18.8
27	CYANO RADICAL,	-92.57122716	-0.46630187	-92.687803	445.495036	445.8626063	6.6	7.0
28	HYDROGEN CYANIDE	-93.28217315	-0.47289886	-93.400398	126.044770	126.4123402	-5.8	-5.4
29	CARBON MONOXIDE	-113.1743295	-0.48347211	-113.295198	-113.034626	-111.7218762	-2.6	-1.3
30	HCO BENT	-113.7008128	-0.50613266	-113.827346	33.036842	34.34959161	-8.8	-7.5
31	H2CO //b3lyp/6-31g*	-114.3435216	-0.52570008	-114.474947	-110.382675	-109.0699246	-1.6	-0.3

32	METHANOL //b3lyp/6-31g*	-115.550409	-0.55489327	-115.689132	-190.044441	-188.7316907	10.8	12.1
33	Nitrogen N2,	-109.3814466	-0.5072224	-109.508252	-3.364461	-3.364460702	-3.4	-3.4
34	H2NNH2 //b3lyp/6-31g*	-111.6913506	-0.57006317	-111.833866	103.123279	103.1232786	7.7	7.7
35	NO radical,	-129.7310831	-0.54952994	-129.868466	83.846145	84.79132463	-6.5	-5.6
36	O2 //b3lyp/6-31g*	-150.1436029	-0.61363961	-150.297013	-7.578968	-5.688608466	-7.6	-5.7
37	HYDROGEN PEROXIDE	-151.3609489	-0.64464995	-151.522111	-119.604846	-117.7144864	16.4	18.3
38	F2 //b3lyp/6-31g*	-199.3185091	-0.67352717	-199.486891	15.044139	18.24724853	15.0	18.2
39	CO2 D*H	-188.3569409	-0.8126363	-188.560100	-413.467662	-411.2097322	-20.2	-17.9
40	na2 //b3lyp/6-31G*	-324.3382455	-0.3766461	-324.432407	143.117590	143.1175905	0.9	0.9
41	SI2 3-SGG	-578.590621	-0.56717268	-578.732414	588.688024	592.2587042	3.3	6.9
42	P2 //b3lyp/6-31g*	-682.3983131	-0.72170314	-682.578739	151.682536	151.6825356	8.2	8.2
43	S2 //b3lyp/6-31g*	-796.0577198	-0.76768704	-796.249642	127.318817	131.9922065	-1.1	3.5
44	CL2 //b3lyp/6-31g*	-920.0354542	-0.66207825	-920.200974	8.116320	15.15265976	8.1	15.2
45	Sodium Chloride	-622.2827039	-0.5161927	-622.411752	-174.054117	-170.5359474	8.4	11.9
46	SIO //b3lyp/6-31g*	-364.5057978	-0.62789739	-364.662772	-97.230998	-94.50047839	5.7	8.4
47	Carbon monosulfide,	-435.9971677	-0.58720058	-436.143968	286.445659	289.1499241	6.5	9.2
48	OS //b3lyp/6-31g*	-473.1208774	-0.69827621	-473.295446	1.627667	4.90954159	-3.4	-0.1
49	CLO 2-PI	-535.053204	-0.61766923	-535.207621	107.409948	111.8732984	6.2	10.6
50	CLF 1-SG	-559.7021447	-0.66483211	-559.868353	-52.719329	-47.59960418	2.5	7.6
51	si2h6 //b3lyp/6-31g*	-582.2783679	-0.66764989	-582.445280	98.667959	102.238639	18.8	22.3
52	Methyl chloride,	-499.8658184	-0.56935033	-500.008156	-74.762213	-70.87647268	7.2	11.1
53	H3C-SH METHANETHIOL	-438.4584546	-0.63405982	-438.616970	-5.834073	-3.129807607	17.2	19.9
54	HOCl //b3lyp/6-31g*	-535.7012164	-0.65650485	-535.865343	-67.422730	-62.95938017	7.1	11.5
55	SO2 //b3lyp/6-31G*	-548.2889653	-1.05339873	-548.552315	-282.863497	-278.6364424	14.2	18.4
56	BF3 PLANAR	-324.2676753	-1.0875862	-324.539572	-1146.885124	-1141.949184	-11.3	-6.4
57	bcl3 B3LYP	-1405.043628	-1.12745527	-1405.325492	-415.029459	-404.3436741	-12.1	-1.4
58	ALf3 B3LYP	-541.8121894	-1.22817957	-542.119234	-1193.187221	-1187.489886	16.0	21.7
59	alcl3 B3LYP	-1622.646633	-1.22973413	-1622.954067	-584.402506	-572.9553258	0.1	11.5
60	cf4 B3LYP	-437.0840159	-1.48622945	-437.455573	-944.841717	-938.0679267	-11.8	-5.0
61	ccl4 B3LYP	-1878.156866	-1.56414718	-1878.547903	-87.183824	-72.74357357	8.6	23.1
62	O=C=S. Singlet	-511.2374448	-0.90394116	-511.463430	-157.809267	-154.1598222	-19.3	-15.7
63	CS2 B3LYP	-834.1145734	-1.00247851	-834.365193	102.544303	107.5852628	-14.2	-9.1
64	COF2 B3LYP	-312.6982075	-1.15028884	-312.985780	-621.852144	-617.3362844	2.0	6.5
65	sif4 B3LYP	-688.6714335	-1.58745164	-689.068296	-1575.778915	-1567.587355	39.2	47.4
66	sicl4, td	-2129.7267	-1.62527672	-2130.133020	-639.863735	-624.0057145	22.9	38.7
67	nno B3LYP	-184.41545	-0.8734768	-184.633819	59.223529	60.16870927	-22.8	-21.8
68	clno B3LYP	-589.7503458	-0.94242243	-589.985951	45.086531	49.54988139	-6.8	-2.3

69	nf3 c3v	-353.7296771	-1.26897817	-354.046922	-139.011070	-134.2064047	-6.8	-2.0
70	pf3 c3v	-640.5853534	-1.32529686	-640.916678	-938.289260	-933.4845946	20.3	25.1
71	ozone 1-a1	-225.1210676	-1.051303	-225.383893	152.117163	154.9527026	9.4	12.3
72	f2o B3LYP	-274.3776159	-0.99484103	-274.626326	35.935894	40.0841835	11.3	15.4
73	CLF3, C2V	-759.050934	-1.40887886	-759.403154	-160.433476	-152.1106406	-1.4	6.9
74	CF2=CF2 D2H	-475.0428917	-1.69291913	-475.466121	-693.623021	-686.4816606	-35.1	-27.9
75	cl2c=ccl2 B3LYP	-1916.187134	-1.76699741	-1916.628883	-18.544281	-3.736461263	-6.0	8.8
76	cf3cn B3LYP	-429.9967011	-1.63436257	-430.405292	-517.000157	-511.4603521	-21.6	-16.1
77	PROPYNE C3V	-116.4413585	-0.655122	-116.605139	192.809708	193.9124183	7.9	9.0
78	ALLENE D2D	-116.4417652	-0.64868808	-116.603937	194.308422	195.4111325	3.9	5.0
79	CYCLOPROPENE C2V	-116.4018497	-0.65790642	-116.566326	293.992947	295.095657	17.0	18.1
80	PROPENE CS	-117.6774782	-0.67827309	-117.847047	38.103788	39.20649774	18.0	19.1
81	CYCLOPROPANE D3H	-117.6635815	-0.68413555	-117.834615	73.222804	74.32551392	20.1	21.2
82	PROPANE C2V	-118.89607	-0.71133712	-119.073904	-77.440739	-76.33802933	27.2	28.3
83	TRANS-1,3-BUTADIENE C2H	-155.6997719	-0.87771438	-155.919201	127.770710	129.2409901	17.7	19.2
84	Dimethyl acetylene	-155.6861906	-0.88365463	-155.907104	159.681739	161.1520194	14.1	15.5
85	Methylene cyclopropane.	-155.6669349	-0.88408816	-155.887957	208.548327	210.0186065	8.1	9.6
86	Bicyclo[1.1.0]butane. C2v	-155.650656	-0.89564916	-155.874568	245.632595	247.1028751	28.5	30.0
87	CYCLOBUTENE b3lyp	-155.6762028	-0.886484	-155.897824	185.005914	186.4761944	28.5	30.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.8999528	-0.91550679	-157.128829	59.944107	61.41438732	31.5	33.0
89	Isobutene. Single	-156.9178394	-0.91155012	-157.145727	10.791013	12.26129255	27.5	29.0
90	Trans butane	-158.1314795	-0.94196349	-158.366970	-88.824068	-87.3537878	36.7	38.2
91	isobutane B3LYP/6-31G*	-158.1324698	-0.94524738	-158.368782	-94.873725	-93.40344521	39.4	40.9
92	Spiropentane. D2d	-194.8962058	-1.12067926	-195.176376	211.302128	213.1399775	26.0	27.8
93	Benzene B3LYP	-231.826232	-1.28858427	-232.148378	92.234902	94.44032168	9.8	12.0
94	DIFLUOROMETHANE C2V	-238.7382825	-0.86975322	-238.955721	-454.430523	-450.8598426	-3.8	-0.2
95	HCF3 TRI-FLUOROMETHANE	-337.9130168	-1.17930339	-338.207843	-704.606687	-699.4344517	-7.6	-2.4
96	CH2CL2 C2V	-959.3021844	-0.89336791	-959.525526	-87.667441	-80.26353098	7.7	15.1
97	chcl3 B3LYP/6-31G*	-1418.733335	-1.22524884	-1419.039647	-94.163135	-83.24105458	9.2	20.1
98	METHYLAMINE b3lyp	-95.68707735	-0.52541199	-95.818430	-10.400332	-10.03276214	12.6	13.0
99	Acetonitrile. CH3-CN.	-132.5351038	-0.69847941	-132.709724	72.801559	73.53669932	-2.5	-1.8
100	NITRO METHANE	-244.6709644	-1.15542093	-244.959820	-79.446509	-77.18857864	-5.0	-2.7
101	Methyl-nitrite. CH3-O-N=O.	-244.666848	-1.14584773	-244.953310	-66.083370	-63.82544001	0.4	2.7
102	Methylsilane. CH3-SiH3.	-330.9770555	-0.57541701	-331.120910	-6.547098	-4.394187641	22.7	24.9
103	Formic Acid.	-189.5205049	-0.83437571	-189.729099	-380.976247	-378.7183166	-2.3	-0.1
104	Methyl formate.	-228.7434506	-1.06191509	-229.008929	-358.210622	-355.5851221	-2.6	0.1
105	acetamide ch3cohn2	-208.9005933	-1.03063237	-209.158251	-233.137557	-231.4572373	5.4	7.0

106	Aziridine. (cyclic	-133.685061	-0.73029558	-133.867635	139.462807	140.1979471	13.1	13.8
107	Cyanogen. NCCN.	-185.3767884	-0.93589828	-185.610763	285.610802	286.3459423	-21.1	-20.3
108	DIMETHYLAMINE b3lyp	-134.9138378	-0.75444923	-135.102450	0.676081	1.41122069	19.1	19.8
109	TRANS ETHYLAMINE	-134.9253658	-0.75560902	-135.114268	-29.414873	-28.67973327	17.9	18.6
110	KETENE B3LYP	-152.37887	-0.73083497	-152.561579	-59.843946	-58.1636263	-12.6	-10.9
111	OXIRANE B3LYP	-153.5488626	-0.76165247	-153.739276	-42.969274	-41.28895391	9.7	11.4
112	Acetaldehyde B3LYP	-153.5944858	-0.75415919	-153.783026	-160.953704	-159.2733841	5.2	6.8
113	Glyoxal, O=CH-CH=O.	-227.5147112	-1.02931777	-227.772041	-219.519864	-216.8943643	-7.4	-4.8
114	ETHANOL TRANS	-154.7911343	-0.78430836	-154.987211	-214.883325	-213.2030054	20.3	21.9
115	DIMETHYL ETHER,	-154.7743972	-0.78141448	-154.969751	-169.883279	-168.2029593	14.2	15.9
116	Thiooxirane. (cyclic	-476.4754849	-0.84677229	-476.687178	96.224251	99.29608647	14.2	17.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.7984628	-1.19673516	-553.097647	-118.431107	-114.414092	33.0	37.0
118	Thioethanol. CH3-CH2-SH.	-477.6945383	-0.86558692	-477.910935	-19.184642	-16.11280727	27.3	30.3
119	ch3sch3 B3LYP	-477.6926293	-0.86760595	-477.909531	-12.972046	-9.900211336	24.3	27.3
120	Vinyl fluoride,	-177.5939081	-0.75944549	-177.783769	-140.389820	-138.0531245	-1.5	0.9
121	Ethyl chloride.	-539.1050377	-0.80020891	-539.305090	-96.071933	-91.81862309	16.1	20.3
122	Vinyl chloride,	-537.8812033	-0.77161054	-538.074106	29.568311	33.82162099	6.6	10.8
123	h2c=chcn B3LYP	-170.5485413	-0.89875752	-170.773231	185.045117	186.1478268	4.3	5.4
124	ACETONE B3LYP	-192.8417075	-0.98418579	-193.087754	-203.402388	-201.3544983	13.7	15.8
125	CH3COOH ACETIC	-228.7691471	-1.06112993	-229.034430	-425.615635	-422.990135	7.0	9.6
126	CH3CFO HCCO	-252.7809498	-1.06935805	-253.048289	-442.588169	-439.3062945	-0.3	2.9
127	ch3c(o)cl hcco	-613.0550426	-1.08616028	-613.326583	-241.417767	-236.2192767	1.3	6.5
128	ch3ch2ch2cl B3LYP	-578.3405581	-1.03109995	-578.598333	-107.825293	-103.204413	24.0	28.6
129	Isopropyl alcohol,	-194.031484	-1.01723685	-194.285793	-242.438789	-240.3908986	30.4	32.4
130	Methyl ethyl	-194.0150271	-1.01145289	-194.267890	-194.885995	-192.8381052	21.4	23.5
131	Trimethyl Amine.	-174.142937	-0.98846056	-174.390052	1.042206	2.144916041	24.9	26.0
132	FURAN B3LYP	-229.6547994	-1.17141304	-229.947653	-29.026091	-26.61063082	5.7	8.1
133	Thiophene b3lyp	-552.5710409	-1.2639347	-552.887025	130.216803	134.0237778	15.2	19.0
134	PYROLE PLANAR	-209.8055963	-1.14297855	-210.091341	112.487310	113.9575902	4.1	5.6
135	C2v Pyridine	-247.8551945	-1.33368027	-248.188615	137.796382	139.6342316	-2.8	-0.9
136	H2 B3LYP/6-31G*	-1.1605759	-0.0354324	-1.169434	6.863444	6.86344398	6.9	6.9
137	SH b3lyp/6-31G*	-398.5883544	-0.36407166	-398.679372	146.798462	149.1351566	3.7	6.0
138	CCH B3LYP	-76.48014432	-0.38934277	-76.577480	578.864335	579.5994751	13.6	14.3
139	C2H3 CS,2-A'	-77.7609747	-0.41067382	-77.863643	303.034569	303.7697089	3.5	4.2
140	ch3co hcco	-152.9524654	-0.73204508	-153.135477	-13.991673	-12.31135293	-4.0	-2.3
141	H2COH C1	-114.897747	-0.52213732	-115.028281	-12.771012	-11.458262	4.4	5.7
142	ch3o CS,	-114.8904781	-0.49515259	-115.014266	20.452334	21.76508411	3.3	4.6

143	ch3ch2o 2A"	-154.1309981	-0.72481527	-154.312202	-4.592803	-2.912483292	10.9	12.6
144	ch3s 2-A'	-437.8252254	-0.59740002	-437.974575	131.017821	133.722086	6.3	9.0
145	c2h5 staggered	-79.00053745	-0.44174075	-79.110973	132.465456	133.2005961	11.5	12.3
146	(ch3)2ch Cs	-118.2407743	-0.6734239	-118.409130	107.835312	108.9380218	17.9	19.0
147	TERT-BUTYL RADICAL	-157.481086	-0.90719812	-157.707886	81.373520	82.84380023	29.9	31.4
148	NO2 RADICAL	-204.8130862	-0.92440539	-205.044188	12.079758	13.97011785	-21.0	-19.1

MAD	**11.5**	**12.8**
LD	**39.4**	**47.4**

Table S5.14b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498637	0.000000	-0.498637
2	li	-7.469599	-0.014722	-7.473279
3	be	-14.639095	-0.054764	-14.652786
4	b	-24.619225	-0.078860	-24.638940
5	c	-37.803292	-0.105763	-37.829732
6	n	-54.537204	-0.136608	-54.571356
7	o	-75.002614	-0.194420	-75.051219
8	f	-99.651190	-0.257973	-99.715683
9	na	-162.159421	-0.173623	-162.202827
10	al	-242.242757	-0.222817	-242.298461
11	si	-289.244033	-0.253137	-289.307318
12	p	-341.126873	-0.282497	-341.197498
13	s	-397.962534	-0.324260	-398.043599
14	cl	-459.982025	-0.295367	-460.055867

Table S5.15a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04902488	-0.04760782	-8.061403	146.107166	146.107166	6.8	6.8
2	BERYLLIUM HYDRIDE	-15.22473298	-0.05603119	-15.239301	319.384650	319.3846505	-22.4	-22.4
3	DOUBLET CH	-38.42238875	-0.14734439	-38.460698	598.826119	599.1936893	2.6	3.0
4	CH2 3-B1	-39.08561392	-0.16641154	-39.128881	395.201383	395.5689534	3.2	3.5
5	Singlet methylene,	-39.06289997	-0.18751261	-39.111653	438.820579	439.1881487	8.7	9.1
6	Methyl radical,	-39.758735	-0.21200143	-39.813855	151.412215	151.7797847	5.0	5.3
7	ch4 //b3lyp/6-31G*	-40.42404631	-0.25460329	-40.490243	-64.529174	-64.16160391	10.4	10.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15308226	-0.19069695	-55.202663	356.800073	356.8000729	0.3	0.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79538547	-0.24535455	-55.859178	185.913860	185.9138596	-2.8	-2.8
10	AMMONIA, //b3lyp/6-31G*	-56.46175812	-0.30047286	-56.539881	-39.803885	-39.80388546	6.2	6.2
11	OH RADICAL	-75.65045935	-0.26262043	-75.718741	40.134829	41.08000896	0.8	1.8
12	Water //b3lyp/6-31G*	-76.3285831	-0.33287431	-76.415130	-232.034176	-231.0889963	9.8	10.7
13	HYDROGEN FLUORIDE,	-100.3474901	-0.34316635	-100.436713	-267.662991	-266.0614358	4.7	6.3
14	SIH2 singlet	-290.461856	-0.31052242	-290.542592	274.877974	276.6633138	2.1	3.9
15	SIH2 3B1	-290.435175	-0.28736091	-290.509889	361.750420	363.5357596	1.1	2.9
16	SIH3 c3v	-291.076815	-0.31580225	-291.158924	203.160493	204.9458329	2.7	4.5
17	SIH4 //b3lyp/6-31G*	-291.7198643	-0.34346972	-291.809166	43.341822	45.12716222	9.0	10.8
18	ph2 doublet	-342.3448058	-0.35026455	-342.435875	138.487980	138.4879798	0.0	0.0
19	PH3 c3v	-342.9728142	-0.38225028	-343.072199	16.710448	16.71044752	11.3	11.3
20	SH2 //b3lyp/6-31G*	-399.2200976	-0.40381056	-399.325088	-10.661660	-8.324965487	9.8	12.2
21	HCL //b3lyp/6-31G*	-460.6301071	-0.34159691	-460.718922	-88.963016	-85.44484593	3.5	7.0
22	DILITHIUM //b3lyp/6-31G*	-14.96379989	-0.05932109	-14.979223	230.080051	230.0800513	14.2	14.2
23	Lithium Fluoride,	-107.3117506	-0.37324937	-107.408795	-339.662278	-338.0607231	-4.5	-2.9
24	ACETYLENE //b3lyp/6-31g*	-77.18998834	-0.42721288	-77.301064	229.937294	230.6724338	3.2	3.9
25	ETHYLENE //b3lyp/6-31g*	-78.43185109	-0.44778325	-78.548275	61.944942	62.68008199	9.6	10.4
26	ETHANE //b3lyp/6-31g*	-79.65500556	-0.4812396	-79.780128	-67.032676	-66.29753621	17.1	17.8
27	CYANO RADICAL,	-92.56695731	-0.46620783	-92.688171	441.638005	442.0055745	2.7	3.1
28	HYDROGEN CYANIDE	-93.2775265	-0.47288332	-93.400476	122.950236	123.3178064	-8.8	-8.5
29	CARBON MONOXIDE	-113.1694802	-0.48346578	-113.295181	-116.081620	-114.7688703	-5.6	-4.3
30	HCO BENT	-113.6957297	-0.50612064	-113.827321	30.012516	31.32526582	-11.8	-10.5
31	H2CO //b3lyp/6-31g*	-114.3381143	-0.52569511	-114.474795	-113.074421	-111.761671	-4.3	-3.0

32	METHANOL //b3lyp/6-31g*	-115.5444473	-0.55489066	-115.688719	-192.048504	-190.7357543	8.8	10.1
33	Nitrogen N2,	-109.3766084	-0.50720668	-109.508482	-6.914139	-6.914139328	-6.9	-6.9
34	H2NNH2 //b3lyp/6-31g*	-111.6853818	-0.5700627	-111.833598	100.881853	100.8818532	5.5	5.5
35	NO radical,	-129.7258022	-0.54952031	-129.868677	80.143518	81.08869803	-10.2	-9.3
36	O2 //b3lyp/6-31g*	-150.1378799	-0.61363825	-150.297426	-12.010494	-10.12013399	-12.0	-10.1
37	HYDROGEN PEROXIDE	-151.3545856	-0.64465536	-151.522196	-123.174325	-121.2839647	12.8	14.7
38	F2 //b3lyp/6-31g*	-199.3117522	-0.67353124	-199.486870	11.752557	14.95566732	11.8	15.0
39	CO2 D*H	-188.3490289	-0.8126227	-188.560311	-418.784374	-416.5264442	-25.5	-23.2
40	na2 //b3lyp/6-31G*	-324.3298175	-0.37664057	-324.427744	142.988422	142.9884222	0.7	0.7
41	SI2 3-SGG	-578.5796385	-0.56715367	-578.727098	588.024735	591.5954152	2.7	6.3
42	P2 //b3lyp/6-31g*	-682.386169	-0.721679	-682.573806	149.682219	149.6822186	6.2	6.2
43	S2 //b3lyp/6-31g*	-796.0446498	-0.76767735	-796.244246	125.398612	130.0720025	-3.1	1.6
44	CL2 //b3lyp/6-31g*	-920.0213245	-0.66207055	-920.193463	7.010441	14.04678105	7.0	14.0
45	Sodium Chloride	-622.2713745	-0.51619546	-622.405585	-174.462054	-170.9438844	8.0	11.5
46	SIO //b3lyp/6-31g*	-364.4972719	-0.62790673	-364.660528	-100.321264	-97.5907444	2.6	5.3
47	Carbon monosulfide,	-435.9886841	-0.58717988	-436.141351	283.857239	286.561504	3.9	6.7
48	OS //b3lyp/6-31g*	-473.1114712	-0.69826835	-473.293021	-1.721092	1.560783028	-6.7	-3.5
49	CLO 2-PI	-535.0432859	-0.61762524	-535.203868	105.176734	109.6400843	3.9	8.4
50	CLF 1-SG	-559.6916818	-0.66483173	-559.864538	-54.789625	-49.6699002	0.4	5.6
51	si2h6 //b3lyp/6-31g*	-582.2657499	-0.66763289	-582.439334	99.659458	103.2301378	19.7	23.3
52	Methyl chloride,	-499.8559927	-0.56934137	-500.004021	-75.735832	-71.85009236	6.3	10.2
53	H3C-SH METHANETHIOL	-438.4488687	-0.63404814	-438.613721	-6.764772	-4.060506925	16.2	19.0
54	HOCl //b3lyp/6-31g*	-535.6909638	-0.65650293	-535.861655	-69.826114	-65.36276445	4.6	9.1
55	SO2 //b3lyp/6-31G*	-548.2764184	-1.0533885	-548.550299	-288.961935	-284.7348795	8.1	12.3
56	BF3 PLANAR	-324.2557399	-1.08758726	-324.538513	-1150.370429	-1145.434489	-14.8	-9.9
57	bcl3 B3LYP	-1405.02074	-1.12743654	-1405.313873	-417.010325	-406.3245404	-14.1	-3.4
58	ALf3 B3LYP	-541.7966604	-1.22818836	-542.115989	-1196.849132	-1191.151797	12.3	18.0
59	alcl3 B3LYP	-1622.620155	-1.22971829	-1622.939881	-585.560204	-574.1130242	-1.1	10.4
60	cf4 B3LYP	-437.0681002	-1.48622197	-437.454518	-950.177964	-943.4041738	-17.1	-10.4
61	ccl4 B3LYP	-1878.126346	-1.56412168	-1878.533017	-91.168964	-76.72871447	4.6	19.1
62	O=C=S. Singlet	-511.225896	-0.90391899	-511.460915	-162.338461	-158.6890163	-23.8	-20.2
63	CS2 B3LYP	-834.099377	-1.00244728	-834.360013	98.641034	103.6819936	-18.1	-13.1
64	COF2 B3LYP	-312.6862996	-1.15027929	-312.985372	-627.217369	-622.7015086	-3.4	1.1
65	sif4 B3LYP	-688.6518855	-1.58744818	-689.064622	-1580.132494	-1571.940934	34.9	43.1
66	sicl4, td	-2129.692548	-1.62525079	-2130.115113	-641.811377	-625.9533572	20.9	36.8
67	nno B3LYP	-184.4075747	-0.87345348	-184.634673	52.363552	53.30873172	-29.6	-28.7
68	clno B3LYP	-589.7379173	-0.94240285	-589.982942	39.428272	43.89162197	-12.5	-8.0

69	nf3 c3v	-353.716898	-1.26897234	-354.046831	-145.263628	-140.4589633	-13.0	-8.2
70	pf3 c3v	-640.5688335	-1.32529396	-640.913410	-942.204623	-937.3999576	16.3	21.2
71	ozone 1-a1	-225.1122896	-1.05127938	-225.385622	142.557341	145.3928814	-0.1	2.7
72	f2o B3LYP	-274.367889	-0.99483936	-274.626547	30.336329	34.48461897	5.7	9.8
73	CLF3, C2V	-759.0335044	-1.40887724	-759.399812	-167.092127	-158.7692922	-8.1	0.2
74	CF2=CF2 D2H	-475.0249378	-1.69290968	-475.465094	-700.449422	-693.3080622	-41.9	-34.7
75	cl2c=ccl2 B3LYP	-1916.154528	-1.76696619	-1916.613939	-23.793365	-8.985544911	-11.2	3.6
76	cf3cn B3LYP	-429.9797614	-1.63433873	-430.404689	-524.742062	-519.2022566	-29.4	-23.8
77	PROPYNE C3V	-116.4343248	-0.65509781	-116.604650	189.844846	190.9475562	4.9	6.0
78	ALLENE D2D	-116.4347279	-0.6486659	-116.603381	191.520458	192.6231676	1.1	2.3
79	CYCLOPROPENE C2V	-116.3947603	-0.65788866	-116.565811	291.096962	292.1996722	14.1	15.2
80	PROPENE CS	-117.6699061	-0.67825336	-117.846252	35.941907	37.04461719	15.9	17.0
81	CYCLOPROPANE D3H	-117.6559405	-0.68412046	-117.833812	71.084498	72.18720774	17.9	19.1
82	PROPANE C2V	-118.8879634	-0.71131952	-119.072906	-79.069129	-77.96641905	25.5	26.6
83	TRANS-1,3-BUTADIENE C2H	-155.6901497	-0.87768646	-155.918348	124.344418	125.8146984	14.3	15.8
84	Dimethyl acetylene	-155.6765723	-0.88362514	-155.906315	156.090214	157.5604938	10.5	12.0
85	Methylene cyclopropane.	-155.6572504	-0.88406483	-155.887107	205.115127	206.5854066	4.7	6.2
86	Bicyclo[1.1.0]butane. C2v	-155.6409032	-0.89562933	-155.873767	242.072741	243.5430211	24.9	26.4
87	CYCLOBUTENE b3lyp	-155.6664937	-0.88646048	-155.896973	181.574476	183.0447562	25.1	26.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8897095	-0.9154853	-157.127736	57.151675	58.62195462	28.7	30.2
89	Isobutene. Single	-156.9076728	-0.91152471	-157.144669	7.903710	9.373989762	24.6	26.1
90	Trans butane	-158.1207873	-0.94193957	-158.365692	-91.130692	-89.66041163	34.4	35.9
91	isobutane B3LYP/6-31G*	-158.1217684	-0.94522354	-158.367527	-97.242573	-95.77229261	37.1	38.5
92	Spiropentane. D2d	-194.8838671	-1.12065443	-195.175237	207.210856	209.048706	21.9	23.7
93	Benzene B3LYP	-231.81234	-1.28854597	-232.147362	86.406775	88.61219504	4.0	6.2
94	DIFLUOROMETHANE C2V	-238.7288739	-0.86975363	-238.955010	-457.325559	-453.754879	-6.7	-3.1
95	HCF3 TRI-FLUOROMETHANE	-337.9003565	-1.17930131	-338.206975	-708.762391	-703.5901556	-11.7	-6.5
96	CH2CL2 C2V	-959.2854683	-0.89335448	-959.517740	-89.467402	-82.06349212	5.9	13.3
97	chcl3 B3LYP/6-31G*	-1418.70972	-1.22522978	-1419.028280	-96.971704	-86.04962439	6.4	17.3
98	METHYLAMINE b3lyp	-95.68132915	-0.52540576	-95.817935	-11.987834	-11.62026389	11.0	11.4
99	Acetonitrile. CH3-CN.	-132.5278723	-0.69845812	-132.709471	69.158727	69.89386743	-6.2	-5.4
100	NITRO METHANE	-244.6597396	-1.15540048	-244.960144	-86.533615	-84.27568478	-12.1	-9.8
101	Methyl-nitrite. CH3-O-N=O.	-244.6556599	-1.14582599	-244.953575	-73.014660	-70.75672955	-6.5	-4.2
102	Methylsilane. CH3-SiH3.	-330.967979	-0.57540291	-331.117584	-6.540505	-4.387594748	22.7	24.9
103	Formic Acid.	-189.5120467	-0.83436996	-189.728983	-385.435116	-383.1771862	-6.8	-4.5
104	Methyl formate.	-228.7324213	-1.06189958	-229.008515	-363.302503	-360.6770034	-7.7	-5.0
105	acetamide ch3cohn2	-208.8897509	-1.03061824	-209.157712	-237.698945	-236.0186248	0.8	2.5

106	Aziridine. (cyclic	-133.6772138	-0.73028311	-133.867087	136.595062	137.3302025	10.2	11.0
107	Cyanogen. NCCN.	-185.367864	-0.93586449	-185.611189	278.715158	279.4502976	-28.0	-27.2
108	DIMETHYLAMINE b3lyp	-134.905508	-0.75443578	-135.101661	-1.558109	-0.822969014	16.9	17.6
109	TRANS ETHYLAMINE	-134.9170325	-0.75559639	-135.113488	-31.670674	-30.93553372	15.6	16.3
110	KETENE B3LYP	-152.3713972	-0.73081935	-152.561410	-63.907136	-62.22681597	-16.6	-14.9
111	OXIRANE B3LYP	-153.5408136	-0.76164252	-153.738841	-46.332634	-44.65231445	6.4	8.1
112	Acetaldehyde B3LYP	-153.5864901	-0.75414773	-153.782569	-164.259394	-162.5790745	1.8	3.5
113	Glyoxal, O=CH-CH=O.	-227.504259	-1.02930419	-227.771878	-225.272239	-222.6467389	-13.1	-10.5
114	ETHANOL TRANS	-154.7825871	-0.78429932	-154.986505	-217.533930	-215.8536096	17.6	19.3
115	DIMETHYL ETHER,	-154.765863	-0.78140341	-154.969028	-172.490782	-170.8104618	11.6	13.3
116	Thiooxirane. (cyclic	-476.4637886	-0.84675501	-476.683945	93.837308	96.90914333	11.8	14.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.783255	-1.19671695	-553.094401	-122.459841	-118.442826	29.0	33.0
118	Thioethanol. CH3-CH2-SH.	-477.682368	-0.86556904	-477.907416	-20.820693	-17.74885819	25.6	28.7
119	ch3sch3 B3LYP	-477.6804663	-0.86758806	-477.906039	-14.680266	-11.60843121	22.6	25.6
120	Vinyl fluoride,	-177.5856816	-0.75943529	-177.783135	-143.228252	-140.8915573	-4.3	-2.0
121	Ethyl chloride.	-539.0926278	-0.80019366	-539.300678	-97.733685	-93.48037476	14.4	18.7
122	Vinyl chloride,	-537.8693213	-0.77159318	-538.069935	27.273006	31.52631594	4.3	8.5
123	h2c=chcn B3LYP	-170.5392668	-0.89872829	-170.772936	180.097249	181.1999589	-0.7	0.5
124	ACETONE B3LYP	-192.8311193	-0.98416729	-193.087003	-207.351985	-205.3040947	9.8	11.8
125	CH3COOH ACETIC	-228.7580981	-1.06111723	-229.033989	-430.637071	-428.0115715	2.0	4.6
126	CH3CFO HCCO	-252.7697036	-1.0693449	-253.047733	-447.306557	-444.0246816	-5.1	-1.8
127	ch3c(o)cl hcco	-613.0401548	-1.08614108	-613.322552	-245.752448	-240.5539575	-3.1	2.1
128	ch3ch2ch2cl B3LYP	-578.3255634	-1.03107849	-578.593644	-110.174639	-105.5537595	21.6	26.2
129	Isopropyl alcohol,	-194.0203427	-1.01722088	-194.284820	-245.805415	-243.7575248	27.0	29.0
130	Methyl ethyl	-194.003907	-1.01143507	-194.266880	-198.155345	-196.107455	18.2	20.2
131	Trimethyl Amine.	-174.1320127	-0.98844048	-174.389007	-1.935538	-0.832827603	21.9	23.0
132	FURAN B3LYP	-229.6425442	-1.17138667	-229.947105	-34.924994	-32.50953359	-0.2	2.2
133	Thiophene b3lyp	-552.5551416	-1.26390151	-552.883756	125.091232	128.8982073	10.0	13.8
134	PYROLE PLANAR	-209.7935323	-1.14295057	-210.090699	107.034610	108.5048898	-1.3	0.1
135	C2v Pyridine	-247.8410957	-1.33364395	-248.187843	131.268686	133.106536	-9.3	-7.5
136	H2 B3LYP/6-31G*	-1.16019332	-0.03543271	-1.169406	6.937418	6.937418493	6.9	6.9
137	SH b3lyp/6-31G*	-398.5816758	-0.36407341	-398.676335	146.730147	149.0668421	3.6	6.0
138	CCH B3LYP	-76.47608946	-0.38932167	-76.577313	576.470530	577.2056699	11.2	11.9
139	C2H3 CS,2-A'	-77.75634806	-0.41065185	-77.863118	301.582519	302.3176593	2.0	2.7
140	ch3co hcco	-152.9448	-0.73202448	-153.135126	-17.577642	-15.89732201	-7.5	-5.9
141	H2COH C1	-114.8921174	-0.52212838	-115.027871	-14.782754	-13.47000438	2.4	3.7
142	ch3o CS,	-114.8848813	-0.49513592	-115.013617	19.068367	20.38111742	1.9	3.2

143	ch3ch2o 2A"	-154.1228166	-0.72478943	-154.311262	-6.630330	-4.950009919	8.9	10.5
144	ch3s 2-A'	-437.8159686	-0.59739168	-437.971290	130.183109	132.8873739	5.5	8.2
145	c2h5 staggered	-78.99536225	-0.44173302	-79.110213	131.628268	132.3634079	10.7	11.4
146	(ch3)2ch Cs	-118.233007	-0.67340613	-118.408093	106.311696	107.4144063	16.4	17.5
147	TERT-BUTYL RADICAL	-157.4707239	-0.90717001	-157.706588	79.115660	80.58594006	27.7	29.1
148	NO2 RADICAL	-204.8047655	-0.92438351	-205.045105	4.850277	6.740637146	-28.2	-26.3

MAD	**11.2**	**12.1**
LD	**-41.9**	**43.1**

Table S5.15b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498637	0.000000	-0.498637
2	li	-7.469062	-0.014721	-7.472889
3	be	-14.638145	-0.054759	-14.652383
4	b	-24.617960	-0.078864	-24.638465
5	c	-37.801693	-0.105769	-37.829193
6	n	-54.535276	-0.136612	-54.570795
7	o	-75.000030	-0.194430	-75.050582
8	f	-99.647971	-0.257983	-99.715046
9	na	-162.155329	-0.173621	-162.200471
10	al	-242.237800	-0.222818	-242.295733
11	si	-289.238717	-0.253139	-289.304533
12	p	-341.121202	-0.282492	-341.194650
13	s	-397.956228	-0.324262	-398.040536
14	cl	-459.975105	-0.295370	-460.051901

Table S5.16a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0481368	-0.04760917	-8.060991	146.164114	146.1641141	6.8	6.8
2	BERYLLIUM HYDRIDE	-15.22365148	-0.05602348	-15.238778	319.700205	319.7002051	-22.1	-22.1
3	DOUBLET CH	-38.42041114	-0.14734831	-38.460195	598.731414	599.0989844	2.5	2.9
4	CH2 3-B1	-39.08346154	-0.16640993	-39.128392	395.068849	395.4364192	3.0	3.4
5	Singlet methylene,	-39.0605723	-0.18750889	-39.111200	438.595756	438.9633255	8.5	8.8
6	Methyl radical,	-39.75614932	-0.21200506	-39.813391	151.216633	151.5842025	4.8	5.1
7	ch4 //b3lyp/6-31G*	-40.42110015	-0.25459743	-40.489841	-64.890100	-64.52253035	10.0	10.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15070186	-0.19070722	-55.202193	356.563161	356.5631612	0.1	0.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79258936	-0.24536159	-55.858837	185.335649	185.3356489	-3.4	-3.4
10	AMMONIA, //b3lyp/6-31G*	-56.45857888	-0.30047413	-56.539707	-40.819229	-40.81922933	5.2	5.2
11	OH RADICAL	-75.64744902	-0.26263079	-75.718359	39.463064	40.40824433	0.1	1.1
12	Water //b3lyp/6-31G*	-76.3251791	-0.33288106	-76.415057	-233.514317	-232.5691369	8.3	9.3
13	HYDROGEN FLUORIDE,	-100.3438668	-0.34317549	-100.436524	-268.838509	-267.236954	3.5	5.1
14	SIH2 singlet	-290.4558815	-0.3105145	-290.539720	275.107285	276.8926252	2.3	4.1
15	SIH2 3B1	-290.429395	-0.28733381	-290.506975	362.090957	363.8762969	1.4	3.2
16	SIH3 c3v	-291.0706597	-0.31578711	-291.155922	203.731227	205.5165672	3.3	5.1
17	SIH4 //b3lyp/6-31G*	-291.7133715	-0.34346064	-291.806106	44.067695	45.853035	9.8	11.5
18	ph2 doublet	-342.3383741	-0.35026417	-342.432945	138.702098	138.7020978	0.2	0.2
19	PH3 c3v	-342.9660547	-0.38224116	-343.069260	16.951615	16.95161466	11.5	11.5
20	SH2 //b3lyp/6-31G*	-399.2130791	-0.4038049	-399.322106	-10.875547	-8.538851844	9.6	12.0
21	HCL //b3lyp/6-31G*	-460.6228359	-0.34159478	-460.715067	-89.252204	-85.73403373	3.2	6.7
22	DILITHIUM //b3lyp/6-31G*	-14.96246185	-0.05931688	-14.978477	229.990973	229.9909734	14.1	14.1
23	Lithium Fluoride,	-107.3075742	-0.37326496	-107.408356	-341.203761	-339.6022062	-6.1	-4.5
24	ACETYLENE //b3lyp/6-31g*	-77.18553965	-0.42719391	-77.300882	227.583074	228.3182144	0.8	1.5
25	ETHYLENE //b3lyp/6-31g*	-78.42686554	-0.447769	-78.547763	60.456827	61.1919675	8.2	8.9
26	ETHANE //b3lyp/6-31g*	-79.64948383	-0.48122803	-79.779415	-67.993346	-67.2582064	16.1	16.8
27	CYANO RADICAL,	-92.5626876	-0.46611388	-92.688538	437.786204	438.1537739	-1.1	-0.7
28	HYDROGEN CYANIDE	-93.27287991	-0.47286778	-93.400554	119.857086	120.2246555	-11.9	-11.6
29	CARBON MONOXIDE	-113.1646309	-0.48345945	-113.295165	-119.127352	-117.8146018	-8.7	-7.4
30	HCO BENT	-113.6906467	-0.5061086	-113.827296	26.989713	28.30246308	-14.9	-13.5
31	H2CO //b3lyp/6-31g*	-114.3327072	-0.52569014	-114.474643	-115.765029	-114.4522786	-7.0	-5.7

32	METHANOL //b3lyp/6-31g*	-115.5384856	-0.55488806	-115.688305	-194.051613	-192.7388627	6.8	8.1
33	Nitrogen N2,	-109.3717703	-0.50719097	-109.508712	-10.462503	-10.46250284	-10.5	-10.5
34	H2NNH2 //b3lyp/6-31g*	-111.6794131	-0.57006223	-111.833330	98.640897	98.64089684	3.2	3.2
35	NO radical,	-129.7205212	-0.54951069	-129.868889	76.442224	77.38740387	-13.9	-13.0
36	O2 //b3lyp/6-31g*	-150.1321569	-0.61363691	-150.297839	-16.440791	-14.55043131	-16.4	-14.6
37	HYDROGEN PEROXIDE	-151.3482225	-0.64466077	-151.522281	-126.742916	-124.8525561	9.2	11.1
38	F2 //b3lyp/6-31g*	-199.3049954	-0.67353532	-199.486850	8.461877	11.66498692	8.5	11.7
39	CO2 D*H	-188.3411169	-0.81260911	-188.560521	-424.098798	-421.8408679	-30.8	-28.5
40	na2 //b3lyp/6-31G*	-324.3213897	-0.37663503	-324.423081	142.859204	142.8592042	0.6	0.6
41	SI2 3-SGG	-578.5686563	-0.5671347	-578.721783	587.362602	590.9332825	2.0	5.6
42	P2 //b3lyp/6-31g*	-682.374025	-0.72165486	-682.568872	147.682664	147.682664	4.2	4.2
43	S2 //b3lyp/6-31g*	-796.0315799	-0.76766767	-796.238850	123.479306	128.1526961	-5.0	-0.3
44	CL2 //b3lyp/6-31g*	-920.0071949	-0.66206284	-920.185952	5.905454	12.94179369	5.9	12.9
45	Sodium Chloride	-622.2600452	-0.51619822	-622.399419	-174.870004	-171.3518344	7.6	11.1
46	SIO //b3lyp/6-31g*	-364.488746	-0.62791607	-364.658283	-103.411329	-100.680809	-0.5	2.2
47	Carbon monosulfide,	-435.9802006	-0.58715919	-436.138734	281.270389	283.974654	1.4	4.1
48	OS //b3lyp/6-31g*	-473.1020652	-0.69826049	-473.290595	-5.068707	-1.786831867	-10.1	-6.8
49	CLO 2-PI	-535.0333678	-0.61758127	-535.200115	102.946602	107.409952	1.7	6.2
50	CLF 1-SG	-559.681219	-0.66483136	-559.860723	-56.859094	-51.73936944	-1.6	3.5
51	si2h6 //b3lyp/6-31g*	-582.253132	-0.66761588	-582.433388	100.652148	104.2228278	20.7	24.3
52	Methyl chloride,	-499.8461671	-0.56933242	-499.999887	-76.708417	-72.82267706	5.3	9.2
53	H3C-SH METHANETHIOL	-438.4392829	-0.63403647	-438.610473	-7.694401	-4.990136088	15.3	18.0
54	HOCl //b3lyp/6-31g*	-535.6807112	-0.65650101	-535.857967	-72.228612	-67.76526183	2.2	6.7
55	SO2 //b3lyp/6-31G*	-548.2638715	-1.05337828	-548.548284	-295.058407	-290.831352	2.0	6.2
56	BF3 PLANAR	-324.2438046	-1.08758833	-324.537453	-1153.853793	-1148.917853	-18.3	-13.4
57	bcl3 B3LYP	-1404.997851	-1.12741783	-1405.302254	-418.989246	-408.3034614	-16.1	-5.4
58	ALf3 B3LYP	-541.7811315	-1.22819715	-542.112745	-1200.509584	-1194.812249	8.7	14.4
59	alcl3 B3LYP	-1622.593676	-1.22970245	-1622.925696	-586.716179	-575.2689985	-2.2	9.2
60	cf4 B3LYP	-437.0521846	-1.48621449	-437.453462	-955.511112	-948.737322	-22.5	-15.7
61	ccl4 B3LYP	-1878.095825	-1.56409618	-1878.518131	-95.151422	-80.71117238	0.7	15.1
62	O=C=S. Singlet	-511.2143473	-0.90389681	-511.458399	-166.865369	-163.2159242	-28.4	-24.7
63	CS2 B3LYP	-834.0841808	-1.00241604	-834.354833	94.740139	99.781099	-22.0	-17.0
64	COF2 B3LYP	-312.6743918	-1.15026975	-312.984965	-632.579968	-628.0641078	-8.7	-4.2
65	sif4 B3LYP	-688.6323375	-1.58744472	-689.060948	-1584.483371	-1576.291811	30.5	38.7
66	sicl4, td	-2129.658395	-1.62522486	-2130.097206	-643.756474	-627.8984539	19.0	34.8
67	nno B3LYP	-184.3996994	-0.87343016	-184.635526	45.505920	46.45110031	-36.5	-35.6
68	clno B3LYP	-589.7254889	-0.94238327	-589.979932	33.772115	38.23546453	-18.1	-13.6

69	nf3 c3v	-353.7041189	-1.26896652	-354.046740	-151.513905	-146.7092397	-19.3	-14.5
70	pf3 c3v	-640.5523137	-1.32529106	-640.910142	-946.118298	-941.3136334	12.4	17.2
71	ozone 1-a1	-225.1035116	-1.05125577	-225.387351	133.000549	135.8360892	-9.7	-6.8
72	f2o B3LYP	-274.3581622	-0.9948377	-274.626768	24.738592	28.88688152	0.1	4.2
73	CLF3, C2V	-759.0160748	-1.40887562	-759.396471	-173.748706	-165.4258707	-14.8	-6.4
74	CF2=CF2 D2H	-475.0069841	-1.69290023	-475.464067	-707.272237	-700.1308774	-48.7	-41.6
75	cl2c=ccl2 B3LYP	-1916.121923	-1.76693499	-1916.598995	-29.039095	-14.23127527	-16.5	-1.7
76	cf3cn B3LYP	-429.9628218	-1.6343149	-430.404087	-532.479944	-526.9401386	-37.1	-31.6
77	PROPYNE C3V	-116.4272912	-0.65507362	-116.604161	186.882249	187.984959	1.9	3.1
78	ALLENE D2D	-116.4276908	-0.64864372	-116.602825	188.734652	189.8373622	-1.6	-0.5
79	CYCLOPROPENE C2V	-116.387671	-0.6578709	-116.565296	288.202931	289.3056411	11.2	12.3
80	PROPENE CS	-117.662334	-0.67823363	-117.845457	33.782005	34.88471496	13.7	14.8
81	CYCLOPROPANE D3H	-117.6482996	-0.68410538	-117.833008	68.947919	70.05062914	15.8	16.9
82	PROPANE C2V	-118.8798569	-0.71130191	-119.071908	-80.695671	-79.59296145	23.9	25.0
83	TRANS-1,3-BUTADIENE C2H	-155.6805276	-0.87765854	-155.917495	120.920893	122.391173	10.9	12.4
84	Dimethyl acetylene	-155.6669542	-0.88359565	-155.905525	152.501537	153.9718167	6.9	8.4
85	Methylene cyclopropane.	-155.647566	-0.88404151	-155.886257	201.684445	203.1547249	1.3	2.7
86	Bicyclo[1.1.0]butane. C2v	-155.6311506	-0.8956095	-155.872965	238.515255	239.9855347	21.4	22.8
87	CYCLOBUTENE b3lyp	-155.6567847	-0.88643695	-155.896123	178.145607	179.6158865	21.7	23.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.8794664	-0.91546381	-157.126642	54.361723	55.83200301	25.9	27.4
89	Isobutene. Single	-156.8975065	-0.9114993	-157.143611	5.019015	6.489295151	21.8	23.2
90	Trans butane	-158.1100953	-0.94191566	-158.364412	-93.434819	-91.96453888	32.1	33.6
91	isobutane B3LYP/6-31G*	-158.1110672	-0.94519971	-158.366271	-99.608901	-98.13862136	34.7	36.2
92	Spiropentane. D2d	-194.8715285	-1.12062961	-195.174098	203.122592	204.9604418	17.8	19.6
93	Benzene B3LYP	-231.798448	-1.28850768	-232.146345	80.582721	82.78814081	-1.8	0.4
94	DIFLUOROMETHANE C2V	-238.7194654	-0.86975405	-238.954299	-460.219145	-456.6484646	-9.6	-6.0
95	HCF3 TRI-FLUOROMETHANE	-337.8876962	-1.17929923	-338.206107	-712.915879	-707.7436443	-15.9	-10.7
96	CH2CL2 C2V	-959.2687524	-0.89334104	-959.509954	-91.265866	-83.86195569	4.1	11.5
97	chcl3 B3LYP/6-31G*	-1418.686105	-1.22521072	-1419.016912	-99.778196	-88.8561156	3.6	14.5
98	METHYLAMINE b3lyp	-95.67558103	-0.52539954	-95.817439	-13.574501	-13.20693125	9.4	9.8
99	Acetonitrile. CH3-CN.	-132.5206409	-0.69843684	-132.709219	65.517905	66.25304484	-9.8	-9.1
100	NITRO METHANE	-244.648515	-1.15538004	-244.960468	-93.617916	-91.35998636	-19.1	-16.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6444719	-1.14580426	-244.953839	-79.943051	-77.68512055	-13.4	-11.2
102	Methylsilane. CH3-SiH3.	-330.9589026	-0.57538881	-331.114258	-6.532720	-4.379810403	22.8	24.9
103	Formic Acid.	-189.5035886	-0.83436422	-189.728867	-389.892188	-387.6342584	-11.2	-9.0
104	Methyl formate.	-228.7213921	-1.06188408	-229.008101	-368.391717	-365.766217	-12.8	-10.1
105	acetamide ch3cohn2	-208.8789086	-1.03060412	-209.157172	-242.258127	-240.5778066	-3.8	-2.1

106	Aziridine. (cyclic	-133.6693668	-0.73027064	-133.866540	133.728845	134.4639848	7.4	8.1
107	Cyanogen. NCCN.	-185.3589396	-0.9358307	-185.611614	271.822526	272.5576659	-34.9	-34.1
108	DIMETHYLAMINE b3lyp	-134.8971784	-0.75442234	-135.100872	-3.790754	-3.055613611	14.6	15.4
109	TRANS ETHYLAMINE	-134.9086993	-0.75558377	-135.112707	-33.924946	-33.18980588	13.4	14.1
110	KETENE B3LYP	-152.3639245	-0.73080374	-152.561241	-67.968251	-66.2879307	-20.7	-19.0
111	OXIRANE B3LYP	-153.5327646	-0.76163256	-153.738405	-49.694230	-48.01390987	3.0	4.7
112	Acetaldehyde B3LYP	-153.5784946	-0.75413627	-153.782111	-167.563248	-165.8829275	-1.5	0.2
113	Glyoxal, O=CH-CH=O.	-227.4938069	-1.02929062	-227.771715	-231.022021	-228.3965209	-18.9	-16.3
114	ETHANOL TRANS	-154.7740399	-0.78429027	-154.985798	-220.182869	-218.502549	15.0	16.6
115	DIMETHYL ETHER,	-154.7573288	-0.78139234	-154.968305	-175.096494	-173.4161736	9.0	10.7
116	Thiooxirane. (cyclic	-476.4520925	-0.84673773	-476.680712	91.452147	94.52398187	9.4	12.5
117	Dimethylsulfoxide. (CH3)2SO.	-552.7680474	-1.19669874	-553.091156	-126.486225	-122.4692095	25.0	29.0
118	Thioethanol. CH3-CH2-SH.	-477.6701979	-0.86555115	-477.903897	-22.455003	-19.38316762	24.0	27.1
119	ch3sch3 B3LYP	-477.6683035	-0.86757016	-477.902547	-16.386744	-13.31490907	20.9	23.9
120	Vinyl fluoride,	-177.5774552	-0.75942509	-177.782500	-146.064939	-143.7282436	-7.2	-4.8
121	Ethyl chloride.	-539.080218	-0.80017841	-539.296266	-99.393785	-95.140475	12.7	17.0
122	Vinyl chloride,	-537.8574393	-0.77157583	-538.065765	24.979509	29.23281856	2.0	6.2
123	h2c=chcn B3LYP	-170.5299925	-0.89869907	-170.772641	175.152165	176.2548751	-5.6	-4.5
124	ACETONE B3LYP	-192.8205313	-0.98414879	-193.086251	-211.299042	-209.2511525	5.9	7.9
125	CH3COOH ACETIC	-228.7470492	-1.06110454	-229.033547	-435.656014	-433.030514	-3.0	-0.4
126	CH3CFO HCCO	-252.7584574	-1.06933176	-253.047177	-452.022425	-448.7405495	-9.8	-6.5
127	ch3c(o)cl hcco	-613.0252672	-1.0861219	-613.318520	-250.084633	-244.8861426	-7.4	-2.2
128	ch3ch2ch2cl B3LYP	-578.3105689	-1.03105702	-578.588954	-112.521670	-107.9007897	19.3	23.9
129	Isopropyl alcohol,	-194.0092014	-1.0172049	-194.283847	-249.169654	-247.1217643	23.6	25.7
130	Methyl ethyl	-193.992787	-1.01141724	-194.265870	-201.422211	-199.3743211	14.9	16.9
131	Trimethyl Amine.	-174.1210886	-0.9884204	-174.387962	-4.911076	-3.808365564	18.9	20.0
132	FURAN B3LYP	-229.630289	-1.1713603	-229.946556	-40.820534	-38.40507415	-6.1	-3.7
133	Thiophene b3lyp	-552.5392424	-1.26386832	-552.880487	119.968995	123.7759697	4.9	8.7
134	PYROLE PLANAR	-209.7814684	-1.14292258	-210.090057	101.585026	103.0553062	-6.8	-5.3
135	C2v Pyridine	-247.8269971	-1.33360763	-248.187071	124.744896	126.5827458	-15.8	-14.0
136	H2 B3LYP/6-31G*	-1.15981076	-0.03543303	-1.169378	7.011317	7.011317128	7.0	7.0
137	SH b3lyp/6-31G*	-398.5749972	-0.36407518	-398.673297	146.661859	148.9985539	3.6	5.9
138	CCH B3LYP	-76.47203469	-0.38930061	-76.577146	574.078389	574.8135288	8.8	9.6
139	C2H3 CS,2-A'	-77.75172152	-0.41062991	-77.862592	300.132160	300.8673003	0.6	1.3
140	ch3co hcco	-152.9371347	-0.73200387	-153.134776	-21.161339	-19.48101923	-11.1	-9.4
141	H2COH C1	-114.8864879	-0.52211946	-115.027460	-16.793216	-15.4804663	0.4	1.7
142	ch3o CS,	-114.8792845	-0.49511928	-115.012967	17.686106	18.99885626	0.5	1.8

143	ch3ch2o 2A"	-154.1146353	-0.72476364	-154.310321	-8.665378	-6.985058336	6.8	8.5
144	ch3s 2-A'	-437.806712	-0.59738336	-437.968005	129.349258	132.0535233	4.7	7.4
145	c2h5 staggered	-78.99018714	-0.44172533	-79.109453	130.792042	131.5271817	9.9	10.6
146	(ch3)2ch Cs	-118.2252398	-0.67338838	-118.407055	104.789916	105.8926258	14.8	15.9
147	TERT-BUTYL RADICAL	-157.4603621	-0.90714193	-157.705290	76.860476	78.33075607	25.4	26.9
148	NO2 RADICAL	-204.7964449	-0.92436164	-205.046023	-2.376629	-0.486269258	-35.4	-33.5

MAD	**11.4**	**11.9**
LD	**-48.7**	**-41.6**

Table S5.16b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498637	0.000000	-0.498637
2	li	-7.468525	-0.014720	-7.472499
3	be	-14.637196	-0.054754	-14.651980
4	b	-24.616696	-0.078867	-24.637990
5	c	-37.800095	-0.105775	-37.828654
6	n	-54.533347	-0.136616	-54.570234
7	o	-74.997446	-0.194441	-75.049945
8	f	-99.644751	-0.257993	-99.714409
9	na	-162.151238	-0.173619	-162.198115
10	al	-242.232844	-0.222819	-242.293005
11	si	-289.233401	-0.253140	-289.301749
12	p	-341.115531	-0.282486	-341.191802
13	s	-397.949921	-0.324265	-398.037472
14	cl	-459.968184	-0.295374	-460.047935

Table S5.17a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04724875	-0.04761053	-8.060580	146.220949	146.2209494	6.9	6.9
2	BERYLLIUM HYDRIDE	-15.22257006	-0.05601578	-15.238254	320.015757	320.0157571	-21.8	-21.8
3	DOUBLET CH	-38.41843358	-0.14735226	-38.459692	598.636788	599.0043577	2.4	2.8
4	CH2 3-B1	-39.08130929	-0.16640834	-39.127904	394.936481	395.3040509	2.9	3.3
5	Singlet methylene,	-39.05824468	-0.18750518	-39.110746	438.371427	438.7389965	8.3	8.6
6	Methyl radical,	-39.75356369	-0.21200871	-39.812926	151.021151	151.3887212	4.6	4.9
7	ch4 //b3lyp/6-31G*	-40.41815404	-0.25459157	-40.489440	-65.250413	-64.88284294	9.6	10.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1483215	-0.19071751	-55.201722	356.325826	356.3258257	-0.2	-0.2
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78979329	-0.24536865	-55.858497	184.757184	184.757184	-3.9	-3.9
10	AMMONIA, //b3lyp/6-31G*	-56.45539969	-0.30047541	-56.539533	-41.834543	-41.83454326	4.2	4.2
11	OH RADICAL	-75.64443872	-0.26264116	-75.717978	38.791315	39.73649492	-0.5	0.4
12	Water //b3lyp/6-31G*	-76.32177514	-0.33288781	-76.414984	-234.994272	-234.0490916	6.8	7.8
13	HYDROGEN FLUORIDE,	-100.3402436	-0.34318463	-100.436335	-270.013992	-268.4124366	2.4	4.0
14	SIH2 singlet	-290.4499071	-0.31050658	-290.536849	275.337120	277.1224597	2.5	4.3
15	SIH2 3B1	-290.4236151	-0.28730674	-290.504061	362.432661	364.218001	1.8	3.6
16	SIH3 c3v	-291.0645045	-0.31577198	-291.152921	204.302725	206.0880651	3.9	5.7
17	SIH4 //b3lyp/6-31G*	-291.7068788	-0.34345155	-291.803045	44.794185	46.57952529	10.5	12.3
18	ph2 doublet	-342.3319424	-0.35026382	-342.430016	138.915929	138.915929	0.4	0.4
19	PH3 c3v	-342.9592952	-0.38223204	-343.066320	17.192976	17.19297609	11.8	11.8
20	SH2 //b3lyp/6-31G*	-399.2060606	-0.40379925	-399.319124	-11.088970	-8.752275064	9.4	11.7
21	HCL //b3lyp/6-31G*	-460.6155648	-0.34159269	-460.711211	-89.541127	-86.0229574	2.9	6.4
22	DILITHIUM //b3lyp/6-31G*	-14.96112389	-0.05931266	-14.977731	229.902002	229.902002	14.0	14.0
23	Lithium Fluoride,	-107.3033978	-0.37328057	-107.407916	-342.745544	-341.143989	-7.6	-6.0
24	ACETYLENE //b3lyp/6-31g*	-77.18109102	-0.42717494	-77.300700	225.230568	225.9657084	-1.5	-0.8
25	ETHYLENE //b3lyp/6-31g*	-78.42188006	-0.44775475	-78.547251	58.970152	59.7052923	6.7	7.4
26	ETHANE //b3lyp/6-31g*	-79.64396219	-0.48121645	-79.778703	-68.952763	-68.21762317	15.1	15.9
27	CYANO RADICAL,	-92.55841803	-0.46602	-92.688904	433.939590	434.3071601	-5.0	-4.6
28	HYDROGEN CYANIDE	-93.26823337	-0.47285224	-93.400632	116.765292	117.132862	-15.0	-14.7
29	CARBON MONOXIDE	-113.1597817	-0.48345312	-113.295149	-122.171799	-120.8590495	-11.7	-10.4
30	HCO BENT	-113.6855638	-0.50609655	-113.827271	23.968423	25.28117263	-17.9	-16.6
31	H2CO //b3lyp/6-31g*	-114.3273	-0.52568517	-114.474492	-118.454424	-117.1416739	-9.7	-8.4

32	METHANOL //b3lyp/6-31g*	-115.5325241	-0.55488545	-115.687892	-196.053652	-194.740902	4.8	6.1
33	Nitrogen N2,	-109.3669322	-0.50717525	-109.508941	-14.009669	-14.0096686	-14.0	-14.0
34	H2NNH2 //b3lyp/6-31g*	-111.6734444	-0.57006177	-111.833062	96.400192	96.40019196	1.0	1.0
35	NO radical,	-129.7152403	-0.54950107	-129.869101	72.742184	73.68736417	-17.6	-16.7
36	O2 //b3lyp/6-31g*	-150.1264339	-0.61363557	-150.298252	-20.869806	-18.97944633	-20.9	-19.0
37	HYDROGEN PEROXIDE	-151.3418593	-0.64466619	-151.522366	-130.310666	-128.4203058	5.7	7.6
38	F2 //b3lyp/6-31g*	-199.2982386	-0.6735394	-199.486830	5.172145	8.37525485	5.2	8.4
39	CO2 D*H	-188.3332051	-0.81259551	-188.560732	-429.410956	-427.1530263	-36.1	-33.9
40	na2 //b3lyp/6-31G*	-324.312962	-0.37662947	-324.418418	142.730037	142.7300367	0.5	0.5
41	SI2 3-SGG	-578.5576741	-0.56711577	-578.716467	586.701651	590.2723307	1.4	4.9
42	P2 //b3lyp/6-31g*	-682.3618811	-0.72163072	-682.563938	145.683913	145.6839129	2.2	2.2
43	S2 //b3lyp/6-31g*	-796.0185101	-0.76765801	-796.233454	121.560866	126.2342561	-6.9	-2.2
44	CL2 //b3lyp/6-31g*	-919.9930654	-0.66205514	-920.178441	4.801306	11.83764596	4.8	11.8
45	Sodium Chloride	-622.248716	-0.51620099	-622.393252	-175.277934	-171.7597643	7.1	10.7
46	SIO //b3lyp/6-31g*	-364.4802202	-0.62792542	-364.656039	-106.501191	-103.7706715	-3.6	-0.8
47	Carbon monosulfide,	-435.9717172	-0.58713849	-436.136116	278.685243	281.3895084	-1.2	1.5
48	OS //b3lyp/6-31g*	-473.0926591	-0.69825262	-473.288170	-8.415109	-5.133234305	-13.4	-10.2
49	CLO 2-PI	-535.0234498	-0.6175373	-535.196360	100.719527	105.1828769	-0.5	3.9
50	CLF 1-SG	-559.6707563	-0.66483099	-559.856909	-58.927768	-53.80804316	-3.7	1.4
51	si2h6 //b3lyp/6-31g*	-582.2405142	-0.66759887	-582.427442	101.645998	105.2166777	21.7	25.3
52	Methyl chloride,	-499.8363415	-0.56932346	-499.995752	-77.680010	-73.79427038	4.3	8.2
53	H3C-SH METHANETHIOL	-438.4296972	-0.63402479	-438.607224	-8.622878	-5.918613182	14.4	17.1
54	HOCl //b3lyp/6-31g*	-535.6704587	-0.65649909	-535.854278	-74.630208	-70.16685761	-0.2	4.3
55	SO2 //b3lyp/6-31G*	-548.2513248	-1.05336806	-548.546268	-301.152958	-296.9259025	-4.1	0.1
56	BF3 PLANAR	-324.2318694	-1.08758941	-324.536394	-1157.335260	-1152.39932	-21.8	-16.9
57	bcl3 B3LYP	-1404.974962	-1.12739911	-1405.290634	-420.966218	-410.2804332	-18.0	-7.4
58	ALf3 B3LYP	-541.7656027	-1.22820595	-542.109500	-1204.168620	-1198.471285	5.0	10.7
59	alcl3 B3LYP	-1622.567198	-1.22968662	-1622.911510	-587.870471	-576.4232915	-3.4	8.1
60	cf4 B3LYP	-437.036269	-1.48620702	-437.452407	-960.841138	-954.0673485	-27.8	-21.0
61	ccl4 B3LYP	-1878.065305	-1.56407068	-1878.503245	-99.131167	-84.69091709	-3.3	11.1
62	O=C=S. Singlet	-511.2027986	-0.90387464	-511.455884	-171.389942	-167.7404974	-32.9	-29.3
63	CS2 B3LYP	-834.0689847	-1.00238481	-834.349652	90.841688	95.88264764	-25.9	-20.9
64	COF2 B3LYP	-312.662484	-1.15026022	-312.984557	-637.939907	-633.4240469	-14.1	-9.6
65	sif4 B3LYP	-688.6127897	-1.58744127	-689.057273	-1588.831536	-1580.639976	26.2	34.4
66	sicl4, td	-2129.624243	-1.62519893	-2130.079299	-645.699008	-629.8409875	17.0	32.9
67	nno B3LYP	-184.3918242	-0.87340685	-184.636378	38.650438	39.59561814	-43.4	-42.4
68	clno B3LYP	-589.7130605	-0.94236369	-589.976922	28.117969	32.58131874	-23.8	-19.3

69	nf3 c3v	-353.6913399	-1.2689607	-354.046649	-157.761936	-152.9572707	-25.5	-20.7
70	pf3 c3v	-640.535794	-1.32528817	-640.906875	-950.030331	-945.2256657	8.5	13.3
71	ozone 1-a1	-225.0947336	-1.05123216	-225.389079	123.446775	126.2823153	-19.2	-16.4
72	f2o B3LYP	-274.3484354	-0.99483604	-274.626990	19.142697	23.29098665	-5.5	-1.4
73	CLF3, C2V	-758.9986454	-1.40887396	-759.393130	-180.403179	-172.0803435	-21.4	-13.1
74	CF2=CF2 D2H	-474.9890304	-1.69289078	-475.463040	-714.091461	-706.9501014	-55.5	-48.4
75	cl2c=ccl2 B3LYP	-1916.089318	-1.76690378	-1916.584051	-34.281421	-19.47360088	-21.7	-6.9
76	cf3cn B3LYP	-429.9458822	-1.63429107	-430.403484	-540.213891	-534.674086	-44.8	-39.3
77	PROPYNE C3V	-116.4202577	-0.65504942	-116.603672	183.922005	185.0247154	-1.0	0.1
78	ALLENE D2D	-116.4206537	-0.64862155	-116.602268	185.951080	187.05379	-4.4	-3.3
79	CYCLOPROPENE C2V	-116.3805817	-0.65785314	-116.564781	285.310882	286.4135922	8.3	9.4
80	PROPENE CS	-117.654762	-0.6782139	-117.844662	31.624188	32.72689842	11.5	12.6
81	CYCLOPROPANE D3H	-117.6406588	-0.68409029	-117.832204	66.813216	67.91592567	13.7	14.8
82	PROPANE C2V	-118.8717506	-0.71128431	-119.070910	-82.320273	-81.21756309	22.3	23.4
83	TRANS-1,3-BUTADIENE C2H	-155.6709057	-0.87763062	-155.916642	117.500268	118.9705482	7.5	8.9
84	Dimethyl acetylene	-155.6573362	-0.88356615	-155.904735	148.915850	150.3861302	3.3	4.8
85	Methylene cyclopropane.	-155.6378817	-0.88401818	-155.885407	198.256456	199.7267358	-2.2	-0.7
86	Bicyclo[1.1.0]butane. C2v	-155.621398	-0.89558967	-155.872163	234.960271	236.4305505	17.8	19.3
87	CYCLOBUTENE b3lyp	-155.6470759	-0.88641343	-155.895272	174.719426	176.1897059	18.2	19.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8692234	-0.91544232	-157.125547	51.574282	53.04456191	23.1	24.6
89	Isobutene. Single	-156.8873402	-0.91147388	-157.142553	2.137044	3.607324234	18.9	20.3
90	Trans butane	-158.0994034	-0.94189174	-158.363133	-95.736327	-94.26604746	29.8	31.3
91	isobutane B3LYP/6-31G*	-158.1003661	-0.94517587	-158.365015	-101.972616	-100.5023356	32.3	33.8
92	Spiropentane. D2d	-194.85919	-1.12060479	-195.172959	199.037424	200.8752741	13.7	15.5
93	Benzene B3LYP	-231.7845562	-1.28846939	-232.145328	74.762934	76.96835406	-7.7	-5.5
94	DIFLUOROMETHANE C2V	-238.710057	-0.86975446	-238.953588	-463.111250	-459.54057	-12.5	-8.9
95	HCF3 TRI-FLUOROMETHANE	-337.875036	-1.17929716	-338.205239	-717.067177	-711.8949418	-20.0	-14.8
96	CH2CL2 C2V	-959.2520365	-0.89332761	-959.502168	-93.062830	-85.65892009	2.3	9.7
97	chcl3 B3LYP/6-31G*	-1418.66249	-1.22519166	-1419.005543	-102.582625	-91.66054474	0.8	11.7
98	METHYLAMINE b3lyp	-95.669833	-0.52539332	-95.816943	-15.160406	-14.79283565	7.9	8.2
99	Acetonitrile. CH3-CN.	-132.5134097	-0.69841555	-132.708966	61.879081	62.61422077	-13.4	-12.7
100	NITRO METHANE	-244.6372904	-1.15535959	-244.960791	-100.699410	-98.44148024	-26.2	-24.0
101	Methyl-nitrite. CH3-O-N=O.	-244.6332841	-1.14578254	-244.954103	-86.868607	-84.61067705	-20.3	-18.1
102	Methylsilane. CH3-SiH3.	-330.9498263	-0.5753747	-331.110931	-6.523749	-4.370838807	22.8	24.9
103	Formic Acid.	-189.4951306	-0.83435848	-189.728751	-394.347415	-392.0894848	-15.7	-13.4
104	Methyl formate.	-228.7103631	-1.06186858	-229.007686	-373.478240	-370.8527399	-17.8	-15.2
105	acetamide ch3cohn2	-208.8680664	-1.03059	-209.156632	-246.815100	-245.1347804	-8.3	-6.6

106	Aziridine. (cyclic	-133.6615199	-0.73025817	-133.865992	130.864156	131.5992957	4.5	5.2
107	Cyanogen. NCCN.	-185.3500153	-0.93579691	-185.612038	264.932778	265.6679175	-41.8	-41.0
108	DIMETHYLAMINE b3lyp	-134.8888489	-0.7544089	-135.100083	-6.021897	-5.286757472	12.4	13.1
109	TRANS ETHYLAMINE	-134.9003663	-0.75557115	-135.111926	-36.177760	-35.44262035	11.1	11.8
110	KETENE B3LYP	-152.3564518	-0.73078814	-152.561073	-72.027243	-70.34692299	-24.7	-23.1
111	OXIRANE B3LYP	-153.5247158	-0.76162261	-153.737970	-53.054026	-51.37370577	-0.3	1.3
112	Acetaldehyde B3LYP	-153.5704991	-0.75412482	-153.781654	-170.865249	-169.1849286	-4.8	-3.1
113	Glyoxal, O=CH-CH=O.	-227.4833548	-1.02927705	-227.771552	-236.769187	-234.1436874	-24.6	-22.0
114	ETHANOL TRANS	-154.7654928	-0.78428123	-154.985092	-222.830057	-221.1497367	12.3	14.0
115	DIMETHYL ETHER,	-154.7487948	-0.78138128	-154.967582	-177.700400	-176.0200802	6.4	8.1
116	Thiooxirane. (cyclic	-476.4403964	-0.84672045	-476.677478	89.068783	92.14061834	7.1	10.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.7528399	-1.19668054	-553.087910	-130.510150	-126.4931346	21.0	25.0
118	Thioethanol. CH3-CH2-SH.	-477.6580279	-0.86553327	-477.900377	-24.087489	-21.01565442	22.4	25.4
119	ch3sch3 B3LYP	-477.6561408	-0.86755227	-477.899055	-18.091399	-15.01956378	19.1	22.2
120	Vinyl fluoride,	-177.5692289	-0.75941489	-177.781865	-148.899804	-146.5631089	-10.0	-7.7
121	Ethyl chloride.	-539.0678083	-0.80016315	-539.291854	-101.052152	-96.79884188	11.1	15.3
122	Vinyl chloride,	-537.8455574	-0.77155848	-538.061594	22.687847	26.94115745	-0.3	3.9
123	h2c=chcn B3LYP	-170.5207183	-0.89866985	-170.772346	170.209901	171.3126105	-10.5	-9.4
124	ACETONE B3LYP	-192.8099433	-0.98413029	-193.085500	-215.243486	-213.1955963	1.9	4.0
125	CH3COOH ACETIC	-228.7360004	-1.06109185	-229.033106	-440.672387	-438.0468873	-8.0	-5.4
126	CH3CFO HCCO	-252.7472114	-1.06931862	-253.046621	-456.735698	-453.453823	-14.5	-11.2
127	ch3c(o)cl hcco	-613.0103796	-1.08610271	-613.314488	-254.414259	-249.2157687	-11.7	-6.5
128	ch3ch2ch2cl B3LYP	-578.2955746	-1.03103556	-578.584265	-114.866322	-110.2454424	16.9	21.6
129	Isopropyl alcohol,	-193.9980603	-1.01718893	-194.282873	-252.531472	-250.4835821	20.3	22.3
130	Methyl ethyl	-193.9816672	-1.01139942	-194.264859	-204.686558	-202.6386682	11.6	13.7
131	Trimethyl Amine.	-174.1101647	-0.98840033	-174.386917	-7.884387	-6.781676576	16.0	17.1
132	FURAN B3LYP	-229.618034	-1.17133394	-229.946007	-46.712644	-44.2971837	-12.0	-9.6
133	Thiophene b3lyp	-552.5233433	-1.26383514	-552.877217	114.850179	118.6571542	-0.2	3.6
134	PYROLE PLANAR	-209.7694046	-1.14289459	-210.089415	96.138530	97.60880961	-12.2	-10.8
135	C2v Pyridine	-247.8128986	-1.33357132	-248.186299	118.225060	120.0629102	-22.4	-20.5
136	H2 B3LYP/6-31G*	-1.15942819	-0.03543334	-1.169350	7.085233	7.085232567	7.1	7.1
137	SH b3lyp/6-31G*	-398.5683187	-0.36407697	-398.670260	146.593636	148.9303313	3.5	5.8
138	CCH B3LYP	-76.46798	-0.38927959	-76.576978	571.687989	572.423129	6.4	7.2
139	C2H3 CS,2-A'	-77.7470951	-0.410608	-77.862065	298.683491	299.4186311	-0.9	-0.2
140	ch3co hcco	-152.9294696	-0.73198324	-153.134425	-24.742734	-23.06241442	-14.7	-13.0
141	H2COH C1	-114.8808585	-0.52211055	-115.027049	-18.802371	-17.48962073	-1.6	-0.3
142	ch3o CS,	-114.8736878	-0.49510267	-115.012317	16.305570	17.61831953	-0.8	0.5

143	ch3ch2o 2A"	-154.106454	-0.72473787	-154.309381	-10.697856	-9.017535863	4.8	6.5
144	ch3s 2-A'	-437.7974555	-0.59737506	-437.964720	128.516362	131.2206267	3.8	6.5
145	c2h5 staggered	-78.98501212	-0.44171766	-79.108693	129.956843	130.6919831	9.0	9.8
146	(ch3)2ch Cs	-118.2174727	-0.67337066	-118.406017	103.270016	104.3727263	13.3	14.4
147	TERT-BUTYL RADICAL	-157.4500003	-0.90711387	-157.703992	74.608081	76.07836142	23.1	24.6
148	NO2 RADICAL	-204.7881243	-0.92433978	-205.046939	-9.601000	-7.710639954	-42.7	-40.8

MAD	**12.2**	**12.4**
LD	**-55.5**	**-48.4**

Table S5.17b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498637	0.000000	-0.498637
2	li	-7.467988	-0.014720	-7.472109
3	be	-14.636247	-0.054749	-14.651576
4	b	-24.615431	-0.078871	-24.637515
5	c	-37.798496	-0.105781	-37.828115
6	n	-54.531419	-0.136620	-54.569673
7	o	-74.994861	-0.194452	-75.049308
8	f	-99.641532	-0.258004	-99.713773
9	na	-162.147146	-0.173617	-162.195759
10	al	-242.227887	-0.222820	-242.290277
11	si	-289.228086	-0.253142	-289.298965
12	p	-341.109860	-0.282481	-341.188955
13	s	-397.943614	-0.324267	-398.034409
14	cl	-459.961264	-0.295377	-460.043969

Table S5.18a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 35%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04103319	-0.04762014	-8.057700	146.614968	146.6149676	7.3	7.3
2	BERYLLIUM HYDRIDE	-15.21500223	-0.05596252	-15.234589	322.225157	322.2251571	-19.6	-19.6
3	DOUBLET CH	-38.4045918	-0.14738031	-38.456175	597.977164	598.3447341	1.8	2.1
4	CH2 3-B1	-39.06624681	-0.166398	-39.124486	394.014861	394.3824311	2.0	2.3
5	Singlet methylene,	-39.0419526	-0.1874792	-39.107570	436.815211	437.1827807	6.7	7.1
6	Methyl radical,	-39.73546578	-0.21203495	-39.809678	149.654775	150.0223446	3.2	3.6
7	ch4 //b3lyp/6-31G*	-40.39753271	-0.25455054	-40.486625	-67.755825	-67.38825519	7.1	7.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13166013	-0.19079036	-55.198437	354.653798	354.6537978	-1.8	-1.8
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77022209	-0.24541854	-55.856119	180.701954	180.7019535	-8.0	-8.0
10	AMMONIA, //b3lyp/6-31G*	-56.43314674	-0.3004844	-56.538316	-48.939051	-48.93905095	-2.9	-2.9
11	OH RADICAL	-75.62336772	-0.26271411	-75.715318	34.089250	35.03443	-5.2	-4.3
12	Water //b3lyp/6-31G*	-76.29794863	-0.33293516	-76.414476	-245.348501	-244.4033211	-3.5	-2.6
13	HYDROGEN FLUORIDE,	-100.3148818	-0.34324869	-100.435019	-278.241125	-276.63957	-5.9	-4.3
14	SIH2 singlet	-290.4080883	-0.31045108	-290.516746	276.960843	278.7461828	4.2	5.9
15	SIH2 3B1	-290.3831622	-0.28711823	-290.483654	364.856354	366.6416938	4.2	6.0
16	SIH3 c3v	-291.0214213	-0.31566642	-291.131905	208.324194	210.109534	7.9	9.7
17	SIH4 //b3lyp/6-31G*	-291.6614319	-0.34338798	-291.781618	49.896162	51.68150191	15.6	17.4
18	ph2 doublet	-342.2869227	-0.35026206	-342.409514	140.404089	140.4040887	1.9	1.9
19	PH3 c3v	-342.9119807	-0.38216815	-343.045740	18.887763	18.88776286	13.4	13.4
20	SH2 //b3lyp/6-31G*	-399.1569334	-0.4037596	-399.298249	-12.569977	-10.23328233	7.9	10.3
21	HCL //b3lyp/6-31G*	-460.5646686	-0.3415778	-460.684221	-91.555154	-88.03698423	0.9	4.4
22	DILITHIUM //b3lyp/6-31G*	-14.95176042	-0.05928308	-14.972509	229.280192	229.2801922	13.4	13.4
23	Lithium Fluoride,	-107.2741645	-0.37339026	-107.404851	-353.546933	-351.9453782	-18.4	-16.8
24	ACETYLENE //b3lyp/6-31g*	-77.14995252	-0.42704214	-77.299417	208.809775	209.5449151	-18.0	-17.2
25	ETHYLENE //b3lyp/6-31g*	-78.38698378	-0.447655	-78.543663	48.602780	49.33791954	-3.7	-3.0
26	ETHANE //b3lyp/6-31g*	-79.60531303	-0.48113541	-79.773710	-75.633901	-74.89876112	8.5	9.2
27	CYANO RADICAL,	-92.52853496	-0.46536536	-92.691413	407.158870	407.5264402	-31.7	-31.4
28	HYDROGEN CYANIDE	-93.23570918	-0.47274351	-93.401169	95.161519	95.52908911	-36.6	-36.3
29	CARBON MONOXIDE	-113.1258386	-0.48340891	-113.295032	-143.446658	-142.1339078	-33.0	-31.7
30	HCO BENT	-113.6499856	-0.50601156	-113.827090	2.862444	4.175194014	-39.0	-37.7
31	H2CO //b3lyp/6-31g*	-114.2894518	-0.52565045	-114.473429	-137.246859	-135.9341089	-28.5	-27.2

32	METHANOL //b3lyp/6-31g*	-115.4907952	-0.55486728	-115.684999	-210.039117	-208.7263671	-9.2	-7.9
33	Nitrogen N2,	-109.333067	-0.5070653	-109.510540	-38.803741	-38.80374063	-38.8	-38.8
34	H2NNH2 //b3lyp/6-31g*	-111.6316659	-0.57005866	-111.831186	80.726686	80.7266858	-14.7	-14.7
35	NO radical,	-129.6782755	-0.54943378	-129.870577	46.879224	47.82440409	-43.5	-42.5
36	O2 //b3lyp/6-31g*	-150.0863745	-0.61362644	-150.301144	-51.837160	-49.94679981	-51.8	-49.9
37	HYDROGEN PEROXIDE	-151.2973191	-0.64470424	-151.522966	-155.260233	-153.3698725	-19.3	-17.4
38	F2 //b3lyp/6-31g*	-199.2509421	-0.67356808	-199.486691	-17.830659	-14.62754933	-17.8	-14.6
39	CO2 D*H	-188.2778234	-0.81250045	-188.562199	-466.531200	-464.2732703	-73.2	-71.0
40	na2 //b3lyp/6-31G*	-324.2539726	-0.37659029	-324.385779	141.825260	141.8252603	-0.4	-0.4
41	SI2 3-SGG	-578.4808031	-0.56698438	-578.679248	582.107395	585.6780749	-3.2	0.3
42	P2 //b3lyp/6-31g*	-682.2768769	-0.72146168	-682.529388	131.713880	131.7138805	-11.8	-11.8
43	S2 //b3lyp/6-31g*	-795.9270243	-0.76759058	-796.195681	108.157500	112.8308901	-20.3	-15.6
44	CL2 //b3lyp/6-31g*	-919.8941611	-0.66200129	-920.125862	-2.903915	4.132425444	-2.9	4.1
45	Sodium Chloride	-622.1694137	-0.51622057	-622.350091	-178.133161	-174.6149911	4.3	7.8
46	SIO //b3lyp/6-31g*	-364.4205421	-0.62799105	-364.640339	-128.123625	-125.3931051	-25.2	-22.5
47	Carbon monosulfide,	-435.9123353	-0.58699369	-436.117783	260.635084	263.339349	-19.3	-16.6
48	OS //b3lyp/6-31g*	-473.0268194	-0.69819737	-473.271188	-31.806607	-28.52473194	-36.8	-33.5
49	CLO 2-PI	-534.9540263	-0.6172298	-535.170057	85.215925	89.67927474	-16.0	-11.6
50	CLF 1-SG	-559.5975189	-0.66482846	-559.830209	-73.386143	-68.26641778	-18.2	-13.0
51	si2h6 //b3lyp/6-31g*	-582.1521928	-0.66747977	-582.385811	108.636134	112.2068144	28.7	32.3
52	Methyl chloride,	-499.7675649	-0.5692608	-499.966806	-84.452955	-80.5672155	-2.4	1.4
53	H3C-SH METHANETHIOL	-438.3625998	-0.63394307	-438.584480	-15.090904	-12.38663929	7.9	10.6
54	HOCl //b3lyp/6-31g*	-535.5986934	-0.65648573	-535.828463	-91.416037	-86.95268652	-16.9	-12.5
55	SO2 //b3lyp/6-31G*	-548.1634996	-1.05329667	-548.532153	-343.759229	-339.5321739	-46.7	-42.5
56	BF3 PLANAR	-324.1483247	-1.08759707	-324.528984	-1181.651859	-1176.715919	-46.1	-41.2
57	bcl3 B3LYP	-1404.814747	-1.12726813	-1405.209291	-434.750648	-424.0648627	-31.8	-21.1
58	ALf3 B3LYP	-541.6569037	-1.2282677	-542.086797	-1229.741868	-1224.044533	-20.6	-14.9
59	alcl3 B3LYP	-1622.381853	-1.22957578	-1622.812205	-595.902608	-584.455428	-11.4	0.0
60	cf4 B3LYP	-436.9248625	-1.48615484	-437.445017	-998.065757	-991.2919668	-65.0	-58.3
61	ccl4 B3LYP	-1877.851668	-1.56389227	-1878.399031	-126.915015	-112.4747649	-31.1	-16.7
62	O=C=S. Singlet	-511.1219606	-0.90371948	-511.438262	-202.996090	-199.346645	-64.5	-60.9
63	CS2 B3LYP	-833.9626153	-1.00216615	-834.313373	63.620507	68.66146653	-53.1	-48.1
64	COF2 B3LYP	-312.5791315	-1.15019361	-312.981699	-675.385916	-670.8700561	-51.6	-47.0
65	sif4 B3LYP	-688.4759574	-1.58741719	-689.031553	-1619.194100	-1611.00254	-4.2	4.0
66	sicl4, td	-2129.385183	-1.62501743	-2129.953939	-659.226667	-643.3686471	3.5	19.4
67	nno B3LYP	-184.3366994	-0.87324373	-184.642335	-9.272977	-8.327797453	-91.3	-90.3
68	clno B3LYP	-589.6260645	-0.94222679	-589.955844	-11.402462	-6.939112428	-63.3	-58.8

69	nf3 c3v	-353.6018886	-1.26892015	-354.046011	-201.435126	-196.6304607	-69.2	-64.4
70	pf3 c3v	-640.4201587	-1.32526804	-640.884002	-977.369235	-972.56457	-18.8	-14.0
71	ozone 1-a1	-225.0332897	-1.05106709	-225.401163	56.656495	59.49203518	-86.0	-83.2
72	f2o B3LYP	-274.2803495	-0.99482457	-274.628538	-19.977239	-15.8289489	-44.7	-40.5
73	CLF3, C2V	-758.8766415	-1.40886284	-759.369743	-226.927913	-218.6050775	-67.9	-59.6
74	CF2=CF2 D2H	-474.8633575	-1.6928248	-475.455846	-761.726830	-754.5854699	-103.2	-96.0
75	cl2c=ccl2 B3LYP	-1915.861087	-1.7666854	-1916.479427	-70.884006	-56.07618577	-58.3	-43.5
76	cf3cn B3LYP	-429.8273084	-1.63412439	-430.399252	-594.240618	-588.7008135	-98.9	-93.3
77	PROPYNE C3V	-116.371026	-0.65488006	-116.600234	163.264366	164.3670761	-21.7	-20.6
78	ALLENE D2D	-116.371397	-0.64846633	-116.598360	166.527378	167.6300882	-23.8	-22.7
79	CYCLOPROPENE C2V	-116.3309594	-0.65772885	-116.561164	265.122039	266.2247493	-11.9	-10.8
80	PROPENE CS	-117.6017611	-0.67807582	-117.839088	16.576451	17.67916076	-3.5	-2.4
81	CYCLOPROPANE D3H	-117.587176	-0.68398476	-117.826571	51.920961	53.02367064	-1.2	-0.1
82	PROPANE C2V	-118.8150094	-0.7111611	-119.063916	-93.639363	-92.53665282	11.0	12.1
83	TRANS-1,3-BUTADIENE C2H	-155.6035554	-0.87743518	-155.910658	93.635403	95.10568314	-16.4	-14.9
84	Dimethyl acetylene	-155.5900135	-0.88335969	-155.899189	123.897813	125.3680928	-21.7	-20.2
85	Methylene cyclopropane.	-155.5700951	-0.88385497	-155.879444	174.333778	175.804058	-26.1	-24.6
86	Bicyclo[1.1.0]butane. C2v	-155.5531332	-0.89545098	-155.866541	210.143777	211.6140572	-7.0	-5.5
87	CYCLOBUTENE b3lyp	-155.5791171	-0.8862488	-155.889304	150.809717	152.2799968	-5.7	-4.2
88	CYCLOBUTANE b3lyp/6-31G*	-156.797526	-0.91529192	-157.117878	32.132169	33.60244875	3.7	5.2
89	Isobutene. Single	-156.8161803	-0.911296	-157.135134	-17.961473	-16.49119333	-1.2	0.2
90	Trans butane	-158.0245641	-0.94172433	-158.354168	-111.774810	-110.3045304	13.7	15.2
91	isobutane B3LYP/6-31G*	-158.0254626	-0.94500904	-158.356216	-118.446701	-116.9764208	15.9	17.3
92	Spiropentane. D2d	-194.7728248	-1.12043113	-195.164976	170.527035	172.3648848	-14.8	-13.0
93	Benzene B3LYP	-231.6873179	-1.28820139	-232.138188	34.141154	36.34657369	-48.3	-46.1
94	DIFLUOROMETHANE C2V	-238.6442002	-0.86975747	-238.948615	-483.315905	-479.7452247	-32.7	-29.1
95	HCF3 TRI-FLUOROMETHANE	-337.7864167	-1.17928276	-338.199166	-746.065654	-740.8934189	-49.0	-43.8
96	CH2CL2 C2V	-959.135029	-0.89323362	-959.447661	-105.599668	-98.19575768	-10.2	-2.8
97	chcl3 B3LYP/6-31G*	-1418.497189	-1.2250583	-1418.925959	-122.156090	-111.2340096	-18.8	-7.9
98	METHYLAMINE b3lyp	-95.62959904	-0.52534981	-95.813471	-26.238372	-25.87080208	-3.2	-2.9
99	Acetonitrile. CH3-CN.	-132.4627931	-0.69826659	-132.707186	36.464361	37.19950102	-38.8	-38.1
100	NITRO METHANE	-244.5587211	-1.15521663	-244.963047	-150.189748	-147.9318176	-75.7	-73.5
101	Methyl-nitrite. CH3-O-N=O.	-244.5549718	-1.14563059	-244.955942	-135.265371	-133.0074411	-68.7	-66.5
102	Methylsilane. CH3-SiH3.	-330.8862949	-0.57527597	-331.087642	-6.427173	-4.274262678	22.9	25.0
103	Formic Acid.	-189.4359266	-0.83431844	-189.727938	-425.482293	-423.2243631	-46.8	-44.6
104	Methyl formate.	-228.6331626	-1.06176017	-229.004779	-409.007809	-406.3823089	-53.4	-50.7
105	acetamide ch3cohn2	-208.7921742	-1.03049133	-209.152846	-278.651061	-276.9707406	-40.2	-38.5

106	Aziridine. (cyclic	-133.6065939	-0.73017097	-133.862154	110.854791	111.5899307	-15.5	-14.8
107	Cyanogen. NCCN.	-185.2875474	-0.93556046	-185.614994	216.788258	217.5233984	-89.9	-89.2
108	DIMETHYLAMINE b3lyp	-134.8305457	-0.75431486	-135.094556	-21.596392	-20.86125157	-3.2	-2.5
109	TRANS ETHYLAMINE	-134.8420379	-0.75548286	-135.106457	-51.905269	-51.17012859	-4.6	-3.9
110	KETENE B3LYP	-152.3041456	-0.73067897	-152.559883	-100.380757	-98.70043656	-53.1	-51.4
111	OXIRANE B3LYP	-153.4683764	-0.76155302	-153.734920	-76.521762	-74.84144189	-23.8	-22.1
112	Acetaldehyde B3LYP	-153.5145334	-0.75404472	-153.778449	-193.926600	-192.2462798	-27.8	-26.1
113	Glyoxal, O=CH-CH=O.	-227.4101932	-1.02918221	-227.770407	-276.925366	-274.2998663	-64.8	-62.2
114	ETHANOL TRANS	-154.7056663	-0.78421799	-154.980143	-241.312588	-239.6322677	-6.2	-4.5
115	DIMETHYL ETHER,	-154.6890596	-0.78130386	-154.962516	-195.876694	-194.1963742	-11.8	-10.1
116	Thiooxirane. (cyclic	-476.3585272	-0.84659952	-476.654837	72.435860	75.50769514	-9.6	-6.5
117	Dimethylsulfoxide. (CH3)2SO.	-552.6463915	-1.19655327	-553.065185	-158.609485	-154.5924704	-7.1	-3.1
118	Thioethanol. CH3-CH2-SH.	-477.5728415	-0.86540806	-477.875734	-35.464738	-32.39290265	11.0	14.0
119	ch3sch3 B3LYP	-477.5710054	-0.86742703	-477.874605	-29.973713	-26.90187813	7.3	10.3
120	Vinyl fluoride,	-177.511647	-0.75934354	-177.777417	-168.694097	-166.3574021	-29.8	-27.4
121	Ethyl chloride.	-538.9809438	-0.8000564	-539.260964	-112.613768	-108.3604585	-0.5	3.8
122	Vinyl chloride,	-537.7623872	-0.77143705	-538.032390	6.697340	10.95065025	-16.3	-12.1
123	h2c=chcn B3LYP	-170.4558015	-0.89846534	-170.770264	135.693281	136.7959909	-45.1	-44.0
124	ACETONE B3LYP	-192.7358312	-0.98400089	-193.080231	-242.781813	-240.7339226	-25.6	-23.6
125	CH3COOH ACETIC	-228.6586621	-1.06100315	-229.030013	-475.715182	-473.0896818	-43.1	-40.5
126	CH3CFO HCCO	-252.6684916	-1.06922672	-253.042721	-489.656826	-486.374951	-47.4	-44.1
127	ch3c(o)cl hcco	-612.9061702	-1.08596848	-613.286259	-284.650372	-279.4518821	-42.0	-36.8
128	ch3ch2ch2cl B3LYP	-578.1906181	-1.03088531	-578.551428	-131.212927	-126.5920466	0.6	5.2
129	Isopropyl alcohol,	-193.9200763	-1.01707716	-194.276053	-275.996323	-273.9484328	-3.2	-1.2
130	Methyl ethyl	-193.9038321	-1.01127471	-194.257778	-227.466351	-225.4184611	-11.2	-9.1
131	Trimethyl Amine.	-174.0337011	-0.98825992	-174.379592	-28.634666	-27.53195587	-4.8	-3.7
132	FURAN B3LYP	-229.5322521	-1.1711494	-229.942154	-87.861111	-85.44565066	-53.1	-50.7
133	Thiophene b3lyp	-552.4120539	-1.26360285	-552.854315	79.114104	82.92107858	-35.9	-32.1
134	PYROLE PLANAR	-209.6849618	-1.14269873	-210.084906	58.100535	59.57081451	-50.3	-48.8
135	C2v Pyridine	-247.7142132	-1.3333172	-248.180874	72.696772	74.53462168	-67.9	-66.0
136	H2 B3LYP/6-31G*	-1.15675034	-0.03543554	-1.169153	7.601790	7.601789715	7.6	7.6
137	SH b3lyp/6-31G*	-398.5215709	-0.36409005	-398.649002	146.117392	148.4540874	3.0	5.4
138	CCH B3LYP	-76.43959971	-0.38913379	-76.575797	555.002058	555.7371983	-10.3	-9.5
139	C2H3 CS,2-A'	-77.71471316	-0.41045539	-77.858373	288.590308	289.3254485	-11.0	-10.2
140	ch3co hcco	-152.8758166	-0.7318383	-153.131960	-49.747390	-48.06706993	-39.7	-38.0
141	H2COH C1	-114.8414552	-0.52204862	-115.024172	-32.829925	-31.51717521	-15.7	-14.4
142	ch3o CS,	-114.8345134	-0.49498717	-115.007759	6.690066	8.002815665	-10.5	-9.2

143	ch3ch2o 2A"	-154.0491885	-0.72455845	-154.302784	-24.854276	-23.17395645	-9.4	-7.7
144	ch3s 2-A'	-437.7326625	-0.59731762	-437.941724	122.711545	125.41581	-2.0	0.7
145	c2h5 staggered	-78.94878954	-0.44166477	-79.103372	124.138137	124.8732767	3.2	4.0
146	(ch3)2ch Cs	-118.1631069	-0.67324738	-118.398743	92.682548	93.78525835	2.7	3.8
147	TERT-BUTYL RADICAL	-157.3774729	-0.90691807	-157.694894	58.917549	60.38782915	7.5	8.9
148	NO2 RADICAL	-204.7298822	-0.92418674	-205.053348	-60.098830	-58.20847014	-93.2	-91.3

MAD	**25.1**	**23.5**
LD	**-103.2**	**-96.0**

Table S5.18b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 54% and a_C = 35%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498637	0.000000	-0.498637
2	li	-7.464230	-0.014715	-7.469380
3	be	-14.629602	-0.054714	-14.648753
4	b	-24.606578	-0.078898	-24.634192
5	c	-37.787308	-0.105825	-37.824346
6	n	-54.517924	-0.136648	-54.565751
7	o	-74.976772	-0.194527	-75.044856
8	f	-99.618997	-0.258075	-99.709323
9	na	-162.118506	-0.173602	-162.179267
10	al	-242.193193	-0.222829	-242.271183
11	si	-289.190878	-0.253152	-289.279481
12	p	-341.070165	-0.282442	-341.169020
13	s	-397.899470	-0.324286	-398.012970
14	cl	-459.912822	-0.295401	-460.016212

Table S5.19a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 23%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05173855	-0.04739154	-8.062639	146.112790	146.1127895	6.8	6.8
2	BERYLLIUM HYDRIDE	-15.22810527	-0.05582238	-15.240944	318.310154	318.3101536	-23.5	-23.5
3	DOUBLET CH	-38.4282946	-0.14669741	-38.462035	599.432023	599.799593	3.2	3.6
4	CH2 3-B1	-39.09212794	-0.16577999	-39.130257	395.763771	396.131341	3.7	4.1
5	Singlet methylene,	-39.06987177	-0.18669537	-39.112812	439.955222	440.3227924	9.8	10.2
6	Methyl radical,	-39.76655529	-0.21117646	-39.815126	152.313405	152.6809755	5.9	6.2
7	ch4 //b3lyp/6-31G*	-40.43297135	-0.25361212	-40.491302	-63.011879	-62.64430856	11.9	12.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.16009585	-0.18996673	-55.203788	358.151463	358.1514627	1.7	1.7
9	NH2,2-B-1, //b3lyp/6-31G*	-55.80357087	-0.24438233	-55.859779	188.700631	188.7006312	0.0	0.0
10	AMMONIA, //b3lyp/6-31G*	-56.47107299	-0.29927337	-56.539906	-35.443175	-35.44317545	10.6	10.6
11	OH RADICAL	-75.65913301	-0.26164364	-75.719311	42.936830	43.88200977	3.6	4.6
12	Water //b3lyp/6-31G*	-76.33832406	-0.33156849	-76.414585	-226.241407	-225.2962272	15.6	16.5
13	HYDROGEN FLUORIDE,	-100.3578041	-0.34193382	-100.436449	-263.178712	-261.5771574	9.2	10.8
14	SIH2 singlet	-290.4798617	-0.30948323	-290.551043	274.304774	276.0901138	1.5	3.3
15	SIH2 3B1	-290.452659	-0.28652548	-290.518560	360.599819	362.3851594	-0.1	1.7
16	SIH3 c3v	-291.0955121	-0.31481743	-291.167920	201.216151	203.0014913	0.8	2.6
17	SIH4 //b3lyp/6-31G*	-291.7396729	-0.34235468	-291.818415	40.797435	42.58277495	6.5	8.3
18	ph2 doublet	-342.3641986	-0.34912433	-342.444497	138.187069	138.1870687	-0.3	-0.3
19	PH3 c3v	-342.9932461	-0.38095679	-343.080866	16.354096	16.35409629	10.9	10.9
20	SH2 //b3lyp/6-31G*	-399.2412489	-0.40246795	-399.333817	-9.612907	-7.2762124	10.9	13.2
21	HCL //b3lyp/6-31G*	-460.6520362	-0.34036429	-460.730320	-87.833860	-84.31569006	4.6	8.2
22	DILITHIUM //b3lyp/6-31G*	-14.96791454	-0.05901512	-14.981488	230.512633	230.5126329	14.6	14.6
23	Lithium Fluoride,	-107.323694	-0.37175635	-107.409198	-333.800646	-332.1990912	1.3	2.9
24	ACETYLENE //b3lyp/6-31g*	-77.20298261	-0.42525992	-77.300792	238.880471	239.6156114	12.1	12.8
25	ETHYLENE //b3lyp/6-31g*	-78.4467041	-0.44591259	-78.549264	67.699980	68.43512049	15.4	16.1
26	ETHANE //b3lyp/6-31g*	-79.67171798	-0.47935416	-79.781969	-63.393949	-62.6588085	20.7	21.4
27	CYANO RADICAL,	-92.5788986	-0.46364357	-92.685537	456.853833	457.2214028	18.0	18.3
28	HYDROGEN CYANIDE	-93.29081646	-0.47066466	-93.399069	135.002959	135.3705286	3.2	3.6
29	CARBON MONOXIDE	-113.1832618	-0.48125865	-113.293951	-104.558790	-103.24604	5.9	7.2
30	HCO BENT	-113.7101458	-0.50388115	-113.826038	41.734198	43.04694789	-0.1	1.2
31	H2CO //b3lyp/6-31g*	-114.353652	-0.52341934	-114.474038	-102.673028	-101.360278	6.1	7.4

32	METHANOL //b3lyp/6-31g*	-115.5619039	-0.55269775	-115.689024	-184.314203	-183.0014526	16.5	17.8
33	Nitrogen N2,	-109.390254	-0.50485869	-109.506371	7.114732	7.114731842	7.1	7.1
34	H2NNH2 //b3lyp/6-31g*	-111.7027609	-0.56775839	-111.833345	110.275862	110.2758615	14.9	14.9
35	NO radical,	-129.7405102	-0.54706469	-129.866335	94.775904	95.72108448	4.4	5.3
36	O2 //b3lyp/6-31g*	-150.1535328	-0.61117736	-150.294104	5.189771	7.080131399	5.2	7.1
37	HYDROGEN PEROXIDE	-151.3724332	-0.64192959	-151.520077	-109.011617	-107.1212566	27.0	28.9
38	F2 //b3lyp/6-31g*	-199.3304224	-0.6707669	-199.484699	24.912753	28.11586267	24.9	28.1
39	CO2 D*H	-188.3713343	-0.80896563	-188.557396	-398.600322	-396.3423918	-5.3	-3.0
40	na2 //b3lyp/6-31G*	-324.3546745	-0.37540095	-324.441017	143.642639	143.6426387	1.4	1.4
41	SI2 3-SGG	-578.6124298	-0.56523759	-578.742434	590.747393	594.3180726	5.4	9.0
42	P2 //b3lyp/6-31g*	-682.4223051	-0.71887013	-682.587645	157.778588	157.7785882	14.3	14.3
43	S2 //b3lyp/6-31g*	-796.0835737	-0.7650924	-796.259545	132.917762	137.5911525	4.5	9.1
44	CL2 //b3lyp/6-31g*	-920.0637237	-0.65955616	-920.215422	11.343991	18.38033105	11.3	18.4
45	Sodium Chloride	-622.3053391	-0.51439772	-622.423651	-173.148593	-169.6304232	9.3	12.8
46	SIO //b3lyp/6-31g*	-364.5220524	-0.62511201	-364.665828	-88.505433	-85.77491295	14.4	17.2
47	Carbon monosulfide,	-436.0137417	-0.58458311	-436.148196	293.783952	296.4882168	13.9	16.6
48	OS //b3lyp/6-31g*	-473.138794	-0.69559583	-473.298781	11.238200	14.52007486	6.2	9.5
49	CLO 2-PI	-535.0723785	-0.61471412	-535.213763	114.431224	118.8945743	13.2	17.6
50	CLF 1-SG	-559.7223382	-0.66222022	-559.874649	-46.613002	-41.49327719	8.6	13.7
51	si2h6 //b3lyp/6-31g*	-582.304175	-0.66543473	-582.457225	96.039445	99.61012542	16.1	19.7
52	Methyl chloride,	-499.885602	-0.56717476	-500.016052	-72.092364	-68.20662405	9.9	13.8
53	H3C-SH METHANETHIOL	-438.4777487	-0.63176986	-438.623056	-3.131737	-0.427471825	19.9	22.6
54	HOCl //b3lyp/6-31g*	-535.7211117	-0.65384609	-535.871496	-60.373041	-55.90969134	14.1	18.6
55	SO2 //b3lyp/6-31G*	-548.3124955	-1.04868435	-548.553693	-265.550552	-261.3234974	31.5	35.7
56	BF3 PLANAR	-324.2901248	-1.08364352	-324.539363	-1137.780341	-1132.844401	-2.2	2.7
57	bcl3 B3LYP	-1405.089828	-1.12318198	-1405.348160	-410.416278	-399.7304929	-7.5	3.2
58	ALf3 B3LYP	-541.8417074	-1.22381605	-542.123185	-1183.637352	-1177.940017	25.5	31.2
59	alcl3 B3LYP	-1622.700141	-1.22541334	-1622.981986	-582.209705	-570.762525	2.3	13.7
60	cf4 B3LYP	-437.1136651	-1.48079052	-437.454247	-930.494256	-923.7204663	2.5	9.3
61	ccl4 B3LYP	-1878.218027	-1.55806278	-1878.576381	-76.993396	-62.55314638	18.8	33.3
62	O=C=S. Singlet	-511.2595564	-0.90010611	-511.466581	-145.077389	-141.4279441	-6.6	-2.9
63	CS2 B3LYP	-834.1444084	-0.99844948	-834.374052	113.524430	118.5653897	-3.2	1.8
64	COF2 B3LYP	-312.7201565	-1.14571281	-312.983670	-606.997088	-602.481228	16.8	21.4
65	sif4 B3LYP	-688.7087179	-1.58194201	-689.072565	-1564.574534	-1556.382974	50.4	58.6
66	sicl4, td	-2129.795737	-1.61946675	-2130.168214	-635.762862	-619.9048419	27.0	42.8
67	nno B3LYP	-184.429335	-0.86919673	-184.629250	79.325950	80.27113042	-2.7	-1.7
68	clno B3LYP	-589.7736727	-0.93789913	-589.989390	61.975942	66.43929231	10.1	14.6

69	nf3 c3v	-353.752609	-1.26365263	-354.043249	-120.428110	-115.6234454	11.8	16.6
70	pf3 c3v	-640.616746	-1.32045751	-640.920451	-927.287344	-922.4826789	31.3	36.1
71	ozone 1-a1	-225.1357362	-1.04566607	-225.376239	179.908402	182.743942	37.2	40.1
72	f2o B3LYP	-274.3946495	-0.99046357	-274.622456	52.775168	56.92345761	28.1	32.2
73	CLF3, C2V	-759.0831876	-1.40282838	-759.405838	-140.731282	-132.4084473	18.3	26.6
74	CF2=CF2 D2H	-475.0762021	-1.68643008	-475.464081	-674.762101	-667.6207415	-16.2	-9.1
75	cl2c=ccl2 B3LYP	-1916.252277	-1.7600148	-1916.657080	-4.977206	9.830613862	7.6	22.4
76	cf3cn B3LYP	-430.0281813	-1.6277607	-430.402566	-495.626285	-490.0864803	-0.2	5.3
77	PROPYNE C3V	-116.4551256	-0.65226276	-116.605146	200.950354	202.0530641	16.0	17.1
78	ALLENE D2D	-116.4554711	-0.64586938	-116.604021	202.247082	203.3497917	11.9	13.0
79	CYCLOPROPENE C2V	-116.4157456	-0.6551134	-116.566422	301.901572	303.0042816	24.9	26.0
80	PROPENE CS	-117.6925737	-0.67546925	-117.847932	44.060463	45.16317333	24.0	25.1
81	CYCLOPROPANE D3H	-117.6789015	-0.68140127	-117.835624	78.855651	79.95836139	25.7	26.8
82	PROPANE C2V	-118.9124971	-0.70852212	-119.075457	-73.116213	-72.01350265	31.5	32.6
83	TRANS-1,3-BUTADIENE C2H	-155.7187477	-0.87397614	-155.919762	137.215210	138.6854902	27.2	28.6
84	Dimethyl acetylene	-155.7051796	-0.87989936	-155.907556	169.413632	170.8839117	23.8	25.3
85	Methylene cyclopropane.	-155.6860918	-0.88041737	-155.888588	217.811253	219.2815325	17.4	18.9
86	Bicyclo[1.1.0]butane. C2v	-155.6700442	-0.89200672	-155.875206	254.878139	256.348419	37.7	39.2
87	CYCLOBUTENE b3lyp	-155.6954744	-0.88278107	-155.898514	194.112804	195.5830843	37.6	39.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.9205709	-0.91182742	-157.130291	67.146924	68.61720424	38.7	40.2
89	Isobutene. Single	-156.9381918	-0.90781423	-157.146989	18.517738	19.98801801	35.3	36.7
90	Trans butane	-158.1531461	-0.93822857	-158.368939	-82.829793	-81.35951347	42.7	44.2
91	isobutane B3LYP/6-31G*	-158.1541624	-0.94149465	-158.370706	-88.764548	-87.29426824	45.5	47.0
92	Spiropentane. D2d	-194.920839	-1.11616078	-195.177556	221.882411	223.720261	36.5	38.4
93	Benzene B3LYP	-231.8535451	-1.28320592	-232.148682	107.632438	109.8378581	25.2	27.4
94	DIFLUOROMETHANE C2V	-238.7559911	-0.8664886	-238.955283	-446.408959	-442.838279	4.2	7.8
95	HCF3 TRI-FLUOROMETHANE	-337.9366767	-1.1749195	-338.206908	-693.283804	-688.1115691	3.8	8.9
96	CH2CL2 C2V	-959.33576	-0.88994252	-959.540447	-82.920324	-75.51641352	12.5	19.9
97	chcl3 B3LYP/6-31G*	-1418.780703	-1.22051682	-1419.061421	-86.890619	-75.9685393	16.5	27.4
98	METHYLAMINE b3lyp	-95.69840449	-0.52331916	-95.818768	-5.573532	-5.205962075	17.4	17.8
99	Acetonitrile. CH3-CN.	-132.5489793	-0.6953755	-132.708916	83.153070	83.88821039	7.8	8.6
100	NITRO METHANE	-244.6915361	-1.1502052	-244.956083	-58.914672	-56.65674225	15.6	17.8
101	Methyl-nitrite. CH3-O-N=O.	-244.6873664	-1.14045982	-244.949672	-45.810336	-43.55240599	20.7	23.0
102	Methylsilane. CH3-SiH3.	-330.9955826	-0.5733673	-331.127457	-6.550139	-4.397229283	22.7	24.9
103	Formic Acid.	-189.5362325	-0.83080082	-189.727317	-368.406721	-366.1487908	10.2	12.5
104	Methyl formate.	-228.7643677	-1.05739799	-229.007569	-343.989000	-341.3635001	11.7	14.3
105	acetamide ch3cohn2	-208.9214283	-1.02630958	-209.157480	-220.194062	-218.5137421	18.3	20.0

106	Aziridine. (cyclic	-133.7004362	-0.7273116	-133.867718	147.596452	148.331592	21.2	22.0
107	Cyanogen. NCCN.	-185.3931521	-0.93136519	-185.607366	305.348252	306.0833919	-1.3	-0.6
108	DIMETHYLAMINE b3lyp	-134.9303867	-0.75143443	-135.103217	7.136735	7.871874919	25.5	26.3
109	TRANS ETHYLAMINE	-134.9419264	-0.7525923	-135.115023	-22.922641	-22.1875011	24.4	25.1
110	KETENE B3LYP	-152.3928862	-0.72757568	-152.560229	-48.335126	-46.65480639	-1.1	0.6
111	OXIRANE B3LYP	-153.5643462	-0.75850488	-153.738802	-33.640803	-31.96048309	19.1	20.8
112	Acetaldehyde B3LYP	-153.6098493	-0.75096257	-153.782571	-151.673775	-149.9934554	14.4	16.1
113	Glyoxal, O=CH-CH=O.	-227.5341879	-1.02480111	-227.769892	-203.349695	-200.7241949	8.8	11.4
114	ETHANOL TRANS	-154.8078673	-0.78119538	-154.987542	-207.544885	-205.8645651	27.6	29.3
115	DIMETHYL ETHER,	-154.791088	-0.77828951	-154.970095	-162.578892	-160.8985715	21.5	23.2
116	Thiooxirane. (cyclic	-476.4988369	-0.84354131	-476.692851	102.648938	105.7207727	20.6	23.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.8283771	-1.19187622	-553.102509	-107.189413	-103.1723981	44.3	48.3
118	Thioethanol. CH3-CH2-SH.	-477.7190638	-0.86236594	-477.917408	-14.737450	-11.6656146	31.7	34.8
119	ch3sch3 B3LYP	-477.7171104	-0.86435625	-477.915912	-8.285077	-5.213241725	29.0	32.0
120	Vinyl fluoride,	-177.6096243	-0.75638824	-177.783594	-132.411854	-130.0751595	6.5	8.8
121	Ethyl chloride.	-539.1300509	-0.79710442	-539.313385	-91.689084	-87.4357738	20.4	24.7
122	Vinyl chloride,	-537.9048782	-0.76848445	-538.081630	35.854859	40.10816938	12.8	17.1
123	h2c=chcn B3LYP	-170.5662678	-0.89470063	-170.772049	199.016751	200.1194608	18.3	19.4
124	ACETONE B3LYP	-192.8623301	-0.9800796	-193.087748	-192.542178	-190.4942882	24.6	26.7
125	CH3COOH ACETIC	-228.7901424	-1.05668157	-229.033179	-411.681960	-409.0564605	20.9	23.6
126	CH3CFO HCCO	-252.8022081	-1.06496688	-253.047150	-429.516693	-426.2348182	12.7	16.0
127	ch3c(o)cl hcco	-613.0841502	-1.08161221	-613.332921	-229.453882	-224.2553915	13.2	18.4
128	ch3ch2ch2cl B3LYP	-578.3708095	-1.02707313	-578.607036	-101.754166	-97.13328605	30.0	34.7
129	Isopropyl alcohol,	-194.0534786	-1.01318729	-194.286512	-233.358021	-231.3101309	39.4	41.5
130	Methyl ethyl	-194.0369575	-1.00740812	-194.268661	-185.943252	-183.8953623	30.4	32.4
131	Trimethyl Amine.	-174.1647406	-0.98448794	-174.391173	9.332963	10.43567347	33.2	34.3
132	FURAN B3LYP	-229.6783738	-1.16646192	-229.946660	-13.056860	-10.64139962	21.7	24.1
133	Thiophene b3lyp	-552.6024501	-1.2588096	-552.891976	143.813736	147.6207109	28.8	32.6
134	PYROLE PLANAR	-209.8290802	-1.13822581	-210.090872	127.347335	128.8176153	19.0	20.5
135	C2v Pyridine	-247.8825835	-1.32804708	-248.188034	155.587678	157.425528	15.0	16.8
136	H2 B3LYP/6-31G*	-1.16135902	-0.03528401	-1.169474	6.878981	6.878980901	6.9	6.9
137	SH b3lyp/6-31G*	-398.601791	-0.36292373	-398.685263	147.192263	149.5289577	4.1	6.4
138	CCH B3LYP	-76.48783538	-0.3874711	-76.576954	585.584192	586.3193318	20.3	21.1
139	C2H3 CS,2-A'	-77.77004647	-0.40889885	-77.864093	307.312527	308.0476669	7.7	8.5
140	ch3co hcco	-152.9670236	-0.72888128	-153.134666	-3.839293	-2.15897265	6.2	7.9
141	H2COH C1	-114.9084924	-0.52003541	-115.028101	-6.910232	-5.597482275	10.2	11.6
142	ch3o CS,	-114.9012758	-0.4931041	-115.014690	24.726574	26.03932355	7.6	8.9

143	ch3ch2o 2A"	-154.147021	-0.72182358	-154.313040	1.351920	3.032240495	16.8	18.5
144	ch3s 2-A'	-437.8438192	-0.59527751	-437.980733	133.471838	136.1761033	8.8	11.5
145	c2h5 staggered	-79.01097996	-0.43999472	-79.112179	134.879840	135.6149804	14.0	14.7
146	(ch3)2ch Cs	-118.2564417	-0.67074739	-118.410714	112.019408	113.1221181	22.1	23.2
147	TERT-BUTYL RADICAL	-157.5019983	-0.90357867	-157.709821	87.392197	88.86247726	35.9	37.4
148	NO2 RADICAL	-204.8275454	-0.9199655	-205.039137	33.239881	35.13024111	0.2	2.1

MAD	**15.7**	**18.0**
LD	**50.4**	**58.6**

Table S5.19b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 23%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498660	0.000000	-0.498660
2	li	-7.470725	-0.014689	-7.474104
3	be	-14.641073	-0.054438	-14.653594
4	b	-24.621803	-0.078463	-24.639849
5	c	-37.806513	-0.105326	-37.830737
6	n	-54.541097	-0.136148	-54.572411
7	o	-75.007625	-0.193788	-75.052196
8	f	-99.657315	-0.257180	-99.716467
9	na	-162.167414	-0.173120	-162.207232
10	al	-242.252605	-0.222148	-242.303699
11	si	-289.254670	-0.252391	-289.312720
12	p	-341.138324	-0.281688	-341.203112
13	s	-397.975257	-0.323304	-398.049617
14	cl	-459.996003	-0.294358	-460.063706

Table S5.20a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04907399	-0.04739546	-8.061397	146.299144	146.2991436	7.0	7.0
2	BERYLLIUM HYDRIDE	-15.22486057	-0.05579932	-15.239368	319.247998	319.2479985	-22.6	-22.6
3	DOUBLET CH	-38.42236156	-0.14670913	-38.460506	599.163576	599.5311464	2.9	3.3
4	CH2 3-B1	-39.08567031	-0.16577506	-39.128772	395.380962	395.7485318	3.3	3.7
5	Singlet methylene,	-39.06288854	-0.18668425	-39.111426	439.309202	439.6767715	9.2	9.6
6	Methyl radical,	-39.75879794	-0.2111872	-39.813707	151.756661	152.1242314	5.3	5.7
7	ch4 //b3lyp/6-31G*	-40.42413259	-0.25359452	-40.490067	-64.052480	-63.68490973	10.8	11.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15295434	-0.18999732	-55.202354	357.462343	357.4623432	1.0	1.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79518216	-0.24440324	-55.858727	187.006598	187.0065985	-1.7	-1.7
10	AMMONIA, //b3lyp/6-31G*	-56.46153482	-0.29927695	-56.539347	-38.430964	-38.43096373	7.6	7.6
11	OH RADICAL	-75.65010162	-0.26167444	-75.718137	40.948190	41.89336995	1.6	2.6
12	Water //b3lyp/6-31G*	-76.32811156	-0.33158838	-76.414325	-230.629226	-229.6840461	11.2	12.2
13	HYDROGEN FLUORIDE,	-100.3469338	-0.34196087	-100.435844	-266.671044	-265.0694888	5.7	7.3
14	SIH2 singlet	-290.4619382	-0.30945958	-290.542398	275.014230	276.7995699	2.2	4.0
15	SIH2 3B1	-290.4353185	-0.28644446	-290.509794	361.625750	363.4110898	1.0	2.8
16	SIH3 c3v	-291.0770459	-0.31477216	-291.158887	202.944919	204.7302589	2.5	4.3
17	SIH4 //b3lyp/6-31G*	-291.7201946	-0.34232757	-291.809200	43.002366	44.78770555	8.7	10.5
18	ph2 doublet	-342.3449031	-0.34912319	-342.435675	138.856239	138.8562388	0.4	0.4
19	PH3 c3v	-342.9729672	-0.38092951	-343.072009	17.115691	17.11569082	11.7	11.7
20	SH2 //b3lyp/6-31G*	-399.2201932	-0.40245101	-399.324830	-10.224832	-7.888136897	10.3	12.6
21	HCL //b3lyp/6-31G*	-460.6302224	-0.34035767	-460.718715	-88.684200	-85.16603043	3.8	7.3
22	DILITHIUM //b3lyp/6-31G*	-14.9639	-0.05900259	-14.979241	230.265080	230.2650798	14.4	14.4
23	Lithium Fluoride,	-107.3111642	-0.37180231	-107.407833	-338.371661	-336.7701056	-3.2	-1.6
24	ACETYLENE //b3lyp/6-31g*	-77.18963651	-0.42520339	-77.300189	231.897606	232.6327461	5.1	5.9
25	ETHYLENE //b3lyp/6-31g*	-78.43174728	-0.44587001	-78.547673	63.309830	64.04497022	11.0	11.7
26	ETHANE //b3lyp/6-31g*	-79.65515244	-0.47931944	-79.779775	-66.199795	-65.46465515	17.9	18.6
27	CYANO RADICAL,	-92.5660903	-0.46336563	-92.686565	445.414305	445.7818748	6.5	6.9
28	HYDROGEN CYANIDE	-93.27687666	-0.47061831	-93.399237	125.823077	126.1906474	-6.0	-5.6
29	CARBON MONOXIDE	-113.1687139	-0.48123975	-113.293836	-113.610904	-112.2981535	-3.2	-1.8
30	HCO BENT	-113.6948967	-0.50384492	-113.825896	32.752975	34.06572491	-9.1	-7.8
31	H2CO //b3lyp/6-31g*	-114.3374302	-0.52340437	-114.473515	-110.653813	-109.3410629	-1.9	-0.6

32	METHANOL //b3lyp/6-31g*	-115.5440185	-0.55268974	-115.687718	-190.238150	-188.9253995	10.6	11.9
33	Nitrogen N2,	-109.3757397	-0.50481182	-109.506991	-3.422311	-3.422311495	-3.4	-3.4
34	H2NNH2 //b3lyp/6-31g*	-111.6848541	-0.56775669	-111.832471	103.660698	103.6606977	8.3	8.3
35	NO radical,	-129.7246673	-0.54703587	-129.866897	83.774667	84.71984697	-6.6	-5.7
36	O2 //b3lyp/6-31g*	-150.1363637	-0.6111735	-150.295269	-8.011921	-6.12156103	-8.0	-6.1
37	HYDROGEN PEROXIDE	-151.3533431	-0.64194544	-151.520249	-119.605351	-117.7149913	16.4	18.3
38	F2 //b3lyp/6-31g*	-199.3101516	-0.67077889	-199.484554	15.129545	18.33265526	15.1	18.3
39	CO2 D*H	-188.3475985	-0.80892507	-188.557919	-414.397826	-412.1398964	-21.1	-18.8
40	na2 //b3lyp/6-31G*	-324.3293903	-0.37538443	-324.426990	143.274259	143.2742593	1.0	1.0
41	SI2 3-SGG	-578.579483	-0.56518105	-578.726430	588.789934	592.360614	3.4	7.0
42	P2 //b3lyp/6-31g*	-682.3858732	-0.71879825	-682.572761	151.871735	151.8717349	8.4	8.4
43	S2 //b3lyp/6-31g*	-796.044364	-0.76506364	-796.243281	127.209911	131.8833008	-1.2	3.4
44	CL2 //b3lyp/6-31g*	-920.0213348	-0.65953312	-920.192813	8.065518	15.10185765	8.1	15.1
45	Sodium Chloride	-622.2713507	-0.51440569	-622.405096	-174.349474	-170.8313041	8.1	11.6
46	SIO //b3lyp/6-31g*	-364.4964743	-0.62513938	-364.659010	-97.665269	-94.93474869	5.3	8.0
47	Carbon monosulfide,	-435.9882913	-0.58452153	-436.140267	286.113332	288.8175967	6.2	8.9
48	OS //b3lyp/6-31g*	-473.1105756	-0.69557202	-473.291424	1.276933	4.558808396	-3.7	-0.5
49	CLO 2-PI	-535.0426248	-0.61458361	-535.202417	107.831199	112.2945488	6.6	11.0
50	CLF 1-SG	-559.6909495	-0.66221897	-559.863126	-52.760591	-47.64086601	2.5	7.6
51	si2h6 //b3lyp/6-31g*	-582.2663212	-0.66538395	-582.439321	99.069224	102.6399044	19.2	22.7
52	Methyl chloride,	-499.8561248	-0.56714792	-500.003583	-74.956340	-71.07060031	7.1	10.9
53	H3C-SH METHANETHIOL	-438.448991	-0.63173489	-438.613242	-5.853844	-3.149578673	17.2	19.9
54	HOCl //b3lyp/6-31g*	-535.6903537	-0.65384018	-535.860352	-67.503352	-63.04000245	7.0	11.4
55	SO2 //b3lyp/6-31G*	-548.2748549	-1.0486537	-548.547505	-283.651139	-279.4240838	13.4	17.6
56	BF3 PLANAR	-324.2543187	-1.08364648	-324.536067	-1148.146625	-1143.210685	-12.6	-7.7
57	bcl3 B3LYP	-1405.021162	-1.12312612	-1405.313175	-416.294027	-405.608242	-13.4	-2.7
58	ALf3 B3LYP	-541.7951202	-1.22384182	-542.113319	-1194.520975	-1188.82364	14.7	20.4
59	alcl3 B3LYP	-1622.620705	-1.22536597	-1622.939300	-585.635304	-574.188124	-1.1	10.3
60	cf4 B3LYP	-437.0659182	-1.48076804	-437.450918	-946.362808	-939.5890177	-13.3	-6.6
61	ccl4 B3LYP	-1878.126466	-1.55798666	-1878.531542	-88.824841	-74.38459088	7.0	21.4
62	O=C=S. Singlet	-511.2249104	-0.90004005	-511.458921	-158.525056	-154.8756115	-20.0	-16.4
63	CS2 B3LYP	-834.0988201	-0.99835646	-834.358393	101.944250	106.9852103	-14.8	-9.7
64	COF2 B3LYP	-312.684433	-1.14568422	-312.982311	-622.944572	-618.4287116	0.9	5.4
65	sif4 B3LYP	-688.6500739	-1.58193143	-689.061376	-1577.513518	-1569.321958	37.5	45.7
66	sicl4, td	-2129.69328	-1.61938933	-2130.114321	-641.527877	-625.6698567	21.2	37.1
67	nno B3LYP	-184.4057094	-0.86912734	-184.631683	58.957876	59.90305566	-23.0	-22.1
68	clno B3LYP	-589.7363876	-0.93784102	-589.980226	45.189316	49.65266631	-6.7	-2.2

69	nf3 c3v	-353.7142716	-1.26363519	-354.042817	-138.992979	-134.1883137	-6.8	-2.0
70	pf3 c3v	-640.5671864	-1.32044855	-640.910503	-938.905632	-934.1009675	19.6	24.5
71	ozone 1-a1	-225.1094023	-1.04559583	-225.381257	151.520481	154.3560212	8.8	11.7
72	f2o B3LYP	-274.3654688	-0.99045851	-274.622988	36.144544	40.29283409	11.5	15.6
73	CLF3, C2V	-759.0308988	-1.40282333	-759.395633	-160.499804	-152.1769694	-1.5	6.8
74	CF2=CF2 D2H	-475.0223409	-1.68640165	-475.460805	-695.053534	-687.912174	-36.5	-29.4
75	cl2c=ccl2 B3LYP	-1916.154461	-1.75992164	-1916.612041	-20.565181	-5.757360861	-8.0	6.8
76	cf3cn B3LYP	-429.9773626	-1.62768953	-430.400562	-518.629732	-513.0899272	-23.2	-17.7
77	PROPYNE C3V	-116.4340247	-0.65219057	-116.603594	192.175349	193.2780587	7.2	8.3
78	ALLENE D2D	-116.4343597	-0.64580315	-116.602268	193.999465	195.1021752	3.6	4.7
79	CYCLOPROPENE C2V	-116.3944775	-0.65506032	-116.564793	293.328158	294.4308678	16.3	17.5
80	PROPENE CS	-117.6698572	-0.67541025	-117.845464	37.690379	38.79308887	17.6	18.7
81	CYCLOPROPANE D3H	-117.6559786	-0.68135607	-117.833131	72.551024	73.65373433	19.4	20.5
82	PROPANE C2V	-118.8881774	-0.70846936	-119.072379	-77.884397	-76.78168685	26.7	27.8
83	TRANS-1,3-BUTADIENE C2H	-155.6898814	-0.87389274	-155.917093	127.089849	128.5601292	17.1	18.5
84	Dimethyl acetylene	-155.6763251	-0.87981128	-155.905076	158.794021	160.2643009	13.2	14.7
85	Methylene cyclopropane.	-155.6570385	-0.88034761	-155.885929	207.660127	209.1304067	7.2	8.7
86	Bicyclo[1.1.0]butane. C2v	-155.640786	-0.89194736	-155.872692	244.345070	245.8153499	27.2	28.7
87	CYCLOBUTENE b3lyp	-155.6663474	-0.88271072	-155.895852	183.969535	185.439815	27.5	29.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.8898412	-0.91176304	-157.126900	58.919396	60.38967646	30.5	31.9
89	Isobutene. Single	-156.9076924	-0.90773819	-157.143704	10.009695	11.47997473	26.7	28.2
90	Trans butane	-158.1210695	-0.93815692	-158.364990	-89.595375	-88.12509537	35.9	37.4
91	isobutane B3LYP/6-31G*	-158.1220583	-0.94142323	-158.366828	-95.715339	-94.24505868	38.6	40.1
92	Spiropentane. D2d	-194.883823	-1.11608644	-195.174005	209.789077	211.6269271	24.4	26.3
93	Benzene B3LYP	-231.8118695	-1.28309155	-232.145473	90.359826	92.56524551	7.9	10.1
94	DIFLUOROMETHANE C2V	-238.7277653	-0.86648959	-238.953053	-454.997636	-451.4269558	-4.4	-0.8
95	HCF3 TRI-FLUOROMETHANE	-337.8986956	-1.17491308	-338.204173	-705.629943	-700.4577077	-8.6	-3.4
96	CH2CL2 C2V	-959.285612	-0.88990233	-959.516987	-88.245054	-80.84114439	7.2	14.6
97	chcl3 B3LYP/6-31G*	-1418.709857	-1.22045987	-1419.027177	-95.218453	-84.29637325	8.1	19.0
98	METHYLAMINE b3lyp	-95.6811597	-0.52330035	-95.817218	-10.242293	-9.874723318	12.8	13.1
99	Acetonitrile. CH3-CN.	-132.5272852	-0.69531195	-132.708066	72.361658	73.09679837	-3.0	-2.2
100	NITRO METHANE	-244.657862	-1.1501441	-244.956899	-79.938532	-77.68060154	-5.5	-3.2
101	Methyl-nitrite. CH3-O-N=O.	-244.6538025	-1.14039502	-244.950305	-66.353300	-64.09536977	0.2	2.4
102	Methylsilane. CH3-SiH3.	-330.9683532	-0.57332512	-331.117418	-6.463349	-4.310438655	22.8	25.0
103	Formic Acid.	-189.5108579	-0.83078347	-189.726862	-381.637275	-379.3793448	-3.0	-0.7
104	Methyl formate.	-228.73128	-1.05735155	-229.006191	-359.079873	-356.4543734	-3.4	-0.8
105	acetamide ch3cohn2	-208.8889011	-1.02626715	-209.155731	-233.694830	-232.0145105	4.8	6.5

106	Aziridine. (cyclic	-133.6768949	-0.72727419	-133.865986	139.121573	139.8567127	12.8	13.5
107	Cyanogen. NCCN.	-185.3663792	-0.93126446	-185.608508	284.873050	285.6081899	-21.8	-21.1
108	DIMETHYLAMINE b3lyp	-134.9053974	-0.75139402	-135.100760	0.565304	1.300444019	19.0	19.7
109	TRANS ETHYLAMINE	-134.9169263	-0.75255434	-135.112590	-29.558589	-28.82344867	17.7	18.5
110	KETENE B3LYP	-152.370468	-0.72752906	-152.559626	-60.388974	-58.70865437	-13.1	-11.4
111	OXIRANE B3LYP	-153.5401992	-0.75847498	-153.737403	-43.603317	-41.92299745	9.1	10.8
112	Acetaldehyde B3LYP	-153.5858623	-0.75092816	-153.781104	-161.459352	-159.7790323	4.6	6.3
113	Glyoxal, O=CH-CH=O.	-227.5028314	-1.02476042	-227.769269	-220.422187	-217.7966869	-8.3	-5.7
114	ETHANOL TRANS	-154.7822253	-0.7811681	-154.985329	-215.371256	-213.6909364	19.8	21.4
115	DIMETHYL ETHER,	-154.7654852	-0.7782562	-154.967832	-170.275238	-168.5949178	13.8	15.5
116	Thiooxirane. (cyclic	-476.4637483	-0.84348963	-476.683056	95.596790	98.66862479	13.6	16.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.782754	-1.19182162	-553.092628	-119.088926	-115.0719113	32.4	36.4
118	Thioethanol. CH3-CH2-SH.	-477.6825531	-0.86231238	-477.906754	-19.537365	-16.46553007	26.9	30.0
119	ch3sch3 B3LYP	-477.6806217	-0.86430268	-477.905340	-13.299303	-10.2274681	23.9	27.0
120	Vinyl fluoride,	-177.5849449	-0.75635763	-177.781598	-140.819473	-138.4827782	-1.9	0.4
121	Ethyl chloride.	-539.0928212	-0.79705873	-539.300056	-96.579461	-92.32615088	15.6	19.8
122	Vinyl chloride,	-537.8692322	-0.76843261	-538.069025	29.065007	33.31831684	6.1	10.3
123	h2c=chcn B3LYP	-170.5384449	-0.89461343	-170.771044	184.349651	185.452361	3.6	4.7
124	ACETONE B3LYP	-192.8305657	-0.98002415	-193.085372	-204.223043	-202.175153	12.9	15.0
125	CH3COOH ACETIC	-228.7569955	-1.05664344	-229.031723	-426.566648	-423.941148	6.1	8.7
126	CH3CFO HCCO	-252.7684694	-1.06492746	-253.045351	-443.509759	-440.2278841	-1.3	2.0
127	ch3c(o)cl hcco	-613.0394871	-1.08155485	-613.320691	-242.300430	-237.1019396	0.4	5.6
128	ch3ch2ch2cl B3LYP	-578.3258256	-1.02700885	-578.592848	-108.669813	-104.0489326	23.1	27.7
129	Isopropyl alcohol,	-194.0200544	-1.01313926	-194.283471	-243.293821	-241.2459305	29.5	31.6
130	Methyl ethyl	-194.0035972	-1.0073546	-194.265509	-195.587799	-193.5399087	20.7	22.8
131	Trimethyl Amine.	-174.1319679	-0.98442766	-174.387919	0.571142	1.673852244	24.4	25.5
132	FURAN B3LYP	-229.6416084	-1.16638311	-229.944868	-30.555182	-28.13972228	4.2	6.6
133	Thiophene b3lyp	-552.5547528	-1.2587105	-552.882018	128.623530	132.4305046	13.6	17.4
134	PYROLE PLANAR	-209.7928885	-1.13814216	-210.088805	111.185736	112.6560159	2.8	4.3
135	C2v Pyridine	-247.8402878	-1.32793857	-248.185552	136.234755	138.0726046	-4.3	-2.5
136	H2 B3LYP/6-31G*	-1.16021124	-0.03528493	-1.169385	7.112704	7.112704224	7.1	7.1
137	SH b3lyp/6-31G*	-398.581755	-0.36292902	-398.676117	147.002484	149.3391789	3.9	6.2
138	CCH B3LYP	-76.47567111	-0.38740838	-76.576397	578.479094	579.2142336	13.2	14.0
139	C2H3 CS,2-A'	-77.75616683	-0.40883354	-77.862464	303.025144	303.7602839	3.5	4.2
140	ch3co hcco	-152.9440277	-0.72881939	-153.133521	-14.468932	-12.78861238	-4.4	-2.7
141	H2COH C1	-114.8916037	-0.52000867	-115.026806	-12.865475	-11.55272513	4.3	5.6
142	ch3o CS,	-114.8844856	-0.49305495	-115.012680	20.649393	21.96214259	3.5	4.8

143	ch3ch2o 2A"	-154.122477	-0.72174721	-154.310131	-4.647110	-2.96678966	10.8	12.5
144	ch3s 2-A'	-437.8160491	-0.59525274	-437.970815	131.024040	133.7283048	6.3	9.0
145	c2h5 staggered	-78.99545437	-0.43997169	-79.109847	132.435771	133.1709114	11.5	12.3
146	(ch3)2ch Cs	-118.2331399	-0.67069436	-118.407520	107.553976	108.6566858	17.6	18.7
147	TERT-BUTYL RADICAL	-157.4709124	-0.90349475	-157.705821	80.762950	82.23323022	29.3	30.8
148	NO2 RADICAL	-204.8025838	-0.91990017	-205.041758	11.762328	13.65268808	-21.3	-19.4

MAD	**11.4**	**12.6**
LD	**38.6**	**45.7**

Table S5.20b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498660	0.000000	-0.498660
2	li	-7.469114	-0.014687	-7.472933
3	be	-14.638225	-0.054423	-14.652375
4	b	-24.618008	-0.078474	-24.638411
5	c	-37.801717	-0.105344	-37.829106
6	n	-54.535313	-0.136159	-54.570714
7	o	-74.999872	-0.193820	-75.050265
8	f	-99.647657	-0.257210	-99.714531
9	na	-162.155139	-0.173113	-162.200148
10	al	-242.237735	-0.222151	-242.295494
11	si	-289.238722	-0.252395	-289.304345
12	p	-341.121310	-0.281671	-341.194545
13	s	-397.956337	-0.323312	-398.040398
14	cl	-459.975242	-0.294367	-460.051777

Table S5.21a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04818586	-0.04739677	-8.060983	146.361018	146.3610177	7.0	7.0
2	BERYLLIUM HYDRIDE	-15.22377915	-0.05579167	-15.238843	319.560657	319.5606572	-22.3	-22.3
3	DOUBLET CH	-38.42038396	-0.14671307	-38.459996	599.074300	599.4418702	2.9	3.2
4	CH2 3-B1	-39.08351801	-0.16577347	-39.128277	395.253705	395.6212746	3.2	3.6
5	Singlet methylene,	-39.06056088	-0.18668055	-39.110965	439.094877	439.462447	9.0	9.3
6	Methyl radical,	-39.75621226	-0.21119083	-39.813234	151.571247	151.9388173	5.1	5.5
7	ch4 //b3lyp/6-31G*	-40.42118644	-0.25358865	-40.489655	-64.398150	-64.03057965	10.5	10.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15057392	-0.19000758	-55.201876	357.231878	357.2318776	0.8	0.8
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79238602	-0.24441025	-55.858377	186.441482	186.4414822	-2.3	-2.3
10	AMMONIA, //b3lyp/6-31G*	-56.45835553	-0.29927815	-56.539161	-39.426710	-39.42671033	6.6	6.6
11	OH RADICAL	-75.64709123	-0.26168474	-75.717746	40.285302	41.23048187	1.0	1.9
12	Water //b3lyp/6-31G*	-76.32470748	-0.33159502	-76.414238	-232.091477	-231.146297	9.7	10.7
13	HYDROGEN FLUORIDE,	-100.3433105	-0.34196989	-100.435642	-267.835052	-266.2334969	4.5	6.1
14	SIH2 singlet	-290.4559638	-0.30945169	-290.539516	275.251757	277.0370968	2.5	4.2
15	SIH2 3B1	-290.4295388	-0.28641753	-290.506872	361.969982	363.7553223	1.3	3.1
16	SIH3 c3v	-291.0708907	-0.31475709	-291.155875	203.522665	205.3080054	3.1	4.9
17	SIH4 //b3lyp/6-31G*	-291.7137019	-0.34231853	-291.806128	43.738503	45.52384272	9.4	11.2
18	ph2 doublet	-342.3384715	-0.34912286	-342.432735	139.078697	139.0786969	0.6	0.6
19	PH3 c3v	-342.9662077	-0.38092041	-343.069056	17.369930	17.3699298	11.9	11.9
20	SH2 //b3lyp/6-31G*	-399.2131747	-0.40244536	-399.321835	-10.427882	-8.091187029	10.1	12.4
21	HCL //b3lyp/6-31G*	-460.6229513	-0.34035546	-460.714847	-88.967029	-85.44885874	3.5	7.0
22	DILITHIUM //b3lyp/6-31G*	-14.96256198	-0.05899841	-14.978492	230.182672	230.1826719	14.3	14.3
23	Lithium Fluoride,	-107.3069876	-0.37181766	-107.407378	-339.895910	-338.2943548	-4.8	-3.2
24	ACETYLENE //b3lyp/6-31g*	-77.18518794	-0.42518455	-77.299988	229.573319	230.3084594	2.8	3.5
25	ETHYLENE //b3lyp/6-31g*	-78.42676182	-0.44585581	-78.547143	61.849257	62.58439696	9.5	10.3
26	ETHANE //b3lyp/6-31g*	-79.64963077	-0.47930786	-79.779044	-67.132621	-66.39748112	17.0	17.7
27	CYANO RADICAL,	-92.56182114	-0.46327316	-92.686905	441.611441	441.979011	2.7	3.1
28	HYDROGEN CYANIDE	-93.27223017	-0.47060286	-93.399293	122.765876	123.1334462	-9.0	-8.7
29	CARBON MONOXIDE	-113.1638647	-0.48123345	-113.293798	-116.625739	-115.3129895	-6.2	-4.9
30	HCO BENT	-113.6898139	-0.5038328	-113.825849	29.762267	31.07501655	-12.1	-10.8
31	H2CO //b3lyp/6-31g*	-114.3320231	-0.52339938	-114.473341	-113.311738	-111.9989881	-4.5	-3.2

32	METHANOL //b3lyp/6-31g*	-115.5380569	-0.55268707	-115.687282	-192.210793	-190.8980432	8.6	9.9
33	Nitrogen N2,	-109.3709017	-0.5047962	-109.507197	-6.932115	-6.932115076	-6.9	-6.9
34	H2NNH2 //b3lyp/6-31g*	-111.6788853	-0.56775613	-111.832179	101.456437	101.4564374	6.1	6.1
35	NO radical,	-129.7193865	-0.54702626	-129.867084	80.110216	81.05539566	-10.3	-9.3
36	O2 //b3lyp/6-31g*	-150.1306408	-0.61117223	-150.295657	-12.410034	-10.51967444	-12.4	-10.5
37	HYDROGEN PEROXIDE	-151.3469799	-0.64195074	-151.520307	-123.134932	-121.2445717	12.8	14.7
38	F2 //b3lyp/6-31g*	-199.3033948	-0.67078289	-199.484506	11.870315	15.07342494	11.9	15.1
39	CO2 D*H	-188.3396867	-0.80891155	-188.558093	-419.659143	-417.4012128	-26.4	-24.1
40	na2 //b3lyp/6-31G*	-324.3209626	-0.3753789	-324.422315	143.151413	143.1514132	0.9	0.9
41	SI2 3-SGG	-578.568501	-0.56516229	-578.721095	588.139713	591.7103935	2.8	6.4
42	P2 //b3lyp/6-31g*	-682.3737294	-0.71877429	-682.567798	149.904295	149.9042952	6.4	6.4
43	S2 //b3lyp/6-31g*	-796.0312943	-0.76505408	-796.237859	125.309098	129.9824876	-3.1	1.5
44	CL2 //b3lyp/6-31g*	-920.0072053	-0.65952544	-920.185277	6.974426	14.01076601	7.0	14.0
45	Sodium Chloride	-622.2600214	-0.51440836	-622.398912	-174.749733	-171.2315631	7.7	11.2
46	SIO //b3lyp/6-31g*	-364.4879484	-0.62514852	-364.656738	-100.718127	-97.9876071	2.2	4.9
47	Carbon monosulfide,	-435.9798079	-0.584501	-436.137623	283.559734	286.2639994	3.7	6.4
48	OS //b3lyp/6-31g*	-473.1011697	-0.69556408	-473.288972	-2.041160	1.240715149	-7.1	-3.8
49	CLO 2-PI	-535.0327071	-0.61454013	-535.198633	105.637238	110.1005881	4.4	8.8
50	CLF 1-SG	-559.6804868	-0.66221856	-559.859286	-54.808207	-49.68848217	0.4	5.5
51	si2h6 //b3lyp/6-31g*	-582.2537035	-0.66536702	-582.433353	100.081462	103.6521423	20.2	23.7
52	Methyl chloride,	-499.8462992	-0.56713898	-499.999427	-75.908996	-72.02325616	6.1	10.0
53	H3C-SH METHANETHIOL	-438.4394053	-0.63172324	-438.609971	-6.758998	-4.054732663	16.3	19.0
54	HOCl //b3lyp/6-31g*	-535.6801012	-0.65383822	-535.856638	-69.878357	-65.41500743	4.6	9.1
55	SO2 //b3lyp/6-31G*	-548.2623082	-1.04864349	-548.545442	-289.680794	-285.4537388	7.4	11.6
56	BF3 PLANAR	-324.2423834	-1.08364747	-324.534968	-1151.598244	-1146.662304	-16.1	-11.1
57	bcl3 B3LYP	-1404.998274	-1.1231075	-1405.301513	-418.249408	-407.563623	-15.3	-4.6
58	ALf3 B3LYP	-541.7795913	-1.22385043	-542.110031	-1198.145985	-1192.44865	11.0	16.7
59	alcl3 B3LYP	-1622.594226	-1.22535018	-1622.925071	-586.773769	-575.3265886	-2.3	9.2
60	cf4 B3LYP	-437.0500027	-1.48076056	-437.449808	-951.646211	-944.8724206	-18.6	-11.8
61	ccl4 B3LYP	-1878.095946	-1.55796129	-1878.516595	-92.763300	-78.32304961	3.1	17.5
62	O=C=S. Singlet	-511.2133618	-0.90001803	-511.456367	-163.002983	-159.353538	-24.5	-20.9
63	CS2 B3LYP	-834.0836242	-0.99832545	-834.353172	98.089002	103.1299615	-18.6	-13.6
64	COF2 B3LYP	-312.6725252	-1.14567471	-312.981857	-628.255182	-623.739322	-4.4	0.1
65	sif4 B3LYP	-688.6305261	-1.58192792	-689.057647	-1581.821187	-1573.629627	33.2	41.4
66	sicl4, td	-2129.659128	-1.61936353	-2130.096356	-643.444536	-627.5865164	19.3	35.2
67	nno B3LYP	-184.3978343	-0.86910422	-184.632492	52.173061	53.11824145	-29.8	-28.9
68	clno B3LYP	-589.7239594	-0.93782166	-589.977171	39.597899	44.0612487	-12.3	-7.8

69	nf3 c3v	-353.7014926	-1.2636294	-354.042673	-145.176751	-140.3720861	-13.0	-8.2
70	pf3 c3v	-640.5506667	-1.32044557	-640.907187	-942.775114	-937.9704493	15.8	20.6
71	ozone 1-a1	-225.1006245	-1.04557243	-225.382929	142.063860	144.8994003	-0.6	2.2
72	f2o B3LYP	-274.3557421	-0.99045684	-274.623165	30.604619	34.7529091	5.9	10.1
73	CLF3, C2V	-759.0134693	-1.40282166	-759.392231	-167.085255	-158.7624199	-8.1	0.2
74	CF2=CF2 D2H	-475.0043873	-1.68639219	-475.459713	-701.810262	-694.6689022	-43.2	-36.1
75	cl2c=ccl2 B3LYP	-1916.121856	-1.75989059	-1916.597027	-25.754466	-10.94664612	-13.2	1.6
76	cf3cn B3LYP	-429.9604232	-1.62766581	-430.399893	-526.289611	-520.7498058	-30.9	-25.4
77	PROPYNE C3V	-116.4269913	-0.65216651	-116.603076	189.254914	190.3576239	4.3	5.4
78	ALLENE D2D	-116.4273227	-0.64578108	-116.601684	191.254616	192.3573257	0.9	2.0
79	CYCLOPROPENE C2V	-116.3873883	-0.65504263	-116.564250	290.474286	291.5769963	13.5	14.6
80	PROPENE CS	-117.6622853	-0.67539059	-117.844641	35.571077	36.67378658	15.5	16.6
81	CYCLOPROPANE D3H	-117.6483378	-0.68134101	-117.832300	70.453067	71.55577683	17.3	18.4
82	PROPANE C2V	-118.880071	-0.70845178	-119.071353	-79.469995	-78.36728459	25.1	26.2
83	TRANS-1,3-BUTADIENE C2H	-155.6802595	-0.87386494	-155.916203	123.720374	125.1906544	13.7	15.2
84	Dimethyl acetylene	-155.6667071	-0.87978191	-155.904248	155.260002	156.730282	9.7	11.1
85	Methylene cyclopropane.	-155.6473543	-0.88032436	-155.885042	204.281628	205.7519075	3.9	5.3
86	Bicyclo[1.1.0]butane. C2v	-155.6310335	-0.89192759	-155.871854	240.838900	242.3091802	23.7	25.2
87	CYCLOBUTENE b3lyp	-155.6566386	-0.88268727	-155.894964	180.593695	182.0639752	24.1	25.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8795983	-0.91174158	-157.125769	56.181867	57.6521469	27.7	29.2
89	Isobutene. Single	-156.8975262	-0.90771285	-157.142609	7.179028	8.649308442	23.9	25.4
90	Trans butane	-158.1103776	-0.93813303	-158.363674	-91.845409	-90.37512918	33.7	35.1
91	isobutane B3LYP/6-31G*	-158.1113572	-0.94139942	-158.365535	-98.027137	-96.55685659	36.3	37.7
92	Spiropentane. D2d	-194.8714846	-1.11606166	-195.172821	205.764065	207.6019153	20.4	22.3
93	Benzene B3LYP	-231.797978	-1.28305342	-232.144402	84.610609	86.81602853	2.2	4.4
94	DIFLUOROMETHANE C2V	-238.7183568	-0.86648993	-238.952309	-457.857652	-454.2869715	-7.2	-3.7
95	HCF3 TRI-FLUOROMETHANE	-337.8860353	-1.17491095	-338.203261	-709.740960	-704.5687246	-12.7	-7.5
96	CH2CL2 C2V	-959.2688963	-0.88988894	-959.509166	-90.016961	-82.61305128	5.4	12.8
97	chcl3 B3LYP/6-31G*	-1418.686242	-1.22044089	-1419.015761	-97.990281	-87.06820103	5.4	16.3
98	METHYLAMINE b3lyp	-95.6754116	-0.52329408	-95.816701	-11.796892	-11.42932204	11.2	11.6
99	Acetonitrile. CH3-CN.	-132.5200539	-0.69529077	-132.707782	68.768546	69.5036861	-6.5	-5.8
100	NITRO METHANE	-244.6466375	-1.15012374	-244.957171	-86.940869	-84.68293895	-12.5	-10.2
101	Methyl-nitrite. CH3-O-N=O.	-244.6426147	-1.14037344	-244.950516	-73.195219	-70.9372886	-6.7	-4.4
102	Methylsilane. CH3-SiH3.	-330.9592769	-0.57331106	-331.114071	-6.432049	-4.279139281	22.9	25.0
103	Formic Acid.	-189.5023999	-0.8307777	-189.726710	-386.043850	-383.7859205	-7.4	-5.1
104	Methyl formate.	-228.720251	-1.05733608	-229.005732	-364.104834	-361.4793336	-8.5	-5.8
105	acetamide ch3cohn2	-208.8780589	-1.02625302	-209.155147	-238.190644	-236.5103242	0.3	2.0

106	Aziridine. (cyclic	-133.6690479	-0.72726172	-133.865409	136.299717	137.0348566	9.9	10.7
107	Cyanogen. NCCN.	-185.3574551	-0.93123089	-185.608887	278.053917	278.7890573	-28.6	-27.9
108	DIMETHYLAMINE b3lyp	-134.8970679	-0.75138055	-135.099941	-1.622069	-0.886929344	16.8	17.5
109	TRANS ETHYLAMINE	-134.9085932	-0.75254168	-135.111779	-31.767575	-31.03243489	15.5	16.2
110	KETENE B3LYP	-152.3629954	-0.72751352	-152.559424	-64.402726	-62.72240561	-17.1	-15.4
111	OXIRANE B3LYP	-153.5321503	-0.75846502	-153.736936	-46.920565	-45.24024503	5.8	7.5
112	Acetaldehyde B3LYP	-153.5778669	-0.7509167	-153.780614	-164.717518	-163.0371977	1.4	3.1
113	Glyoxal, O=CH-CH=O.	-227.4923794	-1.02474687	-227.769061	-226.107820	-223.4823203	-14.0	-11.4
114	ETHANOL TRANS	-154.7736782	-0.78115901	-154.984591	-217.976642	-216.2963219	17.2	18.8
115	DIMETHYL ETHER,	-154.7569512	-0.7782451	-154.967077	-172.837088	-171.1567681	11.3	12.9
116	Thiooxirane. (cyclic	-476.4520523	-0.84347241	-476.679790	93.249680	96.32151495	11.2	14.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.7675466	-1.19180343	-553.089333	-123.050596	-119.0335811	28.4	32.4
118	Thioethanol. CH3-CH2-SH.	-477.6703831	-0.86229452	-477.903203	-21.133752	-18.06191678	25.3	28.4
119	ch3sch3 B3LYP	-477.668459	-0.86428482	-477.901816	-14.967138	-11.89530253	22.3	25.3
120	Vinyl fluoride,	-177.5767186	-0.75634743	-177.780932	-143.618472	-141.281777	-4.7	-2.4
121	Ethyl chloride.	-539.0804116	-0.7970435	-539.295613	-98.206209	-93.95289912	13.9	18.2
122	Vinyl chloride,	-537.8573504	-0.76841533	-538.064822	26.805368	31.0586779	3.8	8.0
123	h2c=chcn B3LYP	-170.5291708	-0.89458437	-170.770709	179.466248	180.5689583	-1.3	-0.2
124	ACETONE B3LYP	-192.8199777	-0.98000567	-193.084579	-208.111494	-206.0636035	9.0	11.1
125	CH3COOH ACETIC	-228.7459467	-1.05663074	-229.031237	-431.523153	-428.897653	1.1	3.7
126	CH3CFO HCCO	-252.7572234	-1.06491433	-253.044750	-448.169036	-444.8871612	-5.9	-2.6
127	ch3c(o)cl hcco	-613.0245997	-1.08153573	-613.316614	-246.577558	-241.3790677	-3.9	1.3
128	ch3ch2ch2cl B3LYP	-578.3108313	-1.02698743	-578.588118	-110.970312	-106.3494322	20.8	25.4
129	Isopropyl alcohol,	-194.0089133	-1.01312325	-194.282457	-246.600954	-244.5530639	26.2	28.2
130	Methyl ethyl	-193.9924773	-1.00733677	-194.264458	-198.797636	-196.7497463	17.5	19.6
131	Trimethyl Amine.	-174.1210439	-0.98440758	-174.386834	-2.344965	-1.242255161	21.5	22.6
132	FURAN B3LYP	-229.6293535	-1.16635684	-229.944270	-36.381159	-33.96569916	-1.7	0.8
133	Thiophene b3lyp	-552.538854	-1.25867747	-552.878697	123.566912	127.3738872	8.5	12.3
134	PYROLE PLANAR	-209.7808249	-1.13811427	-210.088116	105.804770	107.2750505	-2.6	-1.1
135	C2v Pyridine	-247.8261896	-1.32790241	-248.184723	129.791618	131.629468	-10.8	-9.0
136	H2 B3LYP/6-31G*	-1.15982866	-0.03528524	-1.169356	7.190542	7.190542423	7.2	7.2
137	SH b3lyp/6-31G*	-398.5750764	-0.36293082	-398.673068	146.939342	149.2760375	3.8	6.2
138	CCH B3LYP	-76.47161653	-0.38738756	-76.576211	576.114098	576.8492378	10.9	11.6
139	C2H3 CS,2-A'	-77.7515405	-0.40881183	-77.861920	301.599391	302.3345311	2.0	2.8
140	ch3co hcco	-152.9363627	-0.72879872	-153.133138	-18.007568	-16.32724842	-8.0	-6.3
141	H2COH C1	-114.8859743	-0.51999979	-115.026374	-14.847971	-13.53522127	2.3	3.6
142	ch3o CS,	-114.878889	-0.49303863	-115.012009	19.293698	20.60644781	2.1	3.5

143	ch3ch2o 2A"	-154.1142958	-0.72172182	-154.309161	-6.641804	-4.961484141	8.8	10.5
144	ch3s 2-A'	-437.8067927	-0.59524453	-437.967509	130.209919	132.9141839	5.5	8.2
145	c2h5 staggered	-78.99027936	-0.43996407	-79.109070	131.623058	132.3581976	10.7	11.4
146	(ch3)2ch Cs	-118.2253729	-0.67067674	-118.406456	106.069173	107.1718831	16.1	17.2
147	TERT-BUTYL RADICAL	-157.4605508	-0.90346682	-157.704487	78.558633	80.02891293	27.1	28.6
148	NO2 RADICAL	-204.7942634	-0.91987839	-205.042631	4.608266	6.498625907	-28.4	-26.6
						MD	**3.5**	**6.2**
						MAD	**11.2**	**12.0**
						LD	**-43.2**	**41.4**

Table S5.21b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498660	0.000000	-0.498660
2	li	-7.468577	-0.014687	-7.472543
3	be	-14.637275	-0.054418	-14.651968
4	b	-24.616743	-0.078478	-24.637932
5	c	-37.800118	-0.105350	-37.828563
6	n	-54.533384	-0.136163	-54.570149
7	o	-74.997287	-0.193830	-75.049622
8	f	-99.644437	-0.257220	-99.713887
9	na	-162.151047	-0.173111	-162.197787
10	al	-242.232778	-0.222152	-242.292759
11	si	-289.233407	-0.252396	-289.301553
12	p	-341.115639	-0.281666	-341.191689
13	s	-397.950030	-0.323314	-398.037325
14	cl	-459.968321	-0.294371	-460.047801

Table S5.22a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04729776	-0.04739809	-8.060569	146.422736	146.4227359	7.1	7.1
2	BERYLLIUM HYDRIDE	-15.22269781	-0.05578405	-15.238317	319.873332	319.8733322	-22.0	-22.0
3	DOUBLET CH	-38.41840641	-0.14671703	-38.459487	598.985109	599.3526786	2.8	3.1
4	CH2 3-B1	-39.08136582	-0.1657719	-39.127782	395.126665	395.4942348	3.1	3.5
5	Singlet methylene,	-39.05823327	-0.18667684	-39.110503	438.881060	439.2486302	8.8	9.1
6	Methyl radical,	-39.75362664	-0.21119447	-39.812761	151.385915	151.7534851	4.9	5.3
7	ch4 //b3lyp/6-31G*	-40.41824034	-0.25358278	-40.489244	-64.743205	-64.3756352	10.2	10.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14819354	-0.19001786	-55.201399	357.001021	357.0010213	0.5	0.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78958992	-0.24441727	-55.858027	185.876153	185.8761532	-2.8	-2.8
10	AMMONIA, //b3lyp/6-31G*	-56.45517628	-0.29927936	-56.538975	-40.422365	-40.42236452	5.6	5.6
11	OH RADICAL	-75.64408088	-0.26169505	-75.717355	39.622438	40.56761795	0.3	1.2
12	Water //b3lyp/6-31G*	-76.32130345	-0.33160166	-76.414152	-233.553531	-232.6083506	8.3	9.2
13	HYDROGEN FLUORIDE,	-100.3396871	-0.34197892	-100.435441	-268.999062	-267.3975065	3.4	5.0
14	SIH2 singlet	-290.4499895	-0.3094438	-290.536634	275.489820	277.2751598	2.7	4.5
15	SIH2 3B1	-290.4237593	-0.28639062	-290.503949	362.315368	364.1007084	1.7	3.4
16	SIH3 c3v	-291.0647357	-0.31474203	-291.152863	204.101186	205.8865264	3.7	5.5
17	SIH4 //b3lyp/6-31G*	-291.7072093	-0.3423095	-291.803056	44.475255	46.2605953	10.2	12.0
18	ph2 doublet	-342.3320398	-0.34912255	-342.429794	139.300874	139.3008735	0.8	0.8
19	PH3 c3v	-342.9594483	-0.38091132	-343.066103	17.624355	17.62435519	12.2	12.2
20	SH2 //b3lyp/6-31G*	-399.2061563	-0.40243971	-399.318839	-10.630513	-8.293817605	9.9	12.2
21	HCL //b3lyp/6-31G*	-460.6156802	-0.34035326	-460.710979	-89.249585	-85.73141453	3.2	6.7
22	DILITHIUM //b3lyp/6-31G*	-14.96122404	-0.05899423	-14.977742	230.100271	230.1002714	14.2	14.2
23	Lithium Fluoride,	-107.3028111	-0.37183303	-107.406924	-341.420528	-339.8189727	-6.3	-4.7
24	ACETYLENE //b3lyp/6-31g*	-77.18073944	-0.42516571	-77.299786	227.250713	227.9858531	0.5	1.2
25	ETHYLENE //b3lyp/6-31g*	-78.42177644	-0.44584162	-78.546612	60.390087	61.12522676	8.1	8.8
26	ETHANE //b3lyp/6-31g*	-79.64410918	-0.47929629	-79.778312	-68.064182	-67.3290416	16.0	16.8
27	CYANO RADICAL,	-92.55755212	-0.46318078	-92.687243	437.813704	438.1812744	-1.1	-0.7
28	HYDROGEN CYANIDE	-93.26758373	-0.47058741	-93.399348	119.710060	120.0776302	-12.1	-11.7
29	CARBON MONOXIDE	-113.1590156	-0.48122716	-113.293759	-119.639242	-118.3264922	-9.2	-7.9
30	HCO BENT	-113.6847311	-0.50382066	-113.825801	26.773088	28.0858378	-15.1	-13.8
31	H2CO //b3lyp/6-31g*	-114.326616	-0.5233944	-114.473166	-115.968425	-114.6556751	-7.2	-5.9

32	METHANOL //b3lyp/6-31g*	-115.5320953	-0.5526844	-115.686847	-194.182339	-192.8695895	6.6	8.0
33	Nitrogen N2,	-109.3660637	-0.50478059	-109.507402	-10.440675	-10.44067522	-10.4	-10.4
34	H2NNH2 //b3lyp/6-31g*	-111.6729166	-0.56775558	-111.831888	99.252525	99.25252466	3.9	3.9
35	NO radical,	-129.7141057	-0.54701666	-129.867270	76.447076	77.39225553	-13.9	-13.0
36	O2 //b3lyp/6-31g*	-150.1249179	-0.61117097	-150.296046	-16.806813	-14.91645253	-16.8	-14.9
37	HYDROGEN PEROXIDE	-151.3406167	-0.64195603	-151.520364	-126.663560	-124.7731996	9.3	11.2
38	F2 //b3lyp/6-31g*	-199.296638	-0.6707869	-199.484458	8.611931	11.81504107	8.6	11.8
39	CO2 D*H	-188.331775	-0.80889804	-188.558266	-424.918096	-422.6601657	-31.6	-29.4
40	na2 //b3lyp/6-31G*	-324.312535	-0.37537336	-324.417640	143.028557	143.0285571	0.8	0.8
41	SI2 3-SGG	-578.5575192	-0.56514356	-578.715759	587.490726	591.0614058	2.1	5.7
42	P2 //b3lyp/6-31g*	-682.3615857	-0.71875033	-682.562836	147.937624	147.9376242	4.4	4.4
43	S2 //b3lyp/6-31g*	-796.0182247	-0.76504453	-796.232437	123.409130	128.0825199	-5.0	-0.4
44	CL2 //b3lyp/6-31g*	-919.9930759	-0.65951776	-920.177741	5.884144	12.92048408	5.9	12.9
45	Sodium Chloride	-622.2486922	-0.51441103	-622.392727	-175.150004	-171.6318342	7.3	10.8
46	SIO //b3lyp/6-31g*	-364.4794226	-0.62515766	-364.654467	-103.770693	-101.0401725	-0.8	1.9
47	Carbon monosulfide,	-435.9713247	-0.58448048	-436.134979	281.007768	283.7120331	1.1	3.8
48	OS //b3lyp/6-31g*	-473.0917638	-0.69555612	-473.286520	-5.358021	-2.076146214	-10.4	-7.1
49	CLO 2-PI	-535.0227895	-0.6144964	-535.194849	103.446507	107.9098567	2.2	6.7
50	CLF 1-SG	-559.6700241	-0.66221814	-559.855445	-56.855020	-51.73529493	-1.6	3.5
51	si2h6 //b3lyp/6-31g*	-582.2410859	-0.66535009	-582.427384	101.094912	104.6655916	21.2	24.8
52	Methyl chloride,	-499.8364737	-0.56713003	-499.995270	-76.860653	-72.97491274	5.1	9.0
53	H3C-SH METHANETHIOL	-438.4298197	-0.63171158	-438.606699	-7.662999	-4.958733533	15.3	18.1
54	HOCl //b3lyp/6-31g*	-535.6698488	-0.65383626	-535.852923	-72.252445	-67.78909454	2.2	6.7
55	SO2 //b3lyp/6-31G*	-548.2497615	-1.04863328	-548.543379	-295.708461	-291.4814063	1.4	5.6
56	BF3 PLANAR	-324.2304482	-1.08364847	-324.533870	-1155.047982	-1150.112042	-19.5	-14.6
57	bcl3 B3LYP	-1404.975386	-1.12308889	-1405.289851	-420.202852	-409.517067	-17.3	-6.6
58	ALf3 B3LYP	-541.7640625	-1.22385904	-542.106743	-1201.769643	-1196.072308	7.4	13.1
59	alcl3 B3LYP	-1622.567748	-1.22533439	-1622.910842	-587.910547	-576.4633671	-3.4	8.0
60	cf4 B3LYP	-437.0340873	-1.48075308	-437.448698	-956.926629	-950.1528393	-23.9	-17.1
61	ccl4 B3LYP	-1878.065426	-1.55793593	-1878.501648	-96.699131	-82.25888074	-0.9	13.6
62	O=C=S. Singlet	-511.2018134	-0.89999601	-511.453812	-167.478568	-163.8291231	-29.0	-25.3
63	CS2 B3LYP	-834.0684284	-0.99829445	-834.347951	94.236162	99.27712193	-22.5	-17.5
64	COF2 B3LYP	-312.6606176	-1.14566519	-312.981404	-633.563160	-629.0472996	-9.7	-5.2
65	sif4 B3LYP	-688.6109784	-1.5819244	-689.053917	-1586.126284	-1577.934724	28.9	37.1
66	sicl4, td	-2129.624977	-1.61933772	-2130.078391	-645.358689	-629.5006692	17.4	33.2
67	nno B3LYP	-184.3899593	-0.86908109	-184.633302	45.390498	46.33567782	-36.6	-35.7
68	clno B3LYP	-589.7115312	-0.9378023	-589.974116	34.008528	38.47187794	-17.9	-13.4

69	nf3 c3v	-353.6887137	-1.2636236	-354.042528	-151.358401	-146.553736	-19.1	-14.3
70	pf3 c3v	-640.5341471	-1.3204426	-640.903871	-946.643083	-941.8384178	11.9	16.7
71	ozone 1-a1	-225.0918467	-1.04554904	-225.384600	132.610309	135.4458491	-10.1	-7.2
72	f2o B3LYP	-274.3460153	-0.99045517	-274.623343	25.066497	29.21478678	0.4	4.5
73	CLF3, C2V	-758.99604	-1.40281999	-759.388830	-173.668727	-165.3458919	-14.7	-6.4
74	CF2=CF2 D2H	-474.9864339	-1.68638272	-475.458621	-708.563510	-701.42215	-50.0	-42.9
75	cl2c=ccl2 B3LYP	-1916.089252	-1.75985954	-1916.582012	-30.940433	-16.13261327	-18.4	-3.6
76	cf3cn B3LYP	-429.9434839	-1.6276421	-430.399224	-533.945644	-528.4058392	-38.6	-33.0
77	PROPYNE C3V	-116.419958	-0.65214244	-116.602558	186.336826	187.4395358	1.4	2.5
78	ALLENE D2D	-116.4202858	-0.64575901	-116.601098	188.512001	189.6147111	-1.9	-0.8
79	CYCLOPROPENE C2V	-116.3802992	-0.65502493	-116.563706	287.622427	288.725137	10.6	11.7
80	PROPENE CS	-117.6547134	-0.67537092	-117.843817	33.453837	34.55654741	13.4	14.5
81	CYCLOPROPANE D3H	-117.6406971	-0.68132595	-117.831468	68.357002	69.45971232	15.2	16.3
82	PROPANE C2V	-118.8719647	-0.70843419	-119.070326	-81.053665	-79.95095468	23.5	24.6
83	TRANS-1,3-BUTADIENE C2H	-155.6706378	-0.87383714	-155.915312	120.353794	121.8240739	10.3	11.8
84	Dimethyl acetylene	-155.6570893	-0.87975255	-155.903420	151.728900	153.1991801	6.1	7.6
85	Methylene cyclopropane.	-155.6376702	-0.88030111	-155.884155	200.905784	202.3760638	0.5	2.0
86	Bicyclo[1.1.0]butane. C2v	-155.6212811	-0.89190781	-155.871015	237.335237	238.8055169	20.2	21.7
87	CYCLOBUTENE b3lyp	-155.6469299	-0.88266382	-155.894076	177.220521	178.6908013	20.7	22.2
88	CYCLOBUTANE b3lyp/6-31G*	-156.8693555	-0.91172012	-157.124637	53.446873	54.91715252	25.0	26.5
89	Isobutene. Single	-156.8873602	-0.90768751	-157.141513	4.351101	5.821381079	21.1	22.6
90	Trans butane	-158.0996858	-0.93810915	-158.362356	-94.092866	-92.62258633	31.4	32.9
91	isobutane B3LYP/6-31G*	-158.1006562	-0.94137562	-158.364241	-100.336336	-98.86605578	34.0	35.4
92	Spiropentane. D2d	-194.8591464	-1.11603689	-195.171637	201.742167	203.5800169	16.4	18.2
93	Benzene B3LYP	-231.7840866	-1.2830153	-232.143331	78.865617	81.07103703	-3.6	-1.4
94	DIFLUOROMETHANE C2V	-238.7089484	-0.86649027	-238.951566	-460.716263	-457.1455826	-10.1	-6.5
95	HCF3 TRI-FLUOROMETHANE	-337.8733752	-1.17490882	-338.202350	-713.849910	-708.6776751	-16.8	-11.6
96	CH2CL2 C2V	-959.2521806	-0.88987555	-959.501346	-91.787400	-84.38348999	3.6	11.0
97	chcl3 B3LYP/6-31G*	-1418.662627	-1.22042192	-1419.004346	-100.760112	-89.83803186	2.6	13.5
98	METHYLAMINE b3lyp	-95.66966358	-0.52328781	-95.816184	-13.350666	-12.98309635	9.7	10.0
99	Acetonitrile. CH3-CN.	-132.5128228	-0.69526959	-132.707498	65.177479	65.91261857	-10.1	-9.4
100	NITRO METHANE	-244.6354132	-1.15010339	-244.957442	-93.940347	-91.68241719	-19.5	-17.2
101	Methyl-nitrite. CH3-O-N=O.	-244.631427	-1.14035185	-244.950726	-80.034200	-77.7762695	-13.5	-11.3
102	Methylsilane. CH3-SiH3.	-330.9502007	-0.573297	-331.110724	-6.399505	-4.246594896	22.9	25.0
103	Formic Acid.	-189.4939419	-0.83077193	-189.726558	-390.448541	-388.190611	-11.8	-9.5
104	Methyl formate.	-228.7092221	-1.05732061	-229.005272	-369.127014	-366.5015145	-13.5	-10.9
105	acetamide ch3cohn2	-208.8672168	-1.0262389	-209.154564	-242.684218	-241.0038985	-4.2	-2.5

106	Aziridine. (cyclic	-133.6612011	-0.72724926	-133.864831	133.479388	134.2145279	7.1	7.9
107	Cyanogen. NCCN.	-185.3485311	-0.93119732	-185.609266	271.237722	271.9728615	-35.4	-34.7
108	DIMETHYLAMINE b3lyp	-134.8887385	-0.75136709	-135.099121	-3.807889	-3.072748937	14.6	15.3
109	TRANS ETHYLAMINE	-134.9002602	-0.75252903	-135.110968	-33.975024	-33.23988361	13.3	14.0
110	KETENE B3LYP	-152.3555229	-0.72749799	-152.559222	-68.414326	-66.73400604	-21.1	-19.5
111	OXIRANE B3LYP	-153.5241016	-0.75845505	-153.736469	-50.235966	-48.55564635	2.5	4.2
112	Acetaldehyde B3LYP	-153.5698715	-0.75090524	-153.780125	-167.973765	-166.2934455	-1.9	-0.2
113	Glyoxal, O=CH-CH=O.	-227.4819275	-1.02473332	-227.768853	-231.790749	-229.1652489	-19.7	-17.0
114	ETHANOL TRANS	-154.7651312	-0.78114991	-154.983853	-220.580306	-218.8999857	14.6	16.2
115	DIMETHYL ETHER,	-154.7484172	-0.778234	-154.966323	-175.397066	-173.7167459	8.7	10.4
116	Thiooxirane. (cyclic	-476.4403565	-0.84345519	-476.676524	90.904341	93.97617576	8.9	12.0
117	Dimethylsulfoxide. (CH3)2SO.	-552.7523393	-1.19178524	-553.086039	-127.009819	-122.9928043	24.5	28.5
118	Thioethanol. CH3-CH2-SH.	-477.6582133	-0.86227667	-477.899651	-22.728368	-19.65653284	23.7	26.8
119	ch3sch3 B3LYP	-477.6562965	-0.86426696	-477.898291	-16.633168	-13.56133272	20.6	23.7
120	Vinyl fluoride,	-177.5684923	-0.75633723	-177.780267	-146.415686	-144.078991	-7.5	-5.2
121	Ethyl chloride.	-539.068002	-0.79702827	-539.291170	-99.831277	-95.57796653	12.3	16.6
122	Vinyl chloride,	-537.8454687	-0.76839805	-538.060620	24.547544	28.80085371	1.5	5.8
123	h2c=chcn B3LYP	-170.5198968	-0.89455531	-170.770372	174.585689	175.688399	-6.2	-5.1
124	ACETONE B3LYP	-192.80939	-0.97998719	-193.083786	-211.997325	-209.9494354	5.2	7.2
125	CH3COOH ACETIC	-228.7348981	-1.05661805	-229.030751	-436.477058	-433.8515578	-3.9	-1.2
126	CH3CFO HCCO	-252.7459775	-1.06490121	-253.044150	-452.825757	-449.5438822	-10.6	-7.3
127	ch3c(o)cl hcco	-613.0097123	-1.08151662	-613.312537	-250.852131	-245.6536405	-8.2	-3.0
128	ch3ch2ch2cl B3LYP	-578.2958371	-1.026966	-578.583388	-113.268440	-108.6475599	18.5	23.1
129	Isopropyl alcohol,	-193.9977723	-1.01310725	-194.281442	-249.905606	-247.8577156	22.9	24.9
130	Methyl ethyl	-193.9813576	-1.00731893	-194.263407	-202.004934	-199.9570445	14.3	16.4
131	Trimethyl Amine.	-174.1101201	-0.9843875	-174.385749	-5.258858	-4.15614822	18.6	19.7
132	FURAN B3LYP	-229.6170987	-1.16633057	-229.943671	-42.203618	-39.78815841	-7.5	-5.1
133	Thiophene b3lyp	-552.5229553	-1.25864443	-552.875376	118.513725	122.3207002	3.5	7.3
134	PYROLE PLANAR	-209.7687614	-1.13808639	-210.087426	100.426938	101.8972183	-7.9	-6.5
135	C2v Pyridine	-247.8120914	-1.32786625	-248.183894	123.352467	125.1903174	-17.2	-15.4
136	H2 B3LYP/6-31G*	-1.15944608	-0.03528555	-1.169326	7.268364	7.268364343	7.3	7.3
137	SH b3lyp/6-31G*	-398.568398	-0.36293264	-398.670019	146.876215	149.2129097	3.8	6.1
138	CCH B3LYP	-76.46756204	-0.3873668	-76.576025	573.750790	574.4859297	8.5	9.2
139	C2H3 CS,2-A'	-77.74691427	-0.40879014	-77.861376	300.175376	300.9105158	0.6	1.3
140	ch3co hcco	-152.9286977	-0.72877803	-153.132756	-21.543841	-19.86352098	-11.5	-9.8
141	H2COH C1	-114.880345	-0.51999093	-115.025942	-16.829137	-15.51638734	0.3	1.6
142	ch3o CS,	-114.8732925	-0.49302233	-115.011339	17.939776	19.2525263	0.8	2.1

143	ch3ch2o 2A"	-154.1061148	-0.72169646	-154.308190	-8.633924	-6.953604058	6.8	8.5
144	ch3s 2-A'	-437.7975363	-0.59523635	-437.964202	129.396715	132.10098	4.7	7.4
145	c2h5 staggered	-78.98510444	-0.43995648	-79.108292	130.811360	131.5465004	9.9	10.6
146	(ch3)2ch Cs	-118.217606	-0.67065914	-118.405391	104.586304	105.6890144	14.6	15.7
147	TERT-BUTYL RADICAL	-157.4501894	-0.90343891	-157.703152	76.357097	77.8273771	24.9	26.4
148	NO2 RADICAL	-204.785943	-0.91985662	-205.043503	-2.543221	-0.652861171	-35.6	-33.7

MAD	**11.5**	**12.0**
LD	**-50.0**	**-42.9**

Table S5.22b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 55% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498660	0.000000	-0.498660
2	li	-7.468041	-0.014686	-7.472153
3	be	-14.636326	-0.054413	-14.651562
4	b	-24.615478	-0.078482	-24.637453
5	c	-37.798520	-0.105356	-37.828019
6	n	-54.531456	-0.136167	-54.569583
7	o	-74.994703	-0.193841	-75.048978
8	f	-99.641218	-0.257230	-99.713242
9	na	-162.146956	-0.173109	-162.195426
10	al	-242.227822	-0.222153	-242.290025
11	si	-289.228091	-0.252398	-289.298762
12	p	-341.109968	-0.281660	-341.188833
13	s	-397.943724	-0.323317	-398.034253
14	cl	-459.961401	-0.294374	-460.043825

Table S5.23a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04912371	-0.04718552	-8.061392	146.488660	146.4886595	7.2	7.2
2	BERYLLIUM HYDRIDE	-15.2249888	-0.05556984	-15.239437	319.112621	319.1126214	-22.7	-22.7
3	DOUBLET CH	-38.42233563	-0.14608114	-38.460317	599.498477	599.8660473	3.3	3.6
4	CH2 3-B1	-39.0857281	-0.16514427	-39.128666	395.559010	395.9265801	3.5	3.9
5	Singlet methylene,	-39.06287878	-0.18586501	-39.111204	439.793244	440.160814	9.7	10.0
6	Methyl radical,	-39.75886254	-0.21038014	-39.813561	152.098200	152.4657701	5.7	6.0
7	ch4 //b3lyp/6-31G*	-40.42422095	-0.25259442	-40.489895	-63.580505	-63.21293515	11.3	11.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15282792	-0.18930412	-55.202047	358.121900	358.1219003	1.6	1.6
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79498076	-0.24346065	-55.858281	188.094300	188.0942995	-0.6	-0.6
10	AMMONIA, //b3lyp/6-31G*	-56.46131376	-0.29809168	-56.538818	-37.064942	-37.06494181	9.0	9.0
11	OH RADICAL	-75.64974591	-0.26073681	-75.717537	41.758043	42.70322276	2.4	3.4
12	Water //b3lyp/6-31G*	-76.3276425	-0.33031383	-76.413524	-229.230738	-228.2855583	12.6	13.5
13	HYDROGEN FLUORIDE,	-100.3463802	-0.3407654	-100.434979	-265.683406	-264.0818508	6.7	8.3
14	SIH2 singlet	-290.4620235	-0.30840672	-290.542209	275.145932	276.9312723	2.3	4.1
15	SIH2 3B1	-290.4354651	-0.28553573	-290.509704	361.498305	363.2836454	0.8	2.6
16	SIH3 c3v	-291.0772801	-0.31375065	-291.158855	202.725327	204.5106668	2.3	4.1
17	SIH4 //b3lyp/6-31G*	-291.7205286	-0.34119495	-291.809239	42.657612	44.4429522	8.3	10.1
18	ph2 doublet	-342.3450034	-0.34799182	-342.435481	139.220114	139.2201137	0.7	0.7
19	PH3 c3v	-342.9731238	-0.37962027	-343.071825	17.514291	17.51429108	12.1	12.1
20	SH2 //b3lyp/6-31G*	-399.2202919	-0.40110318	-399.324579	-9.792498	-7.455803163	10.7	13.0
21	HCL //b3lyp/6-31G*	-460.6303401	-0.33912918	-460.718514	-88.407539	-84.88936889	4.1	7.6
22	DILITHIUM //b3lyp/6-31G*	-14.96400063	-0.05868902	-14.979260	230.446331	230.4463312	14.6	14.6
23	Lithium Fluoride,	-107.3105814	-0.37036921	-107.406877	-337.090617	-335.4890622	-2.0	-0.4
24	ACETYLENE //b3lyp/6-31g*	-77.18928806	-0.42321556	-77.299324	233.845688	234.5808277	7.1	7.8
25	ETHYLENE //b3lyp/6-31g*	-78.43164729	-0.4439751	-78.547081	64.664236	65.39937588	12.4	13.1
26	ETHANE //b3lyp/6-31g*	-79.65530338	-0.47741586	-79.779432	-65.376202	-64.64106205	18.7	19.5
27	CYANO RADICAL,	-92.56522905	-0.46056494	-92.684976	449.157845	449.5254151	10.3	10.6
28	HYDROGEN CYANIDE	-93.27623058	-0.46837818	-93.398009	128.680077	129.0476467	-3.1	-2.7
29	CARBON MONOXIDE	-113.1679518	-0.47903732	-113.292502	-111.154632	-109.8418822	-0.7	0.6
30	HCO BENT	-113.6940685	-0.50159248	-113.824483	35.478183	36.790933	-6.4	-5.0
31	H2CO //b3lyp/6-31g*	-114.336751	-0.52113654	-114.472247	-108.248387	-106.935637	0.5	1.8

32	METHANOL //b3lyp/6-31g*	-115.5435945	-0.55050832	-115.686727	-188.439704	-187.1269541	12.4	13.7
33	Nitrogen N2,	-109.3748747	-0.50244283	-109.505510	0.052583	0.052583439	0.1	0.1
34	H2NNH2 //b3lyp/6-31g*	-111.684331	-0.56547145	-111.831354	106.425093	106.4250929	11.0	11.0
35	NO radical,	-129.723537	-0.54457772	-129.865127	87.388672	88.33385245	-3.0	-2.0
36	O2 //b3lyp/6-31g*	-150.1348511	-0.60873566	-150.293122	-4.026743	-2.136382843	-4.0	-2.1
37	HYDROGEN PEROXIDE	-151.352106	-0.63926184	-151.518314	-116.053754	-114.1633945	19.9	21.8
38	F2 //b3lyp/6-31g*	-199.3085567	-0.66805395	-199.482251	18.490901	21.6940115	18.5	21.7
39	CO2 D*H	-188.3461763	-0.80526612	-188.555546	-410.039386	-407.7814556	-16.7	-14.5
40	na2 //b3lyp/6-31G*	-324.3289673	-0.3741388	-324.426243	143.555845	143.5558447	1.3	1.3
41	SI2 3-SGG	-578.5793326	-0.56322803	-578.725772	589.547742	593.1184215	4.2	7.8
42	P2 //b3lyp/6-31g*	-682.3855831	-0.71594982	-682.571730	154.043456	154.0434555	10.5	10.5
43	S2 //b3lyp/6-31g*	-796.0440831	-0.76247617	-796.242327	129.012408	133.6857984	0.6	5.2
44	CL2 //b3lyp/6-31g*	-920.0213504	-0.6570192	-920.192175	9.112814	16.14915385	9.1	16.1
45	Sodium Chloride	-622.2713314	-0.51263098	-622.404615	-174.240988	-170.7228179	8.2	11.7
46	SIO //b3lyp/6-31g*	-364.4956827	-0.62240365	-364.657508	-95.029866	-92.29934583	7.9	10.6
47	Carbon monosulfide,	-435.9879035	-0.58189448	-436.139196	288.351345	291.0556096	8.4	11.1
48	OS //b3lyp/6-31g*	-473.1096852	-0.69290255	-473.289840	4.261277	7.543152285	-0.8	2.5
49	CLO 2-PI	-535.0419727	-0.61157836	-535.200983	110.455872	114.9192223	9.2	13.7
50	CLF 1-SG	-559.6902231	-0.6596311	-559.861727	-50.743911	-45.62418586	4.5	9.6
51	si2h6 //b3lyp/6-31g*	-582.2668998	-0.66315413	-582.439320	98.468304	102.0389841	18.6	22.1
52	Methyl chloride,	-499.8562614	-0.56497385	-500.003155	-74.184666	-70.29892595	7.8	11.7
53	H3C-SH METHANETHIOL	-438.4491186	-0.62944195	-438.612773	-4.952758	-2.248492895	18.1	20.8
54	HOCl //b3lyp/6-31g*	-535.6897492	-0.65120302	-535.859062	-65.193984	-60.73063418	9.3	13.7
55	SO2 //b3lyp/6-31G*	-548.2733017	-1.04397117	-548.544734	-278.377626	-274.1505706	18.7	22.9
56	BF3 PLANAR	-324.2529072	-1.0797399	-324.533640	-1145.939888	-1141.003948	-10.4	-5.5
57	bcl3 B3LYP	-1405.021594	-1.11885529	-1405.312496	-415.590443	-404.9046579	-12.7	-2.0
58	ALf3 B3LYP	-541.793591	-1.21953359	-542.110670	-1192.211977	-1186.514642	17.0	22.7
59	alcl3 B3LYP	-1622.621264	-1.22105162	-1622.938738	-585.719251	-574.2720707	-1.2	10.2
60	cf4 B3LYP	-437.0637499	-1.47536156	-437.447344	-942.574523	-935.8007331	-9.5	-2.8
61	ccl4 B3LYP	-1878.126599	-1.55190883	-1878.530095	-86.503965	-72.06371452	9.3	23.7
62	O=C=S. Singlet	-511.223933	-0.89620194	-511.456945	-154.737583	-151.0881377	-16.2	-12.6
63	CS2 B3LYP	-834.0982714	-0.994309	-834.356792	105.223715	110.2646751	-11.5	-6.5
64	COF2 B3LYP	-312.6825775	-1.14113258	-312.979272	-618.700143	-614.1842831	5.1	9.7
65	sif4 B3LYP	-688.648276	-1.57646153	-689.058156	-1574.916820	-1566.72526	40.1	48.3
66	sicl4, td	-2129.694025	-1.61357947	-2130.113556	-641.259019	-625.4009992	21.5	37.3
67	nno B3LYP	-184.4038526	-0.86484985	-184.628714	65.514432	66.45961232	-16.5	-15.5
68	clno B3LYP	-589.7348675	-0.93333423	-589.977534	50.911057	55.3744069	-1.0	3.5

69	nf3 c3v	-353.7116586	-1.25835371	-354.038831	-132.763107	-127.9584422	-0.5	4.3
70	pf3 c3v	-640.5655519	-1.31564729	-640.907620	-935.633310	-930.8286451	22.9	27.7
71	ozone 1-a1	-225.1065249	-1.03998497	-225.376921	160.429832	163.2653719	17.8	20.6
72	f2o B3LYP	-274.3630586	-0.98612606	-274.619451	41.918775	46.06706525	17.2	21.4
73	CLF3, C2V	-759.0283083	-1.39683482	-759.391485	-153.953914	-145.6310791	5.0	13.4
74	CF2=CF2 D2H	-475.0197601	-1.67995315	-475.456548	-689.694006	-682.5526463	-31.1	-24.0
75	cl2c=ccl2 B3LYP	-1916.154409	-1.75294333	-1916.610174	-17.365932	-2.558111921	-4.8	10.0
76	cf3cn B3LYP	-429.9749787	-1.62110472	-430.396466	-512.557588	-507.0177826	-17.2	-11.6
77	PROPYNE C3V	-116.4337301	-0.64931246	-116.602551	194.488985	195.591695	9.6	10.7
78	ALLENE D2D	-116.4339973	-0.6429688	-116.601169	196.461186	197.563896	6.1	7.2
79	CYCLOPROPENE C2V	-116.3942003	-0.6522591	-116.563788	295.543649	296.6463592	18.6	19.7
80	PROPENE CS	-117.6698143	-0.67259356	-117.844689	39.423388	40.52609793	19.3	20.4
81	CYCLOPROPANE D3H	-117.6560224	-0.67861598	-117.832463	74.004034	75.10674431	20.9	22.0
82	PROPANE C2V	-118.8883974	-0.70564391	-119.071865	-76.713724	-75.61101368	27.9	29.0
83	TRANS-1,3-BUTADIENE C2H	-155.6896209	-0.87013583	-155.915856	129.812926	131.2832059	19.8	21.2
84	Dimethyl acetylene	-155.6760854	-0.87603418	-155.903854	161.476296	162.9465757	15.9	17.3
85	Methylene cyclopropane.	-155.6568343	-0.87666489	-155.884767	210.184796	211.6550759	9.8	11.2
86	Bicyclo[1.1.0]butane. C2v	-155.6406763	-0.88829848	-155.871634	246.598608	248.0688879	29.4	30.9
87	CYCLOBUTENE b3lyp	-155.6662089	-0.87899591	-155.894748	186.343536	187.8138157	29.9	31.3
88	CYCLOBUTANE b3lyp/6-31G*	-156.8899809	-0.90807352	-157.126080	60.667936	62.1382164	32.2	33.7
89	Isobutene. Single	-156.90772	-0.90398627	-157.142756	12.095281	13.5655606	28.8	30.3
90	Trans butane	-158.1213598	-0.93440711	-158.364306	-88.078942	-86.60866171	37.4	38.9
91	isobutane B3LYP/6-31G*	-158.1223562	-0.93765595	-158.366147	-94.207196	-92.73691582	40.1	41.6
92	Spiropentane. D2d	-194.8837885	-1.11155893	-195.172794	212.344110	214.1819602	27.0	28.8
93	Benzene B3LYP	-231.8114094	-1.27768862	-232.143608	94.284736	96.49015639	11.9	14.1
94	DIFLUOROMETHANE C2V	-238.7266646	-0.86325431	-238.951111	-452.686485	-449.1158048	-2.1	1.5
95	HCF3 TRI-FLUOROMETHANE	-337.8970456	-1.17056359	-338.201392	-702.520157	-697.3479222	-5.5	-0.3
96	CH2CL2 C2V	-959.285763	-0.88648144	-959.516248	-87.034920	-79.63100996	8.4	15.8
97	chcl3 B3LYP/6-31G*	-1418.710004	-1.21573394	-1419.026095	-93.482752	-82.56067201	9.9	20.8
98	METHYLAMINE b3lyp	-95.68099463	-0.52121348	-95.816510	-8.508634	-8.141064185	14.5	14.9
99	Acetonitrile. CH3-CN.	-132.5267039	-0.6921979	-132.706675	75.544216	76.27935648	0.2	1.0
100	NITRO METHANE	-244.6559958	-1.14494183	-244.953681	-73.384140	-71.12621039	1.1	3.3
101	Methyl-nitrite. CH3-O-N=O.	-244.6519576	-1.13502396	-244.947064	-59.739768	-57.48183818	6.8	9.0
102	Methylsilane. CH3-SiH3.	-330.9687329	-0.57126508	-331.117262	-6.395875	-4.242965405	22.9	25.0
103	Formic Acid.	-189.5096774	-0.82723264	-189.724758	-377.865059	-375.6071288	0.8	3.0
104	Methyl formate.	-228.7301493	-1.05284785	-229.003890	-354.888849	-352.2633487	0.8	3.4
105	acetamide ch3cohn2	-208.888061	-1.02195744	-209.153770	-229.719754	-228.0394336	8.8	10.4

106	Aziridine. (cyclic	-133.6765822	-0.72429249	-133.864898	141.630740	142.36588	15.3	16.0
107	Cyanogen. NCCN.	-185.3649025	-0.92671656	-185.605849	290.995698	291.7308381	-15.7	-15.0
108	DIMETHYLAMINE b3lyp	-134.9052934	-0.74837907	-135.099872	2.671444	3.406583887	21.1	21.8
109	TRANS ETHYLAMINE	-134.9168265	-0.74953911	-135.111707	-27.463442	-26.7283023	19.8	20.6
110	KETENE B3LYP	-152.3695459	-0.7242724	-152.557857	-56.893716	-55.21339553	-9.6	-7.9
111	OXIRANE B3LYP	-153.5395916	-0.75533675	-153.735979	-40.892799	-39.21247904	11.8	13.5
112	Acetaldehyde B3LYP	-153.5852416	-0.74773969	-153.779654	-158.679829	-156.9995094	7.4	9.1
113	Glyoxal, O=CH-CH=O.	-227.5014135	-1.02026281	-227.766682	-215.603467	-212.9779666	-3.5	-0.8
114	ETHANOL TRANS	-154.7818703	-0.77806456	-154.984167	-213.225403	-211.5450827	21.9	23.6
115	DIMETHYL ETHER,	-154.7651146	-0.77513705	-154.966650	-168.077639	-166.3973192	16.0	17.7
116	Thiooxirane. (cyclic	-476.463715	-0.84025406	-476.682181	97.340749	100.4125838	15.3	18.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.7822646	-1.18697353	-553.090878	-115.749903	-111.7328876	35.7	39.7
118	Thioethanol. CH3-CH2-SH.	-477.6827454	-0.85908433	-477.906107	-18.268872	-15.19703655	28.2	31.2
119	ch3sch3 B3LYP	-477.6807844	-0.86104639	-477.904656	-11.933712	-8.861877284	25.3	28.4
120	Vinyl fluoride,	-177.5842151	-0.75330895	-177.780075	-138.428128	-136.0914329	0.5	2.8
121	Ethyl chloride.	-539.0930213	-0.79395149	-539.299449	-95.438132	-91.1848224	16.7	20.9
122	Vinyl chloride,	-537.8691496	-0.76530198	-538.068128	30.842183	35.09549258	7.8	12.1
123	h2c=chcn B3LYP	-170.5376307	-0.89054142	-170.769171	188.574609	189.6773193	7.8	8.9
124	ACETONE B3LYP	-192.8300211	-0.97592001	-193.083760	-201.119261	-199.0713709	16.0	18.1
125	CH3COOH ACETIC	-228.755903	-1.05221259	-229.029478	-422.525778	-419.9002783	10.1	12.7
126	CH3CFO HCCO	-252.7672456	-1.06055225	-253.042989	-439.740944	-436.4590686	2.5	5.8
127	ch3c(o)cl hcco	-613.0388296	-1.07701357	-613.318853	-238.875774	-233.6772842	3.8	9.0
128	ch3ch2ch2cl B3LYP	-578.3260965	-1.02297509	-578.592070	-107.182667	-102.5617869	24.6	29.2
129	Isopropyl alcohol,	-194.019775	-1.00909375	-194.282139	-240.804153	-238.7562629	32.0	34.0
130	Methyl ethyl	-194.0032964	-1.00331041	-194.264157	-193.043083	-190.9951927	23.3	25.3
131	Trimethyl Amine.	-174.1319319	-0.98045039	-174.386849	3.054705	4.157415089	26.9	28.0
132	FURAN B3LYP	-229.6406829	-1.16142691	-229.942654	-26.214592	-23.79913226	8.5	10.9
133	Thiophene b3lyp	-552.5543746	-1.25356898	-552.880303	132.128296	135.9352715	17.1	20.9
134	PYROLE PLANAR	-209.7922541	-1.13337851	-210.086932	115.310258	116.7805383	6.9	8.4
135	C2v Pyridine	-247.839491	-1.32228769	-248.183286	141.168455	143.0063046	0.6	2.4
136	H2 B3LYP/6-31G*	-1.16022945	-0.03513849	-1.169365	7.286944	7.286943956	7.3	7.3
137	SH b3lyp/6-31G*	-398.5818368	-0.36179451	-398.675903	147.272580	149.6092746	4.2	6.5
138	CCH B3LYP	-76.47525599	-0.38551701	-76.575490	580.475328	581.210468	15.2	16.0
139	C2H3 CS,2-A'	-77.75598946	-0.40703389	-77.861818	304.456641	305.1917805	4.9	5.6
140	ch3co hcco	-152.9432624	-0.7256459	-153.131930	-11.381215	-9.700894683	-1.3	0.3
141	H2COH C1	-114.8910949	-0.51790858	-115.025751	-10.960896	-9.648145945	6.2	7.5
142	ch3o CS,	-114.8840957	-0.49099626	-115.011755	22.213408	23.52615767	5.1	6.4

143	ch3ch2o 2A"	-154.1221454	-0.71873667	-154.309017	-2.687220	-1.006900118	12.8	14.5
144	ch3s 2-A'	-437.8161346	-0.5931332	-437.970349	131.856091	134.5603556	7.2	9.9
145	c2h5 staggered	-78.99555038	-0.43822615	-79.109489	133.234658	133.9697975	12.3	13.1
146	(ch3)2ch Cs	-118.2332789	-0.66800687	-118.406961	108.782175	109.8848847	18.8	19.9
147	TERT-BUTYL RADICAL	-157.4711092	-0.89985236	-157.705071	82.390628	83.86090842	30.9	32.4
148	NO2 RADICAL	-204.800411	-0.9154669	-205.038432	18.636401	20.52676115	-14.4	-12.5

MAD	**12.0**	**13.7**
LD	**40.1**	**48.3**

Table S5.23b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498683	0.000000	-0.498683
2	li	-7.469167	-0.014654	-7.472977
3	be	-14.638304	-0.054092	-14.652369
4	b	-24.618056	-0.078090	-24.638359
5	c	-37.801741	-0.104924	-37.829021
6	n	-54.535351	-0.135710	-54.570635
7	o	-74.999715	-0.193214	-75.049951
8	f	-99.647345	-0.256443	-99.714020
9	na	-162.154950	-0.172608	-162.199828
10	al	-242.237672	-0.221490	-242.295259
11	si	-289.238729	-0.251657	-289.304160
12	p	-341.121420	-0.280857	-341.194443
13	s	-397.956449	-0.322369	-398.040265
14	cl	-459.975380	-0.293373	-460.051658

Table S5.24a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04823553	-0.04718679	-8.060976	146.555355	146.5553548	7.2	7.2
2	BERYLLIUM HYDRIDE	-15.22390747	-0.05556226	-15.238909	319.422457	319.4224574	-22.4	-22.4
3	DOUBLET CH	-38.42035804	-0.1460851	-38.459801	599.414561	599.7821308	3.2	3.6
4	CH2 3-B1	-39.08357586	-0.1651427	-39.128164	395.437055	395.8046248	3.4	3.8
5	Singlet methylene,	-39.06055113	-0.18586132	-39.110734	439.589307	439.9568775	9.5	9.8
6	Methyl radical,	-39.75627687	-0.21038376	-39.813080	151.922868	152.2904384	5.5	5.9
7	ch4 //b3lyp/6-31G*	-40.42127481	-0.25258855	-40.489474	-63.911031	-63.54346144	11.0	11.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15044749	-0.18931437	-55.201562	357.897794	357.8977937	1.4	1.4
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79218459	-0.24346762	-55.857921	187.542164	187.5421637	-1.2	-1.2
10	AMMONIA, //b3lyp/6-31G*	-56.45813443	-0.29809281	-56.538619	-38.041289	-38.04128886	8.0	8.0
11	OH RADICAL	-75.64673547	-0.26074704	-75.717137	41.103931	42.04911067	1.8	2.7
12	Water //b3lyp/6-31G*	-76.32423834	-0.33032036	-76.413425	-230.675260	-229.7300803	11.2	12.1
13	HYDROGEN FLUORIDE,	-100.3427567	-0.34077431	-100.434766	-266.836019	-265.2344639	5.5	7.1
14	SIH2 singlet	-290.4560492	-0.30839887	-290.539317	275.391565	277.1769052	2.6	4.4
15	SIH2 3B1	-290.4296856	-0.28550896	-290.506773	361.846223	363.6315633	1.2	3.0
16	SIH3 c3v	-291.0711251	-0.31373566	-291.155834	203.310039	205.095379	2.9	4.7
17	SIH4 //b3lyp/6-31G*	-291.714036	-0.34118595	-291.806156	43.403949	45.18928943	9.1	10.9
18	ph2 doublet	-342.3385718	-0.34799152	-342.432530	139.450868	139.4508675	1.0	1.0
19	PH3 c3v	-342.9663644	-0.37961121	-343.068859	17.781489	17.78148874	12.3	12.3
20	SH2 //b3lyp/6-31G*	-399.2132735	-0.40109754	-399.321570	-9.984862	-7.648166722	10.5	12.9
21	HCL //b3lyp/6-31G*	-460.623069	-0.33912695	-460.714633	-88.684156	-85.16598632	3.8	7.3
22	DILITHIUM //b3lyp/6-31G*	-14.96266263	-0.05868487	-14.978508	230.370381	230.3703815	14.5	14.5
23	Lithium Fluoride,	-107.3064047	-0.37038432	-107.406408	-338.597912	-336.996357	-3.5	-1.9
24	ACETYLENE //b3lyp/6-31g*	-77.18483961	-0.42319684	-77.299103	231.551016	232.2861559	4.8	5.5
25	ETHYLENE //b3lyp/6-31g*	-78.42666193	-0.44396096	-78.546531	63.230933	63.9660729	10.9	11.7
26	ETHANE //b3lyp/6-31g*	-79.64978176	-0.47740429	-79.778681	-66.281363	-65.5462234	17.8	18.6
27	CYANO RADICAL,	-92.56096044	-0.46047396	-92.685288	445.403051	445.7706211	6.5	6.9
28	HYDROGEN CYANIDE	-93.27158419	-0.46836282	-93.398042	125.658402	126.0259716	-6.1	-5.8
29	CARBON MONOXIDE	-113.1631027	-0.47903106	-113.292441	-114.138939	-112.8261894	-3.7	-2.4
30	HCO BENT	-113.6889857	-0.50158028	-113.824412	32.519165	33.83191521	-9.3	-8.0
31	H2CO //b3lyp/6-31g*	-114.3313439	-0.52113153	-114.472049	-110.873945	-109.561195	-2.1	-0.8

32	METHANOL //b3lyp/6-31g*	-115.5376329	-0.55050559	-115.686269	-190.382142	-189.0693922	10.4	11.8
33	Nitrogen N2,	-109.3700368	-0.5024273	-109.505692	-3.419124	-3.419123612	-3.4	-3.4
34	H2NNH2 //b3lyp/6-31g*	-111.6783622	-0.5654708	-111.831039	104.257199	104.2571992	8.9	8.9
35	NO radical,	-129.7182562	-0.54456814	-129.865290	83.760579	84.70575932	-6.6	-5.7
36	O2 //b3lyp/6-31g*	-150.1291282	-0.60873446	-150.293487	-8.393076	-6.502716417	-8.4	-6.5
37	HYDROGEN PEROXIDE	-151.3457427	-0.63926701	-151.518345	-119.544672	-117.654312	16.4	18.3
38	F2 //b3lyp/6-31g*	-199.3017999	-0.66805788	-199.482175	15.262678	18.46578754	15.3	18.5
39	CO2 D*H	-188.3382647	-0.80525268	-188.555683	-415.248167	-412.9902368	-22.0	-19.7
40	na2 //b3lyp/6-31G*	-324.3205396	-0.37413328	-324.421556	143.439272	143.4392725	1.2	1.2
41	SI2 3-SGG	-578.5683509	-0.56320947	-578.720417	588.909350	592.4800299	3.6	7.1
42	P2 //b3lyp/6-31g*	-682.3734395	-0.71592604	-682.566740	152.107663	152.1076634	8.6	8.6
43	S2 //b3lyp/6-31g*	-796.0310136	-0.76246672	-796.236880	127.129775	131.8031653	-1.3	3.4
44	CL2 //b3lyp/6-31g*	-920.007221	-0.65701155	-920.184614	8.035379	15.07171927	8.0	15.1
45	Sodium Chloride	-622.2600021	-0.51263355	-622.398413	-174.633666	-171.1154961	7.8	11.3
46	SIO //b3lyp/6-31g*	-364.4871568	-0.62241258	-364.655208	-98.046017	-95.31549712	4.9	7.6
47	Carbon monosulfide,	-435.9794203	-0.58187413	-436.136526	285.830444	288.534709	5.9	8.6
48	OS //b3lyp/6-31g*	-473.1002794	-0.69289452	-473.287361	0.972356	4.25423123	-4.0	-0.8
49	CLO 2-PI	-535.0320553	-0.61153539	-535.197170	108.297481	112.7608305	7.0	11.5
50	CLF 1-SG	-559.6797604	-0.65963065	-559.857861	-52.769918	-47.65019284	2.5	7.6
51	si2h6 //b3lyp/6-31g*	-582.2542823	-0.66313728	-582.433329	99.499986	103.070666	19.6	23.2
52	Methyl chloride,	-499.8464359	-0.56496492	-499.998976	-75.117551	-71.23181126	6.9	10.8
53	H3C-SH METHANETHIOL	-438.4395329	-0.62943031	-438.609479	-5.833630	-3.129365473	17.2	19.9
54	HOCl //b3lyp/6-31g*	-535.6794967	-0.65120102	-535.855321	-67.541828	-63.0784781	6.9	11.4
55	SO2 //b3lyp/6-31G*	-548.2607551	-1.04396098	-548.542625	-284.341356	-280.1143009	12.7	16.9
56	BF3 PLANAR	-324.240972	-1.07974082	-324.532502	-1149.359981	-1144.424041	-13.8	-8.9
57	bcl3 B3LYP	-1404.998706	-1.11883678	-1405.300792	-417.522561	-406.8367759	-14.6	-3.9
58	ALf3 B3LYP	-541.7780621	-1.21954201	-542.107338	-1195.801925	-1190.10459	13.4	19.1
59	alcl3 B3LYP	-1622.594787	-1.22103588	-1622.924466	-586.840441	-575.3932608	-2.3	9.1
60	cf4 B3LYP	-437.0478345	-1.47535407	-437.446180	-947.808653	-941.0348627	-14.8	-8.0
61	ccl4 B3LYP	-1878.096079	-1.55188359	-1878.515088	-90.399020	-75.95877032	5.4	19.9
62	O=C=S. Singlet	-511.2123847	-0.89618008	-511.454353	-159.167156	-155.5177106	-20.7	-17.0
63	CS2 B3LYP	-834.0830758	-0.99427822	-834.351531	101.413490	106.4544505	-15.3	-10.3
64	COF2 B3LYP	-312.6706699	-1.14112308	-312.978773	-623.959322	-619.4434616	-0.1	4.4
65	sif4 B3LYP	-688.6287283	-1.57645795	-689.054372	-1579.181719	-1570.990159	35.8	44.0
66	sicl4, td	-2129.659874	-1.61355378	-2130.095533	-643.147587	-627.2895668	19.6	35.5
67	nno B3LYP	-184.3959777	-0.86482691	-184.629481	58.801526	59.74670609	-23.2	-22.3
68	clno B3LYP	-589.7224395	-0.93331508	-589.974435	45.383390	49.84673959	-6.5	-2.0

69	nf3 c3v	-353.6988797	-1.25834794	-354.038634	-138.881311	-134.0766459	-6.7	-1.9
70	pf3 c3v	-640.5490323	-1.31564423	-640.904256	-939.459142	-934.6544769	19.1	23.9
71	ozone 1-a1	-225.0977472	-1.03996178	-225.378537	151.071836	153.9073755	8.4	11.2
72	f2o B3LYP	-274.3533318	-0.98612438	-274.619585	36.435839	40.58412937	11.8	15.9
73	CLF3, C2V	-759.010879	-1.39683309	-759.388024	-160.469254	-152.1464191	-1.5	6.8
74	CF2=CF2 D2H	-475.0018067	-1.67994366	-475.455392	-696.385308	-689.2439478	-37.8	-30.7
75	cl2c=ccl2 B3LYP	-1916.121805	-1.75291244	-1916.595091	-22.499465	-7.691644951	-9.9	4.9
76	cf3cn B3LYP	-429.9580396	-1.62108112	-430.395731	-520.140371	-514.6005664	-24.8	-19.2
77	PROPYNE C3V	-116.4266969	-0.64928852	-116.602005	191.610320	192.7130303	6.7	7.8
78	ALLENE D2D	-116.4269605	-0.64294683	-116.600556	193.756946	194.8596557	3.4	4.5
79	CYCLOPROPENE C2V	-116.3871113	-0.65224148	-116.563216	292.729617	293.8323271	15.7	16.9
80	PROPENE CS	-117.6622425	-0.67257395	-117.843837	37.344372	38.44708158	17.3	18.4
81	CYCLOPROPANE D3H	-117.6483817	-0.67860094	-117.831604	71.944478	73.0471879	18.8	19.9
82	PROPANE C2V	-118.8802911	-0.70562634	-119.070810	-78.258698	-77.15598837	26.3	27.4
83	TRANS-1,3-BUTADIENE C2H	-155.6799993	-0.87010815	-155.914928	126.497075	127.9673551	16.5	17.9
84	Dimethyl acetylene	-155.6664677	-0.87600494	-155.902989	157.996398	159.4666776	12.4	13.9
85	Methylene cyclopropane.	-155.6471503	-0.87664171	-155.883844	206.858035	208.3283146	6.4	7.9
86	Bicyclo[1.1.0]butane. C2v	-155.630924	-0.88827875	-155.870759	243.143414	244.6136939	26.0	27.5
87	CYCLOBUTENE b3lyp	-155.6565003	-0.87897253	-155.893823	183.020303	184.4905825	26.5	28.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.8797381	-0.9080521	-157.124912	57.982476	59.45275576	29.5	31.0
89	Isobutene. Single	-156.897554	-0.903961	-157.141623	9.318222	10.78850152	26.1	27.5
90	Trans butane	-158.110668	-0.93438325	-158.362951	-90.275290	-88.80501034	35.2	36.7
91	isobutane B3LYP/6-31G*	-158.1116553	-0.93763218	-158.364816	-96.464857	-94.99457697	37.8	39.3
92	Spiropentane. D2d	-194.8714503	-1.11153421	-195.171565	208.381909	210.2197594	23.0	24.9
93	Benzene B3LYP	-231.7975183	-1.27765067	-232.142484	88.609722	90.81514155	6.2	8.4
94	DIFLUOROMETHANE C2V	-238.7172562	-0.86325457	-238.950335	-455.513255	-451.9425746	-4.9	-1.3
95	HCF3 TRI-FLUOROMETHANE	-337.8843855	-1.1705614	-338.200437	-706.589153	-701.4169176	-9.5	-4.4
96	CH2CL2 C2V	-959.2690474	-0.88646809	-959.508394	-88.780557	-81.37664715	6.6	14.0
97	chcl3 B3LYP/6-31G*	-1418.68639	-1.21571504	-1419.014633	-96.220342	-85.29826195	7.1	18.0
98	METHYLAMINE b3lyp	-95.67524655	-0.52120717	-95.815972	-10.031428	-9.663858386	13.0	13.3
99	Acetonitrile. CH3-CN.	-132.5194728	-0.69217682	-132.706361	71.998349	72.73348903	-3.3	-2.6
100	NITRO METHANE	-244.6447715	-1.14492156	-244.953900	-80.305435	-78.04750545	-5.8	-3.6
101	Methyl-nitrite. CH3-O-N=O.	-244.64077	-1.13500252	-244.947221	-66.496301	-64.23837104	0.0	2.3
102	Methylsilane. CH3-SiH3.	-330.9596567	-0.57125106	-331.113895	-6.341193	-4.188283066	22.9	25.1
103	Formic Acid.	-189.5012194	-0.82722683	-189.724571	-382.221669	-379.9637391	-3.6	-1.3
104	Methyl formate.	-228.7191205	-1.0528324	-229.003385	-359.850193	-357.2246925	-4.2	-1.6
105	acetamide ch3cohn2	-208.877219	-1.0219433	-209.153144	-234.152822	-232.4725024	4.3	6.0

106	Aziridine. (cyclic	-133.6687353	-0.72428003	-133.864291	138.852849	139.5879889	12.5	13.2
107	Cyanogen. NCCN.	-185.3559787	-0.92668321	-185.606183	284.249155	284.9842952	-22.4	-21.7
108	DIMETHYLAMINE b3lyp	-134.8969639	-0.74836559	-135.099023	0.528975	1.264115238	18.9	19.7
109	TRANS ETHYLAMINE	-134.9084935	-0.74952643	-135.110866	-29.627457	-28.89231685	17.7	18.4
110	KETENE B3LYP	-152.3620735	-0.72425694	-152.557623	-60.860612	-59.18029158	-13.6	-11.9
111	OXIRANE B3LYP	-153.5315429	-0.75532677	-153.735481	-44.166099	-42.48577863	8.6	10.2
112	Acetaldehyde B3LYP	-153.5772462	-0.74772822	-153.779133	-161.892709	-160.2123887	4.2	5.9
113	Glyoxal, O=CH-CH=O.	-227.4909617	-1.02024927	-227.766429	-221.225610	-218.6001101	-9.1	-6.5
114	ETHANOL TRANS	-154.7733233	-0.77805543	-154.983398	-215.787632	-214.1073118	19.4	21.0
115	DIMETHYL ETHER,	-154.7565806	-0.77512593	-154.965865	-170.595964	-168.9156437	13.5	15.2
116	Thiooxirane. (cyclic	-476.4520192	-0.84023689	-476.678883	95.031317	98.10315168	13.0	16.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.7670574	-1.18695536	-553.087535	-119.647559	-115.630544	31.8	35.8
118	Thioethanol. CH3-CH2-SH.	-477.6705756	-0.85906651	-477.902524	-19.827666	-16.75583082	26.6	29.7
119	ch3sch3 B3LYP	-477.6686218	-0.86102857	-477.901100	-13.563239	-10.4914041	23.7	26.7
120	Vinyl fluoride,	-177.5759889	-0.75329875	-177.779380	-141.189802	-138.8531068	-2.3	0.1
121	Ethyl chloride.	-539.0806117	-0.79393629	-539.294975	-97.031843	-92.77853293	15.1	19.4
122	Vinyl chloride,	-537.857268	-0.76528477	-538.063895	28.616036	32.86934584	5.6	9.9
123	h2c=chcn B3LYP	-170.5283569	-0.89051251	-170.768795	183.752217	184.8549269	3.0	4.1
124	ACETONE B3LYP	-192.8194333	-0.97590156	-193.082927	-204.949658	-202.901768	12.2	14.2
125	CH3COOH ACETIC	-228.7448544	-1.05219988	-229.028948	-427.420480	-424.7949795	5.2	7.8
126	CH3CFO HCCO	-252.7559997	-1.06053913	-253.042345	-444.344202	-441.0623273	-2.1	1.2
127	ch3c(o)cl hcco	-613.0239423	-1.07699453	-613.314731	-243.098482	-237.8999916	-0.4	4.8
128	ch3ch2ch2cl B3LYP	-578.3111023	-1.0229537	-578.587300	-109.437048	-104.8161683	22.4	27.0
129	Isopropyl alcohol,	-194.0086339	-1.00907772	-194.281085	-244.054605	-242.0067154	28.7	30.8
130	Methyl ethyl	-193.9921767	-1.00329256	-194.263066	-196.196379	-194.1484891	20.1	22.2
131	Trimethyl Amine.	-174.1210081	-0.98043029	-174.385724	0.197530	1.300239919	24.0	25.1
132	FURAN B3LYP	-229.6284282	-1.16140074	-229.942006	-31.971571	-29.556111	2.8	5.2
133	Thiophene b3lyp	-552.5384761	-1.2535361	-552.876931	127.136705	130.9436798	12.1	15.9
134	PYROLE PLANAR	-209.7801907	-1.13335074	-210.086195	109.997317	111.467597	1.6	3.1
135	C2v Pyridine	-247.8253931	-1.32225168	-248.182401	134.805291	136.6431409	-5.8	-3.9
136	H2 B3LYP/6-31G*	-1.15984685	-0.03513879	-1.169334	7.368687	7.368686536	7.4	7.4
137	SH b3lyp/6-31G*	-398.5751583	-0.36179634	-398.672843	147.214484	149.5511786	4.1	6.5
138	CCH B3LYP	-76.47120161	-0.38549644	-76.575286	578.137112	578.8722523	12.9	13.6
139	C2H3 CS,2-A'	-77.75136333	-0.4070124	-77.861257	303.055281	303.790421	3.5	4.2
140	ch3co hcco	-152.9355976	-0.72562518	-153.131516	-14.875218	-13.19489827	-4.8	-3.2
141	H2COH C1	-114.8854656	-0.51789974	-115.025299	-12.915708	-11.60295777	4.2	5.6
142	ch3o CS,	-114.8784993	-0.49098025	-115.011064	20.884014	22.19676383	3.7	5.0

143	ch3ch2o 2A"	-154.1139645	-0.71871168	-154.308017	-4.641984	-2.961664421	10.8	12.5
144	ch3s 2-A'	-437.8068783	-0.59312509	-437.967022	131.061504	133.7657685	6.4	9.1
145	c2h5 staggered	-78.99037547	-0.43821861	-79.108694	132.445278	133.1804181	11.5	12.3
146	(ch3)2ch Cs	-118.2255121	-0.66798937	-118.405869	107.334137	108.4368474	17.4	18.5
147	TERT-BUTYL RADICAL	-157.4607478	-0.89982458	-157.703700	80.236828	81.70710838	28.8	30.2
148	NO2 RADICAL	-204.7920908	-0.91544522	-205.039261	11.554193	13.44455314	-21.5	-19.6

MAD	**11.4**	**12.5**
LD	**37.8**	**44.0**

Table S5.24b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498683	0.000000	-0.498683
2	li	-7.468630	-0.014653	-7.472587
3	be	-14.637355	-0.054088	-14.651959
4	b	-24.616791	-0.078094	-24.637876
5	c	-37.800142	-0.104930	-37.828474
6	n	-54.533422	-0.135714	-54.570065
7	o	-74.997131	-0.193225	-75.049301
8	f	-99.644125	-0.256453	-99.713367
9	na	-162.150859	-0.172606	-162.197462
10	al	-242.232715	-0.221491	-242.292518
11	si	-289.233414	-0.251659	-289.301361
12	p	-341.115749	-0.280852	-341.191579
13	s	-397.950142	-0.322372	-398.037182
14	cl	-459.968460	-0.293377	-460.047672

Table S5.25a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04734738	-0.04718807	-8.060560	146.621935	146.6219346	7.3	7.3
2	BERYLLIUM HYDRIDE	-15.22282621	-0.0555547	-15.238382	319.732317	319.7323166	-22.1	-22.1
3	DOUBLET CH	-38.4183805	-0.14608908	-38.459285	599.330735	599.6983046	3.1	3.5
4	CH2 3-B1	-39.08142374	-0.16514116	-39.127663	395.315289	395.6828591	3.3	3.6
5	Singlet methylene,	-39.05822353	-0.18585763	-39.110264	439.385878	439.7534477	9.3	9.6
6	Methyl radical,	-39.75369125	-0.21038741	-39.812600	151.747638	152.1152075	5.3	5.7
7	ch4 //b3lyp/6-31G*	-40.41832872	-0.25258268	-40.489052	-64.240937	-63.87336654	10.7	11.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1480671	-0.18932465	-55.201078	357.673308	357.6733079	1.2	1.2
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78938847	-0.24347461	-55.857561	186.989802	186.9898021	-1.7	-1.7
10	AMMONIA, //b3lyp/6-31G*	-56.45495514	-0.29809394	-56.538421	-39.017514	-39.01751408	7.0	7.0
11	OH RADICAL	-75.64372506	-0.26075729	-75.716737	40.449857	41.39503693	1.1	2.1
12	Water //b3lyp/6-31G*	-76.32083422	-0.33032689	-76.413326	-232.119561	-231.1743812	9.7	10.7
13	HYDROGEN FLUORIDE,	-100.3391333	-0.34078322	-100.434553	-267.988590	-266.3870345	4.4	6.0
14	SIH2 singlet	-290.450075	-0.30839101	-290.536424	275.637786	277.4231256	2.8	4.6
15	SIH2 3B1	-290.4239064	-0.28548222	-290.503841	362.195273	363.9806128	1.5	3.3
16	SIH3 c3v	-291.0649703	-0.31372068	-291.152812	203.895515	205.6808553	3.5	5.3
17	SIH4 //b3lyp/6-31G*	-291.7075435	-0.34117696	-291.803073	44.150894	45.93623368	9.8	11.6
18	ph2 doublet	-342.3321403	-0.34799126	-342.429578	139.681272	139.6812717	1.2	1.2
19	PH3 c3v	-342.959605	-0.37960214	-343.065894	18.048860	18.04885969	12.6	12.6
20	SH2 //b3lyp/6-31G*	-399.2062552	-0.40109189	-399.318561	-10.176737	-7.840041938	10.3	12.7
21	HCL //b3lyp/6-31G*	-460.615798	-0.33912473	-460.710753	-88.960466	-85.44229552	3.5	7.0
22	DILITHIUM //b3lyp/6-31G*	-14.96132471	-0.05868072	-14.977755	230.294514	230.2945142	14.4	14.4
23	Lithium Fluoride,	-107.3022281	-0.37039944	-107.405940	-340.105486	-338.5039312	-5.0	-3.4
24	ACETYLENE //b3lyp/6-31g*	-77.18039123	-0.42317812	-77.298881	229.258032	229.9931718	2.5	3.2
25	ETHYLENE //b3lyp/6-31g*	-78.42167664	-0.44394682	-78.545982	61.799077	62.53421709	9.5	10.2
26	ETHANE //b3lyp/6-31g*	-79.64426023	-0.47739272	-79.777930	-67.185265	-66.45012502	16.9	17.6
27	CYANO RADICAL,	-92.55669197	-0.46038308	-92.685599	441.653324	442.0208938	2.8	3.1
28	HYDROGEN CYANIDE	-93.26693786	-0.46834746	-93.398075	122.638106	123.005676	-9.2	-8.8
29	CARBON MONOXIDE	-113.1582536	-0.4790248	-113.292381	-117.121936	-115.8091859	-6.7	-5.4
30	HCO BENT	-113.6839031	-0.50156806	-113.824342	29.561732	30.87448217	-12.3	-11.0
31	H2CO //b3lyp/6-31g*	-114.3259369	-0.52112653	-114.471852	-113.498318	-112.1855679	-4.7	-3.4

32	METHANOL //b3lyp/6-31g*	-115.5316713	-0.55050286	-115.685812	-192.323508	-191.0107575	8.5	9.8
33	Nitrogen N2,	-109.365199	-0.50241179	-109.505874	-6.889589	-6.889588803	-6.9	-6.9
34	H2NNH2 //b3lyp/6-31g*	-111.6723935	-0.56547015	-111.830725	102.089728	102.0897282	6.7	6.7
35	NO radical,	-129.7129755	-0.54455856	-129.865452	80.133813	81.07899313	-10.2	-9.3
36	O2 //b3lyp/6-31g*	-150.1234054	-0.60873328	-150.293851	-12.758155	-10.867795	-12.8	-10.9
37	HYDROGEN PEROXIDE	-151.3393795	-0.6392722	-151.518376	-123.034722	-121.1443616	12.9	14.8
38	F2 //b3lyp/6-31g*	-199.295043	-0.66806182	-199.482100	12.035339	15.23844943	12.0	15.2
39	CO2 D*H	-188.3303531	-0.80523925	-188.555820	-420.454651	-418.1967212	-27.2	-24.9
40	na2 //b3lyp/6-31G*	-324.3121121	-0.37412775	-324.416868	143.322677	143.3226772	1.1	1.1
41	SI2 3-SGG	-578.5573694	-0.56319094	-578.715063	588.272089	591.8427693	2.9	6.5
42	P2 //b3lyp/6-31g*	-682.3612961	-0.71590225	-682.561749	150.172586	150.1725864	6.7	6.7
43	S2 //b3lyp/6-31g*	-796.0179442	-0.76245729	-796.231432	125.248072	129.9214621	-3.2	1.5
44	CL2 //b3lyp/6-31g*	-919.9930918	-0.65700389	-920.177053	6.958803	13.99514324	7.0	14.0
45	Sodium Chloride	-622.2486729	-0.51263614	-622.392211	-175.026351	-171.5081805	7.4	10.9
46	SIO //b3lyp/6-31g*	-364.478631	-0.62242153	-364.652909	-101.061920	-98.33140005	1.9	4.6
47	Carbon monosulfide,	-435.9709373	-0.58185377	-436.133856	283.311222	286.0154872	3.4	6.1
48	OS //b3lyp/6-31g*	-473.0908737	-0.69288649	-473.284882	-2.315368	0.966506879	-7.3	-4.1
49	CLO 2-PI	-535.0221381	-0.61149242	-535.193356	106.142108	110.6054575	4.9	9.4
50	CLF 1-SG	-559.6692978	-0.65963019	-559.853994	-54.795159	-49.6754337	0.4	5.6
51	si2h6 //b3lyp/6-31g*	-582.2416649	-0.66312043	-582.427339	100.532862	104.1035424	20.6	24.2
52	Methyl chloride,	-499.8366105	-0.56495599	-499.994798	-76.049430	-72.16368995	6.0	9.8
53	H3C-SH METHANETHIOL	-438.4299474	-0.62941868	-438.606185	-6.713349	-4.009083882	16.3	19.0
54	HOCl //b3lyp/6-31g*	-535.6692443	-0.65119901	-535.851580	-69.888745	-65.4253947	4.6	9.0
55	SO2 //b3lyp/6-31G*	-548.2482086	-1.04395079	-548.540515	-290.303055	-286.0759996	6.8	11.0
56	BF3 PLANAR	-324.2290369	-1.07974174	-324.531365	-1152.778246	-1147.842306	-17.2	-12.3
57	bcl3 B3LYP	-1404.975818	-1.11881826	-1405.289087	-419.452733	-408.766948	-16.5	-5.8
58	ALf3 B3LYP	-541.7625333	-1.21955043	-542.104007	-1199.390531	-1193.693196	9.8	15.5
59	alcl3 B3LYP	-1622.568309	-1.22102014	-1622.910194	-587.959929	-576.5127486	-3.5	8.0
60	cf4 B3LYP	-437.0319193	-1.47534659	-437.445016	-953.039832	-946.2660418	-20.0	-13.2
61	ccl4 B3LYP	-1878.06556	-1.55185836	-1878.500080	-94.291415	-79.85116491	1.5	16.0
62	O=C=S. Singlet	-511.2008365	-0.89615822	-511.451761	-163.594335	-159.9448901	-25.1	-21.5
63	CS2 B3LYP	-834.0678804	-0.99424744	-834.346270	97.605696	102.6466561	-19.1	-14.1
64	COF2 B3LYP	-312.6587624	-1.14111359	-312.978274	-629.215927	-624.700067	-5.4	-0.9
65	sif4 B3LYP	-688.6091808	-1.57645437	-689.050588	-1583.444010	-1575.25245	31.6	39.8
66	sicl4, td	-2129.625723	-1.6135281	-2130.077510	-645.033667	-629.175647	17.7	33.6
67	nno B3LYP	-184.3881029	-0.86480398	-184.630248	52.090901	53.03608089	-29.9	-29.0
68	clno B3LYP	-589.7100116	-0.93329594	-589.971334	39.857769	44.32111912	-12.0	-7.6

69	nf3 c3v	-353.6861009	-1.25834217	-354.038437	-144.997342	-140.1926767	-12.8	-8.0
70	pf3 c3v	-640.5325129	-1.31564118	-640.900892	-943.283415	-938.4787503	15.3	20.1
71	ozone 1-a1	-225.0889696	-1.03993859	-225.380152	141.716932	144.5524725	-1.0	1.9
72	f2o B3LYP	-274.3436052	-0.9861227	-274.619720	30.954708	35.10299773	6.3	10.4
73	CLF3, C2V	-758.9934497	-1.39683137	-759.384563	-166.982623	-158.6597884	-8.0	0.3
74	CF2=CF2 D2H	-474.9838535	-1.67993419	-475.454235	-703.073143	-695.9317831	-44.5	-37.4
75	cl2c=ccl2 B3LYP	-1916.0892	-1.75288156	-1916.580007	-27.629648	-12.82182837	-15.1	-0.3
76	cf3cn B3LYP	-429.9411006	-1.62105753	-430.394997	-527.719244	-522.1794386	-32.3	-26.8
77	PROPYNE C3V	-116.4196637	-0.64926458	-116.601458	188.733983	189.8366929	3.8	4.9
78	ALLENE D2D	-116.4199238	-0.64292486	-116.599943	191.054929	192.1576391	0.7	1.8
79	CYCLOPROPENE C2V	-116.3800223	-0.65222386	-116.562645	289.917607	291.0203165	12.9	14.0
80	PROPENE CS	-117.6546708	-0.67255435	-117.842986	35.267421	36.37013149	15.2	16.3
81	CYCLOPROPANE D3H	-117.6407411	-0.6785859	-117.830745	69.886781	70.9894914	16.7	17.9
82	PROPANE C2V	-118.872185	-0.70560877	-119.069755	-79.801707	-78.69899656	24.8	25.9
83	TRANS-1,3-BUTADIENE C2H	-155.6703778	-0.87008047	-155.914000	123.184087	124.6543671	13.1	14.6
84	Dimethyl acetylene	-155.6568501	-0.87597571	-155.902123	154.519463	155.9897432	8.9	10.4
85	Methylene cyclopropane.	-155.6374665	-0.87661854	-155.882920	203.533971	205.0042512	3.1	4.6
86	Bicyclo[1.1.0]butane. C2v	-155.6211717	-0.88825902	-155.869884	239.690744	241.1610241	22.5	24.0
87	CYCLOBUTENE b3lyp	-155.6467919	-0.87894916	-155.892898	179.699752	181.1700316	23.2	24.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8694955	-0.90803067	-157.123744	55.299583	56.76986285	26.8	28.3
89	Isobutene. Single	-156.8873881	-0.90393573	-157.140490	6.543925	8.01420498	23.3	24.8
90	Trans butane	-158.0999764	-0.9343594	-158.361597	-92.469037	-90.99875658	33.1	34.5
91	isobutane B3LYP/6-31G*	-158.1009545	-0.9376084	-158.363485	-98.719853	-97.24957324	35.6	37.1
92	Spiropentane. D2d	-194.8591123	-1.11150948	-195.170335	204.422868	206.2607175	19.1	20.9
93	Benzene B3LYP	-231.7836273	-1.27761272	-232.141359	82.938945	85.1443648	0.5	2.7
94	DIFLUOROMETHANE C2V	-238.7078478	-0.86325483	-238.949559	-458.338599	-454.7679193	-7.7	-4.2
95	HCF3 TRI-FLUOROMETHANE	-337.8717254	-1.17055922	-338.199482	-710.656012	-705.4837775	-13.6	-8.4
96	CH2CL2 C2V	-959.252332	-0.88645474	-959.500539	-90.524731	-83.12082088	4.9	12.3
97	chcl3 B3LYP/6-31G*	-1418.662775	-1.21569615	-1419.003170	-98.955881	-88.03380086	4.4	15.3
98	METHYLAMINE b3lyp	-95.66949855	-0.52120086	-95.815435	-11.553371	-11.18580087	11.5	11.8
99	Acetonitrile. CH3-CN.	-132.5122419	-0.69215574	-132.706045	68.454527	69.18966685	-6.9	-6.1
100	NITRO METHANE	-244.6335472	-1.1449013	-244.954120	-87.223841	-84.9659114	-12.7	-10.5
101	Methyl-nitrite. CH3-O-N=O.	-244.6295825	-1.13498108	-244.947377	-73.249876	-70.991946	-6.7	-4.5
102	Methylsilane. CH3-SiH3.	-330.9505807	-0.57123704	-331.110527	-6.285294	-4.132383546	23.0	25.2
103	Formic Acid.	-189.4927615	-0.82722104	-189.724383	-386.576417	-384.3184869	-7.9	-5.7
104	Methyl formate.	-228.7080917	-1.05281696	-229.002880	-364.808769	-362.1832685	-9.2	-6.5
105	acetamide ch3cohn2	-208.866377	-1.02192917	-209.152517	-238.583601	-236.9032813	-0.1	1.6

106	Aziridine. (cyclic	-133.6608886	-0.72426757	-133.863684	136.076524	136.8116641	9.7	10.5
107	Cyanogen. NCCN.	-185.3470549	-0.92664985	-185.606517	277.505569	278.2407093	-29.2	-28.4
108	DIMETHYLAMINE b3lyp	-134.8886346	-0.7483521	-135.098173	-1.611892	-0.876752381	16.8	17.5
109	TRANS ETHYLAMINE	-134.9001605	-0.74951375	-135.110024	-31.789920	-31.05477973	15.5	16.2
110	KETENE B3LYP	-152.3546011	-0.72424148	-152.557389	-64.825348	-63.14502841	-17.5	-15.9
111	OXIRANE B3LYP	-153.5234943	-0.7553168	-153.734983	-47.437534	-45.75721412	5.3	7.0
112	Acetaldehyde B3LYP	-153.5692509	-0.74771676	-153.778612	-165.103698	-163.4233781	1.0	2.7
113	Glyoxal, O=CH-CH=O.	-227.4805099	-1.02023574	-227.766176	-226.845086	-224.2195862	-14.7	-12.1
114	ETHANOL TRANS	-154.7647763	-0.77804629	-154.982629	-218.348079	-216.6677593	16.8	18.5
115	DIMETHYL ETHER,	-154.7480468	-0.7751148	-154.965079	-173.112428	-171.4321082	11.0	12.7
116	Thiooxirane. (cyclic	-476.4403235	-0.84021972	-476.675585	92.723754	95.79558949	10.7	13.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.7518502	-1.18693719	-553.084193	-123.542729	-119.525714	27.9	31.9
118	Thioethanol. CH3-CH2-SH.	-477.6584059	-0.85904869	-477.898940	-21.384635	-18.31279984	25.1	28.1
119	ch3sch3 B3LYP	-477.6564594	-0.86101075	-477.897542	-15.190914	-12.11907941	22.0	25.1
120	Vinyl fluoride,	-177.5677627	-0.75328856	-177.778684	-143.949706	-141.6130111	-5.0	-2.7
121	Ethyl chloride.	-539.0682023	-0.79392109	-539.290500	-98.623852	-94.37054214	13.5	17.8
122	Vinyl chloride,	-537.8453865	-0.76526757	-538.059661	26.391741	30.64505112	3.4	7.6
123	h2c=chcn B3LYP	-170.5190831	-0.89048361	-170.768419	178.932692	180.0354016	-1.8	-0.7
124	ACETONE B3LYP	-192.8088457	-0.9758831	-193.082093	-208.777419	-206.7295285	8.4	10.4
125	CH3COOH ACETIC	-228.7338059	-1.05218718	-229.028418	-432.312609	-429.6871094	0.3	2.9
126	CH3CFO HCCO	-252.744754	-1.06052602	-253.041701	-448.944895	-445.6630204	-6.7	-3.4
127	ch3c(o)cl hcco	-613.0090552	-1.07697549	-613.310608	-247.318591	-242.1201009	-4.6	0.6
128	ch3ch2ch2cl B3LYP	-578.2961083	-1.02293232	-578.582529	-111.688993	-107.0681127	20.1	24.7
129	Isopropyl alcohol,	-193.997493	-1.00906169	-194.280030	-247.302582	-245.254692	25.5	27.5
130	Methyl ethyl	-193.9810571	-1.00327471	-194.261974	-199.347078	-197.2991878	17.0	19.0
131	Trimethyl Amine.	-174.1100844	-0.9804102	-174.384599	-2.657372	-1.554662094	21.2	22.3
132	FURAN B3LYP	-229.6161738	-1.16137457	-229.941359	-37.725071	-35.30961096	-3.0	-0.6
133	Thiophene b3lyp	-552.5225778	-1.25350323	-552.873559	122.148584	125.955559	7.1	10.9
134	PYROLE PLANAR	-209.7681275	-1.13332296	-210.085458	104.687563	106.157843	-3.7	-2.2
135	C2v Pyridine	-247.8112953	-1.32221567	-248.181516	128.446158	130.284008	-12.1	-10.3
136	H2 B3LYP/6-31G*	-1.15946425	-0.0351391	-1.169303	7.450406	7.450406011	7.5	7.5
137	SH b3lyp/6-31G*	-398.5684799	-0.36179819	-398.669783	147.156462	149.4931566	4.1	6.4
138	CCH B3LYP	-76.46714732	-0.38547591	-76.575081	575.800599	576.5357395	10.5	11.3
139	C2H3 CS,2-A'	-77.74673731	-0.40699093	-77.860695	301.655635	302.3907748	2.1	2.8
140	ch3co hcco	-152.9279328	-0.72560444	-153.131102	-18.366877	-16.68655676	-8.3	-6.6
141	H2COH C1	-114.8798364	-0.51789091	-115.024846	-14.869186	-13.55643584	2.3	3.6
142	ch3o CS,	-114.8729029	-0.49096426	-115.010373	19.556323	20.8690729	2.4	3.7

143	ch3ch2o 2A"	-154.1057837	-0.71868672	-154.307016	-6.594190	-4.913869911	8.9	10.6
144	ch3s 2-A'	-437.797622	-0.59311701	-437.963695	130.267871	132.9721356	5.6	8.3
145	c2h5 staggered	-78.98520064	-0.43821109	-79.107900	131.656958	132.3920983	10.7	11.5
146	(ch3)2ch Cs	-118.2177454	-0.6679719	-118.404778	105.887988	106.9906984	15.9	17.0
147	TERT-BUTYL RADICAL	-157.4503866	-0.89979682	-157.702330	78.085829	79.55610922	26.6	28.1
148	NO2 RADICAL	-204.7837706	-0.91542354	-205.040089	4.474590	6.36495015	-28.6	-26.7

MAD	**11.2**	**11.9**
LD	**-44.5**	**39.8**

Table S5.25b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498683	0.000000	-0.498683
2	li	-7.468093	-0.014652	-7.472196
3	be	-14.636406	-0.054083	-14.651549
4	b	-24.615526	-0.078098	-24.637393
5	c	-37.798544	-0.104936	-37.827926
6	n	-54.531494	-0.135718	-54.569495
7	o	-74.994546	-0.193235	-75.048652
8	f	-99.640905	-0.256463	-99.712715
9	na	-162.146767	-0.172604	-162.195096
10	al	-242.227759	-0.221492	-242.289776
11	si	-289.228098	-0.251660	-289.298563
12	p	-341.110078	-0.280846	-341.188715
13	s	-397.943836	-0.322374	-398.034100
14	cl	-459.961540	-0.293380	-460.043686

Table S5.26a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04645925	-0.04718935	-8.060144	146.688420	146.6884202	7.4	7.4
2	BERYLLIUM HYDRIDE	-15.22174503	-0.05554716	-15.237854	320.042197	320.0421972	-21.8	-21.8
3	DOUBLET CH	-38.41640299	-0.14609307	-38.458770	599.247017	599.6145874	3.0	3.4
4	CH2 3-B1	-39.07927175	-0.16513965	-39.127162	395.193644	395.5612144	3.2	3.5
5	Singlet methylene,	-39.05589597	-0.18585394	-39.109794	439.182941	439.550511	9.1	9.4
6	Methyl radical,	-39.75110568	-0.21039108	-39.812119	151.572473	151.9400429	5.1	5.5
7	ch4 //b3lyp/6-31G*	-40.41538269	-0.25257681	-40.488630	-64.570287	-64.20271661	10.3	10.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14568675	-0.18933495	-55.200594	357.448422	357.448422	1.0	1.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78659239	-0.24348161	-55.857202	186.437221	186.4372207	-2.3	-2.3
10	AMMONIA, //b3lyp/6-31G*	-56.4517759	-0.29809508	-56.538223	-39.993678	-39.99367761	6.0	6.0
11	OH RADICAL	-75.6407147	-0.26076754	-75.716337	39.795791	40.74097105	0.5	1.4
12	Water //b3lyp/6-31G*	-76.31743015	-0.33033342	-76.413227	-233.563659	-232.6184789	8.3	9.2
13	HYDROGEN FLUORIDE,	-100.3355099	-0.34079213	-100.434340	-269.141117	-267.5395618	3.2	4.8
14	SIH2 singlet	-290.4441008	-0.30838316	-290.533532	275.884494	277.6698344	3.1	4.9
15	SIH2 3B1	-290.4181274	-0.28545552	-290.500910	362.545438	364.3307778	1.9	3.7
16	SIH3 c3v	-291.0588156	-0.31370571	-291.149790	204.481722	206.2670625	4.1	5.9
17	SIH4 //b3lyp/6-31G*	-291.701051	-0.34116796	-291.799990	44.898427	46.68376709	10.6	12.4
18	ph2 doublet	-342.3257088	-0.34799101	-342.426626	139.911418	139.9114178	1.4	1.4
19	PH3 c3v	-342.9528458	-0.37959307	-343.062928	18.316417	18.31641651	12.9	12.9
20	SH2 //b3lyp/6-31G*	-399.1992369	-0.40108624	-399.315552	-10.368188	-8.031493398	10.1	12.5
21	HCL //b3lyp/6-31G*	-460.6085269	-0.33912251	-460.706872	-89.236499	-85.71832877	3.2	6.7
22	DILITHIUM //b3lyp/6-31G*	-14.95998687	-0.05867657	-14.977003	230.218706	230.2187058	14.3	14.3
23	Lithium Fluoride,	-107.2980515	-0.37041458	-107.405472	-341.613333	-340.0117779	-6.5	-4.9
24	ACETYLENE //b3lyp/6-31g*	-77.17594292	-0.4231594	-77.298659	226.966656	227.7017956	0.2	0.9
25	ETHYLENE //b3lyp/6-31g*	-78.41669143	-0.44393268	-78.545432	60.368562	61.10370239	8.1	8.8
26	ETHANE //b3lyp/6-31g*	-79.63873878	-0.47738115	-79.777179	-68.087960	-67.35282049	16.0	16.7
27	CYANO RADICAL,	-92.55242364	-0.4602923	-92.685908	437.908589	438.2761592	-1.0	-0.6
28	HYDROGEN CYANIDE	-93.26229159	-0.46833211	-93.398108	119.619116	119.986686	-12.2	-11.8
29	CARBON MONOXIDE	-113.1534046	-0.47901855	-113.292320	-120.103635	-118.7908846	-9.6	-8.3
30	HCO BENT	-113.6788205	-0.50155582	-113.824272	26.605828	27.9185777	-15.2	-13.9
31	H2CO //b3lyp/6-31g*	-114.3205299	-0.52112153	-114.471655	-116.121504	-114.8087541	-7.3	-6.0

32	METHANOL //b3lyp/6-31g*	-115.5257098	-0.55050013	-115.685355	-194.263858	-192.9511078	6.6	7.9
33	Nitrogen N2,	-109.3603612	-0.50239627	-109.506056	-10.358843	-10.35884337	-10.4	-10.4
34	H2NNH2 //b3lyp/6-31g*	-111.6664248	-0.56546952	-111.830411	99.922586	99.92258586	4.5	4.5
35	NO radical,	-129.7076949	-0.54454898	-129.865614	76.508356	77.45353601	-13.9	-12.9
36	O2 //b3lyp/6-31g*	-150.1176826	-0.60873211	-150.294215	-17.121903	-15.23154325	-17.1	-15.2
37	HYDROGEN PEROXIDE	-151.3330163	-0.63927738	-151.518407	-126.523813	-124.6334526	9.5	11.3
38	F2 //b3lyp/6-31g*	-199.2882863	-0.66806576	-199.482025	8.808896	12.01200556	8.8	12.0
39	CO2 D*H	-188.3224415	-0.80522582	-188.555957	-425.658803	-423.4008725	-32.4	-30.1
40	na2 //b3lyp/6-31G*	-324.3036848	-0.37412221	-324.412180	143.206087	143.2060874	1.0	1.0
41	SI2 3-SGG	-578.546388	-0.56317245	-578.709708	587.636017	591.2066965	2.3	5.9
42	P2 //b3lyp/6-31g*	-682.3491528	-0.71587846	-682.556758	148.238283	148.2382828	4.7	4.7
43	S2 //b3lyp/6-31g*	-796.0048749	-0.76244787	-796.225985	123.367242	128.0406318	-5.1	-0.4
44	CL2 //b3lyp/6-31g*	-919.9789626	-0.65699624	-920.169492	5.883019	12.91935931	5.9	12.9
45	Sodium Chloride	-622.2373437	-0.51263873	-622.386009	-175.419013	-171.9008435	7.0	10.5
46	SIO //b3lyp/6-31g*	-364.4701053	-0.62243047	-364.650610	-104.077551	-101.347031	-1.2	1.6
47	Carbon monosulfide,	-435.9624543	-0.58183342	-436.131186	280.793567	283.4978319	0.9	3.6
48	OS //b3lyp/6-31g*	-473.0814681	-0.69287844	-473.282403	-5.601904	-2.320028646	-10.6	-7.3
49	CLO 2-PI	-535.0122209	-0.61144948	-535.189541	103.989726	108.4530761	2.7	7.2
50	CLF 1-SG	-559.6588352	-0.65962974	-559.850128	-56.819634	-51.6999087	-1.6	3.5
51	si2h6 //b3lyp/6-31g*	-582.2290476	-0.66310357	-582.421348	101.566903	105.1375827	21.7	25.2
52	Methyl chloride,	-499.8267852	-0.56494706	-499.990620	-76.980329	-73.09458855	5.0	8.9
53	H3C-SH METHANETHIOL	-438.420362	-0.62940704	-438.602890	-7.591996	-4.887731349	15.4	18.1
54	HOCl //b3lyp/6-31g*	-535.658992	-0.65119702	-535.847839	-72.234787	-67.77143674	2.2	6.7
55	SO2 //b3lyp/6-31G*	-548.2356622	-1.04394061	-548.538405	-296.262797	-292.0357415	0.8	5.0
56	BF3 PLANAR	-324.2171018	-1.07974267	-324.530227	-1156.194563	-1151.258623	-20.7	-15.7
57	bcl3 B3LYP	-1404.95293	-1.11879975	-1405.277382	-421.381018	-410.695233	-18.5	-7.8
58	ALf3 B3LYP	-541.7470046	-1.21955886	-542.100677	-1202.977650	-1197.280315	6.2	11.9
59	alcl3 B3LYP	-1622.541831	-1.2210044	-1622.895922	-589.077763	-577.6305827	-4.6	6.9
60	cf4 B3LYP	-437.0160041	-1.47533911	-437.443852	-958.267933	-951.4941427	-25.2	-18.5
61	ccl4 B3LYP	-1878.035041	-1.55183312	-1878.485072	-98.181225	-83.74097522	-2.4	12.1
62	O=C=S. Singlet	-511.1892884	-0.89613636	-511.449168	-168.019237	-164.3697918	-29.5	-25.9
63	CS2 B3LYP	-834.052685	-0.99421666	-834.341008	93.800281	98.84124141	-22.9	-17.9
64	COF2 B3LYP	-312.6468549	-1.1411041	-312.977775	-634.469878	-629.9540176	-10.6	-6.1
65	sif4 B3LYP	-688.5896333	-1.5764508	-689.046804	-1587.703599	-1579.512039	27.3	35.5
66	sicl4, td	-2129.591571	-1.61350242	-2130.059487	-646.917284	-631.0592642	15.8	31.7
67	nno B3LYP	-184.3802281	-0.86478104	-184.631015	45.382501	46.32768081	-36.6	-35.7
68	clno B3LYP	-589.6975837	-0.93327681	-589.968234	34.334190	38.79754023	-17.5	-13.1

69	nf3 c3v	-353.6733222	-1.2583364	-354.038240	-151.111145	-146.3064798	-18.9	-14.1
70	pf3 c3v	-640.5159935	-1.31563814	-640.897529	-947.106057	-942.3013917	11.4	16.3
71	ozone 1-a1	-225.0801921	-1.03991542	-225.381768	132.365107	135.2006465	-10.3	-7.5
72	f2o B3LYP	-274.3338785	-0.98612103	-274.619854	25.475409	29.62369896	0.8	4.9
73	CLF3, C2V	-758.9760206	-1.39682965	-759.381101	-173.493973	-165.1711381	-14.5	-6.2
74	CF2=CF2 D2H	-474.9659003	-1.67992471	-475.453078	-709.757436	-702.6160764	-51.2	-44.1
75	cl2c=ccl2 B3LYP	-1916.056596	-1.75285067	-1916.564923	-32.756573	-17.94875275	-20.2	-5.4
76	cf3cn B3LYP	-429.9241617	-1.62103393	-430.394262	-535.294241	-529.7544362	-39.9	-34.4
77	PROPYNE C3V	-116.4126306	-0.64924064	-116.600910	185.859879	186.9625893	0.9	2.0
78	ALLENE D2D	-116.4128872	-0.6429029	-116.599329	188.355009	189.4577191	-2.0	-0.9
79	CYCLOPROPENE C2V	-116.3729334	-0.65220624	-116.562073	287.107524	288.2102342	10.1	11.2
80	PROPENE CS	-117.6470992	-0.67253474	-117.842134	33.192432	34.29514239	13.1	14.2
81	CYCLOPROPANE D3H	-117.6331007	-0.67857086	-117.829886	67.830825	68.93353508	14.7	15.8
82	PROPANE C2V	-118.8640789	-0.7055912	-119.068700	-81.342868	-80.24015797	23.3	24.4
83	TRANS-1,3-BUTADIENE C2H	-155.6607564	-0.87005279	-155.913072	119.873855	121.3441349	9.8	11.3
84	Dimethyl acetylene	-155.6472326	-0.87594647	-155.901257	151.045374	152.5156535	5.4	6.9
85	Methylene cyclopropane.	-155.6277827	-0.87659536	-155.881995	200.212434	201.6827144	-0.2	1.3
86	Bicyclo[1.1.0]butane. C2v	-155.6114197	-0.8882393	-155.869009	236.240379	237.7106587	19.1	20.6
87	CYCLOBUTENE b3lyp	-155.6370835	-0.87892579	-155.891972	176.381756	177.8520362	19.9	21.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.8592529	-0.90800925	-157.122576	52.619084	54.08936362	24.2	25.6
89	Isobutene. Single	-156.8772224	-0.90391045	-157.139356	3.772239	5.242518978	20.5	22.0
90	Trans butane	-158.0892849	-0.93433554	-158.360242	-94.660273	-93.18999311	30.9	32.3
91	isobutane B3LYP/6-31G*	-158.0902539	-0.93758463	-158.362153	-100.972385	-99.50210495	33.3	34.8
92	Spiropentane. D2d	-194.8467745	-1.11148476	-195.169105	200.466771	202.3046207	15.1	17.0
93	Benzene B3LYP	-231.7697364	-1.27757476	-232.140233	77.272227	79.47764681	-5.2	-2.9
94	DIFLUOROMETHANE C2V	-238.6984395	-0.86325509	-238.948784	-461.162531	-457.5918509	-10.5	-7.0
95	HCF3 TRI-FLUOROMETHANE	-337.8590654	-1.17055704	-338.198527	-714.720715	-709.54848	-17.7	-12.5
96	CH2CL2 C2V	-959.2356166	-0.88644139	-959.492685	-92.267428	-84.86351803	3.1	10.5
97	chcl3 B3LYP/6-31G*	-1418.639161	-1.21567726	-1418.991707	-101.689440	-90.7673604	1.7	12.6
98	METHYLAMINE b3lyp	-95.66375063	-0.52119455	-95.814897	-13.074528	-12.70695781	9.9	10.3
99	Acetonitrile. CH3-CN.	-132.505011	-0.69213466	-132.705730	64.912644	65.64778386	-10.4	-9.7
100	NITRO METHANE	-244.6223231	-1.14488103	-244.954339	-94.139446	-91.88151568	-19.7	-17.4
101	Methyl-nitrite. CH3-O-N=O.	-244.6183951	-1.13495964	-244.947533	-80.000569	-77.74263869	-13.5	-11.2
102	Methylsilane. CH3-SiH3.	-330.9415047	-0.57122302	-331.107159	-6.228197	-4.075286535	23.1	25.2
103	Formic Acid.	-189.4843037	-0.82721525	-189.724196	-390.929285	-388.6713553	-12.3	-10.0
104	Methyl formate.	-228.697063	-1.05280153	-229.002375	-369.764667	-367.1391668	-14.1	-11.5
105	acetamide ch3cohn2	-208.8555352	-1.02191504	-209.151891	-243.012207	-241.3318872	-4.5	-2.8

106	Aziridine. (cyclic	-133.653042	-0.72425511	-133.863076	133.301686	134.036826	6.9	7.7
107	Cyanogen. NCCN.	-185.3381313	-0.92661651	-185.606850	270.764864	271.5000045	-35.9	-35.2
108	DIMETHYLAMINE b3lyp	-134.8803054	-0.74833862	-135.097324	-3.751306	-3.016165736	14.7	15.4
109	TRANS ETHYLAMINE	-134.8918277	-0.74950108	-135.109183	-33.950971	-33.21583088	13.3	14.1
110	KETENE B3LYP	-152.3471288	-0.72422603	-152.557154	-68.788005	-67.10768506	-21.5	-19.8
111	OXIRANE B3LYP	-153.5154457	-0.75530683	-153.734485	-50.707196	-49.02687634	2.0	3.7
112	Acetaldehyde B3LYP	-153.5612557	-0.7477053	-153.778090	-168.312810	-166.6324897	-2.2	-0.5
113	Glyoxal, O=CH-CH=O.	-227.4700583	-1.02022221	-227.765923	-232.461951	-229.8364509	-20.3	-17.7
114	ETHANOL TRANS	-154.7562294	-0.77803717	-154.981860	-220.906865	-219.2265448	14.2	15.9
115	DIMETHYL ETHER,	-154.739513	-0.77510367	-154.964293	-175.627111	-173.9467911	8.5	10.1
116	Thiooxirane. (cyclic	-476.4286279	-0.84020255	-476.672287	90.417898	93.48973335	8.4	11.5
117	Dimethylsulfoxide. (CH3)2SO.	-552.7366433	-1.18691902	-553.080850	-127.435516	-123.4185005	24.0	28.0
118	Thioethanol. CH3-CH2-SH.	-477.6462363	-0.85903087	-477.895355	-22.939890	-19.86805494	23.5	26.6
119	ch3sch3 B3LYP	-477.6442972	-0.86099293	-477.893985	-16.816876	-13.7450408	20.4	23.5
120	Vinyl fluoride,	-177.5595367	-0.75327837	-177.777987	-146.707861	-144.3711655	-7.8	-5.5
121	Ethyl chloride.	-539.055793	-0.79390589	-539.286026	-100.214253	-95.9609427	11.9	16.2
122	Vinyl chloride,	-537.8335051	-0.76525036	-538.055428	24.169220	28.42253019	1.2	5.4
123	h2c=chcn B3LYP	-170.5098095	-0.89045471	-170.768041	174.115868	175.2185779	-6.6	-5.5
124	ACETONE B3LYP	-192.7982582	-0.97586465	-193.081259	-212.602642	-210.5547521	4.5	6.6
125	CH3COOH ACETIC	-228.7227575	-1.05217448	-229.027888	-437.202145	-434.5766453	-4.6	-2.0
126	CH3CFO HCCO	-252.7335083	-1.06051291	-253.041057	-453.543034	-450.2611591	-11.3	-8.0
127	ch3c(o)cl hcco	-612.9941682	-1.07695645	-613.306486	-251.536212	-246.3377224	-8.9	-3.7
128	ch3ch2ch2cl B3LYP	-578.2811145	-1.02291094	-578.577759	-113.938705	-109.3178246	17.9	22.5
129	Isopropyl alcohol,	-193.9863523	-1.00904566	-194.278976	-250.548168	-248.5002779	22.2	24.3
130	Methyl ethyl	-193.9699377	-1.00325687	-194.260882	-202.495324	-200.4474341	13.8	15.9
131	Trimethyl Amine.	-174.0991609	-0.98039012	-174.383474	-5.510095	-4.407385203	18.3	19.4
132	FURAN B3LYP	-229.6039194	-1.1613484	-229.940710	-43.475217	-41.05975711	-8.7	-6.3
133	Thiophene b3lyp	-552.5066796	-1.25347035	-552.870186	117.163731	120.9707062	2.1	5.9
134	PYROLE PLANAR	-209.7560644	-1.13329518	-210.084720	99.380830	100.8511099	-9.0	-7.5
135	C2v Pyridine	-247.7971977	-1.32217967	-248.180630	122.090822	123.9286722	-18.5	-16.7
136	H2 B3LYP/6-31G*	-1.15908166	-0.0351394	-1.169272	7.532091	7.532090567	7.5	7.5
137	SH b3lyp/6-31G*	-398.5618015	-0.36180006	-398.666724	147.098428	149.4351231	4.0	6.3
138	CCH B3LYP	-76.46309311	-0.38545543	-76.574875	573.465725	574.2008653	8.2	8.9
139	C2H3 CS,2-A'	-77.7421114	-0.40696949	-77.860133	300.257613	300.992753	0.7	1.4
140	ch3co hcco	-152.9202682	-0.72558368	-153.130687	-21.856234	-20.17591373	-11.8	-10.1
141	H2COH C1	-114.8742074	-0.5178821	-115.024393	-16.821370	-15.50862006	0.3	1.6
142	ch3o CS,	-114.8673067	-0.4909483	-115.009682	18.230320	19.54307043	1.1	2.4

143	ch3ch2o 2A"	-154.0976031	-0.7186618	-154.306015	-8.543918	-6.86359798	6.9	8.6
144	ch3s 2-A'	-437.7883659	-0.59310896	-437.960367	129.475092	132.1793566	4.8	7.5
145	c2h5 staggered	-78.98002591	-0.4382036	-79.107105	130.869557	131.6046967	10.0	10.7
146	(ch3)2ch Cs	-118.2099788	-0.66795445	-118.403686	104.443639	105.5463494	14.5	15.6
147	TERT-BUTYL RADICAL	-157.4400255	-0.89976909	-157.700959	75.937436	77.40771587	24.5	25.9
148	NO2 RADICAL	-204.7754505	-0.91540186	-205.040917	-2.602444	-0.712083525	-35.7	-33.8

MAD	**11.6**	**12.0**
LD	**-51.2**	**-44.1**

Table S5.26b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 56% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498683	0.000000	-0.498683
2	li	-7.467557	-0.014652	-7.471806
3	be	-14.635457	-0.054078	-14.651139
4	b	-24.614261	-0.078102	-24.636910
5	c	-37.796945	-0.104943	-37.827379
6	n	-54.529566	-0.135722	-54.568926
7	o	-74.991962	-0.193246	-75.048003
8	f	-99.637686	-0.256473	-99.712063
9	na	-162.142676	-0.172601	-162.192730
10	al	-242.222802	-0.221494	-242.287035
11	si	-289.222782	-0.251661	-289.295764
12	p	-341.104407	-0.280841	-341.185851
13	s	-397.937529	-0.322377	-398.031018
14	cl	-459.954619	-0.293384	-460.039701

Table S5.27a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0500623	-0.04697672	-8.061806	146.604001	146.6040009	7.3	7.3
2	BERYLLIUM HYDRIDE	-15.22619902	-0.05535026	-15.240037	318.671272	318.6712725	-23.2	-23.2
3	DOUBLET CH	-38.42428859	-0.14545632	-38.460653	599.909451	600.2770208	3.7	4.1
4	CH2 3-B1	-39.08793956	-0.16452067	-39.129070	395.852299	396.2198689	3.8	4.2
5	Singlet methylene,	-39.06519837	-0.18505839	-39.111463	440.466790	440.8343603	10.4	10.7
6	Methyl radical,	-39.76151451	-0.20957657	-39.813909	152.602031	152.9696009	6.2	6.5
7	ch4 //b3lyp/6-31G*	-40.42725755	-0.25160877	-40.490160	-62.797366	-62.42979628	12.1	12.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1550835	-0.18860705	-55.202235	358.996098	358.9960978	2.5	2.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79757752	-0.24251971	-55.858207	189.715984	189.7159842	1.0	1.0
10	AMMONIA, //b3lyp/6-31G*	-56.4642744	-0.29691583	-56.538503	-34.748792	-34.74879187	11.3	11.3
11	OH RADICAL	-75.65240276	-0.25979724	-75.717352	43.209775	44.15495491	3.9	4.8
12	Water //b3lyp/6-31G*	-76.33058017	-0.32904407	-76.412841	-226.411520	-225.4663405	15.4	16.4
13	HYDROGEN FLUORIDE,	-100.3494527	-0.339571	-100.434345	-263.558653	-261.957098	8.8	10.4
14	SIH2 singlet	-290.4680861	-0.30737149	-290.544929	275.019794	276.8051336	2.2	4.0
15	SIH2 3B1	-290.4413939	-0.28466125	-290.512559	361.017573	362.8029135	0.4	2.1
16	SIH3 c3v	-291.0836725	-0.31275253	-291.161861	201.910655	203.6959954	1.5	3.3
17	SIH4 //b3lyp/6-31G*	-291.7273588	-0.34008066	-291.812379	41.551498	43.3368385	7.2	9.0
18	ph2 doublet	-342.3515384	-0.34687055	-342.438256	139.340331	139.3403306	0.8	0.8
19	PH3 c3v	-342.9800434	-0.37833144	-343.074626	17.626328	17.62632826	12.2	12.2
20	SH2 //b3lyp/6-31G*	-399.2274123	-0.3997726	-399.327355	-9.182615	-6.845919993	11.3	13.7
21	HCL //b3lyp/6-31G*	-460.6377314	-0.33791347	-460.722210	-87.862367	-84.34419747	4.6	8.1
22	DILITHIUM //b3lyp/6-31G*	-14.96543983	-0.05838436	-14.980036	230.693357	230.6933571	14.8	14.8
23	Lithium Fluoride,	-107.314179	-0.36893497	-107.406413	-334.328829	-332.7272735	0.8	2.4
24	ACETYLENE //b3lyp/6-31g*	-77.19339138	-0.42126759	-77.298708	238.048531	238.7836711	11.3	12.0
25	ETHYLENE //b3lyp/6-31g*	-78.43653645	-0.44211232	-78.547065	67.415592	68.15073237	15.1	15.9
26	ETHANE //b3lyp/6-31g*	-79.66098002	-0.47554022	-79.779865	-63.683335	-62.94819531	20.4	21.2
27	CYANO RADICAL,	-92.56864173	-0.45789454	-92.683115	456.581656	456.9492264	17.7	18.0
28	HYDROGEN CYANIDE	-93.2802346	-0.46617774	-93.396779	134.509297	134.8768669	2.7	3.1
29	CARBON MONOXIDE	-113.172043	-0.47686431	-113.291259	-105.757324	-104.4445744	4.7	6.0
30	HCO BENT	-113.6983275	-0.49937518	-113.823171	41.117310	42.43006014	-0.7	0.6
31	H2CO //b3lyp/6-31g*	-114.3414837	-0.51889624	-114.471208	-103.263323	-101.9505729	5.5	6.8

32	METHANOL //b3lyp/6-31g*	-115.5491369	-0.54834893	-115.686224	-184.739848	-183.4270977	16.1	17.4
33	Nitrogen N2,	-109.3788513	-0.50011466	-109.503880	6.946180	6.94617973	6.9	6.9
34	H2NNH2 //b3lyp/6-31g*	-111.6897814	-0.56320741	-111.830583	111.307198	111.3071984	15.9	15.9
35	NO radical,	-129.7276918	-0.54215499	-129.863231	94.579156	95.52433581	4.2	5.1
36	O2 //b3lyp/6-31g*	-150.1390649	-0.60632538	-150.290646	4.281564	6.17192369	4.3	6.2
37	HYDROGEN PEROXIDE	-151.3572378	-0.63659906	-151.516388	-109.065742	-107.1753815	26.9	28.8
38	F2 //b3lyp/6-31g*	-199.3137244	-0.66535212	-199.480062	25.035459	28.23856909	25.0	28.2
39	CO2 D*H	-188.3526739	-0.80165857	-188.553089	-400.549585	-398.2916552	-7.3	-5.0
40	na2 //b3lyp/6-31G*	-324.3369761	-0.37290902	-324.430203	143.943599	143.943599	1.7	1.7
41	SI2 3-SGG	-578.5901688	-0.56131266	-578.730497	590.926171	594.4968511	5.6	9.2
42	P2 //b3lyp/6-31g*	-682.3974421	-0.71315666	-682.575731	158.103196	158.1031958	14.6	14.6
43	S2 //b3lyp/6-31g*	-796.0568767	-0.75992378	-796.246858	132.671725	137.3451153	4.2	8.9
44	CL2 //b3lyp/6-31g*	-920.0355005	-0.65453607	-920.199135	11.217062	18.25340152	11.2	18.3
45	Sodium Chloride	-622.2826459	-0.51086862	-622.410363	-173.751351	-170.2331813	8.7	12.2
46	SIO //b3lyp/6-31g*	-364.5034232	-0.61969019	-364.658346	-89.434589	-86.70406926	13.5	16.2
47	Carbon monosulfide,	-435.9960037	-0.57931831	-436.140833	293.061696	295.7659609	13.2	15.9
48	OS //b3lyp/6-31g*	-473.1182057	-0.69026753	-473.290773	10.493429	13.77530374	5.5	8.8
49	CLO 2-PI	-535.0512463	-0.60865177	-535.203409	115.177234	119.6405841	13.9	18.4
50	CLF 1-SG	-559.6999653	-0.65706822	-559.864232	-46.733885	-41.61415994	8.5	13.6
51	si2h6 //b3lyp/6-31g*	-582.2801029	-0.6609599	-582.445343	96.806683	100.3773629	16.9	20.5
52	Methyl chloride,	-499.866228	-0.56282781	-500.006935	-72.506711	-68.62097127	9.5	13.4
53	H3C-SH METHANETHIOL	-438.4588369	-0.62718065	-438.615632	-3.203794	-0.499529197	19.8	22.5
54	HOCl //b3lyp/6-31g*	-535.6994027	-0.64859306	-535.861551	-60.576043	-56.11269316	13.9	18.4
55	SO2 //b3lyp/6-31G*	-548.2843052	-1.03935014	-548.544143	-267.240296	-263.0132406	29.8	34.1
56	BF3 PLANAR	-324.2634406	-1.07586622	-324.532407	-1140.359095	-1135.423155	-4.8	0.1
57	bcl3 B3LYP	-1405.044922	-1.11464189	-1405.323583	-412.988632	-402.3028467	-10.1	0.6
58	ALf3 B3LYP	-541.8076016	-1.21525486	-542.111415	-1186.365036	-1180.667701	22.8	28.5
59	alcl3 B3LYP	-1622.648312	-1.21679037	-1622.952509	-584.706348	-573.2591683	-0.2	11.2
60	cf4 B3LYP	-437.0775103	-1.47000933	-437.445013	-933.624183	-926.8503926	-0.6	6.2
61	ccl4 B3LYP	-1878.157264	-1.5459124	-1878.543742	-80.351597	-65.9113465	15.5	29.9
62	O=C=S. Singlet	-511.234512	-0.89242564	-511.457618	-146.591733	-142.9422881	-8.1	-4.5
63	CS2 B3LYP	-834.1129263	-0.99033467	-834.360510	112.247790	117.2887498	-4.5	0.6
64	COF2 B3LYP	-312.6926406	-1.13663316	-312.976799	-609.272829	-604.7569691	14.6	19.1
65	sif4 B3LYP	-688.6660394	-1.57104145	-689.058800	-1568.116794	-1559.925234	46.9	55.1
66	sicl4, td	-2129.728934	-1.60784599	-2130.130896	-639.141584	-623.2835642	23.6	39.5
67	nno B3LYP	-184.4098791	-0.86064288	-184.625040	78.677946	79.62312604	-3.3	-2.4
68	clno B3LYP	-589.7457849	-0.92890022	-589.978010	62.061111	66.52446091	10.2	14.6

69	nf3 c3v	-353.7218377	-1.25313267	-354.035121	-120.517573	-115.7129078	11.7	16.5
70	pf3 c3v	-640.5804496	-1.31089263	-640.908173	-928.602891	-923.7982258	30.0	34.8
71	ozone 1-a1	-225.1124348	-1.03446808	-225.371052	178.550158	181.3856984	35.9	38.7
72	f2o B3LYP	-274.3703849	-0.98184276	-274.615846	53.088318	57.23660782	28.4	32.6
73	CLF3, C2V	-759.0431623	-1.3909122	-759.390890	-141.005228	-132.6823935	18.0	26.3
74	CF2=CF2 D2H	-475.0351487	-1.67357276	-475.453542	-677.740170	-670.5988099	-19.2	-12.0
75	cl2c=ccl2 B3LYP	-1916.186975	-1.74606097	-1916.623491	-9.113892	5.693927784	3.4	18.2
76	cf3cn B3LYP	-429.9895486	-1.61460676	-430.393200	-499.014662	-493.4748566	-3.6	1.9
77	PROPYNE C3V	-116.4404742	-0.64648681	-116.602096	199.625152	200.7278619	14.7	15.8
78	ALLENE D2D	-116.4406774	-0.64018424	-116.600723	201.571704	202.6744141	11.2	12.3
79	CYCLOPROPENE C2V	-116.4010176	-0.64950215	-116.563393	300.519743	301.6224531	23.5	24.6
80	PROPENE CS	-117.677349	-0.66982241	-117.844805	43.181734	44.28444447	23.1	24.2
81	CYCLOPROPANE D3H	-117.6637125	-0.67591487	-117.832691	77.466498	78.56920803	24.3	25.4
82	PROPANE C2V	-118.8967298	-0.70286038	-119.072445	-74.051134	-72.94842351	30.5	31.7
83	TRANS-1,3-BUTADIENE C2H	-155.6989898	-0.8664427	-155.915600	135.778984	137.249264	25.7	27.2
84	Dimethyl acetylene	-155.6854709	-0.87232235	-155.903551	167.565827	169.0361071	22.0	23.4
85	Methylene cyclopropane.	-155.6663217	-0.87303926	-155.884582	215.966795	217.4370749	15.6	17.0
86	Bicyclo[1.1.0]butane. C2v	-155.6503263	-0.88470187	-155.871502	252.240119	253.7103987	35.1	36.6
87	CYCLOBUTENE b3lyp	-155.6757868	-0.87533881	-155.894622	191.969810	193.4400903	35.5	37.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.9003713	-0.90443768	-157.126481	65.033055	66.5033349	36.6	38.1
89	Isobutene. Single	-156.9179214	-0.90029364	-157.142995	16.886531	18.35681088	33.6	35.1
90	Trans butane	-158.1323499	-0.9307135	-158.365028	-84.436391	-82.96611127	41.1	42.6
91	isobutane B3LYP/6-31G*	-158.1333632	-0.93394499	-158.366849	-90.512251	-89.04197117	43.8	45.3
92	Spiropentane. D2d	-194.8961016	-1.10709603	-195.172876	218.778318	220.6161675	33.4	35.3
93	Benzene B3LYP	-231.8248507	-1.27237418	-232.142944	103.786728	105.9921476	21.4	23.6
94	DIFLUOROMETHANE C2V	-238.7349805	-0.8600472	-238.949992	-447.596668	-444.0259877	3.0	6.6
95	HCF3 TRI-FLUOROMETHANE	-337.9080668	-1.16625451	-338.199630	-695.403226	-690.2309912	1.7	6.8
96	CH2CL2 C2V	-959.3026367	-0.88310465	-959.523413	-84.115999	-76.71208933	11.3	18.7
97	chcl3 B3LYP/6-31G*	-1418.733776	-1.21107011	-1419.036544	-89.058841	-78.13676096	14.3	25.2
98	METHYLAMINE b3lyp	-95.68658208	-0.51915124	-95.816370	-5.295008	-4.927438007	17.7	18.1
99	Acetonitrile. CH3-CN.	-132.5333595	-0.6891364	-132.705644	82.207577	82.94271717	6.9	7.6
100	NITRO METHANE	-244.665365	-1.13981292	-244.950318	-60.026131	-57.76820147	14.4	16.7
101	Methyl-nitrite. CH3-O-N=O.	-244.6613126	-1.12973306	-244.943746	-46.498623	-44.24069342	20.0	22.3
102	Methylsilane. CH3-SiH3.	-330.9781943	-0.56923649	-331.120503	-6.415107	-4.262197193	22.9	25.0
103	Formic Acid.	-189.5169631	-0.82372271	-189.722894	-369.809306	-367.551376	8.8	11.1
104	Methyl formate.	-228.740058	-1.04840317	-229.002159	-345.828410	-343.2029097	9.8	12.4
105	acetamide ch3cohn2	-208.8980728	-1.01770262	-209.152498	-221.400673	-219.7203531	17.1	18.8

106	Aziridine. (cyclic	-133.6841226	-0.72135009	-133.864460	146.858165	147.5933046	20.5	21.2
107	Cyanogen. NCCN.	-185.3723574	-0.92225294	-185.602921	303.761356	304.4964964	-2.9	-2.2
108	DIMETHYLAMINE b3lyp	-134.9135254	-0.74540407	-135.099876	6.859396	7.59453574	25.3	26.0
109	TRANS ETHYLAMINE	-134.9250663	-0.74656304	-135.111707	-23.264600	-22.52946013	24.0	24.7
110	KETENE B3LYP	-152.3761032	-0.72106421	-152.556369	-49.498662	-47.8183424	-2.2	-0.5
111	OXIRANE B3LYP	-153.5470397	-0.75223736	-153.735099	-34.969750	-33.28942954	17.7	19.4
112	Acetaldehyde B3LYP	-153.5926232	-0.74459328	-153.778772	-152.751019	-151.0706985	13.4	15.0
113	Glyoxal, O=CH-CH=O.	-227.5104572	-1.01582407	-227.764413	-205.253895	-202.6283949	6.9	9.5
114	ETHANOL TRANS	-154.7900692	-0.77499751	-154.983819	-208.575555	-206.895235	26.6	28.2
115	DIMETHYL ETHER,	-154.7732851	-0.77205675	-154.966299	-163.421287	-161.7409671	20.7	22.4
116	Thiooxirane. (cyclic	-476.4753844	-0.83706495	-476.684651	101.342782	104.4146169	19.3	22.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.7969941	-1.18219009	-553.092542	-108.606217	-104.5892019	42.9	46.9
118	Thioethanol. CH3-CH2-SH.	-477.6951148	-0.85590227	-477.909090	-15.492264	-12.42042879	31.0	34.0
119	ch3sch3 B3LYP	-477.6931169	-0.85783657	-477.907576	-8.990515	-5.918679969	28.2	31.3
120	Vinyl fluoride,	-177.5917185	-0.750299	-177.779293	-133.327782	-130.9910875	5.6	7.9
121	Ethyl chloride.	-539.1056374	-0.79088673	-539.303359	-92.747387	-88.49407715	19.4	23.6
122	Vinyl chloride,	-537.8809551	-0.76221798	-538.071510	34.799088	39.05239807	11.8	16.0
123	h2c=chcn B3LYP	-170.5460982	-0.88654024	-170.767733	197.536990	198.6396998	16.8	17.9
124	ACETONE B3LYP	-192.8400733	-0.97187271	-193.083041	-194.265405	-192.2175155	22.9	24.9
125	CH3COOH ACETIC	-228.7658694	-1.0478367	-229.027829	-413.678425	-411.0529251	18.9	21.6
126	CH3CFO HCCO	-252.7772779	-1.0562317	-253.041336	-431.449597	-428.1677223	10.8	14.1
127	ch3c(o)cl hcco	-613.0530693	-1.0725355	-613.321203	-231.307183	-226.1086928	11.4	16.6
128	ch3ch2ch2cl B3LYP	-578.34137	-1.01899802	-578.596120	-103.502794	-98.88191447	28.3	32.9
129	Isopropyl alcohol,	-194.0306454	-1.00509991	-194.281920	-235.140194	-233.092304	37.7	39.7
130	Methyl ethyl	-194.0141245	-0.99931982	-194.263954	-187.421935	-185.374045	28.9	30.9
131	Trimethyl Amine.	-174.1428286	-0.97652825	-174.386961	8.315629	9.418338691	32.2	33.3
132	FURAN B3LYP	-229.652022	-1.15654341	-229.941158	-16.211308	-13.79584756	18.5	20.9
133	Thiophene b3lyp	-552.5699051	-1.2485089	-552.882032	140.535897	144.3428723	25.5	29.3
134	PYROLE PLANAR	-209.8036922	-1.12868663	-210.085864	124.656490	126.1267695	16.3	17.8
135	C2v Pyridine	-247.8528028	-1.3167263	-248.181984	152.357483	154.1953333	11.8	13.6
136	H2 B3LYP/6-31G*	-1.16063055	-0.03499306	-1.169379	7.374484	7.374484427	7.4	7.4
137	SH b3lyp/6-31G*	-398.5885998	-0.3606679	-398.678767	147.593502	149.9301974	4.5	6.8
138	CCH B3LYP	-76.47889837	-0.38366754	-76.574815	584.772636	585.5077756	19.5	20.2
139	C2H3 CS,2-A'	-77.76044198	-0.40527389	-77.861760	307.255736	307.9908762	7.7	8.4
140	ch3co hcco	-152.9501689	-0.72252424	-153.130800	-4.862363	-3.182043096	5.2	6.9
141	H2COH C1	-114.8962202	-0.51583663	-115.025179	-7.140522	-5.827772231	10.0	11.3
142	ch3o CS,	-114.8893079	-0.4889752	-115.011552	25.065613	26.37836329	7.9	9.2

143	ch3ch2o 2A"	-154.1300026	-0.71578188	-154.308948	1.167065	2.847384554	16.6	18.3
144	ch3s 2-A'	-437.8254814	-0.59104075	-437.973242	133.455217	136.1594821	8.8	11.5
145	c2h5 staggered	-79.00082517	-0.43650368	-79.109951	134.791813	135.5269532	13.9	14.6
146	(ch3)2ch Cs	-118.2411907	-0.66536074	-118.407531	111.409293	112.5120034	21.5	22.6
147	TERT-BUTYL RADICAL	-157.4816753	-0.89627002	-157.705743	86.104579	87.57485933	34.6	36.1
148	NO2 RADICAL	-204.8065672	-0.91110436	-205.034343	32.486778	34.37713823	-0.6	1.3

MAD	**15.1**	**17.2**
LD	**46.9**	**55.1**

Table S5.27b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 25%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498707	0.000000	-0.498707
2	li	-7.469757	-0.014621	-7.473412
3	be	-14.639334	-0.053772	-14.652777
4	b	-24.619369	-0.077708	-24.638796
5	c	-37.803365	-0.104503	-37.829490
6	n	-54.537318	-0.135261	-54.571133
7	o	-75.002144	-0.192603	-75.050295
8	f	-99.650254	-0.255672	-99.714172
9	na	-162.158855	-0.172108	-162.201882
10	al	-242.242567	-0.220833	-242.297775
11	si	-289.244054	-0.250925	-289.306785
12	p	-341.127203	-0.280056	-341.197217
13	s	-397.962869	-0.321432	-398.043227
14	cl	-459.982442	-0.292385	-460.055538

Table S5.28a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04917404	-0.04697795	-8.061388	146.675657	146.6756566	7.3	7.3
2	BERYLLIUM HYDRIDE	-15.22511769	-0.05534272	-15.239507	318.978372	318.9783722	-22.9	-22.9
3	DOUBLET CH	-38.42231097	-0.14546027	-38.460131	599.830737	600.1983075	3.6	4.0
4	CH2 3-B1	-39.08578727	-0.1645191	-39.128562	395.735415	396.1029853	3.7	4.1
5	Singlet methylene,	-39.06287068	-0.18505471	-39.110985	440.272642	440.6402119	10.2	10.5
6	Methyl radical,	-39.75892879	-0.20958016	-39.813420	152.436653	152.8042228	6.0	6.4
7	ch4 //b3lyp/6-31G*	-40.42431137	-0.25160289	-40.489728	-63.113448	-62.7458776	11.8	12.1
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15270301	-0.18861726	-55.201743	358.778700	358.7786996	2.3	2.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79478127	-0.24252663	-55.857838	189.176933	189.1769328	0.5	0.5
10	AMMONIA, //b3lyp/6-31G*	-56.46109496	-0.29691689	-56.538293	-35.705948	-35.70594783	10.3	10.3
11	OH RADICAL	-75.64939223	-0.2598074	-75.716942	42.564337	43.50951696	3.2	4.2
12	Water //b3lyp/6-31G*	-76.32717589	-0.32905049	-76.412729	-227.838690	-226.8935103	14.0	14.9
13	HYDROGEN FLUORIDE,	-100.3458291	-0.33957979	-100.434120	-264.700042	-263.0984866	7.7	9.3
14	SIH2 singlet	-290.4621118	-0.30736367	-290.542026	275.272998	277.0583376	2.5	4.3
15	SIH2 3B1	-290.4356146	-0.2846346	-290.509620	361.367995	363.153335	0.7	2.5
16	SIH3 c3v	-291.0775176	-0.3127376	-291.158829	202.501546	204.2868865	2.1	3.9
17	SIH4 //b3lyp/6-31G*	-291.7208663	-0.34007171	-291.809285	42.307386	44.09272625	8.0	9.8
18	ph2 doublet	-342.3451068	-0.34687027	-342.435293	139.579573	139.5795735	1.1	1.1
19	PH3 c3v	-342.9732839	-0.3783224	-343.071648	17.906184	17.90618424	12.5	12.5
20	SH2 //b3lyp/6-31G*	-399.2203938	-0.39976694	-399.324333	-9.364796	-7.028101337	11.1	13.5
21	HCL //b3lyp/6-31G*	-460.6304602	-0.33791123	-460.718317	-88.133108	-84.61493798	4.3	7.9
22	DILITHIUM //b3lyp/6-31G*	-14.96410178	-0.05838025	-14.979281	230.623817	230.6238165	14.7	14.7
23	Lithium Fluoride,	-107.3100022	-0.36894983	-107.405929	-335.819038	-334.2174826	-0.7	0.9
24	ACETYLENE //b3lyp/6-31g*	-77.18894299	-0.421249	-77.298468	235.781484	236.5166235	9.0	9.7
25	ETHYLENE //b3lyp/6-31g*	-78.43155111	-0.44209823	-78.546497	66.007957	66.7430968	13.7	14.4
26	ETHANE //b3lyp/6-31g*	-79.65545837	-0.47552865	-79.779096	-64.562259	-63.82711872	19.5	20.3
27	CYANO RADICAL,	-92.56437353	-0.45780496	-92.683403	452.869115	453.2366848	14.0	14.3
28	HYDROGEN CYANIDE	-93.27558826	-0.46616248	-93.396791	131.521353	131.8889234	-0.3	0.1
29	CARBON MONOXIDE	-113.1671939	-0.47685808	-113.291177	-108.712728	-107.3999782	1.7	3.1
30	HCO BENT	-113.6932449	-0.49936292	-113.823079	38.188159	39.50090899	-3.7	-2.3
31	H2CO //b3lyp/6-31g*	-114.3360766	-0.51889122	-114.470988	-105.858098	-104.5453482	2.9	4.2

32	METHANOL //b3lyp/6-31g*	-115.5431752	-0.54834614	-115.685745	-186.653376	-185.3406259	14.2	15.5
33	Nitrogen N2,	-109.3740135	-0.50009924	-109.504039	3.510838	3.510837954	3.5	3.5
34	H2NNH2 //b3lyp/6-31g*	-111.6838125	-0.56320667	-111.830246	109.174960	109.1749597	13.8	13.8
35	NO radical,	-129.7224111	-0.54214542	-129.863369	90.985688	91.93086779	0.6	1.6
36	O2 //b3lyp/6-31g*	-150.133342	-0.60632426	-150.290986	-0.054694	1.835665743	-0.1	1.8
37	HYDROGEN PEROXIDE	-151.3508744	-0.63660412	-151.516391	-112.519368	-110.6290083	23.5	25.4
38	F2 //b3lyp/6-31g*	-199.3069675	-0.66535597	-199.479960	21.836878	25.03998755	21.8	25.0
39	CO2 D*H	-188.3447623	-0.80164521	-188.553190	-405.708779	-403.4508488	-12.4	-10.2
40	na2 //b3lyp/6-31G*	-324.3285484	-0.37290352	-324.425503	143.833194	143.8331941	1.6	1.6
41	SI2 3-SGG	-578.5791872	-0.56129425	-578.725124	590.298267	593.868947	5.0	8.5
42	P2 //b3lyp/6-31g*	-682.3852987	-0.71313305	-682.570713	156.197826	156.1978258	12.7	12.7
43	S2 //b3lyp/6-31g*	-796.0438073	-0.75991445	-796.241385	130.806172	135.4795621	2.4	7.0
44	CL2 //b3lyp/6-31g*	-920.0213712	-0.65452843	-920.191549	10.152293	17.18863288	10.2	17.2
45	Sodium Chloride	-622.2713166	-0.51087111	-622.404143	-174.136581	-170.6184112	8.3	11.8
46	SIO //b3lyp/6-31g*	-364.4948972	-0.61969892	-364.656019	-92.414821	-89.68430057	10.5	13.2
47	Carbon monosulfide,	-435.9875207	-0.57929812	-436.138138	290.571439	293.2757041	10.7	13.4
48	OS //b3lyp/6-31g*	-473.1088	-0.69025942	-473.288267	7.232107	10.51398167	2.2	5.5
49	CLO 2-PI	-535.0413293	-0.60860933	-535.199568	113.050787	117.5141368	11.8	16.3
50	CLF 1-SG	-559.6895026	-0.65706772	-559.860340	-48.739415	-43.61969012	6.5	11.6
51	si2h6 //b3lyp/6-31g*	-582.2674855	-0.66094313	-582.439331	97.856503	101.4271828	17.9	21.5
52	Methyl chloride,	-499.8564026	-0.56281889	-500.002735	-73.421006	-69.53526567	8.6	12.5
53	H3C-SH METHANETHIOL	-438.4492513	-0.62716903	-438.612315	-4.061703	-1.357438103	19.0	21.7
54	HOCl //b3lyp/6-31g*	-535.6891502	-0.64859102	-535.857784	-62.897951	-58.43460082	11.6	16.0
55	SO2 //b3lyp/6-31G*	-548.2717587	-1.03933996	-548.541987	-273.140923	-268.913868	23.9	28.2
56	BF3 PLANAR	-324.2515054	-1.07586706	-324.531231	-1143.750019	-1138.814079	-8.2	-3.3
57	bcl3 B3LYP	-1405.022035	-1.11462347	-1405.311837	-414.899618	-404.2138326	-12.0	-1.3
58	ALf3 B3LYP	-541.7920726	-1.21526309	-542.108041	-1189.921863	-1184.224528	19.3	25.0
59	alcl3 B3LYP	-1622.621834	-1.21677468	-1622.938195	-585.812135	-574.3649546	-1.3	10.1
60	cf4 B3LYP	-437.0615951	-1.47000183	-437.443796	-938.812747	-932.0389566	-5.8	1.0
61	ccl4 B3LYP	-1878.126745	-1.54588729	-1878.528676	-84.206342	-69.76609169	11.6	26.0
62	O=C=S. Singlet	-511.2229639	-0.89240393	-511.454989	-150.975811	-147.3263664	-12.5	-8.8
63	CS2 B3LYP	-834.097731	-0.99030411	-834.355210	108.479644	113.5206038	-8.3	-3.2
64	COF2 B3LYP	-312.6807331	-1.13662368	-312.976255	-614.483817	-609.967957	9.4	13.9
65	sif4 B3LYP	-688.6464917	-1.57103781	-689.054962	-1572.342095	-1564.150535	42.7	50.9
66	sicl4, td	-2129.694783	-1.60782043	-2130.112816	-641.004853	-625.146833	21.7	37.6
67	nno B3LYP	-184.4020043	-0.86062013	-184.625766	72.033779	72.97895934	-10.0	-9.0
68	clno B3LYP	-589.733357	-0.92888128	-589.974866	56.594182	61.05753217	4.7	9.2

69	nf3 c3v	-353.7090589	-1.25312691	-354.034872	-126.573383	-121.7687183	5.6	10.4
70	pf3 c3v	-640.56393	-1.3108895	-640.904761	-932.387251	-927.5825861	26.2	31.0
71	ozone 1-a1	-225.1036573	-1.03444509	-225.372613	169.286359	172.1218991	26.6	29.4
72	f2o B3LYP	-274.3606582	-0.98184106	-274.615937	47.659679	51.80796938	23.0	27.1
73	CLF3, C2V	-759.025733	-1.39091041	-759.387370	-147.453623	-139.130788	11.5	19.9
74	CF2=CF2 D2H	-475.0171954	-1.67356326	-475.452322	-684.370434	-677.2290738	-25.8	-18.7
75	cl2c=ccl2 B3LYP	-1916.154371	-1.74603024	-1916.608339	-14.195598	0.612221863	-1.6	13.2
76	cf3cn B3LYP	-429.9726097	-1.61458327	-430.392401	-506.525186	-500.9853813	-11.1	-5.6
77	PROPYNE C3V	-116.433441	-0.64646299	-116.601521	196.785581	197.8882912	11.9	13.0
78	ALLENE D2D	-116.4336407	-0.64016238	-116.600083	198.905511	200.0082213	8.5	9.6
79	CYCLOPROPENE C2V	-116.3939286	-0.64948459	-116.562795	297.743261	298.8459706	20.8	21.9
80	PROPENE CS	-117.6697772	-0.66980286	-117.843926	41.140641	42.24335084	21.1	22.2
81	CYCLOPROPANE D3H	-117.6560719	-0.67589985	-117.831806	75.443225	76.54593524	22.3	23.4
82	PROPANE C2V	-118.8886235	-0.70284283	-119.071363	-75.557648	-74.45493829	29.0	30.1
83	TRANS-1,3-BUTADIENE C2H	-155.6893683	-0.86641514	-155.914636	132.513409	133.9836886	22.5	23.9
84	Dimethyl acetylene	-155.6758533	-0.87229325	-155.902650	164.136720	165.6069996	18.5	20.0
85	Methylene cyclopropane.	-155.6566378	-0.87301615	-155.883622	212.688794	214.1590741	12.3	13.7
86	Bicyclo[1.1.0]butane. C2v	-155.640574	-0.88468219	-155.870591	248.833054	250.3033339	31.7	33.2
87	CYCLOBUTENE b3lyp	-155.6660783	-0.87531551	-155.893660	188.696125	190.1664055	32.2	33.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8901286	-0.90441628	-157.125277	62.396808	63.8670882	33.9	35.4
89	Isobutene. Single	-156.9077554	-0.90026844	-157.141825	14.160015	15.63029529	30.9	32.4
90	Trans butane	-158.1216581	-0.93068968	-158.363637	-86.582008	-85.11172816	38.9	40.4
91	isobutane B3LYP/6-31G*	-158.1226623	-0.93392125	-158.365482	-92.718690	-91.2484096	41.6	43.1
92	Spiropentane. D2d	-194.8837635	-1.10707134	-195.171602	214.875456	216.7133056	29.5	31.4
93	Benzene B3LYP	-231.8109597	-1.27233639	-232.141767	98.181162	100.3865817	15.8	18.0
94	DIFLUOROMETHANE C2V	-238.725572	-0.86004738	-238.949184	-450.392016	-446.8213363	0.2	3.8
95	HCF3 TRI-FLUOROMETHANE	-337.8954067	-1.16625227	-338.198632	-699.432850	-694.2606146	-2.4	2.8
96	CH2CL2 C2V	-959.2859212	-0.88309134	-959.515525	-85.837147	-78.43323743	9.6	17.0
97	chcl3 B3LYP/6-31G*	-1418.710162	-1.21105129	-1419.025035	-91.764602	-80.84252223	11.6	22.5
98	METHYLAMINE b3lyp	-95.68083393	-0.51914489	-95.815812	-6.787051	-6.419480777	16.2	16.6
99	Acetonitrile. CH3-CN.	-132.5261285	-0.68911542	-132.705299	78.706455	79.4415948	3.4	4.1
100	NITRO METHANE	-244.6541408	-1.13979273	-244.950487	-66.870122	-64.61219209	7.6	9.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6501252	-1.12971175	-244.943850	-53.173664	-50.91573364	13.4	15.6
102	Methylsilane. CH3-SiH3.	-330.9691181	-0.56922252	-331.117116	-6.338392	-4.185482183	22.9	25.1
103	Formic Acid.	-189.5085051	-0.82371687	-189.722671	-374.118327	-371.8603975	4.5	6.8
104	Methyl formate.	-228.7290292	-1.04838776	-229.001610	-350.729472	-348.1039723	4.9	7.5
105	acetamide ch3cohn2	-208.8872308	-1.01768847	-209.151830	-225.773798	-224.0934783	12.7	14.4

106	Aziridine. (cyclic	-133.6762757	-0.72133763	-133.863824	144.122344	144.8574837	17.8	18.5
107	Cyanogen. NCCN.	-185.3634338	-0.9222198	-185.603211	297.083586	297.8187256	-9.6	-8.9
108	DIMETHYLAMINE b3lyp	-134.9051959	-0.74539056	-135.098997	4.759978	5.495118202	23.2	23.9
109	TRANS ETHYLAMINE	-134.9167332	-0.74655034	-135.110836	-25.385495	-24.65035505	21.9	22.6
110	KETENE B3LYP	-152.3686308	-0.72104882	-152.556103	-53.421294	-51.74097382	-6.1	-4.5
111	OXIRANE B3LYP	-153.538991	-0.75222737	-153.734570	-38.201259	-36.52093879	14.5	16.2
112	Acetaldehyde B3LYP	-153.5846279	-0.74458181	-153.778219	-155.920919	-154.2405989	10.2	11.9
113	Glyoxal, O=CH-CH=O.	-227.5000054	-1.01581055	-227.764116	-210.815902	-208.190402	1.3	3.9
114	ETHANOL TRANS	-154.7815221	-0.77498833	-154.983019	-211.096662	-209.416342	24.0	25.7
115	DIMETHYL ETHER,	-154.7647511	-0.77204559	-154.965483	-165.898253	-164.2179331	18.2	19.9
116	Thiooxirane. (cyclic	-476.4636887	-0.83704784	-476.681321	99.068952	102.1407871	17.1	20.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.7817869	-1.18217193	-553.089152	-112.442925	-108.4259097	39.0	43.0
118	Thioethanol. CH3-CH2-SH.	-477.682945	-0.85588448	-477.905475	-17.015559	-13.94372367	29.4	32.5
119	ch3sch3 B3LYP	-477.6809544	-0.85781879	-477.903987	-10.583794	-7.51195913	26.7	29.7
120	Vinyl fluoride,	-177.5834923	-0.7502888	-177.778567	-136.054298	-133.7176028	2.9	5.2
121	Ethyl chloride.	-539.0932279	-0.79087155	-539.298855	-94.310001	-90.05669073	17.8	22.1
122	Vinyl chloride,	-537.8690736	-0.76220084	-538.067246	32.604351	36.8576615	9.6	13.8
123	h2c=chcn B3LYP	-170.5368245	-0.88651149	-170.767317	192.772166	193.8748763	12.0	13.1
124	ACETONE B3LYP	-192.8294855	-0.97185428	-193.082168	-198.040864	-195.9929737	19.1	21.2
125	CH3COOH ACETIC	-228.7548207	-1.04782398	-229.027255	-418.514493	-415.8889926	14.1	16.7
126	CH3CFO HCCO	-252.7660321	-1.0562186	-253.040649	-436.000004	-432.7181286	6.2	9.5
127	ch3c(o)cl hcco	-613.0381821	-1.07251653	-613.317036	-235.478526	-230.2800363	7.2	12.4
128	ch3ch2ch2cl B3LYP	-578.3263759	-1.01897668	-578.591310	-105.713700	-101.0928202	26.1	30.7
129	Isopropyl alcohol,	-194.0195044	-1.00508384	-194.280826	-238.336823	-236.288933	34.5	36.5
130	Methyl ethyl	-194.0030048	-0.99930196	-194.262823	-190.521588	-188.4736977	25.8	27.8
131	Trimethyl Amine.	-174.1319048	-0.97650815	-174.385797	5.514681	6.617391492	29.4	30.5
132	FURAN B3LYP	-229.6397676	-1.15651734	-229.940462	-21.903330	-19.48787012	12.8	15.2
133	Thiophene b3lyp	-552.5540069	-1.24847617	-552.878611	135.605354	139.4123293	20.5	24.4
134	PYROLE PLANAR	-209.7916289	-1.12865895	-210.085080	119.407964	120.8782443	11.0	12.5
135	C2v Pyridine	-247.8387051	-1.31669044	-248.181045	146.069680	147.9075302	5.5	7.3
136	H2 B3LYP/6-31G*	-1.16024794	-0.03499336	-1.169346	7.460079	7.460079403	7.5	7.5
137	SH b3lyp/6-31G*	-398.5819213	-0.36066974	-398.675695	147.540383	149.8770777	4.4	6.8
138	CCH B3LYP	-76.4748441	-0.38364715	-76.574592	582.459244	583.194384	17.2	17.9
139	C2H3 CS,2-A'	-77.75581594	-0.40525258	-77.861182	305.876880	306.6120201	6.3	7.0
140	ch3co hcco	-152.9425041	-0.72250348	-153.130355	-8.314516	-6.634195686	1.7	3.4
141	H2COH C1	-114.890591	-0.51582781	-115.024706	-9.069171	-7.756421211	8.1	9.4
142	ch3o CS,	-114.8837116	-0.48895946	-115.010841	23.760477	25.07322724	6.6	7.9

143	ch3ch2o 2A"	-154.1218218	-0.71575725	-154.307919	-0.750668	0.929652403	14.7	16.4
144	ch3s 2-A'	-437.8162251	-0.59103273	-437.969894	132.679100	135.3833654	8.0	10.7
145	c2h5 staggered	-78.99565027	-0.43649618	-79.109139	134.024624	134.7597637	13.1	13.8
146	(ch3)2ch Cs	-118.2334239	-0.66534333	-118.406413	109.995905	111.0986151	20.0	21.1
147	TERT-BUTYL RADICAL	-157.4713141	-0.89624237	-157.704337	83.998215	85.46849525	32.5	34.0
148	NO2 RADICAL	-204.7982471	-0.91108276	-205.035129	25.472976	27.36333631	-7.6	-5.7

MAD	**13.3**	**15.2**
LD	**42.7**	**50.9**

Table S5.28b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498707	0.000000	-0.498707
2	li	-7.469220	-0.014620	-7.473021
3	be	-14.638384	-0.053767	-14.652364
4	b	-24.618104	-0.077712	-24.638309
5	c	-37.801766	-0.104509	-37.828938
6	n	-54.535390	-0.135265	-54.570559
7	o	-74.999560	-0.192613	-75.049639
8	f	-99.647034	-0.255682	-99.713512
9	na	-162.154764	-0.172106	-162.199511
10	al	-242.237610	-0.220834	-242.295027
11	si	-289.238738	-0.250926	-289.303979
12	p	-341.121532	-0.280050	-341.194345
13	s	-397.956562	-0.321434	-398.040135
14	cl	-459.975521	-0.292388	-460.051542

Table S5.29a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0482858	-0.04697919	-8.060970	146.747173	146.7471731	7.4	7.4
2	BERYLLIUM HYDRIDE	-15.22403644	-0.05533521	-15.238977	319.285463	319.2854633	-22.5	-22.5
3	DOUBLET CH	-38.42033339	-0.14546425	-38.459609	599.752127	600.1196966	3.5	3.9
4	CH2 3-B1	-39.08363511	-0.16451755	-39.128055	395.618695	395.9862648	3.6	3.9
5	Singlet methylene,	-39.06054305	-0.18505102	-39.110507	440.078972	440.4465424	10.0	10.3
6	Methyl radical,	-39.75634312	-0.20958377	-39.812931	152.271377	152.6389468	5.8	6.2
7	ch4 //b3lyp/6-31G*	-40.42136524	-0.25159701	-40.489296	-63.428915	-63.06134534	11.5	11.8
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15032256	-0.1886275	-55.201252	358.560904	358.5609044	2.1	2.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79198508	-0.24253357	-55.857469	188.637612	188.6376118	-0.1	-0.1
10	AMMONIA, //b3lyp/6-31G*	-56.45791558	-0.29691795	-56.538083	-36.663052	-36.66305154	9.4	9.4
11	OH RADICAL	-75.64638173	-0.25981757	-75.716532	41.918972	42.86415199	2.6	3.5
12	Water //b3lyp/6-31G*	-76.32377165	-0.32905691	-76.412617	-229.265610	-228.3204299	12.6	13.5
13	HYDROGEN FLUORIDE,	-100.3422055	-0.33958859	-100.433894	-265.841366	-264.2398106	6.5	8.1
14	SIH2 singlet	-290.4561376	-0.30735585	-290.539124	275.526727	277.3120667	2.7	4.5
15	SIH2 3B1	-290.4298354	-0.28460799	-290.506680	361.719587	363.504927	1.1	2.8
16	SIH3 c3v	-291.0713629	-0.31272268	-291.155798	203.093198	204.8785377	2.7	4.5
17	SIH4 //b3lyp/6-31G*	-291.7143738	-0.34006276	-291.806191	43.063858	44.84919844	8.8	10.5
18	ph2 doublet	-342.3386752	-0.34687002	-342.432330	139.818500	139.8184998	1.3	1.3
19	PH3 c3v	-342.9665246	-0.37831336	-343.068669	18.186179	18.18617859	12.7	12.7
20	SH2 //b3lyp/6-31G*	-399.2133754	-0.39976129	-399.321311	-9.546529	-7.209834246	11.0	13.3
21	HCL //b3lyp/6-31G*	-460.6231891	-0.33790899	-460.714425	-88.403506	-84.88533639	4.1	7.6
22	DILITHIUM //b3lyp/6-31G*	-14.9627638	-0.05837613	-14.978525	230.554285	230.5542852	14.7	14.7
23	Lithium Fluoride,	-107.3058254	-0.3689647	-107.405446	-337.309542	-335.7079871	-2.2	-0.6
24	ACETYLENE //b3lyp/6-31g*	-77.18449466	-0.4212304	-77.298227	233.516134	234.2512739	6.7	7.5
25	ETHYLENE //b3lyp/6-31g*	-78.42656585	-0.44208415	-78.545929	64.601716	65.33685616	12.3	13.0
26	ETHANE //b3lyp/6-31g*	-79.64993681	-0.47551709	-79.778326	-65.439946	-64.70480578	18.7	19.4
27	CYANO RADICAL,	-92.56010546	-0.45771548	-92.683689	449.161566	449.5291364	10.3	10.6
28	HYDROGEN CYANIDE	-93.27094198	-0.46614721	-93.396802	128.534762	128.9023324	-3.3	-2.9
29	CARBON MONOXIDE	-113.1623448	-0.47685186	-113.291095	-111.666789	-110.3540385	-1.2	0.1
30	HCO BENT	-113.6881623	-0.49935063	-113.822987	35.260591	36.57334128	-6.6	-5.3
31	H2CO //b3lyp/6-31g*	-114.3306696	-0.51888621	-114.470769	-108.451646	-107.1388961	0.3	1.6

32	METHANOL //b3lyp/6-31g*	-115.5372136	-0.54834334	-115.685266	-188.565806	-187.2530558	12.3	13.6
33	Nitrogen N2,	-109.3691758	-0.50008381	-109.504198	0.076713	0.076712572	0.1	0.1
34	H2NNH2 //b3lyp/6-31g*	-111.6778437	-0.56320593	-111.829909	107.043107	107.043107	11.6	11.6
35	NO radical,	-129.7171304	-0.54213585	-129.863507	87.393549	88.33872879	-3.0	-2.0
36	O2 //b3lyp/6-31g*	-150.1276192	-0.60632315	-150.291326	-4.389673	-2.499313322	-4.4	-2.5
37	HYDROGEN PEROXIDE	-151.3445111	-0.63660919	-151.516396	-115.972014	-114.0816545	20.0	21.9
38	F2 //b3lyp/6-31g*	-199.3002106	-0.66535983	-199.479858	18.639206	21.84231575	18.6	21.8
39	CO2 D*H	-188.3368508	-0.80163185	-188.553291	-410.865608	-408.6076776	-17.6	-15.3
40	na2 //b3lyp/6-31G*	-324.3201208	-0.37289801	-324.420803	143.722776	143.7227763	1.5	1.5
41	SI2 3-SGG	-578.5682059	-0.56127588	-578.719750	589.671530	593.2422102	4.3	7.9
42	P2 //b3lyp/6-31g*	-682.3731554	-0.71310944	-682.565695	154.293154	154.2931542	10.8	10.8
43	S2 //b3lyp/6-31g*	-796.030738	-0.75990513	-796.235912	128.941523	133.6149133	0.5	5.2
44	CL2 //b3lyp/6-31g*	-920.007242	-0.6545208	-920.183963	9.088420	16.1247598	9.1	16.1
45	Sodium Chloride	-622.2599873	-0.5108736	-622.397923	-174.521780	-171.0036098	7.9	11.4
46	SIO //b3lyp/6-31g*	-364.4863713	-0.61970765	-364.653692	-95.394730	-92.66420972	7.5	10.3
47	Carbon monosulfide,	-435.9790377	-0.57927793	-436.135443	288.082811	290.7870756	8.2	10.9
48	OS //b3lyp/6-31g*	-473.0993943	-0.6902513	-473.285762	3.972016	7.25389071	-1.0	2.2
49	CLO 2-PI	-535.0314123	-0.6085669	-535.195725	110.927373	115.3907227	9.7	14.1
50	CLF 1-SG	-559.6790399	-0.65706723	-559.856448	-50.744142	-45.62441716	4.5	9.6
51	si2h6 //b3lyp/6-31g*	-582.2548682	-0.66092636	-582.433318	98.907485	102.4781646	19.0	22.6
52	Methyl chloride,	-499.8465772	-0.56280997	-499.998536	-74.334250	-70.44850988	7.7	11.6
53	H3C-SH METHANETHIOL	-438.4396658	-0.62715741	-438.608998	-4.918486	-2.214221193	18.1	20.8
54	HOCl //b3lyp/6-31g*	-535.6788977	-0.64858897	-535.854017	-65.218880	-60.75552996	9.3	13.7
55	SO2 //b3lyp/6-31G*	-548.2592123	-1.03932979	-548.539831	-279.039480	-274.812425	18.0	22.3
56	BF3 PLANAR	-324.2395703	-1.0758679	-324.530055	-1147.138990	-1142.20305	-11.6	-6.7
57	bcl3 B3LYP	-1404.999147	-1.11460505	-1405.300090	-416.808618	-406.1228329	-13.9	-3.2
58	ALf3 B3LYP	-541.7765437	-1.21527133	-542.104667	-1193.477248	-1187.779913	15.7	21.4
59	alcl3 B3LYP	-1622.595356	-1.21675899	-1622.923881	-586.916143	-575.4689634	-2.4	9.0
60	cf4 B3LYP	-437.0456799	-1.46999434	-437.442578	-943.998250	-937.2244599	-11.0	-4.2
61	ccl4 B3LYP	-1878.096226	-1.54586219	-1878.513609	-88.058363	-73.61811265	7.8	22.2
62	O=C=S. Singlet	-511.2114158	-0.89238223	-511.452359	-155.357549	-151.7081038	-16.9	-13.2
63	CS2 B3LYP	-834.0825357	-0.99027355	-834.349910	104.713908	109.7548678	-12.0	-7.0
64	COF2 B3LYP	-312.6688256	-1.1366142	-312.975711	-619.692165	-615.1763047	4.1	8.7
65	sif4 B3LYP	-688.6269442	-1.57103416	-689.051123	-1576.564715	-1568.373155	38.5	46.7
66	sicl4, td	-2129.660632	-1.60779487	-2130.094737	-642.865505	-627.0074847	19.9	35.7
67	nno B3LYP	-184.3941296	-0.86059738	-184.626491	65.391847	66.33702667	-16.6	-15.7
68	clno B3LYP	-589.7209292	-0.92886234	-589.971722	51.129351	55.59270148	-0.8	3.7

69	nf3 c3v	-353.6962801	-1.25312115	-354.034623	-132.626947	-127.8222825	-0.4	4.4
70	pf3 c3v	-640.5474106	-1.31088637	-640.901350	-936.170026	-931.3653611	22.4	27.2
71	ozone 1-a1	-225.0948798	-1.0344221	-225.374174	160.025687	162.8612266	17.4	20.2
72	f2o B3LYP	-274.3509315	-0.98183937	-274.616028	42.232882	46.38117194	17.5	21.7
73	CLF3, C2V	-759.0083037	-1.39090863	-759.383849	-153.899949	-145.5771138	5.1	13.4
74	CF2=CF2 D2H	-474.9992423	-1.67355376	-475.451102	-690.997115	-683.8557549	-32.4	-25.3
75	cl2c=ccl2 B3LYP	-1916.121767	-1.7459995	-1916.593187	-19.273861	-4.466040716	-6.7	8.1
76	cf3cn B3LYP	-429.9556709	-1.61455978	-430.391602	-514.031767	-508.4919615	-18.6	-13.1
77	PROPYNE C3V	-116.4264079	-0.64643918	-116.600946	193.948326	195.0510362	9.0	10.1
78	ALLENE D2D	-116.4266041	-0.64014051	-116.599442	196.241519	197.3442291	5.9	7.0
79	CYCLOPROPENE C2V	-116.3868397	-0.64946704	-116.562196	294.968765	296.071475	18.0	19.1
80	PROPENE CS	-117.6622056	-0.66978332	-117.843047	39.101586	40.20429617	19.0	20.1
81	CYCLOPROPANE D3H	-117.6484313	-0.67588483	-117.830920	73.421787	74.52449689	20.3	21.4
82	PROPANE C2V	-118.8805173	-0.70282527	-119.070280	-77.062189	-75.95947871	27.5	28.6
83	TRANS-1,3-BUTADIENE C2H	-155.6797469	-0.86638758	-155.913672	129.250710	130.7209897	19.2	20.7
84	Dimethyl acetylene	-155.6662358	-0.87226414	-155.901747	160.710550	162.1808303	15.1	16.6
85	Methylene cyclopropane.	-155.646954	-0.87299305	-155.882662	209.413429	210.883709	9.0	10.5
86	Bicyclo[1.1.0]butane. C2v	-155.6308219	-0.88466251	-155.869681	245.428478	246.898758	28.3	29.7
87	CYCLOBUTENE b3lyp	-155.6563699	-0.87529221	-155.892699	185.425120	186.8953998	28.9	30.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.8798859	-0.90439489	-157.124073	59.763107	61.23338745	31.3	32.8
89	Isobutene. Single	-156.8975896	-0.90024324	-157.140655	11.436200	12.90647976	28.2	29.6
90	Trans butane	-158.1109665	-0.93066586	-158.362246	-88.724997	-87.25471744	36.8	38.3
91	isobutane B3LYP/6-31G*	-158.1119615	-0.9338975	-158.364114	-94.922498	-93.45221755	39.4	40.9
92	Spiropentane. D2d	-194.8714256	-1.10704666	-195.170328	210.975696	212.813546	25.6	27.5
93	Benzene B3LYP	-231.797069	-1.27229861	-232.140590	92.579822	94.78524202	10.2	12.4
94	DIFLUOROMETHANE C2V	-238.7161636	-0.86004755	-238.948376	-453.185891	-449.6152109	-2.6	1.0
95	HCF3 TRI-FLUOROMETHANE	-337.8827466	-1.16625002	-338.197634	-703.460286	-698.2880513	-6.4	-1.2
96	CH2CL2 C2V	-959.2692058	-0.88307803	-959.507637	-87.556738	-80.15282782	7.8	15.2
97	chcl3 B3LYP/6-31G*	-1418.686547	-1.21103248	-1419.013526	-94.468247	-83.54616656	8.9	19.8
98	METHYLAMINE b3lyp	-95.67508587	-0.51913854	-95.815253	-8.278295	-7.910724869	14.7	15.1
99	Acetonitrile. CH3-CN.	-132.5188976	-0.68909444	-132.704953	75.207335	75.94247543	-0.1	0.6
100	NITRO METHANE	-244.6429167	-1.13977255	-244.950655	-73.711210	-71.45327969	0.8	3.0
101	Methyl-nitrite. CH3-O-N=O.	-244.6389378	-1.12969044	-244.943954	-59.845761	-57.5878312	6.7	8.9
102	Methylsilane. CH3-SiH3.	-330.9600421	-0.56920854	-331.113728	-6.260465	-4.107554718	23.0	25.2
103	Formic Acid.	-189.5000472	-0.82371104	-189.722449	-378.425439	-376.1675087	0.2	2.5
104	Methyl formate.	-228.7180005	-1.04837234	-229.001061	-355.627724	-353.0022243	0.0	2.6
105	acetamide ch3cohn2	-208.8763888	-1.01767433	-209.151161	-230.144673	-228.4643527	8.3	10.0

106	Aziridine. (cyclic	-133.668429	-0.72132517	-133.863187	141.388078	142.1232184	15.0	15.8
107	Cyanogen. NCCN.	-185.3545102	-0.92218666	-185.603501	290.408722	291.1438619	-16.3	-15.5
108	DIMETHYLAMINE b3lyp	-134.8968665	-0.74537706	-135.098118	2.662086	3.397225555	21.1	21.8
109	TRANS ETHYLAMINE	-134.9084002	-0.74653763	-135.109965	-27.504893	-26.76975343	19.8	20.5
110	KETENE B3LYP	-152.3611585	-0.72103343	-152.555838	-57.341763	-55.66144262	-10.1	-8.4
111	OXIRANE B3LYP	-153.5309423	-0.75221739	-153.734041	-41.430922	-39.75060231	11.3	13.0
112	Acetaldehyde B3LYP	-153.5766326	-0.74457034	-153.777667	-159.088889	-157.4085686	7.0	8.7
113	Glyoxal, O=CH-CH=O.	-227.4895537	-1.01579704	-227.763819	-216.375186	-213.7496855	-4.2	-1.6
114	ETHANOL TRANS	-154.7729751	-0.77497915	-154.982219	-213.615985	-211.935665	21.5	23.2
115	DIMETHYL ETHER,	-154.7562172	-0.77203443	-154.964666	-168.373384	-166.6930637	15.7	17.4
116	Thiooxirane. (cyclic	-476.451993	-0.83703072	-476.677991	96.796953	99.86878836	14.8	17.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.7665798	-1.18215377	-553.085761	-116.277114	-112.2600985	35.2	39.2
118	Thioethanol. CH3-CH2-SH.	-477.6707753	-0.85586669	-477.901859	-18.537020	-15.46518517	27.9	31.0
119	ch3sch3 B3LYP	-477.668792	-0.857801	-477.900398	-12.175260	-9.103424596	25.1	28.1
120	Vinyl fluoride,	-177.5752662	-0.75027861	-177.777841	-138.779010	-136.4423154	0.1	2.5
121	Ethyl chloride.	-539.0808186	-0.79085638	-539.294350	-95.870885	-91.61757516	16.3	20.5
122	Vinyl chloride,	-537.8571922	-0.7621837	-538.062982	30.411454	34.66476408	7.4	11.7
123	h2c=chcn B3LYP	-170.5275509	-0.88648275	-170.766901	188.010183	189.1128927	7.3	8.4
124	ACETONE B3LYP	-192.8188979	-0.97183584	-193.081294	-201.813662	-199.7657715	15.3	17.4
125	CH3COOH ACETIC	-228.7437722	-1.04781127	-229.026681	-423.347905	-420.722405	9.3	11.9
126	CH3CFO HCCO	-252.7547863	-1.0562055	-253.039962	-440.547782	-437.2659068	1.7	5.0
127	ch3c(o)cl hcco	-613.0232951	-1.07249756	-613.312869	-239.647268	-234.4487784	3.0	8.2
128	ch3ch2ch2cl B3LYP	-578.311382	-1.01895534	-578.586500	-107.922215	-103.3013351	23.9	28.5
129	Isopropyl alcohol,	-194.0083634	-1.00506779	-194.279732	-241.530989	-239.4830992	31.3	33.3
130	Methyl ethyl	-193.9918852	-0.9992841	-194.261692	-193.618696	-191.5708058	22.7	24.7
131	Trimethyl Amine.	-174.1209811	-0.97648805	-174.384633	2.716022	3.818732153	26.6	27.7
132	FURAN B3LYP	-229.6275132	-1.15649127	-229.939766	-27.591888	-25.17642834	7.1	9.6
133	Thiophene b3lyp	-552.5381088	-1.24844345	-552.875188	130.678242	134.4852167	15.6	19.4
134	PYROLE PLANAR	-209.7795659	-1.12863128	-210.084296	114.162528	115.6328078	5.8	7.3
135	C2v Pyridine	-247.8246076	-1.31665458	-248.180104	139.785838	141.6236884	-0.8	1.0
136	H2 B3LYP/6-31G*	-1.15986532	-0.03499366	-1.169314	7.545685	7.545684881	7.5	7.5
137	SH b3lyp/6-31G*	-398.5752428	-0.3606716	-398.672624	147.487284	149.8239793	4.4	6.7
138	CCH B3LYP	-76.47078991	-0.38362681	-76.574369	580.147550	580.8826898	14.9	15.6
139	C2H3 CS,2-A'	-77.75119002	-0.4052313	-77.860602	304.499679	305.2348188	4.9	5.7
140	ch3co hcco	-152.9348395	-0.72248271	-153.129910	-11.764295	-10.08397535	-1.7	0.0
141	H2COH C1	-114.8849618	-0.51581902	-115.024233	-10.996486	-9.683736173	6.2	7.5
142	ch3o CS,	-114.8781153	-0.48894375	-115.010130	22.457065	23.76981483	5.3	6.6

143	ch3ch2o 2A"	-154.1136412	-0.71573265	-154.306889	-2.665852	-0.985531962	12.8	14.5
144	ch3s 2-A'	-437.8069689	-0.59102474	-437.966546	131.903925	134.6081904	7.2	9.9
145	c2h5 staggered	-78.99047545	-0.43648871	-79.108327	133.258469	133.993609	12.3	13.1
146	(ch3)2ch Cs	-118.2256573	-0.66532594	-118.405295	108.584384	109.6870937	18.6	19.7
147	TERT-BUTYL RADICAL	-157.460953	-0.89621474	-157.702931	81.894587	83.36486693	30.4	31.9
148	NO2 RADICAL	-204.7899271	-0.91106117	-205.035914	18.461794	20.35215411	-14.6	-12.7

MAD	**11.9**	**13.5**
LD	**39.4**	**46.7**

Table S5.29b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498707	0.000000	-0.498707
2	li	-7.468683	-0.014620	-7.472631
3	be	-14.637435	-0.053762	-14.651951
4	b	-24.616839	-0.077715	-24.637822
5	c	-37.800167	-0.104515	-37.828386
6	n	-54.533462	-0.135269	-54.569984
7	o	-74.996975	-0.192624	-75.048984
8	f	-99.643815	-0.255692	-99.712851
9	na	-162.150672	-0.172104	-162.197140
10	al	-242.232654	-0.220836	-242.292279
11	si	-289.233423	-0.250927	-289.301173
12	p	-341.115861	-0.280045	-341.191473
13	s	-397.950256	-0.321437	-398.037044
14	cl	-459.968601	-0.292391	-460.047547

Table S5.30a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0473976	-0.04698042	-8.060552	146.818552	146.818552	7.5	7.5
2	BERYLLIUM HYDRIDE	-15.22295527	-0.05532771	-15.238447	319.592558	319.5925581	-22.2	-22.2
3	DOUBLET CH	-38.41835585	-0.14546824	-38.459087	599.673605	600.041175	3.5	3.8
4	CH2 3-B1	-39.08148306	-0.16451604	-39.127548	395.502148	395.869718	3.5	3.8
5	Singlet methylene,	-39.05821545	-0.18504735	-39.110029	439.885814	440.2533839	9.8	10.1
6	Methyl radical,	-39.7537575	-0.20958741	-39.812442	152.106168	152.4737385	5.7	6.0
7	ch4 //b3lyp/6-31G*	-40.41841917	-0.25159114	-40.488865	-63.743829	-63.37625857	11.1	11.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14794216	-0.18863777	-55.200761	358.342730	358.3427296	1.9	1.9
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78918892	-0.24254052	-55.857100	188.098152	188.0981517	-0.6	-0.6
10	AMMONIA, //b3lyp/6-31G*	-56.45473624	-0.29691901	-56.537874	-37.620005	-37.62000454	8.4	8.4
11	OH RADICAL	-75.64337127	-0.25982776	-75.716123	41.273582	42.21876235	1.9	2.9
12	Water //b3lyp/6-31G*	-76.32036746	-0.32906333	-76.412505	-230.692369	-229.7471888	11.1	12.1
13	HYDROGEN FLUORIDE,	-100.338582	-0.33959739	-100.433669	-266.982644	-265.3810889	5.4	7.0
14	SIH2 singlet	-290.4501635	-0.30734803	-290.536221	275.780956	277.5662962	3.0	4.8
15	SIH2 3B1	-290.4240565	-0.28458141	-290.503739	362.072250	363.8575902	1.4	3.2
16	SIH3 c3v	-291.0652082	-0.31270777	-291.152766	203.685583	205.4709234	3.3	5.1
17	SIH4 //b3lyp/6-31G*	-291.7078814	-0.34005381	-291.803096	43.820890	45.60623038	9.5	11.3
18	ph2 doublet	-342.3322437	-0.34686979	-342.429367	140.057108	140.0571078	1.6	1.6
19	PH3 c3v	-342.9597653	-0.37830432	-343.065691	18.466357	18.46635724	13.0	13.0
20	SH2 //b3lyp/6-31G*	-399.2063571	-0.39975563	-399.318289	-9.727771	-7.391076187	10.8	13.1
21	HCL //b3lyp/6-31G*	-460.6159181	-0.33790676	-460.710532	-88.673616	-85.15544599	3.8	7.3
22	DILITHIUM //b3lyp/6-31G*	-14.9614259	-0.05837201	-14.977770	230.484810	230.4848105	14.6	14.6
23	Lithium Fluoride,	-107.3016486	-0.36897959	-107.404963	-338.800309	-337.1987542	-3.7	-2.1
24	ACETYLENE //b3lyp/6-31g*	-77.18004641	-0.4212118	-77.297986	231.252372	231.9875121	4.5	5.2
25	ETHYLENE //b3lyp/6-31g*	-78.42158066	-0.44207006	-78.545360	63.196860	63.93199968	10.9	11.6
26	ETHANE //b3lyp/6-31g*	-79.64441533	-0.47550552	-79.777557	-66.316407	-65.58126726	17.8	18.5
27	CYANO RADICAL,	-92.55583754	-0.45762611	-92.683973	445.458964	445.826534	6.6	6.9
28	HYDROGEN CYANIDE	-93.26629575	-0.46613195	-93.396813	125.549557	125.9171265	-6.2	-5.9
29	CARBON MONOXIDE	-113.1574958	-0.47684563	-113.291013	-114.619633	-113.3068827	-4.2	-2.8
30	HCO BENT	-113.6830798	-0.49933833	-113.822894	32.334506	33.64725592	-9.5	-8.2
31	H2CO //b3lyp/6-31g*	-114.3252626	-0.51888119	-114.470549	-111.044041	-109.7312915	-2.3	-0.9

32	METHANOL //b3lyp/6-31g*	-115.5312521	-0.54834055	-115.684787	-190.477240	-189.1644902	10.4	11.7
33	Nitrogen N2,	-109.364338	-0.50006839	-109.504357	-3.356092	-3.356092184	-3.4	-3.4
34	H2NNH2 //b3lyp/6-31g*	-111.6718749	-0.5632052	-111.829572	104.911699	104.9116985	9.5	9.5
35	NO radical,	-129.7118498	-0.54212629	-129.863645	83.802714	84.74789414	-6.6	-5.6
36	O2 //b3lyp/6-31g*	-150.1218964	-0.60632204	-150.291667	-8.723415	-6.833054727	-8.7	-6.8
37	HYDROGEN PEROXIDE	-151.3381478	-0.63661425	-151.516400	-119.423845	-117.5334852	16.6	18.4
38	F2 //b3lyp/6-31g*	-199.2934538	-0.66536369	-199.479756	15.442452	18.64556183	15.4	18.6
39	CO2 D*H	-188.3289393	-0.8016185	-188.553392	-416.020205	-413.7622748	-22.7	-20.5
40	na2 //b3lyp/6-31G*	-324.3116934	-0.37289249	-324.416103	143.612347	143.6123465	1.4	1.4
41	SI2 3-SGG	-578.5572246	-0.56125754	-578.714377	589.045916	592.6165956	3.7	7.3
42	P2 //b3lyp/6-31g*	-682.3610122	-0.71308583	-682.560676	152.389168	152.3891679	8.9	8.9
43	S2 //b3lyp/6-31g*	-796.0176687	-0.75989581	-796.230440	127.077790	131.7511804	-1.4	3.3
44	CL2 //b3lyp/6-31g*	-919.9931129	-0.65451317	-920.176377	8.025383	15.06172321	8.0	15.1
45	Sodium Chloride	-622.248658	-0.51087609	-622.391703	-174.906941	-171.3887707	7.5	11.0
46	SIO //b3lyp/6-31g*	-364.4778455	-0.6197164	-364.651366	-98.374446	-95.64392564	4.6	7.3
47	Carbon monosulfide,	-435.9705548	-0.57925774	-436.132747	285.595814	288.3000786	5.7	8.4
48	OS //b3lyp/6-31g*	-473.0899888	-0.69024318	-473.283257	0.713088	3.994963368	-4.3	-1.0
49	CLO 2-PI	-535.0214955	-0.60852448	-535.191882	108.806934	113.2702844	7.6	12.0
50	CLF 1-SG	-559.6685773	-0.65706674	-559.852556	-52.748052	-47.62832715	2.5	7.6
51	si2h6 //b3lyp/6-31g*	-582.242251	-0.66090959	-582.427306	99.959605	103.5302855	20.0	23.6
52	Methyl chloride,	-499.8367519	-0.56280105	-499.994336	-75.246515	-71.3607753	6.8	10.6
53	H3C-SH METHANETHIOL	-438.4300803	-0.62714579	-438.605681	-5.774114	-3.069849064	17.2	19.9
54	HOCl //b3lyp/6-31g*	-535.6686454	-0.64858693	-535.850250	-67.538954	-63.0756037	6.9	11.4
55	SO2 //b3lyp/6-31G*	-548.2466659	-1.03931962	-548.537675	-284.936163	-280.7091079	12.1	16.4
56	BF3 PLANAR	-324.2276353	-1.07586875	-324.528879	-1150.526052	-1145.590112	-15.0	-10.1
57	bcl3 B3LYP	-1404.976259	-1.11458663	-1405.288344	-418.715705	-408.0299197	-15.8	-5.1
58	ALf3 B3LYP	-541.761015	-1.21527956	-542.101293	-1197.031135	-1191.3338	12.1	17.8
59	alcl3 B3LYP	-1622.568878	-1.2167433	-1622.909567	-588.018418	-576.5712384	-3.5	7.9
60	cf4 B3LYP	-437.0297648	-1.46998685	-437.441361	-949.180682	-942.4068918	-16.1	-9.4
61	ccl4 B3LYP	-1878.065707	-1.54583708	-1878.498541	-91.907723	-77.46747346	3.9	18.3
62	O=C=S. Singlet	-511.1998679	-0.89236053	-511.449729	-159.736999	-156.0875539	-21.2	-17.6
63	CS2 B3LYP	-834.0673406	-0.990243	-834.344609	100.950580	105.9915399	-15.8	-10.7
64	COF2 B3LYP	-312.6569183	-1.13660473	-312.975168	-624.897914	-620.3820542	-1.1	3.5
65	sif4 B3LYP	-688.6073968	-1.57103053	-689.047285	-1580.784695	-1572.593135	34.2	42.4
66	sicl4, td	-2129.626481	-1.60776931	-2130.076657	-644.723695	-628.8656752	18.0	33.9
67	nno B3LYP	-184.386255	-0.86057463	-184.627216	58.752229	59.69740917	-23.3	-22.3
68	clno B3LYP	-589.7085015	-0.92884341	-589.968578	45.666548	50.12989819	-6.2	-1.8

69	nf3 c3v	-353.6835014	-1.2531154	-354.034374	-138.678277	-133.8736118	-6.5	-1.7
70	pf3 c3v	-640.5308912	-1.31088325	-640.897939	-939.951175	-935.1465098	18.6	23.4
71	ozone 1-a1	-225.0861023	-1.03439913	-225.375734	150.767936	153.6034762	8.1	10.9
72	f2o B3LYP	-274.3412049	-0.98183768	-274.616119	36.807923	40.95621287	12.1	16.3
73	CLF3, C2V	-758.9908746	-1.39090686	-759.380329	-160.344224	-152.0213891	-1.4	7.0
74	CF2=CF2 D2H	-474.9812892	-1.67354427	-475.449882	-697.620295	-690.4789347	-39.1	-31.9
75	cl2c=ccl2 B3LYP	-1916.089164	-1.74596877	-1916.578035	-24.348824	-9.541003568	-11.8	3.0
76	cf3cn B3LYP	-429.9387322	-1.6145363	-430.390802	-521.534412	-515.9946071	-26.1	-20.6
77	PROPYNE C3V	-116.4193749	-0.64641536	-116.600371	191.113298	192.2160082	6.2	7.3
78	ALLENE D2D	-116.4195676	-0.64011865	-116.598801	193.579637	194.6823473	3.2	4.3
79	CYCLOPROPENE C2V	-116.3797509	-0.64944948	-116.561597	292.196168	293.2988777	15.2	16.3
80	PROPENE CS	-117.654634	-0.66976378	-117.842168	37.064527	38.16723688	17.0	18.1
81	CYCLOPROPANE D3H	-117.6407909	-0.67586981	-117.830034	71.402107	72.50481658	18.3	19.4
82	PROPANE C2V	-118.8724113	-0.70280772	-119.069197	-78.564898	-77.46218757	26.0	27.1
83	TRANS-1,3-BUTADIENE C2H	-155.6701256	-0.86636001	-155.912706	125.990767	127.4610466	16.0	17.4
84	Dimethyl acetylene	-155.6566184	-0.87223503	-155.900844	157.287211	158.7574907	11.7	13.2
85	Methylene cyclopropane.	-155.6372704	-0.87296994	-155.881702	206.140612	207.6108918	5.7	7.2
86	Bicyclo[1.1.0]butane. C2v	-155.6210698	-0.88464283	-155.868770	242.026289	243.4965692	24.9	26.3
87	CYCLOBUTENE b3lyp	-155.6466617	-0.87526891	-155.891737	182.156691	183.6269713	25.7	27.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.8696434	-0.90437349	-157.122868	57.131838	58.60211844	28.7	30.2
89	Isobutene. Single	-156.887424	-0.90021803	-157.139485	8.715016	10.18529604	25.5	26.9
90	Trans butane	-158.100275	-0.93064203	-158.360855	-90.865480	-89.3951999	34.7	36.1
91	isobutane B3LYP/6-31G*	-158.1012608	-0.93387376	-158.362745	-97.123843	-95.65356329	37.2	38.7
92	Spiropentane. D2d	-194.8590878	-1.10702199	-195.169054	207.078884	208.9167342	21.7	23.6
93	Benzene B3LYP	-231.7831783	-1.27226083	-232.139411	86.982510	89.18792991	4.6	6.8
94	DIFLUOROMETHANE C2V	-238.7067553	-0.86004774	-238.947569	-455.978363	-452.407683	-5.4	-1.8
95	HCF3 TRI-FLUOROMETHANE	-337.8700866	-1.16624778	-338.196636	-707.485547	-702.3133119	-10.4	-5.3
96	CH2CL2 C2V	-959.2524905	-0.88306472	-959.499749	-89.274835	-81.87092535	6.1	13.5
97	chcl3 B3LYP/6-31G*	-1418.662933	-1.21101367	-1419.002017	-97.169852	-86.24777193	6.2	17.1
98	METHYLAMINE b3lyp	-95.66933789	-0.51913219	-95.814695	-9.768694	-9.401123551	13.2	13.6
99	Acetonitrile. CH3-CN.	-132.5116668	-0.68907347	-132.704607	71.710207	72.44534671	-3.6	-2.9
100	NITRO METHANE	-244.6316927	-1.13975237	-244.950823	-80.549520	-78.29159004	-6.1	-3.8
101	Methyl-nitrite. CH3-O-N=O.	-244.6277505	-1.12966914	-244.944058	-66.515003	-64.25707326	0.0	2.3
102	Methylsilane. CH3-SiH3.	-330.9509662	-0.56919457	-331.110341	-6.181389	-4.028478858	23.1	25.3
103	Formic Acid.	-189.4915893	-0.82370522	-189.722227	-382.730766	-380.4728362	-4.1	-1.8
104	Methyl formate.	-228.7069719	-1.04835693	-229.000512	-360.523383	-357.8978833	-4.9	-2.3
105	acetamide ch3cohn2	-208.865547	-1.01766019	-209.150492	-234.513332	-232.8330117	4.0	5.7

106	Aziridine. (cyclic	-133.6605824	-0.72131272	-133.862550	138.655356	139.3904964	12.3	13.0
107	Cyanogen. NCCN.	-185.3455868	-0.92215352	-185.603790	283.736806	284.471946	-23.0	-22.2
108	DIMETHYLAMINE b3lyp	-134.8885373	-0.74536356	-135.097239	0.565746	1.300885628	19.0	19.7
109	TRANS ETHYLAMINE	-134.9000673	-0.74652493	-135.109094	-29.622788	-28.88764792	17.7	18.4
110	KETENE B3LYP	-152.3536863	-0.72101805	-152.555571	-61.260217	-59.57989661	-14.0	-12.3
111	OXIRANE B3LYP	-153.5228938	-0.75220741	-153.733512	-44.658821	-42.97850149	8.1	9.7
112	Acetaldehyde B3LYP	-153.5686374	-0.74455887	-153.777114	-162.255042	-160.5747221	3.8	5.5
113	Glyoxal, O=CH-CH=O.	-227.4791021	-1.01578353	-227.763521	-221.931917	-219.3064166	-9.8	-7.2
114	ETHANOL TRANS	-154.7644282	-0.77496997	-154.981420	-216.133664	-214.4533443	19.0	20.7
115	DIMETHYL ETHER,	-154.7476834	-0.77202327	-154.963850	-170.846740	-169.1664204	13.2	14.9
116	Thiooxirane. (cyclic	-476.4402975	-0.83701361	-476.674661	94.526723	97.59855815	12.5	15.6
117	Dimethylsulfoxide. (CH3)2SO.	-552.7513729	-1.18213562	-553.082371	-120.108929	-116.0919139	31.4	35.4
118	Thioethanol. CH3-CH2-SH.	-477.6586058	-0.8558489	-477.898243	-20.056697	-16.98486185	26.4	29.5
119	ch3sch3 B3LYP	-477.6566298	-0.85778322	-477.896809	-13.764974	-10.69313885	23.5	26.5
120	Vinyl fluoride,	-177.5670401	-0.75026842	-177.777115	-141.501990	-139.1652953	-2.6	-0.3
121	Ethyl chloride.	-539.0684093	-0.7908412	-539.289845	-97.430150	-93.17683966	14.7	19.0
122	Vinyl chloride,	-537.8453108	-0.76216656	-538.058717	28.220351	32.47366146	5.2	9.5
123	h2c=chcn B3LYP	-170.5182774	-0.886454	-170.766484	183.250944	184.3536539	2.5	3.6
124	ACETONE B3LYP	-192.8083105	-0.97181741	-193.080419	-205.583953	-203.5360625	11.6	13.6
125	CH3COOH ACETIC	-228.7327238	-1.04779856	-229.026107	-428.178859	-425.5533594	4.4	7.1
126	CH3CFO HCCO	-252.7435407	-1.0561924	-253.039275	-445.093098	-441.8112228	-2.8	0.4
127	ch3c(o)cl hcco	-613.0084082	-1.07247859	-613.308702	-243.813543	-238.6150531	-1.1	4.1
128	ch3ch2ch2cl B3LYP	-578.2963882	-1.018934	-578.581690	-110.128435	-105.5075554	21.7	26.3
129	Isopropyl alcohol,	-193.9972226	-1.00505173	-194.278637	-244.722786	-242.6748957	28.1	30.1
130	Methyl ethyl	-193.9807658	-0.99926625	-194.260560	-196.713354	-194.6654637	19.6	21.6
131	Trimethyl Amine.	-174.1100575	-0.97646795	-174.383469	-0.080432	1.022277709	23.8	24.9
132	FURAN B3LYP	-229.615259	-1.1564652	-229.939069	-33.277121	-30.86166109	1.5	3.9
133	Thiophene b3lyp	-552.5222108	-1.24841073	-552.871766	125.754493	129.561468	10.7	14.5
134	PYROLE PLANAR	-209.7675029	-1.1286036	-210.083512	108.920190	110.3904703	0.6	2.0
135	C2v Pyridine	-247.8105102	-1.31661873	-248.179163	133.505843	135.343693	-7.1	-5.2
136	H2 B3LYP/6-31G*	-1.15948271	-0.03499396	-1.169281	7.631248	7.631248351	7.6	7.6
137	SH b3lyp/6-31G*	-398.5685644	-0.36067348	-398.669553	147.434287	149.7709818	4.3	6.7
138	CCH B3LYP	-76.46673581	-0.38360652	-76.574146	577.837472	578.5726118	12.6	13.3
139	C2H3 CS,2-A'	-77.7465642	-0.40521005	-77.860023	303.124132	303.8592716	3.5	4.3
140	ch3co hcco	-152.9271749	-0.72246191	-153.129464	-15.211827	-13.53150706	-5.2	-3.5
141	H2COH C1	-114.8793327	-0.51581023	-115.023760	-12.922536	-11.60978617	4.2	5.5
142	ch3o CS,	-114.8725192	-0.48892807	-115.009419	21.155311	22.46806121	4.0	5.3

143	ch3ch2o 2A"	-154.1054607	-0.71570809	-154.305859	-4.578639	-2.89831872	10.9	12.6
144	ch3s 2-A'	-437.7977128	-0.59101676	-437.963197	131.129629	133.833894	6.4	9.2
145	c2h5 staggered	-78.98530073	-0.43648126	-79.107515	132.493250	133.2283904	11.6	12.3
146	(ch3)2ch Cs	-118.2178908	-0.66530859	-118.404177	107.174663	108.277373	17.2	18.3
147	TERT-BUTYL RADICAL	-157.450592	-0.89618713	-157.701524	79.793617	81.2638972	28.3	29.8
148	NO2 RADICAL	-204.7816071	-0.91103957	-205.036698	11.453139	13.34349869	-21.6	-19.7

MAD	**11.3**	**12.4**
LD	**-39.1**	**42.4**

Table S5.30b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498707	0.000000	-0.498707
2	li	-7.468146	-0.014619	-7.472240
3	be	-14.636486	-0.053757	-14.651538
4	b	-24.615574	-0.077719	-24.637336
5	c	-37.798569	-0.104521	-37.827835
6	n	-54.531533	-0.135273	-54.569410
7	o	-74.994391	-0.192634	-75.048328
8	f	-99.640595	-0.255702	-99.712192
9	na	-162.146581	-0.172102	-162.194769
10	al	-242.227697	-0.220837	-242.289531
11	si	-289.228107	-0.250929	-289.298367
12	p	-341.110190	-0.280039	-341.188601
13	s	-397.943949	-0.321440	-398.033952
14	cl	-459.961681	-0.292395	-460.043551

Table S5.31a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04650942	-0.04698167	-8.060134	146.889809	146.8898094	7.6	7.6
2	BERYLLIUM HYDRIDE	-15.22187417	-0.05532024	-15.237917	319.899693	319.899693	-21.9	-21.9
3	DOUBLET CH	-38.41637835	-0.14547225	-38.458565	599.595199	599.9627689	3.4	3.7
4	CH2 3-B1	-39.07933113	-0.16451455	-39.127040	395.385796	395.7533656	3.3	3.7
5	Singlet methylene,	-39.05588791	-0.18504367	-39.109551	439.693143	440.0607134	9.6	9.9
6	Methyl radical,	-39.75117194	-0.20959108	-39.811953	151.941034	152.308604	5.5	5.9
7	ch4 //b3lyp/6-31G*	-40.41547314	-0.25158526	-40.488433	-64.058086	-63.6905157	10.8	11.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14556179	-0.18864807	-55.200270	358.124180	358.1241803	1.6	1.6
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78639282	-0.24254749	-55.856732	187.558420	187.5584203	-1.1	-1.1
10	AMMONIA, //b3lyp/6-31G*	-56.45155696	-0.29692008	-56.537664	-38.576912	-38.57691186	7.4	7.4
11	OH RADICAL	-75.64036084	-0.25983795	-75.715714	40.628221	41.57340132	1.3	2.2
12	Water //b3lyp/6-31G*	-76.3169633	-0.32906975	-76.412394	-232.118901	-231.1737212	9.7	10.7
13	HYDROGEN FLUORIDE,	-100.3349585	-0.33960619	-100.433444	-268.123850	-266.5222945	4.3	5.9
14	SIH2 singlet	-290.4441894	-0.30734021	-290.533318	276.035740	277.8210803	3.2	5.0
15	SIH2 3B1	-290.4182778	-0.28455487	-290.500799	362.426055	364.211395	1.8	3.6
16	SIH3 c3v	-291.0590537	-0.31269288	-291.149735	204.278697	206.064037	3.9	5.7
17	SIH4 //b3lyp/6-31G*	-291.701389	-0.34004485	-291.800002	44.578544	46.36388378	10.3	12.1
18	ph2 doublet	-342.3258123	-0.34686959	-342.426405	140.295422	140.2954224	1.8	1.8
19	PH3 c3v	-342.9530061	-0.37829528	-343.062712	18.746728	18.74672783	13.3	13.3
20	SH2 //b3lyp/6-31G*	-399.1993389	-0.39974998	-399.315266	-9.908594	-7.571899361	10.6	12.9
21	HCL //b3lyp/6-31G*	-460.6086471	-0.33790452	-460.706639	-88.943452	-85.42528202	3.5	7.0
22	DILITHIUM //b3lyp/6-31G*	-14.96008809	-0.05836788	-14.977015	230.415345	230.415345	14.5	14.5
23	Lithium Fluoride,	-107.2974719	-0.36899449	-107.404480	-340.291373	-338.6898176	-5.2	-3.6
24	ACETYLENE //b3lyp/6-31g*	-77.17559821	-0.42119321	-77.297744	228.990339	229.7254787	2.2	3.0
25	ETHYLENE //b3lyp/6-31g*	-78.41659555	-0.44205598	-78.544792	61.793416	62.52855599	9.5	10.2
26	ETHANE //b3lyp/6-31g*	-79.63889393	-0.47549395	-79.776787	-67.191581	-66.45644066	16.9	17.6
27	CYANO RADICAL,	-92.55156975	-0.45753684	-92.684255	441.761349	442.1289187	2.9	3.2
28	HYDROGEN CYANIDE	-93.26164958	-0.46611668	-93.396823	122.565714	122.9332839	-9.2	-8.9
29	CARBON MONOXIDE	-113.1526468	-0.47683941	-113.290930	-117.571175	-116.2584247	-7.1	-5.8
30	HCO BENT	-113.6779973	-0.499326	-113.822802	29.409967	30.72271698	-12.4	-11.1
31	H2CO //b3lyp/6-31g*	-114.3198556	-0.51887617	-114.470330	-113.635243	-112.322493	-4.9	-3.5

32	METHANOL //b3lyp/6-31g*	-115.5252906	-0.54833776	-115.684309	-192.387650	-191.0749003	8.4	9.8
33	Nitrogen N2,	-109.3595003	-0.50005297	-109.504516	-6.787686	-6.787685534	-6.8	-6.8
34	H2NNH2 //b3lyp/6-31g*	-111.6659063	-0.56320447	-111.829236	102.780651	102.7806513	7.4	7.4
35	NO radical,	-129.7065693	-0.54211673	-129.863783	80.213185	81.15836541	-10.2	-9.2
36	O2 //b3lyp/6-31g*	-150.1161737	-0.60632094	-150.292007	-13.055952	-11.16559181	-13.1	-11.2
37	HYDROGEN PEROXIDE	-151.3317846	-0.63661932	-151.516404	-122.874822	-120.9844618	13.1	15.0
38	F2 //b3lyp/6-31g*	-199.286697	-0.66536756	-199.479654	12.246636	15.44974599	12.2	15.4
39	CO2 D*H	-188.3210279	-0.80160515	-188.553493	-421.172528	-418.9145982	-27.9	-25.6
40	na2 //b3lyp/6-31G*	-324.3032661	-0.37288696	-324.411403	143.501894	143.5018943	1.2	1.2
41	SI2 3-SGG	-578.5462435	-0.56123925	-578.709003	588.421435	591.9921149	3.1	6.7
42	P2 //b3lyp/6-31g*	-682.3488691	-0.71306221	-682.555657	150.485995	150.4859947	7.0	7.0
43	S2 //b3lyp/6-31g*	-796.0045996	-0.75988651	-796.224967	125.214921	129.8883112	-3.2	1.4
44	CL2 //b3lyp/6-31g*	-919.9789839	-0.65450554	-920.168790	6.963150	13.99949001	7.0	14.0
45	Sodium Chloride	-622.2373289	-0.5108786	-622.385484	-175.292127	-171.7739573	7.1	10.6
46	SIO //b3lyp/6-31g*	-364.4693198	-0.61972515	-364.649040	-101.353913	-98.62339345	1.6	4.3
47	Carbon monosulfide,	-435.962072	-0.57923755	-436.130051	283.110451	285.8147162	3.2	5.9
48	OS //b3lyp/6-31g*	-473.0805833	-0.69023505	-473.280751	-2.544633	0.737241655	-7.6	-4.3
49	CLO 2-PI	-535.0115787	-0.60848207	-535.188038	106.689428	111.1527785	5.4	9.9
50	CLF 1-SG	-559.6581148	-0.65706625	-559.848664	-54.751200	-49.63147522	0.5	5.6
51	si2h6 //b3lyp/6-31g*	-582.2296339	-0.66089282	-582.421293	101.012947	104.5836271	21.1	24.7
52	Methyl chloride,	-499.8269267	-0.56279213	-499.990136	-76.157771	-72.27203069	5.8	9.7
53	H3C-SH METHANETHIOL	-438.420495	-0.62713416	-438.602364	-6.628655	-3.924389715	16.4	19.1
54	HOCl //b3lyp/6-31g*	-535.6583931	-0.64858489	-535.846483	-69.858155	-65.39480526	4.6	9.1
55	SO2 //b3lyp/6-31G*	-548.2341197	-1.03930945	-548.535519	-290.830898	-286.6038427	6.2	10.5
56	BF3 PLANAR	-324.2157003	-1.0758696	-324.527702	-1153.911181	-1148.975241	-18.4	-13.4
57	bcl3 B3LYP	-1404.953372	-1.11456822	-1405.276597	-420.620933	-409.9351482	-17.7	-7.0
58	ALf3 B3LYP	-541.7454863	-1.21528781	-542.097920	-1200.583583	-1194.886248	8.6	14.3
59	alcl3 B3LYP	-1622.542401	-1.21672761	-1622.895252	-589.119114	-577.6719338	-4.6	6.8
60	cf4 B3LYP	-437.0138498	-1.46997937	-437.440144	-954.360038	-947.5862484	-21.3	-14.6
61	ccl4 B3LYP	-1878.035188	-1.54581197	-1878.483473	-95.754541	-81.31429121	0.1	14.5
62	O=C=S. Singlet	-511.18832	-0.89233882	-511.447098	-164.114111	-160.4646662	-25.6	-22.0
63	CS2 B3LYP	-834.0521456	-0.99021244	-834.339307	97.189620	102.23058	-19.5	-14.5
64	COF2 B3LYP	-312.645011	-1.13659526	-312.974624	-630.101035	-625.5851753	-6.3	-1.8
65	sif4 B3LYP	-688.5878495	-1.57102689	-689.043447	-1585.001958	-1576.810398	30.0	38.2
66	sicl4, td	-2129.592331	-1.60774375	-2130.058576	-646.579489	-630.7214692	16.2	32.0
67	nno B3LYP	-184.3783804	-0.86055188	-184.627940	52.114824	53.06000419	-29.9	-28.9
68	clno B3LYP	-589.6960739	-0.92882448	-589.965433	40.205744	44.66909422	-11.7	-7.2

69	nf3 c3v	-353.6707227	-1.25310966	-354.034125	-144.727362	-139.9226971	-12.5	-7.7
70	pf3 c3v	-640.514372	-1.31088013	-640.894527	-943.730654	-938.9259893	14.8	19.6
71	ozone 1-a1	-225.0773249	-1.03437616	-225.377294	141.513162	144.3487019	-1.2	1.7
72	f2o B3LYP	-274.3314783	-0.981836	-274.616211	31.384757	35.53304702	6.7	10.8
73	CLF3, C2V	-758.9734455	-1.39090509	-759.376808	-166.786469	-158.4636344	-7.8	0.5
74	CF2=CF2 D2H	-474.9633363	-1.67353478	-475.448661	-704.239868	-697.0985076	-45.7	-38.5
75	cl2c=ccl2 B3LYP	-1916.05656	-1.74593804	-1916.562882	-29.420529	-14.61270922	-16.9	-2.1
76	cf3cn B3LYP	-429.9217936	-1.61451282	-430.390002	-529.033116	-523.4933108	-33.6	-28.1
77	PROPYNE C3V	-116.412342	-0.64639155	-116.599796	188.280613	189.3833229	3.3	4.5
78	ALLENE D2D	-116.4125312	-0.64009679	-116.598159	190.920003	192.0227129	0.5	1.7
79	CYCLOPROPENE C2V	-116.3726622	-0.64943193	-116.560997	289.425637	290.5283469	12.4	13.5
80	PROPENE CS	-117.6470626	-0.66974423	-117.841288	35.029575	36.13228456	14.9	16.0
81	CYCLOPROPANE D3H	-117.6331505	-0.6758548	-117.829148	69.384281	70.48699065	16.2	17.4
82	PROPANE C2V	-118.8643053	-0.70279017	-119.068114	-80.065664	-78.96295409	24.5	25.6
83	TRANS-1,3-BUTADIENE C2H	-155.6605045	-0.86633245	-155.911741	122.733730	124.2040096	12.7	14.2
84	Dimethyl acetylene	-155.6470012	-0.87220592	-155.899941	153.866866	155.3371458	8.3	9.7
85	Methylene cyclopropane.	-155.6275868	-0.87294684	-155.880741	202.870493	204.3407727	2.5	3.9
86	Bicyclo[1.1.0]butane. C2v	-155.6113179	-0.88462315	-155.867859	238.626600	240.0968798	21.5	22.9
87	CYCLOBUTENE b3lyp	-155.6369535	-0.87524562	-155.890775	178.890918	180.3611985	22.4	23.9
88	CYCLOBUTANE b3lyp/6-31G*	-156.859401	-0.9043521	-157.121663	54.503152	55.97343161	26.1	27.5
89	Isobutene. Single	-156.8772584	-0.90019283	-157.138314	5.996588	7.466868308	22.7	24.2
90	Trans butane	-158.0895837	-0.93061821	-158.359463	-93.003331	-91.53305135	32.5	34.0
91	isobutane B3LYP/6-31G*	-158.0905603	-0.93385001	-158.361377	-99.322495	-97.85221502	35.0	36.5
92	Spiropentane. D2d	-194.8467501	-1.10699732	-195.167779	203.185253	205.023103	17.8	19.7
93	Benzene B3LYP	-231.7692878	-1.27222304	-232.138233	81.389467	83.59488712	-1.0	1.2
94	DIFLUOROMETHANE C2V	-238.697347	-0.86004792	-238.946761	-458.769349	-455.1986688	-8.2	-4.6
95	HCF3 TRI-FLUOROMETHANE	-337.8574267	-1.16624555	-338.195638	-711.508648	-706.3364128	-14.5	-9.3
96	CH2CL2 C2V	-959.2357754	-0.88305141	-959.491860	-90.991491	-83.58758096	4.4	11.8
97	chcl3 B3LYP/6-31G*	-1418.639319	-1.21099486	-1418.990508	-99.869473	-88.94739268	3.5	14.4
98	METHYLAMINE b3lyp	-95.66358999	-0.51912585	-95.814136	-11.258265	-10.89069467	11.8	12.1
99	Acetonitrile. CH3-CN.	-132.5044361	-0.68905249	-132.704261	68.215134	68.95027376	-7.1	-6.4
100	NITRO METHANE	-244.6204687	-1.13973219	-244.950991	-87.385037	-85.1271066	-12.9	-10.7
101	Methyl-nitrite. CH3-O-N=O.	-244.6165633	-1.12964784	-244.944161	-73.181393	-70.92346272	-6.7	-4.4
102	Methylsilane. CH3-SiH3.	-330.9418903	-0.56918059	-331.106953	-6.101088	-3.948177678	23.2	25.3
103	Formic Acid.	-189.4831316	-0.8236994	-189.722004	-387.034268	-384.7763379	-8.4	-6.1
104	Methyl formate.	-228.6959434	-1.04834153	-228.999962	-365.416354	-362.7908541	-9.8	-7.2
105	acetamide ch3cohn2	-208.8547053	-1.01764605	-209.149823	-238.879737	-237.1994174	-0.4	1.3

106	Aziridine. (cyclic	-133.6527358	-0.72130026	-133.861913	135.924190	136.6593303	9.6	10.3
107	Cyanogen. NCCN.	-185.3366634	-0.92212039	-185.604078	277.067836	277.8029762	-29.6	-28.9
108	DIMETHYLAMINE b3lyp	-134.8802081	-0.74535006	-135.096360	-1.529017	-0.793877161	16.9	17.6
109	TRANS ETHYLAMINE	-134.8917345	-0.74651223	-135.108223	-31.739147	-31.00400729	15.5	16.3
110	KETENE B3LYP	-152.3462142	-0.72100267	-152.555305	-65.176514	-63.49619376	-17.9	-16.2
111	OXIRANE B3LYP	-153.5148453	-0.75219743	-153.732983	-47.884900	-46.20457989	4.8	6.5
112	Acetaldehyde B3LYP	-153.5606423	-0.74454741	-153.776561	-165.419330	-163.7390104	0.7	2.4
113	Glyoxal, O=CH-CH=O.	-227.4686506	-1.01577002	-227.763224	-227.486025	-224.8605253	-15.4	-12.7
114	ETHANOL TRANS	-154.7558814	-0.77496079	-154.980620	-218.649591	-216.9692712	16.5	18.2
115	DIMETHYL ETHER,	-154.7391497	-0.77201211	-154.963033	-173.318241	-171.6379206	10.8	12.5
116	Thiooxirane. (cyclic	-476.4286021	-0.83699649	-476.671331	92.258340	95.33017499	10.3	13.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.7361661	-1.18211747	-553.078980	-123.938313	-119.9212978	27.5	31.5
118	Thioethanol. CH3-CH2-SH.	-477.6464363	-0.85583111	-477.894627	-21.574577	-18.50274216	24.9	27.9
119	ch3sch3 B3LYP	-477.6444676	-0.85776543	-477.893220	-15.352858	-12.2810234	21.9	25.0
120	Vinyl fluoride,	-177.5588142	-0.75025823	-177.776389	-144.223141	-141.8864459	-5.3	-3.0
121	Ethyl chloride.	-539.0560001	-0.79082602	-539.285340	-98.987709	-94.73439889	13.1	17.4
122	Vinyl chloride,	-537.8334296	-0.76214942	-538.054453	26.031083	30.28439327	3.0	7.3
123	h2c=chcn B3LYP	-170.509004	-0.88642525	-170.766067	178.494554	179.5972644	-2.3	-1.2
124	ACETONE B3LYP	-192.7977231	-0.97179899	-193.079545	-209.351620	-207.3037301	7.8	9.8
125	CH3COOH ACETIC	-228.7216755	-1.04778586	-229.025533	-433.007267	-430.3817673	-0.4	2.2
126	CH3CFO HCCO	-252.7322951	-1.05617931	-253.038587	-449.635797	-446.353922	-7.4	-4.1
127	ch3c(o)cl hcco	-612.9935214	-1.07245962	-613.304535	-247.977271	-242.778781	-5.3	-0.1
128	ch3ch2ch2cl B3LYP	-578.2813945	-1.01891265	-578.576879	-112.332253	-107.7113728	19.5	24.1
129	Isopropyl alcohol,	-193.986082	-1.00503567	-194.277542	-247.912102	-245.8642118	24.9	26.9
130	Methyl ethyl	-193.9696464	-0.99924839	-194.259428	-199.805430	-197.7575397	16.5	18.6
131	Trimethyl Amine.	-174.0991341	-0.97644786	-174.382304	-2.874604	-1.771894126	21.0	22.1
132	FURAN B3LYP	-229.6030049	-1.15643913	-229.938372	-38.958903	-36.54344263	-4.2	-1.8
133	Thiophene b3lyp	-552.5063129	-1.24837801	-552.868343	120.834163	124.6411376	5.8	9.6
134	PYROLE PLANAR	-209.7554401	-1.12857593	-210.082727	103.681005	105.1512851	-4.7	-3.2
135	C2v Pyridine	-247.796413	-1.31658288	-248.178222	127.229855	129.0677054	-13.4	-11.5
136	H2 B3LYP/6-31G*	-1.1591001	-0.03499425	-1.169248	7.716804	7.716803681	7.7	7.7
137	SH b3lyp/6-31G*	-398.5618861	-0.36067538	-398.666482	147.381304	149.7179995	4.3	6.6
138	CCH B3LYP	-76.4626818	-0.38358627	-76.573922	575.529083	576.2642231	10.3	11.0
139	C2H3 CS,2-A'	-77.74193849	-0.40518882	-77.859443	301.750287	302.4854267	2.2	2.9
140	ch3co hcco	-152.9195105	-0.7224411	-153.129018	-18.657015	-16.97669472	-8.6	-6.9
141	H2COH C1	-114.8737038	-0.51580147	-115.023286	-14.847296	-13.534546	2.3	3.6
142	ch3o CS,	-114.8669231	-0.48891241	-115.008708	19.855217	21.16796717	2.7	4.0

143	ch3ch2o 2A"	-154.0972802	-0.71568356	-154.304828	-6.488914	-4.80859445	9.0	10.7
144	ch3s 2-A'	-437.7884568	-0.59100881	-437.959849	130.356251	133.0605157	5.7	8.4
145	c2h5 staggered	-78.9801261	-0.43647384	-79.106704	131.729055	132.4641946	10.8	11.5
146	(ch3)2ch Cs	-118.2101244	-0.66529126	-118.403059	105.766833	106.8695426	15.8	16.9
147	TERT-BUTYL RADICAL	-157.4402312	-0.89615955	-157.700117	77.695409	79.16568923	26.2	27.7
148	NO2 RADICAL	-204.7732872	-0.91101798	-205.037482	4.447004	6.337363759	-28.6	-26.7

MAD	**11.3**	**11.9**
LD	**-45.7**	**-38.5**

Table S5.31b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498707	0.000000	-0.498707
2	li	-7.467610	-0.014618	-7.471849
3	be	-14.635537	-0.053753	-14.651125
4	b	-24.614309	-0.077723	-24.636849
5	c	-37.796970	-0.104527	-37.827283
6	n	-54.529605	-0.135277	-54.568836
7	o	-74.991806	-0.192645	-75.047673
8	f	-99.637376	-0.255712	-99.711532
9	na	-162.142489	-0.172100	-162.192398
10	al	-242.222741	-0.220838	-242.286784
11	si	-289.222791	-0.250930	-289.295561
12	p	-341.104519	-0.280033	-341.185729
13	s	-397.937643	-0.321442	-398.030861
14	cl	-459.954760	-0.292398	-460.039556

Table S5.32a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04562127	-0.04698291	-8.059716	146.960956	146.960956	7.6	7.6
2	BERYLLIUM HYDRIDE	-15.22079314	-0.05531278	-15.237387	320.206881	320.2068815	-21.6	-21.6
3	DOUBLET CH	-38.4144009	-0.14547628	-38.458044	599.516866	599.8844363	3.3	3.7
4	CH2 3-B1	-39.07717933	-0.16451308	-39.126533	395.269595	395.6371654	3.2	3.6
5	Singlet methylene,	-39.0535604	-0.18503999	-39.109072	439.501018	439.8685885	9.4	9.8
6	Methyl radical,	-39.74858643	-0.20959476	-39.811465	151.775999	152.1435687	5.3	5.7
7	ch4 //b3lyp/6-31G*	-40.41252717	-0.25157938	-40.488001	-64.371760	-64.00419048	10.5	10.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14318147	-0.1886584	-55.199779	357.905221	357.905221	1.4	1.4
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78359675	-0.24255448	-55.856363	187.018514	187.018514	-1.7	-1.7
10	AMMONIA, //b3lyp/6-31G*	-56.44837772	-0.29692114	-56.537454	-39.533687	-39.53368686	6.5	6.5
11	OH RADICAL	-75.63735046	-0.25984816	-75.715305	39.982856	40.92803556	0.7	1.6
12	Water //b3lyp/6-31G*	-76.31355919	-0.32907618	-76.412282	-233.545232	-232.6000524	8.3	9.2
13	HYDROGEN FLUORIDE,	-100.3313351	-0.339615	-100.433220	-269.265042	-267.663487	3.1	4.7
14	SIH2 singlet	-290.4382154	-0.30733239	-290.530415	276.291028	278.0763679	3.5	5.3
15	SIH2 3B1	-290.4124993	-0.28452836	-290.497858	362.780981	364.5663214	2.1	3.9
16	SIH3 c3v	-291.0528993	-0.312678	-291.146703	204.872573	206.6579125	4.5	6.2
17	SIH4 //b3lyp/6-31G*	-291.6948967	-0.3400359	-291.796908	45.336805	47.12214525	11.0	12.8
18	ph2 doublet	-342.319381	-0.34686941	-342.423442	140.533416	140.5334155	2.0	2.0
19	PH3 c3v	-342.946247	-0.37828623	-343.059733	19.027317	19.02731737	13.6	13.6
20	SH2 //b3lyp/6-31G*	-399.1923207	-0.39974434	-399.312244	-10.088938	-7.752242593	10.4	12.7
21	HCL //b3lyp/6-31G*	-460.6013761	-0.33790229	-460.702747	-89.212964	-85.69479405	3.3	6.8
22	DILITHIUM //b3lyp/6-31G*	-14.95875035	-0.05836376	-14.976259	230.345956	230.3459562	14.5	14.5
23	Lithium Fluoride,	-107.2932953	-0.36900941	-107.403998	-341.782725	-340.1811704	-6.6	-5.0
24	ACETYLENE //b3lyp/6-31g*	-77.17115009	-0.42117461	-77.297502	226.729942	227.4650815	0.0	0.7
25	ETHYLENE //b3lyp/6-31g*	-78.41161051	-0.44204189	-78.544223	60.391398	61.12653794	8.1	8.8
26	ETHANE //b3lyp/6-31g*	-79.63337262	-0.47548239	-79.776017	-68.065528	-67.33038848	16.0	16.8
27	CYANO RADICAL,	-92.5473021	-0.45744768	-92.684536	438.068683	438.4362535	-0.8	-0.5
28	HYDROGEN CYANIDE	-93.25700347	-0.46610142	-93.396834	119.583224	119.9507944	-12.2	-11.8
29	CARBON MONOXIDE	-113.1477979	-0.47683319	-113.290848	-120.521413	-119.2086628	-10.1	-8.8
30	HCO BENT	-113.672915	-0.49931365	-113.822709	26.486990	27.7997397	-15.4	-14.0
31	H2CO //b3lyp/6-31g*	-114.3144487	-0.51887116	-114.470110	-116.225238	-114.9124878	-7.4	-6.1

32	METHANOL //b3lyp/6-31g*	-115.5193292	-0.54833498	-115.683830	-194.296997	-192.9842472	6.5	7.8
33	Nitrogen N2,	-109.3546627	-0.50003755	-109.504674	-10.218029	-10.21802915	-10.2	-10.2
34	H2NNH2 //b3lyp/6-31g*	-111.6599377	-0.56320375	-111.828899	100.649996	100.6499959	5.3	5.3
35	NO radical,	-129.7012888	-0.54210717	-129.863921	76.624964	77.57014418	-13.7	-12.8
36	O2 //b3lyp/6-31g*	-150.110451	-0.60631986	-150.292347	-17.387197	-15.49683716	-17.4	-15.5
37	HYDROGEN PEROXIDE	-151.3254214	-0.6366244	-151.516409	-126.324849	-124.4344891	9.7	11.5
38	F2 //b3lyp/6-31g*	-199.2799402	-0.66537143	-199.479552	9.051688	12.25479814	9.1	12.3
39	CO2 D*H	-188.3131165	-0.8015918	-188.553594	-426.322549	-424.0646186	-33.0	-30.8
40	na2 //b3lyp/6-31G*	-324.294839	-0.37288142	-324.406703	143.391448	143.3914485	1.1	1.1
41	SI2 3-SGG	-578.5352626	-0.561221	-578.703629	587.798095	591.3687752	2.5	6.0
42	P2 //b3lyp/6-31g*	-682.3367261	-0.71303859	-682.550638	148.583535	148.5835345	5.1	5.1
43	S2 //b3lyp/6-31g*	-795.9915305	-0.75987722	-796.219494	123.352994	128.0263835	-5.1	-0.4
44	CL2 //b3lyp/6-31g*	-919.9648549	-0.65449791	-920.161204	5.901851	12.93819098	5.9	12.9
45	Sodium Chloride	-622.2259998	-0.51088111	-622.379264	-175.677207	-172.1590367	6.7	10.3
46	SIO //b3lyp/6-31g*	-364.4607941	-0.6197339	-364.646714	-104.333097	-101.6025767	-1.4	1.3
47	Carbon monosulfide,	-435.9535893	-0.57921737	-436.127354	280.626711	283.3309759	0.7	3.4
48	OS //b3lyp/6-31g*	-473.0711779	-0.69022691	-473.278246	-5.801157	-2.519281779	-10.8	-7.5
49	CLO 2-PI	-535.001662	-0.60843967	-535.184194	104.574954	109.0383045	3.3	7.8
50	CLF 1-SG	-559.6476523	-0.65706576	-559.844772	-56.753494	-51.63376895	-1.5	3.6
51	si2h6 //b3lyp/6-31g*	-582.2170169	-0.66087604	-582.415280	102.067468	105.6381482	22.2	25.7
52	Methyl chloride,	-499.8171016	-0.56278321	-499.985937	-77.067991	-73.1822511	4.9	8.8
53	H3C-SH METHANETHIOL	-438.4109098	-0.62712254	-438.599047	-7.482023	-4.777757818	15.5	18.2
54	HOCl //b3lyp/6-31g*	-535.6481409	-0.64858285	-535.842716	-72.176411	-67.71306059	2.3	6.8
55	SO2 //b3lyp/6-31G*	-548.2215735	-1.0392993	-548.533363	-296.723621	-292.4965659	0.3	4.6
56	BF3 PLANAR	-324.2037653	-1.07587046	-324.526526	-1157.294459	-1152.358519	-21.8	-16.8
57	bcl3 B3LYP	-1404.930485	-1.11454981	-1405.264850	-422.524099	-411.8383135	-19.6	-8.9
58	ALf3 B3LYP	-541.7299577	-1.21529606	-542.094546	-1204.134704	-1198.437369	5.0	10.7
59	alcl3 B3LYP	-1622.515924	-1.21671192	-1622.880937	-590.218007	-578.7708266	-5.7	5.7
60	cf4 B3LYP	-436.9979349	-1.46997189	-437.438926	-959.536429	-952.7626388	-26.5	-19.7
61	ccl4 B3LYP	-1878.004669	-1.54578687	-1878.468405	-99.598550	-85.1583002	-3.8	10.7
62	O=C=S. Singlet	-511.1767722	-0.89231712	-511.444467	-168.488897	-164.8394517	-30.0	-26.3
63	CS2 B3LYP	-834.0369506	-0.99018188	-834.334005	93.431104	98.47206435	-23.3	-18.3
64	COF2 B3LYP	-312.6331037	-1.1365858	-312.974079	-635.301566	-630.7857061	-11.5	-7.0
65	sif4 B3LYP	-688.5683023	-1.57102326	-689.039609	-1589.216644	-1581.025084	25.8	34.0
66	sicl4, td	-2129.55818	-1.6077182	-2130.040495	-648.432605	-632.5745851	14.3	30.2
67	nno B3LYP	-184.3705059	-0.86052914	-184.628665	45.479671	46.42485082	-36.5	-35.6
68	clno B3LYP	-589.6836463	-0.92880555	-589.962288	34.747033	39.21038278	-17.1	-12.7

69	nf3 c3v	-353.6579442	-1.25310392	-354.033875	-150.774280	-145.9696148	-18.6	-13.8
70	pf3 c3v	-640.4978528	-1.31087701	-640.891116	-947.508574	-942.7039092	11.0	15.9
71	ozone 1-a1	-225.0685476	-1.03435319	-225.378854	132.261495	135.0970346	-10.4	-7.6
72	f2o B3LYP	-274.3217518	-0.98183433	-274.616302	25.963368	30.11165758	1.3	5.4
73	CLF3, C2V	-758.9560166	-1.39090333	-759.373288	-173.226730	-164.9038948	-14.2	-5.9
74	CF2=CF2 D2H	-474.9453834	-1.67352529	-475.447441	-710.855964	-703.7146037	-52.3	-45.2
75	cl2c=ccl2 B3LYP	-1916.023957	-1.74590731	-1916.547729	-34.488718	-19.68089828	-21.9	-7.1
76	cf3cn B3LYP	-429.9048551	-1.61448935	-430.389202	-536.527945	-530.9881397	-41.1	-35.6
77	PROPYNE C3V	-116.4053092	-0.64636773	-116.599220	185.450217	186.5529265	0.5	1.6
78	ALLENE D2D	-116.4054949	-0.64007493	-116.597517	188.262547	189.3652571	-2.1	-1.0
79	CYCLOPROPENE C2V	-116.3655736	-0.64941438	-116.560398	286.657058	287.7597685	9.7	10.8
80	PROPENE CS	-117.6394913	-0.66972469	-117.840409	32.996645	34.09935544	12.9	14.0
81	CYCLOPROPANE D3H	-117.6255103	-0.67583978	-117.828262	67.368308	68.47101781	14.2	15.3
82	PROPANE C2V	-118.8561995	-0.70277261	-119.067031	-81.564523	-80.46181292	23.0	24.1
83	TRANS-1,3-BUTADIENE C2H	-155.6508835	-0.86630489	-155.910775	119.479523	120.9498029	9.4	10.9
84	Dimethyl acetylene	-155.6373841	-0.87217681	-155.899037	150.449433	151.9197126	4.8	6.3
85	Methylene cyclopropane.	-155.6179034	-0.87292374	-155.879781	199.602970	201.0732497	-0.8	0.7
86	Bicyclo[1.1.0]butane. C2v	-155.6015661	-0.88460348	-155.866947	235.229372	236.6996517	18.1	19.6
87	CYCLOBUTENE b3lyp	-155.6272455	-0.87522232	-155.889812	175.627812	177.0980921	19.1	20.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8491588	-0.90433071	-157.120458	51.876945	53.34722482	23.4	24.9
89	Isobutene. Single	-156.867093	-0.90016762	-157.137143	3.280849	4.75112856	20.0	21.5
90	Trans butane	-158.0788926	-0.93059438	-158.358071	-95.138594	-93.66831352	30.4	31.9
91	isobutane B3LYP/6-31G*	-158.07986	-0.93382627	-158.360008	-101.518603	-100.0483232	32.8	34.3
92	Spiropentane. D2d	-194.8344126	-1.10697264	-195.166504	199.294713	201.1325631	13.9	15.8
93	Benzene B3LYP	-231.7553975	-1.27218526	-232.137053	75.800620	78.00603988	-6.6	-4.4
94	DIFLUOROMETHANE C2V	-238.6879388	-0.86004811	-238.945953	-461.558928	-457.9882483	-10.9	-7.4
95	HCF3 TRI-FLUOROMETHANE	-337.8447669	-1.16624332	-338.194640	-715.529620	-710.357385	-18.5	-13.3
96	CH2CL2 C2V	-959.2190603	-0.88303811	-959.483972	-92.706596	-85.30268595	2.7	10.1
97	chcl3 B3LYP/6-31G*	-1418.615705	-1.21097605	-1418.978998	-102.566953	-91.64487313	0.8	11.7
98	METHYLAMINE b3lyp	-95.65784218	-0.5191195	-95.813578	-12.747015	-12.37944454	10.3	10.6
99	Acetonitrile. CH3-CN.	-132.4972054	-0.68903151	-132.703915	64.722074	65.45721404	-10.6	-9.9
100	NITRO METHANE	-244.6092449	-1.13971201	-244.951158	-94.217685	-91.95975453	-19.7	-17.5
101	Methyl-nitrite. CH3-O-N=O.	-244.6053762	-1.12962655	-244.944264	-79.844863	-77.58693262	-13.3	-11.1
102	Methylsilane. CH3-SiH3.	-330.9328146	-0.56916661	-331.103565	-6.019555	-3.866644614	23.3	25.4
103	Formic Acid.	-189.4746739	-0.82369359	-189.721782	-391.335896	-389.077966	-12.7	-10.4
104	Methyl formate.	-228.6849149	-1.04832612	-228.999413	-370.306554	-367.681054	-14.7	-12.0
105	acetamide ch3cohn2	-208.8438637	-1.01763192	-209.149153	-243.243898	-241.5635784	-4.8	-3.1

106	Aziridine. (cyclic	-133.6448894	-0.72128781	-133.861276	133.194556	133.9296958	6.8	7.6
107	Cyanogen. NCCN.	-185.3277401	-0.92208726	-185.604366	270.401830	271.1369695	-36.3	-35.6
108	DIMETHYLAMINE b3lyp	-134.8718791	-0.74533656	-135.095480	-3.622238	-2.887098257	14.8	15.5
109	TRANS ETHYLAMINE	-134.8834019	-0.74649953	-135.107352	-33.854007	-33.11886697	13.4	14.2
110	KETENE B3LYP	-152.3387422	-0.72098729	-152.555038	-69.090674	-67.41035375	-21.8	-20.1
111	OXIRANE B3LYP	-153.5067969	-0.75218745	-153.732453	-51.109151	-49.42883094	1.6	3.3
112	Acetaldehyde B3LYP	-153.5526473	-0.74453595	-153.776008	-168.581714	-166.9013937	-2.5	-0.8
113	Glyoxal, O=CH-CH=O.	-227.4581992	-1.01575651	-227.762926	-233.037470	-230.4119702	-20.9	-18.3
114	ETHANOL TRANS	-154.7473347	-0.77495161	-154.979820	-221.163785	-219.4834652	14.0	15.7
115	DIMETHYL ETHER,	-154.7306161	-0.77200096	-154.962216	-175.787886	-174.1075657	8.3	10.0
116	Thiooxirane. (cyclic	-476.4169068	-0.83697938	-476.668001	89.991744	93.06357874	8.0	11.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.7209594	-1.18209933	-553.075589	-127.765231	-123.7482158	23.7	27.7
118	Thioethanol. CH3-CH2-SH.	-477.634267	-0.85581332	-477.891011	-23.090654	-20.01881876	23.4	26.4
119	ch3sch3 B3LYP	-477.6323056	-0.85774765	-477.889630	-16.938921	-13.86708585	20.3	23.4
120	Vinyl fluoride,	-177.5505883	-0.75024804	-177.775663	-146.942542	-144.6058474	-8.0	-5.7
121	Ethyl chloride.	-539.0435911	-0.79081085	-539.280834	-100.543534	-96.29022372	11.6	15.8
122	Vinyl chloride,	-537.8215485	-0.76213229	-538.050188	23.843652	28.09696241	0.8	5.1
123	h2c=chcn B3LYP	-170.4997307	-0.88639651	-170.765650	173.740983	174.8436933	-7.0	-5.9
124	ACETONE B3LYP	-192.7871358	-0.97178056	-193.078670	-213.116631	-211.0687407	4.0	6.1
125	CH3COOH ACETIC	-228.7106273	-1.04777316	-229.024959	-437.833054	-435.207554	-5.2	-2.6
126	CH3CFO HCCO	-252.7210496	-1.05616622	-253.037899	-454.175944	-450.8940687	-11.9	-8.6
127	ch3c(o)cl hcco	-612.9786348	-1.07244066	-613.300367	-252.138441	-246.9399507	-9.5	-4.3
128	ch3ch2ch2cl B3LYP	-578.266401	-1.01889131	-578.572068	-114.533686	-109.9128057	17.3	21.9
129	Isopropyl alcohol,	-193.9749415	-1.00501962	-194.276447	-251.099006	-249.0511156	21.7	23.7
130	Methyl ethyl	-193.9585272	-0.99923054	-194.258296	-202.894973	-200.8470827	13.4	15.5
131	Trimethyl Amine.	-174.0882108	-0.97642777	-174.381139	-5.666510	-4.563799628	18.2	19.3
132	FURAN B3LYP	-229.5907509	-1.15641306	-229.937675	-44.637202	-42.22174223	-9.9	-7.5
133	Thiophene b3lyp	-552.4904152	-1.24834529	-552.864919	115.917256	119.7242309	0.9	4.7
134	PYROLE PLANAR	-209.7433774	-1.12854826	-210.081942	98.444915	99.91519531	-9.9	-8.5
135	C2v Pyridine	-247.7823159	-1.31654703	-248.177280	120.957824	122.795674	-19.6	-17.8
136	H2 B3LYP/6-31G*	-1.1587175	-0.03499455	-1.169216	7.802310	7.802309652	7.8	7.8
137	SH b3lyp/6-31G*	-398.5552079	-0.36067729	-398.663411	147.328379	149.6650744	4.2	6.6
138	CCH B3LYP	-76.45862788	-0.38356606	-76.573698	573.222352	573.9574922	8.0	8.7
139	C2H3 CS,2-A'	-77.73731289	-0.40516762	-77.858863	300.378106	301.1132464	0.8	1.5
140	ch3co hcco	-152.9118462	-0.72242027	-153.128572	-22.099843	-20.41952311	-12.1	-10.4
141	H2COH C1	-114.8680749	-0.51579271	-115.022813	-16.770750	-15.4579999	0.4	1.7
142	ch3o CS,	-114.8613271	-0.48889678	-115.007996	18.556820	19.86957026	1.4	2.7

143	ch3ch2o 2A"	-154.0890999	-0.71565905	-154.303798	-8.396693	-6.71637333	7.1	8.8
144	ch3s 2-A'	-437.7792008	-0.59100089	-437.956501	129.583783	132.2880484	4.9	7.6
145	c2h5 staggered	-78.97495156	-0.43646645	-79.105891	130.965851	131.7009906	10.0	10.8
146	(ch3)2ch Cs	-118.2023581	-0.66527395	-118.401940	104.360848	105.4635585	14.4	15.5
147	TERT-BUTYL RADICAL	-157.4298706	-0.89613198	-157.698710	75.599946	77.07022596	24.1	25.6
148	NO2 RADICAL	-204.7649674	-0.91099639	-205.038266	-2.556541	-0.666180858	-35.6	-33.7

MAD	**11.7**	**12.1**
LD	**-52.3**	**-45.2**

Table S5.32b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 57% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498707	0.000000	-0.498707
2	li	-7.467073	-0.014618	-7.471458
3	be	-14.634588	-0.053748	-14.650712
4	b	-24.613045	-0.077727	-24.636363
5	c	-37.795372	-0.104534	-37.826732
6	n	-54.527677	-0.135281	-54.568261
7	o	-74.989222	-0.192656	-75.047019
8	f	-99.634156	-0.255722	-99.710873
9	na	-162.138398	-0.172097	-162.190027
10	al	-242.217784	-0.220839	-242.284036
11	si	-289.217476	-0.250932	-289.292755
12	p	-341.098849	-0.280028	-341.182857
13	s	-397.931337	-0.321445	-398.027770
14	cl	-459.947840	-0.292402	-460.035561

Table S5.33a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04922495	-0.04677271	-8.061386	146.860273	146.8602728	7.5	7.5
2	BERYLLIUM HYDRIDE	-15.22524723	-0.05511792	-15.239578	318.845202	318.8452021	-23.0	-23.0
3	DOUBLET CH	-38.42228756	-0.14484638	-38.459948	600.160483	600.5280535	3.9	4.3
4	CH2 3-B1	-39.08584783	-0.16389946	-39.128462	395.910217	396.2777874	3.9	4.2
5	Singlet methylene,	-39.06286426	-0.18425314	-39.110770	440.747491	441.1150609	10.6	11.0
6	Methyl radical,	-39.75899668	-0.20878714	-39.813281	152.772159	153.1397286	6.3	6.7
7	ch4 //b3lyp/6-31G*	-40.42440386	-0.2506198	-40.489565	-62.651187	-62.28361737	12.2	12.6
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15257959	-0.18793665	-55.201443	359.432814	359.4328141	3.0	3.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79458369	-0.24160107	-55.857400	190.254559	190.2545588	1.6	1.6
10	AMMONIA, //b3lyp/6-31G*	-56.4608784	-0.29575242	-56.537774	-34.353809	-34.3538085	11.7	11.7
11	OH RADICAL	-75.64904055	-0.2588861	-75.716351	43.367251	44.31243056	4.0	5.0
12	Water //b3lyp/6-31G*	-76.32671174	-0.3277982	-76.411939	-226.452949	-225.5077688	15.4	16.3
13	HYDROGEN FLUORIDE,	-100.3452805	-0.33840392	-100.433266	-263.720852	-262.1192969	8.7	10.3
14	SIH2 singlet	-290.4622033	-0.30633026	-290.541849	275.395572	277.1809117	2.6	4.4
15	SIH2 3B1	-290.435767	-0.28374096	-290.509540	361.234924	363.0202637	0.6	2.4
16	SIH3 c3v	-291.0777585	-0.31173289	-291.158809	202.273716	204.0590561	1.9	3.6
17	SIH4 //b3lyp/6-31G*	-291.7212077	-0.33895773	-291.809337	41.951852	43.73719207	7.6	9.4
18	ph2 doublet	-342.345213	-0.34575841	-342.435110	139.934704	139.9347039	1.4	1.4
19	PH3 c3v	-342.9734477	-0.37703572	-343.071477	18.291438	18.29143751	12.9	12.9
20	SH2 //b3lyp/6-31G*	-399.2204988	-0.3984421	-399.324094	-8.941580	-6.60488544	11.6	13.9
21	HCL //b3lyp/6-31G*	-460.6305826	-0.33670367	-460.718126	-87.860716	-84.34254603	4.6	8.1
22	DILITHIUM //b3lyp/6-31G*	-14.96420345	-0.05807613	-14.979303	230.797650	230.7976498	14.9	14.9
23	Lithium Fluoride,	-107.3094266	-0.36754394	-107.404988	-334.556794	-332.9552394	0.6	2.2
24	ACETYLENE //b3lyp/6-31g*	-77.18860129	-0.41930333	-77.297620	237.705236	238.4403762	10.9	11.7
25	ETHYLENE //b3lyp/6-31g*	-78.43145874	-0.44023912	-78.545921	67.341194	68.07633358	15.0	15.8
26	ETHANE //b3lyp/6-31g*	-79.65561741	-0.47365757	-79.778768	-63.757739	-63.02259936	20.3	21.1
27	CYANO RADICAL,	-92.56352369	-0.45508495	-92.681846	456.548635	456.9162054	17.6	18.0
28	HYDROGEN CYANIDE	-93.27494969	-0.46397077	-93.395582	134.347145	134.7147155	2.6	2.9
29	CARBON MONOXIDE	-113.1664401	-0.47470163	-113.289863	-106.284889	-104.9721395	4.2	5.5
30	HCO BENT	-113.6924259	-0.49715582	-113.821686	40.883192	42.19594221	-1.0	0.4
31	H2CO //b3lyp/6-31g*	-114.3354071	-0.51666806	-114.469741	-103.482731	-102.1699812	5.3	6.6

32	METHANOL //b3lyp/6-31g*	-115.5427607	-0.54620291	-115.684773	-184.878807	-183.5660567	16.0	17.3
33	Nitrogen N2,	-109.3731561	-0.4977806	-109.502579	6.952625	6.952624807	7.0	7.0
34	H2NNH2 //b3lyp/6-31g*	-111.6832986	-0.56096205	-111.829149	111.910578	111.9105784	16.5	16.5
35	NO radical,	-129.7212897	-0.53973846	-129.861622	94.566044	95.51122433	4.2	5.1
36	O2 //b3lyp/6-31g*	-150.1318365	-0.60393886	-150.288861	3.904468	5.794828376	3.9	5.8
37	HYDROGEN PEROXIDE	-151.3496482	-0.63397189	-151.514481	-109.001852	-107.1114921	27.0	28.9
38	F2 //b3lyp/6-31g*	-199.3053839	-0.66268447	-199.477682	25.167704	28.37081448	25.2	28.4
39	CO2 D*H	-188.3433564	-0.79806169	-188.550852	-401.405562	-399.1476317	-8.1	-5.9
40	na2 //b3lyp/6-31G*	-324.3281335	-0.37167841	-324.424770	144.106481	144.1064808	1.9	1.9
41	SI2 3-SGG	-578.579047	-0.55937934	-578.724486	591.041691	594.6123715	5.7	9.3
42	P2 //b3lyp/6-31g*	-682.3850201	-0.7103473	-682.569710	158.335014	158.3350138	14.8	14.8
43	S2 //b3lyp/6-31g*	-796.0435364	-0.75737804	-796.240455	132.591456	137.2648459	4.1	8.8
44	CL2 //b3lyp/6-31g*	-920.0213974	-0.65206044	-920.190933	11.184228	18.22056833	11.2	18.2
45	Sodium Chloride	-622.2713062	-0.50912586	-622.403679	-174.036121	-170.5179506	8.4	11.9
46	SIO //b3lyp/6-31g*	-364.4941177	-0.61702457	-364.654544	-89.819682	-87.08916185	13.1	15.8
47	Carbon monosulfide,	-435.9871429	-0.57673182	-436.137093	292.773987	295.4782523	12.9	15.6
48	OS //b3lyp/6-31g*	-473.1079199	-0.68764212	-473.286707	10.189679	13.47155386	5.2	8.5
49	CLO 2-PI	-535.0406946	-0.60567616	-535.198170	115.616275	120.0796252	14.4	18.8
50	CLF 1-SG	-559.6887879	-0.65452844	-559.858965	-46.746915	-41.62718977	8.5	13.6
51	si2h6 //b3lyp/6-31g*	-582.2680783	-0.6587507	-582.439354	97.234077	100.8047571	17.3	20.9
52	Methyl chloride,	-499.8565483	-0.56068275	-500.002326	-72.665068	-68.77932751	9.3	13.2
53	H3C-SH METHANETHIOL	-438.4493892	-0.62491582	-438.611867	-3.180447	-0.476181676	19.8	22.5
54	HOCl //b3lyp/6-31g*	-535.6885566	-0.64600377	-535.856518	-60.614938	-56.15158784	13.9	18.3
55	SO2 //b3lyp/6-31G*	-548.270226	-1.03475911	-548.539263	-267.940337	-263.7132824	29.1	33.4
56	BF3 PLANAR	-324.2501134	-1.07202746	-324.528841	-1141.576850	-1136.64091	-6.0	-1.1
57	bcl3 B3LYP	-1405.022484	-1.11043006	-1405.311196	-414.221205	-403.5354197	-11.3	-0.6
58	ALf3 B3LYP	-541.7905651	-1.21102975	-542.105433	-1187.650390	-1181.953055	21.5	27.2
59	alcl3 B3LYP	-1622.622412	-1.2125346	-1622.937671	-585.913564	-574.4663845	-1.4	10.0
60	cf4 B3LYP	-437.0594539	-1.46468821	-437.440273	-935.077256	-928.3034661	-2.0	4.7
61	ccl4 B3LYP	-1878.126904	-1.53992118	-1878.527283	-81.931391	-67.49114109	13.9	28.3
62	O=C=S. Singlet	-511.222003	-0.88864533	-511.453051	-147.239305	-143.5898604	-8.7	-5.1
63	CS2 B3LYP	-834.0971988	-0.986341	-834.353647	111.712456	116.7534156	-5.0	0.0
64	COF2 B3LYP	-312.6788998	-1.13215686	-312.973261	-610.295184	-605.7793241	13.5	18.1
65	sif4 B3LYP	-688.6447211	-1.5656596	-689.051793	-1569.789049	-1561.597489	45.2	53.4
66	sicl4, td	-2129.695553	-1.60211148	-2130.112102	-640.764860	-624.9068402	22.0	37.8
67	nno B3LYP	-184.4001645	-0.8564373	-184.622838	78.516407	79.46158716	-3.5	-2.5
68	clno B3LYP	-589.7318561	-0.92448101	-589.972221	62.239504	66.70285392	10.4	14.8

69	nf3 c3v	-353.7064724	-1.2479538	-354.030940	-120.423173	-115.6185077	11.8	16.6
70	pf3 c3v	-640.5623207	-1.30617453	-640.901926	-929.167226	-924.3625605	29.4	34.2
71	ozone 1-a1	-225.1007994	-1.02897468	-225.368333	178.091192	180.9267323	35.4	38.3
72	f2o B3LYP	-274.3582677	-0.9776026	-274.612444	53.367805	57.51609518	28.7	32.8
73	CLF3, C2V	-759.0231726	-1.38504893	-759.383285	-140.998201	-132.6753661	18.0	26.3
74	CF2=CF2 D2H	-475.0146468	-1.66723109	-475.448127	-679.082393	-671.9410327	-20.5	-13.4
75	cl2c=ccl2 B3LYP	-1916.154349	-1.73918133	-1916.606536	-11.053549	3.754270608	1.5	16.3
76	cf3cn B3LYP	-429.9702556	-1.60812414	-430.388368	-500.531982	-494.9921766	-5.1	0.4
77	PROPYNE C3V	-116.4331573	-0.6436417	-116.600504	199.065466	200.1681756	14.1	15.2
78	ALLENE D2D	-116.4332899	-0.63738344	-116.599010	201.332710	202.4354199	11.0	12.1
79	CYCLOPROPENE C2V	-116.3936625	-0.64673635	-116.561814	299.927254	301.0299639	22.9	24.0
80	PROPENE CS	-117.6697461	-0.66703778	-117.843176	42.842431	43.9451406	22.8	23.9
81	CYCLOPROPANE D3H	-117.656127	-0.67320733	-117.831161	76.868824	77.97153396	23.7	24.8
82	PROPANE C2V	-118.8888556	-0.70006577	-119.070873	-74.415760	-73.31305006	30.2	31.3
83	TRANS-1,3-BUTADIENE C2H	-155.6891235	-0.86273008	-155.913433	135.191719	136.6619989	25.2	26.6
84	Dimethyl acetylene	-155.6756287	-0.86858792	-155.901462	166.775700	168.2459805	21.2	22.6
85	Methylene cyclopropane.	-155.656449	-0.86940087	-155.882493	215.172495	216.6427751	14.8	16.2
86	Bicyclo[1.1.0]butane. C2v	-155.6404792	-0.88109802	-155.869565	251.048695	252.5189749	33.9	35.4
87	CYCLOBUTENE b3lyp	-155.6659556	-0.87166901	-155.892589	191.027724	192.4980039	34.5	36.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.8902842	-0.90079086	-157.124490	64.106450	65.57672978	35.7	37.1
89	Isobutene. Single	-156.9077988	-0.89658418	-157.140911	16.204325	17.67460516	32.9	34.4
90	Trans butane	-158.1219645	-0.92700419	-158.362986	-85.104124	-83.63384419	40.4	41.9
91	isobutane B3LYP/6-31G*	-158.1229764	-0.93021866	-158.364833	-91.249402	-89.77912152	43.1	44.5
92	Spiropentane. D2d	-194.883748	-1.1026231	-195.170430	217.383526	219.2213759	32.0	33.9
93	Benzene B3LYP	-231.8105204	-1.26703409	-232.139949	102.049603	104.2550228	19.6	21.8
94	DIFLUOROMETHANE C2V	-238.7244874	-0.85686837	-238.947273	-448.114002	-444.5433222	2.5	6.1
95	HCF3 TRI-FLUOROMETHANE	-337.8937787	-1.16197856	-338.195893	-696.367739	-691.1955035	0.7	5.9
96	CH2CL2 C2V	-959.2860866	-0.87973156	-959.514817	-84.651364	-77.24745398	10.7	18.1
97	chcl3 B3LYP/6-31G*	-1418.710329	-1.20641129	-1419.023996	-90.063590	-79.14151014	13.3	24.2
98	METHYLAMINE b3lyp	-95.6806776	-0.51709433	-95.815122	-5.077356	-4.709786158	17.9	18.3
99	Acetonitrile. CH3-CN.	-132.525559	-0.68606399	-132.703936	81.848644	82.58378427	6.5	7.3
100	NITRO METHANE	-244.6522971	-1.13469588	-244.947318	-60.395837	-58.13790653	14.1	16.3
101	Methyl-nitrite. CH3-O-N=O.	-244.6483052	-1.12445734	-244.940664	-46.654179	-44.39624852	19.9	22.1
102	Methylsilane. CH3-SiH3.	-330.9695089	-0.5671972	-331.116980	-6.290622	-4.137711735	23.0	25.2
103	Formic Acid.	-189.507341	-0.82023561	-189.720602	-370.396600	-368.1386698	8.3	10.5
104	Methyl formate.	-228.7279196	-1.0439706	-228.999352	-346.601117	-343.9756172	9.0	11.7
105	acetamide ch3cohn2	-208.8864102	-1.0134596	-209.149910	-221.856482	-220.1761625	16.6	18.3

106	Aziridine. (cyclic	-133.6759755	-0.7184092	-133.862762	146.596685	147.3318247	20.2	21.0
107	Cyanogen. NCCN.	-185.361973	-0.91777323	-185.600594	303.137157	303.8722974	-3.6	-2.8
108	DIMETHYLAMINE b3lyp	-134.905105	-0.74242812	-135.098136	6.831207	7.566346797	25.2	26.0
109	TRANS ETHYLAMINE	-134.9166462	-0.74358764	-135.109979	-23.324460	-22.5893197	24.0	24.7
110	KETENE B3LYP	-152.3677227	-0.71785777	-152.554366	-49.971379	-48.29105894	-2.7	-1.0
111	OXIRANE B3LYP	-153.5383972	-0.74914643	-153.733175	-35.528331	-33.8480107	17.2	18.9
112	Acetaldehyde B3LYP	-153.5840212	-0.74145404	-153.776799	-153.182181	-151.5018605	12.9	14.6
113	Glyoxal, O=CH-CH=O.	-227.498607	-1.0114029	-227.761572	-206.058956	-203.4334565	6.1	8.7
114	ETHANOL TRANS	-154.7811806	-0.771939	-154.981885	-208.984642	-207.3043221	26.2	27.8
115	DIMETHYL ETHER,	-154.7643946	-0.76898139	-154.964330	-163.736726	-162.0564062	20.4	22.0
116	Thiooxirane. (cyclic	-476.4636693	-0.83387051	-476.680476	100.781740	103.8535746	18.8	21.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.7813207	-1.17741608	-553.087449	-109.167359	-105.1503437	42.3	46.3
118	Thioethanol. CH3-CH2-SH.	-477.6831518	-0.85271242	-477.904857	-15.777068	-12.70523331	30.7	33.7
119	ch3sch3 B3LYP	-477.6811317	-0.85461943	-477.903333	-9.249242	-6.177406978	28.0	31.1
120	Vinyl fluoride,	-177.5827765	-0.74729674	-177.777074	-133.697656	-131.3609608	5.2	7.5
121	Ethyl chloride.	-539.0934412	-0.78781852	-539.298274	-93.194753	-88.94144344	18.9	23.2
122	Vinyl chloride,	-537.8690041	-0.75912873	-538.066378	34.351848	38.60515754	11.3	15.6
123	h2c=chcn B3LYP	-170.536026	-0.88252295	-170.765482	196.942740	198.0454499	16.2	17.3
124	ACETONE B3LYP	-192.828959	-0.96782635	-193.080594	-194.987397	-192.9395067	22.2	24.2
125	CH3COOH ACETIC	-228.7537485	-1.04347698	-229.025053	-414.532225	-411.9067245	18.1	20.7
126	CH3CFO HCCO	-252.7648288	-1.05192586	-253.038329	-432.286523	-429.0046482	10.0	13.2
127	ch3c(o)cl hcco	-613.0375448	-1.068063	-613.315241	-232.108117	-226.9096273	10.6	15.8
128	ch3ch2ch2cl B3LYP	-578.326664	-1.01501313	-578.590567	-104.262448	-99.64156824	27.5	32.2
129	Isopropyl alcohol,	-194.0192426	-1.00110903	-194.279531	-235.891372	-233.8434824	36.9	39.0
130	Methyl ethyl	-194.0027223	-0.99532876	-194.261508	-188.022862	-185.9749721	28.3	30.3
131	Trimethyl Amine.	-174.1318864	-0.97260045	-174.384762	7.951563	9.054272946	31.8	32.9
132	FURAN B3LYP	-229.6388625	-1.15165367	-229.938292	-17.621012	-15.20555202	17.1	19.5
133	Thiophene b3lyp	-552.5536497	-1.24343131	-552.876942	139.055152	142.8621271	24.0	27.8
134	PYROLE PLANAR	-209.7910131	-1.1239828	-210.083249	123.479244	124.9495237	15.1	16.6
135	C2v Pyridine	-247.8379303	-1.31114599	-248.178828	150.938876	152.7767258	10.4	12.2
136	H2 B3LYP/6-31G*	-1.16026671	-0.03484952	-1.169328	7.632177	7.632176727	7.6	7.6
137	SH b3lyp/6-31G*	-398.5820083	-0.35955457	-398.675493	147.805926	150.1426213	4.7	7.0
138	CCH B3LYP	-76.47443541	-0.38179839	-76.573703	584.431131	585.166271	19.2	19.9
139	C2H3 CS,2-A'	-77.75564627	-0.4034893	-77.860553	307.286057	308.0211974	7.7	8.4
140	ch3co hcco	-152.9417528	-0.71939162	-153.128795	-5.268454	-3.588133645	4.8	6.5
141	H2COH C1	-114.8900919	-0.5137661	-115.023671	-7.190016	-5.877265794	10.0	11.3
142	ch3o CS,	-114.8833333	-0.48694415	-115.009939	25.290982	26.60373201	8.1	9.4

143	ch3ch2o 2A"	-154.1215063	-0.71280841	-154.306836	1.163081	2.843401408	16.6	18.3
144	ch3s 2-A'	-437.8163205	-0.58895106	-437.969448	133.493300	136.1975655	8.8	11.5
145	c2h5 staggered	-78.99575402	-0.43478154	-79.108797	134.805922	135.5410621	13.9	14.6
146	(ch3)2ch Cs	-118.233575	-0.66270337	-118.405878	111.195512	112.2982223	21.2	22.3
147	TERT-BUTYL RADICAL	-157.4715272	-0.89266431	-157.703620	85.586103	87.05638294	34.1	35.6
148	NO2 RADICAL	-204.7960922	-0.9067468	-205.031846	32.272683	34.16304314	-0.8	1.1

MAD	**14.9**	**16.9**
LD	**45.2**	**53.4**

Table S5.33b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 26%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.469273	-0.014587	-7.473066
3	be	-14.638465	-0.053447	-14.652361
4	b	-24.618153	-0.077338	-24.638261
5	c	-37.801792	-0.104098	-37.828857
6	n	-54.535430	-0.134824	-54.570484
7	o	-74.999406	-0.192017	-75.049330
8	f	-99.646726	-0.254926	-99.713007
9	na	-162.154579	-0.171608	-162.199197
10	al	-242.237550	-0.220185	-242.294798
11	si	-289.238749	-0.250201	-289.303801
12	p	-341.121646	-0.279249	-341.194250
13	s	-397.956678	-0.320507	-398.040010
14	cl	-459.975664	-0.291411	-460.051431

Table S5.34a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04833667	-0.04677391	-8.060966	146.936489	146.9364887	7.6	7.6
2	BERYLLIUM HYDRIDE	-15.22416606	-0.05511046	-15.239046	319.149637	319.1496373	-22.7	-22.7
3	DOUBLET CH	-38.42030999	-0.14485037	-38.459420	600.087119	600.4546889	3.9	4.2
4	CH2 3-B1	-39.08369574	-0.16389794	-39.127948	395.798722	396.1662924	3.8	4.1
5	Singlet methylene,	-39.06053663	-0.18424947	-39.110284	440.564014	440.9315844	10.4	10.8
6	Methyl radical,	-39.75641101	-0.20879076	-39.812785	152.616858	152.9844282	6.2	6.5
7	ch4 //b3lyp/6-31G*	-40.42145774	-0.25061392	-40.489123	-62.951708	-62.5841384	11.9	12.3
8	NH,TRIPLET, //b3lyp/6-31G*	-55.15019913	-0.18794688	-55.200945	359.221291	359.2212907	2.7	2.7
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79178746	-0.24160797	-55.857022	189.728041	189.7280408	1.0	1.0
10	AMMONIA, //b3lyp/6-31G*	-56.45769897	-0.29575342	-56.537552	-35.291796	-35.29179621	10.7	10.7
11	OH RADICAL	-75.64603	-0.25889622	-75.715932	42.730449	43.67562919	3.4	4.3
12	Water //b3lyp/6-31G*	-76.32330742	-0.32780451	-76.411815	-227.862493	-226.9173133	14.0	14.9
13	HYDROGEN FLUORIDE,	-100.3416569	-0.33841261	-100.433028	-264.851011	-263.249456	7.5	9.1
14	SIH2 singlet	-290.4562291	-0.30632248	-290.538936	275.657277	277.4426168	2.9	4.6
15	SIH2 3B1	-290.4299882	-0.28371451	-290.506591	361.590107	363.3754468	0.9	2.7
16	SIH3 c3v	-291.0716039	-0.31171804	-291.155768	202.872227	204.6575672	2.5	4.2
17	SIH4 //b3lyp/6-31G*	-291.7147153	-0.33894882	-291.806231	42.718363	44.50370312	8.4	10.2
18	ph2 doublet	-342.3387816	-0.3457582	-342.432136	140.181727	140.1817269	1.7	1.7
19	PH3 c3v	-342.9666884	-0.3770267	-343.068486	18.584159	18.58415897	13.1	13.1
20	SH2 //b3lyp/6-31G*	-399.2134805	-0.39843644	-399.321058	-9.112777	-6.77608248	11.4	13.7
21	HCL //b3lyp/6-31G*	-460.6233116	-0.33670142	-460.714221	-88.125012	-84.60684225	4.3	7.9
22	DILITHIUM //b3lyp/6-31G*	-14.96286549	-0.05807204	-14.978545	230.734384	230.7343842	14.8	14.8
23	Lithium Fluoride,	-107.3052496	-0.36755859	-107.404490	-336.030708	-334.4291531	-0.9	0.7
24	ACETYLENE //b3lyp/6-31g*	-77.18415308	-0.41928485	-77.297360	235.468894	236.2040339	8.7	9.4
25	ETHYLENE //b3lyp/6-31g*	-78.42647358	-0.44022509	-78.545334	65.961790	66.69692975	13.7	14.4
26	ETHANE //b3lyp/6-31g*	-79.6500959	-0.47364601	-79.777980	-64.608109	-63.87296862	19.5	20.2
27	CYANO RADICAL,	-92.55925616	-0.45499697	-92.682105	452.887551	453.2551208	14.0	14.4
28	HYDROGEN CYANIDE	-93.27030351	-0.46395559	-93.395572	131.395302	131.7628724	-0.4	0.0
29	CARBON MONOXIDE	-113.1615911	-0.47469543	-113.289759	-109.209134	-107.8963839	1.2	2.6
30	HCO BENT	-113.6873435	-0.49714345	-113.821572	37.986631	39.29938112	-3.9	-2.5
31	H2CO //b3lyp/6-31g*	-114.3300001	-0.51666303	-114.469499	-106.044631	-104.7318808	2.7	4.1

32	METHANOL //b3lyp/6-31g*	-115.5367991	-0.54620006	-115.684273	-186.761587	-185.4488369	14.1	15.4
33	Nitrogen N2,	-109.3683184	-0.49776527	-109.502715	3.555754	3.555753695	3.6	3.6
34	H2NNH2 //b3lyp/6-31g*	-111.6773297	-0.56096123	-111.828789	109.814506	109.8145055	14.4	14.4
35	NO radical,	-129.7160091	-0.53972891	-129.861736	91.009401	91.95458051	0.6	1.6
36	O2 //b3lyp/6-31g*	-150.1261138	-0.60393782	-150.289177	-0.399647	1.490713376	-0.4	1.5
37	HYDROGEN PEROXIDE	-151.3432848	-0.63397684	-151.514459	-112.416783	-110.5264227	23.6	25.5
38	F2 //b3lyp/6-31g*	-199.298627	-0.66268826	-199.477553	22.000258	25.20336769	22.0	25.2
39	CO2 D*H	-188.335445	-0.79804841	-188.550918	-406.511125	-404.253195	-13.2	-11.0
40	na2 //b3lyp/6-31G*	-324.319706	-0.37167291	-324.420058	144.002113	144.0021127	1.7	1.7
41	SI2 3-SGG	-578.5680659	-0.55936116	-578.719093	590.426394	593.997074	5.1	8.7
42	P2 //b3lyp/6-31g*	-682.372877	-0.71032386	-682.564664	156.460992	156.4609918	12.9	12.9
43	S2 //b3lyp/6-31g*	-796.0304672	-0.75736884	-796.234957	130.744543	135.4179332	2.3	7.0
44	CL2 //b3lyp/6-31g*	-920.0072683	-0.65205283	-920.183323	10.133709	17.17004933	10.1	17.2
45	Sodium Chloride	-622.2599769	-0.50912827	-622.397441	-174.413934	-170.895764	8.0	11.5
46	SIO //b3lyp/6-31g*	-364.4855918	-0.61703312	-364.652191	-92.763958	-90.03343798	10.2	12.9
47	Carbon monosulfide,	-435.9786602	-0.5767118	-436.134372	290.317182	293.0214472	10.4	13.1
48	OS //b3lyp/6-31g*	-473.0985145	-0.68763391	-473.284176	6.958007	10.2398821	1.9	5.2
49	CLO 2-PI	-535.0307781	-0.60563427	-535.194299	113.527195	117.9905448	12.3	16.7
50	CLF 1-SG	-559.6783252	-0.65452791	-559.855048	-48.730576	-43.61085085	6.5	11.6
51	si2h6 //b3lyp/6-31g*	-582.2554612	-0.658734	-582.433319	98.304185	101.8748647	18.4	22.0
52	Methyl chloride,	-499.846723	-0.56067384	-499.998105	-73.558866	-69.67312569	8.4	12.3
53	H3C-SH METHANETHIOL	-438.4398038	-0.62490422	-438.608528	-4.013310	-1.309045149	19.0	21.7
54	HOCl //b3lyp/6-31g*	-535.6783042	-0.64600169	-535.852725	-62.909371	-58.44602122	11.6	16.0
55	SO2 //b3lyp/6-31G*	-548.2576797	-1.03474896	-548.537062	-273.774766	-269.5477107	23.3	27.5
56	BF3 PLANAR	-324.2381783	-1.07202823	-324.527626	-1144.934904	-1139.998964	-9.4	-4.5
57	bcl3 B3LYP	-1404.999597	-1.11041174	-1405.299408	-416.107381	-405.421596	-13.2	-2.5
58	ALf3 B3LYP	-541.7750362	-1.2110378	-542.102016	-1191.171447	-1185.474112	18.0	23.7
59	alcl3 B3LYP	-1622.595935	-1.21251896	-1622.923315	-587.000605	-575.5534247	-2.5	9.0
60	cf4 B3LYP	-437.0435389	-1.46468071	-437.439003	-940.214431	-933.440641	-7.2	-0.4
61	ccl4 B3LYP	-1878.096385	-1.5398962	-1878.512157	-85.740868	-71.30061767	10.1	24.5
62	O=C=S. Singlet	-511.2104552	-0.88862378	-511.450384	-151.573851	-147.9244057	-13.1	-9.4
63	CS2 B3LYP	-834.0820039	-0.98631066	-834.348308	107.990637	113.0315971	-8.7	-3.7
64	COF2 B3LYP	-312.6669925	-1.1321474	-312.972672	-615.453232	-610.9373719	8.4	12.9
65	sif4 B3LYP	-688.6251737	-1.5656559	-689.047901	-1573.969749	-1565.778189	41.1	49.2
66	sicl4, td	-2129.661403	-1.60208604	-2130.093966	-642.597983	-626.7399628	20.1	36.0
67	nno B3LYP	-184.39229	-0.85641473	-184.623522	71.944614	72.88979447	-10.1	-9.1
68	clno B3LYP	-589.7194285	-0.92446227	-589.969033	56.836556	61.29990573	5.0	9.4

69	nf3 c3v	-353.6936937	-1.24794807	-354.030640	-126.412844	-121.6081795	5.8	10.6
70	pf3 c3v	-640.5458014	-1.30617133	-640.898468	-932.907318	-928.1026528	25.6	30.5
71	ozone 1-a1	-225.0920221	-1.0289519	-225.369839	168.926175	171.7617147	26.3	29.1
72	f2o B3LYP	-274.348541	-0.9776009	-274.612493	47.996408	52.14469763	23.3	27.5
73	CLF3, C2V	-759.0057435	-1.3850471	-759.379706	-147.376378	-139.0535431	11.6	19.9
74	CF2=CF2 D2H	-474.9966939	-1.66722158	-475.446844	-685.644999	-678.5036391	-27.1	-19.9
75	cl2c=ccl2 B3LYP	-1916.121745	-1.73915076	-1916.591316	-16.077173	-1.269353215	-3.5	11.3
76	cf3cn B3LYP	-429.9533171	-1.60810077	-430.387504	-507.963091	-502.4232863	-12.6	-7.0
77	PROPYNE C3V	-116.4261244	-0.64361801	-116.599901	196.269238	197.371948	11.3	12.4
78	ALLENE D2D	-116.4262535	-0.63736167	-116.598341	198.708595	199.8113048	8.3	9.4
79	CYCLOPROPENE C2V	-116.3865738	-0.64671887	-116.561188	297.191929	298.2946395	20.2	21.3
80	PROPENE CS	-117.6621746	-0.6670183	-117.842270	40.843049	41.94575881	20.8	21.9
81	CYCLOPROPANE D3H	-117.6484866	-0.67319233	-117.830249	74.885234	75.98794429	21.7	22.9
82	PROPANE C2V	-118.8807496	-0.70004823	-119.069763	-75.880206	-74.77749593	28.7	29.8
83	TRANS-1,3-BUTADIENE C2H	-155.6795023	-0.86270264	-155.912432	131.981704	133.4519839	21.9	23.4
84	Dimethyl acetylene	-155.6660115	-0.86855894	-155.900522	163.402793	164.8730726	17.8	19.3
85	Methylene cyclopropane.	-155.6467654	-0.86937784	-155.881497	211.948122	213.4184022	11.5	13.0
86	Bicyclo[1.1.0]butane. C2v	-155.6307273	-0.88107839	-155.868618	247.694361	249.1646411	30.5	32.0
87	CYCLOBUTENE b3lyp	-155.6562474	-0.87164579	-155.891592	187.808523	189.278803	31.3	32.8
88	CYCLOBUTANE b3lyp/6-31G*	-156.8800417	-0.9007695	-157.123249	61.524115	62.99439458	33.1	34.5
89	Isobutene. Single	-156.8976332	-0.89655905	-157.139704	13.533339	15.00361916	30.3	31.7
90	Trans butane	-158.1112731	-0.9269804	-158.361558	-87.194145	-85.72386453	38.3	39.8
91	isobutane B3LYP/6-31G*	-158.1122757	-0.93019495	-158.363428	-93.399772	-91.9294924	40.9	42.4
92	Spiropentane. D2d	-194.8714103	-1.10259847	-195.169112	213.545751	215.3836014	28.2	30.0
93	Benzene B3LYP	-231.79663	-1.26699647	-232.138719	96.521309	98.72672926	14.1	16.3
94	DIFLUOROMETHANE C2V	-238.715079	-0.85686847	-238.946433	-450.875270	-447.3045903	-0.3	3.3
95	HCF3 TRI-FLUOROMETHANE	-337.8811187	-1.16197626	-338.194852	-700.353942	-695.1817069	-3.3	1.9
96	CH2CL2 C2V	-959.2693714	-0.87971829	-959.506895	-86.345170	-78.94125986	9.1	16.5
97	chcl3 B3LYP/6-31G*	-1418.686715	-1.20639255	-1419.012441	-92.733652	-81.81157222	10.6	21.5
98	METHYLAMINE b3lyp	-95.67492955	-0.51708794	-95.814543	-6.537230	-6.169659726	16.5	16.8
99	Acetonitrile. CH3-CN.	-132.5183282	-0.68604311	-132.703560	78.395842	79.13098213	3.1	3.8
100	NITRO METHANE	-244.6410732	-1.13467578	-244.947436	-67.157715	-64.89978463	7.3	9.6
101	Methyl-nitrite. CH3-O-N=O.	-244.637118	-1.12443617	-244.940716	-53.242946	-50.98501612	13.3	15.5
102	Methylsilane. CH3-SiH3.	-330.960433	-0.56718327	-331.113572	-6.189652	-4.036742094	23.1	25.3
103	Formic Acid.	-189.4988832	-0.82022976	-189.720345	-374.654876	-372.3969457	4.0	6.3
104	Methyl formate.	-228.716891	-1.04395522	-228.998759	-351.437105	-348.8116049	4.2	6.8
105	acetamide ch3cohn2	-208.8755684	-1.01344545	-209.149199	-226.165735	-224.4854148	12.3	14.0

106	Aziridine. (cyclic	-133.6681289	-0.71839675	-133.862096	143.905729	144.6408686	17.5	18.3
107	Cyanogen. NCCN.	-185.3530498	-0.9177403	-185.600840	296.533216	297.2683563	-10.2	-9.4
108	DIMETHYLAMINE b3lyp	-134.8967757	-0.7424146	-135.097228	4.777616	5.512756311	23.2	23.9
109	TRANS ETHYLAMINE	-134.9083133	-0.74357491	-135.109078	-25.399523	-24.66438283	21.9	22.6
110	KETENE B3LYP	-152.3602506	-0.71784245	-152.554068	-53.845978	-52.16565816	-6.6	-4.9
111	OXIRANE B3LYP	-153.5303486	-0.74913644	-153.732615	-38.714801	-37.03448134	14.0	15.7
112	Acetaldehyde B3LYP	-153.576026	-0.74144257	-153.776215	-156.305761	-154.6254412	9.8	11.5
113	Glyoxal, O=CH-CH=O.	-227.4881555	-1.01138941	-227.761231	-211.556185	-208.930685	0.6	3.2
114	ETHANOL TRANS	-154.7726337	-0.77192977	-154.981055	-211.461495	-209.7811749	23.7	25.4
115	DIMETHYL ETHER,	-154.7558608	-0.7689702	-154.963483	-166.169037	-164.4887167	17.9	19.6
116	Thiooxirane. (cyclic	-476.4519738	-0.83385345	-476.677114	98.546847	101.6186817	16.5	19.6
117	Dimethylsulfoxide. (CH3)2SO.	-552.7661138	-1.17739794	-553.084011	-112.938787	-108.9217724	38.5	42.5
118	Thioethanol. CH3-CH2-SH.	-477.6709823	-0.85269467	-477.901210	-17.261496	-14.18966056	29.2	32.3
119	ch3sch3 B3LYP	-477.6689695	-0.85460168	-477.899712	-10.802956	-7.73112143	26.4	29.5
120	Vinyl fluoride,	-177.5745505	-0.74728655	-177.776318	-136.385746	-134.0490512	2.5	4.9
121	Ethyl chloride.	-539.081032	-0.78780337	-539.293739	-94.723095	-90.46978533	17.4	21.7
122	Vinyl chloride,	-537.8571229	-0.75911165	-538.062083	32.191913	36.44522275	9.2	13.4
123	h2c=chcn B3LYP	-170.5267527	-0.88249435	-170.765026	192.240548	193.3432585	11.5	12.6
124	ACETONE B3LYP	-192.8183716	-0.96780794	-193.079680	-198.703162	-196.6552724	18.4	20.5
125	CH3COOH ACETIC	-228.7427001	-1.04346426	-229.024435	-419.305101	-416.6796005	13.3	15.9
126	CH3CFO HCCO	-252.7535832	-1.05191277	-253.037600	-436.779434	-433.4975587	5.5	8.8
127	ch3c(o)cl hcco	-613.022658	-1.0680441	-613.311030	-236.223558	-231.0250679	6.4	11.6
128	ch3ch2ch2cl B3LYP	-578.3116702	-1.01499183	-578.585718	-106.425472	-101.8045922	25.4	30.0
129	Isopropyl alcohol,	-194.0081017	-1.00109294	-194.278397	-239.029720	-236.9818302	33.8	35.8
130	Methyl ethyl	-193.9916028	-0.99531089	-194.260337	-191.064268	-189.0163778	25.2	27.3
131	Trimethyl Amine.	-174.1209628	-0.97258034	-174.383560	5.210995	6.313704633	29.1	30.2
132	FURAN B3LYP	-229.6266084	-1.1516277	-229.937548	-23.241798	-20.82633847	11.5	13.9
133	Thiophene b3lyp	-552.5377519	-1.24339873	-552.873470	134.191946	137.9989208	19.1	22.9
134	PYROLE PLANAR	-209.7789503	-1.12395523	-210.082418	118.300816	119.7710965	9.9	11.4
135	C2v Pyridine	-247.8238331	-1.31111028	-248.177833	144.733678	146.5715282	4.2	6.0
136	H2 B3LYP/6-31G*	-1.15988407	-0.03484981	-1.169294	7.721618	7.721618323	7.7	7.7
137	SH b3lyp/6-31G*	-398.5753299	-0.35955645	-398.672410	147.757838	150.0945327	4.7	7.0
138	CCH B3LYP	-76.47038142	-0.38177828	-76.573462	582.145612	582.8807517	16.9	17.6
139	C2H3 CS,2-A'	-77.75102054	-0.40346824	-77.859957	305.932820	306.66796	6.4	7.1
140	ch3co hcco	-152.9340883	-0.7193708	-153.128318	-8.674542	-6.994221575	1.4	3.0
141	H2COH C1	-114.8844629	-0.51375734	-115.023177	-9.090167	-7.777416809	8.1	9.4
142	ch3o CS,	-114.8777372	-0.48692874	-115.009208	24.013219	25.3259689	6.9	8.2

143	ch3ch2o 2A"	-154.1133259	-0.7127842	-154.305778	-0.713056	0.967264266	14.8	16.4
144	ch3s 2-A'	-437.8070645	-0.58894317	-437.966079	132.737353	135.4416184	8.1	10.8
145	c2h5 staggered	-78.9905793	-0.43477414	-79.107968	134.062797	134.7979369	13.1	13.9
146	(ch3)2ch Cs	-118.2258085	-0.66268611	-118.404734	109.820224	110.9229342	19.9	21.0
147	TERT-BUTYL RADICAL	-157.4611663	-0.89263683	-157.702178	83.532302	85.00258163	32.1	33.5
148	NO2 RADICAL	-204.7877723	-0.90672529	-205.032588	25.331519	27.22187883	-7.7	-5.8

MAD	**13.2**	**15.0**
LD	**41.1**	**49.2**

Table S5.34b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.468736	-0.014586	-7.472675
3	be	-14.637515	-0.053442	-14.651945
4	b	-24.616888	-0.077342	-24.637770
5	c	-37.800193	-0.104104	-37.828301
6	n	-54.533502	-0.134828	-54.569905
7	o	-74.996821	-0.192028	-75.048669
8	f	-99.643506	-0.254936	-99.712339
9	na	-162.150487	-0.171605	-162.196821
10	al	-242.232594	-0.220186	-242.292044
11	si	-289.233434	-0.250203	-289.300988
12	p	-341.115975	-0.279244	-341.191371
13	s	-397.950372	-0.320510	-398.036909
14	cl	-459.968744	-0.291414	-460.047426

Table S5.35a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04744841	-0.04677511	-8.060545	147.012641	147.0126405	7.7	7.7
2	BERYLLIUM HYDRIDE	-15.22308497	-0.05510303	-15.238514	319.454088	319.4540881	-22.4	-22.4
3	DOUBLET CH	-38.41833246	-0.14485438	-38.458892	600.013842	600.3814125	3.8	4.2
4	CH2 3-B1	-39.08154377	-0.16389644	-39.127435	395.687395	396.0549649	3.6	4.0
5	Singlet methylene,	-39.05820905	-0.18424581	-39.109798	440.381009	440.7485794	10.3	10.6
6	Methyl radical,	-39.7538254	-0.20879439	-39.812288	152.461620	152.8291902	6.0	6.4
7	ch4 //b3lyp/6-31G*	-40.41851168	-0.25060804	-40.488682	-63.251661	-62.88409075	11.6	12.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14781871	-0.18795715	-55.200447	359.009353	359.0093535	2.5	2.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78899128	-0.24161489	-55.856643	189.201272	189.2012723	0.5	0.5
10	AMMONIA, //b3lyp/6-31G*	-56.45451959	-0.29575441	-56.537331	-36.229703	-36.22970252	9.8	9.8
11	OH RADICAL	-75.64301948	-0.25890634	-75.715513	42.093711	43.03889083	2.8	3.7
12	Water //b3lyp/6-31G*	-76.31990315	-0.32781083	-76.411690	-229.271835	-228.3266547	12.6	13.5
13	HYDROGEN FLUORIDE,	-100.3380333	-0.3384213	-100.432791	-265.981102	-264.3795468	6.4	8.0
14	SIH2 singlet	-290.450255	-0.30631469	-290.536023	275.919495	277.7048355	3.1	4.9
15	SIH2 3B1	-290.4242096	-0.28368809	-290.503642	361.946413	363.7317532	1.3	3.1
16	SIH3 c3v	-291.0654495	-0.31170321	-291.152726	203.471496	205.256836	3.1	4.8
17	SIH4 //b3lyp/6-31G*	-291.7082229	-0.33893991	-291.803126	43.485466	45.27080595	9.2	11.0
18	ph2 doublet	-342.3323502	-0.34575801	-342.429162	140.428456	140.4284564	1.9	1.9
19	PH3 c3v	-342.9599292	-0.37701769	-343.065494	18.877057	18.87705686	13.4	13.4
20	SH2 //b3lyp/6-31G*	-399.2064622	-0.39843079	-399.318023	-9.283522	-6.946826884	11.2	13.6
21	HCL //b3lyp/6-31G*	-460.6160405	-0.33669917	-460.710316	-88.388977	-84.87080713	4.1	7.6
22	DILITHIUM //b3lyp/6-31G*	-14.96152762	-0.05806795	-14.977787	230.671200	230.6712	14.8	14.8
23	Lithium Fluoride,	-107.3010728	-0.36757324	-107.403993	-337.504894	-335.9033388	-2.4	-0.8
24	ACETYLENE //b3lyp/6-31g*	-77.17970495	-0.41926637	-77.297100	233.234147	233.9692868	6.5	7.2
25	ETHYLENE //b3lyp/6-31g*	-78.42148849	-0.44021106	-78.544748	64.583774	65.31891376	12.3	13.0
26	ETHANE //b3lyp/6-31g*	-79.64457447	-0.47363445	-79.777192	-65.457246	-64.72210599	18.6	19.4
27	CYANO RADICAL,	-92.55498878	-0.4549091	-92.682363	449.231287	449.5988566	10.3	10.7
28	HYDROGEN CYANIDE	-93.26565739	-0.46394041	-93.395561	128.444774	128.8123441	-3.4	-3.0
29	CARBON MONOXIDE	-113.1567421	-0.47468924	-113.289655	-112.132101	-110.8193506	-1.7	-0.4
30	HCO BENT	-113.6822611	-0.49713106	-113.821458	35.091615	36.40436488	-6.7	-5.4
31	H2CO //b3lyp/6-31g*	-114.3245931	-0.516658	-114.469257	-108.605333	-107.2925832	0.2	1.5

32	METHANOL //b3lyp/6-31g*	-115.5308375	-0.54619721	-115.683773	-188.643311	-187.3305606	12.2	13.5
33	Nitrogen N2,	-109.3634808	-0.49774994	-109.502851	0.160072	0.160071934	0.2	0.2
34	H2NNH2 //b3lyp/6-31g*	-111.671361	-0.56096041	-111.828430	107.718781	107.7187813	12.3	12.3
35	NO radical,	-129.7107286	-0.53971936	-129.861850	87.454084	88.39926415	-2.9	-2.0
36	O2 //b3lyp/6-31g*	-150.1203911	-0.60393679	-150.289493	-4.702473	-2.812113029	-4.7	-2.8
37	HYDROGEN PEROXIDE	-151.3369215	-0.63398179	-151.514436	-115.830784	-113.9404244	20.1	22.0
38	F2 //b3lyp/6-31g*	-199.2918701	-0.66269205	-199.477424	18.833687	22.0367973	18.8	22.0
39	CO2 D*H	-188.3275337	-0.79803513	-188.550983	-411.614411	-409.356481	-18.3	-16.1
40	na2 //b3lyp/6-31G*	-324.3112787	-0.3716674	-324.415346	143.897732	143.8977321	1.6	1.6
41	SI2 3-SGG	-578.5570849	-0.55934302	-578.713701	589.812296	593.3829759	4.5	8.0
42	P2 //b3lyp/6-31g*	-682.360734	-0.71030041	-682.559618	154.587733	154.5877332	11.1	11.1
43	S2 //b3lyp/6-31g*	-796.0173982	-0.75735964	-796.229459	128.898492	133.5718816	0.4	5.1
44	CL2 //b3lyp/6-31g*	-919.9931393	-0.65204522	-920.175712	9.084069	16.12040882	9.1	16.1
45	Sodium Chloride	-622.2486476	-0.50913068	-622.391204	-174.791671	-171.2735007	7.6	11.1
46	SIO //b3lyp/6-31g*	-364.477066	-0.61704167	-364.649838	-95.707965	-92.97744474	7.2	9.9
47	Carbon monosulfide,	-435.9701774	-0.57669177	-436.131651	287.861964	290.5662285	8.0	10.7
48	OS //b3lyp/6-31g*	-473.089109	-0.68762569	-473.281644	3.727583	7.009458498	-1.3	2.0
49	CLO 2-PI	-535.0208616	-0.6055924	-535.190427	111.441081	115.9044307	10.2	14.7
50	CLF 1-SG	-559.6678627	-0.65452738	-559.851130	-50.713445	-45.59372008	4.5	9.6
51	si2h6 //b3lyp/6-31g*	-582.2428442	-0.65871731	-582.427285	99.375488	102.9461684	19.5	23.0
52	Methyl chloride,	-499.8368978	-0.56066493	-499.993884	-74.451644	-70.56590412	7.6	11.4
53	H3C-SH METHANETHIOL	-438.4302185	-0.62489261	-438.605188	-4.845056	-2.140790684	18.2	20.9
54	HOCl //b3lyp/6-31g*	-535.6680519	-0.64599961	-535.848932	-65.202862	-60.73951152	9.3	13.7
55	SO2 //b3lyp/6-31G*	-548.2451335	-1.03473881	-548.534860	-279.607231	-275.3801758	17.5	21.7
56	BF3 PLANAR	-324.2262433	-1.07202901	-324.526411	-1148.291137	-1143.355197	-12.8	-7.8
57	bcl3 B3LYP	-1404.97671	-1.11039342	-1405.287620	-417.991582	-407.3057973	-15.1	-4.4
58	ALf3 B3LYP	-541.7595075	-1.21104587	-542.098600	-1194.691158	-1188.993823	14.5	20.2
59	alcl3 B3LYP	-1622.569458	-1.21250332	-1622.908959	-588.085921	-576.638741	-3.6	7.9
60	cf4 B3LYP	-437.0276239	-1.46467322	-437.437732	-945.348730	-938.5749399	-12.3	-5.5
61	ccl4 B3LYP	-1878.065866	-1.53987122	-1878.497030	-89.547684	-75.10743357	6.3	20.7
62	O=C=S. Singlet	-511.1989074	-0.88860223	-511.447716	-155.906064	-152.2566185	-17.4	-13.8
63	CS2 B3LYP	-834.066809	-0.98628032	-834.342968	104.271207	109.3121673	-12.5	-7.4
64	COF2 B3LYP	-312.6550852	-1.13213795	-312.972084	-620.608703	-616.0928431	3.2	7.7
65	sif4 B3LYP	-688.6056265	-1.5656522	-689.044009	-1578.147874	-1569.956314	36.9	45.1
66	sicl4, td	-2129.627252	-1.60206061	-2130.075829	-644.428538	-628.5705175	18.3	34.2
67	nno B3LYP	-184.3844155	-0.85639216	-184.624205	65.375064	66.32024448	-16.6	-15.7
68	clno B3LYP	-589.707001	-0.92444354	-589.965845	51.435623	55.8989734	-0.4	4.0

69	nf3 c3v	-353.6809151	-1.24794234	-354.030339	-132.400410	-127.5957451	-0.2	4.6
70	pf3 c3v	-640.5292821	-1.30616812	-640.895009	-936.645846	-931.8411807	21.9	26.7
71	ozone 1-a1	-225.0832448	-1.02892912	-225.371345	159.764215	162.5997551	17.1	19.9
72	f2o B3LYP	-274.3388145	-0.9775992	-274.612542	42.626769	46.77505916	17.9	22.1
73	CLF3, C2V	-758.9883145	-1.38504527	-759.376127	-153.752620	-145.4297846	5.2	13.6
74	CF2=CF2 D2H	-474.978741	-1.66721207	-475.445560	-692.204199	-685.0628391	-33.6	-26.5
75	cl2c=ccl2 B3LYP	-1916.089142	-1.73912018	-1916.576096	-21.097444	-6.289624275	-8.5	6.3
76	cf3cn B3LYP	-429.9363786	-1.6080774	-430.386640	-515.390386	-509.8505811	-20.0	-14.5
77	PROPYNE C3V	-116.4190916	-0.64359432	-116.599298	193.475244	194.5779542	8.5	9.6
78	ALLENE D2D	-116.4192172	-0.63733991	-116.597672	196.086605	197.1893154	5.7	6.8
79	CYCLOPROPENE C2V	-116.3794851	-0.64670138	-116.560562	294.458573	295.5612826	17.5	18.6
80	PROPENE CS	-117.6546032	-0.66699881	-117.841363	38.845687	39.94839709	18.8	19.9
81	CYCLOPROPANE D3H	-117.6408463	-0.67317734	-117.829336	72.903441	74.00615099	19.8	20.9
82	PROPANE C2V	-118.8726436	-0.70003069	-119.068652	-77.342767	-76.24005723	27.3	28.4
83	TRANS-1,3-BUTADIENE C2H	-155.6698813	-0.86267519	-155.911430	128.774492	130.2447718	18.7	20.2
84	Dimethyl acetylene	-155.6563943	-0.86852996	-155.899583	160.032735	161.5030149	14.4	15.9
85	Methylene cyclopropane.	-155.637082	-0.86935481	-155.880501	208.726287	210.1965671	8.3	9.8
86	Bicyclo[1.1.0]butane. C2v	-155.6209754	-0.88105876	-155.867672	244.342439	245.8127191	27.2	28.7
87	CYCLOBUTENE b3lyp	-155.6465393	-0.87162256	-155.890594	184.591903	186.0621835	28.1	29.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8697993	-0.90074814	-157.122009	58.944256	60.41453574	30.5	32.0
89	Isobutene. Single	-156.8874677	-0.89653391	-157.138497	10.865009	12.33528859	27.6	29.1
90	Trans butane	-158.1005817	-0.9269566	-158.360130	-89.281606	-87.81132607	36.2	37.7
91	isobutane B3LYP/6-31G*	-158.1015752	-0.93017124	-158.362023	-95.547622	-94.07734227	38.8	40.2
92	Spiropentane. D2d	-194.8590727	-1.10257384	-195.167793	209.710964	211.5488137	24.4	26.2
93	Benzene B3LYP	-231.7827397	-1.26695885	-232.137488	90.997102	93.20252209	8.6	10.8
94	DIFLUOROMETHANE C2V	-238.7056707	-0.85686858	-238.945594	-453.635137	-450.0644568	-3.0	0.6
95	HCF3 TRI-FLUOROMETHANE	-337.8684587	-1.16197397	-338.193811	-704.338067	-699.165832	-7.3	-2.1
96	CH2CL2 C2V	-959.2526563	-0.87970503	-959.498974	-88.037469	-80.63355871	7.4	14.8
97	chcl3 B3LYP/6-31G*	-1418.663101	-1.20637382	-1419.000886	-95.401654	-84.47957434	7.9	18.9
98	METHYLAMINE b3lyp	-95.66918159	-0.51708155	-95.813964	-7.996329	-7.628758772	15.0	15.4
99	Acetonitrile. CH3-CN.	-132.5110976	-0.68602224	-132.703184	74.945012	75.68015175	-0.4	0.4
100	NITRO METHANE	-244.6298494	-1.13465568	-244.947553	-73.916778	-71.6588482	0.6	2.8
101	Methyl-nitrite. CH3-O-N=O.	-244.6259309	-1.124415	-244.940767	-59.828869	-57.57093925	6.7	9.0
102	Methylsilane. CH3-SiH3.	-330.9513572	-0.56716933	-331.110165	-6.087481	-3.934571024	23.2	25.4
103	Formic Acid.	-189.4904254	-0.82022391	-189.720088	-378.911264	-376.6533344	-0.3	2.0
104	Methyl formate.	-228.7058626	-1.04393984	-228.998166	-356.270366	-353.6448663	-0.6	2.0
105	acetamide ch3cohn2	-208.8647267	-1.01343131	-209.148487	-230.472801	-228.7924806	8.0	9.7

106	Aziridine. (cyclic	-133.6602823	-0.7183843	-133.861430	141.216283	141.9514227	14.9	15.6
107	Cyanogen. NCCN.	-185.3441266	-0.91770737	-185.601085	289.932119	290.6672585	-16.8	-16.0
108	DIMETHYLAMINE b3lyp	-134.8884465	-0.74240108	-135.096319	2.725513	3.460653434	21.1	21.9
109	TRANS ETHYLAMINE	-134.8999805	-0.74356218	-135.108178	-27.473140	-26.73799985	19.8	20.5
110	KETENE B3LYP	-152.3527786	-0.71782714	-152.553770	-57.718482	-56.03816223	-10.4	-8.8
111	OXIRANE B3LYP	-153.5223001	-0.74912645	-153.732056	-41.899476	-40.2191556	10.8	12.5
112	Acetaldehyde B3LYP	-153.5680309	-0.7414311	-153.775632	-159.427468	-157.7471479	6.7	8.4
113	Glyoxal, O=CH-CH=O.	-227.477704	-1.01137591	-227.760889	-217.050753	-214.4252529	-4.9	-2.3
114	ETHANOL TRANS	-154.7640868	-0.77192055	-154.980225	-213.936625	-212.2563049	21.2	22.9
115	DIMETHYL ETHER,	-154.7473271	-0.76895902	-154.962636	-168.599548	-166.9192276	15.5	17.2
116	Thiooxirane. (cyclic	-476.4402785	-0.83383639	-476.673753	96.313716	99.38555117	14.3	17.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.7509071	-1.1773798	-553.080573	-116.707803	-112.6907876	34.8	38.8
118	Thioethanol. CH3-CH2-SH.	-477.6588129	-0.85267691	-477.897562	-18.744143	-15.67230824	27.7	30.8
119	ch3sch3 B3LYP	-477.6568074	-0.85458394	-477.896091	-12.354932	-9.283097276	24.9	28.0
120	Vinyl fluoride,	-177.5663245	-0.74727636	-177.775562	-139.072099	-136.7354045	-0.2	2.2
121	Ethyl chloride.	-539.0686229	-0.78778822	-539.289204	-96.249751	-91.99644111	15.9	20.1
122	Vinyl chloride,	-537.8452417	-0.75909458	-538.057788	30.033732	34.2870418	7.0	11.3
123	h2c=chcn B3LYP	-170.5174794	-0.88246576	-170.764570	187.541099	188.6438091	6.8	7.9
124	ACETONE B3LYP	-192.8077842	-0.96778953	-193.078765	-202.416351	-200.3684608	14.7	16.8
125	CH3COOH ACETIC	-228.7316519	-1.04345155	-229.023818	-424.075397	-421.4498972	8.6	11.2
126	CH3CFO HCCO	-252.7423376	-1.05189969	-253.036870	-441.269815	-437.9879403	1.0	4.3
127	ch3c(o)cl hcco	-613.0077713	-1.0680252	-613.306818	-240.336442	-235.1379522	2.3	7.5
128	ch3ch2ch2cl B3LYP	-578.2966766	-1.01497053	-578.580868	-108.586148	-103.9652684	23.2	27.8
129	Isopropyl alcohol,	-193.996961	-1.00107686	-194.277263	-242.165646	-240.1177563	30.6	32.7
130	Methyl ethyl	-193.9804835	-0.99529303	-194.259166	-194.103185	-192.0552945	22.2	24.3
131	Trimethyl Amine.	-174.1100394	-0.97256024	-174.382356	2.472618	3.575327561	26.3	27.4
132	FURAN B3LYP	-229.6143545	-1.15160173	-229.936803	-28.859193	-26.44373329	5.9	8.3
133	Thiophene b3lyp	-552.5218543	-1.24336616	-552.869997	129.332092	133.1390667	14.3	18.1
134	PYROLE PLANAR	-209.7668876	-1.12392765	-210.081587	113.125431	114.5957106	4.8	6.2
135	C2v Pyridine	-247.8097361	-1.31107457	-248.176837	138.532333	140.3701834	-2.1	-0.2
136	H2 B3LYP/6-31G*	-1.15950145	-0.03485011	-1.169259	7.810985	7.81098483	7.8	7.8
137	SH b3lyp/6-31G*	-398.5686516	-0.35955835	-398.669328	147.709798	150.0464934	4.6	7.0
138	CCH B3LYP	-76.46632752	-0.38175821	-76.573220	579.861718	580.5968576	14.6	15.3
139	C2H3 CS,2-A'	-77.74639493	-0.40344719	-77.859360	304.581201	305.3163411	5.0	5.7
140	ch3co hcco	-152.926424	-0.71934995	-153.127842	-12.078269	-10.39794866	-2.0	-0.4
141	H2COH C1	-114.8788339	-0.5137486	-115.022684	-10.988992	-9.676241946	6.2	7.5
142	ch3o CS,	-114.8721412	-0.48691335	-115.008477	22.737105	24.0498546	5.6	6.9

143	ch3ch2o 2A"	-154.1051456	-0.71276002	-154.304718	-2.586724	-0.90640438	12.9	14.6
144	ch3s 2-A'	-437.7978085	-0.5889353	-437.962710	131.982281	134.6865461	7.3	10.0
145	c2h5 staggered	-78.98540468	-0.43476677	-79.107139	133.320611	134.0557506	12.4	13.1
146	(ch3)2ch Cs	-118.2180422	-0.66266887	-118.403589	108.446765	109.549475	18.5	19.6
147	TERT-BUTYL RADICAL	-157.4508056	-0.89260937	-157.700736	81.481152	82.95143207	30.0	31.5
148	NO2 RADICAL	-204.7794526	-0.90670379	-205.033330	18.392897	20.28325705	-14.7	-12.8

MAD	**11.9**	**13.4**
LD	**38.8**	**45.1**

Table S5.35b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.468200	-0.014586	-7.472283
3	be	-14.636566	-0.053437	-14.651529
4	b	-24.615623	-0.077346	-24.637280
5	c	-37.798595	-0.104111	-37.827746
6	n	-54.531573	-0.134832	-54.569326
7	o	-74.994237	-0.192038	-75.048007
8	f	-99.640287	-0.254946	-99.711672
9	na	-162.146396	-0.171603	-162.194445
10	al	-242.227637	-0.220187	-242.289290
11	si	-289.228118	-0.250204	-289.298175
12	p	-341.110304	-0.279238	-341.188491
13	s	-397.944065	-0.320513	-398.033809
14	cl	-459.961823	-0.291418	-460.043420

Table S5.36a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04656018	-0.04677631	-8.060125	147.088643	147.0886427	7.8	7.8
2	BERYLLIUM HYDRIDE	-15.22200395	-0.05509562	-15.237982	319.758552	319.7585524	-22.1	-22.1
3	DOUBLET CH	-38.41635497	-0.1448584	-38.458364	599.940681	600.3082506	3.7	4.1
4	CH2 3-B1	-39.07939191	-0.16389497	-39.126921	395.576272	395.9438422	3.5	3.9
5	Singlet methylene,	-39.05588151	-0.18424214	-39.109312	440.198537	440.5661069	10.1	10.5
6	Methyl radical,	-39.75123984	-0.20879805	-39.811791	152.306475	152.6740452	5.9	6.2
7	ch4 //b3lyp/6-31G*	-40.41556567	-0.25060215	-40.488240	-63.550990	-63.18342033	11.3	11.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14543834	-0.18796744	-55.199949	358.796996	358.7969959	2.3	2.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78619515	-0.24162183	-55.856265	188.674259	188.6742593	0.0	0.0
10	AMMONIA, //b3lyp/6-31G*	-56.45134026	-0.29575541	-56.537109	-37.167534	-37.16753427	8.9	8.9
11	OH RADICAL	-75.64000901	-0.25891648	-75.715095	41.456917	42.40209681	2.1	3.1
12	Water //b3lyp/6-31G*	-76.31649892	-0.32781715	-76.411566	-230.680991	-229.7358107	11.2	12.1
13	HYDROGEN FLUORIDE,	-100.3344097	-0.33842999	-100.432554	-267.111143	-265.509588	5.3	6.9
14	SIH2 singlet	-290.444281	-0.30630691	-290.533110	276.182227	277.9675666	3.4	5.2
15	SIH2 3B1	-290.4184312	-0.28366171	-290.500693	362.303794	364.0891336	1.6	3.4
16	SIH3 c3v	-291.0592952	-0.31168838	-291.149685	204.071471	205.8568108	3.7	5.4
17	SIH4 //b3lyp/6-31G*	-291.7017307	-0.338931	-291.800021	44.253148	46.03848771	9.9	11.7
18	ph2 doublet	-342.3259188	-0.34575784	-342.426189	140.674865	140.6748646	2.2	2.2
19	PH3 c3v	-342.9531701	-0.37700868	-343.062503	19.170112	19.17011175	13.7	13.7
20	SH2 //b3lyp/6-31G*	-399.199444	-0.39842513	-399.314987	-9.453831	-7.117135718	11.0	13.4
21	HCL //b3lyp/6-31G*	-460.6087696	-0.33669692	-460.706412	-88.652655	-85.13448479	3.8	7.3
22	DILITHIUM //b3lyp/6-31G*	-14.96018982	-0.05806386	-14.977028	230.608031	230.608031	14.7	14.7
23	Lithium Fluoride,	-107.2968959	-0.36758791	-107.403496	-338.979366	-337.3778109	-3.8	-2.2
24	ACETYLENE //b3lyp/6-31g*	-77.17525688	-0.4192479	-77.296839	231.001080	231.7362202	4.2	5.0
25	ETHYLENE //b3lyp/6-31g*	-78.41650347	-0.44019703	-78.544161	63.207186	63.94232604	10.9	11.6
26	ETHANE //b3lyp/6-31g*	-79.63905314	-0.47362289	-79.776404	-66.305164	-65.57002355	17.8	18.5
27	CYANO RADICAL,	-92.55072153	-0.45482135	-92.682620	445.579907	445.9474769	6.7	7.0
28	HYDROGEN CYANIDE	-93.26101133	-0.46392524	-93.395550	125.495581	125.863151	-6.3	-5.9
29	CARBON MONOXIDE	-113.1518932	-0.47468305	-113.289551	-115.053814	-113.7410638	-4.6	-3.3
30	HCO BENT	-113.6771788	-0.49711865	-113.821343	32.198114	33.51086435	-9.6	-8.3
31	H2CO //b3lyp/6-31g*	-114.3191862	-0.51665297	-114.469016	-111.164869	-109.8521191	-2.4	-1.1

32	METHANOL //b3lyp/6-31g*	-115.524876	-0.54619436	-115.683272	-190.524008	-189.2112585	10.3	11.6
33	Nitrogen N2,	-109.3586432	-0.49773462	-109.502986	-3.234413	-3.234412861	-3.2	-3.2
34	H2NNH2 //b3lyp/6-31g*	-111.6653923	-0.5609596	-111.828071	105.623413	105.6234133	10.2	10.2
35	NO radical,	-129.7054481	-0.53970982	-129.861964	83.899992	84.8451718	-6.5	-5.5
36	O2 //b3lyp/6-31g*	-150.1146684	-0.60393577	-150.289810	-9.004140	-7.113779751	-9.0	-7.1
37	HYDROGEN PEROXIDE	-151.3305583	-0.63398675	-151.514414	-119.243967	-117.3536067	16.7	18.6
38	F2 //b3lyp/6-31g*	-199.2851134	-0.66269585	-199.477295	15.668001	18.87111092	15.7	18.9
39	CO2 D*H	-188.3196224	-0.79802186	-188.551049	-416.715483	-414.4575526	-23.4	-21.2
40	na2 //b3lyp/6-31G*	-324.3028515	-0.37166188	-324.410633	143.793355	143.7933548	1.5	1.5
41	SI2 3-SGG	-578.5461042	-0.55932492	-578.708308	589.199237	592.7699169	3.9	7.4
42	P2 //b3lyp/6-31g*	-682.3485911	-0.71027697	-682.554571	152.715171	152.7151712	9.2	9.2
43	S2 //b3lyp/6-31g*	-796.0043292	-0.75735046	-796.223961	127.053276	131.7266655	-1.4	3.3
44	CL2 //b3lyp/6-31g*	-919.9790104	-0.65203761	-920.168101	8.035245	15.07158485	8.0	15.1
45	Sodium Chloride	-622.2373185	-0.5091331	-622.384967	-175.169401	-171.6512312	7.3	10.8
46	SIO //b3lyp/6-31g*	-364.4685403	-0.61705022	-364.647485	-98.651740	-95.92121966	4.3	7.0
47	Carbon monosulfide,	-435.9616948	-0.57667174	-436.128930	285.408365	288.1126305	5.5	8.2
48	OS //b3lyp/6-31g*	-473.0797037	-0.68761747	-473.279113	0.498266	3.780141282	-4.5	-1.2
49	CLO 2-PI	-535.0109452	-0.60555055	-535.186555	109.357889	113.8212387	8.1	12.6
50	CLF 1-SG	-559.6574002	-0.65452685	-559.847213	-52.695533	-47.5758077	2.5	7.7
51	si2h6 //b3lyp/6-31g*	-582.2302273	-0.65870061	-582.421250	100.447925	104.0186046	20.5	24.1
52	Methyl chloride,	-499.8270727	-0.56065603	-499.989663	-75.343408	-71.45766806	6.7	10.5
53	H3C-SH METHANETHIOL	-438.4206332	-0.62488101	-438.601849	-5.675709	-2.971444011	17.3	20.0
54	HOCl //b3lyp/6-31g*	-535.6577997	-0.64599753	-535.845139	-67.495478	-63.03212752	7.0	11.4
55	SO2 //b3lyp/6-31G*	-548.2325874	-1.03472866	-548.532659	-285.437787	-281.210732	11.6	15.9
56	BF3 PLANAR	-324.2143084	-1.07202979	-324.525197	-1151.645448	-1146.709508	-16.1	-11.2
57	bcl3 B3LYP	-1404.953823	-1.1103751	-1405.275832	-419.873895	-409.1881097	-17.0	-6.3
58	ALf3 B3LYP	-541.7439788	-1.21105393	-542.095184	-1198.209423	-1192.512088	11.0	16.7
59	alcl3 B3LYP	-1622.542981	-1.21248769	-1622.894602	-589.169547	-577.7223668	-4.7	6.8
60	cf4 B3LYP	-437.0117091	-1.46466573	-437.436462	-950.479911	-943.7061215	-17.4	-10.7
61	ccl4 B3LYP	-1878.035348	-1.53984624	-1878.481903	-93.351864	-78.91161372	2.5	16.9
62	O=C=S. Singlet	-511.1873598	-0.88858068	-511.445048	-160.236032	-156.5865874	-21.7	-18.1
63	CS2 B3LYP	-834.0516143	-0.98624999	-834.337627	100.554090	105.5950495	-16.2	-11.1
64	COF2 B3LYP	-312.6431781	-1.13212851	-312.971495	-625.761614	-621.2457539	-1.9	2.6
65	sif4 B3LYP	-688.5860793	-1.56564851	-689.040117	-1582.323362	-1574.131802	32.7	40.9
66	sicl4, td	-2129.593102	-1.60203517	-2130.057692	-646.256673	-630.3986532	16.5	32.3
67	nno B3LYP	-184.3765411	-0.8563696	-184.624888	58.807661	59.75284136	-23.2	-22.3
68	clno B3LYP	-589.6945736	-0.92442481	-589.962657	46.036679	50.50002884	-5.8	-1.4

69	nf3 c3v	-353.6681366	-1.24793661	-354.030038	-138.385734	-133.5810691	-6.2	-1.4
70	pf3 c3v	-640.512763	-1.30616492	-640.891551	-940.382801	-935.578136	18.2	23.0
71	ozone 1-a1	-225.0744676	-1.02890635	-225.372850	150.605180	153.4407197	7.9	10.8
72	f2o B3LYP	-274.329088	-0.97759751	-274.612591	37.258899	41.40718897	12.6	16.7
73	CLF3, C2V	-758.9708855	-1.38504345	-759.372548	-160.126823	-151.8039882	-1.1	7.2
74	CF2=CF2 D2H	-474.9607882	-1.66720256	-475.444277	-698.759843	-691.6184831	-40.2	-33.1
75	cl2c=ccl2 B3LYP	-1916.056539	-1.7390896	-1916.560875	-26.114374	-11.30655412	-13.6	1.2
76	cf3cn B3LYP	-429.9194403	-1.60805403	-430.385776	-522.813769	-517.2739639	-27.4	-21.9
77	PROPYNE C3V	-116.4120589	-0.64357062	-116.598694	190.683579	191.7862887	5.8	6.9
78	ALLENE D2D	-116.412181	-0.63731815	-116.597003	193.466835	194.5695453	3.1	4.2
79	CYCLOPROPENE C2V	-116.3723966	-0.6466839	-116.559935	291.727203	292.8299133	14.7	15.8
80	PROPENE CS	-117.6470319	-0.66697933	-117.840456	36.850365	37.95307537	16.8	17.9
81	CYCLOPROPANE D3H	-117.633206	-0.67316235	-117.828423	70.923485	72.02619528	17.8	18.9
82	PROPANE C2V	-118.8645378	-0.70001316	-119.067542	-78.803443	-77.70073341	25.8	26.9
83	TRANS-1,3-BUTADIENE C2H	-155.6602604	-0.86264774	-155.910428	125.570130	127.0404105	15.5	17.0
84	Dimethyl acetylene	-155.6467773	-0.86850097	-155.898643	156.665616	158.135896	11.1	12.5
85	Methylene cyclopropane.	-155.6273986	-0.86933178	-155.879505	205.507123	206.9774032	5.1	6.6
86	Bicyclo[1.1.0]butane. C2v	-155.6112237	-0.88103913	-155.866725	240.992983	242.4632635	23.8	25.3
87	CYCLOBUTENE b3lyp	-155.6368314	-0.87159934	-155.889595	181.377932	182.8482118	24.9	26.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.8595571	-0.90072678	-157.120768	56.366928	57.83720789	27.9	29.4
89	Isobutene. Single	-156.8773024	-0.89650878	-157.137290	8.199374	9.669653619	24.9	26.4
90	Trans butane	-158.0898906	-0.92693281	-158.358701	-91.366442	-89.89616237	34.2	35.6
91	isobutane B3LYP/6-31G*	-158.0908749	-0.93014752	-158.360618	-97.692863	-96.22258266	36.6	38.1
92	Spiropentane. D2d	-194.8467353	-1.10254921	-195.166475	205.879316	207.7171664	20.5	22.4
93	Benzene B3LYP	-231.7688496	-1.26692123	-232.136257	85.477103	87.68252255	3.1	5.3
94	DIFLUOROMETHANE C2V	-238.6962624	-0.85686869	-238.944754	-456.393560	-452.8228795	-5.8	-2.2
95	HCF3 TRI-FLUOROMETHANE	-337.8557989	-1.16197167	-338.192771	-708.320030	-703.147795	-11.3	-6.1
96	CH2CL2 C2V	-959.2359414	-0.87969176	-959.491052	-89.728288	-82.32437782	5.7	13.1
97	chcl3 B3LYP/6-31G*	-1418.639487	-1.20635509	-1418.989330	-98.067623	-87.14554301	5.3	16.2
98	METHYLAMINE b3lyp	-95.66343372	-0.51707517	-95.813386	-9.454633	-9.087063079	13.6	13.9
99	Acetonitrile. CH3-CN.	-132.503867	-0.68600136	-132.702807	71.496189	72.23132934	-3.8	-3.1
100	NITRO METHANE	-244.6186256	-1.13463559	-244.947670	-80.673083	-78.41515264	-6.2	-3.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6147439	-1.12439384	-244.940818	-66.411977	-64.15404706	0.1	2.4
102	Methylsilane. CH3-SiH3.	-330.9422815	-0.5671554	-331.106757	-5.984142	-3.83123187	23.3	25.5
103	Formic Acid.	-189.4819677	-0.82021806	-189.719831	-383.165900	-380.90797	-4.5	-2.3
104	Methyl formate.	-228.6948342	-1.04392446	-228.997572	-361.100963	-358.4754628	-5.5	-2.8
105	acetamide ch3cohn2	-208.8538851	-1.01341717	-209.147776	-234.777650	-233.0973297	3.7	5.4

106	Aziridine. (cyclic	-133.6524359	-0.71837186	-133.860764	138.528361	139.2635012	12.2	12.9
107	Cyanogen. NCCN.	-185.3352035	-0.91767445	-185.601329	283.333938	284.0690785	-23.4	-22.6
108	DIMETHYLAMINE b3lyp	-134.8801175	-0.74238756	-135.095410	0.674946	1.410086211	19.1	19.8
109	TRANS ETHYLAMINE	-134.8916478	-0.74354945	-135.107277	-29.545236	-28.81009643	17.7	18.5
110	KETENE B3LYP	-152.3453066	-0.71781183	-152.553472	-61.588895	-59.90857482	-14.3	-12.6
111	OXIRANE B3LYP	-153.5142518	-0.74911646	-153.731496	-45.082364	-43.402044	7.6	9.3
112	Acetaldehyde B3LYP	-153.5600359	-0.74141963	-153.775048	-162.547311	-160.8669909	3.6	5.2
113	Glyoxal, O=CH-CH=O.	-227.4672526	-1.01136242	-227.760548	-222.542736	-219.917236	-10.4	-7.8
114	ETHANOL TRANS	-154.7555401	-0.77191132	-154.979394	-216.410054	-214.7297344	18.7	20.4
115	DIMETHYL ETHER,	-154.7387934	-0.76894784	-154.961788	-171.028236	-169.3479165	13.1	14.7
116	Thiooxirane. (cyclic	-476.4285832	-0.83381933	-476.670391	94.082383	97.15421801	12.1	15.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.7357005	-1.17736167	-553.077135	-120.474428	-116.4574129	31.0	35.0
118	Thioethanol. CH3-CH2-SH.	-477.6466436	-0.85265915	-477.893915	-20.224983	-17.153148	26.2	29.3
119	ch3sch3 B3LYP	-477.6446454	-0.85456619	-477.892470	-13.905094	-10.83325864	23.3	26.4
120	Vinyl fluoride,	-177.5580986	-0.74726617	-177.774806	-141.756668	-139.4199727	-2.8	-0.5
121	Ethyl chloride.	-539.0562138	-0.78777307	-539.284668	-97.774724	-93.52141448	14.4	18.6
122	Vinyl chloride,	-537.8333607	-0.75907751	-538.053493	27.877413	32.13072285	4.9	9.1
123	h2c=chcn B3LYP	-170.5082063	-0.88243717	-170.764113	182.844441	183.9471506	2.1	3.2
124	ACETONE B3LYP	-192.797197	-0.96777113	-193.077851	-206.126960	-204.07907	11.0	13.1
125	CH3COOH ACETIC	-228.7206037	-1.04343884	-229.023201	-428.843169	-426.2176692	3.8	6.4
126	CH3CFO HCCO	-252.7310922	-1.05188661	-253.036139	-445.757664	-442.4757891	-3.5	-0.2
127	ch3c(o)cl hcco	-612.9928848	-1.06800631	-613.302607	-244.446833	-239.2483426	-1.8	3.4
128	ch3ch2ch2cl B3LYP	-578.2816831	-1.01494922	-578.576018	-110.744453	-106.1235728	21.1	25.7
129	Isopropyl alcohol,	-193.9858205	-1.00106078	-194.276128	-245.299187	-243.2512966	27.5	29.5
130	Methyl ethyl	-193.9693643	-0.99527516	-194.257994	-197.139588	-195.0916981	19.2	21.2
131	Trimethyl Amine.	-174.0991161	-0.97254014	-174.381153	-0.263493	0.839216821	23.6	24.7
132	FURAN B3LYP	-229.6021006	-1.15157576	-229.936058	-34.473167	-32.05770657	0.3	2.7
133	Thiophene b3lyp	-552.5059568	-1.24333359	-552.866524	124.475646	128.2826211	9.4	13.2
134	PYROLE PLANAR	-209.7548251	-1.12390008	-210.080756	107.953160	109.4234401	-0.4	1.1
135	C2v Pyridine	-247.7956393	-1.31103887	-248.175841	132.334942	134.1727922	-8.2	-6.4
136	H2 B3LYP/6-31G*	-1.15911882	-0.0348504	-1.169225	7.900369	7.900369452	7.9	7.9
137	SH b3lyp/6-31G*	-398.5619733	-0.35956028	-398.666246	147.661768	149.9984627	4.6	6.9
138	CCH B3LYP	-76.4622737	-0.38173819	-76.572978	577.579505	578.3146446	12.3	13.1
139	C2H3 CS,2-A'	-77.74176942	-0.40342618	-77.858763	303.231270	303.9664098	3.7	4.4
140	ch3co hcco	-152.9187598	-0.71932908	-153.127365	-15.479703	-13.79938315	-5.4	-3.8
141	H2COH C1	-114.873205	-0.51373988	-115.022190	-12.886550	-11.57379975	4.3	5.6
142	ch3o CS,	-114.8665453	-0.48689799	-115.007746	21.462625	22.77537546	4.3	5.6

143	ch3ch2o 2A"	-154.0969654	-0.71273587	-154.303659	-4.457964	-2.777643651	11.0	12.7
144	ch3s 2-A'	-437.7885526	-0.58892746	-437.959342	131.228089	133.9323544	6.5	9.2
145	c2h5 staggered	-78.98023014	-0.43475942	-79.106310	132.579461	133.3146014	11.7	12.4
146	(ch3)2ch Cs	-118.2102759	-0.66265166	-118.402445	107.075160	108.17787	17.1	18.2
147	TERT-BUTYL RADICAL	-157.4404451	-0.89258193	-157.699294	79.432760	80.90303981	28.0	29.4
148	NO2 RADICAL	-204.7711329	-0.90668228	-205.034071	11.456764	13.34712425	-21.6	-19.7

MAD	**11.3**	**12.3**
LD	**-40.2**	**40.9**

Table S5.36b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.467663	-0.014585	-7.471892
3	be	-14.635617	-0.053433	-14.651112
4	b	-24.614358	-0.077350	-24.636790
5	c	-37.796996	-0.104117	-37.827190
6	n	-54.529645	-0.134836	-54.568748
7	o	-74.991652	-0.192049	-75.047346
8	f	-99.637067	-0.254956	-99.711004
9	na	-162.142304	-0.171601	-162.192069
10	al	-242.222681	-0.220188	-242.286536
11	si	-289.222802	-0.250206	-289.295362
12	p	-341.104633	-0.279233	-341.185611
13	s	-397.937759	-0.320515	-398.030708
14	cl	-459.954903	-0.291421	-460.039415

Table S5.37a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04567198	-0.04677752	-8.059705	147.164540	147.1645399	7.8	7.8
2	BERYLLIUM HYDRIDE	-15.22092301	-0.05508823	-15.237449	320.063043	320.0630435	-21.8	-21.8
3	DOUBLET CH	-38.41437753	-0.14486245	-38.457836	599.867565	600.2351348	3.6	4.0
4	CH2 3-B1	-39.07724017	-0.16389353	-39.126408	395.465300	395.8328702	3.4	3.8
5	Singlet methylene,	-39.05355401	-0.18423847	-39.108826	440.016564	440.3841343	9.9	10.3
6	Methyl radical,	-39.74865433	-0.20880173	-39.811295	152.151403	152.5189732	5.7	6.1
7	ch4 //b3lyp/6-31G*	-40.4126197	-0.25059627	-40.487799	-63.849711	-63.48214131	11.0	11.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.143058	-0.18797776	-55.199451	358.584307	358.5843065	2.1	2.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78339906	-0.24162878	-55.855888	188.147080	188.1470799	-0.6	-0.6
10	AMMONIA, //b3lyp/6-31G*	-56.44816098	-0.29575641	-56.536888	-38.105239	-38.10523895	7.9	7.9
11	OH RADICAL	-75.63699857	-0.25892663	-75.714677	40.820172	41.76535215	1.5	2.4
12	Water //b3lyp/6-31G*	-76.31309473	-0.32782347	-76.411442	-232.089915	-231.1447351	9.7	10.7
13	HYDROGEN FLUORIDE,	-100.3307862	-0.33843868	-100.432318	-268.241134	-266.6395788	4.1	5.7
14	SIH2 singlet	-290.4383071	-0.30629912	-290.530197	276.445494	278.2308339	3.6	5.4
15	SIH2 3B1	-290.412653	-0.28363536	-290.497744	362.662314	364.447654	2.0	3.8
16	SIH3 c3v	-291.053141	-0.31167357	-291.146643	204.672197	206.457537	4.3	6.0
17	SIH4 //b3lyp/6-31G*	-291.6952385	-0.33892208	-291.796915	45.021451	46.80679119	10.7	12.5
18	ph2 doublet	-342.3194876	-0.3457577	-342.423215	140.920950	140.9209498	2.4	2.4
19	PH3 c3v	-342.946411	-0.37699966	-343.059511	19.463366	19.46336566	14.0	14.0
20	SH2 //b3lyp/6-31G*	-399.1924258	-0.39841948	-399.311952	-9.623631	-7.286935729	10.9	13.2
21	HCL //b3lyp/6-31G*	-460.6014987	-0.33669468	-460.702507	-88.916059	-85.39788939	3.6	7.1
22	DILITHIUM //b3lyp/6-31G*	-14.95885211	-0.05805976	-14.976270	230.544938	230.5449376	14.7	14.7
23	Lithium Fluoride,	-107.2927192	-0.3676026	-107.403000	-340.454099	-338.852544	-5.3	-3.7
24	ACETYLENE //b3lyp/6-31g*	-77.17080887	-0.41922942	-77.296578	228.769658	229.5047983	2.0	2.7
25	ETHYLENE //b3lyp/6-31g*	-78.41151853	-0.44018299	-78.543573	61.831957	62.56709728	9.5	10.3
26	ETHANE //b3lyp/6-31g*	-79.63353188	-0.47361133	-79.775615	-67.151833	-66.41669348	16.9	17.7
27	CYANO RADICAL,	-92.54645442	-0.4547337	-92.682875	441.933412	442.3009816	3.0	3.4
28	HYDROGEN CYANIDE	-93.25636532	-0.46391006	-93.395538	122.547784	122.9153541	-9.2	-8.9
29	CARBON MONOXIDE	-113.1470443	-0.47467687	-113.289447	-117.974260	-116.6615103	-7.5	-6.2
30	HCO BENT	-113.6720966	-0.49710621	-113.821228	29.306160	30.6189097	-12.5	-11.2
31	H2CO //b3lyp/6-31g*	-114.3137794	-0.51664794	-114.468774	-113.723218	-112.4104677	-4.9	-3.6

32	METHANOL //b3lyp/6-31g*	-115.5189146	-0.54619151	-115.682772	-192.403686	-191.0909361	8.4	9.7
33	Nitrogen N2,	-109.3538057	-0.49771929	-109.503121	-6.627569	-6.627568629	-6.6	-6.6
34	H2NNH2 //b3lyp/6-31g*	-111.6594237	-0.56095879	-111.827711	103.528526	103.5285258	8.1	8.1
35	NO radical,	-129.7001677	-0.53970028	-129.862078	80.347275	81.29245468	-10.0	-9.1
36	O2 //b3lyp/6-31g*	-150.1089458	-0.60393476	-150.290126	-13.304529	-11.4141689	-13.3	-11.4
37	HYDROGEN PEROXIDE	-151.3241951	-0.63399171	-151.514393	-122.656230	-120.7658701	13.3	15.2
38	F2 //b3lyp/6-31g*	-199.2783566	-0.66269964	-199.477166	12.503268	15.70637759	12.5	15.7
39	CO2 D*H	-188.3117112	-0.79800859	-188.551114	-421.814240	-419.5563096	-28.5	-26.3
40	na2 //b3lyp/6-31G*	-324.2944245	-0.37165635	-324.405921	143.688905	143.6889045	1.4	1.4
41	SI2 3-SGG	-578.5351235	-0.55930686	-578.702916	588.587363	592.1580425	3.2	6.8
42	P2 //b3lyp/6-31g*	-682.3364484	-0.71025352	-682.549524	150.843363	150.8433628	7.3	7.3
43	S2 //b3lyp/6-31g*	-795.9912604	-0.75734129	-796.218463	125.209051	129.8824414	-3.2	1.4
44	CL2 //b3lyp/6-31g*	-919.9648816	-0.65203	-920.160491	6.987251	14.02359105	7.0	14.0
45	Sodium Chloride	-622.2259895	-0.50913552	-622.378730	-175.547124	-172.0289537	6.9	10.4
46	SIO //b3lyp/6-31g*	-364.4600146	-0.61705879	-364.645132	-101.595244	-98.86472364	1.3	4.1
47	Carbon monosulfide,	-435.9532122	-0.57665172	-436.126208	282.956391	285.6606556	3.0	5.8
48	OS //b3lyp/6-31g*	-473.0702985	-0.68760923	-473.276581	-2.729742	0.552133141	-7.8	-4.5
49	CLO 2-PI	-535.0010288	-0.60550872	-535.182681	107.277631	111.740981	6.0	10.5
50	CLF 1-SG	-559.6469377	-0.65452632	-559.843296	-54.676818	-49.55709296	0.6	5.7
51	si2h6 //b3lyp/6-31g*	-582.2176105	-0.65868391	-582.415216	101.521530	105.0922096	21.6	25.2
52	Methyl chloride,	-499.8172476	-0.56064712	-499.985442	-76.234201	-72.34846057	5.8	9.7
53	H3C-SH METHANETHIOL	-438.4110481	-0.62486941	-438.598509	-6.505227	-3.800961547	16.5	19.2
54	HOCl //b3lyp/6-31g*	-535.6475475	-0.64599546	-535.841346	-69.787213	-65.32386346	4.7	9.2
55	SO2 //b3lyp/6-31G*	-548.2200413	-1.03471852	-548.530457	-291.266314	-287.0392593	5.8	10.0
56	BF3 PLANAR	-324.2023735	-1.07203057	-324.523983	-1154.997806	-1150.061866	-19.5	-14.5
57	bcl3 B3LYP	-1404.930936	-1.11035678	-1405.264043	-421.754310	-411.0685248	-18.8	-8.1
58	ALf3 B3LYP	-541.7284502	-1.211062	-542.091769	-1201.726183	-1196.028848	7.4	13.1
59	alcl3 B3LYP	-1622.516504	-1.21247205	-1622.880245	-590.251492	-578.8043123	-5.7	5.7
60	cf4 B3LYP	-436.9957943	-1.46465825	-437.435192	-955.608085	-948.8342948	-22.6	-15.8
61	ccl4 B3LYP	-1878.00483	-1.53982127	-1878.466776	-97.153467	-82.71321669	-1.3	13.1
62	O=C=S. Singlet	-511.1758123	-0.88855913	-511.442380	-164.563648	-160.9142032	-26.1	-22.4
63	CS2 B3LYP	-834.0364197	-0.98621965	-834.332286	96.839476	101.8804359	-19.9	-14.9
64	COF2 B3LYP	-312.631271	-1.13211907	-312.970907	-630.911882	-626.3960224	-7.1	-2.6
65	sif4 B3LYP	-688.5665322	-1.56564481	-689.036226	-1586.496135	-1578.304575	28.5	36.7
66	sicl4, td	-2129.558952	-1.60200973	-2130.039555	-648.082335	-632.2243146	14.7	30.5
67	nno B3LYP	-184.3686668	-0.85634704	-184.625571	52.242602	53.18778176	-29.8	-28.8
68	clno B3LYP	-589.6821462	-0.92440609	-589.959468	40.639773	45.10312324	-11.2	-6.8

69	nf3 c3v	-353.6553581	-1.2479309	-354.029737	-144.368837	-139.5641719	-12.2	-7.3
70	pf3 c3v	-640.4962439	-1.30616172	-640.888092	-944.118087	-939.3134225	14.4	19.2
71	ozone 1-a1	-225.0656904	-1.02888359	-225.374355	141.449154	144.2846935	-1.2	1.6
72	f2o B3LYP	-274.3193615	-0.97759583	-274.612640	31.892870	36.0411603	7.2	11.4
73	CLF3, C2V	-758.9534567	-1.38504163	-759.368969	-166.499012	-158.176177	-7.5	0.8
74	CF2=CF2 D2H	-474.9428356	-1.66719306	-475.442993	-705.311961	-698.1706006	-46.8	-39.6
75	cl2c=ccl2 B3LYP	-1916.023936	-1.73905903	-1916.545654	-31.128099	-16.32027929	-18.6	-3.8
76	cf3cn B3LYP	-429.902502	-1.60803067	-430.384911	-530.233224	-524.6934195	-34.8	-29.3
77	PROPYNE C3V	-116.4050263	-0.64354693	-116.598090	187.894124	188.9968338	3.0	4.1
78	ALLENE D2D	-116.4051449	-0.63729639	-116.596334	190.849208	191.9519181	0.5	1.6
79	CYCLOPROPENE C2V	-116.3653081	-0.64666641	-116.559308	288.997760	290.10047	12.0	13.1
80	PROPENE CS	-117.6394607	-0.66695984	-117.839549	34.857022	35.95973223	14.8	15.9
81	CYCLOPROPANE D3H	-117.6255659	-0.67314735	-117.827510	68.945299	70.04800863	15.8	16.9
82	PROPANE C2V	-118.8564321	-0.69999562	-119.066431	-80.262217	-79.15950716	24.3	25.4
83	TRANS-1,3-BUTADIENE C2H	-155.6506396	-0.8626203	-155.909426	122.368536	123.8388165	12.3	13.8
84	Dimethyl acetylene	-155.6371604	-0.86847199	-155.897702	153.301345	154.7716252	7.7	9.2
85	Methylene cyclopropane.	-155.6177154	-0.86930875	-155.878508	202.290502	203.7607824	1.9	3.3
86	Bicyclo[1.1.0]butane. C2v	-155.601472	-0.8810195	-155.865778	237.645945	239.1162249	20.5	22.0
87	CYCLOBUTENE b3lyp	-155.6271235	-0.87157611	-155.888596	178.166547	179.6368272	21.7	23.2
88	CYCLOBUTANE b3lyp/6-31G*	-156.849315	-0.90070542	-157.119527	53.792055	55.26233541	25.3	26.8
89	Isobutene. Single	-156.8671372	-0.89648364	-157.136082	5.536374	7.006653602	22.3	23.7
90	Trans butane	-158.0791995	-0.92690902	-158.357272	-93.448801	-91.97852072	32.1	33.5
91	isobutane B3LYP/6-31G*	-158.0801747	-0.93012381	-158.359212	-99.835584	-98.36530414	34.5	35.9
92	Spiropentane. D2d	-194.834398	-1.10252459	-195.165155	202.050622	203.8884717	16.7	18.5
93	Benzene B3LYP	-231.7549597	-1.26688362	-232.135025	79.961150	82.16656996	-2.5	-0.3
94	DIFLUOROMETHANE C2V	-238.6868543	-0.8568688	-238.943915	-459.150562	-455.5798824	-8.5	-5.0
95	HCF3 TRI-FLUOROMETHANE	-337.8431391	-1.16196939	-338.191730	-712.299824	-707.1275894	-15.2	-10.1
96	CH2CL2 C2V	-959.2192265	-0.87967849	-959.483130	-91.417646	-84.0137361	4.0	11.4
97	chcl3 B3LYP/6-31G*	-1418.615874	-1.20633637	-1418.977775	-100.731637	-89.80955673	2.6	13.5
98	METHYLAMINE b3lyp	-95.65768592	-0.51706879	-95.812807	-10.912063	-10.54449309	12.1	12.5
99	Acetonitrile. CH3-CN.	-132.4966365	-0.68598048	-132.702431	68.049362	68.78450231	-7.3	-6.5
100	NITRO METHANE	-244.607402	-1.1346155	-244.947787	-87.426535	-85.16860473	-13.0	-10.7
101	Methyl-nitrite. CH3-O-N=O.	-244.6035571	-1.12437269	-244.940869	-72.992210	-70.73428048	-6.5	-4.2
102	Methylsilane. CH3-SiH3.	-330.9332058	-0.56714147	-331.103348	-5.879592	-3.726681834	23.4	25.6
103	Formic Acid.	-189.47351	-0.82021222	-189.719574	-387.418645	-385.1607147	-8.8	-6.5
104	Methyl formate.	-228.6838059	-1.04390909	-228.996979	-365.928887	-363.3033872	-10.3	-7.7
105	acetamide ch3cohn2	-208.8430436	-1.01340303	-209.147065	-239.080241	-237.3999214	-0.6	1.1

106	Aziridine. (cyclic	-133.6445895	-0.71835941	-133.860097	135.842000	136.5771398	9.5	10.2
107	Cyanogen. NCCN.	-185.3262805	-0.91764153	-185.601573	276.738697	277.4738369	-29.9	-29.2
108	DIMETHYLAMINE b3lyp	-134.8717885	-0.74237405	-135.094501	-1.374046	-0.638906236	17.0	17.8
109	TRANS ETHYLAMINE	-134.8833152	-0.74353672	-135.106376	-31.615844	-30.88070436	15.7	16.4
110	KETENE B3LYP	-152.3378347	-0.71779652	-152.553174	-65.457247	-63.77692692	-18.2	-16.5
111	OXIRANE B3LYP	-153.5062035	-0.74910647	-153.730935	-48.263445	-46.583125	4.5	6.1
112	Acetaldehyde B3LYP	-153.552041	-0.74140817	-153.774463	-165.665303	-163.984983	0.4	2.1
113	Glyoxal, O=CH-CH=O.	-227.4568014	-1.01134894	-227.760206	-228.032120	-225.4066199	-15.9	-13.3
114	ETHANOL TRANS	-154.7469934	-0.7719021	-154.978564	-218.881777	-217.2014568	16.3	17.9
115	DIMETHYL ETHER,	-154.7302599	-0.76893665	-154.960941	-173.455100	-171.7747801	10.6	12.3
116	Thiooxirane. (cyclic	-476.4168881	-0.83380227	-476.667029	91.852858	94.92469329	9.8	12.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.720494	-1.17734354	-553.073697	-124.238599	-120.2215838	27.2	31.2
118	Thioethanol. CH3-CH2-SH.	-477.6344744	-0.85264139	-477.890267	-21.704030	-18.63219507	24.7	27.8
119	ch3sch3 B3LYP	-477.6324836	-0.85454844	-477.888848	-15.453437	-12.38160158	21.8	24.9
120	Vinyl fluoride,	-177.5498729	-0.74725599	-177.774050	-144.439483	-142.1027876	-5.5	-3.2
121	Ethyl chloride.	-539.043805	-0.78775792	-539.280132	-99.298073	-95.04476266	12.8	17.1
122	Vinyl chloride,	-537.8214797	-0.75906044	-538.049198	25.722846	29.97615616	2.7	7.0
123	h2c=chcn B3LYP	-170.4989332	-0.88240858	-170.763656	178.150568	179.2532783	-2.6	-1.5
124	ACETONE B3LYP	-192.7866099	-0.96775273	-193.076936	-209.835013	-207.787123	7.3	9.4
125	CH3COOH ACETIC	-228.7095556	-1.04342614	-229.022583	-433.608409	-430.9829092	-1.0	1.6
126	CH3CFO HCCO	-252.7198469	-1.05187354	-253.035409	-450.242992	-446.9611169	-8.0	-4.7
127	ch3c(o)cl hcco	-612.9779983	-1.06798742	-613.298395	-248.554707	-243.3562167	-5.9	-0.7
128	ch3ch2ch2cl B3LYP	-578.2666898	-1.01492792	-578.571168	-112.900483	-108.2796029	18.9	23.5
129	Isopropyl alcohol,	-193.97468	-1.0010447	-194.274993	-248.430293	-246.3824025	24.4	26.4
130	Methyl ethyl	-193.9582452	-0.9952573	-194.256822	-200.173498	-198.1256075	16.1	18.2
131	Trimethyl Amine.	-174.088193	-0.97252004	-174.379949	-2.997395	-1.894684822	20.9	22.0
132	FURAN B3LYP	-229.5898469	-1.15154979	-229.935312	-40.083800	-37.66834021	-5.4	-2.9
133	Thiophene b3lyp	-552.4900594	-1.24330102	-552.863050	119.622569	123.4295439	4.6	8.4
134	PYROLE PLANAR	-209.7427627	-1.12387251	-210.079924	102.783956	104.2542358	-5.6	-4.1
135	C2v Pyridine	-247.7815425	-1.31100318	-248.174843	126.141396	127.9792459	-14.4	-12.6
136	H2 B3LYP/6-31G*	-1.1587362	-0.0348507	-1.169191	7.989705	7.989704715	8.0	8.0
137	SH b3lyp/6-31G*	-398.5552952	-0.35956223	-398.663164	147.613813	149.9505082	4.5	6.9
138	CCH B3LYP	-76.45821998	-0.38171822	-76.572735	575.298865	576.0340054	10.0	10.8
139	C2H3 CS,2-A'	-77.73714402	-0.40340519	-77.858166	301.882962	302.6181016	2.3	3.0
140	ch3co hcco	-152.9110957	-0.7193082	-153.126888	-18.878856	-17.19853608	-8.8	-7.2
141	H2COH C1	-114.8675763	-0.51373117	-115.021696	-14.782839	-13.47008945	2.4	3.7
142	ch3o CS,	-114.8609494	-0.48688266	-115.007014	20.189800	21.50254987	3.0	4.3

143	ch3ch2o 2A"	-154.0887853	-0.71271175	-154.302599	-6.326781	-4.646460636	9.2	10.8
144	ch3s 2-A'	-437.7792968	-0.58891963	-437.955973	130.474802	133.179067	5.8	8.5
145	c2h5 staggered	-78.9750557	-0.43475211	-79.105481	131.839228	132.5743684	10.9	11.7
146	(ch3)2ch Cs	-118.2025099	-0.66263447	-118.401300	105.705338	106.8080482	15.7	16.9
147	TERT-BUTYL RADICAL	-157.4300847	-0.89255452	-157.697851	77.386987	78.85726728	25.9	27.4
148	NO2 RADICAL	-204.7628133	-0.90666078	-205.034812	4.523243	6.413603291	-28.5	-26.6

MAD	**11.3**	**11.9**
LD	**-46.8**	**-39.6**

Table S5.37b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.467126	-0.014584	-7.471501
3	be	-14.634668	-0.053428	-14.650696
4	b	-24.613093	-0.077354	-24.636299
5	c	-37.795398	-0.104123	-37.826635
6	n	-54.527717	-0.134839	-54.568169
7	o	-74.989068	-0.192060	-75.046686
8	f	-99.633847	-0.254966	-99.710337
9	na	-162.138213	-0.171599	-162.189693
10	al	-242.217725	-0.220190	-242.283782
11	si	-289.217487	-0.250207	-289.292549
12	p	-341.098963	-0.279227	-341.182731
13	s	-397.931453	-0.320518	-398.027608
14	cl	-459.947983	-0.291425	-460.035410

Table S5.38a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04478381	-0.04677873	-8.059285	147.240287	147.2402869	7.9	7.9
2	BERYLLIUM HYDRIDE	-15.21984214	-0.05508086	-15.236917	320.367570	320.3675705	-21.5	-21.5
3	DOUBLET CH	-38.41240012	-0.1448665	-38.457309	599.794597	600.1621669	3.6	3.9
4	CH2 3-B1	-39.07508856	-0.16389212	-39.125895	395.354477	395.7220473	3.3	3.7
5	Singlet methylene,	-39.05122657	-0.1842348	-39.108339	439.835066	440.2026361	9.7	10.1
6	Methyl radical,	-39.74606888	-0.20880543	-39.810799	151.996403	152.3639734	5.6	5.9
7	ch4 //b3lyp/6-31G*	-40.4096738	-0.25059039	-40.487357	-64.147868	-63.78029808	10.7	11.1
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14067771	-0.18798811	-55.198954	358.371186	358.371186	1.9	1.9
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78060302	-0.24163576	-55.855510	187.619646	187.6196464	-1.1	-1.1
10	AMMONIA, //b3lyp/6-31G*	-56.44498175	-0.29575741	-56.536667	-39.042861	-39.04286092	7.0	7.0
11	OH RADICAL	-75.63398817	-0.25893679	-75.714259	40.183459	41.12863873	0.9	1.8
12	Water //b3lyp/6-31G*	-76.30969058	-0.3278298	-76.411318	-233.498607	-232.5534272	8.3	9.3
13	HYDROGEN FLUORIDE,	-100.3271626	-0.33844738	-100.432081	-269.371029	-267.769474	3.0	4.6
14	SIH2 singlet	-290.4323332	-0.30629133	-290.527284	276.709265	278.4946053	3.9	5.7
15	SIH2 3B1	-290.406875	-0.28360905	-290.494794	363.021913	364.807253	2.4	4.1
16	SIH3 c3v	-291.046987	-0.31165878	-291.143601	205.273622	207.0589621	4.9	6.6
17	SIH4 //b3lyp/6-31G*	-291.6887464	-0.33891317	-291.793809	45.790310	47.57564996	11.5	13.3
18	ph2 doublet	-342.3130564	-0.34575758	-342.420241	141.166745	141.1667449	2.7	2.7
19	PH3 c3v	-342.939652	-0.37699064	-343.056519	19.756838	19.75683828	14.3	14.3
20	SH2 //b3lyp/6-31G*	-399.1854077	-0.39841383	-399.308916	-9.792965	-7.456269715	10.7	13.0
21	HCL //b3lyp/6-31G*	-460.5942278	-0.33669243	-460.698602	-89.179114	-85.66094401	3.3	6.8
22	DILITHIUM //b3lyp/6-31G*	-14.95751447	-0.05805566	-14.975512	230.481860	230.48186	14.6	14.6
23	Lithium Fluoride,	-107.2885424	-0.3676173	-107.402504	-341.929086	-340.3275307	-6.8	-5.2
24	ACETYLENE //b3lyp/6-31g*	-77.16636094	-0.41921094	-77.296316	226.539875	227.2750153	-0.2	0.5
25	ETHYLENE //b3lyp/6-31g*	-78.40653367	-0.44016896	-78.542986	60.458126	61.19326607	8.2	8.9
26	ETHANE //b3lyp/6-31g*	-79.62801071	-0.47359977	-79.774827	-67.997254	-67.26211419	16.1	16.8
27	CYANO RADICAL,	-92.54218745	-0.45464617	-92.683128	438.291759	438.6593294	-0.6	-0.2
28	HYDROGEN CYANIDE	-93.25171937	-0.46389489	-93.395527	119.601324	119.9688943	-12.2	-11.8
29	CARBON MONOXIDE	-113.1421955	-0.47467068	-113.289343	-120.893389	-119.5806389	-10.4	-9.1
30	HCO BENT	-113.6670145	-0.49709376	-113.821114	26.415773	27.72852301	-15.4	-14.1
31	H2CO //b3lyp/6-31g*	-114.3083726	-0.51664291	-114.468532	-116.280343	-114.9675931	-7.5	-6.2

32	METHANOL //b3lyp/6-31g*	-115.5129533	-0.54618867	-115.682272	-194.282289	-192.9695394	6.5	7.9
33	Nitrogen N2,	-109.3489682	-0.49770397	-109.503256	-10.019500	-10.0194996	-10.0	-10.0
34	H2NNH2 //b3lyp/6-31g*	-111.6534552	-0.56095798	-111.827352	101.434004	101.4340038	6.0	6.0
35	NO radical,	-129.6948874	-0.53969074	-129.862192	76.795845	77.74102485	-13.6	-12.6
36	O2 //b3lyp/6-31g*	-150.1032232	-0.60393375	-150.290443	-17.603615	-15.71325528	-17.6	-15.7
37	HYDROGEN PEROXIDE	-151.3178319	-0.63399668	-151.514371	-126.067565	-124.1772048	9.9	11.8
38	F2 //b3lyp/6-31g*	-199.2715999	-0.66270345	-199.477038	9.339439	12.54254901	9.3	12.5
39	CO2 D*H	-188.3038	-0.79799533	-188.551179	-426.910671	-424.6527414	-33.6	-31.4
40	na2 //b3lyp/6-31G*	-324.2859976	-0.37165081	-324.401209	143.584499	143.5844986	1.3	1.3
41	SI2 3-SGG	-578.524143	-0.55928884	-578.697523	587.976568	591.5472478	2.6	6.2
42	P2 //b3lyp/6-31g*	-682.3243057	-0.71023007	-682.544477	148.972302	148.972302	5.5	5.5
43	S2 //b3lyp/6-31g*	-795.9781916	-0.75733213	-796.212965	123.365692	128.0390817	-5.1	-0.4
44	CL2 //b3lyp/6-31g*	-919.9507529	-0.6520224	-920.152880	5.940150	12.97648967	5.9	13.0
45	Sodium Chloride	-622.2146605	-0.50913795	-622.372493	-175.924766	-172.4065962	6.5	10.0
46	SIO //b3lyp/6-31g*	-364.4514891	-0.61706736	-364.642780	-104.538451	-101.8079315	-1.6	1.1
47	Carbon monosulfide,	-435.9447298	-0.5766317	-436.123486	280.506049	283.2103142	0.6	3.3
48	OS //b3lyp/6-31g*	-473.0608934	-0.687601	-473.274050	-5.956584	-2.674708754	-11.0	-7.7
49	CLO 2-PI	-534.9911126	-0.60546689	-535.178807	105.200366	109.6637164	3.9	8.4
50	CLF 1-SG	-559.6364754	-0.6545258	-559.839378	-56.657299	-51.5375743	-1.4	3.7
51	si2h6 //b3lyp/6-31g*	-582.2049939	-0.65866722	-582.409181	102.596298	106.1669785	22.7	26.3
52	Methyl chloride,	-499.8074227	-0.56063821	-499.981221	-77.123941	-73.23820051	4.9	8.8
53	H3C-SH METHANETHIOL	-438.401463	-0.62485781	-438.595169	-7.333579	-4.629313886	15.7	18.4
54	HOCl //b3lyp/6-31g*	-535.6372954	-0.64599338	-535.837553	-72.077983	-67.61463348	2.4	6.9
55	SO2 //b3lyp/6-31G*	-548.2074954	-1.03470839	-548.528255	-297.092846	-292.8657907	0.0	4.2
56	BF3 PLANAR	-324.1904387	-1.07203136	-324.522768	-1158.348269	-1153.412329	-22.8	-17.9
57	bcl3 B3LYP	-1404.908049	-1.11033847	-1405.252254	-423.632730	-412.9469445	-20.7	-10.0
58	ALf3 B3LYP	-541.7129217	-1.21107008	-542.088353	-1205.241507	-1199.544172	3.9	9.6
59	alcl3 B3LYP	-1622.490027	-1.21245641	-1622.865888	-591.331703	-579.8845228	-6.8	4.6
60	cf4 B3LYP	-436.9798796	-1.46465077	-437.433921	-960.733186	-953.9593961	-27.7	-20.9
61	ccl4 B3LYP	-1877.974312	-1.53979629	-1878.451648	-100.952335	-86.51208545	-5.1	9.3
62	O=C=S. Singlet	-511.1642648	-0.88853758	-511.439711	-168.888899	-165.239454	-30.4	-26.7
63	CS2 B3LYP	-834.0212252	-0.98618931	-834.326944	93.127233	98.16819344	-23.6	-18.6
64	COF2 B3LYP	-312.6193639	-1.13210963	-312.970318	-636.059497	-631.5436373	-12.2	-7.7
65	sif4 B3LYP	-688.5469852	-1.56564112	-689.032334	-1590.666255	-1582.474695	24.4	32.5
66	sicl4, td	-2129.524802	-1.6019843	-2130.021417	-649.905466	-634.0474463	12.8	28.7
67	nno B3LYP	-184.3607925	-0.85632448	-184.626253	45.679753	46.62493335	-36.3	-35.4
68	clno B3LYP	-589.669719	-0.92438737	-589.956279	35.244940	39.70828995	-16.6	-12.2

69	nf3 c3v	-353.6425797	-1.24792519	-354.029436	-150.349693	-145.5450284	-18.1	-13.3
70	pf3 c3v	-640.479725	-1.30615853	-640.884634	-947.851710	-943.0470452	10.7	15.5
71	ozone 1-a1	-225.0569133	-1.02886083	-225.375860	132.296223	135.1317634	-10.4	-7.5
72	f2o B3LYP	-274.3096351	-0.97759415	-274.612689	26.528701	30.67699101	1.8	6.0
73	CLF3, C2V	-758.9360279	-1.38503982	-759.365390	-172.869130	-164.5462954	-13.9	-5.6
74	CF2=CF2 D2H	-474.924883	-1.66718357	-475.441710	-711.860521	-704.7191612	-53.3	-46.2
75	cl2c=ccl2 B3LYP	-1915.991333	-1.73902846	-1916.530432	-36.138391	-21.33057135	-23.6	-8.8
76	cf3cn B3LYP	-429.8855639	-1.60800731	-430.384046	-537.648760	-532.1089547	-42.3	-36.7
77	PROPYNE C3V	-116.3979938	-0.64352324	-116.597486	185.106968	186.2096781	0.2	1.3
78	ALLENE D2D	-116.3981089	-0.63727463	-116.595664	188.233779	189.3364887	-2.1	-1.0
79	CYCLOPROPENE C2V	-116.3582197	-0.64664893	-116.558681	286.270335	287.3730447	9.3	10.4
80	PROPENE CS	-117.6318896	-0.66694036	-117.838641	32.865776	33.96848582	12.8	13.9
81	CYCLOPROPANE D3H	-117.6179258	-0.67313236	-117.826597	66.968947	68.07165668	13.8	14.9
82	PROPANE C2V	-118.8483265	-0.69997808	-119.065320	-81.719067	-80.6163572	22.9	24.0
83	TRANS-1,3-BUTADIENE C2H	-155.641019	-0.86259285	-155.908423	119.169807	120.6400871	9.1	10.6
84	Dimethyl acetylene	-155.6275437	-0.868443	-155.896761	149.940046	151.4103262	4.3	5.8
85	Methylene cyclopropane.	-155.6080323	-0.86928573	-155.877511	199.076525	200.5468047	-1.3	0.1
86	Bicyclo[1.1.0]butane. C2v	-155.5917205	-0.88099988	-155.864830	234.301345	235.7716246	17.2	18.6
87	CYCLOBUTENE b3lyp	-155.6174158	-0.87155289	-155.887597	174.957816	176.4280963	18.5	19.9
88	CYCLOBUTANE b3lyp/6-31G*	-156.839073	-0.90068406	-157.118285	51.219720	52.69000021	22.8	24.2
89	Isobutene. Single	-156.8569721	-0.89645851	-157.134874	2.876101	4.346381217	19.6	21.1
90	Trans butane	-158.0685087	-0.92688522	-158.355843	-95.528512	-94.05823231	30.0	31.5
91	isobutane B3LYP/6-31G*	-158.0694746	-0.9301001	-158.357806	-101.975697	-100.5054175	32.3	33.8
92	Spiropentane. D2d	-194.8220609	-1.10249997	-195.163836	198.225048	200.0628984	12.9	14.7
93	Benzene B3LYP	-231.7410699	-1.266846	-232.133792	74.449422	76.65484206	-8.0	-5.8
94	DIFLUOROMETHANE C2V	-238.6774462	-0.85686891	-238.943076	-461.906091	-458.3354106	-11.3	-7.7
95	HCF3 TRI-FLUOROMETHANE	-337.8304794	-1.1619671	-338.190689	-716.277424	-711.1051891	-19.2	-14.1
96	CH2CL2 C2V	-959.2025117	-0.87966523	-959.475208	-93.105454	-85.70154429	2.3	9.7
97	chcl3 B3LYP/6-31G*	-1418.59226	-1.20631764	-1418.966219	-103.393495	-92.47141492	0.0	10.9
98	METHYLAMINE b3lyp	-95.6519382	-0.5170624	-95.812228	-12.368654	-12.00108426	10.6	11.0
99	Acetonitrile. CH3-CN.	-132.4894061	-0.68595961	-132.702054	64.604532	65.33967224	-10.7	-10.0
100	NITRO METHANE	-244.5961784	-1.13459542	-244.947903	-94.177142	-91.91921209	-19.7	-17.4
101	Methyl-nitrite. CH3-O-N=O.	-244.5923703	-1.12435154	-244.940919	-79.569509	-77.31157911	-13.0	-10.8
102	Methylsilane. CH3-SiH3.	-330.9241303	-0.56712753	-331.099940	-5.773847	-3.620936671	23.5	25.7
103	Formic Acid.	-189.4650525	-0.82020638	-189.719316	-391.669525	-389.4115951	-13.0	-10.8
104	Methyl formate.	-228.6727778	-1.04389372	-228.996385	-370.754060	-368.1285599	-15.1	-12.5
105	acetamide ch3cohn2	-208.8322023	-1.0133889	-209.146353	-243.380618	-241.7002976	-4.9	-3.2

106	Aziridine. (cyclic	-133.6367433	-0.71834697	-133.859431	133.157166	133.8923064	6.8	7.5
107	Cyanogen. NCCN.	-185.3173575	-0.91760861	-185.601816	270.146385	270.8815254	-36.5	-35.8
108	DIMETHYLAMINE b3lyp	-134.8634597	-0.74236053	-135.093591	-3.421491	-2.686351214	15.0	15.7
109	TRANS ETHYLAMINE	-134.8749827	-0.743524	-135.105475	-33.684936	-32.94979579	13.6	14.3
110	KETENE B3LYP	-152.3303629	-0.71778122	-152.552875	-69.323431	-67.64311115	-22.0	-20.4
111	OXIRANE B3LYP	-153.4981553	-0.74909649	-153.730375	-51.442664	-49.76234374	1.3	3.0
112	Acetaldehyde B3LYP	-153.5440462	-0.74139671	-153.773879	-168.781374	-167.1010537	-2.7	-1.0
113	Glyoxal, O=CH-CH=O.	-227.4463502	-1.01133545	-227.759864	-233.518817	-230.8933171	-21.4	-18.8
114	ETHANOL TRANS	-154.7384469	-0.77189288	-154.977734	-221.351748	-219.6714279	13.8	15.5
115	DIMETHYL ETHER,	-154.7217265	-0.76892547	-154.960093	-175.880117	-174.1997972	8.2	9.9
116	Thiooxirane. (cyclic	-476.405193	-0.83378521	-476.663666	89.625172	92.69700721	7.6	10.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.7052876	-1.17732542	-553.070259	-128.000311	-123.9832957	23.5	27.5
118	Thioethanol. CH3-CH2-SH.	-477.6223054	-0.85262363	-477.886619	-23.181281	-20.10944551	23.3	26.3
119	ch3sch3 B3LYP	-477.6203218	-0.85453069	-477.885226	-16.999983	-13.92814842	20.2	23.3
120	Vinyl fluoride,	-177.5416472	-0.74724581	-177.773293	-147.120508	-144.7838133	-8.2	-5.9
121	Ethyl chloride.	-539.0313962	-0.78774277	-539.275596	-100.819680	-96.56637013	11.3	15.6
122	Vinyl chloride,	-537.8095989	-0.75904338	-538.044902	23.570139	27.82344911	0.6	4.8
123	h2c=chcn B3LYP	-170.4896603	-0.88237999	-170.763198	173.459493	174.5622026	-7.3	-6.2
124	ACETONE B3LYP	-192.776023	-0.96773433	-193.076021	-213.540393	-211.4925035	3.6	5.7
125	CH3COOH ACETIC	-228.6985076	-1.04341343	-229.021966	-438.371030	-435.7455297	-5.7	-3.1
126	CH3CFO HCCO	-252.7086016	-1.05186047	-253.034678	-454.725701	-451.4438263	-12.5	-9.2
127	ch3c(o)cl hcco	-612.963112	-1.06796853	-613.294182	-252.660019	-247.4615288	-10.0	-4.8
128	ch3ch2ch2cl B3LYP	-578.2516967	-1.01490662	-578.566318	-115.054115	-110.4332352	16.7	21.4
129	Isopropyl alcohol,	-193.9635398	-1.00102862	-194.273859	-251.558953	-249.5110628	21.2	23.3
130	Methyl ethyl	-193.9471263	-0.99523944	-194.255651	-203.204815	-201.1569253	13.1	15.2
131	Trimethyl Amine.	-174.07727	-0.97249995	-174.378745	-5.729032	-4.626322498	18.1	19.2
132	FURAN B3LYP	-229.5775934	-1.15152382	-229.934566	-45.690951	-43.27549086	-11.0	-8.5
133	Thiophene b3lyp	-552.4741622	-1.24326845	-552.859575	114.772918	118.5798934	-0.3	3.5
134	PYROLE PLANAR	-209.7307004	-1.12384494	-210.079092	97.617881	99.08816124	-10.7	-9.3
135	C2v Pyridine	-247.767446	-1.31096748	-248.173846	119.951827	121.7896769	-20.6	-18.8
136	H2 B3LYP/6-31G*	-1.15835359	-0.03485099	-1.169157	8.079006	8.079006109	8.1	8.1
137	SH b3lyp/6-31G*	-398.548617	-0.35956419	-398.660082	147.565944	149.9026388	4.5	6.8
138	CCH B3LYP	-76.45416634	-0.38169829	-76.572493	573.019911	573.7550506	7.8	8.5
139	C2H3 CS,2-A'	-77.73251873	-0.40338423	-77.857568	300.536321	301.2714609	1.0	1.7
140	ch3co hcco	-152.9034317	-0.71928729	-153.126411	-22.275595	-20.59527487	-12.2	-10.6
141	H2COH C1	-114.8619476	-0.51372248	-115.021202	-16.677808	-15.36505772	0.5	1.8
142	ch3o CS,	-114.8553537	-0.48686736	-115.006283	18.918661	20.23141141	1.8	3.1

143	ch3ch2o 2A"	-154.0806054	-0.71268766	-154.301539	-8.193088	-6.512768431	7.3	9.0
144	ch3s 2-A'	-437.7700411	-0.58891183	-437.952604	129.722457	132.4267223	5.0	7.7
145	c2h5 staggered	-78.96988135	-0.43474481	-79.104652	131.100013	131.8351534	10.2	10.9
146	(ch3)2ch Cs	-118.1947439	-0.66261731	-118.400155	104.337397	105.4401073	14.4	15.5
147	TERT-BUTYL RADICAL	-157.4197245	-0.89252712	-157.696408	75.343983	76.81426281	23.9	25.4
148	NO2 RADICAL	-204.7544938	-0.90663927	-205.035552	-2.407703	-0.517343101	-35.5	-33.6

MAD	**11.8**	**12.1**
LD	**-53.3**	**-46.2**

Table S5.38b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.466589	-0.014584	-7.471110
3	be	-14.633719	-0.053423	-14.650280
4	b	-24.611829	-0.077357	-24.635809
5	c	-37.793799	-0.104129	-37.826079
6	n	-54.525789	-0.134843	-54.567591
7	o	-74.986483	-0.192070	-75.046025
8	f	-99.630628	-0.254976	-99.709671
9	na	-162.134122	-0.171597	-162.187317
10	al	-242.212768	-0.220191	-242.281028
11	si	-289.212172	-0.250209	-289.289736
12	p	-341.093292	-0.279222	-341.179851
13	s	-397.925146	-0.320521	-398.024508
14	cl	-459.941063	-0.291428	-460.031406

Table S5.39a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 35%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04123139	-0.04678361	-8.057606	147.542113	147.5421131	8.2	8.2
2	BERYLLIUM HYDRIDE	-15.21551942	-0.05505157	-15.234787	321.585707	321.5857074	-20.2	-20.2
3	DOUBLET CH	-38.40449092	-0.14488289	-38.455200	599.503573	599.8711434	3.3	3.7
4	CH2 3-B1	-39.06648328	-0.16388673	-39.123844	394.912955	395.2805254	2.9	3.2
5	Singlet methylene,	-39.04191722	-0.18422015	-39.106394	439.114201	439.4817709	9.0	9.4
6	Methyl radical,	-39.73572759	-0.20882047	-39.808815	151.377206	151.7447763	4.9	5.3
7	ch4 //b3lyp/6-31G*	-40.39789068	-0.25056687	-40.485589	-65.334363	-64.9667933	9.6	9.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13115696	-0.1880298	-55.196967	357.514779	357.5147789	1.0	1.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.76941931	-0.24166381	-55.854002	185.507799	185.5077987	-3.2	-3.2
10	AMMONIA, //b3lyp/6-31G*	-56.43226533	-0.29576145	-56.535782	-42.792371	-42.79237082	3.2	3.2
11	OH RADICAL	-75.62194695	-0.25897757	-75.712589	37.636651	38.581831	-1.7	-0.7
12	Water //b3lyp/6-31G*	-76.29607442	-0.32785513	-76.410824	-239.131356	-238.1861765	2.7	3.6
13	HYDROGEN FLUORIDE,	-100.3126689	-0.33848219	-100.431138	-273.890097	-272.2885415	-1.5	0.1
14	SIH2 singlet	-290.4084384	-0.30626015	-290.515629	277.769765	279.5551046	5.0	6.8
15	SIH2 3B1	-290.3837651	-0.28350416	-290.482992	364.471432	366.2567719	3.8	5.6
16	SIH3 c3v	-291.022372	-0.31159971	-291.131432	207.686893	209.4722332	7.3	9.1
17	SIH4 //b3lyp/6-31G*	-291.6627785	-0.33887752	-291.781386	48.871711	50.6570515	14.6	16.3
18	ph2 doublet	-342.2873324	-0.34575734	-342.408347	142.146793	142.1467932	3.7	3.7
19	PH3 c3v	-342.9126167	-0.37695456	-343.044551	20.932490	20.93249044	15.5	15.5
20	SH2 //b3lyp/6-31G*	-399.157336	-0.39839124	-399.296773	-10.465656	-8.128961147	10.0	12.4
21	HCL //b3lyp/6-31G*	-460.5651449	-0.33668344	-460.682984	-90.228238	-86.71006834	2.2	5.8
22	DILITHIUM //b3lyp/6-31G*	-14.95216475	-0.05803924	-14.972478	230.229901	230.2299012	14.3	14.3
23	Lithium Fluoride,	-107.2718359	-0.36767623	-107.400523	-347.831824	-346.2302686	-12.7	-11.1
24	ACETYLENE //b3lyp/6-31g*	-77.14856986	-0.41913702	-77.295268	217.637376	218.3725156	-9.1	-8.4
25	ETHYLENE //b3lyp/6-31g*	-78.38659495	-0.44011283	-78.540634	54.976896	55.71203624	2.7	3.4
26	ETHANE //b3lyp/6-31g*	-79.60592688	-0.47355352	-79.771671	-71.366480	-70.63134037	12.7	13.5
27	CYANO RADICAL,	-92.52512096	-0.45429724	-92.684125	423.773527	424.1410965	-15.1	-14.8
28	HYDROGEN CYANIDE	-93.23313612	-0.46383421	-93.395478	107.829164	108.1967341	-24.0	-23.6
29	CARBON MONOXIDE	-113.1228006	-0.47464597	-113.288927	-132.557121	-131.2443709	-22.1	-20.8
30	HCO BENT	-113.6466868	-0.49704372	-113.820652	14.869669	16.18241942	-27.0	-25.7
31	H2CO //b3lyp/6-31g*	-114.2867461	-0.51662282	-114.467564	-126.497021	-125.1842709	-17.7	-16.4

32	METHANOL //b3lyp/6-31g*	-115.4891087	-0.5461773	-115.680271	-201.786333	-200.473583	-1.0	0.4
33	Nitrogen N2,	-109.3296188	-0.4976427	-109.503794	-23.574769	-23.57476943	-23.6	-23.6
34	H2NNH2 //b3lyp/6-31g*	-111.6295818	-0.5609548	-111.825916	93.059917	93.05991691	-2.3	-2.3
35	NO radical,	-129.6737665	-0.53965259	-129.862645	62.603252	63.5484317	-27.8	-26.8
36	O2 //b3lyp/6-31g*	-150.0803332	-0.60392982	-150.291709	-34.787620	-32.89725964	-34.8	-32.9
37	HYDROGEN PEROXIDE	-151.29238	-0.63401658	-151.514286	-139.704119	-137.8137588	-3.7	-1.8
38	F2 //b3lyp/6-31g*	-199.2445734	-0.6627187	-199.476525	-3.306811	-0.103700782	-3.3	-0.1
39	CO2 D*H	-188.272156	-0.79794229	-188.551436	-447.273692	-445.015762	-54.0	-51.7
40	na2 //b3lyp/6-31G*	-324.2522917	-0.37162853	-324.382362	143.166597	143.1665967	0.9	0.9
41	SI2 3-SGG	-578.4802224	-0.55921713	-578.675948	585.544832	589.115512	0.2	3.8
42	P2 //b3lyp/6-31g*	-682.2757361	-0.71013627	-682.524284	141.495342	141.4953422	-2.0	-2.0
43	S2 //b3lyp/6-31g*	-795.9259175	-0.7572956	-796.190971	116.001334	120.6747236	-12.4	-7.8
44	CL2 //b3lyp/6-31g*	-919.8942388	-0.65199199	-920.122436	1.760375	8.796715461	1.8	8.8
45	Sodium Chloride	-622.1693454	-0.50914774	-622.347547	-177.435051	-173.9168812	5.0	8.5
46	SIO //b3lyp/6-31g*	-364.4173877	-0.6171017	-364.633373	-116.308630	-113.5781097	-13.4	-10.7
47	Carbon monosulfide,	-435.9108006	-0.57655162	-436.112594	270.720925	273.4251902	-9.2	-6.5
48	OS //b3lyp/6-31g*	-473.0232736	-0.68756797	-473.263922	-18.851676	-15.56980081	-23.9	-20.6
49	CLO 2-PI	-534.9514485	-0.60529975	-535.163303	96.920775	101.3841253	-4.3	0.1
50	CLF 1-SG	-559.5946265	-0.65452372	-559.823710	-64.571099	-59.45137373	-9.3	-4.2
51	si2h6 //b3lyp/6-31g*	-582.1545283	-0.65860041	-582.385038	106.907293	110.4779726	27.0	30.6
52	Methyl chloride,	-499.7681238	-0.5606026	-499.964335	-80.672810	-76.78707048	1.3	5.2
53	H3C-SH METHANETHIOL	-438.3631238	-0.62481139	-438.581808	-10.635701	-7.931436217	12.4	15.1
54	HOCl //b3lyp/6-31g*	-535.5962877	-0.64598511	-535.822383	-81.232034	-76.76868445	-6.8	-2.3
55	SO2 //b3lyp/6-31G*	-548.1573123	-1.0346679	-548.519446	-320.379372	-316.1523169	-23.3	-19.1
56	BF3 PLANAR	-324.1427002	-1.07203455	-324.517912	-1171.730964	-1166.795024	-36.2	-31.3
57	bcl3 B3LYP	-1404.816503	-1.11026523	-1405.205096	-431.126910	-420.4411253	-28.2	-17.5
58	ALf3 B3LYP	-541.6508086	-1.21110245	-542.074694	-1219.288380	-1213.591045	-10.1	-4.4
59	alcl3 B3LYP	-1622.384121	-1.21239386	-1622.808459	-595.635243	-584.1880628	-11.1	0.3
60	cf4 B3LYP	-436.9162215	-1.4646209	-437.428839	-981.203256	-974.429466	-48.2	-41.4
61	ccl4 B3LYP	-1877.852241	-1.53969641	-1878.391135	-116.121032	-101.6807817	-20.3	-5.9
62	O=C=S. Singlet	-511.1180758	-0.88845141	-511.429034	-186.166798	-182.5173528	-47.7	-44.0
63	CS2 B3LYP	-833.9604485	-0.98606796	-834.305572	78.302337	83.34329666	-38.4	-33.4
64	COF2 B3LYP	-312.5717365	-1.13207193	-312.967962	-656.624009	-652.1081491	-32.8	-28.3
65	sif4 B3LYP	-688.4687983	-1.5656264	-689.016768	-1607.320174	-1599.128614	7.7	15.9
66	sicl4, td	-2129.388205	-1.60188255	-2129.948864	-657.172548	-641.3145281	5.6	21.4
67	nno B3LYP	-184.3292961	-0.85623426	-184.628978	19.450825	20.39600483	-62.6	-61.6
68	clno B3LYP	-589.6200109	-0.92431253	-589.943520	13.685894	18.14924402	-38.2	-33.7

69	nf3 c3v	-353.5914668	-1.2479024	-354.028233	-174.251018	-169.4463527	-42.0	-37.2
70	pf3 c3v	-640.4136501	-1.30614578	-640.870801	-962.770137	-957.965472	-4.2	0.6
71	ozone 1-a1	-225.0218055	-1.02876987	-225.381875	95.714327	98.54986717	-47.0	-44.1
72	f2o B3LYP	-274.27073	-0.97758748	-274.612886	5.090048	9.238337907	-19.6	-15.4
73	CLF3, C2V	-758.8663136	-1.38503262	-759.351075	-198.329343	-190.0065077	-39.3	-31.0
74	CF2=CF2 D2H	-474.8530736	-1.66714562	-475.436575	-738.019531	-730.8781711	-79.5	-72.3
75	cl2c=ccl2 B3LYP	-1915.860925	-1.7389062	-1916.469542	-56.145916	-41.33809643	-43.6	-28.8
76	cf3cn B3LYP	-429.8178124	-1.60791391	-430.380582	-567.271727	-561.7319217	-71.9	-66.3
77	PROPYNE C3V	-116.3698646	-0.64342846	-116.595065	173.981196	175.0839063	-11.0	-9.8
78	ALLENE D2D	-116.3699658	-0.63718761	-116.592981	177.793862	178.8965721	-12.6	-11.5
79	CYCLOPROPENE C2V	-116.3298671	-0.64657901	-116.556170	275.380336	276.4830464	-1.6	-0.5
80	PROPENE CS	-117.6016063	-0.66686242	-117.835008	24.921089	26.02379922	4.8	5.9
81	CYCLOPROPANE D3H	-117.5873666	-0.67307241	-117.822942	59.081820	60.18453023	5.9	7.0
82	PROPANE C2V	-118.8159052	-0.69990793	-119.060873	-87.527451	-86.42474087	17.1	18.2
83	TRANS-1,3-BUTADIENE C2H	-155.6025376	-0.86248307	-155.904407	106.403274	107.873554	-3.6	-2.2
84	Dimethyl acetylene	-155.5890779	-0.86832705	-155.892992	136.523921	137.994201	-9.1	-7.6
85	Methylene cyclopropane.	-155.5693011	-0.86919364	-155.873519	186.246857	187.7171369	-14.2	-12.7
86	Bicyclo[1.1.0]butane. C2v	-155.5527156	-0.88092142	-155.861038	220.947557	222.4178375	3.8	5.3
87	CYCLOBUTENE b3lyp	-155.5785862	-0.87146	-155.883597	162.149241	163.6195208	5.7	7.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.7981065	-0.90059863	-157.113316	40.955417	42.42569749	12.5	14.0
89	Isobutene. Single	-156.8163131	-0.89635797	-157.130038	-7.738101	-6.267820575	9.0	10.5
90	Trans butane	-158.0257466	-0.92679005	-158.350123	-103.821557	-102.3512765	21.7	23.2
91	isobutane B3LYP/6-31G*	-158.0266759	-0.93000524	-158.352178	-110.510297	-109.0400174	23.8	25.3
92	Spiropentane. D2d	-194.7727137	-1.10240151	-195.158554	182.953512	184.7913618	-2.4	-0.6
93	Benzene B3LYP	-231.6855122	-1.26669554	-232.128856	52.444135	54.64955512	-30.0	-27.8
94	DIFLUOROMETHANE C2V	-238.6398145	-0.85686939	-238.939719	-472.913785	-469.3431053	-22.3	-18.7
95	HCF3 TRI-FLUOROMETHANE	-337.7798414	-1.16195801	-338.186527	-732.166267	-726.9940324	-35.1	-29.9
96	CH2CL2 C2V	-959.1356539	-0.87961219	-959.443518	-99.841681	-92.437771	-4.4	3.0
97	chcl3 B3LYP/6-31G*	-1418.497808	-1.20624276	-1418.919993	-114.020324	-103.0982441	-10.7	0.2
98	METHYLAMINE b3lyp	-95.62894816	-0.51703689	-95.809911	-18.186758	-17.8191878	4.8	5.2
99	Acetonitrile. CH3-CN.	-132.4604854	-0.68587611	-132.700542	50.845445	51.58058538	-24.5	-23.7
100	NITRO METHANE	-244.5512852	-1.13451512	-244.948365	-121.151395	-118.8934647	-46.7	-44.4
101	Methyl-nitrite. CH3-O-N=O.	-244.547624	-1.12426698	-244.941117	-105.850036	-103.5921058	-39.3	-37.1
102	Methylsilane. CH3-SiH3.	-330.8878292	-0.56707178	-331.086304	-5.338760	-3.185849838	23.9	26.1
103	Formic Acid.	-189.431223	-0.82018308	-189.718287	-408.654711	-406.3967814	-30.0	-27.7
104	Methyl formate.	-228.6286662	-1.04383227	-228.994008	-390.027841	-387.402341	-34.4	-31.8
105	acetamide ch3cohn2	-208.7888381	-1.01333242	-209.143504	-260.559685	-258.8793653	-22.1	-20.4

106	Aziridine. (cyclic	-133.6053591	-0.71829722	-133.856763	122.433428	123.1685682	-3.9	-3.2
107	Cyanogen. NCCN.	-185.2816667	-0.91747696	-185.602784	243.806454	244.5415944	-62.9	-62.1
108	DIMETHYLAMINE b3lyp	-134.8301454	-0.7423065	-135.089953	-11.595723	-10.86058291	6.8	7.5
109	TRANS ETHYLAMINE	-134.841654	-0.74347313	-135.101870	-41.946110	-41.2109704	5.3	6.1
110	KETENE B3LYP	-152.3004765	-0.71772004	-152.551679	-84.767215	-83.08689525	-37.5	-35.8
111	OXIRANE B3LYP	-153.4659633	-0.74905657	-153.728133	-64.141492	-62.46117232	-11.4	-9.7
112	Acetaldehyde B3LYP	-153.5120678	-0.74135089	-153.771541	-181.226957	-179.5466366	-15.1	-13.4
113	Glyoxal, O=CH-CH=O.	-227.4045464	-1.01128157	-227.758495	-255.439414	-252.8139138	-43.3	-40.7
114	ETHANOL TRANS	-154.7042617	-0.77185601	-154.974411	-231.214415	-229.5340945	3.9	5.6
115	DIMETHYL ETHER,	-154.687594	-0.76888077	-154.956702	-185.561974	-183.8816537	-1.5	0.2
116	Thiooxirane. (cyclic	-476.358414	-0.83371698	-476.650215	80.732491	83.80432634	-1.3	1.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.6444636	-1.17725297	-553.056502	-143.022706	-139.0056908	8.4	12.5
118	Thioethanol. CH3-CH2-SH.	-477.5736304	-0.85255259	-477.872024	-29.072131	-26.00029587	17.4	20.4
119	ch3sch3 B3LYP	-477.5716762	-0.8544597	-477.870737	-23.168086	-20.09625132	14.1	17.1
120	Vinyl fluoride,	-177.5087452	-0.74720509	-177.770267	-157.826799	-155.4901045	-18.9	-16.6
121	Ethyl chloride.	-538.9817622	-0.78768218	-539.257451	-106.889235	-102.6359246	5.2	9.5
122	Vinyl chloride,	-537.7620766	-0.75897513	-538.027718	14.977523	19.23083269	-8.0	-3.8
123	h2c=chcn B3LYP	-170.4525696	-0.88226564	-170.761363	154.723229	155.8259391	-26.0	-24.9
124	ACETONE B3LYP	-192.7336763	-0.96766077	-193.072358	-228.336099	-226.2882089	-11.2	-9.1
125	CH3COOH ACETIC	-228.6543168	-1.04336267	-229.019494	-457.396071	-454.7705706	-24.8	-22.1
126	CH3CFO HCCO	-252.6636216	-1.05180822	-253.031754	-472.631072	-469.3491965	-30.4	-27.1
127	ch3c(o)cl hcco	-612.9035678	-1.067893	-613.277330	-269.055887	-263.8573967	-26.4	-21.2
128	ch3ch2ch2cl B3LYP	-578.1917254	-1.01482141	-578.546913	-123.644952	-119.0240718	8.2	12.8
129	Isopropyl alcohol,	-193.91898	-1.00096432	-194.269317	-264.049240	-262.0013498	8.7	10.8
130	Methyl ethyl	-193.902652	-0.995168	-194.250961	-215.304910	-213.2570204	1.0	3.1
131	Trimethyl Amine.	-174.0335795	-0.9724196	-174.373926	-16.633058	-15.53034772	7.2	8.3
132	FURAN B3LYP	-229.5285802	-1.15141996	-229.931577	-68.085360	-65.66990026	-33.4	-30.9
133	Thiophene b3lyp	-552.4105748	-1.24313819	-552.845673	95.408362	99.21533722	-19.7	-15.8
134	PYROLE PLANAR	-209.6824525	-1.12373468	-210.075760	76.984699	78.45497924	-31.4	-29.9
135	C2v Pyridine	-247.7110611	-1.31082472	-248.169850	95.232828	97.07067839	-45.3	-43.5
136	H2 B3LYP/6-31G*	-1.15682316	-0.03485216	-1.169021	8.436024	8.436023962	8.4	8.4
137	SH b3lyp/6-31G*	-398.5219051	-0.35957222	-398.647755	147.374897	149.7115917	4.3	6.6
138	CCH B3LYP	-76.43795269	-0.38161901	-76.571519	563.920372	564.6555124	-1.3	-0.6
139	C2H3 CS,2-A'	-77.71401864	-0.40330064	-77.855174	295.166334	295.901474	-4.4	-3.7
140	ch3co hcco	-152.8727769	-0.71920348	-153.124498	-35.839369	-34.15904948	-25.8	-24.1
141	H2COH C1	-114.8394338	-0.51368786	-115.019225	-24.244798	-22.93204751	-7.1	-5.8
142	ch3o CS,	-114.8329715	-0.48680642	-115.003354	13.850588	15.16333788	-3.3	-2.0

143	ch3ch2o 2A"	-154.0478867	-0.71259163	-154.297294	-15.633850	-13.95352995	-0.2	1.5
144	ch3s 2-A'	-437.7330194	-0.58888086	-437.939128	126.722009	129.4262744	2.0	4.7
145	c2h5 staggered	-78.94918486	-0.43471592	-79.101335	128.152921	128.8880614	7.2	8.0
146	(ch3)2ch Cs	-118.1636813	-0.66254893	-118.395573	98.883958	99.98666835	8.9	10.0
147	TERT-BUTYL RADICAL	-157.3782854	-0.89241777	-157.690632	67.199035	68.66931515	15.7	17.2
148	NO2 RADICAL	-204.7212162	-0.90655326	-205.038510	-30.106034	-28.21567444	-63.2	-61.3

MAD	**16.9**	**15.9**
LD	**-79.5**	**-72.3**

Table S5.39b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 58% and a_C = 35%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498730	0.000000	-0.498730
2	li	-7.464442	-0.014581	-7.469545
3	be	-14.629923	-0.053404	-14.648614
4	b	-24.606770	-0.077373	-24.633851
5	c	-37.787406	-0.104154	-37.823860
6	n	-54.518077	-0.134859	-54.565278
7	o	-74.976146	-0.192113	-75.043386
8	f	-99.617750	-0.255017	-99.707006
9	na	-162.117758	-0.171588	-162.177814
10	al	-242.192944	-0.220196	-242.270013
11	si	-289.190911	-0.250215	-289.278486
12	p	-341.070610	-0.279200	-341.168330
13	s	-397.899922	-0.320532	-398.012109
14	cl	-459.913383	-0.291442	-460.015388

Table S5.40a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04838813	-0.0465709	-8.060962	147.123423	147.123423	7.8	7.8
2	BERYLLIUM HYDRIDE	-15.22429633	-0.05488799	-15.239116	319.014928	319.0149276	-22.8	-22.8
3	DOUBLET CH	-38.42028784	-0.14424333	-38.459234	600.419547	600.7871168	4.2	4.6
4	CH2 3-B1	-39.08375775	-0.16328378	-39.127844	395.977119	396.3446886	3.9	4.3
5	Singlet methylene,	-39.06053187	-0.18345649	-39.110065	441.044478	441.412048	10.9	11.3
6	Methyl radical,	-39.75648055	-0.20800461	-39.812642	152.959288	153.3268585	6.5	6.9
7	ch4 //b3lyp/6-31G*	-40.42155229	-0.24963915	-40.488955	-62.479349	-62.11177892	12.4	12.8
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1500772	-0.18727242	-55.200641	359.878895	359.8788949	3.4	3.4
9	NH2,2-B-1, //b3lyp/6-31G*	-55.79159175	-0.24069071	-55.856578	190.813355	190.8133547	2.1	2.1
10	AMMONIA, //b3lyp/6-31G*	-56.4574846	-0.29459907	-56.537026	-33.927538	-33.92753784	12.1	12.1
11	OH RADICAL	-75.64568028	-0.25798286	-75.715336	43.538424	44.48360397	4.2	5.2
12	Water //b3lyp/6-31G*	-76.32284564	-0.32656302	-76.411018	-226.465816	-225.5206356	15.4	16.3
13	HYDROGEN FLUORIDE,	-100.3411108	-0.33724622	-100.432167	-263.864925	-262.2633696	8.5	10.1
14	SIH2 singlet	-290.4563237	-0.30529858	-290.538754	275.783298	277.5686384	3.0	4.8
15	SIH2 3B1	-290.4301439	-0.2828284	-290.506508	361.457823	363.2431631	0.8	2.6
16	SIH3 c3v	-291.0718483	-0.31072162	-291.155743	202.647168	204.432508	2.2	4.0
17	SIH4 //b3lyp/6-31G*	-291.7150604	-0.337844	-291.806278	42.367511	44.15285099	8.1	9.8
18	ph2 doublet	-342.3388909	-0.34465591	-342.431948	140.540572	140.5405724	2.1	2.1
19	PH3 c3v	-342.9668557	-0.37575107	-343.068309	18.975460	18.97546033	13.5	13.5
20	SH2 //b3lyp/6-31G*	-399.2135886	-0.39712281	-399.320812	-8.683583	-6.346888057	11.8	14.2
21	HCL //b3lyp/6-31G*	-460.6234364	-0.33550409	-460.714022	-87.848679	-84.3305089	4.6	8.1
22	DILITHIUM //b3lyp/6-31G*	-14.96296769	-0.0577725	-14.978566	230.910895	230.910895	15.0	15.0
23	Lithium Fluoride,	-107.3046775	-0.36616576	-107.403542	-334.761316	-333.1597606	0.4	2.0
24	ACETYLENE //b3lyp/6-31g*	-77.18381486	-0.41735982	-77.296502	237.409419	238.1445585	10.6	11.4
25	ETHYLENE //b3lyp/6-31g*	-78.4263851	-0.43838351	-78.544749	67.311232	68.04637164	15.0	15.7
26	ETHANE //b3lyp/6-31g*	-79.65025902	-0.47179085	-79.777643	-63.785850	-63.0507098	20.3	21.0
27	CYANO RADICAL,	-92.5584125	-0.45231765	-92.680538	456.581458	456.9490279	17.7	18.0
28	HYDROGEN CYANIDE	-93.26966879	-0.46178753	-93.394351	134.240096	134.607666	2.4	2.8
29	CARBON MONOXIDE	-113.1608415	-0.4725614	-113.288433	-106.765800	-105.4530502	3.7	5.0
30	HCO BENT	-113.6865293	-0.49495834	-113.820168	40.697534	42.01028365	-1.1	0.2
31	H2CO //b3lyp/6-31g*	-114.3293354	-0.51446163	-114.468240	-103.652705	-102.3399547	5.1	6.4

32	METHANOL //b3lyp/6-31g*	-115.5363892	-0.54407546	-115.683290	-184.969393	-183.6566433	15.9	17.2
33	Nitrogen N2,	-109.3674648	-0.49547125	-109.501242	7.018062	7.018061982	7.0	7.0
34	H2NNH2 //b3lyp/6-31g*	-111.6768204	-0.55873641	-111.827679	112.571358	112.5713577	17.2	17.2
35	NO radical,	-129.7148922	-0.53734687	-129.859976	94.608302	95.55348175	4.2	5.2
36	O2 //b3lyp/6-31g*	-150.1246119	-0.60157804	-150.287038	3.577274	5.46763384	3.6	5.5
37	HYDROGEN PEROXIDE	-151.342064	-0.63136956	-151.512534	-108.878701	-106.9883414	27.1	29.0
38	F2 //b3lyp/6-31g*	-199.297049	-0.66004273	-199.475261	25.345862	28.54897224	25.3	28.5
39	CO2 D*H	-188.3340473	-0.79450172	-188.548563	-402.184435	-399.9265054	-8.9	-6.6
40	na2 //b3lyp/6-31G*	-324.3192953	-0.37045782	-324.419319	144.277340	144.2773405	2.0	2.0
41	SI2 3-SGG	-578.567931	-0.55746498	-578.718447	591.174086	594.744766	5.8	9.4
42	P2 //b3lyp/6-31g*	-682.3726043	-0.70756867	-682.563648	158.611588	158.6115879	15.1	15.1
43	S2 //b3lyp/6-31g*	-796.0302015	-0.75485742	-796.234013	132.538879	137.2122687	4.1	8.8
44	CL2 //b3lyp/6-31g*	-920.0072998	-0.64960729	-920.182694	11.171247	18.20758707	11.2	18.2
45	Sodium Chloride	-622.2599709	-0.50739736	-622.396968	-174.310086	-170.791916	8.1	11.6
46	SIO //b3lyp/6-31g*	-364.4848184	-0.61438839	-364.650703	-90.153378	-87.42285791	12.8	15.5
47	Carbon monosulfide,	-435.9782876	-0.57417513	-436.133315	292.533804	295.2380692	12.6	15.3
48	OS //b3lyp/6-31g*	-473.0976398	-0.68504183	-473.282601	9.930564	13.21243933	4.9	8.2
49	CLO 2-PI	-535.0301525	-0.60273719	-535.192892	116.097077	120.5604273	14.8	19.3
50	CLF 1-SG	-559.6776164	-0.6520123	-559.853660	-46.729208	-41.6094834	8.5	13.6
51	si2h6 //b3lyp/6-31g*	-582.2560614	-0.65655993	-582.433333	97.690162	101.2608419	17.8	21.3
52	Methyl chloride,	-499.8468733	-0.55855627	-499.997684	-72.791409	-68.90566867	9.2	13.1
53	H3C-SH METHANETHIOL	-438.439947	-0.62267046	-438.608068	-3.118117	-0.413852306	19.9	22.6
54	HOCl //b3lyp/6-31g*	-535.6777162	-0.64343878	-535.851445	-60.613081	-56.14973135	13.9	18.3
55	SO2 //b3lyp/6-31G*	-548.2561574	-1.03021758	-548.534316	-268.546654	-264.3195993	28.5	32.7
56	BF3 PLANAR	-324.236796	-1.06822134	-324.525216	-1142.747800	-1137.81186	-7.2	-2.3
57	bcl3 B3LYP	-1405.000056	-1.10625625	-1405.298745	-415.418784	-404.7329993	-12.5	-1.8
58	ALf3 B3LYP	-541.7735396	-1.2068409	-542.099387	-1188.884662	-1183.187327	20.3	26.0
59	alcl3 B3LYP	-1622.596523	-1.20831526	-1622.922768	-587.093906	-575.6467263	-2.6	8.9
60	cf4 B3LYP	-437.0414113	-1.45941252	-437.435453	-936.457351	-929.683561	-3.4	3.3
61	ccl4 B3LYP	-1878.096557	-1.53398479	-1878.510733	-83.446502	-69.00625151	12.4	26.8
62	O=C=S. Singlet	-511.2095028	-0.88490404	-511.448427	-147.815764	-144.1663186	-9.3	-5.7
63	CS2 B3LYP	-834.0814802	-0.98238878	-834.346725	111.243985	116.2849453	-5.5	-0.4
64	COF2 B3LYP	-312.6651704	-1.12772204	-312.969655	-611.242414	-606.7265536	12.6	17.1
65	sif4 B3LYP	-688.6234168	-1.56032251	-689.044704	-1571.396885	-1563.205325	43.6	51.8
66	sicl4, td	-2129.662186	-1.59642657	-2130.093222	-642.344974	-626.4869543	20.4	36.3
67	nno B3LYP	-184.3904588	-0.85227812	-184.620574	78.460178	79.40535814	-3.5	-2.6
68	clno B3LYP	-589.7179373	-0.92011376	-589.966368	62.505605	66.96895491	10.6	15.1

69	nf3 c3v	-353.6911205	-1.24282776	-354.026684	-120.238737	-115.4340721	12.0	16.8
70	pf3 c3v	-640.5442046	-1.30149843	-640.895609	-929.670924	-924.8662593	28.9	33.7
71	ozone 1-a1	-225.0891741	-1.02354957	-225.365532	177.774402	180.6099421	35.1	37.9
72	f2o B3LYP	-274.3461604	-0.97340808	-274.608981	53.726786	57.87507638	29.0	33.2
73	CLF3, C2V	-759.0031983	-1.3792473	-759.375595	-140.898188	-132.5753529	18.1	26.4
74	CF2=CF2 D2H	-474.9941615	-1.66094626	-475.442617	-680.329004	-673.1876437	-21.8	-14.6
75	cl2c=ccl2 B3LYP	-1916.121737	-1.73236521	-1916.589476	-12.909271	1.898548567	-0.4	14.5
76	cf3cn B3LYP	-429.950978	-1.60170309	-430.383438	-501.934230	-496.3944255	-6.5	-1.0
77	PROPYNE C3V	-116.4258464	-0.64082454	-116.598869	198.573166	199.6758763	13.6	14.7
78	ALLENE D2D	-116.4259087	-0.63460986	-116.597253	201.158296	202.2610055	10.8	11.9
79	CYCLOPROPENE C2V	-116.3863133	-0.64399657	-116.560192	299.399250	300.5019601	22.4	23.5
80	PROPENE CS	-117.6621494	-0.6642785	-117.841505	42.568813	43.67152333	22.5	23.6
81	CYCLOPROPANE D3H	-117.6485476	-0.67052313	-117.829589	76.334843	77.43755347	23.2	24.3
82	PROPANE C2V	-118.8809878	-0.69729488	-119.069257	-74.712705	-73.60999542	29.9	31.0
83	TRANS-1,3-BUTADIENE C2H	-155.6792656	-0.85905276	-155.911210	134.690156	136.160436	24.7	26.1
84	Dimethyl acetylene	-155.6657947	-0.86488878	-155.899315	166.073242	167.5435222	20.5	21.9
85	Methylene cyclopropane.	-155.6465845	-0.8657956	-155.880349	214.462149	215.9324287	14.0	15.5
86	Bicyclo[1.1.0]butane. C2v	-155.6306401	-0.87752593	-155.867572	249.941136	251.4114164	32.8	34.3
87	CYCLOBUTENE b3lyp	-155.6561326	-0.86803274	-155.890501	190.170556	191.6408359	33.7	35.2
88	CYCLOBUTANE b3lyp/6-31G*	-156.8802053	-0.89717549	-157.122443	63.265503	64.73578345	34.8	36.3
89	Isobutene. Single	-156.8976847	-0.89290794	-157.138770	15.609681	17.07996144	32.3	33.8
90	Trans butane	-158.1115876	-0.92332643	-158.360886	-85.682673	-84.2123928	39.8	41.3
91	isobutane B3LYP/6-31G*	-158.112598	-0.92652408	-158.362760	-91.896616	-90.42633562	42.4	43.9
92	Spiropentane. D2d	-194.8714045	-1.09818907	-195.167916	216.092118	217.9299676	30.7	32.6
93	Benzene B3LYP	-231.7962013	-1.26174348	-232.136872	100.434310	102.6397301	18.0	20.2
94	DIFLUOROMETHANE C2V	-238.7140024	-0.85371692	-238.944506	-448.581363	-445.010683	2.0	5.6
95	HCF3 TRI-FLUOROMETHANE	-337.8795016	-1.15773957	-338.192091	-697.270145	-692.0979104	-0.2	5.0
96	CH2CL2 C2V	-959.2695442	-0.87638844	-959.506169	-85.145907	-77.74199658	10.2	17.7
97	chcl3 B3LYP/6-31G*	-1418.686893	-1.20179461	-1419.011377	-91.016522	-80.09444219	12.3	23.3
98	METHYLAMINE b3lyp	-95.67477759	-0.51505512	-95.813842	-4.808260	-4.440689999	18.2	18.6
99	Acetonitrile. CH3-CN.	-132.5177647	-0.68302231	-132.702181	81.564029	82.29916931	6.3	7.0
100	NITRO METHANE	-244.639241	-1.12963037	-244.944241	-60.644513	-58.38658286	13.8	16.1
101	Methyl-nitrite. CH3-O-N=O.	-244.6353107	-1.11923868	-244.937505	-46.687312	-44.42938206	19.8	22.1
102	Methylsilane. CH3-SiH3.	-330.9608294	-0.56517499	-331.113427	-6.128698	-3.975788486	23.2	25.3
103	Formic Acid.	-189.4977273	-0.81678242	-189.718259	-370.909667	-368.6517374	7.7	10.0
104	Methyl formate.	-228.7157921	-1.03958034	-228.996479	-347.277934	-344.6524338	8.4	11.0
105	acetamide ch3cohn2	-208.8747576	-1.00925607	-209.147257	-222.215856	-220.5355357	16.3	18.0

106	Aziridine. (cyclic	-133.667835	-0.71549439	-133.861018	146.405834	147.1409742	20.0	20.8
107	Cyanogen. NCCN.	-185.3515972	-0.91334319	-185.598200	302.622949	303.3580888	-4.1	-3.3
108	DIMETHYLAMINE b3lyp	-134.8966914	-0.73947784	-135.096350	6.875569	7.61070882	25.3	26.0
109	TRANS ETHYLAMINE	-134.9082328	-0.74063789	-135.108205	-23.311363	-22.57622291	24.0	24.7
110	KETENE B3LYP	-152.3593497	-0.71468346	-152.552314	-50.372993	-48.69267301	-3.1	-1.4
111	OXIRANE B3LYP	-153.5297617	-0.7460835	-153.731204	-36.017634	-34.33731438	16.7	18.4
112	Acetaldehyde B3LYP	-153.5754264	-0.73834443	-153.774779	-153.543130	-151.8628101	12.6	14.2
113	Glyoxal, O=CH-CH=O.	-227.4867669	-1.00702563	-227.758664	-206.768225	-204.1427251	5.4	8.0
114	ETHANOL TRANS	-154.772299	-0.76890692	-154.979904	-209.324043	-207.6437234	25.8	27.5
115	DIMETHYL ETHER,	-154.7555114	-0.76593287	-154.962313	-163.982857	-162.3025369	20.1	21.8
116	Thiooxirane. (cyclic	-476.4519615	-0.83070465	-476.676252	100.281032	103.3528665	18.3	21.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.7656594	-1.17268714	-553.082285	-109.632311	-105.6152962	41.8	45.8
118	Thioethanol. CH3-CH2-SH.	-477.6711965	-0.84955003	-477.900575	-16.001064	-12.92922942	30.4	33.5
119	ch3sch3 B3LYP	-477.6691542	-0.85143021	-477.899040	-9.446237	-6.374402444	27.8	30.9
120	Vinyl fluoride,	-177.5738417	-0.74432214	-177.774809	-134.009972	-131.6732772	4.9	7.2
121	Ethyl chloride.	-539.081252	-0.78477688	-539.293142	-93.588429	-89.33511879	18.5	22.8
122	Vinyl chloride,	-537.85706	-0.75606818	-538.061198	33.957420	38.21073025	10.9	15.2
123	h2c=chcn B3LYP	-170.5259623	-0.87854662	-170.763170	196.443564	197.5462744	15.7	16.8
124	ACETONE B3LYP	-192.8178542	-0.96381727	-193.078085	-195.617969	-193.5700791	21.5	23.6
125	CH3COOH ACETIC	-228.7416381	-1.0391582	-229.022211	-415.291727	-412.6662271	17.3	20.0
126	CH3CFO HCCO	-252.7523902	-1.04766032	-253.035258	-433.038912	-429.7570369	9.2	12.5
127	ch3c(o)cl hcco	-613.022031	-1.06363346	-613.309212	-232.827090	-227.6285998	9.8	15.0
128	ch3ch2ch2cl B3LYP	-578.3119671	-1.01106268	-578.584954	-104.946780	-100.3258998	26.8	31.5
129	Isopropyl alcohol,	-194.0078488	-0.9971527	-194.277080	-236.550692	-234.5028022	36.2	38.3
130	Methyl ethyl	-193.9913295	-0.99137243	-194.259000	-188.532994	-186.4851038	27.8	29.8
131	Trimethyl Amine.	-174.1209533	-0.96870669	-174.382504	7.682463	8.785172849	31.5	32.6
132	FURAN B3LYP	-229.6257138	-1.14680934	-229.935352	-18.921070	-16.50560957	15.8	18.2
133	Thiophene b3lyp	-552.5374055	-1.2384012	-552.871774	137.677958	141.4849328	22.6	26.4
134	PYROLE PLANAR	-209.7783441	-1.11932192	-210.080561	122.412205	123.8824848	14.0	15.5
135	C2v Pyridine	-247.8230696	-1.30561794	-248.175586	149.648975	151.4868247	9.1	10.9
136	H2 B3LYP/6-31G*	-1.15990311	-0.03470725	-1.169274	7.896454	7.896453519	7.9	7.9
137	SH b3lyp/6-31G*	-398.5754197	-0.35845077	-398.672201	148.026072	150.3627669	4.9	7.3
138	CCH B3LYP	-76.46997614	-0.37995044	-76.572563	584.131423	584.8665628	18.9	19.6
139	C2H3 CS,2-A'	-77.7508549	-0.40172289	-77.859320	307.354746	308.0898865	7.8	8.5
140	ch3co hcco	-152.9333441	-0.71628894	-153.126742	-5.605739	-3.92541929	4.4	6.1
141	H2COH C1	-114.8839688	-0.51171445	-115.022132	-7.196607	-5.883857112	10.0	11.3
142	ch3o CS,	-114.8773647	-0.48493483	-115.008297	25.552665	26.86541533	8.4	9.7

143	ch3ch2o 2A"	-154.1130185	-0.70986577	-154.304682	1.216789	2.897108636	16.7	18.4
144	ch3s 2-A'	-437.807165	-0.5868801	-437.965623	133.561825	136.26609	8.9	11.6
145	c2h5 staggered	-78.990687	-0.4330747	-79.107617	134.858290	135.5934303	13.9	14.7
146	(ch3)2ch Cs	-118.2259657	-0.66006953	-118.404184	111.041710	112.1444205	21.1	22.2
147	TERT-BUTYL RADICAL	-157.4613878	-0.8890904	-157.701442	85.150012	86.62029212	33.7	35.2
148	NO2 RADICAL	-204.7856265	-0.90243669	-205.029284	32.163842	34.05420225	-0.9	1.0

MAD	**14.7**	**16.7**
LD	**43.6**	**51.8**

Table S5.40b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 27%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498754	0.000000	-0.498754
2	li	-7.468790	-0.014553	-7.472719
3	be	-14.637596	-0.053127	-14.651940
4	b	-24.616937	-0.076974	-24.637720
5	c	-37.800220	-0.103698	-37.828218
6	n	-54.533543	-0.134390	-54.569828
7	o	-74.996669	-0.191437	-75.048357
8	f	-99.643200	-0.254186	-99.711830
9	na	-162.150304	-0.171110	-162.196504
10	al	-242.232536	-0.219542	-242.291812
11	si	-289.233446	-0.249484	-289.300807
12	p	-341.116090	-0.278450	-341.191272
13	s	-397.950490	-0.319591	-398.036779
14	cl	-459.968888	-0.290446	-460.047309

Table S5.41a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04749982	-0.04657207	-8.060540	147.204233	147.2042327	7.9	7.9
2	BERYLLIUM HYDRIDE	-15.22321532	-0.05488063	-15.238582	319.316773	319.3167734	-22.5	-22.5
3	DOUBLET CH	-38.41831032	-0.14424735	-38.458700	600.351484	600.7190539	4.1	4.5
4	CH2 3-B1	-39.08160585	-0.1632823	-39.127325	395.871027	396.2385966	3.8	4.2
5	Singlet methylene,	-39.0582043	-0.18345283	-39.109571	440.871576	441.2391457	10.8	11.1
6	Methyl radical,	-39.75389494	-0.20800824	-39.812137	152.814000	153.1815701	6.4	6.7
7	ch4 //b3lyp/6-31G*	-40.41860624	-0.24963327	-40.488504	-62.764426	-62.39685571	12.1	12.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14769677	-0.18728268	-55.200136	359.673145	359.673145	3.2	3.2
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78879554	-0.2406976	-55.856191	190.299215	190.2992154	1.6	1.6
10	AMMONIA, //b3lyp/6-31G*	-56.45430518	-0.2946	-56.536793	-34.846542	-34.84654186	11.2	11.2
11	OH RADICAL	-75.64266971	-0.25799293	-75.714908	42.910193	43.85537302	3.6	4.5
12	Water //b3lyp/6-31G*	-76.31944129	-0.32656923	-76.410881	-227.857912	-226.9127316	14.0	14.9
13	HYDROGEN FLUORIDE,	-100.3374871	-0.3372548	-100.431918	-264.983931	-263.3823756	7.4	9.0
14	SIH2 singlet	-290.4503497	-0.30529082	-290.535831	276.053388	277.8387276	3.3	5.0
15	SIH2 3B1	-290.4243656	-0.28280214	-290.503550	361.817709	363.6030491	1.2	2.9
16	SIH3 c3v	-291.0656941	-0.31070685	-291.152692	203.253249	205.0385887	2.8	4.6
17	SIH4 //b3lyp/6-31G*	-291.7085682	-0.33783513	-291.803162	43.144575	44.92991524	8.8	10.6
18	ph2 doublet	-342.3324596	-0.34465576	-342.428963	140.795309	140.7953092	2.3	2.3
19	PH3 c3v	-342.9600966	-0.37574208	-343.065304	19.280931	19.28093122	13.8	13.8
20	SH2 //b3lyp/6-31G*	-399.2065704	-0.39711716	-399.317763	-8.843916	-6.507220515	11.7	14.0
21	HCL //b3lyp/6-31G*	-460.6161654	-0.33550183	-460.710106	-88.106556	-84.5883863	4.4	7.9
22	DILITHIUM //b3lyp/6-31G*	-14.96162984	-0.05776843	-14.977805	230.853857	230.8538571	15.0	15.0
23	Lithium Fluoride,	-107.3005005	-0.36618019	-107.403031	-336.219111	-334.6175558	-1.1	0.5
24	ACETYLENE //b3lyp/6-31g*	-77.17936685	-0.41734146	-77.296222	235.203428	235.9385682	8.4	9.2
25	ETHYLENE //b3lyp/6-31g*	-78.42140011	-0.43836953	-78.544144	65.959885	66.69502547	13.7	14.4
26	ETHANE //b3lyp/6-31g*	-79.64473765	-0.4717793	-79.776836	-64.607826	-63.87268637	19.5	20.2
27	CYANO RADICAL,	-92.55414566	-0.45223129	-92.680770	452.970766	453.3383363	14.1	14.4
28	HYDROGEN CYANIDE	-93.26502277	-0.46177244	-93.394319	131.323916	131.6914864	-0.5	-0.1
29	CARBON MONOXIDE	-113.1559926	-0.47255524	-113.288308	-109.659249	-108.3464993	0.8	2.1
30	HCO BENT	-113.6814471	-0.49494586	-113.820032	37.833228	39.14597815	-4.0	-2.7
31	H2CO //b3lyp/6-31g*	-114.3239285	-0.51445659	-114.467976	-106.182039	-104.8692887	2.6	3.9

32	METHANOL //b3lyp/6-31g*	-115.5304277	-0.54407255	-115.682768	-186.821623	-185.5088731	14.0	15.3
33	Nitrogen N2,	-109.3626273	-0.49545602	-109.501355	3.659113	3.659112541	3.7	3.7
34	H2NNH2 //b3lyp/6-31g*	-111.6708516	-0.5587355	-111.827298	110.511056	110.5110562	15.1	15.1
35	NO radical,	-129.7096118	-0.53733734	-129.860066	91.088053	92.03323341	0.7	1.7
36	O2 //b3lyp/6-31g*	-150.1188892	-0.60157709	-150.287331	-0.695121	1.195239081	-0.7	1.2
37	HYDROGEN PEROXIDE	-151.3357007	-0.63137441	-151.512486	-112.255326	-110.364966	23.7	25.6
38	F2 //b3lyp/6-31g*	-199.2902922	-0.66004645	-199.475105	22.209169	25.41227873	22.2	25.4
39	CO2 D*H	-188.3261361	-0.79448852	-188.548593	-407.237002	-404.979072	-13.9	-11.7
40	na2 //b3lyp/6-31G*	-324.3108681	-0.37045232	-324.414595	144.178907	144.1789073	1.9	1.9
41	SI2 3-SGG	-578.5569503	-0.55744703	-578.713036	590.571232	594.1419123	5.2	8.8
42	P2 //b3lyp/6-31g*	-682.3604615	-0.70754539	-682.558574	156.768498	156.7684977	13.3	13.3
43	S2 //b3lyp/6-31g*	-796.0171326	-0.75484835	-796.228490	130.710252	135.3836415	2.3	6.9
44	CL2 //b3lyp/6-31g*	-919.993171	-0.6495997	-920.175059	10.134852	17.17119168	10.1	17.2
45	Sodium Chloride	-622.2486417	-0.50739968	-622.390714	-174.680497	-171.1623266	7.7	11.3
46	SIO //b3lyp/6-31g*	-364.4762925	-0.61439675	-364.648324	-93.062202	-90.33168218	9.9	12.6
47	Carbon monosulfide,	-435.969805	-0.57415526	-436.130569	290.109932	292.8141974	10.2	12.9
48	OS //b3lyp/6-31g*	-473.0882345	-0.68503352	-473.280044	6.728229	10.01010359	1.7	5.0
49	CLO 2-PI	-535.0202364	-0.60269587	-535.188991	114.044706	118.5080561	12.8	17.3
50	CLF 1-SG	-559.6671539	-0.65201173	-559.849717	-48.691265	-43.57154003	6.5	11.7
51	si2h6 //b3lyp/6-31g*	-582.2434446	-0.65654331	-582.427277	98.780409	102.3510894	18.9	22.4
52	Methyl chloride,	-499.8370482	-0.55854738	-499.993441	-73.664835	-69.77909533	8.3	12.2
53	H3C-SH METHANETHIOL	-438.4303618	-0.62265887	-438.604706	-3.926156	-1.221890889	19.1	21.8
54	HOCl //b3lyp/6-31g*	-535.667464	-0.64343666	-535.847626	-62.880328	-58.41697847	11.6	16.1
55	SO2 //b3lyp/6-31G*	-548.2436113	-1.03020745	-548.532069	-274.315758	-270.0887031	22.7	27.0
56	BF3 PLANAR	-324.2248611	-1.06822204	-324.523963	-1146.073327	-1141.137387	-10.5	-5.6
57	bcl3 B3LYP	-1404.977169	-1.10623803	-1405.286916	-417.280310	-406.5945252	-14.4	-3.7
58	ALf3 B3LYP	-541.7580108	-1.20684878	-542.095928	-1192.370357	-1186.673022	16.8	22.5
59	alcl3 B3LYP	-1622.570046	-1.20829967	-1622.908370	-588.162336	-576.7151557	-3.7	7.8
60	cf4 B3LYP	-437.0254965	-1.45940502	-437.434130	-941.543703	-934.769913	-8.5	-1.7
61	ccl4 B3LYP	-1878.066039	-1.53395993	-1878.495548	-87.211129	-72.77087929	8.6	23.0
62	O=C=S. Singlet	-511.1979553	-0.88488263	-511.445722	-152.101325	-148.4518805	-13.6	-10.0
63	CS2 B3LYP	-834.0662857	-0.98235866	-834.341346	107.567861	112.6088207	-9.2	-4.1
64	COF2 B3LYP	-312.6532633	-1.12771261	-312.969023	-616.348070	-611.8322101	7.5	12.0
65	sif4 B3LYP	-688.6038696	-1.56031876	-689.040759	-1575.533438	-1567.341878	39.5	47.7
66	sicl4, td	-2129.628036	-1.59640125	-2130.075029	-644.148221	-628.2902013	18.6	34.5
67	nno B3LYP	-184.3825845	-0.85225573	-184.621216	71.959828	72.90500793	-10.0	-9.1
68	clno B3LYP	-589.70551	-0.92009522	-589.963137	57.165653	61.62900323	5.3	9.7

69	nf3 c3v	-353.678342	-1.24282205	-354.026332	-126.163216	-121.3585506	6.1	10.9
70	pf3 c3v	-640.5276855	-1.30149516	-640.892104	-933.367271	-928.5626065	25.2	30.0
71	ozone 1-a1	-225.080397	-1.02352699	-225.366985	168.706791	171.542331	26.0	28.9
72	f2o B3LYP	-274.3364339	-0.97340637	-274.608988	48.411780	52.56007011	23.7	27.9
73	CLF3, C2V	-758.9857693	-1.37924542	-759.371958	-147.207174	-138.8843386	11.8	20.1
74	CF2=CF2 D2H	-474.9762088	-1.66093673	-475.441271	-686.824656	-679.6832956	-28.3	-21.1
75	cl2c=ccl2 B3LYP	-1916.089135	-1.73233478	-1916.574188	-17.875327	-3.067506705	-5.3	9.5
76	cf3cn B3LYP	-429.9340399	-1.60167983	-430.382510	-509.286795	-503.7469899	-13.9	-8.4
77	PROPYNE C3V	-116.4188138	-0.64080097	-116.598238	195.819908	196.9226181	10.9	12.0
78	ALLENE D2D	-116.4188726	-0.6345882	-116.596557	198.575936	199.6786464	8.2	9.3
79	CYCLOPROPENE C2V	-116.3792248	-0.64397915	-116.559539	296.704823	297.8075334	19.7	20.8
80	PROPENE CS	-117.6545782	-0.66425907	-117.840571	40.610875	41.7135848	20.5	21.6
81	CYCLOPROPANE D3H	-117.6409073	-0.67050816	-117.828650	74.390754	75.49346419	21.3	22.4
82	PROPANE C2V	-118.872882	-0.69727736	-119.068120	-76.135353	-75.03264334	28.5	29.6
83	TRANS-1,3-BUTADIENE C2H	-155.6696448	-0.85902543	-155.910172	131.535316	133.0055964	21.5	23.0
84	Dimethyl acetylene	-155.6561778	-0.86485992	-155.898339	162.756116	164.2263957	17.2	18.6
85	Methylene cyclopropane.	-155.6369012	-0.86577264	-155.879318	211.291026	212.7613057	10.9	12.3
86	Bicyclo[1.1.0]butane. C2v	-155.6208884	-0.87750635	-155.866590	246.639212	248.1094918	29.5	31.0
87	CYCLOBUTENE b3lyp	-155.6464248	-0.86800959	-155.889467	187.005450	188.47573	30.5	32.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.8699632	-0.89715417	-157.121166	60.736793	62.20707277	32.3	33.8
89	Isobutene. Single	-156.8875194	-0.89288287	-157.137527	12.993897	14.46417736	29.7	31.2
90	Trans butane	-158.1008964	-0.92330267	-158.359421	-87.717386	-86.24710568	37.8	39.3
91	isobutane B3LYP/6-31G*	-158.1018977	-0.9265004	-158.361318	-93.991266	-92.52098578	40.3	41.8
92	Spiropentane. D2d	-194.8590672	-1.09816449	-195.166553	212.319030	214.1568804	27.0	28.8
93	Benzene B3LYP	-231.7823114	-1.26170603	-232.135589	94.982727	97.18814662	12.6	14.8
94	DIFLUOROMETHANE C2V	-238.7045941	-0.85371695	-238.943635	-451.308856	-447.7381756	-0.7	2.9
95	HCF3 TRI-FLUOROMETHANE	-337.8668418	-1.15773722	-338.191008	-701.213382	-696.0411468	-4.2	1.0
96	CH2CL2 C2V	-959.2528293	-0.87637521	-959.498214	-86.812572	-79.40866214	8.6	16.0
97	chcl3 B3LYP/6-31G*	-1418.663279	-1.20177596	-1418.999776	-93.651226	-82.72914614	9.7	20.6
98	METHYLAMINE b3lyp	-95.66902965	-0.51504869	-95.813243	-6.236256	-5.868685534	16.8	17.1
99	Acetonitrile. CH3-CN.	-132.5105342	-0.68300153	-132.701775	78.159088	78.89422793	2.8	3.6
100	NITRO METHANE	-244.6280173	-1.12961036	-244.944308	-67.325175	-65.0672448	7.2	9.4
101	Methyl-nitrite. CH3-O-N=O.	-244.6241238	-1.11921765	-244.937505	-53.190904	-50.93297372	13.3	15.6
102	Methylsilane. CH3-SiH3.	-330.9517537	-0.5651611	-331.109999	-6.003623	-3.850712555	23.3	25.4
103	Formic Acid.	-189.4892696	-0.81677655	-189.717967	-375.117688	-372.8597578	3.5	5.8
104	Methyl formate.	-228.7047637	-1.03956499	-228.995842	-352.049412	-349.4239119	3.6	6.2
105	acetamide ch3cohn2	-208.8639161	-1.00924192	-209.146504	-226.461840	-224.78152	12.0	13.7

106	Aziridine. (cyclic	-133.6599886	-0.71548195	-133.860323	143.759358	144.4944978	17.4	18.1
107	Cyanogen. NCCN.	-185.3426743	-0.91331047	-185.598401	296.091944	296.8270837	-10.6	-9.9
108	DIMETHYLAMINE b3lyp	-134.8883623	-0.7394643	-135.095412	4.867439	5.602579392	23.3	24.0
109	TRANS ETHYLAMINE	-134.8999	-0.74062514	-135.107275	-25.340947	-24.60580714	21.9	22.7
110	KETENE B3LYP	-152.3518778	-0.71466822	-152.551985	-54.200026	-52.51970552	-6.9	-5.2
111	OXIRANE B3LYP	-153.5217133	-0.7460735	-153.730614	-39.159405	-37.47908508	13.6	15.2
112	Acetaldehyde B3LYP	-153.5674314	-0.73833296	-153.774165	-156.620780	-154.94046	9.5	11.2
113	Glyoxal, O=CH-CH=O.	-227.4763155	-1.00701216	-227.758279	-212.201301	-209.5758011	-0.1	2.6
114	ETHANOL TRANS	-154.7637522	-0.76889765	-154.979044	-211.756925	-210.0766054	23.4	25.1
115	DIMETHYL ETHER,	-154.7469778	-0.76592166	-154.961436	-166.370807	-164.6904869	17.7	19.4
116	Thiooxirane. (cyclic	-476.4402664	-0.83068764	-476.672859	98.084736	101.1565706	16.1	19.2
117	Dimethylsulfoxide. (CH3)2SO.	-552.7504529	-1.17266902	-553.078800	-113.339153	-109.3221377	38.1	42.1
118	Thioethanol. CH3-CH2-SH.	-477.6590272	-0.8495323	-477.896896	-17.446893	-14.37505814	29.0	32.1
119	ch3sch3 B3LYP	-477.6569923	-0.8514125	-477.895388	-10.960716	-7.888881161	26.3	29.3
120	Vinyl fluoride,	-177.5656158	-0.74431195	-177.774023	-136.659942	-134.3232474	2.2	4.6
121	Ethyl chloride.	-539.068843	-0.78476175	-539.288576	-95.082691	-90.82938116	17.0	21.3
122	Vinyl chloride,	-537.8451791	-0.75605118	-538.056873	31.831937	36.08524675	8.8	13.1
123	h2c=chcn B3LYP	-170.5166893	-0.87851818	-170.762674	191.803369	192.9060794	11.1	12.2
124	ACETONE B3LYP	-192.807267	-0.96379889	-193.077131	-199.274485	-197.2265953	17.9	19.9
125	CH3COOH ACETIC	-228.73059	-1.03914549	-229.021551	-420.001947	-417.3764465	12.6	15.2
126	CH3CFO HCCO	-252.7411448	-1.04764726	-253.034486	-437.474880	-434.1930048	4.8	8.1
127	ch3c(o)cl hcco	-613.0071445	-1.06361463	-613.304957	-236.887101	-231.6886113	5.8	11.0
128	ch3ch2ch2cl B3LYP	-578.2969736	-1.01104142	-578.580065	-107.062200	-102.44132	24.7	29.4
129	Isopropyl alcohol,	-193.9967082	-0.99713659	-194.275906	-239.631147	-237.5832572	33.2	35.2
130	Methyl ethyl	-193.9802103	-0.99135455	-194.257790	-191.516546	-189.4686561	24.8	26.8
131	Trimethyl Amine.	-174.1100301	-0.96868658	-174.381262	5.001802	6.104511619	28.9	30.0
132	FURAN B3LYP	-229.6134601	-1.14678346	-229.934559	-24.471137	-22.05567738	10.3	12.7
133	Thiophene b3lyp	-552.5215083	-1.23836878	-552.868252	132.881549	136.6885243	17.8	21.6
134	PYROLE PLANAR	-209.7662816	-1.11929445	-210.079684	117.303359	118.7736393	8.9	10.4
135	C2v Pyridine	-247.808973	-1.30558239	-248.174536	143.525708	145.3635578	2.9	4.8
136	H2 B3LYP/6-31G*	-1.15952047	-0.03470754	-1.169239	7.989623	7.989622799	8.0	8.0
137	SH b3lyp/6-31G*	-398.5687414	-0.3584527	-398.669108	147.982936	150.3196315	4.9	7.2
138	CCH B3LYP	-76.46592243	-0.3799306	-76.572303	581.873469	582.6086092	16.6	17.4
139	C2H3 CS,2-A'	-77.74622948	-0.40170205	-77.858706	306.026917	306.7620569	6.5	7.2
140	ch3co hcco	-152.92568	-0.71626804	-153.126235	-8.966115	-7.285795427	1.1	2.8
141	H2COH C1	-114.8783399	-0.51170575	-115.021618	-9.068472	-7.755722302	8.1	9.4
142	ch3o CS,	-114.8717689	-0.48491974	-115.007546	24.301929	25.61467885	7.1	8.5

143	ch3ch2o 2A"	-154.1048384	-0.70984197	-154.303594	-0.618189	1.062131458	14.9	16.5
144	ch3s 2-A'	-437.7979091	-0.58687234	-437.962233	132.825807	135.530072	8.1	10.8
145	c2h5 staggered	-78.98551248	-0.4330674	-79.106771	134.139027	134.8741673	13.2	14.0
146	(ch3)2ch Cs	-118.2181996	-0.66005241	-118.403014	109.704317	110.8070265	19.7	20.9
147	TERT-BUTYL RADICAL	-157.4510273	-0.88906309	-157.699965	83.148444	84.61872434	31.7	33.2
148	NO2 RADICAL	-204.777307	-0.90241526	-205.029983	25.294405	27.18476502	-7.8	-5.9

MAD	**13.1**	**14.8**
LD	**40.3**	**47.7**

Table S5.41b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498754	0.000000	-0.498754
2	li	-7.468253	-0.014552	-7.472327
3	be	-14.636647	-0.053122	-14.651521
4	b	-24.615672	-0.076977	-24.637226
5	c	-37.798621	-0.103705	-37.827659
6	n	-54.531614	-0.134394	-54.569245
7	o	-74.994084	-0.191447	-75.047689
8	f	-99.639980	-0.254196	-99.711155
9	na	-162.146213	-0.171107	-162.194123
10	al	-242.227579	-0.219543	-242.289052
11	si	-289.228131	-0.249485	-289.297987
12	p	-341.110420	-0.278444	-341.188384
13	s	-397.944183	-0.319594	-398.033669
14	cl	-459.961968	-0.290449	-460.043294

Table S5.42a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04661154	-0.04657324	-8.060118	147.284901	147.2849015	8.0	8.0
2	BERYLLIUM HYDRIDE	-15.22213438	-0.05487328	-15.238048	319.618673	319.6186731	-22.2	-22.2
3	DOUBLET CH	-38.41633284	-0.14425139	-38.458166	600.283508	600.6510781	4.1	4.4
4	CH2 3-B1	-39.07945407	-0.16328086	-39.126806	395.765085	396.1326553	3.7	4.1
5	Singlet methylene,	-39.05587677	-0.18344918	-39.109077	440.699171	441.0667414	10.6	11.0
6	Methyl radical,	-39.75130938	-0.20801189	-39.811633	152.668793	153.0363632	6.2	6.6
7	ch4 //b3lyp/6-31G*	-40.41566024	-0.24962738	-40.488052	-63.048899	-62.68132889	11.8	12.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14531638	-0.18729296	-55.199631	359.466993	359.4669933	3.0	3.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78599938	-0.2407045	-55.855804	189.784833	189.7848327	1.1	1.1
10	AMMONIA, //b3lyp/6-31G*	-56.4511258	-0.29460093	-56.536560	-35.765442	-35.76544245	10.3	10.3
11	OH RADICAL	-75.63965918	-0.258003	-75.714480	42.281968	43.22714811	3.0	3.9
12	Water //b3lyp/6-31G*	-76.31603698	-0.32657545	-76.410744	-229.249806	-228.3046265	12.6	13.5
13	HYDROGEN FLUORIDE,	-100.3338635	-0.33726339	-100.431670	-266.102884	-264.5013288	6.3	7.9
14	SIH2 singlet	-290.4443757	-0.30528307	-290.532908	276.323988	278.1093281	3.5	5.3
15	SIH2 3B1	-290.4185875	-0.28277592	-290.500592	362.178687	363.9640275	1.5	3.3
16	SIH3 c3v	-291.05954	-0.3106921	-291.149641	203.860017	205.6453575	3.4	5.2
17	SIH4 //b3lyp/6-31G*	-291.702076	-0.33782626	-291.800046	43.922217	45.70755683	9.6	11.4
18	ph2 doublet	-342.3260283	-0.34465563	-342.425978	141.049764	141.049764	2.6	2.6
19	PH3 c3v	-342.9533375	-0.3757331	-343.062300	19.586592	19.58659193	14.1	14.1
20	SH2 //b3lyp/6-31G*	-399.1995522	-0.39711151	-399.314715	-9.003765	-6.667070407	11.5	13.8
21	HCL //b3lyp/6-31G*	-460.6088944	-0.33549957	-460.706189	-88.364152	-84.84598198	4.1	7.6
22	DILITHIUM //b3lyp/6-31G*	-14.96029207	-0.05776437	-14.977044	230.796814	230.7968136	14.9	14.9
23	Lithium Fluoride,	-107.2963236	-0.36619463	-107.402520	-337.677161	-336.0756062	-2.5	-0.9
24	ACETYLENE //b3lyp/6-31g*	-77.1749189	-0.4173231	-77.295943	232.999082	233.7342215	6.2	7.0
25	ETHYLENE //b3lyp/6-31g*	-78.41641519	-0.43835555	-78.543538	64.609927	65.34506662	12.3	13.0
26	ETHANE //b3lyp/6-31g*	-79.63921637	-0.47176774	-79.776029	-65.428588	-64.69344813	18.7	19.4
27	CYANO RADICAL,	-92.54987894	-0.45214504	-92.681001	449.364886	449.7324565	10.5	10.8
28	HYDROGEN CYANIDE	-93.26037681	-0.46175735	-93.394286	128.409047	128.7766174	-3.4	-3.0
29	CARBON MONOXIDE	-113.1511437	-0.47254908	-113.288183	-112.551448	-111.2386979	-2.1	-0.8
30	HCO BENT	-113.676365	-0.49493337	-113.819896	34.970460	36.28321014	-6.9	-5.6
31	H2CO //b3lyp/6-31g*	-114.3185216	-0.51445154	-114.467713	-108.710226	-107.3974759	0.1	1.4

32	METHANOL //b3lyp/6-31g*	-115.5244662	-0.54406964	-115.682246	-188.672852	-187.3601019	12.2	13.5
33	Nitrogen N2,	-109.3577899	-0.49544078	-109.501468	0.301380	0.30138002	0.3	0.3
34	H2NNH2 //b3lyp/6-31g*	-111.6648829	-0.55873461	-111.826916	108.451118	108.451118	13.1	13.1
35	NO radical,	-129.7043314	-0.53732781	-129.860157	87.569071	88.51425134	-2.8	-1.9
36	O2 //b3lyp/6-31g*	-150.1131666	-0.60157614	-150.287624	-4.966265	-3.075904891	-5.0	-3.1
37	HYDROGEN PEROXIDE	-151.3293374	-0.63137925	-151.512437	-115.631075	-113.7407155	20.3	22.2
38	F2 //b3lyp/6-31g*	-199.2835354	-0.66005018	-199.474950	19.073347	22.27645662	19.1	22.3
39	CO2 D*H	-188.318225	-0.79447533	-188.548623	-412.287316	-410.0293861	-19.0	-16.7
40	na2 //b3lyp/6-31G*	-324.302441	-0.37044681	-324.409871	144.080477	144.0804771	1.8	1.8
41	SI2 3-SGG	-578.5459699	-0.55742912	-578.707624	589.969488	593.5401677	4.6	8.2
42	P2 //b3lyp/6-31g*	-682.3483189	-0.70752211	-682.553500	154.926186	154.9261856	11.4	11.4
43	S2 //b3lyp/6-31g*	-796.0040638	-0.75483928	-796.222967	128.882551	133.5559412	0.4	5.1
44	CL2 //b3lyp/6-31g*	-919.9790422	-0.64959212	-920.167424	9.099252	16.13559209	9.1	16.1
45	Sodium Chloride	-622.2373126	-0.50740202	-622.384459	-175.050883	-171.5327135	7.4	10.9
46	SIO //b3lyp/6-31g*	-364.4677668	-0.61440512	-364.645944	-95.970774	-93.24025414	7.0	9.7
47	Carbon monosulfide,	-435.9613226	-0.5741354	-436.127822	287.687701	290.3919657	7.8	10.5
48	OS //b3lyp/6-31g*	-473.0788294	-0.6850252	-473.277487	3.527110	6.808985033	-1.5	1.8
49	CLO 2-PI	-535.0103203	-0.60265457	-535.185090	111.995213	116.4585635	10.7	15.2
50	CLF 1-SG	-559.6566914	-0.65201116	-559.845775	-50.652539	-45.53281399	4.6	9.7
51	si2h6 //b3lyp/6-31g*	-582.2308279	-0.65652669	-582.421221	99.871805	103.4424853	20.0	23.5
52	Methyl chloride,	-499.8272232	-0.55853848	-499.989199	-74.537259	-70.65151853	7.5	11.4
53	H3C-SH METHANETHIOL	-438.4207766	-0.62264729	-438.601344	-4.733068	-2.02880287	18.3	21.0
54	HOCl //b3lyp/6-31g*	-535.6572118	-0.64343455	-535.843808	-65.146695	-60.68334525	9.3	13.8
55	SO2 //b3lyp/6-31G*	-548.2310653	-1.03019732	-548.529823	-280.082917	-275.855862	17.0	21.2
56	BF3 PLANAR	-324.2129262	-1.06822275	-324.522711	-1149.396997	-1144.461057	-13.9	-8.9
57	bcl3 B3LYP	-1404.954283	-1.10621981	-1405.275086	-419.139969	-408.4541845	-16.2	-5.5
58	ALf3 B3LYP	-541.7424822	-1.20685667	-542.092471	-1195.854676	-1190.157341	13.3	19.0
59	alcl3 B3LYP	-1622.543569	-1.20828408	-1622.893972	-589.229166	-577.7819859	-4.7	6.7
60	cf4 B3LYP	-437.0095818	-1.45939753	-437.432807	-946.627102	-939.8533116	-13.6	-6.8
61	ccl4 B3LYP	-1878.035521	-1.53393508	-1878.480362	-90.973231	-76.53298108	4.8	19.3
62	O=C=S. Singlet	-511.1864078	-0.88486123	-511.443018	-156.384605	-152.7351603	-17.9	-14.2
63	CS2 B3LYP	-834.0510913	-0.98232854	-834.335967	103.894213	108.9351731	-12.8	-7.8
64	COF2 B3LYP	-312.6413562	-1.12770319	-312.968390	-621.451185	-616.9353251	2.4	6.9
65	sif4 B3LYP	-688.5843226	-1.560315	-689.036814	-1579.667394	-1571.475834	35.4	43.5
66	sicl4, td	-2129.593887	-1.59637593	-2130.056836	-645.949034	-630.0910136	16.8	32.7
67	nno B3LYP	-184.3747103	-0.85223335	-184.621858	65.461669	66.40684896	-16.5	-15.6
68	clno B3LYP	-589.6930828	-0.92007669	-589.959905	51.827675	56.29102514	-0.1	4.4

69	nf3 c3v	-353.6655635	-1.24281635	-354.025980	-132.085533	-127.2808681	0.1	4.9
70	pf3 c3v	-640.5111665	-1.30149188	-640.888599	-937.061997	-932.2573324	21.5	26.3
71	ozone 1-a1	-225.07162	-1.02350442	-225.368436	159.642120	162.4776599	17.0	19.8
72	f2o B3LYP	-274.3267074	-0.97340467	-274.608995	43.098570	47.2468602	18.4	22.6
73	CLF3, C2V	-758.9683405	-1.37924355	-759.368321	-153.514241	-145.191406	5.5	13.8
74	CF2=CF2 D2H	-474.9582562	-1.66092721	-475.439925	-693.316855	-686.1754952	-34.8	-27.6
75	cl2c=ccl2 B3LYP	-1916.056532	-1.73230436	-1916.558900	-22.838171	-8.030351254	-10.3	4.5
76	cf3cn B3LYP	-429.9171018	-1.60165658	-430.381582	-516.635545	-511.0957397	-21.2	-15.7
77	PROPYNE C3V	-116.4117812	-0.6407774	-116.597607	193.068907	194.1716169	8.1	9.2
78	ALLENE D2D	-116.4118366	-0.63456654	-116.595861	195.995708	197.0984177	5.6	6.7
79	CYCLOPROPENE C2V	-116.3721364	-0.64396173	-116.558885	294.012357	295.1150668	17.0	18.1
80	PROPENE CS	-117.647007	-0.66423965	-117.839636	38.654942	39.75765189	18.6	19.7
81	CYCLOPROPANE D3H	-117.6332672	-0.67049318	-117.827710	72.448425	73.5511353	19.3	20.4
82	PROPANE C2V	-118.8647763	-0.69725984	-119.066982	-77.556115	-76.45340457	27.0	28.1
83	TRANS-1,3-BUTADIENE C2H	-155.6600241	-0.8589981	-155.909134	128.383245	129.8535245	18.3	19.8
84	Dimethyl acetylene	-155.646561	-0.86483106	-155.897362	159.441837	160.9121173	13.8	15.3
85	Methylene cyclopropane.	-155.6272181	-0.86574968	-155.878286	208.122467	209.5927473	7.7	9.2
86	Bicyclo[1.1.0]butane. C2v	-155.6111368	-0.87748677	-155.865608	243.339674	244.8099543	26.2	27.7
87	CYCLOBUTENE b3lyp	-155.636717	-0.86798644	-155.888433	183.842919	185.3131987	27.4	28.8
88	CYCLOBUTANE b3lyp/6-31G*	-156.8597211	-0.89713284	-157.119890	58.210542	59.68082192	29.8	31.2
89	Isobutene. Single	-156.8773543	-0.89285781	-157.136283	10.380755	11.8510348	27.1	28.6
90	Trans butane	-158.0902054	-0.92327891	-158.357956	-89.749571	-88.27929073	35.8	37.2
91	isobutane B3LYP/6-31G*	-158.0911975	-0.92647672	-158.359876	-96.083392	-94.6131123	38.2	39.7
92	Spiropentane. D2d	-194.84673	-1.09813991	-195.165191	208.548959	210.3868089	23.2	25.0
93	Benzene B3LYP	-231.7684217	-1.26166857	-232.134306	89.535261	91.74068071	7.1	9.3
94	DIFLUOROMETHANE C2V	-238.6951859	-0.85371699	-238.942764	-454.034969	-450.4642895	-3.4	0.2
95	HCF3 TRI-FLUOROMETHANE	-337.854182	-1.15773488	-338.189925	-705.154525	-699.9822898	-8.1	-2.9
96	CH2CL2 C2V	-959.2361145	-0.87636198	-959.490260	-88.477798	-81.0738884	6.9	14.3
97	chcl3 B3LYP/6-31G*	-1418.639666	-1.20175731	-1418.988175	-96.283938	-85.36185813	7.1	18.0
98	METHYLAMINE b3lyp	-95.66328179	-0.51504227	-95.812644	-7.663455	-7.295885279	15.3	15.7
99	Acetonitrile. CH3-CN.	-132.5033038	-0.68298075	-132.701368	74.756096	75.49123573	-0.6	0.2
100	NITRO METHANE	-244.6167937	-1.12959035	-244.944375	-74.003093	-71.74516309	0.5	2.7
101	Methyl-nitrite. CH3-O-N=O.	-244.612937	-1.11919663	-244.937504	-59.691706	-57.43377578	6.8	9.1
102	Methylsilane. CH3-SiH3.	-330.9426781	-0.56514721	-331.106571	-5.877392	-3.72448219	23.4	25.6
103	Formic Acid.	-189.4808119	-0.81677067	-189.717675	-379.323878	-377.065948	-0.7	1.6
104	Methyl formate.	-228.6937355	-1.03954965	-228.995205	-356.818238	-354.1927375	-1.2	1.4
105	acetamide ch3cohn2	-208.8530746	-1.00922777	-209.145751	-230.705636	-229.025316	7.8	9.5

106	Aziridine. (cyclic	-133.6521422	-0.71546951	-133.859628	141.114393	141.8495326	14.8	15.5
107	Cyanogen. NCCN.	-185.3337515	-0.91327776	-185.598602	289.563738	290.2988783	-17.1	-16.4
108	DIMETHYLAMINE b3lyp	-134.8800333	-0.73945077	-135.094474	2.860819	3.595958839	21.3	22.0
109	TRANS ETHYLAMINE	-134.8915674	-0.74061239	-135.106345	-27.369083	-26.63394262	19.9	20.6
110	KETENE B3LYP	-152.344406	-0.71465298	-152.551655	-58.024991	-56.34467097	-10.7	-9.1
111	OXIRANE B3LYP	-153.5136651	-0.74606351	-153.730023	-42.299418	-40.61909775	10.4	12.1
112	Acetaldehyde B3LYP	-153.5594365	-0.73832149	-153.773550	-159.696561	-158.0162409	6.4	8.1
113	Glyoxal, O=CH-CH=O.	-227.4658643	-1.00699869	-227.757894	-217.631789	-215.0062895	-5.5	-2.9
114	ETHANOL TRANS	-154.7552055	-0.76888838	-154.978183	-214.188133	-212.5078126	21.0	22.6
115	DIMETHYL ETHER,	-154.7384443	-0.76591045	-154.960558	-168.756980	-167.0766602	15.3	17.0
116	Thiooxirane. (cyclic	-476.4285713	-0.83067063	-476.669466	95.890251	98.96208585	13.9	17.0
117	Dimethylsulfoxide. (CH3)2SO.	-552.7352464	-1.17265091	-553.075315	-117.043519	-113.026504	34.4	38.4
118	Thioethanol. CH3-CH2-SH.	-477.646858	-0.84951458	-477.893217	-18.890933	-15.8190981	27.6	30.6
119	ch3sch3 B3LYP	-477.6448305	-0.85139479	-477.891735	-12.473400	-9.401564561	24.8	27.8
120	Vinyl fluoride,	-177.55739	-0.74430177	-177.773238	-139.308221	-136.9715259	-0.4	1.9
121	Ethyl chloride.	-539.0564342	-0.78474663	-539.284011	-96.575350	-92.32204039	15.6	19.8
122	Vinyl chloride,	-537.8332982	-0.75603418	-538.052548	29.708267	33.9615772	6.7	10.9
123	h2c=chcn B3LYP	-170.5074164	-0.87848974	-170.762178	187.165892	188.2686018	6.4	7.5
124	ACETONE B3LYP	-192.79668	-0.96378051	-193.076176	-202.928509	-200.8806187	14.2	16.3
125	CH3COOH ACETIC	-228.7195419	-1.03913277	-229.020890	-424.709663	-422.0841631	7.9	10.5
126	CH3CFO HCCO	-252.7298995	-1.0476342	-253.033713	-441.908332	-438.6264567	0.3	3.6
127	ch3c(o)cl hcco	-612.9922581	-1.06359581	-613.300701	-240.944649	-235.7461593	1.7	6.9
128	ch3ch2ch2cl B3LYP	-578.2819804	-1.01102016	-578.575176	-109.175348	-104.5544679	22.6	27.2
129	Isopropyl alcohol,	-193.9855677	-0.99712048	-194.274733	-242.709229	-240.6613385	30.1	32.1
130	Methyl ethyl	-193.9690912	-0.99133668	-194.256579	-194.497613	-192.4497231	21.8	23.9
131	Trimethyl Amine.	-174.0991069	-0.96866648	-174.380020	2.323334	3.426043994	26.2	27.3
132	FURAN B3LYP	-229.6012066	-1.14675759	-229.933766	-30.017881	-27.60242132	4.7	7.1
133	Thiophene b3lyp	-552.5056111	-1.23833635	-552.864729	128.088501	131.8954755	13.0	16.8
134	PYROLE PLANAR	-209.7542194	-1.11926698	-210.078807	112.197520	113.6678001	3.8	5.3
135	C2v Pyridine	-247.7948765	-1.30554684	-248.173485	137.406316	139.244166	-3.2	-1.3
136	H2 B3LYP/6-31G*	-1.15913783	-0.03470783	-1.169203	8.082777	8.082776852	8.1	8.1
137	SH b3lyp/6-31G*	-398.5620632	-0.35845465	-398.666015	147.939897	150.2765917	4.8	7.2
138	CCH B3LYP	-76.46186881	-0.3799108	-76.572043	579.617128	580.3522676	14.4	15.1
139	C2H3 CS,2-A'	-77.74160417	-0.40168125	-77.858092	304.700699	305.4358394	5.1	5.9
140	ch3co hcco	-152.918016	-0.71624712	-153.125728	-12.324191	-10.64387084	-2.3	-0.6
141	H2COH C1	-114.8727112	-0.51169707	-115.021103	-10.939048	-9.626297585	6.2	7.5
142	ch3o CS,	-114.8661732	-0.48490468	-115.006796	23.052784	24.36553395	5.9	7.2

143	ch3ch2o 2A"	-154.0966585	-0.70981819	-154.302506	-2.450769	-0.770449426	13.0	14.7
144	ch3s 2-A'	-437.7886534	-0.5868646	-437.958844	132.090707	134.7949719	7.4	10.1
145	c2h5 staggered	-78.98033804	-0.43306012	-79.105925	133.420759	134.1558992	12.5	13.2
146	(ch3)2ch Cs	-118.2104335	-0.66003531	-118.401844	108.368720	109.4714304	18.4	19.5
147	TERT-BUTYL RADICAL	-157.4406671	-0.8890358	-157.698487	81.149523	82.61980307	29.7	31.2
148	NO2 RADICAL	-204.7689875	-0.90239384	-205.030682	18.427439	20.31779865	-14.6	-12.7

MAD	**11.9**	**13.3**
LD	**38.2**	**43.5**

Table S5.42b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498754	0.000000	-0.498754
2	li	-7.467716	-0.014552	-7.471936
3	be	-14.635697	-0.053118	-14.651102
4	b	-24.614407	-0.076981	-24.636732
5	c	-37.797023	-0.103711	-37.827099
6	n	-54.529686	-0.134398	-54.568662
7	o	-74.991500	-0.191458	-75.047022
8	f	-99.636760	-0.254206	-99.710480
9	na	-162.142121	-0.171105	-162.191742
10	al	-242.222623	-0.219544	-242.286291
11	si	-289.222815	-0.249487	-289.295167
12	p	-341.104749	-0.278439	-341.185496
13	s	-397.937877	-0.319596	-398.030560
14	cl	-459.955048	-0.290453	-460.039279

Table S5.43a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04572329	-0.04657441	-8.059696	147.365475	147.3654747	8.0	8.0
2	BERYLLIUM HYDRIDE	-15.22105352	-0.05486595	-15.237513	319.920565	319.9205654	-21.9	-21.9
3	DOUBLET CH	-38.41435541	-0.14425545	-38.457632	600.215577	600.5831475	4.0	4.4
4	CH2 3-B1	-39.0773024	-0.16327944	-39.126286	395.659319	396.0268894	3.6	4.0
5	Singlet methylene,	-39.05354929	-0.18344552	-39.108583	440.527240	440.8948098	10.4	10.8
6	Methyl radical,	-39.74872388	-0.20801557	-39.811129	152.523618	152.8911877	6.1	6.5
7	ch4 //b3lyp/6-31G*	-40.4127143	-0.2496215	-40.487601	-63.332824	-62.96525388	11.6	11.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14293603	-0.18730328	-55.199127	359.260449	359.2604489	2.8	2.8
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78320327	-0.24071142	-55.855417	189.270224	189.2702242	0.6	0.6
10	AMMONIA, //b3lyp/6-31G*	-56.44794647	-0.29460186	-56.536327	-36.684240	-36.68423958	9.3	9.3
11	OH RADICAL	-75.63664869	-0.2580131	-75.714053	41.653761	42.59894052	2.3	3.3
12	Water //b3lyp/6-31G*	-76.31263271	-0.32658167	-76.410607	-230.641458	-229.6962783	11.2	12.1
13	HYDROGEN FLUORIDE,	-100.3302398	-0.33727197	-100.431421	-267.221757	-265.6202021	5.2	6.8
14	SIH2 singlet	-290.4384019	-0.30527531	-290.529984	276.595124	278.3804638	3.8	5.6
15	SIH2 3B1	-290.4128096	-0.28274973	-290.497635	362.540746	364.3260855	1.9	3.7
16	SIH3 c3v	-291.053386	-0.31067736	-291.146589	204.467542	206.2528819	4.1	5.8
17	SIH4 //b3lyp/6-31G*	-291.6955839	-0.33781739	-291.796929	44.700471	46.48581069	10.4	12.2
18	ph2 doublet	-342.3195971	-0.34465553	-342.422994	141.303879	141.303879	2.8	2.8
19	PH3 c3v	-342.9465786	-0.37572411	-343.059296	19.892435	19.89243538	14.5	14.5
20	SH2 //b3lyp/6-31G*	-399.1925341	-0.39710586	-399.311666	-9.163150	-6.826454535	11.3	13.7
21	HCL //b3lyp/6-31G*	-460.6016235	-0.33549731	-460.702273	-88.621431	-85.10326103	3.8	7.4
22	DILITHIUM //b3lyp/6-31G*	-14.95895438	-0.0577603	-14.976282	230.739870	230.7398705	14.8	14.8
23	Lithium Fluoride,	-107.2921466	-0.36620909	-107.402009	-339.135471	-337.5339155	-4.0	-2.4
24	ACETYLENE //b3lyp/6-31g*	-77.17047102	-0.41730474	-77.295662	230.796324	231.5314638	4.0	4.8
25	ETHYLENE //b3lyp/6-31g*	-78.41143035	-0.43834157	-78.542933	63.261300	63.99644048	11.0	11.7
26	ETHANE //b3lyp/6-31g*	-79.63369517	-0.47175618	-79.775222	-66.248144	-65.51300426	17.9	18.6
27	CYANO RADICAL,	-92.54561237	-0.45205892	-92.681230	445.763727	446.1312973	6.9	7.2
28	HYDROGEN CYANIDE	-93.25573091	-0.46174227	-93.394254	125.495493	125.8630633	-6.3	-5.9
29	CARBON MONOXIDE	-113.1462949	-0.47254293	-113.288058	-115.442357	-114.1296068	-5.0	-3.7
30	HCO BENT	-113.6712829	-0.49492085	-113.819759	32.109241	33.42199065	-9.7	-8.4
31	H2CO //b3lyp/6-31g*	-114.3131148	-0.5144465	-114.467449	-111.237208	-109.9244579	-2.5	-1.1

32	METHANOL //b3lyp/6-31g*	-115.5185048	-0.54406674	-115.681725	-190.523040	-189.2102904	10.3	11.6
33	Nitrogen N2,	-109.3529524	-0.49542555	-109.501580	-3.055098	-3.055098038	-3.1	-3.1
34	H2NNH2 //b3lyp/6-31g*	-111.6589143	-0.55873371	-111.826534	106.391565	106.3915653	11.0	11.0
35	NO radical,	-129.6990511	-0.53731828	-129.860247	84.051417	84.99659672	-6.3	-5.4
36	O2 //b3lyp/6-31g*	-150.107444	-0.60157521	-150.287917	-9.236156	-7.345796498	-9.2	-7.3
37	HYDROGEN PEROXIDE	-151.3229741	-0.6313841	-151.512389	-119.005921	-117.1155613	17.0	18.9
38	F2 //b3lyp/6-31g*	-199.2767786	-0.66005391	-199.474795	15.938427	19.14153715	15.9	19.1
39	CO2 D*H	-188.3103139	-0.79446214	-188.548653	-417.335368	-415.0774376	-24.0	-21.8
40	na2 //b3lyp/6-31G*	-324.2940141	-0.37044129	-324.405146	143.981958	143.9819576	1.7	1.7
41	SI2 3-SGG	-578.5349895	-0.55741125	-578.702213	589.368866	592.9395462	4.0	7.6
42	P2 //b3lyp/6-31g*	-682.3361763	-0.70749883	-682.548426	153.084608	153.0846077	9.6	9.6
43	S2 //b3lyp/6-31g*	-795.9909952	-0.75483023	-796.217444	127.055755	131.7291445	-1.4	3.3
44	CL2 //b3lyp/6-31g*	-919.9649135	-0.64958453	-920.159789	8.064533	15.10087309	8.1	15.1
45	Sodium Chloride	-622.2259835	-0.50740435	-622.378205	-175.421249	-171.9030794	7.0	10.5
46	SIO //b3lyp/6-31g*	-364.4592412	-0.61441349	-364.643565	-98.879043	-96.14852311	4.0	6.8
47	Carbon monosulfide,	-435.9528402	-0.57411553	-436.125075	285.267067	287.9713319	5.4	8.1
48	OS //b3lyp/6-31g*	-473.0694243	-0.68501687	-473.274929	0.327201	3.609076304	-4.7	-1.4
49	CLO 2-PI	-535.0004044	-0.60261329	-535.181188	109.948694	114.412044	8.7	13.2
50	CLF 1-SG	-559.646229	-0.6520106	-559.841832	-52.612991	-47.49326618	2.6	7.7
51	si2h6 //b3lyp/6-31g*	-582.2182113	-0.65651007	-582.415164	100.964393	104.5350732	21.0	24.6
52	Methyl chloride,	-499.8173983	-0.55852959	-499.984957	-75.408725	-71.52298499	6.6	10.5
53	H3C-SH METHANETHIOL	-438.4111916	-0.62263571	-438.597982	-5.538877	-2.83461214	17.5	20.2
54	HOCl //b3lyp/6-31g*	-535.6469596	-0.64343243	-535.839989	-67.412097	-62.9487469	7.1	11.5
55	SO2 //b3lyp/6-31G*	-548.2185194	-1.0301872	-548.527576	-285.848059	-281.6210045	11.2	15.4
56	BF3 PLANAR	-324.2009914	-1.06822346	-324.521458	-1152.718740	-1147.7828	-17.2	-12.2
57	bcl3 B3LYP	-1404.931396	-1.10620159	-1405.263256	-420.997656	-410.3118715	-18.1	-7.4
58	ALf3 B3LYP	-541.7269536	-1.20686457	-542.089013	-1199.337530	-1193.640195	9.8	15.5
59	alcl3 B3LYP	-1622.517093	-1.20826849	-1622.879573	-590.294186	-578.8470055	-5.8	5.7
60	cf4 B3LYP	-436.9936672	-1.45939004	-437.431484	-951.707506	-944.9337155	-18.7	-11.9
61	ccl4 B3LYP	-1878.005003	-1.53391023	-1878.465176	-94.732596	-80.29234553	1.1	15.5
62	O=C=S. Singlet	-511.1748605	-0.88483983	-511.440312	-160.665566	-157.0161207	-22.2	-18.5
63	CS2 B3LYP	-834.035897	-0.98229842	-834.330587	100.222863	105.2638233	-16.5	-11.5
64	COF2 B3LYP	-312.6294492	-1.12769377	-312.967757	-626.551680	-622.0358204	-2.7	1.8
65	sif4 B3LYP	-688.5647757	-1.56031125	-689.032869	-1583.798712	-1575.607152	31.2	39.4
66	sicl4, td	-2129.559737	-1.59635062	-2130.038642	-647.747297	-631.8892771	15.0	30.9
67	nno B3LYP	-184.3668362	-0.85221096	-184.622499	58.965751	59.91093111	-23.0	-22.1
68	clno B3LYP	-589.6806556	-0.92005816	-589.956673	46.491748	50.95509757	-5.4	-0.9

69	nf3 c3v	-353.6527852	-1.24281065	-354.025628	-138.005646	-133.2009813	-5.8	-1.0
70	pf3 c3v	-640.4946475	-1.30148861	-640.885094	-940.755103	-935.9504379	17.8	22.6
71	ozone 1-a1	-225.062843	-1.02348185	-225.369888	150.580501	153.4160408	7.9	10.7
72	f2o B3LYP	-274.316981	-0.97340298	-274.609002	37.787162	41.93545243	13.1	17.2
73	CLF3, C2V	-758.9509117	-1.37924168	-759.364684	-159.819233	-151.4963983	-0.8	7.5
74	CF2=CF2 D2H	-474.9403037	-1.6609177	-475.438579	-699.805610	-692.6642497	-41.2	-34.1
75	cl2c=ccl2 B3LYP	-1916.02393	-1.73227394	-1916.543612	-27.797660	-12.98984041	-15.2	-0.4
76	cf3cn B3LYP	-429.9001638	-1.60163332	-430.380654	-523.980457	-518.4406521	-28.6	-23.1
77	PROPYNE C3V	-116.4047488	-0.64075383	-116.596975	190.320094	191.4228037	5.4	6.5
78	ALLENE D2D	-116.4048007	-0.63454488	-116.595164	193.417593	194.520303	3.0	4.1
79	CYCLOPROPENE C2V	-116.3650481	-0.64394431	-116.558231	291.321782	292.4244917	14.3	15.4
80	PROPENE CS	-117.6394359	-0.66422022	-117.838702	36.700961	37.80367077	16.6	17.7
81	CYCLOPROPANE D3H	-117.6256272	-0.67047821	-117.826771	70.507826	71.61053557	17.4	18.5
82	PROPANE C2V	-118.8566706	-0.69724232	-119.065843	-78.975058	-77.87234791	25.6	26.7
83	TRANS-1,3-BUTADIENE C2H	-155.6504036	-0.85897077	-155.908095	125.233884	126.7041638	15.2	16.7
84	Dimethyl acetylene	-155.6369443	-0.8648022	-155.896385	156.130377	157.6006566	10.5	12.0
85	Methylene cyclopropane.	-155.6175351	-0.86572673	-155.877253	204.956435	206.4267151	4.5	6.0
86	Bicyclo[1.1.0]butane. C2v	-155.6013854	-0.87746719	-155.864626	240.042520	241.5127997	22.9	24.4
87	CYCLOBUTENE b3lyp	-155.6270094	-0.86796329	-155.887398	180.682931	182.1532115	24.2	25.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8494792	-0.89711151	-157.118613	55.686687	57.1569671	27.2	28.7
89	Isobutene. Single	-156.8671892	-0.89283274	-157.135039	7.770186	9.240465759	24.5	26.0
90	Trans butane	-158.0795145	-0.92325515	-158.356491	-91.779258	-90.3089784	33.7	35.2
91	isobutane B3LYP/6-31G*	-158.0804974	-0.92645303	-158.358433	-98.173018	-96.70273777	36.1	37.6
92	Spiropentane. D2d	-194.8343929	-1.09811533	-195.163827	204.781832	206.6196822	19.4	21.3
93	Benzene B3LYP	-231.7545321	-1.26163112	-232.133021	84.091760	86.29717984	1.7	3.9
94	DIFLUOROMETHANE C2V	-238.6857777	-0.85371702	-238.941893	-456.759653	-453.1889735	-6.1	-2.6
95	HCF3 TRI-FLUOROMETHANE	-337.8415223	-1.15773254	-338.188842	-709.093519	-703.9212841	-12.0	-6.9
96	CH2CL2 C2V	-959.2193999	-0.87634876	-959.482304	-90.141538	-82.73762758	5.3	12.7
97	chcl3 B3LYP/6-31G*	-1418.616052	-1.20173866	-1418.976574	-98.914568	-87.99248757	4.4	15.4
98	METHYLAMINE b3lyp	-95.65753402	-0.51503585	-95.812045	-9.089866	-8.722296325	13.9	14.3
99	Acetonitrile. CH3-CN.	-132.4960735	-0.68295998	-132.700961	71.355043	72.09018272	-4.0	-3.2
100	NITRO METHANE	-244.6055703	-1.12957034	-244.944441	-80.678160	-78.42022957	-6.2	-3.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6017503	-1.11917561	-244.937503	-66.189603	-63.93167299	0.3	2.6
102	Methylsilane. CH3-SiH3.	-330.9336026	-0.56513332	-331.103143	-5.749960	-3.597050397	23.5	25.7
103	Formic Acid.	-189.4723543	-0.81676481	-189.717384	-383.528231	-381.2703013	-4.9	-2.6
104	Methyl formate.	-228.6827074	-1.03953431	-228.994568	-361.584388	-358.9588883	-5.9	-3.3
105	acetamide ch3cohn2	-208.8422333	-1.00921363	-209.144997	-234.947219	-233.2668986	3.5	5.2

106	Aziridine. (cyclic	-133.6442959	-0.71545707	-133.858933	138.470937	139.2060765	12.1	12.8
107	Cyanogen. NCCN.	-185.3248288	-0.91324504	-185.598802	283.038424	283.773564	-23.6	-22.9
108	DIMETHYLAMINE b3lyp	-134.8717044	-0.73943724	-135.093536	0.855686	1.590825894	19.3	20.0
109	TRANS ETHYLAMINE	-134.8832349	-0.74059964	-135.105415	-29.395745	-28.66060519	17.9	18.6
110	KETENE B3LYP	-152.3369343	-0.71463774	-152.551326	-61.847883	-60.1675628	-14.6	-12.9
111	OXIRANE B3LYP	-153.5056169	-0.74605351	-153.729433	-45.437625	-43.75730461	7.3	9.0
112	Acetaldehyde B3LYP	-153.5514416	-0.73831002	-153.772935	-162.770492	-161.0901723	3.3	5.0
113	Glyoxal, O=CH-CH=O.	-227.4554132	-1.00698522	-227.757509	-223.059675	-220.4341749	-10.9	-8.3
114	ETHANOL TRANS	-154.7466589	-0.76887912	-154.977323	-216.617666	-214.9373463	18.5	20.2
115	DIMETHYL ETHER,	-154.7299108	-0.76589924	-154.959681	-171.141344	-169.4610241	13.0	14.6
116	Thiooxirane. (cyclic	-476.4168763	-0.83065363	-476.666072	93.697498	96.76933283	11.7	14.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.7200401	-1.1726328	-553.071830	-120.745518	-116.7285031	30.7	34.7
118	Thioethanol. CH3-CH2-SH.	-477.634689	-0.84949685	-477.889538	-20.333215	-17.26137951	26.1	29.2
119	ch3sch3 B3LYP	-477.6326688	-0.85137708	-477.888082	-13.984333	-10.9124978	23.3	26.3
120	Vinyl fluoride,	-177.5491644	-0.74429159	-177.772452	-141.954738	-139.6180433	-3.0	-0.7
121	Ethyl chloride.	-539.0440254	-0.78473151	-539.279445	-98.066314	-93.81300408	14.1	18.3
122	Vinyl chloride,	-537.8214175	-0.75601717	-538.048223	27.586374	31.83968355	4.6	8.8
123	h2c=chcn B3LYP	-170.4981436	-0.8784613	-170.761682	182.531141	183.6338515	1.8	2.9
124	ACETONE B3LYP	-192.786093	-0.96376213	-193.075222	-206.579968	-204.532078	10.6	12.6
125	CH3COOH ACETIC	-228.7084939	-1.03912006	-229.020230	-429.414824	-426.789324	3.2	5.8
126	CH3CFO HCCO	-252.7186543	-1.04762114	-253.032941	-446.339275	-443.0574001	-4.1	-0.8
127	ch3c(o)cl hcco	-612.9773719	-1.06357699	-613.296445	-244.999685	-239.8011952	-2.3	2.9
128	ch3ch2ch2cl B3LYP	-578.2669872	-1.01099889	-578.570287	-111.286144	-106.6652644	20.5	25.1
129	Isopropyl alcohol,	-193.9744274	-0.99710437	-194.273559	-245.784918	-243.7370275	27.0	29.1
130	Methyl ethyl	-193.9579723	-0.99131881	-194.255368	-197.476222	-195.4283316	18.8	20.9
131	Trimethyl Amine.	-174.0881839	-0.96864637	-174.378778	-0.352941	0.749768662	23.5	24.6
132	FURAN B3LYP	-229.5889531	-1.14673172	-229.932973	-35.561290	-33.14582982	-0.8	1.6
133	Thiophene b3lyp	-552.4897141	-1.23830394	-552.861205	123.298715	127.1056903	8.2	12.0
134	PYROLE PLANAR	-209.7421572	-1.11923951	-210.077929	107.094709	108.5649891	-1.3	0.2
135	C2v Pyridine	-247.7807801	-1.30551129	-248.172434	131.290702	133.1285524	-9.3	-7.5
136	H2 B3LYP/6-31G*	-1.15875519	-0.03470811	-1.169168	8.175924	8.175923554	8.2	8.2
137	SH b3lyp/6-31G*	-398.555385	-0.35845661	-398.662922	147.896863	150.2335581	4.8	7.1
138	CCH B3LYP	-76.45781528	-0.37989105	-76.571783	577.362359	578.0974987	12.1	12.8
139	C2H3 CS,2-A'	-77.73697897	-0.40166046	-77.857477	303.376086	304.1112261	3.8	4.5
140	ch3co hcco	-152.9103521	-0.71622618	-153.125220	-15.679957	-13.99963739	-5.6	-4.0
141	H2COH C1	-114.8670825	-0.51168841	-115.020589	-12.808366	-11.4956163	4.3	5.7
142	ch3o CS,	-114.8605775	-0.48488964	-115.006044	21.805283	23.11803314	4.7	6.0

143	ch3ch2o 2A"	-154.0884787	-0.70979445	-154.301417	-4.280912	-2.600592271	11.2	12.9
144	ch3s 2-A'	-437.7793977	-0.58685688	-437.955455	131.356466	134.0607309	6.7	9.4
145	c2h5 staggered	-78.9751637	-0.43305287	-79.105080	132.703396	133.438536	11.8	12.5
146	(ch3)2ch Cs	-118.2026676	-0.66001824	-118.400673	107.034897	108.1376066	17.1	18.2
147	TERT-BUTYL RADICAL	-157.430307	-0.88900853	-157.697010	79.153216	80.62349627	27.7	29.2
148	NO2 RADICAL	-204.7606681	-0.90237242	-205.031380	11.563073	13.45343258	-21.5	-19.6

MAD	**11.4**	**12.3**
LD	**-41.2**	**39.4**

Table S5.43b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498754	0.000000	-0.498754
2	li	-7.467179	-0.014551	-7.471544
3	be	-14.634748	-0.053113	-14.650682
4	b	-24.613143	-0.076985	-24.636238
5	c	-37.795424	-0.103717	-37.826539
6	n	-54.527758	-0.134402	-54.568079
7	o	-74.988915	-0.191468	-75.046356
8	f	-99.633541	-0.254216	-99.709806
9	na	-162.138030	-0.171103	-162.189361
10	al	-242.217667	-0.219546	-242.283531
11	si	-289.217500	-0.249488	-289.292347
12	p	-341.099078	-0.278433	-341.182608
13	s	-397.931571	-0.319599	-398.027451
14	cl	-459.948128	-0.290456	-460.035265

Table S5.44a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04483507	-0.04657558	-8.059273	147.445926	147.445926	8.1	8.1
2	BERYLLIUM HYDRIDE	-15.21997273	-0.05485864	-15.236979	320.222501	320.2225014	-21.6	-21.6
3	DOUBLET CH	-38.41237801	-0.14425952	-38.457098	600.147794	600.5153636	3.9	4.3
4	CH2 3-B1	-39.07515086	-0.16327805	-39.125767	395.553709	395.9212792	3.5	3.9
5	Singlet methylene,	-39.05122185	-0.18344186	-39.108089	440.355842	440.7234122	10.2	10.6
6	Methyl radical,	-39.74613843	-0.20801926	-39.810624	152.378556	152.7461265	5.9	6.3
7	ch4 //b3lyp/6-31G*	-40.4097684	-0.24961561	-40.487149	-63.616090	-63.24852012	11.3	11.6
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14055572	-0.18731362	-55.198623	359.053533	359.053533	2.6	2.6
9	NH2,2-B-1, //b3lyp/6-31G*	-55.7804072	-0.24071836	-55.855030	188.755423	188.7554227	0.1	0.1
10	AMMONIA, //b3lyp/6-31G*	-56.4447672	-0.2946028	-56.536094	-37.602960	-37.60295953	8.4	8.4
11	OH RADICAL	-75.63363823	-0.2580232	-75.713625	41.025559	41.9707395	1.7	2.6
12	Water //b3lyp/6-31G*	-76.30922849	-0.32658789	-76.410471	-232.032952	-231.0877723	9.8	10.7
13	HYDROGEN FLUORIDE,	-100.3266162	-0.33728056	-100.431173	-268.340576	-266.7390211	4.0	5.6
14	SIH2 singlet	-290.4324281	-0.30526756	-290.527061	276.866807	278.6521468	4.1	5.9
15	SIH2 3B1	-290.4070319	-0.28272357	-290.494676	362.903935	364.6892749	2.2	4.0
16	SIH3 c3v	-291.0472322	-0.31066264	-291.143538	205.075788	206.8611283	4.7	6.4
17	SIH4 //b3lyp/6-31G*	-291.6890919	-0.33780852	-291.793813	45.479286	47.26462588	11.2	13.0
18	ph2 doublet	-342.313166	-0.34465545	-342.420009	141.557676	141.5576756	3.1	3.1
19	PH3 c3v	-342.9398196	-0.37571512	-343.056291	20.198443	20.19844344	14.8	14.8
20	SH2 //b3lyp/6-31G*	-399.185516	-0.39710021	-399.308617	-9.322066	-6.985370537	11.2	13.5
21	HCL //b3lyp/6-31G*	-460.5943527	-0.33549505	-460.698356	-88.878400	-85.36023	3.6	7.1
22	DILITHIUM //b3lyp/6-31G*	-14.95761676	-0.05775623	-14.975521	230.682994	230.682994	14.8	14.8
23	Lithium Fluoride,	-107.2879698	-0.36622356	-107.401499	-340.594042	-338.9924871	-5.5	-3.9
24	ACETYLENE //b3lyp/6-31g*	-77.16602321	-0.41728638	-77.295382	228.595240	229.3303801	1.8	2.6
25	ETHYLENE //b3lyp/6-31g*	-78.40644558	-0.43832759	-78.542327	61.914118	62.64925836	9.6	10.3
26	ETHANE //b3lyp/6-31g*	-79.62817406	-0.47174463	-79.774415	-67.066444	-66.33130408	17.0	17.8
27	CYANO RADICAL,	-92.54134593	-0.45197291	-92.681458	442.167398	442.534968	3.3	3.6
28	HYDROGEN CYANIDE	-93.25108506	-0.46172718	-93.394220	122.583346	122.9509164	-9.2	-8.8
29	CARBON MONOXIDE	-113.1414461	-0.47253678	-113.287933	-118.332038	-117.0192877	-7.9	-6.6
30	HCO BENT	-113.6662009	-0.49490831	-113.819622	29.249521	30.5622711	-12.6	-11.3
31	H2CO //b3lyp/6-31g*	-114.3077081	-0.51444146	-114.467185	-113.763020	-112.4502703	-5.0	-3.7

32	METHANOL //b3lyp/6-31g*	-115.5125435	-0.54406384	-115.681203	-192.372224	-191.0594742	8.5	9.8
33	Nitrogen N2,	-109.3481151	-0.49541032	-109.501692	-6.410324	-6.410324256	-6.4	-6.4
34	H2NNH2 //b3lyp/6-31g*	-111.6529457	-0.55873282	-111.826153	104.332478	104.3324775	8.9	8.9
35	NO radical,	-129.6937709	-0.53730876	-129.860337	80.535004	81.48018423	-9.8	-8.9
36	O2 //b3lyp/6-31g*	-150.1017215	-0.60157428	-150.288210	-13.504873	-11.61451293	-13.5	-11.6
37	HYDROGEN PEROXIDE	-151.3166109	-0.63138896	-151.512342	-122.379930	-120.4895698	13.6	15.5
38	F2 //b3lyp/6-31g*	-199.2700219	-0.66005764	-199.474640	12.804390	16.00750038	12.8	16.0
39	CO2 D*H	-188.3024029	-0.79444895	-188.548682	-422.381180	-420.1232495	-29.1	-26.8
40	na2 //b3lyp/6-31G*	-324.2855873	-0.37043576	-324.400422	143.883445	143.8834446	1.6	1.6
41	SI2 3-SGG	-578.5240093	-0.55739341	-578.696801	588.769402	592.3400824	3.4	7.0
42	P2 //b3lyp/6-31g*	-682.3240339	-0.70747555	-682.543351	151.243690	151.2436898	7.7	7.7
43	S2 //b3lyp/6-31g*	-795.9779266	-0.75482119	-796.211921	125.229794	129.9031841	-3.2	1.5
44	CL2 //b3lyp/6-31g*	-919.9507849	-0.64957695	-920.152154	7.030666	14.06700606	7.0	14.1
45	Sodium Chloride	-622.2146545	-0.5074067	-622.371951	-175.791564	-172.2733938	6.6	10.1
46	SIO //b3lyp/6-31g*	-364.4507156	-0.61442187	-364.641186	-101.787075	-99.05655474	1.1	3.9
47	Carbon monosulfide,	-435.9443579	-0.57409567	-436.122328	282.848034	285.5522991	2.9	5.6
48	OS //b3lyp/6-31g*	-473.0600193	-0.68500854	-473.272372	-2.871509	0.410365855	-7.9	-4.6
49	CLO 2-PI	-534.9904885	-0.60257204	-535.177286	107.905020	112.3683697	6.7	11.1
50	CLF 1-SG	-559.6357667	-0.65201004	-559.837890	-54.572683	-49.45295828	0.7	5.8
51	si2h6 //b3lyp/6-31g*	-582.2055948	-0.65649345	-582.409108	102.058150	105.62883	22.1	25.7
52	Methyl chloride,	-499.8075734	-0.55852069	-499.980715	-76.279131	-72.39339075	5.7	9.6
53	H3C-SH METHANETHIOL	-438.4016066	-0.62262412	-438.594620	-6.343531	-3.639265666	16.7	19.4
54	HOCl //b3lyp/6-31g*	-535.6367076	-0.64343032	-535.836171	-69.676667	-65.21331705	4.8	9.3
55	SO2 //b3lyp/6-31G*	-548.2059736	-1.03017708	-548.525329	-291.611347	-287.3842915	5.5	9.7
56	BF3 PLANAR	-324.1890567	-1.06822418	-324.520206	-1156.038646	-1151.102706	-20.5	-15.6
57	bcl3 B3LYP	-1404.908509	-1.10618337	-1405.251426	-422.853443	-412.1676576	-19.9	-9.2
58	ALf3 B3LYP	-541.7114251	-1.20687247	-542.085556	-1202.818964	-1197.121629	6.4	12.1
59	alcl3 B3LYP	-1622.490616	-1.2082529	-1622.865175	-591.357544	-579.910364	-6.9	4.6
60	cf4 B3LYP	-436.9777526	-1.45938256	-437.430161	-956.784894	-950.0111041	-23.8	-17.0
61	ccl4 B3LYP	-1877.974485	-1.53388538	-1878.449990	-98.489364	-84.04911388	-2.7	11.8
62	O=C=S. Singlet	-511.1633133	-0.88481844	-511.437607	-164.944282	-161.2948367	-26.5	-22.8
63	CS2 B3LYP	-834.0207029	-0.9822683	-834.325206	96.553937	101.5948973	-20.2	-15.1
64	COF2 B3LYP	-312.6175423	-1.12768435	-312.967124	-631.649645	-627.133785	-7.8	-3.3
65	sif4 B3LYP	-688.5452288	-1.56030751	-689.028924	-1587.927405	-1579.735845	27.1	35.3
66	sicl4, td	-2129.525588	-1.5963253	-2130.020448	-649.543074	-633.6850535	13.2	29.1
67	nno B3LYP	-184.3589621	-0.85218858	-184.623141	52.472069	53.41724862	-29.5	-28.6
68	clno B3LYP	-589.6682286	-0.92003963	-589.953441	41.157813	45.62116301	-10.7	-6.3

69	nf3 c3v	-353.6400069	-1.24280496	-354.025276	-143.923585	-139.11892	-11.7	-6.9
70	pf3 c3v	-640.4781287	-1.30148533	-640.881589	-944.446666	-939.6420007	14.1	18.9
71	ozone 1-a1	-225.054066	-1.02345929	-225.371338	141.521722	144.3572618	-1.2	1.7
72	f2o B3LYP	-274.3072546	-0.97340129	-274.609009	32.477485	36.62577513	7.8	11.9
73	CLF3, C2V	-758.9334831	-1.37923981	-759.361047	-166.122266	-157.7994306	-7.1	1.2
74	CF2=CF2 D2H	-474.9223514	-1.66090818	-475.437233	-706.290858	-699.1494983	-47.7	-40.6
75	cl2c=ccl2 B3LYP	-1915.991328	-1.73224352	-1916.528323	-32.753840	-17.94602039	-20.2	-5.4
76	cf3cn B3LYP	-429.883226	-1.60161007	-430.379725	-531.321432	-525.7816267	-35.9	-30.4
77	PROPYNE C3V	-116.3977164	-0.64073026	-116.596343	187.573596	188.6763062	2.6	3.7
78	ALLENE D2D	-116.3977648	-0.63452323	-116.594467	190.841686	191.9443955	0.5	1.6
79	CYCLOPROPENE C2V	-116.3579599	-0.6439269	-116.557577	288.633217	289.7359275	11.7	12.8
80	PROPENE CS	-117.631865	-0.6642008	-117.837767	34.749070	35.85177981	14.7	15.8
81	CYCLOPROPANE D3H	-117.6179873	-0.67046324	-117.825831	68.569116	69.6718262	15.4	16.5
82	PROPANE C2V	-118.8485651	-0.6972248	-119.064705	-80.392029	-79.28931949	24.2	25.3
83	TRANS-1,3-BUTADIENE C2H	-155.6407832	-0.85894344	-155.907056	122.087430	123.5577105	12.0	13.5
84	Dimethyl acetylene	-155.6273278	-0.86477334	-155.895408	152.821877	154.2921574	7.2	8.7
85	Methylene cyclopropane.	-155.6078522	-0.86570377	-155.876220	201.793062	203.2633423	1.4	2.8
86	Bicyclo[1.1.0]butane. C2v	-155.591634	-0.87744762	-155.863643	236.747857	238.2181374	19.6	21.1
87	CYCLOBUTENE b3lyp	-155.6173019	-0.86794014	-155.886363	177.525632	178.9959122	21.0	22.5
88	CYCLOBUTANE b3lyp/6-31G*	-156.8392374	-0.89709018	-157.117335	53.165425	54.6357047	24.7	26.2
89	Isobutene. Single	-156.8570243	-0.89280768	-157.133795	5.162371	6.632651127	21.9	23.4
90	Trans butane	-158.0688238	-0.92323139	-158.355026	-93.806305	-92.33602482	31.7	33.2
91	isobutane B3LYP/6-31G*	-158.0697975	-0.92642935	-158.356991	-100.259988	-98.78970755	34.0	35.5
92	Spiropentane. D2d	-194.822056	-1.09809076	-195.162464	201.017855	202.8557047	15.7	17.5
93	Benzene B3LYP	-231.7406427	-1.26159367	-232.131737	78.652539	80.85795906	-3.8	-1.6
94	DIFLUOROMETHANE C2V	-238.6763696	-0.85371706	-238.941022	-459.482874	-455.9121943	-8.9	-5.3
95	HCF3 TRI-FLUOROMETHANE	-337.8288627	-1.1577302	-338.187759	-713.030378	-707.8581434	-16.0	-10.8
96	CH2CL2 C2V	-959.2026853	-0.87633554	-959.474349	-91.803779	-84.39986918	3.6	11.0
97	chcl3 B3LYP/6-31G*	-1418.592439	-1.20172001	-1418.964972	-101.543197	-90.62111664	1.8	12.7
98	METHYLAMINE b3lyp	-95.65178632	-0.51502943	-95.811445	-10.515385	-10.14781549	12.5	12.9
99	Acetonitrile. CH3-CN.	-132.4888433	-0.6829392	-132.700554	67.956064	68.69120386	-7.4	-6.6
100	NITRO METHANE	-244.5943469	-1.12955034	-244.944508	-87.350476	-85.09254609	-12.9	-10.6
101	Methyl-nitrite. CH3-O-N=O.	-244.5905637	-1.11915459	-244.937502	-72.684689	-70.42675908	-6.2	-3.9
102	Methylsilane. CH3-SiH3.	-330.9245272	-0.56511942	-331.099714	-5.621301	-3.468391183	23.7	25.8
103	Formic Acid.	-189.4638969	-0.81675894	-189.717092	-387.730801	-385.4728707	-9.1	-6.8
104	Methyl formate.	-228.6716794	-1.03951897	-228.993930	-366.347897	-363.7223973	-10.7	-8.1
105	acetamide ch3cohn2	-208.8313921	-1.00919949	-209.144244	-239.186573	-237.5062528	-0.7	1.0

106	Aziridine. (cyclic	-133.6364498	-0.71544463	-133.858238	135.829083	136.5642228	9.5	10.2
107	Cyanogen. NCCN.	-185.3159061	-0.91321233	-185.599002	276.516087	277.2512268	-30.2	-29.4
108	DIMETHYLAMINE b3lyp	-134.8633757	-0.73942371	-135.092597	-1.147840	-0.412699982	17.3	18.0
109	TRANS ETHYLAMINE	-134.8749025	-0.74058689	-135.104484	-31.420868	-30.6857279	15.9	16.6
110	KETENE B3LYP	-152.3294626	-0.71462251	-152.550996	-65.668709	-63.98838942	-18.4	-16.7
111	OXIRANE B3LYP	-153.4975688	-0.74604352	-153.728842	-48.574041	-46.89372139	4.1	5.8
112	Acetaldehyde B3LYP	-153.5434469	-0.73829856	-153.772319	-165.842583	-164.1622628	0.3	1.9
113	Glyoxal, O=CH-CH=O.	-227.4449622	-1.00697176	-227.757123	-228.484972	-225.8594724	-16.4	-13.7
114	ETHANOL TRANS	-154.7381124	-0.76886985	-154.976462	-219.045459	-217.3651388	16.1	17.8
115	DIMETHYL ETHER,	-154.7213775	-0.76588803	-154.958803	-173.523899	-171.8435787	10.6	12.3
116	Thiooxirane. (cyclic	-476.4051814	-0.83063662	-476.662679	91.506606	94.57844078	9.5	12.6
117	Dimethylsulfoxide. (CH3)2SO.	-552.7048339	-1.17261469	-553.068344	-124.445095	-120.4280805	27.0	31.0
118	Thioethanol. CH3-CH2-SH.	-477.6225201	-0.84947912	-477.885859	-21.773684	-18.70184853	24.7	27.7
119	ch3sch3 B3LYP	-477.6205072	-0.85135937	-477.884429	-15.493428	-12.42159346	21.7	24.8
120	Vinyl fluoride,	-177.5409388	-0.74428141	-177.771666	-144.599472	-142.2627769	-5.7	-3.4
121	Ethyl chloride.	-539.0316168	-0.78471638	-539.274879	-99.555601	-95.3022906	12.6	16.8
122	Vinyl chloride,	-537.8095368	-0.75600017	-538.043897	25.466293	29.71960254	2.5	6.7
123	h2c=chcn B3LYP	-170.4888709	-0.87843286	-170.761185	177.899228	179.0019381	-2.8	-1.7
124	ACETONE B3LYP	-192.7755062	-0.96374376	-193.074267	-210.228803	-208.1809128	6.9	9.0
125	CH3COOH ACETIC	-228.6974461	-1.03910736	-229.019569	-434.117489	-431.4919894	-1.5	1.1
126	CH3CFO HCCO	-252.7074092	-1.04760808	-253.032168	-450.767694	-447.4858192	-8.5	-5.2
127	ch3c(o)cl hcco	-612.9624858	-1.06355817	-613.292189	-249.052216	-243.8537259	-6.4	-1.2
128	ch3ch2ch2cl B3LYP	-578.2519943	-1.01097763	-578.565397	-113.394589	-108.7737089	18.4	23.0
129	Isopropyl alcohol,	-193.9632872	-0.99708827	-194.272385	-248.858180	-246.81029	23.9	26.0
130	Methyl ethyl	-193.9468535	-0.99130094	-194.254157	-200.452277	-198.4043868	15.9	17.9
131	Trimethyl Amine.	-174.0772611	-0.96862628	-174.377535	-3.026912	-1.924202269	20.8	21.9
132	FURAN B3LYP	-229.5766998	-1.14670585	-229.932179	-41.101226	-38.68576557	-6.4	-4.0
133	Thiophene b3lyp	-552.4738173	-1.23827151	-552.857681	118.512423	122.3193983	3.5	7.3
134	PYROLE PLANAR	-209.7300952	-1.11921204	-210.077051	101.995052	103.4653321	-6.4	-4.9
135	C2v Pyridine	-247.766684	-1.30547574	-248.171381	125.179088	127.0169376	-15.4	-13.6
136	H2 B3LYP/6-31G*	-1.15837256	-0.0347084	-1.169132	8.269021	8.269021158	8.3	8.3
137	SH b3lyp/6-31G*	-398.5487069	-0.3584586	-398.659829	147.853900	150.190595	4.8	7.1
138	CCH B3LYP	-76.45376184	-0.37987135	-76.571522	575.109244	575.8443836	9.9	10.6
139	C2H3 CS,2-A'	-77.73235388	-0.40163971	-77.856862	302.053137	302.7882768	2.5	3.2
140	ch3co hcco	-152.9026884	-0.71620522	-153.124712	-19.033414	-17.35309376	-9.0	-7.3
141	H2COH C1	-114.8614539	-0.51167976	-115.020075	-14.676412	-13.36366218	2.5	3.8
142	ch3o CS,	-114.8549819	-0.48487462	-115.005293	20.559435	21.87218456	3.4	4.7

143	ch3ch2o 2A"	-154.0802989	-0.70977074	-154.300328	-6.108665	-4.428344861	9.4	11.1
144	ch3s 2-A'	-437.7701422	-0.58684918	-437.952065	130.623127	133.3273922	5.9	8.6
145	c2h5 staggered	-78.96998945	-0.43304565	-79.104234	131.987046	132.7221864	11.1	11.8
146	(ch3)2ch Cs	-118.1949018	-0.6600012	-118.399502	105.702918	106.8056277	15.7	16.8
147	TERT-BUTYL RADICAL	-157.419947	-0.88898128	-157.695531	77.159666	78.62994624	25.7	27.2
148	NO2 RADICAL	-204.7523488	-0.902351	-205.032078	4.701197	6.591556792	-28.4	-26.5

MAD	**11.4**	**12.0**
LD	**-47.7**	**-40.6**

Table S5.44b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498754	0.000000	-0.498754
2	li	-7.466642	-0.014550	-7.471153
3	be	-14.633799	-0.053108	-14.650263
4	b	-24.611878	-0.076989	-24.635745
5	c	-37.793826	-0.103723	-37.825980
6	n	-54.525830	-0.134406	-54.567496
7	o	-74.986331	-0.191479	-75.045689
8	f	-99.630321	-0.254226	-99.709131
9	na	-162.133939	-0.171101	-162.186980
10	al	-242.212711	-0.219547	-242.280770
11	si	-289.212185	-0.249490	-289.289527
12	p	-341.093408	-0.278428	-341.179720
13	s	-397.925265	-0.319602	-398.024341
14	cl	-459.941208	-0.290460	-460.031250

Table S5.45a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 32%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04394687	-0.04657676	-8.058851	147.526247	147.5262472	8.2	8.2
2	BERYLLIUM HYDRIDE	-15.21889202	-0.05485135	-15.236444	320.524427	320.5244268	-21.3	-21.3
3	DOUBLET CH	-38.41040066	-0.14426361	-38.456565	600.080062	600.4476318	3.9	4.2
4	CH2 3-B1	-39.07299943	-0.16327668	-39.125248	395.448280	395.8158501	3.4	3.8
5	Singlet methylene,	-39.04889445	-0.18343821	-39.107595	440.184937	440.5525071	10.1	10.4
6	Methyl radical,	-39.74355303	-0.20802298	-39.810120	152.233559	152.6011288	5.8	6.2
7	ch4 //b3lyp/6-31G*	-40.40682255	-0.24960972	-40.486698	-63.898765	-63.53119458	11.0	11.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13817546	-0.18732399	-55.198119	358.846184	358.8461839	2.4	2.4
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77761118	-0.24072532	-55.854643	188.240375	188.240375	-0.5	-0.5
10	AMMONIA, //b3lyp/6-31G*	-56.44158797	-0.29460374	-56.535861	-38.521568	-38.52156763	7.5	7.5
11	OH RADICAL	-75.63062782	-0.25803332	-75.713198	40.397366	41.34254583	1.1	2.0
12	Water //b3lyp/6-31G*	-76.30582431	-0.32659411	-76.410334	-233.424192	-232.4790121	8.4	9.4
13	HYDROGEN FLUORIDE,	-100.3229926	-0.33728915	-100.430925	-269.459348	-267.8577934	2.9	4.5
14	SIH2 singlet	-290.4264544	-0.3052598	-290.524137	277.139002	278.9243424	4.3	6.1
15	SIH2 3B1	-290.4012544	-0.28269745	-290.491718	363.268220	365.0535601	2.6	4.4
16	SIH3 c3v	-291.0410784	-0.31064792	-291.140486	205.684826	207.4701661	5.3	7.1
17	SIH4 //b3lyp/6-31G*	-291.6825999	-0.33779965	-291.790696	46.258743	48.04408275	11.9	13.7
18	ph2 doublet	-342.306735	-0.34465539	-342.417025	141.811205	141.8112054	3.3	3.3
19	PH3 c3v	-342.9330608	-0.37570613	-343.053287	20.504669	20.50466942	15.1	15.1
20	SH2 //b3lyp/6-31G*	-399.178498	-0.39709456	-399.305568	-9.480485	-7.143789794	11.0	13.4
21	HCL //b3lyp/6-31G*	-460.5870819	-0.33549279	-460.694440	-89.135050	-85.61687972	3.3	6.8
22	DILITHIUM //b3lyp/6-31G*	-14.95627923	-0.05775216	-14.974760	230.626079	230.6260792	14.7	14.7
23	Lithium Fluoride,	-107.2837929	-0.36623804	-107.400989	-342.052892	-340.451337	-6.9	-5.3
24	ACETYLENE //b3lyp/6-31g*	-77.16157546	-0.41726802	-77.295101	226.395790	227.1309305	-0.4	0.4
25	ETHYLENE //b3lyp/6-31g*	-78.40146089	-0.43831361	-78.541721	60.568288	61.30342785	8.3	9.0
26	ETHANE //b3lyp/6-31g*	-79.62265303	-0.47173307	-79.773608	-67.883511	-67.1483715	16.2	17.0
27	CYANO RADICAL,	-92.53707964	-0.45188703	-92.681683	438.575762	438.9433321	-0.3	0.0
28	HYDROGEN CYANIDE	-93.24643927	-0.4617121	-93.394187	119.672506	120.0400761	-12.1	-11.8
29	CARBON MONOXIDE	-113.1365974	-0.47253063	-113.287807	-121.220401	-119.9076512	-10.8	-9.5
30	HCO BENT	-113.661119	-0.49489574	-113.819486	26.391401	27.70415102	-15.4	-14.1
31	H2CO //b3lyp/6-31g*	-114.3023014	-0.51443642	-114.466921	-116.287652	-114.9749023	-7.5	-6.2

32	METHANOL //b3lyp/6-31g*	-115.5065822	-0.54406093	-115.680682	-194.220332	-192.9075815	6.6	7.9
33	Nitrogen N2,	-109.3432778	-0.4953951	-109.501804	-9.764358	-9.764357973	-9.8	-9.8
34	H2NNH2 //b3lyp/6-31g*	-111.6469773	-0.55873193	-111.825771	102.273733	102.2737327	6.9	6.9
35	NO radical,	-129.6884907	-0.53729924	-129.860426	77.019939	77.96511863	-13.4	-12.4
36	O2 //b3lyp/6-31g*	-150.095999	-0.60157336	-150.288502	-17.772282	-15.88192239	-17.8	-15.9
37	HYDROGEN PEROXIDE	-151.3102478	-0.63139382	-151.512294	-125.752979	-123.8626195	10.2	12.1
38	F2 //b3lyp/6-31g*	-199.2632652	-0.66006138	-199.474485	9.671250	12.87435996	9.7	12.9
39	CO2 D*H	-188.294492	-0.79443576	-188.548711	-427.424671	-425.166741	-34.1	-31.9
40	na2 //b3lyp/6-31G*	-324.2771607	-0.37043022	-324.395698	143.784941	143.7849406	1.5	1.5
41	SI2 3-SGG	-578.5130293	-0.55737562	-578.691389	588.171080	591.74176	2.8	6.4
42	P2 //b3lyp/6-31g*	-682.3118916	-0.70745227	-682.538276	149.403565	149.4035648	5.9	5.9
43	S2 //b3lyp/6-31g*	-795.9648581	-0.75481215	-796.206398	123.404840	128.0782298	-5.0	-0.4
44	CL2 //b3lyp/6-31g*	-919.9366564	-0.64956936	-920.144519	5.997685	13.0340254	6.0	13.0
45	Sodium Chloride	-622.2033257	-0.50740905	-622.365697	-176.161828	-172.6436578	6.3	9.8
46	SIO //b3lyp/6-31g*	-364.4421901	-0.61443026	-364.638808	-104.694798	-101.9642781	-1.8	1.0
47	Carbon monosulfide,	-435.9358757	-0.57407581	-436.119580	280.430632	283.1348967	0.5	3.2
48	OS //b3lyp/6-31g*	-473.0506144	-0.6850002	-473.269814	-6.068967	-2.787091706	-11.1	-7.8
49	CLO 2-PI	-534.9805728	-0.60253081	-535.173383	105.864329	110.3276786	4.6	9.1
50	CLF 1-SG	-559.6253044	-0.65200948	-559.833947	-56.531543	-51.41181758	-1.3	3.8
51	si2h6 //b3lyp/6-31g*	-582.1929784	-0.65647683	-582.403051	103.153105	106.7237851	23.2	26.8
52	Methyl chloride,	-499.7977486	-0.5585118	-499.976472	-77.148542	-73.26280197	4.9	8.7
53	H3C-SH METHANETHIOL	-438.3920218	-0.62261254	-438.591258	-7.147049	-4.442783926	15.9	18.6
54	HOCl //b3lyp/6-31g*	-535.6264556	-0.64342821	-535.832353	-71.940266	-67.47691629	2.5	7.0
55	SO2 //b3lyp/6-31G*	-548.1934279	-1.03016697	-548.523081	-297.372539	-293.1454839	-0.3	3.9
56	BF3 PLANAR	-324.177122	-1.0682249	-324.518954	-1159.356612	-1154.420672	-23.8	-18.9
57	bcl3 B3LYP	-1404.885623	-1.10616515	-1405.239596	-424.707212	-414.0214273	-21.8	-11.1
58	ALf3 B3LYP	-541.6958967	-1.20688038	-542.082098	-1206.298961	-1200.601626	2.9	8.6
59	alcl3 B3LYP	-1622.46414	-1.20823731	-1622.850776	-592.419142	-580.9719618	-7.9	3.5
60	cf4 B3LYP	-436.9618381	-1.45937509	-437.428838	-961.859309	-955.0855195	-28.8	-22.1
61	ccl4 B3LYP	-1877.943968	-1.53386053	-1878.434803	-102.243427	-87.80317744	-6.4	8.0
62	O=C=S. Singlet	-511.1517661	-0.88479704	-511.434901	-169.220619	-165.5711739	-30.7	-27.1
63	CS2 B3LYP	-834.0055088	-0.98223818	-834.319825	92.887433	97.92839313	-23.8	-18.8
64	COF2 B3LYP	-312.6056355	-1.12767494	-312.966491	-636.744976	-632.2291157	-12.9	-8.4
65	sif4 B3LYP	-688.5256821	-1.56030376	-689.024979	-1592.053438	-1583.861878	23.0	31.2
66	sicl4, td	-2129.491438	-1.59629998	-2130.002254	-651.336253	-635.4782332	11.4	27.3
67	nno B3LYP	-184.3510881	-0.8521662	-184.623781	45.980596	46.92577575	-36.0	-35.1
68	clno B3LYP	-589.6558017	-0.92002111	-589.950208	35.825917	40.28926689	-16.1	-11.6

69	nf3 c3v	-353.6272287	-1.24279928	-354.024924	-149.839316	-145.0346511	-17.6	-12.8
70	pf3 c3v	-640.46161	-1.30148207	-640.878084	-948.136597	-943.3319325	10.4	15.2
71	ozone 1-a1	-225.0452892	-1.02343674	-225.372789	132.466071	135.3016114	-10.2	-7.4
72	f2o B3LYP	-274.2975283	-0.97339961	-274.609016	27.169675	31.31796456	2.5	6.6
73	CLF3, C2V	-758.9160545	-1.37923795	-759.357411	-172.423252	-164.1004167	-13.4	-5.1
74	CF2=CF2 D2H	-474.9043991	-1.66089868	-475.435887	-712.772621	-705.6312613	-54.2	-47.1
75	cl2c=ccl2 B3LYP	-1915.958726	-1.73221311	-1916.513034	-37.706618	-22.89879772	-25.2	-10.3
76	cf3cn B3LYP	-429.8662882	-1.60158683	-430.378796	-538.658581	-533.1187755	-43.3	-37.7
77	PROPYNE C3V	-116.3906842	-0.64070669	-116.595710	184.829315	185.9320252	-0.1	1.0
78	ALLENE D2D	-116.3907291	-0.63450157	-116.593770	188.267928	189.3706383	-2.1	-1.0
79	CYCLOPROPENE C2V	-116.3508717	-0.64390948	-116.556923	285.946607	287.0493171	9.0	10.1
80	PROPENE CS	-117.6242942	-0.66418137	-117.836832	32.799160	33.90186954	12.7	13.8
81	CYCLOPROPANE D3H	-117.6103474	-0.67044828	-117.824891	66.632190	67.73489955	13.5	14.6
82	PROPANE C2V	-118.8404598	-0.69720728	-119.063566	-81.807181	-80.70447108	22.8	23.9
83	TRANS-1,3-BUTADIENE C2H	-155.6311629	-0.85891611	-155.906016	118.943726	120.4140061	8.9	10.4
84	Dimethyl acetylene	-155.6177114	-0.86474448	-155.894430	149.516234	150.9865138	3.9	5.4
85	Methylene cyclopropane.	-155.5981694	-0.86568082	-155.875187	198.632253	200.1025331	-1.8	-0.3
86	Bicyclo[1.1.0]butane. C2v	-155.5818828	-0.87742805	-155.862660	233.455563	234.9258429	16.3	17.8
87	CYCLOBUTENE b3lyp	-155.6075945	-0.86791699	-155.885328	174.370889	175.8411687	17.9	19.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.8289957	-0.89706886	-157.116058	50.646588	52.11686774	22.2	23.7
89	Isobutene. Single	-156.8468596	-0.89278261	-157.132550	2.557168	4.027448342	19.3	20.8
90	Trans butane	-158.0581332	-0.92320763	-158.353560	-95.830842	-94.36056231	29.7	31.2
91	isobutane B3LYP/6-31G*	-158.0590978	-0.92640567	-158.355548	-102.344479	-100.8741989	32.0	33.4
92	Spiropentane. D2d	-194.8097192	-1.09806619	-195.161100	197.256869	199.0947188	11.9	13.7
93	Benzene B3LYP	-231.7267535	-1.26155621	-232.130451	73.217356	75.42277577	-9.2	-7.0
94	DIFLUOROMETHANE C2V	-238.6669616	-0.8537171	-238.940151	-462.204714	-458.6340342	-11.6	-8.0
95	HCF3 TRI-FLUOROMETHANE	-337.8162031	-1.15772787	-338.186676	-716.965111	-711.792876	-19.9	-14.7
96	CH2CL2 C2V	-959.1859709	-0.87632231	-959.466394	-93.464477	-86.06056698	1.9	9.3
97	chcl3 B3LYP/6-31G*	-1418.568826	-1.20170137	-1418.953371	-104.169708	-93.24762798	-0.8	10.1
98	METHYLAMINE b3lyp	-95.64603871	-0.51502301	-95.810846	-11.940124	-11.57255383	11.1	11.4
99	Acetonitrile. CH3-CN.	-132.4816131	-0.68291842	-132.700147	64.559034	65.29417364	-10.8	-10.0
100	NITRO METHANE	-244.5831236	-1.12953035	-244.944573	-94.019962	-91.7620318	-19.5	-17.3
101	Methyl-nitrite. CH3-O-N=O.	-244.5793772	-1.11913358	-244.937500	-79.176891	-76.91896079	-12.7	-10.4
102	Methylsilane. CH3-SiH3.	-330.9154519	-0.56510553	-331.096286	-5.491462	-3.338552069	23.8	25.9
103	Formic Acid.	-189.4554394	-0.81675308	-189.716800	-391.931469	-389.6735386	-13.3	-11.0
104	Methyl formate.	-228.6606515	-1.03950363	-228.993293	-371.108664	-368.4831642	-15.5	-12.8
105	acetamide ch3cohn2	-208.820551	-1.00918536	-209.143490	-243.423702	-241.7433821	-4.9	-3.3

106	Aziridine. (cyclic	-133.6286037	-0.7154322	-133.857542	133.188705	133.9238452	6.8	7.6
107	Cyanogen. NCCN.	-185.3069836	-0.91317962	-185.599201	269.996591	270.7317309	-36.7	-36.0
108	DIMETHYLAMINE b3lyp	-134.855047	-0.73941018	-135.091658	-3.149850	-2.41471042	15.3	16.0
109	TRANS ETHYLAMINE	-134.8665702	-0.74057414	-135.103554	-33.444516	-32.70937613	13.8	14.6
110	KETENE B3LYP	-152.321991	-0.71460728	-152.550665	-69.487407	-67.80708675	-22.2	-20.5
111	OXIRANE B3LYP	-153.4895207	-0.74603352	-153.728251	-51.708648	-50.02832816	1.0	2.7
112	Acetaldehyde B3LYP	-153.5354523	-0.7382871	-153.771704	-168.912794	-167.2324745	-2.8	-1.1
113	Glyoxal, O=CH-CH=O.	-227.4345112	-1.0069583	-227.756738	-233.907600	-231.2821003	-21.8	-19.2
114	ETHANOL TRANS	-154.729566	-0.76886059	-154.975601	-221.471548	-219.7912284	13.7	15.3
115	DIMETHYL ETHER,	-154.7128443	-0.76587683	-154.957925	-175.904622	-174.2243023	8.2	9.9
116	Thiooxirane. (cyclic	-476.3934867	-0.83061961	-476.659285	89.317503	92.38933826	7.3	10.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.6896279	-1.17259659	-553.064859	-128.142174	-124.1251594	23.3	27.3
118	Thioethanol. CH3-CH2-SH.	-477.6103513	-0.84946139	-477.882179	-23.212351	-20.14051646	23.2	26.3
119	ch3sch3 B3LYP	-477.6083458	-0.85134165	-477.880775	-17.000716	-13.92888067	20.2	23.3
120	Vinyl fluoride,	-177.5327132	-0.74427123	-177.770880	-147.242477	-144.9057819	-8.3	-6.0
121	Ethyl chloride.	-539.0192082	-0.78470126	-539.270313	-101.043204	-96.78989418	11.1	15.3
122	Vinyl chloride,	-537.7976563	-0.75598318	-538.039571	23.348019	27.60132892	0.3	4.6
123	h2c=chcn B3LYP	-170.4795983	-0.87840443	-170.760688	173.270045	174.3727547	-7.5	-6.4
124	ACETONE B3LYP	-192.7649195	-0.96372539	-193.073312	-213.875087	-211.8271972	3.3	5.3
125	CH3COOH ACETIC	-228.6863983	-1.03909465	-229.018909	-438.817543	-436.1920429	-6.2	-3.6
126	CH3CFO HCCO	-252.6961642	-1.04759503	-253.031395	-455.193556	-451.911681	-12.9	-9.7
127	ch3c(o)cl hcco	-612.9475998	-1.06353935	-613.287932	-253.102202	-247.9037119	-10.4	-5.2
128	ch3ch2ch2cl B3LYP	-578.2370014	-1.01095637	-578.560507	-115.500685	-110.8798052	16.3	20.9
129	Isopropyl alcohol,	-193.9521472	-0.99707217	-194.271210	-251.929038	-249.8811475	20.9	22.9
130	Methyl ethyl	-193.9357348	-0.99128307	-194.252945	-203.425860	-201.3779703	12.9	14.9
131	Trimethyl Amine.	-174.0663384	-0.96860618	-174.376292	-5.698706	-4.595996135	18.2	19.3
132	FURAN B3LYP	-229.5644466	-1.14667998	-229.931384	-46.637830	-44.22236956	-11.9	-9.5
133	Thiophene b3lyp	-552.4579206	-1.23823909	-552.854157	113.729471	117.5364459	-1.3	2.5
134	PYROLE PLANAR	-209.7180333	-1.11918458	-210.076172	96.898435	98.36871543	-11.5	-10.0
135	C2v Pyridine	-247.7525879	-1.3054402	-248.170329	119.071299	120.9091488	-21.5	-19.7
136	H2 B3LYP/6-31G*	-1.15798994	-0.03470869	-1.169097	8.362077	8.36207728	8.4	8.4
137	SH b3lyp/6-31G*	-398.5420289	-0.3584606	-398.656736	147.810998	150.1476927	4.7	7.1
138	CCH B3LYP	-76.44970848	-0.37985168	-76.571261	572.857755	573.5928953	7.6	8.3
139	C2H3 CS,2-A'	-77.7277289	-0.40161898	-77.856247	300.731799	301.4669391	1.2	1.9
140	ch3co hcco	-152.8950247	-0.71618424	-153.124204	-22.384528	-20.70420818	-12.3	-10.7
141	H2COH C1	-114.8558255	-0.51167113	-115.019560	-16.543157	-15.23040738	0.6	1.9
142	ch3o CS,	-114.8493864	-0.48485964	-115.004541	19.315204	20.62795433	2.2	3.5

143	ch3ch2o 2A"	-154.0721193	-0.70974706	-154.299238	-7.933973	-6.25365311	7.5	9.2
144	ch3s 2-A'	-437.7608867	-0.58684151	-437.948676	129.890729	132.594994	5.2	7.9
145	c2h5 staggered	-78.96481529	-0.43303846	-79.103388	131.271642	132.006782	10.4	11.1
146	(ch3)2ch Cs	-118.1871361	-0.65998418	-118.398331	104.372769	105.4754793	14.4	15.5
147	TERT-BUTYL RADICAL	-157.4095872	-0.88895406	-157.694053	75.168757	76.63903694	23.7	25.2
148	NO2 RADICAL	-204.7440295	-0.90232958	-205.032775	-2.158100	-0.267740229	-35.2	-33.3

MAD	**11.9**	**12.2**
LD	**-54.2**	**-47.1**

Table S5.45b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 59% and a_C = 32%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498754	0.000000	-0.498754
2	li	-7.466106	-0.014550	-7.470762
3	be	-14.632850	-0.053103	-14.649843
4	b	-24.610613	-0.076993	-24.635251
5	c	-37.792227	-0.103730	-37.825421
6	n	-54.523902	-0.134409	-54.566913
7	o	-74.983746	-0.191490	-75.045023
8	f	-99.627102	-0.254236	-99.708457
9	na	-162.129848	-0.171099	-162.184600
10	al	-242.207755	-0.219548	-242.278010
11	si	-289.206869	-0.249492	-289.286707
12	p	-341.087737	-0.278422	-341.176832
13	s	-397.918959	-0.319605	-398.021232
14	cl	-459.934288	-0.290463	-460.027236

Table S5.46a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 22%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05288239	-0.04636454	-8.063083	146.878996	146.8789958	7.6	7.6
2	BERYLLIUM HYDRIDE	-15.22983301	-0.05470459	-15.241868	317.384895	317.3848948	-24.4	-24.4
3	DOUBLET CH	-38.43015512	-0.14362304	-38.461752	601.065552	601.4331221	4.8	5.2
4	CH2 3-B1	-39.09458208	-0.16268264	-39.130372	396.661035	397.0286048	4.6	5.0
5	Singlet methylene,	-39.07216726	-0.18269016	-39.112359	442.342544	442.7101141	12.2	12.6
6	Methyl radical,	-39.76948052	-0.20720746	-39.815066	153.977178	154.344748	7.5	7.9
7	ch4 //b3lyp/6-31G*	-40.43637987	-0.24870205	-40.491094	-60.651267	-60.28369683	14.2	14.6
8	NH,TRIPLET, //b3lyp/6-31G*	-55.1618596	-0.18655318	-55.202901	361.526326	361.5263258	5.0	5.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.80537978	-0.23974763	-55.858124	194.398954	194.3989542	5.7	5.7
10	AMMONIA, //b3lyp/6-31G*	-56.47317058	-0.29345049	-56.537730	-28.067316	-28.0673155	18.0	18.0
11	OH RADICAL	-75.66038624	-0.25702753	-75.716932	47.442135	48.38731473	8.1	9.1
12	Water //b3lyp/6-31G*	-76.33940909	-0.32530176	-76.410975	-218.197204	-217.2520242	23.6	24.6
13	HYDROGEN FLUORIDE,	-100.3586868	-0.33604699	-100.432617	-257.342001	-255.7404462	15.0	16.6
14	SIH2 singlet	-290.4862918	-0.30432255	-290.553243	274.523192	276.3085321	1.7	3.5
15	SIH2 3B1	-290.4591957	-0.28208059	-290.521253	359.522077	361.3074174	-1.1	0.6
16	SIH3 c3v	-291.102868	-0.30980693	-291.171026	199.364947	201.1502867	-1.0	0.7
17	SIH4 //b3lyp/6-31G*	-291.747871	-0.3367923	-291.821965	38.085240	39.87057989	3.8	5.6
18	ph2 doublet	-342.3711605	-0.34356394	-342.446745	139.577092	139.5770924	1.1	1.1
19	PH3 c3v	-343.0008229	-0.37453109	-343.083220	17.773192	17.77319164	12.3	12.3
20	SH2 //b3lyp/6-31G*	-399.2487918	-0.39584846	-399.335878	-7.502079	-5.165384176	13.0	15.3
21	HCL //b3lyp/6-31G*	-460.6599193	-0.33432824	-460.733471	-86.310583	-82.7924125	6.2	9.7
22	DILITHIUM //b3lyp/6-31G*	-14.96976078	-0.05749748	-14.982410	231.339157	231.3391566	15.4	15.4
23	Lithium Fluoride,	-107.3249952	-0.36471515	-107.405232	-326.297021	-324.6954663	8.8	10.4
24	ACETYLENE //b3lyp/6-31g*	-77.20572045	-0.41554614	-77.297141	250.250242	250.9853823	23.5	24.2
25	ETHYLENE //b3lyp/6-31g*	-78.45122598	-0.43662878	-78.547284	75.295630	76.03076997	23.0	23.7
26	ETHANE //b3lyp/6-31g*	-79.67803398	-0.47000915	-79.781436	-58.979408	-58.24426812	25.1	25.9
27	CYANO RADICAL,	-92.57890809	-0.45010286	-92.677931	478.144442	478.512012	39.2	39.6
28	HYDROGEN CYANIDE	-93.29226819	-0.45971764	-93.393406	151.501162	151.8687316	19.7	20.1
29	CARBON MONOXIDE	-113.184341	-0.47048003	-113.287847	-89.996074	-88.68332378	20.5	21.8
30	HCO BENT	-113.7111315	-0.49285738	-113.819560	57.585977	58.89872681	15.7	17.1
31	H2CO //b3lyp/6-31g*	-114.3557108	-0.51230701	-114.468418	-88.766390	-87.4536399	20.0	21.3

32	METHANOL //b3lyp/6-31g*	-115.5657929	-0.54198414	-115.685029	-174.058439	-172.7456886	26.8	28.1
33	Nitrogen N2,	-109.3908025	-0.49327705	-109.499323	27.095931	27.09593077	27.1	27.1
34	H2NNH2 //b3lyp/6-31g*	-111.7061609	-0.55653617	-111.828599	125.446316	125.4463164	30.1	30.1
35	NO radical,	-129.7401821	-0.53503688	-129.857890	115.638162	116.5833424	25.3	26.2
36	O2 //b3lyp/6-31g*	-150.1517271	-0.59924791	-150.283562	28.771280	30.66163988	28.8	30.7
37	HYDROGEN PEROXIDE	-151.3726667	-0.62876337	-151.510995	-88.646052	-86.75569231	47.3	49.2
38	F2 //b3lyp/6-31g*	-199.3292615	-0.65740459	-199.473891	44.226316	47.4294261	44.2	47.4
39	CO2 D*H	-188.3722139	-0.79105684	-188.546246	-372.839149	-370.5812187	20.5	22.7
40	na2 //b3lyp/6-31G*	-324.3610268	-0.36927984	-324.442268	145.011161	145.0111614	2.8	2.8
41	SI2 3-SGG	-578.6227049	-0.55567639	-578.744954	594.889745	598.4604245	9.5	13.1
42	P2 //b3lyp/6-31g*	-682.4330515	-0.7049588	-682.588142	169.822412	169.8224123	26.3	26.3
43	S2 //b3lyp/6-31g*	-796.0952855	-0.7524154	-796.260817	143.394960	148.0683499	14.9	19.6
44	CL2 //b3lyp/6-31g*	-920.0779814	-0.64722169	-920.220370	17.330547	24.36688746	17.3	24.4
45	Sodium Chloride	-622.3166166	-0.50566953	-622.427864	-172.393722	-168.8755518	10.0	13.5
46	SIO //b3lyp/6-31g*	-364.5266813	-0.61173211	-364.661262	-73.187829	-70.45730881	29.7	32.5
47	Carbon monosulfide,	-436.0203329	-0.57176592	-436.146121	306.721603	309.4258677	26.8	29.5
48	OS //b3lyp/6-31g*	-473.143797	-0.68251651	-473.293951	28.780695	32.06256971	23.8	27.0
49	CLO 2-PI	-535.0791157	-0.60007928	-535.211133	128.776660	133.2400096	27.5	32.0
50	CLF 1-SG	-559.7292267	-0.64952308	-559.872122	-35.020371	-29.90064554	20.2	25.3
51	si2h6 //b3lyp/6-31g*	-582.3197535	-0.65448657	-582.463741	91.537450	95.10813042	11.6	15.2
52	Methyl chloride,	-499.8961546	-0.55650142	-500.018585	-67.745542	-63.85980161	14.3	18.1
53	H3C-SH METHANETHIOL	-438.4880226	-0.62051368	-438.624536	1.706444	4.410709258	24.7	27.4
54	HOCl //b3lyp/6-31g*	-535.7283959	-0.64091064	-535.869396	-47.109958	-42.64660816	27.4	31.8
55	SO2 //b3lyp/6-31G*	-548.3173761	-1.02578538	-548.543049	-234.792558	-230.5655026	62.3	66.5
56	BF3 PLANAR	-324.2950988	-1.06444365	-324.529276	-1124.072983	-1119.137043	11.5	16.4
57	bcl3 B3LYP	-1405.11496	-1.10222869	-1405.357450	-405.518607	-394.8328219	-2.6	8.1
58	ALf3 B3LYP	-541.8496988	-1.20264157	-542.114280	-1169.333954	-1163.636619	39.8	45.5
59	alcl3 B3LYP	-1622.729507	-1.20422509	-1622.994436	-581.911713	-570.4645328	2.6	14.0
60	cf4 B3LYP	-437.1188715	-1.45422669	-437.438801	-907.485924	-900.7121339	25.5	32.3
61	ccl4 B3LYP	-1878.249333	-1.52825082	-1878.585548	-62.520619	-48.08036906	33.3	47.7
62	O=C=S. Singlet	-511.2662963	-0.88132863	-511.460189	-122.851210	-119.2017652	15.6	19.3
63	CS2 B3LYP	-834.1569374	-0.97865672	-834.372242	132.675992	137.7169524	15.9	21.0
64	COF2 B3LYP	-312.7228952	-1.1233846	-312.970040	-581.738345	-577.2224847	42.1	46.6
65	sif4 B3LYP	-688.7194096	-1.55505249	-689.061521	-1548.328720	-1540.13716	66.7	74.9
66	sicl4, td	-2129.833733	-1.59094174	-2130.183740	-633.188307	-617.3302868	29.6	45.4
67	nno B3LYP	-184.4280073	-0.8482978	-184.614633	117.132570	118.0777504	35.1	36.1
68	clno B3LYP	-589.7785922	-0.91590751	-589.980092	94.566714	99.03006411	42.7	47.1

69	nf3 c3v	-353.7524533	-1.23778783	-354.024767	-84.759339	-79.95467396	47.5	52.3
70	pf3 c3v	-640.6252168	-1.29688386	-640.910531	-908.162925	-903.3582602	50.4	55.2
71	ozone 1-a1	-225.1302215	-1.01832565	-225.354253	231.489056	234.3245956	88.8	91.7
72	f2o B3LYP	-274.3924226	-0.96926869	-274.605662	85.757455	89.90574501	61.1	65.2
73	CLF3, C2V	-759.0878132	-1.37351786	-759.389987	-103.220253	-94.89741836	55.8	64.1
74	CF2=CF2 D2H	-475.0814088	-1.6547747	-475.445459	-642.831350	-635.6899902	15.7	22.9
75	cl2c=ccl2 B3LYP	-1916.284758	-1.72579329	-1916.664433	14.842281	29.65010116	27.4	42.2
76	cf3cn B3LYP	-430.0333448	-1.59548157	-430.384351	-459.492357	-453.9525519	35.9	41.4
77	PROPYNE C3V	-116.4607376	-0.63817558	-116.601136	214.458881	215.5615914	29.5	30.6
78	ALLENE D2D	-116.4607508	-0.63199246	-116.599789	216.339071	217.4417812	26.0	27.1
79	CYCLOPROPENE C2V	-116.4215015	-0.64138651	-116.562606	314.899393	316.0021034	37.9	39.0
80	PROPENE CS	-117.6999873	-0.66166037	-117.845553	53.903606	55.00631591	33.8	34.9
81	CYCLOPROPANE D3H	-117.6868162	-0.66795166	-117.833766	87.331567	88.43427696	34.2	35.3
82	PROPANE C2V	-118.9217626	-0.69465242	-119.074586	-66.616069	-65.51335906	38.0	39.1
83	TRANS-1,3-BUTADIENE C2H	-155.7271413	-0.85557347	-155.915367	152.933527	154.4038073	42.9	44.4
84	Dimethyl acetylene	-155.7136708	-0.8613968	-155.903178	185.089017	186.5592967	39.5	41.0
85	Methylene cyclopropane.	-155.6948282	-0.86236029	-155.884547	232.599152	234.0694315	32.2	33.7
86	Bicyclo[1.1.0]butane. C2v	-155.6793195	-0.8741024	-155.871622	268.467199	269.9374787	51.3	52.8
87	CYCLOBUTENE b3lyp	-155.7045658	-0.864568	-155.894771	208.120916	209.5911961	51.6	53.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.9315889	-0.89371892	-157.128207	77.414744	78.88502381	49.0	50.4
89	Isobutene. Single	-156.9485716	-0.88941442	-157.144243	30.524023	31.9943027	47.3	48.7
90	Trans butane	-158.1653675	-0.91982217	-158.367728	-74.240037	-72.76975728	51.3	52.8
91	isobutane B3LYP/6-31G*	-158.1664315	-0.92300272	-158.369492	-80.165058	-78.69477827	54.1	55.6
92	Spiropentane. D2d	-194.9330959	-1.09394061	-195.173763	237.220291	239.0581411	51.9	53.7
93	Benzene B3LYP	-231.8652325	-1.25672539	-232.141712	131.278984	133.4844044	48.9	51.1
94	DIFLUOROMETHANE C2V	-238.7599762	-0.85059276	-238.947107	-432.804949	-429.2342686	17.8	21.4
95	HCF3 TRI-FLUOROMETHANE	-337.9411954	-1.15355146	-338.194977	-674.662023	-669.4897877	22.4	27.6
96	CH2CL2 C2V	-959.3532996	-0.87315396	-959.545393	-75.729854	-68.32594407	19.7	27.1
97	chcl3 B3LYP/6-31G*	-1418.805149	-1.19733088	-1419.068561	-76.277342	-65.35526221	27.1	38.0
98	METHYLAMINE b3lyp	-95.70337079	-0.51307216	-95.816247	3.907262	4.274832372	26.9	27.3
99	Acetonitrile. CH3-CN.	-132.55336	-0.68013496	-132.702990	101.539994	102.275134	26.2	27.0
100	NITRO METHANE	-244.6935388	-1.12473514	-244.940981	-21.113260	-18.85533043	53.4	55.6
101	Methyl-nitrite. CH3-O-N=O.	-244.6894508	-1.11420154	-244.934575	-8.024009	-5.766078715	58.5	60.8
102	Methylsilane. CH3-SiH3.	-331.0066105	-0.56325273	-331.130526	-6.798668	-4.645758063	22.5	24.6
103	Formic Acid.	-189.538869	-0.81339806	-189.717817	-346.361456	-344.1035264	32.3	34.5
104	Methyl formate.	-228.769846	-1.0353237	-228.997617	-319.558151	-316.932651	36.1	38.7
105	acetamide ch3cohn2	-208.9281655	-1.00517641	-209.149304	-197.333736	-195.6534164	41.2	42.8

106	Aziridine. (cyclic	-133.7067804	-0.71267994	-133.863570	161.931041	162.6661809	35.6	36.3
107	Cyanogen. NCCN.	-185.394767	-0.90915702	-185.594782	341.031588	341.7667275	34.3	35.1
108	DIMETHYLAMINE b3lyp	-134.9382604	-0.73663421	-135.100320	18.802192	19.5373319	37.2	37.9
109	TRANS ETHYLAMINE	-134.9498237	-0.73779014	-135.112138	-11.287625	-10.55248548	36.0	36.7
110	KETENE B3LYP	-152.3958158	-0.71163182	-152.552375	-27.980883	-26.30056303	19.3	21.0
111	OXIRANE B3LYP	-153.5694243	-0.74310824	-153.732908	-17.815722	-16.13540157	34.9	36.6
112	Acetaldehyde B3LYP	-153.6148096	-0.73533286	-153.776583	-135.602862	-133.9225422	30.5	32.2
113	Glyoxal, O=CH-CH=O.	-227.5376452	-1.00277232	-227.758255	-175.110686	-172.4851862	37.0	39.6
114	ETHANOL TRANS	-154.8147063	-0.7659568	-154.983217	-195.222610	-193.5422897	39.9	41.6
115	DIMETHYL ETHER,	-154.7978385	-0.76297826	-154.965694	-150.058420	-148.3781005	34.0	35.7
116	Thiooxirane. (cyclic	-476.5104329	-0.82766867	-476.692520	112.825491	115.8973264	30.8	33.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.8412506	-1.16811125	-553.098235	-88.094900	-84.07788488	63.4	67.4
118	Thioethanol. CH3-CH2-SH.	-477.7322654	-0.84652087	-477.918500	-7.682193	-4.610357874	38.8	41.8
119	ch3sch3 B3LYP	-477.730157	-0.84837457	-477.916799	-0.691731	2.380104139	36.5	39.6
120	Vinyl fluoride,	-177.6142698	-0.74143587	-177.777386	-118.554796	-116.2181008	20.4	22.7
121	Ethyl chloride.	-539.1435246	-0.78185203	-539.315532	-85.130775	-80.87746542	27.0	31.3
122	Vinyl chloride,	-537.9164092	-0.75313753	-538.082099	46.200758	50.45406844	23.2	27.4
123	h2c=chcn B3LYP	-170.571545	-0.87478034	-170.763997	223.569291	224.6720012	42.8	43.9
124	ACETONE B3LYP	-192.8702827	-0.9599551	-193.081473	-174.516930	-172.4690398	42.6	44.7
125	CH3COOH ACETIC	-228.795828	-1.03495613	-229.023518	-388.015739	-385.3902389	44.6	47.2
126	CH3CFO HCCO	-252.8074351	-1.04351281	-253.037008	-407.377207	-404.0953319	34.9	38.2
127	ch3c(o)cl hcco	-613.0958471	-1.05935876	-613.328906	-209.381179	-204.1826887	33.3	38.5
128	ch3ch2ch2cl B3LYP	-578.3872409	-1.00727352	-578.608841	-93.098061	-88.47718137	38.7	43.3
129	Isopropyl alcohol,	-194.063309	-0.99332724	-194.281841	-218.930133	-216.8822431	53.9	55.9
130	Methyl ethyl	-194.0466626	-0.98755765	-194.263925	-171.343629	-169.2957387	45.0	47.0
131	Trimethyl Amine.	-174.1755705	-0.96496722	-174.387863	23.281497	24.38420723	47.1	48.2
132	FURAN B3LYP	-229.6860982	-1.14216439	-229.937374	12.838516	15.25397566	47.6	50.0
133	Thiophene b3lyp	-552.6165563	-1.23361147	-552.887951	164.855019	168.661994	49.8	53.6
134	PYROLE PLANAR	-209.8380596	-1.11486761	-210.083331	151.758138	153.2284177	43.4	44.9
135	C2v Pyridine	-247.8928004	-1.30035383	-248.178878	184.820202	186.6580519	44.2	46.1
136	H2 B3LYP/6-31G*	-1.16183577	-0.03456452	-1.169440	7.585235	7.585234888	7.6	7.6
137	SH b3lyp/6-31G*	-398.6089041	-0.35734493	-398.687520	148.484003	150.8206982	5.4	7.7
138	CCH B3LYP	-76.48984296	-0.37824165	-76.573056	597.291364	598.0265035	32.0	32.8
139	C2H3 CS,2-A'	-77.77382075	-0.4000985	-77.861842	315.311956	316.0470957	15.7	16.5
140	ch3co hcco	-152.9709281	-0.71334113	-153.127863	14.064282	15.74460223	24.1	25.8
141	H2COH C1	-114.9116245	-0.50973353	-115.023766	3.929275	5.242024963	21.1	22.4
142	ch3o CS,	-114.9049775	-0.4830361	-115.011245	33.228554	34.54130429	16.1	17.4

143	ch3ch2o 2A"	-154.1536198	-0.70709453	-154.309181	12.143754	13.82407364	27.6	29.3
144	ch3s 2-A'	-437.8535503	-0.58487391	-437.982223	137.976368	140.680633	13.3	16.0
145	c2h5 staggered	-79.01667205	-0.43142672	-79.111586	139.142268	139.8774083	18.2	19.0
146	(ch3)2ch Cs	-118.2649608	-0.6575613	-118.409624	118.784513	119.8872232	28.8	29.9
147	TERT-BUTYL RADICAL	-157.5134208	-0.88571118	-157.708277	96.550376	98.0206563	45.1	46.6
148	NO2 RADICAL	-204.8250872	-0.89830116	-205.022713	73.003255	74.89361504	39.9	41.8

MAD	**29.0**	**31.6**
LD	**88.8**	**91.7**

Table S5.46b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 22%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.471527	-0.014523	-7.474722
3	be	-14.642423	-0.052840	-14.654047
4	b	-24.623312	-0.076591	-24.640162
5	c	-37.808241	-0.103266	-37.830959
6	n	-54.543226	-0.133936	-54.572692
7	o	-75.009441	-0.190798	-75.051416
8	f	-99.658994	-0.253393	-99.714741
9	na	-162.170580	-0.170628	-162.208118
10	al	-242.257263	-0.218897	-242.305420
11	si	-289.260040	-0.248764	-289.314768
12	p	-341.144562	-0.277689	-341.205654
13	s	-397.982142	-0.318666	-398.052248
14	cl	-460.003637	-0.289468	-460.067320

Table S5.47a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04755183	-0.04637127	-8.060536	147.393332	147.3933317	8.1	8.1
2	BERYLLIUM HYDRIDE	-15.22334631	-0.05466045	-15.238651	319.180589	319.1805887	-22.7	-22.7
3	DOUBLET CH	-38.41828943	-0.14364703	-38.458511	600.686506	601.0540761	4.5	4.8
4	CH2 3-B1	-39.08166932	-0.16267354	-39.127218	396.052938	396.420508	4.0	4.4
5	Singlet methylene,	-39.05820121	-0.18266826	-39.109348	441.357485	441.7250554	11.2	11.6
6	Methyl radical,	-39.75396612	-0.20722887	-39.811990	153.163263	153.530833	6.7	7.1
7	ch4 //b3lyp/6-31G*	-40.41870286	-0.24866671	-40.488330	-62.282173	-61.91460282	12.6	13.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14757631	-0.18661427	-55.199828	360.334205	360.3342049	3.9	3.9
9	NH2,2-B-1, //b3lyp/6-31G*	-55.7886017	-0.23978852	-55.855742	191.392033	191.3920325	2.7	2.7
10	AMMONIA, //b3lyp/6-31G*	-56.45409299	-0.29345563	-56.536261	-33.470404	-33.47040389	12.6	12.6
11	OH RADICAL	-75.64232194	-0.2570874	-75.714306	43.723144	44.66832444	4.4	5.3
12	Water //b3lyp/6-31G*	-76.31898188	-0.32533838	-76.410077	-226.450522	-225.5053418	15.4	16.3
13	HYDROGEN FLUORIDE,	-100.3369435	-0.33609779	-100.431051	-263.991075	-262.3895197	8.4	10.0
14	SIH2 singlet	-290.4504473	-0.30427626	-290.535645	276.182729	277.9680691	3.4	5.2
15	SIH2 3B1	-290.4245246	-0.28192345	-290.503463	361.686198	363.4715378	1.0	2.8
16	SIH3 c3v	-291.065942	-0.30971859	-291.152663	203.030868	204.8162078	2.6	4.4
17	SIH4 //b3lyp/6-31G*	-291.7089171	-0.33673934	-291.803204	42.798267	44.58360653	8.5	10.3
18	ph2 doublet	-342.3325719	-0.34356291	-342.428770	141.157774	141.1577741	2.7	2.7
19	PH3 c3v	-342.9602676	-0.37447734	-343.065121	19.678103	19.67810321	14.2	14.2
20	SH2 //b3lyp/6-31G*	-399.2066816	-0.39581458	-399.317510	-8.408896	-6.072201421	12.1	14.4
21	HCL //b3lyp/6-31G*	-460.6162925	-0.33431458	-460.709901	-87.826298	-84.30812783	4.6	8.2
22	DILITHIUM //b3lyp/6-31G*	-14.96173258	-0.05747333	-14.977825	231.032780	231.0327796	15.1	15.1
23	Lithium Fluoride,	-107.2999318	-0.36480021	-107.402076	-334.942802	-333.3412467	0.2	1.8
24	ACETYLENE //b3lyp/6-31g*	-77.1790321	-0.4154367	-77.295354	237.160292	237.8954322	10.4	11.1
25	ETHYLENE //b3lyp/6-31g*	-78.42131551	-0.43654521	-78.543548	67.325190	68.06032958	15.0	15.8
26	ETHANE //b3lyp/6-31g*	-79.64490485	-0.46993984	-79.776488	-63.768149	-63.03300947	20.3	21.1
27	CYANO RADICAL,	-92.55330812	-0.44959192	-92.679194	456.677964	457.0455339	17.8	18.1
28	HYDROGEN CYANIDE	-93.26439188	-0.45962761	-93.393088	134.187170	134.5547401	2.4	2.8
29	CARBON MONOXIDE	-113.1552472	-0.47044324	-113.286971	-107.200857	-105.8881071	3.3	4.6
30	HCO BENT	-113.6806378	-0.49278235	-113.818617	40.559481	41.87223118	-1.3	0.0
31	H2CO //b3lyp/6-31g*	-114.3232686	-0.51227662	-114.466706	-103.774052	-102.4613019	5.0	6.3

32	METHANOL //b3lyp/6-31g*	-115.5300225	-0.54196632	-115.681773	-185.012138	-183.699388	15.8	17.1
33	Nitrogen N2,	-109.3617775	-0.49318618	-109.499870	7.141325	7.141324743	7.1	7.1
34	H2NNH2 //b3lyp/6-31g*	-111.6703469	-0.55653019	-111.826175	113.288693	113.2886934	17.9	17.9
35	NO radical,	-129.7084995	-0.53497977	-129.858294	94.704936	95.6501159	4.3	5.3
36	O2 //b3lyp/6-31g*	-150.1173909	-0.5992425	-150.285179	3.298952	5.189312462	3.3	5.2
37	HYDROGEN PEROXIDE	-151.3344853	-0.62879171	-151.510547	-108.697215	-106.8068548	27.3	29.2
38	F2 //b3lyp/6-31g*	-199.2887198	-0.65742646	-199.472799	25.569150	28.77226025	25.6	28.8
39	CO2 D*H	-188.3247467	-0.79097806	-188.546221	-402.887627	-400.629697	-9.6	-7.3
40	na2 //b3lyp/6-31G*	-324.3104616	-0.36924708	-324.413851	144.455927	144.455927	2.2	2.2
41	SI2 3-SGG	-578.5568208	-0.55556923	-578.712380	591.322907	594.8935867	6.0	9.6
42	P2 //b3lyp/6-31g*	-682.3601947	-0.70482015	-682.557544	158.931916	158.931916	15.4	15.4
43	S2 //b3lyp/6-31g*	-796.016872	-0.7523615	-796.227533	132.513322	137.1867121	4.1	8.7
44	CL2 //b3lyp/6-31g*	-919.9932079	-0.64717627	-920.174417	11.177832	18.21417156	11.2	18.2
45	Sodium Chloride	-622.2486401	-0.5056829	-622.390231	-174.573363	-171.0551925	7.8	11.4
46	SIO //b3lyp/6-31g*	-364.4755251	-0.61178107	-364.646824	-90.436792	-87.7062725	12.5	15.2
47	Carbon monosulfide,	-435.9694376	-0.57164765	-436.129499	292.339985	295.0442498	12.4	15.1
48	OS //b3lyp/6-31g*	-473.0873652	-0.68246618	-473.278456	9.715316	12.9971906	4.7	8.0
49	CLO 2-PI	-535.0196199	-0.5998345	-535.187574	116.618055	121.0814052	15.4	19.8
50	CLF 1-SG	-559.6664508	-0.64951942	-559.848316	-46.681320	-41.5615948	8.5	13.7
51	si2h6 //b3lyp/6-31g*	-582.2440521	-0.65438734	-582.427281	98.174536	101.7452164	18.3	21.8
52	Methyl chloride,	-499.8372032	-0.55644811	-499.993009	-72.886075	-69.00033527	9.1	13.0
53	H3C-SH METHANETHIOL	-438.4305103	-0.62044429	-438.604235	-3.017356	-0.313090867	20.0	22.7
54	HOCl //b3lyp/6-31g*	-535.6668815	-0.6408977	-535.846333	-60.571170	-56.10781971	13.9	18.4
55	SO2 //b3lyp/6-31G*	-548.2420993	-1.02572463	-548.529302	-269.061203	-264.8341482	28.0	32.2
56	BF3 PLANAR	-324.2234885	-1.06444739	-324.521534	-1143.872575	-1138.936635	-8.3	-3.4
57	bcl3 B3LYP	-1404.977638	-1.10211991	-1405.286231	-416.581822	-405.8960372	-13.7	-3.0
58	ALf3 B3LYP	-541.756525	-1.20268777	-542.093278	-1190.068551	-1184.371216	19.1	24.8
59	alcl3 B3LYP	-1622.570644	-1.20413181	-1622.907801	-588.247649	-576.8004687	-3.7	7.7
60	cf4 B3LYP	-437.0233825	-1.45418163	-437.430553	-937.765459	-930.9916694	-4.7	2.0
61	ccl4 B3LYP	-1878.066224	-1.52810239	-1878.494093	-84.897896	-70.45764576	10.9	25.4
62	O=C=S. Singlet	-511.1970113	-0.88120108	-511.443748	-148.322434	-144.6729889	-9.8	-6.2
63	CS2 B3LYP	-834.0657706	-0.97847728	-834.339744	110.840928	115.8818877	-5.9	-0.9
64	COF2 B3LYP	-312.6514523	-1.12332807	-312.965984	-612.115698	-607.5998379	11.7	16.2
65	sif4 B3LYP	-688.6021263	-1.55502957	-689.037535	-1572.941113	-1564.749553	42.1	50.3
66	sicl4, td	-2129.628833	-1.59079054	-2130.074254	-643.882534	-628.0245144	18.9	34.7
67	nno B3LYP	-184.380762	-0.8481645	-184.618248	78.507121	79.45230129	-3.5	-2.6
68	clno B3LYP	-589.7040284	-0.91579735	-589.960452	62.857386	67.32073646	11.0	15.4

69	nf3 c3v	-353.675782	-1.23775362	-354.022353	-119.966122	-115.1614569	12.2	17.1
70	pf3 c3v	-640.5261014	-1.29686371	-640.889223	-930.115008	-925.3103429	28.4	33.2
71	ozone 1-a1	-225.0775589	-1.01819124	-225.362652	177.596695	180.4322352	34.9	37.8
72	f2o B3LYP	-274.334063	-0.96925833	-274.605455	54.163572	58.31186218	29.5	33.6
73	CLF3, C2V	-758.9832391	-1.37350619	-759.367821	-140.707231	-132.3843956	18.3	26.6
74	CF2=CF2 D2H	-474.9736925	-1.6547174	-475.437013	-681.481334	-674.3399736	-22.9	-15.8
75	cl2c=ccl2 B3LYP	-1916.089142	-1.72561162	-1916.572313	-14.682322	0.125498271	-2.1	12.7
76	cf3cn B3LYP	-429.9317159	-1.59534263	-430.378412	-503.223253	-497.683448	-7.8	-2.3
77	PROPYNE C3V	-116.4185414	-0.63803489	-116.597191	198.147317	199.2500273	13.2	14.3
78	ALLENE D2D	-116.4185338	-0.63186309	-116.595455	201.047613	202.1503226	10.7	11.8
79	CYCLOPROPENE C2V	-116.3789701	-0.64128238	-116.558529	298.934940	300.0376499	22.0	23.1
80	PROPENE CS	-117.654559	-0.66154417	-117.839791	42.360095	43.46280527	22.3	23.4
81	CYCLOPROPANE D3H	-117.6409741	-0.66786194	-117.827975	75.863955	76.96666479	22.7	23.8
82	PROPANE C2V	-118.8731264	-0.69454741	-119.067600	-74.942676	-73.83996585	29.7	30.8
83	TRANS-1,3-BUTADIENE C2H	-155.6694161	-0.85541017	-155.908931	134.273259	135.7435392	24.2	25.7
84	Dimethyl acetylene	-155.6559687	-0.86122439	-155.897112	165.457342	166.9276224	19.9	21.3
85	Methylene cyclopropane.	-155.6367282	-0.86222294	-155.878151	213.834769	215.3050487	13.4	14.9
86	Bicyclo[1.1.0]butane. C2v	-155.6208088	-0.87398515	-155.865525	248.916493	250.3867728	31.8	33.2
87	CYCLOBUTENE b3lyp	-155.6463181	-0.8644295	-155.888358	189.397306	190.8675857	32.9	34.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.8701349	-0.89359114	-157.120340	62.509380	63.97966019	34.1	35.5
89	Isobutene. Single	-156.887579	-0.88926443	-157.136573	15.101669	16.57194872	31.8	33.3
90	Trans butane	-158.1012192	-0.91967981	-158.358730	-86.172922	-84.70264165	39.3	40.8
91	isobutane B3LYP/6-31G*	-158.1022281	-0.92286081	-158.360629	-92.454824	-90.98454423	41.9	43.3
92	Spiropentane. D2d	-194.859071	-1.09379338	-195.165333	214.903018	216.7408681	29.6	31.4
93	Benzene B3LYP	-231.7818934	-1.25650161	-232.133714	98.939379	101.1447993	16.5	18.7
94	DIFLUOROMETHANE C2V	-238.7035254	-0.85059247	-238.941691	-448.999413	-445.4287333	1.6	5.2
95	HCF3 TRI-FLUOROMETHANE	-337.8652356	-1.15353701	-338.188226	-698.111326	-692.9390912	-1.1	4.1
96	CH2CL2 C2V	-959.2530095	-0.87307483	-959.497470	-85.600091	-78.19618103	9.8	17.2
97	chcl3 B3LYP/6-31G*	-1418.663467	-1.19721944	-1418.998688	-91.918413	-80.99633294	11.4	22.3
98	METHYLAMINE b3lyp	-95.66888205	-0.51303336	-95.812531	-4.488393	-4.120822971	18.5	18.9
99	Acetonitrile. CH3-CN.	-132.5099767	-0.68001086	-132.700380	81.352548	82.08768765	6.0	6.8
100	NITRO METHANE	-244.6261965	-1.12461551	-244.941089	-60.774216	-58.51628624	13.7	16.0
101	Methyl-nitrite. CH3-O-N=O.	-244.622329	-1.1140761	-244.934270	-46.600494	-44.34256439	19.9	22.2
102	Methylsilane. CH3-SiH3.	-330.9521556	-0.56316963	-331.109843	-5.929736	-3.776825733	23.4	25.5
103	Formic Acid.	-189.4881219	-0.81336259	-189.715863	-371.349704	-369.0917736	7.3	9.6
104	Methyl formate.	-228.7036754	-1.03523174	-228.993540	-347.860311	-345.2348112	7.8	10.4
105	acetamide ch3cohn2	-208.8631151	-1.00509141	-209.144541	-222.480222	-220.799902	16.0	17.7

106	Aziridine. (cyclic	-133.659701	-0.71260528	-133.859230	146.284654	147.019794	19.9	20.7
107	Cyanogen. NCCN.	-185.34123	-0.90896191	-185.595739	302.216666	302.951806	-4.5	-3.7
108	DIMETHYLAMINE b3lyp	-134.8882846	-0.73655287	-135.094519	6.991567	7.726706561	25.4	26.1
109	TRANS ETHYLAMINE	-134.899826	-0.73771345	-135.106386	-23.226186	-22.49104566	24.1	24.8
110	KETENE B3LYP	-152.3509841	-0.71154075	-152.550215	-50.704600	-49.0242797	-3.4	-1.7
111	OXIRANE B3LYP	-153.5211334	-0.74304817	-153.729187	-36.438526	-34.75820592	16.3	18.0
112	Acetaldehyde B3LYP	-153.5668388	-0.73526399	-153.772713	-153.834843	-152.1545231	12.3	14.0
113	Glyoxal, O=CH-CH=O.	-227.4749367	-1.00269154	-227.755690	-207.383252	-204.7577524	4.7	7.4
114	ETHANOL TRANS	-154.7634242	-0.76590091	-154.977876	-209.594530	-207.91421	25.5	27.2
115	DIMETHYL ETHER,	-154.7466356	-0.76291081	-154.960251	-164.160468	-162.4801478	19.9	21.6
116	Thiooxirane. (cyclic	-476.4402612	-0.82756693	-476.671980	99.839892	102.9117268	17.8	20.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.7500101	-1.16800257	-553.077051	-110.002617	-105.9856019	41.5	45.5
118	Thioethanol. CH3-CH2-SH.	-477.6592487	-0.8464147	-477.896245	-16.164959	-13.09312416	30.3	33.3
119	ch3sch3 B3LYP	-477.6571845	-0.84826851	-477.894700	-9.582323	-6.51048841	27.7	30.7
120	Vinyl fluoride,	-177.564914	-0.74137477	-177.772499	-134.265477	-131.9287819	4.6	7.0
121	Ethyl chloride.	-539.0690698	-0.78176144	-539.287963	-93.928997	-89.6756871	18.2	22.5
122	Vinyl chloride,	-537.8451229	-0.7530359	-538.055973	33.615046	37.86835612	10.6	14.9
123	h2c=chcn B3LYP	-170.5159069	-0.87461057	-170.760798	196.037910	197.1406202	15.3	16.4
124	ACETONE B3LYP	-192.8067588	-0.95984492	-193.075515	-196.158277	-194.1103873	21.0	23.0
125	CH3COOH ACETIC	-228.7295381	-1.03487974	-229.019304	-415.958298	-413.3327985	16.7	19.3
126	CH3CFO HCCO	-252.7399621	-1.04343448	-253.032124	-433.708022	-430.4261475	8.5	11.8
127	ch3c(o)cl hcco	-613.0065277	-1.05924619	-613.303117	-233.465278	-228.2667877	9.2	14.4
128	ch3ch2ch2cl B3LYP	-578.2972792	-1.00714619	-578.579280	-105.556607	-100.9357271	26.2	30.9
129	Isopropyl alcohol,	-193.9964641	-0.99323043	-194.274569	-237.119216	-235.0713258	35.7	37.7
130	Methyl ethyl	-193.9799461	-0.98745034	-194.256432	-188.953354	-186.9054645	27.4	29.4
131	Trimethyl Amine.	-174.1100295	-0.96484651	-174.380187	7.507159	8.609868739	31.4	32.5
132	FURAN B3LYP	-229.6125759	-1.14200971	-229.932339	-20.112905	-17.69744505	14.6	17.0
133	Thiophene b3lyp	-552.5211727	-1.23341782	-552.866530	136.402924	140.2098995	21.3	25.1
134	PYROLE PLANAR	-209.7656849	-1.11470336	-210.077802	121.453984	122.9242639	13.1	14.6
135	C2v Pyridine	-247.8082208	-1.30014136	-248.172260	148.486081	150.3239307	7.9	9.7
136	H2 B3LYP/6-31G*	-1.15953977	-0.03456622	-1.169218	8.167184	8.167184314	8.2	8.2
137	SH b3lyp/6-31G*	-398.5688338	-0.35735636	-398.668894	148.253817	150.5905117	5.2	7.5
138	CCH B3LYP	-76.46552054	-0.37812329	-76.571395	583.872798	584.607938	18.6	19.3
139	C2H3 CS,2-A'	-77.74606785	-0.39997433	-77.858061	307.461277	308.1964169	7.9	8.6
140	ch3co hcco	-152.924943	-0.7132157	-153.124643	-5.875165	-4.194844687	4.2	5.8
141	H2COH C1	-114.8778508	-0.50968141	-115.020562	-7.160870	-5.848120119	10.0	11.3
142	ch3o CS,	-114.8714023	-0.48294686	-115.006627	25.849972	27.16272196	8.7	10.0

143	ch3ch2o 2A"	-154.1045392	-0.70695342	-154.302486	1.327227	3.007547143	16.8	18.5
144	ch3s 2-A'	-437.7980147	-0.5848276	-437.961766	133.660318	136.364583	9.0	11.7
145	c2h5 staggered	-78.98562412	-0.43138293	-79.106411	134.948466	135.6836058	14.0	14.8
146	(ch3)2ch Cs	-118.2183629	-0.65745887	-118.402451	110.947260	112.0499697	21.0	22.1
147	TERT-BUTYL RADICAL	-157.4512572	-0.88554784	-157.699211	84.795406	86.26568579	33.3	34.8
148	NO2 RADICAL	-204.7751703	-0.89817312	-205.026659	32.158186	34.04854561	-0.9	1.0

MAD	**14.6**	**16.5**
LD	**42.1**	**50.3**

Table S5.47b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.468306	-0.014519	-7.472372
3	be	-14.636727	-0.052812	-14.651515
4	b	-24.615722	-0.076614	-24.637174
5	c	-37.798649	-0.103303	-37.827574
6	n	-54.531657	-0.133960	-54.569165
7	o	-74.993933	-0.190861	-75.047374
8	f	-99.639675	-0.253452	-99.710642
9	na	-162.146031	-0.170615	-162.193804
10	al	-242.227523	-0.218904	-242.288817
11	si	-289.228146	-0.248773	-289.297802
12	p	-341.110537	-0.277656	-341.188281
13	s	-397.944303	-0.318682	-398.033534
14	cl	-459.962115	-0.289489	-460.043172

Table S5.48a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0466635	-0.0463724	-8.060111	147.478647	147.4786466	8.2	8.2
2	BERYLLIUM HYDRIDE	-15.22226545	-0.05465316	-15.238115	319.479994	319.4799942	-22.4	-22.4
3	DOUBLET CH	-38.41631196	-0.14365109	-38.457971	600.623652	600.9912219	4.4	4.8
4	CH2 3-B1	-39.0795176	-0.16267212	-39.126693	395.952209	396.3197786	3.9	4.3
5	Singlet methylene,	-39.05587369	-0.18266461	-39.108846	441.195055	441.5626254	11.1	11.4
6	Methyl radical,	-39.75138057	-0.20723252	-39.811478	153.027894	153.3954638	6.6	7.0
7	ch4 //b3lyp/6-31G*	-40.41575688	-0.24866082	-40.487869	-62.551920	-62.18434984	12.3	12.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14519591	-0.18662455	-55.199317	360.134169	360.1341691	3.7	3.7
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78580551	-0.23979539	-55.855346	190.890160	190.8901598	2.2	2.2
10	AMMONIA, //b3lyp/6-31G*	-56.45091357	-0.2934565	-56.536016	-34.370568	-34.37056786	11.7	11.7
11	OH RADICAL	-75.63931136	-0.25709742	-75.713870	43.103372	44.0485518	3.8	4.7
12	Water //b3lyp/6-31G*	-76.31557749	-0.3253445	-76.409927	-227.825306	-226.8801263	14.0	15.0
13	HYDROGEN FLUORIDE,	-100.3333197	-0.33610626	-100.430791	-265.099008	-263.4974526	7.3	8.9
14	SIH2 singlet	-290.4444735	-0.30426854	-290.532711	276.461149	278.2464892	3.7	5.4
15	SIH2 3B1	-290.4187468	-0.28189738	-290.500497	362.050733	363.8360732	1.4	3.2
16	SIH3 c3v	-291.0597881	-0.30970391	-291.149602	203.644420	205.4297601	3.2	5.0
17	SIH4 //b3lyp/6-31G*	-291.702425	-0.33673051	-291.800077	43.585826	45.37116648	9.3	11.1
18	ph2 doublet	-342.3261407	-0.34356282	-342.425774	141.420154	141.4201543	2.9	2.9
19	PH3 c3v	-342.9535086	-0.37446838	-343.062104	19.996217	19.99621745	14.6	14.6
20	SH2 //b3lyp/6-31G*	-399.1996635	-0.39580893	-399.314448	-8.558416	-6.221721283	11.9	14.3
21	HCL //b3lyp/6-31G*	-460.6090216	-0.33431231	-460.705972	-88.077853	-84.55968302	4.4	7.9
22	DILITHIUM //b3lyp/6-31G*	-14.96039483	-0.0574693	-14.977061	230.981833	230.9818334	15.1	15.1
23	Lithium Fluoride,	-107.2957547	-0.36481443	-107.401551	-336.384637	-334.7830818	-1.2	0.4
24	ACETYLENE //b3lyp/6-31g*	-77.17458428	-0.41541846	-77.295056	234.984326	235.7194655	8.2	8.9
25	ETHYLENE //b3lyp/6-31g*	-78.4163307	-0.43653128	-78.542925	66.001605	66.73674467	13.7	14.4
26	ETHANE //b3lyp/6-31g*	-79.63938363	-0.46992829	-79.775663	-64.561978	-63.82683806	19.5	20.3
27	CYANO RADICAL,	-92.54904194	-0.44950718	-92.679399	453.116755	453.4843254	14.2	14.6
28	HYDROGEN CYANIDE	-93.25974603	-0.45961261	-93.393034	131.306198	131.6737684	-0.5	-0.1
29	CARBON MONOXIDE	-113.1503984	-0.47043712	-113.286825	-110.063883	-108.7511332	0.4	1.7
30	HCO BENT	-113.6755558	-0.49276977	-113.818459	37.727127	39.03987697	-4.1	-2.8
31	H2CO //b3lyp/6-31g*	-114.3178618	-0.51227156	-114.466421	-106.271165	-104.9584152	2.5	3.8

32	METHANOL //b3lyp/6-31g*	-115.524061	-0.54196336	-115.681230	-186.834120	-185.5213697	14.0	15.3
33	Nitrogen N2,	-109.3569402	-0.49317104	-109.499960	3.819877	3.819876632	3.8	3.8
34	H2NNH2 //b3lyp/6-31g*	-111.6643781	-0.55652921	-111.825772	111.263858	111.2638577	15.9	15.9
35	NO radical,	-129.7032192	-0.53497026	-129.858361	91.220597	92.16577652	0.8	1.8
36	O2 //b3lyp/6-31g*	-150.1116684	-0.59924163	-150.285448	-0.942125	0.948234929	-0.9	0.9
37	HYDROGEN PEROXIDE	-151.3281219	-0.62879644	-151.510473	-112.035950	-110.1455902	23.9	25.8
38	F2 //b3lyp/6-31g*	-199.281963	-0.65743011	-199.472618	22.462781	25.66589126	22.5	25.7
39	CO2 D*H	-188.3168357	-0.79096494	-188.546216	-407.887777	-405.6298468	-14.6	-12.3
40	na2 //b3lyp/6-31G*	-324.3020346	-0.36924158	-324.409115	144.363345	144.363345	2.1	2.1
41	SI2 3-SGG	-578.5458406	-0.5555515	-578.706951	590.732369	594.3030492	5.4	9.0
42	P2 //b3lyp/6-31g*	-682.3480523	-0.70479704	-682.552443	157.119342	157.1193417	13.6	13.6
43	S2 //b3lyp/6-31g*	-796.0038034	-0.75235255	-796.221986	130.702822	135.3762116	2.3	6.9
44	CL2 //b3lyp/6-31g*	-919.9790792	-0.6471687	-920.166758	10.155391	17.19173097	10.2	17.2
45	Sodium Chloride	-622.237311	-0.50568515	-622.383960	-174.936468	-171.4182984	7.5	11.0
46	SIO //b3lyp/6-31g*	-364.4669993	-0.61178925	-364.644418	-93.310622	-90.58010174	9.6	12.3
47	Carbon monosulfide,	-435.9609553	-0.57162794	-436.126727	289.948667	292.6529323	10.0	12.7
48	OS //b3lyp/6-31g*	-473.0779602	-0.68245777	-473.275873	6.541995	9.823870049	1.5	4.8
49	CLO 2-PI	-535.0097042	-0.59979377	-535.183644	114.601757	119.0651074	13.3	17.8
50	CLF 1-SG	-559.6559884	-0.64951882	-559.844349	-48.622011	-43.5022859	6.6	11.7
51	si2h6 //b3lyp/6-31g*	-582.2314356	-0.6543708	-582.421203	99.284782	102.8554616	19.4	22.9
52	Methyl chloride,	-499.8273782	-0.55643923	-499.988746	-73.739292	-69.85355162	8.3	12.2
53	H3C-SH METHANETHIOL	-438.4209252	-0.62043272	-438.600851	-3.800731	-1.096465503	19.2	21.9
54	HOCl //b3lyp/6-31g*	-535.6566293	-0.64089555	-535.842489	-62.811528	-58.34817829	11.7	16.1
55	SO2 //b3lyp/6-31G*	-548.2295535	-1.02571452	-548.527011	-274.765796	-270.5387412	22.3	26.5
56	BF3 PLANAR	-324.2115536	-1.06444803	-324.520244	-1147.165859	-1142.229919	-11.6	-6.7
57	bcl3 B3LYP	-1404.954751	-1.10210178	-1405.274361	-418.418927	-407.7331424	-15.5	-4.8
58	ALf3 B3LYP	-541.7409963	-1.20269549	-542.089778	-1193.519307	-1187.821972	15.7	21.4
59	alcl3 B3LYP	-1622.544168	-1.20411627	-1622.893361	-589.297685	-577.8505049	-4.8	6.7
60	cf4 B3LYP	-437.007468	-1.45417414	-437.429178	-942.801554	-936.0277638	-9.8	-3.0
61	ccl4 B3LYP	-1878.035706	-1.52807766	-1878.478849	-88.618160	-74.17790995	7.2	21.6
62	O=C=S. Singlet	-511.1854641	-0.88117982	-511.441006	-152.559619	-148.9101744	-14.1	-10.4
63	CS2 B3LYP	-834.0505765	-0.97844737	-834.334326	107.210059	112.2510189	-9.5	-4.5
64	COF2 B3LYP	-312.6395454	-1.12331867	-312.965308	-617.169565	-612.6537054	6.7	11.2
65	sif4 B3LYP	-688.5825794	-1.55502576	-689.033537	-1577.033986	-1568.842426	38.0	46.2
66	sicl4, td	-2129.594684	-1.59076534	-2130.056005	-645.656134	-629.7981136	17.1	32.9
67	nno B3LYP	-184.372888	-0.84814229	-184.618849	72.077338	73.02251848	-9.9	-9.0
68	clno B3LYP	-589.6916014	-0.91577901	-589.957177	57.579542	62.04289204	5.7	10.2

69	nf3 c3v	-353.6630036	-1.23774794	-354.021951	-125.826238	-121.0215729	6.4	11.2
70	pf3 c3v	-640.5095824	-1.29686036	-640.885672	-933.768083	-928.9634179	24.8	29.6
71	ozone 1-a1	-225.0687821	-1.01816886	-225.364051	168.625048	171.4605879	26.0	28.8
72	f2o B3LYP	-274.3243366	-0.96925662	-274.605421	48.904205	53.0524955	24.2	28.4
73	CLF3, C2V	-758.9658104	-1.37350426	-759.364127	-146.948024	-138.6251889	12.0	20.4
74	CF2=CF2 D2H	-474.9557401	-1.65470787	-475.435605	-687.910803	-680.7694427	-29.3	-22.2
75	cl2c=ccl2 B3LYP	-1916.05654	-1.72558134	-1916.556959	-19.591452	-4.783631699	-7.0	7.8
76	cf3cn B3LYP	-429.9147781	-1.59531949	-430.377421	-510.498228	-504.9584226	-15.1	-9.6
77	PROPYNE C3V	-116.411509	-0.63801144	-116.596532	195.436580	196.5392904	10.5	11.6
78	ALLENE D2D	-116.411498	-0.63184153	-116.594732	198.506588	199.6092978	8.1	9.2
79	CYCLOPROPENE C2V	-116.3718818	-0.64126502	-116.557849	296.281042	297.3837524	19.3	20.4
80	PROPENE CS	-117.646988	-0.66152481	-117.838830	40.443234	41.54594374	20.4	21.5
81	CYCLOPROPANE D3H	-117.6333341	-0.66784699	-117.827010	73.958996	75.0617057	20.8	21.9
82	PROPANE C2V	-118.8650207	-0.6945299	-119.066434	-76.323827	-75.22111748	28.3	29.4
83	TRANS-1,3-BUTADIENE C2H	-155.6597957	-0.85538296	-155.907857	131.173017	132.6432973	21.1	22.6
84	Dimethyl acetylene	-155.6463522	-0.86119565	-155.896099	162.195452	163.6657325	16.6	18.1
85	Methylene cyclopropane.	-155.6270452	-0.86220005	-155.877083	210.716436	212.1867158	10.3	11.8
86	Bicyclo[1.1.0]butane. C2v	-155.6110574	-0.87396562	-155.864507	245.666527	247.1368065	28.5	30.0
87	CYCLOBUTENE b3lyp	-155.6366105	-0.86440642	-155.887288	186.285798	187.7560778	29.8	31.3
88	CYCLOBUTANE b3lyp/6-31G*	-156.859893	-0.89356984	-157.119028	60.033840	61.50412034	31.6	33.1
89	Isobutene. Single	-156.877414	-0.88923943	-157.135293	12.540590	14.01087035	29.3	30.7
90	Trans butane	-158.0905283	-0.91965608	-158.357229	-88.152799	-86.6825186	37.4	38.8
91	isobutane B3LYP/6-31G*	-158.0915281	-0.92283716	-158.359151	-94.494177	-93.02389715	39.8	41.3
92	Spiropentane. D2d	-194.8467341	-1.09376885	-195.163927	211.194103	213.0319526	25.8	27.7
93	Benzene B3LYP	-231.7680041	-1.25646432	-232.132379	93.563812	95.7692319	11.1	13.3
94	DIFLUOROMETHANE C2V	-238.6941172	-0.85059243	-238.940789	-451.693506	-448.1228258	-1.1	2.5
95	HCF3 TRI-FLUOROMETHANE	-337.8525759	-1.15353462	-338.187101	-702.012043	-696.8398084	-5.0	0.2
96	CH2CL2 C2V	-959.2362949	-0.87306165	-959.489483	-87.239894	-79.83598405	8.2	15.6
97	chcl3 B3LYP/6-31G*	-1418.639854	-1.19720087	-1418.987042	-94.518093	-83.59601299	8.8	19.7
98	METHYLAMINE b3lyp	-95.66313421	-0.5130269	-95.811912	-5.884760	-5.517190157	17.1	17.5
99	Acetonitrile. CH3-CN.	-132.5027465	-0.67999017	-132.699944	77.994931	78.73007065	2.7	3.4
100	NITRO METHANE	-244.6149731	-1.12459559	-244.941106	-67.374577	-65.11664726	7.1	9.4
101	Methyl-nitrite. CH3-O-N=O.	-244.6111424	-1.11405521	-244.934218	-53.019944	-50.76201429	13.5	15.8
102	Methylsilane. CH3-SiH3.	-330.9430802	-0.56315578	-331.106395	-5.780748	-3.62783806	23.5	25.7
103	Formic Acid.	-189.4796643	-0.81335669	-189.715538	-375.507984	-373.2500544	3.1	5.4
104	Methyl formate.	-228.6926473	-1.03521643	-228.992860	-352.567964	-349.9424642	3.1	5.7
105	acetamide ch3cohn2	-208.8522738	-1.00507726	-209.143746	-226.663536	-224.9832156	11.8	13.5

106	Aziridine. (cyclic	-133.6518547	-0.71259285	-133.858507	143.682316	144.4174557	17.3	18.1
107	Cyanogen. NCCN.	-185.3323075	-0.9089294	-185.595897	295.757629	296.4927688	-10.9	-10.2
108	DIMETHYLAMINE b3lyp	-134.8799557	-0.73653932	-135.093552	5.028535	5.763674558	23.4	24.2
109	TRANS ETHYLAMINE	-134.8914934	-0.73770068	-135.105427	-25.210673	-24.47553324	22.1	22.8
110	KETENE B3LYP	-152.3435124	-0.71152558	-152.549855	-54.484589	-52.80426903	-7.2	-5.5
111	OXIRANE B3LYP	-153.5130852	-0.74303816	-153.728566	-39.536018	-37.85569809	13.2	14.9
112	Acetaldehyde B3LYP	-153.558844	-0.73525252	-153.772067	-156.866999	-155.1866791	9.2	10.9
113	Glyoxal, O=CH-CH=O.	-227.4644857	-1.00267809	-227.755262	-212.752892	-210.1273921	-0.6	2.0
114	ETHANOL TRANS	-154.7548776	-0.7658916	-154.976986	-211.983847	-210.3035271	23.2	24.8
115	DIMETHYL ETHER,	-154.7381021	-0.76289957	-154.959343	-166.504467	-164.8241469	17.6	19.3
116	Thiooxirane. (cyclic	-476.4285663	-0.82754998	-476.668556	97.681862	100.7536971	15.7	18.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.7348039	-1.16798447	-553.073519	-113.645425	-109.6284097	37.8	41.8
118	Thioethanol. CH3-CH2-SH.	-477.6470797	-0.846397	-477.892535	-17.572490	-14.50065523	28.9	31.9
119	ch3sch3 B3LYP	-477.6450228	-0.84825083	-477.891016	-11.057839	-7.98600392	26.2	29.3
120	Vinyl fluoride,	-177.5566884	-0.74136459	-177.771684	-136.877758	-134.5410625	2.0	4.4
121	Ethyl chloride.	-539.056661	-0.78174634	-539.283367	-95.389496	-91.13618606	16.7	21.0
122	Vinyl chloride,	-537.8332423	-0.75301896	-538.051618	31.523742	35.7770519	8.5	12.8
123	h2c=chcn B3LYP	-170.5066343	-0.87458229	-170.760263	191.459020	192.5617303	10.7	11.8
124	ACETONE B3LYP	-192.7961719	-0.95982656	-193.074522	-199.756185	-197.708295	17.4	19.4
125	CH3COOH ACETIC	-228.7184902	-1.03486703	-229.018602	-420.606521	-417.9810207	12.0	14.6
126	CH3CFO HCCO	-252.7287169	-1.04342143	-253.031309	-438.087642	-434.8057674	4.2	7.4
127	ch3c(o)cl hcco	-612.9916416	-1.05922744	-613.298818	-237.470511	-232.2720213	5.2	10.4
128	ch3ch2ch2cl B3LYP	-578.2822862	-1.00712497	-578.574352	-107.624843	-103.0039634	24.2	28.8
129	Isopropyl alcohol,	-193.9853237	-0.9932143	-194.273356	-240.142301	-238.0944113	32.7	34.7
130	Methyl ethyl	-193.9688272	-0.98743245	-194.255183	-191.879556	-189.8316656	24.4	26.5
131	Trimethyl Amine.	-174.0991065	-0.9648264	-174.378906	4.885924	5.988633864	28.7	29.8
132	FURAN B3LYP	-229.6003227	-1.14198393	-229.931498	-25.592977	-23.17751678	9.1	11.5
133	Thiophene b3lyp	-552.5052759	-1.23338555	-552.862958	131.672665	135.4796398	16.6	20.4
134	PYROLE PLANAR	-209.7536229	-1.11467599	-210.076879	116.414046	117.8843258	8.0	9.5
135	C2v Pyridine	-247.7941247	-1.30010596	-248.171155	142.443980	144.28183	1.9	3.7
136	H2 B3LYP/6-31G*	-1.15915712	-0.03456651	-1.169181	8.264075	8.264074979	8.3	8.3
137	SH b3lyp/6-31G*	-398.5621556	-0.35735833	-398.665790	148.215651	150.5523456	5.1	7.5
138	CCH B3LYP	-76.46146711	-0.37810371	-76.571117	581.642044	582.3771842	16.4	17.1
139	C2H3 CS,2-A'	-77.74144274	-0.39995373	-77.857429	306.158547	306.8936866	6.6	7.3
140	ch3co hcco	-152.9172792	-0.71319473	-153.124106	-9.190303	-7.509982671	0.9	2.5
141	H2COH C1	-114.8722222	-0.50967277	-115.020027	-9.004732	-7.691981989	8.1	9.5
142	ch3o CS,	-114.8658067	-0.48293208	-115.005857	24.625902	25.93865164	7.5	8.8

143	ch3ch2o 2A"	-154.0963595	-0.70693002	-154.301369	-0.467097	1.213223469	15.0	16.7
144	ch3s 2-A'	-437.7887591	-0.58481996	-437.958357	132.944096	135.6483613	8.3	11.0
145	c2h5 staggered	-78.98044978	-0.43137572	-79.105549	134.252911	134.9880509	13.3	14.1
146	(ch3)2ch Cs	-118.2105971	-0.65744189	-118.401255	109.647398	110.750108	19.7	20.8
147	TERT-BUTYL RADICAL	-157.4408972	-0.8855207	-157.697698	82.845587	84.31586714	31.4	32.9
148	NO2 RADICAL	-204.766851	-0.89815178	-205.027315	25.359541	27.24990132	-7.7	-5.8

MAD	**13.0**	**14.7**
LD	**39.8**	**46.2**

Table S5.48b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.467769	-0.014519	-7.471980
3	be	-14.635778	-0.052807	-14.651092
4	b	-24.614457	-0.076618	-24.636676
5	c	-37.797050	-0.103309	-37.827010
6	n	-54.529728	-0.133964	-54.568578
7	o	-74.991348	-0.190871	-75.046701
8	f	-99.636456	-0.253462	-99.709960
9	na	-162.141940	-0.170613	-162.191418
10	al	-242.222567	-0.218906	-242.286050
11	si	-289.222830	-0.248775	-289.294975
12	p	-341.104867	-0.277651	-341.185385
13	s	-397.937997	-0.318685	-398.030416
14	cl	-459.955195	-0.289493	-460.039147

Table S5.49a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04577519	-0.04637354	-8.059687	147.563860	147.5638601	8.2	8.2
2	BERYLLIUM HYDRIDE	-15.22118467	-0.05464589	-15.237578	319.779366	319.7793661	-22.1	-22.1
3	DOUBLET CH	-38.41433454	-0.14365516	-38.457431	600.560883	600.9284533	4.3	4.7
4	CH2 3-B1	-39.07736601	-0.16267072	-39.126167	395.851635	396.2192046	3.8	4.2
5	Singlet methylene,	-39.05354621	-0.18266096	-39.108344	441.033150	441.40072	10.9	11.3
6	Methyl radical,	-39.74879507	-0.20723619	-39.810966	152.892624	153.2601939	6.5	6.8
7	ch4 //b3lyp/6-31G*	-40.41281094	-0.24865493	-40.487407	-62.821025	-62.45345466	12.1	12.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14281555	-0.18663486	-55.198806	359.933714	359.9337138	3.5	3.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78300937	-0.23980228	-55.854950	190.388028	190.3880282	1.7	1.7
10	AMMONIA, //b3lyp/6-31G*	-56.4477342	-0.29345736	-56.535771	-35.270652	-35.27065201	10.8	10.8
11	OH RADICAL	-75.63630081	-0.25710745	-75.713433	42.483626	43.42880594	3.2	4.1
12	Water //b3lyp/6-31G*	-76.31217314	-0.32535061	-76.409778	-229.199870	-228.2546897	12.6	13.6
13	HYDROGEN FLUORIDE,	-100.329696	-0.33611474	-100.430530	-266.206944	-264.6053886	6.2	7.8
14	SIH2 singlet	-290.4384997	-0.30426082	-290.529778	276.740088	278.5254281	3.9	5.7
15	SIH2 3B1	-290.4129692	-0.28187135	-290.497531	362.416352	364.2016919	1.8	3.5
16	SIH3 c3v	-291.0536344	-0.30968925	-291.146541	204.258710	206.0440496	3.8	5.6
17	SIH4 //b3lyp/6-31G*	-291.695933	-0.33672168	-291.796950	44.373990	46.15932977	10.1	11.9
18	ph2 doublet	-342.3197096	-0.34356275	-342.422778	141.682242	141.6822424	3.2	3.2
19	PH3 c3v	-342.9467497	-0.37445941	-343.059087	20.314529	20.31452913	14.9	14.9
20	SH2 //b3lyp/6-31G*	-399.1926454	-0.39580329	-399.311386	-8.707457	-6.370762253	11.8	14.1
21	HCL //b3lyp/6-31G*	-460.6017507	-0.33431003	-460.702044	-88.329063	-84.81089322	4.1	7.7
22	DILITHIUM //b3lyp/6-31G*	-14.95905716	-0.05746526	-14.976297	230.930933	230.9309333	15.0	15.0
23	Lithium Fluoride,	-107.2915777	-0.36482866	-107.401026	-337.826759	-336.2252035	-2.7	-1.1
24	ACETYLENE //b3lyp/6-31g*	-77.17013652	-0.41540022	-77.294757	232.810035	233.545175	6.0	6.8
25	ETHYLENE //b3lyp/6-31g*	-78.41134595	-0.43651736	-78.542301	64.679462	65.41460168	12.4	13.1
26	ETHANE //b3lyp/6-31g*	-79.63386249	-0.46991674	-79.774838	-65.354534	-64.61939433	18.7	19.5
27	CYANO RADICAL,	-92.5447759	-0.44942256	-92.679603	449.560221	449.9277913	10.7	11.0
28	HYDROGEN CYANIDE	-93.25510023	-0.45959761	-93.392980	128.426570	128.79414	-3.4	-3.0
29	CARBON MONOXIDE	-113.1455496	-0.470431	-113.286679	-112.925642	-111.6128917	-2.5	-1.2
30	HCO BENT	-113.6704739	-0.49275717	-113.818301	34.896290	36.20904029	-6.9	-5.6
31	H2CO //b3lyp/6-31g*	-114.3124551	-0.5122665	-114.466135	-108.767119	-107.4543691	0.0	1.3

32	METHANOL //b3lyp/6-31g*	-115.5180996	-0.5419604	-115.680688	-188.655079	-187.3423286	12.2	13.5
33	Nitrogen N2,	-109.3521029	-0.4931559	-109.500050	0.499616	0.499616297	0.5	0.5
34	H2NNH2 //b3lyp/6-31g*	-111.6584095	-0.55652823	-111.825368	109.239361	109.2393611	13.8	13.8
35	NO radical,	-129.697939	-0.53496075	-129.858427	87.737540	88.68271996	-2.6	-1.7
36	O2 //b3lyp/6-31g*	-150.1059459	-0.59924077	-150.285718	-5.181964	-3.291604419	-5.2	-3.3
37	HYDROGEN PEROXIDE	-151.3217586	-0.62880119	-151.510399	-115.373802	-113.4834419	20.6	22.5
38	F2 //b3lyp/6-31g*	-199.2752062	-0.65743378	-199.472436	19.357261	22.56037136	19.4	22.6
39	CO2 D*H	-188.3089248	-0.79095183	-188.546210	-412.885712	-410.6277822	-19.6	-17.3
40	na2 //b3lyp/6-31G*	-324.2936077	-0.36923607	-324.404379	144.270700	144.2706996	2.0	2.0
41	SI2 3-SGG	-578.5348606	-0.55553382	-578.701521	590.142924	593.713604	4.8	8.4
42	P2 //b3lyp/6-31g*	-682.33591	-0.70477393	-682.547342	155.307498	155.3074978	11.8	11.8
43	S2 //b3lyp/6-31g*	-795.9907349	-0.75234361	-796.216438	128.893242	133.5666322	0.4	5.1
44	CL2 //b3lyp/6-31g*	-919.9649507	-0.64716114	-920.159099	9.133750	16.17008958	9.1	16.2
45	Sodium Chloride	-622.225982	-0.50568741	-622.377688	-175.299571	-171.7814006	7.1	10.6
46	SIO //b3lyp/6-31g*	-364.4584737	-0.61179744	-364.642013	-96.184162	-93.45364165	6.7	9.5
47	Carbon monosulfide,	-435.9524731	-0.57160823	-436.123956	287.558934	290.2631991	7.6	10.4
48	OS //b3lyp/6-31g*	-473.0685553	-0.68244934	-473.273290	3.369909	6.651784008	-1.7	1.6
49	CLO 2-PI	-534.9997886	-0.59975306	-535.179715	112.588309	117.0516587	11.3	15.8
50	CLF 1-SG	-559.6455261	-0.64951822	-559.840382	-50.561951	-45.44222558	4.7	9.8
51	si2h6 //b3lyp/6-31g*	-582.2188192	-0.65435425	-582.415125	100.396209	103.9668888	20.5	24.1
52	Methyl chloride,	-499.8175534	-0.55643035	-499.984483	-74.591543	-70.70580336	7.4	11.3
53	H3C-SH METHANETHIOL	-438.4113403	-0.62042115	-438.597467	-4.582948	-1.878683343	18.4	21.1
54	HOCl //b3lyp/6-31g*	-535.6463772	-0.6408934	-535.838645	-65.050995	-60.58764525	9.4	13.9
55	SO2 //b3lyp/6-31G*	-548.2170077	-1.02570442	-548.524719	-280.468423	-276.2413681	16.6	20.8
56	BF3 PLANAR	-324.1996189	-1.06444867	-324.518953	-1150.457318	-1145.521378	-14.9	-10.0
57	bcl3 B3LYP	-1404.931865	-1.10208366	-1405.262490	-420.254162	-409.5683771	-17.3	-6.6
58	ALf3 B3LYP	-541.7254677	-1.20270321	-542.086279	-1196.968635	-1191.2713	12.2	17.9
59	alcl3 B3LYP	-1622.517691	-1.20410072	-1622.878922	-590.345995	-578.8988145	-5.8	5.6
60	cf4 B3LYP	-436.9915535	-1.45416665	-437.427803	-947.834704	-941.060914	-14.8	-8.0
61	ccl4 B3LYP	-1878.005189	-1.52805293	-1878.463605	-92.335842	-77.89559222	3.5	17.9
62	O=C=S. Singlet	-511.173917	-0.88115857	-511.438265	-156.794481	-153.1450363	-18.3	-14.7
63	CS2 B3LYP	-834.0353825	-0.97841746	-834.328908	103.581579	108.6225388	-13.2	-8.1
64	COF2 B3LYP	-312.6276385	-1.12330927	-312.964631	-622.220884	-617.705024	1.6	6.1
65	sif4 B3LYP	-688.5630326	-1.55502195	-689.029539	-1581.124275	-1572.932715	33.9	42.1
66	sicl4, td	-2129.560534	-1.59074014	-2130.037756	-647.427293	-631.5692733	15.3	31.2
67	nno B3LYP	-184.365014	-0.84812009	-184.619450	65.649668	66.59484762	-16.4	-15.4
68	clno B3LYP	-589.6791745	-0.91576067	-589.953903	52.303636	56.76698576	0.4	4.9

69	nf3 c3v	-353.6502254	-1.23774226	-354.021548	-131.684275	-126.8796095	0.5	5.3
70	pf3 c3v	-640.4930636	-1.29685702	-640.882121	-937.419581	-932.6149161	21.1	25.9
71	ozone 1-a1	-225.0600052	-1.01814649	-225.365449	159.656329	162.4918692	17.0	19.8
72	f2o B3LYP	-274.3146102	-0.96925492	-274.605387	43.646591	47.79488055	19.0	23.1
73	CLF3, C2V	-758.9483817	-1.37350234	-759.360432	-153.186868	-144.8640335	5.8	14.1
74	CF2=CF2 D2H	-474.9377879	-1.65469834	-475.434197	-694.336835	-687.195475	-35.8	-28.6
75	cl2c=ccl2 B3LYP	-1916.023938	-1.72555108	-1916.541604	-24.497286	-9.689466141	-11.9	2.9
76	cf3cn B3LYP	-429.8978404	-1.59529634	-430.376429	-517.769348	-512.2295435	-22.4	-16.8
77	PROPYNE C3V	-116.4044767	-0.63798799	-116.595873	192.728152	193.8308624	7.8	8.9
78	ALLENE D2D	-116.4044622	-0.63181997	-116.594008	195.967746	197.0704564	5.6	6.7
79	CYCLOPROPENE C2V	-116.3647937	-0.64124767	-116.557168	293.629126	294.7318362	16.6	17.8
80	PROPENE CS	-117.6394171	-0.66150544	-117.837869	38.528422	39.63113167	18.4	19.5
81	CYCLOPROPANE D3H	-117.6256942	-0.66783204	-117.826044	72.055873	73.15858288	18.9	20.0
82	PROPANE C2V	-118.8569152	-0.6945124	-119.065269	-77.703095	-76.60038505	26.9	28.0
83	TRANS-1,3-BUTADIENE C2H	-155.6501754	-0.85535574	-155.906782	128.075623	129.5459026	18.0	19.5
84	Dimethyl acetylene	-155.6367357	-0.86116691	-155.895086	158.936482	160.4067621	13.3	14.8
85	Methylene cyclopropane.	-155.6173624	-0.86217717	-155.876016	207.600734	209.0710137	7.2	8.7
86	Bicyclo[1.1.0]butane. C2v	-155.6013062	-0.87394609	-155.863490	242.419022	243.8893025	25.3	26.7
87	CYCLOBUTENE b3lyp	-155.6269031	-0.86438335	-155.886218	183.176931	184.6472107	26.7	28.2
88	CYCLOBUTANE b3lyp/6-31G*	-156.8496512	-0.89354855	-157.117716	57.560822	59.03110151	29.1	30.6
89	Isobutene. Single	-156.8672492	-0.88921444	-157.134014	9.982201	11.45248102	26.7	28.2
90	Trans butane	-158.0798376	-0.91963235	-158.355727	-90.130045	-88.65976532	35.4	36.9
91	isobutane B3LYP/6-31G*	-158.0808282	-0.92281351	-158.357672	-96.530957	-95.06067656	37.8	39.2
92	Spiropentane. D2d	-194.8343972	-1.09374432	-195.162521	207.488271	209.3261211	22.1	24.0
93	Benzene B3LYP	-231.7541149	-1.25642702	-232.131043	88.192444	90.39786428	5.8	8.0
94	DIFLUOROMETHANE C2V	-238.6847091	-0.85059239	-238.939887	-454.386180	-450.8155005	-3.8	-0.2
95	HCF3 TRI-FLUOROMETHANE	-337.8399163	-1.15353223	-338.185976	-705.910691	-700.7384561	-8.9	-3.7
96	CH2CL2 C2V	-959.2195804	-0.87304846	-959.481495	-88.878228	-81.47431837	6.5	13.9
97	chcl3 B3LYP/6-31G*	-1418.616241	-1.1971823	-1418.975395	-97.115759	-86.19367875	6.2	17.2
98	METHYLAMINE b3lyp	-95.65738646	-0.51302044	-95.811293	-7.280338	-6.912767593	15.7	16.1
99	Acetonitrile. CH3-CN.	-132.4955163	-0.67996949	-132.699507	74.639307	75.37444693	-0.7	0.1
100	NITRO METHANE	-244.6037498	-1.12457566	-244.941123	-73.972181	-71.71425098	0.5	2.8
101	Methyl-nitrite. CH3-O-N=O.	-244.5999559	-1.11403432	-244.934166	-59.436568	-57.17863757	7.1	9.3
102	Methylsilane. CH3-SiH3.	-330.9340048	-0.56314193	-331.102947	-5.630561	-3.477650533	23.7	25.8
103	Formic Acid.	-189.4712068	-0.8133508	-189.715212	-379.664456	-377.4065263	-1.0	1.2
104	Methyl formate.	-228.6816194	-1.03520112	-228.992180	-357.272947	-354.6474471	-1.6	1.0
105	acetamide ch3cohn2	-208.8414326	-1.00506312	-209.142952	-230.844639	-229.1643186	7.6	9.3

106	Aziridine. (cyclic	-133.6440085	-0.71258041	-133.857783	141.081500	141.8166401	14.7	15.5
107	Cyanogen. NCCN.	-185.323385	-0.90889689	-185.596054	289.301462	290.0366024	-17.4	-16.7
108	DIMETHYLAMINE b3lyp	-134.8716269	-0.73652577	-135.092585	3.067024	3.802163771	21.5	22.2
109	TRANS ETHYLAMINE	-134.883161	-0.7376879	-135.104467	-27.193699	-26.45855895	20.1	20.8
110	KETENE B3LYP	-152.3360408	-0.71151042	-152.549494	-58.262511	-56.58219051	-11.0	-9.3
111	OXIRANE B3LYP	-153.5050371	-0.74302816	-153.727946	-42.631713	-40.95139337	10.1	11.8
112	Acetaldehyde B3LYP	-153.5508493	-0.73524106	-153.771422	-159.897255	-158.2169354	6.2	7.9
113	Glyoxal, O=CH-CH=O.	-227.4540347	-1.00266464	-227.754834	-218.119907	-215.494407	-6.0	-3.4
114	ETHANOL TRANS	-154.7463311	-0.7658823	-154.976096	-214.371457	-212.6911366	20.8	22.4
115	DIMETHYL ETHER,	-154.7295688	-0.76288833	-154.958435	-168.846623	-167.1663029	15.2	16.9
116	Thiooxirane. (cyclic	-476.4168715	-0.82753302	-476.665131	95.525691	98.59752625	13.5	16.6
117	Dimethylsulfoxide. (CH3)2SO.	-552.7195978	-1.16796638	-553.069988	-117.285794	-113.2687794	34.2	38.2
118	Thioethanol. CH3-CH2-SH.	-477.6349108	-0.84637931	-477.888825	-18.978218	-15.90638259	27.5	30.5
119	ch3sch3 B3LYP	-477.6328613	-0.84823316	-477.887331	-12.531526	-9.459690506	24.7	27.8
120	Vinyl fluoride,	-177.5484628	-0.74135441	-177.770869	-139.488283	-137.1515882	-0.6	1.8
121	Ethyl chloride.	-539.0442524	-0.78173124	-539.278772	-96.848318	-92.59500838	15.3	19.5
122	Vinyl chloride,	-537.8213617	-0.75300203	-538.047262	29.434256	33.68756558	6.4	10.7
123	h2c=chcn B3LYP	-170.4973617	-0.874554	-170.759728	186.882897	187.9856072	6.1	7.2
124	ACETONE B3LYP	-192.7855851	-0.95980821	-193.073528	-203.351472	-201.303582	13.8	15.8
125	CH3COOH ACETIC	-228.7074423	-1.03485431	-229.017899	-425.252175	-422.6266752	7.4	10.0
126	CH3CFO HCCO	-252.7174719	-1.04340839	-253.030494	-442.464751	-439.1828763	-0.2	3.1
127	ch3c(o)cl hcco	-612.9767556	-1.05920869	-613.294518	-241.473211	-236.2747207	1.2	6.4
128	ch3ch2ch2cl B3LYP	-578.2672932	-1.00710375	-578.569424	-109.690723	-105.0698425	22.1	26.7
129	Isopropyl alcohol,	-193.9741835	-0.99319817	-194.272143	-243.162928	-241.1150378	29.6	31.7
130	Methyl ethyl	-193.9577083	-0.98741457	-194.253933	-194.803187	-192.7552969	21.5	23.6
131	Trimethyl Amine.	-174.0881836	-0.96480629	-174.377625	2.266914	3.369623837	26.1	27.2
132	FURAN B3LYP	-229.5880695	-1.14195815	-229.930657	-31.069619	-28.65415855	3.7	6.1
133	Thiophene b3lyp	-552.4893793	-1.23335328	-552.859385	126.945805	130.7527802	11.9	15.7
134	PYROLE PLANAR	-209.7415611	-1.11464862	-210.075956	111.377204	112.8474841	3.0	4.5
135	C2v Pyridine	-247.7800287	-1.30007056	-248.170050	136.405783	138.2436329	-4.2	-2.3
136	H2 B3LYP/6-31G*	-1.15877447	-0.03456679	-1.169145	8.360958	8.360958292	8.4	8.4
137	SH b3lyp/6-31G*	-398.5554775	-0.35736032	-398.662686	148.177529	150.5142241	5.1	7.4
138	CCH B3LYP	-76.45741377	-0.37808418	-76.570839	579.412919	580.1480589	14.2	14.9
139	C2H3 CS,2-A'	-77.73681774	-0.39993315	-77.856798	304.857469	305.5926093	5.3	6.0
140	ch3co hcco	-152.9096155	-0.71317373	-153.123568	-12.503116	-10.82279551	-2.5	-0.8
141	H2COH C1	-114.8665936	-0.50966415	-115.019493	-10.847315	-9.534564715	6.3	7.6
142	ch3o CS,	-114.8602112	-0.48291733	-115.005086	23.403451	24.71620125	6.2	7.6

143	ch3ch2o 2A"	-154.0881799	-0.70690664	-154.300252	-2.258981	-0.57866059	13.2	14.9
144	ch3s 2-A'	-437.7795036	-0.58481235	-437.954947	132.228775	134.9330401	7.5	10.2
145	c2h5 staggered	-78.97527554	-0.43136854	-79.104686	133.558324	134.2934644	12.6	13.4
146	(ch3)2ch Cs	-118.2028313	-0.65742493	-118.400059	108.349411	109.4521209	18.4	19.5
147	TERT-BUTYL RADICAL	-157.4305373	-0.88549357	-157.696185	80.898544	82.36882365	29.4	30.9
148	NO2 RADICAL	-204.7585318	-0.89813044	-205.027971	18.563414	20.45377435	-14.5	-12.6

MAD	**11.9**	**13.2**
LD	**37.8**	**42.1**

Table S5.49b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.467233	-0.014518	-7.471588
3	be	-14.634829	-0.052803	-14.650670
4	b	-24.613192	-0.076622	-24.636179
5	c	-37.795451	-0.103316	-37.826446
6	n	-54.527800	-0.133967	-54.567990
7	o	-74.988764	-0.190882	-75.046028
8	f	-99.633236	-0.253472	-99.709278
9	na	-162.137849	-0.170611	-162.189032
10	al	-242.217611	-0.218907	-242.283283
11	si	-289.217515	-0.248776	-289.292148
12	p	-341.099196	-0.277645	-341.182490
13	s	-397.931691	-0.318688	-398.027297
14	cl	-459.948275	-0.289496	-460.035123

Table S5.50a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04488692	-0.04637467	-8.059263	147.648935	147.6489352	8.3	8.3
2	BERYLLIUM HYDRIDE	-15.22010397	-0.05463864	-15.237042	320.078747	320.0787471	-21.8	-21.8
3	DOUBLET CH	-38.41235715	-0.14365925	-38.456892	600.498226	600.8657965	4.3	4.6
4	CH2 3-B1	-39.07521454	-0.16266935	-39.125642	395.751215	396.1187853	3.7	4.1
5	Singlet methylene,	-39.05121879	-0.18265732	-39.107843	440.871691	441.2392612	10.8	11.1
6	Methyl radical,	-39.74620962	-0.20723988	-39.810454	152.757434	153.1250043	6.3	6.7
7	ch4 //b3lyp/6-31G*	-40.40986506	-0.24864904	-40.486946	-63.089557	-62.72198712	11.8	12.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14043523	-0.1866452	-55.198295	359.732913	359.7329126	3.3	3.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78021328	-0.23980919	-55.854554	189.885712	189.8857123	1.2	1.2
10	AMMONIA, //b3lyp/6-31G*	-56.44455488	-0.29345823	-56.535527	-36.170596	-36.17059569	9.9	9.9
11	OH RADICAL	-75.6332903	-0.2571175	-75.712997	41.863881	42.8090606	2.5	3.5
12	Water //b3lyp/6-31G*	-76.30876884	-0.32535673	-76.409629	-230.574245	-229.629065	11.3	12.2
13	HYDROGEN FLUORIDE,	-100.3260723	-0.33612322	-100.430271	-267.314743	-265.7131884	5.1	6.7
14	SIH2 singlet	-290.432526	-0.30425309	-290.526844	277.019537	278.8048766	4.2	6.0
15	SIH2 3B1	-290.4071918	-0.28184535	-290.494564	362.783042	364.5683816	2.1	3.9
16	SIH3 c3v	-291.0474807	-0.30967459	-291.143480	204.873708	206.6590475	4.5	6.2
17	SIH4 //b3lyp/6-31G*	-291.6894411	-0.33671286	-291.793822	45.162705	46.94804467	10.9	12.6
18	ph2 doublet	-342.3132786	-0.3435627	-342.419783	141.944003	141.9440035	3.5	3.5
19	PH3 c3v	-342.9399908	-0.37445045	-343.056070	20.633015	20.63301541	15.2	15.2
20	SH2 //b3lyp/6-31G*	-399.1856274	-0.39579764	-399.308325	-8.856020	-6.519325383	11.6	14.0
21	HCL //b3lyp/6-31G*	-460.5944799	-0.33430776	-460.698115	-88.580014	-85.06184377	3.9	7.4
22	DILITHIUM //b3lyp/6-31G*	-14.95771956	-0.05746122	-14.975533	230.880098	230.8800984	15.0	15.0
23	Lithium Fluoride,	-107.2874007	-0.36484291	-107.400502	-339.269070	-337.6675151	-4.1	-2.5
24	ACETYLENE //b3lyp/6-31g*	-77.16568883	-0.41538198	-77.294457	230.637360	231.3724998	3.9	4.6
25	ETHYLENE //b3lyp/6-31g*	-78.40636128	-0.43650343	-78.541677	63.358689	64.09382894	11.1	11.8
26	ETHANE //b3lyp/6-31g*	-79.62834143	-0.46990519	-79.774012	-66.145853	-65.41071294	18.0	18.7
27	CYANO RADICAL,	-92.54050999	-0.44933807	-92.679805	446.008429	446.3759992	7.1	7.5
28	HYDROGEN CYANIDE	-93.25045449	-0.45958261	-93.392925	125.548317	125.9158873	-6.2	-5.9
29	CARBON MONOXIDE	-113.1407009	-0.47042488	-113.286533	-115.786115	-114.4733648	-5.3	-4.0
30	HCO BENT	-113.665392	-0.49274454	-113.818143	32.067025	33.37977497	-9.8	-8.5
31	H2CO //b3lyp/6-31g*	-114.3070484	-0.51226144	-114.465849	-111.261869	-109.9491195	-2.5	-1.2

32	METHANOL //b3lyp/6-31g*	-115.5121383	-0.54195744	-115.680145	-190.474997	-189.1622467	10.4	11.7
33	Nitrogen N2,	-109.3472657	-0.49314076	-109.500139	-2.819304	-2.819303983	-2.8	-2.8
34	H2NNH2 //b3lyp/6-31g*	-111.6524409	-0.55652726	-111.824964	107.215348	107.2153479	11.8	11.8
35	NO radical,	-129.6926588	-0.53495124	-129.858494	84.255825	85.20100503	-6.1	-5.2
36	O2 //b3lyp/6-31g*	-150.1002234	-0.59923991	-150.285988	-9.420619	-7.53025914	-9.4	-7.5
37	HYDROGEN PEROXIDE	-151.3153954	-0.62880593	-151.510325	-118.710782	-116.8204217	17.3	19.2
38	F2 //b3lyp/6-31g*	-199.2684495	-0.65743744	-199.472255	16.252746	19.45585624	16.3	19.5
39	CO2 D*H	-188.3010139	-0.79093871	-188.546205	-417.881365	-415.6234347	-24.6	-22.3
40	na2 //b3lyp/6-31G*	-324.285181	-0.36923055	-324.399643	144.178070	144.1780701	1.9	1.9
41	SI2 3-SGG	-578.5238807	-0.55551617	-578.696091	589.554549	593.1252287	4.2	7.8
42	P2 //b3lyp/6-31g*	-682.3237678	-0.70475081	-682.542241	153.496378	153.4963777	10.0	10.0
43	S2 //b3lyp/6-31g*	-795.9776665	-0.75233468	-796.210890	127.084524	131.7579137	-1.4	3.3
44	CL2 //b3lyp/6-31g*	-919.9508222	-0.64715357	-920.151440	8.112967	15.149307	8.1	15.1
45	Sodium Chloride	-622.214653	-0.50568967	-622.371417	-175.662600	-172.1444303	6.8	10.3
46	SIO //b3lyp/6-31g*	-364.4499481	-0.61180563	-364.639608	-99.057440	-96.32691954	3.9	6.6
47	Carbon monosulfide,	-435.943991	-0.57158853	-436.121183	285.170822	287.8750868	5.3	8.0
48	OS //b3lyp/6-31g*	-473.0591504	-0.6824409	-473.270707	0.199017	3.480892043	-4.8	-1.5
49	CLO 2-PI	-534.9898731	-0.59971238	-535.175784	110.577717	115.0410673	9.3	13.8
50	CLF 1-SG	-559.6350638	-0.64951761	-559.836414	-52.501042	-47.38131722	2.7	7.8
51	si2h6 //b3lyp/6-31g*	-582.2062029	-0.65433771	-582.409048	101.508768	105.0794478	21.6	25.2
52	Methyl chloride,	-499.8077286	-0.55642147	-499.980219	-75.442760	-71.55702013	6.6	10.4
53	H3C-SH METHANETHIOL	-438.4017554	-0.62040959	-438.594082	-5.364078	-2.659812652	17.6	20.4
54	HOCl //b3lyp/6-31g*	-535.6361252	-0.64089125	-535.834802	-67.289553	-62.82620273	7.2	11.6
55	SO2 //b3lyp/6-31G*	-548.204462	-1.02569432	-548.522427	-286.169128	-281.9420729	10.9	15.1
56	BF3 PLANAR	-324.1876842	-1.06444931	-324.517663	-1153.746793	-1148.810853	-18.2	-13.3
57	bcl3 B3LYP	-1404.908979	-1.10206554	-1405.250619	-422.087464	-411.4016795	-19.2	-8.5
58	ALf3 B3LYP	-541.7099392	-1.20271094	-542.082780	-1200.416450	-1194.719115	8.8	14.5
59	alcl3 B3LYP	-1622.491215	-1.20408518	-1622.864482	-591.392659	-579.945479	-6.9	4.6
60	cf4 B3LYP	-436.9756391	-1.45415916	-437.426428	-952.864688	-946.0908978	-19.8	-13.1
61	ccl4 B3LYP	-1877.974672	-1.5280282	-1878.448360	-96.050898	-81.61064794	-0.2	14.2
62	O=C=S. Singlet	-511.16237	-0.88113732	-511.435523	-161.027090	-157.3776447	-22.5	-18.9
63	CS2 B3LYP	-834.0201887	-0.97838755	-834.323489	99.955463	104.9964232	-16.8	-11.7
64	COF2 B3LYP	-312.6157318	-1.12329987	-312.963955	-627.269556	-622.7536957	-3.4	1.1
65	sif4 B3LYP	-688.5434859	-1.55501815	-689.025542	-1585.211819	-1577.020259	29.8	38.0
66	sicl4, td	-2129.526385	-1.59071494	-2130.019507	-649.196021	-633.3380013	13.5	29.4
67	nno B3LYP	-184.3571401	-0.84809788	-184.620050	59.224312	60.16949167	-22.8	-21.8
68	clno B3LYP	-589.6667477	-0.91574233	-589.950628	47.029788	51.49313787	-4.9	-0.4

69	nf3 c3v	-353.6374472	-1.23773659	-354.021146	-137.539951	-132.7352863	-5.3	-0.5
70	pf3 c3v	-640.4765449	-1.29685367	-640.878570	-941.069361	-936.2646956	17.5	22.3
71	ozone 1-a1	-225.0512285	-1.01812412	-225.366847	150.690573	153.526113	8.0	10.9
72	f2o B3LYP	-274.3048839	-0.96925322	-274.605352	38.390824	42.53911395	13.7	17.9
73	CLF3, C2V	-758.9309532	-1.37350043	-759.356738	-159.423623	-151.1007877	-0.4	7.9
74	CF2=CF2 D2H	-474.9198357	-1.65468881	-475.432789	-700.759226	-693.6178657	-42.2	-35.1
75	cl2c=ccl2 B3LYP	-1915.991337	-1.72552081	-1916.526248	-29.399854	-14.59203367	-16.8	-2.0
76	cf3cn B3LYP	-429.8809028	-1.5952732	-430.375437	-525.036482	-519.4966773	-29.7	-24.1
77	PROPYNE C3V	-116.3974445	-0.63796454	-116.595214	190.021955	191.1246651	5.1	6.2
78	ALLENE D2D	-116.3974266	-0.63179841	-116.593284	193.431036	194.5337463	3.1	4.2
79	CYCLOPROPENE C2V	-116.3577056	-0.64123032	-116.556487	290.979147	292.0818566	14.0	15.1
80	PROPENE CS	-117.6318463	-0.66148608	-117.836907	36.615592	37.71830159	16.5	17.6
81	CYCLOPROPANE D3H	-117.6180543	-0.66781709	-117.825078	70.154534	71.25724435	17.0	18.1
82	PROPANE C2V	-118.8488098	-0.6944949	-119.064103	-79.080444	-77.97773443	25.5	26.6
83	TRANS-1,3-BUTADIENE C2H	-155.6405552	-0.85532853	-155.905707	124.980990	126.4512701	14.9	16.4
84	Dimethyl acetylene	-155.6271194	-0.86113817	-155.894072	155.680388	157.1506682	10.1	11.5
85	Methylene cyclopropane.	-155.6076797	-0.86215428	-155.874948	204.487609	205.9578885	4.1	5.5
86	Bicyclo[1.1.0]butane. C2v	-155.591555	-0.87392657	-155.862472	239.173956	240.6442357	22.0	23.5
87	CYCLOBUTENE b3lyp	-155.6171958	-0.86436027	-155.885147	180.070677	181.5409567	23.6	25.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.8394096	-0.89352725	-157.116403	55.090270	56.56054985	26.6	28.1
89	Isobutene. Single	-156.8570845	-0.88918944	-157.132733	7.426473	8.896753152	24.2	25.6
90	Trans butane	-158.069147	-0.91960862	-158.354226	-92.104784	-90.63450364	33.4	34.9
91	isobutane B3LYP/6-31G*	-158.0701284	-0.92278986	-158.356193	-98.565153	-97.094873	35.7	37.2
92	Spiropentane. D2d	-194.8220605	-1.0937198	-195.161114	203.785481	205.6233312	18.4	20.3
93	Benzene B3LYP	-231.7402258	-1.25638973	-232.129707	82.825157	85.03057694	0.4	2.6
94	DIFLUOROMETHANE C2V	-238.675301	-0.85059235	-238.938985	-457.077348	-453.5066682	-6.5	-2.9
95	HCF3 TRI-FLUOROMETHANE	-337.8272567	-1.15352984	-338.184851	-709.807074	-704.6348394	-12.8	-7.6
96	CH2CL2 C2V	-959.202866	-0.87303528	-959.473507	-90.515109	-83.11119895	4.9	12.3
97	chcl3 B3LYP/6-31G*	-1418.592628	-1.19716373	-1418.963749	-99.711401	-88.78932078	3.6	14.6
98	METHYLAMINE b3lyp	-95.65163878	-0.51301398	-95.810673	-8.675014	-8.307443958	14.3	14.7
99	Acetonitrile. CH3-CN.	-132.4882862	-0.67994881	-132.699070	71.285699	72.02083907	-4.0	-3.3
100	NITRO METHANE	-244.5925266	-1.12455575	-244.941139	-80.566974	-78.30904437	-6.1	-3.8
101	Methyl-nitrite. CH3-O-N=O.	-244.5887695	-1.11401343	-244.934114	-65.850340	-63.59241008	0.7	2.9
102	Methylsilane. CH3-SiH3.	-330.9249295	-0.56312808	-331.099499	-5.479182	-3.326271555	23.8	26.0
103	Formic Acid.	-189.4627494	-0.81334491	-189.714886	-383.819111	-381.5611813	-5.2	-2.9
104	Methyl formate.	-228.6705915	-1.03518581	-228.991499	-361.975250	-359.3497504	-6.3	-3.7
105	acetamide ch3cohn2	-208.8305915	-1.00504897	-209.142157	-235.023491	-233.3431713	3.5	5.1

106	Aziridine. (cyclic	-133.6361625	-0.71256798	-133.857059	138.482233	139.2173733	12.1	12.9
107	Cyanogen. NCCN.	-185.3144627	-0.90886439	-185.596211	282.848250	283.5833899	-23.8	-23.1
108	DIMETHYLAMINE b3lyp	-134.8632982	-0.73651223	-135.091617	1.107094	1.842233797	19.5	20.3
109	TRANS ETHYLAMINE	-134.8748286	-0.73767513	-135.103508	-29.175158	-28.44001803	18.1	18.8
110	KETENE B3LYP	-152.3285693	-0.71149526	-152.549133	-62.038330	-60.35801001	-14.8	-13.1
111	OXIRANE B3LYP	-153.496989	-0.74301816	-153.727325	-45.725604	-44.04528389	7.0	8.7
112	Acetaldehyde B3LYP	-153.5428546	-0.73522959	-153.770776	-162.925675	-161.2453546	3.2	4.9
113	Glyoxal, O=CH-CH=O.	-227.4435838	-1.0026512	-227.754406	-223.484348	-220.858848	-11.4	-8.7
114	ETHANOL TRANS	-154.7377846	-0.76587299	-154.975205	-216.757369	-215.0770487	18.4	20.1
115	DIMETHYL ETHER,	-154.7210355	-0.7628771	-154.957527	-171.186970	-169.5066498	12.9	14.6
116	Thiooxirane. (cyclic	-476.4051768	-0.82751607	-476.661707	93.371286	96.44312129	11.4	14.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.7043918	-1.16794829	-553.066456	-120.923761	-116.9067459	30.5	34.6
118	Thioethanol. CH3-CH2-SH.	-477.6227421	-0.84636161	-477.885114	-20.382177	-17.31034193	26.1	29.1
119	ch3sch3 B3LYP	-477.6206998	-0.84821548	-477.883647	-14.003445	-10.93161013	23.2	26.3
120	Vinyl fluoride,	-177.5402373	-0.74134424	-177.770054	-142.097044	-139.7603486	-3.2	-0.9
121	Ethyl chloride.	-539.0318439	-0.78171615	-539.274176	-98.305472	-94.05216167	13.8	18.1
122	Vinyl chloride,	-537.8094812	-0.75298509	-538.042907	27.346551	31.59986066	4.3	8.6
123	h2c=chcn B3LYP	-170.4880893	-0.87452571	-170.759192	182.309584	183.412294	1.6	2.7
124	ACETONE B3LYP	-192.7749984	-0.95978986	-193.072533	-206.944200	-204.8963102	10.2	12.3
125	CH3COOH ACETIC	-228.6963946	-1.0348416	-229.017195	-429.895320	-427.2698205	2.7	5.4
126	CH3CFO HCCO	-252.7062269	-1.04339535	-253.029679	-446.839288	-443.5574129	-4.6	-1.3
127	ch3c(o)cl hcco	-612.9618696	-1.05918994	-613.290219	-245.473419	-240.2749291	-2.8	2.4
128	ch3ch2ch2cl B3LYP	-578.2523004	-1.00708253	-578.564496	-111.754288	-107.1334075	20.0	24.7
129	Isopropyl alcohol,	-193.9630434	-0.99318204	-194.270930	-246.181138	-244.1332483	26.6	28.7
130	Methyl ethyl	-193.9465897	-0.98739669	-194.252683	-197.724363	-195.6764729	18.6	20.6
131	Trimethyl Amine.	-174.0772609	-0.96478619	-174.376345	-0.349803	0.752907185	23.5	24.6
132	FURAN B3LYP	-229.5758165	-1.14193238	-229.929815	-36.542899	-34.12743889	-1.8	0.6
133	Thiophene b3lyp	-552.4734828	-1.23332101	-552.855812	122.222312	126.0292873	7.2	11.0
134	PYROLE PLANAR	-209.7294993	-1.11462125	-210.075032	106.343466	107.8137458	-2.0	-0.6
135	C2v Pyridine	-247.7659329	-1.30003516	-248.168944	130.371505	132.2093551	-10.2	-8.4
136	H2 B3LYP/6-31G*	-1.15839182	-0.03456708	-1.169108	8.457819	8.457818763	8.5	8.5
137	SH b3lyp/6-31G*	-398.5487995	-0.35736233	-398.659582	148.139434	150.4761291	5.0	7.4
138	CCH B3LYP	-76.45336053	-0.3780647	-76.570561	577.185357	577.920497	11.9	12.7
139	C2H3 CS,2-A'	-77.73219285	-0.3999126	-77.856166	303.558001	304.2931407	4.0	4.7
140	ch3co hcco	-152.9019519	-0.71315272	-153.123029	-15.813617	-14.1332966	-5.8	-4.1
141	H2COH C1	-114.8609652	-0.50965555	-115.018958	-12.688628	-11.37587827	4.5	5.8
142	ch3o CS,	-114.8546158	-0.4829026	-115.004316	22.182592	23.49534191	5.0	6.3

143	ch3ch2o 2A"	-154.0800004	-0.70688329	-154.299134	-4.048487	-2.368166733	11.4	13.1
144	ch3s 2-A'	-437.7702482	-0.58480475	-437.951538	131.514361	134.2186258	6.8	9.5
145	c2h5 staggered	-78.97010139	-0.43136139	-79.103823	132.864695	133.5998354	11.9	12.7
146	(ch3)2ch Cs	-118.1950657	-0.657408	-118.398862	107.053211	108.1559205	17.1	18.2
147	TERT-BUTYL RADICAL	-157.4201777	-0.88546647	-157.694672	78.954110	80.42439016	27.5	29.0
148	NO2 RADICAL	-204.7502127	-0.8981091	-205.028626	11.769820	13.66017994	-21.3	-19.4

MAD	**11.4**	**12.3**
LD	**-42.2**	**38.0**

Table S5.50b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.466696	-0.014517	-7.471196
3	be	-14.633880	-0.052798	-14.650247
4	b	-24.611928	-0.076626	-24.635682
5	c	-37.793853	-0.103322	-37.825883
6	n	-54.525872	-0.133971	-54.567403
7	o	-74.986180	-0.190892	-75.045356
8	f	-99.630016	-0.253482	-99.708596
9	na	-162.133758	-0.170608	-162.186647
10	al	-242.212655	-0.218908	-242.280516
11	si	-289.212200	-0.248778	-289.289321
12	p	-341.093526	-0.277640	-341.179594
13	s	-397.925385	-0.318691	-398.024179
14	cl	-459.941354	-0.289500	-460.031099

Table S5.51a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 32%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04399867	-0.04637582	-8.058839	147.733900	147.7339001	8.4	8.4
2	BERYLLIUM HYDRIDE	-15.21902334	-0.05463141	-15.236505	320.378152	320.3781518	-21.5	-21.5
3	DOUBLET CH	-38.4103798	-0.14366335	-38.456352	600.435647	600.8032169	4.2	4.6
4	CH2 3-B1	-39.07306318	-0.162668	-39.125117	395.650968	396.0185377	3.6	4.0
5	Singlet methylene,	-39.0488914	-0.18265367	-39.107341	440.710759	441.0783286	10.6	11.0
6	Methyl radical,	-39.74362423	-0.2072436	-39.809942	152.622274	152.9898435	6.2	6.5
7	ch4 //b3lyp/6-31G*	-40.40691922	-0.24864315	-40.486485	-63.357480	-62.98990995	11.5	11.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13805495	-0.18665556	-55.197785	359.531696	359.5316956	3.1	3.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77741723	-0.23981611	-55.854158	189.383169	189.383169	0.7	0.7
10	AMMONIA, //b3lyp/6-31G*	-56.44137561	-0.29345911	-56.535283	-37.070476	-37.07047584	9.0	9.0
11	OH RADICAL	-75.63027983	-0.25712756	-75.712561	41.244144	42.18932419	1.9	2.9
12	Water //b3lyp/6-31G*	-76.30536458	-0.32536285	-76.409481	-231.948396	-231.0032165	9.9	10.8
13	HYDROGEN FLUORIDE,	-100.3224487	-0.33613171	-100.430011	-268.422528	-266.820973	4.0	5.6
14	SIH2 singlet	-290.4265523	-0.30424537	-290.523911	277.299515	279.084855	4.5	6.3
15	SIH2 3B1	-290.4014146	-0.28181939	-290.491597	363.150828	364.9361677	2.5	4.3
16	SIH3 c3v	-291.0413272	-0.30965995	-291.140418	205.489433	207.2747732	5.1	6.9
17	SIH4 //b3lyp/6-31G*	-291.6829492	-0.33670403	-291.790694	45.951997	47.73733718	11.6	13.4
18	ph2 doublet	-342.3068476	-0.34356268	-342.416788	142.205427	142.2054274	3.7	3.7
19	PH3 c3v	-342.933232	-0.37444149	-343.053053	20.951684	20.9516839	15.5	15.5
20	SH2 //b3lyp/6-31G*	-399.1786095	-0.39579199	-399.305263	-9.004119	-6.667424325	11.5	13.8
21	HCL //b3lyp/6-31G*	-460.5872091	-0.33430549	-460.694187	-88.830625	-85.31245509	3.6	7.2
22	DILITHIUM //b3lyp/6-31G*	-14.95638205	-0.05745718	-14.974768	230.829276	230.8292761	14.9	14.9
23	Lithium Fluoride,	-107.2832238	-0.36485717	-107.399978	-340.711677	-339.1101224	-5.6	-4.0
24	ACETYLENE //b3lyp/6-31g*	-77.1612412	-0.41536374	-77.294158	228.466295	229.2014355	1.7	2.4
25	ETHYLENE //b3lyp/6-31g*	-78.40137669	-0.4364895	-78.541053	62.039248	62.77438838	9.7	10.5
26	ETHANE //b3lyp/6-31g*	-79.62282046	-0.46989364	-79.773186	-66.935991	-66.2008506	17.2	17.9
27	CYANO RADICAL,	-92.53624422	-0.44925371	-92.680005	442.461251	442.8288211	3.6	3.9
28	HYDROGEN CYANIDE	-93.2458088	-0.45956761	-93.392870	122.671375	123.0389453	-9.1	-8.8
29	CARBON MONOXIDE	-113.1358522	-0.47041876	-113.286386	-118.645342	-117.3325923	-8.2	-6.9
30	HCO BENT	-113.6603103	-0.49273189	-113.817984	29.239259	30.55200881	-12.6	-11.3
31	H2CO //b3lyp/6-31g*	-114.3016417	-0.51225639	-114.465564	-113.755491	-112.4427409	-5.0	-3.7

32	METHANOL //b3lyp/6-31g*	-115.5061771	-0.54195448	-115.679603	-192.293888	-190.9811377	8.5	9.9
33	Nitrogen N2,	-109.3424285	-0.49312563	-109.500229	-6.137071	-6.137071143	-6.1	-6.1
34	H2NNH2 //b3lyp/6-31g*	-111.6464724	-0.55652629	-111.824561	105.191673	105.1916735	9.8	9.8
35	NO radical,	-129.6873787	-0.53494173	-129.858560	80.775377	81.72055716	-9.6	-8.7
36	O2 //b3lyp/6-31g*	-150.094501	-0.59923907	-150.286257	-13.658024	-11.76766412	-13.7	-11.8
37	HYDROGEN PEROXIDE	-151.3090322	-0.62881068	-151.510252	-122.046850	-120.1564899	13.9	15.8
38	F2 //b3lyp/6-31g*	-199.2616928	-0.65744111	-199.472074	13.149047	16.35215712	13.1	16.4
39	CO2 D*H	-188.2931031	-0.7909256	-188.546199	-422.874815	-420.616885	-29.6	-27.3
40	na2 //b3lyp/6-31G*	-324.2767545	-0.36922502	-324.394907	144.085395	144.0853954	1.8	1.8
41	SI2 3-SGG	-578.5129009	-0.55549856	-578.690660	588.967279	592.5379587	3.6	7.2
42	P2 //b3lyp/6-31g*	-682.3116257	-0.70472769	-682.537139	151.685921	151.6859214	8.2	8.2
43	S2 //b3lyp/6-31g*	-795.9645982	-0.75232577	-796.205342	125.276697	129.9500874	-3.2	1.5
44	CL2 //b3lyp/6-31g*	-919.9366939	-0.64714601	-920.143781	7.093040	14.1293798	7.1	14.1
45	Sodium Chloride	-622.2033241	-0.50569194	-622.365146	-176.025617	-172.5074469	6.4	9.9
46	SIO //b3lyp/6-31g*	-364.4414226	-0.61181383	-364.637203	-101.930452	-99.19993225	1.0	3.7
47	Carbon monosulfide,	-435.935509	-0.57156882	-436.118411	282.784273	285.4885378	2.9	5.6
48	OS //b3lyp/6-31g*	-473.0497457	-0.68243246	-473.268124	-2.970640	0.311234589	-8.0	-4.7
49	CLO 2-PI	-534.9799577	-0.59967172	-535.171853	108.570010	113.0333603	7.3	11.8
50	CLF 1-SG	-559.6246016	-0.64951702	-559.832447	-54.439351	-49.31962594	0.8	5.9
51	si2h6 //b3lyp/6-31g*	-582.1935867	-0.65432116	-582.402969	102.622495	106.1931747	22.7	26.3
52	Methyl chloride,	-499.797904	-0.55641259	-499.975956	-76.293016	-72.40727649	5.7	9.6
53	H3C-SH METHANETHIOL	-438.3921707	-0.62039802	-438.590698	-6.144097	-3.439832424	16.9	19.6
54	HOCl //b3lyp/6-31g*	-535.6258733	-0.6408891	-535.830958	-69.527180	-65.06382974	4.9	9.4
55	SO2 //b3lyp/6-31G*	-548.1919164	-1.02568423	-548.520135	-291.867869	-287.6408144	5.2	9.4
56	BF3 PLANAR	-324.1757496	-1.06444996	-324.516374	-1157.034434	-1152.098494	-21.5	-16.6
57	bcl3 B3LYP	-1404.886093	-1.10204741	-1405.238748	-423.918809	-413.2330243	-21.0	-10.3
58	ALf3 B3LYP	-541.6944109	-1.20271867	-542.079281	-1203.862862	-1198.165527	5.3	11.0
59	alcl3 B3LYP	-1622.464739	-1.20406964	-1622.850041	-592.437551	-580.9903708	-7.9	3.5
60	cf4 B3LYP	-436.9597248	-1.45415168	-437.425053	-957.891822	-951.1180319	-24.9	-18.1
61	ccl4 B3LYP	-1877.944154	-1.52800348	-1878.433116	-99.763299	-85.32304928	-3.9	10.5
62	O=C=S. Singlet	-511.1508231	-0.88111607	-511.432780	-165.257386	-161.6079407	-26.8	-23.1
63	CS2 B3LYP	-834.004995	-0.97835765	-834.318069	96.331703	101.3726627	-20.4	-15.4
64	COF2 B3LYP	-312.603825	-1.12329048	-312.963278	-632.315696	-627.7998363	-8.5	-4.0
65	sif4 B3LYP	-688.5239394	-1.55501434	-689.021544	-1589.296832	-1581.105272	25.7	33.9
66	sicl4, td	-2129.492237	-1.59068974	-2130.001257	-650.962177	-635.1041573	11.8	27.6
67	nno B3LYP	-184.3492663	-0.84807568	-184.620650	52.801130	53.74631015	-29.2	-28.3
68	clno B3LYP	-589.654321	-0.915724	-589.947353	41.757909	46.22125858	-10.1	-5.7

69	nf3 c3v	-353.6246691	-1.23773092	-354.020743	-143.393544	-138.5888785	-11.2	-6.4
70	pf3 c3v	-640.4600263	-1.29685033	-640.875018	-944.717644	-939.912979	13.8	18.6
71	ozone 1-a1	-225.0424518	-1.01810176	-225.368244	141.727802	144.563342	-0.9	1.9
72	f2o B3LYP	-274.2951577	-0.96925152	-274.605318	33.136813	37.28510329	8.5	12.6
73	CLF3, C2V	-758.9135247	-1.37349851	-759.353044	-165.658405	-157.3355702	-6.7	1.7
74	CF2=CF2 D2H	-474.9018836	-1.65467929	-475.431381	-707.178280	-700.0369204	-48.6	-41.5
75	cl2c=ccl2 B3LYP	-1915.958735	-1.72549054	-1916.510892	-34.299062	-19.49124214	-21.7	-6.9
76	cf3cn B3LYP	-429.8639653	-1.59525006	-430.374445	-532.299882	-526.7600771	-36.9	-31.4
77	PROPYNE C3V	-116.3904124	-0.63794109	-116.594554	187.317969	188.4206789	2.4	3.5
78	ALLENE D2D	-116.390391	-0.63177685	-116.592560	190.896438	191.9991482	0.5	1.6
79	CYCLOPROPENE C2V	-116.3506176	-0.64121297	-116.555806	288.331058	289.4337679	11.4	12.5
80	PROPENE CS	-117.6242756	-0.66146671	-117.835945	34.704740	35.80745008	14.6	15.7
81	CYCLOPROPANE D3H	-117.6104146	-0.66780214	-117.824111	68.254961	69.35767069	15.1	16.2
82	PROPANE C2V	-118.8407046	-0.69447739	-119.062937	-80.455992	-79.35328166	24.1	25.2
83	TRANS-1,3-BUTADIENE C2H	-155.6309351	-0.85530131	-155.904632	121.889101	123.3593812	11.8	13.3
84	Dimethyl acetylene	-155.6175032	-0.86110943	-155.893058	152.427110	153.8973899	6.8	8.3
85	Methylene cyclopropane.	-155.5979972	-0.8621314	-155.873879	201.376983	202.8472633	1.0	2.4
86	Bicyclo[1.1.0]butane. C2v	-155.5818039	-0.87390704	-155.861454	235.931202	237.4014825	18.8	20.3
87	CYCLOBUTENE b3lyp	-155.6074886	-0.86433719	-155.884076	176.966941	178.4372211	20.5	22.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.829168	-0.89350596	-157.115090	52.622135	54.09241471	24.2	25.6
89	Isobutene. Single	-156.8469199	-0.88916444	-157.131453	4.873312	6.343591979	21.6	23.1
90	Trans butane	-158.0584566	-0.91958489	-158.352724	-94.076996	-92.6067157	31.4	32.9
91	isobutane B3LYP/6-31G*	-158.0594288	-0.92276621	-158.354714	-100.596880	-99.1265999	33.7	35.2
92	Spiropentane. D2d	-194.809724	-1.09369527	-195.159706	200.085620	201.9234703	14.7	16.6
93	Benzene B3LYP	-231.726337	-1.25635244	-232.128370	77.461866	79.66728615	-5.0	-2.8
94	DIFLUOROMETHANE C2V	-238.665893	-0.85059232	-238.938083	-459.767179	-456.196499	-9.2	-5.6
95	HCF3 TRI-FLUOROMETHANE	-337.8145973	-1.15352745	-338.183726	-713.701441	-708.5292063	-16.6	-11.5
96	CH2CL2 C2V	-959.1861518	-0.8730221	-959.465519	-92.150452	-84.74654203	3.2	10.6
97	chcl3 B3LYP/6-31G*	-1418.569015	-1.19714517	-1418.952102	-102.304984	-91.38290441	1.0	12.0
98	METHYLAMINE b3lyp	-95.64589119	-0.51300752	-95.810054	-10.068933	-9.701363128	12.9	13.3
99	Acetonitrile. CH3-CN.	-132.4810562	-0.67992813	-132.698633	67.934000	68.66914047	-7.4	-6.6
100	NITRO METHANE	-244.5813036	-1.12453583	-244.941155	-87.158996	-84.90106575	-12.7	-10.4
101	Methyl-nitrite. CH3-O-N=O.	-244.5775832	-1.11399256	-244.934061	-72.261314	-70.00338434	-5.7	-3.5
102	Methylsilane. CH3-SiH3.	-330.9158543	-0.56311422	-331.096051	-5.326660	-3.173750484	24.0	26.1
103	Formic Acid.	-189.454292	-0.81333902	-189.714560	-387.971935	-385.7140052	-9.3	-7.1
104	Methyl formate.	-228.6595638	-1.0351705	-228.990818	-366.674928	-364.0494277	-11.0	-8.4
105	acetamide ch3cohn2	-208.8197505	-1.00503484	-209.141362	-239.200197	-237.5198768	-0.7	1.0

106	Aziridine. (cyclic	-133.6283165	-0.71255555	-133.856334	135.884443	136.6195826	9.5	10.3
107	Cyanogen. NCCN.	-185.3055404	-0.90883188	-185.596367	276.397851	277.1329908	-30.3	-29.6
108	DIMETHYLAMINE b3lyp	-134.8549696	-0.73649868	-135.090649	-0.851346	-0.116205943	17.6	18.3
109	TRANS ETHYLAMINE	-134.8664964	-0.73766236	-135.102548	-31.155202	-30.42006196	16.1	16.9
110	KETENE B3LYP	-152.3210979	-0.7114801	-152.548772	-65.812129	-64.13180893	-18.5	-16.9
111	OXIRANE B3LYP	-153.4889411	-0.74300816	-153.726704	-48.817745	-47.13742476	3.9	5.6
112	Acetaldehyde B3LYP	-153.5348601	-0.73521813	-153.770130	-165.952302	-164.2719817	0.2	1.8
113	Glyoxal, O=CH-CH=O.	-227.433133	-1.00263776	-227.753977	-228.846209	-226.2207087	-16.7	-14.1
114	ETHANOL TRANS	-154.7292383	-0.76586368	-154.974315	-219.141594	-217.4612736	16.0	17.7
115	DIMETHYL ETHER,	-154.7125024	-0.76286587	-154.956619	-173.525581	-171.8452611	10.6	12.3
116	Thiooxirane. (cyclic	-476.3934822	-0.82749912	-476.658282	91.218645	94.29047961	9.2	12.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.6891859	-1.1679302	-553.062924	-124.559307	-120.5422918	26.9	30.9
118	Thioethanol. CH3-CH2-SH.	-477.6105734	-0.84634391	-477.881403	-21.784360	-18.71252486	24.7	27.7
119	ch3sch3 B3LYP	-477.6085386	-0.84819781	-477.879962	-15.473598	-12.40176279	21.8	24.8
120	Vinyl fluoride,	-177.5320118	-0.74133406	-177.769239	-144.704087	-142.3673918	-5.8	-3.5
121	Ethyl chloride.	-539.0194356	-0.78170105	-539.269580	-99.761003	-95.50769344	12.4	16.6
122	Vinyl chloride,	-537.7976008	-0.75296816	-538.038551	25.260626	29.51393636	2.2	6.5
123	h2c=chcn B3LYP	-170.478817	-0.87449742	-170.758656	177.738906	178.8416161	-3.0	-1.9
124	ACETONE B3LYP	-192.7644119	-0.95977151	-193.071539	-210.534414	-208.4865236	6.6	8.7
125	CH3COOH ACETIC	-228.685347	-1.0348289	-229.016492	-434.535958	-431.9104584	-1.9	0.7
126	CH3CFO HCCO	-252.694982	-1.04338231	-253.028864	-451.211341	-447.9294664	-9.0	-5.7
127	ch3c(o)cl hcco	-612.9469839	-1.05917119	-613.285919	-249.471172	-244.2726821	-6.8	-1.6
128	ch3ch2ch2cl B3LYP	-578.2373078	-1.00706131	-578.559567	-113.815538	-109.1946585	18.0	22.6
129	Isopropyl alcohol,	-193.9519035	-0.99316592	-194.269717	-249.197012	-247.1491215	23.6	25.6
130	Methyl ethyl	-193.9354712	-0.98737882	-194.251432	-200.643083	-198.5951934	15.7	17.7
131	Trimethyl Amine.	-174.0663383	-0.96476609	-174.375063	-2.964419	-1.861709068	20.9	22.0
132	FURAN B3LYP	-229.5635636	-1.1419066	-229.928974	-42.012887	-39.59742738	-7.3	-4.9
133	Thiophene b3lyp	-552.4575864	-1.23328874	-552.852239	117.502119	121.309094	2.4	6.2
134	PYROLE PLANAR	-209.7174377	-1.11459388	-210.074108	101.312694	102.7829738	-7.1	-5.6
135	C2v Pyridine	-247.7518372	-1.29999976	-248.167837	124.340994	126.1788444	-16.2	-14.4
136	H2 B3LYP/6-31G*	-1.15800918	-0.03456736	-1.169071	8.554646	8.554646152	8.6	8.6
137	SH b3lyp/6-31G*	-398.5421215	-0.35736436	-398.656478	148.101411	150.4381056	5.0	7.3
138	CCH B3LYP	-76.44930737	-0.37804526	-76.570282	574.959385	575.6945251	9.7	10.4
139	C2H3 CS,2-A'	-77.72756807	-0.39989207	-77.855534	302.260116	302.9952563	2.7	3.4
140	ch3co hcco	-152.8942885	-0.71313169	-153.122491	-19.121852	-17.44153188	-9.1	-7.4
141	H2COH C1	-114.8553368	-0.50964696	-115.018424	-14.528706	-13.21595575	2.6	3.9
142	ch3o CS,	-114.8490205	-0.4828879	-115.003545	20.963353	22.27610251	3.8	5.1

143	ch3ch2o 2A"	-154.071821	-0.70685998	-154.298016	-5.835628	-4.155308351	9.6	11.3
144	ch3s 2-A'	-437.7609929	-0.58479718	-437.948128	130.800788	133.5050532	6.1	8.8
145	c2h5 staggered	-78.96492732	-0.43135427	-79.102961	132.172017	132.9071574	11.3	12.0
146	(ch3)2ch Cs	-118.1873002	-0.6573911	-118.397665	105.758749	106.8614587	15.8	16.9
147	TERT-BUTYL RADICAL	-157.4098181	-0.88543939	-157.693159	77.012311	78.48259058	25.5	27.0
148	NO2 RADICAL	-204.7418936	-0.89808776	-205.029282	4.978764	6.869123865	-28.1	-26.2

MAD	**11.5**	**12.0**
LD	**-48.6**	**-41.5**

Table S5.51b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 32%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.466159	-0.014517	-7.470804
3	be	-14.632931	-0.052794	-14.649825
4	b	-24.610663	-0.076630	-24.635184
5	c	-37.792254	-0.103328	-37.825319
6	n	-54.523944	-0.133975	-54.566816
7	o	-74.983595	-0.190903	-75.044684
8	f	-99.626797	-0.253492	-99.707914
9	na	-162.129667	-0.170606	-162.184261
10	al	-242.207699	-0.218910	-242.277750
11	si	-289.206885	-0.248779	-289.286494
12	p	-341.087855	-0.277634	-341.176698
13	s	-397.919079	-0.318693	-398.021061
14	cl	-459.934435	-0.289503	-460.027075

Table S5.52a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 33%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04311045	-0.04637696	-8.058415	147.818753	147.8187528	8.5	8.5
2	BERYLLIUM HYDRIDE	-15.21794278	-0.0546242	-15.235969	320.677588	320.6775882	-21.2	-21.2
3	DOUBLET CH	-38.4084025	-0.14366747	-38.455813	600.373152	600.7407224	4.2	4.5
4	CH2 3-B1	-39.07091194	-0.16266669	-39.124592	395.550890	395.9184602	3.5	3.9
5	Singlet methylene,	-39.04656406	-0.18265003	-39.106839	440.550327	440.9178966	10.4	10.8
6	Methyl radical,	-39.74103889	-0.20724733	-39.809431	152.487226	152.8547965	6.0	6.4
7	ch4 //b3lyp/6-31G*	-40.40397344	-0.24863726	-40.486024	-63.624802	-63.25723206	11.3	11.6
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13567472	-0.18666596	-55.197274	359.330060	359.3300604	2.9	2.9
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77462123	-0.23982305	-55.853763	188.880405	188.8804055	0.2	0.2
10	AMMONIA, //b3lyp/6-31G*	-56.43819639	-0.29345998	-56.535038	-37.970233	-37.97023311	8.1	8.1
11	OH RADICAL	-75.6272694	-0.25713763	-75.712125	40.624417	41.56959749	1.3	2.2
12	Water //b3lyp/6-31G*	-76.30196036	-0.32536898	-76.409332	-233.322331	-232.3771514	8.5	9.5
13	HYDROGEN FLUORIDE,	-100.318825	-0.33614019	-100.429751	-269.530237	-267.9286822	2.8	4.4
14	SIH2 singlet	-290.4205787	-0.30423764	-290.520977	277.580016	279.365356	4.8	6.6
15	SIH2 3B1	-290.3956376	-0.28179346	-290.488629	363.519692	365.3050321	2.9	4.6
16	SIH3 c3v	-291.0351738	-0.30964532	-291.137357	206.105896	207.8912364	5.7	7.5
17	SIH4 //b3lyp/6-31G*	-291.6764574	-0.3366952	-291.787567	46.741862	48.52720205	12.4	14.2
18	ph2 doublet	-342.3004167	-0.34356269	-342.413792	142.466521	142.4665205	4.0	4.0
19	PH3 c3v	-342.9264733	-0.37443252	-343.050036	21.270526	21.27052567	15.8	15.8
20	SH2 //b3lyp/6-31G*	-399.1715916	-0.39578634	-399.302201	-9.151744	-6.815048838	11.3	13.7
21	HCL //b3lyp/6-31G*	-460.5799384	-0.33430322	-460.690259	-89.080914	-85.56274401	3.4	6.9
22	DILITHIUM //b3lyp/6-31G*	-14.95504462	-0.05745313	-14.974004	230.778501	230.7785013	14.9	14.9
23	Lithium Fluoride,	-107.2790469	-0.36487144	-107.399454	-342.154564	-340.5530087	-7.0	-5.4
24	ACETYLENE //b3lyp/6-31g*	-77.15679364	-0.4153455	-77.293858	226.296903	227.0320431	-0.5	0.3
25	ETHYLENE //b3lyp/6-31g*	-78.39639217	-0.43647557	-78.540429	60.721253	61.45639342	8.4	9.2
26	ETHANE //b3lyp/6-31g*	-79.61729957	-0.46988208	-79.772361	-67.724825	-66.98968523	16.4	17.1
27	CYANO RADICAL,	-92.53197859	-0.44916947	-92.680205	438.918772	439.2863418	0.0	0.4
28	HYDROGEN CYANIDE	-93.24116317	-0.45955261	-93.392816	119.795804	120.163374	-12.0	-11.6
29	CARBON MONOXIDE	-113.1310036	-0.47041265	-113.286240	-121.503288	-120.1905378	-11.0	-9.7
30	HCO BENT	-113.6552286	-0.49271922	-113.817826	26.413065	27.7258148	-15.4	-14.1
31	H2CO //b3lyp/6-31g*	-114.2962352	-0.51225134	-114.465278	-116.247904	-114.935154	-7.5	-6.2

32	METHANOL //b3lyp/6-31g*	-115.5002159	-0.54195152	-115.679060	-194.111733	-192.7989827	6.7	8.0
33	Nitrogen N2,	-109.3375913	-0.49311049	-109.500318	-9.453583	-9.453583052	-9.5	-9.5
34	H2NNH2 //b3lyp/6-31g*	-111.640504	-0.55652532	-111.824157	103.168450	103.1684495	7.8	7.8
35	NO radical,	-129.6820987	-0.53493223	-129.858626	77.296232	78.24141207	-13.1	-12.1
36	O2 //b3lyp/6-31g*	-150.0887786	-0.59923823	-150.286527	-17.894187	-16.00382672	-17.9	-16.0
37	HYDROGEN PEROXIDE	-151.3026691	-0.62881544	-151.510178	-125.382057	-123.4916967	10.6	12.5
38	F2 //b3lyp/6-31g*	-199.2549361	-0.65744478	-199.471893	10.046259	13.24936905	10.0	13.2
39	CO2 D*H	-188.2851923	-0.7909125	-188.546193	-427.865965	-425.6080345	-34.6	-32.3
40	na2 //b3lyp/6-31G*	-324.2683281	-0.36921947	-324.390171	143.992739	143.9927392	1.7	1.7
41	SI2 3-SGG	-578.5019213	-0.55548099	-578.685230	588.381116	591.9517961	3.0	6.6
42	P2 //b3lyp/6-31g*	-682.2994837	-0.70470457	-682.532036	149.876172	149.8761724	6.4	6.4
43	S2 //b3lyp/6-31g*	-795.95153	-0.75231686	-796.199795	123.469773	128.1431631	-5.0	-0.3
44	CL2 //b3lyp/6-31g*	-919.9225656	-0.64713845	-920.136121	6.074047	13.11038728	6.1	13.1
45	Sodium Chloride	-622.1919954	-0.50569421	-622.358874	-176.388550	-172.8703797	6.0	9.6
46	SIO //b3lyp/6-31g*	-364.4328972	-0.61182204	-364.634799	-104.803196	-102.0726764	-1.9	0.9
47	Carbon monosulfide,	-435.927027	-0.57154912	-436.115638	280.399377	283.1036417	0.5	3.2
48	OS //b3lyp/6-31g*	-473.040341	-0.68242401	-473.265541	-6.139069	-2.857194131	-11.2	-7.9
49	CLO 2-PI	-534.9700424	-0.59963108	-535.167921	106.565223	111.0285734	5.3	9.8
50	CLF 1-SG	-559.6141394	-0.64951642	-559.828480	-56.376852	-51.25712679	-1.1	4.0
51	si2h6 //b3lyp/6-31g*	-582.1809706	-0.65430461	-582.396891	103.737387	107.3080667	23.8	27.4
52	Methyl chloride,	-499.7880794	-0.55640371	-499.971693	-77.142181	-73.25644064	4.9	8.7
53	H3C-SH METHANETHIOL	-438.382586	-0.62038646	-438.587314	-6.922944	-4.218679122	16.1	18.8
54	HOCl //b3lyp/6-31g*	-535.6156214	-0.64088695	-535.827114	-71.763892	-67.3005415	2.7	7.2
55	SO2 //b3lyp/6-31G*	-548.1793709	-1.02567414	-548.517843	-297.564626	-293.3375713	-0.5	3.7
56	BF3 PLANAR	-324.1638151	-1.06445062	-324.515084	-1160.320147	-1155.384207	-24.8	-19.8
57	bcl3 B3LYP	-1404.863207	-1.10202929	-1405.226876	-425.748115	-415.0623299	-22.8	-12.1
58	ALf3 B3LYP	-541.6788826	-1.20272641	-542.075782	-1207.307879	-1201.610544	1.9	7.6
59	alcl3 B3LYP	-1622.438263	-1.2040541	-1622.835601	-593.480692	-582.0335124	-9.0	2.5
60	cf4 B3LYP	-436.9438105	-1.4541442	-437.423678	-962.915933	-956.142143	-29.9	-23.1
61	ccl4 B3LYP	-1877.913638	-1.52797875	-1878.417870	-103.472922	-89.03267205	-7.7	6.8
62	O=C=S. Singlet	-511.1392762	-0.88109482	-511.430038	-169.485392	-165.8359474	-31.0	-27.3
63	CS2 B3LYP	-833.9898013	-0.97832774	-834.312649	92.710352	97.75131156	-24.0	-19.0
64	COF2 B3LYP	-312.5919184	-1.12328109	-312.962601	-637.359271	-632.8434108	-13.5	-9.0
65	sif4 B3LYP	-688.5043929	-1.55501054	-689.017546	-1593.379232	-1585.187672	21.6	29.8
66	sicl4, td	-2129.458088	-1.59066454	-2129.983007	-652.725747	-636.8677271	10.0	25.9
67	nno B3LYP	-184.3413925	-0.84805348	-184.621250	46.380166	47.3253456	-35.6	-34.7
68	clno B3LYP	-589.6418943	-0.91570567	-589.944077	36.488086	40.95143584	-15.4	-10.9

69	nf3 c3v	-353.611891	-1.23772526	-354.020340	-149.244939	-144.4402736	-17.0	-12.2
70	pf3 c3v	-640.4435078	-1.29684699	-640.871467	-948.364363	-943.559698	10.2	15.0
71	ozone 1-a1	-225.0336751	-1.0180794	-225.369641	132.767976	135.6035164	-9.9	-7.1
72	f2o B3LYP	-274.2854315	-0.96924983	-274.605284	27.884586	32.03287613	3.2	7.3
73	CLF3, C2V	-758.8960963	-1.37349661	-759.349350	-171.891180	-163.5683447	-12.9	-4.6
74	CF2=CF2 D2H	-474.8839316	-1.65466977	-475.429973	-713.593809	-706.4524486	-55.0	-47.9
75	cl2c=ccl2 B3LYP	-1915.926134	-1.72546028	-1916.495536	-39.194848	-24.38702774	-26.6	-11.8
76	cf3cn B3LYP	-429.8470279	-1.59522693	-430.373453	-539.559375	-534.0195696	-44.2	-38.6
77	PROPYNE C3V	-116.3833805	-0.63791763	-116.593893	184.616281	185.7189908	-0.3	0.8
78	ALLENE D2D	-116.3833556	-0.6317553	-116.591835	188.364048	189.4667579	-2.0	-0.9
79	CYCLOPROPENE C2V	-116.3435297	-0.64119563	-116.555124	285.684982	286.7876921	8.7	9.8
80	PROPENE CS	-117.616705	-0.66144734	-117.834983	32.795990	33.89870003	12.7	13.8
81	CYCLOPROPANE D3H	-117.602775	-0.6677872	-117.823145	66.357248	67.45995771	13.2	14.3
82	PROPANE C2V	-118.8325994	-0.69445989	-119.061771	-81.829570	-80.72686003	22.8	23.9
83	TRANS-1,3-BUTADIENE C2H	-155.6213152	-0.85527409	-155.903556	118.800096	120.2703763	8.8	10.2
84	Dimethyl acetylene	-155.6078871	-0.86108069	-155.892044	149.176795	150.6470752	3.6	5.0
85	Methylene cyclopropane.	-155.5883147	-0.86210852	-155.872811	198.269040	199.7393203	-2.1	-0.7
86	Bicyclo[1.1.0]butane. C2v	-155.572053	-0.87388752	-155.860436	232.690999	234.1612794	15.5	17.0
87	CYCLOBUTENE b3lyp	-155.5977815	-0.86431411	-155.883005	173.865898	175.3361782	17.4	18.9
88	CYCLOBUTANE b3lyp/6-31G*	-156.8189267	-0.89348467	-157.113777	50.156572	51.62685203	21.7	23.2
89	Isobutene. Single	-156.8367555	-0.88913945	-157.130171	2.322909	3.793189418	19.1	20.5
90	Trans butane	-158.0477663	-0.91956116	-158.351221	-96.046586	-94.57630594	29.5	30.9
91	isobutane B3LYP/6-31G*	-158.0487294	-0.92274255	-158.353234	-102.625981	-101.1557005	31.7	33.2
92	Spiropentane. D2d	-194.7973876	-1.09367075	-195.158299	196.388942	198.2267923	11.0	12.9
93	Benzene B3LYP	-231.7124482	-1.25631515	-232.127032	72.102833	74.30825338	-10.3	-8.1
94	DIFLUOROMETHANE C2V	-238.6564851	-0.85059229	-238.937181	-462.455560	-458.8848805	-11.8	-8.3
95	HCF3 TRI-FLUOROMETHANE	-337.8019379	-1.15352507	-338.182601	-717.593626	-712.4213911	-20.5	-15.4
96	CH2CL2 C2V	-959.1694376	-0.87300891	-959.457531	-93.784265	-86.38035524	1.6	9.0
97	chcl3 B3LYP/6-31G*	-1418.545403	-1.19712661	-1418.940454	-104.896456	-93.97437609	-1.6	9.4
98	METHYLAMINE b3lyp	-95.64014368	-0.51300107	-95.809434	-11.461991	-11.09442113	11.6	11.9
99	Acetonitrile. CH3-CN.	-132.4738263	-0.67990745	-132.698196	64.584367	65.31950735	-10.7	-10.0
100	NITRO METHANE	-244.5700806	-1.12451592	-244.941171	-93.748198	-91.4902684	-19.3	-17.0
101	Methyl-nitrite. CH3-O-N=O.	-244.566397	-1.11397168	-244.934008	-78.669403	-76.41147264	-12.1	-9.9
102	Methylsilane. CH3-SiH3.	-330.9067793	-0.56310037	-331.092602	-5.172889	-3.019978887	24.1	26.3
103	Formic Acid.	-189.4458347	-0.81333314	-189.714235	-392.122916	-389.8649864	-13.5	-11.2
104	Methyl formate.	-228.6485361	-1.0351552	-228.990137	-371.371897	-368.7463973	-15.7	-13.1
105	acetamide ch3cohn2	-208.8089096	-1.0050207	-209.140566	-243.374599	-241.6942792	-4.9	-3.2

106	Aziridine. (cyclic	-133.6204706	-0.71254313	-133.855610	133.288249	134.0233892	6.9	7.7
107	Cyanogen. NCCN.	-185.2966182	-0.90879938	-185.596522	269.950395	270.6855353	-36.7	-36.0
108	DIMETHYLAMINE b3lyp	-134.8466412	-0.73648514	-135.089681	-2.808182	-2.073042028	15.6	16.3
109	TRANS ETHYLAMINE	-134.8581643	-0.73764959	-135.101589	-33.133675	-32.39853452	14.1	14.9
110	KETENE B3LYP	-152.3136265	-0.71146494	-152.548410	-69.583766	-67.90344601	-22.3	-20.6
111	OXIRANE B3LYP	-153.4808933	-0.74299816	-153.726083	-51.908021	-50.22770101	0.8	2.5
112	Acetaldehyde B3LYP	-153.5268657	-0.73520667	-153.769484	-168.976987	-167.2966674	-2.9	-1.2
113	Glyoxal, O=CH-CH=O.	-227.4226823	-1.00262432	-227.753548	-234.205399	-231.5798987	-22.1	-19.5
114	ETHANOL TRANS	-154.7206921	-0.76585438	-154.973424	-221.524051	-219.8437313	13.6	15.3
115	DIMETHYL ETHER,	-154.7039693	-0.76285464	-154.955711	-175.862289	-174.1819695	8.2	9.9
116	Thiooxirane. (cyclic	-476.3817877	-0.82748216	-476.654857	89.067846	92.13968104	7.1	10.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.6739802	-1.16791212	-553.059391	-128.192420	-124.1754054	23.3	27.3
118	Thioethanol. CH3-CH2-SH.	-477.5984049	-0.84632622	-477.877693	-23.184704	-20.1128689	23.3	26.3
119	ch3sch3 B3LYP	-477.5963774	-0.84818013	-477.876277	-16.941896	-13.8700608	20.3	23.4
120	Vinyl fluoride,	-177.5237865	-0.74132389	-177.768423	-147.309325	-144.9726301	-8.4	-6.1
121	Ethyl chloride.	-539.0070273	-0.78168596	-539.264984	-101.214781	-96.96147113	10.9	15.2
122	Vinyl chloride,	-537.7857206	-0.75295123	-538.034194	23.176587	27.42989716	0.2	4.4
123	h2c=chcn B3LYP	-170.4695447	-0.87446914	-170.758120	173.171107	174.2738174	-7.6	-6.5
124	ACETONE B3LYP	-192.7538254	-0.95975317	-193.070544	-214.121989	-212.0740987	3.0	5.1
125	CH3COOH ACETIC	-228.6742994	-1.03481619	-229.015789	-439.174008	-436.5485084	-6.5	-3.9
126	CH3CFO HCCO	-252.6837373	-1.04336928	-253.028049	-455.580841	-452.2989656	-13.3	-10.1
127	ch3c(o)cl hcco	-612.9320982	-1.05915245	-613.281618	-253.466301	-248.2678115	-10.8	-5.6
128	ch3ch2ch2cl B3LYP	-578.2223153	-1.00704009	-578.554638	-115.874361	-111.2534813	15.9	20.5
129	Isopropyl alcohol,	-193.9407637	-0.99314979	-194.268503	-252.210399	-250.1625087	20.6	22.6
130	Methyl ethyl	-193.9243528	-0.98736094	-194.250182	-203.559200	-201.5113098	12.8	14.8
131	Trimethyl Amine.	-174.0554159	-0.96474599	-174.373782	-5.576683	-4.473972609	18.3	19.4
132	FURAN B3LYP	-229.5513108	-1.14188083	-229.928131	-47.479372	-45.06391215	-12.8	-10.3
133	Thiophene b3lyp	-552.4416902	-1.23325647	-552.848665	112.785384	116.5923589	-2.3	1.5
134	PYROLE PLANAR	-209.7053762	-1.11456652	-210.073183	96.285097	97.75537657	-12.1	-10.6
135	C2v Pyridine	-247.7377417	-1.29996437	-248.166730	118.314477	120.1523266	-22.3	-20.4
136	H2 B3LYP/6-31G*	-1.15762654	-0.03456765	-1.169034	8.651450	8.651450175	8.7	8.7
137	SH b3lyp/6-31G*	-398.5354436	-0.35736641	-398.653375	148.063415	150.4001096	5.0	7.3
138	CCH B3LYP	-76.4452543	-0.37802586	-76.570003	572.735061	573.470201	7.5	8.2
139	C2H3 CS,2-A'	-77.72294339	-0.39987157	-77.854901	300.963919	301.6990593	1.4	2.1
140	ch3co hcco	-152.8866252	-0.71311063	-153.121952	-22.427696	-20.74737612	-12.4	-10.7
141	H2COH C1	-114.8497085	-0.50963839	-115.017889	-16.367459	-15.05470892	0.8	2.1
142	ch3o CS,	-114.8434252	-0.48287323	-115.002773	19.745723	21.05847332	2.6	3.9

143	ch3ch2o 2A"	-154.0636418	-0.7068367	-154.296898	-7.620311	-5.939991188	7.9	9.5
144	ch3s 2-A'	-437.7517377	-0.58478963	-437.944718	130.088144	132.7924088	5.4	8.1
145	c2h5 staggered	-78.95975335	-0.43134717	-79.102098	131.480331	132.2154712	10.6	11.3
146	(ch3)2ch Cs	-118.1795349	-0.65737422	-118.396468	104.466189	105.5688988	14.5	15.6
147	TERT-BUTYL RADICAL	-157.3994588	-0.88541233	-157.691645	75.073265	76.54354514	23.6	25.1
148	NO2 RADICAL	-204.7335746	-0.89806642	-205.029936	-1.809760	0.080599559	-34.9	-33.0

MAD	**12.0**	**12.2**
LD	**-55.0**	**-47.9**

Table S5.52b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 60% and a_C = 33%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498777	0.000000	-0.498777
2	li	-7.465622	-0.014516	-7.470413
3	be	-14.631982	-0.052789	-14.649402
4	b	-24.609398	-0.076634	-24.634687
5	c	-37.790656	-0.103334	-37.824756
6	n	-54.522016	-0.133979	-54.566229
7	o	-74.981011	-0.190914	-75.044012
8	f	-99.623577	-0.253502	-99.707233
9	na	-162.125576	-0.170604	-162.181875
10	al	-242.202743	-0.218911	-242.274983
11	si	-289.201569	-0.248781	-289.283667
12	p	-341.082185	-0.277629	-341.173802
13	s	-397.912773	-0.318696	-398.017943
14	cl	-459.927515	-0.289507	-460.023052

Table S5.53a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04671604	-0.04617376	-8.060106	147.669912	147.6699119	8.3	8.3
2	BERYLLIUM HYDRIDE	-15.22239717	-0.05443524	-15.238183	319.342361	319.3423608	-22.5	-22.5
3	DOUBLET CH	-38.41629233	-0.14305735	-38.457779	600.961191	601.3287614	4.7	5.1
4	CH2 3-B1	-39.07958252	-0.16206868	-39.126582	396.137582	396.505152	4.1	4.5
5	Singlet methylene,	-39.05587226	-0.18188827	-39.108620	441.686276	442.0538459	11.6	11.9
6	Methyl radical,	-39.75145338	-0.20645983	-39.811327	153.383853	153.7514226	6.9	7.3
7	ch4 //b3lyp/6-31G*	-40.41585556	-0.24770237	-40.487689	-62.060012	-61.69244167	12.8	13.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14507692	-0.18596212	-55.199006	360.798520	360.7985199	4.3	4.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78561353	-0.23889437	-55.854893	191.990241	191.9902414	3.3	3.3
10	AMMONIA, //b3lyp/6-31G*	-56.45070358	-0.29232196	-56.535477	-32.982966	-32.98296564	13.0	13.0
11	OH RADICAL	-75.63896553	-0.25619961	-75.713263	43.921181	44.86636118	4.6	5.5
12	Water //b3lyp/6-31G*	-76.31512043	-0.32412414	-76.409116	-226.407440	-225.4622602	15.4	16.4
13	HYDROGEN FLUORIDE,	-100.3327786	-0.33495849	-100.429917	-264.099563	-262.4980077	8.3	9.9
14	SIH2 singlet	-290.4445742	-0.30326316	-290.532521	276.593643	278.378983	3.8	5.6
15	SIH2 3B1	-290.418909	-0.281026	-290.500407	361.919889	363.7052293	1.3	3.0
16	SIH3 c3v	-291.0600396	-0.30872371	-291.149569	203.424592	205.2099322	3.0	4.8
17	SIH4 //b3lyp/6-31G*	-291.7027777	-0.33564363	-291.800114	43.243906	45.02924551	8.9	10.7
18	ph2 doublet	-342.3262561	-0.34247926	-342.425575	141.786070	141.7860702	3.3	3.3
19	PH3 c3v	-342.9536831	-0.37321436	-343.061915	20.399004	20.39900433	15.0	15.0
20	SH2 //b3lyp/6-31G*	-399.1997779	-0.39451724	-399.314188	-8.117734	-5.781039247	12.4	14.7
21	HCL //b3lyp/6-31G*	-460.6091511	-0.33313501	-460.705760	-87.793777	-84.27560655	4.7	8.2
22	DILITHIUM //b3lyp/6-31G*	-14.9604981	-0.05717852	-14.977080	231.163159	231.1631588	15.3	15.3
23	Lithium Fluoride,	-107.2951895	-0.3634471	-107.400589	-335.101675	-333.5001199	0.0	1.6
24	ACETYLENE //b3lyp/6-31g*	-77.174253	-0.41353363	-77.294178	236.957062	237.6922019	10.2	10.9
25	ETHYLENE //b3lyp/6-31g*	-78.41624998	-0.43472395	-78.542320	67.382356	68.11749643	15.1	15.8
26	ETHANE //b3lyp/6-31g*	-79.6395549	-0.46810433	-79.775305	-63.705295	-62.97015526	20.4	21.1
27	CYANO RADICAL,	-92.54821049	-0.446907	-92.677814	456.836125	457.2036945	17.9	18.3
28	HYDROGEN CYANIDE	-93.25911897	-0.4574906	-93.391791	134.187300	134.5548698	2.4	2.8
29	CARBON MONOXIDE	-113.1496571	-0.46834679	-113.285478	-107.590937	-106.2781871	2.9	4.2
30	HCO BENT	-113.6747513	-0.49062749	-113.817033	40.468256	41.78100609	-1.4	-0.1
31	H2CO //b3lyp/6-31g*	-114.3172068	-0.51011266	-114.465140	-103.847565	-102.5348146	4.9	6.2

32	METHANOL //b3lyp/6-31g*	-115.5236606	-0.53987525	-115.680224	-185.007792	-183.6950417	15.8	17.1
33	Nitrogen N2,	-109.3560943	-0.49092496	-109.498463	7.321294	7.321294367	7.3	7.3
34	H2NNH2 //b3lyp/6-31g*	-111.6638779	-0.55434313	-111.824637	114.061641	114.0616414	18.7	18.7
35	NO radical,	-129.7021114	-0.53263674	-129.856576	94.854830	95.80000964	4.5	5.4
36	O2 //b3lyp/6-31g*	-150.1101737	-0.59693181	-150.283284	3.068542	4.958901995	3.1	5.0
37	HYDROGEN PEROXIDE	-151.3269118	-0.62623794	-151.508521	-108.458393	-106.568033	27.5	29.4
38	F2 //b3lyp/6-31g*	-199.2803962	-0.65483523	-199.470298	25.836589	29.0396992	25.8	29.0
39	CO2 D*H	-188.3154545	-0.7874901	-188.543827	-403.516515	-401.2585852	-10.2	-8.0
40	na2 //b3lyp/6-31G*	-324.3016322	-0.36804604	-324.408366	144.642064	144.6420645	2.4	2.4
41	SI2 3-SGG	-578.5457164	-0.55369176	-578.706287	591.487890	595.05857	6.1	9.7
42	P2 //b3lyp/6-31g*	-682.3477914	-0.70210116	-682.551401	159.294990	159.2949896	15.8	15.8
43	S2 //b3lyp/6-31g*	-796.0035479	-0.74988985	-796.221016	132.514329	137.1877189	4.1	8.7
44	CL2 //b3lyp/6-31g*	-919.9791215	-0.64476703	-920.166104	11.203644	18.23998364	11.2	18.2
45	Sodium Chloride	-622.2373139	-0.5039823	-622.383469	-174.826133	-171.3079631	7.6	11.1
46	SIO //b3lyp/6-31g*	-364.4662379	-0.60920207	-364.642906	-90.671001	-87.94048075	12.3	15.0
47	Carbon monosulfide,	-435.9605931	-0.5691488	-436.125646	292.191645	294.8959096	12.3	15.0
48	OS //b3lyp/6-31g*	-473.0770962	-0.67991468	-473.274271	9.543217	12.82509249	4.5	7.8
49	CLO 2-PI	-535.0090966	-0.59696772	-535.182217	117.177711	121.6410608	15.9	20.4
50	CLF 1-SG	-559.6552913	-0.64704944	-559.842936	-46.603849	-41.48412365	8.6	13.7
51	si2h6 //b3lyp/6-31g*	-582.2320503	-0.65223266	-582.421198	98.686742	102.2574215	18.8	22.3
52	Methyl chloride,	-499.8275378	-0.55435801	-499.988302	-72.949507	-69.06376657	9.1	12.9
53	H3C-SH METHANETHIOL	-438.421079	-0.61823703	-438.600368	-2.878617	-0.174352358	20.1	22.8
54	HOCl //b3lyp/6-31g*	-535.6560523	-0.63838014	-535.841183	-60.489896	-56.02654552	14.0	18.4
55	SO2 //b3lyp/6-31G*	-548.2280518	-1.02127941	-548.524223	-269.485881	-265.2588263	27.6	31.8
56	BF3 PLANAR	-324.2101907	-1.06070517	-324.517795	-1144.951857	-1140.015917	-9.4	-4.5
57	bcl3 B3LYP	-1404.955229	-1.09802047	-1405.273655	-417.710752	-407.0249673	-14.8	-4.1
58	ALf3 B3LYP	-541.7395212	-1.19856985	-542.087106	-1191.203001	-1185.505666	18.0	23.7
59	alcl3 B3LYP	-1622.544775	-1.19998374	-1622.892770	-589.375103	-577.927923	-4.9	6.6
60	cf4 B3LYP	-437.0053675	-1.44899495	-437.425576	-939.002894	-932.229104	-6.0	0.8
61	ccl4 B3LYP	-1878.035905	-1.52227316	-1878.477364	-86.286557	-71.84630737	9.5	24.0
62	O=C=S. Singlet	-511.1845285	-0.87753579	-511.439014	-148.760612	-145.1111675	-10.3	-6.6
63	CS2 B3LYP	-834.0500699	-0.97460575	-834.332706	110.502175	115.5431354	-6.2	-1.2
64	COF2 B3LYP	-312.6377455	-1.11897433	-312.962248	-612.916391	-608.4005309	10.9	15.4
65	sif4 B3LYP	-688.5808497	-1.54978015	-689.030286	-1574.422818	-1566.231258	40.6	48.8
66	sicl4, td	-2129.595493	-1.58520269	-2130.055202	-645.378013	-629.5199931	17.4	33.2
67	nno B3LYP	-184.371074	-0.84409563	-184.615862	78.655082	79.60026187	-3.4	-2.4
68	clno B3LYP	-589.6901295	-0.91153074	-589.954473	63.292855	67.75620478	11.4	15.9

69	nf3 c3v	-353.6604568	-1.23273048	-354.017949	-119.607264	-114.8025989	12.6	17.4
70	pf3 c3v	-640.5080108	-1.29226976	-640.882769	-930.500683	-925.6960176	28.1	32.9
71	ozone 1-a1	-225.0659539	-1.01289824	-225.359694	177.554915	180.3904553	34.9	37.7
72	f2o B3LYP	-274.3219755	-0.96515252	-274.601870	54.676423	58.82471343	30.0	34.1
73	CLF3, C2V	-758.9632951	-1.36782449	-759.359964	-140.427541	-132.1047055	18.6	26.9
74	CF2=CF2 D2H	-474.9532399	-1.6485437	-475.431318	-682.541118	-675.3997582	-24.0	-16.8
75	cl2c=ccl2 B3LYP	-1916.056563	-1.7189196	-1916.555049	-16.373935	-1.566114531	-3.8	11.0
76	cf3cn B3LYP	-429.9124691	-1.58904178	-430.373291	-504.401136	-498.8613313	-9.0	-3.5
77	PROPYNE C3V	-116.4112422	-0.63527229	-116.595471	197.786890	198.8896005	12.9	14.0
78	ALLENE D2D	-116.4111651	-0.62914268	-116.593616	200.999680	202.1023904	10.6	11.7
79	CYCLOPROPENE C2V	-116.3716327	-0.63859339	-116.556825	298.533446	299.6361555	21.6	22.7
80	PROPENE CS	-117.6469748	-0.65883445	-117.838037	42.215359	43.31806854	22.1	23.2
81	CYCLOPROPANE D3H	-117.6334066	-0.66522344	-117.826321	75.455325	76.55803512	22.3	23.4
82	PROPANE C2V	-118.8652712	-0.69182302	-119.065900	-75.106547	-74.00383749	29.5	30.6
83	TRANS-1,3-BUTADIENE C2H	-155.659575	-0.85180179	-155.906597	133.939740	135.4100201	23.9	25.4
84	Dimethyl acetylene	-155.6461508	-0.8575942	-155.894853	164.926734	166.3970141	19.3	20.8
85	Methylene cyclopropane.	-155.62688	-0.85868241	-155.875898	213.289229	214.7595094	12.9	14.3
86	Bicyclo[1.1.0]butane. C2v	-155.6109854	-0.87047525	-155.863423	247.973703	249.4439828	30.8	32.3
87	CYCLOBUTENE b3lyp	-155.6365118	-0.86085881	-155.886161	188.706762	190.1770422	32.2	33.7
88	CYCLOBUTANE b3lyp/6-31G*	-156.8600727	-0.89003737	-157.118184	61.836944	63.30722422	33.4	34.9
89	Isobutene. Single	-156.8774816	-0.88565318	-157.134321	14.679066	16.14934561	31.4	32.9
90	Trans butane	-158.0908592	-0.9160639	-158.356518	-86.576076	-85.1057961	38.9	40.4
91	isobutane B3LYP/6-31G*	-158.0918667	-0.91922842	-158.358443	-92.925220	-91.45493983	41.4	42.9
92	Spiropentane. D2d	-194.8467476	-1.08943551	-195.162684	213.814891	215.6527414	28.5	30.3
93	Benzene B3LYP	-231.7675967	-1.25130773	-232.130476	97.563172	99.76859172	15.1	17.3
94	DIFLUOROMETHANE C2V	-238.6930565	-0.84749462	-238.938830	-449.368987	-445.7983065	1.2	4.8
95	HCF3 TRI-FLUOROMETHANE	-337.8509806	-1.14937039	-338.184298	-698.892347	-693.7201121	-1.8	3.3
96	CH2CL2 C2V	-959.2364824	-0.86979031	-959.488722	-86.014521	-78.61061069	9.4	16.8
97	chcl3 B3LYP/6-31G*	-1418.640052	-1.19268516	-1418.985930	-92.769984	-81.84790442	10.6	21.5
98	METHYLAMINE b3lyp	-95.66299096	-0.51102881	-95.811189	-4.118516	-3.750946469	18.9	19.3
99	Acetonitrile. CH3-CN.	-132.5021949	-0.67702912	-132.698533	81.212986	81.94812604	5.9	6.6
100	NITRO METHANE	-244.6131637	-1.11965045	-244.937862	-60.787183	-58.52925332	13.7	15.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6093602	-1.10896861	-244.930961	-46.396126	-44.13819574	20.1	22.4
102	Methylsilane. CH3-SiH3.	-330.9434877	-0.56118088	-331.106230	-5.694337	-3.541426554	23.6	25.7
103	Formic Acid.	-189.4785248	-0.80997558	-189.713418	-371.717934	-369.4600042	6.9	9.2
104	Methyl formate.	-228.6915695	-1.03092416	-228.990538	-348.349790	-345.7242899	7.3	9.9
105	acetamide ch3cohn2	-208.8514826	-1.00096504	-209.141762	-222.651105	-220.970785	15.8	17.5

106	Aziridine. (cyclic	-133.6515734	-0.70974151	-133.857398	146.232166	146.9673058	19.9	20.6
107	Cyanogen. NCCN.	-185.3308713	-0.9046285	-185.593214	301.916164	302.6513044	-4.8	-4.0
108	DIMETHYLAMINE b3lyp	-134.8798846	-0.73365287	-135.092644	7.178132	7.913272228	25.6	26.3
109	TRANS ETHYLAMINE	-134.8914258	-0.73481397	-135.104522	-23.069988	-22.3348481	24.2	24.9
110	KETENE B3LYP	-152.3426258	-0.70842914	-152.548070	-50.967457	-49.28713715	-3.7	-2.0
111	OXIRANE B3LYP	-153.5125121	-0.74004001	-153.727124	-36.792002	-35.11168171	15.9	17.6
112	Acetaldehyde B3LYP	-153.5582585	-0.73221227	-153.770600	-154.058398	-152.3780781	12.0	13.7
113	Glyoxal, O=CH-CH=O.	-227.4631166	-0.99839991	-227.752653	-207.905612	-205.2801116	4.2	6.8
114	ETHANOL TRANS	-154.7545564	-0.76292062	-154.975803	-209.797091	-208.1167712	25.3	27.0
115	DIMETHYL ETHER,	-154.737767	-0.75991483	-154.958142	-164.270582	-162.5902623	19.8	21.5
116	Thiooxirane. (cyclic	-476.4285681	-0.82445694	-476.667661	99.457444	102.5292787	17.5	20.5
117	Dimethylsulfoxide. (CH3)2SO.	-552.7343729	-1.16336168	-553.071748	-110.279815	-106.2627999	41.2	45.2
118	Thioethanol. CH3-CH2-SH.	-477.6473086	-0.84330605	-477.891867	-16.269567	-13.19773222	30.2	33.2
119	ch3sch3 B3LYP	-477.6452224	-0.84513393	-477.890311	-9.658309	-6.586474318	27.6	30.7
120	Vinyl fluoride,	-177.5559936	-0.73845422	-177.770145	-134.465088	-132.1283929	4.4	6.8
121	Ethyl chloride.	-539.0568945	-0.77877183	-539.282738	-94.217172	-89.96386172	17.9	22.2
122	Vinyl chloride,	-537.8331928	-0.75003144	-538.050702	33.323988	37.57729844	10.3	14.6
123	h2c=chcn B3LYP	-170.5058599	-0.87071413	-170.758367	195.724228	196.8269383	15.0	16.1
124	ACETONE B3LYP	-192.7956727	-0.95590873	-193.072886	-196.609772	-194.5618825	20.5	22.6
125	CH3COOH ACETIC	-228.7174484	-1.03064098	-229.016334	-416.533415	-413.9079153	16.1	18.7
126	CH3CFO HCCO	-252.7275445	-1.03924771	-253.028926	-434.295289	-431.013414	8.0	11.2
127	ch3c(o)cl hcco	-612.991035	-1.05490054	-613.296956	-234.024122	-228.8256324	8.6	13.8
128	ch3ch2ch2cl B3LYP	-578.2826005	-1.00326319	-578.573547	-106.092968	-101.4720881	25.7	30.3
129	Isopropyl alcohol,	-193.9850884	-0.98934176	-194.271998	-237.598242	-235.5503517	35.2	37.2
130	Methyl ethyl	-193.9685721	-0.98356201	-194.253805	-189.285241	-187.2373513	27.0	29.1
131	Trimethyl Amine.	-174.0991148	-0.96101943	-174.377810	7.424327	8.527037102	31.3	32.4
132	FURAN B3LYP	-229.5994489	-1.13725411	-229.929253	-21.198127	-18.78266712	13.5	15.9
133	Thiophene b3lyp	-552.5049512	-1.22848047	-552.861210	135.228536	139.035511	20.2	24.0
134	PYROLE PLANAR	-209.7530357	-1.11012647	-210.074972	120.603040	122.0733202	12.2	13.7
135	C2v Pyridine	-247.7933837	-1.29471545	-248.168851	147.448361	149.2862115	6.9	8.7
136	H2 B3LYP/6-31G*	-1.15917668	-0.03442643	-1.169160	8.444245	8.44424519	8.4	8.4
137	SH b3lyp/6-31G*	-398.5622506	-0.3562712	-398.665569	148.489056	150.8257507	5.4	7.7
138	CCH B3LYP	-76.4610686	-0.37631655	-76.570200	583.654493	584.3896331	18.4	19.1
139	C2H3 CS,2-A'	-77.7412851	-0.39824334	-77.856776	307.605008	308.3401478	8.0	8.8
140	ch3co hcco	-152.9165493	-0.71017141	-153.122499	-6.077852	-4.397531711	4.0	5.6
141	H2COH C1	-114.871738	-0.50766672	-115.018961	-7.083485	-5.770735344	10.1	11.4
142	ch3o CS,	-114.865446	-0.48097986	-115.004930	26.182149	27.49489944	9.0	10.3

143	ch3ch2o 2A"	-154.0960683	-0.70407083	-154.300249	1.493370	3.173689833	17.0	18.7
144	ch3s 2-A'	-437.7888697	-0.58279328	-437.957880	133.788382	136.492647	9.1	11.8
145	c2h5 staggered	-78.98056536	-0.42970601	-79.105180	135.075928	135.8110683	14.2	14.9
146	(ch3)2ch Cs	-118.2107666	-0.65487107	-118.400679	110.911314	112.0140237	21.0	22.1
147	TERT-BUTYL RADICAL	-157.4411354	-0.88203619	-157.696926	84.521122	85.99140217	33.1	34.5
148	NO2 RADICAL	-204.7647234	-0.89395523	-205.023970	32.253571	34.14393134	-0.8	1.1

MAD	**14.6**	**16.4**
LD	**41.4**	**48.8**

Table S5.53b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 29%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498801	0.000000	-0.498801
2	li	-7.467823	-0.014486	-7.472024
3	be	-14.635859	-0.052502	-14.651085
4	b	-24.614507	-0.076260	-24.636623
5	c	-37.797078	-0.102913	-37.826923
6	n	-54.529771	-0.133533	-54.568496
7	o	-74.991199	-0.190289	-75.046383
8	f	-99.636153	-0.252723	-99.709442
9	na	-162.141761	-0.170123	-162.191096
10	al	-242.222513	-0.218272	-242.285812
11	si	-289.222847	-0.248068	-289.294787
12	p	-341.104986	-0.276869	-341.185278
13	s	-397.938119	-0.317781	-398.030276
14	cl	-459.955343	-0.288540	-460.039020

Table S5.54a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04582768	-0.04617486	-8.059680	147.759693	147.7596935	8.4	8.4
2	BERYLLIUM HYDRIDE	-15.22131647	-0.05442803	-15.237645	319.639298	319.6392983	-22.2	-22.2
3	DOUBLET CH	-38.41431491	-0.14306143	-38.457233	600.903529	601.2710994	4.7	5.1
4	CH2 3-B1	-39.07743099	-0.1620673	-39.126051	396.042204	396.4097739	4.0	4.4
5	Singlet methylene,	-39.05354479	-0.18188463	-39.108110	441.534245	441.9018151	11.4	11.8
6	Methyl radical,	-39.74886789	-0.2064635	-39.810807	153.258369	153.6259392	6.8	7.2
7	ch4 //b3lyp/6-31G*	-40.41290963	-0.24769648	-40.487219	-62.314453	-61.94688281	12.6	12.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14269655	-0.18597242	-55.198488	360.604151	360.604151	4.1	4.1
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78281736	-0.23890123	-55.854488	191.500529	191.5005287	2.8	2.8
10	AMMONIA, //b3lyp/6-31G*	-56.44752416	-0.29232277	-56.535221	-33.864432	-33.86443158	12.2	12.2
11	OH RADICAL	-75.63595493	-0.25620959	-75.712818	43.309782	44.25496152	4.0	4.9
12	Water //b3lyp/6-31G*	-76.31171601	-0.32413015	-76.408955	-227.765097	-226.819917	14.1	15.0
13	HYDROGEN FLUORIDE,	-100.3291547	-0.33496686	-100.429645	-265.196575	-263.5950201	7.2	8.8
14	SIH2 singlet	-290.4386005	-0.30325547	-290.529577	276.880311	278.6656508	4.1	5.9
15	SIH2 3B1	-290.4131317	-0.28100012	-290.497432	362.289020	364.0743604	1.6	3.4
16	SIH3 c3v	-291.053886	-0.30870911	-291.146499	204.045558	205.8308984	3.6	5.4
17	SIH4 //b3lyp/6-31G*	-291.6962858	-0.33563485	-291.796976	44.041843	45.82718301	9.7	11.5
18	ph2 doublet	-342.3198251	-0.34247923	-342.422569	142.056003	142.0560034	3.6	3.6
19	PH3 c3v	-342.9469243	-0.37320542	-343.058886	20.729644	20.72964431	15.3	15.3
20	SH2 //b3lyp/6-31G*	-399.1927599	-0.3945116	-399.311113	-8.256541	-5.919845756	12.2	14.6
21	HCL //b3lyp/6-31G*	-460.6018803	-0.33313272	-460.701820	-88.039019	-84.52084899	4.4	7.9
22	DILITHIUM //b3lyp/6-31G*	-14.95916044	-0.05717452	-14.976313	231.118216	231.1182155	15.2	15.2
23	Lithium Fluoride,	-107.2910123	-0.36346111	-107.400051	-336.527753	-334.926198	-1.4	0.2
24	ACETYLENE //b3lyp/6-31g*	-77.16980536	-0.41351551	-77.293860	234.810900	235.5460397	8.0	8.8
25	ETHYLENE //b3lyp/6-31g*	-78.41126534	-0.43471008	-78.541678	66.086388	66.82152836	13.8	14.5
26	ETHANE //b3lyp/6-31g*	-79.63403382	-0.46809278	-79.774462	-64.471069	-63.73592933	19.6	20.4
27	CYANO RADICAL,	-92.54394497	-0.44682389	-92.677992	453.323490	453.6910596	14.4	14.8
28	HYDROGEN CYANIDE	-93.25447327	-0.45747568	-93.391716	131.341245	131.7088152	-0.5	-0.1
29	CARBON MONOXIDE	-113.1448084	-0.4683407	-113.285311	-110.423840	-109.1110895	0.0	1.3
30	HCO BENT	-113.6696695	-0.4906148	-113.816854	37.667498	38.98024766	-4.2	-2.9
31	H2CO //b3lyp/6-31g*	-114.3118001	-0.51010759	-114.464832	-106.312804	-105.0000544	2.5	3.8

32	METHANOL //b3lyp/6-31g*	-115.5176992	-0.53987223	-115.679661	-186.799751	-185.4870006	14.0	15.3
33	Nitrogen N2,	-109.3512571	-0.49090991	-109.498530	4.036966	4.036965574	4.0	4.0
34	H2NNH2 //b3lyp/6-31g*	-111.6579093	-0.55434207	-111.824212	112.071976	112.0719763	16.7	16.7
35	NO radical,	-129.6968313	-0.53262725	-129.856619	91.406025	92.35120509	1.0	2.0
36	O2 //b3lyp/6-31g*	-150.1044512	-0.59693102	-150.283531	-1.141685	0.748675137	-1.1	0.7
37	HYDROGEN PEROXIDE	-151.3205485	-0.62624257	-151.508421	-111.759665	-109.8693047	24.2	26.1
38	F2 //b3lyp/6-31g*	-199.2736394	-0.65483882	-199.470091	22.760167	25.96327666	22.8	26.0
39	CO2 D*H	-188.3075437	-0.78747706	-188.543787	-408.464882	-406.2069522	-15.2	-12.9
40	na2 //b3lyp/6-31G*	-324.2932054	-0.36804054	-324.403618	144.555222	144.5552224	2.3	2.3
41	SI2 3-SGG	-578.5347366	-0.55367425	-578.700839	590.909431	594.4801109	5.6	9.1
42	P2 //b3lyp/6-31g*	-682.3356493	-0.70207821	-682.546273	157.512419	157.5124189	14.0	14.0
43	S2 //b3lyp/6-31g*	-795.9904796	-0.74988103	-796.215444	130.721667	135.3950567	2.3	6.9
44	CL2 //b3lyp/6-31g*	-919.9649931	-0.64475949	-920.158421	10.194958	17.2312983	10.2	17.2
45	Sodium Chloride	-622.2259848	-0.50398447	-622.377180	-175.182024	-171.6638543	7.2	10.8
46	SIO //b3lyp/6-31g*	-364.4577122	-0.60921007	-364.640475	-93.510321	-90.77980094	9.4	12.1
47	Carbon monosulfide,	-435.9521111	-0.56912925	-436.122850	289.832381	292.5366458	9.9	12.6
48	OS //b3lyp/6-31g*	-473.0676915	-0.67990615	-473.271663	6.398562	9.680437409	1.4	4.7
49	CLO 2-PI	-534.9991814	-0.59692761	-535.178260	115.196748	119.6600982	13.9	18.4
50	CLF 1-SG	-559.6448289	-0.6470488	-559.838944	-48.523460	-43.40373487	6.7	11.8
51	si2h6 //b3lyp/6-31g*	-582.2194341	-0.6522162	-582.415099	99.816816	103.3874961	19.9	23.5
52	Methyl chloride,	-499.8177131	-0.55434914	-499.984018	-73.782679	-69.89693932	8.2	12.1
53	H3C-SH METHANETHIOL	-438.4114941	-0.61822548	-438.596962	-3.637514	-0.93324867	19.4	22.1
54	HOCl //b3lyp/6-31g*	-535.6458003	-0.63837795	-535.837314	-62.703662	-58.24031172	11.8	16.2
55	SO2 //b3lyp/6-31G*	-548.2155062	-1.02126932	-548.521887	-275.126807	-270.8997516	21.9	26.2
56	BF3 PLANAR	-324.198256	-1.06070574	-324.516468	-1148.213201	-1143.277261	-12.7	-7.7
57	bcl3 B3LYP	-1404.932343	-1.09800244	-1405.261744	-419.523674	-408.8378895	-16.6	-5.9
58	ALf3 B3LYP	-541.7239926	-1.1985774	-542.083566	-1194.619123	-1188.921788	14.6	20.3
59	alcl3 B3LYP	-1622.518299	-1.19996824	-1622.878290	-590.406893	-578.959713	-5.9	5.5
60	cf4 B3LYP	-436.9894532	-1.44898745	-437.424149	-943.989166	-937.2153756	-11.0	-4.2
61	ccl4 B3LYP	-1878.005388	-1.52224855	-1878.462062	-89.962947	-75.52269682	5.9	20.3
62	O=C=S. Singlet	-511.1729816	-0.87751468	-511.436236	-152.949959	-149.300514	-14.5	-10.8
63	CS2 B3LYP	-834.0348762	-0.97457605	-834.327249	106.915956	111.9569159	-9.8	-4.8
64	COF2 B3LYP	-312.6258388	-1.11896495	-312.961528	-617.918997	-613.403137	5.9	10.4
65	sif4 B3LYP	-688.5613031	-1.54977629	-689.026236	-1578.472465	-1570.280905	36.6	44.7
66	sicl4, td	-2129.561344	-1.58517761	-2130.036898	-647.122347	-631.2643267	15.6	31.5
67	nno B3LYP	-184.3632002	-0.8440736	-184.616422	72.294974	73.24015353	-9.7	-8.8
68	clno B3LYP	-589.6777028	-0.91151258	-589.951157	58.076212	62.53956233	6.2	10.7

69	nf3 c3v	-353.6476786	-1.23272482	-354.017496	-125.403866	-120.5992009	6.8	11.6
70	pf3 c3v	-640.4914921	-1.29226634	-640.879172	-934.110976	-929.3063109	24.4	29.2
71	ozone 1-a1	-225.0571772	-1.01287605	-225.361040	168.677799	171.5133392	26.0	28.8
72	f2o B3LYP	-274.3122492	-0.9651508	-274.601794	49.471929	53.62021918	24.8	28.9
73	CLF3, C2V	-758.9458666	-1.36782252	-759.356213	-146.601064	-138.2782293	12.4	20.7
74	CF2=CF2 D2H	-474.9352879	-1.64853415	-475.429848	-688.905009	-681.7636489	-30.3	-23.2
75	cl2c=ccl2 B3LYP	-1916.023961	-1.71888948	-1916.539628	-21.226696	-6.41887554	-8.7	6.1
76	cf3cn B3LYP	-429.8955316	-1.58901874	-430.372237	-511.599227	-506.0594216	-16.2	-10.7
77	PROPYNE C3V	-116.4042101	-0.63524896	-116.594785	195.118389	196.2210992	10.2	11.3
78	ALLENE D2D	-116.4041295	-0.62912122	-116.592866	198.499697	199.6024072	8.1	9.2
79	CYCLOPROPENE C2V	-116.3645447	-0.63857611	-116.556118	295.919775	297.0224852	18.9	20.0
80	PROPENE CS	-117.639404	-0.65881514	-117.837049	40.339345	41.44205454	20.3	21.4
81	CYCLOPROPANE D3H	-117.6257668	-0.66520851	-117.825329	73.589330	74.69204029	20.5	21.6
82	PROPANE C2V	-118.8571658	-0.69180553	-119.064707	-76.446439	-75.34372886	28.2	29.3
83	TRANS-1,3-BUTADIENE C2H	-155.6499549	-0.85177468	-155.905487	130.893755	132.3640355	20.9	22.3
84	Dimethyl acetylene	-155.6365346	-0.85756558	-155.893804	161.719751	163.190031	16.1	17.6
85	Methylene cyclopropane.	-155.6171974	-0.8586596	-155.874795	210.223380	211.6936598	9.8	11.3
86	Bicyclo[1.1.0]butane. C2v	-155.6012343	-0.87045576	-155.862371	244.775464	246.2457439	27.6	29.1
87	CYCLOBUTENE b3lyp	-155.6268046	-0.8608358	-155.885055	185.648568	187.1188485	29.2	30.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8498311	-0.8900161	-157.116836	59.414312	60.88459161	31.0	32.4
89	Isobutene. Single	-156.867317	-0.88562825	-157.133005	12.172390	13.64267049	28.9	30.4
90	Trans butane	-158.0801686	-0.9160402	-158.354981	-88.501351	-87.03107053	37.0	38.5
91	isobutane B3LYP/6-31G*	-158.081167	-0.91920481	-158.356928	-94.909548	-93.43926753	39.4	40.9
92	Spiropentane. D2d	-194.834411	-1.08941103	-195.161234	210.169844	212.0076939	24.8	26.7
93	Benzene B3LYP	-231.7537079	-1.25127059	-232.129089	92.263222	94.46864164	9.8	12.0
94	DIFLUOROMETHANE C2V	-238.6836484	-0.84749451	-238.937897	-452.029947	-448.4592665	-1.4	2.2
95	HCF3 TRI-FLUOROMETHANE	-337.8383211	-1.14936794	-338.183131	-702.750954	-697.5787194	-5.7	-0.5
96	CH2CL2 C2V	-959.2197681	-0.86977717	-959.480701	-87.627695	-80.22378484	7.8	15.2
97	chcl3 B3LYP/6-31G*	-1418.616439	-1.19266667	-1418.974239	-95.335003	-84.41292288	8.0	18.9
98	METHYLAMINE b3lyp	-95.65724323	-0.51102231	-95.810550	-5.483469	-5.115899023	17.5	17.9
99	Acetonitrile. CH3-CN.	-132.4949649	-0.67700854	-132.698067	77.902318	78.63745771	2.6	3.3
100	NITRO METHANE	-244.6019406	-1.11963061	-244.937830	-67.308103	-65.05017275	7.2	9.4
101	Methyl-nitrite. CH3-O-N=O.	-244.5981738	-1.10894786	-244.930858	-52.732443	-50.47451259	13.8	16.1
102	Methylsilane. CH3-SiH3.	-330.9344125	-0.56116707	-331.102763	-5.521552	-3.368642399	23.8	25.9
103	Formic Acid.	-189.4700674	-0.80996966	-189.713058	-375.827036	-373.569106	2.8	5.1
104	Methyl formate.	-228.6805417	-1.03090888	-228.989814	-352.994238	-350.368738	2.6	5.3
105	acetamide ch3cohn2	-208.8406415	-1.00095089	-209.140927	-226.772260	-225.0919397	11.7	13.4

106	Aziridine. (cyclic	-133.6437273	-0.70972908	-133.856646	143.673654	144.4087936	17.3	18.1
107	Cyanogen. NCCN.	-185.3219492	-0.90459619	-185.593328	295.528371	296.2635112	-11.2	-10.4
108	DIMETHYLAMINE b3lyp	-134.8715559	-0.73363931	-135.091648	5.259941	5.99508114	23.7	24.4
109	TRANS ETHYLAMINE	-134.8830934	-0.73480117	-135.103534	-25.009653	-24.27451315	22.3	23.0
110	KETENE B3LYP	-152.3351543	-0.70841404	-152.547679	-54.700841	-53.02052122	-7.4	-5.7
111	OXIRANE B3LYP	-153.5044641	-0.74003	-153.726473	-39.845580	-38.16526003	12.9	14.6
112	Acetaldehyde B3LYP	-153.5502639	-0.73220081	-153.769924	-157.045440	-155.3651199	9.1	10.7
113	Glyoxal, O=CH-CH=O.	-227.4526658	-0.99838648	-227.752182	-213.212454	-210.5869536	-1.1	1.5
114	ETHANOL TRANS	-154.7460099	-0.76291127	-154.974883	-212.143161	-210.4628406	23.0	24.7
115	DIMETHYL ETHER,	-154.7292337	-0.75990357	-154.957205	-166.570913	-164.8905931	17.5	19.2
116	Thiooxirane. (cyclic	-476.4168735	-0.82444004	-476.664206	97.337465	100.4092998	15.3	18.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.7191669	-1.1633436	-553.068170	-113.859212	-109.8421973	37.6	41.6
118	Thioethanol. CH3-CH2-SH.	-477.6351398	-0.84328838	-477.888126	-17.639073	-14.56723844	28.8	31.9
119	ch3sch3 B3LYP	-477.633061	-0.84511629	-477.886596	-11.095101	-8.023266328	26.1	29.2
120	Vinyl fluoride,	-177.5477681	-0.73844405	-177.769301	-137.039981	-134.7032858	1.9	4.2
121	Ethyl chloride.	-539.044486	-0.77875676	-539.278113	-95.644109	-91.39079917	16.5	20.7
122	Vinyl chloride,	-537.8213124	-0.75001457	-538.046317	31.266600	35.51990991	8.3	12.5
123	h2c=chcn B3LYP	-170.4965876	-0.87068599	-170.757793	191.206127	192.3088369	10.5	11.6
124	ACETONE B3LYP	-192.7850861	-0.9558904	-193.071853	-200.149425	-198.1015353	17.0	19.0
125	CH3COOH ACETIC	-228.7064007	-1.03062827	-229.015589	-421.120179	-418.494679	11.5	14.1
126	CH3CFO HCCO	-252.7162996	-1.03923469	-253.028070	-438.619079	-435.337204	3.6	6.9
127	ch3c(o)cl hcco	-612.9761492	-1.05488186	-613.292614	-237.975042	-232.7765518	4.7	9.9
128	ch3ch2ch2cl B3LYP	-578.2676077	-1.00324201	-578.568580	-108.114254	-103.4933742	23.7	28.3
129	Isopropyl alcohol,	-193.9739483	-0.98932561	-194.270746	-240.564287	-238.5163967	32.2	34.3
130	Methyl ethyl	-193.9574534	-0.98354412	-194.252517	-192.154433	-190.1065429	24.2	26.2
131	Trimethyl Amine.	-174.088192	-0.96099932	-174.376492	4.862165	5.964875452	28.7	29.8
132	FURAN B3LYP	-229.587196	-1.13722843	-229.928365	-26.608668	-24.19320825	8.1	10.5
133	Thiophene b3lyp	-552.4890549	-1.22844834	-552.857589	130.563986	134.3709608	15.5	19.3
134	PYROLE PLANAR	-209.7409741	-1.1100992	-210.074004	115.631622	117.1019021	7.3	8.7
135	C2v Pyridine	-247.7792881	-1.2946802	-248.167692	141.486892	143.324742	0.9	2.7
136	H2 B3LYP/6-31G*	-1.15879402	-0.03442671	-1.169122	8.544833	8.544832558	8.5	8.5
137	SH b3lyp/6-31G*	-398.5555726	-0.35627321	-398.662455	148.455782	150.7924772	5.4	7.7
138	CCH B3LYP	-76.45701546	-0.37629724	-76.569905	581.450643	582.1857829	16.2	16.9
139	C2H3 CS,2-A'	-77.73666031	-0.39822297	-77.856127	306.327172	307.0623117	6.8	7.5
140	ch3co hcco	-152.9088858	-0.71015036	-153.121931	-9.348170	-7.66785031	0.7	2.4
141	H2COH C1	-114.8661095	-0.50765814	-115.018407	-8.899616	-7.58686642	8.3	9.6
142	ch3o CS,	-114.8598506	-0.48096538	-115.004140	24.984451	26.29720121	7.8	9.1

143	ch3ch2o 2A"	-154.0878889	-0.70404781	-154.299103	-0.260705	1.419615337	15.2	16.9
144	ch3s 2-A'	-437.7796143	-0.58278576	-437.954450	133.091785	135.7960498	8.4	11.1
145	c2h5 staggered	-78.97539121	-0.4296989	-79.104301	134.403940	135.1390802	13.5	14.2
146	(ch3)2ch Cs	-118.203001	-0.65485422	-118.399457	109.648842	110.7515518	19.7	20.8
147	TERT-BUTYL RADICAL	-157.4307758	-0.88200921	-157.695379	82.622867	84.09314703	31.2	32.6
148	NO2 RADICAL	-204.7564044	-0.89393397	-205.024585	25.524851	27.41521146	-7.5	-5.6

MAD	**13.0**	**14.7**
LD	**39.4**	**44.7**

Table S5.54b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 30%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498801	0.000000	-0.498801
2	li	-7.467286	-0.014485	-7.471632
3	be	-14.634910	-0.052498	-14.650659
4	b	-24.613243	-0.076263	-24.636122
5	c	-37.795480	-0.102919	-37.826355
6	n	-54.527843	-0.133537	-54.567904
7	o	-74.988614	-0.190300	-75.045704
8	f	-99.632933	-0.252733	-99.708753
9	na	-162.137670	-0.170121	-162.188706
10	al	-242.217557	-0.218274	-242.283039
11	si	-289.217532	-0.248070	-289.291953
12	p	-341.099316	-0.276864	-341.182375
13	s	-397.931813	-0.317784	-398.027148
14	cl	-459.948423	-0.288544	-460.034986

Table S5.55a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04493936	-0.04617596	-8.059254	147.849357	147.8493569	8.5	8.5
2	BERYLLIUM HYDRIDE	-15.22023584	-0.05442084	-15.237106	319.936253	319.9362525	-21.9	-21.9
3	DOUBLET CH	-38.41233753	-0.14306554	-38.456688	600.845936	601.2135061	4.6	5.0
4	CH2 3-B1	-39.07527959	-0.16206595	-39.125520	395.946945	396.314515	3.9	4.3
5	Singlet methylene,	-39.05121737	-0.181881	-39.107600	441.382678	441.7502484	11.3	11.6
6	Methyl radical,	-39.74628245	-0.20646718	-39.810287	153.132966	153.5005361	6.7	7.1
7	ch4 //b3lyp/6-31G*	-40.40996376	-0.24769058	-40.486748	-62.568322	-62.2007516	12.3	12.7
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14031622	-0.18598276	-55.197971	360.409359	360.4093593	3.9	3.9
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78002124	-0.23890811	-55.854083	191.010564	191.0105639	2.3	2.3
10	AMMONIA, //b3lyp/6-31G*	-56.44434479	-0.29232357	-56.534965	-34.745807	-34.74580747	11.3	11.3
11	OH RADICAL	-75.63294437	-0.25621958	-75.712372	42.698392	43.6435721	3.4	4.3
12	Water //b3lyp/6-31G*	-76.30831163	-0.32413617	-76.408794	-229.122535	-228.1773551	12.7	13.7
13	HYDROGEN FLUORIDE,	-100.325531	-0.33497524	-100.429373	-266.293543	-264.6919876	6.1	7.7
14	SIH2 singlet	-290.4326269	-0.30324777	-290.526634	277.167469	278.9528091	4.4	6.2
15	SIH2 3B1	-290.4073546	-0.28097428	-290.494457	362.659215	364.4445552	2.0	3.8
16	SIH3 c3v	-291.0477326	-0.30869452	-291.143428	204.667283	206.4526228	4.3	6.0
17	SIH4 //b3lyp/6-31G*	-291.6897939	-0.33562606	-291.793838	44.840381	46.6257207	10.5	12.3
18	ph2 doublet	-342.3133941	-0.34247922	-342.419563	142.325615	142.3256154	3.8	3.8
19	PH3 c3v	-342.9401655	-0.37319648	-343.055856	21.060474	21.06047359	15.6	15.6
20	SH2 //b3lyp/6-31G*	-399.1857419	-0.39450596	-399.308039	-8.394849	-6.058154208	12.1	14.4
21	HCL //b3lyp/6-31G*	-460.5946095	-0.33313043	-460.697880	-88.283947	-84.76577716	4.2	7.7
22	DILITHIUM //b3lyp/6-31G*	-14.95782287	-0.0571705	-14.975546	231.073351	231.0733515	15.2	15.2
23	Lithium Fluoride,	-107.2868352	-0.36347514	-107.399512	-337.954072	-336.3525172	-2.8	-1.2
24	ACETYLENE //b3lyp/6-31g*	-77.16535779	-0.41349738	-77.293542	232.666338	233.4014783	5.9	6.6
25	ETHYLENE //b3lyp/6-31g*	-78.40628077	-0.4346962	-78.541037	64.791798	65.5269379	12.5	13.2
26	ETHANE //b3lyp/6-31g*	-79.62851282	-0.46808123	-79.773618	-65.235622	-64.50048202	18.9	19.6
27	CYANO RADICAL,	-92.53967959	-0.44674091	-92.678169	449.815414	450.1829836	10.9	11.3
28	HYDROGEN CYANIDE	-93.24982763	-0.45746077	-93.391640	128.496477	128.8640465	-3.3	-2.9
29	CARBON MONOXIDE	-113.1399598	-0.46833461	-113.285143	-113.255494	-111.9427435	-2.8	-1.5
30	HCO BENT	-113.6645878	-0.49060209	-113.816674	34.868272	36.18102174	-7.0	-5.7
31	H2CO //b3lyp/6-31g*	-114.3063935	-0.51010252	-114.464525	-108.776875	-107.4641255	0.0	1.3

32	METHANOL //b3lyp/6-31g*	-115.5117379	-0.53986921	-115.679097	-188.590701	-187.2779511	12.2	13.6
33	Nitrogen N2,	-109.34642	-0.49089487	-109.498597	0.753799	0.753799091	0.8	0.8
34	H2NNH2 //b3lyp/6-31g*	-111.6519407	-0.55434102	-111.823786	110.082660	110.0826602	14.7	14.7
35	NO radical,	-129.6915512	-0.53261775	-129.856663	87.958499	88.90367889	-2.4	-1.5
36	O2 //b3lyp/6-31g*	-150.0987288	-0.59693024	-150.283777	-5.350689	-3.4603285	-5.4	-3.5
37	HYDROGEN PEROXIDE	-151.3141852	-0.62624721	-151.508322	-115.060050	-113.1696902	20.9	22.8
38	F2 //b3lyp/6-31g*	-199.2668827	-0.65484242	-199.469884	19.684638	22.88774758	19.7	22.9
39	CO2 D*H	-188.2996329	-0.78746402	-188.543747	-413.411041	-411.1531109	-20.1	-17.9
40	na2 //b3lyp/6-31G*	-324.2847788	-0.36803503	-324.398870	144.468317	144.468317	2.2	2.2
41	SI2 3-SGG	-578.523757	-0.55365679	-578.695391	590.332060	593.90274	5.0	8.6
42	P2 //b3lyp/6-31g*	-682.3235073	-0.70205526	-682.541144	155.730572	155.7305719	12.2	12.2
43	S2 //b3lyp/6-31g*	-795.9774113	-0.74987221	-796.209872	128.929950	133.6033401	0.5	5.2
44	CL2 //b3lyp/6-31g*	-919.9508648	-0.64475194	-920.150738	9.187144	16.22348385	9.2	16.2
45	Sodium Chloride	-622.2146559	-0.50398665	-622.370892	-175.537853	-172.0196831	6.9	10.4
46	SIO //b3lyp/6-31g*	-364.4491866	-0.60921809	-364.638044	-96.349352	-93.61883155	6.6	9.3
47	Carbon monosulfide,	-435.9436291	-0.5691097	-436.120053	287.474705	290.1789704	7.6	10.3
48	OS //b3lyp/6-31g*	-473.0582868	-0.67989761	-473.269055	3.255186	6.537061472	-1.8	1.5
49	CLO 2-PI	-534.9892663	-0.59688751	-535.174301	113.218673	117.6820226	12.0	16.4
50	CLF 1-SG	-559.6343667	-0.64704816	-559.834952	-50.442246	-45.3225209	4.8	9.9
51	si2h6 //b3lyp/6-31g*	-582.206818	-0.65219973	-582.409000	100.948025	104.5187051	21.0	24.6
52	Methyl chloride,	-499.8078884	-0.55434028	-499.979734	-74.614867	-70.72912673	7.4	11.3
53	H3C-SH METHANETHIOL	-438.4019094	-0.61821393	-438.593556	-4.395294	-1.691029144	18.6	21.3
54	HOCl //b3lyp/6-31g*	-535.6355483	-0.63837577	-535.833445	-64.916532	-60.4531821	9.6	14.0
55	SO2 //b3lyp/6-31G*	-548.2029606	-1.02125924	-548.519551	-280.765792	-276.5387372	16.3	20.5
56	BF3 PLANAR	-324.1863214	-1.06070632	-324.515140	-1151.472681	-1146.536741	-15.9	-11.0
57	bcl3 B3LYP	-1404.909457	-1.09798441	-1405.249832	-421.334670	-410.6488846	-18.4	-7.7
58	ALf3 B3LYP	-541.7084641	-1.19858496	-542.080025	-1198.033796	-1192.336461	11.1	16.8
59	alcl3 B3LYP	-1622.491823	-1.19995275	-1622.863809	-591.436920	-579.9897402	-6.9	4.5
60	cf4 B3LYP	-436.9735389	-1.44897996	-437.422723	-948.972459	-942.1986689	-15.9	-9.2
61	ccl4 B3LYP	-1877.974871	-1.52222394	-1878.446760	-93.636672	-79.19642166	2.2	16.6
62	O=C=S. Singlet	-511.1614349	-0.87749357	-511.433458	-157.137040	-153.4875952	-18.6	-15.0
63	CS2 B3LYP	-834.0196827	-0.97454635	-834.321792	103.332112	108.3730722	-13.4	-8.4
64	COF2 B3LYP	-312.6139321	-1.11895557	-312.960808	-622.919066	-618.4032057	0.9	5.4
65	sif4 B3LYP	-688.5417565	-1.54977243	-689.022186	-1582.519441	-1574.327881	32.5	40.7
66	sicl4, td	-2129.527196	-1.58515253	-2130.018593	-648.864141	-633.0061213	13.9	29.7
67	nno B3LYP	-184.3553265	-0.84405157	-184.616983	65.936997	66.88217709	-16.1	-15.1
68	clno B3LYP	-589.6652762	-0.91149443	-589.947839	52.861534	57.32488376	1.0	5.4

69	nf3 c3v	-353.6349005	-1.23271917	-354.017043	-131.198314	-126.3936492	1.0	5.8
70	pf3 c3v	-640.4749735	-1.29226292	-640.875575	-937.719656	-932.9149908	20.8	25.6
71	ozone 1-a1	-225.0484006	-1.01285387	-225.362385	159.803651	162.6391912	17.1	20.0
72	f2o B3LYP	-274.3025229	-0.96514909	-274.601719	44.269202	48.41749214	19.6	23.7
73	CLF3, C2V	-758.9284381	-1.36782055	-759.352462	-152.772577	-144.4497417	6.2	14.5
74	CF2=CF2 D2H	-474.9173359	-1.64852461	-475.428378	-695.265427	-688.1240673	-36.7	-29.6
75	cl2c=ccl2 B3LYP	-1915.99136	-1.71885937	-1916.524206	-26.076125	-11.26830453	-13.5	1.3
76	cf3cn B3LYP	-429.8785943	-1.58899571	-430.371183	-518.793504	-513.2536993	-23.4	-17.9
77	PROPYNE C3V	-116.3971781	-0.63522563	-116.594098	192.452114	193.5548242	7.5	8.6
78	ALLENE D2D	-116.3970941	-0.62909976	-116.592115	196.001842	197.1045519	5.6	6.7
79	CYCLOPROPENE C2V	-116.3574568	-0.63855882	-116.555410	293.308048	294.4107578	16.3	17.4
80	PROPENE CS	-117.6318334	-0.65879583	-117.836060	38.465293	39.56800309	18.4	19.5
81	CYCLOPROPANE D3H	-117.6181271	-0.66519359	-117.824337	71.725112	72.82782239	18.6	19.7
82	PROPANE C2V	-118.8490606	-0.69178805	-119.063515	-77.784471	-76.68176137	26.8	27.9
83	TRANS-1,3-BUTADIENE C2H	-155.6403349	-0.85174758	-155.904377	127.850521	129.3208011	17.8	19.3
84	Dimethyl acetylene	-155.6269185	-0.85753697	-155.892755	158.515597	159.9858774	12.9	14.4
85	Methylene cyclopropane.	-155.6075149	-0.85863678	-155.873692	207.160097	208.6303771	6.7	8.2
86	Bicyclo[1.1.0]butane. C2v	-155.5914833	-0.87043629	-155.861319	241.579567	243.0498469	24.4	25.9
87	CYCLOBUTENE b3lyp	-155.6170974	-0.86081279	-155.883949	182.592944	184.0632241	26.1	27.6
88	CYCLOBUTANE b3lyp/6-31G*	-156.8395897	-0.88999484	-157.115488	56.994123	58.46440256	28.5	30.0
89	Isobutene. Single	-156.8571525	-0.88560333	-157.131690	9.668299	11.1385786	26.4	27.9
90	Trans butane	-158.0694782	-0.9160165	-158.353443	-90.424098	-88.95381817	35.1	36.6
91	isobutane B3LYP/6-31G*	-158.0704673	-0.91918119	-158.355414	-96.891345	-95.42106503	37.4	38.9
92	Spiropentane. D2d	-194.8220745	-1.08938655	-195.159784	206.527777	208.3656265	21.2	23.0
93	Benzene B3LYP	-231.7398192	-1.25123346	-232.127702	86.967295	89.17271461	4.5	6.7
94	DIFLUOROMETHANE C2V	-238.6742403	-0.8474944	-238.936964	-454.689451	-451.1187707	-4.1	-0.5
95	HCF3 TRI-FLUOROMETHANE	-337.8256616	-1.1493655	-338.181965	-706.607446	-701.4352111	-9.6	-4.4
96	CH2CL2 C2V	-959.2030539	-0.86976403	-959.472681	-89.239378	-81.8354685	6.2	13.6
97	chcl3 B3LYP/6-31G*	-1418.592826	-1.19264818	-1418.962547	-97.897951	-86.97587086	5.4	16.4
98	METHYLAMINE b3lyp	-95.65149557	-0.51101582	-95.809910	-6.847604	-6.480033996	16.2	16.5
99	Acetonitrile. CH3-CN.	-132.487735	-0.67698795	-132.697601	74.593583	75.32872253	-0.7	0.0
100	NITRO METHANE	-244.5907176	-1.11961078	-244.937797	-73.826288	-71.56835798	0.6	2.9
101	Methyl-nitrite. CH3-O-N=O.	-244.5869876	-1.1089271	-244.930755	-59.065961	-56.80803118	7.5	9.7
102	Methylsilane. CH3-SiH3.	-330.9253373	-0.56115326	-331.099295	-5.347631	-3.194720877	23.9	26.1
103	Formic Acid.	-189.46161	-0.80996375	-189.712699	-379.934338	-377.6764077	-1.3	1.0
104	Methyl formate.	-228.669514	-1.0308936	-228.989091	-357.636026	-355.0105264	-2.0	0.6
105	acetamide ch3cohn2	-208.8298006	-1.00093675	-209.140091	-230.891266	-229.2109464	7.6	9.3

106	Aziridine. (cyclic	-133.6358814	-0.70971665	-133.855894	141.116638	141.8517785	14.8	15.5
107	Cyanogen. NCCN.	-185.3130271	-0.90456389	-185.593442	289.143419	289.8785591	-17.5	-16.8
108	DIMETHYLAMINE b3lyp	-134.8632273	-0.73362574	-135.090651	3.343236	4.078375823	21.8	22.5
109	TRANS ETHYLAMINE	-134.8747611	-0.73478838	-135.102546	-26.947889	-26.21274862	20.3	21.1
110	KETENE B3LYP	-152.327683	-0.70839895	-152.547287	-58.432204	-56.75188445	-11.2	-9.5
111	OXIRANE B3LYP	-153.4964161	-0.74001999	-153.725822	-42.897344	-41.21702413	9.8	11.5
112	Acetaldehyde B3LYP	-153.5422693	-0.73218934	-153.769248	-160.030662	-158.3503421	6.1	7.8
113	Glyoxal, O=CH-CH=O.	-227.4422151	-0.99837306	-227.751711	-218.516741	-215.8912413	-6.4	-3.8
114	ETHANOL TRANS	-154.7374636	-0.76290192	-154.973963	-214.487529	-212.8072091	20.7	22.3
115	DIMETHYL ETHER,	-154.7207005	-0.75989231	-154.956267	-168.869443	-167.1891227	15.2	16.9
116	Thiooxirane. (cyclic	-476.405179	-0.82442314	-476.660750	95.219269	98.29110388	13.2	16.3
117	Dimethylsulfoxide. (CH3)2SO.	-552.7039611	-1.16332553	-553.064592	-117.436178	-113.419163	34.0	38.0
118	Thioethanol. CH3-CH2-SH.	-477.6229712	-0.84327072	-477.884385	-19.006791	-15.93495564	27.4	30.5
119	ch3sch3 B3LYP	-477.6208997	-0.84509865	-477.882880	-12.530124	-9.458289014	24.7	27.8
120	Vinyl fluoride,	-177.5395427	-0.73843387	-177.768457	-139.613119	-137.2764242	-0.7	1.6
121	Ethyl chloride.	-539.0320777	-0.77874169	-539.273488	-97.069394	-92.81608388	15.1	19.3
122	Vinyl chloride,	-537.8094321	-0.7499977	-538.041931	29.210985	33.4642949	6.2	10.5
123	h2c=chcn B3LYP	-170.4873154	-0.87065785	-170.757219	186.690707	187.7934175	5.9	7.0
124	ACETONE B3LYP	-192.7744996	-0.95587207	-193.070820	-203.686546	-201.6386559	13.5	15.5
125	CH3COOH ACETIC	-228.6953531	-1.03061555	-229.014844	-425.704436	-423.0789362	6.9	9.5
126	CH3CFO HCCO	-252.7050548	-1.03922166	-253.027213	-442.940344	-439.6584685	-0.7	2.6
127	ch3c(o)cl hcco	-612.9612635	-1.05486317	-613.288271	-241.923489	-236.7249995	0.7	5.9
128	ch3ch2ch2cl B3LYP	-578.2526151	-1.00322083	-578.563614	-110.133259	-105.5123792	21.7	26.3
129	Isopropyl alcohol,	-193.9628084	-0.98930946	-194.269494	-243.527940	-241.48005	29.3	31.3
130	Methyl ethyl	-193.9463349	-0.98352623	-194.251228	-195.021168	-192.9732777	21.3	23.3
131	Trimethyl Amine.	-174.0772694	-0.96097921	-174.375173	2.302159	3.404869074	26.2	27.3
132	FURAN B3LYP	-229.5749433	-1.13720275	-229.927476	-32.015905	-29.60044493	2.7	5.1
133	Thiophene b3lyp	-552.4731587	-1.22841622	-552.853968	125.902730	129.709705	10.8	14.6
134	PYROLE PLANAR	-209.7289127	-1.11007193	-210.073035	110.663174	112.1334539	2.3	3.8
135	C2v Pyridine	-247.7651927	-1.29464494	-248.166533	135.529232	137.3670821	-5.1	-3.2
136	H2 B3LYP/6-31G*	-1.15841136	-0.03442699	-1.169084	8.645405	8.645405224	8.6	8.6
137	SH b3lyp/6-31G*	-398.5488946	-0.35627525	-398.659340	148.422528	150.7592231	5.3	7.7
138	CCH B3LYP	-76.4529624	-0.37627797	-76.569609	579.248389	579.983529	14.0	14.7
139	C2H3 CS,2-A'	-77.73203562	-0.39820261	-77.855478	305.050959	305.7860995	5.5	6.2
140	ch3co hcco	-152.9012225	-0.7101293	-153.121363	-12.616166	-10.9358456	-2.6	-0.9
141	H2COH C1	-114.8604812	-0.50764959	-115.017853	-10.714472	-9.401721504	6.4	7.8
142	ch3o CS,	-114.8542554	-0.48095094	-115.003350	23.788304	25.10105439	6.6	7.9

143	ch3ch2o 2A"	-154.0797097	-0.70402482	-154.297957	-2.012411	-0.33209122	13.5	15.1
144	ch3s 2-A'	-437.7703591	-0.58277827	-437.951020	132.396068	135.1003325	7.7	10.4
145	c2h5 staggered	-78.97021715	-0.42969182	-79.103422	133.732890	134.4680297	12.8	13.6
146	(ch3)2ch Cs	-118.1952356	-0.65483741	-118.398235	108.388118	109.4908282	18.4	19.5
147	TERT-BUTYL RADICAL	-157.4204164	-0.88198225	-157.693831	80.727216	82.19749586	29.3	30.7
148	NO2 RADICAL	-204.7480855	-0.89391271	-205.025198	18.798641	20.68900103	-14.3	-12.4

MAD	**11.9**	**13.2**
LD	**37.4**	**40.7**

Table S5.55b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 31%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498801	0.000000	-0.498801
2	li	-7.466749	-0.014485	-7.471240
3	be	-14.633961	-0.052493	-14.650234
4	b	-24.611978	-0.076267	-24.635621
5	c	-37.793881	-0.102925	-37.825788
6	n	-54.525915	-0.133541	-54.567313
7	o	-74.986030	-0.190310	-75.045026
8	f	-99.629713	-0.252743	-99.708064
9	na	-162.133579	-0.170119	-162.186315
10	al	-242.212600	-0.218275	-242.280266
11	si	-289.212217	-0.248071	-289.289119
12	p	-341.093645	-0.276858	-341.179471
13	s	-397.925507	-0.317787	-398.024021
14	cl	-459.941503	-0.288547	-460.030953

Table S5.56a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 32%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04405106	-0.04617707	-8.058828	147.938894	147.9388938	8.6	8.6
2	BERYLLIUM HYDRIDE	-15.21915529	-0.05441367	-15.236568	320.233222	320.2332221	-21.6	-21.6
3	DOUBLET CH	-38.4103602	-0.14306966	-38.456142	600.788401	601.1559707	4.6	4.9
4	CH2 3-B1	-39.07312831	-0.16206463	-39.124989	395.851830	396.2194	3.8	4.2
5	Singlet methylene,	-39.04889	-0.18187736	-39.107091	441.231593	441.5991626	11.1	11.5
6	Methyl radical,	-39.74369706	-0.2064709	-39.809768	153.007618	153.3751881	6.6	6.9
7	ch4 //b3lyp/6-31G*	-40.40701794	-0.24768469	-40.486277	-62.821607	-62.454037	12.1	12.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13793593	-0.18599312	-55.197454	360.214167	360.2141671	3.7	3.7
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77722517	-0.238915	-55.853678	190.520362	190.5203623	1.8	1.8
10	AMMONIA, //b3lyp/6-31G*	-56.44116548	-0.29232438	-56.534709	-35.627127	-35.62712717	10.4	10.4
11	OH RADICAL	-75.62993384	-0.25622958	-75.711927	42.087058	43.03223781	2.8	3.7
12	Water //b3lyp/6-31G*	-76.30490729	-0.32414219	-76.408633	-230.479727	-229.5345475	11.4	12.3
13	HYDROGEN FLUORIDE,	-100.3219072	-0.33498361	-100.429102	-267.390388	-265.7888333	5.0	6.6
14	SIH2 singlet	-290.4266533	-0.30324008	-290.523690	277.455166	279.2405062	4.7	6.4
15	SIH2 3B1	-290.4015777	-0.28094847	-290.491481	363.030517	364.8158568	2.4	4.2
16	SIH3 c3v	-291.0415792	-0.30867995	-291.140357	205.289716	207.0750556	4.9	6.7
17	SIH4 //b3lyp/6-31G*	-291.6833021	-0.33561727	-291.790700	45.639497	47.42483652	11.3	13.1
18	ph2 doublet	-342.3069632	-0.34247924	-342.416557	142.594889	142.5948888	4.1	4.1
19	PH3 c3v	-342.9334068	-0.37318754	-343.052827	21.391485	21.39148455	16.0	16.0
20	SH2 //b3lyp/6-31G*	-399.178724	-0.39450031	-399.304964	-8.532710	-6.19601475	12.0	14.3
21	HCL //b3lyp/6-31G*	-460.5873387	-0.33312815	-460.693940	-88.528560	-85.01039027	3.9	7.5
22	DILITHIUM //b3lyp/6-31G*	-14.95648538	-0.05716649	-14.974779	231.028464	231.0284644	15.1	15.1
23	Lithium Fluoride,	-107.2826581	-0.36348918	-107.398975	-339.380643	-337.7790884	-4.2	-2.6
24	ACETYLENE //b3lyp/6-31g*	-77.16091029	-0.41347925	-77.293224	230.523372	231.2585116	3.8	4.5
25	ETHYLENE //b3lyp/6-31g*	-78.40129627	-0.43468232	-78.540395	63.498579	64.23371899	11.2	11.9
26	ETHANE //b3lyp/6-31g*	-79.62299191	-0.46806969	-79.772774	-65.998986	-65.26384641	18.1	18.8
27	CYANO RADICAL,	-92.53541434	-0.44665806	-92.678345	446.311922	446.6794917	7.4	7.8
28	HYDROGEN CYANIDE	-93.24518205	-0.45744585	-93.391565	125.653019	126.0205891	-6.1	-5.8
29	CARBON MONOXIDE	-113.1351112	-0.46832852	-113.284976	-116.085879	-114.7731289	-5.6	-4.3
30	HCO BENT	-113.6595062	-0.49058935	-113.816495	32.070609	33.38335851	-9.8	-8.5
31	H2CO //b3lyp/6-31g*	-114.3009869	-0.51009745	-114.464218	-111.239758	-109.9270078	-2.5	-1.1

32	METHANOL //b3lyp/6-31g*	-115.5057766	-0.53986619	-115.678534	-190.380597	-189.0678466	10.5	11.8
33	Nitrogen N2,	-109.3415829	-0.49087982	-109.498664	-2.528172	-2.528172265	-2.5	-2.5
34	H2NNH2 //b3lyp/6-31g*	-111.6459722	-0.55433996	-111.823361	108.093752	108.093752	12.7	12.7
35	NO radical,	-129.6862712	-0.53260826	-129.856706	84.512263	85.45744286	-5.9	-4.9
36	O2 //b3lyp/6-31g*	-150.0930064	-0.59692946	-150.284024	-9.558422	-7.668062446	-9.6	-7.7
37	HYDROGEN PEROXIDE	-151.307822	-0.62625185	-151.508223	-118.359503	-116.4691432	17.6	19.5
38	F2 //b3lyp/6-31g*	-199.260126	-0.65484602	-199.469677	16.610026	19.81313638	16.6	19.8
39	CO2 D*H	-188.2917223	-0.78745099	-188.543707	-418.354908	-416.0969775	-25.1	-22.8
40	na2 //b3lyp/6-31G*	-324.2763524	-0.36802951	-324.394122	144.381392	144.3813922	2.1	2.1
41	SI2 3-SGG	-578.5127776	-0.55363936	-578.689942	589.755788	593.3264677	4.4	8.0
42	P2 //b3lyp/6-31g*	-682.3113654	-0.7020323	-682.536016	153.949442	153.9494416	10.4	10.4
43	S2 //b3lyp/6-31g*	-795.9643432	-0.74986341	-796.204300	127.139045	131.8124354	-1.3	3.4
44	CL2 //b3lyp/6-31g*	-919.9367365	-0.6447444	-920.143055	8.180176	15.21651638	8.2	15.2
45	Sodium Chloride	-622.203327	-0.50398884	-622.364603	-175.893681	-172.3755113	6.5	10.0
46	SIO //b3lyp/6-31g*	-364.4406611	-0.6092261	-364.635613	-99.188064	-96.45754394	3.7	6.5
47	Carbon monosulfide,	-435.9351472	-0.56909015	-436.117256	285.118613	287.8228782	5.2	7.9
48	OS //b3lyp/6-31g*	-473.0488822	-0.67988907	-473.266447	0.113017	3.39489169	-4.9	-1.6
49	CLO 2-PI	-534.9793513	-0.59684744	-535.170342	111.243416	115.7067662	10.0	14.5
50	CLF 1-SG	-559.6239045	-0.64704753	-559.830960	-52.360250	-47.24052505	2.9	8.0
51	si2h6 //b3lyp/6-31g*	-582.194202	-0.65218325	-582.402901	102.080446	105.6511255	22.2	25.7
52	Methyl chloride,	-499.7980638	-0.55433141	-499.975450	-75.446069	-71.56032905	6.6	10.4
53	H3C-SH METHANETHIOL	-438.3923247	-0.61820238	-438.590149	-5.151964	-2.447699032	17.9	20.6
54	HOCl //b3lyp/6-31g*	-535.6252965	-0.6383736	-535.829576	-67.128479	-62.66512883	7.3	11.8
55	SO2 //b3lyp/6-31G*	-548.1904152	-1.02124917	-548.517215	-286.402806	-282.1757511	10.7	14.9
56	BF3 PLANAR	-324.1743868	-1.0607069	-324.513813	-1154.730237	-1149.794297	-19.2	-14.3
57	bcl3 B3LYP	-1404.886571	-1.09796639	-1405.237920	-423.143744	-412.4579588	-20.2	-9.5
58	ALf3 B3LYP	-541.6929358	-1.19859253	-542.076485	-1201.447004	-1195.749669	7.7	13.4
59	alcl3 B3LYP	-1622.465348	-1.19993725	-1622.849327	-592.465253	-581.0180729	-8.0	3.5
60	cf4 B3LYP	-436.9576248	-1.44897247	-437.421296	-953.952706	-947.1789155	-20.9	-14.1
61	ccl4 B3LYP	-1877.944354	-1.52219934	-1878.431458	-97.307755	-82.86750524	-1.5	12.9
62	O=C=S. Singlet	-511.1498882	-0.87747247	-511.430679	-161.321824	-157.6723792	-22.8	-19.2
63	CS2 B3LYP	-834.0044893	-0.97451666	-834.316335	99.750598	104.7915583	-17.0	-11.9
64	COF2 B3LYP	-312.6020256	-1.1189462	-312.960088	-627.916489	-623.4006294	-4.1	0.4
65	sif4 B3LYP	-688.5222101	-1.54976857	-689.018136	-1586.563779	-1578.372219	28.5	36.7
66	sicl4, td	-2129.493047	-1.58512745	-2130.000288	-650.603453	-634.7454331	12.1	28.0
67	nno B3LYP	-184.3474529	-0.84402954	-184.617542	59.581215	60.52639505	-22.4	-21.5
68	clno B3LYP	-589.6528497	-0.91147628	-589.944522	47.648837	52.11218745	-4.2	0.2

69	nf3 c3v	-353.6221225	-1.23271352	-354.016591	-136.990541	-132.1858763	-4.8	0.0
70	pf3 c3v	-640.458455	-1.29225951	-640.871978	-941.326739	-936.5220744	17.2	22.0
71	ozone 1-a1	-225.0396241	-1.0128317	-225.363730	150.932476	153.7680163	8.3	11.1
72	f2o B3LYP	-274.2927968	-0.96514739	-274.601644	39.068278	43.21656778	14.4	18.5
73	CLF3, C2V	-758.9110097	-1.36781858	-759.348712	-158.942017	-150.619182	0.0	8.4
74	CF2=CF2 D2H	-474.899384	-1.64851507	-475.426909	-701.622331	-694.4809707	-43.1	-35.9
75	cl2c=ccl2 B3LYP	-1915.958759	-1.71882925	-1916.508784	-30.922246	-16.11442591	-18.4	-3.6
76	cf3cn B3LYP	-429.8616571	-1.58897268	-430.370128	-525.983927	-520.4441218	-30.6	-25.1
77	PROPYNE C3V	-116.3901461	-0.63520229	-116.593411	189.788076	190.890786	4.9	6.0
78	ALLENE D2D	-116.3900587	-0.6290783	-116.591364	193.506091	194.6088007	3.1	4.2
79	CYCLOPROPENE C2V	-116.3503689	-0.63854154	-116.554702	290.698223	291.8009334	13.7	14.8
80	PROPENE CS	-117.6242628	-0.65877652	-117.835071	36.593207	37.69591657	16.5	17.6
81	CYCLOPROPANE D3H	-117.6104875	-0.66517866	-117.823345	69.862664	70.96537356	16.7	17.8
82	PROPANE C2V	-118.8409554	-0.69177056	-119.062322	-79.120627	-78.01791665	25.5	26.6
83	TRANS-1,3-BUTADIENE C2H	-155.6307151	-0.85172048	-155.903266	124.810048	126.2803277	14.8	16.2
84	Dimethyl acetylene	-155.6173026	-0.85750835	-155.891705	155.314266	156.7845461	9.7	11.2
85	Methylene cyclopropane.	-155.5978325	-0.85861397	-155.872589	204.099316	205.569596	3.7	5.2
86	Bicyclo[1.1.0]butane. C2v	-155.5817325	-0.87041681	-155.860266	238.386065	239.8563449	21.2	22.7
87	CYCLOBUTENE b3lyp	-155.6073905	-0.86078979	-155.882843	179.539831	181.0101113	23.1	24.5
88	CYCLOBUTANE b3lyp/6-31G*	-156.8293483	-0.88997358	-157.114140	54.576388	56.04666783	26.1	27.6
89	Isobutene. Single	-156.8469881	-0.8855784	-157.130373	7.166862	8.637141612	23.9	25.4
90	Trans butane	-158.0587879	-0.9159928	-158.351906	-92.344342	-90.87406214	33.2	34.6
91	isobutane B3LYP/6-31G*	-158.0597679	-0.91915757	-158.353898	-98.870669	-97.40038931	35.4	36.9
92	Spiropentane. D2d	-194.8097382	-1.08936207	-195.158334	202.888693	204.7265433	17.5	19.4
93	Benzene B3LYP	-231.7259307	-1.25119633	-232.126314	81.675377	83.88079672	-0.7	1.5
94	DIFLUOROMETHANE C2V	-238.6648324	-0.8474943	-238.936031	-457.347542	-453.7768623	-6.7	-3.2
95	HCF3 TRI-FLUOROMETHANE	-337.8130022	-1.14936306	-338.180798	-710.461762	-705.2895272	-13.4	-8.2
96	CH2CL2 C2V	-959.1863399	-0.86975088	-959.464660	-90.849597	-83.4456866	4.5	11.9
97	chcl3 B3LYP/6-31G*	-1418.569214	-1.19262969	-1418.950856	-100.458905	-89.53682505	2.9	13.8
98	METHYLAMINE b3lyp	-95.645748	-0.51100932	-95.809271	-8.210949	-7.843378694	14.8	15.2
99	Acetonitrile. CH3-CN.	-132.4805051	-0.67696737	-132.697135	71.286774	72.02191447	-4.0	-3.3
100	NITRO METHANE	-244.5794947	-1.11959095	-244.937764	-80.341683	-78.08375336	-5.9	-3.6
101	Methyl-nitrite. CH3-O-N=O.	-244.5758015	-1.10890635	-244.930652	-65.396623	-63.13869323	1.1	3.4
102	Methylsilane. CH3-SiH3.	-330.9162623	-0.56113945	-331.095827	-5.172507	-3.019596877	24.1	26.3
103	Formic Acid.	-189.4531527	-0.80995784	-189.712339	-384.039792	-381.7818622	-5.4	-3.1
104	Methyl formate.	-228.6584864	-1.03087832	-228.988367	-362.275141	-359.6496411	-6.6	-4.0
105	acetamide ch3cohn2	-208.8189597	-1.00092261	-209.139255	-235.008036	-233.3277157	3.5	5.2

106	Aziridine. (cyclic	-133.6280355	-0.70970423	-133.855141	138.561096	139.2962357	12.2	12.9
107	Cyanogen. NCCN.	-185.3041051	-0.90453159	-185.593555	282.761255	283.4963952	-23.9	-23.2
108	DIMETHYLAMINE b3lyp	-134.8548988	-0.73361218	-135.089655	1.428036	2.163176492	19.8	20.6
109	TRANS ETHYLAMINE	-134.866429	-0.73477559	-135.101557	-28.884624	-28.1494844	18.4	19.1
110	KETENE B3LYP	-152.3202117	-0.70838386	-152.546895	-62.161466	-60.4811457	-14.9	-13.2
111	OXIRANE B3LYP	-153.4883683	-0.74000998	-153.725171	-45.947352	-44.26703178	6.8	8.5
112	Acetaldehyde B3LYP	-153.5342749	-0.73217788	-153.768572	-163.014007	-161.3336869	3.1	4.8
113	Glyoxal, O=CH-CH=O.	-227.4317644	-0.99835964	-227.751240	-223.818374	-221.1928741	-11.7	-9.1
114	ETHANOL TRANS	-154.7289173	-0.76289257	-154.973043	-216.830176	-215.1498559	18.3	20.0
115	DIMETHYL ETHER,	-154.7121675	-0.75988105	-154.955329	-171.166177	-169.4858566	12.9	14.6
116	Thiooxirane. (cyclic	-476.3934846	-0.82440624	-476.657295	93.102799	96.17463398	11.1	14.2
117	Dimethylsulfoxide. (CH3)2SO.	-552.6887554	-1.16330746	-553.061014	-121.010768	-116.9937532	30.5	34.5
118	Thioethanol. CH3-CH2-SH.	-477.6108027	-0.84325305	-477.880644	-20.372734	-17.30089853	26.1	29.1
119	ch3sch3 B3LYP	-477.6087386	-0.84508101	-477.879165	-13.963408	-10.89157309	23.3	26.3
120	Vinyl fluoride,	-177.5313173	-0.7384237	-177.767613	-142.184509	-139.8478139	-3.3	-0.9
121	Ethyl chloride.	-539.0196694	-0.77872662	-539.268862	-98.493015	-94.23970507	13.6	17.9
122	Vinyl chloride,	-537.7975519	-0.74998084	-538.037546	27.157146	31.41045578	4.1	8.4
123	h2c=chcn B3LYP	-170.4780433	-0.87062971	-170.756645	182.178033	183.2807433	1.4	2.5
124	ACETONE B3LYP	-192.7639132	-0.95585375	-193.069786	-207.221121	-205.1732309	9.9	12.0
125	CH3COOH ACETIC	-228.6843056	-1.03060284	-229.014099	-430.286162	-427.6606624	2.3	5.0
126	CH3CFO HCCO	-252.69381	-1.03920864	-253.026357	-447.259095	-443.9772204	-5.0	-1.7
127	ch3c(o)cl hcco	-612.9463779	-1.0548445	-613.283928	-245.869434	-240.6709435	-3.2	2.0
128	ch3ch2ch2cl B3LYP	-578.2376227	-1.00319965	-578.558647	-112.149945	-107.5290654	19.6	24.3
129	Isopropyl alcohol,	-193.9516685	-0.98929331	-194.268242	-246.489206	-244.4413163	26.3	28.4
130	Methyl ethyl	-193.9352165	-0.98350835	-194.249939	-197.885406	-195.8375163	18.4	20.5
131	Trimethyl Amine.	-174.066347	-0.96095911	-174.373854	-0.255663	0.847046588	23.6	24.7
132	FURAN B3LYP	-229.5626906	-1.13717707	-229.926587	-37.419762	-35.00430207	-2.7	-0.3
133	Thiophene b3lyp	-552.4572627	-1.2283841	-552.850346	121.244773	125.0517485	6.2	10.0
134	PYROLE PLANAR	-209.7168513	-1.11004467	-210.072066	105.697725	107.1680052	-2.7	-1.2
135	C2v Pyridine	-247.7510974	-1.29460969	-248.165372	129.575352	131.4132019	-11.0	-9.2
136	H2 B3LYP/6-31G*	-1.1580287	-0.03442727	-1.169045	8.745963	8.745963187	8.7	8.7
137	SH b3lyp/6-31G*	-398.5422167	-0.3562773	-398.656225	148.389328	150.7260232	5.3	7.6
138	CCH B3LYP	-76.44890944	-0.37625874	-76.569312	577.047677	577.7828173	11.8	12.5
139	C2H3 CS,2-A'	-77.72741103	-0.39818229	-77.854829	303.776347	304.5114867	4.2	4.9
140	ch3co hcco	-152.8935592	-0.71010821	-153.120794	-15.881852	-14.20153151	-5.8	-4.2
141	H2COH C1	-114.8548529	-0.50764104	-115.017298	-12.528060	-11.21531005	4.6	5.9
142	ch3o CS,	-114.8486602	-0.48093652	-115.002560	22.593769	23.9065191	5.4	6.8

143	ch3ch2o 2A"	-154.0715305	-0.70400187	-154.296811	-3.761740	-2.0814196	11.7	13.4
144	ch3s 2-A'	-437.7611039	-0.58277079	-437.947591	131.701239	134.4055042	7.0	9.7
145	c2h5 staggered	-78.96504319	-0.42968477	-79.102542	133.062750	133.7978897	12.1	12.9
146	(ch3)2ch Cs	-118.1874703	-0.65482061	-118.397013	107.129194	108.2319035	17.2	18.3
147	TERT-BUTYL RADICAL	-157.4100571	-0.88195531	-157.692283	78.834196	80.30447649	27.4	28.8
148	NO2 RADICAL	-204.7397666	-0.89389145	-205.025812	12.074961	13.96532106	-21.0	-19.1

MAD	**11.5**	**12.4**
LD	**-43.1**	**36.9**

Table S5.56b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 32%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498801	0.000000	-0.498801
2	li	-7.466213	-0.014484	-7.470848
3	be	-14.633012	-0.052488	-14.649808
4	b	-24.610713	-0.076271	-24.635120
5	c	-37.792282	-0.102931	-37.825220
6	n	-54.523987	-0.133545	-54.566721
7	o	-74.983445	-0.190321	-75.044348
8	f	-99.626494	-0.252753	-99.707375
9	na	-162.129488	-0.170117	-162.183925
10	al	-242.207644	-0.218277	-242.277493
11	si	-289.206902	-0.248073	-289.286285
12	p	-341.087975	-0.276853	-341.176568
13	s	-397.919201	-0.317790	-398.020894
14	cl	-459.934583	-0.288551	-460.026920

Table S5.57a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 33%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04316279	-0.04617818	-8.058402	148.028321	148.0283207	8.7	8.7
2	BERYLLIUM HYDRIDE	-15.21807482	-0.05440652	-15.236029	320.530197	320.5301966	-21.3	-21.3
3	DOUBLET CH	-38.4083829	-0.14307379	-38.455597	600.731010	601.0985804	4.5	4.9
4	CH2 3-B1	-39.07097714	-0.16206333	-39.124458	395.756927	396.1244971	3.7	4.1
5	Singlet methylene,	-39.04656267	-0.18187373	-39.106581	441.081033	441.4486033	11.0	11.3
6	Methyl radical,	-39.74111172	-0.20647463	-39.809248	152.882384	153.2499539	6.4	6.8
7	ch4 //b3lyp/6-31G*	-40.40407218	-0.24767879	-40.485806	-63.074283	-62.70671302	11.8	12.2
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13555568	-0.18600351	-55.196937	360.018617	360.0186172	3.5	3.5
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77442914	-0.23892191	-55.853273	190.029994	190.029994	1.3	1.3
10	AMMONIA, //b3lyp/6-31G*	-56.43798621	-0.29232519	-56.534454	-36.508277	-36.508277	9.5	9.5
11	OH RADICAL	-75.62692336	-0.2562396	-75.711482	41.475700	42.4208799	2.1	3.1
12	Water //b3lyp/6-31G*	-76.30150299	-0.32414821	-76.408472	-231.836691	-230.8915109	10.0	10.9
13	HYDROGEN FLUORIDE,	-100.3182835	-0.33499199	-100.428831	-268.487207	-266.8856516	3.9	5.5
14	SIH2 singlet	-290.4206798	-0.30323239	-290.520747	277.743367	279.5287068	4.9	6.7
15	SIH2 3B1	-290.395801	-0.28092269	-290.488506	363.402880	365.1882199	2.7	4.5
16	SIH3 c3v	-291.035426	-0.30866539	-291.137286	205.912873	207.6982133	5.5	7.3
17	SIH4 //b3lyp/6-31G*	-291.6768104	-0.33560848	-291.787561	46.439174	48.22451367	12.1	13.9
18	ph2 doublet	-342.3005324	-0.34247927	-342.413551	142.863900	142.8638996	4.4	4.4
19	PH3 c3v	-342.9266481	-0.3731786	-343.049797	21.722712	21.72271212	16.3	16.3
20	SH2 //b3lyp/6-31G*	-399.1717062	-0.39449467	-399.301889	-8.670050	-6.333354917	11.8	14.2
21	HCL //b3lyp/6-31G*	-460.5800681	-0.33312586	-460.690000	-88.772849	-85.25467886	3.7	7.2
22	DILITHIUM //b3lyp/6-31G*	-14.95514798	-0.05716247	-14.974012	230.983614	230.9836143	15.1	15.1
23	Lithium Fluoride,	-107.2784811	-0.36350324	-107.398437	-340.807467	-339.2059116	-5.7	-4.1
24	ACETYLENE //b3lyp/6-31g*	-77.15646285	-0.41346113	-77.292905	228.382089	229.1172286	1.6	2.3
25	ETHYLENE //b3lyp/6-31g*	-78.39631185	-0.43466845	-78.539752	62.206768	62.94190814	9.9	10.6
26	ETHANE //b3lyp/6-31g*	-79.61747108	-0.46805814	-79.771930	-66.761048	-66.02590828	17.3	18.1
27	CYANO RADICAL,	-92.53114923	-0.44657534	-92.678519	442.813066	443.1806365	3.9	4.3
28	HYDROGEN CYANIDE	-93.24053653	-0.45743094	-93.391489	122.810945	123.1785153	-9.0	-8.6
29	CARBON MONOXIDE	-113.1302626	-0.46832244	-113.284809	-118.914985	-117.6022354	-8.5	-7.1
30	HCO BENT	-113.6544246	-0.49057659	-113.816315	29.274521	30.58727059	-12.6	-11.3
31	H2CO //b3lyp/6-31g*	-114.2955804	-0.51009238	-114.463911	-113.701432	-112.3886824	-4.9	-3.6

32	METHANOL //b3lyp/6-31g*	-115.4998155	-0.53986318	-115.677970	-192.169427	-190.8566769	8.7	10.0
33	Nitrogen N2,	-109.3367458	-0.49086478	-109.498731	-5.808832	-5.808832183	-5.8	-5.8
34	H2NNH2 //b3lyp/6-31g*	-111.6400037	-0.55433892	-111.822936	106.105281	106.1052808	10.7	10.7
35	NO radical,	-129.6809913	-0.53259877	-129.856749	81.067361	82.01254138	-9.3	-8.4
36	O2 //b3lyp/6-31g*	-150.0872841	-0.5969287	-150.284271	-13.764964	-11.87460389	-13.8	-11.9
37	HYDROGEN PEROXIDE	-151.3014588	-0.6262565	-151.508123	-121.658066	-119.7677059	14.3	16.2
38	F2 //b3lyp/6-31g*	-199.2533693	-0.65484962	-199.469470	13.536308	16.73941837	13.5	16.7
39	CO2 D*H	-188.2838116	-0.78743795	-188.543666	-423.296490	-421.0385597	-30.0	-27.7
40	na2 //b3lyp/6-31G*	-324.2679261	-0.36802397	-324.389374	144.294485	144.2944853	2.0	2.0
41	SI2 3-SGG	-578.5017983	-0.55362197	-578.684494	589.180569	592.7512493	3.8	7.4
42	P2 //b3lyp/6-31g*	-682.2992237	-0.70200935	-682.530887	152.169055	152.1690552	8.7	8.7
43	S2 //b3lyp/6-31g*	-795.9512752	-0.74985462	-796.198727	125.349164	130.0225538	-3.1	1.6
44	CL2 //b3lyp/6-31g*	-919.9226084	-0.64473686	-920.135372	7.174102	14.21044211	7.2	14.2
45	Sodium Chloride	-622.1919982	-0.50399103	-622.358315	-176.249402	-172.7312324	6.2	9.7
46	SIO //b3lyp/6-31g*	-364.4321357	-0.60923413	-364.633183	-102.026517	-99.29599693	0.9	3.6
47	Carbon monosulfide,	-435.9266654	-0.5690706	-436.114459	282.764203	285.4684676	2.9	5.6
48	OS //b3lyp/6-31g*	-473.0394777	-0.67988051	-473.263838	-3.027884	0.253991337	-8.0	-4.8
49	CLO 2-PI	-534.9694363	-0.59680739	-535.166383	109.271040	113.7343903	8.0	12.5
50	CLF 1-SG	-559.6134424	-0.64704689	-559.826968	-54.277436	-49.15771083	1.0	6.1
51	si2h6 //b3lyp/6-31g*	-582.1815861	-0.65216678	-582.396801	103.213975	106.7846547	23.3	26.9
52	Methyl chloride,	-499.7882393	-0.55432254	-499.971166	-76.276213	-72.39047303	5.7	9.6
53	H3C-SH METHANETHIOL	-438.3827401	-0.61819084	-438.586743	-5.907434	-3.203168541	17.1	19.8
54	HOCl //b3lyp/6-31g*	-535.6150446	-0.63837142	-535.825707	-69.339483	-64.87613301	5.1	9.6
55	SO2 //b3lyp/6-31G*	-548.1778698	-1.0212391	-548.514879	-292.037811	-287.8107562	5.0	9.3
56	BF3 PLANAR	-324.1624523	-1.06070748	-324.512486	-1157.985918	-1153.049978	-22.4	-17.5
57	bcl3 B3LYP	-1404.863686	-1.09794836	-1405.226008	-424.950822	-414.2650374	-22.0	-11.3
58	ALf3 B3LYP	-541.6774075	-1.19860009	-542.072945	-1204.858796	-1199.161461	4.3	10.0
59	alcl3 B3LYP	-1622.438872	-1.19992176	-1622.834846	-593.491841	-582.0446608	-9.0	2.5
60	cf4 B3LYP	-436.9417107	-1.44896499	-437.419869	-958.930007	-952.1562166	-25.9	-19.1
61	ccl4 B3LYP	-1877.913837	-1.52217474	-1878.416155	-100.976156	-86.53590609	-5.2	9.3
62	O=C=S. Singlet	-511.1383416	-0.87745136	-511.427901	-165.504265	-161.8548201	-27.0	-23.4
63	CS2 B3LYP	-833.989296	-0.97448696	-834.310877	96.171566	101.2125258	-20.6	-15.5
64	COF2 B3LYP	-312.5901191	-1.11893683	-312.959368	-632.911371	-628.395511	-9.1	-4.6
65	sif4 B3LYP	-688.5026637	-1.54976471	-689.014086	-1590.605544	-1582.413984	24.4	32.6
66	sicl4, td	-2129.458899	-1.58510236	-2129.981983	-652.340214	-636.4821937	10.4	26.3
67	nno B3LYP	-184.3395793	-0.84400751	-184.618102	53.227743	54.17292344	-28.8	-27.8
68	clno B3LYP	-589.6404232	-0.91145814	-589.941204	42.438197	46.90154663	-9.4	-5.0

69	nf3 c3v	-353.6093446	-1.23270787	-354.016138	-142.780597	-137.9759316	-10.6	-5.8
70	pf3 c3v	-640.4419366	-1.2922561	-640.868381	-944.932208	-940.1275428	13.6	18.4
71	ozone 1-a1	-225.0308476	-1.01280953	-225.365075	142.064285	144.8998245	-0.6	2.2
72	f2o B3LYP	-274.2830706	-0.96514569	-274.601569	33.869149	38.01743873	9.2	13.3
73	CLF3, C2V	-758.8935814	-1.36781662	-759.344961	-165.109504	-156.7866687	-6.1	2.2
74	CF2=CF2 D2H	-474.8814322	-1.64850554	-475.425439	-707.975784	-700.8344245	-49.4	-42.3
75	cl2c=ccl2 B3LYP	-1915.926158	-1.71879914	-1916.493362	-35.764954	-20.9571344	-23.2	-8.4
76	cf3cn B3LYP	-429.84472	-1.58894966	-430.369073	-533.170481	-527.6306756	-37.8	-32.2
77	PROPYNE C3V	-116.3831143	-0.63517896	-116.592723	187.126313	188.2290229	2.2	3.3
78	ALLENE D2D	-116.3830234	-0.62905685	-116.590612	191.012568	192.1152783	0.6	1.7
79	CYCLOPROPENE C2V	-116.3432812	-0.63852426	-116.553994	288.090417	289.1931269	11.1	12.2
80	PROPENE CS	-117.6166924	-0.65875722	-117.834082	34.723236	35.82594594	14.6	15.7
81	CYCLOPROPANE D3H	-117.602848	-0.66516374	-117.822352	68.002074	69.10478436	14.9	16.0
82	PROPANE C2V	-118.8328503	-0.69175307	-119.061129	-80.454858	-79.35214797	24.1	25.2
83	TRANS-1,3-BUTADIENE C2H	-155.6210954	-0.85169338	-155.902154	121.772452	123.2427319	11.7	13.2
84	Dimethyl acetylene	-155.6076867	-0.85747973	-155.890655	152.115892	153.5861723	6.5	8.0
85	Methylene cyclopropane.	-155.5881503	-0.85859116	-155.871485	201.041240	202.5115196	0.6	2.1
86	Bicyclo[1.1.0]butane. C2v	-155.5719817	-0.87039733	-155.859213	235.195067	236.6653466	18.0	19.5
87	CYCLOBUTENE b3lyp	-155.5976836	-0.86076678	-155.881737	176.489468	177.9597482	20.0	21.5
88	CYCLOBUTANE b3lyp/6-31G*	-156.8191071	-0.88995232	-157.112791	52.161198	53.63147773	23.7	25.2
89	Isobutene. Single	-156.8368238	-0.88555347	-157.129056	4.668136	6.138415717	21.4	22.9
90	Trans butane	-158.0480977	-0.9159691	-158.350368	-94.261940	-92.7916596	31.3	32.7
91	isobutane B3LYP/6-31G*	-158.0490686	-0.91913395	-158.352383	-100.847325	-99.37704503	33.5	34.9
92	Spiropentane. D2d	-194.797402	-1.0893376	-195.156883	199.252764	201.0906142	13.9	15.7
93	Benzene B3LYP	-231.7120424	-1.2511592	-232.124925	76.387735	78.59315471	-6.0	-3.8
94	DIFLUOROMETHANE C2V	-238.6554245	-0.84749419	-238.935098	-460.004220	-456.4335401	-9.4	-5.8
95	HCF3 TRI-FLUOROMETHANE	-337.8003429	-1.14936063	-338.179632	-714.313979	-709.1417435	-17.3	-12.1
96	CH2CL2 C2V	-959.1696259	-0.86973774	-959.456639	-92.458265	-85.05435539	2.9	10.3
97	chcl3 B3LYP/6-31G*	-1418.545602	-1.19261121	-1418.939163	-103.017728	-92.09564837	0.3	11.2
98	METHYLAMINE b3lyp	-95.64000051	-0.51100283	-95.808631	-9.573404	-9.205834397	13.4	13.8
99	Acetonitrile. CH3-CN.	-132.4732754	-0.67694679	-132.696668	67.982052	68.71719237	-7.3	-6.6
100	NITRO METHANE	-244.5682719	-1.11957112	-244.937730	-86.854207	-84.59627723	-12.4	-10.1
101	Methyl-nitrite. CH3-O-N=O.	-244.5646155	-1.10888561	-244.930548	-71.724400	-69.46647037	-5.2	-2.9
102	Methylsilane. CH3-SiH3.	-330.9071873	-0.56112563	-331.092359	-4.996179	-2.843269084	24.3	26.4
103	Formic Acid.	-189.4446955	-0.80995193	-189.711980	-388.143371	-385.8854409	-9.5	-7.2
104	Methyl formate.	-228.6474589	-1.03086305	-228.987644	-366.911553	-364.2860527	-11.3	-8.6
105	acetamide ch3cohn2	-208.808119	-1.00090847	-209.138419	-239.122538	-237.4422184	-0.6	1.0

106	Aziridine. (cyclic	-133.6201897	-0.70969181	-133.854388	136.007184	136.7423242	9.7	10.4
107	Cyanogen. NCCN.	-185.2951832	-0.90449929	-185.593668	276.382110	277.1172502	-30.3	-29.6
108	DIMETHYLAMINE b3lyp	-134.8465704	-0.73359862	-135.088658	-0.485551	0.249589482	17.9	18.7
109	TRANS ETHYLAMINE	-134.8580969	-0.7347628	-135.100569	-30.819815	-30.08467455	16.5	17.2
110	KETENE B3LYP	-152.3127405	-0.70836877	-152.546502	-65.888623	-64.20830287	-18.6	-16.9
111	OXIRANE B3LYP	-153.4803205	-0.73999997	-153.724521	-48.995496	-47.31517584	3.7	5.4
112	Acetaldehyde B3LYP	-153.5262805	-0.73216642	-153.767895	-165.995465	-164.3151446	0.1	1.8
113	Glyoxal, O=CH-CH=O.	-227.4213139	-0.99834622	-227.750768	-229.117393	-226.4918929	-17.0	-14.4
114	ETHANOL TRANS	-154.7203711	-0.76288323	-154.972123	-219.171081	-217.4907611	16.0	17.7
115	DIMETHYL ETHER,	-154.7036345	-0.7598698	-154.954392	-173.461069	-171.7807486	10.6	12.3
116	Thiooxirane. (cyclic	-476.3817903	-0.82438934	-476.653839	90.988242	94.06007676	9.0	12.1
117	Dimethylsulfoxide. (CH3)2SO.	-552.6735499	-1.1632894	-553.057435	-124.582822	-120.5658066	26.9	30.9
118	Thioethanol. CH3-CH2-SH.	-477.5986344	-0.84323539	-477.876902	-21.736837	-18.665002	24.7	27.8
119	ch3sch3 B3LYP	-477.5965776	-0.84506337	-477.875448	-15.394767	-12.32293189	21.8	24.9
120	Vinyl fluoride,	-177.5230921	-0.73841353	-177.766769	-144.754123	-142.4174276	-5.8	-3.5
121	Ethyl chloride.	-539.0072613	-0.77871155	-539.264236	-99.914908	-95.66159842	12.2	16.5
122	Vinyl chloride,	-537.7856718	-0.74996398	-538.033160	25.105155	29.35846475	2.1	6.3
123	h2c=chcn B3LYP	-170.4687714	-0.87060157	-170.756070	177.668186	178.7708959	-3.1	-2.0
124	ACETONE B3LYP	-192.7533269	-0.95583543	-193.068753	-210.753078	-208.7051881	6.4	8.4
125	CH3COOH ACETIC	-228.6732582	-1.03059014	-229.013353	-434.865294	-432.2397943	-2.2	0.4
126	CH3CFO HCCO	-252.6825654	-1.03919563	-253.025500	-451.575306	-448.2934314	-9.3	-6.0
127	ch3c(o)cl hcco	-612.9314925	-1.05482582	-613.279585	-249.812828	-244.6143382	-7.1	-1.9
128	ch3ch2ch2cl B3LYP	-578.2226304	-1.00317847	-578.553679	-114.164213	-109.5433327	17.6	22.3
129	Isopropyl alcohol,	-193.9405288	-0.98927716	-194.266990	-249.447969	-247.4000789	23.3	25.4
130	Methyl ethyl	-193.9240982	-0.98349046	-194.248650	-200.747042	-198.6991517	15.6	17.6
131	Trimethyl Amine.	-174.0554247	-0.96093901	-174.372535	-2.811134	-1.708423713	21.0	22.1
132	FURAN B3LYP	-229.5504381	-1.13715139	-229.925698	-42.820166	-40.40470615	-8.1	-5.7
133	Thiophene b3lyp	-552.4413669	-1.22835197	-552.846723	116.590357	120.3973317	1.5	5.3
134	PYROLE PLANAR	-209.7047901	-1.1100174	-210.071096	100.735515	102.2057947	-7.6	-6.2
135	C2v Pyridine	-247.7370022	-1.29457445	-248.164212	123.625482	125.4633324	-17.0	-15.1
136	H2 B3LYP/6-31G*	-1.15764604	-0.03442755	-1.169007	8.846506	8.846506447	8.8	8.8
137	SH b3lyp/6-31G*	-398.5355388	-0.35627938	-398.653111	148.356227	150.6929219	5.3	7.6
138	CCH B3LYP	-76.44485656	-0.37623956	-76.569016	574.848620	575.58376	9.6	10.3
139	C2H3 CS,2-A'	-77.72278656	-0.39816199	-77.854180	302.503366	303.2385065	2.9	3.7
140	ch3co hcco	-152.8858961	-0.7100871	-153.120225	-19.145180	-17.46485971	-9.1	-7.4
141	H2COH C1	-114.8492248	-0.50763252	-115.016744	-14.340363	-13.02761288	2.8	4.1
142	ch3o CS,	-114.8430651	-0.48092212	-115.001769	21.400863	22.71361268	4.2	5.6

143	ch3ch2o 2A"	-154.0633515	-0.70397894	-154.295665	-5.508647	-3.828327268	10.0	11.7
144	ch3s 2-A'	-437.7518488	-0.58276334	-437.944161	131.007354	133.7116189	6.3	9.0
145	c2h5 staggered	-78.95986931	-0.42967774	-79.101663	132.393651	133.1287905	11.5	12.2
146	(ch3)2ch Cs	-118.1797051	-0.65480385	-118.395790	105.872122	106.974832	15.9	17.0
147	TERT-BUTYL RADICAL	-157.399698	-0.88192839	-157.690734	76.943924	78.41420392	25.5	27.0
148	NO2 RADICAL	-204.7314478	-0.89387019	-205.026425	5.353857	7.244217498	-27.7	-25.8

MAD	**11.6**	**12.1**
LD	**-49.4**	**-42.3**

Table S5.57b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 33%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498801	0.000000	-0.498801
2	li	-7.465676	-0.014483	-7.470455
3	be	-14.632063	-0.052484	-14.649383
4	b	-24.609449	-0.076275	-24.634619
5	c	-37.790684	-0.102937	-37.824653
6	n	-54.522059	-0.133548	-54.566130
7	o	-74.980861	-0.190332	-75.043670
8	f	-99.623274	-0.252763	-99.706686
9	na	-162.125397	-0.170114	-162.181534
10	al	-242.202688	-0.218278	-242.274720
11	si	-289.201586	-0.248074	-289.283451
12	p	-341.082305	-0.276847	-341.173664
13	s	-397.912896	-0.317792	-398.017767
14	cl	-459.927663	-0.288555	-460.022886

Table S5.58a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 34%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04227454	-0.04617929	-8.057975	148.117656	148.1176557	8.8	8.8
2	BERYLLIUM HYDRIDE	-15.21699442	-0.05439938	-15.235490	320.827174	320.8271742	-21.0	-21.0
3	DOUBLET CH	-38.40640565	-0.14307794	-38.455052	600.673669	601.0412395	4.5	4.8
4	CH2 3-B1	-39.0688261	-0.16206206	-39.123927	395.662140	396.0297097	3.6	4.0
5	Singlet methylene,	-39.04423539	-0.18187009	-39.106071	440.930958	441.2985277	10.8	11.2
6	Methyl radical,	-39.73852644	-0.20647838	-39.808729	152.757194	153.1247638	6.3	6.7
7	ch4 //b3lyp/6-31G*	-40.40112646	-0.2476729	-40.485335	-63.326348	-62.95877782	11.6	11.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.13317547	-0.18601392	-55.196420	359.822656	359.8226556	3.3	3.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.77163316	-0.23892883	-55.852869	189.539379	189.5393794	0.8	0.8
10	AMMONIA, //b3lyp/6-31G*	-56.43480699	-0.29232601	-56.534198	-37.389353	-37.38935279	8.6	8.6
11	OH RADICAL	-75.62391291	-0.25624962	-75.711038	40.864389	41.80956872	1.5	2.5
12	Water //b3lyp/6-31G*	-76.29809874	-0.32415424	-76.408311	-233.193459	-232.248279	8.6	9.6
13	HYDROGEN FLUORIDE,	-100.3146598	-0.33500037	-100.428560	-269.583936	-267.9823813	2.8	4.4
14	SIH2 singlet	-290.4147064	-0.30322469	-290.517803	278.032160	279.8175002	5.2	7.0
15	SIH2 3B1	-290.3900246	-0.28089696	-290.485530	363.776338	365.5616784	3.1	4.9
16	SIH3 c3v	-291.0292729	-0.30865084	-291.134214	206.536783	208.322123	6.1	7.9
17	SIH4 //b3lyp/6-31G*	-291.6703187	-0.33559969	-291.784423	47.239519	49.02485875	12.9	14.7
18	ph2 doublet	-342.2941016	-0.34247933	-342.410545	143.132542	143.1325424	4.6	4.6
19	PH3 c3v	-342.9198896	-0.37316966	-343.046767	22.054043	22.05404313	16.6	16.6
20	SH2 //b3lyp/6-31G*	-399.1646884	-0.39448902	-399.298815	-8.806929	-6.470234047	11.7	14.0
21	HCL //b3lyp/6-31G*	-460.5727974	-0.33312358	-460.686059	-89.016847	-85.49867656	3.4	7.0
22	DILITHIUM //b3lyp/6-31G*	-14.95381065	-0.05715845	-14.973245	230.938829	230.9388293	15.0	15.0
23	Lithium Fluoride,	-107.2743041	-0.36351731	-107.397900	-342.234516	-340.6329607	-7.1	-5.5
24	ACETYLENE //b3lyp/6-31g*	-77.15201548	-0.413443	-77.292586	226.242413	226.977553	-0.5	0.2
25	ETHYLENE //b3lyp/6-31g*	-78.3913275	-0.43465457	-78.539110	60.916341	61.65148146	8.6	9.4
26	ETHANE //b3lyp/6-31g*	-79.61195033	-0.46804659	-79.771086	-67.521883	-66.786743	16.6	17.3
27	CYANO RADICAL,	-92.52688426	-0.44649275	-92.678692	439.318743	439.6863134	0.4	0.8
28	HYDROGEN CYANIDE	-93.23589106	-0.45741603	-93.391413	119.970195	120.3377652	-11.8	-11.5
29	CARBON MONOXIDE	-113.1254141	-0.46831636	-113.284642	-121.742837	-120.4300869	-11.3	-10.0
30	HCO BENT	-113.6493432	-0.49056381	-113.816135	26.479951	27.79270126	-15.4	-14.0
31	H2CO //b3lyp/6-31g*	-114.2901739	-0.51008732	-114.463604	-116.161914	-114.8491639	-7.4	-6.1

32	METHANOL //b3lyp/6-31g*	-115.4938544	-0.53986017	-115.677407	-193.957242	-192.6444922	6.9	8.2
33	Nitrogen N2,	-109.3319089	-0.49084974	-109.498798	-9.088320	-9.088320079	-9.1	-9.1
34	H2NNH2 //b3lyp/6-31g*	-111.6340354	-0.55433787	-111.822510	104.117203	104.1172028	8.7	8.7
35	NO radical,	-129.6757113	-0.53258927	-129.856792	77.623744	78.56892429	-12.8	-11.8
36	O2 //b3lyp/6-31g*	-150.0815618	-0.59692794	-150.284517	-17.970241	-16.07988089	-18.0	-16.1
37	HYDROGEN PEROXIDE	-151.2950957	-0.62626115	-151.508025	-124.955727	-123.065367	11.0	12.9
38	F2 //b3lyp/6-31g*	-199.2466126	-0.65485323	-199.469263	10.463502	13.66661246	10.5	13.7
39	CO2 D*H	-188.2759011	-0.78742492	-188.543626	-428.235835	-425.977905	-34.9	-32.7
40	na2 //b3lyp/6-31G*	-324.2594999	-0.36801843	-324.384626	144.207485	144.2074849	2.0	2.0
41	SI2 3-SGG	-578.4908191	-0.55360462	-578.679045	588.606562	592.1772423	3.3	6.8
42	P2 //b3lyp/6-31g*	-682.287082	-0.70198639	-682.525757	150.389308	150.3893083	6.9	6.9
43	S2 //b3lyp/6-31g*	-795.9382073	-0.74984583	-796.193155	123.560108	128.2334982	-4.9	-0.2
44	CL2 //b3lyp/6-31g*	-919.9084803	-0.64472933	-920.127688	6.168879	13.20521903	6.2	13.2
45	Sodium Chloride	-622.1806695	-0.50399323	-622.352027	-176.605103	-173.0869325	5.8	9.3
46	SIO //b3lyp/6-31g*	-364.4236104	-0.60924216	-364.630753	-104.864639	-102.1341186	-1.9	0.8
47	Carbon monosulfide,	-435.9181837	-0.56905105	-436.111661	280.411337	283.1156025	0.5	3.2
48	OS //b3lyp/6-31g*	-473.0300733	-0.67987194	-473.261230	-6.167571	-2.885695509	-11.2	-7.9
49	CLO 2-PI	-534.9595215	-0.59676736	-535.162422	107.301528	111.7648784	6.0	10.5
50	CLF 1-SG	-559.6029803	-0.64704626	-559.822976	-56.193810	-51.07408481	-1.0	4.2
51	si2h6 //b3lyp/6-31g*	-582.1689704	-0.65215031	-582.390701	104.348781	107.9194614	24.4	28.0
52	Methyl chloride,	-499.7784149	-0.55431367	-499.966882	-77.105349	-73.21960882	4.9	8.8
53	H3C-SH METHANETHIOL	-438.3731556	-0.61817929	-438.583337	-6.661822	-3.957556869	16.4	19.1
54	HOCl //b3lyp/6-31g*	-535.6047929	-0.63836924	-535.821838	-71.549568	-67.08621773	2.9	7.4
55	SO2 //b3lyp/6-31G*	-548.1653245	-1.02122903	-548.512542	-297.670881	-293.4438258	-0.6	3.6
56	BF3 PLANAR	-324.1505179	-1.06070807	-324.511159	-1161.239695	-1156.303755	-25.7	-20.8
57	bcl3 B3LYP	-1404.8408	-1.09793034	-1405.214096	-426.756015	-416.0702299	-23.8	-13.2
58	ALf3 B3LYP	-541.6618793	-1.19860767	-542.069406	-1208.269117	-1202.571782	0.9	6.6
59	alcl3 B3LYP	-1622.412397	-1.19990626	-1622.820365	-594.516715	-583.0695347	-10.0	1.4
60	cf4 B3LYP	-436.9257966	-1.44895752	-437.418442	-963.904288	-957.1304983	-30.9	-24.1
61	ccl4 B3LYP	-1877.883321	-1.52215014	-1878.400852	-104.641895	-90.20164521	-8.8	5.6
62	O=C=S. Singlet	-511.1267951	-0.87743026	-511.425121	-169.684436	-166.034991	-31.2	-27.5
63	CS2 B3LYP	-833.9741028	-0.97445726	-834.305418	92.594846	97.63580636	-24.1	-19.1
64	COF2 B3LYP	-312.5782126	-1.11892747	-312.958648	-637.903671	-633.3878113	-14.1	-9.6
65	sif4 B3LYP	-688.4831175	-1.54976086	-689.010036	-1594.644584	-1586.453024	20.4	28.6
66	sicl4, td	-2129.424751	-1.58507726	-2129.963678	-654.074434	-638.2164145	8.7	24.5
67	nno B3LYP	-184.3317058	-0.84398549	-184.618661	46.876401	47.82158112	-35.1	-34.2
68	clno B3LYP	-589.6279969	-0.91144	-589.937886	37.229544	41.69289385	-14.7	-10.2

69	nf3 c3v	-353.5965667	-1.23270224	-354.015685	-148.568478	-143.7638125	-16.4	-11.5
70	pf3 c3v	-640.4254183	-1.2922527	-640.864784	-948.536102	-943.7314369	10.0	14.8
71	ozone 1-a1	-225.0220712	-1.01278736	-225.366419	133.199054	136.0345943	-9.5	-6.6
72	f2o B3LYP	-274.2733445	-0.96514399	-274.601493	28.671818	32.82010816	4.0	8.1
73	CLF3, C2V	-758.8761532	-1.36781467	-759.341210	-171.274973	-162.952138	-12.3	-4.0
74	CF2=CF2 D2H	-474.8634805	-1.64849601	-475.423969	-714.325739	-707.1843795	-55.8	-48.6
75	cl2c=ccl2 B3LYP	-1915.893557	-1.71876903	-1916.477939	-40.604402	-25.7965815	-28.1	-13.2
76	cf3cn B3LYP	-429.827783	-1.58892663	-430.368018	-540.353143	-534.8133378	-45.0	-39.4
77	PROPYNE C3V	-116.3760826	-0.63515562	-116.592036	184.466794	185.5695035	-0.5	0.6
78	ALLENE D2D	-116.3759883	-0.62903539	-116.589860	188.521165	189.6238746	-1.9	-0.7
79	CYCLOPROPENE C2V	-116.3361935	-0.63850697	-116.553286	285.484563	286.5872727	8.5	9.6
80	PROPENE CS	-117.609122	-0.65873791	-117.833093	32.855219	33.95792869	12.8	13.9
81	CYCLOPROPANE D3H	-117.5952086	-0.66514882	-117.821359	66.143278	67.24598839	13.0	14.1
82	PROPANE C2V	-118.8247454	-0.69173559	-119.059935	-81.787196	-80.6844863	22.8	23.9
83	TRANS-1,3-BUTADIENE C2H	-155.6114758	-0.85166627	-155.901042	118.737608	120.2078881	8.7	10.2
84	Dimethyl acetylene	-155.598071	-0.85745111	-155.889604	148.920394	150.3906739	3.3	4.8
85	Methylene cyclopropane.	-155.5784681	-0.85856835	-155.870381	197.985707	199.4559874	-2.4	-1.0
86	Bicyclo[1.1.0]butane. C2v	-155.5622311	-0.87037786	-155.858160	232.006481	233.4767611	14.9	16.3
87	CYCLOBUTENE b3lyp	-155.5879768	-0.86074378	-155.880630	173.441624	174.9119045	17.0	18.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.808866	-0.88993106	-157.111443	49.748470	51.21875035	21.3	22.8
89	Isobutene. Single	-156.8266597	-0.88552854	-157.127739	2.172065	3.642345253	18.9	20.4
90	Trans butane	-158.0374078	-0.9159454	-158.348829	-96.176999	-94.70671873	29.3	30.8
91	isobutane B3LYP/6-31G*	-158.0383694	-0.91911033	-158.350867	-102.821447	-101.3511666	31.5	33.0
92	Spiropentane. D2d	-194.785066	-1.08931313	-195.155432	195.619829	197.4576791	10.3	12.1
93	Benzene B3LYP	-231.6981542	-1.25112207	-232.123536	71.104141	73.30956071	-11.3	-9.1
94	DIFLUOROMETHANE C2V	-238.6460167	-0.84749409	-238.934165	-462.659428	-459.0887482	-12.0	-8.5
95	HCF3 TRI-FLUOROMETHANE	-337.7876837	-1.1493582	-338.178465	-718.164039	-712.9918043	-21.1	-15.9
96	CH2CL2 C2V	-959.1529121	-0.8697246	-959.448618	-94.065443	-86.66153342	1.3	8.7
97	chcl3 B3LYP/6-31G*	-1418.52199	-1.19259272	-1418.927471	-105.574513	-94.65243326	-2.2	8.7
98	METHYLAMINE b3lyp	-95.6342531	-0.51099634	-95.807992	-10.935057	-10.56748722	12.1	12.4
99	Acetonitrile. CH3-CN.	-132.4660457	-0.67692621	-132.696201	64.679262	65.41440211	-10.6	-9.9
100	NITRO METHANE	-244.5570492	-1.1195513	-244.937697	-93.364012	-91.10608213	-18.9	-16.6
101	Methyl-nitrite. CH3-O-N=O.	-244.5534295	-1.10886487	-244.930444	-78.049402	-75.79147185	-11.5	-9.3
102	Methylsilane. CH3-SiH3.	-330.8981124	-0.56111182	-331.088890	-4.818644	-2.665734087	24.5	26.6
103	Formic Acid.	-189.4362384	-0.80994603	-189.711620	-392.245140	-389.9872097	-13.6	-11.3
104	Methyl formate.	-228.6364315	-1.03084778	-228.986920	-371.545291	-368.9197911	-15.9	-13.3
105	acetamide ch3cohn2	-208.7972783	-1.00089434	-209.137582	-243.234857	-241.5545372	-4.7	-3.1

106	Aziridine. (cyclic	-133.612344	-0.70967939	-133.853635	133.454750	134.1898897	7.1	7.8
107	Cyanogen. NCCN.	-185.2862614	-0.904467	-185.593780	270.005786	270.7409265	-36.7	-35.9
108	DIMETHYLAMINE b3lyp	-134.8382421	-0.73358507	-135.087661	-2.397609	-1.662469488	16.0	16.7
109	TRANS ETHYLAMINE	-134.849765	-0.73475001	-135.099580	-32.753508	-32.01836816	14.5	15.3
110	KETENE B3LYP	-152.3052694	-0.70835369	-152.546110	-69.613698	-67.93337803	-22.3	-20.7
111	OXIRANE B3LYP	-153.4722729	-0.73998997	-153.723869	-52.041851	-50.36153089	0.7	2.4
112	Acetaldehyde B3LYP	-153.5182863	-0.73215497	-153.767219	-168.975083	-167.2947634	-2.9	-1.2
113	Glyoxal, O=CH-CH=O.	-227.4108634	-0.99833281	-227.750297	-234.413792	-231.788292	-22.3	-19.7
114	ETHANOL TRANS	-154.711825	-0.76287388	-154.971202	-221.510293	-219.8299735	13.6	15.3
115	DIMETHYL ETHER,	-154.6951017	-0.75985854	-154.953454	-175.754141	-174.0738212	8.3	10.0
116	Thiooxirane. (cyclic	-476.3700961	-0.82437244	-476.650383	88.875427	91.94726234	6.9	9.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.6583445	-1.16327134	-553.053857	-128.152525	-124.1355096	23.3	27.3
118	Thioethanol. CH3-CH2-SH.	-477.5864661	-0.84321772	-477.873160	-23.099149	-20.02731383	23.3	26.4
119	ch3sch3 B3LYP	-477.5844167	-0.84504573	-477.871732	-16.824423	-13.7525878	20.4	23.5
120	Vinyl fluoride,	-177.5148669	-0.73840337	-177.765924	-147.322009	-144.9853141	-8.4	-6.1
121	Ethyl chloride.	-538.9948533	-0.77869648	-539.259610	-101.335158	-97.08184768	10.8	15.0
122	Vinyl chloride,	-537.7737918	-0.74994711	-538.028774	23.054963	27.30827324	0.0	4.3
123	h2c=chcn B3LYP	-170.4594995	-0.87057344	-170.755494	173.161048	174.2637576	-7.6	-6.5
124	ACETONE B3LYP	-192.7427408	-0.95581711	-193.067719	-214.282465	-212.2345745	2.9	4.9
125	CH3COOH ACETIC	-228.6622109	-1.03057744	-229.012607	-439.441914	-436.8164141	-6.8	-4.2
126	CH3CFO HCCO	-252.6713208	-1.03918261	-253.024643	-455.888972	-452.6070966	-13.6	-10.4
127	ch3c(o)cl hcco	-612.9166072	-1.05480715	-613.275242	-253.753720	-248.5552302	-11.1	-5.9
128	ch3ch2ch2cl B3LYP	-578.2076382	-1.00315729	-578.548712	-116.176152	-111.5552723	15.6	20.2
129	Isopropyl alcohol,	-193.9293893	-0.98926102	-194.265738	-252.404362	-250.3564722	20.4	22.4
130	Methyl ethyl	-193.9129801	-0.98347258	-194.247361	-203.606216	-201.5583264	12.7	14.8
131	Trimethyl Amine.	-174.0445025	-0.96091891	-174.371215	-5.364413	-4.261703297	18.5	19.6
132	FURAN B3LYP	-229.5381857	-1.13712571	-229.924808	-48.217224	-45.80176376	-13.5	-11.1
133	Thiophene b3lyp	-552.4254711	-1.22831985	-552.843100	111.939199	115.7461741	-3.1	0.7
134	PYROLE PLANAR	-209.692729	-1.10999013	-210.070126	95.776287	97.24656675	-12.6	-11.1
135	C2v Pyridine	-247.7229072	-1.2945392	-248.163051	117.679438	119.5172882	-22.9	-21.1
136	H2 B3LYP/6-31G*	-1.15726339	-0.03442783	-1.168969	8.947009	8.947008749	8.9	8.9
137	SH b3lyp/6-31G*	-398.528861	-0.35628147	-398.649997	148.323137	150.6598322	5.2	7.6
138	CCH B3LYP	-76.44080378	-0.37622042	-76.568719	572.651102	573.3862422	7.4	8.1
139	C2H3 CS,2-A'	-77.71816219	-0.39814171	-77.853530	301.232002	301.9671425	1.7	2.4
140	ch3co hcco	-152.8782331	-0.71006598	-153.119656	-22.406197	-20.72587695	-12.4	-10.7
141	H2COH C1	-114.8435967	-0.507624	-115.016189	-16.151388	-14.83863762	1.0	2.3
142	ch3o CS,	-114.8374701	-0.48090775	-115.000979	20.209543	21.52229258	3.1	4.4

143	ch3ch2o 2A"	-154.0551726	-0.70395605	-154.294518	-7.253193	-5.572873037	8.2	9.9
144	ch3s 2-A'	-437.7425938	-0.58275591	-437.940731	130.314308	133.0185733	5.6	8.3
145	c2h5 staggered	-78.95469553	-0.42967073	-79.100784	131.725471	132.4606107	10.8	11.5
146	(ch3)2ch Cs	-118.17194	-0.65478711	-118.394568	104.616817	105.7195274	14.7	15.8
147	TERT-BUTYL RADICAL	-157.3893391	-0.88190149	-157.689186	75.056288	76.5265684	23.6	25.1
148	NO2 RADICAL	-204.7231291	-0.89384893	-205.027038	-1.364727	0.525632836	-34.4	-32.5

MAD	**12.2**	**12.3**
LD	**-55.8**	**-48.6**

Table S5.58b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 61% and a_C = 34%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498801	0.000000	-0.498801
2	li	-7.465139	-0.014483	-7.470063
3	be	-14.631114	-0.052479	-14.648957
4	b	-24.608184	-0.076279	-24.634119
5	c	-37.789086	-0.102944	-37.824086
6	n	-54.520131	-0.133552	-54.565539
7	o	-74.978276	-0.190342	-75.042993
8	f	-99.620054	-0.252773	-99.705997
9	na	-162.121306	-0.170112	-162.179144
10	al	-242.197733	-0.218279	-242.271948
11	si	-289.196271	-0.248076	-289.280617
12	p	-341.076634	-0.276842	-341.170761
13	s	-397.906590	-0.317795	-398.014640
14	cl	-459.920744	-0.288558	-460.018853

Table S5.59a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 62% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0476576	-0.0459762	-8.060531	147.764337	147.7643369	8.4	8.4
2	BERYLLIUM HYDRIDE	-15.22361021	-0.05422664	-15.238794	318.911326	318.9113259	-22.9	-22.9
3	DOUBLET CH	-38.41825139	-0.14246597	-38.458142	601.348930	601.7165002	5.1	5.5
4	CH2 3-B1	-39.08180037	-0.16147184	-39.127012	396.411747	396.7793173	4.4	4.7
5	Singlet methylene,	-39.05819997	-0.18112363	-39.108915	442.315724	442.6832936	12.2	12.6
6	Methyl radical,	-39.75411337	-0.2056901	-39.811707	153.852490	154.2200604	7.4	7.8
7	ch4 //b3lyp/6-31G*	-40.41890224	-0.24675781	-40.487994	-61.332558	-60.96498782	13.6	13.9
8	NH,TRIPLET, //b3lyp/6-31G*	-55.14733985	-0.18529531	-55.199223	361.648135	361.6481353	5.2	5.2
9	NH2,2-B-1, //b3lyp/6-31G*	-55.78821967	-0.23799452	-55.854858	193.562535	193.5625355	4.9	4.9
10	AMMONIA, //b3lyp/6-31G*	-56.45367531	-0.29119646	-56.535210	-30.739179	-30.73917921	15.3	15.3
11	OH RADICAL	-75.64163239	-0.25529957	-75.713116	45.338531	46.28371057	6.0	7.0
12	Water //b3lyp/6-31G*	-76.31807035	-0.32290832	-76.408485	-223.655041	-222.7098606	18.2	19.1
13	HYDROGEN FLUORIDE,	-100.3358639	-0.33381167	-100.429331	-262.018170	-260.416615	10.4	12.0
14	SIH2 singlet	-290.4506517	-0.30227442	-290.535289	276.427914	278.2132541	3.6	5.4
15	SIH2 3B1	-290.4248513	-0.28018743	-290.503304	361.414712	363.2000516	0.8	2.5
16	SIH3 c3v	-291.0664478	-0.30776591	-291.152622	202.573745	204.3590851	2.2	3.9
17	SIH4 //b3lyp/6-31G*	-291.7096259	-0.33457424	-291.803307	42.089483	43.8748234	7.8	9.6
18	ph2 doublet	-342.3328055	-0.34140481	-342.428399	141.869571	141.8695713	3.4	3.4
19	PH3 c3v	-342.9606201	-0.37197979	-343.064774	20.452403	20.45240307	15.0	15.0
20	SH2 //b3lyp/6-31G*	-399.2069135	-0.39324194	-399.317021	-7.552556	-5.215860989	12.9	15.3
21	HCL //b3lyp/6-31G*	-460.6165539	-0.33196982	-460.709505	-87.272266	-83.75409587	5.2	8.7
22	DILITHIUM //b3lyp/6-31G*	-14.96193958	-0.05689592	-14.977870	231.380008	231.3800083	15.5	15.5
23	Lithium Fluoride,	-107.2988051	-0.36207865	-107.400187	-332.418169	-330.8166142	2.7	4.3
24	ACETYLENE //b3lyp/6-31g*	-77.17837264	-0.41168628	-77.293645	241.037400	241.7725395	14.3	15.0
25	ETHYLENE //b3lyp/6-31g*	-78.42115765	-0.43294712	-78.542383	70.023677	70.75881743	17.7	18.5
26	ETHANE //b3lyp/6-31g*	-79.64525129	-0.46630718	-79.775817	-62.117972	-61.38283231	22.0	22.7
27	CYANO RADICAL,	-92.55164968	-0.44442552	-92.676089	463.997700	464.3652704	25.1	25.5
28	HYDROGEN CYANIDE	-93.26314127	-0.45540575	-93.390655	139.866937	140.2345073	8.1	8.4
29	CARBON MONOXIDE	-113.1537687	-0.46628377	-113.284328	-102.326736	-101.0139861	8.1	9.4
30	HCO BENT	-113.6790331	-0.48851891	-113.815818	45.966635	47.27938542	4.1	5.4
31	H2CO //b3lyp/6-31g*	-114.3219634	-0.5079796	-114.464198	-99.003181	-97.69043131	9.8	11.1

32	METHANOL //b3lyp/6-31g*	-115.5292262	-0.53780813	-115.679813	-181.429417	-180.1166675	19.4	20.7
33	Nitrogen N2,	-109.3600892	-0.48871711	-109.496930	14.056212	14.05621226	14.1	14.1
34	H2NNH2 //b3lyp/6-31g*	-111.6693511	-0.55217724	-111.823961	118.800531	118.8005305	23.4	23.4
35	NO radical,	-129.7062881	-0.53033631	-129.854782	101.888318	102.8334976	11.5	12.5
36	O2 //b3lyp/6-31g*	-150.1144049	-0.59464699	-150.280906	11.248084	13.13844429	11.2	13.1
37	HYDROGEN PEROXIDE	-151.3320706	-0.62369882	-151.506706	-101.632230	-99.74186952	34.3	36.2
38	F2 //b3lyp/6-31g*	-199.2855919	-0.65226157	-199.468225	32.243542	35.44665197	32.2	35.4
39	CO2 D*H	-188.321992	-0.78406319	-188.541530	-394.271545	-392.0136147	-1.0	1.3
40	na2 //b3lyp/6-31G*	-324.3096607	-0.36686551	-324.412383	144.997981	144.9979814	2.7	2.7
41	SI2 3-SGG	-578.5565768	-0.55186691	-578.711100	592.805005	596.3756846	7.5	11.0
42	P2 //b3lyp/6-31g*	-682.3596782	-0.69945671	-682.555526	163.207715	163.207715	19.7	19.7
43	S2 //b3lyp/6-31g*	-796.0163655	-0.74745951	-796.225654	136.093938	140.767328	7.6	12.3
44	CL2 //b3lyp/6-31g*	-919.9932974	-0.64239429	-920.173168	13.240944	20.27728421	13.2	20.3
45	Sodium Chloride	-622.2486502	-0.50229117	-622.389292	-174.370870	-170.8527003	8.1	11.6
46	SIO //b3lyp/6-31g*	-364.4740081	-0.60663521	-364.643866	-85.245714	-82.51519376	17.7	20.4
47	Carbon monosulfide,	-435.9687177	-0.56671684	-436.127398	296.747668	299.4519329	16.8	19.5
48	OS //b3lyp/6-31g*	-473.0856421	-0.6774041	-473.275315	15.649580	18.93145492	10.6	13.9
49	CLO 2-PI	-535.0184126	-0.59421554	-535.184793	121.675270	126.1386202	20.4	24.9
50	CLF 1-SG	-559.6650622	-0.64460335	-559.845551	-42.697564	-37.57783859	12.5	17.7
51	si2h6 //b3lyp/6-31g*	-582.2452883	-0.65012843	-582.427324	96.930486	100.5011663	17.0	20.6
52	Methyl chloride,	-499.8375266	-0.55230344	-499.992172	-71.352438	-67.46669776	10.7	14.5
53	H3C-SH METHANETHIOL	-438.4308228	-0.61607148	-438.603323	-1.229764	1.474500762	21.8	24.5
54	HOCl //b3lyp/6-31g*	-535.6657329	-0.63589023	-535.843782	-55.992340	-51.52898972	18.5	22.9
55	SO2 //b3lyp/6-31G*	-548.2391058	-1.01690119	-548.523838	-258.660710	-254.4336553	38.4	42.6
56	BF3 PLANAR	-324.220772	-1.05699323	-324.516730	-1139.521424	-1134.585484	-4.0	1.0
57	bcl3 B3LYP	-1404.978601	-1.09399327	-1405.284920	-415.222385	-404.5365995	-12.3	-1.6
58	ALf3 B3LYP	-541.7535854	-1.19447186	-542.088038	-1185.520938	-1179.823603	23.7	29.4
59	alcl3 B3LYP	-1622.571868	-1.19590143	-1622.906720	-588.444225	-576.9970451	-3.9	7.5
60	cf4 B3LYP	-437.0191947	-1.44386679	-437.423477	-930.288071	-923.5142811	2.7	9.5
61	ccl4 B3LYP	-1878.066632	-1.51654528	-1878.491265	-80.339857	-65.89960658	15.5	29.9
62	O=C=S. Singlet	-511.1951478	-0.87394946	-511.439854	-140.840704	-137.191259	-2.4	1.3
63	CS2 B3LYP	-834.0647649	-0.97083247	-834.336598	117.317672	122.3586318	0.6	5.6
64	COF2 B3LYP	-312.6478632	-1.11467893	-312.959973	-603.734435	-599.218575	20.1	24.6
65	sif4 B3LYP	-688.5986799	-1.5445815	-689.031163	-1567.821797	-1559.630237	47.2	55.4
66	sicl4, td	-2129.630463	-1.57971225	-2130.072783	-643.394115	-627.5360947	19.4	35.2
67	nno B3LYP	-184.3771421	-0.84011445	-184.612374	91.491298	92.4364784	9.5	10.4
68	clno B3LYP	-589.7010936	-0.90734884	-589.955151	74.128726	78.59207622	22.2	26.7

69	nf3 c3v	-353.670701	-1.22776875	-354.014476	-107.689803	-102.8851377	24.5	29.3
70	pf3 c3v	-640.5229702	-1.28772294	-640.883533	-923.688401	-918.8837364	34.9	39.7
71	ozone 1-a1	-225.0719119	-1.00771315	-225.354072	195.222365	198.0579045	52.5	55.4
72	f2o B3LYP	-274.3293504	-0.96109328	-274.598456	65.569641	69.71793105	40.9	45.0
73	CLF3, C2V	-758.9782231	-1.36220517	-759.359641	-127.840993	-119.518158	31.2	39.5
74	CF2=CF2 D2H	-474.9687075	-1.64244345	-475.428592	-670.901686	-663.760326	-12.3	-5.2
75	cl2c=ccl2 B3LYP	-1916.089201	-1.71234819	-1916.568658	-8.381773	6.426047146	4.2	19.0
76	cf3cn B3LYP	-429.9271119	-1.58284548	-430.370309	-491.214124	-485.6743186	4.2	9.7
77	PROPYNE C3V	-116.4180128	-0.63258274	-116.595136	202.751115	203.8538247	17.8	18.9
78	ALLENE D2D	-116.4178734	-0.62649095	-116.593291	205.938842	207.0415524	15.6	16.7
79	CYCLOPROPENE C2V	-116.3784771	-0.63596367	-116.556547	303.347409	304.4501187	26.4	27.5
80	PROPENE CS	-117.6545382	-0.65618745	-117.838271	45.811140	46.91384964	25.7	26.8
81	CYCLOPROPANE D3H	-117.6411245	-0.66263713	-117.826663	78.768489	79.87119873	25.6	26.7
82	PROPANE C2V	-118.8736332	-0.68915635	-119.066597	-72.601338	-71.49862792	32.0	33.1
83	TRANS-1,3-BUTADIENE C2H	-155.668982	-0.84828104	-155.906501	139.681514	141.151794	29.6	31.1
84	Dimethyl acetylene	-155.6555731	-0.85405469	-155.894708	170.794261	172.2645414	25.2	26.7
85	Methylene cyclopropane.	-155.6364048	-0.85521903	-155.875866	218.860090	220.3303701	18.4	19.9
86	Bicyclo[1.1.0]butane. C2v	-155.6206718	-0.86703464	-155.863442	253.413270	254.8835496	36.3	37.7
87	CYCLOBUTENE b3lyp	-155.6461279	-0.85736604	-155.886190	194.116636	195.5869157	37.6	39.1
88	CYCLOBUTANE b3lyp/6-31G*	-156.8705019	-0.88655622	-157.118738	65.995168	67.46544832	37.5	39.0
89	Isobutene. Single	-156.8877217	-0.88212345	-157.134716	19.254483	20.72476298	36.0	37.5
90	Trans butane	-158.1018886	-0.9125256	-158.357396	-83.142917	-81.67263717	42.4	43.8
91	isobutane B3LYP/6-31G*	-158.102913	-0.91567368	-158.359302	-89.441340	-87.97106044	44.9	46.3
92	Spiropentane. D2d	-194.8591071	-1.0851638	-195.162953	219.999372	221.837222	34.6	36.5
93	Benzene B3LYP	-231.7810881	-1.24623506	-232.130034	106.766906	108.9723263	24.3	26.5
94	DIFLUOROMETHANE C2V	-238.7014118	-0.84442338	-238.937850	-444.430349	-440.8596691	6.2	9.8
95	HCF3 TRI-FLUOROMETHANE	-337.8620557	-1.14524416	-338.182724	-691.974107	-686.8018716	5.1	10.3
96	CH2CL2 C2V	-959.2533914	-0.86656067	-959.496028	-83.211711	-75.80780149	12.2	19.6
97	chcl3 B3LYP/6-31G*	-1418.663872	-1.18822799	-1418.996576	-88.504623	-77.58254337	14.8	25.8
98	METHYLAMINE b3lyp	-95.66859983	-0.5090543	-95.811135	-1.028995	-0.661425313	22.0	22.4
99	Acetonitrile. CH3-CN.	-132.5088791	-0.67411761	-132.697632	87.678782	88.41392231	12.4	13.1
100	NITRO METHANE	-244.6225884	-1.11477389	-244.934725	-47.792372	-45.53444162	26.7	28.9
101	Methyl-nitrite. CH3-O-N=O.	-244.6187764	-1.10395654	-244.927884	-33.559778	-31.30184767	33.0	35.2
102	Methylsilane. CH3-SiH3.	-330.952976	-0.55923604	-331.109562	-5.811816	-3.658906127	23.5	25.6
103	Formic Acid.	-189.4858509	-0.80663277	-189.711708	-363.889377	-361.6314469	14.8	17.0
104	Methyl formate.	-228.7015299	-1.02668746	-228.989002	-339.576192	-336.9506918	16.1	18.7
105	acetamide ch3cohn2	-208.8615421	-0.9969047	-209.140675	-214.603881	-212.9235606	23.9	25.6

106	Aziridine. (cyclic	-133.6591443	-0.70692755	-133.857084	151.282450	152.0175897	24.9	25.7
107	Cyanogen. NCCN.	-185.338365	-0.9004063	-185.590479	314.363166	315.0983058	7.7	8.4
108	DIMETHYLAMINE b3lyp	-134.8881487	-0.73080465	-135.092774	11.186871	11.92201086	29.6	30.3
109	TRANS ETHYLAMINE	-134.8996969	-0.73196473	-135.104647	-19.048420	-18.31327969	28.2	29.0
110	KETENE B3LYP	-152.3492175	-0.70537816	-152.546723	-43.781878	-42.10155769	3.5	5.2
111	OXIRANE B3LYP	-153.5199937	-0.73707867	-153.726376	-31.053573	-29.37325291	21.7	23.3
112	Acetaldehyde B3LYP	-153.5656746	-0.72921177	-153.769854	-148.324439	-146.6441195	17.8	19.5
113	Glyoxal, O=CH-CH=O.	-227.472208	-0.99417688	-227.750577	-197.839769	-195.2142689	14.3	16.9
114	ETHANOL TRANS	-154.7627884	-0.75998446	-154.975584	-205.321067	-203.6407466	29.8	31.5
115	DIMETHYL ETHER,	-154.7459721	-0.75696715	-154.957923	-159.794432	-158.1141124	24.3	26.0
116	Thiooxirane. (cyclic	-476.4402715	-0.82140798	-476.670266	103.303016	106.3748506	21.3	24.4
117	Dimethylsulfoxide. (CH3)2SO.	-552.7491592	-1.15879992	-553.073623	-103.424832	-99.40781706	48.0	52.1
118	Thioethanol. CH3-CH2-SH.	-477.6597133	-0.84025897	-477.894986	-13.646626	-10.57479077	32.8	35.9
119	ch3sch3 B3LYP	-477.6575906	-0.8420613	-477.893368	-6.872606	-3.800770772	30.4	33.4
120	Vinyl fluoride,	-177.5635311	-0.73558042	-177.769494	-129.528685	-127.1919903	9.4	11.7
121	Ethyl chloride.	-539.0695429	-0.77583779	-539.286778	-91.661161	-87.40785056	20.5	24.7
122	Vinyl chloride,	-537.84503	-0.74708798	-538.054215	37.136652	41.38996238	14.1	18.4
123	h2c=chcn B3LYP	-170.5143654	-0.86691261	-170.757101	204.425388	205.5280982	23.7	24.8
124	ACETONE B3LYP	-192.8057691	-0.95204477	-193.072342	-190.001823	-187.9539332	27.1	29.2
125	CH3COOH ACETIC	-228.7274644	-1.02646677	-229.014875	-407.959090	-405.33359	24.7	27.3
126	CH3CFO HCCO	-252.7376271	-1.03512545	-253.027462	-426.257420	-422.9755445	16.0	19.3
127	ch3c(o)cl hcco	-613.0053242	-1.05063307	-613.299501	-226.702908	-221.5044176	16.0	21.2
128	ch3ch2ch2cl B3LYP	-578.2979161	-0.99945549	-578.577764	-102.599941	-97.9790612	29.2	33.8
129	Isopropyl alcohol,	-193.996002	-0.98551856	-194.271947	-232.162480	-230.1145898	40.6	42.7
130	Methyl ethyl	-193.9794448	-0.97974276	-194.253773	-183.896748	-181.8488576	32.4	34.5
131	Trimethyl Amine.	-174.1100545	-0.95726524	-174.378089	12.447058	13.54976799	36.3	37.4
132	FURAN B3LYP	-229.610838	-1.13259305	-229.927964	-11.484648	-9.069187738	23.2	25.7
133	Thiophene b3lyp	-552.5205329	-1.22365238	-552.863156	143.362615	147.1695896	28.3	32.1
134	PYROLE PLANAR	-209.7645192	-1.10564499	-210.074100	129.674564	131.1448441	21.3	22.8
135	C2v Pyridine	-247.8067491	-1.28940966	-248.167784	158.309212	160.1470625	17.7	19.6
136	H2 B3LYP/6-31G*	-1.15957921	-0.0342873	-1.169180	8.518995	8.518995013	8.5	8.5
137	SH b3lyp/6-31G*	-398.5690263	-0.35519108	-398.668480	148.788768	151.1254625	5.7	8.0
138	CCH B3LYP	-76.46472631	-0.3745681	-76.569605	587.835065	588.570205	22.6	23.3
139	C2H3 CS,2-A'	-77.74575596	-0.39657001	-77.856796	310.296565	311.0317049	10.7	11.5
140	ch3co hcco	-152.9234896	-0.70719779	-153.121505	0.243917	1.924236981	10.3	12.0
141	H2COH C1	-114.876887	-0.50568719	-115.018479	-3.383998	-2.071248052	13.8	15.1
142	ch3o CS,	-114.870686	-0.47906186	-115.004823	28.896741	30.20949079	11.7	13.1

143	ch3ch2o 2A"	-154.1039641	-0.70126282	-154.300318	5.149976	6.830296147	20.6	22.3
144	ch3s 2-A'	-437.7982405	-0.58079172	-437.960862	135.302535	138.0067996	10.6	13.3
145	c2h5 staggered	-78.98585888	-0.42805786	-79.105715	136.540579	137.2757195	15.6	16.4
146	(ch3)2ch Cs	-118.2187075	-0.65233928	-118.401363	113.389701	114.4924114	23.4	24.5
147	TERT-BUTYL RADICAL	-157.4517412	-0.87860871	-157.697752	88.028854	89.49913397	36.6	38.0
148	NO2 RADICAL	-204.7709235	-0.88982454	-205.020074	45.774697	47.66505654	12.7	14.6

MAD	**18.4**	**20.7**
LD	**52.5**	**55.4**

Table S5.59b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 62% and a_C = 28%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498825	0.000000	-0.498825
2	li	-7.468413	-0.014454	-7.472460
3	be	-14.636889	-0.052206	-14.651507
4	b	-24.615823	-0.075902	-24.637075
5	c	-37.798706	-0.102514	-37.827409
6	n	-54.531744	-0.133102	-54.569012
7	o	-74.993635	-0.189702	-75.046751
8	f	-99.639072	-0.251980	-99.709626
9	na	-162.145674	-0.169639	-162.193173
10	al	-242.227417	-0.217643	-242.288357
11	si	-289.228182	-0.247366	-289.297444
12	p	-341.110778	-0.276099	-341.188086
13	s	-397.944550	-0.316881	-398.033277
14	cl	-459.962414	-0.287593	-460.042940

Table S5.60a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 64% and a_C = 35%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.04154656	-0.04559662	-8.057505	148.846610	148.8466098	9.5	9.5
2	BERYLLIUM HYDRIDE	-15.21631451	-0.05375231	-15.235128	320.675733	320.6757328	-21.2	-21.2
3	DOUBLET CH	-38.40437715	-0.14133933	-38.453846	601.703220	602.0707899	5.5	5.9
4	CH2 3-B1	-39.06687942	-0.16028192	-39.122978	396.205590	396.5731601	4.2	4.5
5	Singlet methylene,	-39.0419139	-0.17958539	-39.104769	442.402065	442.7696347	12.3	12.7
6	Methyl radical,	-39.7361695	-0.20420323	-39.807641	153.855492	154.2230619	7.4	7.8
7	ch4 //b3lyp/6-31G*	-40.39848933	-0.24483914	-40.484183	-61.871669	-61.5040988	13.0	13.4
8	NH,TRIPLET, //b3lyp/6-31G*	-55.130447	-0.18407202	-55.194872	361.709504	361.7095035	5.2	5.2
9	NH2,2-B-1, //b3lyp/6-31G*	-55.7682721	-0.23627961	-55.850970	192.536769	192.5367689	3.8	3.8
10	AMMONIA, //b3lyp/6-31G*	-56.43101035	-0.28898015	-56.532153	-33.821148	-33.82114759	12.2	12.2
11	OH RADICAL	-75.61987601	-0.25361086	-75.708640	42.833035	43.77821535	3.5	4.4
12	Water //b3lyp/6-31G*	-76.29333654	-0.32055955	-76.405532	-230.035962	-229.0907815	11.8	12.7
13	HYDROGEN FLUORIDE,	-100.3094262	-0.33161845	-100.425493	-267.515497	-265.9139418	4.9	6.5
14	SIH2 singlet	-290.4090548	-0.30025476	-290.514144	278.827833	280.6131732	6.0	7.8
15	SIH2 3B1	-290.384758	-0.27830169	-290.482164	363.803360	365.5887003	3.1	4.9
16	SIH3 c3v	-291.0238977	-0.30574366	-291.130908	206.595888	208.3812277	6.2	8.0
17	SIH4 //b3lyp/6-31G*	-291.6649086	-0.33238297	-291.781243	47.156086	48.9414264	12.8	14.6
18	ph2 doublet	-342.2880361	-0.33928352	-342.406785	144.610969	144.6109693	6.1	6.1
19	PH3 c3v	-342.9136772	-0.36946178	-343.042989	23.771814	23.77181379	18.3	18.3
20	SH2 //b3lyp/6-31G*	-399.1580333	-0.39067217	-399.294769	-7.467440	-5.130745167	13.0	15.4
21	HCL //b3lyp/6-31G*	-460.5659299	-0.32964753	-460.681306	-88.315086	-84.79691638	4.2	7.7
22	DILITHIUM //b3lyp/6-31G*	-14.95278661	-0.0563073	-14.972494	231.520227	231.5202268	15.6	15.6
23	Lithium Fluoride,	-107.2684504	-0.35950083	-107.394276	-339.586972	-337.9854175	-4.4	-2.8
24	ACETYLENE //b3lyp/6-31g*	-77.14659653	-0.40788786	-77.289357	230.444843	231.1799829	3.7	4.4
25	ETHYLENE //b3lyp/6-31g*	-78.38612544	-0.42931867	-78.536387	64.168919	64.90405876	11.9	12.6
26	ETHANE //b3lyp/6-31g*	-79.60696854	-0.46265411	-79.768897	-65.294372	-64.55923231	18.8	19.5
27	CYANO RADICAL,	-92.52016718	-0.43885539	-92.673767	447.557132	447.9247015	8.7	9.0
28	HYDROGEN CYANIDE	-93.2293886	-0.45116903	-93.387298	126.269655	126.6372248	-5.5	-5.2
29	CARBON MONOXIDE	-113.1183677	-0.46216601	-113.280126	-116.728978	-115.4162278	-6.3	-5.0
30	HCO BENT	-113.6418788	-0.48424684	-113.811365	32.349179	33.66192853	-9.5	-8.2
31	H2CO //b3lyp/6-31g*	-114.282832	-0.50372852	-114.459137	-110.899504	-109.5867543	-2.1	-0.8

32	METHANOL //b3lyp/6-31g*	-115.4867201	-0.53369836	-115.673514	-189.824572	-188.5118221	11.0	12.3
33	Nitrogen N2,	-109.3245584	-0.48423609	-109.494041	-1.332427	-1.33242741	-1.3	-1.3
34	H2NNH2 //b3lyp/6-31g*	-111.6265934	-0.54789038	-111.818355	111.049825	111.0498245	15.7	15.7
35	NO radical,	-129.6671365	-0.52571947	-129.851138	85.584134	86.52931374	-4.8	-3.8
36	O2 //b3lyp/6-31g*	-150.0713777	-0.5901431	-150.277928	-9.701700	-7.811339656	-9.7	-7.8
37	HYDROGEN PEROXIDE	-151.285134	-0.61873047	-151.501690	-116.977876	-115.0875161	19.0	20.9
38	F2 //b3lyp/6-31g*	-199.2351891	-0.64721792	-199.461715	17.931825	21.1349349	17.9	21.1
39	CO2 D*H	-188.2638975	-0.77719617	-188.535916	-419.353715	-417.0957855	-26.1	-23.8
40	na2 //b3lyp/6-31G*	-324.2498926	-0.36448306	-324.377462	145.032890	145.0328901	2.8	2.8
41	SI2 3-SGG	-578.479503	-0.54811531	-578.671343	590.449628	594.0203084	5.1	8.7
42	P2 //b3lyp/6-31g*	-682.2741958	-0.6940482	-682.517113	155.547151	155.5471508	12.0	12.0
43	S2 //b3lyp/6-31g*	-795.9244057	-0.7425912	-796.184313	127.452034	132.1254244	-1.0	3.7
44	CL2 //b3lyp/6-31g*	-919.8945128	-0.63764433	-920.117688	8.491412	15.52775182	8.5	15.5
45	Sodium Chloride	-622.1693758	-0.4989676	-622.344015	-176.526402	-173.0082324	5.9	9.4
46	SIO //b3lyp/6-31g*	-364.4128365	-0.60165227	-364.623415	-99.303344	-96.5728236	3.6	6.4
47	Carbon monosulfide,	-435.9086482	-0.56176136	-436.105265	285.216997	287.9212623	5.3	8.0
48	OS //b3lyp/6-31g*	-473.0181113	-0.67237363	-473.253442	0.101110	3.38298531	-4.9	-1.6
49	CLO 2-PI	-534.9478418	-0.58846455	-535.153804	113.445730	117.90908	12.2	16.7
50	CLF 1-SG	-559.5904623	-0.63977113	-559.814382	-51.770273	-46.65054763	3.5	8.6
51	si2h6 //b3lyp/6-31g*	-582.1582448	-0.64582486	-582.384283	103.956397	107.5270773	24.0	27.6
52	Methyl chloride,	-499.7690979	-0.54816707	-499.960956	-75.274460	-71.38871954	6.7	10.6
53	H3C-SH METHANETHIOL	-438.3640651	-0.61169159	-438.578157	-4.295432	-1.591167464	18.7	21.4
54	HOCl //b3lyp/6-31g*	-535.5928437	-0.63095829	-535.813679	-66.420646	-61.9572964	8.1	12.5
55	SO2 //b3lyp/6-31G*	-548.1483376	-1.00819163	-548.501205	-286.597722	-282.3706674	10.5	14.7
56	BF3 PLANAR	-324.134553	-1.04966567	-324.501936	-1157.419056	-1152.483116	-21.9	-16.9
57	bcl3 B3LYP	-1404.819407	-1.08588496	-1405.199466	-426.116042	-415.4302574	-23.2	-12.5
58	ALf3 B3LYP	-541.6419901	-1.18644353	-542.057245	-1204.256070	-1198.558735	4.9	10.6
59	alcl3 B3LYP	-1622.387805	-1.18770071	-1622.803500	-595.531118	-584.0839381	-11.0	0.4
60	cf4 B3LYP	-436.903664	-1.43367128	-437.405449	-956.811542	-950.0377518	-23.8	-17.0
61	ccl4 B3LYP	-1877.853483	-1.50502383	-1878.380241	-100.719224	-86.27897387	-4.9	9.5
62	O=C=S. Singlet	-511.1124949	-0.86669754	-511.415839	-161.817952	-158.1685065	-23.3	-19.7
63	CS2 B3LYP	-833.9574445	-0.96313674	-834.294542	99.499713	104.5406726	-17.2	-12.2
64	COF2 B3LYP	-312.5609745	-1.10612052	-312.948117	-629.443565	-624.927705	-5.6	-1.1
65	sif4 B3LYP	-688.458465	-1.53427507	-688.995461	-1590.261208	-1582.069648	24.8	33.0
66	sicl4, td	-2129.393115	-1.56864712	-2129.942141	-654.583619	-638.7255987	8.2	24.0
67	nno B3LYP	-184.3184441	-0.8320851	-184.609674	61.222665	62.16784504	-20.8	-19.8
68	clno B3LYP	-589.6112149	-0.89896655	-589.925853	49.974211	54.43756077	-1.9	2.6

69	nf3 c3v	-353.5762279	-1.21794165	-354.002507	-134.857050	-130.0523845	-2.6	2.2
70	pf3 c3v	-640.4042613	-1.27871566	-640.851812	-941.767443	-936.9627782	16.8	21.6
71	ozone 1-a1	-225.0048713	-0.99733233	-225.353938	152.420027	155.2555671	9.7	12.6
72	f2o B3LYP	-274.256594	-0.95308542	-274.590174	41.527723	45.67601278	16.8	21.0
73	CLF3, C2V	-758.8512698	-1.35111892	-759.324161	-157.000533	-148.6776983	2.0	10.3
74	CF2=CF2 D2H	-474.8381265	-1.63031671	-475.408737	-703.682301	-696.5409409	-45.1	-38.0
75	cl2c=ccl2 B3LYP	-1915.86112	-1.69911478	-1916.455810	-35.022622	-20.21480158	-22.5	-7.7
76	cf3cn B3LYP	-429.8040116	-1.57041959	-430.353658	-528.192242	-522.6524372	-32.8	-27.3
77	PROPYNE C3V	-116.3682861	-0.62707356	-116.587762	189.464032	190.5667424	4.5	5.6
78	ALLENE D2D	-116.3679923	-0.62107203	-116.585368	194.093670	195.1963797	3.7	4.8
79	CYCLOPROPENE C2V	-116.3283943	-0.63062258	-116.549112	290.219231	291.3219405	13.2	14.3
80	PROPENE CS	-117.6015497	-0.65079182	-117.829327	36.897793	38.00050319	16.8	17.9
81	CYCLOPROPANE D3H	-117.5878226	-0.65739646	-117.817911	69.350197	70.45290667	16.2	17.3
82	PROPANE C2V	-118.8174298	-0.68373302	-119.056736	-78.855258	-77.75254765	25.7	26.8
83	TRANS-1,3-BUTADIENE C2H	-155.6012449	-0.84109621	-155.895629	124.779781	126.2500612	14.7	16.2
84	Dimethyl acetylene	-155.5879003	-0.84681889	-155.884287	154.709751	156.1800313	9.1	10.6
85	Methylene cyclopropane.	-155.5683396	-0.84818115	-155.865203	203.409781	204.8800606	3.0	4.5
86	Bicyclo[1.1.0]butane. C2v	-155.552312	-0.86006844	-155.853336	236.499032	237.969312	19.3	20.8
87	CYCLOBUTENE b3lyp	-155.5780241	-0.85026884	-155.875618	178.427619	179.8978991	21.9	23.4
88	CYCLOBUTANE b3lyp/6-31G*	-156.7992144	-0.87949193	-157.107037	53.522701	54.99298143	25.1	26.5
89	Isobutene. Single	-156.816749	-0.8749342	-157.122976	6.884673	8.354952872	23.6	25.1
90	Trans butane	-158.027761	-0.90532549	-158.344625	-92.554496	-91.08421635	33.0	34.4
91	isobutane B3LYP/6-31G*	-158.0287368	-0.90844188	-158.346691	-99.274507	-97.80422692	35.0	36.5
92	Spiropentane. D2d	-194.7728311	-1.07651061	-195.149610	200.787011	202.6248605	15.4	17.3
93	Benzene B3LYP	-231.6831122	-1.23589694	-232.115676	78.915030	81.12044999	-3.5	-1.3
94	DIFLUOROMETHANE C2V	-238.6334744	-0.83835611	-238.926899	-457.879259	-454.3085786	-7.3	-3.7
95	HCF3 TRI-FLUOROMETHANE	-337.7703045	-1.13707326	-338.168280	-712.080982	-706.9087474	-15.0	-9.9
96	CH2CL2 C2V	-959.1368071	-0.86006802	-959.437831	-91.623526	-84.219616	3.8	11.2
97	chcl3 B3LYP/6-31G*	-1418.499036	-1.17926686	-1418.911780	-102.412391	-91.49031125	0.9	11.9
98	METHYLAMINE b3lyp	-95.6281023	-0.50509632	-95.804886	-6.528547	-6.160976672	16.5	16.9
99	Acetonitrile. CH3-CN.	-132.4571991	-0.66819658	-132.691068	71.702965	72.43810479	-3.6	-2.9
100	NITRO METHANE	-244.5404686	-1.10498713	-244.927214	-79.000427	-76.742497	-4.5	-2.3
101	Methyl-nitrite. CH3-O-N=O.	-244.5369738	-1.09390628	-244.919841	-63.370622	-61.11269202	3.2	5.4
102	Methylsilane. CH3-SiH3.	-330.8902952	-0.55527095	-331.084640	-4.040014	-1.887104255	25.2	27.4
103	Formic Acid.	-189.4244124	-0.7999885	-189.704408	-384.291865	-382.0339346	-5.6	-3.4
104	Methyl formate.	-228.6222359	-1.01819571	-228.978604	-362.642419	-360.0169188	-7.0	-4.4
105	acetamide ch3cohn2	-208.7841241	-0.98876757	-209.130193	-234.423725	-232.7434054	4.1	5.7

106	Aziridine. (cyclic	-133.6036933	-0.70126144	-133.849135	139.195739	139.9308786	12.8	13.6
107	Cyanogen. NCCN.	-185.2730834	-0.89181179	-185.585218	283.101225	283.8363647	-23.6	-22.9
108	DIMETHYLAMINE b3lyp	-134.829741	-0.72505846	-135.083511	2.800936	3.53607591	21.2	21.9
109	TRANS ETHYLAMINE	-134.8412695	-0.72622331	-135.095448	-27.600352	-26.86521215	19.7	20.4
110	KETENE B3LYP	-152.2951828	-0.69923121	-152.539914	-62.137348	-60.45702812	-14.9	-13.2
111	OXIRANE B3LYP	-153.4625483	-0.73114465	-153.718449	-46.223265	-44.54294478	6.5	8.2
112	Acetaldehyde B3LYP	-153.5085789	-0.72319072	-153.761696	-162.886608	-161.2062877	3.2	4.9
113	Glyoxal, O=CH-CH=O.	-227.3963661	-0.98573294	-227.741373	-224.291113	-221.6656132	-12.2	-9.5
114	ETHANOL TRANS	-154.7023565	-0.7541021	-154.966292	-216.654499	-214.9741795	18.5	20.2
115	DIMETHYL ETHER,	-154.6856068	-0.75104585	-154.948473	-170.712457	-169.0321368	13.4	15.1
116	Thiooxirane. (cyclic	-476.358452	-0.81523907	-476.643786	92.637359	95.709194	10.6	13.7
117	Dimethylsulfoxide. (CH3)2SO.	-552.641918	-1.14964044	-553.044292	-120.737460	-116.7204455	30.7	34.7
118	Thioethanol. CH3-CH2-SH.	-477.5750302	-0.83408373	-477.866960	-19.999909	-16.9280736	26.4	29.5
119	ch3sch3 B3LYP	-477.5729008	-0.83583652	-477.865444	-13.494225	-10.42239047	23.7	26.8
120	Vinyl fluoride,	-177.5046004	-0.72981899	-177.760037	-142.125043	-139.7883477	-3.2	-0.9
121	Ethyl chloride.	-538.9831876	-0.76990946	-539.252656	-98.750855	-94.49754545	13.4	17.6
122	Vinyl chloride,	-537.7618054	-0.74113081	-538.021201	26.885096	31.13840593	3.9	8.1
123	h2c=chcn B3LYP	-170.4479555	-0.85917275	-170.748666	182.310695	183.4134053	1.6	2.7
124	ACETONE B3LYP	-192.7307135	-0.9442571	-193.061203	-207.538545	-205.4906546	9.6	11.7
125	CH3COOH ACETIC	-228.6481005	-1.01811883	-229.004442	-430.933491	-428.3079907	1.7	4.3
126	CH3CFO HCCO	-252.6566221	-1.02687711	-253.016029	-448.049052	-444.7671769	-5.8	-2.5
127	ch3c(o)cl hcco	-612.8999659	-1.04205135	-613.264684	-246.602586	-241.4040958	-3.9	1.3
128	ch3ch2ch2cl B3LYP	-578.1936437	-0.99174733	-578.540755	-112.909005	-108.2881253	18.9	23.5
129	Isopropyl alcohol,	-193.917598	-0.97782409	-194.259836	-246.893291	-244.8454007	25.9	28.0
130	Methyl ethyl	-193.9011532	-0.97204128	-194.241368	-197.854875	-195.8069852	18.5	20.5
131	Trimethyl Amine.	-174.03366	-0.94967203	-174.366045	0.564092	1.666801989	24.4	25.5
132	FURAN B3LYP	-229.5233777	-1.12316874	-229.916487	-39.434522	-37.01906193	-4.7	-2.3
133	Thiophene b3lyp	-552.4086699	-1.21384241	-552.833515	118.893508	122.7004833	3.8	7.6
134	PYROLE PLANAR	-209.6789667	-1.09655885	-210.062762	104.381853	105.8521334	-4.0	-2.5
135	C2v Pyridine	-247.7066615	-1.27862963	-248.154182	127.910614	129.748464	-12.7	-10.8
136	H2 B3LYP/6-31G*	-1.15694085	-0.03401507	-1.168846	9.647197	9.647197305	9.6	9.6
137	SH b3lyp/6-31G*	-398.5224848	-0.35307637	-398.646062	149.182194	151.5188887	6.1	8.4
138	CCH B3LYP	-76.43557808	-0.37095952	-76.565414	576.864065	577.5992051	11.6	12.3
139	C2H3 CS,2-A'	-77.71309129	-0.39309376	-77.850674	304.645276	305.3804164	5.1	5.8
140	ch3co hcco	-152.8684258	-0.70114379	-153.113826	-15.703016	-14.02269584	-5.7	-4.0
141	H2COH C1	-114.836547	-0.5017051	-115.012144	-11.806779	-10.49402875	5.3	6.7
142	ch3o CS,	-114.8308292	-0.47516025	-114.997135	24.024831	25.33758096	6.9	8.2

143	ch3ch2o 2A"	-154.0461709	-0.6955308	-154.289607	-2.583592	-0.903272158	12.9	14.6
144	ch3s 2-A'	-437.7337026	-0.57677526	-437.935574	132.432657	135.136922	7.7	10.5
145	c2h5 staggered	-78.94989318	-0.42474194	-79.098553	133.874340	134.6094801	13.0	13.7
146	(ch3)2ch Cs	-118.1647224	-0.64719238	-118.391240	107.697992	108.8007016	17.7	18.8
147	TERT-BUTYL RADICAL	-157.3797479	-0.87160295	-157.684809	78.942390	80.41266993	27.5	28.9
148	NO2 RADICAL	-204.7084847	-0.88150412	-205.017011	13.561232	15.45159167	-19.5	-17.6

MAD	**12.0**	**12.7**
LD	**-45.1**	**-38.0**

Table S5.60b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 64% and a_C = 35%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498873	0.000000	-0.498873
2	li	-7.464764	-0.014384	-7.469799
3	be	-14.630409	-0.051587	-14.648465
4	b	-24.607073	-0.075236	-24.633406
5	c	-37.787576	-0.101785	-37.823200
6	n	-54.518337	-0.132285	-54.564637
7	o	-74.975251	-0.188634	-75.041273
8	f	-99.615936	-0.250598	-99.703646
9	na	-162.116688	-0.168659	-162.175719
10	al	-242.192625	-0.216413	-242.268370
11	si	-289.191020	-0.245994	-289.277118
12	p	-341.071336	-0.274529	-341.167421
13	s	-397.900664	-0.315131	-398.010960
14	cl	-459.914282	-0.285753	-460.014296

Table S5.61a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 68% and a_C = 39%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.0382143	-0.04485016	-8.055706	150.141227	150.1412268	10.8	10.8
2	BERYLLIUM HYDRIDE	-15.21253887	-0.05290075	-15.233170	321.221644	321.2216435	-20.6	-20.6
3	DOUBLET CH	-38.39641782	-0.13911754	-38.450674	603.021742	603.3893116	6.8	7.2
4	CH2 3-B1	-39.05857032	-0.15797569	-39.120181	396.795451	397.1630215	4.8	5.1
5	Singlet methylene,	-39.03263621	-0.17663569	-39.101524	444.166587	444.5341566	14.1	14.4
6	Methyl radical,	-39.72615628	-0.20126814	-39.804651	155.206730	155.5742999	8.8	9.1
7	ch4 //b3lyp/6-31G*	-40.3871474	-0.2411521	-40.481197	-60.273623	-59.90605305	14.6	15.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.12048258	-0.18158955	-55.191303	363.817762	363.8177624	7.3	7.3
9	NH2,2-B-1, //b3lyp/6-31G*	-55.75636078	-0.23287182	-55.847181	195.477157	195.4771569	6.8	6.8
10	AMMONIA, //b3lyp/6-31G*	-56.41750055	-0.28465016	-56.528514	-31.018371	-31.01837146	15.0	15.0
11	OH RADICAL	-75.6064923	-0.25022059	-75.704078	43.999307	44.94448687	4.7	5.6
12	Water //b3lyp/6-31G*	-76.2779411	-0.31591988	-76.401150	-229.083620	-228.13844	12.8	13.7
13	HYDROGEN FLUORIDE,	-100.292818	-0.32725253	-100.420446	-267.453023	-265.851468	4.9	6.5
14	SIH2 singlet	-290.3856353	-0.29639427	-290.501229	280.805064	282.5904042	8.0	9.8
15	SIH2 3B1	-290.3623836	-0.27487114	-290.469583	364.901748	366.6870877	4.2	6.0
16	SIH3 c3v	-291.0003755	-0.30193569	-291.118130	208.468364	210.2537044	8.1	9.8
17	SIH4 //b3lyp/6-31G*	-291.640438	-0.32818856	-291.768431	49.372685	51.15802525	15.1	16.8
18	ph2 doublet	-342.262844	-0.33514544	-342.393551	147.439810	147.4398101	8.9	8.9
19	PH3 c3v	-342.8874231	-0.36463542	-343.029631	27.180283	27.18028305	21.7	21.7
20	SH2 //b3lyp/6-31G*	-399.1304907	-0.38571135	-399.280918	-5.832474	-3.495778842	14.7	17.0
21	HCL //b3lyp/6-31G*	-460.5374187	-0.32513767	-460.664222	-87.896586	-84.37841561	4.6	8.1
22	DILITHIUM //b3lyp/6-31G*	-14.94786356	-0.05521627	-14.969398	232.277625	232.2776245	16.4	16.4
23	Lithium Fluoride,	-107.2495532	-0.35434619	-107.387748	-339.576997	-337.9754419	-4.4	-2.8
24	ACETYLENE //b3lyp/6-31g*	-77.12756225	-0.40069308	-77.283833	230.929554	231.6646938	4.2	4.9
25	ETHYLENE //b3lyp/6-31g*	-78.36595387	-0.42239045	-78.530686	65.627793	66.36293307	13.3	14.1
26	ETHANE //b3lyp/6-31g*	-79.5856626	-0.45563811	-79.763361	-63.756401	-63.02126062	20.3	21.1
27	CYANO RADICAL,	-92.49992829	-0.42897751	-92.667230	449.934106	450.3016764	11.0	11.4
28	HYDROGEN CYANIDE	-93.20838599	-0.44309734	-93.381194	127.765066	128.1326363	-4.0	-3.7
29	CARBON MONOXIDE	-113.0961025	-0.45423178	-113.273253	-117.016205	-115.7034546	-6.6	-5.2
30	HCO BENT	-113.6184461	-0.4760645	-113.804111	33.318331	34.63108144	-8.5	-7.2
31	H2CO //b3lyp/6-31g*	-114.2586941	-0.49551188	-114.451944	-109.833655	-108.5209047	-1.0	0.3

32	METHANOL //b3lyp/6-31g*	-115.4613774	-0.52571283	-115.666405	-188.468018	-187.155268	12.4	13.7
33	Nitrogen N2,	-109.3019147	-0.47568796	-109.487433	0.977353	0.977352802	1.0	1.0
34	H2NNH2 //b3lyp/6-31g*	-111.600819	-0.53954344	-111.811241	115.711775	115.7117752	20.3	20.3
35	NO radical,	-129.641689	-0.51684667	-129.843259	87.684908	88.63008761	-2.7	-1.7
36	O2 //b3lyp/6-31g*	-150.0425905	-0.5814184	-150.269344	-9.295940	-7.405579659	-9.3	-7.4
37	HYDROGEN PEROXIDE	-151.2549576	-0.60901758	-151.492474	-114.403376	-112.5130162	21.6	23.5
38	F2 //b3lyp/6-31g*	-199.2020179	-0.63737376	-199.450594	20.247500	23.45061015	20.2	23.5
39	CO2 D*H	-188.2269141	-0.76398867	-188.524870	-419.748936	-417.4910062	-26.5	-24.2
40	na2 //b3lyp/6-31G*	-324.2146734	-0.35988143	-324.355027	145.991909	145.9919088	3.7	3.7
41	SI2 3-SGG	-578.4352172	-0.5409868	-578.646202	591.572738	595.1434182	6.2	9.8
42	P2 //b3lyp/6-31g*	-682.2247227	-0.68378282	-682.491398	158.200025	158.2000248	14.7	14.7
43	S2 //b3lyp/6-31g*	-795.8712307	-0.73321113	-796.157183	128.198581	132.8719714	-0.3	4.4
44	CL2 //b3lyp/6-31g*	-919.8382922	-0.62846326	-920.083393	9.150551	16.18689068	9.2	16.2
45	Sodium Chloride	-622.1241697	-0.49245536	-622.316227	-177.234230	-173.7160601	5.2	8.7
46	SIO //b3lyp/6-31g*	-364.375821	-0.59191987	-364.606670	-98.847845	-96.11732482	4.1	6.8
47	Carbon monosulfide,	-435.8733909	-0.5523586	-436.088811	285.909284	288.6135491	6.0	8.7
48	OS //b3lyp/6-31g*	-472.9771626	-0.66266316	-473.235601	0.635214	3.917088675	-4.4	-1.1
49	CLO 2-PI	-534.9059576	-0.57776663	-535.131287	116.808574	121.2719241	15.6	20.0
50	CLF 1-SG	-559.545955	-0.63036906	-559.791799	-50.612084	-45.49235924	4.6	9.7
51	si2h6 //b3lyp/6-31g*	-582.1104066	-0.63758292	-582.359064	106.820150	110.3908299	26.9	30.5
52	Methyl chloride,	-499.7305432	-0.54018596	-499.941216	-74.635550	-70.74980989	7.4	11.3
53	H3C-SH METHANETHIOL	-438.3264614	-0.60325955	-438.561733	-2.656417	0.047848433	20.4	23.1
54	HOCl //b3lyp/6-31g*	-535.5496514	-0.62137964	-535.791989	-64.976137	-60.51278673	9.5	14.0
55	SO2 //b3lyp/6-31G*	-548.09238	-0.99140048	-548.479026	-285.740988	-281.5139332	11.3	15.6
56	BF3 PLANAR	-324.0815761	-1.03536246	-324.485367	-1160.417006	-1155.481066	-24.9	-19.9
57	bcl3 B3LYP	-1404.729988	-1.07026122	-1405.147390	-429.636925	-418.9511398	-26.7	-16.0
58	ALf3 B3LYP	-541.5742122	-1.17070814	-542.030788	-1207.370386	-1201.673051	1.8	7.5
59	alcl3 B3LYP	-1622.284554	-1.17185106	-1622.741576	-599.275883	-587.8287029	-14.8	-3.3
60	cf4 B3LYP	-436.8319063	-1.41385215	-437.383309	-959.716895	-952.9431047	-26.7	-19.9
61	ccl4 B3LYP	-1877.732511	-1.48282071	-1878.310811	-104.464410	-90.02415983	-8.7	5.8
62	O=C=S. Singlet	-511.062758	-0.85282093	-511.395358	-161.618700	-157.9692552	-23.1	-19.5
63	CS2 B3LYP	-833.8948422	-0.94848199	-834.264750	99.970732	105.0116918	-16.8	-11.7
64	COF2 B3LYP	-312.5063956	-1.08954737	-312.931319	-630.557806	-626.0419464	-6.7	-2.2
65	sif4 B3LYP	-688.3736625	-1.51419139	-688.964197	-1594.388610	-1586.19705	20.6	28.8
66	sicl4, td	-2129.260059	-1.54730746	-2129.863509	-659.345707	-643.4876872	3.4	19.3
67	nno B3LYP	-184.2798884	-0.81673954	-184.598417	64.672374	65.61755356	-17.3	-16.4
68	clno B3LYP	-589.5558387	-0.88292434	-589.900179	54.103790	58.56713988	2.2	6.7

69	nf3 c3v	-353.5152181	-1.19890908	-353.982793	-130.942062	-126.1373972	1.3	6.1
70	pf3 c3v	-640.3321787	-1.26119272	-640.824044	-941.619625	-936.8149605	16.9	21.7
71	ozone 1-a1	-224.9586744	-0.97749976	-225.339899	156.080117	158.9156567	13.4	16.2
72	f2o B3LYP	-274.2084595	-0.93757074	-274.574112	45.748018	49.89630765	21.1	25.2
73	CLF3, C2V	-758.7718255	-1.32962243	-759.290378	-153.320892	-144.9980569	5.7	14.0
74	CF2=CF2 D2H	-474.7566759	-1.60677686	-475.383319	-705.246661	-698.1053012	-46.7	-39.5
75	cl2c=ccl2 B3LYP	-1915.731152	-1.67363641	-1916.383870	-39.444549	-24.63672881	-26.9	-12.1
76	cf3cn B3LYP	-429.7273627	-1.54646235	-430.330483	-529.723748	-524.1839433	-34.3	-28.8
77	PROPYNE C3V	-116.3392208	-0.61658871	-116.579690	189.880881	190.9835912	4.9	6.1
78	ALLENE D2D	-116.3386568	-0.61074178	-116.576846	195.691934	196.7946437	5.3	6.4
79	CYCLOPROPENE C2V	-116.2991768	-0.62039434	-116.541131	290.400365	291.5030754	13.4	14.5
80	PROPENE CS	-117.5713518	-0.64046866	-117.821135	38.143409	39.24611863	18.1	19.2
81	CYCLOPROPANE D3H	-117.5576857	-0.64731968	-117.810140	69.489889	70.59259903	16.4	17.5
82	PROPANE C2V	-118.7861502	-0.67332136	-119.048746	-77.626480	-76.52376954	27.0	28.1
83	TRANS-1,3-BUTADIENE C2H	-155.5620672	-0.82737821	-155.884745	125.826372	127.2966517	15.8	17.3
84	Dimethyl acetylene	-155.5488091	-0.83301454	-155.873685	155.016474	156.486754	9.4	10.9
85	Methylene cyclopropane.	-155.5291288	-0.83469299	-155.854659	203.563740	205.0340199	3.2	4.6
86	Bicyclo[1.1.0]butane. C2v	-155.5131941	-0.8466774	-155.843398	235.061470	236.5317499	17.9	19.4
87	CYCLOBUTENE b3lyp	-155.5389842	-0.83666849	-155.865285	178.028665	179.4989452	21.5	23.0
88	CYCLOBUTANE b3lyp/6-31G*	-156.7591514	-0.8659201	-157.096860	53.223132	54.69341214	24.8	26.2
89	Isobutene. Single	-156.7765465	-0.86116636	-157.112401	7.631085	9.101364669	24.4	25.8
90	Trans butane	-157.986509	-0.8915081	-158.334197	-91.681895	-90.21161541	33.8	35.3
91	isobutane B3LYP/6-31G*	-157.9874793	-0.8945623	-158.336359	-98.650965	-97.18068484	35.7	37.1
92	Spiropentane. D2d	-194.7237606	-1.05987412	-195.137112	199.317764	201.1556142	14.0	15.8
93	Benzene B3LYP	-231.6261756	-1.21612756	-232.100465	76.789454	78.99487407	-5.6	-3.4
94	DIFLUOROMETHANE C2V	-238.5917747	-0.82652261	-238.914119	-457.962743	-454.3920632	-7.3	-3.8
95	HCF3 TRI-FLUOROMETHANE	-337.7135265	-1.12116012	-338.150779	-713.468191	-708.295956	-16.4	-11.2
96	CH2CL2 C2V	-959.0708695	-0.84754004	-959.401410	-92.138798	-84.7348877	3.3	10.7
97	chcl3 B3LYP/6-31G*	-1418.405613	-1.16198662	-1418.858788	-104.368899	-93.44681941	-1.0	9.9
98	METHYLAMINE b3lyp	-95.60463653	-0.49743951	-95.798638	-3.630737	-3.263166901	19.4	19.7
99	Acetonitrile. CH3-CN.	-132.4262107	-0.65689016	-132.682398	73.181825	73.91696545	-2.1	-1.4
100	NITRO METHANE	-244.4885958	-1.08616432	-244.912200	-75.730494	-73.47256356	-1.3	1.0
101	Methyl-nitrite. CH3-O-N=O.	-244.48538	-1.07462236	-244.904483	-59.197446	-56.93951596	7.3	9.6
102	Methylsilane. CH3-SiH3.	-330.8557528	-0.54766547	-331.069342	-2.049388	0.103521752	27.2	29.4
103	Formic Acid.	-189.3862069	-0.78712554	-189.693186	-383.713114	-381.4551835	-5.1	-2.8
104	Methyl formate.	-228.5740516	-1.00182299	-228.964763	-361.940922	-359.315422	-6.3	-3.7
105	acetamide ch3cohn2	-208.737815	-0.97306337	-209.117310	-232.437899	-230.7575791	6.1	7.7

106	Aziridine. (cyclic	-133.571327	-0.69033813	-133.840559	140.939231	141.6743705	14.6	15.3
107	Cyanogen. NCCN.	-185.2318394	-0.8754719	-185.573273	284.888308	285.6234477	-21.8	-21.1
108	DIMETHYLAMINE b3lyp	-134.7962912	-0.71398298	-135.074745	5.557413	6.292552653	24.0	24.7
109	TRANS ETHYLAMINE	-134.8078152	-0.71514964	-135.086724	-24.956063	-24.22092276	22.3	23.1
110	KETENE B3LYP	-152.2619127	-0.68743364	-152.530012	-61.226144	-59.54582445	-13.9	-12.3
111	OXIRANE B3LYP	-153.4282196	-0.71968177	-153.708895	-45.715145	-44.03482547	7.0	8.7
112	Acetaldehyde B3LYP	-153.4744177	-0.71158423	-153.751936	-161.835994	-160.1556742	4.3	5.9
113	Glyoxal, O=CH-CH=O.	-227.3493068	-0.96945174	-227.727393	-223.739643	-221.1141427	-11.6	-9.0
114	ETHANOL TRANS	-154.667038	-0.74272071	-154.956699	-215.530278	-213.849958	19.6	21.3
115	DIMETHYL ETHER,	-154.6502935	-0.73960961	-154.938741	-169.224757	-167.5444372	14.9	16.6
116	Thiooxirane. (cyclic	-476.311844	-0.8033805	-476.625162	92.782940	95.85477535	10.8	13.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.579634	-1.13199018	-553.021110	-119.176833	-115.1598175	32.3	36.3
118	Thioethanol. CH3-CH2-SH.	-477.527439	-0.82220952	-477.848101	-18.724146	-15.65231112	27.7	30.8
119	ch3sch3 B3LYP	-477.5252238	-0.82386775	-477.846532	-12.080370	-9.008535088	25.2	28.2
120	Vinyl fluoride,	-177.4690769	-0.71869783	-177.749369	-141.323021	-138.9863262	-2.4	-0.1
121	Ethyl chloride.	-538.9346418	-0.75849383	-539.230454	-98.405370	-94.1520601	13.7	18.0
122	Vinyl chloride,	-537.7142394	-0.72969556	-537.998821	27.188620	31.44193001	4.2	8.4
123	h2c=chcn B3LYP	-170.4079541	-0.84441275	-170.737275	183.666795	184.769505	2.9	4.0
124	ACETONE B3LYP	-192.686577	-0.92926983	-193.048992	-206.806660	-204.7587705	10.3	12.4
125	CH3COOH ACETIC	-228.5999701	-1.0019942	-228.990748	-430.619622	-427.9941224	2.0	4.6
126	CH3CFO HCCO	-252.6071833	-1.01094751	-253.001453	-448.051523	-444.7696475	-5.8	-2.5
127	ch3c(o)cl hcco	-612.8382291	-1.02553824	-613.238189	-246.562525	-241.3640348	-3.9	1.3
128	ch3ch2ch2cl B3LYP	-578.1351309	-0.97691922	-578.516129	-112.952761	-108.3318813	18.8	23.5
129	Isopropyl alcohol,	-193.8722963	-0.96297502	-194.247857	-246.257100	-244.2092098	26.5	28.6
130	Methyl ethyl	-193.855866	-0.9571972	-194.229173	-196.654343	-194.6064527	19.7	21.7
131	Trimethyl Amine.	-173.990204	-0.93505949	-174.354877	2.870385	3.973094749	26.7	27.8
132	FURAN B3LYP	-229.4711105	-1.10506875	-229.902087	-40.735645	-38.32018491	-6.0	-3.6
133	Thiophene b3lyp	-552.3440361	-1.19505631	-552.810108	117.065869	120.8728436	2.0	5.8
134	PYROLE PLANAR	-209.6285915	-1.07912518	-210.049450	104.027363	105.4976429	-4.3	-2.9
135	C2v Pyridine	-247.6475774	-1.25798708	-248.138192	127.320131	129.1579814	-13.3	-11.4
136	H2 B3LYP/6-31G*	-1.15549391	-0.03348171	-1.168552	10.931822	10.9318219	10.9	10.9
137	SH b3lyp/6-31G*	-398.4962141	-0.34893007	-398.632297	150.336140	152.6728351	7.2	9.6
138	CCH B3LYP	-76.4178537	-0.36415759	-76.559875	577.129684	577.8648235	11.9	12.6
139	C2H3 CS,2-A'	-77.69405779	-0.38653775	-77.844808	306.283458	307.0185979	6.7	7.4
140	ch3co hcco	-152.8350185	-0.68956942	-153.103951	-14.605169	-12.92484853	-4.6	-2.9
141	H2COH C1	-114.8122104	-0.4940324	-115.004883	-10.307669	-8.994918657	6.8	8.2
142	ch3o CS,	-114.8071368	-0.46773024	-114.989552	26.371492	27.68424157	9.2	10.5

143	ch3ch2o 2A"	-154.0124728	-0.68462201	-154.279475	-0.302371	1.37794944	15.2	16.9
144	ch3s 2-A'	-437.6972406	-0.56901976	-437.919158	133.792195	136.4964603	9.1	11.8
145	c2h5 staggered	-78.92975007	-0.41834722	-79.092905	135.448774	136.1839137	14.5	15.3
146	(ch3)2ch Cs	-118.1344809	-0.63732254	-118.383037	109.227956	110.330666	19.3	20.4
147	TERT-BUTYL RADICAL	-157.339457	-0.85820712	-157.674158	80.145602	81.61588223	28.7	30.2
148	NO2 RADICAL	-204.6669064	-0.86557805	-205.004482	16.805352	18.69571224	-16.2	-14.4

MAD	**12.8**	**13.6**
LD	**-46.7**	**-39.5**

Table S5.61b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 68% and a_C = 39%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.498971	0.000000	-0.498971
2	li	-7.462836	-0.014254	-7.468395
3	be	-14.626944	-0.050446	-14.646618
4	b	-24.602227	-0.073919	-24.631055
5	c	-37.781310	-0.100314	-37.820433
6	n	-54.510818	-0.130653	-54.561773
7	o	-74.964344	-0.186447	-75.037058
8	f	-99.601885	-0.247797	-99.698526
9	na	-162.099649	-0.166756	-162.164684
10	al	-242.172627	-0.213999	-242.256086
11	si	-289.169873	-0.243301	-289.264761
12	p	-341.049179	-0.271512	-341.155069
13	s	-397.875980	-0.311685	-397.997538
14	cl	-459.887243	-0.282130	-459.997273

Table S5.62a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 75% and a_C = 15%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.05996087	-0.04359176	-8.066500	148.017048	148.0170476	8.7	8.7
2	BERYLLIUM HYDRIDE	-15.23942928	-0.05168768	-15.247182	313.744339	313.7443392	-28.1	-28.1
3	DOUBLET CH	-38.44383236	-0.13531219	-38.464129	605.325844	605.6934141	9.1	9.5
4	CH2 3-B1	-39.11075312	-0.15415593	-39.133877	398.927498	399.2950685	6.9	7.3
5	Singlet methylene,	-39.08860989	-0.17185173	-39.114388	448.483443	448.8510134	18.4	18.7
6	Methyl radical,	-39.78884312	-0.19624761	-39.818280	157.971190	158.3387602	11.5	11.9
7	ch4 //b3lyp/6-31G*	-40.45869532	-0.23516041	-40.493969	-54.801342	-54.43377171	20.1	20.5
8	NH,TRIPLET, //b3lyp/6-31G*	-55.17689655	-0.17713038	-55.203466	371.402058	371.4020579	14.9	14.9
9	NH2,2-B-1, //b3lyp/6-31G*	-55.82227719	-0.22698042	-55.856324	211.449267	211.4492667	22.8	22.8
10	AMMONIA, //b3lyp/6-31G*	-56.49251981	-0.27740542	-56.534131	-5.327809	-5.327809068	40.7	40.7
11	OH RADICAL	-75.6764931	-0.24426161	-75.713132	62.048067	62.99324691	22.7	23.7
12	Water //b3lyp/6-31G*	-76.35665498	-0.30800747	-76.402856	-191.284867	-190.3396867	50.6	51.5
13	HYDROGEN FLUORIDE,	-100.3762196	-0.31970731	-100.424176	-237.170175	-235.5686202	35.2	36.8
14	SIH2 singlet	-290.529922	-0.29016973	-290.573447	272.631388	274.4167281	-0.2	1.6
15	SIH2 3B1	-290.5023295	-0.26986148	-290.542809	354.084185	355.8695246	-6.6	-4.8
16	SIH3 c3v	-291.1500264	-0.29597256	-291.194422	190.058229	191.8435695	-10.4	-8.6
17	SIH4 //b3lyp/6-31G*	-291.7989692	-0.32140885	-291.847180	24.969678	26.75501803	-9.3	-7.6
18	ph2 doublet	-342.4182072	-0.32820551	-342.467438	141.214826	141.214826	2.7	2.7
19	PH3 c3v	-343.0511111	-0.35681944	-343.104634	18.484212	18.48421169	13.0	13.0
20	SH2 //b3lyp/6-31G*	-399.2999533	-0.3775732	-399.356589	-2.305273	0.031422353	18.2	20.5
21	HCL //b3lyp/6-31G*	-460.7130013	-0.31765924	-460.760650	-81.676877	-78.1587072	10.8	14.3
22	DILITHIUM //b3lyp/6-31G*	-14.98072745	-0.05355456	-14.988761	232.953640	232.9536396	17.1	17.1
23	Lithium Fluoride,	-107.3461496	-0.34539201	-107.397958	-301.011912	-299.4103572	34.1	35.7
24	ACETYLENE //b3lyp/6-31g*	-77.23221217	-0.38928173	-77.290604	288.413169	289.1483094	61.6	62.4
25	ETHYLENE //b3lyp/6-31g*	-78.48528495	-0.41124852	-78.546972	99.048743	99.78388271	46.7	47.5
26	ETHANE //b3lyp/6-31g*	-79.7196616	-0.44424486	-79.786298	-46.880206	-46.1450662	37.2	38.0
27	CYANO RADICAL,	-92.59676441	-0.41497312	-92.659010	547.748009	548.1155787	108.8	109.2
28	HYDROGEN CYANIDE	-93.31575122	-0.43015665	-93.380275	206.871504	207.2390745	75.1	75.4
29	CARBON MONOXIDE	-113.2075835	-0.44124312	-113.273770	-39.838948	-38.52619843	70.6	71.9
30	HCO BENT	-113.7350982	-0.46287633	-113.804530	111.213082	112.5258324	69.4	70.7
31	H2CO //b3lyp/6-31g*	-114.3842261	-0.48199924	-114.456526	-42.412754	-41.10000393	66.4	67.7

32	METHANOL //b3lyp/6-31g*	-115.6020046	-0.51246828	-115.678875	-140.837836	-139.5250856	60.0	61.3
33	Nitrogen N2,	-109.4123401	-0.46194893	-109.481632	94.329474	94.32947406	94.3	94.3
34	H2NNH2 //b3lyp/6-31g*	-111.7409214	-0.52565172	-111.819769	173.277304	173.2773041	77.9	77.9
35	NO radical,	-129.7609723	-0.50240368	-129.836333	186.293035	187.2382152	95.9	96.9
36	O2 //b3lyp/6-31g*	-150.1697203	-0.56697147	-150.254766	111.700978	113.5913379	111.7	113.6
37	HYDROGEN PEROXIDE	-151.3996317	-0.59272736	-151.488541	-20.435438	-18.54507838	115.5	117.4
38	F2 //b3lyp/6-31g*	-199.3536434	-0.62089563	-199.446778	109.497260	112.7003698	109.5	112.7
39	CO2 D*H	-188.4076806	-0.7424393	-188.519047	-284.563777	-282.3058475	108.7	111.0
40	na2 //b3lyp/6-31G*	-324.4143912	-0.35232151	-324.467239	148.359074	148.3590743	6.1	6.1
41	SI2 3-SGG	-578.698173	-0.5295843	-578.777611	607.597001	611.1676812	22.3	25.8
42	P2 //b3lyp/6-31g*	-682.5146851	-0.66742605	-682.614799	207.909168	207.9091684	64.4	64.4
43	S2 //b3lyp/6-31g*	-796.1834123	-0.71783191	-796.291087	179.203332	183.8767218	50.8	55.4
44	CL2 //b3lyp/6-31g*	-920.1780371	-0.61335552	-920.270040	36.972464	44.00880431	37.0	44.0
45	Sodium Chloride	-622.39642	-0.48149373	-622.468644	-169.981879	-166.4637089	12.4	16.0
46	SIO //b3lyp/6-31g*	-364.5755673	-0.57563492	-364.661913	-22.007344	-19.27682367	80.9	83.6
47	Carbon monosulfide,	-436.0747585	-0.53738088	-436.155366	349.627673	352.3319383	69.7	72.4
48	OS //b3lyp/6-31g*	-473.1971922	-0.64676955	-473.294208	89.410834	92.69270876	84.4	87.7
49	CLO 2-PI	-535.1402186	-0.56125358	-535.224407	172.616005	177.0793552	71.4	75.8
50	CLF 1-SG	-559.7926022	-0.61471817	-559.884810	3.735687	8.855411733	59.0	64.1
51	si2h6 //b3lyp/6-31g*	-582.4179899	-0.62424783	-582.511627	70.053976	73.6246561	-9.9	-6.3
52	Methyl chloride,	-499.9677775	-0.52710273	-500.046843	-54.478864	-50.59312386	27.5	31.4
53	H3C-SH METHANETHIOL	-438.5579461	-0.58949586	-438.646370	15.418846	18.1231108	38.4	41.1
54	HOCl //b3lyp/6-31g*	-535.7920675	-0.60549017	-535.882891	-2.885712	1.577637567	71.6	76.1
55	SO2 //b3lyp/6-31G*	-548.3837012	-0.96389217	-548.528285	-131.061847	-126.8347924	166.0	170.2
56	BF3 PLANAR	-324.3591781	-1.01142124	-324.510891	-1075.340947	-1070.405007	60.2	65.1
57	bcl3 B3LYP	-1405.283201	-1.04468863	-1405.439905	-387.594310	-376.908525	15.3	26.0
58	ALf3 B3LYP	-541.9373826	-1.14419548	-542.109012	-1118.709698	-1113.012363	90.5	96.2
59	alcl3 B3LYP	-1622.924871	-1.14577575	-1623.096738	-579.764355	-568.3171752	4.7	16.2
60	cf4 B3LYP	-437.2001203	-1.38090623	-437.407256	-826.956383	-820.1825934	106.1	112.8
61	ccl4 B3LYP	-1878.467176	-1.44647281	-1878.684146	-11.752296	2.687953794	84.1	98.5
62	O=C=S. Singlet	-511.3338985	-0.83038278	-511.458456	-47.462004	-43.81255932	91.0	94.7
63	CS2 B3LYP	-834.2564893	-0.92499246	-834.395238	197.117560	202.1585204	80.4	85.4
64	COF2 B3LYP	-312.7803524	-1.06218267	-312.939680	-494.743082	-490.2272217	129.1	133.6
65	sif4 B3LYP	-688.8316537	-1.48066976	-689.053754	-1490.539880	-1482.34832	124.5	132.7
66	sicl4, td	-2130.086134	-1.51232856	-2130.312984	-623.191716	-607.3336963	39.6	55.4
67	nno B3LYP	-184.4567527	-0.79197506	-184.575549	244.196363	245.1415432	162.2	163.1
68	clno B3LYP	-589.844436	-0.85694821	-589.972978	202.325382	206.7887318	150.4	154.9

69	nf3 c3v	-353.8050191	-1.16746069	-353.980138	33.935039	38.7397043	166.1	171.0
70	pf3 c3v	-640.7185332	-1.23203787	-640.903339	-844.113067	-839.3084019	114.4	119.2
71	ozone 1-a1	-225.1502133	-0.94549285	-225.292037	405.826969	408.6625089	263.2	266.0
72	f2o B3LYP	-274.4260802	-0.91191662	-274.562868	195.862653	200.0109434	171.2	175.3
73	CLF3, C2V	-759.1735967	-1.29403832	-759.367702	21.443319	29.76615388	180.4	188.8
74	CF2=CF2 D2H	-475.171173	-1.56774791	-475.406335	-532.868014	-525.7266539	125.7	132.8
75	cl2c=ccl2 B3LYP	-1916.51473	-1.63199841	-1916.759530	84.338171	99.14599054	96.9	111.7
76	cf3cn B3LYP	-430.1187386	-1.50720839	-430.344820	-335.110999	-329.5711941	160.3	165.8
77	PROPYNE C3V	-116.5064959	-0.59982112	-116.596469	259.181797	260.284507	74.2	75.4
78	ALLENE D2D	-116.5055718	-0.59417266	-116.594698	262.175678	263.2783882	71.8	72.9
79	CYCLOPROPENE C2V	-116.4679282	-0.60385245	-116.558506	358.134268	359.2369778	81.2	82.3
80	PROPENE CS	-117.7533678	-0.62380902	-117.846939	84.663716	85.76642554	64.6	65.7
81	CYCLOPROPANE D3H	-117.7419512	-0.63091211	-117.836588	114.321591	115.4243006	61.2	62.3
82	PROPANE C2V	-118.9828678	-0.65642398	-119.081331	-47.993759	-46.89104883	56.6	57.7
83	TRANS-1,3-BUTADIENE C2H	-155.7919368	-0.80531443	-155.912734	203.783725	205.2540053	93.7	95.2
84	Dimethyl acetylene	-155.7787056	-0.81084605	-155.900333	236.496003	237.9662834	90.9	92.4
85	Methylene cyclopropane.	-155.7608842	-0.81285382	-155.882812	281.090868	282.5611479	80.7	82.1
86	Bicyclo[1.1.0]butane. C2v	-155.7472371	-0.82487658	-155.870969	314.118886	315.589166	97.0	98.4
87	CYCLOBUTENE b3lyp	-155.7718094	-0.81465189	-155.894007	254.061633	255.5319129	97.6	99.1
88	CYCLOBUTANE b3lyp/6-31G*	-157.0067701	-0.84385749	-157.133349	109.782892	111.2531721	81.3	82.8
89	Isobutene. Single	-157.0215242	-0.83891089	-157.147361	68.205264	69.67554407	84.9	86.4
90	Trans butane	-158.245973	-0.86909727	-158.376338	-49.044550	-47.57427019	76.5	77.9
91	isobutane B3LYP/6-31G*	-158.2472187	-0.87204637	-158.378026	-54.771041	-53.30076137	79.5	81.0
92	Spiropentane. D2d	-195.0205978	-1.0327869	-195.175516	288.020603	289.8584528	102.7	104.5
93	Benzene B3LYP	-231.957339	-1.1842364	-232.134974	211.975328	214.180748	129.6	131.8
94	DIFLUOROMETHANE C2V	-238.8107385	-0.80675017	-238.931751	-386.935911	-383.3652306	63.7	67.3
95	HCF3 TRI-FLUOROMETHANE	-338.0069878	-1.0946284	-338.171182	-610.558441	-605.3862061	86.5	91.7
96	CH2CL2 C2V	-959.4738268	-0.82699238	-959.597876	-52.003816	-44.59990601	43.4	50.8
97	chcl3 B3LYP/6-31G*	-1418.974388	-1.13366909	-1419.144439	-39.914920	-28.99283968	63.4	74.4
98	METHYLAMINE b3lyp	-95.74190655	-0.48484209	-95.814633	32.901329	33.26889916	55.9	56.3
99	Acetonitrile. CH3-CN.	-132.5962739	-0.6386953	-132.692078	162.549102	163.284242	87.2	88.0
100	NITRO METHANE	-244.7460916	-1.05546251	-244.904411	105.052327	107.3102567	179.5	181.8
101	Methyl-nitrite. CH3-O-N=O.	-244.7422574	-1.04329126	-244.898751	116.184151	118.4420814	182.7	185.0
102	Methylsilane. CH3-SiH3.	-331.0767982	-0.53533303	-331.157098	-12.009804	-9.856893521	17.3	19.4
103	Formic Acid.	-189.5818099	-0.76590761	-189.696696	-272.115649	-269.8577195	106.5	108.8
104	Methyl formate.	-228.8319285	-0.97501044	-228.978180	-238.265304	-235.6398044	117.4	120.0
105	acetamide ch3cohn2	-208.993163	-0.94731045	-209.135260	-122.503586	-120.8232659	116.0	117.7

106	Aziridine. (cyclic	-133.758111	-0.67246504	-133.858981	208.272438	209.0075775	81.9	82.7
107	Cyanogen. NCCN.	-185.4364456	-0.84937061	-185.563851	462.095519	462.8306595	155.4	156.1
108	DIMETHYLAMINE b3lyp	-134.9961599	-0.69587728	-135.100541	54.444449	55.17958871	72.9	73.6
109	TRANS ETHYLAMINE	-135.0077881	-0.69702579	-135.112342	24.399654	25.13479367	71.7	72.4
110	KETENE B3LYP	-152.4355134	-0.66826622	-152.535753	40.324270	42.00459016	87.6	89.3
111	OXIRANE B3LYP	-153.6178542	-0.70085494	-153.722982	34.841253	36.52157314	87.6	89.2
112	Acetaldehyde B3LYP	-153.6626964	-0.69259294	-153.766585	-82.757229	-81.07690856	83.3	85.0
113	Glyoxal, O=CH-CH=O.	-227.5912377	-0.9427839	-227.732655	-79.569337	-76.94383665	132.6	135.2
114	ETHANOL TRANS	-154.8704033	-0.72398423	-154.979001	-155.625267	-153.9449466	79.5	81.2
115	DIMETHYL ETHER,	-154.8532615	-0.72084193	-154.961388	-110.224582	-108.5442623	73.9	75.6
116	Thiooxirane. (cyclic	-476.5930128	-0.78406801	-476.710623	145.871377	148.9432124	63.9	66.9
117	Dimethylsulfoxide. (CH3)2SO.	-552.942387	-1.10312287	-553.107855	-27.182906	-23.16589106	124.3	128.3
118	Thioethanol. CH3-CH2-SH.	-477.8216044	-0.8028709	-477.942035	13.033244	16.10507867	59.5	62.5
119	ch3sch3 B3LYP	-477.819011	-0.80437538	-477.939667	21.775471	24.84730579	59.0	62.1
120	Vinyl fluoride,	-177.6621252	-0.70045251	-177.767193	-72.782949	-70.44625406	66.1	68.5
121	Ethyl chloride.	-539.2345461	-0.73985168	-539.345524	-64.949238	-60.69592771	47.2	51.4
122	Vinyl chloride,	-537.9994698	-0.71111654	-538.106137	80.083024	84.33633419	57.1	61.3
123	h2c=chcn B3LYP	-170.6255961	-0.82071266	-170.748703	305.618942	306.7216525	124.9	126.0
124	ACETONE B3LYP	-192.9378056	-0.90481979	-193.073529	-115.595090	-113.5472002	101.6	103.6
125	CH3COOH ACETIC	-228.8585527	-0.97550747	-229.004879	-308.817070	-306.1915696	123.8	126.4
126	CH3CFO HCCO	-252.8695894	-0.98478295	-253.017307	-332.977484	-329.695609	109.3	112.6
127	ch3c(o)cl hcco	-613.1919492	-0.99858707	-613.341737	-142.412622	-137.2141318	100.3	105.5
128	ch3ch2ch2cl B3LYP	-578.4977634	-0.95274988	-578.640676	-66.288431	-61.66755105	65.5	70.1
129	Isopropyl alcohol,	-194.1386507	-0.93864174	-194.279447	-172.649109	-170.601219	100.1	102.2
130	Methyl ethyl	-194.1215839	-0.93292565	-194.261523	-125.040304	-122.9924144	91.3	93.3
131	Trimethyl Amine.	-174.2530398	-0.91123874	-174.389726	66.082711	67.18542066	89.9	91.0
132	FURAN B3LYP	-229.7597688	-1.07563649	-229.921114	101.197219	103.6126792	135.9	138.3
133	Thiophene b3lyp	-552.7239794	-1.1646646	-552.898679	236.333986	240.1409611	121.3	125.1
134	PYROLE PLANAR	-209.9145954	-1.05082949	-210.072220	234.292388	235.7626677	125.9	127.4
135	C2v Pyridine	-247.9814213	-1.22460122	-248.165111	283.863407	285.7012566	143.3	145.1
136	H2 B3LYP/6-31G*	-1.16484037	-0.03258341	-1.169728	8.760836	8.760836382	8.8	8.8
137	SH b3lyp/6-31G*	-398.6573413	-0.34191392	-398.708628	151.671240	154.0079349	8.6	10.9
138	CCH B3LYP	-76.51253532	-0.35343764	-76.565551	637.032599	637.7677387	71.8	72.5
139	C2H3 CS,2-A'	-77.80419026	-0.37620282	-77.860621	340.487599	341.2227395	40.9	41.6
140	ch3co hcco	-153.0143062	-0.67095701	-153.114950	73.599635	75.27995451	83.6	85.3
141	H2COH C1	-114.9442433	-0.48147354	-115.016464	39.195502	40.50825162	56.3	57.7
142	ch3o CS,	-114.9392806	-0.45576068	-115.007645	58.778132	60.09088206	41.6	42.9

143	ch3ch2o 2A"	-154.2072694	-0.66709213	-154.307333	44.557140	46.23745957	60.0	61.7
144	ch3s 2-A'	-437.9204842	-0.55625492	-438.003922	151.077636	153.7819011	26.4	29.1
145	c2h5 staggered	-79.05500736	-0.40785412	-79.116185	150.965652	151.700792	30.0	30.8
146	(ch3)2ch Cs	-118.3224516	-0.62130394	-118.415647	138.337562	139.4402721	48.4	49.5
147	TERT-BUTYL RADICAL	-157.590309	-0.8365943	-157.715798	123.637320	125.1076001	72.2	73.6
148	NO2 RADICAL	-204.8522967	-0.8398341	-204.978272	207.404371	209.2947312	174.4	176.2

MAD	**75.1**	**77.6**
LD	**263.2**	**266.0**

Table S5.62b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 75% and a_C = 15%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.499145	0.000000	-0.499145
2	li	-7.476097	-0.014051	-7.478205
3	be	-14.650299	-0.048723	-14.657607
4	b	-24.632970	-0.071640	-24.643716
5	c	-37.819937	-0.097695	-37.834591
6	n	-54.557480	-0.127804	-54.576651
7	o	-75.025443	-0.182461	-75.052812
8	f	-99.677195	-0.242797	-99.713614
9	na	-162.196701	-0.163601	-162.221241
10	al	-242.291326	-0.209907	-242.322813
11	si	-289.297706	-0.238739	-289.333517
12	p	-341.186244	-0.266613	-341.226236
13	s	-398.028332	-0.305805	-398.074203
14	cl	-460.054503	-0.275950	-460.095896

Table S5.63a Mean Absolute Deviations from the G2/97 ΔH_f set with ROB2–PLYP/6-311+G(3df,2p) using a_X = 75% and a_C = 40%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)	Hf (298K) (kJ/mol)	Hf (SO) (298K) (kJ/mol)	Theory-Exp (kJ/mol)	Th-Exp (SO) (kJ/mol)
1	LITHIUM HYDRIDE,	-8.03773394	-0.04360905	-8.055178	151.736336	151.7363362	12.4	12.4
2	BERYLLIUM HYDRIDE	-15.2124359	-0.05152487	-15.233046	320.460518	320.4605179	-21.4	-21.4
3	DOUBLET CH	-38.39439846	-0.13541822	-38.448566	605.525882	605.8934523	9.3	9.7
4	CH2 3-B1	-39.05698469	-0.15412688	-39.118635	398.281146	398.6487163	6.2	6.6
5	Singlet methylene,	-39.03042513	-0.17176335	-39.099130	447.879393	448.2469633	17.8	18.1
6	Methyl radical,	-39.72420542	-0.19633702	-39.802740	158.109773	158.4773433	11.7	12.0
7	ch4 //b3lyp/6-31G*	-40.38504981	-0.23501237	-40.479055	-56.304773	-55.93720258	18.6	19.0
8	NH,TRIPLET, //b3lyp/6-31G*	-55.11738119	-0.17738539	-55.188335	368.525502	368.5255024	12.0	12.0
9	NH2,2-B-1, //b3lyp/6-31G*	-55.75236235	-0.22714167	-55.843219	203.254693	203.2546927	14.6	14.6
10	AMMONIA, //b3lyp/6-31G*	-56.41301717	-0.27740567	-56.523979	-21.278241	-21.27824142	24.7	24.7
11	OH RADICAL	-75.60120838	-0.24449309	-75.699006	49.490959	50.43613941	10.2	11.1
12	Water //b3lyp/6-31G*	-76.27151622	-0.30812625	-76.394767	-219.693024	-218.7478435	22.1	23.1
13	HYDROGEN FLUORIDE,	-100.2855916	-0.31988328	-100.413545	-261.034128	-259.4325734	11.3	12.9
14	SIH2 singlet	-290.3806039	-0.28998819	-290.496599	282.277677	284.0630172	9.5	11.3
15	SIH2 3B1	-290.3579918	-0.26926184	-290.465697	364.423376	366.208716	3.8	5.5
16	SIH3 c3v	-290.996251	-0.2956293	-291.114503	207.768218	209.5535581	7.4	9.1
17	SIH4 //b3lyp/6-31G*	-291.6366996	-0.32120271	-291.765181	48.141283	49.92662296	13.8	15.6
18	ph2 doublet	-342.2574525	-0.32821546	-342.388739	150.539852	150.5398524	12.0	12.0
19	PH3 c3v	-342.8821618	-0.35660488	-343.024804	30.778315	30.77831498	25.3	25.3
20	SH2 //b3lyp/6-31G*	-399.1245137	-0.37743316	-399.275487	-2.432179	-0.095483815	18.1	20.4
21	HCL //b3lyp/6-31G*	-460.5312355	-0.31759826	-460.658275	-85.845991	-82.32782135	6.6	10.1
22	DILITHIUM //b3lyp/6-31G*	-14.94728919	-0.05346308	-14.968674	233.676356	233.6763557	17.8	17.8
23	Lithium Fluoride,	-107.241678	-0.34567545	-107.379948	-331.507997	-329.9064416	3.6	5.2
24	ACETYLENE //b3lyp/6-31g*	-77.12106065	-0.38886515	-77.276607	243.840632	244.5757722	17.1	17.8
25	ETHYLENE //b3lyp/6-31g*	-78.36070009	-0.41091858	-78.525068	75.235999	75.97113856	22.9	23.7
26	ETHANE //b3lyp/6-31g*	-79.58165138	-0.44395879	-79.759235	-57.148713	-56.41357261	26.9	27.7
27	CYANO RADICAL,	-92.49029096	-0.41337458	-92.655641	473.330713	473.6982833	34.4	34.8
28	HYDROGEN CYANIDE	-93.1996429	-0.42981106	-93.371567	146.468623	146.8361927	14.7	15.0
29	CARBON MONOXIDE	-113.0863841	-0.44110106	-113.262824	-101.410259	-100.0975091	9.0	10.4
30	HCO BENT	-113.6081037	-0.46252935	-113.793115	50.872437	52.18518678	9.0	10.3
31	H2CO //b3lyp/6-31g*	-114.249071	-0.48186872	-114.441818	-94.106871	-92.79412061	14.7	16.0

32	METHANOL //b3lyp/6-31g*	-115.4529693	-0.51237577	-115.657920	-176.128705	-174.8159552	24.7	26.0
33	Nitrogen N2,	-109.2914489	-0.46160187	-109.476090	23.677362	23.67736227	23.7	23.7
34	H2NNH2 //b3lyp/6-31g*	-111.5916949	-0.52560017	-111.801935	134.896285	134.8962854	39.5	39.5
35	NO radical,	-129.6290037	-0.50216915	-129.829871	111.008699	111.9538786	20.6	21.6
36	O2 //b3lyp/6-31g*	-150.0266788	-0.56697514	-150.253469	15.813217	17.70357653	15.8	17.7
37	HYDROGEN PEROXIDE	-151.2405303	-0.59280982	-151.477654	-91.146147	-89.2557874	44.8	46.7
38	F2 //b3lyp/6-31g*	-199.184719	-0.62096427	-199.433105	41.845530	45.04864003	41.8	45.0
39	CO2 D*H	-188.209957	-0.74213717	-188.506812	-392.397111	-390.139181	0.9	3.2
40	na2 //b3lyp/6-31G*	-324.2037449	-0.35218776	-324.344620	147.982939	147.9829386	5.7	5.7
41	SI2 3-SGG	-578.4237773	-0.52920226	-578.635458	596.580582	600.1512618	11.2	14.8
42	P2 //b3lyp/6-31g*	-682.2112061	-0.66690296	-682.477967	172.560506	172.5605063	29.0	29.0
43	S2 //b3lyp/6-31g*	-795.8567652	-0.71764665	-796.143824	139.721069	144.3944594	11.3	15.9
44	CL2 //b3lyp/6-31g*	-919.8248701	-0.6131738	-920.070140	15.900572	22.93691151	15.9	22.9
45	Sodium Chloride	-622.113194	-0.48152354	-622.305803	-176.556124	-173.0379544	5.9	9.4
46	SIO //b3lyp/6-31g*	-364.36242	-0.57577938	-364.592732	-82.138947	-79.40842701	20.8	23.5
47	Carbon monosulfide,	-435.8627657	-0.5369406	-436.077542	300.231096	302.9353612	20.3	23.0
48	OS //b3lyp/6-31g*	-472.9621295	-0.64651152	-473.220734	19.607631	22.88950644	14.6	17.9
49	CLO 2-PI	-534.8924568	-0.56046813	-535.116644	132.944193	137.4075435	31.7	36.2
50	CLF 1-SG	-559.5310569	-0.61469078	-559.776933	-37.764838	-32.64511325	17.5	22.6
51	si2h6 //b3lyp/6-31g*	-582.1026467	-0.62386113	-582.352191	104.415180	107.9858598	24.5	28.1
52	Methyl chloride,	-499.7221874	-0.52688548	-499.932942	-69.048199	-65.16245919	13.0	16.8
53	H3C-SH METHANETHIOL	-438.3183544	-0.58921356	-438.554040	4.110169	6.814433798	27.1	29.8
54	HOCl //b3lyp/6-31g*	-535.5357795	-0.60542387	-535.777949	-49.962924	-45.49957413	24.5	29.0
55	SO2 //b3lyp/6-31G*	-548.0701065	-0.96364671	-548.455565	-252.490433	-248.2633785	44.6	48.8
56	BF3 PLANAR	-324.0608293	-1.01141408	-324.465395	-1147.103037	-1142.167097	-11.6	-6.6
57	bcl3 B3LYP	-1404.71115	-1.04426814	-1405.128857	-425.692757	-415.0069717	-22.8	-12.1
58	ALf3 B3LYP	-541.5491693	-1.14433189	-542.006902	-1193.417649	-1187.720314	15.8	21.5
59	alcl3 B3LYP	-1622.263064	-1.1454043	-1622.721226	-600.196435	-588.7492547	-15.7	-4.2
60	cf4 B3LYP	-436.8023118	-1.38071789	-437.354599	-936.466444	-929.6926539	-3.4	3.3
61	ccl4 B3LYP	-1877.704382	-1.44589618	-1878.282740	-90.344839	-75.90458893	5.5	19.9
62	O=C=S. Singlet	-511.0453021	-0.82990071	-511.377262	-137.658047	-134.0086017	0.8	4.5
63	CS2 B3LYP	-833.8767523	-0.92431604	-834.246479	120.901761	125.9427207	4.2	9.2
64	COF2 B3LYP	-312.4827285	-1.06195481	-312.907510	-604.141166	-599.6253059	19.7	24.2
65	sif4 B3LYP	-688.3430351	-1.48055619	-688.935258	-1578.646226	-1570.454666	36.4	44.6
66	sicl4, td	-2129.232565	-1.51173939	-2129.837260	-658.121664	-642.2636437	4.6	20.5
67	nno B3LYP	-184.2599718	-0.79147822	-184.576563	106.682389	107.6275689	24.7	25.6
68	clno B3LYP	-589.5338365	-0.85654659	-589.876455	90.541869	95.00521934	38.7	43.1

69	nf3 c3v	-353.4855991	-1.16732395	-353.952529	-91.503812	-86.69914658	40.7	45.5
70	pf3 c3v	-640.305604	-1.23193095	-640.798376	-921.159484	-916.3548191	37.4	42.2
71	ozone 1-a1	-224.9308532	-0.9449944	-225.308851	212.741986	215.5775258	70.1	72.9
72	f2o B3LYP	-274.1829394	-0.91186945	-274.547687	82.522372	86.67066167	57.8	62.0
73	CLF3, C2V	-758.7379181	-1.29397272	-759.255507	-112.268861	-103.9460256	46.7	55.0
74	CF2=CF2 D2H	-474.7224366	-1.56750507	-475.349439	-671.909856	-664.768496	-13.3	-6.2
75	cl2c=ccl2 B3LYP	-1915.699854	-1.63129302	-1916.352371	-19.813289	-5.005469121	-7.3	7.5
76	cf3cn B3LYP	-429.6953941	-1.50666688	-430.298061	-491.596327	-486.0565221	3.8	9.3
77	PROPYNE C3V	-116.3307484	-0.59927579	-116.570459	205.486441	206.5891515	20.6	21.7
78	ALLENE D2D	-116.3297442	-0.59366801	-116.567211	212.355779	213.4584887	22.0	23.1
79	CYCLOPROPENE C2V	-116.2907772	-0.60344168	-116.532154	305.336554	306.4392637	28.4	29.5
80	PROPENE CS	-117.5641446	-0.62334587	-117.813483	50.517762	51.62047217	30.4	31.5
81	CYCLOPROPANE D3H	-117.5509932	-0.63054704	-117.803212	79.965165	81.06787538	26.8	27.9
82	PROPANE C2V	-118.7802643	-0.65599369	-119.042662	-68.451862	-67.34915224	36.1	37.3
83	TRANS-1,3-BUTADIENE C2H	-155.5515115	-0.80467371	-155.873381	144.457824	145.9281036	34.4	35.9
84	Dimethyl acetylene	-155.5383723	-0.81016994	-155.862440	173.334984	174.805264	27.7	29.2
85	Methylene cyclopropane.	-155.5188863	-0.81230692	-155.843809	220.846631	222.3169106	20.4	21.9
86	Bicyclo[1.1.0]butane. C2v	-155.5035175	-0.82440574	-155.833280	250.423523	251.8938035	33.3	34.7
87	CYCLOBUTENE b3lyp	-155.5291945	-0.81410061	-155.854835	194.261773	195.7320533	37.8	39.3
88	CYCLOBUTANE b3lyp/6-31G*	-156.7507819	-0.84333779	-157.088117	65.891536	67.36181563	37.4	38.9
89	Isobutene. Single	-156.7674691	-0.8383105	-157.102793	22.570224	24.04050378	39.3	40.8
90	Trans butane	-157.9787557	-0.86851671	-158.326162	-79.956619	-78.48633877	45.6	47.0
91	isobutane B3LYP/6-31G*	-157.9797717	-0.87146756	-158.328359	-87.017586	-85.54730596	47.3	48.8
92	Spiropentane. D2d	-194.7122551	-1.03219162	-195.125132	216.994991	218.8328413	31.6	33.5
93	Benzene B3LYP	-231.6102463	-1.18336041	-232.083590	102.913229	105.118649	20.5	22.7
94	DIFLUOROMETHANE C2V	-238.5755419	-0.80672515	-238.898232	-443.143482	-439.5728023	7.5	11.0
95	HCF3 TRI-FLUOROMETHANE	-337.690522	-1.09455152	-338.128343	-694.070600	-688.8983648	3.0	8.2
96	CH2CL2 C2V	-959.0560286	-0.82667688	-959.386699	-84.133614	-76.72970381	11.3	18.7
97	chcl3 B3LYP/6-31G*	-1418.384165	-1.13323181	-1418.837458	-93.465198	-82.54311791	9.9	20.8
98	METHYLAMINE b3lyp	-95.59821761	-0.4846689	-95.792085	8.836155	9.203725005	31.8	32.2
99	Acetonitrile. CH3-CN.	-132.4155751	-0.63821176	-132.670860	94.331964	95.0671042	19.0	19.8
100	NITRO METHANE	-244.4655746	-1.05499326	-244.887572	-33.294377	-31.03644743	41.2	43.4
101	Methyl-nitrite. CH3-O-N=O.	-244.4626619	-1.04281304	-244.879787	-16.583653	-14.32572279	49.9	52.2
102	Methylsilane. CH3-SiH3.	-330.8499554	-0.53500184	-331.063956	-0.245957	1.906953285	29.0	31.2
103	Formic Acid.	-189.3703921	-0.76575274	-189.676693	-359.553578	-357.2956479	19.1	21.4
104	Methyl formate.	-228.556281	-0.97463898	-228.946137	-334.752548	-332.1270476	20.9	23.5
105	acetamide ch3cohn2	-208.7221764	-0.94695716	-209.100959	-206.020935	-204.3406152	32.5	34.1

106	Aziridine. (cyclic	-133.561991	-0.67215718	-133.830854	158.193758	158.9288982	31.8	32.6
107	Cyanogen. NCCN.	-185.213486	-0.84862749	-185.552937	324.222637	324.9577766	17.5	18.3
108	DIMETHYLAMINE b3lyp	-134.7879662	-0.6955347	-135.066180	20.734418	21.4695576	39.1	39.9
109	TRANS ETHYLAMINE	-134.7994986	-0.69670008	-135.078179	-9.830608	-9.095468453	37.4	38.2
110	KETENE B3LYP	-152.2487761	-0.66791115	-152.515941	-38.627591	-36.94727061	8.7	10.3
111	OXIRANE B3LYP	-153.4166838	-0.70060317	-153.696925	-27.715647	-26.03532663	25.0	26.7
112	Acetaldehyde B3LYP	-153.4628603	-0.69230737	-153.739783	-143.358682	-141.6783622	22.7	24.4
113	Glyoxal, O=CH-CH=O.	-227.3300142	-0.94245569	-227.706997	-192.819570	-190.1940703	19.3	21.9
114	ETHANOL TRANS	-154.6567567	-0.72373873	-154.946252	-200.613739	-198.9334194	34.5	36.2
115	DIMETHYL ETHER,	-154.6399537	-0.72055377	-154.928175	-153.995430	-152.3151097	30.1	31.8
116	Thiooxirane. (cyclic	-476.3007025	-0.78366281	-476.614168	104.730306	107.8021407	22.7	25.8
117	Dimethylsulfoxide. (CH3)2SO.	-552.5622961	-1.10267789	-553.003367	-96.880563	-92.86354827	54.6	58.6
118	Thioethanol. CH3-CH2-SH.	-477.5174317	-0.80244031	-477.838408	-9.278100	-6.206265424	37.2	40.2
119	ch3sch3 B3LYP	-477.5150247	-0.80394672	-477.836603	-2.014849	1.056986039	35.2	38.3
120	Vinyl fluoride,	-177.4565179	-0.70020016	-177.736598	-125.554004	-123.2173088	13.4	15.7
121	Ethyl chloride.	-538.9243793	-0.73948412	-539.220173	-90.119616	-85.86630609	22.0	26.3
122	Vinyl chloride,	-537.7025189	-0.71071655	-537.986806	39.109228	43.36253833	16.1	20.4
123	h2c=chcn B3LYP	-170.3938708	-0.82005688	-170.721894	211.419557	212.5222674	30.7	31.8
124	ACETONE B3LYP	-192.673188	-0.90437104	-193.034936	-185.903596	-183.8557062	31.2	33.3
125	CH3COOH ACETIC	-228.5823978	-0.97518977	-228.972474	-404.354831	-401.7293309	28.3	30.9
126	CH3CFO HCCO	-252.5885092	-0.98446329	-252.982295	-423.798258	-420.5163825	18.5	21.7
127	ch3c(o)cl hcco	-612.8198732	-0.99814241	-613.219130	-224.433692	-219.2352021	18.2	23.4
128	ch3ch2ch2cl B3LYP	-578.1230049	-0.95223458	-578.503899	-102.121002	-97.50012169	29.7	34.3
129	Isopropyl alcohol,	-193.8601805	-0.93823253	-194.235474	-228.828942	-226.7810523	44.0	46.0
130	Methyl ethyl	-193.8436577	-0.93247796	-194.216649	-178.856204	-176.8083145	37.5	39.5
131	Trimethyl Amine.	-173.9800141	-0.91073688	-174.344309	20.736876	21.83958575	44.6	45.7
132	FURAN B3LYP	-229.4535364	-1.07502556	-229.883547	-12.463026	-10.04756561	22.3	24.7
133	Thiophene b3lyp	-552.3266895	-1.16390898	-552.792253	140.047150	143.854125	25.0	28.8
134	PYROLE PLANAR	-209.6131461	-1.0501804	-210.033218	131.441446	132.9117258	23.1	24.5
135	C2v Pyridine	-247.6291559	-1.22376791	-248.118663	159.902278	161.7401277	19.3	21.2
136	H2 B3LYP/6-31G*	-1.1552683	-0.03258894	-1.168304	12.499563	12.49956282	12.5	12.5
137	SH b3lyp/6-31G*	-398.4904041	-0.34197187	-398.627193	152.419056	154.7557508	9.3	11.7
138	CCH B3LYP	-76.41126965	-0.35301879	-76.552477	590.034311	590.7694509	24.8	25.5
139	C2H3 CS,2-A'	-77.68863393	-0.375754	-77.838936	316.098419	316.8335589	16.5	17.3
140	ch3co hcco	-152.8227926	-0.67041433	-153.090958	5.618836	7.29915638	15.7	17.3
141	H2COH C1	-114.8035679	-0.48127564	-114.996078	2.410909	3.72365893	19.6	20.9
142	ch3o CS,	-114.7994475	-0.45548208	-114.981640	36.744163	38.05691285	19.6	20.9

143	ch3ch2o 2A"	-154.0028566	-0.66662287	-154.269506	12.902712	14.58303218	28.4	30.1
144	ch3s 2-A'	-437.6891434	-0.556097	-437.911582	139.794014	142.4982792	15.1	17.8
145	c2h5 staggered	-78.92568346	-0.40769692	-79.088762	141.641845	142.3769851	20.7	21.5
146	(ch3)2ch Cs	-118.1283683	-0.62091796	-118.376736	118.514872	119.6175817	28.6	29.7
147	TERT-BUTYL RADICAL	-157.3314004	-0.83596504	-157.665786	92.296251	93.76653135	40.8	42.3
148	NO2 RADICAL	-204.6443941	-0.83932462	-204.980124	60.645682	62.53604187	27.6	29.5

MAD	**23.0**	**25.1**
LD	**70.1**	**72.9**

Table S5.63b Atomic species with ROB2–PLYP/6-311+G(3df,2p) using a_X = 75% and a_C = 40%.

	Description	DFT Energy (H)	E2 (H)	B2PLYP E (H)
1	h	-0.499145	0.000000	-0.499145
2	li	-7.462686	-0.014035	-7.468300
3	be	-14.626579	-0.048625	-14.646029
4	b	-24.601350	-0.071743	-24.630047
5	c	-37.779965	-0.097849	-37.819104
6	n	-54.509266	-0.127896	-54.560424
7	o	-74.960816	-0.182716	-75.033902
8	f	-99.596683	-0.243029	-99.693894
9	na	-162.094442	-0.163546	-162.159860
10	al	-242.167430	-0.209945	-242.251408
11	si	-289.164830	-0.238780	-289.260343
12	p	-341.044497	-0.266478	-341.151088
13	s	-397.870697	-0.305889	-397.993052
14	cl	-459.881514	-0.276045	-459.991932