Supporting Information

Examining the Ground and First Excited States of Methyl Peroxy Radical with High-Level Coupled-Cluster Theory

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1 Data for Stationary Points

1.1 CH₃O₂ ($\tilde{X}^2A''$)

1.1.1 CCSD(T)/ANO2 Optimization and Frequencies

Software: CFour 1.0
Theory: CCSD(T)/ANO2
Reference: UHF
CC Convergence: 10^{-10}
SCF Convergence: 10^{-10}
Charge: 0
Multiplicity: 2
Frozen Core: ON
Geometry Convergence: 10^{-9} H/bohr
Equilibrium Geometry (Å):

H	-1.9715478549	0.4931916402	0.0000000000
C	-1.1662002125	-0.2372485708	-0.0000000000
O	0.0535785297	0.5312531795	0.0000000000
O	1.0961886549	-0.2767437253	-0.0000000000
H	-1.1951727886	-0.8537816537	0.8954106256
H	-1.1951727886	-0.8537816537	-0.8954106256

Harmonic Frequencies (cm⁻¹):

150.4895
494.4092
947.4901
1145.7432
1167.7365
1218.7031
1450.3407
1483.9004
1496.9575
3063.8861
3165.6327
3174.9126

1.1.2 CCSD(T)/ANO1 Optimization and Frequencies

Software: CFour 1.0
Theory: CCSD(T)/ANO1
Reference: UHF
CC Convergence: 10^{-10}
SCF Convergence: 10^{-10}
Charge: 0
Multiplicity: 2
Frozen Core: ON
Geometry Convergence: 10^{-9} H/bohr

Equilibrium Geometry (Å):

H	-1.9757680011	0.4896441682	-0.0000000000
C	-1.1671412220	-0.2389183419	-0.0000000000
O	0.0519764191	0.5340179401	-0.0000000000
O	1.0990018882	-0.2777022346	0.0000000000
H	-1.1970712120	-0.8564002979	0.8960315357
H	-1.1970712120	-0.8564002979	-0.8960315357

Harmonic Frequencies (cm^{-1}):

152.7290
493.2919
945.4622
1143.7668
1157.5911
1212.2737
1446.9509
1480.1304
1493.3824
3061.2660
3162.3232
3170.5454

1.1.3 BCCD(T)/ANO1 Optimization and Frequencies

Software: Psi4
Theory: BCCD(T)/ANO1
Reference: Brueckner
CC Convergence: 10^{-9}
SCF Convergence: 10^{-11}
Brueckner Convergence: 10^{-8}
Charge: 0
Multiplicity: 2
Frozen Core: ON
Geometry Convergence: 10^{-6} H/bohr
Equilibrium Geometry (Å):
H -0.958966682798 1.795791386988 0.000000000000
C -0.958674160368 0.707297498933 0.000000000000
O 0.431632483290 0.319472808828 0.000000000000
O 0.529153839342 -1.003085199354 0.000000000000
H -1.437320245925 0.315981593870 0.896048100959
H -1.437320245925 0.315981593870 -0.896048100959
Harmonic Frequencies (cm^{-1}):
153.439
492.694
945.041
1143.163
1150.704
1210.868
1446.300
1479.723
1492.921
3060.747
3162.103
3170.082

1.1.4 Anharmonicity Constants and ZPVE [CCSD(T)/ANO1]

x_1,1 =	-9.66884	x_7,7 =	-8.32992
x_2,2 =	0.19028	x_8,8 =	-6.86582
x_3,3 =	-5.83896	x_9,9 =	-8.08746
x_4,4 =	-2.03363	x_10,10 =	-18.08354
x_5,5 =	-6.89569	x_11,11 =	-33.00780
x_6,6 =	-1.86821	x_12,12 =	-34.25648
x_1,2 =	11.88161	x_4,8 =	-7.67892
x_1,3 =	-2.26047	x_4,9 =	-7.14413
x_1,4 =	1.40740	x_4,10 =	-4.69150
x_1,5 =	-1.42359	x_4,11 =	-5.64316
x_1,6 =	-5.97060	x_4,12 =	-4.63702
x_1,7 =	-1.54107	x_5,6 =	-9.31200
x_1,8 =	-1.31895	x_5,7 =	-4.72378
x_1,9 =	-1.91022	x_5,8 =	-1.48031
x_1,10 =	-0.21871	x_5,9 =	-1.26340
x_1,11 =	0.29112	x_5,10 =	-0.82784
x_1,12 =	-1.84458	x_5,11 =	-0.38546
x_2,3 =	-7.55780	x_5,12 =	-1.40267
x_2,4 =	0.04199	x_6,7 =	-5.13684
x_2,5 =	-4.76345	x_6,8 =	-4.40995
x_2,6 =	-1.79602	x_6,9 =	-4.59645
x_2,7 =	1.39187	x_6,10 =	-3.83133
x_2,8 =	-1.42306	x_6,11 =	-4.63960
x_2,9 =	0.09219	x_6,12 =	-5.34873
x_2,10 =	-0.06486	x_7,8 =	-2.56299
x_2,11 =	0.39065	x_7,9 =	-2.88078
x_2,12 =	-0.61208	x_7,10 =	13.96527
x_3,4 =	-7.52320	x_7,11 =	-8.86739
x_3,5 =	-9.42528	x_7,12 =	-12.02197
x_3,6 =	-6.89756	x_8,9 =	-4.35688
x_3,7 =	-4.86275	x_8,10 =	-2.42817
x_3,8 =	-1.90266	x_8,11 =	-11.33774
x_3,9 =	-2.59308	x_8,12 =	-19.80296
x_3,10 =	0.71644	x_9,10 =	4.52126
x_3,11 =	3.11008	x_9,11 =	-20.47045
x_3,12 =	0.74961	x_9,12 =	-8.81011
x_4,5 =	-2.82357	x_10,11 =	-81.08893
x_4,6 =	-3.32097	x_10,12 =	-68.91635
x_4,7 =	-5.74170	x_11,12 =	-35.74187

Anharmonic ZPVE: 9324.31320 cm-1 26.65956 kcal/mol

Quadratic = 9459.85649 cm-1
Cubic = -23.01921 cm-1
Quartic = -202.55957 cm-1
Z kinetic = 84.82734 cm-1

1.2 CH₃O₂ ($\tilde{A}^2A'$)

1.2.1 CCSD(T)/ANO2 Optimization and Frequencies

Software: CFour 1.0
Theory: CCSD(T)/ANO2
Reference: UHF
CC Convergence: 10^{-10}
SCF Convergence: 10^{-10}
Charge: 0
Multiplicity: 2
Frozen Core: ON
Geometry Convergence: 10^{-9} H/bohr
Equilibrium Geometry (Å):

H	-1.9768010768	0.4169999749	-0.0000000000
C	-1.1362995072	-0.2719180839	-0.0000000000
O	0.0152154969	0.5775828222	-0.0000000000
O	1.1069259259	-0.2873997041	0.0000000000
H	-1.1513370365	-0.8923673166	0.8967847719
H	-1.1513370365	-0.8923673166	-0.8967847719

Harmonic Frequencies (cm⁻¹):

248.8533
384.6010
919.3981
1040.0474
1177.8649
1185.6792
1454.3644
1478.5819
1519.5214
3041.2087
3122.3878
3167.9767

1.2.2 CCSD(T)/ANO1 Optimization and Frequencies

Software: CFour 1.0
Theory: CCSD(T)/ANO1
Reference: UHF
CC Convergence: 10^{-10}
SCF Convergence: 10^{-10}
Charge: 0
Multiplicity: 2
Frozen Core: ON
Geometry Convergence: 10^{-9} H/bohr
Equilibrium Geometry (Å):

H	-1.9817095451	0.4112519670	0.0000000000
C	-1.1370824990	-0.2743519923	-0.0000000000
O	0.0118204545	0.5805207508	0.0000000000
O	1.1113400949	-0.2876661607	0.0000000000
H	-1.1523084472	-0.8962023118	0.8972694559
H	-1.1523084472	-0.8962023118	-0.8972694559

Harmonic Frequencies (cm^{-1}):

248.7078
385.0024
909.5586
1038.9391
1176.3538
1183.3745
1451.2102
1474.2561
1516.9632
3037.9148
3117.7529
3164.2166

1.2.3 BCCD(T)/ANO1 Optimization and Frequencies

Software: Psi4
Theory: BCCD(T)/ANO1
Reference: Brueckner
CC Convergence: 10^{-9}
SCF Convergence: 10^{-11}
Brueckner Convergence: 10^{-8}
Charge: 0
Multiplicity: 2
Frozen Core: ON
Geometry Convergence: 10^{-6} H/bohr
Equilibrium Geometry (Å):
H -1.9819103880 0.4113814263 0.0000000000
C -1.1373832421 -0.2744211720 0.0000000000
O 0.0117287415 0.5804260369 0.0000000000
O 1.1117017930 -0.2875188475 0.0000000000
H -1.1525600178 -0.8962725981 0.8973184818
H -1.1525600178 -0.8962725981 -0.8973184818
Harmonic Frequencies (cm^{-1}):
248.695
384.131
902.484
1036.404
1176.004
1182.509
1450.837
1473.739
1516.666
3037.326
3117.368
3163.808

1.2.4 Anharmonicity Constants and ZPVE [CCSD(T)/ANO1]

x_1,1 =	-6.52892	x_7,7 =	-8.78697
x_2,2 =	0.32996	x_8,8 =	-6.18545
x_3,3 =	1.25366	x_9,9 =	-1.71235*
x_4,4 =	-7.66389	x_10,10 =	-21.06183
x_5,5 =	-2.00752	x_11,11 =	-34.11702
x_6,6 =	-1.88322	x_12,12 =	-44.31269
x_1,2 =	0.14619	x_4,8 =	-2.18160
x_1,3 =	-1.12919	x_4,9 =	-3.36734
x_1,4 =	-1.02279	x_4,10 =	2.19206
x_1,5 =	-3.06804	x_4,11 =	4.25092
x_1,6 =	-0.96704	x_4,12 =	1.12998
x_1,7 =	1.29164	x_5,6 =	-0.16358
x_1,8 =	2.31689	x_5,7 =	-4.51672
x_1,9 =	-4.48388	x_5,8 =	-6.60349
x_1,10 =	-0.37090	x_5,9 =	-11.23674
x_1,11 =	1.71516	x_5,10 =	-5.79357
x_1,12 =	-2.40973	x_5,11 =	-4.01065
x_2,3 =	-3.23193	x_5,12 =	-2.77230
x_2,4 =	-3.30417	x_6,7 =	-8.16560
x_2,5 =	1.21225	x_6,8 =	-5.25823
x_2,6 =	-0.79993	x_6,9 =	-4.84766
x_2,7 =	-0.21917	x_6,10 =	-2.65264
x_2,8 =	-1.57263	x_6,11 =	-3.68611
x_2,9 =	-1.43488	x_6,12 =	-8.06699
x_2,10 =	-0.06885	x_7,8 =	-2.09348
x_2,11 =	0.20747	x_7,9 =	-3.26014
x_2,12 =	-0.81378	x_7,10 =	17.10550
x_3,4 =	-0.31722	x_7,11 =	-8.61476
x_3,5 =	-0.79005	x_7,12 =	-13.73762
x_3,6 =	-0.55075	x_8,9 =	-5.01065
x_3,7 =	-1.35526	x_8,10 =	-3.60288
x_3,8 =	-0.42799	x_8,11 =	-10.23797
x_3,9 =	-0.84182	x_8,12 =	-19.72710
x_3,10 =	-0.02144	x_9,10 =	-22.69884*
x_3,11 =	0.29465	x_9,11 =	-18.36892
x_3,12 =	-1.32001	x_9,12 =	-5.33467
x_4,5 =	-9.58357	x_10,11 =	-99.82969
x_4,6 =	-8.30829	x_10,12 =	-44.57930
x_4,7 =	-7.20543	x_11,12 =	-19.16732

*Near-zero denominators removed

Anharmonic ZPVE: 9220.89658 cm⁻¹ 26.36387 kcal/mol

Quadratic = 9352.12496 cm⁻¹
Cubic = -20.51158 cm⁻¹
Quartic = -111.82760 cm⁻¹
Z kinetic = -1.55898 cm⁻¹