Molecular Structure and Internal Rotation of CF_3 Group of Methyl Trifluoroacetate: Gas Electron Diffraction, Microwave Spectroscopy, and Quantum Chemical Calculation Studies

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ASSOCIATED CONTENT

* Supporting Information

Table S1. Total Intensities (I_T) and the Backgrounds (I_B) of Methyl Trifluoroacetate[a]

s / Å^{-1}	I_T	I_B	s / Å^{-1}	I_T	I_B	s / Å^{-1}	I_T	I_B
4.4590	0.8600	1.0288	14.6860	1.0242	1.0052	24.5720	1.0127	1.0012
4.6620	0.8876	1.0293	14.8840	1.0264	1.0045	24.7610	1.0099	1.0018
4.8640	0.9325	1.0321	15.0820	1.0249	1.0039	24.9500	1.0079	1.0024
5.0660	0.9963	1.0357	15.2800	1.0217	1.0027	25.1390	1.0054	1.0029
5.2690	1.0740	1.0400	15.4770	1.0166	1.0015	25.3270	1.0033	1.0031
5.4710	1.1470	1.0440	15.6740	1.0121	0.9999	25.5150	1.0028	1.0036
5.6730	1.2095	1.0474	15.8710	1.0075	0.9981	25.7030	1.0021	1.0046
5.8750	1.2461	1.0500	16.0680	1.0051	0.9994	25.8910	1.0027	1.0055
6.0770	1.2512	1.0519	16.2650	1.0033	0.9988	26.0790	1.0033	1.0066
6.2790	1.2324	1.0527	16.4620	1.0010	0.9983	26.2660	1.0041	1.0075
6.4810	1.1912	1.0526	16.6580	0.9981	0.9978	26.4530	1.0051	1.0084
6.6830	1.1359	1.0520	16.8550	0.9942	0.9973	26.6400	1.0066	1.0093
6.8850	1.0838	1.0505	17.0510	0.9900	0.9969	26.8270	1.0082	1.0102
7.0860	1.0332	1.0486	17.2470	0.9857	0.9964	27.0130	1.0095	1.0112
7.2880	0.9906	1.0464	17.4430	0.9827	0.9961	27.1990	1.0106	1.0120
7.4900	0.9600	1.0439	17.6390	0.9804	0.9957	27.3850	1.0112	1.0129
7.6910	0.9438	1.0411	17.8350	0.9798	0.9954	27.5710	1.0106	1.0138
7.8920	0.9390	1.0383	18.0300	0.9818	0.9952	27.7570	1.0103	1.0148
8.0940	0.9412	1.0356	18.2250	0.9846	0.9949	27.9420	1.0110	1.0158
8.2950	0.9556	1.0331	18.4210	0.9899	0.9947	28.1270	1.0123	1.0169
8.4960	0.9694	1.0308	18.6160	0.9954	0.9946	28.3120	1.0139	1.0179
8.6980	0.9891	1.0288	18.8100	0.9991	0.9943	28.4970	1.0165	1.0190
8.8990	1.0075	1.0270	19.0050	1.0014	0.9942	28.6810	1.0197	1.0202
9.1000	1.0301	1.0254	19.2000	1.0011	0.9941	28.8660	1.0236	1.0214
9.3000	1.0477	1.0240	19.3940	0.9997	0.9941	29.0500	1.0274	1.0226
9.5010	1.0581	1.0229	19.5880	0.9979	0.9941	29.2330	1.0308	1.0238
9.7020	1.0590	1.0220	19.7820	0.9965	0.9941	29.4170	1.0328	1.0250
9.9030	1.0518	1.0212	19.9760	0.9963	0.9941	29.6000	1.0349	1.0262
10.1030	1.0379	1.0204	20.1700	0.9975	0.9940	29.7830	1.0362	1.0275
10.3040	1.0267	1.0198	20.3630	0.9981	0.9941	29.9660	1.0359	1.0289
10.5040	1.0220	1.0194	20.5560	1.0002	0.9941	30.1480	1.0351	1.0302
10.7040	1.0243	1.0188	20.7490	1.0004	0.9943	30.3310	1.0342	1.0317
10.9040	1.0316	1.0182	20.9420	1.0017	0.9944	30.5130	1.0332	1.0331
11.1040	1.0394	1.0175	21.1350	1.0007	0.9945	30.6950	1.0326	1.0347
11.3040	1.0455	1.0168	21.3280	1.0001	0.9947	30.8760	1.0324	1.0365
11.5040	1.0464	1.0161	21.5200	0.9994	0.9948	31.0580	1.0334	1.0383
11.7040	1.0432	1.0153	21.7120	0.9971	0.9951	31.2390	1.0335	1.0403
11.9040	1.0348	1.0144	21.9040	0.9941	0.9953	31.4200	1.0356	1.0423
12.1030	1.0245	1.0135	22.0960	0.9904	0.9954	31.6000	1.0374	1.0447
12.3030	1.0113	1.0125	22.2880	0.9867	0.9957	31.7810	1.0402	1.0469
12.5020	0.9980	1.0116	22.4790	0.9833	0.9961	31.9610	1.0445	1.0493
12.7010	0.9849	1.0106	22.6710	0.9812	0.9964	32.1410	1.0484	1.0517
12.9000	0.9752	1.0098	22.8620	0.9812	0.9967	32.3200	1.0519	1.0541
13.0990	0.9698	1.0090	23.0520	0.9842	0.9971	32.4990	1.0564	1.0564
13.2980	0.9697	1.0083	23.2430	0.9879	0.9976	32.6790	1.0599	1.0588
13.4970	0.9752	1.0077	23.4340	0.9938	0.9979	32.8570	1.0628	1.0610
13.6950	0.9835	1.0072	23.6240	0.9997	0.9983	33.0360	1.0659	1.0632
13.8940	0.9939	1.0067	23.8140	1.0051	0.9989	33.2140	1.0679	1.0652
14.0920	1.0037	1.0063	24.0040	1.0103	0.9993	33.3930	1.0698	1.0673
14.2900	1.0131	1.0059	24.1930	1.0126	0.9999	33.5700	1.0724	1.0696
14.4880	1.0196	1.0055	24.3830	1.0134	1.0005	33.7480	1.0747	1.0722

[a] Scattering parameter s is defined as $s = (4\pi/\lambda)\sin(\theta/2)$.

Table S2. Observed Rotational Transitions Frequencies with Residuals (MHz) of Methyl Trifluoroacetate in the Ground Vibrational State for Normal Species

Transition						Obs. Freq.		Obs.-Calc.	Transition						Obs. Freq.	Obs.-Calc.
J'	K_{-1}'	K_{+1}'	J	K_{-1}	K_{+1}				J'	K_{-1}'	K_{+1}'	J	K_{-1}	K_{+1}		
6	1	6	5	1	5	16468.95	a	-0.02	11	10	2	10	10	1	31436.6	0.20
6	0	6	5	0	5	16739.86	a	0.27	11	9	3	10	9	2	31443.4	0.38
6	2	4	5	2	3	17445.38	a	-0.36	11	9	2	10	9	1	31443.4	0.38
6	1	5	5	1	4	17575.11	a	0.07	11	8	4	10	8	3	31452.6	0.32
7	1	7	6	1	6	19180.55	a	-0.26	11	8	3	10	8	2	31452.6	0.32
7	0	7	6	0	6	19411.71	a	0.18	11	7	5	10	7	4	31465.6	-0.26
7	2	6	6	2	5	19879.40	a	0.02	11	7	4	10	7	3	31465.6	-0.26
7	3	4	6	3	3	20106.69	a	-0.11	11	6	6	10	6	5	31486.6	-0.44
8	1	8	7	1	7	21882.45	a	0.00	11	6	5	10	6	4	31487.3	0.20
8	0	8	7	0	7	22064.92	a	0.12	11	3	9	10	3	8	31502.0	0.12
8	2	7	7	2	6	22679.80	a	0.03	11	1	10	10	1	9	31520.2	-0.25
8	7	2	7	7	1	22864.63	a	-0.38	11	5	7	10	5	6	31521.7	-0.34
8	7	1	7	7	0	22864.63	a	-0.38	11	5	6	10	5	5	31524.4	-0.11
8	6	3	7	6	2	22873.16	a	0.01	11	4	8	10	4	7	31568.7	0.55
8	6	2	7	6	1	22873.16	a	0.01	11	4	7	10	4	6	31621.4	0.01
8	5	4	7	5	3	22886.95	a	0.09	12	1	11	11	1	10	34186.6	0.07
8	5	3	7	5	2	22886.95	a	-0.02	12	11	2	11	11	1	34294.0	0.50
8	3	5	7	3	4	23035.02	a	-0.14	12	11	1	11	11	0	34294.0	0.50
8	1	7	7	1	6	23276.92	a	0.45	12	10	2	11	10	1	34300.6	0.75
8	2	6	7	2	5	23436.76	a	0.08	12	10	3	11	10	2	34300.6	0.75
9	1	9	8	1	8	24575.05	a	0.00	12	8	5	11	8	4	34319.8	-0.63
9	0	9	8	0	8	24710.66	a	0.05	12	8	4	11	8	3	34319.8	-0.63
9	2	8	8	2	7	25465.29	a	-0.19	12	7	6	11	7	5	34338.6	0.52
9	7	3	8	7	2	25729.20	a	-0.39	12	7	5	11	7	4	34338.6	0.52
9	7	2	8	7	1	25729.20	a	-0.39	12	3	10	11	3	9	34342.3	-0.80
9	6	4	8	6	3	25740.71	a	-0.46	12	6	7	11	6	6	34364.9	-0.71
9	6	3	8	6	2	25740.71	a	-0.47	12	6	6	11	6	5	34364.9	-0.89
9	5	5	8	5	4	25760.45	a	-0.19	12	5	8	11	5	7	34410.3	0.01
9	5	4	8	5	3	25760.45	a	-0.55	12	4	9	11	4	8	34459.5	-0.04
9	3	6	8	3	5	25992.06	a	0.10	12	3	9	11	3	8	35031.7	0.56
9	1	8	8	1	7	26069.54	a	0.25	12	2	10	11	2	9	35215.8	0.31
9	2	7	8	2	6	26422.58	a	0.08	13	1	13	12	1	12	35284.8	0.18
10	1	10	9	1	9	27259.70	a	-0.40	13	0	13	12	0	12	35312.9	-0.16
10	0	10	9	0	9	27355.96	a	-0.23	13	1	12	12	1	11	36827.1	-0.04
10	7	3	9	7	2	28596.24	a	-0.21	13	11	3	12	11	2	37156.3	-0.40
10	7	4	9	7	3	28596.24	a	-0.21	13	11	2	12	11	1	37156.3	-0.40
10	6	4	9	6	3	28612.51	a	0.14	13	9	5	12	9	4	37175.2	-0.44
10	6	5	9	6	4	28612.51	a	0.16	13	9	4	12	9	3	37175.2	-0.44
10	5	6	9	5	5	28639.82	a	0.91	13	7	7	12	7	6	37213.5	0.12
10	5	5	9	5	4	28639.82	a	-0.08	13	7	6	12	7	5	37213.5	0.11
10	2	9	9	2	8	28236.1		0.40	13	6	8	12	6	7	37248.3	-0.12
10	4	7	9	4	6	28678.9		0.31	13	6	7	12	6	6	37248.3	-0.57
10	2	8	9	2	7	29386.0		0.01	13	4	10	12	4	9	37350.9	0.29
11	2	10	10	2	9	30990.4		0.21	14	1	14	13	1	13	37954.0	0.69
11	10	1	10	10	0	31436.6		0.20	14	3	12	13	3	11	39980.6	-0.56

a. Taken from the literature (G. I. L. Jones, T. D. Summers, N. L. Owen, *J. Chem.Soc., Faraday Trans.* 2 1974, **70**, 101.)

Table S3. Structural Parameters, Rotational Constants, Dipole Moments, Energies and Populations for the *anti* and *syn* Conformers of Methyl Trifluoroacetate Obtained by the ab initio and DFT Calculations [a]

	anti			*syn*		
Levels of theory	MP2(fc)/6-311++G(d,p)	B3LYP/6-311++G(d,p)	MP2(fc)/cc-pVTZ	MP2(fc)/6-311++G(d,p)	B3LYP/6-311++G(d,p)	MP2(fc)/cc-pVTZ
Bond lengths/Å						
C1O2	1.3302	1.3272	1.3291	1.3373	1.3339	1.3349
C1O7	1.2057	1.1976	1.2042	1.2028	1.1943	1.2012
C1C8	1.5420	1.5529	1.5386	1.5521	1.5628	1.5488
O2C3	1.4420	1.4471	1.4393	1.4446	1.4494	1.4397
C3H4	1.0871	1.0864	1.0823	1.0876	1.0868	1.0828
C3H5	1.0907	1.0900	1.0859	1.0891	1.0890	1.0844
C3H6	1.0907	1.0900	1.0859	1.0891	1.0890	1.0844
C8F9	1.3402	1.3459	1.3358	1.3459	1.3523	1.3415
C8F10	1.3402	1.3459	1.3358	1.3459	1.3523	1.3415
C8F11	1.3287	1.3330	1.3245	1.3226	1.3266	1.3198
Bond angles/°						
O2C1O7	127.19	127.30	126.97	121.99	122.21	121.85
O2C1C8	109.13	109.51	109.28	118.14	118.13	118.27
C1O2C3	114.22	116.15	113.75	123.51	125.00	122.97
O7C1C8	123.68	123.19	123.75	119.87	119.66	119.88
C1C8F9	110.50	110.73	110.44	110.88	110.70	111.10
C1C8F10	110.50	110.73	110.44	110.88	111.07	111.10
C1C8F11	110.57	110.52	110.41	110.66	111.07	110.20
O2C3H4	105.15	105.16	105.38	104.10	104.30	104.46
O2C3H5	109.95	109.96	110.03	111.05	110.86	111.08
O2C3H6	109.95	109.96	110.03	111.05	110.86	111.08
H4C3H5	111.00	110.95	110.96	109.81	109.96	109.74
H4C3H6	111.00	110.95	110.96	109.81	109.96	109.74
H5C3H6	109.70	109.78	109.42	110.81	110.74	110.57
F9C8F10	108.18	108.07	108.21	107.85	107.65	107.96
F9C8F11	108.50	108.35	108.63	108.23	108.11	108.19
F10C8F11	108.50	108.35	108.63	108.23	108.11	108.19
Dihedral angles/°						
C3O2C1O7	0.00	0.00	0.00	180.00	180.00	180.00
C3O2C1O8	180.00	180.00	180.00	0.00	0.00	0.00
O2C1C8F9	-59.85	-59.93	-59.83	-59.89	180.00	-60.10
O2C1C8F10	59.85	59.93	59.83	59.89	59.89	60.10
O2C1C8F11	180.00	180.00	180.00	180.00	-59.89	180.00
C1O2C3H4	180.00	180.00	180.00	180.00	180.00	180.00
C1O2C3H5	-60.44	-60.50	-60.32	-61.89	-61.70	-61.76
C1O2C3H6	60.44	60.50	60.32	61.89	61.70	61.76
O7C1C8F9	120.15	120.07	120.17	120.11	120.11	119.90
O7C1C8F10	-120.15	-120.07	-120.17	-120.11	-120.11	-119.90
O7C1C8F11	0.00	0.00	0.00	0.00	0.00	0.00
Rotational constants (MHz)						
A	3592.116	3575.817	3614.489	2787.565	2780.186	2798.921
B	1524.240	1504.902	1531.743	2016.333	1986.105	2029.802
C	1331.660	1316.867	1338.382	1491.816	1475.803	1500.200
Dipole moment (D)						
μ_a	0.985	0.984	0.252	0.066	0.079	0.080
μ_b	1.015	1.016	1.392	1.413	1.412	1.412
μ_c	1.000	1.000	1.000	1.000	1.000	1.000
μ_{total}	1.732	1.732	1.732	1.732	1.732	1.732
Energy (Hartrees)						
E	-564.98720	-566.27836	-565.30652	-564.97307	-566.26558	-565.29355
G [b]	-564.95208	-566.24325	-565.27141	-564.93691	-566.22942	-565.25739
Energy differences (kJ mol^{-1})						
ΔE	0.0	0.0	0.0	37.1	33.6	34.1
ΔG	0.0	0.0	0.0	39.8	36.3	36.8
Population (%)[c]						
$X(\Delta E)$	100.0	100.0	100.0	0.0	0.0	0.0
$X(\Delta G)$	100.0	100.0	100.0	0.0	0.0	0.0

[a] See Figure 1 for the atom numbering. [b] Thermal correction to Gibbs free energy is estimated by the vibrational calculation at the MP2(fc)/6-31G(d,p) level. [c] calculated at 294 K.

Table S4. Structural Parameters for the *anti* Orientation of Methyl Trifluoroacetate as a Function of ϕ (O7C1C8F11) Obtained by the ab initio and DFT Calculations[a]

	MP2(fc)/6-311++G(d,p)				
	ϕ = 0°	ϕ = 15°	ϕ = 30°	ϕ = 45°	ϕ = 60°
Bond lengths/Å					
C1O2	1.3302	1.3301	1.3296	1.3292	1.3291
C1O7	1.2057	1.2059	1.2060	1.2064	1.2065
C1C8	1.5420	1.5417	1.5416	1.5417	1.5420
O2C3	1.4420	1.4425	1.4428	1.4433	1.4435
C3H4	1.0871	1.0870	1.0870	1.0870	1.0870
C3H5	1.0907	1.0906	1.0905	1.0905	1.0905
C3H6	1.0907	1.0907	1.0907	1.0906	1.0905
C8F9	1.3402	1.3374	1.3353	1.3330	1.3323
C8F10	1.3402	1.3424	1.3427	1.3417	1.3385
C8F11	1.3287	1.3294	1.3313	1.3348	1.3389
Bond angles/°					
C1O2C3	114.22	114.17	113.98	113.88	113.85
O2C3H4	105.15	105.14	105.09	105.08	105.07
O2C3H5	109.95	109.95	109.94	109.91	109.90
O2C3H6	109.95	109.91	109.92	109.90	109.90
O2C1O7	127.19	127.20	127.14	127.18	127.19
O7C1C8	123.68	123.34	122.51	121.57	121.20
O2C1C8	109.13	109.43	110.27	111.21	111.61
C1C8F9	110.50	111.62	112.58	113.28	113.55
C1C8F10	110.50	109.47	108.89	108.80	109.17
C1C8F11	110.57	110.49	110.21	109.69	109.11
Dihedral angles/°					
C1O2C3H4	180.00	179.43	179.35	179.63	-179.96
C1O2C3H5	-60.44	-61.00	-61.11	-60.81	-60.38
C1O2C3H6	60.44	59.86	59.76	60.02	60.46
C3O2C1O7	0.00	0.77	0.80	0.34	-0.03
C3O2C1C8	180.00	-177.12	-176.06	-177.38	179.80
O7C1C8F9	120.15	135.84	151.15	166.21	-179.07
O7C1C8F10	-120.15	-104.41	-88.84	-73.34	-58.09
O7C1C8F11	0.00	15.00	30.00	45.00	60.00
O2C1C8F9	-59.85	-46.18	-31.82	-15.92	1.09
O2C1C8F10	59.85	73.58	88.20	104.53	122.07
O2C1C8F11	180.00	-167.01	-152.96	-137.13	-119.84

Table S4 (Continued)

	B3LYP/6-311++G(d,p)				
	ϕ = 0°	ϕ = 15°	ϕ = 30°	ϕ = 45°	ϕ = 60°
Bond lengths/Å					
C1O2	1.3272	1.3271	1.3269	1.3263	1.3262
C1O7	1.1976	1.1979	1.1981	1.1985	1.1985
C1C8	1.5529	1.5528	1.5529	1.5530	1.5533
O2C3	1.4471	1.4477	1.4481	1.4483	1.4484
C3H4	1.0864	1.0864	1.0864	1.0864	1.0864
C3H5	1.0900	1.0899	1.0898	1.0898	1.0899
C3H6	1.0900	1.0900	1.0900	1.0900	1.0899
C8F9	1.3459	1.3432	1.3407	1.3394	1.3383
C8F10	1.3459	1.3480	1.3489	1.3472	1.3434
C8F11	1.3330	1.3337	1.3355	1.3389	1.3439
Bond angles/°					
C1O2C3	116.15	116.08	115.94	115.83	115.79
O2C3H4	105.16	105.15	105.15	105.13	105.12
O2C3H5	109.96	109.94	109.92	109.94	109.89
O2C3H6	109.96	109.92	109.89	109.85	109.89
O2C1O7	127.30	127.28	127.24	127.21	127.19
O7C1C8	123.19	122.91	122.26	121.53	121.28
O2C1C8	109.51	109.79	110.46	111.24	111.53
C1C8F9	110.73	111.76	112.65	113.30	113.50
C1C8F10	110.73	109.79	109.19	109.00	109.39
C1C8F11	110.52	110.45	110.23	109.88	109.33
Dihedral angles/°					
C1O2C3H4	180.00	179.92	-179.99	-179.22	-179.92
C1O2C3H5	-60.50	-60.57	-60.48	-59.64	-60.36
C1O2C3H6	60.50	60.40	60.45	61.25	60.52
C3O2C1O7	0.00	0.65	0.55	0.67	-0.03
C3O2C1C8	180.00	-177.71	-177.03	-177.58	179.86
O7C1C8F9	120.07	135.66	151.08	166.19	-179.17
O7C1C8F10	-120.07	-104.46	-88.91	-73.47	-58.28
O7C1C8F11	0.00	15.00	30.00	45.00	60.00

Table S4 (Continued)

	MP2(fc)/cc-pVTZ				
	ϕ = 0°	ϕ = 15°	ϕ = 30°	ϕ = 45°	ϕ = 60°
Bond lengths/Å					
C1O2	1.3291	1.3291	1.3288	1.3283	1.3284
C1O7	1.4393	1.4397	1.4399	1.4403	1.4404
C1C8	1.0823	1.0823	1.0823	1.0823	1.0823
O2C3	1.0859	1.0858	1.0858	1.0858	1.0859
C3H4	1.0859	1.0860	1.0860	1.0859	1.0859
C3H5	1.2042	1.2043	1.2045	1.2049	1.2049
C3H6	1.5386	1.5385	1.5386	1.5387	1.5392
C8F9	1.3358	1.3335	1.3315	1.3299	1.3289
C8F10	1.3358	1.3374	1.3380	1.3367	1.3338
C8F11	1.3245	1.3252	1.3270	1.3299	1.3341
Bond angles/°					
C1O2C3	113.75	113.68	113.53	113.40	113.37
O2C3H4	105.38	105.36	105.34	105.34	105.32
O2C3H5	110.03	110.03	110.01	110.00	109.99
O2C3H6	110.03	110.01	110.01	110.07	109.99
O2C1O7	126.97	126.96	126.90	126.93	126.89
O7C1C8	123.75	123.43	122.64	121.75	121.43
O2C1C8	109.28	109.61	110.46	111.32	111.68
C1C8F9	110.44	111.46	112.32	112.91	113.13
C1C8F10	110.44	109.57	109.02	108.92	109.27
C1C8F11	110.41	110.35	110.12	109.73	109.20
Dihedral angles/°					
C1O2C3H4	180.00	179.78	179.63	180.54	180.00
C1O2C3H5	-60.32	-60.54	-60.70	-59.73	-60.27
C1O2C3H6	60.32	60.08	59.90	60.81	60.27
C3O2C1O7	0.00	0.49	0.54	0.24	0.02
C3O2C1C8	180.00	182.39	183.36	182.32	179.87
O7C1C8F9	120.17	135.75	151.07	166.14	180.81
O7C1C8F10	-120.17	-104.52	-88.98	-73.54	-58.33
O7C1C8F11	0.00	15.00	30.00	45.00	60.00

[a] See Figure 1 for the atom numbering.

Table S5. Internal Coordinates for Methyl Trifluoroacet

1	r(C1O2)	r_1
2	r(O2C3)	r_2
3	r(C3H4)	r_3
4	r(C3H5)	r_4
5	r(C3H6)	r_5
6	r(C1=O7)	r_6
7	r(C1C8)	r_7
8	r(C8F9)	r_8
9	r(C8F10)	r_9
10	r(C8F11)	r_{10}
11	θ(H5C3H6)	θ_1
12	θ(H4C3H5)	θ_2
13	θ(H4C3H6)	θ_3
14	θ(O2C3H4)	θ_4
15	θ(O2C3H5)	θ_5
16	θ(O2C3H6)	θ_6
17	θ(C1O2C3)	θ_7
18	θ(O2C1C8)	θ_8
19	θ(O7C1O2)	θ_9
20	θ(C8C1O7)	θ_{10}
21	θ(C1C8F9)	θ_{11}
22	θ(C1C8F10)	θ_{12}
23	θ(C1C8F11)	θ_{13}
24	θ(F9C8F10)	θ_{14}
25	θ(F9C8F11)	θ_{15}
26	θ(F10C8F11)	θ_{16}
27	τ(C1-O2)	τ_1
28	τ(O2-C3)	τ_2
29	τ(C1-C8)	τ_3
30	ϕ(C8C1O2O7)	ϕ_1

[a] See Figure 1 for the atom numbering.

r: stretching, θ: bending, τ: torsion, ϕ: out-of-plane bending

Table S6. Local Symmetry Coordinates for Methyl Trifluoroacetate [a]

	Symmetry coodinate[b]	Description	Scale factor[c]
A'	$S_1 = r_1$	C1O2 stretching	1.00
A'	$S_2 = r_2$	O2C3 stretching	0.90
A'	$S_3 = r_3 + r_4 + r_5$	CH_3 sym. stretching	0.90
A'	$S_4 = 2r_3 - r_4 - r_5$	CH_3 antisym. stretching	0.85
A''	$S_5 = r_4 - r_5$	CH_3 antisym. stretching	0.95
A'	$S_6 = r_6$	C=O stretching	0.85
A'	$S_7 = r_7$	C-C stretching	0.95
A'	$S_8 = r_8 + r_9 + r_{10}$	CF_3 sym. stretching	0.90
A'	$S_9 = 2r_8 - r_9 - r_{10}$	CF_3 antisym. stretching	0.90
A''	$S_{10} = r_9 - r_{10}$	CF_3 antisym. stretching	0.90
A'	$S_{11} = -\theta_1 - \theta_2 - \theta_3 + \theta_4 + \theta_5 + \theta_6$	CH_3 sym. bending	0.90
A'	$S_{12} = 2\theta_4 - \theta_5 - \theta_6$	CH_3 rocking	0.90
A''	$S_{13} = \theta_5 - \theta_6$	CH_3 rocking	0.90
A'	$S_{14} = 2\theta_1 - \theta_2 - \theta_3$	CH_3 antisym. bending	0.90
A''	$S_{15} = \theta_2 - \theta_3$	CH_3 antisym. bending	0.90
A'	$S_{16} = \theta_7$	C1O2C3 bending	0.90
A'	$S_{17} = 2\theta_8 - \theta_9 - \theta_{10}$	O2C1C8 bending	0.90
A'	$S_{18} = \theta_9 - \theta_{10}$	C=O in-plane wagging	1.00
A'	$S_{19} = \theta_{11} + \theta_{12} + \theta_{13} - \theta_{14} - \theta_{15} - \theta_{16}$	CF_3 sym. bending	1.00
A'	$S_{20} = 2\theta_{13} - \theta_{11} - \theta_{12}$	CF_3 rocking	1.00
A''	$S_{21} = \theta_{11} - \theta_{12}$	CF_3 rocking	1.00
A'	$S_{22} = 2\theta_{14} - \theta_{15} - \theta_{16}$	CF_3 antisym. bending	1.00
A''	$S_{23} = \theta_{16} - \theta_{14}$	CF_3 antisym. bending	1.00
A''	$S_{24} = \tau_1$	C1O2 tortion	1.00
A''	$S_{25} = \tau_2$	O2C3 tortion	1.00
A''	$S_{26} = \tau_3$	CF_3 tortion	1.00
A''	$S_{27} = \phi_1$	C=O out-of-plane wagging	1.00

[a] See Figure 1 for the atom numbering.

[b] See Table S5 for internal coordinates.

[c] Scale factors are used for the force constants calculated at the MP2(fc)/6-31G(d,p) level.

Table S7. Calculated Vibrational Wavenumbers (cm^{-1}) for *anti* Conformer of Methyl Trifluoroacetate

			Unscaled		Scaled[a]		
Assignment[b]		ν_{obs} [c]	ν_{calc}	ν_{calc}-ν_{obs}	ν_{calc}	ν_{calc}-ν_{obs}	Description
ν_1	*A′*	3044	3298	253.6	3044	0.3	CH_3 antisym. stretching
ν_{18}	*A″*	3018	3262	243.5	3007	-11.1	CH_3 antisym. stretching
ν_2	*A′*	2970	3157	187.0	2991	20.9	CH_3 sym. stretching
ν_3	*A′*	1807	1850	42.6	1802	-5.3	C=O stretching
ν_4	*A′*	1469	1554	85.0	1474	5.3	CH_3 antisym. bending
ν_{19}	*A″*	1455	1548	93.1	1469	13.6	CH_3 antisym. bending
ν_5	*A′*	1448	1522	73.8	1450	2.3	CH_3 sym. bending
ν_6	*A′*	1366	1435	69.3	1383	16.8	C1O2 stretching / C-C stretching / CH_3 sym. bending
ν_7	*A′*	1237	1300	62.6	1248	10.9	CF_3 antisym. stretching
ν_8	*A′*	1203	1248	44.9	1204	1.2	C1O2 stretching / CH_3 rocking
ν_{21}	*A″*	1189	1246	56.9	1196	7.1	CF_3 antisym. stretching
ν_{20}	*A″*	1163	1204	41.3	1153	-10.2	CH_3 rocking
ν_9	*A′*	1148	1194	46.1	1143	-4.8	CH_3 rocking
ν_{10}	*A′*	976	1023	47.0	976	0.4	O2C3 stretching
ν_{11}	*A′*	838	853	15.3	822	-15.9	CF_3 sym. stretching / O2C1C8 bending
ν_{22}	*A″*	781	780	-1.2	776	-4.7	C=O out-of-plane wagging
ν_{12}	*A′*	734	731	-3.3	716	-18.1	CF_3 sym. Stretching / CF_3 sym. bending
ν_{13}	*A′*	585	583	-1.8	578	-7.2	CF_3 antisym. bending
ν_{23}	*A″*	525	518	-7.5	516	-9.5	CF_3 antisym. bending
ν_{14}	*A′*	421	419	-1.7	417	-3.7	C=O in-plane wagging / CF_3 rocking / CF_3 antisym. bendi
ν_{15}	*A′*	370	380	9.7	363	-7.0	C-C stretching / CF_3 sym. bending
ν_{16}	*A′*	329	325	-4.1	314	-15.5	C1O2C3 bending / CF_3 rocking
ν_{24}	*A″*	279	281	1.9	282	2.5	CF_3 rocking
ν_{17}	*A′*	189	187	-2.1	184	-4.6	C=O in-plane wagging / CF_3 rocking
ν_{25}	*A″*	133	143	10.1	143	10.1	O2C3 tortion
ν_{26}	*A″*		126		126	126.3	C1O2 tortion
ν_{27}	*A″*	25	28	3.2	28	3.3	CF_3 tortion

[a] Scale factors are shown in Table S6.

[b] See Table S6.

[c] M. E. Defonsi Lestard et al., *J. Raman Spectrosc.* , **40,** 2053-2062(2009).

Table S8. Vibrational Mean Amplitudes and Shrinkage Corrections (Å) for the *anti* Orientation of Methyl Trifluoroacetate[a]

Atom pair																									
				ϕ = 0°				ϕ = 15°				ϕ = 30°				ϕ = 45°				ϕ = 60°			
				$l_{calc.}$	$l_{obs.}$	n^b	r_a	$r_e - r_a$	$l_{calc.}$	$l_{obs.}$	r_a	$r_e - r_a$	$l_{calc.}$	$l_{obs.}$	r_a	$r_e - r_a$	$l_{calc.}$	$l_{obs.}$	r_a	$r_e - r_a$	$l_{calc.}$	$l_{obs.}$	r_a	$r_e - r_a$
C	1 -	O	2	0.045	0.043 (4)	1	1.334	-0.008	0.045	0.043	1.334	-0.008	0.045	0.043	1.333	-0.008	0.045	0.043	1.333	-0.008	0.045	0.043	1.333	-0.008
C	1 -	C	3	0.068	0.062 (6)	2	2.361	-0.028	0.068	0.062	2.361	-0.028	0.068	0.062	2.358	-0.028	0.068	0.062	2.357	-0.028	0.068	0.062	2.357	-0.028
C	1 -	H	4	0.102	0.095 (19)	4	3.207	-0.008	0.102	0.095	3.207	-0.008	0.102	0.095	3.205	-0.008	0.102	0.095	3.204	-0.008	0.102	0.095	3.204	-0.008
C	1 -	H	5	0.207	0.191 (22)	3	2.663	-0.034	0.207	0.191	2.667	-0.034	0.207	0.191	2.664	-0.034	0.207	0.191	2.660	-0.034	0.207	0.191	2.657	-0.034
C	1 -	H	6	0.208	0.191	3	2.664	-0.035	0.208	0.191	2.659	-0.035	0.208	0.191	2.655	-0.035	0.208	0.191	2.656	-0.035	0.208	0.191	2.658	-0.035
C	1 -	O	7	0.038	0.036	1	1.194	-0.003	0.038	0.036	1.194	-0.003	0.038	0.036	1.194	-0.003	0.038	0.036	1.194	-0.003	0.038	0.036	1.195	-0.003
C	1 -	C	8	0.051	0.049	1	1.542	-0.009	0.051	0.049	1.542	-0.009	0.051	0.049	1.541	-0.009	0.051	0.049	1.542	-0.009	0.051	0.049	1.542	-0.009
C	1 -	F	9	0.071	0.064	2	2.352	-0.011	0.071	0.064	2.365	-0.011	0.071	0.064	2.377	-0.011	0.071	0.064	2.385	-0.011	0.071	0.064	2.388	-0.011
C	1 -	F	10	0.071	0.064	2	2.352	-0.011	0.071	0.064	2.339	-0.011	0.071	0.064	2.330	-0.011	0.071	0.064	2.328	-0.011	0.071	0.064	2.332	-0.011
C	1 -	F	11	0.067	0.061	2	2.352	-0.011	0.067	0.061	2.351	-0.011	0.067	0.061	2.348	-0.011	0.067	0.061	2.344	-0.011	0.067	0.061	2.339	-0.011
O	2 -	C	3	0.051	0.049	1	1.430	-0.010	0.051	0.049	1.431	-0.010	0.051	0.049	1.431	-0.010	0.051	0.049	1.432	-0.010	0.051	0.049	1.432	-0.010
O	2 -	H	4	0.105	0.098	2	2.016	-0.018	0.105	0.098	2.017	-0.018	0.105	0.098	2.016	-0.018	0.105	0.098	2.017	-0.018	0.105	0.098	2.017	-0.018
O	2 -	H	5	0.103	0.097	2	2.077	-0.015	0.103	0.097	2.077	-0.015	0.103	0.097	2.078	-0.015	0.103	0.097	2.078	-0.015	0.103	0.097	2.078	-0.015
O	2 -	H	6	0.103	0.097	2	2.077	-0.015	0.103	0.097	2.077	-0.015	0.103	0.097	2.077	-0.015	0.103	0.097	2.077	-0.015	0.103	0.097	2.078	-0.015
O	2 -	O	7	0.053	0.047	2	2.248	-0.013	0.053	0.047	2.248	-0.013	0.053	0.047	2.247	-0.013	0.053	0.047	2.247	-0.013	0.053	0.047	2.247	-0.013
O	2 -	C	8	0.068	0.062	2	2.368	-0.007	0.068	0.062	2.372	-0.007	0.068	0.062	2.383	-0.007	0.068	0.062	2.396	-0.007	0.068	0.062	2.401	-0.007
O	2 -	F	9	0.106	0.089	3	2.750	-0.004	0.106	0.089	2.670	-0.004	0.106	0.089	2.617	-0.004	0.106	0.089	2.589	-0.004	0.106	0.089	2.585	-0.004
O	2 -	F	10	0.106	0.089	3	2.750	-0.004	0.106	0.089	2.857	-0.004	0.106	0.089	2.992	-0.004	0.106	0.099	3.144	-0.004	0.106	0.099	3.286	-0.004
O	2 -	F	11	0.065	0.058	4	3.505	-0.012	0.065	0.058	3.496	-0.012	0.065	0.058	3.466	-0.012	0.065	0.058	3.402	-0.012	0.065	0.058	3.294	-0.012
C	3 -	H	4	0.076	0.074	1	1.099	-0.016	0.076	0.074	1.099	-0.016	0.076	0.074	1.098	-0.016	0.076	0.074	1.099	-0.016	0.076	0.074	1.098	-0.016
C	3 -	H	5	0.077	0.075	1	1.102	-0.015	0.077	0.075	1.102	-0.015	0.077	0.075	1.102	-0.015	0.077	0.075	1.102	-0.015	0.077	0.075	1.102	-0.015
C	3 -	H	6	0.077	0.075	1	1.102	-0.015	0.077	0.075	1.102	-0.015	0.077	0.075	1.102	-0.015	0.077	0.075	1.102	-0.015	0.077	0.075	1.102	-0.015
C	3 -	O	7	0.109	0.093	3	2.704	-0.047	0.109	0.093	2.703	-0.047	0.109	0.093	2.698	-0.047	0.109	0.093	2.696	-0.047	0.109	0.093	2.696	-0.047
C	3 -	C	8	0.072	0.065	4	3.705	-0.017	0.072	0.065	3.707	-0.017	0.072	0.065	3.713	-0.017	0.072	0.065	3.722	-0.017	0.072	0.065	3.727	-0.017
C	3 -	F	9	0.129	0.123 (50)	5	4.089	-0.004	0.129	0.123	4.051	-0.004	0.129	0.123	4.024	-0.004	0.129	0.123	4.007	-0.004	0.129	0.123	4.006	-0.004
C	3 -	F	10	0.129	0.123	5	4.089	-0.004	0.129	0.123	4.144	-0.004	0.129	0.123	4.234	-0.004	0.129	0.123	4.358	-0.004	0.129	0.123	4.485	-0.004
C	3 -	F	11	0.083	0.078	5	4.701	-0.030	0.083	0.078	4.694	-0.030	0.083	0.078	4.667	-0.030	0.083	0.078	4.609	-0.030	0.083	0.078	4.509	-0.030
H	4 -	H	5	0.123	0.117	2	1.806	-0.017	0.123	0.117	1.806	-0.017	0.123	0.117	1.806	-0.017	0.123	0.117	1.806	-0.017	0.123	0.117	1.807	-0.017
H	4 -	H	6	0.123	0.117	2	1.806	-0.017	0.123	0.117	1.806	-0.017	0.123	0.117	1.806	-0.017	0.123	0.117	1.807	-0.017	0.123	0.117	1.805	-0.017
H	4 -	O	7	0.124	0.117	4	3.718	-0.015	0.124	0.117	3.718	-0.015	0.124	0.117	3.713	-0.015	0.124	0.117	3.712	-0.015	0.124	0.117	3.711	-0.015
H	4 -	C	8	0.122	0.117	5	4.351	0.004	0.122	0.117	4.355	0.004	0.122	0.117	4.366	0.004	0.122	0.117	4.381	0.004	0.122	0.117	4.387	0.004
H	4 -	F	9	0.197	0.191	5	4.551	0.015	0.197	0.191	4.469	0.015	0.197	0.191	4.410	0.015	0.197	0.191	4.377	0.015	0.197	0.191	4.372	0.015
H	4 -	F	10	0.196	0.191	5	4.552	0.014	0.196	0.191	4.664	0.014	0.196	0.191	4.820	0.014	0.196	0.191	5.012	0.014	0.196	0.191	5.197	0.014
H	4 -	F	11	0.113	0.107	5	5.477	0.001	0.113	0.107	5.468	0.001	0.113	0.107	5.430	0.001	0.113	0.107	5.348	0.001	0.113	0.107	5.207	0.001
H	5 -	H	6	0.123	0.116	2	1.797	-0.021	0.123	0.116	1.797	-0.021	0.123	0.116	1.797	-0.021	0.123	0.116	1.797	-0.021	0.123	0.116	1.797	-0.021
H	5 -	O	7	0.341	0.324	3	2.691	-0.035	0.341	0.324	2.693	-0.035	0.341	0.324	2.688	-0.035	0.341	0.324	2.684	-0.035	0.341	0.324	2.680	-0.035
H	5 -	C	8	0.174	0.169	5	4.072	-0.030	0.174	0.169	4.090	-0.030	0.174	0.169	4.098	-0.030	0.174	0.169	4.094	-0.030	0.174	0.169	4.079	-0.030
H	5 -	F	9	0.225	0.220	5	4.326	-0.022	0.225	0.220	4.383	-0.022	0.225	0.220	4.435	-0.022	0.225	0.220	4.481	-0.022	0.225	0.220	4.530	-0.022
H	5 -	F	10	0.161	0.156	5	4.725	-0.004	0.161	0.156	4.782	-0.004	0.161	0.156	4.839	-0.004	0.161	0.156	4.896	-0.004	0.161	0.156	4.937	-0.004
H	5 -	F	11	0.229	0.223	5	4.920	-0.045	0.229	0.223	4.882	-0.045	0.229	0.223	4.815	-0.045	0.229	0.223	4.709	-0.045	0.229	0.223	4.570	-0.045
H	6 -	O	7	0.342	0.325	3	2.693	-0.037	0.342	0.325	2.688	-0.037	0.342	0.325	2.681	-0.037	0.342	0.325	2.679	-0.037	0.342	0.325	2.682	-0.037
H	6 -	C	8	0.174	0.169	5	4.072	-0.030	0.174	0.169	4.054	-0.030	0.174	0.169	4.050	-0.030	0.174	0.169	4.063	-0.030	0.174	0.169	4.082	-0.030
H	6 -	F	9	0.161	0.155	5	4.725	-0.004	0.161	0.155	4.662	-0.004	0.161	0.155	4.599	-0.004	0.161	0.155	4.542	-0.004	0.161	0.155	4.496	-0.004
H	6 -	F	10	0.226	0.220	5	4.326	-0.022	0.226	0.220	4.291	-0.022	0.226	0.220	4.317	-0.022	0.226	0.220	4.414	-0.022	0.226	0.220	4.554	-0.022
H	6 -	F	11	0.229	0.224	5	4.921	-0.046	0.229	0.224	4.950	-0.046	0.229	0.224	4.977	-0.046	0.229	0.224	4.994	-0.046	0.229	0.224	4.984	-0.046
O	7 -	C	8	0.064	0.058	2	2.412	-0.006	0.064	0.058	2.408	-0.006	0.064	0.058	2.399	-0.006	0.064	0.058	2.389	-0.006	0.064	0.058	2.385	-0.006
O	7 -	F	9	0.082	0.076	4	3.294	-0.007	0.082	0.076	3.381	-0.007	0.082	0.076	3.440	-0.007	0.082	0.076	3.471	-0.007	0.082	0.076	3.480	-0.007
O	7 -	F	10	0.082	0.076	4	3.295	-0.008	0.082	0.076	3.183	-0.008	0.082	0.076	3.058	-0.008	0.082	0.066	2.932	-0.008	0.082	0.066	2.823	-0.008
O	7 -	F	11	0.112	0.095	3	2.662	-0.004	0.112	0.095	2.669	-0.004	0.112	0.095	2.696	-0.004	0.112	0.095	2.746	-0.004	0.112	0.095	2.827	-0.004
C	8 -	F	9	0.045	0.043	1	1.326	-0.006	0.045	0.043	1.323	-0.006	0.045	0.043	1.321	-0.006	0.045	0.043	1.319	-0.006	0.045	0.043	1.318	-0.006
C	8 -	F	10	0.045	0.043	1	1.326	-0.006	0.045	0.043	1.328	-0.006	0.045	0.043	1.328	-0.006	0.045	0.043	1.327	-0.006	0.045	0.043	1.324	-0.006
C	8 -	F	11	0.045	0.042	1	1.325	-0.006	0.045	0.042	1.325	-0.006	0.045	0.042	1.327	-0.006	0.045	0.042	1.331	-0.006	0.045	0.042	1.335	-0.006
F	9 -	F	10	0.060	0.054	2	2.122	-0.008	0.060	0.054	2.122	-0.008	0.060	0.054	2.121	-0.008	0.060	0.054	2.119	-0.008	0.060	0.054	2.118	-0.008
F	9 -	F	11	0.058	0.052	2	2.169	-0.007	0.058	0.052	2.168	-0.007	0.058	0.052	2.166	-0.007	0.058	0.052	2.167	-0.007	0.058	0.052	2.169	-0.007
F	10 -	F	11	0.058	0.052	2	2.169	-0.007	0.058	0.052	2.172	-0.007	0.058	0.052	2.173	-0.007	0.058	0.052	2.173	-0.007	0.058	0.052	2.173	-0.007

[a] See Figure 1 for the atom numbering. The dihedral angle, ϕ, is difined as O7C1C8F11. Listed values are taken from GED-LAM final data analysis with MP2(fc)/6-311++G(d,p) constraints.

[e] The group of vibrational amplitudes. The vibrational amplitudes belonging to the same group have the same experimental error.

Table S9. Structural Parameters for Methyl Trifluoroacetate[a]

	GED (LAM) with MP2(fc)/6-311++G(d,p) restraints			GED (LAM) with B3LYP/6-311++G(d,p) restraints			GED (LAM) with MP2(fc)/cc-pVTZ. restraints		
	first (r_g, $\angle_\alpha$)	second (r_{h1}, $\angle_{h1}$)	Anh (r_e, $\angle_e$)	first (r_g, $\angle_\alpha$)	second (r_{h1}, $\angle_{h1}$)	Anh (r_e, $\angle_e$)	first (r_g, $\angle_\alpha$)	second (r_{h1}, $\angle_{h1}$)	Anh (r_e, $\angle_e$)
Geometrical parameters									
Bond lengths/Å									
C1-O2	1.330	1.329	1.326	1.332	1.329	1.315	1.330	1.329	1.322
O2-C3	1.434	1.432	1.421	1.433	1.430	1.420	1.434	1.432	1.422
C3-H4	1.107	1.103	1.083	1.102	1.100	1.080	1.109	1.106	1.085
C3-H5	1.111	1.107	1.087	1.106	1.103	1.084	1.113	1.110	1.089
C3-H6	1.111	1.107	1.087	1.106	1.103	1.084	1.113	1.110	1.089
C1-O7	1.196	1.196	1.190	1.194	1.194	1.189	1.197	1.197	1.192
C1-C8	1.545	1.543	1.533	1.543	1.542	1.533	1.544	1.542	1.534
C8-F9	1.331	1.330	1.320	1.324	1.325	1.323	1.333	1.332	1.324
C8-F10	1.331	1.330	1.320	1.324	1.325	1.323	1.333	1.332	1.324
C8-F11	1.324	1.323	1.319	1.334	1.332	1.323	1.321	1.321	1.315
Bond angles/°									
C1-O2-C3	116.2	116.2	116.3	117.6	117.6	117.2	115.9	115.9	115.7
O2-C3-H4	105.2	105.2	105.2	105.2	105.2	105.2	105.4	105.4	105.4
O2-C3-H5	110.0	110.0	110.0	110.0	110.0	110.0	110.0	110.0	110.0
O2-C3-H6	110.0	110.0	110.0	110.0	110.0	110.0	110.0	110.0	110.0
O2-C1-O7	125.2	125.2	125.2	125.9	125.9	126.2	124.8	124.9	125.0
O7-C1-C8	123.7	123.7	123.7	123.2	123.2	123.2	123.8	123.8	123.8
O2-C1-C8	111.1	111.1	111.2	111.0	110.9	110.6	111.4	111.4	111.3
C1-C8-F9	110.2	110.2	110.1	110.2	110.3	110.4	110.2	110.2	110.1
C1-C8-F10	110.2	110.2	110.1	110.2	110.3	110.4	110.2	110.2	110.1
C1-C8-F11	110.2	110.2	110.1	110.2	110.3	110.4	110.2	110.2	110.1
Dihedral angles/°									
C1-O2-C3-H4	-180.0	-180.0	180.0	180.0	180.0	-180.0	180.0	180.0	180.0
C1-O2-C3-H5	-60.4	-60.4	-60.4	60.4	60.4	-60.4	-60.3	-60.3	-60.3
C1-O2-C3-H6	60.4	60.4	60.4	-60.4	-60.4	60.4	60.3	60.3	60.3
O7-C1-O2-C3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C8-C1-O2-C3	-180.0	-180.0	180.0	180.0	180.0	-180.0	-180.0	-180.0	-180.0
O7-C1-C8-F9	118.4	118.5	121.5	120.9	120.9	121.3	118.4	118.4	118.6
O7-C1-C8-F10	-118.4	-118.5	-121.5	-120.9	-120.9	-121.3	-118.4	-118.4	-118.6
O7-C1-C8-F11	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Independent geometrical parameters									
p_1 rCF/CO/CC average	1.354 (1)	1.354 (1)	1.354 (1)	1.354 (1)	1.353 (1)	1.353 (1)	1.355 (1)	1.355 (1)	1.354 (1)
p_2 rCF/CO/CC difference 1	0.220 (5)	0.220 (5)	0.220 (5)	0.219 (4)	0.220 (4)	0.220 (5)	0.219 (5)	0.219 (5)	0.220 (5)
p_3 rCF/CO/CC difference 2	0.131 (5)	0.131 (5)	0.130 (5)	0.131 (4)	0.130 (4)	0.130 (5)	0.131 (5)	0.131 (5)	0.130 (5)
p_4 rCF/CO/CC difference 3	0.047 (10)	0.047 (10)	0.042 (8)	0.037 (8)	0.040 (8)	0.047 (8)	0.050 (9)	0.050 (9)	0.048 (10)
p_5 rCF/CO/CC difference 4	0.061 *	0.061 *	0.061 *	0.071 *	0.071 *	0.071 *	0.058 *	0.058 *	0.058 *
p_6 rCF/CO/CC difference 5	0.134 (10)	0.134 (10)	0.140 (9)	0.137 (8)	0.135 (8)	0.130 (9)	0.132 (9)	0.132 (9)	0.135 (10)
p_7 rCH mean	1.104 (16)	1.104 (15)	1.101 (14)	1.100 (13)	1.101 (13)	1.098 (14)	1.107 (16)	1.107 (16)	1.103 (15)
p_8 ∠OCH average	108.35 *	108.35 *	108.35 *	108.36 *	108.36 *	108.36 *	108.48 *	108.48 *	108.48 *
p_9 ∠OCH difference	4.80 *	4.80 *	4.80 *	4.80 *	4.80 *	4.80 *	4.65 *	4.65 *	4.65 *
p_{10} COCH5 dihedral angle	-60.4 *	-60.4 *	-60.4 *	60.4 *	60.4 *	-60.4 *	-60.3 *	-60.3 *	-60.3 *
p_{11} ∠C1O2C3	116.23	116.19	116.26	117.60	117.58	117.23	115.89	115.85	115.74
p_{12} ∠O2C1C8	111.14 } (59)	111.10 } (58)	111.17 } (47)	110.96 } (47)	110.94 } (48)	110.59 } (49)	111.42 } (67)	111.38 } (63)	111.27 } (56)
p_{13} ∠CCF average	110.19 (32)	110.23 (31)	110.08 (30)	110.17 (28)	110.25 (29)	110.39 (30)	110.19 (28)	110.23 (29)	110.09 (32)
p_{14} ∠CCF difference	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *	0.00 *
p_{15} OCCF9 dihedral angle	118.43 (1)	118.53 (1)	121.50 (1)	120.86 (1)	120.86 (1)	121.28 (2)	118.35 (1)	118.44 (1)	118.61 (1)
p_{16} ∠O7C1C8	123.68 *	123.68 *	123.68 *	123.19 *	123.19 *	123.19 *	123.75 *	123.75 *	123.75 *
V_3 /kJ mol^{-1}	3.8 (5)	3.6 (6)	2.3 (4)	2.2 (4)	2.1 (4)	1.8 (4)	4.6 (5)	4.4 (5)	2.9 (5)
R	0.036	0.035	0.032	0.030	0.030	0.031	0.038	0.037	0.034

[a] See Fig.1 for the atom numbering. See text for the definition of independent geometrical parameters, V_3 and R factor. Errors in parentheses represent 3 times the standard deviation. Structural parameters for the $\phi = 0^\circ$ conformer are listed.

*Fixed at the theoretical values.

†:dependent parameter.

Table S10. Structural Parameters for Pseudoconformers of the *anti* Orientation of Methyl Trifluoroacetate[a]

	Value				
Parameter	ϕ = 0°	ϕ = 15°	ϕ = 30°	ϕ = 45°	ϕ = 60°
Bond lengths/Å					
C1O2	1.3338	1.3337	1.3332	1.3328	1.3327
O2C3	1.4303	1.4308	1.4311	1.4316	1.4318
C3H4	1.0985	1.0986	1.0984	1.0986	1.0984
C3H5	1.1021	1.1020	1.1019	1.1019	1.1019
C3H6	1.1021	1.1021	1.1021	1.1020	1.1019
C1O7	1.1937	1.1939	1.1940	1.1944	1.1945
C1C8	1.5418	1.5415	1.5414	1.5415	1.5418
C8F9	1.3258	1.3230	1.3209	1.3186	1.3179
C8F10	1.3258	1.3280	1.3283	1.3273	1.3241
C8F11	1.3246	1.3253	1.3272	1.3307	1.3348
Bond angles/°					
C1O2C3	116.26	116.21	116.02	115.92	115.89
O2C3H4	105.15	105.14	105.09	105.08	105.07
O2C3H5	109.95	109.95	109.94	109.91	109.90
O2C3H6	109.95	109.91	109.92	109.90	109.90
O2C1O7	125.15	125.16	125.10	125.14	125.15
O2C1C8	111.17	111.47	112.31	113.25	113.65
C1C8F9	110.08	111.20	112.16	112.86	113.13
C1C8F10	110.08	109.05	108.47	108.38	108.75
C1C8F11	110.08	110.00	109.72	109.20	108.62
Dihedral angles/°					
C1O2C3H4	180.00	179.43	179.35	179.63	179.96
C1O2C3H5	-60.40	-60.96	-61.07	-60.77	-60.34
C1O2C3H6	60.40	59.82	59.72	59.98	60.42
C3O2C1O7	0.00	0.77	0.80	0.34	-0.03
C3O2C1C8	180.00	182.88	183.94	182.62	179.80
O7C1C8F9	121.50	137.19	152.50	167.56	182.28
O7C1C8F10	-121.50	-105.76	-90.19	-74.69	-59.44
O7C1C8F11	0.00	15.00	30.00	45.00	60.00
Population (%)					
X	20.6	34.8	23.0	15.2	6.4

[a] See Figure 1 for the atom numbering. The dihedral angle, ϕ, is O7C1C8F11.

Bond distances (r_a) and angles ($\angle_e$) are taken from the final results for GED(LAM)-Anh data analysis.

The geometrical restraints are based on the MP2(fc)/6-311++G(d,p) calculations.

Table S11. Correlation Matrix of Methyl Trifluoroacetate[a]

	k	p_1	p_2	p_3	p_4	p_6	p_7	p_{12}	p_{13}	p_{15}	l_1	l_2	l_3	l_4	l_5	V_3
k	1.00															
p_1	-0.22	1.00														
p_2	-0.21	0.30	1.00													
p_3	0.11	-0.18	-0.33	1.00												
p_4	0.55	-0.14	-0.31	0.10	1.00											
p_6	0.43	-0.12	-0.06	0.61	0.17	1.00										
p_7	-0.24	0.47	0.62	-0.05	-0.30	0.02	1.00									
p_{12}	0.51	-0.43	-0.49	-0.08	0.51	0.15	-0.86	1.00								
p_{13}	-0.67	0.12	0.18	0.17	-0.44	-0.19	0.24	-0.47	1.00							
p_{15}	-0.19	-0.16	0.19	-0.53	-0.43	-0.36	-0.38	0.26	0.01	1.00						
l_1	-0.38	0.40	0.51	0.05	-0.57	-0.07	0.90	-0.91	0.40	-0.27	1.00					
l_2	0.52	0.09	0.01	-0.24	0.44	-0.14	0.14	0.09	-0.43	-0.24	-0.03	1.00				
l_3	-0.26	0.73	0.42	-0.38	-0.27	-0.22	0.42	-0.38	0.11	0.07	0.37	0.05	1.00			
l_4	0.11	0.00	0.12	0.09	0.03	0.16	0.22	-0.15	-0.04	-0.17	0.16	0.09	-0.02	1.00		
l_5	0.35	0.01	-0.52	0.31	0.16	0.25	0.11	-0.02	-0.15	-0.44	0.14	0.22	-0.18	0.08	1.00	
V_3	-0.08	0.47	0.17	-0.10	-0.06	-0.06	0.29	-0.25	0.03	-0.12	0.25	0.09	0.35	0.00	0.03	1.00

[a] k is index of resolution.

p_1-p_{15} are parameters for the differences and averages of the bond lengths and bond angles (see text). Notation for these parameters are same as those in the literature (M. E. Defonsi Lestard et al., J. Raman Spectrosc., 40, 2053-2062(2010).).

l_1-l_5 are the vibrational amplitudes for group 1-5, respectively.

V_3 is potential parameter(see text).

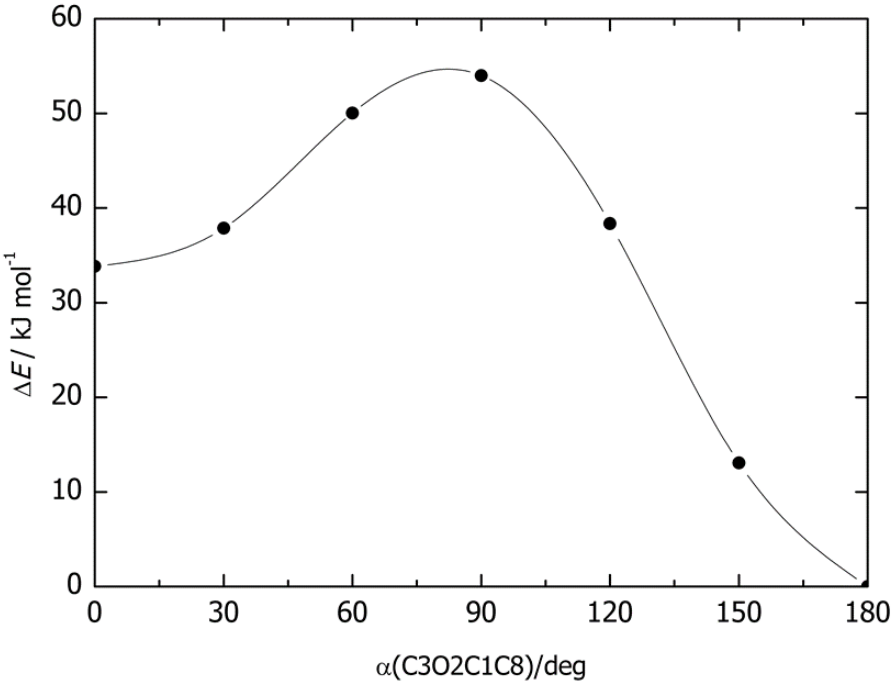

Figure S1. Torsional potential curve about the C(=O)–O bond of methyl trifluoroacetate calculated at the MP2(fc)/cc-pVTZ level of theory.