Solvent Effects on the Intramolecular Conversion of Trimethylsulfonium Chloride to Dimethylsulfide and Methylchloride

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Supplementary Material

S.1 Evaluation of the computational method

The evaluation of a suitable computational method for the analysis of the conversion of trimethylsulfonium chloride is done in two steps. The first step focuses on the properties of dimethylsulfide $(CH_3)_2S$ taken from the National Institute of Standard (NIST) web page for computational benchmark data [1], such as geometries, IR spectra and dipole moments. In the second step, the basis set size is systematically increased until convergence can be observed in barrier height of the nucleophilic substitution reaction at dimethyl sulfide in the vacuum

$$(CH_3)_2S + Cl^- \longrightarrow CH_3S^- + CH_3Cl \quad . \tag{S.1}$$

Dimethyl sulfide was chosen instead of the trimethylsulfonium cation, because a barrier can be observed in reaction S.1 while no barrier has been reported for reaction 1 (main body of the paper) in the vacuum.

Ten methods were tested in the first step: two wave function based methods (HF and MP2), two GGA (generalized gradient approximation) functionals (OLYP and OPBE), four hybrid (B3LYP, O3LYP, X3LYP, PBE1PBE) and two meta-GGA functionals (M05 and M05-2X). These methods were paired with 12 different gaussian basis sets [6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p), D95+(d,p), D95++(d,p), cc-pVDZ, aug-cc-pVDZ, cc-pVTZ, aug-cc-pVTZ] including both polarization and diffuse function. The geometry of the $(CH_3)_2S$ molecule was then optimized in the vacuum under the constraint of a C_s symmetry followed by a normal mode analysis. Methods and basis sets were used as defined in the Gaussian 09 program package [2].

The following data were extracted from the 120 combinations of basis set and method and compared with the NIST reference values given in parentheses: the carbon-sulfur bond length r_{CS} (1.802 Å), the average carbon-hydrogen bond length $\overline{r}_{CH}$ (1.091 Å), the CSC bond angle ω_{CSC} (98.9°), the average HCH bond angle $\overline{\omega}_{HCH}$ (109.6°), the molecular dipole moment μ (1.5 Debye) and three low lying vibrational modes involving the sulfur atom ν_i (CSC scissoring vibration, A_1, 282 cm^{-1}; CS symmetrical stretch, A_1, 695 cm^{-1}, CS asymmetrical stretch, B_2, 743 cm^{-1}). The large amount of data was compressed with the aid of a scoring function

$$\sigma_{tot} = \sqrt{\sum_{i=1}^{2}\left(\frac{\Delta r_i}{r_i^{ref}}\right)^2 + \sum_{i=1}^{2}\left(\frac{\Delta \omega_i}{\omega_i^{ref}}\right)^2 + \left(\frac{\Delta \mu}{\mu^{ref}}\right)^2 + \sum_{i=1}^{3}\left(\frac{\Delta \nu_i}{\nu_i^{ref}}\right)^2} \tag{S.2}$$

where $\Delta x_i = x_i^{calc} - x_i^{ref}$ is the difference between the calculated and the NIST reference value. Table S.1 summarizes the final results for σ_{tot} while the complete data set is presented within the supplementary material.

	HF	MP2	OLYP	OPBE	B3LYP	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	0.2417	0.2117	0.1580	0.1766	0.1685	0.1618	0.1679	0.1935	0.1632	0.2252
6-31+G(d,p)	0.2738	0.2409	0.1729	0.1838	0.1837	0.1777	0.1840	0.2026	0.1777	0.2448
6-31++G(d,p)	0.2730	0.2398	0.1613	0.1740	0.1776	0.1682	0.1773	0.1973	0.1696	0.2408
6-311G(d,p)	0.2574	0.2244	0.1703	0.1797	0.1656	0.1695	0.1655	0.1830	0.1396	0.2161
6-311+G(d,p)	0.2480	0.2130	0.1544	0.1642	0.1514	0.1536	0.1505	0.1693	0.1243	0.2016
6-311++G(d,p)	0.2515	0.2165	0.1541	0.1645	0.1554	0.1547	0.1542	0.1729	0.1262	0.2073
D95+(d,p)	0.3120	0.2804	0.1702	0.1993	0.2037	0.1854	0.2032	0.2310	0.2333	0.2540
D95++(d,p)	0.3087	0.2772	0.1680	0.1961	0.2013	0.1829	0.2008	0.2281	0.2310	0.2504
cc-pVDZ	0.1512	0.1297	0.0894	0.0721	0.0944	0.0651	0.0912	0.0933	0.0513	0.1180
aug-cc-pVDZ	0.2290	0.2132	0.1024	0.1063	0.1343	0.1017	0.1317	0.1437	0.1013	0.1886
cc-pVTZ	0.1862	0.1657	0.0844	0.0911	0.0963	0.0724	0.0919	0.1143	0.0594	0.1409
aug-cc-pVTZ	0.2132	0.1914	0.0955	0.1012	0.1130	0.0917	0.1101	0.1279	0.0729	0.1567

Table S.1: Results from the scoring function σ_{tot} (Equation S.2) for the reproduction of the experimental properties of $(CH_3)_2S$ at various computational levels.

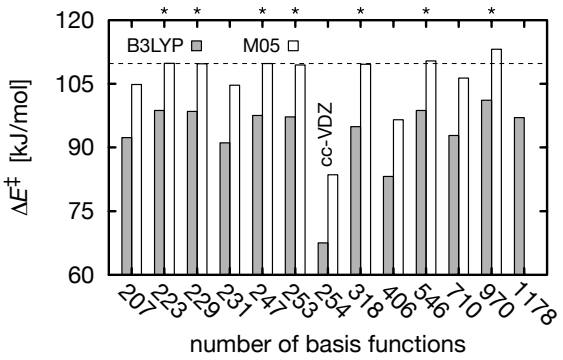

Figure S.1: Barrier height for reaction S.1 relative to the reactants. The basis sets are labeled by the number of basis functions and those including diffuse functions are marked with an asterisk at the top border of the histogram. The dashed line marks the approximate barrier height of 109.81 kJ/mol for the M05 functional.

The data in Table S.1 show that the best results with any method are consistently obtained using either the cc-VDZ or cc-VTZ basis set. However, the overall performance of theses basis sets diminishes markedly as diffuse functions are added to these basis sets. A comparison of the methods along these lines show, that the inclusion of correlation effects (MP2) increases quality of the HF results, but all DFT methods perform better than the MP2 calculations. Moreover, the GGA functionals outperform the significantly more expensive hybrid functionals. This results agrees with data published by Swart *et al.* showing that the GGA functionals OLYP and OPBE are suitable functionals for the analysis of nucleophilic substitution reactions [3]. Truhlar's meta-GGA functional M05 [4] consistently yields the best σ-values, but the quality of the predicted properties decreases as the HF exchange contribution increases going from M05 to M05-2X. In summary, the M05 functional using either the ccp-VDZ or ccp-VTZ basis set performs best for the analysis of dimethyl sulfide.

The winning M05 functional and 13 basis sets [6-311G(d,p) {207}, 6-311G(2d,p) {231}, 6-311+G(d,p) {223}, 6-311+G(2d,p) {247}, 6-311++G(d,p) {229}, 6-311++G(2d,p) {253}, cc-pVDZ {254}, cc-pVTZ {406}, cc-pVQZ {710}, cc-pV5Z {1178}, aug-cc-pVDZ {318}, aug-cc-pVTZ {546}, aug-cc-pVQZ {970}] were used for analysis of the barrier height in comparison with the frequently used B3LYP functional. The number of basis functions for the $[(CH_3)_2S\cdot Cl]$ system is given in curly brackets. Figure S.1 summarizes the results for the barrier height relative to the reactants. The M05/cc-VDZ method which worked very well for the properties of dimethyl sulfide predicts by far the smallest barrier. The barrier height converges quickly with basis sets containing diffuse functions (109.8 kJ/mol for the M05 functional), but this convergence seems to be much slower with correlation consistent basis sets than with the Pople basis sets. Moreover, diffuse functions on the light atoms do not have a large impact on the barrier height and can be neglected in this study. The relatively small 6-311+G(2d,p) {247} basis set predicts a barrier height of 109.8 kJ/mol which compares well with 110.4 kJ/mol obtained with the aug-cc-pVTZ {546}. Further, the scoring function σ_{tot} is 0.0815 for the 6-311+G(2d,p) basis set compared to 0.1243 for the aug-cc-pVTZ basis set. Table S.1 shows further that the M05 functional in combination with a triple ζ basis set provides generally a better description of dimethyl sulfide than the GGA functionals recommended by Swart *et*

al. [3]. Justified by the calculations presented here, the analysis of the conversion of $(CH_3)_3SCl$ was done using the M05 functional with the 6-311+G(2d,p) basis set.

References

[1] National Institute of Standards and Technology *NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 15b, August 2011, Editor: Russell D. Johnson III*.
URL `http://cccbdb.nist.gov/`

[2] M. J. Frisch *et al.*; *Gaussian 09*; Revision B.01; Gaussian, Inc., Wallingford CT 2010.

[3] Swart, M.; Solà, M.; Bickelhaupt, F. M. *J. Comp. Chem.* **2007**, *28*, 1551–1560.

[4] Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103–161106.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	1.808	1.8047	1.8255	1.8218	1.8048	1.8147	1.8236	1.807	1.8087	1.814
6-31+G(d,p)	1.8078	1.8046	1.8259	1.822	1.8044	1.8147	1.8241	1.8069	1.8086	1.8141
6-31++G(d,p)	1.8078	1.8046	1.8258	1.822	1.8043	1.8147	1.824	1.8069	1.8086	1.8141
6-311G(d,p)	1.8087	1.8022	1.8245	1.821	1.8035	1.8138	1.8227	1.8058	1.8076	1.8121
6-311+G(d,p)	1.8085	1.8023	1.8243	1.8208	1.8033	1.8135	1.8225	1.8056	1.8075	1.8119
6-311++G(d,p)	1.8086	1.8026	1.8244	1.8209	1.8035	1.8137	1.8225	1.8058	1.8076	1.812
D95+(d,p)	1.8112	1.8122	1.8265	1.8219	1.805	1.8152	1.8248	1.8083	1.8093	1.8145
D95++(d,p)	1.8111	1.8123	1.8265	1.8218	1.805	1.8152	1.8247	1.8082	1.8092	1.8144
cc-pVDZ	1.8129	1.8144	1.8265	1.8203	1.8033	1.8141	1.8246	1.808	1.8067	1.8152
aug-cc-pVDZ	1.8144	1.8216	1.829	1.8234	1.8059	1.8168	1.8272	1.8101	1.8094	1.8172
cc-pVTZ	1.8059	1.8038	1.819	1.816	1.7993	1.809	1.8172	1.8011	1.8061	1.8067
aug-cc-pVTZ	1.8059	1.8045	1.8191	1.8163	1.7995	1.8092	1.8173	1.8013	1.806	1.8068

Table S.2: CS bond length in $(CH_3)_2S$ calculated at various computational levels. All values given in Å. Reference value from CCCBDB [1]: 1.802 Å.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	1.0829	1.0882	1.0931	1.0968	1.0973	1.0933	1.0928	1.0933	1.0923	1.0894
6-31+G(d,p)	1.0831	1.0892	1.0936	1.0974	1.0976	1.0938	1.0934	1.0937	1.0928	1.0898
6-31++G(d,p)	1.0831	1.0892	1.0936	1.0974	1.0976	1.0939	1.0934	1.0937	1.0928	1.0898
6-311G(d,p)	1.0829	1.0925	1.0913	1.0952	1.0962	1.0919	1.0911	1.0921	1.0918	1.088
6-311+G(d,p)	1.0831	1.0927	1.0915	1.0957	1.0966	1.0923	1.0913	1.0924	1.092	1.0882
6-311++G(d,p)	1.0831	1.0926	1.0915	1.0957	1.0967	1.0923	1.0913	1.0924	1.092	1.0881
D95+(d,p)	1.0835	1.0923	1.0953	1.0992	1.0985	1.0955	1.095	1.0948	1.0931	1.0912
D95++(d,p)	1.0836	1.0921	1.0952	1.0991	1.0986	1.0954	1.095	1.0947	1.0931	1.0912
cc-pVDZ	1.0885	1.1022	1.1011	1.1039	1.1033	1.1005	1.1008	1.1003	1.0994	1.0963
aug-cc-pVDZ	1.1022	1.1006	1.0978	1.1009	1.1013	1.0976	1.0975	1.0978	1.0968	1.0937
cc-pVTZ	1.0811	1.0881	1.0891	1.0944	1.0961	1.0909	1.0889	1.0906	1.0886	1.0857
aug-cc-pVTZ	1.081	1.0887	1.0889	1.0944	1.0962	1.0908	1.0887	1.0905	1.0885	1.0856

Table S.3: Average CH bond length in $(CH_3)_2S$ calculated at various computational levels. All values given in Å. Reference value from CCCBDB [1]: 1.091 Å.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	100.1768	98.4386	99.6475	100.5473	100.6788	100.3624	99.5452	99.4667	99.2485	98.2466
6-31+G(d,p)	100.1173	98.2991	99.6194	100.5045	100.593	100.3117	99.5209	99.4118	99.2278	98.2081
6-31++G(d,p)	100.1104	98.2432	99.6139	100.5036	100.6035	100.3108	99.5142	99.4074	99.2209	98.1915
6-311G(d,p)	100.2581	98.2295	99.6939	100.7274	100.942	100.5057	99.591	99.503	99.2409	98.1633
6-311+G(d,p)	100.2472	98.1259	99.6692	100.69	100.9006	100.4735	99.5669	99.4796	99.2246	98.144
6-311++G(d,p)	100.2606	98.1211	99.6727	100.682	100.8932	100.4677	99.5684	99.4797	99.2153	98.1521
D95+(d,p)	100.1625	98.2278	99.5704	100.3587	100.571	100.1956	99.466	99.3881	99.3489	98.0557
D95++(d,p)	100.1658	98.1892	99.5674	100.3587	100.5783	100.1995	99.4625	99.3952	99.3516	98.0637
cc-pVDZ	100.1994	98.0166	99.4642	100.3346	100.7251	100.2019	99.3476	99.4511	99.0335	98.3055
aug-cc-pVDZ	100.1689	97.7688	99.4903	100.3525	100.5879	100.2006	99.3865	99.368	99.123	98.1733
cc-pVTZ	100.3355	98.0045	99.7695	100.6556	100.8399	100.4642	99.6596	99.5269	99.1877	98.2145
aug-cc-pVTZ	100.3802	97.9307	99.8115	100.7023	100.8723	100.5098	99.7022	99.5533	99.2053	98.2208

Table S.4: CSC bond angle in $(CH_3)_2S$ calculated at various computational levels. All values given in degrees. Reference value from CCCBDB [1]: 98.9°.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	109.0327	108.8533	109.0739	108.9261	108.7506	108.9157	109.069	108.9214	109.009	109.2603
6-31+G(d,p)	109.0383	108.8679	109.0668	108.8915	108.6993	108.8862	109.0607	108.8948	108.9824	109.2542
6-31++G(d,p)	109.0507	108.8949	109.0658	108.8919	108.7098	108.8882	109.0592	108.9001	108.986	109.2578
6-311G(d,p)	109.1832	108.8789	109.1754	109.0920	108.9324	109.0713	109.1731	109.0418	109.1628	109.3329
6-311+G(d,p)	109.1659	108.8685	109.1586	109.0598	108.8944	109.0433	109.1554	109.0224	109.1470	109.3273
6-311++G(d,p)	109.1756	108.8895	109.1697	109.0649	108.9014	109.0500	109.1660	109.0352	109.1570	109.3443
D95+(d,p)	109.1629	109.1276	109.1453	108.9597	108.8178	108.9653	109.1379	109.0060	109.1156	109.2929
D95++(d,p)	109.1647	109.1325	109.1412	108.9554	108.8182	108.9625	109.1336	109.0058	109.1135	109.2933
cc-pVDZ	109.2024	109.0073	109.1492	108.9815	108.8661	108.9969	109.1464	109.0440	109.0584	109.3933
aug-cc-pVDZ	109.2834	109.2912	109.2372	109.0913	108.9904	109.0944	109.2346	109.1423	109.1506	109.4990
cc-pVTZ	109.1802	109.1829	109.2003	109.0866	108.9664	109.0747	109.1965	109.1008	109.3035	109.4394
aug-cc-pVTZ	109.2131	109.3717	109.2394	109.1330	108.9995	109.1174	109.2375	109.1377	109.3311	109.4702

Table S.5: Average HCH bond angle in $(CH_3)_2S$ calculated at various computational levels. All values given in degrees. Reference value from CCCBDB [1]: 109.6°.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	1.8049	1.7796	1.7182	1.7035	1.7395	1.7227	1.7201	1.7589	1.7360	1.8080
6-31+G(d,p)	1.8619	1.8320	1.7463	1.7306	1.7541	1.7509	1.7499	1.7776	1.7605	1.8434
6-31++G(d,p)	1.8607	1.8303	1.7356	1.7106	1.7379	1.7354	1.7384	1.7686	1.7480	1.8368
6-311G(d,p)	1.8479	1.8038	1.7114	1.7196	1.7431	1.7347	1.7155	1.7443	1.6959	1.8054
6-311+G(d,p)	1.8314	1.7875	1.6873	1.6928	1.7188	1.7098	1.6906	1.7221	1.6723	1.7828
6-311++G(d,p)	1.8370	1.7939	1.6939	1.6915	1.7184	1.7111	1.6967	1.7277	1.6753	1.7920
D95+(d,p)	1.9242	1.8965	1.7801	1.7318	1.7761	1.7623	1.7812	1.8174	1.8403	1.8590
D95++(d,p)	1.9191	1.8920	1.7762	1.7280	1.7706	1.7584	1.7773	1.8127	1.8367	1.8535
cc-pVDZ	1.6702	1.6449	1.4711	1.4295	1.5205	1.4698	1.4678	1.5455	1.4840	1.5982
aug-cc-pVDZ	1.8084	1.7922	1.6301	1.5709	1.6001	1.6048	1.6316	1.6614	1.6363	1.7342
cc-pVTZ	1.7257	1.7060	1.5598	1.5046	1.5512	1.5392	1.5586	1.6009	1.5289	1.6658
aug-cc-pVTZ	1.7757	1.7559	1.6037	1.5620	1.5847	1.5913	1.6051	1.6320	1.5663	1.6957

Table S.6: Dipole moment of $(CH_3)_2S$ calculated at various computational levels. All values given in Debye. Reference value from CCCBDB [1]: 1.5 Debye.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	286.5	278.1	258.8	261.3	263.6	264.8	259.5	263.2	275.7	263.5
6-31+G(d,p)	287.3	279.5	259.9	262.5	264.6	265.9	260.7	264.4	277.2	265.3
6-31++G(d,p)	287.1	279.6	259.7	262.4	264.5	265.8	260.5	264.2	277.1	265.1
6-311G(d,p)	284.7	273.5	259.4	261.4	261.8	264.5	260.1	261.8	269.9	267.3
6-311+G(d,p)	285.0	276.7	259.8	261.9	262.5	265.0	260.5	262.2	270.6	267.8
6-311++G(d,p)	285.0	277.1	259.6	261.7	262.1	264.8	260.3	262.0	270.6	268.0
D95+(d,p)	283.2	270.9	259.6	263.4	264.8	266.1	260.3	263.1	276.4	268.1
D95++(d,p)	283.3	271.4	259.6	263.3	264.7	266.1	260.3	263.0	276.4	268.2
cc-pVDZ	282.1	267.1	257.2	262.8	265.5	265.4	257.8	261.4	276.2	259.0
aug-cc-pVDZ	279.5	260.7	254.7	259.0	260.9	261.8	255.4	258.3	274.6	256.6
cc-pVTZ	282.3	264.3	258.6	260.9	260.5	263.7	259.3	259.9	269.4	261.8
aug-cc-pVTZ	282.1	265.5	258.2	260.7	260.5	263.4	258.9	259.5	268.6	262.0

Table S.7: CSC scissoring vibration (A_1) in $(CH_3)_2S$ calculated at various computational levels. All values given in cm^{-1}. Reference value from CCCBDB [1]: 282 cm^{-1}.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	752.5	741.7	685.6	679.5	708.4	696.4	689.4	720.2	712.8	723.7
6-31+G(d,p)	751.8	739.6	683.3	677.3	707.5	694.6	687.1	719.0	711.1	722.6
6-31++G(d,p)	751.8	739.6	683.2	677.2	707.4	694.5	687.0	718.9	711.0	722.5
6-311G(d,p)	743.6	739.3	678.2	672.1	702.1	689.3	682.0	713.5	706.5	716.5
6-311+G(d,p)	744.1	739.1	678.4	672.0	702.1	689.3	682.1	713.6	706.7	716.9
6-311++G(d,p)	744.3	738.8	678.5	672.1	702.1	689.3	682.3	713.7	706.8	717.1
D95+(d,p)	753.9	735.0	689.8	685.0	713.5	701.5	693.5	724.2	720.1	725.8
D95++(d,p)	753.8	734.8	689.7	684.9	713.5	701.4	693.4	724.2	720.1	725.7
cc-pVDZ	737.8	726.7	683.0	680.9	709.5	696.2	686.8	716.9	717.6	718.0
aug-cc-pVDZ	737.6	712.6	678.8	676.5	707.1	692.3	682.5	714.4	712.4	717.7
cc-pVTZ	742.4	727.0	680.6	676.4	707.0	692.8	684.4	716.5	711.3	716.3
aug-cc-pVTZ	741.5	725.1	679.9	675.2	706.0	691.7	683.6	715.6	711.1	716.4

Table S.8: CS symmetrical stretch (A_1) in $(CH_3)_2S$ calculated at various computational levels. All values given in cm^{-1}. Reference value from CCCBDB [1]: 695 cm^{-1}.

	HF	MP2	B3LYP	OLYP	OPBE	O3LYP	X3LYP	PBE1PBE	M05	M05-2X
6-31G(d,p)	816.3	796.9	738.0	731.4	761.9	750.3	742.1	774.6	762.2	779.9
6-31+G(d,p)	815.3	794.3	735.7	729.0	760.6	748.3	739.7	773.2	760.5	778.8
6-31++G(d,p)	815.3	794.0	735.5	728.9	760.7	748.3	739.5	773.1	760.4	778.7
6-311G(d,p)	806.1	791.5	729.4	723.8	756.1	742.8	733.4	766.9	755.4	771.4
6-311+G(d,p)	806.6	790.8	729.6	723.8	756.1	742.8	733.6	767.1	755.6	771.4
6-311++G(d,p)	806.7	790.5	729.7	723.8	756.1	742.9	733.7	767.2	755.7	771.7
D95+(d,p)	816.9	788.8	741.4	736.3	767.1	754.8	745.4	778.1	768.8	781.6
D95++(d,p)	816.6	788.4	741.3	736.2	767.0	754.7	745.2	778.0	768.7	781.5
cc-pVDZ	800.4	779.2	733.5	730.9	762.1	748.4	737.4	770.0	765.9	774.1
aug-cc-pVDZ	800.6	764.6	730.3	727.4	760.1	745.3	734.2	768.1	761.6	775.1
cc-pVTZ	805.3	779.8	732.8	728.4	761.1	746.6	736.7	770.6	760.7	771.7
aug-cc-pVTZ	804.7	777.4	732.2	727.3	760.0	745.7	736.1	769.8	760.6	771.7

Table S.9: CS asymmetrical stretch (B_2) in $(CH_3)_2S$ calculated at various computational levels. All values given in cm^{-1}. Reference value from CCCBDB [1]: 743 cm^{-1}.

S.2 Additional graphics

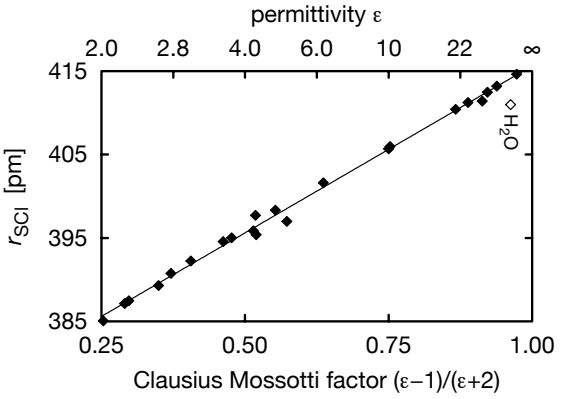

Figure S.2: Distance between S and Cl in $[(CH_3)_3S^+ \cdot Cl^-]^{tri}_{(sol)}$ as a function of *cmf*. The data point for water (marked in the plot with an empty diamond) as an obvious outlier was not included into the data set for the linear regression.

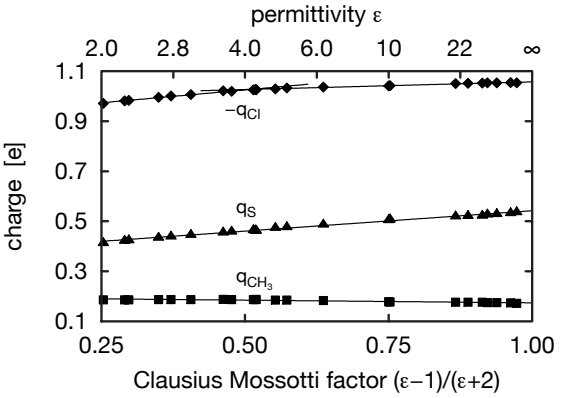

Figure S.3: ATP charges in the tripod ion pair. $-q_{Cl}$: diamonds, q_S: triangles, q_{CH_3}: squares.

S.3 Annotated list of all symbols

$[(CH_3)_3SCl]$	Concentration of the salt $(CH_3)_3SCl$
$[(CH_3)_3S^+ \cdot Cl^-]$	Ion pair concentration
$[(CH_3)_3S]$	Concentration of the $(CH_3)_3S^+$ cation
$[Cl^-]$	Concentration of the Cl^- anion
C_{ax}	C atom in an axial position
C_{eq}	C atom in an equatorial position
$G^\ddagger$	Gibbs free energy of linear transition state
G_{ip}	Gibbs free energy of the tripod ion pair
G_{free}	Gibbs free energy of the free ions
K_{H_2O}	Equilibrium constant for reaction 1 in water
K_A	Association constant
R	Ideal gas constant
T	Temperature
WBI	Wiberg bond index
X_{ip}	Mole fraction of the ion pair in solution.
$\Delta E^\ddagger$	Energy difference between the linear transition state and the free ions
$\Delta E^\ddagger_{H_2O}$	$\Delta E^\ddagger$ for reaction 1 in water
ΔE^{ZP}_{reac}	Zero point corrected version of ΔE_{reac}
ΔE_{reac}	Change in electronic energy for reaction 1
ΔE_{S_N1}	Combined electronic energies of CH_3^+, $(CH_3)_2S$ and Cl^- relative to the combined electronic energies of the free ions
ΔE_{ip}	Electronic energy relative to that of the tripod ion pair
ΔE_{pro}	Electronic energy of the products relative to that of the free ions
ΔE_{see}	Electronic energy of the seesaw ion pair relative to that of the free ions
ΔE_{tri}	Electronic energy of the tripod ion pair relative to that of the free ions
$\Delta G^\ddagger$	Gibbs free energy of the linear transition state relative to that of the free ions
$\Delta G^\ddagger_{EtOH}$	$\Delta G^\ddagger$ in ethanol
$\Delta G^\ddagger_{H_2O}$	$\Delta G^\ddagger$ in water
$\Delta G^\ddagger_{mix}$	Effective value of $\Delta G^\ddagger$ as defined in Equation 33
$\Delta G^\ddagger_{ip}$	Gibbs free energy of the linear transition state relative to that of the tripod ion pair
$\Delta G^\ddagger_{front}$	Gibbs free energy of a transition state for a frontside attack relative to that of the free ions
ΔG_{S_N1}	Combined Gibbs free energies of CH_3^+, $(CH_3)_2S$ and Cl^- relative to the combined Gibbs free energies of the free ions
ΔG_{ip}	Gibbs free energy of the tripod ion pair relative to that of the free ions
ΔG_{diss}	Change in Gibbs free energy for the dissociation of a product cluster
ΔG_{pro}	Gibbs free energy of the products relative to the free ions
ΔG_{reac}	Change in Gibbs free energy for reaction 1
ΔG_{see}	Gibbs free energy of the seesaw ion pair relative to that of the free ions
ΔG_{tri}	Gibbs free energy of the tripod ion pair relative to that of the free ions

$\Delta H^{\ddagger}$	Enthalpy of the linear transition state relative to that of the free ions
ΔH_{reac}	Change in enthalpy for reaction 1
$\Delta U^{\ddagger}$	Inner energy of the linear transition state relative to that of the free ions
ΔU_{reac}	Change in inner energy for reaction 1
$\Delta\mu_i$	Difference in dipole moment between experiment and calculation for $(CH_3)_2S$
$\Delta\omega_i$	Difference in bond angle between experiment and calculation for $(CH_3)_2S$
$\Delta\rho$	Change in electron density, PCM model
$\Delta\rho^{\mathrm{ex}}$	Change in electron density, explicit water molecules
$\Delta\xi$	Change in stoechiometric factors
Δf_i	Difference in frequency between experiment and calculation for $(CH_3)_2S$
Δr_i	Difference in bond length between experiment and calculation for $(CH_3)_2S$
$\Delta^{\mathrm{back}}_{\mathrm{front}} E^{\ddagger}$	Electronic energy difference between a transition states for a frontside attack and that for the backside attack
$\Delta^{\mathrm{back}}_{\mathrm{front}} G^{\ddagger}$	Gibbs free energy difference between a transition states for a frontside attack and that for the backside attack
$\Delta^{\mathrm{back}}_{\mathrm{front}} q^{\mathrm{NBO}}_{\mathrm{CH_3}}$	Difference in NBO charge on the moving CH_3 group between a transition states for a frontside attack and that for the backside attack
$\Delta^{\mathrm{tri}}_{\mathrm{see}} G$	Difference in Gibbs free energy between the seesaw and the tripod ion pair
$\Delta_{12} G$	Change in Gibbs free energy for reaction 12
$\Delta_{14} E^{\ddagger}$	Electronic energy of the transition state of reaction 14 relative to that of the reactants H_2O and $(CH_3)_3S^+$
$\Delta_{14} G^{\ddagger}$	Gibbs free energy of the transition state of reaction 14 relative to that of the reactants H_2O and $(CH_3)_3S^+$
$\Delta_{16} G$	Change in Gibbs free energy of reaction 16
$\Delta_{17} G$	Change in Gibbs free energy of reaction 17
$\Delta_{19} E^{\ddagger}$	Electronic energy of the transition state for reaction relative to that of the reactants CH_3Cl and H_2O
$\Delta_{19} G^{\ddagger}$	Gibbs free energy of the transition state for reaction relative to that of the reactants CH_3Cl and H_2O
$\Delta_{19} G$	Change in Gibbs free energy of reaction 19
$\Delta_{19} H^{\ddagger}$	Enthalpy of the transition state for reaction relative to that of the reactants CH_3Cl and H_2O
$\Delta_{20} G$	Change in Gibbs free energy of reaction 20
χ	Acceleration factor, prototype given in Equation 31
$\chi_{1\mathrm{M}}$	Acceleration factor (Equation 31), using Equation 33 for the difference in Gibbs free energy and an initial $(CH_3)_3SCl$ salt concentration of 1 M
$\chi_{20\mathrm{mM}}$	Acceleration factor (Equation 31), using Equation 33 for the difference in Gibbs free energy and an initial $(CH_3)_3SCl$ salt concentration of 20 mM
$\chi_{10\mathrm{mM}}$	Acceleration factor (Equation 31), using Equation 33 for the difference in Gibbs free energy and an initial $(CH_3)_3SCl$ salt concentration of 10 mM
$\chi_{1\mathrm{mM}}$	Acceleration factor (Equation 31), using Equation 33 for the difference in Gibbs free energy and an initial $(CH_3)_3SCl$ salt concentration of 1 mM
χ_{fi}	Acceleration factor (Equation 31) for reaction 1 starting from free ions
χ_{ip}	Acceleration factor (Equation 31) for reaction 1 starting from an ion pair

δG	Correction to standard Gibbs free energy from quantum calculations for particle densities (Equation 7)
ϵ	Dielectric constant of a solvent
$\mathrm{p}K_\mathrm{A}$	Negative decadic logarithm of the acid constant K_A
μ	Calculated dipole moment
μ^ref	Measured dipole moment of $(CH_3)_2S$ used as reference value
ω_1	Optimised CSC bond angle
ω_2	Optimised, average HCH angle
ω_i^ref	Experimental reference values of the calculated bond angles
ρ	Electron density
$\rho_{C_6H_{12}}$	Electron density in cyclohexane
ρ_{H_2O}	Electron density in water, PCM
$\rho_{H_2O}^\mathrm{ex}$	Electron density in water, explicit solvent molecules
ρ_vac	Electron density in the vacuum
σ_tot	Quality function to judge computational methods on the basis of experimental data for $(CH_3)_2S$
ξ_pro	Stoechiometric factors of the products
ξ_rea	Stoechiometric factors of the reactants
ξ_i	Stoechiometric factors of a compound
c_0	initial $(CH_3)_3SCl$ salt concentration
cmf	Clausius Mossotti factor
e	Elementary positive charge
f_i^ref	Experimental reference values for the frequency of vibrations involving the CS bonds in $(CH_3)_2)S$
$f_{1...3}$	Calculated frequencies for vibrations involving the the CS bonds in $(CH_3)_2S$
h	Planck constant
k_A	Rate constant for the formation of an ion pair (association)
k'_A	Rate constant for the dissociation of an ion pair
k_B	Boltzmann constant
k_{29}	Rate constant as defined in Equation 29
k_{28}	Rate constant as defined in Equation 28
k_{19}	Rate constant as defined in Equation 19
k_{14}	Rate constant as defined in Equation 14
k_fi	Rate constant for the reaction starting from free ions
$k_\mathrm{fi}^\mathrm{EtOH}$	Rate constant for the reaction starting from free ions in ethanol
$k_\mathrm{fi}^{H_2O}$	Rate constant for the reaction starting from free ions in water
k_fi	Rate constant for the reaction starting from free ions
k_ip	Rate constant for the reaction starting from ion pairs
p	Pressure
q^APT	APT charge
$q_\mathrm{Cl}^\mathrm{APT}$	APT charge on the chlorine atom
q^NBO	NBO charge
$q_{CH_3}^\mathrm{NBO}$	NBO charge on the moving CH_3 group
$q_\mathrm{Cl}^\mathrm{NBO}$	NBO charge on the chlorine atom

r	Bond distance
r_1	Calculated CS bond length in $(CH_3)_2S$
r_2	Calculated average CH bond length in $(CH_3)_2S$
r_i^{ref}	Experimental reference values for r_1 and r_2
$r_{\mathrm{C\cdots S}}$	Distance between the C atom in the moving CH_3 group and the S atom
$r_{\mathrm{Cl\cdots C}}$	Distance between the Cl atom and the C atom in the moving CH_3 group
$r_{\mathrm{S\cdots Cl}}$	Distance between the Cl and S atom
v	rate of a reaction
v_{fi}	rate of reaction 1 starting from free ions
v_{ip}	rate of reaction 1 starting from ion pairs
$C_{2\mathrm{v}}$	Point group in Schoenflies notation

S.4 Computational setup for calculations with explicit solvent molecules

These calculations are targeted to create structural models for solvation shells.

- homebrew code
- Gaussian 09 for the calculation of forces and energies
  `oniom(olyp/6-31G(d,p):amber=softfirst)=embedcharge`
- Amber force force field for the solvent
  - Parameter used as defined in Gaussian 09
  - Sulphur parameter from Biochemistry 41 (2002) 7636-7646
    The parameter for the CT-CT-CT-H1 dihedral angle as defined in G09 were used for the CT-SP-CT-H1 dihedral angle, because they reproduce the quantum results better.
  - Chloride parameter from J. Phys. Chem. B 112 (2008) 9020-9041
- oniom(olyp/6-31G(d,p) for $(CH_3)_3S^+$, Cl^-, $(CH_3)_2S$ and CH_3Cl
- spherical boundaries for the reaction vessel, no frozen hydrogen atoms
- sphere radius chosen to reproduce the experimental density of 300 water molecules at 298 K
- molecules placed into the equilibrated H_2O cluster in an optimised position to minimize the number of H_2O molecules to be removed from the cluster
- leap frog algorithm for the integration, 0.5 step size, 40000 steps for production runs
- Berendsen thermostat, 100 fs coupling constant
- size of the solvation shells from radial distribution functions
- DFT calculations on the solute with the first solvation shell every 50 fs

S.5 Detailed data on the chloride ion

solvent	ϵ	E	G
Cyclo hexane	2.0165	−460.350921526	−460.365944
Carbon tetrachloride	2.228	−460.356252664	−460.371275
Benzene	2.2706	−460.357206769	−460.372230
Carbon disulfide	2.6105	−460.363707826	−460.378731
Tetralin	2.771	−460.366225009	−460.381248
Dibutyl ether	3.0473	−460.369938942	−460.384962
Diethyl amine	3.5766	−460.375454872	−460.390478
Diphenyl ether	3.73	−460.376761538	−460.391784
Ethyl phenyl ether	4.1797	−460.380040453	−460.395063
Anisole	4.2247	−460.380330217	−460.395353
Ether	4.24	−460.380427338	−460.395450
Chloroform	4.7113	−460.383110575	−460.398133
1-Bromo octane	5.0244	−460.384615287	−460.399638
Acetic acid	6.2528	−460.389065230	−460.404088
Pentanal	10.0	−460.395890752	−460.410914
Dichloro ethane	10.125	−460.396031427	−460.411054
Acetone	20.493	−460.401727328	−460.416750
Ethanol	24.852	−460.402703381	−460.417726
Methanol	32.613	−460.403795516	−460.418818
Nitro methane	36.562	−460.404173277	−460.419196
Dimethylsulfoxide	46.826	−460.404857156	−460.419880
water	78.3553	−460.405837513	−460.420860
formamide	108.94	−460.406246313	−460.421269

Table S.10: SCF energy (E) with the include thermal correction (G) of the chloride ion in various environments.

S.6 Selected cluster geometries in formamide

S.6.1 $(CH_3)_3S^+$ in formamide

```
Cartesian coordinates (input orientation)
C      0.000000     1.613189     0.267720
H      0.000000     1.493797     1.348817
H      0.891918     2.131560    -0.077967
H     -0.891918     2.131560    -0.077967
C     -1.396301    -0.806489     0.265252
H     -1.394354    -1.838957    -0.077514
H     -1.298429    -0.743108     1.346581
H     -2.291417    -0.297268    -0.085074
C      1.396301    -0.806489     0.265252
H      1.394354    -1.838957    -0.077514
H      2.291417    -0.297268    -0.085074
H      1.298429    -0.743108     1.346581
S      0.000000     0.001537    -0.525133

SCF energy       : -517.694478702
Gibbs free energy: -517.607903

Frequencies
 169.3402   219.5202   228.9316   269.8743   282.1918   317.4057   657.2160
 734.5454   744.4695   904.2649   942.0754   948.3214  1046.9754  1051.9076
1059.8527  1329.0790  1330.1105  1363.9303  1417.8433  1423.1961  1425.1386
1436.0831  1438.3769  1448.1304  3089.2996  3092.3322  3100.1151  3203.5462
3207.9565  3210.2019  3211.6159  3213.7950  3218.8677
```

S.6.2 Tripod ion pair in formamide

```
Cartesian coordinates (standard orientation)
C      0.770451    -0.708220     1.447033
H     -0.311530    -0.644534     1.330990
H      1.116682    -1.737873     1.513963
H      1.126860    -0.139191     2.303588
C      0.748637     1.607033    -0.110020
H      1.083748     2.063916    -1.039394
H     -0.331593     1.462147    -0.087315
H      1.103402     2.188134     0.739091
C      0.743245    -0.900405    -1.334597
H      1.075988    -0.449175    -2.267244
H      1.095245    -1.928380    -1.272079
H     -0.336428    -0.825605    -1.203833
S      1.554305     0.002575    -0.007372
Cl    -2.592074    -0.001241     0.005041
```

```
SCF energy       : -978.107694287
Gibbs free energy: -978.025877

Frequencies
  73.7983    80.1683    96.5763   201.2943   222.8131   224.8322   273.3777
 277.2243   310.6521   653.5617   728.4497   737.9062   910.0168   953.8382
 958.0530  1052.7528  1055.8359  1066.5527  1322.7824  1325.4396  1355.9645
1418.7103  1422.9881  1432.3172  1440.1025  1444.7431  1447.1542  3067.5443
3069.8115  3071.4575  3188.0688  3189.8749  3192.4927  3200.7730  3203.1933
3207.5012
```

S.6.3 Linear ion pair in formamide

```
Cartesian coordinates (standard orientation)
C      2.146903    -1.398078     0.453944
H      1.756754    -1.306445     1.465290
H      1.771843    -2.293090    -0.038020
H      3.234639    -1.393868     0.442367
C      2.146194     1.398474     0.453747
H      1.771270     2.293254    -0.038743
H      1.755472     1.307105     1.464901
H      3.233931     1.394398     0.442798
C     -0.164761    -0.000319    -0.264162
H     -0.563818     0.889049    -0.745394
H     -0.563562    -0.889761    -0.745462
H     -0.374284    -0.000353     0.802215
S      1.612010    -0.000020    -0.540848
Cl    -3.681437    -0.000025     0.102497

SCF energy       : -978.102981873
Gibbs free energy: -978.022196

Frequencies
  49.2308    63.0262    76.0440   165.9737   209.4604   220.2989   270.4543
 278.3271   311.2423   655.5575   734.9000   740.8411   912.8708   945.4531
 954.5043  1040.8156  1057.7884  1060.5935  1328.6157  1336.2070  1365.6360
1415.6126  1424.5259  1428.2589  1433.8104  1434.1870  1447.6554  3093.7083
3097.4291  3111.0030  3209.6370  3211.8062  3212.8341  3215.7583  3227.3705
3229.4757
```

S.6.4 Linear transition state in formamide

```
Cartesian coordinates (standard orientation)
C      1.630742     1.226506     1.388870
H      0.767202     1.889283     1.335623
```

```
H      1.584772     0.626794     2.296531
H      2.555047     1.802304     1.377490
C      1.630742     1.226506    -1.388870
H      1.584772     0.626794    -2.296531
H      0.767202     1.889283    -1.335623
H      2.555047     1.802304    -1.377490
C     -0.676128    -0.561324     0.000000
H     -0.528471    -1.080972    -0.929712
H     -0.528471    -1.080972     0.929712
H     -0.947568     0.479207     0.000000
S      1.630742     0.074621     0.000000
Cl    -2.906679    -1.146946     0.000000

SCF energy       : -978.062540272
Gibbs free energy: -977.983698

Frequencies
-598.9327    70.8926    74.5423    89.3684   163.4433   178.0937   208.8970
 249.7157   257.5035   287.7637   697.4580   748.7533   920.3690   942.3503
 967.7096   997.3177  1004.5227  1046.4356  1057.0836  1318.9779  1344.0390
1357.2082  1365.6073  1428.6011  1436.8972  1441.6286  1446.9927  3069.9910
3070.8488  3167.9129  3171.6595  3171.7171  3181.3366  3182.2231  3374.5829
3383.5083
```

S.6.5 Immediate product cluster in formamide

```
Cartesian coordinates (standard orientation)
C     -1.857306     1.411852     0.519651
H     -0.994425     1.243488     1.165628
H     -1.686732     2.304513    -0.081298
H     -2.754077     1.551003     1.123881
C     -2.325838    -1.309871     0.553925
H     -2.468786    -2.221861    -0.024594
H     -1.452776    -1.425987     1.197453
H     -3.213803    -1.124884     1.159129
C      1.621731    -0.100855    -0.303126
H      1.529768    -0.596524    -1.264580
H      1.246922     0.916876    -0.355633
H      1.109165    -0.662269     0.472674
S     -2.070811     0.032976    -0.630305
Cl     3.363894    -0.030513     0.121737

SCF energy       : -978.097049969
Gibbs free energy: -978.019990
```

```
Frequencies
  31.5210    59.2192    69.7531    75.1645   110.9013   115.8947   195.1474
 200.0102   276.1201   701.5707   730.1288   754.6109   914.4378   956.3481
 987.6363  1033.7728  1037.7112  1061.4718  1319.5721  1342.2055  1365.4611
1433.4378  1442.3363  1445.8308  1447.4356  1452.2637  1462.0072  3060.9132
3064.2296  3104.0602  3145.9164  3153.9599  3171.3025  3174.2806  3214.3999
3221.7435
```

S.6.6 CH_3Cl in formamide

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134645
H      0.000000     1.033617    -1.468236
H      0.895138    -0.516808    -1.468236
H     -0.895138    -0.516808    -1.468236
Cl     0.000000     0.000000     0.659563

SCF energy       : -500.112917812
Gibbs free energy: -500.097799

Frequencies
 722.0195  1029.8359  1030.7071  1356.6864  1449.9848  1450.1278  3100.6679
3214.1278  3214.2659
```

S.6.7 $(CH_3)_2S$ in formamide

```
Cartesian coordinates (standard orientation)
C     -1.381445    -0.510553     0.000001
H     -1.357032    -1.134818     0.894039
H     -2.296975     0.080314    -0.000006
H     -1.357035    -1.134822    -0.894038
C      1.381445    -0.510553     0.000001
H      2.296975     0.080314    -0.000015
H      1.357037    -1.134812     0.894044
H      1.357030    -1.134828    -0.894033
S      0.000000     0.656581     0.000000

SCF energy       : -477.982273002
Gibbs free energy: -477.933766

Frequencies
 187.5543   202.3516   270.5971   699.7143   750.6508   912.7005   948.0089
 981.0100  1036.9320  1313.0675  1335.4274  1430.9159  1440.0397  1445.8738
1450.6268  3050.0491  3053.5234  3135.9841  3144.2772  3163.8294  3165.4571
```

S.6.8 CH_3^+ in formamide

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000005    -0.000020
H      0.172503     1.071625     0.000040
H      0.842245    -0.685124     0.000039
H     -1.014617    -0.386533     0.000040

SCF energy       : -39.5708446881
Gibbs free energy: -39.558408

Frequencies
1377.2830  1382.4684  1405.6089  3084.7643  3286.6614  3292.5066
```

S.7 Selected cluster geometries in water

S.7.1 $(CH_3)_3S^+$ in water

```
Cartesian coordinates (input orientation)
C      0.000000     1.613173     0.271599
H      0.000000     1.493599     1.352669
H      0.891897     2.131585    -0.074039
H     -0.891897     2.131585    -0.074039
C     -1.395752    -0.806475     0.270030
H     -1.394784    -1.838558    -0.073876
H     -1.295826    -0.744311     1.351244
H     -2.291185    -0.296407    -0.078190
C      1.395752    -0.806475     0.270030
H      1.394784    -1.838558    -0.073876
H      2.291185    -0.296407    -0.078190
H      1.295826    -0.744311     1.351244
S      0.000000     0.001559    -0.521293

SCF energy       : -517.694165921
Gibbs free energy: -517.607594

Frequencies
 164.0708   222.4960   229.8099   271.9872   281.6985   317.7987   657.4865
 734.6527   744.4657   904.0014   941.6982   948.7244  1047.6644  1051.6064
1060.4654  1329.1941  1329.7359  1364.3606  1416.9690  1423.2144  1425.4876
1436.4000  1438.2950  1448.5125  3088.7870  3092.4409  3100.1637  3203.0428
3208.2375  3209.9367  3211.6185  3213.8867  3218.9324
```

S.7.2 Tripod ion pair in water

```
Cartesian coordinates (standard orientation)
C      0.726805    -0.132936     1.604861
H     -0.352589    -0.120070     1.449641
H      1.067379    -1.064168     2.053621
H      1.067464     0.712783     2.199442
C      0.755063     1.457872    -0.688064
H      1.108270     1.544516    -1.713651
H     -0.326790     1.332606    -0.633554
H      1.100943     2.307641    -0.102783
C      0.748951    -1.324203    -0.918648
H      1.120793    -1.257858    -1.939134
H      1.072342    -2.259306    -0.465559
H     -0.331979    -1.191790    -0.863583
S      1.544169    -0.002192     0.007265
Cl    -2.565732     0.001548    -0.005269

SCF energy       : -978.107395720
Gibbs free energy: -978.025385

Frequencies
  78.7708    81.4860   101.1909   203.7689   227.2167   234.6869   272.2572
 275.5533   311.0170   652.0566   726.9130   733.5431   911.3167   954.2041
 958.0317  1053.9182  1056.5037  1067.0561  1323.2010  1325.9441  1357.0359
1419.5063  1424.5113  1432.2134  1442.0843  1445.1623  1445.9429  3065.0599
3067.6883  3070.6238  3186.1656  3188.7951  3191.5194  3198.1875  3206.4797
3209.3967
```

S.7.3 Linear ion pair in water

```
Cartesian coordinates (standard orientation)
C     -2.144705     1.398138     0.454116
H     -1.753681     1.306462     1.465130
H     -1.770040     2.293182    -0.038105
H     -3.232457     1.393891     0.443488
C     -2.144929    -1.398004     0.454185
H     -1.770301    -2.293126    -0.037924
H     -1.753993    -1.306279     1.465228
H     -3.232680    -1.393654     0.443452
C      0.166306    -0.000133    -0.265153
H      0.564882    -0.889563    -0.746626
H      0.565009     0.889236    -0.746635
H      0.376416    -0.000140     0.801094
S     -1.610606     0.000000    -0.540974
Cl     3.677442    -0.000001     0.102799
```

```
SCF energy       : -978.102601172
Gibbs free energy: -978.021841

Frequencies
  46.9785    62.6934    78.2546   161.7675   210.3503   218.6146   272.8046
 279.9558   310.9473   655.8748   734.9211   741.0256   914.3529   945.6782
 953.8338  1040.1185  1060.6273  1060.8308  1328.4714  1336.5255  1366.7212
1415.1318  1424.6240  1428.4054  1434.0341  1434.7372  1447.8104  3092.9525
3097.1560  3111.2979  3208.8726  3211.3183  3212.6410  3215.5811  3227.8747
3229.6992
```

S.7.4 Seesaw ion pair in water

```
Cartesian coordinates (standard orientation)
Cl     2.795429    -0.000008    -0.161385
S     -0.917769     0.000005    -0.421684
C     -0.446756    -1.397136     0.604869
C     -2.708851    -0.000047    -0.272016
C     -0.446800     1.397190     0.604836
H     -0.912689    -1.311928     1.584387
H     -2.996498    -0.000053     0.777002
H     -0.912899     1.312088     1.584284
H     -0.774819    -2.294240     0.083606
H     -3.067789     0.891001    -0.782901
H      0.641773     1.357657     0.658793
H      0.641827    -1.357679     0.658638
H     -3.067739    -0.891114    -0.782904
H     -0.774708     2.294282     0.083453

SCF energy       : -978.106476823
Gibbs free energy: -978.024488

Frequencies
  41.6038    94.7495   113.8530   202.4900   216.2330   249.6362   271.1091
 290.4092   322.5209   657.7309   741.3529   744.2917   910.9168   952.0176
 953.8614  1055.7819  1056.9377  1067.0228  1321.9955  1326.7671  1358.1328
1419.5263  1429.2116  1430.8976  1434.6798  1447.0225  1455.0825  3071.4702
3073.7156  3092.3549  3187.2052  3189.6721  3199.5622  3201.6561  3207.5086
3209.9730
```

S.7.5 Linear transition state in water

```
Cartesian coordinates (standard orientation)
C      1.630627     1.225724     1.388862
H      0.766901     1.888285     1.335830
```

```
H      1.585002     0.626003     2.296539
H      2.554799     1.801733     1.377289
C      1.630627     1.225724    -1.388862
H      1.585002     0.626003    -2.296539
H      0.766901     1.888285    -1.335830
H      2.554799     1.801733    -1.377289
C     -0.675332    -0.561010     0.000000
H     -0.528498    -1.080905    -0.929707
H     -0.528498    -1.080905     0.929707
H     -0.946837     0.479504     0.000000
S      1.630627     0.073852     0.000000
Cl    -2.906773    -1.145529     0.000000

SCF energy       : -978.062405924
Gibbs free energy: -977.983541

Frequencies
-598.7029    71.3143    75.5141    89.6547   162.1988   178.4143   209.3640
 249.8799   257.7851   288.2066   697.4962   748.7668   920.3524   942.2073
 967.9324   997.7047  1004.5095  1046.6181  1056.9610  1318.9764  1344.3115
1357.3194  1365.6738  1428.6413  1436.6964  1441.7434  1447.1570  3069.9563
3070.7128  3167.8672  3171.5639  3171.6519  3181.3232  3182.1682  3374.5519
3383.4926
```

S.7.6 Transition state for a frontside attack

```
Cartesian coordinates (standard orientation)
C      1.257235    -0.658095     1.386361
H      2.107376    -1.339159     1.344419
H      1.310332    -0.061560     2.296036
H      0.313680    -1.200473     1.344394
C      1.256828    -0.658503    -1.386275
H      0.313455    -1.201151    -1.343591
H      1.309199    -0.062201    -2.296144
H      2.107213    -1.339281    -1.344638
C     -1.054522     1.838414    -0.000128
H     -2.113519     1.665881    -0.000068
H     -0.580747     2.120319     0.926362
H     -0.580838     2.120027    -0.926773
S      1.342329     0.488991    -0.000141
Cl    -2.024745    -0.685716     0.000147

SCF energy       : -978.013795005
Gibbs free energy: -977.937440
```

```
Frequencies
-431.5468    31.6292    80.7718   111.6569   116.9973   141.1474   162.7692
 209.3373   258.3316   296.1168   665.1265   670.8840   707.9399   757.7844
 922.7695   940.6617   970.9202  1046.9278  1114.2616  1306.9204  1328.4566
1380.5966  1414.2357  1424.4217  1436.9624  1437.9600  1445.7289  3066.6276
3067.3409  3168.8734  3170.7591  3180.8257  3181.6770  3182.3348  3367.2056
3397.2626
```

S.7.7 Transition state for an attack from the seesaw ion pair

```
Cartesian coordinates (standard orientation)
Cl    -2.341495    -0.255508    -0.216337
S      0.907111    -0.188601    -0.532591
C     -0.691864     1.597782     0.651888
C      2.457658     0.656764    -0.170245
C      0.940490    -1.457819     0.747696
H      0.048521     1.344047     1.393226
H      2.426507     1.100447     0.827265
H      1.057284    -1.004675     1.732706
H     -0.387617     2.183044    -0.201391
H      3.287701    -0.046278    -0.236420
H     -0.012448    -1.979235     0.689018
H     -1.707459     1.692275     0.986106
H      2.580571     1.438499    -0.918263
H      1.760868    -2.147237     0.550904

SCF energy       : -978.015569838
Gibbs free energy: -977.938748

Frequencies
-450.3637    60.6308    81.3637    95.5328   124.1995   140.4380   178.4673
 184.8577   276.8650   304.1966   658.7410   694.5404   709.2761   749.7935
 910.2363   945.4087   972.1773  1036.7091  1093.5305  1316.5696  1335.9649
1384.3861  1420.5272  1428.5342  1437.5375  1439.1680  1445.6116  3058.9616
3068.2336  3152.2929  3162.6560  3168.6395  3178.2389  3194.5008  3345.2845
3380.3597
```

S.7.8 Immediate product cluster

```
Cartesian coordinates (standard orientation)
C     -1.788909     1.421537     0.506024
H     -0.913985     1.232237     1.129801
H     -1.607562     2.303823    -0.107009
H     -2.664093     1.592952     1.133247
C     -2.352690    -1.282065     0.576005
H     -2.540739    -2.193061     0.008776
```

```
H     -1.470087    -1.424195     1.200939
H     -3.219786    -1.060986     1.199259
C      1.622886    -0.181805    -0.341708
H      1.572204    -0.878443    -1.173004
H      1.256186     0.797478    -0.633917
H      1.073138    -0.560454     0.514891
S     -2.077713     0.041311    -0.625979
Cl     3.345319    -0.012725     0.135339

SCF energy       : -978.096977080
Gibbs free energy: -978.019962

Frequencies
  49.0210    57.9679    66.0257    74.3909    93.7359   107.6300   186.0817
 196.4710   275.5391   704.0163   724.9299   758.2495   914.2095   954.8969
 986.6001  1029.0010  1037.0126  1046.0114  1318.9364  1342.2677  1356.4985
1433.0721  1442.2275  1445.1822  1446.6327  1450.3607  1459.0278  3058.3851
3061.9710  3109.1800  3144.0719  3152.3421  3170.0301  3172.0868  3220.9668
3224.3485
```

S.7.9 Asymmetric bifurcated product cluster

```
Cartesian coordinates (standard orientation)
C     -1.743604     1.458042    -0.062615
H     -0.731821     1.712610     0.254613
H     -2.001585     2.039841    -0.947176
H     -2.456179     1.678816     0.732816
C     -1.392125    -1.051595     1.042947
H     -1.409074    -2.130241     0.889346
H     -0.390114    -0.745748     1.346773
H     -2.115110    -0.787316     1.815204
C      2.085180    -0.909358    -0.704294
H      2.743630    -0.801370    -1.560953
H      1.043864    -0.960044    -1.011974
H      2.362410    -1.773851    -0.107994
S     -1.838731    -0.286443    -0.533988
Cl     2.275116     0.551051     0.322172

SCF energy       : -978.097787908
Gibbs free energy: -978.020065

Frequencies
  47.0294    55.2539    73.3986    83.3239   106.0617   134.2684   193.0933
 206.9163   271.6113   698.2262   732.2737   751.8455   911.1563   954.6037
 986.1718  1030.2305  1035.9719  1037.0743  1315.1213  1337.0781  1358.4916
```

1432.3808 1440.4088 1446.2819 1449.7899 1452.4860 1459.4662 3061.9789
3067.3725 3093.8993 3153.2634 3160.6696 3168.4649 3177.5454 3204.0919
3215.0693

S.7.10 Symmetric bifurcated product cluster

Cartesian coordinates (standard orientation)

S	1.934730	0.008034	0.593008
C	1.502053	1.446547	-0.416499
C	1.559590	-1.315494	-0.582378
H	1.792033	-2.256410	-0.084545
H	1.700624	2.329772	0.189789
H	0.503164	-1.302129	-0.853428
H	2.177593	-1.219379	-1.475585
H	0.445543	1.423959	-0.686387
H	2.118673	1.482239	-1.315359
C	-2.022099	-0.141895	1.140387
H	-2.492470	0.702056	1.636386
H	-0.943218	-0.125344	1.275781
H	-2.445840	-1.080658	1.484796
Cl	-2.355826	-0.001036	-0.618155

SCF energy : -978.097785144
Gibbs free energy: -978.020424

Frequencies
50.2262 55.4052 77.5997 88.5874 91.3810 101.1546 185.9721
193.4593 275.2195 704.1268 723.3725 759.2197 914.3122 957.4452
988.4886 1030.0352 1036.4432 1040.1050 1319.1131 1341.1746 1362.9730
1433.7734 1441.5406 1448.3654 1449.5036 1454.9402 1456.2953 3054.7595
3060.9264 3092.3094 3144.2935 3152.0656 3166.7442 3176.1099 3204.9421
3214.0604

S.7.11 Single bonded product cluster

Cartesian coordinates (standard orientation)

Cl	-2.636088	-0.357439	-0.079480
S	1.748157	-0.220749	-0.655094
C	-1.781520	1.205440	0.139748
C	2.405256	1.109799	0.378688
C	1.189132	-1.355811	0.637109
H	-1.774475	1.434920	1.201386
H	1.618605	1.535157	1.003728
H	0.420597	-0.888825	1.254851
H	-0.771489	1.082732	-0.244900
H	3.220719	0.742940	1.002631

```
H      0.763914    -2.224243     0.135057
H     -2.324641     1.963098    -0.417345
H      2.784566     1.878416    -0.293937
H      2.027984    -1.672302     1.257930

SCF energy       : -978.097542685
Gibbs free energy: -978.020057

Frequencies
  42.4073    53.8203    57.6086    77.6921   102.4536   153.3299   206.2197
 212.9185   276.2511   702.6299   727.2879   755.6552   913.1048   957.3292
 988.3897  1027.8024  1036.5377  1037.8906  1318.7729  1341.2919  1356.3724
1430.6770  1439.8953  1445.5826  1450.7916  1454.3764  1462.0804  3060.2379
3065.0572  3091.3557  3148.0678  3158.3109  3172.9349  3176.2878  3203.5046
3217.0875
```

S.7.12 $(CH_3)_2S$ in water

```
Cartesian coordinates (standard orientation)
C     -1.381425     0.510555     0.000003
H     -1.356879     1.135002    -0.893912
H     -2.296950    -0.080323    -0.000311
H     -1.357253     1.134649     0.894175
C      1.381425     0.510555     0.000003
H      2.296950    -0.080323    -0.000302
H      1.356884     1.134996    -0.893916
H      1.357248     1.134655     0.894170
S      0.000000    -0.656583     0.000003

SCF energy       : -477.982250689
Gibbs free energy: -477.933742

Frequencies
 187.4440   202.6068   270.7616   699.7619   750.6891   912.6745   947.9694
 981.0965  1037.0052  1313.0872  1335.5248  1430.9794  1440.1721  1445.9049
1450.7273  3050.0174  3053.4758  3135.9257  3144.2043  3163.8061  3165.4251
```

S.7.13 CH_3Cl in water

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134317
H      0.000000     1.033087    -1.468382
H      0.894680    -0.516544    -1.468382
H     -0.894680    -0.516544    -1.468382
Cl     0.000000     0.000000     0.659473
```

SCF energy : -500.112901018
Gibbs free energy: -500.097764

Frequencies
722.5077 1028.6231 1029.4897 1356.2335 1449.6833 1449.8309 3104.1899
3217.6012 3217.7387

S.7.14 CH_3^+ in water

Cartesian coordinates (standard orientation)

C	-0.000022	0.000006	-0.000019
H	0.173027	1.071559	0.000038
H	0.841927	-0.685545	0.000038
H	-1.014822	-0.386049	0.000038

SCF energy : -39.5704249609
Gibbs free energy: -39.557991

Frequencies
1377.0101 1382.2540 1405.6647 3084.5138 3286.3930 3292.2358

S.8 Selected cluster geometries in DMSO

S.8.1 $(CH_3)_3S^+$ in DMSO

Cartesian coordinates (input orientation)

C	-3.114028	-0.037995	-0.036536
H	-2.693168	0.378739	0.875840
H	-2.756320	0.487984	-0.919333
H	-4.201587	-0.031122	-0.013902
C	-3.114990	-2.457030	1.361719
H	-2.759591	-3.485272	1.374715
H	-2.691279	-1.877011	2.178419
H	-4.202628	-2.438899	1.379553
C	-0.828509	-1.649150	-0.033403
H	-0.452993	-2.670135	-0.022573
H	-0.455531	-1.125262	-0.910848
H	-0.579794	-1.120808	0.884137
S	-2.613355	-1.754846	-0.214519

SCF energy : -517.693445130
Gibbs free energy: -517.606883

Frequencies
191.3120 199.9932 220.9626 262.8377 278.6239 320.3446 650.3981
732.6561 736.6032 908.2236 943.9888 946.8580 1043.8850 1050.1227

```
1060.1231  1325.8477  1330.7189  1357.6449  1424.2638  1425.4237  1426.7685
1436.5708  1440.9819  1445.8066  3095.5475  3096.0860  3100.6750  3209.0376
3211.6318  3213.3189  3214.2200  3216.1941  3220.1747
```

S.8.2 Tripod ion pair in DMSO

```
Cartesian coordinates (standard orientation)
C      0.755521     1.537683    -0.482369
H     -0.325871     1.402763    -0.449753
H      1.096252     2.298977     0.216828
H      1.111401     1.767465    -1.484827
C      0.759104    -1.187097    -1.089536
H      1.109073    -2.171648    -0.785287
H     -0.322478    -1.087388    -0.995430
H      1.107129    -0.963155    -2.096045
C      0.735522    -0.351147     1.571086
H      1.078151    -1.334687     1.886736
H      1.074865     0.405348     2.276011
H     -0.344073    -0.319574     1.420518
S      1.550334    -0.000158     0.006081
Cl    -2.581804     0.000458    -0.004773

SCF energy       : -978.106804580
Gibbs free energy: -978.024577

Frequencies
  73.9947    87.9011    92.2911   214.4176   244.7729   255.1577   272.5892
 282.2999   304.9460   653.2901   729.5798   732.0314   908.4241   955.9897
 959.9940  1056.0917  1060.2438  1064.6620  1322.8157  1326.1350  1359.2365
1424.4034  1424.8121  1430.7408  1442.5834  1443.4162  1448.8859  3063.9328
3069.3989  3071.7020  3188.1203  3190.3512  3191.9370  3205.7522  3210.1045
3212.4716
```

S.8.3 Linear ion pair in DMSO

```
Cartesian coordinates (standard orientation)
C      2.142140    -1.397428     0.454256
H      1.751743    -1.304616     1.465426
H      1.767097    -2.293037    -0.036667
H      3.229908    -1.393075     0.442981
C      2.141749     1.397609     0.454173
H      1.766628     2.293100    -0.036908
H      1.751187     1.304820     1.465285
H      3.229512     1.393424     0.443074
C     -0.169627    -0.000111    -0.265224
H     -0.568175     0.889337    -0.746583
```

```
H     -0.568221    -0.889429    -0.746783
H     -0.379518    -0.000192     0.801028
S      1.607288    -0.000016    -0.541410
Cl    -3.669550    -0.000029     0.103087

SCF energy       : -978.101693002
Gibbs free energy: -978.021176

Frequencies
  37.8288    60.7130    81.1965   152.5006   211.1200   214.3345   278.6162
 282.2588   309.8481   656.2556   734.6939   741.1430   916.1563   945.5339
 951.7825  1038.2535  1060.3390  1065.0115  1328.0591  1336.4633  1367.2792
1413.7762  1424.9150  1428.5793  1433.7088  1435.9888  1448.2011  3091.4667
3096.9022  3111.9734  3207.2267  3210.5009  3212.5485  3215.4036  3228.9268
3230.3783
```

S.8.4 Linear transition state in DMSO

```
Cartesian coordinates (standard orientation)
C      1.630691     1.222914     1.388829
H      0.766801     1.885289     1.335808
H      1.585171     0.623220     2.296544
H      2.554778     1.799058     1.377226
C      1.630691     1.222914    -1.388829
H      1.585171     0.623220    -2.296544
H      0.766801     1.885289    -1.335808
H      2.554778     1.799058    -1.377226
C     -0.673517    -0.560222     0.000000
H     -0.529008    -1.080751    -0.929716
H     -0.529008    -1.080751     0.929716
H     -0.944628     0.480381     0.000000
S      1.630691     0.071025     0.000000
Cl    -2.907594    -1.140238     0.000000

SCF energy       : -978.062084655
Gibbs free energy: -977.983181

Frequencies
-598.0719    70.5140    78.8111    90.4800   159.0500   179.0890   209.9630
 250.3300   258.3722   289.2155   697.5546   748.7604   920.3519   941.9001
 968.3699   998.7149  1004.3065  1046.9564  1056.6563  1318.9907  1344.9359
1357.6345  1365.7743  1428.7254  1436.2482  1441.8874  1447.6028  3069.9293
3070.4517  3167.8377  3171.2737  3171.7029  3181.3280  3182.0825  3374.5499
3383.5410
```

S.8.5 Immediate product cluster in DMSO

```
Cartesian coordinates (standard orientation)
C     -1.790400     1.421646     0.505836
H     -0.916585     1.232926     1.131366
H     -1.608130     2.303725    -0.107226
H     -2.666769     1.593238     1.131372
C     -2.352119    -1.282130     0.576096
H     -2.538752    -2.193519     0.009039
H     -1.470231    -1.423404     1.202271
H     -3.220201    -1.061523     1.198149
C      1.622757    -0.181528    -0.341779
H      1.570972    -0.885496    -1.166800
H      1.258684     0.795933    -0.643273
H      1.071077    -0.551055     0.517569
S     -2.076661     0.040898    -0.626100
Cl     3.345005    -0.012536     0.135542

SCF energy       : -978.096893870
Gibbs free energy: -978.019401

Frequencies
  55.3741    62.9423    71.2876    77.6914    99.6651   118.2852   186.8434
 196.1990   275.7459   704.0771   725.1374   758.2977   914.2284   954.9101
 986.5674  1028.9492  1037.1437  1049.3141  1319.0045  1342.3064  1357.1291
1433.2399  1442.3382  1445.8259  1447.2528  1450.8129  1459.8654  3058.4067
3062.0369  3108.8173  3143.9915  3152.3324  3169.9689  3172.1595  3220.8411
3224.0846
```

S.8.6 CH_3Cl in DMSO

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134244
H      0.000000     1.033224    -1.468158
H      0.894798    -0.516612    -1.468158
H     -0.894798    -0.516612    -1.468158
Cl     0.000000     0.000000     0.659408

SCF energy       : -500.112860066
Gibbs free energy: -500.097725

Frequencies
 722.8152  1029.0067  1029.8528  1356.4013  1449.9706  1450.1352  3103.3258
3216.7260  3216.8690
```

S.8.7 $(CH_3)_2S$ in DMSO

```
Cartesian coordinates (standard orientation)
C      1.381365    -0.510568     0.000001
H      1.357096    -1.134847    -0.894050
H      2.296890     0.080311    -0.000013
H      1.357126    -1.134846     0.894051
C     -1.381365    -0.510568     0.000001
H     -2.296890     0.080311    -0.000030
H     -1.357087    -1.134858    -0.894042
H     -1.357135    -1.134835     0.894059
S      0.000000     0.656599     0.000001

SCF energy       : -477.982197688
Gibbs free energy: -477.933684

Frequencies
 187.1327   203.1311   271.1359   699.8742   750.7765   912.6037   947.8670
 981.2839  1037.1643  1313.1275  1335.7424  1431.1260  1440.4762  1445.9800
1450.9620  3049.9690  3053.3921  3135.8133  3144.0603  3163.7823  3165.3814
```

S.8.8 CH_3^+ in DMSO

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000006    -0.000017
H      0.174320     1.071394     0.000034
H      0.841139    -0.686584     0.000034
H     -1.015328    -0.384848     0.000034

SCF energy       : -39.5694182319
Gibbs free energy: -39.556992

Frequencies
1376.3182  1381.6964  1405.7846  3083.8999  3285.7346  3291.5752
```

S.9 Selected cluster geometries in nitromethane

S.9.1 $(CH_3)_3S^+$ in nitromethane

```
Cartesian coordinates (input orientation)
C      0.000016     1.613305     0.266271
H      0.000134     1.493356     1.347325
H      0.891832     2.131897    -0.079318
H     -0.891943     2.131786    -0.079125
C     -1.394890    -0.806451     0.265598
H     -1.393873    -1.838567    -0.078317
H     -1.292742    -0.744428     1.346652
```

```
H     -2.291059    -0.296487    -0.080945
C      1.394860    -0.806549     0.265551
H      1.395032    -1.838078    -0.080112
H      2.290899    -0.295243    -0.079356
H      1.291732    -0.746405     1.346619
S      0.000002     0.001863    -0.526884

SCF energy       : -517.692894402
Gibbs free energy: -517.606327

Frequencies
 144.1690   234.2828   235.3471   280.4719   281.9968   319.9110   658.0504
 734.8124   744.1842   903.1613   940.4220   950.6098  1050.6867  1051.2025
1063.0257  1328.7310  1330.0542  1366.7154  1414.0043  1423.2650  1426.6564
1438.3853  1438.9487  1450.2112  3086.1556  3091.9527  3099.8984  3200.1367
3207.9957  3208.4301  3210.9892  3213.6827  3218.7226
```

S.9.2 Tripod ion pair in nitromethane

```
Cartesian coordinates (standard orientation)
C     -0.750084    -0.518396     1.524861
H      0.330893    -0.470748     1.392009
H     -1.099650     0.158535     2.302038
H     -1.095332    -1.530112     1.729491
C     -0.742100    -1.061378    -1.211173
H     -1.088416    -0.735284    -2.190127
H      0.338343    -0.962702    -1.101796
H     -1.084517    -2.075320    -1.013707
C     -0.752308     1.580411    -0.313119
H     -1.096125     1.914074    -1.290334
H     -1.104039     2.262734     0.458247
H      0.328959     1.444402    -0.281376
S     -1.547964    -0.002256    -0.001752
Cl     2.576721     0.001571     0.001186

SCF energy       : -978.106359667
Gibbs free energy: -978.024043

Frequencies
  82.0079    87.9857    95.1182   215.7793   243.1666   257.4803   272.9514
 274.8634   305.3298   653.7688   729.1284   733.4008   908.5602   956.5965
 959.8440  1056.0223  1059.2400  1064.9948  1323.1942  1325.7560  1358.2817
1423.5238  1424.1320  1431.8450  1443.0913  1444.1055  1447.7519  3062.3635
3069.2643  3070.1650  3186.1724  3190.6296  3191.1390  3205.2673  3207.0932
3210.8602
```

S.9.3 Linear ion pair in nitromethane

This calculation was used for the ΔE_{lin} plots, because the calculated value of ΔE_{lin} fitted better into the line of the energy plot. The frequency calculation automatically done after the convergence of the geometry optimization produced no imaginary frequencies (values listed below) whereas as an independent repetition with the geometry stored in the checkpoint file yielded a single imaginary frequency of -63 cm^{-1}.

```
Cartesian coordinates (standard orientation)
C     -0.454333     2.139841     1.397151
H     -1.465552     1.749758     1.303437
H      0.035791     1.764270     2.292986
H     -0.442753     3.227616     1.393107
C     -0.454333     2.139841    -1.397151
H      0.035791     1.764270    -2.292986
H     -1.465552     1.749758    -1.303437
H     -0.442753     3.227616    -1.393107
C      0.265485    -0.171896     0.000000
H      0.746986    -0.570349    -0.889401
H      0.746986    -0.570349     0.889401
H     -0.800747    -0.381796     0.000000
S      0.541707     1.605058     0.000000
Cl    -0.103319    -3.664025     0.000000

SCF energy       : -978.101063509 (result from opt, used for the plots)
SCF energy       : -978.100994348 (after the opt. step of freq. calc.)
Gibbs free energy: -978.019776

Frequencies
  26.5424    58.5961    81.2296   146.9904   212.0520   212.2836   282.4236
 282.4646   308.8982   656.3560   734.4983   741.1582   916.0804   944.9650
 949.4143  1036.9990  1059.6869  1064.8735  1327.8035  1335.5898  1365.5163
1412.8639  1425.1143  1428.2554  1433.5963  1435.9962  1448.3931  3090.5509
3096.7590  3112.2813  3206.1863  3210.0482  3212.4714  3215.0947  3229.2453
3230.6073
```

S.9.4 Linear ion pair in nitromethane

This calculation was used for the ΔG_{lin} plots, because the calculated value of ΔG_{lin} fitted better into the line of the energy plot.

```
Cartesian coordinates (standard orientation)
C      2.139383    -1.397107     0.454731
H      1.748281    -1.303716     1.465586
H      1.764651    -2.293014    -0.035891
H      3.227170    -1.392660     0.444243
C      2.139113     1.397260     0.454655
```

```
H      1.764349     2.293069    -0.036122
H      1.747855     1.303923     1.465457
H      3.226898     1.392919     0.444332
C     -0.172162    -0.000119    -0.266656
H     -0.570275     0.889252    -0.748441
H     -0.570188    -0.889525    -0.748448
H     -0.382728    -0.000118     0.799433
S      1.605080    -0.000010    -0.541678
Cl    -3.663253    -0.000010     0.103549

SCF energy       : -978.101063648
Gibbs free energy: -978.020952

Frequencies
  27.1967    57.9670    81.3469   147.0651   212.1828   212.4249   282.4575
 282.7932   308.9098   656.3233   734.4172   741.1851   916.0603   945.0150
 948.7756  1036.9046  1059.5224  1064.8197  1327.8412  1335.4346  1365.1838
1412.9634  1425.0529  1428.1086  1433.6706  1436.0738  1448.3862  3090.5082
3096.6910  3112.5355  3206.1242  3210.0346  3212.3984  3215.0108  3229.4932
3230.7374
```

S.9.5 Linear transition state in nitromethane

```
Cartesian coordinates (standard orientation)
C      1.630129     1.222856     1.388827
H      0.765703     1.884605     1.336602
H      1.585790     0.623103     2.296565
H      2.553805     1.799642     1.376541
C      1.630129     1.222856    -1.388827
H      1.585790     0.623103    -2.296565
H      0.765703     1.884605    -1.336602
H      2.553805     1.799642    -1.376541
C     -0.672223    -0.559795     0.000000
H     -0.528550    -1.080644    -0.929678
H     -0.528550    -1.080644     0.929678
H     -0.944166     0.480606     0.000000
S      1.630129     0.071032     0.000000
Cl    -2.907035    -1.140355     0.000000

SCF energy       : -978.061861680
Gibbs free energy: -977.982911

Frequencies
-597.6949    70.3065    81.7417    90.9277   157.7091   179.5634   211.1253
 250.5512   258.9545   290.0624   697.6537   748.8352   920.2799   941.7207
```

```
 968.7902   999.3542  1004.4275  1047.2944  1056.5700  1318.9897  1345.4175
1357.7809  1365.9315  1428.8084  1436.0051  1442.1749  1447.8921  3069.8383
3070.2372  3167.7032  3171.0306  3171.6209  3181.2846  3181.9798  3374.4188
3383.4258
```

S.9.6 Immediate product cluster in nitromethane

```
Cartesian coordinates (standard orientation)
C     -1.858814     1.411683     0.519780
H     -0.995497     1.245077     1.165677
H     -1.690093     2.304751    -0.081095
H     -2.755752     1.549274     1.124153
C     -2.323756    -1.310276     0.554015
H     -2.465031    -2.222576    -0.024434
H     -1.451017    -1.425283     1.198247
H     -3.212432    -1.126632     1.158608
C      1.621433    -0.100172    -0.304197
H      1.529948    -0.595232    -1.266020
H      1.246579     0.917541    -0.356498
H      1.107946    -0.662009     0.470694
S     -2.069923     0.032638    -0.630296
Cl     3.362996    -0.030266     0.122225

SCF energy       : -978.096875273
Gibbs free energy: -978.019743

Frequencies
  32.7214    59.7387    69.9791    76.0999   111.1032   115.9524   195.6531
 199.7193   276.3835   701.8593   730.8844   754.8497   914.3348   956.4154
 987.8468  1033.7362  1037.8268  1061.5028  1319.7874  1342.4846  1365.6554
1433.7841  1442.7004  1446.2284  1447.8588  1452.7973  1462.2608  3060.8116
3064.0979  3104.1578  3145.6448  3153.6661  3171.3050  3174.2345  3214.3628
3221.7341
```

S.9.7 CH_3Cl in nitromethane

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134427
H      0.000000     1.033579    -1.468208
H      0.895106    -0.516790    -1.468208
H     -0.895106    -0.516790    -1.468208
Cl     0.000000     0.000000     0.659482

SCF energy       : -500.112831464
Gibbs free energy: -500.097710
```

```
Frequencies
 722.5983  1029.9065  1030.7381  1356.8949  1450.4274  1450.6045  3100.4498
3213.7628  3213.9095
```

S.9.8 $(CH_3)_2S$ in nitromethane

```
Cartesian coordinates (standard orientation)
C     -1.381383     0.510807     0.000043
H     -1.356638     1.135400    -0.893884
H     -2.297125    -0.080026    -0.000781
H     -1.357043     1.134650     0.894343
C      1.381388     0.510806     0.000043
H      2.297127    -0.080031    -0.000847
H      1.356605     1.135440    -0.893852
H      1.357077     1.134599     0.894377
S     -0.000002    -0.656857     0.000008

SCF energy       : -477.982160959
Gibbs free energy: -477.933633

Frequencies
 188.7089   205.1942   271.6745   699.2727   750.0439   912.8719   947.8883
 981.4864  1037.4424  1313.1251  1335.8767  1431.3677  1440.8471  1446.0415
1451.1369  3049.5449  3052.9397  3135.6966  3143.9137  3162.7321  3164.3245
```

S.9.9 CH_3^+ in nitromethane

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000007    -0.000016
H      0.175255     1.071272     0.000031
H      0.840568    -0.687334     0.000031
H     -1.015691    -0.383980     0.000031

SCF energy       : -39.5687158161
Gibbs free energy: -39.556294

Frequencies
1375.8042  1381.2729  1405.8566  3083.4604  3285.2627  3291.1049
```

S.10 Selected cluster geometries in Methanol

S.10.1 $(CH_3)_3S^+$ in methanol

```
Cartesian coordinates (input orientation)
C      0.000051     1.613326     0.266094
H      0.000242     1.493275     1.347140
H      0.891837     2.131956    -0.079511
```

```
H     -0.891933     2.131833    -0.079197
C     -1.394706    -0.806399     0.265683
H     -1.393571    -1.838595    -0.078007
H     -1.292138    -0.744160     1.346691
H     -2.291060    -0.296612    -0.080650
C      1.394632    -0.806604     0.265519
H      1.395200    -1.837924    -0.080782
H      2.290789    -0.294860    -0.078435
H      1.290678    -0.747168     1.346554
S     -0.000022     0.001931    -0.527141

SCF energy       : -517.692606128
Gibbs free energy: -517.606033

Frequencies
 140.5850   236.4559   237.3415   281.8545   282.4221   320.5176   658.1730
 734.8468   744.1300   902.9988   940.2024   951.0602  1050.5490  1052.0544
1063.5757  1328.5373  1330.2631  1367.3153  1413.4950  1423.2931  1426.8788
1438.9008  1439.1235  1450.6464  3085.6885  3091.8745  3099.8648  3199.6116
3207.9611  3208.1702  3210.8916  3213.6529  3218.7099
```

S.10.2 Tripod ion pair in methanol

```
Cartesian coordinates (standard orientation)
C     -0.739046     1.560633    -0.398665
H      0.341346     1.421114    -0.348608
H     -1.072362     1.839527    -1.396436
H     -1.094690     2.287217     0.329451
C     -0.757583    -0.434707     1.551308
H     -1.107671    -1.432645     1.808643
H      0.324356    -0.397964     1.421008
H     -1.107947     0.284626     2.288956
C     -0.737944    -1.126388    -1.151169
H     -1.096443    -2.124898    -0.908987
H     -1.066914    -0.844452    -2.149540
H      0.342266    -1.035947    -1.031459
S     -1.545314     0.001310    -0.005568
Cl     2.568854    -0.000868     0.003954

SCF energy       : -978.106126826
Gibbs free energy: -978.024082

Frequencies
  73.9786    82.5075    93.9830   207.9170   242.4781   261.8157   272.9734
 275.2915   306.6727   652.3217   727.1523   731.5597   906.8551   956.1436
```

```
 959.5612  1055.1326  1058.9428  1065.6737  1322.4108  1325.3535  1358.3971
1423.2501  1424.2663  1430.3052  1441.9829  1445.2794  1448.4628  3059.5227
3063.1449  3068.4751  3182.3583  3185.1750  3189.3225  3200.6934  3206.5255
3209.6512
```

S.10.3 Linear ion pair in methanol

```
Cartesian coordinates (standard orientation)
C      2.137736    -1.396969     0.454974
H      1.746184    -1.303327     1.465638
H      1.763204    -2.293013    -0.035559
H      3.225534    -1.392488     0.444976
C      2.137600     1.397051     0.454934
H      1.762895     2.293028    -0.035588
H      1.746112     1.303348     1.465618
H      3.225395     1.392725     0.444867
C     -0.173609    -0.000063    -0.267476
H     -0.571436     0.889313    -0.749450
H     -0.571390    -0.889452    -0.749463
H     -0.384634    -0.000066     0.798508
S      1.603787    -0.000007    -0.541809
Cl    -3.659577    -0.000005     0.103812

SCF energy       : -978.100717464
Gibbs free energy: -978.021107

Frequencies
  17.2883    56.3477    80.6840   144.3452   211.2428   213.0965   281.9999
 284.9424   308.3461   656.3303   734.2978   741.1835   915.4982   944.5603
 946.7689  1036.0786  1059.0371  1063.5203  1327.7296  1334.4046  1363.3959
1412.5261  1425.1306  1427.6540  1433.6644  1435.7661  1448.4721  3090.0099
3096.5803  3112.7169  3205.5555  3209.7818  3212.3065  3214.9608  3229.7099
3230.8975
```

S.10.4 Linear transition state in methanol

```
Cartesian coordinates (standard orientation)
C      1.629996     1.222242     1.388822
H      0.765417     1.883812     1.336782
H      1.585945     0.622479     2.296570
H      2.553563     1.799200     1.376378
C      1.629996     1.222242    -1.388822
H      1.585945     0.622479    -2.296570
H      0.765417     1.883812    -1.336782
H      2.553563     1.799200    -1.376378
C     -0.671495    -0.559518     0.000000
```

```
H     -0.528540    -1.080582    -0.929671
H     -0.528540    -1.080582     0.929671
H     -0.943573     0.480849     0.000000
S      1.629996     0.070432     0.000000
Cl    -2.907066    -1.139258     0.000000

SCF energy       : -978.061738733
Gibbs free energy: -977.982769

Frequencies
-597.4603    69.9730    83.2520    91.2371   156.7923   179.8028   211.5028
 250.7174   259.2252   290.5064   697.6868   748.8504   920.2652   941.6298
 968.9818   999.7557  1004.4169  1047.4352  1056.5104  1318.9998  1345.6751
1357.8930  1365.9849  1428.8468  1435.8691  1442.2663  1448.0705  3069.8132
3070.1422  3167.6657  3170.9250  3171.6085  3181.2758  3181.9402  3374.3767
3383.4061
```

S.10.5 Immediate product cluster in methanol

```
Cartesian coordinates (standard orientation)
C     -1.858919     1.411672     0.519759
H     -0.995631     1.245251     1.165764
H     -1.690298     2.304772    -0.081098
H     -2.755944     1.549153     1.124033
C     -2.323647    -1.310281     0.553963
H     -2.464650    -2.222630    -0.024475
H     -1.451066    -1.425169     1.198442
H     -3.212515    -1.126755     1.158317
C      1.621248    -0.100055    -0.303808
H      1.529252    -0.596459    -1.264886
H      1.246745     0.917734    -0.357519
H      1.107667    -0.660562     0.472011
S     -2.069681     0.032592    -0.630354
Cl     3.362897    -0.030283     0.122094

SCF energy       : -978.096843931
Gibbs free energy: -978.019654

Frequencies
  34.4432    59.8553    70.1887    76.2528   111.5815   115.8243   195.6656
 199.6137   276.4324   701.8900   730.9475   754.8748   914.3236   956.4278
 987.8767  1033.8930  1037.8576  1061.3678  1319.8243  1342.5328  1365.6987
1433.8489  1442.7657  1446.2693  1447.9602  1452.8833  1462.2631  3060.7829
3064.0586  3104.0262  3145.5963  3153.6064  3171.2832  3174.2263  3214.2633
3221.5178
```

S.10.6 CH_3Cl in methanol

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134388
H      0.000000     1.033572    -1.468203
H      0.895100    -0.516786    -1.468203
H     -0.895100    -0.516786    -1.468203
Cl     0.000000     0.000000     0.659467

SCF energy       : -500.112815913
Gibbs free energy: -500.097694

Frequencies
 722.7028  1029.9189  1030.7436  1356.9323  1450.5067  1450.6896  3100.4105
3213.6971  3213.8453
```

S.10.7 $(CH_3)_2S$ in methanol

```
Cartesian coordinates (standard orientation)
C     -1.381355     0.510816     0.000043
H     -1.356639     1.135411    -0.893889
H     -2.297103    -0.080009    -0.000781
H     -1.357046     1.134660     0.894348
C      1.381360     0.510814     0.000043
H      2.297106    -0.080015    -0.000848
H      1.356605     1.135452    -0.893857
H      1.357081     1.134609     0.894383
S     -0.000002    -0.656868     0.000008

SCF energy       : -477.982140907
Gibbs free energy: -477.933611

Frequencies
 188.6431   205.4036   271.8074   699.3144   750.0746   912.8516   947.8599
 981.5591  1037.5016  1313.1437  1335.9566  1431.4260  1440.9602  1446.0740
1451.2262  3049.5144  3052.8975  3135.6413  3143.8484  3162.7123  3164.2975
```

S.10.8 CH_3^+ in methanol

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000007    -0.000015
H      0.175783     1.071203     0.000030
H      0.840245    -0.687757     0.000030
H     -1.015895    -0.383489     0.000030
```

```
SCF energy       : -39.5683277672
Gibbs free energy: -39.555909

Frequencies
1375.5091  1381.0274  1405.8923  3083.2136  3284.9977  3290.8418
```

S.11 Selected cluster geometries in ethanol

S.11.1 $(CH_3)_3S^+$ in ethanol

```
Cartesian coordinates (input orientation)
C     -3.113973    -0.038127    -0.036430
H     -2.691046     0.378714     0.874947
H     -2.758554     0.487960    -0.920068
H     -4.201484    -0.031171    -0.011380
C     -3.115168    -2.457061     1.361228
H     -2.759392    -3.485174     1.374859
H     -2.692107    -1.876567     2.178010
H     -4.202823    -2.439668     1.378802
C     -0.828382    -1.649023    -0.033286
H     -0.452608    -2.669884    -0.022297
H     -0.454720    -1.125290    -0.910523
H     -0.580239    -1.120590     0.884396
S     -2.613277    -1.754926    -0.214990

SCF energy       : -517.691822000
Gibbs free energy: -517.605210

Frequencies
 191.8614   202.5247   224.4957   262.1775   279.5058   321.6019   650.3558
 732.5972   736.4471   908.2401   944.2646   947.0550  1043.3471  1050.8703
1060.6643  1325.8504  1330.7525  1358.1146  1424.3559  1425.8268  1428.1938
1436.9432  1441.3066  1446.5880  3095.3484  3096.1012  3101.0925  3208.8099
3211.9285  3213.4607  3214.4644  3215.6716  3220.5681
```

S.11.2 Tripod ion pair in ethanol

```
Cartesian coordinates (standard orientation)
C      0.735193    -0.364545     1.568954
H     -0.345014    -0.330016     1.422925
H      1.078131    -1.350692     1.876708
H      1.079069     0.386846     2.277183
C      0.755041     1.542093    -0.469180
H      1.107570     1.777843    -1.471486
H     -0.326816     1.411174    -0.432313
H      1.102127     2.296664     0.234094
```

```
C      0.743613    -1.177020    -1.100596
H      1.094951    -0.949752    -2.105248
H      1.084144    -2.166703    -0.802353
H     -0.337360    -1.067522    -1.006740
S      1.544520    -0.003650     0.003382
Cl    -2.567777     0.002788    -0.002468

SCF energy       : -978.105457779
Gibbs free energy: -978.023304

Frequencies
  74.9770    87.0435    93.6314   211.2752   242.7212   255.5291   271.9163
 277.9842   304.8135   651.9317   727.8347   731.8792   907.8838   956.0119
 959.7805  1055.0014  1059.9469  1065.2027  1322.0932  1325.5797  1358.2860
1424.0905  1424.2608  1430.6071  1442.7422  1444.2204  1447.8341  3060.3314
3066.6657  3069.5884  3185.9143  3188.3420  3190.3440  3203.5876  3210.0971
3212.4759
```

S.11.3 Linear ion pair in ethanol

```
Cartesian coordinates (standard orientation)
C     -2.128071     1.399293     0.454605
H     -1.728623     1.308316     1.462471
H     -1.757927     2.294493    -0.040802
H     -3.215892     1.393862     0.453054
C     -2.137680    -1.393927     0.456754
H     -1.758895    -2.291396    -0.027919
H     -1.752456    -1.295926     1.469417
H     -3.225452    -1.390965     0.440101
C      0.177838    -0.003949    -0.269984
H      0.573391    -0.894159    -0.752188
H      0.576509     0.884527    -0.752861
H      0.390587    -0.003584     0.795634
S     -1.599907     0.000051    -0.542086
Cl     3.648514    -0.000852     0.104601

SCF energy       : -978.099722650 (result from opt, used for the plots)
SCF energy       : -978.099722607 (after the opt. step of freq. calc.)
Gibbs free energy: -978.020618

Frequencies
  14.1193    52.1226    75.2850   146.7406   211.8836   214.4079   278.4196
 289.5063   306.6713   656.0917   734.0215   741.0978   911.6791   940.3617
 943.2655  1033.7942  1055.2657  1058.0178  1327.5687  1328.7955  1357.2747
1412.8613  1425.2944  1425.8202  1433.7810  1433.9421  1448.5428  3089.1142
```

```
3096.2292  3112.8706  3204.5335  3209.0987  3212.0637  3214.4756  3229.9730
3231.0433
```

S.11.4 Linear transition state in ethanol

```
Cartesian coordinates (standard orientation)
C      1.629668     1.221073     1.388778
H      0.764729     1.882227     1.337183
H      1.586303     0.621318     2.296572
H      2.552989     1.798404     1.375940
C      1.629668     1.221073    -1.388778
H      1.586303     0.621318    -2.296572
H      0.764729     1.882227    -1.337183
H      2.552989     1.798404    -1.375940
C     -0.669764    -0.558747     0.000000
H     -0.528455    -1.080309    -0.929648
H     -0.528455    -1.080309     0.929648
H     -0.942568     0.481428     0.000000
S      1.629668     0.069284     0.000000
Cl    -2.907099    -1.137273     0.000000

SCF energy       : -978.061384544
Gibbs free energy: -977.982370

Frequencies
-596.6292    69.1660    86.5541    92.1107   154.6318   180.3660   212.6435
 251.0614   259.9962   291.6253   697.8173   748.9353   920.1934   941.3771
 969.3988  1000.6791  1004.2623  1047.7766  1056.3045  1319.0118  1346.3328
1358.1506  1366.1494  1428.9661  1435.5651  1442.5512  1448.5828  3069.7784
3069.9242  3167.6059  3170.6798  3171.6166  3181.2848  3181.8702  3374.3359
3383.3594
```

S.11.5 Immediate product cluster in ethanol

```
Cartesian coordinates (standard orientation)
C     -1.859434     1.411628     0.519775
H     -0.995961     1.245969     1.165774
H     -1.691562     2.304872    -0.081082
H     -2.756523     1.548543     1.124099
C     -2.322870    -1.310371     0.554047
H     -2.463257    -2.222861    -0.024322
H     -1.450453    -1.424864     1.198850
H     -3.212035    -1.127299     1.158115
C      1.621107    -0.099900    -0.304263
H      1.529313    -0.596088    -1.265475
H      1.246461     0.917857    -0.357947
```

```
H      1.107152    -0.660567     0.471215
S     -2.069240     0.032440    -0.630365
Cl     3.362464    -0.030162     0.122309

SCF energy       : -978.096754266
Gibbs free energy: -978.019512

Frequencies
  35.6203    60.1434    70.3211    76.6364   111.7752   116.0061   195.8863
 199.6650   276.5493   702.0129   731.3422   754.9761   914.2731   956.4537
 987.9755  1033.8764  1037.9126  1061.4020  1319.9266  1342.6651  1365.8130
1434.0293  1442.9508  1446.4727  1448.1926  1453.1379  1462.4446  3060.7062
3063.9617  3103.9661  3145.4359  3153.4243  3171.2576  3174.2009  3214.1803
3221.3211
```

S.11.6 CH_3Cl in ethanol

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134276
H      0.000000     1.033553    -1.468190
H      0.895083    -0.516776    -1.468190
H     -0.895083    -0.516776    -1.468190
Cl     0.000000     0.000000     0.659425

SCF energy       : -500.112771264
Gibbs free energy: -500.097648

Frequencies
 723.0030  1029.9539  1030.7590  1357.0392  1450.7337  1450.9326  3100.2981
3213.5084  3213.6609
```

S.11.7 $(CH_3)_2S$ in ethanol

```
Cartesian coordinates (standard orientation)
C     -1.381271     0.510840     0.000043
H     -1.356640     1.135441    -0.893903
H     -2.297041    -0.079960    -0.000782
H     -1.357052     1.134691     0.894363
C      1.381276     0.510839     0.000043
H      2.297044    -0.079965    -0.000851
H      1.356605     1.135485    -0.893870
H      1.357088     1.134638     0.894399
S     -0.000002    -0.656900     0.000008

SCF energy       : -477.982083502
Gibbs free energy: -477.933549
```

```
Frequencies
 188.4715   205.9662   272.1672   699.4342   750.1634   912.7939   947.7819
 981.7587  1037.6629  1313.1977  1336.1765  1431.5929  1441.2754  1446.1710
1451.4803  3049.4266  3052.7788  3135.4823  3143.6636  3162.6556  3164.2209
```

S.11.8 CH_3^+ in ethanol

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000008    -0.000013
H      0.177354     1.070994     0.000025
H      0.839279    -0.689015     0.000025
H     -1.016501    -0.382027     0.000025

SCF energy       : -39.5672056981
Gibbs free energy: -39.554796

Frequencies
1374.6117  1380.2749  1405.9795  3082.4841  3284.2137  3290.0677
```

S.12 Selected cluster geometries in acetone

S.12.1 $(CH_3)_3S^+$ in acetone

```
Cartesian coordinates (input orientation)
C      0.000284     1.613412     0.265295
H      0.000841     1.492935     1.346309
H      0.891952     2.132149    -0.080429
H     -0.891786     2.132108    -0.079499
C     -1.393972    -0.806041     0.266313
H     -1.391663    -1.838987    -0.075214
H     -1.290059    -0.741629     1.347099
H     -2.291244    -0.297850    -0.080021
C      1.393590    -0.806973     0.265140
H      1.396525    -1.837010    -0.085030
H      2.290151    -0.292541    -0.073768
H      1.285623    -0.751791     1.346043
S     -0.000241     0.002215    -0.528278

SCF energy       : -517.691029681
Gibbs free energy: -517.604417

Frequencies
 125.3765   242.1978   251.9820   282.8875   289.6466   324.0154   658.6699
 734.9814   743.8330   902.2566   939.2689   953.2029  1049.6869  1056.5027
1066.1950  1327.7044  1331.2427  1370.4127  1411.4442  1423.4881  1427.9030
```

```
1439.9352  1441.7402  1453.0902  3083.5188  3091.4640  3099.6980  3197.1304
3206.8952  3207.7741  3210.4225  3213.4708  3218.6707
```

S.12.2 Tripod ion pair in acetone

```
Cartesian coordinates (standard orientation)
C      0.737774     1.595018    -0.231935
H     -0.342931     1.451119    -0.206110
H      1.087059     2.238971     0.573107
H      1.078728     1.980772    -1.190554
C      0.739182    -0.999629    -1.264112
H      1.089543    -2.020105    -1.120731
H     -0.341587    -0.913779    -1.145505
H      1.079023    -0.621409    -2.226433
C      0.750181    -0.596723     1.497348
H      1.098538    -1.616739     1.648198
H      1.099572     0.038777     2.308728
H     -0.331485    -0.544905     1.369039
S      1.542256     0.002089    -0.003413
Cl    -2.562081    -0.001066     0.002180

SCF energy       : -978.104789575
Gibbs free energy: -978.023187

Frequencies
  71.7576    81.5323   101.7824   193.4348   212.2613   241.7103   262.7629
 267.7001   305.6989   649.5688   724.7790   731.0320   908.9970   951.2775
 956.7375  1048.8489  1055.3132  1066.0227  1321.5899  1323.9626  1353.6607
1419.1743  1424.1299  1431.7577  1441.1553  1444.1816  1445.6235  3058.3566
3064.0070  3067.7159  3179.6038  3185.9487  3189.1339  3199.5072  3200.5191
3207.1367
```

S.12.3 Linear ion pair in acetone

```
Cartesian coordinates (standard orientation)
C     -2.117635     1.400776     0.455368
H     -1.709888     1.312532     1.460172
H     -1.752351     2.295253    -0.044951
H     -3.205406     1.394355     0.462783
C     -2.133514    -1.392248     0.459749
H     -1.754505    -2.290736    -0.022869
H     -1.748525    -1.292336     1.472318
H     -3.221327    -1.389517     0.442887
C      0.183064    -0.006913    -0.276597
H      0.575547    -0.898075    -0.759483
H      0.581003     0.880514    -0.761964
```

```
H      0.400478    -0.005463     0.788055
S     -1.595842    -0.000366    -0.542083
Cl     3.633938    -0.000609     0.106192

SCF energy       : -978.098842540
Gibbs free energy: -978.019252

Frequencies
  22.5936    55.2166    68.3520   155.8102   213.0121   217.0791   273.7567
 292.2737   305.6038   655.8340   733.8640   741.1508   906.0136   933.4266
 942.5359  1031.7636  1047.0712  1056.7265  1318.9166  1328.4188  1353.3467
1414.3127  1423.6926  1425.5275  1432.1680  1434.4800  1448.5233  3088.5871
3095.6675  3113.1526  3203.9354  3208.3686  3211.6455  3214.0205  3230.1857
3231.0055
```

S.12.4 Linear transition state in acetone

```
Cartesian coordinates (standard orientation)
C      1.629484     1.219041     1.388769
H      0.764396     1.880021     1.337196
H      1.586208     0.619285     2.296580
H      2.552732     1.796491     1.375933
C      1.629484     1.219041    -1.388769
H      1.586208     0.619285    -2.296580
H      0.764396     1.880021    -1.337196
H      2.552732     1.796491    -1.375933
C     -0.667947    -0.558167     0.000000
H     -0.528588    -1.080234    -0.929667
H     -0.528588    -1.080234     0.929667
H     -0.940937     0.481955     0.000000
S      1.629484     0.067264     0.000000
Cl    -2.907437    -1.133459     0.000000

SCF energy       : -978.061069343
Gibbs free energy: -977.982047

Frequencies
-595.9766    68.2098    87.7688    92.7174   152.4610   180.8683   213.1022
 251.2972   260.6480   292.4957   697.8627   748.9362   920.1557   941.1018
 969.7902  1001.5259  1004.1268  1047.9610  1056.1257  1319.0083  1346.8376
1358.2446  1366.2112  1429.0406  1435.2790  1442.6769  1449.0306  3069.7265
3069.7436  3167.5481  3170.4697  3171.5928  3181.2823  3181.7992  3374.2207
3383.3075
```

S.12.5 Immediate product cluster in acetone

```
Cartesian coordinates (standard orientation)
C     -1.796276     1.425549     0.500139
H     -0.921805     1.242013     1.126294
H     -1.616640     2.305377    -0.116897
H     -2.672930     1.597814     1.125218
C     -2.350276    -1.278585     0.583504
H     -2.538035    -2.192660     0.021151
H     -1.466583    -1.416795     1.207971
H     -3.216803    -1.055860     1.206986
C      1.631464    -0.202468    -0.353473
H      1.593610    -0.945450    -1.144332
H      1.268857     0.757321    -0.707954
H      1.068578    -0.532700     0.514774
S     -2.079497     0.039010    -0.625462
Cl     3.344955    -0.002953     0.140774

SCF energy       : -978.096627370
Gibbs free energy: -978.018573

Frequencies
  58.2813    69.2365    77.6403    89.1574   105.6901   139.7885   187.2226
 193.4666   276.2112   704.4479   724.1902   758.8242   913.8500   955.2376
 987.0593  1030.3280  1037.1647  1054.8921  1319.3602  1342.5996  1359.5137
1433.5792  1442.4536  1446.1373  1449.7518  1451.5173  1461.1787  3058.1800
3061.8814  3103.9788  3143.3406  3151.7999  3170.0627  3172.2334  3216.0197
3220.9617
```

S.12.6 CH_3Cl in acetone

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.134176
H      0.000000     1.033535    -1.468178
H      0.895068    -0.516768    -1.468178
H     -0.895068    -0.516768    -1.468178
Cl     0.000000     0.000000     0.659388

SCF energy       : -500.112731749
Gibbs free energy: -500.097608

Frequencies
 723.2691  1029.9842  1030.7724  1357.1334  1450.9338  1451.1461  3100.1988
3213.3415  3213.4976
```

S.12.7 $(CH_3)_2S$ in acetone

```
Cartesian coordinates (standard orientation)
C     -1.381196     0.510862     0.000043
H     -1.356639     1.135468    -0.893917
H     -2.296986    -0.079915    -0.000781
H     -1.357053     1.134720     0.894375
C      1.381201     0.510860     0.000043
H      2.296989    -0.079920    -0.000853
H      1.356602     1.135513    -0.893882
H      1.357091     1.134665     0.894412
S     -0.000002    -0.656929     0.000008

SCF energy       : -477.982032899
Gibbs free energy: -477.933494

Frequencies
 188.3398   206.4191   272.4605   699.5404   750.2429   912.7437   947.7169
 981.9246  1037.7957  1313.2462  1336.3605  1431.7398  1441.5432  1446.2612
1451.7024  3049.3486  3052.6763  3135.3411  3143.5030  3162.6056  3164.1542
```

S.12.8 CH_3^+ in acetone

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000009    -0.000011
H      0.178817     1.070795     0.000022
H      0.838377    -0.690184     0.000022
H     -1.017061    -0.380663     0.000022

SCF energy       : -39.5662026546
Gibbs free energy: -39.553801

Frequencies
1374.0047  1379.6287  1406.0416  3081.8124  3283.4929  3289.3597
```

S.13 Selected cluster geometries in dichloro ethane

S.13.1 $(CH_3)_3S^+$ in dichloro ethane

```
Cartesian coordinates (input orientation)
C     -3.113521    -0.037883    -0.036715
H     -2.688009     0.378106     0.873931
H     -2.759653     0.488518    -0.920872
H     -4.201076    -0.028754    -0.009595
C     -3.115387    -2.457412     1.360880
H     -2.757661    -3.484987     1.376040
H     -2.693633    -1.875205     2.177258
```

```
H     -4.203150    -2.442990     1.379001
C     -0.829070    -1.649099    -0.033278
H     -0.452613    -2.669748    -0.021853
H     -0.453679    -1.125754    -0.910126
H     -0.582199    -1.120360     0.884636
S     -2.614123    -1.755237    -0.216039

SCF energy       : -517.686795993
Gibbs free energy: -517.600084

Frequencies
 188.8042   210.6307   231.2214   262.5651   283.8505   324.9881   649.7383
 731.6575   735.8260   907.9232   944.7563   947.6701  1042.1772  1052.2691
1062.1877  1325.7233  1330.8939  1359.1977  1424.4728  1427.0177  1431.2344
1437.8504  1443.1491  1448.8635  3094.1219  3095.8079  3101.5178  3207.4934
3211.7516  3212.7946  3214.1431  3214.5374  3221.3641
```

S.13.2 Tripod ion pair in dichloro ethane

```
Cartesian coordinates (standard orientation)
C     -0.715651     1.428374    -0.745028
H      0.364274     1.299062    -0.657174
H     -1.042095     1.472742    -1.782395
H     -1.072771     2.302694    -0.204059
C     -0.751741    -0.067475     1.610380
H     -1.105581    -0.980226     2.086248
H      0.331354    -0.062368     1.480072
H     -1.105117     0.801517     2.162347
C     -0.721035    -1.361464    -0.861619
H     -1.075693    -2.276233    -0.390015
H     -1.054273    -1.323010    -1.897094
H      0.359505    -1.240373    -0.769338
S     -1.529776     0.001973    -0.010649
Cl     2.529846    -0.001294     0.007023

SCF energy       : -978.101487015
Gibbs free energy: -978.019279

Frequencies
  82.9861    94.6153   113.9460   201.9936   221.5968   240.1977   268.1253
 277.4384   314.1614   650.8369   725.2585   736.9823   906.5490   956.5172
 957.6020  1054.0317  1054.5994  1069.9474  1320.5950  1324.1064  1357.2654
1417.4431  1422.4883  1434.3475  1441.3363  1447.7142  1451.8502  3055.8152
3056.5493  3066.3114  3178.9019  3180.0171  3188.0678  3199.9097  3201.2753
3202.9794
```

S.13.3 Linear ion pair in dichloro ethane

```
Cartesian coordinates (standard orientation)
C      2.122292    -1.389770     0.457619
H      1.747300    -1.284501     1.473443
H      1.736065    -2.289787    -0.016570
H      3.210008    -1.389595     0.430118
C      2.102213     1.400420     0.452239
H      1.733284     2.295386    -0.044685
H      1.698194     1.309965     1.458452
H      3.190060     1.395390     0.455700
C     -0.201022    -0.008478    -0.269481
H     -0.602265     0.877787    -0.753885
H     -0.595471    -0.899833    -0.750008
H     -0.415110    -0.006173     0.795819
S      1.576785    -0.000471    -0.543607
Cl    -3.592443    -0.000831     0.106298

SCF energy       : -978.093834367
Gibbs free energy: -978.014412

Frequencies
  11.8290    57.3245    95.6698   150.9360   220.2102   223.1878   273.9883
 302.4933   303.5638   657.0779   733.1505   741.0075   906.7771   933.8458
 940.5956  1030.4369  1047.7818  1057.3398  1319.1771  1327.6549  1353.1566
1413.9477  1424.4775  1427.0981  1431.2122  1435.7995  1450.6178  3086.0092
3094.9384  3115.3046  3200.6724  3206.8630  3210.9191  3213.2578  3233.0864
3233.6506
```

S.13.4 Linear transition state in dichloro acetone

```
Cartesian coordinates (standard orientation)
C      1.989734    -1.389693     0.460679
H      1.479002    -1.340040     1.422579
H      1.700886    -2.296764    -0.067884
H      3.069562    -1.377801     0.600825
C      1.984639     1.391449     0.460053
H      1.695300     2.297626    -0.069808
H      1.471210     1.340696     1.420059
H      3.064043     1.381723     0.603379
C     -0.827034    -0.001159    -0.231960
H     -0.918245     0.913622    -0.789714
H     -0.910400    -0.946186    -0.738776
H     -0.675557     0.029611     0.832985
S      1.511752     0.000146    -0.587466
Cl    -3.120463    -0.000495     0.120775
```

```
SCF energy       : -978.059205857  (result from the optimisation)
SCF energy       : -978.059206101  (single point calc, used fro the plot)
Gibbs free energy: -977.981253

Frequencies
-593.2042    33.4914    56.6575    79.0002   154.6092   179.4315   240.5032
 247.9439   261.2312   299.8355   701.9738   753.6512   914.5030   941.2447
 966.9524   996.3059  1001.3378  1042.2031  1050.2554  1318.9891  1349.3160
1356.3747  1361.6052  1431.9841  1436.7758  1449.6666  1453.1213  3070.0497
3072.1863  3170.1767  3171.1387  3173.3945  3187.0541  3187.8519  3376.8600
3381.3547
```

S.13.5 Immediate product cluster in dichloro acetone

```
Cartesian coordinates (standard orientation)
C     -1.862711     1.411213     0.519993
H     -0.998755     1.249648     1.166566
H     -1.698472     2.305273    -0.080688
H     -2.760600     1.544980     1.123932
C     -2.318688    -1.311033     0.554208
H     -2.455180    -2.224274    -0.023935
H     -1.447549    -1.423300     1.201311
H     -3.209878    -1.130718     1.156207
C      1.620246    -0.098080    -0.306260
H      1.528779    -0.593787    -1.267777
H      1.245755     0.919746    -0.360525
H      1.103919    -0.658616     0.467828
S     -2.066484     0.031576    -0.630474
Cl     3.360156    -0.029809     0.123355

SCF energy       : -978.096232934
Gibbs free energy: -978.018867

Frequencies
  38.2781    61.2778    70.7910    77.9931   111.9360   115.9530   196.6127
 199.0751   276.8694   702.7984   733.5123   755.6485   913.9500   956.4182
 988.3044  1033.6822  1038.1164  1059.8754  1320.4294  1343.2751  1365.8791
1435.0335  1443.9197  1447.3790  1449.4123  1454.4743  1463.2093  3060.2956
3063.4357  3103.7253  3144.5897  3152.4753  3171.0811  3173.9939  3213.6406
3220.5375
```

S.13.6 CH_3Cl in dichloro ethane

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.133611
H      0.000000     1.033435    -1.468114
H      0.894981    -0.516717    -1.468114
H     -0.894981    -0.516717    -1.468114
Cl     0.000000     0.000000     0.659177

SCF energy       : -500.112508191
Gibbs free energy: -500.097378

Frequencies
 724.7825  1030.1435  1030.8434  1357.6591  1452.0514  1452.3277  3099.6405
3212.3984  3212.5732
```

S.13.7 $(CH_3)_2S$ in dichloro ethane

```
Cartesian coordinates (standard orientation)
C     -1.380757     0.510988     0.000043
H     -1.356605     1.135612    -0.893997
H     -2.296666    -0.079646    -0.000762
H     -1.357021     1.134903     0.894428
C      1.380763     0.510986     0.000043
H      2.296669    -0.079651    -0.000843
H      1.356563     1.135664    -0.893957
H      1.357064     1.134841     0.894470
S     -0.000002    -0.657098     0.000009

SCF energy       : -477.981750038
Gibbs free energy: -477.933190

Frequencies
 187.8836   208.3080   273.7384   700.1408   750.7041   912.4722   947.4076
 982.6969  1038.3978  1313.5288  1337.2390  1432.5554  1442.8884  1446.8316
1452.9144  3048.9046  3052.1356  3134.5355  3142.6386  3162.3246  3163.7933
```

S.13.8 CH_3^+ in dichloro ethane

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000013    -0.000001
H      0.188472     1.069398     0.000002
H      0.832341    -0.697858     0.000002
H     -1.020680    -0.371619     0.000002
```

```
SCF energy       : -39.5603450655
Gibbs free energy: -39.547983

Frequencies
1371.4633  1376.8537  1406.7159  3077.7214  3279.0856  3285.1748
```

S.14 Selected cluster geometries in pentanal

S.14.1 $(CH_3)_3S^+$ in pentanal

```
Cartesian coordinates (input orientation)
C      0.001628     1.613409     0.264355
H      0.003618     1.492416     1.345353
H      0.893062     2.131926    -0.082259
H     -0.890584     2.132911    -0.078975
C     -1.393928    -0.804086     0.268904
H     -1.384558    -1.841395    -0.059301
H     -1.293127    -0.726034     1.349153
H     -2.293047    -0.304944    -0.085908
C      1.391832    -0.808944     0.262735
H      1.404096    -1.833529    -0.103096
H      2.287837    -0.283581    -0.060793
H      1.274475    -0.770643     1.343485
S     -0.001304     0.002492    -0.529695

SCF energy       : -517.686593486
Gibbs free energy: -517.599781

Frequencies
 130.4760   253.3379   262.2743   284.0640   295.8950   332.6419   658.2519
 734.8830   743.1960   901.6584   939.2333   953.9324  1046.0827  1061.9897
1069.1078  1327.5705  1331.4641  1372.3164  1412.3445  1424.2820  1429.4669
1441.7570  1445.8175  1457.6532  3079.8341  3090.7319  3099.2285  3192.7697
3204.4368  3206.9039  3210.1578  3212.7699  3218.6542
```

S.14.2 Tripod ion pair in pentanal

```
Cartesian coordinates (standard orientation)
C      0.734706    -0.261856     1.590925
H     -0.347187    -0.249255     1.449991
H      1.092612    -1.221596     1.959514
H      1.074635     0.537754     2.246576
C      0.715874     1.508233    -0.569337
H      1.064701     1.687412    -1.584673
H     -0.364361     1.362269    -0.521317
H      1.053046     2.309383     0.085915
```

```
C      0.737643    -1.249130    -1.020690
H      1.078859    -1.082868    -2.040622
H      1.095894    -2.212176    -0.661490
H     -0.344390    -1.148689    -0.924434
S      1.528231     0.006569    -0.001922
Cl    -2.528520    -0.004166     0.000936

SCF energy       : -978.101384430
Gibbs free energy: -978.019187

Frequencies
  81.3202    99.1199   109.6053   208.9851   221.6855   253.4544   261.7840
 275.2913   309.7557   649.4856   724.4722   730.9723   908.0438   953.0219
 959.4698  1049.8904  1058.2431  1068.2614  1320.9869  1323.4814  1355.2094
1419.8518  1424.0255  1434.7583  1443.5905  1446.3810  1449.0465  3053.5278
3060.4327  3063.1030  3176.8636  3182.9390  3185.5603  3198.1869  3198.5947
3203.7054
```

S.14.3 Linear ion pair in pentanal

```
Cartesian coordinates (standard orientation)
C      2.124548    -1.388531     0.458276
H      1.753204    -1.281774     1.475272
H      1.736199    -2.289026    -0.013296
H      3.212192    -1.389085     0.426891
C      2.099262     1.401997     0.451466
H      1.732090     2.296059    -0.048387
H      1.691966     1.313572     1.456557
H      3.187075     1.396871     0.458464
C     -0.201300    -0.010792    -0.269563
H     -0.603363     0.874821    -0.754478
H     -0.594714    -0.902758    -0.749802
H     -0.415589    -0.008007     0.795685
S      1.576549    -0.000585    -0.543466
Cl    -3.591700    -0.001022     0.106322

SCF energy       : -978.093713491
Gibbs free energy: -978.013000

Frequencies
  40.7114    57.7793    95.6689   168.1169   219.3859   226.8390   273.8633
 300.0512   302.4623   656.7408   733.0330   741.1497   907.0869   933.9222
 941.3146  1030.4371  1047.9518  1056.2642  1318.8831  1328.3505  1352.6662
```

```
1416.3427  1424.4020  1427.2429  1431.4015  1436.3073  1449.7284  3086.8400
3094.8642  3115.3266  3201.6695  3206.9112  3210.8703  3213.1193  3233.0644
3233.7627
```

S.14.4 Linear transition state in pentanal

```
Cartesian coordinates (standard orientation)
C      1.626975     1.211363     1.388715
H      0.759938     1.870052     1.339450
H      1.587247     0.611461     2.296634
H      2.548862     1.790937     1.374024
C      1.626975     1.211363    -1.388715
H      1.587247     0.611461    -2.296634
H      0.759938     1.870052    -1.339450
H      2.548862     1.790937    -1.374024
C     -0.656971    -0.554149     0.000000
H     -0.527955    -1.079317    -0.929463
H     -0.527955    -1.079317     0.929463
H     -0.933304     0.485151     0.000000
S      1.626975     0.059825     0.000000
Cl    -2.906844    -1.120005     0.000000

SCF energy       : -978.059213205
Gibbs free energy: -977.980067

Frequencies
-591.6858    64.8038    94.5401    97.0253   144.9735   183.4445   217.8220
 252.6343   264.6337   298.2937   698.2824   749.1948   919.7773   940.1210
 972.2910  1003.6936  1006.8676  1048.6544  1056.3941  1319.1809  1350.1241
1358.4352  1366.7166  1429.5973  1434.3165  1443.9446  1451.7130  3068.8343
3069.3868  3166.9930  3169.5170  3171.1256  3181.1991  3181.4255  3373.2345
3382.6188
```

S.14.5 Immediate product cluster in pentanal

```
Cartesian coordinates (standard orientation)
C     -1.862664     1.411169     0.520068
H     -0.998660     1.249622     1.166593
H     -1.698488     2.305253    -0.080595
H     -2.760515     1.544915     1.124070
C     -2.318607    -1.311064     0.554229
H     -2.455206    -2.224275    -0.023934
H     -1.447405    -1.423409     1.201235
H     -3.209723    -1.130744     1.156337
C      1.620308    -0.097869    -0.306727
H      1.529211    -0.592158    -1.269011
```

```
H      1.245626     0.919960    -0.359599
H      1.103847    -0.659641     0.466365
S     -2.066484     0.031572    -0.630433
Cl     3.360049    -0.029888     0.123532

SCF energy       : -978.096222433
Gibbs free energy: -978.018877

Frequencies
  37.6239    61.2942    70.6976    77.9652   111.4160   116.0480   196.6753
 199.1715   276.8620   702.8066   733.6144   755.6530   913.9405   956.4082
 988.3066  1033.5895  1038.1160  1059.7857  1320.4337  1343.2808  1365.8529
1435.0526  1443.9399  1447.4148  1449.4121  1454.4890  1463.2544  3060.2764
3063.4152  3103.7689  3144.5570  3152.4393  3171.0702  3173.9894  3213.6712
3220.5606
```

S.14.6 CH_3Cl in pentanal

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.133598
H      0.000000     1.033432    -1.468113
H      0.894979    -0.516716    -1.468113
H     -0.894979    -0.516716    -1.468113
Cl     0.000000     0.000000     0.659172

SCF energy       : -500.112502817
Gibbs free energy: -500.097373

Frequencies
 724.8190  1030.1471  1030.8450  1357.6716  1452.0779  1452.3556  3099.6272
3212.3757  3212.5510
```

S.14.7 $(CH_3)_2S$ in pentanal

```
Cartesian coordinates (standard orientation)
C     -1.380747     0.510991     0.000043
H     -1.356604     1.135616    -0.893999
H     -2.296658    -0.079639    -0.000761
H     -1.357019     1.134908     0.894429
C      1.380752     0.510989     0.000043
H      2.296661    -0.079645    -0.000843
H      1.356562     1.135668    -0.893959
H      1.357062     1.134845     0.894471
S     -0.000002    -0.657102     0.000009
```

```
SCF energy       : -477.981743308
Gibbs free energy: -477.933183

Frequencies
 187.8776   208.3412   273.7622   700.1552   750.7153   912.4659   947.4011
 982.7123  1038.4095  1313.5357  1337.2572  1432.5747  1442.9177  1446.8463
1452.9427  3048.8938  3052.1233  3134.5160  3142.6186  3162.3179  3163.7850
```

S.14.8 CH_3^+ in pentanal

```
Cartesian coordinates (standard orientation)
C     -0.000022     0.000013    -0.000001
H      0.188736     1.069357     0.000002
H      0.832174    -0.698067     0.000002
H     -1.020777    -0.371371     0.000002

SCF energy       : -39.5602003121
Gibbs free energy: -39.547840

Frequencies
1371.3944  1376.8036  1406.7249  3077.6132  3278.9676  3285.0678
```

S.15 Selected cluster geometries in acetic acid

S.15.1 $(CH_3)_3S^+$ in acetic acid

```
Cartesian coordinates (input orientation)
C      0.002759     1.612834     0.263690
H      0.005479     1.492102     1.344773
H      0.894316     2.130762    -0.083535
H     -0.889168     2.133289    -0.079099
C     -1.395157    -0.802622     0.271095
H     -1.381440    -1.843371    -0.046171
H     -1.298613    -0.713678     1.350950
H     -2.294847    -0.310002    -0.091675
C      1.391598    -0.810277     0.260952
H      1.413221    -1.830159    -0.117612
H      2.285928    -0.274866    -0.050971
H      1.268194    -0.785714     1.341532
S     -0.002270     0.001700    -0.529970

SCF energy       : -517.681421877
Gibbs free energy: -517.594613
```

```
Frequencies
 148.8139   235.3716   255.9336   282.4132   299.1375   339.3489   655.8658
 734.3759   742.5717   901.9543   940.9438   949.1599  1039.7581  1060.0025
1069.3122  1328.6411  1329.1358  1366.0242  1415.3786  1424.7753  1430.1196
1441.2540  1448.0557  1459.4283  3077.3693  3089.9554  3098.6792  3189.9206
3202.3606  3204.9621  3210.8026  3211.9147  3218.6612
```

S.15.2 Tripod ion pair in acetic acid

```
Cartesian coordinates (standard orientation)
C      0.694456    -0.493271     1.533533
H     -0.385054    -0.459611     1.372540
H      1.048626    -1.496788     1.763659
H      1.019542     0.201858     2.305438
C      0.713338     1.576568    -0.342969
H      1.077858     1.900746    -1.316076
H     -0.367677     1.425444    -0.332613
H      1.040041     2.273590     0.426680
C      0.745615    -1.086406    -1.193164
H      1.117609    -0.785991    -2.170960
H      1.085257    -2.094097    -0.960223
H     -0.338140    -0.986583    -1.112339
S      1.516762     0.005961     0.012263
Cl    -2.499218    -0.003252    -0.009219

SCF energy       : -978.097729897
Gibbs free energy: -978.014978

Frequencies
  91.0995    98.8366   114.9043   221.0818   246.2085   260.7906   273.1830
 276.5141   312.0458   649.7742   726.7661   729.8319   909.3659   956.7478
 961.8238  1056.5711  1059.8774  1070.4330  1320.6491  1324.5487  1358.4370
1422.8158  1423.9045  1435.0308  1445.8818  1449.3853  1451.0860  3054.7499
3055.7169  3059.6931  3182.5549  3183.6479  3184.7750  3203.6835  3208.4739
3212.6658
```

S.15.3 Linear ion pair in acetic acid

```
Cartesian coordinates (standard orientation)
C      2.117468    -1.354706     0.501782
H      1.678772    -1.263350     1.493257
H      1.801993    -2.274893     0.014292
H      3.203935    -1.305806     0.538654
C      1.986123     1.434941     0.454506
H      1.594492     2.305622    -0.067722
H      1.548282     1.338703     1.445985
```

```
H      3.071981     1.483603     0.498593
C     -0.225130    -0.078768    -0.347401
H     -0.645551     0.782208    -0.860502
H     -0.559150    -0.992520    -0.832127
H     -0.490069    -0.070827     0.706130
S      1.563243    -0.000280    -0.542171
Cl    -3.499255    -0.000415     0.122638

SCF energy       : -978.088054508
Gibbs free energy: -978.007100

Frequencies
  57.2919    57.6775    94.9027   183.5697   200.0052   235.2899   267.1094
 287.1464   315.8405   648.9160   726.2881   745.0985   899.7450   930.8340
 946.0704  1039.6794  1043.6183  1048.4947  1304.3017  1330.9398  1352.7003
1416.3393  1418.6670  1424.4234  1437.9149  1439.0892  1444.8311  3089.9775
3093.4491  3109.9161  3204.7856  3206.3593  3208.7230  3216.2194  3225.8213
3229.2035
```

S.15.4 Linear transition state in acetic acid

```
Cartesian coordinates (standard orientation)
C      1.623835     1.204645     1.388599
H      0.755508     1.861806     1.340645
H      1.586148     0.604715     2.296628
H      2.544927     1.785448     1.372937
C      1.623835     1.204645    -1.388599
H      1.586148     0.604715    -2.296628
H      0.755508     1.861806    -1.340645
H      2.544927     1.785448    -1.372937
C     -0.644730    -0.550148     0.000000
H     -0.526636    -1.078434    -0.929218
H     -0.526636    -1.078434     0.929218
H     -0.926816     0.487685     0.000000
S      1.623835     0.053289     0.000000
Cl    -2.905417    -1.108366     0.000000

SCF energy       : -978.057099733
Gibbs free energy: -977.977748

Frequencies
-585.3700    64.3807    99.8672   102.9230   143.4319   185.4827   223.3385
 254.4350   268.7577   303.1958   698.6665   749.5271   919.3598   940.0723
 974.2765  1002.7951  1012.5138  1048.5084  1057.8043  1319.7325  1353.0712
1358.7423  1366.9150  1430.4441  1434.3844  1445.5950  1454.2651  3068.3977
```

```
3069.2133  3166.5507  3169.1035  3170.7515  3181.2264  3181.2592  3372.1794
3381.4250
```

S.15.5 Immediate product cluster in acetic acid

```
Cartesian coordinates (standard orientation)
C     -1.796149     1.421756     0.504971
H     -0.921949     1.241043     1.132781
H     -1.619336     2.304835    -0.108333
H     -2.674757     1.589152     1.128698
C     -2.344641    -1.282044     0.577949
H     -2.521887    -2.196356     0.012552
H     -1.466009    -1.416937     1.210503
H     -3.218300    -1.066447     1.194123
C      1.621561    -0.181845    -0.346371
H      1.572240    -0.885317    -1.172056
H      1.255643     0.794439    -0.649729
H      1.065316    -0.552556     0.509739
S     -2.070828     0.038757    -0.626506
Cl     3.339863    -0.010539     0.138031

SCF energy       : -978.095694896
Gibbs free energy: -978.018026

Frequencies
  55.0445    64.3589    73.8941    80.6599   102.3504   115.6031   189.3865
 197.6800   277.1661   705.0970   728.2852   758.9998   913.7031   954.9581
 987.8726  1029.5728  1037.9358  1052.8115  1320.3896  1344.0961  1360.6773
1435.5204  1444.5753  1447.6861  1450.5591  1454.4906  1462.6999  3057.5586
3061.2144  3108.4624  3142.0210  3150.4783  3169.6161  3172.3540  3219.6395
3222.6413
```

S.15.6 CH_3Cl in acetic acid

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.132957
H      0.000000     1.033315    -1.468051
H      0.894877    -0.516658    -1.468051
H     -0.894877    -0.516658    -1.468051
Cl     0.000000     0.000000     0.658935

SCF energy       : -500.112250092
Gibbs free energy: -500.097114
```

```
Frequencies
 726.5480  1030.3028  1030.9145  1358.2517  1453.3115  1453.6387  3099.0050
3211.3125  3211.5042
```

S.15.7 $(CH_3)_2S$ in acetic acid

```
Cartesian coordinates (standard orientation)
C     -1.380239     0.511135     0.000044
H     -1.356539     1.135768    -0.894096
H     -2.296288    -0.079324    -0.000713
H     -1.356924     1.135147     0.894465
C      1.380244     0.511133     0.000044
H      2.296291    -0.079330    -0.000801
H      1.356493     1.135824    -0.894053
H      1.356970     1.135080     0.894511
S     -0.000002    -0.657299     0.000010

SCF energy       : -477.981430345
Gibbs free energy: -477.932854

Frequencies
 187.7863   209.3910   274.5841   700.8251   751.2476   912.1805   947.1359
 983.3051  1038.8497  1313.8644  1337.9872  1433.4656  1444.1617  1447.5797
1454.2305  3048.3880  3051.5715  3133.5971  3141.7094  3162.0014  3163.4005
```

S.15.8 CH_3^+ in acetic acid

```
Cartesian coordinates (standard orientation)
C      0.000022     0.000020    -0.000008
H     -0.203120     1.067031     0.000016
H     -0.822961    -0.709378     0.000016
H      1.025951    -0.357771     0.000016

SCF energy       : -39.5531728474
Gibbs free energy: -39.540862

Frequencies
1369.9181  1374.3957  1406.3065  3071.9811  3272.4669  3280.0950
```

S.16 Selected cluster geometries in 1-bromooactane

S.16.1 $(CH_3)_3S^+$ in 1-bromooctane

```
Cartesian coordinates (input orientation)
C      0.003280     1.612391     0.263305
H      0.006322     1.492040     1.344471
H      0.894876     2.130058    -0.084279
```

```
H     -0.888485     2.133302    -0.079333
C     -1.396098    -0.801951     0.272169
H     -1.381297    -1.844169    -0.040379
H     -1.301658    -0.708392     1.351857
H     -2.295758    -0.311724    -0.094158
C      1.391881    -0.810871     0.260215
H      1.418602    -1.828445    -0.124342
H      2.285092    -0.270354    -0.046367
H      1.265955    -0.792852     1.340696
S     -0.002712     0.000966    -0.529895

SCF energy       : -517.678056186
Gibbs free energy: -517.591351

Frequencies
 156.2801   207.8385   254.0951   285.5373   300.4038   342.7269   654.1474
 733.9928   742.1719   902.3389   941.9712   945.7556  1035.5038  1057.5819
1069.5255  1327.2849  1329.3575  1361.7161  1416.5773  1425.0343  1430.6255
1440.4686  1449.2001  1460.5989  3076.3623  3089.4427  3098.3090  3188.7446
3201.4109  3203.7823  3210.7780  3211.3819  3218.5885
```

S.16.2 Tripod ion pair in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C     -0.686000    -0.886931    -1.345323
H      0.394249    -0.796508    -1.209557
H     -1.025681    -1.919759    -1.291532
H     -1.028266    -0.430156    -2.272339
C     -0.720740     1.610460    -0.094789
H     -1.076926     2.177756     0.763389
H      0.362544     1.472352    -0.081230
H     -1.068373     2.073340    -1.016663
C     -0.704804    -0.721622     1.441480
H     -1.080742    -0.177560     2.306245
H     -1.021885    -1.761861     1.490442
H      0.376403    -0.622219     1.322460
S     -1.504577    -0.007862    -0.004646
Cl     2.465363     0.005822     0.003230

SCF energy       : -978.095399984
Gibbs free energy: -978.013114

Frequencies
  83.5092    98.4434   123.6127   208.1868   223.6205   232.7922   268.5134
 286.0274   317.3643   649.3295   722.5004   734.9430   908.8439   956.6755
```

```
 959.9059  1055.8572  1057.5887  1071.9647  1318.3958  1323.6646  1358.5158
1416.5773  1420.2370  1436.6302  1441.5141  1450.8944  1457.1952  3038.4235
3043.0573  3052.2266  3171.0115  3173.7960  3177.7611  3199.0392  3199.4599
3203.6261
```

S.16.3 Linear ion pair in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C      2.084619    -1.357930     0.512599
H      1.623386    -1.267692     1.493863
H      1.777673    -2.276299     0.016513
H      3.170006    -1.312190     0.574504
C      1.964646     1.431748     0.466512
H      1.598172     2.306050    -0.067753
H      1.495325     1.341147     1.443921
H      3.049130     1.469749     0.544011
C     -0.235467    -0.072322    -0.385752
H     -0.640823     0.790508    -0.907840
H     -0.562695    -0.984598    -0.877796
H     -0.527280    -0.063168     0.660931
S      1.557637    -0.000337    -0.541296
Cl    -3.458110    -0.000417     0.130602

SCF energy       : -978.084533229
Gibbs free energy: -978.003254

Frequencies
  55.9712    63.0656   103.2345   189.8793   210.2602   237.2755   267.2491
 290.3082   317.7428   648.2794   725.5106   744.1028   901.5948   938.4572
 946.6271  1042.4498  1048.3919  1050.4493  1311.9381  1330.7599  1355.8234
1417.4798  1420.8864  1426.4491  1439.2710  1439.8898  1446.9215  3088.6539
3091.5201  3108.4751  3203.2057  3203.7168  3208.3081  3213.3651  3225.0575
3227.6525
```

S.16.4 Linear transition state in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C      1.970203    -1.388776     0.465443
H      1.445016    -1.336852     1.419127
H      1.687908    -2.296143    -0.066256
H      3.047806    -1.378086     0.621378
C      1.969246     1.389175     0.465259
H      1.687001     2.296288    -0.066898
H      1.443479     1.337398     1.418647
H      3.046752     1.378849     0.621876
C     -0.802209    -0.000217    -0.244407
```

```
H     -0.906999     0.927889    -0.777105
H     -0.906377    -0.930961    -0.772637
H     -0.664369     0.002418     0.822371
S      1.508468    -0.000027    -0.588976
Cl    -3.108185    -0.000085     0.122667

SCF energy       : -978.055681505
Gibbs free energy: -977.978975

Frequencies
-581.4053    12.3942    55.1526    68.3690   135.1419   180.3022   232.8383
 251.2869   264.9501   297.9055   703.1385   754.0445   913.9137   938.7182
 965.7874   996.1848   997.1334  1038.3396  1049.1190  1318.5580  1347.8809
1354.4464  1362.8011  1432.5597  1434.7980  1449.7075  1453.2512  3069.5908
3072.9252  3171.2094  3172.5704  3174.8745  3187.6848  3187.9839  3381.4939
3382.1786
```

S.16.5 Immediate product cluster in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C     -1.799108     1.421808     0.504760
H     -0.924933     1.243801     1.133468
H     -1.624135     2.305257    -0.108555
H     -2.678657     1.587396     1.127691
C     -2.342409    -1.282412     0.578147
H     -2.516609    -2.197497     0.013044
H     -1.464760    -1.415288     1.212592
H     -3.217777    -1.068596     1.192561
C      1.621450    -0.181508    -0.346555
H      1.571784    -0.886212    -1.171200
H      1.255499     0.794189    -0.651784
H      1.064369    -0.550747     0.509694
S     -2.069347     0.038059    -0.626696
Cl     3.339127    -0.009917     0.138324

SCF energy       : -978.095395451
Gibbs free energy: -978.017727

Frequencies
  54.2308    64.6434    74.2471    80.8981   102.2484   114.8671   189.7648
 197.0890   277.2185   705.2874   729.1375   759.1061   913.5629   954.9141
 988.0331  1029.5810  1038.0411  1053.4778  1320.7053  1344.4268  1361.3513
1436.0803  1445.0558  1448.0704  1451.4190  1455.3048  1463.1383  3057.4041
3061.0117  3108.2352  3141.5775  3150.0154  3169.5660  3172.4387  3219.1585
3222.2508
```

S.16.6 CH_3Cl in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.132559
H      0.000000     1.033240    -1.468018
H      0.894812    -0.516620    -1.468018
H     -0.894812    -0.516620    -1.468018
Cl     0.000000     0.000000     0.658789

SCF energy       : -500.112093367
Gibbs free energy: -500.096953

Frequencies
 727.6307  1030.3872  1030.9515  1358.6047  1454.0614  1454.4088  3098.6247
3210.6550  3210.8540
```

S.16.7 $(CH_3)_2S$ in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C     -1.379923     0.511224     0.000044
H     -1.356494     1.135858    -0.894158
H     -2.296058    -0.079130    -0.000673
H     -1.356849     1.135306     0.894478
C      1.379928     0.511222     0.000044
H      2.296060    -0.079136    -0.000763
H      1.356447     1.135916    -0.894114
H      1.356896     1.135237     0.894525
S     -0.000002    -0.657420     0.000011

SCF energy       : -477.981239593
Gibbs free energy: -477.932657

Frequencies
 187.8700   209.6241   274.8498   701.2327   751.5780   912.0124   946.9988
 983.5590  1039.0309  1314.0694  1338.3387  1434.0025  1444.8253  1448.0633
1454.9921  3048.0735  3051.2504  3133.0257  3141.1703  3161.8046  3163.1695
```

S.16.8 CH_3^+ in 1-bromooctane

```
Cartesian coordinates (standard orientation)
C      0.000021     0.000024    -0.000013
H     -0.214384     1.065029     0.000025
H     -0.815587    -0.718145     0.000025
H      1.029845    -0.347027     0.000025
```

```
SCF energy       : -39.5485878289
Gibbs free energy: -39.536271

Frequencies
1375.6445  1381.0315  1406.2779  3068.7603  3269.0893  3277.1738
```

S.17 Selected cluster geometries in chloroform

S.17.1 $(CH_3)_3S^+$ in chloroform

```
Cartesian coordinates (input orientation)
C      0.003338     1.612244     0.263399
H      0.006005     1.491946     1.344586
H      0.895157     2.129724    -0.083908
H     -0.888088     2.133525    -0.079582
C     -1.396395    -0.801810     0.272400
H     -1.381256    -1.844425    -0.038864
H     -1.302726    -0.706956     1.352053
H     -2.296046    -0.312357    -0.095069
C      1.392065    -0.810946     0.259952
H      1.419683    -1.828136    -0.125597
H      2.284994    -0.269597    -0.046082
H      1.266100    -0.794018     1.340463
S     -0.002832     0.000808    -0.529790

SCF energy       : -517.676918908
Gibbs free energy: -517.590279

Frequencies
 154.4608   200.1254   252.8596   286.6814   300.6289   343.3210   653.6889
 733.8680   742.0159   902.3543   941.7937   945.0204  1034.0202  1056.9363
1069.3369  1326.7237  1329.4673  1360.5306  1416.5384  1425.0955  1430.7753
1440.3272  1449.4693  1460.8574  3076.0071  3089.2230  3098.1847  3188.3691
3201.0400  3203.4118  3210.5831  3211.2076  3218.5275
```

S.17.2 Tripod ion pair in chlorform

```
Cartesian coordinates (standard orientation)
C     -0.681779     1.508960    -0.567369
H      0.397093     1.366102    -0.472417
H     -0.986758     1.672002    -1.599483
H     -1.052978     2.315971     0.061961
C     -0.747724    -0.260828     1.591726
H     -1.106342    -1.224257     1.950273
H      0.337310    -0.241025     1.471156
H     -1.106681     0.534734     2.242041
```

```
C     -0.694096    -1.250730    -1.017230
H     -1.063185    -2.213158    -0.666173
H     -1.009655    -1.085273    -2.045775
H      0.386032    -1.147028    -0.891080
S     -1.508147     0.006910    -0.018860
Cl     2.475124    -0.004296     0.012265

SCF energy       : -978.094688438
Gibbs free energy: -978.012006

Frequencies
  93.1185   106.7721   121.9003   215.7584   228.1537   258.1968   275.8283
 285.9425   318.7419   648.5442   723.1565   731.2320   909.8518   957.8162
 962.2156  1053.7824  1059.6990  1072.8850  1321.9490  1324.5322  1358.8734
1419.7376  1423.7230  1439.6233  1445.0327  1453.4254  1455.6055  3036.5690
3041.3538  3054.3559  3167.5410  3175.2167  3178.2302  3193.8523  3200.5797
3205.4126
```

S.17.3 Linear transition state in chloroform

```
Cartesian coordinates (standard orientation)
C      1.967770    -1.388841     0.465913
H      1.441081    -1.336683     1.418782
H      1.685956    -2.296147    -0.066154
H      3.045136    -1.378516     0.623462
C      1.967540     1.388936     0.465869
H      1.685749     2.296180    -0.066315
H      1.440698     1.336821     1.418660
H      3.044880     1.378692     0.623597
C     -0.799104    -0.000051    -0.245759
H     -0.905786     0.928962    -0.776550
H     -0.905616    -0.929782    -0.775336
H     -0.663147     0.000664     0.821273
S      1.507937    -0.000006    -0.589130
Cl    -3.106658    -0.000021     0.122854

SCF energy       : -978.055229748
Gibbs free energy: -977.978115

Frequencies
-579.3877    18.3078    58.5672    68.0163   133.6821   180.6708   231.5474
 251.7645   265.3975   297.6148   703.1649   754.0105   913.8923   938.6533
 965.7159   996.6910   996.8110  1038.2944  1048.9339  1318.6197  1347.6800
```

1354.4542 1362.9764 1432.6102 1434.7852 1449.6875 1453.2222 3069.5128
3072.9452 3171.1849 3172.4901 3174.7546 3187.7617 3188.1129 3381.1625
3381.9213

S.17.4 Immediate product cluster in chlorform

Cartesian coordinates (standard orientation)

C	-1.801899	1.422017	0.504483
H	-0.928045	1.245832	1.134173
H	-1.627858	2.305590	-0.108917
H	-2.682359	1.586361	1.126467
C	-2.341067	-1.282805	0.578254
H	-2.513039	-2.198436	0.013351
H	-1.464066	-1.414075	1.213965
H	-3.217615	-1.070220	1.191426
C	1.621698	-0.181582	-0.346277
H	1.571212	-0.891818	-1.166122
H	1.257212	0.792471	-0.658440
H	1.063486	-0.544126	0.512112
S	-2.068613	0.037521	-0.626834
Cl	3.339205	-0.009276	0.138387

SCF energy : -978.095297278
Gibbs free energy: -978.017496

Frequencies

53.8368	66.6490	77.9096	81.1238	103.4850	120.4750	190.1621
196.3525	277.2141	705.2764	729.3975	759.0663	913.5120	954.9560
988.0472	1029.5847	1038.0453	1055.0005	1320.8150	1344.4998	1361.7552
1436.2635	1445.1606	1448.3449	1451.9302	1455.7234	1463.4682	3057.4116
3060.9900	3107.6417	3141.4573	3149.8730	3169.5971	3172.5644	3218.6223
3221.7706						

S.17.5 CH_3Cl in chlorofom

Cartesian coordinates (standard orientation)

C	0.000000	0.000000	-1.132427
H	0.000000	1.033215	-1.468008
H	0.894790	-0.516607	-1.468008
H	-0.894790	-0.516607	-1.468008
Cl	0.000000	0.000000	0.658740

SCF energy : -500.112041727
Gibbs free energy: -500.096900

```
Frequencies
 727.9894  1030.4130  1030.9627  1358.7200  1454.3060  1454.6585  3098.5003
3210.4387  3210.6396
```

S.17.6 $(CH_3)_2S$ in chloroform

```
Cartesian coordinates (standard orientation)
C     -1.379819     0.511253     0.000044
H     -1.356479     1.135887    -0.894179
H     -2.295982    -0.079067    -0.000659
H     -1.356822     1.135360     0.894481
C      1.379825     0.511251     0.000044
H      2.295984    -0.079073    -0.000750
H      1.356432     1.135945    -0.894134
H      1.356870     1.135291     0.894528
S     -0.000002    -0.657461     0.000011

SCF energy       : -477.981177276
Gibbs free energy: -477.932593

Frequencies
 187.9143   209.6437   274.9035   701.3655   751.6865   911.9582   946.9569
 983.6266  1039.0781  1314.1368  1338.4406  1434.1770  1445.0291  1448.2261
1455.2375  3047.9699  3051.1473  3132.8374  3140.9958  3161.7395  3163.0942
```

S.17.7 CH_3^+ in chloroform

```
Cartesian coordinates (standard orientation)
C      0.000021     0.000025    -0.000014
H     -0.218580     1.064245     0.000028
H     -0.812806    -0.721392     0.000028
H      1.031263    -0.343005     0.000028

SCF energy       : -39.5470369074
Gibbs free energy: -39.534713

Frequencies
1378.6836  1384.0825  1405.9497  3067.7554  3268.1264  3276.2049
```

S.18 Selected cluster geometries in ether

S.18.1 $(CH_3)_3S^+$ in ether

```
Cartesian coordinates (standard orientation)
C     -0.914456   -1.332102    0.266013
H     -0.841406   -1.245058    1.348051
H     -1.945247   -1.245561   -0.072677
```

```
H     -0.487156   -2.267225   -0.090364
C      1.612468   -0.123142    0.267613
H      2.196023    0.730570   -0.071602
H      1.497945   -0.123526    1.349333
H      2.069137   -1.045287   -0.086770
C     -0.700925    1.455090    0.266058
H     -0.122841    2.310565   -0.077384
H     -1.727330    1.538157   -0.086523
H     -0.657521    1.351759    1.348171
S      0.002242   -0.000217   -0.522396

SCF energy       : -517.675002419
Gibbs free energy: -517.588909

Frequencies
 150.8517   161.2537   229.6559   264.1786   293.7821   313.7141   650.5798
 730.4532   735.2691   903.0337   937.3910   951.7208  1042.4189  1051.0672
1060.8693  1323.2005  1337.2442  1362.4001  1419.0778  1420.9976  1428.1141
1431.5617  1447.5043  1450.8120  3089.2730  3094.3969  3097.0475  3200.5351
3205.4324  3207.7819  3210.3348  3213.9116  3220.6070
```

S.18.2 Tripod ion pair in ether

```
Cartesian coordinates (standard orientation)
C     -0.686457    -0.445782     1.548306
H      0.394578    -0.408309     1.392125
H     -1.023865     0.270392     2.295781
H     -1.035189    -1.444734     1.804490
C     -0.707569    -1.119358    -1.160638
H     -1.085962    -0.858944    -2.147684
H      0.374574    -0.991956    -1.080208
H     -1.027221    -2.124938    -0.892189
C     -0.703505     1.564952    -0.389226
H     -1.057473     1.854257    -1.377299
H     -1.044974     2.283159     0.354062
H      0.378843     1.418353    -0.360243
S     -1.500148    -0.000249     0.005825
Cl     2.453779     0.000461    -0.004275

SCF energy       : -978.093395163
Gibbs free energy: -978.010905

Frequencies
  91.6263    99.1715   129.4650   200.4743   239.8084   244.4486   269.9507
 279.9330   320.6510   648.3981   724.3868   727.4106   906.8128   957.1449
```

```
 962.3299  1053.4634  1058.1463  1075.9466  1319.9255  1322.2285  1357.7843
1418.2936  1419.9040  1435.4147  1443.9655  1451.8118  1455.2270  3036.1628
3042.2598  3049.5053  3170.8329  3171.2667  3176.5848  3198.0679  3202.6333
3204.1701
```

S.18.3 Linear ion pair in ether

```
Cartesian coordinates (standard orientation)
C      2.032411    -1.393467     0.471355
H      1.612047    -1.293079     1.471398
H      1.662078    -2.291604    -0.022121
H      3.121475    -1.402882     0.492424
C      2.026701     1.396993     0.469374
H      1.652558     2.292866    -0.025354
H      1.606982     1.296258     1.469646
H      3.115728     1.410838     0.490130
C     -0.260432    -0.003584    -0.319774
H     -0.651096     0.884130    -0.812653
H     -0.647984    -0.892540    -0.812861
H     -0.510115    -0.003972     0.738859
S      1.527870     0.000002    -0.547107
Cl    -3.423510     0.000018     0.119913

SCF energy       : -978.080983893
Gibbs free energy: -977.999701

Frequencies
  54.7933    64.2960   112.9472   194.4720   230.0489   232.2322   275.6372
 289.3764   318.5744   643.1941   723.0906   745.8600   908.0535   940.2598
 948.2360  1044.9354  1051.3184  1053.1779  1317.0761  1329.1951  1359.0371
1415.5596  1419.6118  1427.5149  1434.1179  1439.4040  1446.1692  3076.1995
3076.8074  3098.7687  3190.2003  3190.6493  3195.2091  3195.4727  3215.4433
3219.5457
```

S.18.4 Seesaw ion pair in ether

```
Cartesian coordinates (standard orientation)
Cl     2.633799    -0.000002    -0.186443
S     -0.820589     0.000001    -0.404031
C     -0.419974    -1.398556     0.650038
C     -2.620464    -0.000002    -0.342271
C     -0.419969     1.398559     0.650037
H     -0.914892    -1.288692     1.613097
H     -2.967895    -0.000009     0.689381
H     -0.914859     1.288679     1.613107
H     -0.752756    -2.292853     0.126322
```

```
H     -2.957585     0.890022    -0.870683
H      0.667813     1.379201     0.730162
H      0.667806    -1.379179     0.730192
H     -2.957582    -0.890018    -0.870696
H     -0.752782     2.292853     0.126336

SCF energy       : -978.090546376
Gibbs free energy: -978.008413

Frequencies
  33.4119   121.0315   141.4066   202.1858   230.0764   261.1504   280.4427
 282.5037   302.7167   654.8884   736.6493   737.8377   905.4128   950.8644
 951.7063  1048.7195  1051.3237  1060.6438  1312.8990  1322.0955  1349.7049
1415.4916  1428.6951  1434.2465  1438.5178  1450.3147  1463.7380  3065.7307
3070.6033  3084.8224  3184.4561  3188.9632  3196.3273  3197.0210  3199.5674
3200.5147
```

S.18.5 Linear transition state in ether

```
Cartesian coordinates (standard orientation)
C     -1.963663     1.388753     0.466946
H     -1.434345     1.335985     1.418367
H     -1.682719     2.296080    -0.065562
H     -3.040611     1.378974     0.627289
C     -1.963832    -1.388681     0.466979
H     -1.682966    -2.296050    -0.065498
H     -1.434529    -1.335943     1.418410
H     -3.040784    -1.378784     0.627300
C      0.793516    -0.000042    -0.248362
H      0.903890    -0.929323    -0.778011
H      0.903892     0.929209    -0.778064
H      0.660825    -0.000009     0.819098
S     -1.507095    -0.000005    -0.589457
Cl     3.103808    -0.000014     0.123212

SCF energy       : -978.054431293
Gibbs free energy: -977.976844

Frequencies
-575.6346    27.0135    65.9907    68.5041   131.5847   181.3892   228.9956
 252.7976   266.2441   297.0423   703.2019   753.9425   913.8984   938.6963
 965.6820   996.5781   997.7433  1038.5001  1048.5614  1318.8020  1347.3076
1354.6278  1363.2701  1432.6826  1434.8819  1449.5851  1453.1832  3069.4295
3073.0173  3171.1958  3172.2746  3174.6465  3187.9458  3188.4042  3380.3853
3381.6057
```

S.18.6 Transition state for an attack from the seesaw ion pair

```
Cartesian coordinates (standard orientation)
Cl    -2.304256    -0.235866    -0.213264
S      0.881508    -0.172390    -0.530553
C     -0.642365     1.586192     0.637761
C      2.468340     0.597712    -0.154739
C      0.857669    -1.455387     0.735081
H      0.151452     1.411824     1.347640
H      2.458508     1.032430     0.847837
H      0.994894    -1.018013     1.724904
H     -0.423543     2.191773    -0.227861
H      3.267459    -0.140035    -0.227547
H     -0.120805    -1.925395     0.668636
H     -1.636798     1.643752     1.037536
H      2.630768     1.380826    -0.893968
H      1.644412    -2.180301     0.528540

SCF energy       : -978.007758504
Gibbs free energy: -977.929657

Frequencies
-471.9031    71.0954   100.2428   134.6895   143.2819   167.9461   177.1735
 192.7651   274.5309   316.4043   682.6387   699.0433   743.7792   762.1077
 912.1170   948.3760   973.3854  1036.3097  1092.7951  1318.5257  1337.4508
1390.1653  1433.4581  1434.6766  1441.2620  1445.5529  1451.5808  3055.7850
3065.7271  3146.7101  3159.2265  3160.9251  3174.3005  3193.9700  3329.1886
3368.3173
```

S.18.7 Transition state for a direct attack in ether

Results form the `Integral=UltraFineGrid` calculation.

```
Cartesian coordinates (standard orientation)
C     -1.207438    -0.695843    -1.374117
H     -2.013488    -1.426744    -1.306096
H     -1.308234    -0.124700    -2.296156
H     -0.229328    -1.174019    -1.326854
C     -1.202122    -0.636228     1.399365
H     -0.224744    -1.117050     1.369111
H     -1.300239    -0.026135     2.296426
H     -2.008737    -1.368883     1.366036
C      1.003904     1.829075    -0.024926
H      2.020751     1.661154    -0.324207
H      0.336026     2.287227    -0.734939
H      0.798738     1.958750     1.026381
```

```
S     -1.349288     0.474088    -0.011456
Cl     1.997164    -0.661002     0.006568

SCF energy       : -978.007514835
Gibbs free energy: -977.930795

Frequencies
-443.8231    35.7559    63.5773   129.3206   147.9800   156.7984   183.8723
 211.2168   263.0489   299.5426   652.3879   684.3419   711.3592   764.2936
 921.4476   945.5074   975.4022  1047.9836  1088.8196  1307.8710  1330.7660
1381.6247  1419.8020  1425.8700  1439.8166  1446.2836  1456.2652  3056.6504
3057.0745  3159.4981  3164.5889  3166.3294  3175.4661  3176.5236  3342.3720
3371.9093
```

S.18.8 Immediate product cluster in ether

```
Cartesian coordinates (standard orientation)
C     -1.810593     1.422344     0.504228
H     -0.937735     1.251256     1.136735
H     -1.639355     2.306522    -0.109075
H     -2.693773     1.582620     1.123426
C     -2.336875    -1.284693     0.577844
H     -2.502315    -2.201561     0.013005
H     -1.461589    -1.411422     1.216907
H     -3.216694    -1.076151     1.187721
C      1.622078    -0.179592    -0.344714
H      1.568203    -0.901802    -1.153822
H      1.261999     0.791257    -0.671772
H      1.061615    -0.526596     0.518673
S     -2.066632     0.036019    -0.627212
Cl     3.339888    -0.008164     0.138203

SCF energy       : -978.095125966
Gibbs free energy: -978.017229

Frequencies
  50.6655    68.9013    79.1527    83.0488   103.8137   132.6071   189.8270
 194.6749   277.1599   705.0759   729.9186   758.7842   913.3712   954.9942
 988.0097  1029.4153  1037.9769  1057.1552  1321.0083  1344.5972  1362.2939
1436.5861  1445.2730  1448.6560  1452.8914  1456.3760  1463.7331  3057.4749
3060.9357  3105.5756  3141.2519  3149.5363  3169.7356  3172.9592  3216.5889
3220.2066
```

S.18.9 Single bonded product cluster

```
Cartesian coordinates (standard orientation)
Cl    -2.627646    -0.366772     0.011363
S      1.775817    -0.155617    -0.658464
C     -1.810327     1.228223    -0.014722
C      2.418267     1.047690     0.528945
C      1.147282    -1.402435     0.490852
H     -1.875459     1.653708     0.983012
H      1.616507     1.435429     1.159910
H      0.363676    -0.986092     1.125664
H     -0.776010     1.064385    -0.310851
H      3.196847     0.600352     1.147934
H      0.723001    -2.203734    -0.113143
H     -2.326458     1.855708    -0.735758
H      2.847021     1.866415    -0.048100
H      1.956462    -1.802050     1.103147

SCF energy       : -978.095643452
Gibbs free energy: -978.017885

Frequencies
  42.3056    55.4903    69.7539    89.4555    98.6093   135.0475   204.0769
 207.2523   272.9593   710.2082   730.7922   765.2887   912.2632   959.4627
 991.2540  1033.6813  1038.3870  1041.8192  1322.2086  1345.5133  1363.5402
1434.5229  1443.6428  1451.1415  1454.3251  1455.6470  1464.3058  3060.7751
3066.4924  3087.1249  3149.2145  3159.2777  3172.7631  3177.2105  3195.6375
3214.3734
```

S.18.10 CH_3Cl in ether

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.131795
H      0.000000     1.032622    -1.468298
H      0.894277    -0.516311    -1.468298
H     -0.894277    -0.516311    -1.468298
Cl     0.000000     0.000000     0.658568

SCF energy       : -500.111951633
Gibbs free energy: -500.096792

Frequencies
 729.1772  1029.3963  1029.9186  1358.7200  1454.4554  1454.8118  3101.3476
3212.9628  3213.1629
```

S.18.11 $(CH_3)_2S$ in ether

```
Cartesian coordinates (standard orientation)
C     -1.379625     0.511253     0.000030
H     -1.357268     1.135258    -0.895005
H     -2.295875    -0.079574     0.000293
H     -1.356549     1.135899     0.894450
C      1.379631     0.511251     0.000058
H      2.295879    -0.079578    -0.001106
H      1.356473     1.136018    -0.894432
H      1.357341     1.135129     0.895027
S     -0.000002    -0.657386     0.000015

SCF energy       : -477.981078641
Gibbs free energy: -477.932610

Frequencies
 192.2525   198.2836   267.3110   702.1191   752.7408   911.2548   947.4718
 981.0925  1035.9690  1314.4607  1336.2158  1435.6346  1444.2830  1450.5349
1457.0202  3043.6091  3047.5640  3129.9437  3138.4306  3157.5188  3158.8868
```

S.18.12 CH_3^+ in ether

```
Cartesian coordinates (standard orientation)
C      0.000020     0.000028    -0.000016
H     -0.226603     1.062690     0.000031
H     -0.807441    -0.727570     0.000031
H      1.033923    -0.335287     0.000031

SCF energy       : -39.5442704569
Gibbs free energy: -39.531935

Frequencies
1383.4047  1390.7371  1405.1683  3065.8931  3266.2080  3274.5851
```

S.19 Selected cluster geometries in anisole

S.19.1 $(CH_3)_3S^+$ in anisole

```
Cartesian coordinates (input orientation)
C      0.003536     1.612013     0.263269
H      0.006255     1.491965     1.344511
H      0.895393     2.129396    -0.084146
H     -0.887766     2.133541    -0.079736
C     -1.396942    -0.801532     0.272856
H     -1.381589    -1.844766    -0.036432
H     -1.304335    -0.704743     1.352451
```

```
H     -2.296497    -0.312988    -0.096214
C      1.392360    -0.811200     0.259640
H      1.422273    -1.827425    -0.128369
H      2.284720    -0.267653    -0.044338
H      1.265601    -0.797000     1.340132
S     -0.003009     0.000393    -0.529664

SCF energy       : -517.674818317
Gibbs free energy: -517.588283

Frequencies
 154.3740   183.9771   251.9873   288.4526   300.6323   344.6003   652.7626
 733.6147   741.7436   902.5643   941.0891   944.2933  1031.7493  1055.4436
1069.2650  1325.6693  1329.8219  1358.5550  1416.6863  1425.3976  1431.0495
1440.0468  1449.9157  1461.3670  3075.5250  3088.8954  3097.9173  3187.8118
3200.5256  3202.7838  3210.4475  3210.9584  3218.3959
```

S.19.2 Tripod ion pair in anisole

```
Cartesian coordinates (standard orientation)
C      0.721782     1.606500    -0.159188
H     -0.361777     1.469603    -0.148795
H      1.071613     2.204139     0.680839
H      1.076889     2.035955    -1.094433
C      0.688360    -0.942017    -1.307901
H      1.033255    -1.970620    -1.215152
H     -0.391970    -0.850523    -1.171963
H      1.024610    -0.520112    -2.253446
C      0.708525    -0.664814     1.468384
H      1.046968    -1.694409     1.570874
H      1.064694    -0.070641     2.307975
H     -0.373666    -0.594067     1.336642
S      1.506272    -0.006575    -0.004770
Cl    -2.470763     0.005757     0.003294

SCF energy       : -978.093363534
Gibbs free energy: -978.010546

Frequencies
  91.5809   102.2703   125.5561   213.0587   241.9124   258.4606   282.0126
 285.3652   319.6377   651.8890   725.1684   731.7776   913.4474   959.4523
 961.7198  1059.6761  1063.0033  1073.3973  1323.8531  1325.1208  1363.6380
1419.2822  1423.9492  1438.6266  1447.5218  1454.5523  1456.5096  3038.8519
3042.3253  3051.6587  3172.2788  3173.8206  3176.7841  3195.6915  3203.3504
3204.9267
```

S.19.3 Linear transition state in anisole

```
Cartesian coordinates (standard orientation)
C     -1.963535     1.388746     0.466981
H     -1.434136     1.335958     1.418357
H     -1.682620     2.296077    -0.065538
H     -3.040470     1.378979     0.627408
C     -1.963698    -1.388676     0.467013
H     -1.682862    -2.296047    -0.065477
H     -1.434313    -1.335919     1.418398
H     -3.040637    -1.378794     0.627421
C      0.793318    -0.000041    -0.248449
H      0.903829    -0.929314    -0.778088
H      0.903830     0.929210    -0.778127
H      0.660749    -0.000016     0.819027
S     -1.507061    -0.000005    -0.589466
Cl     3.103711    -0.000013     0.123224

SCF energy       : -978.054402556
Gibbs free energy: -977.976798

Frequencies
-575.4942    27.3739    66.3059    68.5567   131.5320   181.4162   228.9164
 252.8408   266.2755   297.0291   703.2038   753.9411   913.8985   938.7024
 965.6849   996.5898   997.7830  1038.5151  1048.5512  1318.8110  1347.2996
1354.6420  1363.2803  1432.6857  1434.8891  1449.5825  1453.1852  3069.4299
3073.0213  3171.1991  3172.2652  3174.6458  3187.9519  3188.4136  3380.3573
3381.5936
```

S.19.4 Immediate product cluster in anisole

```
Cartesian coordinates (standard orientation)
C     -1.804824     1.422083     0.504366
H     -0.931127     1.248111     1.134938
H     -1.632208     2.305953    -0.109013
H     -2.686188     1.584816     1.125520
C     -2.339235    -1.283338     0.578255
H     -2.508665    -2.199526     0.013484
H     -1.462989    -1.412909     1.215416
H     -3.217135    -1.072309     1.190055
C      1.621692    -0.180963    -0.346118
H      1.570370    -0.894087    -1.163418
H      1.258113     0.792234    -0.662046
H      1.062583    -0.539788     0.513285
S     -2.067539     0.036927    -0.626987
Cl     3.338946    -0.008825     0.138503
```

```
SCF energy       : -978.095120197
Gibbs free energy: -978.017298

Frequencies
  52.5047    67.2665    79.2531    81.0226   103.6794   122.7083   190.2448
 195.6520   277.1872   705.3244   729.9170   759.0600   913.4125   954.9395
 988.0930  1029.5419  1038.0671  1055.8506  1320.9936  1344.6620  1362.2025
1436.5918  1445.4132  1448.6237  1452.5218  1456.2422  1463.7248  3057.3369
3060.8645  3107.1117  3141.1984  3149.5721  3169.5902  3172.6604  3217.9877
3221.2398
```

S.19.5 CH_3Cl in anisole

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.132188
H      0.000000     1.033168    -1.467991
H      0.894750    -0.516584    -1.467991
H     -0.894750    -0.516584    -1.467991
Cl     0.000000     0.000000     0.658653

SCF energy       : -500.111948040
Gibbs free energy: -500.096804

Frequencies
 728.6426  1030.4573  1030.9816  1358.9278  1454.7466  1455.1065  3098.2761
3210.0467  3210.2503
```

S.19.6 $(CH_3)_2S$ in anisole

```
Cartesian coordinates (standard orientation)
C     -1.379632     0.511305     0.000045
H     -1.356452     1.135939    -0.894216
H     -2.295844    -0.078953    -0.000632
H     -1.356773     1.135459     0.894485
C      1.379638     0.511303     0.000045
H      2.295846    -0.078959    -0.000723
H      1.356405     1.135998    -0.894171
H      1.356821     1.135389     0.894532
S     -0.000002    -0.657533     0.000012

SCF energy       : -477.981064877
Gibbs free energy: -477.932478
```

```
Frequencies
 188.0115   209.6152   274.9628   701.6044   751.8826   911.8615   946.8840
 983.7308  1039.1499  1314.2588  1338.6103  1434.4903  1445.3822  1448.5248
1455.6760  3047.7820  3050.9631  3132.4960  3140.6828  3161.6211  3162.9584
```

S.19.7 CH_3^+ in anisole

```
Cartesian coordinates (standard orientation)
C      0.000020     0.000028    -0.000016
H     -0.226907     1.062629     0.000032
H     -0.807236    -0.727804     0.000031
H      1.034023    -0.334994     0.000031

SCF energy       : -39.5441703013
Gibbs free energy: -39.531835

Frequencies
1383.4810  1390.9785  1405.1364  3065.8130  3266.1152  3274.5245
```

S.20 Selected cluster geometries in ethyl phenyl ether

S.20.1 $(CH_3)S^+$ in ethyl phenyl ether

```
Cartesian coordinates (input orientation)
C      0.003555     1.611990     0.263256
H      0.006278     1.491968     1.344504
H      0.895414     2.129365    -0.084170
H     -0.887737     2.133540    -0.079752
C     -1.396999    -0.801506     0.272900
H     -1.381638    -1.844798    -0.036204
H     -1.304496    -0.704536     1.352490
H     -2.296541    -0.313041    -0.096322
C      1.392394    -0.811224     0.259611
H      1.422534    -1.827357    -0.128633
H      2.284696    -0.267464    -0.044173
H      1.265564    -0.797287     1.340102
S     -0.003025     0.000349    -0.529649

SCF energy       : -517.674599456
Gibbs free energy: -517.588076

Frequencies
 154.2453   182.3383   251.9165   288.6109   300.6119   344.7125   652.6733
 733.5876   741.7147   902.5869   940.9597   944.2742  1031.5258  1055.2847
```

```
1069.2502  1325.5628  1329.8592  1358.3534  1416.6925  1425.4347  1431.0744
1440.0205  1449.9553  1461.4102  3075.4802  3088.8619  3097.8907  3187.7551
3200.4791  3202.7172  3210.4204  3210.9456  3218.3757
```

S.20.2 Tripod ion pair in ethyl phenyl ether

```
Cartesian coordinates (standard orientation)
C      0.686066    -0.492729     1.534308
H     -0.394499    -0.460335     1.374505
H      1.043288    -1.495268     1.763967
H      1.012796     0.204173     2.304196
C      0.693403     1.576169    -0.342988
H      1.048407     1.897522    -1.320681
H     -0.387944     1.420720    -0.321370
H      1.027305     2.275383     0.421741
C      0.723108    -1.086322    -1.192938
H      1.087748    -0.783658    -2.173055
H      1.066174    -2.093733    -0.963299
H     -0.360727    -0.985495    -1.101889
S      1.501144     0.006352     0.008494
Cl    -2.457430    -0.003744    -0.006489

SCF energy       : -978.093254962
Gibbs free energy: -978.010244

Frequencies
  98.8954   107.4111   127.8035   223.6220   250.7465   260.1100   271.7965
 281.4125   319.1623   648.6500   725.0675   728.4490   909.5494   959.1712
 964.0474  1057.3795  1060.2407  1075.1735  1320.6568  1323.9411  1359.8075
1422.0485  1422.8911  1437.2116  1446.2954  1451.5775  1455.6504  3040.3811
3044.9327  3050.3953  3176.4986  3177.6032  3178.7123  3202.4983  3206.8964
3211.5310
```

S.20.3 Linear transition state in ethyl phenyl ether

```
Cartesian coordinates (standard orientation)
C     -1.963153     1.388726     0.467085
H     -1.433514     1.335879     1.418327
H     -1.682326     2.296066    -0.065465
H     -3.040051     1.378996     0.627763
C     -1.963301    -1.388662     0.467114
H     -1.682552    -2.296039    -0.065414
H     -1.433666    -1.335848     1.418361
H     -3.040200    -1.378824     0.627784
C      0.792730    -0.000037    -0.248710
H      0.903648    -0.929286    -0.778313
```

```
H      0.903643     0.929212    -0.778314
H      0.660524    -0.000035     0.818814
S     -1.506959    -0.000005    -0.589494
Cl     3.103422    -0.000012     0.123260

SCF energy       : -978.054316887
Gibbs free energy: -977.976662

Frequencies
-575.0736    28.3952    67.2465    68.7202   131.3813   181.4969   228.6808
 252.9697   266.3696   296.9899   703.2093   753.9368   913.8990   938.7212
 965.6945   996.6281   997.9020  1038.5619  1048.5208  1318.8378  1347.2763
1354.6843  1363.3108  1432.6950  1434.9115  1449.5746  1453.1913  3069.4316
3073.0332  3171.2093  3172.2366  3174.6447  3187.9702  3188.4416  3380.2741
3381.5572
```

S.20.4 Immediate product cluster in ethyl phenyl ether

```
Cartesian coordinates (standard orientation)
C     -1.805192     1.422085     0.504362
H     -0.931547     1.248350     1.135075
H     -1.632699     2.305989    -0.109005
H     -2.686688     1.584641     1.125378
C     -2.339047    -1.283411     0.578237
H     -2.508189    -2.199655     0.013469
H     -1.462892    -1.412799     1.215568
H     -3.217105    -1.072556     1.189873
C      1.621693    -0.180838    -0.346068
H      1.570280    -0.893923    -1.163398
H      1.258127     0.792376    -0.661957
H      1.062573    -0.539674     0.513327
S     -2.067411     0.036856    -0.627007
Cl     3.338941    -0.008792     0.138506

SCF energy       : -978.095102048
Gibbs free energy: -978.017294

Frequencies
  52.2507    67.2003    79.2047    80.9017   103.5684   122.1414   190.1599
 195.5845   277.1774   705.3261   729.9733   759.0550   913.4005   954.9240
 988.0903  1029.5237  1038.0690  1055.7992  1321.0070  1344.6751  1362.2135
1436.6248  1445.4395  1448.6244  1452.5662  1456.2744  1463.6914  3057.3260
3060.8463  3107.1037  3141.1712  3149.5382  3169.5847  3172.6711  3217.9530
3221.2285
```

S.20.5 CH_3Cl in ethyl phenyl ether

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.132163
H      0.000000     1.033164    -1.467990
H      0.894746    -0.516582    -1.467990
H     -0.894746    -0.516582    -1.467990
Cl     0.000000     0.000000     0.658644

SCF energy       : -500.111938403
Gibbs free energy: -500.096794

 728.7100  1030.4617  1030.9834  1358.9491  1454.7917  1455.1522  3098.2532
3210.0065  3210.2103
```

S.20.6 $(CH_3)_2S$ in ethyl phenyl ether

```
Cartesian coordinates (standard orientation)
C     -1.379613     0.511310     0.000045
H     -1.356450     1.135944    -0.894219
H     -2.295830    -0.078942    -0.000629
H     -1.356768     1.135470     0.894485
C      1.379618     0.511309     0.000045
H      2.295832    -0.078948    -0.000720
H      1.356402     1.136003    -0.894174
H      1.356816     1.135400     0.894533
S     -0.000002    -0.657540     0.000012

SCF energy       : -477.981053363
Gibbs free energy: -477.932466

Frequencies
 188.0226   209.6079   274.9663   701.6288   751.9027   911.8517   946.8767
 983.7403  1039.1563  1314.2714  1338.6267  1434.5223  1445.4173  1448.5557
1455.7207  3047.7627  3050.9444  3132.4609  3140.6509  3161.6089  3162.9445
```

S.20.7 CH_3^+ in ethyl phenyl ether

```
Cartesian coordinates (standard orientation)
C      0.000020     0.000028    -0.000016
H     -0.227821     1.062447     0.000032
H     -0.806621    -0.728505     0.000032
H      1.034322    -0.334113     0.000032

SCF energy       : -39.5438714737
Gibbs free energy: -39.531536
```

```
Frequencies
1383.7022  1391.7194  1405.0418  3065.5753  3265.8392  3274.3466
```

S.21 Selected cluster geometries in diphenyl ether

S.21.1 $(CH_3)_3S^+$ in diphenyl ether

```
Cartesian coordinates (input orientation)
C      0.003732     1.611731     0.263118
H      0.006494     1.492040     1.344436
H      0.895607     2.129048    -0.084433
H     -0.887442     2.133511    -0.079944
C     -1.397638    -0.801232     0.273354
H     -1.382338    -1.845107    -0.033914
H     -1.306221    -0.702471     1.352903
H     -2.297006    -0.313484    -0.097416
C      1.392810    -0.811484     0.259327
H      1.425379    -1.826660    -0.131324
H      2.284484    -0.265483    -0.042496
H      1.265321    -0.800256     1.339812
S     -0.003182    -0.000153    -0.529464

SCF energy       : -517.672123536
Gibbs free energy: -517.585745

Frequencies
 149.8942   166.3277   251.3432   290.0033   300.1788   345.6814   651.7057
 733.2788   741.3816   902.8325   939.1956   944.4161  1029.1930  1053.4420
1068.9961  1324.3967  1330.2616  1356.2409  1416.6997  1425.9099  1431.3395
1439.7401  1450.3031  1461.7676  3075.0107  3088.4756  3097.5617  3187.1871
3199.9854  3202.0387  3210.0768  3210.7573  3218.2022
```

S.21.2 Tripod ion pair in diphenyl ether

```
Cartesian coordinates (standard orientation)
C      0.678136    -1.276065    -0.985030
H     -0.402213    -1.152161    -0.873733
H      1.007140    -1.149872    -2.014950
H      1.030005    -2.230462    -0.596158
C      0.741666    -0.221106     1.597306
H      1.076051     0.609228     2.216852
H     -0.343363    -0.233872     1.470894
H      1.125464    -1.159718     1.993591
C      0.674460     1.494989    -0.604068
H      1.085923     2.322850    -0.029180
```

```
H      0.937534     1.604357    -1.654737
H     -0.401711     1.373235    -0.456933
S      1.499041     0.004508    -0.021287
Cl    -2.450886    -0.002508     0.013865

SCF energy       : -978.091657471
Gibbs free energy: -978.008524

Frequencies
 101.6025   114.7676   133.6391   222.3377   236.6744   263.8618   277.8843
 290.9387   323.9731   651.1277   724.6379   733.8025   913.4033   961.5921
 965.2496  1059.2290  1063.7095  1075.2509  1324.1657  1326.5172  1363.9065
1420.8066  1424.7461  1441.0372  1448.4874  1455.2002  1458.7467  3032.4123
3036.9814  3047.4101  3166.6372  3170.8598  3173.5996  3193.9472  3200.1512
3204.7431
```

S.21.3 Linear transition state in diphenyl ether

```
Cartesian coordinates (standard orientation)
C     -1.958876     1.388506     0.468241
H     -1.426548     1.335001     1.417984
H     -1.679022     2.295955    -0.064658
H     -3.035347     1.379197     0.631727
C     -1.958883    -1.388500     0.468244
H     -1.679103    -2.295946    -0.064696
H     -1.426486    -1.335044     1.417952
H     -3.035344    -1.379144     0.631812
C      0.786119    -0.000005    -0.251638
H      0.901611    -0.929038    -0.780750
H      0.901583     0.929159    -0.780530
H      0.658044    -0.000132     0.816419
S     -1.505805    -0.000001    -0.589796
Cl     3.100196     0.000000     0.123670

SCF energy       : -978.053354454
Gibbs free energy: -977.975284

Frequencies
-570.1580    36.6794    71.1655    77.3675   130.4294   182.4485   226.1448
 254.4597   267.4551   296.5766   703.2732   753.8966   913.9029   938.9829
 965.8941   997.4066   999.3085  1039.3058  1048.1955  1319.1610  1347.0577
1355.1469  1363.6415  1432.7971  1435.2525  1449.4770  1453.3058  3069.5126
3073.1902  3171.3789  3171.8648  3174.7178  3188.1887  3188.7563  3379.3517
3381.1139
```

S.21.4 Immediate product cluster in diphenyl ether

```
Cartesian coordinates (standard orientation)
C     -1.841855     1.424087     0.502043
H     -0.978706     1.268214     1.151611
H     -1.672015     2.308609    -0.111097
H     -2.738533     1.574263     1.104135
C     -2.326333    -1.290277     0.576042
H     -2.470105    -2.211041     0.011658
H     -1.459247    -1.402903     1.228940
H     -3.218300    -1.092742     1.171755
C      1.622032    -0.173968    -0.336006
H      1.557937    -0.924679    -1.118208
H      1.270832     0.788294    -0.697081
H      1.059363    -0.482963     0.540382
S     -2.056338     0.030464    -0.628891
Cl     3.342772    -0.004208     0.136923

SCF energy       : -978.094897643
Gibbs free energy: -978.016869

Frequencies
  50.1785    72.3806    74.8421    90.9829   107.7890   143.1618   182.8810
 196.4604   276.6902   705.0335   730.0832   758.5239   912.9385   953.5700
 986.8466  1029.9711  1037.8964  1060.9892  1320.4852  1344.0007  1364.4816
1436.9902  1445.5929  1448.9997  1454.7295  1456.8699  1462.7164  3058.3597
3061.4284  3099.5631  3141.8891  3149.8049  3170.0479  3174.1125  3211.2109
3214.4081
```

S.21.5 CH_3Cl in diphenyl ether

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.131888
H      0.000000     1.033109    -1.467973
H      0.894699    -0.516555    -1.467973
H     -0.894699    -0.516555    -1.467973
Cl     0.000000     0.000000     0.658544

SCF energy       : -500.111830973
Gibbs free energy: -500.096684

Frequencies
 729.4637  1030.5095  1031.0030  1359.1862  1455.2921  1455.6576  3097.9985
3209.5577  3209.7635
```

S.21.6 $(CH_3)_2S$ in diphenyl ether

```
Cartesian coordinates (standard orientation)
C     -1.379400     0.511370     0.000045
H     -1.356421     1.136003    -0.894261
H     -2.295672    -0.078814    -0.000595
H     -1.356711     1.135585     0.894487
C      1.379405     0.511368     0.000045
H      2.295675    -0.078820    -0.000687
H      1.356373     1.136062    -0.894216
H      1.356759     1.135515     0.894535
S     -0.000002    -0.657622     0.000012

SCF energy       : -477.980925595
Gibbs free energy: -477.932336

Frequencies
 188.1582   209.4746   274.9740   701.8990   752.1260   911.7432   946.7976
 983.8305  1039.2170  1314.4105  1338.7971  1434.8763  1445.7960  1448.9029
1456.2125  3047.5475  3050.7374  3132.0701  3140.2972  3161.4725  3162.7899
```

S.21.7 CH_3^+ in diphenyl ether

```
Cartesian coordinates (standard orientation)
C      0.000019     0.000032    -0.000018
H     -0.238805     1.060185     0.000035
H     -0.799159    -0.736897     0.000035
H      1.037850    -0.323477     0.000035

SCF energy       : -39.5404887448
Gibbs free energy: -39.528169

Frequencies
1383.9059  1396.2311  1402.9862  3062.3383  3262.2745  3271.5266
```

S.22 Selected cluster geometries in diethyl amine

S.22.1 $(CH_3)_3S^+$ in diethyl amine

```
Cartesian coordinates (input orientation)
C      0.003791     1.611632     0.263068
H      0.006564     1.492083     1.344415
H      0.895664     2.128939    -0.084534
H     -0.887344     2.133489    -0.080021
C     -1.397892    -0.801135     0.273518
H     -1.382683    -1.845210    -0.033127
H     -1.306875    -0.701765     1.353056
```

```
H     -2.297178    -0.313598    -0.097799
C      1.392992    -0.811579     0.259232
H      1.426465    -1.826414    -0.132271
H      2.284425    -0.264765    -0.041916
H      1.265304    -0.801322     1.339718
S     -0.003234    -0.000354    -0.529380

SCF energy       : -517.671137182
Gibbs free energy: -517.584820

Frequencies
 145.6068   162.6267   251.2077   290.3464   299.9316   345.9355   651.3436
 733.1533   741.2470   902.9361   938.4555   944.5500  1028.3662  1052.7046
1068.8476  1323.9661  1330.4230  1355.4982  1416.7035  1426.1300  1431.4429
1439.6274  1450.4020  1461.8546  3074.8536  3088.3268  3097.4242  3186.9904
3199.8021  3201.7838  3209.9130  3210.6654  3218.1063
```

S.22.2 Tripod ion pair in diethyl amine

```
Cartesian coordinates (standard orientation)
C      0.695855    -1.341518    -0.895860
H     -0.386254    -1.209886    -0.817594
H      1.049384    -1.283631    -1.923944
H      1.035181    -2.268919    -0.437626
C      0.692295    -0.105939     1.608838
H      1.027267     0.757833     2.180572
H     -0.389547    -0.107566     1.453380
H      1.048000    -1.022724     2.076050
C      0.703379     1.447541    -0.712694
H      1.055402     2.306162    -0.143124
H      1.049428     1.517035    -1.742665
H     -0.379461     1.316764    -0.644911
S      1.497469    -0.002028     0.001625
Cl    -2.448122     0.001581    -0.001638

SCF energy       : -978.091091487
Gibbs free energy: -978.008895

Frequencies
  77.0067    95.4526   124.1692   209.0511   231.4425   240.4519   270.4650
 286.2614   316.6343   648.2886   722.0080   731.0091   910.2972   956.7548
 959.1361  1056.6817  1059.5757  1072.2831  1317.5118  1322.9637  1359.6754
1416.1395  1420.5782  1437.9185  1443.0430  1453.4055  1458.5876  3032.9666
3036.4699  3042.2463  3167.9927  3170.1272  3172.6754  3195.9799  3198.5115
3204.1690
```

S.22.3 Linear transition state in diethyl amine

```
Cartesian coordinates (standard orientation)
C      1.957208    -1.388424     0.468687
H      1.423838    -1.334664     1.417846
H      1.677725    -2.295913    -0.064347
H      3.033513    -1.379280     0.633256
C      1.957169     1.388437     0.468682
H      1.677760     2.295911    -0.064414
H      1.423706     1.334731     1.417793
H      3.033459     1.379266     0.633362
C     -0.783512    -0.000006    -0.252787
H     -0.900813     0.928955    -0.781673
H     -0.900785    -0.929113    -0.781428
H     -0.657099     0.000135     0.815481
S      1.505341     0.000000    -0.589905
Cl    -3.098938    -0.000004     0.123830

SCF energy       : -978.052974419
Gibbs free energy: -977.974777

Frequencies
-568.1252    39.1304    72.3661    80.8939   130.4556   182.8419   225.2220
 255.0652   267.8949   296.4299   703.2990   753.8848   913.9021   939.1050
 966.0164   997.8828   999.8925  1039.7056  1048.0798  1319.2965  1346.9956
1355.3174  1363.7662  1432.8413  1435.4243  1449.4378  1453.3734  3069.5746
3073.2623  3171.4718  3171.7002  3174.7813  3188.2783  3188.8767  3378.9940
3380.9205
```

S.22.4 Immediate product cluster in diethyl amine

```
Cartesian coordinates (Immediate product cluster)
C     -1.809928     1.422263     0.504065
H     -0.936543     1.252089     1.136185
H     -1.639681     2.306577    -0.109344
H     -2.692842     1.582342     1.123750
C     -2.336259    -1.284201     0.578297
H     -2.501398    -2.201341     0.013789
H     -1.461294    -1.410878     1.217897
H     -3.216429    -1.075781     1.187771
C      1.621836    -0.180301    -0.345636
H      1.568939    -0.899882    -1.157188
H      1.260039     0.790885    -0.669849
H      1.061080    -0.530992     0.516123
S     -2.065832     0.035919    -0.627259
Cl     3.338679    -0.007899     0.138626
```

```
SCF energy       : -978.094821679
Gibbs free energy: -978.016937

Frequencies
  50.5455    68.9613    79.9324    82.5723   104.2441   128.6152   189.8072
 194.8012   277.0982   705.4021   730.7896   759.0503   913.2235   954.8973
 988.1397  1029.5302  1038.0788  1057.5002  1321.2661  1344.9026  1363.0270
1437.1366  1445.8404  1449.1268  1453.5888  1457.1024  1464.1973  3057.1845
3060.6126  3105.7763  3140.7490  3149.0261  3169.5542  3172.8121  3216.4727
3220.0062
```

S.22.5 CH_3Cl in diethyl amine

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.131780
H      0.000000     1.033088    -1.467967
H      0.894680    -0.516544    -1.467967
H     -0.894680    -0.516544    -1.467967
Cl     0.000000     0.000000     0.658505

SCF energy       : -500.111788975
Gibbs free energy: -500.096641

Frequencies
 729.7596  1030.5272  1031.0102  1359.2786  1455.4863  1455.8532  3097.8997
3209.3825  3209.5886
```

S.22.6 $(CH_3)_2S$ in diethyl amine

```
Cartesian coordinates (standard orientation)
C     -1.379317     0.511392     0.000045
H     -1.356410     1.136026    -0.894278
H     -2.295611    -0.078764    -0.000582
H     -1.356688     1.135631     0.894487
C      1.379323     0.511391     0.000045
H      2.295614    -0.078770    -0.000674
H      1.356362     1.136085    -0.894233
H      1.356737     1.135560     0.894535
S     -0.000002    -0.657654     0.000013

SCF energy       : -477.980875937
Gibbs free energy: -477.932286
```

```
Frequencies
 188.2163   209.3983   274.9623   702.0036   752.2128   911.7013   946.7676
 983.8586  1039.2355  1314.4646  1338.8580  1435.0133  1445.9378  1449.0396
1456.4021  3047.4635  3050.6575  3131.9175  3140.1602  3161.4190  3162.7297
```

S.22.7 CH_3^+ in diethyl amine

```
Cartesian coordinates (standard orientation)
C      0.000019     0.000033    -0.000018
H     -0.243540     1.059168     0.000037
H     -0.795907    -0.740493     0.000037
H      1.039334    -0.318872     0.000037

SCF energy       : -39.5391400108
Gibbs free energy: -39.526836

Frequencies
1383.1399  1396.3118  1401.3835  3060.8787  3260.7896  3270.0544
```

S.23 Selected cluster geometries in dibutyl ether

S.23.1 $(CH_3)_3S^+$ in dibutyl ether

```
Cartesian coordinates (input orientation)
C      0.003964     1.611259     0.262873
H      0.006757     1.492364     1.344351
H      0.895798     2.128595    -0.084943
H     -0.887038     2.133364    -0.080358
C     -1.398929    -0.800801     0.274104
H     -1.384447    -1.845534    -0.030550
H     -1.309372    -0.699488     1.353632
H     -2.297821    -0.313741    -0.099079
C      1.393821    -0.811939     0.258937
H      1.430710    -1.825573    -0.135538
H      2.284324    -0.262170    -0.039932
H      1.265621    -0.805141     1.339451
S     -0.003387    -0.001195    -0.528988

SCF energy       : -517.666974987
Gibbs free energy: -517.580940

Frequencies
 117.7605   158.5048   251.0573   290.4423   298.6916   346.1667   649.9842
 732.5910   740.6553   903.2953   935.6496   945.1121  1025.5283  1049.7057
1067.9766  1322.4284  1331.0800  1352.7623  1416.7750  1427.1113  1431.8521
```

```
1439.1597  1450.5890  1461.8543  3074.3353  3087.7204  3096.8117  3186.3092
3199.1943  3200.8150  3209.1887  3210.2806  3217.6379
```

S.23.2 Tripod ion pair in dibutyl ether

```
Cartesian coordinates (standard orientation)
C     -0.695382    -1.008327    -1.258335
H      0.387615    -0.909002    -1.145244
H     -1.038406    -2.029568    -1.100870
H     -1.050665    -0.640066    -2.219164
C     -0.688369     1.594426    -0.243784
H     -1.033156     2.242556     0.560394
H      0.394006     1.440017    -0.222104
H     -1.035225     1.973679    -1.203319
C     -0.685922    -0.585706     1.502584
H     -1.030232     0.055049     2.312432
H     -1.030773    -1.605853     1.662084
H      0.396280    -0.528429     1.355352
S     -1.491616     0.000868     0.001895
Cl     2.430850    -0.000861    -0.001922

SCF energy       : -978.088687869
Gibbs free energy: -978.005778

Frequencies
 103.9079   116.1409   137.7271   209.4944   228.8895   268.7060   276.5405
 283.3785   321.4429   647.7048   720.7811   727.0315   911.7978   956.5305
 964.4818  1052.8316  1063.3905  1075.7291  1320.4810  1323.8072  1360.6257
1418.1338  1423.3778  1441.2364  1446.3928  1456.3787  1459.0460  3025.2557
3030.1280  3040.2224  3162.6873  3167.6385  3170.9073  3194.9851  3196.6001
3203.0690
```

S.23.3 Linear transition state in dibutyl ether

```
Cartesian coordinates (standard orientation)
C      1.950308    -1.388140     0.470494
H      1.412623    -1.333380     1.417211
H      1.672368    -2.295766    -0.063151
H      3.025919    -1.379680     0.639532
C      1.950228     1.388169     0.470482
H      1.672288     2.295766    -0.063208
H      1.412485     1.333428     1.417170
H      3.025829     1.379745     0.639593
C     -0.772549    -0.000015    -0.257566
H     -0.897531     0.928614    -0.785481
H     -0.897497    -0.928834    -0.785159
```

```
H     -0.653358     0.000169     0.811604
S      1.503396     0.000000    -0.590307
Cl    -3.093846    -0.000008     0.124491

SCF energy       : -978.051391195
Gibbs free energy: -977.972772

Frequencies
-559.0949    47.3297    77.7723    91.6625   132.7287   184.4600   221.7540
 257.5195   269.7145   295.9136   703.3908   753.8399   913.8773   939.6715
 966.6878  1000.6828  1002.3296  1041.9015  1047.7199  1319.9012  1346.8889
1355.9158  1364.2386  1433.0506  1436.2600  1449.2666  1453.7363  3069.9975
3073.6184  3170.9780  3172.0032  3175.1877  3188.6465  3189.3312  3377.5167
3380.0083
```

S.23.4 Immediate product cluster in dibutyl ether

```
Cartesian coordinates (standard orientation)
C     -1.853808     1.419360     0.508604
H     -0.989365     1.267915     1.157533
H     -1.691546     2.308270    -0.100263
H     -2.751876     1.559117     1.111271
C     -2.317206    -1.298223     0.569550
H     -2.452553    -2.217737     0.001007
H     -1.450431    -1.407118     1.223627
H     -3.211835    -1.110917     1.164636
C      1.621145    -0.147106    -0.332408
H      1.541994    -0.876047    -1.133443
H      1.280303     0.828094    -0.667270
H      1.059141    -0.471984     0.538709
S     -2.056416     0.029660    -0.629271
Cl     3.345179    -0.011667     0.135180

SCF energy       : -978.094500217
Gibbs free energy: -978.017319

Frequencies
  36.6176    61.1652    69.4897    78.6582   104.5775   125.5907   182.0590
 195.7217   276.4331   705.1973   733.9969   758.2149   912.6934   953.3478
 986.7769  1023.9061  1037.9026  1055.9282  1320.8272  1344.4064  1361.4345
1437.6804  1445.9323  1448.9174  1454.7998  1456.8652  1462.3228  3058.1121
3061.0255  3102.2357  3141.2993  3149.0036  3170.0477  3173.5439  3211.8526
3218.4183
```

S.23.5 CH_3Cl in dibutyl ether

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.131335
H      0.000000     1.032998    -1.467947
H      0.894602    -0.516499    -1.467947
H     -0.894602    -0.516499    -1.467947
Cl     0.000000     0.000000     0.658344

SCF energy       : -500.111616578
Gibbs free energy: -500.096465

Frequencies
 730.9822  1030.5936  1031.0341  1359.6538  1456.2755  1456.6437  3097.4977
3208.6646  3208.8697
```

S.23.6 $(CH_3)_2S$ in dibutyl ether

```
Cartesian coordinates (standard orientation)
C     -1.378981     0.511485     0.000046
H     -1.356368     1.136118    -0.894344
H     -2.295361    -0.078566    -0.000525
H     -1.356596     1.135820     0.894485
C      1.378987     0.511483     0.000045
H      2.295363    -0.078572    -0.000616
H      1.356320     1.136178    -0.894299
H      1.356644     1.135750     0.894533
S     -0.000002    -0.657784     0.000014

SCF energy       : -477.980673758
Gibbs free energy: -477.932082

Frequencies
 188.4781   208.9577   274.8374   702.4270   752.5658   911.5328   946.6484
 983.9357  1039.2846  1314.6851  1339.0780  1435.5679  1446.4865  1449.6052
1457.1648  3047.1195  3050.3343  3131.2929  3139.6042  3161.1983  3162.4834
```

S.23.7 CH_3^+ in dibutyl ether

```
Cartesian coordinates (standard orientation)
C      0.000017     0.000038    -0.000020
H     -0.266122     1.053980     0.000040
H     -0.780103    -0.757475     0.000040
H      1.046124    -0.296735     0.000040
```

```
SCF energy       : -39.5334420315
Gibbs free energy: -39.521234

Frequencies
1378.6867  1385.6600  1395.2299  3054.3043  3254.6920  3262.3721
```

S.24 Selected cluster geometries in tetralin

S.24.1 $(CH_3)_3S^+$ in tetralin

```
Cartesian coordinates (input orientation)
C      0.004030     1.611055     0.262760
H      0.006825     1.492643     1.344330
H      0.895807     2.128459    -0.085211
H     -0.886911     2.133273    -0.080584
C     -1.399595    -0.800641     0.274417
H     -1.385830    -1.845674    -0.029387
H     -1.310846    -0.698496     1.353967
H     -2.298199    -0.313611    -0.099685
C      1.394411    -0.812148     0.258819
H      1.433270    -1.825163    -0.137175
H      2.284367    -0.260775    -0.038965
H      1.266118    -0.807184     1.339370
S     -0.003446    -0.001737    -0.528696

SCF energy       : -517.664173670
Gibbs free energy: -517.578352

Frequencies
  98.1989   158.5495   250.7939   289.4467   297.6913   345.5276   649.2092
 732.1995   740.2279   903.4479   934.1273   945.3692  1024.1734  1047.8586
1067.1336  1321.6771  1331.4912  1351.3122  1416.9143  1427.6772  1432.0643
1438.8021  1450.5235  1461.5169  3074.0979  3087.3283  3096.3673  3185.9693
3198.8301  3200.2297  3208.6856  3210.0035  3217.2412
```

S.24.2 Tripod ion pair in tetralin

```
Cartesian coordinates (standard orientation)
C      0.685656    -1.181146    -1.097491
H     -0.396955    -1.072383    -0.985423
H      1.025429    -0.951735    -2.106077
H      1.038902    -2.167410    -0.800879
C      0.691816    -0.361353     1.571332
H      1.037698     0.392175     2.276997
H     -0.391321    -0.330307     1.422100
H      1.041880    -1.346114     1.876034
```

```
C      0.678636     1.541615    -0.472601
H      1.021179     2.299980     0.229619
H      1.023672     1.780703    -1.477102
H     -0.403181     1.386768    -0.426970
S      1.487687     0.002730    -0.002818
Cl    -2.419820    -0.001768     0.001726

SCF energy       : -978.087207965
Gibbs free energy: -978.003907

Frequencies
 111.9300   124.2100   144.0222   224.9705   247.3887   253.0808   272.8849
 287.7377   326.6659   646.8054   722.5440   726.2680   909.0109   961.0415
 964.7515  1056.3603  1059.8202  1078.6351  1321.5511  1323.8022  1360.2621
1420.8172  1421.7253  1439.9022  1444.9241  1455.6666  1460.1810  3023.9526
3034.4592  3040.7520  3169.8628  3171.3274  3172.5011  3200.9661  3205.2530
3208.4702
```

S.24.3 Linear transition state in tetralin

```
Cartesian coordinates (standard orientation)
C      1.945954    -1.387982     0.471624
H      1.405491    -1.332668     1.416754
H      1.669053    -2.295682    -0.062460
H      3.021111    -1.379920     0.643524
C      1.945863     1.388015     0.471609
H      1.668853     2.295682    -0.062472
H      1.405428     1.332658     1.416755
H      3.021026     1.380060     0.643491
C     -0.765326    -0.000017    -0.260640
H     -0.895465     0.928312    -0.787982
H     -0.895402    -0.928660    -0.787451
H     -0.651136     0.000288     0.809136
S      1.502134     0.000000    -0.590516
Cl    -3.090709    -0.000009     0.124906

SCF energy       : -978.050343494
Gibbs free energy: -977.971514

Frequencies
-552.6291    51.8353    81.1596    95.1776   135.6969   185.4072   219.8504
 259.0001   270.7656   295.6845   703.4396   753.8223   913.8152   940.0030
 967.1297  1002.8733  1003.7518  1043.5531  1047.6772  1320.2787  1346.9114
```

1356.1778 1364.4768 1433.2093 1436.8507 1449.1600 1454.0055 3070.3923
3073.8749 3170.5076 3172.4522 3175.5154 3188.8685 3189.5696 3376.5468
3379.3167

S.24.4 Immediate product cluster in tetralin

Cartesian coordinates (standard orientation)

C	-1.855132	1.419482	0.508237
H	-0.991146	1.269198	1.158096
H	-1.693080	2.308343	-0.100774
H	-2.753866	1.558920	1.110027
C	-2.316607	-1.298057	0.569856
H	-2.450889	-2.217931	0.001629
H	-1.450437	-1.406340	1.224897
H	-3.211967	-1.111195	1.164023
C	1.621306	-0.147921	-0.332509
H	1.542241	-0.878772	-1.131844
H	1.280101	0.826291	-0.669933
H	1.058753	-0.470786	0.539046
S	-2.055567	0.029326	-0.629390
Cl	3.344821	-0.011057	0.135387

SCF energy : -978.094294383
Gibbs free energy: -978.017005

Frequencies

38.2521	62.2896	69.9793	79.9081	105.3502	127.0573	182.3210
195.7295	276.3080	705.4870	734.5105	758.4772	912.5867	953.3564
986.8731	1024.1301	1037.9453	1056.7669	1321.0203	1344.5954	1362.0384
1438.0291	1446.3032	1449.2644	1455.4111	1457.3552	1462.9573	3058.0039
3060.8980	3101.7182	3141.0585	3148.7691	3169.9351	3173.4442	3211.1837
3217.8046						

S.24.5 CH_3Cl in tetralin

Cartesian coordinates (standard orientation)

C	0.000000	0.000000	-1.131045
H	0.000000	1.032938	-1.467938
H	0.894551	-0.516469	-1.467938
H	-0.894551	-0.516469	-1.467938
Cl	0.000000	0.000000	0.658240

SCF energy : -500.111504766
Gibbs free energy: -500.096351

```
Frequencies
 731.7821  1030.6311  1031.0459  1359.8948  1456.7805  1457.1464  3097.2407
3208.2000  3208.4025
```

S.24.6 $(CH_3)_2S$ in tetralin

```
Cartesian coordinates (standard orientation)
C     -1.378766     0.511544     0.000046
H     -1.356343     1.136177    -0.894386
H     -2.295200    -0.078441    -0.000486
H     -1.356537     1.135945     0.894481
C      1.378772     0.511542     0.000046
H      2.295202    -0.078447    -0.000578
H      1.356296     1.136237    -0.894341
H      1.356586     1.135874     0.894529
S     -0.000002    -0.657866     0.000015

SCF energy       : -477.980544023
Gibbs free energy: -477.931952

Frequencies
 188.6628   208.5740   274.6966   702.6964   752.7917   911.4261   946.5736
 983.9558  1039.2960  1314.8264  1339.1980  1435.9211  1446.8169  1449.9746
1457.6472  3046.8973  3050.1282  3130.8897  3139.2484  3161.0542  3162.3241
```

S.24.7 CH_3^+ in tetralin

```
Cartesian coordinates (standard orientation)
C      0.000015     0.000042    -0.000020
H     -0.284105     1.049452     0.000040
H     -0.767175    -0.770798     0.000040
H      1.051187    -0.278906     0.000040

SCF energy       : -39.5296029611
Gibbs free energy: -39.517429

Frequencies
1376.7078  1382.5603  1393.2997  3051.8060  3252.1196  3259.5559
```

S.25 Selected cluster geometries in carbon disulfide

S.25.1 $(CH_3)_3S^+$ in carbon disulfide

```
Cartesian coordinates (input orientation)
C      0.004054     1.610931     0.262676
H      0.006858     1.492864     1.344311
H      0.895778     2.128402    -0.085412
```

```
H     -0.886861     2.133202    -0.080740
C     -1.400031    -0.800561     0.274594
H     -1.386884    -1.845729    -0.028875
H     -1.311716    -0.698093     1.354173
H     -2.298427    -0.313392    -0.099944
C      1.394821    -0.812272     0.258782
H      1.434903    -1.824944    -0.138044
H      2.284436    -0.259955    -0.038430
H      1.266538    -0.808350     1.339363
S     -0.003468    -0.002102    -0.528496

SCF energy       : -517.662275408
Gibbs free energy: -517.576615

Frequencies
  85.2230   159.1780   250.5148   288.4487   296.8923   344.7314   648.7367
 731.9296   739.9299   903.5113   933.2503   945.4780  1023.5010  1046.6898
1066.4677  1321.2754  1331.7605  1350.4712  1417.0716  1428.0161  1432.1799
1438.5028  1450.4306  1461.1316  3073.9677  3087.0718  3096.0553  3185.7740
3198.5858  3199.8754  3208.3435  3209.7870  3216.9402
```

S.25.2 Tripod ion pair in carbon disulfide

```
Cartesian coordinates (standard orientation)
C      0.674914     1.544288    -0.468927
H     -0.407055     1.396896    -0.403199
H      1.037513     2.303021     0.222638
H      1.002383     1.777040    -1.480866
C      0.675152    -1.180994    -1.099356
H      1.024045    -2.167758    -0.798804
H     -0.407440    -1.067482    -0.987680
H      1.016542    -0.956736    -2.108677
C      0.697068    -0.365114     1.571660
H      1.058572    -1.346074     1.876218
H      1.039936     0.391822     2.275639
H     -0.386781    -0.342448     1.428310
S      1.482452     0.002449    -0.007681
Cl    -2.410574    -0.000974     0.004651

SCF energy       : -978.086193477
Gibbs free energy: -978.002870

Frequencies
 114.8198   126.3672   146.0029   228.8507   246.1313   251.3475   273.1063
 287.6957   326.8508   645.8020   721.6759   725.8210   909.7354   961.8582
```

```
 964.2891  1057.2104  1059.6680  1078.5487  1321.3584  1323.9412  1359.9127
1420.9471  1421.3846  1440.8617  1444.1697  1456.9089  1459.9679  3020.0915
3032.1447  3040.5871  3167.6913  3170.0416  3171.5161  3197.5413  3203.4240
3205.7329
```

S.25.3 Linear transition state in carbon disulfide

```
Cartesian coordinates (standard orientation)
C      1.943123    -1.387880     0.472365
H      1.400829    -1.332217     1.416442
H      1.666910    -2.295626    -0.062015
H      3.017977    -1.380077     0.646150
C      1.943001     1.387927     0.472343
H      1.666609     2.295629    -0.062014
H      1.400776     1.332183     1.416457
H      3.017868     1.380287     0.646066
C     -0.760540    -0.000027    -0.262666
H     -0.894125     0.928086    -0.789629
H     -0.894043    -0.928542    -0.788944
H     -0.649738     0.000368     0.807512
S      1.501318    -0.000001    -0.590641
Cl    -3.088686    -0.000011     0.125175

SCF energy       : -978.049641371
Gibbs free energy: -977.970693

Frequencies
-548.1767    54.4806    83.2905    96.5316   138.1138   185.9608   218.7369
 259.9320   271.3176   295.5634   703.4688   753.8196   913.7592   940.2046
 967.3940  1004.3456  1004.5924  1044.5727  1047.8321  1320.5186  1346.9441
1356.3050  1364.6182  1433.3352  1437.2529  1449.1007  1454.1849  3070.6831
3074.0409  3170.2065  3172.7737  3175.7359  3189.0055  3189.7009  3375.9063
3378.8145
```

S.25.4 Immediate product cluster in carbon disulfide

```
Cartesian coordinates (standard orientation)
C     -1.827771     1.422402     0.503736
H     -0.957953     1.262253     1.143473
H     -1.661357     2.307795    -0.109187
H     -2.717259     1.575098     1.115951
C     -2.328415    -1.287675     0.577306
H     -2.480849    -2.207144     0.012988
H     -1.457640    -1.406222     1.224382
H     -3.215426    -1.086890     1.179482
C      1.622614    -0.174874    -0.342729
```

```
H      1.563310    -0.908064    -1.141655
H      1.266587     0.792583    -0.684261
H      1.058652    -0.506494     0.524635
S     -2.060583     0.032741    -0.628204
Cl     3.339570    -0.006228     0.138563

SCF energy       : -978.094158785
Gibbs free energy: -978.016453

Frequencies
  42.0107    70.9936    75.9510    85.6187   104.8149   131.4722   183.3429
 195.5135   276.6210   705.6099   732.8551   758.9838   912.7378   953.8816
 987.5010  1028.8802  1038.0774  1059.1541  1321.3713  1345.0168  1364.3028
1438.2898  1446.7854  1449.7995  1455.9799  1458.2759  1463.8630  3056.8853
3060.0410  3102.3592  3139.8878  3147.8730  3169.3919  3173.1895  3212.3783
3217.0502
```

S.25.5 CH_3Cl in carbon disulfide

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.130853
H      0.000000     1.032898    -1.467933
H      0.894516    -0.516449    -1.467933
H     -0.894516    -0.516449    -1.467933
Cl     0.000000     0.000000     0.658172

SCF energy       : -500.111430841
Gibbs free energy: -500.096275

Frequencies
 732.3142  1030.6535  1031.0525  1360.0533  1457.1116  1457.4746  3097.0725
3207.8933  3208.0932
```

S.25.6 $(CH_3)_2S$ in carbon disulfide

```
Cartesian coordinates (standard orientation)
C     -1.378625     0.511582     0.000046
H     -1.356328     1.136217    -0.894413
H     -2.295094    -0.078360    -0.000460
H     -1.356499     1.136027     0.894477
C      1.378631     0.511581     0.000046
H      2.295097    -0.078366    -0.000552
H      1.356281     1.136276    -0.894369
H      1.356547     1.135957     0.894525
S     -0.000002    -0.657921     0.000015
```

```
SCF energy       : -477.980458833
Gibbs free energy: -477.931867

Frequencies
 188.7893   208.2829   274.5804   702.8721   752.9397   911.3566   946.5248
 983.9575  1039.2958  1314.9190  1339.2686  1436.1519  1447.0257  1450.2196
1457.9610  3046.7509  3049.9932  3130.6240  3139.0149  3160.9586  3162.2189
```

S.25.7 CH_3^+ in carbon disulfide

```
Cartesian coordinates (standard orientation)
C      0.000014     0.000044    -0.000020
H     -0.297815     1.045764     0.000040
H     -0.757114    -0.780837     0.000040
H      1.054845    -0.265194     0.000040

SCF energy       : -39.5270007168
Gibbs free energy: -39.514811

Frequencies
1378.7354  1386.8174  1394.3906  3051.8356  3252.1155  3259.3878
```

S.26 Selected cluster geometries in benzene

S.26.1 $(CH_3)_3S^+$ in benzene

```
Cartesian coordinates (input orientation)
C      0.004085     1.610799     0.262636
H      0.006878     1.493585     1.344434
H      0.895693     2.128448    -0.085712
H     -0.886732     2.133270    -0.080971
C     -1.401045    -0.800484     0.274880
H     -1.389106    -1.845913    -0.027999
H     -1.313941    -0.697408     1.354563
H     -2.299040    -0.313179    -0.100733
C      1.395792    -0.812543     0.258708
H      1.438064    -1.824703    -0.139393
H      2.284772    -0.258693    -0.037940
H      1.268088    -0.810368     1.339424
S     -0.003509    -0.002809    -0.527939

SCF energy       : -517.657373781
Gibbs free energy: -517.572168
```

```
Frequencies
  56.7424   162.2241   248.7570   285.2690   294.1970   341.3823   647.6854
 731.2101   739.1650   903.4653   931.6458   945.3801  1022.3091  1044.2442
1064.2746  1320.6616  1332.2846  1348.7697  1417.6224  1428.7148  1432.3818
1437.6197  1449.9436  1459.7237  3073.7744  3086.4616  3095.1635  3185.4612
3197.9377  3199.1342  3207.3914  3209.2279  3216.0357
```

S.26.2 Tripod ion pair in benzene

```
Cartesian coordinates (standard orientation)
C      0.677787    -1.077683    -1.199681
H     -0.405463    -0.976420    -1.078598
H      1.019526    -0.755288    -2.181962
H      1.029713    -2.087612    -0.994553
C      0.668170    -0.501471     1.532035
H      1.013446     0.184377     2.304043
H     -0.414096    -0.447966     1.375677
H      1.009626    -1.512352     1.749662
C      0.682731     1.578358    -0.332408
H      1.027966     2.267559     0.436562
H      1.037547     1.901571    -1.309784
H     -0.401059     1.429433    -0.306875
S      1.478264    -0.001957     0.002901
Cl    -2.396562     0.001928    -0.002368

SCF energy       : -978.083705433
Gibbs free energy: -978.000086

Frequencies
 121.7470   137.0252   152.0875   233.9814   252.7244   257.8030   277.6536
 291.1399   328.7458   647.6215   721.7471   726.8037   910.5636   962.5529
 965.5131  1058.8307  1062.4723  1078.9170  1321.1272  1324.0398  1362.1286
1420.8877  1421.2191  1443.0930  1445.8940  1458.2945  1462.6313  3014.7281
3025.0304  3035.6011  3165.7954  3168.0935  3169.0352  3199.7114  3202.4810
3205.9039
```

S.26.3 Linear transition state in benzene

```
Cartesian coordinates (standard orientation)
C     -1.936187     1.387745     0.473919
H     -1.389871     1.331422     1.415675
H     -1.661407     2.295516    -0.061201
H     -3.010387     1.380548     0.651722
C     -1.936226    -1.387727     0.473928
H     -1.661406    -2.295505    -0.061160
H     -1.389960    -1.331379     1.415710
```

```
H     -3.010436    -1.380539     0.651676
C      0.748443    -0.000010    -0.267458
H      0.890683    -0.927879    -0.792908
H      0.890693     0.927821    -0.792968
H      0.646725     0.000027     0.803743
S     -1.498642    -0.000001    -0.590741
Cl     3.083380    -0.000003     0.125837

SCF energy       : -978.047856232
Gibbs free energy: -977.968631

Frequencies
-536.0514    61.0429    87.9457    99.0700   144.7550   187.4200   216.8771
 262.2209   272.5285   295.6584   703.5508   753.8826   913.5998   940.7131
 968.1495  1006.9644  1007.9544  1046.1279  1049.9109  1321.0878  1347.1720
1356.3939  1364.9890  1433.7260  1438.2413  1449.0807  1454.6559  3071.4462
3074.3647  3169.3605  3173.6083  3176.1948  3189.3137  3189.9331  3374.1957
3377.1139
```

S.26.4 Immediate product cluster in benzene

```
Cartesian coordinates (standard orientation)
C     -1.836046     1.422397     0.503561
H     -0.968272     1.266641     1.147210
H     -1.670842     2.308195    -0.109117
H     -2.728740     1.572011     1.111924
C     -2.325074    -1.289209     0.576811
H     -2.471911    -2.209650     0.012576
H     -1.456296    -1.404303     1.227303
H     -3.215137    -1.091787     1.175640
C      1.623100    -0.172384    -0.341301
H      1.560930    -0.910546    -1.135473
H      1.269188     0.793631    -0.689190
H      1.057944    -0.496760     0.528108
S     -2.058120     0.031304    -0.628650
Cl     3.340068    -0.005478     0.138529

SCF energy       : -978.093821994
Gibbs free energy: -978.016171

Frequencies
  41.2026    71.0654    74.5280    85.7127   105.2787   129.5529   181.7654
 195.9010   276.3308   705.9206   733.9367   759.1650   912.4940   953.2819
 987.1332  1028.5605  1038.1038  1059.5334  1321.3669  1345.0530  1364.9523
1438.8594  1447.3415  1450.2287  1456.9980  1458.7554  1464.0765  3056.8553
```

3059.8988 3100.8718 3139.6122 3147.5313 3169.2917 3173.2238 3210.5210
3215.5098

S.26.5 CH_3Cl in benzene

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.130021
H      0.000000     1.032550    -1.468314
H      0.894215    -0.516275    -1.468314
H     -0.894215    -0.516275    -1.468314
Cl     0.000000     0.000000     0.657945

SCF energy       : -500.111246701
Gibbs free energy: -500.096084

Frequencies
 734.1399  1030.5966  1030.9523  1360.8632  1458.0129  1458.3633  3096.8642
3207.0268  3207.2136
```

S.26.6 $(CH_3)_2S$ in benzene

```
Cartesian coordinates (standard orientation)
C     -1.378280     0.511676     0.000047
H     -1.356295     1.136314    -0.894480
H     -2.294833    -0.078163    -0.000396
H     -1.356408     1.136234     0.894466
C      1.378286     0.511674     0.000046
H      2.294836    -0.078170    -0.000486
H      1.356248     1.136373    -0.894435
H      1.356456     1.136165     0.894514
S     -0.000002    -0.658053     0.000016

SCF energy       : -477.980248388
Gibbs free energy: -477.931658

Frequencies
 189.1144   207.4412   274.2192   703.3025   753.3033   911.1863   946.4042
 983.9252  1039.2717  1315.1468  1339.4188  1436.7181  1447.5162  1450.8315
1458.7274  3046.3879  3049.6604  3129.9653  3138.4381  3160.7188  3161.9568
```

S.26.7 CH_3^+ in benzene

```
Cartesian coordinates (standard orientation)
C      0.000010     0.000051    -0.000019
H     -0.340219     1.033065     0.000037
```

```
H     -0.724882    -0.811235     0.000037
H      1.065040    -0.222134     0.000037

SCF energy       : -39.5202738197
Gibbs free energy: -39.508032

Frequencies
1381.6851  1388.1696  1404.3234  3055.3145  3255.0670  3261.8499
```

S.27 Selected cluster geometries in carbon tetrachloride

S.27.1 $(CH_3)_3S^+$ in carbon tetrachloride

```
Cartesian coordinates (input orientation)
C      0.004089     1.610816     0.262671
H      0.006864     1.493712     1.344491
H      0.895691     2.128483    -0.085698
H     -0.886700     2.133336    -0.080971
C     -1.401177    -0.800490     0.274898
H     -1.389289    -1.845964    -0.027870
H     -1.314313    -0.697291     1.354597
H     -2.299143    -0.313267    -0.100930
C      1.395916    -0.812578     0.258688
H      1.438339    -1.824717    -0.139481
H      2.284844    -0.258649    -0.038023
H      1.268395    -0.810526     1.339433
S     -0.003518    -0.002865    -0.527846

SCF energy       : -517.656654490
Gibbs free energy: -517.571511

Frequencies
  53.7895   162.7453   248.2858   284.7483   293.7174   340.7295   647.5441
 731.1002   739.0549   903.4255   931.4877   945.3075  1022.1670  1043.9595
1063.8811  1320.6185  1332.3269  1348.5597  1417.7099  1428.7818  1432.4001
1437.4833  1449.8323  1459.4780  3073.7661  3086.3795  3095.0187  3185.4441
3197.8438  3199.0443  3207.2393  3209.1409  3215.8890
```

S.27.2 Tripod ion pair in carbon tetrachloride

```
Cartesian coordinates (standard orientation)
C      0.667306    -0.534714     1.521483
H     -0.415539    -0.473462     1.368565
H      1.004592    -1.552634     1.711196
H      1.018756     0.128580     2.310460
C      0.682478     1.586664    -0.298967
```

```
H      1.043924     1.937836    -1.264410
H     -0.401302     1.435311    -0.283566
H      1.020632     2.255843     0.490824
C      0.676183    -1.052757    -1.222847
H      1.021603    -0.713233    -2.197976
H      1.023905    -2.067483    -1.037040
H     -0.407214    -0.951840    -1.102640
S      1.477185    -0.002104     0.002724
Cl    -2.394125     0.002329    -0.002177

SCF energy       : -978.083334675
Gibbs free energy: -977.999749

Frequencies
 127.5114   136.1349   153.2324   232.0990   251.0652   259.9466   277.6256
 292.2768   327.8819   646.4483   718.4019   725.1557   909.6252   961.0566
 966.0900  1057.7123  1062.9477  1077.8868  1320.6134  1323.3345  1362.5331
1420.2656  1421.3278  1443.7346  1446.7944  1458.4368  1462.7971  3014.0402
3020.5251  3033.6431  3164.3300  3165.0380  3166.1835  3195.8716  3200.2487
3202.9248
```

S.27.3 Linear transition state in carbon tetrachloride

```
Cartesian coordinates (standard orientation)
C     -1.935191     1.387721     0.474167
H     -1.388239     1.331298     1.415552
H     -1.660652     2.295499    -0.061071
H     -3.009284     1.380610     0.652615
C     -1.935225    -1.387706     0.474174
H     -1.660633    -2.295489    -0.061027
H     -1.388330    -1.331251     1.415590
H     -3.009329    -1.380615     0.652560
C      0.746673    -0.000008    -0.268179
H      0.890201    -0.927798    -0.793462
H      0.890211     0.927750    -0.793513
H      0.646295     0.000024     0.803169
S     -1.498319    -0.000001    -0.590763
Cl     3.082666    -0.000003     0.125931

SCF energy       : -978.047597572
Gibbs free energy: -977.968336

Frequencies
-534.1296    62.0149    88.6476    99.2319   145.6955   187.5961   216.6082
 262.5458   272.6534   295.6882   703.5568   753.8892   913.5730   940.7825
```

```
 968.2141  1007.1852  1008.4107  1046.1873  1050.3566  1321.1722  1347.2026
1356.4044  1365.0291  1433.7825  1438.3870  1449.0707  1454.7199  3071.5632
3074.4134  3169.2525  3173.7364  3176.2658  3189.3553  3189.9600  3373.9488
3376.8668
```

S.27.4 Immediate product cluster in carbon tetrachloride

```
Cartesian coordinates (standard orientation)
C     -1.834981     1.422651     0.503134
H     -0.967008     1.266699     1.146480
H     -1.669602     2.308206    -0.109854
H     -2.727342     1.572925     1.111829
C     -2.325561    -1.288569     0.577385
H     -2.473116    -2.209112     0.013501
H     -1.456658    -1.403997     1.227662
H     -3.215333    -1.090472     1.176436
C      1.623334    -0.174332    -0.341991
H      1.562495    -0.913411    -1.135421
H      1.268495     0.790892    -0.691153
H      1.057861    -0.498399     0.527338
S     -2.058236     0.031380    -0.628604
Cl     3.339720    -0.004936     0.138805

SCF energy       : -978.093773977
Gibbs free energy: -978.016086

Frequencies
  41.5011    71.8137    74.8335    86.6665   105.3614   129.9722   181.7662
 195.8927   276.3205   705.9849   733.9719   759.2484   912.4722   953.2742
 987.1541  1028.8784  1038.1178  1059.8613  1321.4026  1345.0958  1365.2552
1438.9388  1447.4470  1450.3301  1457.1449  1458.9047  1464.2088  3056.7730
3059.8216  3100.7174  3139.4984  3147.4328  3169.2455  3173.1950  3210.3477
3215.2721
```

S.27.5 CH_3Cl in carbon tetrachloride

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.129954
H      0.000000     1.032537    -1.468311
H      0.894203    -0.516269    -1.468311
H     -0.894203    -0.516269    -1.468311
Cl     0.000000     0.000000     0.657921

SCF energy       : -500.111220414
Gibbs free energy: -500.096057
```

```
Frequencies
 734.3300  1030.6036  1030.9548  1360.9170  1458.1279  1458.4761  3096.8039
3206.9181  3207.1032
```

S.27.6 $(CH_3)_2S$ in carbon tetrachloride

```
Cartesian coordinates (standard orientation)
C     -1.378231     0.511689     0.000047
H     -1.356291     1.136328    -0.894489
H     -2.294796    -0.078136    -0.000386
H     -1.356396     1.136264     0.894464
C      1.378237     0.511687     0.000046
H      2.294799    -0.078142    -0.000477
H      1.356244     1.136387    -0.894444
H      1.356444     1.136195     0.894512
S     -0.000002    -0.658072     0.000016

SCF energy       : -477.980218605
Gibbs free energy: -477.931629

Frequencies
 189.1615   207.3089   274.1601   703.3630   753.3546   911.1624   946.3871
 983.9167  1039.2658  1315.1789  1339.4374  1436.7978  1447.5830  1450.9188
1458.8348  3046.3364  3049.6133  3129.8718  3138.3565  3160.6845  3161.9194
```

S.27.7 CH_3^+ in carbon tetrachloride

```
Cartesian coordinates (standard orientation)
C      0.000010     0.000052    -0.000018
H     -0.347437     1.030706     0.000036
H     -0.719226    -0.816310     0.000036
H      1.066605    -0.214705     0.000036

SCF energy       : -39.5192854934
Gibbs free energy: -39.507072

Frequencies
1375.9585  1381.9957  1405.3956  3055.0122  3254.6286  3261.1183
```

S.28 Selected cluster geometries in cyclohexane

S.28.1 $(CH_3)_3S^+$ in cyclohexane

Used for the calculation of ΔE_{tri}

```
Cartesian coordinates (standard orientation)
C      1.273726    -0.992151     0.268034
H      1.181969    -0.927476     1.350392
H      1.142251    -2.013645    -0.083767
H      2.231773    -0.605252    -0.074609
C      0.224150     1.598429     0.266914
H     -0.564483     2.251261    -0.102736
H      0.175220     1.485476     1.348363
H      1.194743     1.973713    -0.053003
C     -1.498123    -0.604194     0.267878
H     -2.322201    -0.006373    -0.117192
H     -1.622729    -1.641676    -0.036993
H     -1.408969    -0.512759     1.348313
S     -0.000381    -0.000985    -0.524733

SCF energy       : -517.652712158
Gibbs free energy: -517.565936

Frequencies
 202.7920   209.7482   242.6308   278.7824   300.3911   307.6349   652.0551
 729.6279   734.9433   905.1491   942.2428   943.8529  1045.5665  1056.2078
1063.2138  1329.9058  1333.4220  1368.6505  1422.5259  1429.6094  1433.7169
1440.5937  1443.8950  1462.2297  3083.8696  3087.8022  3089.9174  3198.4535
3201.5076  3202.1609  3205.2926  3208.4025  3209.6862
```

S.28.2 $(CH_3)_3S^+$ in cyclohexane

Used for the calculation of ΔG_{tri}

```
Cartesian coordinates (input orientation)
C      0.004074     1.611271     0.263117
H      0.006492     1.494677     1.345051
H      0.895776     2.129011    -0.085096
H     -0.886391     2.134262    -0.080870
C     -1.401654    -0.800692     0.274832
H     -1.389057    -1.846407    -0.027309
H     -1.316363    -0.696750     1.354640
H     -2.299786    -0.314677    -0.102362
C      1.396378    -0.812754     0.258492
H      1.438191    -1.825210    -0.139112
H      2.285462    -0.259667    -0.039568
H      1.270457    -0.810351     1.339469
S     -0.003579    -0.002713    -0.527326

SCF energy       : -517.652635587
Gibbs free energy: -517.567697
```

```
Frequencies
  47.5709   164.5947   243.8716   281.2765   290.7311   336.1823   646.7618
 730.4478   738.4414   902.9116   930.9535   944.3945  1021.4409  1042.7099
1061.2208  1320.5461  1332.2260  1347.4377  1418.0658  1428.8115  1432.4058
1436.7526  1448.9151  1457.8759  3073.7279  3085.9709  3094.1072  3185.4072
3197.3476  3198.5974  3206.2738  3208.6146  3214.9827
```

S.28.3 Tripod ion pair in cyclohexane

```
Cartesian coordinates (standard orientation)
C     -0.664397    -1.318450    -0.929709
H      0.418647    -1.190353    -0.829473
H     -1.017859    -2.255633    -0.502273
H     -1.003820    -1.228089    -1.960578
C     -0.667685     1.466226    -0.674349
H     -1.021004     2.310231    -0.083404
H      0.415722     1.323683    -0.600140
H     -1.008780     1.564352    -1.703669
C     -0.676904    -0.147476     1.605932
H     -1.032595     0.690020     2.203959
H     -1.021586    -1.085949     2.037494
H      0.407066    -0.127356     1.454397
S     -1.470882    -0.000595    -0.004206
Cl     2.379544     0.000401     0.002338

SCF energy       : -978.081387767
Gibbs free energy: -977.997845

Frequencies
 127.3900   133.1445   154.8968   214.6393   254.4892   259.8233   280.6232
 292.7784   333.0392   649.7710   720.7241   728.9598   914.1888   960.9888
 966.0342  1062.9227  1064.2029  1078.0737  1321.9807  1325.4657  1366.7899
1418.5013  1422.6705  1442.2597  1449.0226  1459.3081  1464.6042  3008.1129
3014.5010  3028.2591  3159.8901  3160.8724  3164.2826  3194.2825  3198.7022
3199.7667
```

S.28.4 Linear transition state in cyclohexane

```
Cartesian coordinates (standard orientation)
C      1.930079    -1.387490     0.475559
H      1.379830    -1.330510     1.415005
H      1.656813    -2.295360    -0.060218
H      3.003620    -1.380768     0.657306
C      1.929533     1.387722     0.475447
H      1.656036     2.295441    -0.060459
```

```
H      1.379180     1.330675     1.414834
H      3.003051     1.381371     0.657348
C     -0.736986    -0.000151    -0.272085
H     -0.887714     0.926635    -0.797369
H     -0.887474    -0.928043    -0.795492
H     -0.644054     0.000939     0.800059
S      1.496575    -0.000009    -0.590861
Cl    -3.078838    -0.000043     0.126426

SCF energy       : -978.046166990
Gibbs free energy: -977.966706

Frequencies
-522.9243    67.5641    92.6761   100.2669   151.0072   188.5124   215.5207
 264.3247   273.1236   295.9678   703.5823   753.9406   913.4306   941.1821
 968.4508  1008.1560  1010.5695  1046.3148  1052.9255  1321.6454  1347.3629
1356.4420  1365.2515  1434.1897  1439.1904  1449.0990  1455.0498  3072.1907
3074.6383  3168.6867  3174.4269  3176.6135  3189.5609  3190.0663  3372.5709
3375.4378
```

S.28.5 Immediate product cluster in cyclohexane

```
Cartesian coordinates (standard orientation)
C     -1.851160     1.421267     0.505003
H     -0.987011     1.272017     1.155080
H     -1.688134     2.308552    -0.106108
H     -2.749367     1.564291     1.106879
C     -2.318700    -1.293725     0.573879
H     -2.455405    -2.214958     0.008375
H     -1.453077    -1.403096     1.229666
H     -3.213838    -1.103468     1.167476
C      1.622933    -0.161418    -0.336674
H      1.551891    -0.901008    -1.128824
H      1.274829     0.806211    -0.686054
H      1.057696    -0.479348     0.535135
S     -2.054424     0.029150    -0.629412
Cl     3.342045    -0.006608     0.137396

SCF energy       : -978.093514755
Gibbs free energy: -978.015798

Frequencies
  46.2920    67.7716    72.7917    84.5724   106.5630   132.1065   182.1476
 195.9954   276.0121   706.3860   735.5728   759.3992   912.2389   953.2381
 987.1694  1026.8195  1038.1436  1059.8077  1321.6491  1345.2952  1364.7259
```

```
1439.3458  1447.8163  1450.6196  1457.7292  1459.1894  1464.9422  3057.2156
3060.1462  3099.8089  3139.7582  3147.6095  3169.3425  3173.1467  3209.0002
3214.8897
```

S.28.6 CH_3Cl in cyclohexane

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.129591
H      0.000000     1.032464    -1.468297
H      0.894140    -0.516232    -1.468297
H     -0.894140    -0.516232    -1.468297
Cl     0.000000     0.000000     0.657790

SCF energy       : -500.111076976
Gibbs free energy: -500.095911

Frequencies
 735.3703  1030.6385  1030.9668  1361.2074  1458.7501  1459.0852  3096.4774
3206.3265  3206.5007
```

S.28.7 $(CH_3)_2S$ in cyclohexane

```
Cartesian coordinates (standard orientation)
C      1.377969     0.511760    -0.000047
H      1.356270     1.136404     0.894538
H      2.294597    -0.077990     0.000336
H      1.356330     1.136426    -0.894453
C     -1.377974     0.511758    -0.000047
H     -2.294599    -0.077996     0.000426
H     -1.356223     1.136462     0.894494
H     -1.356377     1.136357    -0.894500
S      0.000002    -0.658173    -0.000017

SCF energy       : -477.980057050
Gibbs free energy: -477.931470

Frequencies
 189.4200   206.5377   273.8069   703.6889   753.6314   911.0333   946.2934
 983.8545  1039.2239  1315.3527  1339.5285  1437.2281  1447.9348  1451.3951
1459.4136  3046.0566  3049.3579  3129.3640  3137.9132  3160.4966  3161.7153
```

S.28.8 CH_3^+ in cyclohexane

```
Cartesian coordinates (standard orientation)
C      0.000005     0.000056    -0.000016
H     -0.393480     1.014290     0.000032
```

```
H     -0.681958    -0.847997     0.000032
H      1.075405    -0.166630     0.000032

SCF energy       : -39.5137765504
Gibbs free energy: -39.501495

Frequencies
1378.5491  1390.3007  1415.3333  3058.6963  3258.6339  3262.5526
```

S.29 Selected cluster geometries in the vacuum

S.29.1 $(CH_3)_3S^+$ in the vacuum

```
Cartesian coordinates (standard orientation)
C     -1.617646    -0.095333     0.265991
H     -1.513334    -0.088220     1.349252
H     -2.190700     0.761501    -0.086492
H     -2.085707    -1.014199    -0.084997
C      0.891851    -1.352538     0.265800
H      1.920932    -1.298663    -0.087457
H      0.835509    -1.264203     1.349028
H      0.435673    -2.277549    -0.084760
C      0.726420     1.448063     0.265575
H      1.755138     1.515087    -0.086452
H      0.165588     2.313304    -0.085990
H      0.679931     1.354816     1.348964
S     -0.000424    -0.000189    -0.519706

SCF energy       : -517.609832488
Gibbs free energy: -517.523689

Frequencies
 178.7937   214.7626   225.2531   267.8453   269.5203   302.8690   644.5839
 724.9535   731.7595   896.2527   938.8708   940.5336  1045.6222  1047.2230
1052.0250  1329.3526  1330.4778  1364.7509  1419.6450  1430.0061  1431.7214
1441.0472  1442.0313  1453.5419  3082.2539  3083.8207  3084.7587  3192.8049
3193.5858  3195.8161  3202.1154  3202.5908  3206.9428
```

S.29.2 Tripod ion pair in the vacuum

```
Cartesian coordinates (standard orientation)
C     -0.630032    -0.266245     1.591704
H      0.456710    -0.244644     1.418645
H     -0.970990     0.532695     2.249344
H     -0.982434    -1.229159     1.959972
C     -0.638980    -1.249217    -1.024270
```

```
H     -0.985462    -1.082247    -2.043676
H      0.448292    -1.121723    -0.915064
H     -0.991789    -2.214913    -0.663522
C     -0.634818     1.513359    -0.566137
H     -1.004304     1.702863    -1.573341
H     -0.960385     2.306630     0.105767
H      0.451818     1.344906    -0.526888
S     -1.438757     0.001583     0.001061
Cl     2.293038    -0.000418    -0.002117

SCF energy       : -978.065762847
Gibbs free energy: -977.982589

Frequencies
 145.2761   147.5332   176.4406   231.4111   251.9752   254.0619   279.1165
 282.4587   336.4008   643.1004   711.6425   717.0560   912.1020   961.1332
 962.8537  1059.6224  1062.1894  1079.4496  1311.5967  1313.2325  1360.8242
1415.2347  1416.2023  1442.6309  1446.8425  1464.4587  1466.4376  2938.6866
2939.9742  2972.5719  3139.7434  3142.5732  3147.1599  3188.8846  3190.8816
3194.1087
```

S.29.3 Linear transition state in the vacuum

```
Cartesian coordinates (standard orientation)
C      1.888747    -1.387977     0.484371
H      1.326329    -1.321889     1.415946
H      1.610394    -2.294079    -0.052148
H      2.960763    -1.391198     0.674788
C      1.888553     1.388068     0.484336
H      1.610115     2.294123    -0.052217
H      1.326137     1.321921     1.415907
H      2.960567     1.391357     0.674758
C     -0.628311    -0.000058    -0.310298
H     -0.860462     0.919602    -0.823327
H     -0.860499    -0.919645    -0.823460
H     -0.639501    -0.000136     0.768066
S      1.473389     0.000000    -0.586576
Cl    -3.053059    -0.000015     0.131556

SCF energy       : -978.032095350
Gibbs free energy: -977.951994

Frequencies
-371.4734    82.3593   104.1301   119.8242   179.6005   187.3538   220.7991
 268.8208   276.6326   305.8919   702.3696   754.0790   907.9140   940.1474
```

```
 940.9431   997.0984  1002.0962  1046.8522  1069.0162  1324.3546  1348.3601
1357.3810  1369.5803  1439.3387  1443.8404  1452.0707  1455.9128  3075.5818
3077.5696  3162.5055  3179.1608  3180.9033  3190.8200  3192.4648  3349.5616
3351.6936
```

S.30 Immediate product cluster in vacuum

```
Cartesian coordinates (standard orientation)
C     -1.888801     1.414848     0.511161
H     -1.034119     1.282615     1.177659
H     -1.732318     2.307600    -0.093826
H     -2.800967     1.539750     1.096391
C     -2.299919    -1.306435     0.563009
H     -2.409835    -2.228332    -0.007424
H     -1.443577    -1.403671     1.233299
H     -3.208557    -1.137421     1.142745
C      1.619736    -0.122331    -0.316911
H      1.512280    -0.861829    -1.105479
H      1.289450     0.852245    -0.665455
H      1.055898    -0.421802     0.562785
S     -2.042471     0.024138    -0.632320
Cl     3.345010    -0.013638     0.131346

SCF energy       : -978.091310779
Gibbs free energy: -978.013517

Frequencies
  47.9916    61.1846    69.9953    86.8684   113.4812   135.8738   187.4475
 192.5189   275.2044   709.3608   748.7990   761.6384   911.1200   953.6050
 988.4857  1023.1867  1038.6416  1059.2567  1323.9211  1347.8276  1366.9492
1442.5761  1451.4349  1453.2472  1462.6174  1463.4079  1470.9755  3056.6990
3059.9875  3095.1204  3138.4132  3146.4675  3168.5596  3170.6927  3201.0647
3209.8466
```

S.30.1 Methylchloride in the vacuum

```
Cartesian coordinates (standard orientation)
C      0.000000     0.000000    -1.126543
H      0.000000     1.031868    -1.468159
H      0.893624    -0.515934    -1.468159
H     -0.893624    -0.515934    -1.468159
Cl     0.000000     0.000000     0.656690

SCF energy       : -500.109839629
Gibbs free energy: -500.094649
```

```
Frequencies
 744.4957  1030.7046  1030.9762  1363.3907  1463.7530  1463.8861  3093.8937
3201.3933  3201.4456
```

S.30.2 $(CH_3)_2S$ in the vacuum

```
Cartesian coordinates (standard orientation)
C      1.375880     0.512311    -0.000050
H      1.356252     1.137032     0.894913
H      2.292981    -0.076891    -0.000135
H      1.355895     1.137860    -0.894262
C     -1.375885     0.512310    -0.000050
H     -2.292983    -0.076896    -0.000054
H     -1.356210     1.137084     0.894873
H     -1.355938     1.137798    -0.894304
S      0.000002    -0.658982    -0.000027

SCF energy       : -477.978724695
Gibbs free energy: -477.930186

Frequencies
 191.4353   197.4953   269.2910   706.2454   755.8298   909.9838   945.4155
 982.5403  1038.4312  1316.7320  1339.8384  1440.6520  1450.3690  1455.4296
1463.9731  3043.7518  3047.2255  3125.1696  3134.2169  3158.8552  3159.9513
```

S.30.3 CH_3^+ in the vacuum

```
Cartesian coordinates (standard orientation)
C     -0.000078    -0.000049    -0.000048
H     -1.036955    -0.338350     0.000097
H      0.225544     1.067297     0.000096
H      0.811877    -0.728652     0.000096

SCF energy       : -39.4545672620
Gibbs free energy: -39.442577

Frequencies
1383.7672  1388.8747  1402.0350  3021.5144  3216.9450  3225.9531
```