Matrix Isolation and Spectroscopic Properties of the Methylsulfinyl Radical $CH_3(O)S^{\bullet}$

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Supplementary Information

Table S1. Experimental (Ar, 10 K) and computed (AE-CCSD(T)/cc-pVTZ, harmonic approximation, no scaling) the IR spectra of **3**.

		3		^{13}C-**3**		D_3-**3**	
Sym.	Approx. Mode	Band Position[a] (Intensity)[b]		Band Position[a] (Intensity)[b]		Band Position[a] (Intensity)[b]	
		Computation	Experiment	Computation	Experiment	Computation	Experiment
a''	CH str.	3151.3 (2.1)	2995.4 (vw)	3139.3 (2.1)	n.o.	2336.4 (1.2)	2247.2 (vw)
a'	CH str.	3149.3 (4.1)		3137.5 (4.0)	n.o.	2334.5 (2.2)	
a'	CH str.	3065.6 (4.3)	2919.4 (vw)	3062.7 (4.5)	n.o.	2194.2 (1.4)	2095.5 (vw)
a'	CH_3 def.	1477.4 (6.5)	1417.1 (w)	1474.8 (6.6)	1414.6 (w)	1062.8 (17.3)	1028.7 (s)
a''	CH_3 def.	1464.4 (7.8)	1405.2 (w)	1461.7 (7.8)	1401.4 (w)	1058.5 (3.7)	1025.6 (w)
a'	CH_3 def.	1324.7 (1.0)	1288.7 (w)	1316.2 (0.8)	1283.8 (w)	1024.8 (2.3)	1000.7 (w)
a'	SO str.	1077.8 (33.7)	1068.2 (vs)	1077.8 (33.8)	1067.9 (vs)	1082.5 (20.4)	1069.5 (vs)
a'	CH_3 rock.	944.7 (9.3)	926.6 (m)	936.5 (9.0)	918.9 (m)	765.5 (12.6)	751.6 (w)
a''	CH_3 rock.	888.8 (1.1)	868.2 (vw)	883.7 (1.2)	863.5 (vw)	671.8 (0.3)	659.2 (vw)
a'	CS str.	690.9 (11.9)	669.9 (w)	676.8 (11.9)	656.0 (m)	630.7 (5.9)	614.2, 618.8 (w)
a'	CSO def.	328.5 (7.1)	340.8 (w)	326.3 (7.)	n.o.	298.8 (6.6)	n.o.
a''	CH_3 twist.	134.0 (0.8)	n. o.	134.0 (0.8)	n.o.	103.1 (1.3)	n.o.

[a] in cm^{-1}; [b] in km mol^{-1} (computation), vw: very weak, w: weak, m: middle, s: strong, vs: very strong, n.o.: not observed (experiment)

Experimental

Preparation of allylmethyl sulfoxide (**4a**) and its labelled derivatives **4b** and **4c** was based on the known protocols.[1] A solution of ally1 bromide (1.94 g, 0.016 mol) and thiourea (1.0 g, 0.016 mol) in methanol (20 mL) was heated under reflux for 1 h and then after addition of a methanolic NaOH (1.28 g in 15 mL) solution heating was continued for additional 1 h. Next, the solution was cooled to –10 °C and MeI (2.28 g, 0.016 mol) was added in small portions. The solution obtained thereby was refluxed for 0.5 h. After this time the mixture was distilled and the product **9** was collected as an azeotrope with methanol (bp 62–64 °C). To this solution 30% H_2O_2 (1.27 g, 0.012 mol) was added dropwise and the reaction mixture was stirred for 6 h at rt. The solvents were evaporated and the liquid residue was distilled to yield allylmethyl sulfoxide (**4a**), bp 48–50 °C/0.25 Torr. The crude distillate contained traces of allylmethyl sulfone and was directly used for the matrix experiments.used. *Note:* The same procedure was applied for the synthesis of **4b** and **4c** using CD_3I and $^{13}CH_3I$, respectively.

Matrix isolation experiments: The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR and BaF_2 windows for UV/Vis measurements. The IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm^{-1}, resolution 0.7 cm^{-1}), the UV/Vis spectra with a JASCO V-670 spectrophotometer (spectral range: 190–2500 nm, resolution: >= 0.1 nm). For the combination of high-vacuum flash pyrolysis (HVFP) with matrix isolation a small home built water-cooled oven directly connected to the vacuum shroud of the cryostat was used. The pyrolysis zone consisted of a completely empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a coax heating wire. The temperature was controlled by a Ni/CrNi thermocouple. The precursors were evaporated from a cooled storage bulb allylmethyl sulfoxide (**4a**) at –30 °C (dimethyl sulfoxide (**8**) at –23 °C) into the quartz pyrolysis tube. Immediately after leaving the tube, at a distance of ca. 50 mm, the pyrolysis products were co-condensed with a large excess of argon on the surface of the 10 K cold matrix window during a time of 2–4 hours. Pyrolysis temperatures were varied between 500 and 900 °C, the optima with respect to the yields of methylsulfinyl radical (**3**) was found at 600 °C for precursor **4a** and 800 °C for **8**. For irradiations a mercury high-pressure lamp (Osram, HBO 200 in connection with long-pass glass

filters or a Bausch & Lomb monochromator (slits set to a spectral half-width of $\Delta\lambda$ = 10 nm), a mercury low pressure lamp (Gräntzel, with vycor filter (λ > 210 nm, main line: λ = 254 nm)), or a KrF excimer laser (Lambda Physik LPX 100, (λ = 248 nm) was used. An unspecific photodegradation of **3** to COS, CS, CO, H_2S, H_2O was observed using λ = 248 and 254 nm (80 min or 16 h irradiation time for complete conversion), but not with visible light (λ > 475 nm). Subtraction of the respective spectra before and after photodegradation were made to discern the IR and UV/Vis spectra of **3** more clearly. The same procedure was applied for the D_3- and ^{13}C-isotopologues **4b** and **4c**.

Computational methods: The electronic structure computations employed the correlation-consistent triple-ξ atomic-orbital basis set cc-pVTZ.[2] Geometry optimizations and evaluations of the analytical harmonic vibrational frequencies were performed with single-reference all-electron coupled-cluster theory, incorporating all single and double excitations, and with perturbative inclusion of connected triple excitations AE-CCSD(T).[3] For energy evaluation of all other structures Gaussian-4 theory (G4) was employed.[4,5] All stationary structures were characterized as minima or transition structures by computing analytical harmonic vibrational frequencies. For computations of electronic excitations within the adiabatic approximation of time dependent density functional theory (TD-DFT)[6] with the B3LYP functional and a large basis set including polarization and diffuse functions (6-311+G(3df,3pd) was employed.[5]

References:

(1) (a) Prabhuswamy, B.; Ambekar, S. Y. *Synth. Comm.* **1999**, *29*, 3477. (b) Kline, M. L.; Beutow, N.; Kim, J. K.; Caserio, M. C. *J. Org. Chem.* **1979**, *44*, 1904. (c) O'Connor, D. E.; Lyness, W. I. *J. Am. Chem. Soc.* **1964**, *86*, 3840.
(2) Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
(3) Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay P. G. with contributions from Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; Cheng, L.; Christiansen, O.; Heckert, M.; Heun, O.; Huber, C.; Jagau, T.-C.; Jonsson, D.; Jusélius, J.; Klein, K.; Lauderdale, W. J.; Matthews, D. A.; Metzroth, T.; Mück, L. A.; O'Neill, D. P.; Price, D. R.; Prochnow, E.; Puzzarini, C.; Ruud, K.; Schiffmann, F.; Schwalbach, W.; Stopkowicz, S.; Tajti, Vázquez, A.; Wang, F.; Watts J. D. and the integral packages *MOLECULE* (Almlöf, J.; Taylor, P. R.), *PROPS* (Taylor, P. R.), *ABACUS* (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.), and ECP routines by Mitin, A. V.; van Wüllen, C. For the current version, see http://www.cfour.de.
(4) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.*, **2007**, *126,* 084108.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G. B.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.
(6) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.*, **1996**, *256***,** 454.

1. Spectroscopic Data

Figure S1. The IR spectrum of matrix isolated pyrolysis products of precursor **4a** (after 1 h pyrolysis at 600 °C, argon matrix, 10 K); bands of **3** and **7** are labelled.

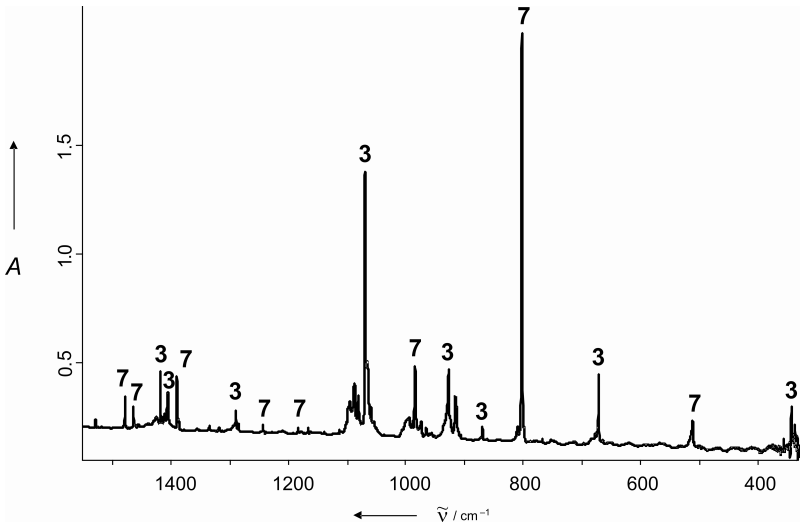


Figure S2. Long wavelength part of the UV/Vis absorption spectrum of the matrix isolated (Ar, 10 K) pyrolysis products of precursor **4a** (2 h pyrolsis at 660 °C), recorded with 0.2 nm resolution, after baseline correction. Spectrum shows the electronic excitation band of allyl radical and n→π* transition of methylsulfinyl radical **3**.

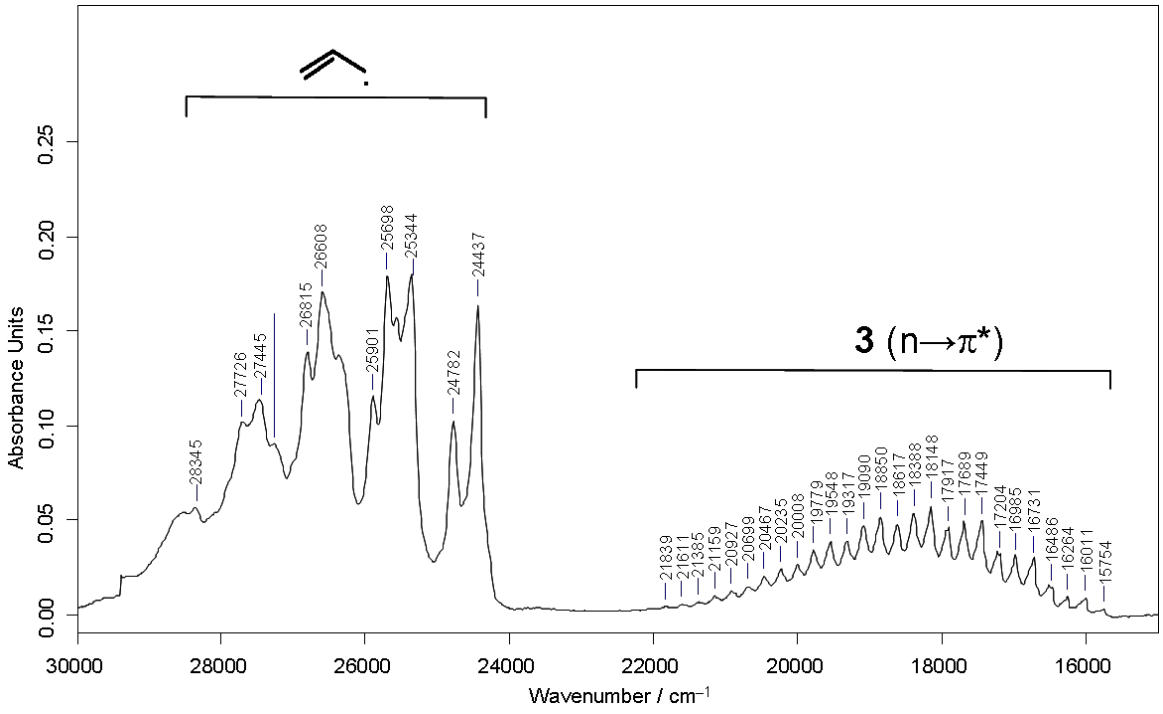


Figure S3. IR spectrum of matrix isolated pyrolysis products of dimethyl sulfoxide (bands marked with ●) (pyrolysis temperature 800 °C, argon matrix, 10 K); bands of methylsulfinyl radical marked with **3**, bands of methyl radical are marked with ***,** bands of sulfine (**4**) marked ○

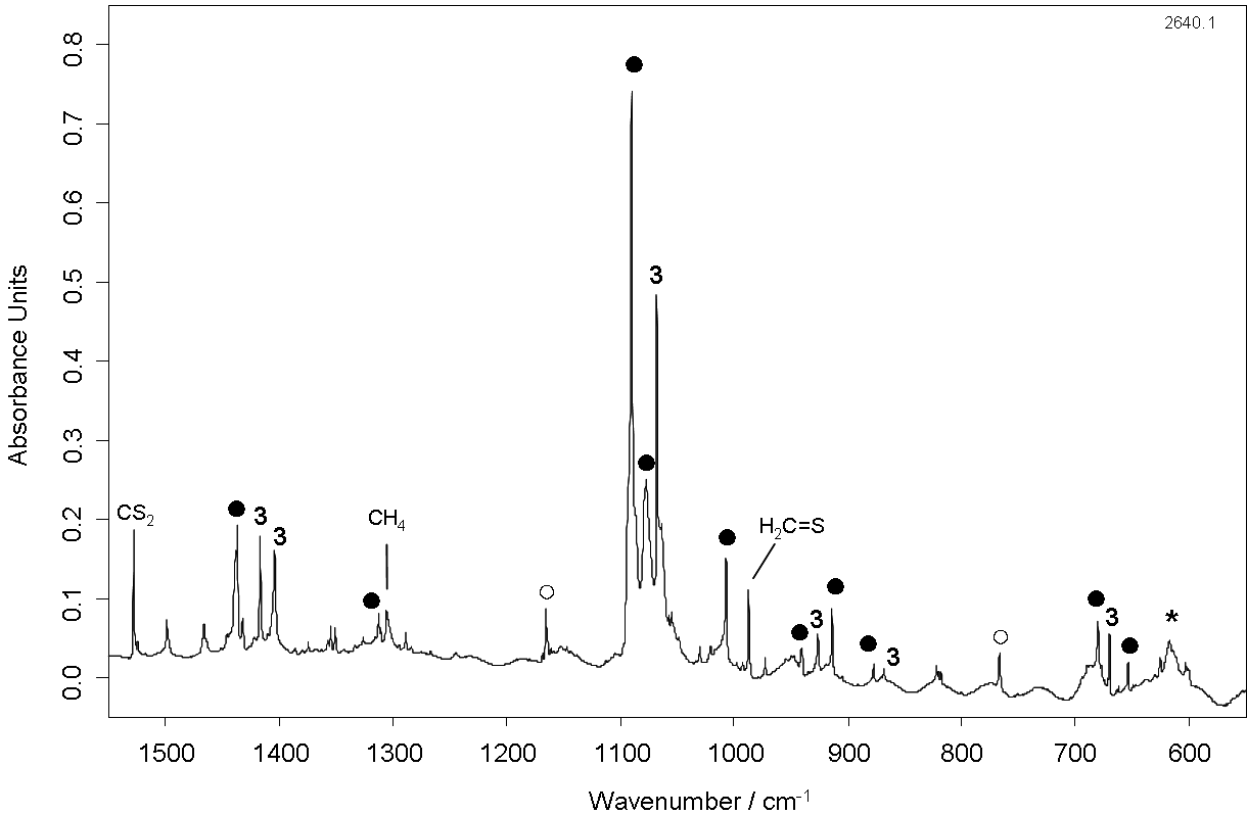


Figure S4. Computed first three electron transitions of methylsulfinyl radical (**3**) at TD-UB3LYP/6-311+G(3df,3pd) level of theory and orbitals involved.

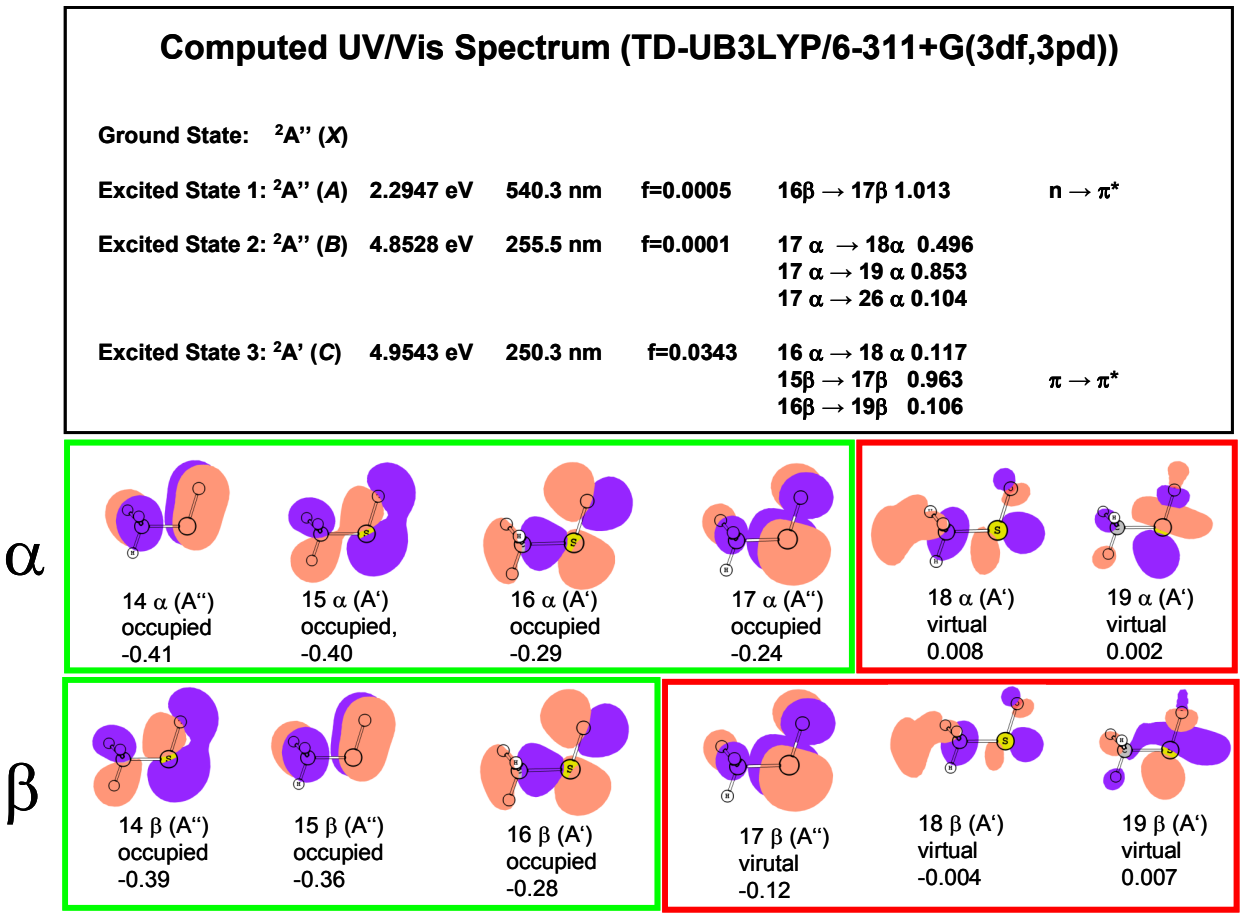
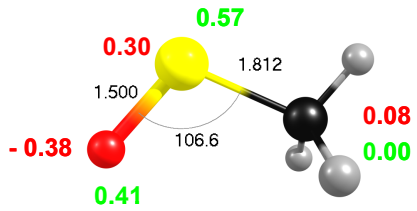


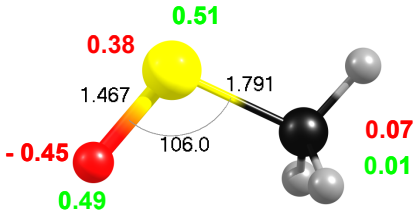
Figure S5. Computed charges and spin densities for **3** for the two lowest lying doublet states.

^{2}A“
0.0 kcal/Mol
(π-radical)

UB3LYP/6-311+G(3df,3pd)

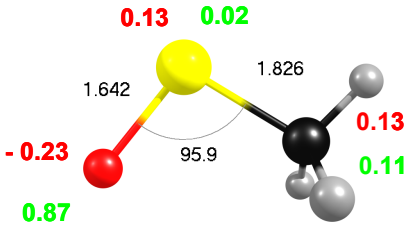


UHF/6-311+G(3df,3pd)



^{2}A‘
+44.0 kcal/Mol
(σ-radical)

UB3LYP/6-311+G(3df,3pd)

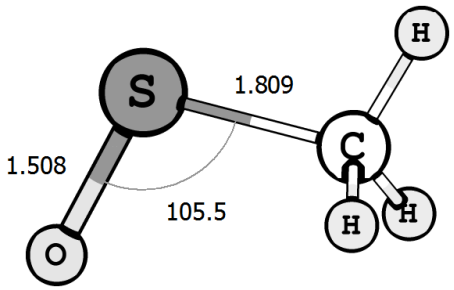


Mulliken **charges (green)** and **spin densities (red)** with hydrogens summed into heavy atoms.

2. Computational Results (optimized geometry, energies, cartesian coordinates, and vibrational harmonic frequencies of optimized geometries)

2.1 UCCSD(T)-AE/cc-pVTZ level of theory

Methylsulfinyl radical (3)



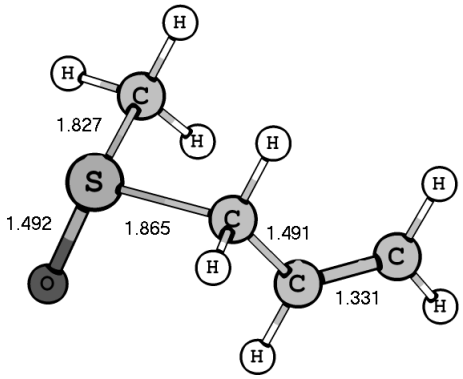
Symmetry: Cs, State = ^{2}A"
CCSD(T)= -512.717177032 Hartree, ZPVE = 25.2991 kcal/mol

Cartesian coordinates (x, y, z, in Å):

O	-1.181270821	0.583232398	0.000000000
S	-0.122737959	-0.490472754	0.000000000
C	1.457670195	0.389252783	0.000000000
H	2.256349040	-0.348236477	0.000000000
H	1.514382465	1.008411771	0.890072942
H	1.514382465	1.008411771	-0.890072942

2.2 Gaussian-4 level of theory

Allylmethyl sulfoxide (4a)



Symmetry: C1, State = ^{1}A

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.111034 E(Thermal)= 0.118864
E(CCSD(T))= -629.328231 E(Empiric)= -0.125046
DE(Plus)= -0.023447 DE(2DF)= -0.269920
E(Delta-G3XP)= -0.661115 DE(HF)= -0.034158
G4(0 K)= -630.330883 G4 Energy= -630.323053
G4 Enthalpy= -630.322109 G4 Free Energy= -630.363059

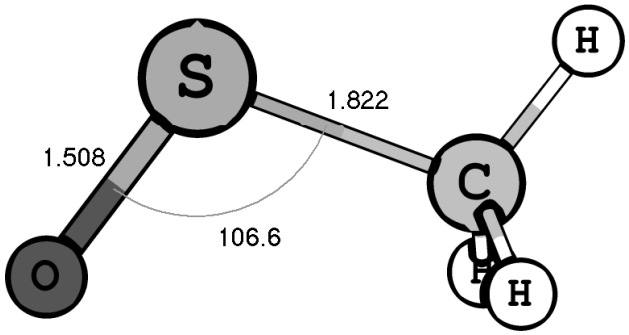
Cartesian coordinates (x, y, z, in Å):

C	-0.863724000	1.583718000	-0.196135000
S	-1.160583000	-0.134240000	0.349079000
C	0.584668000	-0.510006000	0.889472000
C	1.550467000	-0.472745000	-0.245493000
C	2.647528000	0.279772000	-0.284717000
O	-1.416304000	-0.952545000	-0.872477000
H	-0.058776000	1.606391000	-0.932809000
H	-1.798721000	1.926770000	-0.642391000
H	-0.617868000	2.201235000	0.672014000
H	0.489949000	-1.518526000	1.306689000
H	0.837758000	0.182036000	1.698704000
H	1.287632000	-1.107985000	-1.087537000
H	2.932102000	0.925543000	0.541645000
H	3.314059000	0.268308000	-1.140522000

Vibrations (cm^{-1}, km mol^{-1}):

84.415	3.2197
95.1745	1.8944
193.8585	0.9578
199.5775	3.4514
270.6059	0.7752
313.6631	5.3194
386.2907	4.2203
439.595	3.5752
563.3678	13.0386
649.0763	15.2419
709.1242	4.7028
855.4565	0.9829
935.9768	3.2253
940.153	4.1733
954.8002	34.3626
976.3041	26.266
1041.7767	11.5147
1084.2992	34.2245
1120.2403	87.3898
1207.815	4.9109
1235.1742	0.5086
1320.5963	2.1939
1322.4313	1.3265
1437.3429	2.1037
1449.353	4.4802
1462.0097	3.3402
1465.9531	10.3572
1706.484	5.0531
3042.9472	9.3129
3047.2608	4.7232
3102.2864	6.0327
3141.538	5.8635
3146.6951	5.239
3160.3949	0.7194
3172.0433	2.653
3226.5443	11.5876

Methylsulfinyl radical (3)



Symmetry: Cs, State = ^{2}A''

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.039386 E(Thermal)= 0.043602
E(CCSD(T))= -512.401727 E(Empiric)= -0.066593
DE(Plus)= -0.014153 DE(2DF)= -0.153432
E(Delta-G3XP)= -0.486020 DE(HF)= -0.023075
G4(0 K)= -513.105613 G4 Energy= -513.101397
G4 Enthalpy= -513.100453 G4 Free Energy= -513.132634

Cartesian coordinates (x, y, z, in Å):

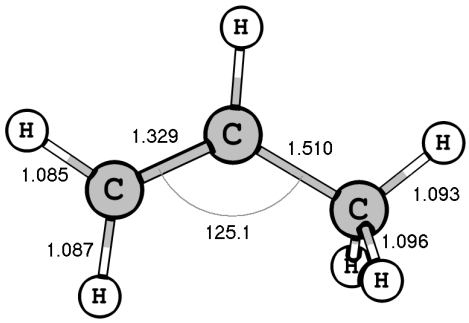
C	-1.409066000	0.300190000	0.000001000
S	0.227625000	-0.500556000	0.000002000
H	-1.510642000	0.919390000	-0.894096000
H	-2.165681000	-0.489386000	-0.001569000
H	-1.511849000	0.916979000	0.895627000
O	1.250070000	0.607597000	0.000000000

Vibrations (cm^{-1}, km mol^{-1}):

126.9414	0.3487
322.4073	5.6456

663.4729	11.1357
882.6132	1.9912
941.4786	10.5653
1057.3296	29.1236
1318.6987	0.1128
1445.2338	6.7194
1460.1082	6.0305
3041.8055	3.2254
3140.955	4.4548
3143.672	2.4449

Propene



Symmetry: Cs, State = ^{1}A’

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.077966 E(Thermal)= 0.081538
E(CCSD(T))= -117.504799 E(Empiric)= -0.062523
DE(Plus)= -0.007466 DE(2DF)= -0.116275
E(Delta-G3XP)= -0.175908 DE(HF)= -0.012217
G4(0 K)= -117.801222 G4 Energy= -117.797650
G4 Enthalpy= -117.796706 G4 Free Energy= -117.825820

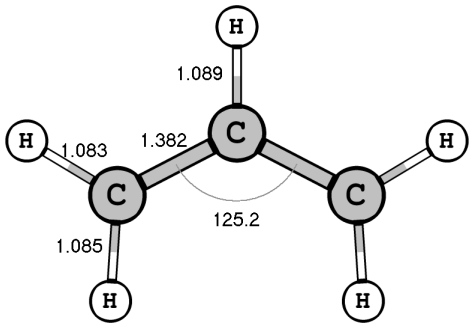
Cartesian coordinates (x, y, z, in Å):

C	1.139640000	-0.512311000	0.000000000
C	0.000000000	0.478765000	0.000000000
C	-1.290517000	0.159938000	0.000000000
H	2.109806000	-0.009160000	0.000000000
H	1.106344000	-1.162702000	0.881069000
H	0.276788000	1.531421000	0.000000000
H	-1.627934000	-0.873555000	0.000000000
H	-2.066088000	0.918344000	0.000000000

Vibrations (cm^{-1}, km mol^{-1}):

-220.654	0.4961
413.8005	0.4674
594.1011	9.8896
919.72	0.8018
942.5992	25.7029
971.6212	0.6248
1024.838	13.1401
1060.4803	1.3461
1171.273	6.2487
1335.0748	0.6781
1404.3952	1.1363
1453.2739	2.0289
1490.3693	4.2047
1492.4111	4.6249
1715.156	9.0195
3034.0927	20.0146
3086.9376	17.8618
3112.4561	12.5234
3137.8122	18.9183
3147.844	11.0411
3221.9823	18.1404

Allyl radical (7)



Symmetry: C2v, State= $^2A_2$

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.065064 E(Thermal)= 0.068919
E(CCSD(T))= -116.869727 E(Empiric)= -0.059465
DE(Plus)= -0.009191 DE(2DF)= -0.106573
E(Delta-G3XP)= -0.173819 DE(HF)= -0.012064
G4(0 K)= -117.165775 G4 Energy= -117.161920
G4 Enthalpy= -117.160976 G4 Free Energy= -117.190276

Cartesian coordinates (x, y, z, in Å):

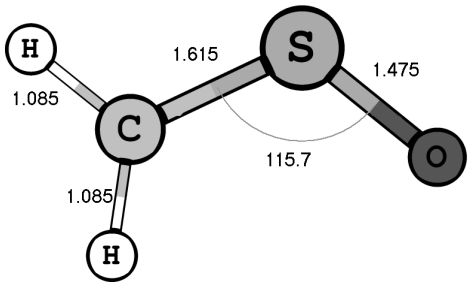
C	0.000000000	1.227567000	-0.195103000
C	0.000000000	0.000000000	0.440771000
C	0.000000000	-1.227567000	-0.195103000
H	0.000000000	1.297226000	-1.278294000
H	0.000000000	2.156677000	0.361628000
H	0.000000000	0.000000000	1.529935000
H	0.000000000	-1.297226000	-1.278294000
H	0.000000000	-2.156677000	0.361628000

Vibrations (cm^{-1}, km mol^{-1}):

422.2656	0.1136
537.0353	10.6503

556.2108	0
784.2134	0
807.6833	59.9847
932.3853	0.0097
1022.7048	12.0494
1041.0988	0.0001
1219.5843	0.0552
1270.7411	1.0472
1421.2495	4.8139
1508.6997	0.287
1519.1119	2.0376
3139.34	14.6531
3148.7362	6.7351
3155.1567	3.6059
3247.0858	4.5363
3249.8513	17.1187

Thioformaldehye *S*-oxide (5)



Symmetry: Cs, State=^{1}A′

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.028574 E(Thermal)= 0.032084
E(CCSD(T))= -511.799053 E(Empiric)= -0.062523
DE(Plus)= -0.015207 DE(2DF)= -0.147969
E(Delta-G3XP)= -0.487131 DE(HF)= -0.022518
G4(0 K)= -512.505826 G4 Energy= -512.502317

G4 Enthalpy= -512.501373 G4 Free Energy= -512.531070

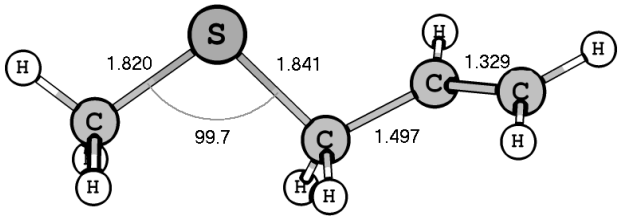
Cartesian coordinates (x, y, z, in Å):

C	1.236160000	-0.607317000	0.000000000
S	0.000000000	0.431235000	0.000000000
H	1.115318000	-1.685120000	0.000000000
H	2.225938000	-0.163449000	0.000000000
O	-1.344777000	-0.175911000	0.000000000

Vibrations (cm^{-1}, km mol^{-1}):

389.3915	7.4542
646.1358	0.0086
794.3802	73.6949
875.1003	3.9127
1004.3269	5.0278
1196.1814	108.4968
1404.3663	19.5828
3147.9822	3.251
3270.6959	1.2693

Allylmethyl sulfide (6)



Symmetry: C1, State = $^{1}A°$

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.107453 E(Thermal)= 0.114494
E(CCSD(T))= -554.332056 E(Empiric)= -0.104205

DE(Plus)= -0.011693 DE(2DF)= -0.208196
E(Delta-G3XP)= -0.575716 DE(HF)= -0.025036
G4(0 K)= -555.149448 G4 Energy= -555.142408
G4 Enthalpy= -555.141463 G4 Free Energy= -555.180789

Cartesian coordinates (x, y, z, in Å):

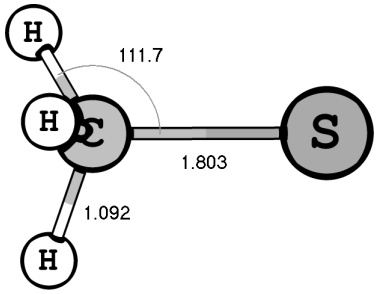
C	-2.408715000	0.420925000	-0.046492000
S	-0.929559000	-0.638804000	-0.088774000
C	0.375093000	0.639299000	0.145400000
C	1.682819000	-0.021167000	0.453384000
C	2.749908000	0.017032000	-0.338619000
H	-2.399228000	1.148835000	-0.861781000
H	-3.271333000	-0.236739000	-0.172104000
H	-2.496156000	0.939513000	0.911914000
H	0.058260000	1.275698000	0.979748000
H	0.448096000	1.255807000	-0.755234000
H	1.721985000	-0.569849000	1.392240000
H	2.738955000	0.547253000	-1.286744000
H	3.677735000	-0.476184000	-0.069691000

Vibrations (cm^{-1}, km mol^{-1}):

62.8045	0.8085
90.4136	0.324
175.5097	0.3427
200.6462	0.6835
305.7867	1.1343
411.4539	1.0448
591.2364	2.0873
714.5258	2.1961
772.228	9.9644
887.6105	4.2358
936.9748	0.2142
956.5036	29.6298
967.9475	3.239

993.0401	3.5904
1036.2592	9.977
1085.3946	3.0622
1214.8779	0.4638
1251.079	31.0259
1326.6274	0.27
1351.3954	7.9342
1448.2478	2.535
1467.0127	6.9644
1479.7073	4.4572
1483.5088	5.0968
1713.5355	5.9346
3028.1965	24.562
3039.0146	26.0196
3085.8668	12.4658
3118.8776	11.9091
3139.1327	6.3469
3143.875	9.0515
3156.5512	6.0174
3229.4629	13.5106

Thiomethoxy radical (2)



Symmetry: C1, State = ^{2}A

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.034939 E(Thermal)= 0.038152
E(CCSD(T))= -437.369373 E(Empiric)= -0.045209
DE(Plus)= -0.003236 DE(2DF)= -0.095534
E(Delta-G3XP)= -0.401012 DE(HF)= -0.013257
G4(0 K)= -437.892682 G4 Energy= -437.889469
G4 Enthalpy= -437.888524 G4 Free Energy= -437.916968

Cartesian coordinates (x, y, z, in Å):

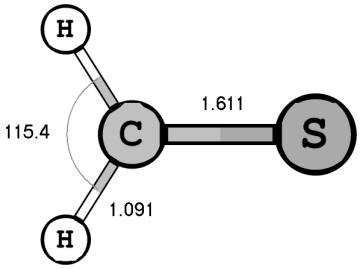
C	-1.109349000	0.000071000	-0.008750000
S	0.693857000	0.000013000	-0.002020000
H	-1.511198000	-0.898385000	-0.482152000
H	-1.422854000	-0.003550000	1.043450000
H	-1.511564000	0.901295000	-0.476482000

Vibrations (cm^{-1}, km mol^{-1}):

577.5586	42.0096
714.9217	0.6738
859.4931	1.3257
1329.2073	4.1741

1372.2927	8.2758
1469.9259	13.6709
3020.9961	4.02
3096.7506	14.222
3122.5268	1.5575

Thioformaldehyde



Symmetry: C2v, State = $^1A_1$

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.024320 E(Thermal)= 0.027260
E(CCSD(T))= -436.790864 E(Empiric)= -0.041682
DE(Plus)= -0.003969 DE(2DF)= -0.086789
E(Delta-G3XP)= -0.400797 DE(HF)= -0.012674
G4(0 K)= -437.312457 G4 Energy= -437.309517
G4 Enthalpy= -437.308573 G4 Free Energy= -437.334776

Cartesian coordinates (x, y, z, in Å):

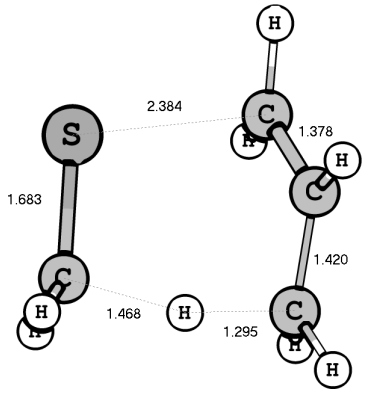
C	0.000000000	0.000000000	-1.025250000
S	0.000000000	0.000000000	0.585517000
H	0.000000000	0.922513000	-1.608389000
H	0.000000000	-0.922513000	-1.608389000

Vibrations (cm^{-1}, km mol^{-1}):

995.5959	3.0648
1032.2275	35.6151
1089.9195	15.5959

1488.2234	7.866
3071.2351	27.523
3156.0161	6.4824

Transition state propene elimination from allylmethyl sulfide (6)



Symmetry: C1, State = ^{1}A

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.102657 E(Thermal)= 0.108668
E(CCSD(T))= -554.260310 E(Empiric)= -0.104205
DE(Plus)= -0.012483 DE(2DF)= -0.211954
E(Delta-G3XP)= -0.577194 DE(HF)= -0.024616
G4(0 K)= -555.088105 G4 Energy= -555.082094
G4 Enthalpy= -555.081150 G4 Free Energy= -555.117578

Cartesian coordinates (x, y, z, in Å):

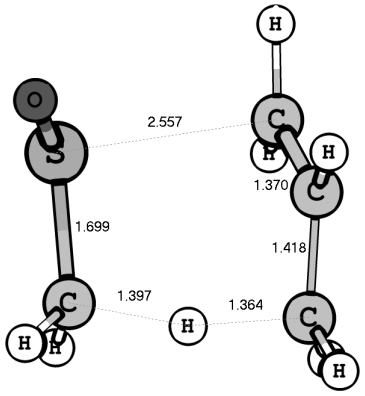
C	-1.109211000	1.209569000	0.076992000
S	-1.364235000	-0.444385000	-0.103776000
C	0.821254000	-1.288517000	0.338742000
C	1.523895000	-0.343731000	-0.376986000
C	1.605162000	0.993334000	0.093152000
H	0.353604000	1.315020000	0.006441000
H	-1.301022000	1.854873000	-0.779953000
H	-1.272731000	1.676510000	1.048378000
H	0.674777000	-2.288206000	-0.054473000
H	0.713222000	-1.191130000	1.412824000
H	1.724248000	-0.535965000	-1.427996000

H	1.732338000	1.137378000	1.166848000
H	2.156718000	1.717758000	-0.503049000

Vibrations (cm^{-1}, km mol^{-1}):

-977.3732	33.1434
120.486	6.0243
237.9018	9.6098
328.6733	1.7455
378.2406	0.853
436.9706	0.1025
499.7319	1.3795
568.0279	3.0916
747.3816	25.4544
813.4524	1.7738
944.341	5.4655
949.6074	1.6372
969.4897	14.5637
986.3211	11.9867
998.005	6.7313
1011.6184	12.8236
1039.3034	0.3719
1196.332	5.1459
1290.6104	3.9014
1301.1181	3.6629
1344.1299	6.558
1413.3109	1.9201
1449.9561	3.7785
1477.0618	3.5845
1511.2563	4.4836
1619.6076	3.15
3076.7669	19.9423
3100.746	8.017
3158.4774	2.5413
3163.2532	3.7509
3164.9922	6.3866
3185.2307	10.4149
3246.4538	2.9531

Transition state propene elimination from allylmethyl sulfoxide (4a)



Symmetry: C1, State = ^{1}A

Temperature= 298.150000 Pressure= 1.000000
E(ZPE)= 0.105396 E(Thermal)= 0.112589
E(CCSD(T))= -629.260566 E(Empiric)= -0.125046
DE(Plus)= -0.024908 DE(2DF)= -0.271466
E(Delta-G3XP)= -0.662129 DE(HF)= -0.034124
G4(0 K)= -630.272843 G4 Energy= -630.265650
G4 Enthalpy= -630.264706 G4 Free Energy= -630.304043

Cartesian coordinates (x, y, z, in Å):

C	0.541144000	1.464029000	-0.252608000
S	1.206518000	-0.095405000	-0.367079000
C	-1.060518000	-1.245589000	-0.642973000
C	-1.655569000	-0.592473000	0.404637000
C	-2.033990000	0.771639000	0.316418000
O	1.713475000	-0.546593000	0.956577000
H	-0.781714000	1.290853000	0.162303000

H	0.928642000	2.063205000	0.569104000
H	0.454076000	1.966028000	-1.215052000
H	-0.692840000	-2.259893000	-0.539680000
H	-1.174924000	-0.883308000	-1.660557000
H	-1.568434000	-1.034205000	1.394809000
H	-2.443587000	1.124523000	-0.630310000
H	-2.479695000	1.246383000	1.187200000

Vibrations (cm^{-1}, km mol^{-1}):

-1206.5672	3.7054
101.3354	3.0677
140.2234	0.6426
219.7983	4.5807
324.118	3.6862
358.4869	4.0921
401.8244	3.4218
436.6861	1.3705
480.4385	5.3272
543.8581	4.9266
723.9255	13.9605
797.1494	0.5198
839.188	13.1969
925.7085	25.3513
942.3853	3.5685
960.4357	24.5445
960.9566	0.9849
1011.933	23.8093
1041.6708	1.7171
1132.7824	135.6195
1147.5321	21.3225
1266.529	2.4961
1301.462	2.2337
1357.7559	3.7416
1384.9111	6.8443
1416.5983	2.0495
1452.2393	3.1522
1508.319	3.6741
1610.7109	9.2507
3105.369	7.8207
3105.9493	0.9727

3146.3429	4.7341
3156.9906	3.6617
3193.2813	8.9602
3213.2027	0.9094
3238.7345	4.2637