

# Reactions of the methylsulfinyl radical [CH<sub>3</sub>(O)S<sup>•</sup>] with oxygen (<sup>3</sup>O<sub>2</sub>) in solid argon

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## Supplementary Information

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### 1. Experimental Methods

Allylmethylsulfoxide (**2**) was prepared as described in reference.<sup>S1</sup> Experiments with isotopically labeled oxygen were performed with 97.1% <sup>18</sup>O<sub>2</sub> enriched oxygen from 'euriso-top' and used without further purification.

*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<sub>2</sub> windows for UV/Vis measurements. IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm<sup>-1</sup>, resolution 0.7 cm<sup>-1</sup>), UV/Vis spectra with a JASCO V-670 spectrophotometer (spectral range: 190–2500 nm, resolution: ≥ 0.1 nm). We employed a small home built water-cooled oven directly connected to the vacuum shroud of the cryostat for the combination of high-vacuum flash pyrolysis (HVFP) with matrix isolation. The pyrolysis zone consisted of an 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. Allylmethylsulfoxide (**2**) was evaporated from a cooled storage bulb at –30 °C into the 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 an argon/oxygen gas-mixtures containing 0, 0.5, 1.0, or 5.0% O<sub>2</sub>, respectively, on the surface of the 10 K cold matrix window during a time of

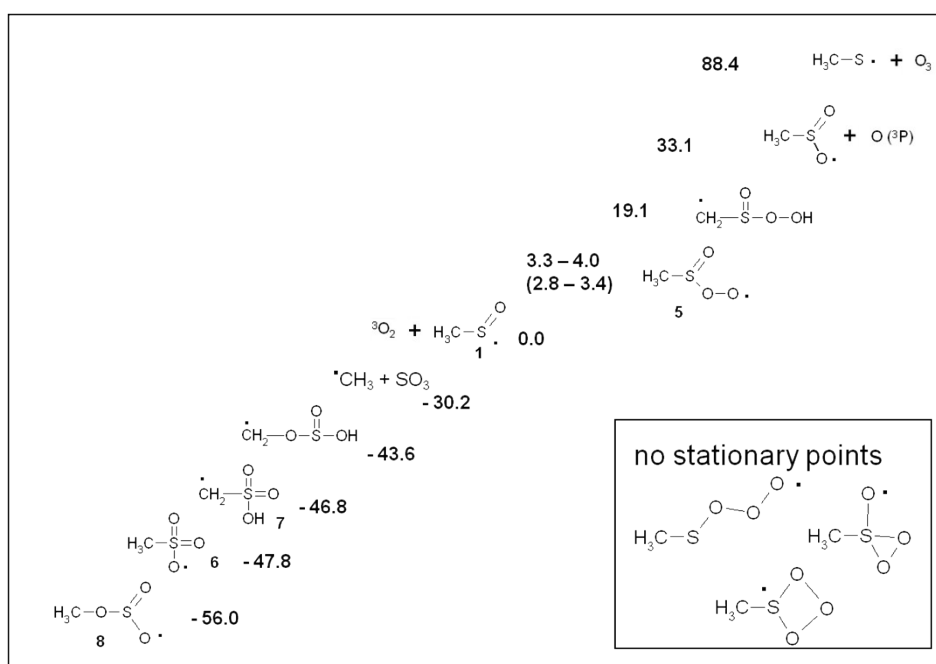
2–4 h. In order to prevent reactions between the methylsulfinyl radical and O<sub>2</sub> in the gaseous phase, the argon/oxygen gas mixture was injected into the cryostat by a separate jet after the pyrolysis tube. Pyrolysis temperatures were varied between 500 and 900 °C; the optimal temperatures with respect to the yields of methylsulfinyl radicals (**1**) was 600 °C. For irradiations a mercury high-pressure lamp (Osram, HBO 200 in connection with a Bausch & Lomb monochromator (slits set to a spectral half-width of  $\Delta\lambda = 10$  nm) was used. The same procedure was applied for the CD<sub>3</sub> isotopologue. The reaction of allyl radicals with <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> was investigated in the same way by matrix isolating the HVFP products (900 °C) of 1,5-hexadiene (evaporated at –115 °C) in an argon matrix containing 5% O<sub>2</sub>.

**Computational methods.** We utilized DFT to assess reaction energies and equilibrium geometries, harmonic vibrational wavenumbers as well as IR intensities of all key structures using the B3LYP<sup>S2,S3</sup> functional with a large basis set including polarization and diffuse functions [6-311+G(3df,3pd)] as implemented in the GAUSSIAN 09 program.<sup>S4</sup> All stationary structures were characterized as minima or transition structures by computing analytical harmonic vibrational frequencies.

#### References:

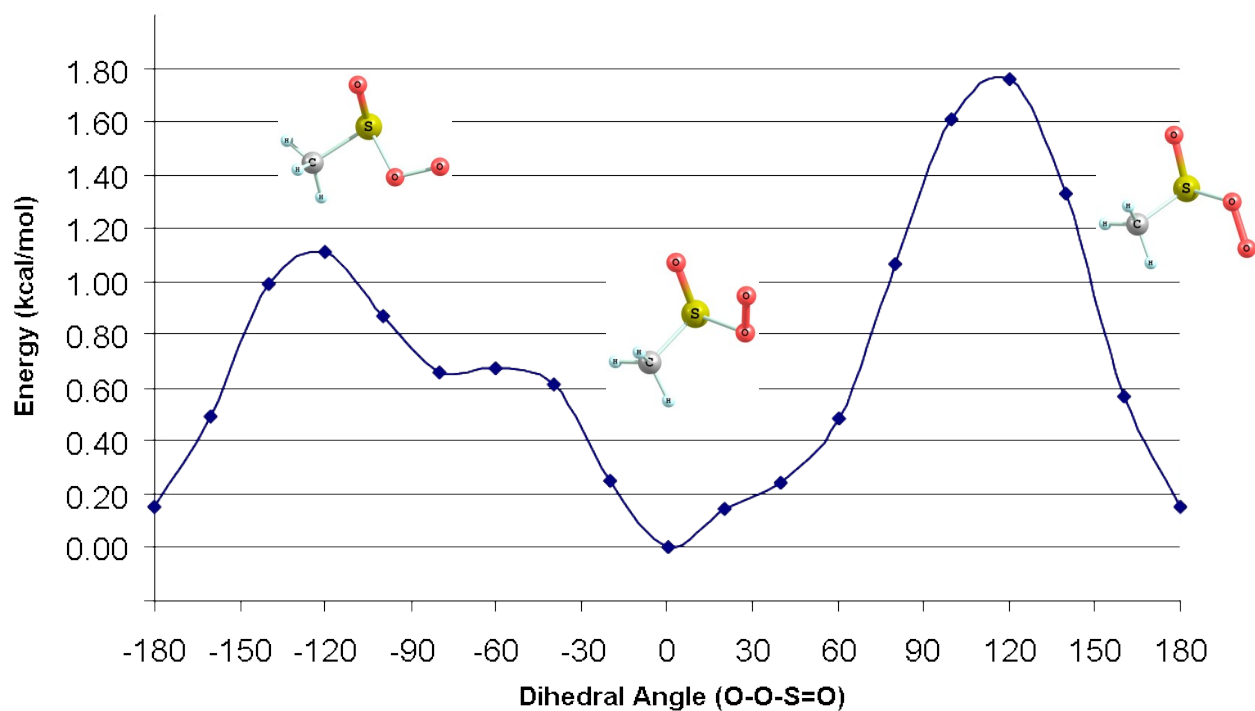
- [S1] H. P. Reisenauer, J. Romański, G. Mlostoń, P. R. Schreiner, *Chem. Commun.* **2013**, *49*, 9467–9469.
- [S2] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [S3] B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206.
- [S4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian09 Revision D.01*, Gaussian Inc., Wallingford CT, 2013.

## 2. Computed Relative Energies of CH<sub>3</sub>SO<sub>3</sub> Isomers



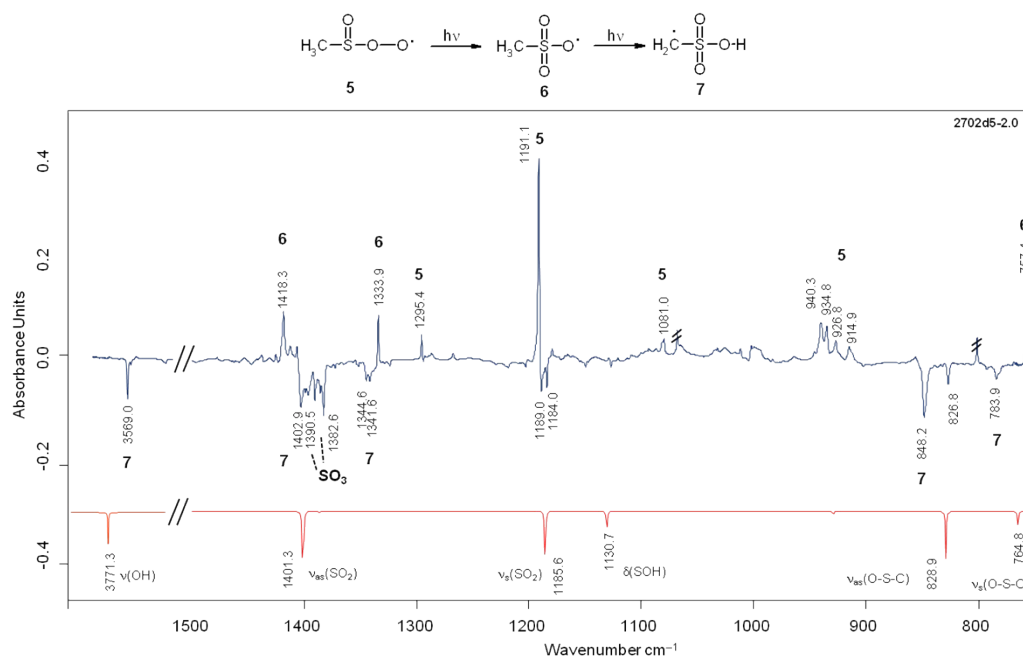
**Figure S1.** Computed relative energies ( $\Delta H_0 + \text{ZPVE}$ ) of conceivable reaction products of the methylsulfinyl radical ( $\text{CH}_3(\text{O})\text{S}^\bullet$ ) and molecular oxygen ( $^3\text{O}_2$ ) in kcal mol<sup>-1</sup> at the UB3LYP/6-311+G(3df,3pd) level of theory, (UMP2/6-311+G(3df,3pd) values in parenthesis).

## 3. Rotamers of Methylsulfinyldioxygen Radical (5) ( $\text{CH}_3(\text{O})\text{SOO}^\bullet$ )

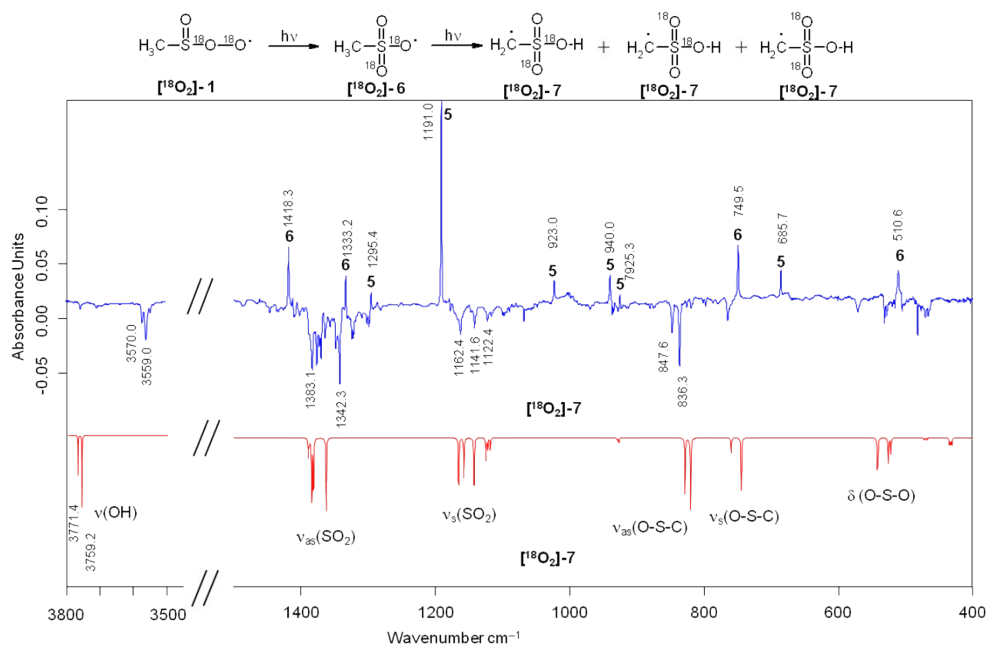


**Figure S2.** Computed energy profile of rotation around the (S-O) single bond of methylsulfinyldioxygen radical 5; relaxed scan at UB3LYP/6-311+G(3df,3pd).

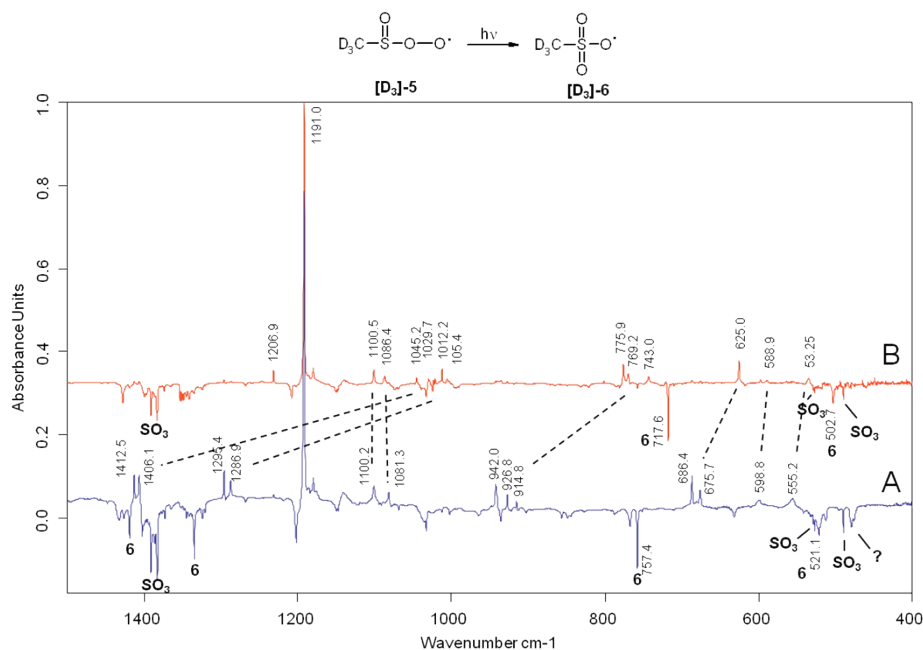
## 4. Additional Spectroscopic Data



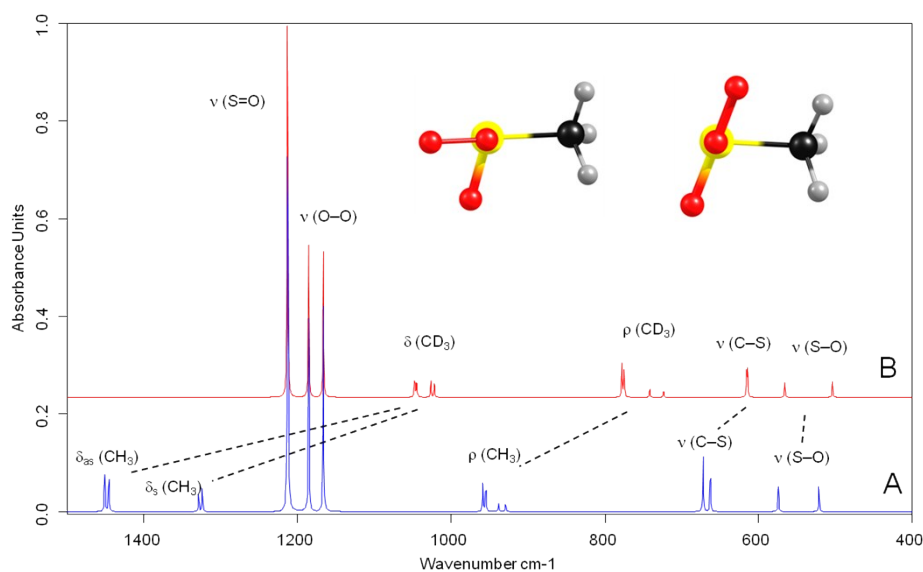
**Figure S3.** Photochemical isomerization of methylsulfonyloxyl radical ( $\text{CH}_3\text{-SO}_3^\bullet$ , **6**, positive bands vanish upon irradiation) to the C-centered radical of methylsulfonic acid (**7**, negative bands appear upon irradiation) with 435 nm light. Insert shows the OH-stretching spectral region. Red line: Computed IR spectrum of **7** at UB3LYP/6-311+G(3df,3pd).



**Figure S4.** Photochemical isomerization of the  $[\text{}^{18}\text{O}_2]$ -methylsulfinylperoxy radical ( $[\text{}^{18}\text{O}_2]$ -1,  $\text{CH}_3(\text{O})\text{C}^{18}\text{O}^{18}\text{O}^\bullet$ ) and  $[\text{}^{18}\text{O}_2]$ -methylsulfonyloxyl radical ( $[\text{}^{18}\text{O}_2]$ -6,  $\text{CH}_3\text{-S}^{16}\text{O}^{18}\text{O}^{18}\text{O}^\bullet$ ) to C-radical of  $[\text{}^{18}\text{O}_2]$ -methylsulfonic acid ( $[\text{}^{18}\text{O}_2]$ -7,  $\text{CH}_2\text{-SO}_3\text{H}$ ) with 435 nm light; positive bands vanish upon irradiation, negative bands appear upon irradiation. Red line: Computed spectrum of an equimolar mixture of the three isotopologues of **7** (B3LYP/6-311+G(3df, 3pd)).



**Figure S5.** Experimental IR band shifts upon deuteration of the methylsulfinyl peroxy radical conformers (difference spectra after irradiation with 366 or 405 nm, Ar matrix, 10 K, positive bands vanish, negative bands appear upon irradiation); A: CH<sub>3</sub>-(O)SOO<sup>•</sup>; B: CD<sub>3</sub>-(O)SOO<sup>•</sup>



**Figure S6.** Computed IR band shifts upon deuteration of methylsulfinyl peroxy radical conformers (1:1 mixture, (UB3LYP/6-311+G(3df,3pd))); A: CH<sub>3</sub>-(O)SOO<sup>•</sup>; B: CD<sub>3</sub>-(O)SOO<sup>•</sup>

**Table S1.**  $^{18}\text{O}_2$  Band shifts of methylsulfinyldioxy radical **5**, valence force constants, and bond orders of the O–O and S–O bonds.

	$^{16}\text{O}_2$	$^{18}\text{O}_2$	$\Delta\nu$ , exp.	$\Delta\nu$ , theor. <sup>a</sup>	valence force constant <sup>b</sup>	bond order <sup>c</sup>
v(O–O)	1100.3	1039.3	–61.0	–62.9	5.7	0.83
	1081.3	1023.0	–58.0	–58.0	5.5	0.81
v(S–O)	598.8	575.2	–23.6	–23.6	2.3	0.71
	555.3	534.0	–21.3	–21.0	1.9	0.64

<sup>a</sup>) 2-Atomic model (*Hooke's law*), <sup>b</sup>) force constants in  $\text{J m}^{-2}$ , <sup>c</sup>) see A. Fadini, S. Kemmer-Sack, *Z. Anorg. Allg. Chem.* **1977**, 435, 210–212.



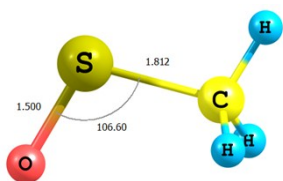
## 5. Computational Results

**Table S3.** Computed four lowest excitation energies and oscillator strengths of CH<sub>3</sub>SO<sub>3</sub> isomers 5–8 (TD-UB3LYP/6-311+G(3df,3pd))

	Excitation Energy [eV]	Absorption Wavelength [nm]	Oszillator Strength
<b>5</b>	1.15	1081	0.0001
	3.19	<b>388</b>	<b>0.005</b>
	3.37	<b>368</b>	<b>0.003</b>
	4.03	308	0.003
<b>6</b>	1.23	1010	0.001
	1.51	819	0.000
	2.60	<b>476</b>	<b>0.022</b>
	4.85	256	0.011
<b>7</b>	3.94	315	0.004
	4.06	305	0.003
	4.39	282	0.009
	5.02	247	0.011
<b>8</b>	2.87	432	0.0001
	3.31	<b>375</b>	<b>0.011</b>
	3.44	<b>361</b>	<b>0.007</b>
	4.05	306	0.021

### Optimized geometries, energies, cartesian coordinates, and vibrational harmonic frequencies of optimized geometries on B3LYP/6-311+G(3df,3pd) level of theory

#### Methylsulfinyl Radical (1)



Symmetry: C<sub>s</sub>, State = <sup>2</sup>A'

E = -513.368757 Hartree, ZPVE = 25.12997 kcal/mol

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

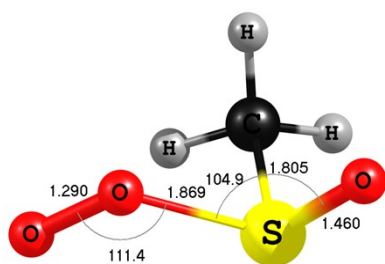
C	-1.152081000	-0.851382000	0.000000000
S	0.000000000	0.546917000	0.000000000
H	-0.988513000	-1.452896000	0.892382000
H	-2.163234000	-0.445226000	0.000000000
H	-0.988513000	-1.452896000	-0.892382000
O	1.381594000	-0.036420000	0.000000000

Vibrational Frequencies (cm<sup>-1</sup>, km mol<sup>-1</sup>):



141.8153	0.4014
336.0001	6.8398
665.7302	13.3015
887.8612	1.0941
948.6347	10.2068
1072.7763	48.313
1326.414	1.5133
1445.4912	9.52
1459.0236	7.6648
3035.4739	2.9797
3129.5424	1.513
3129.909	3.3682

**Methylsulfinyloxyl radical, rotamer a (5a)**



< OOSO: 176.6 °

Symmetry:  $C_1$ , State =  $^2A$

E = -663.7454169 Hartree, ZPVE = 29.32660 (Kcal/Mol)

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

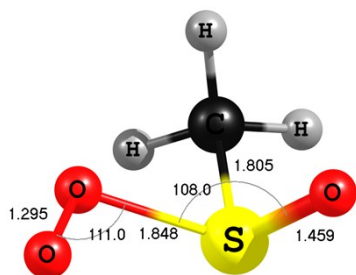
symmetry c1

C	0.500872000	1.520021000	0.203139000
S	0.525565000	-0.168897000	-0.432629000
O	-2.083851000	-0.006834000	-0.142076000
O	-1.081361000	-0.586487000	0.425989000
O	1.548941000	-0.896459000	0.311366000
H	0.563998000	1.476371000	1.288044000
H	1.369164000	2.026176000	-0.215736000
H	-0.417266000	1.997926000	-0.131307000

Vibrational Frequencies ( $\text{cm}^{-1}$ ,  $\text{km mol}^{-1}$ ):

93.4667	2.3443
192.2934	3.4757
202.4701	7.7349
262.1777	5.3343
293.575	1.1981
372.8215	12.6568
574.8375	11.9705
663.2582	20.0221
929.741	4.128
959.4776	12.848
1185.8587	92.2198
1212.8935	120.0462
1324.1689	10.7812
1445.8125	8.3944
1451.5989	10.7656
3046.5355	0.5451
3143.7892	0.1991
3159.476	0.1194

**Methylsulfinylperoxyl radical, rotamer b (5b)**



< OOSO: 72.6 °

Symmetry:  $C_1$ , State =  $^2A$

E = -663.7446155 Hartree, ZPVE = 29.245 (Kcal/Mol)

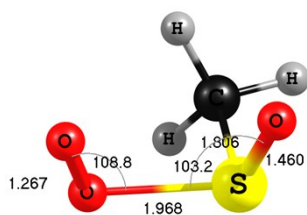
Cartesian coordinates (x, y, z, in Å):

```
symmetry c1
C      -1.480828000    -1.048424000    0.165797000
S      -0.408345000     0.272564000   -0.435587000
O       2.144953000    -0.040406000   -0.005188000
O       1.037183000    -0.668613000    0.227202000
O      -0.621131000     1.433358000    0.421578000
H      -1.345408000    -1.138882000    1.241190000
H      -2.501369000    -0.753353000   -0.068760000
H      -1.222772000    -1.972959000   -0.346560000
```

Vibrational Frequencies ( $\text{cm}^{-1}$ ,  $\text{km mol}^{-1}$ ):

46.3529	1.0902
166.2314	0.1036
191.1556	1.5427
273.0331	3.0157
351.3724	18.7108
380.6603	9.5486
521.9987	11.0968
672.81	21.5658
938.6351	4.5172
955.428	12.4511
1166.8715	79.6131
1213.8063	99.5545
1328.9464	8.0695
1445.8515	8.8809
1451.1437	8.9492
3049.0355	0.4211
3148.9944	0.1921
3155.0656	0.1654

**Methylsulfinylperoxyl radical, rotamer c (5c)**



< OOSO: 0.4 °

Symmetry:  $C_1$ , State =  $^2A$

E = -663.7456571 Hartree, ZPVE = 29.162 (Kcal/Mol)

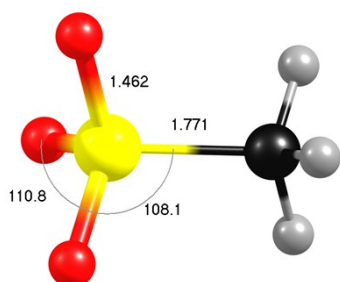
Cartesian coordinates (x, y, z, in Å):

```
symmetry c1
C      -1.354443000    -1.044740000    0.429812000
S      -0.560681000    0.289517000    -0.493752000
O       1.916548000    -0.056960000    0.414736000
O       1.157952000    -0.664141000    -0.398299000
O      -0.371670000    1.410000000    0.423424000
H      -0.870530000    -1.120779000    1.400833000
H      -2.406552000    -0.787274000    0.540514000
H      -1.248013000    -1.966971000    -0.139072000
```

Vibrational Frequencies (cm<sup>-1</sup>, km mol<sup>-1</sup>):

69.7059	0.8479
170.4206	0.0893
200.3881	0.1145
240.9339	1.3223
274.2968	0.5901
360.7645	11.8411
530.9721	4.4624
665.0156	21.0456
920.133	2.4737
953.8744	10.4347
1189.6399	186.1776
1267.9904	63.7963
1326.7391	6.6111
1442.4268	9.6578
1452.4442	9.8338
3042.8643	0.7252
3138.4913	0.2203
3152.6947	0.1308

### Methylsulfonylperoxy radical, (6)



Symmetry: C<sub>3v</sub>, State = <sup>2</sup>A<sub>2</sub>

E = -663.8286783 Hartree, ZPVE = 30.212 (Kcal/Mol)

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

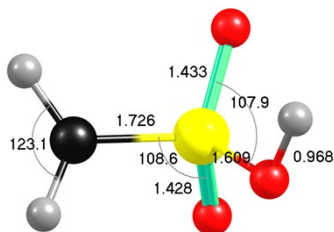
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symmetry c3v
C      0.000000000    0.000000000   -1.647918000
S      0.000000000    0.000000000    0.123573000
H      0.894284000    0.516315000   -1.985596000
H      0.000000000   -1.032630000   -1.985596000
H     -0.894284000    0.516315000   -1.985596000
O      0.000000000    1.390008000    0.577797000
O      1.203782000   -0.695004000    0.577797000
```

O -1.203782000 -0.695004000 0.577797000

Vibrational Frequencies (cm<sup>-1</sup>, km mol<sup>-1</sup>):

138.711	5.3492
138.7764	5.3431
212.2213	0
327.3776	0.4563
327.3808	0.4569
523.3434	44.2182
753.6483	39.6087
969.4714	1.173
969.4735	1.1735
998.2933	3.0524
998.2946	3.0513
1082.1107	115.6575
1369.2291	13.8623
1460.2779	11.2791
1460.2796	11.2783
3068.8382	0.0409
3167.9655	0.3464
3167.9662	0.3464

#### Methylsulfonic acid C-radical, (7)



Symmetry: C<sub>1</sub>, State = <sup>2</sup>A

E = -663.8266458 Hartree, ZPVE = 29.841 (Kcal/Mol)

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

symmetry c1

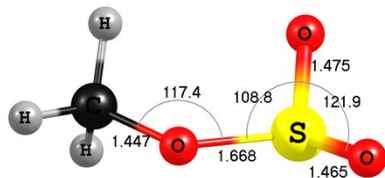
S	0.032664000	0.031628000	-0.143591000
C	-1.564278000	-0.000566000	0.509268000
O	0.921954000	-0.491709000	1.090682000
O	0.139964000	-0.988974000	-1.137009000
O	0.402590000	1.390712000	-0.407300000
H	-1.932198000	-0.926304000	0.921922000
H	-2.183672000	0.870641000	0.372712000
H	1.262851000	0.272785000	1.576227000

Vibrational Frequencies (cm<sup>-1</sup>, km mol<sup>-1</sup>):

62.6811	1.8362
278.1825	59.8586
296.7436	3.1459
345.6317	20.459
444.4069	22.7593
483.4508	5.5739
536.0369	53.7844
545.3805	53.8895
765.407	65.561
829.6665	169.2577
929.8967	9.8335

1131.4295	57.4137
1186.3995	155.9836
1387.5823	5.7988
1401.7489	239.6104
3168.0388	1.4476
3310.4249	4.9468
3771.3517	122.039

**Methylsulfanyl radical, (8)**



Symmetry:  $C_1$ , State =  $^2A$   
 E = -663.7734382 Hartree, ZPVE = 31.088 (Kcal/Mol)

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

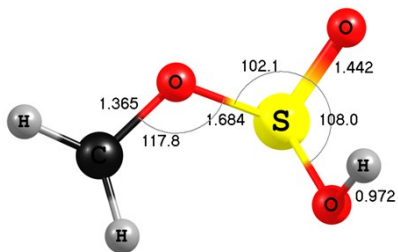
```

symmetry c1
C      2.069133000    -0.027793000    -0.017239000
O      0.826320000    -0.762332000    -0.112589000
S     -0.579734000     0.053423000     0.262910000
O     -0.454215000     1.450063000    -0.193035000
O     -1.657311000    -0.821114000    -0.207123000
H      2.276851000     0.250807000     1.018084000
H      2.823802000    -0.729651000    -0.367582000
H      2.041934000     0.857894000    -0.651656000
  
```

Vibrational Frequencies ( $\text{cm}^{-1}$ ,  $\text{km mol}^{-1}$ ):

92.8641	2.6644
146.5687	1.6338
234.9718	2.6831
377.0915	7.3131
448.3898	3.1679
497.4465	33.4903
620.9881	138.5087
978.5241	140.2357
1038.7573	50.8764
1164.8783	1.3448
1173.1413	0.2292
1211.5421	145.8706
1460.3894	1.3017
1479.9042	13.0708
1495.8265	14.9245
3044.2671	24.2396
3127.0642	12.9511
3154.1043	2.372

**Methylsulfanic acid C-radical,**



Symmetry:  $C_1$ , State =  $^2A$

E = -663.8201055 Hartree, ZPVE = 28.940 (Kcal/Mol)

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

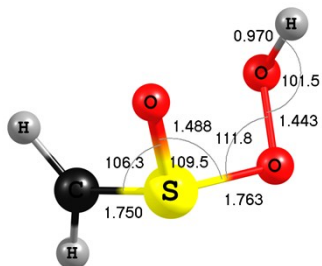
symmetry c1

C	-2.092025000	0.001016000	0.063457000
O	-0.927909000	-0.598023000	-0.323734000
S	0.498136000	-0.099239000	0.419534000
O	1.492884000	-0.868985000	-0.285704000
O	0.543378000	1.425484000	-0.151876000
H	-2.091555000	1.057954000	0.282586000
H	-2.978093000	-0.554672000	-0.191811000
H	0.784795000	1.410642000	-1.093542000

Vibrational Frequencies ( $\text{cm}^{-1}$ ,  $\text{km mol}^{-1}$ ):

105.6286	0.1298
185.9383	4.5819
241.0318	3.5999
284.5637	31.3869
403.6622	20.7167
410.9431	40.4741
444.5713	37.8641
487.5599	53.6129
631.393	230.1165
748.1329	194.752
1096.2028	45.0049
1156.2261	120.8021
1169.2856	50.5155
1269.1817	185.658
1467.6484	3.4352
3149.7319	10.9969
3297.915	0.6543
3694.6087	78.4721

**Methylsulfinic peroxyacid C-radical,**



Symmetry:  $C_1$ , State =  $^2A$

E = -663.6666269 Hartree, ZPVE = 27.846 (Kcal/Mol)

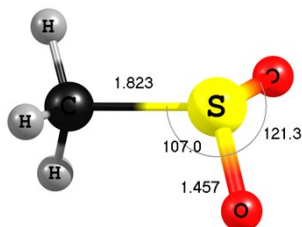
Cartesian coordinates (x, y, z, in Å):

```
symmetry c1
C      -0.858405000    1.400688000    0.330751000
S      -0.655909000    -0.155779000    -0.442971000
O       1.084044000    -0.073895000    -0.713815000
O       1.807339000    0.146087000    0.515749000
H      -1.079534000    1.422804000    1.389851000
H      -0.787846000    2.291935000    -0.279615000
O      -0.948816000    -1.179962000    0.596158000
H       1.971824000    -0.764244000    0.808068000
```

Vibrational Frequencies (cm<sup>-1</sup>, km mol<sup>-1</sup>):

```
89.5913      12.9403
153.103      4.1741
206.1137     1.7946
272.9569     54.2823
340.4187     70.6078
359.29       24.3999
449.8416     5.3589
501.4713     32.5162
572.9958     67.3277
716.0835     15.5519
869.1638     20.2188
906.3959     6.5322
1120.2976    144.7761
1372.675     2.1767
1381.7264    46.0714
3137.9779    1.2011
3287.108     2.6453
3741.5178    63.9521
```

### Methylsulfonyl radical



Symmetry: C<sub>s</sub>, State = <sup>2</sup>A'

E = -588.6059337Hartree, ZPVE = 28.307 (Kcal/Mol)

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

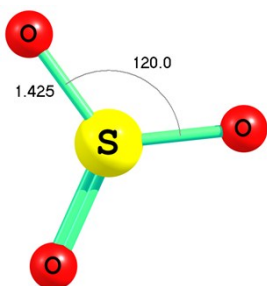
```
symmetry cs
C       0.169385000    -1.572320000    0.000000000
S      -0.281365000     0.194072000    0.000000000
H       1.256896000    -1.608007000    0.000000000
H      -0.240770000    -2.016784000    -0.900975000
O       0.169385000     0.748147000    -1.270480000
```

Vibrational Frequencies (cm<sup>-1</sup>, km mol<sup>-1</sup>):

```
173.5106     0.0541
302.0618     0.0588
380.8776     21.2833
459.1564     15.6838
624.7657     16.1805
933.78       6.8457
```

955.4796	0.0411
1076.4358	66.0962
1271.0911	141.4177
1312.29	0.9349
1446.7774	5.1483
1455.3276	9.6646
3060.62	0.2435
3164.1859	0.5048
3185.1076	0.0109

### Sulfur trioxide



Symmetry:  $D_{3h}$ , State =  $^1A_1'$   
 E = -623.9363146 Hartree, ZPVE = 7.747 (Kcal/Mol)

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

symmetry d3h

S	0.000000000	0.000000000	0.000000000
O	0.000000000	1.425298000	0.000000000
O	1.234345000	-0.712649000	0.000000000
O	-1.234345000	-0.712649000	0.000000000
O	0.169385000	0.748147000	-1.270480000

Vibrational Frequencies ( $\text{cm}^{-1}$ ,  $\text{km mol}^{-1}$ ):

495.1432	33.3189
524.3584	25.7878
524.3688	25.7937
1076.2767	0
1399.5595	196.2911
1399.5625	196.3526