Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for The Methylsulfinyl Radical CH_3SO, Characterized Using High-Level Ab Initio Methods

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All states considered in the present work were doublet states optimized in C_s symmetry.

CH_3SO Ground Electronic State ($\tilde{X}\ ^2A''$)

Occupation numbers:

	A''	A'
α	13	4
β	13	3

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Minimum-Energy Structure (abbreviated GS)

CCSD(T)/ANO1

Software:	CFour 1.0
Theory:	CCSD(T)/ANO1
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	1.0E-9
Equilibrium Geometry (Å):	

H	-2.2591906630	0.3561031197	-0.0000000000
C	-1.4602099596	-0.3875247704	-0.0000000000
S	0.1231740905	0.4885941747	-0.0000000000
O	1.1835752818	-0.5811629339	0.0000000000
H	-1.5230460854	-1.0092567076	0.8931384867
H	-1.5230460854	-1.0092567076	-0.8931384867

Frequencies (cm^{-1}):

139.2032
331.0387
685.8069
890.2235
946.6529
1083.8226
1324.6757
1449.1373
1463.4529
3041.1660
3145.7567
3148.8905

ZPVE:	26.2317 kcal mol^{-1}
SCF Convergence:	1.0E-10
CC Convergence:	1.0E-10
UHF Reference energy	-512.043458240531 E_h
Final energy	-512.679538426120 E_h
$\langle S^2 \rangle$	0.776
T1	0.033
T2	0.02
Gradient	Analytic

CCSD(T)/ANO2

Software:	CFour 1.0
Theory:	CCSD(T)/ANO2
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	1.0E-9
Equilibrium Geometry (Å):	

H	-2.2509697198	0.3613035509	-0.0000000000
C	-1.4559420392	-0.3851022499	-0.0000000000
S	0.1223153099	0.4847998944	-0.0000000000
O	1.1811859407	-0.5761743588	0.0000000000
H	-1.5199830223	-1.0056807712	0.8927955110
H	-1.5199830223	-1.0056807712	-0.8927955110

Frequencies (cm^{-1}):

142.4783
334.1565
695.0646
889.7511
949.8553
1095.3919
1327.1385
1451.5482
1466.0564
3041.9176
3146.9911
3148.9728

ZPVE:	25.2881 kcal mol^{-1}
SCF Convergence:	1.0E-10
CC Convergence:	1.0E-10
UHF Reference energy	-512.048095598701 E_h
Final energy	-512.719438774341 E_h
$\langle S^2 \rangle$	0.787
T1	0.032
T2	0.02
Gradient	Analytic

BCCD(T)/ANO1

Software:	Psi4
Theory:	BCCD(T)/ANO1
Charge:	0
Multiplicity:	2
Geometry Convergence:	RMS Force 1.0E-6
Equilibrium Geometry (Å):	

H	-2.2594566935	0.3558335612	0.0000000000
C	-1.4603694998	-0.3878107179	0.0000000000
S	0.1228335457	0.4891309447	0.0000000000
O	1.1844319104	-0.5819680454	0.0000000000
H	-1.5233592211	-1.0095450019	0.8932064012
H	-1.5233592211	-1.0095450019	-0.8932064012

Frequencies (cm^{-1}):

138.943
330.339
685.228
890.537
946.447
1068.615
1324.281
1448.792
1463.173
3040.193
3144.860
3148.136

ZPVE:	25.2027 kcal mol^{-1}
Final energy	-512.6800499 E_h
Gradient	Numeric

Rotational transition state (abbreviated TS)

CCSD(T)/ANO1

Software:	CFour 1.0
Theory:	CCSD(T)/ANO1
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	1.0E-9

Equilibrium Geometry (Å):

C	-1.4693671390	0.3853395912	0.0000000000
S	0.1258648563	-0.4898561090	0.0000000000
O	1.1853767123	0.5835494121	0.0000000000
H	-1.2343313229	1.4494445999	0.0000000000
H	-2.0379349717	0.1205712899	-0.8920704853
H	-2.0379349717	0.1205712899	0.8920704853

Frequencies (cm^{-1}):

$142.7966i$
354.6870
685.5770
886.6665
925.9689
1078.4911
1316.6356
1452.5510
1464.0369
3042.6275
3141.5675
3159.7328

ZPVE:	25.0310 kcal mol^{-1}
SCF Convergence:	1.0E-10
CC Convergence:	1.0E-10
UHF Reference energy	-512.618840637054 E_h
Final energy	-512.677886444682 E_h
$\langle S^2 \rangle$	0.785
T1	0.033
T2	0.03
Gradient	Analytic

CCSD(T)/ANO2

Software:	CFour 1.0
Theory:	CCSD(T)/ANO2
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	1.0E-9
Equilibrium Geometry (Å):	

C	-1.4647912058	0.3828937921	0.0000000000
S	0.1251703058	-0.4862751136	0.0000000000
O	1.1824656024	0.5789596144	0.0000000000
H	-1.2334134703	1.4468259345	0.0000000000
H	-2.0315186500	0.1160617102	-0.8914816009
H	-2.0315186500	0.1160617102	0.8914816009

Frequencies:

144.7431i
357.0137
695.3994
889.1443
929.6082
1089.8934
1320.2352
1455.9998
1466.7974
3043.4856
3142.3001
3160.4886

ZPVE:	25.0895 kcal mol^{-1}
SCF Convergence:	1.0E-10
CC Convergence:	1.0E-10
UHF Reference energy	-512.046146830428 E_h
Final energy	-512.717729459839 E_h
$\langle S^2 \rangle$	0.787
T1	0.032
T2	0.02
Gradient	Analytic

$\mathbf{CH_3SO}$ ($\tilde{A}\ ^2A'$)

Occupation numbers:

	A''	A'
α	13	4
β	12	4

Minimum-energy structure (abbreviated XS)

CCSD(T)/ANO1

Software:	CFour 1.0
Theory:	CCSD(T)/ANO1
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	1.0E-9
Equilibrium Geometry (Å):	

H	-2.2221601568	0.1737208367	-0.0000000000
C	-1.3676909325	-0.5039113213	-0.0000000000
S	0.0841391191	0.5896686273	-0.0000000000
O	1.1711325837	-0.6707228759	0.0000000000
H	-1.3744586861	-1.1177119764	0.8987375735
H	-1.3744586861	-1.1177119764	-0.8987375735

Frequencies (cm^{-1}):

205.2934
253.0606
682.4609
725.0451
957.2973
978.9611
1330.3587
1445.0348
1485.8584
3052.8142
3156.1938
3161.4989

ZPVE:	24.9215 kcal mol^{-1}
SCF Convergence:	1.0E-10
CC Convergence:	1.0E-10
UHF Reference energy	-511.998265754416 E_h
Final energy	-512.611374451606 E_h
$\langle S^2 \rangle$	0.763
T1	0.031
T2	0.02
Gradient	Analytic

CCSD(T)/ANO2

Software:	CFour 1.0
Theory:	CCSD(T)/ANO2
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	1.0E-9
Equilibrium Geometry (Å):	

H	-2.2144127479	0.1895280279	-0.0000000000
C	-1.3678704294	-0.4965783375	-0.0000000000
S	0.0878554674	0.5849046086	-0.0000000000
O	1.1638318427	-0.6688467415	0.0000000000
H	-1.3782781817	-1.1085931940	0.8986136032
H	-1.3782781817	-1.1085931940	-0.8986136032

Frequencies (cm^{-1}):

208.7370
252.9643
683.1387
734.1697
957.8931
980.0153
1330.1197
1447.4180
1488.7834
3052.9625
3157.4615
3164.1043

ZPVE:	24.9571 kcal mol^{-1}
SCF Convergence:	1.0E-10
CC Convergence:	1.0E-10
UHF Reference energy	-512.001816668576 E_h
Final energy	-512.649312382801 E_h
$\langle S^2 \rangle$	0.763
T1	0.033
T2	0.03
Gradient	Analytic

BCCD(T)/ANO1

Software:	Psi4
Theory:	BCCD(T)/ANO1
Charge:	0
Multiplicity:	2
Frozen Core:	ON
Geometry Convergence:	RMS Force 1.0E-6
Equilibrium Geometry (Å):	

H	-2.222342124016	0.174313836993	0.000000000000
C	-1.368422526616	-0.504079381007	0.000000000000
S	0.084378490184	0.589254071593	0.000000000000
O	1.171279318284	-0.669795298707	0.000000000000
H	-1.374973502616	-1.117793070507	0.898833577500
H	-1.374973502616	-1.117793070507	-0.898833577500

Frequencies (cm^{-1}):

205.3281
252.1836
680.8362
725.8256
956.3662
978.5290
1329.2747
1444.3636
1485.4765
3051.1885
3155.9744
3161.3445

ZPVE:	24.9127 kcal mol^{-1}
Final energy	-512.719438774341 E_h
Gradient	Numeric

Table 1: Energy values (Hartree) used for focal point analysis corrections

State	GS	XS	TS
Frozen Core	−512.666892057105	−512.597077904741	−512.665097275290
All-Electron	−513.106058947981	−513.036081301753	−513.104253347319
MVD1	−1.14331055382883	−1.14353012096674	−1.14331840488828
MVD2	−0.03879361835091	−0.03879607869464	−0.03879371581377
DBOC	+0.0103944588	+0.0103798740	+0.0103910206

Table 2: ZPVE values (kcal mol^{-1}) used for focal point analysis corrections

State	GS	XS	TS
Harmonic ZPVE	25.2317	24.9216	25.0895
Anharmonic ZPVE	-0.3451	-0.3451	–
Brueckner ZPVE	-0.0290	-0.0088	–
Total ZPVE	24.8576	24.5677	25.0895

Descriptions [tight *d* functions are used only for sulfur in cc-pCV(T+d)Z and cc-pV(T+d)Z]:

- Harmonic ZPVE - zero-point vibrational energy for the CCSD(T)/ANO2 harmonic frequencies
- Anharmonic ZPVE - CCSD(T)/ANO1 VPT2 anharmonic correction to the ZPVE
- Brueckner ZPVE - difference between the BCCD(T)/ANO1 harmonic ZPVE and the CCSD(T)/ANO1 harmonic ZPVE
- Frozen Core - CCSD(T)/cc-pCV(T+d)Z energy with core electrons frozen
- All-Electron - CCSD(T)/cc-pCV(T+d)Z energy with no electrons frozen
- MVD1 - CCSD/cc-pV(T+d)Z mass-velocity relativistic correction with one-electron Darwin terms
- MVD2 - CCSD/cc-pV(T+d)Z relativistic correction including two-electron Darwin terms; this must be added to MVD1 number to obtain the total MVD2 correction
- DBOC - HF/cc-pV(T+d)Z diagonal Born-Oppenheimer correction

Table 3: Corrections for GS-XS focal point analysis, kcal mol^{-1}

Core:	0.1026
Relativistic:	−0.1393
ZPVE:	−0.2999
DBOC:	−0.0092

Table 4: Corrections for GS-TS focal point analysis, kcal mol^{-1}

Core:	0.0068
Relativistic:	−0.0050
ZPVE:	−0.1422
DBOC:	−0.0022

Energy Values for FPA

Table 5: Electronic ground state energy values for focal point approach (Hartree)

	Basis			
Theory	cc-pV(D+d)Z	cc-pV(T+d)Z	cc-pV(Q+d)Z	cc-pV(5+d)Z
UHF	-511.9687350	-512.0340500	-512.0478183	-512.0512207
MP2	-512.4128803	-512.6030323	-512.6620159	-512.6842617
CCSD	-512.4495456	-512.6337504	-512.6864678	-512.7036359
CCSD(T)	-512.4640947	-512.6597788	-512.7159919	-512.7344252
CCSDT	-512.4651670	-512.6607039		
CCSDT(Q)	-512.4667102	-512.6624277		

Table 6: Rotational transition state on electronic ground state energy values for focal point approach (Hartree)

	Basis			
Theory	cc-pV(D+d)Z	cc-pV(T+d)Z	cc-pV(Q+d)Z	cc-pV(5+d)Z
UHF	-511.9671655	-512.0321108	-512.0458040	-512.0492043
MP2	-512.4112259	-512.6008681	-512.6598030	-512.6820525
CCSD	-512.4481154	-512.6318921	-512.6845768	-512.7017501
CCSD(T)	-512.4627131	-512.6579651	-512.7141621	-512.7326064
CCSDT	-512.4637905	-512.6588974		
CCSDT(Q)	-512.4653406			

Table 7: Electronic excited state energy values for focal point approach (Hartree)

	Basis			
Theory	cc-pV(D+d)Z	cc-pV(T+d)Z	cc-pV(Q+d)Z	cc-pV(5+d)Z
UHF	-511.9300131	-511.9877195	-512.0006739	-512.0038235
MP2	-512.3458547	-512.5248398	-512.5816924	-512.6030895
CCSD	-512.3906399	-512.5667778	-512.6179486	-512.6343849
CCSD(T)	-512.4033016	-512.5903783	-512.6449429	-512.6626007
CCSDT	-512.4044801	-512.5917619		
CCSDT(Q)	-512.4055911	-512.5931238		

Table 8: methylsulfinyl radical $\mathcal{T}_1$ and $\mathcal{T}_2$ amplitudes for states under study.

	Basis	Ground State	Excited State	Transition State
$\mathcal{T}_1$	ANO1	0.033	0.031	0.033
	ANO2	0.032	0.033	0.032
maxt_{ij}	ANO1	0.02	0.03	0.03
	ANO2	0.02	0.03	0.02

Table 9: Transition properties for electronic transitions $\tilde{X}\ ^2A'' \leftarrow \tilde{A}\ ^2A'$ and $\tilde{A}\ ^2A' \leftarrow \tilde{X}\ ^2A''$. The former transition is relevant to fluorescence, while the latter can be used to study absorption processes. Notation follows that of Ref. 19:

	$\tilde{X}\ ^2A''$	$\tilde{A}\ ^2A'$
	Equilibrium	Equilibrium
$\tilde{\nu}_{\tilde{A}}$	18872 cm^{-1}	11299 cm^{-1}
$\lvert\langle\tilde{X}\rvert\hat{\mu}_z\lvert\tilde{A}\rangle\rvert$	0.098 Debye	0.058 Debye
$f_{\tilde{A}}$	5.5×10^{-4}	1.1×10^{-4}

Vertical excitation energy: $\tilde{\nu}_{\tilde{A}} = \frac{\omega_{\tilde{A}}}{2\pi c}$

Transition dipole moment: $|\langle\tilde{X}|\hat{\mu}_z|\tilde{A}\rangle| \equiv \sqrt{\langle\tilde{X}|\hat{\mu}_z|\tilde{A}\rangle\langle\tilde{A}|\hat{\mu}_z|\tilde{X}\rangle}$

Oscillator strength: $f_{\tilde{A}} = \frac{2}{3}\frac{m_e}{e^2\hbar}\omega_{\tilde{A}}|\langle\tilde{X}|\hat{\mu}|\tilde{A}\rangle|^2$

Table 10: Ground electronic state spin densities calculated using Mulliken population analysis for the CCSD(T)/ANO2 method with a UHF reference. The final two atoms listed are the equivalent hydrogens. A spin density of 0.58099757 resides on the sulfur, with a spin density of 0.40894725 on the oxygen. The remaining atoms contribute only 0.01005518 to the spin density.

Z-matrix center	Population
H	-0.00030509
C	-0.01374331
S	0.58099757
O	0.40894725
H	0.01205179
H	0.01205179

Truncated output of PyVPT2, a program written in Python by Jay Agarwal

Ground State

```
## Anharmonic Script, Version 4.
## J. Agarwal


---- Diagnostics----------------------------------------
      12 normal modes found
      12 modes defined for analysis by user
    50.0 cm-1 cutoff for delta between two fundamentals
    80.0 cm-1 cutoff for minimum phi value
    30.0 bound for large Xrr
   100.0 bound for large Xrs
       0 Xrr value(s) are being set to zero
       0 Xrs value(s) are being set to zero
```

0 additional Fermi resonance(s) has been defined by user

TABLE 1: HARMONIC AND ANHARMONIC FREQUENCIES AND INTENSITIES

	Frequencies(cm-1)			Intensities(km mol-1)	
	Harmonic	Correction	Anharmonic	Harm.	Anharm.
1	139.2032	-13.6538	125.5493	0.4	0.0
2	331.0387	1.1341	332.1728	7.02	0.0
3	685.8069	-16.145	669.6618	12.09	0.0
4	890.2235	-16.986	873.2374	1.32	0.0
5	946.6529	-22.1801	924.4728	9.82	0.0
6	1083.8226	-15.8421	1067.9805	39.19	0.0
7	1324.6757	-33.6579	1291.0178	0.67	0.0
8	1449.1373	-41.5971	1407.5402	8.37	0.0
9	1463.4529	-40.531	1422.9218	6.73	0.0
10	3041.166	-118.21	2922.956	3.6	0.0
11	3145.7567	-147.9725	2997.7841	3.72	0.0
12	3148.8905	-150.562	2998.3285	1.89	0.0

Harmonic ZPVE: 8824.9134 cm-1; 25.2317 kcal/mol

Anharmonic ZPVE: 8702.8915 cm-1; 24.8828 kcal/mol

G_0 = 1.6502 cm-1

E_i w_i/2 = 8824.9134 cm-1

E_i>=j x_ij/4 = -123.672 cm-1

Anharmonic ZPVE (resonance-free): 8702.6041 cm-1; 24.882 kcal/mol

```
     Quadratic: 8824.9134 cm-1
     Cubic: -330.9051 cm-1
     Quartic: 204.8154 cm-1
     Z_kinetic: 3.7805 cm-1
Have a nice day.
```

Excited State

```
## Anharmonic Script, Version 4.
## J. Agarwal

----Diagnostics-----------------------------------------
      12 normal modes found
      12 modes defined for analysis by user
    50.0 cm-1 cutoff for delta between two fundamentals
    80.0 cm-1 cutoff for minimum phi value
    30.0 bound for large Xrr
   100.0 bound for large Xrs
       0 Xrr value(s) are being set to zero
       0 Xrs value(s) are being set to zero
       0 additional Fermi resonance(s) has been defined by user
-----------------------------------------------------

TABLE 1: HARMONIC AND ANHARMONIC FREQUENCIES AND INTENSITIES

                    Frequencies(cm-1)              Intensities(km mol-1)
               Harmonic     Correction     Anharmonic       Harm.     Anharm.
 ------------------------------------------------------------------------------
```

1	205.2934	-7.6999	197.5935	0.03	0.0
2	253.0606	-0.832	252.2286	5.43	0.0
3	682.4609	-19.2216	663.2392	4.03	0.0
4	725.0451	-10.1889	714.8562	1.05	0.0
5	957.2973	-16.7404	940.5569	6.95	0.0
6	978.9611	-17.4755	961.4856	5.14	0.0
7	1330.3587	-35.6941	1294.6646	6.55	0.0
8	1445.0348	-37.4528	1407.582	6.95	0.0
9	1485.8584	-42.1795	1443.6789	9.79	0.0
10	3051.8142	-116.295	2935.5191	11.03	0.0
11	3156.1938	-148.0882	3008.1056	3.87	0.0
12	3161.4989	-151.3441	3010.1547	2.45	0.0

Harmonic ZPVE: 8716.4386 cm-1; 24.9216 kcal/mol

Anharmonic ZPVE: 8595.7293 cm-1; 24.5764 kcal/mol

G_0 = 0.9759 cm-1

E_i w_i/2 = 8716.4386 cm-1

E_i>=j x_ij/4 = -121.6852 cm-1

Anharmonic ZPVE (resonance-free): 8596.7778 cm-1; 24.5794 kcal/mol

Quadratic: 8716.4386 cm-1

Cubic: -192.7418 cm-1

Quartic: 71.0916 cm-1

Z_kinetic: 1.9894 cm-1

Have a nice day.