Electronic Supplementary Information for

Threshold Photoelectron Spectroscopy of Organosulfur Radicals

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Precursor TPES and dissociative photoionization

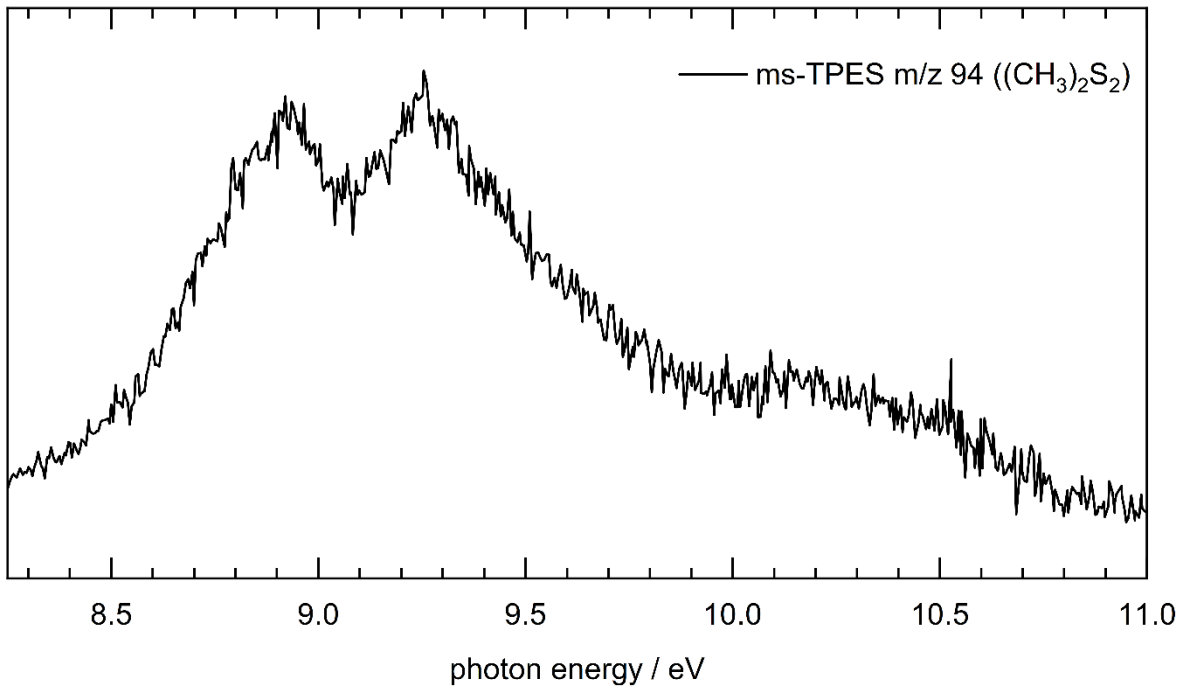

Figure S1: ms-TPES of the precursor m/z 94 from 8.25 – 11.0 eV. A He(I) photoelectron spectrum was first published by Kimura *et al.* in 1980 with an IE of 8.3 eV. In 1993 Li *et al.* published a more precise IE of 8.18 ± 0.03 eV through photoionization efficiency curves. A first TPE spectrum was published by Chiang *et al.* in 1999.[2-5]

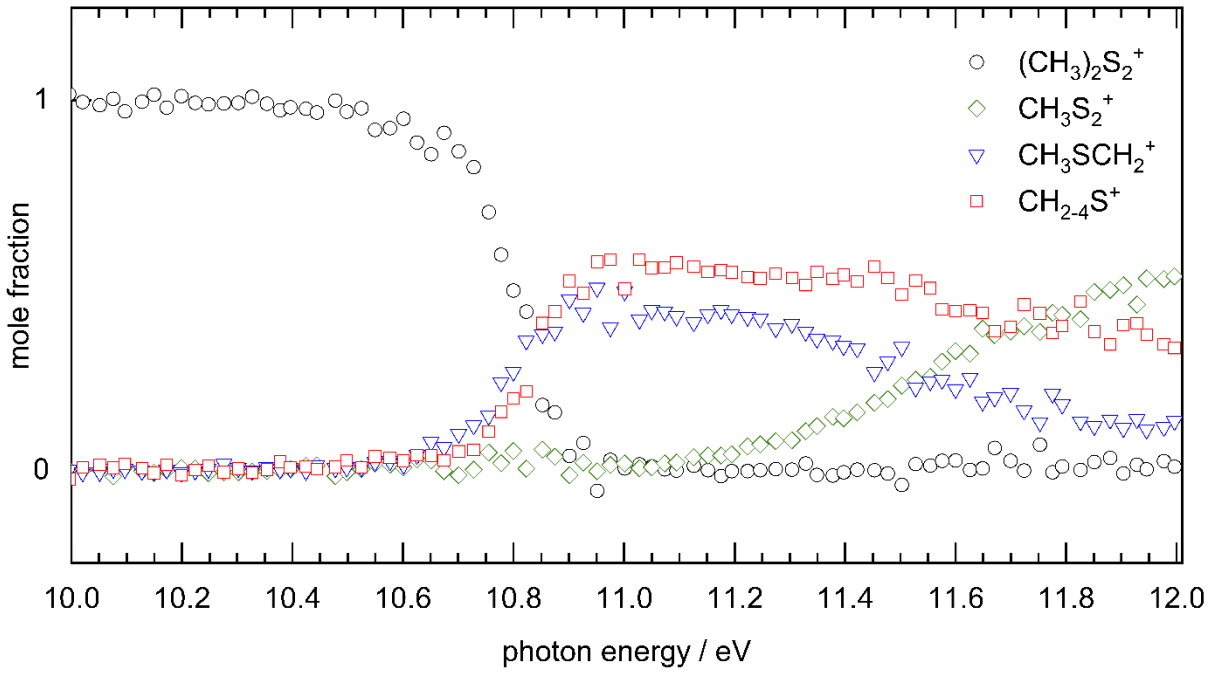

Figure S2: Breakdown diagram of the dissociative photoionization of the precursor $(CH_3)_2S_2$ to $CH_3S_2^+$, $CH_3SCH_2^+$ and $CH_{2\text{-}4}S^+$. It is in agreement with the data from Hrodmarsson et al.[1]

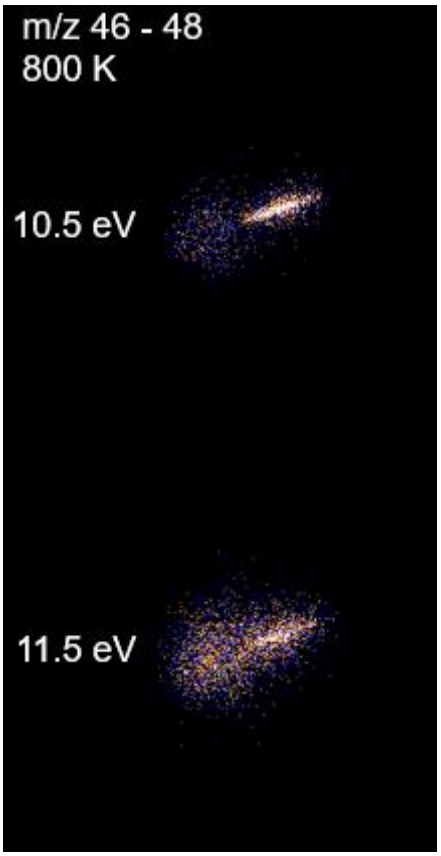

Figure S3: Ion velocity map images (VMI) of m/z 46 – 48 (CH_2S^+, CH_3S^+, CH_3SH^+) at 800 K. The signal at 10.5 eV results from direct photoionization of the pyrolysis products and is not affected by dissociative photoionization (DPI). Even at 11.5 eV DPI only contributes to a lower extend to these mass channels, as evident from the small signals at high kinetic energy release..

Potential energy surface

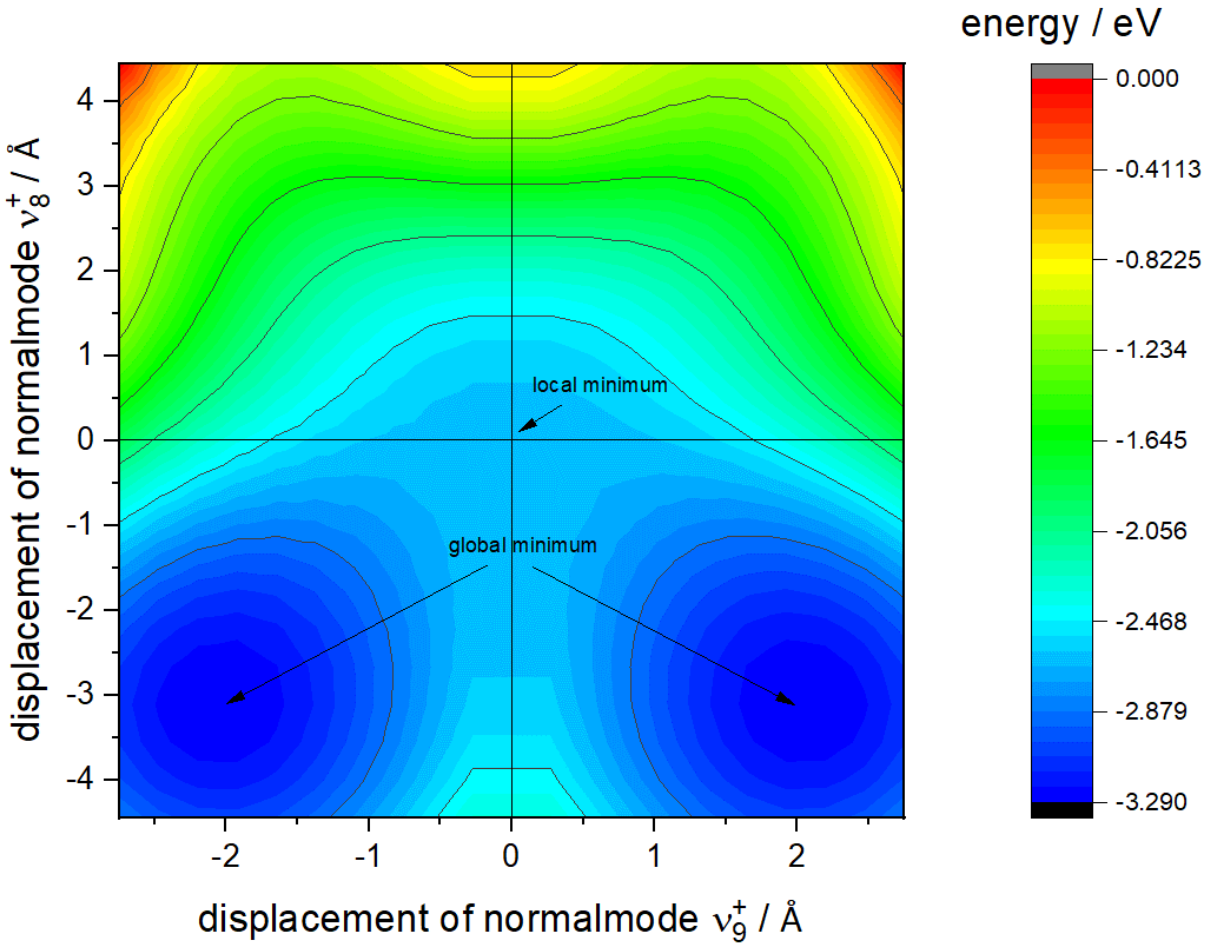

Figure S4: Scan of the displacements of normal modes ν_8^+ and ν_9^+. The local minimum in the middle corresponds to the structure CH_2HS, where the hydrogen sits above the C-S bond. The global minimum corresponds to the mercaptomethyl radical cation CH_2SH^+. A combination of ν_8^+ and ν_9^+ leads barrierless to the global minimum. Hence the ZPE should be sufficient to transfer the local minimum to the global one.

Calculated Ionization Energies, Geometries and Vibrations of several molecules and states

Table 1: Adiabatic Ionization energies using different composite methods

	CBS-QB3	G4	W1BD
$CH_2SH\ X^{+2}B_2 \leftarrow X\ ^1A_1$	7.50	7.52	7.57
$CH_3S\ X^+\ ^3A'' \leftarrow X\ ^2A'$	9.23	9.26	9.37
$CH_3S_2\ X^+\ ^1A' \leftarrow X\ ^2A'$	8.61	8.60	8.61
$CH_3S_2\ X^+\ ^3A'' \leftarrow X\ ^2A'$	9.18	9.21	9.20
$S_2H\ X^+\ ^1A' \leftarrow X\ ^2A''$	9.22	9.22	9.26
$S_2H\ a^+\ ^3A'' \leftarrow X\ ^2A''$	9.59	9.61	9.62
$CH_3SH\ X^+\ ^2A'' \leftarrow X\ ^1A'$	9.45	9.44	9.45
$CH_2S\ X^+\ ^2B_2 \leftarrow X\ ^1A_1$	9.35	9.38	9.39

$\underline{CH_3S_2}$:

Table 2: Cartesian Coordinates in Å of CH_3S_2 in its X ^{2}A" state

Atom	X	Y	Z
S	-2.159822	-0.276096	-0.007522
S	-0.209972	-0.177077	0.003536
C	0.362540	-1.894386	0.000573
H	-0.003027	-2.396821	-0.891238
H	1.451319	-1.874561	-0.000423
H	-0.001234	-2.399696	0.891529

Table 3: Vibrations of CH_3S_2 in its X ^{2}A" state

Vibration	Wavenumbers	Description
ν_1	3180	Asymmetric CH_2 stretching
ν_2	3170	Asymmetric CH_3 stretching
ν_3	3070	Symmetric CH_3 stretching
ν_4	1470	Symmetric CH_3 scissoring
ν_5	1460	Asymmetric CH_3 scissoring
ν_6	1350	CH_3 umbrella
ν_7	980	CH_3 wagging
ν_8	940	CH_3 wagging
ν_9	720	S-C stretching
ν_{10}	630	S-S stretching
ν_{11}	260	S-S-C bending
ν_{12}	110	CH_3 rotation

Table 4: Cartesian Coordinates in Å of CH_3S_2 in its $X^+\ ^1$A' state

Atom	X	Y	Z
S	-1.3135640	0.2813330	0.0014720
S	0.3174530	-0.6257030	0.0014150

C	1.6829900	1.1044050	0.0044360
H	1.6529960	0.0478250	0.9380430
H	2.5923900	-0.0478250	-0.0970400
H	1.5944490	1.1933440	-0.8667160

Table 5: Vibrations of CH_3S_2 in its X^+ $^1A'$ state

Vibration	Wavenumbers	Description
ν_1	3180	Asymmetric CH_2 stretching
ν_2	3090	Asymmetric CH_3 stretching
ν_3	3010	Symmetric CH_3 stretching
ν_4	1410	Symmetric CH_3 scissoring
ν_5	1400	Asymmetric CH_3 scissoring
ν_6	1320	CH_3 umbrella
ν_7	970	CH_3 wagging
ν_8	840	CH_3 wagging
ν_9	740	S-S stretching
ν_{10}	630	S-C stretching
ν_{11}	280	S-S-C bending
ν_{12}	100	CH_3 rotation

Table 6: Cartesian Coordinates in Å of CH_3S_2 in its a^+ $^3A''$ state

Atom	X	Y	Z
S	-2.1382510	-0.2826630	-0.0121410
S	-0.2012290	-0.1708750	0.0081810
C	0.3531130	-1.9208630	0.0009940
H	-0.0097300	-2.4006500	-0.9037830
H	1.4384240	-1.8388600	-0.0033140
H	-0.0025240	-2.4047270	0.9065200

Table 7: Vibrations of CH_3S_2 in its a^+ $^3A''$ state

Vibration	Wavenumbers	Description
ν_1	3210	Asymmetric CH_2 stretching
ν_2	3200	Asymmetric CH_3 stretching
ν_3	3080	Symmetric CH_3 stretching
ν_4	1450	Symmetric CH_3 scissoring
ν_5	1440	Asymmetric CH_3 scissoring
ν_6	1350	CH_3 umbrella
ν_7	980	CH_3 wagging
ν_8	940	CH_3 wagging
ν_9	630	S-S stretching
ν_{10}	620	S-C stretching
ν_{11}	210	S-S-C bending
ν_{12}	110	CH_3 rotation

Table 8: Cartesian Coordinates in Å of CH_3S_2 in its A^+ $^1A''$ state

Atom	X	Y	Z
S	-2.0457850	-0.2041220	0.3990820
S	-0.2906470	-0.2330680	-0.3910150
C	0.3464640	-1.9327200	-0.0526110

H	-0.3159580	-2.6525510	-0.5265220
H	1.3287270	-1.9182640	-0.5217420
H	0.4162220	-2.0680250	1.0233740

Table 9: Vibrations of CH_3S_2 in its A^+ $^1A''$ state

Vibration	Wavenumbers	Description
ν_1	3210	Asymmetric CH_2 stretching
ν_2	3200	Asymmetric CH_3 stretching
ν_3	3080	Symmetric CH_3 stretching
ν_4	1450	Symmetric CH_3 scissoring
ν_5	1440	Asymmetric CH_3 scissoring
ν_6	1330	CH_3 umbrella
ν_7	960	CH_3 wagging
ν_8	940	CH_3 wagging
ν_9	670	S-S stretching
ν_{10}	590	S-C stretching
ν_{11}	210	S-S-C bending
ν_{12}	70	CH_3 rotation

HS_2: CCSD(T)/cc-pVTZ and ωB97x-D3/cc-pVTZ for the excited state

Table 10: Cartesian Coordinates in Å of HS_2 in its X $^2A''$ state

Atom	X	Y	Z
S	-1.6204750	0.1664060	-0.0030270
S	0.3608730	-0.0437240	0.0043110
H	0.7565250	1.2476990	-0.0407860

Table 11: Vibrations of HS_2 in its X $^2A''$ state

Vibration	Wavenumbers	Description
ν_1	2580	S-H stretching
ν_2	900	S-S-C bending
ν_3	590	S-S stretching

Table 12: Cartesian Coordinates in Å of HS_2 in its X^+ $^1A'$ state

Atom	X	Y	Z
S	-1.5770390	0.1668720	-0.0030430
S	0.3186390	-0.0456680	0.0043790
H	0.7553230	1.2491750	-0.0408380

Table 13: Vibrations of HS_2 in its X^+ $^1A'$ state

Vibration	Wavenumbers	Description
ν_1	2520	S-H stretching
ν_2	940	S-S-C bending
ν_3	680	S-S stretching

Table 14: Cartesian Coordinates in Å of HS_2 in its $a^+\ ^3A''$ state

Atom	X	Y	Z
S	-1.5772880	0.2083990	-0.0044930
S	0.3877440	-0.0826400	0.0056700
H	0.6864660	1.2446210	-0.0406790

Table 15: Vibrations of HS_2 in its $a^+\ ^3A''$ state

Vibration	Wavenumbers	Description
ν_1	2570	S-H stretching
ν_2	760	S-S-C bending
ν_3	600	S-S stretching

Table 16: Cartesian Coordinates in Å of HS_2 in its $a^+\ ^3A''$ state

Atom	X	Y	Z
S	-1.5614070	0.2042800	-0.0043490
S	0.3595040	-0.0780490	0.0055100
H	0.6988250	1.2441490	-0.0406630

Table 17: Vibrations of HS_2 in its $a^+\ ^3A''$ state

Vibration	Wavenumbers	Description
ν_1	2550	S-H stretching
ν_2	800	S-S-C bending
ν_3	660	S-S stretching

<u>CH_4S</u>:

Table 18: Cartesian Coordinates in Å of CH_4S in its X $^1A'$ state

Atom	X	Y	Z
S	-2.584560	0.636421	0.000824
H	-2.833893	1.952225	0.001295
C	-0.775553	0.743816	0.000178
H	-0.408946	-0.280115	-0.000419
H	-0.407936	1.244273	-0.891748
H	-0.407243	1.243477	0.892264

Table 19: Vibrations of CH_4S in its X $^1A'$ state

Vibration	Wavenumbers	Description
ν_1	3170	Asymmetric CH_3 stretching
ν_2	3170	Asymmetric CH_2 stretching
ν_3	3080	Symmetric CH_3 stretching
ν_4	2750	S-H stretching
ν_5	1490	Asymmetric CH_3 scissoring
ν_6	1480	Asymmetric CH_3 scissoring
ν_7	1370	CH_3 umbrella
ν_8	1100	H-S-C bending + CH_3 wagging

ν_9	980	CH_3 wagging
ν_{10}	810	H-S-C bending
ν_{11}	740	S-C stretching
ν_{12}	230	H-S-C-H dihedral

Table 20: Cartesian Coordinates in Å of CH_4S in its $X^+ {}^2A''$ state

Atom	X	Y	Z
S	-2.54409	0.63636	0.00116
H	-2.8058	1.96536	0.00086
C	-0.77489	0.71303	0.00022
H	-0.39463	-0.30440	-0.00061
H	-0.44987	1.26542	-0.88753
H	-0.44886	1.26434	0.88829

Table 21: Vibrations of CH_4S in its $X^+ {}^2A''$ state

Vibration	Wavenumbers	Description
ν_1	3200	Asymmetric CH_3 stretching
ν_2	3100	Asymmetric CH_2 stretching
ν_3	3030	Symmetric CH_3 stretching
ν_4	2660	S-H stretching
ν_5	1440	Asymmetric CH_3 scissoring
ν_6	1420	Asymmetric CH_3 scissoring
ν_7	1330	CH_3 umbrella
ν_8	1110	H-S-C bending + CH_3 wagging
ν_9	840	CH_3 wagging
ν_{10}	810	H-S-C bending
ν_{11}	720	S-C stretching
ν_{12}	250	H-S-C-H dihedral

<u>CH_3S</u>:

Table 22: Cartesian Coordinates in Å of CH_3S in its $X {}^2A'$ state

Atom	X	Y	Z
S	-2.38120	0.80604	1.47306
C	-2.92689	-0.04700	-0.00082
H	-2.60388	-1.08583	-0.00891
H	-2.60384	0.46735	-0.90354
H	-4.02025	-0.03315	0.01992

Table 23: Vibrations of CH_3S in its $X^+ {}^2A'$ state

Vibration	Wavenumbers	Description
ν_1	3150	Asymmetric CH_2 stretching
ν_2	3130	Asymmetric CH_3 stretching
ν_3	3050	Symmetric CH_3 stretching
ν_4	1480	Symmetric CH_3 scissoring
ν_5	1380	Aymmetric CH_3 scissoring
ν_6	1350	CH_3 umbrella

ν_7	880	CH_3 wagging
ν_8	750	S-C stretching
ν_9	440	CH_3 wagging

Table 24: Cartesian Coordinates in Å of CH_3S in its $X^+ {}^3A_2$ state

Atom	X	Y	Z
S	-2.37421	0.77506	1.42153
C	-2.95144	-0.04083	0.00767
H	-2.58069	-1.07385	0.01659
H	-2.58065	0.48299	-0.88267
H	-4.04906	-0.03595	0.0166

Table 25: Vibrations of CH_3S in its $X^+ {}^3A_2$ state

Vibration	Wavenumbers	Description
ν_1	3080	Asymmetric CH_2 stretching
ν_2	3080	Asymmetric CH_3 stretching
ν_3	2980	Symmetric CH_3 stretching
ν_4	1360	Asymmetric CH_3 scissoring
ν_5	1350	Symmetric CH_3 scissoring
ν_6	1320	CH_3 umbrella
ν_7	830	CH_3 wagging
ν_8	820	CH_3 wagging
ν_9	780	S-C stretching

Table 26: Cartesian Coordinates in Å of CH_3S in its $b^+ {}^1A_1$ state.

Atom	X	Y	Z
S	0.77331	0.01549	-0.00037
C	2.48722	0.03294	0.00004
H	2.84044	-1.01556	-0.00157
H	2.86290	0.54186	-0.89882
H	2.86250	0.53890	0.90073

Table 27: Vibrations of CH_3S in its $b^+ {}^1A_1$ state.

Vibration	Wavenumbers	Description
ν_1	3110	Asymmetric CH_2 stretching
ν_2	3050	Asymmetric CH_3 stretching
ν_3	2950	Symmetric CH_3 stretching
ν_4	1370	Asymmetric CH_3 scissoring
ν_5	1330	Symmetric CH_3 scissoring
ν_6	1330	CH_3 umbrella
ν_7	890	CH_3 wagging
ν_8	890	CH_3 wagging
ν_9	810	S-C stretching

<u>SCH_2</u>:

Table 28: Cartesian Coordinates in Å of CH_2S in its X $^1A_1$ state

Atom	X	Y	Z
S	-1.59438	1.51332	-0.00005
C	-3.1946	1.51578	0.00003
H	-3.7726	0.59521	-0.03211
H	-3.76982	2.43809	0.03224

Table 29: Vibrations of CH_2S in its X $^1A_1$ state

Vibration	Wavenumbers	Description
ν_1	3190	Asymmetric CH_2 stretching
ν_2	3100	Symmetric CH_2 stretching
ν_3	1510	Symmetric H-C-H bending
ν_4	1130	S-C stretching
ν_5	1060	CH_2 out-of-plane bending
ν_6	1010	Asymmetric S-C-H bending

Table 30: Cartesian Coordinates in Å of CH_2S in its X^+ $^2B_2$ state

Atom	X	Y	Z
S	-1.61405	1.51346	-0.00005
C	-3.19833	1.51569	0.00002
H	-3.76106	0.57883	-0.03268
H	-3.75796	2.45443	0.03282

Table 31: Vibrations of CH_2S in its X^+ $^2B_2$ state

Vibration	Wavenumbers	Description
ν_1	3160	Asymmetric CH_2 stretching
ν_2	3060	Symmetric CH_2 stretching
ν_3	1390	Symmetric H-C-H bending
ν_4	1100	S-C stretching
ν_5	1020	CH_2 out-of-plane bending
ν_6	770	Asymmetric S-C-H bending

Notes and references

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