Supporting Information: A Computational Journey in the CH_2O_2S Land: An Accurate Rotational and Ro-vibrational Analysis of the Sulfene molecule and the S,O- and O,O-Monothiocarbonic Acids

S. Alessandrini[a,b], V. Dell'Isola[b], L. Spada[a,b], V. Barone[a] and C. Puzzarini[b]

[a]Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy; [b]Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via F. Selmi 2, I-40126 Bologna, Italy.

ARTICLE HISTORY
Compiled May 5, 2020

1. Isomer of the CH_2O_2S family considered in the present study.

Figure S1. All isomers of the CH_2SO_2 family: relative energies (in kJ mol^{-1} at the B2-D3+harmonic-ZPE level. The structures of all isomers can be found in Figure S2

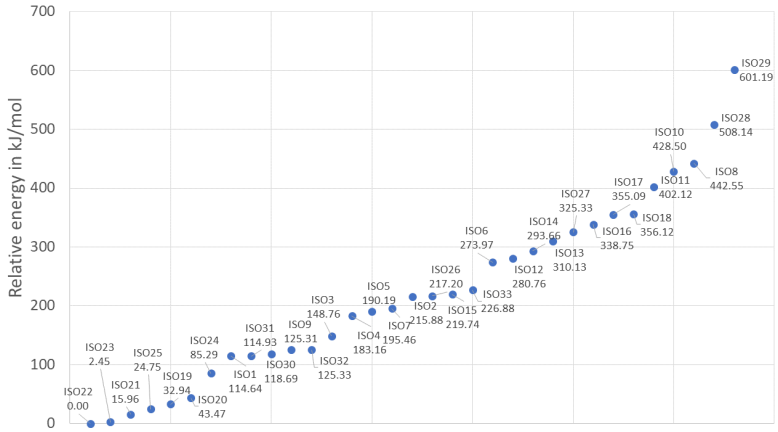
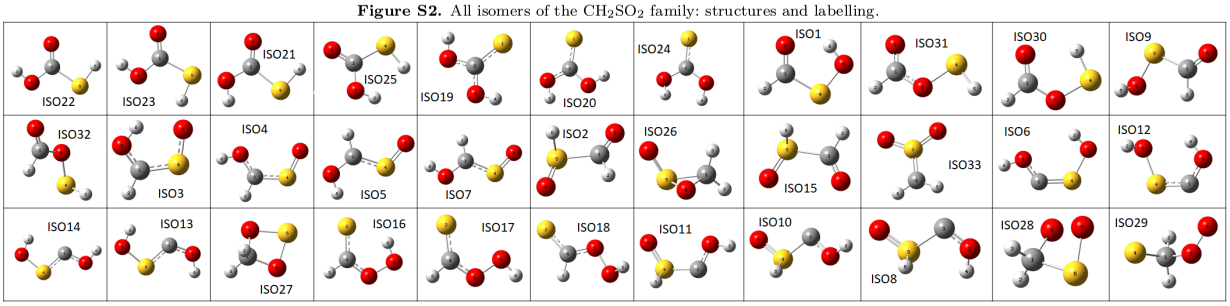


Figure S2. All isomers of the CH_2SO_2 family: structures and labelling.



2. B2-D3 geometries for the most stable CH_2O_2S species and their interconnecting transition states.

Table S1. Geometry of cis,cis conformer of the carbonothionic O,S-acid.

C	-0.490680	0.104115	0.000000
O	-1.026261	-1.135292	0.000000
H	-1.988453	-1.020533	0.000000
O	-1.126366	1.123863	0.000000
S	1.277911	-0.041658	0.000000
H	1.454434	1.283796	0.000000

Table S2. Geometry of cis,trans conformer of the carbonothionic O,S-acid.

C	-0.487327	0.099916	0.000000
O	-1.053948	-1.128340	0.000000
H	-2.012752	-0.983112	0.000000
O	-1.101121	1.132853	0.000000
S	1.281222	0.032296	0.000000
H	1.372508	-1.302741	0.000000

Table S3. Geometry of trans,cis conformer of the carbonothionic O,S-acid.

C	-0.508255	0.104952	0.000000
O	-1.136351	-1.091013	0.000000
H	-0.502959	-1.819451	0.000000
O	-1.108208	1.137011	0.000000
S	1.282974	-0.045305	0.000000
H	1.476596	1.277051	0.000000

Table S4. Geometry of trans,trans conformer of the carbonothionic O,S-acid.

C	-0.504865	-0.098029	0.000000
O	-1.198229	1.061597	0.000000
H	-0.609708	1.823542	0.000000
S	1.287942	-0.012768	0.000000
H	1.439344	1.318707	0.000000
O	-1.049731	-1.160522	0.000000

Table S5. Geometry of cis,cis conformer of the carbonothionic O,O-acid.

S	-1.292832	0.000000	0.000000
C	0.349127	0.000000	0.000000
O	1.126981	1.077979	0.000000
H	0.542282	1.847688	0.000000
O	1.126981	-1.077979	0.000000
H	0.542282	-1.847688	0.000000

Table S6. Geometry of cis,trans conformer of the carbonothionic O,O-acid.

S	1.298687	-0.019976	0.000000
C	-0.330883	-0.012286	0.000000
O	-1.101368	1.091578	0.000000
H	-0.505157	1.853232	0.000000
O	-1.087202	-1.105895	0.000000
H	-2.020209	-0.846022	0.000000

Table S7. Geometry of trans,trans conformer of the carbonothionic O,O-acid.

S	-1.295272	0.000000	0.000000
C	0.323646	0.000000	0.000000
O	1.049887	1.137936	0.015485
H	1.956222	0.986348	-0.283530
O	1.049887	-1.137936	-0.015485
H	1.956222	-0.986348	0.283530

Table S8. Geometry of TS1 (see main text)

C	-0.508762	0.101171	0.001880
O	-1.058209	-1.127993	0.000213
H	-2.021108	-1.001298	0.004171
O	-1.135421	1.121836	0.001293
S	1.308105	-0.002815	-0.042373
H	1.395227	-0.016295	1.293760

Table S9. Geometry of TS2 (see main text)

C	-0.536843	-0.101403	0.001052
O	-1.121897	1.109958	0.000480
H	-0.433068	1.785980	-0.041448
O	-1.154485	-1.117691	0.003497
S	1.310079	-0.016966	-0.041796
H	1.392268	0.082349	1.291737

Table S10. Geometry of TS3 (see main text)

C	-0.495651	0.121631	0.005226
O	-1.090146	-1.118396	-0.059998
H	-1.207085	-1.479527	0.826609
O	-1.098738	1.151740	0.002867
S	1.271569	-0.055415	-0.001811
H	1.508870	1.260066	0.075306

Table S11. Geometry of TS4 (see main text)

C	-0.493233	-0.115668	0.002650
O	-1.144832	1.096007	-0.058002
H	-1.252992	1.456228	0.830207
O	-1.053231	-1.170138	0.001746
S	1.281648	-0.007088	0.004862
H	1.351898	1.322391	-0.123182

Table S12. Geometry of TS5 (see main text)

S	-1.292722	-0.038531	-0.002330
C	0.336157	0.003470	-0.002348
O	1.144254	-1.077996	0.061881
H	1.398875	-1.371365	-0.820418
O	1.070858	1.121175	-0.003588
H	0.453203	1.867122	-0.002845

Table S13. Geometry of TS6 (see main text)

S	1.299181	0.016797	-0.001956
C	-0.316853	-0.013485	-0.003359
O	-1.109988	1.103687	0.057183
H	-1.504461	1.279946	-0.806489
O	-1.030897	-1.149187	-0.009223
H	-1.960417	-0.930130	0.147383

Table S14. Geometry of Sulfene (see main text)

S	0.000000	0.000000	0.012307
O	0.000000	1.257742	0.709585
O	0.000000	-1.257742	0.709585
C	0.000000	0.000000	-1.576023
H	0.000000	-0.952144	-2.074132
H	0.000000	0.952144	-2.074132

3. Rotational and vibrational parameters

Table S15. Rotational[a] and vibrational[b] spectroscopic parameters of the cis,trans-carbonothionic O,S-acid.

Parameter[c]	Theoretical value	Parameter[c]	Theoretical value	Parameter[c]	Harm. value	Anharm. value
A_e	11666.61	D_J	1.12×10^{-3}	ν_1	3743.54 (86.5)	3556.82 (72.4)
B_e	5179.34	D_{JK}	7.85×10^{-3}	ν_2	2725.16 (1.0)	2608.33 (0.7)
C_e	3586.94	D_K	2.61×10^{-3}	ν_3	1778.02 (432.3)	1739.79 (358.4)
$\Delta A_{\rm vib}$	-78.87	d_1	-4.66×10^{-4}	ν_4	1337.07 (49.9)	1303.00 (34.9)
$\Delta B_{\rm vib}$	-28.71	d_2	-1.61×10^{-4}	ν_5	1136.51 (310.2)	1101.21 (284.0)
$\Delta C_{\rm vib}$	-24.68	H_J	-2.33×10^{-10}	ν_6	908.60 (59.4)	884.60 (52.7)
A_0	11587.73	H_K	-4.60×10^{-8}	ν_7	723.90 (74.6)	709.93 (44.4)
B_0	5150.63	H_{JK}	-1.24×10^{-9}	ν_8	478.28 (9.8)	471.83 (8.6)
C_0	3562.26	H_{KJ}	6.42×10^{-8}	ν_9	364.22 (1.3)	360.93 (1.3)
		h_1	1.11×10^{-10}	ν_{10}	696.06 (38.4)	682.39 (19.9)
		h_2	3.51×10^{-10}	ν_{11}	527.98 (82.8)	507.60 (86.4)
		h_3	1.68×10^{-10}	ν_{12}	324.06 (22.8)	332.06 (20.8)

[a] Rotational parameters in MHz [b] Vibrational frequencies in cm^{-1}, intensities in $km{\cdot}mol^{-1}$. [c] Equilibrium rotational constants at the CBS+CV level. Anharmonic corrections, quartic and sextic centrifugal distortion constants as well as vibrational frequencies and intensities at the B2-D3 level.

Table S16. Rotational[a] and vibrational[b] spectroscopic parameters of the trans,cis-carbonothionic O,S-acid.

Parameter[c]	Theoretical value	Parameter[c]	Theoretical value	Parameter[c]	Harm. value	Anharm. value
A_e	11340.80	D_J	1.24×10^{-3}	ν_1	3798.12 (67.2)	3615.03 (58.0)
B_e	5194.39	D_{JK}	7.59×10^{-3}	ν_2	2736.51 (6.1)	2625.56 (4.7)
C_e	3562.62	D_K	4.60×10^{-4}	ν_3	1831.37 (358.6)	1785.71 (246.7)
$\Delta A_{\rm vib}$	-70.90	d_1	-5.16×10^{-4}	ν_4	1287.18 (391.3)	1248.23 (370.0)
$\Delta B_{\rm vib}$	-31.80	d_2	-1.70×10^{-4}	ν_5	1133.00 (160.5)	1098.30 (162.3)
$\Delta C_{\rm vib}$	-24.15	H_J	-3.66×10^{-10}	ν_6	902.87 (29.8)	878.73 (17.9)
A_0	11269.90	H_K	-4.93×10^{-8}	ν_7	732.68 (51.4)	717.31 (33.2)
B_0	5162.58	H_{JK}	-1.67×10^{-9}	ν_8	470.66 (0.7)	465.16 (0.1)
C_0	3538.46	H_{KJ}	6.30×10^{-8}	ν_9	365.73 (13.9)	361.36 (12.3)
		h_1	6.46×10^{-11}	ν_{10}	666.93 (1.0)	655.55 (1.7)
		h_2	3.58×10^{-10}	ν_{11}	447.07 (55.2)	432.87 (50.0)
		h_3	1.76×10^{-10}	ν_{12}	228.65 (70.9)	283.35 (65.2)

[a] Rotational parameters in MHz [b] Vibrational frequencies in cm^{-1}, intensities in $km{\cdot}mol^{-1}$. [c] Equilibrium rotational constants at the CBS+CV level. Anharmonic corrections, quartic and sextic centrifugal distortion constants as well as vibrational frequencies and intensities at the B2-D3 level. The intensities are reported in parentheses after the corresponding vibrational frequencies.

Table S17. Rotational[a] and vibrational[b] spectroscopic parameters of the trans,trans-carbonothionic O,S-acid.

Parameter[c]	Theoretical value	Parameter[c]	Theretical value	Parameter[c]	Harm. value	Anharm. value
A_e	11371.03	D_J	1.24×10^{-3}	ν_1	3836.37 (54.9)	3638.60 (46.5)
B_e	5157.32	D_{JK}	7.40×10^{-3}	ν_2	2699.57 (3.9)	2585.63 (3.0)
C_e	3548.09	D_K	6.71×10^{-4}	ν_3	1821.91 (372.5)	1775.02 (260.9)
$\Delta A_{\rm vib}$	-76.74	d_1	-5.05×10^{-4}	ν_4	1269.95 (412.0)	1229.32 (376.0)
$\Delta B_{\rm vib}$	-34.31	d_2	-1.63×10^{-4}	ν_5	1147.66 (110.9)	1110.09 (106.4)
$\Delta C_{\rm vib}$	-23.63	H_J	-3.28×10^{-10}	ν_6	913.03 (35.7)	904.44 (39.4)
A_0	11294.29	H_K	-4.69×10^{-9}	ν_7	726.69 (50.4)	712.44 (44.7)
B_0	5123.01	H_{JK}	-1.67×10^{-9}	ν_8	464.82 (1.0)	455.63 (1.0)
C_0	3524.46	H_{KJ}	6.16×10^{-8}	ν_9	378.52 (5.7)	363.54 (7.7)
		h_1	7.39×10^{-11}	ν_{10}	669.47 (0.3)	656.83 (0.6)
		h_2	3.38×10^{-10}	ν_{11}	402.68 (113.3)	390.69 (106.0)
		h_3	1.64×10^{-10}	ν_{12}	142.11 (0.2)	288.07 (0.1)

[a] Rotational parameters in MHz [b] Vibrational frequencies in cm^{-1}, intensities in $km\cdot mol^{-1}$. [c] Equilibrium rotational constants at the CBS+CV level. Anharmonic corrections, quartic and sextic centrifugal distortion constants as well as vibrational frequencies and intensities at the B2-D3 level. The intensities are reported in parentheses after the corresponding vibrational frequencies.

Table S18. Rotational[a] and vibrational[b] spectroscopic parameters of the cis,trans-carbonothionic O,O-acid.

Parameter[c]	Theoretical value	Parameter[c]	Theoretical value	Parameter[c]	Harm. value	Anharm. value
A_e	11912.17	D_J	7.73×10^{-4}	ν_1	3773.20 (87.8)	3578.11 (74.5)
B_e	5203.82	D_{JK}	7.40×10^{-3}	ν_2	3754.65 (113.9)	3570.15 (93.8)
C_e	3621.69	D_K	5.79×10^{-3}	ν_3	1493.26 (453.6)	1454.29 (422.4)
$\Delta A_{\rm vib}$	-106.15	d_1	-3.35×10^{-4}	ν_4	1377.05 (188.3)	1335.85 (170.5)
$\Delta B_{\rm vib}$	-19.16	d_2	-1.34×10^{-4}	ν_5	1183.04 (227.8)	1163.45 (178.4)
$\Delta C_{\rm vib}$	-22.88	H_J	5.86×10^{-11}	ν_6	1127.55 (295.1)	1129.06 (147.9)
A_0	11806.02	H_K	-3.10×10^{-8}	ν_7	802.75 (11.0)	790.19 (10.8)
B_0	5184.66	H_{JK}	-2.16×10^{-9}	ν_8	507.40 (20.1)	500.85 (19.0)
C_0	3598.81	H_{KJ}	5.31×10^{-8}	ν_9	417.76 (3.0)	413.66 (2.8)
		h_1	1.47×10^{-10}	ν_{10}	661.19 (4.2)	651.60 (4.5)
		h_2	2.39×10^{-10}	ν_{11}	588.15 (29.8)	558.09 (30.4)
		h_3	1.23×10^{-10}	ν_{12}	484.65 (187.9)	476.56 (179.3)

[a] Rotational parameters in MHz [b] Vibrational frequencies in cm^{-1}, intensities in $km\cdot mol^{-1}$. [c] Equilibrium rotational constants at the CBS+CV level. Anharmonic corrections, quartic and sextic centrifugal distortion constants as well as vibrational frequencies and intensities at the B2-D3 level. The intensities are reported in parentheses after the corresponding vibrational frequencies.

Table S19. Rotational[a] and vibrational[b] spectroscopic parameters of the trans,trans-carbonothionic O,O-acid.

Parameter[c]	Theoretical value	Parameter[c]	Theoretical value	Parameter[c]	Harm. value	Anharm. value
A_e	11711.47	D_J	7.53×10^{-4}	ν_1	3775.99 (103.0)	3593.14 (76.1)
B_e	5192.64	D_{JK}	6.78×10^{-3}	ν_2	1485.63 (214.2)	1446.43 (177.8)
C_e	3607.02	D_K	9.15×10^{-3}	ν_3	1136.05 (435.8)	1110.84 (420.5)
$\Delta A_{\rm vib}$	-60.50	d_1	-3.22×10^{-4}	ν_4	799.35 (0.2)	788.36 (0.1)
$\Delta B_{\rm vib}$	-26.75	d_2	-1.25×10^{-4}	ν_5	531.82 (1.8)	499.36 (65.2)
$\Delta C_{\rm vib}$	-22.85	H_J	4.85×10^{-11}	ν_6	285.22 (70.8)	86.11 (10.6)
A_0	11650.96	H_K	-4.44×10^{-8}	ν_7	3761.22 (13.6)	3579.64 (7.5)
B_0	5165.89	H_{JK}	-1.81×10^{-9}	ν_8	1277.98 (424.2)	1235.66 (402.9)
C_0	3584.17	H_{KJ}	4.74×10^{-8}	ν_9	1149.06 (1.9)	1107.82 (2.2)
		h_1	1.36×10^{-10}	ν_{10}	632.74 (4.0)	626.03 (2.1)
		h_2	2.25×10^{-10}	ν_{11}	424.63 (5.9)	420.43 (4.9)
		h_3	1.14×10^{-10}	ν_{12}	378.34 (207.7)	356.98 (202.4)

[a] Rotational parameters in MHz [b] Vibrational frequencies in cm^{-1}, intensities in $km\cdot mol^{-1}$. [c] Equilibrium rotational constants at the CBS+CV level. Anharmonic corrections, quartic and sextic centrifugal distortion constants as well as vibrational frequencies and intensities at the B2-D3 level. The intensities are reported in parentheses after the corresponding vibrational frequencies.

4. Rotational constants for the exited vibrational modes of the cis,cis-carbonothionic S,S-acid, the cis,cis-carbonothionic O,O-acid, and the sulfene molecule.

Table S20. Rotational constants (in MHz) of the vibrational excited modes considered in the simulation of the ro-vibrational spectrum for the cis,cis-carbonothionic O,S-acid, the cis,cis-carbonothionic O,O-acid and the sulfene molecule.

cis,cis-carbonothionic S,O-acid		
Vibrational mode	Rotational constant[a]	Value
ν_{11}	A_{11}	11624.10
	B_{11}	5159.67
	C_{11}	3566.05
ν_5	A_5	11641.30
	B_5	5160.90
	C_5	3575.50
ν_3	A_3	11627.98
	B_3	5168.95
	C_3	3574.01
ν_1	A_1	11578.42
	B_1	5164.89
	C_1	3568.60
cis,cis-carbonothionic O,O-acid		
Vibrational mode	Rotational constant[a]	Value
ν_8	A_8	11507.10
	B_8	5284.08
	C_8	3614.00
ν_{11}	A_{11}	11492.37
	B_{11}	5287.15
	C_{11}	3620.83
ν_2	A_2	11494.60
	B_2	5294.81
	C_2	3598.96
ν_9	A_9	11495.03
	B_9	5281.97
	C_9	3614.87
Sulfene		
Vibrational mode	Rotational constant[a]	Value
ν_7	A_7	9784.73
	B_7	9319.11
	C_7	4759.92
ν_3	A_3	9816.50
	B_3	9308.79
	C_3	4777.76
ν_{10}	A_{10}	9816.90
	B_{10}	9321.38
	C_{10}	4770.88

[a] Obtained from the equilibrium rotational constants by adding the corresponding vibrational corrections (see main text) at the B2-D3 level.

5. Equilibrium geometrical parameter at the CBS+CV level of theory for the conformers belonging to the carbonothionic O,S- and O,O-acids

Table S21. Equilibrium structural parameters (bond lengths in Å, angles in degrees) of the four conformers belonging to the carbonothionic O,S-acid family at the CBS+CV level of theory. The labelling of the atoms is according to Figure S2.

cis,cis-carbonothionic O,S-acid		cis,trans-carbonothionic O,S-acid		trans,cis-carbonothionic O,S-acid		trans,trans-carbonothionic O,S-acid	
r_{CO_2}	1.3434	r_{CO_2}	1.3457	r_{CO_2}	1.3451	r_{CO_2}	1.3450
r_{CO_4}	1.1970	r_{CO_4}	1.1968	r_{CO_4}	1.1894	r_{CO_6}	1.1897
r_{CS}	1.7658	r_{CS}	1.7617	r_{CS}	1.7862	r_{CS}	1.7842
r_{OH_3}	0.9651	r_{OH_3}	0.9657	r_{OH_3}	0.9615	r_{OH_3}	0.9590
r_{SH_6}	1.3358	r_{SH_6}	1.3366	r_{SH_6}	1.3352	r_{SH_5}	1.3383
$\angle H_3O_2C$	106.30	$\angle H_3O_2C$	105.90	$\angle H_3O_2C$	111.00	$\angle H_3O_2C$	111.17
$\angle O_4CO_2$	124.66	$\angle O_4CO_2$	124.48	$\angle O_4CO_2$	122.19	$\angle O_6CO_2$	122.02
$\angle SCO_4$	126.43	$\angle SCO_4$	122.89	$\angle SCO_4$	124.81	$\angle SCO_2$	118.15
$\angle H_6SC$	92.58	$\angle H_6SC$	95.61	$\angle H_6SC$	93.21	$\angle H_5SC$	98.87

Table S22. Equilibrium structural parameters (bond lengths in Å, angles in degrees) for the three conformers of the carbonothionic O,O-acid family at the CBS+CV level of theory. The labelling of the atoms is according to Figure S2.

cis,cis-carbonothionic O,O-acid		cis,trans-carbonothionic O,O-acid		trans,trans-carbonothionic O,O-acid	
r_{CS}	1.6367	r_{CS}	1.6243	r_{CS}	1.6132
r_{CO}	1.3236	r_{CO_3}	1.3390	r_{CO}	1.3443
r_{OH}	0.9630	r_{CO_5}	1.3239	r_{OH}	0.9623
$\angle OCS$	125.70	$r_{O_3H_4}$	0.9635	$\angle OCS$	122.57
$\angle HOC$	106.72	$r_{O_5H_6}$	0.9644	$\angle HOC$	111.20
		$\angle O_3CS$	125.04	τ(HOCS)	-159.83
		$\angle H_4O_3C$	106.79		
		$\angle O_5CS$	124.45		
		$\angle H_6O_5C$	108.70		

6. Vibrationally averaged dipole moment for the simulation of the rotational spectrum

Table S23. Vibrationally averaged dipole moment components (in debye) obtained at the B2-D3 level for T=298 K. These values were used for the simulation of the rotational spectra for the various species considered.

	μ_a	μ_b	μ_c
Sulfene	-2.85	0.00n	0.00
cis,cis-O,S-acid	0.03	-0.59	0.00
cis,trans-O,S-acid	-0.03	2.27	0.00
trans,cis-O,S-acid	2.36	1.72	0.00
trans,trans-O,S-acid	2.10	3.33	0.00
cis,cis-O,O-acid	-0.50	0.00	0.00
cis,trans-O,O-acid	-2.67	1.48	0.00
trans,trans-O,O-acid	-4.80	0.00	0.00