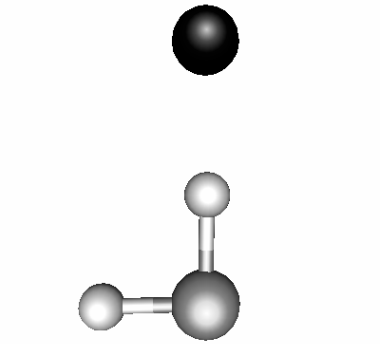
Calculated data for Br^--$(H_2S)_n$ clusters (n=1-4)

Key:

Calculations were performed at either the MP2/aug-cc-pvdz or MP2/aug-cc-pvtz levels of theory. The data are labeled pvdz or pvtz in the tables

Bond lengths are denoted *r*(A-B), and are given in Ångström (10^{-10} metre)
Angles are denoted by θ(A-B-C), and are given in degrees
Zero point energy (zpe), given in kcal/mol
E_{MP2} and $E_{e/BSSE}$ are the electronic energies (MP2, and MP2 corrected for Basis Set Superposition Error), in units of hartrees.
$\Delta E_{e/BSSE}$ is the energy separation between stationary points of the same cluster size. $\Delta E_{e/BSSE/Corr}$ is corrected for zpe differences, both are given in kcal/mol
$\Delta H_{n \rightarrow n+1}^{295K}$ is the enthalpy change for ligand association, in kcal/mol. This is also termed the ligand binding energy in the paper.
Vibrational data given in units of cm^{-1}, while the infrared intensities are in km/mol (bold text following the vibrational wavenumber)

Dimer Structures: Br^--H_2S



C_s symmetry minimum

Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 a′	2764 **3**	2779 **2**
ω_2 a′	2246 **1923**	2157 **2312**
ω_3 a′	1180 **5**	1194 **7**
ω_4 a′	277 **6**	294 **5**
ω_5 a′	119 **28**	134 **33**
ω_6 a″	528 **1**	563 <**1**

	$r(Br^-\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{0\rightarrow 1}^{295K}$
pvdz	2.288	1.392	1.349	177.4	92.4	10.2	-2971.481629	-2971.478801	0.0	0.0	-10.3
pvtz	2.207	1.388	1.336	177.6	92.2	10.2	-2971.704139	-2971.701079	0.0	0.0	-11.1

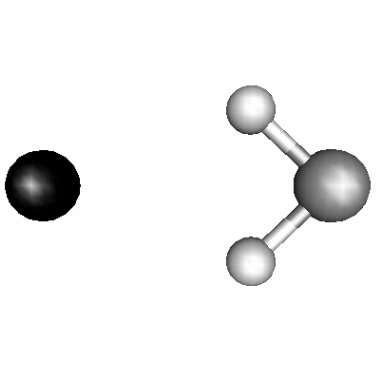
VSCF and LEVEL 7.5 data for Br^--H_2S at MP2/aug-cc-pvdz and -pvtz

	ω_1 a′	ω_2 a′	ω_3 a′	ω_4 a′	ω_5 a′	ω_6 a″	*zpe*
aug-cc-pvdz							
Harmonic	2764 **4**	2246 **1923**	1180 **5**	277 **6**	119 **28**	528 **1**	10.2
vscf	2645	1923	1154	406	119	606	9.8
cc-vscf	2651 **7**	1951 **1912**	1153 **3**	392 **8**	118 **26**	597 **4**	9.8
cc-vscf-qff	2652 **8**	1921 **1970**	1153 **3**	417 **8**	117 **26**	610 **4**	9.8
aug-cc-pvtz							
Harmonic	2779 **2**	2157 **2312**	1194 **7**	294 **5**	134 **33**	563 <**1**	10.2
Vscf	2664	1859	1164	401	128	592	
cc-vscf	2670 **6**	1893 **2073**	1163 **4**	386 **7**	127 **29**	593 **3**	
cc-vscf-qff	2672 **6**	1854 **2149**	1162 **4**	419 **7**	125 **28**	613 **3**	
Level 7.5		1847					

Data for H_2S and Br^- at MP2/aug-cc-pvdz and -pvtz

	H_2S		***Br^-***	
	aug-cc-pvdz	***aug-cc-pvtz***	***aug-cc-pvdz***	***aug-cc-pvtz***
r(S-H)[a]	1.350 (14)	1.336 (0)		
θ(H-S-H)[a]	92.5 (4)	92.2 (1)		
ω_1 (a_1)	2755 <**1**	2773 <**1**		
ω_2 (a_1)	1193 **1**	1211 **1**		
ω_3 (b_2)	2780 <**1**	2793 **1**		
zpe	9.6	9.7		
E_{MP2}	-398.853219	-398.9088179	-2572.609288	-2572.774831

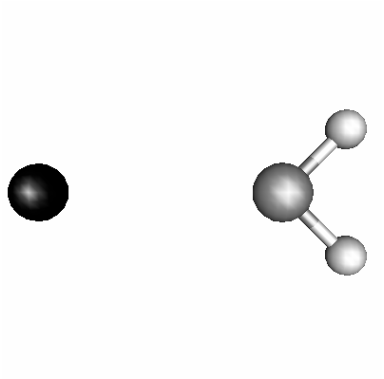
[a] Numbers in parentheses are differences between calculated and experimental values taken from; T. H. Edwards, N. K. Moncur and L. E. Snyder, *J. Chem. Phys.*, 1967, **46**, 2139



C_{2v} symmetry, 1 imaginary frequency (b_2)

	$r(Br^-\ldots H_b)$	$r(S\text{-}H_b)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.917	1.355	117.5	87.5	10.0	-2971.477268	-2971.475395	2.1	1.9
pvtz	2.829	1.343	117.5	87.0	10.1	-2971.699093	-2971.697303	2.4	2.3

Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2718 **96**	2725 **126**
$\omega_2\ a_1$	1111 **74**	1119 **78**
$\omega_3\ a_1$	99 **9**	104 **10**
$\omega_4\ b_1$	385 **8**	399 **5**
$\omega_5\ b_2$	2711 **1**	2711 **2**
$\omega_6\ b_2$	259*i* **14**	285*i* **12**

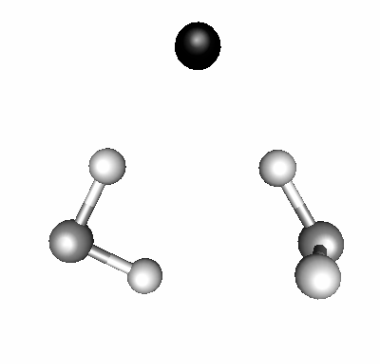


C_{2v} symmetry, 1 imaginary frequency (b_2)

	$r(Br^-\ldots S)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}S\text{-}H_t)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	3.916	1.354	134.8	90.4	9.9	-2971.461387	-2971.460710	11.3	11.0
pvtz	3.828	1.341	135.0	90.1	9.9	-2971.683319	-2971.682604	11.6	11.3

Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2717 **37**	2736 **33**
$\omega_2\ a_1$	1190 **6**	1209 **7**
$\omega_3\ a_1$	40 **6**	44 **7**
$\omega_4\ b_1$	196 **31**	200 **29**
$\omega_5\ b_2$	2744 **8**	2757 **5**
$\omega_6\ b_2$	172*i* **7**	175*i* **6**

Trimer Structures: $Br^-(H_2S)_2$



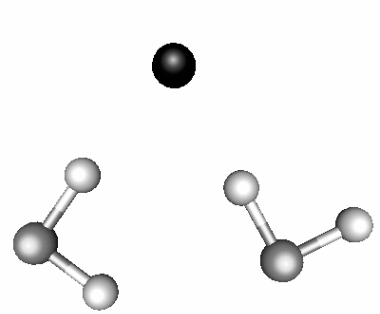
C_1 symmetry, minimum

	$r(Br^-\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_f)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	zpe	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{1\rightarrow 2}^{295K}$
pvdz	2.406 *D* 2.323 *A*	1.376 1.386	1.352 1.350	169.1 175.4	91.1 92.2	71.1	21.0	-3370.353626	-3370.347560	0.0	0.0	-8.7
pvtz	2.313 *D* 2.260 *A*	1.371 1.378	1.338 1.337	171.3 175.1	91.1 91.9	71.4	21.1	-3370.632446	-3370.626615	0.0	0.0	-9.4

D=H-bond donor, A=H-bond acceptor

HSH…SH_2 Hbond angle = 138.3° (apvdz)
132.4° (apvtz)

Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 *a*	2761 **2**	2776 **1**
ω_2 *a*	2739 **12**	2759 **8**
ω_3 *a*	2442 **1046**	2376 **1429**
ω_4 *a*	2311 **1150**	2262 **1185**
ω_5 *a*	1183 **13**	1200 **12**
ω_6 *a*	1180 **5**	1194 **6**
ω_7 *a*	520 **5**	543 **4**
ω_8 *a*	461 **2**	497 **1**
ω_9 *a*	269 **4**	286 **4**
ω_{10} *a*	257 **5**	271 **4**
ω_{11} *a*	241 **1**	234 **1**
ω_{12} *a*	125 **24**	136 **26**
ω_{13} *a*	105 **15**	114 **16**
ω_{14} *a*	61 **2**	58 **1**
ω_{15} *a*	53 **11**	36 **14**



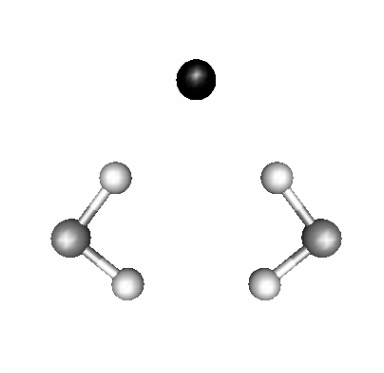
Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 a′	2766 **3**	2778 **2**
ω_2 a′	2757 <**1**	2771 <**1**
ω_3 a′	2409 **1292**	2360 **1534**
ω_4 a′	2322 **1075**	2256 **1251**
ω_5 a′	1197 **4**	1215 **5**
ω_6 a′	1181 **1**	1198 **1**
ω_7 a′	277 **11**	298 **4**
ω_8 a′	273 **7**	289 **12**
ω_9 a′	124 **23**	135 **26**
ω_{10} a′	103 **12**	112 **13**
ω_{11} a′	43 **1**	42 <**1**
ω_{12} a″	492 **1**	523 <**1**
ω_{13} a″	460 <**1**	488 <**1**
ω_{14} a″	107 <**1**	107 <**1**
ω_{15} a″	141*i* **21**	142*i* **19**

***C**s* symmetry, one imaginary frequency (*a*′)

	r(Br⁻…H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Br-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Br-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.377 *D*	1.379	1.350	174.7	92.4	68.8	20.8	-3370.352205	-3370.346267	0.8	0.6
	2.328 *A*	1.384	1.350	180.0	92.6						
pvtz	2.302 *D*	1.372	1.337	175.0	92.3	69.3	20.8	-3370.631051	-3370.625254	0.9	0.6
	2.255 *A*	1.378	1.336	179.5	92.4						

D=H-bond donor, A=H-bond acceptor

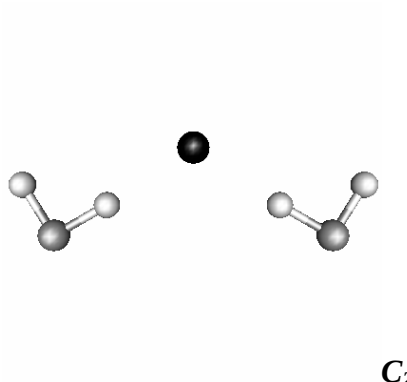
HSH…SH_2 Hbond angle = 133.3° (apvdz)



Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2765 **1**	2780 **1**
$\omega_2\ a_1$	2380 **1471**	2329 **1681**
$\omega_3\ a_1$	1192 **5**	1210 **7**
$\omega_4\ a_1$	279 **16**	298 **13**
$\omega_5\ a_1$	122 **21**	133 **23**
$\omega_6\ a_1$	36 **<1**	33 **<1**
$\omega_7\ a_2$	482 **0**	509 **0**
$\omega_8\ a_2$	154*i* **0**	149*i* **0**
$\omega_9\ b_1$	493 **2**	521 **1**
$\omega_{10}\ b_1$	61 **14**	60 **13**
$\omega_{11}\ b_2$	2762 **6**	2778 **2**
$\omega_{12}\ b_2$	2329 **1034**	2265 **1279**
$\omega_{13}\ b_2$	1180 **1**	1196 **1**
$\omega_{14}\ b_2$	251 **1**	260 **1**
$\omega_{15}\ b_2$	106 **15**	116 **17**

C_{2v} symmetry, one imaginary frequency (a_2)

	$r(Br^{-}\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.345	1.383	1.349	177.1	92.5	78.9	20.6	-3370.352044	-3370.346154	0.9	0.5
pvtz	2.272	1.376	1.336	177.2	82.3	80.3	20.7	-3370.630878	-3370.625030	1.0	0.6

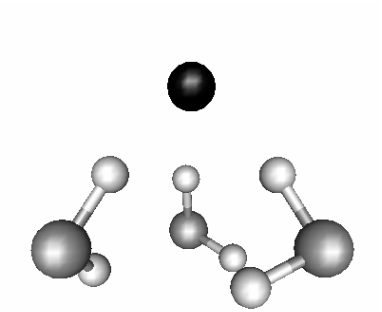


Vibrational Frequencies		
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2765 **5**	2781 **2**
$\omega_2\ a_1$	2398 **541**	2348 **520**
$\omega_3\ a_1$	1187 **5**	1204 **6**
$\omega_4\ a_1$	255 **2**	272 **3**
$\omega_5\ a_1$	107 **7**	116 **6**
$\omega_6\ a_1$	**6** <1	7 **<1**
$\omega_7\ a_2$	485 **0**	515 **0**
$\omega_8\ a_2$	36*i* **0**	32*i* **0**
$\omega_9\ b_1$	481 **3**	508 **2**
$\omega_{10}\ b_1$	19*i* **22**	16*i* **19**
$\omega_{11}\ b_2$	2765 **<1**	2781 **<1**
$\omega_{12}\ b_2$	2361 **2279**	2299 **2901**
$\omega_{13}\ b_2$	1183 **6**	1199 **9**
$\omega_{14}\ b_2$	250 **10**	263 **7**
$\omega_{15}\ b_2$	116 **34**	128 **43**

C_{2v} symmetry, two imaginary frequencies (a_1 and b_2)

	$r(Br^{-}\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.357	1.381	1.349	176.1	92.3	112.8	20.5	-3370.351325	-3370.345916	1.0	0.5
pvtz	2.282	1.374	1.336	176.3	92.1	118.6	20.6	-3370.630247	-3370.624656	1.2	0.7

Tetramer Structures: $Br^-(H_2S)_3$

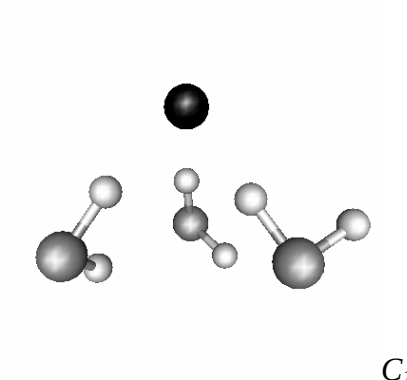


C_3 symmetry, minimum

	$r(Br\text{-}H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_f)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	zpe	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{2\rightarrow 3}^{295K}$
pvdz	2.425	1.375	1.354	167.1	90.9	71.2	32.3	-3769.226633	-3769.216586	0.0	0.0	-8.6

HSH…SH_2 Hbond angle = 142.1° (apvdz)

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 *a*	2719 **1**
ω_2 *a*	2494 **1132**
ω_3 *a*	1182 **16**
ω_4 *a*	469 **<1**
ω_5 *a*	348 **<1**
ω_6 *a*	273 **4**
ω_7 *a*	129 **18**
ω_8 *a*	73 **2**
ω_9 *e*	2725 **34 (68)**
ω_{10} *e*	2443 **392 (784)**
ω_{11} *e*	1181 **9 (18)**
ω_{12} *e*	473 **10 (20)**
ω_{13} *e*	257 **2 (4)**
ω_{14} *e*	221 **9 (18)**
ω_{15} *e*	103 **7 (14)**
ω_{16} *e*	59 **1 (2)**



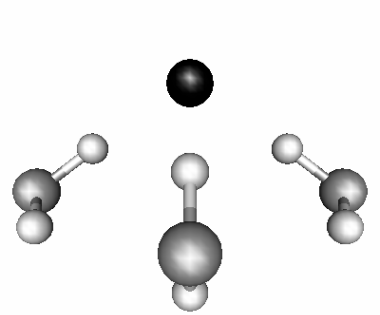
C_1 symmetry, minimum

	r(Br⁻…H$_b$)	***r(S-H$_b$)***	***r(S-H$_l$)***	***θ(Br-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Br-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.436 *l*	1.372	1.353	166.7	91.0	71.7 *l-m*	32.1	-3769.224624	-3769.215008	1.0	0.8
	2.438 *m*	1.374	1.353	166.8	90.9	70.2 *m-r*					
	2.383 *r*	1.378	1.351	173.7	92.0	66.9 *r-l*					

l=left, m=middle, r=right

HSH…SH_2 Hbond angles = 142.8° *l-m*
143.0° *m-r*

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω$_1$ a	2755 **3**
ω$_2$ a	2731 **22**
ω$_3$ a	2722 **23**
ω$_4$ a	2510 **929**
ω$_5$ a	2466 **451**
ω$_6$ a	2412 **635**
ω$_7$ a	1186 **5**
ω$_8$ a	1183 **10**
ω$_9$ a	1181 **9**
ω$_{10}$ a	490 **6**
ω$_{11}$ a	464 **7**
ω$_{12}$ a	430 **5**
ω$_{13}$ a	311 **7**
ω$_{14}$ a	267 **4**
ω$_{15}$ a	254 **5**
ω$_{16}$ a	248 **3**
ω$_{17}$ a	200 **6**
ω$_{18}$ a	149 **11**
ω$_{19}$ a	128 **18**
ω$_{20}$ a	103 **6**
ω$_{21}$ a	101 **7**
ω$_{22}$ a	68 **2**
ω$_{23}$ a	57 **0**
ω$_{24}$ a	28 **0**



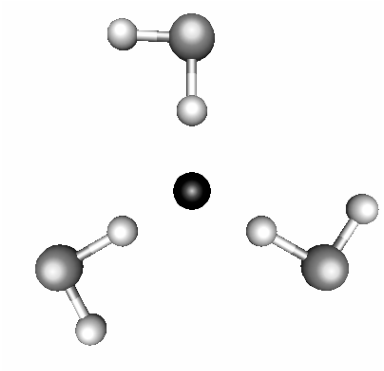
C_s symmetry, minimum

	r(Br⁻…H$_b$)	***r(S-H$_b$)***	***r(S-H$_f$)***	***θ(Br-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Br-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.438 *D* 2.353 *A*	1.372 1.382	1.352 1.351	169.0 174.0	91.3 92.0	113.5 *D-D* 70.1 *A-D*	31.8	-3769.223913	-3769.214714	1.2	0.7

D=H-bond donors, A=H-bond acceptor

HSH…SH_2 Hbond angle = 136.5°

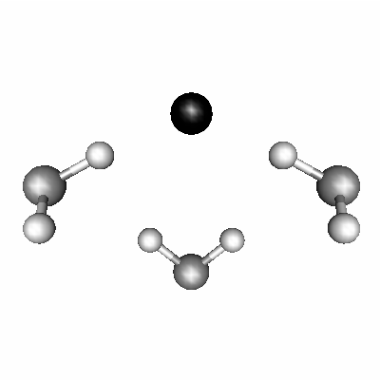
Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 ***a′***	2754 **1**
ω_2 ***a′***	2744 **6**
ω_3 ***a′***	2506 **541**
ω_4 ***a′***	2363 **740**
ω_5 ***a′***	1186 **7**
ω_6 ***a′***	1177 **2**
ω_7 ***a′***	437 **2**
ω_8 ***a′***	260 **8**
ω_9 ***a′***	238 **4**
ω_{10} ***a′***	203 **5**
ω_{11} ***a′***	123 **17**
ω_{12} ***a′***	94 **2**
ω_{13} ***a′***	53 **1**
ω_{14} ***a′***	8 <**1**
ω_{15} ***a″***	2743 **9**
ω_{16} ***a″***	2476 **1079**
ω_{17} ***a″***	1185 **16**
ω_{18} ***a″***	513 **6**
ω_{19} ***a″***	430 **2**
ω_{20} ***a″***	265 <**1**
ω_{21} ***a″***	247 <**1**
ω_{22} ***a″***	114 **26**
ω_{23} ***a″***	65 <**1**
ω_{24} ***a″***	42 **17**



C_{3h} symmetry, six imaginary frequencies ($2a''+2e'+2e''$)

	$r(Br\text{-}H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.402	1.375	1.349	176.6	92.3	120.0	30.9	-3769.219449	-3769.211571	3.2	1.8

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 a'	2766 **0**
ω_2 a'	2486 **0**
ω_3 a'	1185 **0**
ω_4 a'	231 **0**
ω_5 a'	94 **0**
ω_6 a''	438 **7**
ω_7 a''	8*i* <**1**
ω_8 a''	49*i* **31**
ω_9 e'	2766 **3**
ω_{10} e'	2443 **1655**
ω_{11} e'	1188 **8**
ω_{12} e'	231 **10**
ω_{13} e'	112 **21**
ω_{14} e'	5*i* <**1**
ω_{15} e''	448 **0**
ω_{16} e''	25*i* **0**



C_s symmetry, one imaginary frequency (a'')

H_2Ss bound to anion

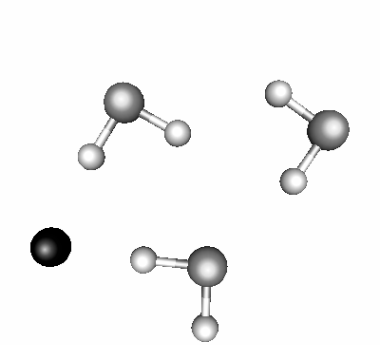
	r(Br⁻…H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Br-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Br-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.319	1.383	1.350	174.6	92.3	128.3	31.3	-3769.220052	-3769.211406	3.3	2.3

Satellite H_2S

	r(S…H$_b$)	***r(S-H$_b$)***	***θ(S-H$_b$-S)***	***θ(H-S-H)***
pvdz	2.809	1.353	164.7	92.1

HSH…SH_2 Hbond angles = 164.7°

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω$_1$ a′	2760 **1**
ω$_2$ a′	2716 **60**
ω$_3$ a′	2380 **478**
ω$_4$ a′	1181 **9**
ω$_5$ a′	1158 **1**
ω$_6$ a′	501 **3**
ω$_7$ a′	328 **4**
ω$_8$ a′	249 **12**
ω$_9$ a′	114 **4**
ω$_{10}$ a′	110 **29**
ω$_{11}$ a′	72 **1**
ω$_{12}$ a′	28 **<1**
ω$_{13}$ a′	8 **<1**
ω$_{14}$ a″	2760 **1**
ω$_{15}$ a″	2732 **95**
ω$_{16}$ a″	2329 **2172**
ω$_{17}$ a″	1183 **<1**
ω$_{18}$ a″	499 **19**
ω$_{19}$ a″	293 **<1**
ω$_{20}$ a″	251 **2**
ω$_{21}$ a″	125 **37**
ω$_{22}$ a″	83 **<1**
ω$_{23}$ a″	59 **<1**
ω$_{24}$ a″	154*i* **22**



C_s symmetry, two imaginary frequencies (2a'')

	$r(Br^-\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.362 *l* 2.270 *b*	1.380 1.391	1.350 1.348	172.2 178.8	91.7 93.6	69.5	30.9	-3769.213204	-3769.205165	7.2	5.8

Satellite H_2S

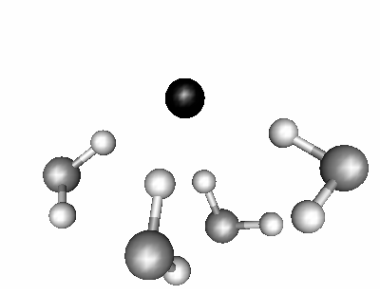
	$r(S\ldots H_b)$	$r(S\text{-}H_b)$	$\theta(H\text{-}S\text{-}H)$
pvdz	3.342 *l* 2.692 *b*	1.350 1.354	92.3

l=left, b=bottom

HSH…SH_2 Hbond angles = 135.8° *l-b*
168.4° *sat-b*
76.4° *sat-l*

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 a'	2769 **3**
ω_2 a'	2763 **4**
ω_3 a'	2762 **1**
ω_4 a'	2718 **80**
ω_5 a'	2390 **1332**
ω_6 a'	2234 **1449**
ω_7 a'	1203 **7**
ω_8 a'	1189 **12**
ω_9 a'	1174 **2**
ω_{10} a'	291 **12**
ω_{11} a'	288 **7**
ω_{12} a'	167 **6**
ω_{13} a'	136 **23**
ω_{14} a'	110 **16**
ω_{15} a'	75 **5**
ω_{16} a'	46 **2**
ω_{17} a'	35 <**1**
ω_{18} a''	498 **1**
ω_{19} a''	454 **1**
ω_{20} a''	220 **2**
ω_{21} a''	89 **3**
ω_{22} a''	15 **1**
ω_{23} a''	165*i* **19**
ω_{24} a''	202*i* **10**

Pentamer Structures: $Br^-(H_2S)_4$



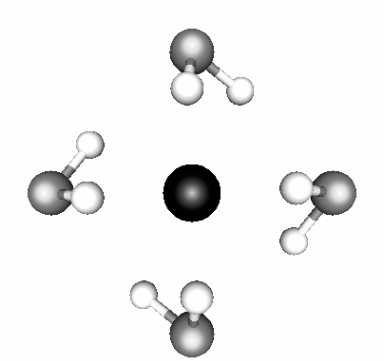
C_1 symmetry, minimum

	$r(Br\text{-}H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_f)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	zpe	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{3\rightarrow 4}^{295K}$
pvdz	2.465 *l* 2.453 *f* 2.483 *b* 2.451 *r*	1.368 1.373 1.369 1.371	1.352 1.356 1.354 1.353	167.6 165.3 164.9 167.5	91.2 90.8 90.9 91.0	70.4 *l-f* 70.5 *f-b* 71.2 *b-r* 129.1 *r-l*	43.2	-4168.096178	-4168.082711	0.0	0.0	-6.8 Checked

l=left, f=front, b=back, r=right

HSH…SH2 Hbond angles = 142.1° *l-f*
146.6° *f-b*
141.9° *b-r*
141.7° *r-f*

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 ***a***	2736 **14**
ω_2 ***a***	2728 **23**
ω_3 ***a***	2721 **19**
ω_4 ***a***	2700 **39**
ω_5 ***a***	2556 **605**
ω_6 ***a***	2520 **475**
ω_7 ***a***	2498 **573**
ω_8 ***a***	2477 **270**
ω_9 ***a***	1186 **13**
ω_{10} ***a***	1184 **6**
ω_{11} ***a***	1184 **13**
ω_{12} ***a***	1180 **3**
ω_{13} ***a***	481 **10**
ω_{14} ***a***	452 **3**
ω_{15} ***a***	448 **8**
ω_{16} ***a***	408 **6**
ω_{17} ***a***	374 **3**
ω_{18} ***a***	270 **5**
ω_{19} ***a***	267 **2**
ω_{20} ***a***	250 **5**
ω_{21} ***a***	244 **5**
ω_{22} ***a***	233 **3**
ω_{23} ***a***	226 **12**
ω_{24} ***a***	189 **7**
ω_{25} ***a***	127 **13**
ω_{26} ***a***	114 **15**
ω_{27} ***a***	99 **5**
ω_{28} ***a***	92 **<1**
ω_{29} ***a***	74 **2**
ω_{30} ***a***	68 **<1**
ω_{31} ***a***	61 **<1**
ω_{32} ***a***	48 **<1**
ω_{33} ***a***	22 **<1**

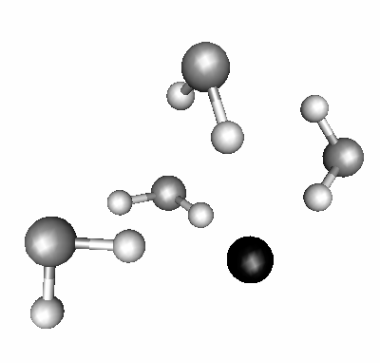


***C*$_4$** symmetry, minimum

	***r*(Br-H$_b$)**	***r*(S-H$_b$)**	***r*(S-H$_t$)**	***θ*(Br-H$_b$-S)**	***θ*(H-S-H)**	***θ*(H$_b$-Br-H$_b$)**	***zpe***	***E*$_{MP2}$**	***E*$_{e/BSSE}$**	**$\Delta E_{e/BSSE}$**	**$\Delta E_{e/BSSE/Corr}$**
pvdz	2.467	1.371	1.353	167.0	91.0	67.7	43.3	-4168.096027	-4168.082724	<0.1	0.1

HSH…SH2 Hbond angles = 142.7°

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 *a*	2720 **2**
ω_2 *a*	2549 **704**
ω_3 *a*	1178 **15**
ω_4 *a*	451 **<1**
ω_5 *a*	358 **4**
ω_6 *a*	258 **8**
ω_7 *a*	124 **12**
ω_8 *a*	58 **1**
ω_9 *b*	2727 **0**
ω_{10} *b*	2497 **0**
ω_{11} *b*	1192 **0**
ω_{12} *b*	463 **0**
ω_{13} *b*	251 **0**
ω_{14} *b*	173 **0**
ω_{15} *b*	90 **0**
ω_{16} *b*	74 **0**
ω_{17} *b*	17 **0**
ω_{18} *e*	2724 **61 (132)**
ω_{19} *e*	2502 **603 (1206)**
ω_{20} *e*	1184 **11 (22)**
ω_{21} *e*	457 **16 (32)**
ω_{22} *e*	268 **7 (14)**
ω_{23} *e*	253 **<1 (1)**
ω_{24} *e*	110 **11 (22)**
ω_{25} *e*	65 **2 (4)**

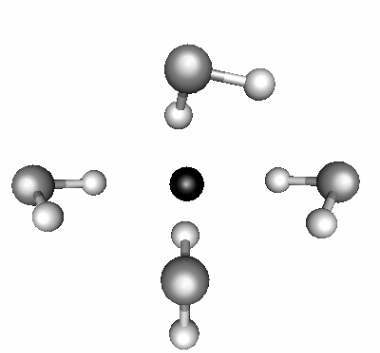


C_1 symmetry, minimum

	r(Br-H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Br-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Br-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.409 *l*	1.374	1.351	173.4	92.0	70.2 *l-b*	43.0	-4168.094283	-4168.081239	0.9	0.7
	2.497 *b*	1.369	1.354	164.5	91.0	70.8 *b-t*					
	2.461 *t*	1.370	1.355	165.2	91.0	70.4 *t-r*					
	2.475 *r*	1.368	1.353	166.9	91.1	126.3 *r-l*					

HSH…SH2 Hbond angles = 143.5° *b-l*
146.8° *t-b*
143.1° *r-t*

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω$_1$ *a*	2757 **2**
ω$_2$ *a*	2732 **20**
ω$_3$ *a*	2722 **26**
ω$_4$ *a*	2710 **33**
ω$_5$ *a*	2564 **622**
ω$_6$ *a*	2530 **397**
ω$_7$ *a*	2510 **308**
ω$_8$ *a*	2461 **697**
ω$_9$ *a*	1188 **9**
ω$_{10}$ *a*	1186 **7**
ω$_{11}$ *a*	1184 **7**
ω$_{12}$ *a*	1182 **5**
ω$_{13}$ *a*	470 **6**
ω$_{14}$ *a*	447 **8**
ω$_{15}$ *a*	442 **6**
ω$_{16}$ *a*	402 **7**
ω$_{17}$ *a*	342 **9**
ω$_{18}$ *a*	261 **5**
ω$_{19}$ *a*	258 <**1**
ω$_{20}$ *a*	249 **5**
ω$_{21}$ *a*	235 <**1**
ω$_{22}$ *a*	230 **7**
ω$_{23}$ *a*	194 **8**
ω$_{24}$ *a*	141 **9**
ω$_{25}$ *a*	125 **13**
ω$_{26}$ *a*	113 **17**
ω$_{27}$ *a*	99 **4**
ω$_{28}$ *a*	92 <**1**
ω$_{29}$ *a*	71 **2**
ω$_{30}$ *a*	63 **1**
ω$_{31}$ *a*	58 <**1**
ω$_{32}$ *a*	26 <**1**
ω$_{33}$ *a*	18 <**1**

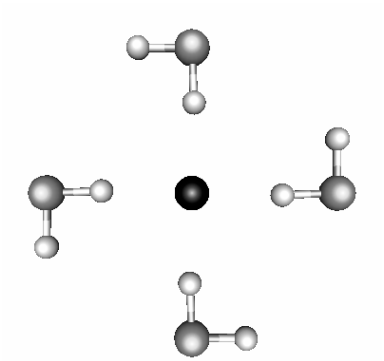


C_1 symmetry, minimum

	$r(Br\text{-}H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Br\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Br\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.478 *l*	1.368	1.352	167.2	91.3	69.0 *l-f*	43.0	-4168.094026	-4168.081028	1.1	0.9
	2.396 *f*	1.375	1.351	177.5	92.0	68.6 *f-r*					
	2.466 *r*	1.370	1.353	167.2	91.1	72.1 *r-t*					
	2.494 *t*	1.367	1.353	163.5	91.0	58.1 *t-l*					

HSH…SH_2 Hbond angles = 141.5° *l-f*
141.7° *r-f*
143.5° *t-r*

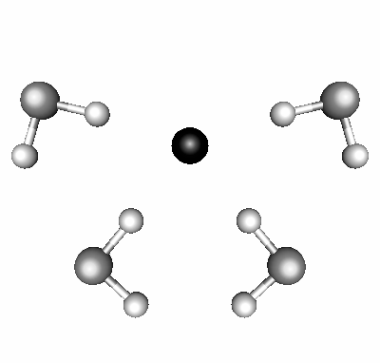
Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 ***a***	2751 **4**
ω_2 ***a***	2738 **12**
ω_3 ***a***	2729 **26**
ω_4 ***a***	2726 **9**
ω_5 ***a***	2573 **555**
ω_6 ***a***	2541 **280**
ω_7 ***a***	2511 **675**
ω_8 ***a***	2437 **482**
ω_9 ***a***	1190 **3**
ω_{10} ***a***	1187 **11**
ω_{11} ***a***	1185 **7**
ω_{12} ***a***	1180 **3**
ω_{13} ***a***	505 **7**
ω_{14} ***a***	441 **7**
ω_{15} ***a***	409 **2**
ω_{16} ***a***	394 **11**
ω_{17} ***a***	322 **7**
ω_{18} ***a***	260 **15**
ω_{19} ***a***	253 **5**
ω_{20} ***a***	249 **1**
ω_{21} ***a***	238 **1**
ω_{22} ***a***	220 **6**
ω_{23} ***a***	215 **11**
ω_{24} ***a***	147 **1**
ω_{25} ***a***	126 **15**
ω_{26} ***a***	112 **15**
ω_{27} ***a***	97 **4**
ω_{28} ***a***	89 **<1**
ω_{29} ***a***	69 **1**
ω_{30} ***a***	62 **<1**
ω_{31} ***a***	50 **1**
ω_{32} ***a***	44 **<1**
ω_{33} ***a***	20 **<1**



C_{4h} symmetry, eight imaginary frequencies ($2a_u$, b_g, b_u, $2e_g$, $2e_u$)

	r(Br-H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Br-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Br-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.432	1.370	1.350	176.2	92.3	90.0	41.2	-4168.086645	-4168.075955	4.2	2.2

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 a_g	2764 **0**
ω_2 a_g	2540 **0**
ω_3 a_g	1185 **0**
ω_4 a_g	220 **0**
ω_5 a_g	90 **0**
ω_6 a_u	405 **9**
ω_7 a_u	5*i* **<1**
ω_8 a_u	92*i* **39**
ω_9 b_g	2764 **0**
ω_{10} b_g	2498 **0**
ω_{11} b_g	1197 **0**
ω_{12} b_g	234 **0**
ω_{13} b_g	86 **0**
ω_{14} b_g	13*i* **0**
ω_{15} b_u	392 **0**
ω_{16} b_u	45 **0**
ω_{17} b_u	8*i* **0**
ω_{18} e_g	421 **0**
ω_{19} e_g	56*i* **0**
ω_{20} e_u	2764 **3 (6)**
ω_{21} e_u	2494 **1740 (3480)**
ω_{22} e_u	1187 **5 (10)**
ω_{23} e_u	218 **17 (34)**
ω_{24} e_u	117 **27 (54)**
ω_{25} e_u	11*i* **<1 (<1)**



C_{2v} symmetry, three imaginary frequencies ($2a_2 + b_1$)

	***r*(Br-H_b)**	***r*(S-H_b)**	***r*(S-H_t)**	**θ(Br-H_b-S)**	**θ(H-S-H)**	**θ(H_b-Br-H_b)**	***zpe***	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.466 *t* 2.406 *b*	1.369 1.374	1.350 1.349	173.9 179.0	92.4 92.8	150.5 *t-t* 67.7 *t-b* 74.2 *b-b*	41.7	-4168.088135	-4168.076283	4.0	2.5

t=top, b=bottom.

HSH…SH2 Hbond angles = 134.9° *t-b*

Vibrational Frequencies	
	MP2/aug-cc-pvdz
ω_1 a_1	2767 **3**
ω_2 a_1	2759 **1**
ω_3 a_1	2550 **3**
ω_4 a_1	2468 **1024**
ω_5 a_1	1204 **<1**
ω_6 a_1	1190 **1**
ω_7 a_1	267 **35**
ω_8 a_1	253 **1**
ω_9 a_1	114 **14**
ω_{10} a_1	90 **1**
ω_{11} a_1	50 **<1**
ω_{12} a_1	25 **<1**
ω_{13} a_2	422 **0**
ω_{14} a_2	380 **0**
ω_{15} a_2	64 **0**
ω_{16} a_2	27*i* **0**
ω_{17} a_2	195*i* **0**
ω_{18} b_1	430 **3**
ω_{19} b_1	389 **3**
ω_{20} b_1	108 **<1**
ω_{21} b_1	5 **<1**
ω_{22} b_1	140*i* **35**
ω_{23} b_2	2764 **5**
ω_{24} b_2	2759 **1**
ω_{25} b_2	2522 **1452**
ω_{26} b_2	2446 **608**
ω_{27} b_2	1200 **5**
ω_{28} b_2	1182 **<1**
ω_{29} b_2	249 **9**
ω_{30} b_2	242 **<1**
ω_{31} b_2	123 **38**
ω_{32} b_2	86 **<1**
ω_{33} b_2	46 **<1**

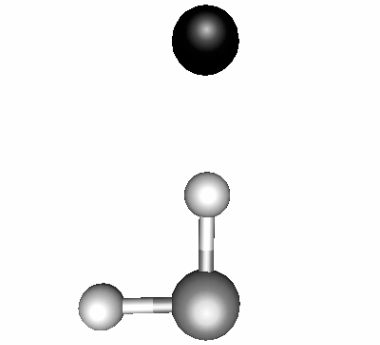
Calculated data for Cl^--$(H_2S)_n$ clusters (n=1-4)

Key:

Calculations were performed at either the MP2/aug-cc-pvdz or MP2/aug-cc-pvtz levels of theory. The data are labeled pvdz or pvtz in the tables

Bond lengths are denoted *r*(A-B), and are given in Ångström (10^{-10} metre)
Angles are denoted by θ(A-B-C), and are given in degrees
Zero point energy (zpe), given in kcal/mol
E_{MP2} and $E_{e/BSSE}$ are the electronic energies (MP2, and MP2 corrected for Basis Set Superposition Error), in units of hartrees.
$\Delta E_{e/BSSE}$ is the energy separation between stationary points of the same cluster size. $\Delta E_{e/BSSE/Corr}$ is corrected for zpe differences, both are given in kcal/mol
$\Delta H_{n \rightarrow n+1}^{295K}$ is the enthalpy change for ligand association, in kcal/mol. This is also termed the ligand binding energy in the paper.
Vibrational data given in units of cm^{-1}, while the infrared intensities are in km/mol (bold text following the vibrational wavenumber)

Dimer Structures: Cl^--H_2S



C_s symmetry minimum

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 *a′*	2760 **6**	2778 **3**
ω_2 *a′*	2004 **2683**	1941 **2938**
ω_3 *a′*	1178 **4**	1194 **6**
ω_4 *a′*	312 **7**	328 **6**
ω_5 *a′*	152 **93**	169 **100**
ω_6 *a″*	597 **2**	626 **1**

	$r(Cl^-\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{0\rightarrow 1}^{295K}$
pvdz	2.034	1.412	1.349	178.4	92.6	10.0	-858.597639	-858.595654	0.0	0.0	-12.7
pvtz	1.990	1.407	1.336	178.4	92.4	10.1	-858.712218	-858.710652	0.0	0.0	-13.6

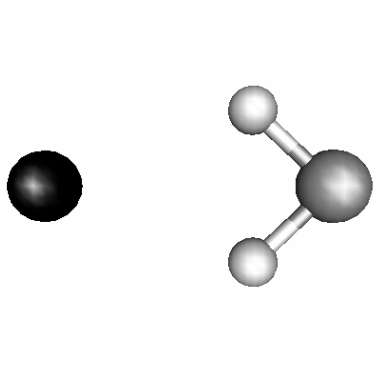
VSCF and LEVEL 7.5 for Cl^--H_2S at MP2/aug-cc-pvdz and -pvtz

	ω_1 *a′*	ω_2 *a′*	ω_3 *a′*	ω_4 *a′*	ω_5 *a′*	ω_6 *a″*	*zpe*
MP2/aug-cc-pvdz							
harmonic	2760 **6**	2004 **2683**	1178 **4**	312 **7**	152 **93**	597 **2**	10.0
vscf	2644	1520	1149	449	155	674	9.4
cc-vscf	2649 **6**	1437 **2920**	1148 **4**	440 **6**	154 **97**	670 **2**	9.3
cc-vscf-qff	2660 **6**	1500 **3019**	1140 **4**	470 **6**	147 **97**	679 **2**	
MP2/aug-cc-pvtz							
harmonic	2778 **3**	1941 **2938**	1194 **6**	328 **6**	169 **100**	626 **1**	10.1
Vscf	2662	1425	1159	438	172	676	9.3
cc-vscf	2669 **4**	1389 **3063**	1156 **6**	425 **5**	170 **105**	670 **1**	9.3
cc-vscf-qff	2675 **11**	1664 **3162**	1151 **4**	465 **8**	165 **101**	686 **5**	
LEVEL 7.5		1438					

Data for H_2S and Cl^- at MP2/aug-cc-pvdz and -pvtz

	H_2S		Cl^-	
	aug-cc-pvdz	*aug-cc-pvtz*	*aug-cc-pvdz*	*aug-cc-pvtz*
r(S-H)[a]	1.350 (14)	1.336 (0)		
θ(H-S-H)[a]	92.5 (4)	92.2 (1)		
ω_1 (a_1)	2755 <**1**	2773 <**1**		
ω_2 (a_1)	1193 **1**	1211 **1**		
ω_3 (b_2)	2780 <**1**	2793 **1**		
zpe	9.6	9.7		
E_{MP2}	-398.853219	-398.9088179	-459.722765	-459.780792

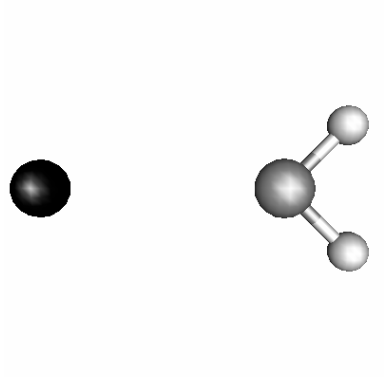
[a] Numbers in parentheses are differences between calculated and experimental values taken from; T. H. Edwards, N. K. Moncur and L. E. Snyder, *J. Chem. Phys.*, 1967, **46**, 2139



C_{2v} symmetry, 1 imaginary frequency (b_2)

	$r(Cl^-\ldots H_b)$	$r(S\text{-}H_b)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.749	1.356	116.7	86.9	10.1	-858.591679	-858.590587	3.2	3.3
pvtz	2.685	1.343	116.7	86.5	10.1	-858.705797	-858.705005	3.5	3.5

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2716 **105**	2725 **131**
$\omega_2\ a_1$	1095 **78**	1107 **80**
$\omega_3\ a_1$	122 **28**	126 **29**
$\omega_4\ b_1$	406 **9.7**	416 **7**
$\omega_5\ b_2$	2705 **2**	2707 **3**
$\omega_6\ b_2$	292*i* **14**	307*i* **12**

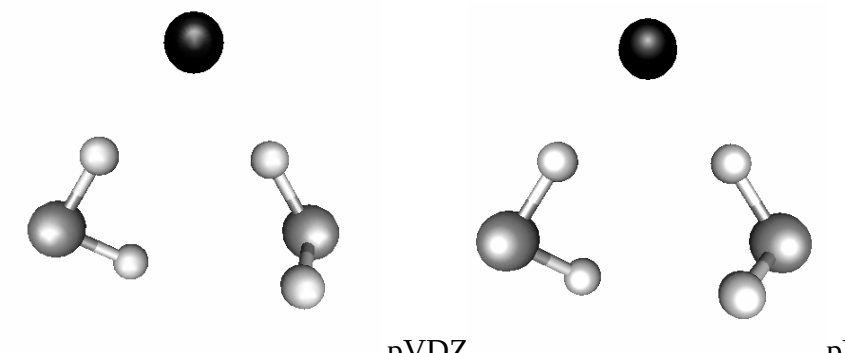


C_{2v} symmetry, 1 imaginary frequency (b_2)

	$r(Cl^-\ldots S)$	$r(S\text{-}H_t)$	$\theta(Cl\text{-}S\text{-}H_t)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	3.740	1.355	135.0	90.1	9.9	-858.574752	-858.574368	13.4	13.3
pvtz	3.662	1.341	135.1	89.8	10.0	-858.689074	-858.688756	13.7	13.6

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2713 **37**	2732 **34**
$\omega_2\ a_1$	1189 **5**	1209 **6**
$\omega_3\ a_1$	48 **21**	54 **22**
$\omega_4\ b_1$	210 **28**	212 **26**
$\omega_5\ b_2$	2740 **10**	2754 **6**
$\omega_6\ b_2$	179*i* **6**	184*i* **5**

Trimer Structures: Cl^--$(H_2S)_2$



pVDZ pVTZ both C_1 symmetry, both minima

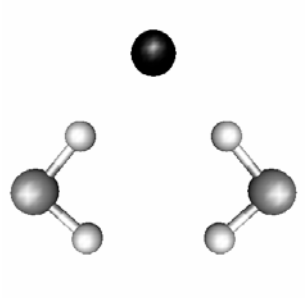
	$r(Cl^-\ldots H_b)$	$r(S\text{-}H_b)$	$R(S\text{-}H_f)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{1\rightarrow 2}^{295K}$
pvdz	2.200 *D*	1.383	1.351	170.6	91.2	21.0	-1257.470562	-1257.466224	0.0	0.0	-9.6
	2.118 *A*	1.394	1.350	175.9	92.3						
pvtz	2.126 *l*	1.379	1.338	173.3	91.5	21.1	-1257.641028	-1257.638018	0.0	0.0	-10.5
	2.097 *r*	1.383	1.337	175.2	91.9						

D=H-bond donor, A=H-bond acceptor
l=left, r=right

HSH…SH_2 Hbond angles
132.9° (apvdz)
123.2° (apvtz)

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 *a*	2759 **2**	2774 **<1**
ω_2 *a*	2744 **6**	2767 **2**
ω_3 *a*	2362 **1259**	2293 **1725**
ω_4 *a*	2196 **1359**	2182 **1181**
ω_5 *a*	1187 **12**	1206 **9**
ω_6 *a*	1181 **5**	1197 **6**
ω_7 *a*	561 **7**	570 **4**
ω_8 *a*	500 **3**	543 **3**
ω_9 *a*	290 **8**	311 **7**
ω_{10} *a*	276 **5**	291 **6**
ω_{11} *a*	227 **1**	225 **1**
ω_{12} *a*	158 **59**	171 **60**
ω_{13} *a*	120 **37**	130 **40**
ω_{14} *a*	60 **1**	59 **1**
ω_{15} *a*	44 **11**	19 **13**

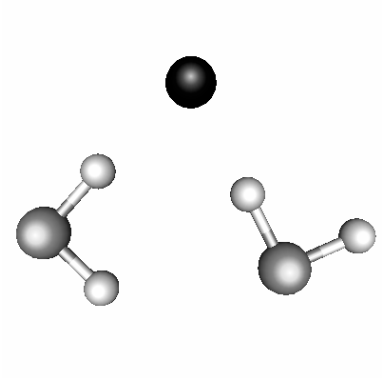
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a_1$	2763 **3**	2779 **2**
$\omega_2\ a_1$	2293 **1597**	2260 **1721**
$\omega_3\ a_1$	1197 **4**	1214 **5**
$\omega_4\ a_1$	300 **21**	319 **19**
$\omega_5\ a_1$	154 **50**	166 **51**
$\omega_6\ a_1$	39 <**1**	37 <**1**
$\omega_7\ a_2$	520 **0**	543 **0**
$\omega_8\ a_2$	153*i* **0**	155*i* **0**
$\omega_9\ b_1$	532 **4**	556 **2**
$\omega_{10}\ b_1$	63 **13**	58 **11**
$\omega_{11}\ b_2$	2760 **7**	2777 **3**
$\omega_{12}\ b_2$	2213 **1380**	2168 **1553**
$\omega_{13}\ b_2$	1182 <**1**	1199 <**1**
$\omega_{14}\ b_2$	273 **2**	283 **2**
$\omega_{15}\ b_2$	125 **44**	135 **48**



C_{2v} symmetry, one imaginary frequency (a_2)

	$r(Cl^-\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Cl\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.141	1.391	1.350	177.8	92.7	82.5	20.6	-1257.469196	-1257.465062	0.7	0.3
pvtz	2.100	1.383	1.336	177.8	92.5	83.2	20.7	-1257.639626	-1257.636697	0.8	0.4

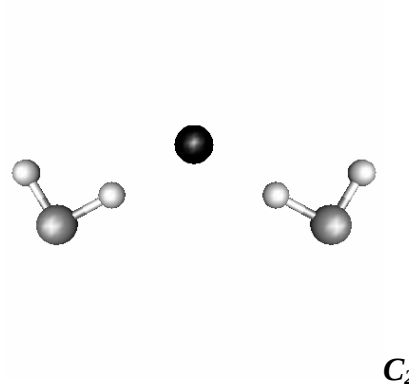
	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
$\omega_1\ a'$	2764 **5**	2778 **3**
$\omega_2\ a'$	2756 **1**	2771 <**1**
$\omega_3\ a'$	2332 **1443**	2297 **1608**
$\omega_4\ a'$	2210 **1353**	2161 **1466**
$\omega_5\ a'$	1203 **4**	1222 **5**
$\omega_6\ a'$	1183 <**1**	1201 <**1**
$\omega_7\ a'$	299 **6**	321 **5**
$\omega_8\ a'$	293 **16**	309 **16**
$\omega_9\ a'$	157 **58**	171 **61**
$\omega_{10}\ a'$	119 **34**	128 **37**
$\omega_{11}\ a'$	42 **1**	42 **1**
$\omega_{12}\ a''$	533 **2**	558 **1**
$\omega_{13}\ a''$	497 **1**	521 <**1**
$\omega_{14}\ a''$	104 <**1**	105 <**1**
$\omega_{15}\ a''$	135*i* **21**	139*i* **19**



C_s symmetry, one imaginary frequency (a')

	$r(Cl^-\ldots H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.178 *l* 2.126 *r*	1.386 1.393	1.350 1.349	175.0 179.6	92.4 92.7	20.7	-1257.469229	-1257.465010	0.8	0.5
pvtz	2.132 *l* 2.082 *r*	1.378 1.386	1.337 1.336	175.3 179.2	92.3 92.5	20.9	-1257.639696	-1257.636733	0.8	0.6

HSH…SH_2 Hbond angles
130.1° (apvdz)
29.9° (apvtz)

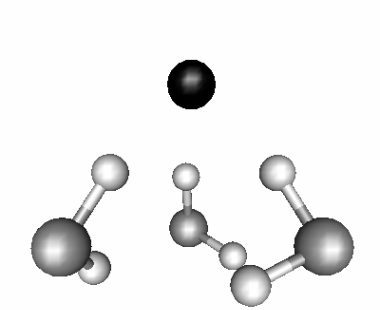


	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 a_1	2764 **7**	2781 **3**
ω_2 a_1	2311 **543**	2278 **442**
ω_3 a_1	1190 **3**	1206 **5**
ω_4 a_1	278 **4**	293 **5**
ω_5 a_1	125 **16**	131 **12**
ω_6 a_1	9 **2**	8 **2**
ω_7 a_2	520 **0**	548 **0**
ω_8 a_2	36*i* **0**	33*i* **0**
ω_9 b_1	518 **6**	541 **4**
ω_{10} b_1	15*i* **23**	18*i* **21**
ω_{11} b_2	2764 **<1**	2781 **<1**
ω_{12} b_2	2250 **2907**	2204 **3519**
ω_{13} b_2	1185 **6**	1201 **8**
ω_{14} b_2	269 **13**	283 **9**
ω_{15} b_2	145 **97**	162 **119**

C_{2v} symmetry, two imaginary frequencies (a_2 and b_1)

	r(Cl…H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Cl-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Cl-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.153	1.388	1.349	176.6	92.5	116.5	20.5	-1257.468413	-1257.464811	0.9	0.4
pvtz	2.107	1.381	1.336	176.9	92.3	124.6	20.6	-1257.638973	-1257.636283	1.1	0.6

Tetramer Structures: $Cl^-(H_2S)_3$



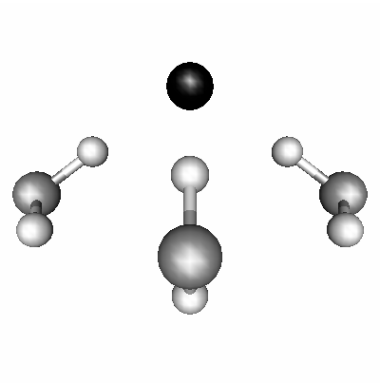
C_3 symmetry, minimum

	$r(Cl\text{-}H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_f)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Cl\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{2\rightarrow 3}^{295K}$
pvdz	2.243	1.378	1.353	168.0	90.9	74.6	32.4	-1656.343825	-1656.336280	0.0	0.0	-9.2
pvtz	2.201	1.369	1.340	169.1	90.9	74.5	32.5	-1656.569665	-1656.564937	0.0	0.0	-10.0

HSH…SH_2 Hbond angle = 138.8° (apvdz)
137.8° (apvtz)

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 *a*	2725 **1**	2741 **1**
ω_2 *a*	2460 **1128**	2443 **1243**
ω_3 *a*	1185 **14**	1200 **14**
ω_4 *a*	496 **<1**	517 **<1**
ω_5 *a*	332 **<1**	325 **<1**
ω_6 *a*	285 **7**	291 **6**
ω_7 *a*	162 **45**	171 **46**
ω_8 *a*	76 **2**	75 **1**
ω_9 *e*	2730 **25**	2745 **30 (60)**
ω_{10} *e*	2389 **494**	2360 **560 (1120)**
ω_{11} *e*	1183 **12**	1199 **11 (22)**
ω_{12} *e*	500 **13**	522 **12 (24)**
ω_{13} *e*	267 **2**	277 **2 (4)**
ω_{14} *e*	209 **9**	204 **9 (18)**
ω_{15} *e*	115 **18**	119 **19 (38)**
ω_{16} *e*	59 **1**	58 **1 (2)**

	MP2/aug-cc-pvtz	*MP2/aug-cc-pvdz*
ω_1 **a′**	2754 **1**	2772 <**1**
ω_2 **a′**	2746 **3**	2761 **6**
ω_3 **a′**	2469 **574**	2449 **658**
ω_4 **a′**	2300 **795**	2275 **818**
ω_5 **a′**	1191 **5**	1207 **6**
ω_6 **a′**	1179 **1**	1197 **2**
ω_7 **a′**	472 **3**	492 **2**
ω_8 **a′**	277 **10**	290 **8**
ω_9 **a′**	252 **7**	268 **7**
ω_{10} **a′**	194 **5**	192 **5**
ω_{11} **a′**	153 **40**	163 **39**
ω_{12} **a′**	102 **8**	106 **9**
ω_{13} **a′**	57 **1**	56 **1**
ω_{14} **a′**	11 <**1**	9 <**1**
ω_{15} **a″**	2746 **5**	2761 **8**
ω_{16} **a″**	2425 **1254**	2396 **1428**
ω_{17} **a″**	1189 **17**	1205 **16**
ω_{18} **a″**	543 **9**	569 **8**
ω_{19} **a″**	459 **3**	478 **2**
ω_{20} **a″**	268 <**1**	278 <**1**
ω_{21} **a″**	246 **1**	248 **1**
ω_{22} **a″**	136 **54**	142 **57**
ω_{23} **a″**	64 <**1**	64 <**1**
ω_{24} **a″**	31 **15**	27 **15**



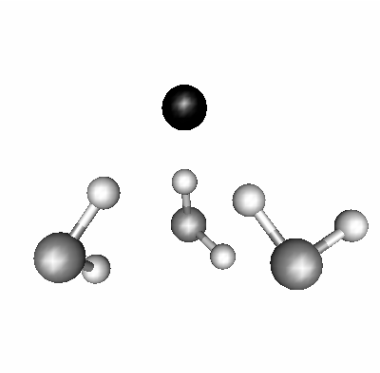
C_s symmetry, minimum

	r(Cl…H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Cl-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Cl-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.256 *D* 2.171 *A*	1.376 1.386	1.351 1.351	170.1 174.4	91.3 92.0	113.3 *D-D* 73.6 *D-A*	31.8	-1656.341390	-1656.334728	1.0	0.4
pvtz	2.216 *D* 2.137 *A*	1.366 1.377	1.338 1.337	171.1 174.2	91.3 91.8	113.4 *D-D* 73.6 *D-A*	32.0	-1656.567430	-1656.563058	1.2	0.7

D=H-bond donors, A=H-bond acceptor

HSH…SH_2 Hbond angle = 132.6° (apvdz)
131.4° (apvtz)

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvdz*
ω_1 ***a***	2756 **4**	2771 **2**
ω_2 ***a***	2736 **16**	2751 **18**
ω_3 ***a***	2727 **18**	2743 **21**
ω_4 ***a***	2477 **955**	2458 **1076**
ω_5 ***a***	2418 **529**	2390 **593**
ω_6 ***a***	2349 **764**	2319 **818**
ω_7 ***a***	1189 **5**	1206 **3**
ω_8 ***a***	1186 **10**	1202 **11**
ω_9 ***a***	1184 **11**	1200 **11**
ω_{10} ***a***	520 **9**	524 **8**
ω_{11} ***a***	491 **9**	512 **8**
ω_{12} ***a***	461 **7**	488 **6**
ω_{13} ***a***	298 **7**	294 **7**
ω_{14} ***a***	278 **5**	284 **8**
ω_{15} ***a***	266 **9**	280 **5**
ω_{16} ***a***	259 **2**	266 **1**
ω_{17} ***a***	191 **6**	183 **6**
ω_{18} ***a***	161 **45**	170 **46**
ω_{19} ***a***	137 **12**	137 **13**
ω_{20} ***a***	116 **19**	120 **20**
ω_{21} ***a***	113 **15**	117 **15**
ω_{22} ***a***	70 **2**	69 **2**
ω_{23} ***a***	58 **1**	55 **<1**
ω_{24} ***a***	25 **1**	27 **1**

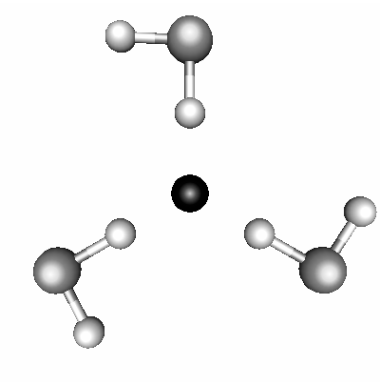


C_1 symmetry, minimum

	r(Cl…H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Cl-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Cl-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.258 *l*	1.375	1.352	167.9	91.0	74.9 *l-m*	32.1	-1656.341928	-1656.334790	0.9	0.6
	2.257 *b*	1.377	1.353	167.6	90.9	73.9 *m-r*					
	2.199 *r*	1.382	1.351	174.4	92.1	72.0 *r-l*					
pvtz	2.217 *l*	1.365	1.339	168.8	91.0	75.0 *l-m*	32.3	-1656.567840	-1656.563262	1.1	0.9
	2.212 *b*	1.368	1.340	168.6	90.8	73.8 *m-r*					
	2.161 *r*	1.373	1.337	175.5	92.0	71.7 *r-l*					

l=left, b=back, r=right

HSH…SH_2 Hbond angle = 139.3° *l-b* (apvdz)
138.1° *l-b* (apvtz)
139.5° *b-r* (apvdz)
138.6° *b-r* (apvtz)

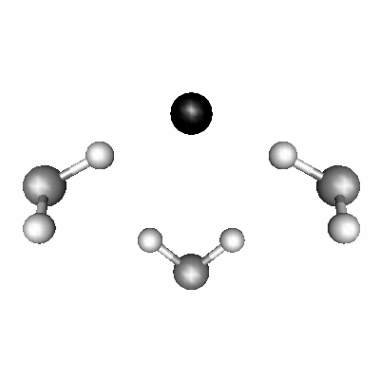


	MP2/aug-cc-pvdz	*MP2/aug-cc-pvtz*
ω_1 ***a′***	2765 **0**	2782 **0**
ω_2 ***a′***	2445 **0**	2422 **0**
ω_3 ***a′***	1187 **0**	1204 **0**
ω_4 ***a′***	247 **0**	261 **0**
ω_5 ***a′***	99 **0**	107 **0**
ω_6 ***a″***	465 **10**	491 **7**
ω_7 ***a″***	7*i* **2**	7*i* **1**
ω_8 ***a″***	54*i* 31	54*i* **29**
ω_9 ***e′***	2765 **4**	2782 **1 (2)**
ω_{10} ***e′***	2383 **1871 (3742)**	2349 **2112 (4224)**
ω_{11} ***e′***	1193 **6 (12)**	1209 **8 (16)**
ω_{12} ***e′***	252 **16 (32)**	266 **14 (28)**
ω_{13} ***e′***	138 **59 (118)**	149 **64 (128)**
ω_{14} ***e′***	7 <**1 (1)**	3*i* <**1 (1)**
ω_{15} ***e″***	473 **0**	496 **0**
ω_{16} ***e″***	26*i* **0**	27*i* **0**

***C*$_{3h}$** symmetry, six imaginary frequencies (2*a″*+ 2*e′*+ 2*e″*)

	***r*(Cl-H$_b$)**	***r*(S-H$_b$)**	***r*(S-H$_t$)**	**θ(Cl-H$_b$-S)**	**θ(H-S-H)**	**θ(H$_b$-Cl-H$_b$)**	***zpe***	***E*$_{MP2}$**	***E*$_{e/BSSE}$**	**$\Delta E_{e/BSSE}$**	**$\Delta E_{e/BSSE/Corr}$**
pvdz	2.221	1.379	1.349	177.3	92.5	120.0	30.9	-1656.372481	-1656.332070	2.6	1.1
pvtz	2.174	1.370	1.336	177.6	92.3	120.0	31.1	-1656.563519	-1656.559811	3.2	1.8

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvdz*
ω_1 *a′*	2759 **3**	2777 **1**
ω_2 *a′*	2704 **81**	2722 **84**
ω_3 *a′*	2288 **485**	2269 **522**
ω_4 *a′*	1180 **6**	1199 **8**
ω_5 *a′*	1164 **3**	1169 **2**
ω_6 *a′*	545 **5**	561 **5**
ω_7 *a′*	339 **5**	339 **4**
ω_8 *a′*	265 **14**	285 **15**
ω_9 *a′*	131 **17**	142 **16**
ω_{10} *a′*	113 **27**	118 **30**
ω_{11} *a′*	77 **<1**	74 **<1**
ω_{12} *a′*	26 **2**	33 **1**
ω_{13} *a′*	11 **1**	7 **1**
ω_{14} *a″*	2759 **1**	2777 **1**
ω_{15} *a″*	2720 **137**	2773 **113**
ω_{16} *a″*	2205 **2759**	2179 **2908**
ω_{17} *a″*	1184 **<1**	1200 **<1**
ω_{18} *a″*	544 **21**	568 **19**
ω_{19} *a″*	315 **<1**	300 **<1**
ω_{20} *a″*	269 **2**	285 1
ω_{21} *a″*	157 **105**	168 **109**
ω_{22} *a″*	98 **1**	90 **<1**
ω_{23} *a″*	72 **1**	56 **<1**
ω_{24} *a″*	87*i* **19**	147*i* **17**



C_s symmetry, one imaginary frequency (*a″*)

H_2Ss bound to anion

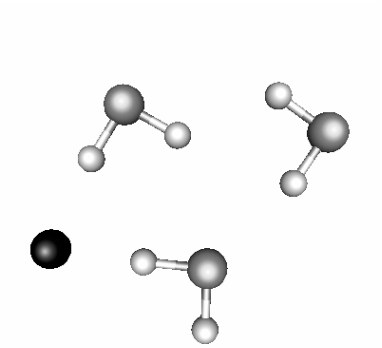
	r(Cl⁻…H$_b$)	***r(S-H$_b$)***	***r(S-H$_f$)***	***θ(Cl-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Cl-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.116	1.391	1.350	175.6	92.5	131.5	31.4	-1656.337462	-1656.330919	3.4	2.4
pvtz	2.085	1.382	1.337	175.8	92.3	130.4	31.5	-1656.563325	-1656.559170	3.6	2.6

Satellite H_2S

	r(S…H$_b$)	***r(S-H$_b$)***	***θ(H-S-H)***
pvdz	2.749	1.354	169.6
pvtz	2.779	1.341	163.4

HSH…SH_2 Hbond angles
169.6° (apvdz)
163.4° (apvtz)

	MP2/aug-cc-pvdz	*MP2/aug-cc-pvdz*
ω_1 ***a′***	2767 **4**	2780 **3**
ω_2 ***a′***	2762 **3**	2775 **2**
ω_3 ***a′***	2761 **2**	2774 **1**
ω_4 ***a′***	2710 **98**	2714 **118**
ω_5 ***a′***	2324 **1411**	2289 **1577**
ω_6 ***a′***	2080 **1822**	2031 **1918**
ω_7 ***a′***	1206 **11**	1224 **13**
ω_8 ***a′***	1192 **7**	1212 **8**
ω_9 ***a′***	1175 **1**	1192 <**1**
ω_{10} ***a′***	**314** 8	340 **8**
ω_{11} ***a′***	306 **17**	326 **16**
ω_{12} ***a′***	171 **3**	189 **2**
ω_{13} ***a′***	170 **67**	184 **72**
ω_{14} ***a′***	123 **38**	132 **39**
ω_{15} ***a′***	78 **8**	80 **7**
ω_{16} ***a′***	49 **3**	52 **3**
ω_{17} ***a′***	36 <**1**	35 <**1**
ω_{18} ***a″***	544 **2**	574 **1**
ω_{19} ***a″***	486 **1**	511 **1**
ω_{20} ***a″***	229 **2**	243 **2**
ω_{21} ***a″***	91 **4**	91 **2**
ω_{22} ***a″***	16 **4**	19 **4**
ω_{23} ***a″***	175*i* **19**	154*i* **17**
ω_{24} ***a″***	205*i* **8**	213*i* **7**



C_s symmetry, two imaginary frequencies (2a'')

	r(Cl…H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Cl-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Cl-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.174 *t* 2.057 *b*	1.386 1.403	1.350 1.348	172.8 178.1	91.7 93.9	73.8	30.9	-1656.330581	-1656.324331	7.5	6.0
pvtz	2.130 *t* 2.019 *b*	1.378 1.397	1.337 1.336	172.8 178.0	91.6 93.7	73.5	31.1	-1656.556559	-1656.552479	7.8	6.4

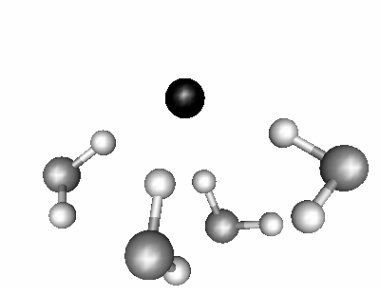
t=top, b=bottom

Satellite H_2S

	r(S…H$_b$)	***r(S-H$_b$)***	***θ(H-S-H)***
pvdz	3.398 *l* 2.665 *b*	1.350 1.354	92.3
pvtz	3.252 *l* 2.639 *b*	1.337 1.343	92.2

HSH…SH_2 Hbond angles
140.3° *s-t* (apvdz)
139.2° *s-t* (apvtz)
168.7° *s-b* (apvdz)
169.4° *s-b* (apvtz)

Pentamer Structures: $Cl^-(H_2S)_4$



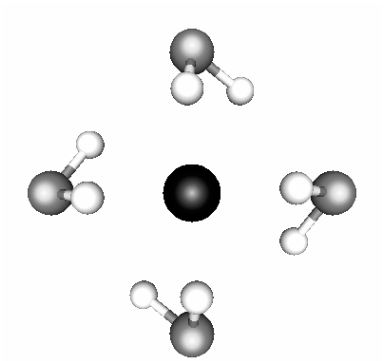
C_1 symmetry, minimum

	***r*(Cl-H_b)**	***r*(S-H_b)**	***r*(S-H_f)**	**θ(Cl-H_b-S)**	**θ(H-S-H)**	**θ(H_b-Cl-H_b)**	***zpe***	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$	$\Delta H_{3\rightarrow 4}^{295K}$
pvdz	2.300 *l*	1.370	1.352	168.5	91.2	73.2 *l-f*	43.3	-2055.213566	-2055.203332	0.0	0.0	-7.4
	2.286 *f*	1.375	1.355	165.9	90.8	73.8 *f-b*						Checked
	2.319 *b*	1.371	1.354	165.8	90.9	73.9 *b-r*						
	2.284 *r*	1.373	1.353	168.5	91.1	135.5 *r-l*						

l=left, f=front, b=back, r=right

HSH…SH_2 Hbond angle = 138.9° *l-f*
143.6° *f-b*
139.3° *b-r*
138.6° *r-f*

	MP2/aug-cc-pvdz
ω_1 *a*	2739 **10**
ω_2 *a*	2732 **18**
ω_3 *a*	2725 **15**
ω_4 *a*	2708 **30**
ω_5 *a*	2542 **566**
ω_6 *a*	2494 **500**
ω_7 *a*	2469 **688**
ω_8 *a*	2447 **301**
ω_9 *a*	1188 **13**
ω_{10} *a*	1187 **7**
ω_{11} *a*	1186 **11**
ω_{12} *a*	1182 **4**
ω_{13} *a*	502 **14**
ω_{14} *a*	473 **6**
ω_{15} *a*	467 **8**
ω_{16} *a*	431 **8**
ω_{17} *a*	360 **3**
ω_{18} *a*	276 **7**
ω_{19} *a*	263 **<1**
ω_{20} *a*	254 **6**
ω_{21} *a*	249 **6**
ω_{22} *a*	237 **6**
ω_{23} *a*	217 **12**
ω_{24} *a*	181 **8**
ω_{25} *a*	155 **31**
ω_{26} *a*	138 **39**
ω_{27} *a*	109 **11**
ω_{28} *a*	92 **<1**
ω_{29} *a*	79 **2**
ω_{30} *a*	70 **1**
ω_{31} *a*	61 **1**
ω_{32} *a*	48 **1**
ω_{33} *a*	24 **1**

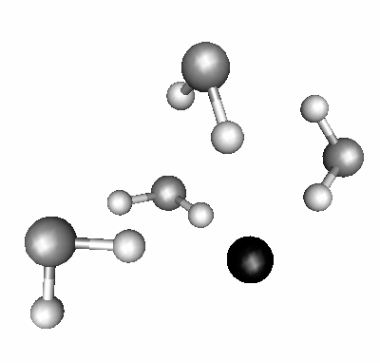


C_4 symmetry, minimum

	$r(Cl\text{-}H_b)$	$r(S\text{-}H_b)$	$r(S\text{-}H_t)$	$\theta(Cl\text{-}H_b\text{-}S)$	$\theta(H\text{-}S\text{-}H)$	$\theta(H_b\text{-}Cl\text{-}H_b)$	*zpe*	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.298	1.372	1.353	168.1	91.0	70.5	43.5	-2055.213351	-2055.203272	<0.1	0.2

HSH…SH_2 Hbond angle = 139.0°

	MP2/aug-cc-pvdz
ω_1 ***a***	2727 **1**
ω_2 ***a***	2535 **625**
ω_3 ***a***	1181 **12**
ω_4 ***a***	473 **1**
ω_5 ***a***	344 **5**
ω_6 ***a***	267 **11**
ω_7 ***a***	151 **25**
ω_8 ***a***	63 **2**
ω_9 ***b***	2733 **0**
ω_{10} ***b***	2467 **0**
ω_{11} ***b***	1197 **0**
ω_{12} ***b***	489 **0**
ω_{13} ***b***	264 **0**
ω_{14} ***b***	163 **0**
ω_{15} ***b***	90 **0**
ω_{16} ***b***	72 **0**
ω_{17} ***b***	17 **0**
ω_{18} ***e***	2730 **44 (88)**
ω_{19} ***e***	2473 **720 (1440)**
ω_{20} ***e***	1188 **13 (26)**
ω_{21} ***e***	477 **19 (38)**
ω_{22} ***e***	262 **1 (2)**
ω_{23} ***e***	255 **7 (14)**
ω_{24} ***e***	128 **29 (58)**
ω_{25} ***e***	69 **2 (4)**

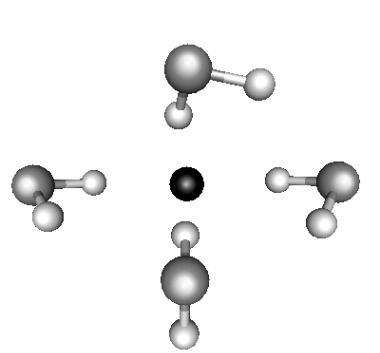


C_s symmetry, minimum

	r(Cl-H$_b$)	***r(S-H$_b$)***	***r(S-H$_t$)***	***θ(Cl-H$_b$-S)***	***θ(H-S-H)***	***θ(H$_b$-Cl-H$_b$)***	***zpe***	***E$_{MP2}$***	***E$_{e/BSSE}$***	***ΔE$_{e/BSSE}$***	***ΔE$_{e/BSSE/Corr}$***
pvdz	2.242 *l*	1.376	1.350	174.0	92.1	73.2 *l-b*	43.1	-2055.211775	-2055.201920	0.9	0.7
	2.333 *b*	1.370	1.353	165.3	91.0	73.9 *b-t*					
	2.295 *t*	1.372	1.354	165.9	90.9	73.1 *t-r*					
	2.309 *r*	1.369	1.352	167.9	91.1	133.3 *r-l*					

HSH…SH_2 Hbond angle = 140.8° *b-l*
143.7° *t-b*
139.9° *r-t*

	MP2/aug-cc-pvdz
ω$_1$ *a*	2757 **3**
ω$_2$ *a*	2736 **15**
ω$_3$ *a*	2726 **22**
ω$_4$ *a*	2717 **25**
ω$_5$ *a*	2550 **582**
ω$_6$ *a*	2506 **438**
ω$_7$ *a*	2483 **349**
ω$_8$ *a*	2425 **813**
ω$_9$ *a*	1191 **6**
ω$_{10}$ *a*	1188 **10**
ω$_{11}$ *a*	1187 **7**
ω$_{12}$ *a*	1184 **7**
ω$_{13}$ *a*	493 **8**
ω$_{14}$ *a*	472 **11**
ω$_{15}$ *a*	460 **7**
ω$_{16}$ *a*	425 **9**
ω$_{17}$ *a*	332 **8**
ω$_{18}$ *a*	266 **7**
ω$_{19}$ *a*	258 **3**
ω$_{20}$ *a*	255 **5**
ω$_{21}$ *a*	243 **3**
ω$_{22}$ *a*	234 **5**
ω$_{23}$ *a*	187 **8**
ω$_{24}$ *a*	153 **30**
ω$_{25}$ *a*	139 **36**
ω$_{26}$ *a*	133 **17**
ω$_{27}$ *a*	109 **10**
ω$_{28}$ *a*	92 **<1**
ω$_{29}$ *a*	75 **2**
ω$_{30}$ *a*	65 **1**
ω$_{31}$ *a*	57 **<1**
ω$_{32}$ *a*	27 **<1**
ω$_{33}$ *a*	20 **1**

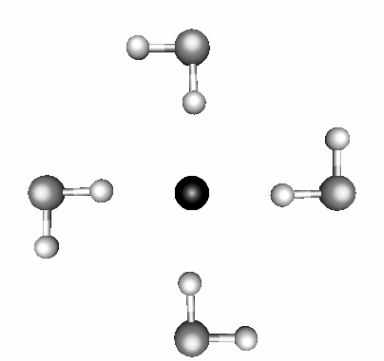


C_1 symmetry, minimum

	***r*(Cl-H$_b$)**	***r*(S-H$_b$)**	***r*(S-H$_t$)**	***θ*(Cl-H$_b$-S)**	***θ*(H-S-H)**	***θ*(H$_b$-Cl-H$_b$)**	***zpe***	***E*$_{MP2}$**	***E*$_{e/BSSE}$**	**Δ*E*$_{e/BSSE}$**	**Δ*E*$_{e/BSSE/Corr}$**
pvdz	2.311 *l*	1.369	1.352	168.2	91.3	72.1 *l-f*	43.1	-2055.211473	-2055.201698	1.0	0.8
	2.230 *f*	1.378	1.351	178.4	92.1	71.8 *f-r*					
	2.299 *r*	1.372	1.353	168.1	91.1	74.8 *r-t*					
	2.331 *t*	1.368	1.353	164.4	91.0	69.8 *t-l*					

HSH…SH_2 Hbond angle = 138.1° *l-f*
140.8° *t-r*
138.7° *r-f*

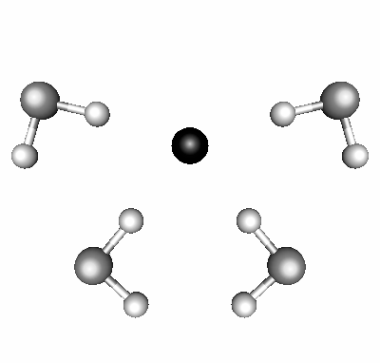
	MP2/aug-cc-pvdz
ω$_1$ *a*	2752 **4**
ω$_2$ *a*	2741 **9**
ω$_3$ *a*	2733 **20**
ω$_4$ *a*	2730 **8**
ω$_5$ *a*	2559 **521**
ω$_6$ *a*	2516 **309**
ω$_7$ *a*	2484 **798**
ω$_8$ *a*	2402 **508**
ω$_9$ *a*	1193 **2**
ω$_{10}$ *a*	1190 **13**
ω$_{11}$ *a*	1187 **8**
ω$_{12}$ *a*	1183 **1**
ω$_{13}$ *a*	524 **11**
ω$_{14}$ *a*	461 **9**
ω$_{15}$ *a*	434 **2**
ω$_{16}$ *a*	417 **13**
ω$_{17}$ *a*	310 **7**
ω$_{18}$ *a*	265 **17**
ω$_{19}$ *a*	260 **7**
ω$_{20}$ *a*	253 **3**
ω$_{21}$ *a*	243 **1**
ω$_{22}$ *a*	216 **6**
ω$_{23}$ *a*	207 **13**
ω$_{24}$ *a*	156 **34**
ω$_{25}$ *a*	140 **3**
ω$_{26}$ *a*	136 **37**
ω$_{27}$ *a*	107 **9**
ω$_{28}$ *a*	89 **1**
ω$_{29}$ *a*	72 **2**
ω$_{30}$ *a*	63 **<1**
ω$_{31}$ *a*	52 **1**
ω$_{32}$ *a*	41 **1**
ω$_{33}$ *a*	21 **1**



C_{4h} symmetry, eight imaginary frequencies ($2a_u$, b_g, b_u, $2e_g$, $2e_u$)

	***r*(Cl-H$_b$)**	***r*(S-H$_b$)**	***r*(S-H$_t$)**	**θ(Cl-H$_b$-S)**	**θ(H-S-H)**	**θ(H$_b$-Cl-H$_b$)**	***zpe***	***E*$_{MP2}$**	***E*$_{e/BSSE}$**	**$\Delta E_{e/BSSE}$**	**$\Delta E_{e/BSSE/Corr}$**
pvdz	2.265	1.373	1.350	176.5	92.4	90.0	41.2	-2055.204480	-2055.197709	3.5	1.4

	MP2/aug-cc-pvdz
ω_1 a_g	2763 **0**
ω_2 a_g	2523 **0**
ω_3 a_g	1186 **0**
ω_4 a_g	226 **0**
ω_5 a_g	95 **0**
ω_6 a_u	421 **12**
ω_7 a_u	51*i* **1**
ω_8 a_u	103*i* **40**
ω_9 b_g	2763 **0**
ω_{10} b_g	2463 **0**
ω_{11} b_g	1199 **0**
ω_{12} b_g	232 **0**
ω_{13} b_g	86 **0**
ω_{14} b_g	16*i* **0**
ω_{15} b_u	401 **0**
ω_{16} b_u	52 **0**
ω_{17} b_u	10*i* **0**
ω_{18} e_g	434 **0**
ω_{19} e_g	62*i* **0**
ω_{20} e_u	2763 **4 (8)**
ω_{21} e_u	2458 **1851 (3702)**
ω_{22} e_u	1188 **3 (6)**
ω_{23} e_u	220 **28 (56)**
ω_{24} e_u	146 **60 (120)**
ω_{25} e_u	17*i* **<1 (1)**



C_{2v} symmetry, three imaginary frequencies ($2a_2 + b_1$)

	***r*(Cl-H_b)**	***r*(S-H_b)**	***r*(S-H_t)**	***θ*(Cl-H_b-S)**	***θ*(H-S-H)**	***θ*(H_b-Cl-H_b)**	***zpe***	E_{MP2}	$E_{e/BSSE}$	$\Delta E_{e/BSSE}$	$\Delta E_{e/BSSE/Corr}$
pvdz	2.304 *t* 2.243 *b*	1.370 1.376	1.350 1.349	174.7 178.4	92.5 92.9	142.6 *t-t* 70.6 *t-b* 76.2 *b-b*	41.8	-2055.205910	-2055.197630	3.6	2.1

t=top, b=bottom.

HSH…SH_2 Hbond angle = 132.0° (apvdz)

	MP2/aug-cc-pvdz
ω_1 a_1	2767 **4**
ω_2 a_1	2759 **1**
ω_3 a_1	2536 **1**
ω_4 a_1	2438 **1105**
ω_5 a_1	1211 **1**
ω_6 a_1	1193 **<1**
ω_7 a_1	284 **40**
ω_8 a_1	263 **4**
ω_9 a_1	139 **34**
ω_{10} a_1	95 **2**
ω_{11} a_1	53 **<1**
ω_{12} a_1	29 **1**
ω_{13} a_2	442 **0**
ω_{14} a_2	395 **0**
ω_{15} a_2	59 **0**
ω_{16} a_2	28*i* **0**
ω_{17} a_2	196*i* **0**
ω_{18} b_1	451 **4**
ω_{19} b_1	407 **4**
ω_{20} b_1	107 **1**
ω_{21} b_1	3 **1**
ω_{22} b_1	137*i* **36**
ω_{23} b_2	2764 **6**
ω_{24} b_2	2759 **<1**
ω_{25} b_2	2496 **1489**
ω_{26} b_2	2415 **677**
ω_{27} b_2	1204 **4**
ω_{28} b_2	1185 **<1**
ω_{29} b_2	261 **15**
ω_{30} b_2	255 **<1**
ω_{31} b_2	157 **91**
ω_{32} b_2	85 **<1**
ω_{33} b_2	49 **1**