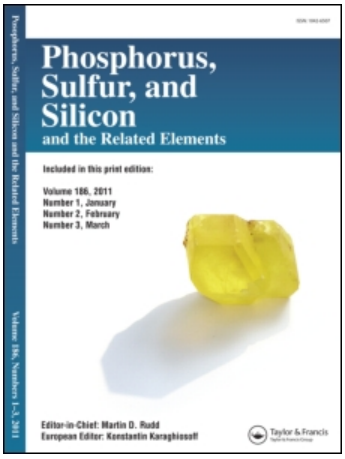

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THEORETICAL PREDICTIONS OF STRUCTURES AND VIBRATIONAL INFRARED FREQUENCIES. I. MERCAPTANS AND SULFIDES

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THEORETICAL PREDICTIONS OF STRUCTURES AND VIBRATIONAL INFRARED FREQUENCIES. I. MERCAPTANS AND SULFIDES

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We report the computed equilibrium geometries and vibrational infrared frequencies of a group of thirteen mercaptans and sulfides. The computations were based on the Gaussian 86 Program Package utilizing 3-21G basis sets. The theoretical bond distances and bond angles are in agreement with the available experimental data. The agreement between computed frequencies and available experimental values seems reasonable. We also used the computations as guidelines for the assignment of available experimental infrared frequencies. We believe that it is possible to make reliable frequency predictions by combining computations with available experimental data for groups of similar molecules. However, it is necessary to introduce different correction factors for different types of vibrational modes if we use 3-21G basis sets.

Key words: Vibrations; infrared; frequencies; mercaptans; sulfides.

I. INTRODUCTION

In recent years infrared spectroscopy has become a favorite method for the detection of unknown substances in the environment. The spectral region between 800 and 1200 cm^{-1} is of particular interest in this respect because it is the region that is most readily accessible to experimental devices in atmospheric testing.

The detection of known substances whose experimental infrared spectra are known is relatively straightforward. However, in many situations we wish to detect substances of unknown composition or substances of known composition whose experimental infrared spectra are not available. In those situations it would be helpful if the spectra could be predicted by means of theoretical computations. Nowadays it is possible to predict infrared vibrational spectra of medium-sized molecules by means of the Gaussian 86 or 88 Program Packages.[1] The accuracy of the various computational procedures was discussed in a recent

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book by Hehre, Radom, Schleyer and Pople[2] and a variety of results were presented and discussed in Chapter 6 of that book.

The theoretical prediction of the vibrational modes and vibrational frequencies of a medium-sized molecule may be useful also in deciding about the frequency assignments of experimental infrared spectra. For instance, the assignment of the vibrational frequencies in methyl alcohol by Noether[3] was based on a comparison of the infrared and Raman spectra of the four molecules CH_3OH, CH_3OD, CD_3OH and CD_3OD. Much time and effort can be saved if the vibrational modes and frequencies of methyl alcohol can be predicted theoretically with sufficient accuracy.

Adams, Handy and Amos[4] have reported results of ab initio computations of infrared spectra based on the use of the Cambridge Analytical Derivative Package (CADPAC). The goal of these computations is the accurate evaluation of the complete spectra of a group of molecules. We are interested in performing somewhat less accurate computations for a larger group of similar molecules. In a typical case experimental infrared spectra are known for about a third of the molecules in a group that we consider. We hope to predict the infrared spectra of all molecules in the group by combining our computational results with the available experimental data. In other words, we hope to fill in the gaps in spectral data base sets by making use of computational results on vibrational infrared spectra.

Our present plan involves a study of a group of mercaptans, sulfides and their fluoro and chloro derivatives. In addition to making numerical predictions we hope to derive a better understanding of the overall features of the spectra from our computational results. It will appear that it is not always possible to predict the whole spectrum of a medium-sized molecule with the desired degree of accuracy. On the other hand, we find that it is possible to make accurate predictions for certain specific vibrational modes such as the S—H, C—S or C—C stretch vibrations, etc. We find that the frequencies of some of those vibrational modes may be predicted with a much higher degree of accuracy than for others. Therefore, we will focus our attention on those features of the spectra that can be predicted theoretically with the highest accuracy and on those features that are essential for the identification process. A similar study was reported by Sosa, Bartlett, KuBulat and Person[5] on four of the molecules that we report here, namely $(ClCH_2CH_2)_2S$, $(C_2H_5)_2S$, $ClCH_2CH_2SH$ and CH_3CH_2SH. We were pleased to note that their results are consistent with ours.

In addition to the vibrational infrared spectra we also report our theoretical results for the molecular geometries. We believe that the computed bond distances and bond angles should be reasonably accurate. Theoretical predictions of the various dihedral angles representing rotations around the carbon–carbon and carbon–sulfur bonds are less reliable.

II. COMPUTATIONAL METHODS

Our computations are all based on the use of the Gaussian 86 or Gaussian 88 Program Package. An extensive discussion of the accuracy of the results and of

the possible errors in both experimental and computed frequencies may be found in the book by Hehre, Radom, Schleyer and Pople.[2] In preliminary work we observed that the use of 3-21G basis sets led to results that were more accurate than STO-3G results. Computations based on the use of the 3-21G basis set are applicable to all molecules that we are interested in. We decided therefore to use the straight Hartree–Fock procedure (no CI or MP) with the 3-21G basis set for all computations in order to be consistent. It is not clear whether the use of larger basis sets leads to improvements in the accuracy of the frequency results. The results and analysis presented by Hehre, Radom, Schleyer and Pople[2] seem to indicate that improvements in the basis set do not lead to significant improvement in the accuracies of the computed frequencies. On the other hand, we felt that it might be helpful to investigate the effects of improvements in the basis set on the theoretical results of at least one of the smaller molecules. In the following section we present a comparison of the optimized geometrics and computed frequencies of methyl mercaptan derived from the 3-21G, 6-31G and 6-31G* basis sets.

It should be noted also that frequency computations are all based on the harmonic approximation but that experimental potential curves may exhibit significant degrees of anharmonicity. For instance, the potential curve of the hydrogen molecule is both anharmonic and asymmetric, in this case the difference between the harmonic and the experimental vibrational frequencies may be as high as 6%. Also in the frequency computations it is assumed that all energy gradients are zero and it was observed by Hehre *et al.*[2] that small errors in the molecular geometries can lead to significant errors in the theoretical frequency results. Therefore, we paid particular attention to the accurate geometry optimizations in our frequency computations.

We consider two different groups of organic molecules, mercaptans and sulfides. We discuss these groups separately in the following sections.

III. METCAPTANS

We have computed the 3-21G optimized geometries and the vibrational frequencies of the following group of mercaptans: CH_3SH, CH_2FSH, CH_2ClSH, CH_3CH_2SH, CH_2FCH_2SH and CH_2ClCH_2SH. The computations were all based on the method outlined in Section II, that is a HF computation with the 3-21G basis set.

We depict the geometry of CH_2ClSH in Figure 1a and the geometry of CH_2ClCH_2SH in Figure 1b. We view both molecules from a direction which is close to the C—S bond. The geometries of the other molecules CH_2XSH and CH_2YCH_2SH are similar. Figures 1a and 1b are therefore suitable for defining the geometry parameters for all six molecules. The definitions of the bond lengths are self-explanatory and our computed values are presented in Tables I and II. It may be seen that the C—S—H bond angle has about the same value for all six molecules, 97.5 ± 0.3 degrees. If we rotate the S—H group around the C—S bond we find an energy minimum when the H—S—C—X dihedral angle is between 60 and 75 degrees. In the case of CH_2FSH and CH_2ClSH there is a second energy

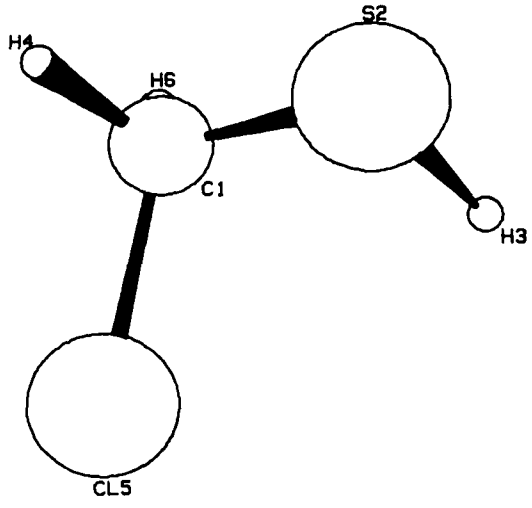

FIGURE 1a. Structure of CH_2ClSH.

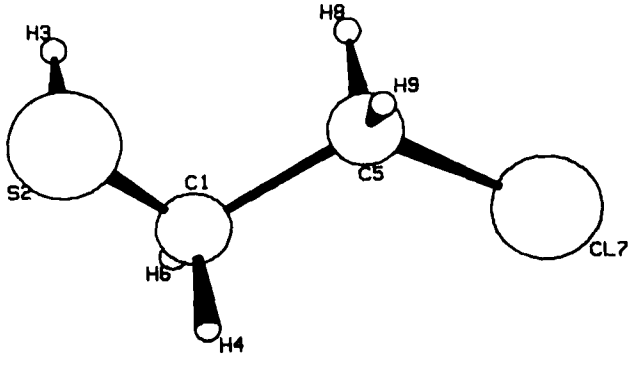

FIGURE 1b. Structure of CH_2ClCH_2SH.

minimum at a dihedral angle of 180 degrees but this energy is higher by 2.90 kCal/mole in the case of CH_2FSH and by 2.70 kCal/mole in the case of CH_2ClSH. It should be noted that there is a slight difference between the S—C—H bond angles. This means that there is a slight tilt in the CH_2X group, the symmetry axis of the CH_2X group is slightly different from the S—C direction, the tilt angle is about 2 degrees in the three methyl mercaptans.

Experimental geometrical parameters for CH_3SH are reported in Hargittai's book,[6] they were derived from Kojimas' microwave measurements.[7] The experimental values are C—S = 1.814, S—H = 1.335, CH = 1.092, C—S—H = 96.5, H—C—H = 109.8. The agreement between theoretical and experimental data seems reasonable except for the C—S bond distance, here our computed value is

TABLE I

Energies, bond lengths and bond angles (in terms of hartrees, angstroms and degrees) of the molecules CH_2XSH. The geometry parameters are defined in Figure 1a

	X = H	X = F	X = Cl
E	−435.526292	−533.831262	−892.234653
C—S	1.8941	1.8774	1.8544
S—H	1.3552	1.3512	1.3508
C—X	1.0773	1.3910	1.8836
C—H	1.0773	1.0740	1.0720
	1.0778	1.0740	1.0720
C—S—H	97.84	97.20	97.51
S—C—X	109.67	110.24	112.86
S—C—H	105.55	105.76	107.79
	109.67	109.56	112.17
X—C—S—H	61.31	63.83	66.68

larger than the experimental result by 0.08 angstroms. It should be noted also that our computed H—C—H bond angles are 110.2, 110.2 and 111.4, one of the three being larger than the other two by 1.2 degrees.

We list the geometry parameters of the ethyl mercaptans CH_2YCH_2SH in Table II. It may be seen that the geometry of the CH_2SH group is similar to the geometry of the methyl mercaptans, the C—S, S—H and C_m—H bond lengths are practically the same and the C—S—H bond angles are also quite similar. The C—C—S—H dihedral angles in the ethyl mercaptans are larger than the X—C—S—H dihedral angles in the methyl mercaptans. The experimental geometry of ethyl mercaptan[8,9] is presented in Hargittai's book,[6] the largest difference between theory and experiment is again in the C—S bond distance,

TABLE II

Energies, bond lengths and bond angles (in terms of hartrees, angstroms, and degrees) of the molecules CH_2YCH_2SH. The geometry parameters are defined in Figure 1b

	Y = H	Y = F	Y = Cl
E	−474.347903	−572.658753	−931.060921
C—S	1.8972	1.8865	1.8851
S—H	1.3531	1.3537	1.3535
C—C	1.5296	1.5154	1.5147
C_c—H	1.0789	1.0783	1.0765
	1.0784	1.0783	1.0747
C—Y	1.0854	1.4009	1.8865
C_m—H	1.0037	1.0815	1.0810
	1.0819	1.0793	1.0747
C—S—H	97.56	97.44	97.16
S—C—C	112.38	112.93	114.04
S—C—H	103.77	104.34	105.21
	107.84	108.96	108.08
C—C—Y	110.53	109.60	110.59
C—C—H	109.96	109.71	111.64
	110.94	111.19	113.44
C—C—S—H	63.47	70.08	73.18

the experimental value is 1.815 angstroms. The other experimental values, S—H = 1.336, C—C = 1.528, C—S—H = 96.6 are quite similar to our computed values. It should be noted also that we obtain a dihedral C—C—S—H angle of around 63 to 73 degrees in the CH_2YCH_2SH molecules. This is between the gauche form where the angle is 0 degrees and the anti form where the angle is 180 degrees but it obviously is closer to the gauche form.

We have listed our frequency results in Table III. The computations produce the detailed forms of the normal coordinates in addition to the frequencies of all normal modes. It is therefore possible to assign the different vibrational modes to specific localized motions. We have identified the various stretch modes corresponding to the C—S, S—H, C—F and C—Cl bond stretch modes. These assignments seem to be quite obvious and we have listed them and their frequencies in Table III. It follows from Table III that these stretch frequencies are similar for similar molecules. For instance, it seems reasonable to assume that the S—H stretch motion is not going to be affected much by substitutions at the other end of the molecule. We conclude that the S—H stretch frequencies for the ethyl mercaptans should be very close to each other, in agreement with Table III. The C—Cl stretch frequencies in the methyl and ethyl mercaptans should be very

TABLE III

Computed vibrational frequencies of methyl and ethyl mercaptans (in terms of cm^{-1}) with relative IR intensities in parenthesis

	CH_3SH	CH_2FSH	CH_2ClSH
C—S stretch	682.0 (27)	700.2 (50)	739.7 (78)
S—H stretch	2626.6 (29)	2636.9 (144)	2637.2 (10)
C—H stretch	3249.9 (23)	3300.3 (25)	3336.9 (3)
	3346.37 (3)	3373.1 (10)	3426.3 (2)
C—X stretch	3348.3 (7)	1168.7 (59)	638.2 (45)
S—H bend	849.5 (4)	854.8 (10)	825.3 (2)
	1186.7 (25)	1126.9 (63)	1063.6 (16)
CH_2X wag	1504.7 (11)	1490.4 (44)	1372.1 (45)
CH_2X SC	1062.5 (6)	1364.7 (4)	1282.8 (11)
	C_2H_5SH	C_2H_4FSH	C_2H_4ClSH
C—S stretch	654.1 (14)	660.0 (12)	667.0 (17)
S—H stretch	2621.3 (29)	2614.6 (30)	2615.6 (27)
C—C stretch	1027.3 (8)	1197.8 (13)	1121.7 (7)
C_m—H stretch	3271.6 (22)	3275.9 (9)	3261.6 (7)
	3328.9 (10)	3339.2 (2)	3333.6 (0)
C—Y stretch	3280.0 (17)	1175.6 (71)	637.9 (32)
C_c—H stretch	3199.3 (22)	3236.0 (30)	3298.5 (11)
	3251.5 (9)	3286.6 (34)	3372.8 (0)
S—H bend	797.2 (2)	836.6 (5)	849.0 (7)
	948.1 (16)	967.9 (3)	1121.7 (7)
S—C—C bend	349.3 (1)	293.1 (5)	281.7 (6)
	1165.9 (3)	1043.4 (5)	1041.4 (24)
C—Y bend	—	488.8 (14)	429.1 (9)
C—H bend	1219.8 (14)	—	974.1 (14)
	1411.9 (5)	1352.8 (4)	1288.8 (7)
	1431.4 (26)	1376.1 (2)	1333.8 (4)
	1580.9 (6)	1466.0 (12)	1437.1 (55)
	1639.9 (6)	1568.7 (20)	1460.9 (11)
	1665.3 (11)	1620.3 (12)	1620.5 (9)
	1668.9 (4)	1694.9 (1)	1635.7 (11)

close to each other, in agreement with Table III. It should be noted that the C—Cl stretch frequencies in the methyl and ethyl compounds are practically the same, this again seems reasonable. The behavior of the C—C stretch frequencies is less predictable. Here it should be realized that the two carbon atoms move in conjunction with the attached hydrogens and halogens and that the C—C stretch motion is less localized and less predictable than the other stretch modes. Nevertheless, the C—C bond stretch mode is easily identified from the normal coordinates. In addition to the bond stretch frequencies we have identified two different S—H bending modes. The H—S—C bending motion occurs in conjunction with a rocking motion of the three hydrogens, the two bending motions may be either in-plane or out-of-plane. Of course, these assignments become more complicated after substituting a halogen for one of the hydrogens and they are also less straightforward for the ethyl than for the methyl mercaptans. We also list the various C—H stretch frequencies. In the case of the ethyl mercaptans it is possible to differentiate between the end and the middle CH_2, groups, but otherwise we are not able to separate the C—H stretch frequencies into more specific modes.

We do not feel confident in making specific assignments for the various H—C—H bending modes. Most of them are nonlocalized and we just list their frequencies as a group. We have singled out a wagging motion which is associated with a very intense infrared transition, we list this frequency separately.

Experimental information is available only for methyl mercaptan and for ethyl mercaptan. The Raman spectra for both molecules were reported by Wagner.[10,11] The experimental infrared spectrum of methyl mercaptan was reported by Hehre *et al.*[2] The IR spectrum of methyl mercaptan was reported by Smith, Selvin and Scott.[12] Some additional, more recent experimental studies on ethyl mercaptans are limited to the far infrared region or the microwave region[13] and they are not particularly relevant to our computations. It should be noted that most of the experimental data that we quote are fairly old but they represent careful measurements that are sufficiently accurate for our purpose. More recent experimental work deals with either the microwave or far infrared region or they are private efforts[14] that were not published in the general literature. In general we have found the spectra of the Aldrich Library of Infrared Spectra[15] sufficiently accurate for our purpose since the accuracy of our computational results is not much better.

We present some of our computed frequencies and the corresponding experimental values of methyl and ethyl mercaptan in Table IV. We are most confident about the assignment of the various bond stretch frequencies and we list all of them. We also list the S—H bend frequencies even though there is some doubt about the assignment of the lower of the two frequencies in ethyl mercaptan. Finally, we list the most intense of the many C—H bending frequencies, we denote it as the CH_2 wag.

In order to investigate the dependence of the theoretical frequencies on the basis sets we report computations for three different basis sets 3-21G, 6-31G and 6-31G* on the methyl mercaptan molecule CH_3SH in Table V. We selected this molecule because it is the smallest of the group and because experimental data are available.

TABLE IV

Comparison of computed and experimental frequencies of methyl and ethyl mercaptan (in terms of cm^{-1})

	CH_3SH			CH_3CH_2SH		
	comp	Ram[16]	IR[2]	comp	Ram[11]	IR[12]
C—S stretch	682.0	702	708	654.1	656	658
S—H stretch	2626.6	2572	2572	2621.3	2569	2551
C—H stretch	3249.9	2839	2931	3199.3	2875	2872
	3346.6	2931	3000	3251.1	2902	
	3348.3	2999	3000	3271.6	2928	2930
				3280.0	2967	2968
				3328.9		2988
C—C stretch				1027.6	973	971
S—H bend	849.5	803	803	797.2	738	736
	1186.7	1055	1074	948.1	871	867
CH_2 wag	1504.7	1319	1319	1431.4	1266	1274

We note that the differences between the 3-21G and 6-31G results are not that large but that the introduction of polarization functions in the 6-31G* basis set leads to significant changes in the results. First, the C—S bond distance in the 3-21G computation is too long by 0.08 angstrom and the 6-31G* bond length agrees almost exactly with experiment. The same improvement may be noted for the S—H bond distance. In Table V we also presented corrected frequency values for the 6-31G* results which we obtain by multiplying all computed frequencies

TABLE V

Comparison of experimental results with theoretical results derived from different basis sets for methyl mercaptan

E	exp.	3-21G −435.5263	6-31G −437.6476	6-31G* −437.7003	(6-31G*) × 0.9
C—S	1.814	1.8941	1.8785	1.8176	—
S—H	1.335	1.3522	1.3545	1.3266	—
C—H	1.092	1.0773	1.0772	1.0809	—
		1.0773	1.0772	1.0809	—
		1.0778	1.0775	1.0815	—
C—S—H		97.84	98.49	97.90	—
S—C—H		109.67	110.23	111.28	—
		109.67	110.23	111.28	—
		105.55	105.91	106.67	—
X—C—S—H		61.31	61.35	61.54	—
torsion	—	227.2	225.2	260.6	235
C—S stretch	708	602.1	708.5	775.5	698
S—H bend	803	849.5	847.3	871.6	784
CH_2 sciss	—	1062.7	1003.3	1079.5	972
S—H bend	1074	1186.7	1190.6	1219.3	1097
CH_2 wag	1319	1504.8	1516.7	1521.1	1369
CH bend	—	1646.5	1633.3	1622.9	1460
CH bend	—	1649.3	1639.4	1634.7	1471
S—H stretch	2572	2626.8	2683.9	2910.7	2620
C—H stretch	2931	3249.7	3247.7	3238.3	2914
	3000	3346.7	3354.1	3325.9	2993
	3000	3347.8	3356.9	3326.2	2994

by a uniform correction value of 0.9. These corrected frequency values agree quite well with the experimental frequencies except for the CH_2 wag.

Unfortunately we cannot use the 6-31G* basis set for all molecules that we are interested in because of the size of the molecules. Instead we use the 3-21G basis set. It follows from the data in Table V that in the 3-21G basis set the C—S bond distance is too large by almost 0.1 angstrom and that the S—H bond length is too large by 0.03 angstrom. We believe that this discrepancy causes the computed C—S stretch frequency to be lowered by 10% and to be very close to the experimental value. Consequently we must introduce different correction factors for different types of frequencies in the 3-21G computation. The correction factors are 1.0 for the computed C—S stretch frequencies, 0.898 for the C—H stretch frequencies, 0.98 for the S—H stretch and 0.95 for the C—C stretch. We will review these correction factors again in Section VI.

IV. DIMETHYL SULFIDES

We have computed the vibrational frequencies and the corresponding normal coordinates of five methyl sulfide molecules, namely CH_3SCH_3, CH_2FSCH_2F, CH_2ClSCH_2Cl, CH_3SCH_2F and CH_3SCH_2Cl from the 3-21G basis set.

The energies and geometries of all five molecules are listed in Table VI. We give a visual representation of the geometries in Figure 2, the molecular plane is

TABLE VI

Energies and geometry parameters of the 3-21G optimized geometries of the five methyl sulfide molecules CH_2XSCH_2Y

	X = Y = H	X = Y = F	X = Y = Cl
E	−474.3486	−670.9640	−1387.7695
C—S	1.885	1.874	1.850
C—X	1.079	1.397	1.885
C—H	1.079	1.073	1.072
C—S—C	99.07	93.58	98.98
X—C—S	109.58	108.25	112.40
$(H—C—S)_O$	109.58	108.25	111.15
$(H—C—S)_P$	105.50	107.61	108.35
	X = F, Y = H	X = Cl, Y = H	
E	−572.6567	−931.0602	
C—S	1.872	1.846	
	1.890	1.886	
C—X	1.399	1.895	
C—Y	1.078	1.078	
C—H	1.075	1.073	
	1.078	1.078	
C—S—C	96.74	99.48	
X—C—S	109.08	112.81	
Y—C—S	109.08	109.52	
H—C—S	109.89	112.35	
	107.38	108.71	
	109.08	109.52	
	106.90	105.98	

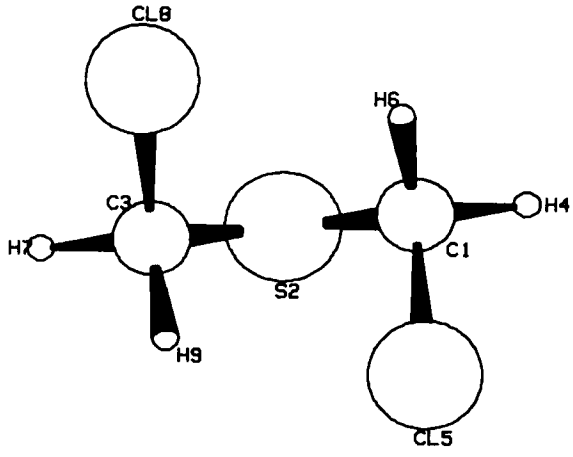

FIGURE 2. Structure of CH_2ClSCH_2Cl.

HCSCH and in the case of CH_2XCH_2X one halogen is above and the other halogen is below the molecular plane.

Experimental data are available for dimethyl sulfide[16] and for monochlorodimethyl sulfide,[17] we compare these results with our computed values in Table VII. It should be noted that our computed S—C bond distances are consistently higher than the experimental values by 0.06 to 0.08 angstroms, our computed C—Cl value is higher than the experimental result by 0.13 angstroms. While the agreement between the theoretical and experimental bond angles is more satisfactory, we are particularly pleased by the agreement between the computed and experimental dihedral C—S—C—Cl angles. Finally, we find that the "tilt" of the methyl and chloromethyl groups is about 2 degrees, which is consistent with experiments.

TABLE VII

Comparison between computed and experimental bond lengths and bond angles in dimethyl sulfides

	CH_3SCH_3	
	comp	exp[16]
S—C	1.885	1.807
C—H	1.079	1.116
C—S	99.07	99.05
H—C—H	110.1	109.3
	110.9	
	CH_3SCH_2Cl	
	comp	exp[17]
S—C(Cl)	1.846	1.785
S—C(H_3)	1.886	1.827
C—Cl	1.895	1.76
C—S—C	99.5	98.9
C—S—C—Cl	64	59

Our results for the vibrational frequencies of the five molecules, together with the relative intensities of the corresponding infrared and Raman spectral lines, are presented in Table VIII. It should be noted that the accuracy of the intensity values is quite low. The only reason we list them is that they are of some help in interpreting the experimental spectra. We have identified the C—S and C—X stretching modes and the C—S—C and H—C—X bending modes. We have listed the H—C—H bending modes and the C—H stretching modes in numerical order, we did not feel justified in making more detailed assignments. It is known empirically that the sulfides are identified by means of the relatively weak S—C

TABLE VIII

Computed frequencies in terms of cm^{-1} of methyl sulfides. We also report in parenthesis the relative IR and Raman intensity, respectively

	CH_3SCH_3	CH_2FSCH_2F	CH_2ClSCH_2Cl
C—X bend	—	74.1 (2, 0)	57.3 (2, 4)
	—	371.6 (5, 4)	296.9 (2, 8)
C—S—C bend	258.8 (0, 4)	425.3 (1, 7)	344.1 (1, 10)
C—S stretch	664.5 (7, 48)	704.4 (39, 43)	732.2 (60, 25)
	716.5 (5, 28)	732.9 (60, 23)	749.7 (80, 12)
C—X stretch	—	1130.5 (116, 2)	643.7 (80, 12)
	—	1144.0 (69, 4)	646.2 (101, 18)
H—C—H bend	1018.4 (0, 2)	992.8 (0, 3)	885.8 (2, 4)
	1045.4 (0, 10)	1082.7 (5, 8)	967.4 (7, 3)
	1075.5 (8, 8)	—	—
	1152.7 (21, 11)	—	—
	1487.3 (10, 0)	1384.1 (5, 1)	1249.1 (1, 1)
	1515.8 (2, 0)	1362.0 (1, 23)	1282.4 (2, 28)
	1637.7 (0, 48)	1462.8 (32, 3)	1354.2 (75, 1)
	1643.1 (19, 0)	1494.0 (27, 1)	1382.7 (21, 2)
	1648.2 (26, 0)	1645.6 (0, 26)	1583.5 (10, 2)
	1652.4 (2, 34)	1660.2 (1, 0)	1588.1 (2, 31)
C—H stretch	3234.2 (24, 201)	3312.2 (3, 153)	3331.4 (0, 132)
	3235.6 (27, 1)	3312.4 (32, 26)	3331.8 (1, 21)
	3325.3 (22, 105)	—	—
	3327.5 (0, 11)	—	—
	3331.9 (5, 104)	3395.6 (4, 44)	3424.5 (4, 53)
	3332.5 (2, 52)	3397.3 (4, 71)	3424.7 (6, 53)

	CH_3SCH_2F	CH_3SCH_2Cl
C—X bend	406.9 (2, 5)	319.8 (2, 9)
C—S—C bend	246.2 (4, 2)	227.6 (3, 4)
C—S stretch	673.4 (12, 47)	647.5 (29, 35)
	728.2 (36, 26)	743.5 (54, 15)
C—X stretch	1139.6 (63, 4)	634.7 (51, 36)
H—C—H bend	1011.2 (1, 3)	908.2 (2, 3)
	1076.5 (4, 8)	1073.5 (4, 9)
	1117.0 (43, 9)	1103.4 (10, 5)
	1348.9 (3, 13)	1263.4 (6, 16)
	1467.8 (30, 2)	1359.3 (51, 1)
	1505.2 (9, 0)	1504.8 (3, 0)
	1638.4 (11, 27)	1590.3 (4, 19)
	1655.6 (13, 13)	1637.5 (16, 20)
	1664.9 (2, 12)	1644.4 (14, 15)

stretching frequencies but also by a CH_2 wagging motion. This wagging mode corresponds to a very strong IR line, the frequency is at 1153 cm^{-1} for methyl sulfide, at 1463 for the difluoro compound and at 1354 cm^{-1} for the dichloro compound.

We should mention also that the CH_3SCH_2F and the CH_3SCH_2Cl spectra may be predicted from a comparison of the CH_2ClSCH_2Cl and CH_3SCH_3 spectra. Three of the sulfides are symmetric, if we were to disregard interactions between the two halves in each molecule then each vibrational mode would be two-fold degenerate since the same vibrational motion occurs in each molecular half. Due to the interaction between the two halves each two-fold degenerate vibrational mode is split into two different modes with slightly different frequencies. Each pair of matching vibrational modes is easily identified by inspecting the normal coordinates. We have found that each vibrational frequency in the CH_3SCH_2Cl molecule corresponds to the average of such a pair of frequencies in either the CH_3SCH_3 molecule or the CH_2ClSCH_2Cl molecule, the average deviation is about 10 cm^{-1}. The same correlation may be found in the corresponding fluoro compounds.

The experimental infrared and Raman spectra of methyl sulfide were reported by Fonteyne[18] and the spectrum of monochlorodimethyl sulfide is listed in the Aldrich Atlas.[15] We were unable to find experimental data for the other molecules. We have matched our theoretical data with the experimental values in Table IX by considering both the frequencies and the intensities of both sets of data. It may be seen that the C—S and C—Cl stretch frequencies agree quite well as they are and that the ratio between the experimental and theoretical H—C—H bend and C—H stretch frequencies is 0.89 ± 0.02. We should point out that the matchup between theoretical and experimental data involves some guesswork in some cases but the main features of the spectra, involving the stretch frequencies and the very strong CH_2 wag line are identified without ambiguity.

TABLE IX

Comparison of theoretical and experimental spectra of dimethyl sulfide and chlorodimethyl sulfide

	CH_3SCH_3			CH_3SCH_2Cl	
	comp	IR[18]	R[18]	comp	IR[15]
C—S—C bend	258.8	—	285	—	—
C—S stretch	663.5	685	690	674.5	697
	716.5	706	742	743.5	749
C—Cl stretch	—	—	—	634.7	640
H—C—H bend	1152.7	1037	1041	908.2	837
	1487.3	1310	1325	1073.5	961
	1515.8	1335	—	1103.4	982
	1637.7	—	1426	1263.4	1152
	1643.1	1435	—	1359.3	1233
	1648.2	1445	—	1504.8	1316
	1652.4	1459	—	1640.4	1433
C—H stretch	3234.2	—	2911	3244.0	2941
	3326	2977	2980	3326.9	3021

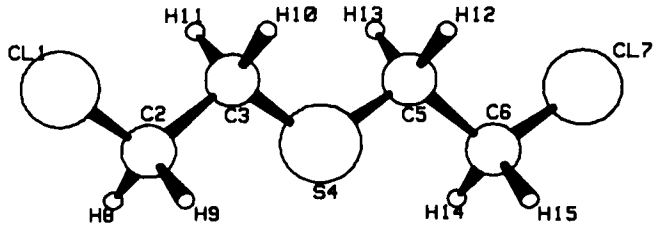

FIGURE 3. Structure of $CH_2ClCH_2SCH_2CH_2Cl$.

V. DIETHYL SULFIDES

We have calculated the structures and the vibrational infrared spectra of two ethyl sulfides, namely diethyl sulfide and dichloroethyl sulfide. In order to determine the most stable geometry of the dichloro molecule we must compute a number of different configurations obtained by rotating the CH_2Cl groups around the C—C bonds since there may be a number of equilibrium geometries. We found that the most stable geometry with the lowest energy ($E = -1465.4236100$ hartrees) corresponds to the geometry of Figure 3. Here all the chlorine and carbon atoms and the sulfur are in one plane and the chlorine is trans to the sulfur. The geometry has two symmetry planes. The equilibrium geometry of diethyl sulfide with the lowest energy ($E = -551.98728128$ hartrees) is also represented by Figure 3 if we replace the chlorine atoms by hydrogens.

The dichloroethyl molecule has another stable geometry where the two CH_2Cl groups are rotated about 120 degrees with respect to Figure 3, but this configuration has an energy which is higher by 3.96 kCal/mole. We also studied the geometry where the two CH_2Cl groups are rotated by 180 degrees relative to Figure 3 but this geometry has a considerably higher energy (14 kCal.mole) and it is not stable.

We list the geometry parameters of the two molecules $CH_2XCH_2SCH_2CH_2X$ (X = Cl, H) in Table X. We were unable to find any experimental data.

TABLE X

Geometry parameters in terms of angstroms and degrees of the two molecules ($CH_2XCH_2SCH_2CH_2X$ with X = Cl and X = H). The geometries are described in Figure 3

	X = Cl	X = H
C—S	1.896	1.891
C—C	1.513	1.533
C—X	1.895	1.085
C—H	1.077	1.080
C—H	1.074	1.083
C—S—C	98.71	100.12
S—C—C	107.40	109.11
S—C—H	108.44	107.85
C—C—X	108.25	109.96
C—C—H	113.04	110.64

Our computed vibrational frequencies for diethyl sulfide and for dichloroethyl sulfide are all presented in Table XI. We have also listed the symmetries of each vibrational mode and in the case of diethyl sulfide the relative infrared and Raman intensities. It should again be noted that the accuracy of these values is low, we only list them because they are helpful in deciding which vibrational modes are experimentally observable in either the IR or Raman spectra and which modes are not likely to be observed. The experimental infrared spectra of diethyl

TABLE XI

Computed frequencies of diethyl sulfide and dichloroethyl sulfide. We report the IR and Ram intensities (in parenthesis) for diethyl sulfide and the symmetry assignments in both cases. Experimental data are due to Kroutil[14] for dichloroethyl sulfide and due to the Aldrich[15] Atlas for diethyl sulfide

	$C_2H_5SCH_5$			$C_2H_4CISC_2H_4Cl$	
	comp	exp[15]		comp	exp[14]
B1 (1, 0)	52.9		B1	27.4	
A2 (0, 1)	78.4		A2	45.4	
A1 (0, 1)	142.2		A1	60.5	
B1 (0, 0)	253.9		A2	109.2	
A2 (0, 0)	255.0		B1	117.3	
A1 (1, 15)	337.1		B2	210.6	
B2 (2, 0)	364.3		A1	219.0	
B2 (9, 23)	683.7	689	A1	329.8	
A1 (1, 46)	696.2		B2	343.1	
A2 (0, 1)	854.9		A1	681.5	
B1 (12, 0)	874.7	778	B2	702.3	722
B2 (4, 15)	1024.1		A1	757.2	
A1 (6, 3)	1031.7	970	A1	795.5	
A2 (0, 11)	1140.4		A2	839.7	
B2 (11, 0)	1153.2	1046	B1	852.5	860
B1 (1, 7)	1154.4		A2	1032.2	
A1 (0, 12)	1196.9		B1	1049.9	905
A2 (0, 20)	1401.2		B2	1082.6	
B2 (63, 0)	1405.7	1256	A1	1114.4	1038
B1 (0, 0)	1409.1		A2	1244.5	
A1 (16, 5)	1449.5		B1	1249.5	1135
B2 (5, 4)	1579.2		B2	1360.2	1213
A1 (8, 5)	1579.2	1370	A1	1387.3	
B2 (14, 0)	1641.3		A2	1433.1	
A1 (1, 33)	1648.7		B2	1436.2	1300
B1 (18, 0)	1667.4	1447	B1	1439.5	
A2 (0, 57)	1667.7		A1	1458.8	
B2 (1, 1)	1672.5		B2	1638.6	
A1 (6, 37)	1673.0		B2	1641.1	1453
B2 (50, 40)	3204.2	2857	A1	1641.1	
A1 (2, 229)	3204.5		A1	1646.4	
B2 (1, 5)	3246.9		A1	3280.3	
A1 (13, 193)	3247.7		B2	3280.4	
B2 (13, 37)	3266.1		A1	3317.9	
A1 (56, 82)	3266.1	2899	B2	3318.1	
A2 (0, 13)	3272.4		B1	3344.5	
B1 (14, 158)	3272.6		A1	3345.5	
B1 (48, 44)	3310.4	2933	B1	3396.5	
A2 (0, 9)	3311.4		A2	3396.8	

sulfide is listed in the Aldrich Atlas.[15] The 689 line corresponds to a C—S stretch, the 970 line to the C—C stretch, the 778 to the CH_3 wagging motion and the three 2800–3000 lines to C—H stretch modes. The other lines are H—C—H bend modes. In the dichloroethyl sulfide molecule we did not derive the intensities but the spectral assignments are relatively straightforward by comparison with the other molecules. The experimental data in Table XI were supplied by Kroutil.[14] In the dichloroethyl sulfide molecule the 722 lines correspond to the C—Cl stretch, the 763 line to the C—S stretch, the 860 to the H—C—H wag, the 1038 line to the C—C stretch and the other lines to C—H bending motions. Again we find that the ratio between experimental and computed frequencies is about 1.0 for the C—Cl and C—S stretch modes, 0.93 for the C—C stretch and 0.9 for the C—H and H—C—H bending modes.

VI. DISCUSSION

We have derived the 3-21G optimized geometries and the corresponding vibrational frequencies of a group of six mercaptans, five dimethyl sulfides and two diethyl sulfides. Experimental data are available for six molecules. By comparing the experimental and computed frequencies we propose the set of correction factors that we have listed in Table XII. If the corresponding computed frequencies are multiplied by the correction factors of Table XII then we should obtain fairly accurate frequency predictions.

It should be noted that these correction factors are applicable to 3-21G computations only. By comparison, in our 6-31G* computations for methyl mercaptan we obtained good agreement by using one uniform correction factor of 0.9. Also, if we were to consider a different group of molecules we may have to use different correction factors.

It is instructive also to inspect the computed geometries of methyl mercaptan that we have listed in Table V. The experimental bond lengths are vibrationally averaged and anharmonic effects cause vibrationally averaged bond lengths to be 0.01 to 0.02 larger than equilibrium values. If we take this effect into account then the agreement for the 6-31G* computed S—H and C—H bond lengths is quite good and the agreement for the C—S bond length is still reasonable. The 3-21G computed C—S bond length is 0.08 angstrom larger than the corresponding

TABLE XII

Correction factors for 3-21G computed frequencies of mercaptans and sulfides

C—S stretch	1.00
C—Cl stretch	1.00
S—H stretch	0.98
C—H stretch	0.90
C—C stretch	0.95
C—H bend	0.90
S—H bend	0.94

6-31G* value. We believe that this error causes the C—S stretch frequency to be decreased by about 10%. The good agreement between the 3-21G computed C—S stretch frequency and the corresponding experimental value is therefore due to the accidental cancellation of the two 10% errors. We suspect that a similar accidental cancellation occurs for the C—Cl stretch frequency. However, in order to make use of 3-21G computations we should use the correction factors of Table XII, no matter what the reasons for their differences.

It may be useful to summarize our geometry results once more. In the case of mercaptans we predict a C—C—S—H dihedral angle of around 70 degrees and we found that this angle, which is somewhere between the gauch and the anti form represents the energy minimum. This prediction is consistent with the experimental information. In the case of dichloroethyl sulfide we predict a planar structure of the molecule as drawn in Figure 3.

In general, we hope that our computations contribute to the general understanding of the structure of mercaptans and sulfides and we hope that our frequency predictions are of sufficient accuracy to be of practical use.

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