New Measurements of the Infrared Spectrum of H_2S_2 and D_2S_2 and Evaluation of the Molecular Force Field *

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The infrared spectrum of H_2S_2 has been reviewed in the range 4000 to 250 cm^{-1} and the spectrum of D_2S_2 has been measured for the first time. No change in the basic assignment of the fundamental bands of H_2S_2 has been made, although the stretching fundamentals and the combination bands can be more precisely assigned on the basis of the new information.

With the six fundamental frequencies of H_2S_2 and the two asymmetric fundamental frequencies of D_2S_2, calculations were made to determine as fully as possible the general valence force field. It was found that only the diagonal force constants could be determined on the basis of the available data:

$F_{SH} = 4.08-4.09$ md/Å, $F_\alpha = 0.83-0.85$ md Å/rad^2,
$F_{SS} = 2.52-2.62$ md/Å, $F_t = 0.0926$ md Å/rad^2.

The basic features of the infrared spectrum of disulfane have been known since 1949, when Wilson and Badger[1] measured the low resolution vapor phase spectrum of the molecule and recorded the combination band $\nu_1+\nu_5$ with a resolution of 0.85 cm^{-1}. However, the spectrum of H_2S_2 has not been investigated as fully as that of the analogous H_2O_2. The Raman spectrum and chemical preparation have been thoroughly studied by Fehér et al.[2], and the infrared spectrum of crystalline H_2S_2 has been measured by Zengin and Giguère[3]. The right-angle chain structure with C_2 symmetry which was strongly indicated by earlier data was confirmed by Redington's observation of the torsional band in 1962[4]. More recently, the structure of the molecule has been established by Winnewisser and Haase[5], including a very exact value for the dihedral angle through a combination of electron diffraction and millimeterwave data. In view of the recent millimeterwave investigation of H_2S_2[6] and the very thorough studies of the vibration-rotation spectrum of H_2O_2 in the last few years[7–11], it should be possible to extract a good deal of information from the vibration-rotation spectrum of H_2S_2. The present work represents the first step in this direction. The results of a medium resolution investigation of H_2S_2 and its deuterated species is presented together with a force constant analysis based on the measurements.

Experimental

Absorption spectra in the range 4000 – 250 cm^{-1} were recorded on a Perkin-Elmer 421 double beam spectrometer with a resolution of approximately 1.0 cm^{-1} and an accuracy of ± 0.5 cm^{-1}.

Samples of H_2S_2 were prepared according to Fehér et al.[2]. The distilled disulfane was allowed to evaporate into a clean glass cell, previously acidified with dry HCl, to the room temperature vapor pressure of approximately 100 Torr. All vapor phase spectra were made with a path length of 10 cm in a large-volume cell designed to reduce wall collisions and thus decrease decomposition as much as possible.

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[2] a) F. Fehér and M. Baudler, Z. Elektrochem. **47**, 844 [1941]; b) F. Fehér and W. Laue, Z. Anorg. Allg. Chem. **288**, 103 [1956]; c) F. Fehér, W. Laue, and G. Winkhaus, Z. Anorg. Allg. Chem. **288**, 113 [1956].

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[5] M. Winnewisser and J. Haase, Z. Naturforsch. **23 a**, 56 [1968].

[6] a) G. Winnewisser, M. Winnewisser, and W. Gordy, Bull. Am. Phys. Soc. **11**, 312 [1966]; b) G. Winnewisser, M. Winnewisser, and W. Gordy, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, September 1966, Abstract AA7; c) G. Winnewisser, Thesis, Duke University 1967.

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[8] R. L. Redington, W. B. Olson, and P. C. Cross, J. Chem. Phys. **36**, 1311 [1962].

[9] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, J. Chem. Phys. **42**, 1931 [1965].

[10] H. Dreizler, Z. Naturforsch. **21 a**, 1628 [1966].

[11] R. H. Hunt and R. A. Leacock, J. Chem. Phys. **45**, 3141 [1966].

Deuterated disulfane was prepared by exchanging a small amount of the raw oil, H_2S_x, in a solution of DCl in D_2O by shaking at room temperature for up to 72 hours. The resulting mixture of isotopic species was then cracked in the usual manner described by Fehér et al.[2]. A full deuteration is not possible by this method, but a yield of approximately 50% DSSD and 40% HSSD was achieved, as estimated from the infrared spectra.

Liquid spectra were obtained at room temperature with a capillary layer of the liquid which was frequently changed.

Gas Phase Spectra

Additional information has been obtained on all bands of H_2S_2 below 4000 cm^{-1}, although no new absorptions were observed. The fundamental assignment of Wilson and Badger is retained, and the combination bands are more specifically assigned on the basis of the new information. The assignment is summarized in Table 5, and the absorptions are discussed in descending order of frequency.

3437 cm^{-1} band

The rather weak band at 3437 cm^{-1} shows clearly a perpendicular component, as illustrated in Fig. 1, but no indication of a parallel component. The band is therefore assigned to the symmetric combination $\nu_5 + \nu_6$. The assignment of the Q branches giving the ground state rotational constant most in agreement with the value from the pure rotational spectrum is indicated in Table 1 and yields a center frequency of 3437.0 cm^{-1}. The rotational constants are given in Table 4. Terms involving the $^RQ_0$ and $^PQ_1$ branches were omitted in averaging the combination differences because the slight asymmetry is sufficient to cause an observable deviation from the symmetric top frequencies expected for these branches. This symmetric stretch-bend combination has not been observed in the spectrum of H_2O_2. On the contrary, the two asymmetric stretch-bend combinations $\nu_1 + \nu_6$ and $\nu_2 + \nu_5$ are observed in H_2O_2 [8], but not in H_2S_2. The band $\nu_2 + \nu_6$, also observed in H_2O_2, could not be detected in the spectrum of H_2S_2 with the available absorption intensity. This indicates the limitation of analogies between the spectra of H_2O_2 and H_2S_2.

3074 cm^{-1} band

This absorption shows a weak parallel structure, sufficing to assign it definitely to the asymmetric combination $\nu_3 + \nu_5$, but too weak to measure detail other than the absorption minimum at 3074 cm^{-1}.

2560 cm^{-1} band

The S – H stretching absorption has the form shown in Fig. 2. There is a strong parallel component, indicative of the asymmetric hybrid vibration ν_5, and perpendicular Q branches which are doubled with an average spacing of 2.95 cm^{-1}. No doubling corresponding to the doubling of these Q branches could be established in the parallel component. Similar data has been obtained by Wilkinson and Wilson[12]. The absence of torsional doubling in the $\nu_5 + \nu_1$ combination band and in the torsional absorption itself, as discussed below, lead to the conclusion that the double Q branches cannot be caused by an energy level splitting due to torsion, as is the case with H_2O_2. The most reasonable explanation, proposed by Redington[4], is that the lower frequency set of Q branches belong to the symmetric vibration ν_1, and the higher frequency set, along with the parallel component, to the hybrid vibration ν_5. This assignment is assumed in Fig. 2. The ap-

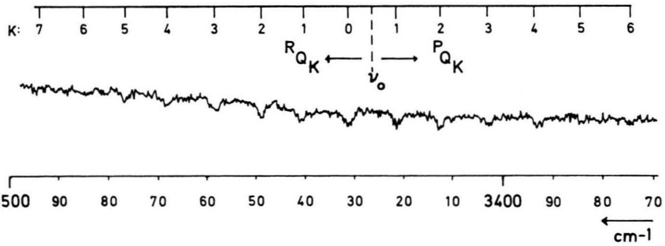

Fig. 1. Infrared spectrum of H_2S_2 in the region 3500 – 3370 cm^{-1}.

K	^RQ_K cm^{-1}	^PQ_K cm^{-1}
0	3441.3	
1	3450.9	3432.7
2	3460.0	3422.9
3	3469.2	3413.4
4	3478.0	3404.3
5	3486.6	3394.8
6		3384.9

Table 1. Measured absorption peaks in the combination band $\nu_5 + \nu_6$.

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[12] G. R. Wilkinson and M. K. Wilson, unpublished.

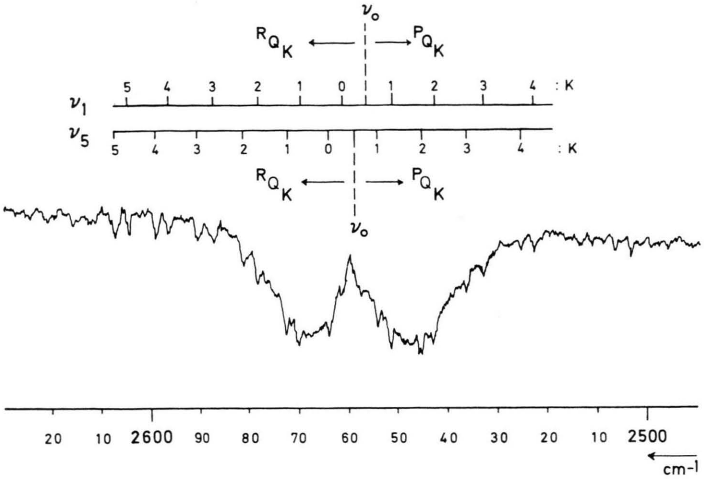

Fig. 2. Infrared spectrum of H_2S_2 in the region 2630−2500 cm^{-1}.

	K	ν_5 cm^{-1}	ν_1 cm^{-1}
^RQ_K:	5	2607.3	2604.4
	4	2598.9	2595.8
	3	2589.7	2586.9
	2	2580.7	2577.8
	1	2572.1	2569.3
	0	2563.1	2560.1
^PQ_K:	1	2553.7	2551.1
	2	2544.5	2541.9
	3	2535.2	2532.1
	4	2525.3	2522.3
^QQ:		2557.0	

Table 2. Measured absorption peaks in the S−H stretching region.

parently identical intensity of the two sets can be explained in terms of the structure determined by WINNEWISSER and HAASE [5], which gives a dihedral angle of 90° 37′, and the fact that the C_2 axis is along the c-axis of the inertial ellipsoid [6]. Therefore the species A vibrations (ν_1 to ν_4) involve c-type transitions and the species B vibrations (ν_5 and ν_6) involve a- and b-type transitions. The perpendicular component of the change in dipole moment is along the c-axis for ν_1, and along the b-axis for ν_5, but because of the 90° angle must be of the same magnitude in both vibrations.

The difference between c-type and b-type transitions gives a means of checking this assignment. Since the Wang asymmetry parameter is known ($b_p = -1.11 \times 10^{-5}$) [6], the effect of the slight asymmetry, noticeable only for the $K=1$ levels, can be calculated. The resulting effective shift of the $^RQ_0$ and $^PQ_1$ absorptions relative to the spectrum of a symmetric top can be estimated. A rough calculation predicts that the $^RQ_0$ branches of the two bands should be at least 0.14 cm^{-1} farther apart, and the $^PQ_1$ branches 0.14 cm^{-1} closer together than the other pairs of Q branches. Differently expressed, a plot of the frequency difference between neighboring Q branches versus the interval number will be a straight line for a symmetric top. For a very slightly asymmetric top it will show a sharp peak at $^RQ_0 - {}^PQ_1$ which is positive for b-type and negative for c-type bands. The data of WILSON and BADGER for $\nu_5 + \nu_1$ (hybrid, perpendicular component b-type) show a peak of 0.7 cm^{-1}. The present data for $\nu_5 + \nu_6$ show a peak of -0.7 cm^{-1}, with the minus sign expected for the c-type transitions. Thus it must be possible to apply this criterion to the Q branches of the S−H stretching absorption. Unfortunately, the accuracy of the measurements of these weak Q branches, listed in Table 2, is not sufficient to definitely establish such a shift or to calculate meaningful rotational constants.

The higher frequency set of Q branches and the minimum of the parallel component yield a center frequency of 2559.5 cm^{-1} for ν_5 and 2556.5 cm^{-1} for ν_1.

882 cm^{-1} band

The parallel shape of the strong band at 882 cm^{-1} identifies it as the asymmetric hybrid bending vibration ν_6. No Q branches which could be attributed to a perpendicular component were observed. As can be seen in Fig. 3, the ^QQ branch of the parallel absorption could clearly be distinguished. It is observed to converge in the high-frequency direction, opposite to the direction of convergence of the ^QQ branch of ν_5. This indicates that $(A' - B') - (A'' - B'')$ is negative for ν_5 and positive for ν_6.

416 cm^{-1} band

The torsional absorption, ν_4, was first observed by REDINGTON with a resolution of 5.0 cm^{-1} (l. c. Ref. [4]). As shown in Fig.4, we have traced it with a resolution of 1.0 cm^{-1}. A broad absorption reported by REDINGTON centered at 475 cm^{-1} cannot be observed in our spectrum, and proved to be an absorption from decomposition products on the cell windows or mirrors. Liquid spectra, described below, gave further confirmation of this explanation.

K	${}^{R}Q_K$ cm^{-1}	${}^{P}Q_K$ cm^{-1}
0	421.1	
1	429.9	412.0
2	439.5	402.1
3	447.9	393.6
4	457.6	384.1
5	466.4	374.3
6	474.9	365.3
7	484.7	357.5 354.7
8	492.1	348.2 345.7
9	501.6	338.6 335.8
10	509.6	327.1 324.4
11	519.1	319.6 316.1
12	527.6	

Table 3. Measured absorption peaks in the torsional band ν_4.

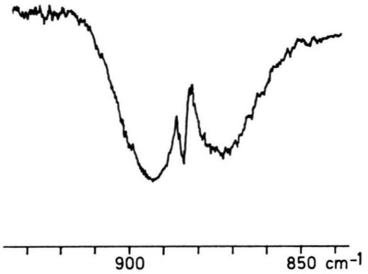

Fig. 3. Infrared spectrum of H_2S_2 in the region 950−850 cm^{-1}.

Our data reduces the upper limit on a torsional doubling to 1.0 cm^{-1}. At the same time, millimeter-wave measurements of molecules in the first excited torsional state indicate a torsional doubling of about 16 MHz [6]. This is not resolvable by means of infrared methods, and is therefore consistent with our data. The irregular splitting of the ${}^{P}Q_K$ branches for $K \geqq 7$ will be discussed when high resolution data are available. The satellites to the low frequency side of each Q branch can be reasonably assigned to the hot band $2\nu_4 - \nu_4$. The Q branch absorption frequencies for the main band, ν_4, are listed in Table 3. The rotational constants from ν_4, given in Table 4, give poor agreement with millimeter values, as compared with the rotational constants of $\nu_5 + \nu_6$. For the latter absorption, the experimental scatter is ±0.4 cm^{-1}, whereas for ν_4 the scatter is ±1.0 cm^{-1}, mainly because of limitations of mechanical accuracy.

Deuterated Species

Due to the fact that the samples of deuterated disulfane contained at most 50% DSSD, the intensity of the signal was correspondingly reduced, and the data are not as complete as the HSSH data. The use of a reflection cell was rejected because of the inevitable increase of decomposition, leading to spurious absorptions such as REDINGTON observed.

Absorption	$A' - \bar{B}'$ cm^{-1}	$A'' - \bar{B}''$ cm^{-1}
$\nu_5 + \nu_1$	4.50 [a]	4.64 [a]
$\nu_5 + \nu_6$	4.62	4.66
ν_4	4.59	4.59
Pure rotational transitions, ground state		4.666 [b]
Pure rotational transitions, ν_4	4.640 [b]	

Table 4. Rotational constants of H_2S_2.
[a] Reference [1], [b] reference [6].

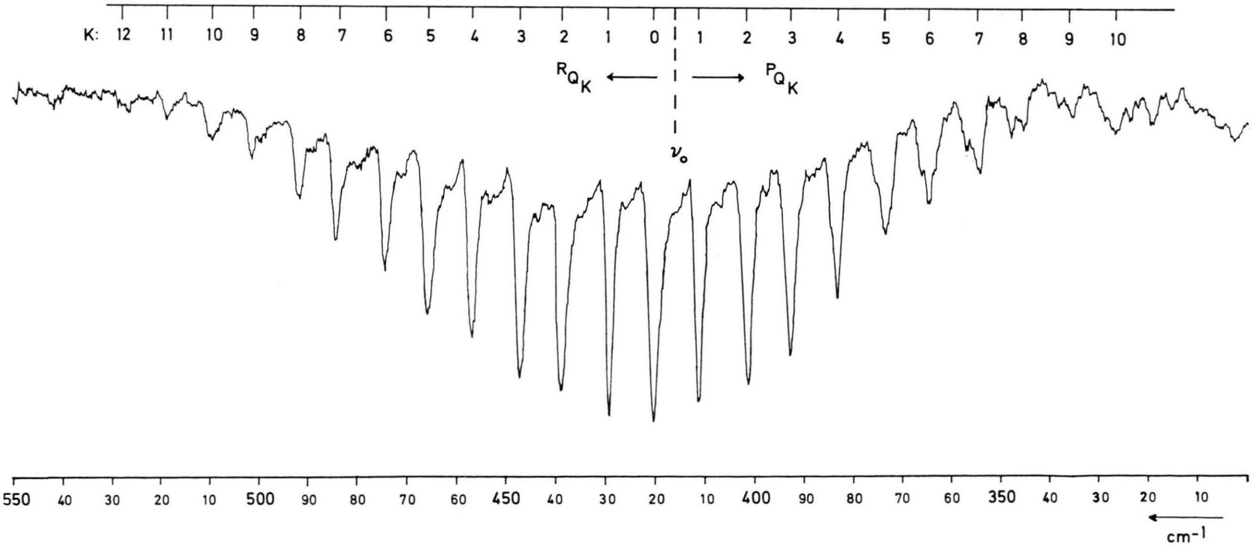

Fig. 4. The infrared torsional absorption ν_4 of H_2S_2 in the region 550−300 cm^{-1}.

The only absorption which could definitely be assigned to HSSD, even when this species attained approximately 50% of the sample, was the torsional vibration. The loss of nuclear spin multiplicity and the change in orientation of the dipole moment relative to the *b*- and *c*-axes in the HSSD species results in a sharp drop in absorption intensity relative to the symmetric species of the molecule.

The fundamentals ν_5 and ν_6 of DSSD as well as the torsional fundamental ν_4 of both species were observed and are shown in Fig. 5. In addition, the combination band $\nu_1 + \nu_5$ of DSSD was observed. The center frequencies of the observed bands are given in Table 5. The band forms are consistent with those of H_2S_2, although no perpendicular Q branches could be distinguished for ν_5 of DSSD. The product rule for the asymmetric vibrations ν_5 and ν_6 predicts a ratio of deuterated to undeuterated frequencies of 0.521. The experimental ratio is 0.531, which, considering anharmonicity, is satisfactory agreement.

The *K* assignment of the Q branches in the torsional bands is somewhat uncertain. However the rotational constants obtained confirm the assignment of the two groups of Q branches to the two deuterated species. The predicted value of $A - \overline{B}$ for HSSD, using structural parameters of HSSH, is 2.98 cm^{-1}; the value obtained from the strongest six lines of the higher frequency absorption in Fig. 5 c is 2.92 cm^{-1}. The predicted value of $A - \overline{B}$ for DSSD is 2.21 cm^{-1}, whereas the average spacing of the thirteen Q branches assigned to DSSD gives a value of 2.26 cm^{-1}.

Liquid Spectra

Traces of the spectra obtained for liquid D_2S_2 and H_2S_2 are shown in Fig. 6 along with that of H_2S_3 for comparison. Although the samples were pure to start with, it was difficult to insure spectra free from absorptions of decomposition products. A comparison of the H_2S_3 spectrum with that of H_2S_2, however, indicates that the absorptions recorded with H_2S_2 are not due to higher sulfanes, in spite of obvious similarities in the spectra. It was noted only that an absorption at 478 cm^{-1} in disulfane, which was very weak in fresh samples, increased in strength until after 15 or 20 minutes it was stronger than the neighboring torsional vibration. H_2S_3 shows a strong absorption at this frequency. This same absorption may be that observed by Redington in the gas phase spectrum at about this frequency, and which appeared in our spectra when decomposition was very far advanced. Since S_8 also has a strong absorption at 475 cm^{-1} (l. c. Ref. [13]), it must be considered that the observed

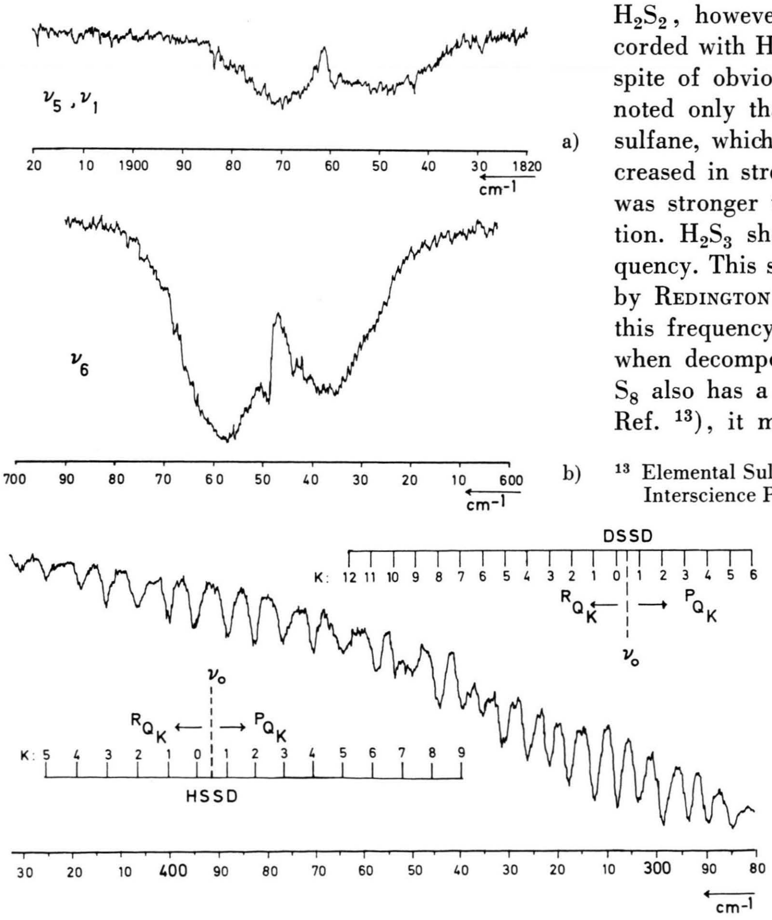

Fig. 5. The infrared spectrum of D_2S_2 in the regions a) 1920 – 1820 cm^{-1} and b) 700 – 600 cm^{-1}, and c) the torsional spectrum of D_2S_2 and HSSD in the region 430 – 280 cm^{-1}.

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[13] Elemental Sulfur, Chemistry and Physics, Beat Meyer, ed., Interscience Publishers, New York 1965, p. 243.

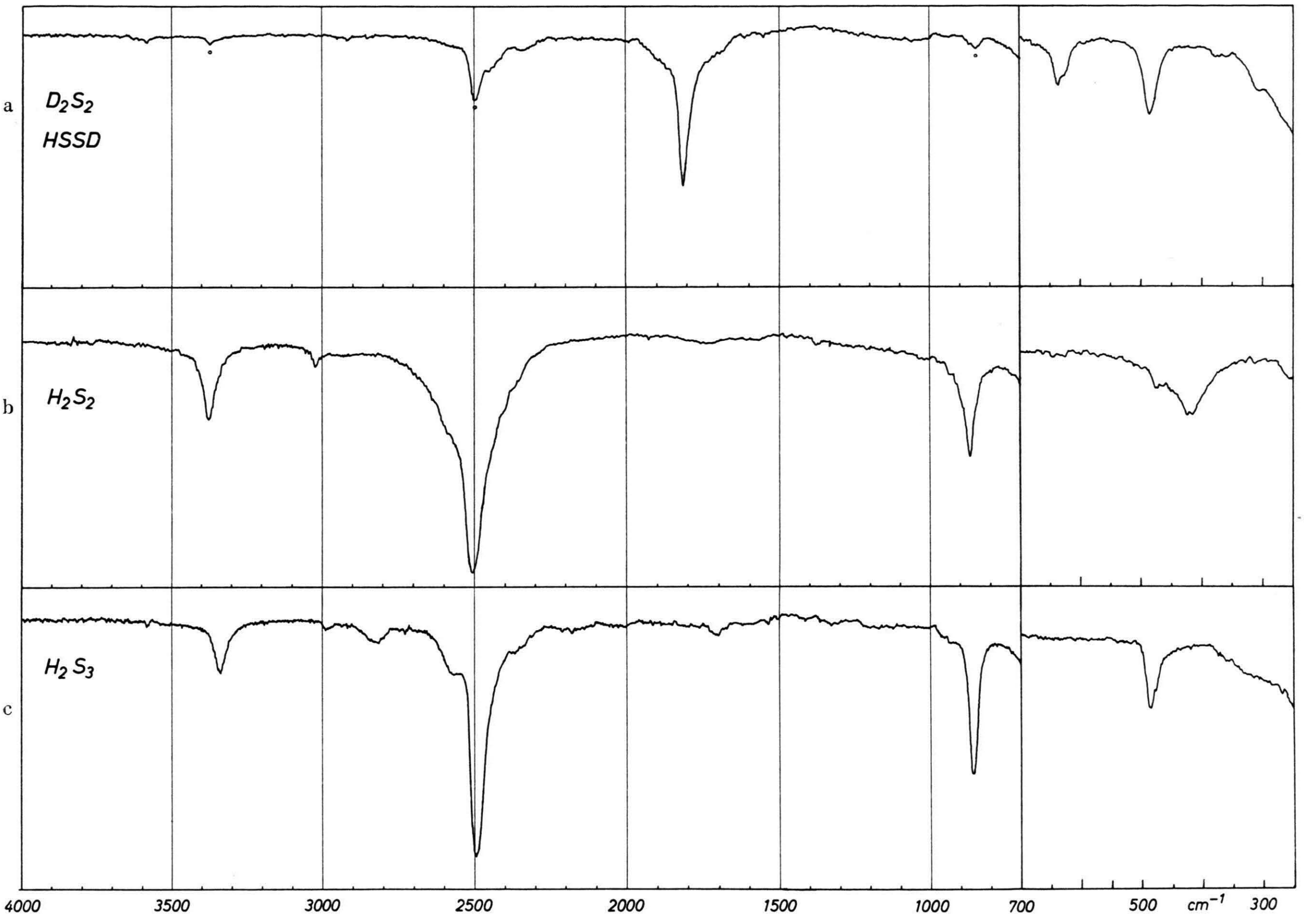

Fig. 6. Infrared absorptions in the liquid of a) deuterated H_2S_2, b) H_2S_2 and c) H_2S_3. In a) absorptions marked with a circle are due to residual H_2S_2 in the sample.

H_2S_2 Raman, liquid cm^{-1}	H_2S_2 Infrared, liquid cm^{-1}	H_2S_2 Infrared, vapor cm^{-1}	Assignment	D_2S_2 Infraed, vapor $cm^{-}r^{1}$	D_2S_2 infra-red, liquid cm^{-1}
		5007.2[b]	$\nu_5+\nu_1$	3663	3508[d]
	3370	3437.0	$\nu_5+\nu_6$		2430
	3020	3074.0	$\nu_3+\nu_5$		
	2505	2559.5	ν_5	1863	1825
2509[a]	2505	2556.5	ν_1		
			ν_1, ν_5 (HSSD) ?		2330
	870	882.0	ν_6	646.4	636
883[a]			ν_2		
509[a]			ν_3		
	478		?		485
	420	416.5	ν_4	306[c]	300[d]
		412	$2\nu_4-\nu_4$		
			ν_4 (HSSD)	365[c]	391[d]

Table 5. Measured frequencies of the Raman and infrared spectrum of H_2S_2 and D_2S_2 in the liquid and vapor phase. [a] Reference [2c]. [b] Reference [1]. [c] Assignment uncertain by ±1 unit of K. [d] Very weak absorption.

absorptions between 475 and 485 cm^{-1} could be due either to sulfur or to H_2S_3 and higher sulfanes. This applies also to the rather strong absorption in the liquid spectrum of the deuterated species at 482 cm^{-1}.

Frequencies and assignments are given in Table 5 for all observed absorptions of H_2S_2 and D_2S_2 including the Raman frequencies.

Force Constant Calculations

From the combined frequencies of the Raman spectrum and of the liquid and gaseous infrared spectra, appropriate gas phase frequencies for a force constant analysis can be derived. By noting the shift from liquid to gas for ν_1, ν_4, ν_5 and ν_6, the liquid-gas shift for those fundamentals of H_2S_2 not observed in the gas, that is ν_2 and ν_3, could be reasonably estimated. The two asymmetric vibrations ν_5 and ν_6 of D_2S_2 were also used, giving a total of 8 frequencies for the calculations. Positive anharmonicity constants were assumed proportional to those known for H_2S for the H – S stretch and the HSS bending modes, and corrections of 3% for the D – S stretch, 1.5% for the DSS bend (so that the product rule is exactly satisfied) and 1% for the torsional mode. The harmonic frequencies used are listed in Table 7 with the results of the force constant calculations.

The force constants were calculated according to the *GF* matrix method of WILSON with an iteration program developed by HÜTTNER[14]. The *G* matrix was evaluated from the *G* matrix elements of H_2O_2 given by DECIUS[15] using the molecular parameters listed in Table 6.

r(S–H) = 1.352 ± 0.015 Å
r(S–S) = 2.055 ± 0.001 Å
α (HSS) = 91°57′ ± 30′
τ (dihedral angle) = 90°37′ ± 3′

Table 6. Molecular structure parameters of H_2S_2 as given in Reference [5].

The six internal valence coordinates correspond to a general valence force field of 13 independent force constants. In calculating the force field of H_2O_2, the assumption is made that the torsional coordinate can be factored out of the matrix of the symmetric vibrations. The basis of this simplification is the near collinearity of the torsion axis with the main axis of the inertial tensor[16]. The greater mass of the S atoms brings these two axes even closer together in H_2S_2, so that this same approximation is possible. The valence force field potential used for these calculations, omitting torsion, has the form

$$\begin{aligned} 2V = {} & F_{\mathrm{SH}}[(\Delta r_{\mathrm{SH_1}})^2 + (\Delta r_{\mathrm{SH_2}})^2] + F_{\mathrm{SS}}(\Delta r_{\mathrm{SS}})^2 \\ & + F_{\alpha}[(\Delta\alpha_1)^2 + (\Delta\alpha_2)^2] \\ & + 2F_{\mathrm{SH,SS}}(\Delta r_{\mathrm{SS}})[(\Delta r_{\mathrm{SH_1}}) + (\Delta r_{\mathrm{SH_2}})] \\ & + 2F_{\mathrm{SH},\alpha}[(\Delta r_{\mathrm{SH_1}})(\Delta\alpha_1) + (\Delta r_{\mathrm{SH_2}})(\Delta\alpha_2)] \\ & + 2F_{\mathrm{SS},\alpha}(\Delta r_{\mathrm{SS}})[(\Delta\alpha_1) + (\Delta\alpha_2)] \\ & + 2F_{\mathrm{SH,SH'}}(\Delta r_{\mathrm{SH_1}})(\Delta r_{\mathrm{SH_2}}) + 2F_{\alpha,\alpha'}(\Delta_1)(\Delta\alpha_2) \\ & + 2F_{\mathrm{SH},\alpha'}[(\Delta r_{\mathrm{SH_1}})(\Delta\alpha_2) + (\Delta r_{\mathrm{SH_2}})(\Delta\alpha_1)]. \end{aligned}$$

As a check on the above assumption, we calculated the force constants both with and without the torsional contribution to the potential, $F_t(\Delta\tau)^2$. The calculations with torsion but with the three torsional interaction constants set equal to zero resulted in a torsional force constant of 0.0926 md Å/rad² or 0.051 md/Å, which agrees well with the value found for S_8 which is 0.040 md/Å[17]. The other force constants in this calculation differed from the values obtained without the torsion only in the fourth significant figure.

Omitting torsion there are 7 frequencies available to calculate 9 force constants. Since one degree of freedom was used in adjusting the harmonic frequencies of the asymmetric vibrations to fit the product rule, we have actually only 6 independent frequencies. The simplest assumption is to set the interaction constants $F_{\mathrm{SH,SH'}}$, $F_{\mathrm{SH},\alpha'}$ and $F_{\alpha,\alpha'}$ equal to zero. This assumption is somewhat justified by the near identity of the two stretching frequencies and of the two bending frequencies, and was applied for the bulk of the calculations.

In spite of this reduction of the number of unknowns, it was found that the three interaction constants included in the calculations, $F_{\mathrm{SH,SS}}$, $F_{\mathrm{SH},\alpha}$ and $F_{\mathrm{SS},\alpha}$, could not be uniquely determined. The calculations converged rapidly for a whole family of different initial force constants, giving nearly the identical diagonal force constants but with all possible combinations of interaction constants within the range investigated. The frequencies are not very sensitive to the interaction constants, and the asymmetric vibrations of the deuterated species are not sufficient to determine them. The force constants given in Table 7 are thus limited to the diagonal force constants, listed as the range of values for which a solution was obtained with various values of the interaction constants within the given limits. Some of the interaction force constants can probably be determined if additional information is obtained in the form of centrifugal distortion constants or Raman data for D_2S_2[17a]. Information from the amplitudes of vibra-

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[14] W. HÜTTNER, Thesis, Technische Hochschule Karlsruhe 1965.

[15] J. C. DECIUS, J. Chem. Phys. **16**, 1025 [1948]. A difference was noticed in the sign of the second term of s_{t2} as given in Molecular Vibrations, E. B. WILSON, J. C. DECIUS, and P. C. CROSS, McGraw-Hill, N. Y. 1955, p. 61, and in this reference. The sign in this reference proved to be correct.

[16] R. L. REDINGTON, Thesis, University of Washington 1961.

[17] D. W. SCOTT, J. P. MCCULLOUGH, and F. H. KRUSE, J. Mol. Spectry **13**, 313 [1964].

[17a] Note added in proof: Calculations using assumed values for the symmetric frequencies of D_2S_2, show that the interaction constante $F_{\alpha,\alpha}$, and $F_{\mathrm{SS},\alpha}$ can be determined, but that these frequencies are not sufficient to determine $F_{\mathrm{SH},\alpha}$, $F_{\mathrm{SH,SS}}$ or $F_{\mathrm{SH},\alpha'}$.

Symmetry		Harmonic frequencies obs. cm^{-1}	calc. cm^{-1}	Force Constants
A	ω_1	2661	2663.7 – 2665.0	$F_{SH} = 4.08 - 4.09$ md/Å
	ω_2	920	906.0 – 917.9	$F_\alpha = 0.83 - 0.85$ md Å/rad^2
	ω_3	509	508.9 – 509.0	$F_{SS} = 2.52 - 2.62$ md/Å
	ω_4	420	420.0	$F_t = 0.0926$ md Å/rad^2
				$F_{SH.SS} = \pm 0.30$ md/Å
B	ω_5	2662	2663.1 – 2665.5	$F_{SH,\alpha} = \pm 0.10$ md/rad
	ω_6	906	904.0 – 911.4	$F_{SS,\alpha} = \pm 0.10$ md/rad
B	ω_5^D	1916	1912.0 – 1914.2	
	ω_6^D	656	657.0 – 662.4	

Table 7. Results of Force Constant Calculations of H_2S_2.

tion of the S – H and S – S bonds as evaluated from the electron diffraction data was considered, but the estimated experimental uncertainties of the vibrational amplitudes are larger than the variations that would be caused by varying the force constants within the ranges given in Table 7.

The S – H stretching force constant is noticeably smaller than the value of 4.28 md/Å obtained for H_2S [18]. This is in keeping with the longer S – H bond length determined by electron diffraction of H_2S_2. The S – S stretching force constant shows the greatest dependence on the interaction force constants. The range of values found includes the value found for $(CH_3)_2S_2$ of 2.55 md/Å [19] but is somewhat higher than the value calculated for S_8 of 2.366 md/Å [17]. The values found correspond more or less to what can be expected for a sulfur-sulfur single bond. Force constants have also been calculated for Cl_2S_2 and Br_2S_2, which have S – S bond lengths of 1.97 and 1.98 Å respectively. In a Urey-Bradley potential the S – S stretching force constant is 2.46 md/Å [20] as oposed to a value of 1.849 md/Å for S_8 with a Urey-Bradley potential [17]. Bond length and S – S stretching force constant in these two halogensulfides indicate a pronounced double-bond character in the S – S bonding. Although the high torsional potential of H_2S_2 can only be explained in terms of 3d orbital interaction, the effect of this interaction on the S – S stretching potential is very small.

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