New Measurements of the Infrared Spectrum of $\text{H}_2\text{S}_2$ and $\text{D}_2\text{S}_2$ and Evaluation of the Molecular Force Field

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The infrared spectrum of $\text{H}_2\text{S}_2$ has been reviewed in the range 4000 to 250 cm$^{-1}$ and the spectrum of $\text{D}_2\text{S}_2$ has been measured for the first time. No change in the basic assignment of the fundamental bands of $\text{H}_2\text{S}_2$ 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 $\text{H}_2\text{S}_2$ and the two asymmetric fundamental frequencies of $\text{D}_2\text{S}_2$, 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:

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

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 $\nu_1 + \nu_2$ with a resolution of 0.85 cm$^{-1}$. However, the spectrum of $\text{H}_2\text{S}_2$ has not been investigated as fully as that of the analogous $\text{H}_2\text{O}_2$. The Raman spectrum and chemical preparation have been thoroughly studied by Fernè et al. 2, 3, and the infrared spectrum of crystalline $\text{H}_2\text{S}_2$ has been measured by Zengin and Giugère 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, 6, 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 $\text{H}_2\text{S}_2$ 5 and the very thorough studies of the vibration-rotation spectrum of $\text{H}_2\text{O}_2$ in the last few years 7–11, it should be possible to extract a good deal of information from the vibration-rotation spectrum of $\text{H}_2\text{S}_2$. The present work represents the first step in this direction. The results of a medium resolution investigation of $\text{H}_2\text{S}_2$ 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 $\text{H}_2\text{S}_2$ were prepared according to Fernè 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.


Deuterated disulfane was prepared by exchanging a small amount of the raw oil, H$_2$S$_2$, in a solution of DC$_2$ in D$_2$O 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 Ferder et al. 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$_2$S$_2$ 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 $v_5 + v_6$. 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 $^bQ_0$ and $^pQ_0$ 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$_2$O$_2$. On the contrary, the two asymmetric stretch-bend combinations $v_1 + v_5$ and $v_2 + v_5$ are observed in H$_2$O$_2$, but not in H$_2$S$_2$. The band $v_2 + v_6$, also observed in H$_2$O$_2$, could not be detected in the spectrum of H$_2$S$_2$ with the available absorption intensity. This indicates the limitation of analogies between the spectra of H$_2$O$_2$ and H$_2$S$_2$.

### 3074 cm$^{-1}$ band

This absorption shows a weak parallel structure, sufficing to assign it definitely to the asymmetric combination $v_3 + v_5$, 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 $v_5$, 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. The absence of torsional doubling in the $v_5 + v_1$ 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$_2$O$_2$. The most reasonable explanation, proposed by Redington, is that the lower frequency set of Q branches belong to the symmetric vibration $v_1$, and the higher frequency set, along with the parallel component, to the hybrid vibration $v_5$. This assignment is assumed in Fig. 2. The ap-

<table>
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Table 1. Measured absorption peaks in the combination band $v_5 + v_6$.

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

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<tr>
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<td>2595.8</td>
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<td>2580.7</td>
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</tr>
<tr>
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<td>2560.1</td>
</tr>
<tr>
<td>$P Q_K$:</td>
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<td></td>
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<tr>
<td>$Q Q$:</td>
<td>2557.0</td>
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The difference between c-type and b-type transitions gives a means of checking this assignment. Since the Wang asymmetry parameter is known ($b_\phi = -1.11 \times 10^{-5}$), the effect of the slight asymmetry, noticeable only for the $K = 1$ levels, can be calculated. The resulting effective shift of the $R Q_0$ and $P Q_1$ absorptions relative to the spectrum of a symmetric top can be estimated. A rough calculation predicts that the $R Q_0$ branches of the two bands should be at least 0.14 cm$^{-1}$ farther apart, and the $P Q_1$ 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 $R Q_0 - P Q_1$ which is positive for b-type and negative for c-type bands. The data of Wilson and Badger for $v_5 + v_1$ (hybrid, perpendicular component b-type) show a peak of 0.7 cm$^{-1}$. The present data for $v_5 + v_6$ 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 $v_5$ and 2556.5 cm$^{-1}$ for $v_1$.

882 cm$^{-1}$ band

The parallel shape of the strong band at 882 cm$^{-1}$ identifies it as the asymmetric hybrid bending vibration $v_5$. No Q branches which could be attributed to a perpendicular component were observed. As can be seen in Fig. 3, the $Q Q$ 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 $Q Q$ branch of $v_5$. This indicates that $(A' - B') - (A'' - B'')$ is negative for $v_5$ and positive for $v_6$.

416 cm$^{-1}$ band

The torsional absorption, $v_4$, 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.

<table>
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<th>$pQ_K$ cm$^{-1}$</th>
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<td>327.1</td>
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<td>11</td>
<td>519.1</td>
<td>319.6</td>
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<tr>
<td>12</td>
<td>527.6</td>
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Table 3. Measured absorption peaks in the torsional band $\nu_4$.

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 $pQ_K$ branches for $K \geq 7$ 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, $\nu_4$, are listed in Table 3. The rotational constants from $\nu_4$, 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 $\pm 0.4$ cm$^{-1}$, whereas for $\nu_4$ the scatter is $\pm 1.0$ 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.

<table>
<thead>
<tr>
<th>Absorption</th>
<th>$A' - B'$ cm$^{-1}$</th>
<th>$A'' - B''$ cm$^{-1}$</th>
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<td>$\nu_5 + \nu_1$</td>
<td>4.50$^a$</td>
<td>4.64$^a$</td>
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<td>$\nu_5 + \nu_6$</td>
<td>4.62</td>
<td>4.66</td>
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<tr>
<td>$\nu_4$</td>
<td>4.59</td>
<td>4.59</td>
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<tr>
<td>Pure rotational transitions, ground state</td>
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<tr>
<td>Pure rotational transitions, $\nu_4$</td>
<td>4.666$^b$</td>
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</table>

Table 4. Rotational constants of H$_2$S$_2$.

$^a$ Reference 1, $^b$ reference 6.

Fig. 4. The infrared torsional absorption $\nu_4$ of H$_2$S$_2$ 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 \( \nu_5 \) and \( \nu_6 \) of DSSD as well as the torsional fundamental \( \nu_4 \) 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 \( \text{H}_2\text{S}_2 \), although no perpendicular Q branches could be distinguished for \( \nu_5 \) of DSSD. The product rule for the asymmetric vibrations \( \nu_5 \) and \( \nu_6 \) predicts a ratio of deuterated to undeuterated frequencies of 0.521. The experimental ratio is 0.531, which, considering anharmonicity, is satisfactory agreement.

The 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 \( A - B \) 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 \( A - B \) 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 \( \text{D}_2\text{S}_2 \) and \( \text{H}_2\text{S}_2 \) are shown in Fig. 6 along with that of \( \text{H}_2\text{S}_3 \) 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 \( \text{H}_2\text{S}_3 \) spectrum with that of \( \text{H}_2\text{S}_2 \), however, indicates that the absorptions recorded with \( \text{H}_2\text{S}_2 \) 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. \( \text{H}_2\text{S}_3 \) 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 \( \text{S}_8 \) also has a strong absorption at 475 cm\(^{-1}\) (l.c. Ref. 13), it must be considered that the observed

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Infrared absorptions in the liquid of a) deuterated H$_2$S$_2$, b) H$_2$S$_2$ and c) H$_2$S$_3$. In a) absorptions marked with a circle are due to residual H$_2$S$_2$ in the sample.

The frequencies and assignments are given in Table 5 for all observed absorptions of H$_2$S$_2$ and D$_2$S$_2$ 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 $v_1$, $v_4$, $v_5$ and $v_6$, the liquid-gas shift for those fundamentals of H$_2$S$_2$ not observed in the gas, that is $v_3$ and $v_4$, could be reasonably estimated. The two asymmetric vibra-
tions \(v_5\) and \(v_6\) of \(D_2^+S_2\) 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 \(-S\) stretch and the HSS bending modes, and corrections of 3\% for the \(-D\) 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 Hüttnerr. The GF matrix was evaluated from the \(G\) matrix elements of \(H_2O_2\) given by Decius using the molecular parameters listed in Table 6.

\[
\begin{align*}
\tau(S-H) &= 1.332 \pm 0.015 \text{ Å} \\
\tau(S-S) &= 2.055 \pm 0.001 \text{ Å} \\
\varphi (\text{HSS}) &= 91.57' \pm 30' \\
\tau (\text{dihedral angle}) &= 90.37' \pm 3'
\end{align*}
\]

Table 6. Molecular structure parameters of \(H_2S_2\) as given in Reference 4.

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. 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

\[
2V = F_{SH}[(\Delta r_{SH})^2 + (\Delta r_{SH'})^2] + F_{SS}(\Delta r_{SS})^2 \\
+ F_\alpha[(\Delta \alpha_1)^2 + (\Delta \alpha_2)^2] \\
+ 2F_{SH,SS}(\Delta r_{SS})[(\Delta r_{SH}) + (\Delta r_{SH'})] \\
+ 2F_{SH,\alpha}(\Delta r_{SH})(\Delta r_{SH'}) + (\Delta r_{SH}) + (\Delta r_{SH'}) \\
+ 2F_{SS,\alpha}(\Delta r_{SS})(\Delta r_{SS}) + 2F_{SS,\alpha}(\Delta \alpha_1)(\Delta \alpha_2) \\
+ 2F_{SH,\alpha,\alpha}(\Delta r_{SH})(\Delta r_{SH'}) + (\Delta r_{SH})(\Delta \alpha_1)
\]

As a check on the above assumption, we calculated the force constants both with and without the torsional contribution to the potential, \(F_1(\Delta r)^2\). 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. 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 \(F_{SH,SS}, F_{SH,\alpha},\) and \(F_{SS,\alpha}\) 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, \(F_{SH,SS}, F_{SH,\alpha},\) and \(F_{SS,\alpha}\), 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 \(D_2S_2\). Information from the amplitudes of vibra-


15 J. C. Decius, J. Chem. Phys. 16, 1025 [1948]. A difference was noticed in the sign of the second term of \(\theta_0\) 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.


17a Note added in proof: Calculations using assumed values for the symmetric frequencies of \(D_2S_2\), show that the interaction constants \(F_{\alpha,\alpha}\), and \(F_{SS,\alpha}\) can be determined, but that these frequencies are not sufficient to determine \(F_{SH,\alpha}, F_{SH,SS}\), or \(F_{SH,\alpha'}\).
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<td>657.0 - 662.4</td>
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Table 7. Results of Force Constant Calculations of H\(_2\)S\(_2\).

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\(_2\)S\(_2\)^{18}. This is in keeping with the longer S—H bond length determined by electron diffraction of H\(_2\)S\(_2\). 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\(_3\))\(_2\)S\(_2\) 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\(_2\)S\(_2\) and Br\(_2\)S\(_2\), 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 opposed 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\(_2\)S\(_2\) can only be explained in terms of 3d orbital interaction, the effect of this interaction on the S—S stretching potential is very small.

Acknowledgments

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