

¹The Deuterium-Sulfide Band at 4,590 cm⁻¹

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The absorption of deuterium sulfide has been observed and measured under high resolution in the region from 4,513 cm⁻¹ to 4,675 cm⁻¹. The rotational structure has been analyzed through the use of published energy and line-strength tables for the rigid asymmetric rotor. A classical centrifugal-distortion correction was applied to the rigid energy levels. The absorption is attributed to the vibrational band having an excited state with the quantum number (n_1, n_2, n_3) = (1, 1, 1). The inertial parameters giving the best fit to the observed absorption are:

Ground state.....	$A=5.473$ cm ⁻¹	$B=4.490$	$C=2.444$
Excited state.....	$A=5.465$ cm ⁻¹	$B=4.482$	$C=2.383$

Using the ground-state inertial constants, the D - S distance is calculated to be 1.345 A , and the D - S - D -angle 92° 16', in excellent agreement with similar structural parameters determined for hydrogen sulfide from infrared studies.

1. Introduction

Although the rotational fine structure of several infrared bands of hydrogen sulfide has been satisfactorily analyzed [1 to 6],⁴ there has been no report of a successful analysis of the rotational fine structure of any infrared band of deuterium sulfide. The spectrum of D₂S has been observed under rather low resolution [7, 8], but no satisfactory analysis of the rotational structure was presented. In order to enable a solution for the cubic and quartic terms of the vibrational potential function of H₂S, the infrared spectrum of D₂S has been reinvestigated under high resolution.

In this paper an analysis of the absorption of D₂S in the region from 4,513 cm⁻¹ to 4,675 cm⁻¹ will be presented.

2. Experimental Procedure

The intensity of the absorption bands of D₂S in the region from 1 to 3 μ is low. With a cell of 6-m path length it was possible to observe the spectrum of the (1,1,1) band of D₂S in the region of 2.2 μ with a pressure of a few centimeters of Hg. The spectrum of this band was measured for several pressures, up to 60 cm of Hg. In figure 1 the spectrum was obtained with a pressure of 42.5 cm of Hg. In this way the weak and the strong lines could both be measured to the best advantage. The spectrometer had a grating with 15,000 lines per inch, and the resolution was about 0.10 cm⁻¹ in the 2- μ region.

In order to measure the lines to a high precision a Fabry-Perot interferometer was employed in a manner similar to that used by Douglas and Sharma [9]. A two pen recorder was used for observing the spectrum. One circuit was connected to a 1P28 photo-

multiplier, which detected the fringe system, and the other circuit was connected to a PbS cell. Suitable amplifiers were used with each detector. Standard atomic lines from krypton were thrown on the fringe system, and in this manner all the maxima of the fringe system could be reduced to wave numbers. The instrument was run continuously while the standards, fringe system, and absorption spectra were recorded.

3. Vibrational Assignment

The absorption at 2.2 μ shows well-defined P and R branches with an extremely strong absorption near the center, which suggests a collected Q branch. This absorption corresponds to an energy range for which there are several possible vibrational assignments. Dennison [10] has shown that as $\rho=B/A$ becomes smaller, the Q branch of A -type bands tends to collect at the center. On the other hand, there is a gap at the center of a B -type band for all values of ρ . Hence, it is concluded that this band is an A -type band, i. e., the electric moment oscillates along the least inertial axis. This axis is perpendicular to the symmetry axis; thus, n_3 must be odd, leaving only two possible vibrational assignments (n_1, n_2, n_3) = (1, 1, 1) and (0, 3, 1). Arguments relating to the relative intensities, to the dependence of the moments of inertia on n_2 , and especially to the value of $\Delta=I_C-I_B-I_A$ indicate a strong preference for the former assignment. However, the rotational analysis is independent of the vibrational assignment except for the effect of the symmetry of the excited vibrational state on the rotational selection rules.

4. Analysis

Initial trial values for the inertial parameters and the band center were estimated from the known parameters of hydrogen sulfide [11]. A trial spectrum was calculated through $J=8$, using published tables of asymmetric-rotor energies [12], and using A -type selection rules, i. e., dipole change along the

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⁴ Figures in brackets indicate the literature references at the end of this paper

lead inertial axis. A classical centrifugal-distortion correction [1] was applied to the rigid energies.⁵ The relative intensities were calculated with the aid of published tables of line strengths [13], using the line strengths tabulated for $K=0.5$. These line strengths were combined with the Boltzmann factor and the appropriate nuclear-spin factor. For D_2S the symmetric rotational states are twice as numerous as the antisymmetric rotational states, hence the relative intensities of all transitions in which the ground state τ is even are multiplied by 2.

The calculated spectrum was compared to the observed absorption. The adjustment of the six inertial parameters and the band center to give the best fit to the observed spectrum is largely a stochastic procedure. The inertial parameters were adjusted by means of the partial derivatives of the energy with respect to the initial parameters [1] until it was possible to assign unambiguously 100 transitions for $J < 8$. In some instances two or more transitions were assigned to the same peak. Final values of the inertial parameters were determined by solving 100 equations of the type

$$E_{\text{obs.}} - E_{\text{calc.}} = \Delta\nu_0 + a' \frac{\partial E}{\partial A'} + b' \frac{\partial E}{\partial B'} + c' \frac{\partial E}{\partial C'} - a \frac{\partial E}{\partial A} - b \frac{\partial E}{\partial B} - c \frac{\partial E}{\partial C'}$$

by the method of least squares. The best values of the seven variables are given in table 1. A comparison between the observed absorption and the spectrum calculated from the constants given in table 1 is shown in figure 1. In the final calculations the mean deviation of about 110 transitions, with $J < 10$, was 0.08 cm^{-1} .

An inspection of figure 1 reveals that most of the absorption in the central region is well accounted

⁵ The correction may be readily evaluated for individual energy levels, and hence has this advantage over methods that involve tedious calculations.

TABLE 1. Constants of the D_2S molecule

	Ground state	Excited state
	A -----	5.473 cm^{-1}
B -----	4.490	4.482
C -----	2.444	2.383
I_a -----	5.114 $\times 10^{-10} \text{ g cm}^2$	5.121 $\times 10^{-10} \text{ g cm}^2$
I_b -----	6.223	6.244
I_c -----	11.451	11.744
Bond angle-----	92°16'	-----
D-S distance-----	1.345 Å	-----
$\nu_0(1,1,1)$ -----	4592.32 cm^{-1}	-----

for. Some of the weaker peaks are due to a piling up of weak transitions that were not plotted. Also, the sample of D_2S contained about 5 percent of HDS, and some of the weaker peaks may arise from absorption by this molecule. The absorption on the ends of the region that is not accounted for arises from higher J transitions. Transitions for $J > 12$ were not calculated because they are beyond the range of presently available energy tables, and the labor involved makes the task unrewarding.

That some errors between calculated and observed values are greater than the mean deviation is ascribed, mainly, to the effect of a finite slit on several close-lying transitions, the integrated result not corresponding uniquely to any single transition. Likewise, some error is introduced by the use of a classical centrifugal-distortion correction, although it is believed that this will not cause errors greater than 0.20 cm^{-1} in the most unfavorable cases. Table 2 gives the assignments and calculated line positions for the main P and R branch transitions.

For a nonlinear triatomic molecule, it has been shown [14] that

$$\Delta = I_c - I_a - I_b = k_1(n_1 + \frac{1}{2}) + k_2(n_2 + \frac{1}{2}) + k_3(n_3 + \frac{1}{2}),$$

For H_2O and H_2S it has been found that k_1 is essentially zero, whereas $k_2 \gg k_3$. The large Δ found for the excited state seems to indicate that $n_2 = 1$. If

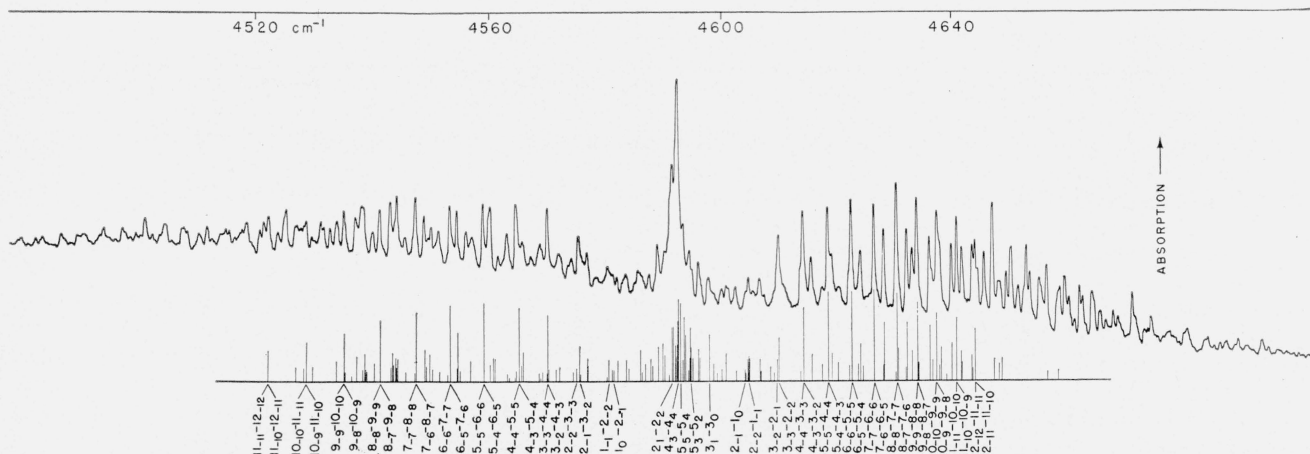


FIGURE 1. The infrared-absorption spectrum of deuterium sulfide in the region from 4,500 to 4,700 cm^{-1} .

The calculated positions and intensities of the lines are shown below the spectrum.

$n_2 > 1$, then one would reasonably expect a larger Δ than is observed.

The Δ for the ground state is about the same as that for the H_2S ground state. One might expect it to be somewhat larger in D_2S . Thus the ground-

TABLE 2. Observed and calculated values for main lines of P and R branches

Transition	Calculated	Observed
	cm^{-1}	cm^{-1}
9 ₋₉ -10 ₋₁₀	4535. 61	4535. 52
9 ₋₈ -10 ₋₉		
8 ₋₈ -9 ₋₉	4541. 62	4541. 62
8 ₋₈ -9 ₋₈		
7 ₋₇ -8 ₋₈	4547. 47	4547. 33
7 ₋₆ -8 ₋₇		
6 ₋₆ -7 ₋₇	4553. 23	4553. 18
6 ₋₅ -7 ₋₆		
5 ₋₅ -6 ₋₆	4558. 84	4558. 80
5 ₋₄ -6 ₋₅		
4 ₋₄ -5 ₋₅	4564. 32	4564. 38
4 ₋₃ -5 ₋₄		
3 ₋₃ -4 ₋₄	4569. 66	4569. 64
3 ₋₂ -4 ₋₃	4569. 68	
2 ₋₁ -3 ₋₂	4574. 99	4574. 92
1 ₀ -2 ₋₁	4580. 44	4580. 41
1 ₋₁ -2 ₋₂	4579. 73	4579. 79
2 ₋₁ -1 ₀	4603. 84	4603. 83
3 ₋₃ -2 ₋₂	4608. 99	4609. 09
4 ₋₄ -3 ₋₃	4613. 30	4613. 30
4 ₋₃ -3 ₋₂	4613. 31	
5 ₋₅ -4 ₋₄	4617. 57	4617. 58
5 ₋₄ -4 ₋₃		
6 ₋₆ -5 ₋₅	4621. 71	4621. 71
6 ₋₅ -5 ₋₄		
7 ₋₇ -6 ₋₆	4625. 67	4625. 70
7 ₋₆ -6 ₋₅		
8 ₋₈ -7 ₋₇	4629. 62	4629. 57
8 ₋₇ -7 ₋₆		
9 ₋₉ -8 ₋₈	4633. 32	4633. 22
9 ₋₈ -8 ₋₇		
10 ₋₁₀ -9 ₋₉	4636. 92	4636. 82
10 ₋₉ -9 ₋₈		

state inertial constants presented here may be somewhat in error due to the inability to assign Q branch transitions uniquely. However, it is felt that this error is small because of the excellent agreement between the structural parameters of the two molecules. As more bands are analyzed, the ground-state inertial constants will be continually refined, removing any small errors in the present determination.

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