

Some Infrared Bands of Deuterium Sulfide¹

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Two regions of the D₂S spectrum have been observed, 5 and 3.6 μ . An analysis of the absorption in the 3.6 μ region attributes it to two overlapping bands with excited states $(v_1, v_2, v_3) = (1, 1, 0)$ and $(0, 1, 1)$. The band center of the $(0, 1, 1)$ band is found to be some 50 cm^{-1} lower than the previously accepted value while the $(1, 1, 0)$ band center is found some 60 cm^{-1} higher than the previous determination. The absorption near 5 μ seems to arise from the $(0, 0, 1)$ band centered near 1906 cm^{-1} . Overlapping atmospheric absorption makes a detailed analysis impossible at this time. This band center is almost 100 cm^{-1} lower than previously reported. The excited state constants for the two bands near 3.6 μ are

$$(1, 1, 0) \quad \nu_0 = 2742.77 \quad A^* = 5.478 \quad B^* = 4.512 \quad C^* = 2.395$$

$$(0, 1, 1) \quad \nu_0 = 2754.44 \quad A^* = 5.531 \quad B^* = 4.521 \quad C^* = 2.405.$$

1. Introduction

Although the spectrum of hydrogen sulfide is now fairly well understood, very little work has been done on the totally deuterated compound. The spectrum of D₂S was investigated with low resolution by Bailey, Thompson, and Hale [1]² and with somewhat higher resolution by Nielsen and Nielsen [2]. In general these two groups agreed as to the regions of absorption, the only real discrepancy arising in the region near 3.6 μ . Although Nielsen and Nielsen resolved the rotational structure in several regions they did not present a rotational analysis of any of their data. The vibrational assignments of the two groups were completely different. With this considerable confusion existing it was thought advisable to reinvestigate the spectrum of D₂S.

One D₂S band has been successfully analyzed [3] previously, and in the present work the analysis of the rotational structure in the region of 2750 cm^{-1} is reported. The fundamental region near 1900 cm^{-1} was also investigated although the atmospheric absorption in this region makes a complete rotational analysis quite impossible at this time.

2. Experimental Procedure

The intensity of absorption of D₂S is weak, thus it was necessary to use several centimeters pressure of the gas and a path length of 10 m to observe the absorption in the 3.6 μ region. The absorption at 5 μ could be observed satisfactorily with a 1 m cell and several centimeters pressure of the gas.

The spectra were recorded with the grating instruments of the Radiometry Section, using a 7,500 lines/in. grating with a ruled surface of about 6 by 8 in. and a cooled PbTe cell as a detector. The resolution was about 0.2 cm^{-1} . The wavelengths of the lines were measured by employing a Fabry-Perot interferometer as previously described [4].

3. Analysis

Figure 1 is a reproduction of a recorder trace of the absorption near 2750 cm^{-1} . The absorption shows a well-defined *P*-, *Q*-, *R*-branch type of structure. The appearance of a collected *Q*-branch indicates that the change in electric moment is along the least inertial axis, hence *A*-type selection rules must be invoked [5].

Assignments of the strong lines in the *P*- and *R*-branches of the band could be made by using the previously determined ground state [3] of D₂S. From these assignments estimates were made of the excited state inertial parameters from which a trial spectrum was calculated using published tables of the reduced energy [6], $E(K)$.

Relative intensities of the transitions were calculated by combining the Boltzmann factor and appropriate nuclear spin statistics with the published values of the line strength [5]. Line strength values were used for $K=0.5$. These were found to be close enough for our purposes. This trial spectrum was compared with the observed spectrum and adjustments were made to improve the agreement by means of the partial derivatives of the energy with respect to the various inertial constants [3]. The final adjustment of the parameters was obtained by carrying out a least squares treatment [3] in which some 90 assignments were used. The agreement between the observed absorption and calculated transitions for these 90 assignments was excellent. The average deviation between the observed and calculated values was 0.07 cm^{-1} .

After assigning the strong transitions of the *A*-type band, it was found that there was a sizable number of strong absorption peaks still unaccounted for. Closer examination revealed that these peaks arose from a second transition obeying the selection rules for a *B*-type band. Proceeding in the same manner as for the *A*-type band it was possible to assign unambiguously about 70 transitions to these absorption peaks with an average deviation of 0.06 cm^{-1} . Strong transitions of these two bands account for almost all the absorption in this region.

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²Figures in brackets indicate the literature references at the end of this paper.

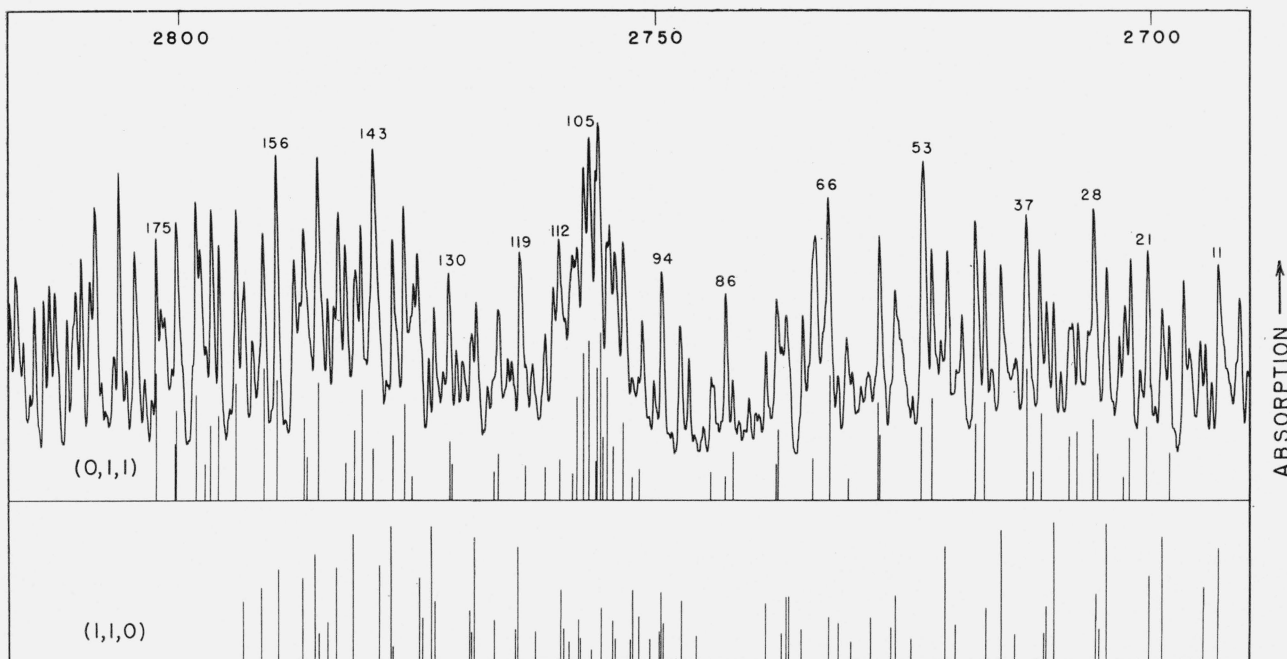


FIGURE 1. Comparison of observed and calculated spectrum of D_2S near 3.6μ .
The numbers on the peaks correspond to the numbers in column 1 of table 1.

The remaining peaks are due to a piling up of weaker transitions or to absorption by HDS which was present to a few percent in the sample. Because the moments of inertia in D_2S are relatively large, the resulting line spacing in the vibrational rotational bands is quite close, resulting in severe overlapping of the absorptions due to neighboring transitions both in the same band and in two closely lying bands. This situation leads to some difficulty in making an analysis for it cuts down the number of assignments that can be made, thus introducing more uncertainty into the determination of the inertial constants than one would like. The strongest transitions in the P - and R -branches of both bands arise from levels that are strongly dependent on C^* . These levels could be readily identified and assigned, hence the value of C^* for each band should be very good. The strong Q -branch transitions of the A -type band arise from levels strongly dependent on A^* . Although the calculated Q -branch reproduces the observed absorption in remarkable detail, indicating a good value for A^* , this may be somewhat fortuitous because many transitions of the B -type band are calculated to fall in this same region. The transitions determining B^* most directly in both bands as well as A^* in the B -type band are spread throughout the band and in general are weaker transitions. As a result these inertial constants are probably somewhat more uncertain than the others although the general excellence of the fit for the transitions in the two bands that could be unambiguously assigned indicates that the constants determined should be fairly reliable.

Figure 1 compares the observed absorption with the two calculated bands whereas table 1 compares the observed and calculated frequencies of some of the stronger transitions.

The excited state constants leading to the fit shown are

$$\begin{aligned} A\text{-type } \nu_0 &= 2754.44 \text{ cm}^{-1} & A^* &= 5.531 & B^* &= 4.521 \\ & & C^* &= 2.403 & & \\ B\text{-type } \nu_0 &= 2742.77 \text{ cm}^{-1} & A^* &= 5.478 & B^* &= 4.512 \\ & & C^* &= 2.395 & & \end{aligned}$$

The previously determined ground [3] state was found to be adequate for both bands.

The absorption in the 5μ region is too complicated by atmospheric absorption to enable a quantitative analysis. However, the D_2S absorption seems to have a Q -branch located near 1906 cm^{-1} indicating an A -type band. The main transitions of the P - and R -branches that are free from contamination by water vapor absorption indicate that the center of the band is $1906 \pm 1 \text{ cm}^{-1}$.

4. Vibrational Assignment

The A -type band at 2754.44 cm^{-1} must have v_3 odd. The most likely transition with v_3 odd that could occur in this frequency region is the transition with the upper state $(v_1, v_2, v_3) = (0, 1, 1)$. The B -type band must have v_3 even and hence the most likely assignment on the basis of frequency is for the excited state to be $(1, 1, 0)$.

TABLE 1. Comparison of observed and calculated spectra ^a

Line	Observed	Transition	Calculated		Intensity calculated	Line	Observed	Transition	Calculated		Intensity calculated
			0,1,1	1,1,0					0,1,1	1,1,0	
	<i>cm</i> ⁻¹		<i>cm</i> ⁻¹	<i>cm</i> ⁻¹			<i>cm</i> ⁻¹		<i>cm</i> ⁻¹		
1	2687.79	{ 9 _s -10 ₋₁₀		2687.71	5.0	68	2732.68				
2	2688.57	{ 9 _s -10 ₋₉		2687.71	2.5	69	2733.41				
3	2689.14	{ 8 _s -9 ₋₆		2689.20	3.9	70	2733.68	2 ₁ -3 ₀	2733.86		1.8
4	2689.84	{ 8 _s -9 ₋₆				71	2734.14				
5	2690.32	{ 8 _s -9 ₋₇				72	2734.72	0 ₀ -1 ₀		2734.85	1.9
6	2690.54					73	2735.13				
7	2691.40					74	2736.16	4 ₀ -4 ₂		2736.20	4.6
8	2691.74					75	2736.42	{3 ₁ -3 ₃		2736.34	1.7
9	2692.50					76	2736.88	{2 ₂ -2 ₀		2736.44	2.1
10	2693.13					77	2737.30	3 ₁ -3 ₁		2736.72	1.9
11	2693.38	{ 8 _s -9 ₋₈	2693.38		5.5	78	2738.15	2 ₋₁ -3 ₋₂	2737.33		4.3
12	2694.12	{ 8 _s -9 ₋₉	2693.38		2.7	79	2738.52			2738.48	3.7
13	2694.78	{ 7 ₋₁ -8 ₋₆	2694.83		4.1	80	2739.33				
14	2695.22	{ 7 ₋₃ -8 ₋₅	2694.83		2.0	81	2739.52	2 ₋₂ -2 ₀		2739.72	1.5
15	2696.10					82	2740.24				
16	2696.33					83	2740.76				
17	2696.83					84	2741.31	3 ₋₃ -3 ₀	2741.33		1.1
18	2698.29	8 ₋₃ -9 ₋₄	2698.22		3.0	85	2741.92	1 ₋₁ -2 ₋₂	2741.91		3.1
19	2698.95	{ 7 ₋₆ -8 ₋₈	2698.96		5.8	86	2742.57	1 ₀ -2 ₋₁	2742.64		1.4
20	2699.78	{ 7 ₋₇ -8 ₋₇	2698.96		2.9	87	2743.04				
21	2700.44	{ 9 ₋₃ -10 ₋₁₀	2700.39		4.6	88	2744.19	4 ₋₁ -4 ₀	2744.35		1.8
22	2701.22	{ 9 ₋₃ -10 ₋₉	2700.39			89	2745.06				
23	2702.12	{ 8 ₋₃ -9 ₋₆	2702.13		3.9	90	2745.82	1 ₁ -1 ₋₁		2745.83	1.5
24	2702.74	{ 8 ₋₄ -9 ₋₇	2702.13			91	2746.44				
25	2703.33	{ 6 ₀ -7 ₋₁	2702.64		1.5	92	2747.33	2 ₂ -2 ₀		2747.42	3.5
26	2704.45	{ 6 ₋₄ -7 ₋₆	2704.45		6.1	93	2748.34				
27	2704.80	{ 6 ₋₁ -7 ₀	2704.76		2.9	94	2749.18	{3 ₁ -3 ₋₁		2749.05	1.9
28	2705.78	{ 8 ₋₇ -9 ₋₈	2705.87		5.3	95	2750.14	{2 ₂ -2 ₋₂		2749.23	2.2
29	2706.42	{ 8 ₋₈ -9 ₋₉	2705.87			96	2751.31				
30	2707.38	{ 7 ₋₃ -8 ₋₆	2707.38		4.4	97	2751.72	{4 ₁ -4 ₂	2751.59		3.3
31	2707.96	{ 7 ₋₄ -8 ₋₅	2707.38			98	2752.38	{4 ₁ -4 ₂		2751.72	2.8
32	2708.26	{ 6 ₋₂ -7 ₋₃	2708.16		1.8	99	2753.24	1 ₀ -1 ₋₁	2752.32		1.3
33	2709.13	{ 6 ₋₁ -7 ₋₂	2708.37		3.6	100	2754.10	{2 ₁ -2 ₂	2753.27		4.9
34	2709.84	{ 5 ₃ -6 ₂	2708.42		3.1	101	2754.56	{5 ₂ -5 ₃	2753.38		2.0
35	2709.84	{ 5 ₋₄ -6 ₋₆	2709.84		6.1	102	2754.84	2 ₋₁ -1 ₀		2754.16	2.5
36	2710.54	{ 5 ₋₃ -6 ₋₆	2709.84		3.1	103	2755.72				
37	2711.22	{ 4 ₋₅ -5 ₂	2710.40		3.9	104	2756.04	4 ₃ -4 ₁	2755.08		7.9
38	2711.22	{ 7 ₋₇ -8 ₋₈	2711.29		5.4	105	2756.71	{3 ₃ -3 ₂	2755.73		6.7
39	2712.56	{ 7 ₋₆ -8 ₋₇	2711.29			106	2757.28	{4 ₃ -4 ₃	2755.74		3.9
40	2713.70	{ 6 ₋₃ -7 ₋₄	2712.53		4.7	107	2758.03	{5 ₄ -5 ₃	2755.80		4.0
41	2714.75	{ 6 ₋₄ -7 ₋₅	2712.54			108	2758.54	{6 ₄ -6 ₂	2756.06		8.0
42	2715.08	{ 5 ₋₁ -6 ₋₂	2712.65		3.0	109	2758.86	{5 ₅ -5 ₄	2756.09		2.4
43	2715.98	{ 5 ₀ -6 ₋₁	2713.59		1.8	110	2759.35	{2 ₂ -2 ₁	2756.09		2.9
44	2716.63					111	2759.75	{1 ₁ -1 ₀	2756.55		2.9
45	2717.40					112	2759.95	{6 ₆ -6 ₅	2756.63		3.6
46	2717.58					113	2760.56	{7 ₆ -7 ₇	2757.31		3.0
47	2718.94					114	2761.48	{7 ₋₇ -7 ₆	2757.38		6.0
48	2719.12					115	2761.80				
49	2719.50					116	2762.60	{6 ₀ -3 ₋₂	2758.56		2.6
50	2720.36					117	2762.90	{4 ₂ -4 ₁	2758.56		1.7
51	2721.06					118	2763.46	5 ₋₁ -5 ₋₃		2759.03	1.2
52	2721.86					119	2764.04	6 ₈ -6 ₁		2759.31	1.2
53	2722.70					120	2764.90	{3 ₋₂ -2 ₂	2759.69		4.4
54	2723.92					121	2765.36	{3 ₁ -3 ₀	2759.69		2.6
55	2725.52					122	2766.34	{3 ₋₃ -2 ₋₁	2759.78		2.2
56	2725.82					123	2766.92				
57	2726.79					124	2767.38				
58	2727.11					125	2768.64	1 ₋₁ -0 ₀	2761.37		2.0
59	2727.54					126	2769.14	2 ₁ -1 ₁		2761.62	1.4
60	2728.28					127	2769.96				
61	2728.45					128	2770.64				
62	2729.01					129	2771.38				
63	2729.84					130	2771.52				
64	2730.28					131	2772.12				
65	2731.24					132	2772.96				
66	2732.14					133	2773.55				
67	2732.44					134	2774.32				

TABLE I. Comparison of observed and calculated spectra ^a—Continued

Line	Observed	Transition	Calculated		Intensity calculated	Line	Observed	Transition	Calculated		Intensity calculated
			0,1,1	1,1,0					0,1,1	1,1,0	
	<i>cm</i> ⁻¹		<i>cm</i> ⁻¹	<i>cm</i> ⁻¹			<i>cm</i> ⁻¹		<i>cm</i> ⁻¹		
141	2777.93	4 ₁ -3 ₁		2778.07		157	2790.75	5 ₀ -4 ₁	2790.85		2.0
142	2778.73	{ 6 ₋₃ -5 ₋₃ 6 ₋₄ -5 ₋₂		2778.68 2778.60	2.6 5.1	158	2791.08	6 ₋₃ -5 ₋₂	2791.29		5.7
143	2779.22	3 ₁ -2 ₂	2779.10		3.2	159	2792.11				
144	2779.61					160	2793.06	8 ₋₄ -7 ₋₂		2793.13	2.3
145	2780.65	{ 5 ₋₃ -4 ₋₄ 5 ₋₄ -4 ₋₃ 4 ₋₁ -3 ₀	2780.61 2780.61 2781.13		6.9 4.4	161	2793.26	8 ₋₃ -7 ₋₃		2793.22	1.9
146	2781.29	{ 8 ₋₅ -7 ₋₄ 8 ₋₇ -7 ₋₇		2781.35 2781.35	7.0 3.5	162	2793.90	{ 8 ₋₈ -7 ₋₇ 8 ₋₇ -7 ₋₆	2793.86 2793.86		7.2
147	2782.26	4 ₋₂ -3 ₁	2782.06		2.3	163	2794.68				
148	2782.97	{ 7 ₋₅ -6 ₋₃ 7 ₋₄ -6 ₋₄		2783.01 2783.03	.6 5.3	164	2795.66	{ 7 ₋₅ -6 ₋₄ 7 ₋₄ -6 ₋₃	2795.66 2795.66		5.6
149	2783.50	6 ₋₂ -5 ₀		2783.54	2.5	165	2796.46	6 ₋₁ -5 ₀	2796.34		4.6
150	2784.18					166	2797.12	6 ₋₂ -5 ₋₁	2797.27		2.3
151	2785.12	{ 6 ₋₃ -5 ₋₄ 6 ₋₆ -5 ₋₅ 6 ₋₁ -5 ₋₁	2785.10 2785.10		7.4	167	2797.68				
152	2786.33	5 ₋₂ -4 ₋₁	2786.21		1.8	168	2798.10	{ 9 ₋₉ -8 ₋₈ 9 ₋₈ -8 ₋₇	2798.12 2798.12		6.2
153	2786.69	5 ₋₃ -4 ₋₂	2786.50		3.6	169	2798.44				
154	2787.20	{ 8 ₋₃ -7 ₋₅ 8 ₋₆ -7 ₋₄		2787.30 2787.30	2.6 5.1	170	2799.64				
155	2787.77					171	2800.18	{ 8 ₋₅ -7 ₋₄ 8 ₋₆ -7 ₋₅ 6 ₁ -5 ₂	2800.04 2800.04 2800.08		5.5 3.5
156	2789.54	{ 7 ₋₇ -6 ₋₆ 7 ₋₆ -6 ₋₅	2789.53 2789.53		7.4	172	2800.73				
						173	2801.44				
						174	2801.78				
						175	2802.28	{ 10 ₋₉ -9 ₋₈ 10 ₋₁₀ -9 ₋₉	2802.29 2802.29		6.0

^a Because so many absorption peaks are composites of several transitions, only those for which definite assignments could be made are included in the table. Line numbers correspond to numbering of peaks in figure 1.

The band center of the (0,1,1) band is some 40 cm^{-1} lower than the Bailey, Thompson, and Hale value whereas it is some 70 cm^{-1} higher than the center of the absorption observed by Nielsen and Nielsen.

The A-type band at 1906 cm^{-2} is in the region where one would normally expect the stretching fundamentals. The band type demands that this absorption be assigned to the (0,0,1) band. Such an assignment places the band center of ν_2 nearly 100 cm^{-1} lower than that reported by Nielsen and Nielsen.

5. Discussion

With the help of these new band centers it is possible to make some estimates of the (0,1,0) band center. The difference between the (0,1,1) and (0,0,1) frequencies is $\sim 848 \text{ cm}^{-1}$. This difference is the band center of the (0,1,0) band minus X_{23} , the interaction between ν_2 and ν_3 . This interaction can be estimated from the corresponding interaction in H_2S as about 10 cm^{-1} leading to a value of 858 cm^{-1} as the frequency of (0,1,0). Using the (1,1,0) frequency, and as ν_1 the Raman [7] line at 1892 cm^{-1} one finds 851 cm^{-1} which includes X_{12} .

This frequency can also be estimated from the spectrum of crystalline [8] H_2S and D_2S which leads to a value of 855 cm^{-1} .

The existing data in this region by Nielsen and Nielsen runs out at 853 cm^{-1} , so this absorption seems to represent only the R-branch of the bending fundamental. Attempts to analyze their data as an R-branch were unsuccessful. Their data show no regular series that can be identified with the main strong R-branch series. However, the three pieces

of evidence offered above strongly argue for a ν_2 band center close to 855 cm^{-1} fully 80 cm^{-1} lower than the value previously suggested [2].

These findings argue strongly for more work on the D_2S spectrum, which will be undertaken shortly at the Bureau.

In conclusion the authors thank R. E. Florin for preparing the D_2S and Carroll Dannemiller for doing the least squares calculations on SEAC.

6. References

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