

Infrared Spectrum of Hydrogen Sulfide in the 6,290-cm⁻¹ Region¹

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The absorption of hydrogen sulfide in the region 6,100 to 6,500 cm⁻¹ has been measured under high resolution. The rotational fine structure has been analyzed through the use of published energy tables for the rigid rotor. A classical centrifugal-distortion correction was applied to the rigid energy levels. It is found that there are two overlapping bands in this region, a normally strong, A-type band, the $(n_1, n_2, n_3) = (1, 1, 1)$, and a normally weak, B-type band, which becomes strong enough to be observed by borrowing intensity from the A-type band through a Coriolis interaction. The B-type band is the lower component of the resonating pair $(2, 1, 0)$ and $(0, 1, 2)$. The excited state inertial parameters giving the best fits are $(1, 1, 1)$ band, $A = 10.398$, $B = 8.935$, $C = 4.548$, $\mu_0 = 6289.26$ cm⁻¹; $(0, 1, 2)$ band, $A = 10.394$, $B = 8.918$, $C = 4.547$, $\mu_0 = 6288.28$ cm⁻¹.

1. Introduction

The absorption of hydrogen sulfide in the 1.6 μ region has been measured previously under low resolution and the rotational fine structure of the band envelope analyzed [1].³ As it is now possible to increase the resolution 10 times, it was thought advisable to remeasure this region. The analysis of the new data confirms the main conclusions of the previous analysis, i. e., the absorption is due largely to the A-type band $(1, 1, 1)$. However, the improved data show a second and weaker band overlapping the $(1, 1, 1)$ band. This second band is a B-type band and is assigned as the lower component of the resonating pair $(0, 1, 2)$ and $(2, 1, 0)$.

2. Experimental Procedure

The measurements of the 1.6- μ band of hydrogen sulfide were made on an infrared grating spectrometer constructed in the Bureau's Radiometry Section. The grating has 15,000 lines/in., and the rulings extend over 7½ in. A lead-sulfide cell is used as the detecting element. Other details of the instrument are given in a previous paper [2]. In the measurement of the hydrogen-sulfide spectra at 1.6- μ it is possible to use narrow slits (0.03 mm), and sharp lines separated by 0.15 cm⁻¹ could be resolved. Two cells were used in the measurements, one 60 cm and the other 600 cm in length. The long cell was so constructed that there was no loss in aperture. This cell transmits about 85 percent of incident energy. A detailed description of this cell is given in another publication [3]. Various pressures were used in the absorption cells so that both weak and strong lines could be observed. Figure 1 shows a recorder tracing obtained on unruled paper for the 600-cm

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³Figures in brackets indicate literature references at the end of this paper.

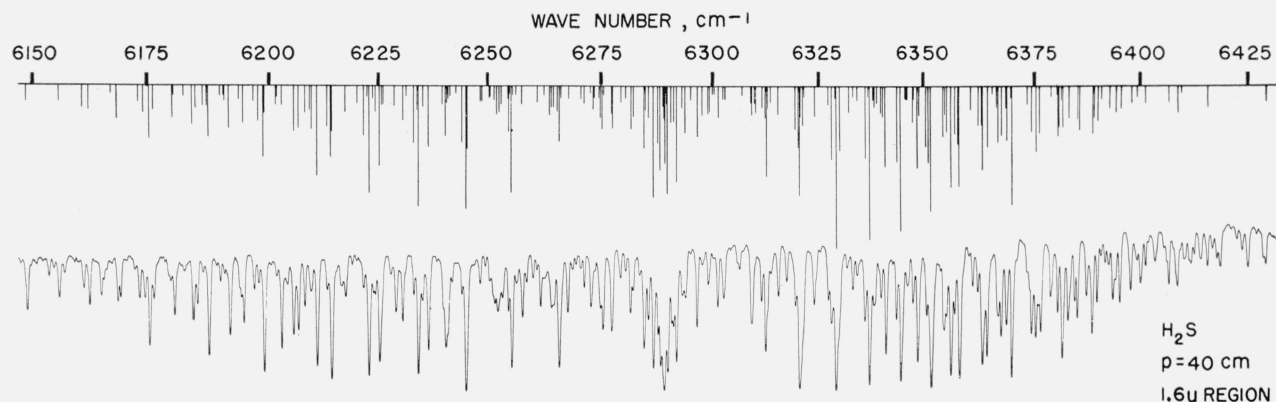


FIGURE 1. Absorption bands $(1, 1, 1)$ and $(2, 0, 1)$ for hydrogen sulfide in the region 6,100 to 6,500 cm⁻¹.

The calculated positions of the lines are shown above the spectra.

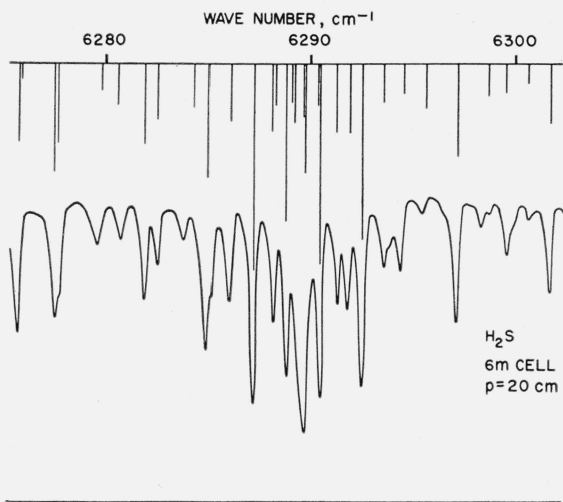


FIGURE 2. Center of (1,1,1) band at slow scanning speed. The calculated positions and their intensities are placed above the spectra.

cell, with hydrogen sulfide at a pressure of 40 cm Hg. Figure 2 represents the center of the same region obtained by using a slower scanning speed.

The frequencies of the absorption peaks were obtained by using a comparison spectrum. Higher orders of the atomic lines of mercury, krypton, argon, and neon were superimposed on the absorption band. An arrangement of shutters was used so that either the absorption lines or the emission line could be recorded on the chart, and thus the shifting of position of the atomic line by the overlapping of the absorption line was avoided. Several tracings were measured, and the frequency given for each line is a result of the average of several determinations. In these measurements the precision of most lines is 0.1 cm^{-1} or better. The experimental determinations of the frequencies are listed in table 1.

TABLE 1. Comparison of observed and calculated spectra in $1.6\text{-}\mu$ region

Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity	Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity
				(111)	(012)						(111)	(012)	
		cm^{-1}		cm^{-1}				cm^{-1}		cm^{-1}			
31	3.8	6148.77	11-10-12-11 11-11-12-12	6148.86	-----	0.6	59	3.3	6175.87	7 ₀ -8-1 5 ₃ -6 ₃	6175.78 ----- 6176.09	----- -----	0.9 ----- .6
32	.5	6149.51					60	.4					
33	.2	6150.19					61	.4	6178.15				
34	.7	6150.65					62	1.5	6178.95	8-5-9-7 8-6-9-6	----- -----	6178.92	.6 ----- .2
35	.3	6151.99					63	1.9	6179.43	6-7 ₅	6179.08	-----	.4
36	1.7	6153.21					64	4.6	6180.19	7-1-8-2 8-3-9-6 8-6-9-7	6180.07 ----- -----	----- ----- -----	.3 ----- 1.5
37	.1	6154.45											
38	3.2	6155.60	10-7-11-8 10-8-11-9	6155.52	-----	.2 .6	65	1.2	6180.71	4-6-5 ₃	6180.79	-----	.6
39	1.3	6156.67					66	.6	6181.49				
40	.1	6157.63					67	1.3	6182.19	6-3-7 ₂	6182.13	-----	.3
41	.6	6158.79	7 ₅ -8 ₄ 5 ₁ -6 ₄	6158.72 6158.82	-----	.1 .1	68	.1	6182.83	7-3-8-3 7-2-8-4	----- -----	6182.60	.6 ----- .2
42	.6	6159.55											
43	2.5	6160.71	9-4-10-5 9-5-10-6 10-9-11-11 10-10-11-10	6160.71	----- ----- 6160.93	.8 .3 .5 .2	69	4.9	6184.17	4 ₁ -5 ₃ 7-3-8-3 7-3-8-4	----- ----- -----	6183.66 ----- 6183.97	.6 ----- 1.4 ----- .5
44	3.7	6162.05	10-10-11-11 10-9-11-10	6162.20	-----	1.1 .4	70	3.7	6184.95	6-6-7-1	6185.02	-----	1.4
45	.2	6163.05					71	1.3	6186.21	8-7-9-9 8-8-9-8 4-3-5 ₅	----- ----- -----	6186.37 ----- 6186.82	1.2 ----- .4
46	.3	6163.58	7 ₁ -8 ₀	6163.41	-----	.2	72	7.3	6187.48	8-8-9-9 8-7-9-8	6187.48	-----	2.5 ----- .8
47	3.0	6164.63	8-2-8-3 8-1-8-2	6164.41 6164.45	-----	.6 .2	73	.1	6189.09				
48	1.8	6165.23	7-4-8 ₃	6165.18	-----	.4	74	1.9	6189.98	5 ₃ -6 ₂	6190.05	-----	.6
49	1.0	6165.83	7-6-8 ₅	6165.63	-----	.2	75	1.3	6190.86	7-5-8-5 7-4-8-6	----- -----	6190.81	1.9 ----- .6
50	.1	6166.80	9-7-10-7 9-6-10-8		6166.70	1.0 .3	76	1.0	6191.37	9-8-9-7 10-8-10-5	6191.24 -----	----- 6191.11	.2 ----- .1
51	3.5	6168.13	5-5-6 ₅ 9-6-10-7 9-7-10-8		6167.82 6168.01	.9 1.0 .3	77	5.7	6192.09	7-4-8-5 7-3-8-6	6192.00	-----	2.1 ----- .7
52	2.9	6168.73					78	.1	6193.37				
53	.2	6168.87					79	2.2	6194.23	6-1-7-3 6-2-7-1	----- -----	6193.95	.8 ----- .3
54	.1	6170.87					80	2.9	6194.69				
55	1.0	6171.79					81	.5	6195.26	6-2-7-3 6-1-7-2	6195.00	-----	1.9 ----- .6
56	3.4	6172.63	8-4-9-5 8-3-9-4	6172.59	-----	.9 .3	82	2.6	6197.53	5-4-6 ₃	6197.54	-----	.9
57	3.2	6173.83	4-2-5 ₅ 9-9-10-9 9-8-10-10	6173.75	----- 6173.81	.2 .8 .3	83	2.2	6198.76	7-7-8-7 7-6-8-7	----- -----	6198.55	1.7 ----- .6
58	6.7	6174.94	6-4-7 ₃ 6-2-7 ₁ 9-9-10-10 9-8-10-9	6174.00 6174.64 6174.90	----- ----- -----	.9 1.2 .6 1.7	84	8.3	6199.62	7-6-8-7 7-7-8-8 5-2-6 ₁	6199.63 ----- 6199.83	----- ----- -----	3.4 ----- 1.1 ----- 1.7

TABLE I. Comparison of observed and calculated spectra in 1.6- μ region—Continued

Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity	Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity
				(111)	(012)						(111)	(012)	
86	1.5	6202.45	6-3-7-5	-----	6202.42	1.2	124	10.0	6244.71	3-2-4-3	6244.83	-----	6.1
			6-4-7-4	-----	-----	.4				3-3-4-4	-----	-----	2.0
			5-2-6-0	-----	6202.49	.7				2-0-3-1	6244.94	-----	4.2
87	6.8	6203.57	6-4-7-5	6202.42	-----	2.8	125	.7				-----	
			6-3-7-4	-----	-----	.9	126	.6	6246.48			-----	
88	1.0	6204.17	5-1-6-1	-----	6203.92	-----	127	2.5	6247.97	2-1-3-0	-----	-----	1.0
89	2.2	6205.01									6248.34	-----	.9
90	5.9	6206.29	5-0-6-1	6206.28	-----	2.4	128	1.0	6249.13			-----	
			3-2-4-4	-----	6206.51	-----	129	1.7	6250.12	4-3-4-1	-----	6250.02	.8
91	5.6	6207.30	4-2-5-1	6207.32	-----	2.8				6-1-6-1	-----	6250.26	.7
92	3.8	6208.70	4-1-5-3	6208.80	-----		130	2.8	6250.90			-----	
93	2.5	6210.11	3-3-4-3	-----	6209.72	1.6	131	3.7	6251.35	6-2-6-1	6251.29	-----	.9
			6-3-7-7	-----	6210.43	2.1	132	4.4	6251.98	5-3-5-1	-----	6251.69	.8
			6-4-7-6	-----	-----	.7				4-4-4-1	6252.01	-----	1.1
94	7.9	6211.46	6-4-7-7	6211.46	-----	4.4	133	3.1	6252.33	1-1-2-1	-----	6252.41	1.7
			6-3-7-6	-----	-----	1.5	134	3.3	6252.95	5-2-5-1	6252.85	-----	1.2
95	2.5	6213.67	5-2-6-4	-----	6213.49	-----	135	4.6	6254.32	2-2-3-2	-----	6254.03	.8
			5-3-6-3	-----	6213.50	-----				7-1-7-1	-----	6254.35	.5
			4-3-5-2	6213.89	-----	.5				2-1-3-3	-----	6254.40	2.5
96	9.0	6214.69	5-2-6-3	6214.63	-----	3.5	136	8.5	6255.17	2-2-3-3	6254.97	-----	5.4
			5-3-6-4	-----	-----	1.2				2-1-3-2	-----	-----	1.8
			4-0-5-1	6214.82	-----	3.0				6-0-6-3	6255.29	-----	.5
97	.1	6215.79					137	2.1	6256.40	7-0-7-1	6256.60	-----	.6
98	2.1	6216.90	8-6-8-3	6216.53	-----	.3	138	4.9	6257.56	1-1-2-0	6257.54	-----	1.2
			8-3-8-4	6216.53	-----	.1	139	2.0	6258.37			-----	
			7-7-7-4	6216.64	-----	.1	140	1.9	6259.80			-----	
			7-6-7-5	6216.66	-----	.4	141	1.4	6260.73	4-1-4-1	-----	6260.74	1.1
99	3.2	6217.93	4-1-5-0	6217.80	-----	.9	142	4.0	6261.66			-----	
			4-1-5-1	-----	6217.68	.8	143	1.7	6262.70	4-0-4-3	6262.36	-----	.5
100	.7	6219.11								3-3-3-1	-----	6262.97	.9
101	.5	6220.37					144	1.7	6263.60	1-1-2-1	-----	6263.50	1.8
102	.3	6221.06	3-1-4-1	-----	6220.86	-----				7-3-7-5	-----	6263.54	.5
103	2.5	6221.89	5-3-6-5	-----	6221.90	2.5	145	4.1	6264.01	3-2-3-1	6264.01	-----	1.4
			5-4-6-6	-----	-----	.9	146	3.9	6264.65	1-1-2-2	6264.75	-----	1.4
104	8.7	6222.98	2-0-3-3	6222.46	-----	.7	147	8.5	6265.85	4-1-4-3	-----	6265.23	.9
			5-4-6-5	6222.94	-----	5.3				1-0-2-2	-----	6265.25	.5
			5-3-6-6	-----	-----	1.8				4-1-4-0	6265.51	-----	.6
105	2.8	6224.03	3-3-4-2	6224.10	-----	.8				5-1-5-1	-----	6265.60	.6
			4-2-5-2	-----	6224.11	.5				1-0-2-1	6265.91	-----	3.7
106	2.9	6224.46	4-1-5-3	6224.44	-----	1.7				7-1-7-3	-----	6266.04	.7
107	8.1	6225.49	4-1-5-3	6225.22	-----	4.0	148	4.5	6267.68	5-3-5-5	-----	6267.20	.7
			4-1-5-2	-----	-----		149	1.4	6268.71	2-1-2-2	6268.42	-----	.4
			2-1-3-3	-----	6225.40	1.3	150	.9	6269.48			-----	
			3-1-4-0	6225.67	-----	1.2	151	1.5	6270.57	2-1-2-1	-----	6270.62	.9
108	1.5	6227.97					152	2.7	6271.38	2-2-2-1	6271.29	-----	1.2
109	4.3	6229.07	7-3-7-2	6228.79	-----		153	4.0	6272.94	0-0-1-0	-----	6273.23	.5
			6-4-6-3	6228.82	-----	.6	154	1.3	6273.73	7-2-7-3	6270.40	-----	.8
			6-3-6-4	6228.85	-----	.2				5-1-5-3	-----	6237.57	1.6
			7-4-7-3	6228.81	-----	.5	155	4.0	6274.96	4-0-4-2	-----	6274.55	.7
110	.2	6229.80								3-1-3-1	-----	6275.00	2.1
111	5.0	6230.40	3-2-4-1	6230.62	-----	2.3	156	5.7	6275.47	0-0-1-1	6275.54	-----	2.8
112	1.3	6231.08	2-2-3-2	-----	6231.13	.6				2-1-2-0	6275.71	-----	0.6
113	3.1	6232.85	4-3-5-5	-----	6232.86	2.8	157	6.3	6277.39	3-1-3-3	-----	6277.36	2.0
			4-4-5-4	-----	-----	.9				3-0-3-1	6277.52	-----	2.8
114	8.9	6233.93	3-0-4-2	-----	6233.60	.5	158	2.3	6279.53	4-1-4-2	6279.71	-----	1.0
			3-1-4-1	-----	6233.83	1.6	159	1.5	6280.70	2-0-2-2	-----	6280.56	.8
			4-4-5-5	6234.06	-----	6.0	160	4.7	6281.81	5-2-5-3	6281.99	-----	2.9
			4-3-5-4	-----	-----	2.0	161	2.7	6282.43	1-1-1-1	-----	6282.43	2.0
115	3.5	6234.81	3-1-4-2	6235.15	-----	1.4	162	1.7	6283.72			-----	
116	7.0	6236.35	3-0-4-1	6236.35	-----	4.0	163	7.1	6284.89	1-0-1-1	6284.88	-----	4.1
117	.4	6238.18								7-4-7-5	6285.15	-----	1.6
118	3.8	6239.73	6-3-6-1	-----	6239.55	.6	164	5.0	6285.93	2-1-2-2	6285.98	-----	2.1
			5-3-5-3	-----	6239.63	.6	165	8.4	6287.17	3-2-3-3	6287.12	-----	7.5
119	6.8	6240.28	2-2-3-1	6240.32	-----	3.3	166	6.1	6288.15	4-3-4-4	6288.10	-----	2.4
120	5.8	6240.66	5-3-5-2	6240.62	-----	.3	167	8.2	6288.80	5-4-5-5	6288.71	-----	5.7
			5-4-5-3	6240.67	-----	.8	168	9.8	6289.62	6-5-6-6	6289.11	-----	1.3
			6-4-6-1	6240.81	-----	.8				7-6-7-7	6289.07	-----	2.2
121	2.1	6241.57	7-2-7-1	6241.29	-----	.6				5-5-5-4	6289.67	-----	1.9
122	.7	6242.67	2-0-3-0	-----	-----	.5				6-6-6-5	6289.82	-----	3.9
123	3.0	6243.76	3-3-4-3	-----	6243.79	2.8						-----	
			3-2-4-4	-----	6243.84	1.0						-----	

TABLE I. Comparison of observed and calculated spectra in 1.6- μ region—Continued

Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity	Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity
				(111)	(012)						(111)	(012)	
169	8.6	6290.44	4 ₁ -4 ₃	6290.36	-----	7.3	211	0.2	6334.50				
			8 ₈ -8 ₇	6290.49	-----	1.2	212	5.7	6335.65	5-5-4-3	-----	6335.71	3.7
170	5.3	6291.33	3 ₃ -3 ₂	6291.22	-----	2.5				5-4-4-4	-----	-----	1.2
171	5.4	6291.80	6 ₄ -6 ₃	6292.09	-----	2.4	213	10.0	6336.75	8-2-8-3	6336.59	-----	.5
172	8.4	6292.48	2 ₂ -2 ₂	6292.37	-----	6.4				5-4-4-3	6336.75	-----	7.8
173	4.0	6293.64	1 ₁ -1 ₀	6293.49	-----	1.4				5-3-4-4	-----	-----	2.6
			1 ₁ -1 ₋₁	-----	6293.91	2.1				6-3-5-5	-----	6336.95	.5
174	3.8	6294.31	5 ₃ -5 ₂	6294.44	-----	1.0	214	4.3	6337.78	7-2-7-5	6337.47	-----	.7
175	.7	6295.50	2 ₂ -2 ₀	6295.53	-----	.8				3 ₁ -2 ₂	6337.57	-----	1.4
176	5.8	6297.14	4 ₂ -4 ₁	6297.07	-----	3.3				4-2-3 ₀	-----	6338.05	.7
177	1.0	6298.45	3 ₃ -3 ₁	-----	6298.37	2.0				6-4-6-5	6338.22	-----	1.1
178	.7	6298.79	-----	-----	-----	-----	215	1.0	6338.85	7-3-7-4	6338.59	-----	
179	3.2	6299.69	4 ₂ -4 ₀	-----	6299.59	.8	216	3.3	6339.37	4-1-3 ₀	6339.41	-----	1.7
			3 ₁ -3 ₀	6299.60	-----	1.0				4-1-3-1	-----	6339.71	2.1
			3 ₁ -3-1	-----	6299.84	2.2	217	7.6	6340.65	4-2-2-1	6340.48	-----	5.4
180	.7	6300.85	1 ₀ -0 ₀	-----	6300.26	.5	218	.2	6341.53				
			5 ₃ -5 ₁	-----	6300.81	1.7	219	.4	6341.97				
			2 ₀ -2-2	-----	6300.93	.5	220	4.8	6342.93	6-5-5-5	-----	6343.10	3.5
181	4.8	6301.81	2 ₀ -2-1	6301.65	-----	2.1				6-6-5-4	-----	-----	1.2
182	4.1	6303.17	1 ₁ -0 ₀	6302.75	-----	.9	221	9.3	6344.12	6-6-5-5	6344.17	-----	7.3
			6 ₂ -6 ₁	6303.28	-----	.9				6-5-5-4	-----	-----	2.4
183	.2	6304.72	-----	-----	-----	-----	222	2.5	6345.57	3 ₂ -2 ₂	-----	6345.22	.8
184	1.5	6306.42	5 ₁ -5-1	-----	6306.58	1.4				8-4-8-5	6345.15	-----	.5
185	1.9	6306.94	5 ₁ -5 ₀	-----	6306.91	.6				7-4-7-7	6345.71	-----	.5
186	.6	6307.65	-----	-----	-----	-----	223	3.9	6346.86	5 ₃ -4-1	-----	6346.75	2.4
187	5.4	6309.77	3 ₂ -3-1	6309.62	-----	1.1				5-2-4-2	-----	6347.06	.8
			4 ₀ -4-1	6309.77	-----	1.9	224	8.0	6347.98	5-2-4-1	6347.92	-----	5.5
188	.7	6310.44	4 ₃ -4 ₁	-----	6310.12	1.0				5-3-4-2	6348.15	-----	1.8
			2-2-1 ₀	-----	6310.38	.6	225	4.5	6350.01	7-7-6-5	-----	6350.09	3.1
			3-1-3-3	-----	6310.82	1.1				7-6-6-6	-----	-----	1.0
189	4.3	6311.73	2-1-1 ₀	6311.67	-----	1.4				3 ₃ -2 ₁	6350.42	-----	1.9
			3-1-3-2	6311.83	-----	.5	226	9.4	6351.32	4 ₆ -3 ₁	6351.04	-----	5.1
190	8.0	6312.83	2-1-1-1	-----	6312.10	2.1				7-6-6-5	6351.19	-----	6.3
			4-1-4-1	-----	6312.74	1.3				7-7-6-6	-----	-----	2.1
			2-2-1-1	6312.77	-----	4.7	227	.2	6352.53	-----	-----	-----	.3
191	4.7	6313.25	3 ₀ -3-3	6313.34	-----	1.5	228	.7	6353.04	8-5-8-3	-----	-----	.1
192	2.3	6314.07	7 ₁ -7-1	-----	6313.94	.6				8-6-8-7	6353.03	-----	.4
			4 ₁ -4-2	6314.12	-----	.5	229	5.6	6353.79	4 ₂ -3 ₃	6353.57	-----	3.4
193	1.2	6314.43	-----	-----	-----	-----	230	5.7	6354.21	4 ₁ -3 ₁	-----	6353.91	1.7
194	4.0	6315.73	6 ₃ -6 ₁	-----	6315.57	.7	231	4.7	6354.48	6-4-5-2	-----	6354.64	.8
			5 ₂ -5-1	6316.01	-----	1.1				6-3-5-3	-----	6354.68	.23
195	3.1	6317.62	6 ₀ -6-1	6318.29	-----	1.1	232	8.8	6355.69	5-1-4 ₁	-----	6355.35	1.2
196	4.8	6319.66	5-1-5-3	-----	6319.07	1.0				6-4-5-3	-----	6355.94	5.1
			3-3-2-1	-----	6319.68	2.9				6-3-5-2	-----	-----	1.7
			6 ₁ -6-1	-----	6319.98	.8	233	5.0	6356.45	8-7-7-7	-----	6356.71	2.4
			3-2-2 ₂	-----	6320.01	1.0				8-8-7-6	-----	-----	.8
197	10.0	6320.75	4-1-4-3	-----	6320.52	.9	234	9.3	6357.79	5 ₀ -4 ₁	6357.65	-----	3.9
			2 ₀ -1 ₁	6320.57	-----	4.1				8-8-7-7	6357.91	-----	5.1
			3-2-2-1	6320.71	-----	6.4				8-7-7-6	-----	-----	1.7
			3-3-2-2	6320.95	-----	2.1	235	2.0	-----	-----	-----	-----	
198	6.7	6321.47	4-2-4-3	6321.30	-----	1.3	236	1.0	6359.73	-----	-----	-----	
			5 ₀ -5-3	6321.39	-----	1.4	237	2.7	6360.63	5-1-4 ₀	6360.29	-----	1.5
199	.1	6322.70	7 ₂ -7 ₁	6322.28	-----	.6				5 ₀ -4 ₀	-----	6360.18	.5
200	4.7	6324.00	2 ₁ -1 ₁	-----	6323.99	2.0	238	2.9	6361.88	7-5-6-3	-----	6361.85	2.0
201	2.2	6324.37	-----	-----	-----	-----				7-4-6-4	-----	6361.86	.7
202	.7	6325.39	-----	-----	-----	-----	239	7.9	6363.07	9-9-8-7	-----	6362.96	1.9
203	4.2	6327.23	3-1-2 ₁	-----	6327.04	1.2				9-8-8-3	-----	-----	.6
204	6.0	6327.98	4-4-3-2	-----	6327.97	1.2				7-4-6-3	6363.07	-----	4.2
			4-3-3-3	-----	6328.01	3.5				7-5-6-4	-----	-----	1.4
205	1.00	6329.01	5-3-5-5	-----	6328.79	.8	240	7.2	6364.14	9-8-8-7	6364.08	-----	3.8
			7 ₀ -7-3	6328.92	-----	.7				9-9-8-8	-----	-----	1.3
			4-4-3-3	6329.01	-----	7.5	241	2.1	6364.52	-----	-----	-----	
			4-3-3-2	-----	-----	2.5	242	1.0	6365.31	6-2-5 ₀	-----	6365.20	.5
206	7.0	6329.51	6-2-6-3	6329.25	-----	1.3	243	5.0	6366.60	6-1-5-1	-----	6366.44	1.4
			3 ₀ -2 ₁	6329.56	-----	3.8				6-1-5 ₀	6368.69	-----	1.2
207	1.9	6331.46	-----	-----	-----	-----	244	5.1	6366.80	-----	-----	-----	
208	1.4	6332.00	3-1-2 ₀	6332.23	-----	1.7	245	7.2	6367.44	6-2-5-1	6367.48	-----	3.3
209	3.7	6332.85	3 ₀ -2 ₀	-----	6332.68	.6				-----	-----	-----	
210	2.7	6333.89	2 ₂ -1-1	6333.85	-----	.9				-----	-----	-----	

TABLE 1. Comparison of observed and calculated spectra in 1.6- μ region—Continued

Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity	Line No.	Intensity	Observed wave number	Transition	Calculated wave number		Intensity
				(111)	(012)						(111)	(012)	
246	6.0	cm^{-1} 6368.65	8-6-7-4	-----	6368.75	0.5	264	4.0	cm^{-1} 6387.15				
			8-5-7-5	-----		1.5							
			5-1-4-2	6368.83	-----	1.4							
247	9.5	6370.00	10-9-9-9	6368.85	-----		265	2.5	6388.03	54-44	-----	6387.79	0.9
			10-9-9-8	-----									
			10-9-9-8	6370.00	-----	2.7							
			10-10-9-9	-----		.9							
			8-6-7-5	6370.02	-----	3.3							
248	1.5	6371.06	8-5-7-4	-----			267	4.7	6389.55	55-43	-----	6389.52	2.2
						1.1							
249	.2	6372.34					268	1.3	6390.47				
250	2.0	6373.39	7-3-6-1	-----	6373.24	1.2	269	2.0	6391.65				
			7-2-6-2	-----		.4							
251	3.0	6373.96				270	2.0	6392.46	72-63	6392.41	-----	1.5	
252	6.7	6374.54	11-11-10-9	-----	6374.33	.9	271	5.0	6393.33				
			11-10-10-10	-----		.3							
253	6.8	6375.49	7-2-6-1	6374.61	-----	3.0	272	3.3	6393.98	8-2-7-1	6393.82	-----	1.7
			7-3-6-2	-----		1.0							
			9-7-8-5	-----	6375.31	.7	273	5.0	6394.97	10-6-9-5	6395.07	-----	1.0
			9-6-8-6	-----		.2							
			6-1-5-2	6375.39	-----	.9							
			11-10-10-9	6375.52	-----	1.8							
			11-11-10-10	-----		.6							
254	4.2	6376.17				274	4.4	6397.55	10-5-9-4	-----		.3	
255	6.7	6376.65	9-6-8-5	6376.62	-----	2.4	281	1.3	6403.69				
255A	3.7	6378.86	9-7-8-6	-----		.8	282	1.2	6405.35				
256	3.6	6379.07	4-4-3-1	6379.03	-----	.7	283	2.0	6406.07				
			12-11-11-11	-----	6379.46	.6							
257	5.0	6380.51	12-12-11-10	-----		.3	284	3.5	6406.67	80-71	6406.95	-----	1.4
			6-3-5-4	6379.87	-----	.5							
			6-0-5-1	6380.23	-----	3.3							
			12-11-11-10	6380.69	-----	.4							
			12-12-11-11	-----		1.2							
			8-3-7-3	-----	6380.54	.8							
			8-2-7-4	-----		.3							
			6-1-5-1	-----	6381.64	.9							
			8-4-7-3	6381.96	-----	2.3							
			8-3-7-2	-----		.8							
258	8.0	6381.72	6-1-5-1	-----	6381.64	.9	285	1.3	6407.67				
			8-4-7-3	6381.96	-----	2.3							
			8-3-7-2	-----		.8							
259	5.6	6382.85	10-8-9-7	6382.87	-----	1.6	286	3.0	6408.34				
			10-7-9-6	-----		.5							
			7-1-6-1	-----	6382.99	.8							
260	-----	-----	6-4-5-5	6383.30	-----	1.1	287	4.1	6408.77	65-55	-----	6408.61	1.6
261	-----	-----					288	1.0	6409.49	66-54	-----	6409.50	.5
262	4.3	6384.43					289	2.0	6410.26				
263	6.0	6385.16	7-0-6-1	6385.23	-----	2.2	290	2.0	6410.60				
			6-2-5-0	-----	6385.47	2.9							
							291	2.2	6411.53				
							292	2.3	6412.08				
							293	1.8	6412.82				
							294	1.8	6414.21				
							295	2.0	6414.48				
							296	2.8	6415.89	82-73	6415.76	-----	1.3
							297	1.3	6417.14				
							298	2.1	6418.26				
							299	2.7	6419.15				
							300	.3	6421.94				
							301	.7	6423.05				
							302	1.5	6424.33				
							303	2.7	6425.52				
							304	.4	6427.40				
							305	2.0	6428.99				
							306	2.4	6429.50	77-65	-----	6249.57	1.0

3. Analysis of Experimental Results

The previous analysis of the low-resolution data showed that the absorption in this region could be accounted for by an A-type band, i. e., the dipole moment change along the least inertial axis. The previously calculated spectrum was compared to the new data, and the strong transitions were brought into agreement with the observed absorption peaks through the use of derivatives of the energy with respect to the inertial parameters [4]. Then all transitions of intensity sufficient to be observed were calculated. The fit between the observed and calculated spectra was very good, except that quite a

few of the weaker peaks were not accounted for. Through the use of known ground-state energies [4] it was possible to determine that many of these unaccounted for peaks resulted from a B-type band centered about 1 cm^{-1} lower than the main band. The excited state inertial parameters for this band were determined as described previously [1]. A classical centrifugal distortion correction was applied to the excited-state energy levels of both bands [4].

The excited vibrational state of the A-type band is undoubtedly the (1,1,1) [1]. The excited vibrational state involved in the B-type band is probably the lower component of the resonating pair (0,1,2) and (2,1,0). A calculation based on the quadratic expression for the vibrational-band system of

hydrogen sulfide [5] predicts this band to be at $6,285\text{ cm}^{-1}$, compared to the observed 6288.30 cm^{-1} .

The parameters giving the best fit of the observed data are (1,1,1) $A=10.398$, $B=8.935$, $C=4.548$, $\nu_0=6289.26\text{ cm}^{-1}$; (0,1,2) $A=10.394$, $B=8.918$, $C=4.547$, $\nu_0=6288.28\text{ cm}^{-1}$.

Many of the listed peak positions cannot be attributed to single transitions. The overlapping of two or more transitions will give an observed peak position that will not be the true frequency of any one transition. In many instances, however, definite assignments can be made. This is generally true for the extremely strong transitions because the observed frequency will not be greatly affected by weaker satellites. In the (1,1,1) band the mean deviation of 76 such assignments is 0.10 cm^{-1} . In the (0,1,2) band some 36 peaks were assigned that do not have a dual assignment in the (1,1,1) band. The mean deviation in this case was 0.09 cm^{-1} . That so many of the individual deviations are greater than the mean must be attributed to the effect of finite slit on overlapping transitions. This is especially true of the (0,1,2) band, which is very weak compared to the main band in this region. The classical centrifugal-distortion correction may also be responsible for some of the large deviations. However, it should be pointed out that for low J the corrections are small in any event, and for high J the correction should become classical. Another advantage of this method is that this correction can be evaluated level for level and applied to the rigid levels calculated from published energy tables. The agreement between the observed and calculated spectra may be seen in figure 1 and in table 1. The relative intensity scale within a given band is the same as that used in the previous analysis. In reporting the intensities, the line strengths in the (1,0,2) band were divided by two to give a better picture of the relative importance of the two bands. The P branch of the (1,1,1) band is roughly three times as strong as the P branch of the (0,1,2) band, and the R branch of the (1,1,1) band is approximately twice as strong as the R branch of the (0,1,2) band. Some transitions of the two bands appear to be different from the intensities that one would predict from simple theory. These intensity discrepancies no doubt arise from the effect of Coriolis interaction between the two bands.

The new values of the inertial parameters of the (1, 1, 1) band agree with those determined previously within the estimated error. As the (0, 1, 2) band is somewhat weaker, and the transitions somewhat harder to identify, it is felt that the inertial parameters for this band are not as well determined as those for the main band.

4. Discussion

In figure 1 it will be noted that the calculated spectrum does not account for all the observed absorption lines at the high and low limits of the band. The calculated spectrum in these regions is incomplete as calculations were not extended above $J=12$, the upper limit of published energy tables [6]. Likewise, the other half of the resonating pair,

(0, 1, 2) and (2, 1, 0), is predicted to fall in the high-frequency region of this absorption. It has not been possible to locate any transitions that can be definitely assigned to a band having this upper state; however, it would in all probability be lost in the other two overlapped bands.

In the infrared spectra of water-type molecules, it has been observed that A-type bands are normally very much stronger than B-type bands. In the hydrogen-sulfide spectrum only two B-type bands, (0, 1, 0) and (0, 2, 0), have been observed. It may be possible that other B-type bands are present in the spectrum of hydrogen sulfide that are completely overlapped by strong A-type bands [5, 7, 8, 9]. In each case observed so far the overlapping bands have fitted the criterion for Coriolis-type interaction [10]. In the analysis of the rotational fine structure of all these bands, it has been possible to account for the observed absorption by calculating a theoretical spectrum with effective moments of inertia. There has been no drastic perturbation of individual energy levels. This is in line with what might be expected. As the inertial parameters of the two excited states are nearly the same, the initial separation of the unperturbed energy levels is very nearly constant. Both the interaction and the energy vary nearly as K^2 ; hence it is possible to fit the observed spectra through the use of effective moments of inertia [5], the effect of the Coriolis interaction being absorbed in the inertial constants. The extent of this effect cannot be ascertained until the vibrational system of hydrogen sulfide is better understood. The fact that these B-type bands are observed only when overlapped by a normally strong A-type band seems to indicate that the intensity is interchanged quite readily.

As has been observed in other B-type bands [11], R branch transitions between high τ levels of adjacent J values are apparently stronger than would be predicted by the simple rigid theory. There is still no adequate explanation for this.

The value of $\Delta = I_c - I_a - I_b$ lends additional support to the vibrational assignments proposed here. In both bands its value is large indicating that n_2 equals at least 1 in each of the excited states. The exact value of Δ is of little significance because of the presence of the Coriolis interaction.

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