Infrared Absorption Bands of Ammonia

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Eight NH_3 absorption bands have been recorded in the spectral region 1.0 to 2.0μ with an automatic recording, prism spectrometer. The fine structure of the bands shows that they all belong to the two general types, "composite" and "double." The 1.6μ band is composite like the 1.97μ band first resolved by Stinchcomb and Barker. The intensity of the lines is very uniform, and the line spacing, 10.2 cm^{-1}, agrees with that of the 1.97μ band, 9.98 cm^{-1}. Bands arising from changes of the electric moment parallel to the symmetry axis are double as was found in the 3μ and 10μ bands. The doublet spacing in the 10μ band is 33 cm^{-1}, but only 1.6 cm^{-1} in the one at 3μ. D. M. Dennison has shown that the doublet spacing should rapidly decrease in the higher levels, and for harmonic bands the separation should be so large that they would not appear double. The 1.51μ and 1.22μ bands both appear as double, and have a separation of 30.3 cm^{-1} and 30.4 cm^{-1}, respectively. Evidently the multiplicity of some of the higher levels is more evident than the present theory predicts.

INTRODUCTION

IN the region 1–2μ the author has recorded eight ammonia bands, two of which are really double bands, and a series of very weak lines between 0.97μ and 1.0μ. The fine structure of the 1.97μ band has been observed and analyzed by Stinchcomb and Barker,[1] and J. D. Hardy[2] has reported resolving the 1.5μ band into several overlapping bands. To my knowledge the rest of the bands have not been previously resolved. An excellent résumé of what has been done experimentally on the symmetrical top-type molecule has been made by Schaefer and Matossi.[3] Some doubt has existed in assigning the four fundamental frequencies that theory requires for the ammonia molecule, but those assigned by Dennison and Barker are well founded.

EXPERIMENTAL PROCEDURE

The spectroscope used is of the Littrow type, consisting of two 60° and one 30° glass prisms, (faces 10×15 cm), and a collimating mirror with a 60 cm focus. The prisms were traversed twice, giving a dispersion equivalent to five 60° prisms. A single junction Bi, Bi-Sn, vacuum, microthermocouple was used as a detector, the tinfoil receiver being 0.1×4 mm and the wires 0.01 mm in diameter. The thermocouple operated a Leeds and Northrup high sensitivity galvanometer with a scale distance of five meters. Automatic recording was obtained on camera film, and the reproducibility was excellent. The time required to cover a range of 2000A was usually one and one-half hours, and the zero shift in this time was negligible. Razor blade slits were used with a setting of 0.08 mm in most cases.

The source of continuous radiation used was a 66 watt series street light, with a single straight filament, operated at 120 watts. Under these conditions it gave about 50 hours service at a temperature of 2600°. Four banks of storage batteries connected in parallel supplied a very constant current for the lamp.

No precautions were taken to purify the ammonia used, but the same results were obtained with the gas from an ammonia solution as from liquid ammonia. No absorption cell was necessary as the gas was released into the case of the spectrometer, giving a three meter absorption path. The spectrometer was calibrated by the use of standard mercury and water-vapor lines; the accuracy of the wave-length measurements being in most cases ±1A.

EXPERIMENTAL RESULTS AND ANALYSIS

Fig. 1B shows the 1.97μ band which was first analyzed by Stinchcomb and Barker,[2] and although there is some fine structure not shown

[1] G. A. Stinchcomb and E. F. Barker, Phys. Rev. 33, 305 (1929).

[2] J. D. Hardy, Washington, D. C. meeting of Am. Phys. Soc., April, 1932.

[3] Scheafer and Matossi, *Das Ultrarote Spektrum.*

TABLE I. *Ammonia bands.*

No.	μ	ν	$\Delta\nu$
	A series of weak unanalyzed lines		
1	0.9760	10245.9	
2	0.9774	10231.2	
3	0.9787	10217.6	
4	0.9798	10206.1	
5	0.9811	10192.6	
6	0.9825	10178.1	
7	0.9839	10163.6	
8	0.9854	10148.1	
9	0.9870	10131.7	
10	0.9887	10114.2	
11	0.9905	10095.9	
12	0.9923	10077.5	
13	0.9936	10064.4	
14	0.9947	10053.2	
15	0.9957	10043.1	
16	0.9968	10032.1	
17	0.9979	10021.0	
18	0.9989	10011.0	
19	1.0008	9992.0	
20	1.0018	9982.0	
21	1.0028	9972.1	
22	1.0039	9962.1	
23	1.0049	9951.2	
24	1.0060	9940.3	
25	1.0070	9930.4	
26	1.0080	9920.6	
27	1.0091	9909.7	
	(See Fig. 3A)		
	1.028μ band		
1	1.0107	9894.1	
			10.8
2	1.0118	9883.3	
			10.7
3	1.0129	9872.6	
			9.7
4	1.0139	9862.9	
			9.8
5	1.0149	9853.1	
			10.6
6	1.0160	9842.5	
			9.7
7	1.0170	9832.8	
			9.6
8	1.0180	9823.2	
			8.7
9	1.0190	9814.5	
			10.6
10	1.0200	9803.9	
			9.6
11	1.0210	9794.3	
			11.5
12	1.0222	9782.8	
			10.5
13	1.0233	9772.3	
			9.6
14	1.0243	9762.7	
			11.4
15	1.0254	9751.3	
			7.6
16	1.0264	9743.7	
			11.4
17	1.0275	9732.3	
			10.4
18	1.0286	9721.9	
			16.0

No.	μ	ν	$\Delta\nu$
	1.028μ band (*Cont.*)		
19	1.0303	9705.9	
			20.7
20	1.0325	9685.2	
			20.5
21	1.0347	9664.6	
			14.9
22	1.0363	9649.7	
			15.8
23	1.0380	9633.9	
			18.6
24	1.0400	9615.3	
			14.7
25	1.0416	9600.6	
			17.5
26	1.0435	9583.1	
			15.6
27	1.0452	9567.5	
			18.3
28	1.0472	9549.2	
			18.1
29	1.0492	9531.1	
			17.3
30	1.0511	9513.8	
			17.2
31	1.0530	9496.6	
	(See Figs. 3A and 2)		
	1.18μ band		
1	1.1678	8563.2	
			10.4
2	1.1692	8552.8	
			7.3
3	1.1702	8545.5	
			10.9
4	1.1717	8534.6	
			11.7
5	1.1733	8522.9	
			9.4
6	1.1746	8513.5	
			8.0
7	1.1757	8505.5	
			13.0
8	1.1775	8492.5	
			11.5
9	1.1791	8481.0	
			15.1
10	1.1812	8465.9	
			15.0
11	1.1833	8450.9	
			14.3
12	1.1853	8436.6	
			9.2
13	1.1866	8427.4	
		Av. $\Delta\nu$ = 11.3	
	(See Figs. 4A and 2)		
	1.219μ band		
1	1.1887	8412.6	
			20.5
2	1.1916	8392.1	
			19.0
3	1.1943	8373.1	
			23.8
5	1.1977	8349.3	
			18.1

No.	μ	ν	$\Delta\nu$
	1.219μ band (*Cont.*)		
7	1.2003	8331.2	
			22.1
9	1.2035	8309.1	
			19.3
11	1.2063	8289.8	
			24.0
13	1.2098	8265.8	
			21.8
15	1.2130	8244.0	
			23.7
17	1.2165	8220.3	
			18.2
A 19	1.2192	8202.1	
			15.5
21	1.2215	8186.6	
			20.1
23	1.2245	8166.5	
			26.5
25	1.2285	8140.0	
			16.5
27	1.2310	8123.5	
			23.1
29	1.2345	8100.4	
31	1.2390	8071.0	
32	1.2415	8054.8	
33	1.2437	8040.6	
34	1.2466	8021.8	
35	1.2497	8001.9	
		Av. $\Delta\nu$ = 20.8	
	1.223μ band		
4	1.1956	8364.0	
			22.4
6	1.1988	8341.6	
			20.7
8	1.2018	8320.9	
			20.8
10	1.2048	8300.1	
			20.6
12	1.2078	8279.5	
			19.8
14	1.2107	8259.7	
			23.9
16	1.2142	8235.8	
			25.6
18	1.2180	8210.2	
			16.8
20	1.2205	8193.4	
			16.0
B 22	1.2229	8177.4	
			23.5
24	1.2264	8153.9	
			23.8
26	1.2300	8130.1	
			16.6
28	1.2325	8113.5	
			26.1
30	1.2365	8087.4	
		Av. $\Delta\nu$ = 21.3	
	(See Figs. 4A and 2)		

No.	μ	ν	$\Delta\nu$
	1.258μ band		
1	1.2520	7987.2	
			11.5
2	1.2338	7975.7	
			11.5
3	1.2553	7966.2	
			10.1
4	1.2569	7956.1	
			9.5
5	1.2584	7946.6	
			12.6
6	1.2604	7934.0	
			13.2
7	1.2625	7920.8	
			14.4
8	1.2648	7906.4	
			16.4
9	1.2673	7890.0	
			11.0
10	1.2692	7879.0	
	(See Figs. 4B and 2)		
	1.304μ band		
1	1.2716	7864.1	
			14.2
2	1.2739	7849.9	
			12.9
3	1.2760	7837.0	
			18.5
4	1.2790	7818.5	
			14.5
5	1.2814	7804.0	
			15.8
6	1.2840	7788.2	
			15.2
7	1.2865	7773.0	
			15.7
8	1.2891	7757.3	
			15.0
9	1.2916	7742.3	
			17.3
10	1.2945	7725.0	
			7.6
11	1.2956	7718.4	
			10.8
12	1.2974	7707.6	
			11.2
13	1.2993	7696.4	
			9.4
14	1.3009	7687.0	
			19.5
15	1.3042	7667.5	
			15.2
16	1.3068	7652.3	
			20.5
17	1.3103	7631.8	
			15.1
18	1.3129	7616.7	
			13.9
19	1.3153	7602.8	
			10.6
20	1.3170	7592.2	
			13.6
21	1.3196	7578.5	
			7.3
22	1.3208	7571.2	
			16.6

TABLE I. (*Continued*).

No.	μ	ν	$\Delta\nu$
1.304μ band (*Cont.*)			
23	1.3237	7554.6	
			16.0
24	1.3265	7538.6	
			13.0
25	1.3288	7525.6	
			8.0
26	1.3302	7517.6	
			10.2
27	1.3320	7507.4	
			11.1
28	1.3340	7496.3	
			6.4
29	1.3350	7489.9	
(See Fig. 4B)			
1.509μ			
1	1.4721	6793.0	
			17.9
3	1.4760	6775.1	
			20.7
5	1.4805	6754.4	
			22.7
7	1.4855	6731.7	
			20.3
9	1.4900	6711.4	
			21.6
11	1.4948	6689.8	
			23.1
13	1.5000	6666.7	
			20.9
15	1.5047	6645.8	
			19.8
A17	1.5092	6626.0	
			20.2
19	1.5138	6605.8	
			19.0
21	1.5178	6587.8	
			16.7
23	1.5218	6571.1	
			17.2
25	1.5258	6553.9	
			17.1
27	1.5298	6536.8	
			19.6
29	1.5344	6517.2	
			17.4

No.	μ	ν	$\Delta\nu$
1.509μ (*Cont.*)			
31	1.5385	6499.8	
			18.9
33	1.5430	6480.9	
			20.1
35	1.5478	6460.8	
			20.4
38	1.5527	6440.4	
			18.2
40	1.5571	6422.2	
			21.4
42	1.5623	6400.8	
			19.2
44	1.5670	6381.6	
			19.5
46	1.5718	6362.1	
			23.4
48	1.5776	6338.7	
		av.	19.7
1.516μ			
2	1.4735	6786.5	
			22.0
4	1.4783	6764.5	
			20.5
6	1.4828	6744.0	
			23.6
8	1.4880	6720.4	
			22.0
10	1.4929	6698.4	
			18.0
12	1.4969	6680.4	
			21.3
14	1.5017	6659.1	
			24.3
16	1.5072	6634.8	
			20.2
18	1.5118	6614.6	
			17.4
B20	1.5158	6597.2	
			17.5
22	1.5198	6579.7	
			17.2
24	1.5238	6562.5	
			18.4
26	1.5281	6544.1	
			18.0
28	1.5323	6526.1	
			17.0

No.	μ	ν	$\Delta\nu$
1.516μ (*Cont.*)			
30	1.5363	6509.1	
			17.7
32	1.5405	6491.4	
			21.0
34	1.5455	6470.4	
			25.0
36?	1.5497	6452.8	
37	1.5515	6445.4	
			16.2
39	1.5554	6429.2	
			21.8
41	1.5607	6407.4	
			18.5
43	1.5652	6388.9	
			18.3
45	1.5697	6370.6	
			19.4
47	1.5745	6351.2	
		av.	19.8
(See Figs. 3B and 2)			
1.66μ*			
1	1.5946	6271.2	
			12.6
2	1.5978	6258.6	
			13.7
3	1.6013	6244.9	
			13.6
4	1.6048	6231.3	
			10.1
5	1.6074	6221.2	
			12.3
6	1.6106	6208.9	
			10.0
7	1.6132	6198.9	
			9.6
8	1.6157	6189.3	
			12.6
9	1.6190	6176.7	
			17.2
10	1.6235	6159.5	
			12.2
11	1.6270	6146.3	
			6.1
12	1.6286	6140.2	
			6.0

No.	μ	ν	$\Delta\nu$
1.66μ (*Cont.*)			
13	1.6302	6134.2	
			12.4
14	1.6335	6121.8	
			10.8
15	1.6364	6111.0	
			10.5
16	1.6392	6100.5	
			9.3
17	1.6417	6091.2	
			11.2
18	1.6447	6080.1	
			9.6
19	1.6473	6070.5	
			9.5
20	1.6499	6061.0	
			9.6
21	1.6525	6051.4	
			10.6
22	1.6554	6040.8	
			7.3
23	1.6574	6033.5	
			11.6
24	1.6606	6021.9	
Center		6018	10.8
25	1.6636	6011.1	
			10.5
26	1.6665	6000.6	
			9.3
27	1.6691	5991.3	
			10.8
28	1.6721	5980.5	
			10.3
29	1.6750	5970.2	
			10.7
30	1.6780	5959.5	
			10.7
31	1.6810	5948.8	
			10.6
32	1.6840	5938.2	
			11.3
33	1.6872	5926.9	
			8.0
34	1.6895	5918.9	
			12.3
35	1.6930	5906.6	
			10.0
36	1.6959	5896.6	
			9.1
37	1.6985	5887.5	
(See Figs. 1A and 2)			

* Lines 1 to 13 are very weak and are either another band or an impurity. Average $\Delta\nu = 10.2$ cm^{-1}.

in their work, the agreement is excellent. Four additional lines on the long wave-length end of the band were observed and found to belong to it (see footnote of Fig. 1). The 1.66μ band shown in Fig. 1A is a composite band of the same type as that at 1.97μ, and has a line spacing of 10.2 cm^{-1} as compared to 9.98 cm^{-1}[(1)]. There are thirteen weak lines on the short wave end of this band that do not fit this analysis.

The fundamental vibrational frequencies[1] of the ammonia molecule are given as: $//\nu_1 = 950$ cm^{-1} (double band); $\perp\nu_2 = 1631$ cm^{-1}; $//\nu_3 = 3335$ cm^{-1} (double band); $\perp\nu_4 = 5059$ cm^{-1}.

(Frequencies arising from vibrations of the electric moment parallel to the symmetry axis are designated //, and those due to vibrations perpendicular to the axis are designated as $\perp$.)

The 1.66μ band[3] has been considered to be $\nu = \nu_1 + 3\nu_2 = 5843$ cm^{-1}, but $\nu = \nu_1 + \nu_4 = 6009$ cm^{-1}

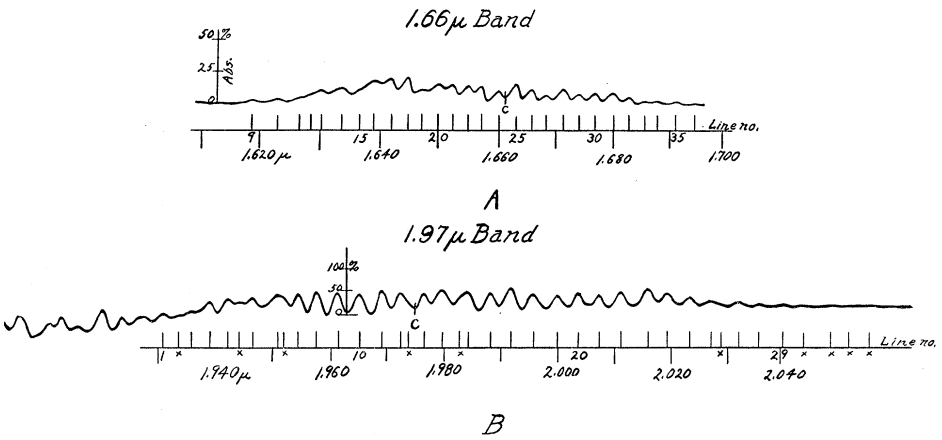

FIG. 1. The 1.66μ band is of the same type as the 1.97μ band first analyzed by Stinchcomb and Barker.[1] These are composite bands with no apparent maximum or minimum of absorption, and extremely uniform line intensity. The line spacing in the 1.97μ band is 9.98 cm^{-1}, in the 1.66μ band, 10.2 cm^{-1}. Four extra lines were found on the long wave-length end of the 1.97μ band that fit the original analysis.[1]

Line No.	ν	$\Delta\nu$	Line No.	ν	$\Delta\nu$
29	4899.7				
30	4890.4	9.3	32	4870.9	8.3
31	4879.2	11.2	33	4861.9	9.0

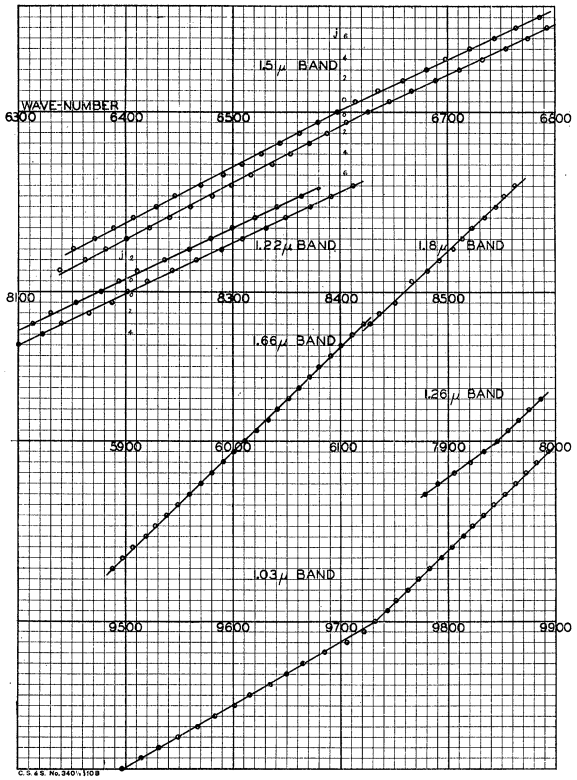

FIG. 2. In each of the graphs the wave number is plotted along the abscissa and the ordinal numbers along the ordinate. Where designated by j, the ordinal numbers represent the initial values of the total angular momentum quantum number.

is more consistent with the selected center of the band, 6018 cm^{-1}.

The 1.5μ band, Fig. 3B, is very intense, but is probably two overlapping bands with a line spacing of 19.7 and 19.8 cm^{-1}, which is in agreement with the 10μ bands,[4] 18.7 and 20.2 cm^{-1}, and the 3μ band,[1] 19.67 cm^{-1}. Because of overlapping the individual structure of the bands cannot be determined, but the spacing in the positive and negative branches seems to be different. The zero branches were selected at the point of convergence. The best lines through the + and − branches are parallel in the two bands and do not show the convergence[4] that the 10.5μ bands do. This might be a composite band, but its general appearance is not such. The extreme overlapping of the lines 1 and 2, Fig. 3B, accounts for the intense absorption at that position in reference to the neighboring lines. Another band at 1.2μ also appears to be double with line spacings 20.8 and 21.3 cm^{-1}. The zero branches A and B were selected because of their prominence.

The average separation of the two bands at 1.2μ is 30.4 cm^{-1}, and 30.3 cm^{-1} for the ones at 1.5μ. The line spacing in these bands might indicate that they are composite, but the general

[4] E. F. Barker, Phys. Rev. 33, 684 (1929).

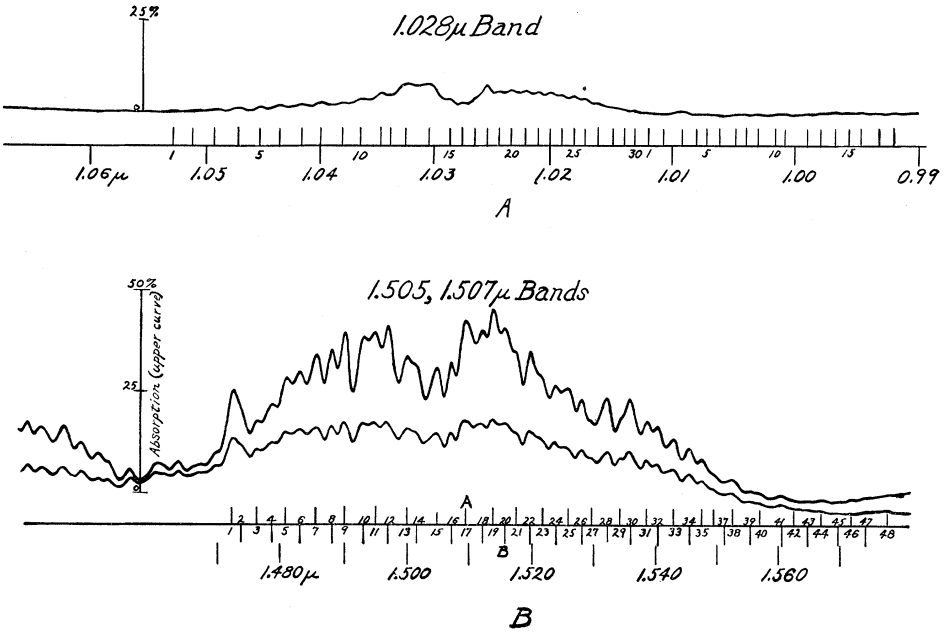

FIG. 3. In the lower figure the upper curve was taken with 0.10 mm slits, and the lower curve with 0.06 mm slits. The absorption lines on the left side of the curves are due to water vapor, which serves as wave-length identification points. The lines *A* and *B* are the assumed zero branches of the two overlapping bands.

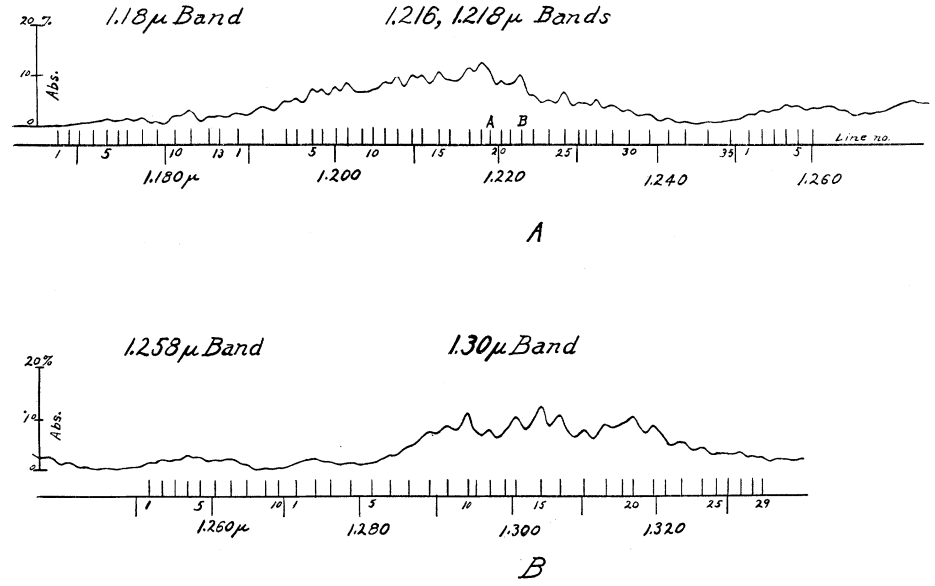

FIG. 4. In the upper curve the lines marked 1 to 35 are two overlapping bands with zero branches marked *A* and *B*. The 1.3μ band shown in the lower curve is evidently a series of overlapping bands with only the strong zero branches resolved.

appearance is that of overlapping bands. The lower vibrational levels of the ammonia molecule are known to be double as is shown by the 10.5μ[4] and 3.0μ[5] bands, but the separation of the doublets in the former is 33 cm^{-1}, while it is only 1.6 cm^{-1} in the latter. Quantum mechanics applied to the problem of symmetrical molecules of the type, YX_3, indicates that all the // vibrational levels are double,[6] and the separation decreases for the higher levels. Multiple levels like $2\nu_1$ and $2\nu_2$ will be double, but the separation should be so large that the bands will not appear double. However the 1.5μ band, which satisfies the condition $2\nu_2 = 6670$ cm^{-1}, is a close double band of 30.3 cm^{-1} separation. The positive and negative branches have slightly different average line spacings, as is shown by the graph in Fig. 2, but this is not uncommon for the symmetrical top-type molecule, due to a small energy of coupling between rotation and vibration.

A number of overlapping bands occur at about 1.3μ, but only the strong zero branches are resolved from the background of fine structure. A more thorough investigation of these bands is now in progress.

[5] D. M. Dennison, Rev. Mod. Phys. 3, 280 (1931).
[6] Dennison and Hardy, Phys. Rev. 39, 938 (1932).

The 1.03μ band has two radically different line spacings; on the high-frequency side it is 10.1 cm^{-1} and on the low-frequency side, 17.3 cm^{-1} (Fig. 2). It is hardly probable that this difference in spacing is due to coupling between rotational and vibrational states, and the two strong lines, 13 and 14, in Fig. 3A may be the zero branches of two unresolved, overlapping bands similar to those at 10μ. The spacing on the high-frequency side suggests the double band, as 10.1 cm^{-1} is half the spacing of the // type bands, and each line on the low-frequency side is wide enough to be an unresolved doublet.

Conclusions

From the above analysis it appears that all the ammonia bands are of two types, // and $\perp$, as theory confirms, but the multiplicity of the higher levels is still to be accounted for. The 1.5μ and 1.2μ bands indicate that there is either a constant separation of some of the higher multiple levels, or that the ground-state levels are separated much more than given by Dennison and Hardy.[6]

I wish to express my appreciation to Dr. A. E. Caswell for his interest in and direction of this work.