THE MOLECULAR SPECTRUM OF AMMONIA
II. THE DOUBLE BAND AT 10μ

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ABSTRACT

Structure of the NH₃ absorption band at 10μ.—The NH_3 absorption band extending from 8μ to 14μ has been sufficiently resolved by means of a grating to reveal the details of its structure. Two very narrow zero branches of nearly equal intensity appear at 10.3μ and 10.7μ, with each of which there is associated a positive and a negative branch consisting of ten or twelve lines spaced at nearly equal frequency intervals. The mean spacing for the higher frequency series is 18.7 cm⁻¹, and for the lower frequency series 20.2 cm⁻¹. Both of these bands must be associated with a single fundamental vibration parallel to the symmetry axis.

Configuration of the molecule as revealed by intensities in the 1.9μ band.—The band structure corresponding to a vibration normal to the symmetry axis is described for symmetrical rotators of the oblate and prolate forms. Line intensities are computed for each from known transition probabilities, and only the oblate form yields intensities in accord with those observed at 1.9μ. The distance of the N atom from the plane of the three H atoms apparently lies between 0.1×10^{-8} and 0.3×10^{-8} cm, which is approximately one fifth of the distance between H atoms.

Interpretation of the double band.—The double character of the 10μ band is shown to be a consequence of the close proximity of the two equilibrium positions for the N atom, one on either side of the plane formed by the H atoms.

THE ammonia absorption band extending over the region from 8μ to 14μ has been partially resolved with a prism spectrometer by Schierkolk[1] and by Robertson and Fox.[2] In both cases the curves reveal certain significant features but just fail to disclose the details of fine structure which are indispensable for an interpretation of the band. The following more complete analysis has resulted from the use of a grating ruled particularly for this purpose, and the rotation series may now be described with some confidence.

The grating is of the echelette type, having 1440 lines per inch ruled upon a surface of tin. It is used with a rock salt fore prism and a collimating mirror of one meter focal length. With a Nernst glower as source and a vacuum thermopile, easily measureable deflections were obtained out to 12μ using 0.5 mm slits, while under the best conditions observations could be extended considerably farther. The spectrum interval included in the slit is about 0.9 cm⁻¹. The absorption cell is a metal cylinder, adjustable in length, with rock-salt windows. A cell length of 2 cm was used for most of the observations, though the positions of stronger maxima were checked with a shorter cell, while the weak regions at the extremities of the band required more gas.

[1] Schierkolk, Zeits. f. Physik **29,** 277 (1924).
[2] Robertson and Fox, Proc. Roy. Soc. **A120,** 161 (1928).

Figure 1 shows the absorption pattern with all observations reduced to approximately 2 cm of ammonia at atmospheric pressure. A striking feature of this curve is the pair of intense absorption maxima near its center, which now appear even narrower than in the prism curves. They lie at approximately 10.3μ and 10.7μ, and are in fact the two zero branches belonging to
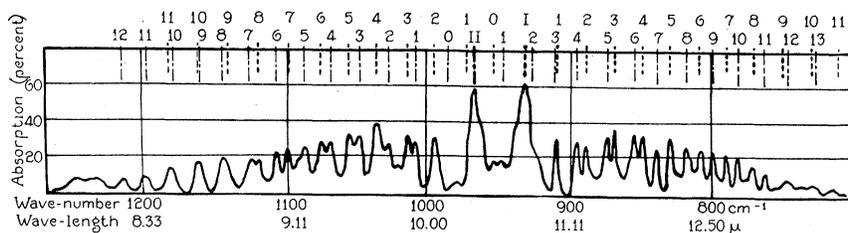
Fig. 1. Absorption pattern for the double band at 10μ.
— — — — — —Series I, with zero branch at 10.71μ.
— — — — —Series II, with zero branch at 10.32μ.

a pair of bands for which the values of ν_0 differ by about 4 percent. The lower frequency band appears to be slightly more intense, although the difference is not great. All of the prominent maxima on either side may be assigned to these two bands, forming series of the usual sort as indicated by the numbering in the figure, which designates the initial rotation states for each transition.

TABLE I. *Wave-numbers and wave-number differences in the 10μ band.*

Band I. 10.7μ or 933 cm^{-1}				Initial	Band II. 10.3μ or 966 cm^{-1}			
+ branch		− branch			+ branch		− branch	
ν	$\Delta\nu$	ν	$\Delta\nu$	j	ν	$\Delta\nu$	ν	$\Delta\nu$
				14	1250	19		
				13	1231	18	726	20
				12	1213	15	746	16
1176	18	711	18	11	1198	19	762	19
1158	18	729	21	10	1179	18	781	18
1140	21	750	20	9	1161	18	799	18
1119	20	770	19	8	1143	18	817	22
1099	22	789	19	7	1125	19	839	17
1077	21	808	20	6	1106	19	856	18
1056	20	828	21	5	1087	18	874	21
1036	21	849	19	4	1069	20	895	14
1015	20	868	21	3	1049	20	909	19
995	20	889	22	2	1029	20	928	21
—	20	911	22	1	1009	18	949	17
955	22			0	981	15		
Mean $\Delta\nu$: 20.2					Mean $\Delta\nu$: 18.7			

The frequencies assigned to each line, after an approximate correction for overlapping has been applied, are shown in Table I, and these numbers are plotted in Fig. 2 against ordinal numbers of the initial states. Neither series shows appreciable convergence. The difference in slope of the two lines indicates that they have not quite the same spacing, which accounts

for the apparent irregularities in the pattern. The mean wave-number differences for the two bands are 20.2 cm^{-1} and 18.7 cm^{-1}, a variation in spacing of about 8 percent. This precludes the possibility of associating them with two independent fundamental vibrations, which should yield precisely the same moment of inertia.
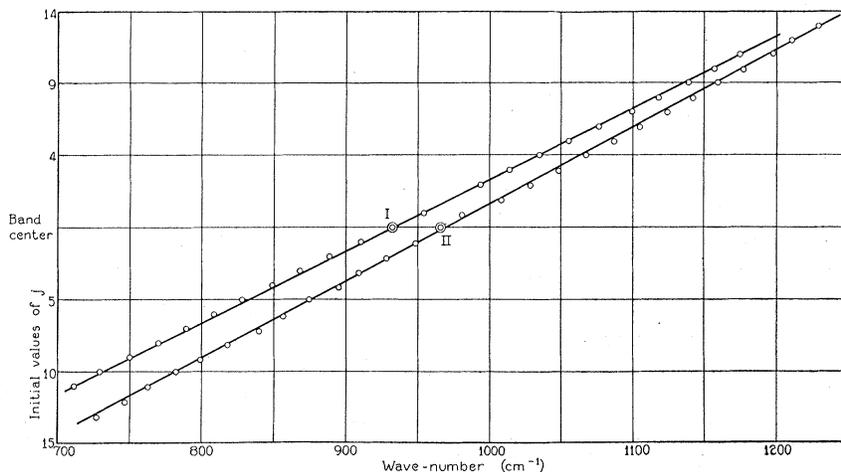
Fig. 2. Line frequencies in the 10μ band as functions of j, for series I and series II.

The simplest assumption regarding atomic configuration is an axially symmetrical triangular pyramid with the nitrogen atom at its vertex. (A special case in which the altitude is zero and all four atoms lie in a plane is not to be excluded a priori.) This system rotates with a simple precession. If $jh/2\pi$ is the total angular momentum, and $ih/2\pi$ the angular momentum about the symmetry axis, then the premissible angles of precession are given by the relation $\cos\theta = i/j$. The rotational energy is

$$W = \frac{h^2}{8\pi^2}\left(\frac{1}{A}(j^2+j)+\left(\frac{1}{C}-\frac{1}{A}\right)i^2+\text{const.}\right)$$

where C and A are respectively the moments of inertia about the symmetry axis and any other axis perpendicular to it.[3] Hence the changes in energy of rotation for changes Δj and Δi in quantum numbers are

$$\Delta W = \frac{h^2}{8\pi^2}\left(\frac{1}{A}[(2j+1)\Delta j+(\Delta j)^2]+\left(\frac{1}{C}-\frac{1}{A}\right)(2i\Delta i+(\Delta i)^2)\right). \tag{1}$$

Such transitions, accompanied by changes in energy of vibration, yield the various infra-red bands according to the following selection rules:

I. $\Delta i = 0$, $\Delta j = 0$ or ± 1 for a symmetrical vibration in which the changes in electric moment are parallel to the symmetry axis.

[3] Cf. Nat. Res. Counc. Bull. No. 57, Molecular Spectra of Gases, p. 60 sq.

II. $\Delta i = \pm 1$, $\Delta j = 0$ or ± 1 when the change in electric moment is normal to the symmetry axis.

Two fundamental frequencies of each sort are to be expected.[4]

The bands observed near 10μ (Fig. 1) obviously follow the first rule. Each of the prominent zero branches corresponding to $\Delta i = 0$, $\Delta j = 0$ is really a composite of lines of very nearly the same frequency absorbed by different molecules having various values of i and j. It is apparent from the sharpness of the absorption maxima that the energy of coupling between vibration and rotation is almost negligible, a fact also indicated by the small convergence in positive and negative branches. For the latter $\Delta i = 0$, $\Delta j = \pm 1$, and Eq. (1) becomes

$$\Delta W = \frac{h^2}{4\pi^2}\left(\frac{1}{A}\left[\pm\left(j+\frac{1}{2}\right)+\frac{1}{2}\right]\right). \tag{2}$$

The corresponding lines form a series spaced $h/4\pi^2 cA$ cm^{-1} apart. For integral values of j there will be one absent member at the center, which position, however, is occupied by the zero branch.

A second band of this type, which, however, does not exhibit the same double character, is found at 3μ, and has already been described.[5] It has a line interval of approximately 19.7 cm^{-1}, which agrees well with the mean for the two series at 10μ. The envelope of the 6μ absorption region as observed with a prism spectrograph very strongly suggests a third band of the same kind. However our observations here, although as yet only in a preliminary stage, seem to indicate that this may be a composite band of a different sort.

For vibrations normal to the symmetry axis the bands are no longer single, but appear in groups. When $\Delta i = \pm 1$ and $\Delta j = 0$, Eq. (1) becomes

$$\Delta W = \frac{h^2}{4\pi^2}\left(\left(\frac{1}{C}-\frac{1}{A}\right)\left(\pm i+\frac{1}{2}\right)\right), \tag{3}$$

while $\Delta i = \pm 1$, $\Delta j = \pm 1$ yields

$$\Delta W = \frac{h^2}{4\pi^2}\left(\left(\frac{1}{A}\left[\pm\left(j+\frac{1}{2}\right)+\frac{1}{2}\right]+\left(\frac{1}{C}-\frac{1}{A}\right)\left(\pm i+\frac{1}{2}\right)\right)\right). \tag{4}$$

Eq. (3) represents a set of zero branches and Eq. (4) the corresponding positive and negative branches for a family of superposed bands, whose positions depend upon the values of i and the sign of Δi. The line spacing in each band (constant i and Δi) is $h/4\pi^2 cA$ cm^{-1} as in Eq. (2), but the zero branches, which may constitute the most noticeable absorption peaks, are separated by $(1/C - 1/A)h/4\pi^2 c$ cm^{-1}. This yields a sequence of maxima with no missing members, of which the two most intense ones correspond to the transitions $0 \rightleftarrows 1$. The envelope of these maxima would not exhibit

[4] Dennison, Phil. Mag. 1, 195 (1926).
[5] Stinchcomb and Barker, Phys. Rev. 33, 305 (1929).

the doublet appearance characteristic of many unresolved infra-red bands. Should it happen that the ratio of the quantities $1/A$ and $(1/C-1/A)$ is

Oblate, $C=2A$

ν_0

Prolate, $C=(2/3)A$

ν_0
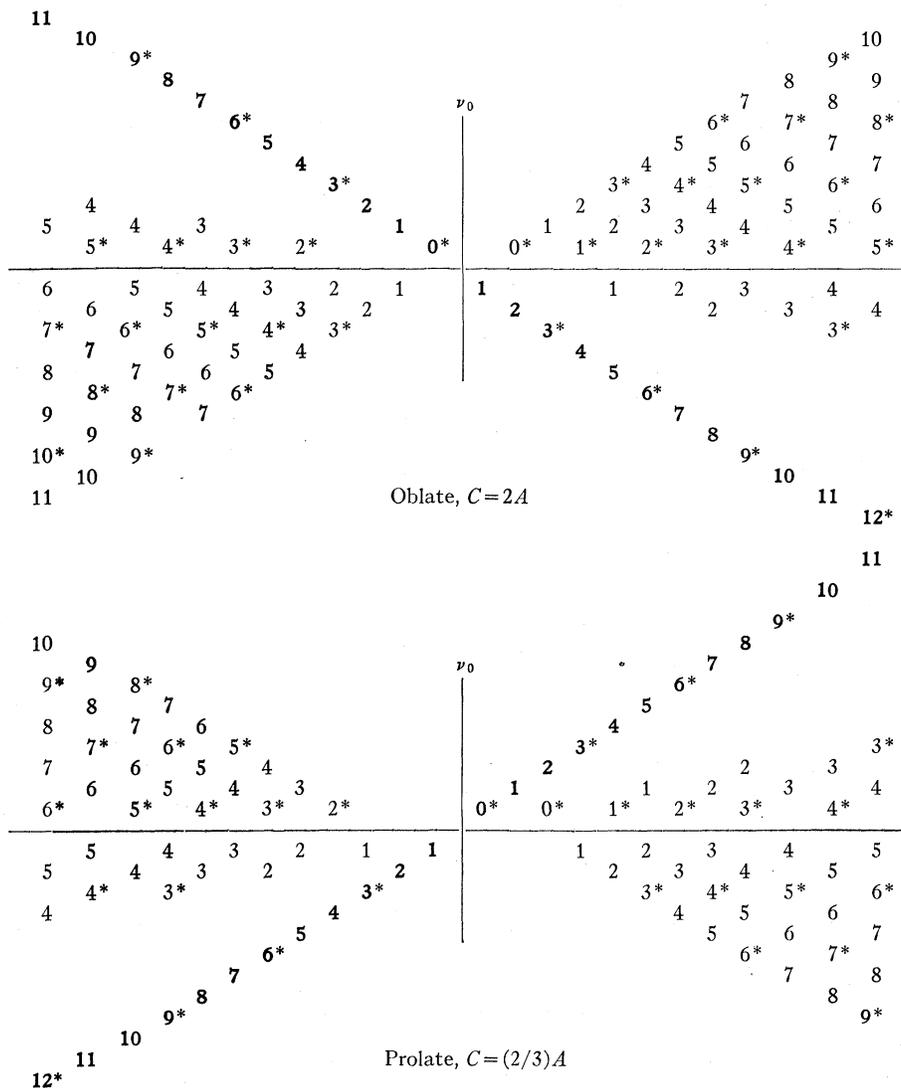
Fig. 3. Structure of vibration-rotation band for vibrations normal to symmetry axis and spacing ratio 2:1.

Diagonals indicate initial i values for zero branches with $\Delta j = 0$.

Associated initial j values are shown for $+$ and $-$ branches.

* indicates levels occupied by molecules having complete three-fold symmetry.

Higher frequencies to the right.

nearly integral, and also that the convergence of the series is small, then the lines represented by Eq. (4) would be superposed upon those of Eq.

(3), and the observed intensity distribution would not be that characteristic of Eq. (3) alone.

The ammonia band near 2μ, previously reported,[5] is of exactly this type. Some twenty lines appear, with spacing and intensity very nearly uniform, and with no obvious feature to indicate the band center. The frequency interval is almost exactly half of that observed in the other bands. This suggests either an arrangement of the four atoms approximately in a plane, $C = 2A$, $(1/A - 1/C) = 1/2A$, or in a pyramid such that $C = 2/3A$, $(1/C - 1/A) = 1/2A$. The rotations of these two structures would . correspond respectively to those of an oblate and a prolate ellipsoid. Figure 3 shows the composition of such a band on the assumption of no convergence, and a spacing ratio of exactly 2:1. The numbers in bold type along the diagonals represent initial i values for the zero branches ($\Delta j = 0$), the transitions $\Delta i = +1$ and $\Delta i = -1$ lying respectively in the upper and lower halves of each figure. With each i transition there is associated a series of j transitions, with positive and negative branches on the sides of higher and lower frequencies. These are arranged in horizontal rows, the numbers representing initial j values. The similarity in arrangement for the oblate and prolate cases makes it apparent that the two cannot be distinguished by a superficial examination.

Because of the nuclear spin of the H atoms two different sorts of NH_3 molecules are to be expected, those which exhibit a three-fold symmetry having all three spins oriented in the same direction, and those which do not because one of the H nuclei is reversed. Those of the former type are distributed only upon the energy levels marked*, which, as a consequence, have their populations doubled.

The relative intensites for all of the lines indicated in this figure may be estimated with the aid of transition probabilities computed by Dennison,[6] and by summing those in each column a result is obtained which may be compared with the observed band. Slightly different intensity distributions are to be expected for the oblate and prolate models, and this apparently offers the only hope of distinguishing between the two possibilities. Table II summarizes the results, showing separately the contributions due to transitions $\Delta j = 0$ and $\Delta j = \pm 1$ when the symmetry in nuclear spins is neglected, and the additional effect resulting from this symmetry. In comparing the totals with line intensities as observed it must be remembered (a) that the actual spacing ratio is probably not exactly 2:1, (b) that there is probably a slight convergence with consequent change in spacing across each component band, and (c) that the computed total intensities should not be directly proportional to the maximum absorption percentages as observed, but more nearly to the logarithms of the squares of these numbers.[7] Thus an exact quantitative agreement is hardly to be expected. However it is at once obvious that the oblate form yields results very closely resembling

[6] Dennison, Phys. Rev. 28, 318 (1926).

[7] Dennison, Phys. Rev. 31, 503 (1928).

the observed curve while those for the prolate form are quite inconsistent.[8] This is true both as to variations in intensity from line to line across the band, and as to the shape of the envelope which, for the prolate case, drops off much too rapidly on each side of the center. If C is slightly less than $2A$, and the finer spacing therefore slightly less than half the coarser, the effects (a) and (b) combined would tend to throw the various components together on the low frequency side and separate them on the high frequency side. This may account for the lack of contrast between lines and background on the left edge of the observed pattern.

TABLE II. *Total intensities for band indicated in Figure 3.*

| \multicolumn{4}{Oblate configuration} | ν for band at 1.9μ | \multicolumn{4}{Prolate configuration} |
Δj=0	Δj=±1	sym.	total		Δj=0	Δj=±1	sym.	total
0.01	1.65	0.48	2.14	5168.8				
.02	2.07	.83	2.92	5158.7	—	1.39	0.84	2.23
.05	2.45	.83	3.33	5148.6	—	1.07	.29	1.36
.10	2.72	.66	3.48	5137.7	—	.76	.05	.81
.18	2.94	1.39	4.51	5126.0	—	1.33	.35	1.68
.30	2.78	.86	3.94	5117.1	.01	.87	.05	.93
.47	2.46	.84	3.77	5107.8	.04	.48	.41	.93
.73	1.97	1.22	3.92	5098.0	.12	.88	.03	1.03
1.08	1.37	.34	2.79	5088.7	.27	.40	.34	1.01
1.53	.69	1.52	3.74	5079.1	.59	.11	.59	1.29
2.06	.25	.25	2.56	5069.4	1.12	.25	.25	1.62
2.59	—	—	2.59 center)	5058.7	1.83	—	—	1.83
2.51	—	2.51	5.02)	5050.1	(2.53	—	2.53	5.06 center
1.91	.23	—	2.14	5040.2	2.47	.—	—	2.47
1.34	.62	—	1.96	5029.1	1.70	—	—	1.70
.91	1.16	1.78	3.85	5019.4	.99	.22	.99	2.21
.58	1.60	.09	2.27	5009.4	.51	.09	.09	.69
.36	1.89	.63	2.88	4999.6	.22	.32	—	.54
.22	2.04	1.24	3.50	4989.7	.08	.67	.22	.98
.12	2.01	.42	2.55	4980.1	.03	.35	.01	.39
.07	1.81	.60	2.48	4970.1	.01	.61	.14	.76
.03	1.56	.69	2.28	4959.6	—	.89	.59	1.48
.02	1.25	.34	1.61	4950.6	—	.49	.12	.61
.01	.94	.29	1.24	4940.2	—	.66	.42	1.08
				4930.6	—	.81	.08	.89

It thus appears that the N atom must lie very close to the plane of the three H atoms, forming a pyramid of very small altitude. A lower limit for this altitude h may be obtained from the electric moment, the value of which is 1.44×10^{-18}.[9] The extreme case where the N is assigned a charge -3 and each H a charge $+1$ requires for h the value 0.1×10^{-8} cm. The upper limit to be assigned for this dimension depends upon the accuracy with which the ratio C/A can be determined. The value of A computed from the mean $\Delta \nu$ for the 3μ and 10μ bands is 2.8×10^{-40}. An equally precise value of C cannot as yet be determined, because in the first place the lines in the band at 1.98μ are all composite and the zero branches cannot be

[8] Cf. Fig. 2, Reference 5.

[9] Zahn, Phys. Rev. **27**, 455 (1926).

located with great accuracy, and secondly, the dependence upon C of line spacing in this band is represented only in first approximation by Eq. (3) and (4), the system being considered as rigid. That perturbations may be of considerable importance in the case of vibrations normal to the symmetry axis appears from the fact that the spacing is often appreciably different in two such bands absorbed by the same molecule. Nevertheless it would seem quite safe to consider that our value of $(1/A - 1/C)$ is not in error by more than 10 percent. The maximum value of h estimated thus is slightly less than 0.3×10^{-8} cm which is about one fifth of the distance between H atoms.

This conclusion that the four atoms in NH_3 lie nearly but not quite in a plane is of especial interest in that it provides an explanation for the doubling of the band at 10μ.[10] In the vibration here concerned the three H atoms move symmetrically, the distances between them increasing as h decreases. The potential energy function plotted in terms of h decreases in either direction from the plane of the H atoms to a minimum corresponding to the equilibrium position, and then rises again. A maximum at $h = 0$ thus separates two adjacent minima corresponding to two possible positions for the N atom. As a consequence each vibrational energy level is divided into a pair of levels of different symmetry character, the antisymmetric lying above the symmetric. Transitions occur only between states of unlike character, e.g. $1_a \rightleftarrows 0_s$ or $1_s \rightleftarrows 0_a$, of which the former corresponds to the larger energy difference and higher frequency. The separation between pairs of levels is a function of the height of the potential energy maximum for $h = 0$, and diminishes rapidly as this maximum increases. For this reason it is observable only when the two minima lie close together. A similar doubling ought to occur in the 3μ band, which also corresponds to a vibration along the symmetry axis. However in this case the distance between H atoms *decreases* as h decreases, so that the potential energy rises much more rapidly as h approaches zero. The consequent reduction in the separation of pairs of levels apparently renders them indistinguishable.

Double bands apparently corresponding to that of NH_3 at 10μ have been observed in about the same region for PH_3 and AsH_3 by Robertson and Fox. In each of these the separation of zero branches is considerably greater than for NH_3, which suggests a still more oblate configuration.

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[10] I am indebted to Professor Dennison for suggesting this explanation.