MARCH 15, 1932 PHYSICAL REVIEW VOLUME 39

THE PARALLEL TYPE ABSORPTION BANDS OF AMMONIA

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(Received February 1, 1932)

Abstract

The form of the ammonia molecule is discussed together with the theory that all of the vibrational levels of the molecule should be double due to the two equivalent positions of equilibrium of the nitrogen atom. This theory serves to explain the doubling of the $\|$ band at 10.5μ and further predicts that the lines of the 3.0μ band should also appear as doublets although with a much finer separation. An experimental search is made for the doubling of the 3.0μ band using an infrared spectrometer of high resolving power. The effect is found, each fine structure line appearing as a doublet with a mean separation of about 1.6 cm^{-1}. The theoretical intensities of the $\|$ type ammonia bands are computed assuming that the hydrogen nucleus possesses a spin of $\frac{1}{2}(h/2\pi)$. When these values are compared with the observed lines of the 3.0μ and the 10.5μ bands, a very satisfactory agreement is obtained. This agreement furnishes a strong argument for the theory of the doubling of the ammonia bands. It further proves that those states of ammonia existing in nature have vibration—rotation—nuclear spin wave functions which are antisymmetrical for an interchange of two of the hydrogen atoms.

Introduction

The infrared spectrum of ammonia, NH_3, appears to prove rather conclusively that the molecule has the form of a regular pyramid where the three hydrogen nuclei lie at the corners of an equilateral triangle with the nitrogen nucleus lying on an axis perpendicular to the plane of the hydrogens and passing through their center of gravity. The regularity of the fine structure lines of the absorption bands at 3.0μ and 10.5μ as well as the uniform spacing of the far infrared lines, guarantees that the molecule is of the symmetrical top variety where two moments of inertia are equal $A=B$, with the third moment of inertia, C, different. It is moreover clear that the atoms can not all be coplanar since then the system would possess a zero permanent electric moment, contrary to the observed datum[1] $\mu=1.5\times 10^{-18}$.

These conclusions as to the form of the molecule are further strengthened by the fact that all the near infrared absorption bands of ammonia may be correlated with the aid of four fundamental frequencies, not six as would be the case if the molecule were unsymmetrical.

Symmetrical molecules of the YX_3 type which are not coplanar exhibit a feature which at first appears to be rather unusual, namely, that all the vibrational levels are double. This phenomenon depends upon the fact that there are two exactly equivalent positions of equilibrium for the Y atom, one, say, above the plane of the X atoms and the other at an equal distance below.

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[1] For a summary of the experimental work, see P. Debye, Polar Molecules (1929) page 40.

Such a circumstance would on the basis of classical mechanics not influence the vibrational levels but a quantum mechanical treatment reveals that it causes the vibrational levels to become double.[2] The magnitude of the doublet separation is in general small compared with the spacing between the vibrational levels themselves and need not be the same for all vibrational levels. It is proposed to discuss in more detail the amount of the doublet spacing elsewhere. For the purposes of this paper it is only necessary to state that it becomes observable spectroscopically (i.e., $\delta\nu$ is at least as large as 0.1 cm^{-1}), only when the Y atom lies quite close to the plane of the X atoms.

The 10.5μ band of ammonia has been resolved into its fine structure lines by E. F. Barker[3] and consists of two similar and complete bands separated by an interval of about 33 cm^{-1}. It has been suggested that the doubling of this band is the result of the doubling of the vibrational levels which has just been described. We have attempted in the present paper to strengthen this explanation in two ways: first, by showing experimentally that the fundamental band at 3.0μ also possesses a double structure but with a much smaller doublet separation, and second, by computing the intensities of the fine structure lines of both the 10.5μ and 3.0μ bands and showing that these agree with the experimental data. This last computation will further allow us to determine the symmetry character of that part of the wave function which is independent of the coordinates and spins of the electrons.

Of the four fundamental frequencies of a symmetrical molecule YX_3, two, ν_1 and ν_3, correspond to vibrations for which the change of the electric moment lies along the symmetry axis. The fine structure of these bands, which are often called $\|$ type bands, is very much simpler than the fine structure of the $\perp$ type bands and consists of a strong zero branch on either side of which lies a set of lines uniformly spaced in frequency. These latter lines constitute the positive and negative branches of the band.

The fine structure of the absorption band of ammonia at 10.5μ proves that this band is of the $\|$ type while its great intensity shows that it must be a fundamental and we may identify it with the frequency ν_3. The band at 3.0μ has been resolved by Stinchcomb and Barker[4] who find that it also corresponds to a $\|$ vibration. This in itself might not with certainty serve to identify it as the second $\|$ frequency ν_1, since the intensity is not so great that it excludes the possibility that the band might be a strong harmonic or overtone frequency. However, in the Raman spectrum of gaseous ammonia,[5] the strongest frequency to be observed just corresponds to the 3.0μ band. This virtually proves that the band in question is a fundamental band and since its fine structure is of the $\|$ type we may conclude that it is the fundamental frequency ν_1.

We have represented the energy level diagram of certain of the lowest

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[2] The qualitative theory which was proposed by F. Hund, Zeits. f. Physik **43,** 805 (1927) is described by D. M. Dennison, Rev. Mod. Phy. **3,** 280 (1931).

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

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

[5] R. G. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34,** 582 (1929).

vibrational states of ammonia in Fig. 1, which for convenience is not drawn to scale. The two lowest levels form the ground state of the vibrational spectrum and are separated by an interval which we call $\delta\nu_0$. The next two levels form the first excited state of the vibration ν_3 and lie about 950 cm^{-1} above the ground state. The separation is here $(\delta\nu_3)_1$. All levels are further given the designation α or β where the states α have wave functions of which the part depending upon the vibrational coordinates alone is symmetrical for an interchange of any two of the hydrogen nuclei. The states β are antisymmetrical for this interchange. Now it may easily be shown[6] that all $\|$ type infrared bands correspond to a transition from an α state to a β state or from a β state to an α state. The transitions giving rise to the fundamental frequency ν_3 are drawn in Fig. 1, and show that this band will appear as two similar and nearly superimposed bands. The doublet spacing which has been measured by Barker represents the sum of $\delta\nu_0$ and $(\delta\nu_3)_1$; thus

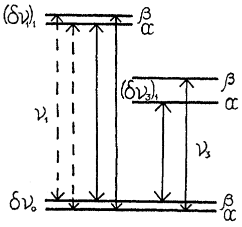

Fig. 1.

$$\delta\nu_0 + (\delta\nu_3)_1 = 33\,\text{cm}^{-1}.$$

Exactly the same argument may be repeated for the fundamental band ν_1. It should consist of two bands with a doublet spacing $\delta\nu_0 + (\delta\nu_1)_1$. It is this quantity the experimental measurement of which will be described in the next section. It is found that $\delta\nu_0 + (\delta\nu_1)_1 = 1.6$ cm^{-1}. Reasons may be given which make it appear very plausible why the doublet spacing should be so much smaller for the band ν_1 than for the band ν_3.

Qualitatively the magnitude of the splitting of the levels depends upon the ratio of the amplitude of the nitrogen atom (relative to the plane of the hydrogens) to the normal distance of the nitrogen atom from this plane. Now the fact that the splitting is sufficiently large to be observed spectroscopically means that the altitude of the regular pyramid in the normal state must be small and this allows us to infer the properties of the motion. In the vibration ν_3, the relative motion of the hydrogen nuclei in their plane is small and the motion consists principally of a vibration of the nitrogen atom relative to this plane. Thus we should expect that $(\delta\nu_3)_1 \gg \delta\nu_0$. It may be remarked that we should similarly expect $(\delta\nu_3)_2 \gg (\delta\nu_3)_1$ and thus if a first harmonic, $2\nu_3$,

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[6] The intensity of a $\|$ type band depends upon such matrix elements as $\int_{-\infty}^{+\infty} x\psi_1\psi_2 dx$. Now x is an odd function, the ψ of an α state is an even function while the ψ of a β state is an odd function of x. The matrix element vanishes unless the integrand as a whole is an even function of x and thus we can only have transitions from states $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$.

should ever be observed it would consist of two bands so widely separated that they would probably not be recognized as a doublet band at all.

In the limiting case of a flat pyramid, the vibration ν_1 consists principally of a motion of the hydrogen nuclei in their plane. The amplitude of the nitrogen nucleus relative to this plane would in general be small and we could infer from this that $(\delta\nu_1)_1$ would be of the same order of magnitude as $\delta\nu_0$.

These considerations are greatly strengthened by measurements of Dickinson, Dillon and Rasetti of the fine structure of the Raman band corresponding to ν_1. The arguments which showed that the $\|$ type infrared bands must be correlated with transitions from levels $\alpha\rightarrow\beta$ or $\beta\rightarrow\alpha$ also show that for a $\|$ type Raman band the transitions must be from $\alpha\rightarrow\alpha$ or from $\beta\rightarrow\beta$. These transitions for the frequency ν_1 are shown in Fig. 1 with dotted lines. Accordingly, the fine structure lines as observed in the Raman spectrum should also be doublets but with the spacing constant $(\delta\nu_1)_1-\delta\nu_0$. The measurements of Dickinson, Dillon and Rasetti show these lines to be single within the limit of observation which is probably at least as good as 1 cm^{-1}. Thus from these experimental data as well as from our theoretical conclusions (which are only presented here in qualitative form) we find $(\delta\nu_1)_1 \cong \delta\nu_0$.

Before leaving this section we would like to remark that the far infrared rotation lines of ammonia which have been observed by Badger and Cartwright,[7] may be regarded as forming part of a $\|$ type vibration. It can easily be shown that they correspond to transitions between the two levels forming the ground state of the vibrational energy diagram. Therefore these pure rotation lines should also be double with a doublet spacing $2\delta\nu_0 \cong 1.6$ cm^{-1}. No trace of a doubling can be noted in the experimental curves obtained by Badger and Cartwright but the dispersion of their spectrometer was certainly not sufficient to separate lines as close together as 1.6 cm^{-1}.

Experimental Procedure and Results

The spectrometer which was used in this experiment has been previously described[8] and for the region of 3μ a 7200 line echelette grating (ruled at the University of Michigan by Professor E. F. Barker) was used. The grating was so ruled as to give a very strong intensity at the 3μ region, thus permitting the use of very narrow slits. The grating spectrometer was preceded by a small prism spectrometer, the latter being used to separate the second order of 1.5μ, which is exceedingly strong, from the first order of 3μ. The separation was considered complete enough for this experiment when the prism was so adjusted that the deflections in the first order of 1.5μ were one fourth the total deflection obtained when the grating was turned to 3μ.

The thermocouple, which is of the Pfund design, was connected to a Leeds and Northrup galvanometer, the deflections of which were amplified by means of a Pfund thermoelectric amplifier. Usually an amplification of about six hundred could be used and the deflections determined to an accuracy of about one percent. The width of the slits was varied between 0.05 and 0.15

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[7] R. M. Badger and C. H. Cartwright, Phys. Rev. **33**, 692 (1929).

[8] J. D. Hardy, Phys. Rev. 38, 2162, (1931).

mm depending upon the kind of work that was being done, but in the final runs both slits were set at 0.07 mm. Under these conditions deflections of 40 cm were obtained with the absorption cell out of the path and 25 cm with the cell in the path. The steadiness of the instrument was such that readings could be made in the daytime as well as at night.

When the slits were 0.15 mm in width they included a wave-length range of ten angstroms or about one frequency unit. For more careful examination of the rotation lines the slits were adjusted to include a little less than one half of one frequency unit.

The cell which was used was six centimeters in length and supplied with KBr windows. The ammonia was introduced from a tank through a liquid air trap, and the pressure of the ammonia in the cell was made to be approximately that of the atmosphere. The readings were made alternately through the cell and through the air in order to correct for water vapor absorption. No correction was applied for the absorption of the windows and the resulting curves cannot therefore be given in percent absorption. The heights of the lines give some measure of their relative intensities although not an accurate one.

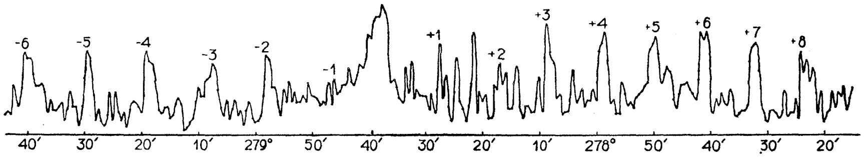

Fig. 2. 3μ ammonia band surveyed with 0.15 mm slits.

Fig. 2 shows a general survey of the 3.0μ band as made with 0.15 mm slits. There is shown the complexity of the background and an indication of the doubling of the rotation lines. The existence of this background can very probably be explained as the first harmonic of the strong ammonia band at 6.0μ. Although it is strong enough to apparently mask the simple structure of the $\|$ type band ν_1, it did not cause any very serious difficulty since after the lines belonging to ν_1 were once located they could be carefully studied individually without mapping the intervening background.

In Fig. 3a is shown the results obtained with narrowed slits. The regions between the rotation lines were not examined carefully and are therefore omitted from this diagram.

The wave-length accuracy is about one in ten thousand or three angstroms. The calibration of the grating was repeatedly checked and the position of the central image determined with each set of readings. The calibration and the position of the central image were found to remain very constant.

The observed positions of the lines in frequency units as well as the frequency intervals between lines are given in Table I. The lines are grouped in pairs by means of a bracket and the upper figure relates to a line of the $\beta\rightarrow\alpha$ band while the lower relates to a line of the $\alpha\rightarrow\beta$ band.

The doublet separation $(\delta\nu_1)_1+\delta\nu_0$ varies from 1.4 cm^{-1} to 2.1 cm^{-1} and

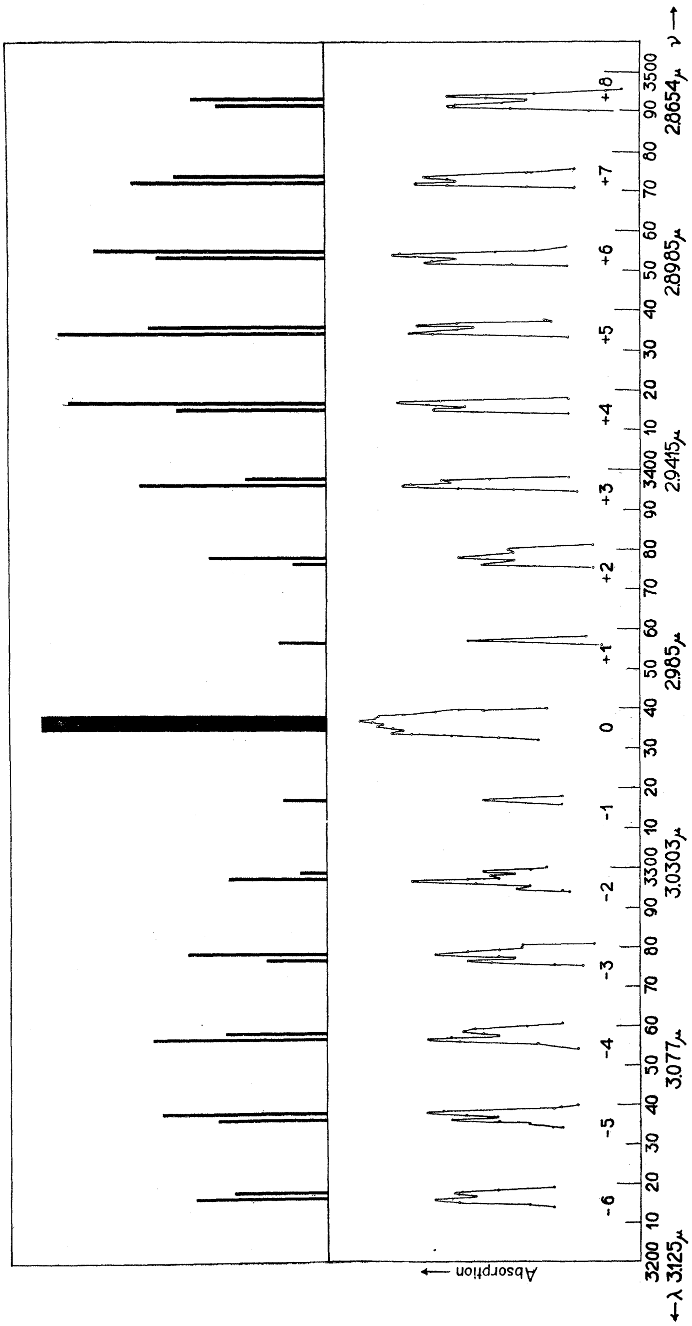

Fig. 3. Showing zero branch and rotation lines as observed under high dispersion. Slits—0.07 mm; 4A; 0.5 cm^{-1}.

has an average value of 1.6 cm^{-1}. It does not appear probable that the accuracy with which we have determined this constant can be greater than 10 to 20 percent. We feel that the considerable variation observed is very possibly due to the presence of the strong and irregularly spaced lines of the background. The average interval between lines of the $\beta \rightarrow \alpha$ band is 19.64 cm^{-1} while the interval for the $\alpha \rightarrow \beta$ band is 19.46 cm^{-1}. These data lead to values for the moment of inertia A of 2.81 and 2.84×10^{-40} respectively in good agreement with the values of A as determined from Barker's measurements on the 10.5μ band,[9] namely, 2.79 and 2.82×10^{-40}. The observations of the Raman band corresponding to the 3.0μ vibration yield $A = 2.79 \times 10^{-40}$ while the far infrared pure rotation lines give $A = 2.78 \times 10^{-40}$. It will be noticed from Table I that while the average value of the line interval is satisfactory, there is a considerable variation in the individual values which appears to be much higher than can be accounted for as experimental error in the spectrometer itself although it might be due to the presence of the strong background lines.

TABLE I.

Line No.	Positive branch	$(\delta\nu_1)_1 + \delta\nu_0$	$\Delta\nu$	Negative branch	$(\delta\nu_1)_1 + \delta\nu_0$	$\Delta\nu$
0	3336.8 cm^{-1}			3336.8 cm^{-1}		
1	3356.6 —	—		— 3316.8	—	— 18.2
			19.7 —			
2	3376.3 3378.0	1.7		3297.1 3298.6	1.5	
			19.8 19.6			20.4 20.4
3	3396.1 3397.6	1.5		3276.7 3278.2	1.5	
			19.1 19.2			20.3 19.9
4	3415.2 3416.8	1.6		3256.4 3258.3	1.9	
			19.1 19.2			20.3 20.6
5	3434.3 3436.0	1.7		3236.1 3237.7	1.6	
			19.0 18.8			20.0 20.2
6	3453.3 3454.8	1.5		3216.1 3217.5	1.4	
			19.1 19.0			
7	3472.4 3473.8	1.4				
			19.2 19.9			
8	3491.6 3493.7	2.1				

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[9] A slight rearrangement of the ordinal numbers given by Barker has been suggested by R. M. Badger, Phys. Rev. **35**, 1038 (1930). This identification is the one we follow here and leads to more probable values for A as well as fitting our intensity curves better.

THE INTENSITIES OF THE || TYPE LINES

The theoretical intensities of the fine structure lines of || type vibration bands may be computed when the moments of inertia of the molecule, A and C, are known. We shall take as an average value $A = 2.80 \times 10^{-40}$. In addition to this datum we require the constant $\beta = (A/C - 1)$. The fact that the doubling of the || type bands is observable spectroscopically insures that the molecule is very flat, that is $\beta \cong -0.5$. It cannot however be exactly -0.5. From estimates based on a quantitative discussion of the doubling which will be published elsewhere we are lead to the value $\beta = -0.412$ and this will be used here in determining the intensities. Fortunately, it appears that the line intensities are relatively insensitive to small variations in β when it is in this neighborhood.

The intensity formulae have been given explicitly by Dennison[10] and need only be modified by introducing weights appropriate for the ammonia molecule. We shall take the spin of the hydrogen nucleus equal to $\frac{1}{2}(h/2\pi)$ and assume that those states which occur in nature have wave functions (the vibration—rotation—nuclear spin part) which are antisymmetrical for an interchange of any two of the hydrogens.

The weights of the states (see Table V, reference 2) may then be expressed in terms of the rotational quantum numbers J and K where the two cases of vibrational symmetry α or β occur.

	VIBRATIONAL SYMMETRY		
	α	β	
$g=$	0	$2(2J+1)$	for $K=0$ and J even.
$g=$	$2(2J+1)$	0	for $K=0$ and J odd.
$g=$	$(2J+1)$	$(2J+1)$	for $K\neq 0$ and not a multiple of 3.
$g=$	$2(2J+1)$	$2(2J+1)$	for $K\neq 0$ and a multiple of 3.

As an example the intensity of the lines of the negative branch of the $\alpha \rightarrow \beta$ band are given by,

$$I_{J-1}^{J} = A \sum_{K=0}^{J-1} ([x](J^2 - K^2)/J) e^{-\sigma(J^2+J)-\sigma\beta K^2}$$

where A is a proportionality constant and $\sigma = h^2/8\pi^2 AkT$. The symbol $[x]$ is 0 for $K=0$ and J even, 2 for $K=0$ and J odd, 1 for $K\neq 0$ and not a multiple of 3 and 2 for $K\neq 0$ and a multiple of 3. The intensities of the positive branch of this band as well as those of the $\beta \rightarrow \alpha$ band may be expressed by means of similar formulae. Their values have been computed (using the values of A and β given above) and are arranged in Table II according to the ordinal number of the line.

In Fig. 3b we have plotted these theoretical intensities in order that they may be compared directly with the experimental curve. The agreement appears to be very good; certainly as close as could be expected when the approximate character of the experimental intensities is taken into account.

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[10] See reference 2, page 315.

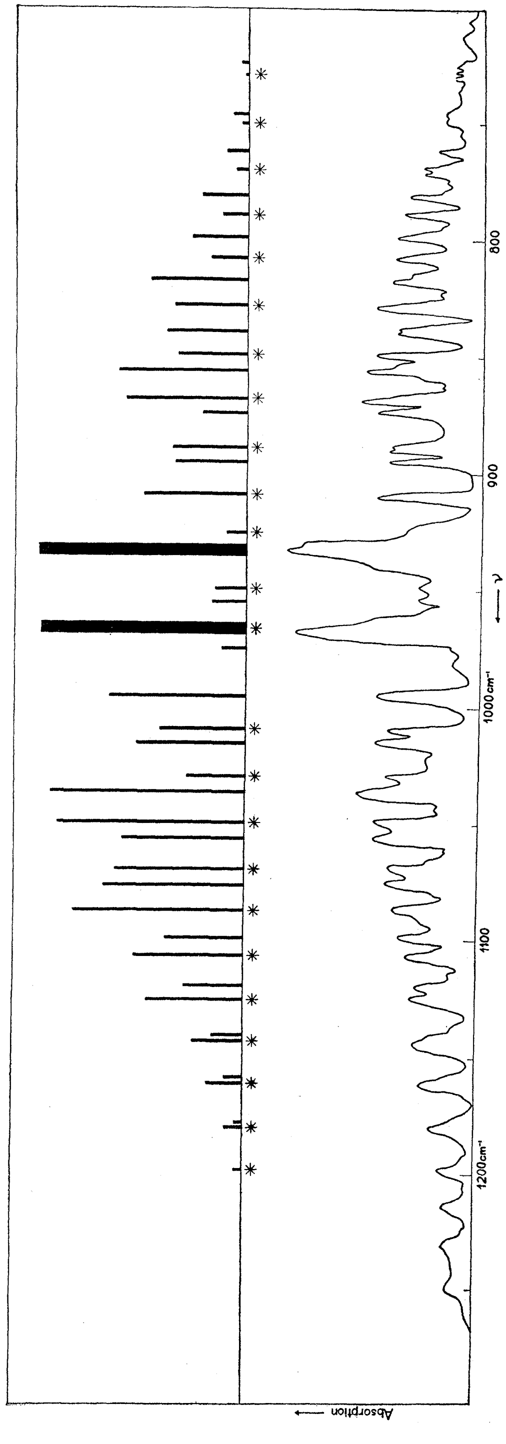

Fig. 4. The 10.5 μ band of ammonia.

TABLE II.

m	$\alpha \rightarrow \beta$ Band		$\beta \rightarrow \alpha$ Band	
	+	−	+	−
1	0.00	1.79	2.00	0.00
2	4.96	1.15	1.37	4.14
3	3.38	5.89	7.87	2.53
4	10.79	4.28	6.30	7.32
5	7.45	6.94	11.24	4.59
6	9.89	3.95	7.07	5.53
7	6.30	4.14	8.13	3.20
8	5.59	2.10	4.52	2.58
9	2.92	1.45	3.48	1.22
10	2.04	0.68	1.78	0.78
11	1.04	0.36	1.05	0.36
12	0.49	0.14	0.45	0.15

Before discussing the significance of this result we might point out that our computation is valid for any of the $\parallel$ type bands of ammonia and hence these theoretical intensities may be compared with the intensities of the lines of the 10.5μ band as observed by Barker. The only difference between the 3.0μ band and the 10.5μ band is that in the former the doublet separation is small compared with the distance between successive rotation lines whereas in the latter case the doublet separation is somewhat greater than the line interval. A comparison between the experimental and theoretical intensities is made in Figs. 4a and 4b and again the agreement is on the whole very good.[11]

We regard the fact that the line intensities in these two ammonia bands can be so satisfactorily accounted for as being one of considerable importance. In the first place, the peculiar intensity distribution (an alternating intensity which gradually becomes uniform for the higher band lines) depends intimately upon our interpretation of the origin of the doubling of these bands, namely, $\alpha \rightarrow \beta$ transitions and $\beta \rightarrow \alpha$ transitions. Since the observed lines show just this same unusual intensity distribution we believe that this constitutes a strong argument for the validity of the underlying theory.

The second point is that we have shown that the states of the ammonia molecule which exist in nature are those for which that part of the wave function which is independent of the electronic coordinates and spins, is totally antisymmetrical for an interchange of the hydrogen nuclei.

If this were not the case we should have found a strong line appearing in the experimental curve where a weak one was predicted and vice versa.

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[11] In Fig. 4b the lines of the $\alpha \rightarrow \beta$ band are marked with a *. The heights of the lines of Fig. 4b represent theoretical intensities while the lines of Fig. 4a are given in percent absorption.