

ABSORPTION BANDS OF AMMONIA GAS  
IN THE VISIBLE

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## ABSTRACT

The article describes an investigation of the absorption spectrum of ammonia gas in the visible region. At 5490Å an absorption region was found which was too weak for a complete investigation with the means at hand. On a second band at 6474Å measurements on 57 lines are given, and the structure of the band is discussed. These two bands are the fifth and fourth overtones of an ammonia band at 3 $\mu$ . Some interesting alternations of intensity are pointed out, and comparison is made with other ammonia bands of the same harmonic series. Some features of other portions of the ammonia spectrum are discussed in connection with the bands here investigated.

## INTRODUCTION

IT WAS recently shown by Badger and Mecke<sup>1</sup> that molecular band spectra of the vibration-rotation type, corresponding to higher members of a harmonic series with a fundamental in the infra-red, may be photographed in the near infra-red or visible regions with the large dispersion of a long focus grating. In the case particularly investigated (ammonia gas) it was found that a complexity of structure was revealed which could only be surmised from the existing investigations on bands lying further in the infra-red and beyond the reach of photographic methods.

Recently, information concerning the spectra of diatomic molecules has been accumulating at a very rapid rate, so that the more important features of this type of spectrum are now quite well understood. Our knowledge of polyatomic molecules is in a much less satisfactory state, and up to the present only relatively small portions of the complete spectrum originating in any molecule of this type have been submitted to anything like a complete analysis.

The study of the vibration-rotation type of band with the relatively high resolution permitted by photography seems to offer important possibilities in the solution of the general problem, and a program for the investigation of a number of the simpler polyatomic molecules by this method has consequently been undertaken.

In the case of certain molecules it has been found that different vibration-rotation bands of the same molecule may have a very different appearance, even in the case of bands of the same harmonic series. Theoretical reasons for this on the basis of symmetry considerations have been discussed by Hund.<sup>2</sup>

<sup>1</sup> Badger and Mecke, *Zeits. f. phys. Chem.* **5**, 333 (1929).

<sup>2</sup> Hund, *Zeits. f. Physik* **43**, 805 (1927).

One of the most interesting cases of the kind mentioned is found in ammonia, which is a relatively simple molecule and one whose spectrum might be expected to be capable of treatment. At  $3\mu$  there is a band which has been investigated by Stinchcomb and Barker<sup>3</sup> and has been interpreted by Dennison<sup>4</sup> as due to a molecular vibration in which the change of electric moment is perpendicular to the symmetry axis. The harmonics of this band are relatively strong as shown by Badger and Mecke,<sup>1</sup> who investigated the fourth and located the fifth members of the series. The two bands of the series which have been studied present considerable difference in appearance and have several features of which the explanation is not immediately evident.

It is the purpose of the investigation described in this paper, as a part of the general program mentioned above, to extend the investigation of this harmonic series to higher members with the expectation that a comparison of several bands, and especially of the intensity alternation of each, will lead to an understanding of the nature of the various rotational and vibrational levels involved.

#### EXPERIMENTAL PROCEDURE

The ammonia gas used in the investigation was a synthetic product and was confined in a steel absorption tube 280 cm long, closed at the ends with plate glass windows. Gas pressures of from one to five atmospheres were employed, but increasing the pressure did not seem to have great advantage, probably due to a broadening of the absorption lines. The source of illumination was a tungsten lamp.

The majority of the exposures were made with a six inch grating of ten foot radius of curvature. This grating gives intense spectra in the first order in the red, and has great freedom from ghosts. Some exposures were also made using the second order of a twenty-foot grating.

When using the ten-foot grating the exposures were made on a process panchromatic film which was very contrasty and fine grained. The exposure times ranged from ten to thirty minutes. Development was carried as far as possible without introducing excessive developer fog. When using the second order of the large grating it was necessary to use a faster film, which unfortunately was less contrasty than the process film, so that only the stronger lines showed up in the exposures. An iron arc calibration spectrum was photographed on each of the films.

Since, at best, the absorption bands studied are very weak, and direct measurements on the films were difficult, as all but the most intense lines disappear under the microscope of a comparator, the following procedures were used in working up the results.

(1) Enlargements of several different films were made on contrast paper. Measurements were made on each with a scale, and the results compared.

<sup>3</sup> Stinchcomb and Barker, *Phys. Rev.* **33**, 305 (1929).

<sup>4</sup> Dennison, *Phil. Mag.* **1**, 195 (1926).

(2) The best film (most contrasty, free from blemishes) was microphotometered and measurements made on the record plate.

(3) Enlargements from four of the best films were made on contrast film and superposed (see Oldenberg, *Zeits. f. Physik*, **58**, 722 (1929)) and measurements made on the resulting composite picture. It is remarkable how this procedure averages out small defects in the plates and intensifies lines which on a single plate would be pronounced doubtful.

TABLE I. *The ammonia band at 6474A.*

$\lambda(\text{A})$	$\nu(\text{cm}^{-1})$	I	$\lambda(\text{A})$	$\nu(\text{cm}^{-1})$	I
6419.5	15573.1	0	{6472.4}	{15445.9}	
{6422.2}	{15566.7}	0	{6474.0}	{15442.0}	9
{6423.3}	{15564.1}		{6474.7}	{15440.5}	
			{6475.7}	{15438.2}	
{6425.5}	{15558.6}	0	{6478.8}	{15430.6}	6
{6426.5}	{15556.2}	1	{6479.6}	{15428.7}	
{6427.8}	{15553.1}	?			
{6428.6}	{15551.1}	?	6483.2	15420.1	6
{6429.7}	{15548.5}	?			
6431.8	15543.4	1	{6485.3}	{15415.3}	
			{6485.8}	{15414.0}	?
{6434.5}	{15536.9}	5	{6486.9}	{15411.5}	
{6435.6}	{15534.3}				
6438.2	15527.9	10	{6488.5}	{15407.7}	5
6442.5	15517.7	9	{6489.5}	{15405.2}	
6446.2	15508.6	8	6492.4	15398.4	1
{6449.5}	{15500.9}	7	{6494.9}	{15392.5}	4
{6450.4}	{15498.6}		{6495.9}	{15390.0}	
6453.1	15492.1	2			
6455.4	15486.7	2	{6498.2}	{15384.6}	?
			{6499.3}	{15382.0}	7
6457.4	15481.9	3			
			{6501.0}	{15377.9}	?
			{6501.8}	{15376.0}	?
			6506.6	15364.7	6
			6510.9	15354.6	1
{6460.1}	{15475.2}	0	6512.9	15349.8	3
{6460.8}	{15473.7}				
			6514.9	15345.1	?
{6363.6}	{15466.9}	0	6517.1	15340.1	?
{6364.7}	{15464.4}				
			6519.9	15333.3	2
{6364.9}	{15463.7}	0			
{6365.6}	{15462.2}		6522.7	15326.8	?
{6367.9}	{15456.7}	0	6525.9	15319.4	1
{6368.2}	{15456.1}				
6370.3	15451.0	?			
			{6528.0}	{15314.4}	?
			{6529.4}	{15311.2}	?

## EXPERIMENTAL RESULTS

In this work two absorption regions were investigated corresponding to the fifth and sixth harmonics of the band at  $3\mu$ . At 6474A a band was found

with a broad *Q* branch, an *R* branch with four intense lines and several rather weak ones, and several irregularly spaced absorption maxima in a *P* branch. The most distinguishing features of the band are the four strong lines of the *R* branch.

In the region at 5490A, evidences of absorption were obtained in all of a number of exposures. The absorption lines were so weak, however, as to be of the same order as non-uniformities in the emulsion of the film, and although the center of the absorption band seemed to lie at about 5490A, the *Q* branch could not be identified with certainty. Consequently no data are given for this band.

In Table I is given a summary of the measurements on the ammonia band at 6474A. The lines for which an intensity is given are well assured as real by several measurements. The lines designated by a point of interrogation are very weak and are possibly somewhat uncertain. Included in braces are broader regions of absorption which are incompletely resolved into lines, but have maxima of absorption at the wave-lengths given. They have possibly a more complex structure than that indicated. All of the lines in the spectrum are rather broad, but this does not seem to be due to a lack of dispersion or resolving power in the means employed, since the spectrograms taken with the second order of the 20 ft. grating showed no better resolution than those taken with the first order of the 10 ft. grating. To secure complete resolution of the lines one would probably have to work at very low gas pressures and a correspondingly long absorption path.

#### DISCUSSION OF THE RESULTS

In Figure 1 is given for purposes of comparison a diagrammatic representation of three of the ammonia bands of the series with fundamental at  $3\mu$ . In the case of the band at 6474A the curve is adapted from a microphotometer investigation of the best spectrogram obtained. The vertical lines represent the position of absorption maxima as taken from the various measurements. The dotted lines indicate the less certain maxima. The band at 7919A is reproduced from the work of Badger and Mecke<sup>1</sup> and the curve for the band at  $3\mu$  is adapted from the figure given by Barker and Stinchcomb.<sup>3</sup>

Below the first two bands is indicated a provisional arrangement of the lines into "series." Each series includes all the lines where one of the quantum numbers characterizing the rotational states, say  $\tau$ , makes the particular transition  $\tau' \rightarrow \tau''$ , the other quantum number, say  $j$ , making all possible transitions (with the restriction of course that  $\Delta\tau$  and  $\Delta j = 0 \pm 1$ ). In the case of the two harmonic bands all of the intense lines, at least, fit into five of these series. Higher series may also be present but the lines of these will nearly coincide with those of the series given, the first and sixth series coinciding, and so on. For the band at 6474A the assignment is possibly in some cases ambiguous owing to incomplete resolution of the lines.

From the figure the following characteristic features are evident. First of all one may note that the bands at 7919A and 6474A include many double

lines with a separation of the two components which is perhaps constant within experimental error, since the resolution is not complete. In general it seems to be the weaker lines which are so resolved, and it is not impossible that the broadness of the stronger lines conceals a similar structure, though in a few cases the stronger lines are relatively sharp and apparently single.

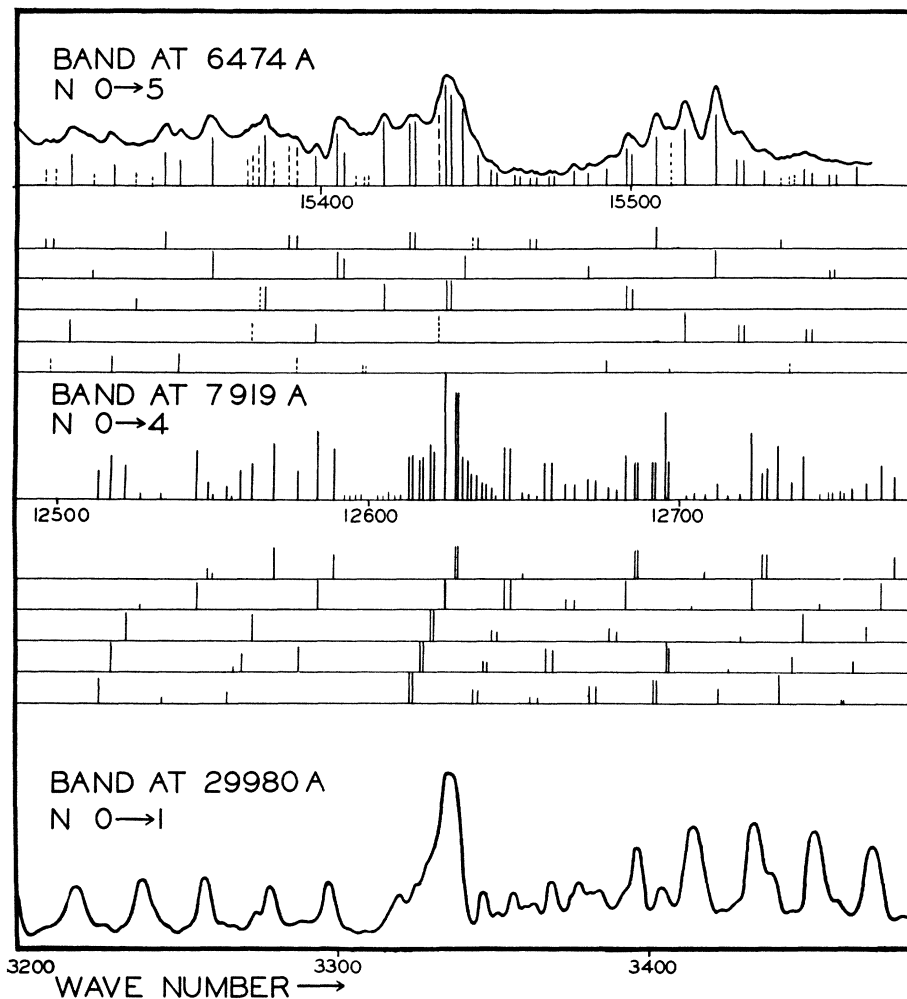


Fig. 1. Two harmonic bands of ammonia and the fundamental band at  $3\mu$ .

Badger and Mecke suggested as an explanation of the doubling that the ammonia molecule becomes slightly unsymmetrical as the amplitude of vibration increases. An alternative explanation has been offered by Barker<sup>5</sup> on the basis of a slight difference in the energy values corresponding to the symmetric and anti-symmetric eigenfunctions representing an oscillational state, this

<sup>5</sup> Barker, Phys. Rev. **33**, 684 (1929).

difference arising from the possibility of the nitrogen atom passing through the plane of the three hydrogen atoms. Barker interprets the bands here considered as due to an oscillation in which all the atoms of the molecule approach each other simultaneously. As the amplitude of this vibration increases the potential energy increases, as the nitrogen atom approaches the plane of the hydrogen, also rises, and the difference between energy levels corresponding to the two types of eigenfunction should decrease. Consequently the doubling of levels might be appreciable only in the lowest energy state, and the doubling of the bands would thus be nearly constant through the harmonic series. This is indeed in agreement with the data. However, it seems very questionable whether the bands here under consideration are due to the type of oscillation mentioned, first on account of the great intensity of transitions in which  $\Delta\tau \neq 0$ , and secondly on account of the convergence of the bands. An extrapolation of the harmonic series yields a dissociation energy of 6.0 volts, which is much less than that required for the complete separation of the molecule into its atoms (about 12 volts) which would result from the vibration in question. Dennison<sup>4</sup> in a treatment of the vibrations of the ammonia molecule by means of normal coordinates, concluded that the  $3\mu$  band arose from an oscillation perpendicular to the symmetry axis. But it is possible that even for this kind of oscillation one should expect a similar situation for the doubling of the vibrational levels.

It is striking that no very appreciable convergence in any series in any of the bands is observed. Furthermore, as one must expect from this fact, the spacing of the lines in a series is sensibly constant for all of the bands, having the approximate mean value  $19.88 \text{ cm}^{-1}$  for the band at  $7919\text{A}$  and  $19.74 \text{ cm}^{-1}$  for the band at  $6474\text{A}$ , corresponding to a moment of inertia of  $2.78 \times 10^{-40} \text{ gm. cm}^2$  or  $2.80 \times 10^{-40} \text{ gm. cm}^2$ , respectively, about an axis perpendicular to the axis of symmetry. It would be very interesting to observe whether the other moment of inertia (about the symmetry axis) is not appreciably changed by the oscillation, as seems not improbable, but the accuracy of measurement scarcely suffices for this. The probable value for this quantity is  $3.49 \times 10^{-40} \text{ gm. cm}^2$  if one assumes a flat pyramidal structure for the ammonia molecule.

A particularly striking feature of the two harmonic bands is the alternation of intensity in each series. There seems to be a great tendency for alternate lines to be weak or to fall out altogether, and an alternation is also observed for corresponding lines through successive series. The irregularity of spacing in the  $P$  branch of the  $3\mu$  band suggests that the strong lines here do not all belong to the same series, and that greater resolution would disclose a similar condition in this case. Indeed this band seems quite similar to the harmonic at  $6474\text{A}$  except that certain series which in the former are quite weak have in the latter become of intensity comparable with the strongest series.

For purposes of clarity the five series of the two harmonic bands have been represented in Figure 2 by means of a scheme similar to that which is frequently used in representing electronic bands. The diagonal lines sloping

to the left indicate the transitions giving rise to the  $P$  branches, and those sloping to the right to the  $R$  branches.  $J'$  and  $J''$  are the probable values of the quantum number associated with the larger spacing of the band structure, in the normal and excited states respectively. The absolute values of the other quantum number  $\tau$  for the several series are somewhat in doubt. The thickness of the diagonal lines represents roughly the intensity of the observed transitions, and as in Figure 1, broken lines indicate doubtful cases. At the bottom of the figure are shown the kinds of transitions which are especially characteristic of the two bands.

In the case of the band  $N, 0 \rightarrow 4$  the results indicate that the rotational levels are alternately of two kinds in both lower and upper states, one of these kinds being considerably the more probable. For the band  $N, 0 \rightarrow 5$  the

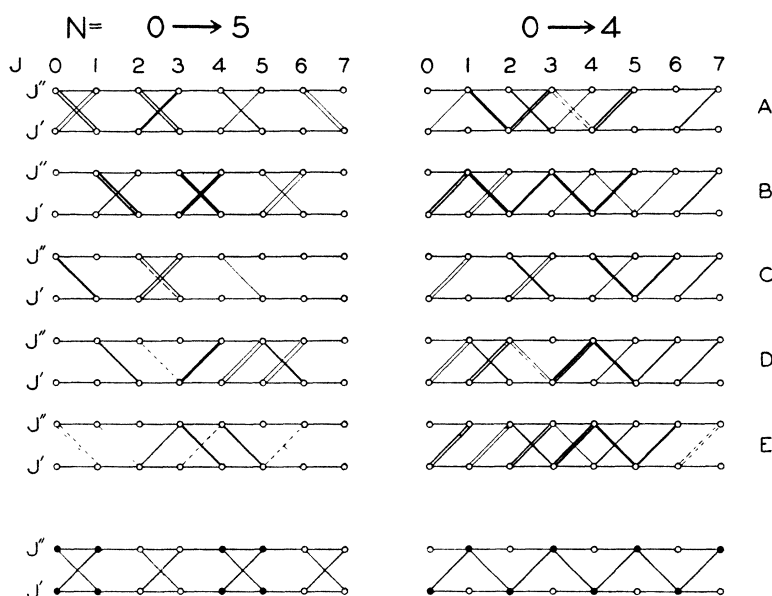


Fig. 2. Scheme of transitions in the ammonia harmonic bands.

situation seems to be quite different and the explanation is not obvious. In neither case is the condition quite what would seem to be predicted by the considerations of Hund.<sup>2</sup>

In this connection it is not out of place to make some remarks on certain other ammonia bands. At  $10\mu$  there is an absorption region which is produced by another type of molecular vibration. This band has been investigated by Barker,<sup>5</sup> who finds a double band of apparently simple structure. According to Barker's analysis this band comprises two component bands, each of which consists of a  $Q$  branch and simple  $P$  and  $R$  branches corresponding to the transitions  $\Delta j = \pm 1, \Delta \tau = 0$ . There is no appreciable convergence of the lines, and one component has a spacing of  $20.2 \text{ cm}^{-1}$  the other of  $18.7 \text{ cm}^{-1}$ . This would mean that the band is produced by two kinds of ammonia mole-

cule whose moments of inertia are the same in the upper and lower states but appreciably different from that of the lower state involved in the bands at  $3\mu$  etc. In other words these bands do not have a common lower level.

It seems to the writer, however, that the absorption curve may equally well be interpreted in a slightly different way, but one which is much more satisfactory when one considers its connection with the other data. The following analysis of the  $10\mu$  band is accordingly suggested.

TABLE II. *The ammonia band at  $10\mu$ . (from the data of Barker<sup>6</sup>).*

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

Mean $\Delta\nu = 19.6\text{ cm}^{-1}$	Mean $\Delta\nu = 19.3\text{ cm}^{-1}$
Weighted mean $\Delta\nu = 19.83\text{ cm}^{-1}$	Weighted mean $\Delta\nu = 19.66\text{ cm}^{-1}$

There is only one region of the absorption curve which does not fit this analysis as well as that given by Barker, and that is the weak maximum at  $981\text{ cm}^{-1}$  which should include two maxima at about  $975\text{ cm}^{-1}$  and  $987\text{ cm}^{-1}$ . It seems, however, that a more complete resolution of this region is necessary to decide definitely which interpretation is the correct one.

In the interpretation here suggested, the band at  $933\text{ cm}^{-1}$  converges slightly in the  $P$  branch, which indicates a decrease of moment of inertia perpendicular to the symmetry axis, in the activated state. This is not surprising if one considers the type of vibration probably responsible for this band. The three hydrogen atoms are presumed to separate at the same time as the nitrogen atom is approaching their plane. The oscillation should be considerably nonharmonic with a tendency for the nitrogen atom to linger near the plane of the hydrogen atoms, causing a decrease of average moment of inertia as the amplitude of vibration increases.

The suggested interpretation of this band gives within experimental error the same moment of inertia for the normal state as that obtained from the other data.

In a study of the pure rotation spectrum of ammonia Badger and Cartwright<sup>6</sup> found an apparent convergence of the lines toward shorter wave-

<sup>6</sup> Badger and Cartwright, Phys. Rev. **33**, 692 (1929).



lengths. This spectrum consists of lines produced when  $j$  increases by unity,  $\tau$  remaining constant. If this convergence is not real the molecular moment of inertia calculated from the lines of shorter wave-length, which were those most accurately measured, is the same as that calculated from the vibration rotation bands. But if the interpretation given for the doubling of these bands is the correct one, one should expect that the pure rotation lines are all double with components of perhaps unequal intensity. In this case it could appear that the unresolved lines were somewhat unequally spaced. A similar effect would not be observed, of course, in the case of the Raman spectrum.

At this point the author wishes to express his thanks to Professor J. Anderson of the Mount Wilson Solar Observatory of the Carnegie Institution for the loan of the ten-foot grating which made the investigation possible; and to Dr. Edison Pettit of the same institution for the microphotometer measurements.