The inversion spectrum of ammonia at centimetre wave-lengths

BY B. BLEANEY AND R. P. PENROSE, Clarendon Laboratory, Oxford

(Communicated by Lord Cherwell, F.R.S.—Received 17 July 1946—Read 27 February 1947)

A technique is described for the investigation of gaseous spectra at high radio-frequencies. The sensitivity of the method is such that an absorption of $2 \times 10^{-4}$ per cm. of path can be detected at wave-lengths around 1 cm.

The inversion spectrum of ammonia in the ground vibrational state has been examined at wave-lengths between 1·1 and 1·6 cm. and found to contain an extensive fine structure, arising from centrifugal distortion of the molecule. Twenty-nine lines have been identified, each corresponding to a different rotational quantum state. The wave numbers of these lines can be accurately represented by the formula

$$\bar{\nu} = 0.7935 + \left[ -0.0050J^2 + J + 0.0070K^2 \right] + 0.63 \left[ -0.0050J^2 + J + 0.0070K^2 \right]^2 \text{ cm}^{-1} \text{ (vacuo)}$$

where $J, K$ are the rotational quantum numbers of the symmetrical top molecule.

Detailed measurements of 18 lines at a pressure of 0·5 mm. Hg show that their half widths, due to collision broadening, lie between 2 and $5 \times 10^{-4}$ cm.$^{-1}$, while their intensities agree with the theoretical values, within the experimental error of $\pm 5\%$. The integrated intensity at a pressure of 4·5 mm. Hg, over the interval 0·67 to 0·87 cm.$^{-1}$, agrees with the calculated intensity to better than 1%.

1. INTRODUCTION

The well-known doubling of most of the lines of the infra-red spectrum of gaseous ammonia is associated with the existence of two equilibrium configurations of the molecule, with the nitrogen atom on either side of the plane containing the three hydrogen atoms. The appropriate potential energy curve of the molecule has two identical minima, separated by a fairly low hump; the associated ‘resonance’
The inversion spectrum of ammonia at centimetre wave-lengths

causes a splitting of the energy levels (‘inversion doubling’). In the ground vibrational state this splitting amounts to 0.67 cm⁻¹, determined by Wright & Randall (1933) from measurements on the pure rotation spectrum in the far infra-red. Transitions between the two sub-levels are allowed, and an absorption line would be expected at a wave-length of about 1.5 cm. The existence of this absorption was verified experimentally by Cleten & Williams (1934) using split-anode magnetrons as sources of radiation. The wave-length was determined by a diffraction grating, and the absorption was measured by inserting ammonia (at atmospheric pressure in a cloth bag) in the path of radiation. The peak of the absorption curve was found to be at about 0.8 cm⁻¹, and the absorption was spread over a considerable frequency range (0.5 cm⁻¹) owing to collision broadening.

This absorption has been re-examined using wave-guide technique. Low gas pressures, down to 0.2 mm Hg, have been employed in order to reduce the effects of collision broadening, and an extensive fine structure of the absorption has thereby been revealed. This fine structure is due to centrifugal distortion of the molecule, the effect of which is comparatively large because the inversion frequency varies very rapidly with the distance between the nitrogen atom and the plane of the hydrogen atoms.

The absorption coefficients to be expected at centimetre wave-lengths are much smaller than those encountered in the infra-red, and direct measurement would require considerable path lengths. The difficulties inherent in such a measurement have been avoided by the use of a resonant cavity, which, effectively, is a short length of wave-guide traversed by the radiation many times before its final decay. The efficiency of such a cavity is measured by its magnification or Q value, defined as 2π times the ratio of the stored energy to the energy dissipated per cycle. On admitting an absorbing gas to the resonator its Q value is reduced, say, from Q₀ to Q₁. The absorption coefficient of the gas is related to Q₀, Q₁ by the expression

\[
\gamma = \frac{2\pi}{\lambda} \left( \frac{1}{Q_1} - \frac{1}{Q_0} \right),
\]

(1)

The Q values were determined from the resonance curve obtained by detuning the cavity, and were subject to errors of a few per cent, owing to fluctuations of the frequency of the oscillator. Since the gaseous absorption is found from the difference of the two values of 1/Q the inaccuracy in its determination is considerable unless 1/Q₁ is appreciably different from 1/Q₀. This method is thus limited to absorptions comparable with the ‘equivalent absorption’ 2π/λQ₀ of the cavity. The value of Q₀ was about 10,000, from which 2π/λQ₀ ≃ 5 × 10⁻⁴ per cm.

To extend the method to smaller absorptions, use was made of the fact that the power output from the oscillator was constant within less than 1 %. When the cavity is tuned to resonance, small fluctuations in the oscillator frequency have only a second order effect on the amplitude of the energy density in the cavity, instead of the first order effect obtained when the resonator is detuned for the measurement of Q. The energy density in the cavity can be determined by a loosely coupled detector,
being proportional to the power registered by this detector, a crystal rectifier. Simple equivalent circuit considerations show that this power $\delta$ varies as $Q^2$, giving

$$\frac{Q_1}{Q_0} = \frac{\sqrt{\delta_1}}{\sqrt{\delta_0}}.$$  \hspace{1cm} (2)

Hence we have

$$\gamma = \frac{2\pi}{\lambda Q_1} \left(1 - \sqrt{\frac{\delta_1}{\delta_0}}\right) = \frac{2\pi}{\lambda Q_0} \left(\sqrt{\frac{\delta_0}{\delta_1}} - 1\right).$$  \hspace{1cm} (3)

Thus it is possible to determine the absorption by measuring either $Q_1$ or $Q_0$ together with the power ratio $\delta_1/\delta_0$. The stability of the oscillator (a reflexion klystron) was such that a difference between $\delta_0$ and $\delta_1$ of 1% could be detected, corresponding to an absorption coefficient of about $2 \times 10^{-6}$ per cm. At the higher attenuations, the values of $\gamma$ given by (1) and (3) were compared, and the agreement was generally satisfactory. The probable error of the mean values of the absorption coefficients obtained from this comparison is estimated at about $\pm 3\%$ or $\pm 2 \times 10^{-6}$ per cm., whichever is the greater.

The wave-length of the radiation was measured by a second resonant cavity. It was carefully designed to give an accuracy of 2 parts in 10,000 or better. Small changes in wave-length, such as were used in measuring the breadths of lines at low pressure, could be measured more accurately, the limit of reading corresponding to a change in wave-number of about 0.00002 cm.$^{-1}$. This wave-meter was used because apparatus for the measurement of frequency by means of the harmonics of quartz crystals was not available. The latter method would give greater accuracy, and would also be desirable because the frequency of a line is more fundamental than the wave-length, through its relation to the quantum of energy.

The essential differences between the technique described in this paper and that normally used in the infra-red may be summarized as follows:

(a) The radiation from the source is collimated by a wave-guide, which produces a beam of radiation less than a wave-length across. This avoids the use of mirrors, which would have to be several metres in diameter to collimate the radiation at these wave-lengths.

(b) The effective multiplication of path length obtained by using a resonator makes it possible to detect absorptions of the order of $10^{-6}$ per cm. The volume of the resonator is less than 10 c.c. and the gas can be rapidly admitted or pumped away. The energy densities in the cavity with and without gas could therefore accurately be compared without requiring long-period stability in the oscillator.

(c) The reflexion klystron is virtually a monochromatic source, and the limit of resolution is determined by the widths of the absorption lines themselves, at the gas pressures used in these experiments. In the infra-red the sources provide a continuous spectrum of radiation and the resolving power is that of the spectrometer.

Although the methods described in this paper for the examination of gaseous spectra have been applied only over a small wave-length interval between 1 and 1.5 cm., they are capable of extension to decimetre, centimetre and millimetre
The inversion spectrum of ammonia at centimetre wave-lengths

wave-lengths. Oscillators and detectors are available at all except millimetre wave-lengths, and it is likely that they will be developed for this region soon, as work at 5 mm. has already been reported. The strength of the absorptions to be expected, and the sensitivity of the apparatus, vary with roughly similar powers of the wave-length. Ceteris paribus, the absorption coefficients vary inversely as the square of the wave-length (see § 5, equation (4)). If the resonant cavity is scaled in proportion to the wave-length, its $Q$ varies with $\sqrt{\lambda}$, and the smallest detectable absorption will, by equation (3), vary with $\lambda^{-1}$. Thus for measurements at wave-lengths between 100 and 1 mm., the effective merit of the method changes by a factor of 10. At wave-lengths beyond this interval, the limitations of the method are mainly mechanical; at decimetre wave-lengths the cavity becomes inconveniently bulky, while its increasing $Q$ requires still greater frequency stability of the oscillator. At the shorter wave-lengths the minute dimensions cause machining difficulties, and the use of a large cavity resonant in many modes, instead of a small cavity resonant in one particular mode (see Autler, Becker & Kellogg 1946) appears more promising.

2. Apparatus

Resonator

A cylindrical cavity was used, shown in figure 1. It was tuned to resonance by moving the plunger $A$ by means of a micrometer head. The $H_0$ mode of resonance was employed because it has the highest $Q$ value for a given size of cavity; a special system of coupling between cavity and wave-guide avoided the excitation of other modes as far as possible. This coupling system is described by the authors elsewhere (1946 a). Further discrimination against unwanted modes was provided by a vacuum-tight glass tube ($B$), containing water, attached to the back of the plunger. All modes except the $H_0$ tend to leak out of the main cavity past the plunger, and are damped by the strong absorption of the water.

To make the cavity vacuum tight, thin mica sheets were waxed over the coupling holes on the outside of the resonator. The problem of moving the plunger inside the vacuum was overcome by sealing the annular space ($C$) between the micrometer spindle and its bushing with a viscous oil of low vapour pressure. By this means the position of the plunger could be controlled with the full accuracy of the micrometer screw; the thrust of the atmosphere on the spindle was sufficient to eliminate back-lash. Other joints in the resonator were waxed over or sealed with oil; the pressure inside could be reduced below $10^{-3}$ mm. Hg by a mercury diffusion pump.

Gas was admitted to the chamber through the hole ($D$) outside the high-frequency field. The higher pressures were measured on a mercury manometer; a McLeod gauge was used for those below 2 mm.

The plunger travel was sufficient to give at least the first two $H_0$ resonances at all the frequencies employed. The plunger movement needed to tune between the half-power points was about 0.005 mm.; the corresponding micrometer head rotation
was measured by a lamp and scale method which gave an over-all magnification of the plunger movement of 12,000.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{resonator.png}
\caption{Resonator.}
\end{figure}

\textit{Wave-meter}

The $H_0$ cavity used for wave-length measurement was coupled in the same way as the experimental cavity, but it was larger in diameter. This makes the readings less sensitive to machining errors in the barrel. Inaccuracies in the barrel diameter and in the micrometer head made roughly equal contributions to the over-all error in the wave-length value; this was believed accurate to 1 part in 5000.
The inversion spectrum of ammonia at centimetre wave-lengths

Oscillator and detector

The power source was a reflexion klystron designed and constructed in this laboratory. The power available on the output side of the resonator was so small that a crystal detector had to be used. The accuracy with which attenuation can be measured depends on the extent to which the detector output is proportional to the incident power. The response characteristics of several crystals were compared with that of a thermocouple, whose reading should give a true indication of power. These experiments indicated that the error introduced in the attenuation values by deviations of the crystals from the square law should be less than 5%.

An attenuator in the resonator output feeder served to adjust the power at the detector to a convenient value.

3. Experimental

At each wave-length the Q value of the resonator was measured by determining the movement of the plunger required to tune the resonator between the half-power points. With the optical magnification this corresponded to deflexions of between 5 and 20 cm. and the average of a number of readings was taken. The scatter in these readings was usually a few per cent, caused mainly by fluctuations in the frequency of the oscillator. A check on the accuracy of this determination was obtained by admitting to the resonator a quantity of ammonia sufficient to diminish the Q appreciably. The new value of Q was measured, together with the power fed through the cavity at resonance before and after admitting the ammonia. The ratio of the square root of these powers should equal the ratio of the two values of Q (equation (2) above). In general the difference between the two ratios was within the experimental error, and an average value of the change in Q was used to calculate the absorption. Measurements of the absorption coefficients at a number of pressures were made, the smaller absorptions being determined from the power change registered by the crystal detector. The absorption coefficients at the various standard pressures (e.g. 4.5, 1.2, 0.5 mm. Hg) were obtained by interpolation on a graph of absorption coefficient against pressure.

Measurements at small frequency intervals were made to delineate each absorption line at pressures of 1.2 and 0.5 mm. Hg. At the latter pressure most of the lines were resolved well enough to make possible an accurate determination of their breadths. A few lines were separated only at a still lower pressure (0.2 mm.).

Whenever possible, the exact centre of each line was found by a brief examination of the absorption at a pressure of less than 1/10 mm. The value thus determined was in close agreement with that deduced from the absorption curve for 0.5 mm. pressure.

4. The spectrum

The absorption curve obtained at a pressure of 1.2 mm. Hg is shown in figure 2. The measurements cover the wave-number band from 0.65 to 0.87 cm.\(^{-1}\), which includes all the more intense lines. The coordinates are given both in terms of
absorption coefficient per centimetre path (the usual spectroscopic unit) and of
decibels per kilometre. The latter unit is customary in radio engineering and is
particularly convenient for the small absorptions to be expected at these wave-
lenghts. The conversion factor is given by

\[
1 \text{ db./km.} = 10^\theta (\log_{10} e) \times \text{absorption coefficient/cm.}
\]

![Figure 2. The spectrum of ammonia near 0.8 cm\(^{-1}\).](image)

The widths of the lines shown in figure 2 are about \(10^{-3}\) cm\(^{-1}\). The widths to be
expected from radiation damping ('natural line breadth') and the Doppler effect
are respectively some \(10^{-17}\) and \(10^{-6}\) cm\(^{-1}\). Thus, even at a pressure of 1.2 mm. Hg,
only collision broadening of the line need be considered, and the lines would be
expected to narrow still further at lower pressures. This has been confirmed using
pressures down to 1/10 mm. Hg. The actual breadths of the lines indicate a collision
diameter several times greater than the kinetic theory value. This may be attributed
to the strong electric field of the ammonia dipole, and will be discussed in another
paper.

Identification of the lines

The theory of the inversion splitting of the energy levels of the ammonia molecule
has been considered by Dennison & Uhlenbeck (1932). Using the Wentzel-Kramers-
Brillouin approximation, they showed that the ratio of the splitting \(A\) to the normal
vibration frequency \(v\) should vary exponentially with the area cut from the potential
hump by the vibrational energy level, being thus a delicate function of the height
of the pyramid. Only in the case of a very flat pyramidal molecule, such as ammonia,
is the splitting in the ground vibrational state large enough to be detected, and in
this case the slight centrifugal distortion of the molecule in the higher rotational
energy levels may cause a considerable change in the splitting, and therefore in the
inversion frequency.
The inversion spectrum of ammonia at centimetre wave-lengths

The effect of centrifugal distortion can be seen qualitatively from the following considerations. When the molecule is rotating mainly about its symmetry axis, the hydrogen atoms tend to fly outwards, thus decreasing the height of the pyramid and increasing the inversion frequency. Rotation about an axis perpendicular to the symmetry axis will have the opposite effect. The energies associated with these two rotations depend on \( K^2 \) and \((J^2 + J - K^2)\) respectively, and, by an extension of Dennison & Uhlenbeck's treatment, Hsi-Yin Sheng, Barker & Dennison (1941) have shown that \( \tilde{\nu} \) should satisfy the relation

\[
\tilde{\nu} = \nu_0 - A'(J^2 + J - K^2) + B'K^2 = \nu_0 - A(J^2 + J) + BK^2.
\]

They have examined the fundamental vibrational band at 10\( \mu \) and have shown that their observations can be represented by a formula of this kind. They have also calculated the constants \( A \) and \( B \), using the potential energy curve proposed by Manning (1935) and obtain values in satisfactory agreement with the experimental determinations. By a similar computation, they find for the ground level of the vibration

\[
\tilde{\nu} = \nu_0 - 0.0011(J^2 + J) + 0.0016K^2 \text{ em.}^{-1}.
\]

In attempting to find a formula of this kind which would adequately represent the system of lines of figure 2, it was assumed that the series of strong lines at the high frequency end of the spectrum corresponded to the levels \( J = K \) which have both large statistical weights and large transition probabilities.

The fact that the levels for which \( K \) is a multiple of three have twice the \textit{a priori} statistical weight (due to nuclear spin) of the others suggested that the lines at 0.797 and 0.836 cm.\(^{-1}\) must be identified as \((J, K) = (3, 3)\) and \((6, 6)\). This yielded the values

\[
A = 0.0050 \text{ em.}^{-1}, \quad B = 0.0070 \text{ em.}^{-1}, \quad \tilde{\nu}_0 = 0.794 \text{ cm.}^{-1}.
\]

With these constants the positions of the remaining lines could be predicted, and fair agreement was found with the frequencies of the lines found experimentally. The discrepancies between the predicted and observed values increased steadily as the observations advanced towards the lower frequencies. This was not surprising, for \((\tilde{\nu} - \nu_0)\) amounted to 20 % of \( \nu_0 \) at the lower limit of the frequency band. In the calculation of Hsi-Yin Sheng, Barker & Dennison the formula for the splitting includes only the first order term in the expansion of an exponential, and other effects which would yield second-order terms are omitted. In the ground vibrational state the fractional change in the splitting is so large that the second-order term from the exponential will be considerable, and it can be included without the introduction of further unknown constants. The formula*

\[
\tilde{\nu} = 0.7935 - 0.0050_3(J^2 + J) + 0.0070_4K^2
+ 0.63\{-0.0050(J^2 + J) + 0.0070K^2\} \text{ cm.}^{-1} \text{ (vacuo)}
\]

* The value for \( \tilde{\nu}_0 \) given here (0.7935 cm.\(^{-1}\)) differs slightly from that in a preliminary report (Bleaney & Penrose 1946 b) where, owing to an error in correcting the wave numbers to vacuum, a value of 0.7940 cm.\(^{-1}\) was given.
B. Bleaney and R. P. Penrose

was adopted as giving the best fit with the experimental results. In table 1 the observed frequencies of the lines are given, together with the values (in italics) calculated from this formula.

The calculated frequencies for the \( K = 0 \) states are included for comparison with the value of the inversion splitting found by Wright & Randall in their experiments on the rotational spectrum (vide infra).

**Table 1. Wave-numbers of lines in the spectrum**

Figures in italics are calculated from the formula

\[
\tilde{v} = 0.7935 - 0.0050(J^2 + J) + 0.0070K^2 + 0.63(-0.0050(J^2 + J) + 0.0070K^2) \text{ cm}^{-1} \text{ (vacuo)}
\]

<table>
<thead>
<tr>
<th>( J )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.7935</td>
<td>0.7934</td>
<td>0.7904</td>
<td>0.7904</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>0.7706</td>
<td>0.7913</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.7638</td>
<td>0.7705</td>
<td>0.7913</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.7352</td>
<td>0.7417</td>
<td>0.7617</td>
<td>0.7964</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.6989</td>
<td>0.7050</td>
<td>0.7240</td>
<td>0.7569</td>
<td>0.8052</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>0.6564</td>
<td>0.6624</td>
<td>0.6797</td>
<td>0.7100</td>
<td>0.7556</td>
<td>0.8183</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.6098</td>
<td>0.6149</td>
<td>0.6308</td>
<td>0.6687</td>
<td>0.7002</td>
<td>0.7582</td>
<td>0.8360</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>0.6939</td>
<td>0.7045</td>
<td>0.7616</td>
<td>0.8581</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>0.6910</td>
<td>0.7750</td>
<td>0.8059</td>
<td>0.8582</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>0.6916</td>
<td>0.7892</td>
<td>0.8015</td>
<td>0.8585</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>0.6954</td>
<td>0.8076</td>
<td>0.8015</td>
<td>0.8583</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td>0.7031</td>
<td>0.8083</td>
<td>0.8015</td>
<td>0.8583</td>
<td>0.8083</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The agreement between the experimental and calculated values is very good. The greatest discrepancy (0.0008 cm.\(^{-1}\)) occurs for the line (5, 1), for which even the third order term in the exponential would be appreciable. The agreement leaves little doubt as to the correctness of the identification of the lines, which is confirmed by comparison of the observed and theoretical intensities (see below).

Since the work described in this paper was completed another investigation of the ammonia spectrum has been briefly reported by Good (1946a). The narrow lines obtained at a pressure of 1/10 mm. Hg or less were displayed on a cathode ray tube screen. The frequencies of the individual lines are not given, except in one case,
The inversion spectrum of ammonia at centimetre wave-lengths

23,878 Mcyc./sec. This is presumably the line (3, 3) and is excellent agreement with our value of \(0.7964 \pm 0.0001\) cm\(^{-1}\), which corresponds to 23,876 ± 3 Mcyc./sec. The formula suggested to represent the wave-numbers of the lines is

\[
\bar{\nu} = 0.7932 - 0.0048(J^2 + J - K^2) + 0.0020K^2.\]

The difference between the coefficients in this expression and the corresponding coefficients in ours may be due to adjustment of the values to give the best fit on all 28 lines observed without the use of a second-order term. This would lead to the choice of a smaller numerical value for the negative coefficient of \((J^2 + J - K^2)\), since the second-order term is essentially positive. There is no doubt that the identification of the lines is the same as made by us.

The experimental values of the constants \(A\), \(B\) of the splitting are considerably greater than those calculated by Sheng, Barker & Dennison. Their calculation rests on the potential energy curve for the ammonia molecule proposed by Manning (1935). This curve has no firm foundation, and was adopted to obtain an exact solution of the wave-equation, the constants being adjusted to fit the energy levels with the observed vibrational frequencies. It gives satisfactory values for the inversion splitting of the vibrational levels, and for the fine structure of the 10\(\mu\) vibrational band. Modification of this potential curve, to give better correlation with the results reported in this paper, would presumably be confined to the region where the potential energy is not much greater than the energy of the ground vibrational level. This would not affect the agreement with the previous observations.

5. Magnitude of the Absorption

Since the experimental errors in the measurement of the absorption coefficients are not expected to amount to more than a few per cent, an accurate comparison with the values predicted by the quantum mechanical intensity formula is possible. This formula is (cf. Van Vleck & Weisskopf, 1945)

\[
\int \frac{\gamma}{\nu^2} d\nu = \frac{8\pi^3 N_{JK}}{3ckT} \left| \mu_{JK} \right|^2,
\]

since \(h\nu \ll kT\) in this region. Here \(N_{JK}\) is the number of molecules per c.c. occupying the level with rotational quantum numbers \((J, K)\) and \(\left| \mu_{JK} \right|^2\) is the transition probability for the inversion. Dennison (1931) has shown that

\[
\left| \mu_{JK} \right|^2 = \frac{\mu^2 K^2}{J^2 + J},
\]

* Note added in proof. In a later paper Good (1946b) gives the formula

\[
\bar{\nu} = 0.79347 - 0.005048(J^2 + J) + 0.007040K^2
\]

\[+ 0.0001546(J^2 + J)^2 - 0.00004260(J^2 + J) K^2 + 0.00002920K^4,
\]

where all the constants are empirical. The close agreement between this formula and that proposed by us, which involves only three empirical constants, has been pointed out elsewhere (Bleaney & Penrose 1946c). The accuracy of determination of the wave-numbers of the lines claimed by Good (±0.02%) is the same as in our experiments.
where $\mu$ is the permanent dipole moment of ammonia, for which the value $1.44 \times 10^{-18}$ e.s.u. is taken in these calculations.

For comparison with the experimental results two methods have been used. The first of these involves a determination of the total absorption due to a number of lines; from equation (4) it is obvious that this requires evaluation of the area contained under a curve of $(\gamma/\nu^2)$ against $\nu$. This area is then to be compared with the theoretical value obtained by summation of the appropriate values of $(N_{JK} | \mu_{JK} |^2)$ for the lines whose wave-numbers lie in the range of integration. In computing the area under the experimental curve greater accuracy is obtained by using a curve determined at a pressure where the individual lines are smoothed over by the pressure broadening. The pressure should not be too high, however, for it is desirable to keep most of the absorption within the band of frequencies covered by the experiments.

The absorption curve measured at 4.5 mm. pressure was chosen as the most suitable and the area between $\nu = 0.67$ and 0.87 cm.$^{-1}$ was found to be

$$\int \frac{\gamma}{\nu^2} d\nu = 44.5 \text{ db./km.cm.}$$

A simple calculation indicated that this figure should be increased by 4% for the tails at the high and low ends of the frequency band, giving 46.3 db./km.cm. This figure includes, of course, the tails of those lines whose centres lie outside the band, but their contribution is less than 1% and can be neglected. The value calculated from the statistical weights and transition probabilities is

$$\int \frac{\gamma}{\nu^2} d\nu = 46.5 \text{ db./km.cm.}$$

The exact agreement of this and the experimental value is somewhat fortuitous, as a difference of several per cent would not lie outside the experimental errors. The latter are however mainly random in nature and the process of computing the integral has a similar effect to taking the mean of a large number of observations.

A second comparison between the theoretical and experimental absorption coefficients can be obtained from the intensities of individual lines. This requires that the lines be sufficiently resolved to make possible a measurement of the total area under each line separately, or, what is equivalent, measurement of the breadths of the lines at half intensity. From the latter and the absorption at the centre of the line the total intensity can be found, assuming the shape of the absorption curve to be given by the usual simple formula

$$\frac{\gamma}{\nu^2} \propto \frac{\Delta \nu}{(\nu - \nu_0)^2 + \Delta \nu^2}.$$ 

In this formula $\Delta \nu$ is half the breadth of the line at half-intensity, i.e. half of what is usually termed the 'breadth' in spectroscopy. We shall refer to it as the 'line-breadth constant'.

To obtain rather better resolution of the lines than at 1.2 mm. pressure (figure 2), a pressure of 0.5 mm. was chosen at which to make a detailed examination of each
The inversion spectrum of ammonia at centimetre wave-lengths

line. At this pressure all but a few lines were well resolved; these few were examined at lower pressures (e.g. 0.2 mm.) to determine their exact frequencies, though not their breadths. A typical absorption curve is shown in figure 3, the readings of the micrometer head being plotted as abscissae. The limit of reading of the micrometer head corresponds to a frequency change of about 0.00002 cm.\(^{-1}\); thus small changes of wave-number can be measured with a probable error of this order. The micrometer reading is linearly related to the length \(l\) of the cavity, and changes in the reading can be reduced to changes in wave-number by the relation

\[
\frac{\Delta \nu}{\Delta \lambda_g} = \frac{n \Delta \nu}{\Delta l} = -\frac{1}{\nu \lambda_g^3},
\]

where \(\lambda_g\) is the wave-length in the cavity, determined from the positions of successive resonances, and \(n\) is the number of full wave-lengths in the cavity at the particular resonance used for the examination of the line. Both \(\nu\) and \(\lambda_g\) and, therefore, the conversion factor are known to a few parts in \(10^4\).

In figure 3. Detail of spectrum at lower pressure (0.5 mm.) showing improved resolution.

In table 2 the experimental values of the absorption coefficient \((\gamma_0)\) at the centre of the line, and the line-breadth constant \((\Delta \nu)\), are given for some seventeen lines (columns 2 and 3). In the fourth column is shown the intensity \(I_{JK}/\bar{\nu}^2\) calculated from the formula

\[
\frac{I_{JK}}{\bar{\nu}^2} = \frac{\pi \gamma_0}{\bar{\nu}^2} \Delta \nu (10^{-5} V_0) \quad (V_0 = \text{molar volume at 0.50 mm. pressure}),
\]
where the constant $10^{-5}V_0$ represents a reduction from a kilometre path to a path length such that a mole of gas would be contained per sq.cm. of cross-section. The units of $I_{JK}/\bar{v}^2$ are therefore decibels per mole. The corresponding values of $I_{JK}/\bar{v}^2$ calculated from the theoretical formula (4) are given in column 5, and do not deviate from the experimental values by more than $\pm 5\%$. The measurements of the line-breadth constants, which range from $2 \times 10^{-4}$ to $5 \times 10^{-4}$ cm.$^{-1}$, are liable to errors of the order $\pm 5\%$. To compare the averages, the values of columns 4 and 5 have been summed separately; they agree very closely showing that there is no consistent deviation.

**Table 2. Comparison of Measured and Calculated Intensities**

<table>
<thead>
<tr>
<th>line $(J, K)$</th>
<th>$\Delta v$ at $p = 0.5$ mm. $\times 10^{-4}$ cm.$^{-1}$</th>
<th>$\gamma_0$ (db./km.)</th>
<th>$I_{JK}/\bar{v}^2$ = ( \frac{\pi \gamma_0}{\bar{v}} \Delta \bar{v}(10^{-5}V_0) ) (db./mol.)</th>
<th>$I_{JK}/\bar{v}^2$ (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 1</td>
<td>2.6</td>
<td>51</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>3, 1</td>
<td>2.4</td>
<td>29</td>
<td>14.5</td>
<td>14</td>
</tr>
<tr>
<td>3, 2</td>
<td>3.2</td>
<td>100</td>
<td>62.5</td>
<td>59</td>
</tr>
<tr>
<td>3, 3</td>
<td>4.5</td>
<td>360</td>
<td>289</td>
<td>289</td>
</tr>
<tr>
<td>4, 4</td>
<td>4.5</td>
<td>190</td>
<td>149</td>
<td>151</td>
</tr>
<tr>
<td>5, 1</td>
<td>1.8</td>
<td>7</td>
<td>3.3</td>
<td>3.5</td>
</tr>
<tr>
<td>5, 2</td>
<td>2.6</td>
<td>20</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>5, 3</td>
<td>3.3</td>
<td>96</td>
<td>71</td>
<td>73.5</td>
</tr>
<tr>
<td>5, 5</td>
<td>4.7</td>
<td>186</td>
<td>148</td>
<td>137</td>
</tr>
<tr>
<td>6, 3</td>
<td>3.1</td>
<td>44</td>
<td>35.5</td>
<td>34</td>
</tr>
<tr>
<td>6, 4</td>
<td>3.6</td>
<td>42</td>
<td>35</td>
<td>34.5</td>
</tr>
<tr>
<td>6, 6</td>
<td>4.7</td>
<td>276</td>
<td>198</td>
<td>210</td>
</tr>
<tr>
<td>7, 5</td>
<td>4.1</td>
<td>28</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>7, 6</td>
<td>3.9</td>
<td>132</td>
<td>100</td>
<td>95.5</td>
</tr>
<tr>
<td>8, 7</td>
<td>4.1</td>
<td>44</td>
<td>34</td>
<td>32.5</td>
</tr>
<tr>
<td>10, 9</td>
<td>4.2</td>
<td>35</td>
<td>25.5</td>
<td>23</td>
</tr>
<tr>
<td>11, 9</td>
<td>2.9</td>
<td>8.5</td>
<td>5.7</td>
<td>6.4</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1237</td>
<td>1236</td>
</tr>
</tbody>
</table>

The good agreement between the theoretical and experimental values of the absorption coefficients by both methods of comparison is in marked contrast with results obtained in the infra-red, where the experimental difficulties generally preclude accurate measurement of intensity. In the case of ammonia these difficulties were largely overcome by Foley & Randall (1941); from the intensity of the line at 270 cm.$^{-1}$ they deduced a value of 1.30 Debye units for the permanent dipole moment. If the measurements reported in this paper are regarded as yielding a dipole moment, the value $1.44 \pm 0.01$ Debye units is obtained. The values obtained by the usual methods are $1.44$ (Zahn 1926), $1.48$ (Watson 1927), $1.44$ (Keyes & Kirkwood 1930) and $1.437$ (Van Itterbeek & De Clippelieir 1946).

### 6. Comparison with Wright and Randall

The most intense lines in the spectrum described in this paper lie in the neighbourhood of 0.8 cm.$^{-1}$. On the other hand, Wright & Randall (1933) found that the splitting of the 4th, 5th and 6th rotational lines in the far infra-red (which should be
The inversion spectrum of ammonia at centimetre wave-lengths 371
twice the inversion frequency) was 1.33 cm$^{-1}$. There is no real discrepancy between these two values, however, because the transition probabilities are different for rotational lines ($\Delta J = \pm 1$) and the lines in the long-wave spectrum for which ($\Delta J = 0$). In fact the lines corresponding to $K = 0$, which are forbidden in the inversion spectrum, are those with the greatest intensity in the rotation spectrum. The inversion frequencies (table 2), observed or predicted by the splitting formula, have been used to calculate the mean splitting of the rotational transition $J = 5$ to $J = 6$, the lines corresponding to different values of $K$ being weighted according to their statistical weights and transition probabilities. The value thus obtained was 1.35 cm$^{-1}$ in good agreement with that observed by Wright & Randall. Only the mean values can be compared, since there is an additional splitting of the $K$ sub-levels due to centrifugal distortion which must also be considered in reconstructing the shape of the unresolved lines observed by Wright & Randall.

We wish to make acknowledgement to Lord Cherwell for extending to us the facilities of his laboratory; and to Mr K. W. H. Stevens for his kind help with the experiments. The work was conducted under the auspices of the Board of Admiralty, to whom we are indebted for permission to publish this paper.

REFERENCES

Autler, Becker & Kellogg 1946 Phys. Rev. 69, 694.
Bleaney & Penrose 1946c Phys. Rev. 70, 775.
Good 1946a Phys. Rev. 69, 539.
Good 1946b Phys. Rev. 70, 213.
Hsi-Yin Sheng, Barker & Dennison 1941 Phys. Rev. 60, 786.
Van Itterbeek & De Clippeleier 1946 Physica, 12, 97.
Zahn 1926 Phys. Rev. 27, 455.