

## The Inversion Spectrum of Ammonia\*

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Ammonia gas is known to exhibit a strong absorption in the region of  $0.8\text{ cm}^{-1}$ . By sweeping the frequency of a continuous wave oscillator and using a balanced wave guide system with one arm of the wave guide serving as an absorption chamber, thirty lines of the fine structure, as predicted by Sheng, Barker, and Dennison, have been observed in this region. Their intensities and frequencies have been measured for two different temperatures and an empirical expression for the frequencies of the lines in terms of their rotational quantum numbers is given. At pressures of  $5 \times 10^{-1}$  mm Hg and below, the lines are very well resolved. At pressures of  $10^{-2}$  mm Hg and below, a definite hyperfine structure appears. The Stark effect is also observed when a d.c. field is applied to the absorbing gas.

### I. INTRODUCTION

AMMONIA gas affords an interesting subject of investigation because it is possible to study one of its molecular transitions by using radiofrequency techniques. In 1934 Cleeton and Williams<sup>1</sup> found that ammonia gas gave a strong absorption line at  $0.8\text{ cm}^{-1}$  (1.25-cm wave-length or 24,000 mc/sec.). With the equipment that is now available in the one-centimeter region, it is possible to carry their work much further.

The ammonia molecule can be considered to be a regular pyramid with the nitrogen atom at the apex and the three hydrogen atoms in a triangle forming the base (see Fig. 1). Dennison and Hardy<sup>2</sup> and Dennison and Uhlenbeck<sup>3</sup> have shown that the vibrational energy levels are split into pairs<sup>4</sup> because of the two positions of equilibrium for the nitrogen atom. The energy difference between the two levels of the lowest pair is the energy difference which Cleeton and Williams investigated and the one in which we are interested. This "inside-out" effect or "inversion" of the molecule also gives rise to a doubling of the far infra-red absorption lines of ammonia<sup>5</sup> and Herzberg<sup>6</sup> has called it "inversion

doubling." It follows that the absorption spectrum in the  $0.8\text{ cm}^{-1}$  region could be called the "inversion spectrum." It is this inversion spectrum that is investigated in this paper.

Unpublished work by Howe<sup>7</sup> and others showed that as the pressure of the ammonia gas is reduced, this main absorption line becomes narrower. Sheng, Barker, and Dennison<sup>8</sup> have predicted a fine structure for this line, which should be observable providing the pressure can be reduced sufficiently to make possible the resolution of the individual lines.

This paper is primarily concerned with the measurement and the interpretation of this fine structure. Thirty absorption lines have been observed and their frequencies and intensities measured.

### II. EXPERIMENTAL

The frequency source used in this investigation is a continuous wave oscillator tube. It is of the type that can be tuned continuously over a broad frequency region and it may be swept

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<sup>1</sup> C. E. Cleeton and N. H. Williams, *Phys. Rev.* **45**, 234 (1934).

<sup>2</sup> D. M. Dennison and J. P. Hardy, *Phys. Rev.* **39**, 938 (1932).

<sup>3</sup> D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).

<sup>4</sup> G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945), pp. 221-224.

<sup>5</sup> N. Wright and H. M. Randall, *Phys. Rev.* **44**, 391 (1933).

<sup>6</sup> Reference 4, p. 27.

<sup>7</sup> H. S. Howe, Doctorate Thesis, University of Michigan (1940).

<sup>8</sup> Sheng, Barker, and Dennison, *Phys. Rev.* **60**, 786 (1941).

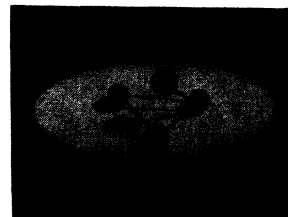


FIG. 1. The  $\text{NH}_3$  molecule.

rapidly in frequency by applying a varying voltage to one of its electrodes.

A wave guide system is used, one section of which (about two meters long) is sealed at the ends with a thin dielectric tape so as to make it pressure tight. This section is the absorption cell and is connected to a vacuum pump and gas filling apparatus. A crystal detector is used to detect the radiofrequency power after it passes through the absorption cell. A block diagram of the apparatus is shown in Fig. 2. The radio waves leave the oscillator and travel down the wave guide past the first variable attenuator (used to adjust the power level in the rest of the system) to the "T" section in the center of the diagram. Here the energy splits and half of it passes through the absorption cell on the right and thus to the right-hand crystal, the other half proceeds down the left wave guide past the various attenuators to the left-hand crystal detector. The rectified currents from the two crystal detectors are passed through two equal resistances ( $R$ ) to ground. A galvanometer is connected across the two resistors. This arrangement permits the system to be balanced by adjusting the variable attenuator in the left-hand arm to give zero galvanometer current. Once this is done fluctuations in the oscillator power will cause approximately equal fluctuations in the two crystal currents and are thus balanced out. This balanced system is particularly useful when measuring small attenuations. To make an absorption measurement the gas cell is evacuated and the left-hand variable attenuator is adjusted to give zero galvanometer current. The gas is then introduced into the gas cell. The unbalance caused by the absorbing gas is corrected by adjusting the calibrated attenuator so that the galvanometer is returned to zero. The attenua-

tion of the gas is read directly from the calibrated attenuator. To measure the absorption of the gas *vs.* frequency, it is necessary to change the frequency step by step and repeat the above for each frequency. When the absorption lines are sufficiently sharp, it is easier to observe a particular line by sweeping the frequency of the oscillator over the frequency range of the line. This can be done by applying a sawtooth voltage to one of its electrodes. This same sawtooth voltage is applied to the horizontal deflection plates of an oscilloscope tube, thus making the horizontal scale a frequency scale, because the oscillator frequency and the oscilloscope spot are being swept in synchronism. A balanced amplifier serves to amplify the difference voltage that is developed across the two resistors and apply it to the vertical deflection plates of the oscilloscope. Thus, if there is no gas in the absorbing cell the trace on the scope should remain flat, as the frequency of the oscillator is swept. However, if the gas that is introduced absorbs energy in a part of the frequency region that is being swept, the system will be unbalanced and the scope trace will be deflected by an amount proportional to the magnitude of the absorption (see Figs. 3 and 4). The scope is connected so that the absorption is positive upwards.

The cavity type wavemeter that is coupled to the right-hand wave guide has the same effect as the absorbing gas. As the oscillator frequency sweeps through the frequency to which the wavemeter is tuned, the wavemeter absorbs energy and its resonance curve is traced out on the scope. Its shape and appearance are very similar to the  $\text{NH}_3$  absorption lines shown in Fig. 3. To measure the frequency of an absorption line, it is only necessary to superpose the wavemeter "pip" on the absorption line and read the wavemeter dial. The wavemeter was calibrated by using the harmonics from an oscillator that was synchronized with the standard frequency from the Bureau of Standard's station WWV. The calibrated attenuator was calibrated using a thermister type bolometer in a bridge circuit.

The inversion spectrum fine structure was found to be very well resolved at pressures below 0.5 mm of Hg. Further reduction of pressure caused the individual lines to become sharper as shown in Figs. 3 and 4. The width and shape

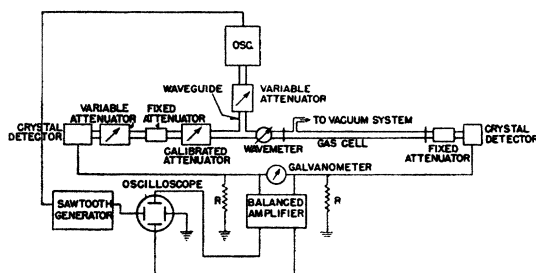


FIG. 2. Block diagram of apparatus.

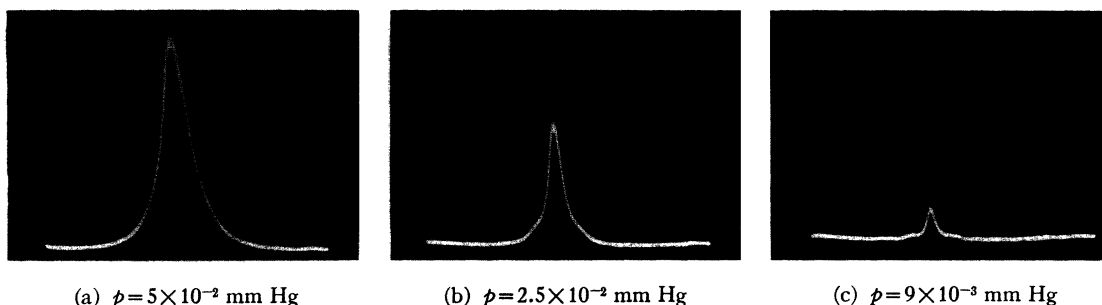


FIG. 3. Oscilloscope picture of absorption *vs.* frequency for one line of the fine structure for different pressures.  $J=3$ ,  $K=3$ ; full scale 22 mc/sec.;  $T=297^\circ\text{K}$ .

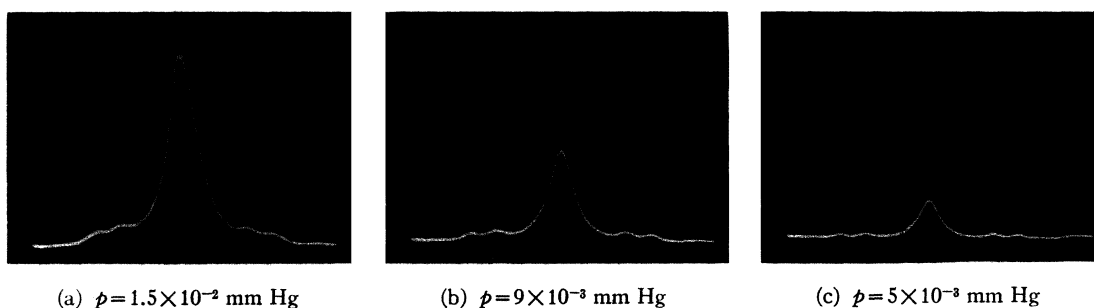


FIG. 4. Oscilloscope picture of absorption *vs.* frequency for one line of the fine structure for different pressures showing the hyperfine structure.  $J=3$ ,  $K=3$ ; full scale 8.6 mc/sec.;  $T=297^\circ\text{K}$ . Note difference in frequency scale between Figs. 3 and 4.

of the line shown is entirely caused by the gas itself and is not affected particularly by this method of observation. This is true because the natural width of the oscillator tube spectrum is extremely small compared to the width of the line being observed.

Two sets of data have been taken. The frequencies and the intensities of the inversion spectrum fine structure have been measured for two different temperatures but approximately the same pressures. These data are plotted in Figs. 5 and 6. To insure the same pressure for a series of measurements the gas was introduced into the absorption cell and left there during the whole run. To obtain a zero balance for each line the frequency of the oscillator was set to one side of the line and the system was balanced. Then the frequency was shifted the few megacycles needed to bring it to the peak of the absorption line (maximum galvanometer deflection) and the calibrated attenuator was adjusted for balance and read.

The measurement of the frequencies is accurate to about  $\pm 5$  megacycles. The measurement of attenuation is accurate to about  $\pm 10$  percent.

Because of the fact that the wave guide wavelength is different from the free space wavelength, a correction factor  $\lambda/\lambda_g$  must be applied to each value of intensity to correct it to the value it would have if it were measured in free space. This correction has been applied to all of the data in this report.

### III. DISCUSSION

As mentioned before, the transition that gives rise to the inversion spectrum is the one between the two levels of the split vibrational ground state. The splitting can be explained by the fact that the nitrogen atom has two positions of equilibrium—one on either side of the plane of the hydrogen atoms. The nitrogen atom may pass through the potential hill, which exists in the region of the plane of the hydrogen atoms, by a tunneling process.<sup>9</sup> The amount of the splitting of the vibrational levels is a sensitive function of the height and breadth of this potential barrier. It is reasonable to expect that the shape of the potential barrier will be a function of the rotational level that a molecule is in.

<sup>9</sup> Reference 4, pp. 221–224.

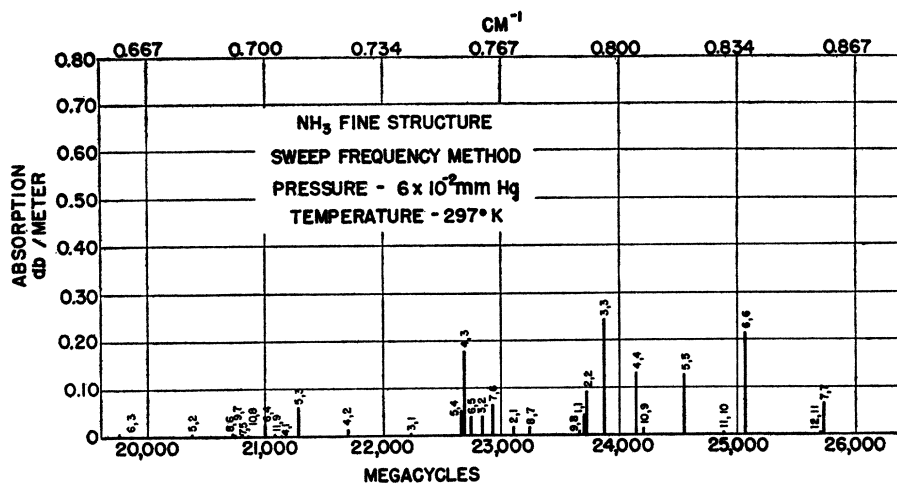


FIG. 5. The inversion absorption spectrum fine structure for ammonia.  $T = 297^\circ\text{K}$ .

Indeed, Sheng, Barker, and Dennison<sup>10</sup> explain this absorption fine structure in terms of the different degrees of centrifugal distortion caused by the various molecules being in different rotational states. With each rotational state, there is associated a definite splitting and thus a definite spectrum line. The two quantum numbers  $J$  and  $K$  are used to indicate the rotational level of a particular molecule.  $K$  is the number of units of angular momentum about the symmetry axis while  $J$  is the total rotational quantum number. Sheng, Barker, and Dennison calculate that the wave numbers of the lines in the inversion fine structure can be represented by

$$\frac{\nu}{hc}(\text{cm}^{-1}) = \frac{\nu_0}{hc} - 0.0011(J^2 + J) + 0.0016K^2. \quad (1)$$

The expression that is obtained from the measured frequencies is

$$\begin{aligned} \frac{\nu}{hc}(\text{cm}^{-1}) = & 0.79347 - 0.005048(J^2 + J) \\ & + 0.007040K^2 + 0.00001546(J^2 + J)^2 \\ & - 0.00004260(J^2 + J)K^2 + 0.00002920K^4. \quad (2) \end{aligned}$$

The average deviation of the measured lines from the above expression (2) is about 0.01 percent. The difference between the two expressions seems to indicate that the theoretical

model needs some modification. The numbers indicated above the lines in Figs. 5 and 6 are the  $J$  and  $K$  values for that line.

The intensities of the lines should be a function of the number of molecules in each rotational level and their transition probabilities. The number of molecules in a given level depends on the distribution of thermal energies and the statistical weights. The statistical weights depend on the value of  $J$  and the nuclear spin of the hydrogen atoms.<sup>11</sup> For this case the levels for  $K = 0, 3, 6, 9$ , etc. will have twice the statistical weight of those for  $K = 1, 2, 4, 5, 7$ , etc. Note the increased intensities of the lines for  $K = 3$  and  $6$  in Figs. 5–8. Because of the symmetry properties,<sup>12</sup> levels for  $K = 0$  are not split but merely displaced so that no inversion line should exist. No lines having  $K = 0$  were found.

Figure 7 shows a plot of the experimental intensities *vs.* frequency for separate  $K$  values. Figure 8 (a) shows the observed intensities for the strongest lines of different  $J$  values, while Fig. 8 (b) shows the relative intensities which were calculated following the suggestions in Herzberg.<sup>13</sup> Note the uniform distribution that would be obtained if the lines for  $K = 3, 6$ , and  $9$  were reduced by a factor of two.

The low temperature data were taken to see if the effect of the thermal distribution "moving

<sup>10</sup> Sheng, Barker, and Dennison, *Phys. Rev.* **60**, 786 (1941).

<sup>11</sup> Reference 4, pp. 27, 413.

<sup>12</sup> Reference 4, p. 413.

<sup>13</sup> Reference 4, pp. 27, 29, 422.

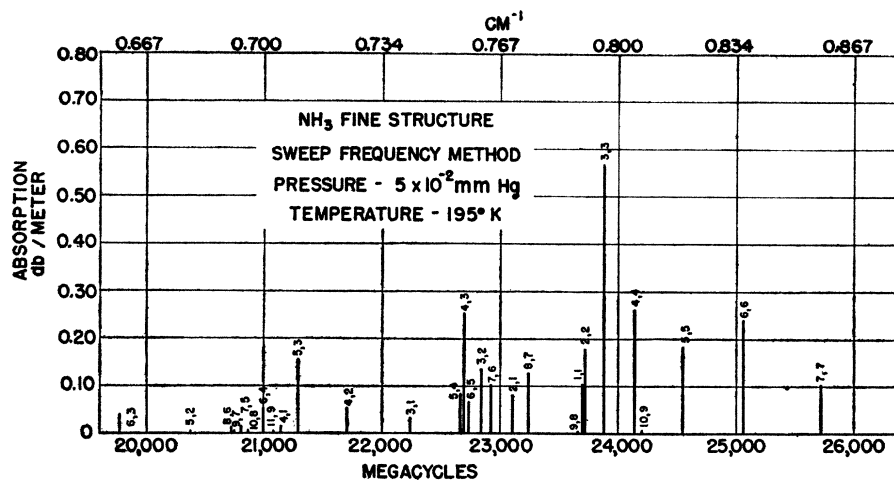


FIG. 6. The inversion absorption spectrum fine structure for ammonia.  $T=195^{\circ}\text{K}$ .

over" could be noticed. It was expected that the intensities of lines having lower values of  $J$  and  $K$  would increase and that of lines having higher values of  $J$  and  $K$  would decrease. This effect is apparent on careful examination of Figs. 5 and 6 but it is obscured by two other effects. First, for a temperature reduction of  $300^{\circ}\text{K}$  to  $200^{\circ}\text{K}$  there will be an increase of  $\frac{3}{2}$  in the number of molecules, providing the pressure remains constant. Second, the average velocity of the molecules will be reduced by the lower temperature, therefore increasing the time between collisions which causes the lines to be sharper and thus relatively more intense. However, the pressure was reduced by 20 percent, so for direct comparison of Figs. 5 and 6 the magnitudes of the lines in Fig. 6 should be decreased by about  $\frac{1}{3}$ .

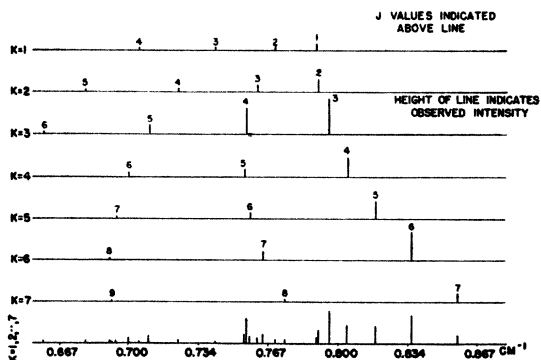


FIG. 7. The  $\text{NH}_3$  inversion spectrum for different values of the rotational quantum number  $K$ . Composite spectrum shown on bottom line.

This collision broadening effect for diminishing pressure is shown graphically in Figs. 3 and 4. The collision broadening process is one of interruption of the absorbed wavetrain by a collision with another molecule. As the number of molecules is reduced, the time between collisions increases, the length of the absorbed wavetrain increases, and the absorption "line" becomes sharper. At a pressure of about  $10^{-2}$  mm Hg the mean free path of the molecules should be about the same as the narrow dimension of the wave guide so that it would be expected that the line breadth would be more or less constant below this pressure.

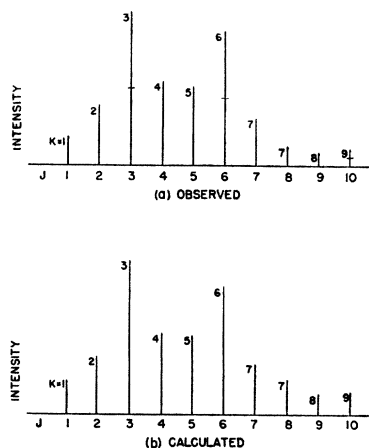


FIG. 8. Intensities of the strongest observed lines of the fine structure of  $\text{NH}_3$  ( $T=300^{\circ}\text{K}$ ). (a) Observed relative intensities; (b) Calculated relative intensities. Note the symmetrical distribution that would result providing the lines for  $K=3, 6,$  and  $9$  were divided by two.

The above explanation would also give weight to the assumption that most of the absorbed energy finally appears as kinetic energy of the gas.

#### IV. CONCLUSIONS

Thirty absorption lines in the fine structure of the inversion spectrum of ammonia gas have been observed and identified with their rotational quantum numbers.<sup>14</sup> An empirical expression has been found which represents the wave numbers of the lines in terms of their  $J$

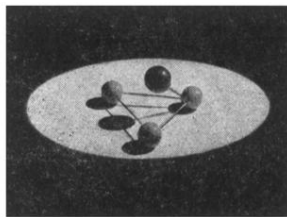
<sup>14</sup> This identification agrees with that of B. Bleaney and R. P. Penrose which is given in their letter to the editor in *Nature* **157**, 339 (1946).

and  $K$  values. The intensities at room temperature compare well with those calculated from the thermal distribution of the rotational levels and the transition probabilities. The intensities at reduced temperature behave as expected and the variation of line breadth with pressure was demonstrated.

Figure 4 shows a definite hyperfine structure for the line  $J=3$ ,  $K=3$ . Other lines show the same type of symmetrical structure but with different separations of the components.

A definite frequency shift (Stark effect) of the various lines was observed when a d.c. field was applied to the absorbing gas.

FIG. 1. The  $\text{NH}_3$  molecule.



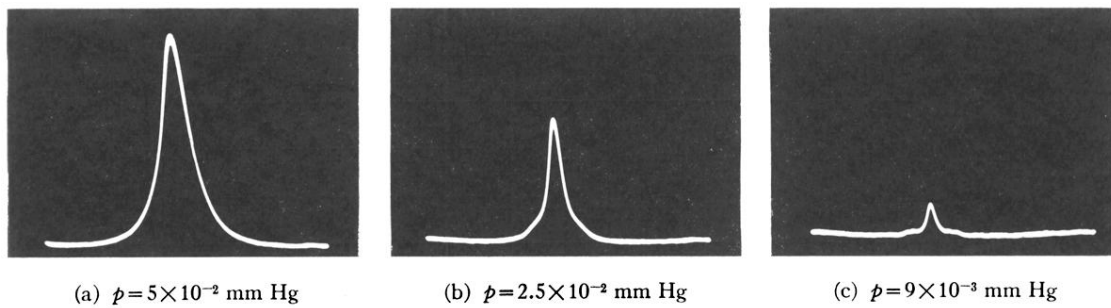


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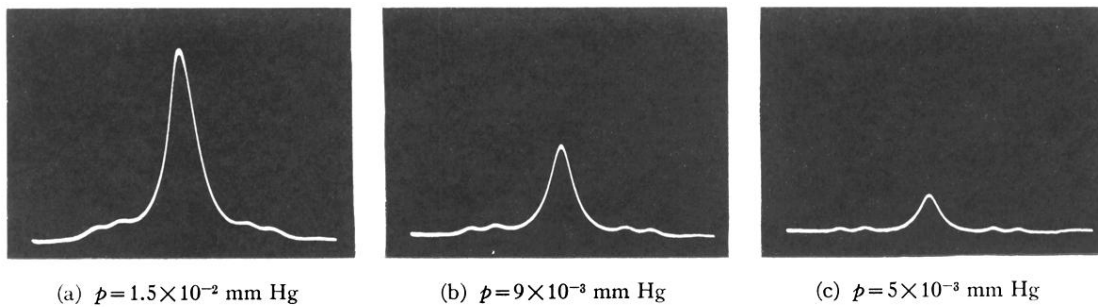


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