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Fine Structure in the Far Infra-Red Spectrum of NH_3

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The pure rotation absorption spectrum of NH_3 for final state $J=11$, 12, 13, 14, 15 has been examined with high resolution. A multiplet splitting is found which may be expressed by the formula

$$\nu=19.89J-0.00294J^3+0.00279JK^2,$$

where K is the quantum number of angular momentum about the symmetry axis. This equation is shown to be in good agreement with the theoretical expression of Slawsky and Dennison when the potential anharmonicities are taken into account. A calculation of the permanent dipole moment is made from the absolute intensity of one absorption, giving the value 1.3×10^{-18} c.g.s. e.s.u.

THE far infra-red rotation spectrum of NH_3 has been observed by Wright and Randall[1] and by Barnes.[2] Wright and Randall examined the 70–100μ region and found three doublets, the centers of which may be represented by the formula

$$\nu=19.89J-0.00178J^3, \tag{1}$$

where J has the values 5, 6, and 7. The value of J corresponds to the total angular momentum quantum number for a symmetric rotator in the final state. The doublet splitting is 1.32 cm^{-1}. As is well known, this is due to the tunnel effect, or resonance between the two equilibrium configurations of the molecule.[3] Barnes, in the 45–65μ region observed the absorptions corresponding to transitions to the final states $J=8$, 9, 10, 11, with less resolving power. The doublet separation is not in evidence.

In this paper are reported observations of the absorptions due to transitions to J values 11, 12, 13, 14, and 15. This work was undertaken because of the recent theoretical investigation of Slawsky and Dennison[4] on the effect of centrifugal distortion on the rotational energy levels of NH_3, which indicates that a fine structure should be observable in the higher rotational lines.

EXPERIMENTAL

The spectrometer employed is the wide-aperture, vacuum instrument with automatic recording, described by Randall and Firestone.[5] The radiation source was a strip of platinum coated with thorium oxide, through which about 60 amperes were passed. This was mounted directly before the entrance slit, the strip being of the right width to fill out the large mirror. Source and spectrometer case were evacuated together to remove atmospheric absorption. To purify the spectrum two filters, composed of selenium evaporated onto nitrocellulose films at six mm pressure, were placed in the optical path. These, together with a single reststrahlen reflection from sodium chloride or calcium fluoride plates, and shutters of potassium bromide, provided pure radiation throughout the 30–50μ region. The thermopile had a polystyrene window, and was evacuated separately with a diffusion pump.

The cell containing the gas was mounted inside the evacuated case of the spectrograph behind the emergent slit. Provision was made to pass the gas into the cell from outside the spectrometer case. The cell is of brass, coated inside with paraffin, and is five cm long. The cell windows are of Pliofilm and are reinforced with a wire grid to hold the gas pressure when in the evacuated case. For the absorptions $J=11$, 12, 13, pressures of 10–12 cm NH_3 were used, and for $J=14$, 15, about 40 cm. The data were

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[1] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

[2] R. B. Barnes, Phys. Rev. **47**, 658 (1935).

[3] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932); D. M. Dennison, Rev. Mod. Phys. **3**, 208 (1931).

[4] Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. **7**, 509 (1939).

[5] H. M. Randall and F. A. Firestone, Rev. Sci. Inst. **9**, 404 (1938).

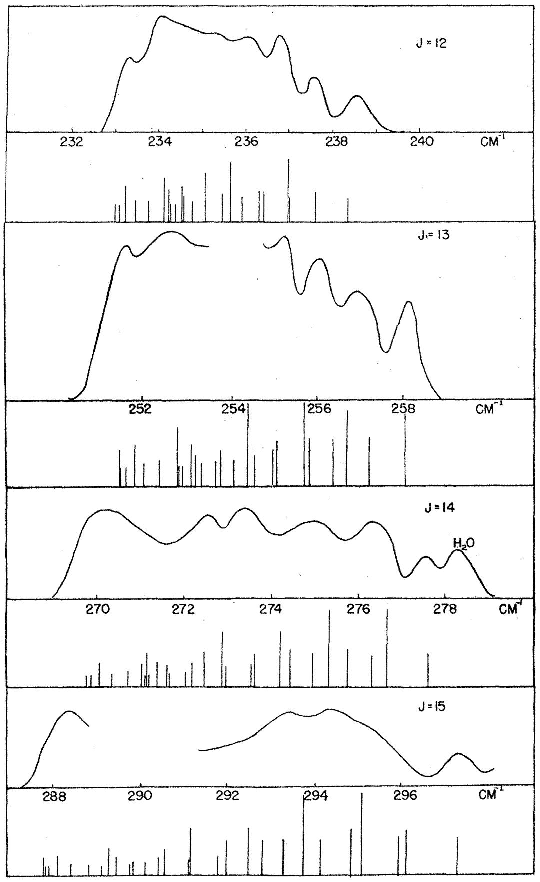

FIG. 1. The absorption lines of ammonia for $J=12$, 13, 14, and 15. Beneath each curve are plotted the positions of the fine structure lines predicted by Eq. (3).

obtained, by the automatic recording device, as photographic records of the galvanometer trace. Three to five records were taken of each absorption. Echelette gratings of 600 and 900 lines per inch, ruled by the Michigan engine, were employed. From the observed zero images it was determined that single lines of 0.5-cm^{-1} separation should be resolved.

The envelopes of the absorptions are shown in Fig. 1 in which the ordinates are proportional to the absorption. Although the ammonia gas was dried and then evaporated from the frozen state, traces of water vapor showed in the spectrum. Possibly this came from the cell walls, which could not be baked out. These lines were easily identified from the known water vapor spectrum,[6] and gaps in the envelopes indicate their positions. The frequencies of the absorption maxima are given in Table I. Most of these positions are considered accurate to a few hundredths cm^{-1}, and all to a tenth cm^{-1}. The $J=14$; 15; absorptions should be the most clearly resolvable, but apparently the larger amount of gas brought on pressure broadening.

COMPARISON WITH THEORY

The effect of centrifugal distortion on a semirigid molecule of the NH_3 configuration has been calculated by Slawsky and Dennison.[4] The influence on the rotational spectrum is predicted to be (1) a displacement of the lines proportional to J^3, and (2) separation of each line into a multiplet with a spread approximately proportional to J^3. Formulas are given, showing the displacement and spread as functions of the normal frequencies and potential constants. These quantities were determined approximately by Slawsky and Dennison, neglecting the effect of anharmonicities in the potentials. They found a formula

$$\nu=19.89J+0.00160J-0.00250J^3+0.00190JK^2. \quad (2)$$

This equation accurately predicts the positions of the lines found by Wright and Randall. However, lines of such a small J value show little spread, and hence no adequate check is possible.

This formula, when applied to the present lines, is in good qualitative, but only fair quantitative agreement. We have fitted a formula of this type to our observed lines. They may all be expressed by the formula

$$\nu=19.89J-0.00294J^3+0.00279JK^2. \quad (3)$$

The deviation of any observed line from this equation is only of the order of magnitude of the experimental error. In Fig. 1 we have plotted the absorption lines $J=12$, 13, 14, and 15, and beneath, the positions of the lines predicted by Eq. (3). The intensities are obtained from the rules given by Slawsky and Dennison.

Dennison[7] has recently made a much better approximation to the normal frequencies and potential constants in the lowest state by taking

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[6] H. M. Randall, D. M. Dennison, N. Ginsburg, and L. Weber, Phys. Rev. 52, 160 (1937).

[7] D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

into account the anharmonicities. In the same paper he has given new values of the internuclear distances and moments of inertia of NH_3. When substituted into the Slawsky and Dennison formula these new constants yield

$$\nu=19.89J+0.00140J-0.00300J^3+0.00271JK^2. \quad (4)$$

It is seen that this is very close to the above empirical formula, and in fact the lines predicted by it would differ only very slightly from the observed lines. The agreement is very satisfactory, and forms an argument for the more recent calculation of the potential constants.

In principle one further effect, not considered by Slawsky and Dennison, might influence the positions of the lines and perhaps account for some of the slight difference between the observed and predicted spectrum. Centrifugal distortion alters the effective double minimum potential, and consequently the resonance splitting. Sheng, Barker, and Dennison,[8] in an analysis of the parallel vibration band of NH_3 have found this perturbation in the excited level. A rough calculation shows that the influence of centrifugal distortion on the splitting in the ground state is about 1/120 of the effect in the excited vibrational level. The ultimate result is a contribution to the doublet separation of

$$-0.00290J^2+0.0040K^2.$$

This will shift the lines by not more than 0.2 cm^{-1}. If we adjust our empirical formula to take care of this, we obtain

$$\nu=19.89J-0.00303J^3+0.00290JK^2. \quad (5)$$

It is evident that this effect will account for the difference between the recalculated Slawsky Dennison formula[4] and the observed positions.

TABLE I. *Observed Absorption Maxima.*

$J=11$	12	13	14	15
214.26 cm^{-1}	233.22	251.63	270.30	288.36
215.16	233.95	252.50	272.56	293.46
216.23	235.41	255.24	273.35	294.40
217.82	235.94	256.08	274.95	297.30
218.59	236.72	256.93	277.60	
	237.53	258.02		
	238.47			

Although these observations were not intended as intensity measurements, certain features make these absorptions a very favorable case to compare the absolute intensities with the theoretically calculated values. The continuous radiation from the spectrometer is very constant across any one absorption, so that the percentage absorption may be calculated easily. More important, large errors in intensity measurement always occur when the absorption coefficient P_ν changes appreciably in a frequency interval equal to the slit width. This effect gives too low an apparent intensity, and consequently too small a value for the dipole moment. In our case, because of the spreading out of a single J line by the multiplet structure, we have in effect a very wide absorption, the spread being more than ten times the slit width. The total intensity of absorption is given by

$$\overset{J-1}{I_J}=\frac{8\pi^2\nu N}{3ch}\mu^2(1-e^{-h\nu/kT})F,$$

where μ is the permanent dipole moment of NH_3, and N the number of molecules per cc.

$$F=\frac{\sum_{K=0}^{J-1} g'_{JK}\exp\left[-E_{JK}/kT\right]}{\sum_{J=0}^{\infty}\sum_{K=0}^{J} g_{JK}\exp\left[-E_{JK}/kT\right]}.$$

We have chosen $J=14$ from which to calculate, as this absorption shows the least structure and is not overlaid with water vapor lines. The pressure here was 21 cm. The sums in this calculation were approximated by the integrals given by Gerhard and Dennison.[9] The measured intensity, integrated across the absorption, is $I=\int P_\nu d\nu=2.8\times10^{10}$. This gives for the dipole moment $\mu=1.3\times10^{-18}$ c.g.s. e.s.u. This value may be compared with the moment obtained from dielectric constant measurements of about 1.45×10^{-18}.[10]

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[8] Unpublished, but see reference 7.

[9] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).

[10] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932).