

## The Far Infrared Absorption Spectra of Ammonia and Phosphine Gases under High Resolving Power

NORMAN WRIGHT AND H. M. RANDALL, *University of Michigan*

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A spectrometer of large aperture employing a reflection grating of the echelette type ruled to concentrate radiation in the region of the 1st order of  $90\mu$  has been applied in the spectral range from  $60$  to  $125\mu$ . The resolving power was several times that hitherto obtained in this region. The pure rotation absorption spectra of water vapor and of the gases  $\text{NH}_3$  and  $\text{PH}_3$  have been investigated. In the case of  $\text{NH}_3$  the absorption lines shown as single in the observations of Badger and Cartwright have been found under the higher resolution of the present work to be doublets with a doublet separation of  $1.33\text{ cm}^{-1}$ .

Despite the similarity of structure of the molecules  $\text{PH}_3$  and  $\text{NH}_3$  the pure rotation lines of  $\text{PH}_3$  exhibit no trace of a doubling. The frequencies of the  $\text{PH}_3$  lines and the mid-frequencies of the  $\text{NH}_3$  doublets have been shown to agree very accurately with formulas of the type  $\nu_J^{J-1} = BJ - DJ^3$ . Determinations of the moments of inertia  $A$  of  $\text{NH}_3$  and  $\text{PH}_3$  have been made and in the case of  $\text{NH}_3$  the measurement of the doublet separation has led to a slight revision of the values for the moment of inertia  $C$  and for the molecular dimensions obtained by Dennison and Uhlenbeck.

### INTRODUCTION

THE spectra dealt with in this work are of the pure rotation type having their origin in changes in the rotational states of molecules possessing permanent electric moments. In general these spectra have their maximum intensities in the far infrared ( $\lambda > 30\mu$ ) and although they are of special interest because of the simplicity of their structure, the experimental difficulties of the far infrared have prevented a development similar to that of the near infrared.

The most important examples of observations of pure rotation spectra are those of Czerny<sup>1</sup> on the hydrogen halides and of Badger and Cartwright<sup>2</sup> on ammonia. While these measurements are of very great value they are nevertheless subject to the experimental limitation of small resolving power.

The present work was undertaken with the purpose of developing a technique for the application of echelette gratings in the far infrared and employing these gratings in a spectrometer of large aperture to bring a high resolving power to bear in this spectral region. High resolving power here refers to frequency difference and means ability to resolve absorption lines as close

together as  $1\text{ cm}^{-1}$ , an amount comparable with the best achieved in the near infrared.

Dennison and Hardy<sup>3</sup> in a recent work on the  $3\mu$  fundamental vibration band of  $\text{NH}_3$  observed a splitting of the rotation-vibration lines into doublets with doublet separation of  $1.6\text{ cm}^{-1}$ . From considerations set forth it was predicted in that work that the far infrared spectrum should also consist of doublets of about the same separation. The work of Badger and Cartwright because of insufficient resolving power showed no trace of this doubling.

The far infrared spectrum of  $\text{NH}_3$  therefore furnished an excellent opportunity both to verify the theory and to demonstrate the resolving power attained by the apparatus. The similar structure of the phosphine molecule ( $\text{PH}_3$ ) made it desirable to investigate this gas also.

### EXPERIMENTAL

The spectrometer used for this investigation has been previously described by Randall.<sup>4</sup> An important feature is its large aperture, the principal mirror having a diameter of  $61\text{ cm}$  ( $24\text{ inches}$ ) and a focal length of  $81.4\text{ cm}$  ( $36$

<sup>1</sup> M. Czerny, *Zeits. f. Physik* **44**, 235 (1927).

<sup>2</sup> R. M. Badger and C. H. Cartwright, *Phys. Rev.* **33**, 692 (1929).

<sup>3</sup> D. M. Dennison and J. D. Hardy, *Phys. Rev.* **39**, 938 (1932).

<sup>4</sup> H. M. Randall, *Rev. Sci. Inst.* **3**, 196 (1932).

inches). In this case a  $10 \times 10$  inch area of grating surface containing around 1200 lines was utilized.

Reflection gratings of the echelette type having cross sections as shown in Fig. 1 were employed.

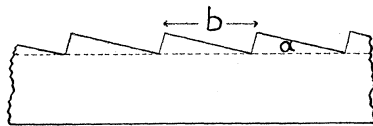


FIG. 1.

The grating used for most of the present work had the characteristics:  $b = 190.50\mu$ ,  $\alpha = 13^\circ 40'$  and blaze at  $90.0\mu$ . The constants of the gratings were obtained from the ruling engine screw which was sufficiently well calibrated to justify wave-length measurements to five significant figures.

The radiation was detected by means of a vacuum thermopile of the Pfund type having two junctions in series. The receivers consisted of silver or tin foil,  $0.6 \times 3.0$  mm, coated with aquadag (graphite). Tests showed that aquadag in layers of the thickness used on the receivers is opaque to radiation of the wave-lengths studied in the present case but the relative amounts reflected and absorbed have not been determined. The thermopile current was amplified about 150 times by means of a Moll thermorelay and the galvanometer deflections were read on a scale 4 meters distant. Under these conditions the Brownian movements were discernible and amounted to 2 or 3 mm scale deflection.

All optical parts of the spectrometer were enclosed in a gas-tight case of sheet metal the outside of which was covered with a layer of Celotex  $\frac{1}{2}$  inch thick. Vessels of  $P_2O_5$  were introduced for drying the air of the interior. The source of radiation, a Welsbach gas mantle which was partly surrounded by a water jacket, was placed directly in front of the entrance slit at a distance of 8 cm. This small space between source and slit was readily accessible for inserting the filters, cell and radiation shutters.

The elimination of overlapping orders of spectra, the greatest problem connected with the use of gratings, had to be accomplished in this case entirely by means of radiation filters and selective reflection, since no orders are suppressed in the blaze of the echelette grating. In all of the

work described here a filter of crystal quartz of at least 5 mm thickness was present in the radiation path. It has been found in agreement with the results of Barnes<sup>5</sup> that a plate of this thickness absorbs all radiation from 4 to about  $45\mu$  beyond which transmission begins and has a general increase, becoming roughly 50 percent at  $90\mu$ . The radiation of wave-length less than  $4\mu$  was partially eliminated by using one or two filters of thin tissue paper or lacquer covered with a layer of soot. Its effect was further decreased by using as shutters a plate of NaCl crystal which transmits all but about 9 percent of the short wave-length radiation but is opaque beyond  $25\mu$ . Finally this 9 percent was corrected for by taking deflections both with the NaCl shutter and with one of metal. As this method of eliminating the short wave-length radiation was employed in all cases no further mention of it will be made. The last step in the elimination of higher orders consisted of a single reflection of the radiation from a residual ray plate.

The methods of purification of the spectrum for the various wave-length regions were as follows: from 70 to  $80\mu$ , a 5 mm crystal quartz filter only; from 80 to  $90\mu$ , a 5 mm quartz filter and reflection from KBr; from 90 to  $105\mu$ , 5 mm quartz and reflection from KI; from 100 to  $125\mu$ , 5 mm quartz and reflection from a plate of pressed TlBr powder.

Despite the fact that all parts of the thermopile circuit were protected by both copper and iron shieldings, all work had to be done at night to avoid electromagnetic disturbances arising in nearby laboratories. Because the thermopile was of the uncompensated type it was necessary to use the utmost care in preventing temperature fluctuations in the surroundings.

The procedure involved in making observations was as follows. The room containing the apparatus was allowed several hours to come to thermal equilibrium after the gas mantle source had been started. The observer took his place at the side of the spectrometer a half hour before taking readings. The steady drift which was usually present was corrected for by averaging the two deflections produced on opening the radiation shutter and on closing it. Also, a

<sup>5</sup> R. B. Barnes, Phys. Rev. 39, 562 (1932).

metronome was used to give the proper intervals between readings. Since the total time of response of the system was 20 seconds, this time was allowed to elapse between opening and closing the shutter. Often as many as six or more of these double deflections were taken at a single setting of the grating and under the best conditions the mean deviation from the average of these was 2 or 3 mm, making the probable error in the neighborhood of 1 mm. The size of the deflections throughout the spectrum varied from 20 to 150 mm as may be seen from the energy curves of Fig. 3.

The absorption spectra of the gases were obtained by placing the cell between the source and slit. The cell consisted of a rectangular glass tube with crystal quartz plates, 2 mm thick, cemented to the ground ends. Because of the strong absorption of the gases observed and the high resolving power of the spectrometer the length of the cell, i.e., internal distance between windows, was made but 1 cm. All observations were made with the gases under reduced pressures, the cell being of sufficient strength to permit evacuation.

The irregular absorption produced throughout the spectrum by the small amount of water vapor, principally in the 8 cm exterior radiation path, necessitated in all cases the taking of two sets of observations, one with the gas in the cell and another with the cell evacuated. This irregularity of the energy distribution introduces an error in the wave-length determinations but no correction was made since it appears of the same order of magnitude as that caused by errors in the deflection measurements.

#### RESULTS

The curves shown in Fig. 2 and Fig. 3 give the galvanometer deflections obtained throughout the spectrum. Readings were taken in steps of 2.5' on the grating circle, an interval corresponding to 0.27  $\mu$  at 95  $\mu$ . The curves are in effect water vapor absorption curves, the numerous deep minima being due to absorption by the water vapor present in that part of the radiation path passing through undried room air. The envelopes of the curves are determined by the emission characteristics of the gas mantle, the absorption of the quartz filter, characteristics of the grating

and reflecting powers of the reststrahlen plates. Curves *A* and *B* were obtained with a 5 mm crystal quartz filter only. Curves *C* and *D* were obtained with the 5 mm quartz filter and in addition by reflecting the radiation from a plate of KI crystal in the case of *C* and from TlBr in *D*. Since the quartz begins to transmit at 45  $\mu$ , second order radiation might be expected to appear in curves *A* and *B* at around 90  $\mu$  and, in fact, comparison of these curves with *C* and *D*, in which the second order is removed, shows this to be the case. The frequent occurrence of strong water vapor absorption lines, or groups of lines, reducing the deflections nearly to zero, was used as an indication of spectral purity, the presence of second orders as in curve *B* preventing the deflections from coming to zero. A grating ruled for the region of 150  $\mu$  was used for curve *E*; here the 5 mm quartz filter was used and although the radiation was reflected from TlBr, the spectral purity is somewhat doubtful.

For all the curves of Fig. 2 the radiation passed through 80 cm of undried air, a focussing mirror having been used outside the spectrometer case. The source was then moved to its final position 8 cm in front of the entrance slit and curves *F*, *G*, and *H* of Fig. 3 were obtained. The extent to which water vapor absorption has been reduced in these curves may be seen by comparing them with *A* and *C*, portions of which are reproduced in this figure. It will be noticed that, in some cases, broad absorption regions have been resolved into two or more sharp lines.

TABLE I. *Water vapor.*

Wave-length ( $\mu$ )	Frequency ( $\text{cm}^{-1}$ )	Wave-length ( $\mu$ )	Frequency ( $\text{cm}^{-1}$ )
134.7	74.22	92.662	107.92
132.3	75.59	89.919	111.21
127.8	78.26	88.520	112.97
126.5	79.02	85.662	116.74
125.6	79.59	84.690	118.08
121.7	87.44	83.196	120.20
113.1	88.42	81.988	121.97
111.7	89.53	78.63	127.2
108.1	92.51	77.66	128.8
104.03	96.125	75.32	132.8
100.96	99.045	71.79	139.3
99.415	100.59	70.98	140.9
98.559	101.46	66.62	150.1
95.613	104.59	65.14	153.5
94.541	105.78	63.34	157.9
93.199	107.30	60.01	166.6

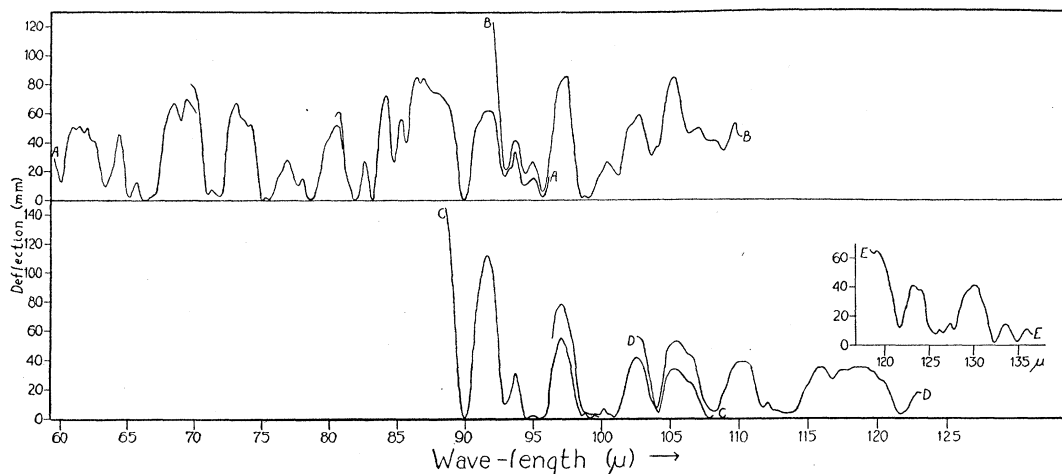


FIG. 2.  $\text{H}_2\text{O}$  vapor: Curve *A*—2 mm slits, 6 mm quartz; *B*—3 mm slits, 6 mm quartz; *C*—3 mm slits, 6 mm quartz, reflection from KI; *D*—3 mm slits, 6 mm quartz, refl. from TlBr; grating with blaze at  $90\mu$  in all cases; Curve *E*—3 mm slits, 6 mm quartz, refl. from TlBr;  $150\mu$  grating.

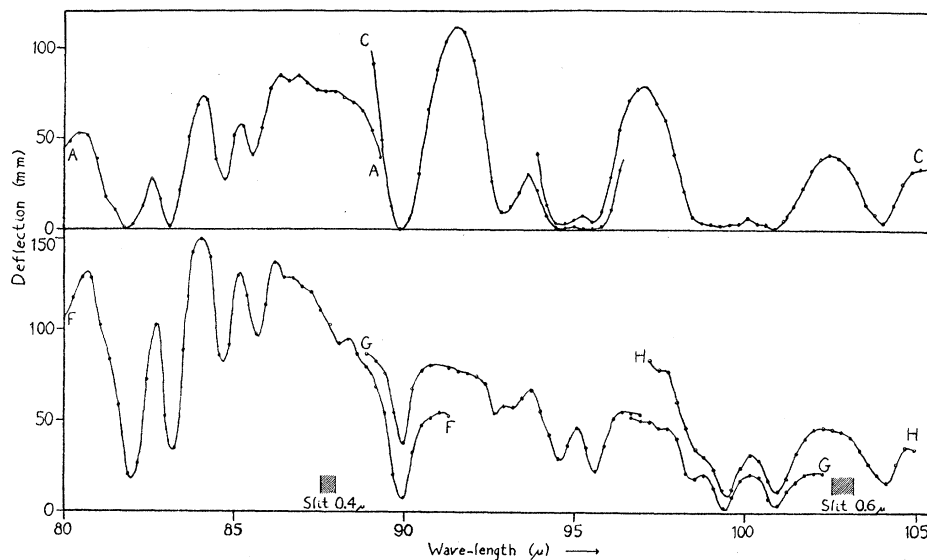


FIG. 3.  $\text{H}_2\text{O}$  vapor: Curves *A* and *C* same as in Fig. 2; undried air path 80 cm; Curve *F*—2 mm slits, 5 mm quartz, refl. from KBr; *G*—2 mm slits, 5 mm quartz, refl. from KI; *H*—3 mm slits, 5 mm quartz, refl. from KI; undried air path 8 cm.  $90\mu$  grating in all cases.

The high practical resolving power attained by the spectrometer is demonstrated by these water vapor absorption curves. That the resolution of lines as close together as  $1\text{ cm}^{-1}$  has been achieved may be seen by consulting Table I which contains a list of the wave-lengths and corresponding frequencies.

In agreement with the prediction of Dennison<sup>3</sup> the pure rotation spectrum of  $\text{NH}_3$  was found to

consist of doublets with doublet separation  $1.33\text{ cm}^{-1}$ . The doublets of ordinal number 5, 6 and 7 were observed and are plotted to a frequency scale in Fig. 4. The precision of the measurements is indicated by the extent to which the experimental points fall on smooth curves. Table II gives a list of the wave-lengths and frequencies of the doublets. The frequencies of the doublets 5 and 6 as measured unresolved by Badger and

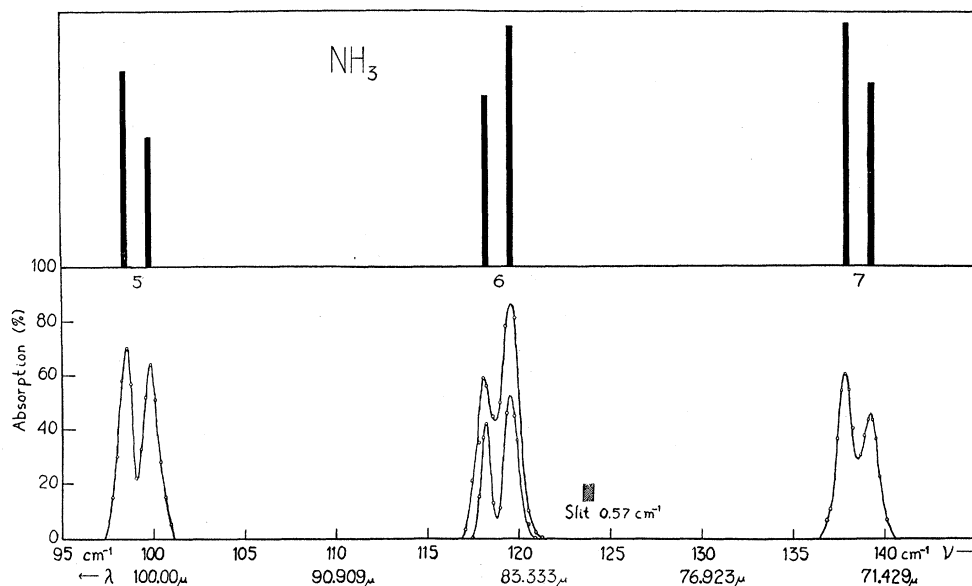


FIG. 4.  $\text{NH}_3$  gas: No. 5—3 mm slits ( $0.60 \text{ cm}^{-1}$ ), 5 mm quartz, refl. from KI, gas pressure 8 cm Hg; No. 6—2 mm slits ( $0.57 \text{ cm}^{-1}$ ), 5 mm quartz, refl. from KBr, pressures 6.5 and 10 cm; No. 7—1.5 mm slits ( $0.58 \text{ cm}^{-1}$ ), 5 mm quartz only, pressure 7.3 cm;  $90\mu$  grating.

TABLE II. Pure rotation lines of  $\text{NH}_3$ .

Final $J$	Wave-length ( $\mu$ )	Frequency ( $\text{cm}^{-1}$ )	$\Delta\nu$	$\bar{\nu}_J^{J-1}$ (Obs.)	$\bar{\nu}_J^{J-1}$ (Calc.)	$\Delta$	$\nu$ (Badger and Cartwright)
5	101.49	98.529	1.30	99.180	99.178	-0.002	99.06
	100.17	99.832					
6	84.591	118.22	1.36	118.90	118.90	0.00	118.60
	83.628	119.58					
7	72.525	137.88	1.33	138.54	138.55	0.01	—
	71.836	139.21					

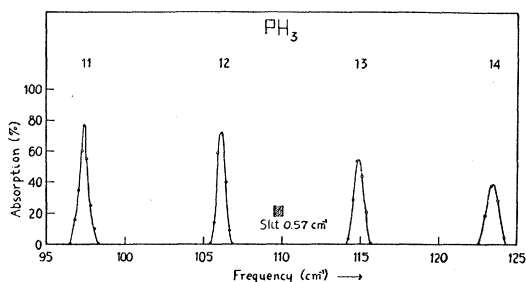


FIG. 5.  $\text{PH}_3$  gas: No. 11—3 mm slits, 5 mm quartz, refl. from KI; No. 12—2 mm slits, 5 mm quartz, refl. from KI; No. 13—2 mm slits, 5 mm quartz, refl. from KBr; No. 14—2 mm slits, 5 mm quartz, refl. from KBr; gas pressure in all cases 30 cm;  $90\mu$  grating.

TABLE III. Pure rotation lines of  $\text{PH}_3$ .

Final $J$	Wave-length ( $\mu$ )	Frequency ( $\text{cm}^{-1}$ )	Frequency (Calc.)	$\Delta$
11	102.72	97.355	97.35	0.00
12	94.255	106.10	106.10	0.00
13	87.073	114.84	114.83	-0.01
14	80.951	123.53	123.53	0.00

due to lack of energy in the  $72\mu$  region.

The pure rotation spectrum of  $\text{PH}_3$ , unlike that of  $\text{NH}_3$ , was found to consist of single lines. The lines of ordinal number 11, 12, 13 and 14 were observed and are plotted on a frequency scale in Fig. 5. A list of the observed wave-lengths and frequencies is given in Table III.

Cartwright<sup>2</sup> are included for comparison in this table; the 7th doublet was not measured by them

## DISCUSSION

The molecule  $\text{H}_2\text{O}$  is of the asymmetrical type, and exhibits a rotation spectrum of great complexity as, indeed, is required for the asymmetrical rotator in the wave-mechanical treatments given by Kramers and Ittmann,<sup>6</sup> Klein,<sup>7</sup> and Dennison.<sup>8</sup> In the last-mentioned treatment a diagrammatical representation of the spectrum in terms of the three unknown moments of inertia has been made. Because, however, of the increasing complexity of the spectrum with higher  $J$  values the transitions depicted in the diagram involve only levels for which  $J < 4$ . In the present investigation the absorption of water vapor has been observed throughout the region from 60 to 125 $\mu$  under varying degrees of resolution. This region, however, is not adequate to permit a correlation with Dennison's diagram. In fact, an examination of the rotational structure of the fundamental vibration bands of  $\text{H}_2\text{O}$  observed by Plyler and Sleator<sup>9</sup> indicates that the pure rotation lines involving the lower levels for which  $J < 4$  lie for the most part at greater wavelengths than those observed in this work.

## Ammonia

The molecule  $\text{NH}_3$  is an example of the symmetrical type, consisting of a triangular pyramid with the nitrogen atom at the apex. As is well known, the frequencies in the pure rotation spectra of symmetrical rigid molecules are given by  $\nu_J^{J-1} = (h/4\pi^2 A)J$ , where  $A$  is the moment of inertia about an axis perpendicular to the axis of symmetry. For actual molecules, however, there is a correction to be applied because of the fact that centrifugal forces set up by the rotation cause a slight deformation. When this effect is taken into account the expression for the frequencies becomes

$$\nu_J^{J-1} = BJ - DJ^3 \quad (1)$$

where  $B$  is but negligibly different from  $h/4\pi^2 A$  and  $D$  is a small constant depending on the two

<sup>6</sup> H. A. Kramers and G. P. Ittmann, *Zeits. f. Physik* **53**, 553 (1929); *Zeits. f. Physik* **58**, 217 (1929) and *Zeits. f. Physik* **60**, 663 (1930).

<sup>7</sup> O. Klein, *Zeits. f. Physik* **58**, 730 (1929).

<sup>8</sup> D. M. Dennison, *Rev. Mod. Phys.* **3**, 317 (1931).

<sup>9</sup> E. K. Plyler and W. W. Sleator, *Phys. Rev.* **37**, 1493 (1931).

moments of inertia of the normal molecule and on various constants involved in the potential energy expression.

In the case of  $\text{NH}_3$  a modification of the spectrum is introduced through the fact that the nitrogen atom can make transitions between equivalent positions of equilibrium on opposite sides of the plane of the hydrogen atoms. The potential energy associated with the distance of the N atom from the plane of the H atoms thus has two minima, one at each position of equilibrium. A discussion of the results of this fact is contained in the papers of Dennison,<sup>8</sup> of Dennison and Hardy<sup>3</sup> and of Dennison and Uhlenbeck.<sup>10</sup>

It is shown that the energy levels are split into pairs with constant separation as illustrated in Fig. 6 which represents levels of the 0th vibra-

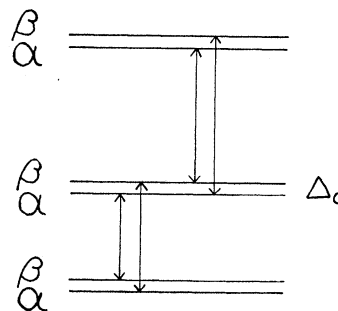


FIG. 6.

tional state. The states designated  $\alpha$  have wave functions of which the part depending on the vibrational coordinates alone is symmetrical for an interchange of any two of the hydrogen nuclei. The states  $\beta$  are antisymmetrical for this interchange. The selection rules for both the parallel vibration bands and the pure rotation spectrum allow transitions only from  $\alpha$  to  $\beta$ -states and *vice versa*. As a consequence the spectral lines also occur in pairs, the doublet difference being the sum of the separations in the initial and final pairs of levels.

The theoretical intensities of the pure rotation doublets of  $\text{NH}_3$  derived by using the weights of the states as given by Dennison<sup>8,3</sup> are plotted

<sup>10</sup> D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).

in Fig. 4 immediately above the corresponding observed lines. Owing to the fact that the various doublets were observed under different gas pressures the intensities of one doublet relative to another have not been determined. It will be noticed, however, that the observed relative intensities of the doublet components possess the alternating character of the theoretical values.

Quantitative expressions for the doublet separations have been derived in the paper of Dennison and Uhlenbeck.<sup>10</sup> The energy level separations,  $\Delta_0$  in the 0th vibrational state and  $\Delta_1$  in the 1st excited state of the vibration  $\nu_3$ , are given by the two simultaneous equations:

$$\Delta_0/h\nu_3 = (2\alpha/\pi^{\frac{1}{2}}) \times \exp[-\alpha^2 - 2(x_0 - \alpha)(\alpha^2 - 1)^{\frac{1}{2}}], \quad (2)$$

$$\Delta_1/h\nu_3 = [(4\alpha^3 - 4\alpha)/\pi^{\frac{1}{2}}] \times \exp[-\alpha^2 - 2(x_0 - \alpha)(\alpha^2 - 3)^{\frac{1}{2}}], \quad (3)$$

in which  $x_0 = [h/4\pi^2\mu\nu_3]^{-\frac{1}{2}}q_0$ ,  $q_0$  is the normal distance of the N atom from the plane of the H atoms, and  $\alpha$  is a parameter of the potential energy curve. From the measurements of the present work the doublet separation  $2\Delta_0$  of the pure rotation doublets is  $1.33 \text{ cm}^{-1}$ , hence  $\Delta_0 = 0.67 \text{ cm}^{-1}$ . The fundamental vibration band  $\nu_3$  observed by Barker<sup>11</sup> yields the values  $\nu_3 = 948 \text{ cm}^{-1}$  and the doublet separation  $\Delta_0 + \Delta_1 = 31.6 \text{ cm}^{-1}$ . Hence  $\Delta_1 = 30.9 \text{ cm}^{-1}$ . Substituting these values in the above equations and solving for  $q_0$ , we obtain

$$q_0 = 0.388 \times 10^{-8} \text{ cm.}$$

(This value is a few percent different from that obtained by Dennison and Uhlenbeck using older data on the  $\nu_3$  band and assuming  $\Delta_0 = 0.8 \text{ cm}^{-1}$ .)

Since the pure rotation lines of  $\text{NH}_3$  occur in pairs, the expression (1) for the frequencies now refers to the mid-frequency of each pair. Fitting this expression to the observed values (Table II) results in the formula

$$\bar{\nu}_J^{J-1} = 19.880J - 0.00178J^3,$$

where  $\bar{\nu}_J^{J-1}$  is the mid-frequency ( $\text{cm}^{-1}$ ) of the  $J$ th doublet. Table II shows the very close agreement of the observed frequencies and those calculated from the above equation. The relation

$h/4\pi^2cA = 19.880$  determines the moment of inertia

$$A = 2.782 \times 10^{-40} \text{ g cm}^2.$$

This is in good agreement with the values obtained in the following investigations:

	Barker <sup>11</sup>	
Band $\nu_3$		$2.80 \times 10^{-40}$
	Dennison and Hardy <sup>3</sup>	
Band $\nu_1$		2.82
	Badger and Cartwright <sup>2</sup>	
Pure rot. spectrum		2.77
	Dickinson, Dillon, and Rasetti <sup>12</sup>	
Raman spectrum		2.79

The values of  $A$  and  $q_0$  yield the following determinations:

$$C(\text{moment of inertia about the axis of symmetry}) = 4.33 \times 10^{-40} \text{ g cm}^2$$

$$N-H (\text{normal distance between N and H nuclei}) = 1.01 \times 10^{-8} \text{ cm}$$

$$H-H (\text{normal distance between H nuclei}) = 1.61 \times 10^{-8} \text{ cm.}$$

It is interesting to note that the combination principle affords a test of the accuracy of the frequency measurements. From a consideration of the energy levels of the 0th vibrational state of the molecule and of the 1st excited states of the parallel vibrations  $\nu_1$  and  $\nu_3$ , it is readily seen that certain relationships exist among the pure rotation frequencies and the rotation-vibration frequencies in the bands  $\nu_1$  and  $\nu_3$ . If the rotational levels of the 0th vibrational state are termed  $R_{\alpha}^{J, K}$  and those of the 1st excited states of  $\nu_1$  and  $\nu_3$  are termed  $V_{1\alpha}^{J, K}$  and  $V_{3\alpha}^{J, K}$ , respectively, the relationships with which the present work is concerned may be expressed:

$$\begin{aligned} &(R_{\beta}^{5, K} - R_{\alpha}^{4, K}) + (R_{\alpha}^{6, K} - R_{\beta}^{5, K}) \\ &= (V_{1\beta}^{5, K} - R_{\alpha}^{4, K}) - (V_{1\beta}^{5, K} - R_{\alpha}^{6, K}) \\ &= (V_{3\beta}^{5, K} - R_{\alpha}^{4, K}) - (V_{3\beta}^{5, K} - R_{\alpha}^{6, K}), \quad (4) \end{aligned}$$

$$\begin{aligned} &(R_{\alpha}^{5, K} - R_{\beta}^{4, K}) + (R_{\beta}^{6, K} - R_{\alpha}^{5, K}) \\ &= (V_{1\alpha}^{5, K} - R_{\beta}^{4, K}) - (V_{1\alpha}^{5, K} - R_{\beta}^{6, K}) \\ &= (V_{3\alpha}^{5, K} - R_{\beta}^{4, K}) - (V_{3\alpha}^{5, K} - R_{\beta}^{6, K}). \quad (5) \end{aligned}$$

<sup>11</sup> E. F. Barker, Phys. Rev. **33**, 684 (1929). (The data quoted here are from unpublished measurements of  $\nu_3$  made recently by Dr. Barker.)

<sup>12</sup> R. B. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34**, 582 (1929).

The frequencies indicated on the left sides of the equations are those of the pure rotation doublets, Nos. 5 and 6, measured in this work. The other frequencies are of band  $\nu_3$ , measured by Barker<sup>11</sup> and of band  $\nu_1$ , measured by Dennison and Hardy.<sup>3</sup> Table IV shows the close agreement of the experimental values.

TABLE IV.

Pure rotation	Band $\nu_1$	Band $\nu_3$
Eq. (4) 99.83+118.22 =218.05	3436.0-3217.5 = 218.5	1065.83-847.68 =218.15
Eq. (5) 98.53+119.58 =218.11	3434.3-3216.1 = 218.2	1034.16-816.25 =217.91

### Phosphine

As has been mentioned the pure rotation lines of PH<sub>3</sub>, unlike those of NH<sub>3</sub>, do not exhibit a doubling but are as sharp, for example, as the

component lines of the NH<sub>3</sub> doublets. The four observed PH<sub>3</sub> lines (Table III) yield the frequency formula:

$$\nu_J^{J-1} = 8.892J - 0.000348J^3.$$

Here again there is accurate agreement of the observed frequencies and those calculated from the formula. From the relation  $h/4\pi^2cA = 8.892$  we find for the moment of inertia  $A$  of PH<sub>3</sub>

$$A = 6.221 \times 10^{-40} \text{ g cm}^2.$$

The fact that no trace of a doubling of the PH<sub>3</sub> lines is observed may be accounted for qualitatively by assuming that  $q_0$  is larger for this molecule than for NH<sub>3</sub>, an assumption supported by the larger moment of inertia  $A$  of PH<sub>3</sub>. Eq. (2) shows that the level separation  $\Delta_0$  is extremely sensitive to  $x_0$  (hence to  $q_0$ ) and that a small increase in the latter could easily lead to a doublet separation far too small for spectroscopic resolution.