TABLE I. *F values.*

Reflection	θ	Area	Relative F Mo $K\alpha$	Relative F Cu $K\alpha$
0002	8° 17′	1.156	0.891	0.897
$10\bar{1}0$	8° 54′	1.000	1.000	1.000
$10\bar{1}1$	9° 49′	4.72	.898	.866

The ($10\bar{1}1$) reflection of the β-line falls very nearly on the ($10\bar{1}0$) reflection of the α-line. The areas in the figure are uncorrected. Measurement of the spectrum of the rays penetrating the zirconium filter give $\beta/\alpha = 0.5/100$. The F values are for pure $K\alpha$ rays.

factor (2 for (0002), 1 for ($10\bar{1}0$), $\sqrt{3}$ for ($10\bar{1}1$)), θ is the Bragg angle of reflection, and F is the atomic structure factor including the effect of thermal vibrations. From the ratio of the areas the ratio of the F's may be obtained. Our final results are shown in Table I. The ratios $F(0002)/F(10\bar{1}0)$ and $F(10\bar{1}1)/F(10\bar{1}0)$ as found by us are shown in the fourth column while Brindley's ratios are shown in the fifth column of the table.

Because of dispersion,[1] the f values (i.e., F values corrected for thermal vibration) should be greater by 2.14 when Mo $K\alpha$ rays are used than when Cu $K\alpha$ rays are used. Hence our value of $F(0002)/F(10\bar{1}0)$ should be slightly less than Brindley's value. Our estimate of Brindley's value for Mo $K\alpha$ rays is 0.894, which is in very good agreement with our value of 0.891. Our estimate of Brindley's value of $F(10\bar{1}1)/F(10\bar{1}0)$ for Mo $K\alpha$ rays is 0.863. We feel that this is really lower than our value of 0.898.

Since Brindley made repeated experiments on $F(10\bar{1}0)$, we take his value of 22.4 for Cu $K\alpha$ rays to be correct. From our ratio, given above, is obtained $F(10\bar{1}1) = 20.1$. If this value is used in Fig. 1 of Jauncey and Bruce's paper,[3] and $f(10\bar{1}1)$ found by using their values of a and b, the f point falls between the curve for $\psi = 0°$ which passes through the f point for (0002) and the curve for $\psi = 90°$ which passes through the f point for ($10\bar{1}0$). This fact gives some support to the idea of asymmetry in the electron structure of the atoms.[3]

The authors wish to thank Professor G. E. M. Jauncey for suggesting this problem and Mr. W. A. Bruce for aid in making the powdered crystals and in the experimental details.

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Fundamental Absorption Bands of the Deuteroammonias

M. V. MIGEOTTE* AND E. F. BARKER, *University of Michigan*

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The four fundamental vibration bands of ND_3 have been obesrved in infrared absorption, ν_3 being a double band as in NH_3. The frequencies of the parallel vibrations, expressed in cm^{-1}, are $\nu_1 = 2420$, $\nu_3 = 749.2$ and 745.8, and of the perpendicular vibrations, $\nu_2 = 2556$ and $\nu_4 = 1191.3$. The rotational structure for ν_3 is completely resolved. The perpendicular bands consist of many components with zero branches spaced at intervals of 1.7 cm^{-1} in ν_2 and 5.2 cm^{-1} in ν_4. The former cannot be resolved: they coalesce into a broad central absorption region, but the spacing of the most intense rotation lines in the composite band indicates the interval between centers. These frequency intervals agree well with the predictions of Johnston and Dennison. The moments of inertia for ND_3 are determined from the structure of the band ν_3, by comparison with observations upon NH_3. They are $C = 8.985 \times 10^{-40}$ g cm^2 with respect to the symmetry axis, and $A = 5.397 \times 10^{-40}$ g cm^2 for any perpendicular axis. From these the molecular dimensions are obtained. The height of the pyramid is 0.360×10^{-8} cm and the distance between hydrogen atoms is 1.645×10^{-8} cm. New information regarding the potential curve is obtained (1) from observations upon the doubling of the first excited levels in the four varieties of ammonia, and (2) from the positions of higher excited levels in ND_3. Four vibration levels are located which lie above the central potential hump, and correspond to oscillations of the nitrogen atom from side to side through the plane formed by the hydrogen atoms.

THE ammonia molecule is known to have the form of a low equilateral triangular pyramid. Its spectrum is rich, including many harmonic and combination bands in addition to the four fundamental frequencies, but the analysis and interpretation of the available observations is by no means complete. The moment of inertia A with respect to an axis normal to the symmetry line may be obtained immediately

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* C. R. B. Fellow 1934–5, now at the University of Liége.

from the line spacing in the parallel bands, and also from the pure rotation frequencies. The spectrum, however, does not yield a direct determination of the moment C with respect to the symmetry axis itself, from which the molecular dimensions could be computed. In the perpendicular bands[1] the dependence of line spacing upon A and C is complicated by an interaction arising from the twofold degeneracy of the vibration. This effect has been completely formulated[2] but is difficult to evaluate precisely. The height of the pyramid may be estimated indirectly[3] in terms of the observed doubling in parallel bands, which serves to define the potential curve representing the bond between N and the H_3 group. The following observations upon the spectrum of ND_3 determine the moment of inertia A for that molecule, from which the molecular dimensions may be computed on the assumption that they are the same for ND_3 as for NH_3.

The gas used at the beginning of this investigation was a mixture of the deuteroammonias, with ND_3 in rather low concentration.[4] Through the courtesy of Professor Taylor we were later privileged to examine a very pure sample of ND_3 prepared at Princeton University by Dr. J. C. Jungers. In transferring this gas to absorption cells with windows of rocksalt, which could not be baked out, some contamination with H was unavoidable: this did not lead to any serious ambiguity in the results, however. The bands were examined under fairly high resolution with the usual prism-grating spectrometer.

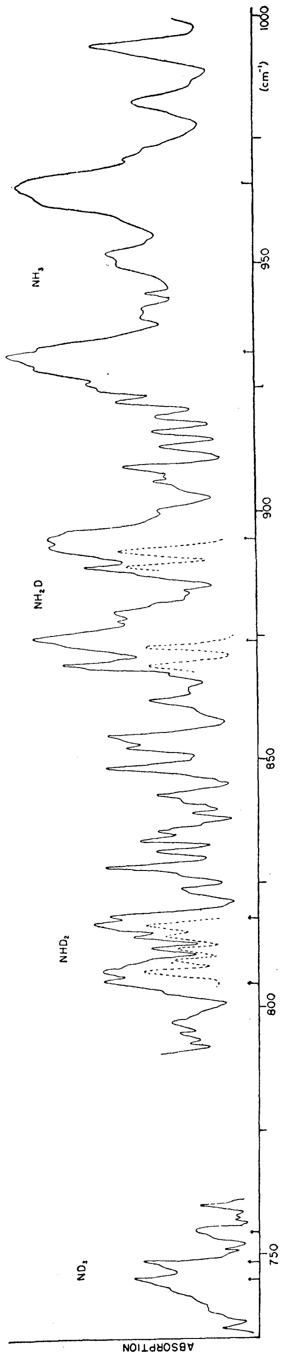

FIG. 1. The double bands ν_3 in a mixed sample. - - - - - NH_3 only.

In the mixed sample the double frequency parallel bands ν_3 for the various ammonias were observed, and these are shown in Fig. 1. The four pairs of zero branches stand out distinctly, but the rest of the structure is extremely complicated due to superposition. Since a considerable amount of NH_3 was present it seemed advisable to remap a part of the pure NH_3 spectrum for comparison. This is represented by the broken lines. The arrows upon the horizontal axis indicate band centers. The lower pair of levels may be designated 0_s, 0_a and the upper pair 1_s, 1_a. The permitted transitions are $0_s \rightarrow 1_a$ and $0_a \rightarrow 1_s$, the former giving the higher frequency. Table I shows the observed positions of the band centers. The computed doublet separations are first approximations obtained by the method

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[1] An analysis of the perpendicular band ν_4 for NH_3 at 6μ has been completed and is soon to be published.

[2] Johnston and Dennison, Phys. Rev. **48**, 868 (1935).

[3] Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932).

[4] This sample was prepared by Mr. W. A. Webb of Berkeley, Cal., and was purchased through a grant from the Faculty Research Fund.

TABLE I. *Positions of band centers in cm^{-1}.*

	$0_s \rightarrow 1_a$	$0_a \rightarrow 1_s$	$\Delta\nu$ obs.	$\Delta\nu$ comp.
NH_3	966	933	33	(33)
NH_2D	894	874	20	10.7
NHD_2	818	808	10	4.5
ND_3	749.2	745.8	3.4	2.2

of Dennison and Uhlenbeck, assuming identical potential curves in each case. It is not surprising that they agree with the observed intervals only moderately well, for the potential energy is actually a function of two variables, depending not only upon the displacement of the nitrogen atom from its equilibrium position, but also upon the distance between the hydrogen atoms. The relative importance of these two coordinates is not the same for vibrating molecules with different mass distributions. Our results indicate, as might be expected, that a section of the two-dimensional potential surface appropriate to one of the heavier molecules has a slightly lower central maximum than does that of NH_3. In the unsymmetrical molecules there is, of course, the added complication that the motion of the nitrogen atom is not precisely along the axis of the pyramid.

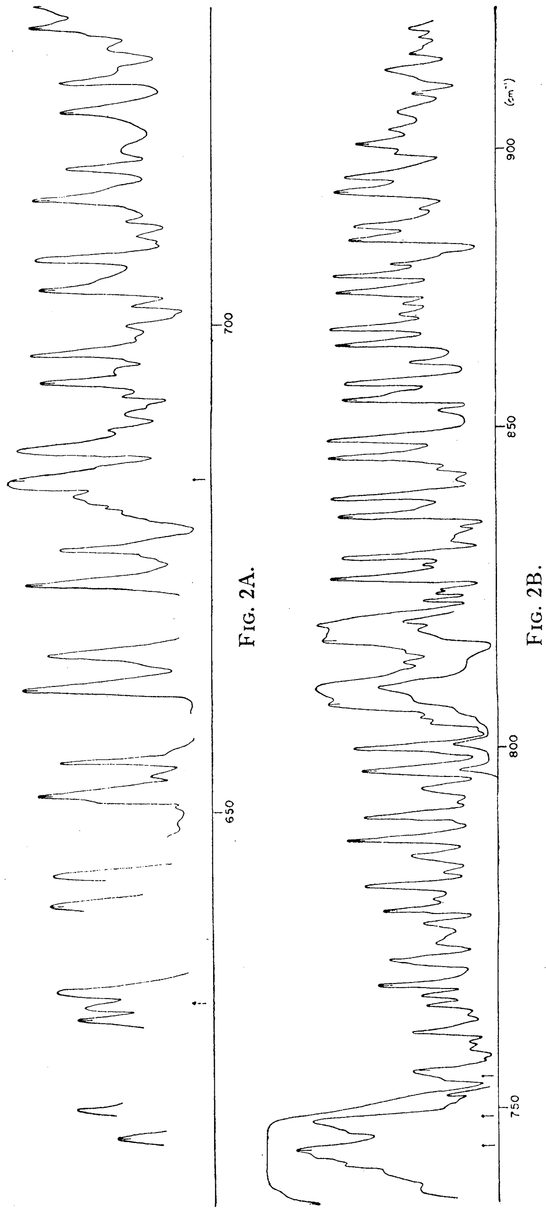

FIG. 2A.

FIG. 2B.

FIG. 2. ν_3 in ammonia with high ND_3 concentration.

The rotational structure of the pair of bands representing ν_3 for ND_3 is shown in Fig. 2, the lines belonging to the component with lower frequency ($0_a \rightarrow 1_s$) being indicated by marks. For these observations ND_3 was used at a pressure of 11 cm in a cell 10 cm long. The windows were KBr plates 6 mm thick. A slight contamination with ordinary hydrogen is indicated by the presence of broad absorption maxima due to NHD_2 at about 808 cm^{-1} and 818 cm^{-1}. Another rather broad line at 683.4 cm^{-1} includes the sixth negative member of the low frequency component band and also a weak zero branch corresponding to absorption by excited ND_3 molecules executing the transition $1_s \rightarrow 2_a$. Similarly, the band center for $2_s \rightarrow 3_a$ appears at 754.5, almost at the +1 position for the low frequency fundamental band. This +1 line is absent, however, while the corresponding member of the $0_s \rightarrow 1_a$ band is clearly present at 759.6, the change is statistics when deuterons replace protons reversing the situation observed in NH_3.[5] The change in spin from $\frac{1}{2}$ for protons to 1 for deuterons also results in a smaller variation in the intensities of the successive lines across the band. At about 632 cm^{-1} there is a weak absorption maximum marked with a broken arrow which is perhaps the $1_a \rightarrow 2_s$ frequency for NHD_2. On the low frequency side these bands extend into the region of intense absorption due to atmospheric CO_2, where satisfactory observations may be made only at intervals between the CO_2 lines.

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[5] Dennison and Hardy, Phys. Rev. **39**, 938 (1932).

TABLE II. *Structure of the bands* ν_3 *for* ND_3.

High frequency component, $\nu_0=749.2$							Low frequency component, $\nu_0=745.8$						
ν obs.	ν comp.	Difference	m	ν obs.	ν comp.	Difference	ν obs.	ν comp.	Difference	m	ν obs.	ν comp.	Difference
759.57	759.42	−0.15	1	739.00	738.92	−0.08	755.96	756.02	+0.06	1	735.32	735.52	+0.20
769.63	769.58	−0.05	2	728.60	728.59	−0.01	766.25	766.20	−0.05	2	724.97	725.20	+0.23
779.63	779.67	+0.04	3	718.16	718.20	+0.04	776.32	776.32	0.00	3	714.66	714.84	+0.18
789.71	789.70	−0.01	4	707.77	707.77	0.00	786.32	786.38	+0.06	4	704.37	704.44	+0.07
799.70	799.66	−0.04	5	697.12	697.28	+0.16	796.40	796.38	−0.02	5	693.97	694.01	+0.04
809.02	809.54	+0.52	6	686.81	686.76	−0.05	806.40	806.32	−0.08	6	683.36	683.55	+0.19
818.95	819.35	+0.40	7	676.28	676.20	−0.08	816.26	816.19	−0.07	7	672.73	673.05	+0.32
829.16	829.09	−0.07	8	665.55	665.60	+0.05	826.00	825.99	−0.01	8	662.18	662.53	+0.35
838.80	838.73	−0.07	9	654.85	654.96	+0.11	835.56	835.72	+0.16	9	651.75	651.99	+0.24
848.28	848.30	+0.02	10	644.21	644.30	+0.09	845.37	845.37	0.00	10	641.45	641.43	−0.02
857.80	857.77	−0.03	11	633.61	633.60	−0.01	855.01	854.94	−0.07	11	630.91	630.85	−0.06
867.26	867.16	−0.10	12	623.13	622.89	−0.24	864.43	864.43	0.00	12	620.55	620.26	−0.29
876.50	876.45	−0.05	13				873.63	873.83	+0.20	13			
885.56	885.64	+0.08	14				883.06	883.14	+0.08	14			
894.77	894.73	−0.04	15				892.22	892.36	+0.14	15			
903.46	903.72	+0.26	16				901.10	901.48	+0.38	16			
							910.16	910.51	+0.35	17			

The positions of the rotation lines in the two bands are very well represented by the two equations

$$\nu = 749.2 \pm 10.25m - 0.029m^2 \mp 0.00050m^3,$$
$$\nu = 745.8 \pm 10.25m - 0.024m^2 \mp 0.00053m^3,$$

where m is the ordinal number of any line counted from the band center. Table II shows the positions of observed lines, and the frequencies indicated by these formulae, expressed in cm^{-1}. The differences are generally small, though in a few cases they clearly exceed the errors in observation. This is the result of blends, either with lines of the upper stage bands or with absorption due to other molecules, such as NHD_2, NH_2D and CO_2.

The curves in Fig. 3 are traced from records of an automatic prism spectrograph, showing (a) the absorption in the region of 16μ due to ND_3 in a 10 cm cell at 40 cm pressure, and (b) the same region with the cell empty. A parallel type band corresponding to the transition $1_a \rightarrow 2_s$ shows very clearly, with its center at 610±2 cm^{-1}. It is not completely separated from the negative branches of the intense fundamental bands whose unresolved zero branches (746 and 749) appear at the left.

In Fig. 4 a small section of the 10μ region is represented, the lower curve indicating absorption due to NH_3, while the upper one shows the changes resulting from the addition of ND_3. A very strong peak at 1081.5 cm^{-1} indicates the $1_a \rightarrow 3_s$ transition, while the weaker absorption at 1066 cm^{-1} is interpreted as the band center for $2_a \rightarrow 4_s$. A much weaker line at 1038.5 may represent the next step from 3_s to 4_a. These observations serve to define the potential curve much more precisely than do any previously available.

Manning[6] has recently discussed the problem of the double minimum in ammonia, utilizing a modified Morse function which may be solved exactly. He has computed the approximate positions for the first eight levels of ν_3 in ND_3, and compared them with numerical values obtained by Benedict from ultraviolet absorption measurements. Our values are in very good agreement with these predictions, and with Benedict's observations. Fig. 5 shows the curve employed by Manning with the observed levels indicated. The separation of the lowest pair, which is predicted to be about 0.2 cm^{-1}, has not yet been determined experimentally. Levels above the central maximum tend to assume an equal spacing, and correspond to vibrations in which the nitrogen atom passes completely through from one side to the other of the plane formed by the hydrogen atoms. Higher levels would, of course, converge as they approach the dissociation level, which lies somewhat above 40,000 cm^{-1}.

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[6] Manning, J. Chem. Phys. 3, 136 (1935).

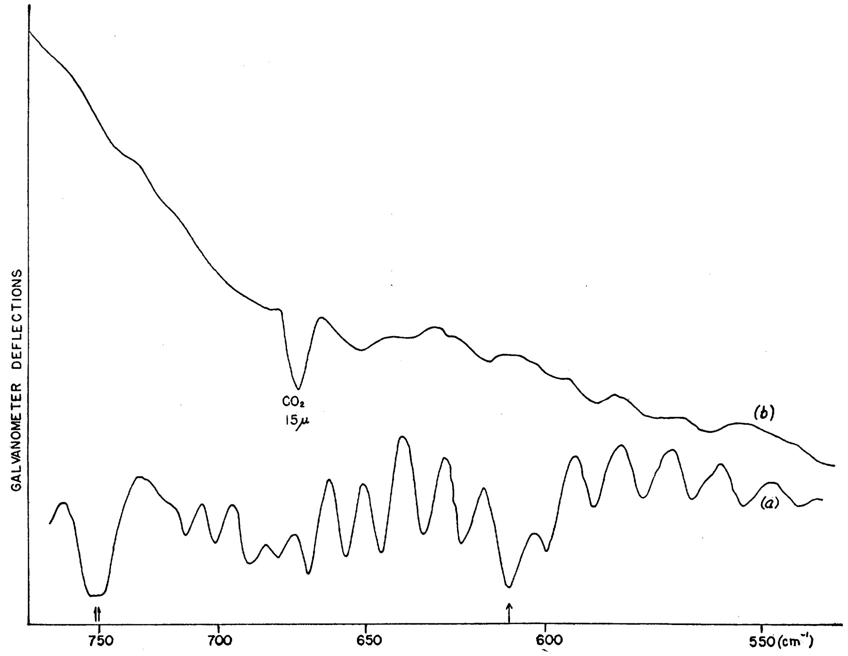

FIG. 3. a. ND_3 band near 16μ, from a recording spectrograph with KBr prism.
b. Empty cell record.

The other parallel vibration, ν_1, corresponds to a symmetrical motion of the three hydrogen atoms approximately in their own plane. For ND_3 it lies at 2420 cm^{-1}, and the zero branch is shown in Fig. 6a. The rotation structure cannot be satisfactorily resolved. It is obscured on the low frequency side by the intense absorption due to atmospheric CO_2, and on the high frequency side by the perpendicular band ν_2 of ND_3. This latter band also is only partially resolved. It consists of a sequence of zero branches spaced approximately 5.2 cm^{-1} apart, the most intense one lying 2.6 cm^{-1} to the high frequency side of the band center at 2556 cm^{-1}. There is some indication of further absorption, perhaps due to NHD_2, at 2570 cm^{-1} and at 2620 cm^{-1}.

The fourth fundamental band, also of the perpendicular variety, has been located at 1191.3 cm^{-1}. This too is an aggregate of many component bands, but their relative displace-

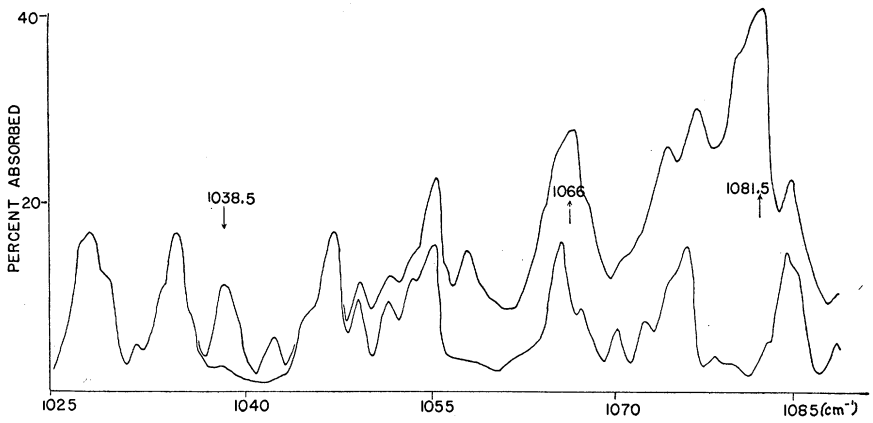

FIG. 4. Absorption of NH_3 (lower curve) and of ND_3+NH_3 (upper curve) near 10μ.

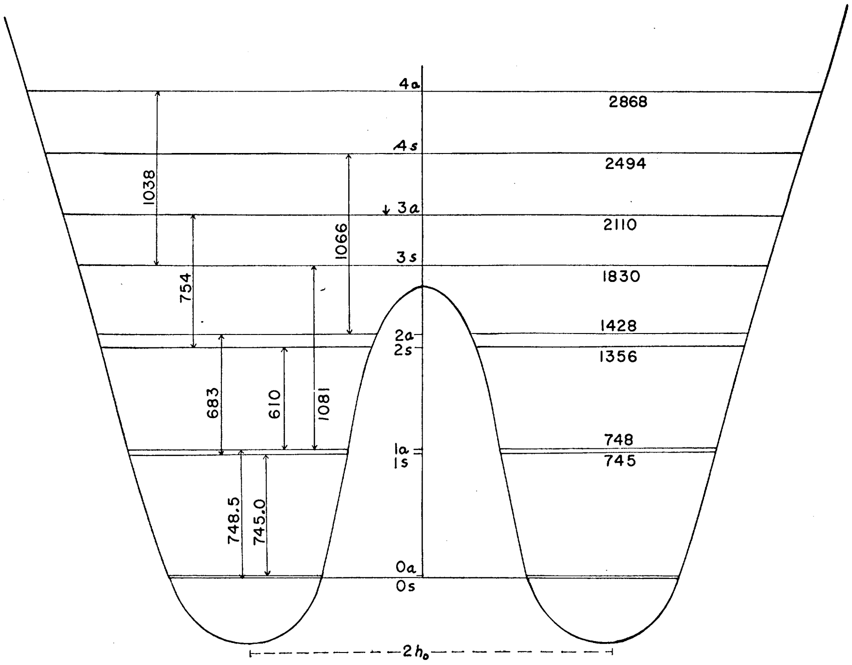

FIG. 5. Potential curve and observed transitions for the low frequency symmetrical vibration in ND_3.

ments are so small that the zero branches are not separated. The observed pattern is indicated in Fig. 6b. On the low frequency side the rotational structure is fairly well resolved, the interval between lines being 8.5 cm^{-1} but on the high frequency side it is not so clear because one of the bands of NHD_2 is superposed upon it. The spacing of successive zero branches is estimated at 1.7 cm^{-1}. Table III shows the measured positions of the lines, and, in the third column, the mean positions by pairs, indicating the convergence.

TABLE III. *Rotational structure of the band $\nu_4 = 1191.3$ cm^{-1}.*

m	Negative	Positive	Mean	Interval
1	—	1200.0		
2	1174.0	1209.0	1191.5	8.8
3	1165.4	1217.0	1191.2	8.6
4	1156.8	1225.0	1190.9	8.5
5	1148.5	1234.1	1191.3	8.6
6	1140.3	1241.8	1191.0	8.5
7	1132.0	1249.5	1190.8	8.4
8	1123.8	1258.1	1191.0	8.4
9	1115.4	1265.8	1190.6	8.4
10	1106.2	1273.5	1189.8	8.4
11	1097.9	1281.3	1189.6	8.3
12	1089.6	—		
13	1081.2	1297.3	1189.2	8.3
14	1073.4			
15	1065.5			
16	1058.2			

The structure and line spacing in these two perpendicular bands is actually in accord with the predictions of band theory. Degenerate vibrations of this type have been discussed in detail by Johnston and Dennison,[2] who show that the resulting internal axial angular momentum $\zeta h/2\pi$ consists of two terms having opposite signs, one due to the mutual rotation of the N atom and the D_3 group, and the other due to the oscillations of the three D atoms, with respect to their own center of mass. Each fundamental or combination band of the perpendicular type has a characteristic ζ, either positive or negative, the value of which may be computed approximately. The line spacing is $[(1-\zeta)/C-1/A]h/4\pi^2$. Dennison's computed values for $\Delta\nu_2$ and $\Delta\nu_4$ in cm^{-1} are 4.8 and 2.7, as compared with our observed spacings 5.2 and 1.7.

The equations representing the bands ν_3 indicated a line interval of 10.25 cm^{-1}. This yields immediately the moment of inertia $A = 5.397 \times 10^{-40}$ g cm^2 for ND_3. The corre-

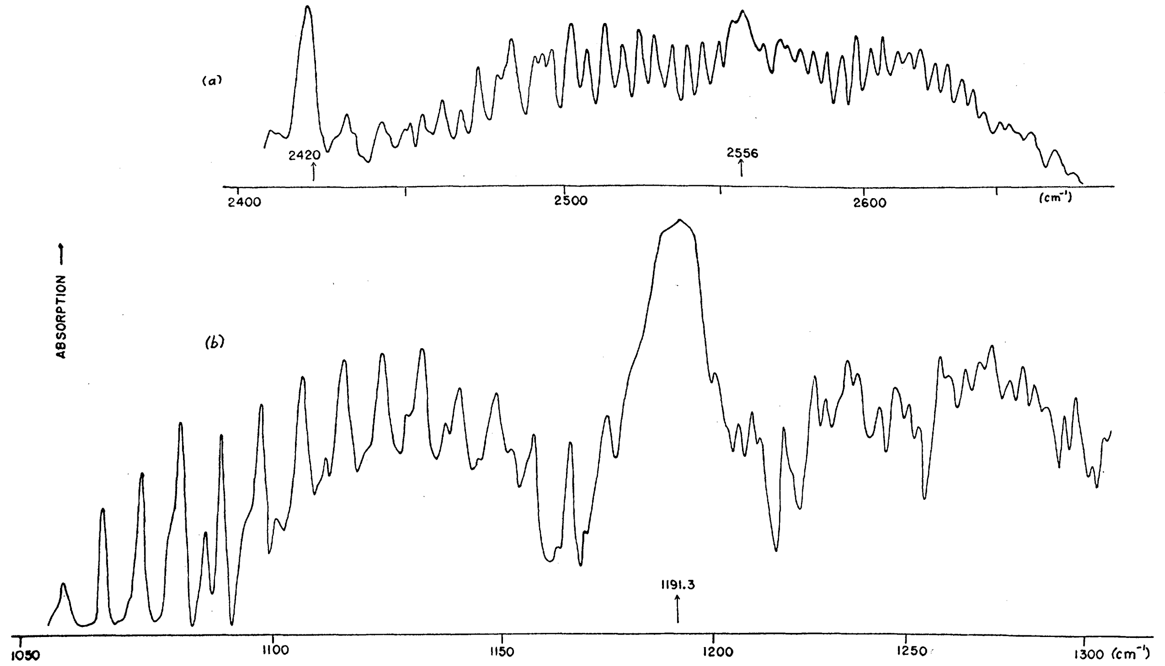

FIG. 6. Fundamental vibration bands of ND_3. a. ν_1 and ν_2 near 4μ. b. ν_4 near 8μ.

sponding value for NH_3 is 2.782×10^{-40}, as indicated by the data of Wright and Randall.[7] From a comparison of these two numbers the molecular dimensions may be computed immediately. Our values agree well with those obtained with somewhat less precision from the pure rotation spectrum of ND_3, by Barnes.[8] They are:

$H-H$ distance	1.645×10^{-8} cm
$N-H$ distance	1.016×10^{-8}
height of pyramid	0.360×10^{-8}

moment of inertia,

$$C=4.497\times10^{-40}\text{ g cm}^2\text{ for NH}_3$$

and $$C=8.985\times10^{-40}\text{ g cm}^2\text{ for ND}_3.$$

The mechanical problem of the vibrations of symmetrical tetratomic molecules has been treated by Rosenthal,[9] though without taking into account the effect of the double minimum. The normal frequencies are represented by her equations (4) consisting of two quadratic expressions containing six arbitrary constants. The four observed frequencies for ND_3, together with any two of those for NH_3, provide information for selecting a consistent set of values for the six constants. Since the effects of anharmonicity and of the double minimum can only be estimated, these coefficients are not precisely determined. The approximate values are useful, however, in the interpretation of the atomic binding, and in the classification of the bands due to NH_2D and NHD_2. We have chosen the following group:

$$A=10.2\times10^{-5},\quad B=5.46\times10^{-5},$$
$$C=1.68\times10^{-5},\quad D=1.18\times10^{-5},$$
$$E=2.12\times10^{-5},\quad F=2.44\times10^{-5}.$$

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[7] Wright and Randall, Phys. Rev. **44**, 391 (1933).

[8] Barnes, Phys. Rev. **47**, 658 (1935).

[9] Rosenthal, Phys. Rev. **47**, 235 (1935).