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The Pure Rotation Spectra of NH_3 and ND_3

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The pure rotation spectra of NH_3 and ND_3 have been measured in the spectral region from 40μ to 170μ. Ten rotation lines of NH_3 corresponding to final J values from 3 to 12 have been observed. These fall upon a curve given by $\nu = 19.880J - 0.00176J^3$. Thirteen lines of ND_3 corresponding to final J's from 8 to 20 have been observed. These fall upon a curve given by $\nu = 10.26J - 0.00045J^3$.

THE pure rotation spectrum of NH_3 was first studied by Badger and Cartwright,[1] who located five lines which fitted the formula $\nu = 19.957J - 0.00508J^3$ with an average deviation of ± 0.173 cm^{-1}. Using a spectrometer which had a very much larger resolution, Wright and Randall[2] measured the three lines corresponding to $J = 5$, 6 and 7, respectively, and made possible an accurate determination of the doublet width. This they found to be 1.33 ± 0.03 cm^{-1}. The centers of the three lines fell upon a curve given by the formula $\nu = 19.880J - 0.00176J^3$ with an average deviation of ± 0.02 cm^{-1}. The accuracy of these results is further guaranteed by their extremely close agreement with combination differences from the accurately measured near infrared bands.

It was the purpose of the present investigation to try to extend the measurements on NH_3 both to longer and shorter wavelengths, and to make similar measurements for the ND_3 molecule. This has been done and the preliminary results reported in a short note.[3] In this present paper the experimental procedure and the final results are given.

Since it was desirable to be able to study as great a portion of the far infrared as possible a wire grating spectrometer was selected rather than one employing an echelette grating. The instrument used was recently described by the author[4] and proved to be quite satisfactory from 30μ to 180μ. Its main features were a Welsbach mantle source, f-2 mirrors of 6-inch diameter, a wire grating having 25 lines to the cm so spaced as to eliminate the even ordered spectra, and a radiometer as a receiving device. In order to obtain pure radiation in the various regions of the spectrum a set of filters, such as those described in the paper just mentioned, was used. As usual the entire spectrometer was enclosed in a metal case, the inside of which could be dried with P_2O_5 in order to remove the water vapor from the air. In spite of this precaution, the energy spectrum contained very clear indications of the rotation spectrum of water vapor. The samples of the gases studied were contained in glass cells of 4 cm diameter which had windows either of 1 mm sheets of paraffin (melting point 68–72°C) or 0.5 mm crystal quartz. These cells were filled by allowing the gases to flow through them until a sufficient quantity of the air had been displaced by the gas to give the desired absorption. They were always used at atmospheric pressure, and ranged in length from 4 cm in the case of NH_3 to 1 cm for ND_3. Transmission measurements were made at each wavelength with the cell and a dummy cell alternately in the path of the radiation, using a 0.5 mm plate of NaCl as a shutter. The deflections finally obtained were of the order of several mm and so a great many readings were necessary for each point, at least 8 being taken at each setting. The individual values of the percent transmission at any given wavelength are believed to be accurate to about ±2 percent. The many other experimental difficulties which are encountered in this region of the spectrum have been discussed elsewhere, and so need not be mentioned here.

The degree of resolution, and therefore the accuracy of the wavelength determinations, is limited in most cases by the finite width of the

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[1] R. M. Badger and C. H. Cartwright, Phys. Rev. **33**, 692 (1929).

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

[3] R. Bowling Barnes, W. S. Benedict and C. M. Lewis, Phys. Rev. **45**, 347 (1934).

[4] R. Bowling Barnes, R. S. I. **5**, 237 (1934).

slits which must be used in order to obtain readable deflections. In these measurements, the slits actually used were as follows: from 30μ to 85μ, 0.75 mm; from 85μ to 122μ, 1.5 mm; from 122μ to 180μ, 2.0 mm. These represent "slit-widths" at 50, 100 and 150μ of 4.42, 1.67 and 1.14 cm^{-1}, respectively. In order to obtain as much resolution as possible readings were taken at intervals of $\frac{1}{5}$ of the slit-width. From the absorption lines of water vapor which were obtained in the background spectrum one sees that minima were located which are separated by about 1.0 cm^{-1}.

The spectrometer was not equipped with a divided circle. It would, however, have been possible to calculate the wavelengths from the geometrical arrangement of the instrument, but as there appeared to be very slight mechanical defects, manifested by small shifts in the measured position of the central image, a semi-empirical method of determining the calibration curve seemed preferable. This curve must have the form $\mu = a \sin (b \cdot \Delta l)$ where Δl is the difference between the scale reading at the central image and at the wavelength μ, and a and b are constants. In the measured energy and absorption curves, several lines appear at long wavelengths which can be accounted for only as lines of stated wavelengths appearing in the third order. For these lines $3 \sin (b \cdot \Delta l_{\mathrm{I}}) = \sin (b \cdot \Delta l_{\mathrm{III}})$, thus determining b. The three lines accurately measured by Wright and Randall; the neighboring NH_3 lines on either side, which should lie closely on their formula; and four strong lines of H_2O, whose calculated position is well known were now chosen as calibration points, and the best value of the constant a found by fitting the curve to these points.

In Fig. 1 the rotation lines of NH_3 are shown, the ordinates giving the actual percent transmissions, no allowance having been made for the slight differences of absorption or selective reflection of the windows of the cell and dummy. These curves have been left as transmission curves purposely, in order to show clearly just exactly what has been measured. Particular attention is directed to the regions between the absorption lines, since they give a very good indication as to the spectral purity of the radiation used. Table I, which gives a summary of the results available on the far infrared of the NH_3 molecule, is self-explanatory. The calculated values of ν were obtained by using the formula of Wright and Randall given above. The observed values agree with the calculated ν's to ± 0.11 cm^{-1}. As may be seen from the curves lines 3 to 6 show definite signs of being double. Line 3 falls in a region where part of the energy comes from overlapping third orders, and so the exact determination of its wavelength is difficult. The line at 152.35μ is the third order of line number 10 which occurs at 50.76μ.

TABLE I. *The far infrared of NH_3.*

Final J	Obs. μ	Obs. ν	Calc. ν	Obs.[2] ν	Obs.[1] ν
12	42.47	235.40	235.48		
11	46.15	216.61	216.31		
10	50.76	196.93	197.02		
9	56.26	177.69	177.622		176.10
8	63.14	158.33	158.129		156.8
7	72.18	138.50	138.549	138.54	
6	84.07	118.92	118.896	118.90	118.60
5	100.78	99.20	99.178	99.180	99.06
4	126.04	79.32	79.406		79.79
10/3	152.35	65.62	65.67		
3	168.42	59.36	59.592		

Samples of heavy ammonia, ND_3, were furnished us by Professor H. S. Taylor. These were prepared by reacting 99+ percent pure heavy water with magnesium nitride.[5] The resulting ammonia contained 97 percent D, as shown by ultraviolet absorption measurements. Fig. 2 shows again the actual transmission measurements. The simplicity of the spectrum found indicates that the absorbing gas in our cell was mostly

TABLE II. *The far infrared of ND_3.*

Final J	Obs. μ	Obs. ν	Calc. ν
20	49.46	202.10	201.60
19	51.85	192.80	191.85
18	54.93	181.99	182.05
17	58.09	172.10	172.20
16	61.66	162.12	162.31
15	65.76	152.02	152.38
14	70.31	142.19	142.41
13	75.13	133.07	132.42
12	80.53	124.14	122.35
11	88.40	113.09	112.26
10	97.70	102.32	102.15
9	108.89	91.81	92.01
8	122.60	81.54	81.85

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[5] H. S. Taylor and J. C. Jungers, J. Am. Chem. Soc. **55**, 5057 (1933).

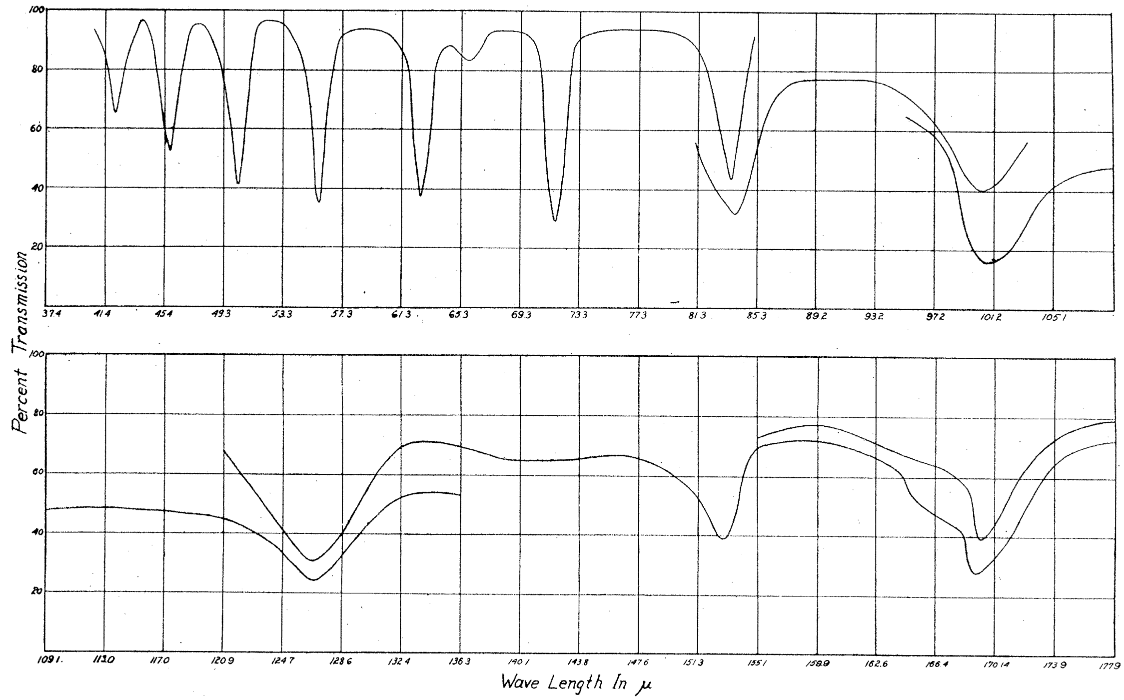

FIG. 1. Pure rotation spectrum of NH_3, showing absorption lines corresponding to final J values from 3 to 12. The line at 152μ is a third order line. (The last numeral in each of the wavelength numbers is a decimal and should be preceded by a decimal point.)

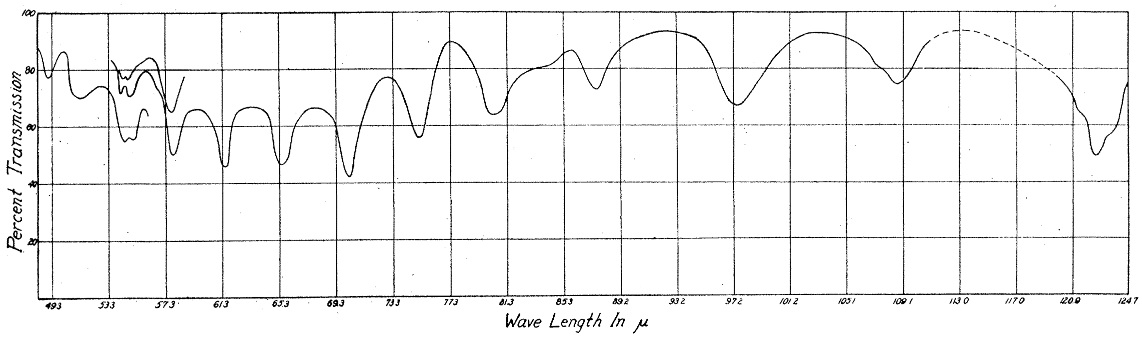

FIG. 2. Pure rotation spectrum of ND_3, showing absorption lines corresponding to final J values from 8 to 20. (The last numeral in each of the wavelength numbers is a decimal and should be preceded by a decimal point.)

ND_3. A general background absorption (absent in the NH_3 curves), however, does suggest the presence of small percentages of unsymmetrical molecules such as ND_2H and NDH_2. This is confirmed by ultraviolet measurements on the sample as used in our cell which indicated a purity of 85 percent D. Considering the crude method of filling the cells made necessary by the thin windows used, the presence of these impurities, due to exchange with atmospheric H_2O, is not at all surprising. Table II gives a summary of the ND_3 results. The calculated frequencies are given by the formula $\nu = 10.26J - 0.00045J^3$. It is seen that the agreement with observation, particularly in lines 11–13, is not good. This is undoubtedly due to the disturbing effect of the NHD_2 absorption, the background being particularly strong in this region. However, the question must be raised how accurately the simple formula, $\nu = 2BJ - 4DJ^3$ derived for linear molecules, is

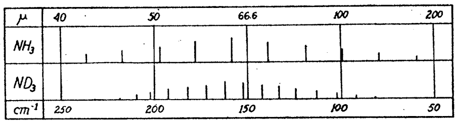

FIG. 3. Schematic representation of the pure rotation spectra of NH_3 and ND_3. Intensities as shown are only approximate.

applicable to the symmetric rotator type. Dr. W. S. Benedict has shown that additional terms in the cubic formula are necessary, and are particularly important in ND_3. Since the present experimental results are not accurate enough to test this point, details will be reserved for a later time. For the present, the simple formula is taken, with $D_{ND_3}=\frac{1}{4}D_{NH_3}$; the resulting value of $B_{ND_3}=5.13$. From this and $B_{NH_3}=9.94$, the height of the pyramid may be calculated, since $1/B\sim I$ and

$$I_{NH_3}=(3/2)m_Ha^2+\frac{3m_Hm_N}{m_N+3m_H}q^2$$

and

$$I_{ND_3}=(3/2)m_Da^2+\frac{3m_Dm_N}{m_N+3m_D}q^2,$$

where a is the distance from the symmetry axis to an H or D atom, and q is the height. Solving, we find $q=0.36A$, $r_{N-H}=a^2+q^2=1.02A$. The accuracy of this result is not high, but the agreement with the value calculated indirectly, 0.37A, is good.[6]

Fig. 3 shows schematically the relative positions of the rotation lines of the two symmetrical ammonias.

The author wishes to express his appreciation to Drs. C. M. Lewis and W. S. Benedict who aided greatly in making these measurements, and to Professor Taylor and Dr. J. C. Jungers who prepared the heavy ammonia.

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

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On Isotopic Shifts in the Spectra of Diatomic Molecules

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An inspection of the theory of diatomic molecules shows that the elementary theory of the dependence of the energy of diatomic molecules on the mass of the nuclei must be supplemented in two ways. In the first place the reaction of the nuclei to the precession of the electronic angular momentum about the internuclear axis gives a term

$$[B_e-\alpha(V+\tfrac{1}{2})][L(L+1)-\Lambda^2].$$

Furthermore there is a second positive term of uncertain magnitude. Both these terms are of importance only for very light molecules especially for the hydrogen molecule. The large electronic shifts observed for some band systems of H_2, HD and D_2 are well accounted for by this theory. A very accurate comparison of the constants of very light isotopic molecules necessitates also taking into account small corrections which appear in the higher order approximations of the energy values for a rotating anharmonic oscillator.

THE study of the spectra of molecules in which one or more of their atoms are substituted by the corresponding isotope can often furnish information about the structure of the molecule which cannot at all, or only with difficulty, be obtained in any other way. This is especially true for those molecules in which a hydrogen atom is replaced by its heavy isotope deuterium, because for this substitution the relative change in the masses is so much greater than for all other isotopic substitutions. In order to make full use of the material which can be obtained in this way it is necessary to know exactly the changes which must be expected in the structure of the corresponding energy levels and wave functions. The approximate theory which was hitherto quite adequate to give a satisfactory account of all the changes as long as only heavy atoms were concerned is not able to explain all the details for proton deuteron substitutions. Kronig[1] called attention to the fact that if certain terms in the Hamiltonian of a diatomic molecule which are usually omitted are taken into account, there is for many states a slight difference in the equilibrium distance even for the

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[1] R. de L. Kronig, Physica 1, 617 (1934).