Rotation Spectra of NH_3 and ND_3

We have measured the pure rotation spectrum of NH_3, using a transmission wire grating spectrometer of large aperture. Ten lines were observed, from No. 3 at 168μ to No. 12 at 42.46μ. The frequencies agree excellently with the formula calculated by Wright and Randall[1] $\nu = 19.880J - 0.00178J^3$, the average deviation being 0.12 cm^{-1}. The resolution attained, although inferior to that of the just-named investigators, is sufficient to give definite indication of the doublet structure in lines No. 4 to No. 6.

Preliminary measurements have been made on a sample of "heavy" ammonia, kindly supplied by Professor H. S. Taylor, the hydrogen being approximately 92 percent deuterium. The spectrum between 49 and 68μ consists of 6 sharp lines, due to ND_3. They have been identified as No. 20 to No. 15. Although the present accuracy is not great (± 1 cm^{-1}), it is sufficient to show that the lines cannot be represented by the usual formula $\nu = 2BJ - 4DJ^3$, unless $4D$ is nearly zero or even negative. We believe this is attributable to the same circumstance that causes the positions of the Raman lines $\Delta J = \pm 1$ to disagree with the usual formula:[2] namely, the existence in the energy of a small term $D_{JK}J(J+1)K^2$, due to the influence of rotations around one axis on the moment of inertia around another. The effect of such a term is to split each "line" into J unresolvable components, corresponding to $0 < K < J-1$. Calculation of the relative intensity of these components shows that their center of gravity would behave much as is observed in both NH_3 and ND_3, the effect resulting in a more noticeable departure from the simple formula in the latter because the observed transitions originate on much higher energy levels. Taking this into account, we obtain for ND_3, $2B = 10.22 \pm 0.05$ cm^{-1}. This value, together with $2B = 19.88$ for NH_3, gives for q_0, the height of the ammonia pyramid, 0.34 ± 0.03A. The slight disagreement of this last figure with $q_0 \cong 0.38$A, as calculated indirectly from assumed potential functions[3] is not disturbing, as the value of $\nu_4 = 770$ cm^{-1}, found in ND_3 by Silverman and Sanderson[4] is incompatible with either of the assumed functions.

It has become necessary to rebuild part of the apparatus, hence we publish these preliminary results at the present time. Needless to say, we will extend them to larger wavelengths and to the limit of our accuracy, and will discuss the theoretical implications more fully later.

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

[2] Lewis and Houston, Phys. Rev. **44**, 903 (1933).

[3] Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); Rosen and Morse, ibid. **42**, 210 (1932).

[4] Silverman and Sanderson, Phys. Rev. **44**, 1032 (1933); this value has also been checked in the ultraviolet by one of us (W. S. B.) and H. S. Taylor.