

DETERMINATION OF THE ROTATIONAL
CONSTANT OF $^{15}\text{NH}_3$ A. F. Krupnov, L. I. Gershtein,
V. G. Shustrov, and V. V. Polyakov

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The rotational spectrum of ^{15}N ammonia has not previously been observed. We have examined the lower rotational transition $J = 0 \rightarrow 1$, $K = 0$ for $^{15}\text{NH}_3$ in the 0.525-mm range, which has given the rotational constant for this species of ammonia.

We used a gas spectroscopy with video detection [1]. The cell contained $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ in the ratio of about 8:1. On sweeping the oscillator frequency (backward-wave tube [2]), the lines for $J = 0 \rightarrow 1$, $K = 0$ for the two forms were clearly seen (Fig. 1). The distance between the lines was deduced from the frequency modulation of the source [3], which was recorded by a ChZ-9 frequency meter. The difference between the two transition frequencies was 384.8 MHz with an error of ± 0.2 MHz. The transition frequency for $^{14}\text{NH}_3$ has been measured [1] as $\nu_{0-1}(\text{N}^{14}\text{H}_3) = 572,499.4 \text{ MHz} \pm 3 \text{ MHz}$, so for $^{15}\text{NH}_3$ we have

$$\nu_{0-1}(\text{N}^{15}\text{H}_3) = 572115 \text{ MHz},$$

with the accuracy as for $\nu_{0-1}(\text{N}^{14}\text{H}_3)$.

The rotational constant B_0 was deduced as for $^{14}\text{NH}_3$ [1] and is

$$B_0(\text{N}^{15}\text{H}_3) = \frac{1}{2} \left[\nu_{0-1}(\text{N}^{15}\text{H}_3) + 4D_J + \frac{\nu_{00} + \nu_{01}}{2} \right],$$

where D_J is the centrifugal perturbation constant and $(\nu_{00} + \nu_{01})/2$ is half the sum of the frequencies for the inversion splitting of the levels $J = K = 0$ and $J = 1$, $K = 0$. No value has been published for D_J for $^{15}\text{NH}_3$, but the quantity is determined by an expression of the form B^3/ω^2 , where B is the rotational constant and ω is the vibrational frequency [3], so the value for $^{15}\text{NH}_3$ is virtually that for $^{14}\text{NH}_3$, which is 19 MHz [3]. It is not possible to measure ν_{00} and ν_{01} because $^{15}\text{NH}_3$ lacks one of the inversion levels in each pair for $K = 0$, so one should use the dependence of the inversion frequency on J and K as found from transitions with $K \neq 0$ by using the corresponding J and K .

An empirical formula [4] for the frequencies in the inversion spectrum of $^{15}\text{NH}_3$ has a standard deviation of 308 MHz and in the appropriate region (J and K small) gives values that differ from experiment by 3-10 MHz, which reduces the accuracy of the calculation. We therefore drew up the following better approximation from the measured frequencies [5]:

$$\begin{aligned} \nu_{JK}^{\text{(MHz)}} = & 22714 \exp \{ -0.6489815 \cdot 10^{-2} J(J+1) + 0.902306 \cdot 10^{-2} K^2 \\ & + 0.850786 \cdot 10^{-6} J^2(J+1)^2 - 0.178945 \cdot 10^{-5} J(J+1) K^2 + 0.52645 \cdot 10^{-6} K^4 \}, \end{aligned} \quad (1)$$

which has a standard deviation of 3.6 MHz and differences of 0.2-4.5 MHz from experiment at small J and K . Use of (1) gives a more accurate B_0 for $^{15}\text{NH}_3$ as

$$B_0(\text{N}^{15}\text{H}_3) = 297379.3 \text{ MHz}.$$

The method of [1] gave $\nu_{0-1}(\text{N}^{15}\text{N}_3) = 572,111.44 \text{ MHz}$ for the frequency of the $J = 0 \rightarrow 1$, $K = 0$ transition in $^{15}\text{NH}_3$, and so

$$B_0(\text{N}^{15}\text{H}_3) = 297377.5 \text{ MHz}.$$

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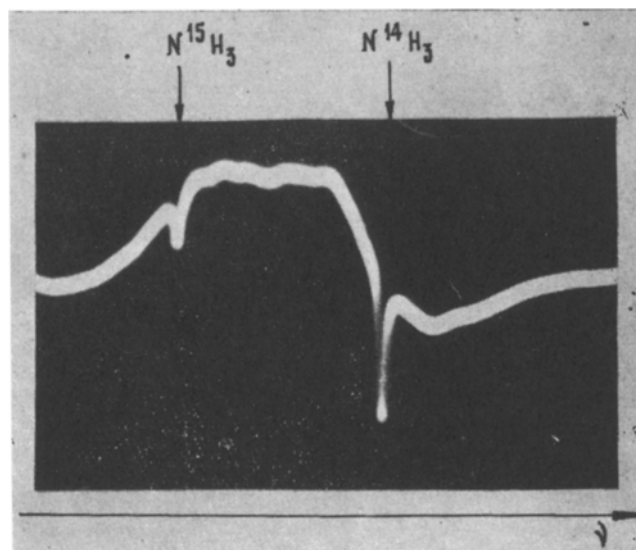


Fig. 1.

The results agree to $6 \cdot 10^{-6}$ or so, and the measured frequency for $^{14}\text{NH}_3$ is $\nu_{0-1}(\text{N}^{14}\text{H}_3) = 572,495.6$ MHz, which corresponds to $B_0(\text{N}^{14}\text{H}_3) = 298,104.2$ MHz. The result for the frequency difference is 384.1 MHz, which agrees well with the value above within the error of the present method.

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