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# LETTERS TO THE EDITOR

## Sub-Millimeter-Wave Rotation–Inversion Transition $J = 1 \leftarrow 0$, $\Delta K = 0$ of $^{14}NH_3$ and $^{15}NH_3$ in the $\nu_2$ State

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Chu and Freund (*1*) have recently reported a direct millimeter-wave observation of the transition between the lower inversion level of the $J = 2$, $K = 1$ rotational state and the upper inversion level of the $J = 1$, $K = 1$ state, which are accidentally close in energy in the $\nu_2$ state of $^{14}NH_3$ and $^{15}NH_3$. A similar situation occurs for the lower inversion level of the $J = 1$, $K = 0$ state and the upper inversion level of the $J = 0$, $K = 0$ state (Fig. 1). The frequency of the transition between these states (encircled transition in Fig. 1) can be obtained from the submillimeter (*2, 3*) and high-resolution infrared data (*4, 5*) for the transitions indicated in Fig. 1. The frequencies obtained in this way are 466.27 GHz (15.553 cm$^{-1}$) for $^{14}NH_3$ and 430.2 GHz (14.35 cm$^{-1}$) for $^{15}NH_3$.

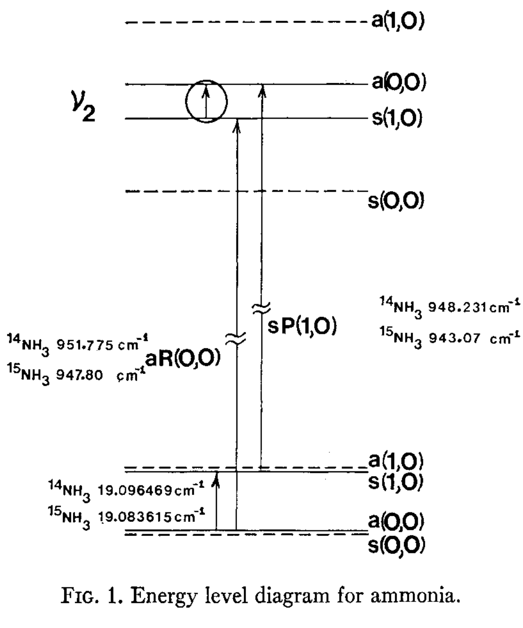


FIG. 1. Energy level diagram for ammonia.




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Table I. Frequencies and the Line Halfwidths of the $J = 1 \leftarrow 0, \Delta K = 0$ Transition in the $\nu_2$ State of $^{14}NH_3$ and $^{15}NH_3$ at Different Pressures (in MHz)

| $(\Delta\nu)_{1/2}$ | $(\overline{\Delta\nu})_{1/2}$ | $\nu_{exp}$ (see[a]) $^{14}NH_3$ | $\nu_{exp}$ (see[a]) $^{15}NH_3$ | $\nu_{exp}(^{14}NH_3) - \nu_{exp}(^{15}NH_3)$ |
|---|---|---|---|---|
| 17.8 | 17.8. | 466 252.7 | 430 045.7 | 36 207.0 |
| 7 | 7 | 466 248.2 | 430 041.3 | 36 206.9 |
| 6 | 6 | 466 247.7 | 430 040.9 | 36 206.8 |
| 3.7 | 3.6 | 466 246.7 | 430 039.8 | 36 206.9 |
| 2.9 | 2.8 | 466 246.3 | | |
| 2.4 | 2.3 | 466 246.1 | | |
| Extrapolated to zero pressure | | $466\,245.1 \pm 0.1$ ($15.55225\ cm^{-1}$) | $430\,038.3 \pm 0.2$ ($14.34452\ cm^{-1}$) | 36 206.8 |

[a] Avarage value from 10 measurements

In this letter we report a direct sub-millimeter-wave observation of this transition in ammonia gas containing 12% $^{15}NH_3$. The sub-millimeter-wave spectrometer with the frequency-stabilized backward-wave oscillator and acoustic detector used for these measurements was described earlier (*6, 7*). Preliminary measurements showed an anomalously large dependence of the line centers on the pressure of the ammonia gas. Because the optimum pressure of the gas in the cell of this spectrometer is approximately

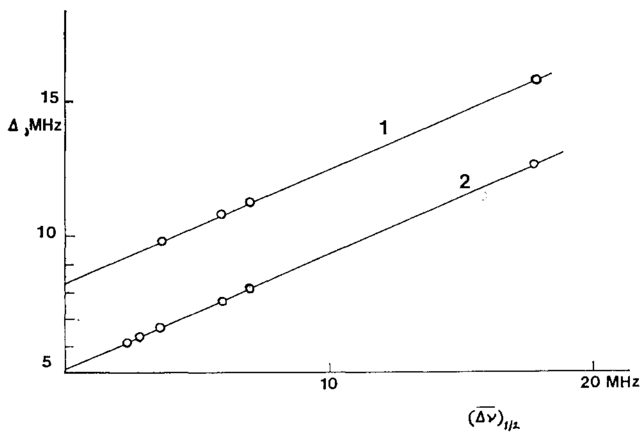


FIG. 2. Dependence of the frequency shifts $\Delta$ on the line half width $(\overline{\Delta\nu})_{1/2}$: (1) $\Delta = \nu_{exp}(^{15}NH_3) - 430\,030$: (2) $\Delta = \nu_{exp}(^{14}NH_3) - 466\,240$.

1 Torr, it was not possible to lower the pressure of the gas to such an extent that the frequency shift due to intermolecular interactions would be eliminated in individual measurements. Instead of this, we measured the frequencies $\nu_{\text{exp}}$ and the line half widths $(\Delta\nu)_{\frac{1}{2}}$ at different pressures (Table I). From $(\Delta\nu)_{\frac{1}{2}}$, we calculated the half widths due to collision broadening $(\overline{\Delta\nu})_{\frac{1}{2}}$ according to the formula

$$(\overline{\Delta\nu})_{\frac{1}{2}} = [(\Delta\nu)_{\frac{1}{2}}^2 - (\Delta\nu)_D^2]^{\frac{1}{2}}, \qquad (1)$$

where the Doppler halfwidth $(\Delta\nu)_D$ is given by

$$(\Delta\nu)_D = 0.84(2kT/m)^{\frac{1}{2}}\nu_{\text{exp}}/c \quad ({}^{14}NH_3). \qquad (2)$$

The frequency shift was found to be a linear function of $(\overline{\Delta\nu})_{\frac{1}{2}}$ (Table I and Fig. 2) which makes it possible to obtain the transition frequencies at zero pressure by linear extrapolation.

The frequencies obtained in this way are given in Table I. The predicted values of these frequencies agree with our sub-millimeter-wave measurements to within the precision of the high-resolution infrared measurements (*4*, *5*).

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