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Rotational Spectra of NH_3 and ND_3 in the 0.5-mm Wavelength Region[1]

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Rotational transitions of NH_3 and ND_3 in the 0.5-mm wavelength region have been observed and measured by microwave techniques. For ND_3 the two inversion components of the $J = 1 \rightarrow 2$ transitions of $^{14}ND_3$ and $^{15}ND_3$ at 0.49-mm wavelength have been measured, and for NH_3 the $J = 0 \rightarrow 1$ transitions of $^{14}NH_3$ and $^{15}NH_3$ at 0.52-mm wavelength have been remeasured with higher precision. With $J = 0 \rightarrow 1$ transition frequencies for ND_3 from previous microwave measurements and with the centrifugal stretching constant D_J for NH_3 measured in the infrared region, these frequencies yield the following spectral constants (in Mc/sec): for $^{14}ND_3$, $B_0 = 154\ 173.38$, $D_J = 5.91$, $D_{JK} = -10.49$; for $^{15}ND_3$, $B_0 = 153\ 600.97$, $D_J = 5.92$, $D_{JK} = -10.54$; for $^{14}NH_3$, $B_0 = 298\ 115.37$; and for $^{15}NH_3$, $B_0 = 297\ 388.12$. The effective ground-state structural dimensions for NH_3 are $d_{NH} = 1.0156$ Å and $< HNH = 107°17'$, and the corresponding values for ND_3 are $d_{ND} = 1.0143$ Å and $< DND = 107°4'$. Various substitution structures are also calculated.

Rotational transitions of NH_3 and ND_3 in the 0.5-mm wavelength region have been observed and measured by microwave techniques. For ND_3 the two inversion components of the $J = 1 \rightarrow 2$ transition of both $^{14}ND_3$ and $^{15}ND_3$ at 0.49-mm wavelength have been measured. Figure 1 shows an oscilloscope tracing of the lower inversion component of the $J = 1 \rightarrow 2$ transition of $^{14}ND_3$ at 615 Gc/sec. When combined with the previous measurements of the $J = 0 \rightarrow 1$ transition (*1*), the present measurements on ND_3 provide the first microwave values of the stretching constants D_J and D_{JK}. The $J = 0 \rightarrow 1$ transition of both $^{14}NH_3$ and $^{15}NH_3$ at 0.52-mm wavelength was earlier measured in this laboratory (*1, 2*). Unfortunately, an error of ~60 Mc/sec was made in the $^{15}NH_3$ line because of an incorrect identification of the frequency marker. We are indebted to A. F. Krupnov of the Radiophysical Research Institute at Gorky (U.S.S.R.) for calling our attention to this error, which is corrected in the present measurement. The value obtained, 572 112.78 ± 0.10 Mc/sec, is in satisfactory agreement with that of 572 111.44 Mc/sec which was obtained by Krupnov and his associates (*3*). In addition, the $J = 0 \rightarrow 1$ transition of $^{14}NH_3$ has been remeasured to greater precision in the present work.

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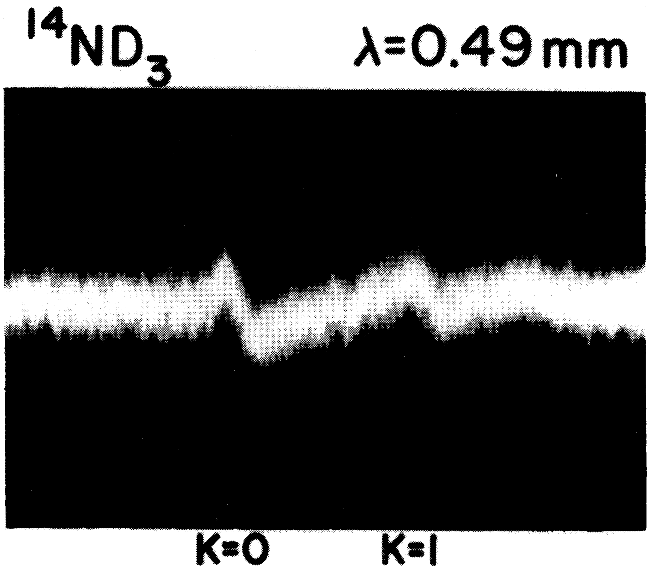

FIG. 1. Oscilloscope tracing of the lower inversion component of the $J = 1 \rightarrow 2$ transition $^{14}ND_3$ at 615 Gc/sec.

TABLE I

MEASURED FREQUENCIES FOR NH_3 AND ND_3

Transition	Lower inversion component (Mc/sec)	Upper inversion component (Mc/sec)	Center frequency (Mc/sec)
$^{14}ND_3$			
$J = 1 \rightarrow 2, K = 0$	614 933.46 ± 0.20	618 075.04 ± 0.25	616 504.25
$J = 1 \rightarrow 2, K = 1$	614 967.54 ± 0.20	618 124.86 ± 0.20	616 546.20
$^{15}ND_3$			
$J = 1 \rightarrow 2, K = 0$	612 800.86 ± 0.15	615 627.96 ± 0.20	614 214.41
$J = 1 \rightarrow 2, K = 1$	612 836.04 ± 0.15	615 677.07 ± 0.15	614 256.56
$^{14}NH_3$			
$J = 0 \rightarrow 1, K = 0$	572 498.15 ± 0.15		596 133.49[a]
$^{15}NH_3$			
$J = 0 \rightarrow 1, K = 0$	572 112.78 ± 0.10		594 680.92[a]

[a] Obtained by the addition to the lower inversion component of half the sum of the inversion splittings of the states $J = 0, K = 0$ and $J = 1, K = 0$. See Ref. (1) and Schnabel, *et al.*, *Z. Physik* **188**, 167 (1965).

The submillimeter microwave power for these observations was generated by a klystron-driven crystal harmonic multiplier of the type described previously (*4*). The measurements reported here were obtained with the 10th and 11th harmonics of an OKI 55V11 klystron. Detection was accomplished with a 1.6° K InSb photoconducting detector obtained from Mullard, Ltd. The sample cell consisted of a copper tube ¾″ in diameter and 1 ft long equipped with teflon windows; the output of the cell matched the input light pipe of the detector.

TABLE II

SPECTRAL CONSTANTS OF NH_3 AND ND_3

Isotopic species	B_0 (Mc/sec)	D_J (Mc/sec)	D_{JK} (Mc/sec)
$^{14}NH_3$	298 115.37	24.31[a]	−45.27[a]
$^{15}NH_3$	297 388.12	23.83[b]	−46.62[b]
$^{14}ND_3$	154 173.38	5.91	−10.49
$^{15}ND_3$	153 600.97	5.92	−10.54

[a] $^{14}NH_3$ infrared values of D_J and D_{JK} from H. M. Mould, *et al.*, *Spectrochim. Acta* **15**, 313 (1959). D_J is used in the evaluation of B_0.

[b] $^{15}NH_3$ infrared values of D_J and D_{JK} from F. O. Shimizu and T. Shimizu, *J. Mol. Spectrosc.* **36**, 94 (1970). D_J is used in the evaulation of B_0.

TABLE III

MOLECULAR DIMENSIONS OF AMMONIA FROM MICROWAVE VALUES OF B_0

Isotopic species	Bond distance[a]	Bond angle
	Effective ground-state structure	
$^{14}NH_3$, $^{15}NH_3$	1.0156 Å	107°17′
$^{14}ND_3$, $^{15}ND_3$	1.0143 Å	107°04′
	Substitution Structure	
$^{14}ND_3$:$^{15}ND_3$, $^{14}NH_3$	1.0136 Å	107°04′
$^{15}ND_3$:$^{14}ND_3$, $^{15}NH_3$	1.0137 Å	107°04′
$^{14}NH_3$:$^{15}NH_3$, $^{14}ND_3$	1.0138 Å	107°14′
$^{15}NH_3$:$^{14}NH_3$, $^{15}ND_3$	1.0138 Å	107°14′

[a] Calculated by use of B (Mc/sec) $= (5.05376 \times 10^5)/I_b$ (amu Å^2). See GORDY and COOK, "*Microwave Molecular Spectra*," (Wiley, New York, 1970).

Microwave power from the harmonic multiplier was directed through the sample cell by means of a metallic horn and a teflon lens. With this spectrometer, molecular rotational frequencies as high as 813 Gc/sec ($\lambda = 0.368$ mm) have been measured (*5*).

The experimental results for NH_3 and ND_3 are listed in Table I. The quadrupole hyperfine structure due to the ^{14}N nucleus contributes a broadening to the $J = 1 \rightarrow 2$ transition of $^{14}ND_3$ and to the $J = 0 \rightarrow 1$ transition of $^{14}NH_3$ but is unresolved because of the large Doppler width. As a result, the estimated errors in the line measurements for these isotopic forms are somewhat larger than those for the ^{15}N species. Rotational constants evaluated from these measurements are presented in Table II. Details of the calculation of B_0 for NH_3 from the single inversion component present for the $J = 0 \rightarrow 1$ transition are given elsewhere (*1*). The spectral constants including the distortion constants for ND_3 shown in Table II were calculated entirely from microwave measurements.

The molecular structure of ammonia from microwave values of B_0 was evaluated in the previous work (*1*). However, correction of the error in the value of B_0 for $^{15}NH_3$ and improvement of the accuracy of the constant for the other isotopic species here obtained justify a recalculation of the structure. The results are presented in Table III. Specific procedures for the evaluation of the effective ground-state structure and the substitution structure for ammonia were discussed in the previous work (*1*).

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