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Microwave rotation-inversion spectrum of NT_3†

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The rotation-inversion spectrum of $^{14}NT_3$ in the ground vibrational state has been measured with high-resolution microwave techniques in the frequency range of 210–633 GHz. Components of the $J = 0 \rightarrow 1$, $1 \rightarrow 2$, and $2 \rightarrow 3$ transitions were observed. Analysis of the results yielded the following rotational constants: $B_0 = 105\,565.373 \pm 0.034$ MHz, $D_J = 2.5981 \pm 0.0024$ MHz, and $D_{JK} = -4.472 \pm 0.006$ MHz, with the ^{14}N nuclear quadrupole coupling $eqQ = -4.170 \pm 0.049$ MHz. The inversion frequency, corrected for rotational distortion, was found to be 305.89 ± 0.11 MHz. Molecular substitution structures obtained were bond length 1.0132 Å and bond angle 107° 13′ for the combination $^{14}NH_3$: $^{15}NH_3$, $^{14}NT_3$; bond length 1.0128 Å and bond angle 107° 2′ for the combination $^{14}ND_3$: $^{15}ND_3$, $^{14}NT_3$.

INTRODUCTION

Although NH_3 was the first molecule to be observed with microwave spectroscopy[1] and although its microwave spectrum has been investigated more thoroughly than that of any other molecule, no previous microwave measurements have, to our knowledge, been made of the tritiated species NT_3. Because of the large change in the reduced mass caused by substitution of T for H, microwave measurements on this species should be useful in testing theoretical treatments of the potential function and other properties of the molecule. Infrared measurements of both the vibrational spectra[2] and the pure rotational spectra[3] of NT_3 have been made, but neither the inversion doubling nor the K splitting has been resolved. Consequently, the molecular constants obtained from these measurements are not accurate. Theoretical efforts[4] to derive the inversion splitting in NT_3 have not been very successful.

Accurate microwave measurements of the ground-state inversion spectrum[5] and the rotation-inversion spectrum[6] of the deuterated species ND_3 have been carried out, and the unresolved microwave measurement of the inversion transition of ND_3 in the excited vibrational state $v_2 = 1$ has been reported.[7] Extensive infrared studies have been made on NH_3 and ND_3 by Benedict and Plyler,[8] who resolved and measured the inversion doubling in these species in several excited vibrational states but made no observations on NT_3. Rao *et al.*[2] measured the fundamental symmetrical vibrational frequency ω_2 of NT_3 at 657 cm^{-1} and estimated the inversion splitting in the $v_2 = 1$ state to be 0.8 cm^{-1}. The splitting theoretically predicted for the $v_2 = 1$ state by Norris and Dowling[4] is 0.3 cm^{-1}.

The present paper reports high-resolution microwave measurements on the rotation-inversion transitions of NT_3 in the ground vibrational state, from which the rotational constants as well as the inversion splitting are accurately determined. Although we have not included observations of the $v_2 = 1$ state in the present study, we hope to be able to observe the microwave transitions of this state in later work.

EXPERIMENTAL PROCEDURE

The measurements of NT_3 in the present work were made with a microwave spectrometer that has been previously described[9] except for a modification of the absorption cell for special handling of the radioactive sample. Microwave energy in the millimeter and submillimeter wavelength region came from a klystron-driven crystal harmonic generator which was referenced to WWVB for precise frequency measurement. Detection of the microwave energy was accomplished by means of an InSb photoconducting detector operated at 1.6°K.

Approximately 10 Ci of NT_3 at a relatively high specific activity was prepared at the Oak Ridge National Laboratory by the reaction of T_2O with calcium nitride. The sample was subsequently loaded into a special absorption cell with an associated gas-handling system designed to be used at the site of the spectrometer without external vacuum connection. All spectral measurements were made at Duke University. The absorption cell consisted of a copper tube 19 mm in diameter, 90 cm in length, with fused-quartz windows and indium vacuum seals. As an additional precaution against vacuum leaks, the quartz windows were bonded to the cell by epoxy resin. The gas-handling system, which was permanently attached to the absorption cell, consisted of primary and recovery reservoirs for sample storage and a thermocouple gauge for the measurement of pressure. The NT_3 pressure in the absorption cell was regulated by liquid-nitrogen trapping. In this work, as in the previous infrared studies,[2,3] NT_3 was observed to decompose into N_2 and T_2 over a period of time as a result of the β activity of the tritium. Because these decay products cannot be trapped by liquid nitrogen, an activated uranium trap was included as a part of the gas-handling system to remove the background pressure due to these gases. Activated uranium[10-12] is an extremely reactive form of metallic uranium suitable as a getter material for many common gases, including nitrogen and hydrogen, but not for the rare gases. Over the period of the measurements on NT_3, a slow increase in the background pressure as a result of the conversion of tritium into ^3He was also noted. This background pressure could not be reduced by use of the getter material.

EXPERIMENTAL RESULTS

Figure 1 shows a recording of the lower inversion component of the $J=2\rightarrow 3$ transition which occurs at submillimeter wavelengths of $\lambda=0.47$ mm. The signal strengths here are limited by the concentration of NT_3 in the samples. This concentration is not known definitely because of its continuous decay through exchange and nuclear radiation. The linewidth, about 4 MHz, is caused by collision broadening, by Doppler broadening, and by unresolved ^{14}N hyperfine structure.

The ^{14}N hyperfine structure was well resolved for the $J=0\rightarrow 1$ transition only. There is a single K component for this transition ($K=0$), and the only inversion component is the lower one. The hyperfine structure is a simple triplet, the measured frequencies of which are given in Table I. The structure was analyzed with first-order nuclear quadrupole coupling theory[13] as applied to the ^{14}N nucleus, which has spin $I=1$. The accuracy, which was limited by the linewidth, did not permit an evaluation of the small effects of the ^{14}N magnetic coupling. The magnetic shifts were estimated from the coupling constant of NH_3 to be only a few kilohertz. In Table I the observed frequencies of the components are compared with those obtained from a least-squares analysis. The resulting ^{14}N nuclear quadrupole coupling constant eqQ and the derived frequency for the hypothetical unsplit rotational frequency are also given in Table I. The magnitude of the eqQ value is somewhat higher than that for $^{14}NH_3$, -4.08 MHz, but the probable error in the NT_3 value overlaps that for $^{14}NH_3$.

In Table II are listed the observed rotational frequencies, including K splitting and inversion splitting but corrected for any nuclear hyperfine splitting. The theoretical frequencies were calculated by a least-squares fitting of observed frequencies to the formula

$$\nu=2B_0(J+1)-4D_J(J+1)^3-2D_{JK}(J+1)K^2 \pm[\nu_i+C_1(J+1)^2+C_2K^2] \,. \qquad (1)$$

Deviations of these theoretical frequencies from the observed lines are given in the last column. The resulting molecular constants obtained from this calculated fitting are listed in Table III. The terms in B_0, D_J, and D_{JK} are the familiar expressions for the pure rotational frequencies of normal symmetric-top molecules without inversion. Thus B_0 is the rotational constant, $h/8\pi^2 I_B$, averaged over the two inversion levels of the ground vibrational state, and D_J and D_{JK} are centrifugal

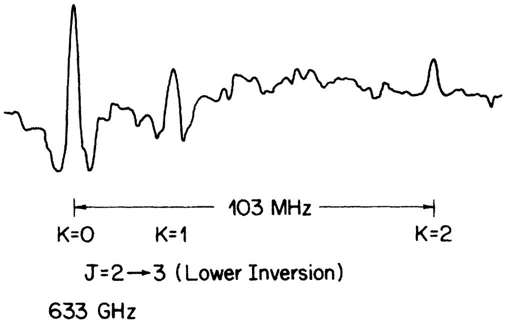

FIG. 1. Recording of the $J=2\rightarrow 3$ transition of the lower inversion component of NT_3 at $\lambda=0.47$ mm (633 GHz).

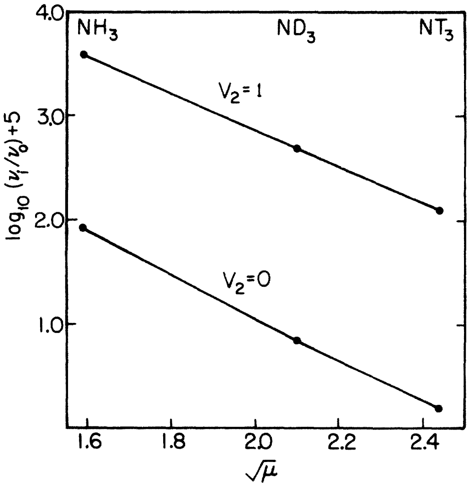

FIG. 2. Correlation of the inversion splitting with the reduced molecular mass for the three isotopic species of ammonia in different v_2 vibrational states.

stretching constants similarly averaged. The term in brackets is the inversion term, in which ν_i is the inversion frequency and C_1 and C_2 represent effects of centrifugal distortion on the inversion transition frequency.

With infrared spectral techniques, McDowell and Jones[3] measured higher rotational transitions of NT_3, from $J = 8 \rightarrow 9$ to $J = 20 \rightarrow 21$. Although the centrifugal stretching effects on these high-J transitions are large, McDowell and Jones could not obtain very accurate values of the stretching constants because neither the K splitting nor the inversion doubling was resolved. They obtained the values $B_0 = 3.521 \pm 0.003$ cm^{-1} (which is equivalent to 105.56 ± 0.09 GHz) and $D_J = (5.8 \pm 0.5) \times 10^{-5}$ cm^{-1} or 1.74 ± 0.15 MHz. McDowell[14] later reanalyzed the data, taking into account the shape of the unresolved K structure, and obtained the values $B_0 = 3.519$ cm^{-1} and $D_J = (7.0 \pm 0.56) \times 10^{-5}$ cm^{-1}. From the corresponding hydrides and deuterides, Sundaram and Cleveland[15] calculated the values $D_J = 2.5486$ MHz and $D_{JK} = -4.3635$ MHz for NT_3, in reasonable agreement with our observed values.

MOLECULAR DIMENSIONS

The rotational constant B_0 for NT_3 with the constants derived from our earlier submillimeter wave measurements on NH_3 and ND_3 allow a number of new combinations for calculation of substitution structures. Methods for these calculations are described elsewhere.[13] Table IV lists the new structural parameters obtained from combinations involving NT_3, along with earlier values obtained from other combinations listed for comparison. The closeness of the different values of bond lengths and bond angles is remarkable in consideration of the large percentage of mass change in the substituted atom. The trend is toward slightly decreasing dimensions, in both bond length and angle, with increasing mass of the combinations employed. This reasonable trend is expected because of the smaller zero-point vibrational energy of the heavier isotope, combined with a slight anharmonicity in the potential function.

TABLE I. Resolved ^{14}N hyperfine structure.

Transition	Observed frequency (MHz)	Theoretically fitted value (MHz)	Difference
$J = 0 \rightarrow 1, K = 0$			
$F = 1 \rightarrow 1$	210 813.830	210 813.843	−0.013
$1 \rightarrow 2$	210 815.115	210 815.094	0.021
$1 \rightarrow 0$	210 816.962	210 816.970	−0.008

Derived constants:
$\nu_0 = 210\,814.885$[a]
$eqQ = -4.170 \pm 0.049$

[a] ν_0 is the $J = 0 \rightarrow 1$ rotational frequency corrected for hyperfine splitting but not for inversion displacement. For the $J = 0 \rightarrow 1$ transition, only the lower inversion component occurs.

INVERSION DOUBLING

The inversion problem in the ammonias, NH_3, ND_3, and NT_3, is of great interest because this group represents the only symmetric isotopic sequence with inversion splitting of the symmetric vibrational states sufficiently large for measurement to good accuracy in the different vibrational states. The inversion splitting in PH_3, the next most promising case, is found from molecular-beam measurements[16] to be less than 1 kHz. A recent effort with high-resolution infrared techniques sets an upper limit of about 0.02 cm^{-1} for the inversion splitting of the $4v_2$ level.[17] There are, however, many related inversion-type oscillations in asymmetric rotors.[13]

Although much theoretical work has been done on the problem of inversion doubling, apparently no one has attempted successfully to predict the splitting in NT_3. The most serious attempt to do so was probably that of Norris and Dowling,[4] who employed a refined Manning potential and predicted the NT_3 splitting to be 0.00 cm^{-1} for the ground vibrational state, and 0.3 cm^{-1} for the $v_2 = 1$ vibrational state. Swalen and Ibers[18] have calculated values that fit well with the known splitting in NH_3 and ND_3, but they did not predict values for NT_3. As explained in our concluding paragraph, we used their method to calculate splittings for NT_3. These agree well with the experimental observations. Swalen and Ibers give an introductory summary of the work on the inversion problem in ammonia, with a rather complete list of references to the many experimental and

TABLE II. Observed and calculated rotation-inversion frequencies of $^{14}NT_3$.

Transition	Inversion component	Observed frequency (MHz)	Calculated frequency (MHz)	Difference (MHz)
$J = 0 \rightarrow 1, K = 0$	lower	210 814.885	210 815.023	−0.138
$J = 1 \rightarrow 2, K = 1$	lower	421 891.743	421 891.608	0.135
$J = 1 \rightarrow 2, K = 0$	upper	422 482.040	422 482.014	0.026
$J = 1 \rightarrow 2, K = 1$	upper	422 500.800	422 500.871	−0.071
$J = 2 \rightarrow 3, K = 0$	lower	632 810.839	632 810.768	0.071
$J = 2 \rightarrow 3, K = 1$	lower	632 836.513	632 836.626	−0.113
$J = 2 \rightarrow 3, K = 2$	lower	632 914.199	632 914.202	−0.003
$J = 2 \rightarrow 3, K = 1$	upper	633 440.324	633 440.321	0.003
$J = 2 \rightarrow 3, K = 2$	upper	633 523.744	633 523.724	0.020

theoretical papers on NH_3 and ND_3. An earlier, general treatment was given by Townes and Schawlow.[19]

The expression derived by Dennison and Uhlenbeck[20] for the ammonia inversion frequency is

$$\frac{\nu_i}{\nu_0} = \frac{1}{\pi} \exp\left(-\frac{2}{\hbar}\int_0^{x_1}[2\mu(V(x) - E_v)]^{1/2}dx\right), \quad (2)$$

where ν_0 is the fundamental vibrational frequency for the symmetrical mode v_2, μ is the reduced mass of the molecule, $V(x)$ is the inversion potential function, and E_v is the total vibrational energy for the v_2 mode. Since ν_i and ν_0 are now known accurately for all three species, NH_3, ND_3, and NT_3, it seems desirable to compare the variation of ν_i/ν_0 with the reduced mass for this sequence. The Dennison-Uhlenbeck equation suggests the relation

$$\ln\frac{\nu_i}{\nu_0} \sim \mu^{1/2}\left(\int_0^{x_1}[V(x) - E_v]^{1/2}dx\right). \quad (3)$$

Evaluation of the integral requires a knowledge of potential functions and barriers and will therefore not be undertaken. It is evident, however, that $V(x)$ should be very nearly the same for the three species and that the integral will differ among the species because E_v will vary. Obviously, if the integral were the same for the different species, $\ln(\nu_i/\nu_0)$ would be a linear function of $\mu^{1/2}$. The curves for the $v_2 = 0$ and $v_2 = 1$ vibrational states plotted in Fig. 2 show, in fact, that the relationship is almost linear, that the omission of the effects of the integral causes only a slight bend in the curve. In these plots we used the reduced mass

$$\mu = 3m(M + 3m\sin^2\theta)(M + 3m)^{-1}, \quad (4)$$

where m is the mass of the hydrogen isotope, M is the nitrogen mass, and $\theta = 22°$ is the angle between the NH bonds and the plane of the three hydrogens in the equilibrium position. The plot for the ground state $v_2 = 0$ was made with precise microwave values of ν_i; the plots for the $v_2 = 1$ state for NH_3 and ND_3 were made from the rather accurate infrared data of Benedict and Plyler,[8] and that for NT_3, from the more approximate values $\nu_i = 0.8\ \text{cm}^{-1}$ and $\nu_0 = 657\ \text{cm}^{-1}$ obtained from infrared measurements by Rao *et al.*[2]

TABLE III. Rotation and inversion constants of $^{14}NT_3$.

Rotation constants (MHz)

$B_0 = 105\,565.373 \pm 0.034$
$D_J = 2.5981 \pm 0.0024$
$D_{JK} = -4.472 \pm 0.006$

Inversion constants (MHz)

$(\nu_i)_0 = 305.89 \pm 0.11$
$C_1 = -0.557 \pm 0.020$
$C_2 = 0.971 \pm 0.038$

Swalen and Ibers[18] considered a potential function in the form of a harmonic oscillator with a Gaussian barrier. The matrix elements of the resulting dimensionless Hamiltonian

$$\mathcal{H} = \tfrac{1}{2}P^2 + \tfrac{1}{2}Q^2 + Ve^{-CQ^2} \quad (5)$$

were evaluated in the harmonic oscillator basis, and a truncated portion of the resulting infinite matrix was diagonalized to give calculated energy levels. Swalen and Ibers used this technique to calculate a potential function which, in general, gives good agreement with observed energy levels of NH_3 and ND_3. We have performed a similar calculation for NT_3 which is based on this potential function. The matrix elements of P^2 and Q^2 were evaluated by the usual techniques while the matrix elements of the Gaussian barrier were evaluated from the equations of Chan and Stelman[21] rather than by direct integration with the Hermite polynomials. This matrix was truncated at $n = 26$ and diagonalized. All calculations were performed in double precision arithmetic on an IBM 370/165. The resulting theoretical values for the inversion splitting are $\nu_i = 0.010\ \text{cm}^{-1}$, or 300 MHz, for the ground state, and $\nu_i = 0.7\ \text{cm}^{-1}$ for the excited $v_2 = 1$ vibrational state. These are in excellent agreement with the observed values of 305.89 MHz and $0.8\ \text{cm}^{-1}$. However, the experimental value for the $v_2 = 1$ state estimated from infrared measurements by Rao *et al.*[2] is highly approximate. We hope later to measure the inversion splitting of the $v_1 = 1$ state with high-resolution microwave spectroscopy.

TABLE IV. Derived isotopic substitution structures of ammonia.

Isotopic species [a]	Bond length (Å)	Bond angle
$^{14}NH_3$: $^{15}NH_3$, $^{14}ND_3$	1.0138	107° 14′
$^{15}NH_3$: $^{14}NH_3$, $^{15}ND_3$	1.0138	107° 14′
$^{14}ND_3$: $^{15}ND_3$, $^{14}NH_3$	1.0136	107° 04′
$^{15}ND_3$: $^{14}ND_3$, $^{15}NH_3$	1.0137	107° 04′
$^{14}NH_3$: $^{15}NH_3$, $^{14}NT_3$	1.0132	107° 13′
$^{14}ND_3$: $^{15}ND_3$, $^{14}NT_3$	1.0128	107° 02′

[a] The data for the NH_3 and ND_3 species were taken from Helminger, De Lucia, and Gordy, J. Mol Spectrosc. 39, 94 (1971).

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