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Submillimeter-Wave Spectra of Ammonia and Phosphine[†]

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Rotational transitions of different isotopic species of ammonia and phosphine have been observed in the $\frac{1}{2}$- to 1-mm region. The frequency of the $J=0\rightarrow 1$ transition of $^{14}NH_3$ is $572\,496.69\pm 0.60$ Mc/sec and that for $^{15}NH_3$ is $572\,053.18\pm 0.50$ Mc/sec. Spectral constants B_0 observed for the different isotopic species (in Mc/sec) are: 298 114.68 for $^{14}NH_3$, 297 359.32 for $^{15}NH_3$, 154 173.25 for $^{14}ND_3$, and 153 600.82 for $^{15}ND_3$. Structural dimensions for the ground vibrational state of ammonia obtained by isotopic substitution are 1.0136 Å for the bond length and $107°3'$ for the bond angle. For PH_3, the rotational constants obtained (in Mc/sec) are: $B_0=133\,480.15$, $D_J=3.95$, and $D_{JK}=-5.18$; for PD_3 they are $B_0=69\,471.09$, $D_J=1.02$, and $D_{JK}=-1.31$. An upper limit of $\frac{1}{2}$ Mc has been put on the unknown inversion frequency of PH_3.

INTRODUCTION

Although there has been an extensive amount of work done in the centimeter-wave region on the inversion spectrum of ammonia and its hyperfine structure, there have been no previous measurements of the pure rotational spectrum by means of microwave techniques, except for the deuterated species.[1] As a consequence, no microwave determination of the ground-state rotational constant B_0 for NH_3 has been available. Work in the infrared region[2-5] has provided a value for B_0 through the analysis of rotation and rotation-vibration spectra, but a much more precise value can be expected from microwave measurements. The reason for the delay in this measurement for this light simple symmetric-top molecule is the occurrence of its lowest rotational frequency at the very-high microwave frequency of 572 Gc/sec, or at a wavelength of 0.52 mm. Although lines of HCl and CO have been measured in the 0.4 to 0.5-mm-wave region,[6] microwave observations in the half-mm-wave region are still relatively difficult, and the present work on NH_3 at $\lambda = 0.52$ mm represents the highest frequency so far measured for a symmetric-top molecule with microwave techniques. The $J = 0 \rightarrow 1$ rotational transition of ND_3, previously measured,[1] falls at the much lower frequency of 310 Gc/sec, $\lambda = 0.97$ mm. These frequencies have been remeasured to greater precision in the present work.

When the $J = 0 \rightarrow 1$ rotational transition of PH_3 was measured[7] in this laboratory, the second transition, $J = 1 \rightarrow 2$, which falls in the submillimeter-wave region at $\lambda = 0.56$ mm could not be reached. For this reason, microwave values for the stretching constants D_J and D_{JK} have not been available. Infrared values of these constants were used to give the "microwave" value of B_0. In the present work, the $J = 1 \rightarrow 2$ transition has been measured under high resolution, and precise values of D_J and D_{JK} have been obtained. The similar stretching constants for PD_3, already measured with the $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ transitions,[7,8] have been improved by measurement of the $J = 2 \rightarrow 3$ transition. In addition, an upper limit has been put on the inversion frequency of PH_3.

SUBMILLIMETER-WAVE SPECTROMETER

The submillimeter-wave energy source and detector are essentially those designed a number of years ago,[9] and used previously for many spectral measurements in the millimeter and submillimeter region.[10] The source is a klystron-driven crystal harmonic generator with a bombarded silicon crystal supplied us by Burrus, of the Bell Telephone Laboratories. The detector is likewise a small silicon crystal mounted in the waveguide with provision for critical adjustment of the contact point and pressure as explained in the original paper.[9] In the present work, we obtained increased power in the half-mm-wave region by driving the crystal multiplier with a klystron of higher frequency (70 Gc/sec) and of higher power (~200 mw) than was used in most of the earlier work. Frequency measurements were made in the usual way, by comparison of the fundamental frequency with harmonic markers multiplied up from the standard 60-kc frequency of station WWVB. Most measurements were made with a video spectrometer, with the marker displayed over the spectral line on a cathode-ray oscilloscope. The weaker lines were measured also with an automatic recording spectrometer which employs a phase-lock-in detector synchronized with a klystron-source modulator. Details of this system are described elsewhere.[11]

EXPERIMENTAL RESULTS ON $^{14}NH_3$ AND $^{15}NH_3$

Measurements were made of the $J = 0 \rightarrow 1$ rotational transitions of $^{14}NH_3$ and $^{15}NH_3$ in the ground vibrational state. Because of spin statistics,[12] the $J = 0 \rightarrow 1$ is a single line rather than an inversion doublet; this single line is displaced downward in frequency from the hypothetical center or unsplit position by an amount equal to half the sum of the inversion splittings of the $J = 0$, $K = 0$ and the $J = 1$, $K = 0$ levels. The $J = 0 \rightarrow 1$ transitions at 572 Gc/sec (0.52-mm wavelength) were recorded and measured by means of lock-in detection and the eighth harmonic of an OKI 70 V11 klystron. Figure 1 shows the recorder tracing of the $J = 0 \rightarrow 1$ transition of $^{14}NH_3$. The samples of $^{14}NH_3$ and $^{15}NH_3$ were contained in a 30-cm-long G-band absorption cell cooled to dry-ice temperatures. Sufficient line strength was obtained for the video observation of the $^{14}NH_3$ transition at approximately twice the noise level.

Although one would expect to observe a triplet quadrupole hyperfine structure (with 3:5:1 intensity ratio) for the $J = 0 \rightarrow 1$ rotational transition of $^{14}NH_3$ from the ^{14}N nucleus (spin $I = 1$), none was observed. Our inability to resolve this structure is due primarily to the rather large Doppler broadening at this frequency which, at the temperature employed, causes linewidths of the order of 1.4 Mc/sec. Additional broadening was produced by the gas pressure and by the source-frequency modulation used to enhance detection of the lines. The predicted frequency separation of the two strong components of the triplet hyperfine structure is only 1 Mc/sec with an over-all spread of approximately 3 Mc/sec for the triplet. It was noted that the $^{14}NH_3$ transition is slightly broader than that of $^{15}NH_3$ for which there is no nuclear splitting (^{15}N has a spin $I = \frac{1}{2}$).

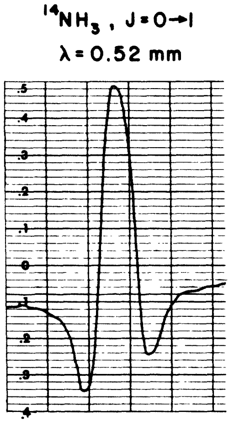

FIG. 1. Recorder tracing of the $J = 0 \rightarrow 1$ rotational transition of $^{14}NH_3$ at 572496.69 Mc/sec.

For the calculation of the rotational constants of $^{14}NH_3$ or of $^{15}NH_3$ one must first ascertain the frequency at which the $J = 0 \rightarrow 1$ rotational transition would occur in the absence of inversion. This frequency is obtained by the addition to the observed $J = 0 \rightarrow 1$ frequency of half the sum of the inversion splittings of the states $J = 0$, $K = 0$ and $J = 1$, $K = 0$. Figure 2 schematically illustrates this procedure. Because of spin statistics, these particular inversion transitions cannot be directly observed; for their evaluation one must resort to the empirical expansions fitting the measured inversion frequencies in the centimeter-wave region and must project backwards for the case of $K = 0$, for which there is no inversion line. The empirical expansions of Schnabel, Törring, and Wilke[13] for $^{14}NH_3$ and $^{15}NH_3$ are used in the present calculation. The center frequencies evaluated by this method are indicated in Fig. 2. Because of the close fitting of the many accurately measured inversion lines, the accuracy of the projected value for $K = 0$ should not be a limiting factor in the evaluation of B_0.

Calculation of the rotational constant B_0 from the center frequency of the $J = 0 \rightarrow 1$ transition is a simple matter: B_0 is determined by substituting the $J = 0 \rightarrow 1$ center frequency just evaluated and the value for the stretching constant D_J into the frequency formula

$$\nu_0 = 2B_0(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \tag{1}$$

for the symmetric-top molecule in the ground vibrational state. Since the last term vanishes for the $K = 0$ lines, D_{JK} is not required for the evaluation of B_0. Because the higher rotational frequencies required for evaluation of the stretching constant D_J fall outside the observable microwave range, a value $D_J = 24.33$ Mc/sec from the infrared vibration-rotation spectrum of $^{14}NH_3$ reported by Mould, Price, and Wilkinson[5] is used. This value is consistent with those published by other investigators[3, 4] and is reported to be somewhat more accurate. The D_J value of $^{14}NH_3$ was used for the $^{15}NH_3$ calculation also, inasmuch as no infrared value for this species was available.

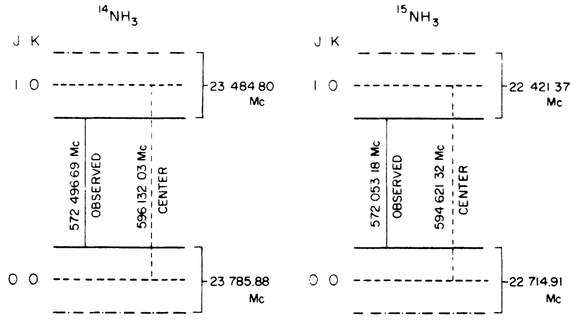

FIG. 2. Energy-level diagrams for the $J=0$ and $J=1$ states of $^{14}NH_3$ and $^{15}NH_3$, showing the observed transitions and the hypothetical levels corresponding to no inversion.

The results of the calculation of the rotational constants for $^{14}NH_3$ and $^{15}NH_3$ as well as a summary of the quantities necessary for their evaluation are presented in Table I. The experimental error may be slightly larger for the rotational constant of $^{15}NH_3$, because the D_J value for $^{14}NH_3$ is assumed in its calculation. However, from the change in D_J with the change in B_0 from $^{14}NH_3$ to $^{14}ND_3$, the difference in D_J for $^{14}NH_3$ and $^{15}NH_3$ is estimated to be within the limits of error of the value for $^{14}NH_3$. Comparison of the microwave value of B_0 for $^{14}NH_3$ with some of the more recent values obtained from infrared measurements (297.99Gc/sec by Hansler and Oetjen,[3] 298.123 Gc/sec by Benedict and Plyler,[4] and 298.114 Gc/sec by Mould, Price, and Wilkinson[5]) indicates that the present microwave measurements increase the accuracy of this constant by a factor of 100.

EXPERIMENTAL RESULTS FOR $^{14}ND_3$ AND $^{15}ND_3$

Measurements were made of the previously unobserved $J = 0 \rightarrow 1$ transition of $^{15}ND_3$, together with a remeasurement of the corresponding transition of $^{14}ND_3$. Rotational transitions for ND_3, like those for NH_3, are split into two components by the inversion. For ND_3, but not for NH_3, the doubling occurs for the $J = 0 \rightarrow 1$ transition also, for which an intensity ratio of 10:1 is predicted by spin statistics for the two components. The frequency separation of the two components of the $J = 0 \rightarrow 1$ transition is again the sum of the inversion splittings of the $J = 0$, $K = 0$ and the $J = 1$, $K = 0$ states. Each of the components of the $J = 0 \rightarrow 1$ transition of $^{14}ND_3$ is further split by the ^{14}N quadrupole coupling into a closely spaced triplet.

Erlandsson and Gordy[1] reported microwave measurements on the two components of the $J = 0 \rightarrow 1$ rotational transition of $^{14}ND_3$, but were unable to obtain sufficient line strength for the measurement of the quadrupole structure of the weaker one. Improvements in submillimeter-wave techniques since that time justify the present remeasurements of this species. The results are listed in Table II. Also given in this Table are our results for $^{15}ND_3$. All of these lines were measured with a spectrometer employing video detection. The fifth harmonic of an OKI 55 V 10 klystron was used for the source power. A 75-cm K-band waveguide was used as the absorption cell during this phase of the experiment.

TABLE I. Values of B_0 for $^{14}NH_3$ and $^{15}NH_3$, and quantities necessary for their calculation.

	$^{14}NH_3$ (Mc/sec)	$^{15}NH_3$ (Mc/sec)
Measured $J=0\rightarrow 1$ transition	572 496.69 ± 0.60	572 053.18 ± 0.50
Inversion splittings[a]		
Δ_{00}	23 785.877	22 714.907
Δ_{10}	23 484.80	22 421.37
$\frac{1}{2}(\Delta_{00}+\Delta_{10})$	23 635.34	22 568.14
$J=0\rightarrow 1$ center frequency	596 132.03	594 621.32
Stretching constant D_J	24.33[b]	24.33[c]
B_0	298 114.68	297 359.32

[a] Reference 13.
[b] $^{14}NH_3$ infrared value of Mould *et al*. (Ref. 5).
[c] Assumed to be the same as that for $^{14}NH_3$ of Ref. b.

Oscilloscope tracings of the two inversion components of the $J = 0 \rightarrow 1$ transition of $^{15}ND_3$ are shown in Fig. 3. The 10:1 intensity ratio of the two inversion components of the $^{15}ND_3$ transition is evident.

A least-squares fit was applied to each inversion component of the $^{14}ND_3$ transition for the simultaneous determination of the quadrupole coupling constant eQq for the ^{14}N nucleus and the frequency of the unsplit inversion component. The results of this calculation are included in Table II, where ν_1 and ν_2 are the frequencies of the respective upper and lower inversion components in the absence of quadrupole splitting. The quadrupole coupling constant −4.10 Mc/sec, derived from the stronger (upper) inversion component, compares favorably with the more accurate value $eQq = -4.080 \pm 0.003$ Mc/sec measured from the low-frequency inversion spectrum of $^{14}ND_3$ by Hermann.[14]

The rotational constant B_0 for ND_3, like that for NH_3, is calculated from the arithmetic mean of the frequencies of the two inversion components of the $J = 0 \rightarrow 1$ transition with the infrared value for the stretching constant D_J. An infrared value of $D_J = 5.85$ Mc/sec from the rotation-vibration analysis of $^{14}ND_3$ by Benedict and Plyler[4] is chosen for this calculation. Assumption of the same value of D_J for $^{15}ND_3$ was made because no infrared data for this species were available. This assumption is justified by the small difference in B_0 for the two species. The values of B_0 for $^{14}ND_3$ and $^{15}ND_3$ which result from this calculation are shown in Table III. The large difference between the present value of the rotational constant for $^{14}ND_3$ and that of Erlandsson and Gordy,[1] 154 162.7 Mc/sec, is partly due to their use of an earlier infrared value, $D_J = 3.4$ Mc/sec, which is considerably smaller and presumably less accurate than the later value used in the present work. The infrared evaluation of B_0 by Benedict and Plyler,[4] when converted to frequency units, is 154 171 Mc/sec for $^{14}ND_3$.

As was pointed out earlier, the separation between the two components of the $J = 0 \rightarrow 1$ transition of ND_3 is the sum of the inversion splittings from the $J = 0$, $K = 0$ and the $J = 1$, $K = 0$ states. The observed separation of the two components of this rotational transition can be compared with measurements made on the direct inversion transi-

TABLE II. Measured frequencies of $^{14}ND_3$ and $^{15}ND_3$.

	Transition	Measured frequency (Mc/sec)	
$^{14}ND_3$	$J=0\rightarrow 1$ upper component		
	$F=1\rightarrow 1$	309 908.46 ± 0.10	$\nu_1 = 309\,909.49$[a] $eqQ = -4.10$
	$F=1\rightarrow 2$	309 909.69 ± 0.10	
	$F=1\rightarrow 0$	309 911.53 ± 0.10	
	$J=0\rightarrow 1$ lower component		
	$F=1\rightarrow 1$	306 735.58 ± 0.20	$\nu_2 = 306\,736.71$[a]
	$F=1\rightarrow 2$	306 736.96 ± 0.20	
	$F=1\rightarrow 0$	306 738.95 ± 0.20	
$^{15}ND_3$	$J=0\rightarrow 1$ upper component	308 606.19 ± 0.05	
	$J=0\rightarrow 1$ lower component	305 750.31 ± 0.07	

[a] ν_1 and ν_2 are transition frequencies corrected for quadrupole splitting.

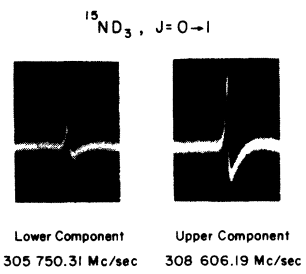

FIG. 3. The two inversion components of the $J = 0 \rightarrow 1$ transition of $^{15}ND_3$ at $\lambda = 0.97$-mm wavelength. The observed intensity ratio of 10:1 agrees with that expected from theory.

tions of ND_3 in the centimeter-wave region.[14], [15] The empirical formula developed by Hermann[14] for the inversion frequencies of $^{14}ND_3$ predicts the sum of the aforementioned splittings to be 3172.64 Mc/sec. This value agrees quite well with the present experimental value for the splitting of the $J = 0 \rightarrow 1$ transition of $^{14}ND_3$, 3172.78 Mc/sec. No such empirical formula for $^{15}ND_3$ is available.

EXPERIMENTAL RESULTS ON PH_3

One purpose of the present work was measurement of the $J = 1 \rightarrow 2$ rotational transition of PH_3 at a wavelength of 0.56 mm in order to obtain the centrifugal stretching constants of PH_3. The $J = 0 \rightarrow 1$ transition was previously measured by Burrus *et al.*[7] In addition to furnishing information on the stretching constants, measurement of the $J = 1 \rightarrow 2$ transition was expected to yield information on the interesting possibility of low-frequency inversion splitting in PH_3 beyond the resolving power available in the infrared region. No evidence of this inversion doubling has been detected[2,16] in the infrared rotational spectrum of PH_3.

If PH_3 has a resolvable inversion doubling, the first transition of the rotational spectrum which will give evidence of this doubling is the $J = 1 \rightarrow 2$ transition. As for NH_3, a single line displaced by the inversion is expected for $K = 0$; but, for $K = 1$, a doublet splitting of twice the inversion frequency of PH_3 should appear. A recording of the $J = 1 \rightarrow 2$ transition of PH_3 at 533 Gc/sec is shown in Fig. 4. These lines were observed through the use of the eighth harmonic of an OKI 70 V11 klystron and a 30-cm *G*-band waveguide absorption cell cooled to dry-ice temperature; measurements were made through use of video detection. Within the resolution of the spectrometer, approximately 1 Mc/sec, there is no evidence of inversion doubling in PH_3. At the temperature and frequency of the observation, the Doppler width is 0.9 Mc/sec. Our measurement places an upper limit of approximately 0.5 Mc/sec on the inversion frequency of PH_3. This result is consistent with the theoretical work of Costain and Sutherland.[17] From an analysis based on the vibrational force constant, they predicted an inversion barrier of 6085 cm^{-1} and a ground-state inversion splitting of 0.14 Mc/sec for PH_3. Jordan,[18] using a semiempirical theory of the low-lying electronic states of the radicals PH and PH_2, predicted a barrier for PH_3 of 12 050 cm^{-1}, which would cause the inversion frequency to be even smaller.

There existed some question as to which of the two components of the $J = 1 \rightarrow 2$ transition should be assigned to $K = 0$ and which to $K = 1$. A calculation of the absorption coefficients for PH_3 (with no inversion splitting) indicates a $K = 0$ to $K = 1$ line-intensity ratio of 4:3. According to the trace of Fig. 4, the stronger of the two components lies at a lower frequency; this component is assigned the value of $K = 0$. For this assignment, the experimentally determined intensity ratio is seen to be in accord with the prediction. Assignment of the lower-frequency line as the $K = 0$ line also indicates that PH_3 has a negative value for the constant D_{JK}, which is found for $^{14}NH_3$ and $^{14}ND_3$[4] as well as for PD_3.

The rotational constant and the two stretching constants for PH_3 are obtained by a substitution of the two measured components of the $J = 1 \rightarrow 2$ transition and the frequency of the $J = 0 \rightarrow 1$ transition, remeasured in the present work, into Eq. (1).

TABLE III. Values of B_0 for $^{14}ND_3$ and $^{15}ND_3$, with quantities necessary for their calculation.

	$^{14}ND_3$ (Mc/sec)	$^{15}ND_3$ (Mc/sec)
$J = 0 \rightarrow 1$ unsplit upper component	309 909.49	308 606.19
$J = 0 \rightarrow 1$ unsplit lower component	306 736.71	305 750.31
$J = 0 \rightarrow 1$ center frequency	308 323.10	307 178.25
Stretching constant D_J	5.85[a]	5.85[b]
B_0	154 173.25	153 600.82

[a] $^{14}ND_3$ infrared value of Benedict and Plyler (Ref. 4).

[b] Assumed to be the same as that for $^{14}ND_3$ of Ref. a.

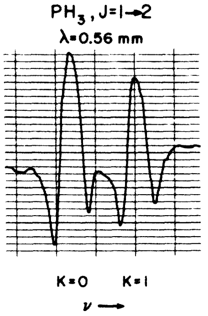

FIG. 4. Recorder tracing of the $J=1\rightarrow 2$ transition of PH_3 at $\lambda=0.56$-mm wavelength. The $K=0$ component has the frequency 533 794.32 Mc/sec and the $K=1$ component has the frequency 533 815.01 Mc/sec.

The measured transitions and calculated constants for PH_3 are given in Table IV.

EXPERIMENTAL RESULTS FOR PD_3

The first microwave investigation[7] of PD_3 included only the $J = 0 \rightarrow 1$ transition. Later, Burrus[8] reported measurement of the $J = 1 \rightarrow 2$ transition. In the present work, these measurements have been extended to include the $J = 2 \rightarrow 3$ transition of PD_3 at 416 Gc/sec (0.72-mm wavelength).

An oscilloscope tracing of the components of the $J = 1 \rightarrow 2$ and $J = 2 \rightarrow 3$ transitions of PD_3 in the ground vibrational state taken during the current investigation is shown in Fig. 5. The technique of displaying different transitions on a common trace is described in an earlier publication.[9] These transitions were observed with the respective fourth and sixth harmonics of an OKI 70 V 11 klystron and a 75-cm K-band absorption cell. The $J = 0 \rightarrow 1$ transition at the second harmonic is eliminated from Fig. 5 by the high-pass filter characteristic of the detector used. The salient feature of the tracing of the $J = 2 \rightarrow 3$ transition is the shift upward in frequency of the components with higher values of K which demonstrates unequivocally that the value of D_{JK} for PD_3 is negative. Burrus has reported a positive value for D_{JK}, reflecting his incorrect assignment of the two components of the $J = 1 \rightarrow 2$ transition.

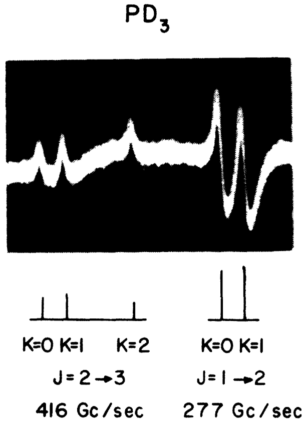

FIG. 5. Simultaneous oscilloscope display of two rotational transitions of PD_3: The $J=1\rightarrow 2$ transition at the fourth harmonic and the $J=2\rightarrow 3$ transition at the sixth harmonic of a klystron oscillating at 69 Gc/sec. The shift upward in frequency of the components with higher values of K demonstrates that the centrifugal stretching constant D_{JK} is negative.

The present measurements of the $J = 2 \rightarrow 3$ transition of PD_3 as well as remeasurements of the $J = 0 \rightarrow 1$ and the $J = 1 \rightarrow 2$ transitions made during the present work are listed in Table V. A least-squares fit was applied to the measured transitions of PD_3 for the calculation of the rotational constants and the two stretching constants. The constants for PD_3 calculated from this fitting are also shown in Table V.

TABLE IV. Measured transitions and calculated constants for PH_3.

Measured transitions	
$J=0\rightarrow 1$, $K=0$	266 944.52 ± 0.04 Mc/sec
$J=1\rightarrow 2$, $K=0$	533 794.32 ± 0.20 Mc/sec
$J=1\rightarrow 2$, $K=1$	533 815.01 ± 0.25 Mc/sec
Calculated constants	
B_0	133 480.15 Mc/sec
D_J	3.95 Mc/sec
D_{JK}	−5.18 Mc/sec

MOLECULAR STRUCTURE OF AMMONIA

In the present work, sufficient data have been obtained from the rotational spectra of several isotopes of ammonia for the undertaking of a number of independent structural calculations. The rotational constants of NH_3 are related to the structural parameters by two equations: that for the moment of inertia about the symmetry axis

$$I_C = 2m_H r^2(1 - \cos\theta) = h/(8\pi^2 C), \tag{2}$$

and that for the moment of inertia about an arbitrary axis perpendicular to the symmetry axis

$$I_B = m_H r^2(1 - \cos\theta) + [m_H m_N r^2/(3m_H + m_N)] \times (1 + 2\cos\theta) = h/(8\pi^2 B), \tag{3}$$

where m_H is the mass of a single hydrogen atom, m_N is the mass of a nitrogen atom, r is the N–H bond distance, and θ is the H–N–H bond angle. Ideally, one would like to have experimental values for both B and C for the simultaneous solution of

TABLE V. Measured transitions and calculated constants for PD_3.

Measured transitions	
$J=0\rightarrow 1,\ K=0$	138 938.17 ±0.03 Mc/sec
$J=1\rightarrow 2,\ K=0$	277 851.71 ±0.04 Mc/sec
$J=1\rightarrow 2,\ K=1$	277 856.93 ±0.04 Mc/sec
$J=2\rightarrow 3,\ K=0$	416 716.39 ±0.20 Mc/sec
$J=2\rightarrow 3,\ K=1$	416 724.18 ±0.20 Mc/sec
$J=2\rightarrow 3,\ K=2$	416 747.81 ±0.20 Mc/sec
Calculated constants	
B_0	69 471.09 Mc/sec
D_J	1.02 Mc/sec
D_{JK}	−1.31 Mc/sec

Eqs. (2) and (3), but use of isotopic substitution is necessary since only the constant B can be extracted from the microwave rotational spectrum.

The method adopted for the evaluation of the ground-state structure of ammonia involves the simultaneous solution of equations for two different isotopic species; a basic assumption for this method is that the bond distance and angle do not change with the isotopic substitution. However, significant changes in the zero-point vibrations can occur when isotopic substitutions of light atoms are made. Because B_0 represents the average over the zero-point vibrations of the reciprocal moment of inertia, the structural parameters are expected to differ slightly for different isotopic species of ammonia, but these differences are neglected in the simultaneous solution of the moment-of-inertia equations for the different isotopic species.

Experimental values for the B_0 of $^{14}NH_3$, $^{15}NH_3$, $^{14}ND_3$, and $^{15}ND_3$ have been obtained in the present work. The ground-state bond distances and angles evaluated through the use of various combinations of these species are shown in Table VI. Values of fundamental constants necessary for these calculations were taken from the work of Cohen and DuMond[19]; atomic masses used were taken from the work of Mattauch, Thiele, and Wapstra.[20]

From their smaller difference in zero-point vibrations, one might expect the most reliable values of Table VI to be those calculated from the pair $^{14}NH_3$ and $^{15}NH_3$ and the pair $^{14}ND_3$ and $^{15}ND_3$. However, the indicated increase in bond length from the N−H to the N−D as obtained from these combinations is in conflict with the decrease in bond length of 0.003-0.005 Å normally observed for a deuterium substitution.[21] Use of the above pairs is believed to be unreliable for the following reason. The substituted N isotope is located only 0.067 Å from the c.m. of $^{14}NH_3$ and 0.113 Å from the c.m. of $^{14}ND_3$. Costain[22] has shown that even for equilibrium constants, isotopic substitution near the c.m. will give large uncertainties in the coordinates.

The substitution method proposed by Costain[22] has also been utilized for the calculation of the structure of ammonia. This method is founded upon the solutions of Kraitchmann[23] for the molecular coordinates in terms of differences of the equilibrium moments of inertia. In the substitution method, the coordinates of an isotopically substituted atom are evaluated in the principal axes of the parent molecule; if possible, isotopic substitutions are made at each atomic position until the structure is determined. Often the use of the c.m. equation is required for the completion of the structure.

Costain has shown that the use of the effective

TABLE VI. Molecular dimensions of ammonia obtained in different ways from microwave values of B_0.

Isotopic species	Bond distance (Å)	Bond angle
	Effective ground-state structure	
$^{14}ND_3$, $^{15}ND_3$	1.0143	107°04′
$^{14}NH_3$, $^{15}NH_3$	1.0139	106°46′
$^{15}NH_3$, $^{15}ND_3$	1.0131	106°32′
$^{14}NH_3$, $^{14}ND_3$	1.0133	106°35′
$^{15}NH_3$, $^{14}ND_3$	1.0133	106°36′
$^{14}NH_3$, $^{15}ND_3$	1.0130	106°31′
	Substitution structure	
$^{14}ND_3$: $^{14}NH_3$, $^{15}ND_3$	1.0136	107°03′ [a]
$^{15}ND_3$: $^{15}NH_3$, $^{14}ND_3$	1.0136	107°03′ [a]
$^{14}NH_3$: $^{14}ND_3$, $^{15}NH_3$	1.0134	106°45′
$^{15}NH_3$: $^{15}ND_3$, $^{14}NH_3$	1.0133	106°45′
	Double-substitution structure	
$^{14}NH_3$, $^{15}NH_3$, $^{14}ND_3$, $^{15}ND_3$	1.0128	107°12′

[a] These are believed to be the most reliable of the structural values.

or ground-state moments of inertia in the Kraitchmann formulation results in a coordinate which is closer to the equilibrium value than is the ground-state coordinate and is virtually independent of the isotopic species employed in its calculation, i.e., zero-point effects are partially canceled. However, substitution structures like ground-state structures suffer from large uncertainties in the coordinates for isotopic substitution near the c.m. In situations where an atom lies close to the c.m., Costain has suggested a procedure for the accurate determination of its position. First the coordinates of atoms away from the c.m. are calculated by means of isotopic substitutions and Kraitchmann's equations. The first-moment equations may then be utilized for the location of the coordinates of the atom near the c.m. In any case, the use of the first-moment equations for the location of light atoms should be avoided.

The structural parameters of ammonia calculated by means of the substitution method are presented in Table VI. One may indeed observe that the spread in the molecular coordinates for the different combinations of isotopic species is much smaller than that for ground-state coordinates. However, a close examination of the substitution method as applied to ammonia reveals that the c.m. condition in an adverse form must be applied for the completion of the structure. Substitutions on the nitrogen atom of the parent molecule lead to equations which may be solved for the nitrogen coordinate along the figure axis. These have the form

$$z_N^2 = \Delta I_1/\mu_1, \qquad (4)$$

where ΔI_1 is the change in the moment of inertia from the parent to the substituted species and μ_1 is the reduced mass for the substitution. This equation may be solved without any additional information. The other possible species of ammonia for which rotational constants are available involves symmetric substitutions of three H or D atoms. A somewhat modified form of Kraitchmann's equations proposed by Chutjian[24] can be applied in these cases for the evaluation of the z and x coordinates of the hydrogen or deuterium atoms. For a parent molecule with hydrogen atoms, these equations have the form

$$\tfrac{3}{2}(m_H - m_D)\, x_H^2 + \mu_2 z_H^2 = \Delta I_2 , \qquad (5)$$

where ΔI_2 is the change in the moment of inertia and μ_2 is the reduced mass for this second type of substitution. It can be seen that the solution of this equation is contingent upon the value for z_N obtained from the previous equation and upon the application of the first-moment equation. In other words, the very small nitrogen coordinate is first located by Kraitchmann's equations; this coordinate is subsequently utilized in the first-moment equation for the location of relatively large coordinates of light atoms.

The double-substitution method of Pierce[25] which is designed for the further reduction of the zero-point vibrational effects on the calculation of a coordinate close to the c.m. was also applied to ammonia; the calculated molecular coordinates are presented in Table VI. In the present application, both the taking of second differences of the moments of inertia of the species involved and the use of first-moment equations are required by this method. The calculated bond distance shows the expected reduction in magnitude; but, because of the stringent requirements placed on the accuracy of the moments of inertia by this method, this bond distance probably contains more uncertainty than do bond distances obtained from the regular substitution method.

Thus, the calculation of the ground-state structure in ammonia is limited in accuracy by the effects of zero-point vibrations and by the uncertainties involved in isotopic substitution near the c.m. Nevertheless, the present microwave structures agree reasonably well with infrared values, especially for ND_3 in which the nitrogen is located at a greater distance from the center of mass than for NH_3. Some uncertainties are also involved in the calculation of the molecular coordinates by the substitution method but the results appear self-consistent and are probably reliable. Perhaps the best of the substitution coordinates are those calculated with the parent molecule $^{14}ND_3$ for which the nitrogen distance from the c.m. is the largest. From experimentally determined infrared values of B_0 and C_0, Benedict and Plyler[4] have calculated a bond distance of 1.0173 Å and an angle of 107°47′ for $^{14}NH_3$ and a bond distance of 1.0155 Å and an angle of 107°35′ for $^{14}ND_3$. From the constants B_e and C_e for $^{14}NH_3$ and $^{14}ND_3$. they obtained the equilibrium bond distances and bond angles: 1.0124 Å and 106°40′ for $^{14}NH_3$, and 1.0108 Å and 106°42′ for $^{14}ND_3$ (theoretically these equilibrium structures should be the same). It may be seen from Table VI that the substitution bond distances calculated from microwave data fall between the ground-state and the equilibrium values of Benedict and Plyler. The bond length obtained from the double substitution method falls quite close to the equilibrium values.

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$K\alpha_2/K\alpha_1$ X-Ray Intensity Ratios for $Z>50$[†]

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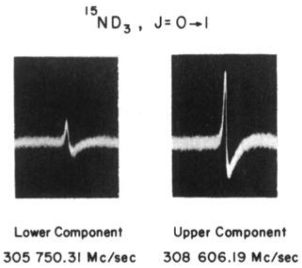
The $K\alpha_2/K\alpha_1$ x-ray intensity ratios for 36 elements between $_{51}$Sb and $_{95}$Am have been measured with a Cauchois-type bent-crystal spectrometer and a Ge(Li) detector. The present experimental results are systematically 5–10% higher than the values reported by Beckman and by Wapstra *et al.*, but agree within experimental errors with the recent theoretical calculations of Scofield.

INTRODUCTION

Measurements of the $K\alpha_2/K\alpha_1$ x-ray ratios have been carried out by Williams $(24 \leq Z \leq 52)$,[1] Meyers $(23 \leq Z \leq 49)$,[2] and Beckman $(73 \leq Z \leq 92)$.[3,4] In addition to these systematic studies, there have been measurements made on a few specific elements. Wapstra *et al.*[5] give a table of $K\alpha_2/K\alpha_1$ x-ray ratios as a function of Z for $16 \leq Z \leq 100$. Their values are derived from a graph drawn smoothly through the experimental values of Williams, Meyers, and Beckman.[1–4]

Relativistic calculations have been carried out by Massey and Burhop,[6] Laskar,[7] Payne and Levinger,[8] Asaad,[9] Taylor and Payne,[10] Babushkin,[11] and recently by Scofield.[12] Only Babushkin and Scofield properly include the effect of retardation. Babushkin uses a Coulomb potential with an effective nuclear charge to account for the screening of the nucleus by the electrons, while Scofield[12] uses the central potential given by the relativistic Hartree-Slater theory. Scofield's theoretical values are larger than those of Babushkin[11] which in turn are larger than the experimental values of Beckman[3,4] and the smooth curve of Wapstra *et al.*[5] Because of these discrepancies and the lack of experimental values between $_{53}$I and $_{72}$Hf, we have measured the $K\alpha_2/K\alpha_1$ x-ray ratios for elements with $Z>50$.



$^{15}ND_3$, $J = 0 \rightarrow 1$

Lower Component
305 750.31 Mc/sec

Upper Component
308 606.19 Mc/sec

FIG. 3. The two inversion components of the $J = 0 \rightarrow 1$ transition of $^{15}ND_3$ at $\lambda = 0.97$-mm wavelength. The observed intensity ratio of 10:1 agrees with that expected from theory.

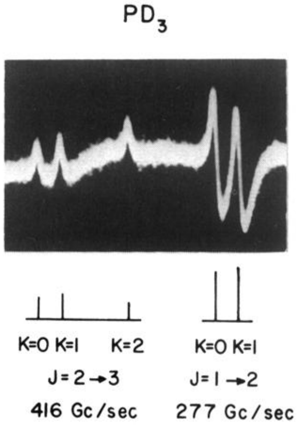


FIG. 5. Simultaneous oscilloscope display of two rotational transitions of PD_3: The $J = 1 \rightarrow 2$ transition at the fourth harmonic and the $J = 2 \rightarrow 3$ transition at the sixth harmonic of a klystron oscillating at 69 Gc/sec. The shift upward in frequency of the components with higher values of K demonstrates that the centrifugal stretching constant D_{JK} is negative.