Hyperfine Structure in the Spectrum of N\textsuperscript{14}H\textsubscript{3}.† I. Experimental Results

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The structure of the hyperfine spectrum of N\textsuperscript{14}H\textsubscript{3} in the microwave region has been carefully re-examined. It has been found that the N\textsuperscript{14} quadrupole line spacings for \( K \neq 1 \) can be fitted within experimental error to previously developed theory, provided a small change in the quadrupole coupling constant \( eQ \) due to centrifugal distortion of the molecule is allowed for. For \( K = 1 \) and \( J = 2, 3, 4 \), a doubling of each line of the quadrupole pattern has been found which increases from about 70 to 150 kc/sec with increasing \( J \). It has been possible to explain these new features of the spectrum in terms of the interactions of the magnetic moments of the protons with the molecular magnetic field caused by rotation and with the magnetic moment of the N\textsuperscript{14} nucleus.

I. INTRODUCTION

SINCE the first measurements by Cleton and Williams\textsuperscript{1} on the inversion spectrum of the symmetric top molecule NH\textsubscript{3} in the radio-frequency range, a great number of increasingly detailed investigations of this spectrum have been made.\textsuperscript{2} A hyperfine spectrum arising from the interaction of the nitrogen quadrupole moment \( Q \) with the gradient of the molecular electric field \( g \) at that nucleus was found and explained. Later a more extended and careful set of measurements\textsuperscript{3} showed that a simple quadrupole interaction would not completely fit the data. The addition of a term \( c I J \) to the molecular Hamiltonian by Henderson\textsuperscript{4} (\( I_N \) is the nitrogen spin, \( J \) the total angular momentum of the molecule exclusive of nuclear spin) accounted for discrepancies within their experimental accuracy. However, experimental errors were on the average about 25 percent of the \( I_N \cdot J \) corrections applied to the quadrupole line spacings. Further, a doubling of the main absorption lines for \( J = 3, 4 \) and \( K = 1 \) (\( K \) is the projection of \( J \) on the molecular symmetry axis) had been observed\textsuperscript{5} and were still completely unexplained.

A careful re-examination of the hyperfine NH\textsubscript{3} spectrum shows that the quadrupole line spacings for \( K \neq 1 \) can be fitted to within our experimental error of ±3 kc/sec provided that, in addition to Henderson’s \( I_N \cdot J \) term, a change in the quadrupole coupling constant \( eQ \), due to centrifugal distortion of the molecule is allowed for. For \( K = 1 \), the above mentioned doubling was found in both the main lines and their satellites for \( J = 2, 3, 4 \). This doubling differs for each line of the quadrupole pattern and increases with \( J \), representative values being from 70 to 150 kc/sec. It has been possible to explain these new features of the spectrum in terms of the interaction of the magnetic moments of the three protons with the molecular magnetic field caused by rotation and with the magnetic moment of the N\textsuperscript{14} nucleus. We shall present the details of the theory in the following article, which we shall refer to as paper II, and make use of the results therein without further justification here.

II. HYPERFINE STRUCTURE IN N\textsuperscript{14}H\textsubscript{3}, WHEN K \neq 1

Experimental Results

Energy due to hyperfine interactions between the nitrogen and the remainder of the NH\textsubscript{3} molecule is given to a good approximation by

\[
W_{JKF_1} = -eQ\left[\frac{1}{J+1} - \frac{3K^2}{J(J+1)}\right] \times \frac{3I_N \cdot J \pm \frac{3I_N \cdot J - I_N(I_N+1)J(J+1)}{2I_N(2I_N-1)(2J-1)(2J+3)}}{J(J+1)} + \left[\frac{(b-a)K^2}{J(J+1)}\right] I_N \cdot J. \tag{1}
\]

The first term of (1) is due to the interaction between the nuclear quadrupole moment \( Q \), and the gradient of the electric field \( g = \nabla V/\nabla \phi \) at the nucleus due to other molecular charges.\textsuperscript{6} The second terms represent the interaction between the magnetic moment of the nitro-

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\textsuperscript{3} J. W. Simmons and W. Gordy, Phys. Rev. 73, 713 (1948).

\textsuperscript{4} R. S. Henderson, Phys. Rev. 74, 107 (1948); Erratum: Phys. Rev. 74, 626 (1948); also see J. M. Jauch, Phys. Rev. 74, 1292 (1948).

\textsuperscript{5} W. E. Good reported this finding to the Ohio State Symposium on Molecular Structure and Spectroscopy in 1947 (unpublished).

\textsuperscript{6} J. Bardeen and C. H. Townes, Phys. Rev. 73, 97 (1948).
gen nucleus and magnetic fields produced by molecular rotation. Magnetic interactions associated with the hydrogen nuclei can be neglected to a good approximation, as will be shown in the following.

The transition $\Delta F = 0, \pm 1$ which are allowed give from (1) three strong lines of identical frequency and two weaker satellites on either side of these.

The experimental data for $K \neq 1$ listed in Table I were initially fitted by the method of least squares to the satellite intervals predicted from Eq. (1). The deviations found between experimental satellite separations and the calculated separations showed a decreasing trend with increasing $J$ and $K$. The square root of the average square deviation, $\delta$, of the inner satellite to main line separation is $3.3$ kc/sec and this quantity is $5$ kc/sec for the outer satellite to main line separations. The experimental error was estimated to be $\pm 3$ kc/sec for $K \neq 1$ (see Sec. III).

An investigation of the theoretically predicted proton effects (see below) revealed that these systematic deviations could not be attributed to them. Previous molecular beam investigations of $I_K \cdot J$ interactions have indicated a possible dependence of the coefficient, $c$, on $J$. Calculation of the corrections needed to a pure quadrupole hyperfine line pattern in order to secure agreement with the experimental data clearly shown that the $I_K \cdot J$ coefficient would have to increase with $J$ for the outer satellites and decrease with $J$ for the inner ones. The dependence of this coefficient on $J$ could be caused by a rotational perturbation of the molecular electronic wave functions but such a perturbation should be independent of the orientation of the nitrogen spin relative to $J$.

Centrifugal distortion of the molecule may be expected to cause the gradient of the electric field $q$ at the nitrogen to be a function of $J$ and $K$. This effect depends on the molecular rotational energy and we may therefore write

$$q = q_0 + d_4 J(J + 1) + d_4 K^2.$$

The values of $d_0$, $d_1$, $d_2$ which minimize $\delta = \frac{1}{n} \sum (r_i - \bar{r}_i)^2/n$ where $\bar{r}_i$ is the deviation of the experimental separation from the calculated one, are $d_0 = 1 - 4 \times 10^{-4}$, $d_1 = 10^{-4}$, $d_2 = 10^{-4}$. These values reduce $\delta$ to $1.7$ kc/sec for the inner satellites and $2.8$ kc/sec for the outer ones. The coupling constants are then:

$$\begin{align*}
 q &= q_0 + 4084.2 \times 10^{-4} J(J + 1) + 10^{-4} K^2 \pm 0.3\text{ kc/sec,} \\
 a &= 6.1 \pm 0.2\text{ kc/sec} \\
 b &= 6.5 \pm 0.2\text{ kc/sec.}
\end{align*}$$

Calculated separations of the satellites from the main lines using the values above, are given in Table I. The errors listed are believed to be random.

On the basis of the above fit of theory and experiment, one can say that the $I_K \cdot J$ coefficient is constant

\[ J \text{ C. Swartz and J. W. Trischka, Phys. Rev. 88, 1085 (1952).} \]

**TABLE I.** Comparison of experiment and theory not including effects due to proton magnetic moments. Intervals are given in kc/sec relative to the inverison transition frequency without hyperfine structure. Theoretical positions were calculated with the aid of (1) assuming

$$\begin{align*}
 q &= -4084.2 \times 10^{-4} J(J + 1) + 10^{-4} K^2 \pm 0.3\text{ kc/sec,} \\
 a &= 6.1 \pm 0.2\text{ kc/sec,} \\
 b &= 6.5 \pm 0.2\text{ kc/sec.}
\end{align*}$$

Within $5\%$ from $J = 2$ to $J = 7$. This is in contrast to the results of some molecular beam experiments\(^8\) in which, for the same range of rotation energies,\(^9\) changes of the coefficient by a factor of as much as $2$ have been reported.

It should be noted that the quadrupole coupling constant, $q$, contains a small percent of pseudo-quadrupole effect\(^10\) in addition to the pure quadrupole coupling of the nitrogen since these two effects are indistinguishable in their dependence on the quantum numbers (see NH\(_3\), paper II).

**III. APPARATUS AND EXPERIMENTAL DETAILS**

**A. Apparatus**

Part of the above measurements were made with a high-resolution balanced bridge spectrometer designed and built by S. Geschwind. A detailed account of the considerations involved in the construction of such an instrument will be found in Geschwind's thesis.\(^11\) The measurements were completed with a modified version of Geschwind's instrument incorporating low-frequency Stark modulation. The original instrument's sensitivity had been limited to minimum detectable absorptions of the order of $c \approx 3 \times 10^{-8}$ because it was not possible to completely eliminate spurious signals arising from bridge unbalances caused by frequency dependent reflections. In addition the sensitivity was also reduced by other undesired signals originating in unsymmetric guide vibrations, minor unstabilities in the sensitive detecting circuits and in pick up on these circuits.

\[ ^{8} \text{M. Danos and S. Geschwind, Phys. Rev. 91, 1159 (1953).} \]

\[ ^{9} \text{This change is reported between } J = 1 \text{ and } J = 25 \text{ for LiF}^{19}. \]

\[ ^{10} \text{Since the moment of inertia of LiF is about nine times that of NH\(_3\), } J = 7 \text{ for NH\(_3\) involves approximately the same rotational energy as } J = 25 \text{ for LiF.} \]

\[ ^{11} \text{H. M. Foley, Phys. Rev. 72, 504 (1947). He has discussed this effect for diatomic molecules.} \]

The spectrometer described above can detect a minimum gas absorption, \( \alpha_e \), of \( \alpha_e \leq 5 \times 10^{-9} \) for an effective band width of 10 cps, and has maintained the high resolution of the original instrument. At present it is impossible to use a recorder with the accompanying reduction in band width of the detecting system because the signal klystron, the source of microwave power, is not sufficiently stable in frequency.

**B. The Measurements**

**For \( K \neq 1 \)**

The data given in Table I were taken at room temperature with satellite lines 100 kc/sec wide at half-amplitude and with main lines, which was slightly power saturated, 150 kc/sec wide. The tabulated separations are one-half the measured intervals between symmetrically placed satellites. In each case the position of the main line was also measured as a check on the expected symmetry of the line pattern. A careful re-examination of the lines for \( J = 2, K = 2; J = 3, K = 3; J = 5, K = 5 \) at \(-78^\circ C\) with satellite line widths of 80 kc/sec revealed no additional features of the spectrum beyond those already discussed. The stated experimental error of \( \pm 3 \) kc/sec represents the average deviations of several measurements. For a few values of \( J \) and \( K \), measurements first made on the original spectrometer and associated frequency measuring devices

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10 R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).
11 We are indebted to Mr. R. Blume who designed and built the frequency standard used.

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**Fig. 1. Schematic diagram of high-resolution spectrometer.**

**Fig. 2. Hyperfine structure of \( N^4H_2 \) inversion spectrum for \( J = 2, K = 1 \). (a) Photograph of oscilloscope trace. (b) Calculated hyperfine spectrum and corresponding line shapes. Frequency increases from left to right.**
were repeated to within 2 kc/sec on the rebuilt machine and frequency measuring system one year later.

For $K = 1$

As described above the splittings encountered here ranged from 70 to 150 kc/sec and thus were of the order of magnitude of the line widths. For this reason every effort was made to obtain narrow lines even at a large sacrifice in their intensity. All the measurements were made at NH$_3$ pressures of less than $10^{-4}$ mm, at power levels of the order of 10 $\mu$w/cm$^2$, and at a temperature of $-78^\circ$C. Under these conditions the mean free path of the gas molecules was several times the cross-sectional dimensions of the x-band Stark guide which was used. Line widths, to which intermolecular collisions contributed negligibly, were determined by wall collisions and Doppler effect. The maximum absorptions, which at these pressures are proportional to the gas density, were down by a factor of about 50 from those given$^2$ for lines broadened only by intermolecular collisions. Theoretical line widths under these conditions are$^5$ Doppler width at half-amplitude = 60 kc/sec = $2\Delta v_D$; wall collision width at half-amplitude = 30 kc/sec = $2\Delta v_w$ and total line width $2\Delta v = 2((\Delta v_D)^2 + (\Delta v_w)^2)^{1/2} = 67$ kc/sec.

Experimentally these line widths were difficult to attain. In order to completely avoid saturation of the lines, the power level had to be reduced to such a low value that the automatic frequency control system did not function very satisfactorily. This, plus the theoretically expected decrease in sensitivity with a decrease in power resulted in rather poor sensitivity under conditions of optimum resolution. The observed spectra reproduced in Figs. 2 and 3 were taken at gas pressures sufficiently high to reduce the above difficulties and hence not at maximum resolution.

In Figs. 2 and 3 the theoretical patterns are drawn for various assumed line widths. At maximum resolution, the separations between line peaks or points of maximum curvature were measured for $J = 2, 3, 4$ with special attention to the case $J = 2$ from which most information could be hoped to be gained. These separations are listed in Table II. Measurements for $J = 3$ were made with a line pattern approximately as drawn in the theoretical plots. In the case $J = 4$, it was possible to completely resolve line No. 7 of the pattern and a direct measurement of its width gave

$$2\Delta v = 64 \pm 8 \text{ kc/sec}.$$  

Choice of the theoretical plots which gave the best fit of the measurements in the case $J = 2$ indicate a line width at maximum resolution of

$$2\Delta v = 68 \pm 5 \text{ kc/sec}.$$  

These measurements confirm the theoretical line widths given above which were calculated according to the theory of Danos and Geschwind.$^8$
Table II. Hyperfine spectrum of NH₂ for \( K = 1 \). Lines are numbered by groups in order of increasing frequency. Measured intervals are all in ksec. Separations are given from a line undisplaced by hyperfine structure. Intensities are in percent of the total intensity of all the transitions.

<table>
<thead>
<tr>
<th>( J = 2 ) Line</th>
<th>Transitions ( F_i, F'_i \rightarrow F_i', F'_i' )</th>
<th>Relative intensity</th>
<th>Measured separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 3/2 \rightarrow 2, 5/2</td>
<td>3.01</td>
<td>-1047 \pm 3</td>
</tr>
<tr>
<td>2</td>
<td>1, 1/2 \rightarrow 2, 3/2</td>
<td>2.35</td>
<td>-968 \pm 3</td>
</tr>
<tr>
<td>3</td>
<td>3, 7/2 \rightarrow 2, 5/2</td>
<td>3.26</td>
<td>-689 \pm 3</td>
</tr>
<tr>
<td>4</td>
<td>3, 5/2 \rightarrow 2, 3/2</td>
<td>2.07</td>
<td>-652 \pm 3</td>
</tr>
<tr>
<td>5</td>
<td>3, 7/2 \rightarrow 3, 7/2</td>
<td>47.5</td>
<td>-24 \pm 3</td>
</tr>
<tr>
<td>6</td>
<td>3, 5/2 \rightarrow 3, 5/2</td>
<td>32.0</td>
<td>36 \pm 3</td>
</tr>
<tr>
<td>7</td>
<td>2, 5/2 \rightarrow 3, 7/2</td>
<td>2.96</td>
<td>646 \pm 3</td>
</tr>
<tr>
<td>8</td>
<td>2, 5/2 \rightarrow 3, 5/2</td>
<td>2.22</td>
<td>708 \pm 3</td>
</tr>
<tr>
<td>9</td>
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<td>3.34</td>
<td>978 \pm 3</td>
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<tr>
<td>10</td>
<td>2, 3/2 \rightarrow 1, 1/2</td>
<td>1.68</td>
<td>1065 \pm 3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( J = 3 ) Line</th>
<th>Transitions ( F_i, F'_i \rightarrow F_i', F'_i' )</th>
<th>Relative intensity</th>
<th>Measured separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2, 3/2 \rightarrow 3, 5/2</td>
<td>1.07</td>
<td>-1426 \pm 3</td>
</tr>
<tr>
<td>2</td>
<td>2, 5/2 \rightarrow 3, 7/2</td>
<td>1.60</td>
<td>-1312 \pm 3</td>
</tr>
<tr>
<td>3</td>
<td>4, 7/2 \rightarrow 3, 5/2</td>
<td>1.19</td>
<td>-1098 \pm 3</td>
</tr>
<tr>
<td>4</td>
<td>4, 9/2 \rightarrow 3, 7/2</td>
<td>1.50</td>
<td>-1004 \pm 3</td>
</tr>
<tr>
<td>5</td>
<td>4, 7/2 \rightarrow 4, 7/2</td>
<td>38.3</td>
<td>-53 \pm 3</td>
</tr>
<tr>
<td>6</td>
<td>3, 5/2 \rightarrow 3, 5/2</td>
<td>35.2</td>
<td>41.6</td>
</tr>
<tr>
<td>7</td>
<td>4, 9/2 \rightarrow 5, 11/2</td>
<td>0.89</td>
<td>71 \pm 4</td>
</tr>
<tr>
<td>8</td>
<td>4, 7/2 \rightarrow 5, 9/2</td>
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<td>1285 \pm 4</td>
</tr>
<tr>
<td>9</td>
<td>4, 9/2 \rightarrow 3, 7/2</td>
<td>0.89</td>
<td>1393 \pm 4</td>
</tr>
<tr>
<td>10</td>
<td>4, 7/2 \rightarrow 3, 5/2</td>
<td>0.69</td>
<td>1539 \pm 4</td>
</tr>
</tbody>
</table>

*Theory shows that these transitions though not observed are not to be associated with the stronger satellites. See Fig. 3.*

IV. A COMPARISON OF EXPERIMENT AND THEORY ALLOWING FOR EFFECTS DUE TO THE PROTON MAGNETIC MOMENTS

Case \( K = 1 \)

Inspection of Figs. 2 and 3 reveals that the spectrum for \( K = 1 \) is quite different from that for other values of \( K \). For low \( J \), the splitting of the quadrupole lines into pairs is small. It is too small for our spectrometer to resolve when \( J = 1 \) but becomes of the same order as the intersatellite spacings for \( J = 4 \). A splitting of the same magnitude was found in the microwave lines of N³H₂ as shown in Table IIIb. Since N¹⁶ has a spin of 1/2 and hence no quadrupole moment, the spectrum of N³H₂ is considerably simpler than that of N¹⁵H₂. The similarity between observed splittings in N¹⁵H₂ and in N³H₂ indicates clearly that they are not primarily due to the nitrogen nucleus. Since the protons interact with the rest of the molecule by virtue of their magnetic moments, one is led to consider (1) the interaction of the protons with the molecular fields due to rotation—an \( I \cdot J \) type interaction, (2) their dipolar interactions
with the nitrogen magnetic moment and (3) their mutual dipolar interactions. In paper II these interactions and other small effects are all considered for the case $K=1$ and for the case $K=1$. The energy levels are derived there in terms of the geometrical parameters of the molecule, of certain magnetic coupling parameters dependent on the electronic states (the $a, b$ of Henderson mentioned above and similar coefficients $a, b, g$ for the protons) and of the angular momentum quantum numbers of the molecule. In order to save space the reader will be referred to this paper for the formulas we are about to discuss. The parameters $a, b, g$ which are dependent on the ground- and excited-state electronic wave functions cannot be evaluated theoretically since little is known about these functions. Because these constants can most readily be evaluated experimentally for the case $K=1$, and because this evaluation does not depend on the coefficients, $a, b$, we shall discuss the case $K=1$ first, returning to the case $K=1$ to show that the proton perturbations do not significantly alter the results obtained from this case.

Close inspection of Figs. 2 and 3 will reveal the following qualitative features. (1) The relative intensities of the two members of each doublet alternate as $J$ varies from odd to even. (2) The splittings of the outer satellites are greatest in all cases. (3) For $J=2$ the lower-frequency satellites are less split than the higher-frequency ones. This effect reverses with $J$ and decreases with increasing $J$. As shown in the following pages, the alternation of relative intensities of the two members of each doublet with $J$ is a consequence of the requirement that the total wave function must be antisymmetric to proton exchange. The formulas for the energy levels are calculated in paper II and an energy level diagram is shown in Fig. 5 of paper II.

These lead to the following expressions for the frequencies of the lines of the NH$_2$ inversion hyperfine spectrum:

\[
\nu = \nu_0 + \left\{ \begin{array}{l}
(a + \beta - \alpha) K^2 / [J(J + 1)]

\times \left[ C(F'_1, J) - C(F_1, J) \right] \\
+ [A + CK^2 / [J(J + 1)] \right] \times \left[ G(J, F'_1, F') - G(J, F_1, F) \right] \\
+ D_2 \left[ \delta(J, F'_1, F') - \delta(J, F_1, F) \right] \{1 - 3 / [J(J + 1)]\} \\
+ \delta_{K_1} (-1)^J \left[ B \left[ G(J, F'_1, F) + G(J, F_1, F) \right] \\
+ D_2 \left[ \delta(J, F'_1, F') + \delta(J, F_1, F) \right] \right],
\end{array} \right.
\]

where

\[
C(F_1, J) = I_N \cdot J, \quad A = \alpha + \rho, \quad B = \rho - \alpha, \quad C = \gamma - (\alpha + \rho).
\]

\[
G(J, F_1, F) = (I \cdot F_1) / [F_1(J + 1)],
\]

\[
D_1 = g_N g_H \delta / \nu R(1 - \frac{3}{2} \sin^2 \theta) / \nu,
\]

\[
\delta(J, F_1, F) = 2(F_1 \cdot F_2) [F_1(J + 1)],
\]

\[
D_2 = g_N g_H \delta / \nu R^3 \sin \theta \nu,
\]

\[
\delta_{K_1} = 1 \quad \text{for} \quad K = 1,
\]

\[
= 0 \quad \text{for} \quad K \neq 1.
\]

$\nu_0$ represents the transition frequency due to the usual inversion energy plus the quadrupole hyperfine structure of the nitrogen nucleus. The parameters employed above which have not been described are identified in paper II, Eqs. (13), (10), and (B1). The first four terms of (2) arise from the parts of the total molecular Hamiltonian which are diagonal in $K$ while the last two terms express the removal of the $K$ degeneracy when $K=1$. The term involving $C(F_1, J)$ arises in the nitrogen $I_N \cdot J$ interaction of (11); terms involving the function $G(J, F_1, F)$ are due to the proton interaction with magnetic field due to molecular rotation $(I \cdot J)$; and finally terms involving the $\delta(J, F_1, F)$ function are due to the nitrogen-proton dipolar interaction. As can be seen from Figs. 2 and 3 the theoretical plots for the line pattern which are discussed below are in good agreement with the experimentally observed patterns. The splitting of the main lines is almost wholly de-
dependent on the $\mathbf{I} \cdot \mathbf{J}$ parameter, $B$, while the satellite splittings are largely but not so exclusively dependent on this parameter. The different splitting of the lower-frequency satellites from the higher-frequency ones depend on the $A$ and $C$ terms which are diagonal in $K$. Finally, the different splitting of the outer and inner satellites is caused by the proton-nitrogen dipolar interaction. Because the order of the allowed energy levels and hence the sequences of line intensities depends on the proton statistics and because the splittings due to the latter interaction can be calculated from the geometrical constants of the molecule, the experiment constitutes another corroboration of these statistics as being Fermi-Dirac (incidentally, this corroboration shows that the phases of the rotational wave functions given in paper II are correct).

Keeping in mind the above discussed dependence of the splittings on the parameters $A$, $B$, $C$, we very carefully measured the splitting of the transition $\Delta F = 0$ (main line) for $J = 4$ under conditions of maximum resolution. This gave a reliable value of the constant $B$. The values of $A$, $C$ were then determined so as to give the best fit to the measured splittings under highest resolution for $J = 2$ where they are most important. We then used the values so determined, which are independent of the constants $a$, $b$ of the Henderson effect, to draw up the predicted spectral patterns assuming several different line widths in cases in which the measured separations would have depended on these line widths. These drawings were used to obtain final values of $A$, $B$, $C$ essentially by a method of trial and error and to check on the measured line widths. It should again be remarked that the photographs given in Figs. 2 and 3 were not obtained under conditions of maximum resolution. For instance for $J = 2$ the intermediate set of theoretical curves with a line width 70 kc/sec comes closest to the pattern actually observed during the course of the measurements. Unfortunately, the splittings are only weakly dependent on $A$, $C$ so that these constants could not be precisely determined. The best fit was obtained with

$$A = -10 \pm 10 \text{ kc/sec}, \quad B = 14.4 \pm 0.2 \text{ kc/sec},$$

$$C = 0 \pm 60 \text{ kc/sec},$$

where the stated errors indicate the range of values for which the fit obtained was still within the experimental error.

The measured, calculated, and corrected splittings are given in Table III(a) together with the similar splittings in $\text{N}^4\text{H}_3$ in Table III(b) for comparison. The fit is within our experimental error but is not as good for $J = 4$ as it is for $J = 2, 3$, probably because of the greater difficulty in making the measurements in this case. Using the above data, and the calculated intensities listed in Table II we have calculated the position of the "centers of gravity" of the unsplit lines for $K = 1$ and have included them in Table I for comparison with the cases for $K \neq 1$. It will be seen that the agreement is approximately as good as that found for $K + 1$ in spite of the larger experimental errors for $K = 1$. The deviation of the calculated average position of the outer satellites for $J = 4$ is several times the probable error of the whole set of measurements. We have not found a satisfactory explanation for this discrepancy.

**Case $K \neq 1$**

In this case the expected is obtained from the first four terms of (2) and has been plotted for a typical case in Fig. 4.

In specie of Fig. 4 might lead one to expect that for $K \neq 1$ the results listed in Table I should still show systematic deviations because of the unsymmetrical nature of the actual satellites which experimentally were not resolved. The splittings of a satellite line in this case as shown in Eq. (2) depend on the constants $A$, $C$. The fact that no structure was found is consistent with the line widths which we were able to achieve and with the values of the constants $A$ and $C$ determined above. Calculation of the shift of the peak of the lines due to the small displaced subsatellites shows that for low $J$ they are separated by about 40 kc/sec from the other two satellite components and, not being resolved, caused negligible shift in the center of gravity, while for higher $J (\approx 7)$ their intensities are so small that this effect is again negligible. We conclude therefore that Eq. (1) represents the results of our experiment satisfactorily when $K \neq 1$.

**Other Effects**

The formula (2) contains, we believe, all the features of the $\text{NH}_3$ hyperfine spectrum observable with a microwave spectrometer of sensitivity and resolving power comparable with what is now available. In the derivation of these relations we have neglected all effects which could reasonably be estimated to be too small to observe by at least two orders of magnitude (see paper II). The only interactions which should be mentioned in addition to those discussed above are the

![Fig. 4. Schematic drawing of the calculated structure of $\text{N}^4\text{H}_3$, inversion spectrum for a low value of $J$ and $K + 1$.](image)
pseudquadrupole effect,\textsuperscript{18} and the interaction of the nuclear magnetic moments with each other through the intermediary of the electronic magnetic moments.\textsuperscript{14} The former effect is not separable from the true nuclear quadrupole effect. The energy involved in the latter effect is less than 1 kc/sec in most known cases. In order to obtain more precise information a few cubic centimeters of liquid \(\text{NH}_3\) were sealed in a thin walled glass tube and Hahn of the Watson Laboratories kindly examined the proton resonance in the \(\text{NH}_3\) vapor in equilibrium with the liquid by means of the spin echo technique.\textsuperscript{15} The resonance was observed with a sample vapor pressure of several atmospheres to a sample vapor pressure of the order of 40 atmospheres. The strong resonance signal was found to be without a trace of the modulations which would be caused by the above-mentioned effect. From this result Hahn was able to inform us that the magnitude of the interaction is certainly less than 300 cps and most probably less than 100 cps. Thus it would not be experimentally detectable by us.

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\textsuperscript{14} N. F. Ramsey and E. M. Purcell, Phys. Rev. \textbf{85}, 143 (1952).
\textsuperscript{15} E. L. Hahn, Phys. Rev. \textbf{80}, 580 (1950); \textbf{88}, 1070 (1952).

\section*{Hyperfine Structure in the Spectrum of \(\text{N}^{14}\text{H}_3\).\textsuperscript{†} II. Theoretical Discussion}

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The new features in the hyperfine spectrum of \(\text{N}^{14}\text{H}_3\) described in the preceding paper are shown to be due to the interactions of the magnetic moments of the three protons with the molecular magnetic field caused by rotation and with the magnetic moment of the \(\text{N}^{14}\) nucleus. Since the protons are off the molecular symmetry axis, these interactions are of a form different from that usually encountered. They possess matrix elements connecting states differing by two units in symmetric top quantum number \(K\) and are capable, therefore, of lifting the degeneracy between states for which \(K = -1\) and \(K = 1\). A systematic treatment of the problem of the hyperfine interactions in this molecule has been made in order to find any other effects detectable with present equipment.

\section*{I. INTRODUCTION}

E\text{A}RLY measurements of the hyperfine structure of the inversion spectrum of ammonia were interpretable\textsuperscript{1} as due to an interaction between molecular electric fields and the quadrupole moment of \(\text{N}^{14}\). More accurate measurements\textsuperscript{2} indicated that small interactions between the \(\text{N}^{14}\) magnetic moment and a magnetic field due to molecular rotation were also present.\textsuperscript{3} The new experimental data presented in the previous paper (which we shall refer to as I) shows that several other types of effects are also of importance. Hence, a systematic and comprehensive treatment of the problem has been undertaken in order to find all effects which could conceivably be observed with a microwave spectrometer of sensitivity and resolving power comparable with what is now available. Doubling of the \(K = 1\) lines is shown to be a new manifestation of magnetic hyperfine interactions.

\section*{II. FORMULATION OF THE PROBLEM}

For the purposes of this calculation, the molecular Hamiltonian based on the Pauli approximation to the wave equation can be written as: \textsuperscript{4,5}

\begin{equation}
\begin{split}
3\mathcal{C} = & A(J_z - L_z)^2 + A(J_y - L_y)^2 + C(J_z - L_z)^2 \\
& + \left(\frac{\mu_0}{c}\right) \sum_{K} r \cdot J
\end{split}
\end{equation}

\begin{equation}
\times \left( v - \left( \frac{Z_K M_I}{g_K M_K} \right) v_k \right) g_K I_K
\end{equation}

\begin{equation}
\text{(1.0)}
\end{equation}

\begin{equation}
\text{(1.1)}
\end{equation}

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\textsuperscript{5} L. H. Thomas, private communication. The equation derived on the basis of footnote (35) of Van Vleck's paper (reference 4) is not entirely correct since factors of \(1/r^2\) and \(1/r^4\) were inadvertently left out of his Eq. (37) and the factor \((1 + Z_K M_I/g_K M_K)\) replaces the factors \(1\) in a fashion evident by comparing the expressions (1.1) and (1.3) with his Eq. (37).