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# Measurement of Ammonia Hyperfine Structure with a Two-Cavity Maser*

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Hyperfine structure of the $J$-$K$ = 1-1, 2-2, 3-3, and 3-2 inversion transitions in $N^{14}H_3$ and the 1-1, 2-2, and 3-3 transitions in $N^{15}H_3$ has been measured with a two-cavity maser spectrometer. This device employs Ramsey's method of separated oscillating fields to obtain a molecular resonance linewidth of 350 cps. The theory of Gunther-Mohr *et al.* and of Gordon has been extended to include all terms off-diagonal in $\mathbf{F}_1 \equiv \mathbf{I}_N + \mathbf{J}$ in an attempt to explain some discrepancies between the previous theory and our measurements. The interactions included in this treatment are the nitrogen quadrupole interaction, the nitrogen $\mathbf{I}_N \cdot \mathbf{J}$ interaction, the hydrogen $\mathbf{I} \cdot \mathbf{J}$ interaction, the hydrogen-nitrogen spin-spin interaction, and the hydrogen-hydrogen spin-spin interaction. The strengths of these interactions are treated as adjustable parameters in least-squares fit programs which determine the parameters by fitting the experimental data. There are still significant deviations between theory and experiment for the 1-1, 3-3, and 3-2 transitions of $N^{14}H_3$ and for the 1-1, 2-2, and 3-3 transitions of $N^{15}H_3$. The largest discrepancies occur for the $N^{14}H_3$ 3-2 transition and the 1-1, 2-2, and 3-3 transitions in $N^{15}H_3$ where the quadrupole interaction vanishes. The discrepancies are greater than 1 kHz in these cases. According to the theory, pairs of satellites of the $N^{15}H_3$ 2-2 transition should occur at the same frequency, and these are all split by 4 kHz. In addition, the values of the $N^{15}H_3$ coupling parameters do not agree with theory.

## INTRODUCTION

THE first detailed measurements of ammonia hyperfine structure were made by Gunther-Mohr, White, Schawlow, Good, and Coles,[1] who used a sensitive waveguide spectrometer with a resolution of 100 kHz. A doubling of the $K=1$ lines was observed and explained by magnetic interactions of the hydrogens with the magnetic field due to molecular rotation, and hydrogen-nitrogen spin-spin interactions. This was followed by an extensive theoretical treatment in which Gunther-Mohr, Townes, and Van Vleck[2] (GTV) enumerated all interactions which they believed would produce effects greater than about 1 kHz on ammonia hyperfine structure.

The maser spectrometer built by Gordon[3,4] was used to make measurements with 7-kHz resolution on four rotational states of ammonia. The theory of GTV was extended by Gordon to include the hydrogen-hydrogen spin-spin interaction which is present for the $J=3$, $K=3$ state.

More recently, Hadley did further calculations on the deuterated ammonias[5] and calculated terms off-diagonal in $\mathbf{F}_1$ for the hydrogen-nitrogen spin-spin interaction in the 3-2 rotational state.[6] Normally the nitrogen quadrupole is much larger than the magnetic terms so the coupling scheme is $\mathbf{F}_1 = \mathbf{I}_N + \mathbf{J}$, $\mathbf{F} = \mathbf{I}_H + \mathbf{F}_1$; but the quadrupole interaction vanishes in the 3-2 state so terms off-diagonal in $F_1$ are much more significant. Measurements of the 3-2 transition with 7-kHz resolution were reported by Shimoda and Kondo.[7,8]

We now have data with a factor-of-20 improvement in resolution (350 Hz) and we will need all the spin-spin and spin-rotational ($\mathbf{I} \cdot \mathbf{F}$) terms off-diagonal in $\mathbf{F}_1$. The methods of Condon and Shortley employed by Hadley make calculations and numerical analysis extremely cumbersome, and we shall find it much more convenient to use the $3n$-$j$-symbol formalism discussed by Edmonds[9] and Thaddeus, Krisher, and Loubser.[10] This greatly facilitates data analysis since we are using a computer (IBM 7094) and the $3n$-$j$ symbols are easily calculated by a subprogram.

## ANALYSIS OF DATA

The Hamiltonian, which will be discussed further in the last section, is used to express the energy levels of a given rotational state $(J,K)$ in terms of five adjustable parameters, $Q$, $R$, $S$, $T$, and $U$. These parameters determine the strength of each interaction. The Hamiltonian for the hyperfine structure is expressed in the form

$$\mathcal{H} = C_Q Q + C_R R + C_S S + C_T T + C_U U\,,$$

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[1] G. R. Gunther-Mohr, R. L. White, A. L. Schawlow, W. E. Good, and D. K. Coles, Phys. Rev. **94**, 1184 (1954).

[2] G. R. Gunther-Mohr, C. H. Townes, and J. H. Van Vleck, Phys. Rev. **94**, 1191 (1954).

[3] J. P. Gordon, Phys. Rev. **99**, 1253 (1955).

[4] J. P. Gordon, H. J. Zeiger, and C. H. Townes, Phys. Rev. **99**, 1264 (1955).

[5] G. F. Hadley, J. Chem. Phys. **26**, 1482 (1957).

[6] G. F. Hadley, Phys. Rev. **108**, 291 (1957).

[7] K. Shimoda and K. Kondo, J. Phys. Soc. Japan **15**, 1125 (1960).

[8] K. Kondo and K. Shimoda, J. Phys. Soc. Japan **20**, 437 (1965).

[9] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1960), 2nd ed.

[10] P. Thaddeus, L. C. Krisher, and J. H. N. Loubser, J. Chem. Phys. **40**, 257 (1964).

where

$$Q=-eQq\left[1-\frac{3K^2}{J(J+1)}\right]=\text{strength of the quadrupole coupling},$$

$$R=\left[a+\frac{(b-a)K^2}{J(J+1)}\right]=\text{strength of the magnetic } \mathbf{I}_{\mathrm{N}}\cdot\mathbf{J} \text{ coupling } (I_{\mathrm{N}}=\text{nitrogen spin}),$$

$$S=\left[A+\frac{CK^2}{J(J+1)}+\delta_{K1}(-1)^{J+V}B\right]=\text{strength of the } \mathbf{I}\cdot\mathbf{J} \text{ coupling } (\mathbf{I}=\text{sum of the hydrogen spins}),$$

$$T=D_1\left[1-\frac{3K^2}{J(J+1)}\right]-D_2\delta_{K1}(-1)^{J+V}=\text{strength of the hydrogen-nitrogen spin-spin interaction},$$

and

$$U=-\tfrac{1}{4}D_3\left[1-\frac{3K^2}{J(J+1)}\right]=\text{strength of the hydrogen-hydrogen spin-spin interaction}.$$

The coefficients are combinations of 6-$j$ and 9-$j$ symbols determined by the quantum numbers $J$, $K$, $I_{\mathrm{N}}$, $F_1$, $I$, $F$ ($F_1=I_{\mathrm{N}}+J$, $F=I+F_1$) as indicated in the last section.

Initial values for the parameters are calculated from known nuclear moments and internuclear distances or obtained from Gordon's data.[3] Calculations of energy levels using these initial values are used along with transition-intensity data and calculations to identify the transitions. Approximate values for $N^{15}H_3$ inversion frequencies were obtained from a paper by Good and Coles.[11]

When the transitions have been identified, the values of the transition frequencies are used in a least-squares fit program to determine the parameters. For $N^{14}H_3$ lines this is done in two steps. First, differences between transition frequencies which are independent of $Q$ and $R$ are used to determine $S$, $T$, and $U$. Then these values of $S$, $T$, and $U$ are used with the transition frequencies in another least-squares fit program to determine $Q$ and $R$.

For all transitions $Q$ is different for the upper and lower inversion states, so we have $Q_0$ and $Q_1$. $V=0$ for the lower inversion state and $V=1$ for the upper state. For $K=1$ states, $S$ and $T$ are different for upper and lower inversion states so we have and $S_0$, $S_1$, $T_0$, and $T_1$ for the 1-1 rotational state.

The significant shifts which are produced by second-order perturbation terms must be included in the data analysis. The magnetic terms off-diagonal in $F_1$ are less than 1 kHz for $N^{14}H_3$, and these are included by subtracting the calculated shift from the data. For $N^{15}H_3$ these shifts are a few kHz or more and the shift must be recalculated after the first fit and the fit procedure repeated. This usually converges to within a few Hz of the correct value after three repetitions. The quadrupole terms off-diagonal in rotational states are a few Hz or less and will be neglected.

The main line ($\Delta F_1=\Delta F=0$) for the 2-2 and 3-3 states contain three components so close together that the Ramsey resonance patterns overlap. The resonance pattern for a single molecular resonance line is the typical "Ramsey" line shape shown in Fig. 1 and may be easily analyzed to determine the resonance frequency. In order to analyze these cases, a line-revolving computer program was written to perform a least-squares fit to the experimental spectrum by using a superposition of the known single-line resonance patterns.

The resonance pattern for a single line is represented by the function

$$A\exp[-b(f-f_0)^2]\sin[\pi(f-f_0)/\Delta f-\phi].$$

The results of a fit to the 3-3 main line are shown in Fig. 2.

The quadrupole interaction is the dominant energy term for $N^{14}$ spectra and produces splitting of a few MHz. Since $I_{\mathrm{N}}=1$ in this case the transitions ($\Delta F_1=\pm1$) result in a pair of quadrupole satellites on each side of

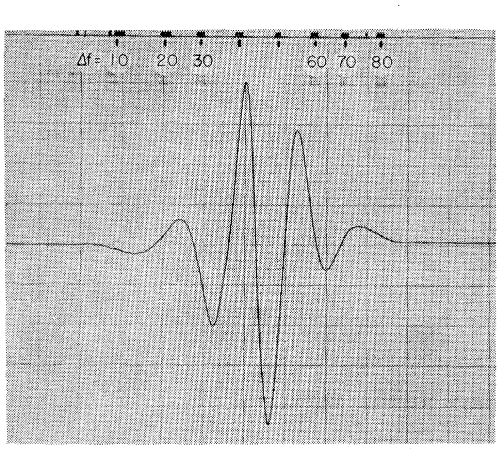

FIG. 1. Single-line resonance pattern. Recorder trace of the $N^{15}$ 3-3 main line ($\Delta F_1=\Delta F=0$). Frequency in kHz=789 419.69 +0.0455$\Delta f$.

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[11] W. E. Good and D. K. Coles, Phys. Rev. 71, 383 (1947).

the main line. These quadrupole satellites are further split by magnetic interactions of magnitude 10 to 50 kHz. The main line consists of transitions $\Delta F_1 = \Delta F = 0$. The transitions $\Delta F_1 = 0$, $\Delta F = \pm 1$ produce magnetic satellites on each side of the main line, separated from the main line by frequencies of the order of 50 kHz.

### *The 1-1 Line*

A recorder tracing with compressed frequency scale of the 1-1 main line is shown in Fig. 3.

The quadrupole satellites have all been observed and completely resolved except the (0,0.5,1,0.5) transition. The transitions beginning on the state $F_1 = 0$ are considerably weaker since the state selection and focusing is much less effective in this case.[3]

Differences between the frequencies of transitions which have the same $\Delta F_1$ are independent of $Q_0$, $Q_1$, and $R$, since $C_Q$ and $C_R$ are independent of $F$. Twelve of these differences have been used in a least-squares-fit program to determine $S_1$, $T_1$, $S_0$, and $T_0$. These values for $S_1$, $T_1$, $S_0$, and $T_0$ are then used in a least-squares fit using the transition frequencies to determine $Q_1$, $Q_0$, and $R$. The results of these fits are combined and shown in Table I.

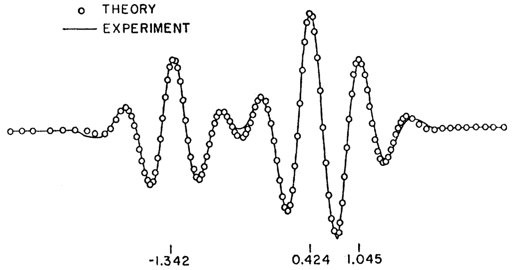

FIG. 2. Results of the line-resolving program for the 3-3 line. Frequencies in kHz relative to 23 870 129.183 kHz.

In Table I and all subsequent tables $F_1'$ and $F'$ are the quantum numbers of the initial state and $F_1$ and $F$ are the quantum numbers of the final state. Dev. is the deviation between the data and calculated frequency and Exp. S.D. is the experimental standard deviation for approximately ten measurements.

The ratio $D_1/D_2$ is only a function of the angle $\beta$ ($\beta$ is the angle between the line perpendicular to the plane of the hydrogens and a line from the nitrogen to a hydrogen nucleus, see Fig. 1 of Ref. 3) so $\beta$ may be determined from $T_0$ and $T_1$. Using the relations $D_1/D_2 = 2(T_1 + T_0)/(T_1 - T_0)$ and $D_1/D_2 = 1 - \frac{2}{3}\sin^2\beta$, we get $\beta = 68°53'$.

We may also calculate $r_{\mathrm{NH}}$ from our values of $T_1$ and $T_0$. We see that $2g_{\mathrm{H}}g_{\mathrm{N}}\mu_0{}^2 r_{\mathrm{NH}}{}^{-3} = -T_0 - 3T_1$, and using nuclear moments from Ramsey[12] we get $r_{\mathrm{NH}} = 0.81394$ Å. When we compare these values with the Hertzberg values[13] of 67°58′ and 1.014 Å (see also Weiss and Strandberg[14]) we see that the angle, which depends on the ratio $D_1/D_2$, deviates much less than the bond length which is a linear combination of $D_1$ and $D_2$. These deviations may be due to modification of the magnetic coupling constants $D_1$ and $D_2$ by a second-order electron coupled interaction.

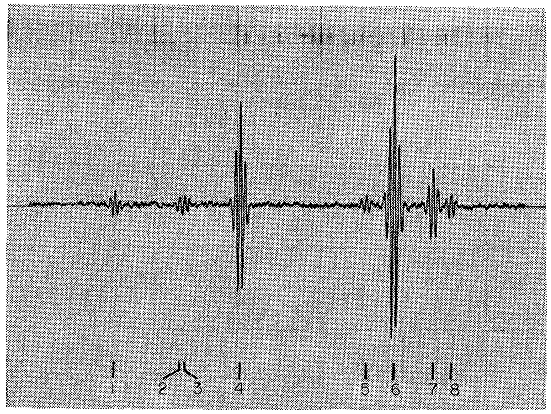

FIG. 3. Recorder trace of the 1-1 main line ($\Delta F_1 = 0$, $\Delta F = 0, \pm 1$).

### *The 2-2 Line*

The main line results from transitions $\Delta F_1 = \Delta F = 0$, and there are three components, one for each value of $F_1$. The line spacings are approximately 1 kHz so the line-resolving program described previously was used for analysis.

TABLE I. Results of 1-1 line measurements and calculations. Frequencies are in kHz relative to 23 694 495.487.

$S_1 = -3.85521$; $S_0 = -33.14220$; $T_1 = -9.26825$; $T_0 = 11.72397$; $Q_1 = -2044.32164$; $Q_0 = -2045.72691$; $R = 6.79999$

| $F_1'$ | $F'$ | $F_1$ | $F$ | Data | Calculated | Dev.[a] | Exp. S.D.[b] |
|---|---|---|---|---|---|---|---|
| 0 | 0.5 | 1 | 1.5 | −1526.658 | −1526.950 | −0.292 | 0.056 |
| 2 | 1.5 | 1 | 0.5 | −623.335 | −623.306 | 0.029 | 0.057 |
| 2 | 2.5 | 1 | 1.5 | −590.375 | −590.338 | 0.037 | 0.058 |
| 2 | 1.5 | 1 | 1.5 | −581.021 | −580.921 | 0.100 | 0.039 |
| 1 | 0.5 | 1 | 0.5 | −36.389 | −36.536 | −0.147 | 0.036 |
| 1 | 1.5 | 1 | 0.5 | −25.453 | −25.538 | −0.085 | 0.028 |
| 2 | 2.5 | 2 | 1.5 | −24.583 | −24.394 | 0.189 | 0.063 |
| 2 | 1.5 | 2 | 1.5 | −15.196 | −14.977 | 0.218 | 0.044 |
| 1 | 0.5 | 1 | 1.5 | 5.941 | 5.848 | −0.093 | 0.059 |
| 2 | 2.5 | 2 | 2.5 | 10.463 | 10.515 | 0.052 | 0.037 |
| 1 | 1.5 | 1 | 1.5 | 16.835 | 16.847 | 0.011 | 0.037 |
| 2 | 1.5 | 2 | 2.5 | 19.832 | 19.932 | 0.100 | 0.047 |
| 1 | 0.5 | 2 | 1.5 | 571.708 | 571.792 | 0.084 | 0.046 |
| 1 | 1.5 | 2 | 1.5 | 582.719 | 582.790 | 0.071 | 0.059 |
| 1 | 1.5 | 2 | 2.5 | 617.689 | 617.700 | 0.011 | 0.050 |
| 1 | 0.5 | 0 | 0.5 | 1534.232 | 1534.050 | −0.182 | 0.048 |
| 1 | 1.5 | 0 | 0.5 | 1545.159 | 1545.049 | −0.110 | 0.038 |

[a] Standard deviation for fit = 0.1303.
[b] Experimental standard deviation = 0.0483.

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[12] N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1961), Chap. 6.

[13] G. Hertzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Princeton, New Jersey, 1945), p. 439.

[14] M. T. Weiss and M. W. P. Strandberg, Phys. Rev. 83, 567 (1951).

TABLE II. Results of 2-2 line measurements and calculations. Frequencies in kHz relative to 23 722 633.335.

$Q_1=-4089.4413$; $Q_0=-4093.6466$; $R=6.7232$; $S=-18.6183$; $T=2.3854$

| $F_1'$ | $F'$ | $F_1$ | $F$ | Data | Calculated | Dev.[a] | Exp. S.D.[b] |
|---|---|---|---|---|---|---|---|
| 1 | 1.5 | 2 | 1.5 | −2099.033 | −2099.027 | 0.006 | 0.033 |
| 1 | 1.5 | 2 | 2.5 | −2058.267 | −2058.265 | 0.001 | 0.039 |
| 1 | 0.5 | 2 | 1.5 | −2053.459 | −2053.464 | −0.006 | 0.034 |
| 3 | 3.5 | 2 | 2.5 | −1297.087 | −1297.079 | 0.008 | 0.058 |
| 3 | 2.5 | 2 | 1.5 | −1296.079 | −1296.096 | −0.017 | 0.057 |
| 3 | 2.5 | 2 | 2.5 | −1255.384 | −1255.335 | 0.049 | 0.106 |
| 1 | 1.5 | 1 | 0.5 | −44.498 | −44.511 | −0.013 | 0.070 |
| 2 | 2.5 | 2 | 1.5 | −41.806 | −41.813 | −0.007 | 0.106 |
| 3 | 3.5 | 3 | 2.5 | −41.456 | −41.444 | 0.012 | 0.086 |
| 2 | 1.5 | 2 | 1.5 | −1.031 | −1.051 | −0.021 | 0.033 |
| 3 | 2.5 | 3 | 2.5 | 0.309 | 0.300 | −0.009 | 0.033 |
| 1 | 0.5 | 1 | 0.5 | 1.054 | 1.051 | −0.003 | 0.033 |
| 2 | 1.5 | 2 | 2.5 | 39.736 | 39.710 | −0.026 | 0.032 |
| 3 | 2.5 | 3 | 3.5 | 42.055 | 42.045 | −0.010 | 0.042 |
| 1 | 0.5 | 1 | 1.5 | 46.621 | 46.614 | −0.008 | 0.022 |
| 2 | 2.5 | 3 | 2.5 | 1254.559 | 1254.584 | 0.024 | 0.125 |
| 2 | 1.5 | 3 | 2.5 | 1295.363 | 1295.345 | −0.018 | 0.064 |
| 2 | 2.5 | 3 | 3.5 | 1296.295 | 1296.328 | 0.033 | 0.050 |
| 2 | 1.5 | 1 | 0.5 | 2053.476 | 2053.464 | −0.012 | 0.063 |
| 2 | 2.5 | 1 | 1.5 | 2058.256 | 2058.265 | 0.009 | 0.057 |
| 2 | 1.5 | 1 | 1.5 | 2099.022 | 2099.027 | 0.004 | 0.123 |

[a] Standard deviation for fit =0.0180.
[b] Experimental standard deviation =0.0700.

All 21 transitions were observed and measured. The results of the fit program are shown in Table II. We see from Table II that the standard deviation for the fit is 0.018 kHz, while the experimental standard deviation (width of the distribution of measurements) is 0.070 kHz. This offers some support to our hypothesis that the measurements are really more accurate than the experimental standard deviation, since there are four times as many points being fitted as there are parameters in the fit. We note that the theory fits the experimental data very well for the 2-2 transition.

TABLE III. Results of 3-3 line measurements and calculations. Frequencies in kHz relative to 23 870 129.183.

$Q_1=-5114.4237$; $Q_0=-5119.7587$; $R=6.7297$; $S=-18.6815$; $T=3.1101$; $U=8.4917$

| $F_1'$ | $F'$ | $F_1$ | $F$ | Data | Calculated | Dev.[a] | Exp. S.D.[b] |
|---|---|---|---|---|---|---|---|
| 2 | 3.5 | 3 | 4.5 | −2324.089 | −2324.577 | −0.488 | 0.022 |
| 2 | 2.5 | 3 | 3.5 | −2312.492 | −2312.558 | −0.066 | 0.045 |
| 2 | 0.5 | 3 | 1.5 | −2304.667 | −2304.415 | 0.251 | 0.112 |
| 2 | 1.5 | 3 | 2.5 | −2302.375 | −2301.989 | 0.386 | 0.020 |
| 4 | 3.5 | 3 | 2.5 | −1690.939 | −1690.763 | 0.177 | 0.047 |
| 4 | 4.5 | 3 | 3.5 | −1688.839 | −1689.154 | −0.314 | 0.024 |
| 4 | 2.5 | 3 | 1.5 | −1682.922 | −1682.925 | −0.003 | 0.071 |
| 4 | 5.5 | 3 | 4.5 | −1679.057 | −1679.029 | 0.029 | 0.071 |
| 2 | 2.5 | 2 | 1.5 | −80.104 | −80.030 | 0.073 | 0.021 |
| 3 | 2.5 | 3 | 1.5 | −64.308 | −64.182 | 0.126 | 0.046 |
| 3 | 4.5 | 3 | 3.5 | −61.780 | −61.951 | −0.171 | 0.053 |
| 4 | 5.5 | 4 | 4.5 | −50.183 | −50.048 | 0.136 | 0.037 |
| 3 | 1.5 | 3 | 1.5 | −1.302 | −1.334 | −0.032 | 0.020 |
| 4 | 2.5 | 4 | 2.5 | 0.433 | 0.445 | 0.011 | 0.020 |
| 2 | 0.5 | 2 | 0.5 | 1.041 | 1.067 | 0.026 | 0.020 |
| 4 | 4.5 | 4 | 5.5 | 51.127 | 50.937 | −0.190 | 0.069 |
| 3 | 3.5 | 3 | 4.5 | 59.143 | 59.283 | 0.140 | 0.066 |
| 2 | 1.5 | 2 | 2.5 | 82.240 | 82.164 | −0.075 | 0.062 |
| 3 | 1.5 | 4 | 2.5 | 1682.148 | 1682.036 | −0.112 | 0.023 |
| 3 | 3.5 | 4 | 4.5 | 1687.971 | 1688.264 | 0.294 | 0.020 |
| 3 | 2.5 | 4 | 3.5 | 1690.070 | 1689.873 | −0.197 | 0.022 |
| 3 | 4.5 | 4 | 5.5 | 1678.235 | 1678.140 | −0.096 | 0.022 |
| 3 | 2.5 | 2 | 1.5 | 2302.080 | 2301.723 | −0.357 | 0.030 |
| 3 | 1.5 | 2 | 0.5 | 2304.227 | 2304.148 | −0.078 | 0.022 |
| 3 | 3.5 | 2 | 2.5 | 2312.291 | 2312.291 | 0. | 0.022 |
| 3 | 4.5 | 2 | 3.5 | 2323.792 | 2324.310 | 0.518 | 0.039 |

[a] Standard deviation for fit =0.2207.
[b] Experimental standard deviation =0.0481.

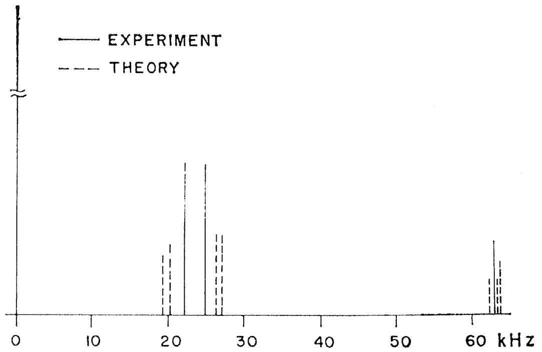

FIG. 4. Results of the 3-2 line measurements and calculations. Frequencies in kHz relative to 22 834 184.96 kHz.

## The 3-3 Line

The main line results from transitions $\Delta F_1=\Delta F=0$ and there is one component for each value of $F_1$. The components are separated by less than 2 kHz so the line-resolving program was used as described previously. The results are shown in Fig. 2.

The results of the fit programs are shown in Table III. The standard deviation for the fits is greater than five times the experimental standard deviation for the 3-3 line. All off-diagonal magnetic terms have been included as discussed previously.

TABLE IV. Results of 3-2 line measurements and calculations. Frequencies in kHz relative to 22 834 184.96. The indicated values of $R$ and $S$ give the best fit to the data.

| $C_R$ | $C_S$ | Shift | Level | $F_1$ | $F$ |
|---|---|---|---|---|---|
| −4.0 | −2.00000 | 0. | 1 | 2 | 1.5 |
| −4.0 | 1.33333 | −2.16 | 2 | 2 | 2.5 |
| −1.0 | −1.83333 | 2.16 | 3 | 3 | 2.5 |
| −1.0 | 1.37500 | −1.42 | 4 | 3 | 3.5 |
| 3.0 | −1.87500 | 1.42 | 5 | 4 | 3.5 |
| 3.0 | 1.50000 | 0. | 6 | 4 | 4.5 |

$R=6.75214$; $S=-18.27612$

| Levels | | Data | Calculated | Dev.[a] |
|---|---|---|---|---|
| 1 | 2 | 62.860 | 63.084 | |
| 5 | 6 | 62.860 | 63.106 | |
| 3 | 4 | 62.860 | 62.224 | −0.056 |
| 6 | 4 | 24.860 | 26.148 | |
| 5 | 3 | 24.860 | 27.030 | 1.729 |
| 4 | 2 | 22.110 | 20.235 | |
| 3 | 1 | 22.110 | 19.374 | −2.305 |

[a] Standard deviation for fit =0.9249.

### *The 3-2 Line*

The data for this line have been reported previously.[15] This line is a special case in the respect that the factor $[J(J+1)-3K^2]$ vanishes and so the only interactions which should be nonzero are the nitrogen magnetic interaction with molecular rotation $R$, and the hydrogen magnetic interaction with molecular rotation $S$.

The satellites result from transitions ($\Delta F_1=0$, $\Delta F=\pm 1$) and ($\Delta F_1=\Delta F=\pm 1$). The results of the fit program are shown in Table IV and Fig. 4. The seven satellites on each side of the main line fall into three groups. The components in each of these groups are unresolved. A recorder tracing for two of the closely spaced groups is shown in Ref. 15.

We see that the fit for the 3-2 line is very poor. It is clear in this case and for the $N^{15}$ data that there must be some additional interaction. The measured lines are symmetric about the main line to within 10 Hz, which supports the previous indication that the experimental accuracy is better than that indicated by the experimental standard deviation for the measurements. The fit is greatly improved by including a term quadratic in $F_1$, but we can find no theoretical justification for such a term.

## Discussion of the $N^{14}H_3$ Coupling Parameters

We may obtain the values of the spin-spin interaction coupling parameters $D_1$ and $D_3$ from the previous data.

$$D_1=g_Hg_N\mu_0^2\langle r_{NH}^{-3}(1-\tfrac{3}{2}\sin^2\beta)\rangle,$$
$$D_3=(g_H\mu_0)^2\langle r_{HH}^{-3}\rangle.$$

The values obtained are shown in Table V. Variations of the parameter $D_1$ were expected to be less than 0.03 kHz for different rotational states on the basis of experimental standard deviations. The possible variation of $\beta$ with $J$ would cause the magnitude of $D_1$ to increase monotonically with $J$ for $J=K$ states.

TABLE V. Coupling parameters (in kHz).

| $J$ | $K$ | $D_1$ | $D_3$ |
|---|---|---|---|
| 1 | 1 | −2.4557 | |
| 2 | 2 | −2.3854 | |
| 3 | 3 | −2.4881 | 27.1734 |

TABLE VI. Data and fit result for $R$ (in kHz).

| | | $a=6.80734$; $b-a=-0.09970$. | | |
|---|---|---|---|---|
| $J$ | $K$ | Data | Calculated | Dev. |
| 1 | 1 | 6.8000 | 6.7575 | 0.043 |
| 2 | 2 | 6.7232 | 6.7409 | −0.018 |
| 3 | 3 | 6.7297 | 6.7326 | −0.003 |
| 3 | 2 | 6.7521 | 6.7741 | −0.022 |

TABLE VII. Data and fit results for $S$ (in kHz).

| | | $A=-17.98191$; $C=-0.95422$ | | |
|---|---|---|---|---|
| $J$ | $K$ | Data | Calculated | Dev. |
| 1 | 1 | −18.4987 | −18.4590 | −0.040 |
| 2 | 2 | −18.6183 | −18.6181 | −0.000 |
| 3 | 3 | −18.6815 | −18.6976 | 0.016 |
| 3 | 2 | −18.2761 | −18.3000 | 0.024 |

TABLE VIII. Data and fit results for $eQq$ (in kHz).

| | | $Q_A=4082.9953$; $Q_B=13.7110$ | | |
|---|---|---|---|---|
| $J$ | $K$ | Data | Calculated | Dev. |
| 1 | 1 | 4090.048 | 4089.851 | 0.198 |
| 2 | 2 | 4091.544 | 4092.136 | −0.592 |
| 3 | 3 | 4093.673 | 4093.278 | 0.394 |

There are two $\mathbf{I}\cdot\mathbf{J}$ coupling parameters, $R$ and $S$. The experimental values of $R$ were fitted to the function $a+(b-a)K^2/J(J+1)$. The results of this fit are shown in Table VI. The experimental values of $S$ were fitted to the function $A+CK^2/J(J+1)$ and the results of this fit are shown in Table VII. These functions were used by Gordon[3] and Gunther-Mohr[2] and discussed by Townes and Schawlow.[16] The indicated values of the terms were determined by a least-squares-fit procedure in both cases.

We see that both of these terms may be fitted with the theoretical expressions to within the experimental standard deviation.

The quadrupole coupling constant $eQq$ also varies with $J$ and $K$. The empirical expansion given by Gordon[3] is $eQq=Q_A+Q_BJ(J+1)$. The results of a fit to this expression are shown in Table VIII.

We see that this expression describes the variation of $eQq$ fairly well. Without more data it would not be meaningful to try more complicated functions.

### *Transition Intensities*

The relative intensities of transitions in the 1-1, 2-2, and 3-3 states were measured. These measurements were compared with values calculated according to the theory of Thaddeus *et al.*[10] The results are shown in Tables IX and X. We have averaged upper and lower satellites since upper satellites are stronger due to focusing effects.[3] The theoretical expression for the intensities is

$$I=[(2F_1'+1)(2F_1+1)(2F'+1)(2F+1)]\times\left[\begin{Bmatrix}J & F_1' & I_N\\ F_1 & J & 1\end{Bmatrix}\begin{Bmatrix}F_1' & F' & I\\ F & F_1 & 1\end{Bmatrix}\right]^2.$$

The main reason for these intensity calculations was to

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[15] S. G. Kukolich, Phys. Rev. **138**, A1322 (1965).

[16] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

aid in the identification of the transitions in terms of the quantum numbers. We see that the agreement between calculated and experimental values is much better than that required for identification.

Table IX. Transition intensities. (Calculated values according to Thaddeus *et al.*) Only relative intensities were measured. Observed values were multiplied by a constant factor to make total intensity the same. For $\Delta F_1=0$ transitions, the tabulated intensities are for the sum of the three possible $F'$, $F$ values and "..." is entered in the $F'$, $F$ columns.

| $F_1'$ | $F'$ | $F_1$ | $F$ | Calculated | Measured |
|---|---|---|---|---|---|
| | | | 1-1 Line | | |
| 0 | 0.5 | 1 | 0.5 | 0.22222 | 0.22388 |
| 0 | 0.5 | 1 | 1.5 | 0.44444 | 0.44776 |
| 1 | 0.5 | 2 | 1.5 | 0.27778 | 0.20896 |
| 1 | 1.5 | 2 | 1.5 | 0.05556 | 0.06716 |
| 1 | 1.5 | 2 | 2.5 | 0.50000 | 0.56716 |
| 1 | 1.5 | 1 | 0.5 | 0.05556 | 0.11194 |
| 2 | 2.5 | 2 | 2.5 | 1.40000 | 2.38806 |
| 2 | 2.5 | 2 | 1.5 | 0.10000 | 0.11194 |
| 1 | 0.5 | 1 | 0.5 | 0.11111 | 0.13433 |
| 1 | 1.5 | 1 | 1.5 | 0.27778 | 0.26866 |
| 1 | 0.5 | 1 | 1.5 | 0.05556 | 0.06716 |
| 2 | 1.5 | 2 | 2.5 | 0.10000 | 0.07463 |
| 2 | 1.5 | 2 | 1.5 | 0.90000 | 0.74627 |
| | | | 2-2 Line | | |
| 1 | 1.5 | 2 | 1.5 | 0.02000 | 0.01509 |
| 1 | 1.5 | 2 | 2.5 | 0.18000 | 0.16097 |
| 1 | 0.5 | 2 | 1.5 | 0.10000 | 0.09557 |
| 3 | 3.5 | 2 | 2.5 | 0.17778 | 0.13833 |
| 3 | 2.5 | 2 | 1.5 | 0.12444 | 0.07545 |
| 3 | 2.5 | 2 | 2.5 | 0.00889 | 0.01509 |
| 1 | 1.5 | 1 | 0.5 | 0.10000 | 0.15091 |
| 2 | 2.5 | 2 | 1.5 | 0.05556 | 0.06036 |
| 3 | 3.5 | 3 | 2.5 | 0.05079 | 0.10563 |
| 2 | ... | 2 | ... | 1.27780 | 1.83702 |
| 3 | ... | 3 | ... | 2.38720 | 2.38707 |
| 1 | ... | 1 | ... | 0.70000 | 0.78395 |

Table X. Transition intensities. (Calculated values according to Thaddeus *et al.*) Only relative intensities were measured. Observed values were multiplied by a constant factor to make total intensity the same. For $\Delta F_1=0$ transitions, the tabulated intensities are for the sum of the three possible $F'$, $F$ values and "..." is entered in the $F'$, $F$ columns.

| $F_1'$ | $F'$ | $F_1$ | $F$ | Calculated | Measured |
|---|---|---|---|---|---|
| | | | 3-3 Line | | |
| 2 | 3.5 | 3 | 4.5 | 0.11338 | 0.11176 |
| 2 | 2.5 | 3 | 3.5 | 0.07775 | 0.08714 |
| 2 | 0.5 | 3 | 1.5 | 0.03175 | 0.03315 |
| 2 | 1.5 | 3 | 2.5 | 0.05079 | 0.06251 |
| 4 | 3.5 | 3 | 2.5 | 0.06150 | 0.06251 |
| 4 | 4.5 | 3 | 3.5 | 0.08185 | 0.09661 |
| 4 | 2.5 | 3 | 1.5 | 0.04592 | 0.03789 |
| 4 | 5.5 | 3 | 4.5 | 0.10714 | 0.14397 |
| 2 | 2.5 | 2 | 1.5 | 0.17778 | 0.14776 |
| 3 | 4.5 | 3 | 3.5 | 0.10003 | 0.08524 |
| 4 | 5.5 | 4 | 4.5 | 0.08766 | 0.06630 |
| 3 | ... | 3 | ... | 2.71175 | 2.88805 |
| 4 | ... | 4 | ... | 4.24474 | 4.24418 |
| 2 | ... | 2 | ... | 1.63990 | 1.61906 |
| 2 | 1.5 | 3 | 1.5 | 0.01270 | Not obs. |
| 2 | 2.5 | 3 | 2.5 | 0.01659 | Not obs. |
| 2 | 3.5 | 3 | 3.5 | 0.01296 | Not obs. |
| 4 | 2.5 | 3 | 2.5 | 0.00738 | Not obs. |
| 4 | 3.5 | 3 | 3.5 | 0.00972 | Not obs. |
| 4 | 4.5 | 3 | 4.5 | 0.00744 | Not obs. |

Table XI. Results of $N^{15}$ 1-1 line measurements and calculations fit with best standard deviation. Frequencies in kHz relative to 22 624 931.128.

$R=-2.79777$; $S_0=-29.15047$; $S_1=-1.60840$

| $F_1'$ | $F'$ | $F_1$ | $F$ | Data | Calculated | Dev.[a] | Exp. S.D.[b] |
|---|---|---|---|---|---|---|---|
| 1.5 | 1 | 0.5 | 0 | −43.685 | −44.563 | −0.878 | 0.088 |
| 1.5 | 1 | 1.5 | 1 | −41.954 | −40.886 | 1.068 | 0.094 |
| 1.5 | 2 | 1.5 | 1 | −31.795 | −30.509 | 1.286 | 0.447 |
| 0.5 | 0 | 1.5 | 1 | −23.690 | −23.795 | −0.105 | 0.379 |
| 0.5 | 1 | 1.5 | 1 | −12.072 | −13.418 | −1.346 | 0.075 |
| 1.5 | 1 | 0.5 | 1 | 0.466 | −0.318 | −0.784 | 0.159 |
| 1.5 | 1 | 1.5 | 2 | 1.999 | 3.359 | 1.360 | 0.190 |
| 1.5 | 2 | 0.5 | 1 | 9.848 | 10.059 | 0.211 | 0.030 |
| 1.5 | 2 | 1.5 | 2 | 15.805 | 13.736 | −2.069 | 0.050 |
| 0.5 | 0 | 0.5 | 1 | 17.410 | 16.773 | −0.637 | 0.055 |
| 0.5 | 1 | 0.5 | 1 | 25.256 | 27.150 | 1.894 | 0.041 |

[a] Standard deviation for fit = 1.2124.
[b] Experimental standard deviation = 0.1988.

### $N^{15}$ *1-1 Line*

The hydrogen spin-rotational coupling parameter is different for the two inversion states, so we have $S_0$ and $S_1$ as discussed previously. For this reason there is no strong central component (main line) and the spectrum is not symmetric. Many different assignments of quantum numbers to the observed transitions were tried and the one giving the best fit to the observed spectrum is shown in Table XI. The standard deviations for each of these fits was greater than 1 kHz.

### $N^{15}$ *2-2 Line*

The transitions

$$(F_1',F',F_1,F)=(1.5,2,2.5,3)$$

and

$$(1.5,1,2.5,2)$$

are shown in Fig. 5. We note that these transitions are separated by 4 kHz. This is the clearest indication that the present theory is incomplete, since the theory indicates that these two transitions should coincide. The transitions are identified from intensity calculations

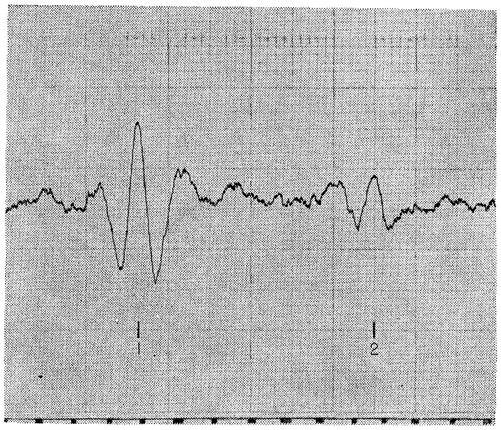

Fig. 5. Recorder trace of the $N^{15}$ 2-2 line satellites at 18.86 and 22.67 kHz relative to 22 649 843.41 kHz($\Delta F_1=\Delta F=+1$).

(see Table XII). This same difficulty occurs for all observed satellites of the $N^{15}$ 2-2 line. The results for these fits are shown in Table XIII and Fig. 6.

The Hamiltonian matrix for the $N^{15}$ 2-2 line in terms of adjustable parameters $R$ and $S$ is

$$\begin{array}{c} (F_1,F) \\ (1.5,1) \\ (1.5,2) \\ (2.5,2) \\ (2.5,3) \end{array} \left[ \begin{array}{cccc} (1.5,1) & (1.5,2) & (2.5,2) & (2.5,3) \\ -1.5R-1.5S & 0 & 0 & 0 \\ 0 & -1.5R+0.9S & -0.489898S & 0 \\ 0 & -0.489898S & R-1.4S & 0 \\ 0 & 0 & 0 & R+S \end{array} \right].$$

When this is diagonalized, we see that the pairs of transitions ($\Delta F_1=0$, $\Delta F=+1$), ($\Delta F_1=0$, $\Delta F=-1$), ($\Delta F_1=\Delta F=+1$), ($\Delta F_1=\Delta F=-1$) all coincide no matter what the values of the parameters $R$ and $S$ are. The measured spectrum is symmetric to within ±50 Hz as may be seen in Table XIII.

TABLE XII. Transition intensities. $N^{15}$ 2-2 line. The line labeled $F_1$, $F$, $F_1$, $F$ is the intensity for the sum of the transitions $\Delta F_1=\Delta F=0$.

| $F_1'$ | $F'$ | $F_1$ | $F$ | Calculated | Measured |
|---|---|---|---|---|---|
| 1.5 | 2 | 1.5 | 1 | 0.090 | 0.135 |
| 2.5 | 3 | 2.5 | 2 | 0.062 | 0.050 |
| 2.5 | 2 | 1.5 | 1 | 0.060 | 0.085 |
| 2.5 | 3 | 1.5 | 2 | 0.093 | 0.200 |
| $F_1$ | $F$ | $F_1$ | $F$ | 3.380 | 2.400 |
| 1.5 | 2 | 2.5 | 2 | 0.007 | Not obs. |

TABLE XIII. Results of $N^{15}$ 2-2 line measurements and calculations. Frequencies in kHz relative to 22 649 843.407.

$R=-8.94536$; $S=-18.59435$

| $F_1'$ | $F'$ | $F_1$ | $F$ | Data | Calculated | Dev.[a] | Exp. S.D.[b] |
|---|---|---|---|---|---|---|---|
| 1.5 | 2 | 1.5 | 1 | −50.014 | −48.100 | 1.914 | 0.062 |
| 2.5 | 3 | 2.5 | 2 | −46.184 | −48.100 | −1.916 | 0.092 |
| 2.5 | 2 | 1.5 | 1 | −22.682 | −20.749 | 1.932 | 0.092 |
| 2.5 | 3 | 1.5 | 2 | −18.793 | −20.749 | −1.956 | 0.047 |
| 1.5 | 1 | 1.5 | 1 | −0.050 | 0. | 0.050 | 0.056 |
| 1.5 | 2 | 2.5 | 3 | 18.855 | 20.749 | 1.894 | 0.059 |
| 1.5 | 1 | 2.5 | 2 | 22.666 | 20.749 | −1.917 | 0.089 |
| 2.5 | 2 | 2.5 | 3 | 46.178 | 48.100 | 1.922 | 0.083 |
| 1.5 | 1 | 1.5 | 2 | 50.024 | 48.100 | −1.924 | 0.069 |

[a] Standard deviation for fit = 1.8121.
[b] Experimental standard deviation = 0.0740.

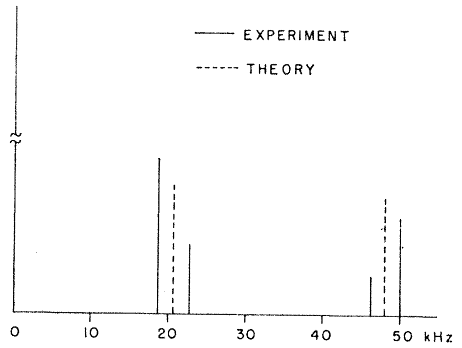

FIG. 6. Results of $N^{15}$ 2-2 line measurements and calculations. Frequencies in kHz relative to 22 649 843.41 kHz.

### $N^{15}$ *3-3 Line*

The main line results from transitions ($\Delta F_1=\Delta F=0$) and is shown in Fig. 1. Many different assignments of quantum numbers to the observed transitions were tried and the one resulting in the best standard deviation is shown in Table XIV. Here the standard deviation is greater than 10 times the experimental standard deviation. The standard deviations for these fits were all greater than 1 kHz.

### $N^{15}$ *Coupling Parameters*

The $N^{15}$ spin-rotational coupling parameters $R$ and $S$ are listed in Table XV. With the exception of $S$ for the 2-2 and 3-3 states these parameters are not consistent and do not agree with $N^{14}$ results or with theory. Using $N^{14}$ data and the ratio of $N^{15}$ to $N^{14}$ nuclear magnetic moments, we expect $R$ to be −4.65 kHz. The values of $S$ for the 2-2 and 3-3 states agree quite

TABLE XIV. Results of $N^{15}$ 3-3 line measurements and calculations. Frequencies in kHz relative to 22 789 421.672.

$R=-5.91871$; $S=-18.62803$; $U=3.39858$

| $F_1'$ | $F'$ | $F_1$ | $F$ | Data | Calculated | Dev.[a] | Exp. S.D.[b] |
|---|---|---|---|---|---|---|---|
| 3.5 | 5 | 3.5 | 4 | −78.964 | −77.631 | 1.333 | 0.078 |
| 2.5 | 4 | 2.5 | 3 | −75.633 | −77.125 | −1.492 | 0.045 |
| 2.5 | 3 | 2.5 | 2 | −72.904 | −71.851 | 1.053 | 0.069 |
| 3.5 | 4 | 3.5 | 3 | −65.987 | −66.462 | −0.475 | 0.059 |
| 3.5 | 3 | 3.5 | 2 | −54.587 | −54.871 | −0.284 | 0.038 |
| 3.5 | 2 | 2.5 | 1 | −21.830 | −22.104 | −0.274 | 0.073 |
| 3.5 | 3 | 2.5 | 2 | −20.355 | −21.597 | −1.242 | 0.116 |
| 3.5 | 5 | 2.5 | 4 | −18.315 | −16.715 | 1.600 | 0.058 |
| 2.5 | 2 | 2.5 | 2 | 0.000 | 0. | −0.000 | 0.055 |
| 2.5 | 4 | 3.5 | 5 | 18.320 | 16.715 | −1.605 | 0.078 |
| 2.5 | 2 | 3.5 | 3 | 20.262 | 21.597 | 1.335 | 0.131 |
| 2.5 | 1 | 3.5 | 2 | 21.749 | 22.104 | 0.355 | 0.034 |
| 3.5 | 2 | 3.5 | 3 | 54.728 | 54.871 | 0.143 | 0.050 |
| 3.5 | 3 | 3.5 | 4 | 66.010 | 66.462 | 0.452 | 0.077 |
| 2.5 | 2 | 2.5 | 3 | 72.916 | 71.851 | −1.065 | 0.090 |
| 2.5 | 3 | 2.5 | 4 | 75.622 | 77.125 | 1.503 | 0.090 |
| 3.5 | 4 | 3.5 | 5 | 78.967 | 77.631 | −1.336 | 0.068 |

[a] Standard deviation for fit = 1.0706.
[b] Experimental standard deviation = 0.0754.

TABLE XV. $N^{15}$ coupling parameters (in kHz).

| $J$ | $K$ | $R$ | $S$ |
|---|---|---|---|
| 1 | 1 | −2.798 | −15.414 |
| 2 | 2 | −8.945 | −18.594 |
| 3 | 3 | −5.919 | −18.628 |

TABLE XVI. Summary of the deviations between theory and experiment for the measured lines. Values in kHz.

| | $J$ | $K$ | Standard deviation for fit | Experimental standard deviation |
|---|---|---|---|---|
| $N^{14}$ | 1 | 1 | 0.130 | 0.048 |
| | 2 | 2 | 0.018 | 0.070 |
| | 3 | 3 | 0.221 | 0.048 |
| | 3 | 2 | 0.925 | 0.050 |
| $N^{15}$ | 1 | 1 | 1.212 | 0.198 |
| | 2 | 2 | 1.812 | 0.074 |
| | 3 | 3 | 1.071 | 0.075 |

well with the previous data; they are, respectively, 0.02 and 0.05 kHz lower than the corresponding $N^{14}$ values. The value of the hydrogen-hydrogen spin-spin parameter $U$ is 3.399 kHz for the $N^{15}$ 3-3 state. The $N^{14}$ value is 8.484 kHz and agrees with theory. The fact that these parameters are inconsistent provides another indication that there must be another interaction which is not included in the theory.

The experimental standard deviation and the standard deviation for the fits are shown on Table XVI. We see that the fit is much poorer for the $N^{14}$ 3-2 transition and the $N^{15}$ transitions. In these cases there is no quadrupole interaction.

## APPARATUS

The maser spectrometer used in these measurements has been described previously.[15]

The frequency measurements are made by comparing the crystal oscillator near 10 MHz with a signal from an atomic clock. The microwave signal used to stimulate the resonance is a multiple of this 10-MHz signal. The time scale used in these measurements is the A1 time scale[17] which locates the cesium hyperfine transition at 9 192 631 770 Hz. The atomic clock used in these measurements incorporates a National 2001 cesium beam tube and the electronics are described in more detail by Badessa *et al.*[18] It provides a signal at 16.415 413 875 MHz, accurate to a few parts in $10^{11}$. This signal is multiplied by 6 and beat with the tenth harmonic of our 10-MHz oscillator. This beat signal is multiplied by 5 and measured on a Hewlett-Packard 524B electronic counter. The reference for the counter is a Hycon 101 C ultrastable oscillator which has a stability of 1 part in $10^9$ per week and is frequently reset by using the atomic clock. Note that the beat signal is smaller than the two compared signals by a factor of 100 so that the measurement accuracy is 100 times the counter accuracy. An electrical output from the tens of Hz digit on the counter is used to provide a frequency marker each time the tens digit is 8 or 9. This marker is recorded on the strip chart recorder along with the resonance signal and provides frequency markers every 454.8 Hz (for the $N^{15}$ 3-3 line, slightly different for other lines). An example of the recorder output is shown in Fig. 1. The frequency scale is expanded by a factor of 10 for actual measurements.

## THEORY OF AMMONIA HYPERFINE STRUCTURE

We shall begin with the Hamiltonian given by Gordon and use the general methods of Edmonds to obtain all diagonal and off-diagonal terms. These off-diagonal terms are particularly important for $N^{15}H_3$, since $N^{15}$ has no quadrupole moment so terms off-diagonal in $F_1$ may be as large as the diagonal terms.

The Hamiltonian is

$$\begin{aligned}\mathcal{H}=\mathcal{H}_Q&+\left[a+\frac{(b-a)K^2}{J(J+1)}\right]\mathbf{I}_{\mathrm{N}}\cdot\mathbf{J}\\&+\left[A+\frac{CK^2}{J(J+1)}-\delta_{K1}(-1)^{J+V}B\right]\mathbf{I}\cdot\mathbf{J}\\&+D_1(\mathbf{I}\cdot\mathbf{I}_{\mathrm{N}}-3I_zI_{\mathrm{N}z})+3D_2(I_{1y}I_{\mathrm{N}y}-I_{1x}I_{\mathrm{N}x})\\&-\tfrac{1}{4}D_3(I^2-3I_z^2).\end{aligned}$$

The derivation of these terms from the basic two-particle electromagnetic interactions has been discussed by many authors.[2,3,5,9,16,19,20] The coupling scheme for $NH_3$ (in the "space" frame) is $\mathbf{F}_1=\mathbf{I}_{\mathrm{N}}+\mathbf{J}$, $\mathbf{F}=\mathbf{F}_1+\mathbf{I}$, where $I$ is the sum of the hydrogen spins, and $I_{\mathrm{N}}$ is the nitrogen spin. For the spin-spin interactions we shall employ the molecular-frame coupling scheme given by Van Vleck.[9,19] In this scheme the signs of the nuclear spins are reversed and the coupling scheme becomes $\mathbf{F}_1=\mathbf{I}'+\mathbf{F}$, $\mathbf{J}=\mathbf{I}_{\mathrm{N}}'+\mathbf{F}_1$. The commutation relations between all angular momenta in both schemes are given by Hadley.[6]

The quadrupole interaction is the scalar product of two tensor operators $\mathcal{H}_Q=\mathbf{V}\cdot\mathbf{Q}$, where $\mathbf{V}$ is due to the electron distribution and depends on $J$, $K$, while $\mathbf{Q}$ is due to the nitrogen nucleus and depends on $\mathbf{I}_{\mathrm{N}}$. In the coupling scheme $\mathbf{F}_1=\mathbf{I}_{\mathrm{N}}+\mathbf{J}$ we have

$$\mathcal{H}_Q=(-1)^{J+I_{\mathrm{N}}+F_1}\begin{Bmatrix}F_1 & I_{\mathrm{N}} & J'\\ 2 & J & I_{\mathrm{N}}\end{Bmatrix}\times(J'K\|V\|JK)(I_{\mathrm{N}}\|\mathbf{Q}\|I_{\mathrm{N}}).$$

$\mathbf{V}$ for a symmetric top is

$$(J'K\|\mathbf{V}\|JK)=\tfrac{1}{2}q[(2J'+1)(2J+1)]^{1/2}\times(-1)^{J'+K}\begin{pmatrix}J' & 2 & J\\ -K & 0 & K\end{pmatrix},$$

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[17] F. H. Reder, Frequency **1**, 32 (1963).

[18] R. S. Badessa, V. J. Bates, and C. L. Searle, IEEE Trans. Instr. Meas. **IM-13**, 175 (1964).

[19] J. H. Van Vleck, Rev. Mod. Phys. **23**, 213 (1951).

[20] Reference 12, Chap. 8.

and $\mathbf{Q}$ is

$$(I_N\|\mathbf{Q}\|I_N)=\tfrac{1}{2}eQ(2I_N+1)\left[\frac{(2I_N+3)(I_N+1)}{I_N(2I_N-1)(2I_N+1)}\right]^{1/2},$$

and so the quadrupole interaction is

$$\mathcal{H}_Q=\tfrac{1}{4}eQq[(2J'+1)(2J+1)]^{1/2}$$
$$\times(-1)^{J'+K}\begin{pmatrix} J' & 2 & J \\ -K & 0 & K \end{pmatrix}(2I_N+1)$$
$$\times\left[\frac{(2I_N+3)(I_N+1)}{I_N(2I_N-1)(2I_N+1)}\right]^{1/2}$$
$$\times(-1)^{J+I_N+F_1}\begin{Bmatrix} F_1 & I_N & J' \\ 2 & J & I_N \end{Bmatrix}.$$

For the special case $J'=J$ this reduces to the expression given by Townes and Schawlow.[16] The factor $eQq$ is approximately 4090 kHz in $NH_3$ and the second-order perturbation shift due to terms off-diagonal in $J$ is typically a few Hz or less. An equivalent expression for the off-diagonal terms is also given by Townes and Schawlow.[16]

The nitrogen $\mathbf{I}_N\cdot\mathbf{J}$ term is given by Gordon[3] and discussed by Townes and Schawlow.

$$\mathcal{H}_{I_N\cdot J}=\left[a+\frac{(b-a)K^2}{J(J+1)}\right]\mathbf{I}_N\cdot\mathbf{J}.$$

This term only has elements diagonal in $F_1$. To be consistent with Gordon we will evaluate the $\mathbf{I}\cdot\mathbf{J}$ matrix elements in the space frame, where $\mathbf{F}_1=\mathbf{I}_N+\mathbf{J}$, $\mathbf{F}=\mathbf{F}_1+\mathbf{I}$. (This avoids an additional minus sign in the coupling coefficient.) In the $F_1$ scheme

$$\langle F_1|\mathbf{I}_N\cdot\mathbf{J}|F_1\rangle=(-1)^{I_N+J+F_1}$$
$$\times[I_N(I_N+1)(2I_N+1)J(J+1)(2J+1)]^{1/2}$$
$$\times\begin{Bmatrix} F_1 & I_N & J \\ 1 & J & I_N \end{Bmatrix}.$$

The hydrogen $\mathbf{I}\cdot\mathbf{J}$ term is given by Gordon and Gunther-Mohr as

$$\mathcal{H}_{I\cdot J}=\left[A+\frac{CK^2}{J(J+1)}-\delta_{K1}(-1)^{J+V}B\right]\mathbf{I}\cdot\mathbf{J}.$$

The third term only occurs for $K=1$, since here matrix elements arise between $K=1$ and $K=-1$ states. $V=0$ for the lower inversion state and $V=1$ for the upper state. It results from diagonalization of the Hamiltonian with respect to $K$ and will be discussed later. We may use the results of Edmonds or of Thaddeus *et al.* to get

$$(F_1'F|\mathbf{I}\cdot\mathbf{J}|F_1F)=(-1)^{1+J+I_N+I+F+2F_1}$$
$$\times[J(J+1)(2J+1)(2F_1+1)(2F_1'+1)$$
$$\times I(I+1)(2I+1)]^{1/2}\begin{Bmatrix} J & F_1' & I_N \\ F_1 & J & 1 \end{Bmatrix}\begin{Bmatrix} F & I & F_1' \\ 1 & F_1 & I \end{Bmatrix}.$$

The hydrogen-nitrogen spin-spin term is given by Gordon as

$$\mathcal{H}_{H-N}=D_1(\mathbf{I}\cdot\mathbf{I}_N-3I_zI_{Nz})+3D_2(I_{1y}I_{Ny}-I_{1x}I_{Nx}),$$

where

$$D_1=g_Hg_N\mu_0^2\langle V|r_{NH}^{-3}(1-\tfrac{3}{2}\sin^2\beta)|V\rangle,$$
$$D_2=g_Hg_N\mu_0^2\langle V|r_{NH}^{-3}\tfrac{3}{2}\sin^2\beta|V\rangle.$$

$\beta$ is shown in Ref. 3. The terms diagonal in $F_1$ for the hydrogen-nitrogen and hydrogen-hydrogen interactions were obtained by Gordon[3] and Hadley.[5] We will need the off-diagonal terms, however, for small corrections in the analysis of $N^{14}H_3$ spectra and as an essential part in the $N^{15}H_3$ spectra.

Here we must use the molecular frame coupling scheme of Van Vleck where the signs of the internal spin angular momenta $(I_1,I_2,I_3,I_N)$ are reversed so that

$$\mathbf{I}'=\mathbf{I}_1'+\mathbf{I}_2'+\mathbf{I}_3',$$
$$\mathbf{F}_1=\mathbf{F}+\mathbf{I}',$$
$$\mathbf{J}=\mathbf{F}_1+\mathbf{I}_N'.$$

We note that $(3I_zI_{Nz}-\mathbf{I}\cdot\mathbf{I}_N)=-(\sqrt{6})T_{20}(I_N,I)$, where $T_{20}$ is a second-rank tensor operator, and

$$(I_{1y}I_{Ny}-I_{1x}I_{Nx})=-T_{22}(I_1,I_N)-T_{2,-2}(I_1,I_N),$$

so we may write the hydrogen-nitrogen spin-spin interactions as

$$\mathcal{H}_{HN1}=-(\sqrt{6})D_1T_{20},$$
$$\mathcal{H}_{HN2}=-3D_2(T_{22}+T_{2,-2}).$$

Evaluating the $K$ dependence of $T_{20}$, we get

$$\langle\mathcal{H}_{HN1}\rangle=-(\sqrt{6})D_1(-1)^{J-K'}\begin{pmatrix} J & 2 & J \\ -K' & 0 & K \end{pmatrix}$$
$$\times(J,I_N,F_1',F,I\|T_2(I,I_N)\|J,I_N,F_1,F,I)$$
$$=\frac{-(\sqrt{6})D_1[3K^2-J(J+1)]}{[J(J+1)(2J+1)(2J+3)(2J-1)]^{1/2}}$$
$$\times(J,I_N,F_1',F,I\|T_2\|J,I_N,F_1,F,I)$$

and

$$\langle\mathcal{H}_{\mathrm{HN2}}\rangle=-3D_2(-1)^{J-K'}$$

$$\times\left[\begin{pmatrix} J & 2 & J \\ -K' & 2 & K\end{pmatrix}+\begin{pmatrix} J & 2 & J \\ -K' & -2 & K\end{pmatrix}\right]$$

$$\times(J,I_{\mathrm{N}},F_1,F,I\|T_2(I_1,I_{\mathrm{N}})\|J,I_{\mathrm{N}},F_1,F,I).$$

We see that the 3-$j$ symbols vanish unless $K'-K=\pm2$. If we require that $K^2$ be the same for both states so that they will have the same rotational energy, then $K^2=1$. This term will only be important therefore for $K=\pm1$. The $K=\pm1$ states are degenerate and GTV[2] have shown that when the Hamiltonian is diagonalized with respect to $K$ the energy shift of the new states produced by $H_{\mathrm{HN2}}$ is $(-1)^{J+V}H_{\mathrm{HN2}}$. It is shown by GTV that $T_2(I_1,I_{\mathrm{N}})=T_2(I,I_{\mathrm{N}})$,

$$\langle\mathcal{H}_{\mathrm{NH2}}\rangle=-D_2\delta_{K1}(-1)^{J+V}$$

$$\times\frac{(\sqrt{6})J(J+1)}{[J(J+1)(2J+1)(2J+3)(2J-1)]^{1/2}}$$

$$\times(J,I_{\mathrm{N}},F_1',F,I\|T_2(I,I_{\mathrm{N}})\|J,I_{\mathrm{N}},F_1,I).$$

The terms $H_{\mathrm{HN1}}$ and $H_{\mathrm{HN2}}$ may be combined to give

$$\langle\mathcal{H}_{\mathrm{NH}}\rangle=[-(\sqrt{6})D_1[3K^2-J(J+1)]$$

$$-(\sqrt{6})D_2\delta_{K1}(-1)^{J+V}J(J+1)]$$

$$\times\frac{(J,I_{\mathrm{N}},F_1',F,I\|T_2(I,I_{\mathrm{N}})\|J,I_{\mathrm{N}},F_1,F\ I)}{[J(J+1)(2J+1)(2J+3)(2J-1)]^{1/2}}.$$

In the coupled system $\mathbf{J}=\mathbf{F}_1+\mathbf{I}_{\mathrm{N}}'$ and $\mathbf{F}_1=\mathbf{F}+\mathbf{I}'$, we have

$$(J,I_{\mathrm{N}},F_1',F,I\|T_2\|J,I_{\mathrm{N}},F_1,F,I)=[(2I_{\mathrm{N}}+1)(I_{\mathrm{N}}+1)I_{\mathrm{N}}(2I+1)I(I+1)(2F_1'+1)(2F_1+1)]^{1/2}$$

$$\times(-1)^{F+I+F_1'+1}(\sqrt{5})(2J+1)\begin{Bmatrix} I & F_1' & F \\ F_1 & I & 1\end{Bmatrix}\begin{Bmatrix} F_1' & F_1 & 1 \\ I_{\mathrm{N}} & I_{\mathrm{N}} & 1 \\ J & J & 2\end{Bmatrix}.$$

It can be shown that for the special case $F_1'=F_1$ this reduces to the hydrogen-nitrogen spin-spin term given by Gordon[3] and Hadley.[5,6]

The hydrogen-hydrogen spin-spin term is given by Gordon as $H_{\mathrm{HH}}=-\frac{1}{4}D_3[(\mathbf{I}\cdot\mathbf{I})-3I_zI_z]$, where $D_3=(g_{\mathrm{H}}\mu_0)^2\times r_{\mathrm{HH}}^{-3}$. Here again we must use the molecular frame coupling scheme. We see that $H_{\mathrm{HH}}=-(\frac{1}{4}\sqrt{6})D_3T_{20}(I)$ and we may evaluate $T_{20}(I)$ in the coupled scheme,

$$(J,K,I_{\mathrm{N}},F_1',F,I\|T_{20}(I)\|J,K,I_{\mathrm{N}},F_1,F,I)=(-1)^{J-K}\begin{pmatrix} J & 2 & J \\ -K & 0 & K\end{pmatrix}(J,I_{\mathrm{N}},F_1',F,I\|T_2(I)\|J,I_{\mathrm{N}},F_1,F,I)$$

$$=\frac{[3K^2-J(J+1)]}{[J(J+1)(2J+1)(2J+3)(2J-1)]^{1/2}}(J,I_{\mathrm{N}},F_1',F,I\|T_2(I)\|J,I_{\mathrm{N}},F_1,F,I).$$

In the coupled scheme $J=\mathbf{F}_1+\mathbf{I}_{\mathrm{N}}'$ so we get

$$(J,I_{\mathrm{N}},F_1',F,I\|T_2(I)\|J,I_{\mathrm{N}},F_1,F,I)=(2J+1)(-1)^{J+I_{\mathrm{N}}+F_1'+F_1+F+3I}[(2F_1'+1)(2F_1+1)]^{1/2}$$

$$\times\begin{Bmatrix} F_1' & J & I_{\mathrm{N}} \\ J & F_1 & 2\end{Bmatrix}\begin{Bmatrix} I & F_1' & F \\ F_1 & I & 2\end{Bmatrix}\left[\frac{(2I+3)(2I-1)}{2I(I+1)(2I+1)3}\right]^{1/2}[I(I+1)(2I+1)].$$

It can be shown that for the special case $F_1'=F_1$ these expressions reduce to the hydrogen-hydrogen spin-spin term given by Gordon[3] and Hadley.[5]

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