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# Structure of the Inversion Spectrum of Ammonia*

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Measurements of the fine structure in the ammonia inversion spectrum have been extended into the millimeter wave region to the 16,16 line at 39941 mc/sec. The relative intensities and positions of the lines are compared with calculated values. The hyperfine structures of 15 lines have been measured. A systematic disagreement is shown to exist between the theoretical and observed separations of the hyperfine components. There is good agreement between the observed and calculated intensities of the hyperfine structure.

## 1. INTRODUCTION

SINCE the first reporting of the fine structure in the inversion spectrum of ammonia by Bleaney and Penrose[1] and by Good,[2] several observers have made measurements on this molecule in the region 20,000 mc/sec. to 26,000 mc/sec. The hyperfine structure in the inversion spectrum was first detected by Good.[2] The formula for predicting the energy of interaction of the nuclear quadrupole moment with the molecular field has been given by Coles and Good[3] and also by Dailey, Kyhl, Strandberg, Van Vleck, and Wilson.[4] More recently it has been derived by Jauch,[5] who also gives a theoretical treatment of the Stark effect. The spacings of the hyperfine structures for the 1,1; 2,2; 3,3; and 4,4 lines have been measured by Dailey *et al.*,[4] and have been remeasured by Watts and Williams,[6] who extended the measurements to the 6,6 line.

The present work extends the observation into the millimeter wave region of the microwave spectrum, to the 16,16 line at 39,941 mc/sec. and extends the measurements of the hyperfine structures to include fifteen lines. Both the relative intensities and the frequencies of the different lines, including the hyperfine components, have been computed and compared with the observed values.

## 2. EXPERIMENTAL PROCEDURE

The observations were made with a single crystal detector employing a filter as described by Gordy and Kessler.[7] The positions of the lines of the fine structure were measured with multiples of the standard frequencies broadcast by WWV. The hyperfine structure was measured by frequency modulation of the microwave oscillator so as to produce moveable images of the main line, following the method used by Dailey, Strandberg *et al.*[4] The signal generator used to produce the images of the hyperfine structure was also calibrated with WWV.

## 3. FINE STRUCTURE

### Frequencies

The frequencies of the new lines observed are given in Table I, beginning with the line for $J=8$. It has been found that these vary widely from those predicted by the various equations for line positions given in previous reports.[2,8,9] An attempt has been made to adjust the constants in the equation as given by Good[2] in order to obtain a better fit. The resulting expression is:

$$\begin{aligned}\nu(\text{mc/sec.}) = 23{,}787 - 151.3J(J+1) \\ +211.0K^2+0.5503J^2(J+1)^2 \\ -1.531J(J+1)K^2+1.055_5K^4.\end{aligned}$$

The r.m.s. deviation predicted from observed frequencies for all fine structure lines so far

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[1] B. Bleaney and R. P. Penrose, Nature **157**, 339 (1946).

[2] W. E. Good, Phys. Rev. **70**, 213 (1946).

[3] D. K. Coles and W. E. Good, Phys. Rev. **70**, 679 (1946).

[4] B. P. Dailey, R. L. Kyhl, M. W. P. Strandberg, J. H. Van Vleck, and E. B. Wilson, Jr., Phys. Rev. **70**, 984 (1946).

[5] J. M. Jauch, Phys. Rev. **72**, 715 (1947).

[6] R. J. Watts and D. Williams, Phys. Rev. **72**, 263 (1947).

[7] W. Gordy and M. Kessler, Phys. Rev. **71**, 640 (1947).

[8] C. H. Townes, Phys. Rev. **70**, 665 (1946).

[9] M. W. P. Strandberg, R. Kyhl, T. Wentink, Jr., and R. E. Hillger, Phys. Rev. 71, 326 (1947); 71, 639 (1947).

Table I. Frequencies and relative intensities of $N^{14}H_3$ absorption lines ($T=297°K$).

| | | | Relative intensities | | | |
|---|---|---|---|---|---|---|
| | | | Calculated | | Observed | |
| $J$ | $K$ | $\nu$ (mc/sec.) | main line only | main line and satellites | main line only | main line and satellites |
| 1 | 1 | 23694.49* | 10.0 | 19.9 | 15. | 30. |
| 2 | 2 | 23722.63 | 30.6 | 38.5 | 37. | 46. |
| 3 | 3 | 23870.13 | 89.3 | 100 | 89. | 100 |
| 4 | 4 | 24139.41 | 49.9 | 53.4 | 57. | 61. |
| 5 | 5 | 24532.98 | 47.9 | 50.2 | 46. | 48. |
| 6 | 6 | 25056.02 | 82.8 | 85.5 | 77. | 79. |
| 7 | 7 | 25715.17 | 32.4 | 33.2 | 29. | 30. |
| 8 | 8 | 26518.91** | → | 23.8 | → | 22. |
| 9 | 9 | 27478.00 | | 31.9 | | 28. |
| 10 | 10 | 28604.73 | | 9.9 | | 9. |
| 11 | 11 | 29914.66 | | 5.8 | | 6. |
| 12 | 12 | 31424.97 | | 6.3 | | 7. |
| 13 | 13 | 33156.95 | | 1.6 | | 1.8 |
| 14 | 14 | 35134.44 | | 0.8 | | 0.8 |
| 15 | 15 | 37385.18 | | 0.7 | | 0.6 |
| 16 | 16 | 39941.54 | | $0.1_5$ | | $0.1_3$ |
| 13 | 12 | 26655.00 | | 1.8 | | 2.8 |
| 14 | 13 | 27772.52 | | 0.3 | | 0.6 |
| 15 | 14 | 29061.14 | | $0.1_5$ | | 0.2 |

* Frequencies of lines with $J=1$ through $J=7$ are as given by Good and Coles.[11]

** Limit of error in frequencies of lines with $J=8$ and higher is ±0.10 mc/sec, except for the 16,16 line for which it is 0.30 mc/sec.

observed is about 26 mc/sec. Although the agreement is fairly good, still higher order terms must be included in order to obtain agreement within the range of possible error in the frequencies. In calculating this deviation, allowance has been made for the shift of the lines of $K=3$ from their normal positions as reported by Strandberg *et al.*[9] and treated theoretically by Nielsen and Dennison.[10] When the observed frequencies are corrected for these shifts, the curves of difference between observed and predicted line frequencies are very smooth. In addition, no apparent shift from a smooth curve of lines for which $K=6$ or higher multiples of 3 has been observed.

Table II. The satellite separations and nuclear quadrupole coupling coefficients in the inversion spectrum of $NH_3$.*

| | | | | | | Ratio $\Delta\nu'/\Delta\nu$ | | $eQ(\partial^2V/\partial z^2)$ | |
|---|---|---|---|---|---|---|---|---|---|
| $J$ | $K$ | $\Delta\nu$ | s.d.** | $\Delta\nu'$ | s.d.** | calc. | obs. | calc. from $\Delta\nu$ | calc. from $\Delta\nu'$ |
| 1 | 1 | 0.609 | ±0.011 | 1.536 | ±0.012 | 2.50 | 2.52 | 4.06 | 4.10 |
| 2 | 2 | 1.286 | 0.005 | 2.064 | 0.006 | 1.56 | 1.61 | 4.00 | 4.13 |
| 3 | 3 | 1.683 | 0.009 | 2.327 | 0.009 | 1.35 | 1.38 | 4.04 | 4.14 |
| 4 | 4 | 1.911 | 0.008 | 2.488 | 0.006 | 1.26 | 1.30 | 4.01 | 4.15 |
| 5 | 5 | 2.075 | 0.005 | 2.613 | 0.010 | 1.20 | 1.26 | 4.00 | 4.18 |
| 6 | 6 | 2.202 | 0.008 | 2.686 | 0.008 | 1.17 | 1.21 | 4.01 | 4.18 |
| 7 | 7 | 2.312 | 0.012 | 2.758 | 0.019 | 1.14 | 1.19 | 4.03 | 4.20 |
| 8 | 8 | 2.374 | 0.029 | 2.795 | 0.028 | $1.12_5$ | 1.18 | 4.01 | 4.19 |
| 9 | 9 | 2.443 | 0.024 | 2.812 | 0.010 | 1.11 | 1.15 | 4.02 | 4.17 |
| 2 | 1 | −0.665 | 0.007 | −1.005 | 0.006 | $1.55_5$ | 1.51 | 4.14 | 4.02 |
| 4 | 3 | 0.465 | 0.005 | 0.642 | 0.007 | 1.26 | 1.38 | 3.90 | 4.28 |
| 5 | 4 | 0.828 | 0.010 | 1.054 | 0.016 | 1.20 | 1.27 | 3.99 | 4.22 |
| 6 | 5 | 1.093 | 0.018 | 1.354 | 0.014 | 1.17 | 1.24 | 3.97 | 4.22 |
| 7 | 6 | 1.305 | 0.020 | 1.577 | 0.022 | 1.14 | 1.21 | 3.98 | 4.21 |
| 4 | 2 | | | −0.656 | 0.010 | | | | 3.83 |

* All readings other than ratio columns are in mc/sec.

** These columns are the standard deviations in the observed readings, of which approximately 16 were made on each satellite.

## Intensities

The calculated and observed relative intensities of the new lines observed are also given in Table I. In order to give an over-all picture of the complete inversion spectrum for the $J=K$ lines, there have been included in the table the lines from $J=1$ to $J=7$ as previously reported by others.[9, 11] The observed intensities of these lines, however, are as recorded in this laboratory. The effect of the hyperfine structure in reducing the height of the center line for values up to $J=7$ is also given. Above this value for $J$ the satellite intensities are too small to detract appreciably from the center line intensity.

The calculated values of intensities have been figured using the expression[12]

$$I(J,K)=\frac{C\nu K^2}{J(J+1)}g_{J,K}\exp\left[\frac{-E(J,K)hc}{kT}\right].$$

Here $g_{J,K}$ is the statistical weight of the lower state, being $(2J+1)$ for $K=1, 2, 4, 5, \cdots$ and $2(2J+1)$ for $K=3, 6, 9, \cdots$, since the effect of the nuclear spins of the three identical hydrogen atoms is to increase the weights of the state for which $K$ is divisible by 3 by a factor of 2 over those for the other states.

Table III. Comparison of nuclear quadrupole coupling coefficients calculated from reported satellite separations in the inversion spectrum of $NH_3$.

| | | $eQ(\partial^2V/\partial z^2)$($mc$/sec.) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Present work | | Dailey, Kyhl *et al.*[4] | | Watts and Williams[6] | |
| $J$ | $K$ | calc. from $\Delta\nu$ | calc. from $\Delta\nu'$ | calc. from $\Delta\nu$ | calc. from $\Delta\nu'$ | calc. from $\Delta\nu$ | calc. from $\Delta\nu'$ |
| 1 | 1 | 4.06 | 4.10 | 4.00 | 4.19 | 4.17 | 4.29 |
| 2 | 2 | 4.00 | 4.13 | 4.04 | 4.10 | 4.14 | 4.20 |
| 3 | 3 | 4.04 | 4.14 | 4.13 | 4.16 | 4.18 | 4.25 |
| 4 | 4 | 4.01 | 4.15 | 4.00 | 4.13 | 4.15 | 4.23 |
| Av. | | 4.03 | 4.13 | 4.04 | $4.14_5$ | 4.16 | 4.24 |

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[10] H. H. Nielsen and D. M. Dennison, Phys. Rev. **72**, 86 (1947).

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

[12] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 421.

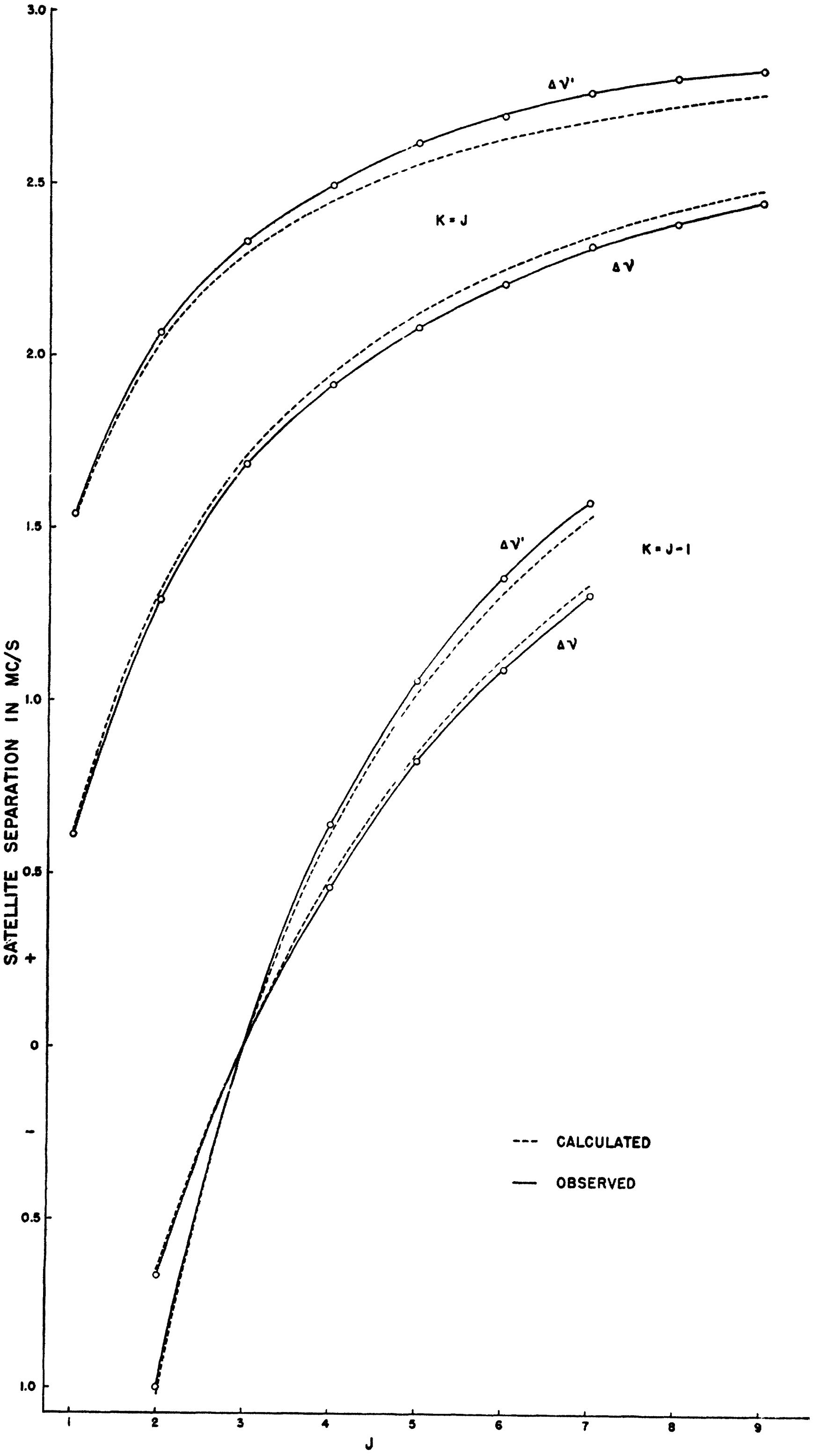

FIG. 1. Comparison of calculated (with $eQ(\partial^2 V/\partial z^2) = 4.08$ mc/sec.) and observed satellite separations for lines of $K=J$ and $K=J-1$.

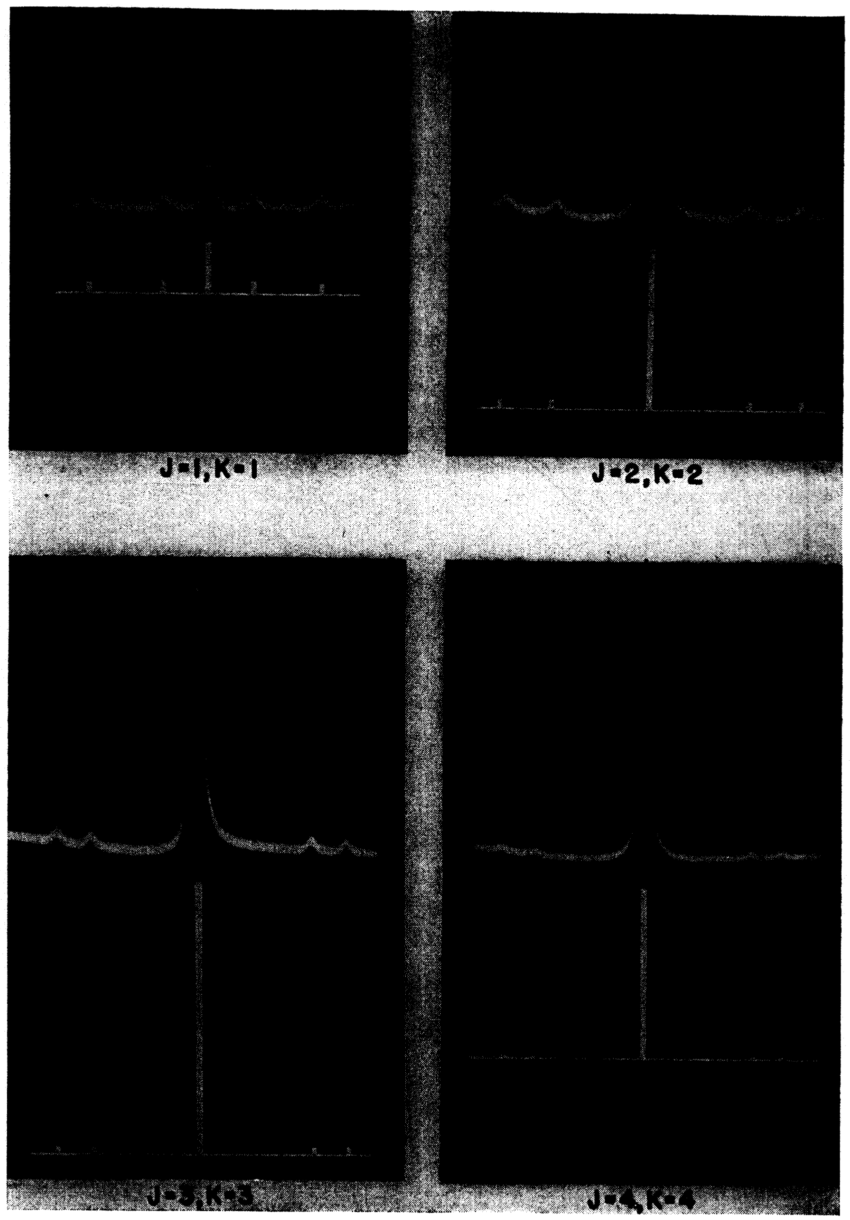

FIG. 2. Comparison of calculated relative intensities of the hyperfine structure with that observed for the first 4 lines with $J=K$.

## 4. HYPERFINE STRUCTURES

### Frequencies

The hyperfine structures of 15 lines of the ammonia spectrum have been measured under very high resolution. These observations revealed a discrepancy between the measured and the theoretically predicted positions of the lines.

Table II lists the observed separations of the satellites from the main lines. Following the usual convention, the separation of the outer satellites is designated as $\Delta\nu'$ and that of the inner satellites as $\Delta\nu$. The nuclear quadrupole coupling factor, $eQ\partial^2 V/\partial z^2$, has been computed from each value of $\Delta\nu$ and $\Delta\nu'$, using the formula

$$E=eQ\frac{\partial^2 V}{\partial z^2}\left(\frac{3K^2}{J(J+1)}-1\right)\times\left(\frac{3/4C(C+1)-I(I+1)J(J+1)}{2(2J+3)(2J-1)I(2I-1)}\right),$$

where

$$C=F(F+1)-I(I+1)-J(J+1),$$

and

$$F=J+I,\ J+I-1,\ \cdots,\ |J-I|.$$

These factors are listed in Table II. It is apparent that the values of $eQ(\partial^2V/\partial z^2)$ determined from $\Delta\nu$ are consistently lower than those from $\Delta\nu'$ except for the 2,1 line and the 4,2 line. The same trend is also shown in another way, i.e., by a comparison of the observed and calculated ratios of $\Delta\nu$ to $\Delta\nu'$. The apparent cause for the reversal of the trend in the 2,1 and 4,2 lines is the reversal in the sign of the energy in these cases.

Figure 1 illustrates the uniformity in the observed data as well as the departure of these data from theory. The dotted curves represent the theoretical values of $\Delta\nu$ and $\Delta\nu'$, calculated with the above formula using a quadrupole coupling coefficients of 4.08 mc/sec. which is the mean of the two values determined from $\Delta\nu$ and $\Delta\nu'$ of the 1,1 line. The solid curves indicate the experimentally determined values for the frequencies.

Table III shows how our values for the coupling coefficients, determined from the first 4 lines, compare with those determined from the data of other groups. Though previous data were not sufficient to show up the disagreement of theory with experiment[13] mentioned above, the trend is noticeable in these data.

Evidently there is an interaction of higher order which measurably affects the hyperfine structure of the ammonia molecule, and which has not been taken into consideration in the theory of the hyperfine structure. A possibility which may be suggested is that a nuclear octupole interaction occurs. However, it seems unlikely that there would be sufficient nuclear asymmetry in an atom with a nuclear spin of one to account for the effects in this way. Perhaps a more promising explanation is that there is a perturbation between energy levels of different $J$ but of the same total angular momentum quantum number $F$. Because of the wide separation of the rotational levels, however, it appears that this type of interaction would not be of the required magnitude. There may exist at the nitrogen nucleus a small magnetic field due to molecular rotation which could interact with the nuclear magnetic moment to cause the observed effects. We are attempting to test the various hypotheses. Further theoretical work is evidently required to explain satisfactorily the anomalous effects which have been found.

## Intensities

In the previous publications no quantitative comparison has been made between calculated and observed intensities of the hyperfine structure. In Fig. 2 the calculated and observed relative intensities are shown for the first 4 lines with $J=K$. The relative intensities were calculated by the methods employed in atomic spectra. The formulae used are[14]

$$I_0=\frac{(2F+1)}{F(F+1)}\cdot R^2(F),\quad \text{for } F\rightarrow F,$$

$$I_\pm=\frac{1}{F}P(F),\quad Q(F-1),$$

$$\text{for } F\rightarrow(F-1) \text{ or } (F+1)\rightarrow F,$$

where

$$P(F)=(F+J)(F+J+1)-I(I+1),$$
$$Q(F)=I(I+1)-(F-J)(F-J+1),$$
$$R(F)=F(F+1)+J(J+1)-(I+1).$$

No similar display of calculated and observed intensities for lines of higher $J$ is feasible because of the small intensity of the satellites compared to that of the main line. For example, for the 6,6 line the satellites are of about equal intensity and are 0.82 percent of the intensity of the main line. For the 9,9 line they are only 0.37 percent as strong as the main line. The photographs show that agreement between theoretical and observed intensities is good. The agreement between the observed intensities and those calculated by Jauch's[5] formulae is not satisfactory.* In making these photographs care was taken to prevent saturation of the molecules with radi-

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[13] Watts and Williams (reference 6), who made measurements on seven lines, state that their results are in agreement with Van Vleck's theory within the limits of their experimental errors. Later Williams (Phys. Rev. **72**, 974 (1947)) reported that satellites near lines with $J$ as high as 10 had been measured. Though he did not state his results he said they were in agreement with theory.

[14] A. C. Candler, *Atomic Spectra and the Vector Model* (University Press, Cambridge, 1937), Vol. II, p. 187.

ation, which could easily cause falsification of the relative intensities.

We wish to acknowledge helpful discussions with Professor L. Nordheim and the assistance of Mr. R. L. Carter in obtaining the photographs.

*Note added in proof:* Through a private communication, Dr. J. M. Jauch has informed us of an error in his intensity formulae (reference 5). The errors involve the values of $Q(J)$, $A_{J-1,\,J}$ and $A_{J,\,J+1}$, which should be

$$Q(J)=\frac{(2J-1)(J-1)(J+1)^3+(2J+3)(J+2)J^3}{2J+1}+[J(J+1)-1]^2$$

$$A_{J-1,\,J}=K^2(2J-1)/3J^3(J+1)$$

$$A_{J,\,J+1}=K^2(2J+3)/3J(J+1)^3$$

rather than the expressions given in the original paper. The corrected forms give values in agreement with the results of the present paper.

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# The Hyperfine Structure of Hydrogen and Deuterium*

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The atomic-beam magnetic resonance method has been applied to measure the h.f.s. separation of the ground state of H and D by observing frequencies of the r-f field required to induce transitions among certain of the magnetic levels of the h.f.s. multiplets in magnetic fields of the order of 1 gauss. The resonance minima were of the theoretical width for transitions which are field independent in the first order. For deuterium we find $\nu_D=327.384\pm0.003$ Mc which agrees with our previously reported value within the precision claimed for that quantity. For hydrogen we find $\nu_H=1420.410\pm0.006$ Mc which is less than the value previously reported by 0.06 percent. The ratio of the measured h.f.s. separations, $\nu_H/\nu_D$, is $4.33867\pm0.00004$.

The h.f.s. separations, $\nu_H$ and $\nu_D$, may be calculated from known values of the magnetic moment of the proton, $\mu_p$, and the magnetic moment of the deuteron, $\mu_d$. The measured $\nu_H$ and $\nu_D$ are larger than the calculated values by 0.24 percent and 0.26 percent, respectively. The ratio $\nu_H/\nu_D$ may be calculated from the known ratio $\mu_p/\mu_d$ using the ordinary reduced mass correction (discussed in the section entitled "Discussion of Results" of this paper). This ratio is independent of $\alpha^2$ and $R_\infty$. The calculated ratio is found to be higher than our value by 0.017 percent. This discrepancy is 18 times the probable error in our measurements.

## 1. INTRODUCTION

THIS paper describes a precision measurement of the hyperfine structure separation of the ground state for the atoms H and D. The experiment depends on the application of the atomic-beam magnetic resonance method previously applied in investigations of the radiofrequency spectra of atoms.[1–3] The h.f.s. separation, $\nu_H$, for hydrogen and the corresponding quantity, $\nu_D$, for deuterium are obtained directly in terms of a fundamental time standard, and depend neither on a knowledge of the gyromagnetic ratio of the nuclear or atomic systems nor on a measurement of magnetic field intensity. None of the experimentally determined constants of physics enter into the measurement.

The h.f.s. splitting of a $^2S_{1/2}$ state in consequence of the perturbing field at the position of the electron produced by the magnetic moment of the nucleus has been calculated by Fermi.[4] The separation, $\nu$, of the h.f.s. doublet terms expressed in absolute frequency units was found to be

$$\nu=(8\pi/3h)(2I+1/I)\mu_0\mu_N\psi^2(0), \qquad (1)$$

where $I$ is the nuclear spin in units of $\hbar$, $\mu_0$ is the Bohr magneton, $\mu_N$ is the nuclear magnetic moment in absolute units, and $\psi(0)$ is the

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[1] P. Kusch, S. Millman, and I. I. Rabi, Phys. Rev. **57**, 765 (1940).

[2] S. Millman and P. Kusch, Phys. Rev. **58**, 538 (1940).

[3] J. R. Zacharias, Phys. Rev. **61**, 270 (1942).

[4] E. Fermi, Zeits. f. Physik **60**, 320 (1930).

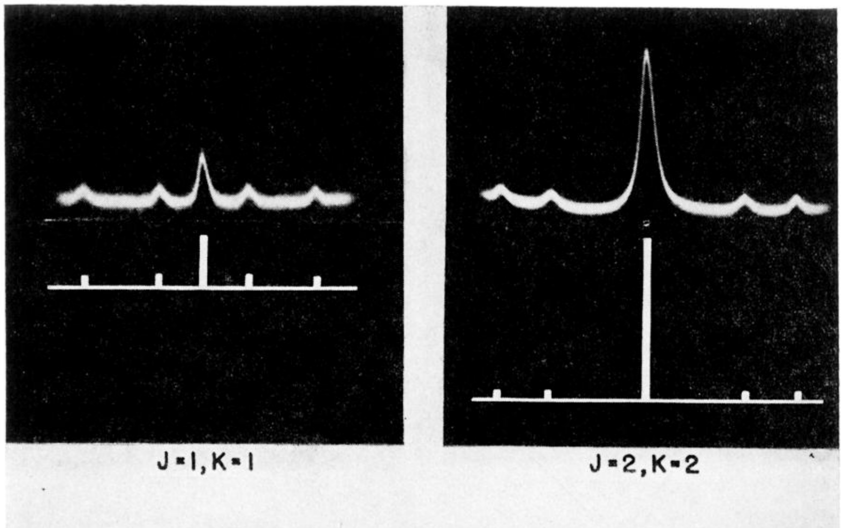

FIG. 2. Comparison of calculated relative intensities of the hyperfine structure with that observed for the first 4 lines with $J=K$.