The Stark Effect of the Ammonia Inversion Spectrum*

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A detailed study of the Stark effect of certain transitions in the inversion spectrum of ammonia has been made. The hyperfine structure due to quadrupole and electric field effects is in agreement with theory. The value 1.468±0.009D has been obtained for the dipole moment. Consideration has been given to possible second-order effects; their influence is shown to be negligible.

I. INTRODUCTION

In this paper we shall report the results of a detailed study of the Stark effect for the $J,K=1,1$; 2,2; and 3,3 transitions in the inversion spectrum of $N^{14}H_3$. In these experiments the combined effects of the electric field and the quadrupole moment of the nitrogen nucleus have been observed and accounted for. The experimental results from the 1,1 and 2,2 transitions in the intermediate and strong-field regions have been compared with exact solutions of the appropriate secular equations. The strong-field behavior of the 3,3 line is in agreement with the calculation of Jauch.[1] A precise value of the dipole moment of ammonia has been obtained from the strong-field measurements of the three lines.

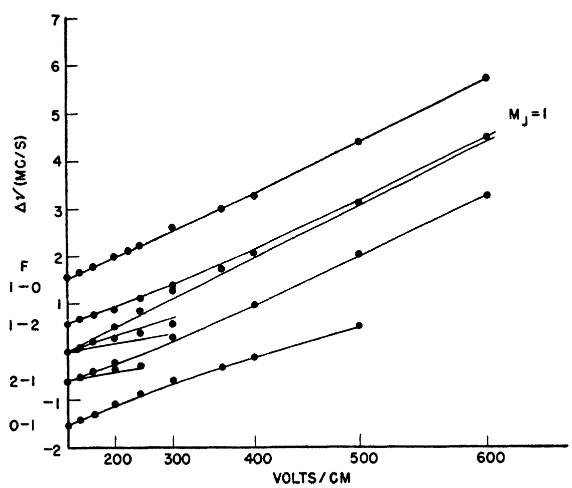

FIG. 1. Stark effect for $J,K=1,1$ ammonia line. Solid lines were computed; circles denote experimentally observed points.

II. EXPERIMENTAL

Measurements of the Stark effect were made using both straight detection[2] and Stark modulation;[3] however, better resolution was obtained with the former method. The constant used in conversion of the voltage applied to the wave guide electrode to electric field strength was checked by a measurement of the dipole moment of OCS. Our value of 0.712±0.005D is in agreement with the careful determinations of Shulman and Townes.[4]

The solid lines of Figs. 1–3 show the computed Stark effect as a function of the electric field for the $J,K=1,1$; 2,2; and 3,3 ammonia lines, respectively. The experimentally determined values, represented by the circles, are seen to be in excellent agreement with theory. In the case of unresolved lines, the observed resultant line falls at the approximate center of gravity of the group. A photograph of the triplet characteristic of the $M_J=1$ transition is shown in Fig. 4. The data given in Fig. 3 for the $J,K=3,3$ line were taken with a

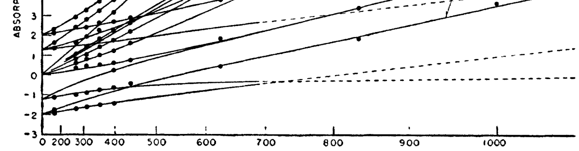

FIG. 2. Stark effect for $J,K=2,2$ ammonia line. Lines shown partially dotted are forbidden at high field strengths. Circles denote experimentally observed points.

* The work reported in this paper was done independently in the Research Laboratories of the General Electric Company and the Westinghouse Electric Corporation. When it was discovered that duplication had occurred, it was decided to publish the results jointly.

[1] J. M. Jauch, Phys. Rev. 72, 715 (1947). The separation of the two satellites of the $M_J=1$ component is just half that given by Jauch; in his quantity Ω, given just after Eq. (18) in this reference, the factor 2 should not appear. This had no effect on the strong field frequencies of the other Stark components.

[2] See, for example, W. E. Good, Phys. Rev. 70, 213 (1946).

[3] R. H. Hughes and E. B. Wilson, Jr., Phys. Rev. 71, 562 (1947).

[4] R. G. Shulman and C. H. Townes, Phys. Rev. 77, 500 (1950).

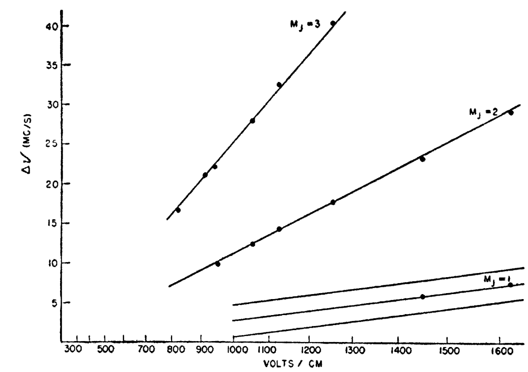

FIG. 3. Stark effect for $J,K=3,3$ ammonia line. Solid lines were computed; circles denote experimentally observed points.

FIG. 4. Photograph of the Stark effect pattern characteristic of the $M_J=1$ transition in ammonia.

Stark modulation spectrograph, and this triplet structure was not resolved.

The dipole moment was calculated from measurements taken at field strengths of 1150 to 2500 volts per cm, using the strong-field approximation

$$\Delta\nu=(2\mu^2E^2/\Delta h^2)[K^2M_J^2/J^2(J+1)^2]\times 10^{-12},$$

where μ is the dipole moment in esu, E is the field strength in esu, Δ is the frequency in mc/s of the J,K ammonia line, and $\Delta\nu$ is the Stark splitting in mc/s. Within the experimental error, the dipole moments obtained from measurements of the three transitions were the same. An extended series of measurements of the $M_J=2$ component of the 2,2 line yielded the value 1.468 ± 0.009D.

III. THEORETICAL

(a) Calculation of the Spectrum

The calculation of the energy levels of ammonia in an electric field has been discussed in detail by Jauch.[1] It was found most convenient to use the strong field representation to calculate the energies for all field strengths; for any transition in the inversion spectrum, this leads to equations which are at most of third degree.

As mentioned earlier, the theoretical frequencies for the 1,1 and 2,2 transitions have been calculated exactly, those for the 3,3 line being the strong-field approximations given by Jauch.

As an aid in the identification, the relative intensities were computed exactly for the 1,1 transition. For the others, the strong-field intensities were used, these being good approximations over the major part of the range of field strengths.

The strong-field Stark spectrum of any transition shows the characteristic triplet structure of the $M_J=1$ component owing to the fact that the quadrupole hamiltonian couples the states $M_J=1$, $M_I=-1$ and $M_J=-1$, $M_I=1$ which remain degenerate in the electric field. All other components ($|M_J|\neq 1$) are single in the strong field approximation.

(b) Possible Corrections to the Energies

There are several small corrections to our computed energies which have been ignored as smaller than the experimental uncertainties. First, the Stark term was taken as $(\pm\mu^2E^2/\Delta)[K^2M_J^2/J^2(J+1)^2]$, where Δ is the separation of the two components of the inversion doublet in question. The contribution of interaction terms between levels of different J can easily be calculated for the 1,1 transition to be less than 0.1 percent of the principal Stark term; for transitions involving higher J, the correction becomes steadily less important.

Second, the first-order quadrupole hamiltonian was used; for nitrogen, the quadrupole coupling is so small that second-order corrections are negligible.

Third, the slight deviations from the quadrupole rule due to magnetic interaction of the nuclear spin with off-diagonal terms of the electronic orbital angular momentum[5] are less than the experimental uncertainties involved in measuring the Stark splitting; indeed, at strong field, such an effect changes only the separations of the two satellites of the principal $M_J=1$ component from that component, an influence it has in common with the quadrupole hamiltonian. Values of the dipole moment obtained from any other components are independent of this correction. This can be seen from the diagonal term of this correction in the strong field representation,

$$2\{[aK^2/J(J+1)]+b\}M_IM_J,$$

where a and b are the constants given by Henderson.[5] This term equally affects the upper and lower Stark states involved in the transitions for which $\Delta M_J=0$.

[5] R. S. Henderson, Phys. Rev. **74**, 107, 626 (1948). We are much indebted to J. H. Van Vleck for a communication on this subject.