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# The Hyperfine Structure and the Stark Effect of the Ammonia Inversion Spectrum

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The expressions for the hyperfine structure separations and the relative intensities in the ammonia inversion spectrum are derived with quantum mechanics under the assumption that the splitting is caused by the interaction of an electric quadrupole moment of the $N^{14}$ nucleus with the electric charge distribution in the rest of the molecule. Furthermore, we consider the displacement of the absorption lines in an electric field $E$ of variable strength. General formulas for the positions of energy levels for weak ($E<E_c$) and strong ($E>E_c$) fields ($E_c\sim 500$ volt/cm) are given and the methods outlined for obtaining solutions of the secular equation for intermediate fields ($E\sim E_c$). The intensities and selection rules for longitudinal and transverse transitions are determined and one particular case ($J=K=3$) is worked out in detail.

## 1. INTRODUCTION

It is well known that the $NH_3$ molecule has the form of a pyramid with the three H atoms at the base of a regular triangle and the N atom at the top. The fact that there exist two equilibrium positions of the N-atom on either side of the base, separated by a potential will give rise to a doubling of each energy level of the whole system of rotational and vibrational states.[1] The transitions from one of the pair of energy levels to the other for all the rotational states and the vibrational ground state can be observed directly since they give rise to a strong absorption in the region of 24,000 megacycles.[2]

With improved techniques of radiofrequency absorption measurements it has recently been possible to separate and identify the lines which arise from different rotational states.[3] W. E. Good observed for the first time the existence of a hyperfine structure with a separation of the four satellites from the main line of several megacycles which was interpreted by various authors as due to the electric quadrupole moment of the $N^{14}$ nucleus.[4] In this paper we shall treat the Stark effect of the inversion spectrum of the $NH_3$ molecule. The hyperfine structure causes the pattern for intermediate values ($E_c\sim 300$–$1000$ volt/cm) to be quite complicated and a general solution of the secular equation does not seem to be feasible although it could in principle be obtained. It is possible, however, to give generally valid expressions for all of the energy levels for very weak fields ($E\ll E_c$) and very strong fields ($E\gg E_c$). For these cases the intensities for both the transverse and longitudinal effects can also be calculated. For intermediate values of the electric field ($E\sim E_c$) one can obtain good approximations for each individual level system by numerical or graphical interpolation.

Although the theory resembles in many respects that of the transition from the weak-field Zeeman effect to the Paschen-Back effect in atomic spectra, there is a characteristic difference for the type of problem considered here. This is due to the fact that a uniform electric field does not interact with the spin of the nucleus (at least not in the approximation considered here). For this reason the spin is never completely decoupled from the orbital angular momentum and thus a splitting of the energy levels with different orientation of the nuclear spin with respect to the orbital angular momentum prevails even for arbitrarily strong fields. This situation holds true for other kinds of radiofrequency absorption spectra as well.

One of the applications of these absorption experiments is the measurement of nuclear spins.[5]

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[1] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932); D. M. Dennison and J. P. Hardy, Phys. Rev. **39**, 938 (1932); H. Y. Sheng, E. F. Barker, and D. M. Dennison, Phys. Rev. **60**, 786 (1941).

[2] C. E. Cleeton and N. H. Williams, Phys. Rev. **45**, 234 (1934).

[3] W. E. Good, Phys. Rev. **70**, 213 (1946); W. E. Good and D. K. Coles, *ibid.* **71**, 383 (1947); D. K. Coles and W. E. Good, *ibid.* **70**, 979 (1946); C. H. Townes, *ibid.* 665 (1946); B. Bleaney and R. P. Penrose, Nature **157**, 339 (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); W. Gordy and M. Kessler, *ibid.* **71**, 639 (1947).

[5] I am indebted to Dr. A. Roberts for numerous discussions on these questions. The electric field is used to modulate the absorption frequency and thus to increase

Since all nuclei with spin values equal to, or greater than, unity seem to have an electric quadrupole moment, it follows that such spin values can be measured in the case of a strong electric field, which simplifies considerably the interpretation of the results.

## 2. THE HYPERFINE STRUCTURE OF THE INVERSION SPECTRUM

The rotational state of the $NH_3$ molecules is given by the well-known formula for the energy levels of the symmetric top.[6] Each level is characterized by three quantum numbers $J$, $K$, $M$, corresponding to the three degrees of freedom of a freely rotating rigid body. The inversion doubling introduces a new quantum number ($s=\pm 1$) which is essentially the symmetry character of the wave function of the molecule under reflection on the base plane. For the energy of a rotational state we have therefore an expression of the form

$$E_{JKs}=J(J+1)/2A+\tfrac{1}{2}(1/C-1/A)K^2 -\tfrac{1}{2}s\Delta(J,K). \quad (1)$$

Here $A$ and $C$ are the two principal moments of inertia;[7] $\Delta(JK)$ is the term for the inversion doubling. The frequency of a particular line in the inversion spectrum is then given by $\Delta(J,K)$. The quantum number $J$ represents the value of the total angular momentum and $K$ is the projection of the angular momentum in the direction of the figure axis. Owing to the rotational symmetry the energy is independent of $M$, the projection of $J$ in a fixed direction in space. The numbers $K$ and $M$ are restricted by the inequalities

$$-J\leqslant M\leqslant +J, \quad -J\leqslant K\leqslant J.$$

We consider now the case in which the nitrogen nucleus has an electric quadrupole moment. Let $\mathbf{i}$ represent the operator of the nuclear spin vector and $\mathbf{J}$ the angular momentum vector of the rotational motion of the molecule. The vector $\mathbf{F}=\mathbf{i}+\mathbf{J}$ represents then the total angular momentum of the system. The energy for the electric quadrupole interaction is given by[8]

$$H_q=\frac{e^2q'Q}{2J(2J-1)i(2i-1)} \times\{3(\mathbf{i}\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{i}\cdot\mathbf{J})-i(i+1)J(J+1)\}. \quad (2)$$

In this expression $Q$ is the nuclear quadrupole moment and the quantity $q'$ represents the expression

$$q'=\langle\sum(3\cos^2\vartheta-1)/r^3\rangle_{J,\,M_J=J}, \quad (3)$$

where the summation is to be extended over all the charges in the molecule other than the nucleus under discussion and the expression thus obtained to be averaged over the rotational state $J$, $M_J=J$. The angle $\vartheta$ is the angle of the radius vector with the fixed 3-direction in space. The expression $eq'$ represents simply the gradient of the 3-component of the electric field in the 3-direction. The expression for $q'$ is not a constant characteristic of the molecule since its value will, in general, still depend on the rotational state of the molecule. We can separate this latter dependence by introducing the characteristic molecular constant $q$ which when multiplied with $e$ represents the gradient of the electric field in the direction of the figure axis. The relationship between $q$ and $q'$ is then given by[9]

$$q'=q\langle\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2}\rangle_{J,\,M_J=J}, \quad (4)$$

where $\theta$ is the angle of the figure axis with the 3-axis. Introducing the normalized wave function[10] for the rotational states

$$\left.\begin{aligned} U_{JKM}(\theta,\phi,\psi)&=\frac{1}{2\pi}\Theta_{JKM}(\theta)e^{i(K\phi+M\psi)} \\ \Theta_{JKM}&=C(1+\cos\theta)^{\frac{1}{2}(J+K)} \\ &\quad\times(1-\cos\theta)^{\frac{1}{2}(J-K)} \end{aligned}\right\}, \quad (5)$$

with the normalization constant given by

$$C^2=(2J+1)!/2^{2J}(J+K)!(J-K)!.$$

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the sensitivity of the absorption measurements. See also R. M. Hughes and E. B. Wilson, Jr., Phys. Rev. **71**, 562 (1947).

[6] C.f. D. M. Dennison, Rev. Mod. Phys. **3**, 311 (1931).

[7] We use here the units $\hbar=c=1$ and cm. The energy is then expressed in wave numbers $cm^{-1}$ and the dimension of $A$ and $C$ is cm.

[8] H. B. G. Casimir, *On the Interaction between Atomic Nuclei and Electrons* (Taylor's Tweede Genootschap, Haarlem, 1936).

[9] See the similar calculation given by A. Nordsieck, Phys. Rev. **58**, 310 (1940).

[10] R. de Kronig and I. I. Rabi, Phys. Rev. **29**, 262 (1927).

We obtain for the average of $\frac{1}{2}(3\cos^2\theta-1)$

$$\langle \tfrac{1}{2}(3\cos^2\theta-1)\rangle_{J,\,M_J=J}=\tfrac{1}{2}C^2\int_0^\pi (1+\cos\theta)^{J+K}\times(1-\cos\theta)^{J-K}(3\cos^2\theta-1)\sin\theta d\theta. \quad (6)$$

This integral can be reduced to three integrals of the type

$$\int_0^1 x^p(1-x)^q dx=p!q!/(p+q+1)!$$

by introducing the substitution $x=\frac{1}{2}(\cos\theta+1)$, $dx=-\frac{1}{2}\sin\theta d\theta$.

$$\begin{aligned}\tfrac{1}{2}\int_0^\pi &(\cos\theta+1)^\alpha(\cos\theta-1)^\beta(3\cos^2\theta-1)\sin\theta d\theta\\ &=2^{\alpha+\beta}\int_0^1 x^\alpha(1-x)^\beta(6x^2-3x+1)dx\\ &=2^{2J}\left\{6\frac{(\alpha+2)!\beta!}{(\alpha+\beta+3)!}-3\frac{(\alpha+1)!\beta!}{(\alpha+\beta+2)!}+\frac{\alpha!\beta!}{(\alpha+\beta+1)!}\right\}\\ &=2^{2J}\frac{\alpha!\beta!}{(\alpha+\beta+3)!}\{(\alpha+\beta)^2-(\alpha+6\alpha\beta+\beta)\}.\end{aligned}$$

This gives finally for Eq. (6)

$$\langle \tfrac{1}{2}(3\cos^2\theta-1)\rangle_{J,\,M_J=J}=\frac{J}{2J+3}\left\{\frac{3K^2}{J(J+1)}-1\right\}. \quad (7)$$

The eigenvalues of the expression in brackets in Eq. (2) are known,[8] and we have

$$\{3(i\cdot J)^2+\tfrac{3}{2}(i\cdot J)-i(i+1)J(J+1)\}=\tfrac{3}{4}N(N+1)-i(i+1)J(J+1)$$

with

$$N=F(F+1)-i(i+1)-J(J+1)$$

and $F=J+i,\ J+i-1,\ \cdots,\ |J-i|$. We finally obtain for the quadrupole energy

$$E_q(J,K,F)=e^2qQ\left(\frac{3K^2}{J(J+1)}-1\right)\times\frac{\frac{3}{4}N(N+1)-i(i+1)J(J+1)}{2(2J+3)(2J-1)i(2i-1)}, \quad (8)$$

with $q$ defined by Eq. (4). This is identical with the formula given by Dailey *et al* in reference 4.

The intensities and selection rules are obtained from the well-known formula[11] for the matrix elements of the electric dipole vector **P** in the representation scheme $(J, i, F, M)$.

Since we shall use later the dependence of the intensities on $M$, we shall give the intensities for the transition to different values of $M$ although they are of course unobservable as long as we have degeneracy with respect to $M$.

(a) *Longitudinal transitions*, electric field parallel to the 3-axis. Selection rules: $\Delta F=0, \pm 1$, $\Delta M=0$. The transition probabilities $A$ are proportional to the squares of the matrix elements of $P_3$

$\Delta F=0$ (center line)

$$A=\frac{K^2}{J^2(J+1)^2}M^2\frac{[J(J+1)-i(i+1)+F(F+1)]^2}{4F^2(F+1)^2}, \quad (9)$$

$F\to F+1$ (satellite)

$$A=\frac{K^2}{J^2(J+1)^2}[(F+1)^2-M^2]\frac{(F+1-i+J)(F+1+i-J)(i+J+2+F)(i+J-F)}{4(F+1)^2(2F+1)(2F+3)}. \quad (10)$$

(b) *Transverse transition*, electric field perpendicular to 3-axis. Selection rules: $\Delta F=0, \pm 1, \Delta M=\pm 1$. In this case the transition probabilities are proportional to the squares of the matrix elements of $P_1$.

$\Delta F=0,\ M\to M\pm 1$

$$A=\frac{1}{4}\frac{K^2}{J^2(J+1)^2}(F\mp M)(F\pm M+1)\frac{[J(J+1)-i(i+1)+F(F+1)]^2}{4F^2(F+1)^2}, \quad (11)$$

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[11] Condon and Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935).

$F\rightarrow F+1,\ M\rightarrow M\pm 1$

$$A=-\frac{1}{4}\frac{K^2}{J^2(J+1)^2}(F\mp M+1)(F\mp M)\frac{(F+1-i+J)(F+1+i-J)(i+J+2+F)(i+J-F)}{4(F+1)^2(2F+1)(2F+3)}. \qquad (12)$$

In addition to the above selection rules we have for the inversion spectrum of course for all transitions $\Delta J=0$, $\Delta K=0$.

We shall now specialize these formulas for the case of the ammonia inversion spectrum. For this case $i=1$. Furthermore we shall sum over all the initial and final states which have the same energy in the field-free case. Making use of the formulas

$$\sum_{-F}^{+F} M^2=\tfrac{1}{3}F(F+1)(2F+1)$$

we obtain for the total transition probabilities:

Center line:

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

with

$$Q(J)=(J+1)^4+J^4+[J(J+1)-1]^2.$$

Satellites:

$$F:\ J-1\rightarrow J,\quad A_{J-1,J}=K^2(2J-1)/3J^3(J+1)^3,$$
$$F:\ J\rightarrow J+1,\quad A_{J,J+1}=K^2(2J+3)/3J^3(J+1)^3.$$

The magnitudes of these quantities for different values of $J$ and $K$ have no direct relation to the relative intensities of the different absorption lines since they must be multiplied with the statistical weight factor, ($=1$ for $K=1, 2, 4, 5, \cdots$ and $=2$ for $K=3, 6, 9, \cdots$) and the Boltzmann factor $\exp[-E(J,\ K)/kT]$. Since we are primarily interested in the relative intensities within one and the same hyperfine structure-level system we calculate instead the ratios of the intensities of the satellites to the intensity of the center line, which is given by

$$\left.\begin{aligned}\alpha_{J-1,J}&=A_{J-1,J}/A_{J,J}\\&=(J+1)^2(2J-1)/(2J+1)Q(J)\\\alpha_{J,J+1}&=A_{J,J+1}/A_{J,J}\\&=J^2(2J+3)/(2J+1)Q(J)\end{aligned}\right\}. \qquad (13)$$

In Table I we summarize these ratios for some values of $J$.

TABLE I. Ratios of the intensities of the hyperfine components to the main lines for different values of $J$.

| $J$ | $\alpha_{J-1,J}$ | $\alpha_{J,J+1}$ |
|---|---|---|
| 1 | $7.4\times10^{-2}$ | $9.3\times10^{-2}$ |
| 2 | 4.42 | 4.6 |
| 3 | 2.5 | 2.53 |
| 4 | 1.56 | 1.58 |
| 5 | 1.06 | 1.07 |
| 6 | 0.769 | 0.769 |

### 3. THE STARK EFFECT OF THE INVERSION SPECTRUM, WEAK FIELD[12]

We consider now the modification of the hyperfine structure when the absorbing molecule is brought into a uniform electric field $E$. Let the field direction be the 3-direction of the fixed-space coordinate system. The total Hamiltonian for the system is then

$$H=H_0+H_q+H',$$

where $H_0$ is the energy for the rotational levels (we disregard the vibrational-level system and consider only the vibrational ground state) given by Eq. (1) including the inversion splitting (last term of Eq. (1)). $H_q$ is the quadrupole energy of Eq. (2) and $H'$ is the interaction energy of the electric dipole moment with the external electric field.

$$H'=(\mathbf{E}\cdot\mathbf{P})=EP_3. \qquad (14)$$

Here $P_3$, as before, is the 3-component of the electric dipole vector of the molecule. Since the symmetry character of $P$ is odd under a reflection of the molecule on its base (the dipole moment has the direction of the figure axis) the matrix elements of the form $(s|P|s)$ are zero. We shall write for $P_3=\mu\cos\theta$, where $\mu$ is the strength of the electric dipole moment and $\cos\theta$ is the operator with the squares of its matrix elements in the $(J, i, F, M)$ representation given by (9), (10).

Two methods of solution suggest themselves:

(a) In the case of sufficiently weak field the splitting due to $H'$ will be small compared to the

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[12] I wish to express my appreciation to Professor J. H. Van Vleck for correspondence and a discussion on the content of this and the following section.

splitting due to $H_q$. In this case one should choose the representation $(J, i, F, M)$ which makes $H_q$ diagonal and treat $H'$ as a perturbation.

(b) For strong fields the Stark-effect splitting is more important than the quadrupole splitting and we start with the representation $(J, i, M_J M_i)$ for which $H'$ is diagonal and treat $H_q$ as a perturbation.

In this section we shall discuss case (a).

The perturbation matrix is then a 6×6 matrix. According to the foregoing remark on the matrix elements of $P_3$, $H'$ will be, with respect to the symmetry character $s$, a matrix of the form

$$H' = \begin{pmatrix} 0 & G \\ G & 0 \end{pmatrix},$$

i.e. the only matrix elements different from zero are those which connect states with different symmetry. The matrix $G_{FF'}$ is a 3×3 matrix which, for each value of $(K, J, M)$, has the following non-vanishing matrix elements (see Eqs. (9)

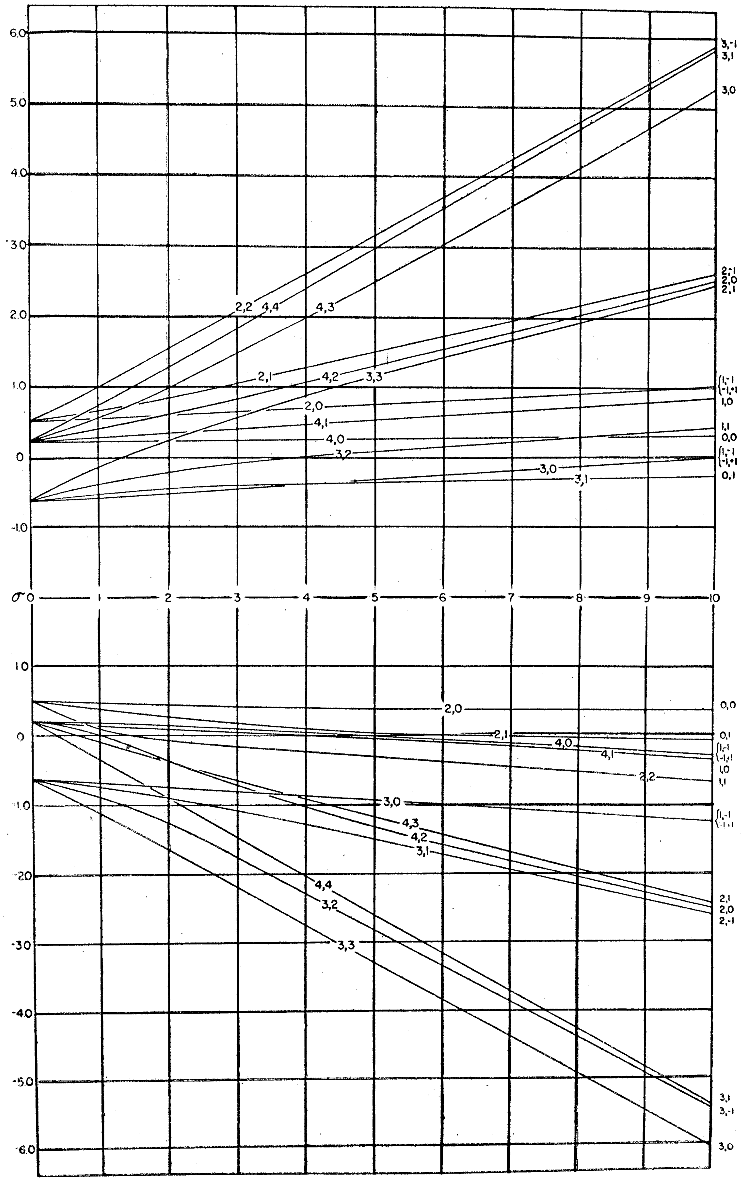

FIG. 1. Energy levels in units $e^2qQ$ for the ammonia inversion line $J=K=3$ as a function of the parameter

$$\sigma = \mu^2 E^2 / [\Delta(J, K) e^2 qQ].$$

The numbers at the right-hand edge denote $M_J$, $M_i$. The numbers in the figure give $F$, $M_F$ for each line.

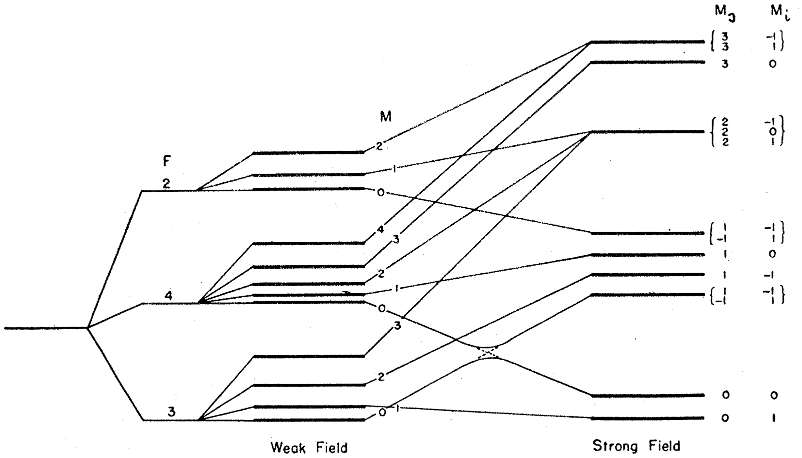

FIG. 2. Coordination of energy levels in the Stark effect of the ammonia inversion line $J=K=3$ for weak and strong fields. Upper state (schematic).

and (10)):

$$
\begin{aligned}
&|M|\leqslant J-1\\
&\left.\begin{aligned}
&G_{J-1,\,J-1}=\mu EKM/J^2\\
&G_{J-1,\,J}=G_{J,\,J-1}=\mu E(K/J^2)\\
&\quad\times[(J+M)(J-M)/(J+1)(2J+1)]^{\frac{1}{2}}
\end{aligned}\right\}, \quad (15a)\\
&|M|\leqslant J\\
&\left.\begin{aligned}
&G_{J,\,J}=\mu EKM[J(J+1)-1]/J^2(J+1)^2\\
&G_{J+1,\,J}=G_{J,\,J+1}=\mu EK(M/(J+1)^2)\\
&\quad\times[(J+M+1)(J-M+1)/J(2J+1)]^{\frac{1}{2}}
\end{aligned}\right\}, \quad (15b)\\
&|M|\leqslant J+1\\
&\qquad G_{J+1,\,J+1}=\mu EKM/(J+1)^2. \quad (15c)
\end{aligned}
$$

The eigenvalue problem leads to a secular equation of the sixth degree. The fact that the separation of the unperturbed levels with different values of $s$ is very much larger than the hyperfine structure splitting (the ratio is about $10^5$), allows the application of Van Vleck's transformation[13] after which the hamiltonian has the form

$$H=H_0+H_q+\bar{H}, \tag{16}$$

where

$$\bar{H}=\begin{pmatrix}\Gamma & 0\\ 0 & -\Gamma\end{pmatrix},$$

and where $\Gamma$ is a $3\times 3$ matrix given by

$$\Gamma_{FF'}=(1/\Delta(J,K))\textstyle\sum_{F''}G_{FF''}G_{F''F'}.$$

Here $\Delta(J,K)$ according to (1) is the energy difference (taken positive) between upper and lower state. The secular equation for the eigenvalue problem is now of third degree. The $\Gamma_{FF'}$ are functions of $M$ as seen from (15).

In the following we shall find it convenient to introduce $e^2qQ$ as unit of energy. Further, we

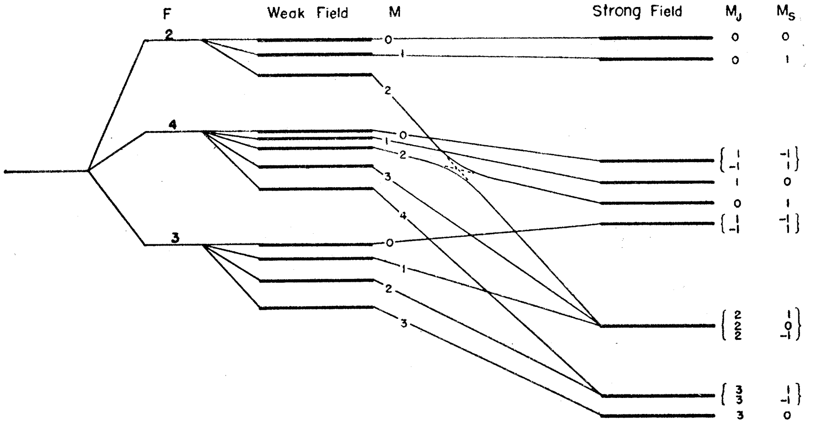

FIG. 3. Coordination of energy levels in the Stark effect of the ammonia inversion line $J=K=3$ for weak and strong fields. Lower state (schematic).

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[13] See E. Kemble, *Principles of Quantum Mechanics* (McGraw-Hill Book Company, New York), p. 395.

Table II. The Stark effect of the inversion line $J=K=3$ for an electric field $E\sim 300$ volt/cm in units of $e^2qQ$.

| Level $F$ | $M$ | Upper state | Lower state |
|---|---|---|---|
| 4 | 4 | 0.771 | −0.355 |
|  | 3 | 0.563 | −0.101 |
|  | 2 | 0.390 | +0.010 |
|  | 1 | 0.270 | 0.150 |
|  | 0 | 0.232 | 0.181 |
| 3 | 3 | −0.167 | −1.127 |
|  | 2 | −0.404 | −0.904 |
|  | 1 | −0.526 | −0.745 |
|  | 0 | −0.562 | −0.687 |
| 2 | 2 | 0.991 | 0.090 |
|  | 1 | 0.666 | 0.380 |
|  | 0 | 0.539 | 0.479 |

Table III. Stark effect of inversion spectrum for $E\sim 300$ volt/cm.

| Initial $F$ | Initial $M$ | Final $F$ | Final $M$ | Energy (arb. units) | Relative intensity |
|---|---|---|---|---|---|
| 4 | 4 | 4 | 4 | 1.126 | 0.563 |
| 4 | 3 | 4 | 3 | 0.664 | 0.316 |
| 4 | 2 | 4 | 2 | 0.334 | 0.141 |
| 4 | 1 | 4 | 1 | 0.120 | 0.035 |
| 3 | 3 | 3 | 3 | 0.960 | 0.473 |
| 3 | 2 | 3 | 2 | 0.500 | 0.210 |
| 3 | 1 | 3 | 1 | 0.219 | 0.053 |
| 2 | 2 | 2 | 2 | 0.926 | 0.444 |
| 2 | 1 | 2 | 1 | 0.286 | 0.111 |
| 4 | 3 | 3 | 3 | 1.690 | 0.0117 |
| 4 | 2 | 3 | 2 | 1.294 | 0.0201 |
| 4 | 1 | 3 | 1 | 1.015 | 0.0251 |
| 4 | 0 | 3 | 0 | 0.919 | 0.0268 |
| 3 | 2 | 2 | 2 | 0.494 | 0.0198 |
| 3 | 1 | 2 | 1 | −0.906 | 0.0317 |
| 3 | 0 | 2 | 0 | −1.041 | 0.0357 |
| 2 | 2 | 3 | 2 | 1.895 | 0.0198 |
| 2 | 1 | 3 | 1 | 1.411 | 0.0317 |
| 2 | 0 | 3 | 0 | 1.226 | 0.0357 |
| 3 | 3 | 4 | 3 | −0.066 | 0.0117 |
| 3 | 2 | 4 | 2 | −0.414 | 0.0201 |
| 3 | 1 | 4 | 1 | −0.676 | 0.0251 |
| 3 | 0 | 4 | 0 | −0.743 | 0.0268 |

introduce the parameter

$$\sigma=[(\mu E)^2/\Delta(J,K)]1/e^2qQ$$

which is a measure of the relative strength of the electric field. $\sigma$ is about equal to unity for a field $E\sim 300$ volt/cm $=1$ e.s.u. If we assume for the dipole moment the value $\mu=1.45\times 10^{-18}$ e.s.u. $=2.58\times 10^{-6}$ cm. We may treat the upper and lower states simultaneously by letting $\sigma>0$ for the upper and $\sigma<0$ for the lower state.

The formula for the perturbation theory gives then in general an expression for the level displacement due to $H_q$ and $H'$.

$$\begin{aligned}\epsilon(J,F,M)&\\ &=\epsilon_q(J,F)+\sigma\Gamma_{FF}+\sigma^2\sum_{F'\pm F}\frac{\Gamma_{FF'}\Gamma_{F'F}}{\epsilon_q(F)-\epsilon_q(F')}\\ &=\epsilon_q{}^0+\epsilon^{(1)}+\epsilon^{(2)}.\end{aligned}\tag{17}$$

The general formulas for these eigenvalues are rather complicated. It is more convenient to evaluate them for each level separately. It may be noted however that for some special values of $M$ the cubic secular equation degenerates into a quadratic and a linear term which can be easily solved. This is the case for $M=J+1$ and $M=J$ and also for $M=0$.

Thus for the line $J=K=3$ there will be twelve levels of which six can be calculated by solving merely a quadratic equation. For the other six the formula (17) must be used for $\sigma<\sim 1$. The case $J=K=3$ is treated explicitly and the results are plotted in Fig. 1 for $\sigma$ ranging from 0 to 10. For the special value $\sigma=1$ the energy values are also given in Table II. Figures 2 and 3 show the coordination of the levels for weak and strong field.

The general expressions for the intensities for longitudinal and transverse absorption spectrum are given by the formulas (9), (10) and (11), (12). In Table III the weak-field spectrum is given for the case of longitudinal transition for the line $J=K=3$.

## 4. THE STARK EFFECT FOR A STRONG FIELD

In the case of strong electric field ($\sigma\gg 1$) we diagonalize first the operator $\bar{H}$ in Eq. (16). The representation which makes $\bar{H}$ diagonal is the $(J, i, M_J, M_i)$ representation. For in this system the matrix $G$ has the simple form

$$G_{M_JM_J'}=\sigma^{\frac{1}{2}}(K/J(J+1))M_J\delta_{M_JM_J'}$$

and

$$\Gamma_{M_JM_J'}=\sigma(K^2/J^2(J+1)^2)M_J{}^2\delta_{M_JM_J'}.$$

Since $M=M_J+M_i$, $M_J$ may assume for any given $M$ the values $M_J=M+1$, $M$, $M-1$. The quadrupole interaction in this representation may best be obtained by using the form of $H_q$ in terms of the operators $J$ and $i$ given by Casimir.[8]

TABLE IV. Longitudinal spectrum of the $J=K=3$ $NH_3$ inversion line for strong electric fields ($\sigma\gg1$).

| Transitions | | | | | |
|---|---|---|---|---|---|
| Initial | | Final | | Relative line position | Relative intensity |
| $M_J$ | $M_i$ | $M_J'$ | $M_i'$ | | |
| 3 | +1 | 3 | +1 | $9\sigma$ | 9 |
| 3 | 0 | 3 | 0 | $9\sigma$ | 9 |
| 3 | −1 | 3 | −1 | $9\sigma$ | 9 |
| 2 | +1 | 2 | +1 | $4\sigma$ | 4 |
| 2 | 0 | 2 | 0 | $4\sigma$ | 4 |
| 2 | −1 | 2 | −1 | $4\sigma$ | 4 |
| $\begin{pmatrix}+1 & -1\\ -1 & +1\end{pmatrix}_+$ | | $\begin{pmatrix}+1 & -1\\ -1 & +1\end{pmatrix}_-$ | | $\sigma+16$ | $\frac{1}{2}$* |
| 1 | 0 | 1 | 0 | $\sigma$ | 1 |
| 1 | +1 | 1 | +1 | $\sigma$ | 1 |
| $\begin{pmatrix}+1 & -1\\ -1 & +1\end{pmatrix}_-$ | | $\begin{pmatrix}+1 & -1\\ -1 & +1\end{pmatrix}_+$ | | $\sigma-16$ | $\frac{1}{2}$* |

* The two states (22) are distinguished by a ± sign.

TABLE V. Transverse spectrum of the $J=K=3$ $NH_3$ inversion line for strong electric field ($\sigma\gg1$).

| Transitions | | | | | |
|---|---|---|---|---|---|
| Initial | | Final | | Relative line position | Relative intensity |
| $M_J$ | $M_i$ | $M_J'$ | $M_i'$ | | |
| 3<br>3 | −1<br>+1 | 2<br>2 | −1<br>+1 | $\frac{1}{2}13\sigma+15/4$ | 3 |
| 3 | 0 | 2 | 0 | $\frac{1}{2}13\sigma-15/8$ | $\frac{3}{2}$ |
| 2 | −1 | +1<br>−1 | −1<br>$+1_+$ | $\frac{3}{2}\sigma-3$ | 5/4 |
| 2 | −1 | +1<br>−1 | −1<br>$+1_-$ | $\frac{3}{2}\sigma+5$ | 5/4 |
| 2 | 0 | 1 | 0 | $\frac{3}{2}\sigma-2$ | 5/2 |
| 2 | 1 | 1 | 1 | $\frac{3}{2}\sigma+1$ | 5/2 |
| $\begin{pmatrix}+1 & -1\\ -1 & +1\end{pmatrix}_+$ | | 0<br>0 | −1<br>+1 | $\sigma+13/3$ | 3/2 |
| 1 | 0 | 0 | 0 | $\sigma-2/3$ | 3 |
| 1 | 1 | 0 | 1 | $\sigma+1/3$ | 6 |
| $\begin{pmatrix}1 & -1\\ -1 & +1\end{pmatrix}_-$ | | 0<br>0 | −1<br>+1 | $\sigma-11/3$ | 3/2 |

$$\begin{aligned}H_q=\Lambda\{&(J_3{}^2-\tfrac{1}{2}J_1{}^2-\tfrac{1}{2}J_2{}^2)(i_3{}^2-\tfrac{1}{2}i_1{}^2-\tfrac{1}{2}i_2{}^2)\\&+\tfrac{3}{8}[J_3(J_1+iJ_2)+(J_1+iJ_2)J_3]\\&\times[i_3(i_1-ii_2)+(i_1-ii_2)i_3]\\&+\tfrac{3}{8}[J_3(J_1-iJ_2)+(J_1-iJ_2)J_3]\\&\times[i_3(i_1+ii_2)+(i_1+ii_2)i_3]\\&+\tfrac{3}{8}(J_1+iJ_2)^2(i_1-ii_2)^2\\&\qquad+\tfrac{3}{8}(J_1-iJ_2)^2(i_1+ii_2)^2,\end{aligned}\tag{18}$$

with

$$\Lambda=2[3K^2-J(J+1)]/J(J+1)(2J-1)(2J+3).$$

Explicitly written out, the matrix elements are the following (we use the abbreviation $(M_JM_J')$ for $\Lambda^{-1}(H_q)_{M_JM_J'}$)

$$\left.\begin{aligned}(M+1,M+1)&=\tfrac{1}{4}\{3(M+1)^2-J(J+1)\}\\(M,M)&=-\tfrac{1}{2}\{3M^2-J(J+1)\}\\(M-1,M-1)&=\tfrac{1}{4}\{3(M-1)^2-J(J+1)\}\end{aligned}\right\},\tag{19}$$

$$\left.\begin{aligned}(M+1,M)&=(M,M+1)\\&=-\sqrt{2}\tfrac{3}{8}(2M+1)\\&\quad\times[J(J+1)-M(M+1)]^{\frac{1}{2}}\\(M+1,M-1)&=(M-1,M+1)\\&=\tfrac{3}{4}[J(J+1)-M(M+1)]^{\frac{1}{2}}\\&\quad\times[J(J+1)-M(M-1)]^{\frac{1}{2}}\\(M,M-1)&=(M-1,M)\\&=\sqrt{2}\tfrac{3}{8}[J(J+1)-M(M-1)]^{\frac{1}{2}}(2M-1)\end{aligned}\right\}.\tag{20}$$

With this matrix one can apply perturbation theory in the usual way for any level except the case $M=0$. In this case, as is easily seen from (19), the zeroth-order energy levels are degenerate for the two states $M_J=+1$, $M_i=-1$ and $M_J=-1$, $M_i=+1$. The first-order correction in the energy is thus not simply the diagonal matrix element of the perturbation energy (18) but must be calculated in the usual way by solving the secular equation of that submatrix which contains all the elements connecting the same energy. If we denote the two states mentioned above for short with $\alpha$ and $\beta$, and an eigenstate of the eigenvalue problem with

$$\psi=x\alpha+y\beta,\tag{21}$$

then the eigenvalue problem is

$$\begin{aligned}-\tfrac{1}{8}x+\tfrac{1}{2}y&=\epsilon x,\\\tfrac{1}{2}x-\tfrac{1}{8}y&=\epsilon y.\end{aligned}$$

The secular equation for $\epsilon$ is

$$(1+8\epsilon)^2-16=0$$

with the solutions

$$\epsilon_1=+\tfrac{3}{8},\quad \epsilon_2=-\tfrac{5}{8}.$$

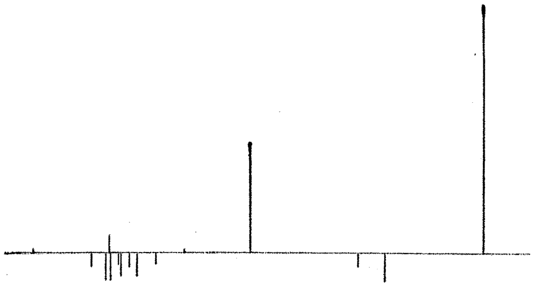

FIG. 4. Stark spectrum of the inversion line $J=K=3$ for a field $E\sim1000$ volt/cm. Upper lines: longitudinal spectrum; lower lines: transverse spectrum.

The corresponding solutions for $x$ and $y$ are:

$$\left.\begin{array}{ll} x^{(1)}=1/\sqrt{2}, & y^{(1)}=1/\sqrt{2} \\ x^{(2)}=1/\sqrt{2}, & y^{(2)}=-1/\sqrt{2} \end{array}\right\}. \tag{22}$$

The eigenstates which represent the zeroth-order wave functions are thus the symmetrical and antisymmetrical combinations of the states $M_J=+1$, $M_i=-1$; $M_J=-1$, $M_i=+1$.

The transition probabilities in this case are given by the square of the matrix elements of $P_3$ and $P_1$ for longitudinal and transverse transitions respectively. In the coordinate system characterized by the quantum numbers $(J, M_J)$ we have the matrix elements

$$(M_J|P_3|M_J)=KM_J/J(J+1), \tag{23}$$

$$(M_J|P_1|M_J+1)=(K/2J(J+1))\times[(J-M_J)(J+M_J+1)]^{\frac{1}{2}}. \tag{24}$$

Together with the selection rules $\Delta M_i=0$ these matrix elements determine the strength and character of each transition uniquely. In the longitudinal case we have for each $|M_J|\geq 2$ six functions corresponding to the six states $M=\pm M_J+1, \pm M_J, \pm M_J-1$.

The total intensity of these transitions is thus given by

$$A=[KM_J/J(J+1)]^2 \quad \text{for} \quad |M_J|\geq 2.$$

For $|M_J|=1$ we have the two states $\psi_+$, $\psi_-$ determined by (21), (22). It is readily seen that only the matrix elements $(+|P_3|-)$ and $(-|P_3|+)$ are different from zero and are given by

$$(+|P_3|-)=(-|P_3|+)=[K/J(J+1)]^2.$$

There are four other transitions corresponding to the states

$$M_J=+1, \quad M_i=0, +1; \quad M_J=-1, \quad M_i=0, -1.$$

The total transition probability for these is then

$$A=[2K/J(J+1)]^2.$$

The transitions for the longitudinal spectrum together with their intensities are given in Table IV.

The transverse spectrum is somewhat more complicated. The transitions and their relative intensities are calculated with the matrix elements (11), (12), and (24) and are tabulated in Table V. In Fig. 4 the longitudinal and transverse spectrum is plotted for a strong field ($E\sim 1000$ volt/cm). For the transverse case only half of the transitions (those with $M_J=-1$) are given. The others are symmetrically situated with respect to the origin (i.e. the undisplaced position of the line).

It is seen from Tables IV and V and also in Fig. 4 that for arbitrarily strong fields there always remains a hyperfine structure with a constant separation. The pattern is particularly simple for the longitudinal case in which only the last component ($M_J=1$) has a hyperfine structure in the form of two satellites on either side of the outer line with one-fourth the intensity of the center line. The transverse spectrum is more complicated and may be not so suitable for an investigation of nuclear spins since it may be difficult to separate all the hyperfine components.