

Theory of the Fine Structure of the Microwave Spectrum of NO_2^\dagger

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The effects of the magnetic interactions between the electronic spin, nuclear spin, and molecular rotation on the rotational energy levels of NO_2 molecule have been investigated and a theory of the fine structure of the microwave spectrum of this molecule is presented. A new method for calculating the matrix elements of the magnetic interaction terms has been developed. Possible extension of this theory to include the general type of polyatomic molecules with $S=\frac{1}{2}$ is discussed.

I. INTRODUCTION

NITROGEN dioxide is one of the very few stable polyatomic free radicals. The interactions between the electronic spin, nuclear spin, nuclear quadrupole moment, and the molecular rotation give rise to very interesting and complicated patterns of fine structure in the rotational spectrum. A summary of the experimental work on the microwave spectrum has been given by Bird.¹ In this paper the theory of the fine structure of the microwave spectra of the NO_2 molecule will be presented. This theory has been applied by Bird and Baird to account for the experimental data and the results of their work will be published in a forthcoming paper.² With proper modification our theory is also applicable to other polyatomic free radicals with $S=\frac{1}{2}$ such as ClO_2 (see Sec. V).

II. THE HAMILTONIAN

The Hamiltonian which describes the interaction between the electronic and nuclear spins and the molecular rotation can be obtained by the procedure of Van Vleck.³ The results of this treatment show that the effective Hamiltonian may be written as

$$H=H_0+H_{S-R}+H_{S-I}+H_F+H_Q, \quad (1)$$

where the five terms in the right-hand side of the preceding equation represent, respectively, the effect of rigid rotation of the molecule, the interaction between electronic spin and molecular rotation (called spin-rotation interaction), the interaction between electronic and nuclear spin (called the spin-spin interaction), the Fermi $|\psi(0)|^2$ coupling,⁴ and nuclear quadrupole coupling. Attention should be called upon the fact that the first order spin-orbit interaction is absent since the orbital angular momentum of the unpaired electron in

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¹ G. R. Bird, J. Chem. Phys. **25**, 1040 (1956).

² J. C. Baird and G. R. Bird, Bull. Am. Phys. Soc. Ser. II, **4**, 68 (1959); J. C. Baird and G. R. Bird (to be published).

³ J. H. Van Vleck, Revs. Modern Phys. **23**, 213 (1951).

⁴ E. Fermi, Z. Physik **60**, 320 (1930); G. Breit and F. W. Doermann, Phys. Rev. **36**, 1732 (1930).

NO_2 is quenched. Each of the five terms in Eq. (1) will be discussed in the following paragraphs.

1. Rigid Rotation

The Hamiltonian for the rigid rotation of the molecule is given by

$$H_0=AN_x^2+BN_y^2+CN_z^2, \quad (2)$$

where A , B , and C are the rotational constants and the N 's are the three components of the rotational angular momentum. Since the molecule NO_2 is a slightly asymmetric prolate top,^{1,5} K (the projection of N along the molecular axis) is nearly a good quantum number and the calculation of the rotational energy levels may be performed by expanding the energy in terms of the "asymmetry parameter."^{6,7} For $\text{N}(\text{O}^{16})_2$ the nuclear spin statistics⁸ require that the rotational energy levels be even with respect to rotation about the line bisecting the $\angle\text{ONO}$. Thus for a given $|K|$ only one energy state out of the pair of Wang functions (symmetric and antisymmetric combination of the symmetric rotor functions) can exist. A discussion on the calculation of the rotational energy levels has been given by Bird.¹ In this paper we will be mainly concerned with various types of magnetic interactions responsible for the fine structure in the rotational spectrum.

2. Spin-Rotation Interaction

The spin-rotation interaction may arise from two causes. The first one is the direct interaction of the electronic spin with the magnetic field of the molecular rotation. Mathematically, this effect may be ascribed to the first term in Eq. (37) of reference 3 which has been shown to be equivalent to

$$\sum_{ij} a_{ij} N_i S_j, \quad a_{ij}=a_{ji}, \quad (3)$$

where the vector \mathbf{N} (instead of \mathcal{K} as used in reference 3) denotes the angular momentum due to the molecular rotation. Here the a_{ij} are complicated functions of the moments of inertia, the internuclear distances, and the

⁵ G. E. Moore, J. Opt. Soc. Am. **43**, 1045 (1953).

⁶ S. C. Wang, Phys. Rev. **34**, 243 (1929).

⁷ H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

⁸ See, for example, G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), p. 135.

average distance of the odd electron to the various nuclei of the molecule. Since very little is known about the electronic structure of the NO_2 molecule, any attempt to calculate a_{ij} from first principles would seem impractical at this time; these coefficients can best be treated as parameters. It should be mentioned that the a_{ij} are different for different isotopic species of the molecule.

Besides the direct coupling between electronic spin and molecular rotation which we have discussed in the preceding paragraph, there is also an indirect coupling via orbital motion and the intermediary of excited orbital states treated by Van Vleck³ and by Henderson.⁹ The indirect mechanism still produces a Hamiltonian of the form (3) and simply changes the values of the coefficients a_{ij} . Henderson has given explicit expressions for the indirect contributions to the a_{ij} under the special assumption that the entire spin-orbit (electronic) interaction can be represented in a simple isotropic form $A(\mathbf{L} \cdot \mathbf{S})$.

When the frequency spacings between the various fine structure components are small compared to the frequencies of the rotational transitions, the matrix elements of H_{S-R} which are nondiagonal in N have very little effect. Hence we shall disregard them. With this approximation, Eq. (3) can be replaced by^{10,11}

$$H_{S-R} = [N(N+1)]^{-1} (\mathbf{N} \cdot \mathbf{S}) \sum_{ij} \epsilon_{ij} N_i N_j, \quad \epsilon_{ij} = \epsilon_{ji}, \quad (4)$$

where ϵ_{ij} is the sum of the two coefficients a_{ij} and η_{ij} which are associated, respectively, with the direct and indirect coupling between the electronic spin and molecular rotation. We can also similarly disregard the effect of matrix elements off-diagonal in K , except that matrix elements of the form $\Delta K = \pm 2$ must be retained for the pair of states $K = \pm 1$. The familiar Wang transformation is used to lift the degeneracy of the pair and the approximate expression for the spin-rotation interaction becomes

$$H_{S-R} = \kappa (\mathbf{N} \cdot \mathbf{S}), \quad (5)$$

where

$$\kappa = \frac{1}{2} (\epsilon_{xx} + \epsilon_{yy}) + [N(N+1)]^{-1} [\epsilon_{zz} - \frac{1}{2} (\epsilon_{xx} + \epsilon_{yy})] K^2 \pm \frac{1}{4} \delta_{|K|=1} (\epsilon_{yy} - \epsilon_{xx}). \quad (6)$$

Here $\delta_{|K|=1}$ is the Kronecker delta, i.e., it is equal to zero unless $|K|=1$. The + and - signs correspond to the symmetric and antisymmetric combination of the symmetric top wave functions involved in the Wang transformation.

The Hamiltonian in Eq. (4) also produces matrix elements connecting the pair of symmetric and antisymmetric Wang functions for $|K|=1$. Matrix elements of this type have not been considered in the derivation of (5). For $\text{N}(\text{O}^{16})_2$ such matrix elements have no effect

on the energy levels since only one of the two energy states with $|K|=1$ is present. In general if both states corresponding to $|K|=1$ are allowed, Eq. (5) is applicable to such states only when the spin-rotation effect is small compared to $(B-C)N(N+1)$, where B and C are the rotational constants for the two principal axes other than the unique axis. In other words, we have neglected terms of the order of

$$[(B-C)N(N+1)]^{-1} [(\epsilon_{xy} + \epsilon_{yx})(\mathbf{N} \cdot \mathbf{S})]^2. \quad (7)$$

For NO_2 we shall simply use (5) as the spin-rotation operator without making the further transformation which carries the Wang representation to the proper asymmetric top representation.

3. Spin-Spin Interaction

The Hamiltonian describing the interaction between the nuclear and the electronic spin can be expressed as

$$-g_S g_I \mu_B \mu_I r^{-3} [\mathbf{I} \cdot \mathbf{S} - 3r^{-2} (\mathbf{I} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})], \quad (8)$$

where μ_B and μ_I are the Bohr and nuclear magneton, respectively, g_I is the nuclear Landé factor and g_S is the g -factor of the electronic spin. The radius vector \mathbf{r} joins the nitrogen nucleus to the odd electron. Equation (8) can be expanded in a coordinate system (x, y, z) fixed in the molecule and expressed in terms of the components of \mathbf{I} and \mathbf{S} in this frame.¹² If we retain only the matrix elements of the form $\Delta K = 0$ and $\Delta K = \pm 2$ in this expansion, the spin-spin interaction term can be replaced approximately by

$$H_{S-I} = \lambda (\mathbf{I} \cdot \mathbf{S} - 3I_x S_x) + \tau (I_y + iI_x)(S_y + iS_x) + \tau^* (I_y - iI_x)(S_y - iS_x), \quad (9)$$

where

$$\lambda = -g_S g_I \mu_B \mu_I \left\langle \frac{3\hat{r}_z^2 - 1}{2r^3} \right\rangle_{Av}, \quad (10)$$

$$\tau = \frac{3}{4} g_S g_I \mu_B \mu_I \left\langle \frac{(\hat{r}_y - i\hat{r}_x)^2}{r^3} \right\rangle_{Av}.$$

Here \hat{r}_x , \hat{r}_y , and \hat{r}_z are the three components of the unit vector $r^{-1}\mathbf{r}$ in the molecular frame. If the electronic wave function in the ground state of NO_2 is real, one has

$$\tau = \tau^* = \frac{3}{4} g_S g_I \mu_B \mu_I \left\langle \frac{\hat{r}_y^2 - \hat{r}_x^2}{r^3} \right\rangle_{Av}. \quad (11)$$

4. Fermi $|\psi(0)|^2$ Coupling and Nuclear Quadrupole Interaction

If the wave function of the odd electron at the point where the nitrogen nucleus is situated [denoted by $\psi(0)$], is different from zero, an additional term,⁴

$$H_F = (16\pi/3) g_I \mu_B \mu_I |\psi(0)|^2 (\mathbf{I} \cdot \mathbf{S}), \quad (12)$$

⁹ R. S. Henderson, Phys. Rev. **100**, 723 (1955).

¹⁰ E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

¹¹ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), p. 61.

¹² See, for example, S. I. Weissman, J. Chem. Phys. **22**, 1378 (1957).

must be inserted in the Hamiltonian to describe the interaction between the electronic and nuclear spin. The value of $|\psi(0)|^2$ has been determined as $6.3 \times 10^{24} \text{ cm}^{-3}$ from the paramagnetic resonance spectrum of NO₂ in solution.¹³

The nuclear quadrupole effects attributable to the nitrogen nucleus are usually very small. For this reason H_Q will not be considered although the theory presented in this paper can easily be extended to include this interaction (see Sec. V and Appendix).

III. ENERGY CALCULATION

To simplify the calculation let us assume that the four coupling terms in Eq. (1) are all very small compared to H_0 , so that the matrix elements non-diagonal in N can be disregarded. Furthermore, the molecule will be approximated by a symmetric rotor, or more precisely, the Wang combinations of the symmetric top wave functions will be taken as the approximate eigenfunctions of H_0 .

To illustrate the structure of the secular equation let us first consider a special case in which

$$H_{S-R} \gg H_{S-I} + H_F. \quad (13)$$

A vector model can be constructed by first coupling the rotational angular momentum \mathbf{N} with \mathbf{S} to form \mathbf{J} which is then compounded with \mathbf{I} to give the total angular momentum \mathbf{F} . The vector \mathbf{F} is a constant of motion, and J is nearly a good quantum number provided that the interaction between the nuclear and electronic spin is much less than H_{S-R} . The energy is then approximately equal to the diagonal matrix elements of H , i.e.,

$$\langle KNJF | H | KNJF \rangle.$$

However, if the condition imposed by (13) is not fulfilled, J will no longer be a good quantum number. In the K, N, J, F scheme of representation (which we shall refer to as the J -representation), the secular equation for a given N and K is a 6×6 determinant corresponding to the following values of J and F :

$$\begin{aligned} J = N + \frac{1}{2}, \quad F = N + \frac{3}{2}; \quad J = N + \frac{1}{2}, \quad F = N + \frac{1}{2}; \\ J = N + \frac{1}{2}, \quad F = N - \frac{1}{2}; \quad J = N - \frac{1}{2}, \quad F = N + \frac{1}{2}; \\ J = N - \frac{1}{2}, \quad F = N - \frac{1}{2}; \quad J = N - \frac{1}{2}, \quad F = N - \frac{3}{2}. \end{aligned}$$

Since F is a constant of motion, the determinant can be factorized immediately into four blocks, according to the four different values of F . Two of the factors are 2×2 matrices while the others are 1×1 .

One may, of course, consider the other extreme case where $H_{S-I} + H_F \gg H_{S-R}$. Now the two spin vectors \mathbf{I} and \mathbf{S} may be first coupled to form \mathbf{G} which then combines with the rotational angular momentum vector giving \mathbf{F} . The 6×6 secular equation for a given N and

K can be set up in this G -representation and again can be factorized into four blocks.

As shown in the previous section, the three types of magnetic coupling, H_{S-R} , H_{S-I} , and H_F , may be written respectively as

$$\begin{aligned} \beta &= \kappa(\mathbf{N} \cdot \mathbf{S}), \\ \alpha &= \lambda(\mathbf{I} \cdot \mathbf{S} - 3I_x S_x) + \tau[(I_y + iI_x)(S_y + iS_x) \\ &\quad + (I_y - iI_x)(S_y - iS_x)], \quad (14) \\ \gamma &= \sigma(\mathbf{I} \cdot \mathbf{S}), \end{aligned}$$

where

$$\sigma = \frac{16\pi}{3} g_I \mu_B \mu_I |\psi(0)|^2. \quad (15)$$

The matrix elements of these operators can be calculated by a procedure similar to that of Frosch and Foley.¹⁴ The computation, though straightforward, is very tedious. In this paper we shall develop a new method for obtaining the matrix elements of the Hamiltonian. The diagonal elements are determined by using Van Vleck's method of "reversed" angular momentum along with the method of projection.^{10,11} With this procedure explicit matrix multiplication is avoided and labor of computation is thereby greatly saved. The off-diagonal elements are obtained by comparing the diagonal sum of the various matrices in the J and G representation. Thus the confusion caused by the different phase conventions for the nondiagonal elements does not arise in our procedure. The details of our method will be presented below.

1. Diagonal Elements in the J Representation

We shall write the 2×2 matrices of α , β , and γ (defined in Eqs. (14)) as

$$\alpha = \begin{pmatrix} \alpha_1 & \alpha_3 \\ \alpha_3 & \alpha_2 \end{pmatrix}, \quad \text{etc.}$$

In the J -representation it is apparent that

$$\langle J | \mathbf{N} \cdot \mathbf{S} | J \rangle = \frac{1}{2} [J(J+1) - N(N+1) - S(S+1)]. \quad (16)$$

Thus for $J = N \pm \frac{1}{2}$, the diagonal matrix elements of β are

$$\beta_1 = \frac{1}{4} \kappa [-1 + (2N+1)], \quad \beta_2 = \frac{1}{4} \kappa [-1 - (2N+1)]. \quad (17)$$

To evaluate α_1 , and α_2 the reversed spin angular momenta are introduced so that

$$\mathbf{F} + \mathbf{I}^r = \mathbf{J}, \quad \mathbf{J} + \mathbf{S}^r = \mathbf{N},$$

where

$$\mathbf{I}^r = -\mathbf{I}, \quad \text{etc.}$$

The diagram of the coupling of the normal and reversed angular momenta is shown in Fig. 1. In this coupling scheme \mathbf{I}^r is precessing about \mathbf{J} , so the matrix elements of I_x and $\mathbf{I} \cdot \mathbf{S}$ diagonal in J can be obtained by the

¹³ Bird, Baird, and Williams, *J. Chem. Phys.* **28**, 738 (1958).

¹⁴ R. A. Frosch and H. M. Foley, *Phys. Rev.* **88**, 1337 (1952).

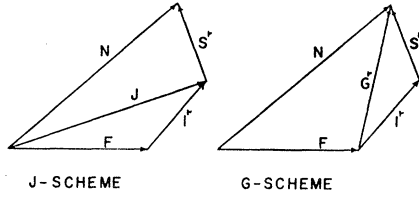


FIG. 1. Diagrams showing the coupling of angular momentum vectors in the J and G scheme.

method of projection^{10,11} as

$$\begin{aligned}
 (J|I_z|J) &= -(J|I_z^r|J) \\
 &= -[J(J+1)]^{-1}(J|\mathbf{I}^r \cdot \mathbf{J}|J)(J|J_z|J) \\
 &= [2J(J+1)]^{-1}[F(F+1) - I(I+1) \\
 &\quad - J(J+1)](J|J_z|J), \quad (18) \\
 (J|\mathbf{I} \cdot \mathbf{S}|J) &= -[J(J+1)]^{-1}(J|\mathbf{I}^r \cdot \mathbf{J}|J)(J|\mathbf{J} \cdot \mathbf{S}|J) \\
 &= [2J(J+1)]^{-1}[F(F+1) - I(I+1) \\
 &\quad - J(J+1)](J|\mathbf{J} \cdot \mathbf{S}|J).
 \end{aligned}$$

As S_z^r is diagonal in J , it is legitimate to write

$$\begin{aligned}
 (J|\mathbf{I} \cdot \mathbf{S} - 3I_z S_z|J) &= [2J(J+1)]^{-1}[F(F+1) \\
 &\quad - J(J+1) - I(I+1)](NJ|\mathbf{S} \cdot \mathbf{J} - 3S_z J_z|NJ). \quad (19)
 \end{aligned}$$

When $S = \frac{1}{2}$ one has

$$\begin{aligned}
 \mathbf{S} \cdot \mathbf{J} - 3S_z J_z &= \mathbf{S} \cdot \mathbf{N} - 3S_z N_z - S^2 + 3S_z^2 \\
 &= \mathbf{S} \cdot \mathbf{N} - 3S_z N_z. \quad (20)
 \end{aligned}$$

Because \mathbf{S}^r is precessing about \mathbf{N} , it follows that

$$\begin{aligned}
 (JN|\mathbf{S} \cdot \mathbf{N} - 3S_z N_z|JN) \\
 &= [2N(N+1)]^{-1}[J(J+1) - N(N+1) - S(S+1)] \\
 &\quad \times (N|N^2 - 3N_z^2|N) = [2N(N+1)]^{-1}[J(J+1) \\
 &\quad - N(N+1) - S(S+1)][N(N+1) - 3K^2]. \quad (21)
 \end{aligned}$$

Substitution of Eqs. (20) and (21) into Eq. (19) leads to

$$\begin{aligned}
 (KNJF|\mathbf{I} \cdot \mathbf{S} - 3I_z S_z|KNJF) &= [4J(J+1)N(N+1)]^{-1} \\
 &\quad \times [F(F+1) - J(J+1) - I(I+1)][J(J+1) \\
 &\quad - N(N+1) - S(S+1)][N(N+1) - 3K^2]. \quad (22)
 \end{aligned}$$

In a similar fashion one can show that

$$\begin{aligned}
 (J|(I_y + iI_x)(S_y + iS_x)|J) &= [4J(J+1)N(N+1)]^{-1} \\
 &\quad \times [F(F+1) - J(J+1) - I(I+1)][J(J+1) \\
 &\quad - N(N+1) - S(S+1)](N|(N_y + iN_x)^2|N). \quad (23)
 \end{aligned}$$

The operator $(N_y + iN_x)^2$ has matrix elements connecting K with $K+2$, in particular, $K=-1$ with $K=1$, i.e.,

$$(N, K=1|(N_y + iN_x)^2|N, K=-1) = N(N+1). \quad (24)$$

Equation (23) can now be rewritten as

$$\begin{aligned}
 (K=1, NJF|(I_y + iI_x)(S_y + iS_x)|K=-1, NJF) \\
 &= [4J(J+1)]^{-1}[F(F+1) - J(J+1) - I(I+1)] \\
 &\quad \times [J(J+1) - N(N+1) - S(S+1)]. \quad (25)
 \end{aligned}$$

The diagonal elements of α are, therefore,

$$\begin{aligned}
 \alpha_{1,2} &= [4N(N+1)(N \pm \frac{1}{2})(N+1 \pm \frac{1}{2})]^{-1} [\pm(N + \frac{1}{2}) - \frac{1}{2}] \\
 &\quad \times [F(F+1) - N(N+1) - I(I+1) \\
 &\quad \mp (N + \frac{1}{2}) - \frac{1}{4}] f(NK\lambda\tau), \quad (26)
 \end{aligned}$$

where the top signs go with α_1 and the bottom signs α_2 , and where

$$f(NK\lambda\tau) = \lambda[N(N+1) - 3K^2] \pm \delta_{|K|1} \tau N(N+1). \quad (26a)$$

The $+$ and $-$ signs in Eq. (26a) are used respectively for the symmetric and antisymmetric Wang functions of the rotating molecule. Equation (26) is valid only for the diagonal elements of the 2×2 sub-matrices of the 6×6 secular equation. The matrix elements for the two 1×1 submatrices are to be calculated from Eqs. (22), (25), and (14) by substituting $N \pm \frac{1}{2}$ for J and $N \pm \frac{3}{2}$ for F .

2. Diagonal Elements in the G Representation

Let us now consider the other extreme case in which the spin-spin coupling becomes the dominant part of the magnetic interaction in the molecule. The electronic and the nuclear spin will first couple to give a vector \mathbf{G} which adds to \mathbf{N} to form \mathbf{F} . In the G -representation let the 2×2 matrices of α , β , and γ be represented by

$$\alpha = \begin{pmatrix} \alpha_{\text{I}} & \alpha_{\text{III}} \\ \alpha_{\text{III}} & \alpha_{\text{II}} \end{pmatrix}, \quad \text{etc.}$$

Note that Arabic subscripts are used for α , β , and γ in the J representation and Roman subscripts in G representation. Figure 1 shows the vector relation between the various angular momenta. By projecting \mathbf{S}^r along the vector \mathbf{G}^r it can easily be verified that

$$\begin{aligned}
 (G|\mathbf{N} \cdot \mathbf{S}|G) &= [4G(G+1)]^{-1}[F(F+1) - N(N+1) \\
 &\quad - G(G+1)][G(G+1) + S(S+1) - I(I+1)]. \quad (27)
 \end{aligned}$$

Remembering the $G = I \pm \frac{1}{2}$ one may express the diagonal elements of β as

$$\begin{aligned}
 \beta_{\text{I, II}} &= \pm \frac{1}{2} \kappa (2I+1)^{-1} [F(F+1) - N(N+1) \\
 &\quad - I(I+1) - \frac{1}{4} \mp (I + \frac{1}{2})]. \quad (28)
 \end{aligned}$$

If when $S = \frac{1}{2}$ we are concerned only with matrix elements diagonal in S , the following simplification can be made:

$$\begin{aligned}
 \mathbf{I} \cdot \mathbf{S} - 3I_z S_z &= \mathbf{G} \cdot \mathbf{S} - 3G_z S_z - (S^2 - 3S_z^2) \\
 &= \mathbf{G} \cdot \mathbf{S} - 3G_z S_z, \quad (29)
 \end{aligned}$$

$$(S_y + iS_x)(I_y + iI_x) = (S_y + iS_x)(G_y + iG_x),$$

since the diagonal matrix elements of $S^2 - 3S_z^2$ and $(S_y + iS_x)^2$ for $S = \frac{1}{2}$ are zero. Upon projecting \mathbf{S}^r along

\mathbf{G}^r we have

$$(G|\mathbf{G}\cdot\mathbf{S}-3G_zS_z|G) \\ = [2G(G+1)]^{-1}[G(G+1)+S(S+1)-I(I+1)] \\ \times (G|G^2-3G_z^2|G), \quad (30)$$

$$(G|(S_y+iS_x)(G_y+iG_x)|G) \\ = [2G(G+1)]^{-1}[G(G+1)+S(S+1)-I(I+1)] \\ \times (G|(G_y+iG_x)^2|G). \quad (31)$$

The matrix elements of $G^2-3G_z^2$ and $(G_y+iG_x)^2$ can be found in Table II of reference 3 with a change of phase and notation. They are

$$(FGNK|G^2-3G_z^2|FGNK) \\ = [N(N+1)-3K^2][2N(N+1)(2N-1)(2N+3)]^{-1} \\ \times \{3R(N)[R(N)+1]-4N(N+1)G(G+1)\}, \quad (32) \\ (FGNK=1|(G_y+iG_x)^2|FGNK=-1) \\ = [2(2N-1)(2N+3)]^{-1}\{3R(N)[R(N)+1] \\ -4N(N+1)G(G+1)\},$$

where

$$R(N)=F(F+1)-G(G+1)-N(N+1).$$

Substitution of Eqs. (32), (31), (30), (29) in Eq. (14) gives

$$\alpha_{I,II}=\pm[N(N+1)(2N+3)(2N-1)(I+\frac{1}{2})]^{-1} \\ \times \{\frac{3}{4}[F(F+1)-N(N+1)-I(I+1)\mp(I+\frac{1}{2})-\frac{1}{4}]^2 \\ +\frac{3}{4}[F(F+1)-N(N+1)-I(I+1)\mp(I+\frac{1}{2})-\frac{1}{4}] \\ -N(N+1)[I(I+1)\pm(I+\frac{1}{2})+\frac{1}{4}]\}f(NK\lambda\tau), \quad (33)$$

where $f(NK\lambda\tau)$ was defined in Eq. (26a). Equation (33) applies only to the 2×2 submatrices; the elements in the 1×1 blocks are determined from Eqs. (32), (31), and (29) rather than from Eq. (33). They are, of course, identical to the corresponding elements in the J -representation.

Finally in the G -representation ($\mathbf{I}\cdot\mathbf{S}$) is diagonal with eigenvalues

$$(G|\mathbf{I}\cdot\mathbf{S}|G)=\frac{1}{2}[G(G+1)-I(I+1)-S(S+1)]. \quad (34)$$

The matrix elements of γ are

$$\gamma_I=\frac{1}{4}\sigma[(2I+1)-1], \quad \gamma_{II}=\frac{1}{4}\sigma[-(2I+1)-1]. \quad (35)$$

3. Evaluation of Nondiagonal Matrix Elements

Since the matrices

$$\begin{pmatrix} \beta_1 & \beta_{III} \\ \beta_{III} & \beta_{II} \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \beta_1 & \beta_3 \\ \beta_3 & \beta_2 \end{pmatrix}$$

are merely two different representations of the same quantity β , they can differ from each other only by an equivalence transformation. The same relation holds for α and thus for $(\alpha+\beta)$ also. The invariance of the

diagonal sum of β , β^2 , α^2 , and $(\alpha+\beta)^2$ gives respectively:

$$\beta_I+\beta_{II}=\beta_1+\beta_2, \\ 2\beta_{III}^2+\beta_I^2+\beta_{II}^2=\beta_1^2+\beta_2^2, \\ \alpha_I^2+2\alpha_{III}^2+\alpha_{II}^2=\alpha_1^2+2\alpha_3^2+\alpha_2^2, \quad (36) \\ (\alpha_I+\beta_I)^2+(\alpha_{III}+\beta_{III})^2+2(\alpha_{II}+\beta_{II})^2 \\ =(\alpha_1+\beta_1)^2+(\alpha_2+\beta_2)^2+2\alpha_3^2.$$

From Eqs. (36) it follows that

$$4\beta_{III}^2=(\beta_1-\beta_2)^2-(\beta_I-\beta_{II})^2, \quad (37)$$

$$4\alpha_{III}\beta_{III}=2\alpha_1\beta_1+2\alpha_2\beta_2-2\alpha_I\beta_I-2\alpha_{II}\beta_{II} \\ =(\alpha_1-\alpha_2)(\beta_1-\beta_2)-(\alpha_I-\alpha_{II})(\beta_I-\beta_{II}). \quad (38)$$

This is essentially an extension of the Goudsmit¹⁵ inspection method as generalized by Van Vleck.³

4. Energy Levels

If one knows all the matrix elements of α , β , and γ in the G -representation, one can derive the equation for the energy for the general case when all the three types of magnetic interactions are of the same order of magnitude. The secular equation is

$$\begin{vmatrix} \alpha_I+\beta_I+\gamma_I-E & \alpha_{III}+\beta_{III} \\ \alpha_{III}+\beta_{III} & \alpha_{II}+\beta_{II}+\gamma_{II}-E \end{vmatrix}=0, \quad (39)$$

with the solution

$$2E=\alpha_I+\alpha_{II}+\beta_I+\beta_{II}+\gamma_I+\gamma_{II}\pm[(\alpha_I-\alpha_{II}+\beta_I \\ -\beta_{II}+\gamma_I-\gamma_{II})^2+4(\alpha_{III}+\beta_{III})^2]^{\frac{1}{2}}. \quad (40)$$

Substituting Eqs. (37), (38), (28), (33), and (35) in Eq. (40) and simplifying, we have

$$2E=\alpha_I+\alpha_{II}+\beta_I+\beta_{II}+\gamma_I+\gamma_{II}+\{(\alpha_I-\alpha_{II})^2 \\ +2(\alpha_1-\alpha_2)(\beta_1-\beta_2)+(\beta_1-\beta_2)^2+(\gamma_I-\gamma_{II})^2 \\ +2(\gamma_I-\gamma_{II})(\alpha_I-\alpha_{II}+\beta_I-\beta_{II}) \\ +[(\beta_1-\beta_2)^2-(\beta_I-\beta_{II})^2]^{-1}[(\alpha_1-\alpha_2)(\beta_1-\beta_2) \\ -(\alpha_I-\alpha_{II})(\beta_I-\beta_{II})]^2\}^{\frac{1}{2}}. \quad (41)$$

Equation (41) gives the energies of the two levels of a given N corresponding to $F=N+\frac{1}{2}$ or the two levels of $F=N-\frac{1}{2}$. For the states with $F=N+\frac{3}{2}$ or with $F=N-\frac{3}{2}$, the energy is simply given by the diagonal matrix element of H in either the J - or G -representation. It should be pointed out that Eq. (41) is not applicable to the case of $F=N\pm\frac{3}{2}$.

5. Energy Levels in a Weak Magnetic Field

The interaction of the electronic spin with the external magnetic field causes an energy level of a given F to split into various components corresponding to the different values of M_F (the projection of \mathbf{F} along the direction of the external field). Here it is assumed that the splittings of the energy levels produced by the

¹⁵ S. Goudsmit, Phys. Rev. **35**, 1325 (1930).

external magnetic field are small compared to those due to the magnetic interaction terms in Eq. (1). In other words, the matrix elements nondiagonal in F need not be considered. The magnetic moments associated with the molecular rotation and the nuclear spin are neglected here. The Hamiltonian representing the Zeeman energy is

$$H_Z = g_{S\mu_B} \mathbf{S} \cdot \mathcal{H} = g_{S\mu_B} S_Z \mathcal{H}, \quad (43)$$

where \mathcal{H} , the external magnetic field, is taken to be coincident with the space-fixed Z axis. The diagonal elements of the Zeeman term in the J and G representation are

$$(S J F | S_Z | S J F) = [J(J+1)F(F+1)]^{-1} (S J | \mathbf{S} \cdot \mathbf{J} | S J) \times (J F | \mathbf{J} \cdot \mathbf{F} | J F) M_F, \quad (44)$$

$$(S G F | S_Z | S G F) = [G(G+1)F(F+1)]^{-1} (S G | \mathbf{S} \cdot \mathbf{G} | S G) \times (G F | \mathbf{G} \cdot \mathbf{F} | G F) M_F.$$

If we denote the matrix (2×2) of H_Z by δ , the non-diagonal elements of this operator can be determined by making use of the invariance property of the trace of matrices δ , δ^2 , and $(\beta + \delta)^2$. The solution of the 2×2 secular equation leads to the following approximate solution:

$$\begin{aligned} 2E' = 2E + \delta_I + \delta_{II} \pm \{ & (\alpha_I - \alpha_{II})^2 + 2(\alpha_1 - \alpha_2)(\beta_1 - \beta_2) \\ & + (\gamma_I - \gamma_{II})^2 + (\beta_1 - \beta_2)^2 + 2(\gamma_I - \gamma_{II})(\alpha_I - \alpha_{II} + \beta_I - \beta_{II}) \\ & + [(\beta_1 - \beta_2)^2 - (\beta_I - \beta_{II})^2]^{-1} [(\alpha_1 - \alpha_2)(\beta_1 - \beta_2) \\ & - (\alpha_I - \alpha_{II})(\beta_I - \beta_{II})]^2 \}^{-1/2} \{ (\beta_1 - \beta_2)(\delta_I - \delta_2) \\ & + (\alpha_I - \alpha_{II})(\delta_I - \delta_{II}) + (\gamma_I - \gamma_{II})(\delta_I - \delta_{II}) \\ & + [(\beta_1 - \beta_2)^2 - (\beta_I - \beta_{II})^2]^{-1} [(\beta_1 - \beta_2)(\delta_I - \delta_2) \\ & - (\beta_I - \beta_{II})(\delta_I - \delta_{II})] [(\alpha_1 - \alpha_2)(\beta_1 - \beta_2) \\ & - (\alpha_I - \alpha_{II})(\beta_I - \beta_{II})] \}, \quad (45) \end{aligned}$$

where

$$\begin{aligned} \delta_I + \delta_{II} &= \frac{1}{2} [F(F+1)]^{-1} g_{S\mu_B} M_F \mathcal{H}, \\ \delta_I - \delta_{II} &= \frac{1}{2} [F(F+1)(I + \frac{1}{2})]^{-1} [F(F+1) + I(I+1) \\ &\quad - N(N+1) + \frac{1}{4}] g_{S\mu_B} M_F \mathcal{H}, \\ \delta_1 - \delta_2 &= \frac{1}{2} [F(F+1)(N + \frac{1}{2})]^{-1} [F(F+1) + N(N+1) \\ &\quad - I(I+1) + \frac{1}{4}] g_{S\mu_B} M_F \mathcal{H}. \end{aligned}$$

Here E' and E denote, respectively, the energies in the presence and in the absence of the external field. Again Eq. (45) pertains only to the energy levels with $F = N \pm \frac{1}{2}$. The Zeeman splittings for the levels with $F = N \pm \frac{3}{2}$ may be calculated from Eqs. (44) and (43).

6. Energy Levels in a Strong Magnetic Field

In a strong magnetic field the angular momenta \mathbf{N} , \mathbf{S} , and \mathbf{I} are decoupled and become spatially quantized separately. If the magnitude of $g_{S\mu_B} \mathbf{S} \cdot \mathcal{H}$ is large compared to the magnetic fine structure interaction terms, the energy is given approximately by the diagonal matrix elements of the Hamiltonian in the represen-

tation which diagonalizes M_I , M_S , and M_N (the components of \mathbf{I} , \mathbf{S} , and \mathbf{N} in the direction of the external field). Here again we shall neglect the interactions of the external field with the nuclear moment and with the molecular rotational magnetic moment, since these terms have no effect on the magnetic resonance transitions of $\Delta M_S = \pm 1$ and $\Delta M_N = \Delta M_I = 0$. Let x, y, z and X, Y, Z be two sets of axes fixed in the molecule and the space, respectively. With the aid of the relations

$$\begin{aligned} I_x &= I_X \lambda_{Xx} + I_Y \lambda_{Yx} + I_Z \lambda_{Zx}, \\ S_x &= S_X \lambda_{Xx} + S_Y \lambda_{Yx} + S_Z \lambda_{Zx}, \end{aligned} \quad (46)$$

$$\mathbf{I} \cdot \mathbf{S} = I_X S_X + I_Y S_Y + I_Z S_Z,$$

(where the λ 's are the direction cosines), the matrix elements of the spin-spin term may be expressed as

$$\begin{aligned} (M_I M_S M_N N K | \mathbf{I} \cdot \mathbf{S} - 3I_z S_z | M_I M_S M_N N K) \\ = (M_N N K | 1 - 3\lambda_{Zz}^2 | M_N N K) M_I M_S. \quad (47) \end{aligned}$$

When the matrix elements of the direction cosines given by Cross, Hainer, and King¹⁶ are used, the above equation becomes

$$\begin{aligned} (M_I M_S M_N N K | \mathbf{I} \cdot \mathbf{S} - 3I_z S_z | M_I M_S M_N N K) \\ = -2[N(N+1)(2N-1)(2N+3)]^{-1} [N(N+1) \\ - 3M_N^2] [N(N+1) - 3K^2] M_I M_S. \quad (48) \end{aligned}$$

Similarly it can be shown that

$$\begin{aligned} (M_I M_S M_N N, K \\ = 1 | (I_y + iI_x)(S_y + iS_x) | M_I M_S M_N N, K = -1) \\ = -2[(2N-1)(2N+3)]^{-1} [N(N+1) \\ - 3M_N^2] M_I M_S. \quad (49) \end{aligned}$$

Since the diagonal matrix elements of the spin-rotation and the Fermi coupling terms are, respectively, proportional to $M_N M_S$ and $M_I M_S$, the energy of the NO₂ molecule in a strong external magnetic field may be written as

$$\begin{aligned} E = E_{\text{rig}} + g_{S\mu_B} M_S \mathcal{H} + \kappa M_N M_S + \sigma M_I M_S \\ - 2f(NK\lambda\tau) [N(N+1)(2N-1)(2N+3)]^{-1} \\ \times [N(N+1) - 3M_N^2] M_I M_S. \quad (50) \end{aligned}$$

Here E_{rig} represents the energy associated with the rigid rotation of the molecule, i.e., the eigenvalue of the operator H_0 in Eq. (2).

IV. THE ROTATIONAL SPECTRUM

In the limiting case where H_{S-R} is much larger than the coupling between the electronic and nuclear spin, intensity considerations show that for a given ΔN the six lines characterized by $\Delta N = \Delta J = \Delta F$ are by far the strongest ones, as compared to the other thirteen possible transitions with $\Delta F \neq \Delta N$ or $\Delta J \neq \Delta N$. For the intermediate case J ceases to be a good quantum number, and the wave functions for the six energy

¹⁶ Cross, Hainer, and King, J. Chem. Phys. 12, 210 (1944).

levels with a given N can be expressed in terms of the wave functions in the J representation (denoted by ψ) as follows:

$$\begin{aligned}
 \Psi_1 &= \psi(J=N+\frac{1}{2}, F=N+\frac{3}{2}), \\
 \Psi_2 &= f\psi(J=N+\frac{1}{2}, F=N+\frac{1}{2}) \\
 &\quad + b\psi(J=N-\frac{1}{2}, F=N+\frac{1}{2}), \\
 \Psi_3 &= b\psi(J=N+\frac{1}{2}, F=N+\frac{1}{2}) \\
 &\quad - f\psi(J=N-\frac{1}{2}, F=N+\frac{1}{2}), \\
 \Psi_4 &= c\psi(J=N+\frac{1}{2}, F=N-\frac{1}{2}) \\
 &\quad + d\psi(J=N-\frac{1}{2}, F=N-\frac{1}{2}), \\
 \Psi_5 &= d\psi(J=N+\frac{1}{2}, F=N-\frac{1}{2}) \\
 &\quad - c\psi(J=N-\frac{1}{2}, F=N-\frac{1}{2}), \\
 \Psi_6 &= \psi(J=N-\frac{1}{2}, F=N-\frac{3}{2}).
 \end{aligned} \tag{51}$$

We can construct six similar wave functions $\Psi_1', \Psi_2', \dots, \Psi_6'$ for the $(N+1)$ th rotational state by merely replacing N by $N+1$ and f, b, c, d by f', b', c', d' in Eqs. (51). These "mixing coefficients" are different for the different rotational states. For the $N \rightarrow N+1$ transitions one may expect ten strong lines corresponding to

$$\begin{aligned}
 \Psi_1 \rightarrow \Psi_1', \quad \Psi_2 \rightarrow \Psi_2', \quad \Psi_3 \rightarrow \Psi_3', \quad \Psi_2 \rightarrow \Psi_3', \quad \Psi_3 \rightarrow \Psi_2', \\
 \Psi_4 \rightarrow \Psi_4', \quad \Psi_5 \rightarrow \Psi_5', \quad \Psi_4 \rightarrow \Psi_5', \quad \Psi_5 \rightarrow \Psi_4', \quad \Psi_6 \rightarrow \Psi_6'.
 \end{aligned}$$

As N becomes large the coefficients f, b, c, d for the N th and $(N+1)$ th state do not differ very much; in such cases the intensities of the transitions

$$\Psi_2 \rightarrow \Psi_3', \quad \Psi_3 \rightarrow \Psi_2', \quad \Psi_4 \rightarrow \Psi_5', \quad \Psi_5 \rightarrow \Psi_4'$$

become greatly reduced and only six strong lines are observed.

This theory has been applied by Bird and Baird to interpret the microwave spectrum. The identification of the spectral lines and the evaluation of the various coupling constants from the experimental data will be discussed in a forthcoming paper by these authors.²

V. HIGHER ORDER CORRECTIONS AND EXTENSION OF THE THEORY

At this point it is well to examine the "higher order" effects which have been disregarded in the derivation of Eq. (41). The more prominent ones are:

1. *Asymmetry of the molecule.*—Equation (41) was derived on the "symmetric top" approximation. To correct for the asymmetry of the molecule, the proper asymmetric rotor wave functions (rather than the Wang functions) are to be used to calculate the matrix elements of H_{S-R} and H_{S-I} ; thus Eq. (41) should be modified accordingly. For the NO₂ molecule the asymmetric rotor functions may be obtained from the Wang functions by first order perturbation method.

2. *Nondiagonality of N .*—The nondiagonal matrix elements ($N|N'$) of the magnetic coupling terms which have been hitherto neglected, may give a substantial

contribution to the energy levels when the magnitudes of these coupling effects become sufficiently large. Under such circumstances, a Van Vleck transformation may be applied to remove the nondiagonality in N , so that in the transformed energy matrix the elements off-diagonal in N become one order of magnitude smaller and can then be safely dropped.

3. *Nuclear quadrupole coupling.*—The nuclear quadrupole interaction can be treated in the same manner as the magnetic coupling terms. The diagonal elements of H_Q are first determined in both the J - and G -scheme. The calculation is given in the Appendix. The nondiagonal terms are obtained by comparing the trace of the various matrices in the two representations.

4. *Pseudoquadrupole correction.*—This type of interaction has been discussed in some detail by Henderson.⁹ Since the ground state of NO₂ has $S=\frac{1}{2}$, a simple group-theoretical argument shows that the diagonal matrix elements of the pseudoquadrupole term are zero.

Some of these effects have been considered by J. C. Baird and the author. The results have been used in the interpretation of the microwave spectrum.

Aside from the approximations made for the specific case of NO₂, this theory should be applicable to other polyatomic molecules with $S=\frac{1}{2}$. For a particular molecule some of these "higher order" effects may be quite important and should be included in the solution of the energy levels at the outset. One interesting example is ClO₂ which has considerably larger asymmetry than NO₂, so that the asymmetry correction discussed above must be made.

VI. THE MAGNETIC RESONANCE SPECTRUM

The magnetic resonance spectrum has been observed by Castle and Beringer¹⁷ at room temperature and a field strength around 3300 gauss. Under a pressure of 5 to 15 mm Hg the spectrum consists of three overlapping lines. A partial resolution of the triplet into a number of lines has been made at lower pressure. The expression for the energy of NO₂ in a strong magnetic field was given by these authors as

$$W = M_{sg} \mu_B \beta C + A M_S M_I + B M_S M_N. \tag{52}$$

Castle and Beringer have pointed out that A and B (not to be confused with the rotational constants) may depend on N and K , but they have not exhibited this dependence. The three overlapping lines were identified as the transitions $\Delta N = \Delta M_I = \Delta M_N = 0$, $\Delta M_S = 1$ with $M_I = 1, 0, -1$, but no explanation was offered for the resolved lines.

Comparison of Eq. (52) with Eq. (50) shows that

$$\begin{aligned}
 B &= K, \\
 A &= \sigma - 2f(NK\lambda\tau) [N(N+1)(2N-1)(2N+3)]^{-1} \\
 &\quad \times [N(N+1) - 3M_N^2].
 \end{aligned} \tag{53}$$

¹⁷ J. G. Castle and R. Beringer, Phys. Rev. **80**, 114 (1950).

Since the value of A varies with different rotational states, according to Eq. (52) and the selection rules given above the magnetic resonance spectrum may be expected to contain a large number of lines. Furthermore, in a magnetic field of 3300 gauss the vectors \mathbf{I} , \mathbf{S} , and \mathbf{N} are not completely decoupled, so that the second order terms of H_{S-R} and H_{S-I} may become quite appreciable. Application of this theory to the spectrum has been investigated by Bird.

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APPENDIX. MATRIX ELEMENTS OF THE NUCLEAR QUADRUPOLE TERM

The Hamiltonian for the nuclear quadrupole effect in a polyatomic molecule has been given by Van Vleck.³ In the case of NO_2 the relevant terms of this operator are the ones which contain matrix elements of the form $\Delta K=0$ and ± 2 , viz.,

$$H_Q = [4I(2I-1)]^{-1} eQ \left[\frac{\partial^2 V}{\partial z^2} (2I_z^2 - I_x^2 - I_y^2) + \left(\frac{\partial^2 V}{\partial y^2} - \frac{\partial^2 V}{\partial x^2} \right) (I_y^2 - I_x^2) + 2 \frac{\partial^2 V}{\partial x \partial y} (I_x I_y + I_y I_x) \right]. \quad (\text{A1})$$

Here Q is the nuclear quadrupole moment as defined in Appendix II of reference 3. If the electronic wave function of NO_2 is real, the last term on the right-hand side of Eq. (A1) may be omitted. The diagonal matrix elements of the operator $2I_z^2 - I_x^2 - I_y^2$ and $I_x^2 - I_y^2$ may be obtained by the projection method and the procedure for the calculation is given in this Appendix.

In the J representation let us first consider the coupling $\mathbf{F} + \mathbf{I} = \mathbf{J}$. It may be shown by a group-theoretical argument that the diagonal matrix elements (in J) of $2I_z^2 - I_x^2 - I_y^2$ are proportional to those of $2J_z^2 - J_x^2 - J_y^2$. The constant of proportionality can be established with the aid of the diagonal matrix elements of $2I_z^2 - I_x^2 - I_y^2$ given in Table II of reference 3. Notice that this is essentially a generalized form of the projection method for the components of the irreducible tensors. Thus we have

$$(J | 2I_z^2 - I_x^2 - I_y^2 | J) = [2J(J+1)(2J-1)(2J+3)]^{-1} \times [3C(C+1) - 4J(J+1)I(I+1)] \times (J | 2J_z^2 - J_x^2 - J_y^2 | J), \quad (\text{A2})$$

where

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

The vector \mathbf{J} can be expanded as $\mathbf{N} - \mathbf{S}^r$, and in this coupling scheme \mathbf{S}^r may be projected along \mathbf{N} . When this is done, it is easily seen that as far as the matrix elements diagonal in J are concerned, we may replace $2J_z^2 - J_x^2 - J_y^2$ by

$$\{1 + 2[N(N+1)]^{-1}(\mathbf{N} \cdot \mathbf{S})\} (2N_z^2 - N_x^2 - N_y^2). \quad (\text{A3})$$

Here we have made use of the fact that the diagonal elements of $2S_z^2 - S_x^2 - S_y^2$ are zero for the $S = \frac{1}{2}$ states. In a similar way we can obtain the matrix elements of $I_y^2 - I_x^2$ connecting the states $K=1$ to $K=-1$. The diagonal elements of H_Q in the J -scheme (with the Wang functions as basis) are

$$eQ [16I(2I-1)J(J+1)(2J-1)(2J+3)]^{-1} \times [3C(C+1) - 4J(J+1)I(I+1)] \times \{1 + 2[N(N+1)]^{-1}(JN | \mathbf{N} \cdot \mathbf{S} | JN)\} \varphi(NK), \quad (\text{A4})$$

where

$$\varphi(NK) = 2 \frac{\partial^2 V}{\partial z^2} [3K^2 - N(N+1)] + \delta_{|K|1} \left(\frac{\partial^2 V}{\partial y^2} - \frac{\partial^2 V}{\partial x^2} \right) N(N+1). \quad (\text{A5})$$

In the G -representation the operator $2I_z^2 - I_x^2 - I_y^2$ can be decomposed into

$$\{1 - 2[G(G+1)]^{-1}(\mathbf{G} \cdot \mathbf{S})\} (2G_z^2 - G_x^2 - G_y^2) \quad (\text{A6})$$

by means of the relation $\mathbf{I} = \mathbf{G} - \mathbf{S}$ and the projection method. The matrix elements of $2G_z^2 - G_x^2 - G_y^2$ in the G -scheme may be found from Eq. (32) and a similar treatment can be applied to $G_y^2 - G_x^2$. The diagonal elements of H_Q in the G -representation then emerge as

$$eQ [16I(2I-1)N(N+1)(2N-1)(2N+3)]^{-1} \times [3C'(C'+1) - 4N(N+1)G(G+1)] \times \{1 - 2[G(G+1)]^{-1}(G | \mathbf{G} \cdot \mathbf{S} | G)\} \varphi(NK), \quad (\text{A7})$$

where

$$C' = F(F+1) - G(G+1) - N(N+1).$$

The matrix elements in (A4) and (A7) may also be obtained by Racah's method.¹⁸ With the diagonal elements of H_Q in the two representations, the off-diagonal terms are determined by the method given in Sec. III-3. The nuclear quadrupole interaction can then be easily incorporated into the secular equation.

Note added in proof.—Dr. John G. Baker has kindly informed us that he has independently developed a somewhat similar theory for the fine structure of the rotational spectra of this type of molecules, and an account of his work will be published in the near future.

¹⁸ G. Racah, Phys. Rev. **62**, 438 (1942).