Theory of the Hyperfine Structure of NO Molecule*

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The theory of the hfs of the NO molecule due to the magnetic moment and the electric quadrupole moment of the N nucleus is worked out. Assuming that the electron which is rotating around the molecular axis is in a pure p state, some relations between coupling constants are derived and were found to agree with experimental relations. Hund's case (a) was taken as a starting point, but the actual deviation from case (a) was found to be not negligible and was also explained satisfactorily. The formula for the nuclear electric quadrupole effect was derived for Hund's case (a) and also for a general coupling case. This electric quadrupole effect was found to be different for Λ-type doublet states. The difference appears for every coupling case including Hund's case (a). The agreement between theory and experimental results is quite satisfactory.

1. INTRODUCTION

THE electronic ground state of the NO molecule is $\Pi_{\frac{1}{2}}$. In this state there are nonvanishing electronic orbital and spin angular momenta. Since the spin orbit coupling is strong compared to the end-over-end rotational energy, the spin is strongly coupled to the molecular axis [Hund's case (a); see Fig. 1]. In this case the molecular magnetic moment is parallel to the molecular axis and has the magnitude $\beta\Lambda+2\beta\Sigma$, where Λ and Σ are the components of the electronic orbital and spin angular momentum, respectively, along the molecular axis and β is the Bohr magneton. In our case, it so happens that since $\Lambda=1$ and $\Sigma=-\frac{1}{2}$, these contributions almost cancel each other, and no net magnetic moment is expected, while in the next excited state $\Pi_{\frac{3}{2}}$, where $\Lambda=1$, $\Sigma=+\frac{1}{2}$, a large magnetic moment exists. This fact was well confirmed by the susceptibility measurements.[1]

Recently Gordy and Burrus[2] and also Gallagher, Bedard, and Johnson[2] have observed the hfs of this molecule in the $\Pi_{\frac{1}{2}}$ state and found that the magnetic interaction is very large, while the nuclear quadrupole term is negligible. This result seems puzzling, since there is no net magnetic moment in this state except that due to the molecular rotation which is of the order of the nuclear magneton.

Recently Frosch and Foley[3] published a theory of the hfs of this kind of molecule. They derived formulas starting from Dirac's equation and discussed the various possibilities. The work done here naturally overlaps their work appreciably, but in this paper more care was taken with the physical meaning of the coupling constant, and the formulas for the electric quadrupole hfs were newly derived.

2. HAMILTONIAN AND WAVE FUNCTION

The magnetic interaction between nucleus and electrons is given by

$$H_1=\sum_k \frac{g_n\beta_n\beta}{r_k{}^3}(\mathbf{l}_k-\mathbf{s}_k)\cdot\mathbf{I}+3\frac{(\mathbf{s}_k\cdot\mathbf{r}_k)(\mathbf{I}\cdot\mathbf{r}_k)}{r_k{}^2}, \qquad (1)$$

where β_n is the nuclear magneton, β is the Bohr magneton, g_n is the gyromagnetic ratio of the nucleus whose spin is I, $\mathbf{r}_k$ is the distance between this nucleus and the kth electron, and $\mathbf{l}_k$, $\mathbf{s}_k$ are the orbital and spin angular momenta of the kth electron, respectively. Although FF took a different expression for this interaction term, it can be seen that their expression is equivalent to that in Eq. (1) when there is no external field and the s-state contribution is negligible, which is our case. It is convenient to express the terms as

$$\sum_k \frac{\mathbf{l}_k}{r_k{}^3}=\xi\mathbf{L}, \qquad (2a)$$

$$\sum_k \frac{1}{r_k{}^3}\left\{-\mathbf{s}_k\cdot\mathbf{I}+3\frac{(\mathbf{s}_k\cdot\mathbf{r}_k)(\mathbf{I}\cdot\mathbf{r}_k)}{r_k{}^2}\right\}$$

$$=\eta\{\zeta(\mathbf{S}\cdot\mathbf{I})-3(\mathbf{S}\cdot\mathbf{L})(\mathbf{I}\cdot\mathbf{L})\}, \qquad (2b)$$

Fig. 1. Hund's case (a).

[1] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (The Clarendon Press, Oxford, 1932), p. 269.
[2] W. Gordy and C. A. Burrus, Phys. Rev. **93**, 419 (1954); Gallagher, Bedard, and Johnson, Phys. Rev. **93**, 729 (1954).
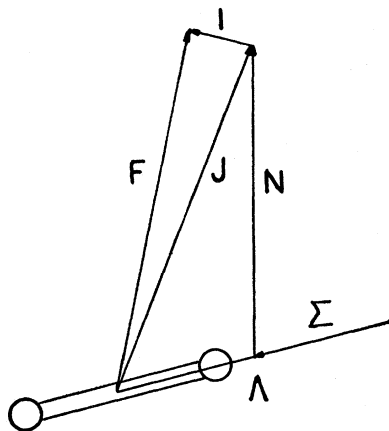[3] R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952). It is called FF in this paper.

where $\mathbf{L}$, $\mathbf{S}$ are now the total electronic orbital and spin angular momenta, ξ is an average value of r_k^{-3}, and η is $\xi/2$ in the classical case. If we assume that only one outer-shell electron is effective in the formula (1), and it is in a p state, then[4] η is $2\xi/5$ and $\zeta=2$. Inserting the formulas (2) into (1), we obtain

$$H_1 = g_n\beta_n\beta\{\xi \mathbf{L}\cdot\mathbf{I} + \eta\zeta(\mathbf{S}\cdot\mathbf{I}) - 3\eta(\mathbf{S}\cdot\mathbf{L})(\mathbf{I}\cdot\mathbf{L})\}. \quad (3)$$

Taking z axis along the molecular axis,

$$\begin{aligned}
H_1 = g_n\beta_n\beta\{&\xi L_z I_z + \eta\zeta S_z I_z - 3\eta S_z L_z{}^2 I_z \\
&- 3\eta(S_+ L_-{}^2 I_+ + S_- L_+{}^2 I_-)/4 - \xi(L_+ I_- + L_- I_+)/2 \\
&+ \eta\zeta(S_+ I_- + S_- I_+)/2 - 3\eta(S_+ L_- I_- L_+ \\
&+ S_- L_+ I_+ L_- + I_+ L_- S_- L_+ + I_- L_+ S_+ L_-)/8\}, \quad (4)
\end{aligned}$$

where

$$L_+ = L_x + iL_y, \quad L_- = L_x - iL_y, \quad \text{etc.}$$

The total wave function is obtained by coupling $\mathbf{J}$ and $\mathbf{I}$ into $\mathbf{F}$ by the usual procedure, where the absolute value of the component of $\mathbf{J}$ parallel to the molecular axis is $\Lambda + \Sigma$ and its perpendicular component is N, the angular momentum of the end-over-end rotation which is not well quantized in our case. There are two kinds of wave functions, in one of which $J_z = \Lambda + \Sigma = \frac{1}{2}$ and in the other $J_z = -(\Lambda + \Sigma) = -\frac{1}{2}$. Owing to the perturbation $-2B(J_x P_x + J_y P_y)$, where B is the rotational constant and P is the total electronic angular momentum, this degeneracy is removed and gives a Λ-type doublet.[5,6] If the wave function with $J_z = +\frac{1}{2}$ is denoted by $(J_+|$ and $J_z = -\frac{1}{2}$ by $(J_-|$, the proper wave functions for the nondegenerate states are $2^{-\frac{1}{2}}\{(J_+| + (J_-|\}$ and $2^{-\frac{1}{2}}\{(J_+| - (J_-|\}$. The perturbation energies due to the above operator are $-2Bf(J,\frac{1}{2})(J_+|P_x|J_-)$ and $+2Bf(J,\frac{1}{2})(J_+|P_x|J_-)$, respectively,[7] so that if we take the sign of the wave function so as to make $(J_+|P_x|J_-)$ positive, the wave function $2^{-\frac{1}{2}}\{(J_+| + (J_-|\}$ corresponds to the lower state. It is customary to denote the lower state by c and the upper state by d.[6]

3. MAGNETIC HYPERFINE STRUCTURE

The magnetic interaction energy is given by the diagonal matrix element of our Hamiltonian (4), that is, for the c state:

$$\begin{aligned}
W_c = 2^{-1}\{&(J_+IF|H_1|J_+IF) + (J_-IF|H_1|J_-IF) \\
&+ (J_+IF|H_1|J_-IF) + (J_-IF|H_1|J_+IF)\} \\
= &(J_+IF|H_1|J_+IF) + (J_+IF|H_1|J_-IF), \quad (5a)
\end{aligned}$$

and for the d state:

$$W_d = (J_+IF|H_1|J_+IF) - (J_+IF|H_1|J_-IF). \quad (5b)$$

[4] See, for example, A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).
[5] J. H. Van Vleck, Revs. Modern Phys. 23, 213 (1951).
[6] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).
[7] f is the function defined in reference 5 as

$$f(J,\tfrac{1}{2}) = \{J(J+1) - \tfrac{3}{4}\}^{\frac{1}{2}}.$$

In Hund's case (a), we have the approximation

$$\begin{aligned}
(J_+IF|H_1|J_+IF) = g_n\beta_n\beta(\xi\Lambda + \eta\zeta\Sigma - 3\eta\Sigma\Lambda^2) \\
\times (J_+IF|\mathbf{z}\cdot\mathbf{I}|J_+IF), \quad (6)
\end{aligned}$$

where $\mathbf{z}$ is a unit vector parallel to the molecular axis. The matrix element of $\mathbf{z}\cdot\mathbf{I}$ is shown in FF and elsewhere to be

$$\begin{aligned}
(J_+IF|H_1|J_+IF) = g_n\beta_n\beta(\xi\Lambda + \eta\zeta\Sigma - 3\eta\Sigma\Lambda^2)(\Lambda + \Sigma) \\
\times \{2J(J+1)\}^{-1}\{F(F+L) - J(J+1) - I(I+1)\}. \quad (7)
\end{aligned}$$

In our case where $\Lambda = 1$, $\Sigma = -\frac{1}{2}$, it is

$$\begin{aligned}
(J_+IF|H_1|J_+IF) = g_n\beta_n\beta(2\xi - \eta\zeta + 3\eta)\{8J(J+1)\}^{-1} \\
\times \{F(F+1) - J(J+1) - I(I+1)\}. \quad (8)
\end{aligned}$$

As was pointed out in FF H_1 has a finite matrix element between the J_+ and J_- states. In our formula (4) this is the $S_+ L_-{}^2 I_+$ or $S_- L_+{}^2 I_-$ term. In calculating the matrix element $(J_+IF|S_- L_+{}^2 I_-|J_-IF)$, integrating over electronic coordinates first, S_- can be replaced by 1 and L_+ by $\{L(L+1)\}^{\frac{1}{2}}$, if the electronic angular momentum L is a good quantum number. Since because of the coupling to the molecular axis, L may not be a good quantum number, we will replace $3\eta S_- L_+{}^2$ by a constant, γ, which is 6η if a p-wave function is a good approximation for the electron under consideration. Thus,

$$\begin{aligned}
&(J_+IF|H_1|J_-IF) \\
&= -g_n\beta_n\beta\gamma(J_+IF|(\mathbf{x}+i\mathbf{y})\cdot\mathbf{I}|J_-IF)/4, \quad (9)
\end{aligned}$$

where $\mathbf{x}$ and $\mathbf{y}$ are unit vectors perpendicular to the molecular axis. Just as in FF, we obtain

$$\begin{aligned}
(J_+IF|H_1|J_-IF) = -g_n\beta_n\beta\gamma(2J+1)\{16J(J+1)\}^{-1} \\
\times \{F(F+1) - J(J+1) - I(I+1)\}. \quad (10)
\end{aligned}$$

Thus, from the formulas (5a), (5b), (8), and (10) we obtain

$$\begin{aligned}
W_c = \{a - b(2J+1)\}\{J(J+1)\}^{-1} \\
\times \{F(F+1) - J(J+1) - I(I+1)\}, \quad (11a)
\end{aligned}$$

$$\begin{aligned}
W_d = \{a + b(2J+1)\}\{J(J+1)\}^{-1} \\
\times \{F(F+1) - J(J+1) - I(I+1)\}, \quad (11b)
\end{aligned}$$

where

$$a = g_n\beta_n\beta(2\xi - \eta\zeta + 3\eta)/8, \quad b = g_n\beta_n\beta\gamma/16. \quad (12)$$

If we take the p-electron approximation, they are

$$a = g_n\beta_n\beta(3\xi/10), \quad b = a/2. \quad (13)$$

The formulas (11a) and (11b) are already given in FF, but the sign before b was not clearly indicated there. According to our procedure there remains no ambiguity on this point. Also the relation (13) was not given in FF.

4. ELECTRIC HYPERFINE STRUCTURE

Many authors have assumed that the conventional formula can be applied in Hund's case (a) even if there

exists a finite electronic spin, but it will be shown here that this is not the case.

The interaction between electrons and the nuclear electric quadrupole moment can be expressed in tensor form as

$$H_2 = \mathbf{Q} \cdot \nabla \mathbf{E}. \tag{14}$$

In Racah's formalism,[8]

$$(JIF|H_2|JIF) = (-1)^{J+I-F}(J\|\nabla E\|J)(I\|Q\|I) \\ \times W(JIJI;F2), \tag{15}$$

where

$$(J\|\nabla E\|J) = (-1)^{-J-m}(Jm|\nabla E_0|Jm)/ \\ V(JJ2;-mm0), \tag{15a}$$

$$(I\|Q\|I) = \tfrac{1}{2}eQ\{(2I+1)(I+1)(2I+3) \\ I(2I-1)\}^{\frac{1}{2}}, \tag{15b}$$

$$W(JIJI;F2) = (-1)^{F-J-I}6\{C(C+1) \\ -(4/3)J(J+1)I(I+1)\}\{(2J+3)(2J+2) \\ \times (2J+1)2J(2J-1)(2I+3)(2I+2)(2I+1) \\ \times 2I(2I-1)\}^{-\frac{1}{2}}, \tag{15c}$$

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

In the above formulas, V is the function defined by Racah's papers[8] and Q is the nuclear electric quadrupole moment.

In calculating the matrix element $(Jm|\nabla E_0|Jm)$, one should be careful to eliminate the electronic spin part of J. In the appendix of this paper it is shown that the wave function of the $\Pi_{\frac{1}{2}}$ state in Hund's case (a) is, if $S = \frac{1}{2}$,

$$(Jm| = (4J+2)^{-\frac{1}{2}}\{(2J-1)^{\frac{1}{2}}(KSJm| \\ + (2J+3)^{\frac{1}{2}}(K+1SJm|\}, \tag{A6}$$

where $K = J - \frac{1}{2}$ is the sum of the angular momenta of the end-over-end rotation and the electronic orbital motion. In our case there are two possible wave functions, in one of which $K_z = 1$ and in the other $K_z = -1$. If we denote them by K_+ and K_-, respectively, the Λ-type doublet can be represented by replacing $(KSJm|$ by $\{(K_+SJm| \pm (K_-SJm|\}/2^{\frac{1}{2}}$ in the formula (A6), the $+$ sign corresponds to the c state according to our definition. Thus,

$$(Jm|\nabla E_0|Jm) = (4J+2)^{-1} \\ \times [(2J-1)(KSJm|\nabla E_0|KSJm) \\ + (2J+3)(K+1SJm|\nabla E_0|K+1SJm) \\ + \{(2J-1)(2J+3)\}^{\frac{1}{2}}\{(KSJm|\nabla E_0|K+1SJm) \\ + (K+1SJm|\nabla E_0|KSJm)\}], \tag{16}$$

where

$$(KSJm|\nabla E_0|K'SJm) \\ = \{(K_+SJm|\nabla E_0|K'_+SJm) \\ \pm (K_+SJm|\nabla E_0|K'_-SJm)\}/2^{\frac{1}{2}},$$

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[8] G. Racah, Phys. Rev. **62**, 438 (1942).

and $K = J - \frac{1}{2}$, $S = \frac{1}{2}$. Using Racah's formula,[8] we have

$$(K\tfrac{1}{2}Jm|\nabla E_0|K'\tfrac{1}{2}JM) \\ = (-1)^{-K+m+\frac{1}{2}}(2J+1)(K\|\nabla E\|K') \\ \times W(KJK'J;\tfrac{1}{2}2)V(JJ2;-mm0), \tag{17}$$

where

$$W(KJKJ;\tfrac{1}{2}2) = (-1)^{-K-J-\frac{1}{2}} \\ \times \{A(A+1) - (4/3)J(J+1)I(I+1)\} \\ \times \{(2J+3)(2J+2)(2J+1)(2J)(2J-1) \\ \times (2K+3)(2K+2)(2K+1)(2K)(2K-1)\}^{-\frac{1}{2}}, \\ A = \tfrac{3}{4} - K(K+1) - J(J+1), \tag{18}$$

and

$$W(KJK+1J;\tfrac{1}{2}2) = (-1)^{-K-J-\frac{1}{2}} \\ \times \{(K+1)^2 - 1 + (J+\tfrac{3}{2})(J-\tfrac{1}{2})\}\{3(K+J+5/2) \\ \times (K-J+\tfrac{3}{2})(K+J+\tfrac{1}{2})(-K+J+\tfrac{1}{2})\}^{\frac{1}{2}} \\ \times \{2K(K+1)(K+2)(2K+1)(2K+3)J(J+1) \\ \times (2J-1)(2J+1)(2J+3)\}^{-\frac{1}{2}}. \tag{19}$$

It is shown by Ito et al.[9] that

$$(K_+\|\nabla E\|K_+) = \tfrac{1}{2}\{3\Lambda^2 - K(K+1)\}(2K+1)^{\frac{1}{2}} \\ \times \{K(K+1)(2K+1)(2K-1)\}^{-\frac{1}{2}}(\partial^2 V/\partial z^2), \tag{20}$$

and using the same procedure, that is, using the formula

$$\nabla E_0 = \tfrac{1}{2}(\partial^2 V/\partial Z^2) = \tfrac{1}{2}\{\Phi_z^2(\partial^2 V/\partial z^2) + \Phi_y^2(\partial^2 V/\partial y^2) \\ + \Phi_z^2(\partial^2 V/\partial z^2) + 2\Phi_x\Phi_y(\partial^2 V/\partial x\partial y) \\ + 2\Phi_y\Phi_z(\partial^2 V/\partial y\partial z) + 2\Phi_z\Phi_x(\partial^2 V/\partial z\partial x)\}, \tag{21}$$

where z is the molecular axis and Φ_x, Φ_y, and Φ_z are the direction cosines between the Z axis and the x, y, and z axes, respectively, and a table of the matrix elements of Φ,[10] we obtain

$$(K_+\|\nabla E\|K+1_+) = -\tfrac{3}{2}\Lambda\{(K+1)^2 - \Lambda^2\}^{\frac{1}{2}} \\ \times \{3K(K+1)(K+2)\}^{-\frac{1}{2}}(\partial^2 V/\partial z^2). \tag{22}$$

When $\Lambda = 1$, ∇E has a finite matrix element between the K_+ and K_-' state also. Using the formula of Ito et al.,[9] we obtain

$$(K_+\|\nabla E\|K_-) = -\tfrac{1}{2}\{K(K+1)(2K+1)\}^{\frac{1}{2}} \\ \times \{(2K+3)(2K-1)\}^{-\frac{1}{2}}(e_+|\partial^2 V/\partial x^2 - \partial^2 V/\partial y^2|e_-), \tag{23}$$

where e_+ and e_- are electronic states. The last factor can be expressed by using ξ which is defined in the formula (2a) as

$$(e_+|\partial^2 V/\partial x^2 - \partial^2 V/\partial y^2|e_-) = -\tfrac{1}{2}(2e\xi + \partial^2 V'/\partial z^2), \tag{24}$$

where $-e$ is the electronic charge and V' is the potential due only to the p electron which is rotating around the molecular axis, so that $\partial^2 V'/\partial z^2$ may be different from

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[9] Ito, Tanabe, and Mizushima, Phys. Rev. (to be published).
[10] See for example, Cross, Hainer, and King, J. Chem. Phys. **12**, 210 (1944).

the $\partial^2 V/\partial z^2$ which appeared in the formula (22). Thus,

$$(K_+\|\nabla E\|K_-) = \tfrac{1}{4}\{K(K+1)(2K+1)\}^{\frac{1}{2}}$$
$$\times\{(2K+3)(2K-1)\}^{-\frac{1}{2}}(2e\xi+\partial^2 V'/\partial z^2). \quad (25)$$

It is not difficult to show that

$$(K_+\|\nabla E\|K+1_-) = -(K+1_+\|\nabla E\|K_-). \quad (26)$$

From the formulas (17), (20), and (25) we find

$$(K\tfrac{1}{2}Jm|\nabla E_0|K\tfrac{1}{2}Jm) = (-1)^{m-3J}V(JJ2;-mm0)$$
$$\times[(\partial^2 V/\partial z^2)12^{-1}\{3\Lambda^2-K(K+1)\}X(K)(2J+1)^{\frac{1}{2}}$$
$$\times\{J(J+1)(2J-1)(2J+3)\}^{-\frac{1}{2}}\pm(2e\xi+\partial^2 V'/\partial z^2)96^{-1}$$
$$\times\{(2J+1)(2J+1)(2J+3)/J(J+1)\}^{\frac{1}{2}}], \quad (27)$$

and

$$(J-\tfrac{1}{2}\tfrac{1}{2}Jm|\nabla E_0|J+\tfrac{1}{2}\tfrac{1}{2}Jm) = (-1)^{m-3J+1}$$
$$\times V(JJ2;-mm0)(\partial^2 V/\partial z^2)3\Lambda\{(J+\tfrac{1}{2})^2-\Lambda^2\}^{\frac{1}{2}}$$
$$\times\{J(J+1)(2J-1)(2J+1)(2J+3)\}^{-\frac{1}{2}}, \quad (28)$$

where

$$X(K) = 2J-1, \quad\text{when}\quad K=J+\tfrac{1}{2},$$

and

$$X(K) = 2J+3, \quad\text{when}\quad K=J-\tfrac{1}{2},$$

and the double sign in the formula (24) means $+$ for the c state and $-$ for the d state.

Inserting the formulas (27), (28), and (16) into (15a) we obtain

$$(J\|\nabla E\|J) = (\partial^2 V/\partial z^2)\{2(2J+1)\}^{-1}$$
$$\times\{J(J+1)(2J+1)\}^{-\frac{1}{2}}$$
$$\times[6^{-1}\{(2J+3)(2J-1)\}^{\frac{1}{2}}\{3\Lambda^2-(J+\tfrac{1}{2})^2\}$$
$$-6\Lambda\{(J+\tfrac{1}{2})^2-\Lambda^2\}^{\frac{1}{2}}]\pm 96^{-1}(2e\xi+\partial^2 V'/\partial z^2)$$
$$\times\{(2J-1)(2J+1)(2J+3)\}^{\frac{1}{2}}\{J(J+1)\}^{-\frac{1}{2}}. \quad (29)$$

Thus from the formula (15) we finally obtain the formula of the nuclear electric quadrupole moment in Hund's case (a) as

$$W_c' = eQY(F)\{A(J)(\partial^2 V/\partial z^2)$$
$$+B(J)(2e\xi+\partial^2 V'/\partial z^2)\}, \quad (30a)$$

$$W_d' = eQY(F)\{A(J)(\partial^2 V/\partial z^2)$$
$$-B(J)(2e\xi+\partial^2 V'/\partial z^2)\}, \quad (30b)$$

where

$$Y(F) = \{\tfrac{3}{4}C(C+1)-J(J+1)I(I+1)\}$$
$$\times\{2(2J-1)(2J+3)I(2I-1)\}^{-1}, \quad (30c)$$

$$A(JF) = (2J+3)(2J-1)\{6J(J+1)\}^{-1}$$
$$\times[\{3\Lambda^2(2J+1)^{-2}-\tfrac{1}{4}\}-36\Lambda\{\tfrac{1}{4}-\Lambda^2(2J+1)^{-2}\}^{\frac{1}{2}}$$
$$\times(2J+1)^{-1}\{(2J+3)(2J-1)\}^{-\frac{1}{2}}], \quad (30d)$$

and

$$B(J) = 48^{-1}(2J-1)(2J+3)/J(J+1). \quad (30e)$$

5. EFFECT OF $\Pi_{3/2}$ STATE

The $\Pi_{\frac{3}{2}}$ state, in which $\Lambda=1$, $\Sigma=+\tfrac{1}{2}$, is the first electronic excited state of this molecule. Since the excitation energy is only 121 cm^{-1}, the effect from this state on

the ground state may be appreciable. The effect comes in two ways: (1) because of the end-over-end rotation, Hund's case (a) is not exactly realized and the actual wave function will be a mixture of the $\Pi_{\frac{3}{2}}$ and $\Pi_{\frac{1}{2}}$ wave functions. This will change the coupling constant of the formulas (11) slightly. (2) Nondiagonal matrix elements of the magnetic interaction between the ground state and this excited state will give the so-called pseudo-quadrupole term[5] which might change slightly the value of $A(J)$ in the formulas (30).

Due to the rotational distortion, the real wave function $(JIF|$ will be

$$(JIF| = \mu(\Pi_{\frac{1}{2}}JIF|+\nu(\Pi_{\frac{3}{2}}JIF|, \quad (31)$$

where μ and ν may be functions of J. If Hund's case (a) is a good approximation, $|\mu|\gg|\nu|$ in the ground state of the NO molecule. $(\Pi_{\frac{1}{2}}JIF|$ and $(\Pi_{\frac{3}{2}}JIF|$ are the wave functions of the pure $\Pi_{\frac{1}{2}}$ and $\Pi_{\frac{3}{2}}$ states, respectively. It is easily seen that

$$(\Pi_{\frac{1}{2}}|H_1|\Pi_{\frac{3}{2}}) = g_n\beta_n\beta(\Pi_{\frac{1}{2}}|\eta\zeta S_-I_+/2-3\eta S_-L_-L_+I_+/4|\Pi_{\frac{3}{2}}). \quad (32)$$

Integrating over the electronic coordinate, S_- will be 1, while $S_-L_-L_+$ will be 2; thus we obtain

$$\tfrac{1}{2}g_n\beta_n\beta\eta(\zeta-3)(JJ_z=\tfrac{1}{2}IF|I_+|JJ_z=\tfrac{3}{2}IF). \quad (33)$$

Since

$$(JJ_z=\tfrac{1}{2}m|\mathbf{x}-i\mathbf{y}|JJ_z=\tfrac{3}{2}m)$$
$$= m\{(J-\tfrac{1}{2})(J+\tfrac{3}{2})\}^{\frac{1}{2}}\{J(J+1)\}^{-1}, \quad (34)$$

we obtain

$$(JJ_z=\tfrac{1}{2}IF|I_+|JJ_z=\tfrac{3}{2}IF)$$
$$= \{(2J-1)(2J+3)\}^{\frac{1}{2}}\{4J(J+1)\}^{-1}$$
$$\times\{F(F+1)-J(J+1)-I(I+1)\}. \quad (35)$$

Thus, when $|\nu|\ll|\mu|$, the correction due to this mixing of states will be

$$\Delta W_{c,d} = \nu g_n\beta_n\beta\eta(\zeta-3)\{(2J-1)(2J+3)\}^{\frac{1}{2}}$$
$$\times\{4J(J+1)\}^{-1}\{F(F+1)-J(J+1)-I(I+1)\}, \quad (36)$$

which is common to the Λ-doublet states.

The second-order perturbation due to the excited $\Pi_{\frac{3}{2}}$ state is

$$-(\Pi_{\frac{1}{2}}|H_1|\Pi_{\frac{3}{2}})^2/\Delta E = -(g_n\beta_n\beta)^2$$
$$\times(\Pi_{\frac{1}{2}}|-\tfrac{1}{2}\xi L_+I_-|\Pi_{\frac{3}{2}})^2/\Delta E$$
$$= -(g_n\beta_n\beta)^2\xi^2(I_x^2+I_y^2)/\Delta E, \quad (37)$$

where ΔE is the energy difference of the $\Pi_{\frac{1}{2}}$ state and the $\Pi_{\frac{3}{2}}$ state. From the Van Vleck formula[5] we can easily see that it gives rise to the so-called pseudo-quadrupole term,

$$\Delta W_{c,d}' = (g_n\beta_n\beta\xi)^2(\Delta E)^{-1}\{3(\Lambda+\Sigma)^2/J(J+1)-1\}$$
$$\times\{3C(C+1)-4J(J+1)I(I+1)\}$$
$$\times\{(2J-1)(2J+3)\}^{-1}, \quad (38)$$

which is also common to the Λ-doublet states.

6. COMPARISON WITH EXPERIMENTAL RESULTS

Gordy and Burrus[2] observed the absorption of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition. In the $J=\frac{1}{2}$ state all quadrupole-type effects vanish, since $3C(C+1)-4J(J+1)I(I+1)$ is zero for all F. Also there is no effect from the $\Pi_{\frac{3}{2}}$ state since this state cannot have $J=\frac{1}{2}$. Thus the energy levels will be simply given by W_c and W_d of the formulas (11). In the $J=\frac{3}{2}$ state, on the other hand, all of these effects appear and the energy level will be given by $W_c+\Delta W_c+W_c'+\Delta W_c'$ or $W_d+\Delta W_d+W_d'+\Delta W_d'$ from the formulas (11), (36), (30), and (38). The energy can be expressed as

$$W=P\{F(F+1)-J(J+1)-I(I+1)\}$$
$$+R\{\tfrac{3}{4}C(C+1)-J(J+1)I(I+1)\}, \quad (39)$$

where P and R are constants. From the experimental data one can find a set of values for these constants as shown in Table I. The calculated frequencies by using these values are compared with the experimental results in Table II. The agreement is quite satisfactory.

Using the values of P from the $J=\frac{1}{2}$ states, one obtains, from the formulas (11),

$$a=23.14 \text{ Mc/sec} \quad \text{and} \quad b=14.065 \text{ Mc/sec}. \quad (40)$$

These values are both positive, as was expected, and give the ratio $b/a=0.608$ which is not far from the value 0.5 predicted in the formula (13); this indicates that the p-electron approximation is reasonably good.

The formulas (11), with the values of a and b shown above, give the values of P for the $J=\frac{3}{2}$ states to be -8.82 Mc/sec and 21.17 Mc/sec for the c and d states, respectively. Both of these are 0.23 Mc/sec smaller than the observed values shown in Table I. Since the correction ΔW given by the formula (36) is common to the doublet states, this $+0.23$ Mc/sec may be attributed to ΔW. In the appendix of this paper ν is shown to be -0.0247 at $J=\frac{3}{2}$. If we adopt the p-electron approximation, $\eta(\zeta-3)$ would be $-2\xi/5$. Since $a=g_n\beta_n\beta(3\xi/10)$ under the same approximation, the coefficient $\nu g_n\beta_n\beta\eta(\zeta-3)$ may be not far in value from $-4a\nu/3$. If we use the value of a given in (40), the corresponding correction to the value of P will amount to $+0.18$ Mc/sec. This is a little too small but not far from the value $+0.23$ Mc/sec required above. The deviation may be attributed to the incorrectness of the p-electron approximation.

Using the value of a shown in (40) and $\Delta E=121$ cm^{-1}, we can estimate the contribution of the pseudoquadrupole effect by the formula (38). Under the p-electron approximation, this contribution to the constant R at $J=\frac{3}{2}$ states is $-(a^2/\Delta E)(20/27)$, which is -1.1×10^{-4} Mc/sec. Since this value is very small compared to the observed values shown in Table I, we may neglect this contribution and assume that the observed values of R are entirely due to the nuclear quadrupole effect.

From the formulas (30), we obtain

$$W_c'+W_d'=2eQ(\partial^2 V/\partial z^2)Y(F)A(J). \quad (41)$$

Table I. Values of coupling constants P and R (Mc/sec).

	$J=1/2$ c	d	$J=3/2$ c	d
P	-6.66	68.37	-8.59	21.40
R	0	0	0.077	0.035

Comparing this formula with the observed value of R_c+R_d, we obtain

$$eQ(\partial^2 V/\partial z^2)=-2.12 \text{ Mc/sec.} \quad (42)$$

In the same way, from the difference R_c-R_d we obtain

$$eQ(2e\xi+\partial^2 V'/\partial z^2)=7.6 \text{ Mc/sec.} \quad (34)$$

If we estimate ξ from a by the p-electron approximation, and assume $Q=0.02\times10^{-24}$ cm^2 according to Townes and Dailey,[11] $2e^2Q\xi$ will be 38 Mc/sec, while the second term $eQ(\partial^2 V'/\partial z^2)$ must be $-\frac{1}{2}$ of the pure p-electron value of the coupling constant which is given by Townes and Dailey[11] as $+24$ Mc/sec or $+10$ Mc/sec. Thus the theoretical value of the coupling constant which is to be compared with the value given in (43) is 26 Mc/sec or 33 Mc/sec. Since they are too large, a smaller value for Q may be preferred.[12] Actually if $Q=0.01\times10^{-24}$ cm^2 the theoretical value for the coupling constant (34) is 7 Mc/sec or 14 Mc/sec.

On the whole we see that the assumption that the electron which is rotating around the molecular axis is in a pure p state works very well.

7. PREDICTION OF THE HFS OF THE NO MOLECULE IN THE $\Pi_{3/2}$ STATE

Since the magnetic interaction H_1 can connect states with $\Delta J_z=0$ or 1 only, the b term in the magnetic hfs formulas (11) vanishes in the $\Pi_{\frac{3}{2}}$ state. The other coupling constant a will be $g_n\beta_n\beta(2\xi+\eta\zeta-3\eta)\frac{3}{8}$, which, under the p-electron approximation, is $g_n\beta_n\beta(21\xi/40)$ or about 40 Mc/sec.

Table II. Comparison between theoretical and experimental frequencies.

$J=1/2\rightarrow3/2$	F	Frequencies (Mc/sec) Observed	Calculated[a]
c band	$3/2\rightarrow5/2$	150 176.54	150 176.52
	$1/2\rightarrow3/2$	150 198.85	150 198.91
	$3/2\rightarrow3/2$	150 218.89	150 218.89
	$1/2\rightarrow1/2$	150 225.75	150 225.70
	$3/2\rightarrow1/2$	150 245.69	150 245.68
d band	$3/2\rightarrow1/2$	150 375.48	150 375.52
	$3/2\rightarrow3/2$	150 439.22	150 439.26
	$3/2\rightarrow5/2$	150 546.50	150 546.51
	$1/2\rightarrow1/2$	150 580.70	150 580.63
	$1/2\rightarrow3/2$	150 644.37	150 644.36

[a] The frequency without hfs was taken to be 150 195.51 Mc/sec and 150 550.63 Mc/sec for the c and d bands, respectively.

[11] C. H. Townes and B. P. Dailey, J. Chem. Phys. 17, 782 (1949).
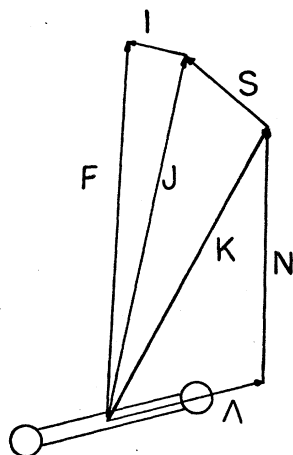[12] J. Sheridan and W. Gordy, Phys. Rev. 79, 513 (1950).

Fig. 2. Hund's case (b).

Referring to the electric hfs, we see that the $B(J)[2e\xi-(\partial^2V'/\partial z^2)]$ term will not change, so that the same difference between the Λ-doublet states will appear. Another term should be calculated using the wave equation formula (A7) of the appendix, instead of (A6). The calculation can be done as before, and the result is

$$W_c'(\Pi_{\frac{3}{2}}) = eQY(F)\{A'(J)(\partial^2V/\partial z^2)$$
$$+B(J)(2e\xi+\partial^2V'/\partial z^2)\}, \quad (44a)$$

$$W_d'(\Pi_{\frac{3}{2}}) = eQY(F)\{A'(J)(\partial^2V/\partial z^2)$$
$$-B(J)(2e\xi+\partial^2V'/\partial z^2)\}, \quad (44b)$$

where

$$A'(J)=[\{3\Lambda^2(4J^2+4J+5)/(2J+1)^2$$
$$-(2J-1)(2J+3)/4\}+36\Lambda\{\tfrac{1}{4}-\Lambda^2/(2J+1)^2\}^{\frac{1}{2}}$$
$$\times\{(2J+3)(2J-1)\}^{\frac{1}{2}}/(2J+1)]/\{6J(J+1)\},$$

and the coupling constants must be about the same as in the $\Pi_{\frac{1}{2}}$ state.

8. ELECTRIC HFS FORMULA FOR GENERAL COUPLING CASE

Our formulas (30) and (44) are applied for Hund's case (a). It is quite easy to extend our method to obtain

$$\begin{vmatrix} D/(2J+1)+B\{(2J-1)(2J+1)-4\Lambda^2\}/4-E & -D\{(2J+3)(2J-1)\}^{\frac{1}{2}}/(4J+2) \\ -D\{(2J+3)(2J-1)\}^{\frac{1}{2}}/(4J+2) & -D/(2J+1)+B\{(2J+1)(2J+3)-4\Lambda^2\}/4-E \end{vmatrix} = 0. \quad (A4)$$

If we neglect B, the solutions are

$$E=D/2 \text{ and } -D/2, \quad (A5)$$

where $E=D/2$ gives the $\Pi_{\frac{3}{2}}$ state, while $E=-D/2$ gives the $\Pi_{\frac{1}{2}}$ state, and they give the wave functions in Hund's case (a),

$$(\Pi_{\frac{3}{2}}J|=\{2(2J+1)\}^{-\frac{1}{2}}\{(2J-1)^{\frac{1}{2}}(KSJ|$$
$$+(2J+3)^{\frac{1}{2}}(K+1SJ|\}, \quad (A6)$$

$$(\Pi_{\frac{1}{2}}J|=\{2(2J+1)\}^{-\frac{1}{2}}\{(2J+3)^{\frac{1}{2}}(KSJ|$$
$$-(2J-1)^{\frac{1}{2}}(K+1SJ|\}. \quad (A7)$$

If we neglect D, on the other hand, we obtain Hund's

the formula for the general coupling case. If the wave function is

$$(J|=a(KSJ|+b(K+1SJ|, \quad (45)$$

where $K=J-\frac{1}{2}$ and $S=\frac{1}{2}$, the corresponding formulas are

$$W_c(\text{general case})= eQY(F)\{A''(J)(\partial^2V/\partial z^2)$$
$$+B(J)(2e\xi+\partial^2V'/\partial z^2)\}, \quad (46a)$$

$$W_d(\text{general case})= eQY(F)\{A''(J)(\partial^2V/\partial z^2)$$
$$-B(J)(2e\xi+\partial^2V'/\partial z^2)\}, \quad (46b)$$

where

$$A''(J)=[\{3\Lambda^2-(J+\tfrac{1}{2})(J+\tfrac{3}{2})\}(2J-1)(2J+1)b^2$$
$$+\{3\Lambda^2-(J-\tfrac{1}{2})(J+\tfrac{1}{2})\}(2J+3)(2J+1)a^2$$
$$-72\Lambda\{\tfrac{1}{4}-\Lambda^2/(2J+1)^2\}ab]/\{6J(J+1)\},$$

and $B(J)$ and $Y(F)$ are given by the formulas (30e) and (30c), respectively. It must be remembered that the $B(J)$ term disappears when $\Lambda\neq 1$.

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APPENDIX

The Hamiltonian of the rotating molecule with electronic spin and orbital angular momentum is

$$H=D\mathbf{S}\cdot\mathbf{\Lambda}+B(\mathbf{K}-\mathbf{\Lambda})^2, \quad (A1)$$

where D and B are constants and $\mathbf{S}$ and $\mathbf{\Lambda}$ are the electronic spin and orbital angular momenta ($\mathbf{\Lambda}$ is parallel to the molecular axis), while $\mathbf{K}=\mathbf{\Lambda}+\mathbf{N}$, where N is the end-over-end rotational angular momentum. Since $\mathbf{N}\cdot\mathbf{\Lambda}=0$,

$$(KSJ|(\mathbf{K}-\mathbf{\Lambda})^2|K'SJ)=\{K(K+1)-\Lambda^2\}\delta_{K,K'}, \quad (A2)$$

and the matrix element of $\mathbf{S}\cdot\mathbf{\Lambda}$ can be obtained by the usual procedure.[8] Thus if we have a wave function

$$(J|=a(KSJ|+b(K+1SJ|, \quad (A3)$$

where $K=J-\frac{1}{2}$ and $S=\frac{1}{2}$, the corresponding secular equation is

case (b) [see Fig. 2]. In that case $(KSL|$ itself is the wave function.

In the case of the NO molecule, it is known[13] that $D=123.8$ cm^{-1}, and $B=1.720$ cm^{-1}. If we use these values and solve the secular equation (A4) for the $J=\frac{3}{2}$ state, we obtain the wave function for the lower energy state:

$$0.5213(1\ \tfrac{1}{2}\ \tfrac{3}{2}|-0.8534(2\ \tfrac{1}{2}\ \tfrac{3}{2}|$$
$$=0.9998(\Pi_{\frac{1}{2}}\ \tfrac{3}{2}|-0.0247(\Pi_{\frac{3}{2}}\ \tfrac{3}{2}|\ ; \quad (A8)$$

Margenau and Henry[13] gave the corresponding energy.

[13] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).