

Hyperfine Structure of Zeeman Levels in Nitric Oxide

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This paper contains a calculation of the energy arising from the magnetic interaction of the extranuclear electrons with the magnetic moment of the nitrogen nucleus in $N^{14}O^{16}$. An operator is derived for the interaction, which is more fundamental than the one, proportional to $\mathbf{I} \cdot \mathbf{J}$, which is commonly used. This operator is employed, together with previously calculated state functions, to compute the hyperfine structure of the ${}^2\Pi_3$ state of $N^{14}O^{16}$. The formula which results from this procedure accounts for the experimental data, which cannot be explained completely if the interaction operator is taken to be proportional to $\mathbf{I} \cdot \mathbf{J}$.

I. INTRODUCTION

IN a paper by Margenau and Henry¹ the magnetic fine structure and hyperfine structure of the ${}^2\Pi_3$ state of $N^{14}O^{16}$ were investigated. NO in this state corresponds closely to Hund's case (a), in which both the orbital and spin angular momenta of the electrons are quantized along the internuclear axis, the quantum numbers associated with these projections being Λ and Σ . For the ${}^2\Pi_3$ state $\Lambda=1$ and $\Sigma=\frac{1}{2}$. The quantum number J has the value $\frac{3}{2}$. In an external magnetic field, \mathbf{H} , the energy level in question is separated into four sublevels in accordance with the four possible values of M_J . The N^{14} nucleus has a spin \mathbf{I} of value 1; hence each magnetic sublevel is divided into $2I+1=3$ hyperfine levels.

The interaction between the nuclear magnetic moment and the magnetic fields caused by the extranuclear electrons is the main cause of this hyperfine structure. Commonly, this interaction is taken to be being proportional to $\mathbf{I} \cdot \mathbf{J}$, where \mathbf{I} is the operator representing nuclear spin and \mathbf{J} is the operator representing the total angular momentum of the electrons; this assumption was made in (MH). However, careful examination of the experimental data shows that the form $A\mathbf{I} \cdot \mathbf{J}$ (A being a proportionality constant) leads to an expression for the energy which is not wholly consistent with the measurements of Beringer and Castle.² Data which they estimate to be accurate to within 1 percent lead to values of the proportionality constant, A , which differ from one another by as much as 7 percent. In this paper we attempt to overcome the difficulty by returning to a more fundamental view of the interaction.

II. THE INTERACTION OPERATOR

It is convenient to describe the $N^{14}O^{16}$ molecule in terms of the coordinate systems pictured in Fig. 1. In this figure there are three Cartesian axis systems. XYZ is fixed in space with its center at C , the center of mass of the $N^{14}O^{16}$ nuclei; $X'Y'Z'$ is a system imbedded in the molecule; $X''Y''Z''$ is a system parallel to XYZ with origin at N , the N^{14} nucleus. θ and ψ are Euler-angles specifying the orientation of $X'Y'Z'$ relative to XYZ ;

these angles are such that the coordinates of a point, xyz , in XYZ are related to the coordinates $x'y'z'$, of that same point in $X'Y'Z'$ by the equations

$$\begin{aligned} x &= x' \cos\psi - y' \cos\theta \sin\psi + z' \sin\theta \sin\psi, \\ y &= x' \sin\psi + y' \cos\theta \cos\psi - z' \sin\theta \cos\psi, \\ z &= y' \sin\theta + z' \cos\theta. \end{aligned} \quad (1)$$

The X' axis lies in the XY plane. In Fig. (1) the line $[NO]=\rho$ represents the internuclear distance. We let $[NP]=r$, $[CP]=r'$, $[PD]=\rho'$, and $[NC]=\xi \equiv \rho M_0 / (M_N + M_0)$; M_0 and M_N are masses of O^{16} and N^{14} nuclei. In the top view $[C''N]$, the projection of $[CN]$ on the $X''Y''$ plane, equals $\xi \sin\theta$. The following relations appear from an examination of the figure.

$$\begin{aligned} x'' &= x + \xi \sin\theta \sin\psi, \\ y'' &= y - \xi \sin\theta \cos\psi, \\ z'' &= z + \xi \cos\theta, \\ z' &= r \cos\chi - \xi = r' \cos\theta', \\ \rho' &= r \sin\chi = r' \sin\theta', \\ r'^2 &= r^2 + \xi^2 - 2r\xi \cos\chi, \\ r^2 &= r'^2 + \xi^2 + 2r'\xi \cos\theta'. \end{aligned} \quad (2)$$

In atomic spectra [see Hargraves,³ Fermi,⁴ Breit and Doermann⁵] the magnetic interaction of an electron in a P state with the nucleus can be described in terms of the operator

$$\mathcal{H}_I = -\frac{eh}{2mcL} \left[\frac{\mathbf{u}_I \cdot \mathbf{L}}{r^3} + \frac{3(\mathbf{S} \cdot \mathbf{r})(\mathbf{u}_I \cdot \mathbf{r})}{r^5} - \frac{\mathbf{u}_I \cdot \mathbf{S}}{r^3} \right], \quad (3)$$

\mathbf{r} =position of the electron relative to the nucleus, \mathbf{u}_I =magnetic moment of the nucleus, \mathbf{S} =spin of the electron, \mathbf{L} =orbital angular momentum of the electron. This comes directly from the non-relativistic approximation for the energy of interaction between a moving electron and a field arising from a vector potential \mathbf{A} , \mathbf{A} in turn being caused by the magnetic moment of the nucleus. The inner shells of electrons are assumed to have no net effect on this magnetic interaction. The non-relativistic approximation is suitable here, although it is not legitimate for S states.

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¹ H. Margenau and A. F. Henry, Phys. Rev. **78**, 587 (1950); henceforth this paper will be referred to as (MH).

² R. Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950).

³ J. Hargraves, Proc. Roy. Soc. **A124**, 568 (1929); **A127**, 141, 407 (1930).

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

⁵ G. Breit and F. W. Doermann, Phys. Rev. **36**, 1262, 1732 (1930).

We assume that (3) can be applied to $N^{14}O^{16}$ without any fundamental change. This is equivalent to regarding the magnetic interaction as taking place between the N^{14} nucleus and an electron outside a cylindrically symmetric cloud of inner electrons. The effect of the inner cloud of electrons is then assumed to be independent of M_J and M_I , the quantum number representing the component of \mathbf{I} in a direction fixed in space.

In applying (3) to NO , the components, $L_{x'}$ and $L_{y'}$, of the operator \mathbf{L} in the X' and Y' directions (perpendicular to the internuclear axis) are ignored. The matrix elements of these components connect neighboring electronic states; as in (MH) we neglect the effect of such states, since the perturbation arising from them is very small. The third component of \mathbf{L} is $L_{z'}$ or Λ whose quantum number is 1 for the ${}^2\Pi_{3/2}$ state. We then obtain

$$\mathcal{H}_I = 4\mu_0\mu_I \left\{ \frac{\mathbf{I} \cdot \mathbf{A}}{r^3} + \frac{3}{r^5} [S_x I_x x''^2 + (S_x I_y + S_y I_x) x'' y'' + (S_x I_z + S_z I_x) x'' z'' + S_y I_y y''^2 + (S_y I_z + S_z I_y) y'' z'' + S_z I_z z''^2] - \frac{S_x I_x + S_y I_y + S_z I_z}{r^3} \right\}. \quad (4)$$

r is the position of the ${}^2\Pi$ electron relative to the N^{14} nucleus (the line $[PN]$ in Fig. (1)); we have written out $\mathbf{S} \cdot \mathbf{r} = S_x x'' + S_y y'' + S_z z''$ and $\mathbf{I} \cdot \mathbf{r} = I_x x'' + I_y y'' + I_z z''$ and have used the abbreviations: $\mu_0 \equiv -e\hbar/2mc$ and $\mu_I = 2\mu_N \mathbf{I} = 2g_I \mu_0 \mathbf{I}/1840$, g_I being the number of nuclear magnetons for one unit (\hbar) of nuclear spin in N^{14} .

III. THE STATE FUNCTION FOR THE ${}^2\Pi_{3/2}$ LEVEL

In (MH), a state function for the ${}^2\Pi_{3/2}$ level in the absence of nuclear spin was computed. This expression is a linear combination of four eigenfunctions $\psi(K, J)$ corresponding to Hund's case (b) and having different values of the rotational quantum number, K , and the total angular momentum quantum number, J . Explicitly, it has the form

$$\Psi = a\psi(1, \frac{3}{2}) + b\psi(2, \frac{3}{2}) + c\psi(2, \frac{5}{2}) + d\psi(3, \frac{5}{2}). \quad (5)$$

The coefficients in the linear expansion are given by

$$\begin{aligned} a &\equiv -S_{ab}(1+S_{ab}^2)^{-\frac{1}{2}}(1+S_{12}^2)^{-\frac{1}{2}}, \\ b &\equiv -S_{ab}(1+S_{ab}^2)^{-\frac{1}{2}}(1+S_{12}^2)^{-\frac{1}{2}}S_{12}, \\ c &\equiv (1+S_{ab}^2)^{-\frac{1}{2}}(1+S_{34}^2)^{-\frac{1}{2}}, \\ d &\equiv (1+S_{ab}^2)^{-\frac{1}{2}}(1+S_{34}^2)^{-\frac{1}{2}}S_{34}, \end{aligned} \quad (6)$$

the quantities S being defined in (MH). The case (b) eigenfunctions, $\psi(K, J)$, are also eigenfunctions of the operators \mathbf{A} , \mathbf{S} , and \mathbf{M}_J . Dependence on vibrational and electronic quantum numbers (other than Λ) will be ignored. It follows as a result of the cylindrical symmetry of the potential energy in the Hamiltonian of the molecule that $\psi(K, J)$ depends on Λ through the factor $\exp(i\Lambda\phi')$, ϕ' being the azimuthal angle of the set of cylindrical coordinates, r', z', ϕ' , in Fig. 1.

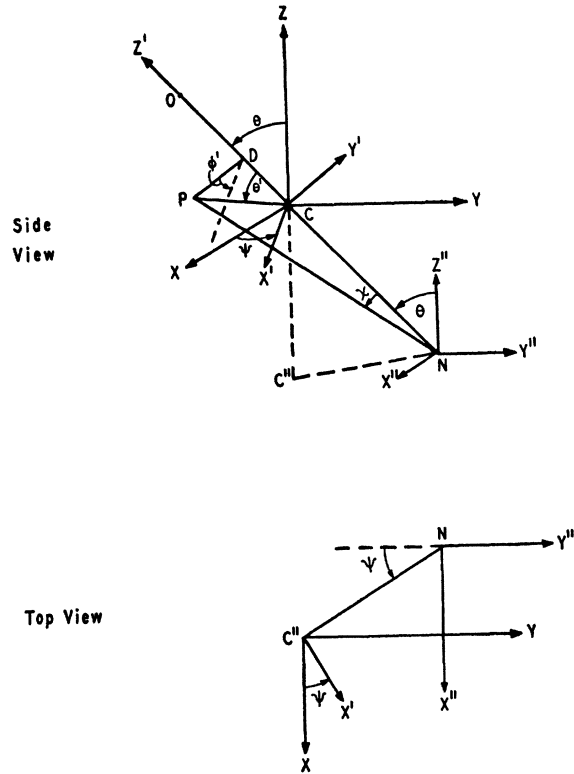


FIG. 1. Axis systems convenient for describing nuclear magnetic interaction in $N^{14}O^{16}$.

To account for the presence of nuclear spin in $N^{14}O^{16}$, we use as state function for the ${}^2\Pi_{3/2}$ levels a product function, $\Psi\Phi(IM_I) \equiv \Psi(M_J, M_I)$, in which $\Phi(IM_I)$ represents an eigenfunction for the nuclear spin, \mathbf{I} , and its component, M_I , in the direction of the external field; Ψ is given by (5). We use the notation $|JKSIM_J M_I\rangle$ for the individual products $\psi(KJ)\Phi(IM_I)$ in the sum $\Psi\Phi(IM_I)$. The different values of M_J and M_I determine the nine sublevels within the ${}^2\Pi_{3/2}$ state.

IV. THE CALCULATION

The magnetic interaction of the nucleus with the electrons is computed by treating the operator (4) as a perturbation on the state functions, $\Psi(M_J M_I)$. The procedure is greatly simplified by the fact that the dependence of the $\psi(K, J)$ on the quantum number, Λ , has the form, $\exp(i\Lambda\phi')$. Since we neglect the small perturbation of neighboring electronic states, all eigenfunctions employed in the calculation are associated with the same value of Λ . Thus, when matrix elements of \mathcal{H}_I are computed, the integration over ϕ' is a simple average. we can perform that average at the start and the resulting operator will still be perfectly general. The advantage of this procedure is that it separates the dependence of \mathcal{H}_I on the rotational coordinates from its dependence on the electronic coordinates. The last of relations (2) shows that the scalar, r is a function of the electronic and vibrational coordinates only. The vector,

\mathbf{r} , depends also on the rotational coordinates, θ and ψ . Thus we need only consider $(\mathbf{S}\cdot\mathbf{r})(\mathbf{I}\cdot\mathbf{r})$ and $\mathbf{I}\cdot\mathbf{S}$ in averaging over ϕ' .

When (1) is substituted in the first three of relations (2) and use is made of the equations: $x' = \rho' \cos\phi' = r \sin\chi \cos\phi'$; $y' = \rho' \sin\phi' = r \sin\chi \sin\phi'$; $z' + \xi = r \cos\chi$, we find

$$\begin{aligned} x'' &= r(\sin\chi \cos\psi \cos\phi' - \sin\chi \cos\theta \sin\psi \sin\phi' \\ &\quad + \cos\chi \sin\theta \sin\psi), \\ y'' &= r(\sin\chi \sin\psi \cos\phi' + \sin\chi \cos\theta \cos\psi \sin\phi' \\ &\quad - \cos\chi \sin\theta \cos\psi), \end{aligned} \quad (7)$$

$$z'' = r(\sin\chi \sin\theta \sin\phi' + \cos\chi \cos\theta).$$

On introducing this result in Eq. (4), averaging over ϕ' , and adopting the notation, $S^\pm \equiv S_z \pm iS_y$; $I^\pm \equiv I_x \pm iI_y$, we obtain

$$\begin{aligned} \langle \mathcal{H}_I \rangle_{\phi'} &= \frac{4\mu_0\mu_I}{r^3} \left\{ \mathbf{I}\cdot\mathbf{A} + \left(\frac{3 \cos^2\chi - 1}{2} \right) [S_z I_z (3 \cos^2\theta - 1) \right. \\ &\quad + \frac{3}{2} I_z \sin\theta \cos\theta (iS^+ e^{-i\psi} - iS^- e^{+i\psi}) \\ &\quad + \frac{3}{2} S_z \sin\theta \cos\theta (iI^+ e^{-i\psi} - iI^- e^{+i\psi}) \\ &\quad - \frac{3}{4} \sin^2\theta (S^+ I^+ e^{-2i\psi} + S^- I^- e^{+2i\psi}) \\ &\quad \left. - \frac{1}{4} (3 \cos^2\theta - 1) (S^+ I^- + S^- I^+) \right\}. \end{aligned} \quad (8)$$

The last two of relations (2) show that r and χ are functions of electronic and vibrational coordinates (r' , θ' and $\rho = \xi(M_N + M_O)/M_O$). Because of this, we may write for the operator representing the effect of the nuclear interaction on rotational states as follows:

$$\begin{aligned} \langle \mathcal{H}_I \rangle_{\phi', \text{elec, vib}} &= A' \mathbf{I}\cdot\mathbf{A} + B' [S_z I_z (3 \cos^2\theta - 1) \\ &\quad + \frac{3}{2} I_z \sin\theta \cos\theta (iS^+ e^{-i\psi} - iS^- e^{+i\psi}) \\ &\quad + \frac{3}{2} S_z \sin\theta \cos\theta (iI^+ e^{-i\psi} - iI^- e^{+i\psi}) \\ &\quad - \frac{3}{4} \sin^2\theta (S^+ I^+ e^{-2i\psi} + S^- I^- e^{+2i\psi}) \\ &\quad - \frac{1}{4} (3 \cos^2\theta - 1) (S^+ I^- + S^- I^+)], \end{aligned} \quad (9)$$

where

$$\begin{aligned} A' &\equiv \langle 4\mu_0\mu_I/r^3 \rangle_{\text{elec, vib}}; \\ B' &\equiv \langle 2\mu_0\mu_I(3 \cos^2\chi - 1)/r^3 \rangle_{\text{elec, vib}}. \end{aligned}$$

We are now in a position to compute the nuclear magnetic interaction energy. Its principal part is the diagonal matrix element,

$$\int \Psi(M_J M_I) \mathcal{H}_I \Psi(M_J M_I) d\tau.$$

There is also a contribution from states differing in M_J by ± 1 and M_I by ∓ 1 . In computing this, we have used only the term $A' \mathbf{I}\cdot\mathbf{A}$ assuming that B' is much less than A' ; analysis of the experimental data under this assumption leads to a ratio of B' to A' of approximately 0.1.

The matrix elements needed for the calculation can be obtained from the article of Rademacher and Reiche⁶

⁶ H. Rademacher and F. Reiche, *Zeits. f. Physik* **41**, 453 (1927).

together with the angular momentum addition laws. These are employed along with the relations

$$\begin{aligned} \mathbf{I}\cdot\mathbf{A} &= \frac{1}{2}(I^+ \Lambda^- + I^- \Lambda^+) + I_z \Lambda_z, \\ I_z |JKSIM_J M_I\rangle &= M_I |JKSIM_J M_I\rangle, \\ I^\pm |JKSIM_J M_I\rangle &= [(I \pm M_I + 1)(I \mp M_I)]^{\frac{1}{2}} |JKSIM_J, M_I \pm 1\rangle, \\ \Lambda_x - i\Lambda_y &\equiv \Lambda^- = e^{-i\psi} \sin\theta (\partial/\partial\phi'). \end{aligned} \quad (10)$$

The elements $(J_1 K_1 SIM_J M_I | I_z \Lambda_z | J_2 K_2 SIM_J M_I)$ can be obtained from formulas given by Hill.⁷ For the elements of the term involving B' we obtain

$$\begin{aligned} &(JKSIM_J M_I | S_m'' | JKSIM_J M_I) \\ &= \frac{M_J M_I}{2K+1} \left[\frac{3\Lambda^2}{K(K+1)} - 1 \right] \frac{2(J-K)(4K-2J+1)}{4J-2K+1} \\ &(JKSIM_J M_I | S_m'' | J, K+1, SIM_J M_I) \\ &= \frac{-6\Lambda M_I M_J}{(K+1)(2K+1)(2K+3)} [(K+1)^2 - \Lambda^2]^{\frac{1}{2}} \\ &(JKSIM_J M_I | S_m'' | J+1, K, SIM_J M_I) \\ &= \frac{M_I}{2(2K+1)} \left[\frac{3\Lambda^2}{K(K+1)} - 1 \right] [(J+1)^2 - M_J^2]^{\frac{1}{2}} \\ &(JKSIM_J M_I | S_m'' | J+1, K+1, SIM_J M_I) \\ &= \frac{3\Lambda M_I (J-K)}{2(K+1)(J+1)(2J-K+1)} \\ &\quad \times \{ [(J+1)^2 - M_J^2] [(K+1)^2 - \Lambda^2] \}^{\frac{1}{2}} \end{aligned} \quad (11)$$

$$\begin{aligned} S_m'' &\equiv B' [S_z I_z (3 \cos^2\theta - 1) \\ &\quad + \frac{3}{2} I_z \sin\theta \cos\theta (iS^+ e^{-i\psi} - iS^- e^{+i\psi})]. \end{aligned}$$

These relations are valid only for the case $S = \frac{1}{2}$.

The principal part of the interaction energy is computed by use of (5), (6), and (11).

The correction for the terms off-diagonal in M_J and M_I is

$$\begin{aligned} \Delta E_I &= \frac{A'^2}{4\nu_0} \left(\frac{a^2}{3} + \frac{2ab\sqrt{3}}{15} + \frac{b^2}{5} \right) \\ &\quad \times \left[2M_J^2 M_I + 4M_J - \frac{15}{2} M_I - 2M_J M_I^2 \right]. \end{aligned} \quad (12)$$

In ΔE_I , we approximate the state function, $\Psi(M_J M_I)$, by $[a | \frac{3}{2}, 1, \frac{1}{2}, 1, M_J M_I \rangle + b | \frac{3}{2}, 2, \frac{1}{2}, 1, M_J M_I \rangle]$ and the energy differences, $E(M_J M_I) - E(M_J - 1, M_I + 1)$ and $E(M_J + 1, M_I - 1) - E(M_J, M_I)$ by ν_0 . The energy of interaction is then

$$E(M_J M_I) = \int \Psi(M_J M_I) \mathcal{H}_I \Psi(M_J M_I) d\tau + \Delta E_I. \quad (13)$$

⁷ E. L. Hill, *Phys. Rev.* **34**, 1507 (1929).

V. COMPARISON WITH EXPERIMENT

The complete theoretical expression for the energy of one of the nine sublevels of the ${}^2\Pi_{3/2}$ energy level of $\text{N}^{14}\text{O}^{16}$ is (see MH)⁸

$$W(M_J M_I) = E_{ab}(M_J) + \Delta E_{ab}(M_J) + E_Q(M_J^2, M_I^2) + E_I(M_J M_I) + (\mu_0 g_I M_I H / 1840). \quad (14)$$

The first two terms are those belonging to the molecular Zeeman effect; the third term accounts for the interaction of the electric quadrupole moment of the N^{14} nucleus with the field of the extranuclear electrons. The term, $\mu_0 g_I M_I H / 1840$, takes account of the interaction of the nuclear spin with the external field.

The experimental data of Beringer and Castle consist of nine values of the external magnetic field strength for which

$$W(M_J M_I) - W(M_J - 1, M_I) = \nu_0,$$

ν_0 being the driving frequency of 0.31220 cm^{-1} . We make use of six of these nine numerical data and determine A' and B' from the following equations:

$$\begin{aligned} W_{\text{H}_1}(\tfrac{3}{2}, 1) - W_{\text{H}_1}(\tfrac{1}{2}, 1) &= W_{\text{H}_3}(\tfrac{3}{2}, -1) - W_{\text{H}_3}(\tfrac{1}{2}, -1), \\ W_{\text{H}_4}(\tfrac{1}{2}, 1) - W_{\text{H}_4}(-\tfrac{1}{2}, 1) &= W_{\text{H}_6}(\tfrac{1}{2}, -1) - W_{\text{H}_6}(-\tfrac{1}{2}, -1), \\ W_{\text{H}_7}(-\tfrac{1}{2}, 1) - W_{\text{H}_7}(-\tfrac{3}{2}, 1) &= W_{\text{H}_9}(-\tfrac{1}{2}, -1) - W_{\text{H}_9}(-\tfrac{3}{2}, -1). \end{aligned} \quad (15)$$

⁸ The equation defining E_{ab} in (MH) contains a typographical error; the first parenthesis on the right should be multiplied by $\frac{1}{2}$.

The subscripts indicate the different values of the magnetic field strength at which the energy differences are taken. The last term in (14), which is proportional to M_I , and the quadrupole term, which is a function of the squares of M_J and M_I , make no contribution to Eqs. (15).

Solving the first and the last of Eqs. (15) for A' and B' leads to $A' = 0.002627 \text{ cm}^{-1}$; $B' = 0.000256 \text{ cm}^{-1}$. These two values satisfy the second Eq. (16) to within 0.1 percent.

VI. DISCUSSION

The fact that consistent values of A' and B' are found as solutions of the three Eqs. (15) is, of course, not conclusive evidence that the operator (9) is the correct one for describing the interaction. All that can be said is that experiments are not in contradiction with (9) whereas they *are* in contradiction with the results of using $A\mathbf{I} \cdot \mathbf{J}$ as the interaction operator.

It can be shown that (9) is equivalent to $A\mathbf{I} \cdot \mathbf{J}$ if the total spin, \mathbf{S} , is zero. The small quantity, B' , is a measure of the error made when $A\mathbf{I} \cdot \mathbf{J}$ is used in place of (9) in treating states for which \mathbf{S} is not zero.

I am indebted to Professor Henry Margenau for his valuable suggestions in carrying out and writing up this research.

Mr. J. G. Castle, Jr. suggested the problem by insisting that the interaction $A\mathbf{I} \cdot \mathbf{J}$ is insufficient to account for the experimental data on $\text{N}^{14}\text{O}^{16}$.