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HYPERFINE SPLITTINGS AND g_F VALUES OF METASTABLE H_2

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The energy arising from the hyperfine interaction, the interaction with the magnetic field and the cross term between them have been studied for ortho H_2 at $c^3\pi_u$ state. The cross term gives rise to a first order correction of the g_F values which accounts for the discrepancies between the theoretical zeroth order g_F and the experimental values. The interactions are expressed as products of irreducible spherical tensors and Racah's method is used to derive all the diagonal and off diagonal matrix elements. The case of rotational level, N = 1 , is presented in detail. The coupling constants of hyperfine structure have been evaluated by using a single configuration electronic wave function for $c^3\pi_u$ state of H_2.

Author

INTRODUCTION

The odd rotational levels of ortho H_2 and the even rotational levels of para H_2 of the $c^3\pi_u$ state are metastable with a life time of the order of milliseconds. Lichten[1,2] measured the fine structure splittings and the g_J values of the rotational level N = 2 of para H_2 to a high precision by atomic beams magnetic resonance method. The hyperfine splittings and the g_F values of the N = 1 level

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of ortho H_2 have recently been measured by Lichten and Brooks.[3] Since hydrogen molecule is the lightest diatomic molecule, pure Hund's case[4] b coupling of angular momenta can be applied to a very good approximation. The properties of the $c^3\pi_u$ state has therefore been of great theoretical interest. The fine structure of this state has been studied by Fontana[5] and by Chiu.[6] Its hyperfine structure has been studied by Frey and Mizuschima,[7] and the relative life time of the fine structure levels due to the perturbation of other electronic states has been studied by Chiu.[8]

The fine structure separations are of the order of 5000 Mc/Sec[2,6] which is not very large in comparison with the hyperfine separations (of the order of 500 Mc/Sec). The second order corrections to the hyperfine energies will therefore be large. Recent measurements[3] indicate that the measured g_F values differ considerably from the zeroth order ($g_F^{(0)}$) values where the perturbations from the nearby fine structure levels have been neglected. These differences are mainly due to a nonvanishing cross term of the hyperfine interaction and the interaction of the molecule with the magnetic field. The corrections to the g_F values from this cross term will be of the first order ($g_F^{(1)}$), and they can take on large values.

In section 1 of this paper we will discuss these corrections on g_F values. The diagonal and off diagonal matrix elements of the hyperfine interacting Hamiltonian will be derived in section 2. In section 3 we will work out the details for the case of rotational level $N = 1$, namely the second order energy corrections $E^{(2)}$ and the corrections on g_F will be given for all the hyperfine states. A set of coupling constants which have been evaluated numerically from a single configuration electronic wave function[6] for the $c^3\pi_u$ state will be given in the last section.

1. ENERGY CORRECTIONS AND g_F CORRECTIONS

The perturbing Hamiltonian, H′, of a diatomic molecule due to its hyperfine interaction (H_{hfs}) and its interaction with the external magnetic field (H_M) is the following:

$$H' = H_{hfs} + H_M ,$$

where

$$H_{hfs} = H_1(hfs) + H_2(hfs) + H_3(hfs)$$

and

$$H_1(hfs) = (g_I \alpha^2/2) \sum_{i,\beta} (\underset{\sim}{\ell}_i \cdot \underset{\sim}{I}_\beta) \frac{1}{r_{i\beta}^3}$$

$$H_2(hfs) = (4\pi g_I \alpha^2/3) \sum_{i,\beta} \delta(r_{i\beta}) \underset{\sim}{S}_i \cdot \underset{\sim}{I}_\beta$$

$$H_3(hfs) = -(g_I \alpha^2/2) \sum_{i,\beta} \left[(\underset{\sim}{S}_i \cdot \underset{\sim}{I}_\beta) - \frac{3(\underset{\sim}{S}_i \cdot \underset{\sim}{r}_{i\beta})(\underset{\sim}{I}_\beta \cdot \underset{\sim}{r}_{i\beta})}{r_{i\beta}^2} \right] \frac{1}{r_{i\beta}^3} \qquad (1\text{-}1)$$

The indices i (= 1, 2) refer to the two electrons and the indices β(= a, b) refer to the two nuclei. $\underset{\sim}{\ell}_i$ and $\underset{\sim}{S}_i$ are the orbital angular momentum and the spin of the electron i ; $\underset{\sim}{I}_\beta$ is the spin of the nucleus β; g_I = 0.003038 for proton and α is the fine structure constant.

H_M is the interaction of the magnetic moments of the molecule with the external magnetic field,

$$H_M = \mu_0 \left(g_S \underset{\sim}{S} + g_N \underset{\sim}{N} + g_I \underset{\sim}{I} \right) \cdot \underset{\sim}{H} \tag{1-2}$$

where μ_0 is the Bohr magneton; S is the total electronic spin, $\underset{\sim}{S} = \underset{\sim}{S}_1 + \underset{\sim}{S}_2$; $\underset{\sim}{N}$ is the total rotational angular momentum which is the resultant of pure rotational angular momentum $\underset{\sim}{O}$ and the projection of electronic orbital angular momentum along the figure axis $\underset{\sim}{\Lambda}$; $\underset{\sim}{I}$ is the total nuclear spin, $\underset{\sim}{I} = \underset{\sim}{I}_1 + \underset{\sim}{I}_2$; and $\underset{\sim}{H}$ is the external magnetic field. $\underset{\sim}{S}$ and $\underset{\sim}{N}$ will couple to give the total electronic angular momentum $\underset{\sim}{J}$, $\underset{\sim}{J} = \underset{\sim}{N} + \underset{\sim}{S}$, and $\underset{\sim}{J}$ will couple with $\underset{\sim}{I}$ to give the total angular momentum $\underset{\sim}{F}$ of the molecule, $\underset{\sim}{F} = \underset{\sim}{J} + \underset{\sim}{I}$.

Due to the closeness of the fine structure separation, there are mixings among the levels of same $\underset{\sim}{F}$ but different J's. In a zero magnetic field, the wave function of a hyperfine level (F, m_F) within a fine structure level J (for a given rotational level N of $c^3\pi_u$ state) is expressed up to first order correction as,

$$\Psi_{J,F,m_F} = \phi^0_{JF,m_F} + \sum_{J'} \frac{\left({}^3\pi_u, FJIN \,|H_{hfs}|\, {}^3\pi_u, FJ'IN \right)}{E_{J,F,} - E_{J',F}} \phi^0_{J',F,m_F} \tag{1-3}$$

where ϕ^0_{J,F,m_F} is the ortho normal zeroth order wave function for level (J,F, m_F) of the $c^3\pi_u$ state where both F and J are good quantum numbers. In the presence of a very weak magnetic field the energy of this hyperfine level is therefore (up to second order correction) the following,

$$E_{J,F,m_F} = E_{J,F}(hfs) + \left(g_F^{(0)} + g_F'\right)\mu_0 m_F H \qquad (1\text{-}4)$$

where

$$E_{J,F}(hfs) = \left({}^3\pi_u, FJIN|H_{hfs}|\,{}^3\pi_u, FJIN\right) + \sum_{J' \neq J} \frac{\left|\left({}^3\pi_u, FJIN|H_{hfs}|\,{}^3\pi_u, FJ'IN\right)\right|^2}{E_{J,F} - E_{J',F}} \qquad (1\text{-}5)$$

The first and the second terms on the right hand side of Eq. (1-5) are the first order energy, $E^{(1)}_{J,F}$ (hfs), and the second order energy, $E^{(2)}_{J,F}$ (hfs), respectively due to the hyperfine interaction and,

$$g_F^{(0)}(J) = \left[F(F+1)\right]^{-1/2}\left(FJINS \,\|\, g_N \underset{\sim}{N} + g_S \underset{\sim}{S} + g_I \underset{\sim}{I} \,\|\, FJINS\right) \qquad (1\text{-}6)$$

$$g_F'(J) =$$

$$\frac{2}{\left[F(F+1)\right]^{1/2}} \sum_{J' \neq J} \frac{\left({}^3\pi_u, FJIN|H_{hfs}|\,{}^3\pi_u, FJ'IN\right)\left(FJ'INS \,\|\, g_N \underset{\sim}{N} + g_S \underset{\sim}{S} \,\|\, FJINS\right)}{E_{J,F} - E_{J',F}}$$

$$+ \sum_{J' \neq J} \left|\frac{\left({}^3\pi_u, FJIN|H_{hfs}|\,{}^3\pi_u, FJ'IN\right)}{E_{J,F} - E_{J',F}}\right|^2 g_F^{(0)}(J') \qquad (1\text{-}7)$$

$g_F^{(0)}(J)$ is the zeroth order g_F value when both F and J are good quantum numbers. The first term on the right hand side of (1-7) is the first order correction, $g_F^{(1)}(J)$, which can be of comparable magnitude to that of $g_F^{(0)}(J)$ due to the energy separation in the denominator is not large. The second term in the RHS of Eq. (1-7) is the second order correction, $g_F^{(2)}(J)$, which is small. The reduced matrix elements in Eq. (1-6) and Eq. (1-7) are defined by Wigner-Eckart's theorem[10] as follows,

$$\left(F', m' \left| T_\mu^{(L)} \right| F, m\right) = C(FLF'; m\mu m')\left(F' \left\| \underset{\sim}{T}^{(L)} \right\| F\right)$$

where $T_\mu^{(L)}$ is the component of the Lth rank irreducible tensor $T^{(L)}$, and $C(FLF'; m\mu m')$ is the Clebsch-Gordan's coefficient.[11]

2. MATRIX ELEMENTS

To obtain the hyperfine energy separations and the corrections on g_F values, one needs to evaluate the diagonal and the off diagonal matrix elements of the interacting Hamiltonian H'. For Hund's case b diatomic molecule, the angular momentum N, S and I are well defined with respect to the space fixed coordinate system. The matrix elements of H_M over the molecular wave function can therefore be easily evaluated.[12] H_1 (hfs) is the sum of the scalar products of the electronic angular momentum $\underset{\sim}{\ell}_i$ and the nuclear spin $\underset{\sim}{I}_\beta$. For matrix elements diagonal in total nuclear spin $\underset{\sim}{I}$, one can write H_1(hfs) in the following form,

$$H_1(\mathrm{hfs}) = \left(g_I\,\alpha^2/4\right)\sum_{i\beta}\left(\frac{1}{r_{i\beta}^{3}}\right)\underset{\sim}{\ell}_i\,(x_i') \cdot \underset{\sim}{I}$$

where x′ refers to the fixed space coordinate system. By considering the above expression as a scalar product of two tensors of first rank, one can evaluate the matrix elements of H_1 (h f s) as follows,

$$\left({}^3\pi_u\,,\, F J' I N \left|\left(\frac{1}{r^3_{i\beta}}\right) \underset{\sim}{\ell}_i(\underset{\sim}{x}')\cdot \underset{\sim}{I}\right| {}^3\pi_u\,,F J I N\right)$$

$$= (-1)^{I+J'-F}\left[(2J'+1)(2I+1)\right]^{1/2} W(J\,I\,J'\,I;\,F1)$$

$$\times\left({}^3\pi_u\,,J'N \,\|\left(\frac{1}{r^3_{i\beta}}\right)\underset{\sim}{\ell}_i(\underset{\sim}{x}')\,\|\, {}^3\pi_u,\ J\,N\right)\left(I\,\|\,\underset{\sim}{I}\,\|\,I\right)\ ,$$

where $W(J\ I\ J'\ I;\ F\ 1)$ is the Racah's coefficient,[13] and $I = 1$ for ortho H_2. The reduced matrix element $(I\,||\underset{\sim}{I}||\,I) = [I(I+1)]^{1/2} = \sqrt{2}$. After $(1/r^3_{i\beta})\,\underset{\sim}{\ell}_i\,(\underset{\sim}{x}')$ been transformed from fixed coordinate system $(\underset{\sim}{x}')$ into molecular moving coordinate system $(\underset{\sim}{x})$, the reduced matrix element of $(1/r^3_{i\beta})\,\underset{\sim}{\ell}_i\,(\underset{\sim}{x}')$ is evaluated as follows.[14]

$$\left({}^3\pi_u\,,\ J'\ N\ \|\left(\frac{1}{r^3_{i\beta}}\right)\underset{\sim}{\ell}_i(\underset{\sim}{x}')\,\|\ {}^3\pi_u,\ J\ N\right)$$

$$= (-1)^{N+J'}\left[(2N+1)(2J+1)\right]^{1/2} W(N\,J\,N\,J'\,;\ 11)\left[N(N+1)\right]^{-1/2}\left\langle\left(\frac{1}{r^3_{i\beta}}\right)\ell_{iz}\,(\underset{\sim}{x})\right\rangle\ ,$$

where $\langle (1/r^3_{i\beta}) \ell_{iz} \rangle$ is to be evaluated in the molecular system $(\underset{\sim}{x})$ over the electronic wave function of $c^3\pi_u$ states, the axis z is the figure axis. The matrix element of H_1 (hfs) is therefore,

$$\left({}^3\pi_u,\ FJ'IN\ |H_1(\text{hfs})|\ {}^3\pi_u,\ FJIN\right)$$

$$= (-1)^{N+1-F}\left[6(2J'+1)(2J+1)(2N+1)/N(N+1)\right]^{1/2}$$

$$\times W(J\,1\,J'\,1;\ F\,1)\ W(N\,J\,N\,J';\ 11)\,\underset{\sim}{a},$$

where $J' = J$, $J \pm 1$ and $\underset{\sim}{a}$ is the coupling constant in terms of the integral $\langle (1/r^3_{i\beta}) \ell_{iz} \rangle$ and it is defined in Eq. (2-9) below.

H_2(hfs) is the contact interaction of electron spin with nuclear spin. It can be written into an equivalent form for matrix elements diagonal in I and S,

$$H_2(\text{hfs}) = \left(\pi g_I\, \alpha^2/3\right) \sum_{i,\beta} \delta(r_{i\beta})\ \underset{\sim}{S} \cdot \underset{\sim}{I}$$

The matrix element of H_2 (hfs) is similarly decomposed into a product of Racah's coefficients and reduced matrix elements,

$$(F\,J'\,I\,N\,S\,|\,\underset{\sim}{S} \cdot \underset{\sim}{I}\,|\,F\,J\,I\,N\,S)$$

$$= (-1)^{N-S-F}\left[(2J'+1)(2J+1)(2I+1)(2S+1)\right]^{1/2}$$

$$\times W(JIJ'I;\ F1)\ W(SJSJ';\ N1)\ \left(I\,\|\,\underset{\sim}{I}\,\|\,I\right)\left(S\,\|\,\underset{\sim}{S}\,\|\,S\right)$$

with $I = 1$, $S = 1$, $(I||\underset{\sim}{I}||I||) = \sqrt{2}$ and $(S||\underset{\sim}{S}||S) = \sqrt{2}$ then,

$$\begin{aligned}&\left({}^3\pi_u,\ FJ'N\,|H_2\,(hfs)|\,{}^3\pi_u,\ FJN\right)\\ &\qquad = (-1)^{N-F-1}\,6\left[(2J'+1)(2J+1)\right]^{1/2}\,W(J1J'\,1;\,F1)\\ &\qquad\qquad \times\ W(1J1J';\,N1)\,\underline{b}\end{aligned}$$

where $\underline{b}$ is in terms of the integral $\langle\delta(r_{i\beta})\rangle$ over the electronic wave function and it is defined in Eq. (2-9) below.

H_3 (hfs) represents spin-spin interaction between electrons and nuclei. For matrix elements diagonal in S and I, it is equivalent to write H_3 (hfs) as,

$$-\left(g_I\,\alpha^2/8\right)\sum_{i,\beta}\left(\frac{1}{r^3_{i\beta}}\right)\underset{\sim}{I}\cdot\left[\underset{\sim}{S} - 3\underset{\sim}{r}_{i\beta}\left(\underset{\sim}{S}\cdot\underset{\sim}{r}_{i\beta}\right)/r^2_{i\beta}\right]$$

Since the doubly degenerate π state is a linear combination of $\Lambda = +1$ state and $\Lambda = -1$ state, and the matrix element of H_3 (hfs) is nonvanishing between state of $\Lambda = +1$ and state of $\Lambda = -1$, we therefore have,

$$\begin{aligned}&({}^3\pi_u,\ FJ'IN\,|\,H_3(hfs)\,|\,{}^3\pi_u,\ FJIN)\\ &\qquad = (FJ'INS,\Lambda = 1\,|H_3(hfs)\,|FJINS,\Lambda=1)\\ &\qquad\quad - (FJ'INS\Lambda \square 1\,|H_3\,(hfs)|\,FJINS,\Lambda = -1),\end{aligned}\tag{2-1}$$

for odd rotational level ($N = $ odd) of ortho H_2.[15] If one expresses H_3(hfs) as a sum of $H_3^{i\beta}$(hfs),

$$H_3\,(hfs) = \sum_{i,\beta} H_3^{i\beta}\,(hfs)$$

where $H_3^{i\beta}(\mathrm{hfs})$ is a scalar product of two first rank tensors and its matrix element can again be decomposed into a product of Racah's coefficient and reduced matrix elements.

$$\left(F\,J'\,I\,N\,S\,\Lambda' \;\middle|H_3^{i\beta}(\mathrm{hfs})\middle|\; F\,J\,I\,N\,S\,\Lambda \right)$$

$$= -\left(g_I\,\alpha^2/8\right)(-1)^{I+J'-F}\left[(2I+1)(2J'+1)\right]^{1/2}\,W(IJIJ';F1)\left(I\,\|\,\mathbf{I}\,\|\,I\right)$$

$$\times\left(J'\,N\,S\,\Lambda'\;\Big\|\;\left(\frac{1}{r_{i\beta}^{3}}\right)\left[\mathbf{S}-3\mathbf{r}_{i\beta}\left(\mathbf{S}\cdot\mathbf{r}_{i\beta}\right)/r_{i\beta}^{2}\right]\;\Big\|\;J\,N\,S\,\Lambda\right)$$

where $(I\,\|\,\mathbf{I}\,\|\,I) = [I(I+1)]^{1/2}$ and $I = 1$ for ortho H_2. Let,

$$\mathbf{x}^{(1)} = \mathbf{S} - 3\mathbf{r}_{i\beta}\left(\mathbf{S}\cdot\mathbf{r}_{i\beta}\right)/r_{i\beta}^{2}\;.$$

where $x^{(1)}$ is a spherical tensor of the first rank and it can be constructed from a first rank spherical tensor $S^{(1)}$ and a second rank spherical tensor $\mathbf{C}^{(2)}(\theta'_{i\beta}\varphi'_{i\beta})$ where $C_m^{(\ell)}(\theta'\varphi') = (4\pi/5)^{1/2}Y_\ell^m(\theta'\varphi')$. We therefore have,[10]

$$x_m^{(1)} = k\sum_{\mu} C(121;\,\mu,\,m-\mu,\,m)\,S_\mu^{(1)}\,C_{m-\mu}^{(2)}\,(\theta'_{i\beta}\varphi'_{i\beta})$$

where $C(121;\mu.m-\mu,m)$ is the Clebsch-Gordan coefficient,[12] and $\theta'_{i\beta}$ and $\varphi'_{i\beta}$ are the polar and azimuth angles of $\mathbf{r}_{i\beta}$ with respect to space fixed coordinate system. The constant $k = \sqrt{10}$ can be obtained by considering the case of $m = 0$. The reduced matrix element of $\mathbf{x}^{(1)}$ are then decomposed into the product of reduced matrix element of $C^{(2)}(\theta'_{i\beta}\;\varphi'_{i\beta})$ and of S, and a 9j symbol. By using the relation of $(S||\underset{\sim}{S}||S) = [S(S+1)]^{1/2}$ and $S = 1$ for triplet electronic state, the reduced matrix element of $\underset{\sim}{x}^{(1)}/r^3_{i\beta}$ may be evaluated as follows,[16]

$$(J'NS\Lambda'||\underset{\sim}{x}^{(1)}/r^3_{i\beta}||JNS\Lambda)$$

$$= \left[180\,(2J+1)\,(2N+1)\right]^{1/2} \begin{Bmatrix} 1 & 1 & 1 \\ N & N & 2 \\ J' & J & 1 \end{Bmatrix} \left(N\Lambda' \,\Big\|\, \frac{\underset{\sim}{C}^{(2)}(\theta'_{i\beta}\varphi'_{i\beta})}{r^3_{i\beta}} \,\Big\|\, N\Lambda\right) \tag{2-3}$$

The above $9j$ symbol is a sum of the products of Racah's coefficients.[16a, 17] For the case of $J' = J, J \pm 1$ the $9j$ symbol can be expressed into the following simple expressions,

$$\begin{Bmatrix} 1 & 1 & 1 \\ N & N & 2 \\ J & J & 1 \end{Bmatrix} = \frac{\left[4+N(N+1)-J(J+1)\right]\left[3J(J+1)+N(N+1)\right]-12}{12\left[5N(N+1)\,(2N+1)\,(2N+3)\,(2N-1)\,J(J+1)\,(2J+1)\right]^{1/2}}$$

$$\begin{Bmatrix} 1 & 1 & 1 \\ N & N & 2 \\ J+1 & J & 1 \end{Bmatrix} = \frac{\left[(J+N+3)\,(N+J)\,(J-N+2)\,(N-J+1)\right]^{1/2}\left[3(J+1)^2-N(N+1)-6\right]}{12\left[5N(N+1)\,(2N+1)\,(2N+3)\,(2N-1)\,(J+1)\,(2J+1)\,(2J+3)\right]^{1/2}} \tag{2-4}$$

After a proper transformation of the fixed coordinate $(\theta'_{i\beta}\ \varphi'_{i\beta})$ into the moving molecular coordinate $(\theta_{i\beta}, \varphi_{i\beta})$ we have,[14]

$$\left(N\Lambda'\,||C^{(2)}(\theta'_{i\beta}\varphi'_{i\beta})/r^3_{i\beta}||\,N\Lambda\right) = (-1)^k\, C(N2N;\ \Lambda'\, k\Lambda)\left\langle\Lambda'|C^{(2)}_{-k}(\theta_{i\beta}\varphi_{i\beta})/r^3_{i\beta}|\Lambda\right\rangle \tag{2-5}$$

where $\langle C^{(2)}_{-k}(\theta_{i\beta}\varphi_{i\beta})/r^3_{i\beta}\rangle$ is independent of the molecular rotation and is to be evaluated over the electronic wave function of the $c^3\pi_u$ state of H_2. By substituting (2-2), (2-3), (2-4) and (2-5) into (2-1) one obtains the matrix element for $H_3(hfs)$ in the following,

$$(^3\pi_u,\ FJ'N\,|H_3(hfs)|\,^3\pi_u,\ FJN) =$$

$$(-1)^{J'+F}\,W(1J1J';F1)\left[\frac{270N(N+1)(2N+1)(2J'+1)(2J+1)}{(2N-1)(2N+3)}\right]^{1/2}$$

$$\times\left[\frac{3-N(N+1)}{N(N+1)}\,\underline{c}-\frac{\sqrt{6}}{2}\,\underline{d}\right]\begin{Bmatrix}1 & 1 & 1\\ N & N & 2\\ J' & J & 1\end{Bmatrix} \qquad (2\text{-}6)$$

where $J' = J,\ J \pm 1$, and the coupling constants $\underline{c}$ and $\underline{d}$ are defined in (2-9). Combining the matrix elements for $H_1(hfs)$, $H_2(hfs)$ and $H_3(hfs)$ we have the matrix elements for H_{hfs} as follows,

$$\left(^3\pi_u,\ F,\ J,\ N\,|H_{hfs}|\,^3\pi_u,\ F,\ J,\ N\right) = \frac{Q_I}{2J(J+1)}\left\{\frac{\left[J(J+1)+N(N+1)-2\right]}{N(N+1)}\,\underline{a}\right.$$

$$+\left[2+J(J+1)-N(N+1)\right]\underline{b}+\frac{\left[4+N(N+1)-J(J+1)\right]\left[3J(J+1)+N(N+1)\right]-12}{2(2N-1)(2N+3)}$$

$$\left.\times\left[\frac{N(N+1)-3}{N(N+1)}\,c+\frac{\sqrt{6}}{2}\,d\right]\right\} \qquad (2\text{-}7)$$

$$\left({}^3\pi_u,\ F,\ J+1,\ N\,\middle|H_{hfs}\middle|\,{}^3\pi_u,\ F,\ J,\ N\right)$$

$$= -\frac{Q_2\,Q_3}{2(J+1)}\left\{\frac{a}{N(N+1)} + b + \frac{\left[3(J+1)^2 - N(N+1) - 6\right]}{2(2N-1)\,(2N+3)}\right.$$

$$\left.\times\left[\frac{N(N+1) - 3}{N(N+1)}\,c + \frac{\sqrt{6}}{2}\,d\right]\right\} \qquad (2\text{-}8a)$$

and

$$\left({}^3\pi_u,\ F,\ J-1,\ N\,\middle|H_{hfs}\middle|\,{}^3\pi_u,\ F,\ J,\ N\right)$$

$$= -\frac{\bar{Q}_2\,\bar{Q}_3}{2J}\left\{\frac{a}{N(N+1)} + b + \frac{\left[3J^2 - N(N+1) - 6\right]}{2(2N-1)\,(2N+3)}\right.$$

$$\left.\times\left[\frac{N(N+1) - 3}{N(N+1)}\,c + \frac{\sqrt{6}}{2}\,d\right]\right\} \qquad (2\text{-}8b)$$

where a, b, c and d are the coupling constants to be evaluated over the electronic wave function of the $c^3\pi_u$ state and they are defined in the following:

$$a = \frac{g_I\,\alpha^2}{4}\left\langle\frac{\ell_{1z}}{r_{1a}^3} + \frac{\ell_{1z}}{r_{1b}^3} + \frac{\ell_{2z}}{r_{2a}^3} + \frac{\ell_{2z}}{r_{2b}^3}\right\rangle$$

$$b = \left(g_I\,\pi\alpha^2/3\right)\ \left\langle\delta\left(r_{1a}\right) + \delta\left(r_{1b}\right) + \delta\left(r_{2a}\right) + \delta\left(r_{2b}\right)\right\rangle$$

$$c = \frac{g_I\,\alpha^2}{4}\left\langle\frac{C_0^{(2)}(\theta_{1a}\varphi_{1a})}{r_{1a}^3} + \frac{C_0^{(2)}(\theta_{1b}\,\varphi_{1b})}{r_{1b}^3} + \frac{C_0^{(2)}(\theta_{2a}\,\varphi_{2a})}{r_{2a}^3} + \frac{C_0^{(2)}(\theta_{2b}\,\varphi_{2b})}{r_{2b}^3}\right\rangle$$

$$d = \frac{g_I\,\alpha^2}{4}\left\langle\frac{C_2^{(2)}(\theta_{1a}\varphi_{1a})}{r_{1a}^3} + \frac{C_2^{(2)}(\theta_{1b}\,\varphi_{1b})}{r_{1b}^3} + \frac{C_2^{(2)}(\theta_{2a}\,\varphi_{2a})}{r_{2a}^3} + \frac{C_2^{(2)}(\theta_{2b}\,\varphi_{2b})}{r_{2b}^3}\right\rangle$$

(2-9)

and

$$C_m^{(\ell)}(\theta\varphi) = \left(\frac{4\pi}{2\ell+1}\right)^{1/2} Y_m^{\ell}(\theta\varphi)$$

The coefficients Q_1, Q_2, Q_3, $\overline{Q}_2$ and $\overline{Q}_3$ appeared in (2-7) and (2-8) are defined as follows,

$$Q_1 \equiv \left[F(F+1) - J(J+1) - 2\right]/2$$

$$Q_2 \equiv \left[(F+J+3)(F+1-J)(F+J)(J-F+2)\right]^{1/2}/2$$

$$Q_3 \equiv \left[\frac{(J+N+3)(J+N)(J-N+2)(N-J+1)}{(2J+1)(2J+3)}\right]^{1/2}$$

$$\overline{Q}_2 \equiv \left[(F+J+2)(F+2-J)(F+J-1)(J-F+1)\right]^{1/2}/2$$

$$\overline{Q}_3 \equiv \left[\frac{(J+N+2)(J+N-1)(J-N+1)(N-J+2)}{(2J-1)(2J+1)}\right]^{1/2} \qquad (2\text{-}10)$$

3. THE CASE OF N = 1

With all the matrix elements developed in the last section, we will now express the hyperfine energy and the g_F values for the rotational level $N = 1$.

$$E_{J,F}(hfs) = E_{J,F}^{(1)}(hfs) + E_{J,F}^{(2)}(hfs)$$

Substituting (2-7) and (2-8) into (1-5) we have,

$$E_{J,F}^{(1)}(hfs) = (Q_1/40)\left\{10a + 20b + \left[16 - 3J(J+1)\right]\left[\sqrt{6}d - c\right]\right\} \qquad (3\text{-}1)$$

and

$$E^{(2)}_{J,F}\,(\mathrm{hfs}) = \left[\frac{Q_2\,Q_3\,P}{40(J+1)}\right]^2 \frac{1}{\Delta E_{J,J+1}(F)}$$

$$+ \left[\frac{\bar{Q}_2\,\bar{Q}_3\,\bar{P}}{40J}\right]^2 \frac{1}{\Delta E_{J,J-1}(F)} \tag{3-2}$$

where

$$\Delta E_{J,J\pm1}(F) = E(J,\,F) - E(J \pm 1,\,F) \tag{3-3}$$

$$P \equiv 10\underline{a} + 20\underline{b} + \left[3(J+1)^2 - 8\right]\left[\sqrt{6}\underline{d} - \underline{c}\right] \tag{3-4}$$

and

$$\bar{P} \equiv 10\underline{a} + 20\underline{b} + [3J^2 - 8]\,[\sqrt{6}\underline{d} - \underline{c}]$$

The Q's and $\underline{a}$, $\underline{b}$, $\underline{c}$, $\underline{d}$ are defined in (2-10) and (2-9).

For g_F values, we neglect the small correcting term $g_F^{(2)}$ (second term) in Eq. (1-7), then, $g_F'(J) = g_F^{(1)}(J)$ and

$$g_F(J) = g_F^{(0)}(J) + g_F^{(1)}(J)$$

For the case of $N = 1$, we have

$$g_F^{(0)}(J) =$$

$$\frac{F(F+1) + J(J+1) - 2}{4F(F+1)}\left(g_S + g_N\right) + \frac{F(F+1) - J(J+1) + 2}{2F(F+1)}\,g_I \tag{3-5}$$

$$g_F^{(1)}(J) = \frac{\left(g_S + g_N\right)}{40F(F+1)}\left[\frac{Q_2^2\,Q_3^2\,P}{(J+1)^2\,\Delta E_{J,J+1}} + \frac{\bar{Q}_3^2\,\bar{Q}_3^2\,\bar{P}}{J^2\,\Delta E_{J,J-1}}\right] \tag{3-6}$$

where P and $\overline{P}$ are defined in Eq. (3-4), and $g_N = \Lambda/N(N+1) = 1/2$, $g_S = 2$ and $g_I = 0.003038$. Since the wave function Ψ_{JFM_F} is normalized up to the first order (see Eq. (1-3)), we therefore have[18]

$$\sum_J g_F^{(1)}(J) = 0 . \tag{3-7}$$

All the values of $g_F^{(0)}(J)$ for different N's have been tabulated[1] by using Eq. (3-5). We now summarize all the $g_F^{(1)}(J)$ and $E_{J,F}^{(2)}(hfs)$ for the case of $N = 1$ in the following, let

$$K_1 \equiv a + 2b - \left(\sqrt{6}d - c\right)/2$$

$$K_2 \equiv a + 2b + 2\left(\sqrt{6}d - c\right)/5 \tag{3-8}$$

we have,

$$g_F^{(1)}(F = 1, J = 0) = -5K_1/3\Delta E_{1,0}(F = 1)$$

$$g_F^{(1)}(F = 1, J = 1) = 25K_2/48\Delta E_{1,2}(F = 1) + 5K_1/3\Delta E_{1,0}(F = 1)$$

$$g_F^{(1)}(F = 1, J = 2) = -25K_2/48\Delta E_{1,2}(F = 1)$$

$$g_F^{(1)}(F = 2, J = 1) = 5K_2/16\Delta E_{1,2}(F = 2)$$

$$g_F^{(1)}(F = 2, J = 2) = -5K_2/16\Delta E_{1,2}(F = 2)$$

$$g_F^{(1)}(F = 3, J = 2) = g_F^{(1)}(F = 0, J = 1) = 0 \tag{3-9}$$

and

$$
\begin{aligned}
E^{(2)}(F = 1,\ J = 0) &= -(K_1)^2 / 3\Delta E_{1,0}(F = 1) \\
E^{(2)}(F = 1,\ J = 1) &= 5(K_2)^2 / 48\Delta E_{1,2}(F = 1) + (K_1)^2 / 3\Delta E_{1,0}(F = 1) \\
E^{(2)}(F = 1,\ J = 2) &= -5(K_2)^2 / 48\Delta E_{1,2}(F = 1) \\
E^{(2)}(F = 2,\ J = 1) &= 3(K_2)^2 / 16\Delta E_{1,2}(F = 2) \\
E^{(2)}(F = 2,\ J = 2) &= -3(K_2)^2 / 16\Delta E_{1,2}(F = 2) \\
E^{(2)}(F = 3,\ J = 2) &= E^{(2)}(F = 0,\ J = 1) = 0
\end{aligned}
\tag{3-10}
$$

Where the $\Delta E_{J,J'}(F)$'s are defined in (3-3). Note that the sum rule relation (3-7) holds for the $g_F^{(1)}$'s in (3-9) and a similar relation $\sum_j E_{J,F}^{(2)} = 0$ also holds for $E^{(2)}$ in (3-10).

Experimentally, one can determine the constants K_1 and K_2 from the fine structure and the hyperfine structure separations and the $g_F^{(1)}$ values. Knowing K_1 and K_2 one can obtain the linear combinations, $(a + 2b)$ and $(\sqrt{6}d - c)$, from Eq. (3-8). Measurements on $N = 1$ rotational level alone therefore cannot determine the coupling constants a, b, c, and d independently. Additional measurements on $N = 3$ level will be needed to determine these hyperfine coupling constants independently.

4. COUPLING CONSTANTS

The coupling constants a, b, c, and d are defined in (2-8). They have been evaluated by using a single configurational electronic wave function[6] of the $c^3\pi_u$ state. The wave function is a linear combination of the Heitler-Condon type with coefficient C_H and ionic-type wave function with coefficient C_I. Both types of wave function are made of Slater-type atomic orbitals of $1s\sigma$ and $2p\pi$ symmetry. For the orbital exponents $\zeta_{1s\sigma}$ (= 1.24108) and $\zeta_{2p\pi}$(= 0.50282) the coefficients C_I (= 0.2808) and C_H (= 0.5612) are the values which minimize the total energy E (= -0.718793 a.u.) of the molecule in a $c^3\pi_u$ state at equilibrium internuclear distance R_e (= 1.96080 a.u.). The values of the coupling constants are evaluated numerically[19] on the IBM 7094 computer, and they are the following.

$$\underline{a} = 17.44 \text{ Mc/Sec}, \qquad \underline{b} = 545.27 \text{ Mc/Sec}.$$

$$\underline{c} = 28.95 \text{ Mc/Sec}, \qquad \underline{d} = -8.27 \text{ Mc/Sec}.$$

Frey and Mizushima[7] have also computed these coupling constant by using Amemiya's wave function.[20] Their c and d values appear to be very different from ours.[21] It seems that they may have defined their constants differently,[22] although the definition of coupling constants was not given by them.

With the calculated coupling constants one can obtain all the first order $g_F^{(1)}$'s from Eq. (3-9) and the second order $E^{(2)}$'s from Eq. (3-10). The g_F values thus corrected by $g_F^{(1)}$'s give a better agreement with the experimental values[3] than the uncorrected $g_F^{(0)}$'s. Since all the operators involved in calculating the coupling constants are one electron operators, a set of much improved coupling constants can therefore be calculated easily when an accurate electronic wave function for $c^3\pi_u$ state is available.

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(16) (a) A. R. Edmonds, Angular Momentum in Quantum Mechanics, p. 110 (Chambridge University Press, New York, 1959). (b) Note the definition of the reduced matrix element, $(J'||\underset{\sim}{T}^{(k)}||J)$, by Edmonds differs from ours by a factor of $(2J'+1)^{1/2}$.

(17) D. M. Brink and G. R. Satchler, Angular Momentum (Oxford University Press, Oxford, 1962).

(18) This is the so called sum rule of g values at different representations. However this relation will not be true if one includes the second order correction $g_F^{(2)}(J)$.

(19) See reference (6) for details of the method used in evaluating the two center integrals involved.

(20) A. Amemiya, Proc. Phys.-Math. Soc. Japan 21, 394 (1939).

(21) Mizuschima's values are as follows, $\underline{a}$ = 23 Mc/Sec, $\underline{b}$ = 417 Mc/Sec, $\underline{c}$ = -168 Mc/Sec and d = 0.6 Mc/Sec.

(22) From Frey and Mizushima's paper (Ref. 6), their "a" appears to be $(g_I\,\alpha^2/4)\left\langle \sum_{ij} 1/r_{ij} \right\rangle$ and it is incorrect. From their Eq. (5) and Eq. (6), "d" is $\sqrt{6}/4$ times of what we have defined here in Eq. (2-8), and this definition is inconsistent with their Eq. (10). Furthermore their Eq. (10)

appears to be incorrect because the ratio of the terms with c and d should be J independent whereas their ratio is J dependent (and this is the reason that c and d cannot be determined independently by measurements on rotational $N = 1$ level alone).