

內部廻轉存在時의 多原子分子에서의 스핀-廻轉相互作用

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Spin-Rotation Interaction in Polyatomic Molecules in the Presence of Internal Rotation

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要約. 多原子分子內의 內部廻轉子 위에 있는 磁氣核은 分子의 全體廻轉으로 因하여 생기는 磁氣場뿐만 아니라 內部廻轉에 基因하는 磁氣場과도 相互作用할 수 있다. 이 論文에서는 多原子分子內의 內部廻轉子 위에 있는 核스핀에 對한 스핀-廻轉相互作用 Hamiltonian을 誘導하였다. 誘導된 Hamiltonian은 스핀과 全體廻轉間의 相互作用을 나타내는 部分 및 스핀과 內部廻轉 間의 相互作用을 나타내는 部分과의 疊으로 이루어져 있음을 밝혔다. 스핀-廻轉相互作用 tensor와 磁氣的 가리움效果 間의 關係도 또한 調査하였다.

ABSTRACT. A magnetic nucleus located on an internal rotor in a polyatomic molecule can interact with the magnetic fields arising from internal rotation as well as end-over-end molecular rotation. In this paper the spin-rotation coupling Hamiltonian for a nuclear spin on a symmetrical internal rotor in a polyatomic molecule is derived. The derived spin-rotation Hamiltonian turns out to be composed of the two parts: the spin-over-all-rotation interaction and the spin-internal-rotation interaction. The relation between the spin-rotation coupling tensor and the magnetic shielding effect is also investigated.

1. INTRODUCTION

It is nowadays well known that when a molecule undergoes end-over-end molecular rotation the motion of its nuclear and electronic charges produces magnetic fields. The interaction between the nuclear magnetic moment and thus produced magnetic fields can usually be expressed

in terms of the following spin-rotation Hamiltonian:¹

$$\hat{H}_{SR} = -\mathbf{I} \cdot \mathbf{C} \cdot \mathbf{J} \quad (1-1)$$

In the above expression \mathbf{I} is the nuclear spin angular momentum vector under consideration, \mathbf{J} the rotational angular momentum of the molecule, and \mathbf{C} the spin-rotation interaction tensor. This spin-rotation interaction may be

detected in the spectroscopy of either nuclear spin (in a molecular beam resonance^{2,3}) or molecular rotation (in microwave spectra^{4,5}). In gases and liquids rotational states of a molecule constantly change because of incessant intermolecular collisions, and as a result the spin-rotation interaction can become an important mechanism for nuclear spin relaxation both in gaseous and liquid phase. Several experimental results have already given indirect evidences for this mechanism.⁶⁻¹⁴

Recently Dubin and Chan¹² have suggested that a magnetic nucleus located on an internal rotor is not only coupled to the rotational magnetic field produced by end-over-end rotation of the molecule but is also coupled to the magnetic field caused by internal rotation of the internal top relative to the molecule-fixed frame and the expression (1-1) should be modified in case there is internal rotational degrees of freedom. This spin-internal-rotation interaction can be quite important since the rotational magnetic field per unit angular momentum is always larger for internal rotation than for end-over-end molecular rotation. The objective of this paper lies in derivation of the interaction Hamiltonian which correctly represents the spin-rotation coupling in the presence of internal rotation. In this paper it will be shown that for a nucleus on a symmetrical internal rotor attached to a frame containing at least two planes of symmetry, such as for a ¹⁹F spin in benzotrifluoride, the spin-rotation Hamiltonian should be modified to

$$\hat{H}_{SR} = -\mathbf{I} \cdot \mathbf{C} \cdot \mathbf{J} - \mathbf{I} \cdot \mathbf{D} \cdot \mathbf{j} \quad (1-2)$$

where \mathbf{J} and \mathbf{j} are the total and internal rotational angular momentum, respectively, and \mathbf{C} and \mathbf{D} are the corresponding coupling tensors for the nuclear spin under consideration. In the expression (1-2) the first term represents the conventional spin-overall-rotation interaction

whereas the second term arises from the interaction between the nuclear spin and the magnetic field due to internal rotation.

Application of the spin-rotation Hamiltonian (1-2) to interpreting the relaxation time data for ¹⁹F spins in benzotrifluoride will be tried in a subsequent paper where we can demonstrate the importance of spin-internal-rotation coupling.

2. ROTATIONAL HAMILTONIAN FOR A POLYATOMIC MOLECULE HAVING A SYMMETRICAL INTERNAL ROTOR

In order to treat the problem of spin-rotation coupling the knowledge regarding rotational motion of a polyatomic molecule is required, and therefore let us briefly review and summarize the results due to Wilson¹⁵ and Lin¹⁶. Consider a rotating frame with a symmetric internal top which can undergo its own rotation with respect to the frame and let ω be the angular velocity of end-over-end rotation of the frame and $\dot{\alpha}$ be the angular velocity for internal rotation with respect to the frame. Then, according to Wilson and Lin the classical kinetic energy of rotation for the entire system is given by

$$T = \frac{1}{2} \omega^+ \cdot \mathbf{I} \cdot \omega + \frac{1}{2} \dot{\alpha}^+ \cdot \mathbf{I}_\alpha \cdot \dot{\alpha} + \frac{1}{2} (\omega^+ \cdot \mathbf{I}_\alpha \cdot \dot{\alpha} + \dot{\alpha}^+ \cdot \mathbf{I}_\alpha \cdot \omega), \quad (2-1)$$

where \mathbf{I} and \mathbf{I}_α represent the inertia tensor of the entire system and the top alone, respectively. Let us designate the three principal axes of the system and the direction cosines of symmetry axis of the internal top with respect to these axes by (a, b, c) and (ξ_a, ξ_b, ξ_c) , respectively. We also denote the three components of ω along the a , b , and c axes and along symmetry axis of the top by $(\omega_a, \omega_b, \omega_c)$ and ω_α , respectively. Then we may write

$$\omega_a = \xi_a \omega_a + \xi_b \omega_b + \xi_c \omega_c \quad (2-2)$$

and

In the component form Eq. (2-1) may be written as

$$T = \frac{1}{2} I_a \omega_a^2 + \frac{1}{2} I_b \omega_b^2 + \frac{1}{2} I_c \omega_c^2 + \frac{1}{2} I_a \dot{\alpha}^2 + I_a \omega_a \dot{\alpha} \quad (2-3)$$

where I_a , I_b , and I_c are the three principal moments of inertia of the entire system, and I_a is the moment of inertia of the internal top about its own symmetry axis.

A conjugate momentum of a canonical variable, say q , is defined by $p = \left(\frac{\partial T}{\partial \dot{q}} \right)$ and thus for T given by (2-3) we may define

$$P_a = \frac{\partial T}{\partial \omega_a} = I_a \omega_a + \xi_a I_a \dot{\alpha},$$

$$P_b = \frac{\partial T}{\partial \omega_b} = I_b \omega_b + \xi_b I_a \dot{\alpha},$$

$$P_c = \frac{\partial T}{\partial \omega_c} = I_c \omega_c + \xi_c I_a \dot{\alpha},$$

and

$$p_\alpha = \frac{\partial T}{\partial \dot{\alpha}} = I_a \dot{\alpha} + I_a (\xi_a \omega_a + \xi_b \omega_b + \xi_c \omega_c) \quad (2-4)$$

It can be shown that P_a , P_b , and P_c are the components of the total rotational angular momentum of the entire system including the internal rotor along a , b , and c axes and p_α is the component of the total rotational angular momentum of the internal top along its symmetry axis. For convenience we introduce an additional angular momentum defined by $p = I_a \dot{\alpha}$, which represents the internal rotational angular momentum of the internal top with respect to the frame (a, b, c) .

In terms of P_a , P_b , P_c , and p , T can be rewritten as

$$T = AP_a^2 + BP_b^2 + CP_c^2 + Dp^2 \quad (2-5)$$

where

$$A = \frac{1}{2I_a}, \quad B = \frac{1}{2I_b}, \quad C = \frac{1}{2I_c}$$

$$D = \frac{1}{2} \left[\frac{1}{I_a} - \left(\frac{\xi_a^2}{I_a} + \frac{\xi_b^2}{I_b} + \frac{\xi_c^2}{I_c} \right) \right] \quad (2-6)$$

It can be seen that p may be written in terms of P_a , P_b , P_c , and p_α as

$$p = \frac{1}{2DI_a} \left[p_\alpha - I_a \left(\frac{\xi_a}{I_a} P_a + \frac{\xi_b}{I_b} P_b + \frac{\xi_c}{I_c} P_c \right) \right] \quad (2-7)$$

which may be considered as a generalized Nielsen transformation.¹⁷ We can also show that quantum mechanical operators corresponding to classical quantities P_a , P_b , P_c , and p_α take the form

$$P_a = -i\hbar \left[\cos \phi \left(\frac{\partial}{\partial \theta} \right)_{\phi\psi\alpha} + \csc \theta \sin \phi \left(\frac{\partial}{\partial \phi} \right)_{\theta\psi\alpha} - \cot \theta \sin \phi \left(\frac{\partial}{\partial \psi} \right)_{\theta\phi\alpha} \right],$$

$$P_b = -i\hbar \times \left[-\sin \phi \left(\frac{\partial}{\partial \theta} \right)_{\phi\psi\alpha} + \csc \theta \cos \phi \left(\frac{\partial}{\partial \psi} \right)_{\theta\phi\alpha} - \cot \theta \cos \phi \left(\frac{\partial}{\partial \phi} \right)_{\theta\psi\alpha} \right],$$

$$P_c = -i\hbar \left(\frac{\partial}{\partial \phi} \right)_{\theta\psi\alpha},$$

and

$$p_\alpha = -i\hbar \left(\frac{\partial}{\partial \alpha} \right)_{\phi\theta\psi}, \quad (2-8)$$

where ϕ , θ , and ψ are the three Eulerian angles (defined in accordance with Goldstein¹⁸) which describe orientation of the molecule-fixed frame (a, b, c) with respect to a stationary frame and α is an internal angle variable which describes rotation of the internal top about its symmetry axis.

Therefore, our rotational Hamiltonian may be written as

$$\hat{H}_{\text{rot}} = AP_a^2 + BP_b^2 + CP_c^2 + Dp^2 + V(\alpha) \quad (2-9)$$

where $V(\alpha)$ is the potential function governing internal rotation of the top.

3. SPIN-ROTATION INTERACTION IN THE PRESENCE OF INTERNAL ROTATION

When a polyatomic molecule with an internal rotor undergoes rotational motion, circulation of electrons and nuclei resulting from molecular rotation produces a rotational magnetic field at the site of a nuclear spin. This magnetic field is supposed to arise from the following two major effects. First, when a molecule executes its rotational motion, electron clouds in it do not perfectly follow the rotation of its nuclear framework. In fact they are supposed to lag slightly behind the nuclear framework, thus producing the net current required to produce a magnetic field. Second, even in the absence of such slippage of electron clouds magnetic fields produced by circulating nuclei and electrons do not exactly cancel each other since electronic charges are not centered on nuclei. Furthermore, there are additional contributions from acceleration of the given nucleus due to the electric field produced by electrons and other nuclei and from the Thomas precession of the given nucleus.

In this section we will formulate the above ideas into a mathematical form in a manner similar to that of Van Vleck¹⁴ and Ramsey.¹⁹ The procedures of formulation are as follows.

(1) Assuming no electronic slippage, we evaluate semiclassically the magnetic field arising from circulation of nuclear and electronic charges. Effect due to acceleration of the given nucleus in the electric field produced by electrons and other nuclei and that of the Thomas precession will be added here. The resulting interaction between the nuclear magnetic moment and thus produced magnetic fields will then be appropriately averaged over electronic states;

(2) To include the perturbing effect of mole-

cular rotation on electronic states we use the Van Vleck formalism where the perturbation is expressed in terms of couplings between rotational and electronic orbital angular momenta. This effect will also be averaged over electronic states using the perturbation theory.

According to classical electrodynamics²⁰ the magnetic field produced by moving nuclear and electronic charges at the site of a given nucleus, say K , may be written

$$H_1 = -\sum'_{K'} \frac{Z_{K'}|e|}{c} \frac{\mathbf{r}_K - \mathbf{r}_{K'}}{r_{KK'}^3} \times \mathbf{v}_{K'} + \sum_k \frac{|e|}{c} \frac{\mathbf{r}_K - \mathbf{r}_k}{r_{Kk}^3} \times \mathbf{v}_k \quad (3-1)$$

where \mathbf{r}_K and \mathbf{r}_k are the position vectors of nucleus K and electron k , respectively, with respect to an appropriately chosen origin (usually chosen at the center of mass of the system) and \mathbf{v}_K and \mathbf{v}_k are the corresponding velocity vectors viewed from the stationary frame. $Z_{K'}|e|$ is the charge of nucleus K' , c the velocity of light, and the summations $\sum'_{K'}$ and \sum_k are performed over all nuclei other than the nucleus K and all electrons in the system, respectively.

Since acceleration of the nucleus K is induced by electric fields due to electrons and other nuclei, we may write the equation of motion in the following form:

$$M_K \frac{d\mathbf{v}_K}{dt} = Z_K |e| \mathbf{E}_K \quad (3-2)$$

where M_K is the mass of nucleus K and \mathbf{E}_K is the electric field at the site of nucleus K . However, to the nucleus moving with velocity \mathbf{v}_K through the electric field \mathbf{E}_K , there will appear to be a magnetic field

$$\mathbf{H}_2 = \mathbf{E}_K \times \mathbf{v}_K / c. \quad (3-3)$$

In addition, there will be the purely kinematical Thomas precession^{20,21} the angular velocity for which is given by

$$\begin{aligned}\omega_K &= (d\omega_K/dt) \times \mathbf{v}_K / 2c^2 \\ &= \frac{Z_K |e|}{2M_K c} \mathbf{E}_K \times \frac{\mathbf{v}_K}{c}\end{aligned}\quad (3-4)$$

where the last step comes from Eq. (3-2). The magnetic field associated with the Thomas precession can be represented by

$$\begin{aligned}\mathbf{H}_3 &= -\frac{\omega_K}{\gamma_K} \\ &= -\frac{Z_K |e|}{2M_K \gamma_K c} \mathbf{E}_K \times \frac{\mathbf{v}_K}{c},\end{aligned}\quad (3-5)$$

where γ_K is the magnetogyric ratio of nucleus K . If we replace γ_K by $g_K \beta_N$, where g_K and β_N are the g -factor of nucleus K and the nuclear magneton, respectively, we may obtain from (3-5)

$$\mathbf{H}_3 = -\frac{Z_K M_P}{g_K M_K} \mathbf{E}_K \times \frac{\mathbf{v}_K}{c}\quad (3-6)$$

where M_P is the mass of proton.

Collecting all the terms in (3-1), (3-3), and (3-6), we may write the internal magnetic field seen at the site of nucleus K due to the motion of electrons and other nuclei in the following form:

$$\begin{aligned}\mathbf{H}_K &= \mathbf{H}_1 + \mathbf{H}_2 + \mathbf{H}_3 \\ &= \sum_{K'} \frac{Z_{K'} |e|}{c} \frac{\mathbf{r}_K - \mathbf{r}_{K'}}{r_{KK'}^3} \times \left(\frac{\mathbf{v}_K}{\beta_K} - \mathbf{v}_{K'} \right) \\ &\quad - \sum_k \frac{|e|}{c} \frac{\mathbf{r}_K - \mathbf{r}_k}{r_{Kk}^3} \times \left(\frac{\mathbf{r}_K}{\beta_K} - \mathbf{v}_k \right),\end{aligned}\quad (3-7)$$

where we have noted that

$$\begin{aligned}\mathbf{E}_K &= \sum_{K'} \frac{Z_{K'} |e| (\mathbf{r}_K - \mathbf{r}_{K'})}{r_{KK'}^3} \\ &\quad - \sum_k \frac{|e| (\mathbf{r}_K - \mathbf{r}_k)}{r_{Kk}^3}\end{aligned}\quad (3-8)$$

β_K is referred to as the nuclear Thomas factor and is defined by

$$\beta_K = \left(1 - \frac{Z_K M_P}{g_K M_K} \right)^{-1}\quad (3-9)$$

For the given nucleus on an internal rotor

the velocity vector \mathbf{v}_K should be replaced by $(\omega + \dot{\alpha}) \times \mathbf{r}_K$ instead of $\omega \times \mathbf{r}_K$.

Then, for the nucleus K which is located on the internal top the magnetic field (3-7) may be rewritten as follows:

$$\begin{aligned}\mathbf{H}_K &= \sum_{K'} \frac{Z_{K'} |e|}{c} \frac{\mathbf{r}_K - \mathbf{r}_{K'}}{r_{KK'}^3} \\ &\quad \times \left\{ \frac{(\omega + \dot{\alpha}) \times \mathbf{r}_K}{\beta_K} - (\omega + \dot{\alpha} \eta_{K'}) \times \mathbf{r}_{K'} \right\} \\ &\quad + \sum_k \frac{|e|}{c} \frac{\mathbf{r}_K - \mathbf{r}_k}{r_{Kk}^3} \times \left\{ \frac{(\omega + \dot{\alpha}) \times \mathbf{r}_K}{\beta_K} - \mathbf{v}_k \right\}\end{aligned}\quad (3-10)$$

where the symbol $\eta_{K'}$ means the value of 1 for nuclei located on the internal top and 0 for otherwise.

The interaction between the nuclear magnetic moment of nucleus K , $\mu_K (= g_K \beta_N \mathbf{I}_K)$, and the magnetic field \mathbf{H}_K can be written in the form

$$\begin{aligned}\hat{H}_1 &= -\mu_K \cdot \mathbf{H}_K \\ &= -g_K \beta_N \mathbf{I}_K \cdot \mathbf{H}_K\end{aligned}\quad (3-11)$$

As we have already pointed out, molecular rotation perturbs the electron clouds surrounding the bare nuclear framework and this perturbing effect may be expressed in terms of couplings between rotational and electronic orbital angular momenta. This coupling effect accounts for the greater part of spin-rotation interaction and can be mathematically formulated by the method of Van Vleck.

When the electron clouds surrounding the nuclear framework are taken into account, the Hamiltonian (2-9) should be modified since only the rotation of bare nuclear framework is involved in the derivation of (2-9). Remembering that only the total angular momentum is conserved when there is some coupling between rotational and electronic orbital angular momenta, we introduce \mathbf{J} and \mathbf{j} defined by

$$\mathbf{J} = \mathbf{P} + \mathbf{L} \quad \text{and} \quad \mathbf{j} = \mathbf{p} + \mathbf{l}\quad (3-12)$$

where, as before, \mathbf{P} is the total rotational angular momentum of bare nuclear framework of the entire molecule in the stationary frame while \mathbf{p} is the internal rotational angular momentum of bare framework of the internal top in the molecule-fixed frame. \mathbf{L} is the total electronic orbital angular momentum in the stationary frame whereas \mathbf{l} may be considered to be the total orbital angular momentum of electrons in the molecule-fixed frame.

Substituting (3-12) into (2-9), we have

$$\begin{aligned} \hat{H}_{rot} = & AJ_a^2 + BJ_b^2 + CJ_c^2 + Dj^2 + V(\alpha) \\ & + AL_a^2 + BL_b^2 + CL_c^2 + Dl^2 \\ & - 2AJ_aL_a - 2BJ_bL_b - 2CJ_cL_c \\ & - 2Dj \cdot l. \end{aligned} \quad (3-13)$$

Since terms involving L_a^2 , etc. is, to a good approximation, a constant of molecular rotation²² we see that the coupling between molecular rotation and electronic motions may be represented by a perturbation term

$$\hat{H}_2 = -2AJ_aL_a - 2BJ_bL_b - 2CJ_cL_c - 2Dj \cdot l. \quad (3-14)$$

In order to obtain an expression for spin-rotation interaction effectively averaged over electronic states we have to evaluate the energy correction due to \hat{H}_1 and \hat{H}_2 using the perturbation theory.*

The first-order energy correction is given by

$$W^{(1)} = \langle 0 | \hat{H}_1 + \hat{H}_2 | 0 \rangle \quad (3-15)$$

while the second-order contribution may be expressed by

$$W^{(2)} = \sum_{n \neq 0} \frac{\langle 0 | \hat{H}_1 + \hat{H}_2 | n \rangle \langle n | \hat{H}_1 + \hat{H}_2 | 0 \rangle}{W_0^{(0)} - W_n^{(0)}} \quad (3-16)$$

where $|0\rangle$ and $|n\rangle$ represent the unperturbed ground and excited electronic states, respectively,

* Average over vibrational states need not be considered since we may assume here the molecule is rigid except that it can undergo internal rotation.

and $W_0^{(0)}$ and $W_n^{(0)}$ are the corresponding energy eigenvalues.

For molecules in their electronic ground state, \hat{H}_2 does not contribute to the first-order energy correction since L_a , etc. have vanishing diagonal elements for the ground state. However, they have nonvanishing off-diagonal elements and give the second-order contribution. The same thing is also true for the term involving v_k in \hat{H}_1 . Thus, we can write

$$\begin{aligned} W^{(1)} = & -g_K\beta_N \sum_K' \frac{Z_{K'}|e|}{c} \langle 0 | \mathbf{I}_K \cdot \frac{\mathbf{r}_K - \mathbf{r}_{K'}}{r_{KK'}^3} \\ & \times \left\{ \frac{(\boldsymbol{\omega} + \dot{\boldsymbol{\alpha}}) \times \vec{r}_K}{\beta_K} - (\boldsymbol{\omega} + \dot{\boldsymbol{\alpha}}\eta_K) \times \vec{r}_K \right\} | 0 \rangle \\ & + g_K\beta_N \sum_K' \frac{|e|}{c} \langle 0 | \mathbf{I}_K \cdot \frac{\mathbf{r}_K - \mathbf{r}_k}{r_{Kk}^3} \\ & \times \frac{(\boldsymbol{\omega} + \dot{\boldsymbol{\alpha}}) \times \mathbf{r}_K}{\beta_K} | 0 \rangle \end{aligned} \quad (3-17)$$

and

$$\begin{aligned} W^{(2)} = & - \sum_{n \neq 0} \frac{4g_K\beta_N}{W_0^{(0)} - W_n^{(0)}} \text{Re} \{ \langle 0 | \mathbf{I}_K \cdot \boldsymbol{\pi}_K | n \rangle \\ & \times \langle n | AJ_aL_a + BJ_bL_b + CJ_cL_c + Dj \cdot l | 0 \rangle \} \end{aligned} \quad (3-18)$$

where the symbol Re means taking real part of the complex function on the righthand side of it and $\boldsymbol{\pi}_K$ is given by

$$\boldsymbol{\pi}_K = \sum_k \frac{|e|}{mc} \frac{(\mathbf{r}_k - \mathbf{r}_K) \times m\mathbf{v}_k}{r_{Kk}^3} \quad (3-19)$$

with m indicating the mass of electron.

According to the Hellmann-Feynman theorem^{23,24} we may write

$$\begin{aligned} & \langle 0 | \sum_K' \frac{\mathbf{r}_K - \mathbf{r}_k}{r_{Kk}^3} | 0 \rangle \\ & = - \frac{\mathbf{F}_K}{Z_K e^2} + \sum_{K'}' \frac{Z_{K'}(\mathbf{r}_K - \mathbf{r}_{K'})}{r_{KK'}^3} \end{aligned} \quad (3-20)$$

where \mathbf{F}_K is the force acting on nucleus K .

Because of the relation (3-20) Eq. (3-17) can further be simplified to

$$W^{(3)} = g_K \beta_N \sum_{K'} \frac{Z_{K'} |e|}{c} \mathbf{I}_K \cdot \left[\frac{\mathbf{r}_K - \mathbf{r}_{K'}}{r_{KK'}^3} \times (\boldsymbol{\omega} + \dot{\boldsymbol{\alpha}}) \times \mathbf{r}_{K'} \right] - \frac{g_K \beta_N}{c Z_K |e|} \mathbf{I}_K \cdot \mathbf{F}_K \times \frac{(\boldsymbol{\omega} + \dot{\boldsymbol{\alpha}}) \times \mathbf{r}_K}{\beta_K} \quad (3-21)$$

Finally, using the relations between components of angular velocities and momenta similar to those given by (2-4) and the vector identity

$$\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B})$$

and collecting from (3-18) and (3-21) the terms bilinear with respect to \mathbf{I}_K and \mathbf{J} or \mathbf{j} , we can show that the spin-rotation interaction for a nucleus on internal top may be written

$$\hat{H}_{SR} = -\mathbf{I}_K \cdot \mathbf{C}(K) \cdot \mathbf{J} - \mathbf{I}_K \cdot \mathbf{D}(K) \cdot \mathbf{j}, \quad (3-22)$$

where the components of spin-rotation coupling tensors $\mathbf{C}(K)$ and $\mathbf{D}(K)$ are given as follows:

$$\begin{aligned} C(K)_{gg'} = & -g_K \beta_N \sum_{K'} \frac{Z_{K'} |e|}{c r_{KK'}^3} \left[\frac{1}{I_g} (\mathbf{r}_K - \mathbf{r}_{K'}) \cdot \right. \\ & \left. \mathbf{r}_{K'} \delta_{gg'} - \frac{1}{I_{g'}} (\mathbf{r}_K - \mathbf{r}_{K'})_{g'} (\mathbf{r}_{K'})_g \right] + \frac{2g_K \beta_N}{I_{g'}} \times \\ & Re \sum_{n \neq 0} \left[\langle 0 | (\boldsymbol{\pi}_K)_g | n \rangle \times \langle n | L_{g'} | 0 \rangle / (W_0^{(0)} \right. \\ & \left. - W_n^{(0)}) \right] + \frac{g_K \beta_N}{c \beta_K Z_K |e|} \left[\frac{1}{I_g} \mathbf{F}_K \cdot \mathbf{r}_K \delta_{gg'} \right. \\ & \left. - \frac{1}{I_{g'}} (\mathbf{F}_K)_{g'} (\mathbf{r}_K)_g \right] \end{aligned} \quad (3-23)$$

and

$$\begin{aligned} D(K)_{gg'} = & g_K \beta_N \sum_{K'} \frac{Z_{K'} |e|}{c r_{KK'}^3} \left[\left(\frac{1}{I_g} - \frac{\eta_{K'}}{I_\alpha} \right) \right. \\ & \left. (\mathbf{r}_K - \mathbf{r}_{K'}) \cdot \mathbf{r}_{K'} \delta_{gg'} - \left(\frac{1}{I_{g'}} - \frac{\eta_{K'}}{I_\alpha} \right) \right. \\ & \left. (\mathbf{r}_K - \mathbf{r}_{K'})_{g'} (\mathbf{r}_{K'})_g \right] \\ & + 4Dg_K \beta_N Re \sum_{n \neq 0} \left[\xi_{g'} \langle 0 | (\boldsymbol{\pi}_K)_g | n \rangle \cdot \right. \\ & \left. \langle n | \mathbf{I} | 0 \rangle / (W_0^{(0)} - W_n^{(0)}) \right] \\ & - \frac{g_K \beta_N}{c \beta_K Z_K |e|} \left[\left(\frac{1}{I_g} - \frac{1}{I_\alpha} \right) \mathbf{F}_K \cdot \mathbf{r}_K \delta_{gg'} \right. \\ & \left. - \left(\frac{1}{I_g} - \frac{1}{I_\alpha} \right) (\mathbf{F}_K)_{g'} (\mathbf{r}_K)_g \right] \end{aligned} \quad (3-24)$$

Thus we have shown that for a magnetic nucleus on a symmetric internal rotor the spin-rotation interaction should be written in the form given by (1-2) of the introductory section. The first part of (3-22) represents the spin-overall-rotation coupling whereas the second part provides the coupling between nuclear spin and internal rotation. For completely rigid molecules where no internal rotation is allowed $\mathbf{j}=0$ and the expression (3-22) is reduced to the ordinary form of spin-rotation Hamiltonian such as given by (1-1).

Although the explicit forms of spin-rotation coupling tensors \mathbf{C} and \mathbf{D} have been derived, nonempirical calculation of them is usually not possible because such calculation requires the knowledge of excited electronic states which are not available in general. In a few cases²⁵ they could be determined semiempirically and were utilized. Nevertheless, the derived result [Eq. (3-22)] is of great importance because we can show that it provides a correct way of interpreting the spin-lattice relaxation time data for ¹⁹F spins in benzotrifluoride. Neglect of the second part of (3-22) has turned out to give erroneous interpretation.²⁶ We will discuss further detail of this problem in a subsequent paper. In the next section we investigate how the spin-rotation coupling tensor is related to the magnetic shielding tensor.

4. THEORY OF MAGNETIC SHIELDING FOR A NUCLEUS ON INTERNAL TOP AND SCHWARTZ RELATION IN THE PRESENCE OF INTERNAL ROTATION

In a molecule exposed to a static field H_0 the local magnetic field "felt" by a nuclear spin at a given site is not usually equal to the external field. This shielding effect is mainly due to the motion of electrons in the molecule induced by the applied external field. Besides

this direct effect the external field can also indirectly change the electronic states via nuclear spin-electron spin coupling, thus giving an additional shielding effect. The induced magnetic field is usually expressed up to the first-order of external field H_0 in the form

$$H_{ind} = -\sigma \cdot H_0, \quad (4-1)$$

where σ is called the magnetic shielding tensor for a given nucleus.

Using the perturbation theory, it can be shown that matrix elements of σ are given by ²⁷

$$\begin{aligned} \sigma(K)_{gg'} &= \frac{e^2}{2mc^2} \langle 0 | \sum_k \frac{r_{Kk}^2 \delta_{gg'} - (r_{Kk})_g (r_{Kk})_{g'}}{r_{Kk}^3} | 0 \rangle \\ &+ \frac{e^2}{2mc^2} \langle 0 | \sum_k \frac{r_{0K} \cdot r_{Kk} \delta_{gg'} - (r_K)_g (r_{Kk})_{g'}}{r_{Kk}^3} | 0 \rangle \\ &+ \frac{|e|}{mc} \text{Re} \sum_{n \neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W_0^{(0)} - W_n^{(0)}} \end{aligned} \quad (4-2)$$

where L and π_K were previously defined and

$$r_{Kk} = r_K - r_k.$$

Application of the Hellmann-Feynman theorem [Eq. (3-21)] to (4-2) gives us

$$\begin{aligned} \sigma(K)_{gg'} &= \frac{e^2}{2mc^2} \langle 0 | \sum_k \frac{r_{Kk}^2 \delta_{gg'} - (r_{Kk})_g (r_{Kk})_{g'}}{r_{Kk}^3} | 0 \rangle \\ &- \frac{e^2}{2mc^2} \sum_{K'} \frac{Z_{K'}}{r_{KK'}^3} [r_K \cdot (r_K - r_{K'}) \delta_{gg'} \\ &- (r_K)_g (r_{K'})_{g'}] \\ &+ \frac{1}{2Z_K mc^2} [r_K \cdot F_K \delta_{gg'} - (r_K)_g (F_K)_{g'}] \\ &+ \frac{|e|}{mc} \text{Re} \sum_{n \neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W_0^{(0)} - W_n^{(0)}} \end{aligned} \quad (4-3)$$

The first term on the righthand side of (4-3) is known to be responsible for diamagnetic shielding while the remaining terms are considered to give the effect of paramagnetic shielding. Thus, for convenience, we write

$$\sigma(K)_{gg'}^D = \frac{e^2}{2mc^2} \langle 0 | \sum_k \frac{r_{Kk}^2 \delta_{gg'} - (r_{Kk})_g (r_{Kk})_{g'}}{r_{Kk}^3} | 0 \rangle \quad (4-4)$$

and

$$\begin{aligned} \sigma(K)_{gg'}^P &= -\frac{e^2}{2mc^2} \sum_{K'} \frac{Z_{K'}}{r_{KK'}^3} [r_K \cdot (r_K - r_{K'}) \delta_{gg'} \\ &- (r_K)_g (r_{K'})_{g'}] \\ &+ \frac{1}{2Z_K mc^2} [r_K \cdot F_K \delta_{gg'} - (r_K)_g (F_K)_{g'}] \\ &+ \frac{|e|}{mc} \text{Re} \sum_{n \neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W_0^{(0)} - W_n^{(0)}}, \end{aligned} \quad (4-5)$$

where the superscripts D and P indicate diamagnetic and paramagnetic shielding, respectively.

Nonempirical calculation of the term

$$\text{Re} \sum_{n \neq 0} \frac{\langle 0 | (\pi_K)_g | n \rangle \langle n | L_{g'} | 0 \rangle}{W_0^{(0)} - W_n^{(0)}} \quad (4-6)$$

requires the knowledge regarding electronically excited states, as we have already pointed out, which is not possible presently. Therefore, in order to calculate theoretically either $C(K)_{gg'}$ or $\sigma(K)_{gg'}$, we cannot help relying on some approximate or semiempirical means. Though there have been several recent successful attempts at the calculation of proton and fluorine chemical shifts, employing the variational procedures²⁸ and the perturbed Hartree-Fock SCF method^{29, 30} calculation of the term such as (4-6) still remains formidable. Therefore, whenever feasible, a direct experimental determination of either $C(K)_{gg'}$ or $\sigma(K)_{gg'}$ is desirable.

In this connection it is of great interest to relate $\sigma(K)_{gg'}$ to $C(K)_{gg'}$ since experimental determination of either of them enables us to calculate the other.

From (3-23) and (4-5) we obtain

$$\begin{aligned} \sigma(K)_{gg'}^P &= -\frac{e^2}{2mc} \sum_{K'} \frac{Z_{K'}}{r_{KK'}^3} [(r_K - r_{K'}) \cdot (r_K \\ &- r_{K'}) \delta_{gg'} - (r_K - r_{K'})_g (r_K - r_{K'})_{g'}] \\ &+ \frac{|e|}{2mc} \frac{I_g C(K)_{gg'}}{g_K \beta_N} \\ &+ \frac{1}{2Z_K mc^2} \left(1 - \frac{1}{\beta_K}\right) [r_K \cdot F_K \delta_{gg'} \\ &- (r_K)_g (F_K)_{g'}] \end{aligned} \quad (4-7)$$

A relation similar to (4-7) was first derived by Schwartz³¹ for the case of completely rigid molecules and is called the Schwartz relation. Comparing (4-7) with that derived by Schwartz, two relations are coincident except that in the presence of internal rotation we have an extra term involving the Hellmann-Feynman force. For completely rigid molecules the forces acting on a given nucleus are balanced out to zero and in this case our relation (4-7) is reduced to that of Schwartz. In case the molecule is symmetrical about its axis of internal rotation, such as in φ -CF₃ and CF₃NO₂ the term $\mathbf{r}_K \cdot \mathbf{F}_K$ vanishes since the position vector \mathbf{r}_K is always perpendicular to the force \mathbf{F}_K . However, even in this case the term $(\mathbf{r}_K)_g (\mathbf{F}_K)_g$ does not vanish, giving an additional effect.

5. CONCLUSION

We have thus far proven that in the presence of internal rotation the spin-rotation Hamiltonian for a magnetic nucleus should be written in the form of (1-2) instead of the usual expression of spin-rotation Hamiltonian (1-1). First part of the derived spin-rotation Hamiltonian is seen to represent the spin-overall-rotation interaction while the second is due to the spin-internal-rotation interaction. We have also derived the explicit forms of corresponding spin-rotation coupling tensor using the method of Ramsey and Van Vleck. Unlike the case of completely rigid molecule coupling tensors are dependent on the internal angle variable α .

The Schwartz relation in the presence of internal rotation has also been investigated and the result shows that except that an extra term involving the Hellmann-Feynman force there is no essential difference between ours and the original Schwartz relation. Finally, application of the result obtained here to the interpretation

of spin relaxation time data will be discussed in a paper subsequent to this work.

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