Spin-Rotational Relaxation of a Nuclear Spin on an Internal Rotor

Jo Woong Lee

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151, Korea

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A magnetic nucleus located on an internal rotor can interact with magnetic fields arising from end-over-end molecular rotation as well as internal rotation. In this paper the expressions for spin-rotational relaxation times, $T_{1,SR}$ and $T_{2,SR}$, are derived for such nucleus with the anisotropy of molecular rotation explicitly taken into consideration. The derived expressions are shown to be composed of two parts, the contribution from spin-overall-rotation coupling and that from spin-internal-rotation coupling. Some remarks on the use of derived expressions are also provided.

Introduction

It has previously been shown[1,2] that a magnetic nucleus located on an internal rotor can interact with magnetic fields arising from rotation of internal rotor itself with respect to the molecule-fixed frames as well as end-over-end rotation of the entire molecule and the corresponding spin-rotation coupling Hamiltonian may be written in the form

$$\mathscr{H}_{SR} = -\boldsymbol{I}\cdot\boldsymbol{C}\cdot\boldsymbol{J} - \boldsymbol{I}\cdot\boldsymbol{D}\cdot\boldsymbol{j} \tag{1}$$

where $\boldsymbol{I}$ is the nuclear spin angular momentum operator, $\boldsymbol{J}$ and $\boldsymbol{j}$ are the total and internal rotational angular momentum, respectively, and $\boldsymbol{C}$ and $\boldsymbol{D}$ are the corresponding coupling tensors for the nuclear spin under consideration. The first term of the righthand side of Eq.(1) will be named as the spin-overall-rotation coupling while the second term may be referred to as the spin-internal-rotation coupling.

Earlier, Dubin and Chan[1] have derived an expression for the spin-rotational relaxation time, $T_{1,SR}$, for a nucleus on an internal rotor assuming the interaction of nucleus with magnetic field arising from rotation of the internal rotor is the dominant relaxation mechanism. Their expression, however, has not found much application to actual interpretation of the spin-rotational relaxation data for a nucleus on an internal rotor because of inherent difficulty in understanding the physical meaning of the correlation time involved in their derivation. Later, Burke and Chan[3] have proposed another expression for $T_{1,SR}$ assuming that the magnetic field arising from internal rotation fluctuates independently of that from overall rotation of the entire molecule, and this expression has usefully been exploited by Jonas and his collaborators[4,5] and Suchanski and Canepa,[6] not to mention Chan and his coworkers.[3,7]

Unfortunately, Burke and Chan have treated the problem under the assumption that overall rotation of the entire molecule is isotropic and that the results obtained by Hubbard[8] can be applied to this case. Such formulation casts some doubts on the applicability of the derived expression to a large number of molecules. In particular, when the effect of anisotropy in rotational motions is emphasized, it cannot provide a proper basis for discussion. Thus a more general expression seems to be required.

In this paper we will derive an explicit expression for $T_{1,SR}$ and $T_{2,SR}$ on the basis of Hubbard's theory of relaxation[9] with the anisotropy of overall rotational motion fully taken into consideration from the outset and some discussion on the application of the derived expression will be presented.

Density Operator Theory of Spin Relaxation

Since the pioneering work of Bloembergen, Purcell, and Pound several classic papers on the microdynamical theory of nuclear spin relaxation have appeared and they are well summarized in the books by Abragam[10] and Slichter.[11] In particular Hubbard[9] has shown that both quantum mechanical and semiclassical forms of density operator relaxation theory can be derived from a common formulation. Before delving into actual treatment of spin-rotational relaxation in the presence of internal rotation we will briefly review and recapitulate the Hubbard's treatment of spin relaxation.

Suppose we have a spin system which can interact with its surroundings and let the Hamiltonian for this spin system and its molecular surroundings (called the "bath") be written as

$$\mathscr{H} = \hbar[E(s) + F(q) + G(q,s)] \tag{2}$$

where $\hbar E(s)$ is the part of the Hamiltonian that depends only on the spin variables s, $\hbar F(q)$ is the Hamiltonian for the bath whose variable is denoted symbolically by q, and $G(q,s)$ represents the interaction between the spin system and the bath.

All the interactions of interest can be written in the form

$$G(q,s) = \sum_k U^k(q)\, V^k(s) \tag{3}$$

where $U^k(q)$ and $V^k(s)$ operate, respectively, on variables of the bath and the spin system. We have to note that $G(q,s)$ must be Hermitian even though $U^k(s)$ and $V^k(s)$ need not be so. This can be accomplished by defining U^k and V^k such that

$$U^{-k} = (U^k)^\dagger, \quad V^{-k} = (V^k)^\dagger \tag{4}$$

Let us define the time-dependent Heisenberg operators $U^k(t)$ and $V^k(t)$ as follows:

$$U^k(t) = e^{iFt}\, U^k\, e^{-iFt} \tag{5}$$

and

$$V^k(t) = e^{iEt}\, V^k\, e^{-iEt} \tag{6}$$

$V^k(t)$ is usually expandable into the following form of series:

$$V^k(t) = \sum_q V_q{}^k \exp(i\omega_q{}^k t) \tag{7}$$

The density operator for the entire system (spin system +bath), $\rho(t)$, evolves according to the equation

$$d\rho/dt = -i[E+F+G, \rho] \tag{8}$$

Since the heat capacity of bath is usually much larger than that of the spin system, to a good approximation the bath can be considered to be at thermal equilibrium at all times. Thus one may write

$$\rho(q, s, t) = \sigma(s, t)\rho^T(q) \tag{9}$$

where $\sigma^T(q)$ is the boltzmann equilibrium density operator for the bath; that is,

$$\rho^T(q) = e^{-\hbar F/kT} / Tr_q(e^{-\hbar F/kT}) \tag{10}$$

with k and T denoting the Boltzmann constant and absolute temperature of the bath, respectively.

After somewhat lengthy discussion Hubbard has shown that at high temperature ($\hbar E << kT$) and in the presence of strong magnetic field the density operator for the spin system alone should satisfy the following equation:

$$\frac{d}{dt}\sigma = -i[E, \sigma] + R(\sigma - \sigma^T) \tag{11}$$

where $R(\sigma-\sigma^T)$ is the so-called relaxation superoperator given by

$$R(\sigma-\sigma^T) = \sum_{k,l,q} J_{lk}(\omega_q{}^l)[[V_q{}^l,\ \sigma-\sigma^T], V^k] \tag{12}$$

with σ^T being the equilibrium density operator for spin system defined by

$$\sigma^T = e^{-\hbar E/kT} / Tr(e^{-\hbar E/kT}) \tag{13}$$

and the spectral density $J_{lk}(\omega)$ is defined as

$$J_{lk}(\omega) = \frac{1}{4}\int_{-\infty}^{\infty} [K_{lk}(\tau) + K_{kl}(-\tau)]\, e^{i\omega\tau}\, d\tau \tag{14}$$

with $K_{lk}(\tau)$ being given by

$$\begin{aligned} K_{lk}(\tau) &= Tr_q[\rho_q{}^T\, U^l(t+\tau)\ U^k(t)] \\ &\equiv \overline{U^l(t+\tau)\, U^k(t)} \end{aligned} \tag{15}$$

It is obvious from Eq. (14) that $J_{lk}(-\omega) = J_{kl}(\omega)$. Eq. (11) will be the starting point for our derivation of spin-rotational relaxation time expressions.

Spin-Rotational Relaxation of a Nuclear on an Internal Rotor

In deriving the expressions for $T_{1,\mathrm{SR}}$ and $T_{2,\mathrm{SR}}$ for a nuclear spin on an internal rotor we shall restrict our attention to the case where the nucleus under consideration is located on the axis of internal rotation which coincides with the molecular symmetry axis. Such limitation has been brought forth not only for mathematical convenience but also for our interest in studying the relaxation of ^{13}C spin on methyl and trisubstituted methyl groups in organic molecules such as toluene, nitromethane, benzotrifluoride, etc. We will denote three principal axes of molecular inertia tensor by a, b, and c, one of which, say the c-axis, is assumed to coincide with the axis of internal rotation as well as with that of molecular symmetry. Also, three principal moments of inertia of the entire molecule are, respectively, denoted by $\mathcal{I}_a$, $\mathcal{I}_b$, and $\mathcal{I}_c$, and the moment of inertia of internal rotor about its axis of rotation by $\mathcal{I}_\alpha$.

It can be shown from the previous results[1,2] that for a nuclear spin on the axis of internal rotation which coincides with the molecular symmetry axis the spin-rotation coupling Hamiltonian given by Eq. (1) can further be simplified to

$$\mathscr{H}_{SR} = -\sum_g C_{gg}\, I_g\, J_g - D_\alpha\, I_c\, j \tag{16}$$

because for such nucleus the coupling tensors $\boldsymbol{C}$ and $\boldsymbol{D}$ become diagonal in the coordinates system $(a, b,\ c)$. In Eq. (16) I_g and J_g are, respectively, the components of the nuclear spin vector $\boldsymbol{I}$ and the rotational angular momentum $\boldsymbol{J}$ along the g-th principal axis, C_{gg} is the principal value of the tensor C along the g-axis, j is the component of internal rotational angular momentum $\boldsymbol{j}$ along the axis of internal rotation, and D_α is the principal value of $\boldsymbol{D}$ along the axis of internal rotation.

In order to facilitate the adaptation of Hubbard's theory to our case we now introduce the following components of first rank spherical tensor of spin operator:

$$I_0 = I_c,\quad I_{\pm 1} = \mp\frac{1}{\sqrt{2}}(I_a \pm i\, I_b) \tag{17}$$

In terms of such components of spherical tensor the interaction $G(q, s)$ may now be expressed as

$$G(q, s) = \hbar^{-1}\mathscr{H}_{SR} = \sum_k A_k\, I_k \tag{18}$$

where

$$\begin{aligned} A_{+1} &= \frac{1}{\sqrt{2}}(C_{aa}\, J_a - i\, C_{bb}\, J_b)/\hbar, \\ A_0 &= -(C_{cc}\, J_c + D_\alpha\, j)/\hbar, \\ A_{-1} &= -\frac{1}{\sqrt{2}}(C_{aa}\, J_a + i\, C_{bb}\, J_b)/\hbar. \end{aligned} \tag{19}$$

In Eqs. (16), (18) and (19) the nuclear spin vector and the rotational angular momentum have both been expressed in terms of their components in the molecule-fixed coordinates in which $\boldsymbol{C}$ and $\boldsymbol{D}$ are diagonal. However, the magnetic resonance experiments are performed in the space-fixed coordinates system (x, y, z) that is determined by the direction of externally applied magnetic field. The two coordinates systems are related to each other by a rotation which can be defined by a set of Eulerian angles $\Omega(\theta, \phi, \psi)$. It is necessary, therefore, to relate the Hamiltonian to the space-fixed coordinates system at least inasmuch as the components of spin vector are concerned. Such transformation may be effected if the Wigner rotation matrix of first-order, $\mathscr{D}^{(1)}(\Omega)$, is employed as follows:[12]

$$I_p = \sum_{q=-1}^{1} \mathscr{D}^{(1)}(\Omega)^*{}_{qp}\, \tilde{I}_q, \tag{20}$$

where $\tilde{I}_q$'s are the components of spherical tensor defined by Eq. (17) in the molecule-fixed coordinates (*a*, *b*, *c*) and $\tilde{I}_q$'s denote the similarly defined components in the space-fixed coordinates (*x*, *y*, *z*).

Application of the transformation defined by Eq. (20) to Eq. (18) will lead to the expression

$$G(q,s)=\sum_k A_k \sum_q \mathcal{D}^{(1)}(\Omega)^*_{qk}\tilde{I}_q = \sum_q U_q \tilde{I}_q \tag{21}$$

where

$$U_q=\sum_k \mathcal{D}^{(1)}(\Omega)^*_{qk} A_k \tag{22}$$

In order to derive the expressions for relaxation times we now return to Eq. (11). Comparing Eq. (21) with Eq. (3), $V^k(s)$ is identified with $\tilde{I}_q$. Multiplying Eq. (11) by $\tilde{I}_q$ and taking the trace, one obtains

$$\frac{d}{dt}<\tilde{I}_q>=-i\,Tr([E,\sigma]\,\tilde{I}_q)+Tr(R(\sigma-\sigma^T)\tilde{I}_q) \tag{23}$$

where $<\tilde{I}_q>$ means $Tr(\sigma\tilde{I}_q)$

Since $E=-\omega_0\tilde{I}_0$, where ω_0 is the Larmor frequency of the nuclear spin of interest, and

$$Tr([E,\sigma]\,\tilde{I}_q)=\omega_0\,Tr(\sigma[\tilde{I}_0,\tilde{I}_q])$$

Eq. (23) may be rewritten as

$$\frac{d}{dt}<\tilde{I}_q>=-i\,\omega_0\,Tr(\sigma[\tilde{I}_0,\tilde{I}_q])+Tr\{R(\sigma-\sigma^T)\tilde{I}_q\}$$

Noting the commutation rule $[\tilde{I}_0,\ \tilde{I}_q]=-(-1)^q q\,\tilde{I}_q$, we have

$$\frac{d}{dt}<\tilde{I}_q>=i(-1)^q\omega_0 q<\tilde{I}_q>+Tr\{R(\sigma-\sigma^T)\tilde{I}_q\} \tag{24}$$

The last term on the righthand side of Eq.(24) may now be calculated as follows. Since $e^{-i\omega_0 I_0 t}\,\tilde{I}_q\,e^{i\omega_0 I_0 t}=e^{-iq\omega_0 t}\,\tilde{I}_q$, we have

$$\begin{aligned}&Tr\{R(\sigma-\sigma^T)\,\tilde{I}_q\}\\&=\sum_{k=-1}^{1}\ \sum_{l=-1}^{1} J_{lk}(-l\omega_0)\ Tr\{[[\tilde{I}_l,\sigma-\sigma^T],\tilde{I}_k]\tilde{I}_q\}\\&=\sum_k\sum_l J_{lk}(-l\omega_0)\ Tr\{(\sigma-\sigma^T)[[\tilde{I}_k,\tilde{I}_q],\tilde{I}_l]\}.\end{aligned} \tag{25}$$

Recalling the commutation relation $[\tilde{I}_k,\tilde{I}_q]=\xi(k,q)\tilde{I}_{k+q}$, where $\xi(0,q)=q$ and $\xi(\pm1,q)=[(1\mp q)(2\pm q)]^{1/2}$, we can obtain from Eq. (25)

$$\begin{aligned}&Tr\{R(\sigma-\sigma^T)\tilde{I}_q\}\\&=\sum_k\sum_l J_{lk}(-l\omega_0)\,\xi(k,q)\xi(k+q,l)\\&\qquad\times(<\tilde{I}_{k+q+l}>-<\tilde{I}_{k+q+l}>_T)\end{aligned} \tag{26}$$

where $<Q>_T$ means $Tr(\sigma^T Q)$.

Substitution of Eq. (26) into Eq. (24) yields

$$\begin{aligned}\frac{d}{dt}<\tilde{I}_q>&=i(-1)^q q\,\omega_0<\tilde{I}_q>\\&\quad+\sum_k\sum_l J_{kl}(-\omega_0)\,\xi(k,q)\,\xi(k+q,l)\\&\quad\times(<\tilde{I}_{k+q+l}>-<\tilde{I}_{k+q+l}>_T).\end{aligned} \tag{27}$$

Setting $q=0$ and $k+l=0$ we have

$$\begin{aligned}\frac{d}{dt}<\tilde{I}_0>&=[J_{1,-1}(-\omega_0)+J_{-1,1}(\omega_0)]\\&\quad\times(<\tilde{I}_0>-<\tilde{I}_0>_T).\end{aligned} \tag{28}$$

Also, by setting $q=\pm1$ and $k+l=0$ we have

$$\begin{aligned}\frac{d}{dt}<\tilde{I}_{\pm1}>&=\mp i\,\omega_0<\tilde{I}_{\pm1}>\\&\quad-[J_{0,0}(0)-J_{1,-1}(-\omega_0)]<\tilde{I}_{\pm1}>\end{aligned} \tag{29}$$

where use has been made of the fact that $<\tilde{I}_{\pm1}>_T=0$.

Thus, from Eqs. (28) and (29) we obtain the following formal expressions for T_1 and T_2:

$$\frac{1}{T_1}=-[J_{1,-1}(-\omega_0)+J_{-1,1}(\omega_0)]=-2J_{-1,1}(\omega_0) \tag{30}$$

and

$$\frac{1}{T_2}=J_{0,0}(0)-J_{1,-1}(-\omega_0) \tag{31}$$

We now have to evaluate $J_{lk}(\omega)$'s from Eqs. (14), (15), and (21). When we try to evaluate $\overline{U_q(t+\tau)U_{q'}(t)}$, the correlation functions involving both the rotational angular momentum and the molecular orientation, such as shown below, will appear.

$$\overline{[J_g\mathcal{D}^{(1)}(\Omega)^*_{qk}]_{t+\tau}\,[J_{g'}\mathcal{D}^{*(1)}(\Omega)^*_{q'k'}]_t} \tag{32}$$

Evaluation of such correlation functions requires that we have to know the probability that the molecule will take the angular momentum $J(t+\tau)$ and orientation $\Omega(t+\tau)$ at a later time $t+\tau$ when it was known to have the angular momentum $J(t)$ and orientation $\Omega(t)$ at time t. Unfortunately, such a knowledge is unavailable as yet. If, however, the correlation time for fluctuation of the rotational angular momentum, τ_J, is very much different from that for the change of orientation, τ_Ω, we may assume

$$\begin{aligned}&\overline{[J_g\mathcal{D}^{(1)}(\Omega)^*_{qk}]_{t+\tau}\ [J_{g'}\mathcal{D}^{(1)}(\Omega)^*_{q'k'}]_t}\\&\approx\overline{J_g(t+\tau)\ J_{g'}(t)}\times\overline{[\mathcal{D}^{(1)}(\Omega)^*_{qk}]_{t+\tau}\,[\mathcal{D}^{(1)}(\Omega)^*_{q'k'}]_t}\end{aligned} \tag{33}$$

Such a separability approximation has also been adopted by Hubbard[8] and Atkins.[13] Of course, the validity of Eq. (33) will depend on the detailed nature of molecular rotation in fluid phase which is not very well known up to the present time. In the rotational diffusion limit where $\tau_J \ll \tau_\Omega$ such validity is well guaranteed; on the other hand, for small and nonpolar molecules, especially at high temperature, the inertial effect plays an important role in which case τ_J is comparable to τ_Ω in magnitude.[14] Thus in the inertial limit the evaluation of correlation functions given by Eq. (32) would be difficult.[15] Therefore we will restrict our attention to the case where end-over-end molecular rotation can be described by the rotational diffusion model.

The orientational correlation functions of the type

$$\overline{[\mathcal{D}^{(\mu)}(\Omega)^*_{qk}]_{t+\tau}\,[\mathcal{D}^{(\mu)}(\Omega)^*_{q'k'}]_t} \tag{34}$$

may be calculated on the basis of Perrin-Favro rotational diffusion equation[16,17] for anisotropic motions if molecular reorientational changes occur as a series of small angle jumps.

and the results have been tabulated up to $\mu=3$ by Lee.[18] In particular when $\mu=1$, we have

$$\overline{[\mathcal{D}^{(1)}(\Omega)_{qk}{}^*]_{t+\tau}[\mathcal{D}^{(1)}(\Omega)^*{}_{q'k'}]_t}$$
$$=\frac{1}{3}(-1)^{q'+k'}\,\delta_{-k,k'}I^{(1)}{}_{q'k'}(\tau)$$
$$(k,k',q,q'=0,\pm1) \tag{35}$$

where

$$I^{(1)}_{1,1}(t)=I^{(1)}_{-1,-1}(t)=\frac{1}{2}e^{-\Delta_c|t|}(e^{-\Delta_a|t|}+e^{-\Delta_b|t|}),$$
$$I^{(1)}_{1,-1}(t)=I^{(1)}_{-1,1}(t)=\frac{1}{2}e^{-\Delta_c|t|}(e^{-\Delta_a|t|}-e^{-\Delta_b|t|}),$$
$$I^{(1)}_{1,0}(t)=I^{(1)}_{0,1}(t)=I^{(1)}_{-1,0}(t)=I^{(1)}_{0,-1}(t)=0,$$
$$I^{(1)}_{0,0}(t)=e^{-(\Delta_a+\Delta_b)|t|} \tag{36}$$

In Eq. (36) Δ_a, Δ_b, and Δ_c represent three principal values of the rotational diffusion tensor Δ. Note that $I^{(1)}_{pq}(t)$'s are even functions of time t.

Substitution of Eq. (2) into Eq. (15) and use of the results obtained in the above discussion will lead us to the following expression:

$$K_{qq'}(\tau)\equiv\overline{U_q(t+\tau)U_{q'}(t)}$$
$$=\frac{1}{3}(-1)^q I^{(1)}_{q',-q}(\tau)\{C_{aa}{}^2\,\overline{J_a(t+\tau)J_a(t)}$$
$$+C_{bb}{}^2\,\overline{J_b(t+\tau)J_b(t)}+C_{cc}{}^2\,\overline{\mathcal{J}_c(t+\tau)\mathcal{J}_c(t)}\}/\hbar^2. \tag{37}$$

In the above expression $\mathcal{J}_c$ has been defined by the relation

$$\mathcal{J}_c=J_c+(D_\alpha/C_{cc})j \tag{38}$$

Eq. (37) can be expressed in an alternative form if we introduce a new coupling constant C_α which has been named as the spin-internal-rotation coupling constant by Dubin and Chan.[1] From the properties of spin-rotation coupling tensor one can show that[1,2]

$$C_\alpha\cong(\mathcal{I}_c/\mathcal{I}_\alpha)\,C_{cc}=\frac{\mathcal{I}_c}{\mathcal{I}_c-\mathcal{I}_\alpha}D_\alpha. \tag{39}$$

Thus we can rewrite Eq. (38) as

$$\mathcal{J}_c=(\mathcal{I}_c/\mathcal{I}_\alpha)j_\alpha=J_c+\frac{\mathcal{I}_c-\mathcal{I}_\alpha}{\mathcal{I}_\alpha}j \tag{40}$$

where j_α is the total rotational angular momentum of the internal rotor; that is,[19]

$$j_\alpha=(\mathcal{I}_\alpha/\mathcal{I}_c)J_c+(1-\mathcal{I}_\alpha/\mathcal{I}_c)j \tag{41}$$

Substitution of Eq. (40) into Eq. (37) and use of Eq. (39) will enable us to rewrite $K_{qq'}(\tau)$ as

$$K_{qq'}(\tau)=\frac{1}{3\hbar^2}(-1)^q I^{(1)}_{q',-q}(\tau)\;\{C_{aa}{}^2\,\overline{J_a(t+\tau)J_a(t)}$$
$$+C_{bb}{}^2\,\overline{J_b(t+\tau)J_b(t)}\,+\,C_\alpha{}^2\,\overline{j_\alpha(t+\tau)j_\alpha(t)}\} \tag{42}$$

In view of Eqs. (36) and (37) it is now obvious that

$$K_{qq'}(\tau)=K_{q'q}(\tau)\qquad(q,q'=0,\pm1)$$

Therefore, the spectral density $J_{qq'}(\omega)$ can now be rewritten as

$$J_{qq'}(\omega)=\int_0^\infty K_{qq'}(\tau)\cos\omega\tau\,d\tau. \tag{43}$$

Assuming the angular momentum correlation functions decay exponentially, we can obtain from Eqs. (30), (31), (42) and (43) the following expressions for $T_{1,\mathrm{SR}}$ and $T_{2,\mathrm{SR}}$ in the extreme narrowing limit:

$$\frac{1}{T_1}=\frac{1}{3\hbar^2}\Big\{C_{aa}{}^2\,\overline{J_a^2}\left(\frac{\tau_{J_a}\tau_{ac}}{\tau_{J_a}+\tau_{ac}}+\frac{\tau_{J_a}\tau_{bc}}{\tau_{J_a}+\tau_{bc}}\right)$$
$$+C_{bb}{}^2\,\overline{J_b^2}\left(\frac{\tau_{J_b}\tau_{ac}}{\tau_{J_b}+\tau_{ac}}+\frac{\tau_{J_b}\tau_{bc}}{\tau_{J_b}+\tau_{bc}}\right)$$
$$+C_\alpha{}^2\,\overline{j_\alpha{}^2}\left(\frac{\tau_{j_\alpha}\tau_{ac}}{\tau_{j_\alpha}+\tau_{ac}}+\frac{\tau_{j_\alpha}\tau_{bc}}{\tau_{j_\alpha}+\tau_{bc}}\right)\Big\} \tag{44}$$

and

$$\frac{1}{T_2}=\frac{1}{6\hbar^2}\Big\{C_{aa}{}^2\,\overline{J_a^2}\left(\frac{2\tau_{J_a}\tau_{ab}}{\tau_{J_a}+\tau_{ab}}+\frac{\tau_{J_a}\tau_{ac}}{\tau_{J_a}+\tau_{ac}}+\frac{\tau_{J_a}\tau_{bc}}{\tau_{J_a}+\tau_{bc}}\right)$$
$$+C_{bb}{}^2\,\overline{J_b^2}\left(\frac{2\tau_{J_b}\tau_{ab}}{\tau_{J_b}+\tau_{ab}}+\frac{\tau_{J_b}\tau_{ac}}{\tau_{J_b}+\tau_{ac}}+\frac{\tau_{J_b}\tau_{cc}}{\tau_{J_b}+\tau_{bc}}\right)$$
$$+C_\alpha{}^2\,\overline{j_\alpha{}^2}\left(\frac{2\tau_{j_\alpha}\tau_{ab}}{\tau_{j_\alpha}+\tau_{ab}}+\frac{\tau_{j_\alpha}\tau_{ac}}{\tau_{j_\alpha}+\tau_{ac}}+\frac{\tau_{j_\alpha}\tau_{bc}}{\tau_{j_\alpha}+\tau_{bc}}\right)\Big\} \tag{45}$$

In these expressions τ_{J_a}, τ_{J_b}, and τ_{j_α} are the characteristic correlation times for fluctuation of J_a, J_b, and j_α, respectively, and τ_{ab}, etc. are defined by the relations

$$\tau_{ab}=(\Delta_a+\Delta_b)^{-1},\ \ \tau_{ac}=(\Delta_a+\Delta_c)^{-1},$$
$$\tau_{bc}=(\Delta_b+\Delta_c)^{-1} \tag{46}$$

Since in the rotational diffusion limit it can usually be assumed that $\tau_{J_a},\tau_{J_b},\tau_{j_\alpha}\ll\tau_{ab},\tau_{bc},\tau_{ac}$, Eqs. (44) and (45) are further simplified to

$$\frac{1}{T_1}\approx\frac{1}{T_2}$$
$$\approx\frac{2}{3\hbar^2}(C_{aa}{}^2\,\overline{J_a^2}\,\tau_{J_a}+C_{bb}{}^2\,\overline{J_b^2}\,\tau_{J_b}+C_\alpha{}^2\,\overline{j_\alpha{}^2}\,\tau_{j_\alpha}) \tag{47}$$

For a small, symmetric internal rotor τ_{j_α} will probably be longer than both τ_{J_a} and τ_{J_b}. Moreover, since $\mathcal{I}_a,\mathcal{I}_b>\mathcal{I}_\alpha$ $C_\alpha{}^2\,\overline{j_\alpha{}^2}$ will be larger than $C_{aa}{}^2\,\overline{J_a^2}$ and $C_{bb}{}^2\,\overline{J_b^2}$. Thus the third term in Eq. (47) will be larger than the other two terms. If we assume that this third term dominates the other two terms, we may write

$$\left(\frac{1}{T_1}\right)_{SR}\cong\frac{2}{3\hbar^2}C_\alpha{}^2\,\overline{j_\alpha{}^2}\,\tau_{j_\alpha} \tag{48}$$

The expression given by Eq. (48) is exactly what Dubin and Chan[1] have suggested and it can approximately describe the spin-rotational relaxation for a nuclear spin on an internal rotor in a large molecule. This expression, however, has not been used very often in the actual interpretation of spin-rotational relaxation data because of difficulties in understanding the physical meaning of correlation time τ_{j_α}. Since j_α is the total rotational angular momentum of the internal rotor only [see Eq. (41)], its fluctuation will be strongly affected by the fluctuation of J_c through coupling of the former to the latter. Therefore, the correlation time τ_{j_α} will depend not only on the motion of the internal rotor but also on the overall rotation of the entire molecule and its temperature dependence will be complicated. Moreover, we have also to note that it is relative motions of internal rotor with respect to the other part of molecule, not the overall motion of the former, that is important in studying the effect of barrier to internal rotation. Hence it will be more convenient if the correlation function of j_α is reexpressed in terms of J_c and j. To do so we return to the calculation of the correlation function $\overline{j_\alpha(t+\tau)j_\alpha(t)}$. It can easily be seen from Eq. (41) that

$$\begin{aligned}\overline{j_\alpha(t+\tau)j_\alpha(t)} &= (\mathcal{I}_\alpha/\mathcal{I}_c)^2\,\overline{J_c(t+\tau)J_c(t)} \\ &\quad+(1-\mathcal{I}_\alpha/\mathcal{I}_c)^2\,\overline{j(t+\tau)j(t)} \\ &\quad+(\mathcal{I}_\alpha/\mathcal{I}_c)(1-\mathcal{I}_\alpha/\mathcal{I}_c)\{\overline{J_c(t+\tau)j(t)}+\overline{j(t+\tau)J_c(t)}\}\end{aligned} \tag{49}$$

Burke and Chan[3] have discussed about two possible limits in which J_c and j are "strongly" correlated or completely uncorrelated. However, we contend here that it is very likely that J_c and j are completely uncorrelated for the following reason. A glance at the rotational Hamiltonian written in terms of J_a, J_b, J_c, and j [20] will tell us that j is not coupled to J_c at all. Thus $\overline{J_c(t)\,j\,(t)}=0$ at any time t. Furthermore, after a long time τ $\overline{J_c(t+\tau)\;j(t)}$ will also vanish. Hence, if $\overline{J_c(t+t_1)j(t)}$ is nonvanishing at any arbitrary time t_1, it will mean that a certain correlation between J_c and j, which has originally not existed, is created by external fluctuating forces. Such a situation is very unlikely in view of randomness of intermolecular collisions in fluid phases. In other words one may say that J_c and j fluctuate independently of each other. Therefore, we obtain from Eq. (49)

$$\begin{aligned}\overline{j_\alpha(t+\tau)j_\alpha(t)} &= (\mathcal{I}_\alpha/\mathcal{I}_c)^2\,\overline{J_c(t+\tau)J_c(t)} \\ &\quad+(1-\mathcal{I}_\alpha/\mathcal{I}_c)^2\,\overline{j(t+\tau)j(t)}\end{aligned} \tag{50}$$

From Eqs. (47) and (50) we now obtain the following expressions for $T_{1,SR}$ and $T_{2,SR}$:

$$\begin{aligned}(1/T_1)_{SR} &= (1/T_2)_{SR} \\ &= \frac{2}{3\hbar^2}(C_{aa}^2\,\overline{J_a^2}\,\tau_{J_a}+C_{bb}^2\,\overline{J_b^2}\,\tau_{J_b}+C_{cc}^2\,\overline{J_c^2}\,\tau_{J_c}) \\ &\quad+\frac{2}{3\hbar^2}C_\alpha^2(1-\mathcal{I}_\alpha/\mathcal{I}_c)^2\,\overline{j^2}\,\tau_j\end{aligned} \tag{51}$$

where τ_{J_c} and τ_j are the correlation times characteristic of fluctuation of J_c and j, respectively. Since j flutuates independently of J_a, J_b, and J_c, τ_j is not influenced by overall rotation of the entire molecule, hence characteristic of internal rotation. The first term on the righthand side of Eq. (51) represents the contribution to $T_{1,SR}$ from the spin-overall-rotation coupling while the second term is due to the spin-internal-rotation coupling.

In case the height of barrier to internal rotation is zero, we have classically

$$\overline{j^2}=(1/\mathcal{I}_\alpha-1/\mathcal{I}_c)^{-1}kT \tag{52}$$

Also, regardless of the presence of barrier, one may write in classical sense

$$\overline{J_a^2}=\mathcal{I}_a\,kT, \qquad \overline{J_b^2}=\mathcal{I}_b\,kT,$$

and

$$\overline{J_c^2}=\mathcal{I}_c\,kT$$

Thus, in case of the zero barrier we may write

$$\begin{aligned}\left(\frac{1}{T_1}\right)_{\mathrm{SR}} &= \frac{2kT}{3\hbar^2}\{\mathcal{I}_a C_{aa}^2\,\tau_{J_a}+\mathcal{I}_b C_{bb}^2\,\tau_{J_b} \\ &\quad+\mathcal{I}_c C_{cc}^2\,\tau_{J_c}+(1-\mathcal{I}_\alpha/\mathcal{I}_c)\,\mathcal{I}_\alpha C_\alpha^2\,\tau_j\}\end{aligned} \tag{53}$$

We have derived Eq. (53) under the assumption that the coupling tensors $\boldsymbol{C}$ and $\boldsymbol{D}$ are diagonal in the principal axis system of molecular inertia tensor, (a, b, c). If the axis of internal rotation coincides with one of three principal axes of molecular inertia tensor, say the c - axis, but the coupling tensors are not diagonal in this axes system, more elaborate calculations will lead to the following expression:

$$\begin{aligned}\left(\frac{1}{T_1}\right)_{\mathrm{SR}} &= \frac{2}{3\hbar^2}\Big\{(\sum_g C_{ga}^2)\,\overline{J_a^2}\,\tau_{J_a}+(\sum_g C_{gb}^2)\,\overline{J_b^2}\,\tau_{J_b} \\ &\quad+(\sum_g C_{gc}^2)\,\overline{J_c^2}\,\tau_{J_c}+(\sum_g D_{gc}^2)\,\overline{j^2}\,\tau_j\Big\}\end{aligned} \tag{54}$$

where C_{pq} and D_{pq} are the pq-element of tensors $\boldsymbol{C}$ and $\boldsymbol{D}$ in the inertial axes system. In deriving Eq. (54) we have assumed that different components of rotational angular momentum are not correlated to one another. In case where the nuclear spin of interest is not located on the axis of internal rotation as for ^{1}H in methyl group and ^{19}F in -CF$_3$ group[7] Eq. (54) must be used instead of Eq. (51).

If the anisotropic nature of rotational motions may be ignored, we can replace τ_{J_a}, τ_{J_b}, and τ_{J_c} by a single correlation time τ_J and $\mathcal{I}_\alpha$, $\mathcal{I}_b$, $\mathcal{I}_c$ by the average moment of inertia $\mathcal{I}=\frac{1}{3}(\mathcal{I}_a+\mathcal{I}_b+\mathcal{I}_c)$, thus producing

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}}=\frac{2kT}{3\hbar^2}\{3\,\overline{\mathcal{I}}\,\overline{C^2}\,\tau_J+(1-\mathcal{I}_\alpha/\mathcal{I}_c)\,\mathcal{I}_\alpha C_\alpha^2\,\tau_j\}, \tag{55}$$

where

$$\overline{C^2}=\frac{1}{3}(C_{aa}^2+C_{bb}^2+C_{cc}^2)$$

Eq. (55) has previously been derived by Burke and Chan[3] by modifying the Hubbard's derivation for spherical top molecules without internal rotational degree of freedom,[8] and has been used by Schmidt and Chan,[7] Jonas and his coworkers[4,5] and Suchanski and Canepa.[6] Unfortunately, however, to our present knowledge not too many investigators seem to try to exploit the usefulness of this equation.

Discussion

In order to extract the informations about molecular motions from NMR relaxation data one usually measures the temperature dependence of T_1 for nuclear spins of interest. Thus one may expect that the measurement of temperature dependence of $T_{1,\mathrm{SR}}$ for a nuclear spin on an internal rotor can provide the informations regarding rotation of the internal rotor. In our case, however, the temperature dependence of $T_{1,\mathrm{SR}}$ for the nuclear spin on the internal rotor alone may not suffice to provide such informations because there are four differerent rotational angular correlation times, τ_{J_a}, τ_{J_b}, τ_{J_c}, and τ_j. To obtain the complete informations of these correlation times one also has to measure the temperature dependence of $T_{1,SR}$'s for the nuclear spins not located on the internal rotor and in this case the components of spin-rotation coupling tensors for all the spins involved must also be known. Unfortunately, however, it is common that not all these data are available. Unless these data are precisely known, one cannot make full use of Eq. (53) and, instead, has to resort to a more approximate formula such as Eq. (55).

Nuclear dipolar and quadrupolar relaxation measurements usually provide the informations about the orientational correlation time, $\tau_Q^{(2)}$, which is the correlation time for the second order spherical harmonics or components of the second order Wigner rotation matrix. Measurements of this correlation time and theoretical interpretations based on an appropriate model usually yield the informations about the orientational changes associated with molecular rotations in liquid phase.

A common method of estimating the magnitude of $\tau_Q^{(2)}$ is based on the Stokes-Debye relation[21]

$$\tau_Q^{(2)} = \frac{4\pi a^3 \eta}{3kT} \tag{56}$$

where a is the molecular hydrodynamic radius and η the viscosity of medium. As is well known, Eq. (56) is based on the isotropic rotational diffusion model where it is assumed that the rotational angular momentum correlation time τ_J is much shorter than $\tau_Q^{(2)}$. Such an assumption has been shown to be well valid for highly viscous and polar liquids. For nonpolar molecules, especially when they are small in size, however, it has often been reported that estimated values from Eq. (56) are much longer than those obtained from the dipolar and quadrupolar relaxation measurements. To correct for this the NMR spectroscopists usually employ either the microviscosity model proposed by Gierer and Wirtz[22] or the slip-stick model proposed by Hu and Zwanzig.[23] Both theories give formally the same fourmula for $\tau_Q^{(2)}$; that is,

$$\tau_Q^{(2)} = \kappa \frac{4\pi a^3 \eta}{3kT} \quad (0 < \kappa \leq 1) \tag{57}$$

where κ may be considered as an adjustable parameter which gives the best agreement with experimental data.

In contrast to this there seems to be no known method of directly estimating τ_J. Only indirect methods are known in which $\tau_Q^{(2)}$ is first estimated and then, using the relation between $\tau_Q^{(2)}$ and τ_J, the latter is evaluated. Recently much progress has been achieved to find the relation between these two correlation times,[24-26] but many experimentalists still prefer to estimate τ_J using the simpler relation proposed by Hubbard[8] which is valid in the rotational diffusion limit.

$$\tau_Q^{(2)} \tau_J = \frac{\overline{\mathcal{I}}}{6kT} \tag{58}$$

Using the method described above, we can gain some insight into the nature of molecular rotation in liquid phase. For example let us consider the toluene molecule in pure liquid state. Fury and Jonas[27] have shown that reasonable value of κ for toluene is 0.11. Using this value of κ and other relevant data for toluene, we can obtain form Eq. (57) $\tau_Q^{(2)} = 1.45 \times 10^{-12}$ sec at 38° C. Substitution of this value into the Hubbard relation gives us $\tau_J = 8.57 \times 10^{-14}$ sec, which means that the contribution from the spin-overall-rotation coupling to the total spin-rotational relaxation rate for ^{13}C spin on methyl group in toluene would approximately be 0.0018 sec^{-1} if we use Eq. (55). However, the measurement carried out in our laboratory[28] indicates that the relaxation rate due to the spin-overall-rotation coupling is approximately 0.021 sec^{-1} at 38° C, which corresponds to $\tau_J = 5.74 \times 10^{-13}$ sec. Thus the observed value for τ_J is larger than the estimated one almost by one order in magnitude. This difference can be understood on the basis of Eq (53), rather than Eq. (55), if if we assume that one of three rotational angular momentum correlation times, τ_{J_a}, τ_{J_b}, and τ_{J_c}, is much longer than the other two. This in turn indicates that rotational motions of toluene molecule in liquid phase are very anisotropic and such a view is consistent with the results obtained by Pecora *et al.*[29]

Unlike the case of overall rotational motion, however, internal rotation of methyl or trisubstituted methyl group about its symmetry axis may be treated as being almost of inertial character. Thus Burke and Chan[3] have proposed that τ_j is proportional to $(\mathcal{I}_\alpha / kT)^{\frac{1}{2}}$; that is,

$$\tau_j = n_j (\mathcal{I}_\alpha / kT)^{\frac{1}{2}} \tag{59}$$

where n_j is an empirical constant obtained by fitting to the experimental data. Burke and Chan,[3] Jonas *et al.*[4,5], and Suchanski and Canepa[6] have all found that $n_j \approx 1.5$ is the most suitable value for describing the internal rotation of $-CH_3$ and $-CF_3$ group in organic molecules. Our measurement for methyl group in toluene[28] also confirms this result.

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