Journal of the Korean Magnetic Resonance Society **1998**, *2*, 66-83

A Study on Spin-Rotational Relaxation of Methyl Carbon-13 in Toluene and 2-Chloro-*p*-Xylene

Hyun Namgoong and Jo Woong Lee*

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Received February 17, 1998

Abstract : Study on spin-rotation relaxation of nuclear spins located on a methyl group can reveal valuable dynamic information related to the internal rotation of methyl group itself. Toward this end we have measured methyl carbon-13 spin-rotational relaxation rate in toluene and 2-chloro-*p*-xylene over the temperature range of 179 - 363K. To interpret the temperature dependence of measured spin-rotational relaxation rate we have revised the expression derived thus far by other authors and reproduced experimental data on the basis of the newly derived expression. The results confirmed that our expression leads to better agreement with experimental data than the previous one over observed temperature range, especially at high temperature.

INTRODUCTION

It is nowadays well known that among several relaxation mechanisms for a nuclear spin (or spins) of $I = 1/2$ those due to intra- and intermolecular dipolar interactions are usually the dominant ones, but for a spin (or spins) located on a rapidly rotating small molecule or an internal rotor such as methyl group the spin-rotation interaction can play an important role in its (or their) relaxation. In particular, the role of spin-rotation interaction in the relaxation of spins located on a methyl and/or trisubstituted methyl group is quite interesting, because these spins can interact not only with magnetic fields arising from end-over-end molecular rotation but with those arising from internal rotation as well. Since a pioneering work by Dubin and Chan nearly three decades ago[1] several investigators actively pursued this interesting research topic until late 1970s [2-5]. Since then, however, this topic has gradually fallen into oblivion as most workers turned their attentions away toward other problems. In view of the importance of methyl group dynamics in the study of biomolecules and polymers, however, we feel that this topic deserves further study. In an attempt to interpret temperature dependence of ^{19}F spin-lattice relaxation times in benzotrifluoride Burke and Chan[6] have proposed that for a nuclear spin (or spins) located on an internal rotor such as methyl and/or substituted methyl group the spin-rotational relaxation rate $(1/T_1)_{\mathrm{SR}}$ could be written as

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}} = \frac{2kT}{3\hbar^2}\left\{3\,\overline{\mathrm{C}}^2\,\overline{\mathrm{I}}\,\tau_J + C_\alpha^2 \mathrm{I}_\alpha\left(1 - \mathrm{I}_\alpha/\mathrm{I}_{cc}\right)\tau_j\right\} \qquad [1]$$

where $\overline{\mathrm{C}}^2$ and $\overline{\mathrm{I}}$ are defined as

$$\overline{\mathrm{C}}^2 = \tfrac{1}{3}\left(\mathrm{C}^2_{a'a'} + \mathrm{C}^2_{b'b'} + \mathrm{C}^2_{c'c'}\right) \qquad [2]$$

and

$$\overline{\mathrm{I}} = \tfrac{1}{3}\left(\mathrm{I}_{aa} + \mathrm{I}_{bb} + \mathrm{I}_{cc}\right) \qquad [3]$$

with C_{ii}'s and I_{jj}'s denoting the principal values of spin-overall rotation coupling tensor **C** for the nuclear spin of interest and the molecular inertia tensor **I**, respectively[7]. I_α denotes the moment of inertia of internal rotor about its symmetry axis and C_α is what has been named as the spin-internal rotation coupling constant for the given nucleus by Dubin and Chan[1]. Using Eq.[1] along with reasonable assumptions on the form of two correlation times τ_J and τ_j, they could successfully explain the temperature dependence of T_1 for ^{19}F spins in benzotrifluoride which was previously unaccounted for. The same equation was also tested by other authors for interpreting their experimental data with remarkable success.

Careful examination of the results published thus far, however, reveals that temperature dependence of $(1/T_1)_{SR}$ predicted by Eq.[1] increasingly deviates from the observed one as temperature is elevated and, as we report in this paper, similar trends are found also in the case of spin-rotational relaxation of methyl ^{13}C in toluene and its derivatives. To find the cause for such deviations we have reexamined this problem on the basis of Hubbard's semiclassical density operator theory of relaxation and found that Burke and Chan unwittingly ignored the fact that the principal axes of the spin-rotation coupling tensor **C** for the nucleus on the internal rotor and those of the molecular inertia tensor **I** do not coincide with each other. In reality, it is quite general that the former will rotate with respect to the latter. Keeping this point in mind, we have rederived the expression for $(1/T_1)_{SR}$ and have applied it to interpret the temperature dependence of spin-rotational relaxation rate of methyl carbon-13 in toluene and its derivatives. Theoretical curves obtained from our modified Burke-Chan expression are found to give better agreement with the observed relaxation data over wide range of temperature.

THEORY

For simplicity, we will consider the situation where the entire molecule has at least a two-fold symmetry axis which coincides with the axis of internal rotation on which the nuclear spin under consideration is located as exemplified by methyl ^{13}C in toluene. For such nucleus it has been shown that the spin-rotation Hamiltonian may be written as[1,8]

$$h^{-1} H_{SR} = -\boldsymbol{I}\cdot\mathbf{C}\cdot\boldsymbol{J} - D_{\alpha}\,\boldsymbol{I}\cdot\boldsymbol{j} \qquad [4]$$

where $\boldsymbol{I}$ is the spin angular momentum for the nucleus under consideration, and $\boldsymbol{J}$ and $\boldsymbol{j}$ are, respectively, the total rotational angular momentum of the molecule and the rotational angular momentum of internal rotor with respect to the molecular inertia axes system. $\mathbf{C}$ has the same meaning as described in the previous section while D_{α} can be shown to be related to C_{α} through the relation $D_{\alpha} = C_{\alpha}(1 - \mathrm{I}_{\alpha}/\mathrm{I}_{cc})$.

Since the principal axes system of spin-rotation coupling tensor $\mathbf{C}$, (a', b', c'), may be taken as fixed on the internal rotor and one of them, say c' axis, may be assumed to coincide with the axis of internal rotation, one can rewrite the above expression as

$$h^{-1}H_{SR} = -\mathrm{C}_{a'a'}\,I_{a'}\,J_{a'} - \mathrm{C}_{b'b'}\,I_{b'}J_{b'} - \mathrm{C}_{c'c'}\,I_{c'}J_{c'} - D_{\alpha}I_{c'}j \qquad [5]$$

where j is the component of $\boldsymbol{j}$ along the c' axis. (Note that $\boldsymbol{j}$ is, by definition, directed along the axis of internal rotation.)

Since the magnetic resonance experiments are performed in the laboratory-fixed coordinates (x, y, z), we must express the Hamiltonian given by Eq.[5] in this coordinates system inasmuch as the nuclear spin operators are concerned. For this coordinates transformation it is convenient to introduce the components of spherical tensor operators defined as follows:

$$\begin{aligned} V_{\pm1} &= \mp\frac{1}{\sqrt{2}}(I_x \pm iI_y), \quad V_0 = I_z, \\ V'_{\pm1} &= \mp\frac{1}{\sqrt{2}}(I_a \pm iI_b), \quad V'_0 = I_c. \end{aligned} \qquad [6]$$

Since the rotational Hamiltonian usually assumes the quadratic form in the molecule-fixed coordinates system, denoted by (a, b, c), where the inertia tensor **I** is diagonal, it will be convenient if we introduce the following additional definitions:

$$\begin{aligned} &J_{\pm 1} = \mp\tfrac{1}{\sqrt{2}}\left(J_a \pm iJ_b\right), \quad J_0 = J_c, \quad j_{\pm 1} = \mp\tfrac{1}{\sqrt{2}}\left(j_a \pm i j_b\right), \quad j_0 = j_c, \\ &J'_{\pm 1} = \mp\tfrac{1}{\sqrt{2}}\left(J_{a'} \pm iJ_{b'}\right), \quad J'_0 = J_{c'}, \; j'_{\pm 1} = \mp\tfrac{1}{\sqrt{2}}\left(j_{a'} \pm i j_{b'}\right), \quad j'_0 = j_{c'} \end{aligned} \qquad [7]$$

Let us denote the relative orientation of (a, b, c) coordinates with respect to the laboratory-fixed frame (x, y, z) by the Eulerian angles $\Omega(\alpha, \beta, \gamma)$ and that of (a', b', c') coordinates with respect to (a, b, c) by $\Omega'(\alpha', \beta', \gamma')$. Then, the transformations of spherical tensor operators, defined by Eqs.[6] and [7], from one coordinates system to another can be effected through the use of Wigner rotation matrices $D^{(j)}_{mn}(\Omega)$ and $D^{(j)}_{mn}(\Omega')$ as following[9]:

$$V'_q = \sum_m \sum_n D^{(1)^*}_{qm}(\Omega) D^{(1)^*}_{mn}(\Omega')\, V_n, \quad J'_q = \sum_n D^{(1)^*}_{qn}(\Omega')\, J_n, \qquad [8]$$

and

$$j'_q = \sum_n D^{(1)^*}_{qn}(\Omega')\, j_n, \qquad [9]$$

where $D^{(1)*}_{qq'}(\Omega)$ is the complex conjugate of $D^{(1)}_{qq'}(\Omega)$. Substitution of Eqs.[8] and [9] into Eq.[5] leads to

$$h^{-1} H_{SR} = \sum_q U_q V_q \qquad [10]$$

where

$$U_q = \sum_k \sum_p A_k\, D^{(1)*}_{kp}(\Omega)\, D^{(1)^*}_{pq}(\Omega') \qquad [11]$$

$$\begin{aligned} A_{\pm} &= \pm\tfrac{1}{\sqrt{2}}(\mathrm{C}_{aa} J_a \mp i\, \mathrm{C}_{bb} J_b) \\ &= \sum_m \{\kappa^{\mp} D^{(1)*}_{1,m}(\Omega) + \kappa^{\pm} D^{(1)*}_{-1,m}(\Omega)\}\, J_m, \end{aligned} \qquad [12]$$

and

$$\begin{aligned} A_0 &= -\,(\mathrm{C}_{cc} J_c + D_\alpha\, j_c) \\ &= -\,(\mathrm{C}_{cc} J_0 + D_\alpha\, j_0), \end{aligned} \qquad [13]$$

with

$$\kappa^{\pm} = \tfrac{1}{2}\,(C_{b'b'} \pm C_{a'a'}). \qquad [14]$$

According to Hubbard[10,11] the spin-lattice and spin-spin relaxation rate due to the spin-rotation mechanism may be expressed as follows:

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}} = -\frac{1}{\hbar^2}\left[J_{1,-1}(-\omega_0) + J_{-1,1}(\omega_0)\right] \qquad [15]$$

and

$$\left(\frac{1}{T_2}\right)_{\mathrm{SR}} = \frac{1}{\hbar^2}\left[J_{0,0}(0) - J_{1,-1}(-\omega_0)\right] \qquad [16]$$

where ω_0 is the Larmor frequency of the nucleus of interest and the spectral densities $J_{q,q'}(\omega)$'s are defined by

$$J_{qq'}(\omega) = \int_0^{\infty}\left\langle U_q(t+\tau)\,U_{q'}(t)\right\rangle \cos(\omega\tau)\,d\tau \qquad [17]$$

with $\langle \quad \rangle$ denoting the statistical average over equilibrium ensemble of lattice.

In the process of calculation of the time correlation functions $\left\langle U_{\mathrm{q}}(t+\tau)\,U_{\mathrm{q}}(t)\right\rangle$ one will have to treat the terms such as

$$\left\langle \left[D^{(1)*}_{\pm k,m}(\Omega')\,D^{(1)*}_{k,p}(\Omega')D^{(1)*}_{p,q}(\Omega)J_m\right]_{t+\tau}\left[D^{(1)*}_{\pm k,m}(\Omega')\,D^{(1)*}_{k,p}(\Omega')D^{(1)*}_{p,q}(\Omega)J_m\right]_t\right\rangle .$$

Unfortunately, however, calculation of such terms is not possible without detailed knowledge of molecular dynamics. Hence, in order to make the calculations tractable we assume that

$$\begin{aligned}&\left\langle \left[D^{(1)*}_{\pm k,m}(\Omega')\,D^{(1)*}_{k,p}(\Omega')D^{(1)*}_{p,q}(\Omega)J_m\right]_{t+\tau}\left[D^{(1)*}_{\pm k,m}(\Omega')\,D^{(1)*}_{k,p}(\Omega')D^{(1)*}_{p,q}(\Omega)J_m\right]_t\right\rangle\\ &\cong \langle\, [D^{(1)*}_{\pm km}(\Omega')D^{(1)*}_{kp}(\Omega')]_{t+\tau}\,[D^{(1)*}_{\pm km}(\Omega')D^{(1)*}_{kp}(\Omega')]_t\rangle \qquad [18]\\ &\qquad \times\langle [D^{(1)*}_{pq}(\Omega)]_{t+\tau}[D^{(1)*}_{pq}(\Omega)]_t\rangle\langle J_m(t+\tau)J_m(t)\rangle\end{aligned}$$

This approximation will hold very well if the correlation times for the modulation of $\Omega(t)$, $\Omega'(t)$, and $J_m(t)$'s are very much different from one another as pointed out by Hubbard[11]. If we assume that the molecule undergoes rotational diffusional motion as a whole, we have[12]

$$I^{(1)}_{pp',qq'}(\tau) \equiv \left\langle \left[D^{(1)*}_{p,q}(\Omega)\right]_{t+\tau} \left[D^{(1)}_{p'q'}(\Omega)\right]_t \right\rangle = \frac{1}{3}\delta_{p,p'} \sum_{k=-1}^{1} \exp(-\lambda_k \tau) Z(\lambda_k)_{q,q'} \tag{19}$$

where $\lambda_0 = D_a + D_b$, $\lambda_1 = D_a + D_c$, $\lambda_{-1} = D_b + D_c$, $Z(\lambda_0)_{q,q'} = \delta_{q0}\delta_{q'0}$, and $Z(\lambda_{\pm1})_{q,q'} = \frac{1}{2}(\delta_{q,1} \pm \delta_{q,-1})(\delta_{q',1} \pm \delta_{q',-1})$ with D_a, D_b, and D_c denoting three principal components of the rotational diffusion tensor **D**.

Substituting Eqs.[12], [13], and [14] into Eq.[17] and invoking the approximations represented by Eq.[18] and [19], we have

$$\begin{aligned} &\left\langle U_1(\mathrm{t}+\tau) U_{-1}(t) \right\rangle \\ &= \{\, 2(\mathrm{k}^+)^2 \left[1 + (\mathrm{k}^- / \mathrm{k}^+)^2 \left\langle \mathrm{e}^{2i\alpha(\mathrm{t}+\tau)} \mathrm{e}^{-2i\alpha(\mathrm{t})} \right\rangle\right] \left\langle J_1(\mathrm{t}+\tau) J_{-1}(t) \right\rangle \\ &\quad - \mathrm{C}^2_{\mathrm{c'c'}} \left\langle \mathrm{J_c}(\mathrm{t}+\tau) \mathrm{J_c}(t) \right\rangle \} I^{(1)}_{11,11}(\tau) \end{aligned} \tag{20}$$

where J_c is defined by

$$\mathrm{J}_c = J_c + (D_a / \mathrm{C}_c) j_c \tag{21}$$

Eq.[20] indicates that internal rotation can influence the spin-rotational relaxation not only by introducing the direct spin-internal rotation coupling but also through its modification of contribution from the spin-overall rotation coupling. For example, if the correlation time τ_J for the components of J is much shorter than that for the modulation of $\exp(2i\alpha)$, $\langle \exp[2i\alpha(t+\tau)]\exp[2i\alpha(\mathrm{t})] \rangle$ can be regarded as unity, and Eq.[20] reduces to the case that Burke and Chan have treated. If the two correlation times are comparable in magnitude, however, this term can play an important role when $|\mathrm{C}_{a'a'} - \mathrm{C}_{b'b'}|$ is comparable to or larger than $|\mathrm{C}_{a'a'} + \mathrm{C}_{b'b'}|$.

In case the end-over-end molecular rotation can be described in terms of rotational diffusion model, the correlation times for the components of rotational angular momentum are considered to be much shorter than those for the modulation of Ω, and one may replace the term $I^{(1)}_{11,11}(\tau)$ by 1/3. Therefore, we have from Eq.[20]

$$\begin{aligned} &< U_1(t+\tau)\,U_{-1}(t) > \\ &= \frac{2}{3}(\kappa^+)^2\left[1+(\kappa^-/\kappa^+)^2\left\langle e^{2i\alpha(t+\tau)}e^{-2i\alpha(t)}\right\rangle\right]\left\langle J_1(t+\tau)J_{-1}(t)\right\rangle \\ &-\frac{1}{3}\,\mathrm{C}^2_{c'c'}\left\langle \mathrm{J}_c(t+\tau)\mathrm{J}_c(t)\right\rangle \end{aligned} \qquad [22]$$

Since the magnetic resonance experiment can rarely provide enough amount of data to allow us to uniquely determine all the parameters involved, we have to introduce further approximations to simplify Eq.[22] as follows:

$$\begin{aligned} &\left\langle \exp[2i\alpha(t+\tau)]\exp[2i\alpha(t)]\right\rangle = \exp(-\tau/\tau^{(2)}_\alpha) \\ &\left\langle J_p(\mathrm{t}+\tau)J_q(\mathrm{t})\right\rangle = \delta_{p,q}\left\langle J_p^2\right\rangle \exp(-\tau/\tau_{Jp}) \quad \text{for } p,\ q = a,\ b,\ c \end{aligned} \qquad [23]$$

In calculating $\langle \mathrm{J}_c(t+\tau)\mathrm{J}_c(t)\rangle$ we are encountered by the cross correlation terms like $\langle J_c(t+\tau)j_c(t)\rangle$. For such terms Burke and Chan[6] have assumed there exists no correlation between J_c and j_c - the so-called uncorrelated limit, and we will also follow the suit. Then, in the extreme narrowing limit where $(\omega_0\tau)^2 << 1$ is valid for all the correlation times involved, we have from Eqs.[15], [17], and [20]

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{\mathrm{SR}} &= \frac{2}{3\hbar^2}\left(\kappa^+\right)^2\left\{\left\langle J_a^2\right\rangle\tau_{Ja}\left[1+\frac{\left(\kappa^-/\kappa^+\right)^2}{1+\left(\tau_{Ja}/\tau^{(2)}_\alpha\right)}\right] + \left\langle J_b^2\right\rangle\tau_{Jb}\left[1+\frac{\left(\kappa^-/\kappa^+\right)^2}{1+\left(\tau_{Jb}/\tau^{(2)}_\alpha\right)}\right]\right\} \\ &+\frac{2}{3\hbar^2}\left(\mathrm{C}^2_{cc}\,J_c^2\tau_{Jc} + D^2_\alpha\, j_c^2\tau_{jc}\right) \end{aligned} \qquad [24]$$

Introduction of the approximations $\tau_{Ja}\approx\tau_{Jb}\equiv\tau_J$ can further simplify the above expression to

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}} = \frac{2}{3\hbar^2}\left(\kappa^+\right)^2\left(\langle J_a\rangle^2+\langle J_b\rangle^2\right)\left[1+\frac{\left(\kappa^-/\kappa^+\right)^2}{1+\left(\tau_J/\tau^{(2)}_\alpha\right)}\right]\tau_J$$

$$+\frac{2}{3\hbar^2}\left(C^2_{c'c'}J^2_c\tau_{Jc}+D^2_\alpha j^2_c\tau_{jc}\right) \qquad [25]$$

The rotational Hamiltonian can be shown to take the following quadratic form in the (a, b, c) coordinates system[12]:

$$H_{\mathrm{rot}}=AJ^2_a+BJ^2_b+CJ^2_c+Dj^2_c+V(\alpha) \qquad [26]$$

where $V(\alpha)$ is the potential function governing the internal rotation and the rotational constants A, B, C, and D are defined as follows:

$$A=\hbar^2/2\mathrm{I}_{aa}\,,\ B=\hbar^2/2\mathrm{I}_{bb}\,,\ C=\hbar^2/2\mathrm{I}_{cc}\,,\ D=\left(\hbar^2/2\right)\left[(1/\mathrm{I}_\alpha)-(1/\mathrm{I}_{cc})\right].$$

Thus we have, classically, $\langle J^2_a\rangle=\mathrm{I}_{aa}kT$, $\langle J^2_b\rangle=\mathrm{I}_{bb}kT$, $\langle J^2_c\rangle=\mathrm{I}_{cc}kT$, and $\langle j^2_c\rangle=[I_\alpha I_{cc}/(I_{cc}-I_\alpha)]kT$.

Substituting these results into Eq.[25], we finally have

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}}=\frac{2kT}{3\hbar^2}\left(\kappa^+\right)^2\left(\mathrm{I}_{aa}+\mathrm{I}_{bb}\right)\left[1+\frac{\left(\kappa^-/\kappa^+\right)^2}{1+\left(\tau_J/\tau^{(2)}_\alpha\right)}\right]\tau_J$$
$$+\frac{2kT}{3\hbar^2}C^2_{cc}\mathrm{I}_{cc}\tau_{Jc}+\frac{2kT}{3\hbar^2}D^2_\alpha\tau_{jc}\,\mathrm{I}_\alpha\mathrm{I}_{cc}/\left(\mathrm{I}_{cc}-\mathrm{I}_\alpha\right). \qquad [27]$$

In case $\tau_J \langle\langle \tau^{(2)}_\alpha$, it can readily be shown that

$$\left(\frac{1}{T_1}\right)_{\mathrm{SR}}=\frac{2kT}{3\hbar^2}\left\{\bar{\mathrm{I}}\left(C^2_{a'a'}+C^2_{b'b'}\right)\tau_J+C^2_{c'c'}\mathrm{I}_{cc}\tau_{jc}\right\}$$
$$+\frac{2kT}{3\hbar^2}D^2_\alpha\tau_{jc}\,\mathrm{I}_\alpha\mathrm{I}_{cc}/\left(\mathrm{I}_{cc}-\mathrm{I}_\alpha\right) \qquad [28]$$

where $\bar{\mathrm{I}}=\frac{1}{2}\left(\mathrm{I}_{aa}+\mathrm{I}_{bb}\right)$, which becomes equivalent to Eq.[1] if we assume $\mathrm{I}_{cc}=\bar{\mathrm{I}}$ and $\tau_{Jc}=\tau_J$.

In order to interpret temperature dependence of $(1/T_1)_{SR}$ we will assume the end-over-end molecular rotation to be of diffusional character so that both τ_J and τ_{Jc} are inversely proportional to the viscosity of medium, η. On the other hand the rotation of small, symmetrical internal rotor is usually assumed to be inertial, in which case τ_{jc} and $\tau_{\alpha}^{(2)}$ are both taken to be proportional to $\exp(-V_0/kT)(I_\alpha/kT)^{1/2}$ where V_0 is the activation energy associated with internal rotation. Thus, in this scheme Eqs.[27] and [28], respectively, may be rewritten into the following forms:

$$\left(\frac{1}{T_1}\right)_{SR} = aT\eta^{-1}\left[1+\frac{b}{1+c\exp(-V_0/kT)T^{1/2}\eta^{-1}}\right]+d\exp(-V_0/kT)T^{1/2} \qquad [29]$$

and

$$\left(\frac{1}{T_1}\right)_{SR} = a'T\eta^{-1}+d'\exp(-V_0/kT)\,T^{1/2} \qquad [30]$$

Since there is no *ab initio* means available to determine the parameters *a*, *b*, *c*, *d*, *a'*, and *d'* for the present, we have to estimate them by fitting these equations with observed data.

EXPERIMENTAL

Commercially available neat toluene and 2-chloro-p-xylene were used without further purification. Each sample was degassed by repeating the standard freezing-pump-thaw cycles at least five times and then sealed under vacuum. The magnetic field was locked to deuterium in THF-d_8 placed in a 5mm o.d. inner tube which was made tightly held coaxially to an outer 12mm o.d. NMR tube by two teflon ring holders. The spin-lattice relaxation time(T_1) was measured by the standard inversion recovery method under broadband proton decoupling. In order to separate the spin-rotational relaxation rate from that of total relaxation, the NOE factors were measured by employing the gated proton noise decoupling technique with a pulse delay of about $10T_1$. All data were taken on a Varian XL-100 NMR spectrometer operating at 25.16MHz for ^{13}C.

RESULTS AND DISCUSSION

It is well known that intramolecular dipole-dipole and spin-rotation interactions are the two major relaxation mechanism for methyl ^{13}C in small molecules at the external magnetic field strength 3T or below.[12,13] Separation of the contributions to the total relaxation rate due to these two mechanisms from each other can be achieved through measurement of conventional NOE factor based on the following relation:[14]

$$(1/T_1)_{DD} = (1/T_1)_{obs}(2\eta\gamma_C/\gamma_H) \qquad [31]$$

where $(1/T_1)_{obs}$ is the total relaxation rate for the ^{13}C spin of interest, $(1/T_1)_{DD}$ the contribution from the dipole-dipole interaction between ^{13}C and ^1H, η the NOE factor, and γ_C and γ_H denote, respectively, the magnetogyric ratio of carbon-13 and proton spin. Hence, the contribution from the spin-rotation relaxation may be expressed as follows:

$$(1/T_1)_{SR} = (1/T_1)_{obs}(1 - 2\eta\gamma_C/\gamma_H) \qquad [32]$$

In Tables 1 and 2, T_1 and the NOE data measured for methyl carbon spin of interest are listed along with dipolar relaxation and spin-rotation relaxation rate estimated from Eqs. [31] and [32]. In Fig.1. thus deduced dipolar and spin-rotation relaxation rate are plotted against temperature. As can be seen from Fig.1, the spin-rotation relaxation rate exhibits quite different temperature dependence from that of dipolar one. The former increases as temperature is elevated while the latter behaves oppositely. Also, we see that spin-rotation relaxation rates for methyl carbon-13 in toluene and 4-methyl carbon-13 in 2-chloro-*p*-xylene exhibit similar temperature dependence but 1-methyl carbon in 2-chloro-*p*-xylene behaves somewhat differently. Spin-rotation relaxation times for 1-methyl carbon seem to be relatively long compared with those for 4-methyl carbon as well as toluene methyl carbon. This can be explained roughly by the fact that ortho-position chlorine atom affects the internal rotational potential barrier such that the role of spin-internal rotation for relaxation of 1-methyl carbon spin becomes less important. Also noteworthy is the fact that the principal axes of inertia tensor and spin-rotation coupling tensor do not always coincide with each other and this may affect the spin-rotation relaxation contribution for 1-methyl carbon in a complicated manner. To see what brings about these different temperature behaviors we have first tested the Burke and Chan spin-rotation expression against the experimental data. The Burke-Chan expression for spin-rotation relaxation rate (Eq.[28]) with very low rotational energy barrier to internal rotation of methyl group may be written, inasmuch as temperature dependence is concerned, as follows:

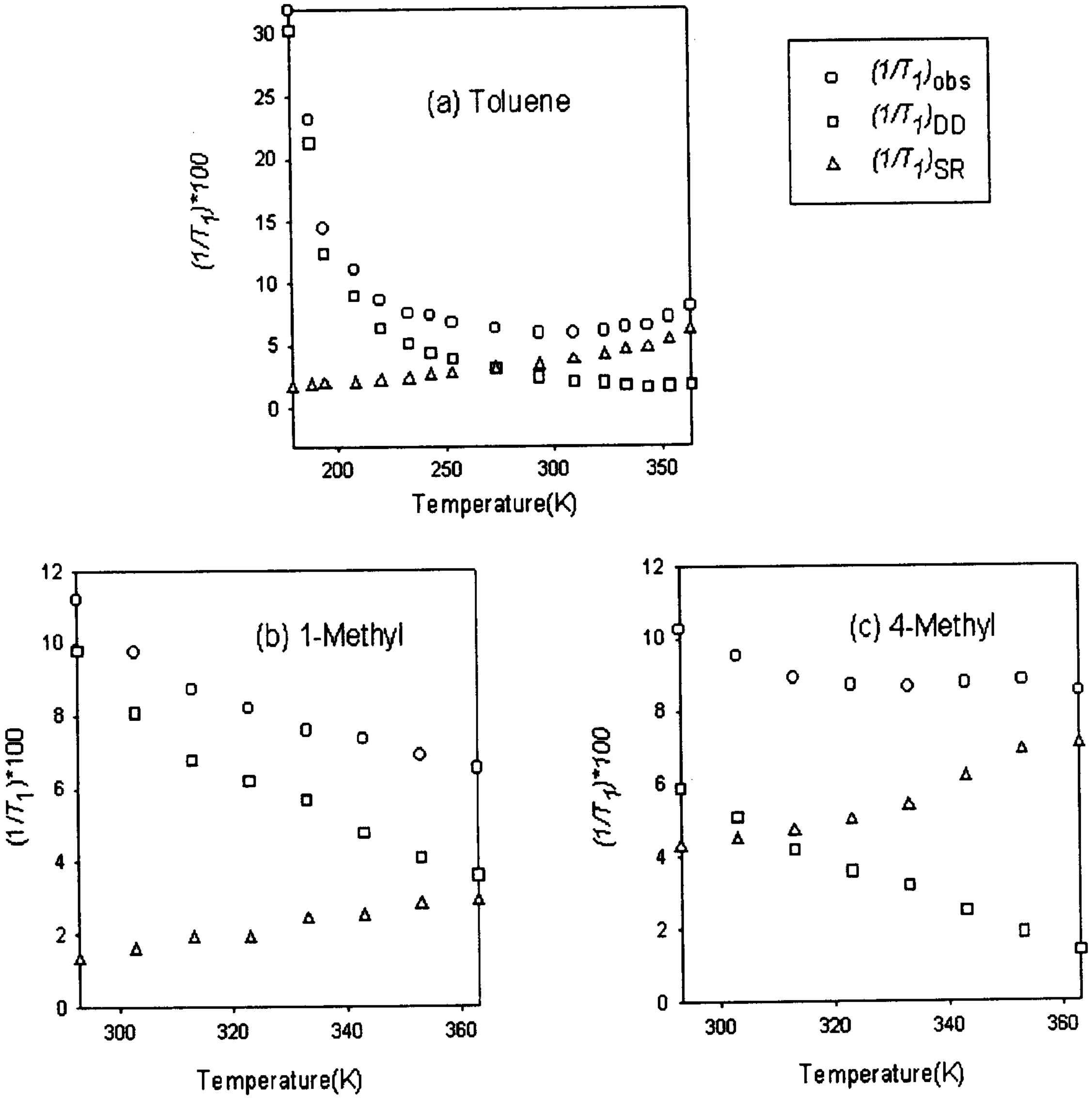

Fig.1 Temperature dependence of relaxation times of (a)Toluene, (b)1-methyl of 2-chloro-*p*-xylene, and (c)4-methyl of 2-chloro-*p*-xylene

$$\left(\frac{1}{T_1}\right)_{SR} = a'T\eta^{-1} + b'T^{1/2}$$

where a' and b' are two adjustable parameters.

The viscosity for toluene and *p*-xylene in liquid is known to depend on temperature as follows:[15]

$$\eta(\text{poise : toluene}) = \exp\left(-7.27 + \frac{409.6}{T - 103.1}\right)$$

$$\eta(\text{poise : } p - \text{xylene}) = \exp\left(-9.43 + \frac{1430}{T}\right)$$

Table 1. Observed Spin Lattice Relaxation Time and NOE Factor along with Estimated $(1/T_1)_{DD}$ and $(1/T_1)_{SR}$ for Methyl Carbon-13 of Toluene

Temperature (K)	$(T_1)_{obs}$	NOE Factor	$(1/T_1)_{DD} \times 100$	$(1/T_1)_{SR} \times 100$
179	3.13	1.88	30.3	1.77
188	4.31	1.83	21.3	1.87
194	6.91	1.72.	12.5	1.96
208	8.95	1.62	9.10	2.08
220	11.5	1.48.	6.46	2.23
233	13.2	1.36	5.17	2.39
243	13.4	1.24	4.4	2.69
253	14.7	1.17	3.99	2.80
273	15.7	1.00	3.21	3.17
293	16.7	0.84	2.53	3.47
309	16.7	0.72	2.17	3.83
323	16.2	0.62	2.08	4.25
333	15.5	0.57	1.84	4.63
343	15.4	0.53	1.73	4.76
353	13.9	0.49	1.77	5.41
363	12.4	0.46	1.86	6.20

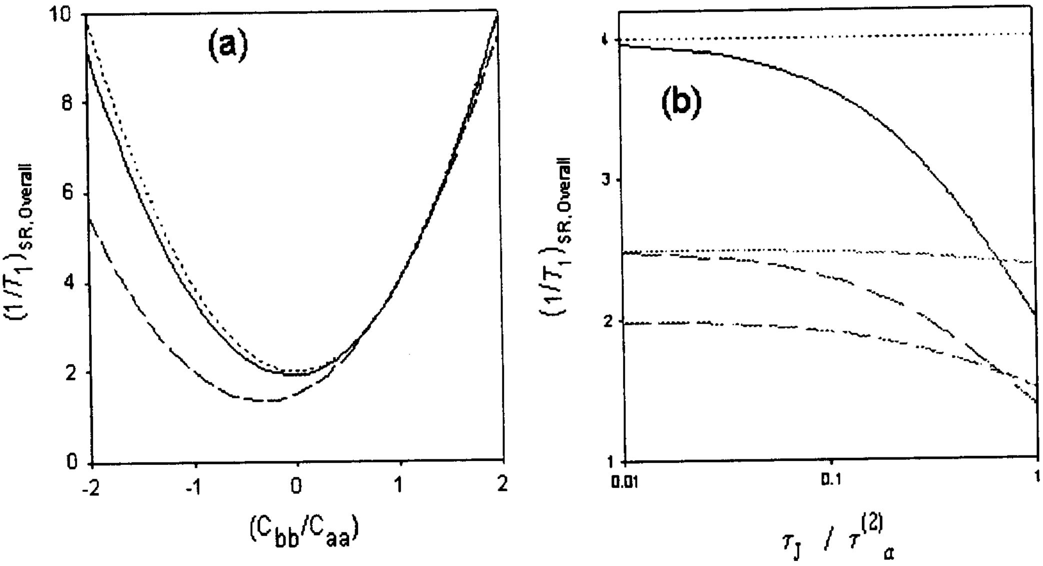

Fig.2(a) Spin-overall relaxation rate (in arbitrary unit) as a function of C_{aa} / C_{bb} with $\tau_J / \tau_\alpha^{(2)} = 0.01, 0.1, 1$ (shown sequentially downward from top to bottom)

(b) Spin-overall relaxation rate (in arbitrary unit) as a function of $\tau_J / \tau_\alpha^{(2)}$ with $C_{aa} / C_{bb} = 1.0, -1.0, 0.5, -0.5, 0.0$ (shown sequentially downward from top to bottom)

The results of nonlinear least-squares fitting are shown in Figs.3 through 5 and in Table 3. The contributions to the spin-rotational relaxation rate from spin-internal rotation coupling and spin-overall rotation coupling are graphically depicted in Figs.3 through 5. Each of the two contributions exhibits distinctive temperature dependence, since rotation of internal rotor is considered largely inertial while that of whole molecule is of diffusional character. In toluene, at room temperature the contribution from spin-internal rotation interaction is seen to be prevailing, as expected; however, the spin-overall-rotation coupling mechanism becomes increasingly important as the temperature goes up, eventually dominating at high temperature (>330K). As pointed out earlier by Burke and Chan, for ^{19}F spins in benzotrifluoride the contribution from spin-internal rotation coupling is significant up to 400K, more prevailing than in the case of methyl carbon-13 in toluene. Temperature dependence of 4-methyl carbon relaxation of 2-chloro-*p*-xylene shown in Fig.1(a)-(c) as well as that of toluene methyl carbon can be well explained by the Burke-Chan model, but $(1/T_1)_{SR}$ for 1-methyl carbon spin in 2-chloro-*p*-xylene exhibits somewhat different temperature behavior from the prediction by this model, increasing less steeply compared to those for 4-methyl carbon in the same molecule

Table 2. Observed Spin Lattice Relaxation Time and NOE Factor along with Estimated $(1/T_1)_{DD}$ and $(1/T_1)_{SR}$ for Methyl Carbon-13's in 2-Chloro-*p*-Xylene

Temperature (K)	$(T_1)_{obs}$		NOE Factor		$(1/T_1)_{DD} \times 100$		$(1/T_1)_{SR} \times 100$	
	1-Met	4-Met	1-Met	4-Met	1-Met	4-Met	1-Met	4-Met
293	8.93	9.75	1.77	1.17	9.8	5.9	1.3	4.3
303	10.25	10.52	1.68	1.07	8.1	5.1	1.6	4.5
313	11.47	11.22	1.58	0.95	6.8	4.2	1.9	4.7
323	12.21	11.50	1.53	0.85	6.2	3.6	1.9	5.0
333	13.20	11.56	1.41	0.73	5.7	3.2	2.4	5.4
343	13.60	11.43	1.32	0.58	4.8	2.5	2.5	6.2
353	14.48	11.31	1.17	0.45	4.1	1.9	2.8	6.9
363	15.32	11.76	1.10	0.34	3.6	1.4	2.9	7.1

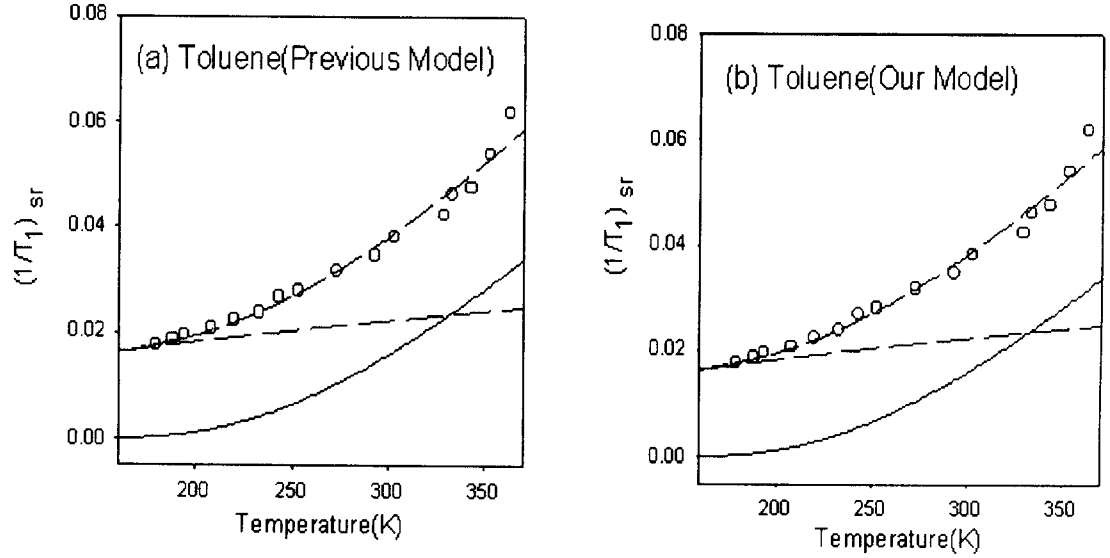

Fig.3 Methyl-13 spin-rotation relaxation rate of toluene with two models : solid line – spin overall contribution, dashed line – spin internal contribution.

and toluene methyl carbon. The Burke-Chan expression could of course give us the better agreement with the experimental data than those expressions that do not take spin-internal rotation coupling into consideration. Nonetheless, there still seems to exist some other factors that differentiate 1-methly carbon from 4-methyl carbon and toluene methyl carbon.

Previously, one has taken it for granted that the correlation function $\langle \exp[2i\alpha(t+\tau)]\exp[-2i\alpha(t)]\rangle$ may be assumed equal to unity, but in general the value of this correlation function may appreciably deviate from unity. On account of this we attempted to interpret the experimental data on the basis of our newly derived expression without such assumption. As can be seen from Eq.[27] the ratio κ^{-}/κ^{+} as well as the relative ratio of the correlation times $\tau_J/\tau_\alpha^{(2)}$ may affect the spin-overall rotational relaxation rate in a delicate manner. In order to understand these effects more clearly the spin-overall rotational relaxation rate was calculated numerically as a function of C_{aa}/C_{bb} as well as $\tau_J/\tau_\alpha^{(2)}$ as shown in Fig.2(a) and Fig.2(b), respectively. From Fig.2(a) the spin-overall rotational relaxation rate can be seen to increase with the absolute value of C_{aa}/C_{bb}. However, it can also be seen that the results are varying significantly depending on whether C_{aa} and C_{bb} has the same or opposite sign. In other words unless $\tau_J/\tau_\alpha^{(2)}$ is very large or small compared to unity, the signs of these two components of the spin-overall rotation coupling tensor can affect the overall relaxation rate substantially–especially when $\tau_J/\tau_\alpha^{(2)}$ gets close to one, as can be seen from Fig.2(b). But if C_{aa} and C_{bb} have the same sign and are equal in magnitude, the spin-overall rotation relaxation rate becomes independent of $\tau_J/\tau_\alpha^{(2)}$. That is to say, for a molecule with a symmetric spin-rotation tensor the spin-overall rotational relaxation rate is not affected by internal rotation.

Before applying Eq.[27] directly to interpret the experimental data, we first attempted preliminary estimation assuming the potential energy term, $\exp(-V_0/RT)$, changes very slowly over the temperature range of interest, which means rotational energy barrier to internal rotation, V_0, is very low. Nonlinear least-squares fitting of Eq.[27] with temperature dependent spin-rotation relaxation rate data, using the four adjustable parameters, are shown in Figs. 3 through 5 and the parameter values thereby deduced are listed in Table 3. One can see from Table 3 that the parameters relevant to the reduced correlation time $\tau_J/\tau_\alpha^{(2)}$ are larger for 1-methyl than for 4-methlyl. This may be ascribed to the fact that ortho-substitution of proton by chlorine in *p*-xylene heightens the barrier to internal rotation, thereby reducing the correlation time $\tau_\alpha^{(2)}$ and, hence, the contribution from nuclear spin internal rotation coupling. To see how the activation energy associated with internal rotation affect the fitting result in a more quantitative way we also attempted the least-squares fitting using the nonzero barrier in Eq.[27] as an adjustable parameter. The values of the parameters obtained in this way are also listed in Table 3. From the goodness of fit (sum of square deviations) we find that, although our modified full expression with five parameters yields merely slight improvement over that with four parameters in reproducing the experimental data, the reasonable potential barrier could be estimated from the fitting process, which predicted that the rotational energy barrier for 1-methyl group in 2-chloro-*p*-toluene could be roughly five times as high as that for 4-methyl group in the same molecule and that for methyl group in toluene.

In conclusion, we have demonstrated that our modified expression for spin-rotational contribution to total relaxation rate yields the better and more useful results in reproducing experimentally observed spin-rotation relaxation data than the original Chan-Burke expression. Unfortunately, for methyl carbon-13 it appears that both C_{aa} and C_{bb} have the same sign and the improvement over the original result is not conspicuous. However, a drastic improvement can be expected if these two components of spin-rotation tensor have mutually opposite sign..

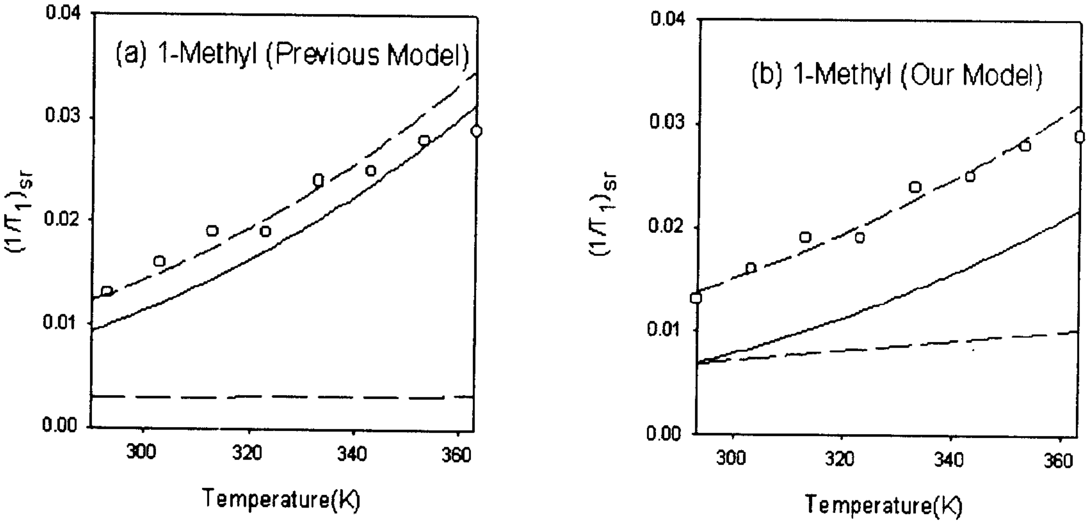

Fig4 1-Methyl-13 spin-rotation relaxation rate of 2-chloro-p-xylene with two models solid line – spin overall contribution, dashed line – spin internal contribution

Table 3. Parameter Values Obtained by Fitting with Experimental Data.

Parameter	Toluene		2-Chloro-p-Xylene			
			1-Methyl		4-Methyl	
a	4.23×10^{-4}	4.03	2.97×10^{-3}	3.12×10^{-3}	2.97×10^{-3}	3.12×10^{-3}
b	0.23	0.43	0.49	0.72	0.96	0.91
c	114.72	526	1.23	7.22	0.12	1.22
d	1.29×10^{-3}	1.43	1.71×10^{-4}	1.22×10^{-4}	1.66×10^{-3}	2.38×10^{-4}
V_0(J/mol)		152.44		4021.89		853.37
Standard Deviation	5.98×10^{-5}	6.23×10^{-5}	5.14×10^{-4}	4.86×10^{-4}	2.34×10^{-4}	2.75×10^{-4}
a'	4.24×10^{-4}		4.28×10^{-3}		4.28×10^{-3}	
b'	1.29×10^{-3}		1.72×10^{-4}		2.00×10^{-3}	
Standard Deviation	5.98×10^{-4}		6.40×10^{-4}		6.18×10^{-4}	

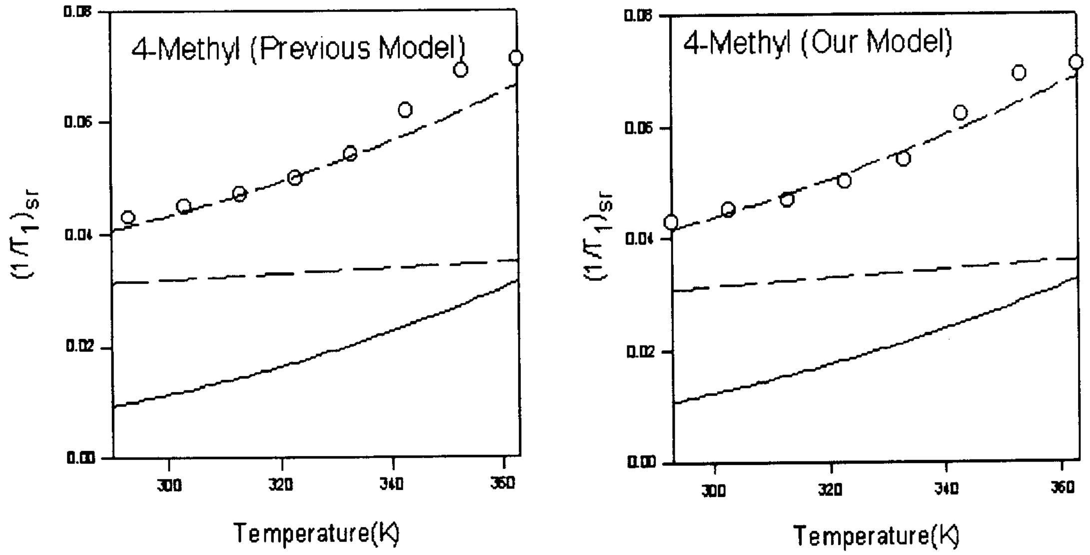

Fig.5 1-Methyl-13 spin-rotation relaxation rate of 2-chloro-p-xylene with two models : solid line – spin overall contribution, dashed line – spin internal contribution

Acknowledgment

This research was supported by a grant (Project No. BSRI 97-3414) from the Basic Science Research Institute Program, Ministry of Education, Korea, 1997.

RERERENCES

1. A. S. Dubin and S. I. Chan, *J.Chem.Phys.* **46**, 4533(1967).
2. K. F. Kuhlmann and D. M. Grant, *J. Chem Phys.* **55**, 2998(1971).
3. K. T. Gillen, U. Heaerlen and D. Schweitzer, *Mol. phys.* **20**, 899(1971).
4. B. D. Nageswara Rao and P.K. Mishra, *Chem. Phys. Lett.* **27**,592(1974).
5. C. F. Schmidt and S. I. Chan, *J. Mag. Res.* **2**, 120(1971).
6. T. E. Burke and S. I. Chan, *J. Mag.Res.* **2**,120(1970).
7. J. W. Lee, *Bull. Kor. Chem.Soc.* **4**, 48(1983).
8. J. W. Lee, *J. Kor. Chem. Soc.* **20**, 364(1976).
9. M. E. Rose, " Elementary Theory of Angular Momentum", John Wiley & Sons, 1957.
10. P. S Hubbard, *Rev. Mod. Phy.* **33**, 249(1961).
11. P. S. Hubbard, *Phy.Rev.* **131**, 1155(1963).
11. H. w. Spiess, D. Schweitzer, U. Haeberlen, and K. H. Hansser, *J. Mag. Res.* 5, 101 (1971).
13. D. Canet, *Prog. in NMR Spectroscopy.* **21**, 237(1989)
14. D. Shaw, *in* "Fourier Transform N.M.R. spectroscopy", pp. 139, Elsevier, Amsterdam (1976).
15. (a) H. D. Kim, M. S. Thesis(Seoul National University,1982, Unpublished).
    (b) S. M. Hong, M. S. Thesis(Seoul National University,1984, Unpublished).