



An NMR Study on Internal Rotation of CH₃ Group in 1,1,1-Trichloroethane

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Abstract : Coupled carbon-13 relaxation study of 1,1,1-trichloroethane dissolved in DMSO has been performed to gain some crucial insight into the dynamics of methyl group in this compound. For this purpose the relaxation behaviors of several observable magnetization modes for CH₃ spin system generated by various perturbing pulse sequences have been carefully investigated and various dipolar spectral densities were estimated by nonlinear numerical fittings of the observed data with the relaxation curves, which were then employed to determine the three principal values for the diffusion tensor for end-over-end molecular rotation as well as internal rotational parameters of methyl group. In this process we could uniquely determine two correlation times $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$ which give valuable information on internal rotor dynamics and thus obtained data were interpreted on the basis of various proposed models for internal rotation. compound undergoes three-fold jumps at 25°. The fact that the ratio $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ is close to 1.0 may be interpreted as indicating that methyl group in this C.

INTRODUCTION

During the past decades, many researchers have made considerable effort aimed for quantitative understanding of detailed molecular dynamics of methyl group in organic molecules in liquid phase.¹⁻³ Previously, studies on methyl group using NMR were primarily focused on the interpretation of measured spin-lattice and transverse relaxation times for ¹H or ¹³C of methyl group.⁴⁻⁶ However, these relaxation times (T_1 , T_2) alone are capable of providing information only on single effective correlation times. Therefore, to fully characterize the motion of molecules undergoing complex anisotropic reorientation, it is necessary to resort also to other sophisticated methodologies or spectroscopic techniques.^{7,8} Of all, the coupled relaxation method for multispin systems pioneered by Grant,⁹ Vold,¹⁰ and Canet¹¹ have a great advantage over other conventional methods used in NMR spectroscopy in that it gives us more detailed information on the dynamics of tumbling molecules

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although long experimental time may be needed. Application of this method to methyl group enables us to determine several dipolar auto- and cross-correlation spectral densities between proton-carbon and proton-proton internuclear vectors as well as other relevant dynamics parameters derived from them.^{12,13} Among these the most useful data were found to be two internal correlation times relevant to reorientation of methyl group, $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$, which cannot be obtained by any other conventional means of measuring T_1 only. The relative ratio of these two correlation times is expected to depend on the internal reorientational dynamics of methyl group. That is, it has been shown that this ratio becomes relatively large for diffusional reorientation of small angular steps while it assumes much smaller value for large angle jump between the potential wells and this fact may serve as a criterion as to which model suits better for describing internal reorientational dynamics of methyl group.

Recently, we have learned from the coupled relaxation experiment that the ratio $\tau_{\text{int}}^{(1)}/\tau_{\text{int}}^{(2)}$ is close to 1.73 for 2,6-dichlorotoluene in CDCl_3 solution at room temperature and have interpreted it as indicating that internal rotation of CH_3 group proceeds through large angle jumps among six-fold potential wells rather than diffusional small angle jumps.¹³ We have also shown on the basis of jump model that, if the methyl group undergoes large angle jumps in the presence of a three-fold symmetry potential well, the relative ratio of these two correlation times would become unity. To confirm this prediction we have performed the coupled C-13 relaxation experiment for 1,1,1-trichloroethane molecule dissolved in DMSO.

THEORY

The dynamical evolution of the magnetization modes for a multispin system can be described by the following Redfield equation;^{11,14}

$$\frac{d\mathbf{v}_i(t)}{dt} = -\sum_j \Gamma_{ij} \mathbf{v}_j(t) \quad (1)$$

where the elements of relaxation matrix Γ_{ij} may be shown to take the form

$$\Gamma_{ij} = \sum_{kk'} \sum_{mm'} (-1)^{m+1} J_{mm'}^{kk'}(\omega_k^m) \text{Tr} \{ [V_k^{-m}, T_i] [V_k^m, T_j] \} \quad (2)$$

The symbols appearing in Eq.(2) are described elsewhere⁹⁻¹¹ and each element of the Γ matrix can be expressed as a linear combination of spectral density terms.

In the case of CH₃ spin system, observable modes are

$$\begin{aligned}
 \nu_1 &= \text{Tr} \left\{ \chi(t) \frac{1}{2} I_Z^C \right\} \\
 \nu_2 &= \text{Tr} \left\{ \chi(t) \frac{1}{2\sqrt{3}} \left(I_Z^H + I_Z^{H'} + I_Z^{H''} \right) \right\} \\
 \nu_3 &= \text{Tr} \left\{ \chi(t) \frac{2}{\sqrt{3}} I_Z^C \left(I_Z^H I_Z^{H'} + I_Z^{H'} I_Z^{H''} + I_Z^{H''} I_Z^H \right) \right\} \\
 \nu_7 &= \text{Tr} \left\{ \chi(t) \frac{1}{\sqrt{3}} I_Z^C \left(I_Z^H + I_Z^{H'} + I_Z^{H''} \right) \right\} \\
 \nu_8 &= \text{Tr} \left\{ \chi(t) 4 I_Z^C I_Z^H I_Z^{H'} I_Z^{H''} \right\}
 \end{aligned} \tag{3}$$

It is straightforward to evaluate various dipolar spectral densities if a model of molecular reorientational process is assumed. In general, the dipolar spectral density between a pair of internuclear vectors ij and mn may be expressed in terms of a correlation time τ_D as follows:

$$J_{ijmn}^D = \frac{3}{40} \frac{\gamma_i \gamma_j \gamma_m \gamma_n \hbar^2}{r_{ij}^3 r_{mn}^3} \tau_D \tag{4}$$

The correlation time τ_D contains the information on not only end-over-end tumbling motion of the molecule as a whole but internal rotation of methyl group as well. In general τ_D is a function of several molecular dynamics parameters and could not easily be expressed in a compact form. However, if we assume the axis of internal rotation of methyl group coincides with one of the principal axes of overall rotational diffusion tensor, say the z-axis, then the correlation time τ_D can be shown to take the form

$$\begin{aligned}
 \tau_D &= \frac{c_1}{E_1 + 1/\tau_{\text{int}}^{(1)}} + \frac{c_1}{E_2 + 1/\tau_{\text{int}}^{(1)}} + \frac{c_2}{E_3 + 1/\tau_{\text{int}}^{(2)}} \\
 &+ \frac{c_3}{E_4 + 1/\tau_{\text{int}}^{(2)}} + \frac{c_4}{E_5 + 1/\tau_{\text{int}}^{(2)}} + \frac{c_3'}{E_4} + \frac{c_4'}{E_5}
 \end{aligned} \tag{5}$$

E_1 through E_5 appearing in Eq.(5) are expressed in terms of the three principal values of rotational diffusion tensor, D_{xx} , D_{yy} , and D_{zz} , as follows:⁹

$$\begin{aligned} E_1 &= 4D_{xx} + D_{yy} + D_{zz} \\ E_2 &= D_{xx} + 4D_{yy} + D_{zz} \\ E_3 &= D_{xx} + D_{yy} + 4D_{zz} \\ E_4 &= 6D + 6\sqrt{D^2 - \ell^2} \\ E_5 &= 6D - 6\sqrt{D^2 - \ell^2} \end{aligned} \quad (6)$$

where

$$\begin{aligned} D &= (D_{xx} + D_{yy} + D_{zz})/3 \\ \ell^2 &= (D_{xx}D_{yy} + D_{yy}D_{zz} + D_{zz}D_{xx})/3 \end{aligned} \quad (7)$$

And the coefficients c_i 's are the function of orientations of two dipolar vectors ij and kl as shown below:

$$\begin{aligned} c_1 &= 6 \cos \theta_{ij} \cos \theta_{kl} \sin \theta_{ij} \sin \theta_{kl} \cos(\phi_{ij} - \phi_{kl}) \\ c_2 &= (3/2) \sin^2 \theta_{ij} \sin^2 \theta_{kl} \cos[2(\phi_{ij} - \phi_{kl})] \\ c_3 &= (3/2) \cos^2(\beta/2) \sin^2 \theta_{ij} \sin^2 \theta_{kl} \cos[2(\phi_{ij} - \phi_{kl})] \\ c_4 &= \sin^2(\beta/2) (3 \cos^2 \theta_{ij} - 1) (3 \cos^2 \theta_{kl} - 1) \\ c_5 &= (3/2) \sin^2(\beta/2) \sin^2 \theta_{ij} \sin^2 \theta_{kl} \cos[2(\phi_{ij} - \phi_{kl})] \\ c_6 &= \cos^2(\beta/2) (3 \cos^2 \theta_{ij} - 1) (3 \cos^2 \theta_{kl} - 1) \end{aligned} \quad (8)$$

where θ_{ij} , ϕ_{ij} , θ_{kl} and ϕ_{kl} denote the polar and azimuthal angles of dipolar vectors ij and kl , respectively. The angle β is defined by

$$\beta = \tan^{-1} \left[\sqrt{3} (D_{xx} - D_{yy}) / \{ 2D_{zz} - (D_{xx} + D_{yy}) \} \right] \quad (9)$$

The correlation functions for internal rotation for methyl group, $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$, are defined as

$$\exp(-t/\tau_{\text{int}}^{(k)}) = \langle \exp[-ik\phi(0)] \exp[ik\phi(t)] \rangle \quad k = 1, 2 \quad (10)$$

with $\phi(t)$ denoting the angle describing internal rotation of methyl group about its axis of symmetry. It has been shown that these two internal correlation times play an important role in revealing the greater details of internal reorientational dynamics of methyl group. In other words, the knowledge of ratio of $\tau_{\text{int}}^{(1)}$ vs $\tau_{\text{int}}^{(2)}$ enables us to learn more about the dynamics of internal rotation of methyl group.

EXPERIMENTAL

A. Sample Preparation

For the coupled relaxation study of a CH₃ spin system, 1,1,1-trichloroethane (sample) and DMSO (solvent), all purchased from Aldrich, were used without further purification. A 50% v/v sample solution was prepared by dissolving 1,1,1-trichloroethane in DMSO. This was placed in a 5mm o.d. NMR tube and then degassed as usual by repeating the freeze-pump-thaw cycles four times before being sealed under vacuum.

B. NMR Experiments

NMR relaxation experiments were performed on a Varian VXR-200S spectrometer operating at 50.3MHz for ¹³C. Temperature was maintained at 298K throughout the measurements.

For the coupled spin relaxation study five different types of initial states for the spin system were prepared by applying the following five types of pulse sequences (Fig. 2 of ref(12)):

(a) total carbon magnetization inversion (carbon hard pulse)	V1V1
(b) total proton magnetization inversion (proton hard pulse)	V2V1
(c) longitudinal two spin order preparation	V7V1
(d) longitudinal three spin order preparation	V3V1
(e) longitudinal four spin order preparation	V8V1

The widths for 90° pulses for ¹³C and ¹H were found to be 12.7 μsec and 14 μsec respectively. The recycle time was set about 6 times the *T*₁ of methyl carbon-13 (in this case, 60sec) and 17 different intervals were taken. For each interval 64 scans were collected to obtain the desirable signal to noise ratio.

C. Calculations

The four observable magnetization modes can be expressed as the linear

combinations of these observed line intensities as follows:

$$\begin{aligned}
 {}^a\nu_1 &\propto L_1 + L_2 + L_3 + L_4 \\
 {}^a\nu_3 &\propto 3L_1 - L_2 - L_3 + 3L_4 \\
 {}^a\nu_7 &\propto -3L_1 - L_2 + L_3 + 3L_4 \\
 {}^a\nu_8 &\propto -L_1 + L_2 - L_3 + L_4
 \end{aligned} \tag{11}$$

where the subscripts in L_1 through L_4 represent the frequency of each methyl quartet peak in increasing order. A standard way to deduce the various parameters involved is by comparing the theoretical values predicted by the derived evolution expressions with the experimental data.

RESULTS AND DISCUSSION

The observable magnetization modes obtained from the coupled relaxation experiments are plotted as a function of the delay time in Figs. 1 through 3. The solid lines in these figures represent the theoretical relaxation curves reproduced by simultaneous least-square fittings of all experimental data. The dipolar and random field spectral densities obtained from these fittings are listed in Table 1.

Each carbon quartet line does not decay at the same recovery rate toward equilibrium. Clearly, the two inner lines relax faster than the two outer lines as can be seen from Fig. 1. The difference in relaxation rate is intimately related to the relative sign of the dipolar cross-correlation spectral density, K_{HCH} .

As shown in Eq.(11), the antisymmetric ${}^a\nu_3$ mode is directly related to the intensity difference between the inner lines and outer lines. The Redfield relaxation matrix elements involving the K_{HCH} are Γ_{13} and Γ_{16} , of which only Γ_{13} can be observed as a single quantum transition.¹⁶

And as expected, it is evident that the random field interaction makes substantial contributions to relaxation of both ^{13}C and ^1H located on a fast internal rotor, which originates from the spin-rotation coupling. Though intermolecular dipole-dipole interactions could also make a substantial influence on the relaxation rate in some cases, it is, however, deemed unimportant for carbon spin relaxation. The large contribution from the spin-rotation mechanism is expected to lower the NOE value. The NOE factor for CH_3 spin system can be formulated as a function of spectral densities in the extreme narrowing limit as⁹

$$\eta_{\text{C-(H)}} = \frac{\gamma_{\text{H}}}{\gamma_{\text{C}}} \frac{15J_{\text{CH}} - 200K_{\text{HCH}}^2}{30J_{\text{CH}} + 6j_{\text{C}} - 400K_{\text{HCH}}^2} \tag{15}$$

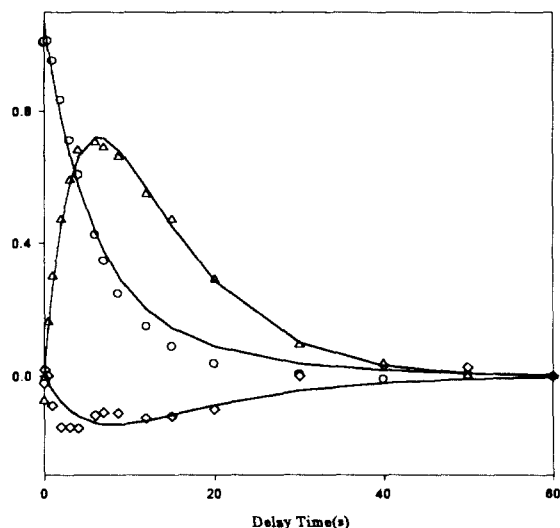


Fig. 1. Plot of Each Magnetization Mode Obtained from the Corresponding Experiment

$$O \quad y_1 = {}^a v_1(t) / \langle I_Z^C(eq) \rangle$$

$$\diamond \quad y_2 = {}^a v_3(t) / \langle I_Z^C(eq) \rangle \text{ using } {}^{13}\text{C}-\pi \text{ pulse}$$

$$\triangle \quad y_3 = {}^a v_1(t) / \langle I_Z^C(eq) \rangle \text{ using } {}^1\text{H}-\pi \text{ pulse}$$

The calculated NOE value from estimated spectral densities is 2.318, which is smaller than its maximum (≈ 2.987) in agreement with our expectation. The obtained spectral density data was utilized to extract the useful information regarding dynamics of the molecule under consideration. The diffusion constants D_{\perp} and D_{\parallel} and the two internal rotational correlation times $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$ were uniquely determined from Eq. (4) and are listed in Table 2. To check how the dipolar spectral densities vary with relative ratio of two internal rotational correlation time, we theoretically produced J_{CH} as a function of $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$.

As can be seen from Fig. 4, the J_{CH} value exhibits strong dependence upon the magnitude of $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$. This means that the relative ratio of internal rotational correlation times is helpful for probing the dynamics of internal rotor. If the molecule as a whole undergoes rotational motions in diffusive steps under the influence of intrinsic potential,

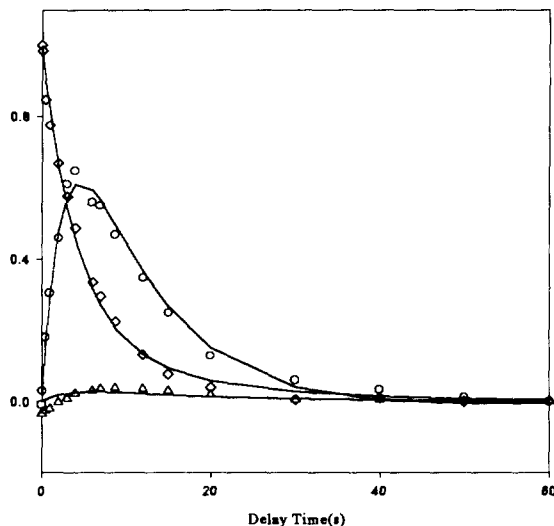


Fig. 2. Plot of Each Magnetization Mode Obtained from the Corresponding Experiment.

- $y_4 = {}^a v_3(t) / \langle I_Z^C(eq) \rangle$ using ${}^1\text{H}-\pi$ pulse
- ◇ $y_5 = {}^a v_3(t) / {}^a v_3(0)$ using Logitudinal Three Spin Order Preparation Pulse
- △ $y_6 = {}^s v_7(t) / {}^s v_7(0)$ using Logitudinal Two Spin Order Preparation Pulse

$$V(\theta) = \frac{\alpha}{2kT} (1 - \cos 3\theta) \quad (16)$$

where the α denotes the parameter describing the potential barrier height, then the rotational Smoluchowski equation for methyl group of 1,1,1-trichloroethane may be used to treat the situation numerically.¹⁷⁻¹⁸ The calculated results based on the Smoluchowski equation are shown in Fig. 5. As is evident from Fig. 5, the value of $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ approaches to that of jump limit (1.0) only when the barrier height is infinitely high. And as the symmetry of potential for the internal rotor changes from three-fold to six-fold, the lower limit of

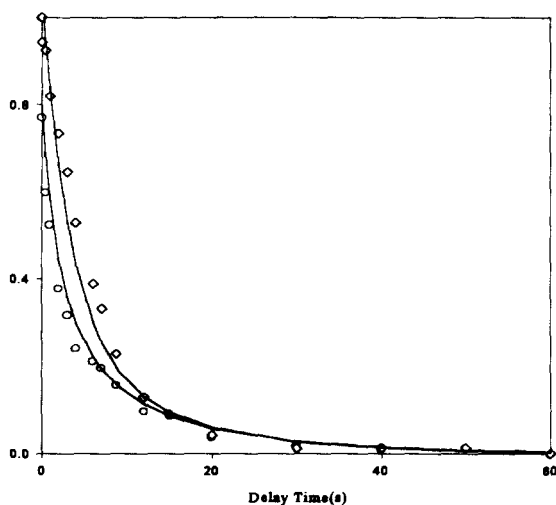


Fig. 3. Plot of Each Magnetization Mode Obtained from Corresponding Experiment.

○ $y_7 = \frac{^s v_8(t)}{^s v_7(0)}$ using Logitudinal Two Spin Order Preparation Pulse

◇ $y_8 = \frac{^s v_8(t)}{^s v_8(0)}$ using Logitudinal Four Spin Order Preparation Pulse

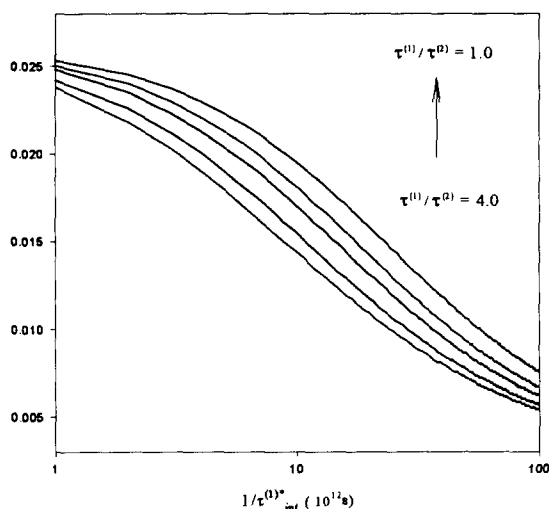
Table 1. Spectral Densities (s^{-1}) Obtained by Fitting with the Magnetization Mode Curves

J_{CH}	K_{HCH}	K_{CHH}	K_{CHHH}	J_{HH}	K_{HHH}
0.0091	-0.0017	0.0020	0.0020	0.0066	-0.0055
(±0.000003)	(±0.000002)	(±0.000001)	(±0.000006)	(±0.000002)	(±0.000002)
		j_C	j_H	k_{HH}	
		0.0230	0.0499	0.0591	
		(±0.000018)	(±0.000010)	(±0.000009)	

Table 2. Rotational Diffusion Parameters Obtained When Overall Rotation of Symmetric Top Is Assumed.

D_{\perp}	D_{\parallel}	$\tau_{\text{int}}^{(1)}$	$\tau_{\text{int}}^{(2)}$	$\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$
$1.14 \times 10^{11} \text{ s}^{-1}$	$1.89 \times 10^{11} \text{ s}^{-1}$	$3.33 \times 10^{-11} \text{ s}$	$3.25 \times 10^{-11} \text{ s}$	1.02

$\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ can be shown numerically to approach 3.0.¹³ Thus small-step diffusion-in-a-potential model with finite barrier height is not adequate for accounting for the present situation. Furthermore, as pointed out earlier in ref. 19, the extended diffusion model, which yields $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ values ranging from 2.0 to 4.0, cannot explain the current experimental results, either.¹³ Therefore, all these considerations and experimental results lead us to the conclusion that the rotation of the methyl group of 1,1,1-trichloroethane can be explained only on the basis of the large angle jump model in which the reorientation occurs *via* 120 jumps among the potential wells rather than the diffusive processes at room temperature.

**Fig. 4.** Spectral Density (J_{CH}) as a Function of Reduced Internal Correlation

Times with $\tau^{(1)}/\tau^{(2)}=4.0, 3.0, 2.0, 1.5, 1.0$ from bottom to top curve (D_{\perp}, D_{\parallel} are set to obtained values)

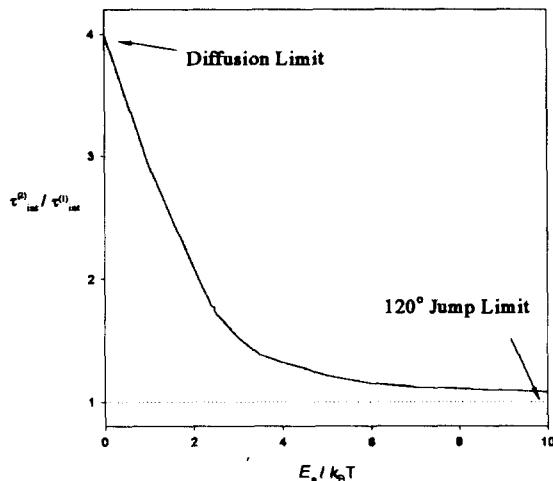


Fig. 5. Internal Correlation Time Ratio $\tau^{(1)}/\tau^{(2)}$ as a Function of Reduced Activation Energy

At higher temperatures, however, smaller angle jumps may be more prevalent, making the ratio $\tau_{int}^{(1)}/\tau_{int}^{(2)}$ larger than unity, which must be probed performing the experiments at several elevated temperatures.

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