



Characterization of Internal Reorientation of Methyl Group in 2,6-Dichlorotoluene

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Abstract : The two correlation times previously obtained in our coupled ¹³C relaxation measurement for the methyl group in 2,6-dichlorotoluene may be used as a criterion for evaluating the reorientation dynamics of an internal rotor. We numerically tested an extended diffusion model and the Smoluchowski diffusion equation to see how the rotational inertial effect and jump character contribute to the internal correlation time ratio of the internal rotor. We also analytically solved the general jump model with three different rate constants in a sixfold symmetric potential barrier. By assuming that the internal rotation of the methyl group in 2,6-dichlorotoluene can be described in terms of jumps among sixfold harmonic potential wells, we can conclude that the jump model satisfactorily reproduce the experimental data and the rate for sixfold jump is at least 1.53 times as great as that of a threefold jump.

Keywords : Correlation time; Internal rotor; Sixfold jump

INTRODUCTION

The NMR relaxation data of nuclear spins located in a methyl group can help us gain a wealth of insight regarding the physical aspects of detailed molecular dynamics.¹⁻³ Previous study on the AX₃ spin system was primarily focused on the conventional spin-lattice relaxation of A(¹³C) or X(¹H) in the methyl group.^{4,5} However, the experimental T₁ data alone cannot fully characterize the motion of molecules undergoing complex anisotropic reorientation because that data gives only one molecular correlation time.⁶⁻⁹ Thus, more

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sophisticated relaxation methods are needed to thoroughly comprehend the molecular motion. The scalar-coupled relaxation experiment pioneered by Grant et al. three decades ago is a suitable and powerful technique for this purpose.¹⁰⁻¹² While exploring the relaxation based on the modulation of intramolecular dipolar interactions they theoretically and experimentally investigated various weakly coupled spin systems. In contrast to the AX_2 spin system, the AX_3 spin system has been the subject of considerable theoretical but relatively little experimental study. Nonetheless, the physical properties of small and large molecules are known to be affected in a delicate manner by the presence of an internal CH_3 group within a given molecule. There is a large difference, for example, in the melting points between benzene and toluene. The white soft rubber poly(methyl acrylate) at room temperature shows quite different physical property from the hard plastic poly(methyl methacrylate); that is, the extra methyl group in the main chain of poly(methyl methacrylate) affects the mobility of the polymer chain. Thus, it is important to experimentally extract the dynamic parameters of the internal rotor.¹³⁻¹⁵

Several useful molecular parameters (such as the dipolar and random spectral densities) can be extracted from the coupled relaxation data. If we assume, firstly, that the whole molecule can be described by the overall anisotropic diffusion and, secondly, that there is a coincidence between the internal rotation axis and one of the principal axes of the overall rotation diffusion tensor, we can formulate the general dipolar correlation time as a function of the diffusion tensors and the internal correlation times. Of these the most useful dynamic parameters for characterizing the internal rotation dynamics are the two internal correlation times for the reorientation of the methyl group, $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$; these parameters can not be uniquely obtained by a conventional T_1 experiment. We expected the relative ratio of these correlation times to depend on the models that were adopted to justify the experimental data.⁹ Abragam pointed out that under the extreme narrowing condition, the effective correlation time $\tau^{(2)}$ for the whole molecule is related to the $\tau^{(1)}$ of the Debye formula as $\tau^{(1)}/\tau^{(2)} = 3$.^{16,17} The relative large value for the overall motion comes from the intrinsic assumption of small angular steps displacement because in a diffusion limit the rotational motion is strongly affected by the intermolecular collisions. Most spherical small molecules such as chloroform and methane show an inertial reorientational character rather than a diffusive character. The internal rotor dynamics in a relatively diluted liquid can

essentially be described by the extended diffusion equation in the same manner. Thus, we tested the extended J -diffusion model by extending the angular diffusion steps to an arbitrary size.^{18,19} The rotational Smoluchowski equation, which encompasses a large angle displacement character of diffusion in a specific potential was also solved under a sixfold trigonometric potential.²⁰ Finally, we propose a model in which the methyl group simultaneously undergoes twofold, threefold and sixfold jumps among six equivalent potential minima. We then analytically solve the master equation for that situation to see which theoretical models reproduce the experimental data.

DIPOLAR SPECTRAL DENSITY AND INTERNAL ROTATION CORRELATION TIME

The dynamical evolution of the magnetization modes for a nuclear spin system can be described by the Redfield equation.^{21,22} Previously we have derived the following expression for the dipolar spectral densities between a pair of dipolar vectors ij and mn .³

$$J_{ijmn}^D = \frac{3}{40} \left(\frac{\gamma_i \gamma_j \gamma_m \gamma_n \hbar^2}{r_{ij}^3 r_{mn}^3} \right) \tau_D \quad (1)$$

The correlation time, τ_D has the information about molecular anisotropic tumbling motion. In general, τ_D is a function of several molecular dynamic parameters and cannot easily be derived in a compact form. Nonetheless, if we assume that the axis of the internal rotation coincides with one of the principal axes of the overall rotational diffusion tensor, say the z -axis, then τ_D is given by

$$\begin{aligned} \tau_D = & \frac{c_1}{E_1 + 1/\tau_{\text{int}}^{(1)}} + \frac{c_1}{E_2 + 1/\tau_{\text{int}}^{(1)}} + \frac{c_2}{E_3 + 1/\tau_{\text{int}}^{(2)}} \\ & + \frac{c_3}{E_4 + 1/\tau_{\text{int}}^{(2)}} + \frac{c_4}{E_5 + 1/\tau_{\text{int}}^{(2)}} + \frac{c_{3'}}{E_4} + \frac{c_{4'}}{E_5} \end{aligned} \quad (2)$$

E_1 through E_5 appearing in Eq.(2) are expressed in terms of the three principal values of rotational diffusion tensor, D_{xx} , D_{yy} , and D_{zz} , like as formulated by Grant¹² And the coefficients c_i 's are the function of the orientations of the two dipolar vectors ij and kl :

$$\begin{aligned} c_1 &= 6 \cos \theta_{ij} \cos \theta_{kl} \sin \theta_{ij} \sin \theta_{kl} \cos(\phi_{ij} - \phi_{kl}) \\ c_2 &= (3/2) \sin^2 \theta_{ij} \sin^2 \theta_{kl} \cos[2(\phi_{ij} - \phi_{kl})] \\ c_3 &= (3/2) \cos^2(\beta/2) \sin^2 \theta_{ij} \sin^2 \theta_{kl} \cos[2(\phi_{ij} - \phi_{kl})] \\ c_{3'} &= \sin^2(\beta/2) (3 \cos^2 \theta_{ij} - 1) (3 \cos^2 \theta_{kl} - 1) \\ c_4 &= (3/2) \sin^2(\beta/2) \sin^2 \theta_{ij} \sin^2 \theta_{kl} \cos[2(\phi_{ij} - \phi_{kl})] \\ c_{4'} &= \cos^2(\beta/2) (3 \cos^2 \theta_{ij} - 1) (3 \cos^2 \theta_{kl} - 1) \end{aligned} \quad (3)$$

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

$$\beta = \tan^{-1} \left[\frac{\sqrt{3}(D_{xx} - D_{yy})}{\{2D_{zz} - (D_{xx} + D_{yy})\}} \right] \quad (4)$$

In this formalism the internal correlation time, $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$, are defined as

$$\exp(-t/\tau_{\text{int}}^{(k)}) = \langle \exp[-ik\varphi(0)] \exp[ik\varphi(t)] \rangle \quad k = 1, 2 \quad (5)$$

where $\varphi(t)$ denotes the angle that describes the reorientation of the methyl group about its axis of symmetry. The two internal correlation times have a key role in revealing the internal rotation of the methyl group.

EXTRACTING DIPOLAR SPECTRAL DENSITIES

For a coupled spin relaxation measurement five different types of initial spin states were prepared by applying the following five pulse sequences³

(a) total carbon magnetization inversion (carbon hard pulse) $\frac{1}{2} I_Z^C$

(b) total proton magnetization inversion (proton hard pulse) $\frac{1}{2\sqrt{3}} (I_Z^H + I_Z^{H'} + I_Z^{H''})$

(c) longitudinal two spin order preparation $\frac{1}{\sqrt{3}} I_Z^C (I_Z^H + I_Z^{H'} + I_Z^{H''})$

(d) longitudinal three spin order preparation $\frac{2}{\sqrt{3}} I_Z^C (I_Z^H I_Z^{H'} + I_Z^{H'} I_Z^{H''} + I_Z^H I_Z^{H''})$

(e) longitudinal four spin order preparation $4 I_Z^C I_Z^H I_Z^{H'} I_Z^{H''}$

The five observable magnetization modes that were perturbed by several pulses were numerically fitted with the well known Redfield Equation.²¹ Table 1 lists the dipolar and random spectral densities obtained by this fitting procedure at two different ¹³C frequency. The dipolar spectral densities are similar in magnitude at both magnetic fields, but the slight difference in the j_c can be ascribed to the coupling between the dipolar interaction and the chemical shift anisotropy of the carbon nucleus. To double-check the proton dipolar spectral density at 200MHz of a ¹H frequency, we conducted a normal inversion recovery proton relaxation experiment with a dilution technique (0.078, 0.035M, 0.012M of 2,6-dichlorotoluene/CDCl₃) that is conventionally used to safely extract the dipolar spectral densities of proton without an interproton dipole-dipole interaction. From these dipolar

spectral densities three overall diffusion constants and two internal correlation time were uniquely determined with Eq.(2) and the results of which are shown in Table 6 of Paper 3. We then used these dynamic parameters to deduce the detailed molecular motion of the internal methyl group.

Table 1. Spectral Densities for Methyl System at Two Magnetic Fields

	50MHz	125MHz
J_{CH}	0.0039 ± 0.00005	0.0039 ± 0.00006
K_{HCH}	0.0020 ± 0.00011	0.0028 ± 0.00014
K_{CHH}	0.0042 ± 0.00010	0.0042 ± 0.00009
K_{CHHH}	0.0022 ± 0.00042	0.0020 ± 0.00048
J_{HH}	0.0067 ± 0.00025 $0.0066 \pm 0.00015^*$	0.0063 ± 0.00024
K_{HHH}	0.0053 ± 0.00025	0.0051 ± 0.00027
j_C	0.0135 ± 0.00069	0.0165 ± 0.00075
j_H	0.0215 ± 0.00095 $0.0221 \pm 0.00084^*$	0.0227 ± 0.00094
k_{HH}	0.0269 ± 0.00143	0.0253 ± 0.00151

(* from the diluted proton inversion recovery pulse sequence)

NUMERICAL RESULTS FOR SEVERAL MODELS AND DISCUSSION

If the internal rotor sits on the a spherical molecule that is undergoing rotational diffusive motion, the dipolar correlation time in Eq.(4) can be simply converted into

$$\tau_D = \frac{2c_1}{6D + 1/\tau_{\text{int}}^{(1)}} + \frac{2c_2}{6D + 1/\tau_{\text{int}}^{(2)}} + \frac{(3 \cos^2 \theta_{ij} - 1)(3 \cos^2 \theta_{kl} - 1)}{6D} \quad (6)$$

This result is equivalent to Woessner's diffusion model in which an internuclear dipolar vector diffuses freely about an internal symmetry axis attached to a tumbling sphere at a specified angle.^{23,24} The ratio between the $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$ of this model is much greater (= 4) than the experimental value (1.73 to 1.75). The higher value is likely due to the inherent nature of the rotational diffusion theory, where molecules incessantly collide with each other thereby yielding a larger value for $\tau_{\text{int}}^{(1)}$ than for $\tau_{\text{int}}^{(2)}$.

The extended diffusion model gives a better description of the experimental data than the simple diffusion theory because it removes the restriction of small angle diffusive steps and allows the inertial effect. Bull applied this model to the symmetric top molecule with an internal rotor.⁵ Later, a successful description of the T_1 of an internal rotor of toluene was reported.²⁵ In this picture, the direction of the internal angular momentum vector is fixed along the axis of the internal rotation and only the magnitude of the internal angular momentum is randomized at the end of each free rotation step.^{6,7} Shin developed a more general expression where the collision simultaneously randomizes both the overall and internal angular momentum. The ratio of the internal correlation times in this framework can be analytically formulated by

$$\frac{\tau_{\text{int}}^{(1)}}{\tau_{\text{int}}^{(2)}} = \frac{\frac{g_{\text{int}}^{(1)}}{1 - \tau_{\alpha}^{-1} g_{\text{int}}^{(1)}}}{\frac{g_{\text{int}}^{(2)}}{1 - \tau_{\alpha}^{-1} g_{\text{int}}^{(2)}}} \quad (7)$$

where $g_{\text{int}}^{(s)} = \sqrt{\frac{\pi}{x_s}} \exp(1/x_s \tau_{\alpha}^2) \operatorname{erfc}(\sqrt{1/x_s \tau_{\alpha}^2})$, $x_s = 2s^2 k_B T / I_{\alpha}$, $s = 1, 2$

The $\operatorname{erfc}(x)$ is the complementary error function and I_{α} the moment of inertia of the internal rotor, $k_B T$ the Boltzman factor. Theoretical values at two limiting cases, namely the diffusion limit (= 2.0) and the free rotation limit (= 4.0) can be obtained with the help of the following identity and the L'Hospital theme;²⁶

$$\lim_{x \rightarrow \infty} e^{x^2} \operatorname{erfc}(x) = 0, \quad \lim_{x \rightarrow \infty} x e^{x^2} \operatorname{erfc}(x) = \sqrt{\frac{2}{\pi}} \quad (8)$$

Fig 1. shows the curve of the internal correlation time ratio. As the momentum inertia of the internal rotor goes to zero and the internal angular momentum correlation time increases rapidly, the value of $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ reaches the free rotor limit of 2. The value of $\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ increases sharply with the value of $\sqrt{1/x_s \tau_{\alpha}^2}$, and the diffusion rotor limit can be read from the curve.

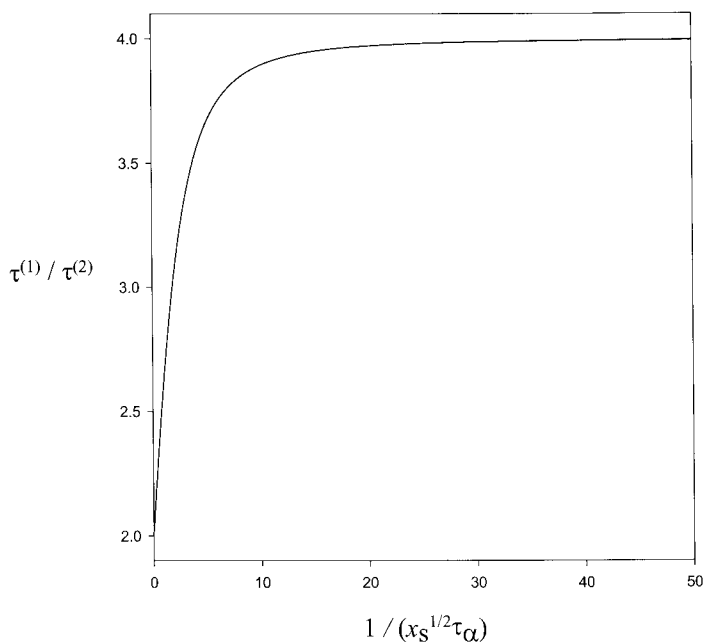


Fig 1. Internal correlation time ratio as a function of reduced internal angular momentum correlation time.

From Fig 1. we can deduce that the extended diffusion model cannot reach the experimental value (1.73 to 1.75) even at the free rotor limit. This occurs because the extended diffusion model has an inherent limitation with respect to the diffusive behavior of the internal rotor; that is it does not consider the effect of the potential barrier around the symmetric internal rotor. Hence, we tested the Smoluchowski equation, which is adequate for describing the mixed behavior of both the diffusion and the jumping between the

potential wells. This equation can be easily solved numerically if the tractable potential is known.²⁰

In this formalism, the correlation times can be shown to have the form

$$\tau_{\text{int}}^{(l)} = \sum_k \beta_k^{(l)} / \lambda_k D \quad l = 1, 2 \quad (9)$$

where $\beta_k^{(l)}$ is a linear combination of elements of eigenvectors \mathbf{Y} for the given potential matrix \mathbf{B} .

Numerical calculations reveal that in the case of the sixfold potential function $V(\varphi) = \eta(1 - \cos 6\varphi)$ the extension of the matrix size to dimensions larger than 100×100 produces very little effect on its first few lowest eigenvalues and the corresponding eigenvectors; hence, we truncated the size of the matrix to 126×126 . First few lowest eigenvalues and the corresponding coefficients $\beta_k^{(l)}$'s calculated at various values of barrier height $2\eta/kT$ for sixfold potential function are listed in Table 2.

From these results, we can see that the magnitude of coefficients $\beta_k^{(l)}$'s sharply decreases as the eigenvalues λ_k 's increase, and, as a result, the series in Eq.(9) rapidly converges. In reality, we found that the sum of the first eigenvalue term is responsible for more than 98% of the series sum and from this sum, we were able to calculate the value of

Table 2. Internal Correlation Time Ratio for Sixfold Barrier.

E_a ($2\eta/k_B T$)	$\tau_{int}^{(1)}/\tau_{int}^{(2)}$	$\beta^{(1)}_1$	$\beta^{(1)}_6$	$\beta^{(2)}_2$	$\beta^{(2)}_5$	$\lambda_1 D$	$\lambda_2 D$	$\lambda_5 D$	$\lambda_6 D$
0.0	4.00	1.000	0.000	1.000	0.000	1.000	4.000	16.000	36.000
1.0	3.86	0.997	0.00346	0.958	0.0405	0.872	3.262	18.403	26.740
3.0	3.37	0.984	0.00930	0.926	0.0567	0.345	1.097	33.470	39.790
5.0	3.17	0.988	0.00940	0.947	0.0409	0.0847	0.257	58.310	63.490
7.0	3.07	0.993	0.00486	0.971	0.0214	0.0168	0.0504	91.004	95.434
9.0	3.06	0.991	0.00032	0.977	0.0197	0.0030	0.0090	128.910	132.520

$\tau_{int}^{(1)}/\tau_{int}^{(2)}$ as a function of the barrier height. The ratio of the two correlation times calculated at several different values of barrier height for sixfold potential function is shown in Table 3.

In the presence of a sixfold potential barrier, this model predicts that the ratio of $\tau_{int}^{(1)}/\tau_{int}^{(2)}$ would ranges from a dilution limit of 4.0 for a zero barrier height to a high barrier limit of 3.0 is closely related to the sixfold jumping model. However, the large value of $\tau_{int}^{(1)}/\tau_{int}^{(2)}$ shows that this model is inadequate for describing the motion of the methyl group in the 2,6-dichlorotoluene.

When we use a threefold potential function, the internal correlation time ratio, $\tau_{int}^{(1)}/\tau_{int}^{(2)}$, tends to vary more widely; that is from a diffusion limit of 4 to 1 with high threefold barrier limit. Nonetheless, it is difficult to envision how the threefold jump comes into play in our system.

Table 3. Internal Correlation Times and Ratios

$\tau_{\text{int}}^{(1)} / \tau_{\text{int}}^{(2)}$ (Exp)	1.73 ~ 1.75	
Free Internal Diffusion	4.0	
Extended Diffusion Model	Diffusion Limit	4.0
	Free Rotor Limit	2.0
Diffusion in a potential	$V(\varphi) = \eta (1 - \cos 3\varphi)$	1.5 ~ 4.0
	$V(\varphi) = \eta (1 - \cos 6\varphi)$	3.0 ~ 4.0
3-fold Jump Limit	$k_2 \neq 0, k_1, k_3 = 0$	1.0
6-fold Jump Model	$k_1 \neq 0, k_2, k_3 = 0$	1.5
	$k_1, k_2 \neq 0, k_3 = 0$	3.0
	$k_1, k_2, k_3 \neq 0$	1.0 ~ 3.0

The presence of two bulky chlorine atoms in the 2,6-dichlorotoluene might have a strong influence on the internal methyl rotor to bring about a high rotational potential barrier. In that case, a large angle jump model based on jumps among the potential wells can describe this situation more elegantly. A jump model that can explain the internal rotation of the methyl group in the presence of a sixfold potential barrier can be described by the following master equation:

$$\frac{d}{dt} P_i = - \left(\sum_{j(\neq i)} R_{ji} \right) P_i + \sum_{j(\neq i)} R_{ij} P_j \quad (i, j = 1, \dots, 6) \quad (10)$$

where the element of the rate matrix, R_{ij} , represents the rate of the $j \rightarrow i$ transition and satisfies the condition of $R_{ij} = R_{ji}$.

Eq.(10) may be solved under boundary conditions in which one of the six P_i 's is equal to 1 at $t = 0$ and all the P_i 's become equal to $1/6$. Suppose that methyl group is in the conformation corresponding to the angle $\varphi = 0$ at $t = 0$; that is $P(\varphi, 0 | 0, 0) = 1$ for $\varphi = 0$ and $P(\varphi, 0 | 0, 0) = 0$ for all other values of φ . If we denote the rate constants for sixfold, threefold, and twofold jump, by k_1 , k_2 , and k_3 , respectively, the rate matrix has the form

$$\mathbf{R} = k_1 \begin{pmatrix} r_d & 1 & r_1 & 2r_2 & r_1 & 1 \\ 1 & r_d & 1 & r_1 & 2r_2 & r_1 \\ r_1 & 1 & r_d & 1 & r_1 & 2r_2 \\ 2r_2 & r_1 & 1 & r_d & 1 & r_1 \\ r_1 & 2r_2 & r_1 & 1 & r_d & 1 \\ 1 & r_1 & 2r_2 & r_1 & 1 & r_d \end{pmatrix} \quad (11)$$

where $r_1 = k_2/k_1$, $r_2 = k_3/k_1$ and $r_d = -2(r_1 + r_2 + 1)$.

To analytically solve Eq.(10) we need diagonalize the 6×6 rate matrix Eq.(11). This task is difficult but we can alleviate the difficulty by considering the symmetry inherent in the present problem. To see how the symmetry work in solving the master equation suppose the methyl group assume the angle $\varphi = 0$ at $t = 0$. Then, due to randomness of its rotational motion, we may expect that at any later time t ,

$$P(\pi/3, t | 0, 0) = P(5\pi/3, t | 0, 0) \text{ and } P(2\pi/3, t | 0, 0) = P(4\pi/3, t | 0, 0). \text{ Therefore,}$$

it will suffice to diagonalize the 4×4 rate matrix given by Eq.(12) instead of the larger matrix (11).

$$\frac{d}{dt} \begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \end{pmatrix} = k_1 \begin{pmatrix} r_d & 2 & 2r_1 & 2r_2 \\ 1 & r_d + r_1 & 1 + 2r_2 & r_1 \\ r_1 & 1 + 2r_2 & r_d + r_1 & 1 \\ 2r_2 & 2r_1 & 2 & r_d \end{pmatrix} \begin{pmatrix} P_0 \\ P_1 \\ P_2 \\ P_3 \end{pmatrix} \quad (12)$$

where P_k is the shorthand notation for $P(k\pi/3, t | 0, 0)$.

It is well known from the linear algebra that the solutions to Eq.(14) have the form

$$P_j = \sum_{k=0}^3 \alpha_{jk} \exp(-\lambda_k t) \quad (13)$$

where λ_k 's are the eigenvalues for the rate matrix given in Eq.(13). Therefore, the

correlation functions $\langle \exp[-i\varphi(0)] \exp[i\varphi(t)] \rangle$ and

$\langle \exp[-i2\varphi(0)] \exp[i2\varphi(t)] \rangle$ take the following form:

$$\langle \exp[-i\varphi(0)] \exp[i\varphi(t)] \rangle = \sum_{k=0}^3 (\alpha_{0k} + \alpha_{1k} - \alpha_{2k} - \alpha_{3k}) \exp(-\lambda_k t) \quad (14)$$

$$\langle \exp[-i2\varphi(0)] \exp[i2\varphi(t)] \rangle = \sum_{k=0}^3 (\alpha_{0k} - \alpha_{1k} - \alpha_{2k} + \alpha_{3k}) \exp(-\lambda_k t) \quad (15)$$

The initial condition $P_j = \delta_{j0}$ at $t = 0$ requires that $\sum_{k=0}^3 \alpha_{jk} = \delta_{j0}$. And the boundary condition $P_j = \frac{1}{6}$ at $t = \infty$ requires that one of the eigenvalues, say λ_0 , must be zero and $\alpha_{j0} = \frac{1}{6}$ regardless of j value. At $t = 0$ both correlation functions in Eq.(13) become equal to 1, respectively, whence the following additional conditions should be satisfied:

$$\sum_{k=0}^3 (\alpha_{0k} + \alpha_{1k} - \alpha_{2k} - \alpha_{3k}) = \sum_{k=0}^3 (\alpha_{0k} - \alpha_{1k} - \alpha_{2k} + \alpha_{3k}) = 1 \quad (16)$$

The condition $\alpha_{j0} = \frac{1}{6}$ regardless of j automatically makes both correlation functions vanish $t = \infty$. The coefficients α_{ij} 's can in general be evaluated from the following eigenvalue equation under constraints imposed by the boundary conditions.

$$\begin{aligned} (\lambda_k - 2 - 2r_1 - 2r_2) \alpha_{0k} + 2 \alpha_{1k} + 2 r_1 \alpha_{2k} + 2 r_2 \alpha_{3k} &= 0 \\ \alpha_{0k} + (\lambda_k - 2 - r_1 - 2r_2) \alpha_{1k} + (1 + 2r_2) \alpha_{2k} + r_1 \alpha_{3k} &= 0 \\ r_1 \alpha_{0k} + (1 + 2r_2) \alpha_{1k} + (\lambda_k - 2 - r_1 - 2r_2) \alpha_{2k} + \alpha_{3k} &= 0 \\ 2r_2 \alpha_{0k} + 2 r_1 \alpha_{1k} + 2 \alpha_{2k} + (\lambda_k - 2 - 2r_1 - 2r_2) \alpha_{3k} &= 0 \end{aligned} \quad (17)$$

for $k = 0, 1, 2,$ and 3 .

The above master equation can be analytically solved to yield the following four eigenvalues:

$$\lambda_k = 0, \quad (1 + 3r_1 + 4r_2)k_1, \quad (4 + 4r_2)k_1, \quad (3 + 3r_1)k_1 \quad (18)$$

These corresponding eigenvalues are fed back into a secular equation to find the α_{kj} 's.

Thus, each conditional probability density is obtained as follows

$$\begin{aligned} P_0 &= \frac{1}{6} [1 + 2 \exp(-\lambda_1 t) + \exp(-\lambda_2 t) + 2 \exp(-\lambda_3 t)] \\ P_1 &= \frac{1}{6} [1 + \exp(-\lambda_1 t) - \exp(-\lambda_2 t) - \exp(-\lambda_3 t)] \\ P_2 &= \frac{1}{6} [1 - \exp(-\lambda_1 t) + \exp(-\lambda_2 t) - \exp(-\lambda_3 t)] \\ P_3 &= \frac{1}{6} [1 - 2 \exp(-\lambda_1 t) - \exp(-\lambda_2 t) + 2 \exp(-\lambda_3 t)] \end{aligned} \quad (19)$$

This produces the following results:

$$\langle \exp[i\varphi(0)] \exp[-i\varphi(t)] \rangle = \exp[-(k_1 + 3k_2 + 4k_3)t] \quad (20)$$

$$\langle \exp[2i\varphi(0)] \exp[-2i\varphi(t)] \rangle = \exp[-(3k_1 + 3k_2)t] \quad (21)$$

which means that

$$\tau_{\text{int}}^{(1)} = (k_1 + 3k_2 + 4k_3)^{-1} \text{ and } \tau_{\text{int}}^{(2)} = (3k_1 + 3k_2)^{-1} \quad (22)$$

and

$$\frac{\tau_{\text{int}}^{(1)}}{\tau_{\text{int}}^{(2)}} = \frac{3k_1 + 3k_2}{k_1 + 3k_2 + 4k_3} \quad (23)$$

We have to note here that twofold jump cannot affect the correlation function of (22) and, hence, $\tau_{\text{int}}^{(2)}$ does not depend on k_3 . If the ratio of the internal correlation times is set at a constant, α , (1.75 in our experiment), then the relation among the jumping rates can be visualized. Fig. 2 shows $\tau_{\text{int}}^{(1)}/\tau_{\text{int}}^{(2)}$ with two relative rate constants (r_1 , and r_2). We can easily see from Fig. 2 that r_1 , and r_2 are linearly and competitively correlated to each other and that k_2 is at least $4\alpha / (3\alpha - 3)$ times greater than k_3 . In our experiment ($\alpha = 1.73$ to 1.75) k_2 is at least three times larger than k_3 so k_3 is not too small to ignore for a good interpretation of the experimental data. This explains why a 180° transition may simultaneously take place in the reorientation of the methyl group of 2,6-dichlorotoluene. Eq.(23) encompasses the ever-existing jump model results, which can easily be tested. First, if we set k_1 , and k_3 to zero, then the ratio of internal correlation time reduces to a simple 120 jump motion important for

the many internal segmental rotations, such as the gauche-trans transition in chain molecules.²⁷⁻²⁹ Second, if the three rate constants are equal, then the $\tau_{\text{int}}^{(1)}/\tau_{\text{int}}^{(2)}$ value is equal to 3/4, and this value is even lower than the 120° jump limit ($= 1.0$), which seems to be unphysical. Experimentally, we can measure the two correlation times $\tau_{\text{int}}^{(1)}$ and $\tau_{\text{int}}^{(2)}$, but, unless we can measure the third, we cannot uniquely determine the three rate constants k_1 , k_2 , and k_3 on the basis of this model. However, even in this case, we can set the upper boundary for the $\tau_{\text{int}}^{(1)}/\tau_{\text{int}}^{(2)}$ ratio. That is, since k_3 , however small, is not zero, we have

$$\frac{\tau_{\text{int}}^{(1)}}{\tau_{\text{int}}^{(2)}} < \frac{3k_1 + 3k_2}{k_1 + 3k_2} \quad (24)$$

which means $k_2/k_1 < 0.56$. In other words, the rate for the threefold jump is at most equal to 0.56 times the rate for the sixfold jump, which sounds very reasonable even from an intuitive perspective.

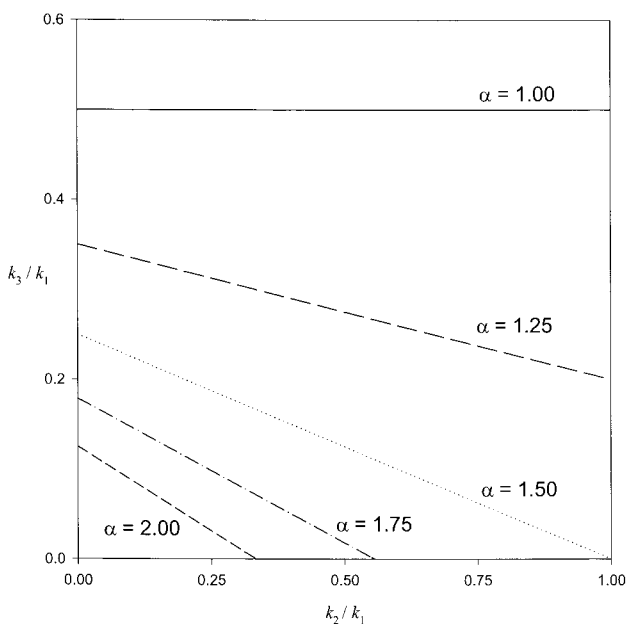


Fig 2. Graphic representation of relative rate constants at a specific internal correlation time ratio.

CONCLUSIONS

In summary, we have shown that the methyl rotor dynamics of 2,6 dichlorotoluene can be described within the framework of a jump in a sixfold harmonic potential well. The relative magnitude of the internal correlation times of the molecule obtained from the ^{13}C -coupled relaxation experiment leads to the conclusion that the jump rate between the nearest potential well is at least 1.53 times as great as that of the next nearest well. The coupled AX_3 multi-pulse spin relaxation experiment together with the inversion recovery process for X_3 spin system is still valuable tool to extract the spectral densities of methyl group to understand the internal rotor dynamics of methyl group, which helps to investigate the more complex motion of side chain as well as overall backbone motion of polymer and natural macromolecules that is currently being studied in our laboratory.

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