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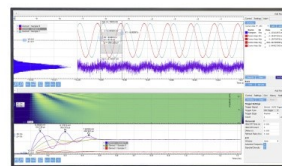
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Extended diffusion theory of reorientation of symmetric top molecules with internal rotation

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The extended diffusion (ED) theory for the reorientational dynamics of a symmetric top molecule with internal rotation is reinvestigated. Based on a unified ED picture, we express, by using the convolution theorem of the Laplace transform, the reorientational correlation time with overall and internal free rotor correlation functions. In this work, Bull's "equal angular momentum correlation time assumption" for both overall and internal rotations is removed. Limiting expressions, for diffusion limit of the overall rotation, are derived and shown to reduce to the results of previous works. As an application, our numerical calculations are compared with experiments on ¹³C nuclear-magnetic-resonance dipolar relaxation times of toluene. Angular momentum correlation times, thus obtained from the comparison, show that our calculations agree with the previous work of Chung *et al.* [Chem. Phys. Lett. **93**, 499 (1982)]. © 1997 American Institute of Physics. [S0021-9606(97)04117-2]

I. INTRODUCTION

Reorientation of simple molecules with internal rotation in liquid has been investigated by many authors, both theoretically¹⁻⁵ and experimentally,⁶⁻¹² for various molecules like toluene,^{5,7,8} mesitylene,^{6,9-11} and alkyl chains.¹² A variety of theoretical models has been proposed for the internal rotation, typical models of which are; diffusion,^{1,2} jump,^{1,2} Fokker-Planck-Langevin,⁴ and extended diffusion models.^{4,13-19} Among these, the extended diffusion (ED) theory gives us advantages in that it allows us to consider the inertial effect of motion, without resorting to the rather complicated Fokker-Planck-Langevin approach. In addition, it is well known that, under a series of approximations, expressions derived by the ED model reduce to the same form as those obtained by the rotational diffusion theory. Originally developed by Gordon, ED theory has been successfully applied to linear,¹³ spherical,¹⁴ and symmetric top¹⁵ molecules.

Conventional theories,^{5,17-19} which adopt the ED model for the internal rotation, usually assume diffusional motion for the overall reorientation. The theories are basically hybrids of models that could not attack the problem with a unified and molecular picture of ED model. Actually, Bull³ has formulated an ED theory for a molecule with an internal rotor and investigated the dependence of the reorientational correlation time on the potential barrier of internal rotation. His formulation is based on the assumption that "collisions" simultaneously randomize both the overall and internal angular momenta (in other words, the internal angular momentum correlation time τ_α is equal to the overall angular momentum correlation time τ_J). One can easily argue that this

assumption may not be valid generally, e.g., for a small internal rotor attached to a massive body.

In this article we develop a general ED theory for the reorientation of a symmetric top molecule with an internal rotor. Using the generic ED picture that both the overall and internal rotors undergo "collision interrupted free rotation," we formulate a theory that removes Bull's assumption ($\tau_J = \tau_\alpha$). Using the convolution theorem of the Laplace transform technique, we express the reorientational correlation time as a contour integral of some function of the overall and internal free rotor correlation functions which are assumed to be independent of each other. In the diffusion limit of the overall rotation, we derive simple expressions which reduce to the results of previous works. As an application, ¹³C nuclear-magnetic-resonance (NMR) dipole-dipole relaxation times of toluene are calculated and compared with experiments. Angular momentum correlation times (τ_J and τ_α), thus obtained, agree with those evaluated in the previous work of Chung *et al.*¹⁸

II. THEORY

A. Reorientational correlation time

In the study of rotational dynamics, one is interested in the Wigner rotation matrix²⁰ at time t , $D[\Omega_{LF}(t)]$, which connects the laboratory coordinate system with the coordinate which diagonalizes the interaction of interest. The sequence of coordinate transform requires the following sets of Euler angles from the laboratory coordinate system:

- (1) $\Omega_{LD}(t)$ to the principal body coordinate system fixed to the molecule at time t ;
- (2) $(\gamma, \eta, 0)$ to the coordinate system whose z axis is coincident with the internal rotation axis;
- (3) $[\alpha(t), \beta, 0]$ to the internal coordinate system fixed to the

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internal rotor and which diagonalizes the interaction of interest.

Thus, the rotation matrix of interest is given by

$$D[\Omega_{\text{LF}}(t)] = D[\Omega_{\text{LD}}(t)]D[\gamma, \eta, 0]D[\alpha(t), \beta, 0]. \quad (1)$$

The reorientational correlation function, $G_{mm}^{(L)}(t)$, is defined as¹⁵

$$G_{mm}^{(L)}(t) = \frac{\langle D_{km}^{(L)*}[\Omega_{\text{LF}}(0)]D_{km}^{(L)}[\Omega_{\text{LF}}(t)] \rangle}{\langle D_{km}^{(L)*}[\Omega_{\text{LF}}(0)]D_{km}^{(L)}[\Omega_{\text{LF}}(0)] \rangle}. \quad (2)$$

Now if we assume that the overall and internal rotations are mutually independent, Eq. (2) can be written as

$$G_{mm}^{(L)}(t) = (2L+1)D_{ab}^{(L)*}[\gamma, \eta, 0]D_{bm}^{(L)*}[0, \beta, 0]D_{a'b'}^{(L)}[\gamma, \eta, 0]D_{b'm}^{(L)}[0, \beta, 0]\langle D_{ka}^{(L)*}[\Omega_{\text{LD}}(0)]D_{ka}^{(L)}[\Omega_{\text{LD}}(t)] \rangle_{\text{Overall}} \langle \exp[ib\alpha(0)]\exp[-ib'\alpha(t)] \rangle_{\text{Internal}}, \quad (3)$$

where $\langle \rangle_{\text{Overall}}$ and $\langle \rangle_{\text{Internal}}$ represent ensemble averages over overall and internal rotations, respectively. It has been assumed that all initial orientations are equally probable, that is,²⁰

$$\langle D_{km}^{(L)*}[\Omega_{\text{LF}}(0)]D_{km}^{(L)}[\Omega_{\text{LF}}(0)] \rangle_{\Omega_{\text{LF}}(0)} = 1/(2L+1).$$

In Eq. (3) and subsequent equations, the summation over repeated indices (Einstein's convention) is implied unless it is explicitly shown. Further defining the overall, $G_{aa'}^{\text{Ovl}}(t)$, and internal, $G_{bb'}^{\text{Int}}(t)$, reorientational correlation functions as

$$G_{aa'}^{\text{Ovl}}(t) = (2L+1)\langle D_{ka}^{(L)*}[\Omega_{\text{LD}}(0)]D_{ka'}^{(L)}[\Omega_{\text{LD}}(t)] \rangle_{\text{Overall}}, \quad (4)$$

$$G_{bb'}^{\text{Int}}(t) = \langle \exp[ib\alpha(0)]\exp[-ib'\alpha(t)] \rangle_{\text{Internal}}, \quad (5)$$

we get

$$G_{mm}^{(L)}(t) = D_{ab}^{(L)*}[\gamma, \eta, 0]D_{bm}^{(L)*}[0, \beta, 0]D_{a'b'}^{(L)}[\gamma, \eta, 0] \times D_{b'm}^{(L)}[0, \beta, 0]G_{aa'}^{\text{Ovl}}(t)G_{bb'}^{\text{Int}}(t). \quad (6)$$

The reorientational correlation time τ_c , which is directly related to NMR relaxation times, is given by¹

$$\tau_c = \int_0^\infty G_{00}^{(L)}(t) dt. \quad (7)$$

Equation (7) can be viewed as a Laplace transform of the reorientational correlation function $G_{00}^{(L)}(t)$,

$$\tau_c = \lim_{s \rightarrow 0} \int_0^\infty e^{-st} G_{00}^{(L)}(t) dt = \lim_{s \rightarrow 0} \mathcal{L}[G_{00}^{(L)}(t)] = \hat{G}_{00}^{(L)}(s=0), \quad (8)$$

where s is the Laplace transformed variable and both $\mathcal{L}[G(t)]$ and $\hat{G}(s)$ denote Laplace transforms of $G(t)$. Finally, from Eqs. (6) and (8), we obtain

$$\tau_c = D_{ab}^{(L)*}[\gamma, \eta, 0]D_{b0}^{(L)*}[0, \beta, 0]D_{a'b'}^{(L)}[\gamma, \eta, 0] \times D_{b'm}^{(L)}[0, \beta, 0] \lim_{s \rightarrow 0} \mathcal{L}[G_{aa'}^{\text{Ovl}}(t)G_{bb'}^{\text{Int}}(t)]. \quad (9)$$

Thus, τ_c can be calculated from the Laplace transform of the product of overall and internal reorientational correlation functions, $\mathcal{L}[G_{aa'}^{\text{Ovl}}(t)G_{bb'}^{\text{Int}}(t)]$, which, in turn, can be evalu-

ated by the convolution theorem once we evaluate $\mathcal{L}[G_{aa'}^{\text{Ovl}}(t)]$ and $\mathcal{L}[G_{bb'}^{\text{Int}}(t)]$, separately. ED expressions of each Laplace transform are derived in the following subsection.

B. Extended J diffusion model

In this subsection, we derive the Laplace transforms of overall and internal rotational correlation functions, respectively. In fact, there are two kinds of ED model,¹³ ‘‘extended J diffusion (EDJ)’’ and ‘‘extended M diffusion (EDM)’’ models. In the EDJ model, collision randomizes both the magnitude and the direction of the angular momentum, while the EDM model assumes that only the direction is randomized by collisions. Here, we use the most commonly used EDJ model, but the general procedure of derivations will be almost the same for EDM model.

Hereafter, we consider the case where the overall rotor is approximated as a symmetric top and the internal rotor is viewed as a one-dimensional rotor with fixed direction with respect to the overall rotor. In the EDJ model, the Laplace transform of the internal correlation function is well known as²¹

$$\hat{G}_{bb'}^{\text{Int}}(s) = \delta_{bb'} \frac{\hat{G}_{b,\text{FR}}^{\text{Int}}(s+1/\tau_\alpha)}{1 - \frac{1}{\tau_\alpha} \hat{G}_{b,\text{FR}}^{\text{Int}}(s+1/\tau_\alpha)}, \quad (10)$$

where $\hat{G}_{b,\text{FR}}^{\text{Int}}(s+1/\tau_\alpha)$ is the Laplace transform of the internal free rotor correlation function given by¹⁷

$$\begin{aligned} \hat{G}_{b,\text{FR}}^{\text{Int}}\left(s + \frac{1}{\tau_\alpha}\right) &= \int_{-\infty}^{+\infty} W_{\text{int}}(\dot{\alpha}) \frac{1}{s + 1/\tau_\alpha + ib\dot{\alpha}} d\dot{\alpha} \\ &= \left(\frac{\pi}{y_b}\right)^{1/2} \exp\left(\frac{(s+1/\tau_\alpha)^2}{y_b}\right) \\ &\quad \times \text{erfc}\left(\frac{(s+1/\tau_\alpha)^2}{y_b}\right)^{1/2}. \end{aligned} \quad (11)$$

The Maxwell–Boltzmann weighting factor for the internal rotation $W_{\text{int}}(\dot{\alpha})$ is

$$W_{\text{int}}(\dot{\alpha}) = \left(\frac{I_\alpha}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{I_\alpha \dot{\alpha}^2}{2k_B T}\right), \quad (12)$$

where $\dot{\alpha}$ is the angular velocity of internal rotor, $k_B T$ the Boltzmann factor, and I_α the moment of inertia of the internal rotor. y_b of Eq. (11) is defined as $y_b = 2b^2 k_B T / I_\alpha$ and $\text{erfc}(x)$ is the complementary error function.²²

The Laplace transform of the overall correlation function is also given by²¹

$$\hat{G}_{aa'}^{\text{Ovl}}(s) = \delta_{aa'} \frac{\hat{G}_{a,\text{FR}}^{\text{Ovl}}(s + 1/\tau_J)}{1 - (1/\tau_J)\hat{G}_{a,\text{FR}}^{\text{Ovl}}(s + 1/\tau_J)}, \quad (13)$$

where the Laplace transform of the overall free rotor correlation function, $\hat{G}_{a,\text{FR}}^{\text{Ovl}}(s + 1/\tau_J)$, is defined as¹⁵

$$\begin{aligned} \hat{G}_{a,\text{FR}}^{\text{Ovl}}\left(s + \frac{1}{\tau_J}\right) &= \int_0^\infty dJ \int_{-1}^{+1} d \cos \theta W_{\text{Ovl}}(J, \theta) \\ &\times \sum_{c=-L}^L \frac{[d_{ac}^{(L)}(\theta)]^2}{s + 1/\tau_J + i(J/I_x)(c + \alpha \xi \cos \theta)}. \end{aligned} \quad (14)$$

The weighting factor for the overall rotation, $W_{\text{Ovl}}(J, \theta)$, is given by¹⁵

$$\begin{aligned} W_{\text{Ovl}}(J, \theta) &= \left(\frac{1 + \xi}{2\pi}\right)^{1/2} (I_x k_B T)^{-3/2} J^2 \\ &\times \exp\left(\frac{-J^2(1 + \xi \cos^2 \theta)}{2I_x k_B T}\right), \end{aligned} \quad (15)$$

where J is the magnitude of the overall angular momentum vector and θ is the polar angle of the Euler angle Ω_{LD} . The asymmetry parameter ξ is defined as $\xi = (I_x - I_z)/I_z$, where $I_x (= I_y)$ and I_z are the moments of inertia of the symmetric top.

C. Reorientational correlation time

With expressions for the Laplace transforms of overall and internal rotational correlation functions given by Eqs. (10) and (13), respectively, we need to know the Laplace transform of the product of two correlation functions [Eq. (9)]. The following describes how one can obtain this by the convolution theorem of the Laplace transform.

From Eq. (9), the reorientational correlation time τ_c for a symmetric top with an internal rotor is given by

$$\begin{aligned} \tau_c &= \sum_{a,b=-L}^L [d_{ab}^{(L)}(\eta)]^2 [d_{b0}^{(L)}(\beta)]^2 \\ &\times \lim_{s \rightarrow 0} \mathcal{L}[G_{aa}^{\text{Ovl}}(t)G_{bb}^{\text{Int}}(t)], \end{aligned} \quad (16)$$

where we have set $\gamma=0$ in Eq. (9) since, for a symmetric top, the choice of x and y coordinates of the principal body frame is arbitrary. We have also used the following relations:²⁰

$$G_{aa'}^{\text{Ovl}} \propto \delta_{aa'}, \quad G_{bb'}^{\text{Int}} \propto \delta_{bb'}$$

and

$$D_{xy}^{(L)}[0, \eta, 0] = d_{xy}^{(L)}(\eta).$$

When the index b of Eq. (16) equals zero, the internal correlation function $G_{bb}^{\text{Int}}(t)$ becomes unity by the definition of Eq. (5). Thus, Eq. (16) is divided into two distinct terms:

$$\begin{aligned} \tau_c &= \sum_{\substack{a,b=-L \\ b \neq 0}}^L [d_{ab}^{(L)}(\eta)]^2 [d_{b0}^{(L)}(\beta)]^2 \lim_{s \rightarrow 0} \mathcal{L}[G_{aa}^{\text{Ovl}}(t)G_{bb}^{\text{Int}}(t)] \\ &+ \sum_{a=-L}^L [d_{a0}^{(L)}(\eta)]^2 [d_{00}^{(L)}(\beta)]^2 \lim_{s \rightarrow 0} \mathcal{L}[G_{aa}^{\text{Ovl}}(t)]. \end{aligned} \quad (17)$$

Now using the convolution theorem²³ for the product of two original functions, one can show that the Laplace transform of the first term in Eq. (17) becomes

$$\begin{aligned} \lim_{s \rightarrow 0} \mathcal{L}[G_{aa}^{\text{Ovl}}(t)G_{bb}^{\text{Int}}(t)] &= (2\pi i)^{-1} \int_{-i\infty}^{+i\infty} \frac{\hat{G}_{a,\text{FR}}^{\text{Ovl}}(u + 1/\tau_J)}{1 - (1/\tau_J)\hat{G}_{a,\text{FR}}^{\text{Ovl}}(u + 1/\tau_J)} \\ &\times \frac{\hat{G}_{b,\text{FR}}^{\text{Int}}(-u + 1/\tau_\alpha)}{1 - (1/\tau_\alpha)\hat{G}_{b,\text{FR}}^{\text{Int}}(-u + 1/\tau_\alpha)} du, \end{aligned} \quad (18)$$

where the integration path is along the vertical line which bisects the complex plane. Defining dimensionless variables as

$$\begin{aligned} \tau_c^* &= \tau_c \sqrt{k_B T / I_x}, \quad \tau_J^* = \tau_J \sqrt{k_B T / I_x}, \\ \tau_\alpha^* &= \tau_\alpha \sqrt{k_B T / I_\alpha}, \quad t^* = t \sqrt{k_B T / I_x}, \end{aligned} \quad (19)$$

$$J^* = \frac{J}{\sqrt{I_x k_B T}}, \quad \dot{\alpha}^* = \dot{\alpha} \sqrt{I_\alpha / k_B T},$$

$$u^* = u \sqrt{I_x / k_B T}, \quad \mu = \sqrt{I_\alpha / I_x},$$

we get the reduced reorientational correlation time τ_c^* as

$$\tau_c^* = \sum_{a,b=-L}^L [d_{ab}^{(L)}(\eta)]^2 [d_{b0}^{(L)}(\beta)]^2 (\tau_c^*)_{a,b}. \quad (20)$$

The components of reorientational correlation time $(\tau_c^*)_{a,b}$ are given by

$$\begin{aligned} (\tau_c^*)_{a,b \neq 0} &= \mu (2\pi i)^{-1} \int_{-i\infty}^{+i\infty} \frac{\hat{G}_{a,\text{FR}}^{\text{Ovl}}(u^* + 1/\tau_J^*)}{1 - (1/\tau_J^*)\hat{G}_{a,\text{FR}}^{\text{Ovl}}(u^* + 1/\tau_J^*)} \\ &\times \frac{\hat{G}_{b,\text{FR}}^{\text{Int}}(-u^* + 1/\tau_\alpha^*)}{1 - (1/\tau_\alpha^*)\hat{G}_{b,\text{FR}}^{\text{Int}}(-u^* + 1/\tau_\alpha^*)} du^*, \end{aligned} \quad (21)$$

$$(\tau_c^*)_{a,b=0} = \frac{\hat{G}_{a,\text{FR}}^{\text{Ovl}}(1/\tau_J^*)}{1 - (1/\tau_J^*)\hat{G}_{a,\text{FR}}^{\text{Ovl}}(1/\tau_J^*)}, \quad (22)$$

where the complex Laplace transforms of the free rotor correlation functions are defined as

$$\hat{G}_{a,FR}^{Ovl}\left(u^* + \frac{1}{\tau_j^*}\right) = \int_0^\infty dJ^* \int_{-1}^{+1} d \cos \theta W_{Ovl}(J^*, \theta) \times \sum_{c=-L}^L \frac{[d_{ac}^{(L)}(\theta)]^2}{u^* + 1/\tau_j^* + iJ^*(c + a\xi \cos \theta)}, \quad (23)$$

$$\hat{G}_{b,FR}^{Int}\left(-u^* + \frac{1}{\tau_\alpha^*}\right) = \int_{-\infty}^{+\infty} d\dot{\alpha}^* W_{Int}(\dot{\alpha}^*) \times \frac{1}{-\mu u^* + 1/\tau_\alpha^* + ib\dot{\alpha}^*} = \left(\frac{\pi}{2b^2}\right)^{1/2} \exp\left(\frac{(-\mu u^* + 1/\tau_\alpha^*)^2}{2b^2}\right) \times \operatorname{erfc}\left(\frac{-\mu u^* + 1/\tau_\alpha^*}{\sqrt{2b^2}}\right). \quad (24)$$

The weighting factors are given as

$$W_{Ovl}(J^*, \theta) = \left(\frac{1+\xi}{2\pi}\right)^{1/2} J^{*2} \exp\left(\frac{-J^{*2}(1+\xi \cos^2 \theta)}{2}\right), \quad (25)$$

$$W_{Int}(\dot{\alpha}^*) = \left(\frac{1}{2\pi}\right)^{1/2} \exp\left(\frac{-\dot{\alpha}^{*2}}{2}\right). \quad (26)$$

General expressions of reorientational correlation time, given by Eqs. (20)–(22), form the central results of this work. Note that, in deriving these equations, we have not made any assumption about the angular momentum correlation times, τ_j^* and τ_α^* . Bull's assumption, thus, does not appear in this formulation. Since Eqs. (21), (23), and (24) cannot be integrated analytically, one needs to resort to numerical method to calculate the components of reorientational correlation time, $(\tau_c^*)_{a,b}$. Making substitution, $u^* = iy$ (y is the real dimensionless quantity), and taking only the real part of integral, we integrated Eq. (21) numerically. The numerical integration routine used is IMSL (version 1.0) subroutine DCADRE, which adopts adaptive Romberg extrapolation for integration. The integrand of Eq. (21) contains $\hat{G}_{a,FR}^{Ovl}(u^* + 1/\tau_j^*)$ and $\hat{G}_{b,FR}^{Int}(-u^* + 1/\tau_\alpha^*)$, which themselves cannot be evaluated analytically but require numerical integrations. We thus need to carry out a triple integration with respect to y , J^* and $\cos \theta$ for the calculation of Eq. (21) and a double integration, with respect to J^* and $\cos \theta$ for Eq. (22). Since the upper limits of the integration with respect to y and J^* extend to infinities, we cut off the upper limits at $y=10^6$ and $J^*=35$, at which convergence of the integrals was obtained. The rapid convergence of the integral with respect to J^* is due to the Gaussian distribution of J^* [see Eq. (25)]. For the calculation of Eq. (24), we used complex error function routine written by Stegun and Zucker.²⁴ As noted from Eq. (21), the $(\tau_c^*)_{a,b \neq 0}$ component depends both on τ_j^* and τ_α^* , whereas the $(\tau_c^*)_{a,b=0}$ component depends

only on τ_j^* which can be seen from Eq. (22). Note that we do not need to evaluate all the possible components of $(\tau_c^*)_{a,b}$, since they have the following symmetry property (see Appendix):

$$(\tau_c^*)_{a,b} = (\tau_c^*)_{-a,b} = (\tau_c^*)_{a,-b} = (\tau_c^*)_{-a,-b}. \quad (27)$$

The quantity directly related to the experiments, though, is the weighted sum of $(\tau_c^*)_{a,b}$ given by Eq. (20) rather than $(\tau_c^*)_{a,b}$ themselves. In Sec. III, we calculate Eq. (20) for a specific molecule, toluene, and relate it to the dipolar relaxation time of ¹³C NMR experiment, which is much facilitated by the above symmetry relations.

D. Diffusion limit of the overall rotation ($\tau_j^* \ll 1$)

In the diffusion limit of overall rotation, the integrand in Eq. (23) can be expanded as a power series of τ_j^* to give

$$(\tau_c^*)_{a,b \neq 0} \cong \frac{\mu}{2\pi i} \int_{-i\infty}^{+i\infty} \frac{1}{u^* + \tau_j^*[L(L+1) + \xi a^2]} \times \frac{\hat{G}_{b,FR}^{Int}(-u^* + 1/\tau_\alpha^*)}{1 - (1/\tau_\alpha^*)\hat{G}_{b,FR}^{Int}(-u^* + 1/\tau_\alpha^*)} du^*, \quad (28)$$

$$(\tau_c^*)_{a,0} \cong \frac{1}{\tau_j^*[L(L+1) + \xi a^2]}, \quad (29)$$

where we have used properties of the rotation matrix²⁵ and neglected terms containing τ_j^* raised to powers greater than 1. Choosing the left-hand half-plane as the contour, we can evaluate the integral in Eq. (28) by the residue theorem as

$$(\tau_c^*)_{a,b \neq 0} \cong \frac{\mu \left(\frac{\pi}{2b^2}\right)^{1/2} \exp(y_{ab}^2) \operatorname{erfc}(y_{ab})}{1 - \frac{1}{\tau_\alpha^*} \left(\frac{\pi}{2b^2}\right)^{1/2} \exp(y_{ab}^2) \operatorname{erfc}(y_{ab})}, \quad (30)$$

where

$$y_{ab} = \frac{\mu[L(L+1) + \xi a^2]\tau_j^* + 1/\tau_\alpha^*}{\sqrt{2b^2}}.$$

Thus for $\tau_j^* \ll 1$, the reorientational correlation time is written as

$$\tau_c^* \cong \sum_{\substack{a,b=-L \\ b \neq 0}}^L [d_{ab}^{(L)}(\eta)]^2 [d_{b0}^{(L)}(\beta)]^2 \times \frac{\mu \sqrt{\pi/2b^2} \exp(y_{ab}^2) \operatorname{erfc}(y_{ab})}{1 - \frac{1}{\tau_\alpha^*} \sqrt{\pi/2b^2} \exp(y_{ab}^2) \operatorname{erfc}(y_{ab})} + \sum_{a=-L}^L [d_{a0}^{(L)}(\eta)]^2 [d_{00}^{(L)}(\beta)]^2 \frac{1}{\tau_j^*[L(L+1) + \xi a^2]}. \quad (31)$$

Equation (31) is valid in the rotational diffusion limit of the overall rotation regardless of the type of motion of the internal rotation. For a special case where the internal rotation

axis is parallel to the molecular symmetry axis ($\eta=0$), Eq. (31) reduces to the same expression as the result of Shin *et al.*,²⁶ provided the following relations hold:

$$D_1 = \frac{k_B T}{I_z} \tau_J \quad \text{and} \quad D_2 = \frac{k_B T}{I_x} \tau_J, \quad (32)$$

where D_1 is the rotational diffusion constant about the principal symmetry axis and D_2 is the rotational diffusion constant about an axis perpendicular to the above axis. Actually, Eq. (32) is known as McClung's relation,²⁷ which was obtained for a simple symmetric top without internal rotation.

Now we further explore the behavior of reorientational correlation time in diffusion and dilute gas limits of internal rotation, respectively. When $\tau_J^* \ll 1$ and $\tau_\alpha^* \ll 1$, the integrand of Eq. (24) can be expanded as a power series of τ_α^* . Then, to the first order in τ_α^* , Eq. (28), with Eq. (29), is evaluated to give

$$\tau_c^* \cong \sum_{a,b=-L}^L [d_{ab}^{(L)}(\eta)]^2 [d_{b0}^{(L)}(\beta)]^2 \times \frac{1}{\tau_J^* [L(L+1) + \xi a^2] + \tau_\alpha^* b^2 / \mu}. \quad (33)$$

Note that the restriction on the summation, $b \neq 0$, was removed. If the internal and overall angular momentum correlation times are the same ($\tau_J = \tau_\alpha$, that is, $\tau_\alpha^* = \tau_J^* / \mu$), Eq. (33) reduces to the same equation as Bull's.²⁸

On the other hand, in the limit where $\tau_J^* \ll 1$ and $\tau_\alpha^* \gg 1$, the reorientational correlation time is approximated as

$$\tau_c^* \cong \mu \sum_{\substack{a,b=-L \\ b \neq 0}}^L [d_{ab}^{(L)}(\eta)]^2 [d_{b0}^{(L)}(\beta)]^2 \left(\frac{\pi}{2b^2} \right)^{1/2} + \sum_{a=-L}^L [d_{a0}^{(L)}(\eta)]^2 [d_{00}^{(L)}(\beta)]^2 \frac{1}{\tau_J^* [L(L+1) + \xi a^2]}, \quad (34)$$

where we have used the limiting relations of

$$y_{ab} \cong \frac{\mu [L(L+1) + \xi a^2] \tau_J^*}{\sqrt{2b^2}}$$

and $e^{a^2} \text{erfc}(x) \cong 1$ for $x \ll 1$ in Eq. (31).²²

III. APPLICATION TO ¹³C NMR RELAXATION OF TOLUENE

¹³C nuclear magnetic relaxation of the methyl group in liquid toluene has been studied by many authors. The dipole-dipole interaction contribution to the spin-lattice relaxation time T_1^{DD} of a ¹³C nucleus directly bonded to several protons is given, in the extreme narrowing limit, by²⁹

$$\frac{1}{T_1^{\text{DD}}} = n \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r^6} \tau_c, \quad (35)$$

where n is the number of protons attached to the relaxing carbon, \hbar is Planck's constant over 2π , and γ are the gyromagnetic ratios.

The overall angular momentum correlation time τ_J^* can be evaluated from T_1^{DD} values of ring carbons via Eq. (35):

$$\frac{1}{T_1^{\text{DD}}(\text{ring})} = \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r^6} \tau_c(\text{ring}), \quad (36)$$

where

$$\tau_c^*(\text{ring}) = \sum_{a=-2}^2 [d_{a0}(\eta)]^2 (\tau_c^*)_{a0}, \quad (37)$$

with $(\tau_c^*)_{a0}$ given as a function of τ_J^* by Eq. (22). Note that there are three distinct ring carbons (ortho, meta, para) in toluene. The angle η has the values of 60°, 120°, and 180° for these carbons, respectively. At 27 °C, Lambert and co-workers⁷ reported: $T_1^{\text{DD}} = 21.7, 20.9, \text{ and } 14.8$ s for ortho, meta, and para carbons, respectively. On the other hand, at 28 °C, Hamza *et al.*⁸ reported: $T_1^{\text{DD}} = 25.1, 23.5, \text{ and } 17.4$ s for ortho, meta, and para carbons, respectively. Using the molecular parameters of toluene,^{30,31} we first calculated the reorientational correlation time $\tau_c^*(\text{ring})$ from the data of three ring carbons. Then comparing the numerical calculation with experiments, we get the overall angular momentum correlation times.

The internal angular momentum correlation time τ_α^* can be obtained from T_1^{DD} value of the methyl carbon by

$$\frac{1}{T_1^{\text{DD}}(\text{methyl})} = 3 \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r^6} \tau_c(\text{methyl}), \quad (38)$$

where $\tau_c(\text{methyl})$ is the reorientational correlation time given in terms both of τ_J^* and τ_α^* by Eq. (20). For the calculation of $\tau_c(\text{methyl})$, we used the average of three τ_J^* values ($\tau_J^* = 0.049$ from Lambert and co-workers and 0.057 from Hamza *et al.*). τ_J^* obtained show that the overall rotation is diffusional ($\tau_J^* \ll 1$).

From these values of τ_J^* , the dipolar relaxation time of methyl carbon can be obtained as a function of τ_α^* and plotted in Fig. 1. From the results of Lambert and co-workers ($T_1^{\text{DD}} = 39.7$ s for methyl carbon), we could not assign a value for τ_α^* , since the curve never crossed the experimental value. Actually, the curve approached very close to the experimental value (our calculation gives $T_1^{\text{DD}} = 37.5$ s at $\tau_\alpha^* = 100$, which is within 6% error of the experimental value). On the contrary, from the T_1^{DD} (30.8 s) of methyl carbon for Hamza *et al.* we could assign τ_α^* by interpolation of experimental value to the curve in Fig. 1. τ_α^* thus obtained ($\tau_\alpha^* = 0.25$) essentially matches the value ($\tau_\alpha^* = 0.29$) of Chung *et al.*¹⁸ and the diffusion constants, calculated using Eq. (32), are very close to experimental values.³² This value of τ_α^* shows that the internal rotation has some inertial character (that is, the motion is in the intermediate motional regime). If we use this τ_α^* and calculate the ratio of τ_α to τ_J , we obtain $\tau_\alpha / \tau_J = 0.5$, which clearly shows that the assumption of equal angular momentum correlation times for both overall and internal rotations is not valid in the present case.

As one can see from Fig. 1, T_1^{DD} is a very slowly increasing function of τ_α^* in the region where τ_α^* is greater than 1. If we consider the sensitivity of NMR relaxation experiments

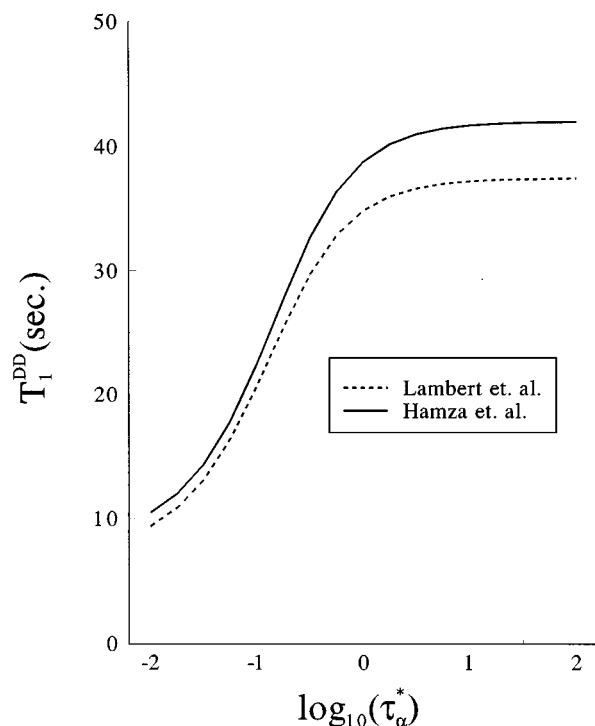


FIG. 1. Numerical calculation of T_1^{DD} for the methyl carbon of toluene as a function of τ_α^* with $\tau_j^* = 0.049$ (from Lambert and co-workers' data) and $\tau_j^* = 0.057$ (from Hamza *et al.*'s data).

(typically 10% error), exact determination of τ_α^* may be inherently difficult for the case where the internal rotation is fast or has some inertial effect. It also reminds us, as Suchanski¹¹ noted, of Spiess and co-workers'¹⁶ conclusions that determination of ^{13}C relaxation rates due to the spin-internal rotation interaction provides a much better quantitative means for a study of fast internal rotation than does the dipolar relaxation. Work on this line is also being carried out in our group.

IV. CONCLUSION

In this article we generalized the extended diffusion theory to investigate the reorientation of a symmetric top

molecule with an internal rotor. Based on a unified ED picture, we expressed the reorientational correlation time with overall and internal free rotor correlation functions. In addition, Bull's "equal angular momentum correlation time ($\tau_j = \tau_\alpha$)" assumption³ is removed in our theory. This generalization was possible through the convolution of Laplace transform technique. Various limiting expressions, Eqs. (31), (33), and (34) are derived and shown to reduce to the results of previous works.

There are only two phenomenological parameters in this formulation; overall (τ_j) and internal (τ_α) angular momentum correlation times. To test our theory, numerical calculations are compared with ^{13}C NMR relaxation experiments of toluene. τ_j obtained from the comparison shows that overall rotation is diffusional. τ_α obtained from Hamza and co-workers'⁸ data agrees with the previous work of Chung *et al.*¹⁸ It is also pointed out, for toluene, that determining the exact τ_α from NMR relaxation experiments is a difficult task because T_1^{DD} increases rather slowly as a function of τ_α^* in the intermediate motional regime and due to the inherent sensitivity problem of NMR relaxation experiments.

Although the overall diffusion approximation is a good one for toluene, as it turned out, our theory differs from conventional ones in that it starts from the clear molecular view of motion, instead of just using rotational diffusion constants as parameters. Therefore, it can be applied to molecules that show intermediate motional behavior for overall reorientation as well as internal rotation.

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APPENDIX: DERIVATION OF EQ. (27)

From the definition of Eq. (23), $\hat{G}_{a,\text{FR}}^{\text{Ovl}}(iy + 1/\tau_j^*)$ can be rewritten as

$$\hat{G}_{a,\text{FR}}^{\text{Ovl}}\left(iy + \frac{1}{\tau_j^*}\right) = \left(\frac{1+\xi}{2\pi}\right)^{1/2} \int_0^\infty dt \exp\left[-t\left(iy + \frac{1}{\tau_j^*}\right)\right] \int_0^\infty dJ^* J^{*2} \exp\left(\frac{-J^{*2}}{2}\right) \sum_{c=-L}^L \exp(-ictJ^*) \\ \times \int_{-1}^{+1} d \cos \theta [d_{ac}^{(L)}(\theta)]^2 \exp\left(-\frac{\xi J^{*2} \cos^2 \theta}{2} - iatJ^* \xi \cos \theta\right), \quad (\text{A1})$$

where we have set $u^* = iy$ ($y = \text{real}$) in Eq. (23). We also used the identity

$$\frac{1}{(p+iq)} = \int_0^\infty dt \exp[-t(p+iq)] \quad (p > 0),$$

and changed the order of integration. It is possible to decompose each rotation matrix into odd and even functions of $\cos \theta$

$$[d_{ac}^{(L)}(\theta)]^2 = [d_{ac}^{(L)}(\theta)]^2|_{\text{even}} + [d_{ac}^{(L)}(\theta)]^2|_{\text{odd}}, \quad (\text{A2})$$

and the rotation matrix has the following symmetry property as

$$[d_{-ac}^{(L)}(\theta)]^2 = [d_{ac}^{(L)}(\theta)]^2|_{\text{even}} - [d_{ac}^{(L)}(\theta)]^2|_{\text{odd}}. \quad (\text{A3})$$

Applying these symmetry properties to Eq. (A1) and noting that only even functions with respect to $\cos \theta$ survive upon integration, one can show that

$$\hat{G}_{a,\text{FR}}^{\text{OvI}}(iy + 1/\tau_j^*) = \hat{G}_{-a,\text{FR}}^{\text{OvI}}(iy + 1/\tau_j^*). \quad (\text{A4})$$

To obtain symmetry properties of $\hat{G}_{b,\text{FR}}^{\text{Int}}$, let us rewrite the integral in Eq. (24) as

$$\hat{G}_{b,\text{FR}}^{\text{Int}}\left(-iy + \frac{1}{\tau_\alpha^*}\right) = \left(\frac{1}{2\pi}\right)^{1/2} \int_0^\infty dt \exp\left[-\left(\frac{1}{\tau_\alpha^*} - i\mu y\right)t\right] \times \int_{-\infty}^{+\infty} d\dot{\alpha}^* \exp\left(\frac{-\dot{\alpha}^{*2}}{2}\right) e^{-ib\dot{\alpha}^*}. \quad (\text{A5})$$

Note that only the real part of $\exp(-ib\dot{\alpha}^*)$ survives when the integration with respect to $\dot{\alpha}^*$ is performed. Thus, it is evident that

$$\hat{G}_{b,\text{FR}}^{\text{Int}}(-iy + 1/\tau_\alpha^*) = \hat{G}_{-b,\text{FR}}^{\text{Int}}(-iy + 1/\tau_\alpha^*). \quad (\text{A6})$$

From Eqs. (A4) and (A6), it immediately follows that Eq. (27) is valid.

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²⁶See Eq. (8) of Ref. 17. One should note that I_z in the reference is equal to the I_α of this article.

²⁷See Eqs. (35) and (36) of Ref. 15.

²⁸See Eq. (44) of Ref. 3. Note that $\tau_{\theta k,m}^{(L)}$ of Ref. 3 corresponds to $(\tau_c^*)_{k,m} \sqrt{I_x/k_B T}$ of the present work. One can also take approximations starting from Eq. (30). In this limit where $\tau_j^* \ll 1$, $\tau_\alpha^* \ll 1$, y_{ab} in Eq. (30) approaches $y_{ab} \cong 1/\sqrt{2b^2} \tau_\alpha^*$, to give $(1/\tau_\alpha^*) \sqrt{\pi/2b^2} \exp(y_{ab}^2) \text{erfc}(y_{ab}) \cong 1 - b^2 \tau_\alpha^{*2}$ (Ref. 22). Then Eq. (30) reduces to $(\tau_c^*)_{a,b \neq 0} = \mu/b^2 \tau_\alpha^*$. Although this expression is different from Eq. (33), μ is usually small so that this expression and Eq. (33) are effectively identical within approximation.

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³²Our calculation shows: $D_1/D_2 = 2.8$, $D_2 = 4.9 \times 10^{10} \text{ s}^{-1}$ for Lambert and co-workers' data and $D_1/D_2 = 2.8$, $D_2 = 5.7 \times 10^{10} \text{ s}^{-1}$ for Hamza *et al.*'s data which are very close to the experimental values ($D_1/D_2 = 2.2$, $D_2 = 5.38 \times 10^{10} \text{ s}^{-1}$ reported in Ref. 7 and $D_1/D_2 = 2.2$, $D_2 = 6.45 \times 10^{10} \text{ s}^{-1}$ in Ref. 8).