

# Extended diffusion theory of reorientation of symmetric top molecules with internal rotation: application to mesitylene

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## Abstract

Our general extended diffusion theory for the reorientational dynamics of a symmetric top molecule with internal rotation is applied to mesitylene which is an oblate symmetric top. The basic idea of independent extended  $J$ -diffusion of both the overall and internal rotations with the different angular momentum correlation times is implemented in the theory. The resulting expressions for the dipole–dipole relaxation times for  $^{13}\text{C}$  nuclei are evaluated numerically and compared with NMR experiments on mesitylene. The angular momentum correlation times obtained from the comparison show that internal rotation is much faster than the overall rotation. © 1997 Elsevier Science B.V.

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## 1. Introduction

Recently, we developed a general extended diffusion (ED) theory for the reorientation of a molecule with an internal rotor [1]. Using the generic ED picture [2] that both the overall and internal rotors undergo ‘collision interrupted free rotations’, we formulated a general ED theory which eliminates Bull’s ‘equal angular momentum correlation time (EAMCT)’ assumption for both the overall and internal rotations [3]. With the Laplace transform technique [4], we obtained an expression for the reorientational correlation time as a contour integral of some function of the overall and internal free rotor correlation functions. In the diffusion limit of the overall rotation, we derived simple expressions which

reduce to the results of previous work. As an application,  $^{13}\text{C}$  NMR dipole–dipole relaxation times of the methyl carbon in toluene, which was approximated to be a prolate symmetric top molecule, were calculated and compared with experiments. The angular momentum correlation times, thus obtained, show that our ED theory is consistent with the experiments and the EAMCT assumption is not valid in that case.

The previous application [1] was focused on the case where the axis of internal rotation is along the major principal axis of the prolate symmetric top. Since our theory is straightforward to implement for arbitrary geometry, within the constraint of an overall symmetric top with internal rotation, it would be interesting to investigate quite a different geometry — an oblate symmetric top minor axis along which lies the internal rotation axis. In the present study, we have chosen mesitylene as such a molecule. One of the advantages of investigating mesitylene is that it is an almost perfect oblate symmetric top. On the

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contrary, toluene is actually an asymmetric top but it has often been approximated as a prolate symmetric top because of easier formulation of tractable theories. As a result, mesitylene is a better candidate for checking a theory of molecular reorientation formulated for a symmetric top.

Some time ago, Shin [5] proposed a theory for an oblate symmetric top with internal rotation assuming that the internal rotation is undergoing extended  $J$ -diffusion while the overall rotation is anisotropic rotational diffusion. At that time, there was a rather big discrepancy [6,7] in reported values of  $^{13}\text{C}$  NMR relaxation times and he could not carry out quantitative analysis. Recently, Suchanski [8] resolved the problem by extensively measuring the dipole–dipole relaxation rates of  $^{13}\text{C}$  over a wide range of temperatures. In this Letter, applying our previous general ED theory to mesitylene, we obtain quantitative information on the reorientational dynamics of mesitylene from Suchanski's relaxation data.

## 2. Theoretical background

The Wigner rotation matrix [9] at time  $t$ ,  $D[\Omega_{\text{LF}}(t)]$ , connects the laboratory coordinate system with the coordinate that diagonalizes the coupling of interest. We need to consider the following sequence of Euler angles; from the laboratory coordinate system, (1)  $\Omega_{\text{LF}}(t)$  to the principal body coordinate at time  $t$ , (2)  $[\gamma, \eta, 0]$  to the coordinate whose  $z$ -axis is coincident with the internal rotation axis, (3)  $[\alpha(t), \beta, 0]$  to the coordinate that diagonalizes the coupling. Then the rotation matrix desired is given by

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

Here we are considering an oblate symmetric top molecule with internal rotation about a minor principal axis which is the axis of tumbling reorientation. The major principal axis is taken to be the  $z$ -axis of the principal coordinate system fixed to the main-body. For mesitylene in which the internal rotation axis is parallel with the molecular symmetry axis,  $\eta$  becomes  $\pi/2$ . We set  $\gamma = 0$  without loss of generality as before [1].  $\alpha(t)$  is the angle of internal rotation

and  $\beta$  is the angle between the internal rotation axis and C–H bond.

The outline of the theory goes as follows: We assume that both the overall and internal rotations undergo independent extended  $J$ -diffusion with different angular momentum correlation times. Using the convolution theorem of the Laplace transform, we can express the reorientational correlation time with the overall and internal free rotor correlation functions. Following the same procedure as in Ref. [1], we get the reduced reorientational correlation time,  $\tau_c^*$ , as

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

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

$$(\tau_c^*)_{a,b \neq 0} = \mu (2\pi i)^{-1} \times \int_{-i\infty}^{+i\infty} \frac{\hat{G}_{a,\text{FR}}^{\text{OvI}}(u^* + 1/\tau_j^*)}{1 - (1/\tau_j^*) \hat{G}_{a,\text{FR}}^{\text{OvI}}(u^* + 1/\tau_j^*)} \times \frac{\hat{G}_{b,\text{FR}}^{\text{Int}}(-u^* + 1/\tau_a^*)}{1 - (1/\tau_a^*) \hat{G}_{b,\text{FR}}^{\text{Int}}(-u^* + 1/\tau_a^*)} du^*, \quad (3)$$

$$(\tau_c^*)_{a,b=0} = \frac{\hat{G}_{a,\text{FR}}^{\text{OvI}}(1/\tau_j^*)}{1 - (1/\tau_j^*) \hat{G}_{a,\text{FR}}^{\text{OvI}}(1/\tau_j^*)}, \quad (4)$$

where  $\tau_j^*$  and  $\tau_a^*$  are the reduced overall and internal angular momentum correlation times, respectively, and  $\mu$  the ratio of moment of inertia defined as  $\mu = \sqrt{I_a/I_c}$ . The complex Laplace transforms of the free rotor correlation functions of the overall,  $\hat{G}_{a,\text{FR}}^{\text{OvI}}$ , and internal,  $\hat{G}_{b,\text{FR}}^{\text{Int}}$ , rotations are defined, respectively, as

$$\hat{G}_{a,\text{FR}}^{\text{OvI}}(u^* + 1/\tau_j^*) = \int_0^\infty dJ^* \int_{-1}^{+1} d(\cos \theta) W_{\text{OvI}}(J^*, \theta) \times \sum_{c=-L}^L \frac{[d_{ac}^{(L)}(\theta)]^2}{u^* + 1/\tau_j^* + iJ^*(c + a\xi \cos \theta)}, \quad (5)$$

$$\begin{aligned} \hat{G}_{b,FR}^{\text{int}}(-u^* + 1/\tau_a^*) &= \int_{-\infty}^{+\infty} d\dot{\alpha}^* W_{\text{int}}(\dot{\alpha}^*) \frac{1}{-\mu u^* + 1/\tau_a^* + i b \dot{\alpha}^*} \\ &= \sqrt{\frac{\pi}{2b^2}} \exp\left[\frac{(-\mu u^* + 1/\tau_a^*)^2}{2b^2}\right] \\ &\quad \times \text{erfc}\left[\frac{-\mu u^* + 1/\tau_a^*}{\sqrt{2}b}\right] \end{aligned} \quad (6)$$

with the weighting factors given by

$$\begin{aligned} W_{\text{ovl}}(J^*, \theta) &= \sqrt{\frac{1+\xi}{2\pi}} \\ &\quad \times J^{*2} \exp\left[\frac{-J^{*2}(1+\xi \cos^2 \theta)}{2}\right], \end{aligned} \quad (7)$$

$$W_{\text{int}}(\dot{\alpha}^*) = \sqrt{\frac{1}{2\pi}} \exp\left[\frac{-\dot{\alpha}^{*2}}{2}\right], \quad (8)$$

where  $J^*$  is the magnitude of reduced overall angular momentum vector,  $\theta$  the polar angle of the Euler angle  $\Omega_{LD}$ , and  $\dot{\alpha}^*$  the reduced angular velocity of the internal rotor. The asymmetry parameter,  $\xi$ , 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.

The above expressions are evaluated numerically as described in Ref. [1]. Numerical calculation is somewhat involved because, unlike the toluene case ( $\eta = 0$ ), nondiagonality of  $d_{ab}^{(L)}(\pi/2)$  makes it necessary to compute the every possible element of  $(\tau_c^*)_{a,b}$  given by Eqs. (3) and (4). In the diffusion limit of the overall rotation ( $\tau_j^* \ll 1$ ), we could carry out analytic contour integration to obtain the same limiting expression as the result reported earlier [5] provided the following relations hold:  $D_1 = (k_B T/I_z)\tau_j$  and  $D_2 = (k_B T/I_x)\tau_j$ .

### 3. Application to $^{13}\text{C}$ NMR relaxation of mesitylene

$^{13}\text{C}$  spin relaxation of mesitylene (1,3,5-trimethyl-benzene) has been studied by several authors [6–8,10,11]. The dipole–dipole relaxation time,

$T_1^{\text{DD}}$  of,  $^{13}\text{C}$  nuclei directly bound to the protons is given by [12]

$$\frac{1}{T_1^{\text{DD}}} = n \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r^6} \tau_c, \quad (9)$$

where  $n$  is the number of protons attached to the relaxing carbon nucleus,  $\hbar$  the Planck constant over  $2\pi$  and  $\gamma$  the gyromagnetic ratios. Our working equations for the ring and methyl carbons, respectively, are as follows:

$$\frac{1}{T_1^{\text{DD}}(\text{ring})} = \frac{0.38}{\sqrt{T}} \tau_c^*(\text{ring}), \quad (10a)$$

$$\frac{1}{T_1^{\text{DD}}(\text{methyl})} = \frac{1.21}{\sqrt{T}} \tau_c^*(\text{methyl}), \quad (10b)$$

where the corresponding reorientational correlation times are given as

$$\tau_c^*(\text{ring}) = \sum_{a=-2}^2 [d_{a0}^{(2)}(90^\circ)]^2 (\tau_c^*)_{a,0}, \quad (11a)$$

$$\begin{aligned} \tau_c^*(\text{methyl}) &= \sum_{a=-2}^2 [d_{ab}^{(2)}(111^\circ)]^2 \sum_{b=-2}^2 \\ &\quad \times [d_{b0}^{(2)}(90^\circ)]^2 (\tau_c^*)_{a,b}. \end{aligned} \quad (11b)$$

Molecular parameters used for mesitylene are [11]: Moments of inertia ( $10^{-40}$  g cm $^2$ );  $I_x = I_y = 486$ ,  $I_z = 957$  and  $I_x = 5.3$ ; C–H bond length; 0.11 nm (ring carbon) and 0.109 nm (methyl carbon); C–C–H bond angle (methyl carbon) =  $111^\circ$ .

At  $T = 313$  K, Kuhlmann and Grant [6] reported  $T_1^{\text{DD}} = 7.8(\pm 1)$  s for the ring carbon and  $T_1^{\text{DD}} = 23(\pm 2)$  s for the methyl carbon of mesitylene. Recently, for the same molecule, Suchanski [8] measured the dipole–dipole relaxation rates of  $^{13}\text{C}$  over a wide temperature range. From his data, fitted into his least-squares fitting equations at  $T = 313$  K, we obtain  $T_1^{\text{DD}} = 8.5$  s and  $T_1^{\text{DD}} = 24.2$  s for the ring and methyl carbon nuclei, respectively.

From Eqs. (4), (5), (7) and (11a) we obtained  $\tau_j^* = 0.038$  from the experimental  $T_1^{\text{DD}}$  data of Kuhlmann and Grant and  $\tau_j^* = 0.042$  from that of Suchanski, which shows that rotational diffusion condition for the overall rotation ( $\tau_j^* \ll 1$ ) is well satisfied in this case. With these  $\tau_j^*$ , the dipole–dipole relaxation times of the methyl carbon are com-

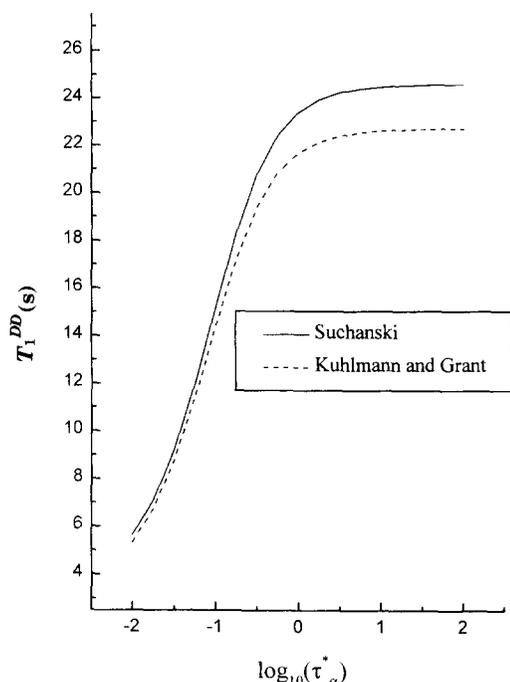


Fig. 1. Numerical calculation of  $T_1^{\text{DD}}$  for the methyl carbon of mesitylene, as a function of  $\tau_{\alpha}^*$  with  $\tau_j^* = 0.038$  (from Kuhlmann and Grant's data) and  $\tau_j^* = 0.042$  (from Suchanski's data).

puted and plotted in Fig. 1 as a function of  $\tau_{\alpha}^*$ . Interpolated value of  $\tau_{\alpha}^*$  to Suchanski's data is  $\tau_{\alpha}^* = 2.53$ , which reveals that the methyl rotation of mesitylene is near, but not in the fully dilute gas limit.

From  $T_1$  measurements, Kuhlmann and Grant [6] deduced that the internal rotation of methyl group is very fast with respect to the overall molecular rotation. The immediate question is 'how much faster it is, on the molecular basis if possible, than the overall motion?'. Our result, together with ED picture, provides the means of some quantitative insights on this question. Calculation of the ratio of root mean square velocities of free rotors yields

$$\left(\sqrt{kT/I_{\alpha}}\right)/\left(\sqrt{kT/I_{\gamma}}\right) = \sqrt{I_{\gamma}/I_{\alpha}} \approx 10 \quad (12)$$

which indicates that the internal rotation is about 10 times faster, during each free rotation step between collisions, than the overall rotation. Moreover, the angular momentum correlation times obtained ( $\tau_{\alpha}/\tau_j = \mu\tau_{\alpha}^*/\tau_j^* = 62$ ) show that the average duration ( $\tau_{\alpha}$ ) of the free rotation steps for the internal

rotation is about 6 times longer than that ( $\tau_j$ ) of the overall rotation. This analysis also leads us to the same conclusion as in the toluene study that EAMCT condition ( $\tau_j = \tau_{\alpha}$ ) is not compatible with experiments. Note that, if we use EAMCT condition for the calculation, we have a poor prediction of the relaxation time,  $T_1^{\text{DD}} = 21.6$  s, for the methyl carbon. The present ratio ( $\tau_{\alpha}/\tau_j = 6.2$ ) is considerably higher than that of toluene ( $\tau_{\alpha}/\tau_j = 0.5$ ) [1]. When the reduced quantities are converted to absolute values, we obtain  $\tau_j \approx 45$  fs and  $\tau_{\alpha} \approx 280$  fs for mesitylene, but  $\tau_j \approx 56$  fs and  $\tau_{\alpha} \approx 28$  fs for toluene. The decrease in  $\tau_j$  is believed to represent the fact that mesitylene is more massive and, as a result, more diffusional in motion than toluene. On the other hand, the enhancement of  $\tau_{\alpha}$  is thought to be originated from the temperature increase (from 301 to 313 K) and the change of molecular geometry. To figure out exactly how and to what extent each of two origins affects the variation of the angular momentum correlation times, further investigation is desired.

It should be noted that our  $\tau_{\alpha}^*$  ( $= 2.5$ ) is somewhat larger than those reported by Suchanski [8]. Our value lies slightly outside the range,  $1 < \tau_{\alpha}^* < 2.3$ , he obtained. Several comments on this difference are in order. First, Suchanski extracted  $\tau_{\alpha}^*$  from the spin-rotational relaxation times but we have drawn it out from the dipole-dipole relaxation time data. Second, as a theoretical model, he used the isotropic rotational diffusion model for the overall rotation. In contrast, we have explicitly taken account the anisotropy of the overall rotation with generalized ED model. Finally, as we pointed out in the previous work [1], exact determination of  $\tau_{\alpha}^*$  from dipole-dipole relaxation data might be a challenging task when we consider the limited experimental accuracy of  $^{13}\text{C}$  NMR relaxation experiments (usually 10% error [11]). It can be easily seen in Fig. 1 that  $T_1^{\text{DD}}$  is nearly insensitive to the increase of  $\tau_{\alpha}^*$  when  $\tau_{\alpha}^*$  becomes larger than 1. In fact,  $\tau_{\alpha}^*$  can not be decided from Kuhlmann and Grant's data because there is no crossing point between the experimental value and the theoretical curve. However, with an increase of  $\tau_{\alpha}^*$ , the curve converges to the point that is placed very close to the experimental value. When we use the same  $\tau_{\alpha}^*$  as Suchanski's data, we get  $T_1^{\text{DD}}(\text{methyl}) = 22.3$  s, which is in agreement with

Kuhlmann and Grant's data within experimental error. If we instead use EAMCT condition,  $\tau_\alpha/\tau_J = 1$ , then we get  $T_1^{\text{DD}} = 20.0\text{ s}$ , which is beyond 10% error bar of the experimental value.

#### 4. Concluding remarks

In this Letter, our generalized ED theory [1] for a molecule with internal rotation is applied to mesitylene which has a different geometry from toluene. It is general in the sense that, through the Laplace transform technique, the 'EAMCT ( $\tau_J = \tau_\alpha$ )' assumption is removed.

Physically, EAMCT implies that collisions (within the ED picture) randomize both the overall and internal angular momenta simultaneously, which, we believe, is not true in general. To test self consistency of our theory and the validity of the EAMCT assumption, numerical calculations are conducted to compare with NMR experiments of mesitylene.  $\tau_\alpha$ , extracted from Suchanski's data, is larger than  $\tau_J$  by a factor of 6, which obviously reveals that the EAMCT condition is not acceptable in this case. Previous reports inferred from NMR measurements, as well as our physical intuition, tell us that the methyl rotation of mesitylene is much more rapid than the overall reorientation. The present analysis based on the ED picture has clarified this point on a quantitative basis. The internal rotation is found to be nearly free rotational ( $\tau_\alpha^* = 2.53$ ). Our  $\tau_\alpha^*$  is rather large, in comparison to those obtained from the spin-rotational relaxation time measurements associated with the isotropic rotational diffusion model for the overall rotor. Possible causes of this difference are discussed.

Whereas angular momentum correlation times are required as input, the ED model has an attractive feature that makes it possible to calculate  $T_1$  with molecular parameters (moments of inertia) and with explicit consideration of temperature through Boltzmann weighting factors. In addition, based on a

'collision interrupted free rotation' picture, it naturally takes inertial effect of rotation into account. The overall rotation of mesitylene was found to be diffusional in the sense that  $\tau_J^*$  is much smaller than 1 and, as a consequence, our expression produces almost the same numerical results as that obtained from the overall rotational diffusion model.

However, the full power of the general expressions, given by Eqs. (3) and (4), of the reorientational correlation times can be realized when it comes to the case where the rotation has intermediate (neither diffusional nor free rotational) character. It is left for future work to apply this theory to a molecule with this 'intermediate' character.

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