Molecular Reorientation of Oblate Symmetric Top Molecules with Internal Extended Rotational Diffusion

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Molecular reorientation of oblate symmetric top molecules with internal rotation is investigated theoretically and an analytic expression for the overall reorientational correlation time in terms of the internal angular momentum correlation time is derived. This expression is quite different from the expression for prolate symmetric top molecules but reduces to the same expresssion in the spherical top limit. Fast internal rotation is treated by a modified version of the extended rotational diffusion while the bulky symmetric top mainbody is treated by the rotational diffusion model.

Introduction

Molecular reorientation in liquid has been investigated by various methods[1] such as NMR, IR, Raman, Rayleigh light scattering, etc. along with several theoretical models.[2] These models include rotational diffusion,[3~5] jump diffusion,[4~6] and extended rotational diffusion.[7,8] Of these, the extended rotational diffusion model proposed by Gordon[7] is well known to give the best description since it can be applied to a rather wide range between small angular step diffusion and free inertial rotation. This model was successfully applied to linear,[7] spherical top,[9] and symmetric top molecules.[10] Another class of molecules which are of great importance in application are those with internal rotations. Application of the extended rotational diffusion model to symmetric top molecules with internal rotation was carried out by Bull[11] some time ago. However, his treatment assigns the same angular momentum correlation time to both the overall reorientation and internal rotation. Experimental evidence shows that internal rotation of side groups such as methyl group is much faster compared to overall reorientation of rather bulky mainbody. Moreover, his expression is not amenable to analytical evaluation. In order to remedy the situation we proposed a theoretical model[12] in which the overall reorientation of a symmetric top molecule is treated by rotational diffusion while the internal rotation is treated by a modified extended rotational diffusion model. Our model calculation leads to an analytical expression for the overall reorientational correlation time as a function of internal angular momentum correlation time. Application of our model to liquid toluene revealed an appreciable degree of inertial effect in internal rotation of methyl group.[13]

When there is no internal rotation it is not necessary to distinguish prolate symmetric tops from oblate symmetric top molecules in the theoretical formulation of molecular reorientation. Existing theories describing internal rotation are dealing implicitly with prolate symmetric top mainbody. Our previous work was also in the same spirit and toluene molecule was assumed to be a prolate symmetric top molecule. However, when the internal rotor is attached to an oblate symmetric top molecule such as mesitylene the situation becomes quite different since the axis of internal rotation is along the minor principal axis of the mainbody. Previous theories are applicable to the case when the axis of internal rotation is along the major principal axis of the prolate symmetric top mainbody. It is the purpose of the present work to complement our earlier work so that internal rotors attached to any type of symmetric top molecules can be properly described. We start from the definition of reorientational correlation function and the overall reorientational correlation time in the presence of internal extended rotational diffusion will be derived as an analytic expression in terms of the internal angular momentum correlation time. As before, only the internal rotation is treated by the extended rotational diffusion and the reorientation of oblate symmetric top mainbody is reasonably assumed to undergo rotational diffusion.

Theory

The overall reorientational correlation function in the presence of internal rotation is given by[8]

$$G_{jk,\,lm}(t)=\frac{\langle D_{jk}^{(2)}[\Omega_{LF}(0)]\,D_{lm}^{(2)*}[\Omega_{LF}(t)]\rangle}{\langle D_{jk}^{(2)}[\Omega_{LF}(0)]\,D_{lm}^{(2)*}[\Omega_{LF}(0)]\rangle} \quad (1)$$

where $\mathbf{D}_{ij}^{(2)}$ is the second rank Wigner rotation matrix element[14] and Ω_{LF} is the Euler angles connecting the laboratory fixed coordinate system and the coordinate system fixed to the internal rotor. $\langle\cdots\rangle$ denotes the ensemble average. Here we are considering an oblate symmetric top molecule with internal rotation about a minor principal axis of the mainbody 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 mainbody. The rotation matrix element can be further decomposed into

$$D_{lm}^{(2)}[\Omega_{LF}]=\sum_{b,d}D_{lb}^{(2)}[\Omega_{LD}]D_{bd}^{(2)}[0,\pi/2,0]D_{dm}^{(2)}[\alpha,\beta,0] \quad (2)$$

where the summation is from -2 to $+2$ and Ω_{LD} is the Euler angles connecting the laboratory fixed frame and the principal coordinate system. The second set of Euler angles represents the transformation from the principal coordinate system to the coordinate system fixed to the mainbody with the z-axis coincident with the minor principal axis. The last set of Euler angles are required to transform to the coordinate

system fixed to the internal rotor such as a methyl group. In this case the z-axis is taken to be along the C-H bond and β is the fixed tetrahedral angle and γ is set to zero without loss of generality. The angle α is the time-dependent internal rotation angle.

The numerator of Eq. (1) then becomes

$$\begin{aligned}&\langle D_{jk}^{(2)}[\Omega_{LF}(0)]\, D_{lm}^{(2)*}[\Omega_{LF}(t)]\rangle\\ &=\sum_{a,b,c,d}\langle D_{ja}^{(2)}[\Omega_{LD}(0)]\, D_{lb}^{(2)*}[\Omega_{LD}(t)]\, D_{ac}^{(2)}[0,\pi/2,0]\\ &\quad\times D_{bd}^{(2)*}[0,\pi/2,0]\, D_{ck}^{(2)}[\alpha(0),\beta,0]\\ &\quad\times D_{dm}^{(2)*}[\alpha(t),\beta,0]\rangle \qquad (3)\\ &\simeq\sum_{a,b,c,d}\langle D_{ja}^{(2)}[\Omega_{LD}(0)]\, D_{lb}^{(2)*}[\Omega_{LD}(t)]\rangle\langle e^{-ic\alpha(0)+id\alpha(t)}\rangle\\ &\quad\times d_{ac}^{(2)}(\pi/2)\, d_{bd}^{(2)}(\pi/2)\, d_{ck}^{(2)}(\beta)\, d_{dm}^{(2)}(\beta).\end{aligned}$$

The second approximate equality is introduced by assuming that the overall reorientation is independent of the internal rotation. Since the reorientation of bulky mainbody may be reasonably assumed to undergo rotational diffusion, the first ensemble average becomes[4]

$$\langle D_{ja}^{(2)}[\Omega_{LD}(0)]\, D_{lb}^{(2)*}[\Omega_{LD}(t)]\rangle=\frac{1}{5}\, e^{-E_a t}\,\delta_{jl}\,\delta_{ab} \qquad (4)$$

where

$$E_a\equiv 6\,D_2+(D_1-D_2)\,a^2$$

and δ_{ij} is the Kronecker delta. D_1 is the rotational diffusion constant for the spinning about the major principal axis and D_2 is for the tumbling about the minor principal axis.

The second ensemble average which represents the internal rotation may be treated by the modified extended rotational diffusion model proposed recently by us.[12,13] In this model, the direction of the internal angular momentum vector is fixed along the minor axis of the principal coordinate system and only the magnitude of the internal angular momentum is randomized at the end of each free rotational step. By following our earlier procedure, it can be shown that

$$\begin{aligned}&\langle e^{-ic\alpha(0)+id\alpha(t)}\rangle=\sum_{n=1}^{\infty}\tau_j^{-(n-1)}e^{-t/\tau_j}\int_0^t dt_{n-1}\cdots\int_0^{t_2}dt_1\\ &\quad\times\langle e^{-ic\alpha(0)+id\alpha(0)}\rangle_{\alpha(0)}\langle e^{id\sum_{m=1}^{n}(t_m-t_{m-1})/I_\alpha}\rangle_{J_m}\\ &\quad\equiv\delta_{cd}\,G_{\rm int}^{(d)} \qquad (5)\end{aligned}$$

where τ_j is the internal angular momentum correlation time and the ensemble averages are over the initial internal rotation angle, $\alpha(0)$, and over the magnitude of the internal angular momentum vector in the m-th free rotational step, J_m, respectively. I_α is the moment of inertia of the internal rotor about the minor axis of the principal coordinate system. The Kronecker delta comes from the first ensemble average and $G_{\rm int}^{(d)}$ represents the rest of the expression on the right hand side of Eq. (5).

Then, Eq. (1) becomes

$$\begin{aligned}G_{jk,lm}(t)=&\sum_{a,b}[d_{ab}^{(2)}(\pi/2)]^2\, d_{bk}^{(2)}(\beta)\, d_{bm}^{(2)}(\beta)\\ &\times e^{-E_a t}\, G_{\rm int}^{(b)}(t)\,\delta_{jl}. \qquad (6)\end{aligned}$$

It is well known that the reorientational correlation time τ_c, which can be evaluated from NMR dipolar or quadrupolar relaxation experiments, is defined by a time integral of $G_{j0,j0}(t)$ component as[4]

$$\tau_c=\sum_{a,b}[d_{ab}^{(2)}(\pi/2)\, d_{b0}^{(2)}(\beta)]^2\int_0^\infty dt\, e^{-E_a t}\, G_{\rm int}^{(b)}(t). \qquad (7)$$

Although the internal rotational correlation function $G_{\rm int}^{(b)}$ cannot be further simplified, the time integral in the above expression is known to be evaluated analytically to give

$$\tau_c^*=\sum_{a,b}[d_{ab}^{(2)}(\pi/2)\, d_{b0}^{(2)}(\beta)]^2\,\frac{\tau_j^*\, Y(a,b)}{\tau_j^*-Y(a,b)} \qquad (8)$$

where

$$\begin{aligned}Y(a,b)\equiv&\frac{1}{|b|}\sqrt{\pi/2}\,\exp[(E_a^*+1/\tau_j^*)^2/2b^2]\\ &\times\mathrm{erfc}\left(\frac{E_a^*+1/\tau_j^*}{\sqrt{2}\,|b|}\right) \qquad (9)\end{aligned}$$

with

$$E_a^*\equiv 6D_2^*+(D_1^*-D_2^*)\,a^2$$
$$\tau^*\equiv\sqrt{k_BT/I_\alpha}\,\tau,\quad D^*\equiv\sqrt{I_\alpha/k_BT}\,D$$

and erfc (x) is the complementary error function. The presence of $d^{(2)}$ matrix elemet with argument $\pi/2$ simplifies Eq. (8) further to give

$$\begin{aligned}\tau_c^*=\tau_j^*\Big[&\frac{1}{4}F(0,0)+\frac{3}{4}F(2,0)+F(1,1)+F(2,1)\\ &+\frac{3}{4}F(0,2)+F(1,2)+\frac{1}{4}F(2,2)\Big] \qquad (10)\end{aligned}$$

where

$$F(a,b)\equiv[d_{b0}^{(2)}(\beta)]^2\,\frac{Y(a,b)}{\tau_j^*-Y(a,b)} \qquad (11)$$

The $d_{b0}^{(2)}(\beta)$ matrix elements can be explicitly written by Rose's formula[14] to yield

$$\begin{aligned}&[d_{00}^{(2)}(\beta)]^2=\frac{1}{4}(3\cos^2\beta-1)^2\equiv A\\ &[d_{10}^{(2)}(\beta)]^2=\frac{3}{2}\cos^2\beta\sin^2\beta\equiv B/2 \qquad (12)\\ &[d_{20}^{(2)}(\beta)]^2=\frac{3}{8}\sin^4\beta\equiv C/2.\end{aligned}$$

The first two terms in Eq. (10) can be simplified further by using the fact that

$$Y(a,0)=\lim_{b\to 0}Y(a,b)=(E_a^*+1/\tau_j^*)^{-1} \qquad (13)$$

to give

$$\tau_j^*F(a,0)=A/E_a^* \qquad (14)$$

which is independent of τ_j^*. Therefore, Eq. (10) may be rewritten as

$$\begin{aligned}\tau_c^*=\tau_0^*+\tau_j^*\Big[&F(1,1)+F(2,1)+\frac{3}{4}F(0,2)\\ &+F(1,2)+\frac{1}{4}F(2,2)\Big] \qquad (15)\end{aligned}$$

where

$$\tau_0^*\equiv\frac{1}{4}\,\frac{1}{6D^*}+\frac{3}{4}\,\frac{1}{4D_1^*+2D_2^*}.$$

In the internal rotational diffusion limit, $\tau_j^*\to 0$, the overall reorientational correlation time can be reduced to

$$\begin{aligned}\tau_c^*(\tau_j^*\to 0)=&A\,\tau_0^*+\frac{B}{2}\left(\frac{1}{D_1^*+5D_2^*}+\frac{1}{4D_1^*+2D_2^*}\right) \qquad (16)\\ &+\frac{C}{2}\left(\frac{3}{4}\,\frac{1}{6D_2^*}+\frac{1}{D_1^*+5D_2^*}+\frac{1}{4}\,\frac{1}{4D_1^*+2D_2^*}\right).\end{aligned}$$

Also, in the internal free rotational limit, $\tau_j^* \to \infty$, τ_c^* is reduced to

$$\tau_c^*(\tau_j^* \to \infty) = A\tau_0^* + \frac{B}{2}\sqrt{\pi/2}\left\{\exp[(D_1^*+5D_2^*)^2/2] \times \operatorname{erfc}\left(\frac{D_1^*+5D_2^*}{\sqrt{2}}\right) + \exp[(4D_1^*+2D_2^*)^2/2]\operatorname{erfc}\left(\frac{4D_1^*+2D_2^*}{\sqrt{2}}\right)\right\} + C\sqrt{\pi/2}\left\{\frac{3}{16}\exp[(6D_2^*)^2/8]\operatorname{erfc}\left(\frac{6D_2^*}{\sqrt{8}}\right) + \frac{1}{16}\exp[(4D_1^*+2D_2^*)^2/8]\operatorname{erfc}\left(\frac{4D_1^*+2D_2^*}{\sqrt{8}}\right) + \frac{1}{4}\exp[(D_1^*+5D_2^*)^2/2]\operatorname{erfc}\left(\frac{D_1^*+5D_2^*}{\sqrt{2}}\right)\right\} \quad (17)$$

Discussion

The overall reorientational correlation time in the presence of internal rotation can be evaluated in terms of the internal angular momentum correlation time and *vice versa via* Eq. (15) which is our main result. However, one must know the values of rotational diffusion constants first. This may be accomplished for a simple oblate symmetric top such as mesitylene by measuring ^{13}C nuclear magnetic relaxation time due to the dipole-dipole relaxation mechanism on the unsubstituted ring carbons. The ring carbon-13 relaxation time is directly related to the overall reorientational correlation time without internal rotation which appeared in Eq. (15) as τ_0^*. The expression for τ_0^* involves both D_1^* and D_2^* and one must know at least the ratio of diffusion constants or the value of one diffusion constant from other experiments. At present, there exist no consistent and complete set of experimental data which are necessary to evaluate τ_j^* from Eq. (15). Moreover, some reported data show rather big differences. For example, Kuhlmann and Grant[15] reported the dipolar relaxation time of methyl carbon-13 for mesitylene as 23.0 sec at 40°C while Tancredo, et al.[16] reported the value of 39.2 sec at 38°C. In view of these situations we do not attempt of extract any number from existing experimental data and hope that these situations would be clarified in the near future.

At this point it would be interesting to compare the present theory with our previous result on toluene[12,13] which was approximated as a prolate symmetric top molecule. This comparison is carried out by taking the limit of $D_1=D_2$ for both results. If this limit is the same for both results, it would show an indication that our theories are consistent. In the limit of $D_1=D_2=D$, Eq. (15) becomes

$$\tau_c^* = \frac{A}{6D^*} + \frac{B\sqrt{\pi/2}\exp[(6D^*+1/\tau_j^*)^2/2]\operatorname{erfc}\left(\frac{6D^*+1/\tau_j^*}{\sqrt{2}}\right)}{\tau_j^* - \sqrt{\pi/2}\exp[(6D^*+1/\tau_j^*)^2/2]\operatorname{erfc}\left(\frac{6D^*+1/\tau_j^*}{\sqrt{2}}\right)} + \frac{C\sqrt{\pi/8}\exp[(6D^*+1/\tau_j^*)^2/8]\operatorname{erfc}\left(\frac{6D^*+1/\tau_j^*}{\sqrt{8}}\right)}{\tau_j^* - \sqrt{\pi/8}\exp[(6D^*+1/\tau_j^*)^2/8]\operatorname{erfc}\left(\frac{6D^*+1/\tau_j^*}{\sqrt{8}}\right)}. \quad (18)$$

In the same limit, Eq. (8) of Ref. 12 gives the same expression which is for a spherical top molecule. The rotational diffusion limit ($\tau_j^* \to 0$) expression, Eq. (16), becomes

$$\tau_c^*(\tau_j^* \to 0) = \frac{1}{6D^*}(A+B+C) \quad (19)$$

which, in turn, reduces to $1/6D^*$ for the tetrahedral angle. The free rotational limit ($\tau_j^* \to \infty$) expression, Eq. (17), becomes

$$\tau_c^*(\tau_j^* \to \infty) = \frac{A}{6D^*} + B\sqrt{\pi/2}\exp[(6D^*)^2/2]\operatorname{erfc}\left(\frac{6D^*}{\sqrt{2}}\right) + C\sqrt{\pi/8}\exp[(6D^*)^2/8]\operatorname{erfc}\left(\frac{6D^*}{\sqrt{8}}\right). \quad (20)$$

The same expressions, Eqs. (19) and (20), can also be obtained from Eqs. (9) and (10) of Ref. 12, respectively.

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