$$-\frac{5}{693}\sqrt{\frac{\pi}{35}}\,F_{18}\,(Y_{4-3}(\Theta,\Phi)+Y_{43}(\Theta,\Phi))+\frac{1}{231}\sqrt{\frac{2\pi}{273}}\,S_1\,(Y_{6-1}(\Theta,\Phi)+Y_{61}(\Theta,\Phi))$$
$$+\frac{1}{77}\sqrt{\frac{\pi}{1365}}\,S_1\,(Y_{6-3}(\Theta,\Phi)+Y_{63}(\Theta,\Phi))+\frac{1}{21}\sqrt{\frac{\pi}{1001}}\,S_1\,(Y_{6-5}(\Theta,\Phi)+Y_{65}(\Theta,\Phi))\Big]$$

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Molecular Reorientation in the Presence of the Extended Diffusion of Internal Rotation in Liquid Perdeuterotoluene

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The effect of internal rotation of methyl group in liquid perdeuterotoluene on nuclear quadrupole relaxation of methyl deuterons is investigated. A model of a spherical diffusor undergoing rotational diffusion is extended to include the extended diffusion of internal rotation. The overall reorientational correlation time in the presence of internal rotation is explicitly given as an analytical function of the angular momentum correlation time. Also, the degree of inertial effect in the internal rotation is evaluated.

1. Introduction

Nuclear magnetic relaxation measurements are widely used in understanding molecular dynamics in liquids.[1-6] Interpretation of the experimental data in terms of the rotational diffusion model[7-9] is a common practice. However, this model is based on the assumption of small angular step diffusion and can not describe the inertial effect properly. In 1966 Gordon[10] proposed an extended version of the rotational diffusion model and applied it to linear molecules. His model is free of the restriction on the size of angular steps but assumes that both the magnitude and direction of angular momentum are randomized at the end of each free rotational step (J-diffusion) or only the direction is randomized (M-diffusion). Since then, Gordon's extended diffusion theory was developed further to deal with spherical top molecules[11] and symmetric top molecules.[12,13]

Recently, Versmold[4] studied the internal rotation of a side group attached to a spherical diffusor in terms of the extended diffusion model. He treated the overall rotation of a spherical diffusor by the isotropic rotational diffusion and proposed a scheme to incorporate the inertial effect of the extended internal rotation. His theory is limited, however, to a certain range of the angular momentum correlation time. Furthermore, all the calculations in his theory have to be carried out by numerical integrations. We have reported earlier[11] a general scheme of calculating the internal correlation time and the overall reorientational correlation time as analytic functions of the angular momentum correlation time without any restriction on the range of validity. The purpose of this work is to apply our general scheme to the nuclear quadrupolar relaxation of methyl group deuterons in liquid perdeuterotoluene and evaluate the degree of inertial effect of the internal rotation.

2. Theoretical Background

Application of the extended diffusion model to describe the internal rotation of a side group such as the methyl group in toluene can be simplified if we assume that the internal rotation about the z-axis of molecular coordinate system is one dimensional. In this case, a modified version of the extended diffusion model of Spiess. *et al.*[2] may be adopted. In this modified version, only the magnitude of angular momentum is randomized at the end of each free rotational step.

The direction of angular momentum vector is fixed along the z axis. Then, the internal correlation time characterizing the internal rotation can be evaluated analytically as[14]

$$\tau_{\rm int}^{(k)*}=\frac{\tau_j^* f_k}{\tau_j^*-f_k} \qquad (k=1,2) \tag{1}$$

where

$$f_k=\frac{1}{k}\sqrt{\pi/2}\,\exp\left(\frac{1}{2k^2\tau_j^{*2}}\right)\mathrm{erfc}\left(\frac{1}{\sqrt{2}\,k\tau_j^*}\right) \tag{2}$$

with

$$\tau_{\rm int}^{(k)*}=\sqrt{k_BT/I_z}\;\tau_{\rm int}^{(k)},\quad \tau_j^*=\sqrt{k_BT/I_z}\;\tau_j \tag{3}$$

and erfc(x) is the complementary error function.

The angular momentum correlation time which represents the average time between collisions is denoted by τ_j.

The degree of inertial effect α is given by[4]

$$\alpha=\tau_{\rm int}^{(1)}/\tau_{\rm int}^{(2)} \tag{4}$$

which becomes 2 in the free rotation limit and 4 in the rotational diffusion limit.

In order to evaluate the angular momentum correlation time from experimental data one has to analyze the overall reorientation of a molecule in the presence of the internal rotation. Corresponding overall reorientational correlation function for a spherical diffusor is well known as[1]

$$\begin{aligned}G(t)=&A\exp(-6Dt)+BG_{\rm int}^{(1)}(t)\exp(-6Dt)\\&+C\,G_{\rm int}^{(2)}(t)\exp(-6Dt)\end{aligned} \tag{5}$$

for a dependent internal rotation with respect to the overall reorientation and

$$\begin{aligned}G(t)=&A\exp(-6Dt)+B\,G_{\rm int}^{(1)}(t)\exp(-5Dt)\\&+C\,G_{\rm int}^{(2)}(t)\exp(-2Dt)\end{aligned} \tag{6}$$

for an independent internal rotation with

$$\begin{aligned}A&=\frac{1}{4}(3\cos^2\theta-1)^2\\B&=3\sin^2\theta\cos^2\theta\\C&=\frac{3}{4}\sin^4\theta\end{aligned} \tag{7}$$

The internal rotational correlation function is denoted by $G_{\rm int}^{(k)}(t)$ and θ is the angle between the relaxation vector and the z-axis of molecular coordinate system, D is the rotational diffusion constant of the whole molecule.

If the internal rotation is governed by the extended diffusion as described above, the overall reorientational correlation time can be evaluated analytically as

$$\tau_c^*=\frac{A}{6D^*}+\frac{B\tau_j^*F_1}{\tau_j^*-F_1}+\frac{C\tau_j^*F_2}{\tau_j^*-F_2} \tag{8}$$

where

$$F_k=\frac{1}{k}\sqrt{\pi/2}\,\exp(Y_k^2)\,\mathrm{erfc}(Y_k) \tag{9}$$

with

$$Y_k=(\tau_j^{*-1}+6D^*)/\sqrt{2}\,k \tag{10}$$

for a dependent internal rotation and

$$Y_k=[\tau_j^{*-1}+(6-k^2)D^*]/\sqrt{2}\,k \tag{11}$$

for an independent case. D^* is the reduced diffusion constant defined by $D^*=\sqrt{I_z/k_BT}\;D$.

In the internal rotational diffusion limit ($\tau_j^*\to 0$) Eq. (8) becomes

$$\tau_c^*=\frac{A}{6D^*}+\frac{B}{6D^*+\tau_j^*}+\frac{C}{6D^*+4\tau_j^*} \tag{12}$$

for a dependent case and

$$\tau_c^*=\frac{A}{6D^*}+\frac{B}{5D^*+\tau_j^*}+\frac{C}{2D^*+4\tau_j^*} \tag{13}$$

for an independent case. Also, in the internal free rotation limit ($\tau_j^*\to\infty$) Eq. (8) becomes

$$\begin{aligned}\tau_c^*=&\frac{A}{6D^*}+B\sqrt{\pi/2}\exp[(6D^*)^2/2]\,\mathrm{erfc}(6D^*/\sqrt{2})\\&+C\sqrt{\pi/8}\exp[(6D^*)^2/8]\,\mathrm{erfc}(6D^*/\sqrt{8})\end{aligned} \tag{14}$$

for a dependent case and

$$\begin{aligned}\tau_c^*=&\frac{A}{6D^*}+B\sqrt{\pi/2}\exp[(5D^*)^2/2]\,\mathrm{erfc}(5D^*/\sqrt{2})\\&+C\sqrt{\pi/8}\exp[(2D^*)^2/8]\,\mathrm{erfc}(2D^*/\sqrt{8})\end{aligned} \tag{15}$$

for an independent case.

3. Application to magnetic relaxation

The above results are applied to nuclear magnetic relaxation of methyl deuterons in liquid perdeuterotoluene. For mathematical simplicity we assume that perdeuterotoluene is a spherical diffusor. Then the isotropic rotational diffusion model for a spherical diffusor with internal rotation undergoing the extended diffusion can be applied here. The quadrupolar contribution to the spin-lattice relaxation time of the methyl deuterons in the extreme narrowing limit is well known as[15]

$$1/T_{1Q}=\frac{3}{2}\pi^2(e^2qQ/h)^2\tau_c \tag{16}$$

where τ_c is given by Eq. (8) and e^2qQ/h is the quadrupole coupling constant. Woessner and Snowden[1] reported T_{1Q} values for the methyl deuterons and ring deuterons of perdeuterotoluene at several temperatures. They evaluated τ_c's from the methyl deuteron data and the rotational diffusion constants were obtained from the ring deuteron data. From their result we obtained the angular momentum correlation time via Eq. (8) and the internal correlation times are evaluated from Eq. (1). The results are given in Table 1 along with the values of the degree of inertial effect α for both independent and dependent internal rotations.

In the kinetic theory of gases the collision frequency which corresponds to $1/\tau_j$ is proportional to $\sqrt{T}$.[16] Hence τ_j values are supposed to decrease as the temperature is increased. But τ_j values for liquid toluene increase with the temperature. One way of explaining this fact might be in terms of the cage effect in liquid. In a liquid each molecule moves in a cage made of its neighbors and the collision frequency becomes larger than that of gas molecules. As the temperature is increased the cage is destroyed and the collision frequency is reduced. This means the larger values of τ_j and hence the smaller values of α. Recalling the rotational diffusion limit

TABLE 1: Various Correlation Times and the Degrees of Inertial Effect at Several Temperatures

T(K)	τ_c^{*a}	D^{*a}	Dependent case			Independent case		
			τ_j^*	$\tau_{int}^{(1)*}$	α	τ_j^*	$\tau_{int}^{(1)*}$	α
227	6.12	0.0054	0.154	6.80	3.62	0.160	6.54	3.59
285	3.47	0.0117	0.220	4.95	3.40	0.237	4.63	3.35
298	3.16	0.0140	0.218	4.97	3.40	0.239	4.60	3.34
313	2.96	0.0155	0.224	4.86	3.39	0.249	4.46	3.31
353	2.41	0.0209	0.258	4.31	3.29	0.295	3.88	3.19

[a] Woessner and Snowden (Ref. 1)

of $\alpha=4$ and the free rotation limit of $\alpha=2$, the above results show that the internal rotation of the methyl group is characterized by a certain degree of inertial effect.

With the knowledge of the diffusion constant from the ring deuteron data one can plot τ_c^* explicitly as a function of τ_j^* according to Eq. (8). Figure 1 shows these curves at two temperatures for both independent and dependent internal rotations.

4. Discussion

When the internal rotation as well as the overall reorientation is treated by the rotational diffusion model, the overall reorientational correlation time is given by Eq. (12) for a dependent case. In order to incorporate the inertial effect for the internal rotation Versmold[4] proposed an iterative scheme by introducing a parameter α defined by Eq. (4) and modified Eq. (12) as

$$\tau_c^* = \frac{A}{6D^*} + \frac{B}{6D^*+D_i^*} + \frac{C}{6D^*+\alpha D_i^*} \tag{17}$$

where the internal rotational diffusion constant D_i may be identified as

$$1/\tau_{int}^{(1)*} = D_i^*, \qquad 1/\tau_{int}^{(2)*} = 4D_i^*. \tag{18}$$

However Eq. (17) is valid only when the internal extended rotational diffusion correlation function is very close to an exponential form. Then, the values of τ_j^* is restricted to a certain range of validity. On the other hand, our Eq. (8) is not restricted by any range of validity for τ_j^* values. Comparison of our result with Versomold's scheme is shown in Figure 2 for a dependent case at 298 K. The curves show that his scheme is in good agreement with ours at small τ_j^* region and deviates from ours at large τ_j^* region. At the large τ_j^* region, τ_j^* values obtained from the curves for a given τ_c^* value could be quite different. But his scheme is still a good approximation as compared to the internal rotational diffusion model which is also shown in Figure 2.

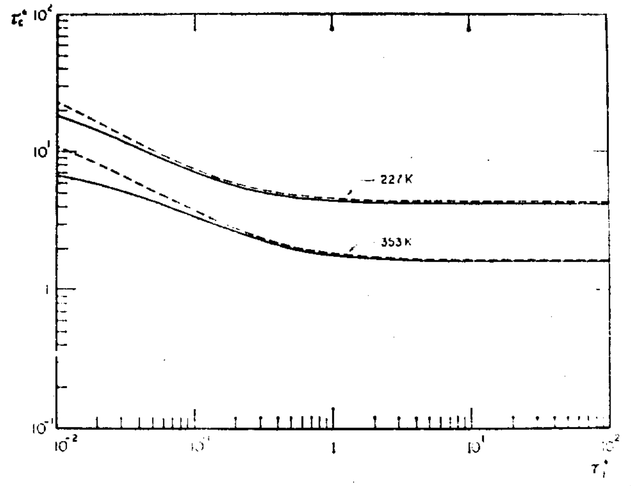

Figure 1. Overall Reorientational Correlation Times τ_c^* as Functions of τ_j^* at two Differen Temperatures: — Dependent Internal Rotation, ······ Independent Internal Rotation.

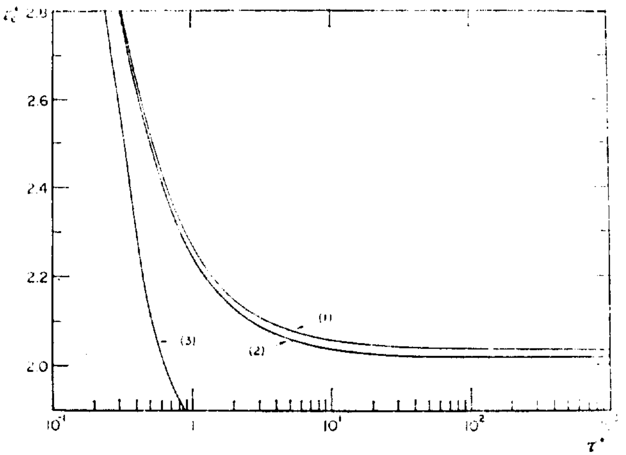

Figure 2. Overall Reorientational Correlation Times τ_c^* as Functions of τ_j^* for a Dependent Internal Rotation at 298 K Calculated by Different Models: Curve (1). Present model, Curve (2). Versmold's model; Curve (3). Rotational Diffusion Model.

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Tunnel Effects in the $H + D_2$ and $D + H_2$ Reactions

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We considered the tunneling effect on the rate constants calculated from transition-state theory for the $H + D_2$ and $D + H_2$ reactions. A method for evaluating the important parameter E_c (potential barrier height) was proposed. A tunnel-effect correction factor (TECF) $\Gamma_t \exp\theta_t$ was estimated from experimental data, and compared with the corresponding values obtained from many theoretical methods. According to our results, the tunneling effect cannot be negligible around 800°K where the TECF value is ca. 0.8 whereas the factor approaches to unity at T>2400°K where the tunneling completely disappears. In addition to the above fact, we also found that the TECF for the $D + H_2$ reaction is greater than that of the $H + D_2$ reaction in agreement with Garrett and Truhlar's result. In contrast to our result, however, Shavitt found that the order is reversed, *i. e.*, TECF for $(D + H_2)$ is greater than that for $(H + D_2)$. We discussed about the Shavitt's result.

1. Introduction

A quantum mechanical tunneling effect is very important for reactions involving light atoms and molecules, and the neglect of this factor often causes the rate constants from activated complex theory to be too small.[1-5] In the past two decades, noteworthy progress in the computation of tunneling factor has been made.[1-12]

The first quantum correction was derived by Wigner in 1932,[7] and this simplified model had been used widely for its computational simplicity. Wigner's quantum correction, however, is justified only when the tunneling correction is small, and the conditions for validity of Wigner's assumptions are seldom to be satisfied. A theoretically more justifiable way is to include tunneling effects involving an exact quantum mechanical transmission probability through a given potential barrier.[1] In simple cases, it is sufficient to use a parabolic or Eckart-type barrier, since for these barriers the transmission probability G(W) can be analytically computed.[1,3,4] But, for more complicated cases, one must calculate the transmission probability numerically to obtain the tunneling factor Γ_t because of the complexity of the potential barrier. Thus, effective potential energy barriers are often employed, the most commonly used models are the CVE (conservation of vibrational energy) barrier[10] and the 'vibrationally adiabatic' (VA) barrier.[10-12] In the latter, there are the MEPVA (minimum energy path vibrationally adiabatic) barrier and the MCPVA (Marcus-Coltrin path vibrationally adiabatic) barrier. These two VA methods and the CVE method are very well compared in Figure 1 of ref. 5. The VA methods, however, are not used in the present paper.

Meanwhile, many *ab initio* and semiempirical methods have been used for constructing the potential energy surface of H_3.[13-18] The most accurate three-dimensional potential energy surface for H_3 is the one obtained by Siegbahn and Liu (SL)[18] by using a configuration interaction method. Among other *ab initio* calculations for obtaining the potential energy surface, however, the method used by Shavitt, Stevens, Minn and Karplus (SSMK)[17] is easier than the SL method, and it yields results of fairly high accuracy. Thus, the SSMK surface has been most widely used, we also employ the SSMK potential energy barrier in the present work.

In view of the experiment, the $H + H_2$ reaction and its isotopic reactions[3,19-22] are not particularly simple to study. Especially, at low temperatures, the experimental procedure is difficult, as a result, the experimental kinetic data are very rare and also are of poor accuracy. This situation has been partly improved at least by the ESR method of Westenberg and de Hass,[21] and Mitchell and LeRoy.[22]

Finally, it should be pointed out that if we calculate the rate constants k' theoretically using the barrier heights (E_c) which were computed by *ab initio* or semiempirical methods, the theoretical values of k' are smaller than the experimental data. Thus, the theoretical barrier height E_c has been adjusted to give agreement with the high-temperature part of the available experimental data.[4]

In this paper we consider the following two reactions which have been studied by many authors[19-22] theoretically and