430 *Bull. Korean Chem. Soc., Vol. 10, No. 5, 1989*

Eun Mi Kim and Kook Joe Shin

Birmingham, England, IV, 73–87, 1974.
17. D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1969).
18. Reference 16, pp 149–150.
19. O. Hassell and C. Romming, *Quart. Rev. Chem. Soc. London*, 16, 1 (1962).
20. I. L. Karle, *J. Chem. Phys.*, 23, 1939 (1955).

21. Reference 10, pD-188.
22. Y. Kim and K. Seff, *J. Phys. Chem.*, 91, 671 (1987).
23. V. Subramanian and K. Seff, *J. Phys. Chem.*, 81, 2249 (1977).
24. Reference 10, pF-159.
25. S. H. Lee and Y. Kim, unpublished work.

Spin-Rotational Relaxation Study of Molecular Reorientation of Oblate Symmetric Top Molecules with Internal Extended Rotational Diffusion

Eun Mi Kim and Kook Joe Shin[†]

Molecular reorientation of oblate symmetric top molecules in the presence of internal rotation is investigated and an analytic expression for the spin-rotational relaxation rate of a nucleus attached to the internal rotor is obtained as a function of the internal angular momentum correlation time. The overall reorientation of the symmetric top is treated by the anisotropic rotational diffusion and the internal rotation is assumed to undergo modified extended rotational diffusion. The result is compared with the previous work for the prolate symmetric top molecule and it is shown that both results reduce to the same expression in the spherical top limit.

Introduction

Study of molecular reorientation in the presence of internal rotation has been carried out for many molecular systems. Theoretically, one usually adopt a certain model for the reorientation and widely employed models are rotational diffusion[1-3], jump diffusion[4-6], and extended rotational diffusion[7-12]. Experimentally[10,13], various techniques of spectroscopy such as NMR, IR, Raman, and Rayleigh light scattering are employed and these techniques can be complemented with one another to extract reliable informaiton on the molecular reorientation.

Recently, we investigated a model of a symmetric-top molecule undergoing anisotropic rotational diffusion in the presence of the extended diffusion of internal rotation[14-17]. Particularly, the effects of internal rotation of methyl group in liquid toluene which is a prolate symmetric top molecule on the ^{13}C nuclear dipolar and spin-rotational relaxation times were investigated[16] to evaluate the internal angular momentum correlation time which reveals the inertial effect in the internal rotation. We also carried out a similar investigation of the effect of the reorientation of oblate symmetric top molecules containing internal rotors on the ^{13}C nuclear dipolar relaxation time[17]. In this case, the overall reorientational correlation time expressed in terms of the internal angular momentum correlation time is quite different from the expression for prolate symmetric top molecules but reduces to the same expression in the spherical top limit.

The purpose of this work is to investigate the effect of reorientation of oblate symmetric top molecules in the presence of internal rotation on the ^{13}C nuclear spin-rotational relaxation time. The result can be compared with the case of

^{13}C nucelar dipolar relaxation and the internal angular momentum correlation time can then be evaluated reliably.

Theory

The spin-rotational contribution to the relaxation rate in the extreme narrowing limit is given by[18]

$$1/T_{1,SR} = \hbar^{-2} \int_0^\infty dt \, [g_{-1,1}(t) + g_{-1,1}(t)] \qquad (1)$$

where

$$g_{kk}(t) = \langle V_k(t) \, V_k(0) \rangle \, (-1)^k \qquad (2)$$

with

$$V_k = \sum_q D_{kq}^{(1)*} A_q. \qquad (3)$$

Here the rotation matrices $D^{(l)}(\Omega)$ defined by Rose[19] are employed and the angular brackets denote the ensemble average. A_q in Eq. (3) appears in the spin-rotational Hamiltonian as follows[20]:

$$H_{SR}/\hbar = \sum_{k=-1}^{1} A_k I_k \qquad (4)$$

where

$$I_0 = I_c, \quad I_{\pm 1} = \mp 2^{-1/2} (I_a \pm i I_b) \qquad (5)$$

and

$$A_{+1} = 2^{-1/2} (C_{aa} J_a - i C_{bb} J_b) \qquad (6a)$$

$$A_0 = - (C_{cc} J_c + D_a j) \qquad (6b)$$

$$A_{-1} = - 2^{-1/2} (C_{aa} J_a + i C_{bb} J_b). \qquad (6c)$$

In Eqs. (4), (5), and (6) the components of nuclear spin vector and total angula momentum (I_a, I_b, I_c and J_a, J_b, J_c) are along the molecule-fixed frame (a,b,c) in which the spin-overall rotation coupling tensor C is diagonal. j is the internal rotational angular momentum along the axis of internal rotation and D_a is defined as $D_a = C_a(1 - I_a/I_{cc})$ where C_a is the spin-internal rotation coupling constant, and I_{cc} and I_a denote the monents of inertia of the whole molecule and the internal rotor, respectively, along the axis of internal rotation.

If we assume that the orientation of molecule is independent of its angular momentum, the time correlation function in Eq. (2) can be expressed as

$$g_{\kappa\kappa'}(t) = (-1)^\kappa \sum_{qq'} < A_q(t) A_{q'}(0) >$$
$$\times < D_{\kappa q}^{(1)*}[\Omega_{LF}(t)] D_{\kappa' q'}^{(1)*}[\Omega_{LF}(0)] > \quad (7)$$

where Ω_{LF} is the Euler angles connecting the laboratory fixed coordinate system and the coordinate system fixed to the internal rotor such as a methyl group. The orientational correlation function can be further decomposed in terms of two sets of Euler angles to give

$$< D_{\kappa q}^{(1)*}[\Omega_{LF}(t)] D_{\kappa' q'}^{(1)}[\Omega_{LF}(0)] >$$
$$= (-1)^{\kappa - q} \sum_{a,b,c,d} < D_{\kappa a}^{(1)*}[\Omega_{LD}(t)] D_{ac}^{(1)*}[0, \frac{\pi}{2}, 0]$$
$$\times D_{cq}^{(1)*}[a(t), 0, 0] D_{-\kappa'b}^{(1)}[\Omega_{LD}(0)] D_{bd}^{(1)}[0, \frac{\pi}{2}, 0]$$
$$\times D_{d-q'}^{(1)}[a(0), 0, 0] > \quad (8)$$

where Ω_{LD} are 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 molecule with the z-axis coincident with the minor principal axis. The last set of the Euler angles are required to transform to the coordinate system fixed to the internal rotor. In this case the z-axis is taken to be along the C-H bond and the angle a is the internal rotation angle. Other angles, β and γ, are set to zero without loss of generality. Then Eq. (8) can be further simplified if we assume that the overall reorientation is independent of the internal rotation to give

$$< D_{\kappa q}^{(1)*}[\Omega_{LF}(t)] D_{\kappa' q'}^{(1)}[\Omega_{LF}(0)] >$$
$$= (-1)^{\kappa - q} \sum_{a,b,c,d} < D_{\kappa a}^{(1)*}[\Omega_{LD}(t)] D_{-\kappa'b}^{(1)}[\Omega_{LD}(0)] >$$
$$\times < \exp i\{ca(t) - da(0)\} > d_{ac}^{(1)}(\pi/2) d_{bd}^{(1)}(\pi/2) \quad (9)$$

As before, we assume that the overall reorientation of the whole molecule, which is also assumed to be a symmetric top, is undergoing the anisotropic rotational diffusion and then the first ensemble average becomes[21]

$$< D_{\kappa a}^{(1)*}[\Omega_{LD}(t)] D_{-\kappa'b}^{(1)}[\Omega_{LD}(0)] > = \frac{1}{3} e^{-E_a t} \delta_{\kappa - \kappa'} \delta_{ab} \quad (10)$$

where

$$E_a = 2D_1 + (D_1 - D_2) a^2.$$

In Eq. (10), δ_{ij} is the Kronecker delta and D_1 and D_2 are the rotational diffusion constants of the spinning along the major • principal axis and the tumbling along the minor principal

axis, respectively.

The second ensemble average in Eq. (9) represents the internal rotational correlation function and here we adopt the modified extended rotational diffusion model proposed recently by us[14]. In this model, the direction of the internal angular momentum vector is fixed along the axis of internal rotation and only the magnitude of internal angular momentum is randomized at the end of each free rotational step. With this model the internal rotational correlation function can be expressed as

$$< \exp i\{ca(t) - da(0)\} > = \sum_{n=1}^{\infty} \tau_j^{-(n-1)} e^{-t/\tau_j} \int_0^t dt_{n-1} \cdots$$

$$\int_0^{t_2} dt_1 < \exp i\{ca(0) - da(0)\} >_{a(0)}$$

$$\times < e^{id \sum_{m=1}^{n} j_m(t_m - t_{m-1})/I_a} > j_m \equiv \delta_{cd} G_{int}^{(d)} \quad (11)$$

where τ_j is the internal angular momentum correlation time and the ensemble averages are over the initial internal rotation angle, $a(0)$, and over the magnitude of the internal angular momentum vector in the mth free rotational step, j_m, respectively.

Substitution of Eqs. (9), (10) and (11) into Eq. (7) gives

$$g_{\kappa\kappa'}(t) = \sum_{qq'} (-1)^q \delta_{\kappa - \kappa'} < A_q(t) A_{-q}(0) > \frac{1}{3} e^{-E_a t}$$
$$\times [d_{aq}^{(1)}(\frac{\pi}{2})]^2 G_{int}^{(q)}(t) \quad (12)$$

The $d_{aq}^{(1)}(\pi/2)$ matrix elements can be explicitly given by Rose's formula to give

$$d_{11}^{(1)}(\pi/2) = d_{1,-1}^{(1)}(\pi/2) = d_{-11}^{(1)}(\pi/2) = d_{-1,-1}^{(1)}(\pi/2) = 1/2$$
$$d_{01}^{(1)}(\pi/2) = d_{-10}^{(1)}(\pi/2) = - d_{10}^{(1)}(\pi/2)$$
$$= - d_{0,-1}^{(1)}(\pi/2) = 2^{-1/2} \quad (13)$$
$$d_{00}^{(1)}(\pi/2) = 0.$$

Then, Eq. (12) becomes

$$g_{\kappa\kappa'}(t) = \frac{1}{3} \delta_{\kappa - \kappa'} \{ \frac{1}{2} [C_{aa}^2 < J_a(t) J_a(0) >$$
$$+ C_{bb}^2 < J_b(t) J_b(0) >] G_{int}^{(1)}(t)$$
$$\times [\exp(-E_0 t) + \exp(-E_1 t)]$$
$$+ [C_{cc}^2 < J_c(t) J_c(0) > + D_a^2 < j(t) j(0) >]$$
$$\times G_{int}^{(0)}(t) \exp(-E_1 t)\} \quad (14)$$

where all the cross correlations are neglected. As usual, we also assume that the angular momentum correlation functions decay exponentially and Eq. (14) can be reduced to

$$g_{\kappa\kappa'}(t) = \frac{1}{3} k_B T \delta_{\kappa - \kappa'} \{ \frac{1}{2} [I_{aa} C_{aa}^2 \exp(-t/\tau_a)$$
$$+ I_{bb} C_{bb}^2 \exp(-t/\tau_b)]$$
$$\times G_{int}^{(1)}(t) [\exp(-E_0 t) + \exp(-E_1 t)] \quad (15)$$
$$+ [I_{cc} C_{cc}^2 \exp(-t/\tau_c) + I_a C_a^2 (1 - I_a/I_{cc})$$
$$\times \exp(-t/\tau_j)] G_{int}^{(0)}(t) \exp(-E_1 t)\}$$

where $k_B T$ is the Boltzmann factor and $\tau_i (i=a,b,c,j)$ is the correlation time for the corresponding component of angular momentum.

By substituting Eqs. (11) and (15) into Eq. (1), we can evaluate the spin-rotational contribution to the spin-lattice relaxation time analytically as shown in APPENDIX to give

$$1/T_{1,SR}^* = (2k_B T/3\hbar^2)\ \{I_{aa}C_{aa}^2[F(a)+F'(a)]+I_{bb}C_{bb}^2$$

$$\times[F(b)+F'(b)]+I_{cc}C_{cc}^2(D_1^*+D_2^*+1/\tau_c^*)^{-1}+I_aC_a^2$$

$$\times(1-I_a/I_{cc})\ (D_1^*+D_2^*+1/\tau_j^*)^{-1}\} \tag{16}$$

where

$$T_{1,SR}^* = (k_B T/I_a)^{1/2}\ T_{1,SR}\quad \tau_i^* \equiv (k_B T/I_a)^{1/2}\tau_i,$$

$$D_i^* \equiv (I_a/k_B T)^{1/2}D_i$$

and

$$F(a) \equiv \tau_j^* f(a)/2[\tau_j^*-f(a)]$$

$$F'(a) \equiv \tau_j^* f'(a)/2[\tau_j^*-f'(a)]$$

with

$$f(a) \equiv (\pi/2)^{1/2}\exp(Y_a^2)\ erfc(Y_a)$$

$$Y_a \equiv 2^{-1/2}\ (D_1^*+D_2^*+1/\tau_a^*+1/\tau_j^*)$$

$$f'(a) \equiv (\pi/2)^{1/2}\exp(Y_a'^2)\ erfc(Y_a')$$

$$Y_a' \equiv 2^{-1/2}\ (2D_2^*+1/\tau_a^*+1/\tau_j^*)$$

and *erfc x* is the complementary error function. $F(b)$ and $F'(b)$ have the same expressions except that τ_a^* is replaced by τ_b^*.

In the internal rotational diffusion limit $(\tau_j^* < 1)$, Eq. (16) can be reduced to

$$1/T_{1,SR}^* \approx (2k_B T/3\hbar^2)\ \{I_{aa}C_{aa}^2[\frac{1}{2}\ ((D_1^*+D_2^*+1/\tau_a^*$$

$$+\tau_j^*)^{-1}+(2D_2^*+1/\tau_a^*+\tau_j^*)^{-1})]$$

$$+I_{bb}C_{bb}^2[\frac{1}{2}\ ((D_1^*+D_2^*+1/\tau_b^*+\tau_j^*)^{-1} \tag{17}$$

$$+(2D_2^*+1/\tau_b^*+\tau_j^*)^{-1})]+I_{cc}C_{cc}^2(D_1^*$$

$$+D_2^*+1/\tau_c^*)^{-1}+I_aC_a^2(1-I_a/I_{cc})$$

$$\times(D_1^*+D_2^*+1/\tau_j^*)^{-1}\}$$

On the other hand, Eq. (16) is reduced in the internal free rotational limit to

$$1/T_{1,SR}^* \approx (2k_B T/3\hbar^2)\ \{I_{aa}C_{aa}^2(\pi/2)^{1/2}/2$$

$$\times[\exp\frac{1}{2}\ (D_1^*+D_2^*+1/\tau_a^*)^2$$

$$\times erfc[2^{-1/2}\ (D_1^*+D_2^*+1/\tau_a^*)]$$

$$\times\exp\frac{1}{2}\ (2D_2^*+1/\tau_a^*)^2 erfc[2^{-1/2}$$

$$\times(2D_2^*+1/\tau_a^*)]]+I_{bb}C_{bb}^2(\pi/2)^{1/2}/2$$

$$\times[\exp\frac{1}{2}\ (D_1^*+D_2^*+1/\tau_b^*)^2 erfc$$

$$\times[2^{-1/2}\ (D_1^*+D_2^*+1/\tau_b^*)]$$

$$+\exp\frac{1}{2}\ (2D_2^*+1/\tau_b^*)^2 erfc[2^{-1/2}\ (2D_2^*+1/\tau_b^*)]]$$

$$+I_{cc}C_{cc}^2(D_1^*+D_2^*+1/\tau_c^*)^{-1}+I_aC_a^2(1-I_a/I_{cc})$$

$$\times(D_1^*+D_2^*)^{-1}\} \tag{18}$$

At this point let us compare Eq. (16) for an oblate symmetric top molecule with the similar result for a prolate symmetric top molecule obtained previously[16]. If we take the spherical top limit $(D_1^* = D_2^* = D^*)$, Eq. (16) becomes

$$1/T_{1,SR}^* = (2k_B T/3\hbar^2)\ \{I_{aa}C_{aa}^2 F''(a)+I_{bb}C_{bb}^2 F''(b)$$

$$+I_{cc}C_{cc}^2(2D^*+1/\tau_c)^{-1}+I_aC_a^2(1-I_a/I_{cc})$$

$$\times(2D^*+1/\tau_j^*)^{-1}\} \tag{19}$$

where

$$F''(a) \equiv \tau_j^* f''(a)/[\tau_j^*-f''(a)]$$

with

$$f''(a) \equiv (\pi/2)^{1/2}\exp(Y_a''^2)\ erfc(Y_a'')$$

$$Y_a'' \equiv 2^{-1/2}\ (2D^*+1/\tau_a^*+1/\tau_j^*).$$

The same expression can be obtained from Eq. (17) of Ref. 16 in the same limit. In both the rotational diffusion limit and the free rotational limit the same situation can be observed in the spherical top limit.

Discussions

In this work we have evaluated the effect of reorientation of oblate symmetric top molecules in the presence of internal rotation on the nuclear spin-rotational relaxation rate. The overall reorientation is assumed to undergo anisotropic rotational diffusion and the internal rotation is treated by the modified extended rotational diffusion in which the direction of the internal angular momentum vector is fixed along the internal rotation axis and only the magnitude of the internal angular momentum is randomized at the end of each free rotational step. Previously we carried out a similar calculation for the nuclear dipolar relaxation rate which is also given as a function of the internal angular momentum correlation time. By comparing both the dipolar and spin-rotational relaxation rates we may now determine τ_j^* reliably. the reliable value of τ_j^* is required to investigate the inertial effect of the internal rotation via the internal rotational correlation time, $\tau_{int}^{(k)}$ difined by

$$\tau_{int}^{(k)} \equiv \int_0^\infty dt\ G_{int}^{(k)}(t). \tag{20}$$

For prolate symmetric top molecules, this kind of analysis is possible with rather plenty experimental data although the agreement among those data is not always satisfactory. As pointed out in our previous work, there exists no consistent and complete set of experimental data for oblate symmetric top molecules at present and we hope that further analysis would be done in the near future.

Appendix

Spin-Rotational Relaxation Study of Molecular

Bull. Korean Chem. Soc., Vol. 10, No. 5, 1989 433

We start from $G_{int}^{(d)}$ in Eq. (11) which can be written as

$$G_{int}^{(d)}(t) = \sum_{n=1}^{\infty} \tau_j^{-(n-1)} \exp(-t/\tau_j) \int_0^t dt_{n-1} \cdots \int_0^{t_2} dt_1$$

$$\times \prod_{m=1}^{n} <\cos [dj_m (t_m - t_{m-1})/I_a]>_{j_m} \qquad (A1)$$

The ensemble average over j_m is performed using a Boltzmann-type weighting function,

$$W(j_m) = (2\pi I_a k_B T)^{-1/2} \exp(-j_m^2/2\pi I_a k_B T) \qquad (A2)$$

and an integration formula[22]

$$\int_0^{\infty} \exp(-\beta x^2) \cos bx \, dx = \frac{1}{2}(\pi/\beta)^{1/2} \exp(-b^2/4\beta).$$

$$(A3)$$

Then,

$$<\cos [dj_m (t_m - t_{m-1})/I_a]>_{j_m}$$
$$= \exp[-d^2 (t_m - t_{m-1})^2 k_B T/2 I_a]. \qquad (A4)$$

The internal rotational correlation function $G_{int}^{(d)}(t)$, cannot be further simplified as it stands but the time integral in the spin-rotational relaxation rate can be evaluated analytically as follows:

$$\int_0^{\infty} dt \, G_{int}^{(d)}(t) = \sum_{n=1}^{\infty} \tau_j^{-(n-1)} \int_0^t dt \exp(-t/\tau_j) \int_0^t dt_{n-1} \cdots$$

$$\times \int_0^{t_2} dt_1 \prod_{m=1}^{n} \exp[-B_d (t_m - t_{m-1})^2] \qquad (A5)$$

$$= \sum_{n=1}^{\infty} \tau_j^{-(n-1)} \int_0^{\infty} dt_1 \int_{t_1}^{\infty} dt_2 \cdots \int_{t_{n-1}}^{\infty} dt_n$$

$$\times \prod_{m=1}^{n} \exp[-(t_m - t_{m-1})/\tau_j] \exp[-B_d (t_m - t_{m-1})^2] \qquad (A6)$$

$$= \sum_{n=1}^{\infty} \tau_j^{-(n-1)} \int_0^{\infty} d(t_1 - t_0) \int_0^{\infty} d(t_2 - t_1) \cdots \int_0^{\infty} d(t_n - t_{n-1})$$

$$\times \prod_{m=1}^{n} \exp[-(t_m - t_{m-1})/\tau_j] \exp[-B_d (t_m - t_{m-1})^2] \qquad (A7)$$

$$= \sum_{n=1}^{\infty} \tau_j^{-(n-1)} \left\{ \int_0^{\infty} dt \exp(-t/\tau_j - B_d t^2) \right\}^n \qquad (A8)$$

where $B_d = d^2 k_B T/2 I_a$ and it is also understood that $t_n = t$ and $t_o = 0$. The integral in Eq. (A7) can be evaluated readily by use of an integration formula[22]

$$\int_0^{\infty} dt \exp(-\alpha^2 t^2 - \beta t) = (\pi/4)^{1/2}$$

$$\times \exp(\beta^2/4\alpha^2) erfc(\beta/2\alpha) \qquad (A9)$$

and the summation formula for an infinite series can be used to evaluate the time integral in Eq. (A5).

References

1. P. Debye, *Polar Molecules* (Dover, New York, 1928).
2. L. D. Favro, *Phys. Rev.* **119**, 53 (1960).
3. K. A. Valiev, *Opt. Spectrosc.* **13**, 282 (1962).
4. D. Wallach, *J. Chem. Phys.* **47**, 5258 (1967).
5. D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyer, *J. Chem. Phys.* **50**, 719 (1969).
6. H. Versmold, *J. Chem. Phys.* **58**, 5649 (1973).
7. R. G. Gordon, *J. Chem. Phys.* **44**, 1830 (1966).
8. R. E. D. McClung, *J. Chem. Phys.* **51**, 3842 (1969).
9. R. E. D. McClung, *J. Chem. Phys.*, **57**, 5478 (1972).
10. R. E. D. McClung, *Adv. Mol. Relax. Int. Processes* **10**, 83 (1977).
11. H. W. Spiess, D. Schweitzer, and U. Haeberlen, *J. Magn. Reson.* **9**, 444 (1973).
12. H. Versmold, *J. Chem. Phys.* **73**, 5310 (1980).
13. J. H. R. Clarke, *Adv. IR Raman Spectrosc.* **4**, 109 (1978).
14. K. J. Shin, D. S. Chung, and B. S. Kim, *J. Chem. Phys.* **77**, 5852 (1982).
15. D. S. Chung, B. S. Kim, J. W. Lee, and K. J. Shin, *Chem. Phys. Lett.* **93**, 499 (1982).
16. D. S. Chung, E. M. Kim, and K. J. Shin, *Chem. Phys. Lett.* **108**, 283 (1984).
17. K. J. Shin, *Bull. Korean Chem. Soc.* **4**, 228 (1983).
18. P. S. Hubbard, *Phys. Rev.* **131**, 1155 (1963).
19. M. E. Rose, *Elementary theory of angular momentum* (Wiley, New York, 1957).
20. J. W. Lee, *Bull. Korean Chem. Soc.* **4**, 48 (1983).
21. C. H. Wang, *J. Magn. Reson.* **9**, 75 (1973).
22. I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products*, (Academic Press, New York, 1980).