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Anisotropic Rotation of Perylene Studied by Fluorescence Depolarization Method

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Synopsis. Rotational diffusion coefficients of perylene in solution were determined by a fluorescence depolarization technique. An asymmetric rotor approximation is more appropriate than an oblate approximation for perylene. The ratio of the diffusion coefficients suggests that a partially slipping boundary condition should be taken into account for this system.

The fluorescence depolarization technique has been utilized to study the rotational Brownian motions of various fluorescent molecules.[1–3] We have investigated the anisotropic rotational diffusion of perylene and its derivatives in solution by a time-resolved technique.[4] In the present work, we reinvestigated the rotational motion of perylene with the asymmetric rotor model as well as with the spheroid model, and precisely analyzed the diffusion coefficients.

Theoretical

A theoretical treatment of the rotational relaxation of fluorescence emission anisotropy was performed in the most general manner by Chuang and Eisenthal.[5] Assuming that the transition vector of absorption is parallel to that of the emission, and coincides with one of the principal axes (z-axis in Fig. 1), we can write a reduced expression for the anisotropy ratio, $r(t)$:

$$r(t) = 0.3(\alpha+\beta)\exp[-(6D+2\Delta)t] + 0.3(\beta-\alpha)\exp[-(6D-2\Delta)t], \qquad (1)$$

with

$$\alpha = (D_x+D_y-2D_z)/3\Delta, \qquad \beta = 2/3,$$
$$\Delta = (D_x^2+D_y^2+D_z^2-D_xD_y-D_yD_z-D_zD_x)^{1/2},$$

and

$$D = (D_x+D_y+D_z)/3,$$

where D_x, D_y, and D_z are the rotational diffusion coefficients about the corresponding axes. These diffusion coefficients can be related to the molecular shape according to a hydrodynamic assumption. In general, with a sticking boundary condition the rotational diffusion coefficient D_r of a rigid body in a fluid medium obeys the expression

$$1/(6D_r) = \eta\zeta V/kT, \qquad (2)$$

where η is the viscosity of the medium, ζ the rotational friction coefficient, V the volume of the body, k the Boltzmann constant, and T the absolute temperature. In the case of a slipping boundary condition, it can be written as

$$1/(6D_r) = \eta\zeta V/kT + \rho_0, \qquad (3)$$

where ρ_0 is related to the inertia of the body (order of picoseconds). The rotational friction coefficient for a sphere (radius R) in a fluid medium with the sticking and the slipping boundary conditions are $8\pi\eta R^3$ and zero, respectively; those for a symmetric rotor could be calculated exactly with the sticking boundary condition,[6] and numerically with the slipping boundary condition.[7] If we approximate perylene by a symmetric rotor (an oblate spheroid) with an axial ratio, $r_x{:}r_y(=r_z)=3{:}11$, the ratio of the diffusion coefficients predicted by the above theory with the sticking boundary condition is $D_{/\!/}/D_\perp=0.816$, where $D_{/\!/}=D_x$, and $D_\perp=D_y=D_z$. In the case of the slipping boundary condition, the friction coefficient about the symmetric axis (x-axis) is zero; thus $D_{/\!/} \gg D_\perp$ is obtained. On the other hand, the friction coefficients for an asymmetric rotor with the slipping boundary condition have been obtained numerically by Youngren and Acrivos.[8] According to their results, the ratio of the friction coefficients is $\zeta_x{:}\zeta_y{:}\zeta_z=1{:}31{:}22$, for the ellipsoid with the axial ratio $r_x{:}r_y{:}r_z=1{:}3.2{:}3.8$, which is estimated by the van der Waals radii of perylene molecule. This is considered to be a more appropriate approximation than the oblate approximation for a perylene molecule. To our knowledge, the friction coefficients for an asymmetric rotor with the sticking boundary condition have not been calculated so far.

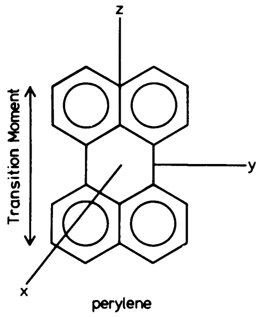

Fig. 1. Molecular fixed coordinate system for perylene.

Experimental

Perylene was dissolved in propylene glycol. The concentration of this solution was 10^{-5} mol dm^{-3}. The solution was degassed for measurement. A time-resolved fluorescence anisotropy measurement was performed using the nanosecond single-photon counting system in our laboratory.[9] The data counts were accumulated to 1.3×10^5 counts at the peak of the fluorescence intensity of the parallel component; this was sufficient for ascertaining good precision regarding the data. The data analysis was executed to fit a biexponential function,

$$r(t) = r_0[a_1 \exp(-t/\rho_1) + a_2 \exp(-t/\rho_2)], \tag{4}$$

to experimental points by the method of nonlinear least-squares fitting which involved a deconvolution procedure.[10] Then, we calculated the diffusion coefficient about each axis by Eq. 1 from the obtained values. Further, to test the oblate spheroid model, the ratio a_1/a_2 was fixed at 1/3 (postulated in this case). The same analysis procedure was executed to find $D_{/\!/}$ and $D_{\perp}$. All these data-analysis procedures were performed on a digital computer FACOM M-382.

Results and Discussion

The results are shown in Tables 1 and 2. As a criteria of the accuracy of the fitting, the reduced sums of the squares of the residuals χ^2 are also shown in Table 1. It can be seen that the ratio $D_{/\!/}/D_{\perp}$ for perylene agrees neither with the theoretical value for the sticking boundary condition ($D_{/\!/}/D_{\perp}=0.816$) nor with that for the slipping boundary condition ($D_{/\!/} \gg D_{\perp}$). Thus, it is considered that the real behavior of perylene is under an intermediate boundary condition between those two ideal boundary conditions. Judging from the values of χ^2, we can say that an approximation with an asymmetric rotor is more appropriate for perylene than that with an oblate spheroid, as might have been expected. This can be clearly seen in Figs. 2 and 3, as the residual plot of the former shows an apparent systematic deviation from the theory. However, as for the values of the diffusion coefficients, it is noticed that a significant discrepancy still exists between theory and experiment, even in the case of an asymmetric rotor approximation. The experimental result is D_x:D_y:D_z=728:1:179 (from Table 2), while the theoretical value (calculated from the ratio of friction coefficients with the slipping boundary condition given in the theoretical section) is 31:1:1.4, provided that the inertia limit ρ_0 is neglected. Thus, the ideal slipping boundary condition seems to be unsatisfactory for perylene; in other words, the 'partially slipping (or sticking)' boundary condition is preferable. In the time region of our experiment, the solvent may not be regarded as a mere continuous medium; also, the discrete chemical structure of the molecules becomes significant: such small-scale molecular motions should be interpreted by jump kinetics[1] rather than by the diffusion model.

Table 1. Best-Fit Parameters for Perylene in Propylene Glycol at 7 °C

Model	r_0	a_1/a_2	ρ_1/ns	ρ_2/ns	χ^2
Oblate	0.290	1/3	6.4	1.0	1.777
Asymmetric	0.303	0.560	4.6	0.74	0.963

Table 2. Diffusion Coefficients Obtained from the Best-Fit Parameters in Table 1

Model	$D_x\times10^{-7}$/s^{-1}	$D_y\times10^{-7}$/s^{-1}	$D_z\times10^{-7}$/s^{-1}	$D_{/\!/}/D_{\perp}$
Oblate	23.2	2.6		8.9
Asymmetric	31.3	0.043	7.7	

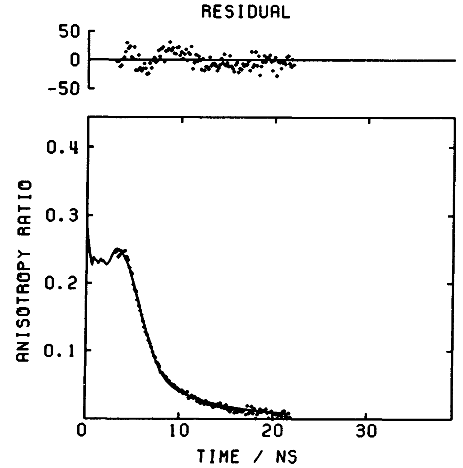

Fig. 2. Anisotropy decay for perylene in propylene glycol at 7 °C. Dots represent experimental data, and a solid curve indicates the theoretical decay convoluted with the best-fit parameters for the oblate model. The weighted residuals are also plotted in an arbitrary scale.

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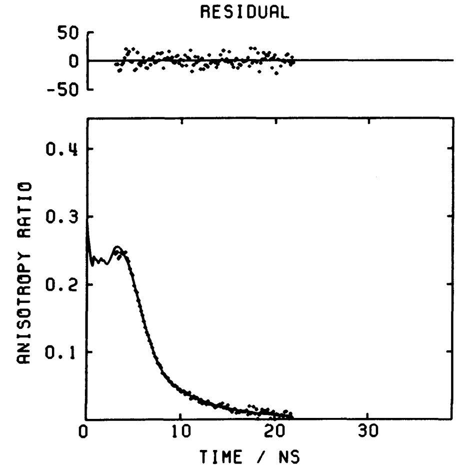

Fig. 3. Anisotropy decay for the sample of Fig. 2. A solid curve indicates the theoretical decay convoluted with the best-fit parameters for the asymmetric rotor model.

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