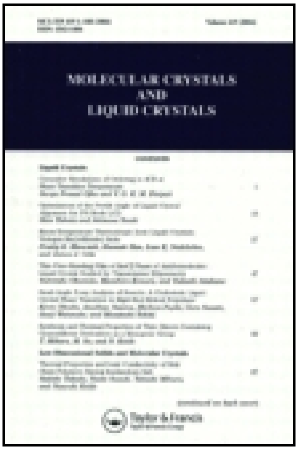

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Unified Theory of Time-Resolved Fluorescence Anisotropy and Stokes Shift of Excited Polar Molecules

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Unified Theory of Time-Resolved Fluorescence Anisotropy and Stokes Shift of Excited Polar Molecules

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Expressions for time-resolved fluorescence anisotropy and dynamic Stokes shift of solute molecules in polar medium were obtained on the basis of continuum model. Distribution function of rotational angles of solute molecules was obtained by solving a rotational analogue of generalized Smoluchowski equation into which a frequency-dependent diffusion coefficient of the rotational motion was introduced according to Nee and Zwanzig. By this distribution function which contained the effect of dielectric friction, expressions of the anisotropy decay and dynamic Stokes shift were derived. Numerical calculations of the both correlation function of the Stokes shift and anisotropy decay were made with common parameters for a model system.

Keywords: time-resolved fluorescence anisotropy; Stokes shift; continuum model; theory

INTRODUCTION

Numerous works have focused on the elucidation of solvent effect upon excited polar molecules, since the works on the Stokes shift of fluorescence spectrum by Lippert [1] and Mataga et al [2]. Recent advances in the time-resolved measurements technique have enabled us to reveal precise feature on the solvation dynamics of polar molecules in the picosecond and femtosecond time region. Theory of time-resolved Stokes shift was worked by several workers [3-4] on the basis of continuum model. A number of workers [5-8] have emphasized the importance of dielectric friction upon the solvation.

Although ultrafast inertial motions of polar solvent are important [5], it is also very important to observe rotational motion of solute for the study of excited state dynamics. The rotational motion of solute is observed by means of fluorescence anisotropy. Because the rotational motion contributes to the Stokes shift[3], we have given here unified treatment for the anisotropy decay and dynamics Stokes shift with the continuum model.

CONTINUUM MODEL

Molecular System

Molecular coordinate system is expressed with (xyz). z-axis was chosen to be along symmetric axis. It was assumed that dipole moment of the excited polar molecule, μ_e, is along z-axis of the spheroid molecule.

Direction of dipole moment in the ground state, μ_g, is arbitrary. Transition moments of absorption and emission are represented by $\mathbf{m}_a$ and $\mathbf{m}_e$, respectively.

Friction for Spheroid Molecule

Friction of solvent is represented as a sum of static friction, ζ_0, and dynamic friction, ζ_d. According to Nee and Zwanzig [6], the dynamic friction is related to the frequency-dependent dielectric constant as Eq. (1).

$$\zeta_d(\omega) = \left(\frac{1}{i\omega}\right) \mu_e^2 \, \frac{3A\,(1-A)\,\{1+(\varepsilon_c-1)\,A\}}{ab^2\{\varepsilon_0+(\varepsilon_c-\varepsilon_0)\,A\}} \, \frac{\varepsilon(\omega)-\varepsilon_0}{\varepsilon(\omega)\,(1-A)+\varepsilon_c A} \tag{1}$$

where ε_c and ε_0 are dielectric constant of the spheroid cavity and static dielectric constant of solvent. A represents an extent of deviation of the molecular shape from sphere and equal to 1/3 for spherical molecule[9]. The frequency-dependent dielectric constant is expressed with a few relaxation times [3].

ROTATIONAL MOTION OF SOLUTE MOLECULES

Diffusion Coefficients

Rotational diffusion coefficient is represented by a tensor with second rank. Among three components the diffusion coefficients around x- and y-axes are frequency-dependent, and one around z-axis is constant. Change in the electric field by the rotational motion of solute may modify motional mode of nearby solvent molecules. This could also modify the rotational motion of the excited dipole in turn. Accordingly, the rotational motion of solute molecule should be a non-Markov process. The rotational diffusion coefficient can be related to frequency-dependent friction by a generalized Einstein relation.

To proceed further we have assumed that the frequency-dependent dielectric constant of solvent is described with two relaxation times. This can be easily generalized to other solvent systems with more than two relaxation times.

Green Function for Rotational Motion of Solute Molecules

Green function for the rotational motion, G(Ω ' Ω t), is represented as a solution of generalized Smoluchowski equation [10] and given by Eq.(2).

$$G(\Omega'\Omega t) = \sum_{r=0}^{\infty} \sum_{s=-r}^{r} \sum_{s=-r}^{r} \Phi_{ss'}^{r*}(\Omega')\, \Phi_{ss'}^{r}(\Omega) \left(A_{rs}e^{-a_{rs}t} + B_{rs}e^{-b_{rs}t} + C_{rs}e^{-c_{rs}t}\right) \tag{2}$$

where $\Phi_{ss'}^{r}(\Omega)$ is an eigen function for rotational motion of spheroid solute. The coefficients, A_{rs}, B_{rs}, C_{rs} and rate constants, a_{rs}, b_{rs} and c_{rs} are obtained as solution of the generalized Smoluchowski equation.

TIME-RESOLVED FLUORESCENCE ANISOTROPY

The time-resolved anisotropy can be obtained by a method of spherical tensor with the Green function of Eq. (2), according to the method described elsewhere [11].

$$A(t) = \frac{2}{5} \sum_{s=-2}^{2} D_{0s}^{(2)*}(\Omega_e)\, D_{0s}^{(2)}(\Omega_a) \left(A_{2s}e^{-a_{2s}t} + B_{2s}e^{-b_{2s}t} + C_{2s}e^{-c_{2s}t}\right) \tag{3}$$

In Eq. (3) Ω_a and Ω_e denote polar coordinates of transition moments, $\mathbf{m}_a(\delta_a\, \varepsilon_a)$ and $\mathbf{m}_e(\delta_e\, \varepsilon_e)$ in molecular system. At t = 0, $A(0) = (1/5)(3\cos\theta - 1)$, which shows limiting polarization anisotropy. When $\varepsilon_0 = \varepsilon_\infty$ as in a non-polar solvent, Eq. (3) becomes the equation identical to one of normal polarization anisotropy of spheroid molecule [12].

DYNAMIC STOKES SHIFT

Energy shift upon solvation in the present system is represented as Eq .(4), according to Bagchi et al [3].

$$\left\langle \Delta E_e \right\rangle = -F\int_0^\infty d\tau \left\{ U e^{-u\tau} + V e^{-v} \right\} \left\langle \mu_e(t)\cdot \mu(t-\tau) \right\rangle \tag{4}$$

where the coefficients, F, U, V, and rate constants, u and v are expressed as function of dielectric constants and relaxation times etc. In Eq. (4) $\langle \mu_e(t)\cdot \mu(t-\tau)\rangle$ is a dipole correlation function and is obtained from Green function of Eq. (2) by means of the method of spherical tensor.

$$\left\langle \mu_e(t)\cdot \mu(t-\tau) \right\rangle = \sum_{s=-1}^{1} \frac{4\pi}{3} Y_{1s}(\omega_\mu) Y_{1s}^{*}(\omega'_\mu) \left(A_{1s} e^{-a_{1s}t} + B_{1s} e^{-b_{1s}t} + C_{1s} e^{-c_{1s}t} \right) \tag{5}$$

where the rate constants of a_{1s}, b_{1s} and c_{1s}, and the coefficients of A_{1s}, B_{1s} and C_{1s} are obtained from Eq .(2) with r = 1. $Y_{1s}(\omega_\mu)$ and $Y_{1s}(\omega'_\mu)$ denote spherical harmonics with rank = 1 and its complex conjugate. ω_μ and ω'_μ are directions of dipole moment expressed with polar coordinates in the molecular system at τ and $\tau = 0$, respectively. The dynamic Stokes shift was obtained from Eqs. (4) and (5) as before [3].

DISCUSSION

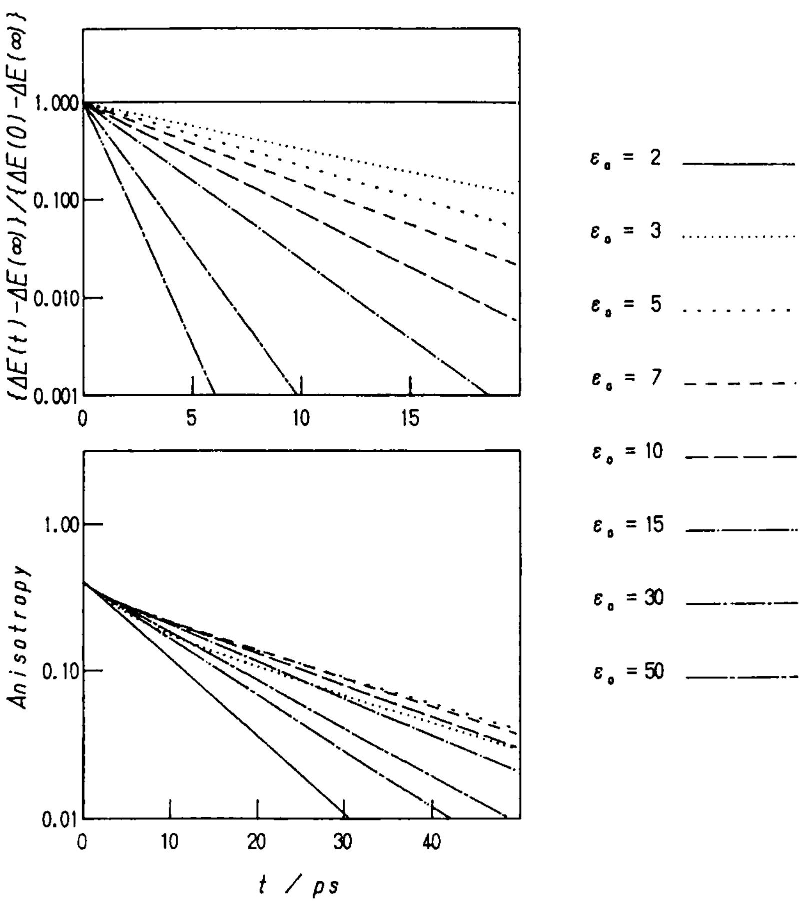

FIGURE 1 Dependence of Correlation Function and Anisotropy on Static Dielectric Constant with Single Relaxation Time Parameters used for the calculations are as follows : a = 1.0 (nm), b = 0.3 (nm), τ = 15 ps, optical dielectric constant ε_{∞} =2, dielectric constant of cavity ε_c = 10, μ_e = 20 (D), μ_g = 5 (D), D_0 = 20 (ns^{-1}) (stick model).

Fig. 1 shows dependence of a energy correlation function, C(t) = $\{\Delta E(t) - \Delta E(\infty)\}/\{\Delta E(0) - \Delta E(\infty)\}$, for time-resolved Stokes shift, and anisotropy on dielectric constant with single relaxation time. At parameters used for the calculation, C(t) seems to be single exponential. The anisotropy decayed with non-exponential functions.

In the present work the rotational dielectric friction is introduced into the both expressions of the time-resolved fluorescence anisotropy and dynamic Stokes shift in the framework of Nee and Zwanzig [6].

As we have seen in the numerical results for the model systems, we may obtain useful information on the solvation dynamics from the observation of anisotropy decay. Since Kivelson and Spears [13] emphasized the importance of dielectric friction on the anisotropy decay of aromatic ions, a number of works have examined the effects of dielectric friction on the anisotropy decays of dyes [14-16]. However, no one has reported on the theoretical equations of both time-dependent decays of anisotropy and energy shift with unique model including the dielectric friction.

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