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Relaxation of Inhomogeneous Spectral Band Width of Dye Molecules in Polar Solvents Studied by Time-Resolved Hole and Fluorescence Spectroscopy

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The comparative studies for time-resolved ground state hole spectra and time-resolved fluorescence spectra of dye molecules in polar solvents have been investigated. A marked difference has been shown clearly in the relaxation times between that are observed from the spectral band width, the solvent fluctuation around average energy, and that from the time resolved peak shift, the average of the solute−solvent interaction energy. The time correlation function of the solvent relaxation observed from the spectral band width was much slower than that from the time dependent peak shift in a fluid solvent at higher temperature, but they became comparable at lower temperature. Some possible mechanisms are discussed for understanding of the time dependences of the behavior. At room temperature, due to the relative preponderance of the rotational diffusion over the translational diffusion of solvent molecules, the energy relaxation takes precedence over the relaxation of the orientational distribution. It is emphasized that the relaxational mechanism presented here is applicable for both the time-resolved fluorescence and the ground state hole spectra.

1. Introduction

Solvation dynamics has been intensively investigated experimentally,[1−15] as well as theoretically,[16−26] in this decade because of its close tie to various chemical reactions in solution. The existence of the ultrafast relaxation processes such as phonon mode, inertial term, and libration of solvent, which largely contribute to the energy relaxation of the solute−solvent system at the early stage of solvation within several tens of femtoseconds, has been elucidated. More recent experiments with ultrashort laser equipments try to give detailed assignment for ingredients of the ultrafast processes. On the other hand, solvation dynamics must not be completely controlled only by the ultrafast relaxations. Slower processes with sub-picosecond up to picosecond time regions originated from diffusive and structural relaxation processes of the solvent molecules also play a key role particularly in alcoholic solvents[8−12] or in nonpolar solvents.[13−15] In contrast to deeper understanding of ultrafast processes, less information was known on how the slower structural processes contribute to the whole solvation mechanisms.

The studies on solvation dynamics in nanoseconds up to femtoseconds have been performed commonly based on the time dependent fluorescence Stokes shift measurements to obtain the time correlation function of solvent fluctuation for energy relaxation. Fluorescence decay curves were measured at several wavelengths by means of fluorescence up-conversion technique applied especially for femtosecond time region or a conventional single-photon-counting method for picoseconds to nanoseconds time region. Time-resolved fluorescence spectra were then reconstructed by using a set of the decay curves. This reconstruction procedure is considered to be adequate to pick out fluorescence maxima, because the spectral peak is a first moment of the reconstructed time-resolved spectra. However, difficulties must be somewhat unavoidable when one tries to reconstruct the entire spectrum based only on the set of the decay curves.

The time dependent spectral broadening governed by the orientational distribution of the solvent molecules also contains essential information on solvation processes. In the previous papers,[10,11] we reported picosecond transient hole-burning spectroscopy of rhodamine 640 in methanol/ethanol mixed solvent at 170 K and observed the recovery of the hole width created in the ground state. Just after the laser excitation, the hole spectrum is rather sharp, and it broadens with time reflecting the distribution relaxation in the ground state. At the same time, the spectral peak of the hole also shifts toward its corresponding peak position at the steady-state absorption. Kinoshita and Nishi[9] also measured time-resolved fluorescence spectra of laser dyes in sub-nanoseconds to nanoseconds time region by a single-photon-counting method at low temperature and reported that the time constants for the fluorescence peak shift and spectral broadening agreed with each other. However, our recent observation for the time-resolved hole-burning spectra of cresyl violet in polar solvents at room temperature showed that the time correlation function of the solvent relaxation expressed by the hole width was different from that expressed by the time dependent peak shift.[12] It remains unclear how the hole and fluorescence spectra behave in time scale at different temperatures.

It is useful for us to survey the theoretical backgrounds on spectral behaviors of the transient hole and fluorescence. For the sake of simplicity, the most essential results will be described based on the two-dimensional configuration coordinate in the continuum model given by Kinoshita[19]. Within his formulation, the two adiabatic potential surfaces for the ground state (ω_g) and the excited state (ω_e) are assumed to be parabolic curves with equal curvatures a and b, but with different energy minima:

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$$\omega_g(Q,q) = aQ^2 + bq^2 \tag{1}$$

$$\omega_e(Q,q) = a(Q - Q_0)^2 + b(q - q_0)^2 + \epsilon' \tag{2}$$

where Q and q indicate the coordinates that give slow and fast relaxations and Q_0 and q_0 are the positions of energy minima on their corresponding axes, respectively. Time evolutions of the population distribution in the excited state followed by the laser irradiation and that in the ground state including spectral depression are treated as stochastic relaxational processes upon the respective potential surfaces, driven by the fluctuation of the solvent molecules surrounding the solute.

The time-resolved hole-burning spectrum I_{THB} defined as the difference between the absorption spectra with and without excitation, and the time-resolved fluorescence spectrum I_{TRF} are given as

$$I_{THB}(\omega_1,\omega_2,t) \propto -\{[A] + [B] + [C]\} + [D] \tag{3}$$

$$I_{TRF}(\omega_1,\omega_2,t) \propto [C] \tag{4}$$

with

$$[A] = \int d\omega g(\omega)\pi^{-1}(\sigma^4 - \sigma_s^4\rho^2)^{-1/2} \exp[-\Delta\omega^2/\sigma^2] \exp[-\{\Delta\omega_2 - \sigma_s^2\rho\Delta\omega/\sigma^2\}^2/\{\sigma^2 - \sigma_s^4\rho^2/\sigma^2\}]$$

$$[B] = e^{-\gamma t} \int d\omega g(\omega)\pi^{-1}(\sigma^4 - \sigma_s^4\rho^2)^{-1/2} \exp[-\Delta\omega^2/\sigma^2] \exp[-\{\Delta\omega_2 + 2bq_0^2 + 2aQ_0^2(1 - \rho) - \sigma_s^2\rho\Delta\omega/\sigma^2\}^2/\{\sigma^2 - \sigma_s^4\rho^2/\sigma^2\}]$$

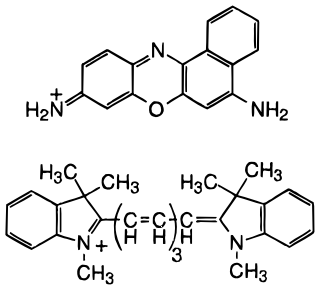
$$[C] = -\gamma \int_0^t d\tau \int d\omega g(\omega)\pi^{-1}(\sigma^4 - \sigma_s^4\rho^2)^{-1/2} \exp[-\Delta\omega^2/\sigma^2] \exp[-\{\Delta\omega_2 + 2aQ_0^2(\rho_1 - \rho) - \sigma_s^2\rho\Delta\omega/\sigma^2\}^2/\{\sigma^2 - \sigma_s^4\rho^2/\sigma^2\}]e^{-\gamma t}$$

where $g(\omega)$ is a normalized spectral function of the exciting light pulse centered at an angular frequency of ω_1. ω_2 is an angular frequency of the probe light. $\Delta\omega = \omega - \epsilon$, $\Delta\omega_2 = \omega_2 - \epsilon$, $\epsilon = \epsilon' + aQ_0^2 + bq_0^2$, $\sigma^2 \equiv \sigma_s^2 + \sigma_f^2$ with $\sigma_s^2 = 4aQ_0^2kT$ and $\sigma_f^2 = 4bq_0^2kT$, k the Boltzmann constant, and T temperature. γ is inverse of the fluorescence lifetime. $\rho \equiv \rho(t)$ is a normalized correlation function of the fluctuation of solvent molecules where the equal relaxation time is assumed for both the ground and excited states, and $\rho_1 \equiv \rho(t - \tau)$. In this expression, the term $[A]$ corresponds to the hole spectrum created in the population distribution in the ground state. The term $[B]$ expresses the induced fluorescence due to the photon field of the probe light. The population in the excited state decays to the ground state with the rate γ to fill the hole spectral shape through the term $[C]$. In addition, the absorption spectrum from the lowest excited state to the higher excited states ($S_n \leftarrow S_1$ spectrum) also contributes to the hole-burning spectra, through the term $[D]$. According to this theory, the time evolutions of I_{THB} and I_{TRF} are characterized by the time correlation function of solvent fluctuation $\rho(t)$.

In the present investigation, we should derive the normalized time correlation function $\rho(t)$ from observed transient hole and fluorescence spectra. The time correlation function of the energy relaxation of the system is evaluated by the following well-known equation,

$$\rho_e(t) = \frac{\tilde{\nu}(t) - \tilde{\nu}(\infty)}{\tilde{\nu}(0) - \tilde{\nu}(\infty)} \tag{5}$$

CHART 1. Molecular Structures of Cresyl Violet (Upper) and HITC (Lower)



where $\tilde{\nu}(0)$, $\tilde{\nu}(t)$, and $\tilde{\nu}(\infty)$ denote the peak energy of the hole or the fluorescence spectrum at $t = 0$, t, and ∞, respectively. On the other hand, the time correlation function for the spectral width comparable to $\rho_e(t)$ is not clear in general. Within the framework of the above theory, the fluorescence Stokes shift is explained with the continuum model as the dielectric dispersion of the surrounding medium and interaction of the solute dipole with the reaction field. The energy shift in the fluorescence spectrum is roughly proportional to the square of the difference of the dipole moments between the ground and excited states of the solute, while the spectral width is linearly related to the difference of the dipole moment under the assumption of the Debye−Onsager model. Then the time correlation function can be given by using the band width as

$$\rho_w(t) = \sqrt{\frac{\tilde{\sigma}(t)^2 - \tilde{\sigma}(\infty)^2}{\tilde{\sigma}(0)^2 - \tilde{\sigma}(\infty)^2}} \tag{6}$$

where $\tilde{\sigma}(t)$ is the spectral width of the hole or fluorescence at time t. Under the context of eqs 1−4 where the unique fluctuation of the solvent is assumed, the time correlation function given by eq 6 derived from the spectral width may just correspond to $\rho_e(t)$ expressed by eq 5.

In this paper we present comparative studies for the transient hole-burning and the time-resolved fluorescence spectroscopy of dye molecules in polar solvents in the time region of the solvent diffusive relaxation. Time dependent spectral broadening and peak shift both for the ground state hole and for the fluorescence spectra are analyzed, and consistency between the results obtained from two experimental methods is discussed.

Recent studies have predicted that in the case of polar solvation dynamics (a dipolar solute is dissolved in a polar solvent) relaxational processes are largely characterized by the solvent−solvent interaction rather than the solute−solvent interaction, except for a specific solute−solvent interaction like a hydrogen bond effect.[8] In the present work we thus employed cresyl violet as a solute molecule for the hole burning spectroscopy and 1,1′,3,3,3′,3′-hexamethylindotricarbocyanine (HITC) for the time-resolved fluorescence measurements, respectively, under the confidence that time evolutions of spectral changes should solely be arisen from the solvation dynamics. Molecular structures are given in Chart 1. Careful examinations on this point will be described in the Results section.

2. Experimental Section

For femtosecond transient hole-burning spectroscopy, the second harmonics of a mode locked Nd^{3+}:YAG laser (Quantronix, 82 MHz) was used as a pumping source. Output of a synchronously pumped dye laser equipped with rhodamine 6G and saturable absorber (DODCI/DQOCI) jets was amplified up to ca. 0.4 mJ/pulse at 606−609 nm by a dye amplifier excited

by a regenerative amplifier (Continuum) with 50 Hz. Transient hole-burning spectra were detected by a pump−probe optical arrangement. The amplified pulse was divided into two parts, and one part was focused into D_2O to generate white continuum and used as probe light. Another part was employed as an excitation source. Spectra were collected by a multichannel photodiode array detector attached to a spectrograph. Time and spectral resolutions of the system were about 150 fs and 3 nm, respectively. Group velocity dispersion arisen from the probe pulse was corrected for the obtained transient spectra.

Temperature dependence of time-resolved fluorescence spectra were detected as follows. Output of a mode locked Ti:sapphire laser pumped with an Argon ion laser (Spectra Physics, 82 MHz, 100 fs fwhm at 745 nm) was employed as an excitation source. The sample was excited under the magic angle conditions. The fluorescence photon flux passed through a spectrograph (Chromex 250IS) was measured with a synchroscaned streak camera controlled by a temporal analyzer (Hamamatsu C2909). Two dimensional streak images were detected by a CCD camera (Hamamatsu A3472), from which time evolutions of the fluorescence spectra were derived. Time and spectral resolutions of the system were determined as 16 ps and 1.5 nm, respectively. The sample solution was contained in a horn-type quartz cuvette to avoid the reflection from the cuvette.

Time-resolved fluorescence spectra were measured through 295 to 170 K. The measurements were carried out in a flow cryostat atmosphere. Temperature control was achieved by changing the flow rate of a nitrogen gas stream evaporated from liquid nitrogen.

For the transient hole burning spectroscopy, commercially available cresyl violet (Exciton) and spectrograde acetonitrile, methanol, ethanol, acetone, and tetrahydrofuran (THF) were used as received. The concentration of the sample solution was ca. 10^{-5} M. For the time-resolved fluorescence measurements, HITC (Nihon Kanko Shikiso) and ethanol were employed, and the concentration of the sample was about 10^{-6} M. The solution was deaerated by a nitrogen gas stream immediately before the measurements.

3. Results

3.1. Femtosecond Transient Hole-Burning Spectra of Cresyl Violet. The steady-state absorption and emission spectra of cresyl violet in the solvents investigated here show good mirror images. The Stokes shift in each solvent is 700−800 cm^{-1} and is comparatively small, which may imply that the potential surfaces of the ground and excited states could be describable as parabolic, and the difference of the dipole moment between the ground and excited states would be rather small. The laser excitation wavelengths were 606−609 nm, corresponding to 0−0 transition bands according to the reference.[27]

Transient hole-burning spectra of cresyl violet in ethanol observed at room temperature are shown in Figure 1. The spectra given in Figure 1 correspond to the summation of the terms [*A*], [*B*], and [*D*] in eq 3, where the term [*C*] can be negligible due to the long fluorescence lifetime of cresyl violet compared to the time domains of present interest. In order to evaluate time evolution of the hole spectrum due to the distribution relaxation of the surrounding solvent molecules, the term [*A*], we should first remove the contribution from the term [*D*], the $S_n \leftarrow S_1$ absorption spectra. The transient hole-burning spectrum detected at sufficiently long time after the excitation (at 40 ps in acetonitrile and 170 ps in alcohols, for example) was assumed to be that the solvation processes are completed and the spectrum is in the thermal equilibrium state. The

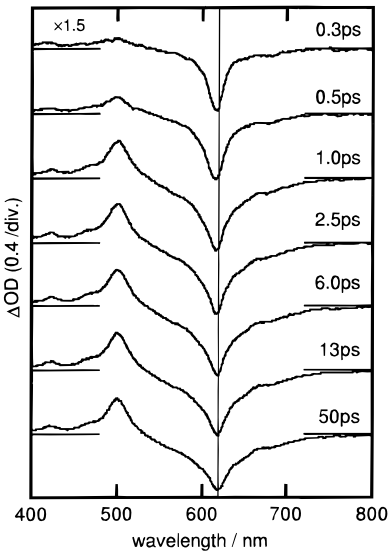


Figure 1. Transient hole-burning spectra of cresyl violet in ethanol excited at 609 nm detected at room temperature. Delay times after the excitation are given in the figure.

transient spectrum in the thermal equilibrium should be the sum spectrum of the steady state absorption and emission spectra and the $S_n \leftarrow S_1$ absorption band. Then, we obtained the $S_n \leftarrow S_1$ absorption spectra at the thermal equilibrium state. Next, the suitably weighted, but not shifted, $S_n \leftarrow S_1$ absorption spectrum was subtracted from the observed transient spectra to obtain the sum spectra of [*A*] and [*B*] at each delay time. We parenthetically note that the estimated $S_n \leftarrow S_1$ absorbance rises with the response function of the experimental setup and decays with the fluorescence lifetime of the solute since the excitation wavelength was chosen to be the 0−0 band. There were some experimental difficulties to measure the correct time resolved fluorescence spectra under the same time resolution as transient absorption measurements. We therefore adopted the half-width at half-maximum (hwhm) at the shorter wavelength region of the transient hole spectra as the hole width, although we inevitably neglected the smaller overlap of the marginal tail of the stimulated fluorescence spectra. The error arising from this approximation was proven to be less than 8%.

In Figure 1, the absorbance with maximum at 500 nm is largely ascribed to the $S_n \leftarrow S_1$ absorption spectrum. The ground state hole and induced emission are responsible for the negative spectra around 610 nm, where the contribution from the $S_n \leftarrow S_1$ absorption is small. As is obviously in Figure 1, the spectral widths of the hole spectra broaden with time.

In all the solvents, hwhm detected at immediately after the excitation already broadened up to 200−300 cm^{-1} within the instrumental response function. The hwhm of the fluorescence spectrum of cresyl violet observed in methanol/ethanol glass matrix at 77 K was also broadened to about 300 cm^{-1}. These results indicate the existence of ultrafast relaxation processes which correspond to the temperature independent modes.

Figure 2 shows normalized time correlation functions $\rho_w(t)$ determined from time evolution of the hole width according to eq 6. Here $\tilde{\sigma}(0) = 30$ cm^{-1} was adopted as the spectral width of the exciting laser pulse, and $\tilde{\sigma}(\infty) = 1300-1400$ cm^{-1} depending on the solvent. Relatively scattered plots of $\rho_w(t)$ obtained particularly in THF is ascribed to a low signal to noise ratio due to the smaller solubility of cresyl violet in a medium polar solvent THF, where the actual measurement was carried out by using the solution of an order of lower concentration (10^{-6} M) compared to other solutions. An error bar for the present $\rho_w(t)$ was estimated based on the spectral resolution of

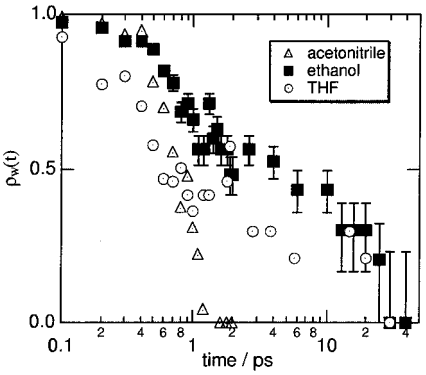


Figure 2. Normalized time correlation functions $\rho_w(t)$ obtained from time evolution of the hole width of cresyl violet in acetonitrile (triangles), ethanol (squares), and THF (circles). Error bars given were estimated according to the spectral resolution of the detecting system.

TABLE 1: Comparison of Mean Relaxation Times

solvent	$\langle\tau_w\rangle$/ps[a]	$\langle\tau_e\rangle$/ps[b]
acetonitrile	0.8	0.26
acetone	6.4	0.58
methanol	13	5.0

[a] Mean relaxation times obtained from the time evolution of the hole spectral width of cresyl violet. [b] Obtained from the time evolution of the fluorescence peak shift of coumarin 153. Taken from the reference 8b. See text.

the detecting system, as shown in Figure 2 in the case of $\rho_w(t)$ in ethanol as the typical example. Due to the definition of $\rho_w(t)$ as given in eq 6, the error bars are not symmetrically extended toward the upper and lower direction from each center of the plot of $\rho_w(t)$, and larger bars were estimated especially when $\rho_w(t) \rightarrow 0$. The $\rho_w(t)$ observed in each solvent decays much slower compared to $\rho_e(t)$ obtained from dynamic Stokes shift measurements reported in the literature. The correlation function $\rho_e(t)$ of LDS750 in acetonitrile[5,6] decays more than 80% in the first 200 fs and that of 1-aminonaphthalene in methanol[21] decays 60% in the first 500 fs. For the comparison of time scales, we also use the mean relaxation times $\langle\tau_w\rangle$ and $\langle\tau_e\rangle$ derived from $\rho_w(t)$ and $\rho_e(t)$, respectively,

$$\langle\tau_w\rangle = \int \rho_w(t)\, dt$$

$$\langle\tau_e\rangle = \int \rho_e(t)\, dt$$

Table 1 compares $\langle\tau_w\rangle$ detected from the hole spectral width with $\langle\tau_e\rangle$ from the time dependent fluorescence peak shift of coumarin 153 in the reference.[8b] In addition, the peak shifts of the hole observed in the present experiments were also much faster compared to spectral broadening. In methanol, ethanol, acetone, and THF, the apparent peak of the negative depression moves toward red within a few picoseconds reflecting the induced emission peak shift due to the excitation at near absorption peak, while hole spectral width broadens until tens of picosecond. As the results, the relaxation processes of the hole width at room temperature in all solvents investigated here are slower than those of the spectral peak shift.

3.2. Temperature Dependence of Time Resolved Fluorescence Spectra of HITC. A good mirror image between absorption and fluorescence spectra was also observed for HITC, and the amount of the Stokes shift is rather small (530 cm^{-1} in ethanol), although the molecule has three ethylene chains. The major part of the spectra can approximately be fit as Gaussian, except the spectral tails at shorter and longer wavelength regions for absorption and fluorescence, respectively. At lower temperatures the contribution from the fluorescence tail to the total spectrum decreases and the entire spectral shape is getting closer to Gaussian. One can thus assume that the difference of the dipole moment of HITC in ethanol between the ground and excited states is small and that the potential curves in the excited and ground states are parabolic, likewise in the case of cresyl violet.

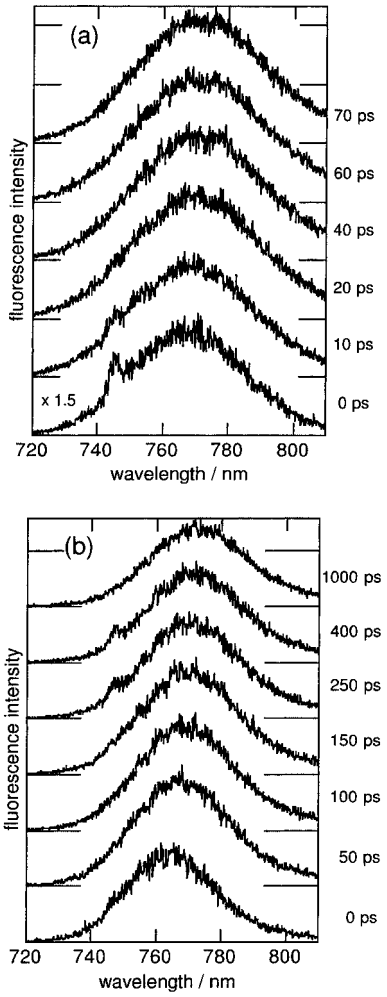


Figure 3. Time-resolved fluorescence spectra of HITC in ethanol excited at 745 nm detected at (a) 295 K and (b) 190 K. Delay times after the excitation are indicated beside the figure. The spectral shoulder in Figure 3a immediately after the excitation corresponds to the scattering light of the excitation pulse.

Figure 3 illustrates time-resolved fluorescence spectra of HITC in ethanol. At room temperature, the minor spectral peak shift and the spectral broadening were observed after the excitation, where the spectral time evolution completed within 60 ps and the spectrum finally reached the steady-state fluorescence spectrum. Spectral developments were more clearly observed at lower temperatures, for instance, as was observed at 190 K. Time dependence of the fluorescence intensity integrated over the entire emission band shows a single exponential decay at each temperature investigated here, where the fluorescence lifetime is 1.1 ns at room temperature and 1.2 ns at 170 K, for example.

On the basis of the time resolved fluorescence spectra, time dependences of the spectral peak $\tilde{\nu}(t)$ and the width $\tilde{\sigma}(t)$ are obtained. $\tilde{\sigma}(\infty)$ becomes monotonically narrower as temperature decreases, whereas $\tilde{\nu}(\infty)$ is rather independent of the temperature higher than the melting point of ethanol 159 K. In order to estimate $\tilde{\nu}(0)$ and $\tilde{\sigma}(0)$, time-resolved fluorescence spectra in the ethanol glass matrix at 77 K were also observed. Time

evolution of the spectra was not detected within the time resolution of the apparatus used, and we adopted $\tilde{\sigma}(0) = 450$ cm^{-1} and $\tilde{\nu}(0) = 13\,180$ cm^{-1} corresponding to the Stokes shift at 77 K of about 300 cm^{-1}, respectively. The excitation of the sample was made with the spectral width of the pulse about 50 cm^{-1} and the central wavenumber at 13 420 cm^{-1} that is close to the 0−0 transition near the absorption peak at 77 K of the solute. The ultrafast relaxations for both the energy and the spectral width exist in the glass matrix, as was observed in the case of cresyl violet. In the calculations of $\rho_e(t)$ and $\rho_w(t)$ we regard the fluorescence spectrum detected at 77 K as the origin of the solvation dynamics. In addition, the similarity of the time resolved spectra at each temperature and the single exponential decay of the fluorescence of HITC in ethanol as described above may justify our assumption that the time evolutions of the fluorescence spectra are free from some intramolecular isomerizations or specific interactions between solute and solvent molecules.

Figure 4 indicates the time correlation functions corresponding to the relaxation of the energy and the spectral width based on eqs. 5 and 6 at different temperatures. At 295 K, the time correlation function derived from the spectral width $\rho_w(t)$ decays much slower than that from the energy $\rho_e(t)$. When the temperature is reduced, $\rho_e(t)$ is getting closer to $\rho_w(t)$ and time constants becoming slower. The time correlation functions detected at 250 K must be critical, where $\rho_w(t)$ decays still slower than $\rho_e(t)$, but the difference is much diminished compared to those observed at higher temperatures. At 240 K or lower temperature to 170 K, however, the two time correlation functions correspond to each other. The agreement of the time dependence between peak shift and spectral broadening at low temperature was reported for hole[11] and fluorescence[9] spectra of rhodamine dyes in alcohols and for nonpolar solute in a nonpolar solvent.[14]

4. Discussion

In the previous papers[10,11] we have shown that the time dependences of the ground state hole shift and the hole broadening of rhodamine 640 were observed at same time scale in sub-nanoseconds to nanoseconds region in methanol/ethanol mixed solvent at 170 K. It is also reported that the time constant of the fluorescence dynamic Stokes shift agreed with that of the broadening of the fluorescence band width in nanosecond time region in the systems of laser dyes in the low-temperature viscous alcoholic solvent.[9] Therefore, the two-dimensional configuration coordinate model seems to work well in viscous alcoholic solvents at low temperature. In the fluid solvent at higher temperature, however, the situation seems to be different. At room temperature the relaxation time for spectral broadening that may be controlled by the solvent orientational distribution relaxation is much slower than that for energy stabilization as described in the previous section.

In the fluid solvents the fast and slow diffusive components are considered to be distributed in the same orders of magnitude in time scale, that is, the rotational relaxation times of the solvent molecule may distribute in tens of femtosecond (rotation of OH for example) to picoseconds (molecular rotation) and the translational motions may distribute in sub-picoseconds to tens of picoseconds. In the course of the energy relaxation, the fast rotational components in the first solvent shell stabilize largely the energy of the system as shown by the studies of molecular dynamics simulations. This fast stabilization of the energy and the ultrafast processes may bring about the disturbance of the solvent configuration which was distributed in the thermal equilibrium one before the abrupt excitation. Some slower rotational and translational motions (collective motion) surrounding the solute molecule follow the rapid motions to achieve the thermal equilibrium distribution in the excited state. After the abrupt change of the electronic state of the solute molecule, the system should relax toward the minimum of the free energy surface. We believe that the average energy of the system observed by the measurements of peak shift will be stabilized

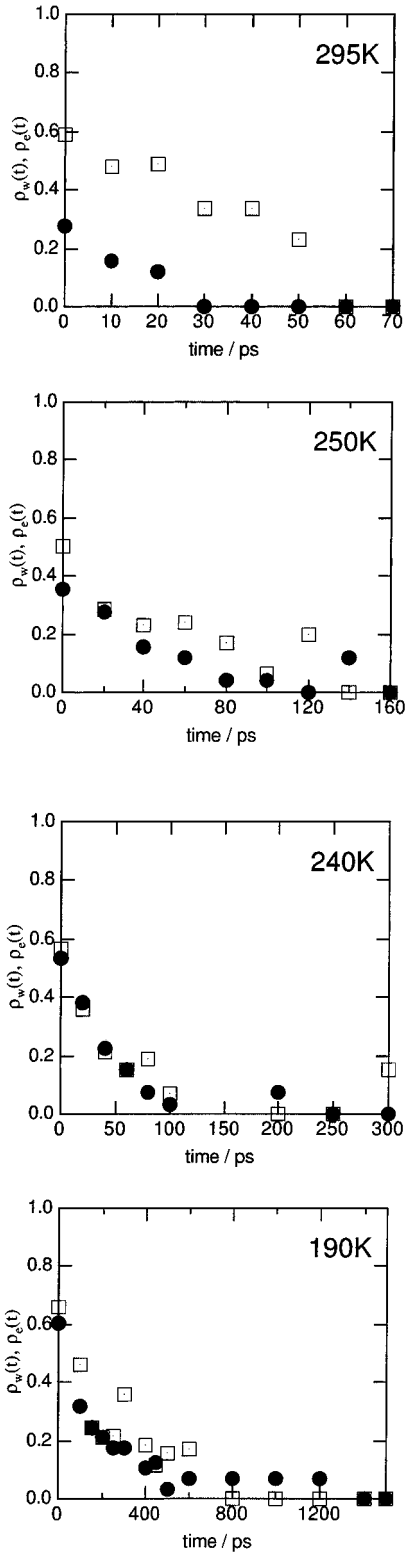


Figure 4. Temperature dependences of normalized time correlation functions obtained from time evolution of the fluorescence spectral width $\rho_w(t)$ (open squares) and the spectral peak shift $\rho_e(t)$ (filled circles) of HITC in ethanol. Temperatures at which the time correlation functions were observed are indicated in the figure.

at first by the rapid response of the solvents nearby the solute, while the free energy of the system controlling the total spectrum of the system will be stabilized by the total response of the solute−solvent interactions, and that the rapid response may minimize the destabilization of the average energy during the stabilization of the free energy including slower rotational or translational motions of solvents. Although the origin of the time dependences of the spectral width is not fully understood at present,[28] the entropy term in the free energy of the system including the solvent reorientational distribution may be considered to be a possible mechanism to broaden absorption and fluorescence spectra. Maroncelli simulated the solvation of monatomic ions in acetonitrile, where the slow component reflected larger amplitude motions involving the reorganization of the local environments and the spectral width depended mainly on the slow component.[20] Similar behavior was also observed by Carter and Hynes as a nonlinear aspect of solvation dynamics.[18]

In Figure 4, at 295 K, $\rho_e(t)$ and $\rho_w(t)$ relax 70% and 40% within the instrumental response function, respectively. At the lowest temperature investigated here, 170 K, about 20% of the total relaxations are the rapid components both for $\rho_e(t)$ and for $\rho_w(t)$. The results indicate that more than 50% of the rapid relaxation observed at room temperature originates from the diffusive components which should be temperature dependent and about 20% arises from ultrafast relaxation including intramolecular vibration, inertial term, and libration of surrounding molecules. Maroncelli et al. pointed out that the ultrafast components are less effective in the case of alcoholic solvents compared to aprotic polar solvents such as nitriles.[8] We hence conclude that the observed relaxation processes in ethanol are mainly ascribed to diffusive motions throughout the whole temperature region investigated here. For the transient hole-burning spectra the hole width broadened up to 200−300 cm^{-1} within the instrumental response function corresponding to its fluorescence spectral width detected at 77 K glass matrix. The contribution from the ultrafast broadening $\rho_w(t)$ is rather small even in acetonitrile. Taking into consideration the general similarity of the temperature dependent behavior of the peak shift and spectral broadening between the hole and fluorescence spectra, it may be plausible that the dynamics of the hole broadening at room temperature are also dominated by diffusive motions of surrounding polar solvent molecules.

It is also important to take into consideration the effect of the site dependent relaxation time. When a solute molecule of a larger size is dissolved into solvent molecules of a smaller size, the relaxation time around each atom of the solute molecule, which has the different charge density in general, may differ from atom to atom due to the different solvent response to the local charge. The solvation dynamics depending on the solute charge, as well as the type of solvent, was studied by computer simulations of molecular dynamics[21,22] and by the theory based on the site−site Smoluchowski−Vlasov equation.[24] The results show remarkable specificity depending on the solvent and the local charge especially in the picosecond time region.

We finally consider the mutual relation between the translational and rotational diffusion with respect to the solvation processes. van der Zwan and Hynes[17,29] predicted the concept on the polarization diffusion, i.e., how the translational diffusion of the solvent molecules contributes toward solvation dynamics. They presented a parameter p which gauges the relative domination of the translational mode against the rotational diffusion as

$$p = \frac{D\tau_D}{a^2} \tag{7}$$

where D is the translational self-diffusion constant of the solvent, τ_D the solvent dielectric relaxation time, and a the radius of the solute molecule. In the case of $p \gg 1$, the measure for the translational diffusion time of the solvent a^2/D is considered to overcome rotational diffusion with its approximate time constant τ_D.

Temperature dependence of the parameter p for the present system in the time resolved fluorescence spectra is given in Figure 5 with the dotted line. Here $a = 5.9$ Å for HITC was assumed. The Stokes−Einstein equation was employed to calculate D, and temperature dependence of τ_D was taken from the literature.[30] In the lower temperature region the lager value of p was obtained, implying that relative contribution from the translational diffusion mode is increasing according to the reduction of the temperature.

In order to emphasize the importance of the translational mode in the interpretation of the obtained experimental results within the context described above, we next introduce an index p_{exp} as follows:

$$p_{exp} = \frac{\langle\tau_e\rangle}{\langle\tau_w\rangle} = \frac{\int \rho_e(\tau)\mathrm{d}t}{\int \rho_w(\tau)\mathrm{d}t} \tag{8}$$

where $\langle\tau_e\rangle$ and $\langle\tau_w\rangle$ denote the mean relaxation times. Obtained values of p_{exp} are also plotted in Figure 5 with triangles. Near room temperature, p_{exp} becomes smaller, reflecting a much faster relaxation of $\rho_e(t)$ than $\rho_w(t)$, and gets close to unity at lower temperatures. On the basis of above discussion, we presume that the relaxation process of the spectral broadening should be essentially controlled by the distribution of the surrounding solvent molecules where the translational diffusion of the solvent is important, while the rotational diffusion in the solvent shell would be mostly responsible for the energy relaxation. At lower temperatures, contribution from the translational diffusion increases, and it enhances the relaxation of the spectral broadening. Eventually, the relaxation time of the spectral broadening catches up with that of energy. Since the polarization diffusion is probably less effective for the energy relaxation in aprotic solvents compared to that in alcohols, the discrepancy of the time scale between the hole broadening and the energy relaxation observed in the present work is more remarkable in aprotic solution compared to the cases of alcohols.

When the temperature is reduced, the experimentally obtained p_{exp} suddenly jumps near to unity, whereas such a jump is not predicted by the theory given in eq 7. Fried and Mukamel[31] studied theoretical correlation functions of the solvation energy and actually calculated them by varying the contribution from the translational diffusion $p' = D_T/2D_R\sigma^2$, where D_T and D_R are the translational and rotational diffusion constants, respectively, and σ is the diameter of the solvent molecule. According to their calculation, especially for Debye and Cole−Davidson solvents, a slight increase of p' affects the solvation dynamics dramatically, in particular, for the smaller value of p'. It is plausible that, even though the increase of p is moderate, the contribution from the translational diffusion to the spectral broadening in the solvation dynamics would be enhanced.

5. Conclusions

Transient hole-burning and time-resolved fluorescence spectra of laser dyes in polar solvents have been scrutinized for the elucidation of spectral and energy relaxations. At room

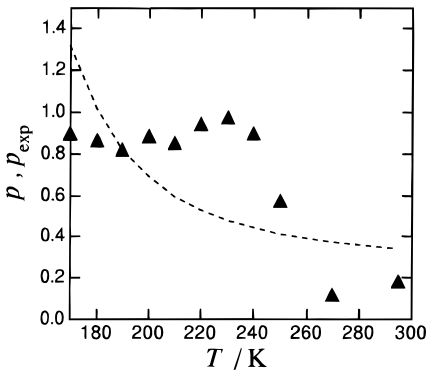


Figure 5. Comparison between the parameter $p = \tau_D/a^2$ which predicts contribution from the polarization diffusion (dotted line) and the relative ratio p_{exp} of the experimentally determined mean relaxation times of the energy $\langle\tau_e\rangle$ to those of the spectral width $\langle\tau_w\rangle$ derived from the time evolution of the fluorescence spectra of HITC in ethanol (triangles) as a function of temperature.

temperature, the time correlation functions for the relaxation of the spectral width decayed much slower compared to those for the energy relaxation, while at lower temperatures, their time correlation functions were corresponding to each other. The major part of the relaxational process of the energy of the system, and that of the spectral width (orientational distribution of solvent molecules) were assigned to be diffusive and temperature dependent processes of solvent molecules surrounding the solute molecule. The components of the diffusive processes are, however, different from each other: the energy relaxation is largely controlled by the rapid rotational diffusion of solvent molecules, whereas the slower, collective, translational diffusion is mainly responsible for the relaxation process of the spectral width. At room temperature, due to the relative preponderance of the rotational diffusion over the translational diffusion of solvent molecules, the energy relaxation takes precedence over the relaxation of the orientational distribution. It is emphasized that the relaxational mechanism presented here is applicable for both the time resolved fluorescence and the ground state hole spectra. A series of the time dependent fluorescence Stokes shift measurements using femtosecond technique reported elsewhere may indeed have brought about important information on solvation dynamics in terms of the energy relaxation. To our knowledge, however, the present experiment first reveals the difference of the two sorts of dynamics: the relaxation of the energy and that of the spectral band width.

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