Nanosecond timescale optical inhomogeneous broadening of dye molecules in liquids at and near room temperature

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Time-resolved fluorescence depolarization measurements of the S_0–S_1 electronic absorption band of rhodamine B in glycerol and propylene glycol have been made at different excitation wavelengths. It was found that electronic excitation transport between the rhodamine B chromophores is dispersive in glycerol at room temperature and in propylene glycol below 250 K. This demonstrates inhomogeneous broadening of the dye absorption spectrum which persists for the time scale of the fluorescence lifetime (nanoseconds) or longer. Measurements of time-resolved emission spectra at a number of different excitation wavelengths and temperatures support this conclusion and suggest that the chromophore-solvent microenvironments causing inhomogeneous broadening are the same as those responsible for the dynamic Stokes shift about an excited chromophore.

1. Introduction

The concepts of dynamical (homogeneous and spectral diffusion) broadening and inhomogenous broadening of an optical transition of a solute have been closely examined in recent years [1,2]. It is now accepted that there are many time scales governing solute–solvent interactions. The solvent fluctuation rates which influence a lineshape measurement depend on a time scale characteristic of the measurement. Those fluctuations which occur faster than or on the time scale of the optical measurement can cause dynamical broadening of a transition. Those which are static on the time scale of the measurement appear as inhomogeneous broadening. When the rates of fluctuations in the solvent change, or the time scale of the measurement is changed, the relative amounts of dynamical and inhomogeneous broadening change.

Over the past several years, electronic excitation transport has been studied both theoretically and experimentally. The field has developed to the point where quantitative information on the spatial distribution of chromophores in a host material can be obtained [3]. Many researchers have examined dispersive energy transport in solids at low temperatures (≈ 4.2), where the inhomogeneous broadening of an optical transition is considerably larger than the dynamical broadening by observing time evolving spectra [4–6]. Dispersive transport refers to electronic excitation transport in a system in which the rate and extent of excitation transfer is dependent upon the electronic excitation frequency. Dispersive excitation transport can occur when a distribution of solvent environments leads to a distribution of electronic transition energies in a solute. Solvent-induced energy differences cause the forward and back rates of transfer between a pair of molecules to differ though the molecules are otherwise identical. Recently measurements of dispersive energy transport in Langmuir–Blodgett films [7] and in polymeric glasses at higher temperatures, up to room temperature, were reported [8,9]. These results [8,9] indicated that dispersive transport can be observed in systems in which the inhomogeneous and dynamical linewidths are comparable, and that long-lived inhomogeneous broadening can occur in room temperature glasses.

Solvent relaxation, the time-dependent relaxation of solvent molecules about an excited chromophore, has been studied extensively by measuring time-resolved fluorescence [10–14] and recently by transient holeburning [15]. Typically the chromophores are assumed to have homogeneously broadened op-

tical transitions, and measurements are performed at one excitation wavelength. Recently, Levshin et al. [16] and Kinoshita et al. [12,13] measured dynamical broadening of fluorescence spectra in viscous liquids, which they attributed to rearrangements of a distribution of solvent shells around dye molecules. Kinoshita and Nishi [13] also reported that the fluorescence emission maximum had an excitation frequency dependence in a solution of rhodamine 6G in vitrified ethanol at 110 K. Their conclusion was that fast and slow processes were contributing to the measured Stokes shift of fluorescence. The fast process always occurred on a time scale faster than their time resolution, but the rate of the slow process could be altered by changing the temperature. A variety of relaxation time scales in this experiment, performed just below the glass transition temperature, is consistent with extensive optical nonlinear experimental studies of chromophores in low temperature ethanol glass [2]. However, long-lived inhomogeneous broadening in the liquid phase has not been addressed in detail.

Glycerol and propylene glycol are well known for their high viscosity at room temperature and their tendency to supercool rather than crystallize [17,18]. Hydrogen bonding networks give these liquids associative properties not found in simple liquids. In this publication we report the results of time-resolved fluorescence measurements of solute electronic excitation transport and solvent relaxation in liquid glycerol and propylene glycol at various excitation wavelengths. Both experiments demonstrate that the optical absorptions of the solute dye molecules are inhomogeneously broadened on the nanosecond time scale in glycerol at room temperature and below, and are inhomogeneously broadened in propylene glycol below 250 K. Inhomogeneous broadening is observed in the liquids ≈ 100 K above their glass transition temperatures. In addition, the experiments indicate that the distributions of solvent environments responsible for the inhomogeneous broadening are the same as those experienced during solvent relaxation about a solute molecule in an excited state.

Recent femtosecond photon echo experiments on similar systems at room temperature reported homogeneous dephasing times of ≈ 60 fs [19]. The experiments reported here show that there is spectral

evolution of chromophores on time scales which are more than five orders of magnitude slower than the fluctuations responsible for homogeneous dephasing. Spectral diffusion occurs much slower than homogeneous dephasing, and in fact, the spectra are still inhomogeneously broadened on the time scale of the fluorescence lifetime.

2. Experimental procedures

Solutions of various concentrations of rhodamine B (rhodamine 610 perchlorate, Exciton) used without further purification, in glycerol (Baker) or propylene glycol (Mallinckrodt) were prepared in an argon atmosphere. Rhodamine B is weak acid, and it was found that there was an ≈ 5 nm blue-shift for low concentration solutions with predominantly deprotonated chromophores relative to high concentration solutions. Therefore, all solution were acidified hydrochloric acid.

It has been found for similar dye molecules in solution that aggregation of the molecules leads to a change in the absorption spectra and a dramatic shortening of the fluorescence lifetime [20,21]. For this reason spectroscopic measurements and lifetime measurements were performed over a wide range of concentrations of rhodamine B in glycerol and propylene glycol. Absorption spectra of low concentration (10^{-5} M) and higher concentration (3×10^{-3} M) solutions were identical over a wide range of temperatures (150–298 K). The fluorescence lifetime was also unchanged for these concentrations, if care was taken to avoid reabsorption. Upon increasing the concentration even further ($\approx 2 \times 10^{-2}$ M), a distinctly different absorption spectrum was measured, and the fluorescence lifetime decreased dramatically, indicating aggregation at this concentration. All concentrations used in the measurements of energy transport and solvent relaxation reported here were 3×10^{-3} M or lower; at these concentrations there is no aggregation of the rhodamine B molecules.

Solutions $\approx 10^{-5}$ M in dye (low concentration samples) were used to measure r_0, the zero time value of the fluorescence anisotropy, the time-dependent rotational diffusion of the chromophore in the solvent at a given temperature, and the solvation dynamics of the excited dye molecules. Higher concen-

tration solutions ($\approx 10^{-3}$ M) were prepared to measure intermolecular excited state transport. The optical density of all samples was kept ≈ 0.1 or less to avoid reabsorption of fluorescence.

All fluorescence measurements were made by time-correlated single photon counting. The instrument [8,9] and technique [22] have been described in detail previously. However, for the fluorescence depolarization measurements the detection optics were modified. Since solvent relaxation about an excited chromophore occurs on the time scale of the fluorescence lifetime in these samples [23,24], the population decay from the S_1 excited state is complicated and non-exponential if detection is made over a narrow spectral region of the fluorescence. Therefore, a double, subtractive–dispersive monochromator was modified to pass a broad band of fluorescence (≈ 60 nm) and block only a narrow band (≈ 1 nm) around the laser excitation wavelength to avoid detecting scattered laser light. After this modification, the population decay could be fit well by a single-exponential function. The detection spectral response is nearly flat over the wavelength region of interest. For the time-resolved emission spectrum measurements, a 1 m monochromator with slit width set for 2 Å resolution was used to measure the fluorescence collected at the magic angle relative to the excitation polarization direction. The spectra are not corrected for the spectral response of the phototube and grating.

Time-dependent decay of the fluorescence anisotropy in low concentration solutions is due to rotational diffusion of the chromophore while in the excited state. Two mechanisms lead to time-dependent depolarization of the fluorescence in higher concentration samples, molecular rotation and excited state energy transfer. Excitation transport takes the excited state into an ensemble of acceptors with an essentially random distribution of transition dipole directions [25–27]. Fluorescence from the acceptor ensemble is depolarized. The anisotropy decays as the probability of the excitation being on the initially excited chromophore decreases [28]. Dividing the fluorescence anisotropy from the higher concentration sample by that of the lower concentration sample removes the contribution to the decay of the anisotropy because of molecular rotation [29], and gives $G^s(t)$, the anisotropy decay caused only by ex-

citation transport [28]. $G^s(t)$, the self-part of the Green function solution to the transport master equation, is quantity of fundamental interest in excitation transport [30]. This procedure has been discussed in detail previously [8,9,28].

3. Results

Fig. 1a shows the experimentally measured $G^s(t)$ for a 3.2 mM solution of rhodamine B in glycerol at 250 K. $G^s(t)$ is the probability that the excitation resides on the initially excited chromophore after a time t. The data was collected for three different excitation frequencies in the S_0–S_1 absorption. The S_0–S_1 absorption spectrum of rhodamine B in acidified glycerol solution at 250 K is shown in the inset to fig. 1a. The three different frequencies excited in the experiments presented here are indicated. These excitation frequencies were chosen near the peak or on the red side of the absorption line to minimize excitation into higher vibrational levels of the S_1 excited state. At the temperatures considered here some excitation from thermally populated vibrational levels in the ground state also occurs on the red side of the absorption.

It can be seen from the figure that as the excitation frequency is moved from the peak of the absorption to the red side of the line the extent of energy transport is decreased ($G^s(t)$ decays more slowly). Fig. 1b shows excitation transfer measurements for rhodamine B in glycerol at room temperature. There is a small but measurable dependence on the excitation frequency. We recently observed this effect [8,9] (dispersive transport), at elevated temperatures up to room temperature, in measurements of excitation transport among naphthyl chromophores in a polymer glass. Previously this effect had been measured in low temperature crystals and glasses using other experimental techniques [4–6], and in Langmuir-Blodgett films at room temperature [7]. Glycerol is a liquid at these temperatures (table 1). This is the first reported measurement of excitation-frequency-dependent electronic energy transfer in a liquid.

A similar series of measurements was made on a 2.5 mM solution of rhodamine B in acidified propylene glycol at room temperature and lower temperatures. The results of measurements at two dif-
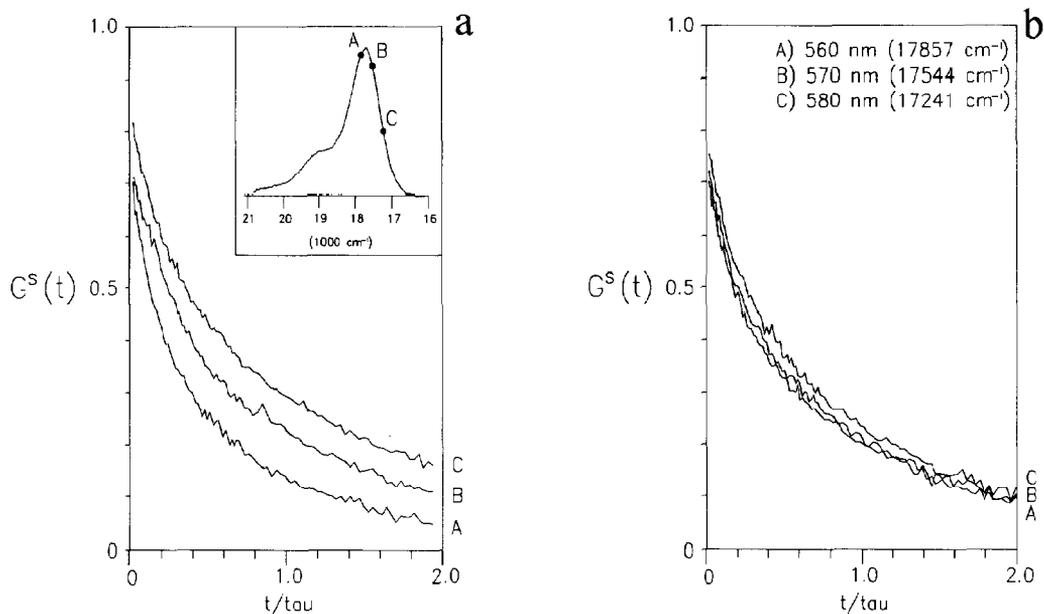
Fig. 1. (a) $G^s(t)$ for a 3.2 mM solution of rhodamine B in glycerol at 250 K. $G^s(t)$ is the probability that an initially excited chromophore is still excited after a time t (excited state lifetime excluded). The experiment was performed at three different excitation wavelengths: (A) 560 nm (17857 cm^{-1}), (B) 570 nm (17544 cm^{-1}), (C) 580 nm (17241 cm^{-1}). The wavelength dependence demonstrates that electronic excitation transport is dispersive in glycerol at this temperature. Tau is the excited state lifetime of RhB in glycerol, which was measured to be 3.5 ns at 250 K. (Inset.) Absorption spectrum of acidified rhodamine B/glycerol solution. The three excitation wavelengths used in this study are indicated. (b) $G^s(t)$ for the same solution as in (a), measured at room temperature. Although the differences with wavelength are small, they are outside experimental error (compare to fig. 2a). There is dispersive transport in glycerol at room temperature as well, indicating some inhomogeneous broadening of the electronic transition on the timescale of energy transport.

Table 1
Bulk properties of glycerol and propylene glycol

	T_g [a] (K)	η [b] (cP)	
		297 K	250 K
glycerol	193	850	250000
propylene glycol	172	40	2600

[a] Ref. [31].
[b] Data for glycerol and propylene glycol obtained from refs. [32,33], respectively.

ferent excitation frequencies, with the sample at room temperature, are shown in fig. 2a. The absorption spectrum of rhodamine B in acidified propylene glycol solution is blue-shifted by ≈ 4 nm relative to glycerol. Thus, the excitation wavelengths were shifted 4 nm from those used for glycerol measurements. In propylene glycol the decay of $G^s(t)$ is identical for excitation at the peak of the absorption

and for excitation on the red side of the line. There is no dispersive transport in propylene glycol at room temperature.

Fig. 2b shows the results of measuring $G^s(t)$ for the rhodamine B in propylene glycol solution at 250 K. $G^s(t)$ depends on the point of excitation in the S_0-S_1 absorption, though to a smaller extent than in glycerol at this same temperature (fig. 1a). Dispersive excitation transport appears in this liquid upon cooling to 250 K, which is still well above the glass transition temperature (≈ 170 K). From table 1 we see that the viscosity of propylene glycol increases dramatically upon cooling to 250 K, and becomes a more viscous liquid at this temperature than glycerol is at room temperature. Comparing figs. 1a and 2b shows that at the same temperature, the more viscous solution shows more dispersive transport.

Dispersive transport has been treated by a number of authors by considering the effect on excitation hopping when the electronic absorption has inho-
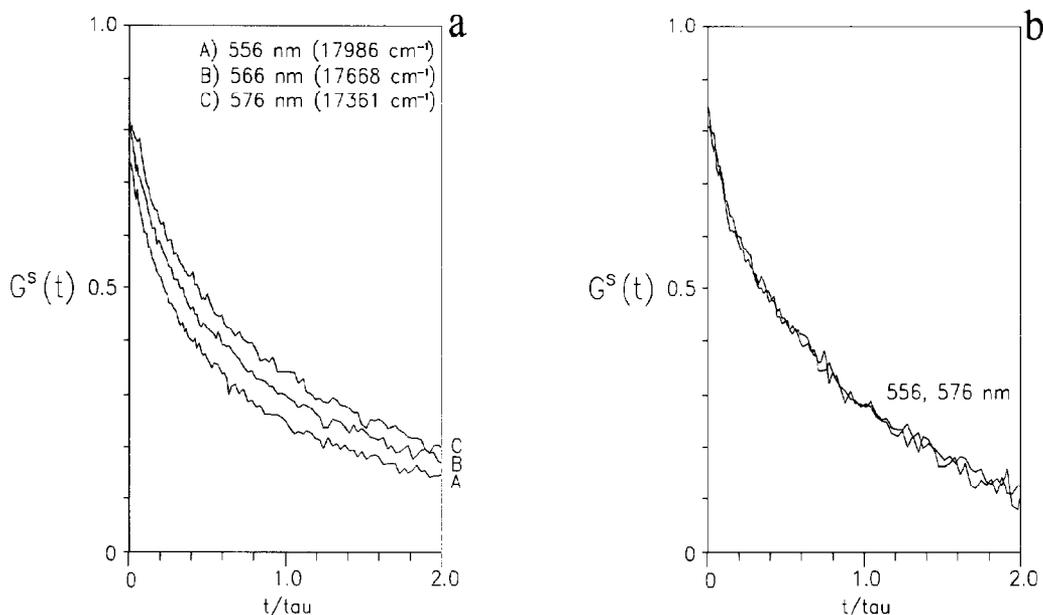
Fig. 2. (a) $G^s(t)$ for a 2.5 mM solution of rhodamine B in propylene glycol at room temperature for two excitation wavelengths, 556 nm (17986 cm^{-1}) and 576 nm (17361 cm^{-1}). At room temperature there is no wavelength dependence to the excitation transport in propylene glycol, i.e. transport is not dispersive. (b) $T=250$ K. The three excitation wavelengths are: (A) 556 nm (17986 cm^{-1}), (B) 566 nm (17668 cm^{-1}), and (C) 576 nm (17361 cm^{-1}). At this temperature the energy transport is dispersive though not to as large an extent as in glycerol at the same temperature.

mogeneous broadening that is similar [8,9] or greater than the dynamical broadening [4,34]. The picture that results is that after an excitation, initially in the higher frequency part of the absorption line, makes a series of hops, it is found in the states on the red edge of the absorption line. As the excitation moves to the red, the hopping frequency decreases due to a lower density of energetically accessible chromophores. The magnitude of the effect is dependent on the inhomogeneous and dynamical linewidths. If an excitation is started on the red side of the absorption there are fewer available transfer sites, and the excitation transfers more slowly than if the excitation is started to the blue.

Observing dispersive transport is complicated by two factors when the inhomogeneous broadening is similar to the dynamical line broadening. As discussed in ref. [9], narrow laser excitation leads to a broad, temperature-dependent distribution of initially excited states, depending on the extent of dynamical broadening. Furthermore, excitations into higher vibrational levels of the S_1 excited state (particularly for excitation wavelengths to the blue) and

excitations from thermally populated levels in the ground state (on the red side of the absorption) also lead to a broad distribution of initially excited states. While having no effect on the actual dispersive transport occurring in the system, both these effects tend to reduce the influence of dispersive transport on observables.

As can be seen from figs. 1 and 2, the data for chromophores dissolved in liquid glycerol and propylene glycol at 250 K, and liquid glycerol at 297 K display the characteristics of dispersive transport. This demonstrates that significant spectral inhomogeneity persists on the time scale of the energy transfer, which is 1 to 2 excited state lifetimes. Additional measurements we have made show that as the temperature is lowered towards the glass transition temperatures the effect of dispersive transport becomes larger, indicating that the dynamical broadening decreases and the absorption has relatively greater inhomogeneous broadening [35].

The fluorescence spectra of rhodamine B in glycerol and propylene glycol for different excitation frequencies were measured at a series of times after ex-

citation using time-correlated single photon counting. These measurements support the conclusion that inhomogeneity exists on the nanosecond time scale in glycerol at room temperature and in propylene glycol at 250 K, and persists for a time much longer than the fluorescence lifetime in glycerol at 250 K. A further observation from this work is that the dynamic Stokes shift, usually associated with solvent relaxation, appears to be intimately related to the inhomogeneous broadening in the solution.

Fig. 3a shows the fluorescence spectra measured 11 ns after excitation for a 10^{-5} M solution of rhodamine B in glycerol excited at 560 nm and at 580 nm. The sample temperature was 250 K, well above the glass transition region (see table 1). The fluorescence spectrum shows a shift with excitation
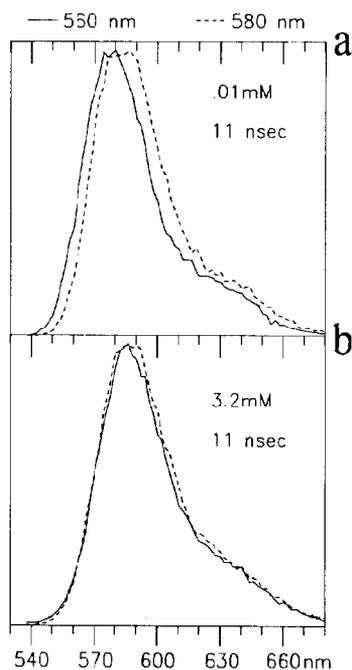
Fig. 3. (a) Fluorescence spectra 11 ns after excitation of a 0.01 mM solution of rhodamine B in glycerol at 250 K. Excitation was at 560 nm (17857 cm^{-1}) and 580 nm (17241 cm^{-1}). The difference in the fluorescence spectra indicates that after 11 ns the optical transition is still inhomogeneously broadened. (b) Fluorescence spectra 11 ns after excitation of a 3.2 mM solution of rhodamine B in glycerol. This sample has a high enough concentration to have a large amount of energy transfer (see fig. 1). This energy transfer takes the electronic excitation to the red side of the inhomogeneous distribution, and the emission is identical for excitation at the peak and on the red side of the absorption spectrum.

wavelength, similar to that reported previously in vitrified solutions [12,13,36]. At this temperature, with excitation at 560 nm, we measure a small shift in the fluorescence spectrum between 0 and 11 ns after excitation, but no shift is measured over this time scale for excitation at 580 nm. The solvent relaxation around the RhB S_1 excited state is much slower than the fluorescence lifetime (3.5 ns) and is different for different excitation wavelengths. The local environments around a guest chromophore in glycerol are inhomogeneous and nearly static on this time scale at 250 K.

When the concentration of chromophores is high enough the excitation transfers to chromophores absorbing on the red side of the absorption line. The fluorescence at long time originates predominantly from these molecules. Fig. 3b shows data for the 3.2 mM solution in glycerol at 250 K. Excitation at either 560 or 580 nm results in identical fluorescence spectra by 11 ns, although initially (<300 ps) the spectra look like fig. 3a. At low concentrations, the extent of solvent relaxation is limited, and the fluorescence spectra are distinct. At high concentration, transport moves the excitation through the inhomogeneous site distribution, resulting at long time in the same fluorescence spectrum regardless of the initial excitation wavelength. The observed spectral evolution is less pronounced, but the same in nature, as that seen in low temperature (4.2 K) crystals and glasses.

Fig. 4 shows the time-dependent fluorescence spectra for excitation at 560 and 580 nm for the low concentration (10^{-5} M) RhB/glycerol solution at room temperature. At room temperature solvent relaxation is occurring on the time scale of the fluorescence lifetime. The figure shows that solvent relaxation occurs to a different extent for excitation at 560 and 580 nm. Initially (<300 ps), the fluorescence from excitation at 560 nm is blue-shifted from that from excitation at 580 nm, similar to the long time behavior at 250 K (fig. 3a). This indicates inhomogeneity in the sample at room temperature. By 6 ns after excitation, the fluorescence following excitation at the two wavelengths is identical. Furthermore, we measure almost zero time-dependent Stokes shift for excitation at 580 nm compared to that for 560 nm.

The spectral evolution in the low concentration sample at room temperature due to solvent relaxa-
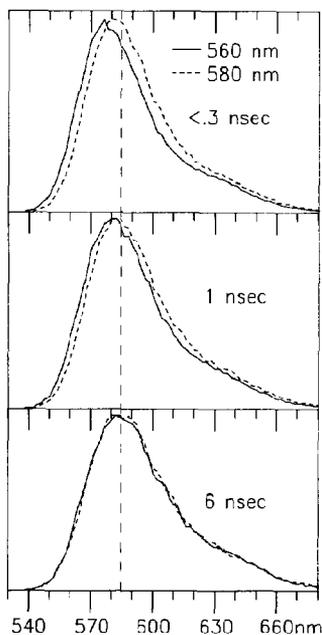
Fig. 4. Time-resolved fluorescence spectrum of 0.01 mM rhodamine B in glycerol at room temperature. This solution has no energy transfer. Initially, excitation at 560 nm leads to fluorescence which is blue-shifted compared to that for excitation at 580 nm. But, after 6 ns, the emission spectra are identical. The solvent-chromophore system has relaxed to the same state, independent of initial excitation wavelength, in contrast to fig. 3a. It is also clear from this figure that different amounts of Stokes shift have taken place for excitation at 560 and 580 nm.

tion is virtually identical to the evolution observed in the high concentration sample at 250 K. At low temperatures hopping between chromophores takes an excitation to the low energy edge of the S_0–S_1 transition. At higher temperatures solvent relaxation leads to states with the same lower energy transitions. From this we conclude that the inhomogeneity in these glycerol samples, responsible for the rhodamine B inhomogeneous broadening and dispersive transport, depends on the same distribution of solvent environments as those involved in the dynamic Stokes shift in the fluorescence at the higher temperatures. Similar results have been obtained for propylene glycol solutions.

Recently Bässler reanalyzed the temperature dependence of the viscosity of glass forming liquids by incorporating a random potential model, which previously was used to explain low temperature disper-

sive excitation hopping in glasses [37]. It was found that the temperature dependence of the frequency of small amplitude elementary steps in the inhomogeneously broadened solvent density of states is well correlated with the temperature dependence of the solvent viscosity. The conclusion was that the width of this density of states was the most important parameter determining T_g and the temperature dependence of the viscosity. If one identifies these elementary steps of solvent fluctuation with the steps leading to spectral diffusion and solvent relaxation, then the viscosity and width of the density of states of the solvent environment would be the key factors in determining whether a chromophore in a liquid is inhomogeneously broadened at a given temperature and time scale.

Recent measurements of photon echoes [19] and transient holeburning [38] of dye molecules in ethylene glycol indicate that homogeneous dephasing times (T_2) are on the order of 60 fs at room temperature. Another study, which analyzed absorption lineshapes and resonant light scattering, concluded that T_2 was 25 fs for azulene in isopentane and cyclohexane at room temperature [39]. Time-dependent spectral holeburning experiments, in which the hole width is found to depend on the amount of time between the burning and reading pulses, are explained by assuming that spectral diffusion, occurring with a rate faster than the time between the burning and reading pulses, broadens the hole, but processes occurring on a slower time scale appear static [40]. The experiments reported here demonstrate that although some electronic dephasing occurs on a tens of femtoseconds time scales, local solvent environments, which are coupled to and determine the transition frequency of a dye molecule, can persist for at least a few nanoseconds. This is five orders of magnitudes longer than the time scale for the fluctuations responsible for homogeneous dephasing in these liquids. The inhomogeneity causes measurements of electronic excitation transfer and solvent relaxation about an excited chromophore to show excitation frequency dependences. The results indicate that the inhomogeneous liquid structures are the same as those involved in the relaxation of the solvent–excited chromophore system to its lowest energy configuration.

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