

SOLUTE-SOLVENT DYNAMICS AND INTERACTIONS IN GLASSY MEDIA: PHOTON ECHO AND OPTICAL HOLE BURNING STUDIES OF CRESYL VIOLET IN ETHANOL GLASS

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Photon echo and non-photochemical hole burning experiments on cresyl violet in ethanol glass are reported. At 1.5 K the optical dephasing time measured by the picosecond echo is eight times longer than the time measured by hole burning because of the difference in the time scales associated with the measurements. The observed temperature dependence arises from the glass's two-level systems and from a pseudolocal phonon mode at higher temperatures. Comparing the ratios of the echo to hole burning dephasing times for cresyl violet and resorufin, suggests that their dephasing is influenced by the nature of their ethanol solvation shells in addition to the dynamics of the bulk ethanol.

1. Introduction

The motions of molecules and the influence of dynamics on internal molecular degrees of freedom fundamentally affect the properties of disordered systems such as glasses, liquids, and proteins. In this article we present the results of a study which provides insights into the dynamics and intermolecular interactions of a solute molecule, cresyl violet, in a glassy ethanol solvent. The results of two kinds of experiments, picosecond photon echoes [1] and non-photochemical optical hole burning [2], are compared. Both of these techniques provide measures of cresyl violet optical dephasing, i.e. the fluctuations in the electronic state energies induced by mechanical motions of the glassy solvent. Because these techniques operate on vastly different time scales (hundreds of picoseconds for the photon echo and hundreds of seconds for the hole burning) they are sensitive to distinct factors which contribute to optical dephasing [3-5]. Analysis of the data, particularly comparison of the echo and hole burning results, provides detailed information on motions of the glass and on the time-dependent interactions of the solute with its environment.

In a glass, as well as in other complex solids such as proteins [6] or complex crystals, dynamics in-

volving the mechanical degrees of freedom can occur on a very wide range of time scales, from subpicoseconds to seconds, or even days to years [7]. This is because an amorphous material has a large number of microscopic structural configurations. Interconversion among local structures occurs by tunneling through or activation over potential barriers which separate local potential minima associated with each structure. The extensive distribution of barrier heights and widths gives rise to a very broad distribution of rates of interconversion. Therefore, solute molecules in a glass, which are influenced by the structural changes because of intermolecular interactions, undergo time-dependent perturbations of their energy levels which range from very fast to exceedingly slow [8,9]. This is in contrast to a simple crystal in which there are no time-dependent structural changes, and all the perturbations are very fast time scale phonon-induced energy fluctuations [10-12].

Recently it has been proven experimentally and theoretically that the range of dynamical time scales inherent in a glass leads inevitably to a difference in the nature of the optical dephasing observable associated with the photon echo (short time scale) and hole burning (long time scale) experiments [3,4]. Cresyl violet is the second molecule to be studied both

with photon echo and hole burning experiments. The photon echo measurements of the optical dephasing yields a dephasing time which is a factor of eight longer than measured with hole burning. The echo is only sensitive to the fast fluctuations of the glassy structures. It measures what is generally referred to as the homogeneous dephasing time [3]. Because the hole burning experiment operates on a time scale which is 11 to 12 orders of magnitude longer than the echo, it is sensitive to very slow evolution of the glassy structure. This slow evolution also causes optical dephasing which is commonly called spectral diffusion. On the time scale of the echo, the slowly evolving structures appear as static inhomogeneity and do not contribute to the measured homogeneous dephasing time. In contrast the hole width is determined by the sum of the homogeneous dephasing and spectral diffusion contributions [3]. By combining both experiments in the appropriate manner it is possible to examine independently the fast and slow time scale evolution of the system. The temperature dependence of the photon echo decays and of the hole widths provides information on the influence of temperature on fast and slow structural evolution of the glass. This is similar in spirit to time-dependent heat capacity measurements in glasses [8,9] except that the optical dephasing measurements can operate over a much broader range of time scales and can examine the influence of structural evolution on a solute.

Previously, resorufin in ethanol glass was studied [3,13]. Like cresyl violet, resorufin also displays a large difference between the optical dephasing times measured with echo and hole burning experiments. Utilization of both the echo and hole burning data for these two molecular ions provides a unique method for comparing the dynamics experienced by distinct species in the same medium. If the hole burning data alone [14] or echo data alone are compared for two molecules, differences can be ascribed to unequal coupling strengths of the solutes to the environment. Berg et al. have shown, however, that by forming the ratio of the hole burning measured dephasing time to the echo measured dephasing time, the coupling strength cancels [3]. The ratio of the dephasing times is thus independent of coupling strength and strictly measures the system's dynamics.

In the simplest picture, the ratio of the dephasing

times, R_d , for two molecules in the same medium would be identical since the dynamics of the medium might be assumed to be unaffected by the solute molecule. Cresyl violet and resorufin, however, have R_d values of 8 and 6 respectively. While the two ions have similar structures, cresyl violet is positively charged and resorufin is negatively charged. The data suggest that the solvent should be considered as two distinct media; bulk ethanol glass with a relaxation rate distribution which is unaffected by the dissolved ions, and ethanol in the solvation shells [15] about the ions with a relaxation rate distribution which is determined by the nature of the ionic species.

2. Experimental methods

Cresyl violet 670 perchlorate (Exciton) and resorufin (Aldrich) were used without further purification. Samples of approximately 2×10^{-4} M were prepared under argon with ethanol-*d* (Aldrich) degassed with argon. (Ethanol-*d* indicates ethanol with only the hydroxyl hydrogen replaced by deuterium.) We chose ethanol-*d* because resorufin/ethanol-*d* and cresyl violet/ethanol-*d* hole burn much more slowly than these chromophores in ethanol-*h* [16,17]. Using the ethanol-*d* glass does not affect the results of either the hole burning or echo optical dephasing measurements [3]. As described previously [13], slow hole burning simplifies the collection of the echo data. Typical burn fluences at low temperatures were $1 \mu\text{W}/\text{cm}^2$ for ethanol-*h* and $10 \mu\text{W}/\text{cm}^2$ for ethanol-*d*.

Detailed descriptions and schematics of the laser systems used to perform these experiments have been published previously [13]. The echo experiments were performed with an amplified sync pumped dye laser having a time resolution of 4 ps and a bandwidth of 3 Å. The pulses are attenuated to approximately 20 nJ/pulse with a spot size of 150 μm to eliminate optical density effects which vanish in the low power and very small flip angle limit [18]. A study of the echo decays versus power demonstrated that the decays were power independent. The hole burning of the sample during the echo measurement is quantitatively corrected for in the manner detailed previously [13]. This involves measuring the echo

signal with fixed pulse separation as a function of time. As the sample undergoes hole burning, the echo intensity is reduced. These "burning curves" are recorded at each temperature and used to normalize the echo decay curves, eliminating the effect of hole burning from the echo decays. The echo data are taken at 615 and 616 nm, well to the red of the low temperature absorption maximum of cresyl violet/ethanol-*d*, 610 nm. This avoids unwanted excitation of vibronic bands.

The holes are burned and detected in transmission at 615 nm with a frequency-stabilized dye laser (Coherent CR-599-21, 1.5 MHz jitter). The normal 30 GHz sweep of the 599-21 is extended to 80 GHz by computer controlling a thin etalon in the laser stabilization loop. This allows detection of holes at higher temperatures where hole widths become very broad.

The lifetime of cresyl violet/ethanol-*d* was measured using a Hamamatsu R1645U-01 microchannel plate and a Tektronix 7912 transient digitizer. The lifetime (T_1) is 5.5 ns at room temperature and at 50 K.

Experimental temperatures (1.2 to 8.5 K) are maintained to 0.05 K. Separate tests showed there is no difference between the temperatures measured with a resistance thermometer actually inside the glass sample and those measured by the GRT in good thermal contact with the surface of the cuvette [19]. Ethanol can form two phases depending on the rate of cooling [20]. Great care was taken to ensure rapid quenching (≈ 100 K/min) of the samples by plunging them into liquid helium. The echo and hole burning data are taken on identically cooled samples of cresyl violet and resorufin in the glassy phase of ethanol-*d* (phase I).

3. Results and discussion

Fig. 1a shows a photon echo decay of cresyl violet taken at 1.48 K. Like the data previously reported for resorufin [3,13], the decay is a single exponential as are the decays measured at all temperatures. Theoretical analysis shows that for the decay to be exponential, the distribution of TLS relaxation rates, $P(R)$, must go as $1/R$ for rates R occurring in the range of rates on the order of the inverse of the time

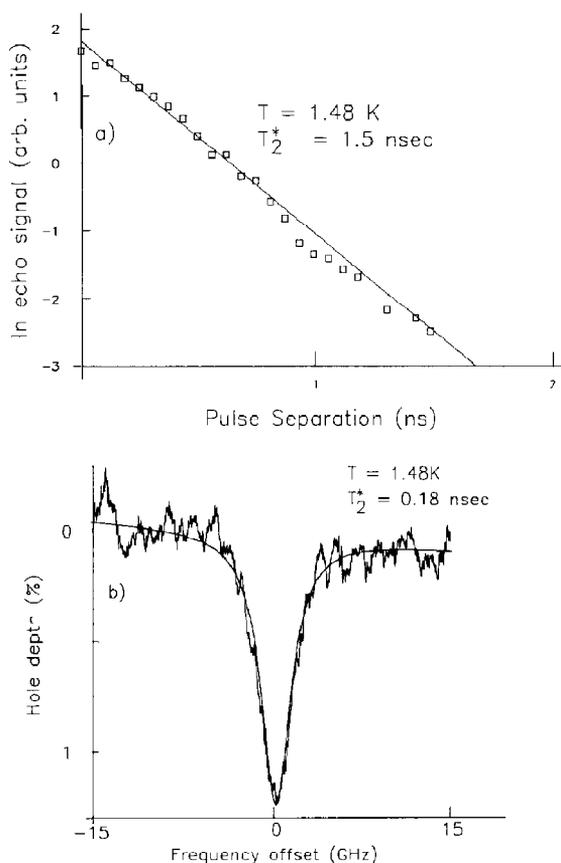


Fig. 1. (a) Photon echo decay from cresyl violet/ethanol-*d* at 1.48 K. Decay is exponential over five factors of e and gives a T_2^{*PE} (optical dephasing time) of 1.5 ns. Exponential decays are caused by dipole-dipole couplings between chromophore and glass TLS and implies a particular e form of the distribution of TLS relaxation rates (see text). (b) Lorentzian hole burned in cresyl violet/ethanol-*d* at 1.48 K (with fit to a Lorentzian accounting for a sloping baseline). T_2^{*HB} is 0.18 ns which is a factor of eight broader than that measured by the photon echo. Because of the long time scale of the hole burning experiment, the hole is sensitive to slow diffusion in addition to the homogeneous dephasing as measured by the echo.

scale covered by the experiment [3]. Furthermore, the coupling of the chromophore to the glassy two-level systems (TLS) must be dipolar [3,5]. In this case, the probability of having a rate, $P(R)$, goes as $1/R$ for rates which are the inverse of a few picoseconds to a few nanoseconds. Thus the functional form of the echo decay establishes the nature of the system dynamics on the fast time scale.

When exciting with fast pulses with bandwidths of

approximately 9 cm^{-1} in the inhomogeneously broadened dye/glass absorption spectrum, it is possible for phonon sideband absorption to contribute to the photon echo signal. This would cause a non-exponential decay consisting of a fast component from the broad phonon side band and a slower component from the zero-phonon line [21]. This type of decay has been observed in systems with strong linear excitation-phonon coupling [21]. We see no evidence of a fast decay in the photon echo data collected in these experiments. This is because of weak linear coupling in the experimental systems, and because any signal from the small amount of phonon sideband absorption will decay very rapidly and be hidden under the $\approx 4 \text{ ps}$ instrument response time. A related effect can be produced by decay processes that occur if molecular vibrations of the organic chromophores are excited. Effects from these 100 cm^{-1} or higher energy modes are eliminated by exciting on the low energy side of the dye absorption band. To avoid any possible contributions from phonon or vibrational states to the "burning curve" normalization [13] of the echo decays, the "burning curves" are recorded with a pulse delay of $> 10 \text{ ps}$, which is well after any ultrafast processes are over.

The echo pure dephasing time, T_2^{*PE} (lifetime contribution removed, $1/T_2^{*PE} = 1/T_2 - 1/2T_1$), determined from the echo decay in fig. 1a is 1.45 ns . (T_2 is four times the echo decay time.) Fig. 1b shows a hole also measured at 1.48 K . As has been previously observed in many systems [14], all holes are Lorentzian. This again requires a dipolar interaction between the chromophore and the TLS but does not give information on $P(R)$ [3]. The hole burning pure dephasing time, T_2^{*HB} , is 0.19 ns ($1/T_2^{*HB} = \pi \text{ hwhm} - 1/2T_1$). T_2^{*PE} is a factor of 8 longer than T_2^{*HB} . The temperature dependences of the pure dephasing times obtained from the echo and hole burning experiments are shown in fig. 2 on a log-log plot. First consider the echo data. On a log-log plot a power law temperature dependence would appear as a straight line. The echo data clearly deviate from a power law as the temperature is increased. The echo data are well fit to a model proposed by Jackson and Silbey [22], i.e. a combination of a power law and an exponentially activated processes:

$$1/T_2^{*PE} = aT^\alpha + be^{-\Delta E/kT}, \quad (1)$$

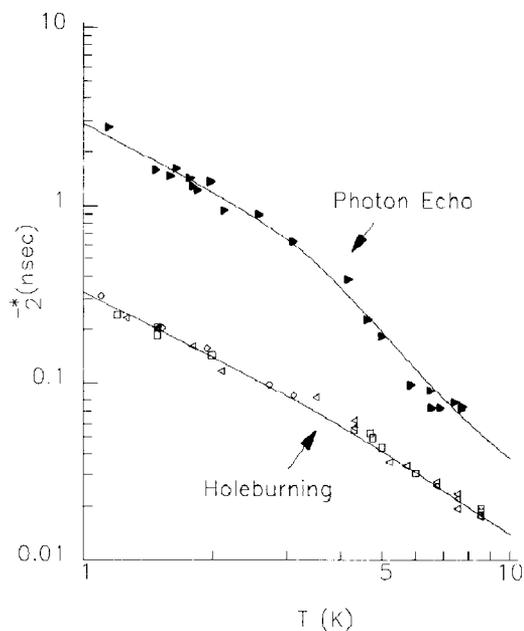


Fig. 2. Log-log plot of temperature-dependent dephasing times, T_2^* , measured by hole burning and photon echoes. The T_2^{*PE} are a factor of eight longer than the T_2^{*HB} at low temperature. At higher temperatures there is a deviation from the $T^{1.2}$ power law because of an exponentially activated pseudolocal mode. The effect of the pseudolocal mode is more prominent in the echo temperature dependence because of the lack of broadening by spectral diffusion. Solid lines are best fits to eq. (2) (photon echo) and eq. (3) (hole burning). (Δ) Holes burnt in cresyl violet/ethanol-*d* (this work); (\square) holes burnt in cresyl violet/ethanol-*h* (this work); and (\diamond) holes burnt in cresyl violet/ethanol-*h* by Völker [14]. (\blacktriangle) Echo decays in cresyl violet/ethanol-*d*.

This model also worked well for the resorufin data [3]. The power law arises from the structural changes of the glass which are described in terms of the TLS [23,24]. The simplest distributions of TLS potential well asymmetries and tunneling parameters, in which the distributions are constant, gives a term linear in T [22,24]. These distributions also yield a linear in T contribution to the heat capacities of glasses [25,26]. More complex distributions result in larger values for α [24]. The exponential term arises from a pseudolocal mode [22], e.g. a librational motion of the chromophore. The pure dephasing of chromophores in mixed molecular crystals is totally dominated by pseudolocal mode dephasing [11,27-29]. Typical frequencies found in crystals for a variety of chromophores are 10 to 30 cm^{-1} . In fig. 2, the best fit to the echo data uses the parameters where

$\alpha=0.35$ (ns K $^\alpha$) $^{-1}$, $\alpha=1.2$, $b=160$ ns $^{-1}$, and $\Delta E=14.1$ cm $^{-1}$.

Fig. 2 also displays the hole burning data for cresyl violet. The five diamond data points were reported earlier by Völker for cresyl violet in ethanol-*h*. The squares are data from this study in ethanol-*h* and the triangles are data taken on ethanol-*d*. As with resorufin, there is no difference in optical dephasing upon deuteration of the hydroxyl hydrogen. Also, in the common temperature range, the current data agree with those of Völker. The hole width determined dephasing time is faster than the echo dephasing time because of the difference in the time scale of the experiments [3]. Hole burning, which takes place on the 100 s time scale, is sensitive to very slow spectral diffusion processes which do not contribute to the echo decay. Spectral diffusion broadens the hole, and therefore yields a faster dephasing time. The hole dephasing time temperature dependence should include the terms in eq. (1) and an additional term which accounts for the temperature dependence of the spectral diffusion [3,30]. This is given by

$$1/T_2^{*HB} = aT^\alpha + be^{-\Delta E/kT} + cT^\beta. \quad (2)$$

The fit to the hole burning data used the parameters from the echo calculation and the additional spectral diffusion parameters $c=2.8$ (ns K $^\beta$) $^{-1}$, $\beta=1.2$.

Subtracting eq. (1) from eq. (2) shows that the temperature dependence of the spectral diffusion can be obtained by subtracting the echo data from the hole burning data [30]. The spectral diffusion optical dephasing time, T_{SD} , is displayed in fig. 3 for both cresyl violet and resorufin. These data give the temperature dependence of the slow time scale dephasing.

The rate of chromophore-glass dephasing depends, in part, on the coupling between the electronic states of the chromophore and the glassy medium. Therefore, in comparing echo data or hole burning data from two different chromophores in the same glass, differences might be simply due to differences in coupling strengths, not differences in dynamics. A recent theory developed by Berg et al. [3] and extended by Bai and Fayer [30] demonstrates that the ratio of the hole burning and echo dephasing times is a more accurate indicator of the underlying glass dynamics. The ratio provides a parameter which is independent of the dipole-dipole coupling re-

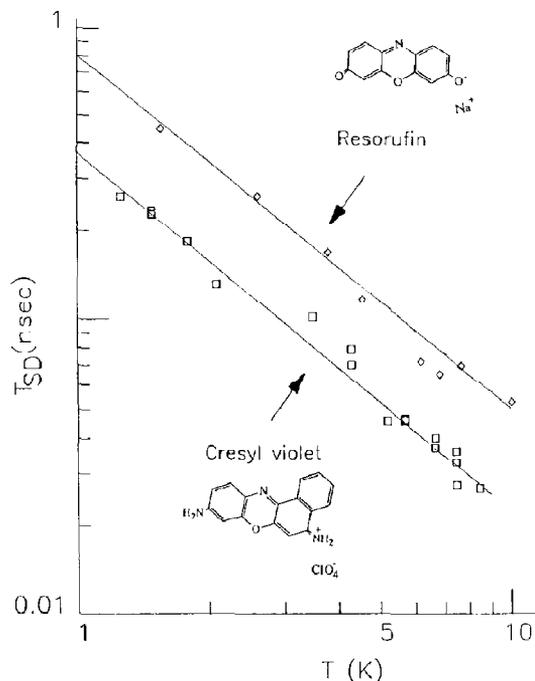


Fig. 3. Log-log plot of the temperature dependence of the contribution of slow time scale relaxations in the glass (spectral diffusion) to the dephasing. Data are shown for both cresyl violet/ethanol-*d* (this work) and resorufin/ethanol-*d* [3,28]. Both sets of data follow the same power law, $T^{1.2}$.

sponsible for TLS-induced dephasing. The ratio is related to the integral of all rates of dynamical processes from the echo time scale to the hole burning time scale. A common approximation is to assume a $1/R$ distribution of rates, R [31-33]. (If a distribution of rates, $P(R)$, equal to $1/R$ is plotted as $P(R) dR$ versus $\ln R$, the result is a constant, see fig. 4.) The observation of exponential decays justifies this approximation for times of the order of T_2 , i.e. picoseconds to several nanoseconds. This topic is discussed in detail in refs. [3,31]. Using a result which relates T_2^{*PE}/T_2^{*HB} to T_2 and a waiting time, T_w [31],

$$R_d = T_2^{*PE}/T_2^{*HB} = [\Theta + \ln(2T_w/T_2)]/\Theta. \quad (3)$$

T_w measures the time scale on which a particular type of dephasing experiment is sensitive to spectral diffusion. For echoes, T_w is zero, and therefore the echo is only sensitive to homogeneous dephasing (fast fluctuations). For hole burning T_w is the time interval from burning through reading the hole, i.e. the

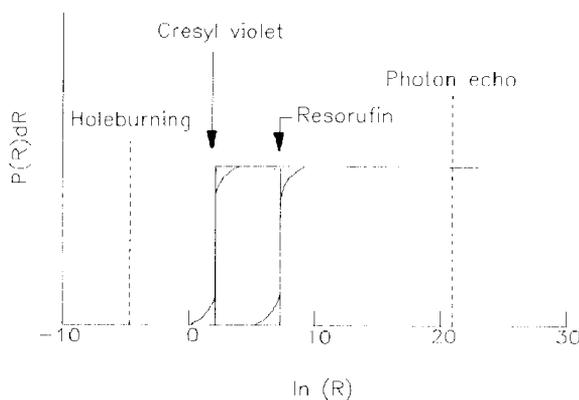


Fig. 4. Plot of the distribution of relaxation rates $P(R) dR$ versus $\ln R$. A horizontal line represents a distribution of rates which goes as $1/R$ for all relaxation rates R . The echo is sensitive to all dynamics in a range about the dashed line ($\ln(1/1 \text{ ps})$ to $\ln(1/2 \text{ ns})$). Hole burning is sensitive to all dephasing rates which occur from very short times to the time required to complete the hole burning experiment ($\ln(1/100 \text{ s})$). Also indicated are suggested positions of the cutoffs in the rate distributions as determined by the parameter R_d (ratio of hole dephasing rate to echo dephasing rate, see text) for cresyl violet and resorufin in ethanol- d .

time required to do the hole burning experiment. If there is a slowest dynamical rate in the glass, $1/T_w$ becomes a measure of where the cutoff or fall off of $P(R)$ occurs (see fig. 4). The Θ parameter depends on the nature of the TLS dynamics. A reasonable description employs an uncorrelated sudden-jump model [34]. Using this model, Θ is 2.63 [31]. Suppose that the distribution of rates is $1/R$ for all R (a continuous horizontal line in fig. 4). Then, for $T_2 = 10^{-9} \text{ s}$ and $T_w = 100 \text{ s}$, the R_d predicted by the model is 10.9.

The observed R_d for cresyl violet in ethanol- d at 1.57 K is 8.0 ± 0.2 . This is substantially less than the 10.9 calculated for a $1/R$ distribution which extends past $1/100 \text{ s}$ where 100 s is the burning time scale. Using eq. (3) one can see that the observed R_d implies a cutoff of the rate distribution at approximately $1/100 \text{ ms}$ (see fig. 4). The low temperature hole burning echo experiments were repeated for resorufin in ethanol- d . The measured R_d is 6.0 ± 0.2 . This implies a cutoff in the rate distribution at approximately $1/1 \text{ ms}$ (see fig. 4).

Examining the R_d of a molecule in a glass yields a parameter which does not depend on coupling strength [3]. It is therefore a measure of the system's

dynamics. Then, in the simplest view, one might expect the R_d 's of two molecules in the same glass to be identical. The fact that the R_d 's for cresyl violet and resorufin both in ethanol- d are substantially different, well outside of experimental error, demonstrates that the dynamics of the two systems differ.

A possible explanation for the difference involves the solvation shells [35] surrounding the two ions. The idea that the R_d 's should be the same assumes that the chromophores interact with bulk glassy ethanol which is unmodified by the presence of the ions. A more realistic view recognizes that a solvation shell exists around an ion and that the structure of the solvation shell, and presumably its dynamics are distinct from the bulk glass. The dipole interaction responsible for dephasing is long range. Therefore a chromophore will interact with both its solvation shell and with bulk material. The interactions between the ionic chromophores and the ethanol permanent dipole moments are strong. The solvation shells could be effectively electrostatically frozen. This would push the distribution of rates in the solvation shells toward slower rates.

Cresyl violet is positively charged while resorufin is a negative ion. This will cause marked differences in the way solvent dipoles are arranged around the ions [35]. Fig. 4 is a plot of $P(R) dR$ versus $\ln R$. The positions of the cutoffs determined with eq. (3) are shown for resorufin and cresyl violet. (Note that the characteristic timescale of the hole burning experiment is well beyond these times.) If there is a cutoff in the rate distribution for bulk ethanol at a faster rate than those obtained for the cresyl violet and resorufin in ethanol systems, then the electrostatic interactions in the solvation shell will push the cutoffs to slower rates. Since the solvation shell structures and therefore the dynamics in the solvation shells are different for the two types of ions, the cutoffs for the ion-glass systems can occur at different rates. This leads to differing R_d values. Thus, in this model, the difference in the R_d values for cresyl violet and resorufin is a measure of the difference in solvation shell dynamics in the two solute-solvent systems.

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