

Bercaw,^{62b} aptly fits. Future exploration includes range of H-H distances, η^1 -H₂ binding (a Pt- η^1 -I₂ complex has been found⁶³), and polyhydrogen ligands (H₃⁺ or H₃⁻). Evidence for the latter and related interactions resembling the four-center transition state in the above scheme has already begun to appear as of this writ-

ing.^{44b,64}

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Time-Resolved Studies of Solvation in Polar Media

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1. Introduction

Interest in the molecular motions associated with chemical reactions in solution has prompted an effort to understand the dynamics of solvation. The effect of macroscopic solvent parameters (i.e., viscosity, polarity) on chemical dynamics has been extensively studied for many decades.¹ Correlations between rate constants and such solvent variables have been reported.²⁻⁴ These studies indicate that to some extent, solvent effects on chemical reactions can be accounted for by the changes the solvent induces in the potential energy barrier and free energy of reaction.

However, for reactions in which the rates are comparable to or faster than solvent fluctuations, the details of the motion and structure of the surrounding solvent can play a deterministic role in the rates of chemical reaction. In order to understand these phenomena, major issues must be addressed: (a) how are the intermolecular forces and molecular motions of solvent perturbed by the chemically reacting system and (b) how do solvent fluctuations couple to the reactive potential energy surface.

In recent years, these issues have received more theoretical⁵⁻¹² than experimental¹³⁻¹⁵ attention. Advances in statistical mechanics have resulted in new treatments for equilibrium solvation which take into account molecular details of the solvent.^{16,17} For non-equilibrium phenomena, the subject of this Account, the solvent is generally modeled as a dielectric continuum.^{18,19} In this treatment the solvent is modeled as a structureless fluid with a frequency-dependent dielectric constant, $\epsilon(\omega)$. Usually $\epsilon(\omega)$ is expressed in the Debye form (eq 1):

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau_D} \quad (1)$$

In eq 1, ϵ_{∞} and ϵ_0 are the high-frequency and zero-frequency dielectric constants, respectively; τ_D is the Debye relaxation time. Dielectric dispersion experiments

on simple liquids (i.e., DMSO²⁰ show that $\epsilon(\omega)$ is well described by eq 1. In contrast, most solvents have more complex dielectric response than given in eq 1. In the case of the normal alcohols, $\epsilon(\omega)$ is generally expressed in terms of multiple regions of Debye-like behavior.^{21,22}

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_{10} - \epsilon_{1\infty}}{1 + i\omega\tau_{D1}} + \frac{\epsilon_{20} - \epsilon_{2\infty}}{1 + i\omega\tau_{D2}} + \frac{\epsilon_{30} - \epsilon_{3\infty}}{1 + i\omega\tau_{D3}} \quad (2)$$

The Debye relaxation times are commonly associated with the following molecular motions:²¹ hydrogen-bonding dynamics in molecular aggregates (τ_{D1}), monomer rotation (τ_{D2}), and rotation of the terminal C-OH group (τ_{D3}). In addition to τ_D , a second relaxation time, the longitudinal relaxation time, or constant charge relaxation time, τ_L , is commonly invoked to gauge dynamical solvent effects. The functional form for τ_L varies slightly depending on the nature of the perturbation and the value used for ϵ_{∞} (n^2 or $\epsilon_{1\infty}$;^{15,25} for the case of a point charge, τ_L is related to τ_D by $\tau_L = (\epsilon_{\infty}/\epsilon_0)$

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τ_D ,^{18,23-27} In polar solvents $\epsilon_0 \gg \epsilon_\infty$ and thus $\tau_L \ll \tau_D$. There have been several recent discussions of the importance of τ_L as a gauge of solvent dynamics. In particular, Kosower and co-workers¹⁵ have reported that the intramolecular charge-transfer rates of several molecules are well correlated with τ_L^{-1} . These results suggest that solvent motions can play a dominant role in determining chemical reaction rates.

Central to all these studies is the desire to understand the dynamic interaction between a solute (chemically active species) and the surrounding solvent. In this Account, we will focus on the present understanding of solvation dynamics in polar solvents. We will examine how studies on electron solvation, molecular rotation, and time-dependent measurements of the evolution of the fluorescence spectrum of a solvated molecule have provided insight into the molecular details of solvation. Our goal is to emphasize how the interplay between picosecond/subpicosecond studies and theoretical advances (computer simulations and analytic developments) have dramatically increased our overall understanding of solvation dynamics on the molecular level.

2. Electrons in Polar Liquids: Mechanism of Solvation

The solvation of electrons in polar fluids has been examined by several research groups, and review articles have recently appeared.²⁹⁻³³ Injection of an electron into a polar media provides an instantaneous perturbation to the liquid. By monitoring the absorption spectrum of this species, the relaxation of the surrounding structure to solvate the charge can be studied.

In both water and alcohol solvents, the experimental data suggest that the solvation process can be described by a two-state model.³²⁻³⁷ At short times, an absorption band in the IR is observed. This band decays and an analogous band grows in the visible. This absorption band is structureless and asymmetric around the maximum with a high-frequency tail. The IR absorption is assigned to the localization of the electron in a preexisting solvent trap. The visible absorption band is characteristic of the electron in equilibrium solvation. No evidence for a time-dependent shift in the absorption spectra reflecting a continuous relaxation process of the surrounding solvent (compare section 4) has been reported.

Recently, Migus et al.³⁷ examined the solvation dynamics of electrons in water using femtosecond absorption spectroscopy. The time-dependent spectra

indicated that the electron thermalizes and reaches a localized trap within 110 fs. This species decays with a lifetime of 240 fs, giving rise to the spectrum of an electron in equilibrium solvation. Once again, no spectral shifts are observed. Thus, similar to the studies in alcohols, these results support solvation occurring by localization followed by structural rearrangement, and the dynamics are well described by a two-state model.

A microscopic picture of the solvation process relies on the theoretical understanding of the effects of solvent structure and dynamics on the spectroscopy of the solvated electron. Feynman path integral simulation techniques have been used by the groups of Berne,³⁸ Klein,³⁹ and Rossky,^{40,41} to examine the equilibrium structure of the solvated electron in water^{38,41} and ammonia.³⁹ These studies show that there is not a sharp shell structure of the solvent around the electron. Recently, Rossky and co-workers extended this technique, coupling path integral techniques to direct calculation of the electronic eigenfunction to evaluate the optical absorption properties of the solvated electron in water. The calculated spectrum qualitatively reproduces both the band shape and high-energy tail found in the experimental spectrum but is shifted to higher energy.⁴¹ These studies are the first to provide a detailed picture of the nature of the electronic transitions monitored by the spectroscopic studies. Extensions of quantum simulations⁴² to look at solvation dynamics of the electron will provide valuable insight into the molecular motions responsible for the experimentally observed spectral changes.

The structure of the solvated electron has also received considerable attention by Robinson and co-workers where threshold ionization is used to inject the electron into water.⁴³ The data suggest that rearrangement of water molecules to accommodate the charge is important in determining the rate of ionization. Further rearrangement of the solvent around the electron is necessary after the charge is transferred. In contrast to the solvated electron structure obtained from the path integral simulations, Robinson and co-workers conclude that the equilibrium state of the hydrated electron may be a hydrated semi-ionic pair ($\text{OH}^- \cdots \text{H}_3\text{O}^+$)(aq).⁴⁴

3. Rotational Diffusion: Evidence of Dielectric Friction

Experimental measurements on rotational diffusion in liquids have been extensively used to probe the interactions between solute and solvent molecules.⁴⁵⁻⁵²

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The rotational motion for many molecules in solution is well described by treating the surrounding solvent as a continuous hydrodynamic fluid. If the solute is assumed to be spherical, Stokes-Einstein-Debye theory predicts that rotational correlation functions of order l decay exponentially, with a time constant given by

$$\tau_r^{(l)} = \frac{6\pi\eta a}{k_B T l(l+1)} (fC) \quad (3)$$

where $\tau_r^{(l)}$ is the rotational relaxation time, η is the viscosity of the solvent, a is the radius of the spherical rotator, T is the temperature, k_B is Boltzmann's constant, and l is the order of the orientational correlation function.

The shape factor, f , takes into account deviations from spherical shape for a solute molecule and has been tabulated by Perrin⁵³ and Tao⁵⁴ for a series of ellipsoids. If the solute has an ellipsoidal shape, the correlation function decays as a sum of at most three exponential terms. However, when the interaction dipole is oriented parallel to the symmetry axis of the molecule, a single-exponential decay results.⁵⁵

The factor C is used to take into account the hydrodynamic boundary condition at the surface of the solute; two extreme conditions, stick and slip, have been discussed in detail. For the stick case, the tangential velocity of the fluid relative to the solute vanishes on the surface of the solute and C is unity. In the slip limit, the tangential component of the normal stress on the surface of the rotator is zero. For spheroids, the values for C have been tabulated by Hu and Zwanzig.⁵⁶

If the solute molecule has a nonzero dipole moment, there are forces in addition to viscosity that can affect the reorientational time. Classically, when a dipole embedded in a dielectric continuum changes its orientation, it produces a time-varying field outside of its own volume.^{57,58} If the response of the medium is not instantaneous, its polarization change lags behind the movement of the dipole. The net effect is the creation of an electric field in the cavity which exerts a torque opposing the reorientation of the dipole. The motional energy of the dipole can be dissipated if there is dielectric loss in the surrounding medium and has the effect of increasing the rotational relaxation time. At a molecular level, this energy dissipation results from reorientation of the surrounding solvent molecules. This dielectric friction has been the subject of several theoretical investigations^{57,59,60} and results in an additive correction to the rotational correlation time.

$$\tau_r^{(l)} = \frac{6\pi\eta a}{k_B T l(l+1)} (fC) + \frac{\zeta_{DF}}{l(l+1)k_B T} \quad (4)$$

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The dielectric friction constant, ζ_{DF} , is given by

$$\zeta_{DF} = \frac{6\mu^2}{a^3} \frac{\epsilon_0 - 1}{(2\epsilon_0 + 1)^2} \tau_D \quad (5)$$

where ϵ_0 is the zero-frequency dielectric constant, a is the cavity radius of the dipole, τ_D is the Debye relaxation time of the solvent, and μ is the dipole moment. It has proven to be difficult to determine experimentally when this effect is important in describing the motions of molecules in solution.^{50,61-63}

Dielectric friction effects are included by a function that depends both on static (ϵ_0), the zero-frequency dielectric constant) and dynamic (τ_D) properties of solvent. In recent papers, Kenney-Wallace and co-workers have reported large deviations from hydrodynamic behavior for several dye molecules in alcohol/water mixtures.⁶² By applying dielectric friction theory, a qualitative agreement is observed. In a pressure-dependent study comparing the rotational dynamics of *p*-terphenyl and rhodamine-6G, Philips et al. reported that the differences between the behavior of the two molecules could be accounted for by dielectric friction.⁵⁰ However, for dye molecules in amide solvents, the inclusion of dielectric friction does not result in good agreement between theory and experiment. Furthermore, for DMSO/H₂O mixtures, a curvilinear dependence of τ_{rot} on η is observed and dielectric friction alone is not able to explain the observed data.⁶¹ Evidence of dielectric friction effects on molecular motion has also been suggested by NMR measurements on rotational diffusion.⁶⁴⁻⁶⁶

In order to examine dielectric friction effects in more detail, we used molecular dynamics simulations to examine the effect of the permanent dipole moment on the rotational dynamics of a model diatomic solute in water.⁶⁷ The dipole moment was varied from 0 to 20 D by changing the atomic charges. From eq 4 and 5, it is expected that the rotational time will scale as the square of the permanent dipole moment of the solute. From 0 to ~ 17 D, the predicted linear correlation is observed. However, beyond 17 D, a dramatic deviation from the hydrodynamic continuum prediction is observed. Examination of pairwise radial distribution functions shows that above 17 D, the local structure of the solvent changes significantly. In addition, the structure at the negative end of the dipole is different from that at the positive end. This change in solvent structure reflects the short-range interactions between the solute and solvent, and this is not adequately handled in dielectric friction theories which use a continuum description of the solvent.

The inability of theory to describe rotational dynamics in some solvent mixtures or the solvent structural changes observed at large dipole moments in the simulations emphasizes the need for inclusion of molecular details of the solvent. In mixed-solvent systems, the

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possibility of specific solvation must be considered. In addition, the dielectric friction due to translational diffusion of solvent molecules can affect the rotational dynamics of the probe molecule.^{68,69}

4. The Time-Dependent Stokes Shift, a Molecular Probe of Microscopic Solvation Dynamics: Laser Experiment, Theory, and Computer Simulation

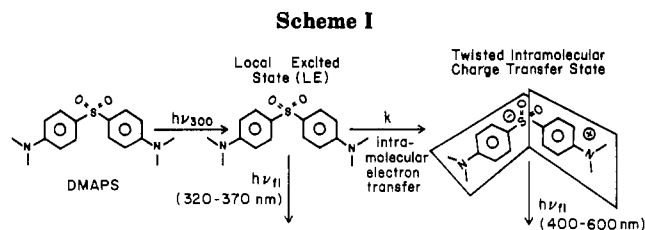
In this section we will explore the dynamics of solvent relaxation around molecules which are perturbed from equilibrium solvation. In the studies to be discussed, the probe molecules are comparable to or larger than the size of the solvent. Thus, unlike electron solvation (section 2), one might expect that collective motions of the medium will be required for solvation, resulting in a continuous relaxation process. The experiments are based on the observation that excitation to an excited electronic state generally results in a change in the permanent dipole moment (magnitude and/or direction) of a molecule. The Franck-Condon principle assures that the formation of the excited state will occur on a time scale much faster than any nuclear rearrangement of the environment. As a result, the excited-state species will be formed out of equilibrium with its surroundings. With increasing time, the solvent restructures, responding to the demands of the new charge distribution. This results in a lowering of the energy of the excited state, and is revealed by a red shift (or Stokes shift) in the emission spectrum. Thus, by studying the time-dependent Stokes shift, one can obtain molecular details of the solvent restructuring process.

Studies on the time-dependent Stokes shift have been reported on several different types of molecular systems.⁷⁰⁻⁷⁹ In addition to states populated by direct excitation, solvation dynamics have been probed by using emission from excited states populated by rapid intramolecular electron-transfer^{71,80} and proton-transfer⁸¹ reactions. In these cases, the time scale of the charge-transfer reaction is much faster than the solvent orientational relaxation.

In order to quantify the time-dependent properties of the emission spectrum, several workers have introduced the following correlation function.^{28,79,82}

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (6)$$

In the above expression, $\nu(t)$, $\nu(0)$, and $\nu(\infty)$ are the



emission maxima at time t , zero, and infinity, respectively. Thus, $C(t)$ is a function that is 1 at time $t = 0$ and decays to 0 as $t \rightarrow \infty$. The time-dependent behavior of $C(t)$ provides a means of examining the relaxation of the surrounding environment on a microscopic level. Dielectric friction effects are expected to play an important role in the structural reorganization dynamics of polar fluids. The connections between dielectric friction theories and $C(t)$ have been discussed by van der Zwan and Hynes.²⁸ In addition to affecting rotational motion (as discussed in section 3), dielectric friction effects can be envisioned in many chemical reactions, i.e., charge transfer and dipole isomerization.^{4,6} If one considers $C(t)$ as a measure of the dielectric friction, one may be able to gain information from the behavior of $C(t)$ of how polar solvents couple to chemical reaction coordinates.

The simplest theoretical model for understanding the underlying solvent dynamics that cause the evolution of the emission spectrum would be to consider a dipole in a spherical cavity embedded in a dielectric continuum.^{28,82} Generally, the frequency-dependent dielectric constant $\epsilon(\omega)$ is expressed as in eq 1. In this case, it has been shown that $C(t)$ decays exponentially with a time constant of the longitudinal relaxation time of the solvent, τ_L . More detailed dielectric continuum treatments by Madden and Kivelson¹⁸ show that for solvents characterized by an $\epsilon(\omega)$ of the form given in eq 1 the relaxation should be biexponential, with time constants of τ_L and τ_D . Relaxation at some single intermediate time has also been discussed by Nee and Zwanzig.⁵⁷ These models attribute the relaxation of the solvent polarization to rotational motion. In solvents which are characterized by slow orientational relaxation, the dominant mechanism for solvent equilibration could involve translational motion of the solvent dipoles. This phenomenon has been termed polarization diffusion. Theoretical work by van der Zwan and Hynes predicts that this relaxation mechanism will dominate when the ratio $D\tau_D/R^2 > 1$.^{28,83,84} In this expression, D and R are the self-diffusion constant of the solvent and the cavity radius of the dipole, respectively. In this case, $C(t)$ is predicted to be nonexponential and relaxes to $1/e$ of its initial value on a time scale much faster than τ_L . In addition, molecular theories and molecular dynamics studies of solvation have been reported. We will discuss the implications of these studies after examining the results of experimental measurements.

In recent publications from our laboratory, we have reported the study of solvation dynamics by monitoring the time-dependent Stokes shift of the emission from the twisted intramolecular charge-transfer (TICT) state of several aminophenyl sulfones.^{70,71} The photophysics

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Table I
Representative Data for Solvation Times Determined by $C(t)$ from Time-Dependent Stokes Shift Measurements^a

solvent	T , K	dielectric parameters				solvation time, ps probe molecule					
		ϵ_0	ϵ_∞	τ_D	τ_L	C311	C102	C153	BA	LDS-750	DMAPS
CH ₃ CN	298	38	1.9	4.3	0.2	0.67	0.89		0.70	0.4	
CH ₃ CH ₂ CN	298	28.6	1.9	4.7	0.31	1.07	1.42		1.4		
CH ₃ (CH ₂) ₂ CN	298	22.3	1.9	6.2	0.53	1.70	1.95		1.98		
EtOAc	313	5.8	2.5	3.8	1.6	2.37	2.5				
THF	293	8.2	2.2	3.1	0.8	1.42					
DMSO	298	46.5	4.8	20.6	2.1					3.1	
<i>N</i> -methylpropylamide	273	215	6	392	10			125			
propylene carbonate	273	81.9	10	171	20			88			
MeOH	298	33.7	5.6	55.6	9.2					3.3	
EtOH	273	26	4.6	337	60						43
EtOH	253	32.4	4.86	643	96			112			113
1-propanol	295	21.1	3.67	430	75			59		(100/53% 17/47%)	
1-butanol	298	17.8	3.5	613	120					(100/53% 17/47%)	
ethylene glycol	298	37.7	4	813	86						100

^aThe corresponding dielectric data are listed for comparison. LDS-750, Styryl 7;⁷⁷ DMAPS, 4,4'-(dimethylamino)phenyl sulfone;^{70,71} C311, Coumarin 311;⁸⁸ BA, bianthryl;⁸⁸ C102, Coumarin 102;⁸⁸ C153, Coumarin 153.⁷⁶ Dielectric data were taken from ref 21, 22, 70, 71, 75, 78, 88, and 92.

(and structure) of this class of molecules is shown in Scheme I.

In alcohol solutions the rate of intramolecular charge transfer for these molecules is significantly faster than either τ_L or the spectral relaxation of the TICT emission.^{70,71} In Figure 1, time-dependent emission spectra at several times after excitation for DMAPS in ethanol at -20°C are shown. The experimental details used to obtain these spectra are described in ref 70 and 71. As can be seen in Figure 1, the emission spectrum shifts to decreasing energy with increasing time after excitation; the total shift is on the order of 40 nm. Static fluorescence data indicate that excitation to the TICT state of this molecule results in a large change in direction ($\sim 90^\circ$) and magnitude (~ 10 D) of the permanent dipole moment.⁸⁵ From these data, $\nu(t)$ is extracted (insert in Figure 1). To generate $C(t)$, $\nu(0)$ and $\nu(\infty)$ need to be determined. Due to the finite time resolution $\nu(0)$ is extremely difficult to measure. Some recent subpicosecond studies suggest that even on such a short time scale, a fast component of the response may be missed, resulting in a misassignment of $\nu(0)$. On the other hand, $\nu(\infty)$ can be determined in an analogous manner to $\nu(t)$. Maroncelli and Fleming have examined the effects of $\nu(\infty)$ on the properties of $C(t)$.⁷⁶ They report that an error in $\nu(\infty)$ can distort $C(t)$ at long time, but has little effect on the time scale of the majority of the response. In figure 2, $\ln[C(t)]$ is plotted for DMAPS in ethanol at -20°C . For comparison, $-t/\tau_L$ is plotted (the continuum prediction), as well as $-t/\tau_D$. It is clear that the function $C(t)$ is not well fit by $-t/\tau_L$ but falls between curves corresponding to the two limiting relaxation times.

To a good approximation, $\epsilon(\omega)$ for ethanol at -20°C is well characterized by eq 1.²² The τ_D reflects the dynamics of hydrogen bonding (ethanol at -20°C is $>90\%$ hydrogen bonded).⁸⁷ However, it could be argued that monomer relaxation or even the fastest di-

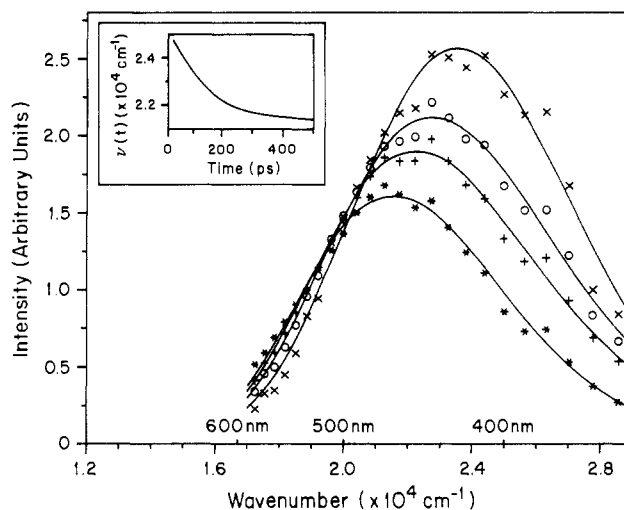


Figure 1. The emission spectrum of the TICT state of DMAPS in ethanol at -20°C is plotted as a function of time. The times plotted are (x) 100, (o) 150, (+) 200, and (*) 400 ps. The solid lines are the best fit of the log-normal line shape function to the experimental data. From the fitted curves, $C(t)$ is generated. The insert is a plot of the emission maximum as a function of time.

electric dispersion region in the alcohols (C-OH rotation) should be included in the response.^{79,82} Both of these motions occur on a faster time scale than the making and breaking of hydrogen bonds. Although not known in ethanol, the three relaxation times in propanol at room temperature are 430, 21.9, and 2.1 ps, respectively.²¹ Contributions from these regions of the $\epsilon(\omega)$ response should result in an acceleration of the solvation from that calculated with just the longest time constant of the dielectric function. This would result in further disagreement between theory and experiment. For the case of two regions of Debye dispersion, Bagchi et al. have derived an expression for $C(t)$ within the continuum model.⁸² In this case, $C(t)$ is a sum of two exponentials, weighted by a function of the dielectric constants associated with the two regions of dispersion. Studies of Coumarin 153 in propanol clearly show that the solvent dynamics are not adequately described by such a model.⁷⁶

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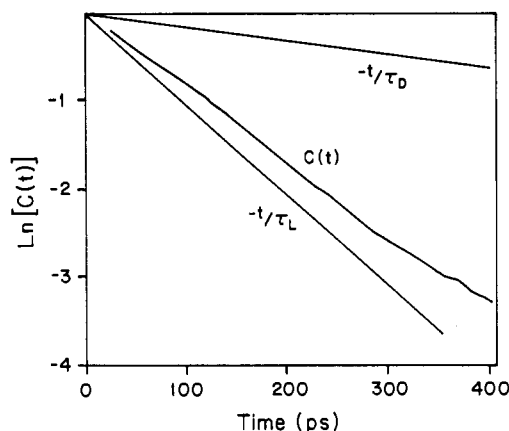


Figure 2. The log of the Stokes shift correlation function, $\ln[C(t)]$, is plotted as a function of time for the TICT emission of DMAPS in ethanol at -20°C . For comparison, $-t/\tau_L$ and $-t/\tau_D$ are also plotted. The data are not adequately described by the continuum model prediction of $-t/\tau_L$ but fall between the curves corresponding to the two relaxation times.

Recently, Castner et al.⁷⁷ and Kahlow et al.⁸⁸ measured $C(t)$ for polar aprotic solvents. For several molecules, nonexponential behavior for $C(t)$ has been observed and the average lifetime for the decay of $C(t)$ is generally longer than τ_L . In Table I, representative data for solvation times and corresponding dielectric data for several polar solvents are listed. The molecules studied represent a range of changes in dipole moment magnitude and direction. In some cases, biexponential fits for $C(t)$ are found to be superior to the single-exponential fits. The times given in Table I reflect an average time for $1/e$ of the relaxation process. It is important to stress that in almost all cases $C(t)$ is a nonexponential function. Several of the molecules examined have been studied in identical solvents and yield, within experimental error, the same solvation time. These results strongly suggest that the observed dynamics are not probe dependent but reflect the restructuring of the surrounding medium. Four general conclusions can be drawn from the data.

1. The time scale for solvation generally falls between τ_L and τ_D . In all cases reported, it is closer to τ_L than τ_D .

2. The relaxation dynamics as determined by $C(t)$ are nonexponential.

3. With increasing values of the static dielectric constant, ϵ_0 , the solvation time and solvent longitudinal relaxation time become more dissimilar. Not only is this true in comparing the variety of solvents examined but is also observed in a single solvent as a function of temperature where ϵ_0 increases with decreasing temperature.

4. In several solvents where $D\tau_D/R^2 > 1$, the observed solvation times are longer than τ_L , in contrast to the prediction of polarization diffusion theory.

These conclusions suggest that dielectric continuum models are not adequate for describing the relaxation dynamics of the solvent. For medium-size molecules, the majority of the relaxation takes place in the first few solvent shells. Thus, the molecular nature of the solvent must be considered. The contribution of a range of relaxation times between τ_L and τ_D was first proposed

by Onsager in discussing solvation of a charge.²⁴ Near the charge, the solvent dipole would need to rotate, a time similar to τ_D . With increasing distance, the continuum model would become applicable, and the time scale for relaxation of the polarization would approach τ_L . Modeling the solvent as a nonequilibrium distribution of dipoles, Calef and Wolynes were able to demonstrate that the time scale for solvation around a charge depended on the distance from the charge.⁷ Nearby, a time similar to τ_D was found. With increasing distance the relaxation time approaches τ_L . The average relaxation time (which would correspond to the experimentally observed dynamics) was nonexponential and had a $1/e$ decay time between τ_L and τ_D but closer to τ_L . Loring and Mukamel have also examined charge solvation.⁹ Expressions for calculating the solvent response are presented, and results similar to the Calef and Wolynes treatment are found. Friedrich and Kivelson recently examined the time-dependent polarization of a dipolar solvent to a stationary and moving ion.⁸⁸ This work demonstrates that the relaxation dynamics are dependent on geometric properties of the solvent molecules.

Wolynes has recently examined nonequilibrium solvent dynamics of an ion in a polar solvent.¹⁰ Solvation was found to occur on a range of time scales. However, to a good approximation, the results could be summarized by introducing a second relaxation time, τ_G , in addition to τ_L , which takes into account the cavity radius of the ion, r_c , and the diameter of the solvent molecule, D_S .

$$\tau_G^{-1} = \tau_D^{-1} \frac{1 + \frac{1}{2}(r_c/D_S)(\epsilon_0 + 3)}{1 + \frac{1}{2}(r_c/D_S)(\epsilon_\infty + 3)} \quad (7)$$

The importance of τ_G to the observed solvation dynamics depends on the polarity of the solvent and the ratio of the volume of the ion to the solvent molecule. For $r_c/D_S \gg 1$, τ_G is similar to τ_L . However, for $r_c < D_S$, τ_G becomes comparable to τ_D . In addition, if the solvent is weakly polar, τ_G will also be close to τ_D . Even though this treatment focuses on charge solvation, the general physical conclusions should apply to the dynamics explored through $C(t)$. Since solvation times are generally longer than τ_L , motion reflected by τ_G may play an important role in the solvation process.

In the above discussion, we have implied that the response is entirely accounted for by solvent motion. However, during the relaxation process, the probe molecules are also undergoing rotational diffusion, resulting in a time-dependent orientation of the probe dipole. This has been treated theoretically by Bagchi et al.⁸² For the molecules presented in Table I, the rotational diffusion times are much longer than the measured solvation times. In the study by Maroncelli and Fleming on the solvation of Coumarin 153, evidence of solvation dynamics was suggested by fast components in the rotational anisotropy.⁷⁶ The time scale of this fast component was found to correlate with the solvation times derived from $C(t)$. This result suggests that there was an initial torque on the molecule, in which the new direction of the dipole moment on the solute tried to realign with the solvation structure that was present around the ground-state molecule. In general, the large difference in solvation and rotational diffusion times indicates that the dominant contribution to the

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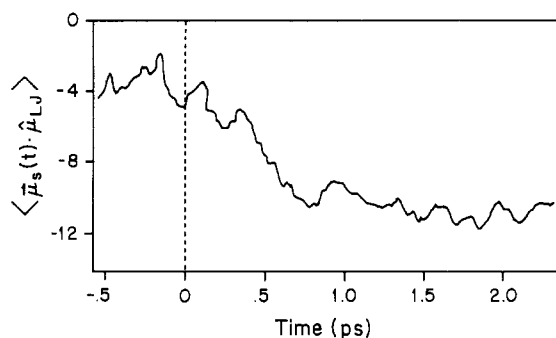


Figure 3. Molecular dynamics simulation of solvent relaxation. The projection of the total solvent dipole moment of a box of 504 TIP4P water, $\hat{\mu}_s(t)$, on the unit vector in the direction of the dipole moment of the LJ solute, $\hat{\mu}_{LJ}$, is plotted as a function of time. The dotted line at $t = 0$ signifies the jumping of the dipole moment of the LJ solute from 4 D to 12 D.

relaxation measured is solvent motion.

Further insight into the molecular details of solvation can be revealed by computer simulation. We have used molecular dynamics (MD) to examine the time scale for the relaxation of TIP4P water to an instantaneous change in the dipole moment of a solvated Lennard-Jones (LJ) sphere.⁸⁹ In order to obtain reasonable statistics, 60 different equilibrated configurations for a solvated 4 D solute were used. For each configuration, the dipole moment was instantly changed to 12 D (in the same direction), and the system was allowed to reequilibrate. The TIP4P water model was used as the dielectric properties for this model of water have been calculated.⁹⁰ This enables comparison between the simulation results and both continuum and molecular models of solvation. The static dielectric constant for TIP4P water is ~ 53 , significantly lower than normal water. Recent MD studies by Anderson et al.⁹¹ demonstrate the importance of including molecular vibrations in order to obtain accurate values for ϵ_0 . In figure 3, results for the 4 D \rightarrow 12 D jump are presented. This plot shows the projection of the total dipole moment of the solvent on the solute dipole moment as a function of time.

For TIP4P water, the Debye relaxation time, τ_D , and the longitudinal relaxation time, τ_L , are ~ 6.5 and 0.12 ps, respectively. The data given in the Figure 3 reveal a solvation time on the order of 0.5 ps, significantly longer than τ_L but shorter than τ_D . This result is similar

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to the trends observed in the experimentally measured $C(t)$ functions. MD simulations of this type are potentially important in revealing the molecular mechanism of solvation in polar fluids. From simulated data, solvation dynamics can be examined for individual solvent shells. We have examined the relaxation dynamics as a function of solvent shell. The first shell is found to relax on a slower time scale than the average solvent relaxation depicted in Figure 3. It is interesting to note that the relaxation time of this solvent shell is well described by eq 8. In addition to our studies, Maroncelli et al. have examined the electric field correlation functions of different solvent shells around charged and uncharged LJ solutes in ST2 water.⁷⁵ These results provide insight into both the nonexponentiality and time scales observed in the experimental measurements of $C(t)$.

5. Conclusions and Future Directions

In this Account, we have examined several experimental probes of the dynamic interactions of molecules in polar solutions. In all cases, experimental data alone are insufficient for a complete understanding of the molecular details of the solvation process. Theoretical models are required.

The experimental studies discussed in this Account show the need for the development of models of non-equilibrium solvation which include molecular details of the solvent. In addition, new experimental probes of solvation dynamics are needed. Advances in our understanding of solvation and the role of solvent fluctuations in chemical reactivity require a concerted effort by both experimentalists and theoreticians. Recent developments in the theory of nonlinear spectroscopies suggest that these techniques will become powerful tools for studying dynamical processes. With advances in computational power, molecular dynamics simulations on more complex systems will become possible. From these simulations it may be possible to identify fundamental microscopic solvent variables which could provide starting points for both analytic theories of solvent dynamics and the design of new experimental probes.

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