

## Solvation dynamics: new insights into chemical reaction and relaxation processes

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**Abstract** - This paper examines the role of dynamic solvation in several chemical processes. The following three phenomena are discussed in detail: rotational diffusion of dipolar molecules in alcohol solvents, the solvation of photogenerated electrons in water and reaction rate constants of intramolecular charge transfer processes in polar solvents. In each case, information on the role of solvent motion in determining the dynamics of the reaction or relaxation process can be assessed by comparison with theoretical models and using information on solvent fluctuation times obtained from time resolved Stokes shift measurements.

### INTRODUCTION

Understanding how solvent fluctuations influence chemical reaction dynamics is necessary for a complete picture of how reactions occur in solution. In the last five years, there has been a substantial effort aimed at elucidating the dynamic role of the solvent on reaction rate constants; ultrafast laser spectroscopy (ref. 1), molecular dynamics simulations (ref. 2) and advances in incorporating molecular aspects of the solvent in analytic theories (ref. 3) have all contributed to an increased understanding of this problem.

This talk examines the role of solvent dynamics in chemical reactions and relaxation processes. Two relaxation processes will be examined: rotational diffusion of a dipolar probe molecule in alcohol solvents and the solvation of photogenerated electrons in water. Finally, a particular class of reactions, intramolecular charge transfer reactions, will be examined. The following discussion emphasizes that our understanding of the dynamic role of the solvent in these chemical processes has resulted from combining insights from analytical theory, molecular dynamics simulations and time resolved measurements.

### ROTATIONAL DIFFUSION AND DYNAMIC SOLVENT RELAXATION

#### Background theory

Rotational diffusion studies have been extensively used to examine the coupling between a solute molecule and the surrounding solvent (refs. 1,4). Several experimental techniques have been developed which are sensitive to the rotational dynamics of molecules in solution (refs. 1,5). These techniques generally measure an autocorrelation function,  $\Phi(t)$ , of the unit vector,  $v$ , along the direction of the molecular transition moment:

$$\Phi_l(t) = \langle P_l [v(0) \cdot v(t)] \rangle \quad (1)$$

In the above expression,  $P_l$  is the  $l^{\text{th}}$  order Legendre polynomial. Experimental measurements of rotational motion of medium size solute molecules in solution are commonly compared to theoretical predictions which treat the surrounding liquid as a hydrodynamic continuum.

However, if one considers a polar molecule in a polar solvent, there are forces in addition to solvent viscosity which can affect the rotational motion. In particular, the permanent dipole moment of the solute induces a polarization in the surrounding dielectric. Since the orientational response of the medium is not instantaneous, the dynamic polarization field is no longer identical to the static polarization for a given orientation of the solute dipole. The result of this effect is the creation of an electric field in the cavity which exerts a torque opposing the reorientation of the solute molecule. This phenomenon, generally referred to as orientational dielectric friction has been the subject of numerous experimental (refs. 6,7) and theoretical (refs. 8-11) investigations. With respect to molecular reorientation, we could partition contributions to the reorientation time as follows:

$$\tau_{\text{rot}} = \frac{1}{6k_B T} \zeta = \frac{1}{6k_B T} (\zeta_{\text{nd}} + \zeta_{\text{d}}) \quad (2)$$

where  $\zeta_{\text{nd}}$  and  $\zeta_{\text{d}}$  refer to the non-dielectric and dielectric friction components of the total solvent friction,  $\zeta$ , respectively. The nondielectric contributions are generally equated to the Stokes-Einstein-Debye (SED) expression (refs. 1,12). Depending on the particular theory used, different expressions have been proposed for  $\zeta_{\text{d}}$ . However, in all the theories to date,  $\zeta_{\text{d}}$  is proportional to the square of the permanent dipole moment of the molecule,  $\mu^2$ .

The validity of the dependence of the dielectric friction constant on  $\mu^2$  has been tested by Cross and Simon (ref. 13) using molecular dynamics simulations. In that study, the permanent dipole moment of a diatomic solute was systematically varied from 0 D to 20 D. From the molecular dynamics trajectories, the second order rotational correlation function,  $\Phi_2(t)$ , was evaluated from which the corresponding diffusion time,  $\tau_{\text{rot}}$ , was determined. For permanent dipole moments less than 15 D, the rotational time correlates with  $\mu^2$ . Unfortunately, the results from that study could not be used to discriminate between the different functional forms for  $\zeta_d$  as the various dielectric properties of the model water solvent were not known.

The most widely used approach for evaluating  $\zeta_d$  is that due to Nee and Zwanzig (ref. 8). Within this approach, the dielectric friction constant is expressed in terms of dielectric properties of the fluid and the Debye solvent relaxation time,  $\tau_D$ . The contribution to the rotational diffusion times is given by the second term in equation (3).

$$\tau_{\text{rot}} = \frac{\zeta_{\text{nd}}}{6k_B T} + \frac{\mu^2 (\epsilon - 1)}{k_B T a^3 (2\epsilon + 1) \tau_D} \quad (3)$$

Most experimental measurements of rotational diffusion have used the Nee-Zwanzig formalism to assess the importance of dielectric friction effects.

The model proposed by Nee and Zwanzig assumes that the relaxation time of the cavity dipole is proportional to the relaxation time of the surrounding solvent. As pointed out in 1978 by Hubbard and Wolynes (ref. 9) there are several problems associated with this description. Perhaps the most serious is that in a real system, rotational motion of the probe molecule is possible even in the fixed field of the surrounding solvent. In order to account for this, Hubbard and Wolynes modeled the solute rotation in the presence of a fluctuating cavity field. This formalism predicts that the magnitude of the dielectric friction constant is reduced from that derived using the Nee-Zwanzig expression. Furthermore, the magnitude of the dielectric friction constant depends on the order of the autocorrelation function being measured.

Madden and Kivelson (ref. 11) have pointed out that the model of Hubbard and Wolynes also ignores several effects, including inertial motion, the contribution of translational diffusion, and anisotropic relaxation of the induced polarization in the dielectric surrounding the rotating solute. Using a Mori formalism, a general expression taking these various effects into account was developed. As found by Hubbard and Wolynes, the magnitude of the dielectric friction constant depends on the order of the orientational autocorrelation function, however, a slightly different functional form was obtained. In particular, these workers examined the role of solvent translational diffusion in detail. Model calculations showed that translational diffusion leads to an acceleration of the relaxation of the surrounding solvent molecules. Similar effects, although in a slightly different context, have been discussed by van der Zwan and Hynes (ref. 14).

The above models focus on calculating the dielectric friction constant by considering solvent forces on the rotational motion of a solute molecule. However, van der Zwan and Hynes (ref. 10) recently proposed that the time dependent dielectric friction can be determined from the experimentally determined time dependent Stokes shift correlation function,  $C(t)$  (refs. 1b-d).

$$C(t) = \zeta_d(t)/\zeta_d(t=0) \quad (4)$$

The initial value of the friction  $\zeta_d(t=0)$  is simply given by static Stokes shift,  $S_{\text{fl}} = \nu_a - \nu_f$ . Thus, for a molecule with dipole moment  $\Delta\mu = \mu_{\text{es}} - \mu_{\text{gs}}$ , the dielectric friction constant can be expressed as

$$\zeta_d = S_{\text{fl}} \int_0^{\infty} dt C(t) = S_{\text{fl}} \tau_s \quad (5)$$

This approach would include all relaxation processes of the fluid which are measured by the experimentally determined function,  $C(t)$ . Although a detailed molecular based understanding of the dynamics sensed by  $C(t)$  is only emerging at present, it is clear that this function is sensitive to orientational and translational relaxation of the solvent in the vicinity of the solute (refs. 3b, 15).

### Oxazine 725: spectroscopy and rotational diffusion measurements

In the present study, we examine the state dependent rotational times of oxazine 725 in alcohol solvents. In order to accurately quantify the effects of dielectric friction on molecular rotation, independent measurements of the molecular dipole moments in the ground and excited electronic states are required. The absorption and emission spectra of oxazine 725 indicate that the steady state Stokes shift is solvent dependent. Within a dielectric continuum description of the solvent, this static Stokes shift can be expressed in terms of the Lippert-Mataga equation from which an estimate of the difference between the dipole moments of the ground and first excited electronic state can be obtained. Using a cavity radius of 4.1 Å (ref. 16), a difference of 4.5 D is found.

For quantitative comparisons to theory the absolute magnitude of the dipole moment for each electronic state is desired. The ground state moment for oxazine 725 has not been experimentally measured, however semi-empirical quantum mechanical calculations reveal a ground state moment of 1.7 D (ref. 15). Combining this result with the

Lippert-Mataga analysis gives a dipole moment of 6.2 D for the first excited singlet state. Reorientation times of ground and electronically excited oxazine 725 have been reported by Blanchard (ref. 17) for the series of n-alcohols from methanol to hexanol. The ground state times are shorter than those observed for the excited state, consistent with the increased molecular dipole moment found upon excitation.

### Comparison of experimental measurements with theory

If we assume that the contribution of nondielectric friction to the rotational motion is not affected by the change in electronic state, the difference between the ground and excited state rotational times can be expressed as in terms of the difference between the dielectric friction contributions to the rotational tumbling in the two electronic states. Under this assumption, using the Nee-Zwanzig result for the magnitude of the dielectric friction constant, one predicts that  $\mu_{es}^2 - \mu_{gs}^2$  is 9.3 D<sup>2</sup>. From static spectroscopy, we know that  $\mu_{es} - \mu_{gs} = 4.5$  D. There is no simultaneous solution to these two equations. The inconsistency between the dynamic and steady state data strongly suggests that the Nee-Zwanzig expression does not give an accurate measure of dielectric friction effect. Using the approach reported by Hubbard and Wolynes for calculating  $\zeta_d$  and comparison with the steady state spectroscopy results in better agreement but suggests that this improved formalism still overestimates the magnitude of the dielectric friction constant.

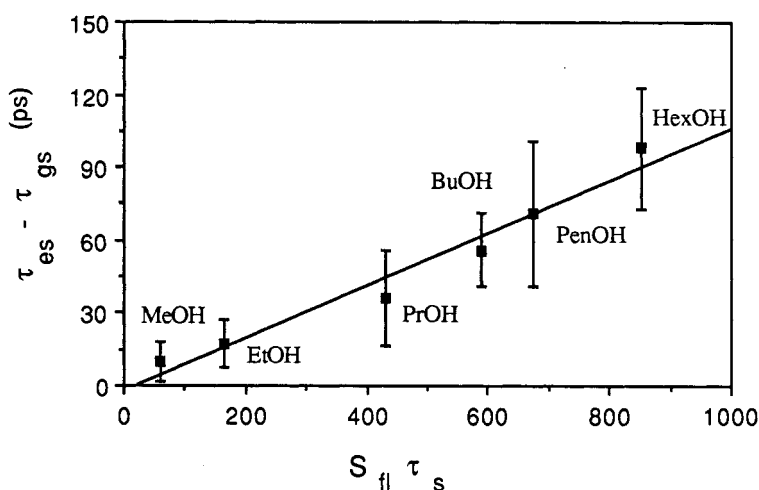


Fig. 1. The difference between the excited and ground state rotational times,  $\tau_{es} - \tau_{gs}$ , of oxazine 725 in the series of alcohols is plotted against the function  $S_{fl} \tau_s$ . Using the connection formula proposed by van der Zwan and Hynes, the resulting slope of this plot can be used to derive an expression relating the squares of the ground and excited state dipole moments.

Finally, we examine the approach of van der Zwan and Hynes in which the magnitude of  $\zeta_d$  can be directly determined from time dependent solvation measurements. In order to evaluate equation (5), the solvation times are needed. Room temperature measurements of  $C(t)$  for MeOH and EtOH reported by Barbara and coworkers (ref. 1d) and our group (ref. 1c), respectively, were used to determine  $\tau_s$  in these solvents; the longitudinal relaxation time,  $\tau_L$ , was used for the longer chain alcohol solvents studied.

In Fig. 1, the difference between the ground and excited state rotational times of oxazine 725 in the series of alcohols from methanol to hexanol are plotted as a function of  $S_{fl} \tau_s$ . Simultaneous solution of the van der Zwan and Hynes equation (using the slope of Figure 1) and the Lippert-Mataga analysis gives  $\mu_{es} = 6.0$  D and  $\mu_{gs} = 1.5$  D, revealing essentially quantitative agreement between steady state spectroscopy, the state dependent rotational times and the calculated ground state dipole moment. This observation supports the conclusion that the magnitude of the dielectric friction constant on the rotational motion of solute molecules in polar solutions can be evaluated using the connection between  $\zeta_d$  and solvation dynamics as determined from time dependent fluorescence measurements.

The above discussion demonstrates how combining analytical theory, molecular dynamics simulations and experimental measurements can lead to new insights into the role of solvent forces on molecular processes in polar solvents.

## SOLVATION OF PHOTOGENERATED ELECTRONS IN WATER

### Background

Because of its deceptive simplicity, the solvated electron and its optical properties have been thought to be ideal probes for studying molecular aspects of liquid structure and dynamics (ref. 18). One challenging and exciting question regarding the solvation of electrons in liquids is whether or not the dynamics are governed by the same molecular processes which are involved in the solvation of ions and polar molecules.

It is generally believed that upon injection into a polar liquid, the electron goes through three distinct solvation states. The first state corresponds to an unsolvated, essentially free, electron scattering through the liquid. Once enough energy has dissipated, the electron enters the second stage of solvation and becomes localized, or trapped in pre-existing sites in the fluid. Finally, the solvent relaxes to give an equilibrium solvated species. Only the last two intermediates are believed to contribute to the near infrared and visible absorption bands observed in the experimental studies of electron solvation. Theoretical studies indicate the likelihood that the electron is first trapped in pre-existing voids in the solvent (ref. 18). Furthermore, computer simulations show that a wide energy distribution of traps are always present; traps with potentials as deep as 1.4 eV have been found in models for water (ref. 19). These calculations suggest that a variety of energetically trapped electron are initially formed after photoionization in fluids; the broad infrared absorption which is experimentally observed immediately following either direct photoionization or pulse radiolysis has been attributed to this large distribution of trapped species. The possible role of very deep traps has been a major topic of discussion (refs. 18-20), as the existence of such solvent sites would indicate that the natural structure of the liquid contains local configurations which resemble that corresponding to the equilibrium structure around the electron. One would expect that electrons which localize in these traps would be characterized by an absorption spectrum similar to the equilibrated species. Questions concerning the initial electronic state of the trapped electron have also been raised (ref. 18).

### Experimental observations

In 1987, Migus et al. (ref. 21) used 100 fs laser pulses to examine the dynamics of electron solvation in liquid water. In Fig. 2A, the transient absorption data observed by these workers is reproduced. Following photoionization, an absorption is observed to grow in throughout the near infrared region of the optical spectrum. With increasing delay time, the transient intensity in this region decreases and the spectrum of the equilibrated electron is observed to rise in the visible region of the spectrum. In developing a physical model to account for these data, it is important to note that several general features must be reproduced; the initial growth of the infrared band, the shoulder at 700 nm observed at zero time, the lack of an isobestic point; the change in slope of the absorption in the region from 900 nm to 1300 nm observed for the <400 fs and >700 fs data, and the time dependent narrowing of the visible absorption band between 700 fs and 2 ps. These complicated spectral features suggest that several dynamical processes are occurring on the subpicosecond time scale.

### Comparison to various models for electron solvation

In the following subsections we compare these data to various physical models for electron localization and solvation in water. The mathematical details of the various models discussed below have been reported by Messmer et al. (ref. 22). The observation of a shoulder near 700 nm observed at zero time supports the conclusion that some of the photogenerated electrons find deep solvent traps (in agreement with theoretical predictions (ref. 19)) which evolve to equilibrium on the time scale of at most 25 fs. In order to quantitatively account for this absorption feature, 20% of the photogenerated electrons need to follow such a mechanism. Thus, in the following three cases considered, 20% of the electron population is assumed to undergo solvation in this manner.

*Activated twostepkinetics* It has been proposed that electron solvation occurs by an activated process between the trapped and equilibrium solvated species. To test this idea, the time dependence of the remaining 80% of the photogenerated electrons was modeled by a two state kinetic process. Convolution of the pump and probe pulse widths (taken to be 100 fs), a trapping rate of  $5 \times 10^{12} \text{ s}^{-1}$ , and an activated rate constant of  $4 \times 10^{12} \text{ s}^{-1}$  for the formation of the equilibrium species from the solvent-trapped intermediates gives the simulated data shown in Fig. 2B. The rate constant of solvent trapping was optimized to give the best fit of the simulated data in the 1100-1250 nm range to the experimental data. The rate constant for the formation of the equilibrated species was chosen to optimize agreement between simulation and experiment for the time dependence of the spectrum in the region from 700 to 800 nm. The values obtained are similar to those reported by Migus and coworkers (ref. 21). This simulation reveals that for time delays greater than 200 fs, the spectra should reveal an isobestic point in the vicinity of 820 nm. This feature is completely absent in the experimental data. In addition, the simulated data exhibit a slope in the region between 1000 and 1250 nm which changes from positive to negative slope at 1000 fs; whereas the experimental data show a change in the sign of the slope between 400 and 700 fs. We conclude from this comparison that the evolution of the optical absorption spectra cannot be accounted for by a simple two state activated process.

*Continuous spectral shift* Spectroscopic studies which focus on the dynamics of molecular solvation suggest that solvent restructuring is manifested by a continuous shift in the optical absorption or emission spectrum of the solute. It is of interest to determine whether or not the solvent relaxation which occurs in the evolution of electrons from the pre-existing solvent traps to equilibrium is also described by a continuous spectral shift. In Fig. 2C, results are presented using a trapping rate of  $5 \times 10^{12} \text{ s}^{-1}$ , and a solvation time similar to that derived from  $C(t)$  measurements,  $\approx 200 \text{ fs}$  (ref. 23). The simulated spectra only reproduce a few features of the experimental data: for example the narrowing of the spectrum observed between 1 ps and 2 ps following photolysis, the early appearance of the shoulder at 700 nm, and the change of slope in the red edge of the spectrum (although at an

earlier delay time than observed experimentally). The relative intensities of the infrared region to that observed in the visible are also not in agreement with the experimental data. Furthermore, the simulated data exhibit time dependent maxima in the region from 800-1100 nm which are completely absent in the experimental data. Allowing the solvation time to vary does not result in superior fits to the experimental data.

**Importance of electronically excited electrons** The above two comparisons clearly demonstrated that the time dependent absorption spectra of Migus and coworkers are revealing the presence of more than one dynamical process. We believe that the femtosecond absorption data can, however, be quantitatively accounted for by postulating three distinct populations of electrons which undergo solvation by different physical mechanisms (ref. 22): 20% are ground state electrons which find equilibrium solvation within 25 fs, 25% are ground state electrons which localize in shallow solvent traps with a rate constant of  $4 \times 10^{12} \text{ s}^{-1}$  and then exhibit a continuous shift in the absorption spectrum ( $\tau_s \approx 200 \text{ fs}$ ) as solvation occurs, 55% of the electrons localize in an excited state and undergo a nonadiabatic transition to the ground state with an excited state lifetime of  $\sim 250 \text{ fs}$ . The predicted spectra for such a model are shown in Fig. 2D. Excellent agreement between these calculated spectra and the experimental data shown in Figure 2A are observed. This partitioning between the three different pathways for relaxation and solvation of photogenerated electrons is also consistent with recent ab initio molecular dynamics simulations reported by Friesner, Rosky and coworkers (ref. 24).

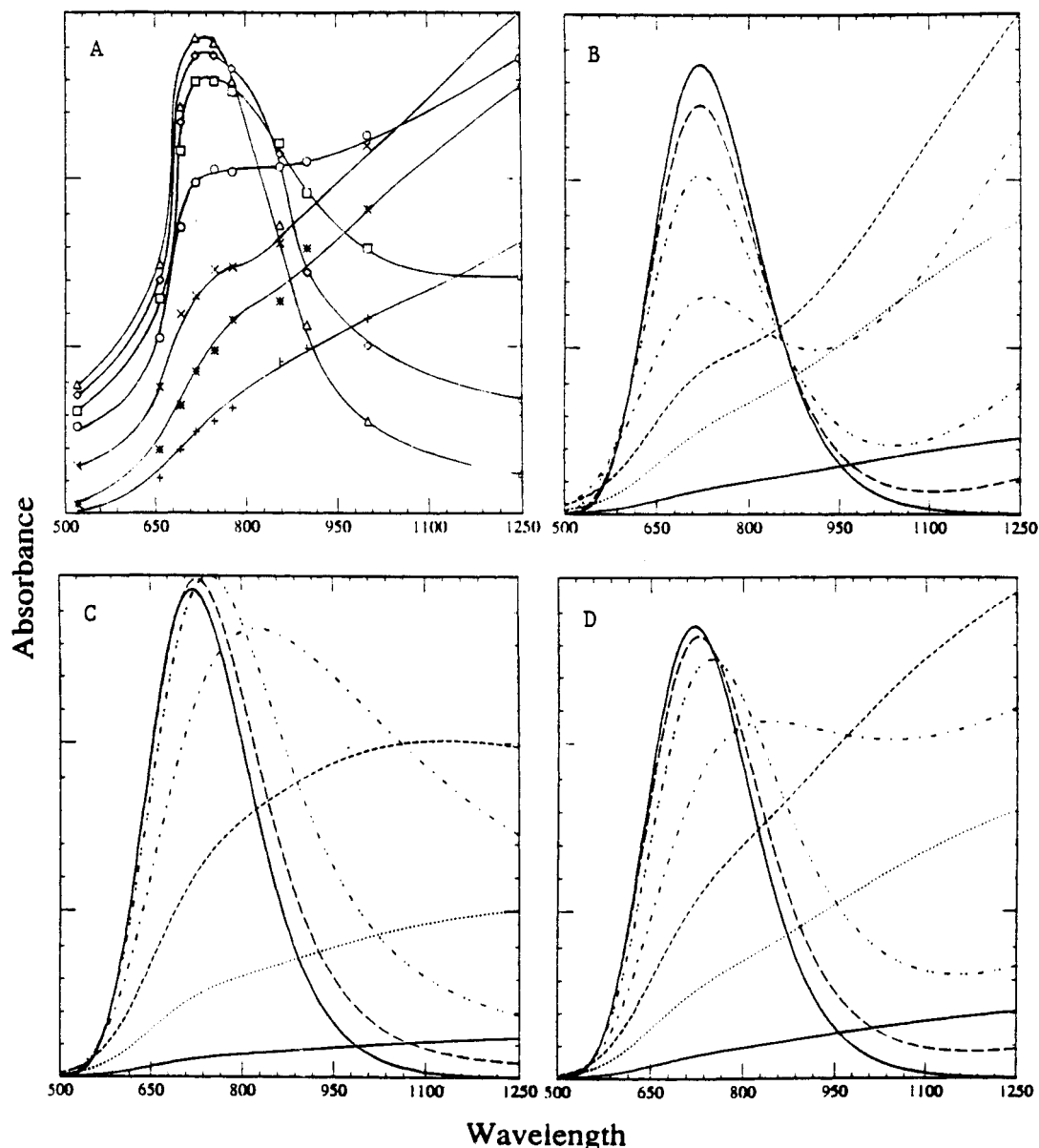


Fig. 2. Experimental and simulated time dependent spectra for the solvation of photogenerated electrons in water. (A) Experimental data reported by Migus and coworkers (ref. 21), (B) Simulated spectra for an activated two-state model, (C) Simulated spectra for continuous spectral relaxation, and (D) Simulated spectra for combined solvent relaxation and contributions from electronically excited trapped electrons. Details of these simulations can be found in reference 22.

Two important conclusions on the nature of electron solvation in polar fluids are revealed by the comparisons between the experimental data and simulated spectra. First of all, the calculations suggest that a large fraction of the photogenerated electrons are electronically excited when they become localized in the solvent. Secondly, we find that the rate of spectral shifting can be described by times scales determined from time dependent Stokes shift studies. This observation suggests that the collective molecular processes associated with the solvent relaxation around ground state photogenerated electrons and electronically excited molecules may, in fact, be similar. As in the previous section, the above discussion demonstrates how experiment, theory and computer simulations can be used in concert to address fundamental issue of condensed phase dynamics.

## DYNAMIC SOLVATION AND EXCITED STATE INTRAMOLECULAR CHARGE TRANSFER REACTIONS

### Background

In the past decade, there has been a significant effort to determine the role of solvent dynamics in electron transfer processes (ref. 25). Efforts have mainly focussed on intramolecular systems; such molecules provide a rigid framework for addressing this question. Elegant work by Barbara and coworkers (ref. 26) on the electron transfer dynamics of electronically excited bianthryl demonstrated that the dynamics and transient emission spectra could be reproduced using the generalized Langevin equation and information on solvent dynamics determined from time resolved Stokes shift measurements.

Recent experiments from our laboratory have found that for dimethylaminobenzonitrile (DMABN) (ref. 27) and bis-(dimethylaminophenyl)-sulfone (DMAPS) (ref. 28), electron transfer rates over an order of magnitude faster than  $\tau_L^{-1}$  or  $\tau_S^{-1}$  are readily observed in alcohol solvents. In addition, the population decay of the reactant state is very nonexponential, indicating a time dependent rate constant for the reaction process. Furthermore, for all of the systems that we have examined, the product twisted intramolecular charge transfer state exhibits a time dependent spectral relaxation, supporting the conclusion that significant solvent relaxation occurs after the electron transfer reaction. These results were interpreted in terms of a recent two-dimensional model proposed by Sumi, Nadler and Marcus (SNM) (ref. 29), in which the effects of fluctuations in both the solvent polarization and the intramolecular vibrational coordinates on the reaction rate are considered. In this model rate constants in excess of  $\tau_L^{-1}$  (or  $\tau_S^{-1}$ ) can be accounted for by concluding that the reaction rate is dominated by vibrational contributions.

However, despite the excellent agreement between theory and experiment, there are other possible sources for the nonexponentiality of the reactant population decays and the seemingly fast reaction rate compared to solvation. Recent studies by Barbara and Weaver and coworkers (ref. 30) suggest that fast components to the solvation dynamics can play a dominant role in determining electron transfer rates, not simply the average time derived from the integral of  $C(t)$ . These effects were more pronounced in alcohol solvents and could lead to the observed fast reaction rates. However, it is unlikely that this effect alone can account for the high degree of nonexponentiality of the population decays observed in our studies of DMABN and DRAPS.

One potential important explanation of the nonexponential decays and the resulting time dependent rate constants is that the assumption that the initial photoprepared population in the locally excited (LE) state is in thermal equilibrium may not be valid. Since the dipole moment of the LE state is different than that of the ground electronic state, dynamic solvation is expected following photoexcitation (ref. 1b-d); this would lead to a time dependent barrier to reaction. In the following subsection, we focus on a simple kinetic model which takes this effect into account. These calculations suggest that this effect could be important; further work is required in order to test the validity of such a model in accounting for the experimentally observed electron transfer dynamics in various intramolecular systems.

### Nonequilibrium solvation around the photogenerated locally excited state: a simple model

As mentioned above, it is possible that excitation does not populate an equilibrium distribution on the excited state reaction surface. In modeling this effect for reactive processes such as excited state electron transfer in DMABN or DMAPS, we assume that relaxation along the torsion angle leading to the twisted intermediate is rapid compared to solvation. This is consistent with our recent experimental results on a series of related bis-(dialkylaminophenyl)-sulfones in which the electron transfer dynamics were insensitive to an increase in the size of the alkyl substituent and changes in solvent viscosity (ref. 31).

In physical terms, we can consider that following excitation, solvent relaxation around the LE state occurs leading to a time dependent change in the height of the reaction barrier. The nonexponential nature of the population decays are then a direct manifestation of the solvation dynamics.

To a first approximation, the effect of dynamic solvation around the LE state on the time dependence of the population decay of the reactant can be examined using a model in which the time dependent barrier to reaction is parameterized in terms of the solvent relaxation function  $C(t)$ . Using the values defined schematically in Fig. 3, the time dependent barrier height can be expressed as:

$$\Delta G^{\ddagger}(t) = \Delta G^{\circ} + [1-C(t)](\Delta G^{\infty} - \Delta G^{\circ}) \quad (6)$$

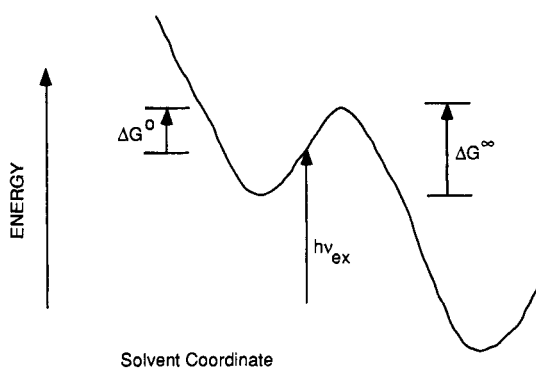


Fig. 3. Schematic of the potential energy surface for excited state intramolecular electron transfer. Excitation results in an initial population which is not in equilibrium with the surrounding solvent structure.

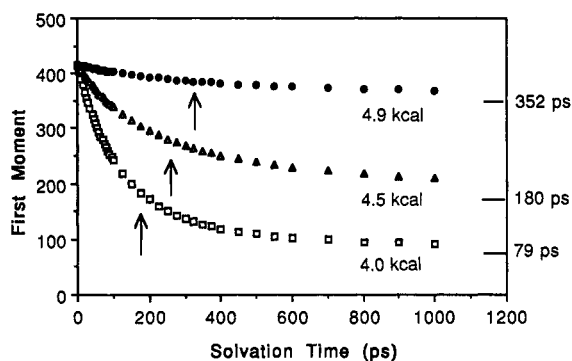


Fig. 4. The integral of  $Q(t)$ , equation (9), is plotted as a function of solvation time,  $\tau_L$ , for several values of initial nonequilibrium,  $\Delta G^0$ . The arrows indicate the points where the solvation time is equivalent to the first moment. The times given on the right axis are the first moments in the limit as  $\tau_L \rightarrow \infty$ .

If we assume that the dielectric response of the solvent can be described by a Debye continuum model, then  $C(t) = \exp(-t/\tau_L)$ . Using this result, the time dependent rate constant is given by:

$$k(t) = A \exp(-\Delta G^\ddagger(t)/RT) \quad (7)$$

where we assume that the prefactor,  $A$ , is independent of the solvent coordinate. The population decay,  $Q(t)$ , of the reactant state is then given by:

$$Q(t) = \exp(-A \int_0^t \exp(-\Delta G^\ddagger(\tau)/RT) d\tau) \quad (8)$$

Within the Debye approximation, this expression can be solved analytically to give the following expression for  $Q(t)$ .

$$Q(t) = \exp(A\tau_L \left[ \text{Ei} \left( \frac{\Delta G^\infty - \Delta G^0}{RT} \exp(-t/\tau_L) \right) - \text{Ei} \left( \frac{\Delta G^\infty - \Delta G^0}{RT} \right) \right]) \exp(-\Delta G^\infty/RT) \quad (9)$$

In the above equation,  $\text{Ei}(z)$  is the exponential integral defined by:

$$\text{Ei}(z) = - \int_{-z}^{\infty} \exp(-t)/t dt \quad (10)$$

We have evaluated equation (9) for various values of  $\tau_L$  and  $\Delta G^0$  and find that in most cases, nonexponential population decays for  $Q(t)$  result (ref. 32). In the remainder of this subsection, the first moment (integral of  $Q(t)$ ) of the population decay is examined. This is instructive as these values are relevant to the interpretation of population decays within the SNM model. In Fig. 4, results as shown for the first moment of  $Q(t)$  as a function of solvation time for various initial values of  $\Delta G^0$ . For these calculations,  $\Delta G^\infty = 5$  kcal/mole and  $RT = 0.6$  kcal/mole and  $A = 1 \times 10^{12} \text{ s}^{-1}$  (1 cal = 4.184 J).

The data shown in Fig. 4 indicate that the reaction dynamics (as measured by the average decay time) can be significantly affected from competition between solvent relaxation and reaction. In particular, if excitation populates the surface 0.5 kcal/mole from equilibrium, for Debye solvents with relaxation times greater than 270 ps, the first moment of the population decay will be faster than solvation. With increasing deviations from equilibrium following excitation or in non-Debye solvents, this effect becomes important even in "fast" relaxing solvents. In alcohol solutions, solvation times on the order of tens to hundreds of picoseconds have been observed from time resolved Stokes shift studies (ref. 33). Thus, for intramolecular electron transfer reactions in these solvents, if the photoexcited reactant is not initially in equilibrium with the surrounding solvent, the reaction dynamics observed can easily be faster than solvation. This model suggests an alternative explanation for the reaction dynamics observed than that derived from a comparison of the experimental data to the SNM model. Furthermore, this effect may be important in a wide variety of excited state chemical reactions (ref. 32).

## CONCLUSIONS

This talk examined the role of solvent dynamics in three fundamental problems: dielectric friction effects on the rotational diffusion of polar molecules, solvation of photogenerated electrons and intramolecular charge transfer reactions. In all three cases, comparisons between the experimental data, solvation times determined from dynamic Stokes shift measurements, computer simulations and analytic theory reveal the important role that solvent relaxation plays in condensed phase chemical processes.

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