Primary Charge Separation in Photosynthetic Bacterial Reaction Centers and Femtosecond Solvation Dynamics


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1. INTRODUCTION.

The capability of generating reliable, tunable femtosecond pulses has given new impetus to the study of condensed phase dynamics. In this paper we describe work in two areas: the dynamics of polar solvation and the primary charge separation step in the reaction centers of photosynthetic bacteria.

2. EXPERIMENTAL.

Two different systems were used to collect the data described in this paper. The experiments on reaction centers used a 20 Hz amplified colliding pulse ring laser system. Two continua were generated, from one of which was selected (via a 10 nm bandwidth filter) the 870 nm pump pulse. This was further amplified in a single pass Bethune type cell using LDS-867 to an energy of about 4 μJ. The second continuum was used as the probe pulse. The polarization of the pump and probe pulses were generally set at the magic angle, although experiments were also performed with parallel and perpendicular polarizations. The instrument response function, determined by monitoring the bleaching of the dye IR-143, was typically 300 fs. Typically 10-15% of the reaction centers were excited by the pump pulse.

The solvation studies utilized a fluorescence upconversion spectrometer based on reflective optics. The design is similar to that of Chesnoy et al. [1], but an elliptical mirror is used to collect and focus the fluorescence. A diagram of the optical arrangement is shown in Figure 1. The excitation pulses were typically 75 fs duration, 1.4 nJ in energy, with center wavelength in the range of 605-608 nm. The sum frequency was generated in a 1 mm LiO₃ crystal and yielded a typical instrument response function of 125 fs (FWHM). At long fluorescence wavelengths (750-775 nm) the instrument function is lengthened by about 45 fs by group velocity mismatch in the crystal [2]. The upconversion bandwidth is about 8 nm.
3. PRIMARY ELECTRON TRANSFER IN BACTERIAL REACTION CENTERS.

The primary charge separation process in bacterial photosynthetic reaction centers occurs with approximately 100% efficiency on the few picosecond time scale. The x-ray structural data [3] raise a number of intriguing issues regarding the mechanism of the primary electron transfer step. The structure shows two apparently similar branches, yet electron transfer proceeds entirely down one branch. The structure also shows an "accessory" bacteriochlorophyll molecule (B) between the primary donor (the special pair, P) and the "primary" acceptor bacteriopheophytin (H_A). The initial step of photosynthesis has been proposed to occur either by a one-step superexchange mechanism (P*BH → P+BH⁻) or by a two-step mechanism corresponding to the scheme [4-11]

\[ P^*BH \rightarrow P^*B^+H \rightarrow P^*BH^- \]

Bixon et al. [11] have presented a theoretical model for the superposition of the two schemes presented above. According to their model the electron transfer path is dominated by the two-step sequential mechanism at room temperature. As the temperature is lowered, their model predicts that the fraction of the sequential mechanism becomes smaller and the contribution from the superexchange process becomes important. Evidence for a real B⁻ intermediate from femtosecond spectroscopy has been controversial. Initial studies did not reveal evidence for a B⁻ state, but the recent work of Zinth and coworkers does suggest a sequential process [12] whereas the parallel work of Kirmaier and Holten was interpreted as
In interpreting the kinetic data a number of complicating factors must be considered. First, a model for the spectrum and its evolution is required. Most studies to date have (usually implicitly) assumed that while the spectra of the various species may overlap the intensity of the absorption bands can be considered as directly proportional to the concentration of the various molecular and ionic states present at a particular time. It is not a priori clear that such a weak coupling picture is appropriate for the reaction center [14-16], and therefore caution must be exercised in interpreting experimental data via simple kinetic schemes. Molecular orbital theory has been applied to the reaction center [17-20] but to date no calculations of the difference spectrum immediately following excitation have been presented. In the absence of further information we will interpret the data presented here in terms of a kinetic scheme, but consider this to be of uncertain validity at the shortest times. Even in the context of a kinetic scheme the possibility of shifts of the absorption bands as a result, for example, of electrochromic effects during charge separation must be considered. This bandshift effect is of particular concern in the B absorption region where a significant electrochromic shift is known to occur.

Given a kinetic picture it is then necessary to include all the species absorbing at a particular probe wavelength, along with the relative orientations of their transition moments. To illustrate this complexity Figure 2 shows data at 665 nm with the probe polarized both parallel and perpendicular to the pump pulse. This wavelength corresponds to the maximum of the bacteriopheophytin anion absorption band. The transition moment of $\text{HA}^-$ is oriented at 65° to that of P [13] resulting in a scaling of parallel and perpendicular curves according to $(1+2\cos^2\theta) / (2-\cos^2\theta)$ for a randomly oriented sample. However, the kinetic information contained in the two curves is the same and thus when properly scaled the curves should superimpose. Figure 2 shows that this is clearly not the case and it is tempting to conclude that these data directly exclude the one-step model. However, when the contribution from the excited state of P ($P^*$) is included the situation changes. Figure 3 shows simulated kinetics for several values of the $P^*$ extinction coefficient. We estimate $\varepsilon(P^*) = 1.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ from a variety of information. Comparison of Figures 2 and 3 leads us to conclude that dichroic measurements at 665 nm in the absence of extremely precise extinction coefficients for all species involved cannot distinguish between the one-step and two-step mechanisms. Our conclusions (and data) at this wavelength are in accord with those of Kirmayer and Holten [13].

Similar experiments were also performed at 680 nm which is close to the peak of the $B^-$ absorption band. Our parallel data look similar to those (at 665 nm) of Zinth and coworkers and lend support to the presence of detectable $B^-$ concentration. Again, however, uncertainty over the contribution of $P^*$ makes unambiguous interpretation difficult and for this reason we turn to a different spectral region.
Figure 2. Transient absorption data at 665 nm with the probe pulse parallel ($||$) and perpendicular ($\perp$) to the 870 nm excitation pulse. The $||$ and $\perp$ curves are scaled to the same height for comparison.

Figure 3. Simulations of the dichroic kinetics with different values of P* extinction coefficients. (a) $\varepsilon(p^*)/\varepsilon(H_A^*)=0.24$; (b) $\varepsilon(p^*)/\varepsilon(H_A^*)=0.3$; (c) $\varepsilon(p^*)/\varepsilon(H_A^*)=0.4$. A single step kinetic model is used for the simulations and the sample is assumed to be randomly oriented. The angles of the transition moments used here for P* and H$_A^*$ absorption are 30° and 65° with respect to P absorption, respectively.

We consider the bacteriopheophytin Q$_X$ absorption region (H$_A$ at 545 nm, H$_B$ at 525 nm) to be capable of providing much less ambiguous information on the mechanism of primary electron transfer for two major reasons. First, the bleaching of H$_A$ (as a result of H$_A^-$ formation) and the absorption of P* give rise to signals with opposite signs and are much more easily disentangled from each other. Second, the fact that the inactive bacteriopheophytin, H$_B$, shows no bleaching allows for a much more direct measure of the P* contribution and a small extrapolation from 526 nm to 545 nm rather than a large one from 545 nm to 665 nm in the determination of the P* contribution. Thus simultaneous fits at 545 nm and 526 nm should prove incisive.
Figure 4. (a) Time-resolved absorption changes measured at 545 nm and 526 nm for \textit{Rb. sphaeroides} R26 at 283 K with excitation at 870 nm. The probe polarization was set at $-55^\circ$ with respect to the pump pulse. (b) A kinetic simulation using a one-step time constant of 2.6 ps results in a poor description of the 545 nm data. (c) Simulation of the 545 nm bleaching kinetics using a two-step model with $k_1^{-1}=2.6$ ps and $k_2^{-1}=1.25$ ps.

Figure 4 shows data at 545 nm and 526 nm for \textit{Rb. sphaeroides} R26 at 283 K. Stimulated emission at 926 nm gives a time constant of 2.6 ± 0.2 ps for the decay of $P^\ast$. Fitting the data in Figure 4 to the one-step superexchange model gives a time constant of 4.0 ± 0.3 ps. Attempts to fit with a single 2.6 ps time constant result in very poor fits and examination of the fits suggests that a model with slower bleaching is required. As Figure 4 shows a two-step simulation with time constants of 2.6 ps for the first step and 1.25 ps for the second step fit the data well at 926 nm, 545 nm and 526 nm. (Of course these parameters will also fit the data at 665 nm and 680 nm but vide supra).

We have also examined the possibility that both sequential and superexchange mechanisms operate at room temperature. Simulations show that the contribution of the single step process can be as much as 25% but beyond that the simulations start to deviate significantly from the data.

Given the prediction of Bixon \textit{et al.} it is of great interest to perform the same analysis at low temperatures. The decay of $P^\ast$ at 22 K gives a time constant of 1.6 ± 0.2 ps consistent with earlier studies [21]. Figure 5 shows data at 545 nm and
526 nm. Attempts to fit to a single step process give a 3.1±0.3 ps time constant. Now, however, attempts to fit with the two-step mechanism with the first step fixed at 1.6 ps do not satisfactorily describe the data. The curve of 1.6 ps for the first step and 0.9 ps for the second step describes the early time portion of the data fairly well but all the curves show poor agreement at longer times. This finding led us to try the parallel pathway model with the superexchange rate being represented by k and the two-step process being described by $k_1$ and $k_2$. Figure 6 shows the fits for $k^{-1} = 3.3$ ps, $k_1^{-1} = 3.1$ ps and $k_2^{-1} = 3.2$ ps. The data are well described by this model and a series of simulations implies that the fractional contribution of the superexchange pathway is 50 ± 10%.

![Figure 5](image)

**Figure 5.** (a) Bleaching kinetics measured at 545 nm and 526 nm for *Rb. sphaeroides* R26 at 22 K. Excitation is at 870 nm. (b) Two-step model simulations of the 545 nm bleaching kinetics with a fixed first step time constant of 1.6 ps and a variable second step time constants of 0.6 ps, 0.9 ps and 1.5 ps.

![Figure 6](image)

**Figure 6.** Fit of the 545 nm data shown in Figure 5a with the parallel electron transfer pathway model. The time constants are $k^{-1}=3.3$ ps, $k_1^{-1}=3.1$ ps and $k_2^{-1}=3.2$ ps.

Very similar data were obtained in the *Rb. capsulatus* mutant Phe$\text{L}^{181} \rightarrow$ Tyr with again roughly equal contributions from the two mechanisms around 20 K. Our results provide a rather different picture of the temperature dependence of the
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decay of \( P^* \) than the conventional one. In this picture the increased decay rate of \( P^* \) at low temperature comes about from the onset of a second electron transfer channel rather than the increase in rate in a single process. In fact, both the initial and second steps slow down slightly in the sequential process. It is of some interest to discuss the temperature dependence of the rate constants, \( k, k_1 \) and \( k_2 \). Figure 7 shows relevant potential surfaces.

According to Bixon et al. [11] the superexchange rate constant \( k \) is

\[
k = \frac{2\pi}{\hbar} \left[ \frac{1}{4\pi\lambda_1 k_B T} \right]^{1/2} \left( \frac{V_{PB} V_{BH}}{\delta E} \right)^2 \exp\left(-\frac{E_a}{k_B T}\right)
\]

and the sequential rate constant \( k_1 \) is

\[
k_1 = \frac{2\pi}{\hbar} \left[ \frac{1}{4\pi\lambda_1 k_B T} \right]^{1/2} \left( \frac{V_{PB}^2}{1 + 4\pi V_{PB}^2 \tau_\rho / \hbar \lambda_1} \right) \exp\left(-\frac{E_{a_1}}{k_B T}\right)
\]

with an analogous expression for \( k_2 \). The \( T^{-1/2} \) terms in these expressions arise from the thermally averaged Franck-Condon factors at high temperatures (\( k_B T > 0 \)). Use of these expressions at 22 K is very likely beyond the range of their validity, however our purpose is simply to make qualitative comparison of the \( k \) and \( k_1 \) temperature dependence. From Figure 7 the simplest arrangement of the three surfaces that is consistent with our data is one in which \( E_a \) is zero and \( E_{a_1} \) has a small positive value. The superexchange rate should increase by roughly 3-4 fold from the \( T^{-1/2} \) term. A very small barrier for \( k_1 \) (\(< 50 \text{ cm}^{-1} \)) is sufficient to counteract the \( T^{-1/2} \) term over such a large temperature range. The second step of the consecutive process lies in the inverted region and the temperature dependence is more complex to predict. Experimental studies on model systems by Miller et al. [22] reveal a very weak temperature dependence in the inverted region consistent with our results. This over simplified analysis neglects changes in the electronic coupling and energy levels as the temperature is lowered and a full analysis will have considered these factors.
The fitting procedure described thus far did not include a reverse rate $k_1$ for the first step in the sequential process. This is equivalent to assuming that $\Delta G_1$ (Fig. 7) is negative so that the $P^+B'H \rightarrow P'BH$ process is uphill. If limits on $k_1$ can be obtained from the data then a rather precise value for the free energy differences of $P'BH$ and $P^+B'H$ can be given. Preliminary analysis suggests that at room temperature $k_1$ cannot be larger than 0.3 $k_1$, otherwise the mechanism reverts to a single step process and the data are poorly fit.

Finally, a comment on why photosynthetic systems require two separate ("peacefully coexisting" [11]) electron transfer mechanisms seems in order. One answer may be that it is not possible to have one without the other and still have efficient electron transfer. Secondly, the two processes, as noted by Bixon et al., allow stability of the electron transfer over a substantial range of energy gaps.

4. SOLVATION DYNAMICS ON FEMTOSECOND TIME SCALES.

The role of polar solvents in the dynamics of electron transfer reactions has been a topic of much interest over the past ten years [23-27]. Such studies have given impetus to direct experimental measures of solvation dynamics using the techniques of ultrafast spectroscopy. Accompanying the experimental work (see [25,27,28] for recent reviews) was a huge burst of theoretical activity aimed at developing molecular descriptions of solvation dynamics [29]. With the notable exception of van der Zwan and Hynes [30] the majority of the treatments did not consider any inertial contribution to the relaxation. In parallel with the experimental and theoretical studies a number of computer simulations of solvation dynamics have been carried out. These molecular dynamics simulations reveal the short-time portion of the solvent response which has been, until recently, inaccessible experimentally. Simulations in water [31], acetonitrile [32], methanol [33] and a methyl chloride like solvent [34] all reveal a 25-150 fs inertial component which contributes 60-80% of the solvent relaxation. It has been suggested that simulations, perhaps because of the neglect of polarizability or internal motions of the solvent, exaggerate the importance of the inertial component in the solvent response [35]. Very recently theoretical models incorporating inertial and viscoelastic effects have been developed by Chandra and Bagchi [36].

Van der Zwan and Hynes [30] showed that the time-dependent fluorescence shift correlation function, $C(t)$ [37] is directly proportional to the time-dependent dielectric friction:

$$C(t) = \zeta_D(t) / \zeta_D(0)$$

Simulations of $\zeta_D(t)$ for ions, ion pairs, electron and proton transfer and $S_N2$ reactions [38-42] reveal the time dependent friction to be dominated by a rapid inertial (Gaussian) component followed by a slow diffusive tail. Hynes and coworkers have demonstrated that chemical dynamics (e.g. transmission...
coefficients) are most strongly influenced by the short time behavior of the time dependent friction. Accordingly experimental verification of the importance of inertial contributions to solvent relaxation is highly desirable.

Experimentally the solvation correlation function \( C(t) \) is accessible from the time resolved fluorescence spectra via

\[
C(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}
\]

where \( v \) is some characteristic frequency such as the peak or the first moment of the spectrum [43]. For our initial set of studies we used the probe molecule LDS-750 dissolved in acetonitrile. Previous work has shown that LDS-750 in polar aprotic solvents gives structureless well behaved time resolved spectra [44]. Evidence for two emitting species has recently been presented by Blanchard [45] in butanol solution so that care in solvent choice is clearly necessary. Fluorescence decays were recorded for 11 wavelengths (approximately one decay for every 10-15 nm of the steady state emission spectrum). Each decay was collected with a 6.67 fs step size and Figure 8 shows a typical data set along with the instrument response function. The time evolving spectra are shown in Figure 9.

Figure 8. Upconversion data, fitted curves and residuals for fluorescence from LDS-750 in acetonitrile at 19°C. Left panel: 654 nm emission. Right panel: 779 nm emission. The instrument response function is also shown in the left panel and has a FWHM of 100 fs.
The solvation time correlation function was constructed from the individual fluorescence decays as described by Maroncelli and Fleming [43]. The result is shown in Figure 10. The solvation response clearly occurs on two time scales. The initial relaxation accounts for ~80% of the amplitude and is well fit by a Gaussian of 120 fs FWHM giving a 1/e decay time of 70 fs. The slower tail appears exponential and has a decay time of ~200 fs. This latter value is probably not well determined in these experiments.

The time resolution of our instrument allows us to be confident about the presence of the ultrafast component in the spectral evolution. In fact, multi-exponential fits to the individual data sets routinely reveal a component of about 60 fs. However, since our measurements are made with significantly higher time resolution than previous solvation studies it is important to consider other possible contributions to the spectral evolution. The most likely complication is that of vibrational relaxation. Excitation at 608 nm prepares \( S_1 \) of LDS-750 with about 1000 cm\(^{-1}\) of excess vibrational energy. For the dye molecules Nile Blue and Oxazine, Chesnoy et al. [1] have shown that excess energy in the range 500-1000 cm\(^{-1}\) leads to shifts of ~5 nm with relaxation times of 500 fs and 800 fs, respectively. These molecules do not have a change in dipole moment upon excitation and the spectral shift arises primarily from vibrational relaxation. The total shift in LDS-750 is more than 70 nm, 50 nm of which occurs in the first 100 fs. It seems difficult to suggest a mechanism other than that resulting from the Coulomb interaction that could induce such a large shift. We conclude, therefore, that the data presented in Figure 10 are dominated by polar solvation dynamics.
The physical origin of the two relaxation components has been discussed by Maroncelli [32], from the perspective of his molecular dynamics simulations. The simulation result for $C(t)$ is strikingly similar to that in Figure 10 with an initial Gaussian contribution accounting for 80% of the relaxation with a decay time of ~100 fs and a slower (mildly oscillatory) decay on a time scale of 0.5 to 1 ps. Maroncelli (private communication) has also carried out a simulation with coumarin 153 in acetonitrile. Here the oscillatory behavior observed (with a frequency of ~30 ps$^{-1}$) is far less prominent than in the small spherical ion simulations [32]. Maroncelli assigns the rapid part of the response to small amplitude inertial rotational motion of the molecules in the first solvation shell. By an elegant series of "rigid cage" simulations in which all except one solvent molecule are fixed in orientation he is able to show that this rapid relaxation results from independent single particle motion. The equilibrium dynamics of the single free molecule are followed and the appropriate correlation function constructed. The results are then averaged over all possible choices of the free molecule. The correlation function constructed in this way is indistinguishable from the full dynamics for the first 100 fs. The uncorrelated angular displacements are in the range of 10°-20° and it is simply the small amplitude of motion that accounts for the rapid relaxation [32]. Interaction between molecules only becomes important for times longer than 0.2 ps and by this time, in acetonitrile, most of the solvation energy is relaxed. The comparatively small amount of further relaxation results from diffusive restructuring of the first shell.

The large amplitude of the Gaussian component in the solvent response
has substantial implications for theoretical descriptions of chemical dynamics in solution. Solvent friction manifests itself in two ways in such dynamics. Firstly, solvent friction enters directly into electron transfer reaction rates, the connection between this friction and the solvation dynamics being made by Hynes [30]. For reactions with very small barriers $C(t)$ is the directly relevant quantity as emphasized by Barbara, Fonseca and coworkers [25,46,47]. When a significant barrier occurs the appropriate time dependent friction must be evaluated in the barrier region [39]. This is a difficult task in general but estimates may be made from $C(t)$ determinations on systems with the same electronic structure as the transition state [39]. Again, the inertial portion of $C(t)$ plays a major role.

Secondly, solvent friction may also impede nuclear motion, such as reorientation, via dielectric effects and again a connection exists between $C(t)$ and the time dependent dielectric friction [30]. This explanation has been explored experimentally [48] and in computer simulation of the reorientation of ion pairs [49]. The latter studies show that the normalized dielectric friction shows very similar time dependence to $C(t)$ and again has a major Gaussian component.

Thus, theories of chemical dynamics in polar liquids must include a full description of the time dependent solvent response - continuum and overdamped approximations are not likely to provide realistic descriptions.

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REFERENCES.

49 J.T. Hynes, Private communication.
DISCUSSION

Tominaga

From the static absorption and emission spectra, you can estimate the t=0s spectrum peak position very roughly, I think. My question is whether the predicted t=0 peak position is consistent with that observed experimentally.

Fleming

Yes, consistent. By estimating the t=0 peak position from the emission spectrum of LDS-750 in frozen acetonitrile we find the reconstructed t=0 peak position is consistent with the steady state estimate, within experimental error.

Tominaga

So it means that there is no more faster component than that observed.

Fleming

Yes.

Wasielewski

1. Holten's central argument for the one step superexchange model in reaction centers involves a physical inhomogeneity of reaction center samples as reflected in the 665 nm band. Do you see any wavelength dependent changes in kinetics across the Q x bands of the pheophytins?

2. Have you examined as yet any of the mutants with somewhat slower electron transfer kinetics? The ratio of 2 step to 1 step processes may change in these cases.

Fleming

1. We do not see evidence for heterogeneity in the fast step kinetics.

2. Not yet. This will be very interesting to look at.

Barbara

It is very interesting that you have observed a large amplitude (80%) fast component of solvation in acetonitrile for the dye LDS-750. We examined C(t) for a coumarine probe in the polar aprotic solvent propylene carbonate with an instrument response function of 200 fs at FWHM (which is about three times as long as your IRF). Our data did not exhibit a very short compound in C(t) although a component as much as 40% might have been missed. Assuming our resolution was sufficient, the message here might be that in bigger more massive solvents,
the inertial components are much less important than acetonitrile. Furthermore, if you consider the impact of the small amplitude fast components of solvation on solvent controlled small barrier ET in BA, you come to the conclusion from stochastic theories that the slower times still dominate picosecond time scale rate process, since the system must still traverse over a broad range of the solvent coordinate.

Fleming

It is clear from the optical Kerr data (OKE) that inertia plays a significant role for light polar liquids. Note the correspondence of the spectral density obtained by deconvolution of the OKE data of Lotshaw et al. and the spectral density fitted to our Stokes shift data. In addition we saw a very similar time constant (60 fs) for the librational modes in the OKE data for CHCl₃. In considering other solvents from the perspective of Mr. Cho's Langevin oscillator mode one needs to consider both the spectral density and the value of the friction constant γ. Different values of even for the same spectral density lead to different amplitudes for the inertial and diffusion contributions.

Tachiya

I would like to make a comment on Onsager's note you referred to. He made that comment in connection with the solvation of an electron, not an ion. In the case of electron solvation, the electron cloud is initially spreaded. It gradually contracts as the solvation proceeds. The longitudinal relaxation time is the relaxation time relevant to the step function change of the electric displacement. In the vicinity of the center the electric displacement gradually increases since the electron cloud flows in, and the solvent there relaxes in response to this gradual increase of the electric displacement. On the other hand, in the region far away from the center the time change of the electric displacement is the step function, and the solvent there relaxes in response to this change. So the solvation is established faster outside than inside. This effect was already pointed out by me (J. Chem. Phys. 66, 3056 (1977)) before Onsager. However, this effect does not apply to the solvation of an ion.

Fleming

You are correct that Onsager was referring to localization of an electron, not solvation of an ion. However, in reading his contemporaneous work with Hubbard on molecular solvation it seems that he believed that similar concepts apply to molecular phenomena. Further information on this topic may be found in an exchange of letters to Physics Today between Gordon Freeman (Edmonton) and Peter Wolynes and myself. (ref. Physics Today 1990 Nov.)

Jortner

A very interesting problem in the area of time–resolved solvation phenomena involves the solvation dynamics of an excess electron in polar liquids. While
solvation dynamics of an ion or a dipole occurs on a single adiabatic potential surface, the electron solvation dynamics may involves nonadiabatic transitions between different electronic states. This state of affairs is similar to electron–hole recombination in semiconductors, which was explored since the pioneering studies of Kubo and Toyozawa. This process seems to involve an initial electron trapping in highly excited electronic states followed by radiationless decay to lower lying electronic configurations. A similar state of affairs pertains to the solvation dynamics of an excess electron in polar solvents, where cascading between electronically excited states occurs, resulting in the interplay between nonadiabatic electronic relaxation and adiabatic solvent relaxation in several electronic states. The multistate description of electron solvation in alcohols by Hirata and Mataga and in water by Migus et al. and by Eisenthal et al. are consistent with this cascading picture. Quantum molecular dynamics simulations of electron localization in water by Rossky et al. also address this issue.

**Fleming**

Thank you.

**Hynes**

Concerning Professor Barbara's comment on inertial Gaussian behavior being less important for more massive solvents: The Gaussian decay rate scales inversely with the square root of the solvent mass [see my contribution to the Proceedings]. The slower decay for more massive solvents allows other, dissipative processes to take over sooner in time, thereby indeed reducing the importance of the Gaussian inertial dephasing.

**Fleming**

I agree. I would, however, like to comment that the Gaussian decay comes from the destructive interference between many frequencies. The net result can be described by a single (“average”) frequency and assigned a mass.

**Mukamel**

1. Your discussion of the applicability of the Brownian oscillator model to the optical Kerr effect is a beautiful demonstration of the nonlinear response function for the multimode Brownian oscillator model which can be calculated exactly [Y. J. Yan and S. Mukamel, J. Chem. Phys., 89, 5160 (1988)] and applies to any four wave mixing process. The stochastic model of line broadening is a special case of the Brownian oscillator model. That model neglects, however, the effects of solvent reorganization (since the stochastic motion is independent on the electronic state of the system) and therefore completely misses the time dependent Stokes shift. In addition it is restricted to the overdamped limit.

2. A careful analysis of the superexchange model using the density matrix shows that in general it is not possible to separate the electron transfer mechanism into a
sequential and a superexchange contributions. Interference terms of mixed origin show as well. (Y. Hu and S. Mukamel, J. Chem. Phys. 91, 6973 (1989)) Also, that work shows a complete analogy of the sequential/superexchange branching and the Fluorescence/Raman branching in electronic spectroscopy. The two calculations are mathematically identical. As the electronic dephasing rate is decreased, the Raman component becomes dominant. The dominance of the superexchange mechanism at lower temperatures may therefore be viewed as a consequence of the reduced dephasing rate with temperature.

Fleming

1. Thank you. The short time behavior in the optical Kerr effect appears to be well described by an inhomogeneous distribution of molecular oscillators. The long time behavior (>2 ps) requires inclusion of diffusive reorientation or slow structural reorganization of the liquid. Our major point is once the short Kerr response can be understood via Brownian oscillators, the response of the solvent to a step function change in the electronic nature of a solute can be understood on the same basis.

2. Our model is based on a weak coupling rapid dephasing approximation. In this limit I believe it is possible to distinguish between direct (superexchange) and sequential mechanisms. When the coupling matrix elements and relaxation times are better characterized (e.g. by non-linear spectroscopy) it will be very interesting to see over what range the Golden rule approach is applicable.