Solvation dynamics for an ion pair in a polar solvent: Time-dependent fluorescence and photochemical charge transfer

Emily A. Carter and James T. Hynes

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

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The results of a molecular dynamics (MD) computer simulation are presented for the solvation dynamics of an ion pair instantaneously produced from a neutral pair, in a model polar aprotic solvent. These time-dependent fluorescence dynamics are analyzed theoretically to examine the validity of several linear response theory approaches, as well as of various theoretical descriptions (e.g., Langevin equation) for the solvent dynamics per se. It is found that these dynamics are dominated for short times by a simple inertial Gaussian behavior, a feature which is absent in many current theoretical treatments, and which is related to the approximate validity of linear response theory. Nonlinear aspects, such as an overall spectral narrowing, but a transient initial spectral broadening, are also discussed. A model photochemical charge transfer process is also briefly considered to elucidate aspects of the connection between solvation dynamics and chemical kinetic population evolution.

I. INTRODUCTION

The theoretical and experimental study of solvation dynamics has seen an explosive growth in recent years. This intense interest stems both from the accessibility of direct experimental scrutiny via picosecond and subpicosecond time-dependent fluorescence and the potential importance of these dynamics in heavy particle charge transfer reactions and electron and proton transfers in solution.

In this paper, we present a molecular dynamics (MD) simulation study of the solvation dynamics of an ion pair instantaneously created from a neutral pair, in a dipolar aprotic solvent. Such simulations are a useful tool in assessing the validity of approximate theoretical descriptions, as well as a source of microscopic insight for the interpretation of experiment (and theory).

Our attention is focused on the time-dependent fluorescence spectral frequency shift and emission spectrum as probes of solvation dynamics, and we attempt to place the MD results in theoretical perspective, with an eye toward experimental consequences. In particular, we establish the major role played by a simple inertial Gaussian time behavior, point out its absence in many popular theoretical treatments, and indicate its assistance in the approximate validity of a linear response treatment. We also discuss some nonlinear aspects of the problem, including an overall spectral narrowing—due to solute-dependent solvent force constants, as well as transient spectral broadening and solute-dependent solvent friction.

We also briefly consider a closely related model photochemical reaction. Our emphasis here is on the relation between the solvation dynamics and the chemical kinetic aspects of the reaction.

The outline of this paper is as follows. In Sec. II, we describe the model and simulation procedures, and present the simulation results. In Sec. III, we interpret the results in terms of linear response descriptions and examine the applicability of a Langevin equation for the solvent coordinate. Here we also demonstrate that a significant fraction of the relaxation can be simply accounted for by short time Gaussian behavior. Section IV is devoted to examination of some details of the molecular trajectories, while Sec. V concludes. Some particular results of our study have been published previously.

II. MODEL DESCRIPTION AND SIMULATION RESULTS

A. Solute and solvent description

We will consider a donor–acceptor solute pair (SP) DA, where D = A, immersed in a solvent of rigid dipolar molecules. This SP will alternately be assigned point charges of zero or plus and minus e, respectively, at the atomic D and A site centers to represent a ground electronic state neutral pair (NP) DA and an electronically excited ion pair (IP) D+ A−. The constituent members of the SP each have mass 40 amu; their centers are rigidly separated by 3.0 Å, but other by a fixed distance of 2.0 Å and with partial charges such that the dipole moment is 2.4 D. The number density is 0.012 Å−3 and the temperature is 250 K. This solvent, which is very roughly similar to methyl chloride, is similar to members of the class of dipolar aprotic solvents currently under experimental investigation for solvation dynamics and charge transfer reactions.

The solvent is composed of 342 rigid dipolar molecules with constituent atoms of mass 40 amu separated from each other by a fixed distance of 2.0 Å and with partial charges ± q such that the dipole moment is 2.4 D. The number density is 0.012 Å−3 and the temperature is 250 K. This solvent, which is very roughly similar to methyl chloride, is similar to members of the class of dipolar aprotic solvents currently under experimental investigation for solvation dynamics and charge transfer reactions.

The total potential energy of interaction U consists of Lennard-Jones and Coulomb potentials

\[ U(r_{ij}) = U_{LJ}(r_{ij}) + Z_i Z_j r_{ij}^{-1} \]  

between each atomic site, with Z, the change on site i. The LJ
parameters are $\epsilon/k_B = 200$ K and $\sigma = 3.5$ Å for each site in the SP and the solvent molecules.

The Hamiltonian of the ground-state NP and the excited-state IP systems are, respectively,

$$H_g = H_{NP}^0 + H_{NP}^0 + H_s + U_{NP,S};$$

(2.2)

$$H_e = H_{IP}^0 + H_{IP}^0 + H_s + U_{IP,S},$$

(2.3)

Here $K_{NP}$ and $K_{IP}$ are the Hamiltonian, comprising the translational and rotational kinetic energies, of the rigid isolated NP and IP solutes, while $H_{NP}^0$ and $H_{IP}^0$ are corresponding constant electronic energies, which include all internal potential energies in the solute pairs. We take

$$\hbar \omega = H_{NP}^0 - H_{NP}^0,$$

(2.4)

to be a positive number, consistent with the excited electronic character of the IP state. The solvent Hamiltonian, including kinetic and potential energy, is $H_s$. Finally, $U_{NP,S}$ is composed of Lennard-Jones interactions between the solvent molecules and the members of the NP, while

$$U_{IP,S} = U_{NP,S} + \Delta E,$$

(2.5)

is the total interaction potential energy between the solvent molecules and the charged members of the IP; $H_e - H_{IP}^0$ thus differs from $H_g - H_{NP}^0$ by the Coulombic potential energy

$$\Delta E = U_{IP,S} - U_{NP,S}$$

(2.6)

of interaction between the charged ions in the IP and the point charges embedded in each of the finite dipolar solvent molecules. It is this energy difference or gap which concerns us in all that follows.

In the point dipole approximation for solvent molecules, $\Delta E$ would be given by

$$\Delta E = -\int dr \mathbf{P}(r) \cdot \left[ \mathbf{E}_A^0 (r - r_A) + \mathbf{E}_B^0 (r - r_B) \right],$$

where $\mathbf{P}(r)$ is the solvent orientational polarization at position $r$ in the solvent and $\mathbf{E}_A^0(r - r_A)$ is the vacuum electric field at $r$ due to ionic sites in the IP. This is in fact the conventional dielectric continuum limit solvent coordinate employed in a number of analytic studies, which are thereby restricted to accounting for the solvent solely via its point polarization field. (The difficulties with this approximation for water are clearly apparent in Ref. 8.) In the present work, however, we employ the full microscopic definition Eq. (2.6) of $\Delta E$. Nonetheless, this indicates that $\Delta E$ is the microscopic solvent coordinate, a perspective also exploited in other studies.

It is worth mentioning here that there are no electronic polarization effects included in either the model solute or solvent. In real systems, such effects would contribute, in a static way, to solvent shifts. These are completely ignored in the present work.

1. **Time-dependent fluorescence**

According to the Franck-Condon principle, the SP and solvent nuclei remain fixed in a fluorescence transition. The instantaneous fluorescent frequency, averaged over the initial conditions, is, from Eqs. (2.2)-(2.6), given by (cf. Fig. 1)

$$\bar{\hbar} \omega (t) = \overline{H_e (t)} - \overline{H_g (t)}$$

$$= \hbar \omega^0 + \overline{\Delta E (t)}.$$  

(2.7)

Thus the dynamics of $\bar{\hbar} \omega (t)$ are governed by the average solvent-excited state IP Coulomb interaction $\overline{\Delta E (t)}$; this will become more negative as the solvent equilibrates to the IP by transiting downward in the IP well. Note that by the Franck-Condon principle, the average energy difference between the (nonequilibrium) free energies of the excited and ground states; there is no entropy change in a transition occurring at fixed nuclear coordinates.

It is convenient to define two measures of this TDF frequency which are independent of the gas-phase frequency $\omega^0$. The first is the dynamic average TDF red shift

$$\delta \hbar \omega (t) = \hbar \omega (t) - \hbar \omega^0 = \overline{\Delta E (t)},$$

(2.8)

and the second is the normalized TDF shift

$$S(t) = \frac{\delta \hbar \omega (t) - \delta \hbar \omega (\infty)}{\delta \hbar \omega (0) - \delta \hbar \omega (\infty)},$$

(2.9)

which characterizes the equilibration in the excited state as $\overline{\Delta E (t)}$ relaxes from its initial value of $\overline{\Delta E (0)}$ to its final equilibrium value $\overline{\Delta E (\infty)}$. [This quantity is termed “$C(t)$” in a number of studies.] Both these measures have been examined in experimental TDF studies.

2. **Photochemical charge transfer**

Our discussion above was appropriate for the TDF problem. We now shift to the perspective of a model photo-
chemical charge transfer reaction, illustrated in Fig. 2. We hasten to stress that such a model is ultrasimplified. A transition from a nonpolar ground state leading to a chemically distinct charge transfer (IP) state will typically occur by initial transition to a locally excited (LE) nonpolar state which is electronically coupled to the IP state. Figure 2 corresponds to the very idealized case where the LE–IP state electronic coupling is very strong and there is no barrier on the upper surface. Our sole purpose for considering the situation depicted in Fig. 2 in the photochemical context is to explore, in the simplest case, the question of the connection of the solvation dynamics per se to the chemical kinetic aspects of the problem, a topic of considerable current interest.\(^1, 10, 11, 20, 21\)

In this case, we can view the role of the frequency \(\hbar \omega \) in the TDF problem to be played by the intrinsic free energy difference

\[
\Delta G^0_{\text{INT}} = H^0_{\text{IP}} - H^0_{\text{NP}} - T\Delta S^0_{\text{INT}}
\]

is the charge shift reaction problem. This internal difference accounts for electronic energy and entropy differences in the isolated IP and NP species, exclusive of solvation free energetic terms. In this case, the essential point is that Eqs. (2.8) and (2.9) provide descriptions of the solvent coordinate time dependence as the nascent IP becomes solvent-equilibrated product after laser excitation from the NP reactant. As discussed in more detail in Sec. III B, this variable gauges the product relaxation insofar as the IP curve illustrated in Fig. 2 is dynamically followed; i.e., no electronically nonadiabatic transition IP → NP occur at the crossing point of the two curves to regenerate the reactant NP.

B. Simulation results

Constant temperature\(^2\) MD simulations were carried out in a periodically replicated cubic box with sides of length 30.52 Å. The integration of the equations of motion was effected via the Verlet algorithm\(^3\) and a time step of \(10^{-2}\) ps. The long range forces were treated by using the Ewald summation method,\(^3\) and the bond constraints for the SP and solvent molecules were implemented with the SHAKE algorithm.\(^3\)

The TDF characteristics Eqs. (2.8) and (2.9) are obtained with a nonequilibrium MD simulation as follows. We focus first on the average dynamic red shift \(\Delta \overline{\omega}(t)\), Eq. (2.8). The NP-solvent system is first equilibrated for 10 ps. The \(\Delta \overline{\omega}\) sampling was performed every 0.1 ps. \(\langle \Delta \omega \rangle_{\text{NP}} = -91.5\) cm\(^{-1}\) with a width of \(\sigma_{\Delta \omega, \text{NP}} = \pm 1.804\) cm\(^{-1}\), while \(\langle \Delta \omega \rangle_{\text{IP}} = -17.659\) cm\(^{-1}\) with a width of \(\sigma_{\Delta \omega, \text{IP}} = \pm 1.456\) cm\(^{-1}\).
The time-dependent red shift Eq. (2.8) is generated by averaging \( \Delta E \) over 198 trajectories at different subsequent times. The result is shown in Fig. 4(a).

The overall dynamics exhibited by the TDF red shift are fairly rapid, and are distinctly bimodal in time. In particular, there is an extensive initial rapid shift of \( \approx 12 \text{,000 cm}^{-1} \) in ~0.3 ps, followed by a much slower relaxation of some further \( \approx 6 \text{,000 cm}^{-1} \), as the solvent ultimately equilibrates to the IP. In a separate simulation of 410 ps duration (after a 10 ps equilibration), the equilibrium distribution of \( \Delta E \) for the solvent in the presence of the IP was determined and is displayed in Fig. 3 (b). Again, as for the NP case, the distribution is fairly Gaussian, but this time is centered about the IP equilibrium average \( \langle \Delta E \rangle_{IP} = -17 \text{,660 cm}^{-1} \); this highly negative value reflects the strongly attractive IP-solvent Coulomb interactions. The distribution is also more narrow than in the NP case, indicating a higher degree of order for the solvent molecules imposed by the Coulomb forces (\textit{vide infra}). Finally, comparison of this \( \langle \Delta E \rangle_{IP} \) value with the long-time average red shift in Fig. 4(a) indicates that equilibration has indeed occurred in the nonequilibrium dynamics.

The relaxation dynamics are presented in the more compact format of the TDF shift function \( S(t) \), Eq. (2.9), in Fig. 4 (b). Again (and of course), the bimodal time-decay character is quite apparent.

More details of the relaxation can be gleaned from other probes not often examined. Inspection of Fig. 3(a) and 3(b) shows that the initial \( \Delta E \) probability distribution—appro...
appropriate for solvent in equilibrium with the NP—is wider than the final distribution—appropriate for equilibrium with the IP. This suggests that the TDF spectrum should exhibit an overall narrowing with time as solvent equilibration to the IP proceeds. We now examine this.

We can formally define the time-dependent red shift spectrum for the distribution \( \delta \tilde{\omega}(t) \) by

\[
I(t,\Delta \epsilon) = \delta(\Delta E(t) - \Delta \epsilon), \tag{2.12}
\]

where \( \Delta \epsilon \) now represents the numerical value of the red shift \( \delta \tilde{\omega} \). We can approximately determine this spectrum by constructing histograms of the observed numerical values \( \Delta E \) of the microscopic dynamical variable \( \Delta E \) at various stages of the relaxation. A number of these are exhibited in Fig. 5. While an overall narrowing trend with time is indeed observed (and this is the major point), there is a discernible initial broadening, and subsequent narrowing, of the red shift spectrum at early times. This is exposed more clearly in Fig. 6 where we display the time-dependent square “width” function

\[
W(t) = \Delta E^2(t) - [\Delta E(t)]^2 \tag{2.13}
\]

for the spectrum. Here the transient broadening followed by a subsequent narrowing is clearly visible. As we will see in Sec. III, the dynamics of \( W(t) \) is entirely governed by nonlinear effects, while the major aspects of the TDF shift \( S(t) \) can be comprehended quite well within a linear framework.

III. THEORETICAL ANALYSIS

In this Section, we provide some theoretical analyses of the simulation results of Sec. II. We discuss in turn the TDF nonequilibrium solvation dynamics in terms of solvation dynamics in equilibrium, and the special issues arising in the photochemical charge transfer case. We then address a Langevin equation description, and finally a short time Gaussian approximation.

A. TDF shift and spectral width

1. Equilibrium time correlation functions and TDF shift

Two forms of what we will call linear response theory may be employed to attempt to connect the nonequilibrium normalized TDF shift \( S(t) \) to equilibrium time correlation functions. In the early linear response treatments of TDF based on a solvent continuum approach,\(^{15-17}\) such a distinction was unnecessary. But as we will see, the distinction is highly relevant for the interpretation of the MD results. In the first linear response treatment, the system initially in equilibrium is subject to a step perturbation at \( t = 0 \), here given by

\[
H'(t) = (\tilde{\omega} + \Delta \epsilon) \theta(t), \tag{3.1}
\]

where \( \theta(t) \) is the step function. This represents the instantaneous Franck-Condon transition to the electronically excited IP state. The average of any observable is then calculated to first order in this perturbation and, as a consequence, is expressed in terms of an equilibrium tcf in the absence of the perturbation. In the present case, this standard procedure\(^{35} \) yields the relation

\[
\delta \tilde{\omega}(t) \quad \delta \tilde{\omega}(\infty) = \beta(\Delta E \Delta E(t))_{NP} \tag{3.2}
\]

involving the tcf of \( \Delta E \) in the ground, NP state, with \( \beta = (k_B T)^{-1} \). The corresponding result for \( S(t) \) is then

\[
S(t) - (\Delta E \Delta E(t))_{NP} = S_{NP}(t) \tag{3.3}
\]

for the spectrum. Here the transient broadening followed by a subsequent narrowing is clearly visible. As we will see in Sec. III, the dynamics of \( W(t) \) is entirely governed by nonlinear effects, while the major aspects of the TDF shift \( S(t) \) can be comprehended quite well within a linear framework.

To begin, we write the nonequilibrium average of \( \Delta E \) for \( t > 0 \) as

\[
\overline{\Delta E}(t) - \int d\Gamma \rho(t) \Delta E = \int d\Gamma (e^{-it\rho_{eq,e}}) \Delta E \\
= \int d\Gamma \rho_{eq,e} \Delta E(t), \tag{3.5}
\]

in which \( iL \) is the Liouville operator \( iL = \{H_e, \} \) appropriate for dynamics in the presence of the IP; \( \Delta E(t) \) is the value of \( \Delta E \) at time \( t \) calculated with those dynamics. Next, since by Eq. (2.6), the difference of excited- and ground-state Hamiltonian is \( H_e - H_g = \tilde{\omega} + \Delta E \), we can write the NP state equilibrium distribution \( \rho_{eq,g} \), Eq. (3.4), in terms of the IP equilibrium distribution \( \rho_{eq,e} \), Eq. (3.6), to give the nonequilibrium average of \( \Delta E \) in the form

\[
\rho_{eq,e} = \frac{e^{-\beta H_e}}{\int d\Gamma e^{-\beta H_e}}, \tag{3.6}
\]

where \( \Gamma \) denotes the totality of phase space coordinates and momenta. But on the other hand, Eqs. (3.2) and (3.3) refer to dynamics, e.g., of the solvent, in the presence of the uncharged NP, whereas in fact the solvent dynamics actually occur in the presence of the charged IP. A shift to this latter perspective on the dynamics gives a second and in principle different “linear response” theory approach, which we now describe.

![Fig. 6. Simulated time-dependent square width function \( W(t) \) [Eq. (2.13)], computed every 0.1 ps from 198 trajectories.](image-url)
\[ \Delta E(t) = \langle e^{\beta \Delta E(t)} \rangle_{IP}, \quad (3.7) \]

where \( \langle \cdots \rangle_{IP} \) denotes the IP excited-state equilibrium average, i.e., with distribution \( \rho_{\text{eq}} \). Expansion of \( \exp(\beta \Delta E) \) through first order in \( \Delta E \) then gives for the average TDF shift the relation

\[ \delta \bar{S} \overline{\Delta E}(t) - \delta \bar{S} \overline{\Delta E}(\infty) = \beta \langle \Delta E \delta E(t) \rangle_{IP}, \quad (3.8) \]

and for the normalized TDF shift

\[ S(t) = \frac{\langle \Delta E \delta E(t) \rangle_{IP}}{\langle (\Delta E)^2 \rangle_{IP}} \equiv \Delta_{IP}(t) \quad (3.9) \]

involving the normalized equilibrium tcf of \( \delta E \) in the excited, IP state [in contrast to Eqs. (3.2) and (3.3)]. We can view Eqs. (3.8) and (3.9) as correctly incorporating the feature that the dynamics occur under the influence of the excited state IP Hamiltonian, but with the approximation that the distribution of initial conditions—which should in fact be those appropriate to the NP—is perturbatively described.

We now have two separate linear response theory results for the TDF shifts \( S(t) \). In a linear dielectric continuum theory,\textsuperscript{15-17} there is no distinction between them. But at a molecular level, they can differ, as first empirically established by Maroncelli and Fleming\textsuperscript{8} for simulated ion solvation in water. We note in passing that the relation Eq. (3.9) has been termed an “Onsager linear regression hypothesis,”\textsuperscript{10-12} and indeed this perspective follows naturally from a focus on relaxation in a nonequilibrium ensemble.\textsuperscript{35} We have emphasized here the (previously unstated) critical physical issues of the different approximations in Eqs. (3.3) and (3.9) for the initial conditions and the dynamics, in order to provide an interpretation below of the simulation results now described.

Figure 7 shows the calculated normalized nonequilibrium TDF shifts compared to the two calculated equilibrium tcf's \( \Delta_{sp}(t) \). (The latter are determined in separate equilibrium simulations of 410 ps duration after a 10 ps equilibrium period.) Both the ground NP state-based tcf \( \Delta_{sp}(t) \) and the excited IP state-based tcf \( \Delta_{IP}(t) \) are in close agreement with \( S(t) \) at short times, while \( \Delta_{IP}(t) \) is clearly in better consonance with the nonequilibrium shift dynamics at longer times. [A similar phenomenon was observed by Maroncelli and Fleming,\textsuperscript{8} who, however, did not discuss the basis for their analog of Eq. (3.9).] This tells us first that the feature that the NP initial conditions are correctly incorporated in \( \Delta_{np}(t) \)—but not in \( \Delta_{IP}(t) \)—appears to have surprisingly little impact on the short time dynamics. It also tells us that a central feature of the longer time relaxation dynamics is its dependence on the presence of the charged IP solute.

From the broader perspective, it is somewhat remarkable that the agreement between \( S(t) \) and, e.g., the linear response approximation \( \Delta_{IP}(t) \) is so good, given the fact that \( \Delta E(t) \) is changing by some 18,000 cm\(^{-1}\). Similar applicability of linear response approximations has been observed in other simulations.\textsuperscript{5,10-14} Our discussion in Sec. III D below sheds some light on this phenomenon.

We will fasten our attention in Secs. III C and III D below on examination of the TDF shift, exploiting this approximate linearity. But first we will explore the nonlinear characteristics of the phenomenon. The deviation from linear behavior is much more clearly exposed in the spectrum, Fig. 5, and in particular, in the square width function \( W(t) \), Eq. (2.12) and Fig. 6. This is worth some inspection, now undertaken.

### 2. Dynamic spectral width

To begin, we note that the Gaussian character of the \( \Delta E \) distributions in Figs. 3(a) and 3(b) indicates that there are, to a good approximation, harmonic free energy curves governing fluctuations in \( \Delta E \) for both the NP and IP cases. In particular, the formal definition for the probability \( P_{sp}(\Delta e) \) that \( \Delta E \) assumes the numerical value \( \Delta e \) in a solvent fluctuation in the presence of a given solute pair (SP) is

\[ P_{sp}(\Delta e) = \langle \delta(\Delta E - \Delta e) \rangle_{sp}, \quad (3.10) \]

where \( \delta \) denotes the delta function. By Fourier representation of the delta function and a second-order cumulant expansion, the harmonic free energy becomes explicit as

\[ P_{sp}(\Delta e) \propto \exp \left[ -\frac{(\Delta e - \langle \Delta e \rangle_{sp})^2}{2(\langle \Delta E - \langle \Delta E \rangle_{sp} \rangle_{sp})^2} \right]. \quad (3.11) \]

![FIG. 7. Normalized nonequilibrium TDF shift function \( S(t) \) (solid lines) and simple linear response theory approximations (dashed lines) to \( S(t) \): the normalized equilibrium time correlation functions (a) \( \Delta_{IP}(t) \) and (b) \( \Delta_{np}(t) \); see Eqs. (3.3) and (3.9). The \( \Delta_{sp}(t) \)'s were each computed every 0.1 ps over 410 ps equilibrium trajectories in separate calculations.](image)
We can use this in turn to define a solvent force constant

\[ k_{SP} = \frac{1}{\Delta_0} \left[ \beta \langle (\Delta E)^2 \rangle_{SP} \right]^{-1} \]

(3.12)

\[ \Delta_0 \equiv \Delta E - \langle \Delta E \rangle_{SP} \]

associated with the harmonic free energies. Figures 8(a) and 8(b) display these free energy curves. It is especially noteworthy that \( k_{IP} > k_{NP} \), i.e., the solvent force constant depends on the solute. The fluctuations in \( \Delta E \) about the average value are more difficult in the presence of the charged IP compared to the uncharged NP. This nonlinear aspect, which we have described in more detail elsewhere, is consistent with the picture that, for this system, the nearby polar solvent molecules are more highly ordered in the presence of the IP charges. In earlier work, we have explored the consequences of this solute dependence of the solvent force constant for the activation energy patterns for electron transfer reactions, and contrasted the estimated magnitudes of such effects with the very much larger values previously suggested by Kakitani, Mataga, and co-workers.

The function \( W(t) \) governs the square width of the time evolving spectrum \( I(t, \Delta E) \), Eq. (2.11); indeed, application to Eq. (2.11) of the procedures used to derive Eq. (3.11) yields the Gaussian approximation

\[ I(t, \Delta E) = (2\pi W(t))^{-1/2} \exp \left\{ -\frac{(\Delta E - \Delta E(t))^2}{2W(t)} \right\} \]

(3.13)

If we develop the averages in Eq. (2.12) up to second order in \( \Delta E \), using Eq. (3.7) for \( \Delta E(t) \) and its analog for \( \Delta E^2(t) \), we obtain

\[ W(t) = W(\infty) + \beta C_{12}(t) + \frac{\beta^2}{2} \left[ C_{22}(t) - 2C_{11}(t) \right] + \langle \Delta E \rangle_{IP} C_{12}(t) \]

(3.14)

where the final equilibrium square width is

\[ W(\infty) = \langle \Delta E^2 \rangle_{IP} - \langle \Delta E \rangle_{IP}^2 \]

(3.15)

with our IP solvent force constant definition (3.12). Here we have defined the assorted time correlation functions

\[ C_{11}(t) = \langle \langle \delta \Delta E \rangle_{IP} \Delta_{1r}(t) - \langle \delta \Delta E \delta \Delta E(t) \rangle_{IP} \rangle \]

\[ C_{12}(t) = \langle \delta \Delta E \delta \Delta E(t) \rangle_{IP} \]

\[ C_{22}(t) = \langle \langle \delta \Delta E \rangle_{IP} \Delta_{2r}(t) - \langle \delta \Delta E \rangle_{IP}^2 \rangle \]

(3.16)

all of which vanish as \( t \to \infty \).

The first nonlinear aspect of the spectrum Fig. 5 is its overall narrowing with time. From Eqs. (3.14)–(3.16) and (3.12), the degree of narrowing in the square width is

\[ W(0) - W(\infty) = (\beta k_{NP})^{-1} - (\beta k_{IP})^{-1} \]

(3.17)

where we have assumed that the IP-solvent free energy is symmetric, even though it is anharmonic to some degree. There are several points we need to make. First, the overall narrowing arises from the larger solvent force constant in the IP state compared to the NP state—the equilibrium distribution is more narrow in the former than in the latter. This narrowing amounts to a change of several hundred cm\(^{-1}\) out of several thousand cm\(^{-1}\) in the width. (Our inference that the NP–IP force constant size could be reversed in water suggests that an overall spectral broadening could occur in that solvent.) It is interesting to note that spectral narrowing has been experimentally observed by Maroncelli and Fleming and by Simon and Su (though it is not clear what role might be played in those systems by vibrational contributions). Second, this narrowing is a completely nonlinear effect: for if the free energy \( G_{IP} (\Delta E) \) for the IP were perfectly harmonic and the corresponding equilibrium distribution \( P_{IP} (\Delta E) \) were perfectly Gaussian, then \( k_{IP} = k_{NP} \) and Eq. (3.17) shows that there would be no narrowing. [The same statement applies to \( G_{NP} (\Delta E) \) and \( P_{NP} (\Delta E) \).] Third, and finally, the entire time dependence of \( W(t) \) arises from nonlinear effects. This follows of course from the second point just made, and in more detail from Eq. (3.14). It is easy to show that for a linear Gaussian system, the tcf relations \( C_{11}(t) = C_{22}(t) = 2C_{12}(t) = 0 \) hold, and there is no dynamic narrowing and indeed no change at all in the width. The transient initial broadening prior to ultimate narrowing observed in Fig. 6 (and Fig. 5) arises from the nonlinear tcf’s in Eq. (3.14); each term in the series displayed rises from zero and ultimately decays to zero. We have attempted to find a simple connection between the ini-
tional transient broadening reflected in $W(t)$ and the deviation of the TDF shift $S(t)$ from its linear approximation, $\Delta_t(t)$ [most apparent in Fig. 7(a) in the 0.25–0.5 ps range], involving only the leading order nonlinear $\Delta E$ tcf $C_{12}(t)$ in Eqs. (3.14):

$$W(t) - W(0) \approx W(\infty) - W(0) + \beta [ C_{12}(t) - C_{12}(0) ].$$

(3.18)

Unfortunately this attempt fails, strongly indicating that the short time transient broadening phenomenon in Fig. 6 is not at all simple in character. We return this question in Sec. IV.

\section*{B. Photochemical reaction}

In the photochemical reaction case (Fig. 2), a natural focus of attention would be on the rate of appearance of the product IP population in the IP well, subsequent to initial excitation from the NP well. Here we assume that any electronic coupling between the NP and IP curves is sufficiently small, and that the passage through the curve crossing region is sufficiently fast; a Landau–Zener perspective then indicates that passage into the IP product well will occur without any electronically nonadiabatic back passage to the NP well.

In the initial Franck–Condon excitation, the initial nearly Gaussian $\Delta E$ distribution in the equilibrated NP well will be transferred up to the repulsive IP curve. This distribution, which will call a “thermal packet,” will then evolve in $\Delta E$ under the influence of the electrostatic forces on the solvent originating from the charged IP solute and will descend into the IP well. We canouch the description of the dynamics of the reaction process in chemical kinetic terms by suitable definitions of the thermal packets to be associated with the reactant and product. The latter plainly should reflect the population near the IP well minimum. The former can be defined by imagining that a suitable laser dump pulse arrangement could transfer, at any time $t$, any residual population on the upper IP surface in the initially FC populated IP region back down to the NP well. In such a (highly idealized) conception, the “reactant” population would be defined by the thermal packet still residing at time $t$ on the IP curve in the neighborhood of the $\Delta E$ values appropriate to the thermal population of the NP well. In effect, this reactant population is the overlap of the thermal packet on the IP surface evolving from the initial FC packet, translated up from the thermal NP distribution, with that thermal NP distribution.

We will extract these product and reactant thermal packets as follows. Rather than use the “exact” MD-generated time-dependent spectrum for this purpose, we employ the time-dependent Gaussian approximation $I(t;\Delta e)$, Eq. (3.13), in terms of the MD-simulated average $\Delta E(t)$ and time dependent square width $W(t)$. To define the “product” population $P_{\text{IP}}(t)$, we integrate $I(t;\Delta e)$ over the region in $\Delta e$ containing most of the equilibrium product distribution $P_{\text{IP}}^{\infty}(\Delta e)$, centered at $(\Delta e)_{\text{IP}}$, with a width $w_{\text{IP}} = 2\sqrt{W(\infty)}$:

$$P_{\text{IP}}(t) = \int_{-w_{\text{IP}}}^{w_{\text{IP}}} I(t;\Delta e) \, d\Delta e;$$

$$\Delta e_{\text{IP}} = (\Delta E)_{\text{IP}} \pm w_{\text{IP}}.$$  

(3.19)

This gives us the formula

$$P_{\text{IP}}(t) = \left[ \frac{2 \text{erf}(w_{\text{IP}}/[2W(\infty)]^{1/2})}{[2W(t)]^{1/2}} \right] - \left[ \frac{\text{erf}\left(\frac{w_{\text{IP}} + (\Delta E)_{\text{IP}}(1 - S(t))}{2W(t)}\right)}{[2W(t)]^{1/2}} \right] - \left[ \frac{\text{erf}\left(\frac{-w_{\text{IP}} + (\Delta E)_{\text{IP}}(1 - S(t))}{2W(t)}\right)}{[2W(t)]^{1/2}} \right],$$

(3.20)

where erf is the error function, $S(t)$ is the MD shift, $W(t)$ is the MD square width function, and $W(\infty) = (\beta k_{\text{IP}})^{-1}$.

The corresponding expression for the initial “reactant” distribution is

$$P_{\text{NP}}(t) = \left[ \frac{2 \text{erf}(w_{\text{NP}}/[2W(0)]^{1/2})}{[2W(t)]^{1/2}} \right] - \left[ \frac{\text{erf}\left(\frac{w_{\text{NP}} - (\Delta E)_{\text{IP}}(1 - S(t))}{2W(t)}\right)}{[2W(t)]^{1/2}} \right] - \left[ \frac{\text{erf}\left(\frac{-w_{\text{NP}} - (\Delta E)_{\text{IP}}(1 - S(t))}{2W(t)}\right)}{[2W(t)]^{1/2}} \right],$$

(3.21)

where $w_{\text{NP}} = [2W(0)]^{1/2}$ with $W(0) = (\beta k_{\text{NP}})^{-1}$ gauges the width of the equilibrium distribution of the reactant distribution $P_{\text{NP}}^{\infty}(\Delta e)$.

Figure 9 displays our results, which illustrate several important features. First, the reactant population very rapidly decreases to nearly zero in consequence of the underlying dynamics propelling the FC thermal packet away from its initial high free energy side down into the $G_{\text{IP}}$ well. By contrast, the product population builds up much more slowly, as significant population growth in the product well requires extensive (and slower) relaxation into the thermal IP region. Both these trends mirror the bimodal relaxation behavior of $S(t)$ [and $\Delta E(t)$]. The first trend illustrates in an MD context the point that passage away from a high energy point with steep slope (as in a high barrier activated electron transfer) is governed by the short time dynamics. This aspect plays a central role in the Hynes theoretical description of electron transfer reactions and has received some experimental support in the studies of Weaver and co-workers. The second trend indicates that in a strongly exothermic process the time dependence of the ap-
Pearce of the lower free energy product species should be sensitive to the longer time relaxation dynamics; this point has been stressed for exothermic electron transfer reactions by Fonseca. 28

C. Langevin equation description

The excited IP state based tcf $A_{IP}(t)$ was seen in Sec. III A 1 to reasonably well describe the nonequilibrium solvation dynamics in the TDF shift $S(t)$ at all times. It is of interest to explore here whether simple models can shed any light on the behavior of this tcf.

One possible model for $A_{IP}(t)$ would be a dielectric continuum description. In this characterization, $A_{IP}(t)$ [and $A_{NP}(t)$ for that matter] would, in the simplest instance, be exponential in time with a decay time proportional to the solvent longitudinal relaxation time $\tau_L$. 11,15-17 A test of this would involve simulation determinations of the Debye relaxation time $\tau_D$ and the static dielectric constant $\varepsilon$ for the pure solvent (since $\tau_D = \varepsilon\tau_L$, $\tau_D/\varepsilon$, and $\varepsilon = 1$ for this nonpolarizable solvent). We have not followed this course here for several reasons. First, the accurate simulation determination of $\varepsilon$ is quite difficult. But more importantly, the lack of validity of a dielectric continuum description for small solutes in solvents of comparable size molecules is easily anticipated (see, e.g., Ref. 17) and is already adequately established in other studies (see, e.g., Ref. 8). Instead, we explore the validity of a more general, yet still simple, description: a Langevin equation (LE) approach.

We note at the outset that the LE description is bound to fail in important ways; this is not unanticipated, given the observed bimodal relaxation character of the solvation dynamics and the very short time scale for the dominant solvent relaxation. Nonetheless, we persist in pursuing this avenue for several reasons. First, the LE approach is already more general than most theoretical descriptions used in discussing TDF dynamics, 15-20 these typically ignore any solvent inertia and describe the solvent as highly overdamped, i.e., diffusive. The LE in contrast includes solvent inertia. 19 Second, we will see that the nature of the failure of a LE description is itself instructive.

A LE for the dynamics of $\delta \Delta E$ in either of the NP or IP harmonic free energy wells can be established 23 with the aid of standard (two variable) projection operator techniques. 35 When applied to the variable of interest, $\delta \Delta E = \Delta E - \langle \delta \Delta E \rangle_{SP}$, one obtains the LE: 17

$$\delta \Delta \ddot{E}(t) = -\omega_{SP}^2 \delta \Delta E(t) - \zeta_{SP} \delta \dot{\Delta} E(t) + R(t).$$

(3.22)

Here $\omega_{SP}^2$ is the square frequency of the SP well, 22,23

$$\omega_{SP}^2 = \frac{\langle (\delta \Delta E)^2 \rangle_{SP}}{\langle (\delta \Delta E)^2 \rangle_{SP}} = \frac{k_{SP}}{m_{SP}},$$

(3.23)

with $k_{SP}$ the force constant and $m_{SP}$ the effective mass associated with the fluctuations in $\delta \Delta E$. Comparison of Eqs. (3.12) and (3.23) shows that in effect $m_{SP}$ is defined by the fluctuations in the "velocity" of $\delta \Delta E$ via the equipartition theorem. 22,23,44

$$\langle (\delta \Delta E)^2 \rangle_{SP} = (\beta m_{SP})^{-1}.\tag{3.24}$$

Finally, the friction constant $\zeta_{SP}$ is defined by

$$\zeta_{SP} = \frac{1}{\langle (\delta \Delta E)^2 \rangle_{SP}} \int_0^\infty dt \langle KK(t) \rangle_{SP};$$

$$-\delta \Delta E + \omega_{SP}^2 \delta \Delta E,$$

(3.25)

which involves the tcf of the fluctuating "random" force (with the systematic harmonic force $-\omega_{SP}^2 \Delta E$ subtracted out). The evolution of $R(t)$ is governed, not by conventional Hamiltonian dynamics, but rather by projection-operator modified dynamics. 35,43 We note, for later reference, that the LE (3.22) is an approximation to an exact generalized Langevin equation (GLE), 43 which involves the time nonlocal friction term

$$\delta \Delta \ddot{E} = -\omega_{SP}^2 \delta \Delta E(t) - \int_0^t d\tau \zeta_{SP} (t-\tau) \delta \dot{\Delta} E(\tau) + R(t),$$

(3.26)

first introduced in an approximate form for solvation dynamics in Ref. 26 and previously used in connection with the MD simulations of activated electron transfer reactions. 23 A reduction to the LE assumes that the random force correlations $\langle RR(t) \rangle_{SP}$ decay very rapidly compared to the timescale of the speed $\delta \dot{\Delta} E$ of the $\delta \Delta E$ fluctuations.

The frequency and friction parameters $\omega_{SP}^2$ and $\zeta_{SP}$ can be obtained via simulation as follows. First, from Eqs. (3.12) and (3.23), $\omega_{SP}^2$ can be determined from separate equilibrium MD simulations of $\langle (\delta \Delta E)^2 \rangle_{SP}$ and $\langle (\delta \Delta E)^2 \rangle_{SP}$ for each of the two SP cases. The results are displayed in Table I. The IP and NP frequencies are quite close to each other, largely as a result of the mild square root dependence of $\omega_{SP}^2$ on the solute-dependent force constant $k_{SP}$.

The second quantities to be determined are the friction constants $\zeta_{SP}$. One can readily show from the LE (3.22) (and in fact also from the GLE 23,41 ) that the time areas of the normalized tcfs $A_{SP}(t)$, Eqs. (3.3) and (3.9), are given by the average relaxation time,

$$\tau_{SP} = \int_0^\infty dt \Delta \ddot{S}(t) = \frac{\zeta_{SP}}{\omega_{SP}^2};$$

(3.27)

such an average time is often used to characterize experimental solvation dynamics. 14 Thus, with known $\omega_{SP}^2$ values, $\zeta_{SP}$ can be extracted from the MD results for the tcf's $A_{SP}(t)$ and $A_{NP}(t)$. The results displayed in Table I indicate the striking feature that the friction for $\delta \Delta E$ in the presence of the charged IP is about twice as large as in the presence of the NP solute. Since the solvent frequencies are comparable, this translates to an average relaxation time which is longer by about a factor of 1.5 for the IP relaxation. The solvent is definitely "slower" in the presence of the field of the

| TABLE I. Simulation results for solute pair properties. | \begin{tabular}{lllll} 
\hline
 & $k_{SP}$ & $\omega_{SP}$ & $\zeta_{SP}$ & $\tau_{SP}$ \\
\hline
NP & 4.9 & 6.2 & 13.3 & 0.35 \\
IP & 8.0 & 7.4 & 29.3 & 0.54 \\
\hline
\end{tabular} |
charges—the solvent relaxation time is solute-dependent; this feature is clearly associated with the differing longer time “tails” of the tcf’s, and not with the initial time behavior. We will return to this point.

We can examine how an LE description, even provided with the correct frequency and friction parameters, fares for the IP tcf [which gives a reasonable approximation to the nonequilibrium shift $S(t)$ in Fig. 3(b)]. The story is mercifully brief: Fig. 10(a) shows that the LE picture begins to fail right from the earliest times and, of course, completely misses the bimodal decay character of $\Delta_{IP}(t)$. These same failures are apparent in the LE comparison with $\Delta_{NP}(t)$ in Fig. 10(b). It is worth stressing that the LE description does not even reproduce the longer time tails for either time correlation function. Obviously a different description on all time scales is required.

D. Short time Gaussian approximation

A quite different tack is suggested by the Gaussian time character of both $\Delta_{IP}(t)$ and $\Delta_{NP}(t)$ evident in Fig. 7 at short times. If we write

$$\Delta_{SP}(t) = 1 - \omega_{SP}^2 t^2/2 + \cdots \approx e^{-\omega_{SP}^2 t^2/2} = \Delta_{SP}^G(t)$$

for suitably short times, then Fig. 10 shows that in each case the short time behavior of the correlation function is quite well reproduced over a significant fraction of the decay. This striking agreement, which also holds for the shift $S(t)$ in Fig. 10(c), has a number of implications, which we now discuss.

First, we have seen in Fig. 10 that both the equilibrium tcf’s $\Delta_{IP}(t)$ and $\Delta_{NP}(t)$ agree well with the nonequilibrium shift $S(t)$ in the initial decay period. That the former should work well is at first glance a cause for surprise since, as discussed in Sec. III A, the initial solvent distribution relevant for the shift $S(t)$ [and $\Delta_{NP}(t)$] is that appropriate for the uncharged NP and not the charged IP; the IP solute charges are not present to induce any average solvent dipolar orientation. Now we see that (a) the initial dynamics for $\Delta_{IP}(t)$ are clearly governed by the frequency $\omega_{IP}$, and (b) that $\omega_{IP}$ is nearly equal to $\omega_{NP}$ which governs the initial decay of $\Delta_{NP}(t)$. Equivalently stated, the extensive initial dynamics of $S(t)$, $\Delta_{IP}(t)$ and $\Delta_{NP}(t)$ are all approximately governed by the solvent frequency, and this is only mildly sensitive to the initial solvent distribution, be it that for the NP or for the IP. This observation goes some way to account for the validity of a linear response treatment. [It also suggests that the approximate validity of linear response is by no means generally guaranteed.]

The physical interpretation of this Gaussian time behavior is the following. In all cases, we can picture a distribution of solvent configurations responsible for the initial $\Delta E$ values. For very short times, the change in those configurations is governed, not by the intermolecular forces and torques, but rather by the free streaming, inertial motion of the solvent molecules, subject to a Maxwellian velocity distribution. These inertial changes in solvent configurations change $\Delta E$, and their average net effect is described by the frequency $\omega_{SP}$.

Second, the extensive initial Gaussian time relaxation for $S(t)$, $\Delta_{NP}(t)$, and $\Delta_{IP}(t)$ dependent upon $\omega_{SP}$ highlights in a particularly stark and instructive fashion the particular inadequacies of a simple LE description. Figures 10(a) and 10(b) indicate that the constant friction assumption, with its requirement that the frictional forces begin to act very quickly [at order $t^3$ for $\Delta_{SP}(t)$], causes a very rapid departure from the simple correct $\exp(-\omega_{SP}^2 t^2/2)$ behavior which is itself completely independent of the frictional forces. Allowance for the finite time scale of the friction forces, i.e., the use of a time-dependent friction kernel $\xi_{SP}(t)$ in a GLE,
will remedy this failing by recognizing that these forces do not act instantly. As shown elsewhere,\textsuperscript{42,43} it is in fact possible to extract $\xi(t)$ from $A_{np}(t)$ via Fourier transform techniques; the result for $\xi_{ip}(t)$ is displayed in Fig. 11.\textsuperscript{46} Comparison of this with Fig. 7(a) shows that the LE assumption that $\xi_{ip}(t)$ decays rapidly compared to the decay of $\Delta E$ fluctuations is simply untenable. Not only does this approximation largely obliterate the important short time Gaussian behavior in $A_{np}(t)$ and $S(t)$ as discussed above, it can be also shown\textsuperscript{43} that in fact explicit retention of the full time dependence of $\xi_{ip}(t)$ is necessary to account for the long time tail behavior in $A_{np}(t)$ and $S(t)$. [Similar remarks apply to $A_{np}(t)$.] Unfortunately, provision of a theory for the full time dependence of $\xi_{ip}(t)$ [or for $\xi_{np}(t)$] is no mean feat; in particular, the physical origin of the bimodal time-dependent structure will need to be understood before the GLE provides a useful nonempirical, nonsimulation route to understanding the tail behavior in the TDF shift $S(t)$. For the present, we content ourselves with the emphasis that a GLE level of description is necessary.

E. Implications for current theories

We have already noted in Sec. III B and III C that even a Langevin equation description including solvent inertia is unable to account for our MD results; instead a Generalized Langevin Equation description is necessary. Much current theoretical effort and experimental attention have been devoted to a different approach which incorporates some microscopic solvent aspects, the dynamical MSA Theory, introduced by Wolynes\textsuperscript{18} and since extended in various ways.\textsuperscript{19} Here we comment briefly on the implications of our results for such interesting MSA theories.

It is important to first point out that the bimodal structure of $S(t)$ and $A_{np}(t)$ that we have observed is unrelated to the (approximately) bimodal time structure found in various MSA studies. As discussed extensively above, the initial time behavior is governed by solvent inertial effects, and solvent inertia has not been included in all the MSA studies to date. (The dielectric continuum non-Debye several relaxation time solvent models studied in the literature\textsuperscript{26} also ignore solvent inertia, as have continuum treatments including solvent translational contributions\textsuperscript{3}(c).\textsuperscript{17} and dielectric saturation;\textsuperscript{47} again, any bimodal time structure arising in these descriptions is unrelated to the present inertial effects.)

In the MSA, the solvent dynamics enters via the dynamical dielectric response $\epsilon(\omega)$ of the solvent in the absence of the solute. At the very least, inclusion of solvent inertial effects via $\epsilon(\omega)$\textsuperscript{17,26} seems necessary. Even then, however, current MSA models must fail to account for the observation that the longer time tails in the saturation dynamics depend on the charge distribution in the solute pair (cf. Fig. 10 and Table I). This points clearly to the need to account for solvation dynamics more directly in terms of solute–solvent interactions, rather than via a purely solvent dynamical property [$\epsilon(\omega)$] as in the MSA approach.

IV. NONEQUILIBRIUM SOLVATION TRAJECTORIES

Immediately after the Franck-Condon transition creating the IP from the initial NP solute, the surrounding polar solvent molecules find themselves out of equilibrium with the IP and subject to the Coulomb interaction with the site charges in the IP. They must then reposition and orient themselves ultimately to achieve a new average equilibrium structure about the IP. Judging from Fig. 4, this accommodation is largely completed within about 3 ps, but with continuing minor adjustments up to times of order 6 ps. Here we attempt to gain some insight on the microscopic details and mechanism of this nonequilibrium solvation process.

The long-time equilibrium spatial and orientational patterns of the solvent about the IP have been previously determined in an MD simulation study by Ciccotti et al.\textsuperscript{21} The results are shown schematically in Fig. 12. The main structural feature is a cylindrical sheath of four solvent molecules whose dipoles are oriented antiparallel to the IP axis, at a radius of approximately 4 Å on the average. There is also a much weaker solvation pattern comprising two solvent molecules each flanking the IP axis and on average parallel to it.

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**FIG. 11.** Time-dependent friction, $\xi_{ip}(t)$, in the presence of the IP. Units are ps$^{-1}$.

**FIG. 12.** Schematic illustration of the equilibrium solvation patterns around the IP.
FIG. 13. Representative trajectories of the first solvent shell molecules subsequent to the excitation NP→IP. The characteristic quantities (z and the parallel and perpendicular components of $\rho$) are described in the text. The panels refer, in sequence, to molecules A–E.
FIG. 13. (continued).
In the absence of the IP electrical charges, there will be no net antiparallel solvent orientation in any cylindrical sheath about the NP, and thus no such net polarization exists initially after the IP has been created in the Franck-Condon transition. In order to examine the ensuing solvation dynamics, we construct a cylindrical coordinate system, whose $z$ axis is anchored to the IP axis and whose zero is located at the midpoint between the two IP members. The spatial position of the center of mass of a solvent molecule is then located by the spatial cylindrical coordinates $z$ (the cylinder height) and $\rho$ (the cylinder radius) and an azimuthal angle $\phi$ that is referenced to some convenient value (see below). The orientation of a solvent molecule can be specified in terms relevant to the solvation as follows. A unit vector $\hat{\mathbf{e}}_z$ is imagined to be attached to the dipolar axis of a solvent molecule, pointing from the negatively charged site to the positively charged site. A corresponding unit vector $\hat{\mathbf{e}}_{\rho}$ is rigidly attached to the IP cylindrical axis pointing from the negative site to the positive site. The signed parallel and perpendicular components of the solvent molecule orientation with respect to the IP axis are then defined by

$$\text{parallel} = \hat{\mathbf{e}}_z(t) \cdot \hat{\mathbf{e}}_{\rho}(t);$$

$$\text{perpendicular} = \hat{\mathbf{e}}_z(t) \cdot \hat{\mathbf{e}}_{\rho}^\perp(t),$$

(4.1)

where $\hat{\mathbf{e}}_{\rho}^\perp(t)$ is a unit vector perpendicular to $\hat{\mathbf{e}}_{\rho}(t)$, defined to have a positive projection along the intermolecular axis from the center of mass of the IP to that of the solvent molecule.

With the above coordinate system, we have followed the fate of (typically) six solvent molecules closest to the newly created IP in a number of trajectories subsequent to the Franck-Condon transition. We have found that there is considerable variation in the detailed dynamics of these molecules between trajectories, but that certain tendencies emerge, involve both reorientational and translational motion. We now discuss two sets of these in detail, but stress that these trajectories should more properly be regarded as representative (and instructive), rather than as necessarily completely typical.

Figures 13(a)–13(c) illustrate the histories of three solvent molecules, labeled A, B and C, which are initially favorably oriented: at $t=0$ they are approximately oriented antiparallel to the IP axis. On a time scale of $\leq 2$ ps, there is a tendency to remain antiparallel or to become more so. On this same time scale (and longer), the solvent molecular centers of mass stay close to the IP bond midpoint $z=0$; an initial motion towards $z=0$ is especially noticeable for B and C. Molecules A and B are typically located near $\rho = 4 \, \text{Å}$ over the 6 ps period examined; in contrast, after $t \approx 3$ ps, molecule C wanders to the periphery—it drifts to somewhat larger $\rho$ away from the $z=0$ midpoint, and loses its antiparallel character; it has exited the inner solvation shell. Solvent molecules D and E [Figs. 13(d) and (e)] have a different behavior than A–C; they illustrate IP-induced antiparallel alignment from initially unfavorable orientations. This occurs fairly rapidly in the case of D, but is rather delayed for E, whose slower alignment coincides with its center of mass positioning near the IP midpoint $z=0$. The interference between all these solvent molecules attempting to accommo-
date to the IP can result in strong disturbances of previously favorable positionings, e.g., molecule C past $t \sim 2$ ps. Finally, Fig. 14 illustrates the azimuthal solvation pattern referenced to molecule D. Within rather large fluctuations, there is a basic pattern of two solvent molecules (A and E) located near 90° (i.e., $\pm 90°$) with respect to D, while the fourth (B) is near 180° (recall that molecule C drifts out of the inner solvation shell).

An impression of the complexity of the solvation trajectories and the frequent mutual interference between them is given in another set of trajectories shown in Fig. 15. Solvent molecule A is initially positioned and oriented favorably with respect to the IP axis but is subsequently (at $\sim 1$ ps) severely perturbed. Molecules B and C rapidly become aligned approximately antiparallel to the IP axis starting from unfavorable orientations (in fact B flips). Molecule D at first succeeds in the induced alignment, but subsequently drifts away from it, eventually exiting the shell at $\sim 6$ ps. Molecules E and F, which are initially flanked away from the IP midpoint $z = 0$ meander toward partial alignment but even wander out of and back into the primary solvation shell (E at $\sim 3$ ps and F at $\sim 2$ ps and 4 ps).

From these two sets of trajectories (and others not shown), we have the impression that initially favorable solvent molecule positionings and alignments tend to strengthen and to be preserved for at least a few picoseconds. Initially unfavorable solvent molecule positionings and alignments can be quickly converted to favorable ones. However, the competition within and between these classes can create considerable complexity, thwarting the attainment of favorable solvation by some molecules and disrupting the pre-existing favorable solvation of others. We think it likely that the initial broadening in the spectrum (Figs. 5 and 6) is associated with the rather large range of solvent molecule trajectories induced by the sudden exertion of the Coulomb forces and torques on them by the newly created IP. Actually, in view of the complexity of the trajectories, it must be counted as remarkable that the spectral shift $S(t)$ can be accounted for so well overall by the linear response approximation $\Delta_{ip}^G (t)$ (Fig. 10) are so accurate at short times.

V. CONCLUDING REMARKS

The present simulation and theoretical studies of time dependent fluorescence have shed some light on the approximate validity of an appropriate linear response treatment, on the importance for the solvation dynamics of the inertial Gaussian time behavior, and on the necessity for a general-ized Langevin equation level of description. The impact of these dynamics on a model photochemical reaction highlights the importance of short time solvation dynamics in the kinetic evolution. In addition, the nonlinear aspects of initial spectral broadening and ultimate spectral broadening have been examined.

The results of the present study suggest a number of avenues for further exploration. The critical role of the inertial Gaussian time behavior of the solvation dynamics, for example, indicates that such a component should be searched for in femtosecond experiments, and be incorporated in future analytical treatments.

An important role should be played by short time Gaussian dynamics in the early time solvation behavior for other solvents, including, e.g., water, and in other environments, e.g., proteins. (These have now also been found for acetonitrile and methanol). A novel feature in aqueous and other hydrogen-bonded solutions should be a relatively early and marked departure from Gaussian behavior associated with, e.g., the high frequency librational dynamics which can contribute at short times. Indeed, Fonseca and Landau have very recently demonstrated this for simulated methanol. They have also found marked departure from linear response theory expectations, and been able to explain this in terms of the methanol dynamics.

The governance of the very extensive initial Gaussian relaxation in the TDF shift $S(t)$ by the solvent frequency $\omega_{ip} \approx \omega_{np}$ suggests that considerable progress might be made in the description of general TDF systems by construction of theories for $\omega_{ip}$. This is an equilibrium time-independent average quantity [cf. Eq. (3.20)], and the application of modern equilibrium statistical mechanical methods for solutes in polar solvents to its calculation could prove useful in providing estimates for more general solute and solvent systems. One can imagine, for example, that such a theory could shed light on the relative importance of solvent translational, librational and reorientational free streaming motion on the initial Gaussian decay, and on the relative importance of solvent shell molecules for this decay. It might also reveal interesting initial relaxation dynamics for a solute in a mixture of solvents of differing polarity, arising from "solvent-sorting" effects. Much remains to be learned here.

In addition, further investigation of the probe dependence of the solvation dynamics and of the overall and transient spectral narrowing and broadening could prove to be useful experimental and theoretical indicators for nonlinear effects. The possibility that these might differ qualitatively in dipolar aprotic versus hydroxylc solvents could provide additional illumination on these solvation nonlinearities.
FIG. 15. A second set of representative trajectories of the first solvent shell molecules subsequent to the excitation NP → IP. The description of various coordinates is as in Fig. 13. The panels refer, in sequence, to molecules A–F.
FIG. 15. (continued.)
ACKNOWLEDGMENTS

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Some recent reviews which address some aspects of these issues include:


For recent reviews, see G. E. M. McManus and M. Weaver, Acc. Chem. Res. (1990) and Refs. 1(a) and 1(d).


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