COMPUTER SIMULATION OF PHOTOCHEMICALLY INDUCED ELECTRON TRANSFER

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We have simulated by molecular dynamics the solvent relaxation immediately after photoinduced electron transfer of an aqueous ferrous–ferric system. The simulations show that the process occurs in a subpicosecond time scale and in a fashion qualitatively consistent with Marcus’ model.

In a recent paper [1], we presented a study of a model for aqueous ferrous–ferric electron transfer. Potential functions were developed, and various equilibrium properties of the model system were computed. The results obtained indicate that the model captures sufficient aspects of the real system to make meaningful predictions about the actual charge transfer process. This work extends the equilibrium results of the first report to the domain of dynamics, examining the nature of the solvent relaxation following the instantaneous transfer of an electron from the ferrous to the ferric ion. The most important conclusions we draw are the following: (1) The solvent relaxation that occurs after the initial charge transfer is remarkably fast, occurring on times scales of tens and hundreds of femtoseconds. (2) This relaxation is complicated involving many more rate constants of frequencies than seem easy to identify. (3) To a reasonable approximation, however, the relaxation follows a course consistent with linear response theory (i.e. Onsager’s regression hypothesis or the fluctuation dissipation theorem). However, our statistics are good enough to discern quantitative deviations from linear behavior.

The qualitative accuracy of a linear relaxation model is especially noteworthy since it provides further evidence of the essential correctness of the spin-boson Hamiltonian as a caricature of the electron transfer system. This Hamiltonian, a two-state system linearly coupled to a harmonic bath, underlies the Marcus theory of electron transfer [2,3]. When the system exists in one of the two redox (i.e. diabatic) states, this theory pictures the relevant degrees of freedom as entirely harmonic, and the free energy surface as parabolic. In ref. [1], we showed that, indeed, the diabatic free energy function is nearly a perfect parabola. In this Letter, we show that the transfer dynamics is qualitatively consistent with a parabolic diabatic potential surface, i.e. a surface for which linear response theory is exact.

Our conclusions are not without precedent. Several years ago, Rao and Berne [4] observed by computer simulation the fast reorganization of the water structure to accommodate an alteration in charge distribution. In a much more recent simulation study, Maroncelli and Fleming [5] have successfully analyzed relaxation dynamics with linear response theory in much the same way as we have done and describe below. A related simulation of aqueous relaxation after a sudden change in charge distribution has been reported by Karim et al. [6]. Our work differs from these earlier studies in the particular system we examine. We have chosen to consider a model for the specific aqueous ferrous–ferric exchange since it is closely tied to experiment and perhaps more realistic than those examined before us.

In our simulations, the model system contains SPC water molecules and two spherical ions with charge +2e and +3e respectively, all coupled by appropriate pair potentials [1]. The interactions were chosen to reproduce important properties of solvated iron ions as discussed in ref. [1]. For the results reported herein, there were 430 solvent molecules in a box of side 23.45 Å. All interactions terminated at half the
box length with a 0.5 Å spline bringing them smoothly to zero. This is a very small periodically replicated system. Based on the system size study carried out in ref. [1], however, we believe our results would not change in any substantial way if a much larger system were employed. For example, the artificial polarization layers that exist at the box edges do no affect transfer energetics by more than about 1 kcal/mole, and such energies are nearly negligible in the current context.

The system evolved by classical molecular dynamics. For the present purposes, quantum mechanical aspects of the dynamics are of minor importance, as discussed below.

Let us now describe our simulation of photoinduced electron transfer. The system of Fe$^{2+}$-Fe$^{3+}$ in water was first equilibrated with iron ions separated a fixed distance $R$. We have used $R = 5.5$ Å, a typical interionic separation during electron transfer. A trajectory run in this diabatic state provides representative solvent configurations equilibrated to Fe$^{3+}$-Fe$^{2+}$. Given such a configuration, the electronic charge was switched to the opposite ion forming the Fe$^{3+}$-Fe$^{2+}$ state. This switch corresponds to a vertical excitation as illustrated schematically in fig. 1. It simulates a photoexcitation of approximately 4 eV energy. The dynamics of the total system – solvent and unconstrained ions – was then followed for several hundred femtoseconds. On a large length scale, this simulation is similar to that of following solvent reorganization after a dipole undergoes an instantaneous change in its direction.

The procedure we have just described was carried out twenty different times, and the results shown in fig. 2 are the averages over all twenty. Each run employed independent equilibrated initial solvent configurations, and for each configuration, independent samples of initial velocities were used. The independent configurations appropriate for water at 300 K and 1 g/mm$^3$ were prepared through separate heating and cooling cycles using a constant temperature molecular dynamics algorithm as discussed in ref. [1]. After initiating the dynamics, however, no temperature controls were used. Since the initiation de-

![Fig. 1. Schematic of two diabatic potential surfaces. The dashed curve depicts the potential energy function for the solvent when the iron ions are in the Fe$^{3+}$-Fe$^{2+}$ redox state. The solid curve is the potential energy when the iron ions are in the Fe$^{3+}$-Fe$^{2+}$ state. The vertical arrow represents the photoinduced excitation that initiates the dynamics investigated herein.](image)

![Fig. 2. The return to equilibrium of ΔE(t) from the excited system. The solid lines correspond to the non-equilibrium results and the dotted lines are calculated from the equilibrium correlation functions of fig. 3. Starting from the top, the three different plots refer to the total relaxation, the bulk relaxation and the first shell (or ligand) relaxation. The standard deviation from averaging over trajectories is roughly 3.0 kcal/mole in each case. The arrows indicate the average values of ΔE and its different components at full equilibrium, t→∞.](image)
posits an excess 4 eV potential energy into the system, the temperature drifts upward during the run. After 350 fs, the increase is approximately 10% (i.e. 30 K).

The forces are so strong that we find that the course of these trajectories are not significantly influenced by the initial choices of velocities provided they are taken from the Maxwell-Boltzmann distribution. The trajectories are, however, noticeably different for different initial configurations.

After the instantaneous transfer of charge from the ferrous to the ferric ion, the change in electric potential at the two ions, termed $\Delta E$, is determined as a function of time. This function is plotted in fig. 2. In tight-binding or two-state approximation, $\Delta E$ is directly proportional to the energy gap between the lowest two electronic states of the charge transfer system. It is this energy gap relaxation that is measured in recent experimental studies [7] of solvent relaxation following electronic transitions. In fig. 2 we show the total $\Delta E$ and also its decomposition into the contribution from the water molecules that are ligands and the contribution from the remaining solvent. This decomposition is unambiguous since the sixfold coordinated ligand structure is extremely stable and long lasting.

At time zero, $\Delta E$ has an initial value characteristic of the equilibrium Fe$^{2+}$–Fe$^{3+}$ solvation structure, whereas the actual ions being solvated have charges 3+ and 2+. The system responds quickly to the charge transfer, reversing direction in 10 to 20 fs. The solvent polarization is then trapped, though highly excited, in the product region, and it never returns to a state which would favor the reactants. In view of the schematic in fig. 1, the system moves from its highly excited configuration to the curve crossing region in approximately $10^{-14}$ s.

Where the diabatic surfaces cross (i.e. where the two redox states are degenerate), there is some probability that the system will leak back onto the initial diabatic surface. We have considered this possibility and computed by perturbation theory the probability for a transition, $p(t)$. That procedure, as used by others too [8] (used in the context of charge transfer, see for example ref. [9]), gives

$$p(t) = \left( \frac{\hbar}{2\Delta} \right)^2 \int_0^t dt' \exp\left( \frac{i}{\hbar} \int_0^{t'} \Delta E(t'') \right)^2,$$

where $\Delta$ is the matrix element coupling the two redox states when $R=5.5$ Å [1]. We have found that $\Delta$ is nearly independent of solvent configurations and since $R$ is virtually unchanged for a subpicosecond trajectory, $\Delta$ can be regarded as a constant. The perturbation estimate is accurate provided $p(t)$ is small, and it is indeed small. When averaged over the ten trajectories, $p(t)$ rises suddenly near $t=10$ fs, from its initial value of $p(0)=0$, to $p(t)=0.005 \pm 0.001$ for all $t>10$ fs. Thus, to within 1% accuracy, transitions from one diabatic surface to the other are negligible.

While electronic transitions between the two diabatic redox states seem unimportant, other ramifications of quantum mechanics may be worthy of future study. In particular, the rapid rate of relaxation suggests that the motion of the solvent nuclei might best be treated quantum mechanically rather than classically. For example, protons can move by tunneling and it is the dynamics of protons through rotations of both inner and outer shell water molecules that occur on the time scale of 10 or 20 fs.

We see from fig. 2 that the inner shell contribution to $\Delta E$ approaches equilibrium in a highly oscillatory fashion. We have analyzed ligand breathing mode spectra and found that these motions occur with periods between 60 to 70 fs, in good agreement with experiment [10]. We have also analyzed the librational motions of the water molecules both in the inner and outer shells. These motions occur on a time scale of approximately 20 fs. Evidently, in view of fig. 2, it is the librations that are responsible for the oscillatory behavior of $\Delta E(t)$.

The outer shell or bulk waters also relax in a complicated fashion. There is an initial fast relaxation of $\Delta E$ followed by a slower decay to the equilibrium value. The decay oscillates with roughly the same timescale as that of the first shell but with a much smaller amplitude. Once again, we attribute these oscillations to librations of water molecules.

It is clear that on the 250 fs timescale of the simulation, the relaxation does not exhibit the simple exponential decay predicted by relatively simple di-electric theories [11] \(^{81}\). Apart from the predictions

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\(^{81}\) The more recently proposed [12] application of the dynamical mean spherical approximation [13] would also seem incapable of explaining the complicated time dependence we observe in our simulation.
of such theories, it is possible to generate equilibrium correlation functions and to use these correlation functions to determine the time evolution from a non-equilibrium state as governed by the Onsager regression hypothesis. Averaging over a series of molecular dynamics simulations of the Fe$^{3+}$-Fe$^{2+}$ system provides the equilibrium correlation function $\langle \delta E(t) \delta E(0) \rangle$. Here, $\delta E(t)$ denotes the instantaneous fluctuation of $E(t)$ from its equilibrium value. The correlation functions for ligand and bulk water molecules, as well as the cross correlations between the ligands and bulk, were calculated as well. These correlation functions along with the equilibrium values $\langle \Delta E \rangle$ are sufficient to determine the relaxation from a non-equilibrium state when all responses are linear. For example, according to linear response theory [14],

$$\frac{\Delta E(t)}{\Delta E(0)} = \frac{\langle \delta E(0) \delta E(t) \rangle}{\langle (\delta E)^2 \rangle}. $$

The correlation functions are shown in fig. 3. These correlations, like the non-equilibrium relaxation results, do not have the simple exponential decay predicted by linearized continuum dielectric theories.

The comparison between the solvent response predicted by the equilibrium correlation functions and the actual non-equilibrium response is shown in fig. 2. While not in perfect agreement, and the difference may be an interesting topic for future research, the linear response approximation and the actual relaxation are remarkably similar. As we noted earlier, this agreement is consistent with Marcus’ hypothesis of a quadratic energy surface since such a model exhibits no non-linear response. It remains a curious and perhaps fundamental issue as to why a non-linear system like the one we have constructed and modeled relaxes to equilibrium from a highly energetic state by a course qualitatively like the relaxation of spontaneous fluctuations in an equilibrium system.

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### References