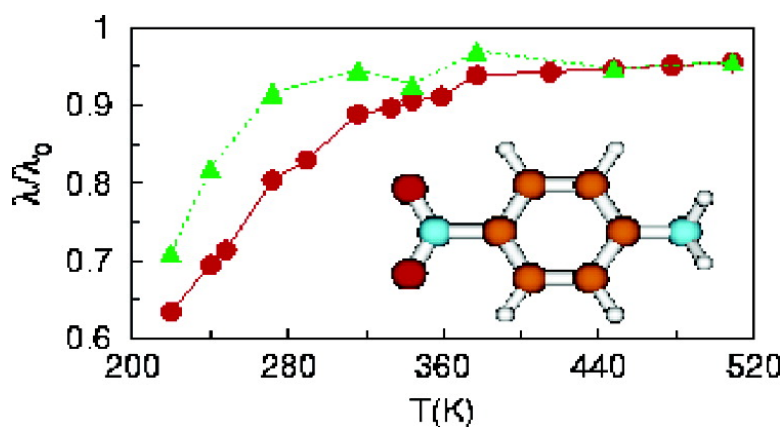Communication

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Dynamical Arrest of Electron Transfer Reorganization in Super-Cooled Water

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This paper reports the results of Molecular Dynamics (MD) simulations of the solvent reorganization energy of electron transfer (ET) reactions in super-cooled water. Simulations are carried out for a model charge-transfer optical dye (*p*-nitroaniline) in SPC/E water in a range of temperatures down to the point of solvent ideal glass transition. We show a significant departure of the solvent reorganization energy, measured on a given time window, from its thermodynamic limit obtained by averaging over long simulation trajectories. Our results thus indicate that optical solvatochromism and activation parameters of ET reactions, measured in viscous solvents, will be significantly affected by the dynamical arrest of nuclear solvation when the experimental time scale becomes comparable to the characteristic relaxation time of the solvent.

ET in simple liquids and in biopolymers is affected by a broad spectrum of nuclear solvent modes with distributed relaxation times. In particular, ET in proteins[1] and DNA[2] is activated by polarization modes characterized by a hierarchy of relaxation times spanning a range from a few picoseconds to nanoseconds.[3] Also, lowering the temperature of a polar molecular liquid slows down solvent dielectric relaxation, leading to a super-Arrhenius (Vogel−Fulcher[4]) temperature dependence of the dielectric relaxation time close to the point of glass transition. Emission energies are strongly affected by freezing of the solvent orientational polarization through liquid crystallization or glass transition.[5] Although some of these effects can be related to the drop of the dielectric constant when a polar fluid freezes,[5a,6] the effect of freezing on ET reactions is actually dynamic in nature.[5c,7]

Slow solvent modes may not achieve equilibrium on the time scale of ET[7,8] or on the excited-state lifetime of the emitting state.[5] This dynamical arrest of nuclear solvation may lead to a significant departure of the measured parameters from their thermodynamic values.[7,8] Most experimental studies have focused on systems undergoing solvent solidification. However, the temperature at which the activation barrier departs from its thermodynamic limit depends on the observation window. For fast reactions, the onset of the dynamical arrest of a given slow mode from a distribution of relaxation times may occur at a temperature well above the freezing transition.[8d] This paper reports the first MD simulation directly showing a significant decrease in the ET reorganization energy in the liquid phase of the solvent. Note that the possibility of this phenomenon has been anticipated in the literature.[8] The dynamical arrest was suggested[6c,8] to be responsible for biphasic temperature dependence of ET rates in redox proteins[8b] and natural photosynthetic reaction centers.[9]

MD simulations of *p*-nitroaniline in SPC/E water were done in the microcanonical NVE ensemble by using the DL_POLY program.[10a] We have studied temperatures from slightly above the point of ideal glass transition of SPC/E water (193 K[10]) up to 490 K. This broad temperature range is allowed by the isochoric conditions of the simulations (466 water molecules, $\rho = 0.997$ g/cm^3). Equilibration was carried out over a time period of 400 ps,

and the production runs were 1.0 ns long. A 16-site model of *p*-nitroaniline with Lennard-Jones atomic sites (OPLS parametrization[11b]) and atomic partial charges has been used. The electronic structure and ground-state geometry of *p*-nitroaniline have been previously reported.[11c−d] The ground-state geometry and charges were obtained here from GAUSSIAN 03 (MP2 for the ground state and CI/S for the excited, S$_4$,[11d] state, 6-31+G*).[12] We note that, although the electronic structure calculations reproduce many experimental properties of *p*-nitroaniline, their accuracy is not critical for our purpose. This molecule is used to represent a small charge-transfer complex,[13] and our main goal is to model the solvent effect on the energy gap $\Delta E(t)$ between the ground state and the excited, charge-transfer (S$_4$) state.

The simulations report the energy gap correlation function $C(t) = \langle \Delta E(t)\Delta E(0)\rangle$. In most practical cases, it is equal to the observable Stokes shift correlation function.[14] $C(t)$ from MD simulations shows a biphasic dependence typical of solvation dynamics in soft media, including polar solvents[14] and proteins.[3] The correlation function is composed of a fast Gaussian component and a slow exponential decay with corresponding two peaks seen in the imaginary part of the Stokes shift susceptibility[15] $\chi''(\omega) = (\pi\omega/kT)C(\omega)$ (Figure 1a), where $C(\omega)$ is the frequency Fourier transform of $C(t)$. The high-frequency Gaussian peak is caused by fast inertial dynamics of the solvent molecules around the solute. This component is absent in the polarization dynamics of the pure solvent, as is seen from the comparison of $\chi''(\omega)$ with the solvent dielectric loss function $\epsilon(\omega)$ (Figure 1b). The Debye peak of the solvent dielectric relaxation shifts to lower frequencies with lowering temperature (see Supporting Information). The exponential solvation relaxation time, corresponding to collective dielectric response of the solvent, shows a super-Arrhenius temperature dependence characteristic of fragile liquids[4] (Figure 2). The relaxation time of the Gaussian peak in $\chi''(\omega)$ is almost independent of temperature (Figure 2), as is its fraction in the overall Stokes shift (not shown here).

The distinction in the temperature dependence of the fast Gaussian and slow exponential components of the Stokes shift dynamics suggests that the slow component may become dynamically arrested once its relaxation time crosses the observation window of the experiment. The observation window is set up by the lifetime of the excited state of the chromophore in time-resolved spectroscopy or by the time of ET in activated kinetics. As was noted previously by Marcus,[6a] only a part of nuclear polarization is frozen when solid or glass is formed. The dynamic (non-ergodic) reorganization energy λ, measured on the finite observation window τ_{obs}, will differ from the thermodynamic reorganization energy λ_0 corresponding to $\tau_{obs} \rightarrow \infty$. The dynamic reorganization energy can be obtained[8d] from $\chi''(\omega)$ by limiting the range of frequencies contributing to the Stokes shift dynamics to frequencies higher than the observation frequency $\omega_{obs} = 2\pi/\tau_{obs}$ (Figure 3, circles).

$$\lambda = \int_{\omega_{obs}}^{\infty} \chi''(\omega)(d\omega/\pi\omega) \qquad (1)$$
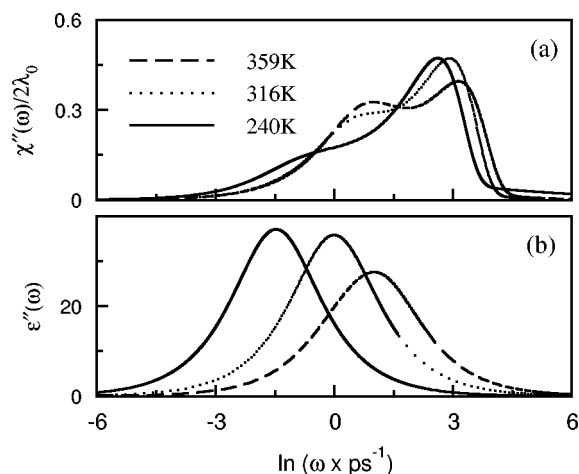
Figure 1. Imaginary part of the Stokes shift susceptibility of *p*-nitroaniline (a) and imaginary part of the frequency-dependent dielectric constant of SPC/E water (b). The data are collected at the temperatures indicated on the plot.
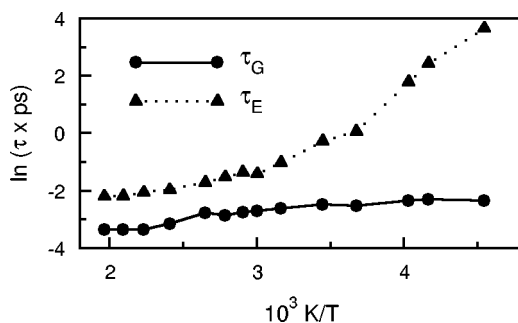

Figure 2. Temperature variation of fast Gaussian (τ_G) and slow exponential (τ_E) relaxation times in the Stokes shift dynamics.
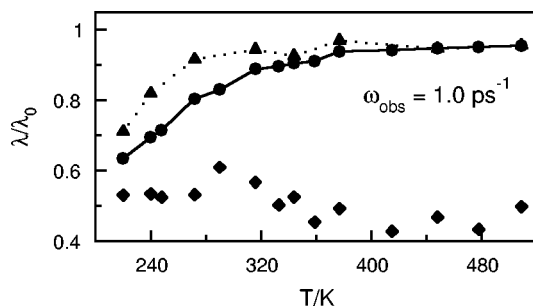

Figure 3. Ratio of the dynamic and thermodynamic reorganization energies obtained from the Stokes shift dynamics limited to observation window $\tau_{obs} = 2\pi/\omega_{obs}$ (triangles) and calculated from eq 1 (circles). Diamonds refer to the reorganization energy originating from the Gaussian component of the Stokes shift dynamics. $\lambda_0(T)$ changes from 0.17 eV at 219 K to 0.12 eV at 509 K.

Alternatively, the dynamic reorganization energy can be obtained by measuring $C(t)$ from simulations on the time window τ_{obs}. In these simulations, mimicking time-resolved spectroscopic experiments, the excited-state of *p*-nitroaniline was instantaneously created from ground-state configurations taken at equal intervals from a long equilibration run. The resulting dynamic reorganization energy is obtained from 50 Stokes shift trajectories averaged on the observation window $\tau_{obs} \cong 6$ ps (Figure 3, triangles). This observation window is chosen here to allow sufficient sampling on the time scale accessible to computer experiment. In experiment,

the excited state has the lifetime of 0.25 ps in water at 295 K,[13b] which increases with cooling resulting in observed fluorescence.[13a]

The direct calculation of the dynamic reorganization energy from simulations is compared to eq 1 in Figure 3. The two approaches agree quantitatively and show that the thermodynamic limit for the reorganization energy is achieved only at high temperatures when the slow component of the Stokes shift dynamics completely relaxes within the observation window. The dynamic reorganization energy tends to its Gaussian component limit (diamonds in Figure 3) with slowing exponential relaxation. It also does not reach its thermodynamic limit on the picosecond time scale typical for primary photosynthetic charge separation[16] in the temperature range up to the physiological temperature of about 300 K. Given that bulk water is the fastest component of the water/protein medium,[3] many fast ET reactions in biology may occur in the regime of (partial) dynamical arrest of nuclear solvation.

Supporting Information Available: Additional experimental details and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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