

The Interplay of Dielectric and Mechanical Relaxation in Solvation Dynamics

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Abstract

Quantum molecular dynamics simulations are used to explore the possible coupling between dielectric solvation, the response of the solvent to a change in charge distribution of the solute, and mechanical solvation, the response of the solvent to a change in solute size or shape. The hydrated electron is chosen as a solvation probe, due to its large increase in spatial extent upon photoexcitation and significant contraction in size upon non-adiabatic relaxation. The strong displacement of translational solvent modes upon excitation hampers the effectiveness of individual solvent molecule rotations in providing relaxation, decreasing the relative amplitude of the inertial response. Following non-adiabatic relaxation, solvent molecules can freely translate and reorient, leading to rapid, effective initial solvation. These results suggest that in many situations where solutes undergo changes in both charge distribution and size, solvation can become rate-limited by the relatively slow viscoelastic solvent response.

I. Introduction

Whenever the electronic states of a solute are coupled strongly to the surrounding environment, the dynamics of the solvent can play a critical role in determining the fate of condensed phase chemical species. Indeed, solvent fluctuations define the reaction coordinate for electron transfer and many other types of chemical reactions.¹ This has prompted an explosion of recent interest in solvation dynamics: the study of the relaxation of the solvent following a sudden perturbation due to a change in the solute.² At the heart of the issue are the specific solvent motions that lead to relaxation. When the solvent rearranges to accommodate the change in the solute, are the motions of individual solvent molecules important or should the response be viewed as inherently collective? In polar solutions, are reorientational or translational motions of the solvent molecules more effective in lowering the energy of the perturbed solute? Are there different types of solvent responses to changes in solute charge distribution versus changes in solute size and shape?

A great deal of progress has been made recently in answering these questions for dielectric relaxation, that is, the response of the solvent accompanying a change in charge distribution of the solute.² Theory predicts that the earliest time motions of the solvent relaxing the perturbed solute are inertial in character.³ This inertial relaxation has now been observed in many simulations and by experiment, which are approaching generally good agreement.⁴ Simulations have established that this early time relaxation can be ascribed to individual molecular behavior,⁵ and theoretical developments have linked these motions to an instantaneous normal mode description of the solvent.⁶ Less well examined, however, are the molecular details for the solvent mechanical response, that is,

the relaxation of the solvent accompanying a change in solute size and/or shape. Transient hole-burning experiments using non-polar solutes have established that the mechanical relaxation of the solvent behaves in a manner qualitatively similar to the dielectric response.⁷ Molecular dynamics simulations changing the dispersion interaction between the solute and the solvent also show similar behavior.⁸ Since real chemical solutes undergo changes in both size and shape and charge distribution upon photoexcitation or chemical relaxation, it is imperative to study the potential interplay between these mechanical and dielectric solvent responses.

In this paper, we present the results of quantum molecular dynamics simulations aimed at a preliminary exploration of the coupling between mechanical and dielectric solvation dynamics. We have chosen the hydrated electron as our solute probe, since the hydrated electron is known to undergo large changes in both size and shape and charge distribution upon photoexcitation, and since experimental results are available for direct comparison. We find that translational motions of the solvent are of key importance in accommodating the change in size of the solute, and that relaxation by solvent rotational motions may in fact be significantly altered by coupling to the mechanically-induced solvent translations.

II. Methodology

The non-adiabatic quantum simulation procedures⁹ we employ have been well described previously in the literature,¹⁰ so we describe them only briefly here. The model system consists of 200 classical SPC flexible water molecules,¹¹ and one quantum mechanical electron interacting with the water molecules via a pseudopotential.¹² The equations of motion were integrated using the Verlet algorithm with a 1 fs time step in the microcanonical ensemble, and the adiabatic eigenstates at each time step were calculated with an iterative and block Lanczos scheme.⁹ Periodic boundary conditions were employed using a cubic simulation box of side 18.17Å (water density 0.997 g/ml).

Twenty configurations from a 35 ps ground state adiabatic trajectory, chosen to be on resonance with the laser bandwidth corresponding to the experiments, were selected as the starting points for non-adiabatic excited state trajectories.¹⁰ A corresponding set of trajectories was run in D₂O, with a model identical in all respects to the work described previously except that the mass of the H atom was changed from 1 to 2 amu, and preliminary results of the behavior in D₂O are included here.

III. Results

Figure 1 presents the dynamical history of the 2 lowest adiabatic eigenstates of the hydrated electron for a typical trajectory. At times before $t=0$, the electron resides in its nearly spherical s-like ground state, with the first p-like excited state lying ~ 2.2 eV higher energies. Solvent fluctuations modulate the energies of these states, and the strength of the coupling is readily manifest in the large changes in energy (nearly an eV on time scales of tens of femtoseconds). Previous work has established that size and shape fluctuations of the solvent environment have different effects on the quantum energy levels.^{13,14} Upon promotion to the first excited state, the electron grows in size by a factor of ~ 2 along the axial lobes of the p-like wavefunction, but remains unchanged in diameter in the other two dimensions.¹⁰ The surrounding solvent cavity takes on a peanut shape to accommodate this change, and the net result is that the energy of the unoccupied nodeless ground state is raised while the energy of the occupied p-like state remains mostly unchanged. The electron eventually makes a non-adiabatic transition back to the ground state (which happens near $t=200$ fs for the trajectory shown, before the excited state equilibrium is attained). After the transition, the eigenenergy of the s-like state rapidly drops so the ground state equilibrium energy gap is quickly recovered, and

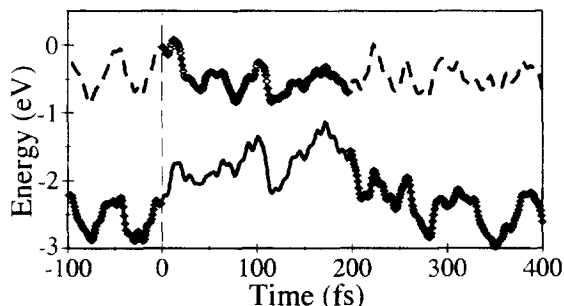


Figure 1. Adiabatic eigenstates of the hydrated electron for a typical trajectory. Solid and dashed lines denote the ground and first excited states, respectively. Diamonds mark the occupied state.

the electronic density quickly becomes localized in one half of the peanut shaped cavity, creating a void in the solvent. As discussed elsewhere,¹⁰ the behavior of the quantum energy levels upon excitation is in good agreement with previous simulations using a different model of the hydrated electron,¹⁵ and the rapid re-establishment of equilibrium following radiationless relaxation is consistent with older, adiabatic calculations.¹⁴

Since the hydrated electron experiences a substantial change in charge distribution upon quantum transition, undergoes a large increase in spatial extent upon photoexcitation, and experiences a corresponding collapse in size upon non-adiabatic relaxation, it serves as an outstanding quantum mechanical probe of the coupling between the mechanical and dielectric solvent responses. To better understand the behavior of the quantum eigenstates following photoexcitation and non-adiabatic relaxation, we have computed non-equilibrium ensemble averages of the quantum energy levels, shown in Figure 2. The left panel shows the response of the adiabatic eigenstates following photoexcitation (the "up" ensemble average); it is an ensemble average that only includes configurations in which the electron still occupies the excited state. Thus, the data at early times contain contributions from all 20 trajectories, but the statistics get poorer at later times as electrons make the radiationless transition to the ground state and are removed from the ensemble. The data clearly show that following photoexcitation, the excited state energy remains essentially unchanged while the ground state energy is raised on two time scales: a rapid increase which takes place in the first 30 fs, and a slower response which takes several hundred femtoseconds. At equilibrium, it is apparent that the gap has decreased from its initial value of ~ 2.2 eV to 0.5-0.6 eV.

The right-hand portion of Figure 2 shows the change in the quantum energy levels following the non-adiabatic transition (the "down" ensemble average); in constructing this average, we have defined $t=0$ to be the point at which the non-adiabatic transition occurs for each trajectory. This is a fairly unusual kind of ensemble average: many of the initial configurations start after radiationless transition from the *equilibrated* excited state, but some initial configurations result from excited state trajectories in which the solvation response is not yet complete (such as the ~ 200 fs point shown in Figure 1). Since all the excited trajectories undergo non-adiabatic relaxation at some point, the traces presented here are averaged over all twenty runs, resulting in good statistics over the entire time period displayed. After radiationless decay over an average gap size of ~ 0.6 eV, solvent relaxation rapidly lowers the energy of the occupied ground state, with most of the response completed within 25 fs. There is evidence for slower relaxation of the ground state on longer time scales, but any slower component of the response plays a much smaller role than that following photoexcitation. Like the upwards transition, the first electronic excited state undergoes little change in energy in response to non-adiabatic

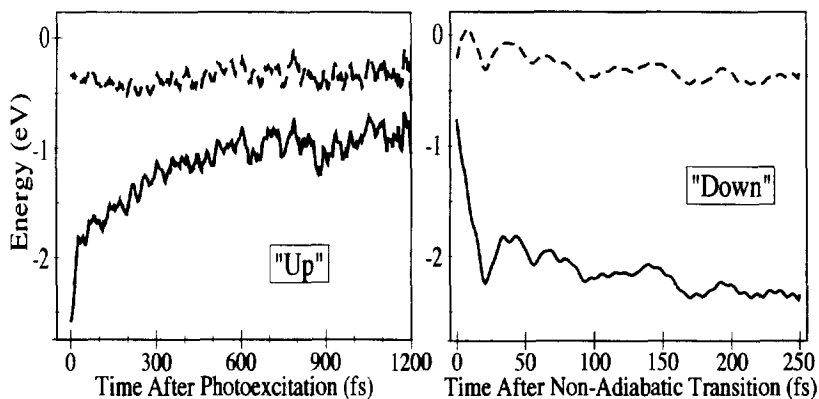


Figure 2. Non-equilibrium ensemble averages of the lowest 2 adiabatic eigenstates of the hydrated electron. Solid line denotes the ground state, dashed line the first excited state. The left panel shows the response of the energy levels following promotion via photoexcitation; the right panel shows the response following the radiationless transition to the ground state. See text for details.

relaxation. Within a few hundred fs of the non-adiabatic transition, the equilibrium structure of the hydrated electron is already re-established, with the gap enlarging to its original value of ~ 2.2 eV. This rapid evolution to equilibrium once the ground state becomes occupied is in agreement with both the results of previous calculations¹⁵ and the observed dependence of the different elements of the calculated ultrafast transient spectroscopy compared to experiment.¹⁶

One interesting feature of the downwards ensemble average lies in the smoothness of the traces present in the right-hand plot of Figure 2. The energy levels of the individual trajectories (cf. Fig. 1) fluctuate by ~ 1 eV on a rapid time scale due to coupling with various modes of the solvent. The fact that these large fluctuations are washed out in the ensemble average following relaxation to the ground state indicates that there is no preferred phase of a particular solvent motion that drives the non-adiabatic transition. If, for example, particular configurations of water molecules characterized by being at the turning point of a collective librational mode were more favorable for non-adiabatic relaxation, then some of the oscillations observed in the individual trajectories would add coherently and hence be enhanced in the ensemble average. The lack of large amplitude oscillations in the average indicate that no special water configurations are responsible for driving the non-adiabatic dynamics. It is also interesting to note the small recurrence in the response between 25 and 30 fs after the downward transition. This oscillation is most likely due to an underdamped librational mode of the solvent, and has been observed in previous aqueous molecular dynamics simulations.¹⁷

IV. Discussion

The effects of mechanical and dielectric solvent fluctuations on the quantum energy gap of a solute are described by the equilibrium solvent response function: $C(t) = \langle \delta U(0) \delta U(t) \rangle / \langle (\delta U)^2 \rangle$ where $U(t)$ is the value of the quantum gap at time t and $\delta U(t) = U(t) - \langle U \rangle$ represents the deviation of the gap from its average value. For small

perturbations, the regression of fluctuations due to a non-equilibrium perturbation should decay in the same manner as those present in equilibrium. Thus, in the limit of linear response, the non-equilibrium correlation function

$$S(t) = (\overline{C}(t) - \overline{C}(\infty)) / (\overline{C}(0) - \overline{C}(\infty)) \quad (1)$$

where the overbar denotes a non-equilibrium average quantity, should be identical to the equilibrium response, $C(t)$. We note that the typical time-dependent Stokes shift experiment which investigates the solvent dielectric response or the transient hole-burning experiment used to explore mechanical solvation measure the non-equilibrium solvent response function $S(t)$.

Figure 3 presents a comparison of the non-equilibrium solvent response functions, Eq (1), for both the photoexcitation ("up") and non-adiabatic ("down") transitions (cf. Fig. 2). The two traces are markedly different: the inertial component for the downwards transition is faster and accounts for a much larger total percentage of the total solvation response than that following photoexcitation. The solvent molecular motions underlying the upwards dynamics have been explored in detail in previous work, where it was also determined that the solvent response falls within the linear regime.¹⁰ Unfortunately, the relatively small amount of time the electron spends in the excited state prevents the calculation of the equilibrium excited state solvent response function due to poor statistics, leaving the matter of linear response for the downwards $S(t)$ unresolved. Whether the radiationless transition obeys linear response or not, it is clear that the upward and downwards solvation response behave very differently, due in part to the very different equilibrium solvation structures of the ground and excited state species. Interestingly, the downwards $S(t)$, with its much larger inertial component, resembles the aqueous solvation response computed in other simulation studies,¹⁷ and bears a striking similarity to that recently determined in experimental work based on a combination of depolarized Raman and optical Kerr effect data.¹⁸

While the difference in the upwards and downwards solvent responses presented in Figure 3 is striking, this is not the first time that variations in solvation dynamics for the same solvent have been observed. Experimental studies have shown differences in solvation response for different probe molecules in the same solvent.² This is a direct indication that probe molecules which have different excited state charge distributions and different mechanical interactions with the solvent produce differing relaxation dynamics. Computer simulations have also observed differing solvation dynamics for the forward and reverse transitions of the sudden appearance of charge, indicative of a solute-dependent solvent response.¹⁷ Moreover, theoretical work has shown that dielectric solvation dynamics is sensitive to the shape of a solute,¹⁹ and that solute size is intimately connected to viscoelastic relaxation.²⁰ It is these effects which are manifest in the

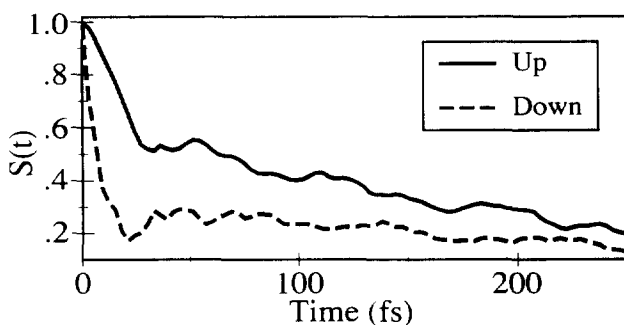


Figure 3. Photoexcitation (up) and non-adiabatic relaxation (down) solvent responses (Eq. 1)

difference between the upwards and downwards solvent responses for the hydrated electron. The size, shape and charge distribution of the electron change continuously (on the time scale of the solvent response) following photoexcitation, creating a situation where the solvent dynamics polarize the solute which then alters the solvent dynamics. The solvent response is determined by both the dynamically changing charge distribution and the mechanical forces of the growing electron pushing on the first solvent shell during its initial expansion. Upon the non-adiabatic relaxation, the electronic density quickly localizes to a shape about that of the final equilibrium ground state. The solvent response to this rapid change in charge distribution is also affected mechanically by the presence of the large void recently occupied by one lobe of the excited state electron. These microscopic differences in the upwards and downwards transitions have profound implications for the coupling of viscoelastic and dielectric solvation dynamics and the nature of the solvent response.

Previous work examining dielectric solvation has ascribed the initial relaxation to rotational motions of individual solvent molecules (i.e., polar solvent molecules inertially reorient to create a more favorable dipole interaction with the new charge distribution of the solute).^{4,5} The rapid expansion of the hydrated electron upon photoexcitation, however, displaces predominantly *translational* modes of the solvent. Water molecules in the first solvation shell are simply pushed back by the Pauli repulsion (mechanical) forces as the electron expands. Thus, much of the initial relaxation of the solvent is the launching of an acoustic wave following this sudden expansion of the solute: the relaxation is predominantly viscoelastic in character. There are three major pieces of evidence pointing towards the strong translational nature of the initial response. First, time-dependent pair distribution functions show large solvent molecule displacements relative to the solute center of mass on the inertial time scale.¹⁰ Second, computed ultrafast transient spectroscopic traces show ringing at frequencies corresponding to intermolecular H-bond stretching and bending motions.¹⁶ Finally, deuteration changes the time scale of the initial relaxation by $\leq 10\%$, a value in accord with motion involving translation of an entire water molecule whose mass has increased from 18 to 20 amu (the corresponding change in moment of inertia if the initial dynamics were predominantly rotational in nature would be $2^{1/2}$, resulting in a $\sim 40\%$ increase in the inertial time scale). This isotope effect is illustrated in Figure 4.

This idea of predominantly displacing translational solvent modes upon excitation leads to an appealing microscopic picture for the coupling of the mechanical and dielectric solvent response. Upon photoexcitation, the free energy will be lowered by both solvent molecule translations, accommodating the new solute size and shape, and solvent molecule rotations, creating favorable electrostatic interactions with the new

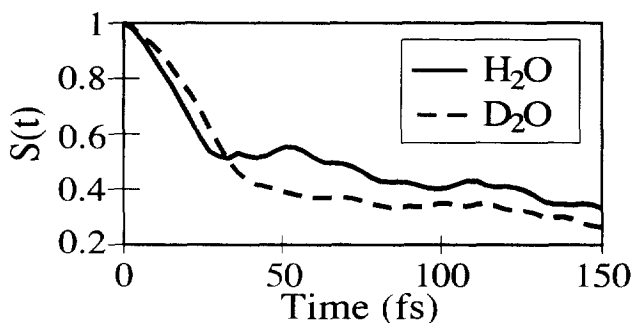


Figure 4. Solvent response following hydrated electron photoexcitation (Eq. 1) for H₂O and D₂O

solute charge distribution. With a continuously expanding solute like the newly excited hydrated electron, the effectiveness of rotational motions of solvent molecules in the first shell will be hindered due to the overwhelming Pauli repulsion forces driving these molecules translationally. This leads to a kind of "dielectric frustration", where the electrostatic relaxation accomplished through solvent rotations is rate-limited by the overall translational rearrangement which accompanies the viscoelastic relaxation. This idea has support in recent experimental work examining the solvent response of the polar solvent propylene carbonate to photoexcitation of a completely non-polar solute, *s*-tetrazine.²¹ In this work, the solvent response function near room temperature, which is well fit by a simple analytic theory incorporating only viscoelastic relaxation,²⁰ is virtually identical to that observed using the polar dye molecule coumarin 152 as a probe.²² This opens up the possibility that in the latter work, the dye molecule undergoes a change in size and shape as well as dipole moment, and that the observed dielectric solvent response is actually rate-limited by the mechanical relaxation, producing the remarkable agreement between the two very different experiments.

The relatively small amplitude of the inertial component of the upwards solvent response may also be the result of this mechanical-dielectric solvation coupling. While the motion of the first shell molecules is inertial in the sense that the solvent-solvent forces play little role in the dynamics, the pressure on these molecules due to the expanding solute hinders their rotational motion. Thus, the decreased effectiveness of these initial ballistic motions can also explain the differences in inertial component amplitude observed in Figure 3 (40%) and in previous aqueous simulation work¹⁷ (80-90%) where only the charge but not the size of the solute was varied. The downward solvent response for the hydrated electron also fits nicely into this picture. The effective size of the ground state electron in one lobe of the excited state peanut-shaped cavity does not significantly change upon non-adiabatic collapse. Molecules in the first solvation shell along the lobe into which the electron localizes do not need to significantly translate to accommodate the newly formed ground state electron. Molecules along the newly vacant lobe can freely translate into the void unhindered, providing rapid solvation. This picture is in accord with the agreement between the downward $S(t)$ and that determined experimentally from the Raman-OKE data; the Raman-OKE experiments are not sensitive to relaxation by solvent translations, and show this same type of dominant rapid inertial response.¹⁸

V. Conclusions

In summary, we have used quantum molecular dynamics simulations of the hydrated electron to investigate the coupling between the mechanical and dielectric solvent responses. The solvation dynamics following photoexcitation shows a strong degree of translational character, because the increase in size of the hydrated electron provides mechanical pressure on the first solvation shell. This mechanical displacement hampers the effectiveness of solvent molecule rotations in providing relaxation, and results in a smaller amplitude of the inertial response. Following non-adiabatic relaxation, molecules in the first solvation shell are either displaced very little, or can freely translate through the newly created void in the solvent, providing for rapid and highly effective solvation. These results suggest that there is strong interplay between the dielectric and mechanical solvent responses, and that in certain cases, "dielectric frustration" can occur in which dielectric relaxation may be altered or even rate-limited by the viscoelastic response of the solvent.

Acknowledgments

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