

## Solvation Dynamics of the Hydrated Electron: A Nonadiabatic Quantum Simulation

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A new algorithm for the quantum dynamical simulation of a mixed classical-quantum system that rigorously includes nonadiabatic quantum transitions is applied to the problem of the solvation dynamics of an initially energetic excess electron in liquid water. Computed results reveal a major channel associated with the appearance of a relatively long-lived solvated excited state postulated earlier; this state is identified as a distorted form of the equilibrium first excited state. The transient spectra evaluated directly from the simulation compare well with experimental data.

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The hydrated electron,  $e_{aq}^-$ , is a ubiquitous transient species in irradiated aqueous systems. Its study also forms the basis for developing a deeper understanding of a broad range of physical problems, ranging from the behavior of hot electrons in amorphous semiconductors to the details of chemical reaction processes in solution.

In this Letter, we consider the relaxation of an initially energetic electron to its equilibrium state in water, a topic of considerable recent interest.<sup>1-11</sup> We use a first-principles quantum molecular-dynamical simulation method,<sup>12</sup> representing the first realization at this level of a nonadiabatic electronic process in a condensed phase.

The process of electron localization proceeds via solvent configurational rearrangement with nonradiative electronic energy loss. The prevailing view has described the relaxation as proceeding via an initial very fast thermalization of the excess electronic energy to form a localized, but only shallowly trapped state, as can be inferred from experiment.<sup>1,13</sup> The further equilibration would proceed under the dominant control of solvent configurational rearrangement.<sup>7,14</sup>

The original ultrafast experiments in water<sup>1</sup> provided the first detailed description of the time-dependent evolution of the optical-absorption spectra. The critical feature is the observation of an apparently stepwise solvation process: an initial rise of absorption in the infrared, followed by a coincident disappearance of this initial state and appearance of the equilibrated state. The experimental evidence for electrons in alcohols<sup>13</sup> suggests a similar type of evolution.

Thus, in contrast to available theories which ascribe the equilibration to solvent configurational relaxation,<sup>7,14</sup> the spectra do *not* manifest a continuous wavelength shift during equilibration. Migus *et al.*<sup>1</sup> tentatively suggested that the second stage corresponded to an electronic transformation.

Using adiabatic quantum dynamics simulation, Rossky and Schnitker<sup>8</sup> investigated the behavior that would be observed if the electron was solvated starting with the

electron already on the ground-state surface. In addition to the observation of a continuous spectral shift, they found that the electron would be solvated in less than 100 fs. Considering the experimental and simulated observations, they postulated that, in fact, the electron is solvated in an effective competition with nonradiative energy loss, so that the electron evolves into a solvated excited state. The rate-limiting time scale would then be determined by the lifetime of this excited state.

A phenomenological analysis based on this postulated description qualitatively reproduces the experimental data.<sup>10</sup> Most recently, Long, Lu, and Eisinger<sup>5</sup> have carried out further experimental studies on the relaxation dynamics and have reported an isosbestic point in the transient spectra at 820 nm (at times longer than about 500 fs), indicative of a true two-state process in this time regime. It is in this spectral region that others observe an approximate, but not true, isosbestic point at times longer than about 400 fs.<sup>1,6</sup> Reference 5 also provides an analysis of the data based on the reported isosbestic point, yielding an absorption spectrum characteristic of the intermediate state.

Here, we investigate the relaxation directly using nonadiabatic quantum dynamics simulation.<sup>12</sup> The calculations are based on a quantum treatment of the electron and a classical solvent. The new algorithm and the numerical implementation are described completely elsewhere.<sup>12</sup> It prescribes a semiclassical simulation of the electronic and solvent nuclear dynamics via a sequence of time steps, each of which is composed of a time propagation of the wave function from an initial time  $t_0$  to a final time  $t$ , a branching among adiabatic electronic eigenstates at time  $t$ , and a time propagation of the nuclear coordinates subject to a total force that recognizes the nature of both the initial and the final quantum state. This is accomplished via a novel combination of the surface hopping idea of Tully and Preston<sup>15</sup> and the nonadiabatic scattering formalism of Pechukas.<sup>16</sup>

The solvent coordinates define a time-dependent electronic Hamiltonian supporting a set of adiabatic eigen-

states  $\{\alpha(t_0)\}$ . The transition amplitudes, defined in terms of the adiabatic states at time  $t$ ,  $\{\beta(t)\}$ , are given in terms of the quantum propagator  $U$  by

$$T_{\beta\alpha} = \langle \beta | U(t, t_0) | \alpha \rangle. \quad (1)$$

The transition to a new state  $\beta$  is determined in accord with the probabilities given by the square of these amplitudes. This is the surface hopping step.<sup>15,17</sup>

The nuclear dynamics are governed by the force prescribed by the sum of the solvent intermolecular forces and a quantum force  $F_Q$  following from the semiclassical scattering theory of Pechukas,<sup>16</sup>

$$F_Q(t') = - \langle \beta | U(t, t') \nabla V_Q(t') U(t', t_0) | \alpha \rangle / T_{\beta\alpha}, \quad (2)$$

where  $V_Q$  is the contribution to the potential depending on the quantum coordinates; in the present context,  $V_Q$  is just the electron-solvent potential. This result follows solely from applying a stationary-phase approximation to the nuclear coordinates in an exact quantum-mechanical expression for the full system propagator. The effective force in Eq. (2) depends implicitly on the nuclear dynamics,<sup>16</sup> requiring that  $F_Q$  be found self-consistently.<sup>12</sup>

The algorithm is not based on *ad hoc* simplifying assumptions. Quantum state transitions are promoted by solvent dynamics and rigorously conserve energy by coupling to the solvent momenta. For short times, the quantum system evolves correctly as a mixed state and the bath evolves with retention of coherence. For longer times, we make a specific assumption in the present implementation of our algorithm: Coherence is dropped for times longer than the step size.<sup>12</sup> Thus, the loss of quantum coherence at long times<sup>18</sup> is also included. A practical but first-principles description of the intermediate time scale describing the dephasing and an estimate of the time involved are difficult.<sup>17-19</sup> However, explicit examination of the approach shows that it is a good approximation in the present context, an aspect that will be addressed in more detail as part of a longer report.

Another recent contribution with related goals has been presented by Tully.<sup>19</sup> He has proposed a convenient nonadiabatic algorithm, based on surface hopping and a plausible assumption regarding energy disposal into the bath. It has been applied to the relaxation of an electron in helium by Space and Coker,<sup>11</sup> using the numerical methods of Webster, Rosky, and Friesner<sup>12</sup> and an approximation of Tully's algorithm.<sup>19</sup>

The simulations here employ a system including 200 solvent molecules, at a density of  $0.977 \text{ g cm}^{-3}$ , with application of the usual periodic boundary conditions. The electronic eigenstates are represented on a three-dimensional cubic grid spanning the simulation cell. The solvent is modeled as rigid molecular species with interactions described by the simple point-charge (SPC) model.<sup>20</sup> The electron-molecule interactions are prescribed by a pseudopotential developed earlier.<sup>21</sup>

The analysis presented here is based on twenty trajec-

tories, each initiated from a statistically independent phase-space point of the pure solvent at 300 K. The electron is initiated at an energy near 2 eV above the vacuum level, comparable to the excess energy associated with the emitted electron in the cited experiments.<sup>1-6</sup> The initial state of the electron is taken as an energy eigenstate of the zero-time solvent configuration. We find this eigenstate is always nonlocalized. While in the experimental case the initial electron is likely described by an outgoing wave packet, we assume here that the basic transient behavior of the electron will be adequately characterized by that of an eigenstate of similar energy.

In Fig. 1, we show the dynamical history of the adiabatic eigenstates for two typical trajectories. Each is

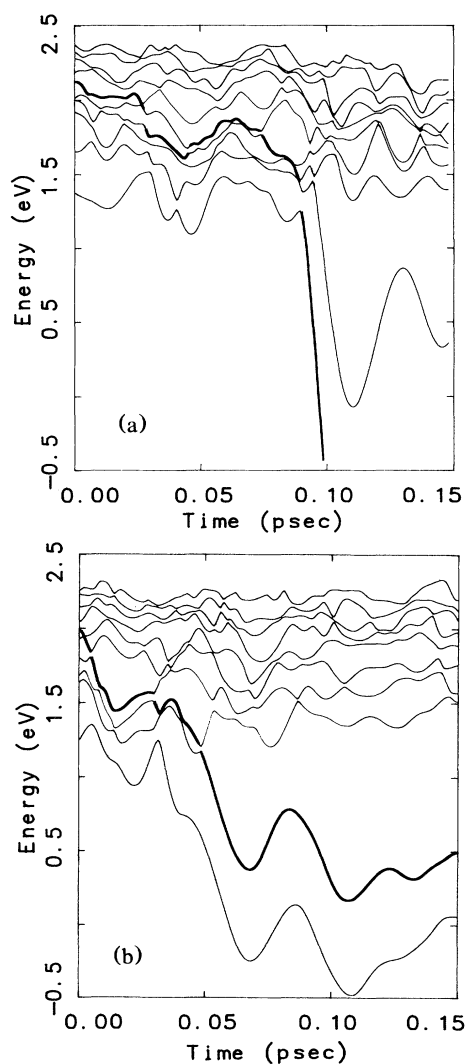


FIG. 1. Dynamical history of adiabatic energies for a trajectory that (a) localizes in the ground state, and (b) localizes in the excited state. The bold line denotes the occupied eigenstate.

representative of roughly half of the trajectories generated. Figure 1(a) typifies the case of a rapid cascade through the excited states directly to the ground state. As can be clearly seen, both curve crossings and energetic discontinuities are observed, with the latter making a major contribution to the process. In parallel with the earlier adiabatic studies,<sup>8</sup> once the electron reaches the ground state, the solvation occurs exceedingly rapidly. In the current study, the time to reach the ground state via such a route is in the range of 50 to 150 fs.

In Fig. 1(b), the alternative behavior postulated earlier<sup>8</sup> is observed. In this case, the electron is clearly characterized by a well-defined isolated excited eigenstate. The time scale for appearance of this state is comparable to that found for the complementary set to reach the ground state. Analysis of the transition amplitudes to the ground state leads to an excited-state lifetime of approximately 1 ps.

Further analysis shows that this excited state is localized and has approximate *p*-type symmetry, analogous to the first three excited states in the equilibrium case.<sup>22</sup> However, we find that the occupied state persists in a distorted cavity characterized by one longer axis; the other two *p*-type states expected in such a cavity occur at significantly higher energy. The effect is analogous to a Jahn-Teller distortion in a molecular system, where the geometry distortion lowers the energy of the occupied level, while raising the energy of unoccupied levels. In accord with the ultrafast time scale for localization,<sup>8</sup> in both cases described here, it is found that the electronic density localizes at the site of a preexisting void in the solvent.

Figure 2 shows the directly computed transient spectra, obtained by evaluation of transition dipole matrix

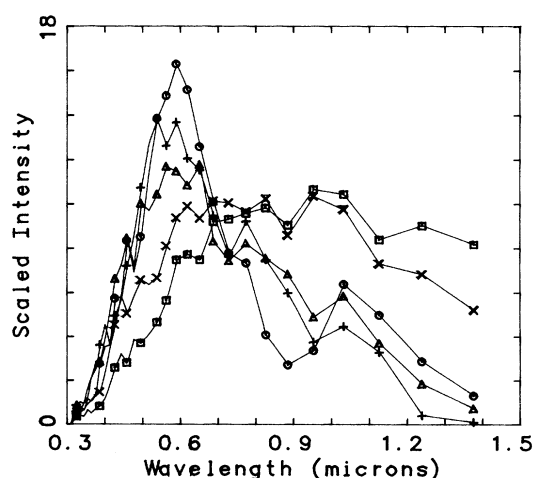


FIG. 2. Calculated transient absorption spectra. The time delays are as follows:  $\square$ , 50 fs;  $\times$ , 100 fs;  $\triangle$ , 200 fs;  $+$ , 300 fs;  $\circ$ , 450 fs. The equilibrium maximum absorption amplitude would be 18 in the scaled units.

elements,<sup>8,22</sup> and convolution with the effective temporal instrument function, a Gaussian with FWHM of 0.1225 ps (see Ref. 10). We note that to obtain computed spectra from the simulated model that coincided accurately with those from experiment would require not only that the spectra of each intermediate species be accurate, but also that each of the separate time scales involved in the relaxation be separately accurately reproduced.

In fact, the overall dynamics appears to evolve somewhat more quickly than seen experimentally.<sup>1</sup> However, the figure shows several important features that parallel the experiment. In particular, at the shortest times, there is a broad absorption peaking well into the infrared, decaying in time with the growth of the peak at the position of the (calculated) equilibrium absorption. An isosbestic point is found for simulated times longer than about 150 fs at roughly the same relative position in the band as seen approximately in Ref. 1 and as has been reported in Ref. 5. The only qualitative discrepancy appears in the relative amplitude of the absorption at the infrared side at early times, where the experimental amplitude<sup>1</sup> is more persistent. The origin of this could lie in the difference in initial conditions between theory and experiment or in the one-electron picture underlying the computed spectra, but this is speculative.

An alternative point of comparison with experiment is derived from the analysis of Long, Lu, and Eisenthal,<sup>5</sup> mentioned above. There are a number of assumptions made in the decomposition of the experimental data, including the value of the branching ratio for entrance into the isolated excited-state channel. Nevertheless, this separation provides a comparison which does not depend on the equivalence of the theoretical and experimental time scales for each of the individual processes. We note that the inferred lifetime of the solvated excited state of 240 fs,<sup>1</sup> or of 540 fs,<sup>5</sup> is not very different from the 1 ps estimated here.

In Fig. 3, we show the computed optical spectrum (averaged from 300 to 600 fs) decomposed into ground- and excited-state components. This may be compared to the result shown in Fig. 4 of Ref. 5, noting that the computed result covers a wider spectral range and that the model is known to produce a ground-state spectrum shifted to higher energy.<sup>22</sup> Over the roughly 1.5-eV range around the maximum that is observed experimentally, the theoretical and experimentally deduced results show an extremely similar relationship between the ground- and excited-state spectra. In both determinations, the excited-state spectrum is somewhat broader than the ground state and is redshifted by about 0.2 eV.

The simulated spectrum shows two additional features. First, there is a distinct absorption peak at about 1 eV that is associated with the excitation across the initial energy gap above this state that is manifest in Fig. 1(b). This feature is observable experimentally, in principle. Second, we compute a net stimulated-emission contribu-

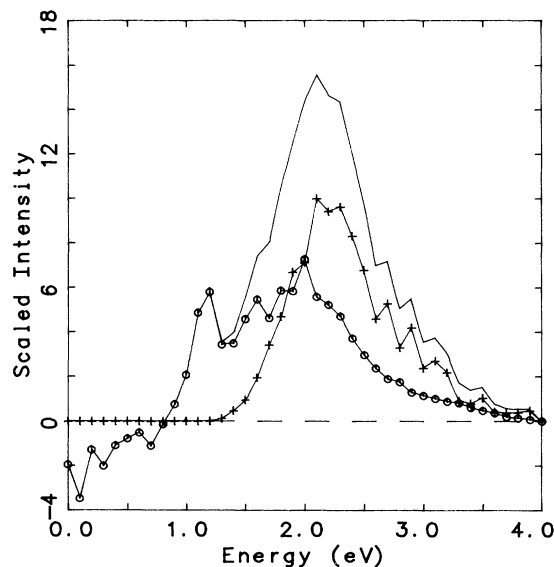


FIG. 3. Decomposition of total absorption spectrum into ground-state and localized excited-state contributions. +, ground state (eleven examples); O, excited state (nine examples).

tion at energies below about 0.5 eV, corresponding to the excited-state to ground-state gap also evident in Fig. 1(b). Because of absorption by liquid water in this region, observation of this emission appears unlikely.

In summary, we have carried out a first-principles simulation of the nonadiabatic relaxation of an initially energetic electron in pure liquid water and compared the results both to physical descriptions of the process postulated earlier and to experimentally determined transient absorption spectra. In both respects, the calculated results are in accord with the earlier postulated picture and in contradiction to the traditional expectation; solvent configurational relaxation *per se* is not rate limiting. It remains to be determined to what extent specific intermediate excited states may play a corresponding role in other solution systems. However, other hydroxylated solvents, where exceptionally rapid readjustment of local order is possible, are likely candidates for a significant channel of this type.

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