

LETTERS

Dynamical Elements of Transient Spectral Hole Burning of the Hydrated Electron

Benjamin J. Schwartz and Peter J. Rossky*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

Received: February 10, 1994*

The transient absorption spectroscopy of photoexcited equilibrium hydrated electrons is computed from quantum nonadiabatic molecular dynamics simulations. The results strongly parallel ultrafast spectral transients measured in recent experiments (Barbara and co-workers, *J. Chem. Phys.* **1993**, *98*, 5996 and *J. Phys. Chem.*, in press), with spectral dynamics that cannot be adequately described by a simple two-state kinetic model. Computed transient spectra with various absorption and bleaching contributions removed are used to explore the microscopic physics underlying the complex behavior. The observed dispersion in excited-state lifetimes and rapid reequilibration of the electron after the radiationless transition to the ground state lead to the conclusion that spectral changes due to solvent cooling after this transition are of little importance to the transient spectroscopy. Instead, the observed complexity of the ultrafast spectral dynamics is shown to be the result of a combination of spectral changes due to excited-state solvation and ground-state bleaching dynamics.

The aqueous solvated electron plays a significant role as an intermediary in the radiation chemistry of water as well as in solution photochemistry and some electron-transfer reactions. For this large class of chemical reactions, the nature of the electronic coupling to solvent fluctuations is of key importance in determining reaction energetics and rates. As the details of this solute-solvent coupling are directly reflected in the electronic absorption spectrum, it is of no surprise that there has been intense experimental¹⁻³ and theoretical⁴⁻⁷ interest in the transient spectroscopy of the hydrated electron.

Experiments first studying the equilibration of electrons injected into liquid water by multiphoton ionization observed a broad infrared absorption which decayed into the known equilibrium spectrum of the hydrated electron on a subpicosecond time scale.^{1,2} These observations were subsequently reproduced by nonadiabatic quantum molecular dynamics simulations,^{5,6} which supported the assignment of the infrared absorption to electronic excited states of the hydrated electron. This suggests that if the electron's spectral properties are characterized by an excited-state absorption spectrum and a ground-state equilibrium spectrum which do not evolve in time, a simple two-state kinetic model could explain the

observed spectral dynamics. If this two-state model of hydrated electron spectroscopy is strictly correct, the transient spectra should show an isosbestic point (wavelength at which the absorption cross sections of the excited and ground states are equal), a matter which has been the subject of some controversy.^{1,2}

More recent experiments have provided complementary information on the radiationless transition rate and electronic solvation dynamics by examining the transient spectroscopy of photoexcited equilibrium hydrated electrons.³ These experiments employ a three laser pulse sequence: first, a UV "synthesis pulse" generates hydrated electrons by multiphoton ionization; next, after a delay of several nanoseconds to allow for equilibration, a near-infrared pump pulse promotes the electrons to their first excited state where a third pulse interrogates the resulting spectral dynamics. In addition to providing insights into the nature of the optical spectrum by bleaching dynamics (hole burning), these experiments also measure spectral contributions due to transient absorption and stimulated emission from the excited state.

If the two-state model were rigorously true, the transient spectral dynamics observed in the above experiments should be identical at every wavelength, and there should also be an isosbestic point where no change in absorption is observed. Instead, the

* Abstract published in *Advance ACS Abstracts*, April 15, 1994.

experiments detected complicated spectral transients, indicating a breakdown of the simple two-state picture.³ The bluest probe wavelengths revealed a net transient bleach with biexponential recovery dynamics. The slower recovery time scale was ~ 2 ps, while the faster recovery time of a few hundred femtoseconds decreased slightly toward longer wavelengths. Just to the red of the 780-nm pump laser, complex spectral kinetics involving an initial bleach which overshoots into a longer-lived transient absorption were observed. Finally, at red probe wavelengths, a net transient absorption with a biexponential recovery similar to the bleach was seen. These complex spectral dynamics could be a reflection of spectral diffusion in the ground-state bleach, spectral evolution due to solvation of the electronic excited state, spectral changes caused by cooling of the reformed ground-state electron after electronic transition, or any combination of these processes not accounted for in the simple two-state model.

To understand the reasons for deviation from the simple two-state picture, we have performed quantum nonadiabatic molecular dynamics simulations of photoexcited aqueous solvated electrons. The calculated transient spectra are in near-quantitative agreement with experiment, indicating that the simulation correctly captures the essential physics of the hydrated electron. We find that the complex spectral dynamics are the result of both excited-state absorption and ground-state bleach spectral evolution. Slower spectral changes on the picosecond time scale are the result of electrons which still remain in the excited state; ground-state cooling after the transition is found to play little role in the resulting transient spectroscopy. This work represents part of a growing body of strongly interrelated experimental and theoretical literature providing detailed knowledge of this important physical system.¹⁻⁷

The nonadiabatic simulation procedures we employ are essentially identical to those used in previous studies of electron localization after injection^{6a} and are described in detail elsewhere.⁵ The model system consisted of 200 classical simple point charge (SPC) water molecules with the addition of internal flexibility⁸ and one quantum electron in a cubic cell of side 18.17 Å (solvent density 0.997 g/mL) with standard periodic boundary conditions at room temperature (300 K). The electron-water interactions were described by a pseudopotential developed previously.⁹ Quantum dynamics were performed using the nonadiabatic method of Webster *et al.*⁵ and the equations of motion integrated with the Verlet algorithm using a 1-fs time step. Spectral calculations included the 40 lowest instantaneous adiabatic eigenstates, computed on a 16^3 grid via an iterative and block Lanczos scheme.⁵

Twenty configurations in which the electronic absorption of the hydrated electron was resonant with the pump laser (2.27 ± 0.01 eV corresponding for the model Hamiltonian¹⁰ to an experimental pump pulse centered at 780 nm with a ~ 200 -cm⁻¹ bandwidth) were selected from a 35-ps equilibrium trajectory^{6a} and used as the starting points for ground-state bleach spectral computations. Excited-state trajectories launched from these same configurations were used to compute excited-state absorption and stimulated emission spectral contributions. The ensemble-averaged bleach, absorption, and emission spectra were then convolved with a 300-fs Gaussian, representing the experimental instrument resolution,³ and combined to produce the full ultrafast spectral response.

Because it is difficult experimentally to determine the relative amplitudes of spectral transients at different wavelengths, we have calculated time domain spectral traces of the type measured directly in the laboratory. The traces in each plot of Figure 1 are normalized to the same maximum amplitude to facilitate comparison of the rise and decay dynamics between wavelengths. The oscillations superimposed on these transients are most likely artifactual, resulting from insufficient sampling over the phase of a low-frequency intermolecular vibration coupled to the

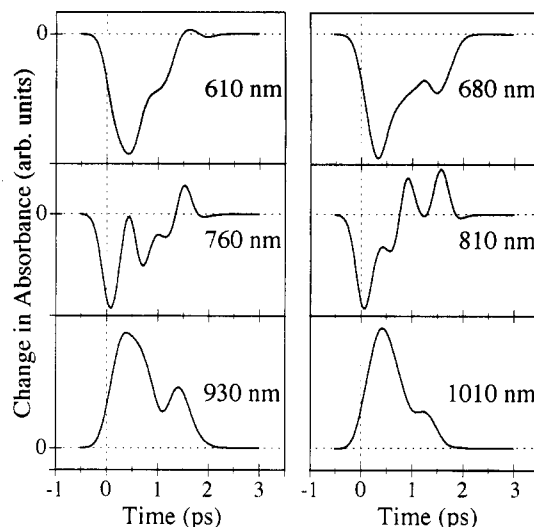


Figure 1. Computed time domain spectral transients for the hydrated electron at various wavelengths.

electronic dynamics. Barring the noise from these oscillations, these traces show remarkable agreement with experiment.³ At the bluest wavelengths (upper two plots), a transient bleach which recovers on multiple time scales is observed. The rate of the fastest portion of the recovery and relative importance of the slower recovery components both decrease toward shorter wavelengths, in accord with experiment. Near the pump laser (center plots), a rapid transient bleach which overshoots into a transient absorption is seen. Like the experiments, the degree of overshoot becomes increasingly important to the red. At the longest wavelengths (lower plots), the calculated spectra show a net transient absorption which recovers in a manner similar to the bleaching dynamics.

The calculated spectral transients for our model differ slightly from those measured experimentally in two ways. First, the computed (shifted¹⁰) spectral dynamics are somewhat blue-shifted from experiment. For example, the calculated trace for 810 nm (center right) most closely resembles the experimental trace^{3b} measured at 860 nm. Second, the simulated spectral traces recover somewhat more rapidly than those measured in the laboratory. This behavior is in agreement with previous work on electron injection using this model of the hydrated electron.^{6a} This faster recovery is likely a reflection of the classical flexible model used for water in the simulations: since the oscillators in classical flexible water can act as a depository for any amount of energy, they can provide for faster relaxation than real water in which energy acceptance is quantized. Despite these slight differences, the excellent agreement between the experimental and theoretical spectral traces indicates that the simulations correctly reproduce the underlying microscopic physics.

Figure 2 presents the complete transient spectroscopy of the hydrated electron in absolute units, shown at various time delays. The region immediately surrounding the pump laser (700–850 nm) is characterized by a dynamic blue shift of the transient spectra. It is this blue shift with time that results in the complicated transients observed in this spectral region and represents the largest deviation from the predictions of the simple two-state kinetic picture.

One attempt to explain this complex spectral behavior incorporated the effects of local heating following the nonadiabatic relaxation to the ground state.^{3b} Since the absorption spectrum of the ground-state electron is temperature dependent,¹¹ the spectral blue shift upon cooling was able to explain much of the deviation from the simple two-state picture. This cooling model yielded an excited-state lifetime of 310 fs and a ground-state cooling time of 1.1 ps.^{3b} The molecular dynamics simulations, however, show that the majority of the electrons remain in the

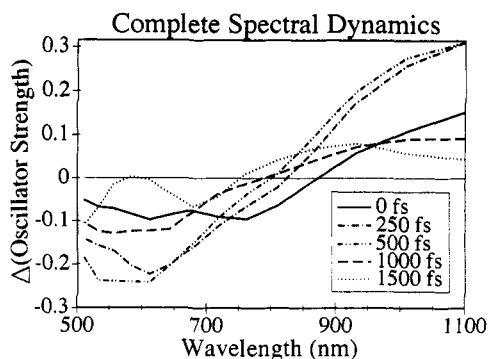


Figure 2. Calculated full spectroscopy of the hydrated electron at various time delays. The data have been smoothed with a simple three-point (1:2:1) sliding average to clarify the observed spectral trends.

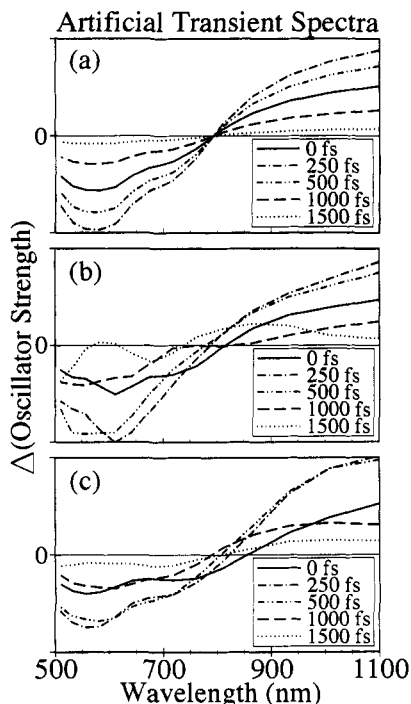


Figure 3. Various computed artificial transient spectra for the hydrated electron; see text for details. (a) Equilibrium bleach, absorption, and ground-state recovery spectra (equivalent to the simple two-state kinetic model). (b) Equilibrium excited-state absorption and ground-state recovery, but calculated bleaching dynamics. (c) Equilibrium bleaching and ground-state recovery, but computed excited-state absorption dynamics. The data have been smoothed in the same manner as Figure 2.

excited state during an appreciable period of the spectral blue shift.¹² Given that the computed nonadiabatic transition rate should be slightly faster than experiment, it is questionable that ground-state cooling dynamics provides the dominant explanation for the observed spectroscopy.

In order to assess the roles of alternative contributions to the spectral evolution, we have computed artificial transients using the static (equilibrium) ground-state^{6a} and excited-state¹³ absorption spectra. Since the emission, absorption, and bleach spectral components are determined independently, the appropriate equilibrium spectra can be substituted for one or more of these spectral components. This allows the construction of transient signals which contain only selected contributions from bleaching dynamics, excited-state evolution, or ground-state cooling. Such traces are shown in Figure 3.

Figure 3a presents transient spectroscopy of the hydrated electron with no component spectral dynamics; that is, at all times, the ground state bleach is assumed to be proportional to the equilibrium spectrum, and the excited-state absorption is

assumed to be due to the equilibrium excited-state spectrum. In addition, the electron is assumed to have its equilibrium spectrum immediately upon making the nonadiabatic jump to the ground state. This set of assumptions, which correspond exactly to that of the simple two-state model, leads to identical spectral dynamics at every wavelength and an isosbestic point near 790 nm. The rise and decay of the red transient absorption and the blue spectral bleach echo the instrumental resolution and nonadiabatic return to the ground state, respectively. Clearly, this representation of electron spectroscopy does a poor job of reproducing the actual spectral dynamics (Figure 2) not only in the central spectral region near the pump laser but also at the extreme red and blue wavelengths.

Figure 3b explores the effects of ground-state bleaching dynamics on the overall spectral signals. In this plot, the excited-state absorption and ground-state absorption after the radiationless transition are assumed to be the equilibrium spectra, as with Figure 3a, but this time the computed bleaching dynamics are used. Since the excitation pulse lies near the red edge of the absorption spectrum, the bleach is characterized by a spectral hole which broadens the blue shifts over several hundred femtoseconds.^{4,7} The region blue of 800 nm in Figure 3b, where the excited-state absorption cross section is small, shows good agreement with the full spectral dynamics (Figure 2). This indicates that much of the deviation from the simple two-state model results from the blue-shifting hole in the transient bleach and that ground-state cooling need not be invoked to explain the complex spectral response in this region. To the red of 950 nm, where the ground-state absorption cross section is low so that the bleaching dynamics are less important, the spectral response is virtually identical to that of the two-state model (Figure 3a). The region between 800 and 950 nm also shows differences from the full calculation. Thus, bleaching dynamics alone can explain much but not all of the observed ultrafast traces.

Figure 3c displays the effects of excited-state relaxation on the full transient spectroscopy. In these traces, both the ground-state bleach and the ground-state absorption after the nonadiabatic transition are assumed to be the equilibrium spectrum, but the computed excited-state absorption dynamics are employed. A large fraction of the excited-state electronic solvation response is observed to take place with a ~ 250 -fs⁻¹ rate in the simulations,¹⁴ leading to an excited-state absorption spectrum which evolves with time. It is interesting to note that the shifting excited-state spectrum has a cross section which is not completely negligible in the 500–700-nm region, as inclusion of the excited-state dynamics causes some deviation from the simple two-state picture (Figure 3a). In the region red of 900 nm, where the bleaching dynamics are less important, the calculation incorporating only excited-state evolution does a reasonable job of reproducing the complete spectral dynamics (Figure 2). Thus, the change in shape of the excited-state absorption due to electronic solvation is responsible for most of the observed spectral dynamics in this region.

Overall, the plots of Figure 3 show that the complex spectral transients demonstrated by the hydrated electron can be explained by a combination of bleaching and absorption dynamics and that spectral changes which occur after the nonadiabatic transition are of little importance. Indeed, artificial spectra constructed from the full bleaching and absorption dynamics, but in which the electron was forced to have the equilibrium spectrum immediately after relaxing to the ground state, are almost indistinguishable from the full spectra presented in Figure 2. This observation is consistent with the calculated relaxation of the electron after the nonadiabatic return to the ground state; nearly 90% of the electronic solvation response is complete within 30 fs of the downward transition,¹⁵ implying that for most purposes the spectrum of the hydrated electron after relaxation to the ground state is, in fact, the equilibrium spectrum. Additional

details concerning the individual spectral components, solvation of the excited state, and relaxation after the radiationless transition will be presented in forthcoming work.⁷

In summary, we have examined the microscopic physics underlying the transient spectroscopy of the hydrated electron via quantum nonadiabatic molecular dynamics simulations. The computed ultrafast spectral traces are in remarkable agreement with experiment and show complex behavior which differs greatly from the predictions of a simple two-state kinetic model. Much of the interesting spectral dynamics take place during the long excited-state residence time, and spectral changes due to ground-state cooling after the nonadiabatic transition are not important to the observed ultrafast transients. Instead, ground-state bleaching dynamics and solvent relaxation leading to evolution of the excited-state absorption spectrum provide the dominant features in the ultrafast spectroscopy. All of the results discussed here highlight the strong interplay between experiment and theory which is continuing to advance our understanding of the microscopic basis underlying ultrafast spectroscopic observations.

Acknowledgment. This work was supported by the NSF. B.J.S. gratefully acknowledges the support of NSF Postdoctoral Research Fellowship Grant CHE-9301479 awarded in 1993 and the allocation of computational resources from the San Diego Supercomputing Center.

References and Notes

- (1) (a) Migus, A.; Gauduel, Y.; Martin, J. L.; Antonetti, A. *Phys. Rev. Lett.* **1987**, *58*, 1559. (b) Pommeret, S.; Antonetti, A.; Gauduel, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9105.
- (2) (a) Long, F. H.; Lu, H.; Eisenthal, K. B. *Phys. Rev. Lett.* **1990**, *64*, 1469. (b) Long, F. H.; Lu, H.; Shi, X.; Eisenthal, K. B. *Chem. Phys. Lett.* **1991**, *185*, 47.

- (3) (a) Alfano, J. C.; Walhout, P. K.; Kimura, Y.; Barbara, P. F. *J. Chem. Phys.* **1993**, *98*, 5996. (b) Kimura, Y.; Alfano, J. C.; Walhout, P. K.; Barbara, P. F. *J. Phys. Chem.*, in press.
- (4) (a) Motakabbir, K. A.; Schnitker, J.; Rosicky, P. J. *J. Chem. Phys.* **1989**, *90*, 6916. (b) Rosicky, P. J. *J. Opt. Soc. Am. B* **1990**, *7*, 1727.
- (5) (a) Webster, F. A.; Schnitker, J.; Friedrichs, M. S.; Friesner, R. A.; Rosicky, P. J. *Phys. Rev. Lett.* **1991**, *66*, 3172. (b) Webster, F. A.; Rosicky, P. J.; Friesner, R. A. *Comput. Phys. Commun.* **1991**, *63*, 494.
- (6) (a) Murphrey, T. H.; Rosicky, P. J. *J. Chem. Phys.* **1993**, *99*, 515. (b) Keszei, E.; Nagy, S.; Murphrey, T. H.; Rosicky, P. J. *J. Chem. Phys.* **1993**, *99*, 2004.
- (7) (a) Schwartz, B. J.; Rosicky, P. J. *Phys. Rev. Lett.*, submitted. (b) Schwartz, B. J.; Rosicky, P. J. Manuscript in preparation.
- (8) Toukan, K.; Rahman, A. *Phys. Rev. B* **1985**, *31*, 2643.
- (9) Schnitker, J.; Rosicky, P. J. *J. Chem. Phys.* **1987**, *86*, 3462.
- (10) Note that the calculated equilibrium absorption spectrum is ~ 0.67 eV blue-shifted from experiment, as seen in ref 6a and Schnitker J.; Motakabbir, K.; Rosicky, P. J.; Friesner, R. A. *Phys. Rev. Lett.* **1988**, *60*, 456. Although a similar probe shift of 0.61 eV results in outstanding agreement between the calculated and experimental transients, all the wavelengths presented here were computed using the 0.67-eV shift for consistency.
- (11) Jou, F.-Y.; Freeman, G. R. *J. Phys. Chem.* **1979**, *83*, 2383 and references therein.
- (12) The average occupation time of the excited state is ~ 730 fs, and the nonradiative lifetime of the excited state after equilibration is found to be ~ 450 fs.
- (13) To avoid contributions from excited-state solvation dynamics, the equilibrium excited state spectrum was computed only from configurations in which the electron had been in the excited state for ≥ 1 ps. The spectrum computed here is very similar but not identical to that presented in ref 6a.
- (14) The ~ 250 -fs electronic relaxation time after promotion of the hydrated electron to the excited state has also been observed by others: Barnett, R. B.; Landman, U.; Nitzan, A. *J. Chem. Phys.* **1989**, *90*, 4413.
- (15) This result is in accord with a growing body of work on aqueous solvation dynamics. See, e.g.: (a) Chang, Y. J.; Castner, E. W., Jr. *J. Chem. Phys.* **1993**, *99*, 7289. (b) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044.