Hydrated Electrons as a Probe of Local Anisotropy: Simulations of Ultrafast Polarization-Dependent Spectral Hole Burning

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Polarized transient hole-burning spectra of the hydrated electron are calculated via quantum nonadiabatic molecular dynamics simulation. The underlying isotropic and anisotropic solvent fluctuations are found to relax on different time scales, leading to polarized spectral holes which are significantly more persistent than unpolarized holes. This separation of time scales leads to a clear spectral signature: transient bleaching in one set of polarizations and transient absorption in the other. This prediction can be directly tested experimentally.

The optical absorption spectrum of the aqueous solvated electron provides a unique probe of the underlying coupling of the electronic states of solutes to solvent fluctuations. The importance of the spectral dynamics of the hydrated electron is evident in the intense interest in its transient spectroscopy. Experiments by Migus *et al.* [1] and Long, Lu, and Eisenthal [2] probed the formation of solvated electrons injected into aqueous solution by multiphoton ionization; the subpicosecond spectral dynamics indicated a stepwise relaxation process characterized by the decay of an infrared absorption into the known equilibrium spectrum of the hydrated electron. Interpretation of these results, supported by molecular dynamics simulations [3], assigned the infrared absorption to the electron trapped in its lowest excited state followed by a nonradiative transition to the ground state. More recently, experiments by Alfano *et al.* [4] have probed the ultrafast spectral dynamics of photoexcited equilibrium hydrated electrons, providing complementary information on the nonadiabatic relaxation and the electronic solvation dynamics. Unlike the injection experiments which detailed the formation of the equilibrium absorption spectrum, these complementary experiments contain spectral components due to bleaching of the ground state, transient absorption from the excited state, as well as stimulated emission from the excited state back to the ground state.

Recent molecular dynamics simulations [5] have been able to reproduce the spectral transients observed in these photoexcitation experiments [4] with a high degree of accuracy. This indicates that such theoretical models are able to capture the essential physics underlying the ultrafast transient spectroscopy of the hydrated electron, giving them utility in providing a detailed picture of the individual spectral components comprising the total observed signal. In this Letter, we present new nonadiabatic quantum calculations which predict the results of polarized ultrafast transient hole-burning (THB) experiments for the aqueous solvated electron. The simulations indicate that isotropic and anisotropic solvent fluctuations coupled to the hydrated electron relax on different time scales, allowing the creation of polarized spectral holes

which are persistent enough to be readily measured with present technology. In addition to a detailed examination of the polarized transient bleaching components, we also present dynamic absorption traces at individual probe wavelengths for the complete polarized transient spectroscopy. Thus, we offer a prediction of the spectral signature of slow anisotropy fluctuations which can be directly tested in the laboratory.

The details of the nonadiabatic simulation method employed are essentially identical to those used in our previous studies [3,5,6], so we describe them only briefly here. The system was modeled by 200 classical simple point charge water molecules with the addition of internal flexibility [7], and one quantum electron in a cubic cell of side 18.17 Å (density 0.997 g/ml) with standard periodic boundary conditions. The temperature was 300 K. The electron-water interactions were described by a pseudopotential developed by Schnitker and Rossky [8]. Quantum dynamics were modeled using the nonadiabatic algorithm of Webster *et al.* [3], and the equations of motion integrated using the Verlet algorithm with a 1 fs time step. Spectral calculations included the forty lowest instantaneous adiabatic eigenstates, computed with a 16^3 plane wave basis via an iterative and block Lanczos scheme [3]. The ensemble averaged transient spectra were convolved with a 300 fs Gaussian representing the experimental instrument response [4,5].

Theoretical modeling has ascribed the broad, featureless absorption band of the hydrated electron to three $(s \to p)$-like transitions, with smaller contributions from absorptions to higher lying continuum states comprising the blue spectral tail [9]. The width of the band arises from both size and shape fluctuations of the electron localized in the solvent cavity. The fluctuation broadening of the individual transitions by roughly 0.4 eV provides only half the total observed spectral width; the remaining width is due to a splitting of these transitions by a comparable amount [9]. This indicates the critical importance of local anisotropy in the spectroscopy of the hydrated electron, removing the normal degeneracy of the p-like excited states that would otherwise be obtained.

The THB experiment offers a method to examine the contribution of these solvent fluctuations to the electronic absorption spectrum. In THB, an initial light pulse which is spectrally narrow compared to the absorption band of interest is used to excite the subset of molecules which are in configurations that bring them into resonance with the pulse. This leaves an absorption deficit, or spectral hole, at the initial pulse frequency which can be measured by a spectrally broad probe pulse as a function of the pump-probe delay time. If the probe pulse also overlaps other ground state electronic excitations, "replica holes" may be observed due to the removal of ground state population which had oscillator strength to these other states. As the delay time increases, solvent fluctuations randomize the configurations of the initially chosen subset, and the spectral hole(s) will broaden, eventually leading to a uniform bleaching of the entire band. Calculations of the bleach component of unpolarized THB for the hydrated electron showed that fast solvent motions coupled to the electronic energy levels lead to a spectrally broad initial hole at the resonant transition, as well as broad overlapping replica holes, making observation of a distinct hole shape difficult [10].

Although the solvent fluctuations that broaden the hydrated electron spectral transitions act rapidly, it is possible that the anisotropic fluctuations which split the otherwise triply degenerate excited state relax on a slower time scale. Since the three excited p states are orthogonal, the three $s \rightarrow p$ transitions have orthogonally polarized transition dipoles, leading to the possibility of using polarized THB spectroscopy to distinguish the local environments which split the states [11]. By exciting the initial subset of configurations with a polarized light pulse, a probe pulse polarized parallel to the initial pulse will tend to probe only the absorption deficit due to the initially prepared state. This effectively masks the replica holes which have probe absorptions polarized perpendicular to that of the initial excitation pulse. This technique has been used recently to examine the solvent anisotropy coupled to the permanganate ion [11] (MnO_4^-) which, like the solvated electron, has a triply degenerate excited state split by local asymmetry in aqueous solution.

To take advantage of this new method to suppress the replica holes, we extended our previous THB calculations [5] to include the effects of polarized light. The starting point for these simulations consisted of injecting an excess electron into neat water and equilibrating the resulting ground state electron for 15 ps [6]. Following equilibration, a 35 ps trajectory was divided into twenty equal segments, and the first configuration in each segment which was found to be resonant with the pump laser (2.27 ± 0.01 eV corresponding for the model Hamiltonian [12] to an experimental pump pulse centered at 780 nm with a ~200 cm^{-1} bandwidth) was chosen as a starting point for the THB runs. Excited state absorption and stimulated emission spectral contributions were computed from separate trajectories following electronic dy-
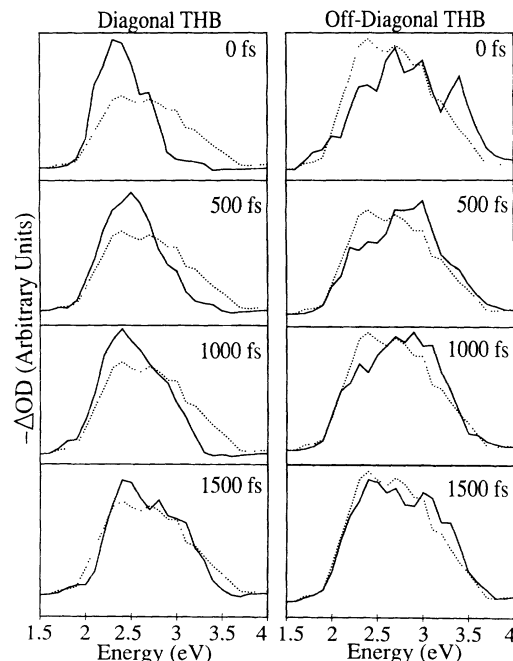

FIG. 1. Diagonal and off-diagonal bleach dynamics (no excited state contributions) of the hydrated electron.

namics on the excited state.

Using the adiabatic eigenstates, the transition dipole matrix elements $\mu_{final}(t) = \langle \psi_{final}(t) | r | \psi_{init}(t) \rangle$ were calculated for each final state, and the absorption spectrum computed directly as the sum over final states. With the starting configuration denoted as $t = 0$, the parallel and perpendicular polarized hole-burning spectra at time t are given by

$$H_\parallel(t;\omega) \propto \sum_i |\mu_\parallel^i(t)|^2 = \sum_i |\mu_i(t) \cdot \mu_i(0)|^2 ,$$

$$H_\perp(t;\omega) \propto \sum_i |\mu_\perp^i(t)|^2 = \sum_i \tfrac{1}{2} [|\mu_i(t)|^2 - |\mu_i(t) \cdot \mu_i(0)|^2] .$$

Since the initial pulse creates a cosine squared distribution of excitations, a probe pulse polarized parallel to the exciting pulse still probes some residual absorption to the two orthogonal excited states. This effect can be compensated for by combining the measured parallel and perpendicular polarized spectra to determine the "diagonal" (probing only the initially prepared state) and "off-diagonal" (probing only the states with transition dipoles perpendicular to the initially prepared state) THB spectra. The appropriate orientational averages have already been computed for the case of a triply degenerate orthogonally polarized excited state [11], giving

$$H_{diag}(t;\omega) = \tfrac{2}{3} H_\parallel(t;\omega) - \tfrac{1}{3} H_\perp(t;\omega) ,$$

$$H_{off\text{-}diag}(t;\omega) = \tfrac{1}{2} H_\perp(t;\omega) - \tfrac{1}{6} H_\parallel(t;\omega) .$$

Figure 1 presents the calculated diagonal and off-diagonal transient bleach spectra (no excited state absorption or emission contributions) for the solvated elec-

tron excited at 2.27 eV (780 nm [12]) at various time delays (solid curves). The calculated equilibrium absorption spectrum (dotted curves), normalized to equal area at each time delay, is also shown to emphasize the shape of the holes. Rapid solvent fluctuations cause the initial ($t = 0$) diagonal hole to be quite broad, corresponding to essentially homogeneous bleaching of the lowest $s \rightarrow p$ transition. Once bleached, the initial hole persists clearly to time delays past 0.5 ps, when it begins to broaden and blueshift. Not until 1.5 ps delay, a time much longer than the nonradiative lifetime of the excited state, does the hole broaden to near uniform bleaching of the entire band. The off-diagonal THB spectra show complementary behavior: The blue edge of the band corresponding to absorption to the upper two p-like states is broadly bleached at $t = 0$, and absorption to the initial state does not grow in until delays > 0.5 ps.

These spectra provide direct evidence that solvent fluctuations with different symmetries are relaxing on different time scales. The initial hole widths of the diagonal and each of the two off-diagonal transitions are comparable, indicating that the very fast fluctuations causing this initial broadening are symmetric in nature. The unpolarized or magic angle bleach also washes out quickly [5,10], confirming the presence of rapid isotropic solvent-solute coupling. The initial bleaching of these polarized spectra is not uniform across the entire band, however, because the anisotropic fluctuations which break the degeneracy occur on a much slower time scale. This asymmetry is persistent: Although coupled strongly to rapid isotropic fluctuations, the three excited states do not interchange roles on a subpicosecond time scale. This separation of time scales by symmetry is a phenomenon which we expect is quite general and one which is presently not considered in microscopic theories of solvation dynamics [13].

Direct measurement of this phenomenon by polarized THB is complicated by the presence of transient absorption and stimulated emission from the excited state as well as the nonadiabatic return to the ground state. The effects of excited state absorption and emission are manifest in the magic angle THB experiments which show a complicated mixture of bleaching and absorption dynamics [4,5]. To account for these complexities and provide a direct prediction of observables, we have calculated the full transient spectroscopy of the hydrated electron including the ground state, excited state, and nonadiabatic contributions.

Figure 2 displays the complete diagonal and off-diagonal spectra at various time delays, presented on the experimentally accessible [4] wavelength scale [12]. The growth and decay of the spectral amplitudes with time reflect the 300 fs instrumental resolution and nonadiabatic return to the ground state, respectively. Near the 780 nm pump wavelength and immediately to the blue, the diagonal spectra show a transient bleach while the off-diagonal spectra show a transient absorption. This is an
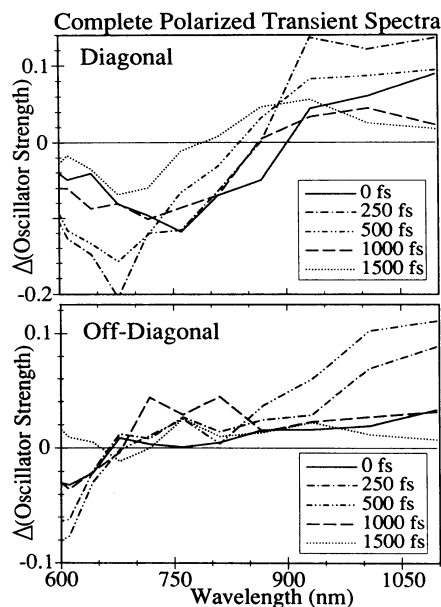

FIG. 2. Complete diagonal and off-diagonal THB including excited state absorption and nonadiabatic relaxation.

immediate consequence of the separation of time scales for the isotropic and anisotropic solvent fluctuations identified here, and provides a basis for direct comparison with experiment.

Because it is difficult experimentally to determine the relative amplitudes of spectral transients at different wavelengths, we have also computed time domain spectral traces of the type measured directly in the laboratory. The traces in each plot of Fig. 3 are normalized to the same maximum amplitude to facilitate comparison of the rise and decay dynamics between wavelengths. The large amplitude oscillations present in these traces are most likely artifactual, resulting from insufficient sampling over the phase of a low frequency intermolecular vibration coupled to the electronic dynamics.

Barring the noise from these oscillations, the figure clearly shows the expected experimental signature of slow anisotropic solvent dynamics. To the red of the excitation wavelength (upper plots) both the diagonal and off-diagonal spectra show an almost instrument limited absorption rise followed by a roughly biexponential decay. Just red of the excitation wavelength, the 870 nm diagonal spectrum (middle left) shows a rapid initial bleach whose recovery overshoots into a longer-lived transient absorption: This type of spectral signature was recently observed in the magic angle THB experiments on the hydrated electron [4]. The 810 nm diagonal trace shows the instrument limited appearance of the bleach of the lowest excited state, while the off-diagonal spectra at these two wavelenths (middle right) show slowly appearing transient absorptions. Just to the blue of the pump (lower plots), the diagonal spectra show the near instrument limited appearance of a bleach which decays on a slower,
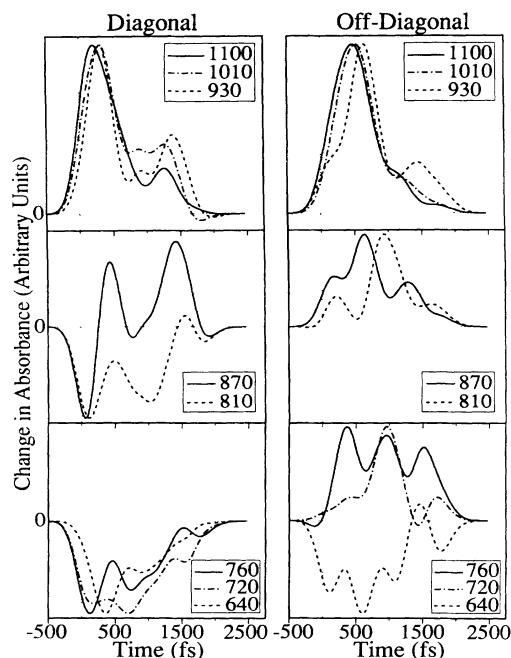
FIG. 3. Calculated single wavelength (nm) spectral transients for polarized THB of the hydrated electron.

~1 ps time scale, while the off-diagonal spectra show more slowly rising (hundreds of fs) and decaying transient absorptions. At the bluest wavelength, 640 nm, both spectra show transient bleaches, with the diagonal bleach appearing and recovering more rapidly than the off-diagonal. As with previous work using this model of the hydrated electron in flexible water, we expect the characteristic time scales of the calculated transients to be slightly faster than those measured experimentally [5,6]. The spectral dynamics at other wavelengths and their connection to the underlying coupling of solvent fluctuations to solute electronic energy levels will be discussed at length in a future publication [5].

In summary, we have used quantum nonadiabatic molecular dynamics simulation to compute the microscopic solvation dynamics of the hydrated electron and provided the first directly testable theoretical predictions of polarized ultrafast spectroscopic transients. The results indicate that anisotropic contributions to electronic solute-solvent coupling occur on a slower time scale than isotropic fluctuations. We expect this to be a general feature of solute-solvent coupling which should be considered in microscopic theories of solvation dynamics. The spectral manifestation of this phenomenon appears as persistent, well-defined, spectral holes in the polarized

THB experiment. Polarized transient spectra calculated from a Hamiltonian based model of the hydrated electron show this signature clearly, predicting a diagonal transient bleach and off-diagonal transient absorption at wavelengths near and just blue of the excitation [12]. The computed dynamics indicate that the spectral changes associated with anisotropic relaxation take place on a time scale of picoseconds or hundreds of femtoseconds, and should be readily observable with current technology.

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[12] Note that the calculated absorption spectrum is ~0.7 eV blueshifted from experiment [5,6,9]. All figures presented in eV use the directly computed transition frequencies; wavelength figures were converted from eV taking this (constant) blueshift into account. As pointed out in [5], the presented transients will likely still be slightly blueshifted from experiment.

[13] See, e.g., M. Maroncelli, J. Mol. Liq. 57, 1 (1993), and references therein.