

Revisiting the pump–probe polarized transient hole-burning of the hydrated electron: Is its absorption spectrum inhomogeneously broadened?

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Abstract

Although simulations have predicted that the hydrated electron's absorption spectrum is inhomogeneously broadened, the experiments in the Literature that test this prediction have produced contradictory results. In this Letter, we describe new polarized transient hole-burning experiments on solvated electrons in both water and methanol. Although we chose excitation wavelengths that should have maximized any polarization dependence in the bleaching dynamics, we were unable to observe any anisotropy. We conclude that the absorption spectrum of the hydrated electron is more homogeneously broadened than suggested by the simulations, although the extent to which the band is inhomogeneously broadened remains an open question.

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1. Introduction

1.1. The origin of the absorption spectrum of the hydrated electron

The optical absorption spectrum of the hydrated electron provides a unique probe to study how solvent fluctuations couple to different electronic states in condensed-phase reactions. The importance of the spectral dynamics of the hydrated electron is evident in the intense experimental [1–9] and theoretical [10–16] interest in its spectroscopy. Although the chemical nature of hydrated electrons is controversial [17], the most widely accepted picture is that hydrated electrons exist as cavity-bound species. In this cavity model, the electron is confined to a quasi-spherical space between solvent molecules and, therefore, its eigenstates are roughly those of a particle in a finite spherical box [10]. This

gives rise to an intense, broad, and featureless optical absorption band centered near 720 nm (see Fig. 1) [1]. One of the most fundamental questions concerning the absorption spectrum of the hydrated electron, and that which we address in this Letter, is whether the absorption spectrum is homogeneously or inhomogeneously broadened.

Mixed quantum/classical molecular dynamics simulations [10–15] suggest that the absorption band of the hydrated electron is dominated by transitions between four cavity-bound electronic eigenstates: an s-like ground state and three p-like excited states. The three p-like states would be degenerate if the cavity were a perfect sphere, but, since on average the cavity is aspherical, the energies of the three p-like states are split. Thus, the simulations assign the absorption spectrum of the hydrated electron to three orthogonally polarized s → p-like transitions, with a tail towards higher energies resulting from s → continuum transitions. This partitioning of the hydrated electron's spectrum is illustrated schematically in Fig. 1. A large asymmetry

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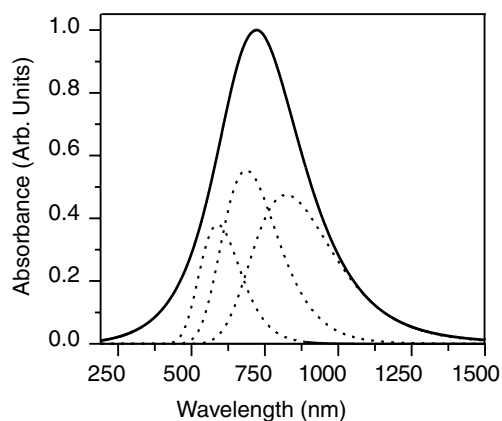


Fig. 1. Absorption spectrum of the hydrated electron (solid curve), reproduced from the Gaussian–Lorentzian fit given in Ref. [1]. The three dotted curves provide a schematic representation of the three $s \rightarrow p$ -like transitions that compose the band (plus a fourth band representing $s \rightarrow$ continuum transitions, which is not shown). In this case, the absorption spectrum was fit to the sum of four Gaussians, with the fitting parameters constrained so that the widths of the three p -like sub-bands were the same (and ≥ 0.3 eV), and so that the relative amplitudes of the three p -like sub-bands were not allowed to vary by more than 20%. The amplitude of the Gaussian representing the continuum band was constrained to be less than 5% of the maximum at 500 nm.

of the hydrated electron's cavity has also been seen in recent Car–Parrinello simulations of the hydrated electron by Boero et al. [16].

Whether the absorption spectrum is homogeneously or inhomogeneously broadened depends on the time scale on which the energies of the three p -like states interchange. Since the relative energies of the three p -like states depend on the instantaneous asymmetry of the cavity, the question boils down to how long memory of the asymmetry of the cavity persists. If the cavity shape changes rapidly, so that the three p -like states interconvert on a time scale faster than the inverse of the absorption line width, then the spectrum would be homogeneously broadened, making the individual sub-bands arising from each of the three excited states experimentally indistinguishable. On the other hand, if memory of the cavity asymmetry persists for a time longer than the inverse of the absorption line width, then the spectrum would be inhomogeneously broadened, allowing experimental delineation of the three sub-bands that compose the absorption spectrum.

1.2. Controversy over the nature of the hydrated electron's spectrum

Mixed quantum/classical calculations by Schwartz and Rossky [12,13] predicted that the absorption spectrum of the hydrated electron should be inhomogeneously broadened: the simulations found that memory of the asymmetry of the electron's cavity should persist

for times of ~ 1 ps. However, these authors noted that a standard *unpolarized* transient hole-burning experiment would not distinguish between the three underlying $s \rightarrow p$ sub-bands because the entire electronic progression would be bleached (thereby producing electronic 'replica holes') even if only a single sub-band were excited. Instead, Schwartz and Rossky [13,18] proposed that the three sub-bands could be experimentally distinguished in a *polarized* transient hole-burning experiment. Since the three p -like excited states are orthogonal, the use of polarized excitation would preferentially bleach a single sub-band, with minimal interference from replica holes that have orthogonal transition dipoles, as described in more detail below.

To investigate the predictions of Schwartz and Rossky's simulations, Barbara and co-workers [4] performed a series of polarized transient hole-burning experiments on the hydrated electron. In their experiments, these authors excited the hydrated electron at 780 nm and probed the resulting polarized bleach dynamics in the near IR. Barbara and co-workers [4] found a difference, or anisotropy, with a decay time of ~ 3 ps in the polarized bleach signals, in good agreement with the predictions of inhomogeneous broadening from the simulations (although the magnitude of the observed anisotropy was somewhat smaller than predicted by the simulations). In a similar series of experiments, however, Laubereau and co-workers [8,9] did not detect any polarization dependence of the bleaching dynamics after exciting the hydrated electron at both 620 and 310 nm and probing at several wavelengths throughout the visible and near-IR. More recently, Barbara's laboratory [19] has been unable to reproduce the polarization dependence they found in their original Letter. One of the purposes of this Letter, is to resolve the conflicting reports as to whether or not there is a polarization dependence to the transient hole-burning of the hydrated electron.

In addition to polarized hole-burning experiments, Wiersma [20] and co-workers performed photon echo experiments on the hydrated electron with ~ 5 fs time resolution to address the question of whether the absorption spectrum is homogeneously or inhomogeneously broadened. These workers reported an echo decay time for the hydrated electron of 1.6 fs, which they argued was consistent with the 1.7-fs dephasing time expected by assuming that the absorption spectrum is homogeneously broadened. Moreover, the photon echo signals were symmetric in time and there was no evidence of quantum beats, which Wiersma and co-workers [20] argued as being consistent with homogeneous broadening. It is worth noting that Schwartz and co-workers [21] had previously calculated the results of the photon echo experiment on the hydrated electron and predicted a fast echo decay similar to that observed in the subsequent experiments done by Wiersma and co-

workers. However, Schwartz and co-workers [21] assigned this fast echo decay to the very large Stokes shift of the excited electron ($\sim 75\%$ of the excitation energy), and argued that for this system, the observation of a fast echo decay is not inconsistent with the inhomogeneous broadening of the spectrum predicted by the simulations.

Finally, both Tauber and Mathies [5,6] and Mizuno and Tahara [7] recently have reported the results of resonance Raman experiments on the hydrated electron. When modeling both the absorption spectrum and the resonance Raman data of the hydrated electron, Tauber and Mathies [5] found an optimal fit assuming that the absorption spectrum had a homogenous linewidth of 4660 cm^{-1} (FWHM) plus an additional inhomogeneous broadening of 2700 cm^{-1} (FWHM). Tauber and Mathies [6] also found that the depolarization ratio of the O–H stretch varied with the excitation wavelength. This changing depolarization ratio is consistent with the idea that the electron's absorption band is not a resonant transition to a single non-degenerate state. Thus, the resonance Raman data suggest that the absorption band is not entirely homogeneously broadened.

In this Letter, we present the results of new polarized transient hole-burning experiments on solvated electrons in both water and methanol. After describing our experimental apparatus, we review a simple model of what is expected in polarized hole-burning experiments and how the results are expected to depend on the excitation wavelength. After analyzing the previous experiments in this area, we then present the results of our new polarized bleach experiments. In particular we explore the polarized dynamics at new excitation wavelengths for the hydrated electron and present the first polarized hole-burning results for solvated electrons in methanol. We find no evidence for any significant polarization dependence in the hole-burning dynamics of solvated electrons either in water or methanol, indicating that their absorption spectra are more homogeneously broadened than suggested by the mixed quantum/classical simulations.

2. Experimental

The details of the laser setup used for our experiments have been described previously [22]. Briefly, the laser system consists of a regeneratively amplified Ti:Sapphire laser (Spectra Physics) that generates $\sim 120\text{ fs}$ pulses at $\sim 790\text{ nm}$ with a pulse energy of $\sim 900\text{ }\mu\text{J}$ at a 1 kHz repetition rate. Like the experiments of Barbara and co-workers [2–4], our experiments consist of a sequential application of three femtosecond laser pulses: the first pulse, or synthesis pulse, creates a population of solvated electrons by multiphoton ionization of I^- ; the second pulse, or pump pulse, arrives $\sim 1.5\text{ ns}$ after the

synthesis pulse and is used to photoexcite the solvated electrons; the third pulse, or probe pulse, arrives at a controlled, variable time-delay after the second pulse, and is used to interrogate the bleaching dynamics of the excited electron population created by the pump pulse. The synthesis pulse is generated by frequency doubling roughly $1/3$ of the 790-nm fundamental beam in a BBO crystal, producing pulses with $\sim 10\text{ }\mu\text{J}$ of energy at 395 nm . The remaining $\sim 2/3$ of the fundamental light is used to pump an optical parametric amplifier (OPA) to create tunable near-IR signal and idler beams. The pump and probe pulses are then generated either by frequency doubling the signal or idler beams, by sum-frequency mixing the signal or idler beams with some of the residual fundamental light in an appropriate non-linear optical crystal, or by splitting off a small fraction of the fundamental beam. The samples consisted of 300 mM potassium iodide solutions in either water ($18\text{ M}\Omega$) flowing through a wire-guided gravity jet [23] or methanol in a 2-mm flow cell¹. All of the experiments were done at room temperature and solutions were changed periodically to avoid the build up of photoproducts.

Polarization information in our experiments on the hydrated electron was obtained by setting the relative polarization of the pump and probe beams to 45° . After passing through the sample, the probe beam was split into components polarized parallel and perpendicular to the pump beam and both components were detected simultaneously and normalized on a shot-by-shot basis using a fast-gated transient digitizer [22]. We performed control experiments to measure coherent artifacts and/or optical Kerr signals in the absence of the 395-nm synthesis pulse, and any pump–probe signals obtained with the 395-nm synthesis pulse blocked were subtracted from the full three-pulse signals.

One issue of particular importance in pump–probe spectroscopy on the hydrated electron is controlling the intensity of the pump pulse to avoid two-photon excitation. We were able to reproduce quantitatively the intensity-dependent results of Barbara and co-workers [3]: Our transient signals changed from the slower bleach recovery associated with excitation into the continuum, to the faster bleach recovery associated with excitation to the p-like state as we lowered the excitation intensity or moved the position of the sample jet out of the focus of the pump beam. Except where noted, we show only the data taken at excitation intensities low enough to ensure that there was no significant two-photon component to our signals.

To calibrate our set-up, we measured the polarized stimulated emission dynamics of $1,1',3,3',3',3'$ -Hexamethylnitrotricarboyanine iodide (HITCI) in methanol,

¹ The 790-nm pump scan in methanol presented in Fig. 4c also was performed using the wire-guided gravity jet.

exciting the dye at 670 nm and probing at 780 nm. We found an initial anisotropy for HITCI of ~ 0.38 [4], with a single-exponential decay time of 360 ps. We obtained similar results when performing the parallel and perpendicular scans separately if we scaled the polarized absorbances to have the same value at long times (when the polarization difference is expected to have decayed). The polarized pump–probe data on solvated electrons in methanol (shown below) were collected and scaled in this fashion, with the parallel and perpendicular signals matched at a time delay of ~ 3 ps. This type of scaling is not possible for transients collected on the hydrated electron, since the hydrated electron's bleach recovers in a very short time; the scaling can be done in methanol, however, because of the presence of a persistent long-time bleach due to reaction of the electrons with the solvent [24].

3. Background and results

3.1. How polarized transient hole-burning can detect inhomogeneous broadening

If solvent fluctuations do not rapidly erase memory of the asymmetry of the hydrated electron's cavity, the electron's absorption spectrum will be inhomogeneously broadened. In this case, the types of motions that exchange the energies of the three p-like states are slow enough to be spectrally separated by a polarized pulse narrow enough in frequency to resolve the individual sub-bands. If the ensemble of electrons created by the synthesis pulse is isotropic, the electrons can be classified in three distinct ways: those with their lowest energy transition (as determined by the direction of the long axis of the aspherical cavity) polarized in the x direction in the lab frame; those with their lowest-energy transition polarized in the y direction; and those with their lowest-energy transition polarized along the z axis. We will refer to these as the N_1 , N_2 , and N_3 types of electrons, respectively (Fig. 2). In a polarized pump–probe experiment, if the light incident on the sample has energy ε_1 and is polarized along the x axis, only the N_1 population of electrons will be excited. Then, if the system is immediately probed at energy ε_1 using light of the same polarization, the signal will show a bleach due to the removal of ground-state N_1 electrons. However, if the system is probed with light polarized perpendicular to the excitation beam, no bleach will be seen at energy ε_1 since the N_2 and N_3 electron populations were not affected by the excitation pulse, but a bleach signal will be observed if the system is probed at energy ε_2 or ε_3 (Fig. 2). As time progresses, solvent fluctuations will exchange the directions of the longer and shorter axes of the electron's cavity, causing the electron to lose memory of its initial polarization. As this occurs, the three

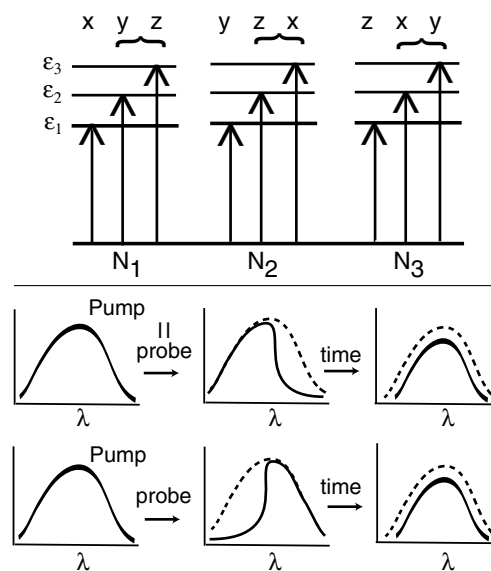


Fig. 2. Schematic for understanding how polarized hole-burning measures the extent of inhomogeneous broadening for the case of three orthogonally-polarized transitions whose degeneracy is broken by local asymmetry. *Top panel:* Energy levels and lab-frame transition dipole orientations of an ensemble of solvated electrons; ε_i represents the transition energy from the ground to the i th p-like excited state (see Ref. [26]). *Bottom panel:* Schematic representation of the polarized transient hole-burning experiment. Exciting the lowest-energy transition (ε_1) with polarized light produces a bleach (solid curves) at low energies when probed with the parallel polarization (top row) and a bleach spread over the two higher-energy transitions when probed with the perpendicular polarization (bottom row). As time progresses (or if the spectrum is homogeneously broadened) and the solvent interchanges the role of the three excited states, the bleach becomes uniform relative to the original absorption spectrum (dashed curves) at all wavelengths and polarizations (see Ref. [13]).

electron populations interchange and the bleach becomes uniform in both polarizations at all probe energies.

Fig. 2 makes it clear that the use of polarized light is essential to separate the roles of the three quasi-degenerate p-like states. If the system were excited with unpolarized light, the removal of electrons from the ground state would deplete oscillator strength from all of the transitions, leading to a uniform bleach of the entire spectrum [12,13]. Anisotropic hole-burning has been observed for the permanganate ion in aqueous glasses, even though there was no evidence of sub-bands in the unpolarized bleach experiment [18]. Moreover, polarized hole-burning has been observed for the charge-transfer-to-solvent (CTTS) transition of the sodium anion in tetrahydrofuran, which, like the hydrated electron, has an absorption spectrum assigned to transitions between an s-like ground state and three non-degenerate solvent-supported p-like excited states [25,26]. The anisotropic dynamics of the sodium anion were well described by a spectral model based on Fig. 2 that incorporates both the full angular distribution of the absorbers and the cosine-squared distribution of transition

dipoles; this model is presented in detail in the Supplementary Information to Ref. [26].

Although polarized transient hole-burning has been seen in other systems, the observation of such signals is more complicated for the hydrated electron. This is due to the fact that the three sub-bands strongly overlap (cf. Fig. 1), making it difficult to excite only one of the three sub-populations of electrons. Thus, the magnitude of any observed anisotropy will depend on the relative weight of the sub-bands that are excited: the more selective the excitation is for a single sub-band, the larger the polarization difference in the transient bleach [26]. Fig. 2 (and the Supplementary Information to Ref. [26]) shows that exciting more than one sub-band would cause the polarization difference (anisotropy) to be much smaller than that expected for excitation of a single sub-band, and that exciting all three sub-bands equally will completely wash out any anisotropy. In the calculations of Schwartz and Rossky [11–13], the simulated excitation was 80% to the lowest excited state and 20% to the second excited state. In the experiments of Barbara and co-workers, however, the 780-nm excitation likely excites a more equal mixture of the two lowest states, with a small component exciting to the third state as well (cf. Fig. 1). Thus, it is not surprising that Barbara and co-workers' [4] experiments found a smaller anisotropy than that predicted from the simulations. The lack of anisotropy observed in the experiments by Laubereau and co-workers [9] exciting at 310 nm is also easy to explain: this excitation wavelength excites only $s \rightarrow$ continuum transitions, which are entirely unpolarized. Thus, no anisotropy is expected in these experiments even if the absorption spectrum of the hydrated electron were inhomogeneously broadened.

Another potential complication for polarized hole-burning experiments on the hydrated electron is the presence of an excited-state absorption that grows in at redder wavelengths [2,3]. The simulations of Schwartz and Rossky [12,13] suggest that this excited-state absorption should be polarized perpendicular to that of the ground-state bleach since the absorption results mainly from transitions between two excited p-like states. Thus, for the hydrated electron, the presence of overlapping bleach and absorption transitions with separate dynamics and opposite polarizations makes it difficult to resolve the anisotropy in the red region of the spectrum. This, along with the fact that 620 nm is close to the crossing point of the two high energy bands (cf. Fig. 1), could potentially explain the lack of anisotropy observed in the 620-nm excitation experiments of Laubereau and co-workers [8]. If the two high energy bands were excited equally, then any anisotropy expected when probing at wavelengths under these two bands would be reduced by a factor of two [26]. Moreover, for 620-nm excitation, the greatest anisotropy would be expected for probe wavelengths interrogating

the low-energy sub-band, where the polarization differences would be more difficult to detect due to the overlapping excited-state absorption in this region. It is for this reason that the probe wavelengths chosen for the experiments presented below are in a region of the spectrum where excited state absorption does not occur and only a bleach signal is seen.

3.2. Polarized transient hole-burning experiments on solvated electrons in water and methanol

Figs. 3A and B show the first set of experiments we performed, which essentially repeat the polarized hole-burning experiments presented by Barbara and co-workers [4], exciting the hydrated electron at 790 nm. As discussed above, this excitation wavelength mixes in considerable contributions from both of the two lowest energy sub-bands, (cf. Fig. 1); we expect based on Fig. 2 and the model in Ref. [26] to see an enhanced bleach in the highest energy sub-bands when probing with the perpendicular polarization. Thus, we chose to probe at both 550 and 620 nm, since these wavelengths should predominantly probe the higher-energy sub-bands without significant contribution from the (unpolarized) continuum. The figure shows no differ-

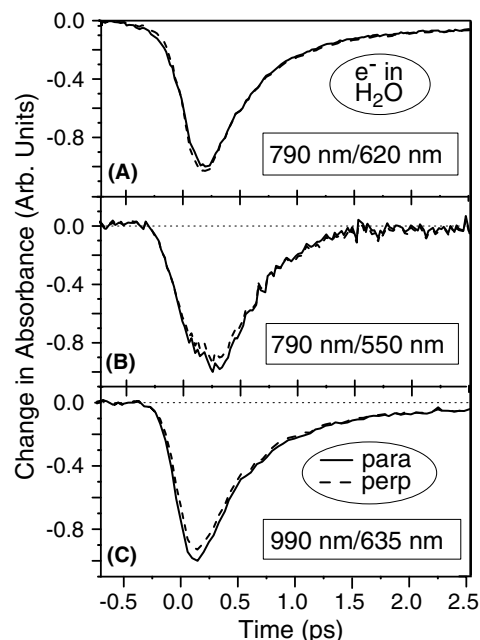


Fig. 3. Pump-probe polarized transient hole-burning signals for the hydrated electron at three different pump-probe wavelength combinations (the pump-probe wavelengths are indicated in the legend of each panel, respectively). For all three panels, the signal with the pump and probe polarizations parallel is shown as the solid curve, and the signal with the pump and probe polarizations perpendicular is shown as the dashed curve. Note that the presence of the coherence artifact (which has been subtracted from the data, see text) prevents analysis of any differences in polarization during the first several hundred fs.

ence in the polarized dynamics outside the time of the coherence artifact (i.e. the signal measured without the synthesis pulse) which persists for ≤ 1 ps. Our experiment is sensitive enough to detect as little as a 5% difference in the parallel and perpendicular signals (corresponding to changes in anisotropy larger than 0.02).

Although we were unable to reproduce the observed anisotropy of Barbara and co-workers [4], it is still possible that the hydrated electron has polarized hole-burning dynamics that could be observed by choosing an excitation wavelength that more cleanly pumps a single sub-band. In our next set of experiments, we therefore chose to excite the hydrated electron at 990 nm, which Fig. 1 suggests should provide a much better contrast for exciting only the lowest energy sub-band. Fig. 3C shows the results of an experiment exciting the hydrated electron at 990 nm and probing the bleaching dynamics at 635 nm. This experiment was challenging for two reasons. First, the absorption cross-section of the hydrated electron is quite small at 990 nm. Second, it is not clear that two-photon excitation would result in a noticeable change in the bleach recovery time [3] (since two photons at this wavelength would still excite the electron to a p-like state rather than to the continuum, as we verified in separate experiments exciting at 500 nm). A significant fraction of two-photon excitation could nonetheless wash out any polarization dependence in the bleaching dynamics, since the p-like states accessed by one- and two-photon excitation are in different sub-bands. Thus, for these experiments, we reduced our excitation intensity to the lowest possible given the sensitivity of our apparatus. Fig. 3C shows a very slight polarization dependence in our 990-nm pump/635-nm probe experiment, but the difference between the two polarizations did not decay with time. Given that the small polarization dependence did not decay and that it goes in the opposite direction for what is expected if the electron's spectrum were inhomogeneously broadened (we would predict that for the 635-nm probe, the bleach should be larger in the perpendicular polarization rather than the parallel), we believe that the small anisotropy observed in Fig. 3C is some form of systematic error, especially given that this experiment so strongly pushes the limits of our sensitivity.

Even though we could not detect any polarization dependence in the transient hole-burning of hydrated electrons, it is still possible that such signals could be observed for solvated electrons in methanol. Since the electron's absorption band in methanol is shifted to the blue ($\lambda_{\text{max}} \sim 640$ nm) [27] relative to that in water ($\lambda_{\text{max}} \sim 720$ nm) [1], pumping the solvated electron in methanol at ~ 800 nm provides a simple method to excite deep into the red side of the band. This makes it easier to cleanly pump the lowest energy sub-band with-

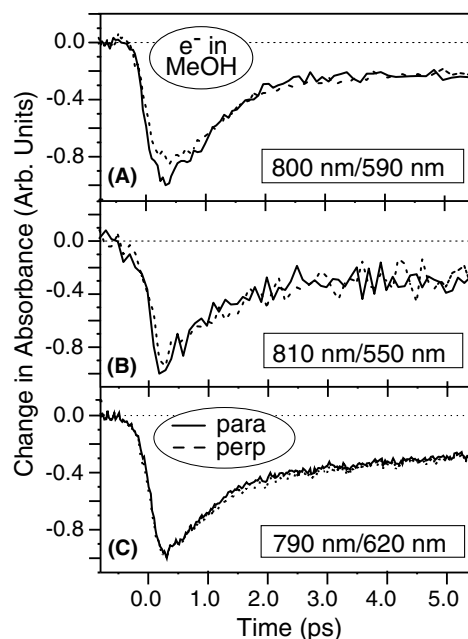


Fig. 4. Pump-probe polarized transient hole-burning signals for the solvated electron in methanol at three different pump-probe wavelength combinations (the pump-probe wavelengths are indicated in the legend of each panel, respectively). Symbols are the same as in Fig. 3.

out significant excitation to any of the higher-energy sub-bands. The anisotropy might also be expected to decay more slowly since the time scale for solvent fluctuations in methanol is slower than that in water [24,28]. Since, to the best of our knowledge, the anisotropic bleaching dynamics have not been previously investigated, solvated electrons in methanol provide a new opportunity for investigating whether cavity shape fluctuations lead to a homogeneously or inhomogeneously broadened absorption spectrum. Fig. 4 shows a series of pump-probe polarized hole-burning experiments on the solvated electron in methanol: 800-nm pump/590-nm probe (panel A), 810-nm pump/550-nm probe (panel B), and 790-nm pump/620-nm probe (panel C). As with the experiments on hydrated electrons, in all cases, no significant polarization dependence to the bleaching dynamics was observed outside the time of the coherence artifact. Thus, we conclude that there is no significant polarization dependence to the bleaching dynamics of solvated electrons in both water and methanol.

4. Discussion

In summary, we have performed polarized pump-probe transient hole-burning experiments on solvated electrons in water and methanol. In contrast to both the results presented by Barbara and co-workers [4] and the simulations of Schwartz and Rossky [13], we find no experimental evidence for a significant polariza-

tion dependence to the bleaching dynamics of solvated electrons. In combination with the results from Laubereau and co-workers [8], this suggests that the absorption spectrum of the hydrated electron is predominantly homogeneously broadened. Thus, we believe that the mixed quantum/classical simulations somehow have overestimated either the asymmetry of the electron's cavity, the stiffness of the cavity (i.e. how long the asymmetry can persist), or both. Since Car–Parrinello simulations of the hydrated electron predict an even larger asymmetry than the mixed quantum/classical simulations [16], we suspect that the fault in the mixed quantum/classical simulations lies in the simulated stiffness of the cavity, which may be a reflection of the approximations inherent in the electron-water pseudopotential.

However, even though we were unable to measure a polarization dependence of the solvated electron's bleaching dynamics, our results do not necessarily imply that the absorption spectrum is purely homogeneously broadened. If the individual sub-bands are broader than what we have suggested in Fig. 1, it would be nearly impossible to cleanly excite a single sub-band, so that teasing the small inhomogeneous component out of the spectrum using polarized hole-burning would be quite challenging. The estimates of the fraction of inhomogeneous broadening from Tauber and Mathies' [5] resonance Raman data suggest that this may indeed be the case.

Could we have missed evidence of anisotropic bleaching in our experiments? The 990-nm excitation experiment in Fig. 3C should have provided the clearest signature of polarization-dependent bleaching, but despite our best efforts, we cannot rule out the possibility of significant two-photon excitation in this experiment. In fact, the small polarization-dependent signal we did see in this experiment would have been more consistent with two-photon excitation, suggesting that we were unable to cleanly probe the dynamics when exciting this far to the red. Another possibility is that the absorption spectrum is inhomogeneously broadened, but the p-like state interchange time is faster than our effective time resolution. Although the cross-correlation of our pump and probe pulses is ~ 200 fs, analysis of our signals requires subtraction of the coherence artifact, which often persists for times nearly as long as 1 ps (likely due to induced birefringence resulting from the optical Kerr effect in the solvent) [29]. Thus, if the polarization dependence to the bleach lasts for significantly less than a picosecond, we would be unable to measure it cleanly in our experiments. Increasing the time resolution of the experiment would not necessarily help the problem: not only are shorter pulses more likely to create interfering optical Kerr signals from the solvent, but the broader bandwidth of the shorter pulses would make it much more difficult to excite only a single sub-band.

Overall, while our results lead us to believe that the absorption spectrum of the hydrated electron is not as inhomogeneously broadened as suggested by the simulations, further work needs to be done to determine whether or not the spectrum is entirely homogeneously broadened.

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