

How Ions Break Local Symmetry: Simulations of Polarized Transient Hole Burning for Different Models of the Hydrated Electron in Contact Pairs with Na⁺

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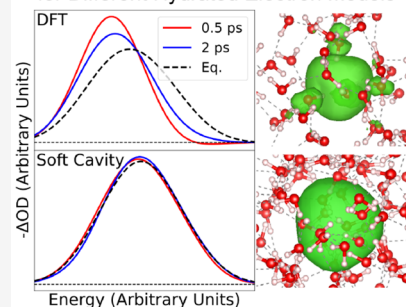
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ABSTRACT: The hydrated electron (e_{aq}^-) is known via polarized transient hole-burning (pTHB) experiments to have a homogeneously broadened absorption spectrum. Here, we explore via quantum simulation how the pTHB spectroscopy of different e_{aq}^- models changes in the presence of electrolytes. The idea is that cation– e_{aq}^- pairing can break the local symmetry and, thus, induce persistent inhomogeneity. We find that a “hard” cavity model shows a modest increase in the pTHB recovery time in the presence of salt, while a “soft” cavity model remains homogeneously broadened independent of the salt concentration. We also explore the orientational anisotropy of a fully *ab initio* density functional theory-based model of the e_{aq}^- , which is strongly inhomogeneously broadened without salt and which becomes significantly more inhomogeneously broadened in the presence of salt. The results provide a direct prediction for experiments that can distinguish between different models and, thus, help pin down the hydration structure and dynamics of the e_{aq}^- .

Polarized Transient Hole Burning Spectrum for Different Hydrated Electron Models



When an excess electron is introduced into liquid water, it becomes stably solvated, forming a species known as the hydrated electron (e_{aq}^-).¹ Hydrated electrons play an important role in radiation chemistry and redox reactions and also provide a rich playground for comparing the results of experiments to quantum many-body simulations.^{2–11} The standard picture of a e_{aq}^- is that of a particle occupying a quasi-spherical cavity in the liquid, with an electronic structure consisting of a *s*-like ground state and three quasi-degenerate *p*-like excited states.¹² The optical transitions between the *s*- and *p*-like states give rise to a broad absorption spectrum that peaks in the near-infrared (IR) and has a Gaussian–Lorentzian shape.^{13,14} Given the unusual line shape, there has been a great deal of work addressing whether the absorption spectrum of the e_{aq}^- is homogeneously or inhomogeneously broadened.^{15–19} In this Letter, we offer new simulation-based predictions for how the homogeneity of the spectrum of the hydrated electron might change in the presence of electrolytes. The results provide a way to distinguish between different simulation models of the e_{aq}^- that have different hydration structures.

Some of the earliest simulation models of the e_{aq}^- predicted that the absorption spectrum of the hydrated electron should be inhomogeneously broadened.¹⁹ The idea was that the cavity containing the hydrated electron is not instantaneously perfectly spherical, causing a splitting in the energies of the three quasi-degenerate *p*-like states. If the solvent motions that cause the splitting are slower than the inverse of the absorption line width of the e_{aq}^- (slow modulation limit), then the spectrum should be inhomogeneously broadened. Examining

this inhomogeneity with a standard transient hole-burning (THB) experiment, however, is not straightforward. This is because photoexcitation of any of the three *s* → *p* transitions removes population from the ground state, causing all three transitions to be bleached, a phenomenon referred to in the THB literature as “replica holes”.^{19–21}

To avoid the issue of replica holes, Schwartz and Rossky¹⁹ proposed examining the homogeneity of the absorption spectrum of the e_{aq}^- via polarized transient hole burning (pTHB).²¹ In pTHB, hydrated electrons are exposed to a polarized pump pulse that selectively excites the e_{aq}^- to one of the three quasi-degenerate *p*-like states, usually the lowest state (red-edge excitation). Because the three *p*-like excited states are orthogonal, they have orthogonal transition dipoles from the ground state. Thus, when the photoexcited system is probed with light polarized parallel to the pump pulse, the pTHB signal shows a bleach of the originally excited transition but no bleach of the orthogonally polarized transitions at higher energies. Conversely, when the system is probed with light that is perpendicularly polarized relative to the pump pulse, the pTHB signal shows a bleach of the non-originally excited transitions but no bleach of the originally excited

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transition. This polarization anisotropy in the bleaching dynamics recovers on the time scale over which solvent motions change the orientations of the transition dipoles of the three quasi-degenerate excited states.^{5,19,21} If the excited states undergo a rapid loss of their initial orientational memory, the absorption spectrum is homogeneously broadened and there is no pTHB signal; if the pTHB signal shows persistent anisotropy, the spectrum is inhomogeneously broadened.

With the idea of pTHB in hand, Schwartz and Rossky simulated this experiment for the e_{aq}^- using mixed quantum/classical (MQC) simulations.¹⁹ In MQC simulations, only the excess electron is treated quantum mechanically, while the water is treated classically, and the interactions of the electron with the water are described by pseudopotentials. Using a standard cavity-forming pseudopotential for the e_{aq}^- ,²² Schwartz and Rossky found that the predicted polarization anisotropy for the pTHB experiment should persist for well over 1 ps, a clear signature that the spectrum of the hydrated electron is inhomogeneously broadened.¹⁹ The reason for this prediction is that the shape of the cavity containing the electron needed to fluctuate to remove the anisotropy, and such shape fluctuations involve translational motions of the first-shell water molecules that are relatively slow.

Motivated by this prediction, several groups set out to perform the pTHB experiment on the e_{aq}^- .^{15,16,18} Although there was some initial controversy over whether there was a pTHB signal or not,¹⁵ consensus was eventually reached that the hydrated electron does not have polarization anisotropy in its THB: the spectrum of the hydrated electron is homogeneously broadened.^{16,18} This means that the reorientation of the excited states of the electron must be quite fast, occurring on a time scale faster than ~ 100 fs. The conclusion that the absorption spectrum is homogeneously broadened is also consistent with the results of experiments measuring the resonance Raman excitation profile of the hydrated electron.⁸ In addition, another group reported a ~ 4 fs decay of the photon echo signal from the e_{aq}^- , which would also be consistent with a homogeneously broadened spectrum,¹⁷ although the photon echo may be reporting more on the very large Stokes shift of the occupied excited state rather than the homogeneity of the absorption spectrum.²³

Here, we propose revisiting the pTHB experiment on the e_{aq}^- with a new twist: adding inert ions to the solution to break the local symmetry of the three quasi-degenerate p-like states of the hydrated electron. Experimentally, when hydrated electrons are solvated in electrolyte solutions, their absorption spectrum blue shifts by a small amount without changing shape.^{24–26} The magnitude of the blue shift increases at higher salt concentrations and depends upon the identities of both the cation and the anion.²⁵ Previous simulation work from both our group^{27–30} and others³¹ has established that the blue shift of the spectrum of the e_{aq}^- in the presence of salts results from ion pairing of the electron with one or more cations in the electrolyte solution. The idea behind performing pTHB in the presence of salt is that the p-like excited state(s) of the e_{aq}^- that are oriented toward the cation(s) will have their energy stabilized relative to those that are not in contact with a cation, potentially breaking the local symmetry on the relatively slow time scale of ion diffusion. Thus, the presence of salt can potentially cause inhomogeneity in what had been a homogeneously broadened e_{aq}^- spectrum.

In this work, we explore predicted results for the pTHB experiment for different simulation models of the hydrated

electron both with and without the presence of different concentrations of NaCl. Previous work has examined the polarized hole burning only for a single model of the hydrated electron in pure water,¹⁹ and here, we show that different hydrated electron models predict quite different results for the pTHB experiment. In particular, we examine the pTHB experiment for the e_{aq}^- both with and without the presence of salt for the well-known MQC “hard” cavity-forming model developed by Turi and Borgis (TB),^{32,33} a “soft” cavity model based on an optimized version of the TB model (TBopt) that uses a polarization potential designed to match the results of CCSD(T) quantum chemistry calculations,³⁴ and a fully *ab initio* density functional theory (DFT)-based model of the hydrated electron that produces a smaller but highly structured cavity.^{35–39} Each of these three models predicts a different hydration structure for the e_{aq}^- , and thus, the three models also show different degrees of ion pairing with Na^+ .³⁹ We find that the TB cavity-forming model, which predicts that the absorption spectrum of the e_{aq}^- is inhomogeneously broadened even without salt, becomes somewhat more inhomogeneously broadened when the electron is paired with Na^+ . The TBopt model, in contrast, predicts a homogeneously broadened spectrum for the bare e_{aq}^- that undergoes little change in transition dipole orientational dynamics upon ion pairing. Finally, the DFT model, which predicts the most inhomogeneously broadened spectrum for the bare electron, becomes significantly more inhomogeneously broadened in the presence of salt. Thus, the way that the pTHB experiment changes in the presence of salt can be used to distinguish between these three different simulation models of the e_{aq}^- .

The time-resolved pTHB spectrum for different simulation models of the e_{aq}^- in this work is calculated using a formalism identical to the previous work by Schwartz and Rossky.¹⁹ Briefly, if the e_{aq}^- has a transition dipole $\mu_i(0)$ at $t = 0$ that is excited with polarized light, the parallel (H_{\parallel}) and perpendicularly polarized (H_{\perp}) probed elements of the pTHB spectrum at time t are given by

$$H_{\parallel}(t, \omega) \propto \sum_j |\mu_{\parallel}^j(t)|^2 = \sum_j |\mu_j(t) \cdot \mu_i(0)|^2 \quad (1)$$

$$H_{\perp}(t, \omega) \propto \sum_j |\mu_{\perp}^j(t)|^2 = \sum_j \frac{1}{2} [|\mu_j(t)|^2 - |\mu_j(t) \cdot \mu_i(0)|^2] \quad (2)$$

where $j = 1, 2, \text{ or } 3$ labels one of the three s-to-p excitations. If the orientations of the three transition dipoles do not change rapidly with time, then the parallel and perpendicularly polarized THB signals will be different, indicating an inhomogeneously broadened spectrum.¹⁹

Of course, if there is an angle θ between the polarizations of either the pump or probe light and one of the transition dipoles of the electron, then there is a $\cos^2(\theta)$ probability for exciting that particular transition dipole. This tends to reduce the difference between the parallel and perpendicularly probed pTHB signals. However, for the particular case of a quasi-triply degenerate excited state with orthogonally oriented transition dipoles, the effects of the $\cos^2(\theta)$ distribution can be removed by calculating^{21,40}

$$H_{\text{diag}}(t, \omega) = \frac{2}{3} H_{\parallel}(t, \omega) - \frac{1}{3} H_{\perp}(t, \omega) \quad (3)$$

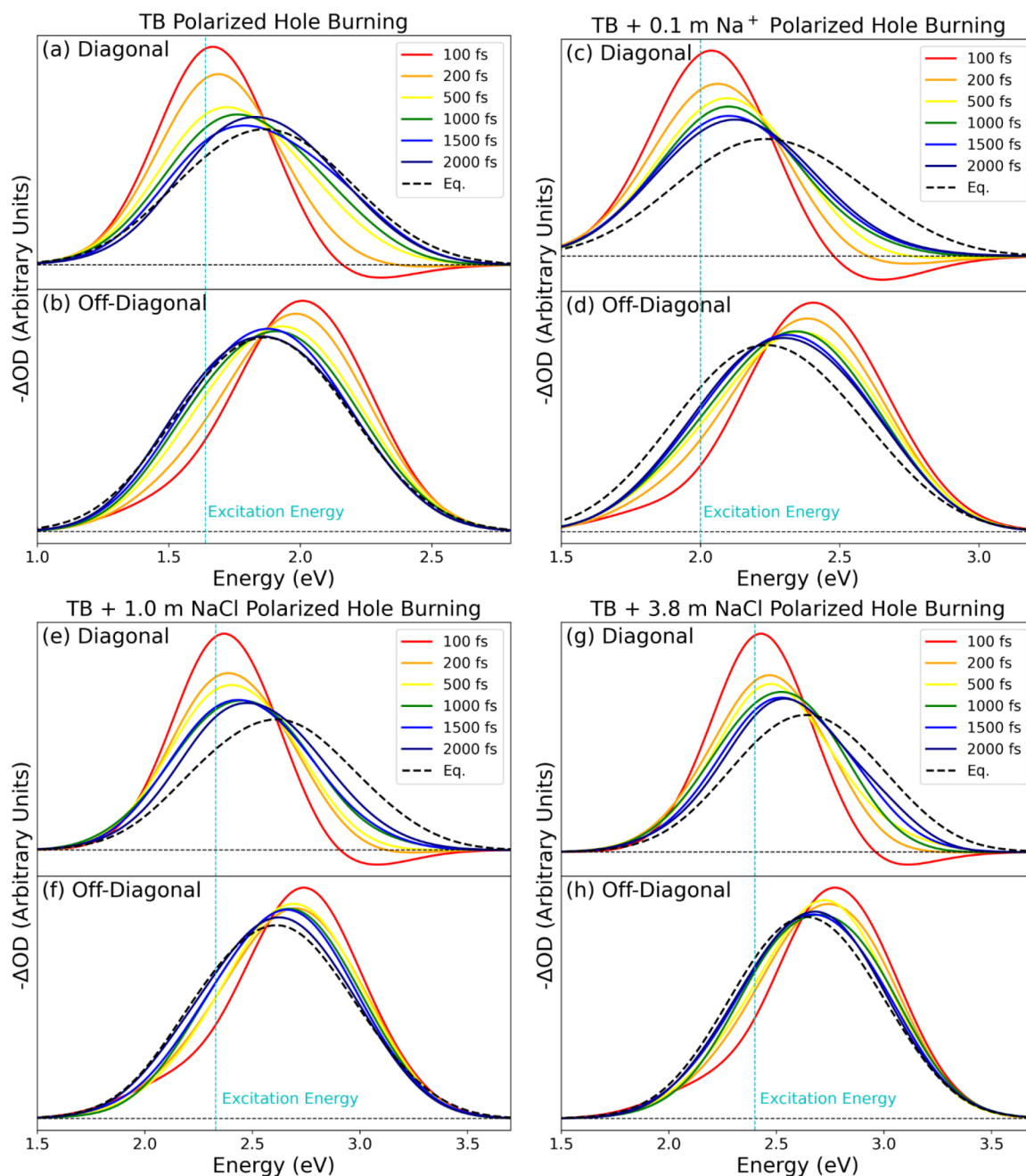


Figure 1. Diagonal and off-diagonal pTHB spectra (eqs 3 and 4, respectively) for the TB cavity model of the hydrated electron at different NaCl concentrations. The time after red-edge excitation is represented by colored curves with time increasing in spectral order from red to blue, and the equilibrium spectra are represented by the black dashed curves. The curves are normalized to have the same total oscillator strength. The pTHB signal of the bare hydrated electron (panels a and b) takes longer than 1 ps to recover to equilibrium, a clear signature of inhomogeneous broadening that is in contrast to experiment. When ions are added, the pTHB recovery to equilibrium extends to ~ 2 ps, indicating enhanced anisotropy as a result of ion pairing. Interestingly, the longest pTHB recovery time is when the e_{aq}^- is paired with a single Na^+ , showing that a single cation is more effective at breaking the local symmetry of the system compared to systems where the electron is paired with multiple cations.

$$H_{\text{off-diag}}(t, \omega) = \frac{1}{2}H_{\perp}(t, \omega) - \frac{1}{6}H_{\parallel}(t, \omega) \quad (4)$$

where the “diagonal” pTHB spectrum probes only the originally excited state and the “off-diagonal” pTHB spectrum probes only the non-originally excited states, enhancing the magnitude of the response. In our simulations, the diagonal and off-diagonal pTHB spectra are convoluted with Gaussians in both energy and time to account for line broadening and the experimental instrumental response, respectively. The standard

deviations of the time and energy Gaussians were chosen to be 50 fs and 0.1 eV, respectively.

The transient absorption spectroscopy of the e_{aq}^- not only consists of a ground-state bleach but also stimulated emission and excited-state absorption components, each of which can have distinctly oriented transition dipoles relative to the originally excited transition.^{10,11,17,41–43} These spectral components can overlap at various probe wavelengths, which can complicate the interpretation of any polarized pump/probe

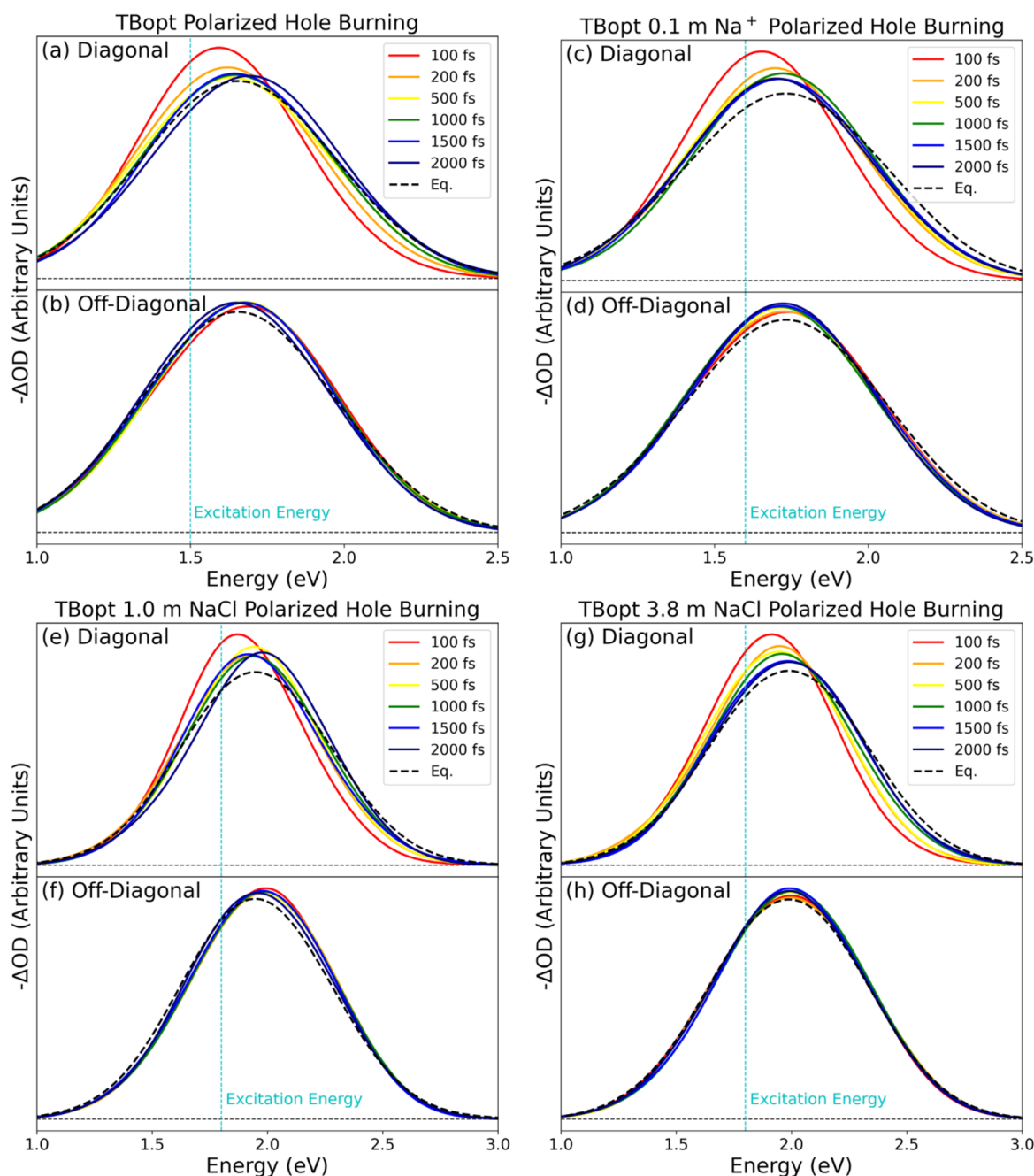


Figure 2. pTHB dynamics of the TBopt soft cavity hydrated electron model for different NaCl concentrations, plotted in the same fashion as for Figure 1. Independent of the salt concentration, the pTHB signals are fully recovered to equilibrium in ~ 200 fs, indicating homogeneous broadening. This is because the highly fluxional first-shell solvent motions can rapidly change the orientation of the excited states whether or not ions are present. Of the three models discussed in this work, this is the only one to correctly predict the experimentally observed homogeneous broadening of the e_{aq}^- in the absence of salt.

signals. Fortunately, the dynamic Stokes shift of the hydrated electron is extremely rapid,^{11,44} so that stimulated emission occurs only well to the red of the initial excitation wavelength. Excited-state absorption between the p-like states also occurs red of the ground-state absorption spectrum of the e_{aq}^- .^{10,11,17,42,43} Thus, the best way to explore the homogeneity of the absorption spectrum of the e_{aq}^- is to excite the lowest energy $s \rightarrow p$ -like transition and then probe the pTHB signal to the higher $s \rightarrow p$ -like transitions that lie to the blue of the excitation wavelength, where only the ground-state bleach contributes.^{11,18}

The pTHB spectra presented in this work were calculated from continuous MQC trajectories that were at least 100 ps long, with the three lowest excited states evaluated at every time step. The transient spectra are ensemble-averaged over at least 300 initial configurations for excitation to the lowest excited state. These initial configurations were chosen as those whose energy gap to the lowest excited state was within 5 meV of the average first excited-state transition energy and were separated in time by at least 250 fs to ensure that they were uncorrelated; further details of the way the calculations were performed are elaborated in the Supporting Information.

Figure 1 shows the calculated diagonal and off-diagonal pTHB spectra for the well-known TB “hard” cavity MQC hydrated electron model at different NaCl concentrations following simulated excitation with polarized light; the spectra at increasing times following the initial excitation are presented in spectral order from red to blue. The black dashed curves mark the simulated equilibrium absorption spectrum in each solution for reference. For the bare hydrated electron (panels a and b), the TB model shows a persistent bleach deficit in the $\sim 2.0\text{--}2.4$ eV spectral region to the blue of the excitation energy in the diagonal pTHB signal and an enhanced off-diagonal pTHB bleach at these same probe energies. The simulations predict that the pTHB signal persists for roughly 1 ps (the time when the pTHB signal becomes indistinguishable from the equilibrium spectrum), a clear signature of inhomogeneous broadening that is similar to that seen in previous simulations with a different hard cavity model.¹⁹ Thus, the TB model fails to reproduce the experimental homogeneity of the spectroscopy of the e_{aq}^- ,¹⁸ although we can still consider how the degree of inhomogeneous broadening changes upon the addition of electrolytes.

Panels c and d of Figure 1 show the results for the pTHB experiment when a single Na^+ is paired with the TB hydrated electron, which we have labeled previously as ~ 0.1 m Na^+ .²⁸ The TB $e_{\text{aq}}^-/\text{Na}^+$ contact pair is highly stable,^{27,39} and the presence of the cation shifts the calculated equilibrium absorption spectrum to the blue by hundreds of meV,^{27,28,30} which is more than an order of magnitude larger than the cation-induced shift seen experimentally.²⁵ The TB e_{aq}^- in 0.1 m Na^+ shows a much more persistent pTHB signal than that in pure water, with significant differences between the diagonal and off-diagonal spectra persisting to delay times well past 2 ps. This is because the orientation of the p-like excited state that is stabilized by the nearby Na^+ remains “pinned” until the ion diffuses. Thus, the prediction is that, if the e_{aq}^- behaves like the TB model, it should have a modestly increased transient polarization anisotropy signature that should be readily observable by experiment.

Panels e–h of Figure 1 show the predicted results for the pTHB experiment on the TB e_{aq}^- in aqueous NaCl solutions with 1.0 and 3.8 m concentrations. For both of these higher salt concentrations, the bleach recovery time is noticeably longer than that of the bare TB hydrated electron, consistent with the argument above that ions break the local symmetry of the electron on the time scale of ion translational motions. Perhaps surprisingly, however, the persistence of the pTHB signal is actually slightly less at these higher NaCl concentrations than at the 0.1 m concentration. This is because the TB e_{aq}^- is simultaneously coordinated by two or three Na^+ at high salt concentrations, providing a more symmetric local environment than when only a single Na^+ is present, as discussed in more detail in the Supporting Information.^{28,30} The fact that the pTHB persistence first increases and then decreases with increasing electrolyte concentration provides an additional experimentally testable signature of the effects of salt on the electronic structure of the hydrated electron.

With these experimental predictions in hand, we turn next to studying how the use of different simulation models affects the homogeneity of the absorption spectrum of the e_{aq}^- in the presence of electrolytes. In Figure 2, we explore the predicted pTHB spectroscopy for the TBopt “soft” cavity model of the hydrated electron, which has a smaller cavity and is much more

fluxional than the TB model; the structural differences between the “hard” and “soft” cavity e_{aq}^- models is discussed in previous work^{34,39} and presented in more detail in depth in the Supporting Information. We note that the TBopt “soft” cavity model is quite different from the so-called LGS “non-cavity” model;⁴⁵ the TBopt model produces a clear cavity, although one that is slightly smaller and with a less distinct hydration structure than the TB model, whereas the LGS model shows essentially no discernible cavity formation. We have shown recently that the TBopt e_{aq}^- model undergoes much weaker ion pairing with Na^+ than the TB model, with the hydration structure of the TBopt electron undergoing relatively little change upon ion pairing.³⁹ Because of this, the TBopt model produces a predicted equilibrium spectral shift in the presence of salt that is in good agreement with the experiment.^{25,39}

Panels a and b of Figure 2 show the calculated pTHB spectrum for the TBopt hydrated electron in pure water. In sharp contrast to the TB model, the predicted pTHB signal for the TBopt model shows almost no persistent anisotropy, with the diagonal and off-diagonal spectra converging to the equilibrium spectrum within 200 fs. This indicates that the TBopt model has a homogeneously broadened absorption spectrum, in generally good agreement with experiment.¹⁸ This is because the hydration structure of the TBopt electron is highly fluxional with first-shell waters that reside well inside of the electron density, so that relatively fast librational or small translational motions of the first-shell waters can reorient the transition dipoles of the three quasi-degenerate p-like excited states, leading to a more homogeneous electronic structure.

Panels c and d of Figure 2 show the calculated pTHB spectra of the TBopt e_{aq}^- paired with a single Na^+ (0.1 m). As with the bare TBopt e_{aq}^- , transient polarization anisotropy is fully recovered in ≤ 200 fs, suggesting that, even with ion pairing, the spectrum remains homogeneously broadened. We believe that this is a direct reflection of the fact that the presence of Na^+ does not perturb the hydration structure of the TBopt electron:³⁹ motions of the first-shell waters are still readily able to scramble the orientations of the quasi-degenerate p-like excited states whether or not there is a nearby Na^+ . Panels e–h of Figure 2 show the predicted pTHB spectroscopy for the TBopt electron at higher salt concentrations. The diagonal and off-diagonal spectra still converge to the equilibrium spectrum within ~ 200 fs, indicating that the absorption remains homogeneously broadened regardless of the electrolyte concentration (we note that the TBopt e_{aq}^- in the 3.8 m NaCl solution might show subtle polarization anisotropy that persists out to ~ 500 fs, but the magnitude of the signal does not seem large enough to be detectable by the experiment). Thus, for a soft cavity electron, the presence of ions makes little difference to the spectral homogeneity. Because the TB and TBopt models show a stark difference in their pTHB dynamics, experiments should be able to readily determine whether the structure of the e_{aq}^- is more like that of the TB or TBopt simulation model.

To make a more direct comparison between our simulations and potential future experiments, we can take advantage of the fact that the cleanest experimental way to examine the pTHB signal is to probe the dynamics in the blue spectral region following excitation on the red edge of the spectrum.¹⁸ Thus, we spectrally integrated the blue region (as defined in more detail in the Supporting Information) of the diagonal (red curves) and off-diagonal (blue curves) pTHB signals for both the TB and TBopt e_{aq}^- models at different salt concentrations,

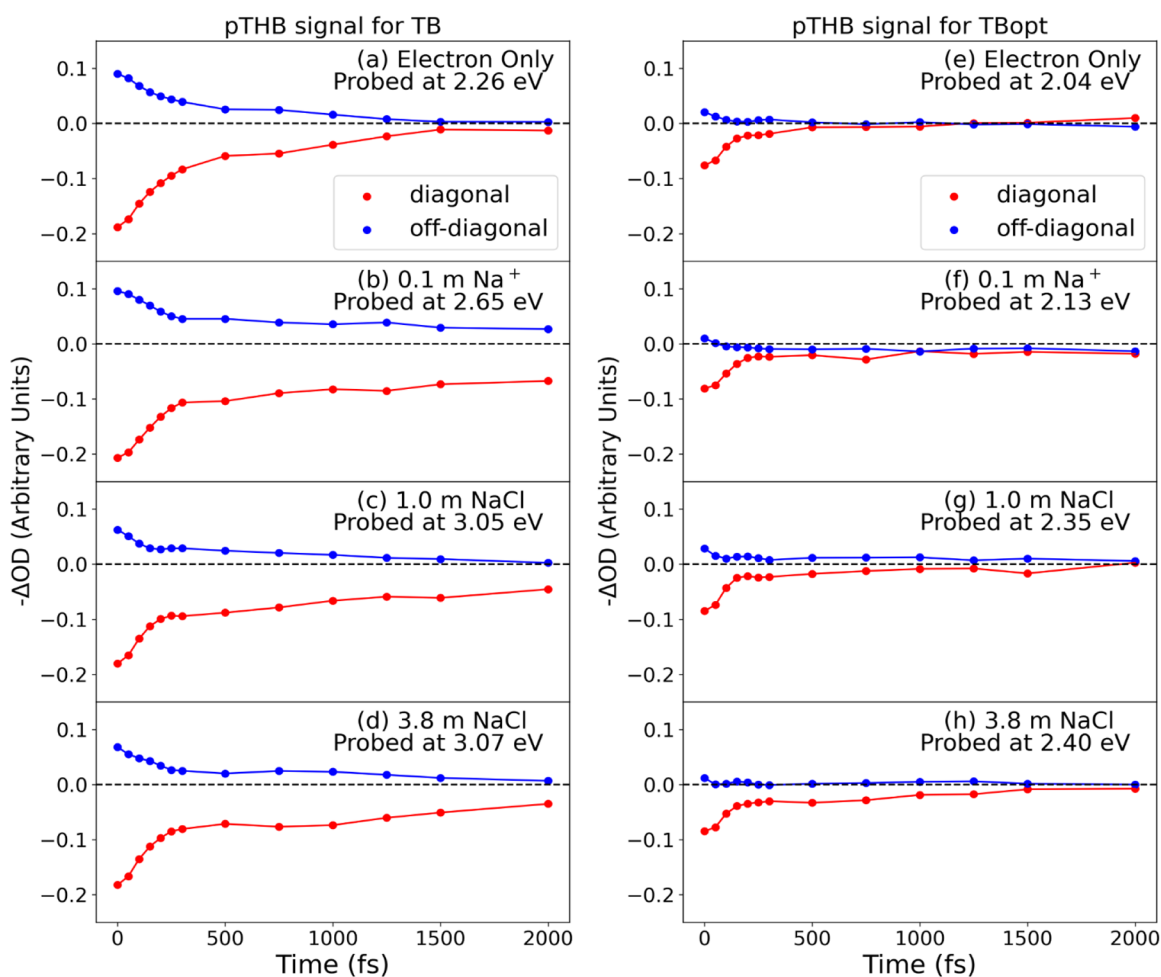


Figure 3. PTHB signal for red-edge excitation probing on the blue side of the absorption band (as with the experiments performed in ref 18) for both the TB (left panels) and TBopt (right panels) hydrated electron models at different NaCl concentrations. The diagonal and off-diagonal pTHB responses are represented with red and blue curves, respectively. As seen in Figures 1 and 2, the bare TB model takes ≥ 1.0 ps for the pTHB signals to fully recover to equilibrium, indicating inhomogeneous broadening. Adding ions to the TB system enhances the anisotropy, because the pTHB signals now persist for longer than ~ 2 ps. For the TBopt model, the pTHB signals are essentially fully recovered by 250 fs, regardless of NaCl concentrations. This indicates that the absorption spectrum of the TBopt hydrated electron is homogeneously broadened and that ions do not break the local symmetry for this model.

with the results shown in Figure 3. The difference between the spectrally integrated diagonal and off-diagonal transients for the TB e_{aq}^- in pure water (panel a) is clearly visible to times beyond 1 ps. As seen in Figure 1, the inclusion of ions causes the polarization anisotropy to persist for longer times, with the persistence time slightly decreasing at the highest NaCl concentration. The results make it clear that, if the experimental e_{aq}^- has similar characteristics to the TB model, experiments would easily be able to see a difference in the pTHB signal in the presence of electrolytes. In contrast to the TB model, the TBopt e_{aq}^- model shows very little pTHB signal, because what little polarization anisotropy there is at early times decays very quickly, independent of the NaCl concentration. Overall, it is clear that different models of the hydrated electron with different local solvation structures should have very different changes in their pTHB spectroscopy in the presence of electrolytes, allowing future experiments to determine which structural features are essential to correctly reproduce the observed pTHB spectroscopy.

Another way to quantify the homogeneity of the absorption spectrum of the e_{aq}^- is to directly examine the solvent motions

that induce reorientation of the transition dipoles to the three quasi-degenerate p-like excited states. If the transition dipoles maintain their orientation, there should be a persistent pTHB signal; if the orientations of the transition dipoles decorrelate quickly, there should be little to no polarization anisotropy. Because the cleanest experiment excites the lowest energy state and then probes the orientation of the higher energy transition dipoles, the most straightforward way to quantify the transition dipole reorientations associated with the pTHB signal is by looking at the autocorrelation, $A(t)$, of a unit vector along the transition dipole between the ground and highest p-like excited state

$$A(t) = \langle \hat{\mu}_{0 \rightarrow 3}(t) \cdot \hat{\mu}_{0 \rightarrow 3}(0) \rangle \quad (5)$$

where $\hat{\mu}$ is the unit vector along the direction of the transition dipole, $0 \rightarrow 3$ indicates that the transition is from the ground to the third excited state, and the brackets denote an ensemble average.

The calculated $A(t)$ functions are shown in Figure 4. The TB e_{aq}^- in pure water (red curve, panel a) shows a slow reorientational decay, taking over 0.5 ps to erase the memory

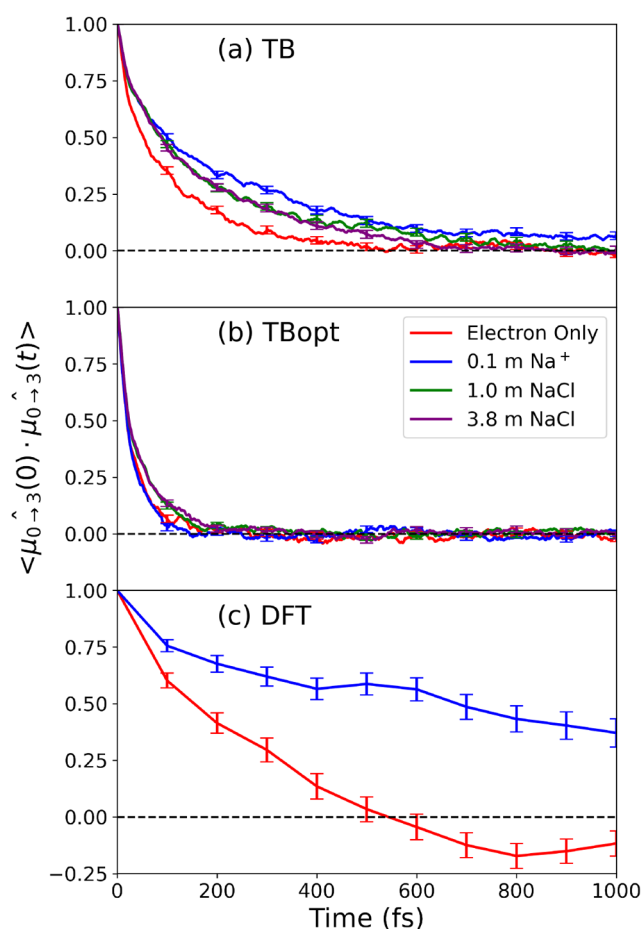


Figure 4. Autocorrelation of a unit vector along the direction of the transition dipole between the ground and third excited state (eq 5) of different models of the hydrated electron in pure water (red curves), with a single Na^+ (blue curves), with 1.0 m NaCl (green curves), and with 3.8 m NaCl (purple curves). The TB hydrated electron model (panel a) shows a slower autocorrelation decay compared to the TBopt model (panel b), verifying that this autocorrelation provides a good proxy for understanding the pTHB experiment shown in the previous figures. This allows us to compare the MQC models to the fully *ab initio* DFT hydrated electron model, which is shown in panel c. The DFT e_{aq}^- shows the slowest transition dipole autocorrelation decay in pure water, indicating strong inhomogeneous broadening that is in disagreement with experiment. Upon the addition of a single Na^+ , the transition dipole autocorrelation becomes ~ 5 times longer, providing a clear signature that could be readily tested by experiment.

of the orientation of the third excited state. As we saw above, adding a single Na^+ nearly doubles the persistence of the orientational memory (blue curve, panel a), and further increases in the NaCl concentration lead to a slightly faster orientational decay (green and purple curves). Panel b shows that the TBopt e_{aq}^- model, in contrast, has a much faster transitional dipole orientational relaxation, with $A(t)$ functions reaching zero by 200 fs and with decays that are nearly independent of the salt concentration. Thus, the equilibrium autocorrelation of the highest excited-state transition dipole provides an excellent proxy for the full pTHB signal when comparing the behavior of different models of the hydrated electron.

The fact that $A(t)$ provides an excellent proxy for the pTHB signal opens the opportunity of exploring the homogeneity of the absorption spectrum for *ab initio* DFT-based models of the

hydrated electron.^{35–39} Direct calculation of the pTHB signal for the DFT-based e_{aq}^- is currently not computationally feasible, because a long (many tens to hundreds of picoseconds) ground-state equilibrium trajectory with time-dependent density functional theory (TD-DFT)-quality excited states is required for sufficient statistics. However, it is possible to calculate the transition dipole autocorrelation function using the TD-DFT-generated excited states of selected configurations over a more modest length trajectory. In previous work, we ran a ≥ 30 ps DFT-based trajectory of the e_{aq}^- with a GGA hybrid functional (PBE0) with 64 waters and an excess electron with periodic boundary conditions;³⁸ we also ran a similar trajectory that included a paired Na^+ .³⁹ We found that the DFT-based e_{aq}^- had its spectrum shift to the red upon the addition of salt, a result in contrast with experiment.³⁹ For the purposes of this paper, however, we can use these previous trajectories to examine the reorientational dynamics of the excited states of an *ab initio* model of the hydrated electron.

Figure 4c shows the reorientational decay of the third excited-state transition dipole, $A(t)$, for both the bare DFT hydrated electron (red curve) and the DFT electron paired with a single Na^+ (blue curve), calculated from our previous trajectories.^{38,39} For the bare DFT hydrated electron, the orientational decorrelation time is similar to that of the TB model, indicating an inhomogeneously broadened spectrum that is inconsistent with experiment. When a single Na^+ is paired with the DFT electron, memory of the transition dipole orientation persists for well beyond 1 ps, the most persistent anisotropy of any of the models explored here. This is due to the fact that the highly structured solvation environment around the DFT electron essentially locks the nearby Na^+ into place, and the tight solvation structure does not allow the orientation of the cavity that determines the directions of the transition dipole moments to easily relax. This extremely slow decay of the transition dipole orientation in the presence of salt should be associated with the largest and most persistent possible pTHB signal of the three models, providing a clear prediction to test if the hydration structure associated with DFT-based models of the e_{aq}^- makes sense.

In summary, we have examined the pTHB spectral dynamics of three different models of the hydrated electron in aqueous electrolyte solutions: a hard cavity model (TB), a soft cavity model (TBopt), and a DFT-based *ab initio* model that gives a highly structured hydration environment. These three models predict dramatically different changes in transient polarization anisotropy upon the addition of salt. The TB model predicts that the spectrum of the e_{aq}^- is inhomogeneously broadened and that the addition of salt leads to increased inhomogeneity that should result in a reasonably significant increase in the persistence of the pTHB signals. In contrast, the TBopt model predicts homogeneous broadening of the spectrum of the e_{aq}^- and that there should be no pTHB signal whether or not salt is present. The DFT model not only predicts inhomogeneous broadening for the bare electron but also predicts a dramatic increase in the persistence of orientational memory in the presence of salt. Because the three models predict very different changes in the pTHB signals upon the addition of salt, the pTHB experiment should provide a straightforward way to test these models and determine which of them, if any, make the most sense in terms of their hydration structure and electronic dynamics.

Given that all three of these hydrated electron models predict that the hydrated electron resides in some type of

cavity, the results presented above show that not all cavity models of the hydrated electron are equivalent: the details of the solvation structure and the dynamics of the first-shell waters cause all three of these models to behave very differently. The TB model creates a fairly large cavity, so that the electronic states of the e_{aq}^- are fairly well-shielded from motions of the first-shell waters. In contrast, the TBopt model has a smaller and more fluxional central cavity with a larger overlap between the electron and first-shell waters. This means that the electronic states can be easily modified by relatively small motions of these waters, leading to rapid reorientational dynamics and homogeneous spectral broadening. The DFT model of the e_{aq}^- has a cavity of intermediate size, but this cavity is surrounded by a highly structured hydration shell whose water molecules are somewhat rigidly locked into place. The much slower first-shell solvent motions cause the DFT hydrated electron to show the largest degree of inhomogeneous broadening.

The problem with distinguishing between cavity models of the hydrated electron is that there is no easy way to measure the hydration structure associated with the e_{aq}^- experimentally, and most simulation models predict absorption spectra and other properties that are very similar to each other. We have argued that studying the behavior of hydrated electrons in the presence of electrolytes provides a sensitive test because ion pairing is very sensitive to the hydration structure of the simulated e_{aq}^- .^{27,39} By exploring how different hydrated electron models behave in the presence of salt, we previously suggested that DFT is too low of a level of quantum chemistry to properly capture the structure and dynamics of the hydrated electron.^{38,39} In this work, we have proposed a new experiment, polarized transient hole burning with and without the addition of NaCl, that should be exquisitely sensitive to the hydration structure and dynamics of the hydrated electron. The fact that experiments have concluded that the absorption spectrum of the hydrated electron is homogeneously broadened suggests to us that the e_{aq}^- must have a highly fluxional solvation structure; hopefully, the pTHB experiment that we have proposed will provide a direct way of determining how the dynamics of the e_{aq}^- change in the presence of salt, thus providing a way to help pin down the true average structure of this fascinating object.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.3c00220>.

Parameters used in the simulation, additional details of the simulation methodology, and additional data analysis (PDF)

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Notes

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