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Ab Initio Studies of Hydrated Electron/Cation Contact Pairs: Hydrated Electrons Simulated with Density Functional Theory Are Too Kosmotropic

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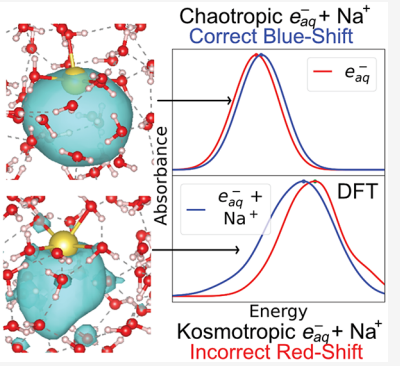
ABSTRACT: We have performed the first DFT-based ab initio MD simulations of a hydrated electron (e^-_{aq}) in the presence of Na^+, a system chosen because ion-pairing behavior in water depends sensitively on the local hydration structure. Experiments show that e^-_{aq}'s interact weakly with Na^+; the e^-_{aq}'s spectrum blue shifts by only a few tens of meV upon ion pairing without changing shape. We find that the spectrum of the DFT-simulated e^-_{aq} red shifts and changes shape upon interaction with Na^+, in contrast with experiment. We show that this is because the hydration structure of the DFT-simulated e^-_{aq} is too ordered or kosmotropic. Conversely, simulations that produce e^-_{aq}'s with a less ordered or chaotropic hydration structure form weaker ion pairs with Na^+, yielding predicted spectral blue shifts in better agreement with experiment. Thus, ab initio simulations based on hybrid GGA DFT functionals fail to produce the correct solvation structure for the hydrated electron.



The hydrated electron (e^-_{aq}), an excess electron dissolved in liquid water, is the primary species produced in radiation chemistry and is known to participate in a variety of radical and other chemical reactions.[1−4] Hydrated electrons also serve as a paradigm system for comparing the results of quantum simulations to experiment. This is both because they are relatively easy to generate in the laboratory by pulse radiolysis or via the charge-transfer-to-solvent excitation of simple anions[5,6] and because they provide one of the simplest quantum many-body problems that can be readily tackled by modern simulation methods. Despite all of the effort aimed at understanding the nature of hydrated electrons, however, there are still open questions concerning their basic features, particularly their solvation structure. The standard picture of the e^-_{aq} (although alternatives have been proposed[7]) is that it occupies a cavity in liquid water.[8−14] But the exact structure of the cavity and the orientation of the waters around the excess electron remain as of yet unresolved.

The question of the solvation structure of the e^-_{aq} is not just academic: the rates of reactions involving hydrated electrons can vary over many orders of magnitude, even when they have similar activation energies, which is not consistent with Marcus theory.[15] This implies that there is something about the reorganization of the waters solvating the e^-_{aq} that critically determines the way that hydrated electrons can interact with other chemical species in an aqueous solution. The purpose of this Letter is to use simulations to study the way that hydrated electrons with different solvation structures interact with other species in solution; in particular, we examine the pairing of a simulated e^-_{aq} with a simple ion, Na^+. The goal is to use experimental knowledge of e^-_{aq}−ion interactions to help determine which simulated structure of the hydrated electron, if any, best matches experiment.

What is known experimentally about hydrated electrons in the presence of electrolytes is that the absorption spectrum of the e^-_{aq} shifts to the blue when salts are present, with the magnitude of the blue shift dependent on the identities of both the cation and anion.[16−18] Salt does not cause the hydrated electron's spectrum to change shape, and the magnitude of the spectral blue shift increases with increasing electrolyte concentration.[16] For e^-_{aq}'s in high-concentration NaCl aqueous solutions, the spectrum shifts by only a few tens of meV.[16] The small magnitude of the spectral shift indicates that the presence of ions provides at most a subtle perturbation to the electron's hydration structure and that any direct overlap of the e^-_{aq}'s charge density with the salt cation is quite small. In previous simulation work, we argued that the blue shift of the e^-_{aq}'s spectrum in the presence of salt was not driven by the salt-induced change in the dielectric constant but instead results from electron−ion pairing.[19−22] Electron−ion pairing, in turn, is a behavior driven by the interaction of the e^-_{aq}'s and ion's hydration structures,[20−22] which form the focus of this work.

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Based on our previous simulations, we argued that the e^-_{aq} in aqueous salt solutions competes with other anions to undergo ion pairing with cations based on their relative positions in the Hofmeister series.[23] The Hofmeister series classifies ions as structure makers, or kosmotropes, when they form tight hydration spheres with negative entropies of solvation; Na^+ and Cl^- are examples. Conversely, larger and more hydrophobic ions are classified as structure breakers or chaotropes, which have less negative or even positive entropies of hydration, such as Cs^+ and ClO_4^-. In general, smaller ions with high charge-to-surface-area ratios tend to be more kosmotropic, although cations such as H^+ and Li^+ are exceptions, as they form complexes with nearby water and the complexes have more chaotropic solvation structures. Kosmotropic ions tend to form pairs with other kosmotropic ions, as there is a favorable enthalpy for placing two high-charge-density ions close together. Chaotropes also tend to pair with chaotropes, as there is a more favorable entropy to solvate a single large paired hydrophobic object rather than two separate smaller ones. Mixed kosmotrope/chaotrope salts, however, tend not to ion pair.[24−29] Hydrated electrons have the largest known solvation entropy of any anion[30,31] and thus should be champion chaotropes; as such, they are expected to pair poorly with kosmotropes such as Na^+.

Our previous simulations of e^-_{aq}/Na^+ pairing used mixed quantum/classical (MQC) methods, where only the hydrated electron was treated quantum mechanically and the water was treated classically, with the water−e^-_{aq} interactions described by a pseudopotential. We chose the standard cavity-forming Turi−Borgis (TB) pseudopotential for our previous work[9,32] and found that the TB hydrated electron experiences a strong interaction with Na^+; the simulations predicted a spectral blue shift of the ion-paired e^-_{aq} that is an order of magnitude larger than that seen experimentally.[19,20] We believe that this overly strong interaction arises because the TB hydrated electron has a hydration structure (see Figure 1(a)) that is somewhat too kosmotropic so that its pairing interactions with simulated kosmotropic Na^+ ions are too strong because there is too much overlap of the electron with the cation. Although we do not know the solvation entropy of the TB hydrated electron, it is clear that the TB model predicts an incorrect solvation structure that leads to a spectral blue shift that is too large.

Recently, there has been a surge of interest in using ab initio approaches to determine the structure and behavior of the e^-_{aq}.[11−14,33−36] To date, all such work has used DFT-based methods (including ref 13, as we discuss in the Supporting Information (SI)). Although different functionals were employed by different groups, all of them appear to yield a similar solvation structure, which is shown in Figure 1(c). To date, however, DFT models have not done a good job predicting the absorption spectrum or vertical detachment energy of e^-_{aq},[36] although it appears that DFT does qualitatively describe the hydrated electron's temperature dependence.[14,36] All of this leads to the principal questions addressed in this work: Does the hydration structure of a DFT-simulated e^-_{aq} have a solvation entropy that allows it to interact with Na^+ in a way that is consistent with experiment? If not, is there another simulation e^-_{aq} model whose solvation structure can predict the correct ion pairing behavior?

In this Letter, we answer these questions by performing the first DFT-based simulations of a hydrated electron in the presence of a sodium cation. Since concentrated ionic solutions are slow to equilibrate, we have elected to examine the interaction of the e^-_{aq} with a single Na^+, reducing the computational expense and also allowing us to compare the results to previous work.[19] We choose to run AIMD with the PBE0 functional, which has been the most popular choice among DFT simulations of the hydrated electron,[12−14,37] providing another detailed basis for comparison. We then compare the results of the DFT calculations to MQC simulations of a e^-_{aq} paired with Na^+. Our MQC simulations use two different pseudopotentials, the TB pseudopotential mentioned above[9] and an altered version of the TB pseudopotential with the polarization interactions optimized

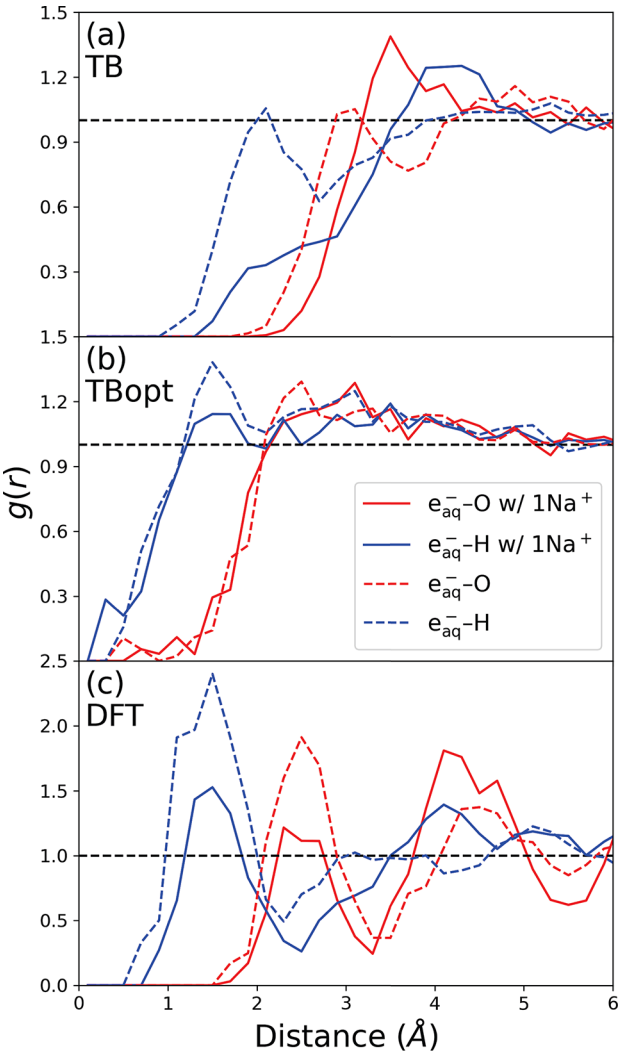

Figure 1. Hydration structure of different models of the hydrated electron. The e^-_{aq}−O and e^-_{aq}−H radial distribution functions are shown as the red and blue curves, respectively, with structures shown for the MQC TB, MQC TBopt, and DFT e^-_{aq} models in panels (a−c), respectively. The dashed curves show the hydration structure of the e^-_{aq} without Na^+, and the solid curves represent the same system with a single paired Na^+. The TB model shows a distinct cavity with a modest hydration structure, and the addition of Na^+ notably decreases the intensity of the e^-_{aq}−H first peak, indicating dehydration of the electron by the adjacent Na^+. The TBopt model is the most chaotropic, showing an indistinct hydration structure with a less-well-defined cavity; the addition of Na^+ makes little change to this e^-_{aq}'s hydration structure. The DFT e^-_{aq} model shows a highly structured hydration shell that resembles a kosmotropic anion such as Cl^-; upon the addition of Na^+, the highly structured solvation peak persists, another indication that the DFT electron is quite kosmotropic.

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to better match the results of CCSD(T) quantum chemistry calculations, which we have referred to as the TBopt potential.[38] We find that the solvation structure of the DFT-simulated e^-_{aq} is so strongly kosmotropic that the spectrum, when paired with Na^+, shifts in the wrong direction. The TBopt model, with the most chaotropic structure, produces a more accurate predicted pairing-induced blue shift, an indication that a better simulation methodology is required to generate correct hydrated electron structures.

The detailed methodology used for both our MQC- and DFT-based ab initio molecular dynamics simulations of hydrated electrons interacting with Na^+ follows that of our previous work[19−21,36] and is elaborated on in the SI. We begin our exploration of how different simulation models of the e^-_{aq} undergo ion pairing with Na^+ by first examining the hydration structure of each model. The dashed curves in Figure 1(a)−(c) show radial distribution functions, $g(r)$'s, for the TB, TBopt, and DFT hydrated electron models without any ions added to the system, respectively; the blue curves show e^-_{aq} center-of-mass to water H atom $g(r)$'s, while the red curves show e^-_{aq}−O radial distribution functions. As is well known, the MQC-based TB model in Figure 1(a) shows a distinct central cavity, with virtually no water O atoms approaching within 2 Å of the electron's center.[9] The TB model has a relatively poorly defined hydration structure, with modestly clear first-shell e^-_{aq}−O and e^-_{aq}−H peaks, suggesting that this species behaves as a weakly kosmotropic or modestly chaotropic anion.

The dashed curves in Figure 1(b) show that the TBopt model has a smaller and more poorly defined central cavity than the TB model. In previous work, we argued that this poorly defined central cavity causes the TBopt e^-_{aq} to have a temperature-dependent structure that yields a spectral red shift with increasing temperature that resembles experiment (although the magnitude of the predicted spectral shift is too small;[38] the TB model, in contrast, shows no temperature dependence whatsoever[39,40]). The TBopt model has a much less well-defined hydration structure than TB, with no visible e^-_{aq}−H first-shell solvation peak, suggesting that this species is more chaotropic.

The dashed curves in Figure 1(c) show that the DFT-based ab initio model not only has a distinct cavity region that lies between TB and TBopt in size but also has a very strongly structured first hydration shell. (Note that the height of the first-shell e^-_{aq}−H peak is ∼2.4, which is twice as large as that of the TB and TBopt models.[36]) This type of hydration structure is typical of what is seen around modestly kosmotropic anions such as Cl^- and Br^- and suggests that the DFT e^-_{aq} has the most negative solvaton entropy and is thus the most kosmotropic of the three models.

The solid curves in Figure 1 show how the structures of the simulated hydrated electrons change in the presence of a single nearby Na^+ cation. After Na^+ is added to the system, the TB model shows a dramatic decrease in the first peak of the e^-_{aq}−H $g(r)$ as well as a restructuring of the e^-_{aq}−O $g(r)$ to move waters from the first to the second solvation shell. We argued previously that this is because some water molecules that were involved in H-bonding with the e^-_{aq} reorient to solvate the nearby Na^+, leaving those waters pointing the "wrong way" toward the hydrated electron.[19] In contrast, this desolvation phenomenon does not take place with the TBopt model, which shows only a slight decrease in its first-shell $g(r)$'s because Na^+ replaces a few water molecules. This is because the TBopt e^-_{aq} is more fluxional than TB so that the TBopt electron can easily distort to help water maintain its natural H-bond network even when there is a paired cation nearby. Finally, the DFT-based e^-_{aq} model shows a hydration structure that is not perturbed by the presence of a nearby Na^+, other than a general decrease in the number of first-shell water molecules due to displacement by the cation. The fact that the hydration structure of each e^-_{aq} model changes differently when Na^+ is added shows that indeed ion pairing is sensitive to the electron's solvation structure, serving as a proxy for comparing the hydration entropy to experiment. Thus, exploring ion pairing should allow us to compare the behavior of the different simulation models to experiment and thus determine which hydration structure makes the most physical sense.

In Figure 2, we show potentials of mean force (PMFs) between the center of mass of each e^-_{aq} model and Na^+. The

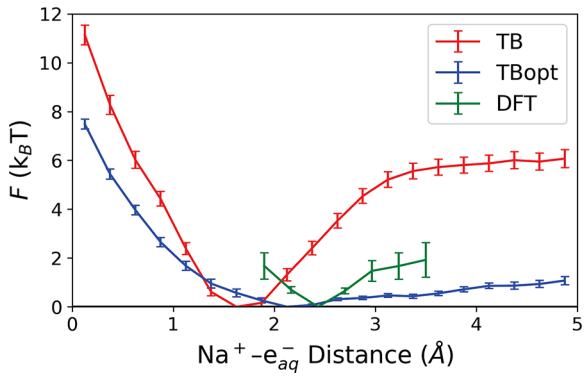

Figure 2. Na^+−e^-_{aq} potentials of mean force for the TB (red curve), TBopt (blue curve), and DFT (green curve) e^-_{aq} models. The TB model shows strong pairing between Na^+ and the e^-_{aq} with a relatively short equilibrium distance, whereas the TBopt model shows much weaker pairing with a longer equilibrium pairing distance. The PMF of the DFT model, which is limited by the simulation statistics, is in between those of the TB and TBopt models, showing a modest pairing strength and equilibrium distance. The stronger pairing seen with the TB and DFT e^-_{aq} models suggests that their hydration structures are more kosmotropic than that of the TBopt model.

stability of the e^-_{aq}−Na^+ contact pair is quite different for the three simulation models. The red curve in Figure 2 shows the PMF for a Na^+ interacting with TB e^-_{aq}, which we have presented previously.[19−21] The contact pair has a stability of roughly 6 k_BT and an equilibrium distance of only ∼1.7 Å, which is smaller than the TB electron's 2.2 Å radius of gyration, thus leading to significant electron−cation overlap.[19] In contrast, the blue PMF curve in Figure 2 for the TBopt e^-_{aq} model shows a much shallower free-energy well, only ∼1.5k_BT deep.[24,26] This means that TBopt e^-_{aq} can move away from Na^+ fairly easily at room temperature, indicative of the type of ion pairing that might be expected between a kosmotropic cation and a chaotropic anion.[24−29] This PMF is consistent with the fact that the presence of Na^+ minimally perturbs the TBopt e^-_{aq}'s hydration structure, as shown in Figure 1.

For comparison, the green curve in Figure 2 shows the limited PMF results available for the DFT-based AIMD e^-_{aq} model. Although we were unable to explore what happens far from equilibrium and thus do not know the full depth of the well, the DFT e^-_{aq} model appears to form a less-stable ion pair with Na^+ than the TB model, with a shallower well and longer equilibrium distance. This is consistent with what we saw in Figure 1(c), where the presence of Na^+ does not significantly

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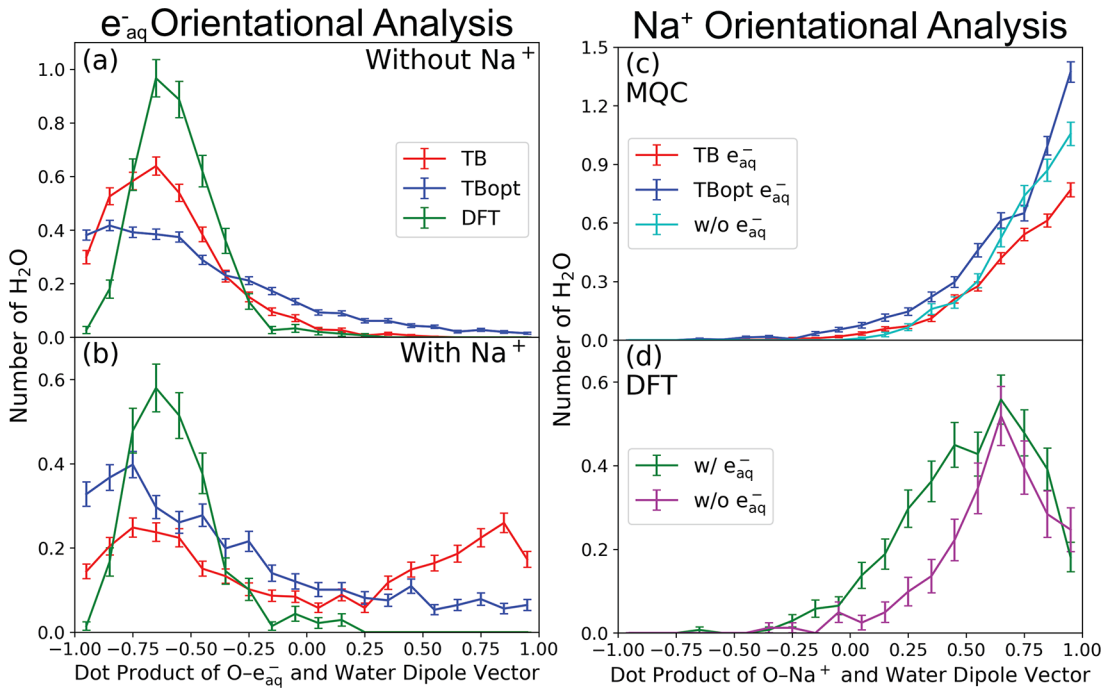

Figure 3. Hydration structure orientational distributions, calculated as the dot product between the dipole vector of first-shell water molecules and the vector connecting the water O and either the e^-_{aq} (panels (a) and (b)) or the Na^+ (panels (c) and (d)). The angular hydration structures of the TB, TBopt, and DFT models are represented by red, blue, and green curves, respectively. Panels (a) and (c) show distributions for the different e^-_{aq} models when no Na^+ is present, and panels (b) and (d) show the distribution after the addition of a single Na^+. The data show that the TB e^-_{aq} becomes dehydrated when Na^+ is in close proximity so that some first-shell waters reorient into an unfavorable configuration. The TBopt e^-_{aq} first-shell water orientation is largely unaffected by Na^+, a sign of weak ion pairing. The DFT e^-_{aq} not only maintains its favorable water H-bond orientation in the presence of Na^+ but also imposes an unfavorable hydration structure on the paired cation, indicating that the DFT e^-_{aq} is actually more kosmotropic than DFT Na^+.

alter the solvation structure of the DFT hydrated electron. However, the DFT-based e^-_{aq} clearly forms a stronger ion pair with Na^+ than the TBopt model with a similar equilibrium distance. We will argue below that these results show not only that the DFT e^-_{aq} is too kosmotropic but also that the hydration structure of the DFT-simulated Na^+ is less kosmotropic than what is seen in the MQC simulations.

To delve deeper into the local solvation structures of the different hydrated electron and sodium cation models, we examined the orientation of the first-shell waters around each species in the different simulated e^-_{aq}–Na^+ ion pairs, which is directly related to the hydration entropy. We define first-shell waters as those whose positions are closer than the distance of the local minimum past the first solvation shell peak in the electron–O $g(r)$. For the orientational analysis, we built distributions of the dot product between the dipole vector of a first-shell water molecule and the vector connecting the O atom of that water molecule to either the e^-_{aq}'s center of mass or the position of Na^+. Figure 3(a) shows the water orientational distributions around each of the three e^-_{aq} models when no cation is present. All three models show a peak near −0.7, which corresponds to the angle expected when water is making an H-bond that points directly toward the e^-_{aq}'s center of mass. We note that the orientational structure is much less distinct for the TBopt model (dark blue curve), which is consistent with the idea that this model is more chaotropic and thus does not impose a strong structure on the surrounding water molecules.

In addition to the hydration of the e^-_{aq}, the cyan curve in Figure 3(c) shows the orientational distribution of first-shell water molecules around a classically simulated Na^+ without the presence of an e^-_{aq}; the peak at +1.0 shows that classical waters strongly prefer to have their dipoles pointing directly to form the sodium cation so that the negatively charged O atoms can sit as closely as possible to the cation, a signature of strongly kosmotropic species with a negative hydration entropy. This distribution is quite different from that when DFT is used to simulate hydrated Na^+ without a nearby e^-_{aq}, as shown by the magenta curve in Figure 3(d). The DFT Na^+ hydration structure has a preferred first-shell water orientation with a significant tilt relative to what is seen in the classical simulations, indicating that the DFT first-shell waters have more of a preference to maintain their H-bonding with the second-shell waters than to strongly solvate the cation. This also suggests that the DFT-based Na^+ is less kosmotropic than what is seen in the classical simulations, a feature that is important to keep in mind when comparing the ion-pairing properties of the different simulation models.

With the water orientations around bare e^-_{aq}'s and Na^+'s established, we now examine how ion-pairing causes changes in the hydration orientation of the two species. Figure 3(b) shows the orientational distribution of the water molecules around the different e^-_{aq} models when they are at their equilibrium distance in contact with Na^+. The red curve shows that for the TB e^-_{aq}, when Na^+ is present, there is a decrease in the number of water molecules making H-bonds to the electron (peak near −0.7) and an increase in water molecules that point their dipoles away from the e^-_{aq}'s center of mass (peak at +1.0). We argued previously that this occurs because the highly kosmotropic classical sodium cation "outcompetes"

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the TB hydrated electron for imposing structure on waters that are in the first shells of both species; these waters prefer to solvate Na^+ and end up oriented in the wrong direction for solvating the e^-_{aq}.[19] Indeed, the red curve in Figure 3(c) shows that pairing with the TB e^-_{aq} has little effect on the water orientation in the first shell surrounding the classical Na^+, with a distribution that is similar to that for a bare classical Na^+.

In contrast, the blue curve in Figure 3(b) shows that the orientation of the first-shell water molecules surrounding the TBopt e^-_{aq} is largely unaffected by the presence of a nearby classical Na^+. This result is consistent with the $g(r)$'s in Figure 1(b), which also argue that the TBopt e^-_{aq}'s hydration structure is largely unaffected by being in a contact-ion pair. Remarkably, the blue curve in Figure 3(c) shows that the orientation of the first-shell waters around classical Na^+ is also unchanged by ion pairing with the TBopt e^-_{aq}. How can water simultaneously maintain its favorable orientation around both species when they are paired? We believe that this is due to the chaotropic nature of the TBopt e^-_{aq}. Unlike the TB model with its rigid cavity, the first-shell waters around the TBopt e^-_{aq}, which has a softer cavity, are more fluxional, as they do not have a tight hydration structure to maintain.[41] This provides them with the opportunity to find an orientation that can favorably solvate both the e^-_{aq} and cation.

The green curves in Figure 3(b) and (d) show the orientations of the first-shell waters around the hydrated electron and sodium cation, respectively, in the DFT-based ab initio simulations. Figure 3(b) shows that the DFT e^-_{aq} experiences no change in first-shell water orientation when placed into contact with Na^+, consistent with the fact that the first-solvation structure also does not change (cf. Figure 1(c)). But strikingly, Figure 3(d) shows that ion pairing with a DFT e^-_{aq} changes the first-shell water orientations around the sodium cation: the number of water molecules solvating the Na^+ increases in the presence of the DFT electron, and the distribution of solvation angles broadens. This indicates that the DFT e^-_{aq} is actually more kosmotropic than the DFT-simulated Na^+. In other words, the DFT hydrated electron outcompetes the cation for imposing structure on the waters in the first shells of both species so that these shared waters more favorably solvate the e^-_{aq} at the expense of the cation. This observation does not fit well with the fact that the hydrated electron is known to have the largest possible solvation entropy of any ion[30,31] and, as we show next, leads to a predicted spectral shift that has the opposite sign compared to what is seen experimentally.

With all of the above analysis, the real arbiter of which simulated e^-_{aq} has the best structure comes by comparing to experiment. Figure 4(a) shows experimental spectra of the e^-_{aq} in pure water (magenta curve) and that in 5 *m* aqueous NaCl (cyan curve), reproduced using the Gauss−Lorentz fits to the spectra given in ref 16. As mentioned above, the hydrated electron's spectrum shifts by only ∼70 meV, without changing shape, in the presence of 5 *m* NaCl.[16] Due to the computational expense of DFT simulations, however, we have only a single Na^+ in the trajectories studied in this work, so our effective electrolyte concentration is smaller than 5 *m*. In previous work, we showed that simulations with a single Na^+ followed the correct concentration-dependent behavior when higher Na^+ concentrations were used.[20,21] Thus, on the basis of this previous work, the effective concentration of Na^+ in our DFT simulations with 64 waters should be roughly 0.85 M and yield a smaller spectral shift than the experiments to which we

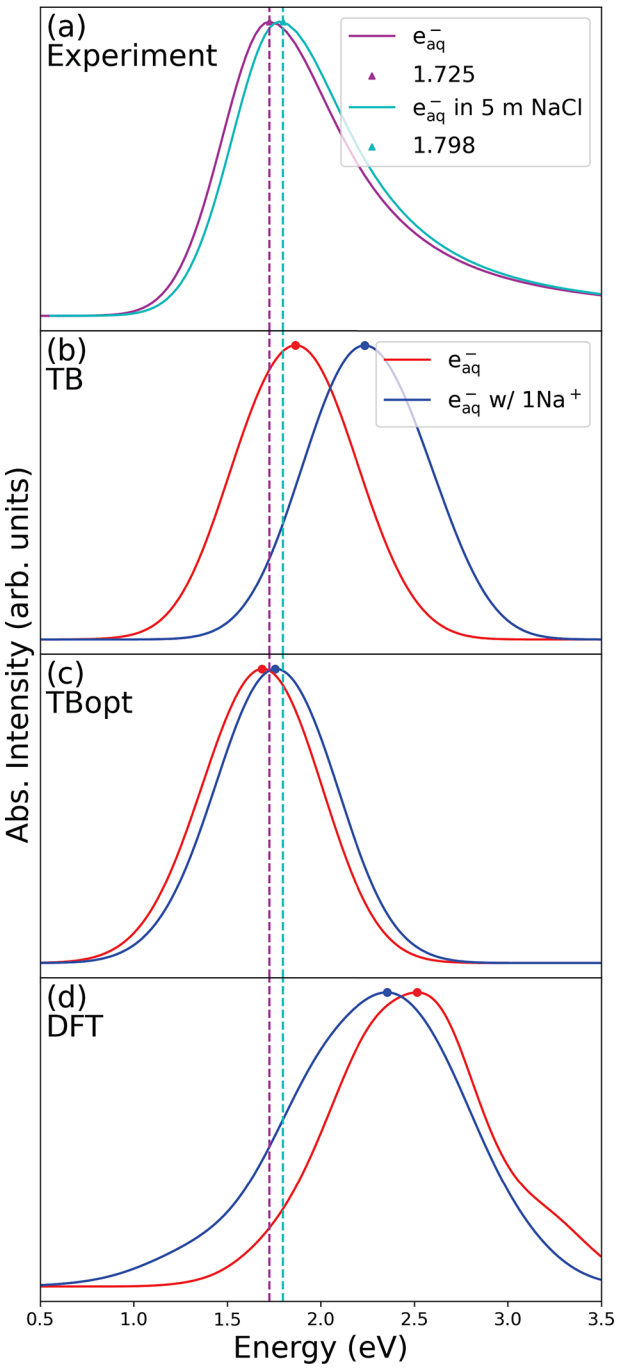

Figure 4. Absorption spectra of hydrated electrons in pure water and when in a contact pair with Na^+. Panel (a) shows the experimental absorption spectrum of the e^-_{aq} in pure water (magenta curve) and in 5 *m* NaCl solution (cyan curve), showing the ∼70 meV shift induced by the high-concentration electrolyte.[16] Panels (b−d) show simulated absorption spectra of the TB, TBopt, and DFT e^-_{aq} models in pure water (red curves) and in the presence of Na^+ at the equilibrium pairing distance (blue curves). The TB model overestimates the spectral blue shift because it makes an e^-_{aq}−Na^+ contact pair that is too tight,[19,20] whereas the DFT model predicts that ion pairing causes a spectral red shift, in disagreement with experiment because the DFT e^-_{aq} is more kosmotropic than the DFT Na^+. The TBopt model, with its chaotropic hydration structure that leads to relatively weak e^-_{aq}−Na^+ contact pairing, predicts the correct magnitude of the spectral blue shift.

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are comparing[16] so that the ∼70 meV shift seen in Figure 4(a) should be an upper limit.

Figure 4(b)−(d) shows the calculated spectroscopy of the three different hydrated electron models (red curves), along with the predicted spectroscopy of the different e^-_{aq}'s at their equilibrium distance in contact pairs with a Na^+ (blue curves). The ab initio spectrum was calculated using TD-DFT with the long-range-corrected ωPBE functional, with the range-separation parameter optimally tuned for each system;[36] detailed procedures for our spectral calculations are given in the SI. Figure 4(b) shows the calculated spectra for the TB e^-_{aq} model, which as we have discussed previously predicts a spectral blue shift that is an order of magnitude larger than that seen experimentally.[19,20] The overly large predicted spectral blue shift is a direct consequence of the fact that the cation and TB e^-_{aq} pair too tightly and that the cation forces a significant reorientation of the water molecules in the hydrated electron's first solvation shell.

Figure 4(d) shows the predicted spectroscopy of the e^-_{aq} in the presence of Na^+ from DFT-based ab initio simulations. The red curve shows that the spectrum of the DFT e^-_{aq} in pure water is blue-shifted from experiment by over 0.5 eV and has an incorrect spectral shape, as we have documented previously.[36] When the DFT hydrated electron is paired with Na^+, the calculated spectrum red shifts by ∼160 meV, a shift that is not only too large but also goes in the wrong direction compared to experiment. The calculated spectrum is also predicted to change shape, which again does not match what is seen experimentally.[16] As mentioned above, this spectral red shift is a direct consequence of the fact that the DFT e^-_{aq} is more kosmotropic than the DFT Na^+, a result that is not consistent with the solvation entropy of the hydrated electron.[30,31] Thus, the distinctively structured solvation shell of the DFT e^-_{aq} is unlikely to have a positive entropy of hydration, indicating that this level of theory is simply inadequate to simulate this system.

On the other hand, Figure 4(c) shows that for the TBopt model, the relative shift of the calculated spectrum in the presence of Na^+ is almost identical with what is seen in experiment. (Both predicted spectra are slightly red-shifted from experiment, but the relative shift and lack of shape change match experiment within the simulation error.) This is a direct consequence of the fact that the TBopt e^-_{aq} model undergoes little change in either the water orientation or coordination number when paired with Na^+, as would be expected when a kosmotropic cation is weakly complexed with a highly chaotropic anion. Of course, the TBopt model is not perfect (as mentioned above, this model underestimates the red shift of the e^-_{aq}'s spectrum with increasing temperature[38]), but the excellent agreement of its predicted ion pairing with experiment suggests that the highly chaotropic hydration structure that this model yields is much more likely to be closer to "correct" than either the TB or DFT e^-_{aq} model. Clearly, even though all three models predict that the hydrated electron occupies a cavity in liquid water, not all cavity models are equivalent: the hydration structure of the electron is important for determining its interactions with other species in aqueous solution, such as pairing with Na^+.

In summary, we examined how different e^-_{aq} models with different hydration structures undergo ion pairing with Na^+. Since ion pairing is directly controlled by the hydration structures of both ions,[23−27,27−29] we can use ion pairing to distinguish which model of the hydrated electron, if any, is consistent with the known experimental behavior of e^-_{aq}'s in aqueous electrolytes. The cavity-forming TB model shows strong pairing with Na^+, as evidenced by the deep PMF and the overly large predicted spectral blue shift, indicating that this model is somewhat too kosmotropic. The TBopt e^-_{aq}, which is the most chaotropic of the three models examined here, shows weak e^-_{aq}−Na^+ contact pairing; this model predicts a spectral shift that is in reasonable agreement with experiment. But perhaps most importantly, the DFT hydrated electron model shows a strikingly strong kosmotropic hydration structure that does not fit with our expectations of hydrated electrons as champion chaotropes.[30,31] The DFT e^-_{aq} is able to alter the hydration structure of the paired Na^+, leading to an erroneously predicted spectral red shift, a result of the fact that the DFT electron is actually more kosmotropic than the DFT Na^+. Given that the direct calculation of the DFT e^-_{aq}'s hydration entropy is not computationally feasible, the examination of ion pairing, as interpreted by the Hofmeister series, provides a useful explanation of the incorrectly predicted spectral shift. In the SI, we also offer predictions for how the vertical detachment energy of the different e^-_{aq} models should change in the presence of Na^+, offering another experimental avenue for distinguishing between the different predicted solvation structures.

It is worth emphasizing that none of the three models that we have examined are able to reproduce all of the known experimental properties of the hydrated electron (e.g., the temperature dependence,[5,14,36,39,40] resonance Raman spectrum,[39,42,43] time-resolved photoelectron spectroscopy,[44−46] molar solvation volume,[47,48] etc.). MQC models have the drawbacks that not only are they extraordinarily sensitive to the pseudopotential employed but also that they cannot allow for mixing of the e^-_{aq}'s wave function into the molecular orbitals of the nearby water molecules, which is undoubtedly important to understanding their solvation and reactivity.[49] Our results show, however, that blindly moving toward ab initio simulations, especially those based on popular DFT functionals, does not necessarily make any improvement.

Given that DFT should constitute a higher-level theory compared to MQC, why does it fail so spectacularly for describing the hydration structure of the hydrated electron? We know that typical hybrid GGA functionals fail to generate the correct structure and dynamics of liquid water because they do a poor job accounting for dispersion and H-bonding interactions.[50,51] Moreover, typical GGA functionals are prone to charge delocalization error, which can be particularly acute when trying to describe the properties of an excess electron that resides primarily between water molecules. Overall, although hydrated electron structures generated with PBE-based functionals are currently considered to be state of the art in the community,[12,14,34,36] they clearly are not accurate enough for this system, as they produce a hydration structure that is incommensurate with experiment.

We believe that it is certainly possible that a well-tweaked pseudopotential can produce an e^-_{aq} with a hydration structure that is "better" than popular DFT functionals, although no MQC simulation will likely be able to fully describe the hydrated electron. Higher levels of quantum chemistry, such as MP2, which is known to handle dispersion interactions better,[52] are currently out of reach due to computational expense, unless hybrid algorithms with DFT are used.[13] Thus, until such methods become affordable, we are left in a situation in which we do not know the true hydration structure of the

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hydrated electron. One alternative and potentially affordable method is to use DFT with a functional that produces more accurate water structures, such as SCAN0.[53] The key point is that any hydrated electron simulation model needs to be tested in situations where small changes in the predicted hydration structure make large changes in the predicted observables, which is exactly the situation we explore here. At the moment, on the basis of ion pairing, which is a highly sensitive measure of hydration structure, we conclude that the hydrated electron likely has a chaotropic structure that is more like the TBopt model and not at all like the kosmotropic structure that is seen with hybrid GGA DFT functionals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c03705.

The parameters used in the simulation, additional details of the simulations methodology, and additional data analysis (PDF)

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Notes

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