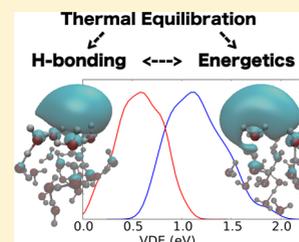


Thermal Equilibration Controls H-Bonding and the Vertical Detachment Energy of Water Cluster Anions

Chen-Chen Zho,[†] Vojtěch Vlček,[‡] Daniel Neuhauser,^{*,†} and Benjamin J. Schwartz^{*,†}[†]Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, United States[‡]Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, California 93106, United States

Supporting Information

ABSTRACT: One of the outstanding puzzles in the photoelectron spectroscopy of water anion clusters, which serve as precursors to the hydrated electron, is that the excess electron has multiple vertical detachment energies (VDEs), with different groups seeing different distributions of VDEs. We have studied the photoelectron spectroscopy of water cluster anions using simulation techniques designed to mimic the different ways that water cluster anions are produced experimentally. Our simulations take advantage of density functional theory-based Born–Oppenheimer molecular dynamics with an optimally tuned range-separated hybrid functional that is shown to give outstanding accuracy for calculating electron binding energies for this system. We find that our simulations are able to accurately reproduce the experimentally observed VDEs for cluster anions of different sizes, with different VDE distributions observed depending on how the water cluster anions are prepared. For cluster anion sizes up to 20 water molecules, we see that the excess electron always resides on the surface of the cluster and that the different discrete VDEs result from the discrete number of hydrogen bonds made to the electron by water molecules on the surface. Clusters that are less thermally equilibrated have surface waters that tend to make single H-bonds to the electron, resulting in lower VDEs, while clusters that are more thermally equilibrated have surface waters that prefer to make two H-bonds to the electron, resulting in higher VDEs.



There are many chemical and radiological processes that create an excess electron in liquid water, known as a hydrated electron. Hydrated electrons are involved in the damage to biological systems caused by ionizing radiation, in the decomposition of radioactive waste,¹ and in many important atmospheric chemistry reactions.² Despite numerous experimental and theoretical studies, there is still great controversy over the basic nature of the hydrated electron, including whether or not it occupies a cavity or encompasses many interior water molecules.^{3–8}

There also have been extensive related studies aimed at understanding the properties of negatively charged water clusters. Water anion clusters with specific sizes have been prepared in gas-phase molecular beams from neutral water clusters that are crossed with an electron beam, expanded through a nozzle, and then mass selected. These water cluster anions can be thought of as nanoscale versions of the bulk hydrated electron, and indeed, many of their properties extrapolate well to the bulk with increasing cluster size.^{9,10}

One of the most basic experiments performed on these cluster anions is photoelectron spectroscopy, which measures the binding energy (or vertical detachment energy, VDE) of the excess electron attached to the water cluster. In nearly every photoelectron experiment on negatively charged water clusters, multiple VDEs of the excess electron are observed.^{10–15} The multiple detachment peaks appear in branches, where the binding energy of the peaks in each branch increase roughly linearly with cluster size, although the

slope of the VDE with cluster size is different for each branch.¹³ Moreover, the relative amplitudes of the different binding energy branches are known to change based on the way the cluster anions are prepared: preparation conditions that allow for greater thermalization of the clusters, such as using lower backing pressures, tend to produce photoelectron spectra with higher VDEs, while conditions that produce more rapid cooling, such as higher backing pressures, tend to create clusters with lower VDEs.^{12,14} With any backing pressure, the temperature of the clusters produced is unknown, although the more rapid cooling with higher backing pressures is generally considered to produce clusters in less equilibrated, more metastable states.¹⁴

It seems clear that the different families of water cluster anion binding energies must correspond to different structural isomers, but the possible structures of these isomers and the reason why these clusters present only a few discrete binding energies per cluster size rather than a broad continuum of energies is still unknown. One possibility is that different VDE branches correspond to different locations in the clusters where the excess electron can localize.^{12,16,17} For example, if electrons sit on the clusters' surfaces, they will be more loosely bound and have lower VDEs, whereas electrons that reside in the clusters' interiors are expected to be more tightly bound

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with larger VDEs. This idea of interior and surface-bound isomers has been supported by some theoretical calculations,^{16–18} although other calculations have suggested that surface-bound electrons also can show multiple VDEs.¹⁹

Of the theoretical calculations that have investigated the water cluster anion VDE problem, many have used post Hartree–Fock methods and/or density functional theory.^{20–29} But essentially all of these calculations have been performed on static water anion cluster structures at absolute zero. This means that none of them has directly mimicked the experimental preparation conditions of the negatively charged water clusters, which is clearly of great importance to understanding the distribution of observed VDEs. Of the few calculations that do incorporate some type of dynamics to simulate different water anion cluster structures, most are either based on one-electron pseudopotentials^{16,18,19,30,31} or based on density functional theory (DFT) methods that have only local exchange (e.g., using the BLYP³² or PBE³³ functionals), both of which suffer from large errors when used to calculate one-electron energies such as VDEs.

In this work, we use Born–Oppenheimer molecular dynamics (BOMD) to simulate the experimental photoelectron spectroscopy of negatively charged water clusters as closely as possible. We focus on three cluster sizes (6, 11, and 20), and we choose a range-separated hybrid functional (the BNL functional^{34,35}) that we show is particularly well-suited to reproducing VDEs in water anion clusters. We then mimic the photoelectron spectroscopy experiments by performing our simulations in two different ways, as summarized in Figure 1. In one set of simulations, we run room-temperature BOMD on neutral water clusters, attach an excess electron to a series of uncorrelated cluster configurations, and then perform an immediate geometry optimization on these configurations to

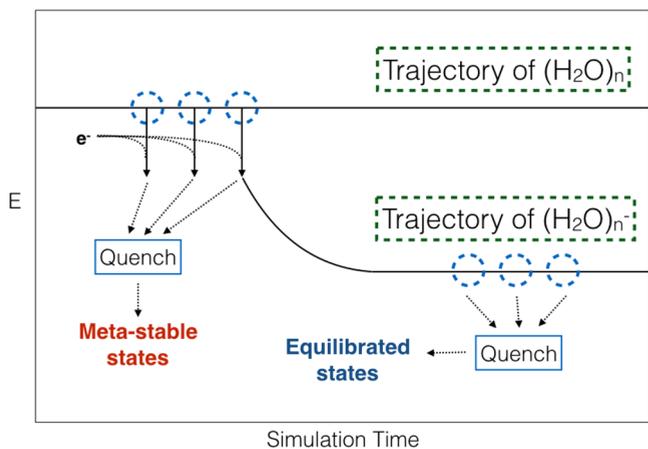


Figure 1. Method of simulating photoelectron spectroscopy experiments on water anion clusters via Born–Oppenheimer molecular dynamics. Starting from snapshots of a neutral water cluster obtained from classical molecular dynamics, BNL-based BOMD is performed at 300 K both before and after charging the water cluster with an excess electron. A geometry optimization search is then performed on uncorrelated configurations from both the neutral (where the extra electron is added instantaneously) and anionic trajectories to find the nearest energy local minimum, thus simulating a thermal quenching process. In this way we are able to sample both metastable and equilibrated structures like those produced experimentally by studying charged water clusters both before and after they have been thermally equilibrated.

represent clusters produced with poor thermalization conditions in the experiments. In the other set, we run room-temperature trajectories on water anion clusters, generating a variety of uncorrelated thermalized configurations that we then geometry optimize to represent the more equilibrated cluster anion experimental preparation conditions. We find that with the two sets of simulations, we are able to accurately reproduce the VDEs of negatively charged water clusters from a variety of experimental groups.^{12,14,15,36} For the sizes of clusters we studied in this work, the excess electron always resides on the cluster surface, so the different binding energy branches are not the result of surface and interior-bound clusters. Instead, we see that the different VDEs result from isomers that have different degrees of hydrogen bonding from the waters on the surface of the cluster, a result that fits well with infrared (IR) spectroscopy.³⁷ The discrete VDE branches thus result from the fact that there are only so many combinations of surface hydrogen bonds available to bind the excess electron.

One of the key features that sets our calculations apart from previous work is our use of an optimally tuned range-separated hybrid (RSH) DFT functional³⁸ that enforces the ionization potential theorem³⁹ and minimizes the spurious electron (de)localization seen with more standard functionals.⁴⁰ RSH functionals are particularly adept at reproducing ionization potentials and electron binding energies given by much higher-level quantum chemistry methods,⁴¹ particularly for calculating the ionization potentials of small neutral water clusters.⁴² Our chosen BNL functional works particularly well for calculating the VDE of negatively charged water clusters, and we show in the Supporting Information that a single value of the range separation parameter is optimum for all the different cluster geometries sampled by our BOMD trajectories. Figure 2 compares the ionization potential of water anion clusters with different geometries and sizes calculated at the eom-CCSD

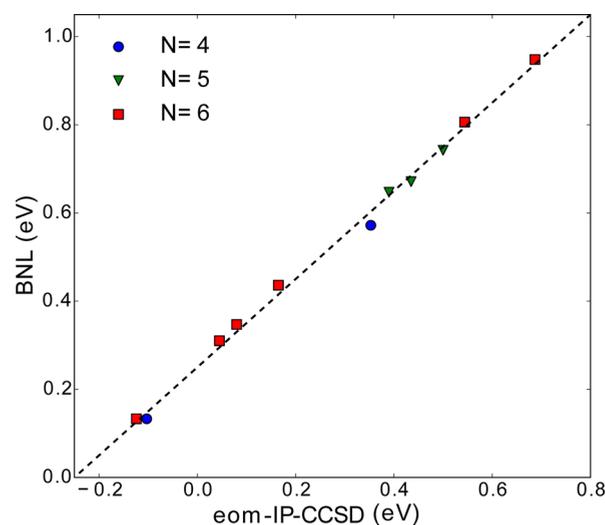


Figure 2. Ionization potentials (IPs) calculated for various $(\text{H}_2\text{O})_4^-$, $(\text{H}_2\text{O})_5^-$, and $(\text{H}_2\text{O})_6^-$ water anion clusters, calculated by both eom-IP-CCSD and DFT using the BNL functional with the optimal range separation parameter; see the Supporting Information for details. Both sets of calculations use the 6-311++G** basis set. The dashed line corresponds to $y = x + 0.25$, showing the excellent agreement between the BNL and eom-IP-CCSD VDE values with a systematic shift of 0.25 eV but with less than 1% fluctuation between the two methods.

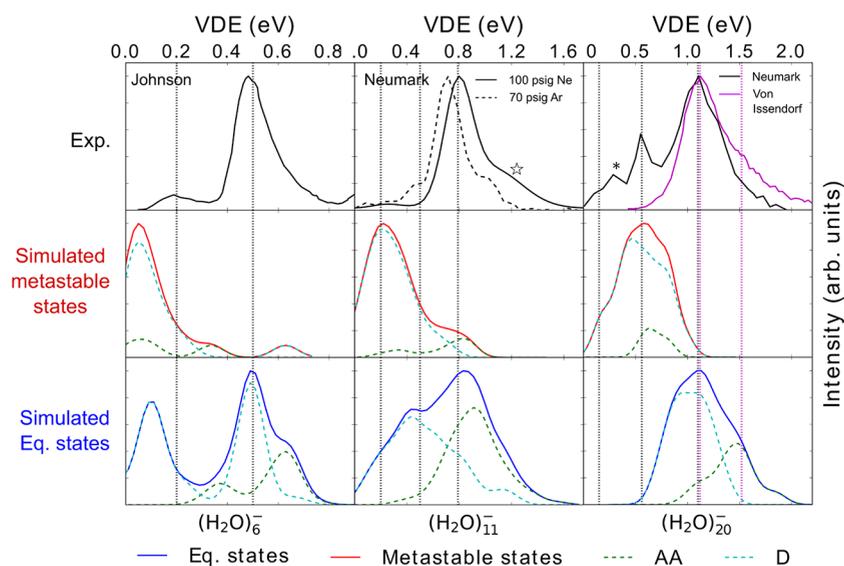


Figure 3. Experimental and simulated photoelectron spectra for $(\text{H}_2\text{O})_6^-$ (left), $(\text{H}_2\text{O})_{11}^-$ (center), and $(\text{H}_2\text{O})_{20}^-$ (right) water anion clusters. The data in each column are plotted on the same x -axis, and the vertical lines indicate the experimental VDEs for ease of comparison. The peaks labeled by stars or asterisks in the upper row are known to be experimental artifacts and were not included in the fits used to determine the experimental VDEs.^{12,14} The apparent tails to negative VDEs in the theoretical calculations result from both the Gaussian broadening applied to mimic the experimental energy resolution, and the 0.25 eV shift added so that the DFT-based energies match those from higher-level quantum chemistry calculations (cf. Figure 2); these structures were not unbound during the BOMD trajectories. The red curves in the middle row show the photoelectron spectra predicted for metastable clusters, where the electron is attached to a neutral water cluster and quenched immediately. The blue curves in the bottom row show the calculated photoelectron spectrum for equilibrated clusters generated from the anion trajectory, representing more thermally equilibrated clusters. The calculated photoelectron spectra are further divided into subpeaks by way of binding motifs, represented by the dashed green (double H-bond acceptor) and cyan (dangling H-bond) curves in the second and third rows; see text for details. These H-bond binding motifs are illustrated in Figure 4 and discussed in the text.

level of theory to those calculated by DFT with our optimally tuned BNL functional; both sets of calculations use the 6-311++G** basis set. Clearly, with the appropriate functional, DFT can provide detachment energies with less than 1% fluctuation compared to what is essentially the “gold standard” of quantum chemistry;⁴³ the DFT results are significantly better than MP2, which is often used for calculating binding energies of water anion clusters, as discussed in the Supporting Information. The DFT results do consistently overbind the electron by 0.25 eV relative to the eom-IP-CCSD results, but this overbinding is independent of cluster size and geometry. Thus, in the results discussed below, all VDE values were calculated using DFT with the BNL functional with a -0.25 eV correction, providing what should be the most accurate possible binding energies.

With our chosen BNL functional properly benchmarked and using the simulation methods described in the Supporting Information, we ran a series of both neutral and anionic water cluster trajectories to produce water anion cluster structures as outlined in Figure 1. Figure 3 shows the calculated VDEs from these trajectories, which are the principal results of this work; there are no adjustable parameters or modification of the theoretical results other than the 0.25 eV shift mentioned above and a Gaussian broadening of 0.25 eV to reflect the experimental photoelectron energy resolution. The left panels in the figure show the results for 6-water-molecule clusters, the center for 11-molecule clusters, and the right panels for 20-molecule clusters. The plots in the upper row (black and magenta curves) show experimental results for each cluster size from different groups (or in the case of $(\text{H}_2\text{O})_{11}^-$ clusters, two results from the same group under different thermalization conditions).^{12,14,15,36} The center row (red curves) shows our results of the VDE distribution from anion configurations

created from the neutral water trajectory, representing metastable or poorly thermalized experimental conditions, while the bottom row (blue curves) shows the VDEs calculated from our anionic cluster trajectories. The vertical gray and magenta lines are the reported experimental VDEs for each cluster size,^{12,14,15,36} drawn to facilitate comparison between the experimental and theoretical results. Clearly, the agreement between the experimental and theoretical VDEs is outstanding.

In addition to the remarkable agreement between experiment and theory, Figure 3 shows that the calculated photoelectron spectra of metastable water anion clusters, generated from the neutral water cluster trajectories manifest lower binding energies relative to the photoelectron spectra of the more thermally equilibrated clusters generated from the water anion cluster trajectories. This finding is also in excellent agreement with the experimental observation that more equilibrated cluster anions have larger VDEs, as seen in experiments from the Neumark group which used different backing pressures (black and dashed black curves in the upper center panel).¹⁴ We also are able to produce the very high binding energy shoulder seen in experiments from the von Issendorff group that worked to make the anion clusters as thermally equilibrated as possible (magenta curve in the upper right panel),¹⁵ a shoulder that was not present in earlier work that presumably produced more metastable clusters.¹² Clearly, the main reason that different groups see different photoelectron spectra for water anion clusters is because of different degrees of thermal equilibration, a finding that is now theoretically justified.

Why does the degree of thermal equilibration affect the VDEs of water anion clusters? As mentioned above, several groups have proposed the idea that the multiple peaks in the

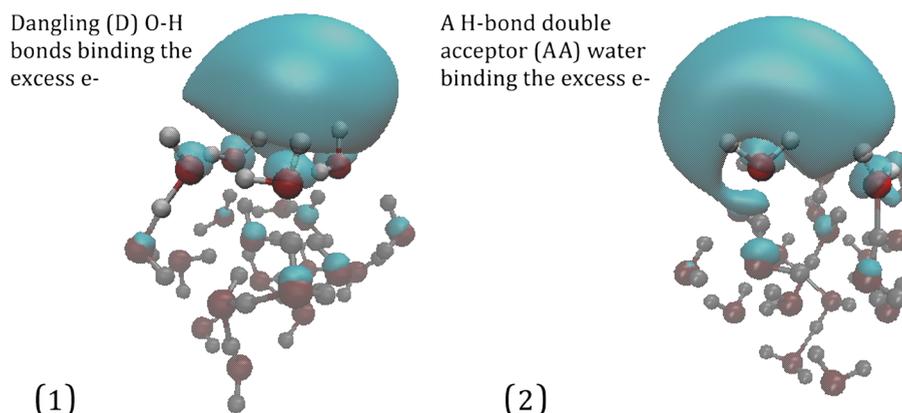


Figure 4. Spin density (blue isosurface plotted at 75% of the maximum density) for two representative $(\text{H}_2\text{O})_{20}^-$ clusters demonstrating that the excess electron is attached to the surface of the water cluster. (1) Structure where single dangling O–H bonds from water molecules on the surface of the cluster are what binds the excess electron; these waters donate their other H-bond to other water molecules in the cluster. (2) Structure where single water molecules make two H-bonds to the excess electron (so-called “double-acceptor” water molecules). In both panels, the water molecules involved in making H-bonds to the excess electron are highlighted with more saturated colors.

photoelectron spectra can be attributed to the presence of different structural isomers in which the excess electron is bound either to the surface of the cluster or in the cluster’s interior. For the clusters studied in this work, we have found that the excess electron always is attached to a cluster’s surface: the majority of the electronic density resides outside the volume defined by the water molecules, as shown for two representative $(\text{H}_2\text{O})_{20}^-$ clusters in Figure 4. In every snapshot we examined, the distance between the centers-of-mass of the water molecules and the excess electron was always ~ 1 Å larger than the radius of the cluster (see the Supporting Information). This verifies that for water anion clusters with up to at least 20 water molecules, there is no (energetically) easy way to solvate the electron in the cluster interior and that interior solvated states are not needed to explain the multiple discrete VDEs observed in photoelectron spectroscopy experiments. This agrees with some previous studies where surface-bound states were argued to be the predominant factor in determining the properties of water cluster anions.^{32,33,44}

Given that the excess electron always resides on the surface in clusters of the size range studied here, the next question we explore is why such clusters have different discrete photodetachment energies. After careful examination of the water anion clusters from our trajectories, we have found that they can always be classified into two categories, with precise definitions given in the Supporting Information. The first category consists of electrons bound to the cluster by accepting single hydrogen bonds from surface water molecules, which we refer to as “dangling H-bond” (D) waters, as illustrated in panel 1 of Figure 4. These types of configurations predominate in the metastable clusters and tend to have lower VDEs, as illustrated by the cyan dashed curves in Figure 3. The second category is when a surface water molecule on the cluster binds the excess electron with both its H-bonds, which we refer to as “double acceptor” (AA) waters because they only accept H-bonds from other waters, as shown in panel 2 of Figure 4. These configurations abound in thermally equilibrated clusters and tend to have higher VDEs, as illustrated by the green dashed curves in Figure 3.

The fact that water anion clusters indeed have different H-bond stabilization motifs is known from IR photodetachment spectroscopy experiments, which observed a splitting of the

water bending vibration consistent with D and AA waters binding the excess electron.^{37,45} For small cluster anions with 7–8 waters, the AA binding motif was shown to correspond to the higher-energy peak in the photoelectron spectrum and the D binding motif to the lower-energy peaks,⁴⁶ a finding consistent with *ab initio* calculations performed on a few static anion cluster geometries.⁴⁷

Our observation that D and AA binding motifs are preferred for metastable and thermally equilibrated water anion cluster configurations makes sense. For the metastable anion clusters with mostly D-type electron stabilization, the neutral water cluster precursors have the surface waters primarily H-bonded to each other, with an occasional dangling H-bond pointing out of the cluster. When the excess electron is attached, the surface waters have little ability to reorganize, so the electron binds to the place on the cluster surface where it can receive the most dangling H-bonds from the water. The single dangling H-bonds do not hold the electron very tightly, however, so these metastable clusters have lower VDEs, with the binding energy dependent on the number of dangling H-bonds. For the thermally equilibrated cluster anions, it is clear that binding the electron with AA waters provides additional stability, and the thermal energy available to these anion clusters permits reorientation of the surface waters to do so. The need to break two H-bonds per AA water produces equilibrated water anion clusters with higher VDEs. Clusters that have different discrete numbers of D and/or AA waters binding the excess electron thus have different discrete VDEs, explaining why different groups see different VDE distributions based on cluster preparation conditions and why a continuum of photodetachment energies from water anion clusters is not observed.

In summary, we have simulated the dynamics of $(\text{H}_2\text{O})_6^-$, $(\text{H}_2\text{O})_{11}^-$, and $(\text{H}_2\text{O})_{20}^-$ clusters using DFT methods that are benchmarked to quantitatively reproduce electron binding energies. We find that by preparing the water anion clusters in two different fashions designed to best mimic the different conditions used experimentally, our calculations successfully reproduce the multippeak features seen in the experimental photoelectron spectra of water anion clusters from different groups. For anion clusters with up to 20 water molecules, our simulations show that the electron is always bound to the

surface of the cluster, with no sign of interior electron solvation states. The different VDEs of different clusters of the same size result from the nature of the hydrogen bonds of the surface water molecules that bind the electron: the more water molecules that make H-bonds to the electron, the higher the binding energy, and waters that make two H-bonds to the electron provide more stabilization than those that make only a single H-bond. The distribution of H-bonds in a given cluster depends sensitively on the preparation conditions, with doubly H-bonded waters playing a greater role in more thermally equilibrated anion clusters. The different discrete VDEs seen experimentally thus reflect cluster geometries with different numbers of water molecules that make discrete numbers of single or double H-bonds with the excess electron. Although all the clusters simulated here were too small to form an interior electron, our goal is that this work will pave the way toward ab initio studies of larger cluster anions and eventually the bulk hydrated electron, eventually addressing the controversy over its cavity or noncavity structure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcclett.8b02152.

Details of how the calculations were performed, including optimization of the BNL range separation parameter and benchmarking of the basis sets used, etc. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: dxn@chem.ucla.edu.

*E-mail: schwartz@chem.ucla.edu.

ORCID

Vojtěch Vlček: 0000-0002-2836-7619

Daniel Neuhauser: 0000-0003-3160-386X

Benjamin J. Schwartz: 0000-0003-3257-9152

Notes

The authors declare no competing financial interest.

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