Probing the Structural Evolution of the Hydrated Electron in Water Cluster Anions $(H_2O)_n^-$, $n \leq 200$, by Electronic Absorption Spectroscopy

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S *Supporting Information*

ABSTRACT: Electronic absorption spectra of water cluster anions $(H_2O)_n^-$, $n \leq 200$, at $T = 80$ K are obtained by photodissociation spectroscopy and compared with simulations from literature and experimental data for bulk hydrated electrons. Two almost isoenergetic electron binding motifs are seen for cluster sizes $20 \leq n \leq 40$, which are assigned to surface and partially embedded isomers. With increasing cluster size, the surface isomer becomes less populated, and for $n \geq 50$, the partially embedded isomer prevails. The absorption shifts to the blue, reaching a plateau at $n \approx 100$. In this size range, the absorption spectrum is similar to that of the bulk hydrated electron but is slightly red-shifted; spectral moment analysis indicates that these clusters are reasonable model systems for hydrated electrons near the liquid−vacuum interface.

$\mathbf{S}$ize-selected water cluster anions have long been discussed as gas phase model systems for the bulk hydrated electrons, a species of fundamental importance in condensed phase chemistry and radiation biology.[1,2] Water cluster anions have been characterized by many experiments, including anion photoelectron spectroscopy,[3−6] electronic and infrared absorption spectroscopy,[7−9] and time-resolved photoelectron spectroscopy.[10−13] These experiments have clearly shown the existence of multiple electron binding motifs; surface and interior states have been proposed to explain these findings, a result also found in many calculations.[14−21] In addition, nanocalorimetry experiments have shown that water cluster anions resemble the bulk in the same way as $F^-(H_2O)_n$ resembles fluoride in bulk aqueous solutions.[22] Despite all efforts, two key questions remain unresolved: which of the proposed electron binding motifs are actually present in experiment, and how large does a cluster have to get to become a valid model system for the bulk? Calculations have predicted that size-dependent electronic absorption spectra are particularly sensitive to the electron binding motif.[15,18] Moreover, the electronic absorption spectrum of the bulk hydrated electron is its best-characterized spectral property and has been extensively investigated with experiment and theory.[23−25] We therefore measured the absorption spectrum via photo-

dissociation spectroscopy on size-selected, temperature-controlled water cluster anions $(H_2O)_n^-$, $n \leq 200$. Two distinct electron binding motifs are evident for $20 \leq n \leq 40$, as is a blue shift of the absorption with increasing cluster size for $n \leq 100$. For clusters beyond $n = 100$, the spectrum no longer changes systematically in position or shape; its appearance is similar to that of the room temperature bulk electron, but it is somewhat red-shifted.

Figure 1 shows optical absorption spectra of $(H_2O)_n^-$ clusters, $20 \leq n \leq 200$, obtained by irradiating mass-selected cluster ions with tunable laser light while they are trapped in the collision-free environment of a Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer at 80 K. The electron can either detach, reaction 1, or water molecules can evaporate, reaction 2. We monitor reaction 1 by the depletion of the total ion signal and reaction 2 by the detection of the fragment ions (see Supporting Information (SI) for details). Figure S3 in the SI shows the contribution of the two dissociation channels to the total cross section.

$$(H_2O)_n^- + h\nu \rightarrow (H_2O)_n + e^- \tag{1}$$

$$(H_2O)_n^- + h\nu \rightarrow (H_2O)_{n-x}^- + xH_2O \tag{2}$$
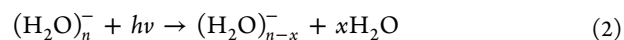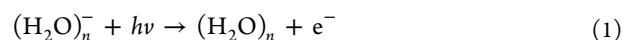
Inspection of Figure 1 shows that there are two contributions for $n = 20−40$ and one dominant contribution for $n \geq 50$. For a quantitative analysis, we assume two isomers I and II in the spectrum for $n \leq 40$, and only isomer I for larger clusters. For each isomer, two fitting Gaussian functions are used, one for the broad lower energy part and one for the blue tail (several constraints were employed to ensure convergence; see the SI). The Gauss−Lorentz fit used in previous studies[5,7] does not describe the whole structure, which we observed for the first time in our spectra.

Figure 2A shows the positions of the main peaks, in comparison with literature values. The absorption maxima reported by Johnson and co-workers[7] lie between the two resolved peaks in our experiment for $n \leq 40$. The peak positions converge to a plateau value around 1.6 eV for $n = 100−200$. For bulk hydrated electrons, the peak maximum is strongly temperature dependent and ranges from 1.8 eV for
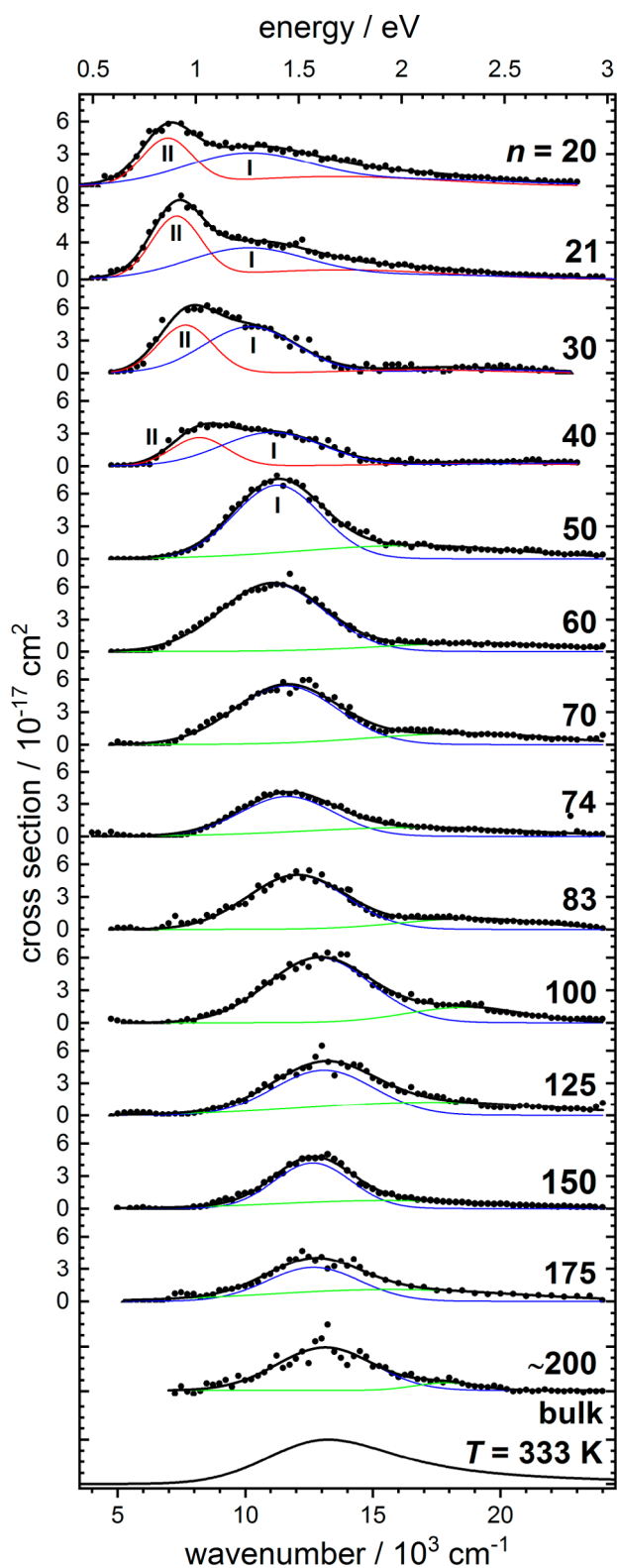
Figure 1. Optical absorption spectra of $(H_2O)_n^-$ in the cluster size region of $n = 20-200$ at $T = 80$ K. The bulk spectrum of the hydrated electron in water at 333 K (60 °C) from ref 23 is shown for comparison.

Figure 2. (A) Optical absorption maxima of Isomers I and II (this work) compared with maxima for clusters $n \leq 50$ from ref 7 and e_{hyd} in bulk liquid at 333 K from ref 23. (B) Electron gyration radius for the systems in panel (A) compared with calculations of the partially embedded isomer from ref 27. (C) Internal conversion (IC) lifetime of the hydrated electron in $(H_2O)_n^-$ clusters from ref 12 and in bulk from ref 25 shown for comparison.

Jacobson and Herbert describe the shape of the bulk hydrated electron absorption spectrum in their theoretical model by $s \rightarrow p$ transitions for the low energy part of the spectrum.[24] Weaker absorptions at higher energies, the blue tail, are assigned to quasi-continuum bound states and a small contribution of continuum states. Our data nicely agree with their calculations and show that the general shape of the bulk hydrated electron optical absorption spectrum can be observed for clusters as small as $n = 50$. We note in passing that the $n = 50$ cluster is an outlier in the overall trend, which coincides with its unusually high intensity in the mass spectrum (Figure S2) and its pronounced stability in photoelectron spectroscopy at $T = 10$ K as observed by von Issendorff and co-workers.[6]

Asmis and co-workers concluded in an infrared multiple photon dissociation (IRMPD) study of $(H_2O)_{15-50}^-$ that the electron is no longer predominantly bound to a single water molecule for clusters larger than $n = 20-25$,[9] as it is for smaller clusters,[8] but is instead delocalized over several water molecules. Our data support the picture of an evolving electron binding motif in this size range. For $n < 30$, electron detachment is the dominant pathway after absorption of a photon. Between $n = 21$ and $n = 30$, this behavior changes

273 K to 1.0 eV at 623 K.[23,26] The peak maximum for the $n > 100$ cluster anions is slightly red-shifted from the room temperature value and matches the bulk value at 333 K.
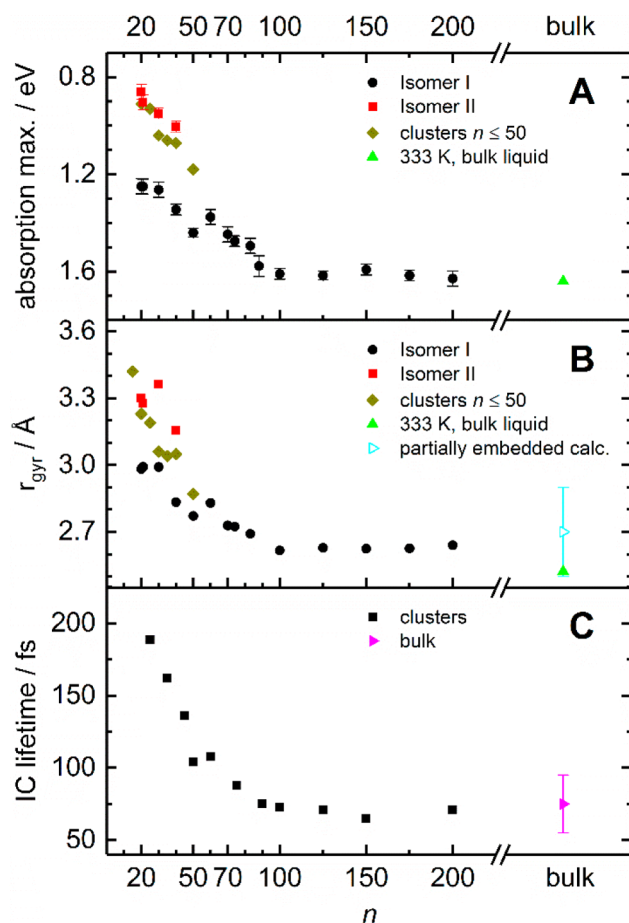
rapidly toward H_2O evaporation, suggesting an electron in a more strongly bound state. We observed the same size-dependent competition between electron detachment and water loss upon heating water cluster anions by blackbody radiation,[28] as did Viggiano and co-workers by collisional thermalization.[29] This competition is an inherent property of water cluster anions.

The observation that water cluster anions exhibit two competing binding motifs in the size region from 20 to 40 water molecules is quite intriguing since the clusters in our experiment are thermalized by exchange of infrared photons with the surrounding blackbody radiation field to 80 K.[30,31] Evaporative cooling limits the available internal energy. To test whether the abundance of the two motifs I and II is sensitive to temperature, we recorded the absorption spectrum of the $n = 40$ cluster also at 140 K and found no significant difference; see Figure S4. This indicates that the two binding motifs are very close in energy and most likely interconvert on the time scale of the experiment. We interpret the gradual disappearance of isomer II with increasing cluster size as an entropic effect; i.e., the phase space of isomer I increasingly outweighs that of isomer II. Possible contributions to this effect are the number of configurations, which may increase faster with cluster size for isomer I than for isomer II, as well as low-lying vibrational modes and internal rotations, which again may favor isomer I with increasing cluster size.

To allow for a compact comparison of our data with theoretical simulations as well as other experimental work, we performed a moment analysis of our spectra as previously described by Bartels.[32] Figure 2B shows the electron radii of gyration r_{gyr} derived from our work, in comparison with earlier experimental results and bulk values. As in the absorption maxima, the gyration radii reach a plateau for $n \geq 100$ that matches the experimental bulk value at 333 K and the calculated value for a near-surface electron in bulk water at 300 K.[27] Neumark and co-workers observed strikingly similar trends in the excited state lifetimes τ_{IC} for $(H_2O)_n^-$ clusters,[12] shown in Figure 2C, where τ_{IC} is the $p \rightarrow s$ internal conversion time. The extrapolated value of 60 fs agrees with the bulk value obtained from several experiments.[25,33,34]

A possible assignment of isomers I and II is suggested by the classification scheme proposed by Jacobson and Herbert.[18] It includes weakly surface bound states, proper surface states, partially embedded states, and internal (cavity) states, each of which has distinct vertical detachment energies and radii of gyration. The weakly surface bound states can be ruled out, since they are significantly less stable than the other motifs and are too short-lived for detection in an ICR apparatus. Based on the relative ordering of the gyration radii r_{gyr}, cluster types I and II can be identified with partially embedded and proper surface isomers, respectively.

While the absorption spectra for the larger clusters match those of the bulk hydrated electron at $T = 333$ K, this is not to say that there is a physical resemblance in terms of solvent structure around the electron between these clusters (which are, after all, at 80 K) and a bulk electron at this temperature. Water cluster anions $n \geq 50$ are exclusively type I, and thus partially embedded isomers. This interpretation is consistent with Jungwirth's model of a near-surface isomer of a hydrated electron,[27] which is considered to be 90% hydrated at room temperature and, within error limits, has the same r_{gyr} as our large clusters. This last correspondence suggests that large water cluster anions are indeed valid model systems for a bulk

hydrated electron, albeit one lying near the liquid/vacuum interface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b10347.

Materials and Methods, details about data fitting, Figures S1−S4 (PDF)

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