

Photoelectron Spectroscopy of Large Water Cluster Anions

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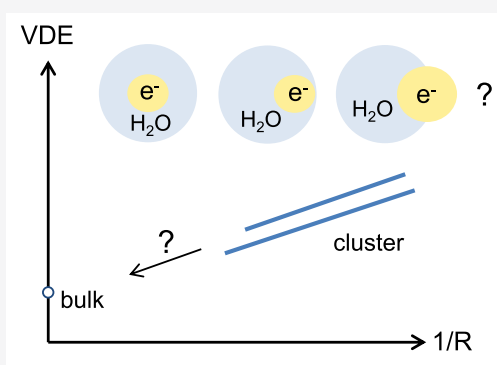
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ABSTRACT: Photoelectron spectra of large size selected water cluster anions $(\text{H}_2\text{O})_n^-$ ($n = 100\text{--}1100$) have been measured at a low cluster temperature (80 K). An extensive peak analysis has been conducted in order to determine average and isomer-resolved vertical detachment energies (VDE) of the hydrated electron. This allows us, in combination with the reevaluated data of the previously reported results on small- and medium-sized water cluster anions (*J. Chem. Phys.* **2009**, 131, 144303), to draw a comprehensive picture of the size-dependent development of the VDEs of water clusters. This allows for an improved extrapolation of the cluster VDEs to the bulk, which yields a value of 3.60 ± 0.03 eV. The general size dependence of the VDEs is in very good agreement with a standard dielectric model.



INTRODUCTION

Since their first observation¹ several decades ago, water cluster anions $(\text{H}_2\text{O})_n^-$ have been the subject of a wide variety of experimental and theoretical studies. The greater interest rests on the fact that $(\text{H}_2\text{O})_n^-$ are considered as simple model systems which might be used to gain further insight into the role of the solvated electron in charge induced chemical reactions like radiation damage.^{2,3}

One important observable, the vertical detachment energy (VDE) of the solvated electron, is readily accessible in cluster experiments by photoelectron spectroscopy (PES). Extrapolating the cluster VDEs toward infinite cluster sizes has in fact been used as one of the few methods to get an estimate of the VDE of the solvated electron in the bulk.⁴ A problem with these early extrapolations is that in more detailed photoelectron spectroscopy experiments on water clusters it was found that at least three well-separated classes of VDEs can be identified. These have been associated with three isomer classes denoted⁵ as isomers I, II, and III with decreasing VDE. Measurements on well-annealed cold medium-sized water cluster anions have additionally shown that isomer class I in fact consists of two classes, which have been termed isomer classes Ia and Ib.⁶ The term isomer class is used here because the hydrogen bond network of water clusters allows for a very large number of similar isomers—even for a given arrangement of the oxygen atoms, the permutation of the hydrogen atom arrangement leads to very many possible structures. Therefore, one cannot assume the structures of water clusters contributing to one of the broad peaks in the photoelectron spectra to be identical.

An additional high binding energy peak has been found in photoelectron spectra of small and medium sized clusters,^{6,7} which was attributed to the excitation of higher energy vibrational modes within the clusters upon photodetachment. Averaging over different isomer classes can lead to extrapolated bulk VDE results that differ from the true value and that furthermore depend on the experimental conditions. Currently extrapolations of various experimental data locate the VDE of the bulk solvated electron at energies between 3.3 and 4.0 eV.^{5,6,8} These results are complemented by measurements of the VDEs of the solvated electron in liquid water-jets,^{9–16} which is currently the experimental method that comes closest to measuring the VDE of the bulk hydrated electron directly. While early water jet VDE values have covered a similar energy range from 3.3 to 3.7 eV, recent investigations, taking inelastic scattering of the photoelectrons into account,¹⁵ have now established a bulk value of the VDE of 3.7 ± 0.1 eV. A very recent measurement at higher photon energies, where these scattering effects are weak,¹⁶ has obtained a value of 3.76 ± 0.05 eV without taking any scattering into account—this can probably also be considered to be compatible with a bulk VDE value of 3.7 eV.

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The localization of the solvated electron in the cluster and its solvation scheme or binding motif has been another long-standing issue and is still controversially discussed. Very early calculations predicted at least two possible localization schemes: surface and interior localized electrons.¹⁷ Since internal solvation requires a minimum amount of surrounding molecules, it becomes possible only at a certain cluster size. First estimates¹⁷ located the transition between surface and interior states between sizes $n = 32$ and $n = 64$. The assignment of experimentally determined VDEs has basically followed that scheme with gradual adaptations the more data became available.

The elusive nature of the hydrated electron and its localization challenged many theoretical groups to develop better theoretical approaches and more sophisticated models of water clusters. More types of electron localization and solvation motifs were predicted, like diffuse surface structures, surface cavity structures, or interior cavity localizations.^{18–21} The VDEs gained from different calculations show, however, a rather large scatter, which makes the comparison with experimental data difficult. The assignment of the VDEs to structures with different electron localizations therefore has remained somewhat ambiguous. Even for the bulk, calculated VDE values have shown rather large variations; nevertheless, one should note that the correct value of about 3.7 eV had already been predicted in 2010 by Jacobson et al.²²

As one can expect that at least at some size internal solution of the electron is energetically preferred, an important question was how the photoelectron spectra of water cluster anions develop toward much larger sizes. Additionally, this could yield a better extrapolation of the VDEs toward the bulk. In this report, we therefore present spectra for large water cluster anions and conduct a complete reevaluation of photoelectron spectra of the full size range we studied up to now.

METHODS

A detailed description of the experiment can be found elsewhere.⁶ In short, water clusters are produced in a liquid nitrogen cooled gas aggregation source by inserting water vapor through a slightly heated tube into a flow of cold helium and argon having a pressure of about 1 mbar. Near the exit aperture of the aggregation tube, the clusters are negatively charged by a pulsed gas discharge. After leaving the tube the cluster ions are guided by a hexapole radio frequency (rf) ion guide and a static quadrupole deflector to a 12-pole rf ion trap. The trap is enclosed by a copper shield attached to a cold head. Collisions of the clusters with helium buffer gas (10^{-3} mbar) inside the trap thermalizes them to the trap temperature, which makes it possible to adjust their temperature between room temperature and 10 K. Most spectra were recorded at a trap temperature of 10 K ($n = 15$ to 150) and 80 K ($n = 100$ to 1100), respectively (at 10 K some of the argon used for the production of the larger clusters freezes out in the trap, leading to surface charging effects and subsequent ion intensity instabilities, which is why a temperature of 80 K was used. For these larger sizes there are no visible differences between spectra measured at the two temperatures). One important detail is the fact that the cluster ions traverse a high pressure (10^{-3} mbar), high temperature (nearly room temperature) region while being guided from the aggregation tube to the low temperature trap. In this region the clusters experience several collisions with helium atoms which heat them up considerably, probably up to the evaporative ensemble temperature. The

subsequent cooling in the trap is slow, taking place on a time scale of several milliseconds, which means that the clusters should be rather well annealed to low energy structures. After thermalization, the clusters are extracted from the ion trap and inserted into a time-of-flight mass spectrometer for mass selection. The size selected clusters are then decelerated before entering the interaction zone of a magnetic bottle type photoelectron spectrometer. Photoelectrons are produced by irradiating the cluster packages with light pulses from a XeCl excimer laser (photon energy 4.02 eV, measured bandwidth <10 meV). The time-of-flight distribution of the detached electrons is recorded and averaged over 30 000 to 100 000 shots. The photoelectron spectra are calibrated with the help of the known spectrum of Pt anions, thus allowing the determination of electron energies with an accuracy of at least 30 meV.

RESULTS

The size range of investigated $(\text{H}_2\text{O})_n^-$ could be extended by nearly a factor of 10 as compared to previously reported experiments^{6,7,23} and covers now clusters consisting of 15 to 1100 water molecules. In addition to the new data, we have reevaluated the spectra previously reported⁶ (size range $n = 20$ –120). Example PES from the size range beyond $n = 120$ are shown in Figure 1. Qualitatively, one finds that the spectra

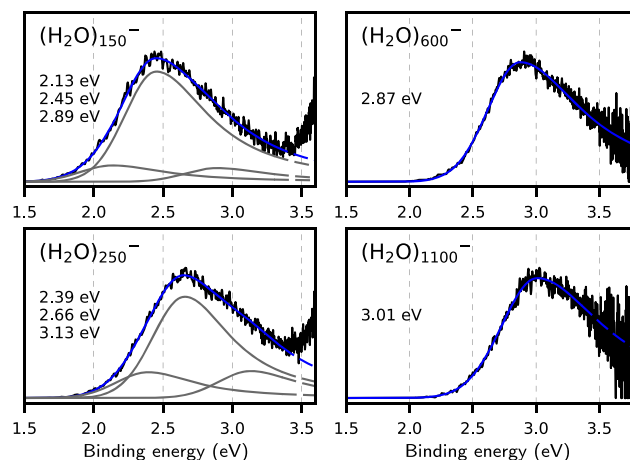


Figure 1. Example photoelectron spectra of cold (80 K) water cluster anions $(\text{H}_2\text{O})_n^-$ from the size range $n = 150$ to 1100. The blue and gray lines indicate the fit function(s) used to model the spectra. The listed energy values give the location of the peak maxima. In the spectra of the sizes $n = 150$ and 250, one can observe the onset of a background signal at 3.5 eV, which has been independently recorded and subtracted from the spectra of larger sizes.

of the larger water cluster anions ($n = 120$ –1100) continue to show a single broad and slightly asymmetric peak. The peak maximum gradually shifts to higher binding energies with increasing cluster size. No indications of additional features or deviations from the general peak shape have been found. In contrast to the small and medium cluster size range the increase of the peak width with size is moderate.

For a more quantitative analysis of the spectra they have been fitted with the often used Gaussian–Lorentzian (GL) function, where the low binding energy side of the peak is modeled by a Gaussian and the high binding energy part by a Lorentzian function:

$$I(E) = \begin{cases} A \exp\left(-\frac{(E - E_0)^2}{2\sigma_G^2}\right) & \text{if } E \leq E_0 \\ \frac{A}{\frac{(E - E_0)^2}{\sigma_L^2} + 1} & \text{if } E > E_0. \end{cases} \quad (1)$$

The use of a GL function is motivated solely by its empirical likeness with the observed line shapes. This function has originally been introduced to fit absorption spectra of bulk solvated electrons²⁴ and was later shown to provide good fits to absorption spectra of water cluster anions as well.²⁵ Coe et al. demonstrated that it can also be used to fit photoelectron spectra of these clusters.⁷ As discussed already by Coe et al.,⁷ it is a bit surprising that absorption and photoelectron spectra have such similar shapes. The photoelectron spectra are certainly dominated by a broad Franck–Condon profile, which results from the strong vibrational excitation due to the severe rearrangement of the water molecules upon photoemission. They will be additionally homogeneously broadened by inelastic scattering effects as well as inhomogeneously broadened due to the unavoidable presence of structural isomers and, at higher temperatures, initial vibrational excitation. While an almost as broad Franck–Condon profile can be expected for the absorption spectra, as the more delocalized excited states of the electron will probably favor similarly strong water molecule rearrangements, these are additionally broadened by the multitude of accessible excited states.^{21,26} It therefore seems to be mainly an interesting coincidence that this convolution of a distribution of electronic transitions with a broad Franck–Condon profile, further broadened by structural diversity, lifetime, and temperature effects, yields peak shapes of the absorption profiles so similar to those of the photoelectron spectra, which mainly reflect an probably even broader Franck–Condon profile.

Besides yielding the energy E_0 of the intensity maximum, fitting the spectra with GL functions also gives information about the peak shape via the independently fitted widths of the Gaussian part σ_G and the Lorentzian part σ_L .

Earlier reports^{5–7} have already shown that for certain size ranges and experimental conditions the PES of water clusters can deviate considerably from the generic single GL peak shape. In such cases, we have used up to 4 GL functions to fit the spectra. For these fits, the amplitude A and the energy E_0 of the peak maximum were used as independent fit parameters for each peak whereas the width parameters σ_G and σ_L were assumed to be the same for all fitted peaks. Using the same width parameters for different substructures is of course an approximation, but unfortunately, the strong overlap of the peaks does not allow for a meaningful determination of independent widths.

The maximum of the fitting function is interpreted as the VDE of the cluster, or, in case of the fit with several GL functions, as the VDE of a specific isomer class. The simplest approach of a peak analysis is to start with a single GL fit function. Although this does not yield a very good fit for many of the intermediate sizes, it can be useful for a comparison with other, less well resolved experimental results, as well as to visualize an average development of the electron binding energy with size. The upper panel of Figure 2 shows the energies of the peak maxima E_0 (or VDEs) versus the cluster size as derived from such a single GL peak analysis (blue rectangles).

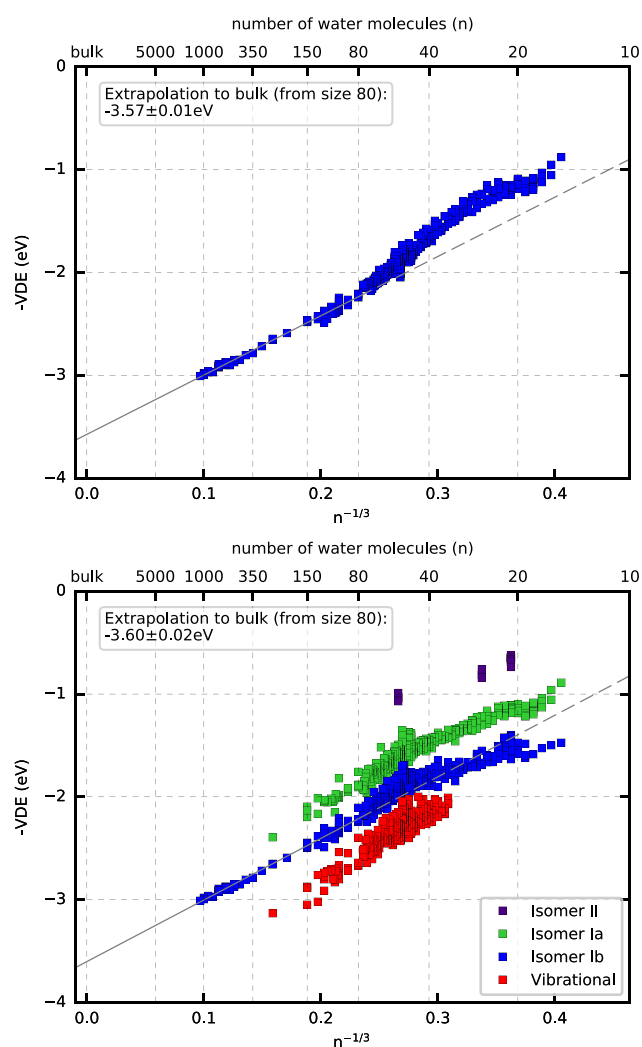


Figure 2. Development of the VDEs with the cluster size $n^{-1/3}$ as derived from different peak analysis. Upper panel: results of fits with a single GL function. Lower panel: results of fits with up to 4 GL functions. The line indicates a linear fit to the VDEs of cluster sizes with $n \geq 80$.

The VDEs increase approximately linearly with the inverse cluster radius, but only in sections, with changes in the slope occurring at about $n = 20$, 30 , and 80 . In conjunction with the new data of the large water clusters, it becomes clear that an actual linear growth motive can only be found starting at about $n = 80$. A linear fit taking into account only VDEs from clusters with size $n \geq 80$ results in an extrapolated bulk value of 3.57 eV (with a statistical error of ± 0.01 eV).

The full width at half-maximum (fwhm) of the peak and the width parameters σ_G and σ_L are plotted in the upper panel of Figure 3 for the single GL peak analysis.

Like the VDEs, the width parameters exhibit a constant growth only for the larger cluster sizes starting somewhere between $n = 60$ and 80 . The fwhm shows a strong increase between $n = 15$ and 40 . It then stays nearly constant and increases slowly again between $n = 150$ and 1100 . Looking at the width parameters, one can see that the increase of the width is mainly caused by a decrease of the slope of the high energy tail of the peak, which is an increase of the Lorentzian width parameter σ_L . The somewhat strong fluctuations of the full width especially for the large clusters with $n > 80$ are

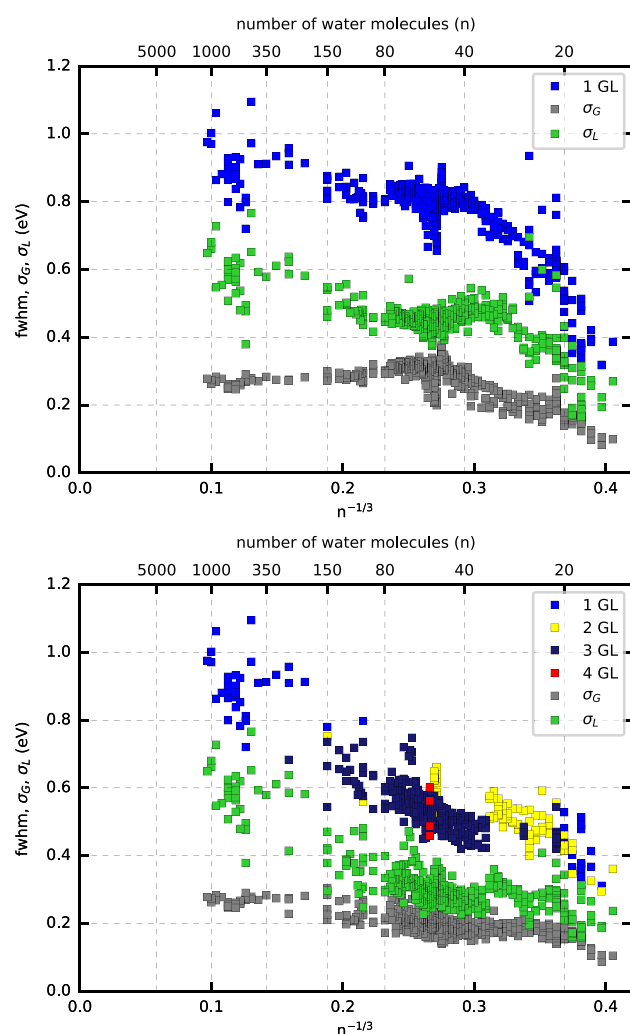


Figure 3. Size-dependent development of the peak width fwhm (indicated by the number of GL functions) and the line shape parameters σ_G and σ_L when using a single GL function (upper panel) and multiple GL functions (lower panel) for fitting.

mainly caused by fluctuations of the Lorentzian width σ_L , which in turn results from uncertainties caused by the background subtraction and the cutoff of the spectra at the photon energy of 4.02 eV. The sizes with about 47–56 water molecules are special. They show strong variations of their peak shapes from one size to the next. For some sizes, this even leads to a significant reduction of the Gaussian width parameter σ_G . For large sizes, the fwhm seems to converge to a width of about 1 eV, which is in good agreement with the bulk peak width measured by Nishitani et al.¹⁶ An interesting difference remains, though; while Nishitani et al. obtained a symmetric Gaussian peak shape, the cluster photoelectron spectra retain their GL shape even for the largest size studied.

Using a single GL function is of course a rough approximation. As already shown before, especially for clusters with $n \leq 65$, one gets a much better representation of the data by the use of multiple fit functions.^{6,7} This requires, however, several assumptions: a function representing the individual contributions must be selected, and the number of contributors to the overall peak shape has to be determined. Unfortunately, there is no unambiguous way to determine either of them from the experimental data. Since the use of an

asymmetric function for the underlying substructures (mainly isomer classes) seems plausible, we continued to use GL functions. The determination of the number of GL functions is more problematic. There are only few cluster sizes for which the experimental data allow to derive a minimum number of underlying substructures with some amount of certainty. One can expect that in neighboring sizes the same isomer classes are present as well, but if these do not exhibit clear substructures in the peak shapes, fitting is less robust. Additionally, one is forced to make assumptions about the peak shapes. Although it is quite possible that different isomer classes exhibit different peak shapes, due to the strong overlap of the peaks it is not possible to extract these individual shapes; we therefore had to assume the same peak parameters for all GL functions used in the fit. Ideally these peak parameters should not change if at a certain size a new isomer class appears, requiring the use of an additional GL function in the fit. But of course the peak widths will reduce if a very similar spectrum is fitted with a larger number of GL functions—discontinuities in the peak parameters upon changes of the number of GL fitting functions therefore hint at the fact that either the peak shapes of different isomer classes are not identical or that the number of GL functions used does not match the actual number of isomer classes contributing to the spectrum.

The lower panels of Figures 2 and 3 show the VDEs and peak width parameters of a multi GL peak analysis, for which we tried to find a best compromise between optimally fitting especially the most structured spectra, while avoiding too strong discontinuities of the peak parameter σ_L (σ_G is rather firmly determined by the shape of the onset of the spectrum, under the assumption that all GL functions have the same shape). The results for small and medium sized water clusters reproduce essentially our previous findings of two isomers classes Ia and Ib. It should be noted, however, that due to the inclusion of additional measurement data in the size interval 80–120 and the reevaluation of the data the VDEs of isomer Ib now shifted by about 50 to 60 meV to lower binding energies. One can observe a jump of the peak parameter σ_L between the sizes $n = 33$ and $n = 34$, which shows that in this size range the fitting is not yet fully self-consistent—this calls for further studies of these sizes.

The data of the large water clusters show that isomer class Ib continues to be the dominant isomer structure for larger sizes. As can be seen in the lower panel of Figure 2, like for the single GL analysis the size dependence of the VDEs changes slopes at several sizes. The VDEs of the dominant isomer class Ib show a constant slope for sizes starting around $n = 80$. This is a consistent result of all peak analysis approaches and supports the claim that any extrapolation to the bulk should start around that size. A linear fit to the VDEs of isomer Ib of sizes starting at $n = 80$ results in a bulk value of 3.60 eV with an statistical error of 0.02 eV. All variants of the peak analysis we investigated yield a bulk value between 3.57 and 3.60 eV. Due to uncertainties in the exact determination of the VDEs (experimentally as well as concerning the peak analysis), we estimate the accuracy of the extrapolation to be 0.03 eV. This means that all peak analysis methods agree in this result within the error.

Before starting the discussion of the results, we would like to comment on the temperature dependence of the PES. A detailed analysis is beyond the scope of this report, as only smaller sizes exhibit stronger temperature effects. We would like just to make a few qualitative remarks. The shapes of the

spectra change with the temperature, which is due to a slight increase of the width of the contributions of the different isomer classes as well as changes in their relative contributions. Thereby, although the overall width of the observed band does increase only very moderately, for higher temperatures the spectra become rather featureless and in most cases resemble single GL-functions. The main changes occur in the temperature range between 100 and 140 K, the region where melting (or rather a glass transition) of the clusters has been observed.²⁷ The changes in peak shape have a measurable impact on the fitting results when using multiple fit functions. In order to show the full range of VDEs of the different isomer classes we obtained experimentally, for the smaller sizes we included measurements done at many temperatures between 10 and 150 K (which is the evaporative ensemble temperature, so the maximum temperature the clusters can have on the time scale of the experiment). All measurements for $n \geq 150$ have been done at 80 K. If we include only measurements done at $T \leq 100$ K in the size range $80 \leq n \leq 150$, the extrapolation of the VDE to the bulk results in a value of 3.59 eV, with a slightly larger statistical error, so practically the same result as given above.

DISCUSSION

The data show that no clearly different isomer class appears in the size range up to $n = 1100$. As we have discussed before,⁶ comparison of the magic numbers in mass spectra of anionic water clusters and neutral or protonated water clusters indicate that in the size range of $n \approx 50$ the electron replaces a water molecule in the water hydrogen bond network, without changing its overall structure except for swapping of the hydrogen atom orientations, and therefore can be assumed to reside in a 4-fold coordinated cavity. This gives strong evidence that isomer class Ib indeed consists of structures with an internally solvated electron. This is also in accordance with its extrapolation to the bulk, which results in a value agreeing with the newer bulk electron binding energies within the error margins.

As there has been an intense discussion in the past about the correct interpretation of the photoelectron spectra of water cluster anions, it is interesting to compare these results to earlier experimental and theoretical results, as well as simple model predictions.

Comparison to Earlier Data. In Figure 4, we compare our data to data published by Coe et al.,⁷ Verlet et al.,⁵ and Young et al.²³ The position of the main peak observed in these measurements, assigned to an isomer class termed isomer I by Verlet et al., shows an almost perfect agreement with our single GL analysis results. Only for larger water clusters with $n > 80$ are the data of Verlet et al. shifted to slightly lower binding energies. Later measurements on water clusters produced in coexpansion with Ne instead of Ar, which are considered to be warmer,²³ lead to VDEs in even better agreement with our data. This probably indicates that the water clusters in the former measurements were not fully annealed. The excellent agreement of the experimental results from three different experimental setups, with different cluster sources and cluster temperatures, demonstrates that the general size dependence of the VDE of water clusters in this medium size range is well established. The main reason these data did not yield a correct interpolation to the bulk binding energy is that in these earlier measurements it was not recognized that isomer class I in fact consists of two isomer classes, with the size dependence of

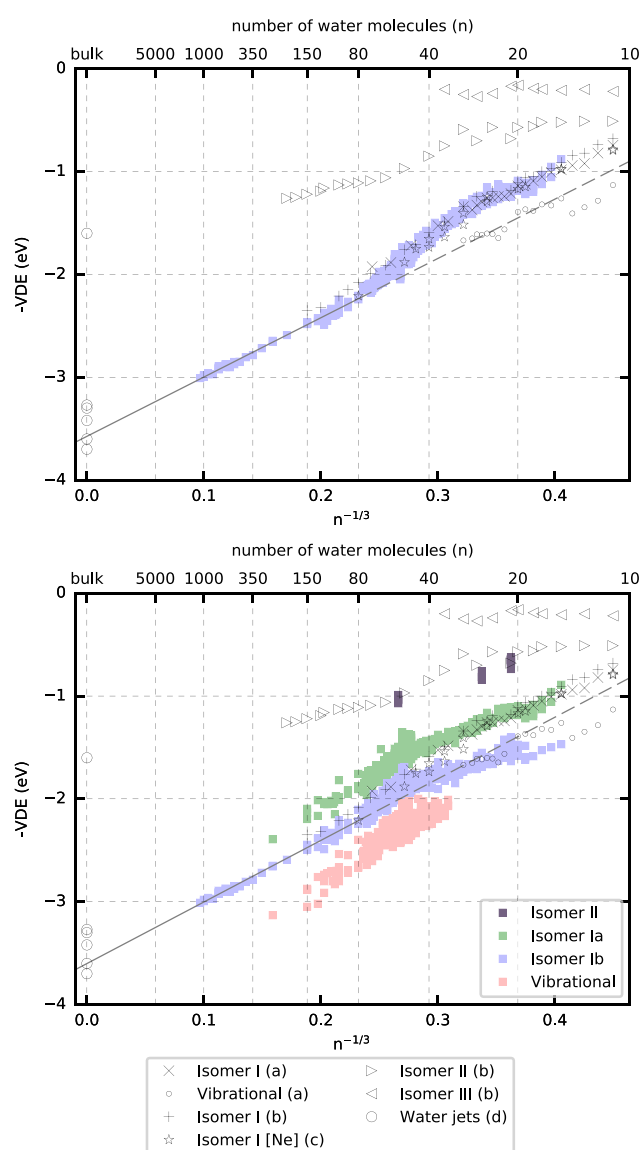


Figure 4. Comparison of the VDEs derived from single GL (upper panel) and multi GL (lower panel) analysis (colored rectangles) with data published by other groups (black markers; a,⁷ b,⁵ c,²³ d^{9–15}).

their relative contributions leading to an additional shift of the mean VDE.

Figure 4 also shows the VDEs gained by various experiments on liquid water microjets.^{9–15} The results cover a range between 3.27 and 3.7 eV. As mentioned above, one of the most recent experimental values amounts to 3.7 ± 0.1 eV,¹⁵ which is in very good agreement with the extrapolation of our data for the larger clusters (3.60 ± 0.03 eV).

If we interpret the VDEs of isomer I as weighted average of isomers Ia and Ib, all available experimental results yield a consistent picture: the two low binding energy isomers II and III (as named in⁵) are metastable isomers, which exist only for not well-annealed clusters. An exception is isomer II, which appears even for a few well-annealed sizes, presumably because these sizes have rather stable structures as neutrals.⁶ Isomers Ia and Ib are stable isomer classes in the sense that at least for medium sized clusters they exist for all experimentally accessible cluster temperatures and annealing times.

The high binding energy peak, found more or less explicitly for sizes between 45 and 65, is most likely of vibrational origin. It has an offset to the isomer Ib peak of 0.3–0.4 eV, compatible with a perturbed hydrogen stretch vibration. Furthermore, it does not show a size dependence of its intensity independent of that of isomer Ib, as one would expect for a different isomer class. Finally, its vibrational energy seems to be smaller for heavy water clusters,⁶ although for these it is only barely detectable, making it difficult to precisely determine its position.

Similar considerations apply to peak Ib for sizes <33, where it clearly exhibits an offset to peak Ia which is different for water and heavy water clusters, in accordance with what one would expect for a hydrogen stretch vibration. So for these small sizes, one has to assume that peak Ib is mainly of vibrational origin, and in the transition size region up to $n \approx 40$ at least partially.^{6,7} For very large clusters, the high energy shoulder is not recognizable anymore. This could indicate that here the excitation of a hydrogen stretch vibration upon electron emission is less probable, but it could also just mean that the broadening of the spectra due to the ever increasing number of contributing structures renders it difficult to detect.

Dielectric Model. The general relationship between VDE and cluster size is usually derived from a simple dielectric continuum model, which describes the energy of an excess electron in a dielectric sphere.^{17,28} It establishes a linear dependence of the VDEs on the inverse cluster radius:

$$\text{VDE}(n) = \text{VDE}_\infty + An^{-1/3} \quad (2)$$

The intercept, VDE_∞ , corresponds to the vertical detachment energy of the bulk. The slope A depends on the relative permittivity $\epsilon_{r,\nu}$ at close to optical frequencies and the relative static permittivity $\epsilon_{r,s}$:

$$A = \frac{e^2}{2r_{bu}} \left(1 + \frac{1}{\epsilon_{r,\nu}} - \frac{2}{\epsilon_{r,s}} \right) \quad (3)$$

where e is the charge of the electron and r_{bu} the effective radius of the water molecule. Figure 5 compares the predictions of the dielectric sphere model (eq 2) for different slopes (A) and bulk VDEs (VDE_∞) with the experimental cluster VDEs.

The black slope ($A = 5.84$ eV) is calculated from the liquid water permittivities at 300 K ($\epsilon_{r,s} = 78.5$, $\epsilon_{r,\nu} = 1.7$) and a density of 1 g/cm³. It agrees within the accuracy of our analysis with the slopes gained from multi (green, $A = 5.75$ eV) and single (blue, $A = 6$ eV) GL analysis, respectively. Accordingly all slope values fit very well to the isomer Ib VDEs if one chooses 3.6 eV as bulk value. When assuming a bulk VDE of 3.3 eV, which formerly was seen as the correct bulk VDE, one has to assume a slope value of $A = 3$ eV to connect to the measured VDE of the largest cluster (red line). Analogously, connecting to the probable bulk value of 3.7 eV yields a slope of $A = 7$ eV. Although especially the latter value of A seems not too far from the predicted value, it is difficult to obtain within the simple model. Water clusters could have a different density than bulk water, but as a higher density leads both to a smaller radius and, following the Clausius–Mossotti relation, an increased value of $\epsilon_{r,\nu}$, the influence of the density partially cancels out. A slope of 7 eV for example can only be obtained assuming a density of 1.6 g/cm³. The value of A of about 5.8 eV should therefore be valid for a rather broad range of cluster structures and temperatures. This is corroborated by measurements of the cluster size dependence of the VDEs of iodine

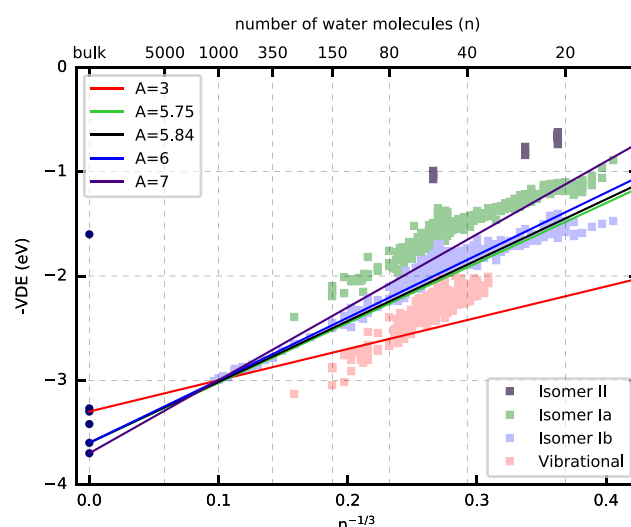


Figure 5. Prediction of the dielectric sphere model for various slope values A when starting at three different bulk VDEs.

anion doped water clusters, which exhibit a slope close to 5.76 eV.²⁹

One should remark, though, that the model described above assumes the electron to be located at the center of the cluster, which is not necessarily the case. Nevertheless this simplification does not have significant consequences. Makov and Nitzan have demonstrated that within a classical dielectric model the solvation energy of a charged conducting sphere in a dielectric droplet is practically independent of its position within the droplet (exhibiting a variation of less than about 15 meV), except for positions where the sphere almost touches the droplet surface.³⁰ This means that classically there is no preferred position of the electron within the cluster as long as the electron is fully solvated. Their model furthermore shows that also the detachment energy of a negatively charged conducting sphere in a droplet is practically independent of its position (with a variation of less than about 40 meV), again except for positions very close to the surface. This means that one can use the simplified model even if the electron is not located at the cluster center.

Therefore, the slope observed for the VDEs of isomer class Ib for larger water clusters is in perfect agreement with expectations, indicating that performing measurements on much larger clusters most probably would not lead to significant changes of the asymptotic value of 3.6 eV. At some point, of course, inelastic scattering of the electron would have to be taken into account for a correct determination of VDEs, which does not seem to play an important role yet in the size range studied here. Inelastic scattering would lead to a lowering of the kinetic energies of the photoelectrons and therefore to an apparent increase of the electron binding energies. Such a deviation from the simple behavior described by eq 2 is not observed in the measured data. In fact this is expected; the largest cluster studied has a radius of about 2 nm, while the inelastic mean free path of electrons with a kinetic energy of about 1 eV is about 3 nm.¹⁵ This means that even if all electrons were located at the cluster center, only about 50% would experience an inelastic collision upon photoemission. If the electrons have rather random positions within the cluster, which is more probable, this percentage will be even lower. Therefore, at this size, the influence of inelastic scattering can

be expected to be still rather weak. Of course this will not be the case anymore for clusters with significantly larger radii, which could be a motivation to extend the study to much larger water cluster anions.

Comparison to Ab Initio Calculations. More details about the binding motif of the hydrated electron and its interaction with the solvent can only be derived in combination of the experimental results with theoretical calculations and models. Although a large number of model calculations with different levels of approximations has been made in the past few decades, the results are not fully conclusive. The charge solvation motif and consequently the structure of the clusters remains somewhat controversial. The complexity of the problem is reflected in the strongly varying results for the calculated VDEs of water clusters, which makes the assignment of different types of electron localization difficult.

Figure 6 shows a comparison of various theoretical VDEs with our data (multi GL analysis). Barnett et al. found three

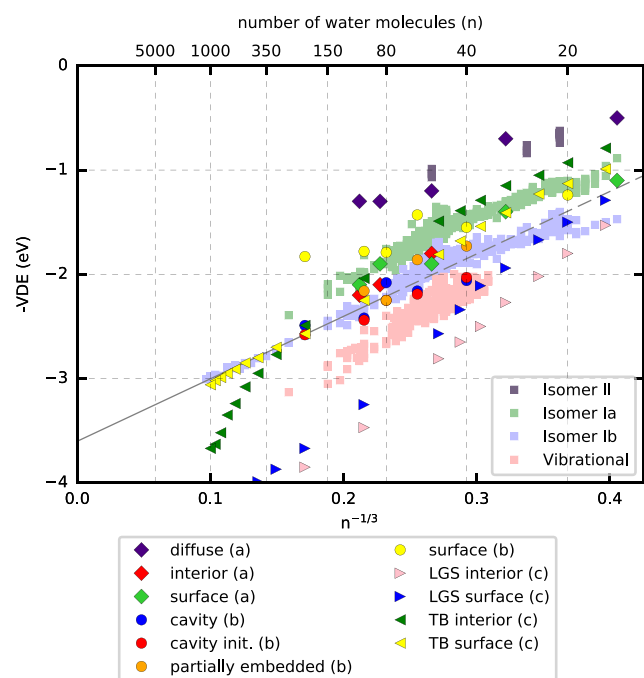


Figure 6. Comparison of the VDEs from various theoretical calculations (a,¹⁸ b,¹⁹ c³¹) with the results of the multi GL analysis of our data.

isomers,¹⁸ with diffuse, surface, and interior localization of the electron, which coincide (with few exceptions) fairly well with our isomer II, Ia, and Ib VDEs.

A similarly good agreement can be found for the VDEs of surface, partially embedded, and cavity solvated electrons calculated by Jacobson and Herbert,¹⁹ although they are consistently slightly below the measured values.

In a recent study³¹ Turi calculated VDEs of water cluster anions for a large size range which covers nicely our measured sizes. The cluster structures were calculated by molecular dynamics simulations employing two different pseudopotentials (Turi–Borgis (TB) and Larsen–Glover–Schwartz (LGS) potential). Both potentials yielded cluster configurations with internal and surface electron localization. The TB model predicts, however, a cavity structure for internal solvation, in

contrast to the LGS model which supports a noncavity structure. As Figure 6 demonstrates the LGS-based VDEs show basically no overlap with the experimental data, which corroborates critical assessments of the model.³² A slightly better agreement can be found for the TB-based VDEs: The VDEs of the TB interior state somewhat agree with isomer Ib values around size 200, but they are too small for smaller sizes and diverge more and more for larger sizes due to a strong change in slope around $n = 400$. For these larger sizes, the size dependence of the VDEs strongly deviates from the prediction of the simple dielectric model, extrapolating to a bulk value much higher than the measured one. This indicates that the calculation does not fully reproduce the dielectric properties of water, as has been discussed before.²² The TB surface state VDEs show an excellent agreement with the VDEs of the larger clusters; nevertheless, given the problems of the calculation mentioned before, this probably has to be considered as fortuitous.

Which conclusions can now be made about the structure assignment of the experimentally found isomers? Although the agreement of experiment and theory is not perfect, it seems highly probable that isomer class II are clusters with surface bound electrons, while in the classes Ia and Ib, the electron is partially and fully embedded in the cluster, respectively.

This means that starting from sizes around size $n = 40$ clusters with fully solvated electrons can be observed, which becomes the dominant structure around size $n = 80$.

CONCLUSIONS

We have measured the PES of large water cluster anions up to sizes consisting of 1100 water molecules. Additionally, medium sized clusters were measured and in combination with previous measurements the whole size range ($n = 15$ to 1100) underwent a detailed peak analysis. The determined VDEs confirm the earlier findings of two dominant stable isomer classes (Ia/Ib) of which Ia is dominant for small cluster sizes and Ib for the larger clusters while they coexist in the intermediate size regime. The peak analysis suggests that these isomer classes are present in all reported experimental studies.

The VDEs of large clusters, starting around $n = 80$, exhibit a size dependence in very good agreement with a simple dielectric model. The VDE extrapolates to 3.60 ± 0.03 eV for $n = \infty$, which within the error bars agrees with a recently determined VDE of bulk water. Comparison with calculated VDEs indicate that isomer class Ia represents structures with a partially embedded surface localized excess electron, while isomer class Ib represents structures with an electron internally embedded in a cavity.

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Notes

The authors declare no competing financial interest.

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