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Photoelectron spectroscopy of the 'missing' hydrated electron clusters $(H_2O)_n^-$, $n = 3, 5, 8$ and 9: Isomers and continuity with the dominant clusters $n = 6, 7$ and $\geqslant 11$

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Abstract

We report photoelectron spectra for the small anionic water clusters, W_n^- ($n = 2$–11, excluding the tetramer), to explore the nature of the trace species surrounding the intense parents appearing at magic numbers $n = 2, 6, 7$ and $\geqslant 11$. Two isomeric forms are observed for most of these anions, which are distinguishable by their vertical electron detachment energies (VDE). While the band corresponding to the more strongly bound form continuously evolves from the band characteristic of the larger ($n \geqslant 11$) clusters, the smaller clusters display a dramatically smaller sequential solvation shift, resulting in a sharp break in the cluster radius ($\propto n^{1/3}$) dependence of the VDEs. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The attachment of an 'excess electron' to water clusters:

$$e^- + W_n + M \rightarrow W_n^- + M \qquad (1)$$

(where M = Ar, for example) occurs with surprisingly distinct discontinuities, generally leading to the characteristic W_n^- cluster distribution displayed in Fig. 1. The 'magic numbers' occur at $n = 2, 6$ and 7 before the sharp onset of a continuous distribution for $n \geqslant 11$. This pattern occurs for a variety of different ion sources [1–5] and has been shown to directly reflect the formation step (Eq. (1)), even in complex environments (e.g., discharged free jets, Rydberg electron attachment, etc.). [1] Bowen and co-workers [2,3] measured the photoelectron spectra of the relatively intense $n = 2, 6, 7$ and $\geqslant 11$ clusters (as well as the weak $n = 10$ parent) [4] and reported the presence of two isomeric forms for $n = 6$ and 7 (denoted I and II corresponding to the lower and higher electron binding forms, respectively) on the basis of the isotope and source–condition dependence of the photoelectron bands. Interestingly, that study revealed a linear dependence of the vertical detachment energies (VDE) of the $n \geqslant 11$

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[1] This occurs because, for $n < 15$, the decay kinetics of warm clusters are dominated by electron evaporation [6,7] (i.e., thermionic emission), which neutralizes the ionic clusters upon condensation and prior to evaporation of water monomers.

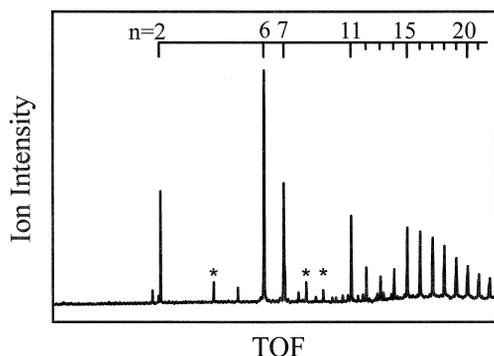* Corresponding author. E-mail: mark.johnson@yale.edu

Fig. 1. Time-of-flight mass spectrum of water anions, W_n^-. Intense features correspond to $n = 2, 6, 7$ and 11. The small peaks marked by asterisks are due to Ar complexes.

follow the evolution of these isomeric forms from the $n = 6$ and 7 'island' to the continuous distribution above $n = 11$ by acquiring the photoelectron spectra of the minor species ($n = 3,5$ and $8–10$). We then combine these results with previous measurements to formulate a self-consistent model for the coarse nature of the isomers based on the extent of charge delocalization and deformation of the neutral network relative to the equilibrium geometries of the corresponding neutral water clusters.

2. Experimental

The water cluster anions, W_n^-, are formed by attachment of slow secondary electrons (generated by high energy electron impact ionization) at the throat of a free jet containing the vapor pressure of water at 0°C seeded in 3–4 atm of Ar. Photoelectron spectra were recorded with a pulsed spectrometer described previously [12], modified to incorporate a 'magnetic bottle' electron spectrometer [13] to improve the collection efficiency of our field-free instrument. This improvement enabled routine collection of the spectra for even the weakest parent ions in the distribution. Unfortunately, we could not generate a sufficiently intense beam of W_4^- to yield an unambiguous (i.e. distinguishable from background) photoelectron spectrum, and therefore omit this species from the present discussion. Photoexcitation was carried out using the Nd:YAG fundamental (1.165 eV), with a typical spectrum resulting from an average of 20000 laser shots. To minimize the degradation in resolution arising from the velocity of the ion beam, the parent ions were impulsively decelerated down to several hundred eV kinetic energy prior to photodetachment. The resolution is therefore mass dependent, ranging from about 0.08 eV (for 1 eV photoelectrons) in the heavier clusters to 0.15 eV for the W_2^- dimer. The spectra were calibrated using Br^- and I^-, photodetached at 355 nm.

3. Results

3.1. Survey of the W_n^- ($n = 2–11$) photoelectron spectra: assignment of the bands to isomers

Photoelectron spectra of the small negatively charged water clusters are displayed in Fig. 2. One
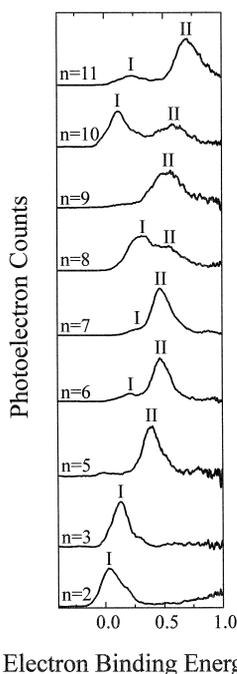
clusters versus inverse cluster radius ($\propto n^{-1/3}$), and surprisingly, found the *lower* binding isomer (I) of the $n = 6$ and 7 ions to correlate with the trend established by the larger clusters. This led those authors to the intriguing suggestion [3] that the more *weakly* bound isomer was related to the morphology established in the large cluster regime, then thought to correspond to internal electron solvation. Kim et al. [8,9] have considered the nature of these isomers in the context of calculations on various plausible neutral water networks, however, and concluded that species I has a more diffuse charge distribution than the isomer with higher binding energy (II), a prediction subsequently supported by measurements [10] of the different photodetachment cross-sections for the two species. Further complicating Bowen's initial 'internal hypothesis' for $n = 6$ and 7, Ayotte and Johnson [11] have recently obtained electronic absorption spectra of the larger clusters and found them consistent with surface solvation of the excess electron. This rules out a simple surface versus internal assignment of the two isomers in $n = 6$ and 7, since the electron will not be internally solvated in small clusters if it does not do so in substantially larger ones. Because these previous studies [2–4] have, understandably, focussed on the abundant parent ions, the resulting sparse data set leaves open important questions regarding the nature of the weak clusters ($n = 3–5$ and $8–10$), such as whether they also display multiple isomeric forms and whether, once formed, they achieve binding energies comparable to those of the nearby intense parents. In this Letter, we

Fig. 2. Photoelectron spectra of small negative water clusters, W_n^- taken at 1.165 eV. The two isomeric forms are labeled as I and II. The VDEs of W_n^- are tabulated in Table 1.

immediate feature of these spectra is many of them display two prominent bands. As mentioned earlier, Bowen and co-workers [2–4] have previously reported two electronic bands for $n = 6$ and 7 and assigned them to two different isomers, labeled I and II in our spectra (Fig. 2). A key element of Bowen's original isomer assignment of the $n = 6$ and 7 was the observation that the relative intensities of the two envelopes could be changed with source conditions, thereby establishing that the ion ensemble was comprised of a heterogeneous mixture of distinct species. In the new spectra reported here, there are two peaks in the spectra of the $n = 8$ and 10 parents, one of which falls in line with the trend established for isomer II. In Fig. 3, we display the spectra of $n = 10$ for two different source conditions, indicating that the relative contribution of the two peaks are quite different, as expected for a mixture of two species. We have not been able to achieve a similar modulation of the spectrum in $n = 8$; however, we have recorded the spectrum of the argon solvated cluster, $W_8^- \cdot Ar$, which is displayed in Fig. 4. Clearly, the

spectrum from the solvated cluster has inverted the intensity of the two bands such that the higher energy band becomes dominant. Since the spectral features arising from these two clusters can be changed by perturbation, we conclude that they are similarly due to two isomers. We denote them, in keeping with the convention established for $n = 6$ and 7, by I and II for the lower and higher VDE forms, respectively. When only one band is observed (i.e., for $n = 2, 3, 5$ and 9) we label the band in a manner consistent with the behavior of the nearest cluster which displays two bands. Thus, both $n = 2$ and 3 are assigned to I, while $n = 5$ and 9 are assigned as II. The VDE values of the isomers are collected in Table 1.

3.2. Continuous evolution of the large cluster VDEs into isomer II

The VDEs of the weaker binding isomers (I) evolve non-monotonically, with $n = 8$, for example, having a much larger VDE than that of $n = 10$ (0.32
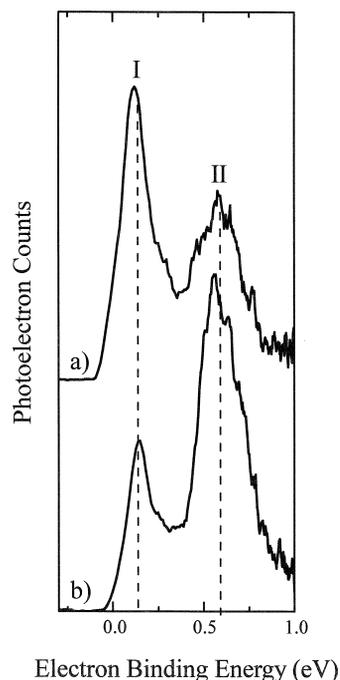

Fig. 3. Photoelectron spectra of W_{10}^- taken at 1.165 eV. Traces (a) and (b) display spectra at two different source conditions.

Fig. 5. The VDEs of water anions plotted as a function of $n^{-1/3}$. The experimental values for VDEs of isomer I and isomer II are represented as open squares ($\square$) and circles ($\bullet$), respectively. Linear fits to isomer I (———) and II (– · –) data are also shown. The experimental values obtained from Ref. [10] are displayed as diamonds ($\blacklozenge$). The line (---) corresponds to the linear least squares fit to the data in Ref. [3].
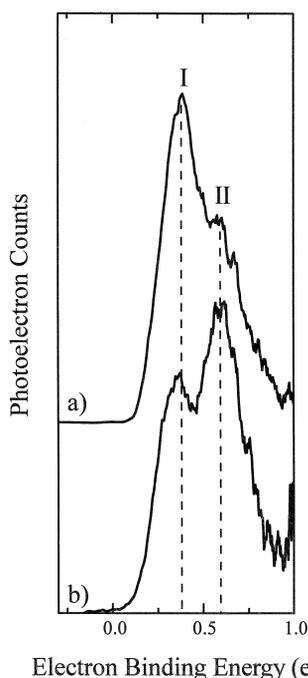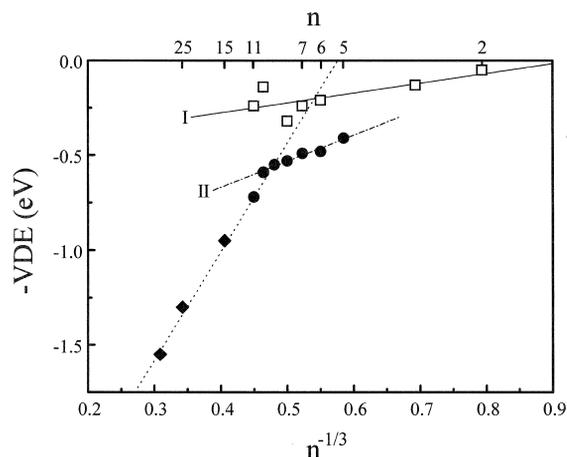

Fig. 4. Photoelectron spectra of (a) W_8^- and (b) $W_8^- \cdot Ar$ taken at 1.165 eV.

vs. 0.14 eV, respectively). Isomer II, on the other hand, smoothly increases from the pentamer, the smallest cluster in which it is apparent. To illustrate this propensity, we plot in Fig. 5 the VDEs of the isomers versus $n^{-1/3}$, with the open and closed symbols denoting isomers I and II, respectively. (The peak locations of the two overlapping bands were extracted by convoluting the spectra with two gaussians.) The characteristic band established in the large

Table 1
The VDEs (± 0.03 eV) for isomers I and II of W_n^- ($n = 2$–11)

n	I	II
2	0.05	–
3	0.13	–
5	–	0.41
6	0.21	0.48
7	0.24	0.49
8	0.32	0.53
9	–	0.55
10	0.14	0.59
11	0.24	0.72

cluster regime continuously evolves into isomer II in the small cluster regime. Isomer I appears as another branch (starting at the dimer) which dies out above $n = 11$.

4. Discussion

4.1. Reduction in sequential solvation for n < 11

While isomer II smoothly evolves from the spectra above $n = 11$, it is of interest that the VDEs for this species become much less sensitive to cluster size than anticipated by the $n^{-1/3}$ scaling followed at larger sizes, resulting in a pronounced break in the slope at $n = 11$ (see Fig. 5). This complete data set indicates that the VDEs of isomer I for $n = 6$ and 7 accidentally fall on the extrapolated curve from the higher clusters [2,3]; therefore, there is no reason to suspect (as previously suggested [3]) that these isomers arise from an 'island' at $n = 6$ and 7 which is analogous to the species $n \geqslant 11$. Although isomer II is most directly related to the large clusters, we note that there is some type of change occurring below $n = 11$ which results in a break in the *slope* of the

VDE versus $n^{-1/3}$ plot. Moreover, the two isomers have different slopes such that isomer I displays much smaller sequential solvation than does II (0.52 vs. 1.37 eV/$n^{-1/3}$ for I and II, respectively), which is, in turn, much smaller than the slope corresponding to the larger clusters (5.73 eV/$n^{-1/3}$). This trend, where the sequential solvation shift for each water becomes smaller with decreasing cluster size, is opposite to that found in the solvation of localized (i.e. valence) anions [14–16], where the first few water molecules provide the largest increases in electron binding energies.

In considering an explanation for the pronounced break in the VDE of form II at $n = 11$ (Fig. 5), we note that a linear binding energy versus inverse radius plot arises from 'missing polarization energy' in a model [17] where a continuous dielectric medium is removed from a charged sphere with fixed radius. While this model indeed accounts for the behavior of solvated halides, for example, down to very small clusters [18], it is not obvious that it provides even a qualitative framework in which to discuss the small W_n^- clusters. Most importantly, the expectation value of radius of gyration of the excess electron has been measured [19] (by direct inversion of the electronic absorption spectra) and found to increase rapidly below $n = 15$ or so, finally converging toward a very diffuse ($R \sim 30$ Å), dipole bound state [20,21] at the dimer. Since the usual increase in VDE with increasing cluster size arises from the larger solvation energy of the anion relative to neutral, these sequential shifts must become smaller for a diffuse charge since it is ineffectively solvated [22]. The extent of charge delocalization can also be determined using the photodetachment cross-section, which displays a rapid fall-off when the De Broglie wavelength of the outgoing electron is much smaller than the orbital describing the excess electron [19,23,24]. Bailey and Johnson used saturated photoelectron spectroscopy [10] to independently measure the detachment cross-sections of the $n = 6$ and 7 isomers, and established that isomer I has a more diffuse excess electron than that in II, and also that the photoelectron spectra from I display less activity in the free OH stretch. Thus, we have a self-consistent picture emerging where we trace the different VDE versus $n^{-1/3}$ slopes for the two isomers to the diffuse nature of the excess electron in the small clusters.

4.2. Isomers: rearrangements and the VDEs

The ubiquitous presence of isomers in the intermediate size range suggests that the clusters suffer significant rearrangement upon electron attachment. Some aspects of the intramolecular rearrangements have been reported previously for isomer II. In the case of the hexamer, for example, the dramatically different IR spectrum of the anion [25,26] relative to that of the neutral [27] (in the OH stretching region), and the presence of H_2O vibrational activity in the photoelectron spectrum [2–4], both point to significant intramolecular distortions (involving both stretching and bending modes) in isomer II. On the other hand, isomer I does not display vibrational fine structure in the PES envelope; unfortunately, the IR spectrum of I could not be measured since the vibrational features are broadened beyond recognition due to strong vibrational autodetachment in this weakly bound species.

Since form I has a more diffuse charge and less intramolecular distortion than II, it seems reasonable to hypothesize that I has the lower VDE because it has not relaxed to a more stable form of the anion (presumed to be II), and therefore form I has a morphology closer to that of the neutral. In this picture, we regard isomer (I) as an intermediate on the rearrangement path:

$$e^- + W_n \rightarrow W_n^- (I)^* \rightarrow W_n^- (II). \qquad (2)$$
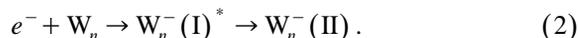
The larger VDE of form II can obviously result from two effects: the increased intrinsic stability of the anion (i.e., adiabatic EA) and/or the increased potential energy induced in the neutral upon photodetachment, arising from more extensive distortion of the anion. A key unresolved question is the adiabatic binding energies of the two isomers, and the nature of the barriers which separate them. Since we know that form II is more distorted than I and also has a more localized electron cloud, it makes sense to seek an explanation of the photoelectron band locations in terms of this known distortion before invoking changes in the EA. Moreover, since both isomers often co-exist in the ensemble, we assume that these minima lie at similar energies on the anionic surface. If so, the differences in VDEs arise from distortion; a similar situation was found [28–30] in the $(CO_2)_n^-$

clusters, where two isomers [corresponding to $CO_2^- \cdot (CO_2)_{n-1}$ and $C_2O_4^- \cdot (CO_2)_{n-2}$] lie very close in energy on the anionic surface, but are readily distinguished (even though they interconvert on the timescale of the laser pulse! [28]) using photoelectron spectroscopy. In that case, the isomers have quite different VDE values because much more potential energy is imparted to the $(CO_2)_n$ neutral cluster (in the CO_2 bending coordinate) upon photodetachment of the $C_2O_4^-$ dimer core than occurs in detachment from the CO_2^- monomer core. It seems reasonable to adopt an analogous picture for W_n^-, where the two anionic isomers lie close in energy, while the photoelectron spectra are distinguishable because of the different potential energy imparted to the neutrals upon photodetachment.

In this context, the non-monotonic variation in VDE of form I, and its more diffuse charge cloud can be rationalized in the context of its similarity to the parent neutral network. These networks display dramatic, discontinuous morphology changes [31–34] (i.e., cyclic pentamer, caged hexamer, and cubic octamer), and such species tend to have low dipole moments and should lead to diffuse excess electron states with little intramolecular distortion. As the network deforms to accommodate and localize the excess electron, however, the clusters apparently relax to analogous binding motifs in the homologous series II, which evolve monotonically into the continuous distribution for $n \geqslant 11$. Since isomer II displays a pronounced intramolecular distortion, we anticipate that it also suffers rearrangement of the soft modes, leading to a change in the water network. In other words, the energetics of form II can be viewed as trade off where increased binding to the electron compensates the increased distortion in the neutral framework. Upon photodetachment, this distortion dominates the location of the photoelectron band until the electron becomes localized in the $n = 10–15$ range, after which the solvation occurs as in a 'normal' negative ion.

What is the nature of this rearrangement in isomer II? At very small size, it is likely that cyclic structures (like that of the trimer) are opened into chains upon addition of the electron, such was recently observed in the $(HF)_n^-$ clusters [35]. Perhaps it is not accidental that the shift between the VDE of forms I and II is typically about 0.25 eV, close to the dissociation energy of a single hydrogen bond. The situation for rearrangement of the three-dimensional frameworks is not so clear; perhaps isomer II results from a local rearrangement of a few water molecules to a common binding motif, such as the 'tweezers' suggested by Kim et al. [9].

4.3. No obvious correlation between PES spectra and the electron attachment process

Since the VDEs of species I is size-specific, one is tempted to seek a correlation between this value and the highly size-specific electron attachment propensity (i.e., magic numbers in the parent distribution). Unfortunately, there is no obvious connection between the VDE (I) value and the intensity of the corresponding parent ion. For example, the VDE values of $n = 8$ and 10 bracket that of $n = 7$, while both of the former are very weak parents (by $20 \times$ or more) relative to $n = 7$. Moreover, the intensity of a parent peak is not simply related to the presence of isomers, since both $n = 8$ and 9 are weak parents while $n = 8$ has a dominant I form and $n = 9$ is almost exclusively II. Thus, it appears that the attachment cross-section is determined by subtleties of the nascent, transient negative ion, W_n^{-*}:

$$e^- + W_n \rightleftharpoons W_n^{-*} \rightarrow W_n^- \tag{3}$$

which must distort in order to trap the electron via a Born–Oppenheimer breakdown process. This distortion presumably involves the low frequency modes of the neutral network, which we anticipate will be high cluster size-specific, especially at small sizes where the clusters adopt robust networked morphologies. We note that form I becomes insignificant at the onset of the continuous distribution above $n = 11$, and it is likely that these are correlated effects. One can imagine, for example, that for $n = 8–10$, the barrier to rearrangement is near or above the neutral surface so that autodetachment quenches the anion intensity. The increase in intensity at $n = 11$ could then result if the barrier falls below the neutral at this size, enabling efficient anion formation into form II, which eventually completely overwhelms the population trapped in form I.

5. Conclusion

Photoelectron spectroscopy of the small W_n^- clusters reveals that, despite the dramatic size dependence of their formation propensity, the anions possess one isomeric form which evolves from the species formed continuously starting at $n = 11$. While continuously evolving, however, this isomer displays a change in character below $n = 11$, as evidenced by a break in the VDE versus $n^{-1/3}$ plot. The dramatic decrease in sequential solvation is consistent with the previous observation that the excess electron becomes more diffuse at the smaller cluster sizes. The VDE of the low binding energy isomer does not monotonically evolve with increasing cluster size, and the distribution of the two isomers is not simply related to the 'magic numbers' which appear in the parent cluster ion distribution.

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