

Low temperature photoelectron spectra of water cluster anions

Lei Ma,^{1,2} Kiran Majer,¹ Fabien Chirof,¹ and Bernd von Issendorff^{1,a)}

¹Fakultät für Physik, Universität Freiburg, Hermann-Herder-Straße 3, 79104 Freiburg, Germany

²The Department of Physics, Nanjing University, 210093 Nanjing, China

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Photoelectron spectra of cold (10 K) size selected water cluster anions $(\text{H}_2\text{O})_n^-$ and $(\text{D}_2\text{O})_n^-$ have been measured in the size range $n=20-120$. A new isomer with a higher binding energy than the so-called isomer I has been identified, which appears in the size range $n=25-30$ and for $(\text{H}_2\text{O})_n^-$ becomes dominant at $n=46$. Magic numbers observed in the mass spectra of the cluster anions provide evidence that this new isomer class consists of clusters with an internal electron. © 2009 American Institute of Physics. [doi:10.1063/1.3245859]

I. INTRODUCTION

Water cluster anions have been intensively investigated in the last decades, as a better understanding of the properties of the solvated electron at a microscopic level could lead to important insights into radiative damage processes or other charge induced chemical reactions.¹ Until now, however, it is not clear at what cluster size an electron is actually solvated by the water cluster, i.e., at what size it is located within a closed hydration shell. How the electron is bound to a water cluster has therefore been one of the central questions of the research ever since water cluster anions were discovered.² Despite a huge experimental and theoretical effort this question is still not answered. Photoelectron spectroscopy (PES) on water cluster anions³⁻⁸ has shown that at least three different classes of isomers with different vertical detachment energies (VDE) exist, which are usually labeled as isomers I, II, and III with decreasing VDE (here and in the following the term “isomer” is used in the sense of “isomer class,” describing clusters with related, but not necessarily identical structures⁹). For most cluster sizes larger than roughly $n=20$ the isomers II and III are metastable species, which can only be produced by the attachment of low energy electrons to cold neutral water clusters.⁴ Of the three isomers only isomer I exhibits the dependence of the VDE on cluster size, which one would expect from a classical estimate of the potential energy of a charge inside a dielectric sphere;¹⁰ for the isomers II and III the size dependence is weaker.⁷ Time resolved PES additionally showed that the relaxation time of the attached electron in its first excited state in isomer I clusters smoothly converges to the value for the bulk solvated electron with increasing size, while isomer II clusters exhibit much larger relaxation times with a negligible size dependence.⁷ These results seemed to indicate that in the isomers II and III the electron resides in a surface state, while it is bound internally in isomer I. Unfortunately the situation is more complex. First of all the size dependence of the VDE does not really yield specific information about the location of the electron. It has been shown that an internal state and a *localized* surface state can exhibit practically the same size

dependence of the VDE.¹⁰ Indeed the increase in the VDE of an iodine anion in a water cluster exhibits exactly the size dependence expected for a charge inside a dielectric sphere,¹¹ although in the size range studied the iodine anion probably resides on the surface of the water cluster.¹² Relaxation times of excited states are not very decisive, either. They depend on the difference between the optimal geometric structure of the cluster in the ground and the excited state of the electron; so if a surface state leads to a strong reorganization of the water molecule network, it can in principle exhibit relaxation times very similar to that of internal states. However most importantly infrared spectroscopy on water cluster anions has shown that clusters consisting mainly of isomer I structures exhibit vibrational features related to the presence of a double acceptor (AA) water molecule.¹³⁻¹⁵ Such a AA configuration can only be formed at the cluster surface, with two unbound hydrogen atoms directed into the negative charge cloud of a surface bound electron, indicating that at least for smaller sizes in isomer I the electron is in a surface state as well. This means that for larger sizes either the electron in isomer I clusters will get gradually more and more internalized, or that yet another isomer class will appear at some size. Without favoring one of these alternatives, Neumark⁷ has remarked that a distinct change of the size dependence of several cluster properties occurs in the size range $n=25-30$, indicating that possibly here the internalization sets in.

Theoretical calculations have contributed strongly to the understanding of water cluster anions. Very soon after the discovery of their existence Landman and co-workers¹⁶⁻¹⁸ showed that an attached electron can reside either in a surface or in an internal state. They estimated the cluster size where the internal state becomes energetically more favorable to be about $n=64$. Since then many groups have worked on this problem, but no agreement has been achieved. Estimates for the critical size range from $n=14$ (Ref. 19) to $n=200$.²⁰ The reason for this strong discrepancy is the high complexity of the problem. Already neutral water clusters are difficult to treat, as *ab initio* calculations of these systems are extremely expensive. Even with semiempirical models for the water-water interaction²¹⁻²⁴ global structural optimizations become very difficult for larger sizes because of which

^{a)}Electronic mail: bernd.von.issendorff@uni-freiburg.de.

the geometrical structures of neutral clusters beyond size 30 or so are not really known yet.^{25,26} The diffuse electron present in the cluster anion adds significantly to the complexity. Although enormous progress has been achieved in the understanding of very small sizes,^{27,28} as well as in the treatment of larger clusters,^{29–32} the question about the ground state structures of water cluster anions with several ten atoms is not fully answered yet.

In this report we present photoelectron spectra of cold annealed water cluster anions, which show that in the size range $n=25–30$ a new feature appears, indicating that here either a new geometrical structure is formed or that a specific vibrational excitation becomes more probable. Following the approach of Bowen and co-workers,⁵ we have measured spectra of both water and heavy water clusters, in order to distinguish between these two effects. The analysis shows that the new feature indeed can be attributed to a new isomer. In the following we will briefly describe the experiment, then present the measured results and their evaluation, and finally discuss the nature of the newly found isomer with the help of magic numbers observed in the mass spectra.

II. EXPERIMENT

The water cluster anions are produced in a gas aggregation source. Inside a liquid nitrogen cooled 100 mm diameter aggregation tube water vapor is injected into a stream of helium with a pressure of about 0.7 mbar, where neutral water clusters are formed. About 200 mm downstream from the water source and close to the exit aperture of the aggregation tube the water clusters get negatively charged by a pulsed gas discharge, which is ignited by applying a short high voltage pulse (about 1000 V, 10 μ s) to an isolated ring of stainless steel wire (diameter 60 mm). The charged clusters leaving through the exit aperture are guided by a radio frequency (rf) hexapole ion guide and a static quadrupole deflector over a distance of about 40 cm into a rf 12-pole trap attached to a cold head, where they are stored. The design of the trap is very similar to that of the 22-pole trap developed by Gerlich.³³ Inside the trap, which is cooled to a temperature of 10 K, the clusters thermalize by collisions with helium buffer gas with a pressure of about 10^{-3} mbar. Small fractions of the total number of clusters stored in the trap are extracted by pulsing the trap exit aperture; this allows thermalization times of more than 100 ms although the experiment is run at a repetition rate of 100 Hz. Note that the clusters undergo several collisions with room temperature helium atoms during the passage through the hexapole ion guide; here they are most probably heated to a temperature close to or above their evaporative ensemble temperature, that is above their melting points.³⁴ This should strongly reduce the presence of metastable structures in the beam. The extracted cluster ion packages are inserted into a time-of-flight mass spectrometer, where a given size is selected, decelerated, and injected into the interaction region of a magnetic bottle type photoelectron spectrometer. Here they are irradiated by a laser pulse from a XeCl excimer laser (photon energy 4.02 eV), and the time-of-flight distribution of the detached electrons is recorded, typically averaging over

30 000 shots. The photoelectron spectrometer has been calibrated by measuring the known spectrum of Pt^- , which leads to a systematic error of the determined binding energies of less than 30 meV.

III. RESULTS

Figure 1 shows examples of the PES obtained for $(\text{H}_2\text{O})_n^-$ and $(\text{D}_2\text{O})_n^-$ clusters. The results are very similar to those of Coe *et al.*⁵ and Verlet *et al.*⁴ In all spectra a broad hump is visible, which based on the earlier work indicates photodetachment from clusters belonging to isomer class I. Features at lower binding energies, which would hint at the presence of isomers II or III, do not appear in most of the spectra. This underlines the observation by Verlet *et al.*⁴ that in this size range isomers II and III are metastable structures. Only for a small number of sizes ($n=21, 25, 26, 51,$ and 53) a peak assignable to isomer II is clearly visible in the spectra. For these sizes isomer II is obviously close to energetically degenerate with the dominant isomer I.

Further inspection shows that the broad hump visible in all spectra actually consists of more than one peak. At size $n=25$ a shoulder on the high energy side of the main peak is clearly present in both the water and the heavy water cluster spectra. It gets more intense with size, until it becomes dominant at size $n=46$ for water and $n=49$ for heavy water clusters. At size $n=49$ for water and $n=52$ for heavy water clusters again a shoulder develops at the high energy side of the now dominant peak; for the larger sizes therefore at least three peaks are visible, which is most clearly seen in the case of $(\text{H}_2\text{O})_{52}^-$. For the sizes $n \geq 60$ unfortunately no clear details can be distinguished anymore. While the broad hump at size $n=60$ still shows a rather triangular shape, which indicates that it consists of several peaks, for larger sizes the profile converges more and more to a single, slightly asymmetric peak.

Two additional observations can be directly made. While for most of the size range studied the spectra develop rather smoothly with size, in the range $n=48–58$ quite strong variations are visible, not only with respect to the intensity ratios of the peaks, but to their positions as well. This hints at a strong interplay between geometrical structure and the binding of the electron in this range. Second, as was seen already by Coe *et al.*,⁵ for a given size the relative intensities of lower binding energy peaks are always higher in the case of the heavy water clusters. This shows the influence of the zero point energy onto the relative energies of different isomers.

IV. FITTING THE SPECTRA

In order to give a more quantitative description of the evolution of the spectra with cluster size, the peak positions have to be determined. For this a simple fitting function is needed. It has been shown that the peaks in the photoelectron spectra of water cluster anions can be well fitted by Gaussian–Lorentzian (GL) functions.⁸

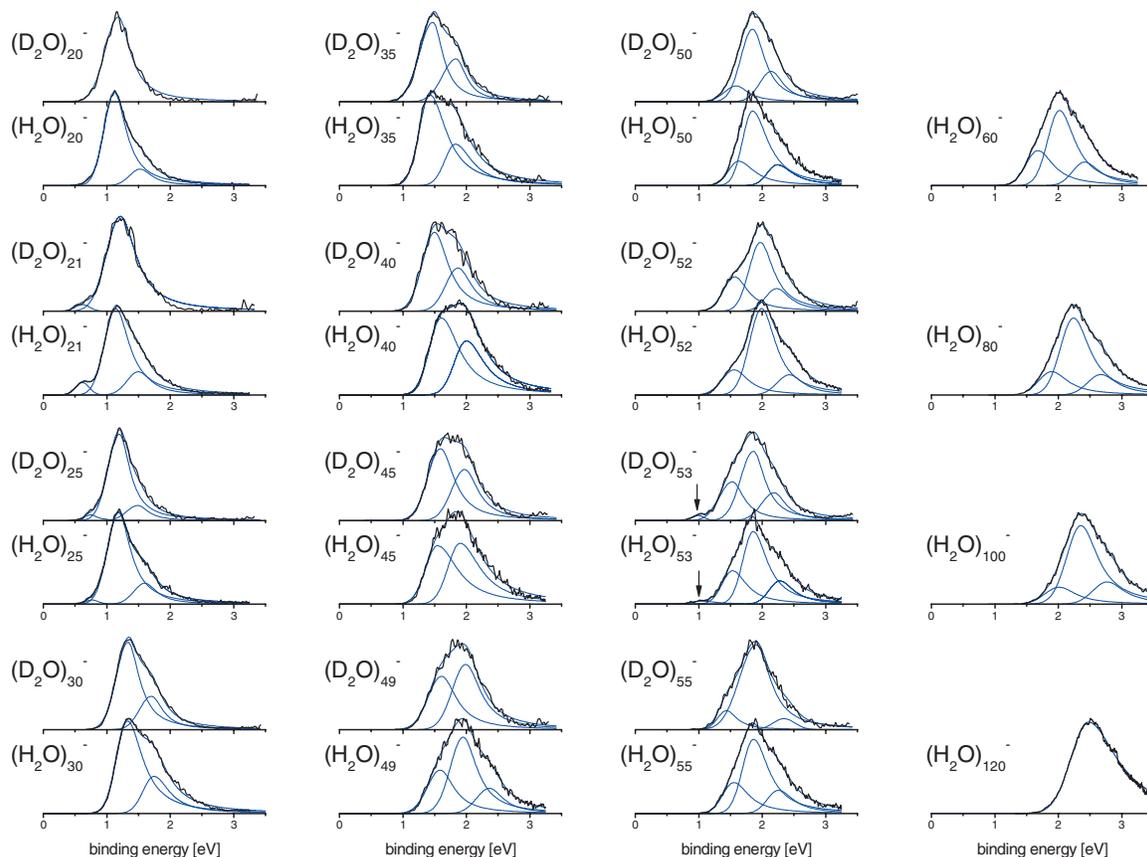


FIG. 1. Photoelectron spectra of cold ($T \approx 10$ K) water cluster anions $(\text{H}_2\text{O})_n^-$ and $(\text{D}_2\text{O})_n^-$, measured at a photon energy of 4.02 eV. The blue (gray) lines show fits with the fitting function given in Eq. (1). The arrows indicate the presence of Isomer II clusters for size $n=53$.

$$I(E) = \begin{cases} A \exp\left(-\frac{(E-E_0)^2}{2\sigma_1^2}\right) & E \leq E_0 \\ \frac{A}{\left(\frac{(E-E_0)^2}{\sigma_2^2} + 1\right)} & E > E_0 \end{cases} \quad (1)$$

Here E_0 is the peak position, σ_1 the width of the Gaussian (low binding energy) side, σ_2 the width of the Lorentzian (high binding energy) tail, and A the maximum amplitude. In cases where several peaks appear to be present in the spectrum, a superposition of these GL functions was used for the fit. Although different isomers could well exhibit different widths, the same values of σ_1 and σ_2 were used to fit all peaks in a spectrum because the measured data simply do not allow to determine these values independently. Only for the low binding energy peak attributed to isomer II, which appears for a small number of sizes, a different fitting function was employed. Here a simple Gaussian with an independent width was used.

The results of the fits are presented in Fig. 2, where the positions of the peaks in the spectra are plotted as a function of the inverse cluster radius. Additionally shown are the results of Verlet *et al.*;⁴ their assignment of the peaks to the isomers I, II, and III is indicated. The overall agreement is very good, with the exception that instead of the single peak assigned to isomer I we now observe up to three peaks at this energy.

This is not a completely new observation: for the sizes

$n=2-30$ a peak on the high binding energy side of the isomer I peak has already been observed by Coe *et al.*⁵ Based on the fact that the offset energy of this peak to the main peak for water clusters is a factor of $\sqrt{2}$ larger than for heavy water clusters, they concluded that it is a vibrational feature, being due to an additional excitation of an OH stretch upon photodetachment. However, this vibrational peak, which can be clearly seen for the sizes $n=2-14$, becomes practically invisible at size $n=21$. The question arises whether the feature appearing at size $n=25$ at about the same energy has the same origin. We have therefore done the same evaluation as Coe *et al.*,⁵ plotting the ratio between the energy offsets for the water and the heavy water clusters as a function of size. The result is shown in Fig. 3. For $n=25$ the ratio between the offset energies is still about $\sqrt{2}$, hinting at a vibrational origin of the second peak; for larger sizes, however, the ratio rapidly converges to 1, indicating that here it is not a vibrational peak anymore. This gives strong evidence that in the size range $n=25-30$ a new cluster structure appears, which exhibits a VDE about 0.4 eV larger than the “normal” isomer I. In the following this new structure will be called isomer Ib, the former one isomer Ia.

This opens the possibility that the third peak observed, the high binding energy shoulder of the peak of isomer Ib appearing at about $n=49$, indicates yet another isomer class. Unfortunately in this size range the measured spectra are too broad to allow a precise determination of the peak positions. Especially in the case of the heavy water clusters, where the

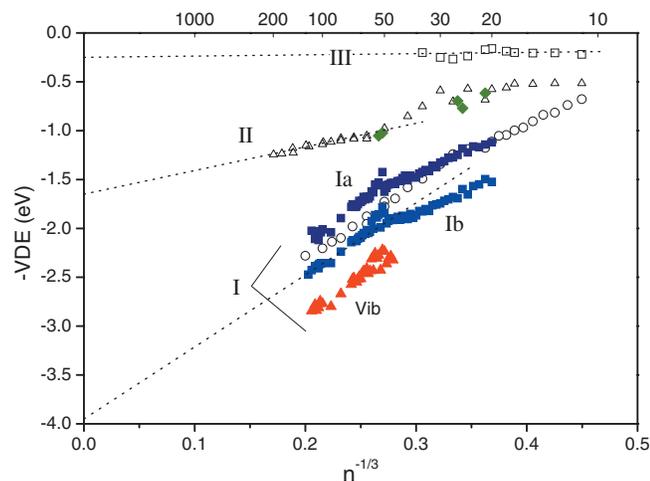


FIG. 2. Positions of the peaks observed in the photoelectron spectra of cold $(\text{H}_2\text{O})_n^-$ clusters as a function of the inverse cluster radius (filled symbols). The empty symbols give the results of Verlet *et al.* (Ref. 4); their assignment of the peaks to the Isomers I, II, and III is indicated. Our results show that the peak usually attributed to Isomer I in the size range studied consists of up to three peaks. Isomer II is only seen for a small number of sizes ($n=21, 25, 26, 51,$ and 53), which shows that for these sizes the Isomers I and II are energetically quasidegenerate. The dashed lines tentatively extrapolate the size dependencies of the detachment energies to larger sizes.

shoulder has a smaller intensity, the statistical error of the positions is too large to calculate a meaningful ratio of the energetic offsets. Nevertheless the fact that this feature is only clearly visible around size $n=52$, and vanishes again for larger sizes, gives some evidence that it is a vibrational excitation which occurs with a high probability only for certain cluster structures. We therefore tentatively assign this third peak to an OH stretch vibration excited upon the photodetachment from isomer Ib clusters.

V. DISCUSSION

It seems that with isomer Ib an up to now unknown structure has been found, which exhibits a higher VDE than isomer Ia, but the same size dependence of the VDE. Could this new isomer be the long sought-after cluster structure with an internal electron?

Some evidence that this really might be the case comes from the observation of magic numbers in the mass spectra. In Fig. 4 a mass spectrum of water cluster anions thermalized at a trap temperature of $T=121$ K is shown. This temperature is close to the evaporative ensemble temperature of water clusters in this size range,³⁴ which means that clusters with a slightly lower binding energy will evaporate a molecule on the timescale of the experiment, while clusters with a slightly enhanced one will not. At this temperature magic numbers are therefore most clearly seen. Obviously the sizes $n=50, 52, 54,$ and 56 are magic numbers, indicating enhanced stability. This is in an interesting contrast to earlier experiments on water cluster anions produced by low energy electron attachment to cold water clusters. In these experiments the magic numbers $n=51, 53, 55,$ and 57 were observed.^{35,36} As the low energy electron attachment does not heat a cluster sufficiently for the evaporation of a molecule, these numbers are the magic numbers of the neutral

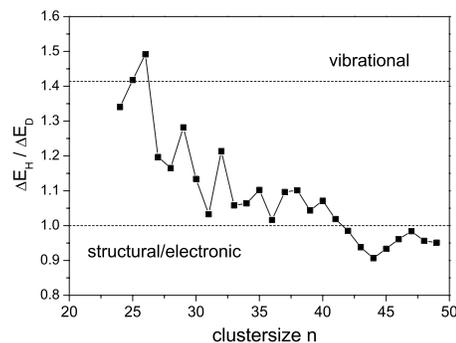


FIG. 3. Ratio of the energy offsets of the two main peaks in the spectra of $(\text{H}_2\text{O})_n^-$ and $(\text{D}_2\text{O})_n^-$, for $n=24-49$. If the second peak is a vibrational satellite of the first one, the offset gives the energy of the excited vibrational mode, which should change by a factor of $\sqrt{2}$ upon deuteration. If the second peak is due to the detachment of an electron from a different structural isomer, the peak positions for water and heavy water cluster should be close to identical. The results show that at least for sizes larger than $n \approx 30$ the latter is the case.

clusters. Exactly the same numbers appear as magic numbers for protonated water clusters $(\text{H}_2\text{O})_n\text{H}^+$.³⁷ In clusters where one of the water molecules has been replaced by a protonated ammonium molecule or a protonated amine group of an organic molecule, the ones with 50, 52, and 54 water molecules are most stable.^{37,38} It therefore seems that for water clusters with 51, 53, 55, and 57 molecules very stable structures exist, which even can tolerate the slight change in the interactions caused by the protonation of one of the water molecules or by the replacement of one of them by an analogous but different molecule. This makes it highly probable that also the magic sizes $n=50, 52, 54,$ and 56 we are observing for the negatively charged clusters adopt these structures, but here with one of the water molecules replaced by the electron. Indeed a possible location for an electron inside a water cluster is a tetraordinated cavity with a volume very close to that of a water molecule^{39,40} (the distance between the cavity center and the four neighboring oxygen

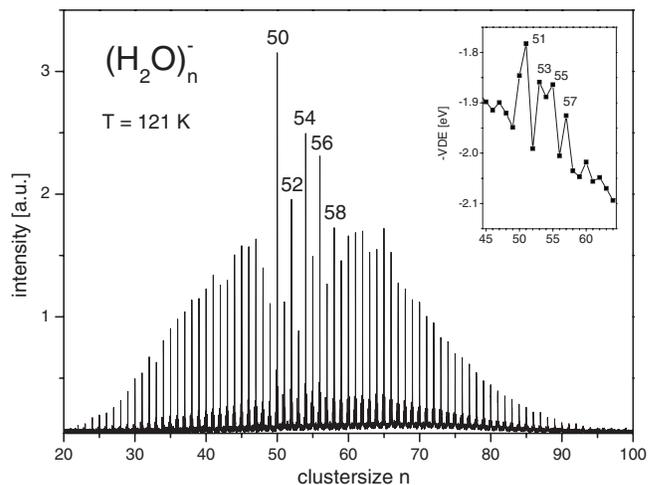


FIG. 4. Mass spectra of $(\text{H}_2\text{O})_n^-$ thermalized at a temperature of $T=121$ K. Magic sizes with increased intensity are observed, which indicates enhanced stability. The inset shows that the VDE of the dominant isomer for each of the clusters exhibits a strong size dependence exactly in the region where the magic numbers appear; this indicates a strong interplay between the geometrical structure and the strength of the bonding of the single electron.

atoms is close to a normal oxygen-oxygen distance in the water network). Replacing a water molecule inside the cluster by an electron could therefore leave the overall structure intact, and would require just a reshuffling of donating and accepting hydrogen bonds (which leads to a reduction of dangling hydrogen bonds on the surface).

The stability of the neutral clusters explains as well why the sizes $n=51$ and 53 are the only larger cluster where a peak at low binding energy can be seen, which indicates the presence of an isomer II structure: as the neutral clusters are very stable, the isomer with a weakly bound surface electron is isoenergetic to the isomers Ia and Ib, where the AA bonding motif or the formation of a cavity significantly perturbs the hydrogen bond network of the clusters. So although in the latter two isomers the electron is more strongly bound, the reorganization energy necessary obviously makes the isomers II and Ia/Ib quasidegenerate. This type of competition between an optimum hydrogen bond network and an optimum bonding of the electron is probably also the reason for the strong size dependence of the VDE for $n=49-58$.

One could argue that in principle the magic numbers in the mass spectrum could also be explained by a structure where a surface water molecule of the neutral cluster is replaced by an electron. It is, however, hard to believe that in such a case the majority of the electron wave function would stay in this rather small and half open cavity. Therefore the magic numbers observed provide evidence that around size $n=50$ in most of the clusters the electron is occupying an internal state. As in this size range isomer Ib is dominating, it seems that all structures of this isomer class have an internal electron. This would mean that the appearance of isomers with an internal electron sets in the size range $n=25-30$, in full agreement with the conclusion of Neumark.⁷

In principle this assignment should make it possible now to extrapolate the binding energy of the internal electron all the way to the bulk. Unfortunately this is not trivial, as the VDE of isomer Ib does not depend fully linearly on the inverse cluster radius in the size range studied. A naive linear extrapolation seems to indicate a bulk VDE close to 4 eV (Fig. 2), that is a higher value than assumed up to now.⁸ Due to the uncertainty of this extrapolation, however, this value is definitely not well founded, and much larger cluster sizes have to be studied before a final statement can be made.

VI. CONCLUSION

Photoelectron spectra have been recorded for water cluster anions from $n=20$ to 120 , thermalized at 10 K . Due to an intermediate heating of the clusters between production and thermalization metastable structures are strongly suppressed. Isomer II structures therefore only appear for certain cluster sizes, namely, for $n=21, 25, 26, 51,$ and 53 , which yields evidence that these sizes have an enhanced stability as neutral clusters. Isomer III clusters are not seen at all. In the size range $n=25-30$ a new isomer with a slightly higher VDE than isomer I appears, which becomes dominant at $n=46$. The magic numbers of the cluster anions observed in this size range give evidence that in this new isomer the electron resides in a cavity inside the cluster. If this assignment is

correct, it follows that a full internalization of the electron in a water cluster starts to become possible at about $n=25$, and gets energetically preferred at $n=46$.

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