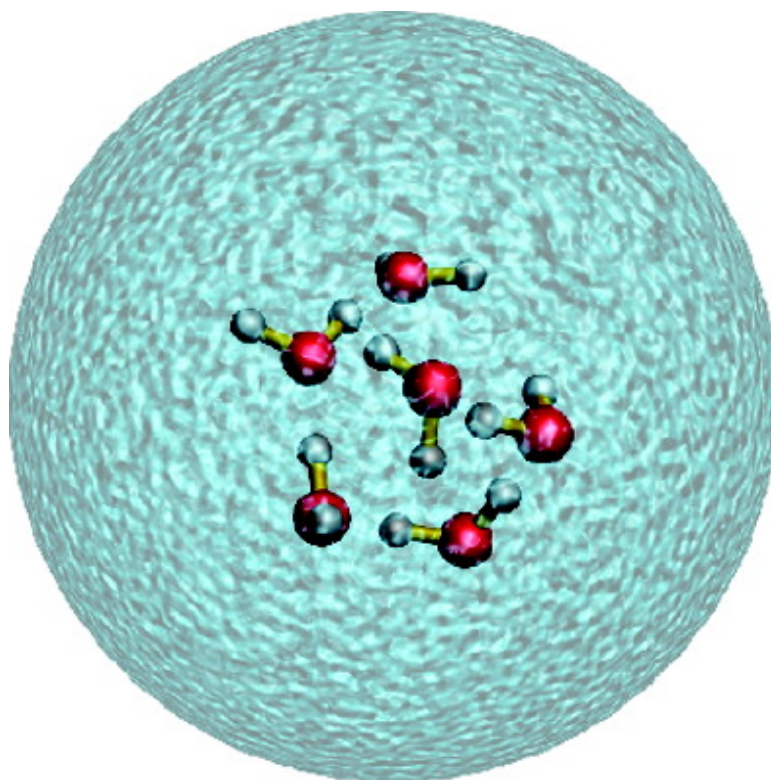


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Ultracold Water Cluster Anions

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Abstract: Attachment of free electrons to water clusters embedded in helium droplets leads to water-cluster anions $(\text{H}_2\text{O})_n^-$ and $(\text{D}_2\text{O})_n^-$ of size $n \geq 2$. Small water-cluster anions bind to up to 10 helium atoms, providing compelling evidence for the low temperature of these complexes, but the most abundant species are bare cluster anions. In contrast to previous experiments on bare water clusters, which showed very pronounced magic and anti-magic anion sizes below $n = 12$, the presently observed size distributions vary much more smoothly, and all sizes are easily observed. Noticeable differences are also observed in the stoichiometry of fragment anions formed upon dissociative electron attachment and the energy dependence of their yield. Spectroscopic characterization of these ultracold water-cluster anions promises to unravel the relevance of metastable configurations in experiments and the nature of the still controversial bonding sites for the excess electron in small water-cluster anions.

1. Introduction

The hydrated electron, discovered in 1962,¹ plays a crucial role in a variety of environments, including materials used for fission reactors, water droplets in the atmosphere, and living tissue exposed to ionizing radiation. It has been shown to facilitate electron-transfer reactions on water-covered TiO_2 surfaces and between proteins.²

Studies of water clusters containing an excess electron are aimed at unraveling structural details and the dynamics of the hydrated electron in bulk water. The situation is more complex in clusters because new reaction channels (electron detachment) play a role, a variety of additional bound states exist for the electron, and the cluster temperature is difficult to control. Even so, an analysis of spectral features and lifetimes as a function of cluster size provides valuable insight into the microscopic nature and dynamics of the hydrated electron.^{3–5}

Haberland and co-workers succeeded in forming $(\text{H}_2\text{O})_n^-$ for $n \geq 11$ by injecting electrons into high-density water vapor.⁶ Subsequently Echt and co-workers demonstrated that these anions could also be formed by attachment of low-energy

electrons to pre-existing clusters.⁷ Smaller anions are more difficult to form by free-electron attachment because their adiabatic electron affinities are smaller than the cluster dissociation energy (i.e., the activation energy for loss of a monomer); the temporary anion cannot be stabilized by evaporation of H_2O molecules.^{7,8} Very cold neutral precursors must be synthesized before small anions can be observed, for example by expanding water vapor from high stagnation pressures or in seeded expansions.^{9–11}

Several groups have reported spectroscopic studies of water cluster anions. Particularly valuable are electronic absorption spectra,¹² vibrational (IR) absorption spectra,^{13,14} photoelectron spectra,³ and time-resolved femtosecond photoelectron spectra.^{5,15,16} Photoelectron spectra provide information on the vertical detachment energies (VDE). Three groups of peaks have been identified. Each group shows an approximately linear depen-

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dence of the VDE on $n^{-1/3}$, that is, on the inverse cluster radius evaluated in a continuum approximation. The first group, with the lowest VDE, is observed in the range of $2 \leq n \leq 35$. This group has been attributed to dipole-bound anions with diffuse electron clouds.^{3,15,17} The second group appears for $6 \leq n \leq 16$ under standard expansion conditions and up to $n = 200$ for cold expansions; it has been attributed to localized surface states.¹⁸ The third group, with the highest VDE, is observed for $n \geq 11$. It is favored in H₂O as opposed to D₂O clusters and by expansion conditions producing warmer clusters. It has been attributed to an interior or cavity state or bulk embryons because its VDE extrapolates to the bulk value.³

The interpretation of the experimental data in terms of dipole-bound, surface, and bulk states has been inspired by the pioneering path-integral molecular dynamics simulations by Barnett et al. which predict a transition from surface-to-internal localization between $n = 32$ and 64 .¹⁹ The interpretation of the experimental spectra has been challenged in recent theoretical work, which suggests that interior states are not thermally populated below $n \approx 100$.^{20,21} There are several contentious issues in the spirited debate that has ensued,^{22,23} including the numerical accuracy of calculated VDE,²⁴ the existence of several rather than just one bound surface states,²⁵ the lack of correlation between cluster energy and VDE,²⁶ the difficulties of identifying the most stable anion structures in theoretical work,^{27,28} the possibility that cluster anions formed by attachment to cold, pre-existing clusters fail to relax into the most stable structures,^{20,26,29,30} and the effect of cluster temperature.^{21,25}

Novel experimental approaches are needed before a coherent model of excess electrons in water clusters can be developed. In the present work, we demonstrate the formation of water cluster anions embedded in helium nanodroplets. These clusters have a well-defined temperature of 0.37 K, which is 2–3 orders of magnitude below the values in previous studies.³¹ These ultracold cluster anions may be even less likely to be in their ground-state configurations; even their neutral precursors possibly remain in configurations far from equilibrium.^{32,33} However, spectroscopic studies of these clusters will provide new insight, because it would be fairly straightforward to anneal the

clusters without increasing the spectral congestion, because the annealed cluster would quickly return to 0.37 K via helium evaporation from the droplet. Here, we report on the energy dependence of the yield of small anions that are formed by electron attachment to unannealed water clusters embedded in helium nanodroplets. One surprising observation is a cluster anion-size distribution that is much more statistical than the ones previously reported. Although magic and anti-magic clusters are still discernible, the features are much less pronounced. The novel growth scheme employed in the current work helps identify the factors that lead to magic numbers in spectra of water cluster anions.

2. Experimental Section

Details of the experimental setup and data analysis have been published elsewhere.³⁴ Neutral helium nanodroplets are produced by expanding helium from a pressure of 15 bar through a 5 μ m nozzle, cooled to 9.6 K by a closed-cycle refrigerator, into vacuum. These conditions are between sub- and supercritical;³⁵ the average number of atoms per droplet is expected to be a few times 10^4 .³⁶ The pressure in the expansion chamber is maintained below 0.01 Pa by a 1200 L/s turbomolecular pump.

The resulting supersonic beam is skimmed by a 0.8 mm conical skimmer, located 5 mm downstream. The skimmed beam enters a pickup cell that is 10 cm long and 5 cm wide, with entrance and exit holes of 5 mm in diameter. Water vapor enters the cell from an external oven. In the current study, we use heavy water because the various product ions that could possibly be formed by dissociative attachment can be more easily identified. The cell is kept at 373 K by resistive heaters in order to prevent water condensation on the walls. After the pickup cell, the cluster beam enters the ionization chamber of a modified Varian MAT CH5-DF two-sector-field mass spectrometer. The pressure in the mass spectrometer is better than 8×10^{-6} Pa; in the ion source, it is approximately 10^{-4} Pa. The energy resolution of the electron beam is 1 eV; resonances can be determined with an accuracy of a few tenths of an electronvolt.

3. Results

3.1. Mass Spectra. A mass spectrum of anions formed by attachment of 2 eV electrons to clusters formed with a water vapor pressure of 8 nbar in the pickup cell is shown in the lower part of Figure 1. Peaks that are due to pure $(D_2O)_n^-$ are marked by dots. Several impurity peaks occur in the low-mass range, in particular at 125 and 193 u; they result from previous experiments with thymine and other biomolecules. The abundance distribution is reminiscent of distributions obtained by attachment to bare water clusters formed in seeded expansions.⁹ In particular, the dimer and hexamer form local maxima. However, we also see relatively strong signals for cluster sizes $n = 3, 4, 5, 8, 9$, and 10, which had been reported missing or barely observable.^{9,10,37–39}

The spectrum in the upper part of Figure 1 was recorded with an increased water vapor of 15 nbar, giving rise to larger water

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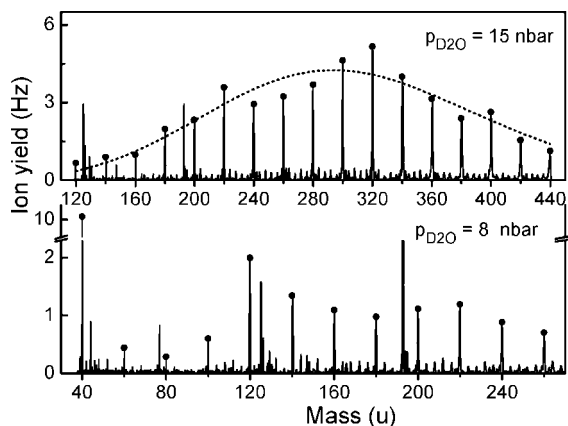


Figure 1. Mass spectra of anions formed by attachment of low-energy electrons to $(\text{D}_2\text{O})_n$ clusters embedded in helium droplets, grown with high and low water-vapor pressures (top and bottom, respectively). Dots mark mass peaks at multiples of 20 u. The dashed line shows a fitted Poisson distribution with a size-dependent coagulation coefficient.

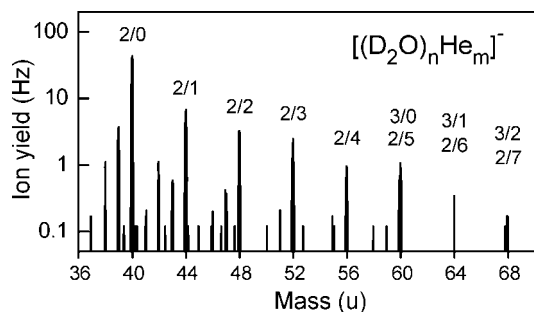


Figure 2. Mass spectrum acquired at low water-vapor pressure showing the presence of mixed $(\text{D}_2\text{O})_n\text{He}_m^-$ cluster anions.

clusters. The distribution of neutral clusters formed in helium droplets has been shown to follow a modified Poisson distribution $P_n(n_{\text{av}})$; the average size n_{av} depends on the coagulation coefficient γ which increases approximately linearly with the size n .⁴⁰ We have fitted such a distribution to our data. The result is shown as a dashed line; it matches the recorded spectrum quite well. Note that there are no strong abundance anomalies in this spectrum, which covers sizes $6 \leq n \leq 22$.

Figure 2 shows a mass spectrum recorded with a water vapor of only 3 nbar and 2 eV electron energy. Water cluster anions containing several helium atoms are observed. The smoothly decreasing abundance distribution suggests that up to 7 helium atoms are attached to $(\text{H}_2\text{O})_2^-$. However, we cannot exclude that the mass peaks at 64 and 68 u are due to the water trimer with one or two helium atoms attached. Close inspection of the spectra in Figure 1 reveals the presence of mixed $(\text{H}_2\text{O})_n\text{He}_m^-$ anions for n as large as 21.

3.2. Energy Scans. Figure 3 displays the yield of anions in the mass range $36 \leq m \leq 44$ u as a function of the electron energy. The energy scale was calibrated with the 0 eV resonance of SF_6^- . The dimer ion at 40 u shows a strong resonance at low energies with a maximum at 1.5 eV and another distinct resonance at 22.5 eV with a satellite peak at 25.4 eV. Another feature is seen at higher energies. We have recorded this range with improved statistics (see insert); the shape of this feature is similar to the one at 22.5 and 25.4 eV but shifted upward by 20.9 eV.

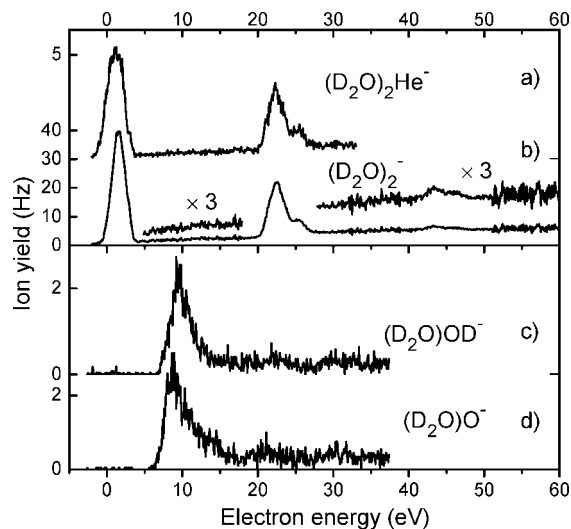


Figure 3. Energy dependence of the yield of $(\text{D}_2\text{O})_2\text{He}^-$, $(\text{D}_2\text{O})_2^-$, and its fragments.

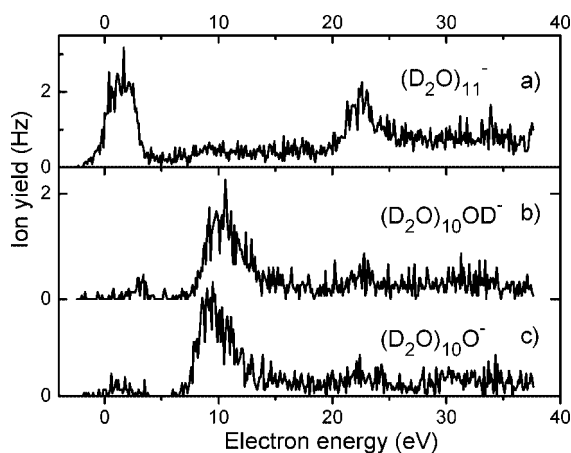


Figure 4. Energy dependence of the yield of $(\text{D}_2\text{O})_{11}^-$ and its fragments.

The anion at 44 u, attributed to $(\text{D}_2\text{O})_2\text{He}^-$, shows the same features as the bare dimer ion within the statistical uncertainty. In contrast, the anions at 36 u ($(\text{D}_2\text{O})\text{O}^-$) and 38 u ($(\text{D}_2\text{O})\text{OD}^-$) show only one resonance each, at 8.8 and 9.7 eV, respectively. These resonances are an order of magnitude weaker than the low-energy resonance of $(\text{D}_2\text{O})_2^-$. The anion yields of the 11-mer and its fragments (Figure 4) and of the trimer and hexamer anions and their fragments (not shown) follow very similar patterns.

4. Discussion

4.1. Energy Scans. We begin with a review of previous work which is limited to free, isolated water clusters and water monomers. We will not differentiate between H_2O and D_2O . Isotope effects have been observed, especially for electron attachment to water monomers,⁴¹ but the differences are not significant enough to warrant a separate discussion.

The formation of $(\text{H}_2\text{O})_n^-$ anions by attachment of free electrons to bare water clusters, with an energy resolution similar

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to ours, has been reported for sizes $n \geq 11$ ($n \geq 12$ for $(D_2O)_n^-$).^{7,42,43} Another study performed at much higher resolution (1.2 meV) included smaller clusters ($n = 2, 6,$ and 7) but was restricted to energies below 80 meV.³⁸ The small clusters exhibited very narrow 0 eV resonances; larger clusters exhibited resonances around 0.05 eV.³⁸ In low-resolution work, these resonances appear as 0 eV resonances.

No intact water cluster anions were detected at elevated electron energies.^{7,42,44} Anions of the stoichiometry $(D_2O)_{n-1}OD^-$ exhibit a resonance at 7 eV and a shoulder at 9 eV for sizes $2 \leq n \leq 50$.^{7,44} A very weak signal of $(D_2O)_{n-1}O^-$ was observed at 7 eV; Klots and Compton have studied its energy dependence for small n .^{7,44} The reported yield of $(D_2O)_{n-1}OD^-$ anions has an energy dependence similar to that of the total anion yield from (undeuterated) water molecules.⁴¹ However, the total anion yield from molecules is predominantly due to H^- . O^- contributes only a few percent, and its energy dependence differs substantially from that of H^- . OH^- contributes even less to the total yield.

In summary, the key features of our results, compared to those reported in the literature for bare water clusters, are the following.

(a) In helium, the intensity of $(D_2O)_{n-1}O^-$ is strongly enhanced relative to $(D_2O)_{n-1}OD^-$.

(b) Below 20 eV, bare and embedded clusters yield qualitatively similar spectra for $(D_2O)_n^-$ and $(D_2O)_{n-1}OD^-$ anions, except for an upward shift of the resonances by 1.5 eV in the helium matrix.

(c) Additional resonances are observed in helium for $(D_2O)_n^-$, shifted by 21.0 and 41.9 eV (with an accuracy of a few tenths of an eV) relative to the low-energy resonance.

Concerning observation (a), frictional and caging effects in helium will tend to suppress fragmentation.⁴⁵ It is not apparent to us, though, how these effects could enhance the $(D_2O)_{n-1}O^-$ yield. Still, fragment ions are of little relevance to our discussion on the hydrated electron; we will not consider them any further.

The well-known energetics of excess electrons in helium nanodroplets provides a rationale for findings (b) and (c). The bottom of the conduction band in bulk helium is at $V_0 = 1.06$ eV above the vacuum level and slightly less in droplets.⁴⁶ V_0 constitutes an energy threshold for electron capture, in close agreement with an observed threshold value of 1.29 eV.⁴⁷ The capture cross-section reaches a maximum at ~ 2 eV for undoped droplets with a small dependence on size.⁴⁷ Likewise, attachment to helium droplets doped with one or more thymine molecules gives rise to a resonance at 2 eV in the yield of thymine (cluster) anions.⁴⁸ In the present work, we report a resonance at 1.5 eV. This is in reasonable agreement with the 2 eV literature value, given the relatively poor energy resolution in the present work and the difficulty of accurately calibrating the energy scale at low energies.

Inside helium, the electron will thermalize within picoseconds and localize in a bubble of 17 Å radius (bulk value, slightly less in droplets).⁴⁶ For bulk helium, the bubble energy is ~ 0.1 eV above the vacuum level; the energy increases with decreasing droplet size.⁴⁶ Thus, a negatively charged helium droplet is not stable with respect to autodetachment; its lifetime is 0.06 s.⁴⁰ If a molecule or cluster with a large positive electron affinity is embedded in the droplet, the electron will localize at the impurity once the bubble comes in contact with the impurity, and the anion will be stable with respect to autodetachment.⁴⁰ The energy released in the reactions (bubble formation and relocalization of the electron at the impurity) can be dissipated by evaporation of helium atoms at a cost of 0.616 meV per atom (bulk value), thus quickly cooling the matrix back to 0.37 K where it is superfluid. The net result would be a relatively small decrease in the size of the helium droplet. Why, then, are the water anions detected in the present study dressed by few, if any, helium atoms? Photodissociation studies of doped helium droplets reveal the existence of another process, namely the ejection of the excited molecule from the droplet.⁴⁹ Even though this may be a minor channel, it is the only channel that our spectrometer with its limited mass range is able to register.

The resonances in the $(D_2O)_n^-$ signal at 22.5 and 25.4 eV can be attributed to electronic excitation of an helium atom in the droplet by the hot electron that is subsequently trapped at the water cluster. The anion yield of the embedded molecule will thus reflect the excitation spectrum of the medium. This kind of autoscavenging process has been observed before in, for example, clusters of SF_6 and Xe.⁵⁰ The luminescence yield of helium droplets shows two prominent bands at 21.02 and 21.55 eV, which are assigned to transitions into $2s^1 S$ and $2p^1 P$, and a band above 23.0 eV assigned to excitations into $3p$ and $4p$ states.⁵¹ In electron attachment spectra, these excitations are blue-shifted by V_0 . Henne and Toennies have measured electron capture cross-sections of pure helium clusters; for the smallest clusters (size $n = 93\ 000$) they observed resonances at 21.93, 22.92 and 25.58 eV.⁴⁷ These values agree well with ours, given that the first two peaks merge under lower energy resolution. For larger bare helium clusters, the resonances shift upward by a few tenths of an electronvolt, and the high-energy feature is barely discernible.⁴⁷

The resonance in the anion yield at 41.9 eV is interpreted as double excitation of the helium droplet by the electron, with subsequent attachment of the thermalized electron to the water cluster.

4.2. Cluster Size Distributions. A remarkable feature in our mass spectra is the relatively smooth variation of cluster abundance with size. In previous work, anions containing 6, 7, 11, and $n \geq 15$ water molecules showed comparable abundances, whereas anions containing 12, 13, or 14 water molecules were significantly less intense, and those with 3, 4, 5, 8, 9, or 10 water molecules were difficult to detect.^{10,37–39} In contrast, Figure 1 shows a very smooth distribution for $n \geq 6$.

Concerning smaller sizes, only the dimer was readily observed, and $n = 4$ was not identified until Johnson and co-workers developed a special scheme in which water molecules are added to cluster anions that are complexed with argon atoms.³⁹ In this approach, thermal-electron detachment upon

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addition of a water molecule may be suppressed even if the condensation energy exceeds the electron affinity of the newly formed complex, because evaporation of argon atoms offers a more efficient cooling channel. Even in this growth scheme, though, the water tetramer is an order of magnitude less intense than the trimer. In contrast, in our spectra, the tetramer is only a factor two less abundant.

Why do our spectra not show the pronounced abundance differences of previously reported mass spectra? What is the origin of those differences? In principle, there are at least three possible reasons for the low abundance of, for example, the tetramer anion in previous experiments: (i) energetics or kinetics disfavors the formation of the neutral precursor; (ii) the tetramer features a particularly low adiabatic electron affinity (AEA), which results in a short lifetime of the anion; and (iii) the VDE of the tetramer in the configuration of the neutral precursor is particularly low.

Explanation (i) can be discarded. For example, the lowest energy forms of the trimer, tetramer, and pentamer have a ring structure; growth occurs readily by successive ring insertion, even at subkelvin temperatures.^{33,52} More generally, there is no reason why the abundance of the neutral tetramer should be low in beam experiments; the computed binding energy of small neutral water clusters do not show anomalies that would correlate with the anion abundances (see refs 53, 54, and references therein).

Explanation (ii) has been proposed by Lee and co-workers to explain the commonly observed abundance spectra.⁵⁴ Clearly, cluster anions would be more likely to undergo autodetachment, especially under expansion conditions favoring warm clusters, if the corresponding neutrals have low AEA. In fact, the computed AEA of most anti-magic clusters is negative (nonbinding).^{27,54} However, it is difficult to accurately calculate AEAs, because it is difficult to locate the ground-state configuration of the anion, and experimental values for the AEA are not available.

If the AEA of anti-magic clusters is, indeed, negative, their long-lived anions might be formed more readily by electron attachment to pre-existing clusters in nonequilibrium structures (explanation (iii)). Indeed, detailed comparisons of computed VDEs with photoelectron spectra have led to the conclusion that the anions probed experimentally are not the energetically lowest ones but the ones with high VDEs.^{26,30} VDEs of small clusters have been computed by several groups,^{26,29,30,55} but the large number of local minima on the potential energy surface makes it difficult to decide which structures are relevant in a comparison with experimental data. Herbert and Head-Gordon find that the neutral tetramer in its equilibrium configuration does not bind with an electron (in other words, its VDE is negative).²⁶ In this scenario, the poorly known height of energy barriers between the various configurations of the neutrals and the anions would also play a crucial role.

A tentative explanation for our rather smooth abundance spectra could then be the freezing-in of metastable water-cluster structures as they grow by successive monomer addition in the

ultracold helium matrix. Miller and co-workers have shown that structures grown in helium may differ from those obtained in gas-phase nucleation.³³ In particular, the presumably metastable cyclic structure was observed for the hexamer, whereas the tetramer and pentamer occurred in the same cyclic structures as in experiments at higher temperatures. Still, noncyclic structures may have gone undetected in their studies. As suggested by an anonymous referee, a fraction of the neutral water clusters could conceivably grow in linear structures that are so prevalent for HCN clusters.³² The large dipole moments of the chains, increasing with the cluster size n ,⁵⁶ would give rise to a positive AEA for all sizes. Another fraction of clusters, occurring in more conventional structures, would explain why the abundance spectra are not completely statistical. A different explanation would be that the yield of long-lived anions at these very low temperatures simply depends on the initial capture process, which does not directly depend on the size of the embedded cluster.

4.3. Annealing the Cluster Anions. It is quite likely that the water cluster anions in our study are formed in nonequilibrium configurations.⁵⁷ The growth mechanism of the neutral precursors is such that one cold molecule at a time is added to a cold cluster. Miller and co-workers have found that, under these conditions, small $(\text{HCN})_n$ are grown into metastable chain configurations; the heat of condensation released upon growth is removed so quickly by the matrix that the cluster does not rearrange into its cyclic equilibrium structure.³² In contrast, structural rearrangement does occur in the growth of water cluster.³³ The hexamer, in particular, is found to be cyclic, which implies that a water molecule can overcome the barrier toward insertion into the cyclic pentamer, or the barrier is so small that the hydrogen atoms tunnel through the barrier. On the other hand, the ring does not rearrange into the cage structure, which appears to be the ground-state structure,³³ although the exact energetic order of competing structures is still a matter of debate.⁵⁸

In the second step, when an electron is attached to the neutral cluster, the AEA is released. The ground-state structures of anions differ drastically from those of neutrals.^{26,59,60} The height of energy barriers between anion isomers are not known, not even for the extensively studied $(\text{H}_2\text{O})_6^-$.^{3,13,17,24,30,60,61} However, comparison of theoretical with experimental work suggests that nonequilibrium structures dominate previously reported photoelectron and IR spectra of water cluster anions.^{20,26,29,30} If anions formed under those conditions (estimated cluster temperatures ≈ 50 K for clusters solvated in argon and 150–200 K for bare clusters^{23,25,26}) fail to rearrange into their ground states, they will certainly fail to do so if they are embedded in helium.

In helium, however, it may be possible to anneal the cluster anions by photoexcitation. An intriguing aspect would be the low temperature to which the anions would return after the excitation pulse. In experiments on small isolated water cluster

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anions, IR irradiation leads to electron detachment and loss of specific isomers rather than annealing.⁶² In helium, electron detachment and dissociation are likely to be suppressed, although extremely fast transfer of vibrational energy into the helium bath may suppress annealing as well. In one of the few annealing experiments that we are aware of, Miller and co-workers have shown that the bent HF–HCN isomer embedded in helium can be annealed into the linear HCN–HF isomer by IR excitation. Whether annealing is a viable mechanism for water cluster anions remains to be seen.⁶³

5. Conclusion

In summary, we have succeeded in forming ultracold water cluster anions. One surprising observation is the relatively large yield of the tetramer and octamer anions (and a few other cluster sizes) that are exceedingly difficult to synthesize in experiments involving warmer water clusters. Although we cannot yet tell whether these features point to thermodynamic or kinetic factors

being responsible for the anti-magic nature of the tetramer and octamer in previous experiments, future work aimed at annealing clusters embedded in helium may lead to photoelectron and absorption spectra that provide a more detailed view of the structure of the hydrated electron in small water clusters.

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- (63) Concerning much larger systems, a molecular dynamics study by Rossky and co-workers reveals that an excess electron initially at the surface of bulk water will relax into the more stable interior state within 10 ps if the water is liquid (300 K), whereas it will not relax if the water is either in the form of ice or a supercooled liquid at 200 K.⁶⁴
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