

Ionization of Water Clusters is Mediated by Exciton Energy Transfer from Argon Clusters

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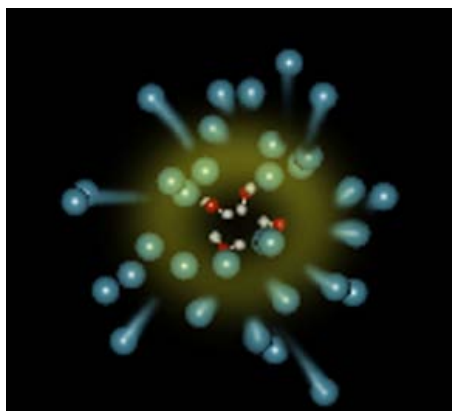
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Abstract- The exciton energy deposited in an argon cluster, (Ar_n , $n < 20$) using VUV radiation is transferred to softly ionize doped water clusters, $(\text{H}_2\text{O})_n$, $n=1-9$ leading to the formation of non-fragmented clusters. Following the initial excitation, electronic energy is channeled to ionize the doped water cluster while evaporating the Ar shell, allowing identification of fragmented and complete water cluster ions. Examination of the photoionization efficiency curve shows that cluster evaporation from excitons located above 12.6 eV are not enough to cool the energized water cluster ion, and leads to their dissociation to $(\text{H}_2\text{O})_{n-2}\text{H}^+$ (protonated) clusters.



Keywords: Excitons • Clusters • Energy transfer • Water • VUV • Ionization

The ionization of water clusters is of paramount interest in a number of fields spanning biology, chemistry and physics.¹⁻⁷ Understanding the changes in electronic structure that occur in these ionic clusters is critical to unveil their structure and function, and is important in fields as diverse as cloud nucleation in earth's atmosphere, radiation biology, and interstellar chemistry. From the brief summary of experimental studies on the ionization of water clusters discussed here, it is readily apparent that, while there is a great deal of information available on the dimer and isolated water molecules, very little is known about the larger clusters. Only rarely have non-protonated water clusters (here non-protonated is denotes $(\text{H}_2\text{O})_n^+$, while protonated is denoted by $((\text{H}_2\text{O})_n\text{H}^+)$, beyond the dimer been observed experimentally. Typically, even when one-photon soft-ionization methods are used, water clusters fragment on ultrafast timescales to give rise to protonated species.⁸ Only very recently have infrared spectroscopy been performed on size-selected non-protonated water clusters.⁹

Here we describe a facile method to generate non protonated water clusters using exciton energy transfer from argon clusters. The idea behind this approach is based on the fact that excited electronic states can decay in two ways, namely, radiatively by emission of a fluorescence photon or non-radiatively by the ejection of an electron and ionization. Moreover, a part of the electronic energy can be used to initiate nuclear dynamics, such as conformation changes or dissociation. This is very similar to an interatomic Coulombic decay (ICD) process.¹⁰ This has been shown to occur in weakly bound aggregates (hydrogen bonded network or a van der Waals cluster). Upon core level photoionization, the created hole state undergoes ultrafast relaxation due to energy transfer to a neighbouring atom, and emits an electron from that neighbouring site.¹¹⁻¹³

The first successful attempt to measure non-protonated $(\text{H}_2\text{O})_n^+$ ($2 \leq n \leq 10$) clusters was by Shinohara et al.¹⁴ who used the argon emission lines at 11.62 and 11.83 eV to ionize a mixed argon/water molecular beam. Since protonated water clusters and mixed $(\text{H}_2\text{O})_n\text{Ar}_m^+$ clusters were also observed, it was suggested that electron emission and Ar evaporation from these clusters led to the formation of the non-protonated species. Shiromaru *et al.* measured appearance energies for the water dimer, trimer and also for the protonated dimer and trimer

using synchrotron radiation.¹⁵ The reported appearance energies for the non-protonated and protonated dimer and trimer were all consistently below literature values (by about 0.3-0.5 eV) and this discrepancy was recently discussed.^{2,16} Jongma *et al.* carried out an extensive reflectron time-of-flight (TOF) analysis of the fragmentation of water clusters in an argon expansion which was photoionized with VUV light (12.2 and 13.4 eV).¹⁷ They saw evidence for the formation of “unprotonated” water clusters and suggested that upon ionization, water clusters take the form $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k \bullet \text{OH}$, and the hydroxyl radical formed upon ionization is outside the first solvation shell but is captured within the cluster. A process termed active parent ion cooling was coined, where argon atoms effectively carried away the excess energy upon evaporation. Electron impact ionization of water clusters embedded in helium nano-droplets have also shown evidence of water cluster ions (typically at the 10% level when compared to protonated ones),^{18,19} as does ion bombardment of ice in a recent secondary ion emission experiment.²⁰ These studies suggest non-dissociative ionization of small water clusters may be feasible only with an ultra-soft ionization method and here we show how an argon cluster can take the role of both electronic energy transport and a heat bath to achieve ultra-soft ionization. In the studies mentioned above, “Pure” (non-protonated) water cluster ions were formed by gas phase ionization of mixed water and rare gas clusters. However, the role of the rare gas atoms in the ionization process was not fully understood and here we suggest a pathway of how this process occurs using tunable VUV radiation and time of flight mass spectrometry (TOF-MS).

This study uses the technique of single photon ionization mass spectrometry to probe the electronic exciton levels of argon doped water clusters formed in a supersonic molecular beam expansion. Following the excitation, a multi-step reaction is initiated. First, electronic energy transfers from the excited argon cluster to the doping water network forming an ionized water cluster. Next, evaporation of the surrounding argon atoms adds additional cooling to the water cluster cation. This series of events leads to ionization resulting in an array of cold water cluster cations of different sizes. A cut-off value to the internal energy removed by the evaporating argon atoms (~ 1.2 eV) can be evaluated by monitoring the water cluster ion yield over a series of argon excitons.

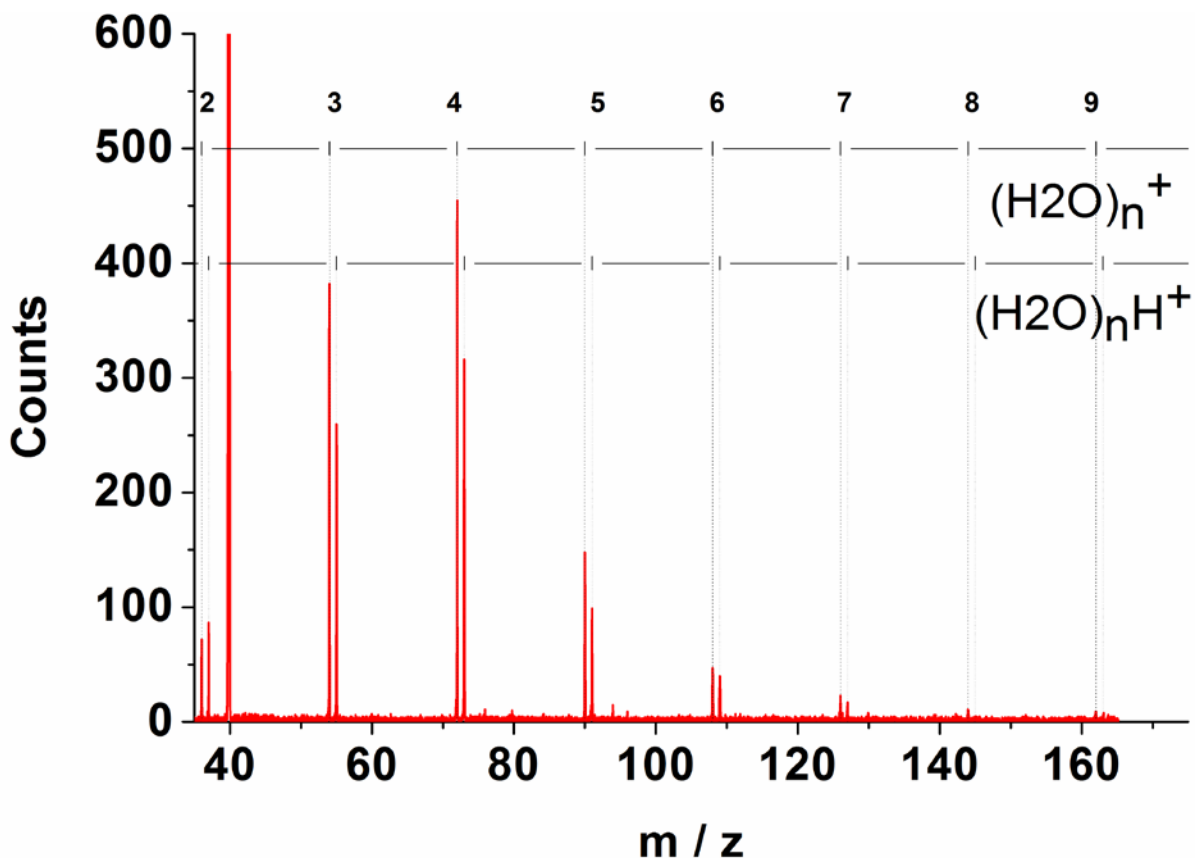


Figure 1. Mass spectrum recorded at 11.95 eV photon energy showing ions of small water clusters (n=2-9).

Figure 1 shows a typical mass spectrum recorded at 11.95 eV. A series of doublet lines separated by 18 amu on the mass to charge (m/z) axis represent the ion counts for water and protonated clusters [(H₂O)_n⁺ and (H₂O)_nH⁺ (n=2-9) respectively]. From n=3 to n=9, the water cluster intensity is higher than the protonated peak of the same n. For both series, n=4 shows the highest intensity. The distribution of the water and the protonated clusters reported here resembles closely that observed by Shinohara *et al.*¹⁴ apart from the fact that the presence of mixed Argon-water clusters is very small in our work (peaks at m/z 76 and 94 are attributed to (H₂O)₂Ar⁺ and (H₂O)₃Ar⁺ respectively). The most prominent peak at m/z 40 is assigned to the Ar monomer resulting from the higher harmonics that are present with the fundamental of the undulator radiation. A gas filter filled with Neon is used to remove these harmonics, but the

presence of the charged Ar peak suggests that there is some penetration of the harmonics and higher orders will be reflected from the grating.

Buck and Krohne have measured the cluster size distribution of argon clusters under exactly the same expansion conditions used in this work by using diffractive He atom scattering.²¹ For a 50 μm nozzle, with an expansion of 7 bar of Ar, an average cluster size distribution of 20 was reported. At room temperature, the vapour pressure of water is around 20 torr, the beam is composed of 99.6% Ar under our conditions, and thus we believe that the average Ar cluster distribution is also around 20 for the work reported here. Using scaling laws for cluster distributions, it would appear that Shinohara *et al.*¹⁴ were producing average cluster sizes of 30 Ar atoms with 5 bar backing pressure and a 100 μm nozzle.

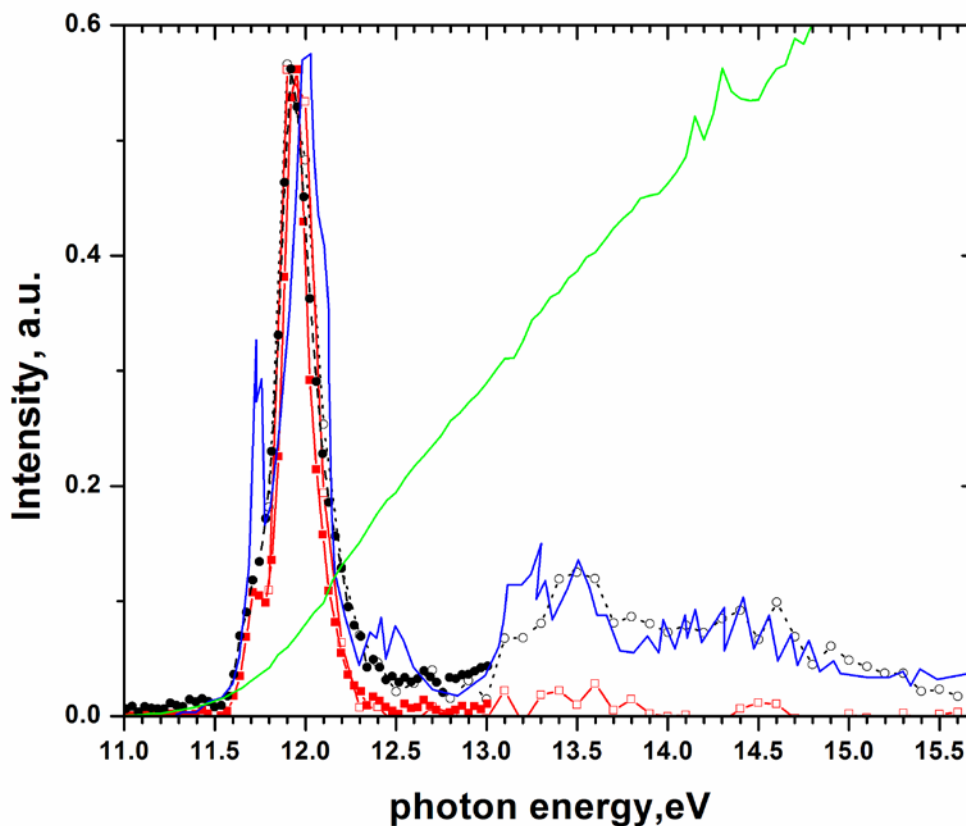


Figure 2. Photoionization efficiency (PIE) curves of water tetramer, $(\text{H}_2\text{O})_4^+$ (red filled (30 meV step size) and unfilled squares (100 meV step size)) and protonated tetramer, $(\text{H}_2\text{O})_4\text{H}^+$ (black filled (30 meV step size) and unfilled (100 meV step size) circles). The fluorescence spectra of Ar_n clusters $\langle n=20 \rangle$ taken from Ref. 22 is shown as a blue solid line. Also shown is a 1.3 bar Ar backing pressure protonated tetramer, $(\text{H}_2\text{O})_4\text{H}^+$, PIE curve as a green dashed line.

Mass spectra were recorded between 10.8 and 15.5 eV. Next, summing the area under a desired mass peak at each photon energy, yielded a photoionization efficiency curve (PIE). The PIE curve for $(\text{H}_2\text{O})_4^+$ and $(\text{H}_2\text{O})_4\text{H}^+$ are shown in Figure 2. The most prominent feature is a peak starting at 11.4 eV, peaking at 11.92 eV and tailing at 12.4 eV, with a slight shoulder to the red at 11.71 eV. Following the main peak, the $(\text{H}_2\text{O})_4^+$ shows a low signal with structure extending out to 15.5 eV. In contrast, the protonated tetramer $(\text{H}_2\text{O})_4\text{H}^+$ (normalized in intensity at 11.92 eV) shows substantial signal beyond 12.4 eV, with a series of peaks extending from 12.8 eV to 15.5 eV. Also shown is a PIE for the protonated tetramer $(\text{H}_2\text{O})_4\text{H}^+$ recorded with 1.3 bar backing pressure of Ar, which dramatically shows the absence of the peak between 11.4-12.4 eV. The PIE curves of the other protonated and non-protonated clusters measured at the higher backing pressure of 7 bar are not shown here (see supplementary material (SM)) as they match exactly those shown for $(\text{H}_2\text{O})_4^+$ and $(\text{H}_2\text{O})_4\text{H}^+$ in Figure 2. Shiromaru *et al.*¹⁵ measured the PIE curves for the protonated and non-protonated dimer and trimer using synchrotron radiation between 11.13 and 11.62 eV and these agree well with ours in the general shape and appearance energies. However, the observed onset did not explain the underlying photoionization dynamics. Only upon comparison of the PIE curves of the water clusters to the fluorescence of small $\text{Ar}_{\langle 20 \rangle}$ clusters is the dynamics revealed. The similarity of the PIE to pure Ar cluster fluorescence suggests that it is the Ar cluster that is absorbing the photon creating an exciton. However, since water clusters ions are formed only when the Ar cluster is absorbing, we conclude that the exciton energy is transferred to a) ionization of the water cluster and b) the evaporation of the Ar cluster.

A set of experiments that provides insight into the formation of non-protonated water clusters is from the group of Thomas Moller,²²⁻²⁴ who studied the optical and electronic properties of argon

clusters with VUV irradiation. The fluorescence upon VUV excitation of Argon clusters was recorded as a function of size, providing two series of spectral features. Excitation of small clusters ($\langle n \rangle$ 5-50) between 11.27-12.91 eV were dominated by the 4s and 4s' states with strong bands located at 11.98 and 11.70 eV.²² By comparison to solid state Ar absorptions recorded in a matrix, these bands were associated with n=1 surface excitons. In addition there is a broad continuum between 13.77 and 15.5 eV with additional peaks centered at 13.52, 13.19 and 12.46 eV being observed. The broad continuum was attributed to Rydberg states, while the bands at 13.19 and 13.52 eV were from n=2,2' surface excitons. A representative spectrum for an average cluster size of 20 is shown in Figure 2 and aids in interpretation of our data.

The VUV fluorescence excitation spectra for Ar clusters between 11.4 and 12.4 eV matches the PIE curve for the non-protonated tetramer very well, suggesting that it is excitation of the Ar part of the mixed cluster that gives rise to this species. This is contrary to what has been previously thought to give rise to ionization of these water clusters, where it was believed that the VUV radiation was directly ionizing the water component of the cluster, and Ar merely acted as a matrix to soak up the excess energy of ionization and evaporate.^{14,15}

An insight into the nature of this indirect ionization process can be found from previous reports in the literature, in the VUV photoionization of benzene/argon clusters,²⁵⁻²⁷ electron impact ionization of methanol/argon clusters,²⁸ and VUV photoionization of doped rare gases in Helium droplets.²⁹⁻³¹ Kamke *et al.*²⁵ observed resonance structures in the PIE curves for C₆H₆ and C₆H₆Ar_n (n=1-4), which showed the typical broad structures observed here and in the C₆H₆Ar⁺ PIE curve recorded by them. The authors suggested an intra-cluster Penning ionization process where excitation of Ar (the Ar 4s ³P_{2,0} excited states located at 11.55 and 11.72 eV respectively) within the mixed cluster leads to energy transfer to the benzene moiety followed by dissociative ionization, and evaporation of the argon cluster. Similar arguments were made for the observation of CH_xO⁺ (x=0-4) ionic species clustered with Ar and methanol in the energy range of 11.3-11.8 eV in an expansion of methanol/argon clusters.²⁸ More recently, the same phenomenon has been invoked by using photoelectron imaging²⁹ and photoionization mass spectroscopy^{30,31} to explain the ionization of doped rare gases in large helium droplets. Features

associated with absorption into the $2p\ ^1P_1$ excited state at 21.6 eV were observed, suggesting that an indirect ionization mechanism via excitation transfer was operational in this process.

In our case it would appear that the excitons located between 11.4-12.4 eV are also coupling very efficiently into the water cluster and the subsequent electronic energy transfer leads to ionization and evaporation of the Ar cluster. This is not the case for the protonated water clusters where beyond 12.4 eV, the signal starts to rise again and follows the general shape of that observed in the VUV fluorescence excitation measurements. It should be noted that a direct photoionization channel leading to protonated water clusters is operational and will be superimposed on the indirect Penning ionization type signal. This result suggests that the coupling of electronic energy leading to the formation of protonated water clusters is different in this energy range compared to the non-protonated case, or that the ions leading to non-protonated clusters are not stable above 12.4 eV and leads to fragmentation and conversion to protonated water clusters.

Huisken and co-workers used IR spectroscopy of size selected water clusters where 7.6 bar Ar were expanded through a 50 μm nozzle and suggested that the average cluster size was around 50.³² Spectra were recorded for water clusters, $n=2-5$, and it was suggested that the water clusters were solvated by argon, but the interactions were weaker than that observed in an argon matrix. Very recently an FTIR experiment on water clusters generated under conditions very similar to ours (less than 1% of water seeded in argon with high backing pressure) suggest that small water clusters ($n=2-5$) were completely solvated by argon clusters composed of between 17-22 atoms.³³ This was based on comparison of the vibrational spectrum with *ab-initio* calculations. Suhm and coworkers have also discussed argon coating of hydrogen-bonded clusters and suggest that these should be situated inside the argon system.^{34,35}

Finally we discuss the nature of the excitation process that is occurring in these mixed $\text{Ar}_m(\text{H}_2\text{O})_n$ clusters and postulate a mechanism that leads to the formation of ionized water clusters. The appearance energies for protonated water clusters reported by our group² previously for $(\text{H}_2\text{O})_n\text{H}^+$ are 11.76 eV for $(\text{H}_2\text{O})_1\text{H}^+$, 11.15 eV for $(\text{H}_2\text{O})_2\text{H}^+$, 10.94 eV for $(\text{H}_2\text{O})_3\text{H}^+$ and $(\text{H}_2\text{O})_4\text{H}^+$, 10.93 eV for $(\text{H}_2\text{O})_5\text{H}^+$, 10.91 eV for $(\text{H}_2\text{O})_6\text{H}^+$, 10.92 eV for $(\text{H}_2\text{O})_7\text{H}^+$, and 10.88 eV for $(\text{H}_2\text{O})_8\text{H}^+$. For the non-protonated dimer, an experimental adiabatic ionization energy of 11.2

eV was also reported in agreement with previous values in the literature and recently to calculations.¹⁶ The protonated cluster appearance energies agree well with those measured earlier² but the photoionization efficiency curve follows the shape of the argon cluster absorption spectrum quite dramatically. This is reflected in the enhancement of signal around 11.5 eV, peaking at 11.92 eV, dropping down and then rising again. For the non-protonated clusters, the signal rises around 11.5 eV, peaks at 11.92 eV and then drops down to the baseline around 12.5 eV. This would suggest that the adiabatic ionization energies for non-protonated water clusters should be below 11.5 eV in agreement with our previous indirect measurements² and with other experiments.⁴

Theory has shown that the structure of the water cluster ions are very different from their neutral ground state geometries, and gives rise to poor Franck-Condon (FC) factors, leading to a vibrationally excited cluster ion upon vertical excitation.^{4,16,36-38} This vibrationally excited cluster ion will rearrange via proton transfer to form a complex of the form $(\text{H}_3\text{O})^+\text{OH}$ in the case of the dimer, and it is stable to dissociation at threshold. Indeed, the non-fragmented dimer has been observed in photoionization experiments,^{16,39} where at the appearance of $(\text{H}_3\text{O})^+$ at 11.71 eV is reflected directly in a lowering of signal of $(\text{H}_2\text{O})_2^+$. Since the AIE of the water dimer is 11.21 eV, this would suggest that the dissociation energy of the dimer is 0.5 eV. Direct *ab-initio* dynamics performed on ionizing water clusters have shown that larger clusters (n=4-6) can either form a complex of the form $((\text{H}_3\text{O})^+\text{OH})(\text{H}_2\text{O})_n$ or lead to dissociation of OH.⁴⁰ This dissociation was shown to occur in two steps, a proton transfer process from the initially ionized H_2O^+ to the nearest hydrogen bonded H_2O , followed by a second proton transfer process to the nearest neighbour water molecule to form a structure of the form $(\text{H}_3\text{O})^+(\text{H}_2\text{O})\text{OH}$. Upon this transfer, the OH dissociates and the lifetimes of the intermediate complexes $((\text{H}_3\text{O})^+(\text{H}_2\text{O})\text{OH})$ are in the range of 50-200 fs. Recent direct dynamics studies on water clusters have suggested similar time scales for ionization and proton transfer.^{41,42} This would explain the predominance of protonated species in most ionization experiments on water clusters.

In our case, it appears that solvation of the ionized water cluster by argon atoms stabilizes the $(\text{H}_3\text{O})^+\text{OH}$ core, and the excess energy formed upon ionization leads to the evaporation of the argon atoms and/or water molecules.^{15,17} Very recently, infrared experiments have shown ionized

water clusters maintain a structure of $\text{H}^+(\text{H}_2\text{O})_{n-1}(\text{OH})$ very similar to that observed for protonated water clusters.⁹ Our experimental data shows that following the water cluster ionization onset, the non-protonated water cluster signal appear over the first Ar cluster exciton region, and then decreases dramatically. Protonated water clusters, on the other hand, follow the Ar fluorescence signal for the full measured region. This difference in behaviour leads us to postulate that the evaporative cooling of the Ar cluster is absorbing the excess electronic energy up to a limit of ~ 1.2 eV after ionization. A rough estimate of the binding energy per atom, using a liquid drop model for a neutral Ar cluster can be made using an empirical expression from literature:⁴³

$$E_b(N) = AN - BN^{2/3}$$

where A is the bulk binding energy per atom or molecule and B is related to the surface tension. A and B are 80.5 meV and 44.4 meV, respectively, for Ar. For a cluster composed of 20 atoms, we derive a value of 1.27 eV which is comparable to the observed value. Presumably, larger Ar clusters will be able to provide more evaporative cooling and sustain non-fragmented water clusters at higher photon energies. An example of this has been demonstrated by Jongma *et al.* when large non-protonated water clusters were observed with N up to 80 and for photoionization with 12.2 eV and 13.41 eV VUV photons.¹⁷

To conclude, these results demonstrate that although the ionization energy of water is considerably lower than that of argon – it is the argon shell that absorbs the photon and not water, contrary to what was previously thought in the literature. In this regard, water doped Ar clusters behave in a similar way to an ICD process where electronic energy excited at one site is channelled to a neighbouring location where an electron is ejected. Here, following the electronic excitation of the argon cluster, a multi-step reaction begins. First, electronic energy transfers from the excited argon cluster to the doping water network forming an ionized water cluster. Next, evaporation of the surrounding argon atoms adds additional cooling to the water cluster cation. This series of events yields an ultra-soft ionization resulting in cold water cluster cations of different sizes. Furthermore a cut-off value to the internal energy (~ 1.2 eV) removed by the

evaporating argon atoms can be evaluated by monitoring the water cluster ion yield over a series of argon excitons, located between 13-13.5 eV.

It is easy to foresee that ultrafast experiments will be able to follow the electronic energy transfer directly and shed light on this stepwise transition from a neutral doped cluster to an isolated charged water cluster. Structural information may be available via incorporation of infrared spectroscopy.

Experimental Section:

The experimental apparatus used to generate water clusters has been described previously.² Briefly, 7 bar of argon (100 psi) is passed through a water reservoir maintained at room temperature, and expanded into vacuum through a 50 μm nozzle. The resulting cluster beam is skimmed through a 2 mm orifice and ionized with tunable VUV radiation and extracted into a reflectron time-of-flight mass spectrometer. Mass spectra are recorded at photon energies between 10.5-15.5 eV, and photoionization efficiency curves are extracted from these data sets.

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Supporting Information Available: Mass spectra recorded between 14.0-15.5 eV and the photoionization efficiency curves for $(\text{H}_2\text{O})_n^+$ and $(\text{H}_2\text{O})_n\text{H}^+$ ($n=3-9$). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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