

# Thermal effects on energetics and dynamics in water cluster anions $(\text{H}_2\text{O})_n^-$

Ryan M. Young,<sup>1</sup> Margaret A. Yandell,<sup>1</sup> Sarah B. King,<sup>1</sup> and Daniel M. Neumark<sup>1,2,a)</sup>

<sup>1</sup>Department of Chemistry, University of California, Berkeley, California 94720, USA

<sup>2</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

(Received 9 December 2011; accepted 6 February 2012; published online 2 March 2012)

The electron binding energies and relaxation dynamics of water cluster anions  $(\text{H}_2\text{O})_n^-$  ( $11 \leq n \leq 80$ ) formed in co-expansions with neon were investigated using one-photon and time-resolved photoelectron imaging. Unlike previous experiments with argon, water cluster anions exhibit only one isomer class, the tightly bound isomer I with approximately the same binding energy as clusters formed in argon. This result, along with a decrease in the internal conversion lifetime of excited  $(\text{H}_2\text{O})_n^-$  ( $25 \leq n \leq 40$ ), indicates that clusters are vibrationally warmer when formed in neon. Over the ranges studied, the vertical detachment energies and lifetimes appear to converge to previously reported values. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3689439>]

## I. INTRODUCTION

The hydrated electron,  $e_{aq}^-$ , has received much attention in recent years owing to its importance as a highly reactive chemical transient in many important processes ranging from atmospheric chemistry<sup>1</sup> to low-energy radiation damage to biological systems.<sup>2</sup> It is also of fundamental interest as the simplest quantum solute. While there is still some controversy as to the exact nature of how  $e_{aq}^-$  is solvated in water,<sup>3–9</sup> the prevailing picture is that the electron resides within a  $\sim 2\text{--}3$  Å radius cavity defined by  $\sim 6$  water molecules in a quasi-octahedral arrangement.<sup>10</sup> In the gas phase, water cluster anions  $(\text{H}_2\text{O})_n^-$  offer another avenue to understand electron solvation, as they can be thought of as precursors to bulk hydrated electrons.<sup>11</sup> However, there are concerns about the validity of inferring the energetics and dynamics of bulk hydrated electrons from extrapolations of cluster data given the controversies surrounding the nature of electron binding to water clusters<sup>12,13</sup> and the differences in temperature between cluster and bulk experiments.<sup>14</sup> In this work, we examine how cluster formation conditions affect binding energies and relaxation times in water cluster anions by preparing them in neon carrier gas and comparing the results to previous studies in argon and in ion traps.

Much of our information on  $(\text{H}_2\text{O})_n^-$  clusters derives from one-photon photoelectron spectroscopy,<sup>11,15–17</sup> which yields size-dependent vertical detachment energies (VDEs), and infrared spectroscopy,<sup>18–20</sup> which yields a more direct structural probe of these species. The first photoelectron spectra, measured by Bowen and co-workers<sup>16</sup> for clusters as large as  $n = 69$ , showed that the VDE of these clusters increased linearly as a function of the inverse cluster radius,  $1/R = n^{-1/3}$ , extrapolating to a value of 3.3 eV in the limit of  $n \rightarrow \infty$ . This implied value for the VDE of  $e_{aq}^-$  agrees with several recent direct measurements of this quantity via photoelec-

tron spectroscopy of electrons in liquid water microjets,<sup>21–24</sup> which yielded VDEs in the range of 3.3–3.6 eV.

However, this picture of a straightforward extrapolation of cluster to bulk properties is complicated by several factors. First, depending on the clustering conditions, water clusters can bind electrons in multiple ways. In our laboratory,<sup>15</sup> we found that clusters formed in argon at low backing pressures ( $\sim 30$  psi (gauge)) had binding energies similar to those previously reported,<sup>16</sup> but at higher backing pressures ( $\sim 70$  psi (gauge)), conditions normally associated with colder expansions, the spectra were dominated by a new, low binding energy peak. This weakly bound feature was labeled “isomer II” and attributed to a surface bound state, while the original, higher binding energy feature first observed by Bowen and co-workers<sup>16</sup> was termed “isomer I” and was deemed the best candidate for an internally solvated electron; these assignments were motivated by theoretical work by Barnett *et al.*<sup>25</sup> A third peak at very low binding energies ( $\sim 0.2$  eV) was also found and labeled “isomer III.” Isomers II and III were attributed to metastable, higher energy structures formed by attaching electrons to very cold neutral clusters. VDEs for isomers II and III extrapolate to  $\sim 1.7$  eV and  $\sim 0.6$  eV, respectively, much lower than the value for the bulk hydrated electron. Recently, von Issendorff<sup>26</sup> measured photoelectron spectra of water cluster anions cooled to  $\sim 10$  K in an ion trap and found that in these very cold clusters, the isomer I peak splits into multiple features beginning around  $n = 25\text{--}30$ . The higher binding energy feature (labeled “isomer Ib”) extrapolates to about 4.0 eV, notably higher than the values from the near-room temperature liquid jet experiments. The effect of cluster temperature and other initial conditions on the electron binding energy and motif has been considered theoretically by the groups of Rossky,<sup>27</sup> Barnett,<sup>28</sup> Herbert,<sup>29</sup> and Jungwirth.<sup>30–32</sup>

Another set of experiments has focused on characterizing excited state dynamics in  $(\text{H}_2\text{O})_n^-$  clusters. Here, time-resolved photoelectron (TRPE) spectroscopy experiments have been carried out<sup>33–36</sup> in which one excites the clus-

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: dneumark@berkeley.edu. Fax: 510 642 3635.

ter analog<sup>37</sup> of the  $s \rightarrow p$  transition of  $e_{aq}^-$  and follows the resulting relaxation dynamics. These experiments yield internal conversion lifetimes for the  $p$ -state as a function of cluster size that can be compared to lifetimes inferred from transient absorption experiments in the bulk. The internal conversion lifetimes of isomer I clusters were shown to be between 300 fs for  $n = 15$  and  $\sim 70$  fs for  $n = 200$ . Extrapolating to infinite cluster size gave an estimate of the bulk internal conversion lifetime of 60 fs, very close to one of the time scales measured in transient absorption experiments.<sup>38</sup> This comparison helped solidify the idea that large isomer I clusters are precursors to the hydrated electron in the bulk and supported the “non-adiabatic” relaxation mechanism<sup>39</sup> for bulk hydrated electrons. Again, however, one must consider the validity of this type of extrapolation since the dependence of these dynamics on cluster temperature, which is estimated at 160 K in these experiments using the evaporative ensemble model,<sup>40</sup> is not well understood.

The body of experimental and theoretical work on water cluster anions indicates that probing the effect of temperature on the energetics and dynamics of these species is of considerable interest. As indicated above, one approach has been to measure photoelectron and infrared spectra of clusters that are trapped and cooled to cryogenic temperatures.<sup>26</sup> Alternatively, in experiments based on free jet ion sources, the cluster temperature can be varied by adjusting the carrier gas backing pressure, as was demonstrated in our experiments with Ar,<sup>15</sup> or by changing the carrier gas itself, as is described in this paper. Here, we generate clusters in a Ne expansion, which is generally expected to result in warmer clusters because Ne is a less efficient energy transfer medium than Ar.<sup>41–43</sup> By carrying out one-photon and time-resolved photoelectron imaging, we test how this substitution affects the vertical detachment energies and the excited state internal conversion dynamics of the anion clusters.

Our key results are as follows. Unlike previous studies with argon as the carrier gas, only the strongly bound isomer I is observed here, even at pressures much higher than previously used. We demonstrate that the vertical detachment energies of water cluster anions are relatively insensitive to the temperature of the cluster as determined by the source conditions. Conversely, the internal conversion lifetimes of excited water cluster anions are influenced by the cluster temperature, becoming shorter for nominally warmer clusters. However, both the binding energies and time scales appear to converge to previously reported values.

## II. EXPERIMENTAL

A detailed description of the time-resolved photoelectron imaging apparatus has been published previously.<sup>44</sup> Briefly, the carrier gas of interest is flowed over a heated (50–75 °C) water reservoir, creating a mixture that is then expanded into a vacuum chamber through a solenoid valve pulsed at 600 Hz.<sup>45</sup> Clusters form from collisions with the carrier gas during the adiabatic expansion. They then pass through a ring-shaped hot filament cathode emitting electrons which are accelerated to  $\sim 200$  eV and ionize the clusters via secondary electron attachment. These ions are then extracted perpendicularly into

a mass spectrometer to achieve mass separation.<sup>46</sup> Additional mass selection is accomplished with a pulsed electrostatic switch. The isolated ion packet of interest is then interrogated by the pump and probe laser pulses. Detached electrons are accelerated and analyzed using velocity map imaging<sup>47</sup> which maps the emitted photoelectron velocity vectors onto a two-dimensional detector comprising a set of chevron-mounted microchannel plates and a phosphor screen. Images are captured using a CCD camera and inverted using the BASEX method after being 4-way symmetrized.<sup>48</sup> Inverted images are then converted to electron kinetic energy (eKE) distributions, which are transformed to binding energy distributions:  $eBE = hv_{probe} - eKE$ .

The femtosecond laser pulses are generated using a commercial Ti:sapphire oscillator/chirped-pulse multipass amplifier (KM Labs Griffin oscillator/Dragon amplifier). Half ( $\sim 1$  mJ/pulse) of the 30 fs, 790 nm fundamental is then used to pump a continuum-seeded optical parametric amplifier (Light Conversion TOPAS-C) to create  $\sim 50$   $\mu$ J/pulse of signal light between 1220 nm (0.98 eV) and 1260 nm (1.01 eV) for use as the pump pulse to excite the  $p \leftarrow s$  transition for the smaller clusters.<sup>37</sup> The remainder of the amplifier output is attenuated and used as the probe ( $\sim 100$   $\mu$ J/pulse) for the time-resolved experiments. Temporal resolution is determined by measuring the cross-correlation time of the pump and probe pulses using a second nonlinear crystal for sum-frequency mixing; typical time resolution is 150 fs full-width at half-maximum (FWHM). For the one-photon experiments, the fundamental is frequency-doubled in a 29.1°  $\beta$ -barium borate crystal yielding 395 nm (3.14 eV) light that is attenuated to  $\sim 50$   $\mu$ J/pulse. The resolution of the photoelectron spectrometer is limited by the bandwidth of the femtosecond laser and is about 45–50 meV FWHM for both the 1.57 eV and 3.14 eV detachment pulses.

## III. RESULTS AND ANALYSIS

Figure 1 shows a mass spectrum of  $(H_2O)_n^-$  formed in an expansion of 250 psi (gauge) Ne. Clustering is seen out to  $n \sim 45$ . Mass spectra for cluster anions generated in Ar extend considerably further. Cheshnovsky and co-workers<sup>28</sup>

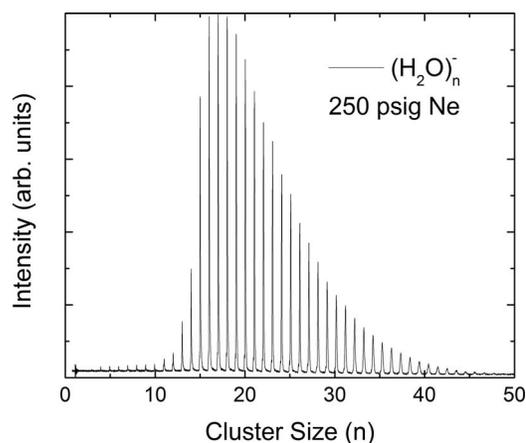


FIG. 1. Time-of-flight mass spectrum for water cluster anions  $(H_2O)_n^-$  formed in Ne carrier gas.

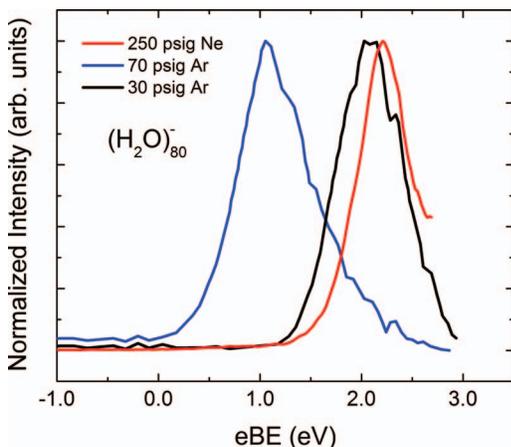


FIG. 2. Photoelectron spectra of  $(\text{H}_2\text{O})_{80}^-$  with  $h\nu = 3.14$  eV for different source gases and pressures: 250 psi (gauge) neon (red); 70 psi (gauge) argon (blue); 30 psi (gauge) argon (black). Spectra taken in argon are adapted from Verlet *et al.*<sup>15</sup>

recently observed water cluster dianions using a Ne expansion; we do not see them here, but our cluster distribution cuts off below the minimum size ( $n = 83$ ) found to support a dianion in their experiment. Intensities for ions formed in co-expansions with neon were lower than for ions made in argon, while co-expansions with helium did not generate significant clustering in our source. No evidence was seen for fragmentation of the electronically excited size-selected clusters in the mass spectrum.

Photoelectron spectra taken with  $h\nu = 3.14$  eV for  $(\text{H}_2\text{O})_{80}^-$  formed under various source conditions are shown in Figure 2. The spectra show the same broad, structureless shape seen in previous studies. In stark contrast to these earlier results,  $(\text{H}_2\text{O})_n^-$  formed in neon exhibits only the high-binding energy isomer (isomer I) for all cluster sizes ( $n = 11$ –80) and pressures (70–250 psi (gauge) Ne) studied here. No evidence for any additional other isomers with significantly lower (or higher) binding energies was found over this size range in either Ar or Ne.

Fitting the peak of the photoelectron binding energy distribution yields the vertical detachment energy for each cluster. A Gaussian–Lorentzian (G–L) profile is assumed:<sup>26,49,50</sup>

$$I(eBE;n) = \begin{cases} I_0 + A \exp[-(eBE - VDE_n)^2/w_G^2] & eBE < VDE_n \\ I_0 + A \left[ \frac{w_L^2}{(eBE - VDE_n)^2 + w_L^2} \right] & eBE \geq VDE_n \end{cases}, \quad (1)$$

where  $I_0$  is the baseline intensity,  $A$  is a scaling factor,  $VDE_n$  is the VDE of the cluster of size  $n$ , and  $w_G$  and  $w_L$  are the half-widths of the Gaussian and Lorentzian sides, respectively. VDEs for selected clusters  $n = 11$ –80 formed in 100 psi (gauge) and 250 psi (gauge) neon are plotted in Figure 3 against  $n^{-1/3}$  along with previously reported values.<sup>17</sup> Over the size range reported here, the VDEs range from 0.78 eV to 2.21 eV and are generally in good agreement with the isomer I VDEs measured in argon (red squares).

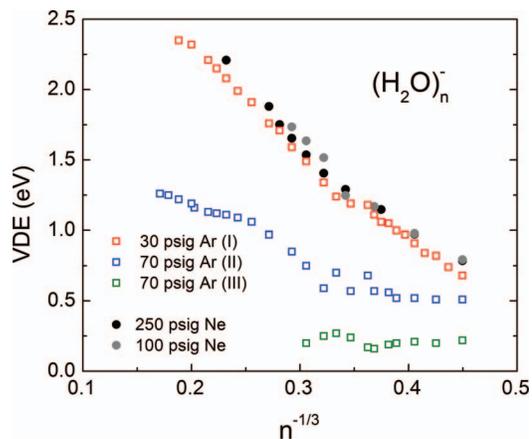


FIG. 3. Vertical detachment energies (VDEs) of  $(\text{H}_2\text{O})_n^-$  under various source conditions: 250 psi (gauge) neon (black circles); 100 psi (gauge) neon (grey filled circles); 30 psi (gauge) argon (red squares); 70 psi (gauge) argon (isomer II: blue squares; isomer III: green squares). Previously reported values are adapted from Verlet *et al.*<sup>15</sup>

Time-resolved photoelectron spectra were taken from  $n = 25$ –40. A representative TRPE spectrum is shown in Figure 4 for  $(\text{H}_2\text{O})_{30}^-$ . TRPE spectra are similar to those measured previously for water cluster anions formed in argon. Four main features are seen: excited-state autodetachment at very low eKE (feature A), direct probe detachment from the ground state (feature B) around 0.25 eV, resonant two-photon detachment (R2PD) from the pump (feature C) around 0.6 eV, and transient excited-state signal (pump-probe, feature D) appearing between 1.00 and 1.50 eV kinetic energy.

Integrated intensities of these features yield their associated population dynamics. The intensities of features B and D are shown in the inset of Figure 4. Feature B is depleted and D is created at the zero of pump-probe delay ( $t_0$ ) before recovering and decaying on the same time scale, respectively. Feature B does not recover to its initial population owing to R2PD from the pump depleting the ground state population at positive pump-probe delays. Because the excited state lifetime and temporal resolution of the laser are comparable, the

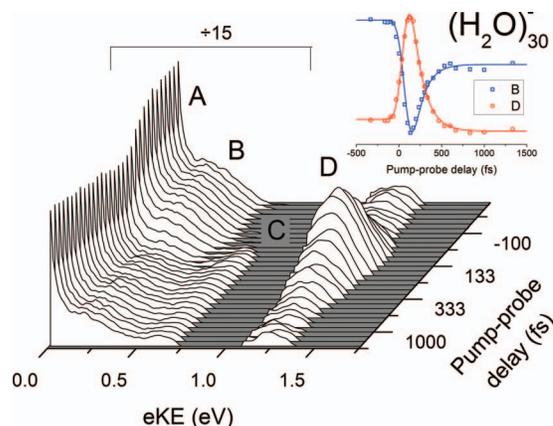


FIG. 4. Time-resolved photoelectron spectrum of  $(\text{H}_2\text{O})_{30}^-$ . The  $p \leftarrow s$  transition is excited with  $h\nu_{\text{pump}} = 1.00$  eV ( $\lambda_{\text{pump}} = 1250$  nm); electrons are detached with  $h\nu_{\text{probe}} = 1.57$  eV. TRPEs of these clusters strongly resembles the spectra of isomer I water cluster anions reported previously.<sup>34,35</sup> The spectrum below 1.0 eV is scaled by a factor of 15.

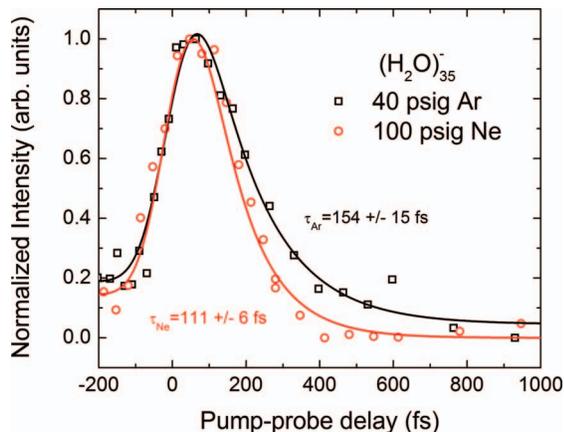


FIG. 5. Integrated intensities of feature D for  $(\text{H}_2\text{O})_{35}^-$  clusters formed in a seeded expansion of 40 psi (gauge) argon (black squares) and 100 psi (gauge) neon (red circles). Relaxation is  $\sim 30\%$  faster in the clusters from the neon expansion.

integrated intensities are fit to the convolution of a single exponential decay with a time scale  $\tau_{IC}$  and the instrumental response function (a Gaussian with width  $\sigma$ , where  $\text{FWHM} = 2\sigma\sqrt{2\ln 2}$ ):

$$I_p(t) = e^{-t^2/\sigma^2} * \begin{cases} I_0 & t < t_0 \\ I_0 + A \exp[-(t - t_0)/\tau_{IC}] & t \geq t_0 \end{cases}. \quad (2)$$

The  $\sigma$  parameter is taken as the cross-correlation time of the laser pulses taken either *in situ* from cross-correlation-limited above-threshold signals or from a measurement outside the vacuum chamber.

Based on the complementary behavior of the ground- and excited-state dynamics, the lifetime of the excited state feature D is taken as the internal conversion time. Figure 5 shows an overlay of the integrated intensity of feature D for  $(\text{H}_2\text{O})_{35}^-$  clusters formed in 100 psi (gauge) neon (red circles) and 40 psi (gauge) argon (black squares). Both traces have the same functional form, and the rise times are very similar (within 10 fs); however the decay time is shorter in the neon-born clusters: 111 vs 154 fs. Following previous arguments,<sup>33,35,51,52</sup> internal conversion lifetimes were plotted against the inverse cluster size,  $1/n$ . Internal conversion times are shown in Figure 6 for  $n = 25$ –40 vs.  $1/n$  with error bars estimated as the standard error from the fit. While the data follow the same qualitative trend and extrapolate to roughly the same bulk time constant (50–60 fs), it can be seen that the lifetimes for clusters born in neon are systematically shorter than for those in argon.

#### IV. DISCUSSION

The results in the Sec. III indicate that in our ion source, the mass spectrum of  $(\text{H}_2\text{O})_n^-$  clusters produced using Ne as a carrier gas cuts off at smaller cluster sizes than when Ar is used. The largest observable size with sufficient intensity to take a photoelectron spectrum was  $n = 80$  for clusters formed in neon, compared to  $n = 200$  for those formed

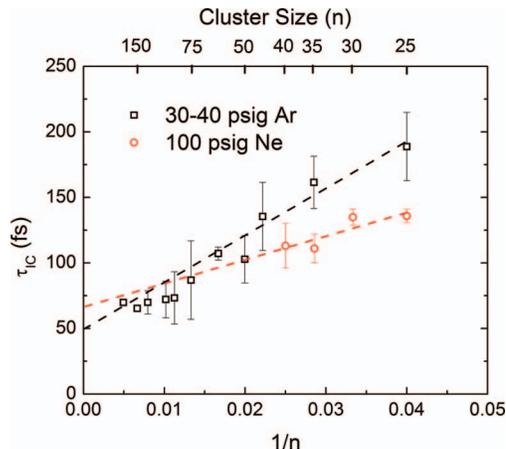


FIG. 6. Time scales for internal conversion following resonant excitation ( $p \leftarrow s$ ) for  $(\text{H}_2\text{O})_n^-$  isomer I clusters from different source conditions: 100 psi (gauge) neon (black circles); 40 psi (gauge) argon (red squares), adapted from Griffin *et al.*<sup>35</sup> The values and slopes are different while appearing to converge to the same bulk limit (50–60 fs).

in argon.<sup>17,35</sup> These effects are reminiscent of those seen in the size distribution of  $\text{Na}_n$  clusters formed in free jet expansions with various seed gases.<sup>53</sup> In addition, our photoelectron spectra show that only isomer I clusters are formed in the adiabatic expansion with neon even at backing pressures as high as 250 psi (gauge); under similar conditions in Ar, isomer III was found to dominate the photoelectron spectrum. In the earlier work by Bowen<sup>49</sup> with argon carrier gas, isomer I was found to be dominant under warm source conditions for clusters  $n \geq 14$ , suggesting that while neon is not necessary to solely produce isomer I clusters, it is helpful and eliminates the need for tuning the backing pressure. Neon has previously been observed to be less effective than argon at deactivating vibrationally excited organic molecules such as toluene<sup>54,55</sup> and azulene.<sup>56,57</sup> It is, therefore, reasonable to expect less efficient cooling of water cluster anions using Ne as the carrier gas, and we can understand our results in this context.

Although the detailed mechanism for water cluster anion formation is not fully understood; it most likely proceeds from attachment of a low energy electron to a neutral water cluster. The resulting anion cluster can grow via collisions with other water molecules in the free jet. Both electron attachment and additional aggregation add to the internal energy of the cluster, whereas it can lose energy by collisions with the carrier gas in the higher pressure region of the expansion and by evaporation of water molecules, which can continue to occur in the collisionless regime of the free jet. When Ne rather than Ar is used as a carrier gas, one expects the distribution of neutral water clusters prior to electron attachment to be shifted toward smaller sizes, and for cooling collisions subsequent to electron attachment to be less efficient. These effects combine to yield smaller anion clusters compared to experiments in Ar, as is observed here.

In fact, not only the mass spectrum but also the isomer distribution suggests that the clusters formed in Ne are warmer. The formation of isomers II and III under “cold”, i.e., high pressure, expansion conditions in Ar has been attributed

by us and others to the trapping of water cluster anions in a metastable state.<sup>14,15,26,29</sup> Such a scenario is not unreasonable, because the lowest energy structures in neutral water clusters are generally quite different from those in water cluster anions.<sup>58</sup> Indeed, warmer neutral clusters are more likely to deviate from their minimum energy geometries, and electron attachment to one of these clusters could result in a more tightly bound electron, as suggested by Madarász *et al.*<sup>59</sup> Once electron attachment occurs, rapid energy removal by the Ar carrier gas then traps the anion in the isomer II (or III) well. In a Ne expansion, we expect the neutral clusters to be warmer prior to attachment, and energy removal from the anion by the Ne to be less efficient, resulting initially in a warmer anion cluster distribution in Ne, prior to evaporative cooling. These effects lessen the probability of trapping in a local minimum as opposed to the global minimum corresponding to isomer I (or Ib (Ref. 26)). While we can rationalize the differing isomer distributions in the two carrier gases, it is nonetheless remarkable that there is no evidence for anything other than isomer I clusters when Ne is used.

We now examine the one-photon and time-resolved PE spectra in more detail. Figure 3 shows that the VDEs from the one photon PE spectra are in agreement with those of isomer I previously reported by our group,<sup>15</sup> although they are systematically higher by  $\sim 50$ – $100$  meV. The photoelectron spectra also appear slightly narrower (e.g., 0.68 eV FWHM in Ne, compared to 0.75 eV in Ar for  $n = 80$ ). Preparing the clusters in neon thus presents a smoother way to anneal the anion structures than in argon. The VDEs in Figure 3 lie between those found by von Issendorff and co-workers<sup>26</sup> for isomers 1a and 1b in their investigation of cold ( $\sim 10$  K) water clusters; as discussed by Jacobson and Herbert,<sup>29</sup> isomers 1a and 1b may be “partially embedded” surface states and cavity states of the excess electron, respectively. Our spectra were well fit to a single G–L profile, as compared to a sum of multiple G–L functions needed to fit their spectra. These differences may reflect not only the temperature but also the rather different means of ion formation in their study,<sup>26</sup> in which relatively warm ions formed in a gas aggregation source were then cooled in an ion trap prior to spectroscopic interrogation. In any case, there is mounting evidence that “isomer I” comprises multiple close-lying structures rather than a single geometry for a given cluster size.<sup>26,29,49</sup> One can therefore envision that the cluster anions at 10 K are trapped in multiple minima separated by small barriers, while the warmer cluster anions in our experiment represent a more averaged structure and thus result in a single-peaked photoelectron spectrum.

The time-resolved spectra show more pronounced differences between clusters formed in Ne and Ar; the results in Figures 5 and 6 clearly show faster internal conversion using Ne as the carrier gas. This result is consistent with increased vibrational energy in the cluster, which can promote faster internal conversion. There are several possible explanations for this effect, which is seen in the gas phase as well as in more complex environments.<sup>60,61</sup> In the case of water cluster anions, we note that the dynamics of internal conversion for bulk hydrated electrons have been shown to be driven by solvent fluctuations.<sup>60,61</sup> The electronic energy level gap

is structurally sensitive and will fluctuate with the solvent configuration. Some of these variations will bring the energy gap to near zero, inducing an electronic transition back to the ground state. These effects will be more pronounced at higher temperatures as the amplitude of the fluctuations increases. Figure 6 suggests that internal conversion time scales for clusters born in neon and argon converge at larger sizes. More data points are necessary to make a definitive statement to this as well as the extrapolation to bulk. Moreover, although there is some temperature dependence, the time scales still yield a rapid,  $<100$  fs internal conversion time in the bulk limit, supporting the validity of previous extrapolations of cluster dynamics.<sup>33,35</sup> However, it should be emphasized that the clusters in this experiment do not represent a fully equilibrated system and that even when formed in neon, the clusters are still far colder than the bulk experiments considered in the extrapolation.

We close by discussing the evaporative ensemble limit<sup>40,62,63</sup> often used to estimate cluster temperatures. In this limit, solvent evaporation continues until the cluster temperature drops sufficiently so that no more evaporation occurs on the time scale of the experiment. As formulated by Klots, the cluster temperature within this limit depends only on the solvent binding energy, and is estimated to be 160 K for water clusters, based on a binding energy of 320 meV.<sup>64</sup> Hence, this model predicts the same temperature for water cluster anions formed in Ar or Ne, whereas our data point to warmer clusters in Ne. This apparent discrepancy can be resolved by realizing that the cluster temperature from the evaporative ensemble model is taken as an upper limit. It applies when water cluster anions emerge from the high pressure region of the free jet with sufficient internal energy for solvent evaporation to continue even after collisional cooling is no longer effective. Our results then suggest that while clusters in the Ne expansion might be described by the evaporative ensemble limit, that those produced in Ar are colder because the more efficient collisional cooling in Ar largely eliminates solvent evaporation once collisions have stopped.

It would be of great interest to explore the effects seen here in other solvent cluster anions. The ability to bind excess electrons in multiple ways is not unique to water: methanol cluster anions have been shown in both photoelectron experiments<sup>65,66</sup> and simulations<sup>67</sup> to have at least two binding motifs. Time-resolved measurements similar to those performed on water have been carried out,<sup>52</sup> so the effect could be readily observed. This may help resolve some of the discrepancy between the bulk electron binding energies extrapolated from the clusters and those measured in liquid jets.<sup>68</sup> Additionally, ammonia cluster anions  $(\text{NH}_3)_n^-$  have been formed and analyzed out to  $n = 1100$ ,<sup>69</sup> but dielectric continuum analysis suggests that the clusters are more likely to be solid than liquid. Forming the clusters in neon could provide a way to generate *liquid* ammonia cluster anions to help us better understand the nature and validity of the  $n^{-1/3}$  extrapolation for the VDEs. However, it is still unclear if the temperatures reached by the clusters in the evaporative ensemble are above or below the cluster “melting” point, so it may very well be that warming those clusters will only result in fragmentation or evaporation.

## V. CONCLUSIONS

One-photon and time-resolved photoelectron imaging were used to investigate the effects of the carrier gas on electron binding and dynamics in water cluster anions. Only isomer I clusters are produced while using neon at backing pressures as high as 250 psi (gauge), whereas for clusters formed in argon the photoelectron spectra are dominated by more weakly bound isomers at pressures as low as 70 psi (gauge). These results are consistent with the formation of warmer water cluster anions in Ne. VDEs were determined to be relatively insensitive to the carrier gas, while the internal conversion lifetimes subsequent to  $p \leftarrow s$  excitation were shorter in Ne. Extending this study to larger cluster sizes in order to explore the tentative lifetime extrapolation presented here as well as the validity of the  $1/n$  extrapolation in general would be very useful. Studies in other solvent clusters such as methanol would also shed more light on how cluster formation conditions affect the nature of electron binding and solvent dynamics in aggregate systems.

## ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF) under Grant No. CHE-0649647. M.A.Y. acknowledges funding from a National Defense Science and Engineering Graduate (NDSEG) Fellowship through the Air Force Office of Scientific Research (AFOSR), 32 CFR 168a. S.B.K. is grateful for funding through an NSF Graduate Research Fellowship. We thank one of the referees for insightful comments about the evaporative ensemble model.

- <sup>1</sup>F. Arnold, *Nature (London)* **294**, 732 (1981).
- <sup>2</sup>J. Simons, *Acc. Chem. Res.* **39**, 772 (2006).
- <sup>3</sup>H. F. Hameka, G. W. Robinson, and C. J. Marsden, *J. Phys. Chem.* **91**, 3150 (1987).
- <sup>4</sup>R. E. Larsen, W. J. Glover, and B. J. Schwartz, *Science* **329**, 65 (2010).
- <sup>5</sup>L. D. Jacobson and J. M. Herbert, *Science* **331**, 1387 (2011).
- <sup>6</sup>L. Turi and Á. Madarász, *Science* **331**, 1387 (2011).
- <sup>7</sup>R. E. Larsen, W. J. Glover, and B. J. Schwartz, *Science* **331**, 1387 (2011).
- <sup>8</sup>J. M. Herbert and L. D. Jacobson, *J. Phys. Chem. A* **115**, 14470 (2011).
- <sup>9</sup>B. Abel, U. Buck, A. L. Sobolewski, and W. Domcke, *Phys. Chem. Chem. Phys.* **14**, 22 (2012).
- <sup>10</sup>L. Kevan, *Acc. Chem. Res.* **14**, 138 (1980).
- <sup>11</sup>J. V. Coe, S. M. Williams, and K. H. Bowen, *Int. Rev. Phys. Chem.* **27**, 27 (2008).
- <sup>12</sup>L. Turi, W.-S. Sheu, and P. J. Rossky, *Science* **309**, 914 (2005).
- <sup>13</sup>D. M. Neumark, *Mol. Phys.* **106**, 2183 (2008).
- <sup>14</sup>O. Marsalek, F. Uhlig, T. Frigato, B. Schmidt, and P. Jungwirth, *Phys. Rev. Lett.* **105**, 043002 (2010).
- <sup>15</sup>J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, *Science* **307**, 93 (2005).
- <sup>16</sup>J. V. Coe, G. H. Lee, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewig, H. Haberland, and D. R. Worsnop, *J. Chem. Phys.* **92**, 3980 (1990).
- <sup>17</sup>A. Kammrath, J. R. R. Verlet, G. B. Griffin, and D. M. Neumark, *J. Chem. Phys.* **125**, 076101 (2006).
- <sup>18</sup>N. I. Hammer, J.-W. Shin, J. M. Headrick, E. G. Diken, J. R. Roscioli, G. H. Weddle, and M. A. Johnson, *Science* **306**, 675 (2004).
- <sup>19</sup>J. R. Roscioli, N. I. Hammer, and M. A. Johnson, *J. Phys. Chem. A* **110**, 7517 (2006).
- <sup>20</sup>K. R. Asmis, G. Santambrogio, J. Zhou, E. Garand, J. Headrick, D. Goebbert, M. A. Johnson, and D. M. Neumark, *J. Chem. Phys.* **126**, 191105 (2007).
- <sup>21</sup>K. R. Siefertmann, Y. Liu, E. Lugovoy, O. Link, M. Faubel, U. Buck, B. Winter, and B. Abel, *Nat. Chem.* **2**, 274 (2010).
- <sup>22</sup>Y. Tang, H. Shen, K. Sekiguchi, N. Kurahashi, T. Mizuno, Y.-I. Suzuki, and T. Suzuki, *Phys. Chem. Chem. Phys.* **12**, 3653 (2010).
- <sup>23</sup>A. T. Shreve, T. A. Yen, and D. M. Neumark, *Chem. Phys. Lett.* **493**, 216 (2010).
- <sup>24</sup>A. Lubcke, F. Buchner, N. Heine, I. V. Hertel, and T. Schultz, *Phys. Chem. Chem. Phys.* **12**, 14629 (2010).
- <sup>25</sup>R. N. Barnett, U. Landman, C. L. Cleveland, and J. Jortner, *J. Chem. Phys.* **88**, 4429 (1988).
- <sup>26</sup>L. Ma, K. Majer, F. Chiro, and B. v. Issendorff, *J. Chem. Phys.* **131**, 144303 (2009).
- <sup>27</sup>Á. Madarász, P. J. Rossky, and L. Turi, *J. Chem. Phys.* **130**, 124319 (2009).
- <sup>28</sup>R. Barnett, R. Giniger, O. Cheshnovsky, and U. Landman, *J. Phys. Chem. A* **115**, 7378 (2011).
- <sup>29</sup>L. D. Jacobson and J. M. Herbert, *J. Am. Chem. Soc.* **133**, 19889 (2011).
- <sup>30</sup>T. Frigato, J. VandeVondele, B. Schmidt, C. Schutte, and P. Jungwirth, *J. Phys. Chem. A* **112**, 6125 (2008).
- <sup>31</sup>O. Marsalek, F. Uhlig, and P. Jungwirth, *J. Phys. Chem. C* **114**, 20489 (2010).
- <sup>32</sup>O. Marsalek, F. Uhlig, J. VandeVondele, and P. Jungwirth, *Acc. Chem. Res.* **45**, 23 (2011).
- <sup>33</sup>A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, *Science* **306**, 669 (2004).
- <sup>34</sup>A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, *J. Am. Chem. Soc.* **127**, 15283 (2005).
- <sup>35</sup>G. B. Griffin, R. M. Young, O. T. Ehrler, and D. M. Neumark, *J. Chem. Phys.* **131**, 194302 (2009).
- <sup>36</sup>D. H. Paik, I.-R. Lee, D.-S. Yang, J. S. Baskin, and A. H. Zewail, *Science* **306**, 672 (2004).
- <sup>37</sup>P. Ayotte and M. A. Johnson, *J. Chem. Phys.* **106**, 811 (1997).
- <sup>38</sup>Y. Kimura, J. C. Alfano, P. K. Walhout, and P. F. Barbara, *J. Phys. Chem.* **98**, 3450 (1994).
- <sup>39</sup>K. Yokoyama, C. Silva, D. H. Son, P. K. Walhout, and P. F. Barbara, *J. Phys. Chem. A* **102**, 6957 (1998).
- <sup>40</sup>C. E. Klots, *Z. Phys. D: At., Mol. Clusters* **20**, 105 (1991).
- <sup>41</sup>J. R. Barker and B. M. Toselli, *Int. Rev. Phys. Chem.* **12**, 305 (1993).
- <sup>42</sup>R. G. Gilbert, *Aust. J. Chem.* **48**, 1787 (1995).
- <sup>43</sup>J. Westergren, S. Nordholm, and A. Rosen, *Eur. Phys. J. D* **22**, 81 (2003).
- <sup>44</sup>A. V. Davis, R. Wester, A. E. Bragg, and D. M. Neumark, *J. Chem. Phys.* **118**, 999 (2003).
- <sup>45</sup>U. Even, J. Jortner, D. Noy, N. Lavie, and C. Cossart-Magos, *J. Chem. Phys.* **112**, 8068 (2000).
- <sup>46</sup>W. C. Wiley and I. H. McLaren, *Rev. Sci. Instrum.* **26**, 1150 (1955).
- <sup>47</sup>A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3477 (1997).
- <sup>48</sup>V. Dribinski, A. Ossadtchi, V. A. Mandelshtam, and H. Reisler, *Rev. Sci. Instrum.* **73**, 2634 (2002).
- <sup>49</sup>J. V. Coe, S. T. Arnold, J. G. Eaton, G. H. Lee, and K. H. Bowen, *J. Chem. Phys.* **125**, 014315 (2006).
- <sup>50</sup>R. M. Young, M. A. Yandell, M. Niemeyer, and D. M. Neumark, *J. Chem. Phys.* **133**, 154312 (2010).
- <sup>51</sup>S. F. Fischer and W. Dietz, *Z. Phys. Chem.* **221**, 585 (2007).
- <sup>52</sup>A. Kammrath, G. B. Griffin, J. R. R. Verlet, R. M. Young, and D. M. Neumark, *J. Chem. Phys.* **126**, 244306 (2007).
- <sup>53</sup>M. M. Kappes, R. W. Kunz, and E. Schumacher, *Chem. Phys. Lett.* **91**, 413 (1982).
- <sup>54</sup>H. Hippler, J. Troe, and H. J. Wendelken, *J. Chem. Phys.* **78**, 6709 (1983).
- <sup>55</sup>B. M. Toselli, J. D. Brenner, M. L. Yerram, W. E. Chin, K. D. King, and J. R. Barker, *J. Chem. Phys.* **95**, 176 (1991).
- <sup>56</sup>H. Hippler, L. Lindemann, and J. Troe, *J. Chem. Phys.* **83**, 3906 (1985).
- <sup>57</sup>J. Shi and J. R. Barker, *J. Chem. Phys.* **88**, 6219 (1988).
- <sup>58</sup>J. M. Herbert and M. Head-Gordon, *J. Phys. Chem. A* **109**, 5217 (2005).
- <sup>59</sup>A. d. m. Madarász, P. J. Rossky, and L. s. Turi, *J. Phys. Chem. A* **114**, 2331 (2010).
- <sup>60</sup>R. Englman and J. Jortner, *Mol. Phys.* **18**, 145 (1970).
- <sup>61</sup>R. Borrelli and A. Peluso, *Phys. Chem. Chem. Phys.* **13**, 4420 (2011).
- <sup>62</sup>S. Wei, K. Kilgore, W. B. Tzeng, and A. W. Castleman, *J. Phys. Chem.* **95**, 8306 (1991).

- <sup>63</sup>T. D. Vaden, C. J. Weinheimer, and J. M. Lisy, *J. Chem. Phys.* **121**, 3102 (2004).
- <sup>64</sup>A. E. K. Sunden, K. Stochkel, S. Panja, U. Kadhane, P. Hvelplund, S. B. Nielsen, H. Zettergren, B. Dynefors, and K. Hansen, *J. Chem. Phys.* **130**, 224308 (2009).
- <sup>65</sup>A. Kammrath, J. R. R. Verlet, G. B. Griffin, and D. M. Neumark, *J. Chem. Phys.* **125**, 171102 (2006).
- <sup>66</sup>A. Kammrath, G. B. Griffin, J. R. R. Verlet, R. M. Young, and D. M. Neumark, *J. Chem. Phys.* **126**, 244306 (2007).
- <sup>67</sup>L. Mones, P. J. Rossky, and L. Turi, *J. Chem. Phys.* **135**, 084501 (2011).
- <sup>68</sup>H. Shen, N. Kurahashi, T. Horio, K. Sekiguchi, and T. Suzuki, *Chem. Lett.* **39**, 668 (2010).
- <sup>69</sup>H. W. Sarkas, S. T. Arnold, J. G. Eaton, G. H. Lee, and K. H. Bowen, *J. Chem. Phys.* **116**, 5731 (2002).