THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 7517−7520

Published on Web 05/25/2006

Infrared Spectroscopy of Water Cluster Anions, $(H_2O)_{n=3-24}^-$ in the HOH Bending Region: Persistence of the Double H-Bond Acceptor (AA) Water Molecule in the Excess Electron Binding Site of the Class I Isomers

Joseph R. Roscioli, Nathan I. Hammer,[†] and M. A. Johnson*

Sterling Chemistry Laboratory, Yale University, P.O. Box 208107, New Haven, Connecticut 06520

Received: April 1, 2006; In Final Form: April 27, 2006

We report vibrational predissociation spectra of water cluster anions, $(H_2O)_{n=3-24}^-$ in the HOH bending region to explore whether the characteristic red-shifted feature associated with electron binding onto a double H-bond acceptor (AA) water molecule survives into the intermediate cluster size regime. The spectra of the "tagged" $(H_2O)_n^-\cdot$Ar clusters indeed exhibit the signature AA band, but assignment of this motif to a particular isomer is complicated by the fact that argon attachment produces significant population of three isomeric forms (as evidenced by their photoelectron spectra). We therefore also investigated the bare clusters since they can be prepared exclusively in the high binding (isomer class I) form. Because the energy required to dissociate a water molecule from the bare complexes is much larger than the transition energies in the bending region, the resulting (linear) action spectroscopy selectively explores the properties of clusters with most internal energy content. The $(H_2O)_{15}^-$ predissociation spectrum obtained under these conditions displays a more intense AA feature than was found in the spectra of the Ar tagged species. This observation implies that not only is the AA motif present in the class I isomer, but also that it persists when the clusters contain considerable internal energy.

Introduction

There has been a resurgence of interest in the water cluster anions, $(H_2O)_n^-$, as model systems with which to explore how an excess electron is accommodated by well-defined water networks.[1−12] This activity is, in turn, driven by a long-standing quest[13−21] to understand the molecular-level mechanics underlying the curious properties of the bulk hydrated electron, a key intermediate in biological radiation damage.[22,23] Recent studies have focused on the nature of three isomeric classes of the cluster anions that are differentiated according to their vertical electron detachment energies (VDE), with the three species denoted I, II, and III in decreasing order of their respective VDE values.[3,4,11,24] In this paper, we report vibrational predissociation spectra of $(H_2O)_n^-$ in the intramolecular HOH bending region to highlight the evolution of the cluster properties in the size range where the VDEs of types I and II rapidly diverge.[4,11] This spectral region was chosen because it provides a distinct, well-isolated spectral signature when the excess electron binds primarily to a single water molecule that is attached to the network in a double H-bond acceptor (AA) motif. In this arrangement, both hydrogen atoms on the AA water molecule point directly into the electron cloud. The AA motif was established in the structures of the type I clusters in the small size ($n = 3-9$) range,[11,12,25] and it is therefore of interest to determine whether this binding site is maintained in the larger type I clusters.

There are presently two scenarios in the literature that account for the differences between isomer classes I and II. Specifically, the Neumark group has considered the results of their recent ultrafast pump−probe studies of the electronically excited-state relaxation dynamics, as well as the size dependence of the cluster binding energies within each class, in the context of excess electron binding on either the cluster interior (type I) or the cluster surface (type II).[4,26] Our group, on the other hand, has emphasized that, in addition to the overall solvation morphology, local binding may also play a crucial role in the determination of the cluster VDE. The latter suggestion was motivated by our spectroscopic observation that the I and II isomers of the hexamer anion both occur as surface states, but differ primarily in the molecular nature of the binding site.[11] In particular, the type II form of the hexamer does not display the spectral signature of the AA motif, exhibiting instead a band pattern consistent with the excess electron binding through the collective action of many water molecules. In this arrangement, several molecules stabilize the excess electron cloud by orienting one of their hydrogen atoms toward the electron while incorporating the other into the hydrogen bonding network.

Recent simulations by Rossky[8] indicate that surface states can account for trends in the observed type I cluster properties, thus implicitly raising the issue of how different local binding motifs contribute to the distinction between the isomer classes. Moreover, Jordan and co-workers,[27] using a quantum Drude model coupled with Monte Carlo calculations, identified several AA-type motifs that survive at finite temperatures. These structures have vertical detachment energies similar to those found experimentally for isomer I. Interestingly, that study also

---

* To whom correspondence should be addressed: mark.johnson@yale.edu.

[†] Current address: Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

10.1021/jp062029g CCC: $33.50

recovered a new type of low-dipole-moment binding motif ("network-permeating") in which correlation effects and polarizability are the primary forces at play in binding the electron.[27]

The AA binding site identified in the smaller type I clusters yields a clear spectral signature in which the two stretching vibrations of the hydrogen atoms pointing into electron cloud account for a strong, red-shifted doublet in the OH stretching region, and its intramolecular bending fundamental appears *uniquely* red-shifted relative to the ν_2 band in the isolated water molecule. In an attempt to clarify the binding motifs at play in the larger members of the type I isomer class, we recently reported their OH stretch spectra through $n = 30$. Although aspects of the AA signature are retained in the larger clusters, the characteristic doublet evolved into a more red-shifted triplet around $n = 11$. Moreover, the AA stretching bands become increasingly embedded in the broad background arising from the H-bonded OH stretches of more remote water molecules, somewhat obscuring the features associated with the excess electron binding site. Therefore, in this study we extend the spectroscopic survey to cover the intramolecular bending region, where the red-shifted transition associated with the AA water molecule occurs well-separated from those arising from the supporting water network.[28]

Because the photon energies necessary for excitation of the water bending transitions (1500−1700 cm^{-1}) are lower than the nominal water binding energy,[29] $D_o \approx 3000$ cm^{-1} (and the fact that the modest pulse energies available with tabletop laser sources in this energy range preclude multiphoton dissociation), acquisition of the bending region with action spectroscopy requires either the argon-tagged "messenger" technique[30] or working with warm bare clusters. Here, we use both approaches, and the resulting spectra establish that the AA motif not only survives throughout the $n = 11-24$ size range, but that it is actually most pronounced when the clusters contain the maximum internal energy possible within the evaporative ensemble ansatz.[31,32]

Experimental Section

$(H_2O)_n^-$ cluster ions were generated by secondary electron attachment to neutral water clusters, where the slow electrons were introduced by ionizing a pulsed nozzle (Parker-Hannefin general valve series #9, 0.5 mm orifice) expansion with a 1 keV counterpropagating electron beam. The expansion was formed by passing 4 atm Ar carrier gas over liquid water at room temperature. Coverage of the 600−1900 cm^{-1} energy range was carried out via nonlinear mixing in a $AgGaSe_2$ crystal, using the 1.5 and 3 μm outputs of a tunable solid-state IR laser source (8 ns Nd:YAG pumped Laser Vision OPO/OPA). Vibrational predissociation spectra were acquired by monitoring either argon loss

$$(H_2O)_n^-\cdot Ar_m + h\nu \rightarrow (H_2O)_n^-\cdot Ar_p + (m-p)Ar \qquad (1)$$

or water molecule evaporation

$$(H_2O)_n^- + h\nu \rightarrow (H_2O)_{n-1}^- + H_2O \qquad (2)$$

as a function of photon energy. The reported spectra resulted from the addition of 5−30 individual scans and were corrected for laser pulse energy variation over the scan range. Size-selective measurements were carried out using a double-focusing, tandem time-of-flight photofragmentation mass spectrometer described previously.[33,34]

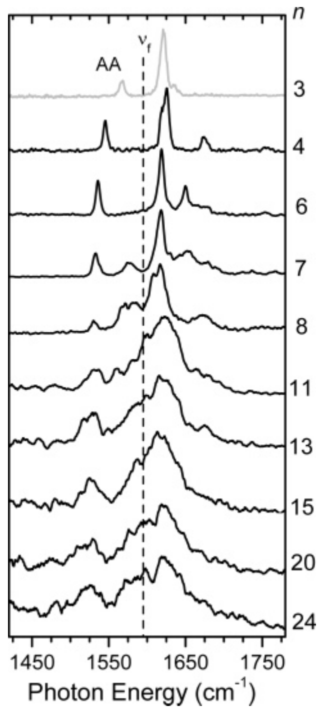

Figure 1. Predissociation spectra of $(H_2O)_n^-\cdot Ar_m$ clusters in the HOH bending region. The dotted line (ν_f) indicates the position of the free water bend (1595 cm^{-1}). The upper trace shown in gray presents the spectrum of the $(D_2O)_3^-\cdot Ar_6$ isotopologue, which is scaled by the ratio of bending frequencies in the isolated D_2O and H_2O molecules. Activity in the 1600−1700 cm^{-1} range is associated with water molecules that donate at least one hydrogen bond to the cluster network. The band near 1535 cm^{-1} is assigned to a water molecule in a double H-bond acceptor (AA) arrangement that interacts directly with the excess electron cloud. The persistence of this feature establishes that the AA motif plays an important role in this intermediate size range.

Results and Discussion

Intramolecular Bending Spectra of the $(H_2O)_n^-\cdot Ar_m$ Species. The argon predissociation spectra of the $(H_2O)_n^-\cdot Ar_m$ ($n = 4-24$) species in the HOH bending region are presented in Figure 1, along with the scaled spectrum of the $(D_2O)_3^-\cdot Ar_6$ isotopologue[12] included in the top trace. Most importantly, all these species display the signature AA transition near 1535 cm^{-1}, which is red-shifted relative to the band in the isolated water molecule[35] (1595 cm^{-1}, dashed line labeled ν_f in Figure 1), establishing the persistence of an AA binding motif in the excess electron binding site over all sizes investigated. Interestingly, at $n = 7$ and 8, although the AA transition is readily apparent, a *second* bending transition (labeled *) appears with about one third the red shift (relative to free water) as that displayed by the AA transition. The assignment of this new feature is not clear at present, and extended studies of these clusters are currently underway in our laboratory to clarify the motion responsible for this transition.

Isomer Distribution of the $(H_2O)_{15}^-\cdot Ar_m$ Species. The use of argon-tagging to obtain predissociation spectra in the bending region introduces a complication because, as Verlet et al.[4] have shown in their photoelectron study of the $(D_2O)_n^-$ isotopologues, colder source conditions yield larger contributions from the more weakly bound (II and III) isomers. Since attachment of Ar likely results in even colder clusters, we must consider the possible role of isomers II and III in the $(H_2O)_n^-$ system, even though only type I has been previously observed for the lighter isotope species in the larger ($n > 14$) size regime. To survey the possible role of isomers in the tagged $[(H_2O)_n^-\cdot Ar]$ clusters, we recorded

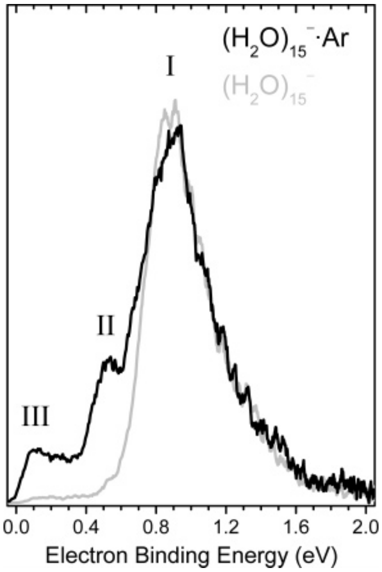

Figure 2. Photoelectron spectra of $(H_2O)_{15}^-$ (gray) and $(H_2O)_{15}^-\cdot Ar$ (black) clusters. Addition of argon atom to the cluster reduces the available internal energy and increases the fractional population of isomers II and III.

the (2.33 eV) photoelectron spectrum for $n = 15$ with the result compared with that of the bare cluster in Figure 2. Types II and III are indeed both present in the tagged cluster spectrum, and it should be noted that their relative contributions were highly dependent upon source conditions. In fact, it was often observed that isomer III was produced in greater abundance than isomer II. Because all three isomers contribute to the Ar-tagged ensemble, we are obliged to further investigate which of these is the carrier of the AA feature observed in the bending region (Figure 1), as discussed in the next section.

Isolating the Bending Spectrum of the Type I $(H_2O)_{15}^-$ Isomer in Warm Clusters. Inspection of the photoelectron spectra in Figure 2 indicates that the bare $(H_2O)_n^-$ clusters can be prepared exclusively in their type I form, thus presenting the possibility of isolating the spectrum of I in the bending region. Application of predissociation spectroscopy in the low-energy bending region is complicated, however, by the fact that the photon energy is significantly lower than the energy required to evaporate either a water molecule ($D_o \approx 3000$ cm^{-1})[29] or the excess electron (at least in the large size regime).[36] This limitation is not straightforward to overcome with multiphoton absorption since the pulse output energy of our tabletop laser system is rather modest (~150 microjoules/pulse) in the bending region. We therefore must rely on selective excitation of clusters with sufficient internal energy that the photoexcited clusters decompose on the time scale of our experiment (10 μs).

The predissociation spectrum of the bare $(H_2O)_{15}^-$ cluster is presented in Figure 3 along with that obtained from the Ar-tagged complex. The photofragment yield at 1525 cm^{-1} (the AA bend frequency) was indeed found to increase linearly as a function of pulse energy as expected for a one-photon process, and thus must reflect the character of parent clusters that contain considerable internal energy prior to photoexcitation. Interestingly, under these conditions, the AA feature is much *more* pronounced than that displayed in the Ar-tagged complex. This result, when combined with the photoelectron results (Figure 2), suggests that the more weakly binding isomers may not display the AA spectral signature, much like the situation observed earlier in the hexamer anion.[11]

The persistence of the AA signature band in the bending region is significant because it indicates that the AA motif is retained as a feature of the type I isomers in the clusters above $n = 11$. This was not obvious in our earlier survey[10] of the OH stretching bands, as the characteristic doublet in the $n = 4-9$ range evolved into a more red-shifted triplet that persists above $n = 11$ (at least up to $n = 30$). Also, having established that the AA motif is present in the larger clusters, it is now important to revisit the nature of the triplet found in the OH stretching bands in the vicinity of the features expected for the AA binding site. Note that the AA transition in the bending region does start to broaden at $n = 11$, suggesting that many structures likely contribute, perhaps arising from the plethora of H-bonding arrangements anticipated to be available for the supporting network at the larger sizes.[37,38] Interestingly, the position of the AA feature of the bare complex appears somewhat red-shifted relative to the band in the colder, Ar-tagged clusters.

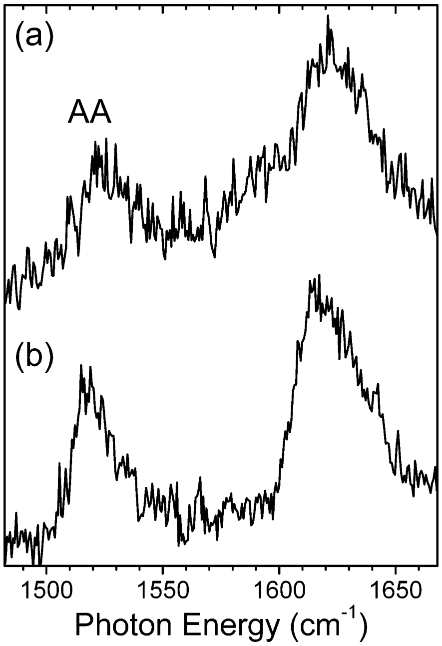

Figure 3. Comparison of the predissociation spectra arising from (a) $(H_2O)_{15}^-\cdot Ar$, and (b) bare $(H_2O)_{15}^-$. The enhancement of the strong transition at 1525 cm^{-1} establishes that the AA motif is present in the type I isomer at $n = 15$. The AA peak intensity in trace (b) was found to increase linearly with laser fluence, indicating that this action spectrum reflects a one-photon excitation process and thus results from clusters which contain significant internal energy prior to excitation.

It is noteworthy that the signature band in the bending region is enhanced in the members of the ensemble that contain the most internal energy, indicating that it is a robust arrangement. This stability in the presence of high amplitude distortions of the neutral network was also observed theoretically by Herbert et al.,[39] where they found that the AA water molecule retains its relationship to the excess electron cloud even when the internal energy of the cluster is large enough to break hydrogen bonds elsewhere in the cluster scaffold. Although assignment of dependable temperatures to cluster ensembles formed in free jets is often problematic, the water clusters in this size range present a more favorable scenario, as Viggiano and co-workers have carried out high-pressure flow tube measurements to determine their reactivity and stability at well-defined temperatures.[29] The important observation for the present study is that the $(H_2O)_n^-$ clusters were observed to spontaneously decompose by thermionic emission

$$(H_2O)_n^- \rightarrow (H_2O)_n + e^- \qquad (3)$$

above 130 K in the size range around $n = 15$. This sets a reasonable upper limit on the (isokinetic) temperature characterizing the internal energy content of cluster ions in an evaporative ensemble.[31] Thus, it would be most useful to engage theoretical analyses of the observed spectra with this starting point in mind.

Summary

Predissociation spectra of the $(H_2O)_n^-\cdot Ar_m$ clusters in the HOH intramolecular bending region display the signature absorption arising from a double H-bond acceptor water molecule with both hydrogen atoms oriented into the excess electron cloud. A band is also recovered starting at $n = 7$, which occurs with about one third the red-shift as that of the AA molecule, whose assignment is presently unknown. Photoelectron spectra establish that many isomers contribute to the $n =$ 15 Ar-tagged ensemble, but the bending predissociation spectrum of the type I form adopted by the bare cluster displays an intense transition in the location expected for the signature AA band. This indicates that the AA motif is retained for the high-binding class I isomers into the intermediate size regime, and that it survives as a persistent local binding site in clusters with considerable internal energy content.

References and Notes

(1) Coe, J. V. *Int. Rev. Phys. Chem.* **2001**, *20*, 33.

(2) Paik, D. H.; Lee, I.-R.; Yang, D.-S.; Baskin, J. S.; Zewail, A. H. *Science* **2004**, *306*, 672.

(3) Bragg, A. E.; Verlet, J. R. R.; Kammrath, A.; Cheshnovsky, O.; Neumark, D. M. *Science* **2004**, *306*, 669.

(4) Verlet, J. R. R.; Bragg, A. E.; Kammrath, A.; Cheshnovsky, O.; Neumark, D. M. *Science* **2005**, *307*, 93.

(5) Herbert, J. M.; Head-Gordon, M. *J. Phys. Chem. A* **2005**, *109*, 5217.

(6) Lee, H. M.; Lee, S.; Kim, K. S. *J. Chem. Phys.* **2003**, *119*, 187.

(7) Lee, H. M.; Suh, S. B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2005**, *122*, 044309.

(8) Turi, L.; Sheu, W.-S.; Rossky, P. J. *Science* **2005**, *309*, 914.

(9) Shin, J.-W.; Hammer, N. I.; Headrick, J. M.; Johnson, M. A. *Chem. Phys. Lett.* **2004**, *399*, 349.

(10) Hammer, N. I.; Roscioli, J. R.; Bopp, J. C.; Headrick, J. M.; Johnson, M. A. *J. Chem. Phys.* **2005**, *123*, 244311.

(11) Hammer, N. I.; Roscioli, J. R.; Johnson, M. A. *J. Phys. Chem. A* **2005**, *109*, 7896.

(12) Hammer, N. I.; Roscioli, J. R.; Johnson, M. A.; Myshakin, E. M.; Jordan, K. D. *J. Phys. Chem. A* **2005**, *109*, 11526.

(13) Hart, E. J.; Boag, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4090.

(14) Barnett, R. N.; Landman, U.; Cleveland, C. L.; Jortner, J. *J. Chem. Phys.* **1988**, *88*, 4421.

(15) Long, F. H.; Lu, H.; Eisenthal, K. B. *Phys. Rev. Lett.* **1990**, *64*, 1469.

(16) Schwartz, B. J.; Rossky, P. J. *J. Chem. Phys.* **1994**, *101*, 6917.

(17) Silva, C.; Walhout, P. K.; Yokoyama, K.; Barbara, P. F. *Phys. Rev. Lett.* **1998**, *80*, 1086.

(18) Kambhampati, P.; Son, D. H.; Kee, T. W.; Barbara, P. F. *J. Phys. Chem. A* **2002**, *106*, 2374.

(19) Baltuška, A.; Emde, M. F.; Pshenichnikov, M. S.; Wiersma, D. A. *J. Phys. Chem. A* **1999**, *103*, 10065.

(20) Pshenichnikov, M. S.; Baltuška, A.; Wiersma, D. A. *Chem. Phys. Lett.* **2004**, *389*, 171.

(21) Beyer, M. K.; Fox, B. S.; Reinhard, B. M.; Bondybey, V. E. *J. Chem. Phys.* **2001**, *115*, 9288.

(22) *Radiation Chemistry*; Farhataziz, Rodgers, M. A. J., Eds. VCH Publishers: New York, 1987.

(23) Garrett, B. C.; Dixon, D. A.; Camaioni, D. M.; Chipman, D. M.; Johnson, M. A.; Jonah, C. D.; Kimmel, G. A.; Miller, J. H.; Rescigno, T. N.; Rossky, P. J.; Xantheas, S. S.; Colson, S. D.; Laufer, A. H.; Ray, D.; Barbara, P. F.; Bartels, D. M.; Becker, K. H.; Bowen, H.; Bradforth, S. E.; Carmichael, I.; Coe, J. V.; Corrales, L. R.; Cowin, J. P.; Dupuis, M.; Eisenthal, K. B.; Franz, J. A.; Gutowski, M. S.; Jordan, K. D.; Kay, B. D.; LaVerne, J. A.; Lymar, S. V.; Madey, T. E.; McCurdy, C. W.; Meisel, D.; Mukamel, S.; Nilsson, A. R.; Orlando, T. M.; Petrik, N. G.; Pimblott, S. M.; Rustad, J. R.; Schenter, G. K.; Singer, S. J.; Tokmakoff, A.; Wang, L. S.; Wittig, C.; Zwier, T. S. *Chem. Rev.* **2005**, *105*, 355.

(24) Coe, J. V.; Lee, G. H.; Eaton, J. G.; Arnold, S. T.; Sarkas, H. W.; Bowen, K. H.; Ludewigt, C.; Haberland, H.; Worsnop, D. R. *J. Chem. Phys.* **1990**, *92*, 3980.

(25) Hammer, N. I.; Shin, J.-W.; Headrick, J. M.; Diken, E. G.; Roscioli, J. R.; Weddle, G. H.; Johnson, M. A. *Science* **2004**, *306*, 675.

(26) Kammrath, A.; Verlet, J. R. R.; Bragg, A. E.; Griffin, G. B.; Neumark, D. M. *J. Phys. Chem. A* **2005**, *109*, 11475.

(27) Sommerfeld, T.; Jordan, K. D. *J. Am. Chem. Soc.* In press.

(28) Paul, J. B.; Provencal, R. A.; Chapo, C.; Roth, K.; Casaes, R.; Saykally, R. J. *J. Phys. Chem. A* **1999**, *103*, 2972.

(29) Arnold, S. T.; Morris, R. A.; Viggiano, A. A.; Johnson, M. A. *J. Phys. Chem.* **1996**, *100*, 2900.

(30) Ayotte, P.; Weddle, G. H.; Kim, J.; Johnson, M. A. *Chem. Phys.* **1998**, *239*, 485.

(31) Klots, C. E. *Z. Phys. D: At., Mol. Clusters* **1987**, *5*, 83.

(32) Klots, C. E. *J. Chem. Phys.* **1985**, *83*, 5854.

(33) Posey, L. A.; DeLuca, M. J.; Johnson, M. A. *Chem. Phys. Lett.* **1986**, *131*, 170.

(34) Johnson, M. A.; Lineberger, W. C. In *Techniques for the Study of Ion−Molecule Reactions*; Farrar, J. M., Saunders, W. H. J., Eds.; Wiley: New York, 1988; Vol. XX, p 591.

(35) *NIST Chemistry WebBook*; National Institute of Standards and Technology: Gaithersburg, MD, 2001.

(36) Campagnola, P. J.; Cyr, D. M.; Johnson, M. A. *Chem. Phys. Lett.* **1991**, *181*, 206.

(37) Tsai, C. J.; Jordan, K. D. *J. Phys. Chem.* **1993**, *97*, 11227.

(38) Tharrington, A. N.; Jordan, K. D. *J. Phys. Chem* **2003**, *107*, 7380.

(39) Herbert, J. M. International Symposium on Molecular Spectroscopy, 2005, Columbus, OH.