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Photoelectron spectroscopy of sodium iodide clusters containing single hydroxyl ions or water molecules

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We have obtained photoelectron spectra of mixed clusters $(\mathrm{NaI})_n\mathrm{Na}_m\mathrm{OH}^-$ $(n=2,3,\ m=1,2,3)$ and $(\mathrm{NaI})_n\mathrm{H}_2\mathrm{O}^-$ $(n=3,4,6)$. Comparison with results obtained for pure sodium iodide clusters provides a microscopic view of the initial stages of the solvation process. We find that an $(\mathrm{NaI})_n\mathrm{Na}_m\mathrm{OH}^-$ cluster incorporates the OH^- ion in the same way it would an I^- ion, whereas an $(\mathrm{NaI})_n\mathrm{H}_2\mathrm{O}^-$ cluster appears to accommodate its intact water molecule on the edge of its ionic lattice.

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I. INTRODUCTION

Studies of the interactions of alkali-halide clusters with hydroxyl ions and water molecules offer insight into both the fundamental processes of molecular solvation and the effects of spatially varying electric fields on polar molecules. The presence of more and more adsorbed water molecules must eventually cause alkali-halide clusters to dissociate and dissolve, even as those clusters position and orient the polar adsorbate molecules around themselves. The possibility of a water molecule itself dissociating complicates solvation and makes it necessary to understand the interactions of hydroxyl ions with alkali-halide clusters. In addition to their academic interest, such studies relate to effects that occur frequently in our atmosphere and can thus find application in atmospheric chemistry [1,2].

Despite these motivations, such systems have not been extensively studied. While several calculations concerning $(MX)\mathrm{H}_2\mathrm{O}$ systems exist [3–7], where M is an alkali atom and X is a halogen atom, only two theoretical reports have examined clusters with more than one alkali-halide monomer unit [8,9]. Experimental detection of such systems has proved relatively difficult. To date, only measurements of the abundances of $\mathrm{Na}_n(\mathrm{OH})_m$ clusters [10] and of the adsorption reactivity between $(\mathrm{NaF})_n\mathrm{Na}^+$ clusters and $\mathrm{H}_2\mathrm{O}$ [11], as functions of cluster size, have been reported in the literature. The study of alkali-halide solvation itself has been performed only with alcohol as the solvent [12], and not with water.

To help improve the understanding of how alkali-halide clusters interact with hydroxyl ions and water molecules, we conducted a systematic study of those combined systems. Using a laser-based cluster source, we performed photoelectron spectroscopy on two types of mixed clusters: $(\mathrm{NaI})_n\mathrm{Na}_m\mathrm{OH}^-$ $(n=2,3,\ m=1,2,3)$ and $(\mathrm{NaI})_n\mathrm{H}_2\mathrm{O}^-$ $(n=3,4,6)$. Among the quantities revealed by these measurements are each cluster's electron vertical binding energy (EVBE) — the energy difference between the ground electronic state of the anionic cluster and the ground electronic state of the neutral cluster in the geometry of the anion cluster [13]. EVBEs are found by locating intensity maxima in the photoelectron spectra. Since EVBEs can also be predicted by calculations, we can combine our measurements with theory to identify each cluster's geometry and the manner in which it accommodates excess electrons.

Our results indicate that $(\mathrm{NaI})_n\mathrm{Na}_m\mathrm{OH}^-$ systems use the hydroxyl ion as a substitute for a halogen ion. The EVBEs, when compared to experimental and theoretical EVBEs of pure alkali-halide clusters, allow us to assign spatial structures to the mixed systems. Photoelectron spectra of $(\mathrm{NaI})_n\mathrm{H}_2\mathrm{O}^-$ systems are consistent with a model in which an intact water molecule is bound to an edge of the ionic lattice.

II. EXPERIMENT

The clusters we study are produced in a room-temperature laser vaporization cluster source [14] from compacted sodium iodide powder. Before compaction, sodium iodide's hygroscopic character causes ambient water vapor to adsorb to the loose powder and to donate hydroxyl ions through dissociation. That situation persists even after the pressed sample is placed in the vacuum chambers used for the experiment itself.

To form clusters, the pulsed beam from an ArF excimer laser (193 nm) strikes the surface of the sodium iodide disk and sends a plume of vapor into a narrow, helium-filled channel. Helium is injected into this channel by a pulsed valve just prior to the laser pulse. The mixed vapor then travels about 1 cm before undergoing a free-jet expansion into the surrounding vacuum. The final cluster abundances in the resulting molecular beam are determined by cluster growth and decay dynamics within the channel [14–16].

After leaving the channel, the beam of clusters passes through a skimmer to a tilted-plate time-of-flight mass spectrometer [17]. The pulsed field plates of the mass spectrometer extract the cluster anions and direct them toward a magnetic bottle photoelectron spectrometer [18]. The cluster anions disperse in time according to their charge-to-mass ratios and a dual microchannel plate detector located just beyond the spectrometer entrance allows us to observe the arriving anions. We find that they include both pure sodium iodide clusters $(\mathrm{NaI})_n\mathrm{Na}_m^-$ and mixed clusters $(\mathrm{NaI})_n\mathrm{Na}_m\mathrm{OH}^-$ and $(\mathrm{NaI})_n\mathrm{H}_2\mathrm{O}^-$.

When the clusters that we wish to study pass through the magnetic bottle, we expose them to the beam of a pulsed Nd:YAG (Yttrium Aluminum Garnate) laser. Photons from

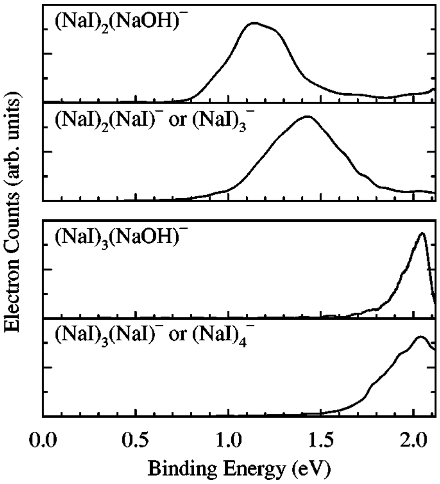

FIG. 1. Photoelectron spectra of $(NaI)_n(NaOH)^-$ and $(NaI)_n(NaI)^-$ ($n=2,3$). Although only the portion of each spectrum below 2.1 eV binding energy is shown, the $(NaI)_n(NaOH)^-$ spectra were taken with 2.33 eV photons and the $(NaI)_n(NaI)^-$ spectra were taken with 3.49 eV photons.

this beam photodetach electrons, which then travel through the electron spectrometer to a second dual microchannel plate detector. We determine the kinetic energies of photodetached electrons from their travel times through the spectrometer. By subtracting their kinetic energies from the photon energy, we are able to determine how much energy was needed to remove each electron from its cluster anion. We record a large number of photodetachment events to obtain a complete photoelectron spectrum.

All of the clusters were studied with 2.33 eV photons from the second-harmonic beam of the Nd:YAG laser. However, $(NaI)_n^-$ and $(NaI)_3Na_2^-$ clusters were also probed with 3.49 eV photons from the laser's third harmonic beam. That higher photon energy allowed us to look at more deeply bound electrons that lie at or beyond the 2.33 eV cutoff of the second-harmonic light. Nonetheless, for ease of comparison with other spectra, only the lower binding-energy portions of these spectra are shown in the figures.

III. RESULTS AND DISCUSSION

A. $(NaI)_nNa_mOH^-$ clusters

Photoelectron spectra for five $(NaI)_nNa_mOH^-$ clusters are shown in Figs. 1 and 2. Paired with each of these spectra is another spectrum in which the OH^- ion has been replaced by an I^- ion. The pairs match almost perfectly, except for small shifts in the electron binding energies. Figure 1 shows that $(NaI)_2(NaOH)^-$ and $(NaI)_2(NaI)^-$ both bind an electron weakly, while $(NaI)_3(NaOH)^-$ and $(NaI)_3(NaI)^-$ both exhibit a single photoelectron peak associated with a more tightly bound electron. A similar comparison of spectra can be made for the pairs of clusters shown in Fig. 2. Since photoelectron spectra are quite sensitive to a cluster's mode of electron accommodation and to its overall geometry, these two cluster characteristics appear to be essentially unchanged when an I^- ion is replaced by an OH^- ion. Evidently, these clusters incorporate an OH^- ion in the same manner that they would an I^- ion.

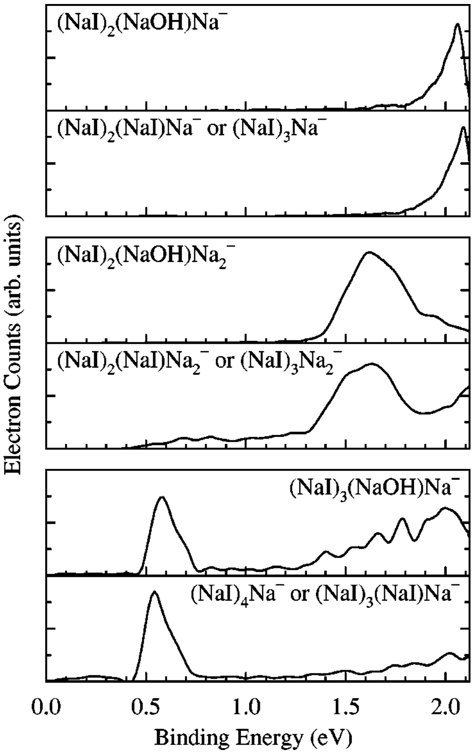

FIG. 2. Photoelectron spectra of $(NaI)_n(NaOH)Na^-$ and $(NaI)_n(NaI)Na^-$ ($n=2,3$) and of $(NaI)_2(NaOH)Na_2^-$ and $(NaI)_2(NaI)Na_2^-$. The $(NaI)_2(NaI)Na_2^-$ spectrum was taken with 3.49 eV photons, while the others were taken with 2.33 eV photons.

Pure sodium-halide cluster anions, containing neither hydroxyl ions nor water molecules, have been extensively studied experimentally and theoretically [13,18–21] and can help us assign ground-state structures to the mixed cluster anions $(NaI)_n(NaOH)Na_m^-$. Mixed clusters of that form consist of $n+m+1$ Na^+ cations, n I^- anions, and $m+1$ excess electrons — that is, electrons not directly associated with any particular ion.

Work on pure sodium-halide clusters identified $(NaI)_2(NaI)^-$ as a 3×2 sheet of ions, with the excess electron bound in a diffuse surface state near the long edge that contains one central I^- ion and two corner Na^+ ions [20]. The anion $(NaI)_3(NaI)^-$ was identified as a 3×3 sheet of ions, with the excess electron occupying the empty corner site that would otherwise be an I^- anion vacancy [13,20]. From the similarities between pairs of spectra in Fig. 1, we believe that $(NaI)_2(NaOH)^-$ and $(NaI)_3(NaOH)^-$ have these same geometries, except that one I^- anion has been replaced by an OH^- anion in each case.

The clusters in Fig. 2 all contain more than one excess electron. The single, high-binding-energy peaks observed in the photoelectron spectra of $(NaI)_2(NaOH)Na^-$ and $(NaI)_2(NaI)Na^-$ are typical of the spin-paired electrons seen in many small alkali-halide clusters with two excess electrons. This electron pair is probably localized in the otherwise vacant corner site of a $2\times2\times2$ cube of ions. That cubic structure has been used to explain similar spectra in $(NaCl)_3Na^-$ [18] and $(KI)_3K^-$ [22].

$(NaI)_2(NaI)Na_2^-$ has been described in terms of an Na_2^- metal ion phase separated from an $(NaI)_3$ hexagonal ring[21]. From the similarities of the spectra, we believe that a similar phase-separated structure exists for $(NaI)_2(NaOH)Na_2^-$.

While $(NaI)_3(NaI)Na^-$ and $(NaI)_3(NaOH)Na^-$ yield similar photoelectron spectra and probably have the same structure, we cannot predict that structure. The spectra are complicated by the fact that the strong photoelectron peaks near 0.5 eV do not originate from the cluster anions themselves. Instead, these peaks come from Na^- ions that are produced during the laser pulse by photofragmentation of the original cluster anions [23]. The similarities that matter most in this pair of spectra are thus the weaker peaks at higher binding energies.

Our results provide an interesting contrast to those obtained by Honea *et al*. [10] in their photoionization mass spectrometry of $Na_n(OH)_m$ aggregates. They obtained mass spectra showing a dominant $Na_n(OH)_{n-1}$ sequence with "magic numbers" at $n=4$, 9, 18, 20, and 24. These "magic" sizes were not the same as those they found in a similar study of alkali-halide clusters, indicating that substitution of OH^- anions for all of the halogen anions produces a new lattice structure. Our results show that substituting a single OH^- anion for a halogen anion does not cause any significant structural rearrangement. These observations agree with predictions by Barnett and Landman [9].

B. $(NaI)_nH_2O^-$ clusters

Photoelectron spectra of $(NaI)_nH_2O^-$ ($n=3,4,6$) cluster anions are shown in Fig. 3, along with spectra for the corresponding water-free sodium iodide cluster anions. For $n=3$ and $n=4$, photoelectron peaks in the water-containing systems are redshifted relative to those obtained from pure sodium iodide clusters of identical *n*. That redshift corresponds to a reduced electron binding energy for the water-containing clusters.

A similar redshift occurs for $n=6$, but is partially masked by an isomer effect: $(NaI)_6^-$ exists in two different isomeric forms that have somewhat different electron affinities. The single peak in $(NaI)_6H_2O^-$ appears to correspond to the higher-binding-energy form of $(NaI)_6^-$ and is slightly redshifted from its position in the water-free cluster anion. The lower-binding-energy form of $(NaI)_6^-$ has no matching peak in the spectrum of $(NaI)_6H_2O^-$, indicating that this isomeric form of the water-containing cluster anion does not exist in our experiment.

While a complete structural understanding of these clusters will require detailed calculations, both $(NaI)_3H_2O^-$ and $(NaI)_4H_2O^-$ probably involve a water molecule attached to one edge of a planar sodium iodide cluster anion. Since $(NaI)_3^-$ consists of a 3×2 ionic sheet, with its excess electron diffusely spread across one edge [20], its opposite edge offers a good binding site for a water molecule. The Na^+ cation in the middle of that opposite edge attracts the water molecule's negatively charged oxygen atom while the two I^- anions at the corners of the sheet attract the molecule's positively charged hydrogen atoms.

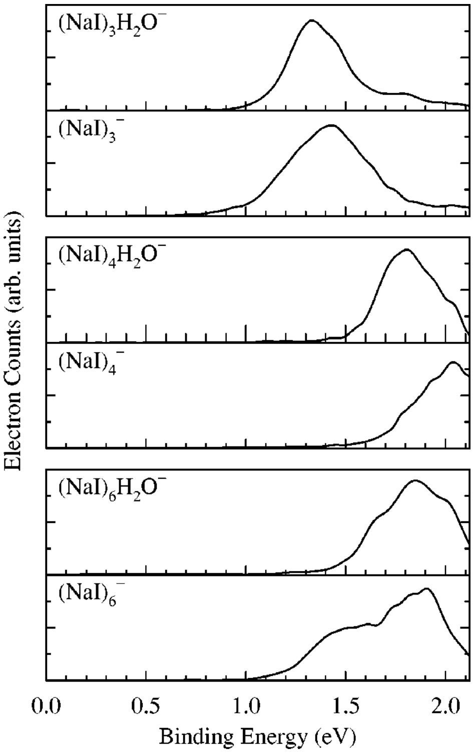

FIG. 3. Photoelectron spectra of $(NaI)_nH_2O^-$ and $(NaI)_n^-$ ($n=3,4,6$). The $(NaI)_nH_2O^-$ spectra were taken with 2.33 eV photons, while the $(NaI)_n^-$ spectra were taken with 3.49 eV photons.

A similar arrangement is likely for $(NaI)_4H_2O^-$. Since the $(NaI)_4^-$ cluster anion forms a 3×3 sheet, with its excess electron occupying the corner anion vacancy, the two edges opposite that anion vacancy are good binding sites for a water molecule. Once again, the edge's central Na^+ cation attracts the molecule's oxygen atom and the two corner I^- anions attract the hydrogen atoms.

Although the calculations performed by Woon and Dunning for $(MX)H_2O$ [7] and the modeling of $(LiF)_2H_2O$ reported by Woon [8] pertain to smaller clusters, those studies provide an interesting background for our experiments. Woon and Dunning's work on alkali-halide monomers examined the relative strength of the binding between H_2O and either an alkali cation or a halogen anion. They found that for both $M^+(H_2O)$ and $X^-(H_2O)$, the binding energy decreases substantially with increasing ion size. At the same time, the corresponding M^+-O and X^--H bond lengths increase with increasing ion size and these changes in bond length carry over to $MX(H_2O)$ systems.

In the clusters we studied, their calculations predict that the Na^+-O bond length should be smaller than the I^--H bond length. Thus the water molecule should orient itself with the negative end of its permanent dipole turned toward the alkali-halide portion of the cluster and its excess electron. That dipole orientation should weaken the electron's attachment to the cluster and redshift the photoelectron spectrum, consistent with the experimental result.

Their calculations also predict a preference for planar, cyclic structures in which the H_2O becomes part of a four-member ring. The ring forms when the water's oxygen atom and one of its hydrogen atoms pair with two of the alkali-halide's oppositely charged atomic ions. For example, $(LiF)_2H_2O$ involves a planar arrangement in which the water molecule attaches to an edge of the rhombic $(LiF)_2$ dimmer [8]. The accommodation of the water molecule on an edge of the alkali-halide system, rather than above the ionic substrate, is consistent with the structures we suggest for $(NaI)_3H_2O^-$ and $(NaI)_4H_2O^-$.

Unfortunately, we cannot predict the structure of $(NaI)_6H_2O^-$, as the structure of $(NaI)_6^-$ is itself unknown. Even calculations on $(NaCl)_6^-$, a simpler alkali-halide system, were only able to predict the most weakly bound portion of that cluster's photoelectron spectrum [20]. Future theoretical work on these systems is encouraged.

IV. CONCLUSION

From our studies of $(NaI)_nNa_mOH^-$ cluster anions, we conclude that the single OH^- ion mimics an I^- ion almost perfectly and that the properties of the resulting mixed cluster anions are essentially unchanged from those of the equivalent pure NaI systems. In contrast, our work with $(NaI)_nH_2O^-$ cluster anions indicates that the H_2O simply attaches itself to a pure NaI particle and orients itself so as to decrease that particle's electron affinity slightly. This lowered electron affinity is consistent with a model in which the water molecule binds to the edge of the ionic lattice and orients the negative end of its permanent dipole toward the weakly attached electron.

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