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Experimental and theoretical studies of single excess electrons in sodium chloride cluster anions

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We have obtained photoelectron spectra for the photodetachment of $(\mathrm{NaCl})_n{}^-$ ($n = 1-13$) cluster anions that are in excellent, quantitative agreement with our calculated values. These anions have a single excess electron attached to a neutral, ionically bound molecule. Their predicted structures, determined by constant-temperature molecular dynamics and simulated annealing, identify three modes for electron attachment. In most cases, the excess electron significantly deforms the cluster anion away from its neutral geometry.

The substantial current interest in ionic clusters with excess electrons[1–9] reflects both their intrinsic value as members of an exotic class of molecules and their conceptual value as model systems in which to study the electron accommodation modes of bulk ionic solids.[10,11] Measuring the electronic binding energies of these clusters can help to clarify our understanding of them. When combined with careful theoretical studies, such measurements can provide considerable insight into the clusters' geometrical and electronic structures and test molecular-level theories for electron accommodation in bulk ionic solids.

In this paper we report photoelectron spectroscopic and theoretical studies of a class of negatively charged clusters $(\mathrm{NaCl})_n{}^-$. Unlike previous studies of similar clusters,[1,2] all the photoelectrons are collected in our experiment, allowing a relatively unambiguous identification of the electron vertical binding energies of the clusters. We have also made systematic calculations of the structures and electron vertical binding energies of the clusters, using simulated annealing and constant-temperature molecular dynamics. Our calculated electron vertical binding energies agree well with the experimental values and identify three very different modes in which various clusters accommodate their extra electrons. These three electron accommodation modes were proposed previously by several other groups.[11,1,2]

We also observed a strong correlation between the experimental abundances of the clusters and their calculated electron adiabatic binding energies. This correlation suggests that our clusters grow by electron attachment to neutral ionic clusters. Furthermore, our calculations show that electron attachment usually induces substantial structural deformation in these clusters and that the neutral and anionic clusters often have quite different spatial structures.

The apparatus used to obtain experimental photoelectron spectra consists of a laser vaporization cluster source, a time-of-flight mass spectrometer, and a magnetic bottle time-of-flight photoelectron spectrometer.[12] Clusters are produced in the source by vaporizing an NaCl sample disk with the focused beam from a 193-nm ArF excimer laser (Lambda Physik EMG103MSC). Cluster anions leaving the source are then dispersed in the mass spectrometer. As mass-selected clusters of a particular size pass through the active region of the electron spectrometer, they are exposed to a brief pulse of 2.33-eV or 3.50-eV photons from a Nd:YAG (yttrium aluminum garnet) laser (Spectra Physics DCR-3). Photodetached electrons are guided along magnetic-field lines in the spectrometer flight tube until they reach a dual-microchannelplate detector.

We determine the kinetic energies of the photoelectrons from their flight times through the electron spectrometer. We can obtain each electron's binding energy (the energy used to remove the electron from the cluster) by subtracting that electron's measured kinetic energy from the photon energy. Repeating such measurements for a great many photodetachment events produces a photoelectron spectrum. Our photoelectron spectra are calibrated using the known electron affinities of K^- and Na^-. A full set of photoelectron spectra for $(\mathrm{NaCl})_n{}^-$ cluster anions ($n = 1-13$) will be published separately.[12] These spectra do not resolve vibrational structure.

The electron vertical binding energy of a cluster anion is defined as the difference between the ground-state energy of that anion and the energy of a neutral cluster having the same (unrelaxed) geometry as the anion but without the extra electron. Because electron photodetachment gives a cluster anion little time for structural rearrangement as the electron leaves, a peak in the cross section occurs when no relaxation is required during photodetachment. Much of the width of each peak in an experimental photoelectron spectrum comes from quantum-mechanically-allowed rearrangements of the ions during photodetachment. The shape of each peak is determined by Franck-Condon coefficients between the anion's ground state and various vibrationally excited states of the resulting neutral cluster. The peak in the Franck-Condon profile occurs when very little rearrangement is required and corresponds to the electron vertical binding energy. Thus, we obtain experimental electron vertical binding energies by locating intensity maxima in the photoelectron spectra.

Theoretically, we view each cluster as a collection of sodium cations, chlorine anions, and one electron.[13] The ions are treated as classical particles, while the electrons are handled quantum mechanically. The interactions between ions are modeled by a pairwise long-range Coulomb interaction term and a Born-Mayer repulsive term.[14] A smooth version of the Shaw pseudopotential is chosen as the electron-ion potential.[15]

The motion of the ions is described by classical molecular dynamics. The electron wave function is defined on a grid of 16^3 uniformly spaced points, with a grid spacing of 1.8 a.u. The electron is assumed to be in the ground state of the instantaneous ionic configuration. The initial electron wave function is obtained by evolving a randomly generated wave function in imaginary time, using the fast-Fourier-transformation method. Subsequent evolution of the ions and the electron wave function is followed with Car-Parinello molecular dynamics for the electron.[16] The temperature of the system is maintained by regularly scaling the ion velocities and by collisions. The initial temperature of 1500 K is gradually lowered at a rate of 10^{-5} T every molecular dynamics step (each step takes 20 a.u.). When the temperature has reached approximately 100 K, the minimum energy configuration is found by the steepest-descent method. The electron vertical binding energy can then be calculated from the resulting structure.

Table I lists the measured and calculated electron vertical binding energies of the cluster anions $(NaCl)_n{}^-$ ($n = 1-13$). These clusters are classified into three types according to their electron-accommodation modes, as determined by our structural calculations. These three electron-accommodation modes are the following: *Type 1*, the electron localized about a single Na^+ ion to form a polarized neutral atom; *Type 2*, the electron occupying an anion vacancy in a cubic lattice to form the microscopic equivalent of an *F* color center in the bulk; and *Type 3*, the electron residing on the surface of the cluster, not associated with either a vacancy or a specific Na^+ ion.

The $(NaCl)_5{}^-$ cluster anion is an example of the Type-1 electron-accommodation mode: the electron localized about a single Na^+ ion. The calculated structure of this species appears in Fig. 1(a), together with its experimental and theoretical photoelectron spectra. The calculated electron vertical binding energy is 2.14 eV, in excellent agreement with the experimental result of 2.19 eV. The theoretical spectrum is produced by following the electron vertical binding energy with constant-temperature molecular dynamics at 100 K. The theoretical spectrum is narrower than the experimental result because it includes only thermal broadening effects. The theory treats the ions classically and cannot reproduce the broader Franck-Condon profile[17] that should reflect the quantum nature of the ions. The experimental spectrum is also broadened somewhat by the limited instrumental resolution.

As shown in Fig. 1(a), four of the sodium cations and the five chlorine anions in $(NaCl)_5{}^-$ form a slightly distorted 3 × 3 square lattice. The remaining sodium cation is almost neutralized by the excess electron, becoming a polarized atom that is bound to one of the corner chlorine ions. The binding energy of the electron in this and other Type-1 clusters is very high. Of the five Type-1 clusters listed in Table I, only $(NaCl)_7{}^-$ has an electron vertical binding energy of less than 2.0 eV. The reason for the relatively low electron affinity of $(NaCl)_7{}^-$ (1.44 eV measured and 1.34 eV calculated) is that its polarized sodium atom has not one but two nearby Cl^- anions. The sodium atom is thus highly polarized and binds the extra electron somewhat less strongly than in the other Type-1 cluster anions.[13]

The $(NaCl)_{13}{}^-$ cluster anion is an example of the Type-2 electron-accommodation mode: the electron occupies a chlorine anion vacancy in a cubic lattice. The

TABLE I. Measured and calculated electron vertical binding energies of the clusters $(NaCl)_n{}^-$, for $n = 1-13$. Clusters are classified into three types according to their electron accommodation modes (see text). All energies are in eV. The experimental uncertainty is approximately ±0.05 eV.

	E_{exp}	E_{cal}		E_{exp}	E_{cal}
		Type-1 clusters			
$(NaCl)_5{}^-$	2.19	2.15	$(NaCl)_9{}^-$	2.05	2.28
$(NaCl)_7{}^-$	1.44	1.34	$(NaCl)_{10}{}^-$	2.40	2.45
$(NaCl)_8{}^-$	1.98	2.03			
		Type-2 clusters			
$(NaCl)_1{}^-$	0.75	0.92	$(NaCl)_{11}{}^-$	1.63,2.10	1.88,2.05
$(NaCl)_2{}^-$	1.55	1.58	$(NaCl)_{13}{}^-$	1.98	1.99
$(NaCl)_4{}^-$	1.72	1.65			
		Type-3 clusters			
$(NaCl)_3{}^-$	1.06	0.89	$(NaCl)_6{}^-$	0.18,1.66	0.025

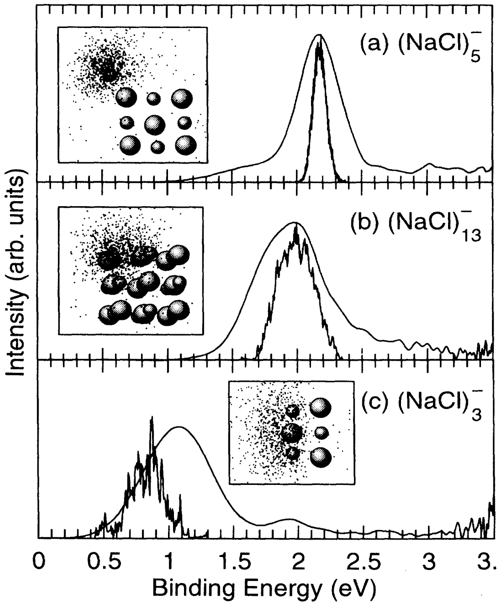

FIG. 1. Experimental and theoretical photoelectron spectra for (a) $(NaCl)_5{}^-$, (b) $(NaCl)_{13}{}^-$, and (c) $(NaCl)_3{}^-$ cluster anions, along with their predicted structures at 100 K. The broad, smooth curves are the experiment, the jagged curves are the theory. The large spheres are Cl^- and the small spheres are Na^+. These three cluster anions are representative of the three types of electron accommodation in such clusters. Only the rectangular isomer of $(NaCl)_3{}^-$ is considered for the theoretical curve in (c).

calculated structure of this species appears in Fig. 1(b), along with its experimental and theoretical photoelectron spectra. The experimental (1.96 eV) and theoretical (1.99 eV) electron vertical binding energies are in excellent agreement. As shown in Fig. 1(b), the 26 atomic ions and single excess electron form a complete 3 × 3 × 3 cube, with the electron occupying one corner lattice site.

Five of the clusters listed in Table I accommodate their excess electrons by forming *F* color centers in the manner of $(\mathrm{NaCl})_{13}{}^-$. One of these species, $(\mathrm{NaCl})_{11}{}^-$, was not expected to accommodate an electron as an *F* color center because it cannot form a perfect cuboid. Instead, its ions form a 2 × 3 × 3 cuboid with an L-shaped four-atom cap on its face. Surprisingly, we calculate that the electron occupies an anion vacancy adjacent to that cap, a prediction supported by the moderately good agreement between the experimental (1.60 eV) and theoretical (1.88 eV) electron vertical binding energies. A second peak in the experimental spectrum at a binding energy of 2.10 eV indicates the probable existence of an isomer of $(\mathrm{NaCl})_{11}{}^-$. This observation is supported by our theoretical prediction of a near-ground-state isomer with an electron vertical binding energy of 2.05 eV.

In the final mode of electron accommodation, Type 3, the electron is delocalized on the surface of the cluster. Only two of the clusters listed in Table I belong to Type 3. Figure 1(c) contains a calculated structure for one of these species, $(\mathrm{NaCl})_3{}^-$, and its experimental and theoretical photoelectron spectra. The calculated electron vertical binding energy for this 2 × 3 rectangle plus electron is 0.89 eV, very close to the measured value of 1.05 eV.

However, the calculation predicts a second, linear isomer of $(\mathrm{NaCl})_3{}^-$ with essentially the same overall binding energy as the rectangular form. This linear isomer has a much larger vertical electron binding energy than is observed experimentally, so that we do not believe that it occurs commonly in the experiment. The model potentials used in the calculations are approximate and the diffuse nature of the electron in Type-3 clusters makes theoretical studies of these clusters very susceptible to imperfections in the model. The rectangular isomer appears to be the true ground state of $(\mathrm{NaCl})_3{}^-$ and we have chosen to report the vertical electron binding energy of that isomer in Table I. While generating the theoretical electron binding energy spectrum in Fig. 1(c), we considered only thermally excited $(\mathrm{NaCl})_3{}^-$ clusters of the rectangular form.

In both Type-3 clusters, the electrons are relatively weakly attached. $(\mathrm{NaCl})_6{}^-$ is predicted to have an electron vertical binding energy of only 0.025 eV, slightly less than the experimental value of 0.16 eV. A second photoelectron peak at 1.66 eV indicates the presence of an isomer of $(\mathrm{NaCl})_6{}^-$ with a much larger electron affinity and almost certainly a different mode of accommodating the electron. We have not yet identified a theoretical candidate for this second isomer. A very similar pair of peaks was reported in the photoelectron spectrum of $(\mathrm{KI})_6{}^-$.[6]

One additional observation we can make concerns the relationships between the cluster anions and the associated neutral clusters. Our calculations indicate that in almost all cases, the attachment of an electron substantially distorts the neutral cluster. Thus, anions usually have spatial structures that are significantly different from the neutrals and the photoelectron spectra should be treated only as measures of electron vertical binding energies and not electron adiabatic binding energies. The outgoing photoelectron almost certainly leaves behind a neutral cluster that is far from its ground-state in both structure and energy.

As an example of the dramatic distortions that may occur between the neutral and anionic form of a particular cluster, consider the ground-state structures of $(\mathrm{NaCl})_4$ and $(\mathrm{NaCl})_4{}^-$. $(\mathrm{NaCl})_4$ is a 2×2×2 cube of ions with an electron affinity close to zero. However, add an electron and it becomes $(\mathrm{NaCl})_4{}^-$, a 3 × 3 sheet with the electron occupying a corner lattice site. The electron vertical binding energy of this sheet-shaped *F* color center anion is 1.72 eV experimentally and 1.65 eV theoretically.

Thus the experimental photoelectron spectra give us the electron vertical binding energies but usually provide little information about the electron adiabatic binding energies. Measuring the threshold energy for electron photodetachment is of little value.[18] It merely identifies the detectable edge of the Franck-Condon overlap between the anion and neutral structures, a measure of neither the vertical nor adiabatic binding energies.

We find that the experimental abundances of the cluster anions $(\mathrm{NaCl})_n{}^-$ ($n = 1 - 13$) [Fig. 2(a)] are closely correlated to their calculated electron adiabatic binding energies [Fig. 2(b)], indicating that adiabatic electron attachment to neutral clusters may be the primary mechanism for forming the cluster anions in our cluster source. It is not unreasonable to assume that the abundances of neutral, fully ionic clusters in the source do not depend strongly on cluster size and that the main limitation on the production of $(\mathrm{NaCl})_n{}^-$ anions is their ability to attract electrons through various charge exchange mechanisms. These two assumptions lead us to expect more of clusters that have large adiabatic electron affinities and less of clusters that have small adiabatic electron affini-

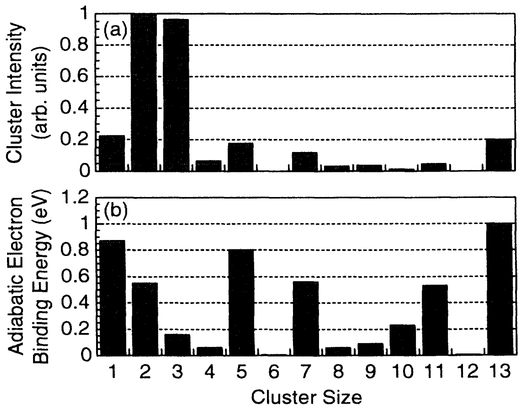

FIG. 2. (a) The experimental abundances of $(\mathrm{NaCl})_n{}^-$ cluster anions and (b) the calculated electron adiabatic binding energies for these same clusters.

ties. That is exactly what we observed in the distribution of cluster anions produced by our source.

Of course, the populations of neutral clusters are not truly independent of cluster size. Neutral $(NaCl)_3$ is predicted to be particularly strongly bound[19,20] so that it should be unusually abundant in our source. That may explain why $(NaCl)_3{}^-$ is so common, despite its relatively modest electron adiabatic binding energy.

In summary, we have made experimental and theoretical studies of the behavior of sodium chloride clusters with single excess electrons, $(NaCl)_n{}^-$. We find three different modes of electron accommodation in these clusters. In many cases, the electron localizes near a specific Na^+ cation to form a polarized neutral sodium atom. In many other cases, the electron occupies an anion vacancy in an ionic cluster lattice, forming an F color center. In a small number of cases, the electron is weakly attached to the cluster in a surface state. Regardless of accommodation mode, the electron's presence usually induces a significant deformation in the cluster's structure. We find a good correlation between the calculated electron adiabatic binding energies and the abundances of these cluster anions, suggesting that they are formed in our source by electron attachment to neutral clusters.

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