Accommodation of Two Excess Electrons in Sodium Chloride Cluster Anions

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We report photoelectron spectra of sodium chloride cluster anions, $(NaCl)_nNa^-$ (n = 1–21), which contain two excess electrons. We observe three distinct types of spectra, corresponding to three different modes for accommodating the two electrons. Our evidence suggests that, in some clusters, the electrons form spin pairs that either occupy a single anion vacancy as an F' color center or localize on a Na^+ cation to form a Na^- anion. In other clusters, the two electrons separately occupy a pair of anion vacancies as a double F color center.

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Recent studies have significantly increased our understanding of how a single excess electron is accommodated in an alkali-halide cluster [1–7]. These experiments and calculations provide insight both into the properties of an interesting class of ionic molecules and into how single-electron defects in ionic solids develop out of molecular structure. To a good approximation, such clusters can be viewed as having a single, quantum-mechanical electron residing in or on the surface of a lattice of classical ions.

In this paper, we extend such studies to alkali-halide clusters with two excess electrons and investigate the behavior of a pair of electrons as they interact with a small ionic lattice. The clusters we have studied are $(NaCl)_nNa^-$ (n = 1–21), which consist of n Cl^- anions, $n+1$ Na^+ cations, and two weakly attached electrons. In addition to being the simplest ionic clusters in which exchange effects are important, these metal-atom rich, two-electron systems reside in the middle ground between alkali-halide clusters and alkali metal clusters. Thus, they are also useful in our understanding of metal-insulator transitions in finite systems.

In alkali/alkali-halide melts, interactions between the ions and excess electrons have been investigated for decades [8]. In the extremely dilute limit, it has been established that the excess electrons localize in anion vacancies, forming structures that are the liquid-state counterpart to F color centers in solids. As the metal concentration increases, the density of excess electrons also increases and there is strong evidence for aggregates of F color centers, electron spin pairing, and eventually metal liquid and nonmetal liquid phase separation [9,10]. However, to date, relevant experimental and theoretical studies on finite cluster systems have been scarce [7].

We have studied the structures of $(NaCl)_nNa^-$ (n = 1–21) cluster anions using visible and ultraviolet photoelectron spectroscopy. We observe three distinct types of photoelectron energy spectra, reflecting three distinct modes of electron accommodation in the cluster anions. These experimental results suggest that two excess electrons in certain sodium chloride cluster anions are spin paired, localizing in a single anion vacancy or on one Na^+ cation to form a Na^- anion. Measurements in other cluster anions indicate that the two excess electrons occupy two different anion vacancies as a double F color center.

Our experimental apparatus combines a laser vaporization cluster source (LVCS), a time-of-flight mass spectrometer, and a magnetic bottle time-of-flight photoelectron spectrometer [11]. The pulsed negative cluster beam is generated in the LVCS, using a Lambda-Physik EMG103MSC ArF excimer laser as the light source. Mass-selected cluster anions are photodetached by a Spectra Physics DCR-3 Nd:YAG laser with photon energies of 2.336 and 3.504 eV. The photodetached electrons are guided along a magnetic bottle time-of-flight tube to a dual-microchannel plate detector. The kinetic energies of the photoelectrons are determined by their flight time and the binding energies of the electrons are obtained by subtracting their kinetic energies from the photon energy. The measured electron vertical binding energies (EVBEs) of the clusters are obtained by locating intensity maxima in the photoelectron spectra [5]. All photoelectron spectra are calibrated by the known electron affinities of K^- and Na^-.

Table I lists the EVBEs for $(NaCl)_nNa^-$ (n = 1–21) cluster anions. When the spectra of a particular cluster anion contains two or more intensity maxima, each peak is reported as a separate EVBE. Several cluster anions in this sequence are not produced in sufficient quantity to permit accurate measurements and are omitted. Other clusters are produced in quantities sufficient only for measurements at 2.336 eV but not 3.504 eV.

The clusters in Table I are grouped into three types, according to the characteristics of their photoelectron spectra. Type I clusters are characterized by a single peak with a large EVBE. Type II clusters have two EVBEs, the first of which is at approximately 0.5 eV. Type III clusters also have two EVBEs, but the first EVBE is above 0.5 eV and the gap between the two EVBEs is between 0.65 and 1.0 eV. To illustrate these three types of photoelectron spectra, Fig. 1 shows the results for $(NaCl)_3Na^-$, $(NaCl)_9Na^-$, and $(NaCl)_{12}Na^-$, which are type I, II, and III clusters, respectively.

While a full understanding of these spectra will require extensive theoretical calculations, we can draw from the

TABLE I. The electron vertical binding energies (EVBEs) for $(NaCl)_nNa^-$ cluster anions. All energies are in eV. The clusters are grouped into three types, according to the characteristics of their photoelectron spectra (see text). Some larger clusters could not be studied with 3.504 eV light, so that EVBEs above 2.3 eV could not be located precisely.

Type I clusters	EVBE		Type III Clusters	EVBE I	EVBE II
$(NaCl)_2Na^-$	2.39		$(NaCl)_1Na^-$	0.98	1.70
$(NaCl)_3Na^-$	2.02		$(NaCl)_6Na^-$	1.38	2.04
$(NaCl)_5Na^-$	1.95		$(NaCl)_{12}Na^-$	1.48	2.19
$(NaCl)_7Na^-$	2.29		$(NaCl)_{21}Na^-$	0.97	1.97
Type II clusters	EVBE I	EVBE II and III		EVBE I	EVBE II&III
$(NaCl)_4Na^-$	0.67	2.55	$(NaCl)_{13}Na^-$	0.59	2.83
$(NaCl)_8Na^-$	0.63	2.45	$(NaCl)_{16}Na^-$	0.60	1.12,>2.3
$(NaCl)_9Na^-$	0.51	2.78	$(NaCl)_{17}Na^-$	0.54	>2.3
$(NaCl)_{11}Na^-$	0.53	2.05,2.65	$(NaCl)_{19}Na^-$	0.61	>2.3

work on alkali/alkali-halide melts to formulate a likely explanation for what we observe. Theoretical calculations concerning such melts predict that, at low metal concentrations, two electrons with antiparallel spins have a strong tendency to attract one another and form a single-center localized state, called a bipolaron (equivalent to an F' color center in bulk solids). In contrast, two electrons with parallel spins repel one another and form two distinct F color-center states [10]. For the particular case of sodium/sodium-halide solutions, two electrons with antiparallel spins can also localize about Na^+ cations to form a Na^- anion or a Na_2 dimer [8,12].

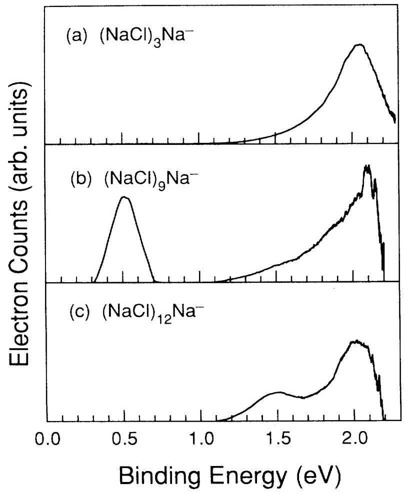

FIG. 1. Three examples of photoelectron spectra taken with 2.336 eV detaching photons: (a) a type I cluster anion, $(NaCl)_3Na^-$, having an electron spin pair localized in a single anion vacancy as an F' color center; (b) a type II cluster anion, $(NaCl)_9Na^-$, having an electron spin pair localized on a Na^+ cation to form a Na^- anion; and (c) a type III cluster anion, $(NaCl)_{12}Na^-$, having two spin-parallel electrons localized at separate anion vacancies as a double F color center. The abrupt ends of the spectra above about 2.2 eV are caused by the 2.336 eV photon energy limit. The spectra continue when 3.504 eV photons are used.

Based on the photoelectron spectra and the alkali/alkali-halide melt calculations, we propose that the two excess electrons in a type I cluster form a spin pair, localized in a single anion vacancy as the cluster equivalent of a bipolaron in a melt or an F' color center in a bulk solid. Because the two electrons occupy a single molecular orbital, they are equivalent and produce only a single feature in the photoelectron spectrum. The four type I clusters we observe can each form a simple cuboid or hexagonal ring structure if the electron pair occupies a single lattice site. For example, $(NaCl)_3Na^-$ can form a 2 × 2 × 2 cube, consisting of four Na^+ cations, three Cl^- anions, and the electron spin pair. Clusters with complete cuboid structures or stacked hexagonal rings are very tightly bound [13,14], permitting the two electrons to overcome their mutual Coulomb repulsion and occupy a single orbital. Because the two equivalent electrons in type I clusters complete very stable structures and have three Na^+ cations as nearest neighbors, they are very tightly bound. Each such cluster exhibits only one large EVBE. While it may be possible to leave the remaining electron in an excited molecular orbital, that orbital should lie several eV above the ground state and beyond the reach of our experimental energies [11].

Further evidence for this structural interpretation of type I clusters is the remarkable abundance of these clusters in our beam. The mass spectrum in Fig. 2 shows that $(NaCl)_3Na^-$ is by far the most abundant species we observe among the negative ions. It is even more abundant than fully ionic species of similar mass, such as $(NaCl)_3Cl^-$. Thus $(NaCl)_3Na^-$ not only has a single, large EVBE, it is also very tightly bound. The 2 × 2 × 2 cubic structure, incorporating an F' color center, is the only structure that satisfies these requirements.

Two spin-antiparallel electrons can also localize on a Na^+ cation, forming a Na^- anion. We believe that type II clusters accommodate their two excess electrons in this manner. The photodetachment threshold energy for Na^- is 0.548 eV [15], very close to the first EVBE in type II clusters. This similarity suggests that type II clusters actually have a Na^- anion attached to an otherwise normal

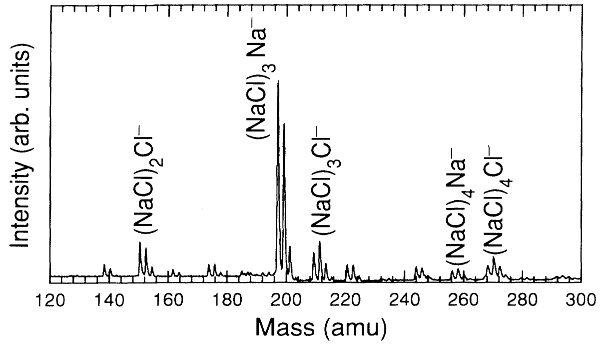

FIG. 2. A mass spectrum of cluster anions produced by our laser vaporization cluster source. Despite its complicated composition, which includes two excess electrons, $(NaCl)_3Na^-$ is by far the most abundant cluster anion we observe. This abundance reflects its unique stability as a 2 × 2 × 2 cube with the pair of excess electrons occupying a single site in that cube. The multiplet structure is due to the two isotopes of chlorine.

ionic lattice. The photodetachment process removes one of the electrons from the Na^-, leaving the other electron in either the 3*s* atomic ground state or the 3*p* excited state, about 2.1 eV to higher energy. The second EVBE in type II cluster anions, observed approximately 2.1 eV above the first EVBE, is due to photodetachment events in which the Na atom is left in the 3*p* excited state.

If you omit one Na^+ and both excess electrons, many of the type II clusters listed in Table I form complete cuboids or stacked hexagonal rings. For example, $(NaCl)_9Na^-$ without one Na^+ and the two electrons becomes a stack of three hexagonal rings. Adding the Na^+ and the two electrons does little to improve the stability of such cuboid structures. Thus, it is not unreasonable for these three unwanted items to group together as a Na^- anion, weakly attached to the otherwise neutral cuboid or stack of hexagonal rings.

At least two of the type II clusters, $(NaCl)_{11}Na^-$ and $(NaCl)_{16}Na^-$, exhibit an additional EVBE between the two associated with the Na^- anion. We attribute this extra EVBE to isomeric content in the beam, with the second, minority isomer being of type III, which is discussed in the next paragraph.

Type III clusters also exhibit two distinct EVBEs, separated by 0.65 to 1.00 eV, which we attribute to two inequivalent final states of the neutral cluster following photodetachment. But unlike type I or II clusters, we suspect that type III clusters accommodate the two extra electrons at separate sites. Whether these electrons are spin parallel or antiparallel depends on exactly how those electrons interact with each other and with the rest of the cluster and cannot be determined without detailed structure and electronic calculations. These electrons can either occupy anion vacancies as *F* color centers or they can reside on Na^+ cations to form polarized, neutral atoms. Supporting this interpretation of the spectra is the fact that the four type III clusters listed in Table I will all form cuboid structures if the two electrons separately occupy anion vacancies. For example, $(NaCl)_{12}Na^-$ can form a 3 × 3 × 3 cube composed of thirteen Na^+ cations, twelve Cl^- anions, and the two electrons. $(NaCl)_1Na^-$ is most likely a chain, with the electrons at either end of a $Na^+Cl^-Na^+$ sequence. Whether the electrons in $(NaCl)_1Na^-$ occupy lattice sites or form polarized Na atoms depends on your point of view.

We can relate these observations in NaCl cluster anions to those observed in KI cluster anions [4] and NaF clusters [16,17]. Photoelectron spectra of $(KI)_3K^-$, $(KI)_5K^-$, and $(KI)_7K^-$ show the same single energy band we observe for NaCl type I clusters, leading Yang *et al.* [4], to suggest that these clusters have electron spin pairs occupying single anion vacancies. Type II clusters are not observed in KI cluster anions [4,11]. Evidently, K^- anions do not form in KI clusters. This observation is in agreement with the studies of alkali/alkali-halide melts, which indicate that Na^- anions and Na_2 dimers are stable in the sodium-based melts, but that analogous anions and dimers do not form in melts of the heavier alkali systems: K, Rb, and Cs [8,12].

Honea [16] found that $(NaF)_{12}Na_2$ is unusually abundant, prompting Rajagopal, Barnett, and Landman [17], to suggest that it is a 3 × 3 × 3 cube with an electron spin pair occupying a single anion vacancy. Miller and Lineberger reported photoelectron spectra of several $(NaF)_nNa^-$ clusters ($n = 5, 7, 12$), using 488 nm detaching radiation [7]. They observed sharp features on top of a diffuse background in the $(NaF)_5Na^-$ photoelectron spectrum. For $(NaCl)_5Na^-$, however, we observe only a single energy band in the spectrum, which we attribute to the two electrons occupying a single anion vacancy. The different features in these two corresponding clusters, as well as the different magic numbers observed in the mass spectra, may be due to differences in cluster generation techniques and cluster internal temperatures [11]. Specific differences in the photoelectron spectra may also be due to differences in ion sizes between Cl^- and F^- and different electronic structures that result from a particular choice of anion.

In summary, we find clear experimental evidence for electron spin pairing states and double *F* color-center states in sodium chloride cluster anions with two excess electrons. These states resemble those found in alkali/alkali-halide melts. In certain clusters, the excess electrons are spin paired, localizing in a single anion vacancy as an *F′* color center or on a Na^+ cation to form a Na^-. In other clusters, the excess electrons are localized at separate sites. These sites can include anion vacancies, where they form *F* color centers, and Na^+ cations, which become polarized, neutral Na atoms. We find four cluster anions in which a pair of *F* color centers appear to be present. We also find evidence for isomers of at least two cluster anions, with one isomer having its two excess electrons localized on a Na^+ ion and the other isomer having its two excess electrons occupying separate lattice sites.

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