Photodesorption of Alkali Anions from Alkali-Halide Cluster Anions

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Using photoelectron spectroscopy, we have observed alkali anion photodesorption from alkali-halide cluster anions that contain two weakly bound electrons. In the alkali iodides, we have found this type of desorption in almost every $(M\mathrm{I})_nM^-$ cluster we have studied ($M = \mathrm{Na}$, K, Cs; $n < 9$), although it depends on the probe laser frequency and cluster temperature. Using pump-probe techniques, we have shown that the process occurs on a picosecond time scale by way of an electronic excitation of the cluster's spin-paired electrons.

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Alkali-halide clusters (AHCs) have long served as model systems in which to study the finite-size analogs of various bulk behaviors and transitions [1]. Equivalents of bulk melting [2–4], lattice charge defects [5,6], and composition-induced metal-insulator transitions [7–9] have all been examined experimentally and theoretically in AHCs. The simplicity of their ionic bonding permits accurate and detailed theoretical studies of their behaviors and, by extrapolating to larger particles, helps to explain the physics of extended systems.

AHCs can also assist in the understanding of photon-stimulated desorption, which has been intensely studied in surface physics for several decades [10,11]. In alkali-halide crystals, the desorbed species are often ground state alkali-metal atoms or cations [12,13], halogen atoms or anions [14–17], or excited-state alkali-metal atoms [18]. The electronic processes leading to the desorption of these particles are a matter of considerable debate, and one of our main motivations in this work is to elucidate those processes. The desorption of atoms from small clusters is also fascinating in light of the recent interest in photodissociation of highly vibrationally excited ion pairs [19] and collisional processes, such as dissociative electron attachment, in which one of the products is an alkali-metal atom or ion.

When extra electrons are added to AHCs, their ionic frameworks can accommodate the excess electrons in several ways. In particular, clusters with two-excess electrons, of the form $(MX)_nM^-$, usually bind those electrons in one of three manners. First, both electrons can attach loosely to a single alkali positive ion to form a polarized negative ion. Second, the two electrons can separately inhabit two independent halogen vacancies. The third and most common accommodation mode places the two electrons in a single halogen vacancy as a spin pair, effectively acting as a single particle. These paired electrons are tightly bound in their cluster and, together with the other atomic ions, usually form a cluster with a cubic or ring geometry [20]. Based on their photoelectron spectra and an analysis of their possible geometries, we believe that all of the cluster systems discussed in this Letter contain such vacancy-filling spin pairs. While a few clusters display mixed isomeric forms in our experiments, only those isomers containing spin pairs appear significant.

In this Letter, we present evidence for negative alkali ion photodesorption from these two-excess electron AHC anions. That result is intriguing because, while alkali atoms exist as positive ions in ionic materials, they can evidently carry away two electrons when desorbing from certain cluster anions.

Such alkali anion photodesorption (AAP) is not rare, occurring instead in almost all of the clusters we studied. The mechanism we propose for AAP has strong parallels to the photon-stimulated desorption caused by low energy photons at alkali-halide surfaces [21]. In addition to its fundamental interest, efficient photon-stimulated desorption from solids has been suggested as a potential photoatom source [22].

We produce the AHCs by laser vaporization of an alkali-halide sample disk [6]. The resulting plume of vapor is entrained in a burst of helium gas, released from a valve just before the laser flash. Helium cools the AHC-rich vapor and sweeps it through a temperature-controlled tube into a vacuum chamber. The free jet expansion from this tube produces a cluster beam that is then collimated by a skimmer and enters a time-of-flight mass spectrometer.

This spectrometer accelerates the beam's negatively charged AHCs at right angles and they disperse in space according to their charge-to-mass ratios. As the desired anions enter a magnetic-bottle photoelectron spectrometer, they are exposed to a pulse of infrared laser light. This radiation can excite clusters or photodetach electrons from them or their possible photofragments. Freed electrons traverse the spectrometer to a dual microchannel-plate detector. We determine electron kinetic energies from their travel times and then subtract these kinetic energies from the photon energy to obtain electron binding energies. We record several thousand photodetachment events to obtain each photoelectron spectrum. The spectral resolution is limited by both homogeneous and inhomogeneous broadenings in these complicated, rovibrationally excited clusters and by spreading and noise introduced by the spectrometer and its electronics.

While laser-induced photofragments could be detected by reanalyzing the clusters in a second mass spectrometer, one type of photofragment is immediately visible in the photoelectron spectra of two-excess electron AHCs: negative alkali ions. Because they lack rovibrational substructure, negative atomic ions create strikingly narrow features in a spectrum. Those features are two photon events: One photon detaches the negative alkali ion from the cluster and a second photon detaches an electron from that atomic anion.

We have studied AAP at a variety of wavelengths and pulse durations. We use 5 ns pulses of 0.65–1.55 eV light from a Nd:YAG-pumped optical parametric oscillator (OPO) to detect AAP and 1 ps pulses of both 1.55 eV light from a Ti:sapphire laser and 0.50–1.06 eV light from a traveling-wave optical parametric amplifier of superfluorescence to study its time dynamics.

$(KI)_3K^-$ is a good example of a cluster that photodissociates into a negative alkali ion and a neutral cluster. Figure 1(a) shows the photoelectron spectrum of this cluster taken with 2.33 eV photons from the Nd:YAG laser. The intensity maximum at 1.73 eV corresponds to the electron vertical binding energy (EVBE) of the cluster—the energy required to remove the weakest-bound electron without allowing the cluster to relax. That value is consistent with an octagonal ring of ions and electrons in which the two-excess electrons form a spin pair in a halogen vacancy [4]. The spectrum is otherwise empty and there is no evidence for other isomers with lower EVBEs.

However, when we use photons with energies between 1.0 and 1.55 eV, we see a strong spectral feature at 0.51 eV [Fig. 1(b)]—the electron affinity of the potassium atom itself. This feature's sharp, double-peaked shape is the result of a kinematic effect: The photodetaching laser is polarized along the cluster beam direction and the *p*-wave continuum electrons ejected from the potassium anions tend to emerge either parallel or antiparallel to the beam direction. Parallel emission boosts the kinetic energy of a photoelectron (the left peak) while antiparallel emission lowers it (the right peak). The separation of these peaks increases with photon energy and cluster velocity.

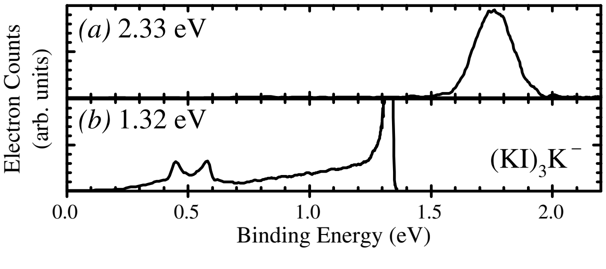

FIG. 1. Photoelectron spectra of $(KI)_3K^-$ recorded with (a) 2.33 eV photons and (b) 1.32 eV photons. The feature centered at 0.51 eV in (b) is due to electrons detached from K^- ions desorbed from the cluster. The large signal near 1.3 eV in (b) is due to the large cross section for photodetachment of threshold electrons.

Seeking further evidence for AAP, we sent particles leaving the laser interaction region through a second time-of-flight mass spectrometer. This spectrometer accelerates negatively charged particles forward so that lighter charged fragments pull ahead of their parent anions, while neutral fragments lag behind. Taking the difference between mass spectra recorded with and without the laser pulse, we obtained a flat line except for a downward peak due to photodepletion of the original cluster anions and two upward peaks: late arriving neutral fragments and early arriving alkali anions (Fig. 2).

To date, we have observed alkali anion photodesorption in $(KI)_nK^-$ ($n = 1$–9), $(CsI)_nCs^-$ ($n = 1$, 3, 5–9), and $(NaI)_nNa^-$ ($n = 3$–8) anions. AAP can also be seen in data from earlier studies conducted in this laboratory on sodium-chloride clusters, including $(NaCl)_nNa^-$ ($n = 4$, 8, 9, 11, 13, 16, 17, 19) [23]. It appears that AAP is a nearly universal process in two-excess-electron AHCs.

Using ~1 mJ, ~5 ns pulses from the OPO, we were able to detect AAP in KI and CsI cluster anions from a threshold of 1.0–1.2 eV up to the 1.55 eV end of the OPO's tuning range (which lies roughly 0.1 eV below the EVBEs of most of these clusters). In NaI cluster anions, which have much higher EVBEs (2.5–3.5 eV), the AAP threshold lies above the OPO's range. Nonetheless, AAP can be observed with 2.33 eV photons from the Nd:YAG.

The absorptions leading to AAP in two-excess-electron AHCs are quite broad. In a previous study, on one-excess-electron AHCs, we attributed such broad absorptions to strong couplings between electronic and vibrational excitations [24] and found that those absorptions often lead to substantial heating or cooling of the clusters.

Not surprisingly, AAP is also at least partly thermal. The clusters in this study bind their spin-paired electrons in halogen vacancies (F' centers in color-center

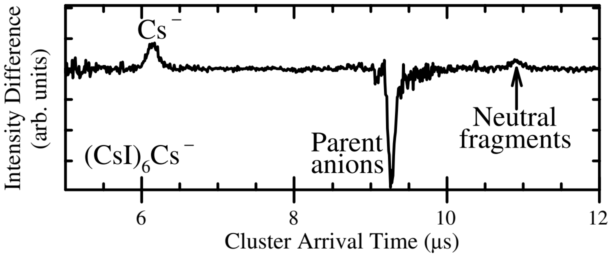

FIG. 2. Difference of $(CsI)_6Cs^-$ mass spectra, with and without exposure to 1.32 eV light. That light desorbs Cs^- (left peak) from the parent anions (downward peak). Neutralized fragments appear as the right peak.

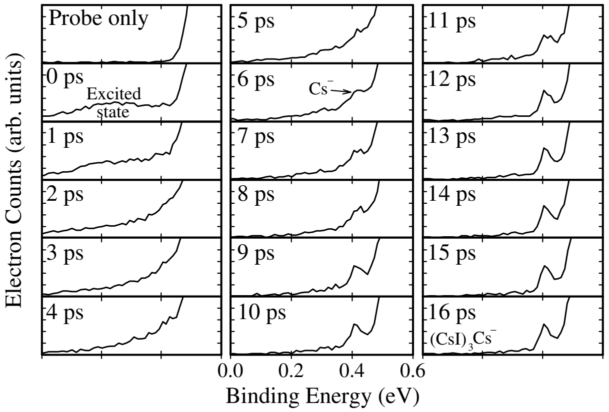

FIG. 3. Photoelectron spectra of $(CsI)_3Cs^-$ probed with 1.55 eV photons after the cluster has been pumped by 1.03 eV photons. After the excited state at 0.24 eV decays, a sharp peak gradually emerges at 0.4 eV. That peak is the leftmost peak of the desorbed Cs^- signal (see Fig. 1). Source temperature was 300 K.

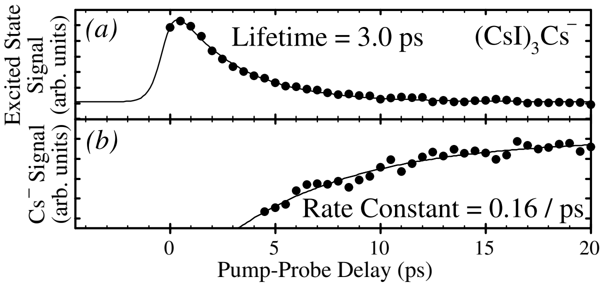

FIG. 4. Excited state and alkali anion signals in $(CsI)_3Cs^-$ as functions of pump-probe delay. Source temperature was 300 K.

terminology), making those spin pairs structurally important and coupling them strongly to vibrations. Optical absorptions in these clusters therefore cause both electronic and vibrational excitations and induce rapid heating and fragmentation.

From the subpicosecond vibrational times of ions in AHCs, we expected desorption to occur on picosecond time scales. We therefore turned to picosecond-laser pump-probe experiments to follow the desorption dynamics. The pump pulse was tuned to an energy known to cause AAP and the probe pulse was tuned elsewhere to look for time dependence in the photoelectron spectrum.

Figure 3 shows photoelectron spectra of $(CsI)_3Cs^-$ taken over a range of pump-probe delays, beginning with no pump pulse at all. At short delays, we observe an electronic excited state centered at 0.24 eV. As this excited state decays, a broad hump appears around 0.4 eV, although it overlaps with the much stronger single-photon feature to its right. Still later, a sharp peak emerges out of that hump—the leftmost of the two Cs^- peaks seen in Fig. 1. The rightmost Cs^- peak is buried under the single-photon feature.

We carefully integrated the excited-state and alkali anion portions of the spectrum to determine the time scales for the desorption process. Figure 4 shows that the excited state has a lifetime of 3.0 ps and the alkali anions are desorbed at a rate of 0.16 ps^{-1}. The hump seen at intermediate delays is too entangled with the single-photon feature for us to measure its time evolution accurately.

From these data, we see that it takes roughly 5 to 15 ps for the alkali anion to photodesorb from the cluster. The first step in this process is an electronic excitation of the spin-paired electrons. Although that excitation decays within a few picoseconds, the alkali anion does not fully emerge from the cluster for several more picoseconds. Instead, we see a broadened spectral hump produced by alkali anions that have not yet separated completely from their parent clusters.

That broad hump also appears in photoelectron spectra taken with nanosecond pulses. In such spectra, the hump forms a pedestal on which the alkali anion signal resides. We find that the relative height of this pedestal decreases when we increase either photon energy (Fig. 5) or cluster temperature (Fig. 6). Evidently, the added optical or thermal energy speeds the ejection of alkali anions from the parent anion. With enough added energy, the alkali anion spends so little time before leaving its parent ion that the pedestal disappears almost completely.

The picosecond pump-probe technique also detects this increase in desorption rate with increasing cluster temperature. For example, raising the temperature of the cluster source from 300 to 400 K when studying $(KI)_4K^-$ leads to an increase in the K^- desorption rate from 0.34 to 0.45 ps^{-1}.

We can understand AAP classically in terms of charge transfer. As background, note that alkali-halide crystals have large photodesorption cross sections for neutral alkali atoms. In one picture of that process, an excited *F* center or valence electron neutralizes an alkali ion and the resulting alkali atom is subsequently ejected from the crystal surface [25]. Similarly, the cluster anions in which we observe AAP contain F'-center charge defects that mediate the alkali anion desorption.

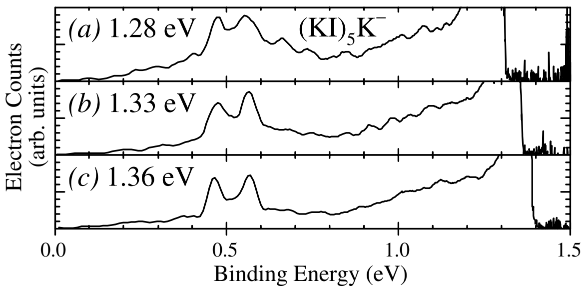

FIG. 5. Photoelectron spectra of $(KI)_5K^-$ at three photon energies. Lower energy photons provide less internal energy to the cluster, making it more likely that an electron will photodetach from it before alkali anion desorption occurs. Source temperature was 300 K.

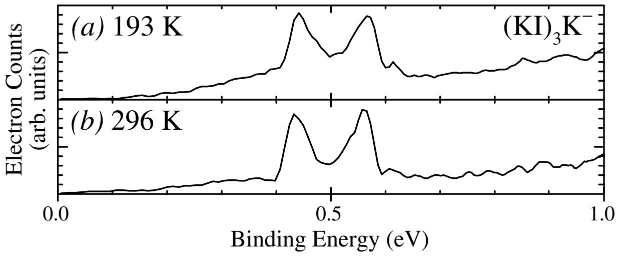

FIG. 6. Photoelectron spectra of $(KI)_3K^-$ at two source temperatures (indicated) and thus at two initial cluster internal temperatures [2]. Desorption occurs more slowly in colder clusters, leading to a broad pedestal of photoelectrons from alkali anions that have not yet had time to leave their parent clusters.

Excitation of that F' center, which is strongly coupled to the cluster's "lattice," abruptly neutralizes one of the alkali cations and changes the cluster's charge distribution. The sudden shift in charge forces dramatically alters the cluster's vibrational energy and may heat it to the point where the weakly bound neutral alkali atom can evaporate thermally. As the cluster and atom separate during this evaporation, they compete for the remaining excess electron. In its hot, distorted form, the cluster may have such a low electron affinity that it allows the outgoing alkali atom to carry away the remaining excess electron. In fact, if the electron affinity of the cluster fragment is less than that of the alkali atom, it is energetically favorable for the atom to evaporate as an anion rather than in its neutral form. While some fraction of the photodetaching atoms may remain neutral, neutral atoms are difficult for us to detect, and we have not yet been able to study their abundances.

The complicated vibrational mode structures of clusters slow the desorption process as compared to diatomic systems. After excitation, a cluster can vibrate many times before the anion desorbs. That desorption can be viewed either as a transition between a bound vibrational mode and a dissociative state, which takes place at their avoided crossing, or as the time evolution of an ionic wave packet along a manifold of admixed vibrational and dissociative states. It can also be viewed as the persistent motion of the cluster's internal coordinates over a complicated, multidimensional potential energy surface as the vibrationally excited cluster searches for a passage between its bound and dissociated forms.

In summary, we have shown that alkali anions can photodesorb from two-excess-electron alkali-halide cluster anions. This process occurs in a variety of AHC anions, all of which accommodate their two-excess electrons as a spin pair in a halogen vacancy, the equivalent of a bulk F' center. We suggest a possible mechanism for this photodesorption, wherein the excited F' center mediates the desorption indirectly by neutralizing a nearby alkali cation. Although the high work function of bulk alkali-halide surfaces should inhibit alkali anion photodesorption from neutral surfaces, negatively charged alkali halides may exhibit this effect.

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