Ultraviolet photoelectron spectroscopy and photofragmentation studies of excess electrons in potassium iodide cluster anions

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Ultraviolet photoelectron spectroscopy (UPS) and photofragmentation data for $(KI)_n^-$, $K(KI)_n^-$, and $K_2(KI)_n^-$ (n up to 13) are presented. The excess electrons in these clusters are all loosely bound with vertical detachment energies below 1.6 eV, and the photofragmentation data correlated well with the UPS results. Our results for the stoichiometric clusters are in good agreement with theoretical predictions, and the ground state geometry of these clusters are discussed. For the excess potassium cluster series, we suggest the possible existence of electron spin pairs in some of these cluster anions.

I. INTRODUCTION

The fully ionic alkali halide clusters have been studied extensively during the past decade and are now relatively well understood. In these particles, each alkali atom exists as a cation and each halide atom as an anion. The simple electrostatic forces that hold these clusters together permit straightforward but reliable calculations of their ground state geometries and binding energies. Experimentally, bulk-like alkali halide particles in the form of $M(MX)_n^+$ and $X(MX)_n^-$, where M^+ are alkali ions and X^- are halide ions, are easily produced in conventional cluster sources. Their relative abundances in mass spectra vary dramatically with the number of atoms in the cluster, a feature which is directly related to their structures and binding properties.[1]

However, the mass spectra of alkali halide cluster ions include several other classes of clusters, in addition to the fully ionic species. One class, the subject of this paper, consists of clusters containing one or more extra electrons, not associated with halogen ions. In the negative ion series, the clusters with one, two, and three loosely bound electrons take the form of $(MX)_n^-$ (the stoichiometric sequence), $M(MX)_n^-$ (the one extra cation series), and $M_2(MX)_n^-$ (the two extra cation series). These excess electrons in small, isolated clusters are the focus of much current interest, as they provide microscopic views of such problems as metal–insulator transitions and the structures of defects in ionic crystals. Being finite systems, the clusters are particularly well suited to test new theoretical models. An extra electron in an alkali halide cluster can be related to an F center in the bulk crystal,[2] and clusters containing more than one extra electron can be microscopic equivalents of F' or M centers or molten alkali metal–alkali halide solutions.[3,4]

Landman, Scharf, and Jortner investigated the properties of an electron interacting with a cluster consisting of n Na^+ and m Cl^- ions at finite temperatures.[5] They predicted that the electron could exist in the cluster in one of several situations, depending on the structure of the cluster. It could be localized about a specific Na^+ ion or local dipole. It could occupy a vacant crystalline lattice site as though it were a Cl^- ion, much like an F center in the bulk crystal. Finally, if there is no favorable site for the electron to localize, it would be delocalized throughout the cluster or at its surface as a conduction electron. Honea *et al.* measured the threshold ionization energies of the excess electron of neutral Na_nF_{n-1} clusters with a tunable dye laser.[6] These results and a subsequent report[7] on R2PI meaurements of bound excited states agree well with the theoretical predictions. Studies of the formation and mass spectrum of stoichiometric sodium chloride clusters by Yang *et al.*[8] also show good agreement with the theoretical results and in particular, their measured vertical detachment energy of $(NaCl)_2^-$ is very close to the value obtained by *ab initio* calculations,[9] indicating that the ground state structure of this molecule is a bent chain.

Nevertheless, there are two weaknesses in the previous experimental schemes. First, measurements with a tunable dye laser are time consuming and in most cases, only the photodetachment threshold is obtained, while the energetics of more tightly bound electrons or the presence of isomers with higher vertical detachment energies are unknown. Second, the measurements are indirect in collecting the photoionized or photodepleted particles instead of photoelectrons. This is acceptible if one assumes that photofragmentation does not take place. However, as we will discuss below, these clusters do decay when they absorb photons near the photodetachment threshold. Thus one needs to be very careful when interpreting the results. A direct measurement of the photoelectrons detached by laser interaction, therefore, is very desirable.

Ultraviolet photoelectron spectroscopy (UPS) of mass selected negative cluster ions has proven to be a very efficient technique for studying the vertical detachment energies and energy levels of metal and semiconductor clusters.[10] In the work described in this paper, we use the ultraviolet photoelectron spectrometer developed at Rice University to measure the vertical detachment energies and binding energies of

alkali halide clusters with one or more extra electrons, produced by a laser vaporization cluster source. Specifically, we have obtained photoelectron spectra of $(KI)_n^-$, $K(KI)_n^-$, and $K_2(KI)_n^-$, n up to 13. Photofragmentation measurements were done at the University of Virginia at several different photon energies on the former two cluster series, from which we obtain information on their fragmentation channels and how fragmentation relates to photodetachment. We have analyzed the structures of a number of these clusters and compared them with the defects in bulk alkali halide crystals and dilute liquid alkali metal–alkali halide solutions.

II. EXPERIMENTAL DETAILS

The supersonic cluster beam apparatus and the magnetically focused time-of-flight photoelectron spectrometer at Rice University have been described previously.[11] Briefly, potassium iodide cluster anions are produced by vaporization of a solid KI sample by the fourth harmonic output of a Nd:YAG laser at 1–3 mJ/pulse. The clusters are cooled and carried downstream by a dense pulse of helium gas. Due to the ionic nature of the material, anions are easy to produce, and it is not necessary to use a second laser to generate attachment electrons, as is usually done when making metal or semiconductor cluster anions.

The negative clusters are extracted from the supersonic beam by a Wiley–McLaren-type time-of-flight mass-spectrometer,[12] and individual clusters are selected by a three-grid mass gate. For small clusters, the selected clusters are then decelerated to 100–150 eV and allowed to drift through the laser detachment region. A KrF excimer laser (248 nm, 5.01 eV) is used to detach the electrons. Data are sums of about 10^4 laser shots at 10 Hz and contain up to 200 counts per 10 ns time channel. Calibration of the spectrometer is done by recording the UPS spectra of Au^- and I^-, which have known electron affinities.

The laser vaporization source (LVCS) at Virginia is similar to the one described above and a detailed description appears elsewhere.[13] Of course, a comparison between the UPS spectra and the photofragmentation data will only be meaningful if we are sure that clusters generated by the two apparatuses are identical. Care has been taken to make the experimental conditions similar, and we have noticed that mass spectra from the two sources are very similar. In the source used at Virginia, a channel about 1.5 cm long is used between the vaporization region and the supersonic expansion to allow interaction and growth of the particles. The fourth harmonic of a Nd:YAG laser is used as the vaporization laser, focused on the sample to a spot about 1 mm square with an energy of about 1 mJ/pulse. A higher laser energy density will increase the abundance of the fully ionic clusters $I(Ki)_n^-$ while reducing the abundance of the clusters with extra electrons, indicating these clusters are loosely bound and vulnerable to photodetachment or photofragmentation.

Photodetachment and photofragmentation experiments are done in the mass spectrometer, in the region between the acceleration region and the microchannel plate detector. We mass select a specific cluster size, expose those

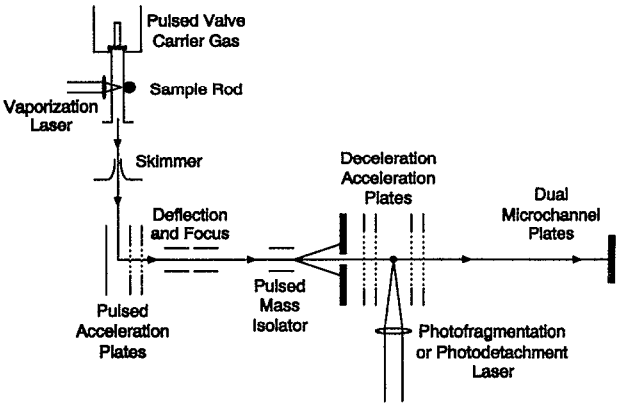

FIG. 1. The overall apparatus and four plate decelarating/reaccelerating scheme for studying photofragmentation. The negative clusters are slowed by a retarding potential in the first region, photofragmented or photodetached in the central region, and the remaining negative ions are reaccelerated to the initial energy in the third region.

clusters to laser radiation, and use a four plate deacceleration/reacceleration scheme[14] (Fig. 1) to look at the daughter particles. The two outer plates are grounded while the two central plates are at a potential slightly less than the acceleration potential. Three regions are formed, a decelerating region, a field-free region, and a reaccelerating region. The particles are slowed by the first region, they interact with the laser beam in the second region, and the negatively charged daughter particles are reaccelerated in the third region. Alternate shots with the photofragmentation/photodetachment laser on and off are subtracted from one another to yield the mass resolved photodepletion peak and daughter ion peaks. The fundamental, the second harmonic, and the fourth harmonic of a Nd:YAG laser, as well as an excimer laser pumped dye laser operating at several wavelengths in the yellow–red region are used as the photodetachment/photofragmentation laser. In order to avoid saturation and multiphoton effects, the laser beam is kept below 1 mJ/pulse and defocused to a radius of about 0.25 cm at the interaction region. As a result, only a small portion of the clusters are photofragmented or photodetached.

III. RESULTS AND DISCUSSIONS

UPS results for negatively charged potassium iodide clusters with one, two, and three loosely bound electrons $(KI)_n^-$, $K(KI)_n^-$, and $K_2(KI)_n^-$ (n up to 13), appear in Fig. 2. Although the spectra extend to approximately 5 eV, we have only plotted up to 3.5 eV so as to emphasize the low energy features. Only one cluster, $(KI)^-$, has a significant peak above 3.5 eV and the UPS spectrum of this cluster appears separately as Fig. 3. We have placed an arrow in each spectrum at what we estimate to be the vertical detachment energy. This value is obtained by following a tangent line, drawn through the leading edge of the first major peak, back to the baseline. We then add 200 meV to account for finite temperature population of vibrationally excited states of the anion.

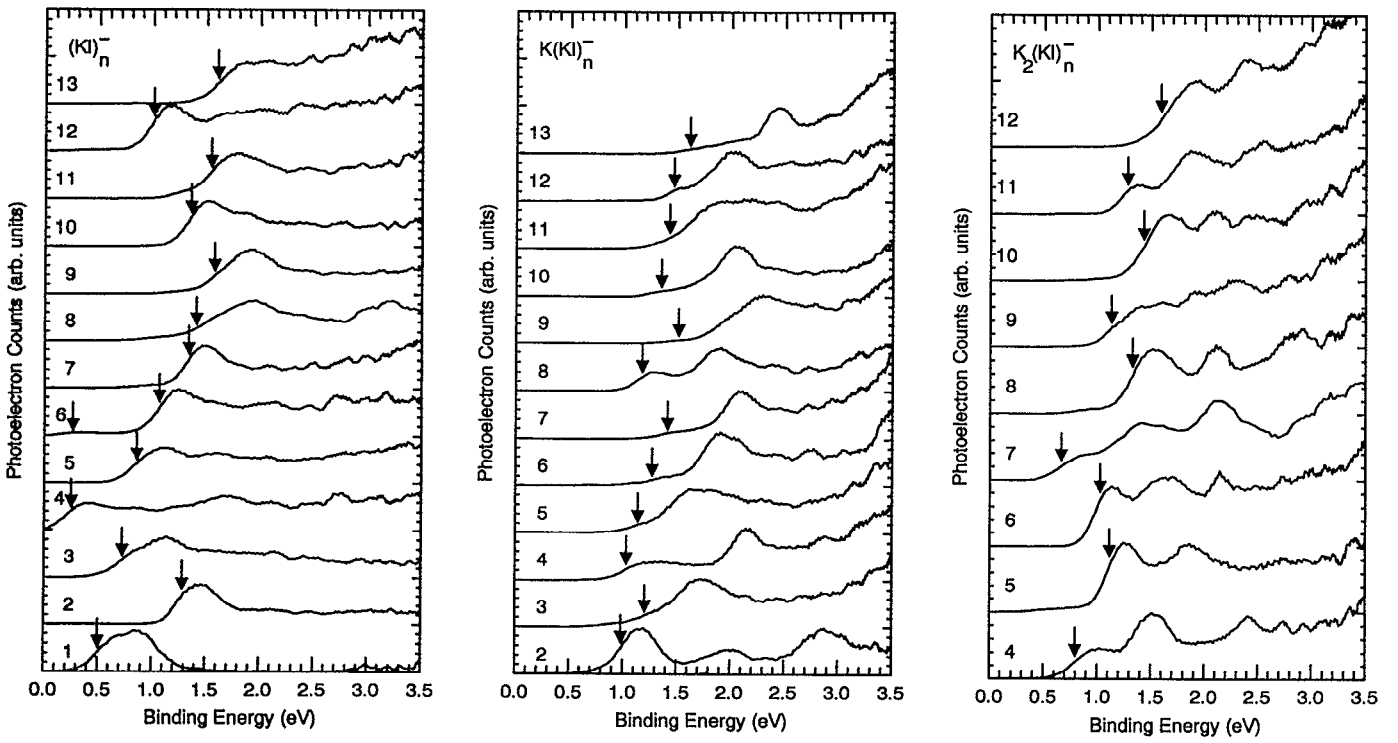

FIG. 2. UPS spectra of (a) $(KI)_n^-$, (b) $K(KI)_n^-$, and (c) $K_2(KI)_n^-$, n up to 13. The intensities are not scaled to one another. Vertical detachment energies are noted with arrows.

These vertical detachment energies are plotted for each cluster of the $(KI)_n^-$ and $K(KI)_n^-$ series in Figs. 4(a) and 4(b). Because we are not able to measure cluster temperatures and because negative and neutral states of the clusters may have significantly different geometries, accurate adiabatic electron affinities cannot be obtained from these data alone. However, considering the substantial number of collisions these clusters experienced in the supersonic source and their small sizes, we expect their internal temperatures to be near or even below room temperature. The values plotted in Fig. 4 are thus reasonable estimates of the vertical detachment energies of these clusters.

The photofragmentation results of $(KI)_n^-$ and $K(KI)_n^-$ (n up to 13, except for $n = 10$ whose signal was too small to make any measurements) are shown in Tables I and II, respectively. Except for a few clusters [noticably $K(KI)_9^-$ and $K(KI)_{13}^-$, photodissociation is not observed with photons above 2 eV. As the photon energy is reduced below 2 eV, photofragmentation is observed, first for the heavier clusters then the lighter ones. Eventually, at low

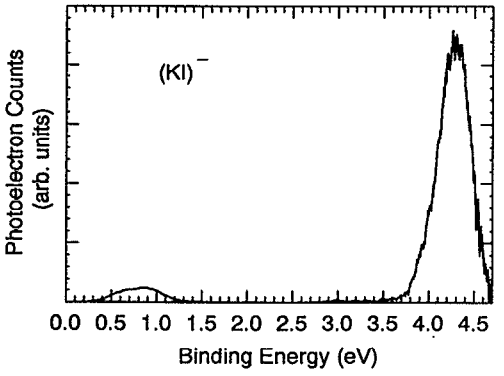

FIG. 3. UPS spectrum of $(KI)^-$.

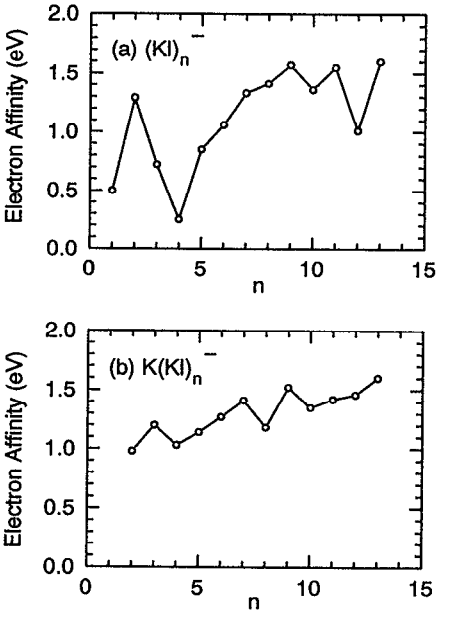

FIG. 4. Vertical detachment energies of (a) $(KI)_n^-$, and (b) $K(KI)_n^-$, derived from photoelectron onset signals in Figs. 2(a) and 2(b).

TABLE I. Results of exposing $(KI)_n^-$ to radiation at several photon energies. The number given is the percentage of decaying cluster anions that decay by losing a K atom. The remaining percentage of decaying cluster anions decay by losing an electron. These numbers are accurate to approximately 10%.

	266 nm	532 nm	580 nm	634 nm	690 nm	730 nm	1064 nm
$(KI)_2^-$	...	...	...	...	...	...	4
$(KI)_3^-$	...	...	...	...	...	...	...
$(KI)_4^-$	...	...	...	...	...	...	...
$(KI)_5^-$	...	...	...	...	...	...	23
$(KI)_6^-$	...	...	...	...	...	...	...
$(KI)_7^-$	...	...	...	...	...	...	82
$(KI)_8^-$	...	...	...	...	...	15	76
$(KI)_9^-$	...	...	...	10	11	33	70
$(KI)_{11}^-$	...	...	...	...	8	17	100
$(KI)_{12}^-$	...	...	...	...	...	...	50
$(KI)_{13}^-$	...	...	...	10	13	26	100

photon energies, photofragmentation replaces photodetachment as the dominant decay channel. In most cases, photofragmentation data continues to occur at a photon energy of 1.17 eV (1.06 μm). We note, however, that at that energy $(KI)_3^-$, $(KI)_4^-$, and $(KI)_6^-$ exhibit only photodetachment and $K(KI)_9^-$ and $K(KI)_{13}^-$ undergo neither photodetachment nor photofragmentation.

There is one fragmentation channel for the stoichiometric series

$$(KI)_n^- \rightarrow I(KI)_{n-1}^- + K,$$

while there are two channels for $K(KI)_n^-$

$$K(KI)_n^- \rightarrow (KI)_n^- + K,$$

$$K(KI)_n^- \rightarrow I(KI)_{n-1}^- + K_2.$$

We know that the second channel, direct loss of a K_2 molecule rather than sequential loss of two K atoms, is present because there are many cases in which one of the sequential channels is not observed. For examle, $K(KI)_5^-$ never loses a single K atom, so that it is not possible for its $I(KI)_4^-$, fragment to be formed by the loss of two separate K atoms. It is certainly more energetically favorable for the two K atoms to leave together as K_2. However, there are cases where we cannot rule out the sequential loss of two K atoms from a cluster because both sequential steps are observed. These cases are noted in Table II.

The relative abundances of clusters in the mass spectra for the three series are very similar to one another. They are also very similar to the mass spectrum of the $(NaCl)_n^-$ ions produced under helium fast cooling conditions, which was published and analyzed in detail previously.[8] These similarities suggest that the series that contain extra K atoms are probably formed by K atoms sticking to previously formed $(KI)_n^-$ anions.

A. The stoichiometric series

A detailed interpretation of the UPS results is difficult because of both the geometry changes that occur during photodetachment and the possible presence of isomers in the

TABLE II. Results of exposing $K(KI)_n^-$ to radiation at several photon energies. The numbers given are the percentages of decaying cluster anions that decay by losing a K atom and by losing a K_2 molecule. The remaining percentage of decaying cluster anions decay by losing an electron. These numbers are accurate to approximately 10%.

	266 nm		532 nm		580 nm		634 nm		690 nm		730 nm		1064 nm	
	K	K_2	K	K_2	K	K_2	K	K_2	K	K_2	K	K_2	K	K_2
$K(KI)_2^-$	...	...	...	...	...	...	...	...	...	...	...	...	2	3[a]
$K(KI)_3^-$	...	...	...	...	...	...	...	...	...	...	...	...	35	16
$K(KI)_4^-$	...	...	...	...	...	...	...	...	...	...	...	...	4	8
$K(KI)_5^-$	...	...	...	...	...	...	...	...	...	...	...	10	...	72
$K(KI)_6^-$	...	...	...	...	...	...	...	...	...	...	...	...	...	50
$K(KI)_7^-$	...	...	...	...	...	...	...	13	...	36	...	52	...	70
$K(KI)_8^-$	...	...	...	...	...	...	...	...	...	28	...	46	...	73
$K(KI)_9^-$	...	...	...	8	...	11	...	25	...	43	20	50[a]	[b]	[b]
$K(KI)_{11}^-$	...	...	...	...	...	...	...	35	...	50	5	60[a]	...	85
$K(KI)_{12}^-$	...	...	...	...	...	...	...	...	...	50	...	65	...	90
$K(KI)_{13}^-$	...	...	25	...	42	...	70	17[a]	40	20[a]	42	21[a]	[b]	[b]

[a] May include cluster anions losing two K atoms sequentially.
[b] Neither photodetachment nor photofragmentation occurs at this wavelength.

cluster beam. Extensive theoretical calculations are thus needed in order to fully understand the data. However, several features are readily observed.

One very important piece of information that previous studies of the UPS spectra of metal and semiconductor clusters have revealed is the existence of the HOMO-LUMO gap of any cluster anion whose neutral counterpart has a closed shell electronic structure.[10] Assuming the extra electron produces only a small geometry change (i.e., Koopmans' theorem), the least bound electron in the negative cluster resides alone in what corresponds to the LUMO (lowest unoccupied molecular orbital) of the neutral cluster. The next most weakly bound electron resides in the HOMO (highest occupied molecular orbital) of the neutral, and normally one expects there will be many of these electrons—either because the Homo has high degeneracy, or because there are several molecular orbitals clustered near the top of the "valence band" in these clusters. In the limit of bulk semiconductor or insulator surfaces this picture corresponds to the UPS of valence band electrons and one extra electron originating from the conduction band. The UPS pattern expected from the negative ion of a closed-shell cluster is therefore expected to start with a small bump corresponding to one electron in the LUMO, followed (after a gap) by a large signal from the many electrons in the HOMO and other nearby orbitals in the valence band.

This feature is clearly present in the UPS spectrum of $(KI)^-$, the smallest cluster in the series (Fig. 3). The small peak centered at 0.8 eV is produced by photodetachment of the extra electron, while the much bigger peak, centered at 4.3 eV, is the result of photodetachment of a $5p$ electron from an I^- anion. Not surprisingly, the 3.5 eV HOMO-LUMO gap is much larger than that of any semiconductor cluster. Because both K^+ and I^- have closed electronic shells and because they bind ionically, we expect every neutral stoichiometric cluster to have a closed electronic structure. However, due to the long-range Coulomb attraction, the $5p$ electrons in I^- usually have higher vertical detachment energies when in bigger clusters, making the HOMO electrons of most of the clusters undetachable with a 248 nm photon. Consequently, most of the features in the UPS spectra result from photodetachment of the loosely bound extra electron.

$(KI)_2^-$ has a comparatively high vertical detachment energy of about 1.30 eV. Because the ground state of its neutral counterpart has the rhombus structure,[1,15] which should have a very small vertical detachment energy, we think that adding an electron has substantially changed the ground state geometry. Such a change is consistent with previous studies on $(NaCl)_2^-$.[8,9] $(KI)_3^-$, on the other hand, has a low vertical detachment energy. The neutral trimer is a ring of six atoms with alternating charge.[1,15] The extra electron may be loosely bound inside the ring and shared by the three K^+ ions, producing only a small change in the ground state configuration.

$(KI)_4^-$ has a vertical detachment energy of less than 0.25 eV, the lowest we have ever seen for any cluster. Mass spectra also show that this species [a well as $(KI)_6^-$ and $(KI)_{12}^-$] is very rare.[8] Scharf *et al.* carried out detailed quantum path-integral dynamics (QUPID) calculations on $(NaCl)_4^-$ at various temperatures.[16] They predicted that at low temperatures ($T < 500$ K), there is no major configuration change from the neutral structure, which is a very stable $2\times2\times2$ cube, and the electron is loosely attached to the cube as a surface electron. Only at elevated temperatures will substantial isomerization occur and several configurations exist. The prominent structure at intermediate temperatures ($500\text{ K} < T < 750$ K) is a distorted 3×3 planar configuration, in which the excess electron occupies a corner position equivalent to one occupied by a Cl^- ion in the $Cl(NaCl)_4^-$ cluster. While the calculations were performed for NaCl, the similarities between different alkali halides[17] permit us to apply their predictions qualitatively to KI as well. Because expect the temperature of clusters from our LVCS sources to be much lower than 500 K, there is not enough thermal energy for the neutral $(KI)_4$ to open into the energetically unfavorable planar structure. Hence most of the $(KI)_4^-$ clusters have the $2\times2\times2$ cubic configuration, with a loosely bound extra electron that is vulnerable to photodetachment.

The same reasoning also holds for two other stoichiometric clusters with very low vertical detachment energies: $(KI)_6^-$ and $(KI)_{12}^-$. Their neutral counterparts are $2\times2\times3$ and $2\times3\times4$ cubes, respectively, with low electron affinities. When an extra electron is added, it becomes loosely attached to the cube and shared by all the K^+ ions in the cluster, not causing substantial change to the ground state geometry, at least at low temperatures. However, two different detachment thresholds are marked for $(KI)_6^-$ because there appear to be two different isomers present in the beam. A small fraction of the $(KI)_6^-$ clusters exhibit the weak electron binding, while a large fraction appear to adopt some new geometry that binds the electron more strongly.

In contrast to these cluster ions, in which extra electrons are loosely bound and delocalized, $(KI)_{13}^-$ forms a $3\times3\times3$ cube with the extra electron occupying a lattice site. Since the ground state geometry of the neutral $(KI)_{13}$ cluster is a $3\times3\times3$ cube missing a corner I^- ion, adding an electron to fill this vacant site does not change the geometry much and is energetically favorable.[18] Consequently, the $(KI)_{13}^-$ ion is abundant and has a relatively high vertical detachment energy of 1.6 eV, the highest we have seen in the stoichiometric $(KI)_n^-$ series. This is the first cluster in the series which resembles an F center in the bulk crystal. The next one would probably be $(KI)_{22}^-$, which is a $3\times3\times5$ cube with the extra electron occupying a missing I^- site. Unfortunately, the small signal (although it is more abundant than its neighbors in the series) and the limited mass resolution of the apparatus prevent us from making UPS or photofragmentation measurements of this species.

The true electron affinity is the difference between the total energies of the excess electron cluster anion and its neutral counterpart. In their studies of excess electron in neutral Na_nF_{n-1} clusters, Honea *et al.* proposed a very simple model for predicting the electron binding energies of F center clusters by assuming that the electron distribution is sufficiently localized so that its contribution to the potential energy is that of a halogen ion.[6] In our case, this leads to an electron binding energy E_b of

$$E_b(n) = (E[I(KI)_n^-] - T) - E[(KI)_n],$$

where T is the kinetic energy of the excess electron and $E[\ ]$ is the total energy of the cluster in the brackets. The total energy of a cluster is calculated using the rigid ion model with the parameters for the repulsive interaction taken from the Tosi–Fumi data set[18–20] obtained from crystalline data. T is estimated to be 0.8 eV, the kinetic energy of an electron localized within a lattice site, a cube of dimension $2a$ where a is the lattice constant of crystalline KI.

Applying this formula to $(KI)_{13}^-$, we obtain $E_b = 2.1$ eV, about 30% higher than the experimental value. For the non-F center clusters $n = 3$, 4, and 6 (the low electron affinity isomer only), the formula estimates electron affinities of 1.0, 0.9, and 0.6 eV, respectively. For these three clusters, the prediction is considerably larger than the observed vertical detachment energy, indicating once again that these clusters probably do not resemble F center clusters.

Photofragmentation measurements demonstrate that the characteristic decay channel is one in which the electron neutralizes a K^+ ion to produce a weakly bound K atom, which is in turn ejected from the cluster by vibrations. This observation agrees with previous theoretical predications.[5] In general, larger clusters more readily detach a K atom. For $n = 8$, 9, 11, and 13, a significant percentage of the clusters that have absorbed photons at 1.7 eV fragment so that both the photodetachment and photofragmentation cross sections are quite large. Smaller clusters, on the other hand, are more resistant to decay either by photodetachment or by photofragmentation. Clusters that bind their extra electrons weakly, $n = 3$, 4, 6, and 12, exhibit little or no photofragmentation. Their electrons are easily removed, and the K^+ and I^- ions in these clusters form stable cubes (a ring in the case of the trimer) which are difficult to break.

B. The two and three extra electron series

When there is more than one electron loosely attached to a cluster, the UPS spectrum is a superposition of the individual spectra produced by each electron. An apparent difference between UPS spectra of the one extra electron cluster series and the three extra electron cluster series is that members of the latter series usually have one or more peaks immediately following the onset peak, with intensity comparable to the first peak. In contrast, members of the single electron series do not have this feature. The UPS spectra of the two extra electron series is somewhere in between: Some clusters exhibit several resolved photodetachment peaks while others do not. We suspect that these multiple peak features reflect the fact that two or more electrons may bind differently in a cluster. The large widths of the individual photodetachment peaks may be a result of vibrational excitations that occur when the electron is removed, but the separate peaks are the result of significantly different environments for the removed electrons. While it is possible that the multiple peaks in the photoelectron spectra of a specific cluster are due to the presence of different isomers with different vertical detachment energies, the fact that UPS data from the single extra electron series do not show any multiple peaks near the onset makes us believe that isomer contribution to this feature is rare, if not nonexistent. Finally, the photon energy is too low to remove electrons associated with the closed shell ions so that they do not contribute to the spectra.

Consequently, we may conclude from our UPS data that, in the $K(KI)_n^-$ cluster series, the two extra electrons in $n = 2$, 4, 8, and 12 interact with the cluster differently and yield different resolvable peaks in the photoelectron spectra. It could be, for example, that the two electrons take two different sites or bind to two different K^+ ions; or one electron binds as a surface electron and the other binds locally. UPS data show that these clusters usually have low vertical detachment energies, and photofragmentation results also show that they are less likely to decay by emitting K atoms than other species.

For those clusters in the two extra electron series which do not yield multiple peak photoelectron spectra, we think that a number of them may bind their extra electrons identically within the limitations of our current experimental resolution. In this case, there is a possibility that the two electrons form spin pairs. Theoretical calculations show that in alkali halide crystals, two electrons with antiparallel spins have a strong tendency to attract each other and form localized bielectronic complexes.[3] ESR and paramagnetic susceptibility measurements[4] of electron localization in molten alkali metal–alkali halide solutions also have shown strong indication of spin-paired states. There is no work so far on whether similar states exist in alkali halide clusters. If electron pairs are possible within a small cluster, then $n = 3$, 5, and 7 in the $K(KI)_n^-$ series are likely candidates. These clusters may form $2\times2\times2$, $2\times2\times3$, and $2\times2\times4$ cubes, respectively, to minimize their free energy, with the electron pair localized in one lattice site and shared by adjacent K^+ ions. Our experimental results show that they usually have higher vertical photodetachment energies than their neighbors, and they are also more readily fragmented.

IV. CONCLUSION

In the present study of potassium iodide clusters, the stoichiometric cluster anions $(KI)_n^-$ and the potassium-rich anions $K(KI)_n^-$ and $K_2(KI)_n^-$ were produced by a laser-vaporization cluster source. Photofragmentation studies show that the typical decay channel for the $(KI)_n^-$ clusters is the detachment of a K atom, while for the $K(KI)_n^-$ clusters, a neutral K_2 molecule is detached. UPS measurements show that all these clusters have vertical detachment energies below 1.6 eV. Several stoichiometric clusters, namely, $n = 3$, 4, 6, and 12, have particularly low vertical detachment energies, indicating the attachment of the extra electron does not change significantly the ground state geometry of the neutral cluster at low temperatures, and that the electron is probably in a surface state of a cluster ring or cube. $(KI)_{13}^-$, on the other hand, has a relatively high vertical detachment energy. It forms a $3\times3\times3$ cube with the electron taking a missing I^- site at a corner. Our results are in good agreement with QUPID calculations. Finally, we have suggested the possibility of electron spin pairs in the potassium-rich clusters.

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[1]T. P. Martin, Phys. Rep. **95**, 167 (1983).
[2]See, for example, *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).
[3]A. Selloni, R. Cor, M. Parrinello, and P. Carnevali, J. Phys. Chem. **91**, 4947 (1987).
[4]N. Nicoloso and W. Freyland, J. Phys. Chem. **87**, 1997 (1983).
[5]U. Landman, D. Scharf, and J. Jortner, Phys. Rev. Lett. **54**, 1860 (1985).
[6]E. C. Honea, M. L. Homer, P. Labastie, and R. L. Whetten, Phys. Rev. Lett. **63**, 394 (1989).
[7]G. Rajagopal, R. N. Barnett, A. Nitzen, U. Landman, E. C. Honea, P. Labastie, M. L. Homer, and R. L. Whetten, Phys. Rev. Lett. **64**, 2933 (1990).
[8]Y. A. Yang, C. W. S. Conover, and L. A. Bloomfield, Chem. Phys. Lett. **158**, 279 (1989).
[9]K. K. Sunil and K. D. Jordan, J. Phys. Chem. **91**, 1710 (1987).
[10]See, for example, O. Cheshnovsky, K. J. Taylor, J. Conceicao, and R. E. Smalley, Phys. Rev. Lett. **64**, 1785 (1990); S. H. Yang, K. J. Taylor, M. J. Craycraft, J. Conceicao, C. L. Pettiette, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **144**, 431 (1988).
[11]O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, and R. E. Smalley, Rev. Sci. Instrum. **58**, 2131 (1987).
[12]W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. **26**, 1150 (1951).
[13]C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, Phys. Rev. B **38**, 3517 (1988).
[14]L. A. Bloomfield, R. R. Freeman, and W. L. Brown, Phys. Rev. Lett. **54**, 2246 (1985).
[15]N. G. Phillips, C. W. S. Conover, and L. A. Bloomfield, J. Chem. Phys. **94**, 4980 (1991).
[16]D. Scharf, J. Jortner, and U. Landman, J. Chem. Phys. **87**, 2716 (1987).
[17]Y. J. Twu, C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, Phys. Rev. B **42**, 5306 (1990).
[18]C. W. S. Conover, Ph.D. thesis, University of Virginia (unpublished).
[19]M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25**, 45 (1964).
[20]D. O. Welch, O. W. Lazareth, G. J. Dienes, and R. D. Hatcher, J. Chem. Phys. **64**, 835 (1976).