

Electronic Excitation and Thermal Effects in Alkali-Halide Cluster Anions

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We have observed electronically excited states in alkali-halide cluster anions with one excess electron. Using photoelectron spectroscopy, we have found two narrow states in $(\text{KI})_2^-$, $(\text{NaI})_2^-$, and $(\text{NaCl})_2^-$, consistent with a dipole-bound electron, while larger cluster anions exhibit a single broad excited state. In the larger systems, electronic excitation is often accompanied by vibrational excitation and thus a change in cluster temperature. Such temperature changes affect cluster structure and in some cases lead to rapid thermal isomerization.

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Located midway between atoms and condensed matter, clusters provide a conceptual bridge across a region where bulk properties are developing out of atomic and molecular ones, and where finite size effects have their greatest influence on spatial and electronic structure. Clusters also offer a fascinating laboratory in which to examine thermodynamics in reduced dimensions, particularly the finite-system equivalents of temperature and phase transitions. In this Letter, we describe experiments in which we optically excite the weakly bound electrons of alkali-halide cluster anions to study the evolution of electron binding with cluster size and to examine the relationships between electronic, vibrational, and thermal excitations.

We chose alkali-halide clusters because of their relatively simple ionic bonding. That bonding facilitates modeling of experimental results [1–5] and studies of excess electron accommodation in alkali-halide clusters have already provided substantial insight into the origins of charge defects in solids [3,6], composition-induced metal-insulator transitions [4,7], and the influence of temperature on cluster structure [8].

But while previous studies of alkali-halide clusters have focused on ground-state properties [3,9,10] or the excited states of neutral or positively charged clusters [11–13], our present work explores the excited states of cluster anions. Most importantly, this shift to negatively charged clusters permits us to look for excited states in dipole-bound systems, the focus of considerable recent theoretical effort [14–16]. While a static dipole field greater than 1.62 D should support an infinite number of bound excited states [17], real molecules are not pure, stationary dipoles and more realistic models have found that a dipole moment near 10 D is required just to support two levels [18]. Although calculations have predicted the energies of excited states in anionic alkali-halide monomers and dimers [14,19], few experimental results are available [20].

It is thus significant that we find two narrow excited states in each of the $(MX)_2^-$ systems ($M = \text{Na}, \text{K}$ and $X = \text{Cl}, \text{I}$) and at least one broad absorption band, comparable to the bulk F -center band, in each of the $(MX)_n^-$

($n > 2$) cluster anions. These results are consistent with dipole binding in the $n = 2$ clusters but more complicated binding in the $n > 2$ clusters. Moreover, the strong electron-phonon coupling in the $n > 2$ clusters allows a single photon absorption to heat one of these clusters substantially, sometimes resulting in a rapid structural transition to another isomer.

A beam of alkali-halide clusters is produced when a helium gas pulse sweeps a plume of laser-vaporized alkali halide through a narrow, temperature controlled nozzle and into a vacuum chamber [21,22]. This beam continues through a skimmer to a time-of-flight mass spectrometer, where pulsed field plates direct the cluster anions toward a magnetic bottle photoelectron spectrometer [23].

When the anions reach the magnetic bottle, they are exposed to pulsed radiation from a Nd:YAG-pumped optical parametric oscillator (OPO). Tunable between 0.65 and 1.50 eV, at about 1 mJ per pulse in a 1 mm \times 7 mm line focus, this radiation photodetaches electrons from the clusters. From their flight times to a dual microchannelplate detector, we determine the electrons' kinetic energies and then subtract those kinetic energies from the photon energy to obtain binding energies. We record a large number of photodetachment events to obtain a complete photoelectron spectrum.

The intensity maximum of the lowest binding energy peak in a normal photoelectron spectrum identifies the electron vertical binding energy (EVBE)—the energy required to remove the most weakly bound electron from the ground state cluster anion when the remaining neutral cluster does not relax. However, when we record photoelectron spectra with photon energies below this EVBE, we sometimes find new peaks at very low binding energies. These peaks correspond to resonant two-photon processes in which the first photon promotes the excess electron to an electronically excited state and the second photon photodetaches it from the anion.

$(\text{KI})_2^-$ is an excellent example of a dipole bound anion. When studied with 2.33 eV light, its photoelectron spectrum [Fig. 1(a)] displays a single peak with an EVBE

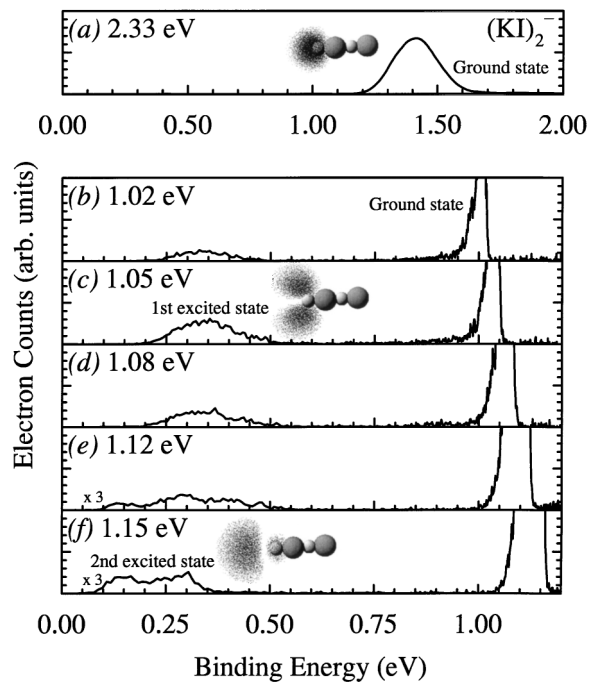


FIG. 1. (a) Photoelectron spectrum of $(\text{KI})_2^-$ anions recorded with 2.33 eV photons, showing the electronic ground state of the cluster at an EVBE of 1.42 eV. The calculated structure, inset above, has an EVBE of 1.49 eV. (b)–(f) Photoelectron spectra of $(\text{KI})_2^-$ anions using photons from 1.02 to 1.15 eV. The ground state peak cuts off naturally at the photon energy. The additional peaks centered at 0.35 and 0.22 eV represent the first and second bound electronic excited states. The calculated structures, inset above, have EVBEs of 0.37 and 0.31 eV, respectively. For clarity, (e) and (f) have been scaled by a factor of 3.

of 1.42 eV. This EVBE is consistent with a linear chain structure [3] and our calculations [24] yield the geometry shown in the figure.

However, spectra recorded with photon energies below 1.42 eV can contain additional low binding energy peaks due to photodetachment from clusters that have already been electronically excited. We find two distinct excited states in this cluster, one bound by 0.35 eV and another by 0.22 eV. The first excited state can be populated by photons with energies between about 1.00 and 1.13 eV, reaching a maximum at about 1.06 eV [Figs. 1(b)–1(e)], and the second excited state can be populated by photons between about 1.10 and 1.20 eV (Figs. 1(e)–1(f)). In both cases, the maximum transition cross section occurs when the photon energy is almost exactly equal to the energy spacing between the ground state EVBE and the excited state EVBE. This equivalence indicates that the transitions occur without much vibrational excitation or deexcitation, and that the equilibrium ion geometries for the ground and excited states are nearly identical.

Recent calculations on alkali-halide monomer anions have used the equilibrium geometries of the neutral molecules to obtain accurate predictions of the electronic

structures for those dipole bound systems [14,16]. We have made similar predictions for the dimer anions, $(\text{NaCl})_2^-$, $(\text{NaI})_2^-$, and $(\text{KI})_2^-$ [24], and have indicated our expected geometries for the two excited states in Figs. 1(c) and 1(f). The first excited state is doubly degenerate, with an equivalent state rotated 90° about the chain axis. The second excited state is sufficiently *s*-like in character to yield a *p*-like outgoing electron. Since the laser is polarized along the cluster beam axis, most of the photoelectrons emerge either parallel or antiparallel to the beam velocity and experience energy shifts as a result. The up-shifted and down-shifted populations give the photoelectron peak in Fig. 1(f) its double-hump appearance.

Our results for the larger clusters, $(\text{MX})_n^-$ ($n > 2$), are quite different—their photoelectron spectra contain only one broad excited state peak and that excited state can be populated by almost any infrared photon. For example, in $(\text{NaI})_3^-$, which has an EVBE of 1.40 eV, the only electronically excited state we find is bound by 0.35 eV (Fig. 2), yet any OPO photon (0.67–1.2 eV) populates this state. We could not locate precise maxima in the two photon transition cross sections for these larger cluster anions because of the large background of threshold electrons photodetaching directly from the ground states.

We can understand why the transitions to excited states are so much narrower in the alkali-halide dimer anions than they are in the larger alkali-halide anions in terms of the ground and excited state energy surfaces. The more similar those two surfaces are, the less vibrational excitation can occur during a transition and the sharper that transition. The narrow widths in the spectra of the linear dimer anions indicate that the ground state, the excited states, and the neutral energy surfaces are all quite similar—a property of dipole bound systems—and that the extra electron has only a weak influence on the ion positions. This observation is consistent with recent high resolution measurements [25] and calculations [26] on $(\text{HF})_2^-$, which reveal

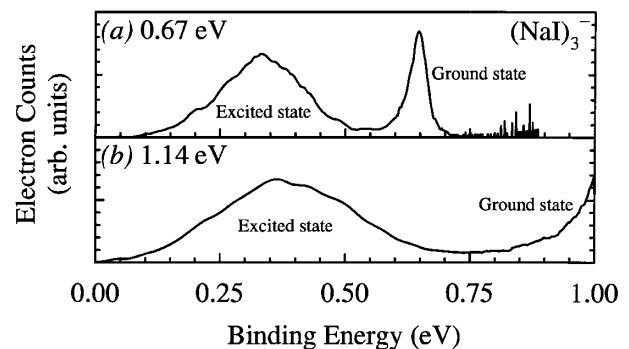


FIG. 2. Photoelectron spectra of $(\text{NaI})_3^-$ recorded with (a) 0.67 eV and (b) 1.14 eV photons. The low binding energy peak is due to an excited state and is present for all photon energies studied (0.67–1.20 eV). The high binding energy feature is due to photodetachment directly from the ground state and cuts off naturally at the photon energy. The change in width of the excited state peak is discussed in the text.

considerable similarity between the equilibrium structures of $(\text{HF})_2$ and $(\text{HF})_2^-$.

However, theoretical studies of the larger alkali-halide clusters have shown that their neutral and anionic forms often have completely different equilibrium shapes and symmetries [27]. Since electron attachment usually causes major structural rearrangements in these clusters, it is likely that their excited state equilibrium geometries are also very different from their ground state geometries and that electronic excitation is therefore accompanied by a broad range of vibrational excitations and deexcitations.

This vibrational redistribution has some interesting implications. Figure 2 shows that while $(\text{NaI})_3^-$ absorbs photons over a broad energy range, the EVBE of the excited state remains constant at 0.35 eV. Evidently, all of these different photons are exciting the same electronic state and any missing or excess photon energy is causing vibrational transitions. Photons with more than the energy required for electronic excitation heat the cluster, while photons with less than the required energy cool it.

A similar effect has long been used to heat metallic clusters and is often explained in terms of plasmon resonances or plasmon-enhanced single-electron excitations [28]. However, in the alkali-halide clusters, the heating/cooling phenomenon involves only one electron and parallels photon absorption by charge defects in insulating solids. In those solids, photon absorption quickly leads to reorganization of the surrounding ions and generation or absorption of phonons as the electron settles into its "relaxed excited state" [29,30]. In clusters, the electronic energy is also exchanged with the vibrational levels, but because the cluster is so small, a single photon can heat or cool it considerably.

This heating effect is apparent in another aspect of the photoelectron spectrum—the width of its features. These features broaden with increasing temperature because the enhanced thermal motion of its ions carries a cluster farther from its equilibrium geometry and the associated EVBE. Figure 2 shows the heating and broadening that occurs as the photon energy increases from 0.67 to 1.14 eV. The full width at half maximum is 0.17 eV when using 0.67 eV photons, and 0.28 eV for 1.14 eV photons. These results are interesting in light of recent attempts to quantify heating and vibrational energy relaxation in SF_6Ar_n^+ cluster ions following the introduction of a single quantum of vibrational energy [31].

Heating during electronic excitation is even more obvious in clusters that change shape when heated. While the sodium- and potassium-halide clusters discussed to this point do not exhibit spontaneous isomerization in our experiments, we have previously observed that many cesium-iodide clusters isomerize on subnanosecond time scales when hot [8]. In those experiments, the clusters were heated by contact with a warm source. But the results above suggest that we can heat the cluster far hotter with leftover energy during an electronic excitation. When

distributed among the $3N - 6$ vibrational modes, even 0.10 eV of excess internal energy will raise the temperature of a 10-particle cluster by about 50 K.

$(\text{CsI})_7^-$ is susceptible to thermal isomerization and is quite sensitive to this optical heating effect. Near room temperature, its two isomeric forms produce a pair of ground-state photoelectron peaks [Fig. 3(a)], but cooling the cluster source virtually eliminates the high EVBE peak [Fig. 3(b)]. Evidently, clusters from the cold source rarely have enough thermal energy to isomerize into the high EVBE form.

To show that this missing thermal energy can be provided by optical heating, we have recorded photoelectron spectra of $(\text{CsI})_7^-$ over a range of source temperatures and photon energies (Fig. 4). At the coldest source temperature (-140°C) and lowest photon energy (0.67 eV), only a single excited state peak appears in the spectrum, centered at 0.38 eV [Fig. 4(a)]. Since only the low energy isomer is present in the beam at that source temperature, this lone peak belongs to the excited state of the low energy isomer. However, the EVBE of this excited state is 0.84 eV less than the EVBE of the ground state, so the 0.67 eV photon cannot provide all of the energy needed to reach this state. Some of that energy comes from vibrations so that the cluster cools during the excitation process.

In contrast, about half the clusters leaving the warmer source (23°C) are high energy isomers and produce a second peak in the photoelectron spectrum, centered near 0.5 eV. Again, some of the energy needed to reach this excited state of the high energy isomer comes from vibrations, so the cluster cools.

But this same peak near 0.5 eV appears when clusters from the cold source (-140°C) are exposed to 0.90 eV photons [Fig. 4(b)]. Now, one photon has more than enough energy to electronically excite the low energy isomer and the resulting heating causes it to isomerize into the high energy form. Evidently, whether the energy

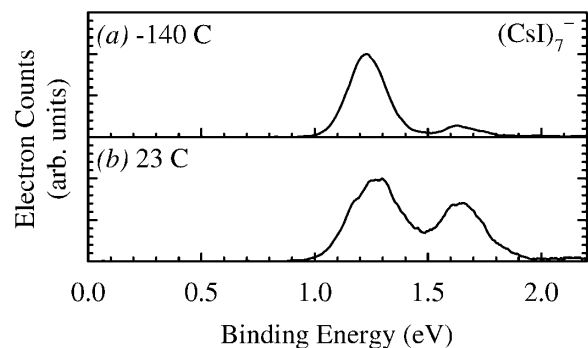


FIG. 3. Photoelectron spectra of $(\text{CsI})_7^-$ recorded with 2.33 eV photons at (a) -140°C and (b) 23°C . Temperature dependent photoelectron spectra suggest spontaneous conversion between two isomers. The low EVBE isomer is more common at low temperatures, while the high EVBE is more common at high temperatures.

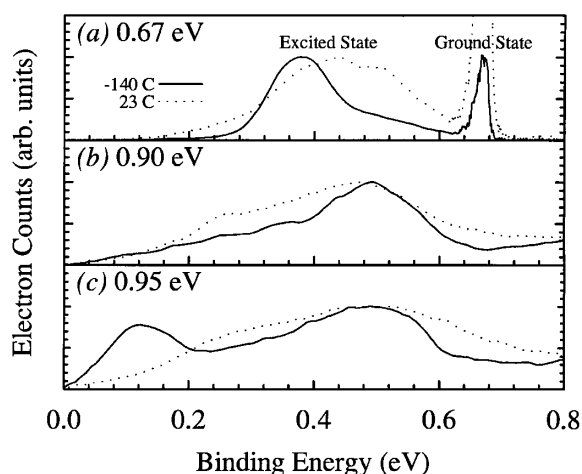


FIG. 4. Photoelectron spectra of $(\text{CsI})_7^-$ recorded at -140°C (solid line) and 23°C (dashed line) with three different photon energies. The traces in this figure have been scaled, and comparisons of peak heights should not be made. At -140°C , only one isomer is created, yet we see evidence in (b) of a state belonging to a different isomer.

comes from the cluster source or from the exciting photon, most clusters that are hot enough end up in the electronically excited state of the high energy isomer and produce similar photoelectron spectra.

Exposing low energy isomers from the cold source to still higher energy photons (0.95 eV) yields evidence of a second electronically excited state, with an EVBE of 0.12 eV [Fig. 4(c)]. Again, the photon energy is insufficient to reach this state unassisted, so some vibrational energy is used and the cluster cools during the excitation. The second excited state does not appear in the spectrum taken with warm clusters, most probably because it is dwarfed by the photodetachment signal from the excited state of the high EVBE isomer. However, it is also possible that the second excited state peak is truly absent because warm low EVBE isomers might isomerize following excitation.

In conclusion, we have found that the smallest systems, $(\text{MX})_2^-$, contain essentially dipole-bound electrons, with neutral cores that change relatively little when the electron is promoted to either of two bound excited states. In contrast, the larger clusters have cores that rearrange significantly when the electron is excited, leading to strong couplings between electronic and vibrational degrees of freedom. We have exploited this coupling to optically cool or heat the clusters and have observed, as in the case of $(\text{CsI})_7^-$, that this heating can lead to spontaneous isomerization. An interesting continuation of these experiments will be to study the time evolution of cluster geometries using ultrafast lasers. We are also currently investigating optical excitation of clusters with more than a single excess electron.

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- [1] T. P. Martin, *Phys. Rep.* **95**, 167 (1983).
- [2] J. P. Rose and R. S. Berry, *J. Chem. Phys.* **96**, 517 (1992).
- [3] P. Xia, N. Yu, and L. A. Bloomfield, *Phys. Rev. B* **47**, 10 040 (1993).
- [4] D. J. Fatemi, F. K. Fatemi, and L. A. Bloomfield, *Phys. Rev. B* **55**, 10 094 (1997).
- [5] E. C. Honea, M. L. Homer, P. Labastie, and R. L. Whetten, *Phys. Rev. Lett.* **63**, 394 (1989).
- [6] D. Scharf, J. Jortner, and U. Landman, *J. Chem. Phys.* **87**, 2716 (1985).
- [7] G. Rajagopal, R. N. Barnett, and U. Landman, *Phys. Rev. Lett.* **67**, 727 (1991).
- [8] D. J. Fatemi, F. K. Fatemi, and L. A. Bloomfield, *Phys. Rev. A* **54**, 3674 (1996); F. K. Fatemi, D. J. Fatemi, and L. A. Bloomfield, *Phys. Rev. Lett.* **77**, 4895 (1996); F. K. Fatemi, D. J. Fatemi, and L. A. Bloomfield, *J. Chem. Phys.* **110**, 5100 (1999).
- [9] D. Fatemi, Ph.D. thesis, 1995.
- [10] H. W. Sarkas, L. H. Kidder, and K. H. Bowen, *J. Chem. Phys.* **102**, 57 (1995).
- [11] G. Rajagopal, R. N. Barnett, A. Nitzan, U. Landman, E. Honea, P. Labastie, M. L. Homer, and R. L. Whetten, *Phys. Rev. Lett.* **64**, 2933 (1990).
- [12] P. Labastie, J.-M. L'Hermite, Ph. Poncharal, and M. Sence, *J. Chem. Phys.* **103**, 6362 (1995).
- [13] X. Li and R. L. Whetten, *Z. Phys. D* **26**, 198 (1993).
- [14] G. L. Gutsev, M. Nooijen, and R. J. Bartlett, *Chem. Phys. Lett.* **276**, 13 (1997).
- [15] M. Gutowski, K. D. Jordan, and P. Skurski, *J. Phys. Chem. A* **102**, 2624 (1998).
- [16] G. L. Gutsev and L. Adamowicz, *J. Phys. Chem.* **99**, 13 412 (1995).
- [17] O. H. Crawford, *Mol. Phys.* **20**, 585 (1971).
- [18] W. R. Garrett, *J. Chem. Phys.* **77**, 3666 (1982).
- [19] K. K. Sunil and K. D. Jordan, *J. Phys. Chem.* **91**, 1710 (1987).
- [20] Y. A. Yang, C. W. S. Conover, and L. A. Bloomfield, *Chem. Phys. Lett.* **158**, 279 (1989).
- [21] C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, *Phys. Rev. B* **38**, 3517 (1988).
- [22] Y. J. Twu, C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, *Phys. Rev. B* **42**, 5306 (1990).
- [23] P. Xia and L. A. Bloomfield, *Phys. Rev. Lett.* **70**, 1779 (1993).
- [24] F. K. Fatemi and L. A. Bloomfield (unpublished).
- [25] J. H. Hendricks, H. L. de Clercq, S. A. Lyapustina, and K. H. Bowen, Jr., *J. Chem. Phys.* **107**, 2962 (1997).
- [26] M. Gutowski and P. Skurski, *J. Chem. Phys.* **107**, 2968 (1997).
- [27] U. Landman, R. N. Barnett, and C. L. Cleveland, in *Physics and Chemistry of Small Clusters*, edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987), p. 169.
- [28] H. Fallgren and T. P. Martin, *Chem. Phys. Lett.* **168**, 233 (1990).
- [29] J. J. Markham, in *Solid State Physics* (Academic Press, New York, 1966), Suppl. 8.
- [30] G. Baldacchini, in *Optical Properties of Excited States in Solids*, edited by S. Di Bartolo (Plenum Press, New York, 1991), p. 255.
- [31] S. Atrill and A. J. Stace, *J. Chem. Phys.* **108**, 1924 (1998).