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Spontaneous thermal isomerization in isolated alkali-halide clusters

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Photoelectron spectra obtained from $(\mathrm{Cs}X)_3\mathrm{Cs}^-$ (X=Cl,Br,I) cluster anions are strongly dependent on the temperature of the laser vaporization source in which they were produced. Spectral features that were present in clusters emerging from the source at room temperature disappear when the source is cooled to low temperature. This effect is consistent with spontaneous thermal isomerization in the isolated clusters, a precursor to the melting transition in bulk materials. [S1050-2947(96)04810-X]

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In recent years, substantial effort has been made to develop a theoretical framework in which to describe phase transitions in small systems [1]. While this work has been motivated in part by a desire to gain insight into analogous bulk phenomena, it has also been driven by a curiosity about the dynamics of finite aggregates. One hallmark of the solidlike to liquidlike transition is an increase in the frequency with which a cluster visits various minimum energy configurations. At the transition, this frequency approaches that of vibrations about individual minima.

In addition to looking at solidlike to liquidlike transitions, this theoretical work has also studied solidlike to less-solidlike transitions and has prompted considerable interest in small systems that exhibit structural transformations [2,3]. But despite this theoretical work, there have been few experimental studies of the role of temperature in these processes. Knochenmuss *et al.* [4], found that varying the temperature of a source producing $(\mathrm{C}_6\mathrm{D}_6)\mathrm{Ar}_n$ $(20<n<35)$ clusters led to changes in their resonant two-photon ionization spectra. This effect was interpreted as a temperature dependence in the structural content of the cluster beam. More recently, Buck and Ettischer [5] reported a temperature dependence in the infrared-dissociation spectra of methanol hexamers. These spectral changes were shown [6] to be consistent with the emergence of a second structural isomer at increased nozzle temperatures.

Because the isomerization process depends strongly on how a cluster is bound, theoretical discussions have proceeded for several different cluster types, with substantial interest shown in the alkali halides [2,3,7–16]. While attempting to understand the isomerization dynamics in a given alkali-halide cluster, investigators have also sought to determine how these transformations depend on the specific alkali and halogen ions involved.

In this paper, we report an observation of spontaneous thermal isomerization in alkali-halide clusters. We observe a temperature dependence in the photoelectron spectra of $(\mathrm{Cs}X)_3\mathrm{Cs}^-$ (X=Cl,Br,I) cluster anions, indicating that the cluster beam contains additional isomers when it emerges from a warm source. Because of the way clusters are formed in this experiment, it is likely that the warm clusters continue to undergo structural transformations even as isolated particles in the cluster beam.

The cesium-halide clusters are produced in a laser vaporization cluster source [17,18]. The pulsed beam from an ArF excimer laser (193 nm) strikes the surface of a cesium-halide disk, sending a plume of vapor into a narrow helium-filled channel. The helium, released by a pulsed valve, cools the vapor and sweeps it out of the channel into the surrounding vacuum chamber.

Regardless of whether clusters are ejected directly from the sample disk during the vaporization process [19] or grow from atomic vapor, they form at very high temperatures and cool during their travels through the source channel. While they are not in the channel long enough to reach thermal equilibrium with it [20], their final temperatures are almost certainly correlated to the channel's temperature. The colder the channel, the faster it should extract heat from the hot clusters. Cooling the channel also slows the helium gas so that the clusters have more time to cool before entering the vacuum.

After leaving the channel, the beam of clusters passes through a skimmer to a time-of-flight mass spectrometer [17,18]. The pulsed field plates of this mass spectrometer extract the cluster anions and direct them toward a magnetic bottle photoelectron spectrometer [21]. When the $(\mathrm{Cs}X)_3\mathrm{Cs}^-$ anions reach the magnetic bottle, they are exposed to the second-harmonic beam of a pulsed Nd:YAG laser (where YAG denotes yttrium aluminum garnet), photodetaching electrons, which then travel through the electron spectrometer to a dual microchannel plate detector.

We determine the kinetic energies of these photodetached electrons from their travel times through the spectrometer. By subtracting these kinetic energies from the 2.33 eV photon energy, we are able to determine how much energy was needed to remove each electron from its cluster anion. We record approximately 10^5 photodetachment events to obtain a complete photoelectron spectrum. Such spectra are quite reproducible from day to day and depend only on the temperature of the source.

Figures 1(a), 2(a), and 3(a) are typical photoelectron spectra of $(\mathrm{Cs}X)_3\mathrm{Cs}^-$ (X=Cl, Br, and I) cluster anions produced with the source channel at room temperature (297 K). Since each of these clusters is composed of four Cs^+ ions, three X^- ions, and two electrons, it is not surprising that the photoelectron spectra are typical of alkali-halide clusters with two excess electrons. All three spectra are similar, except for a slight shift toward higher binding energies as the atomic number of the halogen ion increases and the absence of a discernible peak near 1.15 eV in $(\mathrm{CsBr})_3\mathrm{Cs}^-$.

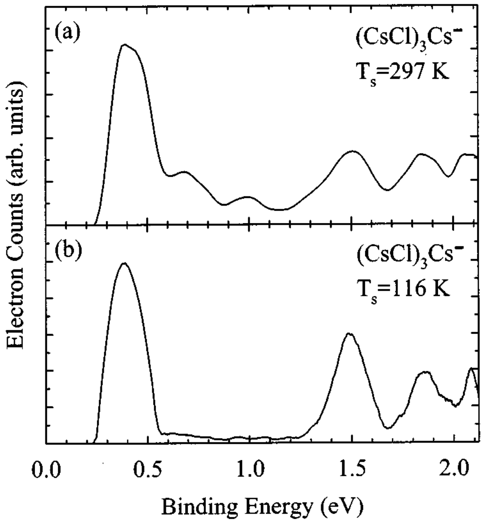

FIG. 1. Photoelectron spectra of $(CsCl)_3Cs^-$ taken with 2.33-eV photons for source temperatures of (a) 297 K and (b) 116 K.

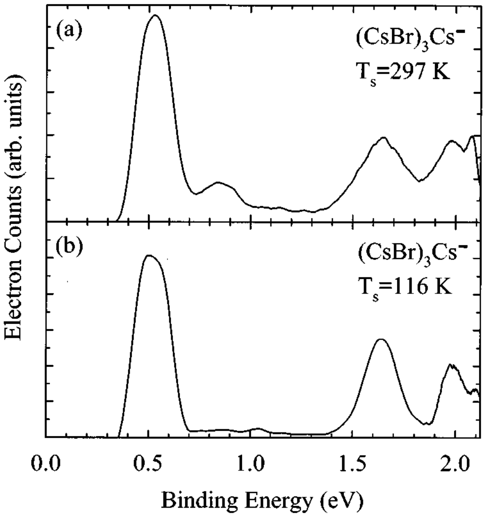

FIG. 2. Photoelectron spectra of $(CsBr)_3Cs^-$ taken with 2.33-eV photons for source temperatures of (a) 297 K and (b) 116 K.

We can assign the peaks in these spectra with the help of previous results for clusters with two excess electrons [21–23]. The spectra are actually less complicated than they appear, because the peaks at binding energies above 1.4 eV involve photodetachment events that leave the remaining neutral clusters in electronically excited states [21–23]. With only three peaks representing ground-state to ground-state photodetachment events, each spectrum is produced by at most three isomers of $(CsX)_3Cs^-$.

The lowest-energy peaks in Figs. 1(a), 2(a), and 3(a) (at 0.39 eV, 0.51 eV, and 0.61 eV respectively) come from a $(CsX)_3Cs^-$ isomer in which both excess electrons localize near one Cs^+ ion, forming a polarized Cs^- ion. These alkali anions are common in sodium- and cesium-halide clusters containing two excess electrons [21,23]. Because the Cs atom has an electron affinity of 0.47 eV [24], a cluster containing a Cs^- ion exhibits an electron vertical binding energy of approximately 0.47 eV.

Further evidence for the presence of a Cs^- ion in this isomer comes from higher-energy peaks in Figs. 1(a), 2(a), and 3(a). Located at 1.50 eV, 1.64 eV, and 1.81 eV, respectively, these peaks represent photodetachment events in which the loss of an electron by the Cs^- ion leaves the neutral Cs atom in the 6*p* excited state. Although the separation between the 6*s* and 6*p* states of the isolated Cs atom is approximately 1.4 eV, polarization effects reduce that spacing in the cluster. Because alkali-halide trimers $(MX)_3$ are known to form stable hexagonal rings [25,26], the most likely structure for this $(CsX)_3Cs^-$ isomer is a hexagonal ring containing three Cs^+ ions and three X^- ions, capped by the Cs^- ion [Fig. 4(a)].

The peaks in Figs. 1(a), 2(a), and 3(a) at 0.68 eV, 0.84 eV, and 0.97 eV, respectively, probably come from a $(CsX)_3Cs^-$ isomer in which the two excess electrons occupy a single corner site in a $2\times2\times2$ cubic crystal [Fig. 4(b)]. Spin pairs of this type are common in two excess electron alkali-halide clusters that are capable of forming complete cuboid crystals and an equivalent $2\times2\times2$ cubic structure was reported for $(NaCl)_3Na^-$ [21]. This structural assignment is also consistent with work done in alkali–alkali-halide melts, which predicted the existence of states in which two electrons localized in a single site [27].

The peaks in Figs. 1(a) and 3(a) at 0.99 eV and 1.28 eV, respectively, are less easy to explain. Although they could reflect final-state excitations in the two isomers just discussed, those excited states would have to involve very small energies. Instead, we believe that these peaks come from a third isomeric form of $(CsX)_3Cs^-$. It is possible that this isomer is an eight-membered ring, with the spin-paired electrons occupying one corner of the octagon. Eight-membered alkali-halide rings are known to be relatively stable [25,26] and have also been observed in molecular-dynamics simulations [2,3].

Figures 1(b), 2(b), and 3(b) are typical photoelectron spectra of $(CsX)_3Cs^-$ (X=Cl, Br, and I) cluster anions produced with the source channel cooled to 116 K. These spectra are obviously different from those obtained with a warm source. The most important difference is in the relative peak heights. While the lowest-energy peak and the corresponding excited-state peak in each low-temperature spectrum remain strong, the peaks associated with the other two isomers are much weaker or absent altogether. Thus, when the source channel is cold, only the hexagonal ring isomer is abundant in the beam.

As we remarked earlier, the three highest-energy peaks in Figs. 1–3 represent photodetachment events in which the remaining neutral clusters are left in electronically excited states. They are produced by the same three isomers that produced the three lowest-energy peaks, but are shifted upward in binding energy by about 1.1 eV. That shift is the difference between the ground and excited states of the remaining neutral clusters and agrees well with spectroscopic measurements made in neutral alkali-halide clusters with single excess electrons [28]. Moreover, recent experiments have found that when infrared light is used to detach electrons from a specific isomer, in order to remove that isomer from the beam prior to photoelectron spectroscopy, the higher-energy peak for that isomer disappears together with

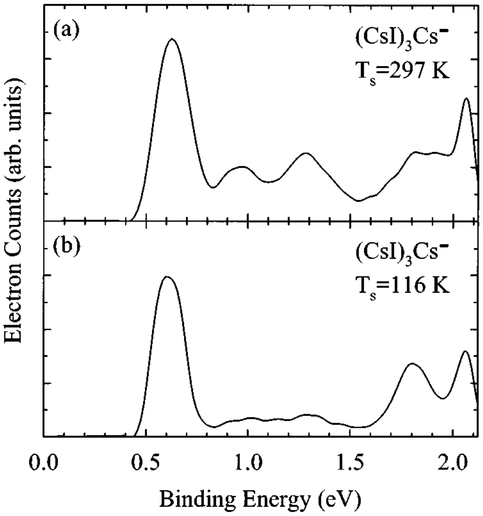

FIG. 3. Photoelectron spectra of $(CsI)_3Cs^-$ taken with 2.33-eV photons for source temperatures of (a) 297 K and (b) 116 K.

the lower-energy peak [29]. Thus each cesium-halide isomer contributes two peaks to the spectra we observe.

As further evidence for the one-to-one correspondence between the three lowest-energy peaks and the three highest-energy peaks, we note that the two higher energy peaks in each group diminish relative to the group's lower-energy peak when the source is cooled. (The third peak is missing in Fig. 3 because it cannot be produced with 2.336-eV photons.) This effect is less obvious in the highest-energy group because the two peaks near 2 eV are enhanced by the large photodetachment cross sections that accompany near threshold photodetachment.

We do not see a temperature dependence of this sort in the photoelectron spectra of other alkali-halide clusters. While we detect structural isomers in many alkali-halide clusters, we are not able to change their relative abundances by varying the temperature of the source. Only the $(CsX)_3Cs^-$ (X=Cl, Br, and I) cluster anions respond to temperature changes.

The isomeric distributions of most clusters are insensitive to source temperature because they were fixed when the clusters were still very hot. Shortly after the laser pulse, the clusters were so hot that they transformed easily between various isomers. But as they cooled, these transformations became more and more difficult until they ceased altogether. Below a certain temperature, a cluster cannot cross the potential barrier from one isomer to another during the time of the experiment.

The population of isomers in the final beam is the equilibrium population that was present when the hot clusters stopped crossing the potential barrier between isomers. Although this population is not in equilibrium at lower temperatures, the equilibration times are exceedingly long. Thus high-energy isomers are essentially frozen into the beam and minor changes in the beam's final temperature have no effect on its isomer distribution.

$(CsX)_3Cs^-$ (X=Cl, Br, and I) clusters are an exception to this rule. Since the isomeric populations change as the source channel is cooled, these clusters must continue to transform from one isomer to the other near room temperature. These clusters are still experiencing spontaneous thermal isomerizations as they emerge from the room-temperature source channel and probably continue to fluctuate in shape as they travel through the mass spectrometer.

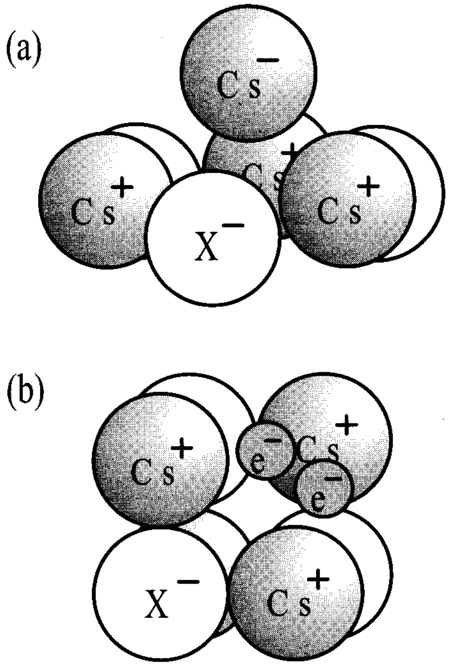

FIG. 4. Proposed structures for the isomers of $(CsX)_3Cs^-$ clusters. (a) is a hexagonal ring, capped by a Cs^- ion. (b) is a $2\times2\times2$ cube, with the two excess electrons occupying a corner site.

We do not know the exact temperature below which these special clusters stop isomerizing; however, it is clear that the potential barriers separating the three isomers are remarkably low. Thus the path by which one isomer converts to the other evidently does not involve any high-energy intermediate states.

Transforming the cubic isomer [Fig. 4(b)] to the hexagonal ring isomer [Fig. 4(a)] is surprisingly easy. If you view the cube as a six-ion chair, with the two ions in the upper left as the chair back, then the chair back simply reclines to the left to form the hexagonal ring. As the two upper left ions pivot toward the lower left, the two extra electrons join with the Cs^+ ion to form a Cs^- ion. Once the chair has reclined into a 3×2 sheet, it opens into a hexagonal ring with the Cs^- ion centered above it.

The cube can also transform into an octagonal ring by opening first into a 4×2 sheet. It does this by reclining both the chair back and the ''footrest'': the electron pair and the Cs^+ ion next to it. Once the 4×2 sheet is formed, it can pop open into the octagonal ring. This type of transformation has been observed in molecular-dynamics simulations of $(KCl)_4$ [2] and $(NaCl)_4$ [3].

These isomeric transformations are facilitated in cesium halides by the large size of the Cs^+ ion. One explanation for why $(NaX)_3Na^-$ and $(KX)_3K^-$ clusters do not exhibit this thermal isomerization is that the Na^+ and K^+ cations are so much smaller than the halogen anions that they raise the energies of the intermediate states. While the size of the alkali ions varies substantially with type (Cs^+ is over 70%

larger than Na^+), the different halogen ions used in our studies are nearly identical in size. The largest, I^-, is less than 20% larger than the smallest, Cl^-. As a result, the choice of halogen does not play the vital role that the choice of alkali does in determining whether the cluster can interconvert between separate isomers.

This analysis is similar to the one used by Buck, Schmidt, and Siebers [6] to predict the results of an experiment on $(CH_3OH)_6$ clusters. In that experiment, Buck and Ettischer found that the infrared-dissociation spectra depended on nozzle temperature and that increasing the temperature of the nozzle produced evidence for the emergence of a second structure in their cluster beam [5]. In the theoretical treatment, the high-temperature situation was described as one involving an interconversion between two different forms [6].

In the future, we would like to obtain better control of the temperature of our cluster beam. While the nozzle temperature clearly affects the clusters' abilities to transform between different isomers, the clusters are not in the source long enough to come into thermal equilibrium with it. An improved source design with a well-defined cluster beam temperature would allow us to determine the internal energies of the clusters, thus aiding theoretical studies seeking to determine the potential-energy surfaces for the $(CsX)_3Cs^-$ systems. Such a source would make measurements at intermediate temperatures worthwhile.

In summary, the temperature-dependent photoelectron spectra of $(CsX)_3Cs^-$ (X=Cl, Br, and I) clusters lead us to conclude that these particles undergo thermal isomerizations at surprisingly low temperatures. Their isomers are readily distinguishable spectroscopically, making them excellent candidates for the study of solidlike to liquidlike transitions in finite systems. Moreover, their simple ionic binding should make them accessible to detailed theoretical examination.

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