Thermal Isomerization in Isolated Cesium-Halide Clusters

F. K. Fatemi, D. J. Fatemi, and L. A. Bloomfield
Department of Physics, University of Virginia, Charlottesville, Virginia 22903

(Received 2 August 1996)

We have used photoelectron spectroscopy to observe thermal isomerization in cesium-halide cluster anions. In many of the $(\mathrm{Cs}X)_n\mathrm{Cs}_m{}^-$ ($X = \mathrm{Cl, Br, I}$; $n = 2-7$; $m = 0, 1$) systems we have studied, small changes in the source nozzle temperature produce dramatic changes in the distribution of cluster isomers. When specific isomers are selectively photodepleted, isomer interconversion quickly reestablishes the thermal isomer distribution, even though the clusters are isolated in a cluster beam. [S0031-9007(96)01845-5]

PACS numbers: 36.40.Ei, 36.40.Sx

Phase transitions in finite systems have attracted considerable interest in recent years [1]. Several theoretical investigations have analyzed the thermodynamic properties and structural transformations of clusters undergoing solidlike to liquidlike transitions [2–9]. These transitions are marked by an increase in the frequency with which a cluster visits various minimum energy geometries. At the transition, this frequency approaches that of vibrations about individual minima.

Unlike bulk materials, small systems have distinct melting and freezing temperatures, with phase coexistence in between [2]. The nature of a cluster's interatomic bonds plays a major role in the character of solid-liquid coexistence. Rare gas clusters with weak, short-range interactions offer a multitude of energetically available isomers and can exhibit truly liquidlike states [2,3]. However, alkali halides have strong ionic bonds, which leave few accessible configurations. In very small alkali-halide systems, coexistence is not between solid and liquid forms; instead, it is between a countable number of distinct isomers [4]. The simple pairwise interaction of pure ionic systems has made the study of coexistence in alkali halides amenable to many molecular dynamics simulations [4–9].

Few experimental results exist to support these calculations and theoretical predictions. Buck and Ettischer [10] reported a temperature dependence in the infrared-dissociation spectra of methanol hexamers. These spectral changes were shown [11] to be consistent with the emergence of a second structural isomer at increased nozzle temperatures. More recently, Ellert *et al.* [12] found a strong temperature dependence in the optical absorption of small sodium cluster ions, explained by a liquid state of the hot clusters.

In this Letter, we report the first direct observation of thermal isomerization in isolated cesium-halide clusters. Not only does the distribution of isomers emerging from our cluster source depend dramatically on the temperature of that source, as we observed earlier for $(\mathrm{Cs}X)_3\mathrm{Cs}^-$ [13], but the thermal distribution of isomers is maintained in flight by structural interconversions in the cluster beam.

The cesium-halide clusters are produced in a laser vaporization cluster source [14,15]. Pulsed light 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 through a temperature controlled nozzle into the surrounding vacuum chamber. Although the clusters are not in the nozzle long enough to reach full thermal equilibrium with it [16] and may experience some cooling as the helium expands into the vacuum, they emerge from the nozzle with a thermal distribution of internal energies and a temperature that is linearly related to the nozzle temperature.

After leaving the nozzle, the cluster beam passes through a skimmer to a time-of-flight mass spectrometer [14,15]. The pulsed field plates of this spectrometer direct cluster anions toward a magnetic bottle photoelectron spectrometer [17]. When the anions reach the magnetic bottle, they are exposed to 532 nm of radiation from a pulsed Nd:YAG laser, photodetaching electrons which then travel through the electron spectrometer to a dual microchannelplate detector. From the electron travel times, we determine their kinetic energies. Their binding energies are found by subtracting their kinetic energies from the 2.33 eV photon energy. We record a large number of these photodetachment events to obtain a complete photoelectron spectrum.

The different isomers of a particular cluster anion generally have different electron affinities and produce distinct peaks in that cluster's photoelectron spectrum. While we have often observed isomers in sodium- and potassium-halide cluster anions, the abundance ratios of those isomers do not depend on the source nozzle temperature (up to 300 K). Evidently their isomer abundance ratios are established while the clusters are still hot from the laser pulse and can still sample many configurations. As the clusters cool in the helium gas, the isomerizations become less frequent and finally cease altogether. Below 300 K, the sodium- and potassium-halide clusters no longer have enough thermal energy to cross the activation barriers between isomers.

0031-9007/96/77(24)/4895(4)$10.00

In contrast, the isomer abundance ratios of several cesium-halide cluster anions depend strongly on the temperature of the source nozzle. The photoelectron spectra of $(CsI)_4^-$ and $(CsI)_3Cs^-$, shown in Figs. 1 and 2, respectively, exhibit this sort of temperature dependence. Other cluster anions that behave this way include $(CsX)_3Cs^-$ ($X = Cl, Br$), $(CsX)_5^-$ ($X = Br, I$), and $(CsX)_7^-$ ($X = Cl, Br$). The isomer abundance ratios for $(CsCl)_5^-$ and $(CsI)_7^-$ may also be temperature dependent but these species are too rare in the cluster beam to produce reliable spectra.

Unfortunately, the isomer abundance ratios are also somewhat sensitive to the source conditions, indicating that the clusters are not always in perfect thermal equilibrium with the nozzle. While we thus cannot determine the exact internal temperatures of the clusters, we normally keep the source conditions constant and vary only the nozzle temperature while producing the different photoelectron spectra. However, reaching the lowest nozzle temperature, 130 K, requires the use of liquid nitrogen with the source, a change that may affect the source conditions. Since these spectra are quite reproducible as long as the source conditions do not change, we are confident that the cluster internal temperature depends linearly on the nozzle temperature. We hope that further source development will allow us to establish the cluster temperature exactly.

The center of each low-energy peak in a photoelectron spectrum is the electron vertical binding energy (EVBE) for the associated cluster isomer. All of the cluster anions studied in this work have at least one weakly bound electron that is accommodated near a cesium positive ion, in a lattice anion vacancy, or in a diffuse surface state. From previous photodetachment studies [17–19], we have learned to associate certain EVBEs with particular electron accommodation modes. In a cluster with only one weakly attached electron, an EVBE above 1.0 eV probably indicates that the electron is localized near a cesium positive ion. An EVBE near 0 eV is most likely due to a diffuse surface state. An intermediate EVBE probably reflects partial electron localization in an anion vacancy, analogous to an *F* center in a bulk ionic crystal. In general, the lower an isomer's EVBE, the more delocalized is its weakly attached electron.

Remarkably, in every cluster that exhibits a temperature dependent photoelectron spectrum, it is the isomer with the lowest EVBE that becomes dominant at low temperature. This result suggests that isomers with relatively delocalized electrons are favored at low temperature while those with relatively localized electrons are favored at high temperature.

This behavior is clearly seen for $(CsI)_4^-$ (Fig. 1). At low temperature, the most abundant isomer has an EVBE of only 0.18 eV, indicating a delocalized electron. The eight ions in this isomer are probably arranged in a $2 \times 2 \times 2$ cube with the weakly attached electron distributed over its surface. At high temperature, the most abundant isomer has an intermediate EVBE of 0.90 eV, typical of an electron in a lattice vacancy. The eight ions in this isomer probably form an octagonal ring with the electron localized in the vacancy at the center of that ring. These observations are consistent with calculations for $(NaCl)_4^-$, which predicted the low temperature form to be a cube with a surface electron and a high temperature form to be a planar octagon with a central localized electron [8].

For the relative abundances of these two isomers to be sensitive to the nozzle temperature, the clusters must be able to isomerize at temperatures near that of the nozzle. The energy barrier separating the two isomers must be minimal. One possible isomerization pathway begins with the unfolding of the $2 \times 2 \times 2$ cube—two opposite faces of the cube fold away from one another,

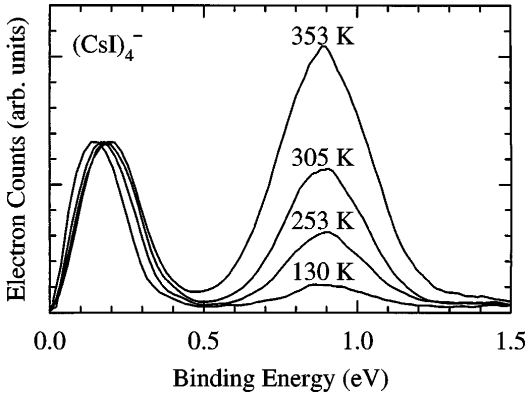

FIG. 1. Photoelectron spectra of $(CsI)_4^-$ cluster anions taken with 2.33 eV photons at four different nozzle temperatures. The traces are scaled so that the low binding energy peaks have equal heights. As the nozzle temperature is reduced, the isomer with the low EVBE increases in abundance relative to the isomer with the high EVBE.

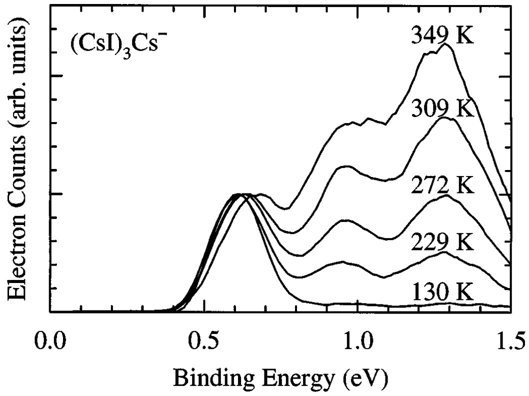

FIG. 2. Photoelectron spectra of $(CsI)_3Cs^-$ cluster anions taken with 2.33 eV photons at five different nozzle temperatures. The traces are scaled so that the low binding energy peaks have equal heights. As the nozzle temperature is reduced, the isomer with the lowest EVBE increases in abundance relative to the two other isomers.

forming a 2 × 4 ladder which then pops open to the octagonal ring. Several molecular dynamics calculations have predicted the cube → ladder → ring isomerization process in neutral $(MX)_4$ systems [4–6] and the presence of an extra electron should not alter this transformation significantly. The fact that we see no evidence of a ladder isomer in the spectra suggests that the clusters move through that form very quickly.

A similar unfolding pathway may explain the isomerization of $(CsI)_3Cs^-$ (Fig. 2) [13]. This cluster has two weakly attached electrons [19] that arrange themselves in a spin pair. The isomer with a low EVBE of only 0.61 eV, dominant at low nozzle temperatures, is probably a hexagonal ring of ions, capped by the remaining Cs^+ ion and the relatively delocalized electron spin pair. The second isomer, with an EVBE of 0.97 eV, is probably a 2 × 2 × 2 cube with the spin-paired electrons occupying a corner lattice site. The third isomer, with an EVBE of 1.28 eV, probably has the spin-paired electrons occupying one position in an octagonal ring. The cubic isomer acts as an intermediate between the two ring forms, allowing isomerization to proceed by folding and unfolding the cluster. In both of the higher temperature isomers, the extra electrons are more localized than in the lower temperature isomer.

The easy isomerization in these cesium-halide cluster anions not only allows their abundance distributions to change with temperature, it also allows them to change form in the cluster beam. To demonstrate that clusters continue to isomerize even in isolation, we selectively photodetached electrons from one isomer and observed its repopulation from the other isomer(s).

In one such study, we used 0.65 eV photons (the Nd:YAG laser fundamental, Raman shifted in H_2) to deplete the cubic isomer of $(CsI)_4^-$ and then performed photoelectron spectroscopy on the remaining cluster anions. As shown in Fig. 3, the resulting photoelectron spectrum indicated that both isomers were partially depleted. By studying the dependence of this effect on laser fluence and remeasuring the cluster masses after exposure to light, we determined that neither multiphoton processes nor fragmentation effects were present in the experiment. Since 0.65 eV photons have too little energy to photodetach the ring isomer, the decrease in this isomer must have been due to in-flight isomerization. This isomerization reestablished the thermal distribution of isomers after one isomer was selectively depleted.

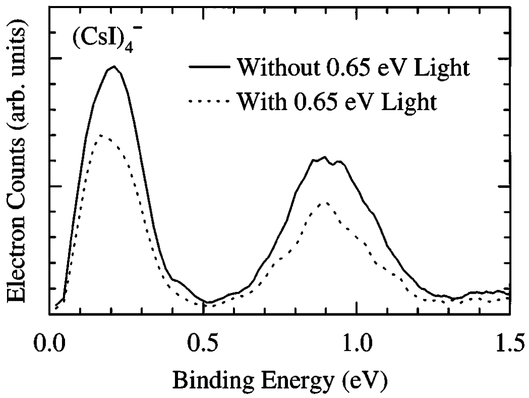

FIG. 3. Photoelectron spectra of $(CsI)_4^-$ cluster anions at 296 K, taken with 2.33 eV photons before and after exposure to 0.65 eV photons. Although the 0.65 eV photons can deplete only one of the two isomers, the peaks for both isomers decrease. This result indicates that the clusters isomerize in the beam and repopulate the depleted isomer.

We also observed this isomer redistribution in $(CsX)_3Cs^-$ and $(CsX)_7^-$ cluster anions. We attempted to measure how long the redistribution takes by varying the delay between the infrared laser pulse that depletes one isomer and the visible laser pulse that produces the photoelectron spectrum of the remaining cluster anions. Over a delay range from 0 to 100 ns, we observed no change in the photoelectron spectra. This result indicates that the isomer redistribution is so rapid that our 5 ns laser pulses are unable to observe it, and is consistent with molecular dynamics calculations on neutral $(MX)_4$ systems [4] which predict picosecond time scales for the isomerization. Observing the isomerization in real time will require femtosecond laser pulse-probe experiments.

To demonstrate that the infrared light pulse depletes only one isomer, we also studied its effect on clusters that do not exhibit thermal isomerization. In such clusters, only isomers with EVBEs below the photon energy showed any depletion. For example, while there are two isomers of $(CsI)_2^-$, the relative abundances of those isomers do not depend on the temperature of the nozzle. Evidently, the barrier to isomerization is large and the relative abundances of the isomers are established at a temperature well above that of the nozzle. When these clusters were exposed to 0.65 eV light, only the isomer with an EVBE of 0.3 eV was depleted (Fig. 4). Similarly, 0.65 eV light depleted only one isomer of $(CsCl)Cs^-$, which also has isomer abundances that do not depend on the nozzle temperature.

The relative strengths of the photoelectron peaks provide information about the time a cluster spends in each isomeric form. At low temperature, the cluster has little internal energy and spends most of its time near the global minimum of the potential energy surface—its excursions to other local minima are infrequent and brief. But at high temperatures, its increased internal energy allows the cluster to escape from the global minimum frequently and it spends much or even most of its time in other isomeric forms. The spectra we record can be viewed as measures of the average time a cluster spends in each isomeric form. However, because the strength of each isomer's photoelectron peak also depends on its relative photodetachment cross section, we cannot assign exact population percentages without further study.

Since the time spent transforming from one isomer to another is exceedingly small, on the order of a vibrational

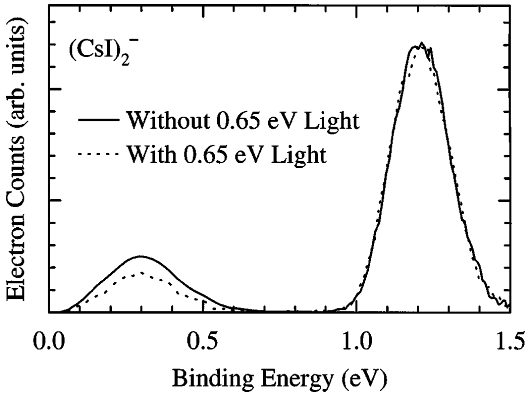

FIG. 4. Photoelectron spectra of $(CsI)_2^-$ cluster anions at 296 K, taken with 2.33 eV photons before and after exposure to 0.65 eV photons. The 0.65 eV photons can deplete only one of the two isomers. Since no thermal isomerization is occurring in this cluster, only the peak corresponding to the depleted isomer is affected.

period, the clusters spend the vast majorities of their times in specific isomeric forms. As a result, photodetachment rarely occurs during a transformation and the photoelectron spectra show distinct peaks corresponding to specific isomers. If the clusters were fully liquidlike, spending large fractions of their times transforming from one isomer to another [5], we would expect to see significant amounts of photodetachment occurring during those transformations. This photodetachment from transition states should blur the peaks of specific isomers. At the highest nozzle temperature we have used, 360 K, there is some evidence in our data for photodetachment occurring during the transformations between isomers. However, the individual isomer peaks remain relatively distinct, with full widths at half maximum that are only about 10% broader than at much lower nozzle temperatures. This peak broadening reflects the larger amplitude motions of a cluster's ions at elevated temperatures, a motion that distorts the cluster and affects both its EVBE and the Franck-Condon overlap between the anion and the neutral.

Because the relative abundances of the cesium-halide cluster isomers continue to change with temperature even at the coldest nozzle temperatures studied (130 K), it appears that the barriers to isomerization are exceptionally small in these systems. The large size and polarizability of cesium ions make it easy for these clusters to transform from one isomer to another. Our inability to detect thermal isomerization in the sodium- or potassium-halide clusters is probably due in large part to the small sizes and polarizabilities of the Na^+ and K^+ ions. Likewise, the bulk melting points of alkali halides tend to decrease as the atomic weights of the constituent ions increase, and are particularly low for cesium halides.

We have shown that small cesium-halide cluster anions isomerize easily at temperatures between 130 and 360 K, and that this isomerization permits the relative abundances of the isomers to change with the temperature of the source nozzle. We have also demonstrated that this isomerization occurs even in the isolation of the cluster beam. We expect these observations to provide insight into the potential energy surfaces of these clusters and into the analogs to phase transitions that are present in finite systems such as molecules and clusters. We hope that future experiments will be able to establish accurate cluster temperatures, activation energies of isomerization, and isomerization rates.

This work was supported by NSF Grant No. DMR-9412618.

[1] See D. J. Wales and R. S. Berry, Phys. Rev. Lett. **73**, 2875 (1994), and references therein.
[2] C. Chakravarty, J. Chem. Phys. **103**, 10 663 (1995).
[3] J. B. Maillet, A. Boutin, and A. H. Fuchs, Phys. Rev. Lett. **76**, 4336 (1996).
[4] A. Heidenreich, I. Schek, D. Scharf, and J. Jortner, Z. Phys. D **20**, 227 (1991).
[5] J. P. Rose and R. S. Berry, J. Chem. Phys. **96**, 517 (1992).
[6] A. Heidenreich and J. Sauer, Z. Phys. D **35**, 279 (1995).
[7] J. P. Rose and R. S. Berry, J. Chem. Phys. **98**, 3246 (1992).
[8] 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.
[9] A. Heidenreich, J. Jortner, and I. Oref, J. Chem. Phys. **97**, 197 (1992).
[10] U. Buck and I. Ettischer, J. Chem. Phys. **100**, 6974 (1994).
[11] U. Buck, B. Schmidt, and J. G. Siebers, J. Chem. Phys. **99**, 9428 (1993).
[12] C. Ellert, M. Schmidt, C. Schmitt, T. Reiners, and H. Haberland, Phys. Rev. Lett. **75**, 1731 (1995).
[13] D. J. Fatemi, F. K. Fatemi, and L. A. Bloomfield, Phys. Rev. A **54**, 3674 (1996).
[14] C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, Phys. Rev. B **38**, 3517 (1988).
[15] Y. J. Twu, C. W. S. Conover, Y. A. Yang, and L. A. Bloomfield, Phys. Rev. B **42**, 5306 (1990).
[16] B. A. Collings, A. H. Amrein, D. M. Rayner, and P. A. Hackett, J. Chem. Phys. **99**, 4174 (1993).
[17] P. Xia and L. A. Bloomfield, Phys. Rev. Lett. **70**, 1779 (1993).
[18] D. J. Fatemi, F. K. Fatemi, and L. A. Bloomfield (to be published).
[19] P. Xia, N. Yu, and L. A. Bloomfield, Phys. Rev. B **47**, 10 040 (1993).