

## Time-Resolved Dynamics of Thermal Isomerization in Cesium-Halide Cluster Anions

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We have performed time-resolved studies of the dynamics of thermal isomerization occurring in certain cesium-halide cluster anions. Using a pump-probe technique, we have observed the repopulation of a photodepleted isomer within an ensemble as a function of time by monitoring the photoelectron spectrum. The rates of isomerization increase and the isomer lifetimes decrease as functions of temperature. The clusters undergo a gradual phase transition from solidlike to liquidlike states with liquidlike behavior obtained at  $\sim 500$  K, much lower than the bulk melting temperatures of  $\sim 900$  K.

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The properties exhibited by bulk materials grow out of the interactions of their constituent atoms. Clusters form a middle ground between these atoms and the bulk materials. By studying clusters, one can learn more about the underlying mechanisms that produce the properties exhibited by the bulk. One such property that has gained much attention in the past two decades is that of a phase transition [1]. For a bulk material, the freezing/melting point is a sharp, well-defined transition and occurs at a particular temperature for each pressure. For finite systems such as clusters, however, the transition from solid to liquid is not well defined and may even exhibit a phase coexistence [2–4]. Depending on the type of interaction between the atoms and the size of the cluster, some clusters have a regime of phase coexistence separating solidlike and liquidlike states.

Theorists have developed a framework for describing phase transitions in finite systems in terms of the underlying potential energy surface (PES) [5]. Depending on the topology of the PES at different energies, a cluster can exhibit solidlike or liquidlike behavior based on its ability to isomerize into different forms. The more liquidlike a cluster becomes, the higher the frequency with which it isomerizes. Rare gas clusters have weak, short-range interactions and are able to form a large number of energetically close isomers. Large rare gas clusters can exhibit freezing/melting behavior similar to the bulk [4]. The strong interactions within alkali-halide clusters, on the other hand, allow for only a small number of isomers. For small alkali-halide clusters, phase coexistence is a regime in which several distinct isomers can exist and the cluster frequently visits each isomeric form [3].

Many theorists have examined these subjects by performing molecular dynamics simulations on a variety of clusters. In particular, several studies have been done using alkali halides because of the simplicity of their models. Heidenreich *et al.* performed simulations of the isomerization of  $(\text{NaCl})_4$  clusters [6,7] while Rose and Berry did the same with  $(\text{KCl})_4$  and  $(\text{KCl})_5$  clusters [8]. A small number of stable isomers were found for each of these clusters, corresponding to minima on the PES.

Molecular dynamics simulations and Rice-Ramsperger-Kassel-Marcus theory calculations determined the temperature dependence of the rates of isomerization between the different isomers.

Experimental studies of isomerization are few and have mostly been limited to the mere observation that it is occurring. Fatemi *et al.* have shown that certain cesium-halide clusters have a temperature dependent photoelectron spectrum [9–11]. This dependence is attributed to the existence of multiple isomers within the cluster beam with different isomers becoming the dominant structures at different nozzle temperatures. In flight isomerization was proven by photodepleting one isomer a few nanoseconds before the spectrum was taken and observing that the other isomers had also been depleted as a result of their isomerization into the depleted form [10,11]. In this Letter, we report on studies that use ultrafast laser pulses to probe the dynamics of thermal isomerization occurring in these systems.

The cesium-halide clusters are produced in a laser vaporization cluster source [12,13]. A plume of cesium-halide vapor, ejected from a sample disk by a laser pulse (193 nm), is swept through a narrow channel by a pulse of helium gas. The channel's nozzle end is temperature controlled and the helium brings the cluster vibrational temperatures into approximate thermal equilibrium with it. A cluster beam forms in the supersonic expansion of this gas into the surrounding vacuum chamber, and that beam continues through a skimmer and into a time-of-flight mass spectrometer [14]. The pulsed field plates of the spectrometer direct the cluster anions toward a magnetic bottle photoelectron spectrometer [15].

When anions of the desired mass reach the magnetic bottle, they are exposed to an ultrafast pulse (1–2 ps duration) of laser light that may photodetach electrons from them. We determine the kinetic energies of these electrons by measuring their flight times to a set of microchannel plates at the end of the photoelectron spectrometer. To find the amount of energy required to remove an electron from a cluster, we subtract the electron kinetic energy from the photon energy. Recording

a large number of photodetachment events yields a photoelectron spectrum for the cluster. This spectrum generally contains multiple peaks, each corresponding to a different isomer. The center of each peak is the electron vertical binding energy (EVBE) for the associated isomer.

Each repetition of the experiment creates an ensemble of clusters whose distribution of energies is determined by the temperature of the nozzle. Once the clusters leave the nozzle, their paths are virtually collisionless and each cluster maintains a constant internal energy. The clusters isomerize in flight so that, when the ensemble reaches the laser interaction region, a steady state has been established for the populations of the isomers. The photoelectron spectrum provides us with a measure of the relative abundances of the isomers.

Preceding the spectroscopic “probe” pulse with a depleting pulse selectively removes certain isomers from the ensemble by photodetaching their electrons. We can then observe changes in the spectrum due to the thermal isomerizations occurring within the ensemble. Figure 1 shows the photoelectron spectrum for  $\text{Cs}_4\text{I}_3^-$  before and after the depleting pulse. This spectrum contains three peaks that correspond to three different isomers. The depleting pulse was tuned to selectively deplete the lowest EVBE isomer. A continuously variable delay from 0–1000 ps between the deplete and probe pulses allows us to observe that the initially depleted isomer regains some of its population at the expense of the other two isomers as time passes. This is due to the isomerization of the nondepleted isomers into the depleted form as the ensemble evolves to reestablish the steady state.

In the simplest model, the atoms within alkali-halide clusters exist as closed-shell ions. Therefore  $\text{Cs}_4\text{I}_3^-$  has four  $\text{Cs}^+$  ions, three  $\text{I}^-$  ions, and two electrons which are referred to as excess electrons. These two excess electrons can arrange themselves as a spin pair in a halogen va-

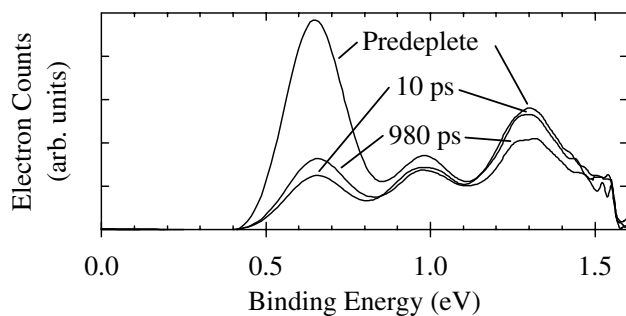


FIG. 1. Photoelectron spectra of  $\text{Cs}_4\text{I}_3^-$  taken with 1.55 eV photons and a nozzle temperature of 300 K. The traces were taken before and after (10 and 980 ps delay) the 0.60 eV depleting pulse. The lowest EVBE isomer was substantially depleted but is replenished at the expense of the other two isomers as the isomer populations within the ensemble return to a steady state.

cancy [15]. Electronic structure calculations [16,17] for the minimum energy structures of a very similar cluster whose spectrum also contains three peaks,  $\text{Cs}_4\text{Cl}_3^-$ , suggest that the lowest EVBE isomer is a cubic structure, the middle EVBE isomer is a ladderlike structure, and the highest EVBE isomer is an octagonal ring. Time-resolved studies could only be performed on  $\text{Cs}_4\text{I}_3^-$  and, due to its similarity to  $\text{Cs}_4\text{Cl}_3^-$ , we assume that the isomer identifications are the same. Therefore, in our experiments, we are selectively depleting the cube isomer.

We collected photoelectron spectra at a number of deplete-probe delays for several temperatures of the source nozzle. A set of three Gaussian peaks was fit to each spectrum, and the area of each Gaussian represents the abundance of a particular isomer in the ensemble. In Fig. 2, the peak areas as a percentage of their predeplete values are plotted as a function of deplete-probe delay for each nozzle temperature.

Figure 2 shows that, at each temperature, the cube isomer is depleted to 20%–50% of its original abundance. There is also some slight depletion of the ladder and ring isomers by direct two-photon photodetachment. Over the

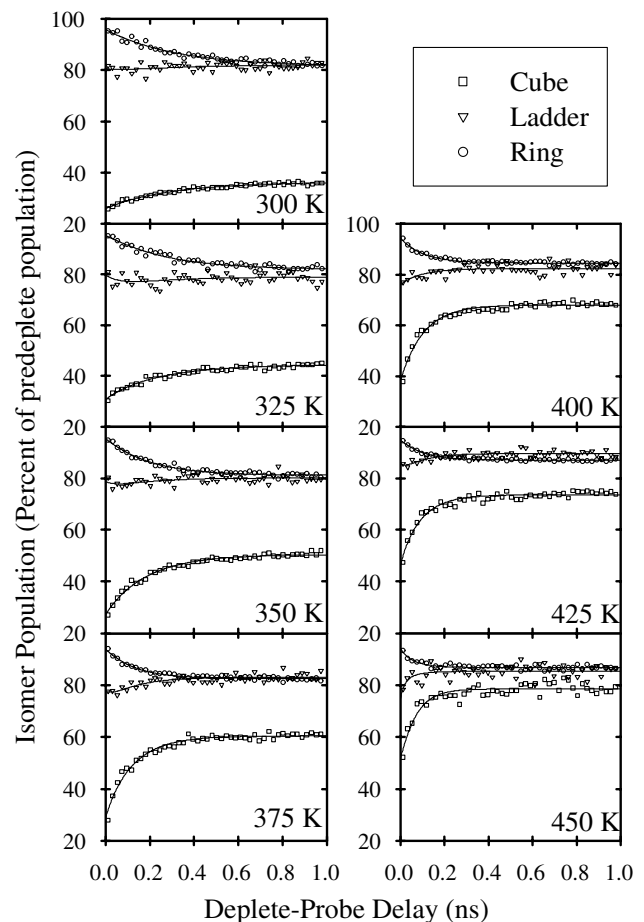


FIG. 2. Reequilibration of the isomer distribution of  $\text{Cs}_4\text{I}_3^-$  at several nozzle temperatures.

next nanosecond, the cube isomer regains some of its population at the expense of the other two isomers. As the nozzle temperature is increased, this repopulation occurs more quickly. This is because it becomes easier for the cluster to isomerize as its internal energy increases.

A cluster's ability to isomerize depends on several things. First, it must have sufficient energy to cross a potential energy barrier. Each shape corresponds to a minimum on the PES and isomerization occurs when a cluster crosses the saddle point connecting two minima. Since quantum tunneling is too slow to observe on our experimental time scale, clusters exhibiting isomerization in our experiment must have internal energies that are well above the potential energy barriers.

Second, there must be a significant number of transition and final states into which the cluster can move as it isomerizes. The cluster has a large amount of phase space it can explore, and it will explore this phase space within a particular isomer until it is able to find a pathway to isomerization. The more pathways there are available, the easier it is to isomerize. In other words, there must be an overlap in the density of states of the original, transition, and final shapes. If there is not good overlap, even when there is sufficient energy, then the time scales for transitions are exceedingly long. Since the density of states is a rapidly increasing function of the energy, the more energy a cluster has the higher the density of states becomes and the easier it is for the cluster to find a passage to isomerization. Therefore, with increased vibrational energy, isomerizations occur more often and the increased number of isomerizations per unit time reduces the amount of time needed to repopulate the depleted isomer.

In order to analyze the dynamics, we must identify the isomerization reactions that can occur. Based on the predicted shapes, there is no obvious way for the cube to convert directly into the ring [16]. However, there are a few ways to envision cube  $\leftrightarrow$  ladder and ladder  $\leftrightarrow$  ring isomerizations. For the cube  $\leftrightarrow$  ladder isomerization, the cube can fold out to form the ladder by breaking the bond between two adjacent atoms on a face containing the electron spin pair, allowing the cluster to open as the electron pair travels with the lonely Cs<sup>+</sup>. Alternatively, the lonely Cs<sup>+</sup> can vibrate around to the side of the ladder creating a hexagon with a central Cs atom. This shape has been shown to be unstable and would subsequently convert to the cube [16]. For the ladder  $\leftrightarrow$  ring isomerization, the interior rungs of the ladder can break, allowing the cluster to pop open to form the ring. Therefore we assume that the cube  $\leftrightarrow$  ring isomerization must go through the ladder and cannot convert directly [16]. This same sort of cube  $\leftrightarrow$  ladder  $\leftrightarrow$  ring transition is predicted by Heidenreich *et al.* in simulations of the isomerization of (NaCl)<sub>4</sub> [7].

When a cluster arrives at the laser interaction region, it is in a complicated state that includes amplitude in all

three of the isomeric forms. The depleting laser pulse selectively quenches amplitude corresponding to the cube isomer. In essence, the depleting pulse creates an anti-wave-packet: a broad superposition of states that is missing amplitude in the cube isomer. This anti-wave-packet evolves across the PES just as a normal wave packet would. The probe pulse samples the subsequent dynamics of this anti-wave-packet. Because of the enormous number of energy eigenstates involved in this anti-wave-packet, coherent quantum effects such as beating are not observed, and the evolution of the system follows the classical trajectory of a three state system approaching a steady state.

If we consider the isomerizations as unimolecular reactions, the dynamics of this system can be modeled by the following set of differential rate equations:

$$C \xrightleftharpoons[k_2]{k_1} L \xrightleftharpoons[k_4]{k_3} R, \quad (1)$$

$$\frac{dC}{dt} = -k_1 C + k_2 L, \quad (2)$$

$$\frac{dL}{dt} = -(k_2 + k_3)L + k_1 C + k_4 R, \quad (3)$$

$$\frac{dR}{dt} = -k_4 R + k_3 L, \quad (4)$$

where  $C$ ,  $L$ , and  $R$  represent the populations of the cube, ladder, and ring isomers, respectively, and  $k$  are the rate constants for each isomerization reaction. The solutions to these equations are of the general form

$$X(t, E) = A_{X,1} + A_{X,2}e^{A_{X,4}t} + A_{X,3}e^{A_{X,5}t}, \quad (5)$$

where  $X = \{C, L, R\}$  and the  $A_{X,i}$  contain the rate constants and initial populations of the isomers. This set of equations assumes all the clusters have the same internal energy,  $E$ , and the rate constants are associated with that energy. However, the clusters in our experiment have a distribution of energies determined by the temperature of the source. This means that each cluster will undergo isomerizations at a different rate, depending on its internal energy. In order to describe the experimental data, the probability function for the energy distribution,  $P(E, T)$ , should be used to create a weighted sum of the above solutions as

$$X(t, T) = \int P(E, T)X(t, E)dE, \quad (6)$$

where the rate constants are functions of energy. If we knew  $P(E, T)$ , our data could be described fully; however, finding  $P(E, T)$  is a complicated task. As a simple approximation, we take  $P(E, T)$  as a delta function in energy at each temperature. This allows us to fit Eqs. (5) to our

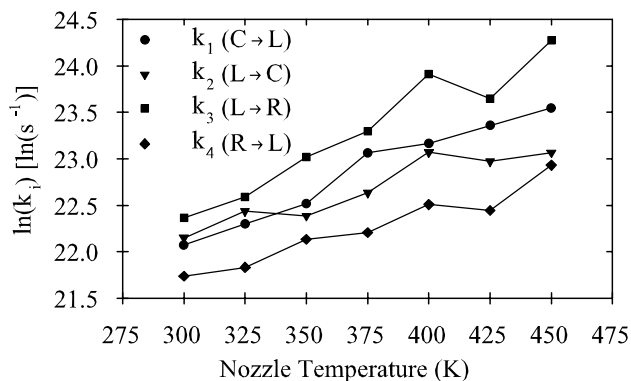


FIG. 3. Rate constants for the different isomerization reactions of  $\text{Cs}_4\text{I}_3^-$  as a function of temperature.

data to obtain a set of rate constants  $k_i$  for each temperature. Model curves fitted to the data are shown in Fig. 2.

The rate constants obtained from these fits are shown in Fig. 3. All of the rate constants increase with temperature, suggesting it is becoming easier for all of the isomers to interconvert. These rate constants can be used to determine the Arrhenius activation energies for the different reactions. The largest activation barrier was calculated to be  $\sim 0.15$  eV, which is small enough to allow even room temperature thermal energy to initiate isomerization.

In order to determine the time scales involved in the isomerizations, the rate constants were used to calculate the lifetimes of the isomers (Fig. 4). As the temperature increases, the lifetimes shrink. At the highest temperatures, the lifetimes approach the tens-of-picoseconds range. The time scale for interconversion is on the order of an atomic vibrational period, which for this cluster is on the order of hundreds of femtoseconds to a few picoseconds [17]. Therefore, the clusters are not spending much more time in a particular shape than it takes to convert from one shape to another. This is the hallmark of a phase transition from a solidlike to a liquidlike state in finite systems.

In addition to studying  $\text{Cs}_4\text{I}_3^-$ , we also studied the dynamics of  $(\text{CsCl})_7^-$ . The same sort of increase in the rates of isomerization and corresponding decrease in isomer lifetimes were observed [14,18]. It is interesting to note that the bulk melting temperatures for CsI and CsCl are around 900 K and that the clusters in these studies appear to be approaching a liquidlike state at  $\sim 500$  K. That observation agrees with experimental studies dating to the early 1900s, in which the melting temperature of materials decreased with particle size [1,19].

In summary, we have observed the dynamics of thermal isomerization occurring in cesium-halide clusters. We have determined the rate constants for the isomerization reactions occurring in these clusters and have used them to calculate the isomer lifetimes. These life-

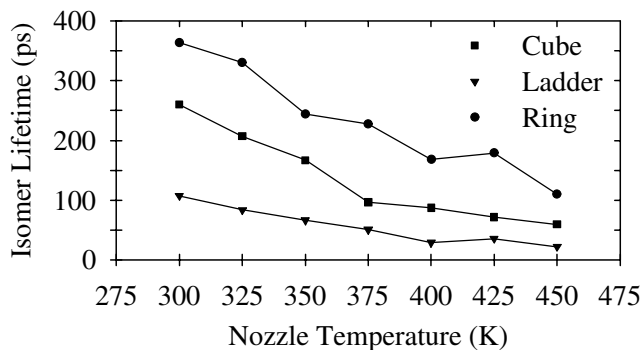


FIG. 4. Lifetimes of the different isomers of  $\text{Cs}_4\text{I}_3^-$  as a function of temperature.

times decrease as the cluster temperature increases and approach the time scales for interconversion at  $\sim 500$  K, indicating a phase transition into a liquidlike state.

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