Dissipation Effects in Cluster Fission

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The fission of Sr_n^{2+} is studied from time-of-flight (TOF) measurements. The TOF acts both as a mass spectrometer and as a velocity dispersion analyzer. Evidence of the postfission ejection of a fast neutral atom is shown. It is explained assuming a strong deformation of the fissioning system at the transition state. The relaxation of the deformation energy into vibrations promotes the evaporation of the large fragment.

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Fragmentation is a ubiquitous phenomenon, which manifests itself on a wide variety of scales ranging from large structures to elementary particles. Although fragmentation has been extensively studied for many years, the process itself is still ill understood. For finite systems, the dynamical aspect of the fragmentation is usually analyzed in the framework of statistical theories. This is the case for nuclei fragmentation. It has been shown that energy deposited initially in nuclei is mostly released by neutron evaporation before the system fissions. However, in the high energy collision regime, the postfission neutron ejection presents anomalies against statistical models that are still under debate [1,2]. The great similarity, which exists between nuclei and metallic clusters, also manifests itself in the fission process that is driven by electrostatic repulsion. Since the first experimental evidence of asymmetric fission of doubly charged alkali clusters, analogous to α-particle decay in nuclei [3], the transition towards symmetrical fission has been observed as the fissility parameter, which is the Coulomb energy, divided by twice the surface energy increases [4]. In the cluster size range, where fission dominates the fragmentation processes, theoretically demonstrated is the importance of shape deformation on the energetics [5] through the most favorable fission channels [6,7]. However, the question of how the shape deformation influences the dynamics of the fission and can induce, by dissipative effects, the ejection of an atom is not solved. It is related to the fundamental problem of the dynamical aspect of the transition across the barrier.

In this Letter, we present experimental evidence of postfission evaporation of doubly charged strontium clusters taking its origin in Coulomb energy. In contrast to our previous experiments where only the kinetic energy release of the ionic fragments has been measured [8], the current ones allow one to focus on the kinetics of the ejection of neutral atoms that may accompany the fission process. Moreover, our studied systems are at a temperature low enough to undergo only one unimolecular event during the observational time window.

As previously reported, for multiply charged clusters, there exists a critical size which above the evaporation of neutral species is the dominant dissociation channel, whereas below the critical size the fission into two charged fragments is more favorable [3]. For doubly charged strontium clusters, the critical size is Sr_7^{2+}. We first verify that, for thermally excited clusters above the critical size of stability, the evaporation of one atom is the main decay channel, and that the kinetic energy release of the evaporating atom is statistical in nature. For Sr_7^{2+}, the fission into two singly charged fragments, $Sr_6^+ + Sr$ or $Sr_5^+ + Sr_2^+$, prevails. We show evidence that the fission channel $Sr_6^+ + Sr$ is accompanied by the ejection of a neutral atom. These two correlated fragmentation events, fission and atom ejection, cannot be explained by classical statistical considerations, involving only the thermal excitation of the cluster parent, but rather can be explained assuming that the system is strongly deformed when passing the Coulombic barrier. The resulting deformation energy relaxes into the large fragment after the scission point and generates its evaporation. We also demonstrate how the measured kinetic energy of the ejected atom enables us to deduce the deformation energy.

The experimental setup consists of a gas aggregation cluster source generating a log-normal mass distribution of neutral strontium clusters. The clusters enter an ionization/acceleration region where they are ionized and photoexcited by a 15 ns laser pulse, operating at two different photon energies, either 3.5 or 5.0 eV. At 3.5 eV, clusters are only singly ionized, whereas at 5.0 eV singly and doubly charged clusters are formed. In both cases, a rapid sequential evaporation follows the warming of the clusters for 2–3 μs (i.e., the residence time in the ionizing region). This results in a charged cluster distribution shifted down to smaller sizes, called "evaporative ensemble" [9]. The cluster temperature T_0 associated with the evaporative ensemble is estimated at $T_0 = 700 \pm 100$ K, under our experimental conditions. The ionized clusters enter a tandem time-of-flight (TOF) mass spectrometer. Parents of interest are mass selected according to their mass/charge ratio in the first TOF region. Because they are at a given temperature, subsequent unimolecular dissociation takes place and the resulting ionic fragments are mass analyzed in the second TOF device. In order to

achieve a complete determination of the fragmentation process, we also analyze the neutral products by deflecting all the ions. The resulting mass spectra are shown in Fig. 1. The broadening of the neutral peak with respect to the ion peak portrays the kinetic energy released in the evaporation process. In a first set of experiments, we focus on the evaporation of Sr_n^+. In a second set of experiments, when the ionizing photon energy allows the formation of doubly charged species, we focus on the unimolecular dissociation of Sr_n^{++} with $n = 7, 9, 11$.

For singly charged species, the unimolecular dissociation channel is

$$Sr_n^+ \rightarrow Sr_{n-1}^+ + Sr. \quad (1)$$

Beyond the detection of Sr_{n-1}^+, we have analyzed the dynamical aspect of the evaporation by measuring the kinetic energy released by the corresponding neutral atom. This latter takes the major part of the kinetic energy and it is free of any electric field perturbation. Since the evaporation is statistical in nature, it manifests itself by a broadening of the TOF profile [10,11]. Figure 2 shows the TOF peak of the neutral atom from evaporation of Sr_{11}^+. It is analyzed by comparing its shape with the predictions of the two main statistical models (Fig. 2). Following the Weisskopf theory [12], the probability distribution for the kinetic energy release ϵ of an evaporative process is

$$I(\epsilon) = A\epsilon \exp -\epsilon/kT. \quad (2)$$

Here kT is the temperature of the cluster fragment at the breakup time. The measured neutral peak is fitted by a time profile deduced from (2) and convoluted by the apparatus function. Using the width of the calculated profile as a fitting parameter, the best fit is given in Fig. 2(a). It is clearly seen that such a fit is not satisfactory. Better agreement is obtained using a Langevin model [13] or by assuming that the velocity distribution of the emitted atom follows a Maxwell-Boltzmann distribution:

$$I(v) = Av^2 \exp -(v/v_{\max})^2. \quad (3)$$

This corresponds to a kinetic energy distribution:

$$I(\epsilon) = A\sqrt{\epsilon} \exp -\epsilon/kT, \quad (4)$$

and displays a Gaussian shape profile versus time:

$$I(t) = A \exp -\frac{(t - t_n)^2 v_n^4}{(Lv_{\max})^2}, \quad (5)$$

where t_n and v_n are the time of flight and the velocity of the center of mass of the fragmenting cluster parent,

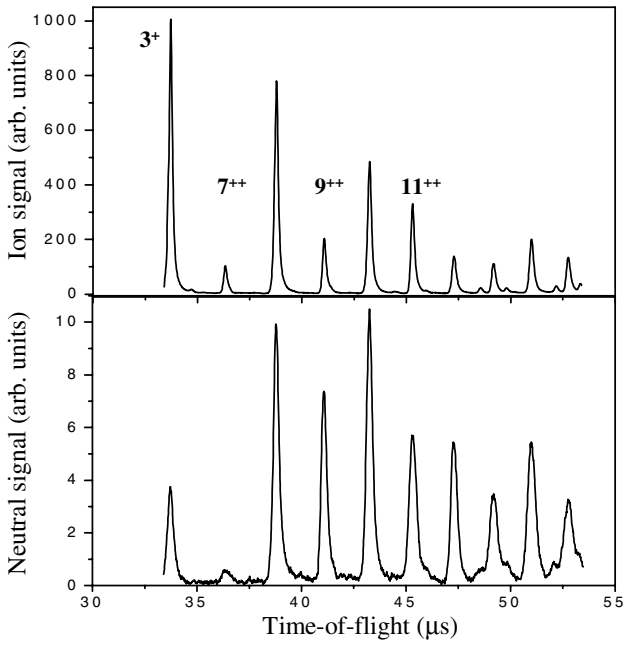

FIG. 1. TOF mass spectra of strontium cluster distribution ionized with a photon energy $h\nu = 5.0$ eV: upper trace ion signal; lower trace neutral signal after deflecting all the ions.

$$Sr_{11}^+ \rightarrow Sr_{10}^+ + Sr$$

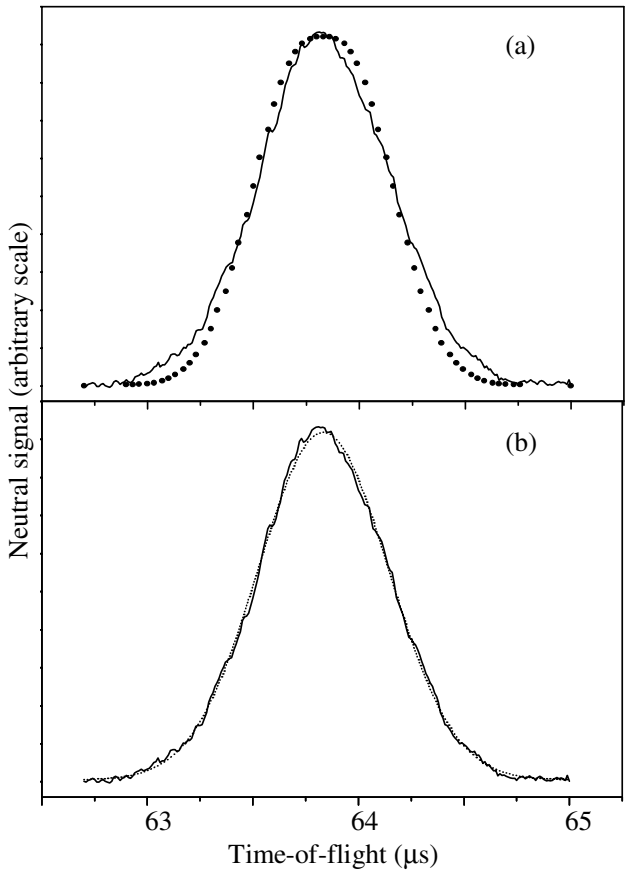

FIG. 2. Fit of the neutral signal associated with the evaporation of the Sr_{11}^+ parent, according to the Weisskopf model (a) and using statistical Maxwell-Boltzmann velocity distribution for the evaporating atom (b) (see text).

respectively, L is the distance between the fragmenting region and the detector, and v_{max} is the relative velocity of the atom in the center of mass, at the maximum of its velocity distribution. The convolution with the apparatus function also leads to a Gaussian profile. Only v_{max}, in the exponent of Eq. (5), is used as a fitting parameter. The quantities t_n, v_m, and L are given by the experimental device. The best fit is given in Fig. 2(b). We deduced the translational temperature $kT = \frac{1}{2}mv_{max}^2$ at the breakup time, which is plotted in Fig. 3 as a function of cluster size (m is the mass of the atom).

For doubly charged species, we studied the unimolecular dissociation of odd numbered atom clusters, since they are not superimposed to singly charged species. For $n \geq 9$, the evaporation dominates:

$$Sr_n^{2+} \rightarrow Sr_{n-1}^{2+} + Sr.$$

For $n = 7$ the fission dominates. The mass analysis of the ionic fragments gives Sr_6^+, Sr_5^+, Sr_2^+, and Sr^+. No doubly charged fragment has been observed. This indicates two fission channels:

$$Sr_7^{2+} \rightarrow Sr_6^+ + Sr^+ \hookrightarrow Sr_5^+ + Sr_2^+.$$

Surprisingly, after deflecting all the ions, a neutral signal appears [Fig. 1]. From mass and charge conservation, the only possibility is the ejection of a neutral atom:

$$Sr_7^{2+} \rightarrow Sr_5^+ + Sr + Sr^+.$$

To go further, we have analyzed the TOF profiles of the emitted neutral atoms from doubly charged clusters as we have done for singly charged ones. Figure 4 displays the neutral signals from Sr_{11}^{2+}, Sr_9^{2+}, and Sr_7^{2+}. For $n = 9$ and 11, the neutral signal reveals a pure Gaussian profile. The deduced temperatures are similar to those observed for singly charged species, in agreement with a cooling by the evaporative process (Fig. 3). For $n = 7$, the neutral signal is difficult to fit by a Gaussian profile [Fig. 4], and if so the apparent temperature attributed to the Sr_7^{2+} fragmenting system is much larger than those of the Sr_7^+ (Fig. 3). What is the origin of the neutral atom ejection observed for the fissioning Sr_7^{2+} and why does its profile present shape and width anomalies? Two possibilities should be considered. The neutral ejection could occur either before or after the scission point. We envisage first the evaporation of Sr_7^{2+} before its fission. It should be followed immediately by the fission of the unstable barrierless Sr_6^{2+}, since Sr_6^{2+} has never been observed in the ion mass spectra:

$$Sr_7^{2+} \rightarrow Sr_6^{2+} + Sr \rightarrow Sr_5^+ + Sr^+ + Sr.$$

In such a case, the profile broadening of Sr should reflect the temperature of the evaporative ensemble and be comparable to those observed for the other parents. In fact, we obtained a temperature out of scale by a factor of 5 (Fig. 3), that rules out this mechanism. The other possibility is to consider a *spontaneous* ejection of an atom induced by the fission mechanism during or after the fission:

$$Sr_7^{2+} \rightarrow Sr_6^+ + Sr^+ \rightarrow Sr_5^+ + Sr^+ + Sr.$$

In that case the translational kinetic energy of the emitted atom results from both the Coulomb energy release of Sr_6^+ from the descent of the fission barrier (Fig. 5) and the kinetic energy originating from the internal energy of

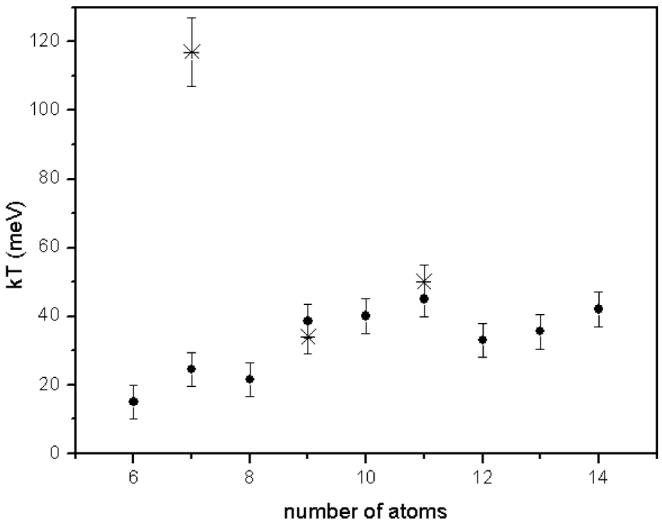

FIG. 3. Translational temperature at the breakup time (see text) of the evaporating atom versus cluster size: ●, singly charged clusters; *, doubly charged clusters.

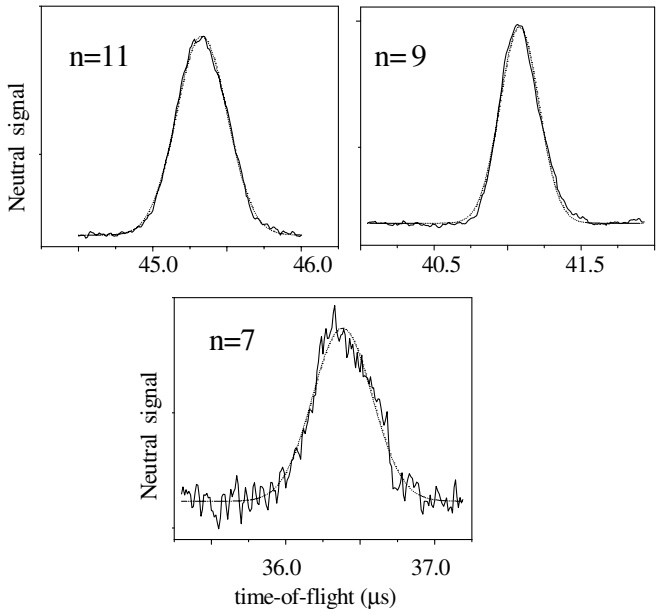

FIG. 4. Fit of the neutral signals associated with the Sr_{11}^{2+}, Sr_9^{2+}, and Sr_7^{2+} parents, with Gaussian profiles according to a statistical Maxwell-Boltzmann velocity distribution model.

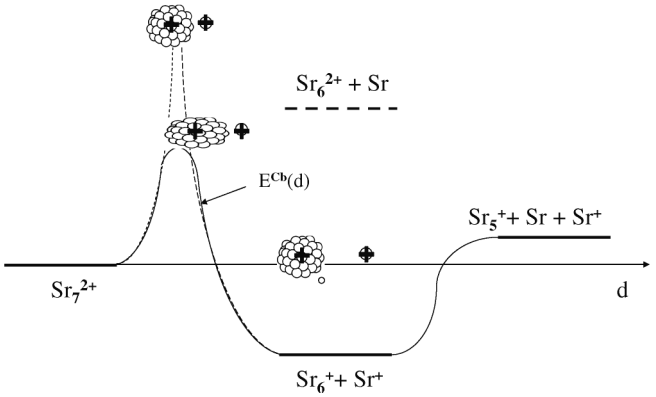

FIG. 5. Schematic potential energy diagram of the fissioning Sr_7^{2+} system against the distance between the fragments.

Sr_6^+. In this latter hypothesis, let us consider the two extreme situations.

First, we assume that the neutral signal broadening comes exclusively from the internal energy of the parent Sr_6^+. This means that the atom ejection takes place at the top of the fission barrier just after the scission point (Fig. 5). One deduces from the width of the profile an internal energy of 2.0 eV for Sr_6^+. With such an energy all the Sr_6^+ would evaporate so fast that none of them can be observed on the detector. This is in contradiction with the observation of Sr_6^+ after the fission of Sr_7^{++}.

On the other hand, we assume that the Coulombic kinetic energy release is exclusively responsible for the observed broadening of the neutral peak. This corresponds to a postfission evaporation, with a two step process and a delay between the two processes long enough to ensure a complete separation of the two singly charged products before the evaporation of Sr_6^+. Assuming a quasirectangular shaped time-of-flight profile, as expected for a well-defined energy release [14], one obtains a translational energy release of 0.06 ± 0.02 eV, after deconvolution with the apparatus function. This value should equate the kinetic Coulombic energy of Sr_6^+ induced by the fission process, i.e., $\frac{1}{7}E^{Cb}(\infty)$ (see Fig. 5). It gives for the outer part of the fission barrier $E^{Cb}(\infty) = 0.42$ eV. In a complementary experiment as described in [8,14], we measured the Coulombic kinetic energy $E^{Cb}(\infty)$ from the recoil velocity of the ionic fragment Sr_6^+ and we found $E^{Cb}(\infty) = 1.2$ eV. In a two step process, these two independent measurements should converge to the same value. It is clear that the latter value is larger than the one deduced for the neutral atom profile showing evidence of an atom ejection along the descent of the fission barrier. The profile related to the ejection of a neutral atom during the fission of Sr_7^{2+} is the interplay between the Coulomb and the evaporation processes.

The observation of atom ejection along the descent of the fission barrier demonstrates an excess of internal energy of Sr_6^+ of the order of magnitude of its dissociation energy (i.e., $\simeq 1$ eV). This energy is taken from the deformation driven by the electrostatic repulsion that is large enough to promote the heating of the system when it relaxes, and finally induces an accompanied evaporation event during the descent of the fission barrier.

In summary, we have shown that the measure of the kinetic energy release of the evaporation of atoms from thermally exited doubly charged clusters is a powerful tool to understand the complex mechanism of the Coulombic fission process of finite systems. We demonstrate that the fission can be accompanied by the emission of an atom resulting from the deformation at the scission point. This deformation driven by the repulsive Coulombic forces leads to a deformed ionic fragment which relaxes by emitting an atom. This provides the impetus for further experimental and theoretical studies of fragmentation dynamics in finite nanoscale systems.

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