Experimental Evidence for the Entropy Effect in Coulombic Cluster Fission

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Coulombic fission of warmed triply charged potassium ion clusters K_n^{3+}, with $n = 54-105$, is studied by unimolecular dissociation mass spectroscopy. Binary fission is shown to occur predominantly with an asymmetrical character which attenuates as the size of the cluster increases. Such a result cannot be interpreted by energetic considerations unless the entropy contribution of discrete atoms is taken into account. [S0031-9007(96)00485-1]

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Fragmentation is an ubiquitous phenomenon which occurs in microscopic systems such as nucleons and in macroscopic objects as well. However, such a phenomenon is in most cases very complex and ill understood. One aspect of cluster studies is to use free clusters as a tool to get insight into fragmentation processes.

In the case of metallic clusters many qualitative properties can be explained with the *jellium model* [1]. In this model, the valence electrons are treated as a Fermi liquid confined in an effective potential well. The discrete nature of the positive ions is replaced by a homogeneous background charge, and the shape of the cluster is determined by the shape of the background. It became apparent that electronic properties of metallic clusters can be accounted for within a shell model [2], very similar to the one used in nuclear physics [3]. In this context it has been shown that Coulombic fission in metallic clusters presents certain analogies to the nuclear fission and α radioactivity despite the differences in the nature of binding in nuclear and metallic clusters [3–5]. The discrete nature of the ions may, however, become important for clusters at rather high temperature when the motion of individual atoms becomes important. It strongly affects the number of possible fission channels since the same fragments may consist of different atoms. The influence of the number of channels grows with an increase in the number of atoms and should play a crucial role for large clusters.

In this Letter we present the first experimental evidence of such an effect, which agrees with the predictions of a simple qualitative model based on the allowance of the entropy contributions of the ions. Our model does not pretend to give a quantitative description of the experimental data but just intended to give a qualitative explanation on the tendencies observed. We have studied experimentally the unimolecular decay of triply charged cluster ions that enables us to observe Coulombic fission of species larger than those which have only two charges [4,6,7]. The role of discrete atoms comes to light at full extent for potassium clusters of size $n = 50-105$ atoms. The observed Coulombic fission channels significantly deviate from the prediction based on energetic considerations. These latter predictions give the wrong dependence for the asymmetrical fission on the cluster size unless the entropy contribution of discrete atoms to the free energy of clusters is taken into account. We have employed the Boltzmann statistic and concentrated here only at the atomic contribution which is the largest one. At this level of consideration we have ignored the weaker effects of the electronic entropy and the vibrational partition function.

The experimental setup is similar to the one described in Ref. [8]. Metallic potassium clusters produced in a gas aggregation source are ionized and warmed up by the radiation of the KrF excimer laser having an energy of $\hbar\omega = 5$ eV. Within our experimental conditions this photon energy enables us to produce singly, doubly, and triply charged cluster ions. The doubly and triply charged clusters are directly identified in the mass spectrum from their appearance critical sizes $n_c^{++} = 21 \pm 1$ and $n_c^{+++} = 53 \pm 1$ for doubly and triply charged clusters, respectively, in agreement with the sizes observed in Ref. [9]. A tandem time-of-flight system allows us to select in the first drift tube the charged cluster ions K_n^{q+} of a given size-to-charge ratio n/q, and to analyze the products of their unimolecular decay during the first time of flight in the second drift tube by applying a properly chosen retarding potential. Unimolecular fragmentation has been extensively studied in the size-to-charge ratio n/q range of 16 to 33.

Figure 1 presents the unimolecular dissociation spectra of the selected ion packet K_n^{q+} for two values of the size to charge ratio $n/q = 17$ and $n/q = 18$. For $n/q = 17$ the selected parent packet contains K_{17}^{+} and K_{34}^{2+} only. K_{51}^{3+} is missing from the selected packet because its size is below the appearance size of stability of triply charged clusters. The unimolecular dissociation spectrum (Fig. 1, upper trace) shows that neutral evaporation dominates in agreement with the fact that K_{34}^{2+} is far above the critical size of stability of the doubly charged clusters [8]. For

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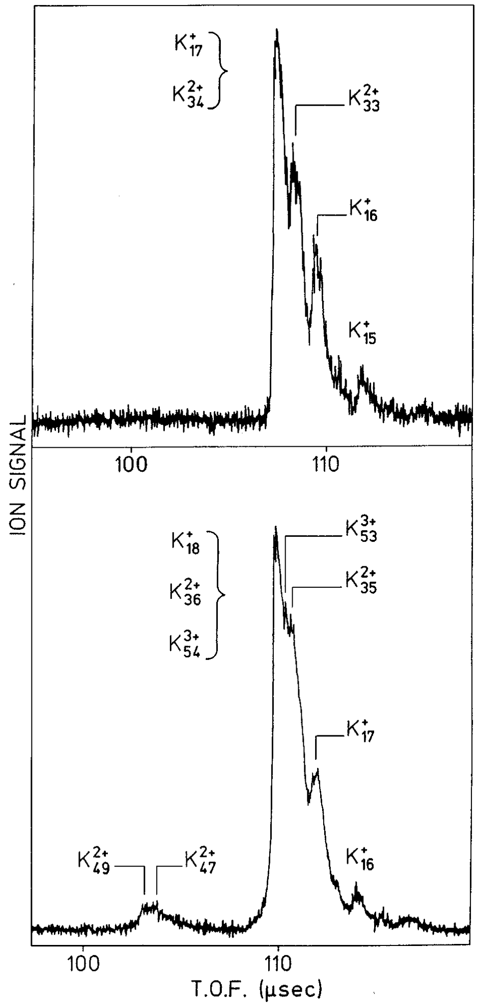

FIG. 1. Unimolecular fragmentation patterns for two selected mass-to-charge ratios $n/q = 17$ (top) and $n/q = 18$ (bottom). Peaks arriving earlier than the parent arrival time are due to the largest fragments of the fission process. Peaks arriving later are the ionic fragments from neutral evaporation.

$n/q = 18$ the selected ion packet contains K_{18}^{+}, K_{36}^{2+}, and K_{54}^{3+} which yield two kinds of unimolecular fragments (Fig. 1, lower trace). The ions produced by neutral evaporation from K_{18}^{+}, K_{36}^{2+}, and K_{54}^{3+} arrive later than the parent because they have a smaller mass-to-charge ratio than the parent's ratio. Fragments arriving earlier than the arrival of the parent correspond to a larger mass-to-charge ratio than 18, and they are identified as the heaviest doubly charged fragments from the fission of K_{54}^{3+} only, since K_{36}^{2+} dissociates by neutral evaporation as K_{34}^{2+}. From the mass analysis of the unimolecular dissociation spectrum, we found that Coulombic fission of K_{54}^{3+} is of asymmetrical character leading to two competitive fission channels: $K_{49}^{2+} + K_5^{+}$ and $K_{47}^{2+} + K_7^{+}$ with two charges on the heaviest fragment.

Coulombic fission of triply charged clusters has been clearly observed for all sizes from K_{54}^{3+} to K_{105}^{3+}. As the cluster size increases the mass resolution cannot discriminate between the competitive fission channels; therefore, only the center of mass and the distribution width of the heaviest fragment have been determined. It should be noted that for parents with larger sizes successive unimolecular events occur during the observational time window [10]. For $n = 100$ we have found that at most three successive unimolecular events can occur which leads to an apparent decrease of at most two mass units for the heaviest fragment of the fission process. No indication is found dealing with multifragmentation processes; binary fission processes always prevail. Moreover, as the size of the parent increases the size of the light fission fragment increases as well. The upper limit of our studied size range gives

$$K_{105}^{3+} \longrightarrow K_{85(\pm 1)}^{2+} + K_{20(\pm 1)}^{+}. \qquad (1)$$

Assuming that the energy balance considerations determine the preferred decay channel, asymmetric fission is already favored in the liquid drop model [9], and it is pronounced even more by shell effects because K_3^{+}, comparable to an α particle in nuclear physics, has the highest stability [11,12]. This prediction, which enhances the asymmetrical fission even more as cluster size increases, is inconsistent with our experimental results.

To go further we should consider that the preferential dissociation channels are not governed by the enthalpy change of the system but by the free energy change which takes into account the different combinations of atoms that constitute the fragments. For the sake of simplicity, we focus on the separation process between the initial triply charged parent and the ultimate fission products. Although this provides a rather incomplete description of fission process, it gives a qualitative description of the predominant fission channels.

According to the classical metallic drop model the enthalpy change $\Delta_{n,p}^{3+}$ of the fission process,

$$X_n^{3+} \longrightarrow X_{n-p}^{2+} + X_p^{+}, \qquad (2)$$

is the sum of two terms $\Delta_{n,p}^{3+} = \Sigma + C$ where Σ is the surface term and C the Coulombic term [8]:

$$\Sigma = a_s[p^{2/3} + (n - p)^{2/3} - n^{2/3}], \qquad (3)$$

$$C = -\frac{e^2}{r_s}\left[\frac{33}{8}n^{-1/3} - \frac{7}{4}(n - p)^{-1/3} - \frac{3}{8}p^{-1/3}\right]; \qquad (4)$$

the Wigner-Seitz radius r_s for potassium is $r_s = 2.57$ Å from Ref. [13], and the surface energy is $a_s = 0.98$ eV/atom [10]. The evolution of the enthalpy change $\Delta_{n,p}^{3+} = \Sigma + C$ with p for $n = 100$ (Fig. 2, upper trace) shows that $\Sigma + C$ is minimum for $p = 2$.

If we now assume that the entropy S plays a role in the determination of the predominant fission channel,

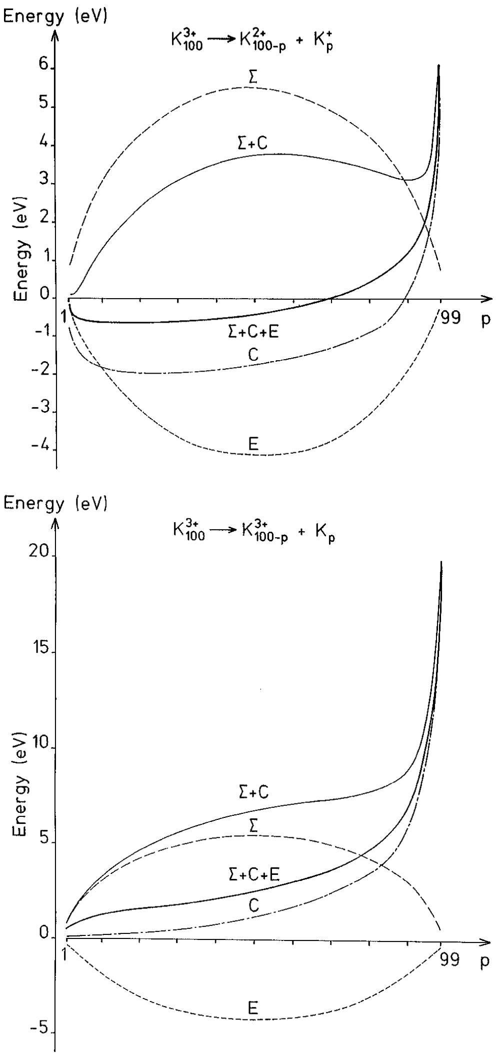

FIG. 2. Different energy contributions involved in the fission and evaporation processes $K_{100}^{3+} \rightarrow K_{100-p}^{2+} + K_p^+$ (top) and $K_{100}^{3+} \rightarrow K_{100-p}^{3+} + K_p$ (bottom), as a function of p. The Σ and C curves are the surface and the Coulomb terms from the drop model, Eqs. (3) and (4). The $\Sigma + C$ curve is the enthalpy change. $E = -kTS$ is the entropy contribution, Eq. (5), and the continuous line $\Sigma + C + E$ is the net result for the free energy change. The minimum of these curves gives the predominant dissociation channel.

the most probable fission products are determined by minimizing the free energy $F = \Sigma + C - kTS$, where T is the cluster temperature. For a cluster of n atoms which splits in two fragments of p and $n - p$ atoms the total number of possible channels is given by the binominal coefficient $n!/p!\,(n-p)!$. Therefore, using the Stirling formula we obtain the entropy change

$$S = \ln \frac{n!}{p!\,(n-p)!} \cong -n\left[\frac{p}{n}\ln\left(\frac{p}{n}\right) + \left(1-\frac{p}{n}\right)\ln\left(1-\frac{p}{n}\right)\right] \quad (5)$$

in the course of fission. Comparing Eqs. (3), (4), and (5) one sees that since the Coulomb contribution scales with the size of the parent clusters as $n^{-1/3}$ and the surface contribution scales as $n^{2/3}$, the role of the entropy contribution which scales as n becomes more and more important as the cluster size increases.

The top panel of Fig. 2 shows the three contributions Σ, C, $E = -kTS$ as a function of p for $T = 600$ K related to the fission process $K_{100}^{3+} \rightarrow K_{100-p}^{2+} + K_p^+$. This temperature is suggested by the parameters of the "evaporative ensemble" of clusters [10,14]. It can be seen that the enthalpy change $\Sigma + C$ is minimum for $p = 2$, whereas the change of free energy $\Sigma + C + E$ has a minimum at $p \cong 20$, which is in a better agreement with the experimental results.

Results of the same kind of calculations applied for the neutral evaporation process are plotted in the bottom panel of Fig. 2. They show that in this case both the enthalpy and the free energy change lead to monomer evaporation as the preferential channel in agreement with experimental results.

The evolution of the asymmetrical character of Coulombic fission with the parent size can be quantified by an asymmetry parameter η defined as the ratio $\eta = (n - 2p)/n$ between the size difference of the two fragments $n - 2p$ to the parent size n. The value $\eta = 1 - 2/n$ corresponds to the detachment of an atomic ion, whereas $\eta = 0$ corresponds to the fission into two fragments with equal size. In Fig. 3 we depict the value of η calculated from the condition $\partial F(n,p)/\partial p = 0$ as a function of n at different temperatures along with the experimental values. For $kT = 0$ the asymmetrical character of the fission increases with size due to the predominant effect of the surface term. For $kT \neq 0$ the asymmetry parameter increases in the low mass range and decreases in the higher mass range due to the predominance of the entropy effect.

This model predicts an increasing role of the entropy contribution, which is the most rapidly rising function of the size. However, a direct extrapolation of the results at the macroscopic scale is illegal, since the model ignores the channels of multifragmentation, that is, the decay at three, four, or more fragments associated with a much larger change of the electrostatic, the surface energies, and the entropy [15]. We do not discuss here whether such multifragmentation may be observed in our experimental conditions, since the kinetic effects should be of much more importance for this phenomenon [11].

The experimental behavior of triply charged clusters agrees reasonably with this simple model calculation in a temperature range compatible with the experiment. However, an important discrepancy remains. The trends of the experimental and theoretical curves suggest that the model fails for 150 atom clusters. This agrees with a simple estimation of the validity range of the model: At n larger

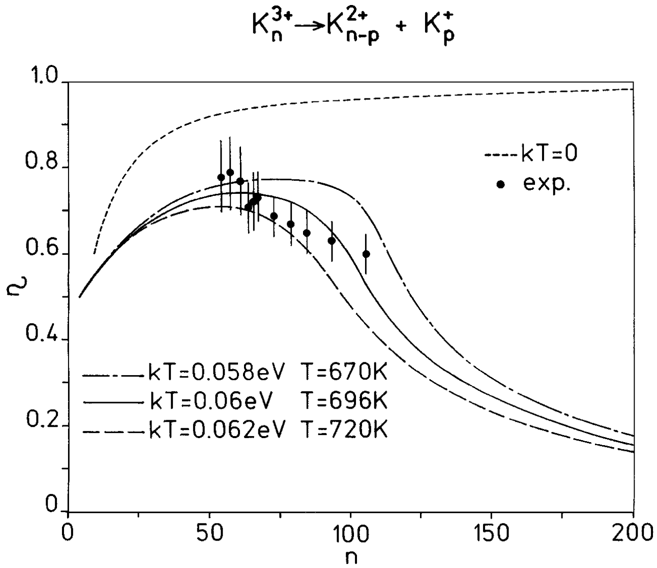

FIG. 3. Comparison between calculated, at several temperatures, and experimental (dots) determination of the asymmetry parameter η of binary fission channels vs cluster size. η is defined as the difference in the product sizes normalized to the parent size.

than 150, one has to take into account multifragmentation. Another possible reason for the discrepancy is the extreme sensitivity of the calculated asymmetry parameter to the temperature which is estimated only within several percents and may vary slightly with the cluster size.

In conclusion, experimentally observed unimolecular mass spectra of decaying clusters deviate from predictions traditionally based on the balance of the Coulomb and the surface energies. They clearly show a trend toward the most symmetrical cluster fission. This fact finds its explanation in the framework of a simple model which takes into account the discreteness of atoms. Allowance for the number of different possible distributions of the atoms among the fission products results in a significant increase of the number of different decay channels. It gives an entropy contribution to the free energy of clusters, which plays a crucial role for large species.

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