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Fission of doubly charged binary metal clusters

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Abstract. The coulombic fission of binary metal clusters composed of lithium and calcium atoms has been studied by time-of-flight mass spectrometry following multi-photon ionization. The determined appearance sizes are compatible with predictions of a simple model which assumes a liquid droplet picture for all but the very small clusters involved. Electronic shell effects on the fission process are discussed.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Qv Stability and fragmentation of clusters

1 Introduction

One of the goals of cluster research has always been to establish a link between microscopic phenomena and the physics of bulk matter. The coulombic fission, i.e. charged fragment emission of clusters can be related to several bulk properties and has therefore been an active subject of experimental and theoretical research in the past years. In experiments with nanosecond laserpulses and multi-photon ionization only very large clusters are multiply charged, far away from where fission comes into play. Due to simultaneous strong heating of the clusters by the ionizing light they evaporate many atoms during the laser pulse, until at a certain point they undergo fission rather than evaporate another atom. Therefore, in such experiments multiply charged clusters are observed only above a certain "appearance size".

While the observed appearance sizes of the alkali metals can be reasonably well understood using a liquid droplet approximation (for a recent review see [1]), for many other systems the observations cannot be explained in such a simple manner. For example, the alkaline earth elements show strikingly smaller appearance sizes than expected from such a model [2]. Recent experiments find the singly charged monomer to be the dominant fragment in the fission of triply charged strontium [3] or calcium clusters [4], also at variance with a liquid droplet picture. Studies of fragment distributions provide valuable information on the fission process. Particularly conclusive are the measurements carried out on clusters caught in an ion trap [5]. The experiments at the ion beam facility in Grenoble allow to study the influence of temperature on the fission process [6]. Temperature effects have also been subject of several theoretical studies recently [7, 8] and might play an important role in the process.

The fission process can be further investigated by studying clusters composed of two different metals. In this paper the appearance sizes for doubly charged binary metal clusters are reported, which in our case consist of calcium and lithium atoms. The results for all but the very calcium rich clusters are shown to be compatible with predictions of a simple model. In addition, we present evidence of an electronic shell closing which can be followed through the entire range of compositions. Its influence on the fission process is discussed.

2 Experimental

The binary metal clusters were produced in a low pressure inert gas condensation cell by evaporation of the elements from two resistively heated ovens into a liquid nitrogen cooled helium atmosphere of about 2 mbar. The calcium was contained in a molybdenum crucible at about 500 °C and lithium was evaporated from a nickel crucible at 450 °C. The average cluster composition could be controlled by varying the oven temperatures. A high resolution mass spectrometer is needed in order to identify the composition and charge state of each peak in the resulting mass spectra unambiguously. Our setup has been described earlier in detail [9]. In short, it consists of a two-stage reflectron time-of-flight mass spectrometer with acceleration perpendicular to the neutral beam axis and quadrupole ion optics for neutral beam velocity compensation. Twofold ionization of the clusters was acheived using light of an ArF excimer laser (193 nm) focussed into the ionization region of the spectrometer.

The elements calcium and lithium were chosen for two reasons: First, in experiments on the stability of binary clusters composed of elements with very different vapor pressures [4] one frequently encounters a situation where in the series of evaporation steps after ionization/heating most of the more volatile component is eliminated from the

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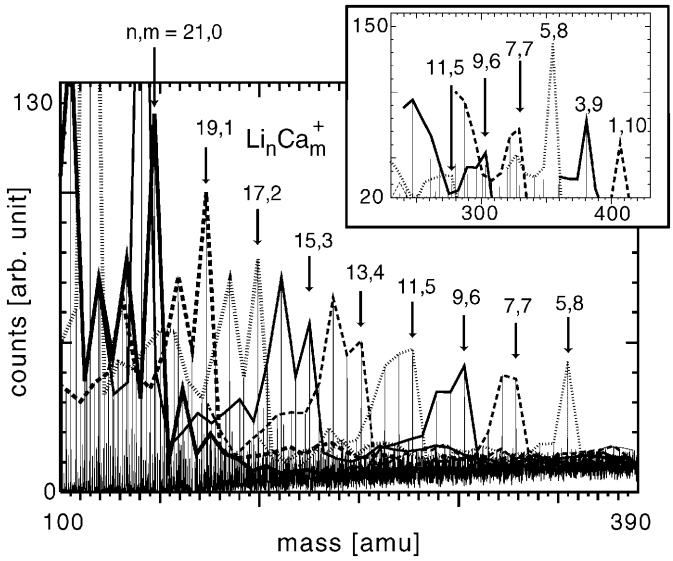

Fig. 1. Two mass spectra of lithium-calcium binary metal clusters with two different average compositions, ionized and heated by ArF excimer laser light (193 nm). Peaks belonging to clusters with a fixed number of calcium atoms have been connected by lines in order to guide the eye. An electronic shell closing is observed for clusters with composition $Li_{21-2n}Ca_n^+$ corresponding to 20 valence electrons independent of composition.

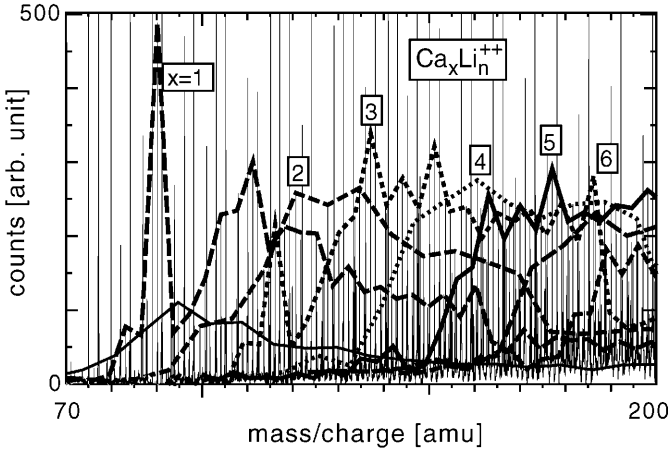

Fig. 2. At high laser fluence, doubly charged clusters are observed above a specific appearance size. Below this size the clusters undergo fission on the experimental timescale. Again, peaks corresponding to a fixed number of calcium atoms are connected by lines.

cluster. Lithium is the only alkali metal with a vapor pressure comparable to the alkaline earth elements. Secondly, a narrow isotope distribution is an important prerequisite for a successful analysis of the complex mass spectra of binary clusters. Of the alkaline earth elements (except for beryllium) calcium has the narrowest one (^{40}Ca: 96.94%, ^{42}Ca: 0.65%, ^{44}Ca: 2.09%, others: 0.32%). Lithium has two natural isotopes (^{6}Li: 7.5%, ^{7}Li: 92.5%), forcing us to use isotopically pure ^{7}Li.

3 Results

First the stability of the singly charged species of the calcium-lithium system must be examined. Spectra of clusters with two different choices of oven temperature, and therefore different average compositions, and taken at moderate ionization laser intensity are reproduced in Fig. 1. Peaks belonging to a series with constant number of calcium atoms are connected by lines in order to guide the eye. In each of these series a sudden drop of intensitiy is observed when going from $Li_{21-2n}Ca_n^+$ to $Li_{22-2n}Ca_n^+$, which corresponds to a step from 20 to 21 valence electrons. This is a manifestation of the electronic shell closing at 20 electrons predicted for electrons in a spherical potential well. In our experiment it can be observed for any composition, indicating that the clusters may be described as homogeneous metallic droplets in spite of their obvious inhomogenity.

If the laser power is increased, additional peaks appear which can be identified as doubly charged species. Figure 2 shows the relevant part of such a spectrum from which appearance sizes can be extracted. The count rates of this spectrum and one with higher calcium content (not shown) can be used to draw the map of stability shown in Fig. 3. Note that for clusters with an even number of atoms of each element the intensity could not be read from the spectra due to mass/charge-coincidence with a singly charged cluster.

It can be seen in Fig. 3 that for $n \leq 6$ the appearance sizes lie very close to the series $Li_{20-2n}Ca_n^{++}$ marked by a dashed line. These clusters have a total number of valence electrons $N_e = 18$, which is an electronic shell closing number. Since the free-electron radii of lithium and calcium are almost equal ($r_e(\mathrm{Li}) = 1.72$ Å; $r_e(\mathrm{Ca}) =$

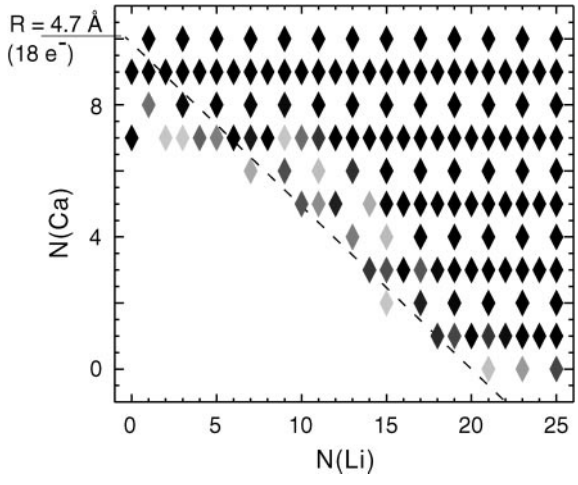

Fig. 3. Map of experimentally determined intensities of doubly charged lithium-calcium clusters. On the lithium rich side the appearance sizes correspond to clusters with approximately 18 valence electrons.

1.73 Å)[11], this also corresponds to a constant jellium radius of $R = 4.7$ Å, which is given by $R^3 = N(\mathrm{Li})r_e(\mathrm{Li})^3 + 2N(\mathrm{Ca})r_e(\mathrm{Ca})^3$. Calcium rich clusters deviate from this rule: Of the clusters $\mathrm{Li}_x\mathrm{Ca}_7^{++}$ we observe the pure calcium cluster ($x = 0$) and those with $x \geq 4$. LiCa_8^{++} is observed only weakly, while the strong signal of $\mathrm{Li}_x\mathrm{Ca}_8^{++}$ with $x \geq 3$ indicates negligible fission probability. Doubly charged clusters containing nine or more calcium atoms all seem to be stable.

The smallest doubly charged lithium cluster found in our spectra is Li_{21}^{++}, which is below the appearance size of 25 reported in [10]. For doubly charged calcium clusters we find an appearance size of seven, one atom less than reported in [2].

4 Discussion

To simplify matters we assume that the rate k for a given fragmentation process depends on its activation energy D as $k = \nu \cdot \exp(-D/k_\mathrm{B}T)$, ν being an attempt frequency and T the temperature. The appearance size is the size below which the rate for any fission process exceeds neutral evaporation rates. If the values of ν do not differ largely for different processes, this corresponds to at least one fission barrier D_f being smaller than the evaporation energy D_e. In the following we will adapt the simple model of [1] to the fission of binary metal clusters and compare the thus estimated appearance sizes to the results of our experiment. We start with three assumptions:

(1) The cohesive energy E_coh of neutral binary clusters of calcium and lithium is approximated by an averaged liquid droplet term which only depends on the number of atoms N, not on the species.
(2) For all effects involving Coulomb forces, namely polarization and ionization, the cluster is treated as a metallic sphere.
(3) For small fragments the liquid droplet approximation is abandoned and experimental cohesive energies are used.

Let us work out these assumptions in more detail: In our simple model the total energy of a neutral cluster with N atoms and arbitrary composition is taken to be

$$-E_\mathrm{coh}(N) = E_\mathrm{tot}(n) = a_\nu N + a_\mathrm{s} N^{2/3} \,. \qquad (1)$$

Averaged values of -1.6 and 1.1 eV are used for a_ν and a_s, respectively. This rather crude treatment is justified by the fact that not too different parameters are obtained for lithium and calcium (Li: $-1.55/0.93$ eV; Ca: $-1.73/1.23$ eV) from bulk vapor pressures and surface tensions [12]. Our recent observation [4] that the more abundant species is evaporated with higher probability from singly charged calcium-lithium clusters, also supports this hypothesis.

If the cohesive energy of a Z-fold charged cluster is defined as the energy needed to disintegrate the cluster into $N - Z$ neutral and Z singly charged atoms, the difference between ionization potentials of the atoms and the cluster has to be added. This yields

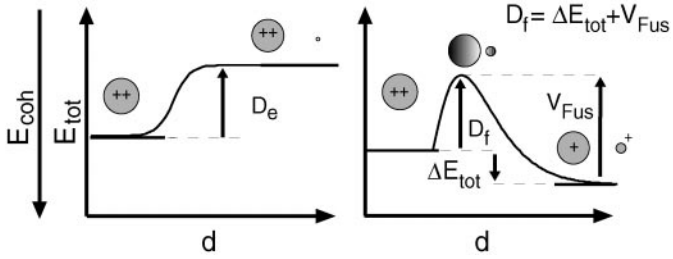

Fig. 4. Schematic picture of the energetics of the two processes considered: the evaporation of a neutral atom and the emission of a charged fragment over a Coulomb barrier.

$$E_\mathrm{C}(R, Z) = Z\left[\frac{(Z + 2\alpha - 1)e^2}{2R} + W_\mathrm{b} - IP\right] \qquad (2)$$

where R is the jellium radius and for $W_\mathrm{b} - IP$ an averaged value of -3.1 eV is used (Li: -3.0 eV; Ca: -3.3 eV). The parameter α is taken to be 0.4 in accordance with experimental determinations, although a value of 0.5 is expected classically (see discussion in [1]). The cohesive energy of a cluster of N atoms, radius R and charge Z is the negative of the sum of (1) and (2):

$$-E_\mathrm{coh}(N, R, Z) = E_\mathrm{tot}(N) + E_\mathrm{C}(R, Z) \,. \qquad (3)$$

Note that specifying N and R is equivalent to specifying $N(\mathrm{Ca})$ and $N(\mathrm{Li})$.

With respect to the expected fission products we make use of the information gathered in the pure systems: Twofold charged lithium clusters fission mainly by emission of a singly charged trimer [10], while for calcium we have exclusively found Ca^+ and Ca_2^+ as the small fission product [4]. As the most probable mixed fragment we consider the diatomic molecule LiCa^+, which as a two-valence-electron system might be unusually stable. So Ca^+, Ca_2^+, LiCa^+, Li^+, Li_2^+ and Li_3^+ are believed to be possible fission fragments. A liquid droplet model (LDM) certainly is not appropriate for such small systems. Instead we want to use experimental values for their cohesive energies. For Li_2^+ and Li_3^+ the cohesive energies have been derived [15] to be 1.30 and 2.79 eV, respectively. The bond strength of LiCa^+ is given as $E_\mathrm{coh} = 1.11$ eV by Kimura *et al.* [13]. For Ca_2^+ to our knowledge E_coh has been neither measured nor calculated, but for Sr_2^+ a value of 1.1 eV has been determined [14]. Remembering the equal dissociation energies of Ca_2 and Sr_2 [14], we will use 1.1 eV as a guess value for $E_\mathrm{coh}(\mathrm{Ca}_2^+)$. It should be stressed that a 20% change does not qualitatively alter the results reported here.

During the emission of a charged particle configurations are passed which are energetically less favorable than the initial one. The saddle point energy, or fusion barrier, is released as kinetic energy of the fission fragments. The fission barrier D_f can be calculated as the sum of net change in total energy ΔE_tot and the fusion barrier V_Fus, as drawn schematically in Fig. 4. We estimate V_Fus as the energy

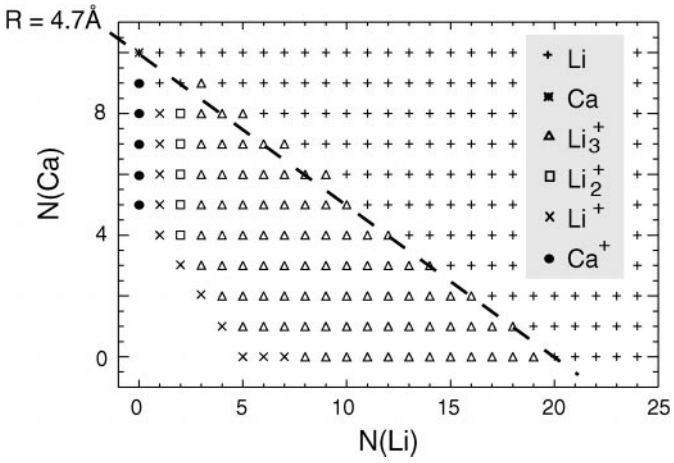

Fig. 5. Predicted fragmentation channels for doubly charged lithium-calcium clusters: for clusters with at least three lithium atoms the experimental appearance sizes are reproduced well.

needed to bring an elementary point charge (the small fragment) into contact with a conducting sphere of charge z and radius r, the jellium radius of the large fragment plus an additional electron spill-out of 0.7 Å. The interaction energy as a function of center distance d is

$$E_{\rm pol}(d) = e^2(z/d - r^3/2d^4) \qquad (4)$$

and its maximum should correspond to $V_{\rm Fus}$. For the decay of $Li_{26}^{++} \rightarrow Li_{23}^+$ and Li_3^+ a value of $V_{\rm Fus} = 1.29\,{\rm eV}$ is obtained from (4), which agrees well with a recent experiment [16] yielding $V_{\rm Fus} = 1.19 \pm 0.10\,{\rm eV}$. At the potential maximum the distance between the point charge and the surface of the large fragment is 3.5 Å, well above the jellium radius of Li_3^+.

We may now calculate the values of $D_{\rm e}$ resp. $D_{\rm f}$ for the various fragmentation channels, and draw the map shown in Fig. 5 indicating the lowest fragmentation pathway for a given doubly charged initial cluster. Clusters containing three or more lithium atoms are predicted to emit a Li_3^+ fragment when they reach a certain size. These sizes define a straight line in the composition plane very close to the line determined experimentally. Clusters with less than three lithium atoms have to follow a different fission path and the appearance sizes shift towards smaller radii, in qualitative agreement with the experimental observation. In no case is the emission of Ca_2^+ predicted, due to its small cohesive energy. In contrast, if one used the LDM estimate (3) of 2.4 eV for the cohesive energy of Ca_2^+, the dimer would become the dominant fission channel and shift the line of appearance sizes to clusters with more than 50 valence electrons, in striking disagreement with experiment. This illustrates the importance of using realistic cohesive energies for the small fragments.

Regarding the simplicity of the model, its good agreement with experiment for lithium rich clusters may be fortuitous to some extent. However, the calculations indicate the approximate size at which fission is expected to set in. The appearance of doubly charged clusters in the spectra is further sharpened by the 18-electron shell closing that coincidentally occurs exactly in this size range. These closed shell clusters are less likely to decay by either mechanism, evaporation or fission.

In summary, we have observed appearance sizes of doubly charged calcium-lithium clusters. Our results illustrate the importance of a good knowledge of the cohesive energies of small clusters, for which the LDM is not applicable, for the prediction of appearance sizes, and show the influence of electronic shell closings. The failure of our description on the calcium rich side is not surprising: The properties of alkaline earth metal clusters converge towards a LDM description rather slowly [17]. For fission of calcium rich clusters in the size range considered here, probably not even the initial cluster is adequately described by the droplet model.

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Note added in proof

Recently, Chien *et al.* [18] have calculated the cohesive energy of Ca_2^+ to be 1.264 eV. Using this value in the analysis of Sect. 4 instead of the assumed 1.1 eV does not alter any of the results reported here.