Critical Sizes against Coulomb Dissociation of Highly Charged Sodium Clusters Obtained by Ion Impact

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The multiple ionization of alkali-metal clusters by low energy ions is investigated experientially for the first time. Multi-ionized clusters possibly undergoing Coulomb dissociation are formed and detected. Free sodium clusters of a few hundred atoms have been bombarded by different ion beams (H^+, O^{5+}, Ar^{8+}) of velocity ranging from 0.5×10^8 to 2.2×10^8 cm/s. Critical sizes for stability against charge excess have been deduced for cluster charges up to 6. They are found to depend upon the projectile charge. Observed differences are discussed in terms of temperature effects.

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As a prototype of a finite system under long range forces a multicharged metal cluster is expected to undergo Coulomb dissociation. However, how the dissociation proceeds is still an open question both experimentally and theoretically. Simple metal clusters, such as sodium clusters, are characterized by a delocalization of valence electrons that already occurs at sizes as small as less than ten atoms. This delocalization leads to the now well-known electronic shell structure and other quantal features typical of finite fermionic systems [1]. How does such a microscopic metallic cluster respond to an excess of charge? Does a highly charged metal cluster behave as a classical charged liquid drop? The answer to these questions reminds one immediately of the fission of atomic nuclei. The basic theoretical understanding of heavy element nuclear fission is provided by the liquid drop model [2]. In analogy with a charged liquid drop, fission occurs when the surface tension due to strong forces cannot counterbalance the disrupting effect of Coulomb repulsion between protons. The liquid drop model predicts that nuclei of mass A and charge Z are unstable with respect to a small deformation when the ratio Z^2/A exceeds the critical nuclear fissility, $(Z^2/A)_C = 50$, in reasonable agreement with empirical observation. It is, however, well known that many features of nuclear fission go far beyond the physics of a classical droplet, and require one to account for the quantal nature of nuclear excitations and dynamics. There are, however, major differences between atomic nuclei and metal clusters even considering both as charged liquid drops. Whereas the electric charge is distributed over the whole volume in the atomic nucleus, metal clusters should have their charge distributed on the surface. The stabilizing influence of surface tension is much weaker in metal clusters than in nuclei, thus leading to a much lower predicted critical cluster fissility. Let n_C^0 be the critical size of a multiply charged cluster below which no fission barrier exits. As the size exceeds n_C^0, the barrier increases with n.

Recent experiments performed on free multiply charged clusters report critical sizes of stability against Coulomb dissociation [3–7]. However, what is actually measured is the size below which no clusters of a given charge are observed in a yield spectrum. Since the cluster is thermally excited, fission decay is competing with evaporation of neutral atoms, so that the empirical size for appearance of fission, which corresponds to the fission barrier getting lower than the activation barrier, is larger than the size n_C^0 [3]. Thus the conditions of preparation of the highly charged cluster may influence strongly the onset of fission and the eventual Coulomb fragmentation process.

The experimental method to produce multiply charged metal clusters that has been used so far consists in irradiating clusters by a laser beam. A maximum charge state q, such that the corresponding ionization potential overcomes the photon energy, is reached during the laser pulse duration of the order of nanoseconds [4]. However, experimental and energetics considerations make a q-fold ionization possible only for sodium clusters with sizes well above the corresponding critical size. It is therefore necessary to heat considerably the cluster in order to evaporate a large number of atoms and bring the residue in the vicinity of the critical size [4].

In the present paper, we discuss and give first results of an alternative method that is characterized by a fast preparation of the order of femtoseconds and a broad range from low to high temperatures. A (multicharged) ion collides with a neutral sodium cluster at a relative velocity of the order of the Fermi velocity. Note that the present method has been used to prepare highly charged fullerenes [8].

For a highly charged ion (O^{5+}, Ar^{8+}), collisions at large impact parameters are effective due to the capture of electrons into Rydberg states of the ion. This process is indeed similar to the neutralization of a highly charged ion approaching a surface [9] with, however, the essential differences that the cluster is isolated, thus modifying the image charge, and that the ionization potential increases after each electron escape. In peripheral collisions, only electrons near the Fermi level can escape, thus leaving the

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cluster in a weakly excited state. In central collisions, the conduction electrons screen the passing charge and induce a strong density oscillation leading to a high electronic excitation and ionization of the cluster; in addition, the ion may capture some electrons. For both peripheral and central collisions, the reaction time is given by the passing time of the order of $2R/v$, where R is the cluster radius and v is the ion velocity, that is, of the order of a few 10^{-15} s, much shorter than the ionic vibrational time scale of order of 10^{-12} s. the sodium ions in the cluster are frozen as the projectile passes by.

The experimental setup consists in intersecting a neutral cluster gas jet by an ion beam. The latter is delivered by the Accélérateur d'Ions Multichargés (AIM) at Gernoble. A typical intensity of about 10 μA is available for high emittance O^{5+} and Ar^{8+} beams accelerated under a voltage ranging from 1 to 20 kV. H^+ beams from 1 to 19 keV energies are also available. Neutral sodium clusters are formed in a gas aggregation source in which the metal vapor mixes with helium gas at a pressure between 1 and 10 mbar and cooled at liquid nitrogen temperature. The condensation process leads to the formation of a broad distribution of Na_n clusters in the size range $n \leq 800$. The cluster stream is conveyed to the ionization region of a modified two-stage Wiley-McLaren time-of-flight mass spectrometer, where it is intersected by the ion beam. The residual pressure is around 10^{-9} Torr in the interaction zone. With a view to calibration and comparison, the ion beam can be replaced by a Nd-YAG laser beam. Ionized clusters are extracted and accelerated to enter the drift tube (length $\sim$ 1 m) with a typical energy of about 5 keV per charge. After a drift time between 20 and 200 μs (depending on the ratio n/q) the ions are postaccelerated to a final energy of $24q$ keV to eventually hit a coated (CsI) copper plate. Secondary electrons are detected by a scintillator connected to a photomultiplier. Details of the spectrometer are given in Ref. [10]. The spectrometer resolution allows one to fully separate Na_{700}^+ and Na_{701}^+ and to identify charges up to 6 for $n/q \leq 100$.

Raw n/q abundancy spectra are shown in Fig. 1. In the upper window we show the n/q distribution obtained when bombarding the neutral sodium cluster jet with a laser beam of low fluence ($\simeq$1 μJ/cm^2) and of 4.67 eV photon energy. At this low flux, double ionization and evaporation of atoms are very unlikely; therefore the spectrum is reasonably well representative of the neutral distribution, within the dependency of ionization cross section upon size and the response function of the spectrometer. It is worth noting that Na atoms and Na_2 molecules are not ionized at the present laser wavelength [11]. This broad distribution peaks at $n \simeq 180$ and decreases slowly from this value to more than 600 atoms. In the middle windows we show the distributions that we obtain when intersecting the cluster jet, prepared under the same source conditions as above, with a H^+ beam of 5 and 19 keV kinetic energy, respectively. In the lowest window the n/q distribution is that obtained after interaction with a O^{5+} beam at 5 keV per nucleon.

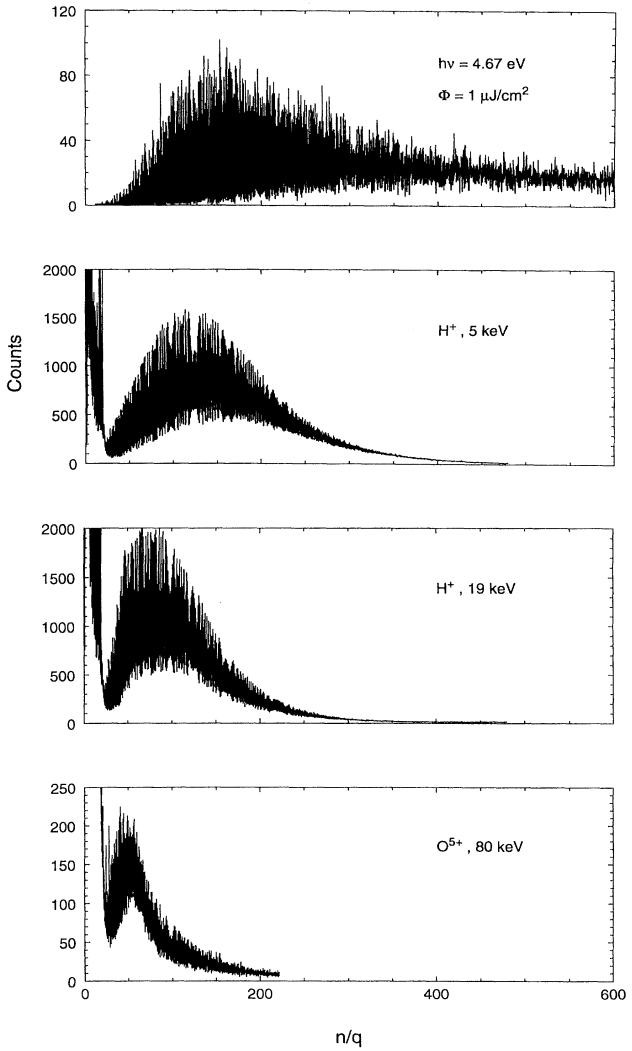

FIG. 1. Abundancy spectra (n/q) of sodium clusters ionized by a Nd-YAG laser ($h\nu$ = 4.67 eV), a 5 keV H^+ ion beam, a 19 keV H^+ ion beam, and a 80 keV O^{5+} ion beam.

The striking feature is a strong shrinking of the n/q distribution compared to that obtained with laser ionization. One observes that the depopulation of the high n/q part of the spectrum increases with the projectile velocity and with the projectile charge. Note that the important counting rate in the lower side of the spectrum is due mainly to organic molecules in the residual gas, prohibiting an unambiguous analysis in the range $n/q \simeq 20$. These spectra are direct evidence for multiple ionization of the sodium clusters.

The multiple ionization is revealed very clearly when magnifying the high resolution spectra. As an example, we show in Fig. 2 the part in the range n/q from 57 to 58 with full resolution. The laser induced ionized spectrum shows intense peaks for integer values of n/q (57 and 58

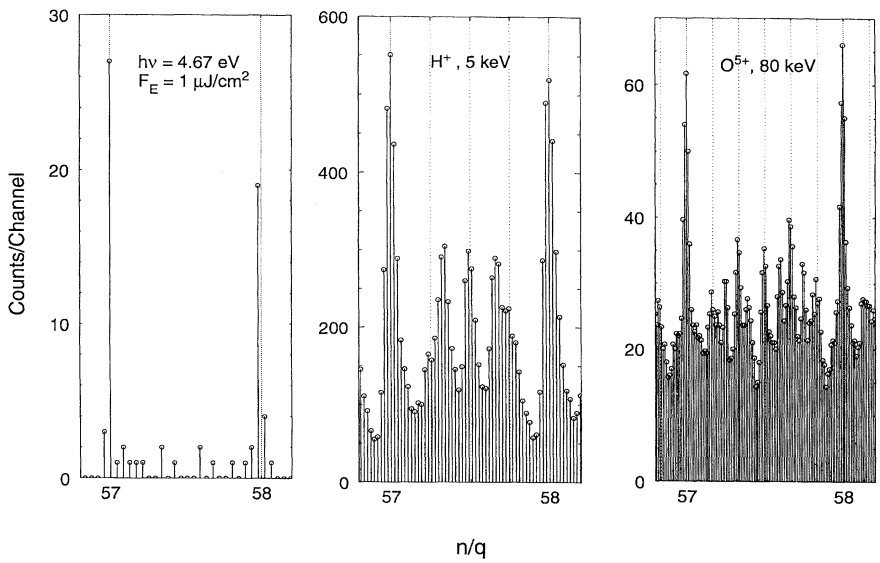

FIG. 2. Magnified abundancy spectra (in the range $n/q = 57-58$) of sodium clusters ionized by a Nd-YAG laser ($h\nu = 4.67$ eV), a 5 keV H^+ ion beam, and a 80 keV O^{5+} ion beam.

in the present figure) and almost no signal in between. By contrast the H^+ induced spectrum exhibits important contributions from peaks centered at half-integer values and at ratios of $n/3$. Higher q values appear in the O^{5+} induced spectrum where resolved peaks give evidence of charges up to 6.

Out of the experimental n/q distribution, we infer the size distribution for a given charge. For that purpose, some reasonable assumptions in reducing the data are necessary; they essentially amount to assigning to a given n/q bin a population equal to the average sum of the two neighboring bins $(n-1)/q$ and $(n+1)/q$, and to fitting a sum of properly separated Gaussian distributions to the data. As examples, we show in Fig. 3 the size distributions of fivefold charged sodium clusters ionized by collision with either a 19 keV H^+ beam or a 40 keV Ar^{8+}. The H^+-like distribution is characterized by a steep falloff on its low size side, whereas the Ar^{8+}-like distribution exhibits a milder one. The appearance size is defined by extrapolating to the zero counting rate.

Appearance critical sizes are reported in Table I. Only critical sizes for charges higher than 3 can be extracted from the ion induced spectra, since critical sizes for charges 2 and 3 lie in the contaminated part. In order to assess the method we extract the critical sizes for charges 2 and 3 from a laser induced spectrum obtained at high fluence thus allowing for multiple ionization. The values 27 ± 1 for $q = 2$ and 62 ± 2 for $q = 3$ agree perfectly with those of Ref. [4]. For charges above 3 we compare critical sizes obtained by laser ionization [4] and by ion induced ionization. Note that the critical sizes obtained in 19 keV H^+ induced collisions are very close to those obtained by laser multiple ionization [4], whereas the corresponding values from 80 keV O^{5+} and 40 keV Ar^{8+} tend to be systematically lower. A temperature effect may explain this shift. As discussed earlier, multiple ionization in collisions of clusters with highly charged ions occurs already at large impact parameters with little heating, whereas multiple ionization by H^+ is only possible through central collisions. In the latter case the energy ΔE lost by the passing ion may be estimated by assuming the cluster to be a finite piece of sodium metal with bulk stopping power. A rough estimate, using tables [12], leads to $\Delta E(\text{a.u.}) = 0.48 n^{1/3} v^{0.9}$ at zero impact parameter. For a 200 atom sodium cluster

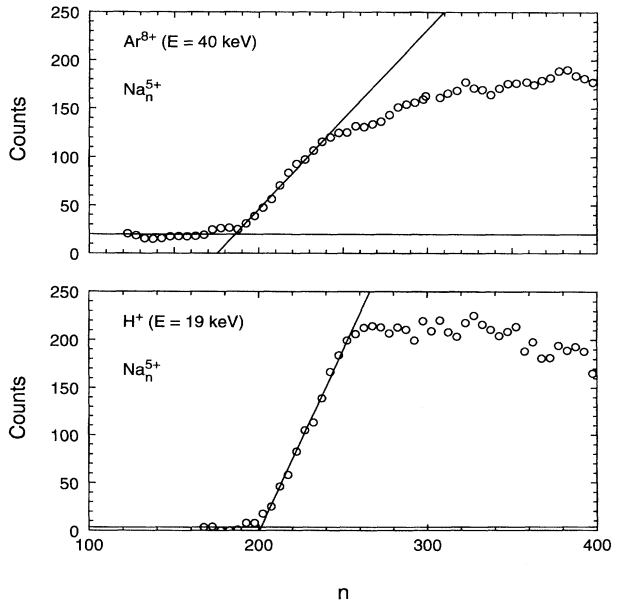

FIG. 3. Size distribution of residual clusters of charge 5 from the $Na_n + H^+$ collision at 19 keV (lower window) and from the $Na_n + Ar^{8+}$ collision at 40 keV (upper window).

TABLE I. Critical sizes of multiply charged sodium clusters (of charge q) extracted from ionized cluster distribution resulting from ionization induced either by laser or ion bombardment. The present values should be considered as upper values. See text.

q	2	3	4	5	6
Laser [4]	27 ± 1	63 ± 1	123 ± 2	206 ± 4	310 ± 10
H^+ (5 keV)			122 ± 2	210 ± 9	
H^+ (19 keV)			118 ± 2	200 ± 5	
$^{16}O^{5+}$ (80 keV)				180 ± 8	253 ± 10
$^{40}Ar^{8+}$ (40 keV)			115 ± 5	187 ± 4	252 ± 8

hit by a 19 keV proton, the energy loss is 67 eV. Note that a microscopic calculation of the energy loss of a proton passing through a jellium cluster, based on the Vlasov equation, yields very similar values [13]. This energy is partly converted into electron emission on a short time scale (of the order of 10^{-15}–10^{-13} s), thus explaining the observed high charge states but mainly into vibrational heating on a longer time scale. As in the laser case of Ref. [4] a hot multi-ionized cluster is formed with a temperature of the order of 1000 K or more. Evaporation of neutral atoms is then competing with Coulomb fission. The ratio of fission to monomer evaporation widths can be written as $(\alpha_F/\alpha_E)\exp[(B_E - B_F)/T]$, where B_E ($\simeq$1 eV) and B_F are the activation energy and the fission barrier, respectively. The ratio of fission to evaporation prefactors α_F/α_E is expected to be smaller than unity, since fission requires the preformation of the charged nascent fragments. Thus one actually measures the onset of fission as B_F becomes lower than $B_E + T\ln(\alpha)$. Within this assumption, the appearance size is expected to slightly decrease with increasing temperature. When the temperature is so low that evaporation does not occur on the experimental time scale of about 40 μs (corresponding to $T_0 \simeq 500$ K), Coulomb fission is possible within the measurement time if B_F is lower than $T[B_E/T_0 + \ln(\alpha)] \simeq TB_E/T_0$. In this low temperature regime, the appearance size decreases with decreasing temperature. The highest appearance size should be observed for the temperature T_0.

The above argumentation is consistent with the experimental values for appearance sizes of Table I and with the typical spectra shown in Fig. 3. The lower values obtained with multiply charged ions give evidence that low temperature (probably well below 500 K) highly charged clusters have been produced in peripheral capture reactions. The smaller slopes of the abundancy curves at threshold indicate that a broad range of temperatures, which arises from the impact parameter distribution, characterizes the multicharged ion collisions. Note that the upper inflection point in the size distribution is at about the same position.

We have shown the first data on multiple ionization of simple metal clusters by proton and multicharged ion impact. From the analysis of the abundance spectra it was possible to extract critical sizes and show temperature dependency. Furthermore, we have given evidence for strong electronic excitation in H^+ induced collisions.

This experiment was performed at the Accélérateur d'Ions Multichargés (AIM) at Grenoble. The AIM is a joint facility of Commissariat à l'Energie Atomique (CEA) and Centra National de Recherche Scientifique (CNRS). We would like to thank A. Brenac, G. Lamborley, and T. Lamy for efficient mastering of the ion beams. We are indebted to C. Bréchignac, Ph. Cahuzac, and their collaborators for giving us their cluster source drawings and for valuable advice. We acknowledge numerous fruitful discussions with S. Blundell and M. Gross.

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