Rayleigh Instabilities in Multiply Charged Sodium Clusters

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The stability of multiply charged sodium clusters Na_n^{q+} ($q \leq 10$) produced in collisions between neutral clusters and multiply charged ions A^{z+} ($z = 1$ to 28) is experimentally investigated. Multiply charged clusters are formed within a large range of temperatures and fissilities. They are identified by means of a high-resolution reflectron-type time-of-flight mass spectrometer ($m/\delta m \approx 14\,000$). The maximum fissility of stable clusters is obtained for $z = 28$ and is $X \approx 0.85 \pm 0.07$, slightly below the Rayleigh limit ($X = 1$). It is mainly limited by the initial cluster temperature ($T \approx 100$ K).

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Charge instabilities in finite systems result from a competition between cohesive surface energy and disruptive Coulombic forces. Lord Rayleigh was the first to address this problem theoretically in 1882 [1]. He calculated the maximum electric charge a liquid conducting drop can stand and concluded that it becomes spontaneously unstable regarding the loss of charged fragment(s) when

$$E_{\mathrm{Coulomb}}^{(\mathrm{sphere})} \geq 2E_{\mathrm{surface}}^{(\mathrm{sphere})}, \tag{1}$$

where $E_{\mathrm{Coulomb}}^{(\mathrm{sphere})}$ and $E_{\mathrm{surface}}^{(\mathrm{sphere})}$ are the Coulomb and the surface energy of the drop in the spherical equilibrium shape, respectively. Many experimental studies on charged microscopic droplets followed this work in order to prove the validity of Eq. (1) [2–4]. The experiments yielded disruption thresholds which are lower than the Rayleigh limit, a discrepancy which has been attributed to external perturbing electric fields in the experimental setups, to contaminants in the droplets or to aerodynamic effects [3].

On a totally different length scale, the atomic nucleus proved to be another model system with the discovery of nuclear fission and its interpretation within the liquid-drop model [5,6]. In this case the charge is volume distributed. Nevertheless, the Rayleigh limit remains valid for a liquid drop of nuclear matter [6]. Nuclear fission is usually observed even for $X < 1$, X being the fissility parameter defined as

$$X = \frac{E_{\mathrm{Coulomb}}^{(\mathrm{sphere})}}{2E_{\mathrm{surface}}^{(\mathrm{sphere})}}. \tag{2}$$

For $X < 1$ the drop must overcome a barrier in order to fission, the height of which converges towards 0 as X approaches 1 [6]. The shell structure of the nucleus modifies this simple picture but, nevertheless, the stability of natural and synthesized nuclei is in reasonable agreement with this model. For example, the fissility of ^{235}U is $X \approx 0.72$ and about 0.9 for the recently discovered $Z = 114$ element [7]. Higher fissilities require the synthesis of heavier elements at low excitation energies which seems to be out of reach for the moment.

More recently, with the advent of performant cluster sources, Coulomb instabilities were studied in atomic clusters [8,9]. Among these, clusters of the alkali or noble metals behave as nanometric conducting droplets, and they are therefore the most suited for addressing Rayleigh's problem (see [10] for a review). For a metal cluster of size n and charge q, the fissility parameter writes as $X = \alpha(q^2/n)$ with $\alpha \approx 2.5$ for sodium (of interest in this paper) [10]. As in nuclei, there is a fission barrier against the loss of charged fragment(s) which is expected to disappear for $X = 1$. In order to reach this limit, a neutral cluster must be brought into a charge state around $q_{\mathrm{crit}} = \sqrt{n/\alpha}$ (e.g., $q_{\mathrm{crit}} = 6$ for Na_{90}) at a low temperature in order to minimize thermal activation. In most experiments, neutral clusters are ionized by laser absorption. This method unavoidably leads to hot multiply charged clusters where fission competes with evaporation of atoms [11–14]. The maximum fissility which can be studied in this way corresponds to the size where the fission barrier equates the energy required to evaporate an atom ($X_{\mathrm{max}} \approx 0.3$ for sodium clusters) [13]. There is no such limit when clusters are ionized in peripheral collisions with multiply charged ions. The strong Coulomb field associated with the projectile allows one to remove a large number of electrons in a single collision during a few fs, resulting in highly charged clusters spanning a large range of fissilities around $X = 1$ [15,16]. Moreover, theory predicts that the excitation energy transferred to the cluster can be very low, so that the stability is limited only by the initial cluster temperature [17]. This opens up the possibility to study charge instabilities in "cold" systems and to prove the validity of Eq. (1).

In this Letter, we report on a study of highly charged sodium clusters Na_n^{q+} formed in collisions between neutral clusters and low energy ions A^{z+} ($z \leq 28$, kinetic energy $E = 20 \times z$ keV). The limit of stability of Na_n^{q+} corresponds to an appearance size $n_{\mathrm{app}}(q)$ which is the smallest size of a cluster with charge q observed in the experimental spectrum. We used a high resolution reflectron-type time-of-flight mass spectrometer (RTOFMS) with a characteristic resolution of $m/\delta m \approx 14\,000$ which allows one to extract appearance sizes for charges up to $q = 10$. This is significantly higher than previously reported [12].

Details on the experimental apparatus can be found elsewhere [18]. In brief, clusters are condensed in a gas aggregation source with helium as the buffer gas. The clusters are formed in a condensation channel cooled with liquid nitrogen and are thermalized at approximately 100 K [19]. A thermostated heat bath (5 cm in length) can be added to increase this temperature [20]. A beam of neutral sodium clusters is formed, and after passing through differential pumping stages it enters the interaction region of the RTOFMS where it is intercepted perpendicularly by a pulsed beam of ions A^{z+}. The ionized clusters Na_n^{q+} are separated and detected according to their time-of-flight and therefore to their size to charge ratio n/q. An event-by-event acquisition mode is performed by registering successive arrival times of all fragments.

The optimal mass resolution of the RTOFMS is $m/\delta m \approx 14\,000$ (measured for Na_{100}^{+}) which allows one to identify peaks of 10-fold charged clusters as displayed in Fig. 1 for Xe^{28+} projectile ions ($E = 560$ keV, $v \approx 0.41$ a.u.). Figure 1a shows the overall spectrum with the superposition of the distributions for the different charge states. In the magnified part (see Fig. 1b) peaks of clusters Na_n^{q+} for $q \leq 10$ are identified.

In such spectra, the appearance of a higher charge state results in a new series of peaks which partially overlap with peaks of lower charge states. In Fig. 2a, the maxima of the peaks of Na_n^{5+}, obtained with Ar^{11+} projectiles ($E = 220$ keV, $v \approx 0.47$ a.u.) are connected by a dotted line. The appearance size is easily extracted from the integrated distribution as the threshold of the rising distribution (see Fig. 2b). In the present case, we obtain $n_{\text{app}}(q = 5) = 106 \pm 2$ corresponding to a fissility $X = 0.590 \pm 0.011$. Note that this latter value is significantly higher than what is obtained for "hot" sequentially ionized clusters $[n_{\text{app}}(q = 5) = 206 \pm 5, X = 0.303 \pm 0.007]$ [11–14].

The observed appearance size depends on the cluster temperature. As the excitation energy transferred to the cluster during the ionizing collision depends on the projectile charge z, we can vary the cluster temperature by changing z [17]. We performed the same analysis as in Fig. 2 for projectiles with charges $z \leq 28$ and cluster charges $q \leq 10$. The projectile kinetic energy is $E = 20 \times z$ keV corresponding to velocities in the range 0.3–0.5 a.u. (atomic units). The results are displayed in Fig. 3. The data at $z = 0$ correspond to sequential photoionization and represent photoheated clusters where fission competes with evaporation [12]. Three remarks are made as follows: (i) For $z = 1$ (protons), $n_{\text{app}}(q \leq 5)$ coincides with the laser data (when available) which indicates that hot multiply charged clusters are produced in this case. Indeed, for projectiles in low charge states, central collisions where the ion penetrates the cluster are predominant,

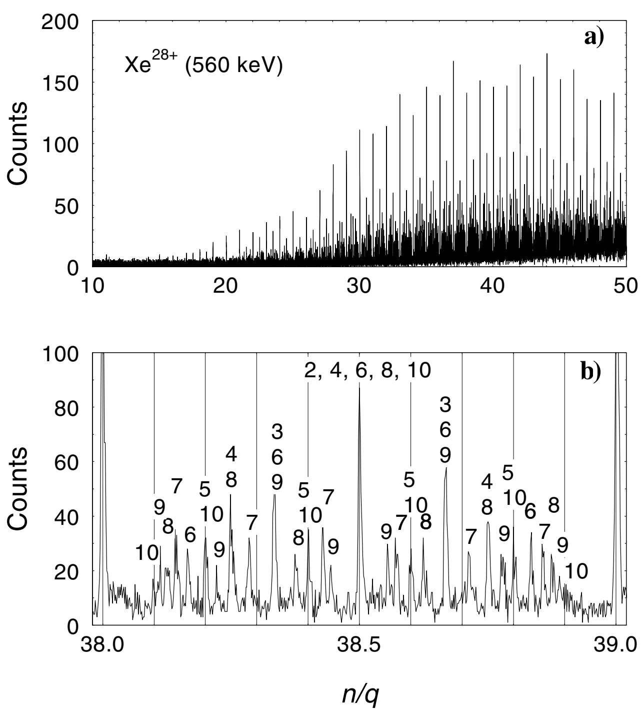

FIG. 1. (a) Time-of-flight mass spectrum of multiply charged sodium clusters Na_n^{q+} following the interaction of neutral clusters Na_n with Xe^{28+} projectiles (kinetic energy $E = 560$ keV, velocity $v \approx 0.4$ a.u.). (b) Details of the same spectrum showing peaks of q-fold charged clusters with $q \leq 10$ (the given numbers indicate the charge state).

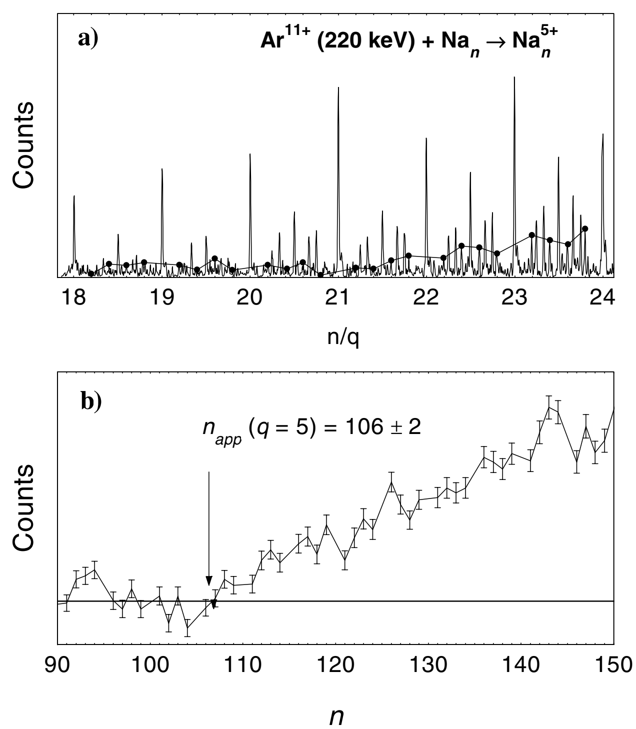

FIG. 2. (a) Time-of-flight mass spectrum obtained with Ar^{11+} ($E = 220$ keV, $v \approx 0.47$ a.u.) projectiles. The dotted line connects the peaks of fivefold charged clusters Na_n^{5+}. (b) Resulting integral distribution of fivefold charged clusters Na_n^{5+} with the extracted appearance size $n_{\text{app}}(q = 5)$.

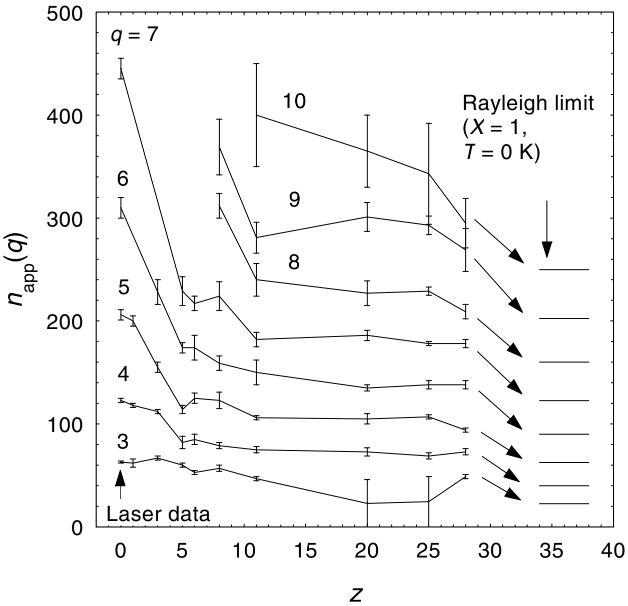

FIG. 3. Appearance size $n_{app}(q)$ of q-fold charged clusters Na_n^{q+} as a function of the projectile charge z. The data at $z = 0$ labeled "Laser data" correspond to photoionized clusters where fission competes with evaporation (from Ref. [12]). On the right side the Rayleigh limit, calculated with Eq. (1), is indicated.

resulting in highly excited multiply charged clusters [21]. (ii) When z increases, the appearance size $n_{app}(q \leq 7)$ decreases. Because of the increasing Coulomb field associated with the projectile, multi-ionization to a given charge state occurs in collisions with larger and larger impact parameters. Therefore, the electronic excitation energy decreases with increasing projectile charge [17], as well as the appearance size. (iii) At high projectile charges $n_{app}(q)$ saturates at a value larger than the Rayleigh limit. In this case, the transferred vibrational energy is smaller than the initial internal energy corresponding to 100 K.

We can estimate the minimum barrier height of a cluster, thermalized at 100 K, which survives the experimental time scale. In order to be observed as a "stable" cluster with a given n/q value, a cluster must not decay before leaving the reflector, otherwise it contributes to the background in the spectra. For a later decay, parent and fragment clusters are not further separated. In the present experiment, the corresponding time is $t(Na_n^{q+}) \approx 12\sqrt{n/q}$ (given in μs) and the fission rate $k_{\text{fission}}(Na_n^{q+})$ has to satisfy the condition $k_{\text{fission}}(Na_n^{q+}) \leq 1/t(Na_n^{q+})$. Assuming an Arrhenius-type fission rate, which depends exponentially on the ratio B_{fission}/T and with a prefactor analog to the evaporation process (see, e.g., [20]), we obtain a typical value of $B_{\text{fission}}/T \approx 21$ which for $T = 100$ K gives $B_{\text{fission}} \approx 180$ meV. These are characteristic values which are determined by the present experimental setup and do not depend significantly on the cluster size as the exponential term dominates.

According to Bohr and Wheeler [6], the following relation holds for X close to 1 where the saddle configuration remains close to a sphere:

$$B_{\text{fission}}(Na_n^{q+}) = \frac{98}{135} E_s (1 - X)^3 \propto n^{2/3}(1 - X)^3, \quad (3)$$

where $E_s = a_s n^{2/3}$ is the surface energy and where a_s corresponds to the surface tension (between 0.7 and 1 eV for sodium depending on the temperature [10,22]). This relation shows that for a constant value of B_{fission} the fissility X approaches the value of 1 with increasing n. We find a similar behavior in the experiment. This is demonstrated in Fig. 4, where the measured appearance sizes for Xe^{28+} projectile ions are shown in a double-log-plot of cluster size n and cluster charge q. The experimental values are well above the laser data corresponding to $X \approx 0.3$, and they strongly approach the Rayleigh limit at $X = 1$ as n is increased. The maximum value obtained is $X \approx 0.85 \pm 0.07$ for $q = 10$. The data are also compared with Eq. (3) (dashed line), where a barrier height of 180 meV has been assumed. In order to further approach the Rayleigh limit, the cluster size (i.e., charge) has to be increased and/or the initial cluster temperature has to be decreased in future experiments.

In order to demonstrate the temperature dependence of the appearance size, we measured $n_{app}(q)$ for a given projectile $(O^{5+}, E = 100 \text{ keV}, v \approx 0.5 \text{ a.u.})$ colliding with neutral clusters thermalized at different initial heat bath temperatures T_{hb}, varying from 100 to 377 K. The results for four-times charged sodium clusters are shown in the left half of Table I. They are compared with those obtained by varying the projectile charge z at a fixed temperature of 100 K (right half of Table I) to emphasize the similar effect of decreasing T_{hb} or rising z on the appearance size. At the highest temperatures T_{hb}, $n_{app}(q)$

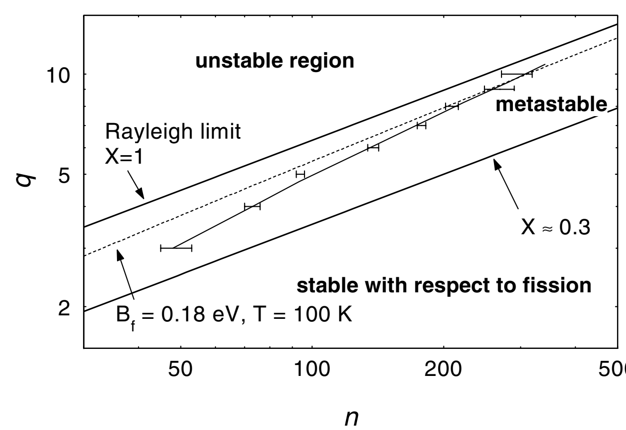

FIG. 4. Appearance size $n_{app}(q)$ of q-fold charged clusters Na_n^{q+} obtained with Xe^{28+} ($E = 560$ keV, $v \approx 0.41$ a.u.) projectiles in a double-log-plot of cluster charge q and cluster size n. The thick lines correspond to the Rayleigh limit ($X = 1$) and to photoionization experiments ($X \approx 0.3$, see Ref. [12]). The dashed line corresponds to $n_{app}(q)$ deduced from Eq. (3) for $B_{\text{fission}} \approx 180$ meV.

TABLE I. Appearance size for fourfold charged sodium clusters produced in collisions between ions and neutral clusters. Left half: variation of $n_{\mathrm{app}}(q=4)$ with the initial cluster temperature T_{hb} for $z=5$; right half: variation of $n_{\mathrm{app}}(q=4)$ with the projectile charge z for $T_{\mathrm{hb}}=100$ K.

T_{hb} (K)	$n_{\mathrm{app}}(q=4)$ ($z=5$)	$n_{\mathrm{app}}(q=4)$ ($T_{\mathrm{hb}}=100$ K)	z
		123 ± 2	Laser
373	117 ± 2	118 ± 2	1
326	118 ± 2		
		112 ± 2	3
272	104 ± 6		
223	99 ± 5		
		82 ± 6	5
100	82 ± 6	85 ± 4	6
0	80	79 ± 3	8
	(extrapolated)	75 ± 3	11
		73 ± 4	20
		69 ± 3	25
		73 ± 3	28

saturates at a value slightly below the laser value. In that case, the excitation energy added by the ion during the collision is enough to form hot multiply charged clusters where fission competes with evaporation and the appearance size does not depend on the initial temperature. When the heat bath temperature decreases further, the appearance size decreases. By extrapolating to 0 K, we obtain a value of $n_{\mathrm{app}}(q=4)=80$, corresponding to $X \approx 0.5$. For that size, Eq. (3) does not apply but the fission barrier can be estimated from the image charge model which gives $B_{\mathrm{fission}} \approx 0.63$ eV [10,23]. From the ratio $B_{\mathrm{fission}}/T \approx 21$ and substracting the initial cluster temperature (100 K) we estimate the energy transfer during the collision to be around 5 eV, in good agreement with what is expected from theory [17].

In conclusion, we have measured the appearance size $n_{\mathrm{app}}(q)$ of multiply charged sodium clusters Na_n^{q+} ($q \leq 10$) formed in collisions of neutral clusters with low energy multiply charged ions $\mathrm{A}^{z+}(z \leq 28, v \approx 0.4$ a.u.). The present experimental setup has allowed us to form highly charged clusters with fission barriers as low as 180 meV for the first time. We have shown that the appearance size is strongly decreasing with the projectile charge z, saturating for higher z values. This behavior is attributed to the fact that electron capture takes place in increasingly distant peripheral collisions when z is increased, resulting in colder clusters as the projectile charge z increases. This is confirmed unambiguously by the increase of $n_{\mathrm{app}}(q)$ when raising the initial cluster temperature in a heat bath from 100 to 377 K. The fissilities reached in this work ($X \approx 0.85$) are far above those measured in laser experiments, and they approach the Rayleigh limit for large cluster sizes and charges. The fact that X is slightly below the value of 1 is due to the initial cluster temperature of 100 K. The results support the validity of the Rayleigh limit for the systems studied in this experiment. Furthermore, they confirm that collisions with multiply charged ions are an efficient way to form highly charged complex systems with rather low excitation energies.

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