Asymmetric Fission of Na_n^{++} around the Critical Size of Stability

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Unimolecular dissociation channels of mass-selected doubly charged sodium clusters Na_n^{++} have been determined for cluster sizes near and above the critical size, $n_c=27$, from which doubly charged clusters are detectable in mass spectra. On a time scale of 50 μs with respect to ionization, doubly charged clusters of size $n=n_c$ are found to fission asymmetrically. For cluster sizes above n_c, however, evaporation of a neutral monomer is the dominant channel for delayed dissociation. An estimation of the height of the Coulombic barrier is given for Na_n^{++} near the critical size, using the framework of statistical theory.

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Small multiply charged clusters X_n^{q+} are often unobservable in mass spectra unless their size exceeds a well defined critical size $n_c(q)$. Values of n_c, for charge states up to $q=4$, have been reported for van der Waals as well as for metal clusters.[1,2] Although it is commonly admitted that small multiply charged clusters below the critical size are not stable because the Coulomb repulsive energy between positive holes exceeds the binding energy, no clear picture has emerged concerning their stability and their dissociation channels. On the theoretical side, energetics has often been considered as a key point to predict the preferred decay channel and the charge and size distribution of the fission products[3,4] even if the existence of energy barriers has been evoked.[5,6] On the experimental side, little information is available about the unimolecular dissociation mechanism of multiply charged clusters making it impossible to confirm or deny the theoretical predictions. Only two recent experiments on van der Waals clusters contribute to a better knowledge of Coulomb explosion. Delayed fission was observed for $(CO_2)_n^{+++}$ but no singly charged fragment ions were detected to be produced by Coulomb explosion from $(CO_2)_n^{++}$.[7] On the other hand, the dissociative double ionization of argon clusters into singly charged fragments was indirectly observed in electron-impact-ionization-potential curves. However, the possible metastable decay of Ar_n^{++} into singly charged fragments has not been observed directly.[8]

In this Letter we present the measurements of size distributions of fragment ions from mass-selected doubly charged sodium clusters Na_n^{++} on a time scale of 50 μs with respect to ionization. For cluster sizes larger than the appearance critical size Na_{27}^{++} the main dissociation channel is the loss of one neutral atom as has been previously mentioned for K_n^{++}.[9] Near the critical size we observe the first experimental evidence of fission into singly charged fragments for delayed dissociation. Competition between the two dissociation pathways, i.e., loss of a neutral atom, and asymmetric fission into singly charged fragments, shows that the decay of metastable doubly charged clusters is not only governed by energetics but also by dynamics. Such a behavior allows us to determine the Coulombic barrier for the fission channel.

A neutral-sodium-cluster distribution, produced by neat adiabatic expansion of metallic vapor, is photoionized by a pulsed uv laser focused between the first two plates of an ion-focusing and accelerating system. The accelerated cluster-ion bunches enter a field-free tube where they spatially resolve into separated ion packets according to the size-to-charge ratio n/q. These are then detected by an electron multiplier located at the end of the flight tube. Depending on the ionizing energy different charge states of the clusters can appear. At $h\nu=3.67$ eV only singly charged clusters are present irrespective of the laser flux density. At $h\nu=4.66$ eV, with high laser fluence, both singly and doubly charged clusters are observed. The doubly charged clusters can be directly identified since odd-numbered clusters appear at the half-integer size-to-charge ratio (Fig. 1). A complementary experiment on ionization of mass-selected singly charged clusters Na_n^+ shows that the ionization of Na_n^+,

$$Na_n^+ + h\nu \rightarrow Na_n^{++} + e^- , \quad (1)$$

with $h\nu=4.66$ eV takes place from $n>80$. The smallest doubly charged clusters Na_n^{++} present in mass spectra from the critical size $n_c=27$ arise from the double ionization of higher masses followed by evaporation of neutral atoms or neutral dimers as has been previously seen for K_n^{++}.[9]

We performed an experiment on selected size-to-charge-ratio ion packets for the two different ionizing situations. This concerns the unimolecular dissociation of ion packets which takes place in the field-free tube downstream from the ionizing region. During the flight "metastable" cluster ions undergo unimolecular dissociation with the parents as well as the fragments proceeding with the center-of-mass velocity. In order to analyze the dissociation, deflection plates located in the flight tube remove all the ions from the beam path except when the

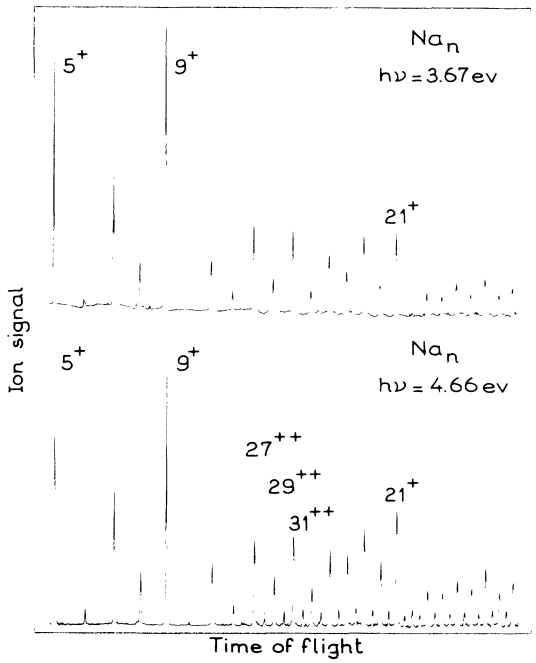

FIG. 1. Mass spectra of photoionized neutral-sodium-cluster distribution. Upper trace, obtained with photon energy $h\nu = 3.67$ eV, shows only singly charged clusters Na_n^+. Lower trace, obtained at higher photon energy $h\nu = 4.66$ eV, puts into evidence doubly charged clusters Na_n^{++} from $n_c = 27$.

packet of interest arrives at the deflection plates. Then the voltage momentarily pulses off to allow the selected packet to proceed further. This packet is then decelerated before entering a final field-free region where the ions are again spatially dispersed according to their size-to-charge ratio. The time interval Δt between the time arrival of the selected n/q ratio and the time arrival of the n'/q' unimolecular product is

$$\Delta t = A\left[\left(\frac{U_0}{n/q} - \frac{V}{n'/q'}\right)^{-1/2} - \left(\frac{U_0 - V}{n/q}\right)^{-1/2}\right], \quad (2)$$

where A depends on the geometry of the experimental arrangement, U_0 is the accelerating voltage in the ionizing region, and V is the decelerating voltage.

Figure 2 shows typical unimolecular dissociation spectra for several selected n/q ratios near the critical size. The right-hand side of the figure shows the delayed dissociation of pure mass-selected singly charged clusters produced with a laser of lower ionization energy $h\nu = 3.67$ eV. As is shown in a previous paper[10] unimolecular dissociation exhibits the loss of neutral monomers or dimers as the dominant channels. The left-hand side of the figure shows the delayed dissociation for several selected parents obtained by ionization with a laser of higher ionizing energy $h\nu = 4.66$ eV. Selecting half-integer size-to-charge ratios makes it possible to focus on unimolecular dissociation of doubly charged Na_n^{++} exclusively, whereas by selecting a integer size-to-charge ratio unimolecular dissociations of both Na_n^{++} and $Na_{n/2}^+$ are present. The dissociation spectrum of Na_n^{++} is then obtained by comparison with the dissociation spectrum of pure mass-selected $Na_{n/2}^+$ produced with the laser of lower energy. For the sake of clarity we have mentioned the main assignment of the daughter unimolecular fragments. According to Eq. (2) the unimolecular fragments on the right-hand side of the parent (Fig. 2) correspond to $n'/q' < n/q$. The unimolecular fragments on the left-hand side correspond to $n'/q' > n/q$ showing the heaviest singly charged fragments from the asymmetric fission of Na_n^{++} when they exist. It has to be noted that such a procedure cannot be used to detect symmetrical fission (from even-numbered doubly charged clusters), since in that case $\Delta t = 0$. From Fig. 2 it is clearly seen that both neutral-atom evaporation and asymmetric fission contribute to the delayed dissociation of Na_n^{++}. For large cluster size evaporation of neutral atoms as was shown[9] for K_n^{++} prevails. For $31 < n \leq 27$ both neutral evaporation and fission coexist. For $n = 26$ and 24 fission is seen to dominate, although Na_{24}^{++} must be the by-product of neutral evaporation from Na_{26}^{++}. Since the heavier singly charged fragments Na_{n-p}^+ with $p = 1,3,5,7,9$ are observable, one would expect other peaks in the fragment size distribution corresponding to Na_p^+ (or below if fission is accompanied by a loss of neutral fragments). Neither of these peaks were detected. This discrimination between heavy and light fission fragments is due to the Coulomb repulsion, which imparts a kinetic energy of about 1 eV to the charged fragments. In our experimental arrangement, the recoil velocity isotropically adds to the center-of-mass velocity and suppresses the intensity of the lighter fragment ions by more than 1 order of magnitude relative to the heavier ones.

It is interesting to compare these first results on the fission process of doubly charged clusters with theoretical predictions. Rao *et al.*[3] as well as Baladron *et al.*[4] assume that energetic considerations determine the preferred decay channel. Considering the energy balance of the fragmentation process,

$$Na_n^{++} \rightarrow Na_{n-p}^+ + Na_p^+, \quad (3)$$

$$\Delta E_n = E(Na_n^{++}) - E(Na_{n-p}^+) - E(Na_p^+), \quad (4)$$

where $E(X)$ is the formation energy of X, they calculated the critical size below which fragmentation is exothermic and the fission products for intrinsically unstable doubly charged clusters. From Ref. 3 the size number beyond which spontaneous fragmentation is not possible is higher than 50, and from Ref. 4 the emission of an atomic ion must be the preferred dissociation channel. This contrasts with our results. The measured critical number is 27 and Coulombic fission around this size occurs along several possible channels. All channels are not observed; the size distribution of the main heavier

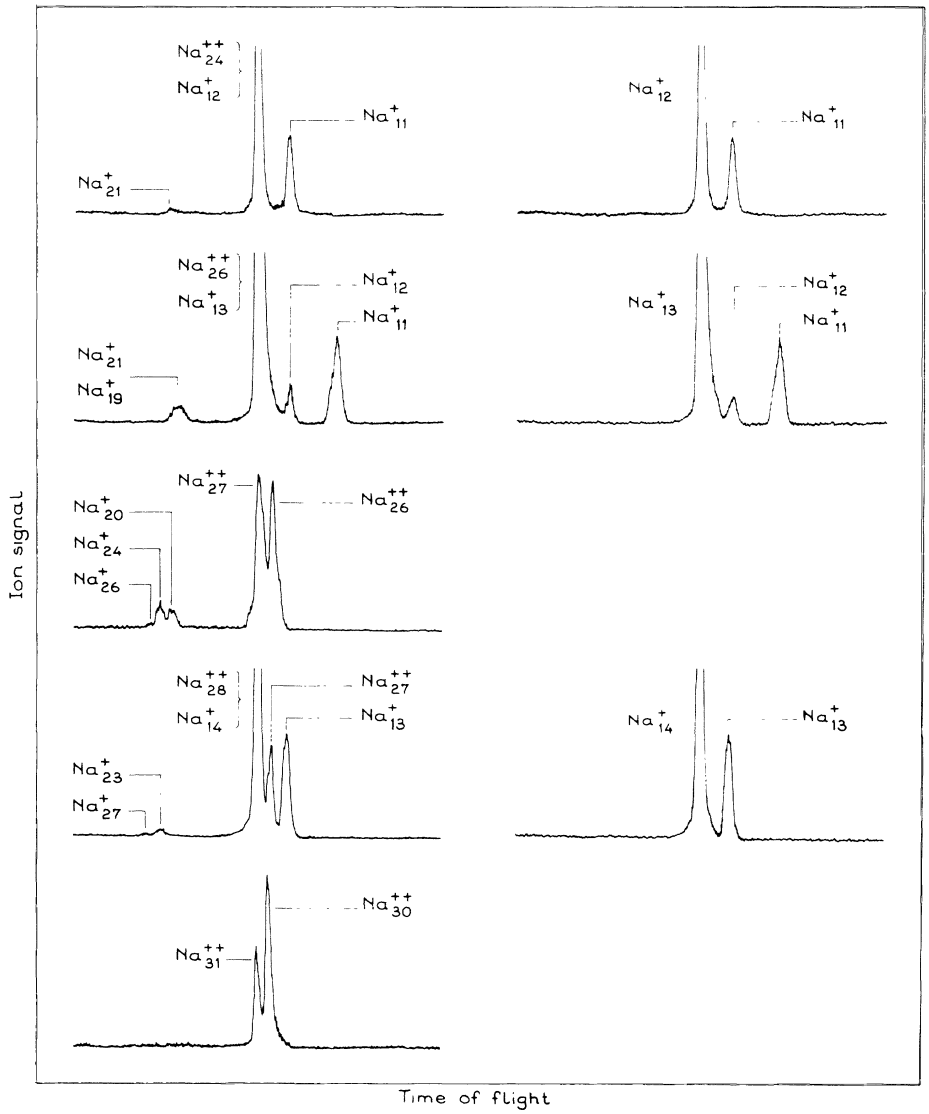

FIG. 2. Unimolecular dissociation spectra for several clusters selected by the size-to-charge ratio. Right-hand side, the unimolecular evaporation of pure singly charged clusters. Left-hand side, unimolecular dissociation of $Na_{n/2}^{+}$ and Na_n^{++}.

fission fragments is centered around $n=21,23$ depending on the parent (Fig. 2). These differences between predictions and experimental observations indicate that energetic considerations are not sufficient to predict the more complex reality.

One of the first questions is what does critical size mean? In fact, the critical size n_c below which multiply charged clusters are not observable in mass spectra depends strongly on the cluster formation. When X_n^{++} are formed by neutral evaporation from higher masses, n_c is the size number for which fission in singly charged fragments dominates the neutral-evaporation process. Then the production of X_n^{++} stops for $n=n_c$. The critical size is dictated here by the dynamics of the dissociation. In the classical limit of Rice-Ramsberger-Kassel theory[11] the rate constant for fracture of a cluster is

$$k=gv(1-E_b/E^*)^{s-1}, \tag{5}$$

where v is the vibrational frequency mode, s is the number of modes, g is the degeneracy factor, E^* is the internal energy, and E_b is the energy to surpass to obtain dissociation. For the reactive channel without potential barrier,

$$Na_n^{++} \rightarrow Na_{n-1}^{++} + Na, \tag{6}$$

E_b equals the dissociation energy D_n:

$$D_n = E(Na_n^{++}) - E(Na_{n-1}^{++}) - E(Na). \tag{7}$$

Conversely, for fission process (3) E_b is the Coulombic

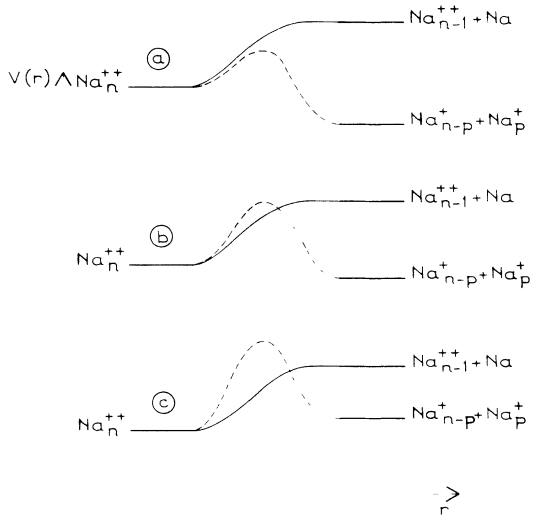

FIG. 3. Schematic drawing of the three main situations which occur in the fragmentation of Na_n^{++}. Curve *a* corresponds to $n \leq 26$, curve *b* corresponds to Na_{27}^{++} where both fission and evaporation coexist, and curve *c* corresponds to $n \geq 31$ when neutral evaporation is the dominant unimolecular dissociation channel.

energy barrier which has to be surpassed before dissociation can occur. As the cluster increases in size, the barrier to dissociation increases in height (Fig. 3). If the vibrational temperature is sufficient to promote unimolecular dissociation of a doubly charged cluster during the flight time, neutral-evaporation processes dominate for higher masses. When the height of the Coulombic barrier roughly equals the dissociation energy the two processes will compete (7). This size region is the observed critical-size region. For Na_n^{++} we found $n_c = 27$. From our binding-energy measurements[10] this leads to a Coulombic barrier height of about 0.8 eV, which is close to the Coulombic repulsion energy of the two singly charged fragments. So a rough estimation of the critical size can be obtained by the method we previously used for K_n^{++}.[9] We found $n_c = 23$ in close agreement with the measured value. Charged clusters X_n^{++} can also be formed by two-step ionization from cold neutral clusters. If, during ionization, the internal energy is maintained lower than the Coulombic barrier, metastable doubly charged clusters must exist below the previous critical size as has been found for Pb_n^{++}.[12,13]

Another question about the stability of doubly charged clusters is how to predict the dissociation channels. If for neutral or singly charged clusters the dissociation channels are given by the energetics because of the absence of barriers, the answer is not so simple for multiply charged clusters, and the knowledge of the multidimensional total-energy surface is also needed. Up to now this has been known only for small doubly charged clusters $n \leq 5$.[14,15] Then statistical methods may be used to determine the fragmentation pathway after excitation. So there is no reason to find only one critical size from which all doubly charged clusters fission into singly charged fragments. There may exist, in some cases, islands of stability for X_n^{++} which may be observed by direct ionization from "cold" clusters.

In conclusion, this new step into the study of the stability of doubly charged clusters Na_n^{++} puts into evidence for the first time asymmetric fission into singly charged fragments on a time scale of 50 μs with respect to ionization. Competition between the two deexcitation pathways, neutral evaporation and fission into singly charged fragments, is understood by the statistical dynamics of unimolecular dissociation, showing that delayed fission can be observed around the critical size of stability. For larger clusters sequential neutral ejection is the dominant deexcitation pathway.

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