Charge-Induced Fragmentation of Sodium Clusters

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The fission of highly charged sodium clusters with fissilities $X > 1$ is studied by *ab initio* molecular dynamics. Na_{24}^{4+} is found to undergo predominantly sequential Na_3^+ emission on a time scale of 1 ps, while Na_{24}^{Q+} ($5 \leq Q \leq 8$) undergoes multifragmentation on a time scale ≥ 0.1 ps, with Na^+ increasingly the dominant fragment as Q increases. All singly charged fragments Na_n^+ up to size $n = 6$ are observed. The observed fragment spectrum is, within statistical error, independent of the temperature T of the parent cluster for $T \leq 1500$ K. These findings are consistent with and explain recent trends observed experimentally.

Starting with the work of Sattler *et al.* [1] on van der Waal's clusters, the study of the fragmentation (fission) of charged atomic or molecular clusters has proved a valuable experimental tool for investigating the intrinsic stability and binding forces of these objects. These studies and others yield important insights into the behavior of matter at the small size limit and the size-dependent evolution toward bulk properties. Much recent work on fission has been devoted to metallic clusters, both experimentally [2–11] and theoretically [4,9,12–16]. Fission of metallic clusters is particularly interesting on account of the similarities and differences with the nuclear fission process [12]. Over a century ago, Lord Rayleigh [17] studied the problem of the time development of the Coulomb instability of a surface-charged liquid drop and conjectured that the excess charge would be removed by the emission of jets, rather than by fission into two parts of more or less equal size (as occurs for nuclei, where the charge is distributed uniformly through the volume).

According to the Rayleigh criterion [17], a charged liquid drop is unstable against Coulomb forces when its fissility $X > 1$, where $X = E_{Coul}/(2E_{surf})$ is proportional to the ratio of the Coulomb to surface energy of the drop. For a metallic cluster M_N^{Q+}, assumed spherical with radius $r_s N^{1/3}$ (r_s is the Wigner-Seitz radius for the metal), this gives $X = (16\pi r_s^3 \sigma)^{-1} Q^2/N$, where σ is the surface tension, or $X \approx 2.5 Q^2/N$ for Na_N^{Q+}. Now, fission experiments on metallic clusters where the cluster is charged by laser ionization [2–7] have so far produced only clusters with $X < 1$, for which an energy barrier exists against fission. Thermally activated fission may be observed, however, and the dominant charged fragment is found to be Na_3^+, which has a closed electronic shell and is particularly stable; Na^+ has not so far been observed. In a different type of experiment [8–11], sodium clusters are ionized by collision with a beam of highly charged ions, a technique that is expected to allow study of a much wider range of X and cluster temperatures. Coincidence measurements reveal multifragmentation processes in some cases, often with Na^+ as the dominant fragment.

In this Letter, we offer the first systematic dynamical study of metallic cluster fission in the regime $X > 1$ using *ab initio* molecular dynamics (MD) [18]. We find that for X close to unity, sequential emission of mainly Na_3^+ is the dominant decay channel, while for $X \gg 1$, multifragmentation with Na^+ as the dominant fragment occurs. Our simulations provide detailed spatial and temporal information on the fission process and explain some of the trends observed experimentally.

On each time step of the cluster dynamics, we compute the density of valence electrons (and hence the forces on the ions) within the temperature-dependent Kohn-Sham (KS) formalism [19], using the local density approximation (at zero temperature) for the exchange-correlation functional $E_{xc}[\rho]$. We use a real-space finite-difference method, recently developed by us [20], incorporating a novel system of adaptive simulation cells that surround, adapt to, and follow each distinct fragment during a multifragmentation, permitting the simulation to continue efficiently up to large fragment separations. To achieve better fragmentation statistics, at the expense of some loss of first-principles accuracy, we employ a soft, phenomenological pseudopotential [21], which permits a relatively large real-space grid step $\Delta = 1.35$ a.u. We do not expect our choice of functional $E_{xc}[\rho]$ or pseudopotential to affect significantly the main results for barrierless fission.

To study the fragmentation of a single species Na_N^{Q+} at an "initial temperature" T_{in}, we run M dynamical simulations arising from an ensemble of M initial conditions constructed as follows: (i) We optimize the geometry of the neutral cluster Na_N at 0 K; (ii) we perform an MD run of ≥ 20 ps for Na_N at 400 K (which is roughly the temperature of the clusters Na_N output by the cluster source in the collision experiments [8–11]); (iii) we take M ionic (nuclear) configurations $\{R_I^{(n)}\}$ with velocities $\{V_I^{(n)}\}$ ($n = 1-M$) at regular intervals from this simulation; (iv) for each $\{R_I^{(n)}\}$, we remove Q electrons and reequilibrate the remaining electrons to an electronic temperature $T_{el} = T_{in}$; and (v) we start the dynamics with configuration $\{R_I^{(n)}\}$ and velocities $\{\lambda V_I^{(n)}\}$, with λ chosen to give

an ionic (kinetic) temperature $T_{ion} = T_{in}$. While the fragmentation spectra may depend to some extent on the initialization procedure, the above procedure has been chosen to approximate the heavy-ion collision experiments [8–11]. The collision time is fast, of order 10 fs, so the ionic coordinates $\{\mathbf{R}_I\}$ are effectively frozen during the ionization process, as above. The scaling factor λ in the initial conditions is intended to approximate the extra energy "injected" into the ionic system by relaxation of the valence electrons, which are excited during the collision. Steps (iv) and (v) above effectively assume this relaxation to be very rapid. We discuss the relative sizes of relaxation and fragmentation times below.

Although we are mainly concerned with barrierless fission $X > 1$, to assess the accuracy of our KS approach, and to make contact with previous experiment and theory, we first consider briefly the binary fission of small doubly charged clusters. Our lowest-energy geometries for Na_N ($4 \leq N \leq 8$) agree with previous density-functional theory (DFT) studies [13,22], and our pseudopotential is adjusted to give a good fit to ionization and atomization energies for this size range, to within the scatter of previous DFT results [13,22]. We find doubly charged clusters Na_N^{2+} to be unstable for $N \leq 6$, in agreement with Ref. [13]. In dynamical simulations with $M = 10$ initial conditions for each N and with $T_{in} = 600$ K, Na_N^{2+} ($5 \leq N \leq 10$) undergoes binary fission with Na_3^+ as the dominant fragment, in agreement with experiment [2,3] and previous theory [13]. Fission products other than Na_3^+ are found in only two cases: $Na_6^{2+} \rightarrow Na_5^+ + Na^+$ with about a 20% branching ratio, and $Na_{10}^{2+} \rightarrow 2Na_5^+$ with about a 40% branching ratio.

To understand the result for Na_{10}^{2+} further, we show in Fig. 1 the energy barriers for the two observed fission channels, obtained by constrained energy minimization with the separation of the centers of mass of the two fragments specified. A double-humped fission barrier is found for each channel, and in the dynamics the cluster elongates to a "precursor state" where it may remain for
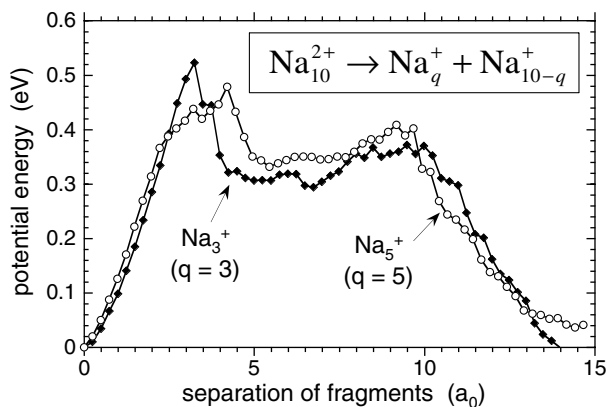

FIG. 1. Fission barriers for two fission channels of Na_{10}^{2+}, as a function of the separation of the centers of mass of the two fragments, with zero corresponding to the initial cluster.

several ps before fissioning, as also found previously in Ref. [13]. Our barrier height for Na_3^+ emission is about 0.5 eV, in reasonable agreement with the 0.7 eV found in Ref. [13]. The discrepancy may be due in part to our phenomenological pseudopotential.

Let us now turn to a systematic study of the effect of fissility on the fragmentation spectrum for fissilities greater than one. We consider the fragmentation of Na_{24}^{Q+} for $Q = 4$–8 ($X = 1.7$–6.7) with initial temperatures $T_{in} = 400$, 800, and 1500 K. We find Na_{24}^{Q+} to be unstable (at 0 K) in our KS model for $Q \geq 4$; Na_{24}^{3+} ($X = 0.94$) is just stable, with a barrier of about 0.2 eV for removal of Na_3^+. For each Q and T_{in}, we run $M = 10$ simulations, each lasting up to 5 ps ($Q = 4$), 3 ps ($Q = 5$–6), or 2 ps ($Q = 7$–8). A distinct final-state fragment Na_n^{q+} is considered to have formed when all n ions in it are separated from the remaining ions by more than a cutoff distance $r_{cut} = 14.0$ a.u. Its charge q is calculated as the total charge inside a box centered on the fragment with a border of at least 7.0 a.u. from any ion. Usually, q is integral to better than a few percent, and the identification of the fragment is unambiguous. But this is not guaranteed by the KS formalism: when two virtual orbitals centered on different clusters are nearly degenerate and overlap, the resulting KS orbital may "split" between the two centers yielding fractional charges. This turns out to be particularly likely to happen with monomers or dimers emitted toward the end of a multifragmentation process.

In such cases, it is usually possible to assign integral charges unambiguously by interpreting the electron wave functions statistically. A typical example would be

$$Na_{24}^{8+} \rightarrow 4Na^+ + Na_{18}^{2.85+} + Na^{0.53+} + Na^{0.70+}. \tag{1}$$
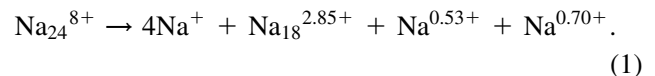
The first four fragments emitted here are Na^+ with very close to integer charge, but when the simulation is stopped (here after 2 ps), the remaining fragments are fractionally charged. We round the large fragment up to Na_{18}^{3+} and assume that the total remaining charge of 1.08 shared by the two monomers is to be interpreted, in a statistical sense, as $Na + Na^+$, with the probability for finding the charge $+1$ on a particular monomer given by the fractional charges. In this way, we often find neutral monomers or dimers emitted in the final stages of a multifragmentation (but never among the initial fragments), which we interpret as evaporation from a hot residual fragment. Note that the slight excess of positive charge $\sum_i q_i = 8.08$ on the right-hand side of Eq. (1) is due to spillout of electron density from the boxes used to calculate the total charge, which results in a slight underestimate of the negative electronic charge. When simple rounding or charge redistribution among equivalent species does not give a clear assignment of integral charges, we discard the simulation, which was the case for less than 5% of simulations.

Some typical snapshots of Coulomb fission processes illustrating the main points are shown in Fig. 2. For
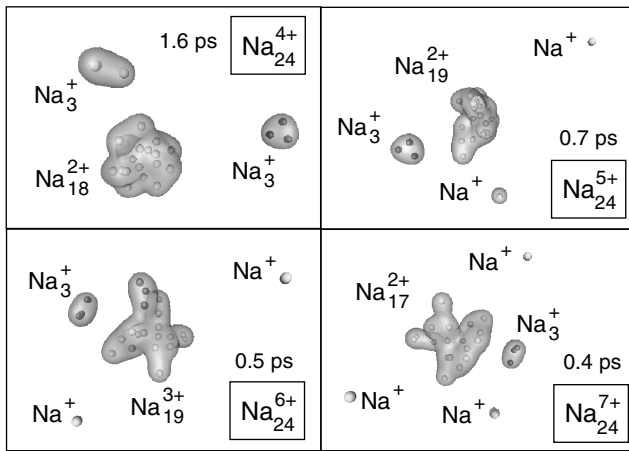
FIG. 2.   Snapshots of the Coulomb fission of $Na_{24}{}^{Q+}$ for $Q = 4-7$ and an initial temperature $T_{in} = 800$ K. The time t for each snapshot (with $t = 0$ the initial condition) is shown.

$Q = 4$ $(X = 1.7)$ (and also for $Q = 3$, $X = 0.94$), we find mainly sequential emission of $Na_3{}^+$ on a 1 ps time scale, with only rarely Na^+ emission. Such emission continues until the large residual fragment (which ultimately develops a fission barrier) is too cool to emit further fragments, at least on the time scale of our simulation, here 5 ps. (It is possible that with a longer simulation time we would occasionally observe emission of an additional singly charged fragment.) As Q increases, we find emission of increasing quantities of Na^+, which is the dominant fragment for $Q \gtrsim 5$. All singly charged fragments up to size six are observed in some quantities.

Figure 3 shows in detail a disintegration of $Na_{24}{}^{7+}$ $(X = 5.1)$ as a function of time. In Fig. 3(a), taken at $t = 0.10$ ps, two Na^+ at the top and bottom left are about

to leave the cluster. After 0.2 ps [Fig. 3(b)], a third Na^+ and a $Na_3{}^+$ start to leave from the rear. At $t = 0.3$ ps [Fig. 3(c)], the residual cluster is already highly deformed, and eventually emits a further Na^+ and $Na_3{}^+$ after about 0.7 ps, leaving a $Na_{14}{}^+$ residue that remains stable up to 2 ps, when the simulation was terminated. The first few Na^+ ions emitted at about $t \sim 0.1$ ps were initially at the surface, where the valence electron density is low (the excess positive charge tends to be located near the surface in a metallic cluster). We conclude that these ions were sufficiently weakly bound that they simply accelerated outwards starting at $t = 0$.

The precise fragmentation pattern found in a given run for large X is very sensitive to the initial condition, even for a given T_{in}. However, averaging over initial conditions, we find the mean number of a given fragment emitted to be, within statistical error, essentially independent of T_{in} for $T_{in} = 400$, 800, and 1500 K. This is perhaps not surprising, since the Coulomb energy of $Na_{24}{}^{Q+}$ is $E_{Coul} \approx 1.2Q^2$ eV, while the ionic kinetic energy is only $E_{kin} \approx 0.3$ eV per 100 K and is thus small compared to E_{Coul} for all cases considered here. Therefore, in Fig. 4 we have combined our results for the three T_{in} and show the average number of singly charged fragments $Na_n{}^+$ $(n = 1-5)$ emitted per fragmentation, averaged now over 30 initial conditions for each parent charge Q. The most striking trend observed in Fig. 4 is the smooth increase in the number of Na^+ emitted with increasing Q, accompanied by a reduction in the number of $Na_3{}^+$ emitted. For $Na_{24}{}^{4+}$ $(X = 1.7)$, $Na_3{}^+$ dominates; for $Na_{24}{}^{8+}$ $(X = 6.7)$, on average 20 times more Na^+ are emitted than $Na_3{}^+$.

The average time elapsed before the emission of the first fragment varies from 0.1–0.2 ps for $Q = 6-8$, where the first fragment is nearly always Na^+, to 0.4–0.6 ps for $Q = 4-5$, where $Na_3{}^+$ is most often the first fragment. A combined electronic-ionic dynamical study within time-dependent KS [16] suggests that electron-ion relaxation times τ_r may be of order $\tau_r \lesssim 100$ fs and thus competitive with the time scale τ_f of some faster fragmentation
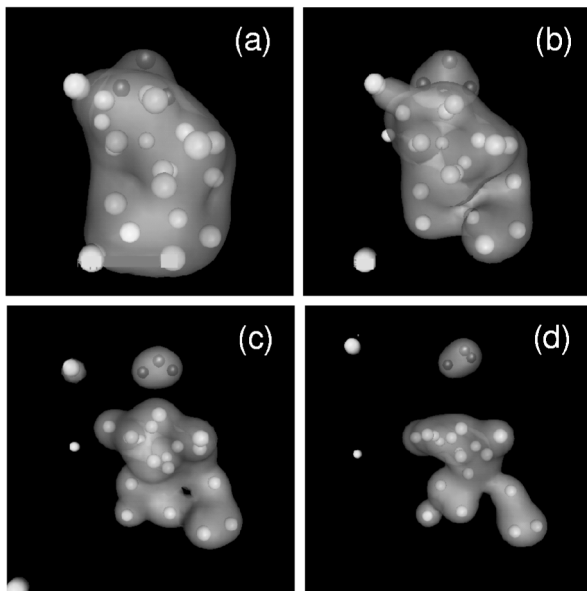

FIG. 3.   Coulomb fission of $Na_{24}{}^{7+}$ at times of (a) 0.1 ps, (b) 0.2 ps, (c) 0.3 ps, and (d) 0.45 ps. Shown are isocontours of the valence electron density, with Na^+ ions in the interior.
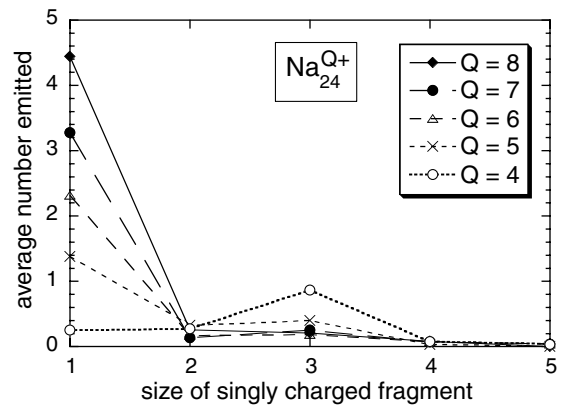

FIG. 4.   Average number of $Na_n{}^+$ fragments emitted per event versus the size n of the fragment, for the Coulomb fission of $Na_{24}{}^{Q+}$ $(Q = 4-8)$.

processes ($\tau_f \gtrsim 50$ fs). However, as we have seen, these faster processes involve immediate acceleration of Na^+ away from the surface region of the cluster, a process which does not require electron-ion relaxation to occur. Moreover, our mean fragment spectra are found to be essentially independent of T_{in} up to at least $T_{in} = 1500$ K. We do not believe, therefore, that our approximate treatment of electron-ion relaxation via the parameters λ and T_{in} will lead to a significant qualitative error in our results.

The trend shown in Fig. 4 is consistent with the observation in a heavy-ion collision experiment [10] that Na^+ dominates the inclusive small fragment spectrum when Xe^{20+} is the projectile, while Na_3^+ dominates when Ar^{3+} is the projectile, since the heavier ion Xe^{20+} should produce clusters Na_N^{Q+} with higher charge Q. Our results are consistent also with another collision experiment [11], in which Na_3^+ is found to dominate in events with a single light fragment, while Na^+ dominates in events with a multiplicity p of light fragments $p \geq 2$. We conclude that in the latter events one is observing multifragmentation of parent clusters with $X > 1$.

We note that the preference for Na^+ emission for $X \gg 1$ is qualitatively consistent with simple considerations of the total energy released (Q value) in a charged liquid-drop model [12], which favors the distribution of the parent charge over many small fragments. Also, in a statistical model [14] that assumes an ergodic distribution of fission fragments for a system confined to a small volume, evidence was found for a first-order "fragmentation phase transition" from a regime with a large residual fragment at low excitation energies to a regime with only small fragments at high excitation energies. We do not observe clear evidence for such an effect in the present data, although our statistics and range of study are too limited. However, we note that, in addition to providing detailed spatial and temporal information, the present dynamical approach avoids the ergodic assumption in the statistical model.

Our test system Na_{24}^{Q+} is perhaps too small to be able to observe jets unambiguously. We observe only small fragments, which tend to be emitted isotropically, although the cluster has a tendency to elongate during the process (see Figs. 2 and 3). We stress that these conclusions pertain to the regime of barrierless fission $X > 1$. We have also searched for symmetric fission when $X < 1$, where experimental evidence exists for the emission of large fission fragments [6]. We found symmetric fission for Na_{10}^{2+}, and as a rare event ($<10\%$) for Na_{18}^{2+}, which has a favorable closed-shell final state Na_9^+. However, in a low-statistics study of Na_{40}^{4+} ($X = 1$), we observed only sequential Na_3^+ emission (and for Na_{40}^{8+} we observed predominantly Na^+ emission).

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