Charge-Induced Fragmentation of Sodium Clusters

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The fission of highly charged sodium clusters with fissilities \( X > 1 \) is studied by \textit{ab initio} molecular dynamics. \( \text{Na}_{24}^{1+} \) is found to undergo predominantly sequential \( \text{Na}_{3}^{+} \) emission on a time scale of 1 ps, while \( \text{Na}_{24}^{2+} (5 \leq Q \leq 8) \) undergoes multifragmentation on a time scale \( \geq 0.1 \) ps, with \( \text{Na}^{+} \) increasingly the dominant fragment as \( Q \) increases. All singly-charged fragments \( \text{Na}_{n}^{+} \) 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.

36.40.Qv, 36.40.Wa, 31.15.Qg, 31.15.Ew

Starting with the work of Sattler et al. \cite{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 \cite{2–11} and theoretically \cite{4,9,12–16}. Fission of metallic clusters is particularly interesting on account of the similarities and differences with the nuclear fission process \cite{12}. Over a century ago, Lord Rayleigh \cite{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 \cite{17}, a charged liquid drop is unstable against Coulomb forces when its fissility \( X > 1 \), where \( X = E_{\text{total}}/(2E_{\text{coul}}) \) 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 \( X = (16\pi\sigma/s)^{-1}Q^{2}/N \), where \( \sigma \) is the surface tension, or \( X \approx 2.5Q^{2}/N \) for \( \text{Na}_{N}^{Q+} \). Now, fission experiments on metallic clusters where the cluster is charged by laser ionization \cite{22} 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 \( \text{Na}_{3}^{+} \), which has a closed electronic shell and is particularly stable; \( \text{Na}^{+} \) has not so far been observed. In a different type of experiment \cite{13,14}, 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 \( \text{Na}^{+} \) as the dominant fragment.

In this Letter, we offer the first systematic dynamical study of metallic cluster fission in the regime \( X > 1 \) using \textit{ab initio} molecular dynamics (MD) \cite{15}. We find that for \( X \) close to unity, sequential emission of mainly \( \text{Na}_{3}^{+} \) is the dominant decay channel, while for \( X \gg 1 \), multifragmentation with \( \text{Na}^{+} \) 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 \cite{19}, using the local density approximation (at zero temperature) for the exchange-correlation functional \( E_{\text{xc}}[\rho] \). We use a real-space finite-difference method, recently developed by us \cite{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 \cite{21}, which permits a relatively large real-space grid step \( \Delta = 1.35 \) a.u. We do not expect our choice of functional \( E_{\text{xc}}[\rho] \) or pseudopotential to affect significantly the main results for barrierless fission.

To study the fragmentation of a single species \( \text{Na}_{N}^{Q+} \) at an “initial temperature” \( T_{\text{in}} \), 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 \( \text{Na}_{N} \) at 0 K; (ii) we perform an MD run of \( \geq 20 \) ps for \( \text{Na}_{N} \) at 400 K (which is roughly the temperature of the clusters \( \text{Na}_{N} \) output by the cluster source in the collision experiments \cite{13,14}); (iii) we take \( M \) ionic (nuclear) configurations \( \{ \mathbf{R}^{(n)}_{i} \} \) with velocities \( \{ \mathbf{V}^{(n)}_{i} \} \) (\( n = 1-M \)) at regular intervals from this simulation; (iv) for each \( \{ \mathbf{R}^{(n)}_{j} \} \), we remove \( Q \) electrons and...
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re-equilibrate the remaining electrons to an electronic
temperature \( T_{el} = T_{\text{in}} \); and (v) we start the dynamics
with configuration \( \{ \mathbf{R}_I \} \) and velocities \( \{ \lambda \mathbf{V}_I \} \), with \( \lambda \)
chosen to give an ionic (kinetic) temperature \( T_{\text{ion}} = T_{\text{in}} \).
While the fragmentation spectra may depend to some ex-
tent on the initialization procedure, the above procedure
has been chosen to approximate the heavy-ion collision
experiments \[\text{[1]}.\] 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 fac-
tor \( \lambda \) in the initial conditions is intended to approximate
the extra energy “injected” into the ionic system by re-
laxation 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 the-
tory, we first consider briefly the binary fission of small
doubly-charged clusters. Our lowest-energy geometries
for \( \text{Na}_N \) \( (4 \leq N \leq 8) \) agree with previous density-
functional theory (DFT) studies \[\text{[22,13]},\] and our pseu-
dopotential is adjusted to give a good fit to ionization
and atomization energies for this size range, to within
the scatter of previous DFT results \[\text{[22,13]},\] . We find
doubly-charged clusters \( \text{Na}_N^{2+} \) to be unstable for \( N \leq 6 \),
in agreement with Ref. \[\text{[13]}\]. In dynamical simulations
with \( M = 10 \) initial conditions for each \( N \) and with
\( T_{\text{in}} = 600 \) K, \( \text{Na}_N^{2+} \) \( (5 \leq N \leq 10) \) undergoes binary fission
with \( \text{Na}_3^{+} \) as the dominant fragment, in agreement
with experiment \[\text{[22]}\] and previous theory \[\text{[13]}\]. Fission
products other than \( \text{Na}_3^{+} \) are found in only two cases:
\( \text{Na}_6^{2+} \rightarrow \text{Na}_5^{+} + \text{Na}_+ \) with about a 20% branching ratio,
and \( \text{Na}_{10}^{2+} \rightarrow 2\text{Na}_5^{+} \) with about a 40% branching ratio.

To understand the result for \( \text{Na}_{10}^{2+} \) further, we show
in Fig. 2 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
several ps before fissioning, as also found previously in
Ref. \[\text{[3]}\]. Our barrier height for \( \text{Na}_3^{+} \) emission is about
0.5 eV, in reasonable agreement with the 0.7 eV found
in Ref. \[\text{[3]}\]. 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 shall consider the fragmentation of
\( \text{Na}_{24}^{Q+} \) for \( Q = 4–8 \) \( (X = 1.7–6.7) \) with initial temperatures
\( T_{\text{in}} = 400 \) K, 800 K, and 1500 K. We find \( \text{Na}_{24}^{Q+} \) to be unstable
(at 0 K) in our KS model for \( Q \geq 4 \); \( \text{Na}_{24}^{3+} \) \( (X = 0.94) \) is just stable, with a barrier of about
0.2 eV for removal of \( \text{Na}_3^{+} \). For each \( Q \) and \( T_{\text{in}} \), 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 \( \text{Na}_n^{q+} \) is considered to have formed when
all \( n \) ions in it are separated from the remaining ions by
more than a cutoff distance \( r_{\text{cut}} = 14.0 \) 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 per-
cent, and the identification of the fragment is unambigu-
ous. 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 frac-
tional 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

\[
\text{Na}_{24}^{8+} \rightarrow 4\text{Na}_+^+ + \text{Na}_{18}^{2.85^+} + \text{Na}_{0}^{0.53^+} + \text{Na}_{0}^{0.70^+}. \tag{1}
\]

The first four fragments emitted here are \( \text{Na}_+ \) 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
\( \text{Na}_{18}^{3^+} \), and assume that the total remaining charge of
1.08 shared by the two monomers is to be interpreted, in
a statistical sense, as \( \text{Na}_+ + \text{Na}_+ \), 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 mul-
tifragmentation (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 r.h.s. of Eq. \( \text{(1)} \) 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 $Q = 4 \ (X = 1.7)$ (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 $Q \geq 5$. 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 $T_{in} = 400$ K, 800 K, and 1500 K. This is perhaps not surprising, since the Coulomb energy of Na$_{24}$$^{Q+}$ is $E_{\text{Coul}} \approx 1.2Q^2$ eV, while the ionic kinetic energy is only $E_{\text{kin}} \approx 0.3$ eV per 100 K and is thus small compared to $E_{\text{Coul}}$ for all cases considered here. Therefore, in Fig. 4 we have combined our results for the three $T_{in}$, and show the average number of singly-charged fragments Na$_{n+}$ $(n = 1\text{-}5)$ emitted per fragmentation, averaged now over 30 initial conditions for each parent charge $Q$. The most striking trend observed in Fig. 4 is the smooth increase in number of Na$_{+}$ emitted with increasing $Q$, accompanied by a reduction in the number of Na$_{3+}$ emitted. For Na$_{24}$$^{4+}$ $(X = 1.7)$, Na$_{3+}$ dominates; for Na$_{24}$$^{8+}$ $(X = 6.7)$, on average 20 times more Na$_{+}$ are emitted than Na$_{3+}$.
We have also searched for symmetric fission when $X < 1$, where experimental evidence exists for the emission of large fission fragments [1]. We found symmetric fission for Na$_{40}^{2+}$, and as a rare event (< 10%) for Na$_{48}^{2+}$, which has a favorable closed-shell final state Na$_3^+$. However, in a low-statistics study of Na$_{40}^{1+}$ ($X = 1$), we observed only sequential Na$_3^+$ emission (and for Na$_{40}^{8+}$ we observed predominantly Na$^+$ emission).

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