Patterns and Barriers for Fission of Charged Small Metal Clusters

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Asymmetric fission of small doubly-charged sodium clusters, investigated via a local-spin-density molecular-dynamics method, is shown to occur predominantly via $Na_n^{+2} \rightarrow Na_{n-3}^{+} + Na_3^{+}$, for $4 \leq n \leq 12$. For the smallest clusters ($n \leq 6$), fission is barrierless, while fission of larger ones involves barriers. For $n=8$, 10, and 12 the barriers are 0.16, 0.71, and 0.29 eV, respectively, reflecting the closed-shell stability of the parent with $n=10$. The fission barriers for $n>8$ exhibit a double-hump shape, and the dynamics of fission involves a precursor mechanism.

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Recent studies of metallic clusters [1] (particularly of simple metals) unveiled systematic energetic, stability [1,2], spectral [3], and fragmentation [1,4–6] trends of intrinsic interest for understanding the properties of matter at the small aggregation limit and the size-dependent evolution toward bulk behavior. Moreover, several properties of atomic clusters (e.g., electronic shell structure [1] and, most recently, supershells [2(b)], portrayed by the occurrence of magic numbers in the abundance spectra and ionization potentials; the influence of shape fluctuations analyzed within the jellium model [1]; giant spectral resonances interpreted as evidence for collective plasma oscillations [1,7]; and fragmentation, fission, and patterns of ionized clusters [1,4–6]) bear close analogies to corresponding phenomena exhibited by atomic nuclei. These observations suggest an intriguing universality of the physical behavior of finite-size aggregates, though governed by interactions of differing spatial and energy scales.

These analogies have led to the adaptation of several established concepts used in the context of nuclear phenomena [8] for interpretation of recent studies of atomic clusters. In particular, experimental results pertaining to fragmentation patterns (symmetric versus asymmetric fission) and fission barriers have been interpreted [5,8] using the framework of the celebrated liquid-droplet model (LDM) of nuclear fission [9], and predictions of fission channels were made using the jellium model [1,10,11].

In this paper we show, by means of a newly developed method [6], that Na_n^{+2} clusters, $4 \leq n \leq 12$, fission into $Na_{n-3}^{+} + Na_3^{+}$ (note the shell closing in the product Na_3^{+} cluster). While fission for $n \leq 6$ is barrierless, that of larger clusters involves barriers, which for $n=8$, 10, and 12 are 0.16, 0.71, and 0.29 eV, respectively. The relatively high barrier for Na_{10}^{+2} portrays a shell-closing effect in the parent cluster. Furthermore, the fission barriers for $n>8$, in the favored channel, exhibit a double-hump shape and the dynamics of the fission process involves a precursor mechanism.

These predictions, which differ from results obtained via jellium model calculations [11(a)] (predicting fission according to $Na_n^{+2} \rightarrow Na_{n-1}^{+} + Na^{+}$ for $n \leq 12$) and those obtained from an adaptation of the LDM (predicting [5(b)] barrierless fission for $n \leq 12$), illustrate the importance of nonjellium and dynamical effects in investigations of charged-cluster fragmentation.

Since the calculational method which we developed is a modification of that described by us recently [6], we limit ourself to pertinent details. Our method combines classical molecular dynamics, or energy minimization, on the Born-Oppenheimer (BO) ground-state potential surface with electronic-structure calculations via the Kohn-Sham (KS) formulation of the local-spin-density (LSD) functional method. The ionic pseudopotentials and exchange-correlation functional used here are those employed previously [6].

Determination of the electronic structure for a given ionic configuration involves the following: (i) The solution of the KS-LSD equations on a spatial Cartesian grid with spacing $\Delta=0.8a_0$. The number of grid points (n_x, n_y,n_z) is determined by requiring that the amplitude of each KS orbital is negligible on the grid surface. This amounts to using a basis of $n_x n_y n_z$ plane waves with maximum energy of 210 eV. (n_x,n_y,n_z) varies from (32,32, 24) for Na_4 to (36,36,64) for the dynamic fission of Na_{12}^{+2}. (ii) The self-consistent solution of the KS equation is accomplished via the subspace iteration method [13] to obtain the eigenfunctions of the effective KS Hamiltonian. The modified Broyden density-mixing scheme [14] is used for accelerated convergence to self-consistency. For nearly degenerate KS eigenvalues, a Fermi function with $k_B T \leq 0.015$ eV is used to determine the occupation numbers [6].

In dynamical simulations, the classical equations of motion were integrated using a fifth-order predictor-corrector algorithm with a time step of 1–5 fs to assure energy conservation. The electronic ground state was redetermined after each classical step. Minimum-energy structures were obtained by a steepest-descent-like method [12], starting from configurations selected from finite-temperature simulations. [Note that the existence of a (local) minimum-energy-configuration implies a barrier for fission.] Barrier heights and shapes were obtained by constrained energy minimization, with the center-of-mass distance, $R_{\text{c.m.-c.m.}}$, between the fragments specified.

TABLE I. Potential energies E_p for Na_n^{+2} ($4 \leq n \leq 12$) clusters, in the minimum-energy configurations [12]. Values marked with an asterisk indicate energies for systems which fragment with no barrier, and are calculated for the minimum energy configuration of Na_n^+. Dissociation energies, $\Delta_m = E(Na_{n-m}^+) + E(Na_m^+) - E(Na_n^{+2})$, for $4 \leq n \leq 12$ ($\Delta_m < 0$ indicates exothermic fragmentation). IV_k and IA_k ($k = 1,2$), the vertical and adiabatic ionization energies for $Na_n \rightarrow Na_n^+$ and $Na_n \rightarrow Na_n^{+2}$, respectively; IV^+ and IA^+, the ionization potentials for $Na_n^+ \rightarrow Na_n^{+2}$. Energies in eV.

	n							
	4	5	6	7	8	9	10	12
E_p	−10.50*	−19.00*	−23.46*	−30.29	−36.95	−43.47	−50.36	−62.83
Δ_1	−2.48	0.10	−1.78	−1.07	−1.08	−0.74	−0.43	−0.26
Δ_2	−2.03	−0.24	−1.70	−1.22	−0.68	−0.82	−0.10	−0.23
Δ_3			−2.50	−1.59	−1.28	−0.87	−0.65	−0.94
Δ_4					−0.85	−0.67	0.10	−0.27
Δ_5							−0.13	−0.44
Δ_6								+0.00
IV_1	4.41	4.33	4.67	4.24	4.62	3.83	4.11	3.93
IA_1	4.38	4.11	4.40	4.07	4.35	3.70	4.04	
IV_2	12.92	12.44	12.94	12.45	12.72	11.40	11.37	10.65
IA_2	10.30*	10.11*	9.80*	11.81	11.61	11.02	10.48	10.28
IV^+	8.40	6.25	7.90	8.01	7.69	7.61	7.09	
IA^+	5.92*	6.01*	5.40*	7.74	7.26	7.32	6.44	

From the energetics of the clusters and of the various fragmentation channels, given in Table I, we observe first that in all cases the energetically favored channel (see Δ) is $Na_n^{+2} \rightarrow Na_{n-3}^+ + Na_3^+$ ($n \leq 12$), i.e., asymmetric fission (except for $n = 6$), in contrast to results obtained from spherical jellium calculations where fragmentation via ejection of Na^+ is favored [11(a)]. Moreover, for many of these clusters the single-ion fission channel is not even the energetically second-best competing channel. Second, the first vertical and adiabatic ionization potentials (IV_1 and IA_1) exhibit an odd-even oscillation [1,2] in the number of particles in the cluster as well as shell-closing effects for systems containing eight electrons. Similar effects are seen for the other ionization energies, though they are complicated by structural changes upon ionization [12]. Finally, for $n > 6$, fission involves energy barriers. The barriers for $n = 8$, 10, and 12 have been determined via constrained minimization to be 0.16, 0.71, and 0.29 eV for the energetically favored channel, and larger barriers were found for the ejection of Na^+ from these clusters (0.43 and 1.03 eV for $n = 8$ and 10, respectively). The barriers for Na_{10}^{+2} are higher because of the closed-shell structure of this parent cluster, an effect that usually has been discussed only in the context of stability (abundance) and ionization potentials [1,2].

The potential energies along the reaction coordinates for the energetically favored channel and for Na^+ ejection, in the case of Na_{10}^{+2}, are shown in Fig. 1. The most interesting feature seen from the figure is the rather unusual shape of the barrier for the favored fission channel (also found for the asymmetric fragmentation of Na_{12}^{+2}). While double-hump barriers have been long discussed in the theory of nuclear fission [15], to our knowledge this is the first time that they have been calculated in the context of asymmetric fission of charged atomic clusters. The existence of the "double-humped" barrier is reflected in the dynamics of the fission process of Na_{10}^{+2} displayed in Fig. 2. This simulation started from a 600-K Na_{10} cluster from which two electrons were removed (requiring 11.23 eV) and additional 0.77 eV was added to the classical ionic kinetic energy. The variation of the center-of-mass distance with time [Fig. 2(a)] exhibits a plateau for $750 \leq t \leq 2000$ fs [see also the behavior of the electronic contribution to the potential energy of the system versus time in Fig. 2(c)]. The contours of the electronic charge density of the system [Figs. 2(d)–2(f)], at selected times, and the corresponding cluster configurations [Figs. 2(g)–2(i)] reveal that the fission process involves a precursor state which undergoes a structural isomerization prior to the eventual separation

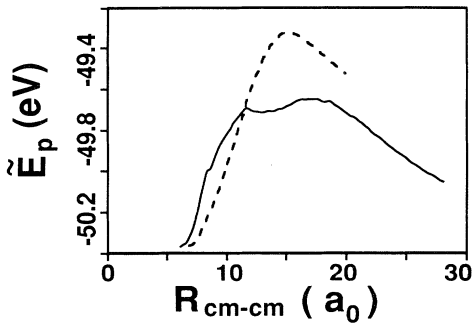

FIG. 1. Potential energy ($\tilde{E}_p$, in eV) vs distance (in a_0) between the centers of mass for the fragmentation of Na_{10}^{+2} into Na_7^+ and Na_3^+ (solid) and Na_9^+ and Na^+ (dashed), obtained via constrained minimization of the LSD ground-state energy of the system.

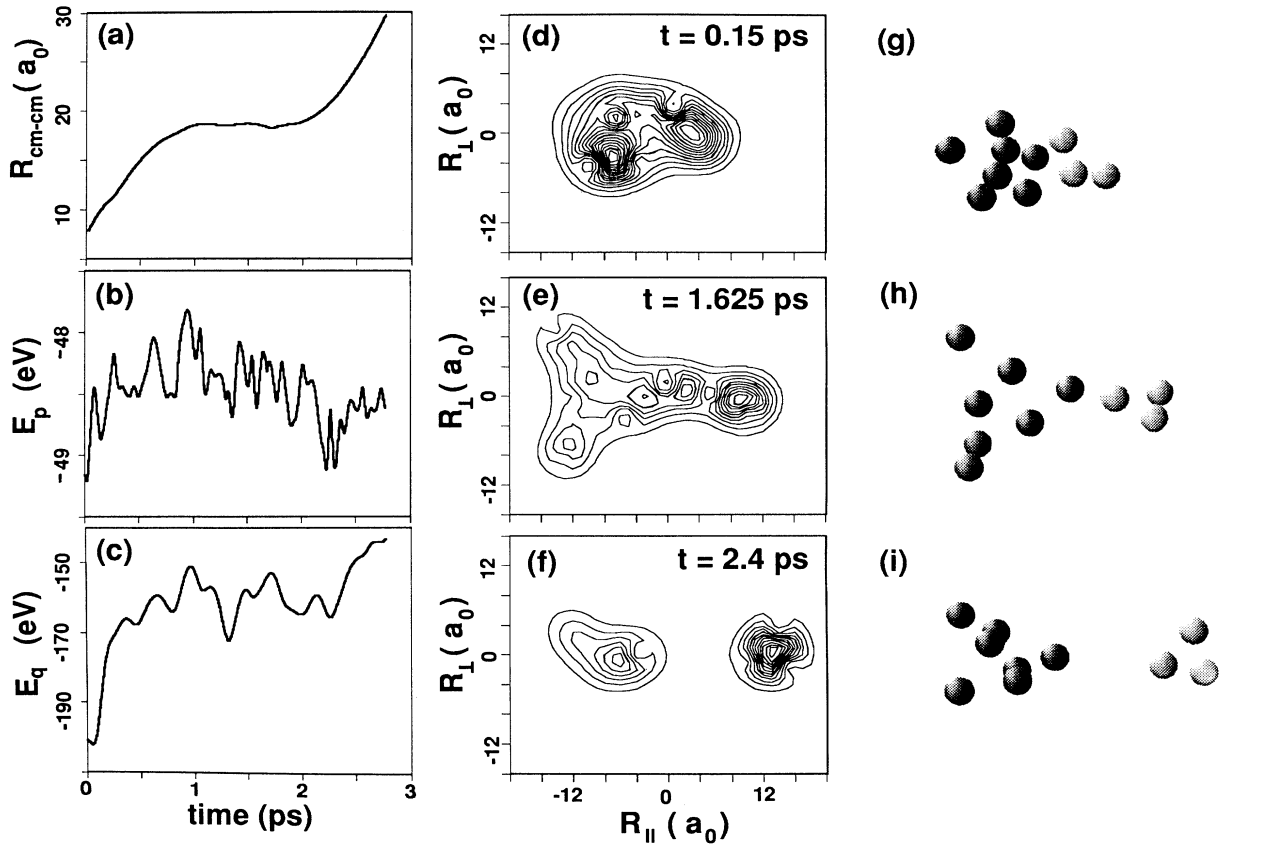

FIG. 2. Fragmentation dynamics of Na_{10}^{+2}. (a)–(c) Center-of-mass distance between the eventual fission products ($R_{c.m.-c.m.}$), total potential energy (E_p), and the electronic contribution (E_q) to E_p, vs time. (d)–(f) Contours of the total electronic charge distribution at selected times calculated in the plane containing the two centers of mass. The $R_\parallel$ axis is parallel to $\mathbf{R}_{c.m.-c.m.}$. (g)–(i) Cluster configurations for the times given in (d)–(f). Dark and light balls represent ions in the large and small fragments, respectively. Energy, distance, and time in units of eV, bohr (a_0), and ps, respectively.

of the Na_7^+ and Na_3^+ fission products. In this context, we remark that examination of the contributions of individual Kohn-Sham orbitals to the total density for the intermediate stage [Fig. 2(e)] reveals that the lowest-energy orbital (s-like) is localized on the Na_7^+ fragment, the next orbital (s-like) is localized on the Na_3^+ fragment, the third is a p-like bonding orbital distributed over the two fragments, and the highest orbital is localized on the larger fragment.

In summary, our prediction of the predominant fragmentation channel, $Na_n^{+2} \rightarrow Na_{n-3}^+ + Na_3^+$ ($4 \leq n \leq 12$), based on constrained-energy minimization and dynamical simulations on the BO potential-energy surface is different from that obtained from jellium calculations. We find that fission for $n > 6$ involves barriers, in contrast to results obtained from adaptation of the LDM to atomic clusters. The shell closing for Na_{10}^{+2} is reflected in the high fission barrier for this cluster. From the fission barrier shapes for the energetically favored channel for $n = 10$ and 12 (but not for the ejection of Na^+, or for $n \leq 8$), as well as from the fission dynamics, we conclude that the fission process involves a precursor mechanism. In addition, energetic data (single and double ionization energies) were calculated, which could assist future experiments.

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