Spontaneous Fragmentation of Multiply Charged Metal Clusters

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Fragmentation channels of metal clusters are studied as functions of their size and charge state by the use of *ab initio* self-consistent theories. Results for geometry-optimized microclusters agree quite well with the jellium model and lend credibility to the latter for the study of Coulomb explosion in multiply charged metal clusters.

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In this Letter we report an analysis of the fragmentation channels as multiply charged metal clusters explode under the influence of electrostatic repulsion. Our results are derived from two differing self-consistent theories. The first one is based upon self-consistent field, linear combination of atomic orbitals, molecular orbitals (SCF-LCAO-MO) method with no approximations for the geometrical structure of the clusters. The second one is based upon the jellium model where clusters are assumed to have spherical geometry with positive charges distributed uniformly inside a sphere. The stability of clusters as a function of size and charge state is studied on the basis of ground-state energetics.

The emergence of atomic clusters as a new state of matter and the promise that studies of these systems can bridge our knowledge between atoms and solids have created considerable excitement[1] in the research community. One of the fundamental questions concerns the stability of these clusters in both neutral and charged states and its dependence on the nature of the chemical bonding. While a lot of work[2-4] has been done on this subject in recent years, no clear picture has emerged concerning the dissociation channels and the charge and mass distribution of fragments as clusters explode when exposed to excessive ionizing radiation. The important questions are as follows: Does fission occur symmetrically? Are the charges shared uniformly by the daughters? How do the positive charges distribute as electrons are stripped from clusters just before the explosion? Does the enhanced stability of certain neutral and singly charged clusters predetermine the dominant fragmentation channel? How does the energy released upon fragmentation compare with the energy used to charge the parent cluster?

In this Letter we answer these questions by analyzing the energetics of neutral, singly, doubly, and triply charged clusters of alkali-metal atoms consisting of up to 40 atoms. We have used two rather distinct but complementary models. The first model is based upon the SCF-LCAO-MO[5,6] method where the atoms constituting the cluster are initially put at random locations. The total energy of this cluster is calculated by our including electrostatic and exchange interactions in the unrestricted Hartree-Fock approximation and correlation contributions involving configuration interaction of all pair excitations. From the energy, the gradient forces at the atomic positions are calculated and the atoms are moved along the path of steepest descent to a new location. The above two steps are repeated until the forces at each atomic site vanish. To avoid local minima in the potential-energy surface, a different initial configuration is chosen and the above processes are repeated. The global minimum thus reached yields the ground-state geometry and total energy of the cluster. The changes in the total energy of the charged clusters are calculated by our stripping one electron at a time and obtaining the total energy of the charged state by keeping the initial geometry unchanged. The argument used for this is that multiply charged clusters may be unstable and may spontaneously decay into smaller species before the atoms in the charged cluster have sufficient time to relax. The reader is referred to a recent paper[5] for details on the calculational procedure.

The second method is based upon the jellium model,[7] where the clusters are assumed to be spheres with the positive charges of the ions distributed uniformly inside the sphere. The total energy of the electrons screening this positive charge distribution,

$$n_+(\mathbf{r}) = n_0\theta(\mathbf{R}-\mathbf{r}), \tag{1}$$

is calculated self-consistently with the use of the density-functional theory in the local-density approximation. Here $n_0 = Z/\Omega_0$ is the positive-ion density of the cluster approximated by the bulk value: Ω_0 is the bulk Wigner-Seitz volume and Z is the ionic valence charge. The radius R of the jellium sphere is related to the number of atoms in the cluster, N, through the relation

$$R = (NZ)^{1/3} r_s, \tag{2}$$

where r_s is the conventional electron-density parameter. While such a jellium model for the cluster appears to be rather crude, it has provided many meaningful results[8,9] and certainly has merit when one considers "large" clusters where the more realistic SCF-LCAO-MO model[5] is all but impossible to apply. While this paper was under consideration for publication, we became aware of the work of Iniguez *et al.*,[10] who applied the jellium model to study the stability of doubly ionized Na and Mg clusters. Our results on doubly charged Li clusters are consistent with their work.[10] Our emphasis here, however, is the comparison between the results of the jellium model and exact geometries for microclusters ($N \le 7$). We clearly show that the shell structure provides the correct picture for multiply charged clusters and can be useful for studying dissociation channels and critical sizes for stabilities of large clusters.

We assume that the energetic considerations are important in determining the preferred decay channel and the charge and size distribution of the fission products. Clearly other factors such as vibronic polarization and temperature could play a role. However, a recent analysis[4] based upon the energetics of a liquid-drop model has quantitatively explained the dissociation channels of $(\mathrm{CO}_2)_N{}^{++}$ clusters. We define the energy released in a fragmentation channel as

$$\Delta E_N^{i+} = E_N^{i+} - \textstyle\sum_{j,m} E_m^{j+}, \qquad 0 \le j \le i, \quad 1 \le m \le N, \tag{3}$$

where E_N^{j+} is the total energy of an N-atom cluster carrying the positive charge j. The parent cluster contains N atoms and i ($i = 0,1,2,3$) positive charges. Charge and mass conservation dictate that $\sum j = 1$ and $\sum m = N$. A positive ΔE in Eq. (3) implies[11] that energy is released and that the fragmentation is spontaneous. A negative ΔE, on the other hand, implies that the parent cluster is stable against that particular dissociation channel and that external energy is necessary should fragmentation be desired along the forbidden path.

In order to answer some of the questions raised earlier and to facilitate the discussions to follow, we plot in Fig. 1 the second derivative of the total energy ($E_{N+1} + E_{N-1} - 2E_N$) obtained from the jellium model as a function of N for clusters corresponding to the density of metallic lithium ($r_s = 3.25$ a.u.) for neutral, singly, doubly, and triply charged clusters. The peaks for $N = 2$, 8, 20, 34 for neutral clusters are all too familiar[7] and result from the electronic shell filling. For charged clusters, these peaks shift for each additional positive charge that is put on the cluster. The reasons are, of course, simple. For example, a 9^+ cluster contains eight electrons that fill s and p shells completely. Thus, for singly charged alkali-metal cluster, 3^+, 9^+, $21^+, \ldots$ are the "new" magic numbers. A similar analysis of the *real* Li clusters obtained from SCF-LCAO-MO calculations also confirms this point. In simple monovalent metals it is thus the number of valence electrons in the cluster which determines the magic number. This has also been observed experimentally[12] for positively and negatively charged noble-metal clusters.

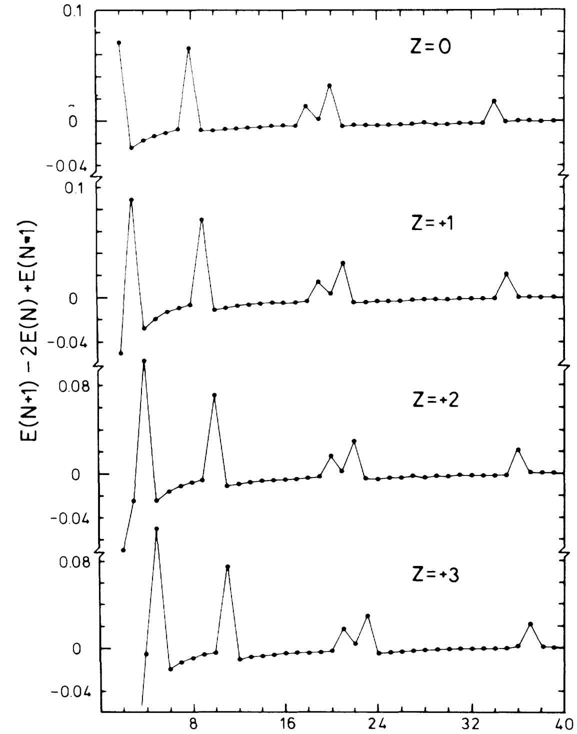

FIG. 1. Second derivative of the total energy ($E_{N+1} + E_{N-1} - 2E_N$) (in Hartree units) as a function of N for Li_N, $\mathrm{Li}_N{}^+$, $\mathrm{Li}_N{}^{2+}$, and $\mathrm{Li}_N{}^{3+}$. The results are based upon the jellium model.

In Fig. 2 we compare the maximum energy released, ΔE, and the dissociation channels between the two models. In all cases, both models predict identical dissociation channel and charge state of the daughter ions (e.g., $7^{+++} \rightarrow 3^+, 3^+, 1^+$). We define this channel as the one for which ΔE is maximum if there is spontaneous fission and ΔE is minimum if the parent clusters are stable against fragmentation and fission has to be induced. Even the agreement between the magnitudes and trends of ΔE's for doubly and triply charged clusters is quite good. For singly charged clusters, however, the agreement is poor: The jellium model predicts spontaneous fragmentation of 5-, 6-, and 7-atom clusters whereas

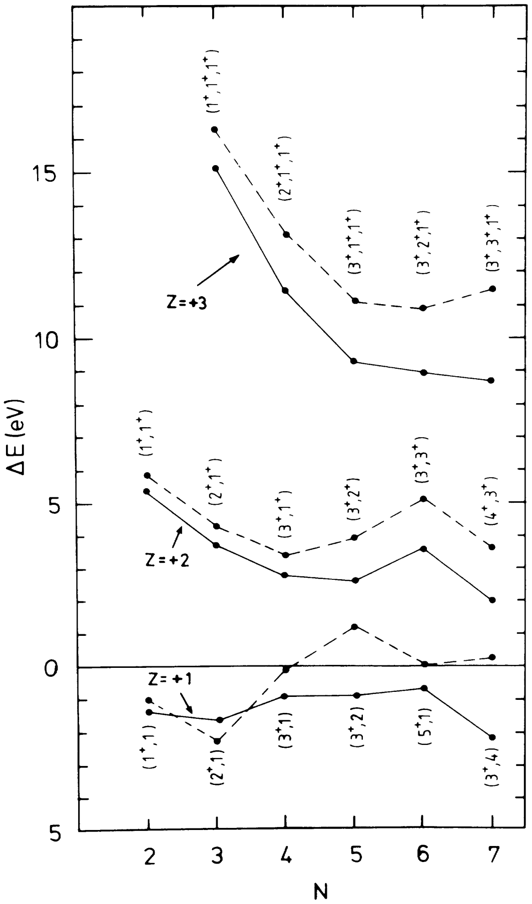

FIG. 2. The energy differences between parent and daughters obtained in the SCF-LCAO-MO (solid curve) and jellium model (dashed curve). The fragmentation products along the energetically most preferable channel in both models are the same and are given in parentheses.

in the *real* model all are stable. This discrepancy arises from the fact that jellium clusters at high densities (low r_s) are intrinsically unstable and the jellium always has a tendency to relax towards its equilibrium electron density (around $r_s = 4$ a.u., "Na"). This is an artifact of the jellium model. It is, however, quite clear that for multiply charged clusters, the jellium model does provide qualitatively the correct trend and correct fragmentation products.

The doubly charged microclusters fragment usually into two unequal pieces with each piece carrying a unit charge. For triply charged clusters, however, there are three fission products, each carrying equal charge. This is in contrast to a recent experiment[4] on $(CO_2)_N{}^{3+}$ clusters where 92% of the mass was carried by doubly charged clusters. The qualitatively different behavior of $Li_N{}^{3+}$ and $(CO_2)_N{}^{3+}$ may arise from the different numbers of total atoms involved in the clusters. Another feature that is also striking in Fig. 2 is that for clusters with $N \geq 4$, the 3^+ cluster is almost always a by-product. Note that in Fig. 1, the 3^+ cluster is a magic-number cluster. To explore this further, we have analyzed the fragmentation products of clusters with up to 40 atoms obtained from the jellium model. We find that for clusters containing $N > 9$, 9^+ is a by-product, and for $N > 21$, 21^+ is also a by-product. Reference to Fig. 1 again reveals that magic numbers are produced in spontaneous fragmentation. This is in agreement with the recent findings of Iniguez *et al.*[10] These results, therefore, provide a unique method for producing and analyzing most stable charged clusters without any ambiguity in experimental conditions.

From the jellium results for $N < 40$ it is difficult to pinpoint the critical size of the clusters beyond which spontaneous fragmentation is *not* possible. For doubly charged clusters, this number is probably more than 50, whereas for triply charged clusters it is much higher. This should be contrasted with Pb clusters[13] where the critical number was found to be 32, 55, and 70 for doubly, triply, and quadruply charged clusters. For weakly bound clusters such as van der Waals clusters, this critical number is much higher. These differences could arise not only as a result of the nature of chemical binding between various clusters, but also as a result of the possible existence of energy barriers against "spontaneous" fragmentation. We also find that the energy release, although tending to decrease with cluster size, is a *nonmonotonic* function of N with minima corresponding to magic numbers for the appropriate charge state. Thus, charged clusters with complete electron-shell filling yield relatively little energy as they explode.

We have also calculated the energy yields for doubly and triply charged microclusters from the SCF-LCAO-MO method. We find that, in agreement with the jellium model, the smallest clusters yield the maximum energy upon fragmentation. This is because a larger cluster with the same charge is more strongly bound than a smaller one. Thus, some of the ionization energy is stored inside the cluster.

We next turn to the last question regarding the distribution of charge in the parent ionized cluster. One can imagine that when ionizing energy is focused on a neutral cluster, holes are created in the delocalized valence-electron states. This causes redistribution of the electron density and the hole density is presumably increased at the surface of the cluster. Electrostatic energy is built up which eventually makes the cluster unstable. Where do the charges actually reside? Do they follow a classical pattern and become localized on individual atoms or are they spread uniformly? As an illustration let us start with a doubly charged dimer. Under the assumption that the positive charges residing on the atom are pointlike, the electrostatic energy (e^2/r) to keep them apart at the neutral dimer distance is 5.44 eV. The energy release in the fragmentation of Li_2^{2+} is 5.4 eV from SCF-LCAO-MO calculation. For a triply charged trimer, the same exercise, putting three point charges at three atom positions corresponding to neutral Li_3 geometry, yields an electrostatic energy of 10.88 eV. The energy yield in the SCF-LCAO-MO study when Li_3^{3+} fragments is 10.85 eV. These remarkable agreements imply that spontaneous fragmentation takes place to release all of the stored electrostatic energy.

The situation becomes more complicated when the number of charges on a cluster is less than the number of atoms in it. Classically, one does not have an *a priori* guideline in distributing them. If one locates them as point charges on atoms most distant from each other, the actual energy yield in the quantum mechanical calculation is less than the stored electrostatic energy. To gain insight into these situations, we have calculated the charge-density contours for doubly and triply charged clusters. We find that the charges are localized around atom centers in triply charged trimers, whereas in doubly charged Li_3 the charges are unequally shared by the atoms as dictated by the geometric configuration.

In conclusion, we have performed self-consistent calculations of the energetics of multiply charged Li clusters containing up to 40 atoms. While fragmentation of singly charged clusters has to be induced, the clusters containing two or more charges fragment spontaneously. For singly charged clusters, it is the largest fragment that carries the charge, while for multiply charged clusters, the charges are equally shared by the daughters. For clusters where the numbers of atoms are equal to the numbers of charges, the charge distribution is localized in the neighborhood of the atomic sites, whereas in other situations it is relatively delocalized and shared by all the atoms in the parent cluster before explosion. The fission products always contain the most stable singly charged cluster[10] (magic number) unless forbidden by the conservation of mass requirement in the fragmentation process. This seems to be a unique method in looking for magic-number clusters.

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