Coulomb fragmentation of doubly ionized molecular clusters

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Using a simple liquid-droplet model, we give a comprehensive description of the process by which doubly charged molecular clusters disintegrate into singly charged fragments. The minimum calculated sizes of stable clusters are in good agreement with experiment. The failure to observe the fragments of doubly charged clusters is also explained, while we claim that triply charged CO_2 clusters fragment by a different thermal process.

When a small cluster (with a size of the order of a few tens of atoms or molecules) is doubly ionized, the Coulomb repulsion between the two positive charges may lead to its fragmentation into two singly charged fragments. The term "Coulomb explosion" has been coined for this process.[1] However, if the cluster is larger than a given critical size the intermolecular forces are sufficient to resist the Coulomb repulsion and the cluster does not fragment. When more than two charges are present in the cluster, the size must be larger for it to be stable. Thus, there are also critical sizes for triply and fourfold ionized clusters, etc. These critical sizes are well defined as sharp onsets in mass spectra of clusters condensed in beam expansions and subsequently ionized by electron impact or otherwise.[1] However, there is some evidence that these critical sizes do not necessarily represent a threshold of absolute stability and that they depend on the formation and ionization mechanisms. Thus, a sharp increase in the concentration of Pb_n^{2+} occurs at $n \approx 30$,[2] but, under certain circumstances,[3] a weak concentration of smaller doubly charged clusters is also observed and even clusters as small as Sb_3^{2+} or Bi_3^{2+} have been observed to form by field evaporation from surfaces.[4] Also, triply charged CO_2 clusters which have survived for a few microseconds, have been observed to fragment in a longer time.[5]

Even so, the well-defined onsets observed in mass spectra of cluster beams present considerable interest, as they reveal the cohesive forces and dynamic properties of very small aggregates of condensed matter, which play an essential role in a number of practical fields, from catalysis[6] to photography.[7] We have presented recently a simple liquid-droplet model which gives very good agreement with the observed critical sizes.[5] The present work is an extension of that model which clarifies further the precise mechanisms by which the clusters fragment.

The simplest and most intuitive model for Coulomb fragmentation is that the cluster fragmentation will occur if the decrease in electrostatic energy is greater than the decrease in binding energy. Since the total volume of the fragments is, approximately, equal to the initial volume, the decrease in binding energy may be best described as an increase in surface energy. Thus, one would expect the critical size to be roughly determined by a balance between the electrostatic energy of a charged sphere of radius R with Z charges ($\approx Z^2e^2/R$) and its surface energy ($\approx \gamma R^2$, where γ is the surface tension). This reasoning gives a relation $R^3 \propto Z^2$ such that the critical number of atoms or molecules n_0^{Z+} is proportional to Z^2. Thus, the predicted critical sizes obey the relation $n_c^{2+}:n_c^{3+}:n_c^{4+}=1:2.25:4$. This relation is in fact very closely confirmed by experiments for most molecular clusters. Although it can be based on very general grounds, it was at first adduced as evidence for symmetric disintegration into equal fragments. However, as long as 100 years ago, Lord Rayleigh[8] developed a theory for Coulomb instability of liquid droplets which also predict the same relation. According to his theory, droplets smaller than a critical size given by $R^3=Z^2e^2/(16\pi\gamma)$ become unstable and emit a jet of smaller charged droplets, in a highly nonsymmetric fragmentation. Rayleigh's qualitative and quantitative predictions were later confirmed by experiments with small but macroscopic droplets. However, when his equation is applied to microscopic doubly, triply, and fourfold ionized clusters, one obtains critical sizes which are smaller than the experimental ones by a factor of approximately 3. In other words, small clusters are more unstable than predicted. This is not very surprising since multiple ionization of neutral clusters surely leaves them in a highly excited state.

Before ionization, the cluster can be assumed spherical. If we assume that two opposite atoms are ionized (which gives the most stable configuration), they will repel each other, stretching the cluster to elongated shape. The inertia of the excited mode will in fact bring the elongation beyond the equilibrium shape, eventually producing the cluster fragmentation. This mechanism for Coulomb fragmentation was proposed by Gay and Berne[9] who performed a molecular-dynamics simulation of the process for Xe_n^{2+}. They also obtained a critical size of $n_c^{2+} \approx 53$, in agreement with experiment, while Rayleigh's number would be $n_c^{2+}=29$. In a macroscopic droplet, the charge is evenly distributed on its surface and there is no preferred direction for elongation. Or, in other words, there is not an initial accumulation of energy concentrated in a particular stretching mode. The same is also partially true for triply and higher ionized clusters.

In the preceding model, the cluster will fragment if the initial repulsion energy in the spherical cluster is larger than the energy barrier for fragmentation. Thus our aim is to calculate this energy barrier with a simple but realistic model. We will use a liquid-droplet model[5] which includes the possibility of cluster shape deformations. The cohesive energy of the cluster is given by a bulk, E_v, and a surface term, E_s:

$$E = E_v + E_s = -bV + \gamma S \ , \tag{1}$$

where b and γ are the energies per unit volume and unit area, respectively. For a charged cluster we have to add the electrostatic energy. This includes the repulsion between the (screened) charges and a polarization term. The latter can be expressed[10] as the interaction between the point charges and the induced surface charge $\sigma(\mathbf{r})$:

$$E_{es} = (1/2\varepsilon) \sum_{\substack{i,j \\ i \neq j}} (e^2/|\mathbf{r}_i - \mathbf{r}_j|) + \tfrac{1}{2} \sum_i \left[\int_s d^2r \, e\sigma(\mathbf{r})/|\mathbf{r} - \mathbf{r}_i| \right] . \tag{2}$$

The approximation of considering the positive charges in an ionized cluster as point charges is justified in molecular clusters because the formation of dimer ions[11] in the cluster produces a rapid localization of the charges (in a few picoseconds). The induced surface charge distribution can be obtained from the total electric field[10]

$$\sigma(\mathbf{r}) = \mathbf{P} \cdot \hat{\mathbf{n}} = \alpha \mathbf{E} \cdot \hat{\mathbf{n}} \ , \tag{3}$$

where $\mathbf{P}$ is the polarization vector, $\hat{\mathbf{n}}$ is a unit vector normal to the surface, and $\alpha = (\varepsilon - 1)/(4\pi\varepsilon)$ is the polarizability. $\mathbf{E}$ is the total electric field which in principle should be calculated self-consistently from $\sigma(\mathbf{r})$. This requires the use of complex Green's-function methods for a cluster of arbitrary shape. But, since we are going to deal with clusters of low dielectric constants the induced surface charge is small and it is reasonable to approximate $\mathbf{E}(\mathbf{r})$ as the electric field created by the point charges only:

$$\mathbf{E}(\mathbf{r}) = \sum_i e^2(\mathbf{r} - \mathbf{r}_i)/(\varepsilon |\mathbf{r} - \mathbf{r}_i|^3) \ . \tag{4}$$

We should keep in mind, however, that this approximation is not acceptable for clusters of polar molecules, with high dielectric constants, such as water and ammonia.

For a doubly charged cluster of a given volume, and for each distance between the two point charges, the total energy [Eqs. (1) and (2)] is a function of cluster shape. We minimize numerically this function, finding the shape of minimum energy. Figure 1 represents the minimized energy for three xenon clusters as a function of distance between charges. For each cluster size there is a critical distance between charges beyond which there is no stable cluster shape and the cluster breaks spontaneously into two pieces when one tries to minimize the energy. There is also a (smaller) distance for which the absolute minimum of the total energy is achieved. Thus, the energy difference between the absolute minimum and the point of fission is the energy barrier of the cluster for fission in two charged fragments. In Fig. 2, we show some of the characteristic shapes (at the points labeled a, b, c, and d in Fig. 1) for a xenon cluster with a volume corresponding to 50 atoms. As one looks at clusters of decreasing size, the point of instability becomes closer to that of minimum energy and the energy barrier for fission decreases. Eventually one achieves a cluster size for which the two points coincide and the energy barrier disappears; clusters smaller than this size are intrinsically unstable. For xenon this critical size is approximately

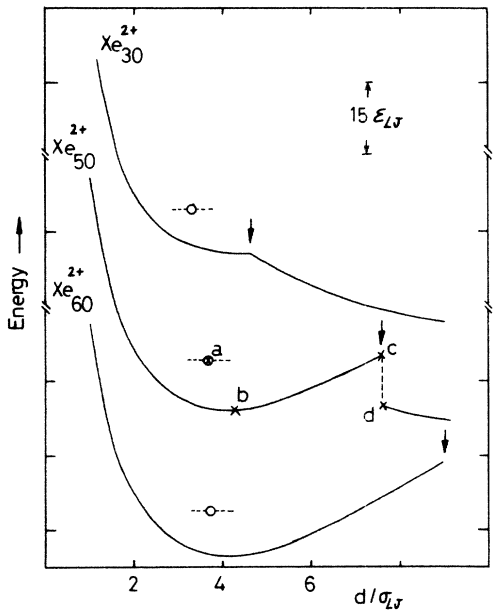

FIG. 1. Minimum energy, as a function of the distance between charges (in Lennard-Jones reduced units, $\varepsilon_{LJ} = 221$ K, $\sigma_{LJ} = 4.1$ Å), for three xenon clusters. The arrows show the critical distance beyond which the cluster breaks spontaneously into two fragments. Open circles represent the minimum energy for the initial spherical shape. The shapes at the points labeled $a \rightarrow d$ are shown in Fig. 2.

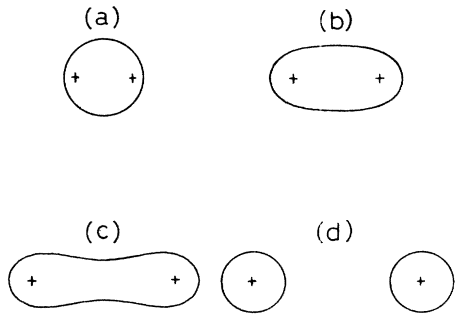

FIG. 2. Shapes of minimum cluster energy of Xe_{50}^{2+} at the corresponding points in Fig. 1. Crosses inside the clusters indicate the locus of the charges (holes). (a) corresponds to the initial spherical cluster just after ionization, with the charges at the position of minimum energy for that shape; (b) represents the shape of absolute minimum energy; (c) shows the critical-distance shape; (d) shows the two fragments just after fission.

equal to 30, in approximate agreement with that obtained with Rayleigh's equation but far from the experimental value of 53.

In Fig. 1 we also show the minimum energy level for a spherical cluster. Since the neutral clusters are expected to be roughly spherical, this is the minimum energy of the cluster immediately after ionization, when the repulsive forces have not yet deformed it. Figure 1 trivially suggests a criterion for cluster fission: If the initial energy after ionization is larger than the fission energy barrier, the repulsion between the two charges will stretch the cluster beyond its maximum stable elongation and it will break. If the initial energy is lower than the barrier, the elongation will bounce back and forth, rapidly dissipating the stretching-mode energy into thermal energy, uniformly shared by all the vibrational degrees of freedom. We have represented in Fig. 3 the minimum initial energy together with the energy barrier for fission as a function of cluster size for xenon. The crossing of the two curves gives the critical size for cluster fragmentation. Below this size, all clusters have an initial energy larger than the energy barrier for fission and therefore we will not expect to find any doubly charged cluster below this size in the mass spectra of ionized clusters. Above this size, most of the clusters will have an initial energy smaller than the energy barrier for fission and they will not fragment. The values obtained for the critical sizes of Xe, CO_2, and Ar doubly charged clusters are 49, 45, and 95, respectively, which compare very well with the experimental ones (53, 44, and 91, respectively[1,12,13]). In particular, the critical size for Ar is in much better agreement with experiment than the previously calculated[5] size of 121, using a simpler spherical-droplet model for Coulomb fragmentation. For Xe and CO_2 the agreement is similar. However, in the simpler model, the surface tension for CO_2 was obtained from an intermolecular interaction parameter smaller than usual[5] while in this work the standard value is used. This means that the simpler model,[5] although with a considerable predictive power (it predicts the critical sizes of about 20 doubly, triply, and fourfold charged molecular clusters with an error of less than 10%[14]), also lacks some important details of the fission mechanism which in some cases may lead to errors in the critical sizes of up to 30%. The present calculations are thus much more reliable, although also much more involved.

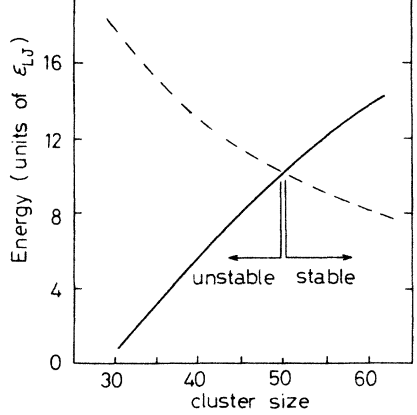

FIG. 3. Calculated energy barrier for fission (solid line) for doubly charged xenon clusters, as a function of cluster size. The minimum initial energy is also shown (dashed line). The crossing of the two curves gives the critical size for cluster fragmentation.

Another issue of considerable interest is the relative size of the fragments of the fission. If we increase slowly the distance between charges, finding at each distance the shape of minimum energy, as in Figs. 1 and 2, the cluster finally splits into two equal fragments for all initial sizes. However, if one minimizes the final energy of the two fragments, as a function of their relative size (but keeping the total volume constant), the result depends on the initial size; for small initial cluster sizes, the minimum final energy corresponds to two equal fragments, but beyond a given initial size (generally smaller than the critical size for fragmentation previously obtained) the preferred final state is nonsymmetric, with one fragment much larger than the other. Furthermore, the absolute size of the smaller fragment decreases with increasing initial size. Also, the simulation of Gay and Berne for Xe_{51}^{2+} resulted in a rather nonsymmetric fission, with the smaller fragment holding only one-third of the initial atoms. The solution of this apparent paradox lies with the fact that we have calculated "minimum energy" shapes for every distance between charges, while the true barrier should rather be a "saddle point" in the configuration space of cluster shapes.

To deal with this problem we have developed another computational technique, consisting in the solution of the Euler differential equation associated with the minimization of the total energy E as a function of cluster shape $z(x,y)$. For a given volume and distance between charges, the cluster shape $z(x,y)$ is given by the solution of

$$\delta E = 0 = \delta[E_s(z(x,y)) + E_{es}(z(x,y))] \ . \tag{5}$$

The saddle-point configurations (shapes) can be found with this technique because the solution to the Euler equation, associated to this variational equation, requires only that the first-order derivatives with respect to changes in shape be zero. For a given volume and distance between charges we find, in addition to the previously found shape of minimum energy, one or two other stationary solutions to Eq. (5), with higher total energy. One of the solutions gives a symmetric shape and the other, when it exists, is nonsymmetric and has a lower energy than the symmetric one. The extra solutions are in fact saddle points and not local minima because they are unstable with respect to small changes in shape; a steepest-descent minimization from them leads either to the minimum energy solution or to fission into two, equal or unequal, fragments, for the symmetric and nonsymmetric solutions, respectively. Two of these saddle-point shapes for xenon clusters are shown in Fig. 4(a) as well as some of the energy barriers in Fig. 4(b). Notice that for the critical cluster size, about Xe_{50}^{2+}, the nonsymmetric barrier is only slightly lower than the symmetric one. Thus, although the minimum barrier fragmentation leads

to very unequal fragment sizes (with ~85% and ~15% of the mass), in practice one should expect nearly any possible relative distribution of sizes. In particular, the relative fragment size found by Gay and Berne[9] for Xe_{50}^{2+} is entirely compatible with our results. Also, the distance between charges at the time of fission[9] ($\approx$29 Å) is also very similar to the distance for which we find the minimum barrier (25 Å, Fig. 5).

In Fig. 5 we present the energy of the nonsymmetric saddle-point configuration for Xe_{50}^{2+}, together with the minimum energy configuration for the unbroken cluster and the energy of the fragmented state (solid lines). Notice that to go from the unfragmented to the fragmented states, the cluster must deform and, in doing so, pass through the barrier indicated by the dashed line. Notice also that the minimum barrier for fission (point *A* in Fig. 5) is lower than that obtained by slowly stretching the cluster by separating the two charges (point *B*). The difference, however, is rather small. Thus, if we calculate the critical cluster size for Xe_n^{2+} by using the energy barriers given by points *A* rather than *B*, in Fig. 5, we find a value of 52 instead of 49. Thus, the previously reported critical sizes are barely affected by this difference, although the relative sizes of the fragments are.

An unfortunate fact is that the experiments will not likely be able to confirm the predicted fragments sizes nor, in fact, to observe them. According to the molecular-dynamics simulation[9] the fragmentation takes place in approximately 100 ps after ionization. Since the minimum time required to separate a given cluster size from others is approximately 1 μs with available experimental techniques, the fragments cannot in practice be distinguished from singly ionized clusters and the only trace of the fission remaining in the mass spectrum is the absence of doubly charged clusters up to the critical size. Product ions, resulting from the fission of triply charged clusters have been observed, however. To be observed, these fissions must occur several microseconds after ionization, rather than in hundreds of picoseconds. In fact, one of the most striking differences between the doubly and triply ionized clusters is the absence of "delayed" fissions in the first.

To be precise, what we have described up to this point is the process of "immediate" or "direct" Coulomb fragmentation. We have calculated the critical size for the occurrence of the process by comparing the fission barrier with what we have called (somewhat loosely) the "initial energy" available immediately after ionization. In fact, the formation of a dimer ion in the cluster,[15] subsequent to its ionization, gives rise to an excitation energy[11] which is orders of magnitude larger than the energy in-

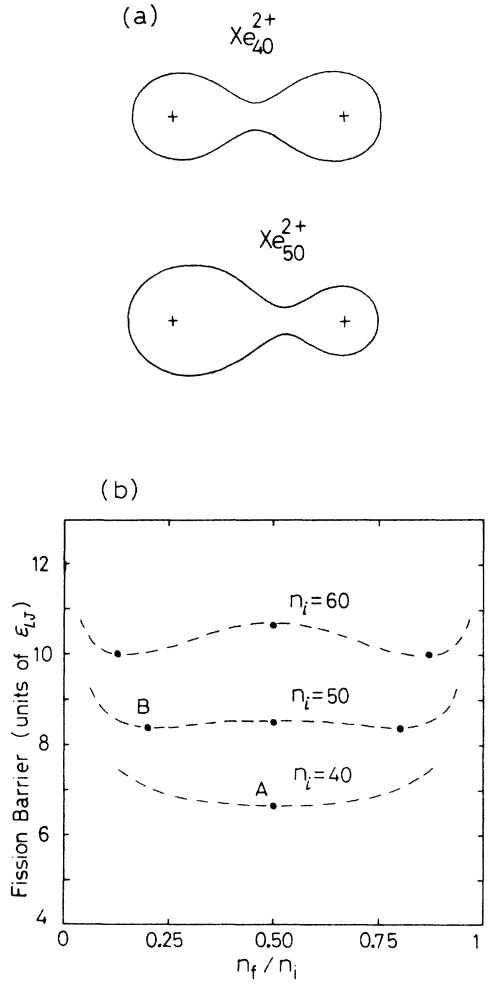

FIG. 4. (a) Saddle-point shapes at the minimum fission barrier for two Xe clusters; nonsymmetric fission is obtained for cluster sizes $n > \approx 40$. (b) Fission barriers, for different cluster sizes, as a function of fragment size n_f, for different initial cluster sizes. Points *A* and *B* refer to shapes shown in (a).

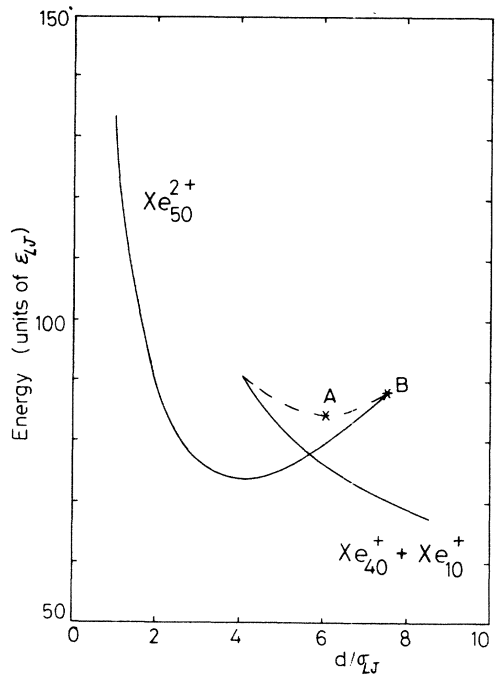

FIG. 5. Energy scheme for the typical reaction $Xe_{50}^{2+} \rightarrow Xe_{40}^{+} + Xe_{10}^{+}$. Solid lines show the energy for the unbroken, Xe_{50}^{2+} (left), and the fragmented state, $Xe_{40}^{+} + Xe_{10}^{+}$ (right), as a function of the charge separation. Dashed line shows the (saddle points) fission barrier, i.e., the pathway from one state to the other.

duced by the relaxation of the cluster shape (which is the initial energy considered previously). However, the ignored energy is initially localized in the dimer ions (pairs of atoms which share a positive charge, reacting strongly) and spreads later (in approximately 500 ps) through the cluster homogeneously, in the form of thermal excitation.[11] Therefore, it adds little to the stretching mode excitation which produces the immediate fission (in approximately 100 ps) as described by the molecular dynamics simulation.[9]

On the other hand, the large amount of thermal excitation might be expected to produce a delayed fission in a much later time, compatible with its experimental observation. In fact, molecular-dynamics simulations with singly ionized clusters[11] show abundant evaporations of neutral monomers subsequent to the cluster ionization. In a doubly charged cluster, thermal excitation may also produce evaporation of neutral monomers but also its fission into two singly charged fragments. Which of the two processes will occur is determined by which of the energy barriers is lower. For Xe, the evaporation barrier is approximately 0.1 eV while the fission barriers for larger than critical clusters is approximately 0.15 eV (see Fig. 3). Since the probability for one process is proportional to $\exp(-\Phi/kT)$, (with Φ the energy barrier) and $kT \ll \Phi$, a difference of 50% in energy barriers makes an enormous difference in probability of the two processes. Therefore, it is extremely unlikely that a xenon cluster larger than the critical size will disintegrate into two charged fragments by thermal excitation. Instead, it will get rid of the thermal energy by a sufficient number of evaporations, until it becomes cold enough to be stable.[11] For smaller clusters the barrier for fission in charged fragments becomes smaller (see Fig. 3) than that of evaporations but this is irrelevant because these clusters have already been exploited by the immediate process. For Ar and CO_2 clusters we obtain the same results.

There remains the problem of the difference between doubly and triply charged clusters of CO_2. The lower symmetry of triply charged clusters has not permitted us, up to now, to extend our calculations for the energy barriers of these clusters. However, we expect that in this case the critical size is not determined by the "direct" or "immediate" fission but rather by the "delayed" or "thermal" one. That is, we expect that the critical size will be that for which the energy barriers for evaporation of neutral monomers will be roughly equal to that for fission in charged fragments. The absence in this case of the immediate fission process is reasonable if we think of the likely dynamics of the events immediately after ionization: If the three charges are initially in an equilateral triangle (minimum energy configuration) they will repel simultaneously outwards, while the most favorable pathway to fission would preferably be that two of the charges approach each other while the other one moves outwards.

In conclusion, we have tried to give a thorough view of the process of Coulomb fragmentation in molecular clusters which explains comprehensively the phenomenology of the experimental observations. The agreement between the calculated and experimental critical sizes is also very good. Although an extension of the computational techniques will be necessary to deal with some cases (notably polar molecules and triply and fourfold charged clusters), there are simple and reasonable arguments to explain the phenomenology also in these cases. Finally, we think that the Coulomb fragmentation of molecular clusters may be already considered as a reasonably well understood phenomenon. The same cannot be said about metal clusters,[2,3] and we think that this is a notable challenge in the near future of cluster research.

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