Evidence for Coulomb Explosion of Doubly Charged Microclusters

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(Received 26 March 1981)

Mass spectra of Pb, NaI, and Xe microclusters show that below a critical number of atoms per cluster, n^{**}, doubly charged particles are not stable. These numbers are 30 for Pb_n, 20 for $(NaI)_n$ and 52 for Xe_n. The two positive charges generated at one atom by electron bombardment are likely to move to opposite sides of the cluster which then explodes into singly charged fragments as long as the Coulomb repulsion energy is greater than the binding energy.

PACS numbers: 34.90.+q, 35.20.Gs

Most doubly ionized molecules are not stable because the Coulomb repulsion energy between the two positive holes exceeds the molecular binding energy. Only a few highly bound covalent molecules have been found, for example $(HCl)^{2+}$, $(HBr)^{2+}$, $(HI)^{2+}$, $(N_2)^{2+}$, $(O_2)^{2+}$, $(NO)^{2+}$, $(CO)^{2+}$, $(CO_2)^{2+}$, and $(NH_3)^{2+}$,[1] whose lifetimes may depend on the ionization method (low-energy electron impact or x-ray absorption).[2] Energy distribution and kinetics of the dissociation products after a Coulomb explosion have been determined by mass spectrometry considering the ionization cross section in the threshold region[3] and by collision experiments of fast molecular ions with solid targets[4] or molecules.[5]

We report the first evidence for Coulomb explosion of microclusters. Only if the particle size exceeds a critical value, doubly charged clusters are stable. This is found for particles with different kinds of bonding: metal clusters (Pb_n), ionic clusters [$(NaI)_n$], and van der Waals clusters (Xe_n).

The condensation occurs by cooling and supersaturation of an atomic gas or vapor. The metallic and ionic particles are generated by inert gas condensation[6] whereby thermal energy is transferred to a cold inert gas. Growth to xenon particles is achieved by expanding the gas under high pressure through a nozzle into vacuum.[7] The mass analysis is performed by electronic time-of-flight spectrometry, including electron impact ionization.[8]

For an ionizing energy of $E_i = 70$ eV we measured the cross-section ratio for double to single ionization of Pb atoms to be $\tilde{\alpha}_{Pb} = 12\%$. A cluster can be doubly charged by removal of two electrons from a single atom or from two different atoms. In the first case we would expect the same $\tilde{\alpha}$ as for the free atom because the energy of the ionizing electrons is high compared to the threshold energy. The existence of the second process would even enlarge the effective $\tilde{\alpha}$. Each mass peak M_n^+ of single ionized clusters therefore should be accompanied by a corresponding M_n^{++} peak.

In the mass spectrometer these doubly charged clusters M_n^{++} are expected at an apparent mass $\frac{1}{2}M_n$. Pb_{13}^{++} for example should appear between Pb_6^+ and Pb_7^+, for $E_i = 70$ eV with an abundance compared to Pb_{13}^+ of at least 12%.

Figure 1(a), however, shows that the low-mass range of the Pb spectrum is free of Pb_n^{++} peaks. Only if n exceeds a critical value $n_{Pb}^{**} = 30$, doubly charged Pb clusters are detected.

The cross section for double ionization decreases considerably if E_i is lowered to values near the threshold energy. For $E_i = 35$ eV we measured $\tilde{\alpha}_{Pb} = 2\%$. Consequently all Pb_n^{++} peaks have disappeared from the mass spectrum [Fig. 1(b)].

The absence of doubly charged particles below $n < 30$ may have two reasons:

(i) Dissociation into Pb^{++} atoms and neutral clusters Pb_{n-1}. This case can be excluded because the measured Pb^{++} intensity is too low ($< 6\%$ compared to the Pb^+ intensity).

(ii) The two positive holes, originally localized at *one* single atom, begin to oscillate along the surface region and come to rest at opposite sides of the particle after having dissipated their motional energy. The relaxation time of the defect electrons is expected to be small compared to the time for the atomic rearrangement. If the repulsive Coulomb energy E_C of the two separated holes exceeds the binding energy of the cluster atoms, E_B, the particle breaks to singly charged pieces. Only if the diameter of the cluster exceeds a critical value, the condition $E_C < E_B$ is fulfilled and doubly charged clusters are stable.

For a 30-atom Pb particle the repulsive energy of two point charges in 12 Å distance (assumed diameter of Pb_{30}, calculated from bulk data) is

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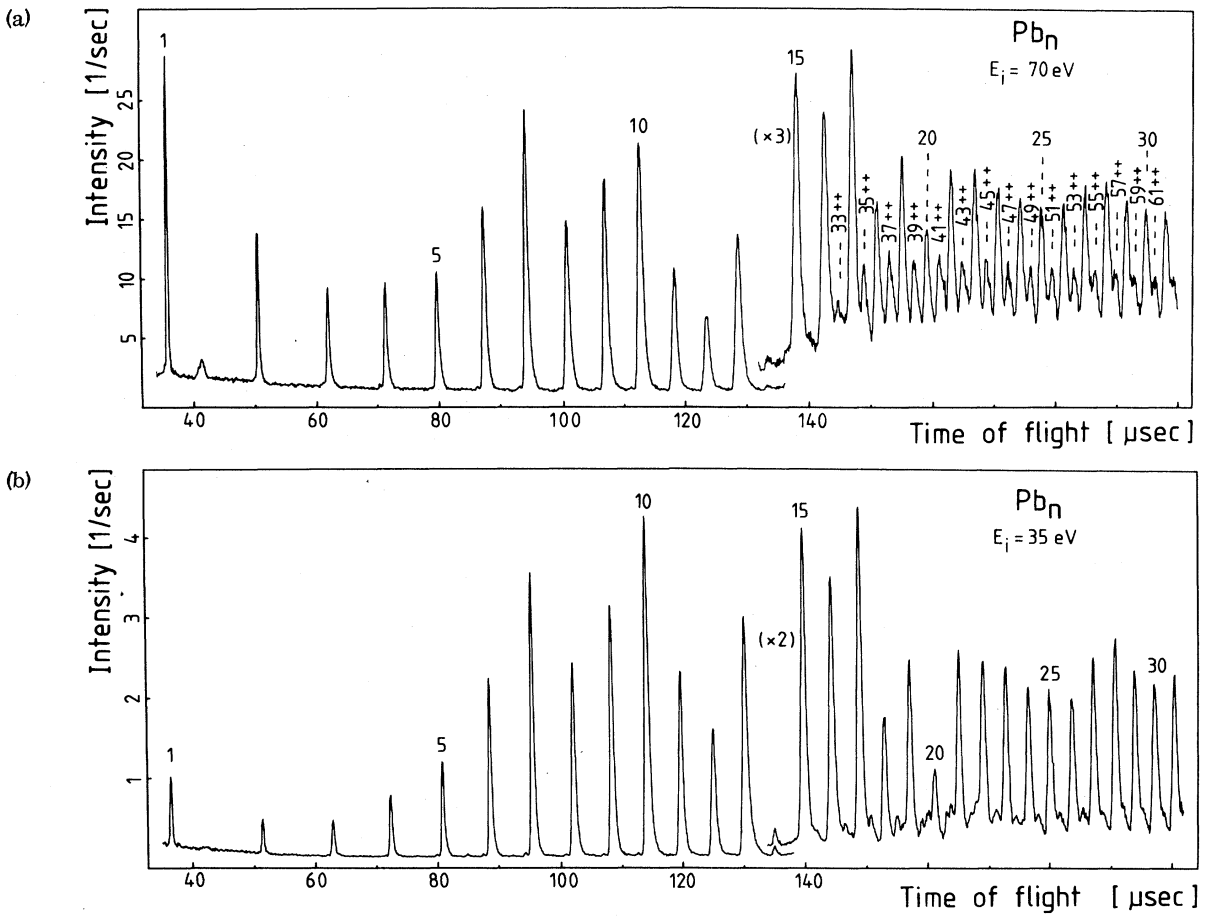

FIG. 1. (a) Mass spectrum of Pb clusters (electron ionizing energy E_i = 70 eV). (b) Mass spectrum of Pb clusters; E_i = 35 eV.

E_C = 1.2 eV which lies in the range of the binding energy of a surface atom to the cluster, taking into account that E_B per bonding is between 0.3 eV (bulk) and 0.8 eV (determined up to Pb_4)[9] and that the minimal coordination number is 3.

The $\tilde{\alpha}$ values have been determined from the Knudsen spectrum without inert gas applied. In the cluster spectrum however a Pb_1^{++} peak does not exist. All Pb atoms have been condensed to agglomerates and the Pb_1^{+} peak is completely caused by fragmentation events in the ionization process. At present it is open to question if these fragments are split off from singly or doubly ionized parent particles.

As for metallic particles we also obtained evidence of Coulomb explosion and critical sizes for ionic clusters $(NaI)_n$, (Fig. 2) and for van der Waals clusters Xe_n (Fig. 3). The critical numbers are $n_{NaI}^{**} = 20$ and $n_{Xe}^{**} = 52$. The value $\tilde{\alpha}_{(NaI)_1}$ is nonexistent because $(NaI)_1^{++}$ is unstable. For xenon, ionized by 50-eV electrons, $\tilde{\alpha}_{Xe} = 10\%$ is obtained, in agreement to the cluster spectrum (Fig. 3). The structure of the spectra as well as fragmentation events after single ionization will be discussed elsewhere.

The binding energy of Xe clusters is expected to be much smaller than for Pb and NaI, explaining qualitatively the higher value of n^{**}. However, the energy per bond in the clusters which may lie between 1.4×10^{-2} eV for solid xenon and 3.0×10^{-2} eV for[10] Xe_2 is too small to explain n_{Xe}^{**}. Yet, because of positive charge depletion at the surface arising from the high degree of correlation between the positions of the holes it is likely that, compared to neutral xenon clusters, the surface region of Xe_n^{++} is bound stronger.[11]

In general it is questionable whether the type of bonding is the same for the solid and the microcluster. Neutral metallic and ionic clusters and

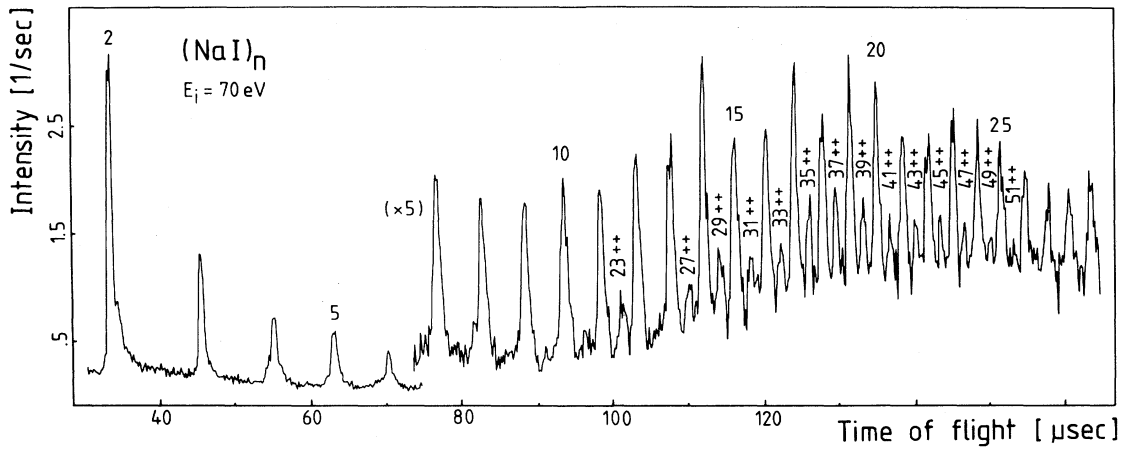

FIG. 2. Mass spectrum of NaI clusters; E_i = 70 eV. Fragmentation after electron bombardment effects that $(Na_nI_{n-1})^+$ and $(Na_nI_{n-2})^{2+}$ particles are detected.

charged van der Waals dimers exhibit reduced atomic distances.[10,12,13] Consequently, cluster matter may be similar to highly compressed solid-state matter, which differs considerably from normal matter.[14,15]

A calculation of the total energy of doubly charged atomic clusters should be based on refined considerations. The electrostatic repulsion of the holes is influenced by atomic, electronic, and vibronic polarization effects of the medium in between. If we assume the holes to be localized, then a redistribution of the electrons of the cluster will occur. As a consequence there is a charge transfer of electrons from the center to the surface, leading to a region with net positive charge in the center. The generation of such a "frozen" plasmon costs a high amount of interelectronic Coulomb repulsion energy. This is compensated by a movement of the positive ions in response to the new negative charge density distribution, which lowers the total energy. Consequently a blowup of the structural configuration of the particles should occur.

The determination of the critical numbers requires the knowledge of the dielectric data of the cluster media, which are not available at present. A continuum model seems to be adequate, because the observations are made for cluster

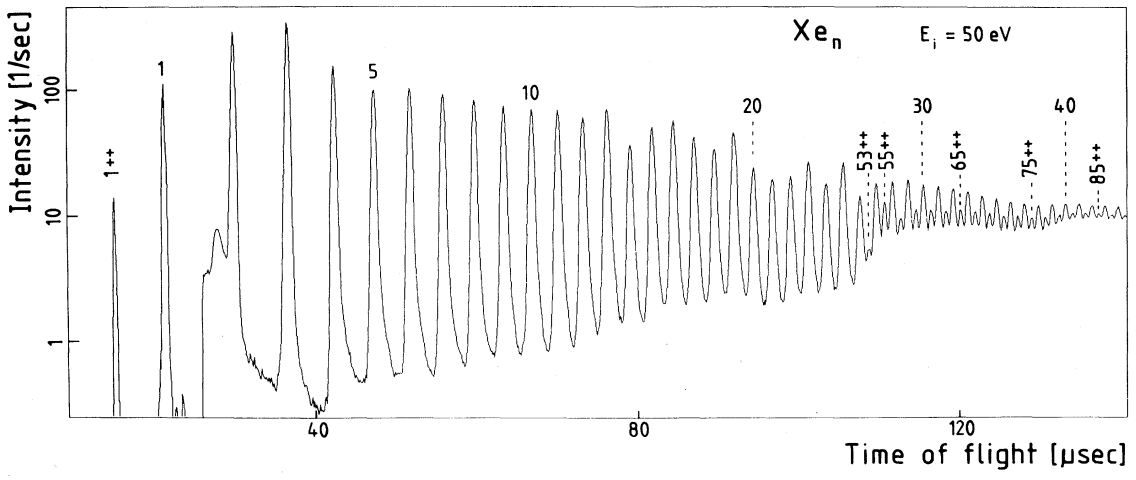

FIG. 3. Mass spectrum of Xe clusters; E_i = 50 eV. The intensities of Xe_1^+ and Xe_1^{++} have been electronically reduced.

matter with different binding character which suggests a similar behavior with regard to propagation and relaxation of defect charges as well as to the subsequent explosion.

This work was partly supported by the Deutsche Forschungsgemeinschaft.

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Exact Closed-Form Solution of the Generalized Debye-Smoluchowski Equation

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(Received 9 April 1981)

The first exact solution of the time-dependent Debye-Smoluchowski equation for diffusional drift under a general interaction in the presence of a reactive sink is presented. Associated time-dependent rates of chemical reactions in a dense gas are formulated and display the basic physical transition from reaction control to transport control as time progresses for a system initially in Boltzmann equilibrium.

PACS numbers: 34.10.+x, 51.10.+y, 82.30.-b, 87.15.-v

The number density $n^-(R,t)$ at time t of some species A (e.g., negative ions) drifting under interaction $V(R)$ across a sphere of radius R towards a central species B (positive ion) in a gas Z (or liquid) under the action of a reactive spherical sink of extent S from B is governed by the generalized Debye-Smoluchowski equation,

$$-\frac{dn^-(R,t)}{dt}=-\frac{\partial n^-(R,t)}{\partial t}+R^{-2}\frac{\partial}{\partial R}[R^2 j(R,t)]$$
$$=\Gamma_3 n^-(R,t)\,\delta(R-S). \qquad (1)$$

Here Γ_3 is the speed of reaction (via ion-pair–gas collisions) for ions after being brought to S by the net inward diffusional-drift current,

$$j(R,t)=D\exp\left(\frac{-V}{kT}\right)\frac{\partial}{\partial R}\left[n(R,t)\exp\left(\frac{V}{kT}\right)\right], \qquad (2)$$

in terms of the diffusion coefficient D ($\mathrm{cm^2\ s^{-1}}$) for relative diffusion of A and B in Z.

The number density N_i of all ion pairs AB with internal separation $R \geq S$ then decays at a rate,

$$-\frac{dN_i}{dt}=-\frac{d}{dt}\int_S^\infty 4\pi R^2 N^+ n^-(R,t)\,dR$$
$$=-\frac{\partial N_i}{\partial t}+N^+[F_\infty-4\pi S^2 j(S-\epsilon,t)]$$
$$=4\pi S^2\Gamma_3 n^-(S,t)N^+=\alpha(t)N^+N^-, \qquad (3)$$

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