straightforward to scan the microwave frequency at a fixed ΔW. In fact, one can easily imagine raising the power and observing the absorption of two microwave photons during the collisions.

In conclusion, we have observed microwave-assisted collisional energy transfer between two colliding Na atoms. The observed collisional resonances are continuously tunable in energy defect ΔW, and the cross sections are 10^{+5} times larger than the largest analogous cross sections for the laser-assisted collisions. The low power requirements of such collisions open a way to investigate systematically such radiatively assisted collisions.

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Computer Simulation of Coulomb Explosions in Doubly Charged Xe Microclusters

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In recent experiments on doubly charged microclusters of Xe, no Xe_n^{++} clusters were observed for n less than 53 atoms. Computer simulations of microclusters have been carried out in which the Xe atoms interact via Lennard-Jones pair potentials and a point polarizability-dipole electrostatic model. From these simulations, it is inferred that Xe_{51}^{++} clusters have lifetimes ~100 ps while Xe_{55}^{++} clusters have lifetimes ~10 μs in agreement with the experimental result that 55-atom clusters are much more stable.

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In a recent paper, Sattler *et al.*[1] have investigated the stability of charged microclusters. A polydisperse "molecular beam" of clusters of Xe, among other species, was bombarded with a low-intensity beam of electrons of sufficient energy to produce Xe^+ and Xe^{++} clusters, which were then detected by mass spectrometry. No Xe_n^{++} clusters were observed for n less than 53 atoms. The absence of small doubly charged clusters implies that Xe_n^{++} clusters consist of two Xe^+

ions and $n-2$ Xe atoms, since a cluster consisting of one Xe^{++} and $n-1$ Xe atoms will always be stable as a result of solvation. Sattler *et al.*[1] state that electron impact produces either $Xe^{++}(Xe)_{n-1}$ by direct inelastic scattering or $(Xe^{+})_2(Xe)_{n-2}$ by secondary scattering, with Xe^{++}-$(Xe)_{n-1}$ subsequently decaying to $(Xe^{+})_2(Xe)_{n-2}$. In either case, they presume that the two Xe^{+} ions are initially in close proximity, and suggest that there is rapid charge transport by electron-hole recombination leading to the migration of the positive charges to opposite sides of the cluster, giving $Xe^{+}(Xe)_{n-2}Xe^{+}$. They then propose that the cluster will be stable or unstable as the repulsive energy is smaller or larger than the binding energy of the cluster atoms.

This explanation ignores the temperature or kinetic energy of the clusters which is an important factor. Let us examine the two different mechanisms for the production of doubly charged clusters. Consider first that the formation of $Xe^{+}(Xe)_{n-2}Xe^{+}$ proceeds by

$$\underset{\text{(a)}}{(Xe)_n} \xrightarrow[\text{impact}]{\text{electron}} \underset{\text{(b)}}{Xe^{++}(Xe)_{n-1}} \rightarrow \underset{\text{(c)}}{Xe^{+}Xe^{+}(Xe)_{n-2}} \rightarrow \underset{\text{(d)}}{Xe^{+}(Xe)_{n-2}Xe^{+}}. \tag{1}$$

The ionization potentials for Xe are 12.08 eV ($Xe \rightarrow Xe^{+}$) and 21.1 eV ($Xe^{+} \rightarrow Xe^{++}$).[2] The energy change in the reaction (b) → (d) is

$$\Delta E = -9.02 \text{ eV} + e^2/r + \Delta E_{\text{solv}}, \tag{2}$$

where r is the separation between the two ions in (d) and ΔE_{solv} represents the change in the solvation energy; that is, $E_{\text{solv}}(Xe^{+}\ldots Xe^{+}) - E_{\text{solv}}(Xe^{++})$. We estimate the energy change of Eq. (2) to be about 6 eV and so the mechanism of Eq. (1) is highly exoergic. If it is assumed that this energy is equipartitioned among the atoms, the increase in temperature of the cluster will be $2\Delta E/3nk_B$ where k_B is Boltzmann's constant. For $n=79$, the temperature increase is 350 K: over twice the triple-point temperature of Xe. Using simulation techniques described below, we have found that an initially cold Xe_{79}^{++} cluster subjected to this temperature rise immediately breaks up into singly charged fragments.

In the second mechanism,

$$\underset{\text{(a)}}{(Xe)_n} \xrightarrow[\text{impact}]{\text{electron}} \underset{\text{(b)}}{Xe^{+}Xe_m\overbrace{Xe^{+}Xe_{n-m-2}}^{r_i}} \rightarrow \underset{\text{(c)}}{Xe^{+}(Xe)_{n-2}\overbrace{Xe^{+}}^{r}}. \tag{3}$$

The energy change corresponding to the reaction (b) → (c) is

$$\Delta E = [e^2 r - e^2/r_i] + [\overbrace{E_{\text{solv}}(Xe^{+}\ldots Xe^{+})}^{r} - \overbrace{E_{\text{solv}}(Xe^{+}\ldots Xe^{+})}^{r_i}], \tag{4}$$

where r_i and r are the initial and final separations between the two Xe^{+} ions. Now the exoergicity is much smaller, so that the temperature rise need not be great enough to lead to fracture of the cluster. Moreover, the electron mean free path between ionizations in Xe, estimated from scattering data,[3] is such that the diameter of Xe_{53} is on the order of two mean free paths. Thus, it is possible that the ionization process produces configuration (c) of Eq. (3) directly without any initial temperature rise at all. These considerations lead us to believe that the mechanism of Eq. (3) is responsible for the formation of doubly charged clusters. We cannot, however, exclude the possibility that the energy of Eq. (2) is carried off in some manner, e.g., by radiative charge transfer and/or by evaporation of neutral atoms from a larger doubly charged parent.

We investigate the dynamics of Coulomb explosions of Xe microclusters assuming the mechanism of Eq. (3). We study n-atom clusters consisting of $n-2$ neutral atoms and two singly ionized atoms. All atoms interact pairwise through Lennard-Jones (LJ) 6-12 potentials with the parameters of Xe: $\sigma = 4.1$ Å, and $\epsilon/k_B = 222.3$ K.[4] We employ reduced units of σ for length, ϵ for energy, and $(m\sigma^2/\epsilon)^{1/2} = 2.76$ ps for time where m is the atomic mass of Xe. In addition, each atom is given the point polarizability of Xe, $\alpha = 4.11$ Å^3.[5] Thus, the Xe^{+} ions are distinguished from the Xe atoms only by the fact that they are charged. The potential energy of a given configuration is calculated as follows:

$$V(\vec{r}_1\ldots\vec{r}_N) = \sum_{i>j}[V(r_{ij}) + z_i z_j e^2/r_{ij}] - \tfrac{1}{2}\sum_i \vec{\mu}_i^{(\text{ind})} \cdot \vec{E}_i^{(\text{Coul})}, \tag{5}$$

where $\sum_{i>j}V(r_{ij})$ is the sum of all LJ pair potentials, $(\vec{r}_i,\vec{r}_j)$ and (z_i,z_j) are the positions and charges of the atoms labeled i and j (when an atom i is neutral $z_i=0$), r_{ij} is the pair separation of the charges, $\vec{\mu}_i^{(\mathrm{ind})}$ is the induced dipole moment of atom i, and $\vec{E}^{(\mathrm{Coul})}$ is the electric field at atom i due to the charges only. Note that[6]

$$\vec{\mu}_i^{(\mathrm{ind})}=\alpha\vec{E}_i, \tag{6}$$

$$\vec{E}_i=-\sum_j\vec{Q}_{ij}q_j-\sum_j\vec{\vec{T}}_{ij}\cdot\vec{E}_j, \tag{7}$$

$$\vec{E}_i^{(\mathrm{Coul})}=-\sum_j\vec{Q}_{ij}q_j, \tag{8}$$

where

$$\vec{Q}_{ij}\equiv\vec{r}_{ij}/r_{ji}^3 \tag{9}$$

and

$$\vec{\vec{T}}_{ij}\equiv(\vec{\vec{I}}-3\vec{r}_{ij}\vec{r}_{ij}/r_{ij}^2)/r_{ij}^3 \tag{10}$$

are the Coulomb and dipole propagators.

In this Letter, we report molecular dynamics simulations based on the numerical integration of Newton's equations using this potential model. Note that the only mechanism for motion of the ionic charges in the simulations is ionic motion. Motion by electron hopping is not incorporated.

In the experiment[1] many more Xe_{55}^{++} clusters were observed than Xe_{53}^{++} clusters, indicating that the Xe_{55}^{++} clusters are significantly more stable. Consequently, we elected to perform simulations with these more stable clusters and to compare them with simulations of Xe_{51}^{++} clusters, which are experimentally unstable. The clusters were constructed in the following way. We assembled a neutral 55-atom cluster consisting of a central atom and the first four spheres of neighbors of the face-centered-cubic structure. The cluster was then aged using a force-bias Monte Carlo procedure[7] to bring it into apparent thermodynamic equilibrium at a temperature $T=0.3\epsilon/k_B$. This is 40% of the melting temperature which is a best estimate of the initial cluster temperature in the experiments.[8] This neutral cluster will maintain its configuration over times long compared to the simulations we describe. The cluster consists of twelve symmetrically disposed atoms surrounding a 43-atom core. We constructed a 51-atom cluster by removing two pairs of atoms from the outer shell of the 55-atom cluster: a pair consisting of an atom and its counterpart on the opposite side of the cluster. This cluster was then further aged to bring it back to thermodynamic equilibrium.

There are a large number of ways of ionizing the clusters. Many of these are manifestly unstable. For example, ionizing a surface atom and an atom directly beneath it will be unstable for clusters of any size, since Coulomb repulsion will immediately eject the surface ion from the cluster. We have chosen to concentrate on initial configurations in which a surface atom and the atom most distant from it (clearly another surface atom) are ionized. This is obviously a relatively stable configuration since the direct Coulomb repulsion is minimized (although solvation forces may drive the ions toward each other; cf. Fig. 1). It is also likely to occur in the experiments since, as already noted, estimates from inelastic electron-scattering data of the mean free path between ionizations shows that the distance between the ions is less than two mean free paths. There are four such most distant pairs for the Xe_{51}^{++} cluster and six for the Xe_{55}^{++} cluster. The results of simulations involving these ten initial configurations may be succinctly stated: The four Xe_{51}^{++} clusters are unstable, and the six Xe_{55}^{++} clusters are apparently stable. Figure 1 compares a typical Xe_{51}^{++} simulation and a typical Xe_{55}^{++} simulation. What is observed is that the Xe_{51}^{++} fractures into an Xe_{15}^{+} and Xe_{36}^{+} cluster at about 30 reduced time units while the Xe_{55}^{++} cluster remains intact for 120 time units and displays no tendency to fracture at that time. This is gratifying agreement with experiment considering that our simple point-dipole model has no disposable parameters.

Molecular dynamics cannot determine the ultimate stability of Xe_{55}^{++} clusters. To address this question and to gain insight into the different short-term behavior of the 51- and 55-atom clusters, we have determined the cluster potential energy curves at $T=0$ as a function of the ion-ion separation reaction coordinate. This was done by constructing symmetric cluster configurations at various ion-ion separations and cooling them by means of dissipative forces with the ion-ion separation held fixed. To within the accuracy that we have been able to determine the curves, they have the same shape for both 51- and 55-atom clusters. The curve of Fig. 2, which is plotted with the well minimum as the zero of energy, thus applies to both sizes.

The total energy of the 55-atom cluster at the well minimum is about -280ϵ whereas the total energy of the six starting configurations is about -211ϵ. Thus the thermal energy of the starting Xe_{55}^{++} configurations is $E_T\sim69\epsilon$. Since the height of the barrier to fracture is only $E_b\sim5\epsilon$, we see that the Xe_{55}^{++} clusters are unequivocally unsta-

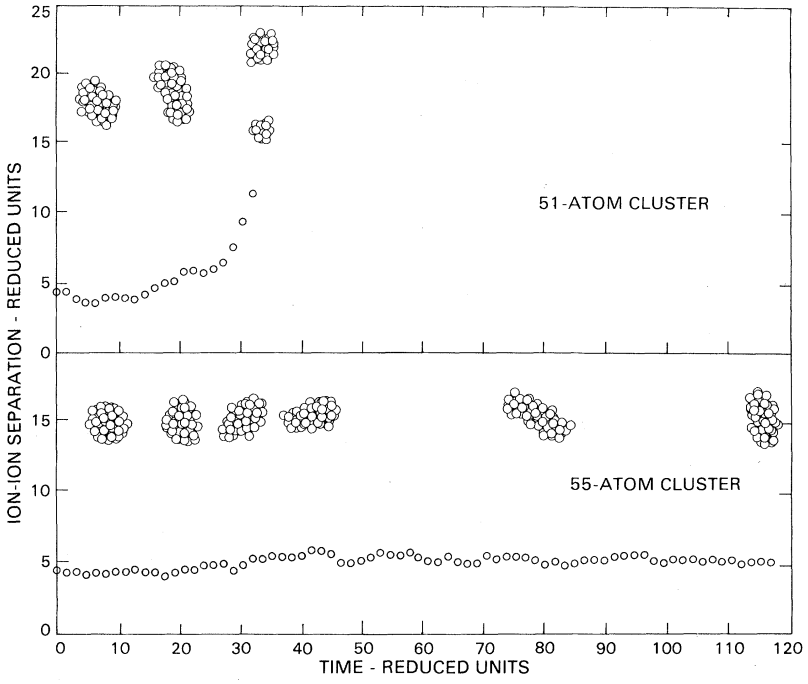

FIG. 1. Ion-ion separation as a function of time for an Xe_{51}^{++} cluster and an Xe_{55}^{++} cluster. The insets along the top of each panel depict the evolution of the clusters during the simulation. The temperature at the start of the simulation was 40% of the melting temperature in accord with experimental conditions. The Xe_{51}^{++} cluster is seen to fracture in approximately 30 time units (83 ps) into a Xe_{15}^{+} and an Xe_{36}^{+}. The Xe_{55}^{++} is apparently stable showing no tendency to fracture in 120 time units.

ble. Indeed, we may infer that much larger clusters will be unstable.

Why then do the 55-atom clusters appear stable whereas the 51-atom clusters fragment quickly? The thermal energy of the Xe_{51}^{++} cluster is $E_T \sim 260\epsilon - 173\epsilon = 87\epsilon$. This is larger than the value for Xe_{55}^{++} because the Xe_{55}^{++} starting configuration has extra stability gained by filling its outer shell of neighbors. In the initial configurations of both cluster sizes E_T is not equipartitioned but is disproportionately localized as compression of the reaction (ion-ion) coordinate. From the simulation results, we infer that sufficient thermal energy resides in the reaction coordinate of the Xe_{51}^{++} cluster that the system crosses the barrier shown in Fig. 2 faster than the reaction coordinate mode loses energy and equipartitions with the other vibrational modes. On the other hand, because E_T is smaller for the Xe_{55}^{++} clusters, vibrational relaxation is successful in preventing immediate fracture. This explanation is supported by the simulation result that a Xe_{51}^{++} cluster started from the well minimum with 87ϵ of kinetic energy equipartitioned among its vibrational modes is apparently stable.

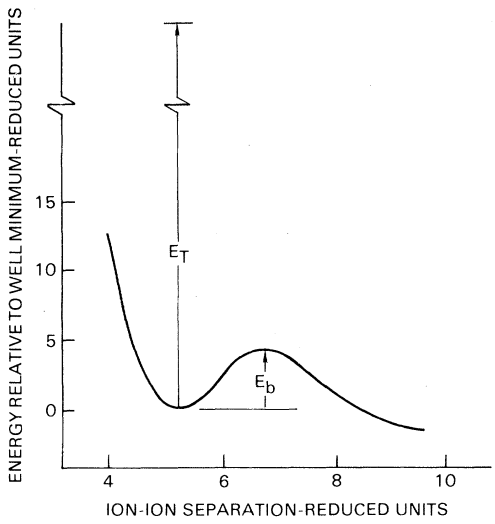

FIG. 2. Microcluster potential energy at $T = 0$ as a function of ion-ion separation for symmetric cluster configurations. To the accuracy that it has been determined the curve applies to both Xe_{51}^{++} and Xe_{55}^{++}. E_T is the thermal energy of the cluster. $E_T \sim 87\epsilon$ for the Xe_{51}^{++} and $E_T \sim 69\epsilon$ for Xe_{55}^{++}. Thus both clusters are unstable.

There remains the question of the lifetime of the 55-atom clusters once equipartition occurs. In the classical limit of Rice-Ramsberget-Kassel-Marcus theory[9] the rate constant for fracture of a cluster is

$$k = \nu(1 - E_b/E_T)^{s-1}, \quad (11)$$

where ν is the reaction-coordinate normal-mode frequency and s the number of degrees of freedom. From the oscillations in the Xe_{55}^{++} ion-ion coordinate visible in Fig. 1, we estimate $\nu \sim 20$ ns^{-1}. Then, using E_b and E_T determined above, we find $k \sim 9\times10^4$ s^{-1}, giving a predicted Xe_{55}^{++} lifetime of 11 μs. While small changes in E_b or in E_T (because, e.g., the cluster temperature was overestimated) can easily change the lifetime by an order of magnitude, this predicted lifetime is consistent with experiment[1] in which the Xe_{55}^{++} clusters are detected only if they survive the acceleration phase of the spectrometer ($t \sim 10$ μs).[8] We have assumed that the symmetric fracture channel is the dominant one. If other channels contribute, their effect would be to reduce the lifetime.

In summary, we find that Xe_{51}^{++} clusters have lifetimes ~100 ps while Xe_{55}^{++} clusters have lifetimes ~10 μs. This sudden increase in lifetime at just the size range that doubly charged clusters are first observed experimentally suggests that our simple point-dipole model contains the essential physics governing Coulomb explosions in Xe.

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