Energetics and dynamics of Coulomb explosion of highly charged clusters

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Ultrafast femtosecond Coulomb explosion of charged homogeneous (Xe_n) and heterogeneous doped ($HIAr_n$) small and medium sized clusters ($n<60$) is studied resting on the picture of a vertical high-order multiphoton ionization from the ground state nuclear configuration. The final average atomic velocity (simulated at constant charge) increases with increasing the cluster size, and at constant cluster size increases linearly with the ion charge, in accord with the predictions of an analytical model. The linear dependence of the reciprocal explosion time on the charge is also in accord with the analytical prediction. From the energetics of the Coulomb explosion (reflecting a probable initial atomic distribution of the cluster size for small clusters), a nonvertical multiphoton ionization during the Coulomb explosion cannot be inferred. © *1997 American Institute of Physics.* [S0021-9606(97)01641-3]

I. INTRODUCTION

Energy acquisition, storage, and disposal in finite systems, e.g., elemental rare-gas clusters,[1–3] is of considerable current interest. The ionization[4–6] or excitation[7,8] of a R_n cluster distorts its nuclear equilibrium configuration, resulting in energy disposal. The released excess energy in small clusters is transformed mostly into the kinetic energy of the cluster constituents, which may induce unimolecular fragmentation of the cluster. In the case of a singly charged rare gas cluster, R_n^+, the excess energy is provided mainly by the valence interaction of the open shell R^+ ion with neighboring neutral R atoms, which leads to the formation of an ionic core, either R_2^+ or R_3^+.[1–3,9–13] An additional, but much smaller, energy release is contributed by the many-body polarization attraction of neutral atoms to the ionic core.[12] The total excess energy release of a singly charged rare gas cluster is of the order of 1 eV. In small and intermediate size clusters this energy release leads to the evaporation of a number of neutral atoms[14–18] or to the detachment of the ionic core.[19]

When the energy of the impact electron or photon is sufficiently large, double or multiple charged clusters can be formed. The doubly charged clusters are unstable and exhibit Coulomb explosion, which results in the cluster fission into two singly charged clusters.[20–26] The Coulomb explosion is accompanied by the formation of ionic molecules and by neutral atoms evaporation,[23] like in the case of singly charged clusters. The molecular dynamics study of doubly charged Xe_n^{2+} and Ar_n^{2+} clusters shows that the character of the Coulomb explosion depends on the cluster size.[27] In the case of small clusters, the Coulomb explosion cannot be described as a real fission, but rather as the almost complete dissociation of the cluster. The final products of the Ar_{13}^{2+} Coulomb explosion on the time scale of 2 ps correspond to two Ar_2^+ dimers with high kinetic and vibrational energy, one or two small Ar_n ($n=2-5$) clusters, and a few monomers.[27] On the other hand, the Coulomb explosion of an intermediate size cluster, e.g., Ar_{55}^{2+}, leads to a slightly asymmetrical fission on a time scale of about 20 ps.[27,28] These dynamic size effects on the Coulomb explosion of Ar_n^{+2} clusters reflect the ''transition'' from dissociative dynamics of small clusters to nondissociative vibrational energy relaxation in larger clusters.

The double ionization of a cluster proceeds via subsequent single ionizations of two atoms, but not by a double ionization of a single atom.[23,24,29] In the same way, the triply charged clusters are formed.[30] The double ionization potentials of the Ar_n and Xe_n ($n=6-43$) clusters have been shown to exceed the first ionization potentials of two atoms by not more than 3 eV.[31] The differences are larger for the triple ionization potentials.[31] Multicharged ions can be produced in clusters by x-ray excitation of an inner electron with a subsequent Auger decay. The charge of the multicharged ions is subsequently distributed between surrounding atoms, leading to the Coulomb explosion and the fragmentation into singly charged clusters.[32] Multicharged ionic species were not detected in this experiment.[32]

Multicharged ions are known to be produced by multiphoton ionization, exposing atoms or molecules to a strong laser field.[33–39] In the case of diatomic molecules, both atoms become charged, being followed by the Coulomb explosion and by the production of multicharged atomic ions.[35–38] The kinetic energy of these ions was found to increase with the ion charge making, for example, ~20 eV for N^{3+} formed from multicharged N_2.[35] The multicharged atomic ions were detected also in the case of a polyatomic molecule UF_6.[39] Recently Purnel, Snyder, Wei, and Castleman[40] found that the multicharged atomic ions can be produced by exposing clusters to a strong laser field. These ions are formed as the result of Coulomb explosion, like in the case of molecules, but with much higher kinetic energies.

In this paper we analyze the energetics and dynamics of Coulomb explosion of clusters containing multicharged ions. We shall treat the Coulomb explosion of small $HIAr_n$ clusters, which was studied experimentally by Castleman *et al.*,[40] and elemental clusters, such as the homonuclear Xe_n, whose constituents are characterized by a relatively low ionization potential (IP). The dynamics of Coulomb explosion is of

central importance in the area of ultrafast femtosecond phenomena. The separation of ions on a repulsive Coulomb potential surface occurs on the fs time scale,[41] constituting one of the fastest processes in molecular dynamics.

II. VERTICAL IONIZATION AND CHARGE TRANSFER

In the study performed by Castleman *et al.*,[40] the small $(HI)_n$ and $HIAr_n$ clusters were irradiated by a strong ($\sim 10^{15}$ Wcm^{-2}) and short (350 fs) laser pulse at the wavelength of 625 nm. As a result of the cluster ionization and the subsequent Coulomb explosion, the multicharged atomic ions are formed up to I^{17+} in the case of $(HI)_n$ and I^{6+} and Ar^{7+} in the case of $HIAr_n$. Since the photon energy is 1.98 eV, the production of such highly ionized ions involves hundreds of photons. The kinetic energy of the multicharged ions increases strongly with the charge q. An intriguing finding of the study is the absence of the multicharged Ar ions when only pure Ar_n clusters are present in the beam.[40] Castleman *et al.* reported that in the $HIAr_n$ cluster the iodine atom is the particle which is losing electrons in the strong laser field, whereas the Ar atoms become ionized by subsequent charge transfer,[40] or by subsequent multiphoton ionization of the Ar cluster atoms in the electric field of the HI cation.[42,32]

In the case of molecules, two different mechanisms of the Coulomb explosion have been proposed. The vertical mechanism considers multiphoton ionization which occurs at the equilibrium geometry of the neutral molecule.[35] The nonvertical mechanism, on the other hand, assumes that the cluster atoms are losing their electrons during the Coulomb explosion when the interatomic distances are larger than in the neutral molecule.[38] According to a recent theoretical study, such nonvertical ionization takes place in some restricted interval of interatomic distances which do not depend on the pulse duration, e.g., around 4 Å in the case of $Cl^{q+}Cl^{q+}$.[43] It is important to note that the nonvertical ionization provides lower kinetic energies of the fragment ions than the vertical one for the same final ionic charges.

Regarding cluster multiphoton ionization, we have also to take into account the problem of charge transfer from ions with a higher charge to those with a lower one. This charge transfer, like in the case of ionization, can be of either vertical or nonvertical character. The effect of the charge transfer dynamics on the kinetic energy of ions is not obviously clear. In our model of the multicharged cluster Coulomb explosion, we shall accept the vertical mechanism for both the charge transfer and ionization. In addition, we assume that at the onset of the heavy particle motion all atoms are ionized and that the ions are in their ground electronic state. Due to these assumptions it is possible to neglect the polarization energy, which is small compared to the Coulomb repulsion energy. For example, the maximal expected polarization energy, which is provided by the pair $I^{8+}Ar^{+}$ at the equilibrium distance of 4.06 Å, is smaller than 2.7 eV, while the Coulomb energy is 28.3 eV. The van der Waals interactions, which are smaller in ionic systems than in neutral systems, are also neglected. Consequently, we are left with the Coulomb interactions only, which can be treated in the point charges approximation. As was mentioned above, the total charge of the ionized cluster is assumed to be distributed in some way among all cluster atoms, being characterized by the atomic charges q_i (in e-charge numbers), which provide minimal cluster energy. The electronic energy is the sum of the inner energy of all ions (taking the neutral atoms as the reference state) and the Coulomb energy U_c, i.e.,

$$E=\sum_i E_i+U_c, \tag{1}$$

$$E_i(q_i)=\sum_{q=0}^{q_i-1} I_{i,q}, \tag{2}$$

$$U_c=14.4\sum_i \sum_{j(>i)} q_i q_j/R_{ij}, \tag{3}$$

where ij stand for atomic indexes, $I_{i,q}$ is the ionization potential of the A_i^{q+} ion (atom), R_{ij} are the interatomic distances in Å, and the energy values are given in eV. The experimental multi-ionization potentials, unfortunately, are not available for all ions we need.[44] The multi-ionization potentials $I_{i,q}$ can be taken from the *ab initio* data.[45]

III. COULOMB EXPLOSION ENERGY OF $HIAr_n$ CLUSTERS

The total kinetic energy T of all ions in the Coulomb explosion of a multiply charged $HIAr_n$ cluster is equal to the initial potential energy, Eq. (3), so that

$$T=\sum_i T_i=U_c \tag{4}$$

So far as H is a light particle (as compared to I and Ar) the H^+ kinetic energy is close to the Coulomb interaction between H^+ and the rest of the cluster. Accordingly, it is possible to ignore the H^+ ion effect on the heavy ions motion and to consider the total energy of these ions as equal to the Coulomb potential energy of the $(IAr_n)^{q+}$ cluster. In order to calculate this energy, one needs to know the IAr_n geometry in the neutral $HIAr_n$ cluster.

The initial potential energy U_c was calculated by us for an IAr dimer and for the clusters IAr_5 and IAr_{12} in the case when all Ar atoms bear the same charge. We included in our consideration the IAr_{12} cluster because of its simple structure (see below), although in the experiments in Ref. 40 the maximal cluster size was $HIAr_{10}$. The exact geometry of the $HIAr_n$ clusters is unknown to us, but taking into account the weak dependence of the Coulomb potential U_c on the interatomic distances, it is possible to conclude that U_c is not very sensitive to the cluster geometry. As the van der Waals attraction of Ar atoms to the hydrogen atom is much weaker than to the iodine atom, the IAr_n geometry is expected not to be affected considerably by the H atom.

The most stable IAr_{12} geometry has been found with the I atom occupying a vertex of the icosahedron so that IAr_{12} resembles the slightly deformed Ar_{13} cluster.[46] The inter-

TABLE I. The initial Coulomb potential energy U_c of the multicharged IAr_n clusters and the experimental[a] total kinetic energy T_t of ions forming these clusters (in eV). q_I and q_{Ar} are the charges of iodine and argon atoms, respectively. All Ar atoms of IAr_n clusters bear the same charge.

	q_{Ar}	2		4		6	
	q_I	U_c	T_t	U_c	T_t	U_c	T_t
IAr	2	14.1	180	28.2	362	42.4	548
	4	28.2	426	56.5	608	84.7	794
	6	42.4	556	84.7	738	127	924
	8	56.5	802	113	984	169	1170
IAr_5	2	215	596	722	861	1520	2444
	4	285	850	861	1760	1729	2690
	6	354	980	1000	1890	1938	2820
	8	424	1226	1139	2136	2146	3066
IAr_{12}	2	938	1240	3491	3242	7650	5288
	4	1069	1486	3752	3488	8050	5534
	6	1199	1616	4014	3618	8440	5664
	8	1330	1862	4274	3864	8830	5910

[a]Reference 40.

TABLE II. The energy E [Eq. (1)], the initial Coulomb potential energy U_c, and the experimental[a] total kinetic energy T_t (in eV) of the multicharged IA_{12} cluster for different charge distributions. q_t is the total charge, and q_I, q_0, and q_i are the charges of I, the central Ar atom, and 11 peripheral Ar atoms, respectively.

q_t	q_I	q_0+q_i	E	U_c	T_t
26[b]	4	$1+1+2\times10$	1518	895	1430[c]
26	4	$1+1\times4+2\times2+3\times4$	1597	908	1490
52[b]	7	$1+4\times11$	5692	3560	3707
52	6	$4+2+3\times4+4\times2+5\times4$	5872	3733	3468
78[b]	8	$3+6\times10+7$	12 652	8186	5982
78	8	$6+4+5\times4+6\times2+7\times4$	12 946	8407	5636

[a]Reference 40.
[b]Equilibrium charge distribution obtained by the minimization of energy (1).
[c]Ar^+ experimental energy (absent in Ref. 40) was estimated by extrapolation.

atomic I–Ar distance in Ref. 46 is equal to 4.06 Å and the Ar–Ar distance is equal to that of the Ar_2 dimer (3.76 Å). We accepted this structure decreasing only the Ar–Ar distance to 3.72 Å, which is the interatomic distance in the Ar_{13} cluster.[12] The IAr_5 cluster is assumed to have the C_4 symmetry with the I atom and one of the Ar atoms is located on the symmetry axis, and four other Ar atoms are located in between. The interatomic distances are taken to be the same as in the IAr_{12} cluster. The I–Ar distance was estimated to be equal to 4.08 Å.

The results of the initial potential energy U_c calculation are presented in Table I and are compared with the experimental kinetic energies T_t of Castleman *et al.*[40] From the data of Table I we infer that for the IAr dimer the experimental kinetic energy of different pairs of ions is of the order of magnitude higher than the potential energy. In the case of the IAr_5 cluster the experimental kinetic energy of all six ions still exceeds the potential energy, with the differences being 40%–60% for $q_{Ar}=6$ but 200%–300% for $q_{Ar}=2$. Only in the case of the IAr_{12} cluster the agreement between the calculated U_c and the experimental T_t[40] is reasonable, i.e. for $q_{Ar}=2$, T_t exceeds U_t by 20%–30%, while for $q_{Ar}\geqslant4$ the potential energy exceeds the experimental kinetic energy by about this amount. Taking into account that the potentials U_c provide the upper limits for the kinetic energy of atomic ions, the Coulomb explosion model advanced by us leads to a large discrepancy between the theoretical and experimental T_t values for small IAr_{n-1} $(n=2-5)$ clusters.

The relation between the calculated potential energy and the experimental kinetic energy is not changed much when the Ar atoms bear different charges. Some examples are presented in Table II for the IAr_{12} cluster, including the equilibrium charge distributions obtained by the minimization of the multicharged cluster energy, Eq. (1).

The results presented in Tables I and II show that the potential energy U_c for given ionic charges increases sharply with the size of IAr_n, with the increase of U_c being superlinear in the number of atoms $n+1$. Consequently, the kinetic energy T_i of individual ions is expected to increase with the size of the cluster. For example, the I^{6+} and Ar^{6+} ions generated by the Coulomb explosion of IAr are expected to have kinetic energies of 30.4 and 96.7 eV, respectively, while the kinetic energies of the same ions which originate from the IAr_5 and IAr_{12} clusters are expected to be ~320 and ~700 eV, respectively. Our simple calculations predict a broad distribution of the kinetic energies. However, the experimental data of Castleman *et al.*[40] give a relatively narrow distribution of the kinetic energy, namely 408–492 eV for I^{6+} and 444–504 eV for Ar^{6+}. It looks like the dimers and very small clusters $(n\leqslant5)$ do not contribute to the generation of multicharged ions. If this is the case, it may also at least partly explain the results of Table I, as for larger clusters ($n>5$, probably), the discrepancy between the theoretical U_c and the experimental (T_i) values is not large (i.e., does not exceed 20%–30%). We may suggest that diatomics and small clusters are not effectively ionized in the laser field, due to the presence of a barrier for electron tunneling at the equilibrium configuration.[43,47]

IV. COULOMB EXPLOSION DYNAMICS OF Xe_n CLUSTERS

In the case of monatomic clusters it is possible to calculate not only the total energy, as done in the previous chapter, but also the kinetic energy of individual ions and the time evolution of the Coulomb explosion. We studied the homonuclear Xe_n clusters with $n=2,3,6,13$. In view of the relatively low ionization potential of Xe and the similarity in the electronic structure of Xe and of I (in HI), it is possible to expect that Xe and HI are ionized in the strong laser field with roughly the same efficiency, which was recently demonstrated experimentally.[48]

The dynamics of Coulomb explosion constitutes an ultrafast (femtosecond) process on the time scale of the nuclear motion of the ions on the repulsive potential surface. The time evolution of the Coulomb explosion of a pair of ions was expressed analytically,[35] and will be presented here in a more detailed way. The time of the atoms' separation from the initial distance R_0 to R can be found as

$$\tau(R)=\int_{R_0}^{R} dr/v=\int_{R_0}^{R}(\mu/2T(r))^{1/2}dr, \tag{5}$$

where v is the velocity, μ is the reduced mass, and $T(r)$ is the total kinetic energy, which is equal to the change in the Coulomb potential,

$$T(r)=e^2q_1q_2\left(\frac{1}{R_0}-\frac{1}{r}\right). \tag{6}$$

Performing the integration one obtains

$$\overline{\tau}=t_0Z(\xi), \tag{7}$$

where

$$t_0=1.905\cdot 10^{-15}R_0\left(\frac{\mu R_0}{q_1q_2}\right)^{1/2} \tag{8}$$

and

$$Z(\xi)=\frac{\sqrt{1-\xi}}{\xi}+\frac{1}{2}\,ln\left(\frac{1+\sqrt{1-\xi}}{1-\sqrt{1-\xi}}\right);\quad \xi=\frac{R_0}{R}\leqslant 1. \tag{9}$$

In Eqs. (7)–(9) the values are in the following dimensions: (t_0/s), $(R/\text{Å})$, $(R_0/\text{Å})$, and (μ/AM). We note that t_0 in Ref. 35 was overestimated by a numerical factor of $\sqrt{8}$.

The expression for the separation time $\tau(R)$ can be generalized for symmetrical clusters with equally charged atoms. To this end we denote R_{cm} as the distance between the moving atoms and the cluster center of mass, and express it and the Coulomb potential energy U_c by the interatomic distance R

$$R_{\mathrm{cm}}=\beta R \tag{10}$$

$$U_c(r)=\frac{14.4}{R}\,S(q). \tag{11}$$

The coefficients β and $S(q)$ are as follows

$$\begin{aligned}
&R_2:\ \beta=\frac{1}{2},\ S=q^2,\\
&R_3:\ \beta=\frac{1}{\sqrt{3}},\ S=3q^2,\\
&R_6:\ \beta=\frac{1}{\sqrt{2}},\ S=14.12q^2,\\
&R_{13}:\ \beta=1,\ S=(49.34q+12q_0)q,
\end{aligned} \tag{11a}$$

where q_0 is the central atom charge and q are the charges of all other atoms. The dependence of the time $\tau(R)$ on the interatomic distance R is expressed by the same function (9) as for the pair of atoms, but the t_0 expression is modified to the form

$$t_0=1.905\cdot 10^{-15}R_0\left(\frac{\beta^2n'mR_0}{S(q)}\right)^{1/2}, \tag{12}$$

where n' is the number of moving atoms ($n'=12$ for R_{13} but $n'=n$ for R_3 and R_6) and m is the atomic mass (not reduced) of the atom R. The kinetic energy per ion is

TABLE III. The Coulomb explosion time τ_c (in fs) and the final kinetic energy per ion T_i (in eV) of Xe_n clusters. $\tau_c=t(2R_0)$ is determined by Eqs. (7), (9), (12), and (14). T_i is determined by Eq. (13). All Xe atoms in a cluster bear the same charge q except for Xe_{13}, where the central atom bears a smaller charge ($q_0<q$) to provide stable charge distribution ($q_0=0$ for $q=2,4$ and $q_0=1,4,8$ for $q=6,8,10$).

	q	2	4	6	8	10
τ_c (fs)	Xe_2	155	77.7	51.8	38.8	31.1
	Xe_3	127	63.5	42.3	31.7	28.8
	Xe_6	101	50.6	33.8	25.3	20.4
	Xe_{13}	108	54.2	35.5	25.6	19.9
T_i (eV)	Xe_2	6.7	26.8	60.3	107	167
	Xe_3	13.4	53.6	121	214	335
	Xe_6	31.5	126	284	504	788
	Xe_{13}	55.1	220	516	988	1646

$$T_i=\frac{14.4}{R_0n'}\,S(q). \tag{13}$$

There are different ways to define the Coulomb explosion time τ_c.[41] We shall determine it as the time corresponding to the doubling of the interatomic distances ($R=2R_0$), so that

$$\tau_c=\tau(2R_0)=t_0Z(0.5). \tag{14}$$

The results of the calculation of the kinetic energy per ion T_i and the Coulomb explosion time τ_c are presented in Table III for Xe_2, Xe_3, Xe_6, and Xe_{13}. The ion kinetic energy increases superlinearly with increasing the cluster size, like in the case of IAr_n (Table I), and is proportional to q^2. The explosion time τ_c decreases with increasing the cluster size. It is inversely proportional to the charge q. The time scale for Coulomb explosion is indeed ultrashort, being tens of femtoseconds for $q>2$ and ~100–150 fs for $q=2$.

V. MOLECULAR DYNAMICS SIMULATIONS OF COULOMB EXPLOSION

Our constant energy molecular dynamics (MD) simulations study Coulomb explosion of two cases: Xe_n ($n=2,3,4,6,13,43,55$) and $HIAr_n$ ($n=1,5,12$), clusters all equilibrated at the temperature $T=10$ K.

A. Potentials for neutral clusters

The dipole moment of the HI molecule is relatively small,[49] being 0.38 Debye. The polarization energy of Ar atoms in the field of such a dipole is less than $6\cdot 10^{-4}$ eV, which is negligibly small compared to the van der Waals interaction, and hence ignored in our simulations.

H–I interaction is described by Morse potential, fitted to the empirical values of this molecule.[50]

$$u(r)=D_e[\exp(-2\alpha(R-R_e))-2\exp(-\alpha(R-R_e))], \tag{15}$$

where the well depth $D_e=3.2$ eV, the equilibrium distance $R_e=1.609$ Å, the exponential parameter $\alpha=1.75$ Å^{-1}, and the frequency $\omega_e=2309$ cm^{-1}.

Ar–Ar, Ar–H, and Ar–I interactions are described by the Lennard-Jones potentials:

$$u(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}], \tag{15a}$$

where

for Ar–Ar:[51] $\epsilon=10.41$ meV, $\sigma=3.40$ Å,

for Ar–H:[11] $\epsilon=4.15$ meV, $\sigma=3.22$ Å,

for Ar–I:[52] $\epsilon=16.1$ meV, $\sigma=3.59$ Å.

The $HIAr_n$ clusters are thermally equilibrated at 10 K, where the HI molecule actually occupies the vertex site of an otherwise Ar atom in the ideal structure of an Ar_{n+1} cluster, which is the most stable geometry. This exchange slightly deforms the geometry of the Ar_{n+1} cluster, where the hydrogen atom tends to align itself close to the Ar atoms (but not sticking out the cluster).

The Xe–Xe interactions in the symmetrical Xe_n clusters also are described by the Lennard-Jones potential with the parameters:[53]

Xe–Xe: $\epsilon=24.2$ meV, $\sigma=4.39$ Å.

B. Potentials for charged clusters

As mentioned above, we suggested all atoms to be charged so it is possible to neglect the polarization, van der Waals, and valence forces. Consequently, we are left with repulsive Coulomb forces only. However, in order to prevent the nonphysical mutual penetration of the ions in the case of collisions, we will keep the Lennard-Jones potential, which provides a strongly repulsive term. The interatomic potential between any two charged ions is as follows:

$$U_{1,2}(R)=\frac{14.4}{R}\,q_1q_2+4\epsilon_{1,2}\left[\left(\frac{r_1+r_2}{R}\right)^{12}-\left(\frac{r_1+r_2}{R}\right)^{6}\right]. \tag{16}$$

The ions radii r, except for H^+ with $r_H=0$, are determined roughly as

$$r=r_0/\gamma,\quad \gamma=\left(\frac{n_0}{n}\right)^{2}\left(\frac{Z}{Z_0}\right), \tag{17}$$

where n is the principal number of the outer electrons, Z is the effective atomic charge (according to Slater rules), r_0, n_0, Z_0 stand for neutral $(q=0)$ atoms, and $r_0=\sigma$ in the Lennard-Jones potential. Using approximate fittings we express γ as follows:

Ar: $\gamma=1+0.052$, $0\leqslant q\leqslant 7$; $\gamma=4.62+0.117(q-8)$,

$8\leqslant q\leqslant 15$; $r_0=1.675$Å;

I: $\gamma=1+0.055q$, $0\leqslant q\leqslant 6$; $\gamma=3.38+0.085(q-7)$,

$7\leqslant q\leqslant 16$; $\gamma=5.87+0.085(q-17)$,

$17\leqslant q\leqslant 24$; $r_0=1.942$ Å.

For pairs of ions we take the same ϵ as for neutral atoms:

HI: $4\epsilon=0.0274$, ArH: $4\epsilon=0.0166$, ArI: $4\epsilon=0.0646$,

ArAr: $4\epsilon=0.041$ eV.

C. Details of simulations

We performed constant-energy MD calculations using a fifth-order preditor-corrector procedure based on the Nordsieck optimization[54] to simulate the high energetic fragmentation of the Xe_n and $HIAr_n$ clusters, initially prepared at 10K. In view of the fast (sub femtosecond) mechanism of the fragmentation, the integration time step is taken as ~ 0.5 fs.

In each simulation we study three kinds of observables:

(a) Time development of kinetic (KE) and potential (PE) energies of the neutral as well as the ionic fragments, both for Xe_n and $HIAr_n$ clusters.
(b) Time development of the interparticle distances.
(c) Coulomb explosion time, t_{ce} (defined as the time when first interatomic distance reaches twice the equilibrium distance).

D. Simulations of Coulomb explosion

Simulations were performed for $(Xe^{+q})_n$ $(n=2-55,\ q=1-10)$ and for $HI^{q_I^+}(Ar^{q_{Ar}^+})_n$ clusters. The simulations span a cluster size domain which is considerably larger than that treated by the analytical model, Eqs. (7)–(9), and also provides information on heteroclusters which cannot be treated by our analytical model.

Figure 1 portrays the time dependence of the potential energy and the total kinetic energy of the $(Xe^{+q})_n$ $(n=2-55)$ clusters. The Coulomb explosion is manifested in the decay of the Coulomb potential energy towards zero and the rise of the kinetic energy of the ion fragments towards a constant value KE(∞). The final average Xe velocity $V(\infty)=[2m_{Xe}\mathrm{KE}(\infty)]^{1/2}$ at constant q increases with increasing the cluster size due to the increase of U_c prior to the Coulomb explosion. $V(\infty)$ at a constant cluster size increases linearly with increasing the ion charge q (Fig. 2), in accord with Eqs. (11) and (11a). The linear dependence of the simulated $V(\infty)$ vs q (Fig. 2) agrees within 5% with the prediction of Eqs. (11) and (12). The Xe–Xe distance dependence for the Coulomb explosion of Xe_{55}^+ (Fig. 3) reveals specificity on the location of the Xe atom. We defined (Sec. IV) the characteristic time τ_c for the Coulomb explosion in terms of Eq. (14). The cluster size dependence of τ_c for the Coulomb explosion of Xe^{+q} increases with increasing the number of constituents n at a fixed charge q, and reaches saturation for large n (Fig. 4). The linear dependence of $1/\tau_c$ vs q (Fig. 6) is in agreement with Eqs. (7), (9), (11a), (12), and (14).

The Coulomb explosion dynamics of the heteronuclear $HI^{q_I^+}(AI^{q_{Ar}^+})_n$ $(n=5,12)$ clusters bears similar characteristics to those of the homonuclear $(Xe^{+q})_n$ clusters. The asymptotic velocity [Figs. 5(a) and 5(b)] and the reciprocal time (Fig. 6) show a linear dependence on both q_{Ar} and q_I. This behavior of the $HI^{q_I^+}(Ar^{q_{Ar}^+})_n$ system is in accord with the predictions of Eqs. (7), (12), and (13), together with (11a), derived for a homonuclear system.

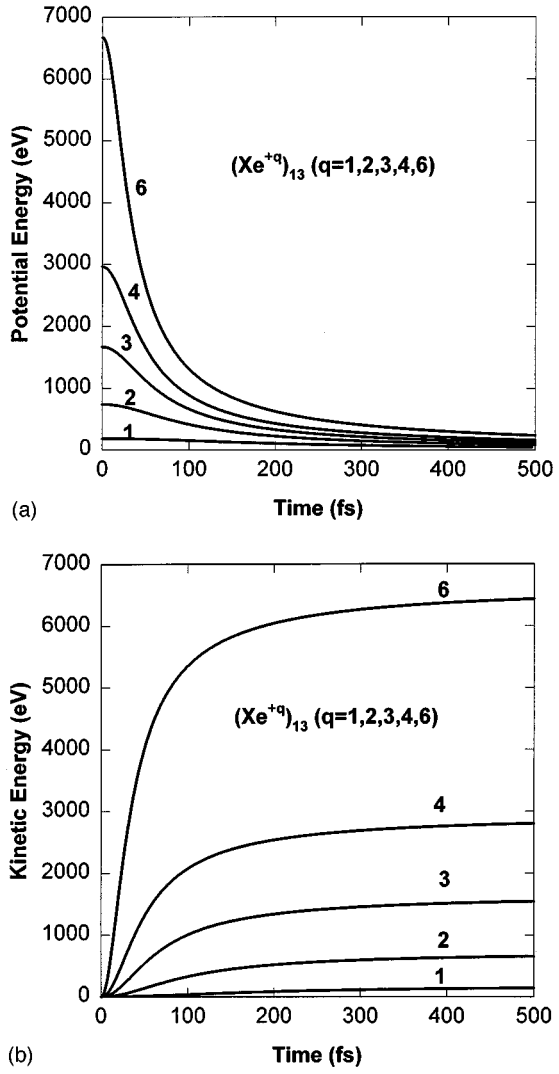

FIG. 1. Time evolution of the potential and kinetic energies of the $(Xe^{+q})_{13}$ cluster for several charges ($q=1,2,3,4,6$). (a) Potential energies; (b) kinetic energies.

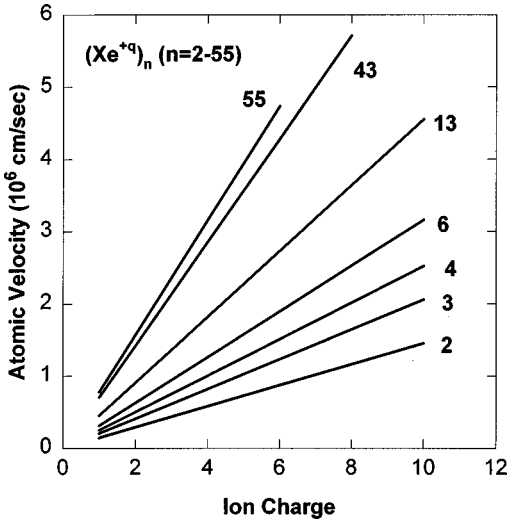

FIG. 2. The dependence of the final average atomic Xe velocity of several clusters $(Xe^{+q})_n$ ($2 \leqslant n \leqslant 55$) on the charge. Notice the linear dependence as predicted by Eqs. (11) and (12).

VI. DISCUSSION

We presented an analysis of the energetics and the time scale of the ultrafast (femtosecond) Coulomb explosion of clusters. Our starting point rests on the picture of a vertical high-order multiphoton ionization of the elemental Xe_n or of the doped $HIAr_n$ clusters, where the configurational onset of Coulomb explosion corresponds to the ground state nuclear configuration of the cluster. This assumption is admittedly oversimplified. Recent experimental work on multiphoton ionization of diatomic molecules indicates that the kinetic energies of the atomic fragments resulting from Coulomb explosion of a variety of molecules correspond to a constant fraction of the Coulomb repulsion experienced by the multicharged molecular ion at the equilibrium distance.[55] This observation indicates a two-step nonvertical ionization model[43,55–57] for Coulomb explosion, where the molecule first loses a few electrons at the equilibrium internuclear distance, then starts separating, and subsequently enhanced ionization occurs at a stretched nuclear configuration. It was suggested[43,56] that the ionization enhancement at the stretched internuclear distance originates from nonadiabatic electron localization near the nuclei. The prevailing parameter of the ionization enhancement model is the critical distance R_{cr}, which determines the region of the high ionization rate. The ionization is enhanced only when R_{cr} exceeds the initial (equilibrium) distance R_e. The critical distance of Ar may be estimated considering that the ionization is enhanced in ionic systems, lacking any valence properties. Consequently R_{cr} of Ar ions has to be comparable to R_{cr} of Cl ions. The one-dimensional quantum model puts R_{cr} in the interval of ~4–5 Å,[43] whereas an estimation based on experimental data provides $R_{cr}=2.8$ Å.[43] Comparing this last value with the Ar–Ar equilibrium distance $R_e=3.72$ Å, we conclude that in argon systems the condition $R_{cr} \geqslant R_e$ may not be fulfilled, which tentatively explains the absence of multicharge ions when pure Ar_n clusters are irradiated.[40] It is possible to speculate that in the doped $HIAr_n$ cluster the I–Ar pair is responsible for the ionization enhancement. Our calculations of the energetics of Coulomb explosion indicate that for very small clusters the vertical ionization provides potential energy U_c(calc), which is considerably smaller than the experimental energy of product ions, presumably reflecting the absence of these clusters in the Coulomb explosion process. On the other hand, for larger clusters ($5 < n \leqslant 13$) with large values of q, it is observed that U_c(calc) is close to T_t or even a little higher than T_t. The suggestion can be made that just these clusters are responsible for the production of the highly charged ions and that the ionization takes place in the vicinity of the equilibrium geometry. If a nonvertical ionization at R_{cr}, which is much larger than R_e, is responsible for the multicharged ion production, then the kinetic energy T would be significantly lower than U_c(calc). Since this is not the case, the evidence for nonvertical cluster multielectron ionization during Coulomb explosion cannot be inferred. It appears that the high-order multiphoton atomic ionization in an elemental cluster does not occur, in view of the observa-

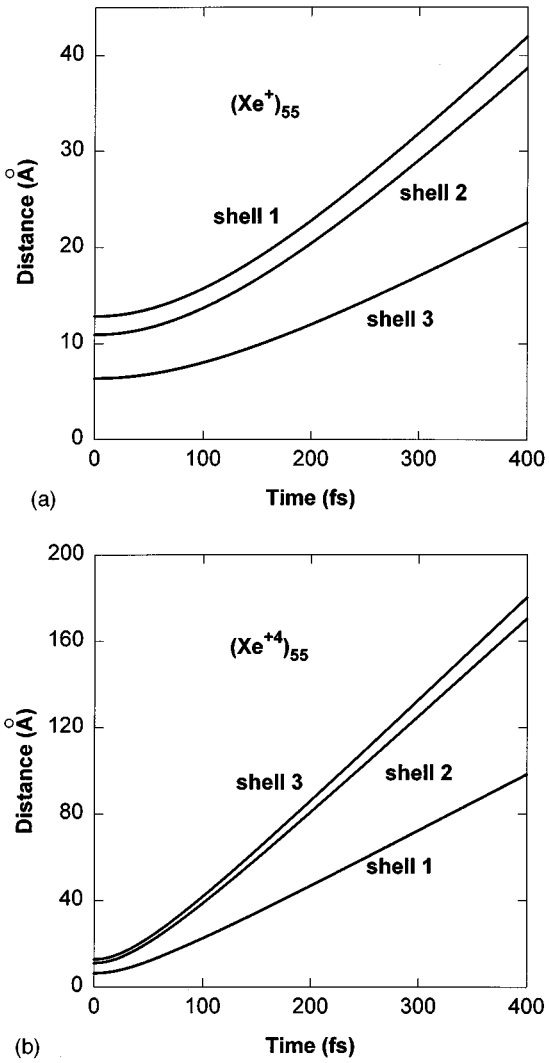

FIG. 3. The time evolution of the Xe–Xe distances for the Coulomb explosion of $(Xe^{+})_{55}$. Distances are shown for typical atoms at the first, second, and third layers beyond the central atom. (a) $q=1$; (b) $q=4$.

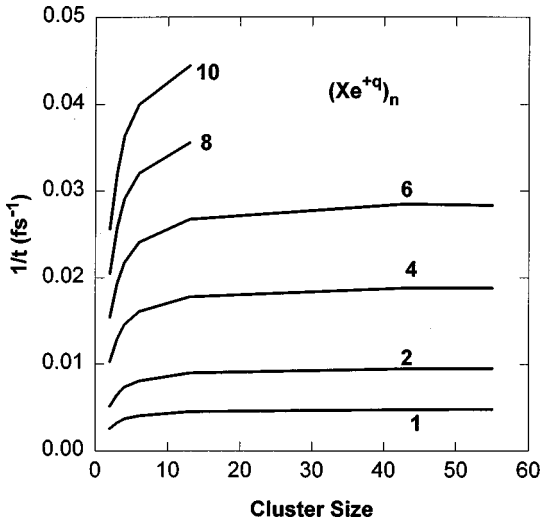

FIG. 4. Cluster size dependence ($2 \leqslant n \leqslant 55$) of the reciprocal Coulomb explosion times of $(Xe^{+q})_n$ for several charges ($1 \leqslant q \leqslant 10$).

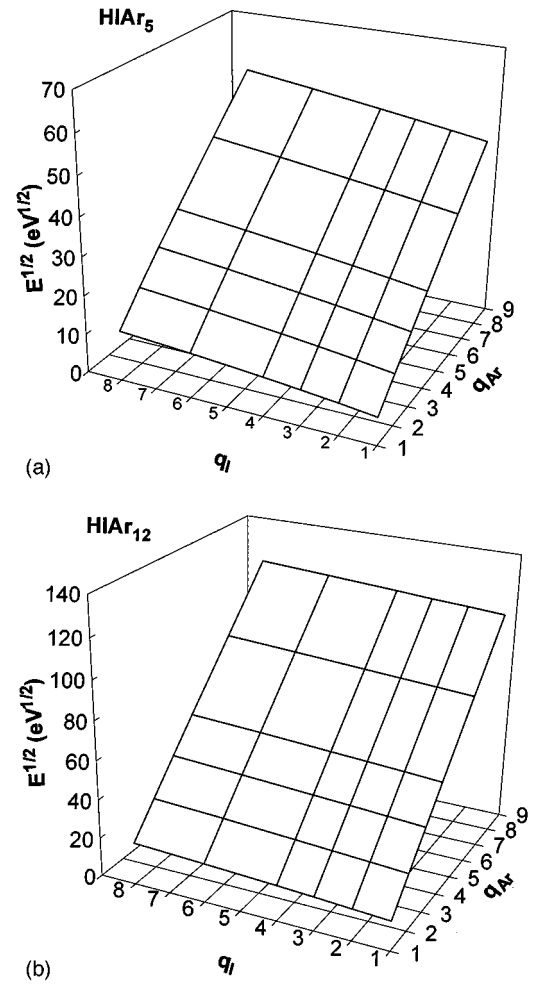

FIG. 5. Dependence of the asymptotic average velocity (in terms of the root of the kinetic energy) of $HIAr_n$ on the iodine and argon charges, respectively. Notice the linear dependence on both charges. (a) $n=5$; (b) $n=12$.

tion of highly multicharged species from a cluster beam and not from an atomic beam.[48] Castleman *et al.*[48] have proposed that the ionization ignition model[57] accounts for many features of cluster multiphoton ionization. In this model[48,57] initial ionization events, which leave behind heavy ions, result in a very large and inhomogeneous electric field, lowering the ionization barrier and allowing subsequent ionization processes to occur. This mechanism[48] is in accord with the low ionization potential of the cluster constituents and predicts a weak cluster size dependence, in accord with experiment. The ionization ignition model may result in contraction of the interatomic distances in an initially weakly ionized elemental cluster, e.g., $(Xe^{+})_m Xe_{n-m}$, with the incipient formation of Xe_2^{+} centers prior to subsequent ionization. Further explorations of the interatomic distance dependence of Xe_2^{+} ionization efficiency in the context of nonadiabatic electron localization will be of interest. In the broad context of the unique features of energy acquisition due to multiphoton ionization of clusters, further experimen-

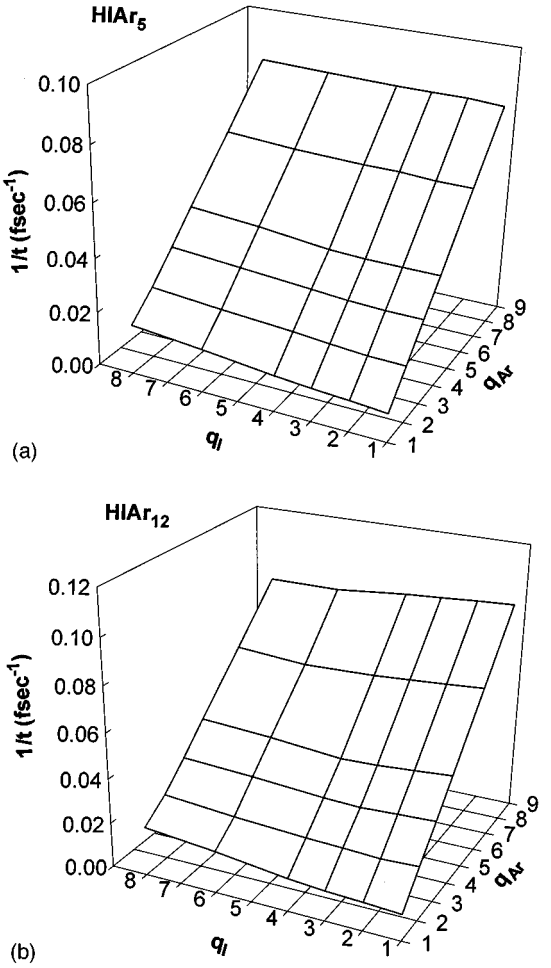

FIG. 6. Dependence of the reciprocal explosion time of $HIAr_n$ on the iodine and argon charges, respectively. Notice the linear dependence on both charges, as predicted by Eqs. (11a), (12), and (13). (a) $n=5$; (b) $n=12$.

tal information on the energetics and femtosecond dynamics of Coulomb explosion in these finite systems will be of considerable interest.

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