Coulomb explosion in dicationic noble gas clusters: A genetic algorithm-based approach to critical size estimation for the suppression of Coulomb explosion and prediction of dissociation channels

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(Received 24 January 2010; accepted 10 May 2010; published online 16 June 2010)

We present a genetic algorithm based investigation of structural fragmentation in dicationic noble gas clusters, Ar_n^{+2}, Kr_n^{+2}, and Xe_n^{+2}, where n denotes the size of the cluster. Dications are predicted to be stable above a threshold size of the cluster when positive charges are assumed to remain localized on two noble gas atoms and the Lennard-Jones potential along with bare Coulomb and ion-induced dipole interactions are taken into account for describing the potential energy surface. Our cutoff values are close to those obtained experimentally [P. Scheier and T. D. Mark, J. Chem. Phys. **11**, 3056 (1987)] and theoretically [J. G. Gay and B. J. Berne, Phys. Rev. Lett. **49**, 194 (1982)]. When the charges are allowed to be equally distributed over four noble gas atoms in the cluster and the nonpolarization interaction terms are allowed to remain unchanged, our method successfully identifies the size threshold for stability as well as the nature of the channels of dissociation as function of cluster size. In Ar_n^{2+}, for example, fissionlike fragmentation is predicted for $n=55$ while for $n=43$, the predicted outcome is nonfission fragmentation in complete agreement with earlier work [Golberg *et al.*, J. Chem. Phys. **100**, 8277 (1994)]. © *2010 American Institute of Physics*. [doi:10.1063/1.3439690]

I. INTRODUCTION

Cluster physics has emerged as a research field of great interest in recent times, especially the problems that deal with the dynamics of clusters under external perturbations. The term "Coulomb explosion" is frequently used to describe the charge separation process in cluster ions. Within the cluster, the repulsion between the charges is too high; as a result, the two fragments separate with a high center of mass kinetic energy.

The study of atomic and molecular clusters has witnessed a phenomenal growth in the past decades. Both experimental and theoretical chemists have contributed to the understanding of structure, spectroscopy, and dynamics of these systems.[1–3] Within this field, a hotly pursued area is the field of noble gas clusters, both neutral and ionic. These apparently inert systems can show up interesting structures if ionized; its dynamics can give us rich chemical information from the point of view of the forces which bind them together. The search for global minima of noble gas clusters has been a challenging field of work. The apparently simple looking Lennard-Jones (LJ) potential, which is used to describe interaction among pairs of atoms constituting these clusters, can be an acid test for any optimization technique that claims to be a truly global one.[4,5] The difficulty stems from the fact that the number of critical points on a LJ hypersurface rises astronomically with the size of the system. A host of stochastic optimization techniques, such as genetic algorithm (GA), simulated annealing, basin hopping Monte Carlo, and quantum annealing, have been used by researchers to create a rich database of cluster geometries for these systems.[6–9] Going beyond finding the global minimum of noble gas clusters, these systems can be looked at from other angles. As the critical points are innumerable in number, one can look for transformations in these systems to map out a reaction path for going from one minimum to another through a first order saddle point, which is characterized by a single negative eigenvalue of the Hessian. This is a nontrivial search with the direction of the next move always pointing toward the direction, which maintains a single negative eigenvalue. A number of publications have already come out in this field.[10–12] Ionized clusters offer even stiffer challenges.

Experiments have been performed to promote the Coulomb explosion in a range of doubly charged atomic and molecular clusters.[13] Here selected clusters of Ar_n^{+2}, $(CO_2)_n^{+2}$, $(H_2O)_n^{+2}$, etc., have been subjected to collisional activation with a background gas. For species, close to the Coulomb cutoff, each collision removes sufficient number of atoms or molecules to render the clusters unstable or unviable. The molecular systems have been studied and they show evidence of asymmetric charge separation, with some singly charged fragments. Sattler *et al.*[14] showed that doubly charged microclusters are stable only above a critical size. Smaller clusters are destroyed as a result of the Coulomb

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explosion. This effect, which occurs at electron ionization energies ≥ 30 eV, explains why most doubly charged molecules are not stable as the Coulomb repulsion energy between the two positive holes exceeds the molecular binding energy. Experiments have been done to investigate the stability of multiply charged C_{60} and C_{70} fullerene ions through studies of charge transfer reactions.[15]

Fragmentation of doubly charged clusters was reported by Rühl *et al.*[16] in which symmetric and asymmetric charge separation reactions were identified in clusters below the critical size required for stable dication formation.

Ishikawa and Blenski[17] experimentally studied the explosion dynamics of rare gas clusters containing up to 147 atoms induced by an intense femtosecond laser pulse along with the Monte Carlo classical particle dynamics simulations. Detailed analysis of ion kinetic energy reveals that the cluster ions are accelerated mainly by the Coulomb repulsion among themselves.

The phenomenon of Coulomb explosion can be seen in certain types of ionized clusters. If a cluster is ionized, opposing forces will come into play, some of which will try to stabilize it and others which will do the reverse. In general, if more than one atom posses charges of similar sign, strong repulsive Coulombic forces will operate and the attractive ones originating from LJ interaction, dipole-dipole, and dipole-induced dipole interactions will try to nullify the effect of the repulsive interaction. A competition will result and it is generally seen that for a critical size of the cluster, which is specific for the system concerned, the attractive forces outweigh the repulsive ones and the cluster becomes stable.[18–23] For sizes less than the critical one, an explosion of the system into fragments induced by the strong Coulombic repulsion becomes operational.

In this communication, we address the problem where the aim partly is to see if GA-based search on a classical potential energy hypersurface can give us reasonably good estimates of the critical sizes for dicataionic noble gas clusters, namely Ar_n^{+2}, Kr_n^{+2}, and Xe_n^{+2}, beyond which the cluster does not undergo Coulomb explosion. There is a second purpose of the work being reported.

Numerous studies for understanding the behavior of charged noble gas clusters using molecular dynamics (MD) simulation are available in literature. In a work by Goldberg *et al.*,[24] the authors modeled the Ar_n^{+2} system to be composed of two pairs of charged atoms and $(n-4)$ neutral Ar atoms. For a small cluster such as Ar_{13}^{+2}, Coulomb explosion leads mostly to the detachment of ionic dimers. In large clusters $(n \geq 55)$, Coulomb explosion leads to fission of the doubly charged clusters to singly charged clusters of similar sizes. They found out the critical size (n_c) for the attainment of stability in Ar_n^{+2} systems to be $n_c = 92-95$. Other than the correct prediction of the critical size, there has been attempt to find out in detail what the fragmentation channels would be in multicharged $(Ar^{+m})_n$ clusters.[25,26] The important parameter to be evaluated is the fissibility parameter, $X = E(\text{Coulomb})/2E(\text{surface})$. MD has established that for $X < 1$, the result is cluster fission into a number of large multicharged clusters, and for $X > 1$, the result is Coulomb explosion into a large number of individual ions and small ionic fragments. The Rayleigh instability limit $X = 1$ separates between the spatially anisotropic fission and spatially isotropic Coulomb explosion. In a recent experimental study,[27] systems were analyzed around the Rayleigh instability barrier. The fragmentation patterns obtained are in close agreement with theoretical predictions.[25,26] We show with Ar_n^{2+} as a test case that our GA-based approach also correctly identifies the predominant fragmentation channels as functions of n if the positive charges are allowed to be symmetrically spread over four Ar atoms—that is, if partial account is taken of charge delocalization; the predicted critical cluster size for the stability of the dications, however, remains unaffected.

II. METHODOLOGY

To study the Coulombic explosion in these clusters, we start by defining a simple potential energy function which hopefully would account for the major interactions among the constituents of the clusters. To evaluate only the cutoff sizes above which the clusters are stable, we have used the potential given as follows:

$$V = \sum_{i>j} \left[V_{ij}^{\mathrm{LJ}} + \frac{z_i z_j e^2}{r_{ij}} \right] - 1/2 \sum_i \mu_i^{\mathrm{ind}} E_i^{\mathrm{Coul}}, \tag{1}$$

$$V_{\mathrm{LJ}}^{ij} = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]. \tag{2}$$

Here V is the total potential energy of the cluster and V_{ij}^{LJ} is the LJ[10–12,18–21] interaction among the constituents i and j. We do not make any distinction among the charged and the uncharged atoms while evaluating V_{ij}^{LJ}. For studying different types of clusters, the standard values of σ and ϵ are used. The second term is the Coulombic interaction with z_i and z_j being the magnitudes of the charges on the interacting atoms, e is the electronic charge, and r_{ij} is the distance between the charges i and j. In the simplest formulation, of the n atoms, $n-2$ are neutral and the other two possess one unit of positive charge each. The third term calculates the energy contribution due to induced dipole effects. μ_i^{ind} is the induced dipole moment of atom i and E_i^{Coul} is the electric field at atom i due to charges only. The induced dipole moment will obviously depend on the polarizability α of the particular atomic species concerned. Hence it is expected that among the three types of clusters we are studying, Xe_n^{+2} should have the largest attractive interaction originating from this term. So we expect that the critical size for Xe_n^{+2} cluster above which no Coulomb explosion will occur would be comparatively smaller. We note here that in real dipositive inert gas clusters, the two units of positive charges are expected to get rapidly delocalized over the n atoms by charge transfer (covalent) interaction following the creation of the charges. The potential in Eq. (1) used by us neglects this charge delocalization. The critical size for stability of the dipositive clusters is not expected to be strongly affected by this approximation as the charge delocalization will only add slightly to the overall stabilization of the cluster. However, the fragmentation pattern may be strongly affected by the presence or absence of charge delocalization effects. For finding out the

fragmentation patterns, we have used the potential of Goldberg *et al.*,[24] a discussion of which is presented in Sec. III.

Now, having defined the problem, our task is to minimize V defined in Eq. (1) for the three systems at various cluster sizes and check whether the global minimum structure preserves the entire cluster framework or ejects some entities in the process. As we have stated earlier, the problem is a nontrivial one and getting trapped in a local minimum which might give counterintuitive results is a high possibility. To be able to assess critical sizes below which the cluster fragments spontaneously, we need the global minimum unequivocally. So we need a true global optimizer and GA is the one which we have used in the present study.

GA[6,28–33] mimics the Darwinian concept of survival of the fittest and the biological processes of crossover and mutation to solve optimization problems of high degrees of complexity. It starts by creating a pool of starting trial solutions. So, from inception it is different from other techniques. In GA, one evolves a pool of trial solutions and not a single one. The trial solutions which we call strings in GA terminology contain simply the Cartesian coordinates of the n atoms of the clusters and are represented as follows:

$$S_1 = x_1^1, y_1^1, z_1^1, x_1^2, y_1^2, z_1^2, \ldots, x_1^n, y_1^n, z_1^n,$$

$$S_2 = x_2^1, y_2^1, z_2^1, x_2^2, y_2^2, z_2^2, \ldots, x_2^n, y_2^n, z_2^n,$$

$$\vdots$$

$$S_k = x_k^1, y_k^1, z_k^1, x_k^2, y_k^2, z_k^2, \ldots, x_k^n, y_k^n, z_k^n,$$

$$\vdots$$

$$S_m = x_m^1, y_m^1, z_m^1, x_m^2, y_m^2, z_m^2, \ldots, x_m^n, y_m^n, z_m^n.$$

Here S_k denotes the kth solution and we have m number of plausible solutions in the population to start with. For each string, we evaluate the energy using Eq. (1) which leads to a quantity called the fitness of each solution. The fitness F is defined as

$$F = \exp\{-(V - V_L)^2\}, \tag{3}$$

where V_L is a suitable lower bound to the energy. The idea of introducing V_L is to guide the search to as low energy structures as possible. In the limit of V reaching V_L, the fitness F will rise to 1. Obviously the randomly selected initial strings will have low F values. Now we apply a sequence of operations, which are termed selection, crossover, and mutation in GA terminology. The selection operation selects a set of m solutions from the existing set discarding the strings with low fitness and keeping the better ones and possibly increasing the frequencies of occurrence of the better ones. Obviously, as the size of the solution set is kept constant, we hope to get multiple copies of the better strings. There are various methods of doing the selection and the one we use is called the Roulette wheel procedure.[28] The selection process has a bias and is expected to increase the average fitness of the population. To evolve our solution set, we need to introduce new information into the starting set. In GA, crossover creates new string by interpolation. In crossover, we select a certain number of strings, say, about a quarter randomly and collect them in pairs. One of the pairs is chosen for which we select a site for crossover (say, the ith site randomly) with a preset probability p_c and swap information to create two new strings as shown below. If string S_1 and S_2 have been selected, then the process goes as follows:

$$S_1 = x_1^1, y_1^1, z_1^1, x_1^2, y_1^2, z_1^2, \ldots, x_1^i, y_1^i, z_1^i, \ldots, x_1^n, y_1^n, z_1^n,$$

$$S_2 = x_2^1, y_2^1, z_2^1, x_2^2, y_2^2, z_2^2, \ldots, x_2^i, y_2^i, z_2^i, \ldots, x_2^n, y_2^n, z_2^n,$$

which becomes

$$S_1' = x_1^1, y_1^1, z_1^1, x_1^2, y_1^2, z_1^2, \ldots, x_2^i, y_2^i, z_2^i, \ldots, x_2^n, y_2^n, z_2^n,$$

$$S_2' = x_2^1, y_2^1, z_2^1, x_2^2, y_2^2, z_2^2, \ldots, x_1^i, y_1^i, z_1^i, \ldots, x_1^n, y_1^n, z_1^n$$

after crossover and the other pairs undergo a similar process. After crossover, it is the turn of mutation. Mutation is designed to occur with a very low probability as it does in real biological systems. The coordinates in a string are selected randomly with a probability p_m for mutation. If the x_1^2 coordinate, for example, is selected then after mutation it becomes

$$x_1^2(\text{mut}) = x_1^2 + (-1)^i r\Delta.$$

Here i is a random integer, r is a random number between 0 and 1, and Δ is the amplitude of mutation. So mutation basically changes a given coordinate by a random positive or negative increment. After all these changes have been done, the transformed strings are checked for their fitness, compared to the ones we started with, the best m among these are picked up, and the procedure is carried on iteratively until a string of maximum fitness emerges. The string of maximum fitness is hopefully the solution we are seeking, with optimized coordinates and hence the optimized interatomic lengths and orientations. The search process is manifestly derivative-free and trivially parallelizable. The ease of implementation and global character of the search makes our GA-based method a viable and powerful alternative tool for understanding noble gas cluster ions.

III. RESULTS AND DISCUSSION

We have carried out calculations on Ar_n^{+2}, Kr_n^{+2}, and Xe_n^{+2} clusters for various values of n. To depict the Coulomb explosion in a succinct pictorial manner, we calculate the deviation of a given interatomic length from the mean. If $\vec{R}_i$ are the individual length vectors, we calculate $\vec{R}_0 = (1/n)\Sigma_i \vec{R}_i$, which is the mean length vector. Now for each atom we calculate $r_i = |\vec{R}_i - \vec{R}_0|$ and then plot the number of interatomic lengths falling within the range r_i and $r_i + dr_i$. The plots for the nine clusters studied are given. In cases where explosion occurs, the plots show finite number of lengths at significantly high values of r_i and the tail of the figures plotted extends up to large r_i.

The GA used by us works with a population of ten trial solutions. The Roulette wheel selection was used. The crossover operation was carried out with a fixed crossover probability ($p_c = 0.5$) while mutation was allowed to occur with probability $p_m = 0.05$.

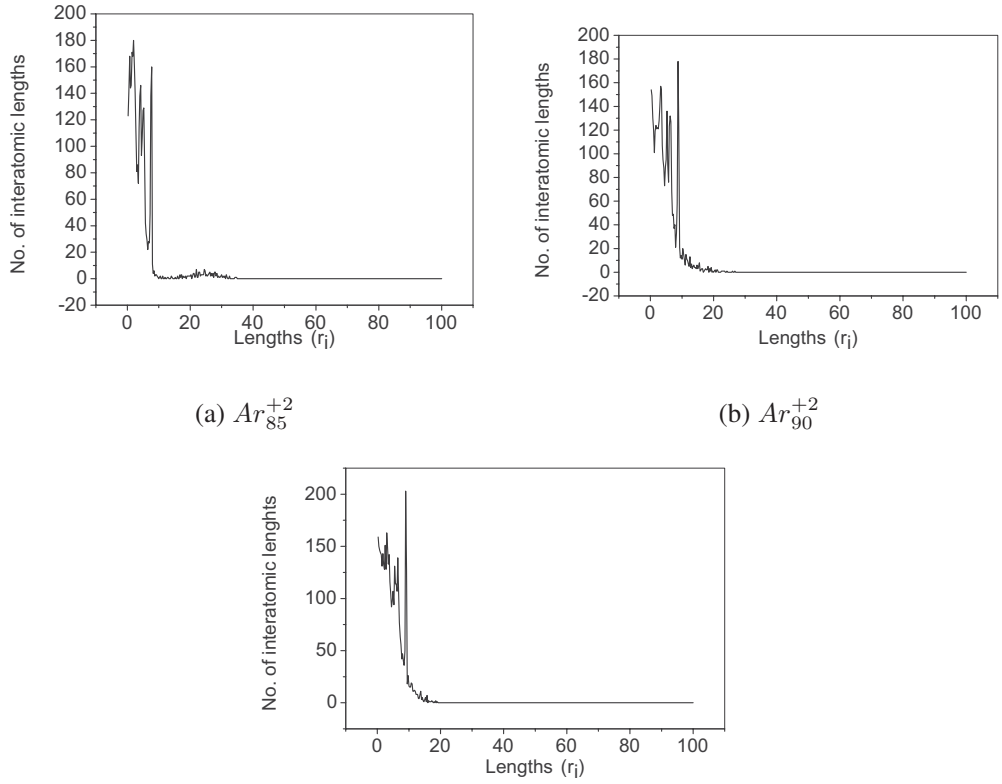


FIG. 1. For Ar clusters (doubly charged) [(a)–(c)]: distribution of distances (in Å) of atoms to the center of the cluster.

For Ar_n^{+2} the experimental critical value of n above which clusters are stable is $n=89-91$.[18,19] We have carried out GA optimizations for various sizes and report the ones with $n=85$, 90, and 95. For $n=85$, we show a graph depicting the number of interatomic lengths for increments of 5 Å in Fig. 1(a). The result clearly shows that there is a substantial number of lengths at very high values, i.e., above 50 Å. So for $n=85$, the Coulombic repulsive force has prevailed over the attractive ones and the cluster is no more stable as one unit. The results for $n=90$ and $n=95$ are shown in Figs. 1(b) and 1(c), respectively. At $n=90$ all the lengths are within 35 Å. This is a reasonably compact structure [Fig. 2(b)], taking into consideration the large size. Hence, at this value of $n=90$, the forces balance out to give a stable entity. The predicted structures are shown in Figs. 2(a)–2(c). For $n=95$, the cluster is stable as expected as now the stabilizing forces have started to prevail over the repulsive ones. In Table I, we have compared three energy components V_{LJ}, V_{Coul}, and $V_{ion\text{-}dipole}$ for Ar_{85}^{+2}, Ar_{90}^{+2}, and Ar_{95}^{+2}, respectively.

For Kr_n^{+2}, the experimental cutoff value for stability is $n=72-73$.[34] The cutoff value is expectedly lower than argon since the polarizability of Kr is greater. The dipole-dipole and dipole-induced dipole interactions will be stronger for systems with larger polarizability. So even at a lower value of n, the Coulombic repulsion is outweighed and a stable system results. We show the results for three values: $n=70$, 72, and 75. In Fig. 3(a) which is for $n=70$, a large number of interatomic lengths is seen to be above 55 Å. The cluster is thus unstable as a single unit. For $n=72$, all lengths are within 25 Å [Fig. 3(b)]. The cluster has achieved stability and Coulomb explosion does not occur. The threshold value for stability is correctly predicted. For $n=75$, the cluster is already above the critical limit and stable as a single entity as expected [Fig. 3(c)].The predicted stable structures for Kr_{70}^{+2}, Kr_{72}^{+2}, and Kr_{75}^{+2} are shown in Figs. 4(a)–4(c), respectively. The energy components are reported in Table II.

In Xe_n^{+2}, the experimental cutoff limit for cluster stability[14] is much smaller and is around $n=53-55$. This is

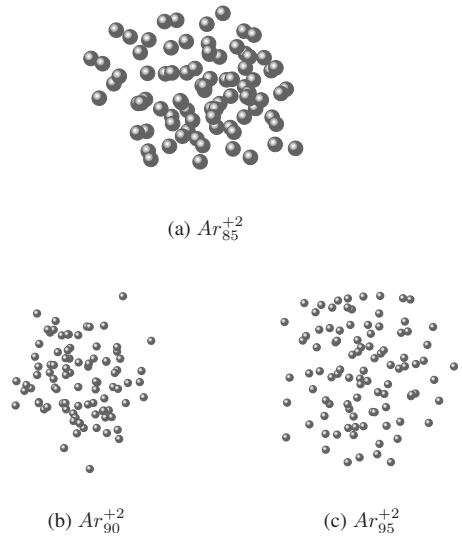


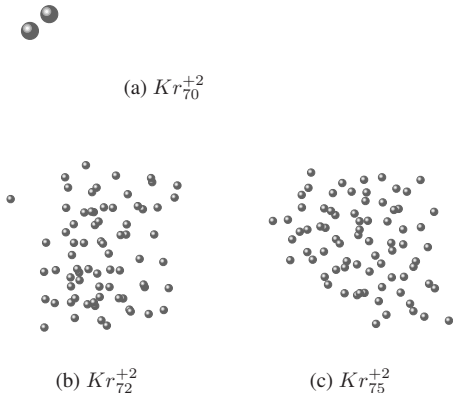
FIG. 2. Optimized structures of doubly charged Ar clusters [(a)–(c)].

TABLE I. Energy components.

	V_{LJ} (a.u.)	$V_{Coulomb}$ (a.u.)	$V_{ion\text{-}dipole}$ (a.u.)	V_{tot} (a.u.)
Ar_{85}^{+2}	−613.63	34.53	−110.93	−690.03
Ar_{90}^{+2}	−698.17	37.97	−64.34	−724.54
Ar_{95}^{+2}	−775.02	91.48	−82.75	−766.293

an expected result, as compared to argon or krypton; xenon has the larger polarizability. For $n=50$, a large number of lengths is above 55 Å. The cluster is unstable and the Coulomb explosion has occurred [Fig. 5(a)]. For $n=55$ all lengths are within 25 Å and for $n=60$ the cluster is stable with a very compact distribution of interatomic lengths [Figs. 5(b) and 5(c)]. The correct threshold for Xe_n^{+2} is thus predicted.[14,19] The predicted structures of Xe_{50}^{+2}, Xe_{55}^{+2}, and Xe_{60}^{+2} are depicted in Figs. 6(a)–6(c), respectively. The energy components are predicted in Table III. One would be curious to know how the computed energy of the best string in a population evolves under the evolution. A representative energy evolution profile, under GA, for Xe_{50}^{+2} is given in Fig. 7. The same pattern has been observed in almost all the cases reported. We note here that our results are valid for the Coulomb explosion at zero temperature. For nonzero temperatures, the algorithm needs to be modified (see later).

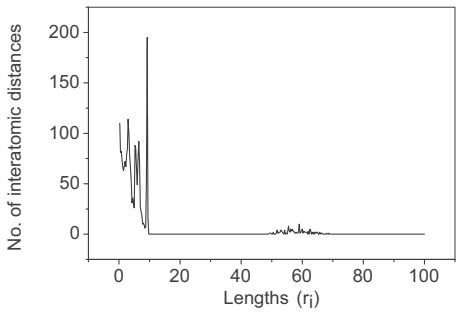
The immediate question that confronts us in the study of cluster explosion and fragmentation is whether we can predict not only the critical size for the suppression of explosion in dipositive noble gas clusters but also the actual fragmentation pattern in situations where the cluster indeed breaks up. The fragmentation pattern for Ar_n^{2+} clusters is very well studied by MD simulation and substantial amount of impressive literature exists in the subject.[24–27] The fragmented products largely follow two patterns: For certain size the



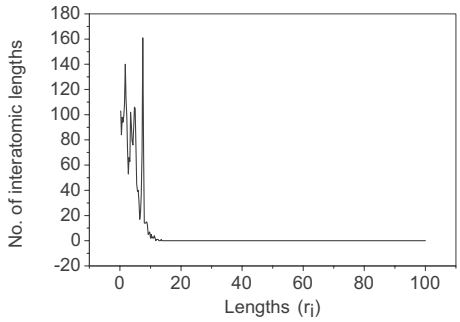
(a) Kr_{70}^{+2}

(b) Kr_{72}^{+2} (c) Kr_{75}^{+2}

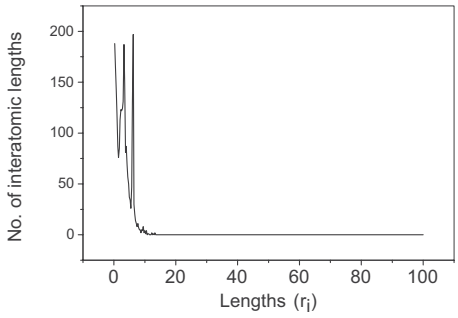
FIG. 4. Optimized structures of doubly charged Kr clusters [(a)–(c)].



(a) Kr_{70}^{+2}



(b) Kr_{72}^{+2}



(c) Kr_{75}^{+2}

FIG. 3. Doubly ionized Kr clusters of different sizes. [(a)–(c)]: distribution of distances (in Å) of atoms to the center of the cluster.

TABLE II. Energy components.

	V_{LJ} (a.u.)	$V_{Coulomb}$ (a.u.)	$V_{ion\text{-}dipole}$ (a.u.)	V_{tot} (a.u.)
Kr_{70}^{+2}	−378.67	19.16	−506.89	−866.40
Kr_{72}^{+2}	−376.09	75.11	−577.11	−878.09
Kr_{75}^{+2}	−398.72	71.59	−680.27	−1007.40

product is predominantly fission type, while in others it is nonfission type with one predominantly large charged unit and a few very small neutral or charged units. Our preliminary investigations indicated that the potential defined in Eq. (1) was unable to predict the fragmentation channels, although it predicted the size threshold for stability correctly. It appeared that unless the charges on two noble gas atoms delocalize further and provide additional nuclei around which the atoms can regroup, fragmentation channels would not possibly appear.

For Ar_n^{2+}, previous studies by Goldberg *et al.*[24] showed that for $n \geq 55$, the product is fission type and for smaller sizes it is nonfission type. The simplest potential model that could explain such findings is as follows:[24] The Ar_n^{2+} system is considered to be made up of two pairs of unipositive charged atoms Ar_2^+ and $(n-4)$ neutral atoms. The distance of separation between atoms of different charged pairs is supposed to be much larger than the distances within the pairs.

The potential energy of interactions is calculated as a sum of pairwise interactions,

$$U = U^v + U^c + U^w + U^q, \tag{4}$$

where U^v is the potential energy of two valence-bound Ar_2^+ dimers,

$$U^v = U_{12}^v + U_{34}^v, \tag{5}$$

if atom pairs 1, 2 and 3, 4 are the ones carrying one unit positive charge each.

U^c is the Coulombic repulsion interaction between the $Ar_2^+ - Ar_2^+$ units,

$$U^c = \frac{U_{13}^c + U_{14}^c + U_{23}^c + U_{24}^c}{4}. \tag{6}$$

U^w is the potential of the van der Waals interaction between neutral atoms

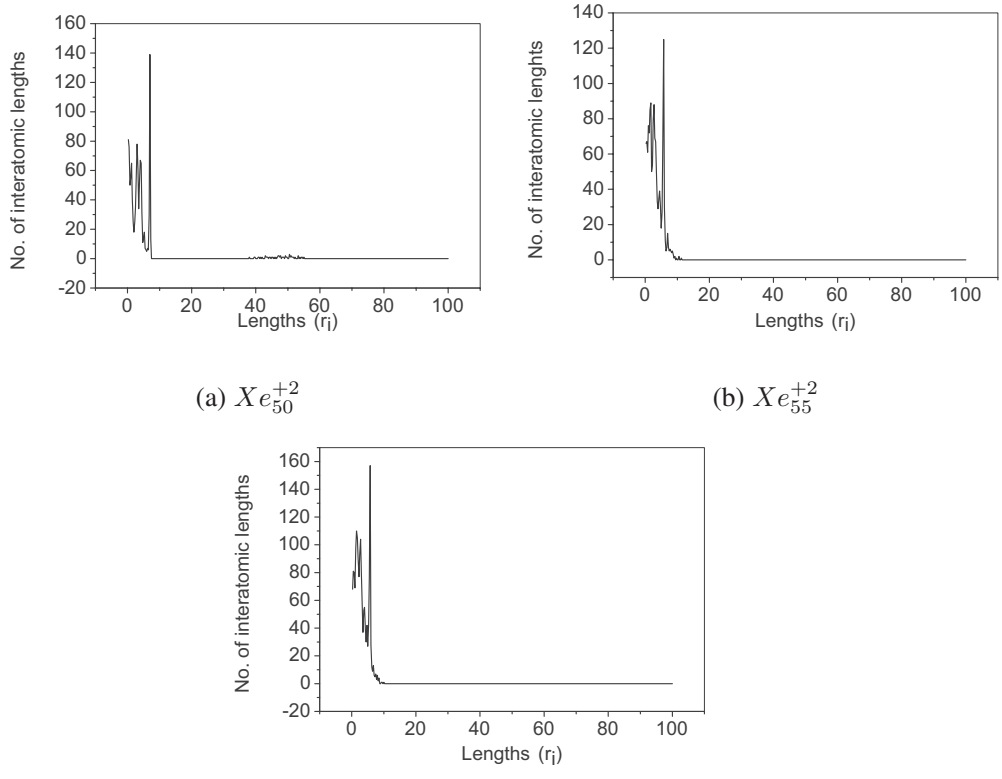
$$U^w = \sum_{i_1=5}^{n-1} \sum_{i_2=i_1+1}^{n} U_{i_1 i_2}^w \tag{7}$$

and U^q is the nonpolarization part of the $Ar^+ - Ar$ interactions in the absence of valence forces,

$$U^q = \sum_{i_1=1}^{4} \sum_{i_2=5}^{n} U_{i_1 i_2}^q. \tag{8}$$

For explicit expressions of the different types of pairwise individual energy components, a detailed discussion can be found in Ref. 24.

To make the potential energy expression even more realistic, one might include the polarization energy which in-



(a) Xe_{50}^{+2} (b) Xe_{55}^{+2}

(c) Xe_{60}^{+2}

FIG. 5. For Xe cluster [(a)–(c)]: distribution of distances (in Å) of atoms to the center of the cluster.

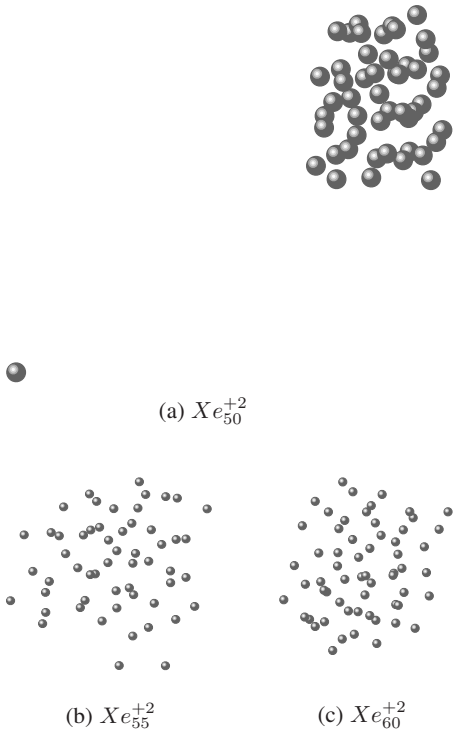


FIG. 6. Optimized structures of doubly charged Xe clusters [(a)–(c)].

volves interaction between the charged atoms and the polarized neutral atoms. This interaction will obviously not be pairwise in character because of more than one charged atom and the dipole-dipole interactions of polarized neutral atoms. However, for argon systems this polarization energy is small and if neglected should not lead to unphysical results. In actual calculations the critical size for stability is correctly predicted. Does it predict the correct fragmentation pattern?

We have carried out GA search for optimum structures for two sizes of dipositive argon clusters, one with 43 atoms and another with 55 atoms. Figure 8(a) depicts two separated cluster units accommodating one unit of positive charge for the Ar_{55}^{2+} cluster. For Ar_{43}^{2+}, an ejection of an Ar_2^+ unit and the formation of a large cluster accommodating the other positive charge is the observed fragmentation pattern, as depicted in Fig. 8(b). Goldberg *et al.*[24] predicted that Ar_n^{+2} clusters with $n \geq 55$ undergo fissionlike fragmentation. Our results echo the same finding.

Thus stability threshold as well as the predominant fragmentation channels in dipositive inert gas clusters can be predicted by our simple GA-based approach when the potential energy surface (PES) is appropriately chosen. We note here that the classical PES used by us has limitations although it provides low cost and fairly accurate predictions of stability threshold and fragmentation channels. It could be

TABLE III. Energy components.

	V_{LJ} (a.u.)	$V_{Coulomb}$ (a.u.)	$V_{ion\text{-}dipole}$ (a.u.)	V_{tot} (a.u.)
Xe_{50}^{+2}	−329.63	26.82	−548.43	−851.24
Xe_{55}^{+2}	−323.87	91.22	−751.45	−984.10
Xe_{60}^{+2}	−395.35	115.86	−808.33	−1087.82

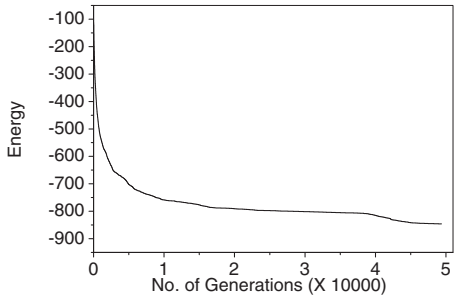


FIG. 7. Energy (in a.u.) evolution profile for Xe_{50}^{+2}.

possible, although quite costly to undertake *ab initio* quantum chemical calculations on the structures and stabilities of the noble gas cluster ions. The global minimum could still be missed unless the electronic structure calculation is interfaced with a global optimizer. In fact, a tight-binding GA-density functional theory (DFT) method has recently led to the prediction of certain unusual and hitherto unknown lower energy structures in ZnS clusters[35] and it would be interesting to explore the possibilities in the present context as well. *Ab initio* Car–Parinello dynamics[36] could be ideally invoked to explore the PES for locating globally minimum energy structures, thereby providing a means for calibrating the empirical PES used in our calculations and comparing fragmentation products. The fragmentation dynamics can also be followed by classical MD simulation and the effects of temperature on the fragmentation pattern can be understood. In principle a thermal GA (with Boltzmann selection) can be constructed and coupled with classical MD simulation for predicting fragmentation channels at nonzero temperatures. We are presently exploring these possibilities. The classical pair potential used in our study has limitations and these limitations arise from neglect of three and higher body effects and quantum corrections. While quantum effects would be important in situations dominated by tunneling, higher body effects would be important when energy differences are calculated. In the present context their neglect may not be unrealistic.

IV. CONCLUSION

We have shown for the first time that a GA-based search on a suitable hypersurface can predict finer properties of clusters such as fragmentation patterns, stability threshold, etc. For noble gas systems, one can write down classical

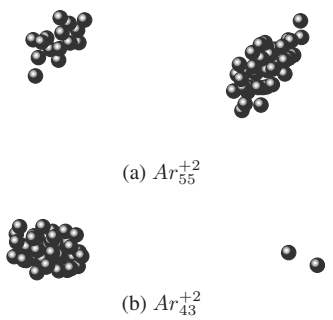


FIG. 8. Optimized structures of doubly charged Ar clusters Ar_{55}^{2+} (a) and Ar_{43}^{2+} (b).

potential energy functions incorporating all the necessary interactions that are important. We wish to extend our technique to other clusters such as metallic ones. For these systems a GA-based search coupled with energy calculations at the DFT level might give us valuable information about their relative stabilities and properties.

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