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A parallel tempering based study of Coulombic explosion and identification of dissociating fragments in charged noble gas clusters

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In this communication, we would like to test the feasibility of a parallel tempering based study of dissociation in dicaticonic noble gas clusters, namely, Ar$_n^{2+}$, Kr$_n^{2+}$, and Xe$_n^{2+}$, where “$n$” is the size of the cluster units. We would like to find out the correct limit for sizes of each of these systems, above which the clusters stay intact as a single unit and does not dissociate into fragments by the process of Coulomb explosion. Moreover, we would also like to, for a specific case, i.e., Ar$_n^{2+}$, study in detail the fragmentation patterns and point out the switchover from the non-fission way to the fission mechanism of dissociation. In all these calculations, we would like to analyse, how close we are in our predictions with that of experimental results. As a further check on the dissociating patterns found out by parallel tempering, we also conduct basin hopping based study on representative sizes of the clusters and find that parallel tempering, as used for this present work as an optimizer, is able to predict correct features when compared with other celebrated methods like the basin hopping algorithm. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4825404]

I. INTRODUCTION

The study of clusters, both atomic and molecular, bound to each other by the so called weakly interacting chemical forces like van der Waals or hydrogen bonding has become an increasing and popular area of activity for theoretical and experimental work in the field of Chemical Physics.1–11 These systems are interesting from different points of view. These clusters, with the increase in size, can support innumerable stable structures, which can be probed experimentally by the subtle difference in spectroscopic properties. The theoretical study of finding out these stable structures, especially the low lying minima and in particular the global, is an onerous task in itself. Several studies exist in literature which point out the inadequacies of using deterministic optimizers in evaluating these structures as the Potential Energy Surface (PES) of these cluster systems are highly rugged and support multiple minima, which increases at an astronomical rate with the increase in size of the cluster. Hence, increasing activity in this field has seen the use of non-deterministic or stochastic techniques, which have endowed them special powers to surmount the barriers separating the low lying or global minimum from the higher energy local minima. Several techniques are in vogue and the use of Simulated Annealing (SA),12,13 Genetic Algorithm (GA),14,15 and Basin Hopping (BH) Monte Carlo16,17 deserves special attention as successful techniques in this field. It must also be mentioned that the success of Molecular Dynamics (MD) Simulation18–20 in predicting structure and properties of loosely bonded cluster systems is commendable. Weakly bonded clusters are interesting from other aspects too, besides the great structural diversity they possess. These structures, for example, an Ar$_n$ system with a specific value of “$n$,” can transform from one configuration to another through a first order saddle point or Transition State (TS). The study of this entire transformation process and mapping out of a so called reaction path or minimum energy path (MEP) is a non-trivial one and reasonable success21–28 has been achieved in this regard by using the so called non-deterministic techniques.

A more interesting aspect of noble gas cluster dynamics comes in when the clusters are made electron deficient with the cationic charge becoming two units or more. In these systems, while the van der Waals forces between neutral atoms and the ion-induced-dipole forces try to hold the cluster together as a single unit, the extremely high coulombic repulsion between the charged units try to dissociate it. A competition thus results and it is seen that only above a particular size of $n = n_c$ (critical size), does the stabilizing forces outweigh the repulsion and the cluster remains intact without dissociating.29–45 The cut-off limit or critical size is lowest for Xe and highest for Ar. This is expected since the polarizability of these noble gas atoms decrease in the following order Xe > Kr > Ar. Experiments involving mass spectrometry corroborates the cut-off limits, which is $n_c ≈ 55$ for Xe, $n_c ≈ 70$ for Kr, and $n_c ≈ 92$ for Ar.34–36 The prediction of $n_c$ merely is not sufficient to study the dissociating dynamics of the clusters. All classical simulation studies try to allocate the two units of positive charge (for dicaticonic clusters) on certain number of atoms. The most obvious way is to allocate one unit on two different atoms, measure the potential energy of the system, and then evolve the structure to reach a minimum using MD or SA/GA and check the structure once a minimum is reached. The work by Berne30 on (Xe)$_n^{2+}$ clusters deserves a special mention in this context. Though this allocation predicts the correct $n_c$, the details of fragmenting patterns for smaller sizes of clusters are somewhat erroneous and lacking in accuracy. For (Ar)$_n^{2+}$ clusters, the model proposed by Goldberg et al.41 where two (Ar)$_2^2$ units accommodate...
the entire positive charge is a more acceptable description of reality. Not only does this model and the following potential predict the correct $n_c$, it is also successful in predicting the correct patterns of dissociation. It is known from experimental studies that for $(\text{Ar})_{2n}^+$, if $n \leq 55$, the dissociation is of non-fission type, and above it fission like pathway is the dominant form of dissociation. The fission type fragmentation is popularly known as coulomb explosion. The parameter which can explain the switchover from non-fission to fission is the Rayleigh instability limit $Z$. $Z$ is defined as the ratio of the coulomb energy $E$ (coulomb) and the surface energy of the cluster $E_s$ (surface). If $Z > 1$, the result is a coulomb explosion with fission like fragments and for $Z < 1$ only non-fission like phenomenon occurs. In this communication we would like to use the potentials as proposed by Berne and Goldberg and couple it with the optimization technique of Parallel Tempering (PT) to see how a randomly chosen set of coordinates defining a guess structure of a $(X_n)^{2+}$ cluster (where $X = \text{Ar, Kr, Xe}$) evolve and does it really predict dissociation or stability with change in size “$n$.”

As these cluster systems with van der Waals interaction can support a large number of structures, we envisage that only the global minimum or the one which is close to it can predict the right structural patterns. So one must resort to the use of a non-deterministic global strategy and we take PT as our choice. PT is a technique which creates replicas of guess structures at various temperatures and keep a provision for exchanging information or swapping among replicas. The power of the method lies in the fact that since parallel simulations are carried on at various temperatures ranging from high to the low, one can do a large sampling of search space (at higher temperature) and a more focused narrow search (at lower temperature). The allowance of exchange makes it possible to efficiently switch over from a gross search to a refined search and quickly converge to the minimum. The method is more sensitive and the identification of the cores with the right parameter to evaluate, little deviation from expected results is incorporated. However, the fragmentation patterns are not allowed. Since the cut-off value $n_c$ is a less sensitive parameter to evaluate, little deviation from expected results is expected, even if widespread smearing of the positive charges is not incorporated. However, the fragmentation patterns are more sensitive and the identification of the cores with the right size and the right amount of positive charge is of paramount importance, if we expect to do a better job in finding the details of the individual fragments. To this end, we have used a more refined potential as suggested by Goldberg et al. specifically for the study of $(\text{Ar})_{2n}^+$ dissociation.

In this model, the $(\text{Ar})_{2n}^+$ system is thought of as comprising of $(n - 4)$ neutral atoms and four charged atoms which are present as two $\text{Ar}_2^+$ cores. It is also assumed that the distance between the atoms of the same charged pair is much smaller than the distance between two different charged pairs. The potential energy of the system is then evaluated as a sum of different pair terms

$$V(\text{total energy}) = V^u + V^c + V^w + V^q.$$ (2.3)

Now $V^u$ is energy of interaction between two $\text{Ar}_2^+$ dimers which are valence bound

$$V^u = V_{12}^u + V_{34}^u.$$ (2.4)

where we have assumed that atoms 1, 2 and 3, 4 are the two charged pairs.
$V^c$ is the coulombic interaction between atoms in two different Ar$_2^+$ unit

$$V^c = \frac{V^c_{13} + V^c_{14} + V^c_{23} + V^c_{24}}{4}. \tag{2.5}$$

$V^w$ calculates the interaction between neutral atoms which is of van der Waals type

$$V^w = \sum_{i=5}^{n-1} \sum_{j=i+1}^{n} V^w_{ij}, \tag{2.6}$$

where the fact that the numbering of the neutral atoms starting from “5” is taken into account. Finally, the $V^q$ term is the Ar$^+ -$ Ar interaction without taking into account the polarization effect or this is the non-polarization part of the interaction only

$$V^q = \sum_{i=1}^{4} \sum_{j=5}^{n} V^q_{ij}. \tag{2.7}$$

A more elaborate discussion on the different terms of the potential can be found in Ref. 41. One can also refine this potential still by including terms which depends on the polarization aspect. This will make the potential depend on terms which have beyond two body interactions. However, for “Ar” which has only a moderate value of polarizability, even if this is not incorporated, the results are in the right line signifying the rather weak contribution of the polarization effect.

A logical question might come to mind at this point, as to why two different potentials have been used? This has been done purposely so that one can follow the improvement in the quality of results (finer points of coulomb explosion and not just the cut-off limit for suppression of coulomb explosion) with the improvement in the inherent model taken, to depict the system. The basic difference between the two is the allocation of charge on a dimer core Ar$_2^+$ and not on an isolated atom. Though the study involves use of these classical potentials, one might not forget about the quantum effects which will try to distribute the total magnitude of charge on a greater number of atoms rather than allocating one unit on a single atom. The identification of a dimeric unipositive core is a step in that direction. It will be shown in Sec. III that follows, the potential of Goldberg$^{41}$ (incorporating Ar$_2^+$ core) not only predicts the correct cut-off limits but also the finer details of fragmentation in comparison to the one of Brene et al.$^{36}$

One can thus write the overall partition function as

$$Q = \prod_{i=1}^{K} \frac{q_i}{N!} \int dr_i^N \exp \left[-\beta_i U(r_i^N)\right]. \tag{2.8}$$

Now $q_i = \prod_{j=1}^{N}(2\pi M_j/k_B T_j)$, which arises when the momenta are integrated. $r_i^N$ denotes the position of the N particles in the system, $M_j$ the mass of the jth particle, and $\beta_i = \frac{1}{k_B T_i}$ or the reciprocal temperature. $U(r_i^N)$ is the potential energy of the system and can be the energy described by any one of the two potential energy functions described in Sec. II A. If other factors are kept the same, then swapping or exchanging information between any two ensembles, ith and jth can happen with an accepting probability

$$P_{\text{swap}} = \min \left\{ 1, \exp \left[ (\beta_i - \beta_j) (U(r_i^N) - U(r_j^N)) \right] \right\}. \tag{2.9}$$

Generally, swaps are performed between ensembles at adjacent temperatures, however, it is not a hard and fast rule. If swaps between two systems, hugely differing in temperatures is performed, the acceptance probability of such a move becomes nominal. At this moment, a parallel can be drawn with the simulated annealing method and it is worth doing. The swaps happening between systems differing largely in temperature makes the method extremely potent. The temperature, in a way, controls the degree of movement in the search space and parallel large jumps as well as minute detailed moves can happen simultaneously as dictated by the magnitude of the temperature. However, in SA if one has to do a search at lower temperature, one needs to wait a long time for the initial high annealing temperature to drop to a low value. Having discussed the advantage that PT has over SA, it obviously gives the impression that, we in the present study intend to use PT as an optimizer. This is bound to raise certain valid questions and queries. However, we believe the caution and conditions in which we use PT makes its role as an optimizer justified. PT is a method, which is normally used to compute thermodynamic properties and total energy density of states. This is the overwhelmingly important area of using PT. It is true that replicas are created at various temperatures, ranging from a high to a low value and the simulation proceeds with evaluation of thermodynamic properties, which are functions of temperature. It is also expected that at finite temperature, entropic effects should also be pronounced. Keeping in mind, the above obvious features of PT, we have used the method in a way in which the replica at the lowest temperature (close to zero) is the one which gives the correct structural predictions regarding dissociating channels of charged clusters (discussed in detail in Sec. III). As the replica with temperature close to zero is the one we are focusing on, our results are essentially zero temperature results and the structural minimum at that temperature can be viewed as a critical point on the corresponding PES. Our logic of using PT as an optimizer to solve the current problem is based on these considerations, which are rigidly followed.

B. The PT method

In PT simulation,$^{36}$ one does not start with a single guess solution but “K” replicas of the system to be handled are generated, where each replica is in the canonical ensemble, but the replicas are assigned “K” different temperature values from $T_1$ to $T_K$ with gradual increase in magnitude. So $T_1 < T_2 < T_3 < \ldots < T_K$. So one can think of the partition function of the larger ensemble as a product of the individual partition functions as they are a set of non-interacting replicas. In PT simulation,$^{36}$ one does not start with a single guess solution but “K” replicas of the system to be handled are generated, where each replica is in the canonical ensemble, but the replicas are assigned “K” different temperature values from $T_1$ to $T_K$ with gradual increase in magnitude. So $T_1 < T_2 < T_3 < \ldots < T_K$. So one can think of the partition function of the larger ensemble as a product of the individual partition functions as they are a set of non-interacting replicas.

C. How the simulation is actually carried out

To calculate the energy of a system, one needs to know the distance between each and every particle in the system.
“$K$” replicas of the system are created by initially guessing the co-ordinates of each atom. Once the initial co-ordinates are set up, the energy ($E$) of the system is evaluated using the potential energy function. The cost function is defined as

$$\text{cost} = |E_i - E|,$$

where $E_i$ is the lower bound of energy. The $E_i$ is supplied and may be updated during simulation. The simulation proceeds with the objective of lowering the cost.

To evolve the structures, some randomly chosen co-ordinates in a replica are picked up and are also randomly changed or mutated in the following manner:

$$r^K_i = r^K_i \pm r.\Delta.$$  

(2.11)

Here, $r^K_i$ is the $i$th co-ordinate in the $K$th replica and it is changed by an amount $r.\Delta$, where “$r$” is a random number between 0 and 1 and $\Delta$ is a changing or mutation amplitude supplied by the user. The change can happen randomly in the positive or negative direction. With new $r^K_i$, the new energy of the $K$th replica is calculated. The entire operation is carried out consecutively for all the replicas. Periodically, swaps are performed with the defined acceptance criteria between pairs of replicas and a track is kept as to the lowering of energy of the system (a flowchart of the simulation is given in Fig. 1). When further lowering in energy is not achieved, even after a number of swaps, the lowest energy solution is taken out and analysed to check the results of the process. A profile of cost function vs. PT simulation steps (for $Ar_{85}^{3+}$ of potential mentioned in Ref. 26) is presented in Fig. 2 to show how the convergence occurs. This is only a representative profile. Similar types of profile may be drawn for each cluster system.

III. RESULTS AND DISCUSSION

A. PT simulation with potential having charges located on two different atoms only

To calculate the correct cut-off limit for suppression of coulomb explosion ($n_c$), we use the potential energy function as given in Eq. (2.1). As has been discussed in Sec. II, we only expect to get the correct $n_c$ from this kind of potential as it does not account for a greater charge delocalization and is devoid of any particular core within the cluster which contains the positive charges. To get a measure as to whether a cluster of ($X_n$)$^{2+}$ [$X = Ar, Kr, Xe$] has indeed dissociated, we also do a calculation of the numbers of inter atomic lengths that falls within a narrow range so as to generate a distribution function. From the optimized structures of the clusters, one can calculate the individual length vectors $\vec{R}$, where “$i$” corresponds to a given atom. Then one can proceed with the calculation of a distribution function of lengths by counting the numbers of $R_i$’s within a small range $R$ and $R + dR$. The existence of substantial number of length vectors $\vec{R}$ at sufficiently high “$R$” signifies dissociation of the cluster. The approach used by us in this paper to evaluate the distribution of interatomic distances in predicting coulomb explosion is obviously not an unique one. There are equally impressive method which can be employed to solve the problem like the depth-first search algorithm as discussed by Wales et al. or the procedure of Stillinger to identify a fragment of dissociated atoms if they lie within a given assigned distance which is meaningful for a fragment. However, the simple approach used by us also satisfies the ultimate objective. For ($Ar_n$)$^{2+}$, we have calculated through PT simulations the optimized structures for $n = 80, 85, 88, 90, 95$. The structures are shown in Figs. 3(a)–3(e). It is observed that while $n = 80, 85$, and 88 clusters are not stable as a single unit (ejecting a positively charged Ar atom), the $n = 90$ and 95 clusters remain as a single entity. This result with $n_c = 90$ is the correct estimate for suppression of coulomb explosion in ($Ar_n$)$^{2+}$ systems and has been observed in experimental studies. The plots of the distribution of inter atomic lengths also support the findings. While for $n = 80, 85$, and 88 there are peaks in the distribution function at sufficiently high lengths (above 60 Å), the corresponding plots for $n = 90$ and 95 only show significant peaks at lower lengths (less than 25 Å). These plots are shown in Figs. 4(a)–4(e). For ($Kr_n$)$^{2+}$ systems, we have done simulation at $n = 70, 72$, and 75. While the cluster at $n = 70$ dissociates, the ones at $n = 72$ and 75 stay intact as a single unit. The cutoff $n_c = 72$ for ($Kr_n$)$^{2+}$ systems is again supported by experimental findings. The plots for the structures are shown in Figs. 5(a)–5(c) and the corresponding distribution of inter atomic lengths in Figs. 6(a)–6(c). In Fig. 6(a), as dissociation occurs one observes noticeable peaks at length values greater than 30 Å.
FIG. 3. (a)–(e) Optimized structures of $\text{Ar}_n^{2+}$ obtained by using the potential as given in Eq. (2.1).

FIG. 4. (a)–(e) Distribution of distances (in Å) of $\text{Ar}_n^{2+}$ structures presented in Fig. 3.
than 80 Å. For (Xe$_n$)$_2^+$, the results are presented for $n = 50$, 52, 55, and 60. The correct experimentally determined cutoff is around $n = 55$.$^{35}$ We observe the expected trends, with the clusters at $n = 50$ and 52 dissociating and the ones at $n = 55$ and 60 remaining intact as a single unit.$^{36}$ The structures are shown in Figs. 7(a)–7(d). The corresponding plots of the distribution of lengths are in Figs. 8(a)–8(d). The tail of the distribution extends to large values for $n = 50$ and 52 (signifying dissociation) while for $n = 55$ and 60 the distribution dies off at much shorter values of around 25 Å.

**B. PT simulation for (Ar$_n$)$_2^+$ system with two Ar$_2^+$ cores**

The earlier potential, though successful in one aspect (predicting the correct $n_c$) fails to account for the correct mode and channels of dissociation. To this end, we carry out a second set of PT simulation with the potential as given in Eq. (2.3). It is known in literature that only for $n \geq 55$ does a fission type pattern exists with each fission fragment containing an Ar$_2^+$ core while for $n < 55$, only non-fission is the resulting feature. So technically one should call $n \geq 55$ as the onset of discernible coulomb explosion which extends up to a size of nearly 88 or 89 and at $n = 90$ the cluster becomes
stable as a single unit (the cutoff in \((\text{Ar}_n)^{2+}\) systems for suppression of coulomb explosion). With this potential, we have done simulations for \(n = 40, 45, 50, 55, 65, 70, 85, 90,\) and 95. The structures of the optimized clusters are shown in Figs. 9(a)–9(i). While in \(n = 40, 45,\) and 50 only single atomic units come out, for \(n = 55, 65, 70, 85\) two fission fragments of significant sizes separate out.\(^{41}\) For \(n = 90\) and 95, the clusters are stable, as expected since \(n_e = 90\) for \((\text{Ar}_n)^{2+}\). The corresponding interatomic lengths distribution plots are shown in Figs. 10(a)–10(i). In situations where the clusters suffer dissociation, whether it is non-fission or fission, the tail of the distribution extends to higher values of lengths (up to about 45 Å). For stable clusters \(n = 90\) and 95, a sharp and much shorter tail is observed with the plot decaying at a value of around 20 Å. If one compares the situations where dissociation occurs for the two different potentials chosen for the study, the first potential with no \(\text{Ar}_2^{2+}\) core has a much longer distribution tail. This is excepted since here two \(\text{Ar}\) atoms possess one unit of positive charge and the overriding tendency is to eject out one \(\text{Ar}^+\) unit away from the main bulk of the cluster as far as possible.

C. Detail analysis of PT based simulation results

While analysing the results of PT simulation, where various replicas are created at different temperatures ranging from a high \(T_{\text{max}}\) to a low \(T_{\text{min}}\) (Table I), certain clarifications and comments must be made to avoid obvious conclusions which might not be correct. It must be emphasized that the temperature at which the search proceeds in a given replica is not the temperature of the system. It is only a parameter in the optimization process which controls the degree of exploration of the search space. So the conclusion that a replica at a higher temperature, owing to its higher entropy should dissociate and if swapped with a low temperature zone would have no chance to re-adjust and come back to a compact structure is not strictly applicable. During the swapping process, the fact that the system at the lowest temperature should ultimately converge to the global minimum is also justified. This is because as the simulation proceeds with routine mandatory swaps, near the termination of the optimization process the replica at \(T_{\text{min}}\) gives the best fine tuned results, as at \(T_{\text{min}}\) a more focused narrow search with minor adjustments in optimization parameters can take place easily. The fine tuning, rather than large hopping on the search space at higher temperature holds the key to find the best solution to the problem being solved. If the final cluster is a dissociated one, one gets that particular solution and if a compact, undissociated cluster is a global solution, as is the case for certain sizes in certain systems, the corresponding expected result is obtained. So in a nutshell, it is not the fact that higher temperature simulations will give a fragmented cluster not in keeping with reality or experimentally observed data.

To demonstrate this point, we show in Fig. 11 the state of four instantaneous systems (after full optimization) at different temperatures. Fig. 11(a) is the highest temperature one with \(T_{\text{max}} \approx 5 \times 10^3\) and Fig. 11(d) is the one at \(T_{\text{min}}\). The other two, Figs. 11(b) and 11(c) have intermediate...
temperatures. The system observed here is $\text{Ar}^{2+}_{85}$. The experimentally observed structure for this size is a dissociated cluster with nearly unsymmetrical fission. This is the solution or the global minimum for the problem and is in keeping with experimental observations. Fig. 11(d) where $\frac{T}{T_{\text{min}}} = 1$ is the correct solution and this is the one with minimum energy as $\frac{E - E_{\text{min}}}{E_{\text{min}}} = 0$ (since the “$E$” is also the minimum energy $E_{\text{min}}$ obtained from among the different energy clusters present among all the replicas).

To establish the analysis further, we take up a cluster system $\text{Xe}^{2+}_{55}$ which does not dissociate or in which the global minimum is not a coulomb exploded structure. Here, Fig. 12(d) is the one at $T_{\text{min}}$ ($\frac{T}{T_{\text{min}}} = 1$) and it is a compact undissociated cluster with $\frac{E - E_{\text{min}}}{E_{\text{min}}} = 0$. The higher temperature clusters in Figs. 12(a)–12(c) have less compactness or show signs of ejection of atomic/ionic entities as in Fig. 11(c).

To conclude this section, we have clearly showed that the temperatures of the replicas are only optimizational parameters which control the degree or extent of search and has no relation with the actual temperature of the system.

D. Comparison with GA based results

A study on these systems had been carried out with GA as the global optimizer as opposed to PT used in this study. If we look at Fig. 9 of the present study, a large number of simulation results for various sizes have been shown for $\text{Ar}^{2+}_n$ system with $n = 40, 45, 50, 55, 65, 70, 85, 90,$ and $95$. These studies are based on the potential in which two $\text{Ar}^{2+}$ cores have been considered. The prediction of Goldberg et al., that for $n \leq 55$ non-fission is the expected product, is also visible. The earlier GA study with the potential, as given by Goldberg, showed optimized structural results for $n = 43$ and 55 only. Hence, the present PT based study is a more in-depth one. For the other results using the potential as given by Berne, the PT results are in close correspondence with the earlier GA study but in the present PT based study a larger number of structures for $\text{Ar}^{2+}_n$, above and below the critical limit for suppression of coulomb explosion, have been studied. This is shown in Fig. 3, where $n = 80, 85, 88, 90,$ and $95$ size clusters have been studied. The gradual progress towards a compact undissociated structure is clearly evident.
FIG. 10. (a)–(i) Distribution of distances (in Å) of Ar$_{2}^{2+}$ structures presented in Fig. 9.

Though the PT and GA based studies give nearly the same cutoff for suppression of coulomb explosion, we believe that in PT the different temperatures of the different replicas give a search strategy which is simultaneously focused for low temperature replicas and broad based for high temperature ones. This feature gives PT a high potency and achievement of global minimum structures with relatively less computational effort. However, it must be stated that GA is also a highly potent procedure but the use of temperature as a dictator of the extent of sampling of the search space is something which it lacks.

TABLE I. Details of parallel tempering simulation.

<table>
<thead>
<tr>
<th>No. of temp. zone</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{i}/T_{i+1}$</td>
<td>Varies 0.5–0.65 for different systems</td>
</tr>
<tr>
<td>$T_{\text{min}}$</td>
<td>$\sim 10^{-4}$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Gradually decreased from 3.0 to 0.1</td>
</tr>
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E. Results on Coulomb explosion using the basin hopping algorithm

Having used PT as our algorithmic choice in elucidating the cutoff “$n_{c}$” for suppression of coulomb explosion and predicting the switchover from a non-fission to a fission like dissociative mechanism for Ar$_{n}^{2+}$ clusters, we try to analyse, how our results stand vis-a-vis the celebrated BH strategy. A logical and expected question that might arise in using PT is that it uses simulations at finite temperatures and entropic effects are expected to be substantial. The other question that might come in mind is that PT should be a better choice for evaluating quantities like density of states and thermodynamic averages, rather than as an optimization strategy. However, it must also be kept in mind that the use of PT as an optimization tool endowed with stochasticity is already pursued by other workers and is not totally uncommon, though not that frequent as other methods. If we look at the results presented by us using PT minutely, we see that in all the simulations on different sizes of the clusters, we report only those as our results, which are obtained after longtime samplings.
and are the equilibrium stable structures for that particular size. Moreover, it is also clear that the correct coulomb explosion features which corroborate with experimental findings are obtained for the replica, where the simulation temperature is $T_{\text{min}}$ and $T_{\text{min}} \approx 0$ for all the results. As $T_{\text{min}} \approx 0$, we safely conclude that for the specific problem we have dealt with, the entropic contribution is negligible and the simulation temperature has no relation with the actual system temperature. Since “PT” must be carefully used with caution, if it is to be considered as an optimizer, we have proceeded to do a BH search also in addition to the previously published results with GA. BH is a scheme which uses the strong points of both deterministic search as well as stochastic Metropolis sampling. In BH the surface on which the search is carried out, is effectively transformed into basins, where each basin is the presence of a local minimum of the system. The maxima on the original surface becomes inconsequential and the effective surface becomes much simple, though regions having high energy barriers separating the local minima might remain. Then a sampling scheme using an effective simulation temperature can help one to hop from one basin to another and effectively locate the global minimum. BH and its variants, i.e., the multi-canonical BH scheme has been successful in solving problems of true complexity and the range

![Diagram](image_url)
of work of Wales\textsuperscript{1,2,10,11} and other workers\textsuperscript{63,64} is a testimony to that fact. We apply PT along with BH\textsuperscript{65} in order to obtain the global minimum structures for the cluster systems. In our previous discussion, we have already mentioned about the two interatomic potentials, the first one being successful in predicting the correct cut-off limit \( n_c \) for suppression of coulomb explosion in \( \text{Ar}_n^{2+} \), \( \text{Kr}_n^{2+} \), and \( \text{Xe}_n^{2+} \). In Figs. 13(a) and 13(b), we show the results for \( \text{Ar}_{85}^{2+} \) and \( \text{Ar}_{95}^{2+} \) while in Figs. 13(c)–13(f) the respective results for \( \text{Kr}_{75}^{2+} \) and \( \text{Kr}_{75}^{2+} \) and \( \text{Xe}_{50}^{2+} \) and \( \text{Xe}_{65}^{2+} \) are given. These sizes were purposely chosen as they bracket the correct cut-off limits in each case \([n_c \sim 90 \text{ for } \text{Ar}_n^{2+}, n_c \sim 72 \text{ for } \text{Kr}_n^{2+}, n_c \sim 55 \text{ for } \text{Xe}_n^{2+} \]). In each, the size slightly lower than the correct cut-off shows dissociating trends while those above remain intact. Having obtained the correct cut-off using the potential according to Berne,\textsuperscript{36} we further examined for \( \text{Ar}_n^{2+} \) using the second potential according to Goldberg et al.\textsuperscript{41} These simulations were carried out for \( \text{Ar}_{55}^{2+}, \text{Ar}_{65}^{2+} \), and \( \text{Ar}_{75}^{2+} \) and the structures are shown in Fig. 14. \( \text{Ar}_{95}^{2+} \) remains intact, as expected, being larger in size than \( n_c \sim 90 \text{ for } \text{Ar}_n^{2+} \). \( \text{Ar}_{75}^{2+} \) dissociates but the pattern is one of non-fission, with a few isolated “Ar” atoms being ejected from the main core. For \( \text{Ar}_{65}^{2+} \), a relatively larger chunk is ejected from the main body of the system and this can be viewed as a fission like fragmenting pattern as is expected for this size. As the “BH” results corroborate with a high degree of accuracy the results of PT based simulations, we conclude that “PT,” keeping in mind the cautions that we have been exercised, is a justified algorithm to solve the present problem.

If one looks at the results obtained from the Berne potential by using PT and BH techniques, one notices some discrepancies. In Fig. 3, which shows the PT results, the clusters which fragment ejects out only a single atom from the main body. In BH method, for the same potential (Fig. 13) ejection of a fragmented unit rather than a single atom is observed. This we believe is due to the BH method having been successful in finding out alternative fragmented structures from the search space, which PT has not been able to do. Ejecting out a single atom on account of the strong electrostatic repulsion is one obvious solution to the problem but other possibilities also remain, which the BH method has been able to find out. These results also correspond to the results reported in Ref. 66.

### IV. CONCLUSION

We have shown that non-deterministic simulation techniques in conjunction with adequately defined potential energy functions and models of cluster structure can correctly predict the essential features of fragmentation and dissociation in charged dicaticonic noble gas clusters. Both the gross feature of the cut-off limit for coulomb explosion to be suppressed as well as the details of the fragmentation patterns can be quickly arrived at. Better is the model for the cluster structure, the more successful will be the endeavor in finding out the finer details of cluster fragmentation dynamics.

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