Alkali-metal ion in rare gas clusters: global minima

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Abstract

Structural optimization for heteronuclear clusters consisting of one alkali-metal ion and of up to 79 neutral rare gas atoms has been carried out. The basin-hopping Monte Carlo minimization method of Wales and Doye is used. Rare gas atoms interact with the Lennard–Jones potential, whereas the interaction between a neutral atom and an ion impurity is given by the Mason–Schamp potential. Starting from eight rare gas atoms the alkali-metal ion is always inside a cluster.

Key words: Global optimization, Basin-hopping method, Nanoparticles

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1 Introduction

Rare gas clusters are important and often studied aggregates of atoms [1]. Their mass spectra show the presence of magic numbers which correspond to

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the most stable geometrical structures [2]. Because of the simple form of van der Waals chemical bonding rare gas clusters are very suitable for theoretical studies. For each cluster size different isomeric structures exist. They are local minima in the multidimensional potential energy surface. The number of these isomers increases rapidly with the size of a cluster. Several methods of a search for global minima were invented [3,4,5,6,7,8,9,10,11,12,13,14]. When the size of clusters increases it becomes more difficult to find the lowest minimum on the potential energy surface. Optimization methods locate only the candidate for a global minimum.

The problem of interaction between various clusters and impurities generated intensive research [15,16,17,18,19,20]. For example, impurities in helium nanoparticles were studied [15]. One goal was to determine whether impurity ions, atoms, or molecules preferably reside in the interior of the cluster, or on its surface. In general, the impurities substantially perturb the cluster matrix. It was found that a single metal atom drastically modifies the properties of silicon clusters [16,17]. Therefore, it is interesting to explore the shape deformation and the energy change induced by impurities. In this context rare gas clusters are especially interesting. They are inert and could play a role of the nanoscale chemical laboratory. A global optimization is one of theoretical methods suitable for investigation of the impurity-cluster interaction.

The most successful methods of global optimization for clusters are genetic algorithms [3,4,5,6] and a basin-hopping method [7,8,9,10,11,12,14]. The genetic algorithm methods select a fraction of the initial population of relaxed cluster structures as “parents” using their energies as the criteria of fitness. The next generation of cluster structures (“children”) is formed by “mating” these parents and the process is repeated until the minima are found. The
basin-hopping approach of global optimization for clusters was developed by Wales and Doye [7]. This method uses the energy minimization and the Monte Carlo simulation. The potential energy is transformed to a new surface which has the form of a multi-dimensional staircase. The steps correspond to the basins of attraction surrounding energy minima [21]. Each basin of attraction contains the set of configurations which after geometry optimization generate a particular minimum. The basin-hopping method is very powerful and, for example, finds all known energy minima for the Lennard–Jones clusters containing up to 110 atoms [7]. A similar method was used in the study of protein folding [22]. The Lennard–Jones nanoparticles play a role of the test system for global optimization methods. Molecule-doped rare gas clusters, in particular $H_2$ in $Ar_N$ [6], $Cl_2$ in $Ar_N$ [10], and $NO$ in $Ar_N$ [11], were also studied.

In general, the clusters with impurities are less studied by optimization methods than homonuclear ones. A small perturbation, for example one impurity atom, or ion, in a cluster may shed light on the global minima formation. In addition, new morphologies in the set of cluster structures may appear for some impurities. The methods of global optimization produce the candidates for minima of the free energy only close to $T = 0$ K. At higher temperatures kinetics effects are important and may change the order of stability of cluster isomers.

In this work I present the results of structural optimization for model heteronuclear clusters consisting of one impurity ion and of up to $N = 79$ rare gas atoms. The Lennard–Jones and Mason–Schamp potentials are used to describe interactions. The basin-hopping method is applied for structural optimization. The results show that an impurity ion is at the surface for a small number of rare gas atoms. It is always trapped in a cluster for $N \geq 8$ atoms. As
in homonuclear Lennard–Jones clusters, several particularly stable structures are found. In the following the computational method is described in Sec. II. Results and discussion are presented in Sec. III. A summary and conclusions are given in Sec. IV.

2 Computational method

The pairwise additivity and the spherical symmetry of the interaction for rare gas atoms are reasonably well described by the Lennard–Jones potential. This potential is one of the most used models of interaction. It is given by

\[ V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \tag{1} \]

where \( \epsilon \) is the depth of the potential energy minimum, and \( 2^{1/6} \sigma \) is the equilibrium pair separation [23]. The \( \sim r^{-6} \) is the leading term in the dispersion energy interaction for neutral atoms. Mason and Schamp proposed the additional term \( \sim r^{-4} \) to model the interaction of an ion and a neutral rare gas atom [24]. The Mason–Schamp potential is given by

\[ V(r) = \frac{\epsilon}{2} \left[ (1 + \gamma) \left( \frac{\sigma}{r} \right)^{12} - 4\gamma \left( \frac{\sigma}{r} \right)^{6} - 3(1 - \gamma) \left( \frac{\sigma}{r} \right)^{4} \right]. \tag{2} \]

The coefficients in this potential were determined from the ion mobility measurements in rare gases and calculations within the kinetic theory. Three parameters in algebraic form (2) specify the depth and position of the potential energy minimum, and the relative strength of various terms. The Mason–Schamp potential was used in the studies of impurities in rare gas crystals [25]. For example, the parameters of this potential for the \( Cs^+–Xe \) system
Fig. 1. The Mason–Schamp potential for \(Cs^+–Xe\) (full line), \(Rb^+–Kr\) (dotted line), and \(K^+–Ar\) (dashed line). The inset shows a comparison of the Mason–Schamp potential (dashed line) and the Lennard–Jones potential (full line) in reduced units where \(\epsilon = 1, \sigma = 1\).

are: \(\epsilon = 0.106\) eV, \(\sigma = 3.88\) Å, and \(\gamma = 0.2\). Figure 1 shows the Mason–Schamp and Lennard–Jones potentials. The Mason–Schamp potential was taken here in its reduced form as a model of a class of the alkali-metal ion and rare gas atom interaction. In the same sense the Lennard–Jones potential represents interaction between rare gas atoms in investigations of the global minima for homonuclear clusters \([4,5,13]\). The Lennard-Jones and Mason–Schamp potentials in the inset of Fig. 1 are drawn in reduced units where \(\epsilon\) and \(\sigma\) are chosen as the units of energy and distance. In the calculations the total potential was modelled by a pairwise sum of potentials given by Eq. (1) for each rare gas/rare gas pair of atoms, and by Eq. (2) for each rare gas/ion pair of particles. For both potentials reduced units for \(\epsilon\) and \(\sigma\) were employed.

I used a basin-hopping method and a modified program gmin of Wales and collaborators \([14]\). The constant temperature Monte Carlo method based on the
standard Metropolis scheme [26] is applied. Energy minimization is performed using the limited memory Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm for the unconstrained minimization problem [27]. For each cluster size five series of runs were done starting from different configurations. Each run consisted of 30000 Monte Carlo steps at a constant reduced temperature of 0.8. Control runs for homonuclear Lennard–Jones clusters have been carried out, and the same global minima were found as by Wales and Doye [7]. For sizes $N < 75$, direct optimizations from random configurations were able to produce known minima for homonuclear Lennard–Jones clusters within less than 10000 Monte Carlo steps. For $N \geq 75$, additional effort was necessary, either the increase of the number of steps, and/or seeding with configurations derived from the best structures around a chosen cluster size. For both homonuclear and heteronuclear clusters the lowest-energy structures were found at different Monte Carlo steps in five series of runs. Sometimes, different lowest-energy structures were found in these runs. Differences between various runs were especially pronounced for $N \geq 75$. Similar type of potentials are used for the atom-atom and atom-ion interactions and it is plausible that the same procedure is adequate for unknown energy minima of heteronuclear clusters. However, in heteronuclear systems the forces are determined not only by distances between particles, but their chemical identity is also important. In homonuclear clusters swapping the position of the particles does not change structural properties of the aggregate. For the system and the method presented in this work (where only one impurity particle, two similar potentials, and the Monte Carlo minimization method are used) the optimization tasks for homonuclear and heteronuclear clusters are analogous. In theoretical analysis of global optimization and NP-hard problems, the case of heteronuclear clusters is more difficult [28].
3 Results and discussion

Figures 2 and 3 show several configurations of an alkali-metal impurity in a rare gas cluster. This visualization is performed using the Rasmol package [29,30]. It is found that all lowest-energy structures of heteronuclear clusters are compact. The spacial distributions of particles does not change much in comparison with homonuclear Lennard–Jones clusters. The ion-atom distance is smaller than the atom-atom one. The lengths of the bonds and the angles between them change slightly. The ratio of the numbers of the atom-atom and ion-atom bonds increases with the cluster size. Therefore, a difference between corresponding homonuclear and heteronuclear clusters decreases when their size increases. The energy minima are presented in Table 1.

The situation where the alkali-metal ion is at the surface of a cluster is shown in Fig. 2(a-f). Figures 2(f) and 2(g) present configurations around the transitional regime of the ion. In Fig. 2(f) the impurity ion is deeply buried in the surface of the cluster, and lies closer to its centre than one rare gas atom. The ion is in the interior of the cluster the first time for eight rare gas atoms, as shown in Fig. 2(g). The impurity ion is also always in the cluster for more than eight rare gas atoms (Figs. 2(h-j) and Fig. 3). When the alkali-metal ion is solvated by rare gas atoms it is not always situated in the centre of the cluster. For example, the impurity ion takes a non-central position in clusters shown in Figs. 3(b-d).

The energies per particle are presented in Fig. 4(a). This quantity varies rather monotonically. However, mild minima occur for certain sizes and show particularly stable structures. This is further confirmed by the first energy differences
Fig. 2. The global minima configurations for one alkali-metal ion and: (a) 2, (b) 3, (c) 4, (d) 5, (e) 6, (f) 7, (g) 8, (h) 9, (i) 10, (j) 11 rare gas atoms. Light and dark balls correspond to the rare gas atoms and the alkali-metal ion, respectively. When the number of rare gas atoms is equal or greater than 8, the impurity ion is always inside the cluster.
Table 1

Energy divided with $\epsilon$ for the calculated putative lowest energy atomic configurations of $(N - 1)$ rare gas atoms and one alkali-metal ion.

| N | Energy/$\epsilon$ | N | Energy/$\epsilon$ | N | Energy/$\epsilon$ | N | Energy/$\epsilon$ | N | Energy/$\epsilon$ |
|---|-------------------|---|-------------------|---|-------------------|---|-------------------|---|-------------------|
| 3 | -3.000000        | 19 | -74.117047       | 35 | -157.959698      | 51 | -255.561479      | 67 | -352.320332      |
| 4 | -6.000000        | 20 | -78.669480       | 36 | -164.131670      | 52 | -262.641668      | 68 | -358.620511      |
| 5 | -9.170198        | 21 | -83.223757       | 37 | -169.413923      | 53 | -269.723630      | 69 | -364.991246      |
| 6 | -12.833944       | 22 | -88.512937       | 38 | -175.688479      | 54 | -276.837164      | 70 | -372.140719      |
| 7 | -16.609860       | 23 | -94.747096       | 39 | -182.644656      | 55 | -283.982317      | 71 | -378.708743      |
| 8 | -20.267149       | 24 | -99.271061       | 40 | -187.934276      | 56 | -288.408595      | 72 | -384.001154      |
| 9 | -24.603991       | 25 | -104.437908      | 41 | -193.313553      | 57 | -293.124190      | 73 | -390.193626      |
| 10| -29.845315       | 26 | -110.531823      | 42 | -199.171591      | 58 | -299.182087      | 74 | -396.341772      |
| 11| -34.559546       | 27 | -115.202264      | 43 | -205.377149      | 59 | -304.564977      | 75 | -401.715686      |
| 12| -38.823624       | 28 | -120.217617      | 44 | -210.799981      | 60 | -310.725716      | 76 | -407.874621      |
| 13| -44.948660       | 29 | -126.039309      | 45 | -217.099260      | 61 | -316.885236      | 77 | -414.039706      |
| 14| -48.507280       | 30 | -130.940143      | 46 | -224.073078      | 62 | -322.259510      | 78 | -420.198993      |
| 15| -53.015985       | 31 | -136.316374      | 47 | -229.513961      | 63 | -328.423273      | 79 | -427.364107      |
| 16| -57.557929       | 32 | -141.606686      | 48 | -235.929062      | 64 | -334.583581      | 80 | -433.748290      |
| 17| -62.572600       | 33 | -147.154918      | 49 | -242.915907      | 65 | -339.974002      |     |                   |
| 18| -67.609864       | 34 | -152.348526      | 50 | -248.498878      | 66 | -346.146925      |     |                   |
Fig. 3. The global minima configurations for $N + 1$ equal to: (a) 13, (b) 19, (c) 39, (d) 46, (e) 49, (f) 55, (g) 70, (h) 79 particles, where $N$ is the number of rare gas atoms. These structures are the most stable ones. Details as in Fig. 2.
\[ \Delta_1 = E(N) - E(N-1) \] shown in Fig. 4(b). Two minima at \( N = 13 \) and \( N = 55 \) correspond to well known filled icosahedral shells. In addition, minima occur for \( N = 19, 39, 46, 49, 70, 79 \). These most stable structures of rare gas clusters with an alkali-metal ion are shown in Fig. 3. Minima at \( N = 19, 46, 49, 70, 79 \) also exist for Lennard–Jones clusters (for example, see Fig. 4 in [5]). However, in homonuclear Lennard–Jones clusters minimum exist for \( N = 38 \). Figure 4(b) shows that for heteronuclear clusters corresponding minimum is \( N = 39 \). Shapes of \( N = 38 \) and \( N = 39 \) (see Fig. 3(c)) heteronuclear clusters are similar to each other and to Lennard–Jones \( N = 39 \). The Lennard–Jones \( N = 38 \) cluster is slightly more compact (see Fig. 1 in [12]). A shape of the \( N = 39 \) structure shown in Fig. 3(c) is closer to the third lowest energy minimum of Lennard–Jones \( N = 38 \), than to the first and second one. In connection with the complex double-funnel energy landscape of the non-icosahedral 38-atom Lennard–Jones cluster [12], it is interesting to point out that this magic size in heteronuclear nanoparticles is replaced by \( N = 39 \). Other non-icosahedral Lennard–Jones global minima occur for \( N = 75–77 \), and these clusters are Marks decahedra [7]. For clusters with the impurity ion, sizes \( N = 75–77 \) are decahedral in origin. As for icosahedral minima, these structures are distorted in comparison with homonuclear Lennard–Jones clusters. The flat region in Fig. 4(b) exist for \( 51 \leq N \leq 55 \). In these clusters the impurity ion is situated in the central position and the magic icosahedral \( N = 55 \) structure builds up. For homonuclear Lennard–Jones clusters a such flat region is \( 52 \leq N \leq 55 \) [5], and it also corresponds to the filling of the magic \( N = 55 \) structure.
Fig. 4. (a) Energies per number of particles $N$, and (b) the first energy difference, $\Delta_1 = (E(N) - E(N - 1))/\epsilon$, for globally optimized clusters plotted vs $N$.

4 Conclusions

The global optimization based on a basin-hopping method is carried out to study structural properties of model nanoparticles consisting of one impurity alkali ion and a rare gas cluster. The catalog of energy minimum candidates for these clusters containing up to 80 particles is presented. It is found that the impurity ion is lying in the surface of a nanoparticle for a small number of atoms.
An alkali-metal ion is solvated by rare gas atoms when their number is greater or equal than eight. The predicted magic numbers 13, 19, 46, 49, 55, 70, 79 of heteronuclear clusters are the same as for homonuclear Lennard–Jones ones. The magic structure $N = 39$ of heteronuclear clusters replaces $N = 38$ of homonuclear nanoparticles. Therefore a small perturbation, such as the presence of the closest alkali-metal ion neighbour from the periodic table, may change the list of magic sizes for rare gas clusters. The system studied in this work is useful as a test example for theoretical analysis of global optimization and NP-hard problems for heteronuclear clusters [28]. The methods of global optimization are helpful as a guide in low-temperature experimental studies of nanoparticles with impurities.

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