ION-SIZE EFFECTS IN THE GROWTH SEQUENCES OF METAL-ION-DOPED NOBLE GAS CLUSTERS

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We have studied the stability and the structure of doped noble gas cluster ions of the type M^+X_n , ($M = \text{In, Al, Na}$, $X = \text{Ar, Kr, Xe}$) by systematically changing the composition M/X and observing changes in the magic number patterns appearing in the mass spectra. When the metal ion radius is comparable to the radius of the noble gas atom, the mass spectra show the familiar icosahedral magic numbers $n + 1 = 13, 19, 23, 26, 29, 32, 46, 55, \dots$. In contrast, for metal ions with radii significantly smaller than the noble gas atoms, we observe a new series of magic numbers $n + 1 = 9, 11, 17, 21, 24, 26, \dots$. This series converts into the icosahedral one for larger clusters. Using a simple hard sphere packing model, we show that this new series of magic numbers is consistent with a cluster growth sequence which is based on a capped square antiprism (CSA) geometrical structure of the clusters.

Keywords: Doped noble gas clusters; magic numbers; metal-ions; time-of-flight analysis

1. INTRODUCTION

After intensive experimental and theoretical investigations in the last ten years, it is well established that the geometrical structure of the atomic van der Waals clusters can be inferred from hard sphere packing models. This is a direct consequence of the electron

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localization on the individual atomic orbitals. As a result, atoms can be treated as hard spheres, thereby allowing the application of geometrical models for determining the cluster structure.

The appearance of magic numbers patterns, observed in mass-spectroscopic studies on Xe_n clusters by Echt *et al.* [1] and on Ar_n by Harris *et al.* [2] could be explained by the adaptation of icosahedral sphere packing. These results are also confirmed by electron diffraction studies from Farges *et al.* [3] on Ar_n clusters. The atoms in these systems arrange themselves in shells around a central atom. When the total number of atoms is $n = 13, 55, 147, \dots$ shell closing occurs, giving rise to very stable clusters, which have icosahedral geometry (Mackay-icosahedra[4]). Stable clusters also are observed for $n = 19, 23, 26, 29, 32, \dots$ where in this case subshells are filled and the cluster geometry is characterized as polyicosahedral [5]. The completion of shells and subshells takes place at a certain sequence (growth sequence), such that every additional atom occupies the position which offers the maximum number of neighbors (contacts).

Icosahedral structures have been observed recently on the mixed ionic clusters Al^+Ar_n [Refs. 6, 7] and Mg^+Ar_n [Ref. 8], where the icosahedral magic numbers appearing at total number of atoms $N = n + 1$ are identical with those observed in the noble gases. Since, experimental techniques for producing such mixed cluster ions M^+X_n (M = metal atom, X = noble gas atom) with different compositions are readily available, metal-doped noble gas clusters are the ideal systems for studies addressing the following questions: i) What happens with the charge delocalization as function of the electronic configuration of metal ion? ii) Where in the cluster does the metal ion reside? And iii) if the charge is localized on the metal ion and the sphere packing model is applicable, what will be the structure of the cluster as a function of the size ratio of metal ion to the noble gas atom?

In this report we present our experimental results for several metal-doped noble gas cluster ions. While for some of them the familiar icosahedral magic numbers are observed, others show magic numbers which cannot be explained with icosahedral packing. We present a simple sphere packing model which is based on capped square antiprism structure and is able to explain the observed non-icosahedral magic numbers.

2. EXPERIMENTAL

Details of the employed experimental setup have been reported previously [9,10]. In brief, clusters ions of the type MX_n are produced using a combination of laser ablation of the metallic target and supersonic expansion of the noble gas into vacuum. The ablation laser is a Nd:YAG laser ($\lambda = 1064$ nm, pulse duration 10 ns, repetition rate 12.5 Hz) with an output energy of 10–100 mJ/pulse. The noble gas is expanded from a pulsed nozzle (diameter 0.8 mm, backing pressure 2–8 bar, room temperature) and is mixed with the metal ions contained in the plasma plume at 0.5–5 mm away from the nozzle orifice. The cluster ions produced from this mixing are then analyzed with a Time-of-Flight (TOF) device, which can be used either as a linear or as a reflectron spectrometer. The pulsed nozzle, the ablation laser firing and the triggering of the TOF are synchronized through coupled delay generators, which are sequentially optimized for maximum signal. The TOF-signal is recorded with a digital storage scope and can be accumulated for an arbitrary number of laser shots. In situations when the ion intensity is low the mass-spectra are recorded with the linear TOF setup.

3. RESULTS AND DISCUSSION

In Figures 1 and 2 we present the TOF-spectra of the In^+X_n , and Al^+X_n ($X = Ar, Kr, Xe$) respectively and in Figure 3 the spectra of Na^+X_n ($X = Ar, Kr$). These spectra are averaged over ≈ 2000 laser shots. The pronounced intensity irregularities (magic numbers) in the spectra are labeled with the total number N of atoms in the corresponding clusters. We check the reproducibility of the magic numbers for each system, by recording a series of averaged spectra obtained under different source conditions (backing pressure, laser fluence, etc.). The magic numbers indicated in Figures 1–3 correspond to peaks whose intensity differs from that of the neighboring ones by at least 10%, and simultaneously show the *same* behavior in *all* recorded spectra for a given system.

In the cases of In^+Ar_n , In^+Kr_n , Al^+Ar_n and Al^+Kr_n , the spectra exhibit the familiar icosahedral magic number sequence $N = 13$,

FIGURE 1 TOF-Spectra of the In^+Ar_n , In^+Kr_n , and In^+Xe_n clusters. The most stable clusters are indicated by the total number of atoms $n+1$.

19, 23, 26, 29, 32, $\dots$, 55. In contrast, in the systems In^+Xe_n , Al^+Xe_n , Na^+Ar_n and Na^+Kr_n with $N < 40$, an unusual stability pattern is observed, namely very stable clusters for sizes $N=9, 11, 17, 21, 24, 26, (27), 30$. As N increases this sequence changes into the icosahedral one. The magic numbers $N=9, 11, 14, 17, 21$ have been previously observed from Saito *et al.* [11] in the Al^+Xe_n clusters formed by ion sputtering of an Al target with Xe ions, the origin of these magic numbers however could not be explained.

FIGURE 2 TOF-Spectra of the Al^+Ar_n , Al^+Kr_n , and Al^+Xe_n clusters.

Geometrical Model of Hard Sphere Packing

For close packing of spheres, the most stable clusters expected are those which have closed shells of atoms around a central one. For clusters of the type MX_n , we can assume that the metal ion M is confined in the center of the cluster and is surrounded by the n noble gas atoms X . In order to obtain high symmetry and dense packing (the requirements for high stability), the most obvious way to arrange the noble gas atoms around the metal ion is represented by the polyhedra

FIGURE 3 TOF-Spectra of the Na^+Ar_n , and Na^+Kr_n clusters.

indicated in Figure 4. These polyhedra can be formed by joining two identical regular polygons, each of them being made from $k = n/2 = 2, 3, 4, 5, \dots$ atoms, and one of which being twisted by an angle of π/k with respect to the other one. The first four polyhedra formed in this way are the tetrahedron ($n=4$), the octahedron ($n=6$), the square antiprism ($n=8$), and the pentagonal antiprism ($n=10$). From the above polyhedra, only the tetrahedron and the octahedron are closed shell structures, while for $k=4$ and $k=5$, two additional atoms are needed in order to acquire the closed shell structures, the capped square antiprism ($n=10$) and the icosahedron ($n=12$) respectively. It should be also mentioned, that only the tetrahedron, the octahedron and the icosahedron are regular polyhedra.

We expect that the polyhedra of Figure 4 represent stable cluster structures only if the size of the central atom fits into the cavity

FIGURE 4 High-symmetry polyhedra formed from two twisted polygons, each of them shaped from $k=2, 3, 4, 5$ atoms. $k=2$ and $k=3$ are closed structures and represent the tetrahedron ($n=4$) and the octahedron ($n=6$) respectively. $k=4$ and $k=5$ can each accept two additional capping atoms to form closed structures, the capped square antiprism ($n=10$) and the icosahedron ($n=12$) respectively.

dimensions. By applying simple geometrical considerations (see also Ref. 12) this condition is fulfilled when the radius R_M of the central atom and the radius R_X of the noble gas atoms have the following relation:

$$R^* = R_M/R_X \leq \left\{ \left[2 + \cos\left(\frac{\pi}{k}\right) - \cos\left(\frac{2\pi}{k}\right) \right] / \left[1 - \cos\left(\frac{2\pi}{k}\right) \right] \right\}^{1/2} - 1 \quad (1)$$

where, $k = n/2$ represents the numbers of atoms per ring. This formula gives the maximum radii ratio for each symmetry in order to keep the exterior atoms in contact with each other. Thus we obtain the maximum R^* -values of Table I for $k = 2$ to 5. That is, for $0.902 \geq R^* > 0.645$ icosahedral packing is preferred, for $0.645 \geq R^* > 0.414$ CSA-packing, etc.

The case of icosahedral packing is well known and the corresponding magic numbers sequence has been deduced by Harris *et al.* [2] and

TABLE I Limits of the radius ratio R^* for forming clusters which have the symmetry of the polyhedra in Figure 4. The values are obtained from Eq.(1). The specification “closed” refers to closed shell structures

k	Maximum $R^* = R_M/R_X$	Number of surrounding atoms	Geometrical Structure
2	0.225	4	Tetrahedron (closed)
3	0.414	6	Octahedron (closed)
4	0.645	8 8+2	Square antiprism Capped square antiprism (closed)
5	0.902	10 10+2	Pentagonal antiprism Icosahedron (closed)

Farges *et al.* [5]. In particular Harris *et al.* have been able to develop a cluster growth model for Ar_n clusters using the closed icosahedral second shell with $N=13$ atoms where they placed additional atoms either at adjacent triangular faces (face packing FP) or at adjacent edge sites (edge packing EP). Every time a pentagonal ring is formed, the next atom is placed on the enclosed vertex-site forming a pentagonal pyramid. The geometrical structures resulting from this procedure correspond to 6-atom pentagonal caps on the 13-atom icosahedron, and can be considered as the closing of subshells with pentagonal symmetry. This operation maximizes the number of the bonds and for the case of FP this occurs at $N=19, 23, 26, 29$ and 32 , whereas for EP this occurs for $N=39, 43, 46, 49, 55$.

Regularly the FP is preferred when the second shell is relatively empty, whereas the EP is favorable when the shell is nearly complete. As a result, a crossover region of cluster sizes exist, where no particular stable clusters are expected. This is a consequence of the balance between the surface density of atoms and the number of nearest-neighbor contacts [5], or equivalently is due to the balance between the surface energy and the interior energy of the cluster [13].

Since this simple model seems to reproduce very well the observed magic number sequences for icosahedral “aufbau”, it will also be worthwhile to attempt to deduce similar growth sequences for the other polyhedra of Figure 4. In the cluster systems M^+X_n studied here, we successively go from lighter to heavier noble gases X. This is equivalent to decreasing the radius of the central ion in comparison with that of the noble gas. Since the first packing appearing (e.g. in In^+X_n) is

the icosahedral one, then according to the results of the model presented above, the square antiprism can be the basic structure for the new magic numbers sequence appearing in the case of e.g. In^+Xe_n .

A cluster of the kind MX_n which has the same symmetry as the square antiprism includes $N=9$ atoms. This structure contains, apart from the triangular faces, two quadratic faces, which are able to accept capping atoms in order to result in a more closed structure. This capped square antiprism (CSA) structure with 11 atoms (see Fig. 5a), has then 16 triangular faces, 10 vertexes and 24 edges.

Generally, the total number of atoms N_m in a cluster with m filled shells and having the symmetries shown in Figure 4, is given by:

$$N_m = N_{m-1} + V + F_3 m(m-2)/2, \quad (2)$$

where V is number of vertices and F_3 the number of triangular faces. For all the polyhedra $N_1 = 1$, while $N_2 = 13$ for the icosahedron and $N_2 = 11$ for CSA. Thus, for the case of the icosahedron, the successive icosahedral shells are filled at $N = 13, 55, 147, 309, \dots$ atoms, whereas,

FIGURE 5 a) The skeleton of the capped square antiprism. It consists of 10 vertexes, 16 triangular faces and 24 edges. The two capping atoms lying at the square faces are shaded. b) The Schlegel diagram of the capped square antiprism representing the polyhedral core with triangular faces, where the new added atoms are placed, in order to explain the observed cluster growth sequence (see text).

for the CSA-structure, we get $N = 11, 45, 119, 249, \dots$. Similar formulas for a variety of polyhedra are given by Martin *et al.* [14].

In the remainder of the present paper, we concentrate only on the case of the CSA and we work in a similar manner as Harris *et al.* did for the icosahedral clusters. In order to represent in two dimensions what happens in three dimensions, we use the so called *Schlegel diagram* [15] shown in Figure 5b for the eleven-atom CSA-core. Such a diagram shows schematically all the elements (faces, edges and vertexes) of a three dimensional polyhedron in two dimensions. The numbers at the triangular faces of the Figure 5b represent the successively added atoms, whereas the small subscripts accompanying, represent the number of the neighboring atoms which are present before the atoms are added – i.e. the number of newly formed bonds. In Figure 6 we display these numbers as function of the corresponding cluster size. Several maxima occur at $N = 17, 21, 24, 27, 30$ and $32-35$. These numbers coincide with the observed ones in In^+Xe_n for $N \leq 21$, in Al^+Xe_n for $N \leq 30$, in Na^+Ar_n for $N \leq 21$ and in Na^+Kr_n for $N \leq 30$.

FIGURE 6 Plot of number of bonds as the clusters grow after the completion of the second CSA-shell at $N = 11$. The number of bonds is taken from Figure 5b.

Assuming that the contribution of every new added atom to the total binding energy of the cluster, is proportional to the number of nearest neighbor bonds, these maxima should then correspond to the binding energy differences of the clusters. This quantity reflects the magic numbers in the cluster stability [2]. According to the above points, the magic number sequence $N=9, 11, 17, 21, 24, 27, 30$ may be due to CSA-packing in these clusters. The corresponding cluster geometries are plotted in Figure 7.

It is interesting to compare the experimental results with the predictions of the model presented above, using the radius of the involved elements obtained from the literature. Generally the effective ionic radius depends on the coordination number of the metal ion [16], but due to electronic configuration of In^+ , Al^+ , and Na^+ we expect that $R_{\text{In}}^+ > R_{\text{Al}}^+ > R_{\text{Na}}^+$. Butterfield and Carlson [17], using Hartree-Fock-Slater calculations, could obtain the ionic radius for many closed

FIGURE 7 The geometrical structure of the magic numbers clusters whose growth is based on the capped square antiprism symmetry. The gray-shaded atoms represent the atoms needed to form 6-atom pentagonal caps to result in partial shell closures.

shell ions. Although their absolute values cannot be taken as very accurate, since these have been obtained in an uniform manner, they allow comparisons between different ions in the Periodic Table of elements. Thus the ionic radii of In^+ , Al^+ , and Na^+ are $R_{\text{In}}^+ = 1.37\text{\AA}$, $R_{\text{Al}}^+ = 1.22\text{\AA}$ and $R_{\text{Na}}^+ = 0.95\text{\AA}$. Taking also the van der Waals radii of noble gases $R_{\text{Ar}} = 1.88\text{\AA}$, $R_{\text{Kr}} = 2\text{\AA}$, $R_{\text{Xe}} = 2.2\text{\AA}$, from Ref. 18, we obtain the $R_{\text{M}}/R_{\text{X}}$ values which are plotted in Figure 8 (solid symbols) for the systems considered here. The solid lines in Figure 8 are the limiting radii ratios from Table I for each symmetry. We observe that, in almost all cases the radii ratio renders very well the observed symmetry. Only in the case of Al^+Kr_n there is a disagreement, where R^* seems to be lower than the observed icosahedral symmetry allows. Our results indicate that, $R_{\text{Al}}^+/R_{\text{Kr}} \geq 0.645$. Therefore we increase slightly (6%) the ionic radius of Al^+ to the value $R_{\text{Al}}^+ = 1.29\text{\AA}$ (open circles in Fig. 8) in order to fit our experimental observations. This value can be considered as the lower limit of R_{Al}^+ .

FIGURE 8 Diagram showing the radii of metal ion R_{M} and the noble gas atom R_{X} . The solid lines are the constant $R_{\text{M}}/R_{\text{X}}$ -values, which define the kind of symmetry expected to have the M^+X_n clusters, according to the sphere packing model (see Tab.I). The solid symbols are the ionic radius values from Ref. 17, whereas the open circles correspond to the corrected Al^+ ionic radius in order to fit our experimental results.

Finally, we should mention that, although the magic numbers for $N < 30$ fit very well to CSA-packing, we do not observe the CSA-third-shell closure at $N=45$. Instead, we observe the icosahedral magic numbers at $N=23, 26, 29, 32, 49$ and at $N=55, 147$ (icosahedral third and fourth shell respectively) and also some icosahedral subshells at 71, 81 are clearly visible (see e.g. In^+Xe_n). These structural transitions as a function of cluster size (number of atoms) are caused by the energetics of the system and can be explained as follows: For $N < 11$, the interaction of the central ion with the atoms placed in the third shell is not as strong as it is for the atoms which are in direct contact with the central ion (polarization energy). Thus as more and more noble gas atoms are added on the third shell to build larger clusters, the noble gas-noble gas interaction becomes more important, resulting in an increase of the cluster surface energy, which forces the noble gas atoms to be placed in a more compact fashion. This corresponds effectively to a decrease of the R_X -value, so that the ratio R_M/R_X increases. These changes of R_M and R_X radii as a function of cluster size, can be seen in the numerical results from molecular dynamics calculation in the K^+Ar_n clusters in Ref. 19. Thus, the cluster at some critical cluster size, rearranges from CSA-symmetry to icosahedral one, which is more favorable for larger R^* -values (see Tab. I). This critical cluster size for structural changes seems to depend also on the radius ratio R^* (e.g. compare In^+Xe_n to Al^+Xe_n). The examination of this topic, based on molecular dynamics simulations of the cluster energetics and structure, will be presented in a forthcoming paper [20].

4. CONCLUSIONS

In mass spectrometric studies concerning the stability and structure of metal ion-doped noble gas clusters, we could observe the icosahedral packing as well as a new cluster packing, which is consistent with a capped square antiprism geometry. A simple hard sphere packing model, which assumes that the metal ion resides in the center of the cluster, can adequately predict the experimental observations and the cluster structure, as a function of radius ratio of metal ion to noble gas atom. Furthermore, we observed structural transitions from the CSA-geometry to icosahedral one as the cluster size increases. To our

knowledge, the present study of metal ion-doped noble gas clusters provides the first example of such a change of geometrical structure in small atomic cluster systems.

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