Potential Functions, Static, and Dynamic Properties of $Mg^{m+}Ar_n$, $m = 1, 2$ and $n = 1 - 18$, clusters

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Abstract

Analytical potential functions have been constructed for $Mg^{m+}Ar_n$, $m = 1, 2$, clusters by combining ab initio calculations with the electrostatic model of ion - induced dipole and induced dipole - induced dipole interactions. The most stable structures and dynamic properties are investigated with Molecular Dynamics techniques. For Mg^+Ar_{12} an icosahedral geometry is predicted. For Mg^+Ar_n clusters and with $n = 7-12$ two series of minima with small differences in energy are found; in one the magnesium ion stays inside the cluster (solvated), and in the other on the surface of the system. For $n > 9$, clusters with Mg on the surface are slightly more stable and have a distinguishable high vibrational frequency relative to those with magnesium ion inside. We find no such trends for $Mg^{2+}Ar_n$ clusters in which Mg cation is always solvated. The absolute minimum of $Mg^{2+}Ar_4$ is a regular tetrahedron, and that of $Mg^{2+}Ar_6$ a regular octahedron. The stability of all these clusters is investigated by studying caloric curves, root mean square bond length fluctuations, radial distributions, and power spectra.

1 Introduction

The interest in investigating the structures and dynamical properties of small finite systems such as atomic and molecular clusters[1] has led theoretical work to the study of several kinds of forces exerted among the atoms: van der Waals,[2] hydrogen bonding,[3–6] metallic,[7] ionic,[8,9] and covalently bonding[10–12] clusters have been explored.

Ionic clusters are particularly favored in experimental studies, since they are directly detected with a mass spectrometer. Thus, metal ions interacting with inert gases serve as proper models for studying solvation effects, and generally, the dependence of the properties of the clusters on their sizes.[1]

The work presented in this article has been motivated from the recent experimental investigation of Mg^+Ar_n and $Mg^{2+}Ar_n$ clusters by Velegrakis and Lüder.[13] These researchers used the laser ablation technique to form metal cations which are perpendicularly ejected into the Ar flow direction to form atomic aggregates. It is believed, that the clusters are formed at the early stage of the adiabatic expansion by adding Ar atoms to the smaller size clusters. The highly energized species are cooled by collisions, and the final products are detected by a time of flight apparatus.

From the analysis of the mass spectra some particularly stable structures (known as magic numbers) were detected for both types of clusters. Mg^+Ar_n yielded higher intensity peaks relative to the neighboring ones for $n = 12, 18, 22, 25, 28, 31, 45, 54$, whereas $Mg^{2+}Ar_n$ gave markedly different behavior showing only one sharp peak at $n = 6$ and a broad peak at $n = 14$.[13]

The magic numbers of the mono-positive clusters coincide with those of pure argon clusters.[14] This led to the speculation that the structures of Mg^+Ar_n are the same as those of Ar_{n+1} clusters. The structure of Ar_{13} is that of a regular icosahedron which has an argon atom in the center, and larger magic number aggregates are formed with the construction of additional regular pentagons. For the double-charged magnesium-argon complexes an octahedral and a fcc type geometry were conjectured for $n = 6$ and 14 respectively.

The ionic character of magnesium and the number of electrons in this species allow for detailed experiments and accurate theoretical calculations of the small aggregates of magnesium cation with inert gases. Indeed, Pilgrim et al.[15] have recently studied the photodissociation spectroscopy of Mg^+ with rare gases (Ar, Kr, Xe) bimers. Vibrational frequencies, dissociation energies, and spin-orbit splittings were measured for the bimers. Their results have been reanalyzed by Le Roy[16] using near dissociation theories in order to obtain improved estimates of the dissociation energies.

Bauschlicher and co-workers[17–19] have carried out high level ab initio calculations for Mg^+Ar and Mg^+Ar_2 complexes. They concluded that the nature of the interaction is mainly electrostatic. The calculated dissociation energy of Mg^+Ar (3.25 kcal/mol) is in good agreement with the spectroscopically estimated one (3.66 kcal/mol). In a recent article Bauschlicher and Partridge[20] calculate the ground and the electronic excited state of Mg^+ with Ar and Kr, and make a direct comparison with the experimental results of Pilgrim et al.[15] Good agreement between computed and experimental results is found.

Density functional theory has been applied by Eriksson[21] to compute equilibrium geometries, energetics, and hyperfine coupling constants for a number of charged magnesium clusters and magnesium-rare gas complexes in matrices.

Patil[22] analyzed the interactions of inert gases with closed shell alkali and alkaline earth ions using a perturbative approach. He predicts a binding energy for $Mg^{2+}Ar$ of 45 kcal/mol, and a bond length of 3.78 a_o.

The recent production of larger mono- and double-charged magnesium - argon clusters[13] calls for further theoretical work on these systems. It is interesting to find the minimum energy geometries, and compare their dynamical properties in parallel for the mono- and double-charged metal atom. In this article we undertake such a study.

In order to investigate large clusters we construct analytical potential functions based on the electrostatic asymptotic expansion model,[8] and utilize the ab initio results for the small clusters. For the mono-cation we use Partridge et al.[19] calculations, but for Mg^{2+} we perform self consistent field (SCF) computations in association to MØller Plesset[23] 2nd order perturbation (MP2) calculations. We indeed confirm the icosahedral geometry of Mg^+Ar_{12} and the extra stability of this cluster implied from the mass spectrum. However, the interesting finding of the present study is the prediction that Mg ion may sit either in the interior of the cluster or on the surface. For

$Mg^{2+}Ar_6$ a regular octahedron of O_h symmetry is predicted.

The article is organized as follows: In section 2 we construct the potential energy surfaces (pes), in Section 3 the minimum energy geometries are located for different size Ar clusters, in Section 4 dynamic and equilibrium properties are calculated, and finally, in Section 5 we summarize the main results.

2 Potential Energy Surfaces

Since we are aiming to study the dynamics of large size atomic aggregates, there is a need for constructing analytical potential functions. As we mentioned it earlier, ab initio calculations suggest that the electrostatic forces prevail in the interactions of Mg^+ with Ar,[19] and therefore, we adopt an electrostatic model. The potential is written as[8]

$$V_{tot} = \sum_{k=2}^{n+1} V_n^+(1,k) + \sum_{j=2}^{n}\sum_{k=j+1}^{n+1} V_{nn}(j,k). \tag{1}$$

The first sum describes the interactions of Mg ion (labeled as atom 1) with the atoms of argon (labeled as atoms 2,3,...,$n+1$). The second term in Equation (1) denotes the interactions among argon atoms.

The first term is developed as

$$\begin{aligned} V_n^+(1,k) &= V_0(r_{1k}) + V_{dis}(r_{1k}) - \frac{1}{2}a_k E_k^2 \Phi(r_{1k}) - \frac{1}{2}a_1 \vec{E}_{1k}\vec{E}_1 \\ &+ \frac{a_1 a_k E_1 E_k}{r_{1k}^3}[\hat{E}_1\hat{E}_k - 3(\hat{E}_1\hat{r}_{1k})(\hat{E}_k\hat{r}_{1k})], \end{aligned} \tag{2}$$

where

- $\vec{r_j}$ is the position vector of atom j in a space fixed cartesian coordinate system, $\vec{r}_{jk} = \vec{r_j} - \vec{r_k}$, and its norm $r_{jk} = |\vec{r_j} - \vec{r_k}|$.
- a_1 is the polarizability of magnesium cation.
- $a_k = a_{Ar}$ is the polarizability of argon atom k, $k = 2, 3, \ldots, n+1$.
- $\vec{E}_k$ is the intensity of the electric field at the position of atom k,

$$\vec{E}_k = \frac{Q}{r_{k1}^2}(1-\delta_{k1})\hat{r}_{k1} + \sum_{l=1, l\neq k}^{n+1} \frac{a_l E_l}{r_{kl}^3}[3(\hat{r}_{kl}\hat{E}_l)\hat{r}_{kl} - \hat{E}_l], \tag{3}$$

where Q is the electric charge on atom 1, and δ_{k1} is Kronecker's delta function.

- $\vec{E}_{1k}$ is the intensity of the electric field at the position of the ion which is due to the dipole moment of atom k.

- $\hat{E}_k$, $\hat{r}_{jk}$ are the unit vectors of the intensity of the electric field on the atom k, and of the position of atom k relative to atom j respectively.

- $\Phi(r_{1k})$ is a switching function which takes care the smooth interpolation between short range and charge - induced dipole interactions.

The first two terms in Equation (2) denote the repulsive and the dispersion potentials respectively. Both these terms are described with a diatomic Morse type function

$$V_0(r) + V_{dis}(r) = Ae^{2B(1-\frac{r}{D})} - 2Ce^{B(1-\frac{r}{D})}. \tag{4}$$

The third term in Equation (2) is the the charge - induced dipole interaction, the forth term describes the effect of all other atoms on the ion, and the fifth term is due to the induced dipole - induced dipole interactions.

The part of the potential which yields the Ar-Ar interactions, is written as

$$V_{nn}(j,k) = V(r_{jk}) + \frac{a_j a_k E_j E_k}{r_{jk}^3}[\hat{E}_j\hat{E}_k - 3(\hat{E}_j\hat{r}_{jk})(\hat{E}_k\hat{r}_{jk})]. \tag{5}$$

This is the sum of a potential valid for a free argon dimer and an electrostatic induced dipole - induced dipole interaction. $V(r_{jk})$ is given by an empirical function produced by Aziz and Slaman[24]

$$V(x) = \varepsilon\left(Ae^{-ax+bx^2} - \left\{\begin{array}{ll} e^{-(\frac{d}{x}-1)^2} & x < d \\ 1 & x \geq d \end{array}\right\}\left[\frac{c_6}{x^6} + \frac{c_8}{x^8} + \frac{c_{10}}{x^{10}}\right]\right), \tag{6}$$

where

$$x = r/r_0.$$

For the completeness of this paper the values of the parameters in the above potential are displayed in Table I. The polarizabilities of the atoms are $a_{Ar} = 11.13\ a_o^3$,[19] $a_{Mg^+} = 37.11\ a_o^3$,[19] and $a_{Mg^{2+}} = 0.6\ a_o^3$.[22]

We must note that Equation (1) is not a pairwise additive function, but many body interactions are introduced through the electrostatic terms. The induced dipole moment on atom k depends on the positions of all other atoms. To fit the parameters that appear in the above functional form we separately study the small clusters of Mg^+ and Mg^{2+}.

2.1 Pes of Mg^+Ar_n

Bauschlicher and co-workers[19] employed the self-consistent-field method and the modified coupled-pair functional approach (SCF MCPF) for the electron correlation to calculate the binding energies and geometries of a number of metal ions with inert gases. For Mg^+ they determined the energy and geometry of the minima with one and two argon atoms in their electronic ground states, $^2\Sigma^+$ and $^2A_1$, respectively. An extended basis set was used for magnesium consisted of (21s16p8d6f) and contracted to [7s7p4d3f], and for argon (17s12p6d4f)/[6s5p3d1f].

The ab initio results for the bimer are employed to fit the parameters of the Morse type potential (Equation (4)), and these are: the minimum energy, −3.25 kcal/mol, the harmonic frequency, 92 cm^{-1}, and the equilibrium bond length, $r_m = 5.47 a_o$. The zero of the total energy is defined with all atoms separated at their electronic ground state. In the Morse type function we fix the parameter D to be equal to the equilibrium bond length, r_m, and the other parameters are fitted such that the total potential of the diatomic (Equation(2)) exactly reproduces the ab initio results.

The following switching function $\Phi(r)$ (Equation(2)) was chosen

$$\Phi(r) = \tanh\left(\frac{r - E}{F}\right). \tag{7}$$

We adjust the parameters E and F in such a way that the potential of the triatomic reproduces the energy and geometry of the minimum (an isosceles triangle) obtained from the ab initio calculations of Partridge et al.[19] These values are $E_0 = -6.2$

kcal/mol, and the equilibrium geometry is at the Mg^+Ar bond length $r = 5.56\ a_o$, and the angle between the two Mg^+Ar bonds is equal to 82.5^o. The fitted values of the parameters, $A, B, C, D, E,$ and F, are tabulated in Table II.

Figure 1 shows the potential curve for Mg^+Ar. The continuous line labeled with [1] is the total potential. [2] denotes the charge - induced dipole interaction term, [3] the Morse type potential, and [4] the last two terms in Equation (2).

The analytical function for the triatomic system Mg^+Ar_2 gives a minimum of -6.06 kcal/mol, at $r = 5.62\ a_0$, and the angle between the two bond lengths is 77^o. This potential function is used to study larger clusters.

2.2 Pes of $Mg^{2+}Ar_n$

We have used the package of programs GAMESS[25] to calculate the geometries and energies of the most stable structures of $Mg^{2+}Ar_n$ for n =1, 2, and 3. SCF type calculations were performed, and the electron correlation energy was treated at the MP2 level. The basis set which we used for Mg is (12s8p2d)/[8s5p2d] (Triple-Zeta Valence plus Polarization, TZV+P), and for Ar (13s10p2d)/[8s5p2d] (TZV+P). The MP2 calculations were done with no frozen core orbitals.

Table III presents the electronic energies for $Mg^{2+}Ar_n$, $n = 1, 2, 3$. A linear geometry ($D_{\infty h}$) was found for the triatomic system, and a planar minimum of D_{3h} symmetry for the tetratomic with magnesium ion in the center of the triangle.

In the fitting process of $Mg^{2+}Ar_n$ the switching function $\Phi(r)$ (Equation(2)) was chosen as

$$\Phi(r) \ = \ 1 \ - \exp\left[-(r/E)^4\right]. \tag{8}$$

As in the case of mono-cation we have used the ab initio results to fit the parameters in the Morse type potential and switching function. Table II stores their values. Figure 2 shows the total potential curve [1] and the contributing terms. As before [2] denotes the charge-induced dipole term, [3] the Morse function for the short range interactions, and [4] the last two terms in Equation (2).

The parameters in the switching function (Equation (8)) were chosen such that to reproduce the energy and geometry of the triatomic. The values in the parentheses shown in Table III are those that are calculated with the analytical function. In Table IV we compare the energies for some other configurations of the triatomic system far from the minimum. We can see, that the energies predicted from the analytical potential function are in satisfactory agreement with the ab initio calculations.

3 Minimum Energy Structures

Generally, we are interested in finding not only the absolute minima of the small size clusters, but also a number of relative minima and saddle points that separate them. The knowledge of the stationary points of a dynamical system provides a zero order approximation to the dynamical properties of the system.[26]

In this work, we apply the same minimization techniques used in previous studies on water clusters.[3,4] These are the Newton-Raphson method, and the method of integration of friction equations. The Newton-Raphson technique is an iterative method to locate the roots of the non linear algebraic equations

$$\vec{f}_i = 0, \quad i = 1, 2, \ldots, n+1, \tag{9}$$

where $\vec{f}_i$ are the forces exerted on the atom i

$$\vec{f}_i = -\frac{\partial V(\vec{r})}{\partial \vec{r}_i}, \quad i = 1, 2, \ldots, n+1. \tag{10}$$

The friction method requires the integration of the first order differential equations

$$\dot{\vec{r}} = \frac{d\vec{r}}{dt} = -\kappa \frac{\partial V(\vec{r})}{\partial \vec{r}_i}, \tag{11}$$

where κ^{-1} is the friction coefficient. We use standard integrators[27] to solve the above system of differential equations.

Although the Newton-Raphson method converges quadratically, very often it diverges because of a bad starting point. We have found that the combination of the above two techniques guarantees convergence. The way we apply it is to locate first the stationary point with the friction method requiring low accuracy. Then, we find the root of Equation (9) with the Newton-Raphson method and with higher precision. The stability properties of the stationary point are determined by linearizing the Hamilton's equations of motion, and then, diagonalizing the matrix of the second derivatives of the hamiltonian.[26] If all eigenvalues are pairs of imaginary numbers, $\pm i\mu$, then, the stationary point is stable (minimum), whereas if there are k pairs of real eigenvalues, $\pm\mu$, then, we have a saddle point of $k\ th$ order.

We have investigated and compared other minimization techniques, such as the conjugate gradient and the variable metric methods, and the results will be presented in another publication.[28]

In the search of locating different minima of low energy we select starting points for the minimization procedure using several algorithms. We employ a Monte Carlo method for obtaining random positions of the atoms, or we construct initial configurations systematically using a building up principle. Finally, to find minima which are dynamically connected we integrate the classical equations of motion and at regular time intervals we store the phase space points that are visited, and these points provide initial conditions for the minimization algorithms. By increasing the total energy of the cluster new regions of phase space are explored.

In the application of the minimization techniques we have benefit a lot from the PVM (Parallel Virtual Machine) package of programs,[29] which allows us to use simultaneously several distributed computers.[6]

3.1 Mg^+Ar_n, $n = 3 - 14$

The lowest energy minima found for the clusters of Mg^+Ar_n and for $n = 3 - 14$ are shown in Figure 3, whereas in Table V we tabulate the total energies (E), and the energy per argon atom (E/n).

The geometries of the absolute minima of the first clusters $n = 3, 4, 5, 6$ are: a trigonal pyramid of C_{3v} symmetry, two triangular pyramids which share a common side, the previous structure with one more Ar atom in the middle of a triangle formed with Mg ion and two argon atoms, and a regular pentagon with the sixth argon atom in the middle of the one side of the pentagon, and the magnesium in the opposite side (C_{5v}).

By adding more Ar atoms we generate two series of minima with small differences in the energies of the isomers. One with the extra atoms on the same side as magnesium, thus, closing the cation in the interior of the cluster, and the other in the opposite side keeping the metal atom always on the surface. The first type of minima which correspond to clusters with a solvated magnesium ion, are denoted with the letter *(a)* and the second type, with a non-solvated cation, with the letter *(b)*.

The energy differences between the two isomers *(a)* and *(b)* are small, and as can be seen from Table V, this difference increases for the large cluster. The geometries of the Mg^+Ar_{12} isomers are an icosahedral structure of I_h symmetry for *(a)* and C_{5v} symmetry for *(b)*. With $n = 12$ the first shell is completed and larger clusters are formed by filling the second shell. We find that in the case of Mg^+Ar_{12}-*(b)* isomer the extra Ar atoms prefer to stay on the same side with the other argon atoms and not on the side of magnesium.

Looking at Table V we make the following interesting remarks. The binding energy per argon atom decreases by increasing the size of the cluster, but for $n = 12$ we can see a small increase. This is an indication of the extra stability of Mg^+Ar_{12}.

For $n = 10$ and larger clusters the *(b)* isomers have lower energy than the *(a)*, reversing the trend observed in the smaller clusters for which the *(a)* structures were the absolute minima. In other words, energetically, Mg^+ prefers to remain non-solvated in the large clusters.

This behavior can be elucidated with the analysis of the total energy into the contributing terms. Figure 4 shows the total energy, V_{tot}, the ion - induced dipole interaction, V_{Mg^+Ar}, the Ar-Ar interaction given by Equation (6), V_{ArAr}, and the induced dipole - induced dipole interactions, V_{dd}, among argon atoms, as functions of the size of the cluster. Dashed lines denote the series *(a)* and continuous lines the series *(b)*. For the small clusters (up to $n = 6$) the repulsive term V_{dd} balance the attractive term V_{ArAr} as can be seen from the approximately symmetric split of these two curves in Figure 4. Therefore, the stability of the cluster is determined mainly by the attractive V_{Mg^+Ar} term.

The symmetric split of the two contributing terms of the Ar-Ar interaction is destroyed for larger clusters, and both terms, V_{dd} and V_{ArAr}, favor the non-solvated magnesium-argon clusters. For the isomers *(b)* the repulsion of the induced dipole - induced dipole interaction is less because of the better orientation of the dipole moments, and also the Ar-Ar attraction becomes more efficient. Contrary to that, the ion-induced dipole interaction favors a solvated magnesium. The balance of the terms V_{Mg^+Ar}, V_{ArAr}, and V_{dd}, determines the stability of the cluster. For example, for Mg^+Ar_{12} the numerical values for the above three terms are -17.219, -9.242, and $+3.405$ kcal/mol for isomer *(a)*, and -15.365, -10.464, and $+2.239$ kcal/mol for isomer *(b)*.

We may conclude that the icosahedral structure of Mg^+Ar_{12} has two isomers, one with the metal atom in the center and the other with the ion on the surface. Our potential predicts as a lower energy minimum the one with Mg on the surface. However, taking into account the small difference in energy between these two isomers, it is difficult to claim that this is a final conclusion. Ab initio calculations or spectroscopic experiments are needed.

We have made a harmonic frequency analysis for all minima that we have located. For Mg^+Ar_6 the highest frequency is about 80 cm^{-1} and for the clusters of type *(a)* this value decreases as the size increases. On the contrary, for the type *(b)* structures the highest frequency increases, reaching the values of 160 cm^{-1} at $n = 12$. The normal coordinate that corresponds to this eigenfrequency describes mainly vibrations of the metal ion and of the argon atom which is in the center of the icosahedral structure. In the following sections we argue that this is a characteristic to discern the two isomers.

3.2 $Mg^{2+}Ar_n$, $n = 3 - 18$

We have seen that a double-charged ion increases the binding energy with Ar by almost an order of magnitude compared to the singly charged metal, and decreases the equilibrium bond length. That means, that the induced dipole moments on the argon atoms are larger and the minimum energy geometries of $Mg^{2+}Ar_n$ clusters are expected to be markedly different than those of mono-cation.

Figure 5 shows the geometries for $n = 3-18$, and Table VI tabulates their energies. For $n = 3$ a planar triangular D_{3h} geometry is found with Mg ion in the center, for $n = 4$ a regular tetrahedron (T_d) is predicted, whereas for $n = 5$ a C_{2v} symmetry structure is located. A regular octahedron is the geometry of Mg^+Ar_6 (O_h). By adding one more Ar atom this high symmetry is destroyed.

It is worth mentioning that the same geometries were found in SCF calculations which we have done, but with a smaller basis set than that used before.

For $Mg^{2+}Ar_8$ a square antiprism is formed as the lowest energy minimum. The next two clusters in the series are obtained by putting one argon atom above and one below and in the center of each square respectively. Larger clusters are constructed by adding argon atoms on the sides of $Mg^{2+}Ar_{10}$ as shown in Figure 5. The series is completed with the $Mg^{2+}Ar_{18}$ cluster. For all these complexes we have not located a minimum with the metal atom on the surface.

If we adopt the assumption that magic numbers correspond to the clusters of high symmetry or result after the completion of a shell of atoms, then, we would expect that the second peak in the mass spectrum would be for $n = 18$. This is not in agreement with the experimental observation which shows a broad peak at $n = 14$. Such a minimum could be resulted by filling a second shell of Ar atoms putting them in the centers of the sides of the regular octahedral geometry of $Mg^{2+}Ar_6$, thus, obtaining a fcc type geometry (Figure 6). We have located this minimum but it is of higher energy (-145.016 kcal/mol).

The geometries which we find for the clusters with $n > 6$ are the result of the electrostatic model. However, we must point out that the ab initio calculations have shown a significant charge transfer, and that means, that the electrostatic potential may not be very accurate for the larger clusters.

In conclusion, we may say that the energetics of $Mg^{2+}Ar_n$ aggregates favor solvated structures as a result of the strong ion - induced dipole interaction.

4 Dynamic Properties

The stationary points of the potential energy surface provide a zero order approximation to the dynamics of the cluster, since for small excitation energies a harmonic approximation of the pes is satisfactory, and thus, the motions around the stationary points are known (both classically and quantum mechanically). However, dealing with highly anharmonic and strongly coupled potential functions it is necessary to study the full dynamics as the excitation of the system becomes appreciable. In particular, we are interested in finding out at which energy the system ceases to explore only the minimum well, and the atoms start moving erratically through an extended phase space. In other words, the trajectory of the cluster at some particular energy overcomes the potential barrier(s) and visits other minima of the pes in which it can be trapped for appreciable time intervals. Numerous studies have been done for investigating these transitions, which are now accustom to be referred as phase transitions from solid like to liquid like. Most of these studies have been done for Ar_n clusters and using pair additive Lennard-Jones potentials.[30,31]

Equilibrium properties at some particular energy are evaluated using either Monte Carlo or Molecular Dynamics techniques. For relatively small size systems, like the clusters we are studying, Molecular Dynamics methods are more efficient. The latter requires the solution of the classical equations of motion, and in our case we integrate the Hamilton's equations of motion.

The atomic aggregate is described in a space fixed cartesian coordinate system. A variable order, variable time step algorithm is used to integrate Hamilton's equations.[27] The properties that we are interested in are the same with those computed in our previous work on water clusters.[3–6] These are: Average values of the distances Mg^{m+}-Ar, and Ar-Ar, and root mean square fluctuations of the distances from the average values, δ,

$$\delta = \frac{2}{n(n+1)} \sum_{i=1}^{n} \sum_{j=i+1}^{n+1} \frac{[< r_{ij}^2 >_t - < r_{ij} >_t^2]^{(1/2)}}{< r_{ij} >_t}. \tag{12}$$

$<>_t$ denotes time average values. Equation (12) defines the root mean square fluctuations of all distances. Similar equations are valid for the fluctuations of the Mg^{m+}Ar and ArAr bond lengths separately.

We also compute the average kinetic energy, and using the equipartition law we estimate a temperature for the cluster, caloric curves, that is the total energy as function of the temperature, velocity autocorrelation functions, $C(t)$,

$$C(t) = \frac{< \vec{v}(t_0 + t) \cdot \vec{v}(t_0) >_t}{< \vec{v}^2(t_0) >_t}, \tag{13}$$

and from it power spectra, as well as radial distribution functions.

To obtain the average values we integrate one trajectory at total energy E, for time intervals which vary between 500 ps to 1 ns. The energy of the system is increased by scaling the momenta, and then, we leave the system to relax by integrating the new trajectory for times of 100-200 ps before we start selecting points for the evaluation of the average values. To test for convergence, in a few runs we compare the results by doubling the integration time of the trajectory and by increasing the energy with smaller energy steps. Negligible differences were found in these tests.

4.1 Mg^+Ar_n

We first examine possible phase transitions for the clusters of magnesium monocation. Such events are portraited in the caloric curves and in plots of the root mean square bond length fluctuations. Figure 7a shows the caloric curves for the clusters with $n = 4 - 13$. Figure 7b presents the caloric curve of $Mg^+Ar_{12} - (a)$ for a better inspection.

As is well known the temperature at the phase transition is better estimated in plots of the root mean square fluctuations of the distances, and Figure 8 shows the results of Mg^+ clusters for $n = 7 - 13$. Here the *(b)* isomers are studied. It is found that at the temperature where the system starts exploring large regions of phase space the δ function exceeds the value of 0.1 (Lindemman's criterion).[32]

From Figure 8 we can see that the icosahedron of Mg^+Ar_{12} is the most stable cluster having a transition temperature at about 45 K. The stability of the cluster is further examined by computing distributions of the average distances at different energies. For example, Figure 9 shows such distributions for the $Mg^+Ar_{12}-(a)$ at four different energies. At low energies where the cluster remains in the potential well the histograms reveal the distances of Mg-Ar and Ar-Ar encountered in the icosahedron. The plot at the energy -20.35 kcal/mol which corresponds to the transition region in the caloric curve, shows that the distributions are broader but still around the peak values found at lower energies. Finally, at very high energies the distributions tend to become uniform.

We have found two series of minima for Mg^+Ar_n $n > 7$ clusters. One with Mg ion inside and the other with the ion on the surface of the cluster. Now, we address the question which of these two isomers is dynamically more stable for $n = 12$. In Figure 10 we compare the caloric curves, the average Mg-Ar distances, and their root mean square fluctuations, $\delta(T)$. We estimate the transition temperature to be 35 K for the isomer *(a)* and 45 K for the isomer *(b)*.

Figure 11 shows the power spectra obtained from the Mg ion velocity autocorrelation function of the two Mg^+Ar_{12} isomers and at temperatures that correspond to the phase transition. The characteristic band at 130 cm^{-1} is red-shifted from the harmonic frequency (160 cm^{-1}) and this can be used to discern the isomer *(b)* from isomer *(a)*. Similar plots at lower energies show narrower bands.

From the above we may conclude, that the icosahedral structures of Mg^+Ar_{12} are dynamically stable as well as energetically, and between the two isomers *(a)* and *(b)* the one with Mg ion on the surface is the most stable.

4.2 $Mg^{2+}Ar_n$

A dynamic analysis of Mg^{2+} clusters has been carried out for $n = 5 - 7$. Figure 12 shows the root mean square fluctuations of all distances for $n = 5, 6, 7$. We can see an almost linear increase for $n = 6$ up to 600 K. It is interesting to note that for $n = 7$ a rather low transition energy is observed (20 K). This is due to the asymmetric geometry of this cluster which makes the movements of Ar atoms easy.

Figure 13 shows average distances as functions of the temperature for the clusters $n = 5, 6, 7$. The mobility of Ar atoms in the clusters $Mg^{2+}Ar_5$ and $Mg^{2+}Ar_7$ can be seen. In contrast, $Mg^{2+}Ar_6$ shows a linear dependence with the temperature up to 600 K. For all these energies the octahedral geometry of the cluster is not destroyed on the average, and this is considered as an indication of the extra stability of this conformer.

5 Discussion and Conclusions

Using ab initio calculations for the small clusters of $Mg^{m+}Ar_n$, $m = 1, 2$, we have constructed analytical potential functions based on the electrostatic expansion of charge - induced dipole and induced dipole - induced dipole interactions. Minimum energy geometries and equilibrium properties have been investigated with Molecular Dynamics techniques.

The main results are:

1) The lowest minimum energy structures of Mg^+Ar_n, $n = 1 - 14$ are similar to those of Ar_{n+1} clusters, with a regular icosahedral geometry for the Mg^+Ar_{12} cluster, and this in spite of the much stronger attraction of Ar atoms by the Mg ion. However, we have found for $n > 6$ two equivalent isomers. Isomer *(a)* has Mg in the center, and isomer *(b)* has the ion on the surface and an argon atom in the center. Our potential function predicts that isomer *(b)* is more stable in absolute energy for $n > 9$.

The coexistence of solvated and non-solvated isomers for heterogeneous clusters havei been observed in the literature before. A case similar to ours is that of the transition metal V^+Ar_n[33] clusters. The authors have made an analysis of the potential function terms to investigate when the metal atom is pull out onto the surface of the aggregate.

However, a more interesting case is that of the neutral clusters of SF_6Rg_n[34] for Rg = Ar and Kr. Isomers with the rare gas (Rg) atoms covering the molecule and isomers with the Rg atoms stacked on one face of SF_6 were found. The investigators tried to rationalize these tendencies by analyzing the total potential to two contributing terms. They showed that the competition between the pulling of the Rg-SF_6 anisotropy of the potential, and the tendency for the rare gas atoms to achieve the best packing geometries results in the two types of isomers, solvated and non-solvated. What is striking as far as the argon clusters are concerned, is the similarities in the geometries of the lowest minima with those of Mg^+Ar_n aggregates that involve a spherically symmetric solute atom. For example, the cluster with 6 argon atoms forms a regular pentagon, whereas for $n = 12$ the argon atoms form the icosahedral structure using one of the protruding F atoms on the surface. Thus, this structure corresponds to the *(b)* type isomers that we found for the magnesium cation.

2) Caloric curves, radial distributions, distance mean square fluctuations, and power spectra point out that the icosahedron of Mg^+Ar_{12}, for both isomers solvated and non-solvated, is more stable with respect to the temperature at which a phase transition is observed compared to the smaller and larger clusters. The same indicators show that isomer *(b)* has a transition temperature at about 45 K whereas isomer *(a)* at 35 K.

3) Analysis of the harmonic frequencies reveals that clusters of type *(b)* have a

distinguishable large frequency compared to clusters *(a)*. For Mg^+Ar_{12} isomers the maximum harmonic frequency for *(a)* is about 50 cm^{-1} and for *(b)* 160 cm^{-1}.

4) Ab initio calculations at the SCF-MP2 level have been performed for $Mg^{2+}Ar_n$, $n = 1, 2, 3$. Based on these calculations an electrostatic potential function was constructed to study larger clusters.

5) For the minimum of $Mg^{2+}Ar_6$ a regular octahedron of O_h symmetry is found. The $n = 8$ atomic aggregate has a square antiprim geometry, and the $n = 10$ a capped structure obtained from the square antiprism with the extra argon atoms in the middle and above (below) the squares.

The charge transfer found in the SCF calculations of $Mg^{2+}Ar_n$, $n = 1 - 6$ clusters, sheds some doubts about the accuracy of the electrostatic expansion for the larger clusters. Therefore, further work is needed, both theoretical and experimental, to elucidate this point.

Acknowledgment

We are grateful to Dr. M. Velegrakis for many helpful discussions.

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$$
\begin{aligned}
A &= 2.26210716 \times 10^5 \\
a &= 10.77874743 \\
b &= -1.8122004 \\
c_6 &= 1.10785136 \\
c_8 &= 0.56072459 \\
c_{10} &= 0.34602794 \\
d &= 1.36 \\
\varepsilon &= 0.28462 \quad \text{kcal/mol} \\
r_0 &= 7.098756333 \quad a_0
\end{aligned}
$$

TABLE I

Values for the parameters of the Ar-Ar potential function (Equation (6)) taken from ref. [24].

	A/Hartrees	B/a_o^{-1}	C/Hartrees	D/a_o	E	F
Mg^+Ar	0.00760454	4.15781215	0.00226453	5.47 (r_m)	4.5	0.4
$Mg^{2+}Ar$	0.03507768	3.94447024	$C = A$	4.47858086	7.0	0.0

TABLE II

Fitted values of the parameters used in the Morse type potential and switching functions (Equations (4,7,8)). $r_m = D$ is the equilibrium bond length of the bimer Mg^+Ar.

n	$r(a_0)$	E_{SCF}	$E_{SCF-MP2}$	$E^{\infty}_{SCF-MP2}$	E_0
1	4.44 (4.44)	−725.671989	−726.036925	−725.992666	−27.772 (−27.772)
2	4.48 (4.51)	−1252.516465	−1253.117368	−1253.032757	−53.093 (−52.23)
3	4.53 (4.57)	−1779.353432	−1780.190837	−1780.072847	−74.038 (−73.51)

TABLE III

Minima of $Mg^{2+}Ar_n$ clusters. E_{SCF} is the electronic ground state energy at the SCF level, $E_{SCF-MP2}$ is the energy at the MP2 level, and $E^{\infty}_{SCF-MP2}$ is the electronic energy with the atoms separated at large distances. Energies are in Hartrees. E_0 is the binding energy of the cluster in kcal/mol with the zero of the energy defined with all atoms separated in their electronic ground states. The numbers in parentheses are calculated values with the analytical potential.

r_1	4.5	4.74	5.87	5.19	5.87	6.64
r_2	4.5	4.74	5.87	7.50	5.19	6.24
r_3	9.0	8.60	8.60	12.67	7.60	10.10
ab-initio	-50.10	-50.59	-29.29	-30.56	-23.81	-20.74
analytical	-49.74	-50.61	-30.30	-31.54	-25.07	-22.17
r_1	6.64	5.39	5.66	6.09	5.19	5.45
r_2	6.64	4.41	3.86	4.46	5.87	6.64
r_3	10.60	9.60	8.60	8.60	8.60	9.00
ab-initio	-18.10	-46.16	-32.94	-39.48	-35.60	-27.87
analytical	-19.72	-46.09	-32.49	-40.04	-36.56	-28.95

TABLE IV

Comparison of SCF - MP2 and analytical function binding energies for configurations far from the equilibrium point of $Mg^{2+}Ar_2$ cluster. r_3 is the distance of the two argon atoms.

n	**−E**	**−E/n + 1**	**−E/n**	**type**
3	8.692	2.173	2.897	
4	10.520	2.104	2.630	
5	12.088	2.015	2.418	
6	13.864	1.980	2.311	
	15.080	1.885	2.154	*a*
7	15.072	1.884	2.153	*b*
	16.567	1.840	2.071	*a*
8	16.532	1.837	2.067	*b*
	18.029	1.802	2.003	*a*
9	18.013	1.801	2.001	*b*
	19.522	1.775	1.952	*a*
10	19.730	1.794	1.973	*b*
	21.113	1.759	1.919	*a*
11	21.530	1.794	1.957	*b*
	23.056	1.774	1.921	*a*
12	23.589	1.815	1.966	*b*
	24.125	1.723	1.856	*a*
13	24.744	1.767	1.903	*b*
	25.440	1.696	1.817	*a*
14	26.120	1.741	1.866	*b*

TABLE V

Total energies, E, energy per atom, and energy per argon atom of the minima of $Mg^{+}Ar_n$ clusters. Isomers *(a)* are those with magnesium ion in the interior and isomers *(b)* on the surface. Energies are in kcal/mol. The zero of the energy is defined with all atoms separated in their electronic ground states.

$\mathbf{n}$	$\mathbf{-E}$	$\mathbf{-E/n+1}$	$\mathbf{-E/n}$
3	73.506	18.377	24.502
4	92.526	18.505	23.132
5	107.877	17.980	21.575
6	123.313	17.616	20.552
7	129.156	16.144	18.450
8	135.887	15.098	16.986
9	139.202	13.920	15.476
10	142.320	12.938	14.232
11	144.559	12.047	13.142
12	146.881	11.298	12.240
13	149.043	10.646	11.465
14	151.303	10.087	10.807
15	153.484	9.593	10.232
16	155.724	9.160	9.733
17	157.848	8.769	9.285
18	160.038	8.423	8.891

TABLE VI

Total energies, E, energy per atom, and energy per argon atom of the minima of $Mg^{2+}Ar_n$ clusters. Energies are in kcal/mol. The zero of the energy is defined with all atoms separated in their electronic ground states.

Figures

1. The fitted potential curve for the electronic ground state ($^2\Sigma$) of the bimer Mg^+Ar. The continuous line, [1], is the total potential given by Equation (2). The dashed line, [2], describes the charge - induced dipole interaction, the dotted line, [4], is the last two terms of Equation (2), and the double dashed line, [3], is the Morse type potential.

2. The fitted potential curve for the electronic ground state ($^1\Sigma$) of the bimer $Mg^{2+}Ar$. The continuous line, [1], is the total potential given by Equation (2). The dashed line, [2], describes the charge - induced dipole interaction, the dotted line, [4], is the last two terms in Equation (2), and the double dashed line, [3], is the Morse type potential. The dots along the total potential curve denote the ab initio points.

3. Minimum energy structures for the clusters Mg^+Ar_n, $n = 3 - 14$. For $n > 6$ two isomers are shown, one with Mg ion in the interior of the cluster *(a)*, and one on the surface *(b)*.

4. Plots of the total energy, (V_{tot}), ion-induced dipole interaction, (V_{Mg^+Ar}), Ar-Ar interaction, (V_{ArAr}), given by Equation(6), and the induced dipole - induced dipole interactions, (V_{dd}), among argon atoms, as functions of the size of the cluster.

5. Minimum energy structures for the clusters $Mg^{2+}Ar_n$, $n = 3 - 18$.

6. A fcc type minimum of $Mg^{2+}Ar_{14}$ with energy equal to -145.016 kcal/mol.

7. (a) Caloric curves of Mg^+Ar_n and for $n = 4 - 13$. (b) The caloric curve of $Mg^+Ar_{12} - (a)$ isomer.

8. Bond length root mean square fluctuations, $\delta(T)$, of all distances for the clusters Mg^+Ar_n and with $n = 7 - 13$.

9. Time average distributions of all distances of $Mg^+Ar_{12} - (a)$ for four different energies. Energies are in kcal/mol.

10. Comparison of the caloric curves, the average Mg-Ar distances, and their root mean square fluctuations, $\delta(T)$, of the isomers *(a)* and *(b)* of Mg^+Ar_{12}.

11. Power spectra of Mg^+Ar_{12} at the temperatures 35 K for the isomer *(a)* and 45 K for the isomer *(b)*. For the latter, the characteristic band at 130 cm^{-1} that discerns this isomer, can be seen (see text).

12. Root mean square fluctuations, $\delta(T)$, of $Mg^{2+}Ar$ distances for the clusters $Mg^{2+}Ar_n$ and with $n = 5 - 7$.

13. Average values of the distances of $Mg^{2+}Ar_n$ clusters. $< r >$ is the average value of all distances in the cluster.