Mass spectra and structures of Cu^+Rg_n clusters (Rg = Ne, Ar)

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Abstract

The mass spectra of copper(I) doped neon and argon clusters obtained in a time-of-flight apparatus are presented. Electronic structure calculations with density functional theory reveal that the first closed shell of Cu^+Ne_n complexes consists of 12 atoms with icosahedral geometry, whereas for Cu^+Ar_n complexes, six atoms form an octahedral structure. These results are in accord with the mass spectra, which show a substantial decrease in the intensities for the clusters with $n > 12$ neon atoms and $n > 6$ argon atoms. For both inert gas atoms the calculated geometry of Cu^+Rg_4 aggregates is found planar and not tetrahedral as it is expected for a cation with a spherical symmetry. © 2002 Published by Elsevier Science B.V.

1. Introduction

Copper(I) has a fully occupied d orbital electronic configuration. Nevertheless, its chemistry shows a minimum resemblance with that of alkali metals because the d orbitals do not shield the nuclear charge as efficiently as the p orbitals. Copper even differs from the other elements of group 11, Ag and Au. The study of complexes of Cu^+ with ligands L has lead to a linear geometry for Cu^+L_2, triangular with copper in the center for Cu^+L_3, and tetrahedral for Cu^+L_4 [1]. Extracting the structures of the most stable complexes (magic numbers) is one of the main objectives of cluster science. Particularly, metal cations doped inert gas clusters have played the role of prototype systems in investigating the geometries and the spectroscopy of these species with the metal atom acting as a chromophore group [2–5].

In the last years Velegrakis and coworkers [6–15] have carried out a systematic study of noble gas clusters doped with a variety of metal cations by using a time-of-flight mass spectrometer, combined with laser sources for the ablation of the metal ions and the electronic excitation of the selectively separated clusters. Theoretical calculations and modelling [8,10,16,17] have shown that for alkali and alkaline earth ions, which have the electronic configuration of an inert gas atom or occupied s orbitals, the geometries of the most

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stable aggregates follow that of the hard sphere packing model. In contrast, transition metal atoms having not fully occupied d orbitals show geometries which are determined by the localization of the d orbitals. Such systems have been studied in previous publications and they involved Ni^+, $Pt^+(d^9)$ [14], $Ti^+(d^3)$ [12] and $Fe^+(d^6)$ [13], whereas other research groups have studied Co^+, $Rh^+(d^8)$ [18–20] and Nb^+, $V^+(d^4)$ [19,20].

Extended ab initio calculations for metal ion doped inert gas complexes were carried out by Bauschlicher et al. [3]. Binding energies and geometric factors for a variety of transition metals with one and two noble gas atoms were reported. Recently, the doubly charged group 11 metal/argon complexes have been studied experimentally and theoretically [21]. In this work the stability found for the dimer ions was considered unexpected and aggregates with four and six argon atoms were shown to be more stable than the neighboring size clusters. Theoretical calculations for Au^+Rg have also been carried out [22,23] and show the formation of covalent character bonds for the heavier inert gas atoms.

Cu^+ has a fully occupied d orbital (d^{10}) electronic configuration and it is interesting to investigate its complexes with noble gas atoms and compare them with those of alkalis and alkaline earths. This is the purpose of the present article. Time-of-flight mass spectra and ab initio electronic structure calculations have been combined to study Ne and Ar aggregates with copper(I). One important outcome of this study is that the expected tetrahedral geometry for the ground state of Cu^+Rg_4 is not found, but instead, planar structures are predicted. Furthermore, copper(I) can accommodate as many as 12 neon atoms in the first closed shell resulting in an icosahedral structure, but only six argon atoms in an octahedral geometry.

The article is organized as follows. In Section 2 the experimental and theoretical techniques are briefly summarized. In Section 3 the mass spectra and theoretical calculations for the minimum energy structures in the ground electronic states of Cu^+ doped neon and argon clusters with sizes up to the first closed shell are presented and discussed. Finally, in Section 4 we summarize the conclusions of this study.

2. Experimental and theoretical methods

The experimental apparatus used for the production of Cu^+Rg_n has been described in detail in our previous studies [7,11a]. However, for completeness of the paper we give in the following a brief description.

The molecular beam apparatus consists of three differentially pumped chambers and it is equipped with a time-of-flight (TOF) mass spectrometer. The Cu^+ doped noble gas clusters are formed in a laser vaporization source, where a pulsed excimer (308 nm) laser produces plasma from a pure Cu target. The plasma plume is mixed with an expanding gas pulse provided by a home built pulsed nozzle. The adiabatic expansion results in cooling of the nascent clusters, thus forming a cluster beam, which contains neutral clusters as well as ionic species. We study the positive ions, which are produced directly from the plasma/noble gas mixing without the use of post-ionization. Hence, it is expected that these clusters are sufficiently relaxed and the measured size distribution reflects the stability of these species. The mass spectra are obtained by accelerating the ions produced by each laser shot in a two-field TOF spectrometer towards a microchannel detector and recording the arrival time of the different masses in a digital storage oscilloscope. The spectra that will be discussed are the result of averaging several hundreds laser shots.

All calculations for the ground electronic state of Cu ion doped neon and argon aggregates were performed at the level of density functional theory (DFT) with the GAUSSIAN 98 program package [24]. The three-parameter hybrid functional of Becke [25] using the Lee–Yang–Parr correlation functional [26] (B3LYP) was employed for the geometry optimizations. The atomic basis set that we use, include Gaussian functions of triple zeta quality augmented by d-polarization functions (6-311G*) [27]. The same methods were used and tested in our previous calculations of Ti^+Ar_n [12] and Ni^+Ar_n [14]. Nevertheless, in order to check the accuracy of our theoretical model, we also performed calculations either with methods treating better the electron correlation like Möller–Pleset [27] or using larger basis sets like 6-311+G*.

In both tests the results were in satisfactory agreement with those of B3LYP/6-311G*. All the geometries presented here are fully optimized with the method mentioned.

3. Results and discussion

The mass spectra obtained for Cu^+Ne_n and Cu^+Ar_n are depicted in Fig. 1. The intensity is displayed as a function of the number of noble gas atoms contained in the cluster by transforming the time-of-flight to mass.

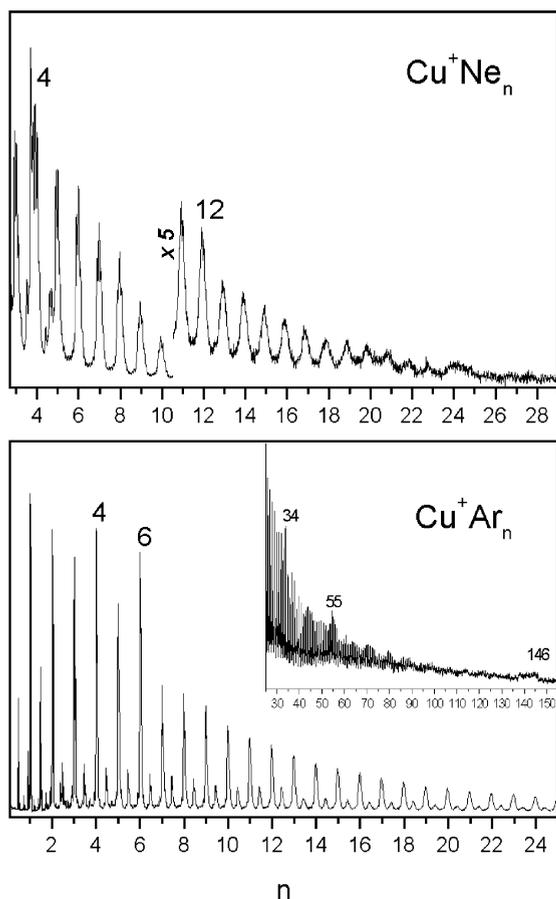For Cu^+Ne_n (Fig. 1, top) the intensity drops smoothly, exhibiting some irregularities at $n = 4$

Fig. 1. Mass spectra of Cu^+Ne_n (top) and Cu^+Ar_n (bottom) clusters. The number n of the noble gas atoms is obtained from the time-of-flight of the corresponding mass. The most stable cluster sizes are denoted.

and 12. Clusters larger than $n \sim 25$ are not formed with appreciable intensities. In addition, the spectrum contains small amounts of $Cu^+(H_2O)_m Ne_n$ ($m = 1–4$, $n = 0–2$) species, which are due to water impurities in the gas inlet line. For the case of Cu^+Ar_n (Fig. 1, bottom), clusters with sizes $n > 150$ are formed. The small peaks between the main series are attributed to Ar_n^+ series. We find increased relative intensities at $n = 4$ and 6 and a substantial drop of the intensity after $n = 6$. Furthermore, as the inset in the figure shows, magic numbers of Cu^+Ar_n clusters appear also at $n = 34$, 55 and 146. This spectrum is very similar to that of Li^+Ar_n [15].

It should be mentioned that laser ablation of Cu produces Cu-ions in ground state $(3d^{10})$ as well as in the excited metastable state $(3d^9 4s^1)$. As experiments however have shown the relative density of these long lived species is less than 10% of the ground state ones [28]. Therefore, only ground state ions are taken into account.

Calculations for the minimum energy geometries for both Cu^+Ne_n and Cu^+Ar_n clusters have been performed. Various initial geometries were tested for each complex at the B3LYP/6-311G* level of theory in our search for the absolute minimum. The total energy, E_{tot}, the binding energies, $E(n) = E_{tot} - E(Cu^+) - nE(Rg)$, of these minima and the charge on Cu (obtained from a Mulliken population analysis) are listed in Table 1. The geometrical parameters of the clusters are tabulated in Table 2.

The ground electronic state of Cu^+Ne is a $^1\Sigma^+$ state with a bond length of 2.164 Å and binding energy of 0.25 eV, while for Cu^+Ar our calculations reveal a state of the same symmetry with a bond distance of 2.291 Å and binding energy of 0.49 eV. Bauschlicher et al. [29] carried out modified coupled-pair functional (MCPF) calculations with an extended triple zeta basis set and found a bond length for Cu^+Ne 2.375 Å and a similar distance for Cu^+Ar of 2.374 Å. However, the corresponding binding energies are significantly different; 0.096 eV for Cu^+Ne and 0.405 eV for Cu^+Ar. In comparison to our DFT results we systematically predict a shorter bond length and an increased dissociation energy. The same trend was found for Li^+Ar. This could be attributed not

Table 1
Total energy E_{tot}, binding energies $E(n)$ and binding energy differences $\Delta E(n) = E(n) - E(n-1)$ of Cu^+Ne_n ($n = 1$–13) and Cu^+Ar_n ($n = 1$–7) clusters obtained at the B3LYP/6-311G* level of theory

n	Cu^+Ne_n				Cu^+Ar_n			
	E_{tot} (hartree)	$E(n)$ (eV)	$\Delta E(n)$ (eV)	q	E_{tot} (hartree)	$E(n)$ (eV)	$\Delta E(n)$ (eV)	q
0	−1640.103615	0.00		1.00	−1640.103615	0.00		1.00
1	−1769.065280	0.25	0.25	0.97	−2167.675719	0.49	0.49	0.91
2	−1898.031295	0.63	0.38	0.92	−2695.254299	1.16	0.67	0.78
3	−2026.987324	0.73	0.10	0.92	−3222.810558	1.23	0.07	0.78
4	−2155.945855	0.91	0.18	0.90	−3750.367391	1.31	0.08	0.78
5	−2284.901156	0.99	0.08	0.90	−4277.922815	1.35	0.04	0.78
6	−2413.862154	1.23	0.24	0.88	−4805.478625	1.40	0.05	0.78
7	−2542.820041	1.38	0.15	0.88	−5333.032721	1.41	0.01	0.78
8	−2671.777600	1.53	0.15	0.88				
9	−2800.734520	1.66	0.13	0.87				
10	−2929.689991	1.75	0.09	0.87				
11	−3058.645198	1.82	0.07	0.88				
12	−3187.601998	1.95	0.13	0.88				
13	−3316.559801	1.99	0.04	0.88				

The charge q on the Cu^+ atom is that from a Mulliken population analysis.

Table 2
Structural characteristics of Cu^+Ne_n and Cu^+Ar_n ($n = 1$–7) clusters obtained at the B3LYP/6-311G* level of theory

System	Symmetry	Structural characteristics	
Cu^+Ne	$C_{\infty v}$	Cu–Ne = 2.164	
Cu^+Ne_2	$D_{\infty h}$	Cu–Ne = 2.087	
Cu^+Ne_3	C_{2v}	Cu–Ne$_{top}$ = 2.395	Cu–Ne$_{bot}$ = 2.119
		Ne$_{top}$–Cu–Ne$_{bot}$ = 91°	Ne$_{top}$–Ne$_{bot}$ = 3.227
Cu^+Ne_4	D_{4h}	Cu–Ne = 2.233	Ne–Ne = 3.158
Cu^+Ne_5	C_{4v}	Cu–Ne$_{top}$ = 2.452	Cu–Ne$_{base}$ = 2.253
		Ne$_{top}$–Ne$_{base}$ = 3.368	Ne$_{base}$–Ne$_{base}$ = 3.186
Cu^+Ne_6	C_{2v}	Cu–Ne = 2.310	Ne–Ne = 3.623
Cu^+Ne_7	C_1	Cu–Ne = 2.317	Ne–Ne = 2.718
Cu^+Ar	$C_{\infty v}$	Cu–Ar = 2.291	
Cu^+Ar_2	$D_{\infty h}$	Cu–Ar = 2.260	
Cu^+Ar_3	C_{2v}	Cu–Ar$_{top}$ = 3.046	Cu–Ar$_{bot}$ = 2.278
		Ar$_{top}$–Cu–Ar$_{bot}$ = 93°	Ar$_{top}$–Ar$_{bot}$ = 3.892
Cu^+Ar_4	D_{2h}	Cu–Ar = 2.312	Ar–Ar = 3.765
		Cu–Ar = 2.971	
Cu^+Ar_5	C_{2v}	Cu–Ar$_{top}$ = 3.234	Cu–Ar$_{base}$ = 2.327
		Cu–Ar$_{base}$ = 3.007	Ar$_{base}$–Ar$_{base}$ = 3.797
		Ar$_{top}$–Ar$_{base}$ = 3.952	
Cu^+Ar_6	D_{4h}	Cu–Ar$_{top}$ = 2.355	Cu–Ar$_{base}$ = 3.048
		Ar$_{base}$–Ar$_{base}$ = 4.311	Ar$_{top}$–Ar$_{base}$ = 3.852
Cu^+Ar_7	C_1	Ar–Ar$_{oct}$ = 4.5	

Bond lengths are in Angstroms and bond angles in degrees.

only to the method but also to the different basis sets that we use.

For both Cu^+Ne_2 and Cu^+Ar_2 a linear geometry is predicted for the minimum in the $^1\Sigma_g^+$ ground electronic state. The equilibrium bond distances are 2.087 and 2.260 Å, respectively, and the binding energies are 0.63 and 1.16 eV as can be seen in Tables 1 and 2. Any attempt starting from a bent

triangular geometry, after the geometry optimization ends up into the linear configuration, indicating that there is no bent local minimum. Our calculations on Cu^+Ar_2 can also be compared with those of Bauschlicher et al. [29] who found a bond length of 2.338 Å and binding energy of 0.85 eV.

Cu^+Ne_3 is a planar C_{2v}, T-shape structure with the copper ion in the middle connected with the three Ne atoms. The Ne–Cu–Ne angle is 91°. The Cu^+Ar_3 ground state geometry is also T-shaped with the Ar–Cu–Ar angle to be 93°. The difference in Cu^+Ne_3 and Cu^+Ar_3 minimum energy formation can be explained with geometrical arguments since the longer Ar–Ar bonds open the Ar–Cu–Ar angle to 93°. It is worth reporting that all pyramidal, three-dimensional initial geometries, after the geometry optimization end up planar. For all clusters with $n < 4$ we have tested the B3LYP results with MP2 calculations. The agreement is satisfactory.

In Cu^+Ne_4 and Cu^+Ar_4 clusters the ground state geometries are planar but of different symmetry. Cu^+Ne_4 is a planar D_{4h} structure, while the Cu^+Ar_4 ground state geometry is a D_{2h} rhombic geometry with the copper ion in the center. Analysis of the highest occupied molecular orbitals (HOMO), shown in Fig. 2, reveal that for neon only the $3d_{xy}$ atomic orbital participates and that justifies the high symmetry of the complex. On the other hand, for argon HOMO contains the $3d_{xy}$ and $4s$ orbitals. This results in forming two non equal pairs of bonds as can be seen in Fig. 2. There is an increased electron density along the longer bonds than the short ones.

For the corresponding clusters of alkalis and alkaline earths tetrahedral geometries have been obtained [15,17]. The planar structures of copper(I) aggregates could be understood on energetic arguments. The distances Ar–Ar (3.765 Å) and Ne–Ne (3.158 Å) in Cu^+Rg_4 are very close to those of the free dimers, 3.76 and 3.10 Å, respectively, for the planar geometries. This is confirmed from calculations, which keep the tetrahedral structure (T_d) of the cluster during the energy optimization. The energies of the optimized T_d-symmetry structures were 0.15 eV for neon and 0.17 eV for argon above their absolute minima, and they have longer bond lengths (2.31 and 2.56 Å). The imaginary

frequencies found for these stationary points preclude these geometries to be minima.

Cu^+Ne_5 and Cu^+Ar_5 are the smallest complexes, which possess a three-dimensional ground state. Cu^+Ne_5 is a squared pyramid, constructed from Cu^+Ne_4 with the addition of an extra Ne atom at 2.452 Å above copper. Similarly, Cu^+Ar_5 is a rhombic pyramid with the Ar–Cu distance to be equal to 3.234 Å. In both ground state geometries the copper atom has a small z-distortion inside the pyramid. As in the case of Li^+Rg_5 clusters [15], there is a relative minimum (triangular bipyramid) a few kcal/mol higher in energy than the ground state. With the present accuracy of our calculations it is difficult to unequivocally determine the absolute minimum.

Cu^+Ne_6 is a strongly distorted octahedron of C_{2v} symmetry, whereas the Cu^+Ar_6 is an almost octahedral structure with two strong Cu–Ar bonds of 2.355 Å and four weaker of 3.048 Å. In both systems no other local minima were traced.

Previous calculations in inert gas complexes doped by transition metal cations have shown that the first closed shell is completed with the octahedral structure. The second shell is formed by capping the faces of the octahedron with extra atoms [12–14]. This is the case in Cu^+Ar_7 cluster. The Ar–Ar$_{caped}$ distance is approximately 4.5 Å and the octahedron is slightly deformed. In contrast, for the Cu^+Ne_n clusters the first closed shell is formed with 12 atoms, which form icosahedral geometry. The geometry of Cu^+Ne_7 is shown in Fig. 3 while the structural characteristics are given in Table 2. The different behavior of Cu^+Ne_7 has mainly, a geometrical explanation. The Ne atoms are smaller in comparison to Ar atoms so that Cu^+ can accommodate more than six Ne atoms around it, maximizing thus the Cu–Ne interactions. In the case of Cu^+Ar_7, as well as in other metals [12–14], no more than six Ar atoms can be placed around the cation. We checked the basis set dependence of this result by reoptimizing Cu^+Ne_7 with a larger basis set including diffuse functions ($6\text{-}311+G^*$) and the results were consistent.

The geometries of clusters larger than Cu^+Ne_6 are exhibited in Fig. 3. The Cu^+Ne_8 structure is a square antiprism with D_{4d} symmetry. The Cu–Ne bonds are 2.333 Å while the Ne–Ne bonds are
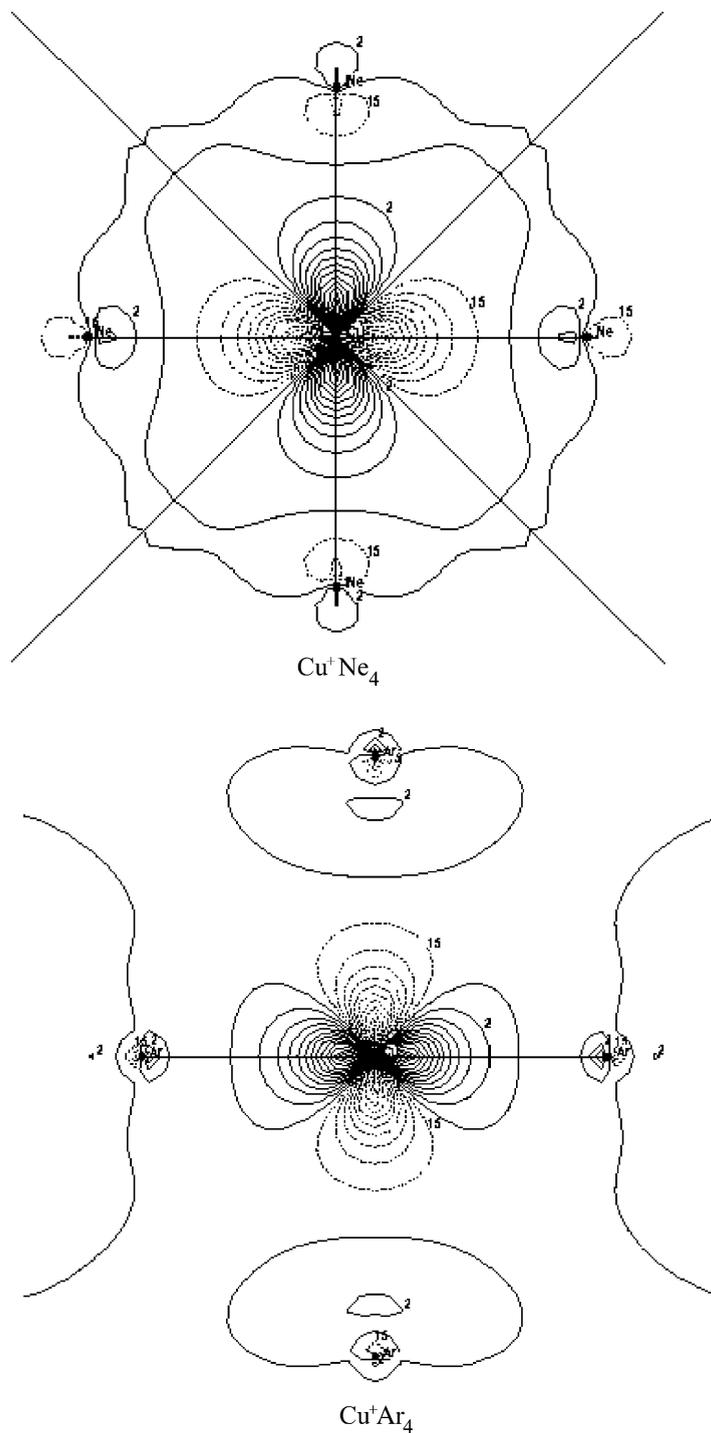
Cu^+Ne_4

Cu^+Ar_4

Fig. 2. The highest occupied molecular orbital (HOMO) of Cu^+Ne_4 and Cu^+Ar_4. For Cu^+Ne_4 the HOMO is mainly a $3d_{xy}$ orbital, while for Cu^+Ar_4 the HOMO is a combination of $3d_{xy}$ and 4s orbitals.
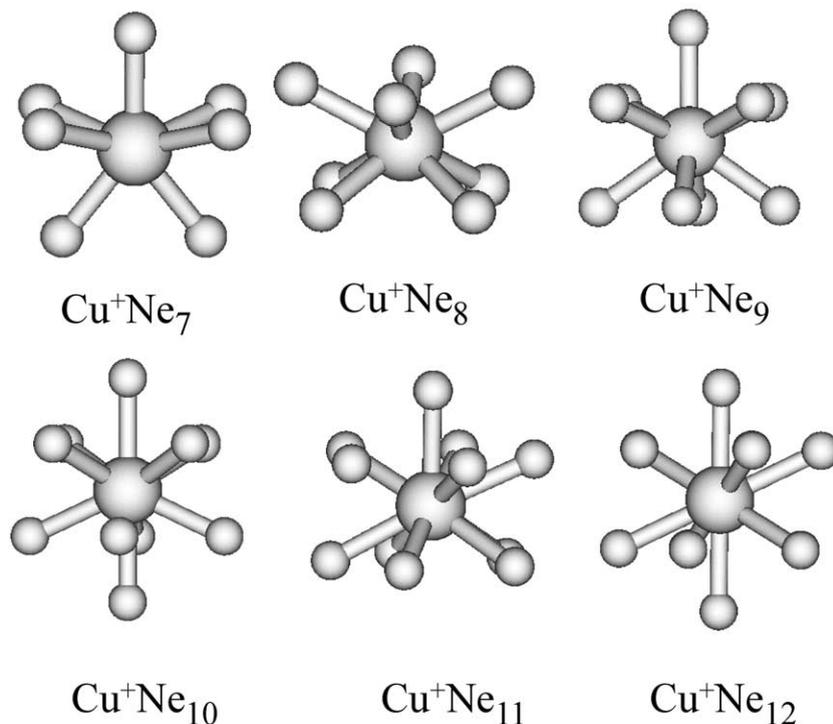
Fig. 3. Minimum energy geometries of Cu^+Ne_n clusters and for $n = 7$–12.

2.919 Å between atoms in the same square and 2.687 Å between atoms of different squares. The cubic isomer is a relative minimum that lies 1.12 eV above the absolute minimum.

The Cu^+Ne_9 cluster is produced form Cu^+Ne_8 with the addition of one Ne atom at the top of one square base and at 2.696 Å from the Cu^+ ion. The symmetry of this cluster is C_{4v}. The Cu^+Ne_{10} forms a capped square antiprism. In this cluster there are two kinds of Cu–Ne bonds: eight at 2.385 Å (with the Ne atoms of the two squares) and two at 2.470 Å (with the two extra Ne atoms). If we compare the geometries of Cu^+Ne_{10} with Cu^+Ne_8 we can observe the elongation of the eight Cu–Ne bonds, but not enough to reach the Cu–Ne_{extra} value. This is an indication that the maximum coordination number of Cu^+ ion has not been achieved yet. In order to do so, we have to add two more atoms to form Cu^+Ne_{12}, a symmetric icosahedral structure with copper ion in the center.

After the icosahedral Cu^+Ne_{12}, the addition of Ne ligands will lead to the capping of the trian-

gular faces of the icosahedron filling the second shell. Cu^+Ne_{13} has also been optimized to give the Ne–Ne_{13} distance at 2.7 Å.

For a comparison between these theoretical results and the experimental mass spectra we show in Table 1 the calculated binding energy differences $\Delta E(n) = E(n) - E(n - 1)$ of the Cu^+Ne_n and Cu^+Ar_n clusters. Irregularities in these energy differences indicate the stability of a cluster with respect to neighboring ones. The theory reproduces the observed extra stability of Cu^+Ne_4, Cu^+Ne_{12}, Cu^+Ar_4 and Cu^+Ar_6 (see Fig. 1). Since, the formation of clusters in a molecular beam, as in these experiments, proceed via association collisions (heating) and evaporation of atoms (cooling) until a particular cluster reaches a bound state [30], it is reasonable to assume that the measured mass spectrum reflects the binding energy differences of the clusters.

For Cu^+Ar_n clusters with $n > 7$ we did not perform DFT calculations. It has been shown in previous studies for similar systems, that the

intensity pattern appearing in the mass spectra gives the fingerprint of the structure of the clusters. As mentioned above the relative intensity irregularities in the Cu^+Ar_n clusters resemble those of Li^+Ar_n [15]. Therefore, it is expected that similar structural trends will characterize both systems, at least for the larger sizes. Thus, we can infer from the Li^+Ar_n study [15] that the complexes are growing from the octahedral structure of Cu^+Ar_6 by close packing of Ar atoms on triangular faces and vertexes. This results in clusters without special stability but keeping an intact octahedral core. This growth ends at $n = 34$, where a dense packing around an octahedron gives a symmetric and stable Cu^+Ar_{34} cluster (see [15]). For large clusters the observed stability at $n = 55$ and $n = 146$ suggests icosahedral structures since at these cluster sizes second and third closed shell occurs [30]. This means that between $n = 34$ and $n = 54$ a structural change occurs, as it has also been observed in many other metal ion doped noble gas (MRg_n) systems [8,10]. There is a critical cluster size, n_t, where this transition occurs. This critical size depends mainly on the radius ratio $\sigma^* = R_{M-Rg}/R_{Rg-Rg}$ and increases as σ^* decreases [8]. For Cu^+Ar $\sigma^* \approx 0.61$ and for Cu^+Ne $\sigma^* \approx 0.71$. Thus, the Cu^+Ne_n clusters adopt earlier $(n_t < 12)$ icosahedral geometry than the Cu^+Ar_n clusters $(34 < n_t < 55)$. Finally, the similarity in the stability pattern of large Cu^+Ar_n and Li^+Ar_n clusters can be attributed to their similar size ratios $(\sigma^*_{Li^+-Ar} \approx 0.62)$.

4. Conclusions

The mass spectra of Cu^+Ne_n and Cu^+Ar_n obtained in a time-of-flight apparatus are reported together with density functional theory calculations employed to determine the geometries of the most stable configurations. It is found that for neon the first closed shell consists of 12 atoms forming an icosahedral structure whereas for argon six atoms form an octahedral geometry. Although the octahedral geometry of argon is in accord with other transition metals which have not fully occupied d orbitals, the icosahedral geometry of neon clusters seem to follow the behavior of

alkaline earth cations such as Mg^{+17}. Furthermore, for both Cu^+Ne_4 and Cu^+Ar_4 we do not find a tetrahedral geometry, as in the most electronic spherically symmetric cations, but planar.

Finally, the comparison of Cu^+Ar_n and Li^+Ar_n mass spectra implies close packing structures for the large size aggregates.

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