DENSITY FUNCTIONAL STUDY ON Cu AND Zn CLUSTERS:
Comparison with Na and Mg clusters

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The geometrical structure of Cu_2-Cu_8 and Zn_2 - Zn_8 clusters were optimized by Amsterdam Density Functional method. The Cu clusters up to hexamers exhibit the equilibrium structures with triangles joined by edges. While, the Zn clusters have the structures with tetrahedrons joined by edges or vertices. The trend for Cu clusters is almost similar to that for the Na clusters. On the other hand, the trend for Zn clusters is somehow different from that for Mg clusters, though both metals have similar outermost electronic structure, $(s)^2$ configuration.
Key words: density functional theory, metal cluster, geometry optimization

1. INTRODUCTION

Metal clusters are found to exhibit some properties different from those of bulk: bond length [1], ionization energy [2], magnetic moment [3,4], and so on. One of the most interesting features of the metal clusters is their geometrical structure that is often different from their bulk structures.

The geometric structure of the metal clusters is of interest from both fundamental and practical points of view. Since the 3d orbital of both copper (Cu) and zinc (Zn) is filled with electrons, their valence structures are similar to those of alkali metal (AM) and alkaline earth metal (AE) elements, respectively: one s-electron for Cu and AM, while two s-electrons for Zn and AE. This predicts that Cu and Zn have properties similar to those of AM and AE, respectively.

The geometric structure of the AM and AE clusters are well explained by the jellium (shell) model [5], which is defined by a Hamiltonian that treats the electrons as usual but the ionic cores as an uniformly positive charge [6]. The AM clusters are well described by the jellium model with ellipsoidal distortion [5] and the AE ones by a simple spherical jellium model [7]. In Fig. 1, equilibrium structures for Na_2 - Na_8 clusters [8-10] and in Fig. 2 those for Mg_2 - Mg_8 [11-13] clusters are shown.

For Cu clusters, Yannouleas and Landman reported that the ellipsoidal shell model well explains their ground-state properties such as ionization potentials and electron affinities [14]. Actually, first-principle calculations have clarified that the geometries up to Cu octamers [15-19] are almost similar to those of Na_n clusters [5,8,9,20,21]. Here, the Cu_6 hexamer have different structure from that of Na_6 hexamer. Therefore, in this study we reconfirm the Cu_6

clusters, as well as other Cu clusters up to octamers.

For Zn clusters, Katakuse et al. reported that the abundance of Zn clusters is explained by shell-closing effect of s-valence electrons which are bound in a spherically symmetric potential well of the cluster [22,23]. Recently, Flad et al. reported the equilibrium structured of Zn clusters up to hexamer [24]. The obtained structures by them are the same for those of Mg clusters up to pentamer. However, the structure of hexamer is somehow different: it was the bicapped tetrahedral structure.

In order to clarify whether the Zn clusters have the similar property of Mg clusters, it is useful to examine the geometrical structure of the Zn clusters systematically. The first aim of the present work is to obtain the equilibrium structures of Zn clusters up to octamers by a density functional method. We use Amsterdam Density Functional method, which have successfully applied for the calculation of V, Cr, and Fe clusters [25,26]. Then we examine whether the structure of Cu and Zn clusters are similar to AM and AE clusters, respectively. Furthermore, we focus our attention on the tetramers of these metals, because the structures of $(AM)_4$ and Cu_4 are quite different from those of $(AE)_4$ and Zn_4. The former is reported to be in rhombus while the latter is tetrahedron. Recently, we successfully analyzed the nature in chemical bond of AM and AE tetrahedrons by using DV-Xα method [27]. In the present study, this approach would be helpful.

2. COMPUTATIONAL METHOD

The geometries of the Cu and Zn clusters were energetically optimized using a program package of Amsterdam Density Functional (ADF) [28]. A triple-ζ Slater-type orbital (STO) basis set was
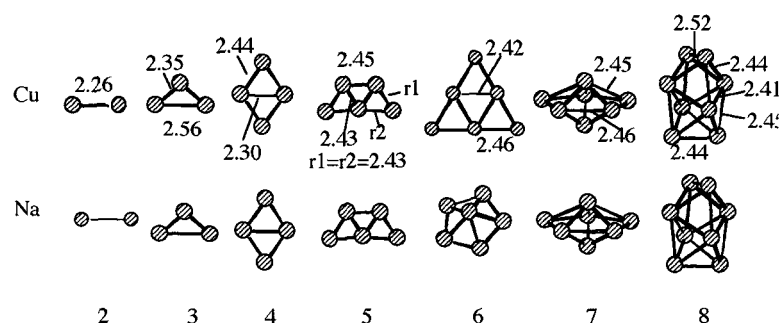
Fig. 1. Lowest energy equilibrium configurations of neutral Cu and Na [8-10] clusters.

used for the electronic state of the clusters. The $1s \sim 2p$ orbitals were treated using the frozen core approximation. A local part and so-called non-local part of the exchange and correlation potentials were given by Vosko, Wilk, and Nusair [29] and Perdew and Wang [30], respectively.

For trimers, we tried an equilateral triangle (D_{3h}), an isosceles triangle (C_{2v}, both obtuse and acute), and a linear structure. We considered a rhombus, a rectangle, a square, a tetrahedron, and a linear structure for tetrameter. For pentamer, a trapezoid, a pyramid, a trigonal bipyramid, a pentagon, and a linear structure were examined. A tetrahedron with an atom on the top was also considered as pentamer. We calculated a planar hexagon, a pentagon pyramid, a trigonal prism, a trigonal antiprism, a planer double triangle, an octahedron, a bicapped tetrahedron, and a linear structure as hexamer. For heptamer, we examined a pentagon bipyramid, a planar hexagon with a center atom, a hexagon pyramid, two types of trigonal prism with an add-atom, an octahedron with an add-atom, and two tetrahedrons joined by a vertex. We investigated a rhombohedron, a rectangular prism, a cube, three types of trigonal prism with two add-atoms, a stacked tetrahedrons, hexagon bipyramid, a square antiprism, and a C_{2v} structure shown in Fig. 1 and a C_s structure in Fig. 2 for octamer.

In order to elucidate the contribution of individual atomic orbitals to chemical bonding of the metal clusters, the discrete-variational (DV) $X\alpha$ molecular orbital method was used [31]. This method is suitable for analyzing the roles of individual atomic orbitals in chemical bonding, because the atomic orbitals used as the basis functions are automatically optimized in the molecular potential [32]. The computational details of the DV-$X\alpha$ method have been described in Ref. 32. Chemical bonds between atomic orbitals were extracted with the Mulliken population analysis [33]. The basis functions used were $1s \sim 4p$. The DV-$X\alpha$ calculations were performed with the Slater exchange parameter α of 0.7 for all the calculations.

3. RESULTS AND DISCUSSION
3.1 Optimized Geometry for Cu Clusters
   Fig. 1 shows optimized geometry for $Cu_2 \sim Cu_8$

clusters obtained by the ADF method in the present study. Structures for Na clusters taken from literature are also shown [8-10]. Since the Cu small clusters are typical system for those who perform quantum chemical or first-principle molecular dynamics calculation, it is useful to examine whether the ADF method can reproduce the results appeared in the literature. The Re (bond length) and B.E. (Binding Energy) of Cu_2 were obtained to be 2.26 Å and -2.54 eV, respectively. The most stable structures for Cu_3 was isosceles triangle (C_{2v}) with Re $=2.35$ and 2.56Å and B.E.$= -3.82$ eV. On the other hand, the most stable structure for the tetramer was the rhombus (D_{2h}) with Re $= 2.30 \sim 2.44$Å and B.E.$= 4.30$ eV. For the Cu_5 pentamer, the most stable structure was the trapezoid (C_{2v}) with Re $= 2.43 \sim 2.45$ Å and B.E.$=-8.77$ eV. For the hexamer, the most stable structure was found to be the double triangle (D_{3h}) structure with Re $= 2.42 \sim 2.46$ Å and B.E.$= -11.75$ eV. Furthermore, the most stable structure for the Cu_7 heptamer was the pentagonal bipyramid (D_{5h}) with Re$= 2.45 \sim 2.46$Å and B.E.$=-14.47$ eV. Finally, the most stable structure for the octamer was C_{2v} symmetry with Re$= 2.41 \sim 2.52$Åand B.E.$=-17.37$ eV.

The geometries for Cu_3 to Cu_8 obtained in the present calculation completely reproduce the results obtained by Massobrio et al. [15] and partially do those by Jackson [16]. Experimentally, the bond length for Cu_2 dimer has been obtained to be 2.22 Å [34], which is well reproduced by the present calculation. Theoretical values reported in the literature are $2.17 \sim 2.18$ Å [15,16], which are comparable.

Comparing the structures for Cu clusters and Na ones, one can easily find that the geometries are almost the same for these metals, except for hexamers. As to hexamer, Martins [9] and Röthlisberger [10] have reported that the most stable structure for Na_6 was the pentagonal pyramid instead of double triangle. While for Cu clusters, in our calculation, the difference in total energy of the most stable Cu_6 with double triangle (B.E.$= -11.75$ eV) and the second most one with pentagonal pyramid (B.E. $=-11.68$ eV) is not so large. As a result, we can conclude that the trend in the geometry for Na and Cu clusters is similar. This result is explained from the fact
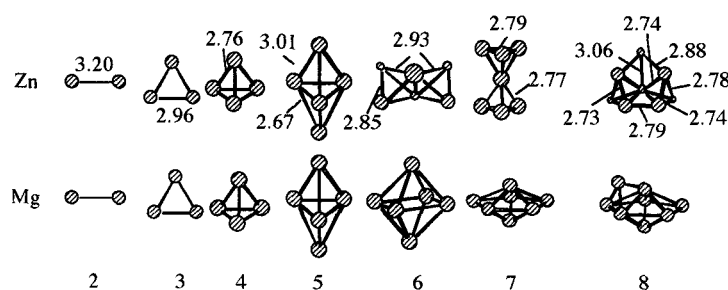
Fig. 2. Lowest energy equilibrium configurations of neutral Zn and Mg [11-13] clusters.

that the electronic configuration is the same, $(s)^1$, for Na and Cu atoms. Furthermore, this result suggest that d electrons in Cu clusters up to octamer are not determinant factor of geometry.

3.2 Optimized Geometry for Zn Clusters

Fig. 2 shows optimized geometry for Zn_2~Zn_8 clusters obtained using the ADF. Structures of Mg clusters taken from references are also shown [11-13]. The Re and B.E. of Zn_2 were obtained to be 3.20 Å and -0.08 eV, respectively. The most stable structures of Zn_3 was equilateral triangle (D_{3h}) with Re =2.96 and B.E.= -0.33 eV, while that of the tetramer was the tetrahedron (Td) with Re = 2.76Å and B.E.= -0.96 eV. For the Zn_5 pentamer, the most stable structure was the distorted trigonal bipyramid (D_{3h}) with Re = 2.67 Å (equatorial) and 3.01 Å (axial) and B.E.=-1.17 eV. For the hexamer, it was found to be the jointed tetrahedron (C_{2v}) structure with Re = 2.85 ~ 2.94 Å and B.E.= -1.47 eV. Furthermore,

the most stable structure of the Zn_7 heptamer was the jointed pyramid (D_{3d}) with Re= 2.77 ~ 2.79 Å and B.E.= -1.98 eV. Finally, that of the octamer was C_s symmetric structure with Re= 2.73 ~ 3.06 Å and B.E.= -2.38 eV. The structures of Zn clusters up to hexamers obtained in the present work well reproduces those obtained by Flad et al. However bond lengths obtained by them are longer than ours by 0.2 to 0.7 Å.

Although the trend in the geometry up to pentamer is the same for Mg and Zn clusters, it is different for hexamers, heptamers, and octamers. For Mg clusters, the spherical geometries are always stable. On the other hand, for Zn clusters, the structure consisted with tetrahedrons are preferable. The clarification of the difference in structure of Mg and Zn clusters is the further problem.

3.3. Comparison of the $(s)^1$ and $(s)^2$ clusters

In order to elucidate the nature in bonding of

Table I.   orbital overlap population (P_O) for Na, Mg, Cu and Zn tetramers

		Rhombus (Rh)								
	P_B				P_O					
		s-s			s-p			p-p		
		r_{11}	r_{12}	av	R_{11}	r_{12}	av	r_{11}	r_{12}	av
Na_4	0.392	0.286	0.128	0.160	0.158	0.222	0.210	0.070	0.012	0.024
Mg_4	0.196	-0.244	-0.158	-0.174	0.484	0.294	0.332	0.052	0.034	0.038
Cu_4	0.422	0.100	0.084	0.097	0.260	0.113	0.231	0.001	0.065	0.014
Zn_4	0.040	-0.062	-0.022	-0.030	0.128	0.047	0.063	0.017	0.004	0.007

		Tetrahedron (Td)		
	P_B		P_O	
		s-s	s-p	p-p
Na_4	0.076	-0.136	0.184	0.028
Mg_4	0.234	-0.156	0.328	0.062
Cu_4	0.372	0.051	0.198	0.050
Zn_4	0.157	-0.084	0.202	0.040

P_B: overlap population per bond, P_O: orbital overlap population per bond.
r_{11}: diagonal pair, r_{12}: side pair,
av: average, where $av = \{P_O(r_{11}) + 4 P_O(r_{12})\} / 5$

Cu and Zn clusters, we chose tetramers of these clusters as a typical example and compared them with Na and Mg tetramers that are representative of AM and AE metals, respectively. For the convenience of comparison, in the case of Td structure for Cu and Rh structure for Zn clusters were also calculated. Then we obtained the bond orbital overlap population (P_O) [27]. Table I shows the P_O values of the s-s, s-p, and p-p atomic orbital pairs for the metal clusters. The term "P_B" represents the sum of P_O values over these pairs. The average value, $P_O(av)$, was estimated in terms of $\{P_O\ (r_{11}) + 4\ P_O\ (r_{12})\}/5$, where r_{11} is bond length for the diagonal pair and r_{12} is that for the side pair. The P_O values concerned with d-orbitals are less than 0.079 for Cu and less than 0.003 for Zn. Although the values for the former are not negligible small, these terms were omitted in the table.

In the previous work treating with the AM and AE tetramers [27], we concluded as follows. The s-s antibonding contribution is the main factor, which the AM tetramers to avoid the Td closely packing geometry. On the other hand, for the AE tetramers, the large s-p and p-p bonding interactions stabilize the tetrahedral geometry. This difference in the bonding character of the AE clusters arises from the increase in the p contribution, originating from the promotion of s orbital electrons that form a closed shell in an isolated AE atom.

The above discussion is applied to Cu and Zn tetramers. For Cu tetramer in Td, the s-s interaction is not negative but very small (0.051). The smaller difference between Td and Rh is due to the d-component which was not indicated in the table. In any way the P_B value is larger for Cu tetramer with Rh structure. On the other hand for Zn tetramer, p electrons play an important role in the preference of the closed shell geometry. That is, the s-p and p-p interactions become large for Td geometry.

4. SUMMARY

The most stable structure for Cu and Zn clusters up to octamers are obtained by Amsterdam Density Functional method. The geometries of Cu and Zn clusters are almost the same for those of Na and Mg clusters, respectively. Interactions between the atomic orbitals for Cu and Zn clusters are also similar to those for Na and Mg clusters, respectively.

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