

# Cu<sub>n</sub>、Ag<sub>n</sub> 和 Au<sub>n</sub>( n ≤ 9 ) 团簇的静电极化率 \*

王红艳<sup>a\*\*</sup>, 李喜波<sup>a,b</sup>, 唐永建<sup>b</sup>, 毛华平<sup>a</sup>, 朱正和<sup>a</sup>

( a. 四川大学原子与分子物理所, 成都 610065 ; b. 中国工程物理研究院激光聚变中心, 绵阳 621900 )

**摘要:** 采用 B3LYP 密度泛函的方法计算了 Cu<sub>n</sub>, Ag<sub>n</sub> 和 Au<sub>n</sub>( n ≤ 9 ) 团簇的静电极化率和极化率的各向异性, 并与 Na 原子团簇进行比较. 结果表明, Cu<sub>n</sub> 和 Ag<sub>n</sub> 团簇的极化率与团簇大小的关系与 Na 原子团簇类似, 而 Au<sub>n</sub> 团簇的极化率有所不同; Au 原子的极化率较小, 而从 Au<sub>2</sub> 至 Au<sub>7</sub>, Au<sub>n</sub> 团簇极化率变化趋势与 Cu<sub>n</sub> 和 Ag<sub>n</sub> 团簇相似. 重金属元素团簇的极化率小于 Na 原子团簇的极化率, 具有更加紧致结构.

**关键词:** Cu<sub>n</sub> 团簇; Ag<sub>n</sub> 团簇; Au<sub>n</sub> 团簇; 极化率; 各向异性

中图分类号: O561.2 文献标识码: A

## Static Polarizabilities of Cu<sub>n</sub>, Ag<sub>n</sub> and Au<sub>n</sub>( n ≤ 9 ) Clusters \*

Wang Hongyan<sup>a\*\*</sup>, Li Xibo<sup>a,b</sup>, Tang Yongjian<sup>b</sup>, Mao Huaping<sup>a</sup>, Zhu Zhenghe<sup>a</sup>

( a. Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065 ;

b. Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang 621900 )

**Abstract** The static polarizabilities and polarizability anisotropies of Cu<sub>n</sub>, Ag<sub>n</sub> and Au<sub>n</sub>( n ≤ 9 ) clusters have been calculated by the B3LYP density functional method, which is a three-parameter mixture of density functional and "exact" Hartree-Fock exchange. The calculated results are compared with experimental polarizabilities of sodium clusters. It is shown that the size dependency of the static polarizabilities per atom of Cu<sub>n</sub>, and Ag<sub>n</sub> clusters possesses the same trend as that observed in sodium clusters exception of the Au<sub>n</sub> clusters while the polarizability of Au atom is much smaller than these of Cu and Ag. The  $\bar{\alpha}$  of Au atom is the smallest and the  $\bar{\alpha}$  per atom of Au approach to the values of Cu from the dimer to the hexamer. It indicates that in Au clusters the electrons are more strongly attracted by the nuclei because of the more electrons. However, the absolute polarizabilities of the noble-metal clusters are considerably smaller than those of the sodium clusters and the electronic structures of the noble-metal are much more compact.

**Keywords** Cu<sub>n</sub> cluster, Ag<sub>n</sub> cluster, Au<sub>n</sub> cluster, Static polarizability, Polarizability anisotropy

### 1 Introduction

In the last few years the static polarizabilities of atoms and free clusters have been extensively studied both theoretically and experimentally. The static polarizability (  $\alpha$  ) represents one of the most important observables for the understanding of the electronic proper-

ties of clusters, since it is very sensitive to the delocalization of valence electrons, as well as the structure and shape. Despite numerous investigations on metal clusters, static polarizability measurements are only available for alkali-metal clusters such as sodium, lithium and potassium. The electronic configuration of the noble metals Cu, Ag and Au are characterized by a

\* Project supported by the National Natural Science Foundation of China( 10276028 )

\*\* Corresponding author, Email: wanghyxx@163.net

Received 16 December 2003; in final form 11 April 2004.

closed  $d$  shell and a single valence electron and are therefore closely related to that of the alkali metals<sup>[1]</sup>. The study of Calaminici *et al.* demonstrated that the density functional theory can be used to predict fairly accurate values of static polarizabilities for sodium clusters<sup>[2,3]</sup>. Clusters of noble metals are expected to exhibit certain similarities to alkali-metal clusters. However, no measurements of static electric polarizabilities are until now available for homonuclear noble metal clusters. In this paper the B3LYP method is used to calculate the static polarizabilities and polarizability anisotropies for noble-metal clusters up to the nonamer. The obtained results of the static polarizabilities will be compared with available experimental data from sodium clusters.

## 2 Computational details

The static response properties of a molecule can be defined in two different ways. The field-dependent energy  $E(F)$  can be expanded in a series :

$$E(F) = E(0) - \sum_i \mu_i F_i - \frac{1}{2} \sum_{ij} \alpha_{ij} F_i F_j - \dots \quad (1)$$

where  $E(0)$  is the total energy of the molecular system in the absence of the electric field and the quantities,  $\mu_i$  and  $\alpha_{ij}$  are components of the static dipole moment and polarizability tensor, respectively. In an alternative way the static response properties of a molecule can be defined by expanding the field-dependent dipole moment, calculated from the field-induced charge distribution, as a series of the external electric field :

$$\mu_i(F) = \mu_i(0) + \sum_j \alpha_{ij} F_j + \dots \quad (2)$$

The equivalence of these two definitions for field-independent basis sets follows the Hellmann-Feynman theorem<sup>[4]</sup>. We have used the dipole moment expansion in our density functional calculation.

Calculations are carried out using the popular density functional : the " hybrid " B3LYP functional, which is a three-parameter mixture of density functional and " exact " Hartree-Fock exchange<sup>[5]</sup>. DFT is nowadays one of the best methods to study small and medium-size systems, because it yields results comparable to those

obtained with standard correlated *ab initio* methods. However, the computational cost is similar to the lowest level of Hatree-Fock without the important electron correlation contribution<sup>[6-8]</sup>. The effective core potential ( ECP ) and basis set ( LANL2DZ ) with a double- $\xi$  type suggested by Los Alamos National Laboratory have been used to optimize the geometry of all topologically different clusters. In order to have only one electron with the same angular momentum quantum number  $l$ , the positive ion with the electron removed from the outer  $(n+1)$  orbital was used as the starting point for generating the ECP's. Then, the 19 valence electronic pseudo-orbitals were defined with the  $ns$ ,  $np$  and  $nd$  orbitals. The numerical potentials were derived and fitted to analyse Gaussian functions in the form  $r^2 [ U_l - U_L ], l = 0, 1, \dots, L-1, r^2 [ U_L - N_c/r ], l = L$  where  $L$  is the lowest angular momentum not represented in the core and  $N_c$  is the number of core electrons. The Gaussian functions have the form  $\sum_k d_k r^{n_k} \exp[ -\xi_k r^2 ]$ , where  $n_k = 0, 1$ , or 2. The analytic representations for the ECP's are given in the Ref.[ 5 ].

From the calculated polarizabilities components, the mean polarizability can be calculated :

$$\bar{\alpha} = \frac{1}{3} ( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} ) \quad (3)$$

and the polarizability anisotropy can be calculated.

$$\begin{aligned} |\Delta\alpha|^2 &= \frac{3\text{tr}\alpha^2 - (\text{tr}\alpha)^2}{2} \quad (\text{general axes}) \\ &= \frac{1}{2} [ ( \alpha_{xx} - \alpha_{yy} )^2 + ( \alpha_{xx} - \alpha_{zz} )^2 + \\ &\quad ( \alpha_{yy} - \alpha_{zz} )^2 ] \quad (\text{principal axes}) \quad (4) \end{aligned}$$

## 3 Result and discussion

Since these are some controversies about the geometrical shape of transition-metal clusters containing a few atoms, all possible structures of Cu, Ag and Au clusters have been optimized with B3LYP method and the Lanl2DZ basis set. Meanwhile the total energy has been calculated and the geometrical structure with the lowest energy was as the ground state geometry. All calculations are performed using the Gaussian 98 program. The structures of these ground state geometries

are illustrated in Fig. 1, whose parameters are given in Table 1. In Table 1 the average distance between atoms in the cluster can be defined as

$$\bar{R} = \frac{1}{N_b} \sum_i R_{ij}$$

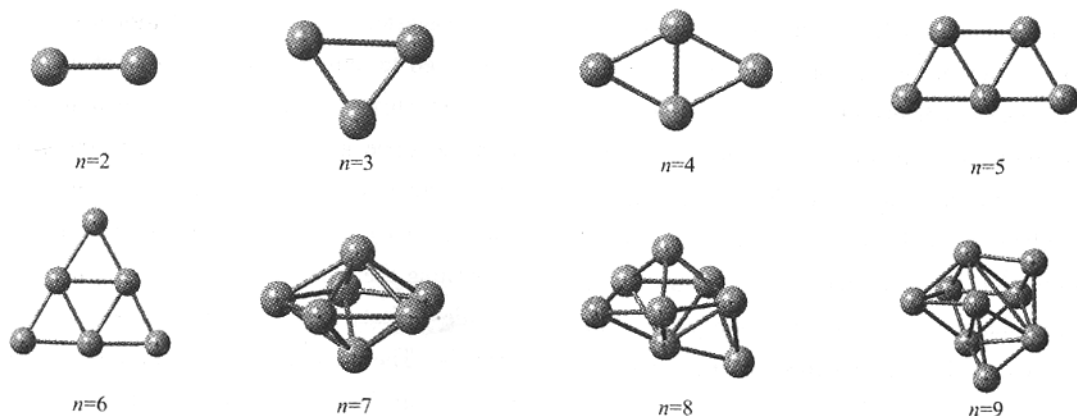


Fig. 1 Ground-state structures of  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$  ( $n \leq 9$ )

Table 1 The geometry parameters of  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$  ( $n \leq 9$ )

$n$	$\text{Cu}_n$		$\text{Ag}_n$		$\text{Au}_n$	
	$\bar{R}/\text{nm}$	$E/\text{a. u.}$	$\bar{R}/\text{nm}$	$E/\text{a. u.}$	$\bar{R}/\text{nm}$	$E/\text{a. u.}$
2	0.2259	-392.3077	0.2611	-291.5744	0.2573	-270.9484
3	0.2485	-588.4612	0.2695	-437.3576	0.3418	-406.4205
4	0.2423	-784.6592	0.2784	-583.1748	0.2751	-541.9305
5	0.2434	-980.8434	0.2801	-728.9847	0.2814	-677.4343
6	0.2447	-1177.0518	0.2800	-874.8166	0.2769	-812.9703
7	0.2508	-1373.2358	0.2888	-1020.6107	0.2876	-948.4230
8	0.2516	-1569.4352	0.2905	-1166.4349	0.2837	-1083.9580
9	0.2579	-1765.6084	0.2899	-1312.2280	0.2893	-1219.4251

The static mean polarizabilities and the polarizability anisotropies of Cu, Ag and Au clusters up to the nonamer were calculated at the optimized ground state geometries. Therefore, the same method and the same basis set were used to calculate the electronic properties of the noble metal clusters. And these clusters were oriented with their permanent dipole moment along the  $z$  axis pointing in the positive  $z$  direction. The obtained results of  $\bar{\alpha}$  and  $|\Delta\alpha|$  are listed in Table 2. Table 2 shows that the static mean polarizabilities of the noble-metal clusters increase monotonically from the atom to nonamer. The same behavior was observed for the static polarizability of sodium clusters<sup>[3]</sup>. Our

where  $R_{ij}$  is the nearest-neighbor distance less than 15% of the minima distance.

calculated polarizability values of the copper clusters are fairly close to that of the Ref. [9], in which the polarizability calculation for the copper clusters has been carried out by Calaminici *et al.* using a finite field approach implemented in the density function program Allchem. It is noted that the calculated polarizability value of Cu atom is smaller than that of Ag atom and larger than that of Au atom, but for the clusters ( $n = 2 \sim 9$ ) the order of the polarizability value is:  $\text{Cu}_n < \text{Au}_n < \text{Ag}_n$ .

In Fig. 2 the mean polarizabilities per atom of  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$  ( $n = 1 \sim 9$ ) clusters are plotted. The  $\bar{\alpha}$  per atom has an obvious varying behavior. For the

Table 2 Static mean polarizabilities and polarizability anisotropies of  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$  ( $n \leq 9$ )

$n$	$\text{Cu}_n$		$\text{Ag}_n$		$\text{Au}_n$	
	$\bar{\alpha}/\text{a. u.}^a$	$ \Delta\alpha /\text{a. u.}$	$\bar{\alpha}/\text{a. u.}$	$ \Delta\alpha /\text{a. u.}$	$\bar{\alpha}/\text{a. u.}$	$ \Delta\alpha /\text{a. u.}$
1	49.502(47.02)	0.000	53.280	0.000	36.786	0.000
2	76.735(78.50)	45.958	94.057	70.323	78.849	60.142
3	131.563(130.06)	106.156	173.588	214.126	143.06	178.153
4	153.839(151.49)	142.235	193.850	191.149	160.20	149.655
5	195.647(192.07)	141.363	247.780	212.875	204.81	176.404
6	221.339(217.64)	154.063	282.911	209.835	234.67	170.772
7	242.819(233.11)	67.083	305.979	96.603	267.80	100.766
8	253.549(256.83)	22.685	344.495	66.240	312.53	44.558
9	327.362(295.17)	178.299	441.336	176.747	364.22	194.103

a. The values in parentheses are taken from the Ref.[9].

$\text{Cu}_n$  clusters and the  $\text{Ag}_n$  clusters, the trends are analogous, i. e. from the pentamer, as the  $\bar{\alpha}$  per atom decreases with a minimum for the octamer, and then it increases again from the octamer to the nonamer. However, there is a different trend for the  $\text{Au}_n$  clusters: the  $\bar{\alpha}$  of Au atom is the smallest. The  $\bar{\alpha}$  per atom of Au approaches to the values of Cu from the dimer to the hexamer. Although the atomic radius of Au is larger than that of Cu, these results indicate that in Au clusters the electrons are more strongly attracted by the nuclei because of the more electrons. Therefore their electronic structure is more compact. The comparison of Table 2 with the values of the experimental polarizability per atom of sodium clusters reported by Knight *et al.*<sup>[10]</sup> shows that the calculated polarizabilities per atom of noble-metal clusters present the same trend,

ranging from the atom to the nonamer exception with the Au atom.

The calculated polarizability anisotropies for  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$  ( $n = 2 \sim 9$ ) are also given in Table 2. For  $\text{Cu}_n$  cluster the polarizability anisotropies increase from the dimer to the hexamer and decrease from the hexamer to the octamer. For Ag and Au cluster, the polarizability anisotropies increase from the dimer to the pentamer and decrease from the pentamer to the octamer. Similar to the calculated mean polarizability per atom, a minimum value for the polarizability anisotropies is found at the octamer. From these data it is obvious that the polarizability anisotropies are directly related to the particular cluster structure. In fact, in the planar clusters it increases with an increasing number of cluster atoms. For the pentamer and the hexamer very similar values for the polarizability anisotropies are calculated. When the cluster structures become three-dimensional the polarizability anisotropies decrease to a minimum value for the octamer, which is the cluster with the most compact structure and with the highest binding energy per atom. It increases again as the cluster structure becomes more open, as the case of the nonamer. The obtained relation of the polarizability anisotropies with the cluster structures is very similar to that obtained in the study of solidium cluster polarizabilities<sup>[10]</sup>.

From these results it is concluded that the electronic and geometric structures of  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$

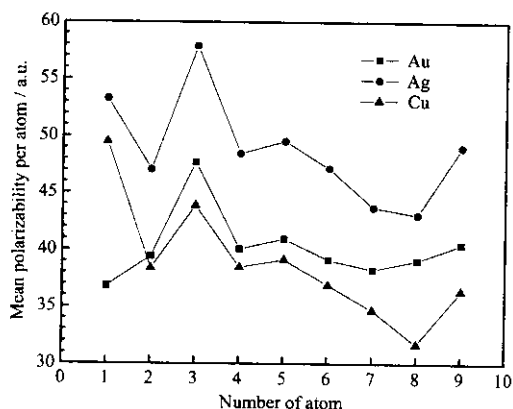


Fig. 2 Calculated mean polarizabilities per atom of  $\text{Cu}_n$ ,  $\text{Ag}_n$  and  $\text{Au}_n$  ( $n = 1 \sim 9$ )

( $n=2\sim 9$ ) clusters follow a similar trend as for sodium clusters. But the polarizability of Au atom is an exception, In fact a minimum is obtained for Au atom. Since the mean polarizability per atom of noble-metal clusters is about three times smaller, the electronic structures of the noble-metal clusters are much more compact than those of the sodium clusters. Although for noble-metal clusters there are no experimental data can be compared with the calculated static polarizabilities, the calculations are highly valuable for the understanding of the influence of the electronic structure of these systems.

### References

- [ 1 ] Alonso J A. *Chem. Rev.* ,2000 ,**100** :637  
[ 2 ] Calaminici P , Jug K , Köster A M. *J. Chem. Phys.* ,1998 ,**109** :7756  
[ 3 ] Calaminici P , Jug K , Köster A M , *Chem. Phys.* ,1999 ,**111** :4613  
[ 4 ] Guan J G , Duffy P , Carter J T , *et al. J. Chem. Phys.* ,1993 ,**98** :4753  
[ 5 ] Hay P J , Wadt W R. *J. Chem. Phys.* ,1985 ,**82** :299  
[ 6 ] Wang Hongyan , Zhu Zhenghe , Meng Daoqiao , Zhang wanxiang , Liu Xiaoya. *Chin. J. Chem. Phys.* ,2001 ,**14** :285  
[ 7 ] Wang Hongyan , Zhu Zhenghe , Fu Yibei , Wang Xiaolin , Sun Ying. *Chin. J. Chem. Phys.* ,2003 ,**16** :265  
[ 8 ] Chi Xianxing , Tian Shanxi , Zhuang Youyi , Xu Kezun. *Chin. J. Chem. Phys.* ,2002 ,**15** :269  
[ 9 ] Calaminici P , Köster A M , Vela A. *J. Chem. Phys.* ,2000 ,**113** :2199  
[ 10 ] Ilia A. Solov 'you , Andrey V. Solov 'you , Walter Greiner. *Phys. Rev.* ,2002 ,A65 :053203