Theoretical Study on Structures of Gold, Silver and Copper Clusters Using Relativistic Model Core Potentials

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Abstract: - We investigated the lowest-energy structures of Au, Ag and Cu clusters up to octamer using model core potentials (MCPs). We utilized several levels of theory, such as density functional theory (B3LYP, BLYP, PBEPBE, LC-BLYP, LC-BOP), second-order perturbation theory (MP2) and coupled cluster method (CCSD(T)). The MP2 calculations predicted that the Au, Ag and Cu clusters have the crossover from planar to non-planar at heptamer. In contrast, all the DFT and coupled cluster methods predicted that all the gold clusters up to octamer are planar but for the Ag and Cu clusters the crossover from planar to non-planar occurs at heptamer.

Key-words:- Au clusters, Ag clusters, Cu clusters, stable structure, relativistic effect, model core potential, molecular orbital calculation, correlation energy

1 Introduction

The properties of metal clusters have attracted much attention in recent years for their interesting properties and potential applications in nanotechnology. Small gold clusters have also special properties, which are promising new materials for electronic and other functional nanoscale devices. Thus the investigation for their structures is greatly important for not only scientific interests but also engineering purposes.

There have been a number of papers dedicated to the structure of neutral gold clusters over the past decade, most of them have utilized density functional theory (DFT) calculations using effective core potentials (ECPs) [1~3]. It is well known, however, that nodeless ECPs do not adequately estimate electron correlation. Therefore, results of previous ECPs works are somewhat questionable. On the other hand, we have developed pseudo potentials called model core potentials (MCPs) for all elements up to Ra [4~8]. They include relativistic effects and express node structures appropriately for valence orbitals. Thus, compared with other ECPs, MCPs can describe more precisely electron-electron repulsion interaction such as electron correlation.

The purpose of this study is to investigate structures of small noble metal (Au, Ag and Cu) clusters with the use of our MCPs, which are expected to describe more appropriately the electronic structures of noble metal clusters than previous ECPs works.

2 Computational details

In all the calculations, we utilized model core potentials (MCPs) for Au, Ag and Cu and the basis set of a triple-zeta quality, MCP-tzp, which includes

major relativistic effects except spin-orbit interaction. Using the MCPs, we performed geometry optimization of neutral Au_n, Ag_n and Cu_n (n = 2~8) clusters at levels of second order Møller-Plesset perturbation (MP2) approach and several density functional approaches. We utilized BLYP, B3LYP, PBEPBE, LC-BLYP, and LC-BOP functionals for exchange and correlation.

In addition to these calculations, we carried out single-point coupled cluster (CCSD(T)) calculations at optimized geometries given by MP2 calculations to investigate further accurate electronic structures. The initial geometries of Au, Ag and Cu clusters in this work were taken from previous works [2]. The MP2 and all the DFT calculations were performed on GAMESS [9] and the CCSD(T) calculations were performed on MOLCAS program [10].

3 Results and discussion

Fig.1 shows the most stable structures of neutral Au, Ag and Cu clusters up to hexamer given by all the methods used in the present study. Most of previous theoretical calculations have predicted the same results for these clusters [2~3]. Thus it is safe to say that the most stable structures for the Au, Ag and Cu clusters up to hexamer are planar.

For heptamer and octamer, the most stable structures for Au are different from those for Ag and Cu. The most stable structures of the Ag_7, Cu_7, Ag_8 and Cu_8 clusters are shown in Fig. 2. All the present calculations indicate that Ag_7 and Cu_7 are non-planar structures, Fig.2(a), and Ag_8 and Cu_8 are also non-planar structures, Fig.2(b). Thus the crossover from planar to non-planar takes place at the cluster size N=7 for Ag and Cu clusters. The most stable structures of Au_7 and Au_8 are shown in Fig. 3. In the DFT and CCSD(T) calculations, the most stable structures of Au_7 and Au_8 are planar, Fig.3(c) and Fig.3(d), respectively. In contrast, the MP2 calculations predicted non-planar, Fig.3(e) and Fig.3(f), respectively, for Au_7 and Au_8. Thus, all the Au clusters up to octamer have non-planar structures at the DFT and CCSD(T) calculations, while at the MP2 calculations the Au cluster has the crossover from planar to non-planar at heptamer.

To explain these results, we analyzed energies of clusters in terms of correlation energy. Table 1 shows relative energies of the non-planar structure

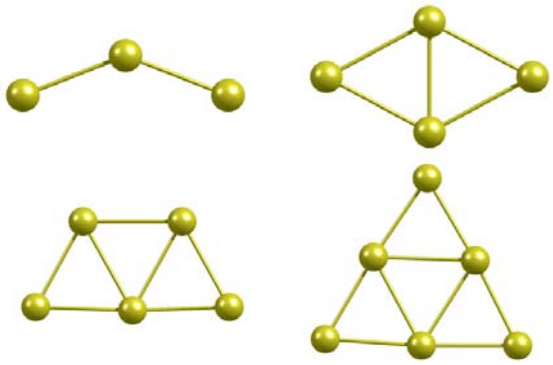

Fig. 1. The most stable structures of Au, Ag and Cu clusters up to 6 atoms.

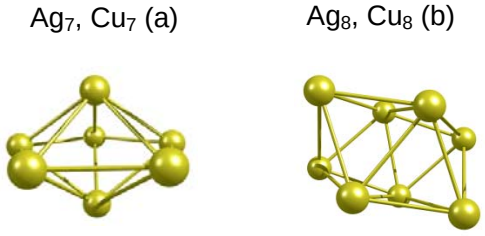

Fig. 2. The most stable structures of Ag_7, Cu_7, Ag_8, and Cu_8 clusters.

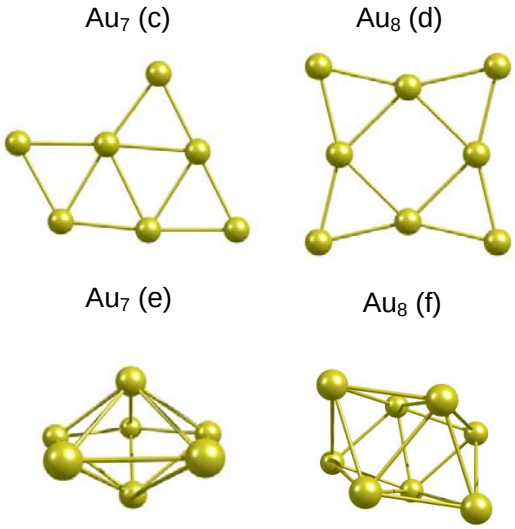

Fig. 3. The most stable structures of Au_7 and Au_8 clusters.

(Fig.3(f)) with respect to those of the planar structure (Fig.3(d)) for the Au, Ag and Cu octamers. From Table 1, we can find the following fact that the planar structure of the Au octamer is the most stable among the Au, Ag and Cu octamers at uncorrelated (Hartree-Fock) calculations. In the MP2 calculations, a large negative value of the relative correlation

Table 1. The relative energies of the non-planar structure with respect to those of the planar structure for the Au, Ag and Cu octamers, in eV. (Hartree-Fock energy: ΔE_{HF}, correlation energy: ΔE_{corr}, and total energy: ΔE_{total})

	ΔE_{HF}	ΔE_{corr}^{MP2}	ΔE_{total}^{MP2}	$\Delta E_{corr}^{CCSD(T)}$	$\Delta E_{total}^{CCSD(T)}$
Au_8	37.9	-54.8	-16.9	-30.5	7.4
Ag_8	14.1	-50.7	-36.6	-33.5	-19.4
Cu_8	8.5	-58.3	-49.8	-44.1	-35.6

energy for the Au octamer brings the non-planar structure the most stable. In CCSD(T) calculations, however, the relative correlation energy of the Au octamer is not large enough to cover the unstability of the non-planar structure. Therefore, the planar structure remains the most stable. This result is sharply different from a previous work by Olson *et al*. at CCSD(T) using ECPs [1], where they concluded that the most stable structure of Au_8 is the non-planar structure (Fig.3(f)). Judging from our best calculations at CCSD(T) their conclusion is erroneous and clearly caused by ill description of the ECP method they used for electron correlation.

On the other hand, for the Ag and Cu clusters, since the stability of the planar structures becomes small at uncorrelated calculations, large negative values of the relative correlation energies bring the non-planar structures the most stable.

4 Conclusions

We investigated the lowest-energy structures of Au, Ag and Cu clusters up to octamer using model core potentials (MCPs) at various levels of calculation including highly correlated CCSD(T) calculations. Our MCP calculations revealed that the Au clusters up to octamer are planar, while the crossover from planar to non-planar occurs at heptamer for the Ag and Cu clusters.

For the Au clusters, planar structures tend to be much more stable than non-planar structures at uncorrelated calculations, whereas the stabilization of non-planar structures by considering electron correlation at CCSD(T) is not large enough to cover the unstability of the non-planer structures. Thus, the most stable planar structures of the Au clusters up to octamer are lower than the most stable non-planer structure.

For the Ag and Cu clusters, however, the stabilization of planar structures compared with non-planar structures is not much large as is in the case of the Au clusters and a large amount of relative correlation energies of non-planar structures with respect to planar structures make the Ag and Cu clusters non-planar.

Therefore, the Au clusters prefer planar structures compared with the Ag and Cu clusters.

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