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Optical and electronic properties of Cu doped Ag clusters

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ABSTRACT

The optical and electronic characteristics of Ag_{13}, $Ag_{12}Cu$ and Cu_{13} clusters with Ih symmetry were investigated using density functional theory (DFT) methods. Absorption peak red shifts clearly with increasing the Cu atoms in comparison of the absorption spectra of $[Ag_{13}]^+$, $[Ag_{12}Cu]^+$ and $[Cu_{13}]^+$ clusters at the singlet state. The electronic state densities show that the d-electrons play a crucial role in the $Ag_{12}Cu$ cluster. Mulliken charge analysis reveals the electrons of outer shell silver atoms in $Ag_{12}Cu$ cluster are more active than these of Ag_{13} and Cu_{13} clusters when excited from ground state to singlet state. HOMO–LUMO gaps of three clusters show the $Ag_{12}Cu$ cluster has a better metallic nature. The values of ionization potential (IP) and electronic affinity (EA) indicate that the $Ag_{12}Cu$ cluster has a more electronic activity than that of Ag_{13} or Cu_{13} cluster, which is interested to understand a catalytic mechanism of bimetallic nanoalloys.

1. Introduction

The optical properties of metal nanoparticles are a subject of great interest in fundamental sciences and technological applications, such as optoelectronic devices [1], thermal treatment of cancer [2], cell imaging, that is colorimetric probes for DNA detection, surface enhanced Raman scattering and the strong absorption of light by silver colloids [3], Solar cells for enhancing the absorption of sunlight [4], catalysis as a catalyst [5]. The reason of such interest is due to the fact that nanoparticles of specific metals support a surface plasmon resonance (SPR), which is a very intense optical absorbance in the UV–visible region due to the coherent and collective oscillation of free electrons in the metal when subjected to electromagnetic radiation of proper wavelength. SPR is responsible for a host of phenomena [1–5] unique to nanometals and dominated in the interaction of light with metals at the nanoscale.

The optical spectra of metal nanoparticles have been modeled in many theories. For pure metal cluster, ab initio optical spectra of small metal neutral Ag_n (n = 2–8) and Ag_n^+ (n = 2–4) clusters have been studied [6,7]. Time-dependent density functional theory (TD-DFT) calculation has been performed for Ag_n (n = 2–11) [8–12], Ag_n (n = 4–22) [13], Ag_n (n = 1–9) [14], Au_n (n = 2–14 and 20) [15–17], and Cu_n (n = 2–22) [18] clusters. For bimetallic nanoalloys, structural properties of small Ag–Au nanoalloys [19–21] have been widely calculated using DFT. Some other bimetallic nanostructures, for example, M_2Au_n (M = Ag, Cu; n = 1–10) clusters [22], $Au_{19}X$ (X = Li, Na, K, Rb, Cs, Cu, and Ag) clusters [23], Ag_nCu_{34-n} (n = 0–34) nanoparticles [24], AuCu nanoparticles [25], and AgCu [26] clusters. However, there are a few papers about optical properties of bimetallic nanoparticles investigated in the framework of DFT. The spectral characteristics of the Ag_3Au_{10} nanoalloy and alloying effects on the optical properties of Ag–Au nanoclusters are just a few of examples [27,28].

Bimetallic nanoparticles, composed of two different metal elements, are of greater interest than monometallic ones, from both the scientific and technological views, for the improvement of the optical and catalytic properties of metal particles. This is because bimetallization can improve performance of the original pure single-metal nanoparticle and create a new property, which may not be achieved by monometallic particles. Although many bimetallic cluster structures have been found and reported, the optical properties of most bimetallic nanoalloys have not been made known. Alloying effects on electronic and optical properties in small bimetallic nanoparticle have been unrevealed. It is well-known that the interaction of light with a spherical particle in Mie theory is described in the framework of classical optics [29], assuming that the particle and the medium are continuous, homogeneous, and characterized by their dielectric function. However, there are many unresolved issues in calculation of the absorption spectrum for small metal nanoclusters using Mie theory [30]. As far as we know, a complete development of these calculations hasn't been given even for metal nanoclusters in Mie theory [31–35], it is significant for us to address these issues from the electronic structure interpretation.

In this paper, we have a theoretical study of the UV–visible absorption spectra and electronic properties of $[Ag_{13}]^+$, $[Ag_{12}Cu]^+$ and $[Cu_{13}]^+$ clusters. The optical characteristics of the $Ag_{12}Cu$ cluster as a bimetallic nanoparticle were revealed. The HOMO–LUMO

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gap, ionization potential and electronic affinity indicate that the $Ag_{12}Cu$ cluster has a more electronic activity than Ag_{13} and Cu_{13} clusters, which is helpful to understand the catalytic mechanism of bimetallic nanoparticles.

2. Computational details

In this study, we present DFT level investigations of the geometries and optical properties of Ag_{13}, $Ag_{12}Cu$ and Cu_{13} clusters with Ih symmetry based on previous papers [36]. The initial unbiased global searches of the configuration spaces were performed using the genetic algorithm, and putative global minimum geometries, with atomic interactions modeled by the empirical Gupta many-body potential, have been found.

The UV–visible spectra of metallic nanoclusters are described by TD-DFT calculations, and the structures from the empirical potential searches were optimized at the DFT level using the DMol3 program package [37]. The spin-polarized DFT calculations were performed in the framework of the all electron with double numerical basis sets with d-polarization functions. A global cutoff of 5.5 Å was used for grid integration. The self-consistent-field procedures were performed with a convergence criterion of 1.0×10^{-6} a.u. on the total energy and electron density. Both the generalized gradient approximation (GGA) of Perdew et al. [38] and Perdew–Burke–Ernzerhof (PBE) [38] correlation were used as exchange-correlation functions for the calculation of geometries. The adiabatic local density approximation (ALDA) as a simulated method has been employed to simulate the UV–visible spectra [39].

To study the stability of the cluster, we define average binding energy of the clusters as follows:

$$E_b = [-E_{cluster} + nE_{Ag} + mE_{Cu}]/13 \quad (1)$$

where $n = 12$, $m = 1$ for $Ag_{12}Cu$; $n = 13$, $m = 0$ for Ag_{13}; $n = 0$, $m = 13$ for Cu_{13}.

To study the electronic properties of the cluster, the energy gap, adiabatic ionization potential (IP), and adiabatic electron affinity (EA) is defined as:

$$IP = -E_{cluster} + E_{cluster^+} \quad (2)$$

$$EA = -E_{cluster} + E_{cluster^-} \quad (3)$$

3. Results and discussion

3.1. The structural properties of Ag_{13}, Cu_{13}, and $Cu@Ag_{12}$ clusters

Three structural motifs of Ag_{13}, $Ag_{12}Cu$ and Cu_{13} clusters with Ih symmetry, as shown in Fig. 1, were applied in the present work. For all the three structures, the cluster geometries were optimized using functional GGA-PBE method, and on the geometries obtained from these optimizations the absorption spectra were calculated using ALDA method. In general, the electronic structure of neutral clusters can present an incomplete occupation of the highest-occupied molecular orbital (HOMO) which would give a rise to a Jahn–Teller structural distortion. To prevent this effect, charged systems were considered to achieve electronic shell closure: $[Ag_{13}]^+$, $[Ag_{12}Cu]^+$ and $[Cu_{13}]^+$, so that the spin restricted calculations were performed for optical properties. This simplification is effective in keeping configuration, but affects hardly the absorption spectrum, as discussed in other articles [15].

Seeing Table 1, we can find clearly that the $Ag_{12}Cu$ [25], Ag_{13} [40] and Cu_{13} clusters have a binding energy with 1.04 eV, 1.43 eV, 1.83 eV, respectively [27]. It is obvious that the $Ag_{12}Cu$ cluster has the lowest binding energy, which indicates the $Ag_{12}Cu$ nanoalloy has a lower stability among Cu_{13}, $Ag_{12}Cu$, and Ag_{13}. Compared with HOMO–LUMO gaps of the three clusters, the energy gap with 0.381 eV for $Ag_{12}Cu$ cluster is the lowest (0.408 eV for Ag_{13}, 0.490 eV for Cu_{13}), which indicates $Ag_{12}Cu$ cluster has a more active metallicity than Ag_{13} or Cu_{13} cluster. The IP values of Ag_{13}, $Ag_{12}Cu$, and Cu_{13} are 154.77 Kcal/mol, 121.76 Kcal/mol, 141.73 Kcal/mol, respectively. It is obvious that the $Ag_{12}Cu$ cluster loses more easily some electrons than Ag_{13} or Cu_{13} cluster. From the list of EA values, it is distinct that the $Ag_{12}Cu$ cluster hangs

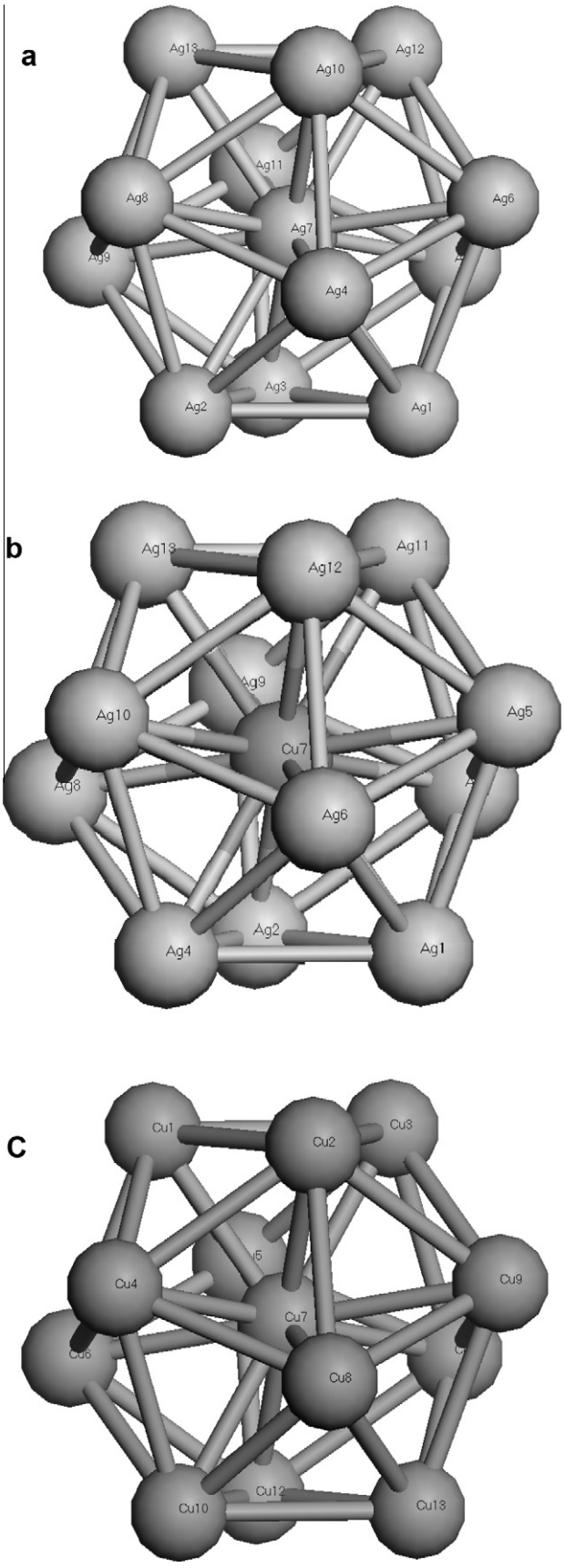

Fig. 1. The three structures of Ag_{13}, $Ag_{12}Cu$, and Cu_{13} clusters with Ih symmetry.