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A series of quasi-icosahedral gold fullerene cages: Structures and stability

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ABSTRACT

An icosahedron-based template has been proposed and applied to produce a series of initial icosahedral Au_n ($n=32$, 42, 72, 92, and 122) cages. Relativistic density functional theory calculations have subsequently been performed on these structures. The results show that two new, large cages for Au_{92} and Au_{122} have good stability, and that the optimized cages with I_h symmetry are quasi-icosahedron and low-lying in energy. Moreover, the HOMO–LUMO gaps of the Au_{92} and Au_{122} cages are very small, suggesting strong metallicity. Analyses of the electronic orbitals show sp–d hybridization in the Au_{92} and Au_{122} cages.

1. Introduction

Gold nanoclusters have attracted considerable attention over the past two decades due to their wide applications in biology, catalysis, and nanotechnology [1–4]. Many recent studies have shown that a series of gold cage-like structures have unusual stability, resulting from relativistic effects in Au–Au bonding. Xing et al. predicted theoretically that the lowest-energy configurations of the small Au_n clusters transform from planar to three-dimensional structures in the range $n=$ 12–15 [5–9], which is supported by experimental photoelectron spectra [10–13]. Furthermore, an unexpected macrotetrahedral configuration of Au_{20} with T_d symmetry was indicated by photoelectron spectroscopy combined with first principles density functional theory (DFT) calculations [14]. For larger Au_n clusters with $n>20$, the most exciting result is that based on DFT calculations the highly stable icosahedral Au_{32} fullerene [15,16] was predicted to prevail over conventional compact structures. Recently, Wang et al. [17] constructed a number of fullerene-like cages for the medium-sized Au_n ($n=32$, 38, 44, 50, and 56) clusters and compared their energies with those of the space-filling structures generated by genetic arithmetic. They found that the cage-like structure of Au_{50} [17,18], following the $2(k+1)^2$ aromatic rule [19], is more stable than the space-filling isomers, and that clusters of other sizes prefer conventional compact structures, again on the basis of DFT calculations. More recently, a new chiral Au_{72} gold cluster, which satisfies the $2(k+1)^2$ aromatic rule [19], has been reported by Karttunen et al. [20]. The structure of Au_{72} with spherical aromaticity and I symmetry is similar to that of an icosahedron. Another stable icosahedral hollow cage of Au_{42}, which unlike the Au_{32} and Au_{50} cages, does not satisfy the $2(k+1)^2$ rule [19], has also been proposed as a local energy minimum [21]. Wei Fa et al. found that a fullerene-cased cage with a hollow tube-like structure is predicted to be a possible ground state for Au_{24} and Au_{26-28} [22,23].

Although no large cage-like structures have yet been synthesized in the laboratory, gold clusters with a hollow cage structure would be of both fundamental and practical interest because of their larger surface area (compared to a space-filling structure) and their potential applications. Recently, two methods have been proposed to construct gold cages from carbon fullerene cages, namely omnicapping and dualization [15–18,21]. From a theoretical point of view, the Au_{32} cage with I_h symmetry [15,16] can be obtained either by omnicapping a C_{20} fullerene or by dualization of a C_{60} fullerene. Similarly, the Au_{42} cage [21] with I_h symmetry can be obtained by dualization of a C_{80} fullerene isomer and the D_{6d} cage of Au_{50} [18] can be constructed from C_{96} by the dualization method. The Au_{92} cage can also be constructed from C_{60} plus 32 atoms at the center of the rings [15].

In the present paper, we have found a new icosahedron-based template for constructing gold cages from an icosahedral Au_{12} cage and analyzed a series of stable and metastable hollow cages of Au_n ($n=32$, 42, 72, 92, and 122). The structural stability and electronic structures of these new larger Au_{92} and Au_{122} cages are discussed.

2. Computational details

We have employed the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof functional [24] (PBE) for the exchange–correlation interaction. A DFT-based relativistic semi-core pseudopotential [25] (DSPP) and a double-numeric-polarized (DNP) basis set were utilized in the calculations. Geometry optimization was performed without symmetry constraint

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and a spin-polarized calculation was used. The convergence requirements were set at 5×10^{-4} Hartree/Å for the force, 5×10^{-3} Å for the displacement and 1×10^{-6} Hartree for the energy change. Self-consistent field (SCF) calculations were carried out with a convergence criterion of 1×10^{-6} eV on the total energy and 1×10^{-6} e/Å^3 on the electron density. The real-space global orbital cutoff radius was chosen to be 4.5 Å so as to ensure reliable calculation of the wavefunctions.

In order to confirm the stability of the Au_{92} and Au_{122} cages, we first compared the optimized cages with the space-filling structures on the basis of the binding energy, and then performed two calculations in order to verify the stability of the cages. One was to optimize the energy of the cages by displacing each atom randomly over distances between 0 and 0.5 Å. The other approach was to carry out DFT molecular dynamics calculations for the cage. The dynamic evolution of the cage was followed for 50 steps, each of 2 fs, assuming an initial temperature of 600 K. In the molecular dynamics calculation, we chose the NVE base set that carries out dynamics calculations at fixed volume and constant energy. With fixed volume and constant energy, the temperature falls over the course of the calculation, and the atoms in the structures vibrate. The atoms undergo typical displacements of a few tenths of an Angstrom, which given the typical Au–Au bond length of 2.7–2.8 Å, is a suitable range for verifying the stability of the clusters. All computations were performed in the DMol^3 package [25,26].

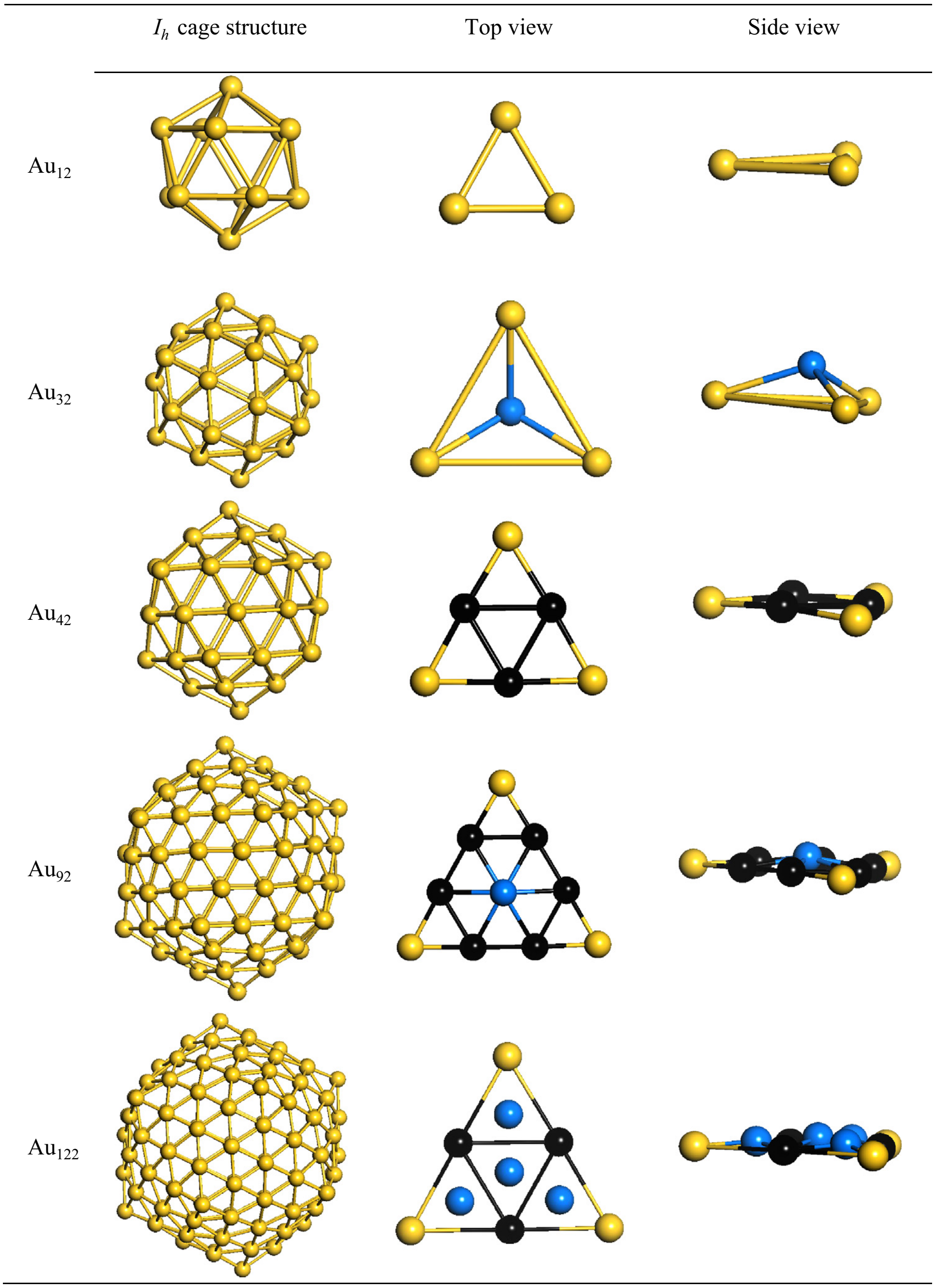

Fig. 1. The optimized cagelike configurations of Au_n, $n=32$, 42, 72, 92, and 122, and their top view and side view of triangular unit. Gray balls and black balls refer to edge atoms and center atoms, respectively.