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Detecting the lowest-energy structures of CAu_{16}^{q} $(q = -1, 0)$

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ABSTRACT

Using scalar relativistic density-functional simulations, we have performed a detailed study of the structural and electronic properties of CAu_{16}^{q} $(q = -1, 0)$. We have discovered that the most stable configurations of both the neutral and anionic C-doped gold clusters are not endohedral structures but distorted close-flat cages, in which the carbon atom prefers forming covalent bonds with its four nearest-neighboring gold atoms. Despite the geometrical similarity between the CAu_4 and $SiAu_4$, the lowest-energy CAu_{16}^{q} $(q = -1, 0)$ show a square-pyramid local structure around the dopant carbon just like the cases of $GeAu_{16}^{-}$ and $SnAu_{16}^{-}$, displaying different photoelectron spectroscopy with those of isomers with a dangling gold atom atop carbon.

Interest in doped gold clusters has undergone a notable increase since doping can offer chemical versatility for fine tuning the structural, electronic, and catalytic properties of gold clusters [1–16]. Pyykkö and Runeberg were the first to predict theoretically highly stable icosahedral clusters constructed by 12 gold atoms with an encapsulated central impurity atom, $M@Au_{12}$ $(M = W, Ta^{-}, Re^{+})$ [1], which were subsequently confirmed by the anion photoelectron spectroscopy (PES) experiments [2,3]. However, since the icosahedral Au_{12} is not a stable cage, the stability of these gold-covered clusters has been attributed to relativistic effects and aurophilic attractions in accordance with the 18-electron rule [17–19].

Recently, Bulusu et al. have reported their experimental and theoretical evidence that the Au_{16}^{-} cluster is a hollow cage with an inner diameter of about 5.5 Å [20], providing the possibility to design novel endohedral gold-caged clusters by filling the cage with a guest atom. For example, they have validated subsequently, using the same combined PES and density-functional theory (DFT), that the cage structure of Au_{16}^{-} can be maintained with a very little structural change by doping a copper atom [21]. The charge-transfer interactions between the Au_{16}^{-} cage and its Cu dopant are reminiscent of the behavior of endohedral fullerenes [22,23], giving more inspiration for doping the stable Au_{16}^{-} cage with different guest atoms.

However, our earlier DFT simulations have shown that the stability of filling the Au_{16}^{-} cage with a foreign metal atom is dependent on the atom's size [24]. For example, doping both Ag and K atoms into the Au_{16}^{-} cage would make the combined structures unstable, evolving to the more stable lowest-energy structures with Ag and K atoms lying on the surface of the Au_{16}^{-} cage. On the other hand, the nature of the dopant-Au local interactions is believed to play an important role in determining the stability of endohedral doped Au_{16}^{-} cage. Theoretical and experimental studies had already revealed that the Si and Ge as well as Sn atom cannot be doped stably into the sixteen-atom golden cage, for which the dopant atom is found to be exohedral (Ge and Sn) or becomes a part of the gold cage (Si) [25,26]. Different from the Cu-doped Au_{16}^{-} cage in which the copper transfers its single valence electron to the surrounding Au, the charge analysis on the neutral clusters shows that all dopants (Si, Ge, and Sn) entail a small negative charge [25]. The local structure around the doped atom in the lowest-energy MAu_{16}^{-} $(M = Si, Ge, Sn)$ is similar to that of the corresponding MAu_4 cluster [27], which possesses a T_d geometry ($SiAu_4$) or a square-planar structure ($GeAu_4$ and $SnAu_4$). Since the ground-state CAu_4 and $SiAu_4$ are the same as their corresponding hydrides with a tetrahedral geometry [27–29], it is interesting to explore the lowest-energy structure of CAu_{16}^{-}, which will be benefit to understanding the Au/H analogy and carbon–gold bond formation.

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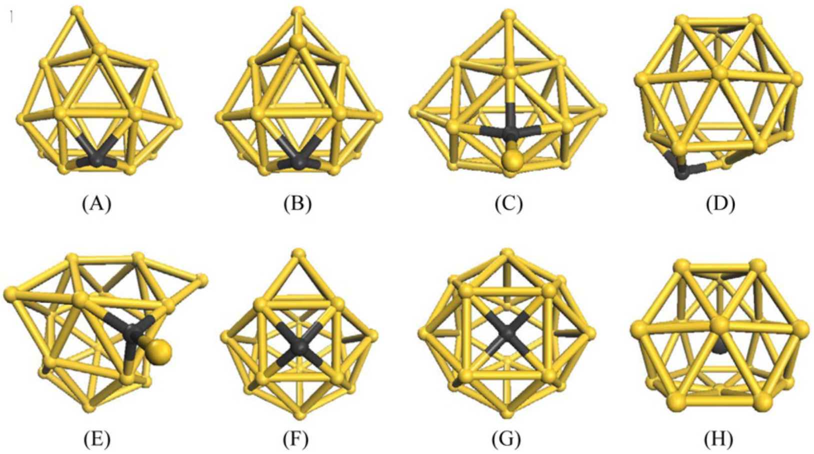

Fig. 1. (Color online.) Optimized ground-state (A) and selected low-lying isomers [(B)–(H)] of CAu_{16}^{q} $(q=-1,0)$. The pictures are drawn according to the coordinates of anion isomers, for which the bond lengths and bond angles change for the neutral counterparts. The dopant carbon atoms are shown in dark gray. The local geometry around C exhibits a square pyramid in the isomers (A), (B), (F), and (G). A dangling gold atom atop C is present in the isomers (C) and (E). The isomers (D) and (H) show most similarity to the parent cage Au_{16}^{-}, in which the carbon atom lies outside or inside the cage, respectively.

Table 1
Point group symmetries, relative energy (ΔE), HOMO–LUMO gap (E_g), and Hirshfeld charge on the C atom (Q) of the ground-state and selected low-lying CAu_{16}^{q} $(q=-1,0)$. The values given outside and inside the parentheses are those for the anion and neutral isomers, respectively. All energies are in eV

Isomer	Group	ΔE	E_g	Q
A	C_1	0 (0)	0.418 (0.767)	−0.242 (−0.186)
B	C_s	0.018 (0.046)	0.466 (0.772)	−0.244 (−0.184)
C	C_s	0.308 (0.115)	0.175 (1.238)	−0.217 (−0.210)
D	C_s	0.403 (0.596)	0.100 (0.228)	−0.218 (−0.187)
E	C_1	0.539 (0.320)	0.143 (0.999)	−0.234 (−0.225)
F	C_s	0.653 (0.798)	0.150 (0.248)	−0.259 (−0.226)
G	C_{2v}	1.258 (1.334)	0.150 (0.914)	−0.205 (−0.179)
H	C_{3v}	1.632 (1.613)	0.092 (0.919)	−0.116 (−0.087)

Therefore, we have examined the stability of CAu_{16}^{q} $(q=-1,0)$ by using the relativistic DFT simulations. We have shown that both the neutral and anionic CAu_{16}^{q} $(q=-1,0)$ do not possess the endohedral structures. The lowest-energy structures of CAu_{16}^{q} $(q=-1,0)$ are similar to that of Ge/Sn doped Au_{16}^{-}, in which the dopant carbon and its nearest-neighbor four gold atoms form a square pyramid with the C atom at the apex and the four Au atoms forming the base.

Our numerical simulations were carried out using the spin-polarized DFT at the level of a generalized gradient approach via the Perdew–Wang exchange-correlation functional [30]. The molecular DFT DMol^3 package was applied first [31], in which a double-numerical basis set together with polarization functions was chosen to describe the electronic wave functions. The scalar relativistic effects, such as the mass velocity and Darwin correction terms, were included in the all-electron calculations. More than 30 possible initial geometries were considered for each charge state, which were optimized by the Broyden–Fletcher–Goldfarb–Shanno algorithm [32] without symmetry constraints until the total energy was converged to 10^{-6} eV in the self-consistent loop and the force on each atom was less than 5 meV/Å.

The accuracy of the above results has been further verified by performing independent calculations with the Amsterdam density functional (ADF) program [33] on the top-ten lowest-lying isomers plus one endohedral C@Au_{16}^{q} $(q=-1,0)$ obtained from the DMol^3 package. These isomers were fully optimized with an energy gradient converging to 10^{-4} Hartree/Å by using the relativistic scheme of zero-order regular approximation formalism without the spin–orbit effects [34]. A frozen core approximation including the $1s$–$4f$ orbitals was used for the Au atoms with basis sets of triple-zeta quality plus p- and f-polarizations functions (TZ2P), while C is represented with all-electron basis sets of TZ2P quality. The frequency check has been performed to make sure that the obtained structures are real local minima rather than saddle stationary points on the potential energy surface. Benchmark calculations for the Au_2 and AuC^{+} have been carried out, obtained consistent results with previous experimental and theoretical data [35,36]. Taking the AuC^{+} as an example, the calculated bond length of 1.763 Å and vibrational frequency of 892.2 cm^{-1}, agree well with the previous DFT values of 1.766 Å and 873.1 cm^{-1}, respectively, done by Barysz and Pyykkö [36]. All results shown here are those done by the ADF program.

Fig. 1 illustrates the derived low-lying isomers of CAu_{16}^{q} $(q=-1,0)$, for which their relative energies are summarized in Table 1. Both the neutral and anionic CAu_{16}^{q} $(q=-1,0)$ has the same ground-state configuration, which is a distorted close-flat cage similar to the lowest-energy structures of GeAu_{16}^{-} and SnAu_{16}^{-}. The isomer (B) with C_s symmetry resembles to the configuration of the isomer (A) and is nearly degenerate in energy to the ground state. The structures with endohedral doping of carbon are unstable for the neutral and anionic complexes, which are higher-lying isomers separated from the corresponding ground states by 1.613 and 1.632 eV, respectively. Though the global minima of MAu_{16}^{-} (M = Si, Ge, Sn) exhibit likeness to the corresponding MAu_4 clusters, a close look at the local geometries around the dopant carbon atom indicates that a square pyramidal structure with the carbon atom at the apex and four surrounding gold atoms forming the base is preferred in the CAu_{16}^{q} $(q=-1,0)$ to a tetrahedral configuration although the latter has a much higher stability than the former for the CAu_4 [27]. For example, the isomer (E) possesses a T_d local geometry around C but its energy is higher than the ground state by 0.539 eV for the anion CAu_{16}^{-}. Also, the dan-