Structure, stability, and electronic property of carbon-doped gold clusters $\text{Au}_n\text{C}^-$ ($n = 1$–$10$): A density functional theory study

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The equilibrium geometric structures, relative stabilities, and electronic properties of $\text{Au}_n\text{C}^-$ and $\text{Au}_{n+1}^-\text{C}^-$ ($n = 1$–$10$) clusters are systematically investigated using density functional theory with hyper-generalized gradient approximation. The optimized geometries show that one Au atom capped on $\text{Au}_{n-1}^-\text{C}^-$ clusters is a dominant growth pattern for $\text{Au}_n\text{C}^-$ clusters. In contrast to $\text{Au}_{n+1}^-\text{C}^-$ clusters, $\text{Au}_n\text{C}^-$ clusters are most stable in a quasi-planar or three-dimensional structure because C doping induces the local non-planarity while the rest of the structure continues to grow in a planar mode, resulting in an overall non-2D configuration. The relative stability calculations show that the impurity C atom can significantly enhance the thermodynamic stability of pure gold clusters. Moreover, the effect of C atom on the $\text{Au}_n^-\text{host}$ decreases with the increase of cluster size. The HOMO-LUMO gap curves show that the interaction of the C atom with $\text{Au}_n^-\text{clusters}$ improves the chemical stability of pure gold clusters, except for $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters. In addition, a natural population analysis shows that the charges in corresponding $\text{Au}_n\text{C}^-$ clusters transfer from the $\text{Au}_n^-\text{host}$ to the C atom. Meanwhile, a natural electronic configuration analysis also shows that the charges mainly transfer between the $2s$ and $2p$ orbitals within the C atom. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4852179]

I. INTRODUCTION

In the past, bulk gold was an ignored element because of its chemical inactivity. However, since Haruta first discovered the prominent catalytic reactivity of gold nano-clusters supported on oxide substrates, 1 considerable attention has been devoted to studying gold clusters for clarifying their catalytic mechanisms and controlling their catalytic activities. 2–10 To date, the structures of small-to-medium sized pure gold clusters, $\text{Au}_n^-$, have been determined through a variety of joint experimental and theoretical studies. 11–27 We have previously determined that the small-sized gold clusters, $\text{Au}_n^-$ ($n = 4$–$12$), exhibit two-dimensional (2D) planar structure, 11–13 noting that the 2D to 3D structural transition occurs at $n = 12$, which has been proven by using argon tagging. 14 The $\text{Au}_n^-$ ($n = 16$–$18$) clusters exhibit a hollow cage shape 15,16 and the $\text{Au}_{32}^-$ cluster possesses a tetrahedral structure (the smallest gold pyramid). 17 For medium-sized gold clusters, $\text{Au}_{34}^-$ possesses a tubular structure, 18,19 and core-shell structure appears in the size range of $n = 25$–$35$ 18,20–22 and 55–64. 23–26 However, the $\text{Au}_n^-$ ($n = 36$–$54$) clusters have not been verified due to a lack of experimental and computational evidence. The electronic property as well as the structural evolution of the above $\text{Au}_n^-$ clusters are summarized by Wang et al. 27

To enhance the stability of gold clusters and tune their chemical reactivity more precisely, a considerable amount of experimental and theoretical work has been implemented on gold clusters doped with impurity atoms, most commonly transition metal impurities. For example, Guo et al. reported the double-doped $\text{Au}_n\text{Pd}_2$ and $\text{Au}_n\text{Pt}_2$ ($n = 1$–$4$) clusters. 28,29 Different from the single-doped analogue, the results show that the gold-impurity interaction is strong enough to change the known growth pattern of pure gold clusters, implying that the larger the clusters, the smaller the deformation caused by the two dopants. Compared with the $\text{Au}_n\text{M}_2$ ($\text{M} = \text{Pd}, \text{Pt}; n = 1$–$4$) clusters, $\text{Au}_n\text{Ni}_2$ clusters show an inverse odd-even alternation phenomenon in magnetic property. 30 A density functional theory (DFT) study of $\text{Au}_n\text{M}_2$ ($\text{M} = \text{Si}, \text{P}; n = 1$–$8$) clusters 31 indicates that the most stable isomers for $\text{Au}_n\text{Si}_2$ and $\text{Au}_n\text{P}_2$ ($n = 1$–$8$) clusters prefer a 3D structure when $n$ is equal to or greater than 2 and 3, respectively. For single doping, Wang and co-workers reported that isoelectronic replacement of Au by Cu or Ag changes the onset of the 2D to 3D structural transition to a smaller size. 32 Yuan et al. studied the $\text{Au}_n\text{M}$ ($\text{M} = \text{Ni, Pd, Pt}$) clusters 33 and found that Ni cannot change the geometry of the host clusters, while for Pd- and Pt-doped Au clusters, the ground state structures change significantly. Dong et al. studied the $\text{Au}_n\text{M}$ ($\text{M} = \text{Sc, V, and Mn}$) clusters 34–36 and concluded that the ground state structures prefer a planar configuration with M occupying the higher coordination site. Li et al. reported that the lowest-energy structures of $\text{Au}_n\text{Zn}^-$ ($n = 2$–$10$) clusters 37 favor 2D configuration, as in the $\text{Au}_n^-$ clusters.
Although a large number of studies have been focused on the transition metal-doped gold clusters, there have been relatively few studies on gold clusters with non-transition elements as dopants. Majumder and Kandalam\textsuperscript{48} have proven that when gold clusters are doped with impurity elements possessing \( p \) electrons, the whole structure would prefer a three-dimensional (3D) configuration because of the \( sp^3 \) hybridization, which can be verified by gold clusters doped with various elements, such as Al, Si, P, and S.\textsuperscript{38–42} There are many studies on the gold clusters containing Si, Ge, and Sn elements. Though these dopants are from the same main group, there are two differences in the growth mode of Si-doped Au clusters from Ge- and Sn-doped clusters. On one hand, \( Au_XSi^{1−1/0} \) clusters exhibit \( T_d \) symmetry,\textsuperscript{43} which are similar to \( SiH_4^{1−1/0} \).\textsuperscript{44} On the other hand, the dopant atom in corresponding \( Au_XGe^{1−1/0} \) and \( Au_XSn^{1−1/0} \) clusters have \( Cs \) symmetry\textsuperscript{47} rather than the \( T_d \) configuration; thus, the Au/H analogue does not exist in \( Au_XGe^{1−1/0} \) and \( Au_XSn^{1−1/0} \) clusters. Moreover, the structure of \( Au_XSi^{1−1/0} \) clusters has a dangling Au-Si unit, which reflects the competition between the tendency to form a Au-Si local unit and the tendency to grow without destroying the integrity of the pure gold clusters. However, a DFT study shows that the lowest-energy structures of \( Au_{16}C^{1−1/0} \) clusters\textsuperscript{50} are similar to those of \( Au_{16}Ge^{1−1/0} \) and \( Au_{16}Sn^{1−1/0} \) clusters in that they do not possess the local Au-Si unit with \( T_d \) geometry.\textsuperscript{47} In addition, two DFT studies show that both \( Au_{16}C^{1−1/0} \) and \( CH_{16}^{1−1/0} \) clusters\textsuperscript{47,51} have \( T_d \) configuration, but whether there exists an Au/H analogy between them is still questionable. In short, in addition to theoretical calculation, experimental evidence is needed to further identify the global minimum of \( Au_{16}C^{1−1/0} \) and \( Au_{16}C^{1−1/0} \) clusters.

Though there are some studies\textsuperscript{47,50,52–58} on clusters that contain Au and C elements, as far as we know, there are relatively few systematic studies on the geometric structure, stability, and electronic property of C-doped Au clusters, which brings about an important question: are their structures and properties different from the pure gold or Si/Ge/Sn-doped Au clusters? In light of this question, this paper reports a systematic study of the geometries, stabilities, and electronic properties of \( Au_{16}C^n \) clusters by means of a density functional method. The goal of this work is to provide effective guidelines for future experimental studies and contribute to further understanding the structures and electronic properties of C-doped Au clusters, which may be useful in creating a new type of C-Au nanostructure for nanocatalysis.

### II. Computational Methods

The calculations were carried out in three steps. In the first step, we used the basin-hopping (BH) algorithm\textsuperscript{59–61} coupled with DFT in the DMol3 software package\textsuperscript{62} to search the potential energy surfaces of \( Au_{16}C^n \) (\( n = 1–10 \)) clusters at the BLYP/DNP (DNP is the abbreviation of double-numerical polarized basis set) level of theory. After the BH global search program, we chose a few tens of low-energy isomers for each species from a few hundreds searched structures. Then, we ran the second step (optimization), implemented in the NWChem 6.0 software package,\textsuperscript{63} in which the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) functional form was chosen. All of the low-lying structures were optimized at the PBE/aug-cc-pVDZ(AVDZ) level of theory. Additionally, the scalar relativistic effective core potential and the CRENBL basis set are for the Au atom in the present work, except for the (U)CCSD(T)-F12 calculation in Tables I and II. Next, we selected a few of low-lying isomers for re-optimization at the PBE0/aug-cc-pVTZ(AVTZ) level of theory. To verify the stability of each isomer, we calculated the harmonic vibrational frequency using the GAUSSIAN 09 program,\textsuperscript{64} which is at the same theoretical level as the second-run optimization. If an imaginary vibrational mode appears, a relaxation along the coordinates of the imaginary vibrational mode will be performed until the true minimum is actually obtained.

It is well known that relativistic effects play an important role in the growth pattern of gold clusters.\textsuperscript{55–71} The preference for planar structure of gold clusters has been attributed to strong relativistic effects, which enhance the \( s-d \) hybridization by stabilizing the \( 6s \) orbital and destabilizing the \( 5d \) orbital of the Au atom. Therefore, to obtain accurate information regarding the \( Au_{16}C^n \) (\( n = 1–10 \)) clusters, the spin-orbit (SO) effects\textsuperscript{72–74} were included in the single-point energy calculation, which was based on the re-optimized structures at the SO-PBE0/AVTZ level of theory in the NWChem 6.0 software package. Additionally, inclusion of the SO effects can make the computed photoelectron spectroscopy (PES) more in line with the experimental data.\textsuperscript{32,75–80} The first vertical detachment energy (VDE) was calculated as the energy difference

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>Isomers</th>
<th>PBE0/AVTZ</th>
<th>B3LYP/6-311+G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 2</td>
<td>Isomer 1</td>
<td>0.000</td>
<td>0.647</td>
</tr>
<tr>
<td></td>
<td>Isomer 2</td>
<td>0.000</td>
<td>0.419</td>
</tr>
<tr>
<td>n = 3</td>
<td>Isomer 1</td>
<td>0.000</td>
<td>1.366</td>
</tr>
<tr>
<td></td>
<td>Isomer 2</td>
<td>0.000</td>
<td>0.799</td>
</tr>
<tr>
<td>n = 4</td>
<td>Isomer 1</td>
<td>0.000</td>
<td>1.020</td>
</tr>
<tr>
<td></td>
<td>Isomer 2</td>
<td>0.000</td>
<td>1.537</td>
</tr>
<tr>
<td></td>
<td>Isomer 3</td>
<td>0.000</td>
<td>0.438</td>
</tr>
<tr>
<td></td>
<td>Isomer 4</td>
<td>0.000</td>
<td>6.456</td>
</tr>
<tr>
<td>n = 5</td>
<td>Isomer 1</td>
<td>0.000</td>
<td>1.529</td>
</tr>
<tr>
<td></td>
<td>Isomer 2</td>
<td>0.000</td>
<td>2.360</td>
</tr>
<tr>
<td></td>
<td>Isomer 3</td>
<td>0.000</td>
<td>1.108</td>
</tr>
<tr>
<td></td>
<td>Isomer 4</td>
<td>0.000</td>
<td>2.109</td>
</tr>
</tbody>
</table>

\textsuperscript{2}The (U)CCSD(T)-F12 calculations are performed in MOLPRO 2010.1. CCSD(T)-F12 is for close-shell construction and UCCSD(T)-F12 is for open shell. In addition, the aug-cc-pVTZ basis set is for Au and 6-31+G* is for the C atom. The lowest energy for each of the corresponding isomers is set to 0.000 kcal/mol.
between the anionic and neutral species of each isomer based on the corresponding anion geometry. The binding energies of the deeper occupied orbitals of the anion were then added to the first VDE to give VDEs for the excited states. The simulation of the lowest unoccupied molecular orbital (HOMO-LUMO) gaps of the three levels of theory are all based on the optimized geometries of the clusters at the PBE0/AVTZ level of theory.

### TABLE II. The computed relative energies of the top several low-lying isomers at the SO-PBE0/AVTZ, SO-B3LYP/6-311+G*, and (U)CCSD(T)-F12/6-31+G* levels of theory.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>SO-PBE0/AVTZ</th>
<th>SO-B3LYP/6-311+G*</th>
<th>(U)CCSD(T)-F12/6-31+G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>14.395</td>
<td>...</td>
</tr>
<tr>
<td>2</td>
<td>0.000</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>3</td>
<td>0.000</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>0.000</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

The lowest energy for each of the corresponding isomers is set to 0.000 kcal/mol.

The computed relative energies of the lowest-energy structure, the energy order, and the energy difference from the (U)CCSD(T)-F12 energy, we concluded that the performance of SO-PBE0/AVTZ energy was better than that of SO-B3LYP/6-311+G* side from several defects. Thus, we select the PBE0/AVTZ group for optimization and single-point energy calculations in the present work. Although it is difficult to confirm that we have achieved the lowest-energy structures of Au$_n$C$^-$ (n = 1–10) clusters because of the lack of experimental data, it is worth mentioning that we have performed an extensive search to the best of our ability.

### III. RESULTS AND DISCUSSIONS

#### A. Structures and VDEs

To study the effect of impurity atom on gold clusters, we first performed some optimization and energy calculations on pure gold clusters, Au$_{n+1}^-$ (n = 1–10), by using the same method, basis set, and software as in Au$_n$C$^-$ clusters. Although many possible initial structures were taken into account, only the most stable isomers for each size were selected and shown in Figs. 1 and 2. A few low-energy isomers are listed in Table S1. It is interesting to note that the geometric structures are in good agreement with the previous results, which are the lowest in energy for the Au$_n$C$^-$ cluster. To affirm the global minimum, we calibrated the single-point energy at the CCSD(T)-F12/6-31+G* level of theory in MOLPRO 2010.1. The results reveal that the W-like structure is more stable than the triangle structure by 0.005 eV. Moreover, the calculated VDE value of W-like structure is 2.89 eV, which is in good agreement with the experimental values (2.98 eV$^{91}$ and 3.09 eV$^{12}$), while the corresponding value of triangle structure is 3.62 eV, far larger than the experimental value. Thus, the W-like structure is actually the global minimum for the Au$_5^-$ cluster. For the Au$_6^-$ cluster, the recognized lowest-energy structure in previously published literature is the triangle configuration, which is the second lowest-energy structure in the present work (see Table S1), unfortunately. Moreover, the triangle structure is 0.225 eV higher in energy than the cart-like ground-state structure. To confirm the global minimum in theory, we performed higher level single-point energy calculation for the first three lowest-energy structures at the MP2/AVTZ level of theory in NWChem 6.0. The MP2 calculation results show that the triangle structure is more stable than the cart-like and hat-like structures by 0.371 and 0.214 eV, respectively. Furthermore, the computed VDE value (1.83 eV) of the triangle structure is in reasonable agreement with the experimental values (2.00 eV$^{99}$ and 2.13 eV$^{12}$), while the corresponding VDE values of other two isomers are 3.41 eV (for the cart-like structure) and 2.40 eV (for the hat-like structure). Thus, we adopt the triangle structure in the present work. Additionally, the averaged atomic
FIG. 1. Lowest-energy structures of Auₙ⁻ and Auₙ⁺ (n = 1–5) clusters and a few of the low-lying isomers for doped clusters at the SO-PBE0/AVTZ//PBE0/AVTZ level of theory. The first number represents the cluster size and the data after the comma represent the geometry symmetries and the relative energies (in eV) with respect to the ground state isomers for Auₙ⁻ (n = 1–5) clusters.

Au₂⁻ D₆h 1a,C₆v - - - -
Au₃⁻ D₆h 2a,C₂v 0.000 2b,C₄ 0.624 - - -
Au₄⁻ Cᵥ 3a,C₃v 0.000 3b,C₃ 0.302 3c,C₃ 0.302 - -
Au₅⁻ Cᵥ 4a,C₃s 0.000 4b,C₃ 0.607 4c,C₃ 0.607 4d,C₃ 0.783 4e,C₃ 0.783

FIG. 2. Lowest-energy structures of Auₙ⁻ and Auₙ⁺ (n = 6–10) clusters and a few of the low-lying isomers for doped clusters at the SO-PBE0/AVTZ//PBE0/AVTZ level of theory. The first number represents the cluster size and the data after the comma represent the geometry symmetries and the relative energies (in eV) with respect to the ground state isomers for Auₙ⁻ (n = 6–10) clusters.

Au₆⁻ C₃h 5a,C₃v 0.000 5b,C₁ 0.645 5c,C₁ 0.645 5d,C₁ 1.181 5e,C₁ 1.181

Au₇⁻ Cᵥ 6a,C₃s 0.000 6b,C₃s 0.415 6c,Cᵥ 0.415 6d,C₁ 0.192 6e,C₁ 0.359 6f,C₁ 0.525

Au₈⁻ C₄h 7a,C₁ 0.000 7b,C₁ 0.000 7c,C₁ 0.154 7d,C₄ 0.406 7e,C₁ 0.538 7f,C₁ 0.650

Au₉⁻ Cᵥ 8a,C₃s 0.000 8b,C₁ 0.159 8c,C₃ 0.159 8d,C₄ 0.164 8e,C₁ 0.299 8f,C₁ 0.312 8g,C₁ 0.420

Au₁₀⁻ C₁ 9a,C₃ 0.000 9b,C₁ 0.005 9c,C₃ 0.005 9d,C₄ 0.020 9e,C₁ 0.143 9f,C₁ 0.149
binding energies, attachment energies, second-order difference of energies, the first VDEs, and the HOMO-LUMO gaps of pure gold clusters are also calculated and compared with the available experimental values.

1. Structures

Figure 1 shows the lowest-energy structures of Au\(_n\)C\(^-\) and Au\(_{n+1}\)^- (n = 1–5) clusters in addition to a few of low-lying isomers for doped gold clusters at the SO-PBE0/AVTZ/PBE0/AVTZ level of theory. The corresponding structures of Au\(_n\)C\(^-\) and Au\(_{n+1}\)^- clusters for n = 6–10 are shown in Fig. 2. According to the total energy from lowest to highest, the low-lying isomers are designated by na, nb, nc, nd, ne, and nf, where n is the number of Au atoms in the clusters. Meanwhile, the symmetries and relative energies with respect to each of the corresponding ground-state isomers are also presented in Figs. 1 and 2. Moreover, the VDE values are listed in Table III, HOMO-LUMO gaps are shown in Table IV, and the corresponding computed PES are shown in Figs. S2–S10.88

Regarding the ground-state geometries of the Au\(_n\)C\(^-\) (n = 1–10) clusters, our calculation results show that the equilibrium bond length of Au-C in the Au\(_1\)C\(^-\) cluster is 1.818 Å, which is smaller than the calculated value of Au-Au (2.660 Å) in the Au\(_2\)^- cluster. This is because the radius of a C atom is less than that of a Au atom. The lowest-energy isomer (2a) of the Au\(_2\)C\(^-\) cluster is an isosceles triangle structure with C\(_{2v}\) symmetry and an apex angle of 101.01°, which resembles the lowest-energy structures of Au\(_2\)Si\(^-\) and Au\(_2\)Sn clusters.92 A linear chain structure (2b) with the C atom located at the edge of the Au-Au bond is 0.642 eV higher in energy than Isomer 2a. The chain structure can be obtained by adding one Au atom connecting to the Au atom of Isomer 1a, one C atom on the edge of the Au\(_2\)^- cluster, or by replacing a side Au atom in the Au\(_3\)^- cluster. In addition, the triangle structure can be taken as Au\(_1\)C\(^-\) with another Au atom binding with the C atom.

For the Au\(_3\)C\(^-\) cluster, a 3D structure (3a) is found to be the global minimum with C\(_{3v}\) symmetry and different Au-C bond lengths (1.951, 1.951, and 1.960 Å), which is

#### Table III. Point group symmetry and the computed first VDEs of the lowest-energy Au\(_n\)C\(^-\) and Au\(_{n+1}\)^- (n = 1–10) clusters, along with the experimental VDE values of Au\(_n\)\(^-\) (n = 1–10) clusters in Refs. 12, 91, and 95. All of energies are in eV.

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>Au(_n)C(^-) VDE</th>
<th>Au(_{n+1})^- VDE</th>
<th>Au(_n)(^-) VDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1</td>
<td>C(_{2v}) 1.23</td>
<td>D(_{2h}) 1.89</td>
<td>2.01(3) 1.90</td>
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<tr>
<td>n = 2</td>
<td>C(_{2v}) 2.04</td>
<td>D(_{2h}) 3.49</td>
<td>3.88(2) 3.77</td>
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<tr>
<td>n = 3</td>
<td>C(_{3v}) 2.81</td>
<td>C(_{2v}) 2.64</td>
<td>2.75(3) 2.63</td>
</tr>
<tr>
<td>n = 4</td>
<td>C(_s) 2.00</td>
<td>C(_{2v}) 2.89</td>
<td>3.09(3) 2.98</td>
</tr>
<tr>
<td>n = 5</td>
<td>C(_{3v}) 3.60</td>
<td>C(_{4h}) 1.83</td>
<td>2.13(2) 2.00</td>
</tr>
<tr>
<td>n = 6</td>
<td>C(_s) 2.80</td>
<td>C(_{2v}) 3.26</td>
<td>3.46(2) 3.38</td>
</tr>
<tr>
<td>n = 7</td>
<td>C(_1) 3.29</td>
<td>C(_{4h}) 2.69</td>
<td>2.79(2) 2.79</td>
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<tr>
<td>n = 8</td>
<td>C(_1) 2.98</td>
<td>C(_{2v}) 3.69</td>
<td>3.83(2) 3.78</td>
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<td>C(_1) 3.80</td>
<td>3.91(2) 2.98</td>
</tr>
<tr>
<td>n = 10</td>
<td>C(_1) 3.51</td>
<td>C(_1) 3.60</td>
<td>3.80(2) 3.71</td>
</tr>
</tbody>
</table>

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88Reference 12. The numbers in parentheses represent the experimental uncertainties in the last digits.
89Reference 91.
90Reference 95.

#### Table IV. HOMO/LUMO energies and the gaps between them for the lowest-energy Au\(_n\)C\(^-\) and Au\(_{n+1}\)^- (n = 1–10) clusters. All of energies are in eV.

<table>
<thead>
<tr>
<th>Cluster size</th>
<th>Au(_n)C(^-) HOMO</th>
<th>Au(_n)C(^-) LUMO</th>
<th>Au(_n)C(^-) HOMO-LUMO gap</th>
<th>Au(_n)(^-) HOMO</th>
<th>Au(_n)(^-) LUMO</th>
<th>Au(_n)(^-) HOMO-LUMO gap</th>
</tr>
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<tr>
<td>n = 1</td>
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<td>2.30</td>
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<td>n = 2</td>
<td>−0.46645</td>
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<td>n = 3</td>
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<td>n = 4</td>
<td>−0.71031</td>
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<td>0.67913</td>
<td>1.87</td>
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<tr>
<td>n = 5</td>
<td>−2.25984</td>
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<td>0.81033</td>
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<tr>
<td>n = 6</td>
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<td>1.99</td>
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<tr>
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<tr>
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<td>...</td>
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<td>−0.53154</td>
<td>1.98</td>
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similar to the lowest-energy structures of Au$_3$Si$^-$ and Ag$_3$C$^-$ clusters.\cite{33, 93} The structure of Isomer 3a can be obtained from Isomer 2a after another Au atom connecting to the C atom. Meanwhile, the calculation shows that the second lowest-energy structures are an ax-like structure (3b) and a Y-shaped structure (3c), which are entirely degenerate (0.302 eV for both of them). The former can be taken as the Isomer 2a or 2b with a Au atom added to the corresponding site of these isomers, and the latter can be considered to be the Au$_4$$^-$ cluster with a C atom replacing the top Au atom.

In the case of the Au$_4$C$^-$ cluster, a distorted tetrahedron configuration (4a) is proven to be the global minimum with C$_s$ symmetry, which can be described as Isomer 3a after another Au atom connecting to the C atom. Additionally, if another Au atom connects to the Au atom in Isomer 3a, a new isomer (4e) with C$_s$ symmetry will emerge, which is 0.783 eV higher in energy than Isomer 4a. However, a DFT study shows that the Au$_4$C$^-$ cluster has T$_d$ symmetry\cite{17} rather than C$_s$ symmetry, thus the true global minimum for the Au$_4$C$^-$ cluster is still unknown, further emphasizing the necessity of the relevant experiments.

Among the stable isomers of the Au$_n$C$^-$ cluster, an isomer (5a) with C$_3$ symmetry is proven to be the ground state, which is derived from Isomer 4a with one Au atom top-capped and has the same structure as the Au$_5$Si$^-$ cluster.\cite{94} Moreover, four other isomers (5b, 5c, 5d, and 5e) are taken into account with different symmetries and relative energies from Isomer 5a (C$_1$, 0.645 Å; C$_s$, 0.645 Å; Cs, 1.181 Å; and Cs, 1.181 Å; respectively).

When one central Au atom is replaced by a C atom in the second lowest-energy structure of the Au$_5$$^-$ cluster (see Table S1),\cite{88} another isomer (6a) will be generated with C$_s$ symmetry. As a result of the incorporation of the C atom, six Au atoms in Isomer 6a are no longer coplanar. Additionally, it can be observed from Fig. 2 that the energy of Isomer 6b is higher than that of Isomer 6a by 0.415 eV. Furthermore, Isomers 6b and 6c can also be obtained by adding one Au atom to Isomers 5b and 5c, respectively.

In our search for the global minimum of the Au$_n$C$^-$ cluster, we find two 3D structures (7a, 7b) to be the lowest in energy and entirely degenerate. Both of them are lowly symmetrical (C$_1$), and the former can be taken as Isomer 6d with one added-Au atom binding with the C atom, and the latter is the analogous structure of Isomer 6a by the same manner. Moreover, Isomer 6a has another derivative, Isomer 7c, that is top-capped with a Au atom. To obtain the global minimum in theory, we conducted higher level MP2/AVTZ single-point energy calculation in NWChem 6.0, which showed that Isomer 7b is more stable than Isomer 7a by 0.545 eV; thus, we chose Isomer 7b as the global minimum in the present work.

For the Au$_8$C$^-$ cluster, a deformed planar structure (8a) is found to be the global minimum with C$_1$ symmetry, which can be derived from the Au$_8$$^-$ cluster by a dangling C-Au unit replacing one of the top Au atoms. Moreover, if a C atom displaces a bottom Au atom in the Au$_8$$^-$ cluster and then the overall structure undergoes partial structural relaxation, a new structure (8c) will form. According to our calculations, the lowest-energy structure of the Au$_n$C$^-$ cluster possesses the same symmetry (C$_1$) as Isomer 8a, and the overall structure is derived from 8a by the addition of a Au atom binding with the C atom. Additionally, Isomer 8c has two derivatives (9b and 9f) in which another Au atom binds with the Au or C atom, respectively.

As for the Au$_{10}$C$^-$ cluster, the global minimum is still non-planar, which can be visualized as Isomer 9b with an added-Au atom binding with the C atom. At the same time, Isomer 9b has another derivative (10e) after being capped by a Au atom. Furthermore, if a Au atom binds with the dangling Au atom in Isomer 9a, another structure (10f) will emerge.

On the basis of the above discussion regarding Au$_n$C$^-$ (n = 1–10) clusters, it is remarkable that the lowest-energy structures favor 3D configuration for n = 3, 4, 5, 7, and 9; quasi-2D configuration for n = 6, 8, and 10; and, as expected, 1D for Au$_1$C$^-$ and 2D for Au$_3$C$^-$ cluster. To gain insight on the structural evolution of these Au$_n$C$^-$ clusters, the extent of dimensionality change has been measured by using the average dihedral angle of the C atom with respect to the connected Au atoms in Mercury 3.1. These values are summarized in Table S2.\cite{88} In addition, the coordination numbers of the C atoms and the average Au-C bond lengths are also shown in this table. As seen from Table S2,\cite{88} we can draw a conclusion that the degree of dimensionality change only depends on the Au-C dangling unit in Au$_n$C$^-$ (n = 6–10) clusters. Also, the extent of dimensionality change of clusters with only one Au-C dangling unit will be smaller than that of clusters with two Au-C dangling units (see the supporting information for detailed analysis).

Combining Figs. 1 and 2, and Table S2,\cite{88} we can conclude that the lowest-energy structures of Au$_n$C$^-$ (n = 1–10) clusters are not purely planar configurations anymore, except for the Au$_{12}$C$^-$ clusters. Furthermore, the C doping induces local non-planarity, while the rest of the structure continues to grow in a planar mode, resulting in an overall quasi-2D or 3D structure. Therefore, the doped C atom dramatically changes the ground-state geometries of Au$_{n-1}$$^-$ (n = 1–10) clusters. Moreover, one Au atom capped on a Au$_{n-1}$$^-$ structure is the dominant growth pattern for Au$_n$C$^-$ clusters.

2. VDEs

The computed first VDE values of the lowest-energy Au$_n$C$^-$ and Au$_{n+1}$$^-$ (n = 1–10) clusters, along with the experimental VDE values of the Au$_n$$^-$ (n = 1–10) clusters in previous literatures,\cite{11, 12, 91, 95} are listed in Table III. The corresponding curves for the cluster size, n, are presented in Fig. 3, where only the experimental data from Refs. 12 and 91 are shown because of the considerably detailed experimental and theoretical data. From Fig. 3, we can see that the computed VDE values of Au$_n$$^-$ (n = 1–10) clusters are generally lower than the experimental values, and generally present the odd-even alternation phenomenon with the exception of the Au$_{10}$$^-$ cluster.

As for the Au$_{10}$$^-$ cluster, there are two very weak features at 2.98 and 3.5 eV in the photoelectron spectrum,\cite{12, 91} with the first weak peak being attributed to the first VDE value of the
cluster in Refs. 11 and 91. However, our calculations show that the triangular structure is the global minimum with the VDE value of 3.80 eV, which is smaller than the first strong PES peak by 0.11 eV. This difference in values is within the range of 0.1–0.3 eV when the SO effects are included in the single-point energy calculation, as shown in Ref. 78. Moreover, the difference of experimental spectra between the Au9− and Au10− clusters is very small, implying that the structural change between them is equally small. Thus, there is little doubt that the triangular structure is the global minimum. In the present work, a planar structure with C2 symmetry (the third lowest-energy structure of the Au10− cluster in Table S18) has the VDE value of 2.72 eV and is identified as the minor isomer because of the excellent agreement with the first weak peak. The corresponding structure is also shown in the inset of Fig. 3, and the violet square frame stands for the theoretical value for one of the Au10− clusters, and the inset shows the corresponding structure.

For Au9C− (n = 1–10) clusters, the VDE values also follow the odd-even alternation phenomenon, with the exception of the Au1C− cluster. The Au1C− cluster has the smallest VDE value of 1.23 eV, which suggests that only 1.23 eV is required to remove an extra electron from the Au1C− cluster by means of photoelectron spectroscopy. At the same time, Au9C− has the largest VDE value of 3.60 eV. By comparison of the VDE values of Au9C− and Au9+− (n = 1–10) clusters, we can see that there is no obvious relationship between them. In addition, the VDE values at the same cluster size are anti-correlative on the whole because of the typical odd-even electronic effect: Au9C− clusters have three valence electrons more than the corresponding Au9+− clusters. Unfortunately, there has been no experimental VDE data for Au9C− clusters until now. Thus, more efforts need to be fully invested in the theoretical and experimental studies on them.

B. Relative stabilities

To predict the relative stabilities of Au1C− and Au2− (n = 1–10) clusters, the average atomic binding energies, E9(n); Au attachment energies, ΔAuE(n); C attachment energies, ΔcE(n); and the second-order difference of energies, Δ2E(n), for the lowest-energy structures of these two kinds of clusters are calculated. For Au1C− clusters, E9(n), ΔAuE(n), and Δ2E(n) are defined as follows:

\[
E_9(n) = E(C^-) + nE(Au) - E(Au_nC^-) / n + 1,
\]

\[
Δ_{Au}E(n) = E(Au_{n-1}C^-) + E(Au) - E(Au_nC^-),
\]

\[
Δ_{c}E(n) = E(Au_n^-) + E(C^-) - E(Au_nC^-),
\]

\[
Δ_2E(n) = E(Au_nC^-) + E(Au_{n+1}C^-) - 2E(Au_n^-),
\]

where E(Au), E(C), E(C−), E(Au−), E(Au+nC−), E(Au+nC), E(Au+n−C−), E(Au+nC−), and E(Au+n+1C−) denote the total energy of Au, C, C−, Au−, Au+n−C−, Au+nC−, and Au+n+1C− clusters, respectively. For Au9− clusters, E9(n), ΔAuE(n), and Δ2E(n) are defined as follows:

\[
E_9(n) = E(Au^-) + (n-1)E(Au) - E(Au_{n-1}^-) / n,
\]

\[
Δ_{Au}E(n) = E(Au) + E(Au_{n-1}^-) - E(Au_n^-),
\]

\[
Δ_2E(n) = E(Au_{n-1}^-) + E(Au_{n+1}^-) - 2E(Au_n^-),
\]

where E(Au), E(Au−), E(Au−), E(Au+n−), and E(Au+n−1−) denote the total energy of Au, Au−, Au+n−, Au+n−1−, and Au+n+1− clusters, respectively.

The E9(n), ΔAuE(n), ΔcE(n), and Δ2E(n) values of the lowest-energy structures for Au9C− and Au2− (n = 1–10) clusters measured against the corresponding cluster size, n, are plotted in Fig. 4. In general, the average atomic binding energies, E9(n), of Au9C− clusters are higher than those of the corresponding Au9− clusters, indicating that the substitution of Au by C atom in the Au9− clusters leads to the improvement of overall relative stability. The enhanced-stability effect of the C atom is most prominent for Au9C− and Au2− clusters, whose binding energies are 1.01 and 2.27 eV, respectively. The variation trend of E9(n) for Au9C− clusters is to increase until n = 3 and then follows a plateau down to n = 10 with very small peaks or hollows for specific clusters, reflecting their relative stabilities. The clusters with an odd number of Au atom are more stable than even-numbered clusters, excluding the Au1C− cluster. The odd-even alternation phenomenon can be explained by the electron pairing effect. As for Au2− clusters, though E9(n) values do not present an odd-even nature, the overall change trend is rising. Regardless of whether the average atomic binding energies of Au9C− and Au2− (n = 1–10) clusters increase, they exhibit a convergent tendency close to a limit, which reflects the fact that the larger the clusters, the smaller the effect of impurity on the host framework. Additionally, a large jump appears between the Au1C− and Au2C− clusters, the Au2− and Au3−
clusters, respectively, indicating that the Au$_2$C$^-$ and Au$_3$$^-$ clusters exhibit a skipping increase of relative stability.

It is well known that the attachment energies, $\Delta_{Au}E(n)$ and $\Delta_{C}E(n)$, along with the second-order difference of energies, $\Delta_2E(n)$, are sensitive indicators of the relative stability. The attachment energies of Au or C atoms on the specific size cluster stand for its ability towards spontaneous single-atom dissociation. The corresponding attachment energy curves as a function of the cluster size, $n$, are shown in Fig. 4(b). It is clear that the interaction of C atom with Au$_n$$^-$ clusters is energetically more favorable than the Au atom with Au$_n$$^-$ or Au$_{n-1}$$^-C$ clusters. That is, the dissociation of C atom from Au$_n$$^-$ clusters requires more energy than that of Au atom from Au$_n$$^-$ or Au$_{n+1}$$^-C$ clusters because the attachment energies of C are larger than those of Au. Combined with Fig. 4(a), we can see that the impurity C atom can significantly enhance the stability of pure gold clusters, which is the purpose of the study on gold clusters doped with impurity atom. We have also compared the Au attachment energies of Au$_{n+1}$$^-$ and Au$_n$$^-$ clusters, and the results show that both of them obey the odd-even alternation phenomenon, which can be explained by the odd-even electron pairing effect. Additionally, because Au$_n$$^-$ clusters have three valence electrons more than the corresponding Au$_{n+1}$$^-C$ clusters, it is very easy to understand that the variation trends are anti-correlative. To our surprise, the open-shell Au$_2$C$^-$ cluster is unexpectedly more stable than the close-shell Au$_3$$^-$ cluster. The NBO analysis in GAUSSIAN 09 shows that the average Wiberg bond order of Au-C bond are 1.1276 a.u. and 1.0903 a.u. in the Au$_2$C$^-$ and Au$_3$$^-$ clusters, respectively, implying that the extent of electron cloud overlap of Au and C atoms in Au$_2$C$^-$ is larger than that in the Au$_3$$^-$ cluster, i.e., the interaction of Au and C atoms in Au$_2$C$^-$ is stronger. Intuitively, the Au-C bond length of the Au$_2$C$^-$cluster (1.959 Å) is smaller than that of the Au$_3$$^-$ cluster (1.993 Å). Thus, there is no question of the higher attachment energy of Au atom in the Au$_2$C$^-$ cluster in spite of the odd numbers of electrons. Furthermore, for $n = 2, 3, 5, 7, 9$, it is found that the dissociation of Au from Au$_n$$^-$ clusters requires more energy than that from Au$_{n+1}$$^-C$ clusters; however, this trend is reversed for $n = 4, 6, 8, 10$. The reason for such a difference is the close-shell system for Au$_n$$^-$ clusters at $n = 3, 5, 7, 9$, and the open-shell structures for Au$_{n+1}$$^-C$ clusters in the same size. Certainly, $n = 2$ is an exception because of its surprisingly high stability.

According to the total energy calculations, it is possible to confirm few stable clusters by plotting the second-order difference of energies as a function of cluster size, $n$. On the basis of the definition, as illustrated by Eqs. (4) and (7), one can determine that the clusters with positive $\Delta_2E(n)$ values would be more stable than their vicinity clusters. The odd-even electron pairing effect in the relative stabilities of Au$_{n+1}$$^-C$ (n = 2–9) clusters can be reflected by the sharp oscillation of the $\Delta_2E(n)$ values in Fig. 4(c). However, the appearance of the C atom changes the pattern for a series of clusters. The Au$_2$C$^-$ (n = 2–9) clusters with odd numbers of Au atoms are more stable than even-number clusters, except for the Au$_3$$^-$ cluster. The exceptional stability of the Au$_2$C$^-$ cluster is in line with that in Fig. 4(b). In addition, the maximum $\Delta_2E(n)$ value of Au$_n$$^-$ (n = 2–9) clusters is found at $n = 9$.

In conclusion, the relative stabilities of Au$_n$$^-$ and Au$_{n+1}$$^-C$ (n = 1–10) clusters have been verified based on various energy parameters, namely, average atomic binding energies, $E_b(n)$, atom attachment energies, $\Delta_{Au}E(n)$, and second order difference in energy, $\Delta_2E(n)$, as shown in Fig. 4. The higher atomic binding energies of Au$_n$$^-$ over Au$_{n+1}$$^-C$ (n = 1–10) clusters (see Fig. 4(a)), along with the higher C atom attachment energy over Au attachment energy (see Fig. 4(b)), reflect that the impurity C atom can greatly

![Fig. 4](image-url)

**Fig. 4.** Size dependence of the average atomic binding energies, $E_b(n)$ (a); Au attachment energies (C attachment energies, $\Delta_{Au}E(n)$, of Au$_n$$^-$ clusters marked with the filled triangles), $\Delta_{Au}E(n)$ (b); and the second-order difference of energies, $\Delta_2E(n)$ (c), for the lowest-energy structures of Aun$^+$ and Aun$^-$ (n = 1–10) clusters.
enhance the relative stability of pure gold clusters. This is the purpose of the study on gold clusters doped with impurity atoms, including C atom. Moreover, the convergent tendency of average atomic binding energies for $\text{Au}_n^-$ and $\text{Au}_{n+1}^-$ clusters (see Fig. 4(a)) suggests that the larger the clusters, the smaller the effect of impurity atom on the host framework. Moreover, as seen from Figs. (4b) and (4c), the $\text{Au}_{2,3,5,7,9}^-$ clusters are more stable than the nearest clusters. These more stable structures are of 3D configuration (but 2D for the $\text{Au}_4^-$ cluster), and the C atom is saturated with coordination numbers of four, except for $\text{Au}_{2,3}^-$ clusters.

C. Electronic properties

The electronic properties of $\text{Au}_n^-$ and $\text{Au}_{n+1}^-$ ($n = 1–10$) clusters can be described by using the energy gap between the HOMO and LUMO, which reflects the ability for electrons to jump from an occupied orbital to an unoccupied orbital, as well as the ability for the molecule to participate in chemical reactions to some extent. A large value corresponds to an enhanced chemical stability. The HOMO and LUMO energies and the energy gaps for the lowest-energy $\text{Au}_n^-$ and $\text{Au}_{n+1}^-$ ($n = 1–10$) clusters are listed in Table IV, with the corresponding curves shown in Fig. 5. As seen from Fig. 5, we can gain some important information about the most stable $\text{Au}_n^-$ and $\text{Au}_{n+1}^-$ ($n = 1–10$) clusters. (a) The HOMO-LUMO gaps for the most stable $\text{Au}_n^-$ ($n = 1–10$) clusters range from 1.58 to 3.15 eV, where $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters have the largest and smallest gap values, respectively. As for $\text{Au}_{n+1}^-$ ($n = 1–10$) clusters, the HOMO-LUMO gaps range from 1.20 to 3.42 eV, where the gap value of $\text{Au}_3^-$ is the largest and that of $\text{Au}_8^-$ is the smallest. Additionally, the $\text{Au}_{10}^-$ cluster has a nearly identical gap value (1.21 eV) with the $\text{Au}_8^-$ cluster. By comparing the energy gaps of $\text{Au}_n^-$ and $\text{Au}_{n+1}^-$ ($n = 1–10$) clusters, we can see that both of them show the same odd-even alternation phenomenon except for the $\text{Au}_1^-$ cluster. (b) It is well known that the doping of an impurity atom can increase or decrease the energy gap depending on its interaction with the host cluster. In the present work, we can see that the interaction of C with $\text{Au}_n^-$ clusters enlarges the energy gaps, except for $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters. In other words, the doped C atom can enhance the chemical stability of pure gold clusters. In particular, the gap difference between $\text{Au}_{10}^-$ and $\text{Au}_{10}^-$ clusters is the largest (0.75 eV), which suggests that the $\text{Au}_{10}^-$ cluster has skipping-increase chemical stability.

In light of the unusual phenomenon where the gaps of $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters are less than those of $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters, respectively, the eigenvalues of molecular frontier orbitals for these clusters are displayed in Fig. 6. Ten frontier orbitals are chosen for each kind of clusters. According to Fig. 6(a), we can see that both $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters are obviously characteristic of the degeneration of energy level nearby the HOMO and LUMO. Because of the incorporation of the C atom, the energy levels of the HOMO and LUMO are partially increased by 0.5 eV and 0.22 eV, respectively, thus leading to a net decrease in the energy gap of $\sim 0.28$ eV. Although the eigenvalues of the frontier orbitals in the $\text{Au}_3^-$ and $\text{Au}_4^-$ clusters (see Fig. 6(b)) are very close, the energy levels are not degenerate. Furthermore, the participation of the C atom also increases the energy levels of the HOMO and LUMO by 0.49 eV and 0.19 eV, respectively, which results in a slight net decrease in the energy gap of $\sim 0.3$ eV. Generally, the incorporation of the C atom improves the energy levels of the HOMO and LUMO for $\text{Au}_3^-$.
TABLE V. Natural population analysis (NPA) and natural electron configuration (NEC) of C atoms in the lowest-energy AuₙC− (n = 1–10) clusters at the PBE0/6-311G level of theory.

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</tbody>
</table>

°NPA and NEC are obtained from the NBO analysis in GAUSSIAN 09.

and Auₙ⁻ clusters, but decreases the corresponding HOMO-LUMO gaps.

In the present work, it must be mentioned that various energy parameters in Fig. 4 are based on the total energy values of clusters and reflect the total thermodynamic stability. However, the HOMO-LUMO energy gap of a given cluster accurately lies on the eigenvalues of the HOMO and LUMO, which reflects its chemical stability. The VDE is the energy required to remove an extra electron from the anion by means of photoelectron spectroscopy, i.e., the energy difference between the HOMO and infinity. Therefore, all of them need not correlate directly with each other. 41,100

It is well known that the NPA can provide a reasonable explanation for the localization of natural charge in clusters. To study the electronic properties, we have summarized the natural atomic charge population of C atom in the lowest-energy AuₙC− (n = 1–10) clusters in Table V. As shown in Table V, the atomic charges of C atom are negative, indicating that the charges in the corresponding clusters transfer from the Auₙ⁻ host to the C atom owing to the larger electronegativity of C than that of Au. Focusing on all the clusters, we can see that the charge-transfer values between Auₙ⁻ host and C atom are less than an electron, except for Au₄C−, Au₅C−, Au₆C−, Au₇C−, and Au₁₀C− clusters. Moreover, we also calculated the average ionic character of Au-C bonds for each kind of clusters based on the NBO analysis in GAUSSIAN 09, and the ionicity of the Au-C bond defined as follows:

\[ i_{Au-C} = \frac{C_{C}^{2} - C_{Au}^{2}}{C_{C}^{2} + C_{Au}^{2}} \]

where \( C_{Au}^{2} \) and \( C_{C}^{2} \) denote the polarization coefficients of Au and C atoms, respectively. The average ionicities of Au-C bonds in Au₄C−, Au₅C−, Au₆C−, Au₇C−, and Au₁₀C− clusters are 28.49%, 25.78%, 27.81%, 27.91%, and 34.14%, respectively, all of which are less than 50%. Therefore, Au and C atoms interact with each other mainly through covalent bond rather than ionic bond, which can also be verified through the difference in electronegativity, \( \Delta_{EN} \). Covalently bonded interactions will exist in clusters if \( \Delta_{EN} < 1.7 \), and \( \Delta_{EN} = 0.15 \) for Au₄C− clusters. Moreover, in order to further understand the above phenomenon, the internal charge transfer of the C atom is also taken into account by natural electronic configuration (NEC), which is also shown in Table V. With regard to the free C atom, the configuration of valence electrons is 2s²2p². When the C atom is doped into gold clusters, the NEC analysis reveals that the 2s orbital loses 0.13–0.56 electrons, while the 2p orbital receives 0.74–1.74 electrons. In short, the charges mainly transfer between the 2s and 2p orbitals, and the effects of 3s and 3p orbitals can be neglected within the C atom.

IV. CONCLUSIONS

The geometrical structures, relative stabilities, and electronic properties of AuₙC− and Auₙ⁻ clusters have been investigated using hyper-GGA in PBE0 functional form, including the spin-orbit coupling effects (aiming at considering the relativistic effect). All of the results are summarized as follows:

1. The optimized geometries show that one Au atom capped on Auₙ₋₁C− clusters is a dominant growth pattern for AuₙC− clusters. The lowest-energy structures of Auₙ⁻ clusters are planar, at least up to n = 10. The equilibrium geometries of C-doped Au clusters favor 3D configuration for n = 3, 4, 5, 7, and 9; quasi-2D configuration for n = 6, 8, and 10; and, as expected, 1D for Au₆C− and 2D for Au₁₀C− cluster. According to the ground-state geometries of AuₙC− (n = 3–10) clusters, we can see that C doping induces local non-planarity while the remainder of the structure continues to grow on a planar mode, which results in an overall quasi-2D or 3D configuration. Thus, the C atom can dramatically alter the ground-state geometries of Auₙ⁻ (n = 1–10) clusters.

2. The global minimum of the Au₄C− cluster is not perfectly established because of the lack of experimental validation. In addition, the different performances of X in the corresponding AuₙX− and Au₁₆X− (X = C, Si, Ge, and Sn) clusters may be related to the extent of sp³ hybridization and the Au-X bonding energy, etc., which deserves to be investigated further in terms of both theory and experimentation.

3. The higher atomic binding energies of AuₙC− over Auₙ₋₁⁻ (n = 1–10) clusters, along with the higher C atom attachment energy over Au attachment energy, reflect that the impurity C atom can significantly enhance the thermodynamic stability of pure gold clusters. Moreover, the convergent tendency of the average atomic binding energies for AuₙC− and Au₁₆⁻ clusters suggests that the effect of the C atom on the Auₙ⁻ host decreases with the increase of cluster size. Additionally, Figs. 4(b) and 4(c) show that the Au₁₆₋₁C− clusters are very stable clusters.

4. The electronic properties of Auₙ₋₁C− (n = 1–10) clusters are discussed based on the HOMO-LUMO energy gaps and the NBO analysis. The HOMO-LUMO gap curves show that the interaction of the C atom with Auₙ⁻ clusters improves the chemical stability of pure gold clusters, except for Au₇⁻ and Au₁₀⁻ clusters. Furthermore, the NPA shows that the charges in corresponding AuₙC−...
clusters transfer from $\text{Au}_n^-$ to host the C atom. Meanwhile, the NEC analysis also shows that the charges mainly transfer between the 2s and 2p orbitals within the C atom.

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See supplementary material at http://dx.doi.org/10.1063/1.4852179 for more information on top-several low-lying structures of Au$_n$C$^{-}$ (n = 2–11) clusters, structural parameters of the lowest-energy Au$_n$C$^{-}$ (n = 1–10) clusters, main methods, basis sets, and software packages used for optimization and single-point energy calculations, and simulated photoelectron spectra of Au$_n$C$^{-}$ (n = 1–10) clusters.


