Density functional study of structural and electronic properties of bimetallic copper–gold clusters: comparison with pure and doped gold clusters

Supplementary Information

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1. Supplementary calculated results using three different functionals.

In the following, we present more detailed geometrical structure and relative energies between the energetically lowest structures for $\text{Au}_{n-1}\text{Cu}^\lambda$ ($\lambda = 0, +1, -1$; $2 \leq n \leq 9$) using three different DFT calculations (BPW91, BP86 and B3LYP), these results underline that the geometries of all the clusters obtained within the three functionals are similar, although the order of isomers is reversed in some cases. From Table 1, it can be seen that for the $\text{Au}_{n-1}\text{Cu}$ cluster ($2 \leq n \leq 9$), the ground state structures predicted by the BP86 and BPW91 methods are consistent with those predicted by B3LYP method. In the case of $n=7$ and $9$, the energies of 7-N-c and 9-N-c predicted by B3LYP method are lower than those of 7-N-d and 9-N-d by 0.005 and 0.031 eV, respectively, while the BP86 and BPW91 methods predict 7-N-c and 9-N-c to lie slightly higher than 7-N-d and 9-N-d by 0.01, 0.004 eV (BP86) and 0.032, 0.03 eV (BPW91). For the $\text{Au}_{n-1}\text{Cu}^+$ cluster the only difference of the geometrical structure among the three functionals is that BP86 and BPW91 predict 9-C-b to lie higher than 9-C-c by 0.013 and 0.033 eV, respectively (see Table S2). The geometries of the $\text{Au}_{n-1}\text{Cu}$ cluster anions calculated by BP86 and BPW91 functionals are also essentially similar to those obtained by B3LYP functional except for $n=8$. The ground state structure is either a $C_2$ structure 8-A-a or a $C_1$ structure 8-A-b, depending on the theoretical method. The B3LYP method predicts 8-A-a to lie lower in energy than 8-A-b by 0.023 eV, while the BP86 and BPW91 methods predict 8-A-a to lie higher than 8-A-b by 0.059 and 0.050 eV, respectively. Thus structures 8-A-a and 8-A-b are essentially degenerate in energy. In addition, structure 6-A-b is predicted to be lower than 6-A-c by the B3LYP and BPW91 methods, while it is predicted by the BP86 method to lie above structure 6-A-c by 0.006 eV. The order of structures 7-A-b and 7-A-c predicted by the B3LYP is consistent with that predicted by BP86, but contrary to the result of BPW91. The corresponding results are listed in Table S3.

It can be seen from Tables S1-S3 that although the B3LYP results give small
relative energies than by the BPW91 and BP86 functionals systemically, they show very similar geometries and the other features. This suggests that geometries of all the clusters should be correctly predicted by all functionals.
Table S1. Geometries (Geo), symmetries (sym), electron states, and relative energies (in eV) between the energetically lowest structures for AuₙCu (2 ≤ n ≤ 9), optimized at the different methods.

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<th>Geo</th>
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<tr>
<td>4-N-a</td>
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<td>¹A'</td>
<td>0</td>
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Table S2. Geometries (Geo), symmetries (sym), electron states, and relative energies (in eV) between the energetically lowest structures for Au_{n-1}Cu^+(2 ≤ n ≤ 9), optimized at the different methods.

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<th></th>
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<td>2B_2</td>
<td>0</td>
<td>C_{2v}</td>
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Table S3. Geometries (Geo), symmetries (sym), electron states, and relative energies (in eV) between the energetically lowest structures for Au_{n-1}Cu^- (2 ≤ n ≤ 9), optimized at the different methods.

<table>
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<tr>
<th>Geo</th>
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2. Structural and energetic characteristics of the lowest-energy isomers as a function of size for doped and bare gold clusters.

**Figure S1.** Average nearest-neighbor distance of the lowest-energy isomers as a function of size for $\text{Au}_{n-1}\text{Cu}^\lambda$ (charge $\lambda = 0, \pm 1$; $2 \leq n \leq 9$) clusters as well as their corresponding bare gold clusters. (a), (b), and (c) correspond to neutral ($\lambda = 0$), cationic ($\lambda = +1$), and anionic ($\lambda = -1$) species, respectively.
Figure S2. The calculated binding energy per atom of neutral and charged clusters (\(\text{Au}_n\text{Cu}^\lambda\) and \(\text{Au}_n^\lambda\) (charge \(\lambda = 0, \pm 1; 2 \leq n \leq 9\)) is represented versus the number of atoms. (a), (b), and (c) correspond to neutral (\(\lambda = 0\)), cationic (\(\lambda = +1\)), and anionic (\(\lambda = -1\)) species, respectively.
Figure S3. Size dependence of dissociation energies for the lowest structures of \( \text{Au}_{n-1}\text{Cu}^\lambda \) and \( \text{Au}^\lambda \) (charge \( \lambda = 0, \pm 1; 2 \leq n \leq 9 \)).
Figure S4. Second total energy differences versus number of atoms for neutral, anionic, and cationic clusters of the lowest-energy structure of $\text{Au}_{n-1}\text{Cu}^\lambda$ and $\text{Au}_n^\lambda$ (charge $\lambda = 0, \pm 1; \ 2 \leq n \leq 9$) clusters. (a), (b), and (c) correspond to neutral ($\lambda = 0$), cationic ($\lambda = +1$), and anionic ($\lambda = -1$) species, respectively.