



Density functional study of NO_x binding on small Au_nCu_m ($n + m \leq 5$) clusters

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ABSTRACT

Density functional theory calculations were performed to investigate the structural and energetic properties of NO, NO₂ and NO₃ binding on small bimetallic Au_nCu_m clusters ($n + m \leq 5$). The adsorbates prefer binding to Cu atoms when both Au and Cu co-exist in the cluster. In general NO is located at top site via the N atom while NO₂ and NO₃ are located at bridge site via the O atoms. The binding energies and the electron transfer from metal clusters to the adsorbates follow the same order NO₃ > NO₂ > NO. Besides, the dope of Cu atoms in Au_n clusters can greatly increase the binding energy with respect to pure Au_n. The N–O vibrational properties of the complex clusters were also discussed and analyzed.

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1. Introduction

In contrast to the inert nature of the bulk material, coinage metals in cluster form were extensively used in catalysis, electrochemistry and medical science [1–8]. As the first and the last coinage metal elements, copper and gold have the similar electronic structure: a completely filled *d* shell and a singly occupied *s* shell. The electronegativity of Au is 2.54 while that of Cu is 1.91. The ionic radii of Au and Cu are 1.44 and 1.28 Å, respectively. In recent years, there is a growing interest in bimetallic Au/Cu clusters both experimentally and theoretically [9–16]. Regarding the differences in ionic radii and electronegativity, it is expected that the combining of Cu atoms into Au_n clusters may have some influence on the structural, physical and chemical properties of the bimetallic Au/Cu clusters. Janssens et al. performed the temperature-dependent Ar tagging on the optical absorption spectra of cationic Au_nCu⁺ ($n = 1–16$) clusters. They found that the substitution of one Au atom by one Cu atom does not significantly change the geometric structure of the clusters [9]. The photoelectron spectra of the anionic Au_nCu[−] ($n = 2–7$) has been performed at a photon energy of 4.661 eV [10]. Wang et al. reported the structures, relative stabilities, growth-patterns and electronic properties of Cu₂Au_n ($n = 1–10$) clusters [11]. The lowest energy geometries of Au_nCu clusters can be considered as assemblies of triangular Au₃ moieties substituted with one Cu atom at the highest coordinated site [12]. Besides, the thermodynamic stability of Au_nCu clusters can be enhanced to some extent after doping with one Cu atom.

Although many of the studies were focused on geometric and electronic properties of the bare Au/Cu clusters, much less is known how the mixing of Au and Cu will influence the chemical reactivity of metal clusters towards atoms or small molecules. A recent experiment has suggested that the bimetallic Au/Cu nanoparticles have much better performance than monometallic particles in catalyzing CO oxidation even with the presence of excess H₂ [17]. CO prefers binding on Cu site of cationic Au/Cu clusters and the binding energy generally decreases with the increase of Cu composition [18]. To our knowledge, there has been no report on chemisorption of nitrogen oxides (NO_x) on bimetallic Au/Cu clusters. In this contribution, we systematically investigate the interaction between NO_x and small Au_nCu_m ($n + m \leq 5$) clusters using the first principles methods on the basis of density functional theory (DFT). The sequence from NO to NO₃ was considered here. The results of geometry, binding energy, electron transfer and vibrational frequency for bimetallic and monometallic clusters were analyzed and discussed in section 3. Before presenting the results, we summarize the computational details in section 2. Finally, the conclusion is drawn in section 4.

2. Computational details

The calculations were carried out using GAUSSIAN 03 package [19]. The PW91PW91 [20] exchange and correlation functional was employed for all the calculations in this study. The Stuttgart–Dresden effective core potential (ECP) plus DZ basis set [21] was used for Au and Cu atoms. The 6-311++G(d, p) basis set was used on N and O atoms. To calibrate the accuracy of this approach, we first compared the calculated spectroscopic parameters of the smallest Au₂, AuCu and Cu₂ clusters with previous experimental

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Table 1

Comparison of calculated and experimental values of the bond length (R in Å), dissociation energies (DE in eV) and vibrational frequencies (freq. in cm^{-1}) of Au_2 , AuCu and Cu_2 clusters.

Species	Au_2			AuCu			Cu_2		
	R	DE	Freq.	R	DE	Freq.	R	DE	Freq.
Cal.	2.56	2.18	170	2.37	2.40	238	2.22	2.17	271
Exp.	2.47 ^a	2.29 ^a	191 ^a	2.33 ^b	2.39 ^c	248 ^b	2.22 ^a	2.08 ^d	265 ^a

^a From Ref. [29].

^b From Ref. [33].

^c From Ref. [34].

^d From Ref. [35].

data. The PW91PW91 results in Table 1 show good agreement with experimental values. The NO_x binding energy (BE) is defined by the following equation:

$$\text{BE} = E(\text{Au}_n\text{Cu}_m) + E(\text{NO}_x) - E(\text{Au}_n\text{Cu}_m\text{NO}_x)$$

where $E(\text{Au}_n\text{Cu}_m)$ and $E(\text{Au}_n\text{Cu}_m\text{NO}_x)$ are the total energies of the bare cluster and the complex cluster, respectively. The more positive the BE is, the stronger the bond is. All binding energies were corrected with basis set superposition error (BSSE) estimated by using the counterpoise corrections method [22]. All calculations were performed with (99,590) pruned grid (ultrafine grid as defined in Gaussian 03). Natural bond orbital (NBO) [23] analysis was used to provide the natural charge distribution. Vibrational frequency calculations including thermochemical analysis were carried out at 298.15 K and 1 atmosphere of pressure. These frequency calculations also guarantee the optimized structures locating the minima, not as transition structures.

3. Results and discussions

3.1. Bare Au/Cu clusters

To have the results of bare clusters and complex clusters for comparison, we also studied the geometries and properties of bare Au/Cu clusters up to five atoms. Results for the most stable metal clusters are displayed in Fig. 1. Bimetallic trimers have triangular structures with the Au–Cu–Au angle of 71.4° and the Cu–Au–Cu angle of 53.4° . Bimetallic neutral tetramers tend to assume rhombic structures in which the gold atoms prefer exposed positions while the copper atoms form a higher number of bonds. Such

topologies are convenient for charge transfer from Cu to Au and easily decrease geometrical reconstruction. Stable bimetallic pentamers assume planar trapezoidal structures with triangular sub-units. Like the case of tetramers, Au atoms favor to occupy outer positions in pentamers. The structures of bimetallic Au/Cu clusters are in good agreement with previous theoretical reports [11–14,18].

3.2. Structures and stability of complex clusters

The most stable structures of $\text{Au}_n\text{Cu}_m\text{NO}$ are displayed in Fig. 2. In all cases the NO molecule is bound to the cluster via the N atom. The Au_nNO clusters are calculated to have the lowest possible spin multiplicities, whereas the triplet state is preferred for all the Cu-containing trimers and pentamers except for AuCu_2NO and Au_4CuNO . The most stable structures of Au_nNO are all with the nitrogen on-top binding to the gold clusters, in consistent with previous theoretical report [24]. For Cu_nNO the most preferred binding site is top site for $n = 2-4$ while bridge site for $n = 5$. It seems that NO prefers bound with Cu when both Au and Cu sites co-exist in the cluster. For example, NO is attached to top-Cu site of bimetallic dimer and all the bimetallic tetramers.

In atop configuration the Au–N–O angle is $\sim 125^\circ$ and the Cu–N–O angle is $\sim 139^\circ$, respectively. This bent structure is related with the symmetry and shape of the $2p\pi^*$ orbital of NO which interacts with metal cluster, which has been fully interpreted in previous theoretical studies [24–28]. However, the most stable AuCu_2NO cluster contains Cu–Cu bridge bound NO. For bimetallic pentamers with only one Cu atom (Au_4Cu), the Au–Cu bridge site is the most favorable, while other bimetallic pentamers all prefer Cu–Cu bridge site. Earlier theoretical study also indicated that NO is adsorbed in bridge configuration on Ag_5 and the underlying reason for the bridge preference may be related with the electronic structure of the metal cluster [26,28]. The HOMO level of the trapezoidal pentamer is a bonding orbital between the two metal atoms connected to NO, which forms efficient interaction with the $2p\pi^*$ orbital of NO [26]. The N–O distance is elongated upon adsorption. The orbital interaction of bridge configuration mentioned above is also supported by the longer N–O distance in bridge configurations (1.20–1.23 Å) than that in atop configurations (1.16–1.17 Å for top-Au binding and 1.17–1.20 Å for top-Cu binding).

Different from NO, NO_2 is bound to the metal clusters via the O atoms in bridge configuration except for Au_2NO_2 and AuCuNO_2 (see in Fig. 3). In Au_3NO_2 two O atoms of the NO_2 were attached

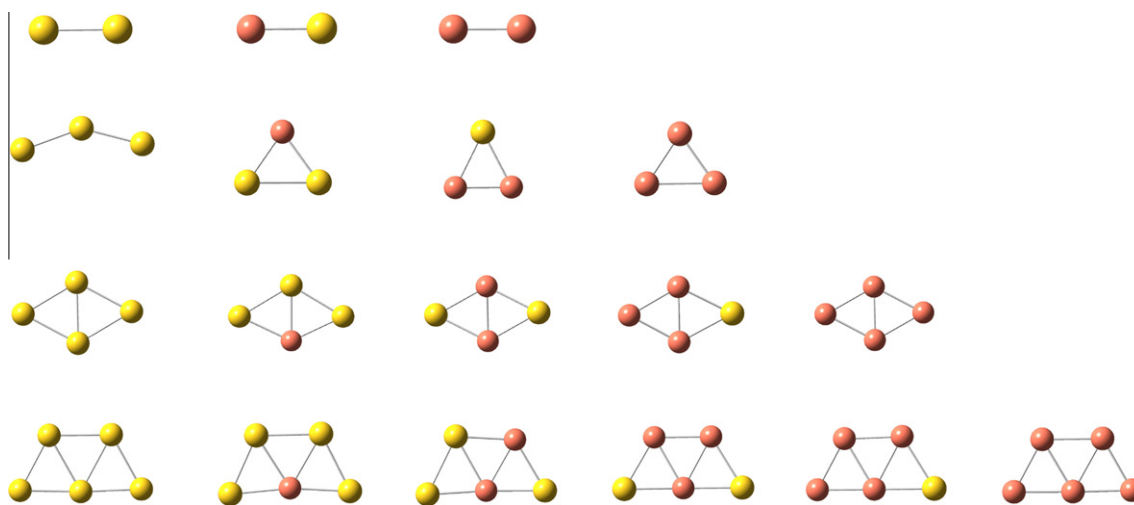


Fig. 1. The most stable structures for Au_nCu_m clusters, with $n + m \leq 5$. The structures are arranged in the order of increasing Cu composition.

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