First-principles study of interaction of cluster Au$_{32}$ with CO, H$_2$, and O$_2$

Yao Wang  
Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China

X. G. Gong
Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai 200433, China

(Received 13 February 2006; accepted 14 August 2006; published online 22 September 2006)

First-principles calculations are performed to study the interaction of cluster Au$_{32}$ with small molecules, such as CO, H$_2$, and O$_2$. The cagelike Au$_{32}$(I$_6$)$_{12}$ shows a higher chemical inertness than the amorphous Au$_{32}$(C$_1$)$_{12}$ with respect to the interaction with small molecules CO, H$_2$, and O$_2$. H$_2$ can only be physically adsorbed on Au$_{32}$(I$_6$)$_{12}$, while it can be dissociatively chemisorbed on Au$_{32}$(C$_1$)$_{12}$. Although CO can be chemically adsorbed on Au$_{32}$(I$_6$)$_{12}$ and Au$_{32}$(C$_1$)$_{12}$ with one electron transferred from Au$_{32}$ to the antibonding $\pi^*$ orbit of CO, it is bound more strongly on Au$_{32}$(C$_1$)$_{12}$ than on Au$_{32}$(I$_6$)$_{12}$. Spin polarized and spin nonpolarized calculations result almost identical ground state structures of Au$_{32}$(I$_6$)$_{12}$–O$_2$ and Au$_{32}$(C$_1$)$_{12}$–O$_2$, in which O$_2$ is dissociatively chemisorbed. © 2006 American Institute of Physics. [DOI: 10.1063/1.2352749]

I. INTRODUCTION

Nanosized gold clusters have attracted much attention from both industrial and scientific areas due to their unique physical and chemical properties strongly dependent on the cluster size. Although bulk Au is one of the most chemically inert metals, small Au clusters, the size of which is as small as 2–3 nm, are efficient catalysts for various chemical reactions. Previous studies reported that nanosized Au catalysts could be applied to many oxidation and hydrogenation reactions at low temperatures. These reactions include CO and NO oxidations, partial oxidation of propylene, partial hydrogenation of acetylene, and hydrogenations of ethylene, 1,3-butadiene, 1-butene, acrolein, and so on. However, up to now, the mechanism of such fantastic size-dependent catalytic activity of Au clusters has not been clearly revealed. Therefore, Au clusters and the interactions of Au clusters with small molecules, such as O$_2$, H$_2$, CO, NO, and CH$_4$, have become hot topics in both experimental and theoretical fields.

The interactions of Au clusters with small molecules have been extensively studied. Previous studies found that the interaction behaviors of small molecules with Au clusters were dependent on the size and structural properties of the clusters. For the interaction of Au clusters with O$_2$, it was experimentally found that an odd-even alteration as a function of the number of Au atoms in the interaction of Au clusters with O$_2$, was also found by theoretical calculations, while the theoretical results of adsorption states of O$_2$ (molecular adsorption or dissociative adsorption) and the number of adsorbed O$_2$ molecules were not exactly coincident with the experimental results. For the interaction of Au clusters with CO, theoretical calculations found that CO was a two-electron donor; therefore, Au$_n^+$ bound CO more strongly than Au$_n^-$ and Au$_n^-$ bound CO adsorbed on Au$_n^+$ and Au$_n^-$ with the size of gold cluster were different from each other, it decreased for Au$_n^+$ bit increased for Au$_n^-$. For all Au clusters, the most favorable adsorption site of CO was the top of the cluster with low coordination sites. An experimental study reported that each Au cluster had a critical CO number (nc), exactly equal to the number of the available low-coordination apex sites on this cluster. In addition, both experimental and theoretical studies revealed that O$_2$ and CO were able to be coadsorbed on Au clusters, because the adsorption of one kind of molecule favored that of another kind of molecule. Meanwhile the coadsorption could induce the oxidation of CO, i.e., Au clusters behaved as a catalyst facilitating the oxidation of CO. The studies of the interaction of Au clusters with H$_2$ were relatively rare. Early experiment reported that the reaction of Au$_n^+$ with H$_2$ might be observed under high pressure and temperature conditions; recent experiments found no reactivity of Au$_n^+$ toward H$_2$ under usual experimental condition, because the binding between Au$_n^+$ and H$_2$ was weak and the reaction of Au$_n^+$ with H$_2$ needed to overcome a high barrier. A theoretical study found that H$_2$ could be molecularly bound to Au$_2$ and Au$_3$, but could not be bound to Au$_4$ and Au$_5$. Besides, the gas-phase Au clusters, Au clus-

*Electronic mail: xggong@fudan.edu.cn
ters supported by metal oxides, have also been extensively studied. Recently, joint experimental and theoretical studies on \( \text{Au}_n (2 \leq n \leq 20) \) supported by MgO surface revealed that \( \text{Au}_8 \) was the smallest gold heterogeneous catalyst for the oxidation of CO. It was reported that when \( \text{Au}_8 \) was bound to oxygen vacancy F centers of MgO surface, it was catalytically active; while it was catalytically inert when bound to MgO defect-free surface.32 Some theoretical studies found that oxide enhanced the catalytic activity of Au clusters.33,34 Meanwhile it was found experimentally that different oxides showed different effects on the activity of Au clusters: the activity of Au clusters supported by the reducible oxides (TiO\(_2\) and Fe\(_2\)O\(_3\)) was higher than that supported by irreducible oxides (MgO, Al\(_2\)O\(_3\), and SiO\(_2\)).35 It was also found experimentally that the lowest temperature, at which TiO\(_2\) supported Au clusters catalyzed the oxidation of CO, was 65 K.36

Recent experimental and theoretical studies found that the relativistic effect played a significant role in the structures of small Au clusters, resulting in the structures of Au clusters different from the clusters of other metals. For example, neutral and anionic clusters \( \text{Au}_n \) and \( \text{Au}^-_n \) favored planar structure up to \( n = 13 \), cationic cluster \( \text{Au}^+_n \) favored planar structure up to \( n = 8 \), while the clusters of five to seven atoms of other metals would transfer to three-dimensional structure.37,38 The photoelectron spectroscopy combined with the relativistic density functional calculations revealed that \( \text{Au}_{20} \) possessed a tetrahedral structure with a wide highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap of 1.77 eV. This suggested that \( \text{Au}_{20} \) should be highly inert and stable. CO favored to be molecularly adsorbed on the apex sites of the \( \text{Au}_{20} \) tetrahedron and the HOMO-LUMO gap of the tetrahedral \( \text{Au}_{20} \) was slightly decreased upon CO adsorption.39 Another x-ray photoelectron spectroscopy showed that \( \text{Au}_{32} \) supported by silicon substrate presented a maximum oxidation resistance; therefore it might exhibit unusual catalytic properties.40 Recently, the first-principles calculations have found that clusters \( \text{Au}_n \) (\( n = 32 \sim 35 \)) can appear in cage-like structure with a wide HOMO-LUMO gap. The most typical example is cluster \( \text{Au}_{32}(I_h) \) of icosahedral symmetry; its gap is as wide as 1.56 eV. This suggested that \( \text{Au}_{32}(I_h) \) should have a high chemical inertness.41 Although \( \text{Au}_{32}(I_h) \) is the most stable one at zero temperature, experimental and theoretical studies have found that its amorphous isomer \( \text{Au}_{32}(C_1) \) becomes most stable above 300 K.42

In this paper, in order to investigate the chemical properties of cluster \( \text{Au}_{32} \), first-principles calculations are carried out to compare the interactions of clusters \( \text{Au}_{32}(I_h) \) and \( \text{Au}_{32}(C_1) \) with selected small molecules, i.e., CO, H\(_2\), and O\(_2\). It is found that \( \text{Au}_{32}(I_h) \) shows a high chemical inertness with respect to these interactions.

II. DETAILS OF CALCULATIONS

The present calculations are based on the density functional theory43,44 and plane-wave basis set45,46 with generalized gradient approximation (GGA).47,48 which are implemented in the \text{VASP} code.49 The interaction between core and valence electrons is described with the projector augmented wave (PAW) potential.50,51 The structures of the clusters are optimized by the conjugate gradient (CG) method.52 A simple cubic supercell with a lattice constant of 25 Å is adopted, which is large enough to neglect the interaction between the cluster and its periodic images. Due to the large supercell, only \( I \) point is used for the summation in the Brillouin zone. The structures of \( \text{Au}_{32}(I_h) \) and \( \text{Au}_{32}(C_1) \) (see Fig. 1) are first optimized to make them coincident with the previous theoretical studies,41,42 then the small molecules, i.e., CO, H\(_2\), and O\(_2\), or their atomic forms, such as C, O, and H, are added on. Finally, the structure with the highest binding energy is taken as the ground-state structure. If, for example, the structure with two O atoms separately absorbed on the cluster is of higher binding energy than that of the structure with O\(_2\) molecularly absorbed, we say O\(_2\) can dissociatively adsorb on the cluster, without calculating the exact barrier. In order to test the accuracy of the present method, the bond lengths of \( \text{Au}_{32} \), CO, H\(_2\), and O\(_2\) are calculated. The results are 2.49, 1.14, 0.75, and 1.31 Å, respectively, in agreement with the experimental results of 2.47, 1.13, 0.73, and 1.21 Å.

III. RESULTS AND DISCUSSIONS

A. Interaction between cluster \( \text{Au}_{32} \) and CO

For the present calculations, two types of cluster \( \text{Au}_{32} \) are selected to study the interaction with small molecules: one is \( \text{Au}_{32}(I_h) \), which is the ground state structure of cluster...
Au$_{32}$ at 0 K; and the other is Au$_{32}$($C_1$), which is the most stable structure of cluster Au$_{32}$ above 300 K.$^{31,42}$ First, the structural and electronic properties of Au$_{32}$($I_b$) and Au$_{32}$($C_1$) (shown in Fig. 1) are discussed. Au$_{32}$($I_b$) is of high symmetry: there are only two different kinds of site on the cage, i.e., 12 five-coordinated sites and 20 six-coordinated sites. The HOMO charge density of Au$_{32}$ is plotted in Fig. 1. It is shown that the HOMO spreads symmetrically over the outer surface of the Au$_{32}$ ($I_b$) cage: protrudes outwards at the five-coordinated sites and sinks inwards at the six-coordinated sites. Thus, at the five-coordinated sites, the HOMO of Au$_{32}$ should overlap with those of other molecules more than at the six-coordinated sites. This means that the atoms at the five-coordinated sites should be more active than those at the six-coordinated sites and small molecules should be adsorbed more favorably on the five-coordinated sites. However, for Au$_{32}$($C_1$), the structure without any symmetry results in the distribution of its HOMO charge density without any symmetry.

In order to study the interaction between cluster Au$_{32}$ and CO, the structures of both Au$_{32}$($I_b$)–CO and Au$_{32}$($C_1$)–CO complexes are optimized. The structural and electronic properties of Au$_{32}$–CO complexes are displayed in Figs. 2 and 3 and listed in Table I. Figure 2 shows the optimized structures of Au$_{32}$($I_b$)–CO (a) and Au$_{32}$($C_1$)–CO (b), while the binding energy of CO, HOMO-LUMO gap, and bond lengths of C–O and Au–C of each complex are listed in Table I. The HOMO charge densities of the isomers of Au$_{32}$($I_b$)–CO complex are shown in Fig. 3.

Because of the high symmetry of Au$_{32}$($I_b$), the possible binding sites of CO are very few. Therefore, in the present calculations, only five stable structures of Au$_{32}$($I_b$)–CO complex are obtained. All of them are shown in Fig. 2(a). For the first two most stable structures of Au$_{32}$($I_b$)–CO [(I) and (II) of Fig. 2(a)], CO molecules are adsorbed on the on-top sites of the Au$_{32}$($I_b$) cage. In the ground state of Au$_{32}$($I_b$)–CO [(I) of Fig. 2(a)], CO is adsorbed on the five-coordinated site; while in the first isomer [(II) of Fig. 2(a)], CO is adsorbed on the six-coordinated site. The binding energy of CO of the former is 0.86 eV, while it is 0.40 eV for the latter. This indicates that CO should be adsorbed much more favorably on the five-coordinated sites, the lower-coordinated sites, showing the higher activity of the Au atoms at the five-coordinated sites. This result is in agreement with previous experimental and theoretical studies on the adsorption of CO on small gold clusters: CO ought to prefer to be bound on the low-coordinated sites of small gold clusters.$^{20-24}$ Examination on these two most stable structures of Au$_{32}$($I_b$)–CO shows that Au$_{32}$($I_b$) cages only change slightly upon CO adsorption. The C atom of CO likes to be bound to one single Au atom with C–O bond length of 1.15 Å, which is equal to that of CO$^-$ and 0.01 Å longer than that of a free CO molecule (1.14 Å). In previous study, the interaction between CO and transition metal surface was generally characterized by the charge transfer from the metal to the antibonding ($\pi^*$) orbit of CO (donation) and back donation to the metal from the CO bonding ($\sigma$) orbit.$^{53}$ The present calculation suggests that for the two most stable
structures of $\text{Au}_{32}(I_h)$—CO one electron might transfer from $\text{Au}_{32}(I_h)$ to the $\pi^*$ orbit of CO, i.e., CO could be chemisorbed on $\text{Au}_{32}(I_h)$ cage. The plots of the HOMO charge densities of these two most stable structures are shown in Fig. 3 [(I) and (II)]. It can be clearly seen that CO molecules gain electrons, while the Au atoms, on which CO are bound, lose electrons. The charge transfer from $\text{Au}_{32}(I_h)$ to the $\pi^*$ orbit of CO results in the formation of Au–C bonds. The chemical adsorption of CO leads to a slight decrease of the HOMO-LUMO gap of $\text{Au}_{32}(I_h)$ to 1.45 eV for the ground-state structure [(I) in Fig. 2(a)] and 1.26 eV for the first isomer [(II) in Fig. 2(a)]. Comparison of the geometric and electronic properties of the two most stable structures of $\text{Au}_{32}(I_h)$—CO with those of cluster $\text{Au}_{32}(I_h)$ shows that the influence of CO adsorption on $\text{Au}_{32}(I_h)$ is not noticeable.

As for the third stable structure of $\text{Au}_{32}(I_h)$—CO [(III) in Fig. 2(a)], CO stays on the outer surface of the $\text{Au}_{32}(I_h)$ cage with CO binding energy of 0.12 eV, while for the fourth stable structure of $\text{Au}_{32}(I_h)$—CO [(IV) in Fig. 2(a)], CO stays at the inner center of the $\text{Au}_{32}(I_h)$ cage, with a much less CO binding energy of 0.01 eV. This means that in these two cases, CO does not strongly interact with $\text{Au}_{32}(I_h)$ cages. In fact, CO molecule keeps its free molecule state, with a bond length of 1.14 Å, while the $\text{Au}_{32}(I_h)$ cages also keep their original structures unchanged. The HOMO charge densities of these two structures are shown in Fig. 3, which confirm the argument mentioned above: for each case the HOMO keeps the same distribution as a free $\text{Au}_{32}(I_h)$ cluster, independent of the CO adsorption. Therefore, in these two structures, neither charge transfer nor bond formation could occur between $\text{Au}_{32}(I_h)$ and CO. Meanwhile, the wide HOMO-LUMO gap of the $\text{Au}_{32}(I_h)$ cage is also not obviously affected by CO adsorption, it is 1.53 and 1.56 eV for the third and the fourth stable structures, respectively. In comparison, the HOMO-LUMO gap of a free cluster $\text{Au}_{32}(I_h)$ is 1.56 eV. Briefly CO adsorption has no noticeable effect on the geometric and electronic structures of the free $\text{Au}_{32}(I_h)$ cage. Therefore, it can be concluded that CO can freely stay either on the outer surface or at the inner center of $\text{Au}_{32}(I_h)$ cages. This behavior of $\text{Au}_{32}(I_h)$ cage is different from that of $\text{C}_{60}$ cage which destabilizes the CO staying at its center.54

All the above four stable structures of $\text{Au}_{32}(I_h)$—CO are formed exothermically. However, the CO binding energy of the fifth structure of $\text{Au}_{32}(I_b)$—CO complex [(V) in Fig. 2(a)] is $-0.08$ eV, which means its formation is endothermic. In this structure, CO stays on the bridge site between two six-coordinated Au atoms. Two Au–C bonds formed with slightly different bond lengths, 2.19 and 2.22 Å, which are longer than the Au–C bonds in the two most stable structures. The adsorption of CO makes $\text{Au}_{32}(I_b)$ cage broken; the bond length between the two six-coordinated Au atoms increases to $3.16$, $0.3$ Å longer than the original bond length, while the bond length of CO increases to $1.17$, showing that more than one electron transfer from $\text{Au}_{32}(I_b)$ to the antibonding $\pi^*$ orbit of CO. The HOMO available charge density of this structure shown in Fig. 3 (V) provides

\[
\begin{array}{c|c|c|c}
\text{System} & E_a & E_g & r(C-O) \\
\hline
\text{Au}_{32}(I_b) - \text{CO} & & & \\
I & 0.86 & 1.45 & 1.15 \\
II & 0.40 & 1.26 & 1.15 \\
III & 0.12 & 1.54 & 1.14 \\
IV & 0.01 & 1.56 & 1.14 \\
V & -0.08 & 0.47 & 1.17 \\
\hline
\text{Au}_{32}(C_1) - \text{CO} & & & \\
I & 1.10 & 0.29 & 1.15 \\
II & 1.08 & 0.46 & 1.15 \\
III & 1.03 & 0.85 & 1.19 \\
\end{array}
\]

*orbit of CO, i.e., CO could be chemically adsorbed on Au \(32\) cluster. The plots of the HOMO charge densities of these two most stable structures are shown in Fig. 3 [(I) and (II)]. It can be clearly seen that CO molecules gain electrons, while the Au atoms, on which CO are bound, lose electrons. The charge transfer from Au \(32\)(I) to the \(\pi^*\) orbit of CO results in the formation of Au–C bonds. The chemical adsorption of CO leads to a slight decrease of the HOMO-LUMO gap of Au \(32\)(I) to 1.45 eV for the ground-state structure [(I) in Fig. 2(a)] and 1.26 eV for the first isomer [(II) in Fig. 2(a)]. Comparison of the geometric and electronic properties of the two most stable structures of Au \(32\)(I)—CO with those of cluster Au \(32\)(I) shows that the influence of CO adsorption on Au \(32\)(I) is not noticeable.

As for the third stable structure of Au \(32\)(I)—CO [(III) in Fig. 2(a)], CO stays on the outer surface of the Au \(32\)(I) cage with CO binding energy of 0.12 eV, while for the fourth stable structure of Au \(32\)(I)—CO [(IV) in Fig. 2(a)], CO stays at the inner center of the Au \(32\)(I) cage, with a much less CO binding energy of 0.01 eV. This means that in these two cases, CO does not strongly interact with Au \(32\)(I) cages. In fact, CO molecule keeps its free molecule state, with a bond length of 1.14 Å, while the Au \(32\)(I) cages also keep their original structures unchanged. The HOMO charge densities of these two structures are shown in Fig. 3, which confirm the argument mentioned above: for each case the HOMO keeps the same distribution as a free Au \(32\)(I) cluster, independent of the CO adsorption. Therefore, in these two structures, neither charge transfer nor bond formation could occur between Au \(32\)(I) and CO. Meanwhile, the wide HOMO-LUMO gap of the Au \(32\)(I) cage is also not obviously affected by CO adsorption, it is 1.53 and 1.56 eV for the third and the fourth stable structures, respectively. In comparison, the HOMO-LUMO gap of a free cluster Au \(32\)(I) is 1.56 eV. Briefly CO adsorption has no noticeable effect on the geometric and electronic structures of the free Au \(32\)(I) cage. Therefore, it can be concluded that CO can freely stay either on the outer surface or at the inner center of Au \(32\)(I) cages. This behavior of Au \(32\)(I) cage is different from that of \(C_{60}\) cage which destabilizes the CO staying at its center.54

All the above four stable structures of Au \(32\)(I)—CO are formed exothermically. However, the CO binding energy of the fifth structure of Au \(32\)(I)–CO complex [(V) in Fig. 2(a)] is $-0.08$ eV, which means its formation is endothermic. In this structure, CO stays on the bridge site between two six-coordinated Au atoms. Two Au–C bonds formed with slightly different bond lengths, 2.19 and 2.22 Å, which are longer than the Au–C bonds in the two most stable structures. The adsorption of CO makes Au \(32\)(I) cage broken; the bond length between the two six-coordinated Au atoms increases to $3.16$, $0.3$ Å longer than the original bond length, while the bond length of CO increases to $1.17$, showing that more than one electron transfer from Au \(32\)(I) to the antibonding $\pi^*$ orbit of CO. The HOMO available charge density of this structure shown in Fig. 3 (V) provides

\[
\begin{array}{c|c|c|c}
\text{System} & E_a & E_g & r(C-O) \\
\hline
\text{Au}_{32}(I_b) - \text{CO} & & & \\
I & 0.86 & 1.45 & 1.15 \\
II & 0.40 & 1.26 & 1.15 \\
III & 0.12 & 1.54 & 1.14 \\
IV & 0.01 & 1.56 & 1.14 \\
V & -0.08 & 0.47 & 1.17 \\
\hline
\text{Au}_{32}(C_1) - \text{CO} & & & \\
I & 1.10 & 0.29 & 1.15 \\
II & 1.08 & 0.46 & 1.15 \\
III & 1.03 & 0.85 & 1.19 \\
\end{array}
\]
an evidence for this charge transfer. It can be seen that considerable part of the HOMO concentrates around CO and two Au atoms, on which CO is bound, showing that CO gains more electrons in this structure of Au$_{32}$($I_b$)–CO than its four counterparts. Accompanying with the geometric structure change of the Au$_{32}$($I_b$) cage, its electronic properties also change upon CO adsorption. For instance, the HOMO-LUMO gap of this structure is much narrower, only 0.47 eV.

The amorphous Au$_{32}$ cluster Au$_{32}$($C_1$) has a structure without any symmetry, resulting in many sites available to bind CO to form Au$_{32}$($C_1$)–CO. In fact, the present calculations give many stable structures of Au$_{32}$($C_1$)–CO. Only the three most stable structures are selected and shown in Fig. 2(b). It can be seen that the behavior of CO on Au$_{32}$($C_1$) is similar to that on Au$_{32}$($I_b$). CO is adsorbed on the on-top sites of Au$_{32}$($C_1$) cluster with C atom attached to Au atom. The ground-state structure (I) and the first isomer structure (II) of Au$_{32}$($C_1$)–CO complex are very similar to each other, and the total energy difference between them is only 0.01 eV. In these two structures, CO is bound to a single Au atom, but at different sites. The C–O bond length increases to 1.19 Å, a bond length of CO$^-$, while the Au–C bond length is 1.96 Å. Therefore, it is suggested that one electron might transfer from Au atom to the $\pi^*$ orbit of CO, indicating chemical adsorption of CO on Au$_{32}$($C_1$). However, in the third stable structure of Au$_{32}$($C_1$)–CO (III), CO is bound to the surface of Au$_{32}$($C_1$) in such a way that three Au–C bonds are formed simultaneously, and the C–O bond is stretched to 1.19 Å. This means that more than one electron transfer from Au atoms to the antibonding $\pi^*$ orbit of CO. Compared with the highest binding energy of CO in the Au$_{32}$($I_b$)–CO complex, 0.86 eV, the binding energy of CO in the Au$_{32}$($C_1$)–CO complex is even higher, i.e., 1.09, 1.08, and 1.03 eV, respectively, for the three most stable structures of Au$_{32}$($C_1$)–CO shown in Fig. 2(b), indicating that Au$_{32}$($I_b$) is more inert than Au$_{32}$($C_1$) with respect to the interaction with CO.

In summary, present calculation shows that CO can be chemically adsorbed on Au$_{32}$ cluster for both Au$_{32}$($I_b$) and Au$_{32}$($C_1$), but the CO adsorption on Au$_{32}$($C_1$) is stronger than that on Au$_{32}$($I_b$). Accompanying with the chemisorption of CO, electrons transfer from Au$_{32}$ cluster to the antibonding $\pi^*$ orbit of CO, resulting in the increase of C–O bond length and formation of Au–C bond. Au$_{32}$($I_b$) shows a higher chemical inertness than Au$_{32}$($C_1$). Although CO can be chemically adsorbed on Au$_{32}$($I_b$), the adsorption of CO does not bring out remarkable effects on Au$_{32}$($I_b$). In addition, the five-coordinated sites of Au$_{32}$($I_b$) are the active sites, more favorable for CO adsorption.

**B. Interaction between cluster Au$_{32}$ and H$_2$**

The interactions between cluster Au$_{32}$ and H$_2$ are also investigated in the present work. First, the possible structures of Au$_{32}$–H$_2$ complexes are explored. The structures are optimized, and the most stable ones are shown in Fig. 4 for Au$_{32}$($I_b$)–H$_2$ (a) and Au$_{32}$($C_1$)–H$_2$ (b). Their structural and electronic properties, i.e., the binding energy of H$_2$, HOMO-LUMO gap, and the bond lengths of H–H and Au–H, are listed in Table II. In addition, HOMO charge densities of Au$_{32}$($I_b$)–H$_2$ complexes are calculated and plotted in Fig. 5.

For Au$_{32}$($I_b$)–H$_2$, many structures are obtained from the present calculation, only the six most stable ones are shown in Fig. 4(a), according to the sequence of their stability. In the ground state structure of Au$_{32}$($I_b$)–H$_2$ (I), molecule H$_2$ is adsorbed on the top of the five-coordinated site, forming one

![Figure 4](image-url)

**Table II.** The calculated structural and electronic properties for the interaction of H$_2$ molecule with cluster Au$_{32}$($I_b$) and cluster Au$_{32}$($C_1$): binding energy of H$_2$ $E_b$ (eV), HOMO-LUMO gap $E_g$ (eV), H–H bond length $r$(H–H) (Å), and Au–H bond length $r$(Au–H) (Å).

<table>
<thead>
<tr>
<th>System</th>
<th>$E_b$</th>
<th>$E_g$</th>
<th>$r$(H–H)</th>
<th>$r$(Au–H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{32}$($I_b$)–H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.33</td>
<td>1.56</td>
<td>0.76</td>
<td>2.40</td>
</tr>
<tr>
<td>II</td>
<td>0.30</td>
<td>1.56</td>
<td>0.75</td>
<td>3.15</td>
</tr>
<tr>
<td>III</td>
<td>0.30</td>
<td>1.56</td>
<td>0.75</td>
<td>…</td>
</tr>
<tr>
<td>IV</td>
<td>0.10</td>
<td>1.33</td>
<td>0.75</td>
<td>…</td>
</tr>
<tr>
<td>V</td>
<td>−0.12</td>
<td>0.77</td>
<td>…</td>
<td>1.77 1.78 1.84 1.94 1.95</td>
</tr>
<tr>
<td>VI</td>
<td>−0.24</td>
<td>0.63</td>
<td>…</td>
<td>1.75 1.75 1.80 1.80</td>
</tr>
<tr>
<td>Au$_{32}$($C_1$)–H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.98</td>
<td>0.86</td>
<td>…</td>
<td>1.76 1.76 1.77 1.77</td>
</tr>
<tr>
<td>II</td>
<td>0.64</td>
<td>0.78</td>
<td>…</td>
<td>1.87 1.88 1.89 1.90 1.91 2.00</td>
</tr>
<tr>
<td>III</td>
<td>0.62</td>
<td>0.73</td>
<td>…</td>
<td>1.74 1.76 1.76 1.80</td>
</tr>
</tbody>
</table>
Unlike that of C_60 cage which destabilizes H_2 staying at its vicinity, the Au_{32} cage keeps almost unchanged, with the H–H bond length increasing to 0.76 Å, 0.01 Å longer than that of a free H_2, 0.75 Å. The interaction of H_2 with Au_{32}(I_h) is weak, with the binding energy of only 0.33 eV. The HOMO charge density shown in Fig. 5 confirms this weak adsorption. Although the HOMO of Au_{32}(I_h) cage is disturbed somehow by H_2 adsorption, it is far away from H_2, indicating no charge transfer from Au_{32}(I_h) to H_2 occurred, i.e., physical adsorption of H_2 on Au_{32}(I_h). Upon H_2 adsorption, the geometric and electronic structures of Au_{32}(I_h) cage experience only negligible changes; therefore Au_{32}(I_h) keeps its wide HOMO-LUMO gap unchanged, 1.56 eV. The present calculation shows that H_2 is only physically adsorbed on the five-coordinated sites of Au_{32}(I_h), it cannot be adsorbed on the six-coordinated sites at all. This is another evidence to reveal that the five-coordinated sites have higher chemical activity than the six-coordinated sites of Au_{32}(I_h).

H_2 stays on the outer surface of Au_{32}(I_h) cage in the second stable structure of Au_{32}(I_h)–H_2 (II), while it stays at the inner center of Au_{32}(I_h) cage in the third stable structure of Au_{32}(I_h)–H_2 (III). In these two cases, H_2 keeps its free molecule state with a H–H bond length of 0.75 Å, while Au_{32}(I_h) cages keep their structures unchanged, too. The HOMO densities of these two structures are shown as (II) and (III) in Fig. 5. It is clearly seen that addition of H_2 molecules does not disturb the HOMO distributions of Au_{32}(I_h), and no part of it exists around H_2. This confirms that upon addition of H_2, the wide HOMO-LUMO gaps in these two structures do not change either, but keep the value of 1.56 eV. The binding energy of H_2 in the two structures is calculated to be 0.30 eV, suggesting that H_2 can stay either on the outer surface or at the inner center of the Au_{32}(I_h) cage. Therefore, Au_{32}(I_h) cage can stably store H_2 inside, unlike that of C_{60} cage which destabilizes H_2 staying at its center.

Only weak interaction between Au_{32}(I_h) and H_2 exists in the fourth stable structure of Au_{32}(I_h)–H_2 (IV) with a low binding energy of H_2, 0.10 eV, where H_2 keeps its free molecule state. It is shown that adsorption of H_2 leads to part of the structure of Au_{32}(I_h) close to the adsorbed H_2 distorted. The structural distortion of Au_{32}(I_h) causes part of the HOMO close to the adsorption site of H_2 redistributed, while the other part of the HOMO keeps unchanged. However, no part of the HOMO concentrates around the adsorbed H_2. Upon adsorbing H_2 the HOMO-LUMO gap of Au_{32}(I_h) decreases to a slightly narrower value, 1.33 eV. Briefly, adsorption of H_2 does not bring out a remarkable influence to Au_{32}(I_h).

Besides the H_2 molecularly adsorbed structures, the structures of Au_{32}(I_h)–H_2, in which H_2 is dissociatively adsorbed, should also be taken into consideration. In the present calculation such kind of structures is also optimized. All the structures, in which the H_2 is dissociatively adsorbed, have higher total energy than those in which the H_2 is molecularly adsorbed, indicating that the latter is more stable. In this paper, only two most stable H_2 dissociatively adsorbed structures of Au_{32}(I_h)–H_2 are selected and shown in Fig. 4(a) as (V) and (VI). The binding energy of H_2 is positive in the case of H_2 molecularly adsorbed on Au_{32}(I_h), i.e., the molecular adsorption of H_2 is exothermic; while it is negative in the case of H_2 dissociatively adsorbed on Au_{32}(I_h), i.e., the dissociative adsorption of H_2 is endothermic. Since the dissociation of H_2 needs a fairly high energy, H_2 molecule would rather like not to be adsorbed than dissociatively adsorbed on Au_{32}(I_h). Therefore H_2 can only be molecularly adsorbed on Au_{32}(I_h), and Au_{32}(I_h) shows a high inertness with respect to the interaction with H_2. Previous studies reported that the hydrogenation occurred only at high temperature and under high pressure, though H_2 can be dissociated and adsorbed on small Au_n clusters. Similar to the case of small Au_n clusters, it is proposed that the hydrogenation of Au_{32}(I_h) is very difficult except under special conditions. When H_2 is dissociatively adsorbed on Au_{32}(I_h), each H atom would like to contact with two or three Au atoms, resulting in the Au_{32}(I_h) cage broken and the electronic structures of Au_{32}(I_h) changed. The HOMO charge densities of such kind of structures shown in Fig. 5 indicate that H atoms gain electrons from Au_{32}(I_h), inducing the redistribution of the HOMO of Au_{32}(I_h). In addition, upon dissociative adsorption of H_2 on Au_{32}(I_h), HOMO-LUMO gaps of the clusters decrease remarkably to 0.77 and 0.63 eV for structures (V) and (VI), respectively.

For the amorphous cluster Au_{32}(C_1), the interaction with H_2 leads to only two kinds of stable structures: one is H_2 dissociatively adsorbed on Au_{32}(C_1), and the other is molecular H_2 staying on the outer surface of Au_{32}(C_1) without chemically bonding with Au_{32}(C_1). The present calculations show that the former is more stable than the latter, opposite to the case of Au_{32}(I_h). Figure 4(b) shows the three most stable structures of Au_{32}(C_1)–H_2 obtained; in all these three structures, upon adsorption on Au_{32}(C_1) H_2 dissociates to two H atoms, each H atom tends to connect with two or three Au atoms. The binding energy of H_2 of Au_{32}(C_1)–H_2 is positive and much more than those of Au_{32}(I_h)–H_2, it is 0.98, 0.64, and 0.62 eV for the three most stable structures of Au_{32}(I_h)–H_2.
Au$_{32}(C_1)$–H$_2$, respectively, by comparison it is only 0.33 eV for the most stable Au$_{32}(I_6)$–H$_2$. This shows that during H$_2$ desorption on Au$_{32}(C_1)$ enough energy is released to overcome the high energy barrier of H$_2$ dissociation. Therefore molecular H$_2$ can be dissociatively chemisorbed on Au$_{32}(C_1)$. It illustrates that Au$_{32}(I_6)$ has higher chemical inertness than Au$_{32}(C_1)$ with respect to the interaction with H$_2$.

In summary, H$_2$ can only be physically adsorbed on the five-coordinated sites of Au$_{32}(I_6)$, while it can be dissociatively chemisorbed on Au$_{32}(C_1)$. Au$_{32}(I_6)$ has a higher chemical inertness than Au$_{32}(C_1)$ with respect to the interaction with H$_2$, and it almost keeps its original state unchanged in this interaction.

C. Interaction between cluster Au$_{32}$ and O$_2$

The interaction of Au$_{32}$ cluster with O$_2$ would be more complicated than the interaction of Au$_{32}$ clusters with CO and H$_2$ because of the many adsorption mechanisms involved for O$_2$. These mechanisms are accompanied by a different number of electrons transferred from Au clusters to the antibonding $\pi^*$ orbit of O$_2$, e.g., (a) physical adsorption corresponding to zero electron transfer; (b) molecular chemisorption to yield superoxide, O$_2^-$, corresponding to one electron transfer; (c) molecular chemisorption to yield peroxide, O$_2^2-$, corresponding to two electron transfer; and (d) dissociative chemisorption to yield two oxide adsorbates corresponding to four electron transfer. In addition, the properties of O$_2$ molecule are also more complicated because of its two kinds of spin states: ground state [spin-triplet, O$_2$(triplet)] and excited state [spin-singlet, O$_2$(singlet)]. Therefore, in order to study the interaction of Au$_{32}$ clusters with O$_2$ molecules, both spin polarized and nonpolarized calculations, for spin-triplet O$_2$(triplet) and spin-singlet O$_2$(singlet), respectively, should be carried out.

First, consider the spin polarized calculations. Figure 6 displays the most stable structures of Au$_{32}$–O$_2$(triplet) complexes obtained for Au$_{32}(I_6)$–O$_2$(triplet) (a) and Au$_{32}(C_1)$–O$_2$(triplet) (b). Their structural and electronic properties, i.e., the binding energy of O$_2$(triplet), HOMO-LUMO gap, magnetic moment, and the bond lengths of O–O and Au–O, are listed in Table III. In addition, the HOMO charge densities of Au$_{32}(I_6)$–O$_2$(triplet) complexes are plotted in Fig. 7.

Similar to Au$_{32}$–H$_2$ complexes, both molecular adsorption and dissociative adsorption of O$_2$ should be considered for Au$_{32}$–O$_2$ complexes. Therefore, a great number of possible structures of Au$_{32}$–O$_2$ complexes are obtained. Here only six most stable structures of Au$_{32}(I_6)$–O$_2$(triplet) and three most stable structures of Au$_{32}(C_1)$–O$_2$(triplet) are selected and shown in Fig. 6.

In the ground state structure of Au$_{32}(I_6)$–O$_2$(triplet) (I), upon adsorption on Au$_{32}(I_6)$ molecular O$_2$ is dissociated symmetrically into two O atoms, resulting in the Au$_{32}(I_6)$ cage broken. The dissociative chemisorption of O$_2$ not only breaks the geometric structure of the Au$_{32}(I_6)$ cage but also changes its electronic property. The HOMO charge density [see (I) in Fig. 7] shows that the HOMO mostly concentrates around the O atoms and those Au atoms nearby, indicating the electron transfer from Au$_{32}(I_6)$ to the antibonding $\pi^*$ orbit of O$_2$, leading to the O–O bond broken and the Au–O bond formed. Due to the interaction of Au$_{32}(I_6)$ with O$_2$, its HOMO-LUMO gap remarkably decreases to 0.34 eV. Compared to other structures of Au$_{32}(I_6)$–O$_2$(triplet), this ground state structure of O$_2$ dissociative chemisorption is energetically favorable.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_b$ (eV)</th>
<th>$E_{t}$ (eV)</th>
<th>$\mu$ (B)</th>
<th>r(O–O) (Å)</th>
<th>r(Au–O) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_{32}(I_6)$–O$_2$(triplet)</td>
<td></td>
<td></td>
<td></td>
<td>2.12</td>
<td>2.14</td>
</tr>
<tr>
<td>Au$_{32}(C_1)$–O$_2$(triplet)</td>
<td></td>
<td></td>
<td></td>
<td>2.12</td>
<td>2.14</td>
</tr>
</tbody>
</table>

FIG. 6. Structures of Au$_{32}$–O$_2$(triplet): (a) Au$_{32}(I_6)$–O$_2$(triplet) and (b) Au$_{32}(C_1)$–O$_2$(triplet). The white balls represent O atoms. The bond lengths of O–O and Au–O are given in Å. What shown in brackets are the relative energies to the total energy of the ground state structures of Au$_{32}(I_6)$–O$_2$(triplet) and Au$_{32}(C_1)$–O$_2$(triplet), respectively, in eV.
The HOMO charge densities of these two structures are plotted to show that the five-coordinated sites are more energetically most favorable, which has the highest binding energy of $O_2^{\text{triplet}}$, 1.16 eV. However, as both the dissociation of $O_2^{\text{triplet}}$ and break of $Au_{32}(I_b)$ need to overcome high energy barriers, some special conditions must be available to promote this interaction. Similar to the present calculations, previous theoretical and experimental studies reported that dissociative adsorption of $O_2$ on $C_{60}$ cage, accompanied with the cage broken, only happened at the temperatures higher than 200 °C.\(^{55,56}\)

$O_2$ is molecularly adsorbed on the top of the five-coordinated site of $Au_{32}(I_b)$ in the second stable structure of $Au_{32}(I_b)$—$O_2^{\text{triplet}}$ (II) and on the top of the six-coordinated site of $Au_{32}(I_b)$ in the third stable structure (III), only one $Au$—$O$ bond formed in both structures. The energy difference of these two structures is 0.23 eV. This is a more evident evidence to show that the five-coordinated sites are more active than the six-coordinated sites of $Au_{32}(I_b)$. The present calculation shows that, for these two structures, adsorption of $O_2$ (triplet) does not make any noticeable change of the $Au_{32}(I_b)$ structure, the $O$—$O$ bond length only slightly increases to 1.34 and 1.33 Å, respectively, 0.03 and 0.02 Å longer than that of a free $O_2$, 1.31 Å. It is interesting to notice that the binding energies of $O_2$ (triplet) for these two structures are only 0.48 and 0.35 eV, respectively, much smaller than that for the ground state structure. This suggests that no electron is transferred from $Au_{32}(I_b)$ to $O_2$ in these two structures, i.e., $O_2$ (triplet) is only physically adsorbed on $Au_{32}(I_b)$. The HOMO charge densities of these two structures are plotted in Fig. 7 [(II) and (III)], supporting the above analysis. The figure shows only slight distortion of the HOMO distribution of $Au_{32}(I_b)$ cage, i.e., the HOMO around the $Au$ atom binding the $O_2$ molecules spreads a little towards the $O_2$ but without any charge transfer between $Au$ and $O$. Though $O_2$ (triplet) is only physically adsorbed in the second and third stable structures of $Au_{32}(I_b)$—$O_2$ (triplet), they are obviously different from the ground state structure of $Au_{32}(I_b)$—$O_2$ (triplet), their HOMO-LUMO gap also decreases remarkably. The gaps of the second and third stable structures of $Au_{32}(I_b)$—$O_2$ (triplet) are 0.47 and 0.62 eV, respectively.

In the fourth and the fifth stable structures of $Au_{32}(I_b)$—$O_2$ (triplet) [(IV) and (V) in Fig. 6], $O_2$ molecule stays on the outer surface and at the inner center of $Au_{32}(I_b)$ cage, respectively. $O_2$ molecules keep in free molecular state, and $Au_{32}(I_b)$ cages keep their original geometric structures unchanged, too. Examination of the HOMO charge densities [(IV) and (V) in Fig. 7], shows no change of the HOMO of both $Au_{32}(I_b)$ and $O_2$ occurred, indicating no charge transfer between them. The weak interaction of $Au_{32}(I_b)$ and $O_2$ corresponds to very small binding energies of $O_2$ for these two structures, only 0.30 and 0.24 eV, respectively. Even though, the adsorption of $O_2$ does influence $Au_{32}(I_b)$ somehow for both fourth and fifth stable clusters. For example, the wide HOMO-LUMO gap of $Au_{32}(I_b)$ decreases to 0.51 and 0.52 eV, respectively.

In the sixth stable structure of $Au_{32}(I_b)$—$O_2$ (triplet) complex, though $O_2$ molecule is dissociatively adsorbed on $Au_{32}(I_b)$, the $Au_{32}(I_b)$ cage is only slightly distorted. This is different from the ground state structure of $Au_{32}(I_b)$—$O_2$ (triplet), in which the $Au_{32}(I_b)$ cage is broken. In this structure, $O$ atoms are located at the bridge sites between five-coordinated $Au$ atom and six-coordinated $Au$ atom. Dissociative adsorption of $O_2$ should be accompanied with charge transfer, which is proved by the HOMO charge density shown in Fig. 7 (VI). It can be seen that the HOMO mostly concentrates around $O$ atoms and those $Au$ atoms nearby. Therefore $O_2$ gains electrons from $Au_{32}(I_b)$ and the electrons occupy the $\pi^*$ orbit of $O_2$, which makes $O_2$ molecule dissociatively chemisorbed on $Au_{32}(I_b)$. Although $O_2$ molecule is dissociated and chemisorbed on $Au_{32}(I_b)$ in both ground state structure and sixth stable structure, the binding energies of $O_2$ (triplet) are very different, which are 1.16 and 0.24 eV, respectively. Energy difference comes from the structural difference: $O_2$ dissociation and chemisorption make $Au_{32}(I_b)$ cage of the ground state structure broken but $Au_{32}(I_b)$ cage of the sixth stable structure only slightly distorted. This shows that $O_2$ dissociative adsorption on $Au_{32}(I_b)$ should favor the structural break of $Au_{32}(I_b)$.

Although the molecular chemisorption of $O_2$ can also be found in some isomers of $Au_{32}(I_b)$—$O_2$ (triplet) and $O_2$ appears in $O_2^-$ or $O_2^{2-}$ state, their binding energy of $O_2$ (triplet) is negative and those isomers are unstable. Therefore for spin-triplet $O_2^-$, superoxide or peroxide cannot be formed through the interaction with $Au_{32}(I_b)$.

For amorphous $Au_{32}(C_1)$—$O_2$ (triplet) complexes, both $O_2$ dissociatively chemisorbed and molecularly chemisorbed structures are found. Figure 6(b) shows three most stable ones of them. Similar to $Au_{32}(I_b)$—$O_2$ (triplet), $O_2$ is dissociatively adsorbed in the ground state structure of $Au_{32}(C_1)$—$O_2$ (triplet) [(I) of Fig. 6(b)] and gets four electrons from $Au_{32}(C_1)$. However, in the second and third stable structures [(II) and (III) of Fig. 6(b)], $O_2$ molecules are molecularly chemisorbed on different sites and the O—O bond lengths increase to 1.41 and 1.53 Å, respectively. The value of 1.41 Å is close to the bond length of $O_2^-$, and the value of

![Diagram showing the highest occupied states (HOMO) of $Au_{32}(I_b)$—$O_2$ (triplet) complexes. The plots show equal density surface of 0.04 electrons/Å².](image-url)
1.53 Å is close to the bond length of $O_2^–$. Therefore $O_2$ forms superoxide state and gets one electron from Au$_{32}$($C_1$) in the second stable structure, while $O_2$ forms peroxide state and obtains two electrons from Au$_{32}$($C_1$) in the third stable structure. The binding energy of $O_2$(triplet) in Au$_{32}$($C_1$)–$O_2$(triplet) is much higher than in Au$_{32}$($I_b$)–$O_2$(triplet). For example, the binding energy of $O_2$(triplet) for the ground state structure of Au$_{32}$($C_1$)–$O_2$(triplet) is 2.06 eV, 0.90 eV higher than that for the ground state structure of Au$_{32}$($I_b$)–$O_2$(triplet). Meanwhile, $O_2$ can be molecularly chemisorbed on Au$_{32}$($C_1$), but can only be physically adsorbed on Au$_{32}$($I_b$). Therefore Au$_{32}$($I_b$) is more inert than with respect to the interaction with $O_2$(triplet).

It can be seen from the spin polarized calculations that the corresponding ground state structures are that, in which $O_2$ is dissociatively chemisorbed for both Au$_{32}$($I_b$)–$O_2$(triplet) and Au$_{32}$($C_1$)–$O_2$(triplet). Although the $O_2$ dissociative chemisorption is energetically favorable in Au$_{32}$($I_b$)–$O_2$(triplet), it is suggested that the formation of this structure should require some special condition, since both the dissociation of $O_2$ and break of Au$_{32}$($I_b$) need to overcome high barriers. Except the dissociative chemisorption of $O_2$, no stable molecular chemisorption of $O_2$ is found in the Au$_{32}$($I_b$)–$O_2$(triplet), and $O_2$ is only physically adsorbed on Au$_{32}$($I_b$) or freely stays outside or inside the Au$_{32}$($I_b$). However, for Au$_{32}$($C_1$)–$O_2$(triplet), in addition to the dissociative chemisorption of $O_2$, the molecular chemisorption of $O_2$ is also favorable, and both superoxide and peroxide can be found. Both dissociative chemisorption and molecular chemisorption of $O_2$ are accompanied with the charge transfer from cluster Au$_{32}$ to $O_2$, resulting in the transition of $O_2$ from spin triplet to spin singlet. Compared to Au$_{32}$($C_1$), Au$_{32}$($I_b$) is more chemically inert with respect to the interaction with spin-triplet $O_2$. Besides, the interaction with spin-triplet $O_2$ leads to the HOMO-LUMO gap of Au$_{32}$($I_b$) decreased.

Next, let us discuss the spin nonpolarized calculations. Figure 8 displays the most stable structures of Au$_{32}$($I_b$)–$O_2$(singlet) (a) and Au$_{32}$($C_1$)–$O_2$(singlet) (b). Their structural and electronic properties, i.e., the binding energy of $O_2$(singlet), HOMO-LUMO gap, and the bond lengths of $O$–$O$ and Au–$O$, are listed in Table IV. In addition, HOMO charge densities of Au$_{32}$($I_b$)–$O_2$(singlet) complexes are plotted in Fig. 9.

The six most stable structures of Au$_{32}$($I_b$)–$O_2$(singlet) are shown in Fig. 8(a). The results of the spin nonpolarized calculations show that in all the five most stable structures of Au$_{32}$($I_b$)–$O_2$(singlet) O$_2$ is dissociatively chemisorbed, except the sixth one ([VI] in Fig. 8(a)]. The ground state structure of Au$_{32}$($I_b$)–$O_2$(singlet) (I) is almost as the same as the ground state structure of Au$_{32}$($I_b$)–$O_2$(triplet). The binding energies of O$_2$(singlet) and O$_2$(triplet) are 2.06 and 1.16 eV, respectively; the difference between them, 0.9 eV, is equal to the difference between the total energy of spin-singlet O$_2$ and that of spin-triplet O$_2$. Because the magnetic moment of this structure is 0$\mu_B$ and the dissociation of O$_2$ induces the transition of O$_2$ from spin triplet to spin singlet, the spin polarized calculations and spin nonpolarized calculations lead to the same results. In the second stable structure of Au$_{32}$($I_b$)–$O_2$(singlet) ([II] in Fig. 8(a)], O$_2$ is dissociated and chemisorbed on the outer surface of Au$_{32}$($I_b$), accompanying with the Au$_{32}$($I_b$) cage broken, too. In the third, fourth, and fifth stable structures ([III], [IV], and [V] in Fig. 8(a)], although O$_2$ molecules are dissociated, the Au$_{32}$($I_b$) cages keep unbroken but slightly distorted. It is found that the binding energies of O$_2$(singlet) for the two most stable structures of

<table>
<thead>
<tr>
<th>System</th>
<th>$E_b$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$E_{O–O}$ (eV)</th>
<th>$E_{Au–O}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.20</td>
<td>0.35</td>
<td>2.02 2.02 2.20 2.14 2.14</td>
<td>2.12 2.13 2.15 2.17 2.20</td>
</tr>
<tr>
<td>II</td>
<td>1.97</td>
<td>0.42</td>
<td>2.01 2.03 2.07 2.12 2.25 2.35</td>
<td>2.15 2.16 2.17 2.18 2.20</td>
</tr>
<tr>
<td>III</td>
<td>1.49</td>
<td>0.37</td>
<td>2.07 2.10 2.15 2.17 2.19 2.20</td>
<td>2.17 2.18 2.19 2.20 2.21</td>
</tr>
<tr>
<td>IV</td>
<td>1.45</td>
<td>0.41</td>
<td>2.03 2.03 2.14 2.14 2.16 2.26</td>
<td>2.18 2.19 2.20 2.21 2.22</td>
</tr>
<tr>
<td>V</td>
<td>1.28</td>
<td>0.45</td>
<td>2.03 2.03 2.03 2.04 2.05 2.06</td>
<td>2.10 2.11 2.12 2.13 2.14</td>
</tr>
<tr>
<td>VI</td>
<td>1.12</td>
<td>0.14</td>
<td>1.42</td>
<td>2.10 2.11 2.12 2.13 2.14</td>
</tr>
</tbody>
</table>

Au$_{32}$($I_b$)–O$_2$(singlet)
**As to the amorphous clusters, three most stable structures of Au$_{32}(I_b)$–O$_2$(singlet) are shown in Fig. 8(b). The ground state structure of Au$_{32}(C_1)$–O$_2$(singlet) [(I) in Fig. 8(b)] is almost as the same as the ground state structure of Au$_{32}(C_1)$–O$_2$(triplet) [(II) in Fig. 6(b)], in which O$_2$ is dissociatively chemisorbed on Au$_{32}(C_1)$. This is because from the present spin nonpolarized calculations, the interaction with O$_2$ causes the energy gap of Au$_{32}(I_b)$ narrowed.

Au$_{32}(I_b)$–O$_2$ (singlet) [(I) and (II)] are much higher than those for the other structures [(III), (IV), and (V)]. The reason is that the break of Au$_{32}(I_b)$ cage would make the dissociative adsorption of O$_2$ more stable. Moreover, the HOMO charge density (Fig. 9) show that for all the first five structures considered the HOMO is mostly distributed around O atoms and those Au atoms binding the O atoms, corresponding to that O$_2$ is dissociatively adsorbed on Au$_{32}(I_b)$, no matter whether the cage is broken or not. This means that the dissociative adsorption of O$_2$ is accompanied with the charge transfer from Au$_{32}(I_b)$ to O$_2$. In the sixth stable structure of Au$_{32}(I_b)$–O$_2$(singlet) [(VI) in Fig. 8(a)], O$_2$ is molecularly chemisorbed on Au$_{32}(I_b)$ and bound on the bridge site between five-coordinated Au atom and six-coordinated Au atom with O–O bond length increased to 1.42 Å, which is close to the value of O$_2$. This suggests that electrons transfer from Au$_{32}(I_b)$ to O$_2$, leading to the formation of superoxide. The HOMO charge density supports this analysis. The HOMO distribution shown in (VI) of Fig. 9 shows that a considerable part concentrates around O$_2$ and those Au atoms nearby. For these six structures of Au$_{32}(I_b)$–O$_2$(singlet), HOMO-LUMO gaps are all narrow, i.e., the spin nonpolarized calculations also indicate that the interaction with O$_2$ causes the energy gap of Au$_{32}(I_b)$ narrowed.

As to the amorphous clusters, three most stable structures of Au$_{32}(C_1)$–O$_2$(singlet) are shown in Fig. 8(b). The ground state structure of Au$_{32}(C_1)$–O$_2$(singlet) [(I) in Fig. 8(b)] is almost as the same as the ground state structure of Au$_{32}(C_1)$–O$_2$(triplet) [(II) in Fig. 6(b)], in which O$_2$ is dissociatively chemisorbed on Au$_{32}(C_1)$. This is because from the spin nonpolarized calculation, the magnetic moment of this structure is 0, i.e., O$_2$ is in spin singlet in this structure. The second stable structure of Au$_{32}(C_1)$–O$_2$(singlet) [(III) in Fig. 8(b)] is almost as the same as the third stable structure of Au$_{32}(C_1)$–O$_2$(triplet) [(III) in Fig. 6(b)], while the third stable structure of Au$_{32}(C_1)$–O$_2$(singlet) [(III) in Fig. 8(b)] is almost as the same as the second stable structure of Au$_{32}(C_1)$–O$_2$(triplet) [(II) in Fig. 6(b)]. This means that from the spin nonpolarized calculation, the binding energy of O$_2$(singlet) of Au$_{32}(C_1)$–O$_2$(singlet) is higher than that of Au$_{32}(I_b)$–O$_2$(singlet), indicating the high chemical inertness of Au$_{32}(I_b)$.

Briefly, the present spin nonpolarized calculation show that the peroxide is most favorable for both Au$_{32}(I_b)$ and Au$_{32}(C_1)$. For Au$_{32}(I_b)$–O$_2$(singlet), of all the six most stable structures five are that, in each of them O$_2$ is dissociatively chemisorbed, except one is that, in which O$_2$ is molecularly chemisorbed. For Au$_{32}(C_1)$–O$_2$(singlet), the structure in which O$_2$ is dissociatively adsorbed is most stable, the peroxide is the second stable structure. In conclusion, first-principles calculations have been carried out on the interactions of Au$_{32}(I_b)$ and Au$_{32}(C_1)$ with CO, H$_2$, and O$_2$.

CO can be chemically adsorbed on Au$_{32}(I_b)$ and Au$_{32}(C_1)$, but it is bound more strongly on Au$_{32}(C_1)$ than on Au$_{32}(I_b)$. Accompanied with the chemisorption of CO, electrons transfer from cluster Au$_{32}$ to the antibonding $\pi^*$ orbit of CO, resulting in the C–O bond length increased and the
Au–C bond formed. The chemisorption of CO exerts only a slight influence on \( \text{Au}_{32}(I_6) \) for both geometric and electronic properties. The five-coordinated sites of \( \text{Au}_{32}(I_6) \) are the active sites, and CO favors more to be adsorbed on these sites. \( \text{H}_2 \) can only be physically adsorbed on the five-coordinated sites of \( \text{Au}_{32}(I_6) \), while it can be dissociatively chemisorbed on \( \text{Au}_{32}(C_1) \). The physical adsorption of \( \text{H}_2 \) almost does not affect the structural and electronic properties of \( \text{Au}_{32}(I_6) \). From both the present spin polarized and spin nonpolarized calculations, the ground state structures of both \( \text{Au}_{32}(I_6)–\text{O}_2 \) and \( \text{Au}_{32}(C_1)–\text{O}_2 \) are \( \text{O}_2 \) dissociatively chemisorbed structures and they are very similar to each other, because the chemisorption of \( \text{O}_2 \) is accompanied with the charge transfer from \( \text{Au} \) cluster to \( \text{O}_2 \) and the transition of \( \text{O}_2 \) from spin triplet to spin singlet. For \( \text{Au}_{32}(I_6) \), because the break of \( \text{Au}_{32}(I_6) \) cage and the chemisorption of \( \text{O}_2 \) both need to overcome high barriers, the formation of the \( \text{O}_2 \) dissociatively chemisorbed structure of \( \text{Au}_{32}(I_6)–\text{O}_2 \) (triplet) must be under some special conditions. Otherwise, spin-triplet \( \text{O}_2 \) only prefers to be physically adsorbed on \( \text{Au}_{32}(I_6) \); therefore the spin polarized calculations show no stable \( \text{O}_2 \) molecularly chemisorbed structure of \( \text{Au}_{32}(I_6)–\text{O}_2 \) (triplet) existing. For \( \text{Au}_{32}(C_1) \), both spin polarized calculations and spin nonpolarized calculations show that dissociative \( \text{O}_2 \) chemisorption on \( \text{Au}_{32}(C_1) \) is more favorable than molecular chemisorption. In summary, for all three small molecules considered, i.e., CO, \( \text{H}_2 \), and \( \text{O}_2 \), their interaction with \( \text{Au}_{32}(C_1) \) is stronger than that with \( \text{Au}_{32}(I_6) \). Therefore, \( \text{Au}_{32}(I_6) \) exhibits higher chemical inertness with respect to the interaction with small molecules, CO, \( \text{H}_2 \), and \( \text{O}_2 \).

ACKNOWLEDGMENTS

The authors would like to thank Professor P. Jiang for a critical reading of the manuscript. This work is supported by the National Science Foundation of China and the National Basic Research Program. One of the authors (X.G.G.) is also supported by the Shanghai Science and Technology Foundation. The computation is performed in the Supercomputer Center of Shanghai, the Supercomputer Center of Fudan University and CCS, HFCAS.