Probing the Interactions of O₂ with Small Gold Cluster AuₙQ (n = 2−10, Q = 0, −1): A Neutral Chemisorbed Complex Au₅O₂ Cluster Predicted

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Supporting Information

ABSTRACT: Enormous progress has been made in catalytic oxidation reactions involving nanosized gold particles. However, the reaction mechanism of O₂ with neutral gold clusters remains complicated. Here, we have performed an unbiased structure search for AuₙQ and Au₅O₂⁺ (n = 2−10, Q = 0, −1) clusters by means of CALYPSO structure searching method. Subsequently, the lowest-energy candidate structures were fully optimized at the B3PW91/Au/LANLDZ/O−6−311+G(d) level of theory to determine the global minimum structures. Based on the ground-state structures of Auₙ− and Au₅O₂⁺ (n = 2−10), we have simulated the photoelectron spectra (PES) using time-dependent density functional theory. The good agreement between simulated PES and the corresponding experimental data suggest that the current ground-state structures are the true minima. The locally maximized value of the adsorption energy in Au₅O₂, where the unpaired electron of Au₅ can transfer to O₂, makes it the most promising candidate of the chemisorbed complex. A comprehensive analysis of molecular orbitals and chemical bonding of the Au₅O₂ cluster reveals that O₂ can be chemisorbed onto the neutral Au₅ cluster.

1. INTRODUCTION

As the noblest of all metals, gold has fascinated humankind since ancient times due to its enchanting color and chemical stability.¹−³ In the extended state, gold does not, for instance, form any stable oxides at ambient conditions, though some have been proposed for low temperatures or high pressures.⁴,⁵ Added interest in gold has arisen because, different from the properties of bulk counterparts, gold at the nanometer scale possesses a rich array of new properties. Haruta et al. discovered that Au can express extraordinary catalytic activity when it is dispersed on certain catalyst supports.⁶ Subsequently, nanosized gold particles have been found to exhibit unusually strong catalytic capabilities in a wide variety of chemical reactions such as CO oxidation,⁷−⁹ propylene epoxidation,¹⁰ water−gas shift,¹¹−¹³ and hydrogenation of unsaturated hydrocarbons.¹⁴ Among these, CO oxidation catalyzed by nanosized gold particles has attracted considerable attention.

In the past decade, many experimental and theoretical studies of CO oxidation have been devoted to revealing the essence of the catalytic activity of Au nanoparticles.¹⁶−₂₄ Haruta et al. suggest that CO reacts with molecularly adsorbed oxygen on gold catalysts to form carbonate species (CO₃²⁻), which are then converted to CO₂.²⁵ To reveal the catalytic mechanism of gold, it is therefore important to fundamentally understand the interaction of gold clusters with O₂. A systematic study of the interaction between Auₙ− and O₂ supported by photoelectron spectroscopy calculations revealed that O₂ was chemisorbed to Au₅− clusters where n is an even number.²⁶ Subsequently, the group of Wang determined there are two modes of O₂ activation by small even-sized Au₅− clusters: superoxo and peroxo chemisorption, with O₂ binding to Au₅− via one or both oxygen atoms.²⁷ Lee et al.²⁸ theoretically studied the geometrical and electronic characteristics of Au₅O₂− clusters (n = 2−7). Most of the theoretical studies have shown an even−odd alternation of several observables for anionic clusters, which is consistent with experimental reactivity observations. However, despite the enormous progress that has been made, the picture for the neutral clusters is still not entirely clear because of the shortage of direct experimental probes for the uncharged species. Then, theoretical studies are of paramount importance.

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for these systems. Landman et al. hold that neutral Au clusters are insufficient to activate molecular oxygen.\textsuperscript{26} Jena and co-workers argued that, because of the high electronegativity of Au, electron transfer should take place from O\textsubscript{2} to Au\textsubscript{n} and Au\textsubscript{14} in the neutral Au\textsubscript{O} and Au\textsubscript{O} clusters.\textsuperscript{27} Ab initio calculations support that neutral Au clusters can interact with O\textsubscript{2}.\textsuperscript{28,29} Vibrational spectroscopy has been used to study O\textsubscript{2} adsorption on small neutral Au\textsubscript{n} clusters, and it was concluded that adsorbed oxygen is activated due to charge transfer from the gold cluster.\textsuperscript{30} Very recently, structural transformations of Au\textsubscript{n} clusters upon O\textsubscript{2} adsorption have been surveyed computationally, focusing on isomerization and transition pathways.\textsuperscript{31} Clearly, more accurate theoretical calculations are needed to understand whether and how neutral gold clusters interact with oxygen molecules.

In order to explore the mechanism of oxygen adsorbed on neutral Au\textsubscript{n} clusters, we have carried out a systematic study on small gold clusters. Here, we obtained the ground-state structures of Au\textsubscript{n} as well as Au\textsubscript{O} \textsuperscript{Q} (Q = 0, −1) clusters in the size range of n = 2−10 by employing the crystal structure analysis by particle swarm optimization (CALYPSO) method and density functional theory (DFT). In the first part of this work, we studied the ground state geometric structures of Au\textsubscript{Q} and Au\textsubscript{O} \textsuperscript{Q} (n = 2−10, Q = 0, −1) clusters. For the anionic clusters, we simulated the PES of Au\textsubscript{Q}− and Au\textsubscript{O} \textsuperscript{Q}− (n = 2−10) and compared them with experimental results. Subsequently, the inherent stability and the adsorption energy were calculated. On the basis of the calculated results, there is a promising candidate among the neutral Au\textsubscript{O} clusters that can chemisorb oxygen particularly strongly. In order to gain further insight into the reaction mechanisms of the neutral species, detailed chemical bonding analysis is presented. Finally, we also explored the adsorption mechanism behind the electronic properties of neutral and anionic Au\textsubscript{O} clusters and provide relevant information for unraveling the mechanistic details of CO catalysis by oxygenated gold clusters.

2. COMPUTATIONAL DETAILS

To identify the ground-state structures of Au\textsubscript{Q} and Au\textsubscript{O} \textsuperscript{Q} (n = 2−10, Q = 0, −1) clusters, unbiased structure searches were carried out using the CALYPSO\textsuperscript{32−36} software, where a high search efficiency is achieved by implementing the PSO (particle swarm optimization) algorithm. The validity of this method in structure prediction has been certified by the successful identification of the structures in various systems, ranging from clusters to extended crystal structure.\textsuperscript{37−41} To predict low-lying isomers for each cluster size, we followed 50 generations of structures, where each generation contains 30 structures. Subsequently, the top 50 isomers are collected as candidates for the lowest energy structure and reoptimized using the Gaussian 09 package\textsuperscript{42} if within 5 eV among the initial candidate structures. Spin unrestricted density functional theory calculations with the B3PW91 functional\textsuperscript{43,44} are performed to reoptimize the geometries. The LANL2DZ\textsuperscript{45} basis set was chosen as suitable for the gold atom and 6-311+G (d)\textsuperscript{46} for the oxygen atom. Subsequently, frequency calculations were performed to verify the obtained structures were true minima on the potential energy surface. Different spin multiplicities, up to sextet and quintet for the neutral and anionic clusters, were considered in the geometry optimization process. We simulated the photoelectron spectra of the anionic Au\textsubscript{n} and Au\textsubscript{O} clusters using time-dependent density functional theory (TD-DFT).\textsuperscript{47} The natural charges of oxygen molecule (NC(O\textsubscript{2})) were calculated by natural bond orbital (NBO). Adaptive natural density partitioning (AdNDP)\textsuperscript{48} bonding analyses were performed using the Multiwfn 3.3.8\textsuperscript{49} program package, to gain further insight into the nature of the bonding.

3. RESULTS AND DISCUSSIONS

3.1. Geometric Structure. The ground-state structures of Au\textsubscript{Q} and Au\textsubscript{O} \textsuperscript{Q} (n = 2−10, Q = 0, −1) clusters are exhibited in Figures 1 and 2, respectively, together with their low-lying isomers. Each isomer of the neutral cluster is denoted by the label n\textsubscript{x}, where n stands for the number of gold atoms and x represents alphabetically the xth low-lying isomer of the cluster (e.g., “a” for the lowest energy isomer). Similarly, the anionic species are denoted by n\textsubscript{x}−.

As seen in Figure 1, pure gold clusters, whether neutral or anionic, all favor planar structures up to at least n = 10 in our work. This is due to strong hybridization of the atomic 5d and 6s orbitals of Au because of relativistic effects.\textsuperscript{50,51} The transition from 2D to 3D structures in gold clusters is debated in the computational literature, but a consensus seems to put the onset of 3D cluster structures around n = 11.\textsuperscript{52−61} The structures we find are in agreement with previous studies.\textsuperscript{62−64} The corresponding electronic states, symmetries, average binding energies E\textsubscript{b}, and HOMO−LUMO energy gaps E\textsubscript{gap are summarized in Table S1 (see the Supporting Information). The ground-state structures of Au\textsubscript{n} with n ≤ 8 have the same configurations for neutral and anionic clusters, except for Au\textsubscript{3} and Au\textsubscript{4}, where the structures show some deformations due to the acquisition of an electron. Likewise, the acquisition of an
electron changes the energetic order for Au[n/10] switching 9a to 9b− and 10a to 10c− and vice versa. Similarly, the second-most stable structures nb are the same as those of nb+ for n = 3, 4, 7, 8, and 10. Among the metastable structures, there are also some three-dimensional structures. As for the Au[n]O2− (n = 2−10, Q = 0, −1) clusters, in Figure 2, the ground-state structures are all quasi-planar geometries; that is, the Au atoms form a plane, and only the oxygen molecule potentially departs from the Au plane. We have also obtained some structures which contained two separate oxygen atoms and not an oxygen molecule; such structures are never the lowest-energy structure. This is not unexpected: the O−O bond is much stronger than the Au−O bond, so the oxygen molecule does not segregate and bind to multiple Au atoms. Note that only molecularly adsorbed oxygen on gold catalysts can react with CO to form carbonate species (CO2−), which are subsequently converted to CO2. From now on, we only focus on structures that contain oxygen molecules. It is apparent that an oxygen molecule makes mainly two kinds of bonds with Au clusters (an exception is Au4O2− where both oxygen atoms are bonded to the same Au atom). In the first kind of bonding arrangement, O2 forms a bent-triatomic unit with one Au atom (as in the 3a− structure); in the other, O2 binds to two Au atoms to form a cyclic structure (as in the 3a structure). This agrees with the conclusions reported by Mills et al. and the classification by Pal et al. The lowest-energy structures of Au[n]O2− clusters (n = 2, 4, 6) exhibit the former (superoxo) binding and n = 8 and 10 exhibit the latter (peroxo) binding motif. At the turnover point n = 8, the lowest-energy structure exhibits peroxo chemisorption, while the 8b− isomer exhibits superoxo chemisorption. This phenomenon is consistent with the transition discussed by Pal and co-workers. In the metastable structures 5c−, 6b−, and 7b−, the O2 bonds to Au clusters in the same cyclic way as seen in 3a. In the ground-state structure of the Au6O2− cluster, the parent Au4O2− is not the global minimum D3h isomer but the 10c− structure; this agrees with earlier findings that the low-lying isomers are reactive with O2 and the global minimum can only form a physisorbed Au10(O2)− van der Waals complex. For the neutral Au6O2 clusters, if n = 2, 4, 6, 8, 9, and 10, O2 forms a bent-triatomic unit with one Au atom across all relevant structures, except for 9c and 10c. For the global minimum structures of Au6O2 (n = 3, 5, 7) clusters, O2 binds to two Au atoms to form a cyclic structure. In particular, the ground-state structures 3a and 5a are of C2v symmetry.

3.2. Photoelectron Spectra. In order to verify the accuracy of all of the ground-state configurations obtained in this work, the PES of the global minima of anionic Au− as well as Au[n]O2− clusters have been simulated using the TD-DFT method. The theoretical vertical detachment energies (VDEs) were obtained as the energy differences between the neutrals and anions both at the geometries of the anionic species. At the same time, the corresponding binding energy of the first peak position of the simulated PES represents the value of the VDE. The simulated spectra of the ground-state structures of anionic Au[n−] clusters are displayed in Figure 3, along with available experimental spectra for comparison. Generally, the theoretical PESs of Au[n−] clusters are in agreement with the measurements. The simulated spectrum of Au7− shows three major peaks and fits well to the experimental result. For the Au8− cluster, there are three major peaks, and the third peak of the simulated spectrum corresponds to a weak shoulder of the experimental spectrum. As for the Au9− and Au10−, the positions of the simulated peaks are coincident with the experimental ones, disregarding splitting of the peaks. For n = 2, 5, 7, and 8,
there are more peaks in the experimental spectra, but the first
peaks are always in good agreement, which indicates that the
ground-state structures we obtained are the true minima, while
the experimental spectra might involve several isomers. As an
important evaluation criterion of our theoretical results, the
location of the first peak in the simulated PES is of particular
importance, which represents a transition from the ground state
of the anionic clusters to their neutral ground state ones. The
theoretical as well as experimental VDE values of Au\textsuperscript{−} and
Au\textsubscript{2}O\textsubscript{2}− clusters are collected in Table 1. The values for all Au\textsubscript{n}−
clusters agree very well with the experimental data, and all
differences are within 0.20 eV. These observations suggest that the
structures of Au\textsubscript{n}− clusters obtained here are the true minima structures.

Compared to the PES of the Au\textsubscript{n}− clusters, the PESs of
Au\textsubscript{2}O\textsubscript{2}− clusters contain substantially more peaks, as seen in
Figure 4. In the simulated PES of Au\textsubscript{2}O\textsubscript{2}−, there are six obvious
peaks, with the first peak located around 3.13 eV. This onset
and the increase in spectral strength around 5 eV agree very
well with the experimental data. In the experimental PES of
Au\textsubscript{3}O\textsubscript{2}−, there is a very small peak around 3.90 eV, close to the
first peak of pure Au\textsubscript{1}−, which suggests that this peak originates
from a physisorbed Au\textsubscript{1}(O\textsubscript{2}) \textsuperscript{−} species.\textsuperscript{22} In agreement with this,
the simulated PES of the Au\textsubscript{2}O\textsubscript{2}− cluster shows five major peaks with a first peak corresponding to a VDE of 3.90 eV, in
accordance with the physisorption picture. For Au\textsubscript{4}O\textsubscript{2}−,
ignoring the relative intensities of the peaks, the peak structure
and positions are similar to the experimental data. For n = 5
and 7, there are fewer features in the simulated spectra
compared to the experimental results. There is also a missing
feature between 3.50 and 4.00 eV in the PES of Au\textsubscript{4}O\textsubscript{2}−. For
Au\textsubscript{4}O\textsubscript{2}− and Au\textsubscript{10}O\textsubscript{2}−, the shapes and the positions of the first
peak coincide with the experimental data. Summarized in Table
1, we conclude that the theoretical VDE values of the Au\textsubscript{2}O\textsubscript{2}−
clusters agree well with the experimental values. Most
differences are less than 0.20 eV, with a maximum of 0.22 eV
for n = 3. As stated above for the anionic Au\textsubscript{n}− clusters, these
results confirm that the lowest-energy structures obtained are
true ground-state structures and provide further support to the
accuracy of our calculations.

3.3. Relative Stabilities. As an effective criterion of the
inherent stability of a cluster, the average binding energies (E\textsubscript{b})
of the Au\textsubscript{n}− clusters as well as the Au\textsubscript{2}O\textsubscript{2}− \textsuperscript{Q} (n = 2–10; Q = 0,
−1) clusters are defined as follows:

\[
E_b(Au_nO_2^{-}) = \frac{\sum_{i=1}^{n} E(Au) + E(O_2) - E(Au_nO_2^{-})}{n+2}
\]

(1)

\[
E_b(Au_{n-1}O_2^{-}) = \frac{\left(n-1\right) E(Au) + E(Au_n^{-}) + E(O_2) - E(Au_{n-1}O_2^{-})}{n+2}
\]

(2)

E is the total energy of the corresponding cluster or atom.
Larger values of E\textsubscript{b} represent stronger chemical stability. To facilitate comparison across the clusters, the binding energies
for the Au\textsubscript{2}O\textsubscript{2}− \textsuperscript{Q} (n = 2–10; Q = 0, −1) clusters are plotted in
Figure 5a, with the corresponding values summarized in Table

Table 1. Calculated Vertical Detachment Energy VDE (eV)
for Anionic Au\textsubscript{n} and Au\textsubscript{2}O\textsubscript{2} Clusters, together with the
Experimental Data for Comparison

<table>
<thead>
<tr>
<th>Cluster</th>
<th>VDE (eV)</th>
<th>Cluster</th>
<th>VDE (eV)</th>
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<td>Au\textsuperscript{−}</td>
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<td>Au\textsubscript{2}O\textsubscript{2}\textsuperscript{−}</td>
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<td>Au\textsubscript{−}</td>
<td>3.68</td>
<td>Au\textsubscript{3}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.88</td>
</tr>
<tr>
<td>Au\textsubscript{2}−</td>
<td>2.85</td>
<td>Au\textsubscript{4}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.70</td>
</tr>
<tr>
<td>Au\textsubscript{3}−</td>
<td>3.17</td>
<td>Au\textsubscript{5}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.09</td>
</tr>
<tr>
<td>Au\textsubscript{4}−</td>
<td>2.20</td>
<td>Au\textsubscript{6}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.13</td>
</tr>
<tr>
<td>Au\textsubscript{5}−</td>
<td>2.82</td>
<td>Au\textsubscript{7}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.91</td>
</tr>
<tr>
<td>Au\textsubscript{6}−</td>
<td>3.95</td>
<td>Au\textsubscript{8}O\textsubscript{2}\textsuperscript{−}</td>
<td>4.09</td>
</tr>
<tr>
<td>Au\textsubscript{7}−</td>
<td>4.09</td>
<td>Au\textsubscript{9}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.91</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cluster</th>
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<th>Cluster</th>
<th>VDE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au\textsubscript{8}−</td>
<td>3.38</td>
<td>Au\textsubscript{10}O\textsubscript{2}\textsuperscript{−}</td>
<td>3.91</td>
</tr>
</tbody>
</table>

References are as follows:
1. Reference 63.
2. Reference 22.
3. Reference 23.
4. Reference 65.
5. Reference 62.

Figure 4. Calculated photoelectron spectra of Au\textsubscript{2}O\textsubscript{2}− (n = 2–10)
clusters, along with the available experimental data ([n = 2–5 and 7],\textsuperscript{22}
[n = 6 and 8],\textsuperscript{22} and [n = 10]\textsuperscript{65}) for comparison. The blue curves show
the theoretical results, while the gray curves represent the experimental results.

Figure 5. Size dependence of (a) the averaged binding energies E\textsubscript{b} and
(b) second-order energy differences ΔE\textsubscript{ff}, (c) HOMO–LUMO energy
gaps E\textsubscript{gap}, and (d) absolute value of the adsorption energy E\textsubscript{ads} for the
lowest energy Au\textsubscript{2}O\textsubscript{2}− \textsuperscript{Q} (n = 2–10; Q = 0, −1) clusters.

2. From this figure, we can see that all neutral Au\textsubscript{2}O clusters
have lower binding energies than their anionic counterparts,
and E\textsubscript{b} of the Au\textsubscript{2}O\textsubscript{2}− \textsuperscript{Q} (n = 2–10; Q = 0, −1) clusters generally
increases with cluster size. As an obvious outlier from a mostly
linear trend, Au\textsubscript{2}O\textsubscript{2}− can be considered as a local optimum.
Clusters Au3O2 and Au5O2 are more stable than their neighbors. The trend for the anionic clusters shows the standard even oscillation behavior. For anionic Au

with remarkable chemical stability. We have calculated the

bonded van der Waals complexes. For neutral clusters, the

chemisorbed complexes are more stable than the weakly bonded van der Waals complexes. The molecularly

oscillation, a phenomenon corroborating that Au

For the anionic species, there is an obvious odd oscillation behavior, which again highlights the conclusion that small gold cluster anions with even-numbered atoms can molecularly chemisorb O2, whereas clusters with odd-numbered atoms are inert toward O2. The results of natural charges of O2 in anionic clusters are in line with this conclusion. From Table 3, we can see that the charges of O2 are always negative, and the absolute value of the charges are much larger for even n than for odd n, which shows the more significant charge transfer from the parent Au

cluster to the oxygen molecule. The anion species are better electron donors than the corresponding neutral species, because the electron affinities are always smaller than ionization potentials. Thus, the Au

clusters with even-number n have larger absolute values of adsorption energies. For neutral Au

clusters, the absolute value of adsorption energy of Au2O2 with n = 3, 5, and 7 is relatively larger than those of their adjacent neutral clusters. This is consistent with the conclusion that Au

clusters with an odd number of electrons hold the promise of chemisorbing an O2 molecule, for charges transferring from Au

to O2 is the dominant mechanism of the chemisorption process. Correspondingly, the natural charges of the oxygen molecule in Au

clusters with n = 3, 5, and 7 have the largest absolute values (with the exception of n = 4). The large charge transfer in the Au

cluster is probably due to its special geometry and oxygen binding motif, and since it does not

promising among these. It is worth noting that our results generally fit well with earlier conclusions that O2 binds more strongly to clusters with an odd number of electrons than with an even number.

3.4. Adsorption Analysis. Based on the optimized geometries, we have calculated the natural charges of the oxygen molecule and the adsorption energy of O2 on Au clusters, which is defined as the energy difference between the ad sorption system with the individual cluster and oxygen molecule:

\[ E_{ads}(Au_{n}O_{2}^{Q}) = E(Au_{n}O_{2}^{Q}) - E(Au_{n}^{Q}) - E(O_{2}), \]

where

\[ Q = 0, \ \pm 1 \]

is the adsorption energy of the corresponding cluster. The results of both E_{ads} and natural charges of the oxygen molecule are summarized in Table 3. By construction, the more negative the adsorption energy, the more stable the corresponding adsorption reactions. For better observation, we have plotted the absolute value of adsorption energy in Figure 5d for all Au

clusters. The adsorption energy of the Au

clusters reveals the even–odd oscillation behavior, which again highlights the conclusion that small gold cluster anions with even-numbered atoms can molecularly chemisorb O2, whereas clusters with odd-numbered atoms are inert toward O2. The results of natural charges of O2 in anionic clusters are in line with this conclusion. From Table 3, we can see that the charges of O2 are always negative, and the absolute value of the charges are much larger for even n than for odd n, which shows the more significant charge transfer from the parent Au

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Table 2. Calculated Electronic States, Symmetries, Averaged Binding Energies E_{bp} (eV), and HOMO–LUMO Energy Gaps E_{g} (eV) for the Ground-State Au

clusters (n = 2–10, Q = 0, –1) Clusters

<table>
<thead>
<tr>
<th>Au2O2</th>
<th>Au2O2^{−}</th>
</tr>
</thead>
<tbody>
<tr>
<td>n  sta. sym. E_{bp} E_{g}</td>
<td>sta. sym. E_{bp} E_{g}</td>
</tr>
<tr>
<td>2  'A' C_{2} 0.93 2.44</td>
<td>'A' C_{2} 1.12 3.31</td>
</tr>
<tr>
<td>3  'A' C_{2} 0.98 3.13</td>
<td>'A' C_{2} 1.23 3.57</td>
</tr>
<tr>
<td>4  'A' C_{2} 0.96 2.12</td>
<td>'A' C_{2} 1.34 2.60</td>
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<td>5  'A' C_{2} 1.30 3.10</td>
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<td>6  'A' C_{2} 1.23 1.53</td>
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</tr>
<tr>
<td>7  'A' C_{2} 1.41 2.65</td>
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<td>8  'A' C_{2} 1.51 2.49</td>
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<tr>
<td>10 'A' C_{2} 1.56 3.36</td>
<td>'A' C_{2} 1.66 1.38</td>
</tr>
</tbody>
</table>

A more sensitive quantity reflecting the relative stability of clusters, the second-order differences of the energy (\Delta^2 E) are calculated for all Au

clusters (Q = 0, –1) as

\[ \Delta^2 E(Au_{n}O_{2}) = E(Au_{n-1}O_{2}) + E(Au_{n+1}O_{2}) - 2E(Au_{n}O_{2}) \] (3)

\[ \Delta^2 E(Au_{n}O_{2}^{−}) = E(Au_{n-1}O_{2}^{−}) + E(Au_{n+1}O_{2}^{−}) - 2E(Au_{n}O_{2}^{−}) \] (4)

Figure 5b shows the size dependence of \Delta^2 E for the Au

clusters (n = 2–10; Q = 0, –1) clusters. For the neutral clusters, two distinct peaks are found at n = 3 and 5, indicating that the clusters Au3O2 and Au5O2 are more stable than their neighbors. For the anionic species, there is an obvious odd–even oscillation, a phenomenon corroborating that Au

clusters with even n are more stable than those with odd n.

The HOMO–LUMO energy gap (E_{g}) is a reflection of the energy cost for an electronic excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and thus serves as further support to the stability of a cluster. A large E_{g} often tends to correlate with remarkable chemical stability. We have calculated the E_{g} values for the neutral and anionic Au

clusters and summarize them in Table 2. Figure 5c gives the E_{g} values of Au

clusters as functions of cluster size. The

results of natural charges of O2 in anionic clusters are in line with earlier conclusions that O2 binds more strongly to clusters with an odd number of electrons than with an even number.

The adsorption energy, the more stable the corresponding adsorption reactions. For better observation, we have plotted the absolute value of adsorption energy in Figure 5d for all Au

clusters. The adsorption energy of the Au

clusters reveals the even–odd oscillation behavior, which again highlights the conclusion that small gold cluster anions with even-numbered atoms can molecularly chemisorb O2, whereas clusters with odd-numbered atoms are inert toward O2. The results of natural charges of O2 in anionic clusters are in line with this conclusion. From Table 3, we can see that the charges of O2 are always negative, and the absolute value of the charges are much larger for even n than for odd n, which shows the more significant charge transfer from the parent Au

cluster to the oxygen molecule. The anion species are better electron donors than the corresponding neutral species, because the electron affinities are always smaller than ionization potentials. Thus, the Au

clusters with even-number n have larger absolute values of adsorption energies. For neutral Au

clusters, the absolute value of adsorption energy of Au2O2 with n = 3, 5, and 7 is relatively larger than those of their adjacent neutral clusters. This is consistent with the conclusion that Au

clusters with an odd number of electrons hold the promise of chemisorbing an O2 molecule, for charges transferring from Au

to O2 is the dominant mechanism of the chemisorption process. Correspondingly, the natural charges of the oxygen molecule in Au

clusters with n = 3, 5, and 7 have the largest absolute values (with the exception of n = 4). The large charge transfer in the Au

cluster is probably due to its special geometry and oxygen binding motif, and since it does not

Table 3. Adsorption Energy E_{ads} (eV) of the Oxygen Molecule and the Natural Charges of O2 NC(O2) in the Ground-State Au

clusters (Q = 0, –1) Clusters

<table>
<thead>
<tr>
<th>Au2O2</th>
<th>Au2O2^{−}</th>
</tr>
</thead>
<tbody>
<tr>
<td>n  E_{ads} NC(O2) E_{ads} NC(O2)</td>
<td></td>
</tr>
<tr>
<td>2  –1.83 0.00</td>
<td>–2.67 0.65</td>
</tr>
<tr>
<td>3  –2.11 0.42</td>
<td>–1.79 0.17</td>
</tr>
<tr>
<td>4  –0.85 0.44</td>
<td>–2.44 0.59</td>
</tr>
<tr>
<td>5  –2.32 0.53</td>
<td>–1.87 0.33</td>
</tr>
<tr>
<td>6  –0.29 0.20</td>
<td>–2.51 0.65</td>
</tr>
<tr>
<td>7  –2.01 0.53</td>
<td>–1.70 0.20</td>
</tr>
<tr>
<td>8  –1.75 0.02</td>
<td>–2.43 0.58</td>
</tr>
<tr>
<td>9  –1.88 0.17</td>
<td>–1.73 0.21</td>
</tr>
<tr>
<td>10 –1.74 0.02</td>
<td>–2.27 0.56</td>
</tr>
</tbody>
</table>
possess a high negative value of adsorption energy or high inherent stability, we will not analyze it in detail here. The large negative values of the natural charges of O$_2$ of Au$_5$O$_2$ clusters with $n = 3, 5,$ and 7 give confidence to the conclusion that O$_2$ is chemisorbed onto the parent Au$_n$ cluster. Using the relatively large absolute values of adsorption energies as a criterion to indicate the chemisorption of O$_2$ molecules, these results give further support to the assumption that O$_2$ molecules can be chemisorbed onto neutral Au$_n$ clusters, especially in the case of Au$_5$O$_2$, which possesses the largest absolute value of adsorption energy.

3.5. Chemical Bonding Analysis. According to the analysis above, the neutral Au$_5$O$_2$ cluster exhibits an unexpected stability along with a large absolute value of adsorption energy and charge transfer and can therefore be regarded as the most promising candidate of chemisorption between neutral Au$_n$ clusters and a O$_2$ molecule. To gain insight into its bonding properties, the corresponding molecular orbitals (MO) of Au$_5$O$_2$ were analyzed and are presented in Figure 6. Despite

![Figure 6](image)

Figure 6. Molecular orbitals and energy levels of the neutral Au$_5$O$_2$ cluster.

their different shapes, they are combinations of two sets of atomic orbitals: mostly d-type Au orbitals and p-type O orbitals. For the LUMO, the bottom two Au atoms possess s-type character, and there is a strong Au–Au bond over two of the middle three Au atoms. For the occupied MOs HOMO, HOMO–2, and HOMO–4, the O p$_z$ orbitals (taken as in-plane) interact with the Au 5d$_z^2$ orbitals to form Au–O σ bonding. The HOMO–$n$ for $n = 1, 7,$ and 9 involve the same d$_{xy}$ and d$_{yz}$ atomic orbitals of Au atoms and the p$_z$ atomic orbital (taken as out-of-plane) of the O atomic orbitals, while the HOMO–5 is formed primarily by d$_{xy}$ orbitals of Au atoms. The remaining MOs shown involve bonding and antibonding combinations with the O p$_z$ atomic orbitals. The Au–Au interaction (mainly the interactions of the d orbitals) of the HOMO–2, HOMO–4, and HOMO–6 contribute to the stability of the C$_{2v}$ structure. On the basis of the MO configuration, the Au$_5$O$_2$ cluster possesses two σ bonds and one antibonding π* bond (HOMO–1) between Au and O atoms, because one of the three σ bonds and the antibonding π* bond (HOMO–8) cancel each other. These molecular orbitals indicate that there are strong interactions in the cyclic arrangement between the O atoms and the Au atoms they are bound to.

To improve our understanding of the bonding properties in the Au$_5$O$_2$ cluster further, we performed a chemical bonding analysis using the AdNDP approach, which is a visual and efficient algorithm to interpret the nature of molecular orbitals. The AdNDP approach obtains electron pairs by partitioning the electron density matrix into $n^c–2e$ terms ($n$ ranges from 1 to the maximum number of atoms in the system), and the electron pair serves as a unit to describe the chemical bonding. Figure 7 gives the representative results of AdNDP for Au$_5$O$_2$.

![Figure 7](image)

Figure 7. AdNDP chemical bonding analysis of the neutral Au$_5$O$_2$ cluster. LP represents lone pair localized bond. ON stands for the occupation number.

(they remaining can be seen in the Supporting Information, Figure S1), and the following discussion is about the revealed chemical bonds. The occupation numbers (ONS) of all chemical bonds maintain the ideal values 2.00 for σ bonds and one Au–Au π bond. The rest of the valence electron density is, except for one lone pair (LP), totally delocalized. There are five delocalized σ bonds and three delocalized π bonds (only considering the representative results). Except for the 6c–2e σ bond, 7c–2e σ bond, and 7c–2e π bond shown in the bottom row of Figure 7, the remaining delocalized bonds describe the chemical bonding among Au atoms only. The 6c–2e σ bond, 7c–2e σ bond, and 7c–2e π bond then visualize the strong bond between Au and O atoms, which make the C$_{2v}$ structure of Au$_5$O$_2$ so stable. Accordingly, the Au$_5$O$_2$ cluster does not exist in the form of a weakly bonded van der Waals complex but a chemisorbed complex for the strong interactions between O and Au atoms.

4. CONCLUSIONS

In summary, we have reported a detailed investigation of the neutral and anionic Au$_n^Q$ and Au$_5$O$_2^Q$ ($n = 2–10, Q = 0, −1$) clusters on the basis of the CALYPSO structure searching method and density functional theory. The ground-state structures of neutral and anionic Au$_n$ clusters are planar, and there are two ways the oxygen molecule binds to the parent gold clusters. The reasonable agreement between our simulated photoelectron spectra and the experimental PES give forceful support that the ground-state structures we obtained are truly global minima. Based on the optimized geometries, we have calculated the inherent stability and the corresponding adsorption energies. The results showed that neutral gold clusters with an odd number of electrons bind O$_2$ more strongly, because the presence of an unpaired electron makes them better electron donors. Furthermore, the molecular orbital and chemical bonding analysis of the Au$_5$O$_2$ cluster.
confirm the chemical adsorption of an oxygen molecule to a neutral gold cluster. We hope this work can provide the reference for further theoretical and experimental investigations of the adsorption behavior between O\textsubscript{2} and neutral gold clusters.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b09022.

Electronic states, symmetries, average binding energies $E_{b}$ and HOMO−LUMO energy gaps $E_{gap}$ of the ground-state Au\textsubscript{n} cluster. (PDF)

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**Notes**
The authors declare no competing financial interest.

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