Density functional theory investigation of gold cluster geometry and gas-phase reactivity with $O_2$

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We have conducted a density functional theory investigation into the gas-phase reactivity of small gold cluster ions in the interest of understanding gold cluster reactivity in several catalytic systems. Previously unreported geometries for $Au_9$ and $Au_{10}$ anions are obtained and reported from geometry optimizations. Predicted values of the vertical detachment energy match well with experiment, as does a rough simulation of its ultraviolet photoelectron spectrum—we found that comparison of predicted spectra with experimental data is a more sensitive analysis of geometry differences. Several binding sites for $O_2$ with different energies are identified on $Au_{10}$, but we show that the strongest binding site and orientation is predicted by frontier orbital theory. In addition, weakly stable adsorbed states for $O_2$ on the anion clusters $Au_5^-$, $Au_{10}^-$, and $Au_{11}^-$ are predicted in agreement with frontier orbital theory. The calculated binding energies are consistent with the experimentally observed patterns in adsorption of $O_2$ on anionic Au clusters. The binding energy for $O_2$ to $Au_{10}$ was calculated to be 19 kcal/mol, higher than for $O_2$ to either $Au_5^-$ (4 kcal/mol) or $Au_{11}^-$ (5 kcal/mol), and the calculated O–O bond length was found to increase from its gas-phase value of 1.27 angstroms to 1.38 angstroms when adsorbed on the $Au_{10}$ cluster, approaching the calculated bond length of 1.41 angstroms for the gas-phase superoxide ion $O_2^\cdot$. © 2002 American Institute of Physics. [DOI: 10.1063/1.1520137]

I. INTRODUCTION

The remarkable catalytic properties of small gold particles ($\leq 5$ nm) are well documented. Catalysts made from highly disperse gold on titania and TS-1 are active for reactions such as CO oxidation\(^1\) and the epoxidation of propylene with $H_2$ and $O_2$.\(^ {2\text{–}4}\) The reaction rates in these systems are highly dependent on the Au particle size,\(^5\) and are completely different from the behavior of bulk Au.\(^6\) Describing such unusual activity at an atomic level is a challenge.

With an eye towards eventual understanding of these complicated chemical systems, we turn to a simpler setting, the gas-phase reactivity of small Au clusters with $O_2$ molecules. The geometry and chemistry of gas-phase clusters may differ from supported particles, but their study provides insight into the unique reactivity of gold ensembles, in particular the strong dependence of reaction rate with particle size. The reaction rate of gas-phase $Au_3^-$ anion clusters with $O_2$ shows a marked pattern of even–odd reactivity\(^7\text{–}9\) for $N \leq 20$. The even-numbered anion clusters adsorb one molecule of $O_2$ per cluster, while the odd-numbered anions show extremely small or zero reactivity.\(^8\) The issue of whether the odd-number anions might show some slight interaction with $O_2$ is not fully resolved. Some have found no adsorption on odd-number anions ($N$ up to 20).\(^10\) After consideration of the experimental uncertainty, however, Lee and Ervin found that odd-numbered anion clusters of Au might have a low reactivity with gas-phase $O_2$ for anion clusters with up to 7 gold atoms.\(^9\) Their measured effective bimolecular rate constant for $Au_7^-$ with $O_2$ was $\leq 0.11 \pm 0.09 \times 10^{-11}$ cm$^3$ s$^{-1}$, very near their limit of detection.

Proposed explanations of this reactivity pattern point to the electron affinity of the Au clusters as a key variable. The bonding process envisioned involves donation of one electron from an even-$N$ gold anion cluster to the $1\pi^*$ molecular orbital of $O_2$, leaving the cluster with a stable, closed-shell electron configuration. The adsorbed $O_2$ superoxide ion polarizes the Au cluster further stabilizing the complex. This electron transfer process is not energetically favorable for the odd-numbered cluster; since the odd-number anion cluster already has a closed-shell configuration, electron transfer would first require an energetically costly electron promotion. As predicted by this simple picture, there is good qualitative correlation between electron affinity (of $Au_N^0$) and the reactivity of $Au_N^-$ toward $O_2$. Larger electron affinity means an electron is more difficult to remove from the anion and subsequent reactivity towards oxygen is lower. This is well explained in the paper by Salisbury et al.\(^8\)

Early \textit{ab initio} studies of small gold clusters focused on the characteristics of bare Au clusters.\(^{11\text{–}13}\) Bravo-Pérez et al.\(^{11}\) using Møller–Plesset (MP2 and MP4) real-space methods predicted planar structures for the neutral 4-atom ($D_{2h}$), 5-atom ($C_{2v}$), and 6-atom ($D_{3h}$) clusters. Grönbeck and Andreoni,\(^{12}\) using periodic density functional theory (DFT) methods, local spin density approximation (LSDA), and Becke–Lee–Yang–Parr (BLYP), also predicted that neutral clusters with up to 5 atoms had planar geometries, though in some cases different DFT methods lead to different planar geometries. Grönbeck and Andreoni predicted that anionic Au clusters up to 5 atoms would also be planar. They

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reported several cases where Jahn–Teller distortions made highly symmetric singlet structures unstable. Häkkinen et al., using periodic plane wave DFT codes, studied cluster sizes up to 10 atoms. They predicted that anion Au clusters (Au$_N^-$) with $N$ below 7 atoms would be planar structures, with a transition to nonplanar three-dimensional structures at $N=7$. In Häkkinen’s and our work, calculated values for vertical detachment energies (VDE) are typically within 0.2 eV of experiment. It has also been reported, as expected, that optimal computed geometries are sensitive to the electronic structure method employed. For example, the neutral 4-atom cluster yields two different optimal geometries: $D_{2h}$ using MP2$^{11}$ or PBE-GGA,$^{12}$ and $C_{2v}$, using LDA$^{12}$ or BLYP$^{12}$.

More recently, computational studies have addressed the reactivity of gas-phase and supported Au clusters interacting with O$_2$. Using DFT (Becke 3-parameter exchange and Lee–Yang–Parr correlation) with the LANL2DZ pseudopotential/basis set for Au and O, Okumura et al. reported an adsorption geometry for O$_2$ on an icosahedral 13-atom neutral gold cluster. The O$_2$ molecule is attached in an end-on bent arrangement. The binding energy depends on the spin state of the ensemble. With doublet spin, the binding energy is 11.8 kcal/mol while for quartet spin, the binding energy is 12.1 kcal/mol. Higher spin states were not reported.

In this paper we present DFT calculations on Au cluster geometries (cation, neutral, and anion) and the interaction of anion Au clusters with O$_2$. We predict previously unreported geometries for Au$_6^-$ and Au$_{10}^-$. and support the results with a comparison of predicted UPS spectra to experimental data.

II. COMPUTATIONAL METHOD

We used density functional theory (DFT) methods from the GAUSSIAN 98 suite$^{17}$ programs. We conducted calculations using B3LYP (Becke’s 3-parameter exchange with Lee–Yang–Parr correlation energy functional). Two different effective core pseudopotentials (ECP) for gold were utilized: the Stegans/Basch/Krauss ECP triple-split valence basis set (CEP-121G)$^{18}$ and the Los Alamos LANL2DZ double-split basis.$^{19–21}$ In the LANL2DZ basis set for Au, the O atoms are represented by Dunning/Huzinaga full double-zeta basis sets. The cluster geometries were obtained using B3LYP/CEP-121G. Different starting geometries were used for each cluster size and no symmetry constraints were imposed. Optimal geometries and spin multiplicities for Au$_9$, Au$_{10}$, and Au$_{11}$ clusters in the anion charge state were obtained. Two different spin multiplicities were investigated (generally singlet/triplet or doublet/quartet depending on the cluster size). Only relaxed geometries in the lowest spin multiplicity were sought in the case of the neutral and cation clusters. Having established optimal geometries and spin multiplicities at this level of theory, we used the B3LYP/LANL2DZ combination to relax anion clusters with absorbed O$_2$.

One test of the validity of the geometry is the predicted vertical detachment energy (VDE). For each of the anion clusters, a separate calculation was made for a corresponding neutral cluster with nuclei positions fixed in the corresponding anion configuration. The energy difference between this “frozen neutral” and the relaxed anion is an estimate of the vertical detachment energy. This energy difference corresponds to electron ejection followed by rapid relaxation of the remaining electron density. The nuclear ions are assumed to remain fixed on the time scale of the ejection event. Ultraviolet photoelectron spectra were simulated by Lorentzian broadening of the discrete electron energy levels (Kohn–Sham orbital energies) given by

$$F(e) = \sum_i c[(a+e-e_i)^2+b],$$

where $e_i$ are the Kohn–Sham energy levels in eV, $e$ is the energy in eV, $a$, $b$, and $c$ are constants established by qualitative fit to experimental data (values $b=0.008$ eV$^2$ and $c=1.0$ eV was used in both spectra, $c$ is an arbitrary nondimensionalizing factor as the photoelectron count in the UPS spectra is treated here and in Ref. 22 as nondimensional). The resulting spectra were shifted in energy (parameter $a$) to match the first experimental peak in the UPS spectra. The spectra were also scaled to match the (arbitrary) scale of the experimental data. That the broadening is approximately correct can be seen by the match with the first spectral peak. The scattering process, particularly for photoelectrons with kinetic energies
$5 \text{ eV or more below the energy of incoming photons (i.e., 5 eV down), is not accounted for in this very simplified approach; thus, the match to experimental data is not expected to be other than qualitative.}$

Cluster binding energies were calculated from the cluster and atom total energies as

$$E_b = \frac{E(AU_n^\ast) - nE(Au)}{n},$$

where sat = +, −, or 0, $n$ is the number of atoms in the cluster, $E_b$ is the binding energy of the cluster in eV, $E(AU_n^\ast)$ is the energy of the cluster in eV, and $E(Au)$ is the energy of an isolated neutral Au atom in eV.

### III. RESULTS AND DISCUSSION

#### A. Geometry

The lowest energy geometries found for the Au clusters investigated are shown in Fig. 1 through Fig. 3. For $\text{Au}_{11}^+$, the geometries of each charge state are all identical, having $C_{2v}$ symmetry as shown in Fig. 3. This is not the case for the $\text{Au}_{10}$ clusters. In the $\text{Au}_{10}^+$ cluster (Fig. 2) the symmetry is $C_2$, showing that the symmetry plane present in both the neutral and anion ($C_{2v}$) has been lost. An alternate $\text{Au}_{10}$ structure predicted by Häkkinen and Landman\(^{13}\) is also shown in Fig. 3. Comparison of these two structures is presented below. Our convergence $\text{Au}_9$ cation cluster geometry, shown in Fig. 1, has $C_{2v}$ symmetry, unlike our predicted $\text{Au}_{10}^0$ and $\text{Au}_{10}^-$ geometries, which are $C_{4v}$.

We tried to replicate the alternate $\text{Au}_{10}^-$ geometry reported by Häkkinen and Landman\(^{13}\) by relaxing the published structure in doublet and quartet spin multiplicities. The quartet spin configuration converged readily. Some difficulty was observed in attempting to tightly converge the doublet spin configuration. The doublet multiplicity initially stabilized at an energy level lower than the optimal quartet spin state, but as the geometry relaxation proceeded, large shifts in the electronic configuration were observed.\(^{23}\) The doublet spin also developed negative eigenvalues in the energy Hessian matrix, which suggests to us that the relaxed geometry of the alternate $\text{Au}_{10}$ structure has a Jahn–Teller instability. Further relaxation was unsuccessful, so the geometry prior to the instability was taken as the best achievable for this arrangement. The final geometry ($C_{4v}$) is that of two stacked square planar arrays capped by Au atoms on top and below (Fig. 3); however, the square planar arrays are slightly different in size, which breaks the ground-state degeneracy.

In further assessing the cluster geometries, we consider only the anion clusters. The $\text{Au}_{10}^-$ cluster is of particular interest since O$_2$ adsorption on this anion has been observed experimentally.\(^{7,9}\) VDE for $\text{Au}_9$ to $\text{Au}_{11}$ are shown in Table I. Good agreement is obtained with experimental values, generally within $\pm 0.2$–0.3 eV. However, we believe VDE agreement with experiment is not sufficient evidence to identify the lowest energy geometry. For example, both the alternate and optimal $\text{Au}_{10}$ configurations result in nearly identical calculated values for VDE, both in fair agreement with experiment.

A more sensitive test of cluster geometry is the predicted versus the experimental ultraviolet photoelectron spectra. Very detailed experimental spectra are available for $\text{Au}_N$ clusters in work done by Taylor et al.\(^{22}\) We have done com-

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**FIG. 2.** Projection views of the gas-phase clusters: $\text{Au}_{10}^+$, Optimal $\text{Au}_{10}^0$, and $\text{Au}_{10}^-$ in their ground-state configurations (note, there is no significance to the lines connecting nuclear positions; these are only an aid for the eye). Geometries were optimized at the B3LYP/CEP-121G approximation.

**FIG. 3.** Projection views of the gas-phase clusters: Alternate $\text{Au}_{10}^-$, $\text{Au}_{11}^+$, $\text{Au}_{10}^0$, and $\text{Au}_{11}^-$ in their ground-state configurations (note, there is no significance to the lines connecting nuclear positions; these are only an aid for the eye). Geometries were optimized at the B3LYP/CEP-121G approximation.
B. Anion clusters with adsorbed O$_2$

Having established reasonable ground-state geometries for the $N$=9, 10, and 11 anion clusters, we next consider their reaction with O$_2$ in the gas phase. An early report of gas-phase reactions between small gold clusters and molecules like H$_2$ and O$_2$ by Kaldor et al. found O$_2$ adsorption on Au$_N$ clusters with $N$ odd. Later, more quantitative work determined that O$_2$ relative reactivity with Au$_N$ clusters follows the general pattern

$$6 > 4 \sim 20 > 8 > 12 > 18 > 14 > 10 > 2 > \text{odd sizes}$$

and established that nondissociative dioxygen adsorption was the only significant interaction between O$_2$ and the cluster. As Cox et al. have noted, O$_2$ adsorption on Au$_N$ clusters correlates with electron affinity of the (neutral) cluster. This even–odd pattern in O$_2$ reactivity/electron affinity of Au$_N$ clusters correlates with electron affinity of the neutral cluster, which is given in Table I. The calculated spectra are obtained from the one-electron energies which have been Lorentzian broadened (as discussed above) and shifted to match the initial peak to the observed experimental energy. Examination of the spectra in Fig. 4 that qualitatively, the optimal Au$_{10}^{2-}$ geometry from our calculations predicts the two experimental peaks at 2.4 and 2.45 eV. The calculated peaks are separated in energy by 0.5 eV and are only shifted slightly (~0.2 eV) from the experimental values. The spectra obtained from the alternate Au$_{10}^{2-}$ geometry shows two peaks in this region as well, but their separation is much larger (approximately 1 eV) and the offset from experimental values is +0.5 eV in one case and −0.5 eV in the other. Neither spectrum does well at lower electron kinetic energies, presumably due to secondary scattering and other effects not considered here. Our reported optimal geometry gives a better qualitative fit to UPS experimental data and also has lower energy, so we have higher confidence in this geometry.

![Graph A](image1.png)

![Graph B](image2.png)

**Table I. Au cluster data.**

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Energy (Hartree/cluster)</th>
<th>Preferred spin</th>
<th>Binding energy (kcal/atom)</th>
<th>Calculated VDE(eV)</th>
<th>Measured VDE(eV)$^a$</th>
</tr>
</thead>
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<td><strong>Anions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$-1 \ 225.392\ 27$</td>
<td>singlet</td>
<td>40</td>
<td>3.6</td>
<td>3.8</td>
</tr>
<tr>
<td>10 (optimal)</td>
<td>$-1 \ 361.522\ 30$</td>
<td>doublet</td>
<td>39</td>
<td>2.8</td>
<td>3.0</td>
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<tr>
<td>10 (alternate)</td>
<td>$-1 \ 361.48^b$</td>
<td>singlet</td>
<td>2.75$^c$</td>
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</tr>
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<td>11</td>
<td>$-1 \ 497.673\ 36$</td>
<td>singlet</td>
<td>39</td>
<td>3.4</td>
<td>3.7</td>
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<td></td>
<td></td>
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<tr>
<td>9</td>
<td>$-1 \ 225.266\ 50$</td>
<td>doublet</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$-1 \ 361.430\ 03$</td>
<td>singlet</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$-1 \ 497.551\ 25$</td>
<td>doublet</td>
<td>36</td>
<td></td>
<td></td>
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<tr>
<td><strong>Neutrals with ions fixed at anion location</strong></td>
<td></td>
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</tr>
<tr>
<td>9</td>
<td>$-1 \ 225.260\ 31$</td>
<td>doublet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$-1 \ 361.420\ 47$</td>
<td>singlet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$-1 \ 497.549\ 76$</td>
<td>doublet</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Cations</strong></td>
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<tr>
<td>9</td>
<td>$-1 \ 225.045\ 85$</td>
<td>singlet</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$-1 \ 361.164\ 88$</td>
<td>doublet</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$-1 \ 497.307\ 16$</td>
<td>singlet</td>
<td>42</td>
<td></td>
<td></td>
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</table>

$^a$Reference 22.

$^b$See the text.

$^c$Reference 13.
clusters is associated with the filling of electronic shells,\(^22,24\) and leads to the conceptual model discussed in the Introduction. Considering that each Au atom in the cluster contributes one electron valence shell (6s) and adding the additional anion electron, an even number of electrons (and closed-shell stability) results for clusters with an odd number of atoms. Consequently, the odd-number anion clusters either do not adsorb O\(_2\) at all, or adsorb O\(_2\) only weakly. For our calculations, the electron affinity of the neutral cluster is approximately the same as the vertical detachment energy of the equivalent anion cluster. The difference between the electron affinity and the vertical detachment energy is the energy difference associated with relaxing the neutral cluster. For the clusters considered here, the difference amounts to 0.1–0.3 eV (vertical detachment energies being greater; see Table I).

The appealing qualitative correlation between reactivity and electron affinity or vertical detachment energy has its shortcomings, however. For example, the measured VDE of an Au\(_{5}\) cluster, 3.0 eV, is the same as that of a Au\(_{10}\). Though the neutral clusters have the same electron affinity, they have very different reactivities toward O\(_2\). The odd-numbered 5-atom cluster has very low or no reactivity toward O\(_2\), while the even-sized 10-atom cluster is reactive.

One additional factor to consider in the reactivity of O\(_2\) and Au\(_N\) clusters is electron spin. Wigner’s spin selection rule\(^25\) predicts a spin inversion barrier for the interaction of odd-sized anion Au clusters (singlet ground state) with triplet oxygen if the product complex is singlet. In fact, the weakly bound complexes of O\(_2\) with Au\(_9\) and Au\(_{11}\) were predicted to have triplet states as the lowest energy states, so the spin barrier should not be a factor in their formation. Nor does a spin barrier exist for the even-sized clusters, since they have a doublet ground state and reaction with triplet oxygen can lead to the product with doublet spin multiplicity.

We have predicted several different stable binding configurations for O\(_2\) and Au\(_N\) clusters. The electron affinity of the neutral cluster is approximately the same as the vertical detachment energy of the equivalent anion cluster. The difference between the electron affinity and the vertical detachment energy is the energy difference associated with relaxing the neutral cluster. For the clusters considered here, the difference amounts to 0.1–0.3 eV (vertical detachment energies being greater; see Table I).

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**FIG. 5.** (Color) Au\(_{10}\) cluster with O\(_2\) adsorbed at the rear binding site. Frontier orbitals shown are the Kohn–Sham orbitals for O\(_2\) (LUMO) and the optimal Au\(_{10}\) cluster (HOMO) suggesting the preferred overlap. (a) 23 kcal/mol binding energy without BSSE correction.

**FIG. 6.** Views of other adsorption geometries for O\(_2\) and Au\(_{10}\) (higher energy, but still stable binding energy). (a) 10 kcal/mol binding energy uncorrected for BSSE. (b) 7 kcal/mol binding energy uncorrected for BSSE.

**FIG. 7.** Adsorption geometries for O\(_2\) with Au\(_9\) and Au\(_{11}\) (both triplet). (a) 8 kcal/mol binding energy uncorrected for basis set superposition error (BSSE). (b) 9 kcal/mol binding energy uncorrected for basis set superposition error (BSSE).
figurations for \( \text{O}_2 \) on \( \text{Au}_{10} \) clusters. Figure 5 and 6 show three configurations. One of these, Fig. 6, is similar to the bent-end-on binding configuration calculated by Okumura et al.\(^{14}\) However, in this case, we find that the bent-end-on arrangement is not the most stable. Frontier orbital theory suggests a better binding site. As illustrated in Fig. 5, the best frontier orbital overlap is obtained at the “wide” end of the 10-anion cluster. This is where the greatest HOMO density is found and the HOMO overlap with the \( \text{O}_2 \) LUMO is symmetry allowed. Electron transfer from the cluster to oxygen is consistent with a weakened O–O bond. The calculated binding energy of \( \text{O}_2 \) on the \( \text{Au}_{10} \) cluster is 23 kcal/mol. A separate calculation for the electronic structure of \( \text{O}_2 \) utilizing the additional basis set functions of the \( \text{Au}_{10} \) cluster gives an energy 4 kcal/mol lower than a stand-alone calculation for \( \text{O}_2 \). Accounting for this basis set superposition error (BSSE) decreases the binding energy from 23 to approximately 19 kcal/mol. The same 4 kcal/mol value is used in making BSSE adjustments for the other cluster/O\(_2\) complexes.

Adsorption of \( \text{O}_2 \) on the odd-size anion clusters in our investigation depended on spin multiplicity. No bound complexes of \( \text{O}_2 \) with \( \text{Au}_{9}\) or \( \text{Au}_{11}\) were found where the final ensemble had singlet spin. Weakly bound complexes with triplet spin are shown in Fig. 7. When the BSSE correction for the \( \text{Au}_{10} \) complex with \( \text{O}_2 \) is applied, these binding energies were reduced to approximately 5 kcal/mol for \( \text{Au}_{10}\) and 4 kcal/mol (\( \text{Au}_{9}\))—both substantially lower than the value for the 10-atom anion cluster of 19 kcal/mol. The binding of \( \text{O}_2 \) to the \( \text{Au}_{12} \) cluster has the bent-end-on configuration, similar to the configuration found for \( \text{O}_2 \) on neutral \( \text{Au}_{13} \) by Okumura et al.\(^{14}\) and they predicted a binding energy for \( \text{O}_2 \) of about 12 kcal/mol (no mention of BSSE corrections). This is comparable to the weakly bound energies of \( \text{O}_2 \) found in our work for \( \text{Au}_{9} \) (8 kcal/mol), \( \text{Au}_{11} \) (9 kcal/mol), and the weak adsorption sites on the \( \text{Au}_{10} \) cluster (front 10 kcal/mol and side 7 kcal/mol).

The Mulliken charge distribution obtained for our most stable configuration shows the shift of electron density accompanying adsorption of \( \text{O}_2 \) on the \( \text{Au}_{10} \) cluster. Figure 8 illustrates that electron density is not distributed uniformly on the bare anion cluster. Electron richer regions appear at the apexes of the structure, while the center (two stacked triangles) is neutral to electron deficient. This electron density distribution is distorted upon adsorption of oxygen as the \( \text{O}_2 \) molecule draws electron density away from the cluster, particularly from the two Au atoms most closely coordinated with \( \text{O}_2 \). Activation of the O–O bond is also seen in the stretch of the O–O bond distance from 1.27 angstroms (calculated using the same DFT method and pseudopotential) in the gas phase to 1.37 angstroms when adsorbed in the \( \text{Au}_{12} \) cluster at the highest binding energy site. This stretched bond length is approaching that of a free superoxide ion \( \text{O}_2^- \), 1.41 angstroms (calculated). Table II gives the bond distances for the other weakly bound configurations which are not stretched to the same extent. Activation of the O–O bond may be an important step for Au in the epoxidation of propylene with \( \text{H}_2 \) and \( \text{O}_2 \). It has been speculated\(^{5}\) that peroxy species are formed on small gold clusters from \( \text{H}_2 \) and \( \text{O}_2 \). Further work will be needed to explore this possibility.

![FIG. 8. Mulliken electron distribution on Au\(_{10}\) before and after adsorption of O\(_2\) (done at the B3LYP/LANL2DZ level).](image)

**TABLE II. Properties of bound O\(_2\) in Au\(_{10}\)**

<table>
<thead>
<tr>
<th>Cluster w/O(_2)</th>
<th>Adsorption site</th>
<th>Pseudopotential/basis set</th>
<th>Binding energy (kcal/mol)(^a)</th>
<th>O(_2) bond length (angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Au}_{10} )</td>
<td>side</td>
<td>LANL2DZ(^a)</td>
<td>7</td>
<td>1.308</td>
</tr>
<tr>
<td>( \text{Au}_{10} )</td>
<td>front</td>
<td>LANL2DZ(^a)</td>
<td>9</td>
<td>1.367</td>
</tr>
<tr>
<td>( \text{Au}_{10} )</td>
<td>rear</td>
<td>LANL2DZ(^a)</td>
<td>23</td>
<td>1.370</td>
</tr>
<tr>
<td>( \text{O}_2 ) Molecule</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^1\text{O}_2 )</td>
<td>CEP-121G(^b)</td>
<td></td>
<td>1.273</td>
<td></td>
</tr>
<tr>
<td>( ^3\text{O}_2 )</td>
<td>LANL2DZ(^b)</td>
<td></td>
<td>1.268</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Unadjusted for BSSE (calculated to be 4 kcal/mol for the \( \text{Au}_{10}/\text{O}_2 \) rear bonded complex).

\(^b\)References 19–21.
IV. CONCLUSIONS

We predict a new minimum energy geometry for Au$_{10}$ and identify relatively weak binding sites for O$_2$ on this cluster as well as on an Au$_{11}$ cluster. We have also predicted a new stable geometry for Au$_{10}$. Predicted values of the vertical detachment energy match well with experiment, as does a rough simulation of its UPS spectra. Comparison of predicted UPS with experimental data is more sensitive to geometry differences. No Jahn–Teller instabilities are seen with the new structure. Several binding sites for O$_2$ with different energies are identified on Au$_{10}$, but the strongest binding site and orientation is predicted by frontier orbital geometry differences. No Jahn–Teller instabilities are seen with the new structure. Several binding sites for O$_2$ with different energies are identified on Au$_{10}$, but the strongest binding site and orientation is predicted by frontier orbital theory. The strongest bonding of O$_2$ with the Au$_{10}$ cluster is edge-on attachment to the HOMO region of the cluster. Of the three clusters studied, Au$_9$, Au$_{10}$, and Au$_{11}$, the Au$_{10}$ cluster binds O$_2$ the tightest (19 kcal/mol including BSSE correction) and is also experimentally the more reactive cluster size in this group of anions. O$_2$ does not dissociate completely on the Au$_{10}$ cluster, but the bond length is stretched from 1.27 angstroms to approximately 1.38 angstroms after adsorption. Activation of O$_2$ may be important in explaining the role of Au in epoxidation of propylene using H$_2$ and O$_2$ over Au/TiS-1 catalysts.

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17M. J. Frisch et al., Gaussian 98, Revision A.7 Gaussian, Inc., Pittsburgh, PA, 1998.
23Evidenced by a jump in the number of self-consistent field iterations (from 4 cycles to 287 cycles) followed by a jump back to the prior electronic configuration as evidenced by another jump in the number of SCF iterations (from 475 cycles to 7 cycles), the pattern of many steps with low number of SCF iterations followed by 2 steps with very high SCF iterations repeated several times.