

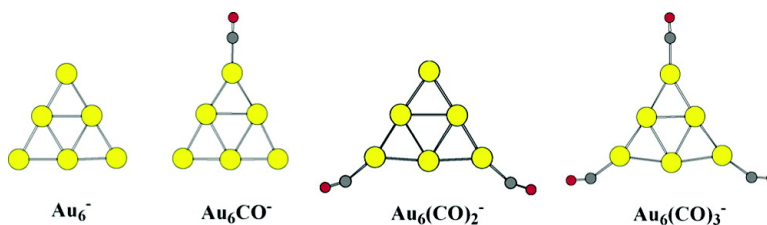
Article

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Unique CO Chemisorption Properties of Gold Hexamer: Au₆(CO)_n⁻ (n = 0–3)

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Abstract: Elucidating the chemisorption properties of CO on gold clusters is essential to understanding the catalytic mechanisms of gold nanoparticles. Gold hexamer Au₆ is a highly stable cluster, known to possess a D_{3h} triangular ground state structure with an extremely large HOMO–LUMO gap. Here we report a photoelectron spectroscopy (PES) and quasi-relativistic density functional theory (DFT) study of Au₆–CO complexes, Au₆(CO)_n⁻ and Au₆(CO)_n (n = 0–3). CO chemisorption on Au₆ is observed to be highly unusual. While the electron donor capability of CO is known to decrease the electron binding energies of Au_m(CO)_n⁻ complexes, CO chemisorption on Au₆ is observed to have very little effect on the electron binding energies of the first PES band of Au₆(CO)_n⁻ (n = 1–3). Extensive DFT calculations show that the first three CO successively chemisorb to the three apex sites of the D_{3h} Au₆. It is shown that the LUMO of the Au₆–CO complexes is located in the inner triangle. Thus CO chemisorption on the apex sites (outer triangle) has little effect on this orbital, resulting in the roughly constant electron binding energies for the first PES band in Au₆(CO)_n⁻ (n = 0–3). Detailed molecular orbital analyses lead to decisive information about chemisorption interactions between CO and a model Au cluster.

1. Introduction

The discovery of remarkable catalytic activities of highly dispersed gold nanoparticles for low-temperature CO oxidation as pioneered by Haruta et al.¹ has stimulated considerable research on gold clusters.² Because of their potentials for industrial applications, extensive research efforts have been directed at the elucidation of the catalytic mechanisms of nanogold.^{3–13} Different models have been proposed, including

the perimeter sites model,² the nonmetallic gold model,³ the extra electron model,¹¹ and the low-coordination sites model.^{8,13} However, the exact catalytic mechanisms are still being debated.^{2,13,14} Size-selected cluster deposition studies^{11,12} and gas-phase experimental^{15–23} and theoretical^{24–30} studies have

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been carried out to model this catalytic reaction in a well-controlled manner, providing fundamental mechanistic information at the molecular level. Chemisorbed gold cluster complexes serve as ideal model systems for nanogold catalysts, even though the role of substrates cannot be addressed.³¹ Numerous mass spectrometric,¹⁹ photoelectron spectroscopic,¹⁵ and density functional theory (DFT)^{15,25,26,29} studies have established that O₂ adsorbs on gold clusters molecularly. Evidence for molecular chemisorption of O₂ on TiO₂-supported gold nanoparticles has also been observed recently.⁵ Co-adsorption of CO and O₂ on small gold clusters has been investigated by mass-spectrometry-based experiments, and it was revealed that CO and O₂ adsorb cooperatively, rather than competitively.^{17,18}

However, little experimental information is available on how CO molecules interact with gold clusters and gold nanoparticles.^{19–23} Chemical reactions of gold clusters with CO have been studied,^{19–22} and pronounced size dependence and saturation were observed. Infrared spectra of Au–CO complexes formed in a rare gas matrix have been reported,²³ and complexes such as Au(CO)_{*n*} (*n* = 1–5) and Au_{*n*}(CO)₂ (*n* = 1, 2) were assigned. However, definitive electronic and structural information on the Au_{*m*}(CO)_{*n*} complexes is still elusive. Such information would be valuable in the mechanistic understanding for the catalytic CO oxidation by gold nanoparticles.

In a recent communication,³² we reported the generation of several series of gold carbonyl cluster anions Au_{*m*}(CO)_{*n*}[–] (*m* = 2–5, *n* = 1–7) in the gas phase and characterized their electronic structure using photoelectron spectroscopy (PES). We observed that the first few CO groups induce significant red shifts to the photoelectron spectra, suggesting that CO acts as electron donors to the gold clusters. For a given gold cluster, CO adsorption reaches a critical number, beyond which further CO adsorption changes the spectra very little. The critical CO numbers correspond exactly to the available low coordination apex sites on the respective bare gold clusters. It was suggested that CO first chemisorbs to the apex sites and additional CO then only physisorbs to the chemisorption-saturated Au_{*m*}(CO)_{*n*}[–] complexes. The observation that CO chemisorption induces significant decreases to the electron binding energies of the Au_{*m*}(CO)_{*n*}[–] complexes is important, suggesting that CO chemisorption would promote O₂ adsorption because the latter involves electron transfers from the cluster. Thus the previous experimental results provided electronic and spectroscopic basis for the cooperative chemisorption of CO and O₂ on gold clusters and may hold the key for the mechanistic understanding of nanogold catalysts for CO oxidation. However, a detailed molecular understanding about how CO interacts with gold is still lacking.

In the current paper, we report a combined PES and DFT investigation of the CO chemisorption behavior on the gold hexamer from one to three CO groups, Au₆(CO)_{*n*}[–] (*n* = 0–3). Bare gold hexamer has unique electronic and structural properties.^{33–36} Structurally, Au₆ and Au₆[–] were well-character-

ized to possess a close-packed planar triangular structure with D_{3h} symmetry.³⁶ This highly symmetric structure, stabilized by strong relativistic effects,³⁷ aromaticity, and aurophilic attraction,³⁸ may be viewed as a small piece of Au(111) surface or an ideal model catalytic surface composed of apex and edge sites only. Electronically, Au₆ is known to possess the largest HOMO–LUMO gap among gold clusters^{34,35} and has been proposed to be a six-electron magic cluster within a two-dimensional electronic shell model.³⁹ Upon CO chemisorption, we observed surprisingly that the first three CO chemisorptions do not significantly change the electron binding energies of the first PES band in Au₆(CO)_{*n*}[–] (*n* = 1–3), in direct contrast to our previous study on the smaller Au_{*m*}(CO)_{*n*}[–] (*m* = 2–5) complexes. Only the binding energies of the second PES band in Au₆(CO)_{*n*}[–] were observed to be red-shifted, resulting in a closing of the HOMO–LUMO gaps upon CO chemisorption. We also performed extensive quasi-relativistic DFT calculations to examine chemisorption structures in Au₆(CO)_{*n*}[–] and Au₆(CO)_{*n*} (*n* = 1–3). We found that the first three CO successively chemisorb to the apex sites of the triangular Au₆ without significantly perturbing the parent Au₆ structure. The unique CO chemisorption behavior and its influence on the electronic structure of Au₆ are understood using molecular orbital analysis, providing detailed information about the molecular and electronic interactions between CO and Au₆.

2. Experimental and Computational Methods

2.1. Photoelectron Spectroscopy. The experiments were carried out using a magnetic-bottle-type PES apparatus equipped with a laser vaporization supersonic cluster source, details of which were described elsewhere.⁴⁰ Briefly, Au_{*m*}(CO)_{*n*}[–] cluster anions were produced by laser vaporization of a pure gold target in the presence of a helium carrier gas seeded with 2% CO. Various Au_{*m*}(CO)_{*n*}[–] clusters were generated and mass-analyzed using a time-of-flight mass spectrometer. The Au₆(CO)_{*n*}[–] (*n* = 1–3) species were each mass-selected and decelerated before being photodetached. Three detachment photon energies were used in the current study: 532 nm (2.331 eV), 266 nm (4.661 eV), and 193 nm (6.424 eV). Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectra of Au[–] and Rh[–], and the energy resolution of the apparatus was Δ*E*_{*k*}/*E*_{*k*} ~2.5%, that is, ~25 meV for 1 eV electrons.

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2.2. Density Functional Calculations. In the DFT calculations, we used the Stuttgart 19-valence-electron energy-consistent pseudopotentials⁴¹ and basis sets augmented with two f-type and one g-type polarization functions ($\zeta_f = 0.498$, 1.461, and $\zeta_g = 1.218$) for gold as recommended by Martin and Sundermann⁴² and Dunning's all-electron basis set aug-cc-pVTZ for oxygen and carbon.⁴³ Scalar (mass-velocity and Darwin) relativistic effects were taken into account via the quasi-relativistic pseudopotentials. A variety of exchange-correlation functionals were tested for accuracy and consistency. We found that the B3LYP hybrid functional, which makes use of the Hartree–Fock exact exchange and Becke's exchange functional and Lee–Yang–Parr correlation functional,⁴⁴ gave electron binding energies in good agreement with the experimental data. Harmonic frequency calculations were performed to verify that the obtained structures are minima on the potential energy surfaces. All calculations were spin-restricted for closed-shell molecules and spin-unrestricted for open-shell species. Adiabatic detachment energies (ADEs) were calculated via the total energy difference (i.e., Δ SCF method), whereas the vertical detachment energies (VDEs) for the anionic clusters were calculated using the combined Δ SCF-TDDFT approach.^{45,46} For all calculations, the extra fine integration grid was used to obtain highly accurate DFT results. All calculations were accomplished using the NWChem 4.6 program and the Molecular Science Computing Facility located at the Environmental Molecular Sciences Laboratory.⁴⁷ Molecular orbitals were visualized using GaussView 3.0.⁴⁸

3. Experimental Results

The PES spectra of $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$) were obtained at three detachment photon energies (532, 266, and 193 nm). Figure 1 compares the 193 nm spectra of all the species. The spectra at all three photon energies are given as Supporting Information in Figures S1–S4. The lower photon energy spectra had better spectral resolution and yielded more accurate ADEs and VDEs, which are summarized in Table 1 for the first two detachment features (bands X and A in Figure 1). Since no vibrational structures were resolved in the PES data, the ADEs, that is, the electron affinities of the corresponding neutral clusters, were evaluated by drawing a straight line at the leading edge of the ground-state feature X and then adding the instrumental resolution to the intersections with the binding energy axis. Although this is an approximate procedure, we were able to obtain consistent ADEs from spectra taken at different photon energies due to the relatively sharp onset of the data. The VDE differences between bands A and X give approximately the experimental measures for the HOMO–LUMO gap of the neutral complexes and are given in Table 2. The VDE and ADE difference of band X defines the reorganization energy (Table 2), which is a measure of the geometry changes between the anion and neutral ground states. The VDEs for all

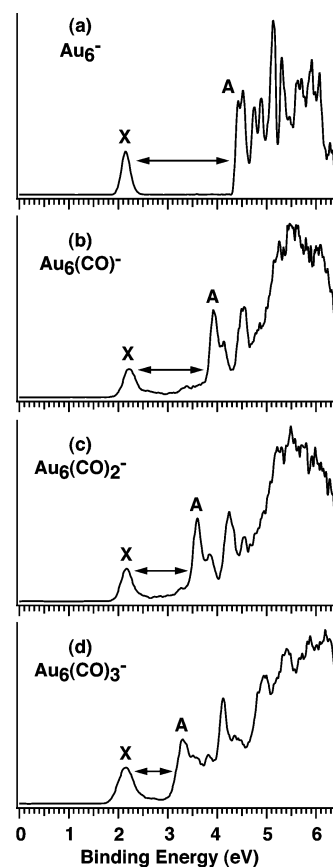


Figure 1. Photoelectron spectra of $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$) at 193 nm. The arrows indicate the observed energy gaps.

Table 1. Observed Adiabatic and Vertical Detachment Energies from the Photoelectron Spectra of $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$), and Comparison with Theoretical Detachment Energies^a

	feature	exptl ^{b,c}		theor ^{b,d}		
		ADE	VDE	ADE	state (MO)	VDE
Au_6^-	X	2.06 (2)	2.13 (2)	2.02	$^1\text{A}_1'$ ($6a_1'$)	2.12
	A		4.43 (2)		$^3\text{E}'$ ($7e'$)	4.43
$\text{Au}_6(\text{CO})^-$	X	2.04 (5)	2.20 (3)	2.10	$^1\text{A}_1$ ($11b_2$)	2.26
	A		3.92 (2)		$^3\text{B}_2$ ($15a_1$)	3.91
$\text{Au}_6(\text{CO})_2^-$	X	2.03 (5)	2.15 (3)	2.16	$^1\text{A}_1$ ($17a_1$)	2.30
	A		3.60 (2)		$^3\text{B}_2$ ($13b_2$)	3.75
$\text{Au}_6(\text{CO})_3^-$	X	1.95 (5)	2.15 (3)	1.86	$^1\text{A}_1$ ($20a_1$)	2.15
	A		3.32 (3)		$^3\text{B}_2$ ($14b_2$)	3.53

^a For complete data sets, see Supporting Information Tables S1–S4. ^b All detachment energies are in eV. ^c The ground-state ADE also represents the electron affinity of the corresponding neutral species. ^d “State (MO)” denotes the final neutral triplet and singlet states upon electron detachment from the corresponding molecular orbital of the anion.

Table 2. Comparison of Experimental and Theoretical X–A Energy Gaps and Reorganization Energies of $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$)

	energy gap ^a		reorganization energy ^a	
	exptl ^b	theor	exptl ^b	theor
Au_6^-	2.30	2.31	0.07	0.10
$\text{Au}_6(\text{CO})^-$	1.72	1.65	0.16	0.16
$\text{Au}_6(\text{CO})_2^-$	1.45	1.45	0.12	0.14
$\text{Au}_6(\text{CO})_3^-$	1.17	1.38	0.20	0.29

^a All energies are in eV. ^b The estimated uncertainty is ± 0.03 eV.

the observed features for each species are given as Supporting Information in Tables S1–S4, where the calculated VDEs are also listed (see below).

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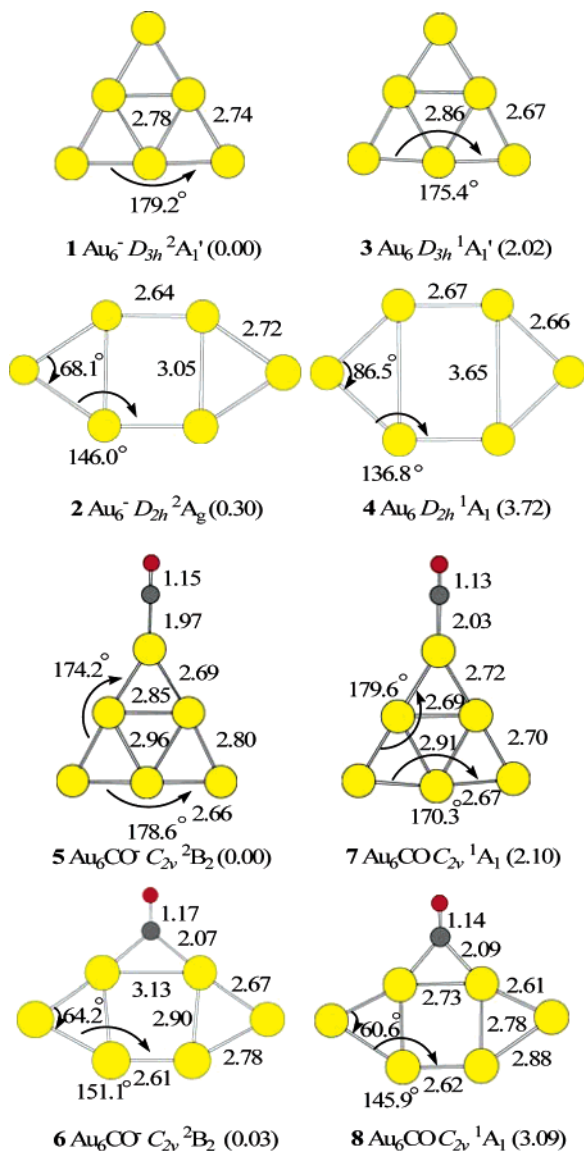


Figure 2. Optimized structures of the ground state and a low-lying isomer for Au_6^- , $\text{Au}_6(\text{CO})^-$, and their corresponding neutrals. All bond lengths are in Å, and all relative energies (in eV) are referenced to the anion ground state.

Well-resolved PES spectra for Au_6^- were presented in our previous work.³⁴ The ADE and VDE of the ground-state X were measured to be 2.06 and 2.13 eV, respectively, where the ADE is in good agreement with a previous ZEKE measurement (2.05 eV).³⁵ The VDE of band A at 4.43 eV defines an extremely large HOMO–LUMO gap of 2.30 eV for neutral Au_6 , which is the largest among all gold clusters.^{34,35} Upon adsorption of the first CO, the ground state feature X broadened (Figure 1b), but its binding energies (ADE: 2.04 eV; VDE: 2.20 eV) showed very little change relative to that of the bare cluster. This is completely different from the chemisorption behavior of the smaller gold clusters, where a red shift of as much as 0.6 to 0.7 eV was observed upon the first CO chemisorption for Au_n^- ($n = 2–5$).³² However, the second VDE, corresponding to electron detachment from the anion ground state to the first neutral excited state (A), was measured to be 3.92 eV, significantly red-shifted by 0.51 eV with respect to that of Au_6^- and resulting in a much smaller X–A energy gap (1.72 eV).

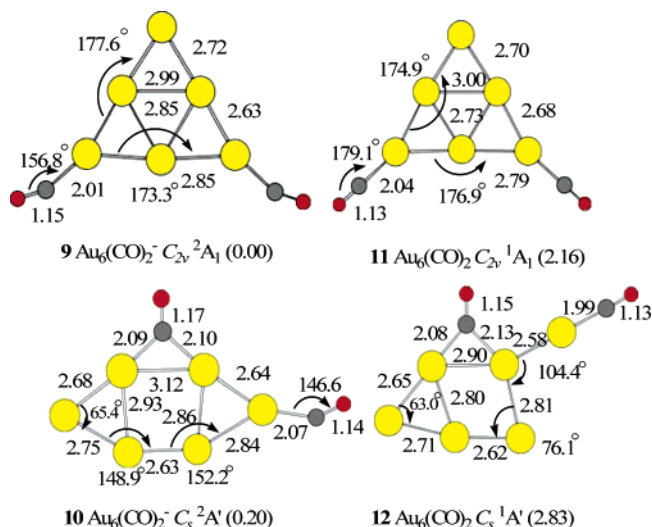


Figure 3. Optimized structures of the ground state and a low-lying isomer for $\text{Au}_6(\text{CO})_2^-$ and $\text{Au}_6(\text{CO})_2$. All bond lengths are in Å, and all relative energies (in eV) are referenced to the anion ground state.

Upon further CO adsorption, the overall spectral patterns of $\text{Au}_6(\text{CO})_2^-$ (Figure 1c) and $\text{Au}_6(\text{CO})_3^-$ (Figure 1d) appeared similar to that of $\text{Au}_6(\text{CO})^-$: the first PES band X showed very little dependence on the number of CO ligands, whereas the higher binding energy features displayed continued red shifts, resulting in smaller and smaller X–A energy gaps: 1.45 eV for $\text{Au}_6(\text{CO})_2^-$ and 1.17 eV for $\text{Au}_6(\text{CO})_3^-$. Very weak signals were observed in the X–A gap region in the spectra of the CO chemisorbed species (Figure 1). These weak signals were likely due to minor structural isomers in the CO-chemisorbed complexes. Stronger signals were observed in the X–A gap region in the 266 nm spectra (Figures S2–S4). In fact, weak signals were also present in the 266 nm spectrum of the bare Au_6^- (Figure S1b). These enhanced signals in the X–A gap region in the chemisorbed species at 266 nm were most likely due to autodetachment, which has been observed in other clusters with large HOMO–LUMO gaps, in particular for C_{60}^- and Au_{20}^- .^{46,49}

4. Computational Results

To find the CO chemisorption sites on the gold hexamer, we searched a variety of isomers for $\text{Au}_6(\text{CO})_n$ and $\text{Au}_6(\text{CO})_n^-$ ($n = 0–3$). Optimized ground state and selected low-lying isomers for $\text{Au}_6(\text{CO})_n$ and $\text{Au}_6(\text{CO})_n^-$ (1–18) are presented in Figures 2–4. Optimized structures for other isomers and their relative energies are presented as Supporting Information in Figures S5–S7. The computed ADEs for the ground state and computed VDEs for the ground and first excited states of the lowest energy isomers are compared with the experimental data in Table 1. The computed VDEs for all the detachment channels up to the 193 nm photon energy for the global minimum structures are given in Tables S1–S4. On the basis of these computed VDEs, we simulated the photoelectron spectra by convoluting each vertical detachment energy with a Gaussian function, as shown in Figure 5. In addition, the CO chemisorption energies were also computed, as compared with previous DFT results^{27,28} in Table 3. Since we were only concerned with the trend of the adsorption energies, no zero-point energy corrections and basis set superposition error (BSSE) corrections were pursued.

(49) Wang, X. B.; Ding, C. F.; Wang, L. S. *J. Chem. Phys.* **1999**, *110*, 8217.

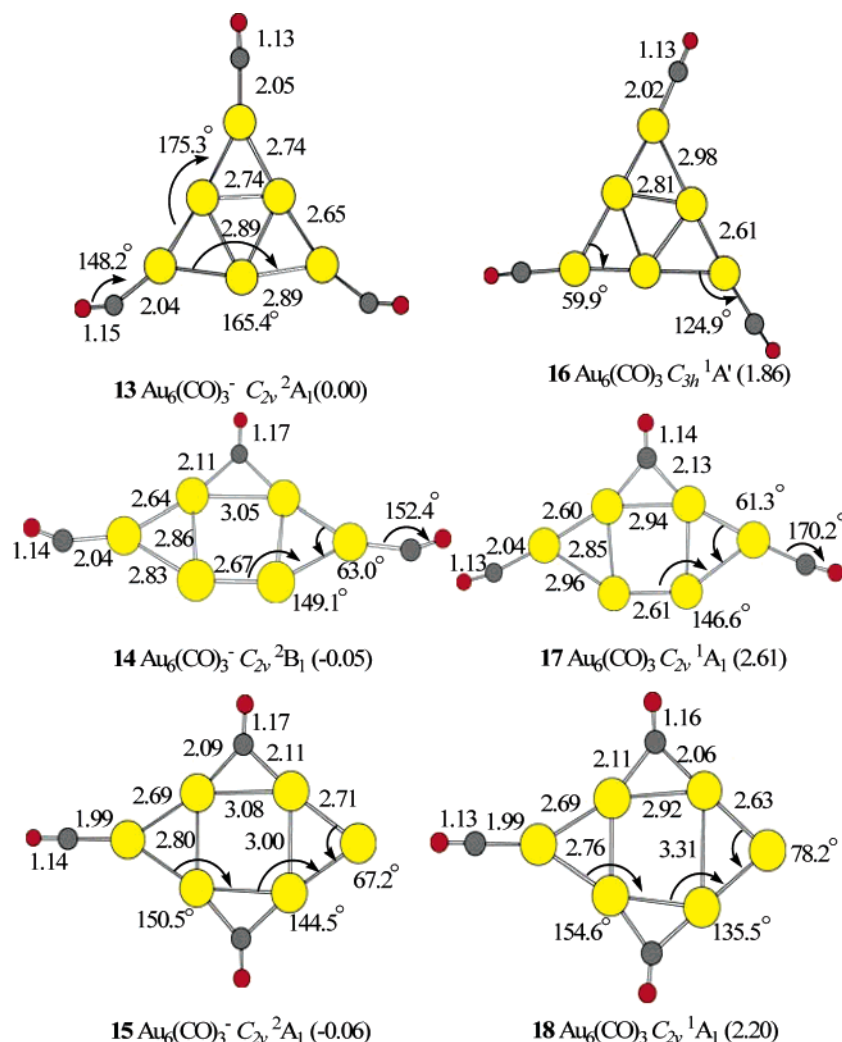


Figure 4. Optimized structures of selected low-lying isomers of $\text{Au}_6(\text{CO})_3^-$ and $\text{Au}_6(\text{CO})_3$. All bond lengths are in Å, and all relative energies (in eV) are referenced to the anion ground state.

4.1. Au_6^- and Au_6 . The identified ground state (**1**) of Au_6^- is $^2A_1'$ with one electron occupying the 6s-derived antibonding a_1' orbital of D_{3h} symmetry, in agreement with numerous previous theoretical calculations.^{33,34,36} As shown in Figure 2, the structure (**1**) can be viewed as composed of an inner triangle made from the three edge atoms and an outer triangle made from the three apex atoms. The ground state of Au_6 (**3** D_{3h} $^1A_1'$) is similar to the anion with some minor geometrical changes. In the anion ground state **1**, all Au–Au bond distances are almost equal, and the bond angle of the three edge atoms is almost linear ($\angle\text{Au}–\text{Au}–\text{Au} = 179.2^\circ$). Upon detachment of the extra electron, the inner triangle is slightly expanded while the outer triangle is slightly contracted because the extra electron is removed from the outer triangle. The anion-to-neutral structural changes from **1** to **3** can be understood from the LUMO of Au_6 or the singly occupied anion MO (SOMO $6a_1'$, Figure 6A), which is largely localized on the apex sites and exhibit weak bonding within the inner triangle and weak antibonding characters between the inner triangle and the apex atoms. We located a low-lying isomer for Au_6^- (**2** D_{2h} 2A_g , Figure 2), which was found to be only 0.30 eV higher in energy. The corresponding neutral D_{2h} structure (**4**) was found to be 1.70 eV higher in energy.

4.2. $\text{Au}_6(\text{CO})^-$ and $\text{Au}_6(\text{CO})$. The ground state and a low-lying isomer for $\text{Au}_6(\text{CO})^-$ and $\text{Au}_6(\text{CO})$ are also given in Figure 2. The anion ground state **5** is 2B_2 with C_{2v} symmetry, in which CO chemisorbs to an apex site of the triangular Au_6^- cluster. The CO chemisorption results in a slight and interesting structural distortion in the Au_6^- motif: the inner triangle is slightly expanded, and the overall shape of the Au_6 motif appears slightly elongated along the CO direction. A C_{2v} (2B_2) isomer **6** of $\text{Au}_6(\text{CO})^-$, derived from the D_{2h} isomer of Au_6^- **2**, was found to be almost degenerate with the C_{2v} ground state structure, only 0.03 eV higher in energy at the current level of theory. For neutral $\text{Au}_6(\text{CO})$, the triangular structure **7** was found to be the ground state, whereas the C_{2v} isomer **8** was found to be substantially higher in energy (by 0.99 eV). Our calculated CO chemisorption energy is 0.69 eV in $\text{Au}_6(\text{CO})^-$ and 0.61 eV in the neutral complex (Table 3).

4.3. $\text{Au}_6(\text{CO})_2^-$ and $\text{Au}_6(\text{CO})_2$. The second CO also chemisorbs to an apex site on the triangular gold hexamer (Figure 3). The geometry of the $\text{Au}_6(\text{CO})_2^-$ ground state (**9** C_{2v} 2A_1) is similar to that of $\text{Au}_6(\text{CO})^-$ **5**: the second CO appears to cause the two Au–Au bonds between the two chemisorption sites to lengthen. The only notable structural change between the ground state of $\text{Au}_6(\text{CO})_2^-$ **9** and that of the neutral **11** is with respect

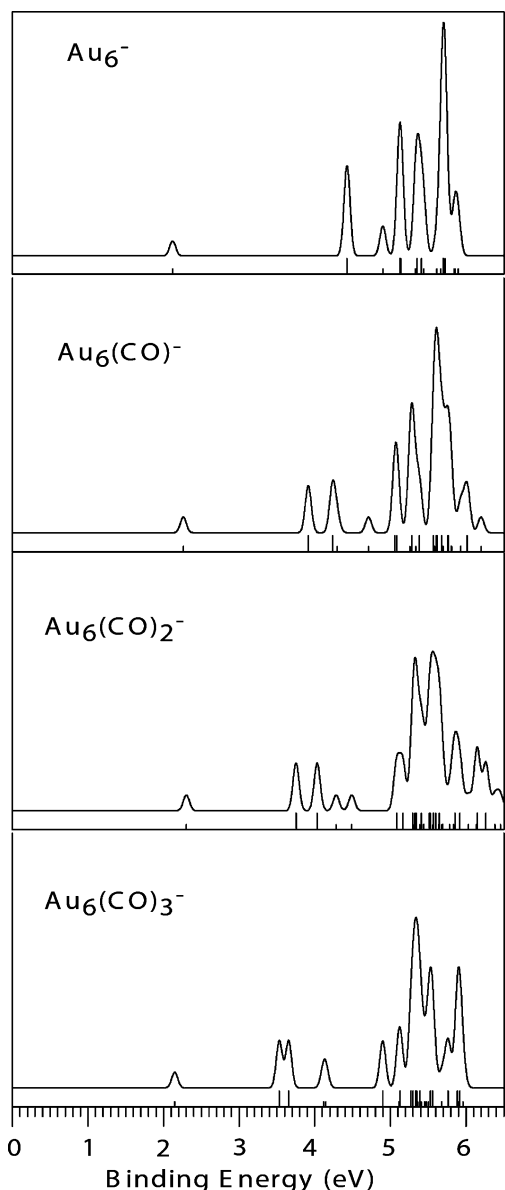


Figure 5. Simulated photoelectron spectra for the ground-state structures of $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$). The spectra were constructed by fitting the distribution of the calculated VDEs with unit-area Gaussian functions of 0.04 eV width.

Table 3. Computed Average Chemisorption Energy per CO (in eV) in $\text{Au}_6(\text{CO})_n^-$ and $\text{Au}_6(\text{CO})_n$ ($n = 1-3$)^a

species	B3LYP ^{b,c}	PW91 ^c
$\text{Au}_6(\text{CO})^-$	0.69	0.98 ^d , 1.14 ^e
$\text{Au}_6(\text{CO})_2^-$	0.62	1.06 ^e
$\text{Au}_6(\text{CO})_3^-$	0.47	0.92 ^e
$\text{Au}_6(\text{CO})$	0.61	0.89 ^d
$\text{Au}_6(\text{CO})_2$	0.56	
$\text{Au}_6(\text{CO})_3$	0.53	

^a All data are for optimized geometric structures based on the triangular Au_6 motif. ^b This work. ^c About 0.4–0.6 eV discrepancy between B3LYP and PW91 numbers was documented in ref 27. ^d From ref 27. ^e From ref 28.

to the $\angle\text{AuCO}$ bond angle, which is 156.8° in the anion, but almost linear in the neutral structure. The D_{2h} Au_6 -based structure, **10** C_s ($^2A'$), was found to be a low-lying isomer for $\text{Au}_6(\text{CO})_2^-$ only 0.20 eV higher, where one CO adsorbs to a terminal site and the other on a bridging site. The neutral

structure related to the C_s isomer of the anion was found to be a low-lying isomer for neutral $\text{Au}_6(\text{CO})_2$ **12**, which is 0.67 eV higher in energy than the triangular structure **11**. But the structure of this $\text{Au}_6(\text{CO})_2$ isomer is completely distorted, in which one Au–Au bond is broken, leading to the low symmetry C_s ($^1A'$) structure **12**. The chemisorption energy per CO in $\text{Au}_6(\text{CO})_2^-$ and $\text{Au}_6(\text{CO})_2$ decreases only slightly relative to the mono-CO chemisorbed systems (Table 3).

4.4. $\text{Au}_6(\text{CO})_3^-$ and $\text{Au}_6(\text{CO})_3$. Three anion structures (**13**–**15**) were identified for $\text{Au}_6(\text{CO})_3^-$, which are energetically degenerate at the B3LYP level and cannot be differentiated without accurate account of the dispersion electron correlation effects. Their corresponding neutral structures (**16**–**18**) were also identified as minima. However, in the neutrals, the triangular Au_6 -based structure C_{3h} ($^1A'$) is clearly the ground state (**16**), with the D_{2h} Au_6 -based structures (**17** and **18**) being 0.75 and 0.34 eV higher, respectively. Note that structures **13** and **16** are significantly different in the CO chemisorption angles. Structure **13** is derived from the ground-state structure of $\text{Au}_6(\text{CO})_2^-$ (**9**) by adsorbing a CO to the third apex site. In structure **16**, CO is almost collinear with one of the edges of the triangular Au_6 , forming a propeller shaped C_{3h} structure. Structures **14** and **15** are derived from the D_{2h} isomers of Au_6^- (**2**) with CO adsorbed at different positions. The chemisorption energy per CO in the triangular $\text{Au}_6(\text{CO})_3^-$ (**13**) seemed to decrease slightly relative to that in $\text{Au}_6(\text{CO})_2^-$, whereas in neutral $\text{Au}_6(\text{CO})_3$ the per CO chemisorption energy is nearly the same as that in $\text{Au}_6(\text{CO})_2$ (Table 3).

5. Discussion

5.1. Comparison between the Experimental Data and Theoretical Calculations. The calculated ADEs for the ground-state transitions, i.e., the electron affinities for neutral $\text{Au}_6(\text{CO})_n$ ($n = 0-3$), are compared to the experimental values in Table 1. These values, computed from the differences between the total energies of the ground states of the anions and that of the neutrals, were all based on the triangular Au_6 . Excellent agreement was observed between the calculated and experimental ADEs. For $\text{Au}_6(\text{CO})_3^-$, there are three nearly degenerate structures competing for the ground state (Figure 4). However, only the triangular Au_6 -derived structure (**13**) yielded an ADE that agrees with the experiment. The ADEs calculated for the two structures derived from the D_{2h} Au_6 isomer (**14**, **15**) were both much higher than the experimental value because the corresponding neutrals were found to be significantly higher in energy than the triangular structure (Figure 4). The calculated VDEs from the triangular Au_6 derived ground-state $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$) are also in excellent agreement with the experiment (Table 1).

The computed reorganization energies are compared with the experimental values in Table 2. Excellent agreement was also observed. The relatively small values of the reorganization energies are consistent with the small geometrical changes between the anion and the neutral ground states from the triangular Au_6 derived complexes (Figures 2–4). The largest reorganization energy was for the three CO chemisorbed complex, largely due to the CO bond angle changes between the anion **13** and the neutral **16** (Figure 4).

The calculated VDEs for the first excited state of neutral $\text{Au}_6(\text{CO})_n$ ($n = 0-3$) are also compared with the experimental

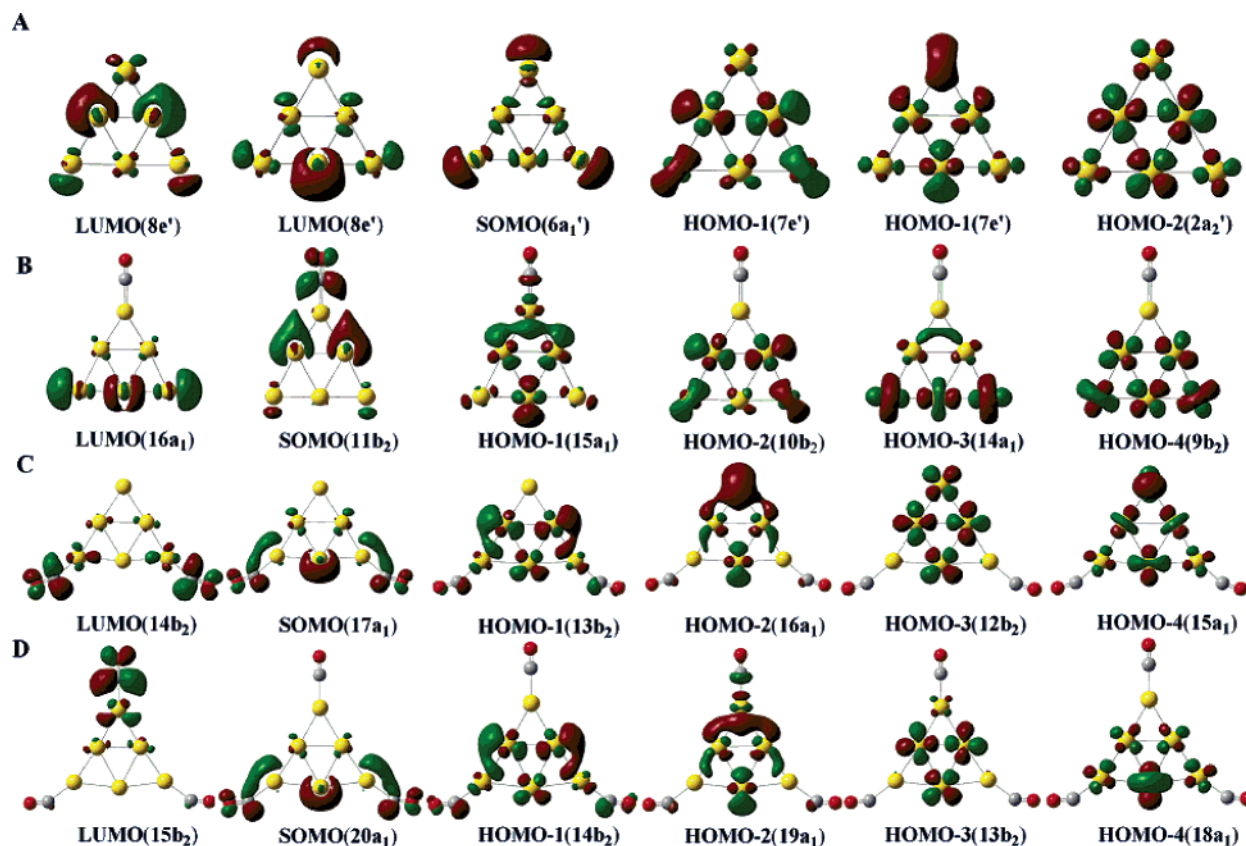


Figure 6. Molecular orbital pictures of (A) Au_6^- , (B) $\text{Au}_6(\text{CO})^-$, (C) $\text{Au}_6(\text{CO})_2^-$, and (D) $\text{Au}_6(\text{CO})_3^-$.

values in Table 1. The theoretical results are in perfect agreement with the experiment. The difference between the VDEs of the first excited state and of the ground-state detachment transitions defines the X–A energy gap, an approximate measure of the HOMO–LUMO gap of the neutral complexes. We see from Table 2 that the computed HOMO–LUMO gaps agree very well with the experimental values. In particular, the large HOMO–LUMO gap of Au_6 was well reproduced, as well as the trend of the decreasing gaps in the $\text{Au}_6(\text{CO})_n$ complexes with increasing CO chemisorption.

The PES spectra beyond the first excited-state become much more complicated with a very high density of electronic states. We also computed VDEs for the higher detachment channels up to the 193 nm photon energy. Numerical values are given in Tables S1–S4 for $\text{Au}_6(\text{CO})_n^-$ ($n = 0–3$), respectively. Simulated spectra based on the computed VDEs are shown in Figure 5. The simulated spectra agree qualitatively with the experimental spectra (Figure 1). As discussed above, the first two detachment transitions, as well as the trend of the energy gap, reproduced well the experimental observation. The weak signals observed in the HOMO–LUMO gap region in the experimental spectra of the chemisorbed complexes (Figure 1) were most likely due to the D_{2h} Au_6^- derived isomers. The computed ADEs and VDEs for these isomers (Tables S2–S4) agree with the experimental observation.

5.2. Electronic Structure and Chemical Bonding in Au_6 .

Before the discussion of the chemical interactions between Au_6 and CO, it is instructive to examine the bare Au_6 neutral. The bonding in Au_6 can be understood by mainly considering the orbital interactions of the Au $6s^1$ electrons; the Au $5d^{10}$ manifold can be qualitatively viewed as being simply broadened upon

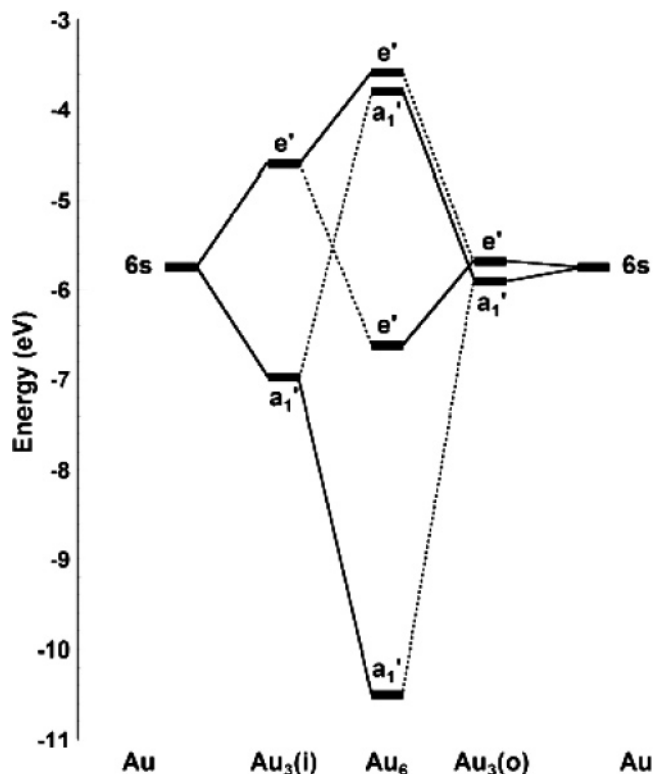


Figure 7. Orbital interaction diagram for Au_6 . $\text{Au}_3(\text{i})$ and $\text{Au}_3(\text{o})$ represent the inner and outer triangles, respectively, for the D_{3h} Au_6 (1 in Figure 2). Only one of the three degenerate Au $6s$ orbitals is shown at the far-left and far-right.

orbital overlap. As shown in Figure 7, the $6s$ orbitals of the inner $\text{Au}_3(\text{i})$ and outer $\text{Au}_3(\text{o})$ triangles in Au_6 both form $a_1' +$

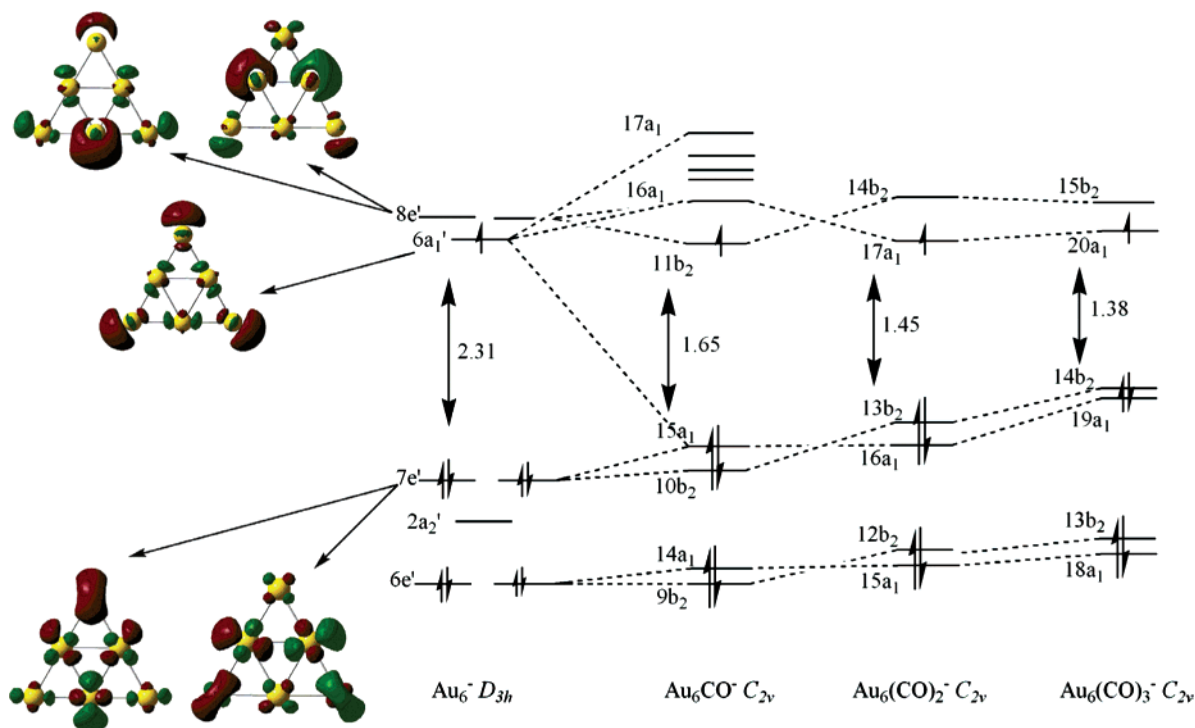


Figure 8. Schematic energy level diagrams of $\text{Au}_6(\text{CO})_n^-$ ($n = 0-3$) based on TD-DFT calculations.

e' representations. The orbital interaction between the inner and outer Au_3 fragments leads to the formation of a bonding and antibonding pair of $a_1' + e'$. The six $6s^1$ electrons fully occupy the $a_1' + e'$ bonding orbitals, giving rise to a $(a_1')^2(e')^4(a_1')^0 - (e')^0$ electron configuration, which is analogous to the delocalized π electrons in benzene. The antibonding $a_1' + e'$ orbitals, which are nearly degenerate, are unoccupied and become the LUMO and LUMO+1, respectively (Figure 7). This unique electron configuration and the delocalized nature of the $a_1' + e'$ orbitals render Au_6 a highly σ -aromatic system, explaining its special stability and its extremely large HOMO–LUMO gap. As shown in Figure 6A, the a_1' LUMO of Au_6 (the $6a_1'$ SOMO in Au_6^-) is mainly from the outer Au_3 fragment, whereas the e' LUMO+1 orbitals ($8e'$) are mainly from the inner Au_3 fragment. The different spatial distributions of these orbitals and their near degeneracy turn out to be the key in understanding the interaction of Au_6 and CO.

5.3. Electronic Structure Evolution and Chemical Bonding in $\text{Au}_6(\text{CO})_n^-$. As noted above, there are two major surprising experimental observations for CO interacting with Au_6^- . In contrast to the smaller gold clusters, chemisorptions of CO on Au_6^- do not alter significantly the electron binding energies in the $\text{Au}_6(\text{CO})_n^-$ complexes, whereas the X–A band gap decreases continuously with increasing CO chemisorption (Figure 1). This indicates that the LUMO of the neutral $\text{Au}_6(\text{CO})_n$ complexes, into which the extra electron occupies in the anions, is energetically not affected by the CO chemisorption, while the HOMO is pushed up in energy. These observations can be understood from the above MO analysis for Au_6 and the schematic MO level diagram depicted in Figure 8. The HOMO of Au_6 is the degenerate $7e'$ orbitals (Figure 6A), which involve strong s–d hybridization and are highly delocalized. The LUMO of Au_6 is $6a_1'$ (Figure 6A), which is mainly distributed on the three apex atoms (outer triangle). In the Au_6^- anion the extra electron enters the $6a_1'$ orbital and the charge is distributed on

the outer triangle. What is unique to Au_6 is that its LUMO+1 ($8e'$) (Figure 6A), which is mainly concentrated on the inner triangle, is very close in energy to the LUMO, as shown in Figure 8. The consequence of this energetic proximity between the LUMO and LUMO+1 in Au_6 will become clear when CO is adsorbed.

When one CO is coordinated to an apex atom of Au_6 , the symmetry of the molecule is lowered from D_{3h} to C_{2v} , and the degenerate LUMO+1 ($8e'$) of Au_6 is split into a_1 and b_2 orbitals. The a_1 component of the $8e'$ orbital strongly mixes with the $6a_1'$ orbital, which are both destabilized (Figure 8). On the other hand, the b_2 component of the $8e'$ orbital interacting with the CO 2π orbitals becomes the LUMO, into which the extra electron enters in $\text{Au}_6(\text{CO})^-$. Consequently, the CO chemisorption to Au_6^- induces an internal electron transfer from the outer triangle to the inner triangle. Since the b_2 LUMO of Au_6CO ($11b_2$) does not change much energetically relative to that in the bare Au_6 species, similar electron binding energies are expected for the two systems. In $\text{Au}_6(\text{CO})_2^-$ and $\text{Au}_6(\text{CO})_3^-$, the a_1 component of the $8e'$ orbital becomes the LUMO, which is again localized on the inner triangle (Figure 6) and whose binding energy is not expected to change significantly relative to that of Au_6^- . This situation is unique to the D_{3h} Au_6 structure, where there exist two spatially distinct but energetically similar regions in the molecule. Thus, in the anions, the extra electron shuttles from the outer triangle to the inner triangle upon chemisorption, resulting in a relatively constant electron binding energy for the SOMO in both Au_6^- and $\text{Au}_6(\text{CO})_n^-$ ($n = 1-3$) (Figure 8). In other words, since the extra electron in $\text{Au}_6(\text{CO})_n^-$ ($n = 1-3$) is localized on the inner Au atoms, it is not sensitive to the CO chemisorption, which only involves the outer Au atoms. This is also reflected in the similar CO binding energies between the $\text{Au}_6(\text{CO})_n$ neutrals and the $\text{Au}_6(\text{CO})_n^-$ anions and their relative independence of the CO numbers (Table 3).

The CO chemisorption also lifts the degeneracy of the $7e'$ HOMO of the D_{3h} Au_6 , forming a_1 and b_2 orbitals under the C_{2v} symmetry in $Au_6(CO)_n$. The a_1 or b_2 orbital from the HOMO mixes with the corresponding orbital from the LUMO, pushing up the HOMO level in the chemisorbed complexes, $15a_1$ for $n = 1$, $13b_2$ for $n = 2$, and $14b_2$ for $n = 3$ (Figure 8). The destabilization of the HOMO in the chemisorbed systems is further enhanced by the CO 5σ -donation, which is repulsive due to closed-shell/closed-shell interactions. The relatively constant LUMO level plus the destabilization of the HOMO level in $Au_6(CO)_n$ gives rise to the decreasing band gaps observed in the chemisorbed complexes.

The large HOMO–LUMO gap in Au_6 arises from the σ -aromaticity of the Au_6 $6s$ manifold. Accordingly, the Au_6 cluster is quite inert chemically, and it is known not to be reactive to O_2 . The destabilization of its HOMO upon CO chemisorption provides an important activation mechanism. Thus it is expected that neutral chemisorbed $Au_6(CO)_n$ complexes should be reactive toward O_2 . This cooperative chemisorption behavior seems to be an essential feature in considering the catalytic mechanisms of nanogold for CO oxidation.

6. Conclusions

We report a combined photoelectron spectroscopic and theoretical investigation of $Au_6(CO)_n^-$ ($n = 0–3$). Photoelectron spectra were obtained at several photon energies and revealed surprisingly that the electron affinities of $Au_6(CO)_n$ are relatively independent of the CO chemisorption, whereas the HOMO–LUMO gap decreases with CO chemisorption. Extensive density functional calculations were carried out, showing that CO prefers to bind to the apex sites of the triangular Au_6 in both $Au_6(CO)_n$ and $Au_6(CO)_n^-$ ($n = 1–3$). The experimental observation was elucidated through molecular orbital analyses, yielding detailed information about the molecular interactions between CO and Au_6 . The unique triangular structure of Au_6 is responsible for the surprising experimental observation. It turns out that the LUMO ($6a_1'$) and LUMO+1 ($8e'$) of Au_6 are nearly degenerate

and they are localized on the outer and inner Au_3 triangles of the D_{3h} Au_6 , respectively. Upon CO chemisorption, the symmetry of the chemisorbed complexes is lowered and the degeneracy of the LUMO+1 is lifted. One component of the LUMO+1 orbital in Au_6 becomes the LUMO in the $Au_6(CO)_n$ complexes. Since the LUMO in the $Au_6(CO)_n$ complexes is mainly localized in the inner triangle of the Au_6 substrate, it is not affected energetically by the CO chemisorption; i.e., an electron shuttling from the outer triangle to the inner triangle takes place upon CO chemisorption in the negatively charged systems. On the other hand, the HOMO of Au_6 is destabilized upon CO chemisorption due to both HOMO–LUMO orbital interactions and the CO 5σ -donation, causing the decreasing HOMO–LUMO gap. This series of complexes thus provides ideal molecular models of nanogold catalysts for CO oxidation. The destabilization of the HOMO of Au_6 upon CO chemisorption should promote reactions with O_2 , providing a mechanism for cooperative chemisorption and catalytic reactions.

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Supporting Information Available: The complete sets of photoelectron spectra for $Au_6(CO)_n^-$ ($n = 0–3$) at 532, 266, and 193 nm, experimental and theoretical electron detachment energies, and alternative structures optimized for the anions and neutrals along with their relative energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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