Interactions of Au cluster anions with oxygen

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Experimental and theoretical evidence is presented for the nondissociative chemisorption of O_2 on free Au cluster anions (Au_n^-, n=number of atoms) with $n = 2, 4, 6$ at room temperature, indicating that the stabilization of the activated di-oxygen species is the key for the unusual catalytic activities of Au-based catalysts. In contrast to Au_n^- with $n = 2, 4, 6$, O_2 adsorbs atomically on Au monomer anions. For the Au monomer neutral, calculations based on density functional theory reveal that oxygen should be molecularly bound. On Au dimer and tetramer neutrals, oxygen is molecularly bound with the O–O bond being less activated with respect to their anionic counterparts, suggesting that the excess electron in the anionic state plays a crucial role for the O–O activation. We demonstrate that interplay between experiments on gas phase clusters and theoretical approach can be a promising strategy to unveil mechanisms of elementary steps in nanocatalysis.

I. INTRODUCTION

Gold (Au) particles, which are inert in the bulk form, become efficient catalysts for various chemical reactions in the size range below 2–3 nm.[1–5] This unusual size-dependent catalytic behavior of Au is currently one of the most extensively studied subjects in chemistry, and physics.[1–23] However, no generally accepted picture for the O_2 adsorption on Au nanoclusters has appeared yet, which is believed to be responsible for the size-selectivity of Au-based catalysis.[10] In spite of extensive studies in the past, it is still controversial, whether O_2 dissociates or not on Au-based catalysts at room temperature.[6–11]

Catalytically active Au particles were suggested to be negatively charged through the charge transfer from defect sites of the oxide supports to Au.[6] It was recently shown that the mass-selected Au cluster anions (Au_n^-, n=number of gold atoms) in the gas phase exhibit comparable catalytic activities to those of oxide-supported Au particles, confirming the importance of the negative charge on Au clusters for the catalytic activities.[6,12–14] This result suggests that Au_n^- in the gas phase is a good model system to unveil the origin of the size-dependent variations of chemical activities and reaction mechanisms of Au nanocatalysts.[12–14] It is important to mention that the sizes of the gas phase clusters can be better controlled with respect to those of the metal islands grown on oxide surfaces, even though efforts have recently been made to deposit mass-selected clusters to obtain mono-dispersed clusters on the surface.[6,7] Moreover, gas phase cluster data allow direct comparisons with theoretical results. Therefore, size-dependent changes of the chemical activities can be much more precisely followed by studying gas phase clusters.

To shed light on adsorption properties of oxygen on Au cluster anions, we have studied oxygen adsorption on Au cluster anions consisting of 1, 2, 4, and 6 Au atoms using ultraviolet photoelectron spectroscopy (UPS) and density functional theory (DFT) calculations. In particular, Au_2^-, Au_4^-, and Au_6^- have recently been shown to be very active toward CO-oxidation at room temperature, and thus are suitable model systems to study interaction mechanisms of the Au-based catalysts.[9,13] We demonstrate that the formation of activated molecular oxygen is an important step for the catalytic reactions of Au nanoparticles.

II. TECHNICAL DETAILS

To synthesize $Au_nO_2^-$, Au clusters were produced in the Pulsed Arc Cluster Ion Source (PACIS),[24] and subsequently exposed to O_2. In agreement with previous results, even-numbered Au cluster anions smaller than Au_{21}^- generally react with O_2, whereas most of the odd-numbered ones are inert in O_2 environments.[12,13,25] There are, however, some exceptions for this even/odd rule of the chemical activities. Au_{16}^- is inert toward O_2 adsorption, and Au_1^- and Au_3^- partially form $Au_nO_2^-$ ($n = 1,3$). The temperature of the clusters is estimated to be room temperature. The mass of clusters was selected using a time-of-flight mass spectrometer, and the UPS spectra of the mass-selected clusters were taken using UV Laser pulse (photon energy=4.66 or 6.4 eV). The energy resolution of our UPS spectra is about 0.1 eV.

For theoretical studies, we have used the self-consistent linear combination of atomic orbital-molecular orbital approach. The total energies are calculated using DFT with the generalized gradient approximation for exchange–correlation potential, which is taken as Perdew–Wang 91 prescription (commonly referred to as PW91). The atomic orbitals are represented by a Gaussian basis. We have used the $6\text{-}311++G(3df,3pd)$ basis set for oxygen and the Stuttgart relativistic effective core potential basis set for gold.[26] The structures for the anionic and neutral clusters

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TABLE I. Establishing the accuracy of the basis set and exchange correlation potential by comparing the experimental values of ionization potential (IP), electron affinity (EA), bond length (d), and binding energy (BE).

	IP (eV)		EA (eV)		d (Å)		BE (eV)	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
Au	9.46	9.22	2.33	2.31				
O	14.08	13.62	1.72	1.46				
O_2	12.33	12.07	0.44	0.45	1.22	1.21		
AuO							2.47	2.30±0.2
Au_2			2.06	2.02	2.56	2.47	2.12	2.31
Au_4			2.82	2.77				

were optimized without symmetry constraint using the GAUSSIAN 98 code.[27] The convergence for energy and force are 0.000 01 eV and 0.003 eV/Å, respectively. To check the accuracy of the exchange–correlation potential, we calculated the ionization potential (IP), electron affinity (EA), binding energy (BE) and bond length (d) of Au, O, O_2, AuO, Au_2, and Au_2, and these are compared with the experimental data, as shown in Table I. The good agreement between theory and experiment provides confidence on the accuracy of our numerical procedure.

III. RESULTS AND DISCUSSIONS

In the following, we discuss our results on Au_n^-, Au_nO^-, and $Au_nO_2^-$. The results are contrasted with calculations of the interaction of O_2 with the neutral Au clusters.

A. Bare Au cluster anions

In Fig. 1, the calculated structures of pure Au cluster anions consisting of 1–4 Au atoms are presented. The Au–Au bond lengths are generally about 2.6–2.7 Å, which are significantly shorter than the bulk value. Au_3^- shows a slightly bent structure, and the Au_4^- exhibits a triangle frame with the fourth Au atom attached to the apex of the triangle. These results are in line with previous studies.[28,29]

For Au^-, the calculated detachment energy from the singlet state of the anion to the doublet of the neutral amounts to 2.33 eV, which is in agreement with the experimentally determined vertical detachment energy (2.31 eV). For Au_2^-, the experimentally found peaks at 2.1 and 4 eV can be assigned to the vertical detachments from the doublet state of

the anion to the singlet and triplet state of the neutral, respectively. For Au_3^-, the experimentally determined vertical detachment energy corresponds to the calculated transition energy from the singlet state of the anion to the doublet of the neutral. For Au_4^-, the peaks at 2.8 and 4.2 eV in the UPS spectrum are consistent with the theoretically determined energies arising from the transitions from the doublet to singlet and doublet to triplet transitions, respectively. The good agreement between theory and experiment demonstrates a high reliability of the computational method in the present work.

B. Chemisorption of atomic oxygen on Au cluster anions (Au_nO^-)

To shed light on the electronic and geometric structures of the Au cluster anions reacted with a single oxygen atom, UPS studies and DFT calculations were carried out, as shown in Fig. 2. In our cluster source, the partial pressure of atomic oxygen generated by the dissociation of molecular oxygen in the arc is eventually quite high, leading to the formation of gold monoxide clusters.[24,29]

Analogous to the case of the pure Au cluster anions, peak positions in the UPS spectra of Au_nO^- are in agreement with the calculated transition energies (Fig. 2), demonstrating that our calculation method is suitable for dealing with the interactions between oxygen and Au clusters. It is interesting to note that upon the chemisorption of atomic oxygen, the geometric structure of Au_4^- is significantly modified. The Au–Au bond length located nearest to the oxygen atom is changed from 2.76 to 2.63 Å upon oxygen adsorption. Contraction of the metal–metal bonding upon oxygen adsorption has also been found on transition metal surfaces, which can be roughly explained by the transfer of electrons from antibonding bands of metals to oxygen, leading to the enhanced metal–metal bonding.[30] In addition to the change in bond length, the triangle structure becomes slightly distorted upon oxygen adsorption.

C. Chemisorption of O_2 on Au cluster anions ($Au_nO_2^-$)

In Fig. 3, the UPS spectra of $Au_nO_2^-$ (produced in O_2 atmosphere) with $n = 1, 2, 4, 6$ taken using a laser with a photon energy of 4.66 eV are compared. UPS spectra for

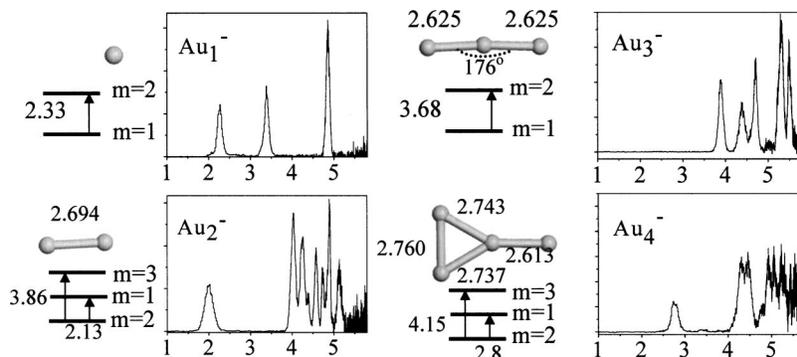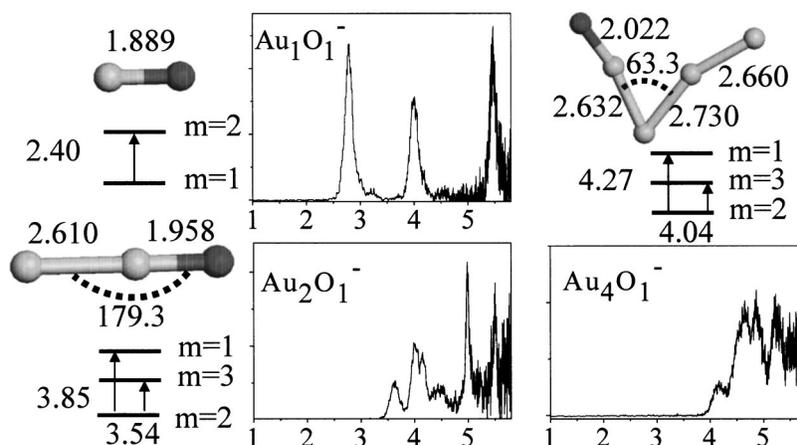
FIG. 1. Calculated transition energies from the anionic to the neutral state for the Au_n^- with $n = 1-4$, and their equilibrium structures. Experimentally taken UPS spectra (photon energy = 6.4 eV) are displayed for comparison.

FIG. 2. Calculated transition energies from the anionic to the neutral state for the AuO_n^- with $n = 1$–4, and their equilibrium structures. Experimentally taken UPS spectra (photon energy = 6.4 eV) are displayed for the comparison.

$Au_nO_2^-$ with $n = 2, 4, 6$, exhibit vibrational fine structures of about 150–180 meV corresponding to the O–O stretching frequencies, indicative of the nondissociative adsorption of O_2. The vibrational frequencies in Fig. 3 are much higher than those found for the di-oxygen species on transition metal surfaces.[31] However, note that the vibrational frequencies in the UPS spectra correspond to those of the neutral clusters having geometries of their respective anions. In the anionic states, the additional electrons occupy the antibinding $2\pi^*$ orbitals of O_2, further activating the O–O bonding, and decreasing the O–O stretching frequencies.[14] The fact that we can observe the strong vibrational structures of O–O indicates that the O–O bond length should be significantly altered upon the one electron detachment. The additional electron in the anionic state is strongly localized on oxygen, in line with recent theoretical studies, which found strong resonances of the O_2–$2\pi^*$ and the highest occupied molecular orbitals (HOMOs) of the Au cluster anions.[32]

To obtain a better understanding on chemisorption mechanism of O_2 on catalytically active Au clusters, UPS spectra of $Au_nO_2^-$ with $n = 2, 4$ are collected using a laser with a higher photon energy (6.4 eV), as indicated in Fig. 4. The distinct features of the pure Au cluster anions existing at the binding energies below about 4.7 eV completely disappear upon O_2 adsorption, and broad features between 3 and 4.5 eV (marked with A in Fig. 4) appear, followed by several narrower peaks. Comparing the UPS spectra of the $Au_nO_2^-$ with those of the respective pure Au cluster anions, the valence band structures of Au_n^- are completely changed upon O_2 adsorption, indicating significantly large interactions between O_2 and these Au cluster anions. It should be noted that not only HOMOs but also other occupied MOs of the Au cluster anions with higher binding energies participate in the O_2 chemisorption (Fig. 4). As a result of the charge transfer from the HOMOs of the Au cluster anions to oxygen, O_2 can approach closer to Au atoms, which then allows contribution of other localized MOs of the Au cluster anions with higher binding energies to the O_2 chemisorption. Due to this strong interaction between Au and oxygen, O_2 can be highly activated, leading to enhanced chemical activities toward vari-
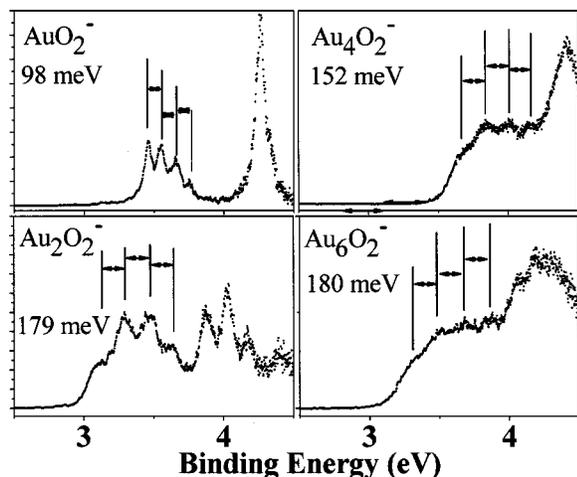

FIG. 3. UPS spectra of $A_nO_2^-$ for $n = 1, 2, 4, 6$ using a laser with a photon energy of 4.66 eV. For $n = 2, 4, 6$, vibrational fine structures are resolved, which correspond to the stretching frequencies of dioxygen species.
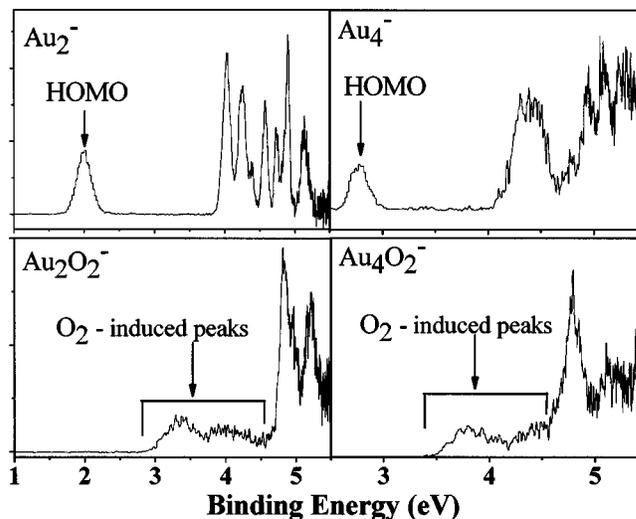

FIG. 4. Comparison of the UPS spectra for Au_n^- and $A_nO_2^-$ with $n = 2, 4$ (photon energy = 6.4 eV).
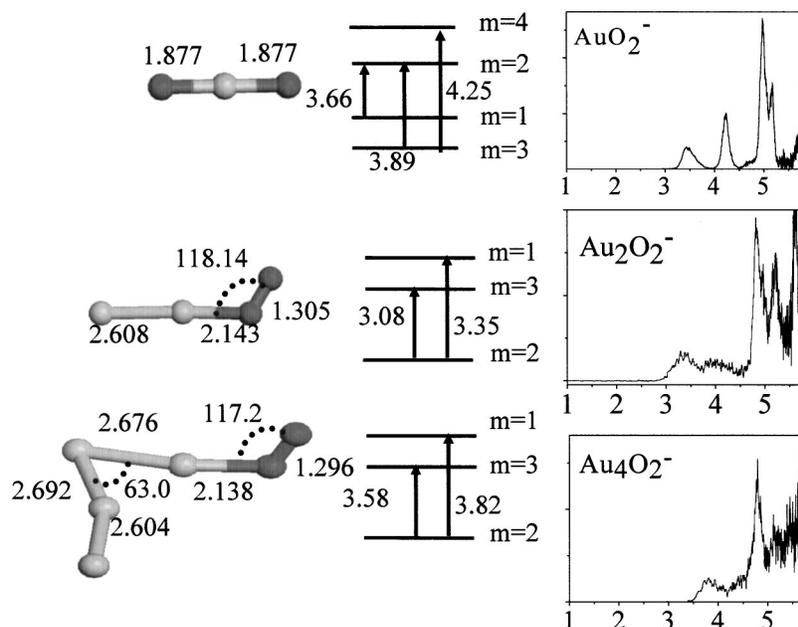
FIG. 5. Equilibrium structures of $Au_nO_2^-$ with $n = 1, 2, 4$ obtained from DFT calculations. Transition energies from the anionic to the neutral states are also shown. For comparison, experimentally taken UPS spectra (photon energy = 6.4 eV) are displayed.

ous chemical reactions such as CO-oxidation, in which activation of the O–O bonding is essential.

To better understand the structure of adsorbed oxygen on these Au cluster anions, first principle calculations were carried out. First, we focus on the even-numbered Au cluster anions. Theoretical results show that di-oxygen species are attached to Au cluster anions with one oxygen atom, and the O–O bond lengths amount to about 1.30 Å, which are significantly larger than that of an O_2 molecule (1.21 Å) (Fig. 5). To establish the accuracy of these calculated structures, we compare the calculated vertical detachment energies with the peaks in the photodetachment spectra in Fig. 5. For AuO_2^-, there are two spin multiplet structures (singlet and triplet) that are 0.23 eV apart in energy. The resulting transitions from the anion with spin multiplicity M to the neutral with spin multiplicities, $M \pm 1$, are identified in Fig. 5. Note that the calculated transition energies again compare very well with the measured peaks, demonstrating a high reliability of the theoretical calculations. Electron affinities and vertical detachment energies of the $Au_nO_2^-$ from theory agree with the experimentally found values within 0.2 eV (Table II). The O–O stretching frequencies in the DFT calculations are 142 and 145 meV for the Au_2O_2 and Au_4O_2 clusters which are close to the experimental values (150–180 meV).

TABLE II. Comparison of experimental and theoretical electron affinities (EA), vertical detachment energies (VDE), and vibrational frequencies (f) for AuO_2^-, $Au_2O_2^-$, and $Au_4O_2^-$.

	EA (eV)		VDE (eV)		f (meV)	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
AuO_2	2.95	3.30	3.66	3.46	87	88–108
Au_2O_2	2.96	2.94	3.35	3.11	142	169–189
Au_4O_2	3.44	3.50	3.82	3.70	145	142–162

For Au monomer anions, the vibrational frequency is much lower than those for the other clusters (Fig. 3). The 98 meV can be tentatively assigned to the Au–O stretching frequency, indicating that O_2 dissociatively adsorbs on Au monomer anions. In the DFT calculations for Au monomer anions, dissociative adsorption of oxygen on Au^- forming a linear O–Au–O^- structure is energetically more favorable than the molecular adsorption by about 0.7 eV, in agreement with our assignments of the vibrational fine structures in the UPS spectrum (Figs. 3, 5, and 6). Again, the electron affinity, the vertical detachment energy, and the vibrational frequency of AuO_2^- from the theoretical calculations are consistent with experimental data (Table II).

To study the dissociation process of O_2 as it approaches an Au monomer anion in detail, we have calculated the total energies of AuO_2^- as a function of the O–Au–O bond angle. The results are plotted in Fig. 6. Note that the two energy minima corresponding to molecular versus dissociative adsorption are separated by a large energy barrier of about 2 eV. In the neutral case, the energy barrier that separates the two minima is also of the same order. The only difference is that the O_2 binds dissociatively to Au^- and molecularly to the neutral Au atom. The large energy barriers suggest that the dissociative adsorption of O_2 on Au^- can only be observed under some suitable experimental conditions, for example in the presence of large amounts of atomic oxygen in the reagent atmosphere.

Our results suggest that activated molecular oxygen is an important intermediate in Au-based catalysts. On Pt-group metal surfaces, CO oxidation usually takes place through the Langmuir–Hinshelwood mechanism, in which O_2 first dissociates and then reacts with CO to form CO_2.[33] On Au cluster anions, in contrast, the stabilization of the activated molecular oxygen at room temperature can open new reaction channels (e.g., CO oxidation mediated by
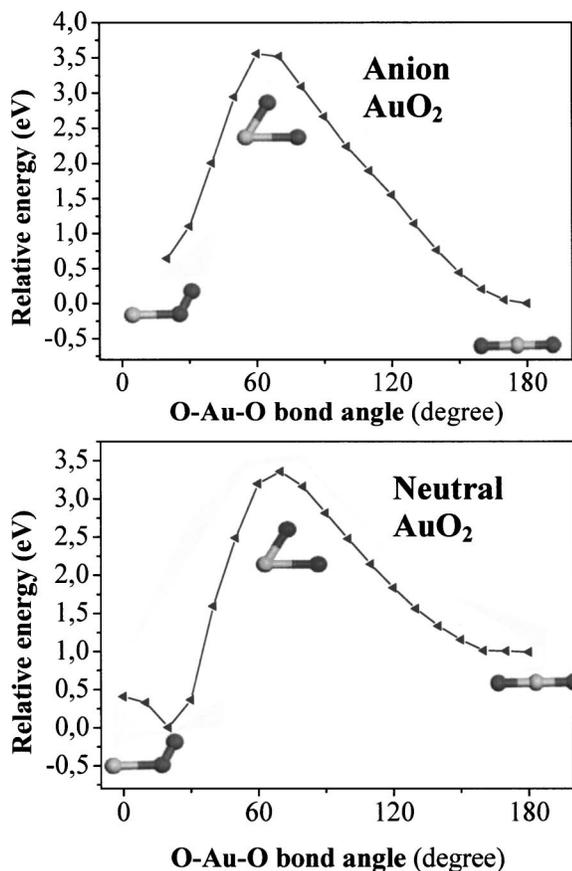
FIG. 6. Energy diagram for the dissociation of oxygen molecule on anionic and neutral Au monomer calculated based on DFT calculations.

FIG. 7. Equilibrium geometries of molecularly bound oxygen on neutral Au clusters from DFT calculations are displayed.

carbonate-like species),[2] responsible for the low temperature CO oxidation. Molecular adsorption of oxygen can play a vital role for the enhanced activities of gold clusters toward many other catalytic reactions such as partial oxidation of propylene, in which formation of hydroperoxide (H_2O_2) is suggested to be important.[15] Note that for the formation of the hydroperoxide, nondissociative adsorption of oxygen is essential.

D. O_2 adsorption on Au neutral clusters

DFT calculations are carried out for the O_2 adsorption on neutral Au clusters to study the role of the additional charge in the anionic state for the O_2 chemisorption. As mentioned before, for Au monomer, molecular adsorption is more stable than the dissociative adsorption of O_2, which is different from the result of Au monomer anions (Fig. 6). An additional charge on Au plays a crucial role for the dissociation of O_2. It is interesting to note that it is not only the activation barrier for the dissociative adsorption on Au monomers, which is influenced by the existence of the additional charge, but the metastable and ground state in the chemisorption can be exchanged depending on the charge state in the Au monomer.

The calculated structures of O_2 adsorbed on Au dimers and tetramers show that the O–O bond lengths in the neutral states are shorter with respect to the O–O bond lengths in their anionic counterparts by about 0.05 Å (Fig. 7). Obvi-
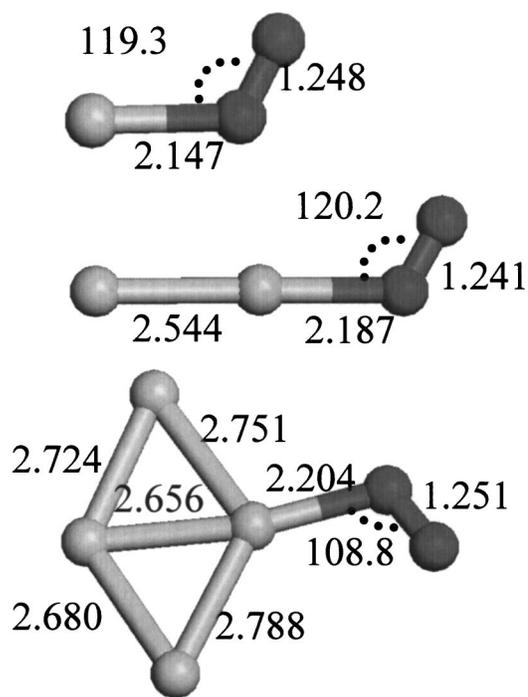
ously, the additional electron in the anionic state is important for the activation of the O–O bonding.

E. Interaction mechanism

We now examine electronic structures of neutral and anionic Au_nO_2 clusters to answer two fundamental questions in nano-gold catalysis: what role does the extra electron play and what role does the reduced size play? Note that the electronic ground state of O_2 is in the triplet state, having two unpaired electrons in the degenerate $2\pi^*$ antibonding orbitals. It can be expected that charge transfers from metal systems to these orbitals would occur when O_2 is adsorbed, which is favorable for electron pairing and adsorption. However, it should be noted that Au is the most electronegative metal, comparable to selenium, and only slightly more electropositive than sulfur (S) and iodine (I). Its electron affinity is actually greater than that of O, and therefore it can form compounds such as Au^-Cs^+ where gold becomes anionic.[34] Due to the high electronegativity of Au, charge transfers take place from oxygen to Au, when an O_2 molecule interacts with even-numbered neutral Au clusters, forming partially negatively charged Au. In Au_2O_2 and Au_4O_2, Mulliken population analysis indicates that there are 0.08 and 0.04 electrons transferred from O_2 to Au_2 and Au_4, respectively. The minor charge transfer results in very weak interactions giving small energy gains of 0.45 and 0.41 eV for Au_2 and Au_4, respectively (see Table III).

In contrast to the case of neutral clusters, anionic clusters can better facilitate electron donation to adsorbates, resulting in stronger interactions between Au and oxygen through large charge transfers. For $Au_2O_2^-$, 0.36 electrons are transferred to O_2, and the Au–O_2 interaction energy and the O–O bond length increase to 1.25 eV and 1.31 Å, respectively. For

TABLE III. Comparison of electronic and structural parameters for anion and neutral clusters. Δq is the charge transfer from Au cluster to O_2 molecule. ΔE is the energy gain when O2 interacts with Au cluster. $R1$ is the bond length between the two O atoms, $R2$ is the nearest distance between Au and O.

	AuO_2		Au_2O_2		Au_4O_2	
	Anion	Neutral	Anion	Neutral	Anion	Neutral
Δq (e)	+1.22	+0.04	+0.36	−0.08	+0.27	−0.04
ΔE (eV)	−1.04	−0.43	−1.25	−0.45	−1.07	−0.41
$R1$ (Å)	3.75	1.25	1.31	1.24	1.30	1.25
$R2$ (Å)	1.88	2.15	2.14	2.19	2.14	2.20

$Au_4O_2^-$, Au_4^- transfers 0.27 electrons to O_2 with an adsorption energy of 1.07 eV. The O_2–Au binding energies calculated in the present work agree better with experimentally determined values in comparison to the previous theoretical calculations.[35] Table III gives a comparison of the structural and electronic parameters of anion and neutral clusters, showing that the more charge O_2 gets, the longer the O–O bond length becomes, the shorter the Au–O distance becomes, and the larger the adsorption energy becomes. In AuO_2^-, there are 1.22 electrons transferred from Au^-. This significant charge transfer activates the O–O bond greatly, and dissociates O_2.

Combining UPS experiments and DFT calculations, we found that even at the smallest size, the even-numbered neutral Au cluster interacts very weakly with O_2. Thus, for the even-numbered Au cluster anions, quantum size effects do not appear to be a dominant mechanism for the reactivity. However, when an additional charge is introduced to Au clusters, the reactivity with O_2 is increased significantly. In Au monomer anions, dissociative chemisorption of O_2 takes place, indicative of a very strong Au–O interaction. Due to the large electronegativity of gold atom, Au clusters easily attract electrons from support materials to become negatively charged. This electron transfer to the Au catalysts enhances interactions with O_2, as does the catalytic activity. Therefore the substrate effects (charge transfer from substrate to Au clusters) can be important to understand the Au nanocatalysis.[6]

IV. CONCLUSION

A synergistic study involving UPS experiments and DFT calculations revealed that high chemical activities of even-numbered Au nanoclusters result from the stabilization of molecular oxygen on negatively charged Au clusters. For the anionic Au monomer, in contrast, dissociative adsorption of oxygen was found. For the neutral clusters, O_2 is less activated with respect to the anionic clusters. These results indicate that the additional electrons in the anionic states of these Au clusters are crucial for the activation of the O–O bonding. We demonstrate that interplay between cluster physics in combination with theoretical approach is a promising strategy to unveil mechanisms of elementary steps on various nanocatalysts.

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