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How O₂-Binding Affects Structural Evolution of Medium Even-Sized Gold Clusters Au_n^- (n = 20-34)

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ABSTRACT: We report the first joint anion photoelectron spectroscopy and theoretical study on how O₂-binding affects the structures of medium even-sized gold clusters, Au, (n = 20-34), a special size region that entails a variety of distinct structures. Under the temperature conditions in the current photoelectron spectroscopy experiment, O_2 -bound gold clusters were observed only for n = 22-24 and 34. Nevertheless, O₂ binding with the clusters in the size range of n = 20-34 can be still predicted based on the obtained global-minimum structures. Consequently, a series of structural transitions, from the pyramidal to fused-planar to core-shell structures, are either identified or predicted for the $Au_n O_2^{-}$ clusters, where the O_2 -binding is in either superoxo or peroxo fashion. The



identified global-minimum structures of Au_nO₂⁻ (n = 20-34) also allow us to gain improved understanding of why the clusters Au_n (n = 26-32) are less reactive with O₂ in comparison to others.

old nanoparticles show remarkable capability to catalyze ${f J}$ a variety of industrially and environmentally important chemical reactions, such as CO oxidation,¹ ethylene epoxidation,^{2,3} selective hydrogenation,⁴ C-C bond formation,⁵ and water-gas shift reaction.⁶ Many of these reactions involve activation of oxygen molecule as a key step, which is particularly challenging because of the high kinetic stability of molecular oxygen owing to its triplet ground state and strong oxygen-oxygen bond. Many efforts have been made to seek more efficient nanoscale catalysts for the activation of molecular oxygen.⁷⁻²¹ Particularly, both experimental and theoretical studies have been devoted toward the use of gold nanoclusters for oxygen activation in the CO oxidation reaction.^{22–24}

The binding of molecular oxygen on bare gold cluster anions can help in understanding the oxygen activation process. Kaldor^{25,26} and Whettan²⁷ first studied the adsorption of O₂ on a series of gold cluster anions in cluster beam experiments. They observed that only small even-sized clusters (Au_n⁻, $n \leq$ 20) were reactive toward oxygen, because the even-sized cluster anions possessed an open-shell electronic configuration with low electron binding energies which were conducive to charge transfers from Au_n^- to O_2 . Subsequent anion photoelectron spectroscopy (PES) studies showed that the molecular oxygen was chemisorbed on these even-sized Au_n clusters.^{28,29} Another PES study confirmed the molecular chemisorption and physisorption of O2 on small-sized anionic gold clusters with even and odd number of atoms, respectively.³⁰ Among the even-sized clusters, Au₁₀ and Au₁₆ showed unusual behavior, with Au16⁻ being unreactive and Au₁₀⁻ being significantly less reactive toward molecular oxygen.²⁷ The chemical inertness of Au₁₆⁻ is due to its unique hollow-cage type structure and high electron binding energy (or high electron affinity).³¹ The global-minimum structure of Au_{10}^{-} which possesses D_{3h} structure is unreactive toward O_{2h} whereas its other low-lying isomers are reactive.³² Using infrared multiple photon dissociation spectra of Au_nO₂clusters, Woodham et al.33 provided direct experimental evidence for O₂ adsorption in *superoxo* mode (binding through one oxygen atom). Previously, while studying O_2 adsorption on even-sized gold clusters in the range of n = 2-20, we have revealed a superoxo-to-peroxo (binding through both the oxygen atoms) binding transition of the O2 molecule on anionic gold clusters that occurs at Au₈^{-.34} Specifically, it was observed that n = 2, 4, 6 involve superoxo binding and n = 10, 12, 14, 18 involve peroxo binding, whereas a re-emergence of superoxo binding occurs at n = 20 because of the highly symmetrical pyramidal structure of Au₂₀⁻, which possesses a low electron affinity. O₂-derived low binding energy features were observed in the experimental spectrum of $Au_n O_2^-$ (n = 2, 4, 6, 8, and 20). Note that no direct comparison of the experimental and theoretical PES spectra was presented for $Au_{20}O_2^{-}$ at that time. Hence, the superoxo O_2 binding site on the pyramidal Au₂₀⁻ cluster and possible presence of any minor isomer contributors toward the experimental PES spectrum were not reported.

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Figure 1. 193 nm experimental photoelectron spectra (a and b) in comparison with the simulated spectra (c and d) for the low-lying isomers of $Au_{20}O_2^-$ and bare Au_{20}^- (see ref 60). The oxygen molecule is in red.

Table 1. The Experimental First VDE (X) Shown in Figures 1–4, X–A Binding-Energy Gap from the 193 nm Spectra for $Au_nO_2^-$ (n = 20-24, 34), Isomer Label, Spin Multiplicity (M_s), Relative Energies Calculated at PBE0/CRENBL-ECP (ΔE_a) and PBE0/CRENBL-ECP (with inclusion of the SO effects for Au) (ΔE_b) Levels (here, all isomers are optimized at the PBE0/CRENBL-ECP level), Theoretical First VDE, X–A Binding-Energy Gaps, and Root-Mean-Square Deviation (RMSD) between the Identified Theoretical Peaks with respect to the Experimental Peaks. ΔE_a and ΔE_b are Calculated with respect to the Lowest Energy Isomer with Molecularly Adsorbed O₂. In Case Where Multiple Isomers are Assigned, the RMSD Value is Calculated Using the Peaks from all the Assigned Isomers. All Energies and Binding-Energy Gaps are in eV. The X–A Gaps of the Major/Singly Assigned Isomers are Highlighted in Bold

	experim	theoretical							
anion cluster	VDE	X—A gap	isomer	M _s	ΔE_{a}	$\Delta E_{\rm b}$	VDE	X–A or X'–A gap	RMSD
$Au_{20}O_2^{-}$	3.81 (X')	0.54	VII	2	0.000	0.000	4.08	0.14	
	3.62 (X)		XIV	2	0.263	0.253	3.47	0.51	0.057
			XIX	2	0.335	0.333	3.78	0.16	
$Au_{22}O_{2}^{-}$	3.65 (X)	0.45	XVII	2	0.098	0.387	3.53	0.50	0.037
	3.49 (X')		XXXVIII	2	0.505	0.835	3.34	0.61	
Au2402	3.44 (X)	0.40	XVI	2	0.227	0.511	3.35	0.40	0.067
Au ₃₄ O ₂ ⁻	4.37 (X)	0.10	Ι	2	0.000	0.000	4.20	0.15	0.058
	3.93 (X')		XII	2	0.539	0.535	3.84	0.53	
	4.11 (X")		XVI	2	0.577	0.573	4.00	0.37	
^a Experimental ur	1 = 0.01	eV.							

Apart from the experimental studies, several computational studies have also been performed to investigate O_2 binding on bare gold clusters.^{35–44} Mills et al.³⁹ reported that O_2 binds more strongly with neutral and anionic gold clusters that have an odd number of electrons. Yoon et al.³⁶ found that smallersized anionic gold clusters (n = 1-3) favor molecular adsorption, whereas relatively larger-sized clusters (n = 4-8) favor dissociative adsorption. It was also reported that O_2 dissociation requires very high activation energy. The high activation barriers are consistent with the experimental observation of only chemisorbed O_2 species on the evensized Au_n^- for $n \le 20^{25,27-29,45}$ and physisorbed odd-sized Au_n^- for n = 3, 5, 7.³⁰ Several other computational studies have been carried out to examine the effect of charge state,⁴⁶⁻⁴⁸ doping,⁴⁹⁻⁵² coadsorption,^{4,53} and substrate support^{52,54-56} on the O_2 interactions with gold clusters.

Thus far, the experimental O₂-binding studies have mostly been focused on small-sized gold clusters. As mentioned above, O2 reactivity with even-sized gold cluster anions was observed only up to Au₂₀ previously.²⁵⁻²⁷ To our knowledge, there have been no joint experimental and theoretical studies on the effect of O2-binding on the structural evolution of mid-sized gold clusters. One possible reason for the lack of study of O₂bound gold clusters beyond Au₂₀⁻ is due to the relatively weak binding between O2 and medium-sized clusters in general. Indeed, in our experiment, we were unable to observe the photoelectron spectra of O_2 -bound Au_n^- clusters for n = 26-32, at least under the state-of-the-art experimental temperature conditions. Nevertheless, we observed photoelectron spectra of the three relatively small O_2 -bound gold clusters n = 20-24, as well as the largest O_2 -bound cluster Au_{34} , in the size range of gold clusters considered.

Herein, we report the first combined experimental anion PES and computational study of O₂ binding on medium evensized Au_n^- clusters (n = 20-24, 34). The medium-sized range of gold clusters (n = 20-34) is particularly interesting because the gold clusters in this size region exhibit diverse structural evolution and transition, and several distinct structures coexist for each size.^{57,58} Specifically, the Au₂₀⁻, a well-known magicnumber cluster, is a highly symmetric pyramid; the Au₂₁₋₂₅ clusters exhibit flat-planar or hollow-tubular structures; the Au₂₆⁻ cluster has the smallest core-shell structure; and the Au₃₄⁻, another known magic-number cluster, has a fluxional core-shell structure with a highly symmetrical tetrahedral Au₄ core. In view of the strong size-dependent structural evolution of gold clusters in this size range, we focus especially on the chemical interplay between the O2-binding and the structures of the gold clusters, e.g., the O₂ binding mode, and on how the O_2 binding affects the structural evolution in the host gold cluster anions. Notably, we observe a core-shell type structure for $Au_n O_2^-$ at n = 24. In fact, this is the smallest $Au_n O_2^-$ cluster with a gold core. In their bare Au_n^- counterparts, the smallest core-shell gold cluster is $Au_{26}^{-.59}$ Moreover, the identified global-minimum structures of $Au_nO_2^-$ (n = 20-34) offer an explanation of why the clusters Au_n^- (n = 26-32) are less reactive with O₂ compared to other sizes considered.

Experimental Photoelectron Spectra. Figures 1-4 present the comparison between the experimental PES spectra of $Au_n O_2^{-}$ (*n* = 20, 22, 24, and 34) at 193 nm (or 6.424 eV) photon energy and the simulated spectra of the corresponding low-energy (both major and minor) isomers. The observed major binding-energy features are designated by uppercase letters X, A, B, C, ..., where X represents the transition from the ground state of the anionic cluster to that of the neutral cluster and A, B, C, ... represent the detachment transitions to the excited states of the neutral cluster. Low binding-energy features, labeled with X', A', ... signify the presence of minor isomers of the cluster. Additionally, in some experimental spectra, the very low intensity features are marked with * to represent the existence of minor isomers that are unidentified. In Figures 1–4, we also show the 193 nm experimental spectra as well as the simulated spectra of the assigned isomers of the bare clusters, Au_n^{-} (n = 20, 22, 24, and 34), obtained from previous studies. 57,58,60,61

Table 1 shows the first vertical detachment energies (VDEs) measured from the PES experiment and the binding-energy gap (the binding-energy difference between the two peaks marked X and A), as well as the first VDEs, the spin multiplicities, and relative energies from DFT calculations for the best candidate isomers. The DFT calculations are performed at the PBE0/CRENBL-ECP level of theory, with and without considering the spin-orbit (SO) effects for gold. Note that the inclusion of SO coupling effects in the theoretical calculations results in a minor systematic reduction in the theoretical VDEs with respect to the experimental ones. Therefore, the experimental and theoretical VDE values cannot be directly compared. Rather, we have used root-mean-square deviation (RMSD) and X-A energy gaps (see below) as quantitative tools to compare the simulated spectra with the experimental spectra. The first VDE from the calculation was aligned with the first VDE (X) from the experimental measurement. Next, the RMSD was computed for the following binding-energy peaks of the simulated spectra with respect to the corresponding peaks in the experimental spectra. There is a very good agreement between the computed and

experimental energy gaps, as indicated by small average deviation (less than a tenth of an electronvolt). The X-A binding-energy gaps (of the major/singly assigned isomers highlighted in bold) and the RMSD values given in Table 1 confirm that the chosen level of theory is suitable for the $Au_n O_2^{-}$ species in the present study. Previously, we successfully used visual analysis in conjugation with the relative energy comparison, as well as RMSD in bindingenergy peak positions to identify the most stable structures of the bare gold cluster anions and CO-bound gold cluster anions.^{62–65} The structures for each cluster size are designated with the roman numerals (I, II, III, ...) which are based on the increasing values of energies computed at PBE0/CRENBL-ECP level of theory (see Supporting Figures S1-S8 and Tables S1-S9). In the following discussions, we refer to the PBE0/ CRENBL-ECP and PBE0/CRENBL-ECP//PBE0/CRENBL-ECP (with inclusion of the SO effects for Au) levels of theory as PBE0 and SO-PBE0, respectively.

 $Au_{20}O_2^{-}$. The 193 nm spectrum (Figure 1a) of $Au_{20}O_2^{-}$ exhibits broad weak peaks. Seven major peaks (X, A–F) were identified, as well as one minor peak. The initial band, designated X, at 3.62 eV denotes the region where an anion cluster transitions to that of the neutral state. The smaller band, X' at 3.81 eV, represents the contribution from another isomer. These two weak bands are attributed to the unresolved O–O vibrational progressions due to photodetachment of a superoxo unit.^{29,30,34} Subsequent regions, labeled A–F, represent excited-state transitions of the neutral cluster. They can be found at 4.16, 4.35, 4.58, 4.78, 4.96, and 5.24 eV.

A total of 44 low-lying isomers were examined (see Figure S1), out of which the simulated spectra of three candidate isomers are presented in Figures 1c. The Supporting Information shows simulated spectra of the remaining isomers identified. A combination of three isomers (with isomer XIV as the major contributor, and isomers VII and XIX as the minor contributors, toward the experimental PES spectrum) is found to accurately replicate the experimental spectrum. The RMSD between the peaks of the experimental spectrum and the peaks of the combined simulated spectrum of the assigned isomers is calculated to be 0.057. The major isomer XIV shows superoxo O_2 binding with the gold nanocluster. The two minor isomers exhibit peroxo O_2 binding. In all three isomer structures, the stable tetrahedral pyramidal Au₂₀⁻ motif is present.^{34,61} Energetically, isomer VII is the lowest in energy, computed at both PBE0 and SO-PBE0 levels of theory, whereas isomers XIV and XIX are higher in energy. Isomer XIV has a relative energy of 0.263 and 0.253 eV at both PBE0 and SO-PBE0 levels of theory, respectively. Isomer XIX is even higher in energy with relative energy of 0.335 and 0.333 eV at both PBE0 and SO-PBE0 levels of theory, respectively.

In the major isomer XIV, the oxygen is adsorbed in superoxo mode on an apex site of the Au_{20} pyramid. Its simulated PES spectrum has 12 bands within the experimental window, from 3.47 to 5.87 eV. Out of the 12 bands, 3 bands are found to contribute significantly to the experimental spectrum. The band with peak at 3.47 eV describes experimental peak X; the band at 3.97 eV reproduces experimental peak A; the peak at 4.55 eV reproduces peak D; the peak at 4.81 eV reproduces peak E; and the peak at 5.14 eV reproduces peak F.

The minor isomer XIX has the oxygen adsorbed in a peroxo fashion on one of the near-apex edges of its pyramidal structure. Like isomer XIV, its PES spectrum also demonstrates 12 peaks within the experimental range. Three peaks at 3.78,



Figure 2. 193 nm experimental photoelectron spectra (a and b) in comparison with the simulated spectra (c and d) for the low-lying isomers of $Au_{22}O_2^-$ and bare Au_{22}^- (see ref 57). The oxygen molecule is in red.



Figure 3. 193 nm experimental photoelectron spectra (a and b) in comparison with the simulated spectra (c and d) for the low-lying isomers of $Au_{24}O_2^-$ and bare Au_{24}^- (see ref 57). The gold atoms in the core of the cluster are denoted in green. The oxygen molecule is in red.

3.94, and 4.43 eV reproduce the measured peaks X', A, and C, respectively, of the experimental PES spectrum.

The minor isomer VII has the oxygen adsorbed on the lateral edge of the pyramidal cluster in a peroxo fashion. In the simulated PES spectrum, again there are 12 peaks within the experimental range. Band peaks are found at 4.08, 4.22, 4.33, 4.51, 4.57, 4.83, 4.89, 5.20, 5.50, 5.69, 5.84, and 5.97 eV. Three of these peaks (4.22, 4.57, and 4.83 eV) reproduce three experimental peaks for bands B, D, and E within the experimental spectrum.

 $Au_{22}O_2^-$. The 193 nm spectrum of $Au_{22}O_2^-$ (Figure 2a) shows broad weak peaks. However, sharp well-defined peaks are also present at higher binding energies. This suggests that there are superoxo and peroxo isomers coexisting. There exist two weak initial peaks corresponding to individual ground states of the two coexisting isomers. The major isomer band at

 \sim 3.65 eV is denoted X, and the minor isomer band X' is at \sim 3.49 eV. Subsequent bands are denoted A, B, C, D, E, and F, located at 4.10, 4.35, 4.46, 4.58, 4.71, and 4.89 eV, respectively. The remaining bands are too poorly resolved to meaningfully analyze.

A total of 45 low-lying isomers were examined. Two of these isomers (XVII and XXXVIII) are found to reproduce the experimental PES spectrum (Figure 2a,c). Although the major isomer XVII possesses a degree of symmetry lower than that of the $Au_{20}O_2^-$ clusters, a deformed tetrahedral pyramidal motif is clearly visible in its case. The tetrahedral pyramidal motif is completely absent in the case of the minor isomer XXXVIII, which exhibits a flat-cage type structure with relatively higher degree of symmetry (C_2). The O_2 binding is in a peroxo fashion in the case of the major isomer, whereas a superoxo type binding on an apex site is observed in the case of the



Figure 4. 193 nm experimental photoelectron spectra (a and b) in comparison with the simulated spectra (c and d) for the low-lying isomers of $Au_{34}O_2^-$ and bare Au_{34}^- (see refs 61 and 87). The gold atoms in the core of the cluster are denoted in green. The oxygen molecule is in red.

minor isomer. The simulated PES spectrum of the major isomer can accurately reproduce seven major peaks of the experimental spectrum: X, A, B, C, D, E and F at 3.53, 3.99, 4.21, 4.32, 4.45, 4.62, and 4.78 eV, respectively. The minor isomer can account for the weak band X' (3.49 eV). This feature results from the O-O vibrational excitation upon photodetachment from the minor isomer.^{29,30,34} TThe other bands of the minor isomer are buried under those of the major isomer in the combined PES spectrum. The RMSD between the peaks of the experimental spectrum and the peaks of the combined spectrum of the assigned isomers is calculated to be 0.037. Isomer XVII has a relative energy of 0.098 and 0.387 eV at both PBE0 and SO-PBE0 levels of theory, respectively, whereas the minor isomer XXXVIII has a relative energy of 0.505 and 0.835 eV at both PBE0 and SO-PBE0 levels of theory, respectively.

The minor isomer XXXVIII has a striking resemblance to one of the assigned bare isomers (isomer III) of Au_{22}^{-} . The structures are nearly identical except for a displaced gold atom, reflecting that the superoxo type binding on an apex site has little effect on the host structure. The major isomer XVII, on the other hand, is quite different from the assigned bare clusters as the tetrahedral pyramidal motif is absent in the case of the bare Au_{22}^{-} isomers. It seems that the peroxo O_2 binding has a much greater effect on the structure of the Au_{22}^{-} cluster than on the magic-number and high-symmetry Au_{20}^{-} cluster.

 $Au_{24}O_2^{-}$. The experimental PES spectrum (Figure 3a) showed eight clear peaks at 3.44, 3.84, 4.16, 4.58, 4.92, 5.11, 5.21, and 5.38 eV. Following the naming scheme outlined earlier, the first peak was designated X, while subsequent peaks were labeled A–G, respectively. The sharper nature of the bands in comparison to those of $Au_{20}O_2^{-}$ and $Au_{22}O_2^{-}$ and the absence of weak features in the low-binding region indicate that the O_2 binding is in the peroxo mode.

Out of the 42 examined low-lying isomers, isomer XVI (Figure 3c) can accurately reproduce the experimental PES spectrum. The initial X band of isomer XVI is at 3.35 eV, and the bands A–G are at 3.76, 4.03, 4.48, 4.78, 4.87, 5.13, and 5.34 eV, respectively. After accounting for the 0.09 eV red shift, the calculated RMSD between the experimental and theoretical

spectrum was 0.067. Isomer XVI as predicted has O_2 binding in a peroxo mode. Unlike the bare Au_{24}^{-} clusters where a hollow-tubular structure is populated, ^{57,58} the $Au_{24}O_2^{-}$ exhibits a core–shell with one Au-atom core. This illustrates that upon peroxo O_2 binding the structure of Au_{24}^{-} cluster changes significantly. This is the smallest reported O_2 -bound gold cluster with a core atom. Energetically, isomer XVI has a relative energy of 0.227 and 0.511 eV at both PBE0 and SO-PBE0 levels of theory, respectively.

Au_nO₂⁻ (n = 26-32). As mentioned above, O₂-bound gold clusters in this size range were not observed under the current experimental conditions, likely because of either relatively weak binding between O₂ and these clusters or the high electron binding energy (electron affinity) of the bare clusters. As a result, their photoelectron spectra were not able to be observed. We speculate that if the cluster beam could be generated below room temperature in future photoelectron spectroscopy experiments, PES spectra of certain sized gold clusters (e.g., n = 30, see below) with relatively strong O₂ adsorption ability might be observed. Hence, we report the speculative simulated spectra based on the obtained globalminimum clusters Au_nO₂⁻ (n = 26-32).

In Supporting Figures S4–S7 and S9 and Tables S4–S7, the simulated spectra for each cluster size in this range and their corresponding relative energies, computed first VDE, and X–A gap data are presented, respectively. Without the experimental spectra to compare with, for now, we tentatively assign the lowest-energy isomers for each cluster size as the global minima (see Figure S9). Definite assignments could be made if the experimental data become available in the future. The structures of the assigned isomers are presented in Figure 6.

Au₃₄**O**₂⁻. The experimental PES spectrum of $Au_{34}O_2^-$ consists of weak bands in the low-binding-energy spectrum, followed by the binding-energy features with relatively higher intensity and a high degree of overlap. The unique character and high degree of overlap made the determination of the global minimum structure especially difficult. Eight major peaks X, A–G are observed at 4.37, 4.47, 4.51, 4.68, 4.82, 5.02, 5.25, and 5.41 eV. The two minor peaks are labeled X' at 3.93 eV and X" 4.14 eV, respectively. These two features are likely



Figure 5. Size dependences of (a) O_2 adsorption free energies (ΔG_{ads}) for the best candidate isomer of $Au_nO_2^-$ (n = 20-34) clusters identified, (b) Hirshfeld charges (H_c) for the host gold cluster Au_n^- and the adsorbed O_2 for the best candidate isomer of $Au_nO_2^-$ (n = 20-34) clusters, and (c and d) the Mayer bond orders (M_{bo}) for the O–O and Au–O bonds of the best candidate isomer of the $Au_nO_2^-$ (n = 20-34) clusters, and (c and d) the Mayer bond orders (M_{bo}) for the O–O and Au–O bonds of the best candidate isomer of the $Au_nO_2^-$ clusters. The horizontal dashed line at -0.61 eV in panel a separates the more reactive gold clusters (n = 20-24 and 34) and less reactive gold clusters (n = 26-32) with O_2 . The more reactive gold clusters exhibit more negative adsorption free energy (< -0.61 eV). For the $Au_{32}O_2^-$ cluster, both the doublet and quartet spin states are very close in energy. Therefore, ΔG_{ads} , H_{c} and M_{bo} data are presented for both doublet and quartet spin states. The quartet spin state is denoted by the "×" symbol.

due to the O–O vibrational excitation upon photodetachment of O₂ binding in relatively weak superoxo mode.^{29,30,34} A small unresolved peak, designated *, at approximately 3.42 eV is similar to the peak labeled X in the experimental spectrum of Au₃₄⁻ cluster. This peak could be from the bare Au₃₄⁻ cluster which might have been formed after the photodissociation of Au₃₄O₂⁻ cluster. The experimental spectrum shows a strong similarity to that of the bare Au₃₄⁻ cluster. This indicates that the Au₃₄⁻ structure changes little upon O₂ binding.

We examined 64 low-lying isomers, of which isomer I (Figure 4c,d) accurately reproduces the major bands of the experimental PES spectra. The simulated PES spectrum of isomer I can mimic the bands X and A-G at 4.21, 4.33, 4.37, 4.52, 4.68. 4.86, 5.10, and 5.27 eV, respectively. The two minor bands X' and X" in the low-binding-energy region can be assigned to the isomers XII and XVI, respectively. Both isomers are the minor contributors toward the experimental PES spectrum. A red shift of about 0.088 eV is observed in the theoretical peaks, and the RMSD is calculated to be 0.058. Overall, the combined simulated spectra of three isomers agrees well with the experimental spectrum. Isomer I is the lowest in energy at both PBE0 and SO-PBE0 levels. Isomer XII has a relative energy of 0.539 and 0.535 eV at PBE0 and SO-PBE0 levels, respectively. Isomer XVI has a relative energy of 0.577 and 0.573 eV at both PBE0 and SO-PBE0 levels of theory, respectively. In the case of isomer I, the oxygen molecule is chemisorbed in the peroxo style, whereas the two minor isomers exhibited superoxo type O₂ binding. The superoxo adsorption observed in the minor isomers is

supported by the fact that both X' and X" are very broad peaks. The major as well as two minor isomers contain a tetrahedral Au_4 core, the same as the one observed in the case of the bare Au_{34} cluster.⁶¹ The structures of isomer I and the bare Au_{34}^- are very similar. This is confirmed by the very small RMSD of 1.18 Å for the atomic coordination of gold atoms between the two structures.

Adsorption Free Energies, Hirshfeld Charges, and Mayer Bond Orders. The adsorption free energies of O_2 on the Au_n^- clusters at 25 °C are computed as follows:

$$\Delta G_{\text{ads}} = G(\text{Au}_n \text{O}_2^-) - G(\text{Au}_n^-) - G(\text{O}_2)$$

where G represents the free energy. A more negative value of $\Delta G_{\rm ads}$ indicates stronger adsorption. Here, adsorption free energy calculations were performed using the PBE exchangecorrelation functional and the LANL2DZ basis set⁶⁶⁻⁶⁸ with the corresponding effective core potential (ECP), provided in the Gaussian16 package. The change in the calculated ΔG_{ads} versus the cluster size (the number of gold atoms n) is displayed in Figures 5a. When multiple isomers are assigned, the ΔG_{ads} is shown only for the major isomer. As expected, $Au_n O_2^-$ complexes which show superoxo O_2 -binding have a ΔG_{ads} lower than the ones which exhibit peroxo type O₂binding. Among the five weakly reactive gold clusters with O_{2} , $Au_{30}O_2^-$ shows the most favorable O_2 -binding, whereas $Au_{32}O_2^-$ shows the least favorable O_2 -binding. The extremely small adsorption free energy of $Au_{32}O_2^{-}$ indicates O_2 physisorption rather than chemisorption. Although the ΔG_{ads} of $Au_{30}O_2^-$ is only 0.006 eV higher than that of the $Au_{24}O_2^-$



Figure 6. Structural evolution of the O₂ adsorbed on even-numbered anionic gold clusters $Au_nO_2^-$ (n = 20-34). Major isomers are plotted in larger size than the minor isomers. The gold atoms in the core of the cluster are denoted in green. The oxygen molecule is in red.

cluster, it is still not observed in the cluster beam. This is because the electron ADE (adiabatic detachment energy) of 3.50 eV serves as a threshold to disfavor the O₂-binding on Au_n⁻ clusters, and the ADE (~3.70 eV) of low-lying isomers of Au₃₀⁻ is above the threshold.⁶⁹ Nevertheless, our DFT computation suggests that among the five less reactive gold clusters within the range of n = 26-32, the O₂-bound cluster is most likely to be observed at n = 30 in future photoelectron spectroscopy experiments if the cluster beam could be generated below room temperature.

To understand the charge transfer upon the O_2 binding, the Hirshfeld charge analysis⁷⁰ (implemented in Gaussian16 package) of the Au_nO₂⁻ clusters was performed. The Hirshfeld charges (H_c) of the Au_n⁻ and O₂ components of the Au_nO₂⁻ cluster are shown in Figure 5b. A charge transfer of about 0.25–0.40 e from Au_n⁻ to O₂ is observed in all the cases except Au₃₂O₂⁻ where only 0.19 e of charge is transferred. This confirms the O₂ physisorption in the case of Au₃₂O₂⁻. From Figure 5b, it appears that the larger sized cluster entails slightly less charge transfer to O₂, except the largest cluster Au₃₄⁻. Indeed, Au₃₄⁻ is a special case because it is a magic-number cluster.

To further assess the O_2 adsorption, we calculated the Mayer bond order⁷¹ (implemented in Gaussian16 package) of the O– O and Au–O bonds in the Au_nO₂⁻ clusters. The Mayer bond orders (M_{bo}) of the O–O and Au–O bonds in the Au_nO₂⁻ cluster are presented in panels c and d of Figure 5, respectively. For the clusters with peroxo O₂-binding, the bond orders of the two Au–O bonds were averaged. The O–O bonds are stronger in the case of clusters with superoxo O₂-binding than the ones with peroxo O₂-binding. The Au–O bonds show the similar trend except for Au₃₂O₂⁻ and Au₃₄O₂⁻. The Au–O bond is strongest in the case of Au₃₄O₂⁻ (averaged bond order = 0.76), which is consistent with the large ΔG_{ads} and high charge transfer observed in its case. For Au₃₂O₂⁻, the O–O bond is strongest (bond order = 1.11), and the Au–O bond is the weakest (bond order = 0.55) among the Au_nO₂⁻ clusters, reconfirming the O₂ physisorption.

Structural Evolution of $Au_nO_2^-$ (n = 20-34) Clusters with Even Numbered Gold Atoms. The identified most stable structures of the O2-bound anionic gold clusters are presented in Figure 6. This particular size range of bare gold clusters exhibits diverse structures, which include pyramidal, hollow-tubular, fused-planar, and core-shell. For the size of n= 20, the highly symmetric pyramidal motif is observed in both major and minor isomers, with the O₂ binding in the superoxo fashion in the major isomer and a peroxo fashion in both the minor isomers. A distorted pyramidal Au₂₀ motif (shown in blue) with an intact triangular Au_{10} face is observed again in the major isomer of $Au_{22}O_2^{-}$. The minor isomer at n = 22 has a fused-planar structure. The O2 shows peroxo binding in the major isomer but superoxo O_2 binding in the minor isomer at n = 22. A core–shell structure emerges at n = 24 with one core gold atom and with the O_2 binding in the peroxo fashion. Note that Au_{24}^{-} is the smallest cluster anion which transforms to a core-shell cluster upon O₂ binding. The core-shell structures with core atom remain dominant in the n = 24-28 range with the O_2 binding in superoxo fashion at n = 26 and in peroxo fashion for n = 28 and 30. Au₃₂O₂⁻ exhibits a triangular Au₃ core, whereas the highly symmetric tetrahedral Au₄ core is observed in the major as well as minor isomers of $Au_{34}O_2^{-}$. A superoxo O_2 binding is observed in the case of $Au_{32}O_2^-$, and a peroxo O2 binding is observed in the case of the major isomer of $Au_{34}O_2^-$. Both the minor isomers of $Au_{34}O_2^-$ exhibit a superoxo O₂ binding.

In conclusion, we present a combined experimental and theoretical study of O₂ binding on medium-sized evennumbered gold anion clusters, Au_n^- (n = 20-34). Photoelectron spectra were measured for the clusters Au_n^{-} (n = 20-24, 34) and used to compare with theoretical calculations for the identification of the structures and sites of O₂ adsorption on the gold clusters. The global minima of the O₂-bound gold clusters $(Au_nO_2^{-})$ are searched using the basin-hopping global optimization technique in conjugation with DFT calculations. Vertical detachment energies are obtained for the low-lying isomers based on the DFT computation with the inclusion of spin-orbit effects for gold to make simulated photoelectron spectra and to compare with the experimental PES data for clusters n = 20-24, and for the magic-number cluster n = 34. The global-minimum search resulted in a wide variety of structures for the O₂-bound gold clusters, such as pyramidal, fused-planar, and core-shell structures. Transitions from the pyramidal to fused-planar to core-shell structures for the host Au_n^- clusters and the adsorbed O_2 in either superoxo or peroxo fashion are observed. Notably, the O2-bound Au24O2is the smallest cluster with a core-shell type structure for the gold. This is in contrast with the hollow-tubular type structures found dominant for the bare Au24 cluster. Moreover, the identified global-minimum structures of $Au_n O_2^-$ (n = 20-34) allow us to examine why the Au_n^- clusters in the range of n =26-32 are less reactive with O_2 than other sizes. Our DFT computation of the O₂ adsorption free energies show that the more reactive gold clusters (n = 20-24, 34) exhibit more negative adsorption free energy (< -0.61 eV) whereas less reactive gold clusters (n = 26-32) exhibit less negative adsorption free energy (> -0.61 eV). Among the gold clusters Au_n^{-} (n = 26-32), the O₂-adsorbed Au_{30}^{-} is most likely to be observed in future photoelectron spectroscopy experiments if the cluster beam could be generated below room temperature.

METHODS

Experimental Methods. The photoelectron spectroscopy (PES) experiment was performed using a magnetic-bottle apparatus equipped with a laser vaporization cluster source. The details of this experimental measurement have been published previously.⁷²⁻⁷⁴ In brief, a pulsed laser was used to vaporize a gold disk target to produce a plasma within a largewaiting-room cluster nozzle. Meanwhile, a helium carrier gas pulse was delivered to the nozzle which cooled the plasma and initiated cluster nucleation. For the O2 binding experiment, a helium carrier gas was seeded with 0.1% O2. The latter reacted with the gold clusters within the nozzle, forming various $Au_nO_2^-$ clusters. These cluster anions were then entrained in the helium carrier gas and underwent a supersonic expansion. After passing through a skimmer, the cluster anions from the collimated cluster beam were extracted at 90° into a time-offlight mass spectrometer. Clusters of particular size for the study of interest were mass-selected and decelerated before they were photodetached by radiation from the 193 nm ArF excimer laser. A magnetic bottle was used to collect the photoelectrons at almost 100% efficiency into a 3.5 m long electron flight tube. These photoelectrons were collected for kinetic energy analyses. The known spectra of Au⁻ were used to calibrate the photoelectron kinetic energies. The latter were then subtracted from the photon energies to obtain the photoelectron binding energy spectra. The apparatus has an electron kinetic energy resolution of $\Delta E_k/E_k \approx 2.5\%$, i.e., about 25 meV for 1 eV electrons.

Computational Methods. The search for global-minimum structures of Au_nO₂⁻ was carried out using the basinhopping global optimization method^{75,76} along with density functional theory optimization. During the basin-hopping search, the local-minimum structure obtained after each accepted Monte Carlo move was reoptimized using a DFT method, i.e., the Perdew-Burke-Ernzerhof (PBE) exchangecorrelation functional⁷⁷ and the double-numerical polarized (DNP) basis set with effective core potential (ECP), given in the DMOL³ 4.0 program.^{78,79} A loose integration grid was used for the DFT calculations at this step. Both biased and unbiased BH searches were performed. In the biased search, the coordinates of the two oxygen atoms were fixed and all the gold atoms could relax. In the unbiased BH search, all oxygen and gold atoms could move. More than 1000 different isomers were recorded for every size of clusters. This isomer population consisted of the structures with both molecularly chemisorbed oxygen (O₂ binding) as well as dissociated oxygen (atomic O binding). Extensive studies have shown that although dissociated oxygen isomers are generally the global minimum, the high energy barrier for O_2 dissociation cannot be overcome under the experimental PES conditions.³² Therefore, among the isomers obtained from the BH global search we focused mainly on the ones with molecularly adsorbed oxygen as the candidates for the lowest-energy structures. These isomers were then reoptimized by employing the DMOL³ 4.0 program using the fine integration grid. Both doublet and quartet multiplicities were considered at this step.

Next, the candidate isomers with the lower-energy spin multiplicity were also reoptimized based on the PBE0 functional⁸⁰ with the CRENBL-ECP⁸¹ basis set, given in the Gaussian16 package.⁸² However, for candidate isomers in the n= 26-32 range, the re-optimization was performed at the PBE0/TZP level, with inclusion of the relativistic effects under zeroth-order regular approximation (ZORA) as given in the ADF2013 program.⁸³⁻⁸⁵ During this re-optimization step, some isomers were found to converge to the same structure. This lowered the number of candidate isomers for each size of cluster. Lastly, single-point energy calculations of the reoptimized structures were performed based on the PBE0 functional with CRENBL-ECP basis set and with incorporation of the spin-orbit (SO) effects for the gold, given in the NWCHEM 6.6 program.⁸⁶ The incorporation of SO effects for the gold has been proven to provide a nearly quantitative agreement between the experimental and simulated spectra for bare gold, doped gold, and CO-bound gold clus-ters.^{57,62-65,87-89} The first VDE for each structure was computed as the difference between the energies of the neutral and anionic cluster at the optimized (PBE0 level) anion geometry. The electronic density of states was obtained by adding the binding energies of the occupied deeper orbitals to the first VDE. Each VDE feature was added with a Gaussian width of 0.035 eV to produce simulated spectra, which were then used to compare with the experimental spectra of $Au_n O_2^{-1}$ in order to determine the structures that give the best agreement between the simulation and the measurement. The binding-energy gap (eV) between the first and second highest occupied molecular orbitals, which is viewed as the gap between peaks labeled X and A, was also computed for each candidate isomer.

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ASSOCIATED CONTENT

Supporting Information

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Additional simulated spectra, relative energies, and Cartesian coordinates (PDF)

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The authors declare no competing financial interest.

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