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# Determination of CO Adsorption Sites on Gold Clusters $Au_n^-$ (n = 21-25): A Size Region That Bridges the Pyramidal and Core-Shell Structures

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Supporting Information

ABSTRACT: We perform a joint photoelectron spectroscopy and theoretical study to investigate CO adsorption sites on midsized gold clusters,  $Au_n^-$  (n = 21-25), a special size region that bridges the highly symmetric pyramidal cluster Au<sub>20</sub><sup>-</sup> (Li et al. Science 2003, 299, 864) and the prevailing core-shell clusters starting from Au<sub>26</sub><sup>-</sup> (Schaefer et al. ACS Nano 2014, 8, 7413). Particular attention is placed on whether the CO binding can significantly change structures of the host clusters in view of the fact that the size-dependent structural change already occurs for bare gold clusters in this size range. A transition from hollow-tubular to fused-planar structures is identified for the  $Au_nCO^-$  clusters even though the CO molecule mostly binds to an apex gold atom. The computed CO adsorption energy and HOMO-LUMO gap of the gold clusters suggest that among the five gold clusters the  $Au_{23}^{-}$  cluster exhibits the strongest CO binding and thereby could be a good catalytic model system.



hereas bulk gold is chemically inert, gold nanoparticles show remarkable catalytic activities.<sup>1–6</sup> Several important reactions have been found to be catalyzed by gold nanoparticles, such as epoxidation,  $^{7-16}$  C–C bond formation,<sup>17</sup> selective or partial oxidation of methanol,<sup>18,19</sup> and water-gas shift reaction.<sup>20,21</sup> In particular, the CO oxidation reaction has been studied extensively.<sup>22-24</sup> The size, shape, and net charge of the gold clusters can have a great effect on their chemical activity toward CO oxidation.<sup>25–29</sup> The smaller gold clusters show higher reactivity toward CO and  $O_2^{.30,31}$  The role of the support is also vital.<sup>6,32–34</sup> The gold clusters tend to become more reactive for the CO oxidation when they are supported on oxide surfaces, in particular, reducible oxide surfaces.<sup>35–38</sup> The charge transfer from the oxide support to the gold cluster is responsible for the enhanced activity of the cluster.<sup>35,36,39</sup>

There have been numerous studies devoted to the understanding of CO or O<sub>2</sub> adsorption on gold clusters.<sup>40-51</sup> For example, the  $O_2$  binding is shown only by certain even numbered anionic gold clusters, <sup>52–56</sup> whereas anionic, <sup>44–47,57</sup> neutral,<sup>58</sup> and cationic<sup>59</sup> gold clusters are capable of binding CO on their surface. Several studies have shown that the CO adsorbs on the low-coordinated apex or corner atoms of the gold clusters.  $^{41,45-47,60,61}$  In general, the structures of the gold clusters exhibit little change upon adsorption of a single CO molecule.<sup>41,45,57,58,61</sup> For example, the Au<sub>17</sub><sup>-</sup> cage remains intact in Au<sub>17</sub>CO<sup>-</sup>, whereas the Au<sub>16</sub><sup>-</sup> and Au<sub>18</sub><sup>-</sup> cages undergo minor structural change to optimize the interactions with CO.62 The adsorption of multiple CO molecules can induce a significant change in the small-sized gold cluster structures.<sup>42,46,60,63</sup> A unique 2D-3D-2D structural transition is observed upon subsequent adsorption of four CO molecules

in the case of  $Au_7^{-.42}$  In our previous studies, we observed that the chemisorption of CO on gold clusters induces a decrease in the binding energies of the host clusters.<sup>41,42,47</sup> This decrease in the binding energies upon CO chemisorption enhances the O<sub>2</sub> coadsorption, which requires electron transfer from the host gold cluster to  $O_2$ .

To understand the interaction between CO and gold clusters, the cluster size is of principal importance. The size range of  $Au_n^{-}$  (n = 21-25) is particularly interesting because in this range more than one structural transition occurs as well as coexistence of different structures for each size. In our previous studies, we showed that several different structural motifs such as pyramidal, hollow-tubular, fused-planar, and core-shell can be seen in this size range.<sup>64,65</sup> In this Letter, we report a joint photoelectron spectroscopy (PES) and density functional theory (DFT) study of the interaction of a single CO molecule with the gold clusters in this special size range of  $Au_n^{-}$  (n = 21-25). To our knowledge, this size range of gold clusters is the largest one thus far for the PES experimental study of CO binding.

The experimental photoelectron spectra of  $Au_n CO^-$  (*n* = 21-25) at 193 nm (6.424 eV) photon energy and their comparison with the theoretical photoelectron spectra of the lowest-lying isomers are shown in Figures 2-6, respectively. The observed features are labeled by capital letters X, A, B, C, ..., where X denotes the transition from the ground state of the anion to that of the neutral and A, B, C, ... denote detachment

Received: August 2, 2018 Accepted: September 4, 2018 Published: September 5, 2018 Table 1. Experimental First VDE Labeled as X, X', or X'' in Figures 2–6, the Energy Gap between Peaks Labeled X and A and Peaks Labeled X' and A' from the 193 nm PE Spectra for  $Au_nCO^-$  (n = 21-25), Point Group, Relative Energies Computed at PBE0/CRENBL-ECP ( $\Delta E_a$ ) and PBE0/CRENBL-ECP (with SO effects for Au) ( $\Delta E_b$ ) Levels (with all isomers being optimized at the PBE0/CRENBL-ECP level), Theoretical First VDE, Energy Gaps (X–A and X'–A'), and Root-Mean-Square Deviation (rmsd) in the Theoretical Peak Positions with Respect to the Experimental Peak Positions<sup>a</sup>

anion cluster	experimental <sup>0</sup> VDE	gap	isomer	point group	$\Delta E_{\mathrm{a}}$	$\Delta E_{ m b}$	VDE	Gap	rmsd
3.81 (X')	0.52 (X'-A')	II	$C_s$	0.024	0.043	3.650	0.552	0.024	
		Ι	$C_s$	0.000	0.000	3.452	0.753		
Au <sub>22</sub> CO <sup>-</sup>	3.37 (X)	0.59 (X–A)	Ι	$C_s$	0.000	0.000	3.218	0.592	0.009
	3.45 (X')		III	$C_1$	0.102	0.095	3.329	0.428	0.015
	3.74 (X'')		IV	$C_1$	0.130	0.124	3.587	0.123	0.042
			II	$C_1$	0.096	0.128	3.154	0.855	
Au <sub>23</sub> CO <sup>-</sup>	3.69 (X)	0.12 (X–A)	VII	$C_1$	0.069	0.079	3.820	0.121	0.021
			Ι	$C_1$	0.000	0.000	3.723	0.317	
Au <sub>24</sub> CO <sup>-</sup>	3.42 (X)	0.60 (X–A)	II	$C_1$	0.015	0.003	3.318	0.584	0.063
			Ι	$C_s$	0.000	0.000	3.700	0.072	
Au <sub>25</sub> CO <sup>-</sup>	3.98 (X)	0.13 (X–A)	Ι	$C_s$	0.000	0.000	3.760	0.177	0.071
	4.07 (X')	0.17 (X'-A')	II	$C_s$	0.013	0.029	3.875	0.177	0.039
			III	$C_1$	0.068	0.081	3.936	0.063	
a . 11 .	<i>b</i>	2 1							

<sup>*a*</sup>All energies are in electronvolts. <sup>*b*</sup>Experimental uncertainty:  $\pm 0.01$  eV.

transitions to the excited states of the neutral cluster. Weaker features labeled with X', X'', A', A'', ... indicate that they are from minor isomers. Also, in some Figures, the weak features are labeled with \*, representing the presence of unidentified minor isomers. For the sake of discussion, the 193 nm experimental PES along with the theoretical spectra of assigned structures of pristine gold clusters,  $Au_n^-$  (n = 21-25), from a recent study<sup>65</sup> are also presented in Figures 2-6. The experimental first VDEs and the energy gap (energy difference between peaks labeled X and A and peaks labeled X' and A') are given in Table 1, along with the computed first VDEs and relative energies calculated at the PBE0/CRENBL-ECP (with and without the inclusion of spin-orbit (SO) effects for gold) level of theory for the top candidates. Note that a systematic shift to the lower binding energy side is typically observed in the theoretical VDEs with respect to the experimental one due to the SO coupling used for the theoretical calculations. Because of this, we did not directly compare the first VDE values obtained from experimental and theoretical PES. Instead, in Figure 1, we show the change of experimental and theoretical X-A energy gaps of the assigned major isomers with respect to number of gold atoms. The theoretical X-A



**Figure 1.** Experimental and theoretical X–A gaps of  $Au_nCO^-$  (n = 21-25) versus the number of gold atoms.

energy gaps show excellent agreement with the experimental values with an average deviation of 0.025 eV. Furthermore, we calculated root-mean-square deviation (rmsd) in the spectral peak positions for the isomers presented in Table 1 and Figures 2-6. In the case where more than one isomer is assigned, the rmsd in spectral peak positions is also calculated for the overlay of the spectra of the major and minor isomers (Table S11). The first peak of the simulated spectra was aligned with the first experimental VDE (X); then, the rmsd was calculated for the subsequent peaks of the simulated spectra with respect to the corresponding experimental peaks. The rmsd values given in Table 1 and Table S11 and the X-A gap comparison shown in the Figure 1 all confirm that the selected level of theory is appropriate for the Au<sub>n</sub>CO<sup>-</sup> species in the current study. Note that in our previous studies we have successfully used a combination of visual inspection, relative energy comparison, and rmsd in spectral peak positions for the identification of the global-minimum structures of bare and alloy gold clusters.<sup>66,67</sup> For each cluster size, the structures are named with roman numerals (I, II, III, ...) which are based on the order of increasing energies at the PBE0/CRENBL-ECP level of theory. Hereafter, the PBE0/CRENBL-ECP and PBE0/CRENBL-ECP//PBE0/CRENBL-ECP (with SO effects for Au) levels of theory are referred to as PBE0 and SO-PBE0, respectively.

 $Au_{21}CO^-$ . The 193 nm spectrum (Figure 2c) of Au<sub>21</sub>CO<sup>-</sup> shows three well-resolved bands labeled A, B, and D at 4.27, 4.42, and 4.68 eV, respectively, and three broad bands labeled X', X, and C around ~3.80, ~3.90, and ~4.50 eV. Band A possesses a shoulder band labeled A' on its higher binding side at 4.33 eV. The relatively lower intensities of bands X' (compared to X) and A' (compared to A) along with the presence of weak features D' and E' at 4.84 and 5.08 eV, respectively, suggest the presence of minor isomers in the cluster beam. Beyond band E', the PES spectrum signals are almost continuous, and no definitive PES bands can be identified. The PES spectrum of  $Au_{21}CO^-$  differs significantly from that of the  $Au_{21}^-$  (Figure 2a).



Figure 2. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of Au<sub>21</sub>CO<sup>-</sup>.



Figure 3. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of Au<sub>22</sub>CO<sup>-</sup>.

We examined a total of 43 low-lying structures. The simulated spectra of isomers I, II, and IV are compared with the experimental 193 nm spectrum in Figure 2c-e. The simulated spectra of the rest of the isomers can be found in the Supporting Information. Isomers I, II, and III (Table 1 and Table S1) are almost degenerate at both PBE0 and SO-PBE0

levels of theory, with isomer I being the lowest energy isomer at both the levels. Isomer IV is slightly higher in energy at both PBE0 (0.174 eV) and SO-PBE0 (0.115 eV) levels of theory. A combination of the simulated spectra of isomers IV and II (with isomer IV being the major and isomer II being the minor contributor toward the experimental PES spectrum) is also

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 $\begin{bmatrix} (a) Au_{23}^{-} \\ EXP. 193 nm \\ & & & \\ &$ 

Figure 4. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of Au<sub>23</sub>CO<sup>-</sup>.

presented in Figure 2d. The intensities of the bands of minor isomer II are reduced to 90% for better visualization. Despite a systematic red shift of ~0.18 eV, isomers IV and II can successfully reproduce X–A and X'–A' (see Table 1) gaps, respectively, as well as all of the major features of the experimental spectrum, with bands X, A, B, C, and D coming from isomer IV, while bands X', A', D', and E' come from isomer II.

Features C and D are also present in the simulated spectrum of isomer II but are buried under those of isomer IV. Lowest energy isomer I can be neglected for assignment because its spectrum is unable to reproduce bands X, A, A', and B of experimental spectrum. Also, the energy gap between the first two peaks in the case of isomer I is much larger than the X-A gap of the experimental PES spectrum. Note that although isomers I and II are structurally and energetically very similar, we only assign isomer II as the minor isomer because a combination of isomer IV as the major and isomer II as the minor gives a very small rmsd of 0.018 in the spectral peak positions. On the contrary, a combination of isomer IV as the major and isomer I as the minor is presented in Figure \$33, giving a relatively large rmsd of 0.310 in the spectral peak positions. Because of the lack of bands X', X, and C in its simulated spectrum (Figure S1(III)), isomer III can also be ruled out. Hence isomer IV is assigned as the major and isomer II is assigned as the minor isomer in the case of Au<sub>21</sub>CO<sup>-</sup>. Note that the hollow-tubular structure of major isomer IV is derived directly from that of the major isomer I of the bare Au<sub>21</sub><sup>-</sup>cluster. The minor isomer II contains the pyramidal Au<sub>20</sub> motif and is directly derived from isomer V of bare Au<sub>21</sub><sup>-</sup>cluster.<sup>65</sup>

 $Au_{22}CO^-$ . The 193 nm spectrum (Figure 3c) of  $Au_{22}CO^-$  shows three broad bands X, X', and X'' at ~3.35, ~3.45, and ~3.75 eV, respectively and three well-resolved bands labeled A, D, and E at 3.96, 4.66, and 4.95 eV, respectively. The bands A

and D are relatively sharp, whereas bands B, C', and D'' at 4.27, 4.33, and 4.40 eV, respectively, are closely spaced. Relatively weak bands X', X'', C', D'', and E' indicate the presence of minor isomers in the cluster beam. The 193 nm spectrum displays continuous signals beyond 5.0 eV. Note that the PES spectrum of  $Au_{22}CO^-$  differs significantly from that of the  $Au_{22}^-$  (Figure 3a), indicating that CO either induces an appreciable geometry change in the gold cluster or favors to bind with some higher energy isomers of bare  $Au_{22}^-$ .

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A total of 51 isomers were examined, out of which the theoretical spectra of the top four lowest-lying isomers are compared with the 193 nm experimental spectrum in Figure 3c-e. Isomer I is the lowest energy isomer at both PBE0 and SO-PBE0 levels of theory. At the PBE0 level, isomer II is the second lowest in energy, but at the SO-PBE0 level, isomer III is the next lowest energy isomer behind isomer I. Isomers II-IV are very close in energy at both theoretical levels. Considering isomer I as the major, and isomers III and IV as the minor contributors toward the experimental spectrum, an overlay of the simulated spectra of isomers I, III, and IV is also presented in Figure 3d. The peak intensities in the spectra of the minor isomers III and IV are reduced to 90% for better visualization. The spectra of these three isomers can successfully reproduce all of the bands present in the experimental spectrum, with bands X, A, B, D, and E coming from isomer I, bands X', C', and E' coming from isomer III, and bands  $X^{\prime\prime}$  and  $D^{\prime\prime}$  coming from isomer IV. The other spectral features of isomers III and IV are buried under the bands A and E of the spectrum of isomer I. The X–A gap value of isomer I is very close to the corresponding value from the experimental spectrum. Isomer II can be ruled out because its simulated spectrum cannot reproduce bands X', X'', A, and E. The absence of band A results in a much larger gap (0.855 eV)between its first two bands of the spectrum of isomer II. Thus on the basis of both the simulated spectra and the computed



Figure 5. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of Au<sub>24</sub>CO<sup>-</sup>.

energetics we assigned isomer I as the major and isomers III and IV as the minor isomers.

The fused-planar major isomer I of  $Au_{22}CO^-$  does not resemble any of the structures of bare  $Au_{22}^-$  isomers determined from our previous study.<sup>65</sup> This means that CO induces appreciable structural change in the gold cluster upon CO adsorption. The minor isomers III and IV of  $Au_{22}CO^-$ , both of which possess hollow-tubular structures, are derived from the major isomer II and minor isomer III of their bare counterparts.<sup>65</sup>

 $Au_{23}CO^-$ . The 193 nm spectrum (Figure 4d) of  $Au_{23}CO^$ shows three broad bands labeled X, A, and B at ~3.70, ~3.80, and 4.0 eV, respectively, followed by four relatively sharp bands labeled C, D, E, and \* at 4.27, 4.52, 4.84, and 5.04 eV, respectively. Compared with other bands the band E is relatively weak. Beyond the band labeled as \*, the PES spectrum signals are continuous, and no definitive PES bands can be identified. The PES spectrum of  $Au_{23}CO^-$  looks somewhat simpler than that of the bare  $Au_{23}^-$  (Figure 4a), indicating the presence of a single dominant isomer in the cluster beam. Also, the spectral patterns of  $Au_{23}CO^-$  and  $Au_{23}^$ are quite different, suggesting that CO induces a notable change in the host gold cluster.

The top 38 low-lying structures were examined, and isomer I was found to be the lowest energy candidate at both of the theoretical levels. At PBE0 and SO-PBE0 levels, a total of 11 and 9 structures, respectively, are within relative energy of 0.1 eV. It must be noted that a systematic blue shift instead of a red shift is observed in the case of the simulated spectra of all of the low-lying candidates of Au<sub>23</sub>CO<sup>-</sup>. This seems to be the unique electronic property of the 23-atom gold cluster anion because it is also seen in the case of the bare Au<sub>23</sub><sup>-</sup> cluster in our previous study.<sup>65</sup> The theoretical spectrum of isomer VII can successfully reproduce most of the bands (X, A, B, C, D, and E) present in the experimental spectrum. The X–A gap

(0.121 eV) of isomer VII also matches pretty well with that of the experimental spectrum (0.12 eV). The theoretical spectrum of isomer I does not seem to exhibit bands A and C of the experimental spectrum. The absence of band A leads to a larger X-A gap (0.317 eV) in the case of isomer I. On the basis of the relative energies and X-A gap comparison with experiment, all of the other low-lying candidates except isomer V can be ruled out for the assignment. Isomer V can also be rejected because its simulated spectrum does not seem to exhibit bands D and E and has an extra band between bands B and C. Thus isomer VII is identified as the only structure in the cluster beam of Au<sub>23</sub>CO<sup>-</sup>. It must be noted that the band labeled as \* is not reproduced by the theoretical spectrum of isomer VII, indicating the presence an unidentified minor isomer in the cluster beam.

In Figure 4b, we present an alternative assignment for bare  $Au_{23}^{-}$  cluster, which is different from the one presented in the previous study.<sup>65</sup> We assign hollow-tubular isomer IX with  $C_{2\nu}$  symmetry as the major isomer and fused-planar isomer V as the minor isomer. This combination can successfully reproduce most of the bands of the experimental PES spectrum with bands X, A, B, C, and D coming from isomer IX and bands C' and D' coming from isomer V. The previous assignment for bare  $Au_{23}^{-}$ , is also presented in Figure 4c for comparison. For more details such as the relative energies and X–A gap, please refer to our previous paper.<sup>65</sup> The assigned fused-planar isomer VII of  $Au_{23}CO^{-}$  does not resemble any of the structures of bare  $Au_{23}^{-}$  clusters. This means again that CO induces a marked structural change in the gold cluster upon CO adsorption.

 $Au_{24}CO^{-}$ . The 193 nm spectrum (Figure 5c) of  $Au_{24}CO^{-}$  displays a broad band labeled as X at ~3.40, followed by two closely spaced bands A and B at 4.02 and 4.09 eV, respectively, and two sharp bands labeled as C and D at 4.33 and 4.56 eV, respectively. There is an unresolved shoulder (labeled as \*) to

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Figure 6. Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of Au<sub>25</sub>CO<sup>-</sup>.

the band X on its low binding-energy side (~3.30 eV). No discernible PES spectral features are observed beyond the band D. Upon comparison with the PES spectrum of bare  $Au_{24}^{-}$ , it seems that upon CO adsorption the PES spectrum becomes much simplified. This indicates that all of the major features of the experimental spectrum of  $Au_{24}CO^{-}$  must come from a single isomer. Overall, the PES spectrum of  $Au_{24}CO^{-}$  looks quite different from that of the bare  $Au_{24}^{-}$  (Figure 5a), indicating that the structure of CO-adsorbed  $Au_{24}^{-}$  cluster differs notably from that of the bare  $Au_{24}^{-}$ .

A total of 46 isomers were examined, and isomers I and II emerged as the top two candidates at both the PBE0 and SO-PBE0 levels of theory. The theoretical spectrum of isomer II seems to match quite well with experimental spectrum because it can reproduce all of the bands *X*, *A*, *B*, *C*, and D of the experimental spectrum. Isomer I can be ruled out due to the absence of bands X and C in its simulated spectrum. For now, we assign isomer II as the single isomer present in the cluster beam, but there is a possibility of a minor isomer owing to the presence of the weak feature on the low binding-energy side of the X band in the experimental spectrum.

The assigned fused-planar isomer II of  $Au_{24}CO^-$  is derived directly from that of the isomer VII of bare  $Au_{24}^-$  cluster. The CO adsorption seems to stabilize a high-energy structure of bare  $Au_{24}^-$ .

 $Au_{25}CO^-$ . The 193 nm spectrum (Figure 6c) of  $Au_{25}CO^$ displays four congested bands labeled X, X', A, and A' at 3.98, 4.07, 4.11, and 4.24 eV, respectively, followed by three relatively well-spaced bands labeled B, C', and C at 4.45, 4.54, and 4.74 eV, respectively. Following band C, there are two weak bands labeled D and D' at 4.82 and 4.87 eV, respectively. Beyond 5 eV, no identifiable features are observed in the 193 nm PES spectrum. The PES spectrum of  $Au_{25}CO^-$  is even more congested than that of the bare  $Au_{25}^-$  (Figure 6a). The two PES spectra look quite different, suggesting that the structures of the CO-adsorbed  $Au_{25}^{-}$  cluster are different from that of the bare  $Au_{25}^{-}$ .

A total of 58 isomers were examined, and isomers I, II, and III emerged as the top candidates with very close energies at both PBE0 and SO-PBE0 levels of theory. Isomers I and II are considered as major and minor contributors, respectively, and an overlay of their theoretical spectra is presented in Figure 6d. The peak intensities in the spectrum of the minor isomer II are reduced to 90% for better visualization. The spectrum of isomer III is shown in Figure 6e for the sake of discussion. All of the bands of the experimental spectrum are well reproduced by the combined spectra of isomer I and II with bands X, A, B, C, and D coming from isomer I and bands X', A', C', and D' coming from isomer II. The absence of bands X', A, C', D, and D' in the simulated spectrum of isomer III and a very small X–A gap compared with the experimental data rule out isomer III as a candidate.

The major and minor isomers of  $Au_{25}CO^-$  both possess the same fused-planar Au skeleton of the isomer I of bare  $Au_{25}^-$  cluster.<sup>65</sup> It must be noted that although the bare  $Au_{25}^-$  cluster has a hollow-tubular structure, the CO prefers to adsorb on the fused-planar one.

Adsorption Energies, HOMO-LUMO Gap, and Bader Charges. The adsorption energies of CO on the  $Au_n^-$  clusters is calculated as follows

$$\Delta E_{ads} = E_{ZPE,BSSE}(Au_nCO^-) - E_{ZPE}(Au_n^-) - E_{ZPE}(CO)$$

where *E* represents the electronic energy. The subscript ZPE represents that the electronic energy includes the zero-point energy correction. For cluster–CO (Au<sub>n</sub>CO<sup>-</sup>) complexes, the basis set superposition error (BSSE) was taken into the account in which gold cluster Au<sub>n</sub><sup>-</sup> and CO were treated as two separate fragments. A more negative value of  $\Delta E_{ads}$  reflects more favorable adsorption. The change in the calculated  $\Delta E_{ads}$ 

and the HOMO-LUMO (H–L) gaps of the assigned major isomers of  $Au_n^-$  and  $Au_nCO^-$  clusters with respect to number of gold atoms *n* are shown in Figure 7a,b, respectively. The



**Figure 7.** Size dependences of adsorption energies ( $\Delta E_{ads}$ ), HOMO–LUMO (H–L) gaps, and Bader charges ( $B_c$ ) of the global-minimum Au<sub>n</sub>CO<sup>-</sup> (n = 21-25) clusters.

HOMO and LUMO levels of the Au<sub>n</sub><sup>-</sup>, Au<sub>n</sub>CO<sup>-</sup> clusters, and CO molecule are compared in Figures S34–S38. We note that the Au<sub>n</sub><sup>-</sup> clusters here were constructed by removing the CO molecule from the corresponding Au<sub>n</sub>CO<sup>-</sup> clusters. Among the five clusters, Au<sub>23</sub>CO<sup>-</sup> shows the most favorable adsorption of CO, while Au<sub>25</sub>CO<sup>-</sup> shows the least favorable adsorption. The H–L gaps show an even–odd trend, with the closed orbital clusters (n = 21, 23, 25) exhibiting higher H–L gaps. Upon adsorption of CO, the gap increases in the case of n = 23 and 24 but decreases in the case of n = 21, 22, and 25, with

 $Au_{23}CO^-$  showing the largest increase and  $Au_{25}CO^-$  showing the largest decrease.

To gain deeper insight into the mechanism of CO adsorption, we perform the Bader charge analysis<sup>68–70</sup> of the Au<sub>n</sub>CO<sup>-</sup> clusters. The Bader charges ( $B_c$ ) of the Au<sub>n</sub><sup>-</sup> and CO fragments of the Au<sub>n</sub>CO<sup>-</sup> cluster are presented in Figure 7c. A small charge transfer from Au<sub>n</sub><sup>-</sup> to CO is observed in the case of n = 21-24, whereas charge transfer in the reverse direction (from CO to Au<sub>n</sub><sup>-</sup>) is observed for n = 25.

Structural Evolution of  $Au_nCO^-$  (n = 21-25). The identified global-minimum structures for the CO-adsorbed gold cluster anions are shown in Figure 8. This special size range is known for exhibiting a variety of bare-gold structures, including pyramidal, hollow-tubular, and fused-planar. For n = 21, the major isomer possesses a hollow-tubular structure, whereas the most stable pyramidal  $Au_{20}$  motif is present in the minor isomer. A transition from hollow-tubular to fused-planar structure is observed at n = 22. The fused-planar structures remain dominant in the n = 22-25 range, as the major isomer of  $Au_{22}CO^-$ , singly assigned isomers of  $Au_{23}CO^-$  and  $Au_{24}CO^-$ , as well as the major and minor isomers of  $Au_{25}CO^-$  all exhibit the fused-planar structures. The minor isomer of  $Au_{22}CO^-$  possesses a hollow-tubular structure.

As seen in Figure 8, the CO molecule prefers to adsorb predominantly on the apex sites of the  $Au_n^-$  clusters. The minor isomer of  $Au_{25}CO^-$  is the only exception, where the CO molecule adsorbs on a nonapex and somewhat flat surface site. The Au atoms of the apex-sites are typically coordinated to five and four neighboring Au atoms, while the Au atom of the surface site is coordinated to five of the neighboring Au atoms.

In summary, we report a combined theoretical and experimental photoelectron spectroscopy study of adsorption of carbon monoxide on a special size range of gold anion clusters,  $Au_n^{-}$  (n = 21-25). Photoelectron spectra are obtained for these clusters and used to compare with theoretical calculations for structure elucidation. The basin-hopping (BH) search for this size range yielded diverse structures for the COadsorbed gold clusters, such as pyramidal, fused-planar, and hollow-tubular. The transition from the hollow-tubular to fused-planar structures for host  $Au_n^-$  and CO adsorption on the apex-sites is observed. The n = 23 size is the most favorable for CO adsorption because it possesses the highest adsorption energy, and the computed HOMO-LUMO gap also increases upon the adsorption of CO in its case. We speculate that the  $Au_{23}^{-}$  cluster might be a good model catalytic system among the five clusters. Because the activation barrier to the reaction also depends on other factors such as change in the electronic structure of the catalyst upon adsorption of the reactants and the local cone angle and local coordination number of the active Au sites,<sup>31</sup> computation of the full reaction profile in a



Figure 8. Structural evolution of the CO adsorbed gold cluster anions  $Au_nCO^-$  (n = 21-25). The size of the minor isomers is plotted smaller than that of the major isomers.

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future study would be needed to confirm our speculation of high catalytic activity of  $Au_{23}^{-}$ .

## METHODS

Experimental Methods. The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been published elsewhere.<sup>1,71,72</sup> In brief, a gold disk target was vaporized by a pulsed laser to generate a plasma inside a large-waiting-room cluster nozzle. A high-pressure helium carrier gas pulse was delivered to the nozzle simultaneously, cooling the plasma and initiating nucleation. For the CO chemisorption experiment, we used a helium carrier gas seeded with 0.01% CO, which reacts with the gold clusters inside the nozzle to form various  $Au_n(CO)_m^-$  complexes. A low CO concentration was used to optimize the formation of one CO chemisorbed complex. Clusters formed inside the nozzle were entrained in the helium carrier gas and underwent a supersonic expansion. After a skimmer, anions from the collimated cluster beam were extracted at 90° into a time-of-flight mass spectrometer. Clusters of interest were selected by a mass gate and decelerated before being photodetached by a 193 nm laser beam from an ArF excimer laser. Photoelectrons were collected by a magnetic bottle at nearly 100% efficiency into a 3.5 m long electron flight tube for kinetic energy analyses. The photoelectron kinetic energies were calibrated by the known spectra of Au<sup>-</sup> and subtracted from the photon energies to obtain the reported electron binding energy spectra. The electron kinetic energy resolution of our apparatus is  $\Delta E_k/E_k \approx 2.5\%$ , that is,  $\sim$ 25 meV for 1 eV electrons.

Theoretical Methods. The BH global optimization method in combination with DFT optimization was used for the search of global-minimum structures of the CO-adsorbed Au, clusters in the size range under study. During the BH search, after each accepted move, the resulting local-minimum geometry was further optimized by using generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchangecorrelation functional<sup>73</sup> and the double-numerical polarized (DNP) basis set with effective core potential (ECP), implemented in the DMOL<sup>3</sup> 4.0 program.<sup>74,75</sup> More than 1500 isomers were collected for each cluster size. The top 40-60 low-energy isomers obtained from the BH global optimization were considered as candidates for the lowestlying structures. These candidates were reoptimized using the PBE0 functional<sup>76</sup> with the CRENBL-ECP<sup>77</sup> basis set implemented in the Gaussian16 package.<sup>78</sup> During the reoptimization for each cluster, some of the structures were found to converge to the same geometry. Next, single-point energy computations of the reoptimized geometries were performed using the PBE0 functional with CRENBL-ECP basis set and with inclusion of the SO effects for the gold atoms, all implemented in the NWCHEM 6.6 package.<sup>79</sup> The inclusion of SO effects for gold has been proven to result in a quantitative match between the experimental and simulated PES spectra for pure gold and gold-alloy anion clusters.<sup>65,80-83</sup> The first vertical detachment energy (VDE) was calculated as the energy difference between the neutral and anion at the PBE0-optimized anion geometry. The binding energies of deeper occupied orbitals were added to the first VDE to generate electronic density of states. Each VDE was fitted with a Gaussian of 0.035 eV width to yield simulated PES spectra, which were compared with the experimental PES spectra to identify the lowest energy structures. The energy gap

(eV) between the first and second highest occupied molecular orbitals, representing the gap between peaks labeled X and A or peaks labeled X' and A', was also calculated for all of the candidate isomers.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.8b02372.

Tables S1–S10: Experimental and theoretical first VDEs, energy gaps, and relative energies for Au<sub>21</sub>CO<sup>-</sup>, Au<sub>22</sub>CO<sup>-</sup>, Au<sub>23</sub>CO<sup>-</sup>, Au<sub>24</sub>CO<sup>-</sup>, and Au<sub>25</sub>CO<sup>-</sup>. Table S11. Assigned isomers of Au<sub>n</sub>CO<sup>-</sup> clusters and rmsd in the peak positions. Figures S1–S32: Comparison of the simulated spectra with the 193 nm experimental spectra for the low-lying isomers of Au<sub>21</sub>CO<sup>-</sup>, Au<sub>22</sub>CO<sup>-</sup>, Au<sub>23</sub>CO<sup>-</sup>, Au<sub>24</sub>CO<sup>-</sup>, and Au<sub>25</sub>CO<sup>-</sup>. Figure S33. Comparison of the combined simulated spectrum of isomers IV and I with the 193 nm experimental spectra of Au<sub>21</sub>CO<sup>-</sup>. Figures S34–S38. Comparison between the energies of HOMO and LUMO levels of Au<sub>n</sub><sup>-</sup>, Au<sub>n</sub>CO<sup>-</sup> (n = 21-25) clusters, and the free CO molecule. (PDF)

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Notes

The authors declare no competing financial interest.

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