Structural Transition of Gold Nanoclusters: From the Golden Cage to the Golden Pyramid

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old is the most inert metal in the periodic table. However, at nanometer scale, supported gold particles have been shown to display a remarkable repertoire of catalytic activities.1 This discovery has stimulated a renaissance of investigations on the structures and properties of gaseous gold clusters, which provide atomically defined models for understanding the mechanisms of the catalytic effects of gold nanoparticles. A diverse set of structures has been observed experimentally and proposed theoretically for a variety of gold clusters. In particular, the structures of gold cluster anions Au18− in the size range from n = 3 to 20 have been well-established using a combination of experimental techniques and density functional theory (DFT) calculations, ranging from the planar (2D) clusters for n < 13,2 the tetrahedral Au19− and the cage clusters for n = 16−18.3 The 2D Au18− clusters were first discovered in an ion mobility experiment2 and have been confirmed by both photoelectron spectroscopy (PES)3 and trapped ion electron diffraction (TIED) experiment.6 However, the 2D-to-3D transition has been controversial7 and is only resolved recently in a combined TIED and DFT study.5 Both the Au16− cage and the Au20− pyramid have been confirmed in a series of experimental and theoretical studies,6,9−13 but how the clusters evolve from the cage to the pyramidal structure has not been understood. In the initial PES/DFT study,4 Au18− and Au17− were shown definitively to be cages, whereas Au19− was shown to be pyramidal, similar to Au20−. The global minimum of Au18− was concluded to be a cage, but the PES spectrum of Au18− suggested the presence of another minor isomer, which could be interpreted by either cage-like structures or a pyramidal structure. Thus, no definitive assignment was possible. A subsequent PES/DFT study confirmed the presence of isomers in Au18− and suggested that the PES data contain a mixture of cage and pyramidal structures.9 However, using the same theoretical data, a simultaneous TIED/DFT study assigned Au18− to the pyramidal structure.6 Recent catalytic studies suggest that supported gold nanoparticles in the size range of 10−20 atoms may be the active species.16 Hence, understanding the structures and structural transitions of gold clusters in this size range is of critical importance.

Because of the theoretical challenges presented by gold clusters as a result of the strong relativistic and spin−orbit effects,8,17 definitive experimental data are essential in helping elucidate their structures and chemical reactivity. In particular, in cases of multiple isomers, it is critical to be able to identify contributions from different isomers and to obtain isomer-specific chemical and spectroscopic information. This is especially true when there is a

ABSTRACT How nanoclusters transform from one structural type to another as a function of size is a critical issue in cluster science. Here we report a study of the structural transition from the golden cage Au16− to the pyramidal Au18−. We obtained distinct experimental evidence that the cage-to-pyramid crossover occurs at Au18−, for which the cage and pyramidal isomers are nearly degenerate and coexist experimentally. The two isomers are observed and identified by their different interactions with O2 and Ar. The cage isomer is observed to be more reactive with O2 and can be preferentially “titrated” from the cluster beam, whereas the pyramidal isomer has slightly stronger interactions with Ar and is favored in the Au18Ar− van der Waals complexes. The current study allows the detailed structural evolution and growth routes from the hollow cage to the compact pyramid to be understood and provides information about the structure−function relationship of the Au18− cluster.

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structural transition, where isomers from different structure types may become degenerate and coexist experimentally, such as the 2D-to-3D crossover at Au12 . On the other hand, different structures may exhibit different chemical and physical properties, which can be used to provide isomer-specific information. Recently, we have shown that the main isomer of Au10 , which is a D3h triangle, is not reactive with O2 whereas minor isomers of Au10 are reactive with O2 and can be titrated out to produce a clean D3h Au10 beam.19 We have also observed that planar Au10 clusters (including the pyramidal Au20 ) have stronger van der Waals interactions with Ar and used this property to obtain isomer-specific PES spectra for Au12 .19 We found that Ar can titrate out the 2D Au12 isomer from the beam, whereas the Au12Ar complexes contain a larger proportion of the 2D isomer.

In the current article, we use the O2 titration and Ar tagging to probe the structural transition from the golden cages starting at Au10 to the pyramidal structure in Au20 . We found that the crossover size is Au18 , for which both the cage and pyramidal isomers coexist experimentally. The cage isomer is observed to be slightly more reactive with O2, while the pyramidal isomer has slightly stronger interactions with Ar, similar to Au20 .19 These different chemical and physical properties are used to provide definitive isomer information. The confirmation of the two coexisting isomers at Au18 in conjunction with a detailed structural analysis provides an atom-by-atom view about the growth routes and structural transitions from the golden cage to the golden pyramid.

O2 Titration. Figure 1a shows the 193 nm photoelectron spectrum of Au18 produced using a laser vaporization cluster source with a pure helium carrier gas and taken using a magnetic bottle PES apparatus (see Methods).20 This spectrum is the same as that reported before.4 The threshold peak X at a vertical detachment energy (VDE) of 3.32 eV was assigned to the cage structure, whereas the weaker features X′ (VDE = 3.63 eV) and A′ (VDE = 3.97 eV) were suggested to originate from another minor isomer. Previous chemical studies21–23 showed that for small Au10 clusters (n < 24) only even-sized clusters are reactive with O2 (except Au16 ) because the even-sized Au10 neutral clusters are closed shell and the corresponding anions possess relatively low electron binding energies24 so that the extra electron can be transferred to O2 to form chemisorbed Au10O complexes. Using a helium carrier gas seeded with a 0.1% O2, we found that indeed, in the size range from Au16 to Au18 , only Au18 reacts with O2 to form a Au18O2 complex, in agreement with the previous works.21–23 However, the photoelectron spectrum of the unreacted portion of the Au18 beam with the 0.1% O2/He carrier gas was very different from that taken with a pure helium carrier gas, as shown in Figure 1b: the X′ and A′ peaks were greatly enhanced and became even stronger than the X band. This observation indicates that the X′ and A′ features indeed come from a Au18 isomer, which is less reactive with O2 than the global minimum cage isomer. This is understandable because the electron binding energy (VDE = 3.32 eV) of the cage isomer is lower than the X′ isomer (VDE = 3.63 eV), and thus it is expected to be easier for it to transfer an electron to O2. At a higher O2 concentration (0.5%), we found that the majority of the Au18 beam is converted to Au19O2, suggesting that the X′ isomer of Au18 is also reactive with O2, preventing us from obtaining an isomer-clean spectrum for the low-lying isomer. The Au18 case is different from Au10, for which we were able to use a 0.5% O2/He carrier gas to completely titrate out reactive isomers to yield an isomer-clean D3h Au10 spectrum because the D3h Au10 isomer is inert toward O2.18

Ar Tagging. The question now is what is the minor isomer observed for Au18 ? In our original PES/DFT study,4 this was not definitively answered because several low-lying isomers, including the pyramidal isomer, seemed to give PES bands consistent with the X′ and A′ features. A subsequent PES/DFT study yielded similar structures for Au18 and suggested similarly that the spectrum of Au18 consists most likely of a combination of low-lying isomers, including the ground state cage isomer, the pyramidal isomer, and another higher-lying cage structure.9 However, a simultaneous TIED study using the same DFT result concluded that the pyramidal Au18 fits best the TIED data.6 Because of the pairwise additive nature of the van der Waals interactions between a rare gas atom and a cluster,25 a 2D structure is expected to have stronger interactions with Ar than a 3D structure of the same cluster size. This was recently observed to be the case for all 2D Au10 clusters, which exhibit a strong propensity to form van der Waals complexes with Ar.19 The pyramidal Au10 cluster was also shown to readily form Au20Ar complexes because of...
its four Au(111) faces. Similar effects were observed previously in Xe/Au₉/He complexes. If the minor isomer of Au₁₈/Xe/He is pyramidal, we may be able to use Ar tagging to distinguish it because it should have a stronger interaction with Ar than the cage structure. This has indeed been observed, as shown in Figure 2.

Figure 2a shows a Au₁₈ spectrum taken with a 5% Ar/He carrier gas, under which Au₁₈Arₓ⁻ van der Waals complexes are readily formed in our cluster source. The relative intensities of the weak features (X’ and A’) in (a) and their increases in the spectra of the Ar-tagged species from x = 1–3, together with the decrease of the relative intensities of the weak features (X and A) in (a) compared to those of Au₁₈/He in Figure 1a, suggest that Ar preferentially forms van der Waals complexes with the pyramidal isomer. The weak features (X and A) in (a) are also observed on the pure Au₁₈ spectrum with a 5% Ar/He carrier gas and should be Ar-induced, as shown in Figure 1a.

Comparison with Simulated Spectra for the Cage and Pyramidal Structures of Au₁₈⁻. To further confirm the assignment of the pyramidal isomer, we compare the simulated spectra for the cage and pyramidal structures with the new isomer-dependent PES data in Figure 3. As discussed in the Supporting Information, a decrease of the relative intensities of the weak features (X and A) in (a) and their increases in the spectra of the Ar-tagged species from x = 1–3, together with the decrease of the relative intensities of the weak features (X and A) in (a) compared to those of Au₁₈/He in Figure 1a, suggest that Ar preferentially forms van der Waals complexes with the pyramidal isomer. The weak features (X and A) in (a) are also observed on the pure Au₁₈ spectrum with a 5% Ar/He carrier gas and should be Ar-induced, as shown in Figure 1a.
Structure Evolution from the Au$_{16}^-\text{Cage}$ to the Au$_{20}^-\text{Pyramid}$.

The next question is how the cage structures evolve to the pyramidal structures. What is the intrinsic link between Au$_{16}^-$ and Au$_{20}^-$? Historically, the pyramidal Au$_{20}^-$ was discovered first, and the structure of the Au$_{16}^-$ cage was found later. The golden cage Au$_{16}^-$ has been viewed as removing the four apex atoms from the pyramidal Au$_{20}^-$ while simultaneously popping up the face-center atoms (see Figure 4). The pyramidal Au$_{20}^-$ cluster is close-packed, similar to bulk gold, and possesses four Au(111) faces. While Au$_{16}^-$ maintains the tetrahedral symmetry of the parent Au$_{20}^-$, the popping up of the four face-center atoms created a central volume and a distinctly hollow cage structure in Au$_{16}^-$, which has been shown to be able to entrap a variety of external atoms analogous to the fullerenes.

**Origin of the Hollow Golden Cage Au$_{16}^-$: Spherical Aromaticity.** Recent chemical bonding analyses$^{22,33}$ show that the pyramidal Au$_{20}^-$ can be described by 10 four-center two-electron (4c-2e) bonds localized on 10 intertwining Au$_4$ tetrahedra. More importantly, the closed-shell Au$_{16}^-$ cage has been shown to contain three globally delocalized 16c-2e bonds derived from its triply degenerate tetrahedra. More importantly, the closed-shell Au$_{16}^-$ cage has been shown to contain three globally delocalized 16c-2e bonds derived from its triply degenerate frontier orbital, in addition to six 4c-2e bonds.$^{33}$ We note that the three globally delocalized 16c-2e bonds are responsible for the caging in Au$_{16}^-$ because removal of these three electron pairs promptly returns the Au$_{16}^+$ cluster to a compact $T_d$ structure,$^{33}$ which is an exact fragment of Au$_{19}$ by removing the four corner atoms. The six globally delocalized electrons in Au$_{16}^-$ give rise to spherical aromaticity, which is also analogous to the fullerenes.$^{34}$ The spherical aromaticity provides extra electronic stability and explains the unique hollow cage structure in the Au$_{16}^-$ and Au$_{16}^-$ golden cages. The idea of spherical aromaticity has been proposed for other larger gold cage clusters suggested computationally.$^{35-43}$ Apparently, the removal of one electron from Au$_{16}^-$ does not destroy the spherical aromaticity in Au$_{16}^-$, but the removal of two electrons seems to destroy the spherical aromaticity in the neutral Au$_{16}$ because the global minimum of the neutral Au$_{16}$ is no longer the cage structure.$^{44}$

Cage Growth: From Au$_{16}^-$ to Au$_{19}^-$. However, in reality, the pyramidal clusters grow from the Au$_{16}^-$ cage by nucleation of additional Au atoms. Figure 4 delineates two growth pathways from Au$_{16}^-\text{Cage}$: the cage growth route (Figure 4a) and the pyramidal path (Figure 4b). To help visualize the structures and understand the growth path, the atoms are color-coded in Figure 4. The Au$_{16}^-$ cage can be viewed as consisting of three layers. The bottom layer contains a six-membered ring with one central atom, which is out of plane, giving rise to the curvature for the cage (note that Au$_{16}^-$ possesses tetrahedral symmetry, and there are three more such atoms in the green-colored middle layer). This layer is related to the Au$_{15}^-\text{base plane}$. The middle layer (green color) contains six atoms to form a six-membered ring,
which is related to the second layer of \( \text{Au}_{20}^- \) (similarly colored, Figure 4b). The top layer of \( \text{Au}_{16}^- \) is a triangle, which can be viewed as due to the truncation of an apex atom from \( \text{Au}_{20}^- \). The ground state structure of \( \text{Au}_{17}^- \) is formed by adding a Au atom into the top layer of \( \text{Au}_{16}^- \) with a slight rearrangement to give a butterfly-four atom top layer (Figure 4a), whereas the bottom and middle layers are essentially unaffected relative to \( \text{Au}_{16}^- \). Our previous work showed that the structure along the pyramidal growth route by adding a Au atom to the top triangular site of \( \text{Au}_{16}^- \) is much less stable. Addition of a capping atom to the top layer of \( \text{Au}_{17}^- \) leads to the ground state \( \text{Au}_{18}^- \) cage (Figure 4a). The butterfly top layer of \( \text{Au}_{17}^- \) is slightly distorted, but the bottom and second layers are again essentially unaffected in the \( \text{Au}_{18}^- \) cage relative to those in \( \text{Au}_{16}^- \) and \( \text{Au}_{17}^- \). However, in \( \text{Au}_{18}^- \), the pyramidal structure becomes competitive and nearly degenerate with the cage. The pyramidal structure of \( \text{Au}_{18}^- \) is formed by adding two atoms to the bottom layer of the \( \text{Au}_{16}^- \) cage (Figure 4). Note that the addition of these apex atoms induces a significant "de-caging" effect, considerably flattening the four atoms that give rise to the curvature in the \( \text{Au}_{16}^- \) cage. These four atoms transform naturally to the face centers of the pyramidal \( \text{Au}_{20}^- \). The flattening effect in the \( \text{Au}_{18}^- \) pyramidal structure is directly responsible for the enhanced van der Waals interactions with \text{Ar}, relative to the cage isomer.

Addition of one more apex atom to the pyramidal \( \text{Au}_{18}^- \) structure further flattens the structure and leads to a very stable pyramidal \( \text{Au}_{19}^- \) (Figure 4b), for which the cage isomer derived from the \( \text{Au}_{18}^- \) cage becomes much less stable according to our previous DFT calculations. Addition of one more apex atom to \( \text{Au}_{19}^- \) produces a perfect tetrahedral \( \text{Au}_{20}^- \) with four \( \text{Au}(111) \) faces and completes the cage-to-pyramid evolution from \( \text{Au}_{16}^- \) to \( \text{Au}_{20}^- \).

**METHODS**

The experiment was carried out with a magnetic bottle photoelectron spectroscopy apparatus equipped with a laser vaporization cluster source, details of which has been reported elsewhere. A gold disk target was vaporized by a pulsed laser to generate a plasma inside a cluster nozzle with a large waiting room. A high-pressure helium carrier gas pulse was delivered to the nozzle simultaneously, cooling the plasma and initiating nucleation. Clusters formed inside the nozzle were entrained in the helium carrier gas and underwent a supersonic expansion for further cooling. After a skinner, anions from the collimated cluster beam were extracted perpendicularly 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 \( \text{Au}^- \) and subtracted from the photon energies to obtain the reported electron binding energy spectra. The electron kinetic energy \( E_k \) resolution of our apparatus is \( \Delta E_k/E_k \approx 2.5\% \) (i.e., \( \sim 25 \) meV for 1 eV electrons).

As shown previously, by carefully controlling the residence time of the clusters in the nozzle, relatively cold clusters can be produced from our laser vaporization supersonic cluster source. The cooling effects have been confirmed recently by the observation of van der Waals clusters of gold cluster anions with \( \text{Ar}^- \). In the present study, the \( \text{Au}_{19}\text{Ar}^- \) clusters were produced using a helium carrier gas seeded with 5% \text{Ar}. For the \( \text{O}_2 \) titration experiment, a 0.1% \text{O}_2/\text{He} carrier gas was used.

**CONCLUSIONS**

The current study shows that chemical titration and van der Waals complex formation are effective techniques to deconvolute complex photoelectron spectra of size-selected clusters due to coexisting isomers at major structural transitions, thereby providing critical structural and isomeric information. Such information is crucial in comparing with computational results in order to elucidate the size-dependent structures and structural evolution of clusters. Both electronic and atomic structures are important in determining the novel chemical and physical properties of nanoclusters. The present results reveal that the higher \( \text{O}_2 \) reactivity of the \( \text{Au}_{18}^- \) cage isomer is distinctly an electronic effect. Detailed structures of supported gold catalysts are still elusive. Thus, continued progress in understanding the structures of size-selected gold nanoclusters and the structure—function relationships will be important in the understanding of the catalytic effects of gold and may suggest new strategies to design more efficient catalysts.

**REFERENCES AND NOTES**


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**Supporting Information Available:** Intensity ratios of the X to the X band in the \( \text{Au}_{18}^- \) spectra under different experimental conditions and that in the \( \text{Ar}^- \) van der Waals complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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