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Probing the electronic properties and structural evolution of anionic gold clusters in the gas phase

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Gold nanoparticles have been discovered to exhibit remarkable catalytic properties in contrast to the chemical inertness of bulk gold. A prerequisite to elucidate the molecular mechanisms of the catalytic effect of nanogold is a detailed understanding of the structural and electronic properties of gold clusters as a function of size. In this review, we describe joint experimental studies (mainly photoelectron spectroscopy) and theoretical calculations to probe the structural properties of anionic gold clusters. Electronic properties and structural evolutions of all known Au_n⁻ clusters as experimental efforts in resolving the isomeric issues of small gold clusters using Ar-tagging, O₂-titration and isoelectronic substitution are also discussed.

1. Introduction

Materials at the nanometre scale exhibit a rich array of new properties, which are usually not found in their bulk counterparts. This is especially the case for gold: while bulk gold is

^aDepartment of Physics and Astronomy, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA ^bDepartment of Chemistry, Brown University, Providence, Rhode Island 02912, USA. E-mail: lai-sheng_wang@brown.edu known as the most chemically inert metal in the periodic table, nanometre-sized gold particles are exceptionally active as catalysts in a wide range of chemical transformations.^{1,2} The remarkable catalytic reactivity of gold nanoparticles supported on oxide substrates was first discovered by Haruta,³ and it has sparked a flurry of research interests aimed at elucidating its catalytic mechanisms and controlling the catalytic activities.⁴ It has been shown that catalytic properties of nanogold are sensitive to many factors, such as the nature of the substrate and the



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spectroscopy. Research in his group has led to the discovery of golden buckyballs and the golden pyramid, as well as aromatic clusters and planar boron clusters. His group has also pioneered spectroscopic studies of free multiply charged anions and complex solution-phase anions using electrospray ionization. size, shape and charge state of the gold particles.¹⁻⁴ However, despite extensive research efforts on supported gold nanoparticles,^{5.6} there has not been a conclusive picture concerning the origin of the peculiar catalytic properties of nanogold. To understand nanogold catalysis and to reveal its size/shape– function relationship, intrinsic structural information of free gold clusters and its size dependence are essential.

Structural determination of free clusters has been a grand challenge in cluster science because of the lack of direct experimental probes. Bare clusters are usually produced and sizeselected in a molecular beam, but typically with rather low number density. Thus, their structures usually cannot be characterized directly with traditional microscopic or diffraction techniques. Over the last two decades, a variety of experimental techniques have been developed to study the size-dependent properties of gas phase clusters. These experimental advances, usually combined with quantum chemistry calculations, have allowed structural information to be obtained for many gas phase clusters. The experimental techniques include: (i) ion mobility spectrometry (IMS),^{7,8} (ii) photoelectron spectroscopy (PES),⁹⁻¹⁷ (iii) trapped ion electron diffraction (TIED),^{18,19} and (iv) infrared multi-photon dissociation spectroscopy (IR-MPD).^{20,21} Each of these experimental techniques measures a certain property of a given cluster (e.g. collision cross-section by IMS, electron binding energies by PES, molecular scattering intensity by TIED, and IR absorption by IR-MPD), which is sensitively dependent on its geometric structure. To fully interpret the experimental measurement and determine the cluster structure, comparison with high-level quantum calculations is often required for all these experimental probes. With the significantly improved computing capabilities of modern supercomputers, the combination of a structure-sensitive experiment with advanced quantum calculations has made it possible to routinely determine the structures of a wide range of clusters with substantial level of credence.

We have been interested in probing the structural and electronic properties of atomic clusters using high-resolution photoelectron spectroscopy. PES measurements are performed on negatively charged clusters, because (i) charged particles are easily sizeselected and the anions usually have low valence electron binding energies that are accessible for most of the commercial lasers and (ii) PES on anionic clusters yield spectroscopic information about the corresponding neutral species, which are often of interest. An anion photoelectron spectrum directly measures the adiabatic detachment energy (ADE), the vertical detachment energy (VDE) and the electronic excitation energies, which constitute an electronic fingerprint for the underlying cluster. The most stable cluster structure can be obtained through comparison of the wellresolved PES spectrum with simulated density of states (DOS) for a pool of candidate structures gathered from either known structural motifs or global minimum search algorithms. In addition, with the spectroscopic and computational data, one can analyze the chemical bonding of the clusters, as well as other electronic and chemical properties, which may further rationalize their specific structures. The potential and power of joint PES/ theory in resolving the complex structures of atomic clusters have been demonstrated in the structural determination of e.g. boron clusters,^{22,23} gold clusters^{14,24} and tin clusters,^{25,26} all of which have led to unexpected discoveries.

Motivated by the surprising catalytic effects of nanogold particles, we started our PES work on anionic gold clusters in early 2000's. Over the last decade, the structures of anionic gold clusters with less than about 20 atoms in size have been well established through a variety of joint experimental and theoretical studies.^{27,28} For clusters larger than Au_{20}^{-} , only specific sizes (ranges) have been experimentally probed. The chemistry of gold is dominated by its strong relativistic effect^{29–32} and so-called aurophilic attractions.^{33–35} As a result, some intriguing and surprising structural motifs have been discovered for gold clusters, such as the planar structures up to Au_{12}^{-} ,^{7,24} the hollow golden cage Au_{16}^{-} ,³⁶ the golden pyramid Au_{20}^{-} ,¹⁴ and the non-icosahedral low-symmetry Au_{55}^{-} .^{16,37,38}

In this review, we summarize the structures of all known gold cluster anions Au_n⁻ as experimentally confirmed, covering the size ranges of n = 3-35 and 55–64 (no joint experimental and computational report on n = 36-54 yet). While the major focus is on the structural evolution of elemental gold clusters, topics to be covered also include our recent efforts in resolving the isomeric issues of small gold clusters using various techniques such as Artagging, ³⁹ O₂-titration⁴⁰ and isoelectronic substitution, ^{41,42} and doping of the special gold cage clusters, it is beyond the scope of this review to cover all the works. The focus is placed on the work from the authors' laboratory with relevant literature selectively discussed.

2. Experimental method

In this section, we briefly describe the PES experimental method used in our laboratory in probing atomic clusters. PES experiments were carried out using a magnetic-bottle time-of-flight photoelectron spectrometer coupled with a laser vaporization supersonic cluster source, details of which have been published elsewhere.⁴⁷ Fig. 1 shows a schematic diagram of the experimental setup. Briefly, a disk target containing desired materials is ablated by an intense focused laser beam (usually 532 nm from a pulsed Nd:YAG laser). The laser-induced plasma is cooled by a high-pressure helium carrier gas, initiating nucleation for cluster formation. The nascent clusters entrained in the carrier gas then undergo a supersonic expansion through a nozzle to form a collimated cluster beam. Very strong supersonic expansion is enabled by a specially designed nozzle with a large waiting room,47 which substantially cools and thermalizes the formed clusters.48 Recently, by using helium carrier gas seeded with a small amount of Ar or O_2 , we have observed physisorption of Ar and O₂ onto gold clusters,^{39,49} evidencing the very low internal temperatures of the clusters. A sufficiently cold cluster beam is essential for obtaining high resolution photoelectron spectra.

When the cluster beam reaches the ion extraction (repeller) zone, the negatively charged clusters are extracted perpendicularly from the beam and are subjected to a time-of-flight (TOF) mass analysis. A mass gate is used to select the clusters of desired size to enter the interaction zone of the magnetic-bottle photoelectron analyzer. The selected clusters are decelerated before being intercepted by a laser beam for photodetachment. The detachment lasers used in our experiments usually include two harmonics of a Nd:YAG laser, 355 nm (3.496 eV) and 266 nm (4.661 eV), and a 193 nm (6.424 eV) from an ArF excimer laser.



Fig. 1 The schematic view of the laser vaporization, magnetic-bottle photoelectron spectrometer. (1) Target and nozzle; (2) skimmer; (3) pulsed ion extraction stack; (4) ion deflector; (5) Einzel lens; (6) horizontal and vertical deflector; (7) mass gate and decelerator; (8) magnet; (9) ion detector; (10) detachment laser beam; (11) 3.5 m electron flight tube; and (12) electron detector. The red dots represent clouds of clusters.

High photon energies are used to reveal more electronic transitions, which are essential for comparison with simulated spectra, while low photon energies in general yield better resolved spectral features, allowing more accurate determination of ADE/VDEs and vibrational fine structures in favorable cases. Photoemitted electrons are collected by the magnetic-bottle at nearly 100% efficiency and analyzed in a 3.5 m long electron time-of-flight tube. The photoelectron time-of-flight spectra are calibrated using the known spectra of Au⁻ and/or Rh⁻ and converted to binding-energy spectra by subtracting the kinetic-energy spectra from the photon energies. The resolution of the magnetic-bottle PES spectrometer is $\Delta E/E \approx 2.5\%$, that is, about 25 meV for 1 eV electrons.

3. Au_n^- (n = 3-15): planar gold clusters and 2D-to-3D transition

The first systematic experimental investigation of the structures of Au_n^- was reported by Kappes' group using ion mobility combined with density functional theory (DFT).⁷ In the ion mobility measurement, it was found that small gold cluster anions (n < 13) have significantly larger cross-sections than the corresponding cations of the same sizes (Fig. 2). The enhanced collision cross-sections imply more open structures, which led to the surprising discovery that anionic gold clusters are of planar structures up to n = 12. The two-dimensional (2D) to threedimensional (3D) transition was convincingly shown to be at Au_{12}^- on the basis of a bimodal arrival time distribution, which indicates the co-existence of both 2D and 3D structures.⁷ The planar gold clusters in this size range are surprising because metal clusters are expected to form compact 3D structures. The unusual planarity of gold clusters was attributed to the strong relativistic effects of gold,²⁹ which reduce its 5d–6s energy gap and enhance its s–d hybridization.^{50–52} The directional bonding and reduced Au–Au bond length as favored by the Au 5d electrons lead to the preference of planar geometries of the small gold clusters.

A PES experiment of size-selected Au_n^- clusters has been performed by several groups in early 1990's.^{53–55} However, those prior PES data were either of poor resolution or of limited size range, and no structural information was obtained. In 2003, we reported the first systematic high-resolution PES/DFT investigation of Au_n^- clusters in the size range of n = 4-14.²⁴ The joint



Fig. 2 Cross-sections obtained from the ion mobility measurements for gold cluster anions and cations. Reproduced from ref. 7 with permission. Copyright 2002 American Institute of Physics.

study confirmed the planar structures of small gold clusters discovered in the previous IMS experiment (Fig. 3).7 Briefly, for the size range investigated, the lowest energy isomers from the DFT calculation are all of planar structures (Fig. 3). For Au₄⁻, a "Y" shaped structure (4B) gives the best agreement with the experiment. For n = 5, 6, 8 and 10, the lowest energy 2D structure was assigned as the major isomer for each case based on their simulated PES spectra; while for n = 7, 9, 11 and 13, satisfactory agreement between experimental and theoretical PES spectra was not achieved. The PES of Au12⁻ showed evidence of the co-existence of multiple isomers, and a mixture of 3D (12C) and 2D (12A) structures was assigned, consistent with the IMS observation.⁷ For n = 14, the spectrum suggested that the 3D structure (14B) is dominant though its calculated energy is higher than for the 2D (14A) isomer. The planar structures of gold cluster anions and the 2D-to-3D structural transition at Au_{12}^{-} have been further confirmed by several subsequent experiments using inert gas complex depletion⁵⁶ and trapped ion electron diffraction.^{19,57} Several recent theoretical works have shown that the discrepancy between the calculated energetic stabilities of 2D structures and the various experimental observations of 3D ones around the transition size range (e.g. n = 12, 13, 14) can be reconciled if appropriate functionals are chosen in the DFT calculations.⁵⁷⁻⁵⁹ More details of small gold clusters in this size range can be found in two recent reviews.^{27,28}

4. On the isomeric issues of small gold clusters

There is a general paucity of effective ways to resolve different structural isomers if they are energetically very close and simultaneously present in the experiment. Except for Au_{12}^{-} , the ion mobility measurement did not reveal evidence of multiple isomers for small gold cluster anions.7 Our initial PES study, however, suggested a population of multiple isomers for several sizes, though not definitely identified.24 Recently, we have improved our cluster source conditions by seeding the He carrier gas with a small amount of Ar for better cooling. In the meantime, a theoretical survey of a large pool of candidate structures was made possible by global minimum search algorithm.^{60,61} We have also recently shown the importance of including spin-orbit (SO) effects in the PES simulation of gold clusters, in order to achieve quantitative comparison between the experimental and simulated PES spectra.41,42,62 With the improved experimental and theoretical capabilities, we re-visited the small gold clusters Au_n^{-} . Isomeric structures were identified and resolved for most of the sizes for n = 7-15.

4.1. Au_{10}^{-} : multiple isomers and structure-dependent O_2 reactivity

The PES spectrum of Au_{10}^{-} differs from that of all other evensized gold clusters in that it does not show an energy gap,²⁴ suggesting an open-shell triplet electronic configuration of its neutral with two unpaired electrons. The major isomer of Au_{10}^{-} that contributes to the PES spectrum is the global minimum D_{3h} structure (10A in Fig. 3). The open shell configuration and high electron affinity of the neutral D_{3h} Au₁₀ have been explained by Häkkinen²⁸ using a 2D electron shell model proposed by Lievens and co-workers.⁶³ However, weak features observed in the

Fig. 3 Optimized low-energy isomeric structures of Au_n^- (n = 4-14). The calculated ground state structure is labeled "A" for each size. See the text for detailed structural assignments. From ref. 24.



Fig. 4 Comparison of the 193 nm PES spectra of $Au_{10}Ar_{-}^{-}$ and $Au_{10}Ar_{2}^{-}$ to that of the parent Au_{10}^{-} . Note the reduction of the relative intensities of the weak peaks (X', X'', X''') in the spectra of the Ar-tagged species, X'' in particular. From ref. 40.

original PES spectrum at the low binding energy side (see Fig. 4a)^{24,55} suggest the presence of minor isomers.

Our recent experiments using Ar-tagging and O2-titration have shed more light on the isomeric issue of Au₁₀^{-.40} In the experiment using helium carrier gas seeded with 5% argon, clustering of several Ar atoms to gold clusters has been observed, demonstrating a very cold cluster beam. The spectra of Au₁₀Ar⁻ and $Au_{10}Ar_2^-$ are nearly identical to that of bare Au_{10}^- (Fig. 4), consistent with the weakly bound nature of these van der Waals complexes. However, in the spectra of the Ar-tagged clusters, which are expected to be colder than the pure gold cluster, the relative intensities of the weak signals in the low binding energy range (X', X", X"') are reduced, confirming that they are from minor isomers other than the major D_{3h} carrier. In particular, the relative peak height of the X" band is significantly decreased in the spectra of the complexes, suggesting that this isomer is relatively higher lying. The change in the intensity ratio between X' and X''' is not as pronounced, indicating that they are close in energy.

When He carrier gas is seeded with 0.1% O₂, the weak lowbinding energy features (X', X'', X''') in the Au₁₀⁻ spectra are also greatly reduced, as shown in Fig. 5. With a 0.5% O₂-He as carrier gas, the weak features are completely gone. These observations again confirm the X', X'', and X''' features to be due to low-lying isomers of Au₁₀⁻. Unlike the cooling effect of Artagging, the disappearance of the minor PES features in the O₂seeded experiments arises from isomer-dependent reactivity towards O₂: the D_{3h} global minimum structure of Au₁₀⁻ (10A in Fig. 3) is inert towards O₂ due to its high electron binding energy,^{64,65} while the minor isomers indicated by X', X'', and X''' have lower electron binding energies and are reactive with O₂.



Fig. 5 Comparison of the 193 nm and 266 nm PES spectra of Au_{10}^- produced using pure He (or Ar-seeded) with those using He seeded with different amount of O₂ as carrier gases. Note that the weak features (X', X'', X''') are titrated out with increasing O₂ concentration. From ref. 40.

These reactive species are thus gradually "titrated" out of the beam upon increasing O_2 concentration, leaving a clean beam of unreactive D_{3h} Au₁₀⁻. With Ar-tagging and O₂-titration, four distinct isomers of Au₁₀⁻ co-existing in the cluster beam are readily distinguished. The structures of the three low-lying isomers of Au₁₀⁻ are completely identified in a later experiment of isoelectronic substitution in conjunction with DFT calculations (*vide infra*).⁴²

4.2. Au₁₂⁻: 2D-to-3D structural transition reaffirmed by Artagging

Weakly bound rare gas complexes can be used to provide structural information of clusters, because different isomeric structures may have different strengths of van der Waals interactions with rare gases.56,66,67 In the experiment using He carrier gas seeded with 1% to 3% Ar, we observed the formation of $Au_nAr_m^-$ complexes.³⁹ As seen in the mass spectra of $Au_nAr_m^$ displayed in Fig. 6, in the size range of n = 6-30 extensive Arclustering was observed, in particular for Au₇₋₁₁⁻ and Au₂₀⁻, where more than four Ar atoms are physisorbed onto the gold clusters and the corresponding bare Au_n^{-} become minor species. The enhanced Ar-physisorption at these sizes is associated with their planar structures. Au_{20}^{-} is a 3D cluster, but its unique tetrahedral structure consists of four Au(111) faces (vide infra). This observation is due to the fact that the van der Waals interactions between the Ar atom and a 2D surface are stronger than those between a rare gas atom and a 3D structure.⁶⁸ The enhanced Ar complexation with the planar Au_n^{-} and the abrupt drop of Ar clustering at Au_{12}^{-} provide clear evidence for the 2D to 3D structural transition.

The enhanced van der Waals interactions between Ar and planar structures of Au_n^- were further revealed by the photoelectron spectra of Au_{12}^- and $Au_{12}Ar_m^-$ shown in Fig. 7. The





Fig. 6 Mass spectra of $Au_nAr_m^-$ produced from laser vaporization of a gold target with a helium carrier gas seeded with 1–3% Ar. From ref. 39.

spectrum of Au_{12}^{-} taken with a pure He carrier gas contains contributions of two isomers,²⁴ as shown in Fig. 7a, in which the X and X' peaks correspond to the 3D C_{2v} (12C) and 2D D_{3h} (12A in Fig. 3) structures, respectively. The relative ratio of X/X' (*i.e.* 3D/2D) is $\sim 3/1$, showing that the 3D structure is slightly more stable than the 2D isomer and represents the global minimum. With 1-3% Ar seeded in the He carrier gas, the X' feature in the PES spectrum is almost completely gone (Fig. 7b), indicating that the 2D isomer of Au_{12}^{-} has been titrated out by Ar to form Au₁₂Ar_m⁻ complexes because of its enhanced physisorption interaction. Indeed, in the spectrum of Au₁₂Ar⁻ (Fig. 7c), the contribution from the 2D isomer (X') was seen to be significantly enhanced, while the overall pattern of Au₁₂Ar⁻ was similar to that of the bare Au_{12}^{-} and the Ar complexation induced negligible spectral shift. For Au₁₂Ar₂⁻, the 2D isomer becomes the dominant species (Fig. 7d). The Ar-tagging experiment demonstrated vividly the co-existence of isomers of different dimensionalities and confirmed unequivocally the 2D-to-3D structural transition of Au_n^- clusters at n = 12.

4.3. $Au_n^{-} vs. MAu_{n-1}^{-}$ (n = 7-15, M = Ag, Cu): isoelectronic substitution

In a series of recent work,^{41,42,62} we have shown that isomeric information can also be extracted by isoelectronic substitution in Au_n^- clusters by Cu or Ag. Replacing a gold atom in Au_n^- with a copper or silver atom in general does not significantly change the structure of the parent gold cluster. However, in cases where multiple isomers are present, the isoelectronic substitution alters the relative stabilities of different isomers, thereby their relative populations in the cluster beam. Fig. 8 shows the comparison of the PES spectrum of Au_7^- with that of $AgAu_6^-$ and $CuAu_6^-$. Clear similarities are seen between the spectrum of the pure gold cluster and that of the isoelectronically substituted species,



Fig. 7 193 nm PES spectra of Au_{12}^- using (a) pure He, (b) He seeded with 1-3% Ar as carrier gas, and spectra of (c) $Au_{12}Ar^-$ and (d) $Au_{12}Ar_2^-$. From ref. 39.

except that the relative intensities of different peaks are changed. Specifically, the intensity of the X' peak is increased while those of the X and A peaks are decreased in the spectrum of AgAu₆⁻ and CuAu₆⁻ relative to the Au₇⁻ spectrum. However, the peak height ratio of X to A or X' to A' remains nearly unvaried. These observations provide definite evidence that features X/A and X'/ A' are associated with different isomers of Au₇⁻. Besides the global minimum C_{2v} structure (7A in Fig. 3), a triangle Au₆ with a dangling gold atom was identified as a low-lying isomer of Au₇⁻ (Fig. 8d). This isomer was first identified by the isoelectronic substitution⁴¹ and had not been recognized in previous experimental or theoretical studies, despite the relatively small size of Au₇⁻.

With the aid of isoelectronic substitution, isomeric structures were identified and resolved systematically for Au_n^- with n = 7-15.^{41,42,62} Au_8^- also has two isomers with D_{4h} (8A) and C_{2v} (8B in Fig. 3) symmetries, respectively. For Au_9^- there is only one isomer (9A in Fig. 3). Four planar isomeric structures are resolved for $Au_{10}^{-,42}$ consistent with the Ar-tagging and O_2 titration experiment.⁴⁰ For Au_{11}^- , a C_8 structure (11A in Fig. 3) is the major carrier, while a D_{2h} isomer (11C in Fig. 3) also has a minor contribution. Au_{13}^- has two 3D isomers; only the global minimum C_{2v} structure (13C in Fig. 3) had been reported before, while a C_{3v} isomer⁶² with nearly equal population had not been



Fig. 8 193 nm photoelectron spectra of (a) Au_7^- , (b) $AgAu_6^-$ and (c) $CuAu_6^-$, compared with the simulated spectra for corresponding structures in (d), (e), and (f), respectively. From ref. 41.

recognized in previous IMS,⁷ PES²⁴ or TIED^{19,27} studies. Au₁₄⁻ has a single isomer of C_2 symmetry,⁶² different from the C_{2v} structure (14B in Fig. 3) reported in earlier PES²⁴ and TIED¹⁹ studies, but consistent with a more recent TIED measurement.¹⁸ Finally, for Au₁₅⁻, the major isomer is a C_{2v} structure,⁶² consistent with the recent TIED observation;¹⁸ and a C_1 structure was identified as a minor isomer.⁶² Isomers of Au₁₃₋₁₅⁻ all have similar 3D structural motifs, *i.e.* the shell-like flat cage structures. They can all be viewed as grown from the 3D isomer of Au₁₂⁻ (12C in Fig. 3).

5. $Au_{16}^{-}-Au_{19}^{-}$: golden cages and cage-to-pyramid transition

Our joint PES/DFT investigations³⁶ of Au_n⁻ clusters in the size range of n = 15-19 first revealed in 2006 that the major isomers of Au₁₆⁻-Au₁₈⁻ are dominated with hollow cage motifs (Fig. 9). Particularly, the Au₁₆⁻ cluster is a highly symmetric cage with tetrahedral (T_d) symmetry, which can be derived from the previously discovered T_d Au₂₀⁻ pyramid¹⁴ by removing its four apex atoms and allowing subsequent pop-up of the four facecenter atoms. The Au₁₇⁻ and Au₁₈⁻ cages are both of C_{2v} symmetries; they can be viewed as evolved from the tetrahedral Au₁₆⁻ cage by adding one and two gold atoms to its top, respectively, followed by slight structural relaxation (Fig. 9). Au₁₆⁻-Au₁₈⁻ are the first experimentally confirmed golden cages



Fig. 9 Structural evolution of Au_n^- clusters from n = 16 to 19. From ref. 36.

and their structures have been further substantiated by subsequent TIED^{18,19} and PES⁷³ studies. A number of larger gold cage clusters have been theoretically proposed,^{69–72} however, none has been observed or is expected to be the global minimum.

The beautiful golden cage of Au_{16}^{-} is particularly interesting. The PES spectrum^{36,55} of Au_{16}^{-} is rather simple relative to its neighboring sizes, reflecting its high symmetry. It has a high VDE and does not exhibit an energy gap, breaking the even-odd alternation observed in this size range. This suggests an openshell with two unpaired electrons for neutral Au_{16} , similar to the Au_{10} case discussed above. In a follow-up study,⁷⁴ Häkkinen and Walter explained the large VDE and high stability of the Au_{16}^{-} cage in terms of the electron shell model,^{75,76} showing that Au_{16}^{-} is only one electron short from a major electron shell closure $(1S^21P^61D^{10})$, which led to a perfect T_d 18-electron close-shell Au_{16}^{2-} dianion.

A more recent quantum chemical bonding analysis⁷⁷ further showed that the close-shell Au_{16}^{2-} has three sixteen-center twoelectron (16c–2e) bonds occupied by six globally delocalized electrons. This is an important result. We believe that the six globally delocalized electrons give rise to spherical aromaticity analogous to the fullerenes.⁷⁸ It is the spherical aromaticity that provides extra electronic stability and leads to the unique hollow cage structure of Au_{16}^{-} and Au_{16}^{2-} .

5.1. Cage to pyramid transition: Au₁₈

For n > 18, our initial PES study³⁶ as well as several subsequent experiments^{18,19,73} all concluded that Au₁₉⁻ has a single isomer of pyramidal structure (Fig. 9), similar to the T_d Au₂₀⁻ but with a missing apex atom. Therefore, from n = 16 to 19, there exists a major structural transition from the golden cage to the golden pyramid. The earlier PES measurements^{36,73} have suggested coexistence of multiple isomers for Au₁₈⁻, but the TIED studies reached inconsistent conclusions.^{18,19} Definite evidence of structural transition at Au₁₈⁻ has been provided by our recent Ar/O₂tagging PES experiment.⁷⁹ The spectrum of Au₁₈⁻ is



Fig. 10 Comparison of the simulated PES spectra of (a) the cage isomer and (b) the pyramidal isomer of Au_{18}^- with (c) the experimental spectra. The experimental spectra taken with pure He carrier gas and the one with 0.1% O₂/He are overlapped after normalizing to the first band. Note the increase of the relative intensities of the X' and A' bands under the O₂ titration condition (blue), which correspond to the pyramidal isomer. From ref. 79.

quantitatively reproduced by a weighted superposition of both a cage and a pyramidal structure, while the relative populations of the two isomers can be varied under Ar-tagging or O₂-titration conditions (Fig. 10). In the same work, detailed growth pathways from the hollow Au_{16}^- cage to the closed-packed Au_{20}^- pyramid were proposed. Similar to the case of Au_{12}^- , the co-existence of both structural motifs evidenced the cage-to-pyramid structural transition of Au_n^- at n = 18.

5.2. M@Au₁₆⁻: doping the golden buckyball

The large empty space inside the Au_{16}^{-} cage allows for possible endohedral doping to form a new class of endohedral golden cages, analogous to the endohedral fullerenes.80,81 A gold cluster containing a central atom was first predicted by Pyykkö and Runeberg for a series of icosahedral clusters $M@Au_{12}^{-}(M = W,$ Ta, Re),⁸² and was subsequently confirmed experimentally.^{83,84} However, the central dopant in this class of clusters plays the role of "structure maker" because the bare Au_{12}^{-} cluster is not an empty cage. The first experimentally observed endohedral doping of the hollow golden cage was for Cu@Au₁₆^{-.45} The PES spectrum of Cu@Au₁₆⁻ is remarkably similar to that of the parent Au₁₆⁻ cluster except for some enhancement of the intensity for the ground state transition band (X, Fig. 11), revealing that the Cu atom doping does not significantly alter the geometric and electronic structure of the Au₁₆⁻ cluster but simply donates its valence electron to the cage. In a subsequent study,⁴⁶ we have shown that Ag, Zn, and In can all be doped inside the Au₁₆⁻ cage with little structural distortion. Similar to Cu, they



Fig. 11 Photoelectron spectra of $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$, compared to those of Au_{16}^- and Au_{17}^- . From ref. 45.

transfer their valence electrons to the golden cage and form endohedral charge transfer complexes.

However, in contrast to a previous theoretical calculation by Walter and Häkkinen,⁷⁴ our combined PES and DFT study showed that doping the Au_{16}^{-} cluster with a Si, Ge, or Sn atom led to completely different structures, in fact, to the complete destruction of the Au_{16} cage.⁴⁴ In the case of SiAu₁₆⁻, we found that it consists of a Si atom coordinating to a square face on the surface of a Au_{15} cluster and a terminal (dangling) Au atom on Si, whereas both Ge and Sn coordinate to the square face on the surface of a non-cage Au_{16} . In a DFT calculation reported in the meantime, Jena *et al.* reached the same structure for SiAu₁₆⁻ with the dangling Au atom on the Si atom.⁸⁵

In a combined PES, TIED and DFT investigation,⁴³ we concluded that magnetic doping of the Au₁₆⁻ cage with Fe, Co and Ni results in endohedral structures but with considerable distortion to its T_d symmetry. Atomic-like magnetism was retained in the distorted endohedral M@Au₁₆⁻ (M = Fe, Co, Ni) clusters. Possible doping of the golden cage Au₁₆⁻ with other elements has also been examined computationally.⁸⁶⁻⁸⁹ Doping offers an additional dimensionality to fine tune the electronic and magnetic properties of the golden cage clusters.

6. Au₂₀⁻: a tetrahedral golden pyramid

Historically, the remarkable tetrahedral structure of Au₂₀⁻ was discovered prior to other Au_n⁻ in the size range of n = 15-19, because of its special PES spectrum.¹⁴ During our experiment on small gold clusters, the photoelectron spectrum of Au₂₀⁻ was observed to have an extremely large HOMO-LUMO gap of 1.77 eV (Fig. 12), reminiscent of that of $C_{60}^{-.90}$ With the exception of Au2 and Au6, the HOMO-LUMO gap observed for Au20 is the largest among all known coinage-metal clusters,55 even exceeding that of C₆₀.⁹⁰ The unusually large HOMO-LUMO gap suggests that neutral Au₂₀ should be chemically inert and possibly possess a highly symmetric geometry. An extensive structural search for both the neutral and the anion using relativistic DFT calculations revealed that the most stable structure of Au₂₀ is a perfect tetrahedral (T_d) structure (Fig. 13A), which is more stable than the previously predicted "global minima" C_1 and C_{2v} (Fig. 13B and C)^{91,92} by 1.4 eV and 1.8 eV, respectively. The $T_{\rm d}$ Au₂₀ is a closed shell with a calculated HOMO-LUMO gap of 1.8 eV, in excellent agreement with the experiment. Very little structural change was observed upon electron addition to the $T_{\rm d}$



Fig. 12 Photoelectron spectra of Au_{20}^- taken at (A) 355 nm, (B) 266 nm, and (C) 193 nm. From ref. 14.

Au₂₀; the Jahn–Teller geometry distortion expected for the openshell Au₂₀⁻ was found to be quenched by the spin–orbit coupling. When spin–orbit coupling is included, the calculated electron affinity (EA, defined as the total energy difference between the optimized anion and the neutral structures) of the T_d Au₂₀ is 2.741 eV, again in excellent agreement with the experimental value of 2.745 eV, confirming unequivocally its T_d structure.

The tetrahedral Au_{20} pyramid can be viewed as a small piece of bulk gold with a slight relaxation. Each of its four triangular faces resembles, on the nanoscale, a (111) surface of facecentered cubic (fcc) gold. It has a very high surface area with all the atoms being on the cluster surface. The 20 gold atoms in the $T_{\rm d}$ Au₂₀ can be classified into three categories: 4 at the apexes with a three-coordination to nearest neighboring atoms; 4 ninecoordinated atoms at the center of each face; and 12 six-coordinated atoms at the edge sites. The rich abundance of different coordination environments may provide preferential sites to bind different molecules, making Au₂₀ an ideal molecular model to study nanogold catalysis.

6.1. Further experimental and computational evidence of the golden pyramid

The tetrahedral structure and various properties of Au_{20} have been studied and confirmed by numerous subsequent works. Experimentally, in a TIED work,19 Xing et al. observed characteristic diffraction patterns for Au₁₈⁻-Au₂₀⁻ and interpreted them as strong evidence for the presence of fcc packing inherent to bulk gold. They found that the $T_{\rm d}$ Au₂₀⁻ gives the best fit to the experiment. In a related work by Yoon et al.,73 the same set of theoretical structures as presented in ref. 19 have been used to compare with the PES experiment, which also confirmed the T_d structure for Au₂₀⁻. In a more recent TIED measurement,⁹³ Lechtken et al. conducted a comparative study of the structures of the 20-atom clusters of copper, silver, and gold with different charge states, and found that Au_{20}^{-} is indeed tetrahedral whereas Au20⁺ contains a mixture of tetrahedral and distorted icosahedral structures. Gruene et al. studied neutral gold clusters using FIR-MPD,²⁰ in which the pyramidal structures of both Au₁₉ and Au₂₀ were unambiguously identified through their simple vibrational spectra. Neumaier *et al.*⁹⁴ studied the reactivity of Au_n^+ (n = 1-65) towards the CO molecule with Fourier transform ion cyclotron resonance mass spectrometry and found a local minimum at Au_{20}^{+} in the first CO adsorption rate, indicative of a stable Au_{20}^{+} cluster.

Computationally, the T_d structure of Au₂₀ has been confirmed in several DFT and empirical calculations.⁹⁵⁻⁹⁸ It has been shown that relativistic effects play vital roles in stabilizing the T_d structure,^{99,100} consistent with our initial work. King *et al.*¹⁰¹ explained the stability of Au₂₀ in terms of aromaticity and showed that its tetrahedral structure can be generated from



Fig. 13 Selected optimized structures of Au₂₀. (A) The ground state tetrahedral structure (T_d). (B) Amorphous structure (C_1). (C). Capped decahedron (C_{2v}). (D) Planar structure (C_{2h}). (E) Octahedral structure (O_h). (F) Dodecahedral structure (I_h). From ref. 14.

a regular dodecahedron by forming two transannular Au-Au bonds across each face while preserving T symmetry. More recently, by chemical bonding analysis, Zubarev and Boldyrev⁷⁷ reinforced the concept of spherical aromaticity and showed that the pyramidal Au_{20} can be described by 10 four-center twoelectron (4c-2e) bonds localized on 10 intertwining Au₄ tetrahedra. Krishnamurty et al.¹⁰² studied the finite temperature behavior of the tetrahedral Au₁₉ and Au₂₀ clusters using ab initio molecular dynamics. Molina et al. 103 theoretically examined the competition between Jahn-Teller effect and spin-orbit coupling in $T_d \operatorname{Au}_{20}^{\gamma \pm}$ with $\gamma = 1, 2, 3$, and concluded that except for Au_{20}^{3-} , all other ions tend to conserve the original tetrahedral symmetry of Au₂₀, consistent with our original finding. The optical properties of T_d Au₂₀ have been first studied by Wu et al.,¹⁰⁴ and more recently by Aikens and Schatz,¹⁰⁵ both using time-dependent DFT (TD-DFT) calculations. Shiga and Haruta¹⁰⁶ have simulated the CO oxidation catalyzed by T_d Au₂₀ using paired interacting orbitals (PIO) analysis. The structure and catalytic reactivity of Au₂₀ upon deposition onto an oxide substrate (MgO) have been theoretically investigated by Molina and Hammer,¹⁰⁷ and more recently by Yoon and Landman.¹⁰⁸

6.2. Attempts to synthesize ligand-protected golden pyramids

The high symmetry and high stability of Au₂₀ as discovered in the gas phase have also stimulated synthetic works. We have successfully demonstrated that the tetrahedral Au₂₀ can be formed in solution, coordinated with eight triphenyl phosphine (PPh₃) ligands.¹⁰⁹ The Au₂₀(PPh₃)₈ complex exists as doubly charged cations in solution as determined from its mass spectrum taken by a high-resolution mass spectrometer coupled with an electrospray ionization source. A collision-induced dissociation experiment showed that four PPh3 ligands can be easily removed from $Au_{20}(PPh_3)_8^{2+}$, resulting in a highly stable $Au_{20}(PPh_3)_4^{2+}$ ion. This is consistent with the tetrahedral structure of Au_{20} , in which the four apex sites are expected to bond to the PPh₃ ligands strongly. Theoretical calculations performed on a model Au₂₀(PH₃)₄ complex predicted strong Au–PH₃ bonds with bond energies of ~ 1 eV, confirming the high stability of the $Au_{20}(PPh_3)_4^{2+}$ ion, and giving more hopes of synthesizing ligandstabilized tetrahedral Au₂₀ in large quantities. Recently, Zhu et al.¹¹⁰ reported the synthesis and observation of highly stable thiolate-capped Au₂₀ clusters in the formula of Au₂₀(SCH₂CH₂Ph)₁₆. The optical absorption spectrum of these clusters showed multiple-band structures with a large absorption band gap of ~ 2.15 eV. In a subsequent DFT study by Pei et al.,¹¹¹ the structure of the above synthesized Au₂₀(SCH₂CH₂Ph)₁₆ was predicted to contain a prolate Au₈ core, in which the tetrahedral structure of Au₂₀ is not retained due to the strong thiolate-Au bond. Phosphine ligands are more promising in allowing the Au₂₀ pyramid to be realized.

7. Au₂₁⁻-Au₃₅⁻: structural evolution from pyramidal to tubular to core-shell

Structural information for medium-sized gold clusters is of particular importance for understanding the growth dynamics of gold nanoparticles, but it becomes increasingly more challenging to obtain structural information for these systems due to the large number of possible isomers. Beyond Au_{20}^{-} , only a few structural studies have been carried out experimentally. A joint TIED/DFT study by Xing et al.¹⁹ suggested an elongated cage structure for Au₂₁⁻ and a highly symmetric tube structure for Au₂₄⁻. The PES/DFT study by Yoon et al.,⁷³ using the same set of calculated structures as presented in ref. 19, showed that the simulated DOS of the tubular Au24⁻ is in reasonable agreement with the experimental PES spectrum. In the later work,⁷³ it was suggested that Au₂₁⁻ has a tetrahedral-based ground state structure while Au22⁻ and Au23⁻ adopt double-layer pocket-like structures. Similar observations were made in our systematic PES/DFT study of Au_n⁻ in the range of n = 21-25.¹¹² We have shown that the low energy isomers of Au₂₁⁻ are dominated by pyramidal structures which are based on the $T_{\rm d}$ Au₂₀. For Au₂₂ and Au₂₃⁻, pyramidal and fused-planar (double-layer) structures are found to be competitive in energies. A low symmetry tubular structure was suggested for Au₂₄⁻, different from the high symmetry one suggested by the TIED study. It is worth mentioning that definite structural assignments were not achieved for these intermediate-sized gold clusters due to the lack of quantitative agreement between the experiment and the simulation; and the presence of multiple isomers cannot be excluded. However, all these joint studies seem to consistently suggest the structural motif evolution from pyramidal Au₂₀⁻ and Au₂₁⁻, to fused-planar (double-layer) Au_{22}^{-} and Au_{23}^{-} , to tubular Au_{24}^{-} . Significantly, our study¹¹² revealed that Au₂₅⁻ has a core-shell structure with a single-atom core and a 24-atom shell, suggesting another structural transition from tubular to core-shell structures between n = 24 and 25. The Au₂₅⁻ cluster is thus the smallest anionic gold cluster that features an atom in the core.

For n > 25, Au₃₂ has been theoretically predicted by Johansson *et al.*⁷¹ to be "a 24-carat golden fullerene" which has a highly stable cage structure with the same icosahedral (I_h) symmetry as C_{60} and can be constructed by decorating one atom to each of the 32 faces of C_{60} . The high-symmetry hollow cage structure is unexpected for a metal cluster of such size. Our subsequent photoelectron spectroscopy on the corresponding anion together with DFT calculations,¹¹³ however, revealed that Au₃₂⁻ possesses a low-symmetry (C_1) compact core–shell structure with a three-atom triangular core. Further theoretical calculations by Jalbout *et al.*¹¹⁴ and Johansson *et al.*¹¹⁵ supported this conclusion that for the anionic Au₃₂⁻ compact structures are preferred over the fullerene-like isomer, while the neutral golden fullerene Au₃₂ yet remains to be verified experimentally.

Au₃₄⁻ has also attracted major experimental efforts, since its PES spectrum displays well-resolved features with a large HOMO–LUMO energy gap reflecting a major electron shell closing ($1S^{2}1P^{6}1D^{10}2S^{2}1F^{14}$) for its neutral.⁵⁵ In a combined TIED, PES and DFT work,¹¹⁶ Lechtken and co-workers concluded that the best fit to the TIED data for Au₃₄⁻ is a chiral structure with C_3 symmetry which consists of a four-atom tetrahedral core and a thirty-atom shell. This C_3 structure has been described by Doye and Wales before.¹¹⁷ Our initial joint PES/DFT study¹¹⁸ found a similar structural motif for Au₃₄⁻, *i.e.* a core–shell structure with a four-atom tetrahedral core, but with notable difference in the details of the outer shell from the proposed C_3 structure. Two low-symmetry C_1 structures were shown to compete for the global minimum, which could not be distinguished at that time based on their simulated spectra.



Fig. 14 Structural evolution from Au_{32}^- to Au_{35}^- . Newly added atoms are highlighted in red. From ref. 119.

Very recently, we systematically investigated the structures of Au_n⁻ with n = 27-35.¹¹⁹ In the new study, PES experiments were conducted using Ar-seeded He supersonic beams to achieve better cluster cooling, yielding better resolved spectra. Simulation of the photoelectron spectra was also improved by including the spin-orbit coupling which was not considered in our previous study. Quantitative comparison between the experimental and simulated spectra has been achieved for most of the sizes investigated (with the exceptions of n = 29 and 31), leading to significantly more convincing assignments of their structures. Au_{27}^{-} , Au_{28}^{-} , and Au_{30}^{-} all have core-shell structures with a one-atom core. A C_1 structure containing a three-atom core (Fig. 14) was newly identified for Au_{32}^{-} , which was found to be more stable than all previously reported core-shell structures of Au₃₂⁻ and agrees best with the experiment. Au₃₃⁻ has a C_{3v} coreshell structure with a four-atom tetrahedral core.

For Au_{34}^{-} , nine well-resolved spectral features up to 5.5 eV in PES are amazingly well-reproduced in the simulation (Fig. 15),

confirming unequivocally the C_1 global minimum structure, consistent with the conclusion in our previous study.¹¹⁸ The C_3 structure proposed in the TIED work¹¹⁶ was found to be only 0.03 eV higher above the global minimum at the PBE/CRENBL/ SO DFT level. However, its simulated spectrum disagrees with the experiment and can be excluded as a major carrier (Fig. 15); finally Au₃₅⁻ is of a C_1 structure, which can be derived from the C_1 Au₃₄⁻ by attaching one atom to its surface.

A cluster growth path was therefore revealed from Au_{25}^{-} to Au_{35}^{-} (Fig. 14): from Au_{25}^{-} to Au_{30}^{-} , all of which have coreshell structures with a single-atom core, clusters grow by expanding the shell ($Au@Au_m^{-}$, m = 24-29); Au_{33}^{-} ($Au_4@Au_{29}$) can be viewed as adding an Au atom to the core of Au_{32}^{-} ($Au_3@Au_{29}$) whereas Au_{34}^{-} ($Au_4@Au_{30}$) can be viewed as adding an Au atom to the structure of Au_{34}^{-} is quite robust, and Au_{35}^{-} can be viewed as attaching an Au atom onto the surface of Au_{34}^{-} : [($Au_4@Au_{30}$) + Au]. The core–shell growth pathway may provide valuable clues for structural searching of larger gold clusters.



Fig. 15 PES spectrum of Au_{34}^- compared with simulated spectra of candidate structures. From ref. 119.



Fig. 16 Photoelectron spectra of Cu_n^- , Ag_n^- and Au_n^- (n = 53, 55, 57, 58) obtained at a photon energy of 6.424 eV. Reproduced from ref. 16 with permission. Copyright 2004 American Physical Society.



8. Au₅₅⁻-Au₆₄⁻: low-symmetry core-shell gold nanoclusters

In the nanometre regime, the 55-atom clusters are of particular interest because they correspond to a magic number in the Mackay icosahedron series. However, several theoretical calculations have suggested Au₅₅ to possess a disordered amorphous structure as opposed to an ordered icosahedron.^{37,117,120} In 2004, Issendorff and co-workers¹⁶ reported systematic high resolution PES spectra of coinage metal clusters Cu_n⁻, Ag_n⁻ and Au_n⁻ with

n = 53-58. It was observed that while the spectra of Cu_n⁻ and Ag_n^{-} were practically identical to each other, Au_n^{-} clusters displayed completely different spectral patterns (Fig. 16). Particularly, the spectra of Cu₅₅⁻ and Ag₅₅⁻ were found to be rather simple with several well-separated peaks in the s-band region (corresponding to the delocalized electron shells 1G, 2P and 1F),⁵⁵ while that of the Au₅₅⁻ exhibited one broad (yet congested) band with numerous fine structures (Fig. 16). The relatively simple spectral features observed for Cu₅₅⁻ and Ag₅₅⁻ are a signature of high-symmetry structures. Comparison of the PES spectra with simulated DOS for a number of candidate structures indeed concluded that Cu_{55}^{-} and Ag_{55}^{-} have icosahedral (I_h) ground state structures, whereas the low-lying isomers of Au₅₅are all of low symmetries. It was demonstrated that the preference of Au₅₅⁻ to adopt a low-symmetry structure was due to a relativistic effect, since the reference nonrelativistic calculations would give rise to a fictitious $I_{\rm h}$ ground state Au₅₅⁻ very similar to Cu_{55}^- or Ag_{55}^- .

We have carried out a joint PES/DFT investigation³⁸ of Au_n⁻ with n = 55-66, providing a detailed mechanism of how the relativistic effect leads to the low-symmetry structure of Au₅₅⁻. More significantly, we found that Au₅₈⁻ is a highly spherical core–shell cluster. Clusters up to Au₆₄⁻ are formed simply by nucleating additional atoms onto the surfaces of the robust Au₅₈⁻ clusters.

During structural optimization of Au₅₅⁻ starting from the I_h symmetry, it was observed that the surface atoms underwent several steps of rearrangement, in which a number of surface bonds were broken and surface "holes" were formed (Fig. 17). Several interior atoms subsequently moved outward to fill the surface holes, leading to a highly disordered amorphous-like final structure, which is 1.65 eV more stable than the I_h Au₅₅⁻ (Fig. 17). The structural reconstruction resulted in shorter Au–Au bond length for the surface atoms (2.83 Å) than that in an I_h structure (2.91 Å). Such surface contraction has also been observed for bulk Au(100) surface, but not for the corresponding



Fig. 18 Optimized structures of (A) Au_{56}^- , (B) Au_{57}^- , and (C) Au_{58}^- ; (D) the 12-atom inner part (one atom core + 11-atom first shell) of Au_{58}^- ; (E) the 46-atom outer shell of Au_{58}^- , where the surface square-defects are highlighted; and (F) structure of Au_{58}^- where the inner core is highlighted. From ref. 38.

Ag(100), which is entirely due to the relativistic effect.¹²¹ Therefore, the relativistic-driven structural distortion of Au_{55}^{-} from the ideal $I_{\rm h}$ structure is to optimize surface interactions at the expense of the interior, analogous to the reconstruction in bulk gold surfaces.¹²¹

Filling the surface holes of the distorted Au₅₅⁻ led to a spherical Au₅₈⁻ with a core-shell structure (Fig. 18). The structures of Au_{56}^{-} and Au_{57}^{-} were constructed in a similar way by filling the surface holes of the core-constrained Au₅₅⁻ with one and two atoms, respectively (Fig. 18). Despite its low symmetries, starting from n = 56 and onward, the structures of Au_n⁻ clusters displayed clear core-shell motifs, in contrast to the amorphous-like Au₅₅⁻ (Fig. 19). Specifically, Au₅₆⁻ and Au₅₇⁻ consist of a central atom core and a 10-atom first shell with a 45-atom and 46-atom second shell, respectively; Au_{58}^{-} possesses a central atom core, an 11-atom first shell, and a 46-atom outer shell with 6 surface "square-defects" (Fig. 18). The Au₅₈⁻ cluster is nearly spherical, with the ratio between its three principal axes of 1.0: 1.0: 1.0; and structurally very robust. The neutral Au₅₈ is a major shell closing $(1S^21P^61D^{10}2S^21F^{14}2P^61G^{18})$. PES spectra of Au₅₈⁻ indeed revealed a large HOMO-LUMO gap (Fig. 16). Thus, the Au_{58} cluster is both a geometrically and electronically stable cluster. Our high-resolution PES data further revealed that the spectra of Au₅₉⁻-Au₆₄⁻ displayed remarkable similarities to that of Au₅₈⁻; the effect of the additional atoms seemed simply to contribute its one valence electron, which successively fills up the LUMO or SOMO following the aufbau principle. This observation suggested that additional atoms in the larger clusters from Au_{59}^{-} to Au_{64}^{-} were grown from Au_{58}^{-} by adding extra atoms to the square defects on its surface. Our optimized structures in this size range showed very little structural distortions to the Au₅₈



Fig. 19 Plots of the atomic distances from the center atom for the optimized structures of Au_n^- (n = 55-64). Two atomic shells are clearly revealed for n = 56-64. From ref. 38.

core (Fig. 19). The unique low-symmetry structures of gold clusters observed in this critical size regime may provide key insights into the catalytic effects of gold nanoparticles. The protruding surface atoms are expected to become the active sites for chemical reactions.

9. Conclusions and outlook

Structural determination of size-selected clusters is a challenging task, in particular for clusters with more than 20 atoms. It requires close collaborations between sophisticated experimental techniques that are sensitive enough to probe the trace amount of gas phase samples and advanced theoretical calculations. In this paper, we reviewed recent experimental studies leading to structural information on anionic gold clusters, primarily focusing on joint photoelectron spectroscopy and theoretical works from the authors' laboratory. Structural evolution of Au_n^{-} clusters as revealed to date by joint experimental and theoretical studies can be summarized as follows. (1) Small gold cluster anions have planar structures up to n = 12, where a 2Dto-3D structural transition occurs. (2) Au13⁻-Au15⁻ adopt 3D flat shell-like structures. (3) Hollow cages are found for Au_{16}^{-1} and Au₁₇⁻. The cage structure evolves into tetrahedral structure at n = 19 and 20. Au₁₈⁻ is the transition size from cage to pyramid, where both cage and pyramidal isomers co-exist. (4) Au₂₀ is a perfect golden pyramid with a large HOMO-LUMO gap. (5) For n > 20, a gradual transition was observed from pyramidal-based Au₂₁⁻, to fused-tubular (n = 22, 23), to tubular (n = 24). (6) At n = 25, a core-shell type of structure appears and Au25⁻ contains a single core-atom and a 24 atom shell. The lowsymmetry core-shell structures are the dominant structural feature for $25 \le n \le 35$ and beyond. (7) In the nanometre size regime, Au₅₅⁻ features a low-symmetry amorphous structure, instead of the icosahedral structure, due to the relativistic effects analogous to the surface reconstruction in bulk gold. (8) Adding three Au atoms to Au_{55}^{-} results in a robust and spherical Au_{58}^{-} , which has a clear core–shell structure. (9) For n > 58 up to Au₆₄⁻ the clusters are all evolved from the robust Au₅₈⁻ core in a layered growth manner by nucleating additional atoms to the surface of Au₅₈⁻.

Despite the impressive progresses advanced by recent joint experimental and theoretical efforts, which have provided a panoramic view of the structural evolution of gold clusters and a reasonable library of structure-property information, there are many issues yet to be resolved. First, there is an obvious need to systematically solve the structures of Au₃₆⁻-Au₅₅⁻. We have shown that medium-sized Au_n^- (n = 33-35) clusters have coreshell structures with a 4-atom tetrahedral core, while at the nanometre size Au₅₆⁻-Au₆₄⁻ have core-shell structures with two atomic shells. Thus, it is expected that gold clusters in the missing size range from n = 36 to 54 are likely all of core-shell compact structures. Recently, based on DFT-basin hopping global minimization, Jiang and Walter¹²² suggested that Au₄₀ features a twisted pyramidal geometry with an Au₄-tetrahedral core. Its structure was shown to be built upon an Au₄@Au₃₂ core-shell framework with four adatoms in tetrahedral symmetry, in line with the core-shell growth pattern discovered for Au₂₇⁻-Au₃₅⁻ as discussed in Section 7. For larger clusters, Au₄₂,⁶⁹ Au₅₀,⁷² and Au₇₂¹²³ have been suggested to be spherical golden cages, similar to Au_{32} . However, none of these structures has been experimentally confirmed. A structural study of even larger gold clusters is of paramount importance, since these clusters are likely directly related to the unique nanogold catalysis. Gold nanoclusters with more than one hundred atoms are accessible with the experimental techniques now available, whereas current limitation in addressing the larger gold clusters lies in the computational challenges.

While this review was focused on anions, gold clusters of other charge states are of equal interest and importance, particularly the singly charged cation states and neutral states. Experimental determination of structures of singly charged cationic gold clusters has been carried out mainly by Kappes' group using ion mobility spectrometry and rare-gas-complex photodissociation spectroscopy.^{124–127} Structures of Au_n^+ cluster cations up to n =20 have been summarized in a recent review article by the same group.²⁷ So far, structure determination of neutral gold clusters has been performed only for a few sizes in a recent IR multiphoton dissociation study of Au_nKr (n = 7, 19, 20).²⁰ It is interesting to note that only at a very few sizes (e.g. n = 20) gold clusters have uniform geometries in three different charge states, while the majority of Au_n⁺ and Au_n⁻ display different structures in the small size regime.²⁷ For example, the onset of 3D structures for Au_n^+ appears at n = 8, much smaller than that for the anions. For the seven-atom gold cluster, each charge state (+, -, 0) has a different structure. However, it is expected that for large clusters, the influence of charge on structures will be diminished, in particular for stable and high symmetry structures, such as Au₂₀ and Au₅₈. Chemical doping of gold clusters is another interesting issue. As mentioned above, doping gold clusters with other atoms offers additional opportunities for fine tailoring their physical and chemical properties. A number of bimetallic gold clusters have been studied experimentally.¹²⁸⁻¹³¹ A few examples of doping the "golden buckyball" Au₁₆⁻ have been mentioned. It is expected that doped gold clusters will represent new dimensions in the study of gold nanoclusters.

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