

New insight into the electronic shell of Au₃₈(SR)₂₄: a superatomic molecule†

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Based on the recently proposed super valence bond model, in which superatoms can compose superatomic molecules by sharing valence pairs and nuclei for shell closure, the 23c-14e bi-icosahedral Au₂₃⁽⁺⁹⁾ core of Au₃₈(SR)₂₄ is proved to be a superatomic molecule. Molecular orbital analysis reveals that the Au₂₃⁽⁺⁹⁾ core is an exact analogue of the F₂ molecule in electronic configuration. Chemical bonding analysis by the adaptive natural density partitioning method confirms the superatomic molecule bonding framework of Au₃₈(SR)₂₄ in a straightforward manner.

Thiolate-protected gold (Au-SR) nanoparticles with core diameter of 0.5–2 nm are of significant interest due to their distinct electronic transition in optical absorption, intrinsic magnetism, enhanced photoluminescence, discontinuous charge transport and redox properties, and applications in catalysis.¹

Crystallization and structural determination of Au₁₀₂(SR)₄₄ was a breakthrough in nanogold research.² The seminal X-ray crystal structure determination showed that the thiolate ligands do not simply passivate a large gold core but instead form Au_n(SR)_{n+1} (*n* = 1, 2) oligomers that bind to a smaller gold core. This packing agrees with the previous “divide-and-protect” model³ in concept. The 44 thiol groups of Au₁₀₂(SR)₄₄ form 21 staple motifs⁴ on the surface, 19 Au(SR)₂ and 2 Au₂(SR)₃ units. Later, the Au₂(SR)₃ units were also observed in the crystal structure of Au₂₅(SR)₁₈[−].⁵ Knowledge of the binding motifs of Au₂₅(SR)₁₈[−] has been obtained from density functional theory (DFT) predictions⁶ independent of and in agreement with X-ray crystal structure determination. DFT⁷ and X-ray⁸ investigations

of Au₃₈(SR)₂₄ have revealed that these motifs are ubiquitous. Moreover, based on the model of a gold core surrounded by gold thiolate oligomers, DFT calculations have been used to predict the structures of Au₁₀(SR)₈,⁹ Au₁₂(SR)₉⁺,¹⁰ Au₂₀(SR)₁₆,¹¹ Au₂₄(SR)₂₀,¹² Au₄₄(SR)₂₈^{2−},¹³ and Au₁₄₄(SR)₆₀,¹⁴ which have not yet been determined by experiments. All of these clusters have molecule-like electronic structures in which the highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap can be correlated to measured optical and electrochemical values.

Electronic shell closure based on the jellium model has successfully explained the observed experimental abundances of alkali-metal clusters in the gas phase.¹⁵ The spherical jellium model assumes a uniform background of positive charge of the cluster's atomic nuclei and the innermost electrons, in which valence electrons move and are subjected to an external potential. To explain the electronic stability of Au-SR nanoparticles, Hakkinen *et al.*¹⁶ extended the superatom model to treat Au-SR nanoparticles by accounting for ligand interactions with the nanoparticle core. The electron count of the Au_N(SR)_M^z compound is determined as *n** = *N* − *M* − *z*, where *N* and *M* are related to the cluster stoichiometry, and *z* is the charge state of the compound. The appropriate Aufbau rule of delocalized “superatomic orbitals” of Au clusters is |1S²|1P⁶|1D¹⁰|2S²1F¹⁴|2P⁶1G¹⁸|2D¹⁰3S²1H²²|..., and exceptional stability is associated with the magic numbers (*n** = 2, 8, 18, 34, 58, 92, ...). Superatom theory has achieved great success in Au-SR nanoparticles, of which the stability of many clusters can be understood with the magic numbers, such as Au₁₀₂(SR)₄₄ (*n** = 58),² Au₆₈(SR)₃₄ (*n** = 34),¹⁷ Au₄₄(SR)₂₈^{2−} (*n** = 18),¹³ Au₂₅(SR)₁₈[−] (*n** = 8),⁵ and Au₁₂(SR)₉⁺ (*n** = 2).¹⁰

Besides the electronic shell closure based on the superatom model, geometric shell closure is also very important for Au-SR clusters. Among the ligand-protected gold nanoparticles with a superatom core, Au₂₅(SR)₁₈[−] is most interesting in both electronic and geometric shell closure,⁵ which has a nearly idealized icosahedral core of Au₁₃, where twelve vertexes of the icosahedron are stapled by six Au₂(SR)₃ oligomers. The icosahedral core

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is a 13-center 8-electron (13c-8e) superatom. Electronic structures of $\text{Au}_{25}(\text{SR})_{18}^-$ are consistent with the superatom model, in which the large HOMO–LUMO gap (~ 1.3 eV) can be viewed as P–D superatom orbitals.¹⁸

The superatom model can treat only those clusters with a spherical core, and the stability of clusters with a non-spherical core, such as $\text{Au}_{38}(\text{SR})_{24}$,⁸ cannot be understood. As shown in Fig. 1a, $\text{Au}_{38}(\text{SR})_{24}$ also has a magic geometric shell, which has a face-fused bi-icosahedral Au_{23} core. Eighteen vertexes of the bi-icosahedron are stapled by six $\text{Au}_2(\text{SR})_3$ and three $\text{Au}(\text{SR})_2$ oligomers, of which each oligomer withdraws one electron and there are 14 valence electrons delocalized in the $\text{Au}_{23}^{(+9)}$ core (Fig. 1b). $\text{Au}_{38}(\text{SR})_{24}$ has a sizable HOMO–LUMO gap (~ 0.9 eV) and a large adiabatic ionization potential,^{7a} indicating a high electronic stability. However, the 14 valence electrons delocalized in the bi-icosahedral Au_{23} core disagree with the count in the superatom model. The electronic stability of $\text{Au}_{38}(\text{SR})_{24}$ has been explained by Aikens *et al.*^{7b} using the parameter-based particle-in-a-cylinder model, a variation of Clemenger's ellipsoidal shell model,¹⁹ with certain parameters. However, the parameters give no direct physical picture, and the model is entirely structureless.

Recently, we proposed a super valence bond (SVB) model²⁰ to explain the electronic stability of non-spherical shells of metal clusters, and found that Li_8 , Li_{10} , and Li_{14} are exact analogues of CH_4 , N_2 , and F_2 , respectively, in electronic state and bonding patterns. Note that the Au_{23} core of $\text{Au}_{38}(\text{SR})_{24}$ is a union of two 13c-7e icosahedral units and has 14 valence electrons, of which a three-nucleus triangle face is shared by the two 13c-7e icosahedral units (Fig. 1c). Is the $\text{Au}_{23}^{(+9)}$ core an analogue of the F_2 molecule in electronic structure (just like $\text{Au}_{13}^{(+5)}$ is an analogue of Ne)? Is the SVB model applicable to the Au-SR clusters?

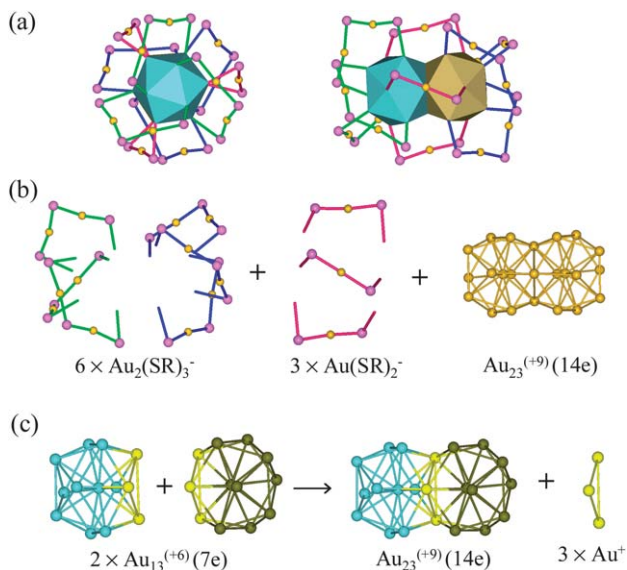


Fig. 1 (a) Top and side views of $\text{Au}_{38}(\text{SR})_{24}$ compounds. R groups are removed for clarity. The $\text{Au}(\text{SR})_2$ and $\text{Au}_2(\text{SR})_3$ oligomers are given as ball-and-stick models (Au: yellow; SR: pink), in which the sticks are shown in different colors by their groups. The Au cores are shown as polyhedra. (b) Model of $\text{Au}_{23}^{(+9)}$ core plus $\text{Au}(\text{SR})_2^-$ and $\text{Au}_2(\text{SR})_3^-$ oligomers. (c) Superatomic model of the prolate $\text{Au}_{23}^{(+9)}$ core.

To verify such a supposition on the chemical bonding of $\text{Au}_{38}(\text{SR})_{24}$, we first studied the electronic structure of the $\text{Au}_{23}^{(+9)}$ core of $\text{Au}_{38}(\text{SR})_{24}$ for simplicity and clarity. Based on the SVB model, $\text{Au}_{23}^{(+9)}$ can be seen as an analogue of F_2 in chemical bonding. To verify this point of view, Fig. 2a compares their canonical Kohn–Sham molecular orbital (MO) diagrams of the valence shell. Chemical bonding of F_2 is a classical case of valence bond (VB) theory in textbooks, in which there are three lone pairs in each F and one covalent pair shared by two F. In the canonical MO of F_2 , the two s atomic orbitals (AOs) are split into two sets (σ_s and σ_s^*), the four p_x and p_y AOs are split into two doubly degenerate sets (π_{p_x,p_y} and π_{p_x,p_y}^*), and the p_z AOs are also split into two sets (σ_{p_z} and $\sigma_{p_z}^*$). The electronic configuration is $(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_{p_z})^2 (\pi_{p_x,p_y})^4 (\pi_{p_x,p_y}^*)^4 (\sigma_{p_z}^*)^0$, where the $(\sigma_{p_z})^2$ MO consists of the F–F σ -bond and the HOMO–LUMO gap is $(\pi_{p_x,p_y}^*) - (\sigma_{p_z}^*)$. To our surprise, the canonical MO diagrams of $\text{Au}_{23}^{(+9)}$ are obviously analogous of those of F_2 both in MO shapes and orders (except for the order of σ_{p_z} and π_{p_x,p_y}). The 23c-14e bi-icosahedral core can be taken as a superatomic molecule bonded by two 7-electron superatoms, of which two electrons are shared by the two superatoms for 8-electron shell closure each. It is noted that here we focused only on the comparison of the valence shells of $\text{Au}_{23}^{(+9)}$ and F_2 . If one includes inner and/or outer shells, there will be both similarities and dissimilarities between the atomic and superatomic shells. For example, Al_{13} is a well known super-halogen, but the electronic configuration of Al_{13} ($[1S^2]1P^6|1D^{10}2S^2|1F^{14}2P^5|\dots$) is of course different from that of Br.

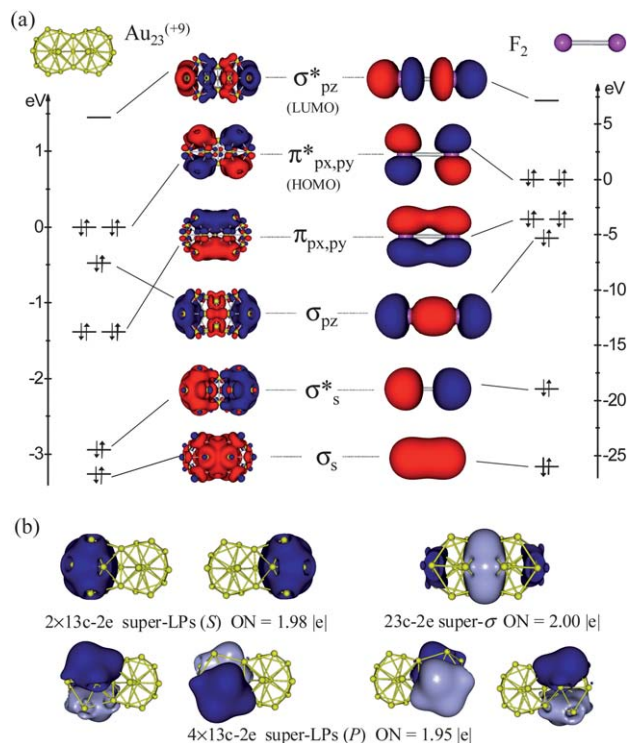


Fig. 2 (a) Comparison of the Kohn–Sham MO diagrams between $\text{Au}_{23}^{(+9)}$ (left) and F_2 (right). Energies of the HOMOs are reset to zero. (b) AdNDP localized natural bonding orbitals of the $\text{Au}_{23}^{(+9)}$ cluster, where the Au(5d) lone pairs (ON = 1.96–1.99|e|) are not shown.

Next, to give a direct view on the chemical bonding of a cluster, we selected the adaptive natural density partitioning (AdNDP) method as a tool for chemical bonding analysis. This method was recently developed by Zubarev and Boldyrev²¹ and used to analyze chemical bonding in organic molecules, boron clusters, and Au clusters.²² AdNDP recovers both Lewis bonding elements (1c-2e and 2c-2e objects) and delocalized bonding elements (*nc*-2e), which achieves seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. The 8e-superatom model of Au₂₅(SR)₁₈⁻ is successfully confirmed by AdNDP analysis, and direct evidence for the delocalized superatomic orbitals (S²P⁶) is given (see Fig. S1 in ESI†).

Chemical bonding analysis by AdNDP confirms further the superatomic molecule model of Au₂₃⁽⁺⁹⁾. As shown in Fig. 2b, AdNDP analysis reveals three 13c-2e super lone pairs (LPs) (super S, P_x, and P_y) in each 13c-superatom, and one 23c-2e super σ -bond in the Au₂₃⁽⁺⁹⁾ cluster. The Au(5d) orbitals are viewed as LPs with ON = 1.86–1.98|e|, and are not plotted in this figure. Such a bonding framework shows clearly that the Au₂₃⁽⁺⁹⁾ cluster can be viewed as a superatomic molecule bonded by two 13c-7e superatoms, of which two electrons and three nuclei are shared by the two superatoms.

Ligand effects are also very important for Au-SR clusters. Lastly, we carried out a total bonding analysis of Au₃₈(SR)₂₄ using AdNDP. The R groups do not affect much of the overall bonding patterns of the compound, thus we used SH instead of SR for simplicity and clarity in the chemical bonding analysis. Fig. 3 plots the bonding framework of the valence shells of Au₃₈(SH)₂₄ from AdNDP analysis. As expected, the Au(5d) orbitals are viewed as LPs with ON = 1.86–1.98|e|, which are excluded in this analysis. AdNDP analysis reveals 24 LPs of S atoms with ON = 1.94–1.95|e|, 24 2c-2e localized SH σ -bonds with ON = 1.98–1.99|e|, and 48 2c-2e localized AuS σ -bonds with ON = 1.90–1.93|e|. The remaining 14 electrons are delocalized in the Au₂₃ bi-icosahedral core: two s-type 13c-2e super-LPs, four p-type 13c-2e super-LPs, and one 23c-2e super- σ . The

bonding analysis confirms that the Au₂₃ core of Au₃₈(SR)₂₄ is a superatomic molecule in electronic structure.

In summary, based on the SVB model, the 23c-14e double-icosahedral Au₂₃⁽⁺⁹⁾ core of Au₃₈(SR)₂₄ is an exact analogue of the F₂ molecule in both MO diagrams and bonding patterns, of which electronic shell closure is obtained beyond the magic numbers of superatoms. Superatom theory has achieved great success in ligand-protected Au nanoclusters. However, the SVB model gives new physical insight into the shell closure of delocalized electrons, and extends the superatom model. Geometric shell closure is as important as electronic shell closure, and unusual stability requires both geometric and electronic shell closure in Au-SR clusters. Although the superatomic molecule shell may be less stable than the superatom shell, it is more diverse and flexible in matching the geometric shell. We believe that such an electronic shell closure of a superatomic molecule may exist in some other ligand-protected Au nanoparticles, and the SVB model is helpful in guessing the structure of some other Au-SR clusters which are isolated but not yet crystallized. For example, in a recent surfactant-free synthesis of small Au-SR clusters,²³ some 10e compounds (Au₂₉(SR)₁₉, Au₃₀(SR)₂₀ and Au₃₁(SR)₂₁) were viewed as stable clusters from mass spectra. Although the structures of these 10e compounds have not yet been given, we expect that the electronic shells of these 10e compounds are analogues of N₂ molecules based on the SVB model.

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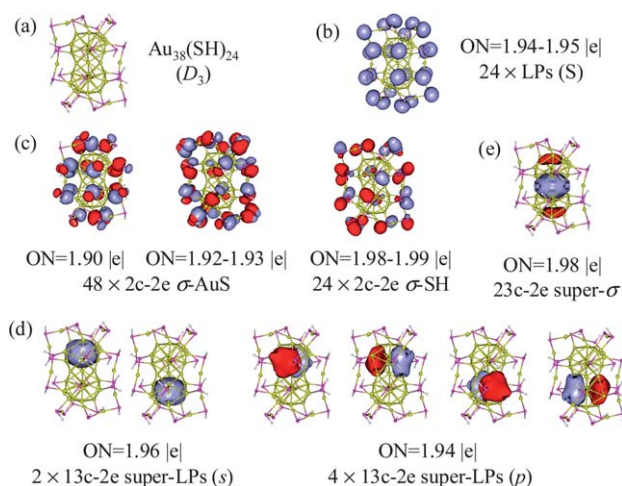


Fig. 3 (a) Geometry (Au: yellow, S: pink, H: white) and AdNDP localized natural bonding orbitals of Au₃₈(SH)₂₄. (b) lone pairs, (c) localized AuS and SH bonds, (d) 13c-2e delocalized bonding, and (e) 23c-2e delocalized bonding.

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