

Correspondence: Reply to 'On the bonding in ligand-protected gold clusters'

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In the recent Correspondence¹, Professor Henrik Grönbeck made several comments on the recently developed grand unified model (GUM)², in particular using the ligand-protected gold cluster [Au₂₅(SR)₁₈]¹⁻ as an example. We noted that the latter cluster can be viewed as belonging to a special group of ligand-protected gold clusters that contain one or several icosahedral Au₁₃ motifs³. For this group of clusters, a secondary block Au₁₃(8e) has been identified as a more convenient way to describe their structure anatomy and evolution. Another extension of the GUM is the identification of the new elementary block, Au₃(μ₃-S), with zero valence electron [referred as Au₃(μ₃-S)(0e)] to describe all crystallized ligand-protected gold clusters containing μ₃-S motifs⁴. In this correspondence, first, we discuss the purpose of GUM development in more detail. Next, we briefly discuss the secondary block Au₁₃(8e) and show new computational results on the stabilities of Au₃(2e) and Au₄(2e) elementary blocks. Then two Au₆²⁺ clusters are used as the simplest example (a suggestion credited to a reviewer of ref. ²) to better explain the GUM and high stability of Au₃(2e), followed by a summary and perspective.

Purpose of GUM development: First of all, we reiterate a statement pointed out clearly in the abstract of ref. ², that is, "GUM is a predictive heuristic and may not be necessarily reflective of the actual electronic structure". In other words, the development of GUM is not intended to describe actual electronic structures or electron re-hybridization within the Au core or between the Au core and ligands at atomic level. Density functional theory (DFT) can already serve that purpose.

GUM is a model to highlight a universal correlation between the number of valence electrons in the Au core and the number of elementary blocks, with consideration of the ligand effect. As a rule of thumb, GUM can be used to describe structure anatomy and evolution of the ligand-protected clusters. When using the GUM, the focus is placed on treating the ligand-protected clusters in a coarse-grained fashion in terms of elementary blocks² or secondary blocks³, while the counting of valence electrons is at the elementary block level. As such, the assignments of the 1

valence electron for Au atom in the Au core, 0 valence electron for the PR₃ ligand, and -1 valence electron for halides are empirical descriptions of electronic structure of the ligand-protected gold clusters. Such a description is not intended to reflect the exact electron distribution at the atomic level because these assignments neglect many details in atomic level electronic structures, such as the *s*-*d* hybridization, spin-orbit effects, ligands' constraint effects, etc. Nevertheless, these detailed assignments of valence electrons and valence electron counting are widely used as rules of thumbs in general chemistry and hence employed in GUM as well.

In summary, the development of GUM is to introduce a generic rule of thumb—a rule derived after analyzing a "big data" of all 71 clusters available in the literature. In practice, we would like the GUM to be used simply as a rule of thumb, particularly for the design and prediction of new ligand-protected Au clusters. If a new ligand-protected cluster, either designed from theory or determined based on mass spectroscopy or transmission electron microscopy (TEM) experiments, does not satisfy the rule of thumb as described in GUM, the predicted structure of the cluster would be questionable or likely unrealistic for next step crystallization effort.

A secondary block icosahedral Au₁₃(8e): Among the 71 ligand-protected clusters illustrated in ref. ², there is a special group of ligand-protected gold nanoclusters that all contain one or several icosahedral Au₁₃ motifs. For these ligand-protected clusters, according to the electron counting protocols for effective detachment of ligands in GUM, each icosahedral Au₁₃ motif can be assigned to have 8e valence electrons [Au₁₃(8e)], as each icosahedral Au₁₃ motif can be viewed as packing of four elementary blocks. For example, the Au₁₃(8e) in [Au₂₅(SR)₁₈]¹⁻ consists of two Au₃(2e) and two Au₄(2e) elementary blocks. Note that this decomposition is not intended to reflect the electronic structure of the Au₁₃ core at the atomic level but simply to indicate that the 8e valence electrons of Au₁₃(8e) can be viewed as a sum of four pairs of valence electrons of the four elementary blocks. Au₁₃(8e)

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can be also viewed as an electron shell closure species, in analog of that of the stable Ne atom. As such, the $\text{Au}_{13}(8e)$ may be regarded as a secondary block (or coarse-grained block) to constitute the gold cores of the special group of ligand-protected gold clusters with one or several icosahedral Au_{13} motifs.

The introduction of secondary block $\text{Au}_{13}(8e)$ into GUM appears to be a convenient supplement to understand this special group of ligand-protected gold clusters with icosahedral Au_{13} motifs. It can be also exploited for predicting new ligand-protected gold clusters by design (see ref. ³ for more detail).

Stabilities of $\text{Au}_3(2e)$ and $\text{Au}_4(2e)$: The high stabilities of the trimer $\text{Au}_3(2e)$ and tetramer $\text{Au}_4(2e)$ elementary blocks are in part due to the strong electronic delocalization among the three- and four-Au atom clusters, and associated strong electron shell closure. From the computed formation energy (Supplementary Table 3 in ref. ²), one can see that the $\text{Au}_4(2e)$, although not as

stable as $\text{Au}_3(2e)$, is still highly favorable in formation energy, compared to the isoelectronic dimer Au_2 . In addition, the dissociation barrier from Au_4^{2+} to Au_3^+ and Au^+ is computed to be ~ 1 eV (Fig. 1), suggesting the Au_4^{2+} can be a stable species in the gas phase at room temperature. Thus, Au_3^+ and Au_4^{2+} , if could be made in the laboratory, would very likely be a standing-alone/stable species without the ligand protection, largely due to the strong electronic delocalization among Au_3^+ and Au_4^{2+} , and associated strong electron shell closure.

Using Au_6^{2+} as the simplest example to illustrate GUM: Here, two Au_6^{2+} clusters are used as the simplest examples to illustrate the view of the elementary blocks introduced in GUM. The molecular orbital analysis showed that the HOMO-30 and HOMO-31 of the D_{2d} Au_6^{2+} core in $[\text{Au}_6(\text{dppp})_4]^{2+}$ (dppp = 1,3-Bis(diphenylphosphino)propane)⁵ can be viewed as the anti-bonding and bonding orbitals of two HOMO-15 of the Au_3^+ cluster (Fig. 2a), respectively, suggesting that the HOMO-30 and HOMO-31 of the D_{2d} Au_6^{2+} can be viewed as the linear combination of two 1S orbitals of $\text{Au}_3(2e)$. Similar behavior can be seen in the HOMO (Fig. 2d) and HOMO-1 (Fig. 2e) of the ligand-protected $[\text{Au}_6(\text{dppp})_4]^{2+}$. Thus, we use this simple example to demonstrate that the ligand-protected $[\text{Au}_6(\text{dppp})_4]^{2+}$ and associated D_{2d} Au_6^{2+} core can be well described by GUM in terms of the elementary block $\text{Au}_3(2e)$.

Likewise, the HOMO-30 and HOMO-31 of the D_{2h} Au_6^{2+} core of $[\text{Au}_6(\text{PR}_3)_6]^{2+6}$ can be viewed as the anti-bonding and bonding orbitals of two HOMO-20 of Au_4^{2+} cluster (Fig. 2b), suggesting that the HOMO-30 and HOMO-31 of the D_{2h} Au_6^{2+} can be viewed as a linear combination of two 1S orbitals of $\text{Au}_4(2e)$. Similar behavior can be seen in the HOMO (Fig. 2f) and HOMO-18 (Fig. 2g) of the ligand-protected $[\text{Au}_6(\text{PR}_3)_6]^{2+}$. Again, the ligand-protected $[\text{Au}_6(\text{PR}_3)_6]^{2+}$ and its D_{2h} Au_6^{2+} core can be described by GUM as well.

Finally, we note that the orbital analyses on $[\text{Au}_6(\text{dppp})_4]^{2+}$ and $[\text{Au}_6(\text{PR}_3)_6]^{2+}$ are quite similar to that on Mg_2 , in which 3s orbital (HOMO) of two Mg atoms can form the bonding

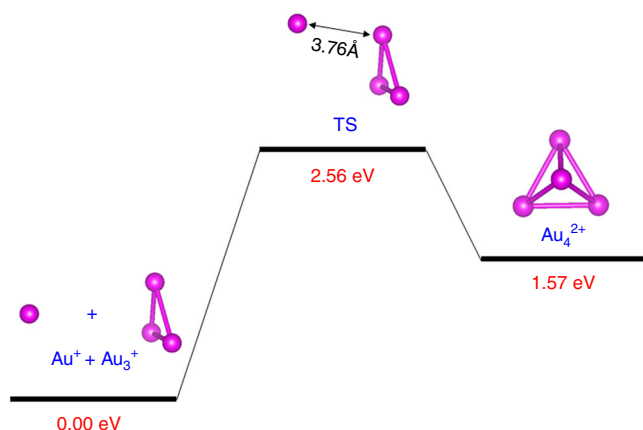


Fig. 1 The computed reaction pathway for the $\text{Au}^+ + \text{Au}_3^+ \leftrightarrow \text{Au}_4^{2+}$ reaction. Color code: Au—magenta

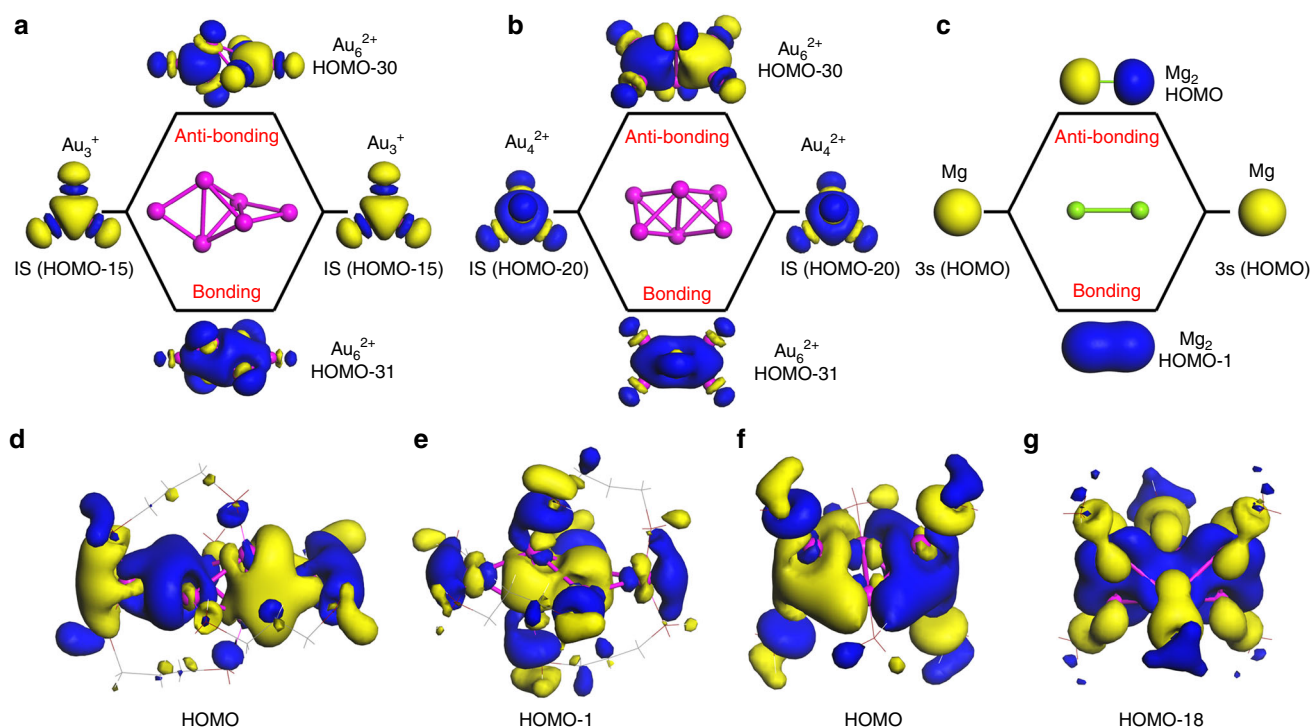


Fig. 2 The anti-bonding and bonding orbital diagrams of clusters. **a** D_{2d} Au_6^{2+} , **b** D_{2h} Au_6^{2+} , and **c** Mg_2 . The HOMO **d** and HOMO-1 **e** of $[\text{Au}_6(\text{dppp})_4]^{2+}$, HOMO **f**, and HOMO-18 **g** of $[\text{Au}_6(\text{PR}_3)_6]^{2+}$. Color code: Au—magenta, Mg—green

(HOMO-1) and anti-bonding (HOMO) orbitals of Mg_2 , as shown in Fig. 2c.

Summary and perspective: With introducing two groups of elementary blocks in the GUM, $Au_3(2e)$, and $Au_4(2e)$, a variety of ligand-protected gold nanoclusters, e.g., spherical and non-spherical, or magic-number and non-magic-number, can be viewed as an aggregate of the elementary groups by applying electron counting rule, a notion analog to Mingo's united atom model for understanding weakly bound condensed icosahedra with $8e$ valence electrons for each unit⁷. A recent experiment showed that the localization effect is highly important for the interpretation of the spectroscopy of gold nanoclusters⁸. Moreover, the triangle Au_3 and tetrahedral Au_4 can be considered as the basic units of face-centered cubic bulk gold. As such, one may view the ligand-protected gold clusters as the trapped intermediates on the path toward the bulk phase, but being stabilized by the ligands bounded to the surface metal atoms. A similar view has been reported previously for Al and Ga clusters⁹.

In closing, GUM provides a generic, empirical, and coarse-grained model to understand and to assess the structural stabilities and structural evolution of ligand-protected gold clusters, a model that may be extended beyond gold.

Methods

The reaction pathway for the $Au^+ + Au_3^+ \leftrightarrow Au_4^{2+}$ reaction in Fig. 1 was computed using DFT methods with the TPSS functional¹⁰ and pseudopotential basis set LANL2DZ for Au, as implemented in the Gaussian 09 program package¹¹. The orbitals of nanoclusters shown in Fig. 2 were computed based on the DFT method implemented in DMol³^{12,13}. The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE)¹⁴ functional and the double numeric polarized (DNP) basis set coupled with semi-core pseudopotential were employed.

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Author contributions

All authors contributed intellectual input and assistance to this correspondence. W.W.X., X.C.Z., and Y.G. developed ideas for additional data analysis. W.W.X. performed the data analysis. W.W.X., X.C.Z., and Y.G. wrote this correspondence. All the authors read and approved this correspondence.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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