Here, an approach based on synchrotron resonant photoemission is employed to explore the transition between quantization and hybridization of the electronic structure in atomically precise ligand-stabilized nanoparticles. While the presence of ligands maintains quantization in Au_{25} clusters, their removal renders increased hybridization of the electronic states at the vicinity of the Fermi level. These observations are supported by DFT studies.

Ligand-stabilized metallic nanoparticles contain a metallic core with a continuous electronic conduction band in which the electrons move freely. However, quantization of the electron energy has been observed when nanoparticles become ultra-small (<2 nm in diameter). This transition is important as many of the physical and chemical properties – such as nature of energy spectra (continuous band to discrete), optical, crystal structure, chirality, magnetism, redox potential, femto-second dynamics and charge states of metallic nanoparticles – are altered when confined to this ultra-small size regime. Unraveling the size-dependent physical, chemical, electronic and magnetic properties of ligand-stabilized metallic nanoparticles is of critical importance to understanding their catalytic properties. Although there are many studies on ultra-small metal nanoparticles, to our knowledge, no investigations have studied the transition between the widely observed discrete (consisting of atomic and molecular orbital like states) and continuous or band like electronic structure (i.e. strongly hybridized states with band width). Here, synchrotron-based resonant photoemission spectroscopy (schematically represented in Fig. S1) and density functional theory (DFT) are combined to investigate this transition in the ligand-stabilized Au_{25} cluster [Au_{25}(PPh_3)_{10}(SC_{12}H_{25})_5Cl_2]^{2+} (denoted herein as Au_{25-bi}) which is compared with [Au_{25}(SCH_2CH_2Ph)_{18}] – (Au_{25-i}).

These Au_{25} clusters were selected because the phosphine ligands on Au_{25-bi} are easily removed under UHV conditions at room temperature, without aggregation or any major structural changes to the Au_{25} cores (based on experimental evidence as discussed below) to provide in situ generation of partially “undressed” gold cores and further comparison to the completely “dressed” Au_{25-i} clusters. Significantly, that “undressing” method is proven to be exclusively passive toward possible UHV assisted alteration (at least for the larger Au_{38} clusters) - the only condition left under consideration in reported herein study which might influence the Au_{25} core.

The approach reported here is based on resonant photoemission enhancement from the 5d level of gold. Gold is a filled 5d^{10} system. Thus, resonant enhancement cannot be observed for atomic and molecular-like states due to the forbidden photoemission transition to a fully occupied 5d state at the 4f_{7/2} and 4f_{5/2} gold thresholds (Fig. S1). The resonant enhancement can only take place if 5d states hybridize with s and/or p state orbitals i.e. the atomic level broadens into hybridized band. This situation leads to a partial depletion of the d-band, permitting a photoemission resonant transition to a (s+p)-d hybridized 5d state (Fig. S1). The core-hole
contribution to the valence band photoemission signal is from Au$_{25}$
the cluster can include the same two vertex-shared icosahedra but
molecularly monodisperse and one of the smallest NCs with well-
known structure, optical, chemo-physical properties, and
established synthetic protocols. X-ray crystallographic analysis of the Au$_{25}$(SR)$_{18}$ cluster revealed an icosahedral Au$_{13}$ core, capped by an exterior shell composed of twelve Au atoms which are
complexed with eighteen thiolate ligands. Au$_{25}$ clusters exhibit multiple molecular-like transitions in their optical absorption spectrum (see Fig. S2), with at least three well-defined bands at 1.8,
2.75, and 3.1 eV, consistent with literature report. The study of its
electronic structure by time-dependent DFT determined that the
three lowest unoccupied MOs are mainly composed of 6sp hybrid atomic orbitals of gold, comprising the sp band, whereas the
HOMO-1 through HOMO-5 are mainly weighted from the 5
atomic orbitals of gold and thus constitute the d-band. Single-
crystal X-ray crystallographic analysis of mixed thiol/phosphine protected Au$_{25}$([PPh$_3$])$_{10}$[SC$_2$H$_2$Cl$_2$]Cl (Au$_{25}$-bi) revealed that the core of the Au$_{25}$ cluster is comprised of two vertex-shared Au$_{13}$
icosahedra, i.e., a bi-icosahedron (see schematic on Fig.1). Recently the same group revealed a Au$_{25}$ isomer, specifically that the cluster can include the same two vertex-shared icosahedra but
rotated along a shared axis, forming the “twisted” rotamer. The
overall structure can be described as four layers of Au pentagons having a staggered-eclipsed-staggered configuration, with ten PPh$_3$
ligands coordinated on top of peripheral Au atoms in layers one and four, five ethanethiolates bridging two of the Au$_{25}$ pentagon rings in
layers two and three, and two chlorides coordinating to two apical
Au atoms.

In general, studies of the electronic structure of ligand-stabilized clusters exhibit a high level of complexity, wherein the overall
electronic structure is strongly influenced by the Au core-ligand interaction. Therefore, to gain insight into this ligand effect, we
compared two Au$_{25}$ clusters: the fully thiolated Au$_{25}$(SC$_2$H$_2$CH$_2$)$_{18}$
(Au$_{25}$-thiol) cluster and the mixed thiol/phosphine Au$_{25}$([PPh$_3$])$_{10}$[SC$_2$H$_2$Cl$_2$]Cl (Au$_{25}$-bi) cluster. Both clusters were
synthesized using established synthetic protocols with slight modifications. Importantly, in the case of Au$_{25}$-bi, we found that ligand desorption could be facilitated simply in UHV, partially “undressing” the gold core and opening an avenue to study the surface of pristine, undressed clusters as well.

Sedimentation velocity-analytical ultracentrifugation (SV-AUC) was used to confirm size uniformity, where the majority of species, ca 85%, are Au$_{25}$ clusters (Fig. S3), assuring that the main contribution to the valence band photoemission signal is from Au$_{25}$ species.

Photon energy dependent photoemission was employed to study the electronic structure of ligand-stabilized Au$_{25}$-bi and Au$_{25}$-i clusters. The photoemission spectra of both types of Au clusters deposited on the SiO$_2$ support were acquired at room temperature. The spectra acquired for the Au$_{25}$-bi cluster revealed shallow 4f7/2 and 4f5/2 core levels, observed at 84.25 and 87.82 eV, respectively (Fig. 2a, Fig. S4); two valence band features are observed at about 4.0 and 6.0 eV (Fig. 2b, Fig. S5). In general the electronic structure of thin films supported on various substrates is affected by film-substrate interaction. To exclude any influence from the substrate on the VB structure of the Au NC film, the films were made several hundreds of nanometers thick, i.e. three orders of magnitude thicker than the (ultra)thin film limit, at which the substrate might affect the interaction. Moreover the photon energy range that was used in the synchrotron photoemission experiments was selected to provide the highest surface sensitivity, limiting the sample probing depth to the topmost layers only. The XPS (which probes deeper layers compared to UPS) VB structures of the Au NC thick films deposited on various substrates looked virtually identical (Fig. S6), proving that the substrates were fully screened by Au cluster films.

Strongly enhanced photoemission at both the Au 4f core level and Au 5d valence band region observed for the Au$_{25}$-bi cluster compared to the Au$_{25}$-i cluster (Fig. 2, S5). This is due to enhanced phosphine (compared to thiol) ligand desorption from the gold clusters under the UHV conditions, which is consistent with much weaker Au-P, compared to Au-S, bonds. The desorption of weakly bound phosphine ligands results in freeing Au orbitals of Au$_{25}$-bi cluster and hence the observed photoemission enhancement. This enhancement clearly supports the role of ligand-controlled hybridization in determining the transition to continuous spectrum, as a significant portion of initially quantized gold valence band becomes delocalized when freed from gold-phosphine bonding.

The stoichiometry of the Au cluster, investigated by X-ray core
level photoemission (XPS), confirms a 1:4 Au/S ratio for the Au$_{25}$-i cluster (Fig. S11), as expected. In the case of the Au$_{25}$-bi cluster, measured ratios of Au/S=1 and Au/P=10 were obtained, indicating desorption of approximately 50% the thiol ligands and 80% of phosphine ligands, i.e. 11 out of 15 ligands have desorbed (Fig. 1, Fig. S10). That significant difference in ligand-to-core ratios remains after mild annealing (Fig. S4, Fig. S5) while demonstrating (similarly to room temperature) suppressed intensity of the valence band features as well as 4f gold core levels by thiol ligands (cluster Au$_{25}$-i) in comparison to Au$_{25}$-bi cluster capped by mixed ligands. The chemistry of phosphines is dominated by their strong nucelphilicity and reducing character. The presence of
nucleophile phosphines in vicinity to the thiols weakens Au-S bonds in Au25-bi, so about of half of thiol ligands desorb as well. The measured S 2p3/2 BE which is lower in Au25-bi compared to Au25-i supports this picture (see Fig. S10, S11).

The great advantage of UHV-assisted ligand removal is the possibility to “undress” Au25-bi clusters, allowing the electronic structure of the Au metal core to be probed exclusively, without any contribution from the ligand shell. This reduced level of complexity makes the study of the resonant photoemission enhancement from the gold valence band at the 4f7/2 and 4f5/2 threshold possible, which is indicative of an f-to-d transition. As mentioned, resonant enhancement of valence states in the photoemission spectra cannot be observed in atomic gold, as gold has fully occupied 5d orbitals. The photoemission resonance can only occur if s-p-d hybridization occurs, leading to partial depletion of the valence 5d bands in Au25. Such resonant enhancement of the valence band photoemission was observed for Au25-bi at photon energies corresponding to the gold 4f7/2 and 4f5/2 thresholds, indicative of an f-to-d transition (Fig. 3). The under-coordinated Au orbitals liberated upon ligand desorption, tend to couple with each other partially depleting the valence 5d band and resulting in allowed f-d transitions. The photoemission studies of completely ligand free Cu, Ag and Au clusters26, 27 reveal such hybridization effects through the formation of a continuous valence band for just 20 atoms per all clusters studied (the smallest 7 gold atoms cluster27 was reported to exhibit either molecularlike or bulklike properties). Similarly, completely ligand free Au clusters very likely lose high symmetry geometry and demonstrate s-d hybridization.28 The surface Au orbitals do not intercouple for Au25-i because they are engaged in the core-thiolate ligand bonds. Thus, the resonance enhancement observed for Au25-bi clusters is strongly suppressed for thiolate-protected Au25-i clusters (Fig. 3, see for more detailed explanation SM, sections Ultraviolet Photoelectron Spectroscopy and Resonant Photoemission). This finding is in agreement with the superatom picture29 extended by Häkkinen and co-workers to account for the closed electronic shell structure of gold-phosphine and gold-thiolate clusters.30

One might argue that the observed photoemission resonance originates from the larger size species comprised of agglomerated Au25-bi clusters, caused by ligand desorption under vacuum in “undressing condition”. To rule out this possibility, we performed grazing incident wide-angle X-ray scattering (GIWAXS) study that probes the sample’s inter-particle distance on the macroscopic scale. The study revealed that the thin film formed by Au25-bi clusters deposited onto the SiO2, followed by UHV treatment, exhibits an ordered structure in the (001) orientation, with the (001) and (002) peaks along the qx direction (Fig. S12). The interparticle spacing is 1.91nm from the (001) peak in GIWAXS pattern, whereas the nominal size of Au25 is 2.1 nm (including ligand shell).23 The result confirms unaltered size of the Au25-bi clusters and absence of any noticeable agglomeration after UHV treatment. Note, that for GIWAXS experiments we used the same sample that was previously characterized with XPS i.e. after the exposure to X-ray radiation under UHV. The cluster stability is also supported by observed d-band size trend and reduced DOS at the Fermi level (Fig. S7, S8), consistent with previously reported theoretical and experimental findings.31-37

DFT calculations were also conducted to probe the hybridization in gold and found to be consistent with the results from resonant photoemission. The DFT calculations were performed for a simple model, where the “undressed” Au25 cluster was adsorbed on SiO2 (111) surface. The optimized structure of the Au25:SiO2 model is shown in Fig. S13. The Au25 cluster was found to be slightly positively charged. The projected density of states (PDOS) at the vicinity of the Fermi level (Fig. 4) reveals that electronic structure is intermixed with comparable density of 6s states, along with noticeable contributions from the Au 6p states. We also found clear overlaps between the occupied and unoccupied Au 6s, 6p, and 5d states in the vicinity of the Fermi level (Fig. 4) for bulk gold, the free Au25 cluster, and Au25:SiO2 suggesting the existence of s-p-d hybridization. PDOS away from Fermi region is dominated by Au 5d states (Fig. S14). It is worth noting that the substrate contribution to

![Figure 3](image-url)
the Au$_{25}$ cluster electronic structure (one cluster thickness) deliberately was not excluded from our model, but even for such condition a significant mixing of gold 5$d$ and 6$s$ states at Fermi level along with notable density of 6$p$ states emerges in calculation. This 6$p$ and 6$s$ somewhat weaker hybridization channel likely may supplement stronger s-d hybridization that facilitates the catalysis.

Conclusions

The synchrotron-based resonant photoemission spectroscopy revealed enhanced valence band photoemission that is much stronger at the 4$f$ and weaker at the 5$p$ core level Au thresholds (i.e. photoemission resonance enhancements) in partially “undressed” Au$_{25}$-bi clusters (a manifestation of s-p-d hybridization) while strongly suppressed in the “dressed” Au$_{25}$-i clusters. This observation unambiguously proves that noble metal clusters, even ultra-small size just of 25 gold atoms, still retain some bulk properties of gold. The DFT calculations that reveal overlap states – a necessary condition for the photoemission resonance to occur. While the investigations reported here are the first attempts to study the influence of ligands in effecting the transition from hybridized band to discrete states in Au$_{25}$ clusters, the methodology and the experimental techniques are broadly applicable to not only different sizes of Au clusters stabilized by various ligands but also to other types of metallic clusters. This approach is anticipated to pave new avenues for designing materials in correlation with their atomic or electronic constituents.

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