

Characterization of electronic structures of ligand-protected superatoms and superatomic molecules by gas-phase photoelectron spectroscopy

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Gold/silver clusters protected by organic ligands have been gathering much interest as next-generation functional nanomaterials.¹ Extraordinary stabilities of $[\text{Au}_{25}(\text{PET})_{18}]^-$ (PET = 2-PhC₂H₄S) with an icosahedral Au₁₃ core and its derivatives have been well explained by the electronic shell closure of superatomic orbitals.² Superatom concept was extended to supervalence bond (SVB) model to rationalize an anisotropic bi-icosahedral Au₂₃ core of Au₃₈(PET)₂₄.³ To probe the superatomic orbitals directly, we have developed and conducted gas-phase photoelectron spectroscopy (PES) on mass-selected beam of $[\text{Au}_{25}(\text{PET})_{18}]^-$, $[\text{M}\text{Ag}_{24}(\text{DMBT})_{18}]^-$ (M = Ag, Au, Pd⁻, Pt⁻, DMBT = 2,4-Me₂C₆H₃S),⁴ and $[\text{MAu}_{37}(\text{PET})_{24}]^-$ (M = Pd, Pt)⁵ by using a home-built apparatus (Figure 1a) equipped with an electrospray ionization (ESI) source, a quadrupole linear ion trap, a time-of-flight mass spectrometer, and a magnetic-bottle type photoelectron spectrometer. PES on $[\text{Au}_{25}(\text{PET})_{18}]^-$ and $[\text{M}\text{Ag}_{24}(\text{DMBT})_{18}]^-$ (M = Ag, Au, Pd⁻, Pt⁻) revealed that doping of Pd/Pt upshifted the energy levels of 1P superatomic orbitals while the effect of Au/Ag exchange was small (Figure 1b).⁴ PES on $[\text{MAu}_{37}(\text{PET})_{24}]^-$ (M = Pd, Pt) exhibited two distinct peaks, which is in accordance with the SVB model theoretically predicted (Figure 1c).⁵

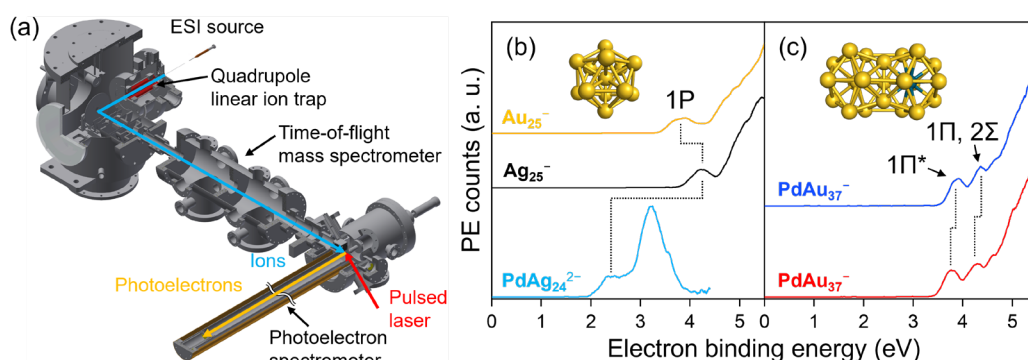


Figure 1. (a) Schematic view of an apparatus. PE spectra of (b) $[\text{Au}_{25}(\text{PET})_{18}]^-$, $[\text{PdAg}_{24}(\text{DMBT})_{18}]^-$, and $[\text{PtAg}_{24}(\text{DMBT})_{18}]^-$ and (c) $[\text{MAu}_{37}(\text{PET})_{24}]^-$ (M = Pd, Pt).

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