

## Observation of spin-orbit splitting in gold/silver superatoms by gas-phase photoelectron spectroscopy

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Spin-orbit coupling (SOC) is known to play an important role in thiolate-protected gold clusters.<sup>1</sup> For example, it has been theoretically predicted that superatomic 1P orbitals of  $[\text{Au}_{25}(\text{SR})_{18}]^-$  (Figure 1a), in which an icosahedral  $\text{Au}_{13}$  superatomic core is passivated by  $\text{Au}_2(\text{SR})_3$  units, are split into  $1P_{1/2}$  and  $1P_{3/2}$  by SOC. The purpose of this study is to reveal what structural factors cause the SO splitting of the 1P orbitals of ligand-protected  $\text{Au}_{13}$  superatoms. To better understand the impact of gold as a heavy element, single Au atom-doped Ag clusters were studied in addition to Au clusters by anion photoelectron spectroscopy (PES)<sup>2</sup> and two-component density functional theory (2c-DFT) calculations. Specifically, we evaluated the energy levels of the 1P orbitals of  $[\text{Au}_{25}(\text{SC8})_{18}]^-$  (SC8 =  $\text{SC}_8\text{H}_{17}$ ; denoted as  $\text{Au}_{25}^-$ ),  $[\text{Ag}_{25}(\text{DMBT})_{18}]^-$  (DMBT = 2,4- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{S}$ ;  $\text{Ag}_{25}^-$ ), and  $[\text{AuAg}_{24}(\text{DMBT})_{18}]^-$  ( $\text{AuAg}_{24}^-$ ) (Figure 1a). The SO splitting of 1P orbitals was clearly observed by using a home-built PE spectrometer equipped with a newly designed liquid nitrogen-cooled ion trap. Low temperature PES showed that the 1P orbitals of  $\text{AuAg}_{24}^-$  split into two, to the same extent as those of  $\text{Au}_{25}^-$ , while those of  $\text{Ag}_{25}^-$  did not (Figure 1b). The 2c-DFT calculation well reproduced the SO splitting in the PE spectra, and the origin of the large SO splitting in  $\text{AuAg}_{24}^-$  was explained by the symmetry-dictated coupling<sup>3</sup> between triply degenerated 1P orbitals formed by the  $\text{Ag}_{12}$  shell and an SO-split 6p orbital of the central Au atom. 2c-DFT calculation of putative regioisomers of  $\text{AuAg}_{24}^-$  revealed that the “central” doping of an Au atom is crucial for the SO splitting of 1P orbitals.

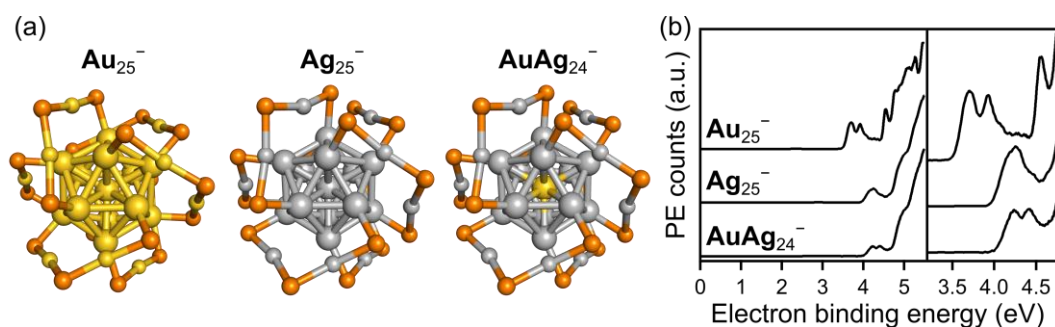


Figure 1. (a) Geometric structures and (b) low-temperature PE spectra of thiolate-protected superatoms.

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