

Probing the Electronic Structure of Ligand-Protected Metal Nanoclusters Using Atomically-Precise Spectroscopic Methods

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Nanostructured particles hold much promise as “designer materials,” but full realization of this promise requires a detailed understanding of the geometric and electronic effects driving their behavior. While some smaller particles, often called nanoclusters, can be synthesized monodispersely and crystallized to determine their geometric structures, this is not generally true and no similarly powerful technique exists for the determination of their electronic structures. We have extended mass-selective absorption spectroscopy techniques to small ligand-protected metal nanoclusters synthesized using standard solution-phase protocols. These experiments reveal dramatically more information than do typical UV/Vis spectra in solution, near the limit of spectroscopic resolution. Using new benchmark-quality spectra, we find that a simple explicit implementation of the superatomic model, the dominant approach to describing qualitative features of nanocluster electronic structure, yields semiquantitative energy level spacings with accuracy on the order of what can be achieved using much more expensive density functional theory approaches. We further show that this framework is sufficient to understand the spectral perturbations upon silver doping of the Au₂₅ nanocluster, where isomer-selective double resonance spectroscopy shows that a single isomer is created despite the presence of three distinct dopant sites. Finally, we show surprisingly large presumably through-space electronic coupling between two Au₂₅ clusters bound in a long-distance dimer configuration.

