

ELECTRONIC SPECTROSCOPY OF MASS-SELECTED LIGAND-PROTECTED METAL NANOCCLUSERS

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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 action spectroscopy techniques to small ligand-protected metal nanoclusters synthesized using standard solution-phase protocols. These clusters are mass-selected from a mixture and stored in a variable-temperature ion trap where they adsorb weakly-bound “tag” molecules that act both as action spectroscopy messengers and a mildly perturbative environment. These experiments reveal dramatically more information than do typical UV/Vis spectra in solution, likely at the limit of resolution considering lifetime effects and the high density of states of the clusters. We find that minor functionalization of the protecting ligands has a drastic impact on the cluster electronic structure, even for transitions between two nominally metal-based states. Even more surprisingly, very subtle environmental effects, such as solvation by He or N₂, yield notable shifts to the spectra, suggesting that even weakly interacting ligands and solvents can have major effects. Taken together, these spectra provide the first experimental windows into using subtle chemical effects to tune the properties of these clusters for chemical and technological applications.