# State-resolved Dynamics in Structurally Precise Monolayer-Protected Gold Clusters Using Two-Dimensional Electronic Spectroscopy

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Superatom state-resolved electron relaxation dynamics of structurally precise $Au_{25}(SC_8H_9)_{18}^-$ nanoclusters were studied using Two-Dimensional Electronic Spectroscopy. The 2-D data allowed for for hot electron and hot hole carrier dynamics occuring in the < 300 fs time scale to be distinguished.

Monolayer-protected clusters (MPCs) represent an emerging class of structurally precise nanomaterials. MPCs provide unique opportunities to examine the structural influence on the electronic properties of nanoscale domains. However, state-specific descriptions of the electron dynamics have been difficult to achieve using traditional 1-D spectroscopic techniques due to spectral congestion of the transient spectra. Here, two-dimensional electronic spectroscopic measurements on these systems will be described. The excitation laser bandwidth overlapped two discrete transitions originating from the superatomic P to D orbital manifolds with sub-20 fs temporal resolution. At early $t_2$ waiting times (150 < fs), several distinguishable cross peaks are observed corresponding to excited state absorption (ESA) transitions from the LUMO+n to higher energy continuum of conduction band *sp* states. Through the use of 2DES carried out using visible excitation and detection frequencies, we have been able for the first time to resolve electron and hole dynamics in specific Superatom states.

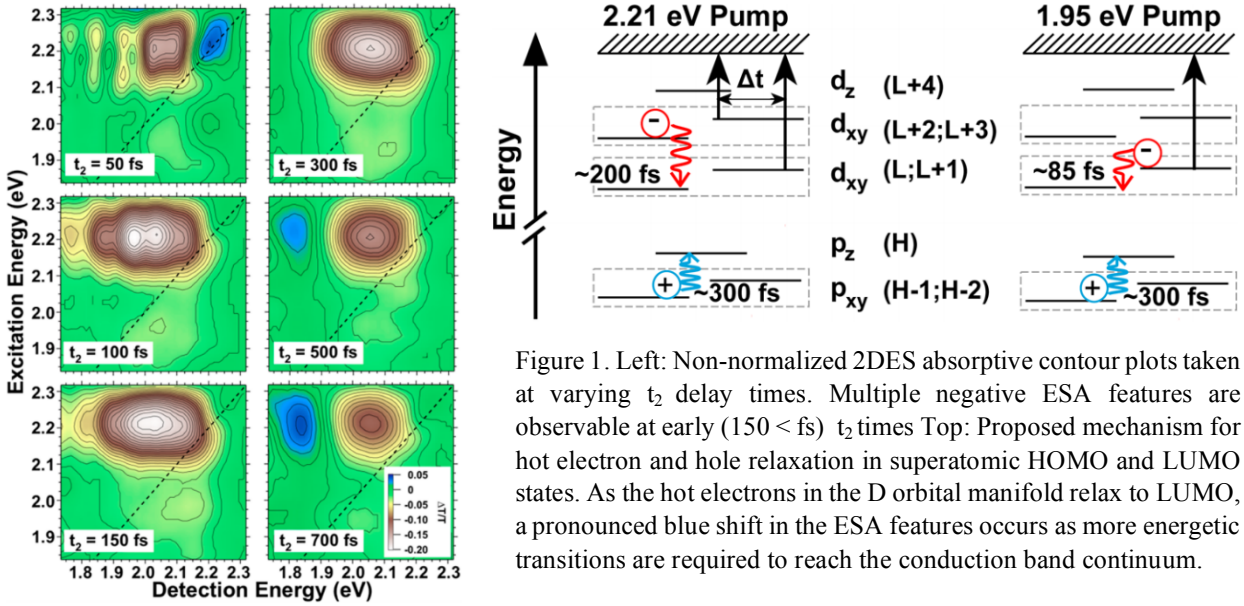


Figure 1. Left: Non-normalized 2DES absorptive contour plots taken at varying $t_2$ delay times. Multiple negative ESA features are observable at early (150 < fs) $t_2$ times Top: Proposed mechanism for hot electron and hole relaxation in superatomic HOMO and LUMO states. As the hot electrons in the D orbital manifold relax to LUMO, a pronounced blue shift in the ESA features occurs as more energetic transitions are required to reach the conduction band continuum.