

MAPPING ELECTRONIC RELAXATION DYNAMICS IN METAL NANOCCLUSERS USING POLARIZATION-SELECTIVE TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

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Gold monolayer protected clusters (MPCs) are a class of quantum-confined metal nanostructures that span the transition from molecular to metallic electron dynamics. MPCs are well-described by three structural motifs that include (i) an all-metal atom core, (ii) an inorganic semiring of alternating Au-S staple units, and (iii) passivating organic ligands. The structure and composition of these domains influence the nanocluster optical and electronic properties, providing a well-defined platform to elucidate structure-dependent energy relaxation mechanisms in quantum confined metals. In this presentation, ultrafast electronic and charge carrier relaxation will be discussed. Coherent two-dimensional electronic spectroscopy (2DES) provides an excitation-detection frequency-frequency correlation by spreading the transient signal over two axes that spectrally and temporally resolves state-to-state electron dynamics on the femtosecond timescale. Here, 2DES was used to distinguish several electronic fine-structure peaks that comprise a charge transfer resonance in molecular-like $\text{Au}_{38}(\text{SC}_6\text{H}_{13})_{24}$ nanoclusters. By manipulating the polarization vector of the femtosecond pulses, additional insights on the coupling of transition dipole moments were obtained from cross-peak specific spectra. These results revealed a low-amplitude excited state absorption signal that uniquely relaxed through a charge transfer resonance within 150 femtoseconds. Evidence of population changes of excited vibrational states within the electronic manifold, which undergo intramolecular vibrational relaxation (IVR), were quantified by fitting time-dependent amplitudes of 2DES-detected cross-peaks spanning a frequency range of 1000 cm^{-1} . Anisotropy and orientation parameters obtained from polarization-selective 2DES were applied to better understand state-specific relaxation through coupled electronic states. Solvent dependences on charge carrier relaxation will be discussed. These results demonstrate the ability of polarization-selective 2DES to map state-resolved electron dynamics in molecular-like metal nanoclusters.