State-Resolved Electron Dynamics in Structurally Precise Metal Clusters

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Introduction

Metal nanoparticles represent a class of nanomaterials of growing interest due to their size-dependent optical and electronic properties, as well as their potential application in catalytic and light-harvesting technologies, among others. Quantum-confined gold nanoclusters are an ideal system to study nanoscale phenomena due to facile synthetic routes to truly monodisperse samples of several sizes with known crystal structures. Although the number of gold atoms and thiolated ligands varies between nanocluster sizes, a structure consisting of a solid gold core protected by an outer shell of mixed gold-thiolate "semiring" units is common to all structures determined to date. This motif is believed to be responsible for the observation of near infrared photoluminescence (PL) in several nanoclusters. Our work on the temperature-dependent PL of $Au_{25}(SC_8H_9)_{18}$ and $Au_{38}(SC_{12}H_{25})_{24}$ has revealed direct evidence of electron-vibration coupling in these systems.

Experimental

Experiments were performed using the 17.5 T superconducting magnet (SCM3) in the DC Field facility of the NHMFL. A sample consisting of metal nanoparticles dispersed in a polymer film were attached to the sample probe and loaded into the cryostat. Electronic excitation was achieved using the frequency doubled output (3.1 eV) of a regeneratively amplified Ti;Sapphire femtosecond laser operating at 1 KHz repetition rate. Resulting PL was collected via optical fiber in transmission geometry, filtered to isolate PL from residual excitation light, and detected using a 0.75 m spectrometer (McPherson) for energy-resolved measurements, or an avalanche photodiode (Quantique) for time resolved measurements.

Results and Discussion

The NIR PL spectra of both nanocluster species exhibited a broad band comprised of multiple overlapped peaks. The data were fit to Gaussian peaks, and the temperature-dependent energy shift of each peak was analyzed independently to extract the vibration energy and coupling strength. For both $Au_{25}(SC_8H_9)_{18}$ and $Au_{38}(SC_{12}H_{25})_{24}$, each peak was determined to couple to a vibrational mode of approximately 21 meV, however the coupling strength was peak specific. Additionally, for the $Au_{25}(SC_8H_9)_{18}$ nanocluster, the temperature-dependent peak width data revealed another vibrational mode of approximately 13 meV. The 21 meV and 13 meV modes were assigned to the Au – S stretch of the semirings and the Au(0) – Au(I) stretch between core gold and semiring gold, respectively.

Time-resolved PL data were fit to a biexponential decay function, with one component stretched. An Arrhenius analysis of the low temperature average rates revealed an activation energy of 0.95 $\pm$ 0.03 meV for $Au_{25}(SC_8H_9)_{18}$ and 0.79 $\pm$ 0.02 meV for $Au_{38}(SC_{12}H_{25})_{24}$. These small energy barriers were interpreted as small energy gaps in the hole fine structure in the ligand band. These results were published in the Journal of Physical Chemistry.[1] Other manuscripts describing a series of nanoclusters are being prepared.

Conclusions

Energy- and time-resolved PL measurements were carried out. Temperature-dependent peak shifts and peak widths revealed two vibrational modes that mediate the PL. These vibrations were assigned to the Au – S stretch of the semirings and the Au(0) – Au(I) stretch between core god and semiring gold atoms. An Arrhenius analysis of the rates extracted from lifetime data revealed small activation barriers on the order of 1 meV were attributed to fine structure in the ligand band. These results highlight the importance of the surface ligands, indicating the ability to tailor application specific nanomaterials for photochemical devices. This research is providing important predictive nanostructure-function insights for designing photonic nanomaterials.

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References

[1] Green, T.D., *et al.*, J. Phys. Chem. A, **118**, 10611-10621 (2014).