Supporting Information: Ultrafast Relaxation Dynamics of Rod-Shaped 25-Atom Gold Nanoclusters

Matthew Y. Sfeir,[1] Huifeng Qian,[2] Katsuyuki Nobusada[3] and Rongchao Jin[2]

[1] Brookhaven National Laboratory, Center for Functional Nanomaterials, Upton, NY 11973
[2] Carnegie Mellon University, Department of Chemistry, Pittsburgh, PA 15213
[3] Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan

To verify that an internal conversion process is responsible for the sub-ps decay component observed in the carrier relaxation of Au_{25} rods, we have excited the system with near-IR light. This results in an excitation of only the lowest energy (i.e. HOMO-LUMO) optical transitions. This wavelength was chosen to be slightly off-resonance to avoid the complications from scattered light in a degenerate pump-probe experiment. The sub-ps dynamics are absent under these excitation conditions as would be expected for an internal conversion process. Slight differences in the transient spectra at 0.35 and 3.5 ps are the result of electronic coupling to coherent phonons (Fig. S1), which results in a shift of the wavelength of the absorption features as a function of time.

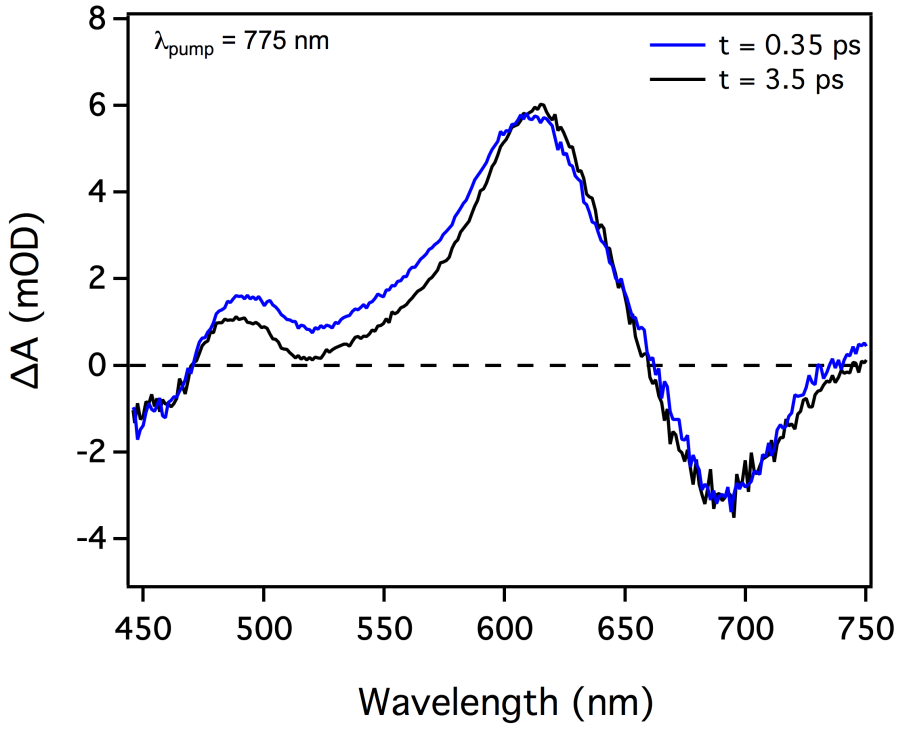

Fig. S1 Transient absorption spectra at 0.35 ps (blue) and 3.5 ps (black) of Au_{25} rod clusters excited at 775 nm.