Heterogeneity of gold nanorod studied with two-dimensional electronic spectroscopy

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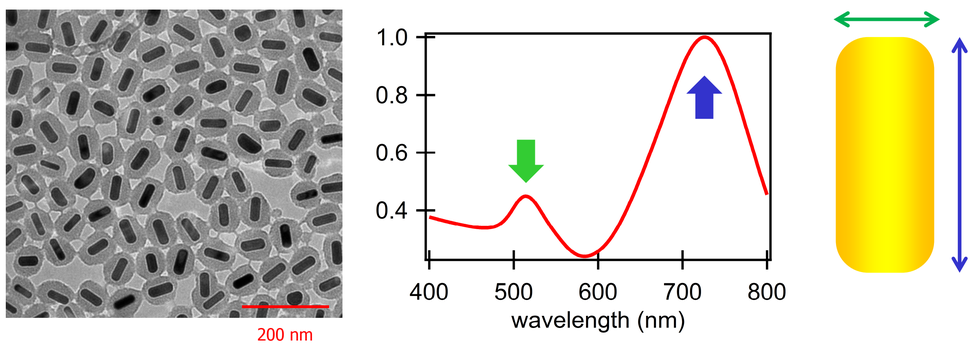
1. Introduction

Gold nanorods (AuNRs) have shown great potentials in biological and biomedical application such as molecular imaging, drug delivery, or photothermal therapy. The optical properties of these elongated nanoparticles depend on their shape anisometry and surface plasmon absorption. The AuNR-based longitudinal localized surface plasmon resonance (longitudinal LSPR) band is very sensitive to the AuNR's aspect ratio and the surrounding local environment. Upon photo excitation, we are able to follow the electron dynamics (electron-phonon and phonon-phonon scattering) in these metal nanoparticles. With two-dimensional electronic spectroscopy, the heterogeneity of these noble metal nanorods can be investigated.

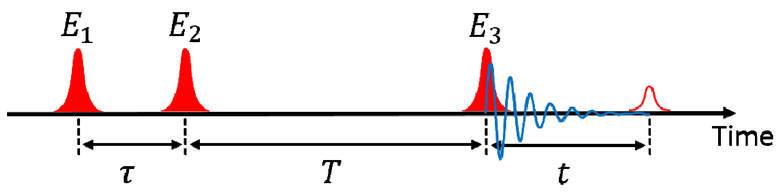
2. Experiment

Gold nanorods

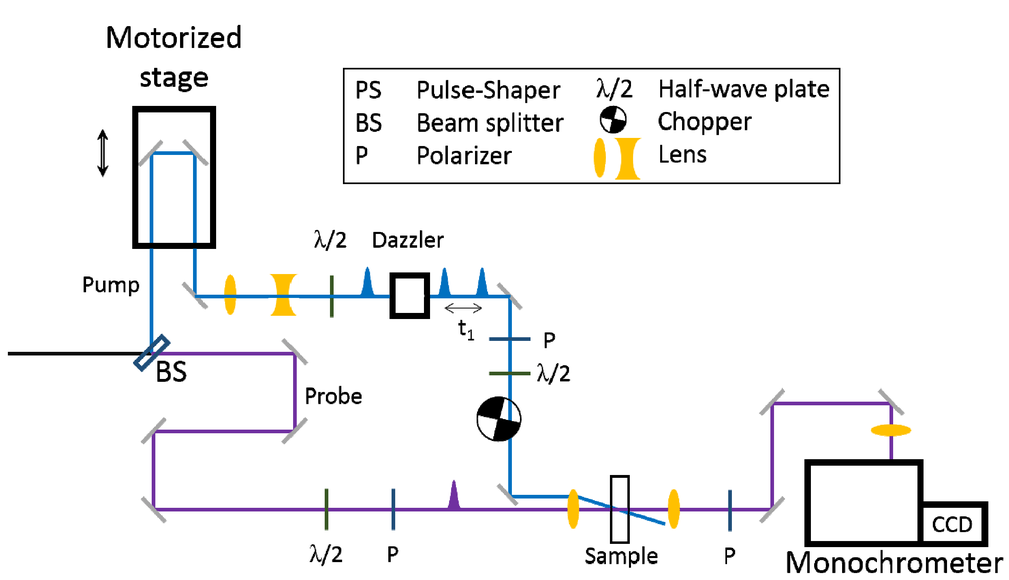


- Aspect ratio ~ 4.
- Transverse mode ~520 nm and longitudinal mode ~740 nm.

Two-Dimensional Electronic Spectroscopy (2D ES)



- Three femtosecond optical pulses interact with the sample to generate a third order nonlinear signal.

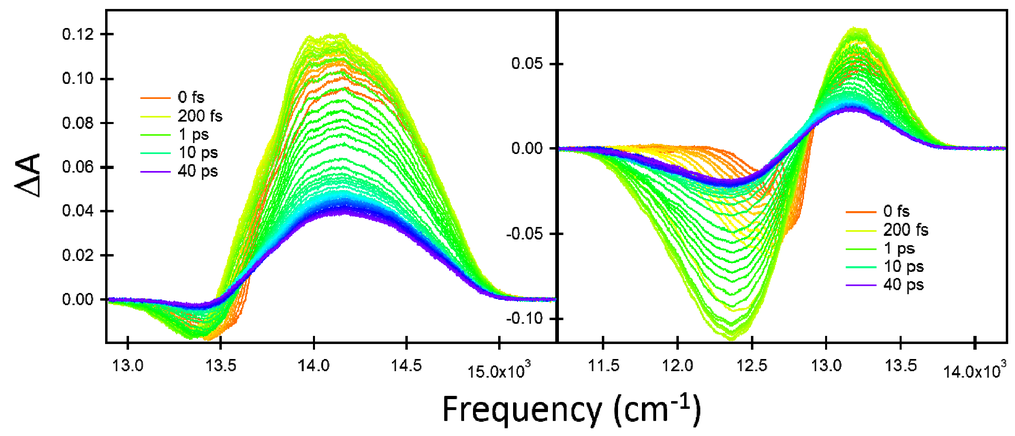


- The Dazzler was used to produce a duplicated pulse pair and control the variable time delay τ and the phase shift between those replica pulses.

Reference: X. Huang *et al.*, Adv. Mater. 21, 4880 (2009).
S. Link *et al.*, J. Phys. Chem. B 103, 8410 (1999).

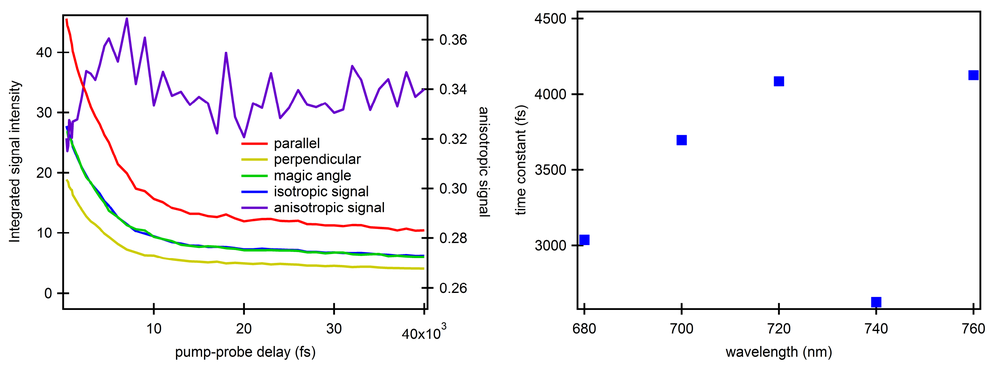
3. Results and discussion

3.1. Transient Absorption



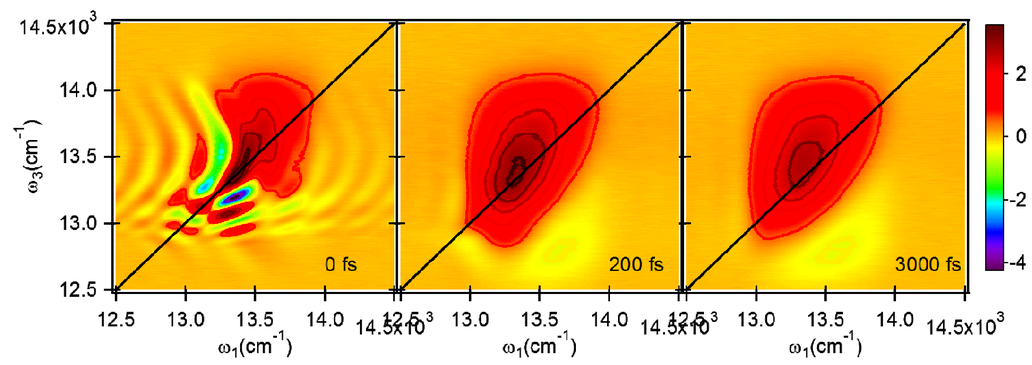
- The spectral range of the laser is too narrow to cover the whole absorption spectrum, but we can still observe the 0→1 and 1→2 transition upon excitation.

3.2. Relaxation Dynamics



- The electron-phonon relaxation times is ~3 ps, and is independent of wavelength.
- The anisotropy signal remains constant within 40 ps, showing that the reorientation and Forster energy transfer of AuNRs in water solutions are much slower than the electron-phonon relaxation process.

3.3. 2D ES of AuNR



- The 0→1 transition lies along the diagonal line upon excitation at t=0, showing that the broad absorption band of the AuNRs solution results from inhomogeneous line broadening.
- The ultrafast energy redistribution within 200 fs results from electron-electron interactions. The 2D spectra remain the same from 200 fs to 3 ps. There is no coupling between different electronic mode, due to low concentration of the solution and long distance between nanoparticles.

5. Conclusion

We have investigated the dynamics of AuNR in water solution using time-resolved two-dimensional electronic spectroscopy. Our data show that this heterogeneous system has very slow reorientation and Forster energy transfer rate compared with the relaxation process, which is within 200 fs for electron-electron energy relaxation and ~ 3 ps for electron-phonon energy relaxation.