Probing state- and size-dependent line broadening in CdSe nanocrystals using 2D ES

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Two-dimensional electronic spectroscopy (2D ES) can separate the homogeneous and inhomogeneous linewidths of CdSe nanocrystals. We find that, in contrast to inhomogeneous linewidths, homogeneous linewidths are relatively insensitive to both electronic state and nanocrystal size. This suggests that solvent effects dominate homogeneous line broadening.

Technologies based on semiconductor nanocrystals harness key optical properties for applications in high-efficiency photovoltaics, quantum computing, and biological imaging [1, 2]. The performance of these technologies depends critically on the ability of nanocrystals to convert and tune a spectrum. While transient absorption and photoluminescence studies have provided crucial insight into relaxation dynamics, these measurements are unable to isolate contributions from overlapping relaxation pathways [3]. 2D ES excels at resolving state-dependent dynamics in spectrally congested and inhomogeneous systems [4, 5].

Here we use 2D ES to extract homogeneous and inhomogeneous linewidths in CdSe nanocrystals. Isolating these spectral features demands accurate phase corrections for fitting 2D spectral features to rotated Gaussian distributions. While previous studies have examined the sources of inhomogeneous line broadening, homogeneous linewidths are relatively unexplored.

Experimental results are modeled by a particle-in-a-sphere potential within the framework of the effective mass approximation. In two initial samples, we observe that the homogeneous linewidth depends modestly on excitonic state and minimally on nanocrystal radius. Future experiments across a broader range of nanocrystal sizes will further explore these dependencies and support a microscopic mechanism of line broadening controlled by solvent effects as opposed to acoustic phonon interactions.

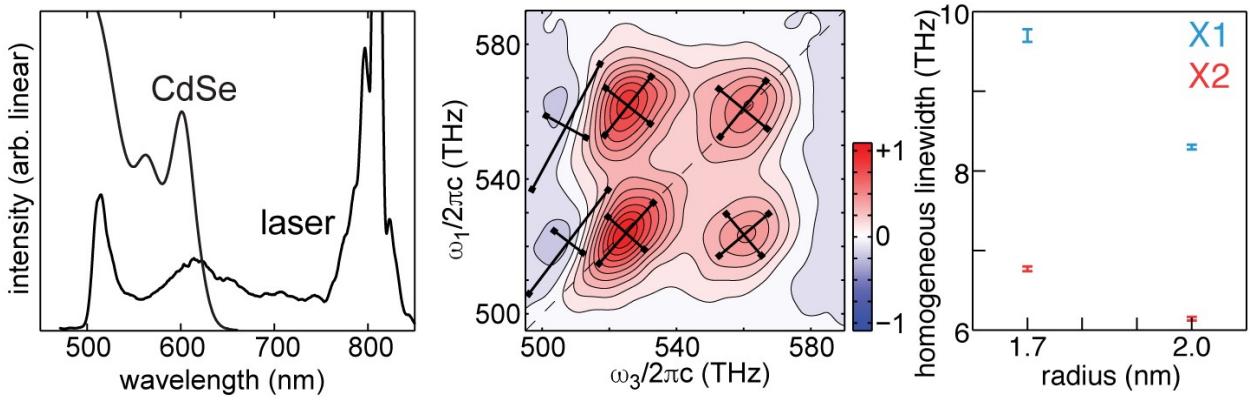

Fig. 1 (left) Pulse spectrum is plotted against the absorption spectrum of zinc-blende CdSe nanocrystals (r = 2.0 nm) in hexane. (middle) Experimental 2D ES (τ_2 = 10 ps, r = 2.0 nm). Black lines mark the diagonal and antidiagonal linewidths. (right) Homogeneous linewidths for the first two transitions across two sizes of nanocrystal samples.

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