

# Multi-dimensional coherent spectroscopy of CdSe colloidal quantum dots at cryogenic temperatures

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**Abstract.** One-quantum and zero-quantum multi-dimensional coherent spectroscopy are used to study CdSe colloidal quantum dots at cryogenic temperatures. Each technique reveals unique aspects of the electron-phonon coupling dynamics in the material.

## 1 Colloidal Quantum Dots and MDCS

Colloidal quantum dots (CQDs), which are quantum dots dispersed in solution, are the continued focus of intense study due to their wide range of applications such as biological tagging, photovoltaics, and tunable light absorbers/emitters [1]. Despite the numerous studies on CQDs that have been performed, knowledge of the carrier-phonon interactions at low temperatures is limited. The inhomogeneous broadening of CQDs obscures the dynamics exhibited by dots of a given size, and can usually only be studied by techniques such as single dot measurements and spectral hole burning. A technique able to circumvent the inhomogeneous broadening is multi-dimensional coherent spectroscopy (MDCS), which has the ability to correlate absorption, intraband(Raman) coherence, and emission spectra. MDCS has already been used to study many aspects of carrier dynamics in CQDs such as exciton and biexciton state coherences [2-3] as well as below-gap interfacial states [4]. Because these experiments have primarily been performed at room-temperature however, many features of CQD 2-D spectra are hidden beneath thermally broadened linewidths. MDCS of CQDs at cryogenic temperatures is thus required to resolve low-energy features such as the excitonic fine structure and phonon coupling.

The pulses used to perform the MDCS experiment are sourced from an optical parametric amplifier tuned to the 1S exciton energies of each CQD sample. A device called the Multi-Dimensional Optical Nonlinear Spectrometer (MONSTR) [5] then splits the pulses into four identical copies that are independently delayed in time and focused onto the CQD sample. A four-wave mixing signal is emitted in the phase-matched direction and heterodyne detected via a co-propagating local oscillator pulse. The excitation pulse

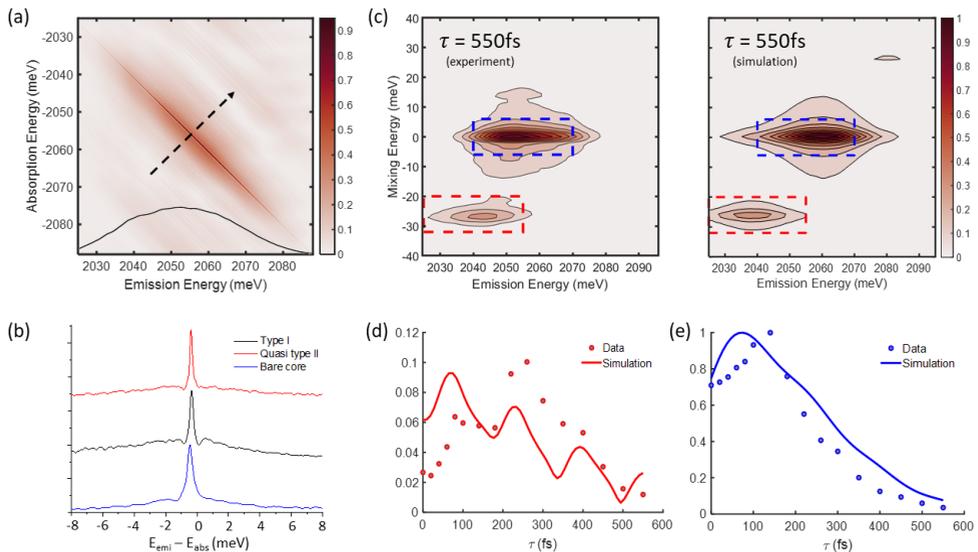
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parameters used are 90 fs pulses at an average power of 120  $\mu\text{W}/\text{beam}$  and 250 kHz repetition rate, or approximately 0.48 nJ/pulse. All pulses are collinearly polarized.

## 2 One-Quantum Spectra

In one-quantum spectra, which correlate the absorption and emission spectra of a material, inhomogeneous and homogeneous broadening manifest as peak elongation along the diagonal ( $E_{\text{emi}} = E_{\text{abs}}$ ) direction and the perpendicular cross-diagonal direction. By taking slices along the cross-diagonal direction, the ensemble-averaged response of dots with a specific resonance energy is revealed. In figure (a) a representative one-quantum 2-D spectrum of CdSe/CdZnS Type I core/shell CQDs (2 nm core radius, 2.5 nm shell thickness) is presented, in which a sharp zero-phonon line can be seen overlayed on a broad pedestal due to coupling with lattice acoustic phonon modes. To examine the effect of the shell configuration on the CQD electronic properties, additional one-quantum 2-D spectra of CdSe/CdS quasi-Type II core/shell CQDs (2 nm core radius, 2.5 nm shell thickness) and bare-core CQDs (2 nm core radius) are taken. In figure (b) slices from 2-D spectra taken of each material are plotted. One notable behaviour is observed, which is the variation of the zero-phonon line homogeneous linewidth with respect to the shell configuration. It is observed that the bare-core CQDs have the broadest linewidth, followed by the Type I CQDs, and then quasi-Type II with the narrowest linewidth. This trend implies that delocalization of the carriers out of the core material and into the shell decreases the decoherence rate. At 4.5 Kelvin, the temperature at which the data was taken, the optical phonon modes of the lattice are frozen out. The main external decoherence mechanism should therefore be the remaining acoustic modes, and from the linewidth trends the effect of the shell configuration on the piezoelectric acoustic mode coupling can be inferred.



Though not shown in the slices plotted, additional sidebands appear at  $E_{\text{emi}} - E_{\text{abs}} = \pm 26\text{ meV}$ , matching reported LO-phonon energies of the CdSe lattice. These sidebands exhibit oscillations as a function of waiting time  $T$ , which are indicative of intraband coherence Liouville pathways [6].

### 3 Zero-Quantum Spectra

At the LO-phonon sidebands observed in one-quantum spectra, the responses of pathways involving intraband coherences and population states during waiting time  $T$  overlap. Zero-quantum spectra [6] are thus acquired, which are uniquely capable of separating intraband coherence pathway responses from that of their population state counterparts by correlating waiting time evolution energies (which we call the mixing energy  $E_{\text{mix}}$ ) and emission spectra, at  $\tau$  delays from 0 fs to 550 fs. As shown in figure (c), a sideband appears at  $E_{\text{mix}} = -26$  meV with increasing  $\tau$ . Interestingly, the evolutions of the integrated peak intensities of the  $E_{\text{mix}} = -26$  meV sideband and the  $E_{\text{mix}} = 0$  peak do not follow the usual exponential dephasing lineshapes and instead exhibit rises over 250fs and 130 fs respectively. Such rises have been shown to arise from pulse time-ordering ambiguities at times shorter than the pulse duration and photon echo integration for inhomogeneously broadened samples.

To study the origin of these rises, simulations of a four-level system composed of the zero LO vibrational-quantum ground and excited states  $\{|g\rangle, |e\rangle\}$  and their one LO vibrational-quantum counterparts  $\{|g'\rangle, |e'\rangle\}$  are performed. With exponential dephasing, no rise due to echo formation is possible. The non-Markovian dephasing lineshape [7] resulting from the Kubo correlation function  $C(t) = \Delta\omega^2 \exp(-t/\tau_c)$  is thus used, where  $\Delta\omega$  is the spectral diffusion amplitude and  $\tau_c$  is the correlation time. Crucially, by assigning different dephasing parameters to coherences involving the vibrational-quantum states  $\{|g'\rangle, |e'\rangle\}$  the correct sideband asymmetry is observed. As evident in figure (d) however, the 250 fs rise of the sideband peak could not be reproduced. We attribute this behaviour to non-Markovian dynamics beyond the second-order cumulant truncation applied.

Though it is difficult to directly ascertain the nature of the non-Markovian dephasing from this study, the unique lineshapes observed will constrain possible microscopic theories. Previous studies have focused on free surface charges and surface ligand rearrangement as causes for the band-edge Stark shift that leads to spectral diffusion, but these results point to coupling with lattice vibrational modes as a major factor in the spectral diffusion dynamics.

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