Supplementary Information:
Exploring Size and State Dynamics in CdSe Quantum Dots Using Two-Dimensional Electronic Spectroscopy

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I. EXPERIMENTAL DETAILS

A. Synthesis of Quantum Dots

To synthesize large CdSe quantum dots, 0.2 mmol of cadmium myristate, 0.2 mmol of selenium dioxide and 0.04 mmol of cadmium acetate were mixed in 12.6 mL of 1-octadecene according to a literature procedure. The mixture was stirred and heated to 240 °C (heat rate ca. 20 °C/min). When the temperature reached 230 °C, 0.2 mL of oleic acid was added to ensure stable growth of nanocrystals. After an hour the solution was cooled to room temperature. Quantum dots were precipitated with ethanol and re-dispersed in toluene. Washing was repeated 2 times. UV-Vis absorption and photoluminescence (PL) spectra of QD dispersions were recorded using a Cary 5000 UV-Vis-NIR spectrophotometer and FluoroMax-4 spectrofluorimeter (HORIBA Jobin Yvon), respectively. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai F30 microscope operated at 300 kV. Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 diffractometer with CuKα X-ray source. The TEM image and XRD pattern are shown in figure S1a and S1b. We also plot a histogram of sizes generated by examining the TEM image (S3c) and the expected size-dependent inhomogeneity in figure S1d according to equation 1 in the main text. We utilize zinc-blende QDs rather than wurtzite to eliminate confounding effects from crystal field splitting.

Figure S1: a) TEM image of zinc-blende CdSe quantum dots. b) X-ray diffraction data verifying zinc-blende crystallinity. c) Radial distribution derived from TEM image. d) Inhomogeneous
lineshape for the first three excitons derived from equation 1 in the main text using the radial distribution shown in (c).

**B. Continuum Generation**

To generate continuum white light we focused the 4W output (38 fs FWHM) of a seeded regenerative amplifier (Coherent Micra and Legend Elite) into a 2 m path length argon cell held at 2 atm (total power stability 0.4% SD/mean, 10 Hz). We characterize this pulse using multiphoton intrapulse interference phase scan (MIIPS) and transient grating frequency resolved optical gating (TG-FROG), and we compress the pulse to approximately 8 fs autocorrelation width (figure S2a and S2b) using a spatial light modulator (Biophotonics Inc.).

Figure S2: a) Transient grating in neat solvent (chloroform) and b) MIIPS autocorrelation for a typical experiment (pulse duration ~8fs). c) Diagram of the experimental setup. Four beams are generated using beamsplitters (BS) and pass through compensating windows (CW) and differentially delayed using retro-reflectors (RR) angled mirrors using all-reflective interferometric delay (ARID). An 30 degree off-axis parabolic mirror (PM) focuses the beams to a 100 µm point on the sample (SC). The beams are all blocked (BB) except the signal and LO. They are focused and interfered on a camera for various time delays and Fourier transformed into a 2D spectrum. d) Schematic diagram of ARID describing how the time delays are
generated by angling the stage. The distance \(\Delta d\) represent the translation of the stage, while \(\Delta x\) represents the forward motion of the mirror.

C. All-Reflective Delay Generation and Beam Geometry

A diagram of the experimental apparatus is shown in figure S2c and S2d. Beams 1 and 2 are delayed relative to 3 and 4 using a retroreflector mounted to a mechanical delay stage. Beam 1 is delayed relative to 2 using a separate stage mounted at a small angle (0.3°) from the plane perpendicular to the direction of beam propagation. The small offset angle provides nanometer precision in the relative delay between each beam (34 fs/mm) as the position of the stage is scanned with negligible effect on beam position (<6 μm). Delays are calibrated via spectral interferometry.\(^3\) This approach provides the well-controlled, small-magnitude time delays required for 2DES. In contrast, previous passively phase-stable 2D spectrometers relied on glass wedges to introduce these delays, implicitly adding frequency dependent phase while scanning coherence time.\(^4\) This dispersion can result in phase-twisted lineshapes and false cross-peaks, especially in systems with broad spectral response and inhomogeneity like QDs.\(^5\) Each beam passes through an identical amount of glass (including neutral density) before reaching the sample, and all dispersion is compensated by the MIIPS-based compression scheme prior to arrival at the sample. We show a spectrum taken from a separate run with twice the power in figure S3 to demonstrate that we are operating in the single exciton regime.
In this instrument, four continuum white light beams are arranged in a boxcar geometry with a 1.2 cm separation and focused onto the sample with an 30 degree off-axis parabolic mirror (EFL: 45 cm), achieving a 100 µm spot size. This soft-focus approach minimizes frequency-dependent directional filtering. The sample (QDs in toluene) is pumped through a 0.2mm thick fused silica cell (Starna) at room temperature.

II. RELATIONSHIP TO STATE-SELECTIVE TA

In Figure S4, we plot the fit of the projected 2D spectrum at 900fs to broadband pump broadband probe transient absorption, using equation 3 in the main text. In Figure S5, we illustrate the relationship between C-2DES and previous state-selective transient absorption (TA) studies. Pump-probe studies share the same signal as 2D studies, though 2D studies add frequency resolution to the pump-domain. Thus, 2D electronic spectra provide state-specific lineshape and dynamics. The connection between pump-probe and TA has been rigorously described elsewhere. Others have characterized the location of the features in the nonlinear response of QDs in TA using the second derivative of the absorption spectrum as a sample-independent marker. ESA below the band edge was labeled A₁, and two resolvable GSB/SE features were
referred to as B1 and B2 (which line up with the energies of |X1⟩ and |X2⟩). A persistent ESA feature appears at higher energies labeled A2 and a final GSB/SE feature labeled B3. State-selective TA, however, shows that, depending on the energy of initial excitation, these features may or may not appear in the TA spectra. For instance, the A1 ESA peak is absent when the QDs are directly excitated to |X1⟩. In figure S5, we evaluate slices at the input energies taken from our fit of the linear absorption spectrum of our sample, showing good agreement to the state-selective TA work done by Kambhampati and coworkers. Due to inhomogeneity in our sample and the relatively close spacing between states for dots of this size, we do not resolve separate B1 and B2 features.11-14

Figure S4: A typical fit to broadband pump-probe. The blue line shows the summed down 2D spectrum, while the red line shows the broadband-pump broadband-probe spectrum. We fit the summed down spectrum using equation 3 in the main text. We sequentially fit each parameter, first fitting the amplitude and phase (A, ϕc), then fitting amplitude, phase and the 3/4 timing correction (A, ϕc, tc), and finally fitting all parameters simultaneously, initializing each nonlinear regression with the parameters from the prior fit. Only ϕc and A varied more than 1% of their magnitude during a run.
Figure S5: a) C-2DES spectrum at T = 500 fs. b) Traces taken from input energies corresponding to the first 3 excitons, indicated by vertical lines in part A. For comparison, we plot the second derivative of the absorption spectrum, commonly used as a sample independent marker of peak positions. Generally positive and negative features conform to expected positions, though the peaks are broader near the band-edge.

Figure S6: We plot the results for two traces taken from the band-edge and X₃> features for three different runs. Each run had the same spacing, but a different number of total time points. Traces are offset to improve overlap for facile comparison, but traces are normalized. While each trace appears relatively “noisy,” the noise is partially reproducible, implying that it reflects that underlying molecular signals. (See Fig. S7 for analysis.)
Figure S7: Mean power spectrum of the data shown in Fig S6 indicating that the beating signal is significantly stronger than the noise. Error bars are 1 s.d.

III. MOVIE OF 2D SPECTRA

A movie of the raw spectra is attached separately. Spectra are acquired every 5 fs between T=0 fs and T=1000 fs. The 2D spectra are shown on the left. To highlight changes during the first 500fs, frames in this portion movie are linearly interpolated between raw spectra to slow down playback (frames every 1 fs). All spectra are individually normalized and plotted with the same color bar and contour lines. On the top right and bottom right, we highlight in insets the spectra of the band edge exciton (1.83eV<ωτ<1.94eV, 1.81eV<ωt<2.04eV) and the spectra near the stimulated emission feature below the main diagonal (2.06eV<ωτ<2.27eV, 1.92eV<ωt<2.13eV).
REFERENCES