Supporting Information for:

Auger Heating and Thermal Dissipation in Zero-Dimensional CdSe Nanocrystals **Examined Using Femtosecond Stimulated Raman Spectroscopy**

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Experimental Details

Details of our femtosecond stimulated Raman spectroscopy experiment have been detailed elsewhere.¹ For each sample, the actinic pump was tuned to 400 nm and focused to a spot size of 250 um. The Raman pump was tuned to the low energy full-width at half-maximum (FWHM) of the absorption feature (see Figure 1b in main text). For the samples with radius R = 1.3 and 1.5 nm, the chirped continuum probe was generated with a 2 mm sapphire plate and spectra were collected using a grating with 1200 lines/mm with a 600 nm blaze. For the R = 2.0 nm sample the probe was generated with a 1:1 H₂O:D₂O mixture in a 5 mm quartz cuvette and spectra were collected using a grating with 2400 lines/mm with a 400 nm blaze. Chirped probe pulses were not compressed for experimental simplicity and owing to observations that the time-resolution is minimally impacted as a result of the high spectral resolution and broad bandwidth.² All spectra were collected using a 1.0 mm quartz cuvette with optical density (OD) around 0.2 at the peak of the lowest energy transition. Samples were stirred during data acquisition to minimize sample

degradation and the effects of local heating. The CdSe NCs were dispersed in hexanes for both stability and to ensure that the ligands and solvent are thermally similar.

LO Phonon Mode

In order to aid visualization of the LO phonon mode studied, we provide an illustration (Figure S1). Phonon frequencies and vectors were obtained from the referenced website³ and are displayed using the VESTA visualization package.⁴



Figure S1. Lattice motion corresponding to the LO phonon. Cd²⁺ ions are shown in blue and Se²⁻ ions in orange.

Background Subtraction Process

In order to monitor the dynamics of only the LO phonons, the Raman features and background were fit to a sum of two Gaussians (for the LO and SO phonon modes) and a polynomial, respectively. Both were fit simultaneously in a MATLAB script before the polynomial was subtracted. An example of a fit is given in Figure S2.



Figure S2. The anti-Stokes LO phonon feature for the R = 2.0 nm CdSe along with fits. (Top) Raw data with the overall fit (Gaussians plus polynomial) and polynomial baseline. (Bottom) Baseline-subtracted data overlaid with Gaussian fits for LO and SO phonon modes.

Normalized Kinetics



Figure S3. Data presented in Figure 2b with minima normalized allowing better comparison of lifetimes. Inset shows the same data with a smaller time range.

Multiexciton Fitting Process

In order to determine the lifetimes due to Auger heating, all data were fit to both the single-exciton component (determined from fits of the lowest pump fluence for each sample) and one or two additional exponentials. As pump fluence is increased not only do the population of multiexcitons increase, but the number of NCs with single excitons decreases, so the single-exciton components have fixed lifetimes and relative amplitudes but were allowed to vary collectively in amplitude.

All fits were done using a MATLAB script. An example fit is given for R = 2.0 nm CdSe ($\langle N \rangle =$ 0.6) in Figure S4.



Figure S4: Fits for the R = 2.0 nm CdSe NCs sample (Stokes, $\langle N \rangle = 0.6$) where the data is fit to a combination of single- and multiexciton components.

Multiexciton Fits and Errors

The average of our multiexciton fits are compared to literature values for AR in Table S1.

Sample	FSRS Lifetime (ps)	AR Lifetime (ps)
R = 1.3 nm	16	8
R = 1.5 nm	25	15
R = 2.0 nm	100	41

Table S1: LO Phonon Lifetimes vs Auger Recombination Lifetimes

In order to not crowd Figure 3c, errors were not included. Representative errors of the different sizes, derived from the fit of a single <N> for each size are given in Table S1 below.

Table S2: Errors derived from multiexciton fits		
Sample	FSRS Lifetime (ps)	95% Confidence Interval (ps)
R = 1.3 nm, <n> = 1.45</n>	12.7	± 0.8
R = 1.5 nm, <n> = 1.04</n>	32.7	± 5.3
$R = 2.0 \text{ nm}, \langle N \rangle = 0.6$	99.3	± 12.1

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Fast Component Lifetimes

Given in Figure S3 are the lifetimes for the fast component that is most evident above $\langle N \rangle = 0.8$ compared to triexciton lifetimes in the literature.⁵



Figure S5. (a) Reprint of the inset from Figure 3a (R = 2.0 nm CdSe, Stokes) highlighting the fast decay. (b) Lifetimes of fast decay component compared to triexciton lifetimes from Ref. 5 on a log-log plot. Multiple excitation fluences for a given particle radius relate some variability in fitting of lifetimes.

Effect of Actinic Pump Fluence and Timing on Solvent Modes

In order to ensure that our peak shifts are not due to experimental artifacts we monitored the solvent (hexanes) modes at the same actinic pump powers used for R = 2.0 nm CdSe NCs. We saw no change in the peak positions suggesting that any peak shifts observed for the NCs were intrinsic to the material.



Figure S6. Hexane Raman modes as a function of time showing no change in position upon optical excitation with the actinic pump. Actinic pump powers of 20 nJ and 500 nJ correspond to the powers used to generate $\langle N \rangle = 0.1$ and $\langle N \rangle = 2.8$ for the R = 2.0 nm CdSe NCs. Inset: magnified view of the peaks between 1025 and 1100 cm⁻¹.

References

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