Electronic Supplementary Material (ESI) for Nanoscale.

Probing Surface Interactions in CdSe Quantum Dots with Thiocyanate Ligands

Samadhan H. Deshmukh[§,†], Sushma Yadav[#], Tubai Chowdhury[§,†],Akhil Pathania[§,†], Sameer Sapra[*,#], Sayan Bagchi[*,§,†]

[§]Physical and Materials Chemistry Division, National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune - 411008, (India)

[#]Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

[†]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad- 201002, India

Table of contents

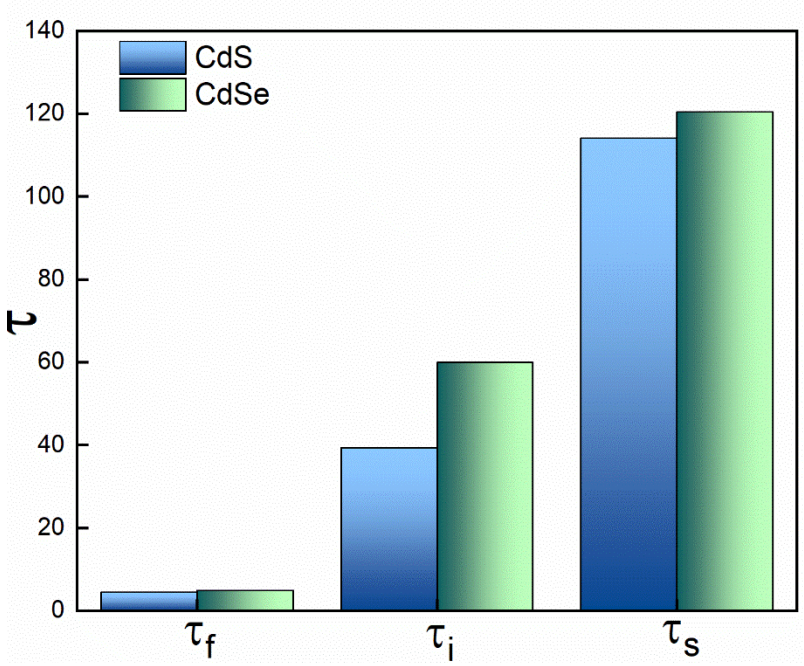

Fig. S1: Comparison of fast, intermediate, and slow time scales of CdS and CdSe quantum dots.[1]

System	FTIR peak positions (cm^{-1}) and FWHM (cm^{-1})	CLS fitting parameters					
		a_1	τ_1	a_2	τ_2	a_3	
NH_4SCN	2056.1 13.1	0.26±0.05	1.2±0.02	0.25±0.02	6.8±0.40		
CdSe_SCN	2056.2 15.5	0.20±0.06	0.8±0.39	0.24±0.14	4.9±1.61	0.18±0.01	60. 0±5.0
	2072.6 11.46	0.25±0.04	1.65±0.14	0.72±0.02	120.5±10.92		

Table S1. FTIR, and CLS fitting parameters of the nitrile stretch of free SCN^- and SCN^-capped CdSe.

* All cases show a ~1 ps timescale. This ultrafast timescale, common in all the cases, was not considered while comparing the timescales.

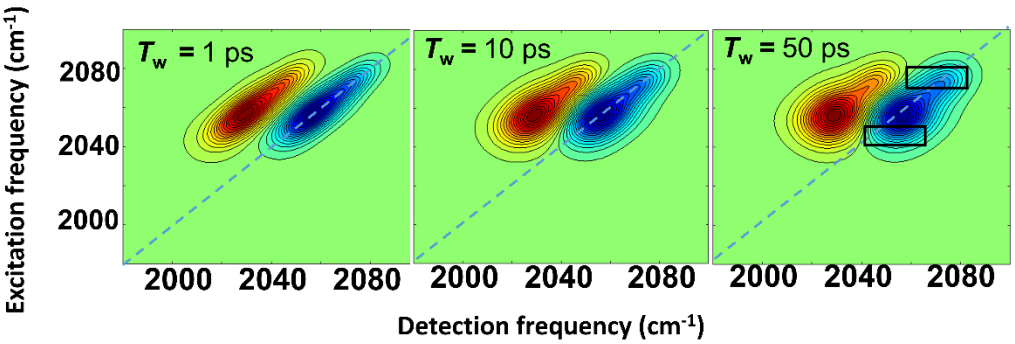

Fig. S2: Simulated 2D IR spectra at three different waiting times (T_w). The simulations used peak positions and relative intensities from the experimental 2D IR spectrum, and the experimentally obtained spectral diffusion timescales and amplitudes to define the lineshape functions (Kubo model). The black boxes represent the spectral region from where the CLS is calculated. To check whether the overlapping bands introduce any error bar in the estimated timescales.

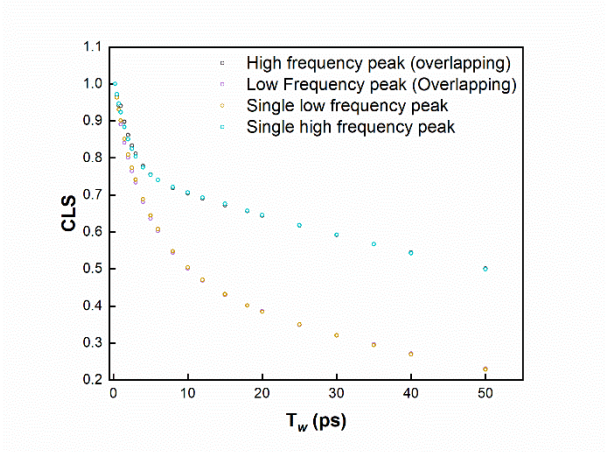

Fig. S3: CLS obtained from 2D IR simulations using single and overlapping peaks. To determine if overlapping bands introduce any errors in the estimated timescales, CLS was calculated from the simulated 2D IR spectra of a single peak. An overlapping peak was then added, maintaining the same frequency difference between the two peaks as obtained from FTIR peak fitting. Various spectral regions were examined to identify the region that provides comparable CLS decays between single peak and overlapping peak simulations. This identified spectral region was then used to extract the CLS from the experimental 2D IR spectra.

References.

1. Deshmukh, S. H.; Chatterjee, S.; Ghosh, D.; Bagchi, S., Ligand Dynamics Time Scales Identify the Surface–Ligand Interactions in Thiocyanate-Capped Cadmium Sulfide Nanocrystals. *J. Phys. Chem. Lett.* **2022,** *13*, 3059-3065.