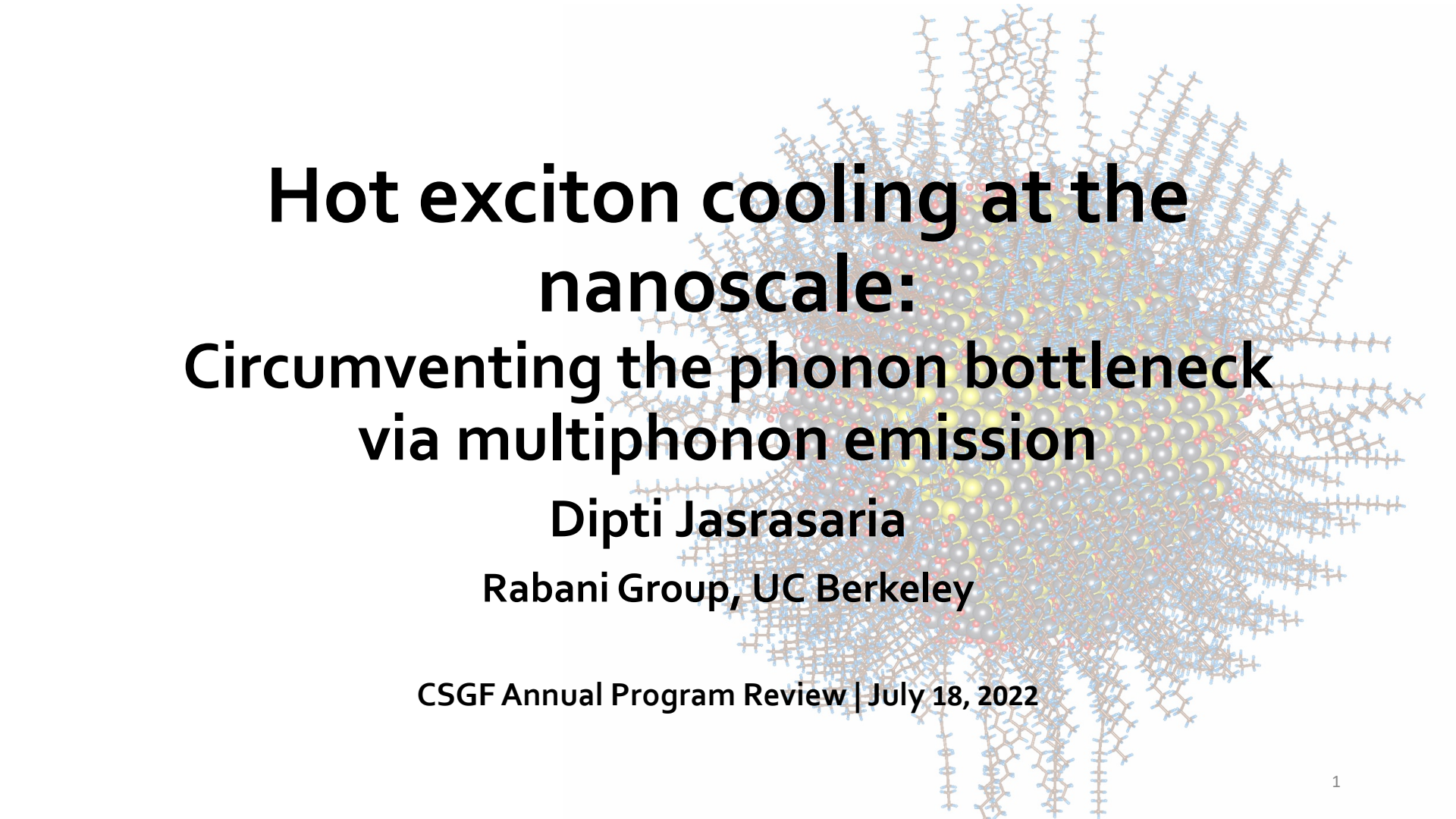

Hot exciton cooling at the nanoscale:
Circumventing the phonon bottleneck via multiphonon emission

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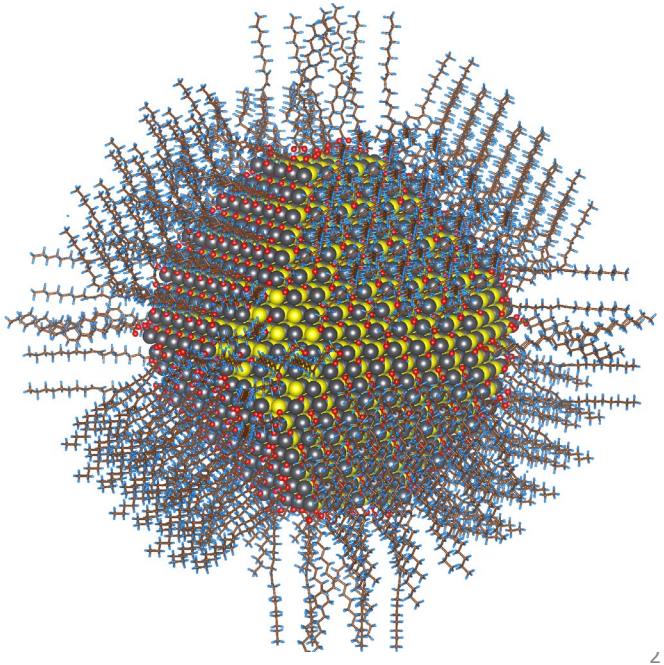
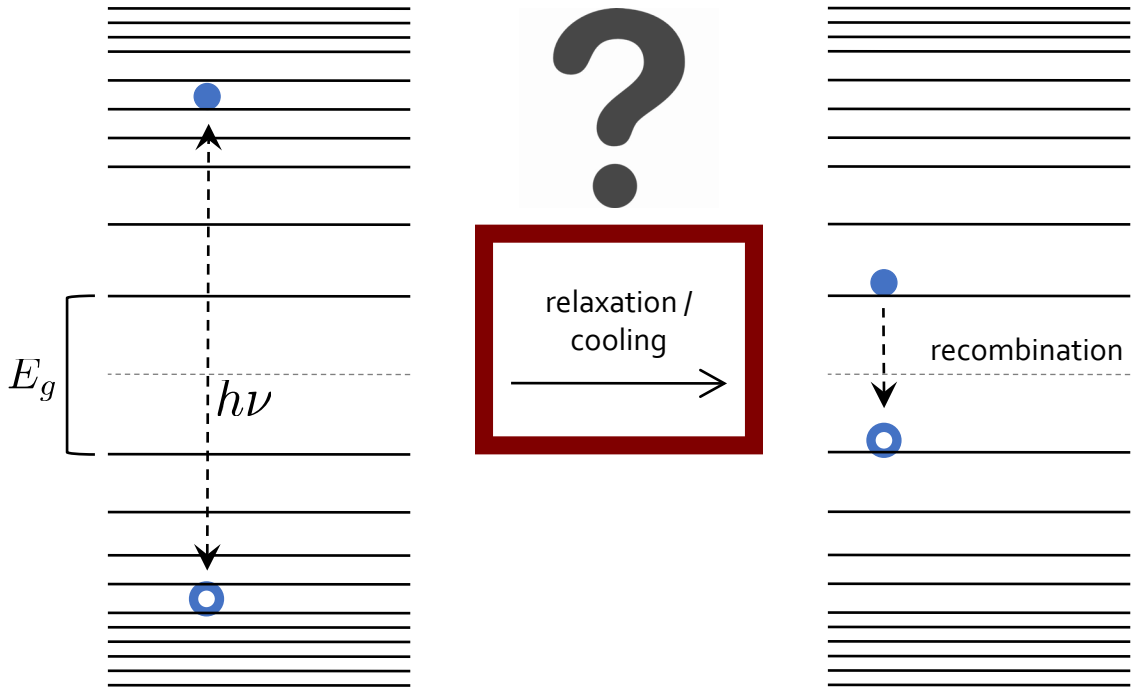
Quantum dots: semiconducting nanocrystals

- Optoelectronic properties can be tuned by changing size, material composition, etc.
- Variety of applications: TVs, solar cells, lasers, bio-imaging devices

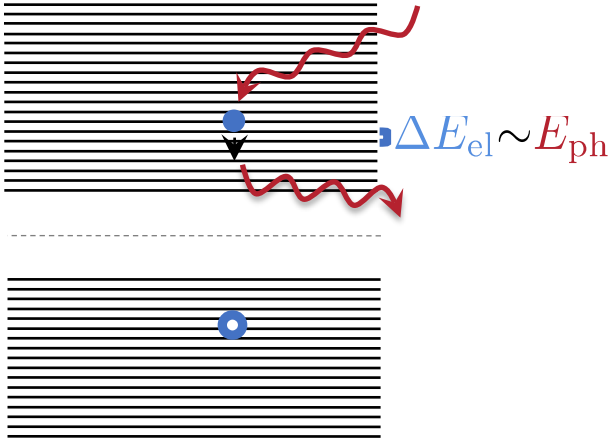


Carriers in quantum dots

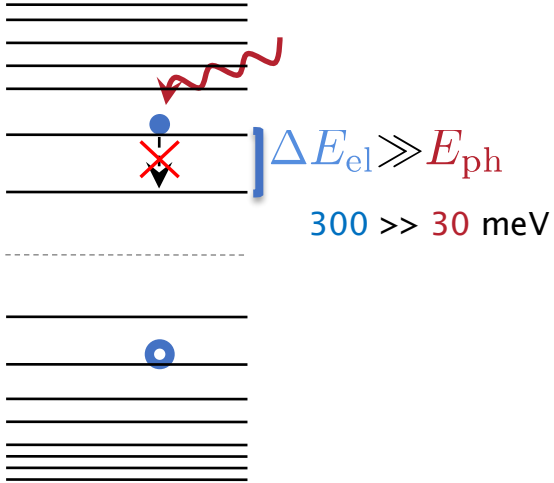


Hot exciton cooling

- All semiconductors, excitons coupled to phonons (lattice vibrations)
- Bulk
  - Continuous density of states
  - Phonon-mediated decay ~1 ps



- Quantum dots
  - Discrete density of states
  - Phonon bottleneck?



Contradictory experimental data

Group	QD material	Relaxation time	Group	QD material	Relaxation time
Sugawara (1)	InGaAs	~10 ps to ~1 ns	Bhattacharya (5)	InGaAs	~5 ps
Gfroerer (2)	GaAs	~1 ns	Murray (6)	PbSe	~1 ps
Murray (3)	InAs, GaAs	~500 ps	Klimov (7)	CdSe	~300 fs
Heitz (4)	InAs, GaAs	~40 ps	Engel (8)	CdSe	<30 fs

- System-specific mechanisms introduced to explain data
- **Necessitates unified theory to understand exciton cooling in QDs instead of imposing system-specific mechanisms**

(1) JJAP **37**, 5451 (1998); APL **68**, 3013 (1996); APL **71**, 2791 (1997); (2) PRB **53**, R16474 (1996); (3) APL **69**, 4087 (1996)
(4) PRB **56**, 10435 (1997); PE **2**, 578 (1998); (5) PRB **57**, R9423 (1998); (6) PRB **72**, 195312 (2005)
(7) PRB **60**, 13740 (1999); PRB **61**, R13349 (2000); (8) JCP **138**, 014705 (2013)

Hot exciton cooling in quantum dots

1. What is the timescale and mechanism of hot exciton cooling to band edge in QDs?

2. How does this process depend on excitation energy and QD properties (*i.e.*, size, dimensionality, composition)?

3. Ultimately, how we can design experimental QD systems with increased quantum yield?

Our approach: open quantum systems

- Hamiltonian describing system of excitons coupled to phonon bath

$$H = H_S + H_B + V_S \otimes V_B$$

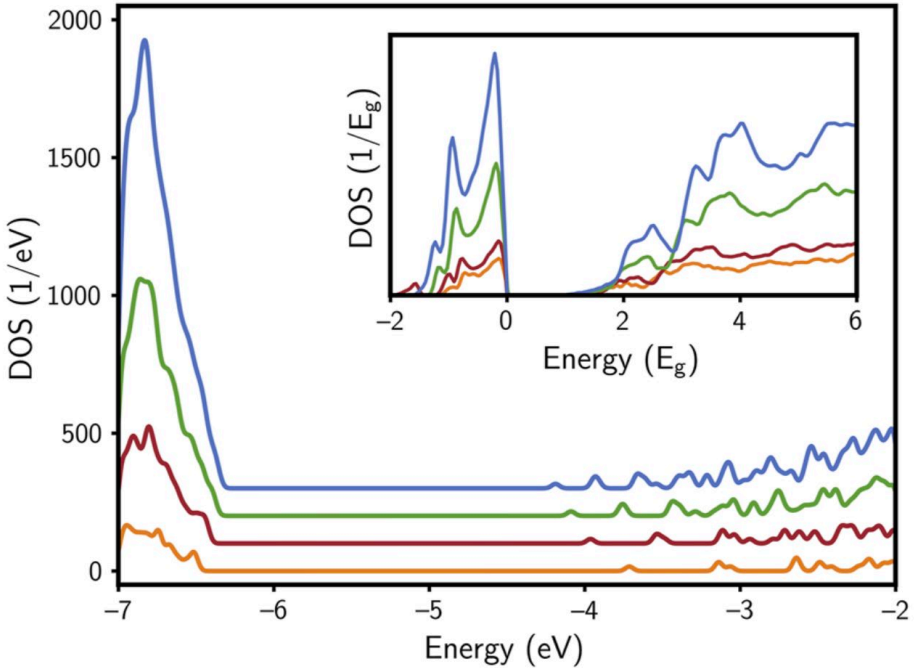
- Calculate golden rule rates between system states:

$$\Gamma_{n\to m} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt e^{i(E_n - E_m)t/\hbar}\langle V_{nm}(t)V_{mn}(0)\rangle_{\mathrm{eq}}$$

  - Build master equation and propagate system dynamics

Atomistic calculations on QDs of experimentally relevant sizes

- Nanoscale regime presents computational challenge
  - No translational symmetry
  - Many degrees of freedom: ~10^3 atoms, ~10^4 electrons
- HPC resources and theoretical/ computational tricks are essential



Dipti Jasrasaria, D. Weinberg, J. P. Philbin, E. Rabani. *J. Chem. Phys.* **157**, 020901 (2022).

Atomistic calculations on QDs of experimentally relevant sizes

- Excitons: semiempirical pseudopotential method and Bethe-Salpeter Equation approach to obtain correlated electron-hole states

$$H_S = \sum_{n}^{\text{exc}} E_n |\psi_n\rangle\langle\psi_n|$$

- Phonons: atomic force field to obtain full range of phonon frequencies and modes

$$H_B = \sum_{\alpha}^{\text{phonon}} \hbar\omega_\alpha b_\alpha^\dagger b_\alpha$$

Dipti Jasrasaria, D. Weinberg, J. P. Philbin, E. Rabani. *J. Chem. Phys.* **157**, 020901 (2022).

$V_S \otimes V_B$: Exciton-phonon coupling

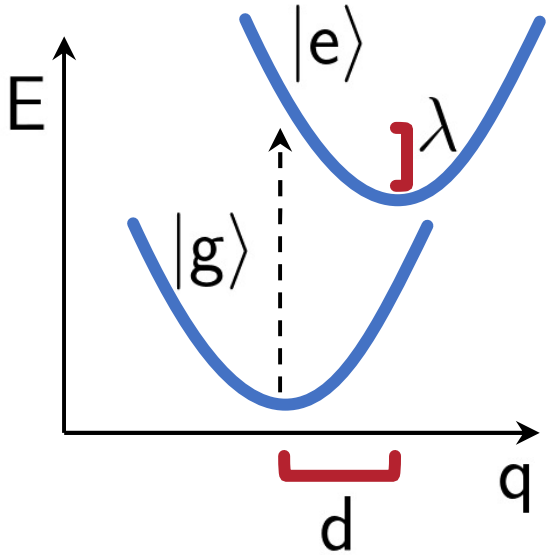
- Open questions about role of quantum confinement on exciton-phonon coupling

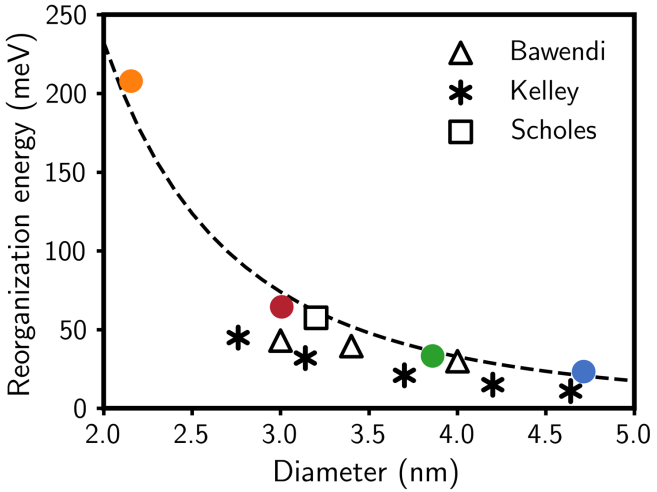
$$V_{SB} = \left\langle \psi_n \left| \left(\frac{\partial v(\boldsymbol{r})}{\partial R_{\mu k}} \right)_{\boldsymbol{R}_0} \right| \psi_m \right\rangle (\boldsymbol{R} - \boldsymbol{R}_0)$$

Dipti Jasrasaria, E. Rabani. *Nano Lett.* **21**, 8741 (2021).

$V_S \otimes V_B$: Exciton-phonon coupling

- Open questions about role of quantum confinement on exciton-phonon coupling – validate by computing reorganization energies

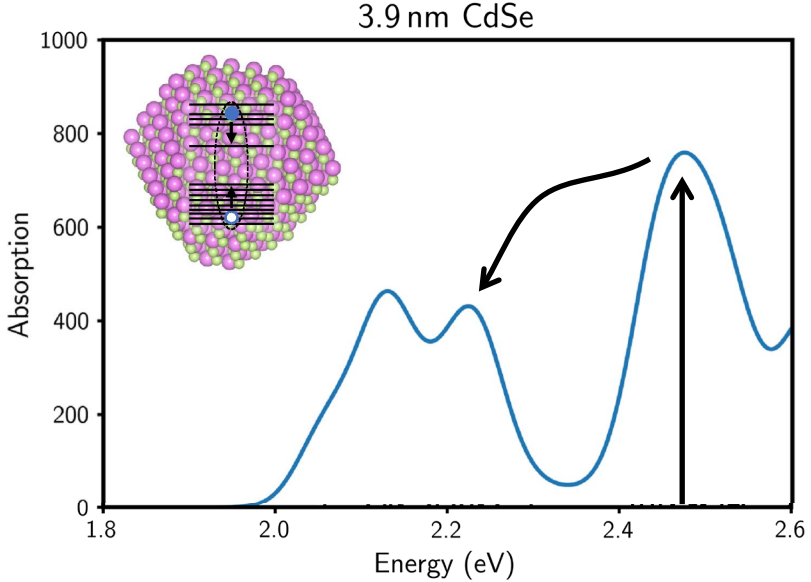




Dipti Jasrasaria, E. Rabani. *Nano Lett.* **21**, 8741 (2021).

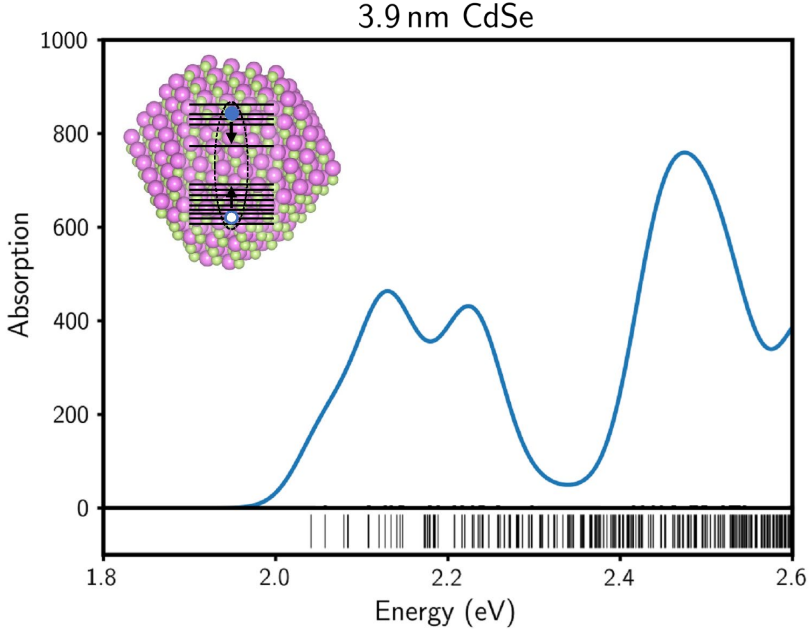
… back to hot exciton cooling!

- Cooling would require simultaneous emission of ~10 phonons… slow!

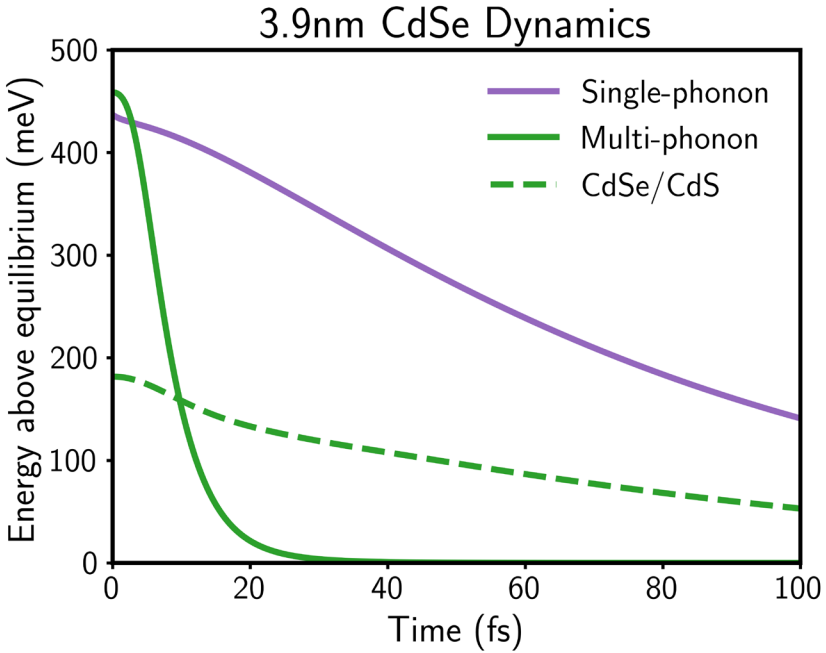


… back to hot exciton cooling!

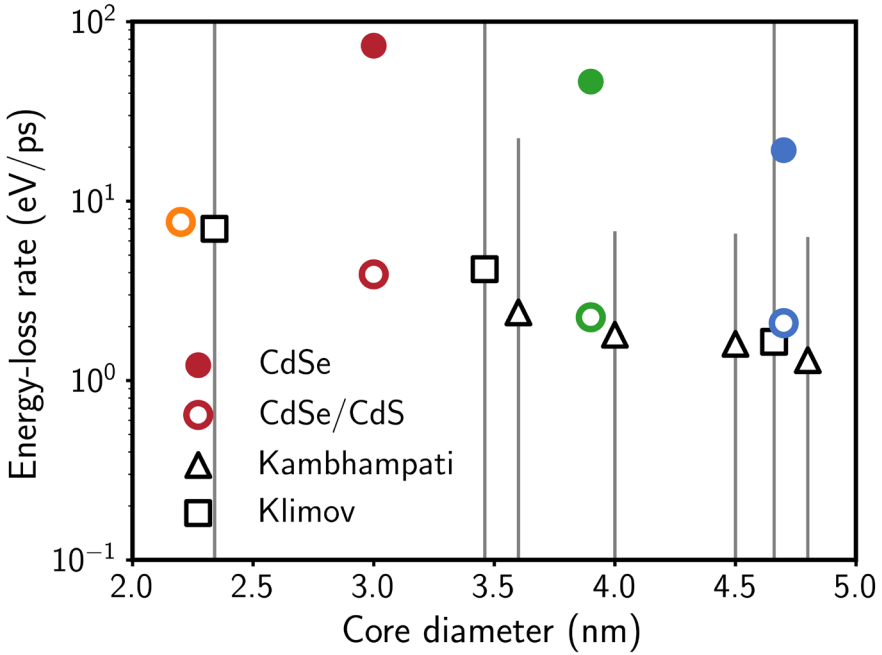
- Spectrum consists of many excitonic states with smaller energy gaps – no phonon bottleneck
- Perform polaron transform to allow multi-phonon processes



Ultrafast cooling enabled by multiphonon emission



Cooling rate decreases with decreasing exciton-phonon coupling

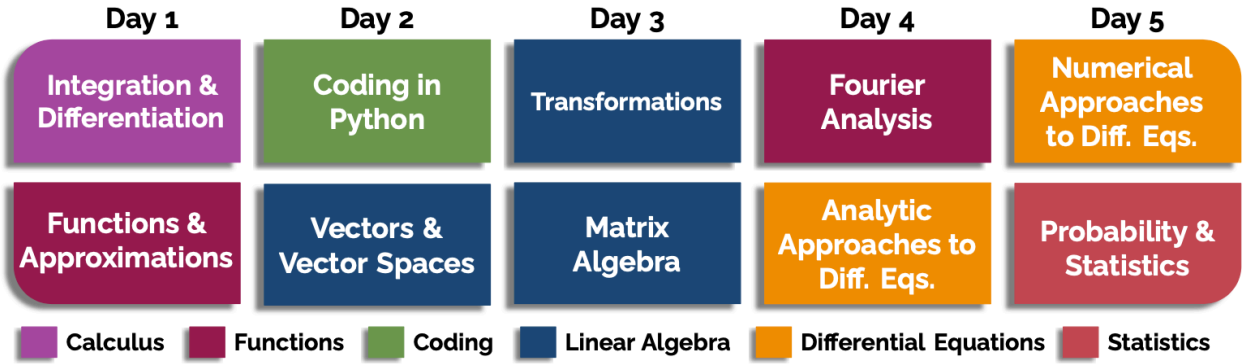


Summary and looking forward

- Unified framework for hot exciton cooling in NCs
  - Electron-hole correlations, exciton-phonon coupling, multi-phonon processes
  - Dense manifold of excitonic states and efficient multiphonon processes
  - no phonon bottleneck!!
- Understanding exciton cooling…
  - dependence on excitation energy (stochastic approach?)
  - in other materials (anisotropic nanoplatelets, perovskites, etc.)

College of Chemistry Math Bootcamp

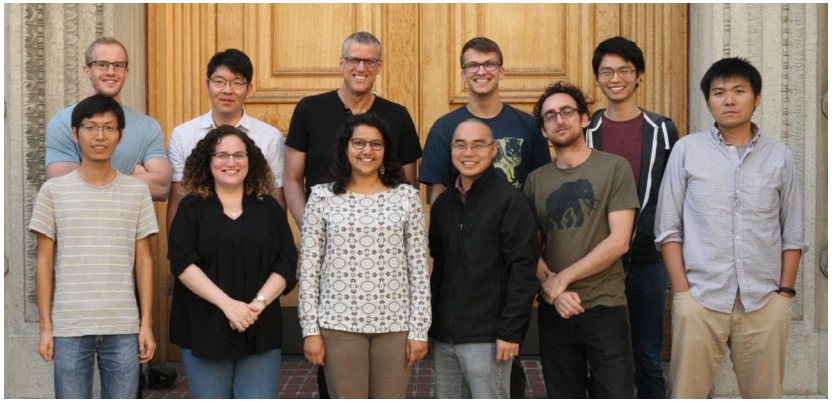
- Student-initiated, designed, and taught for incoming physical chemistry students
- Five-day intensive course centered around group problem solving



- Content freely available at chemmathbootcamp.com

Co-leaders: Rachel Clune, Orion Cohen, Avishek Das, Elliot Rossomme

Acknowledgements



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PTL PHOTONICS AT THERMODYNAMIC LIMITS

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