Ultrafast transient absorption spectroscopy investigations of charge carrier dynamics of methyl ammonium lead bromide ($CH_3NH_3PbBr_3$) perovskite nanostructures

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Outline

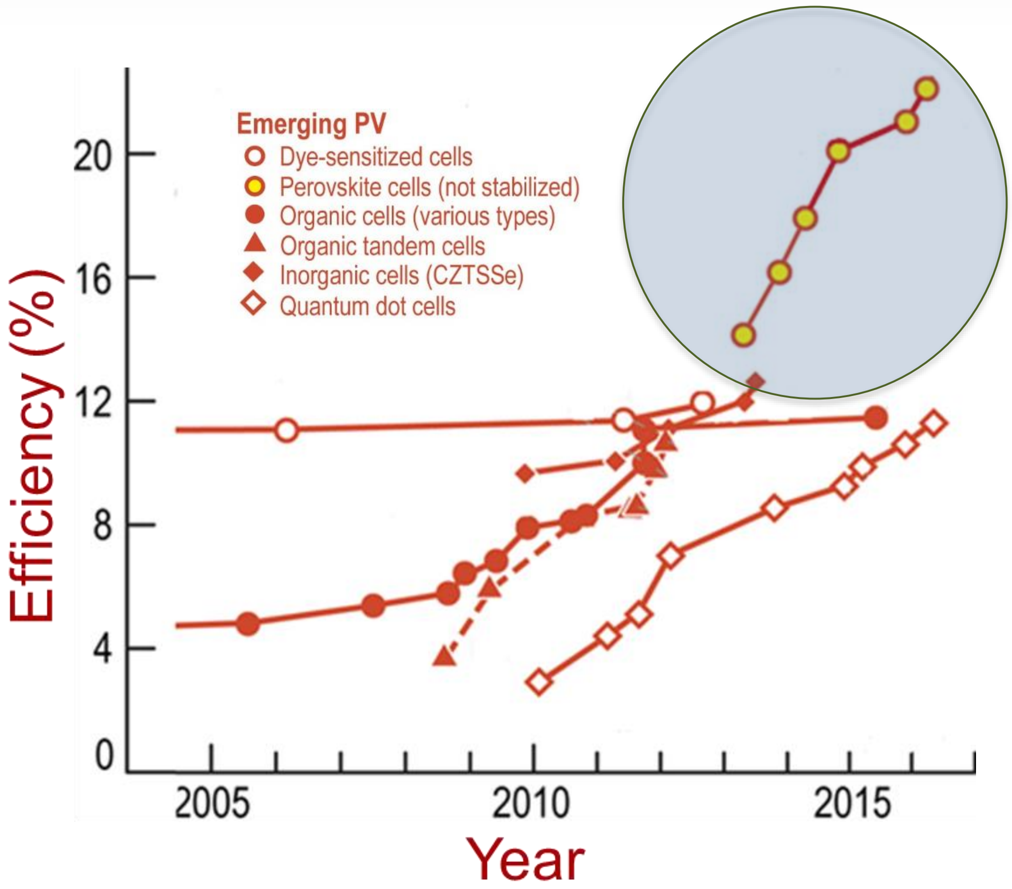
- Motivation: why we want to study excited-state dynamics of perovskites.
- Perovskite structure
- Sample synthesis.
- Transient absorption (TA) measurements
  - Experimental
  - Results
    - Pump fluence dependence measurements
  - Proposed kinetic model
  - Global fitting
- Conclusions.

Motivation

- High demand for alternative energy sources of higher efficiency
- Perovskites are promising light absorbers for photovoltaic devices [1] as well as materials in light-emitting diodes [2], photodetectors [3], and lasers [4].
- Ultimately, increasing efficiency relies on optimization of photo-induced processes in photovoltaic materials.
- Transient absorption (TA) spectroscopy is a powerful tool for the study of photo-induced processes in photovoltaic materials.

1. Nature Photon. 8, 133–138 (2014).
2. Nature Nanotech. 9, 687–692 (2014).
3. Nature Photon. 9, 679–686 (2015).
4. Nature Mater. 14, 636–642 (2015).

Photovoltaic Efficiency Chart



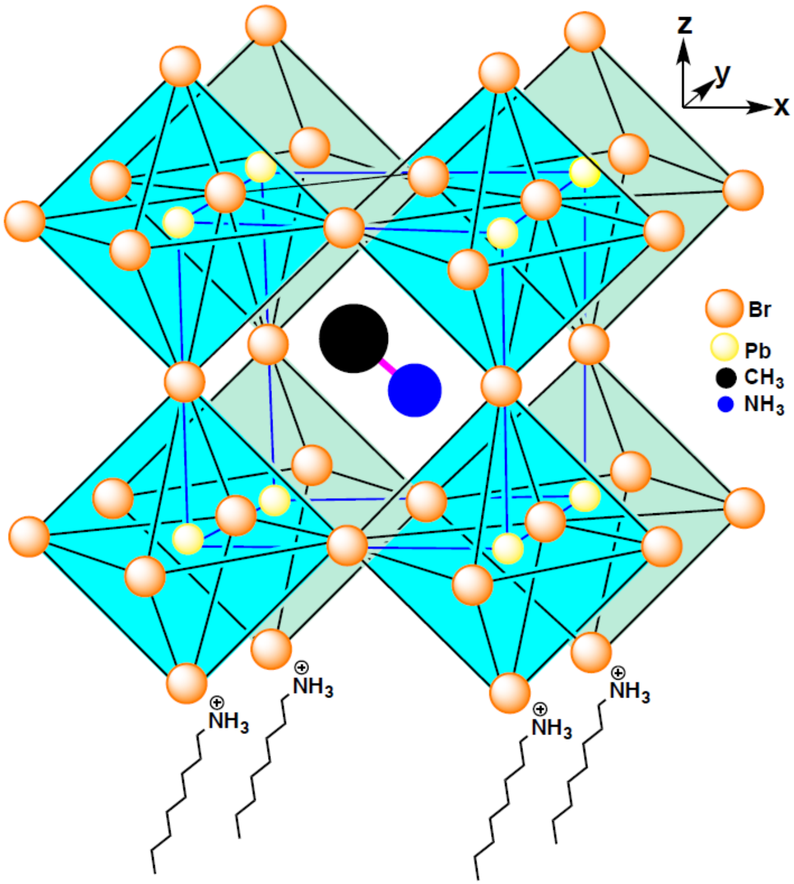
Advantages of perovskites:

- Strong absorption across the solar spectrum,
- Low exciton binding energy (~16 meV),
- High charge-carrier mobility,
- Long diffusion length (>1 µm) ,
- Band gap tunability.

➢ **Higher efficiencies**

http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

Samples, Synthesis and Characterization



Nano-Crystals (NCs)

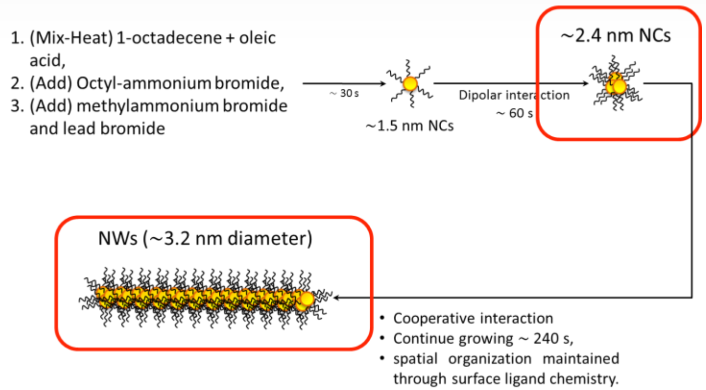
Nano-Wires (NWs)

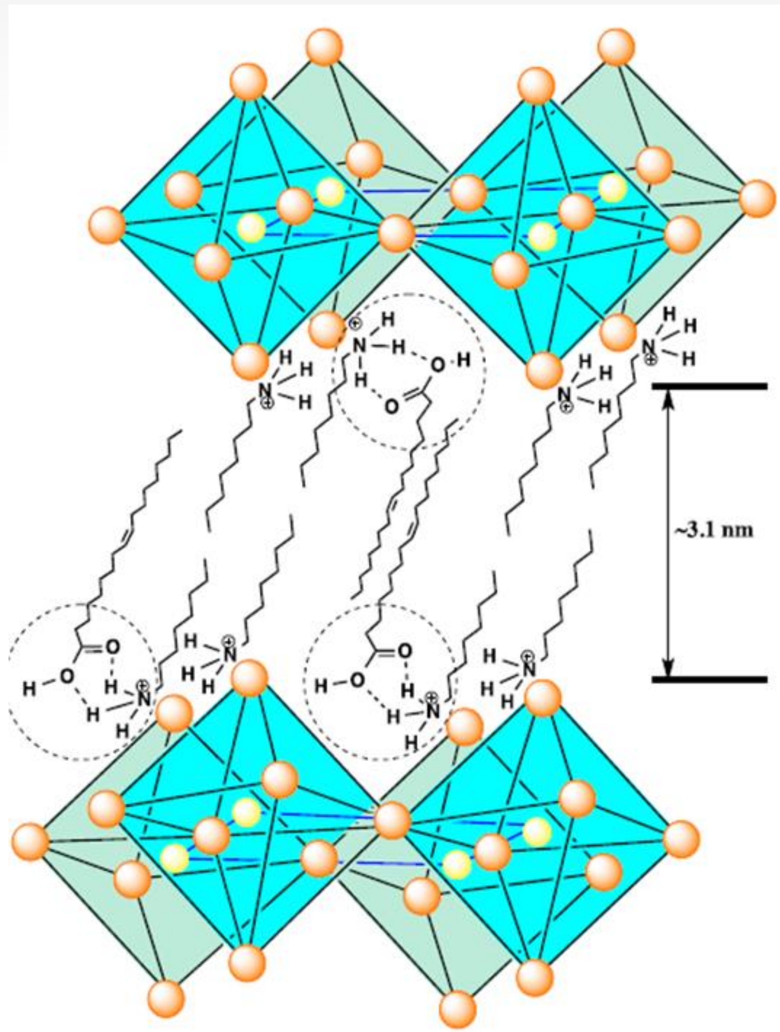
Nano-Plates (NPs)

Chem. Mater. 2016, 28, 5043–5054

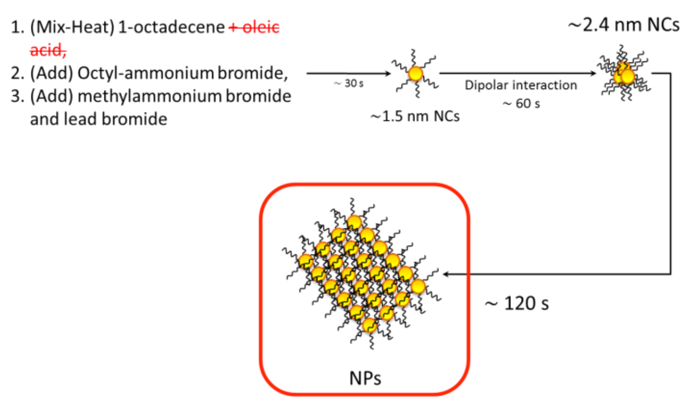
Samples

Synthesis, NCs and NWs





and NPs



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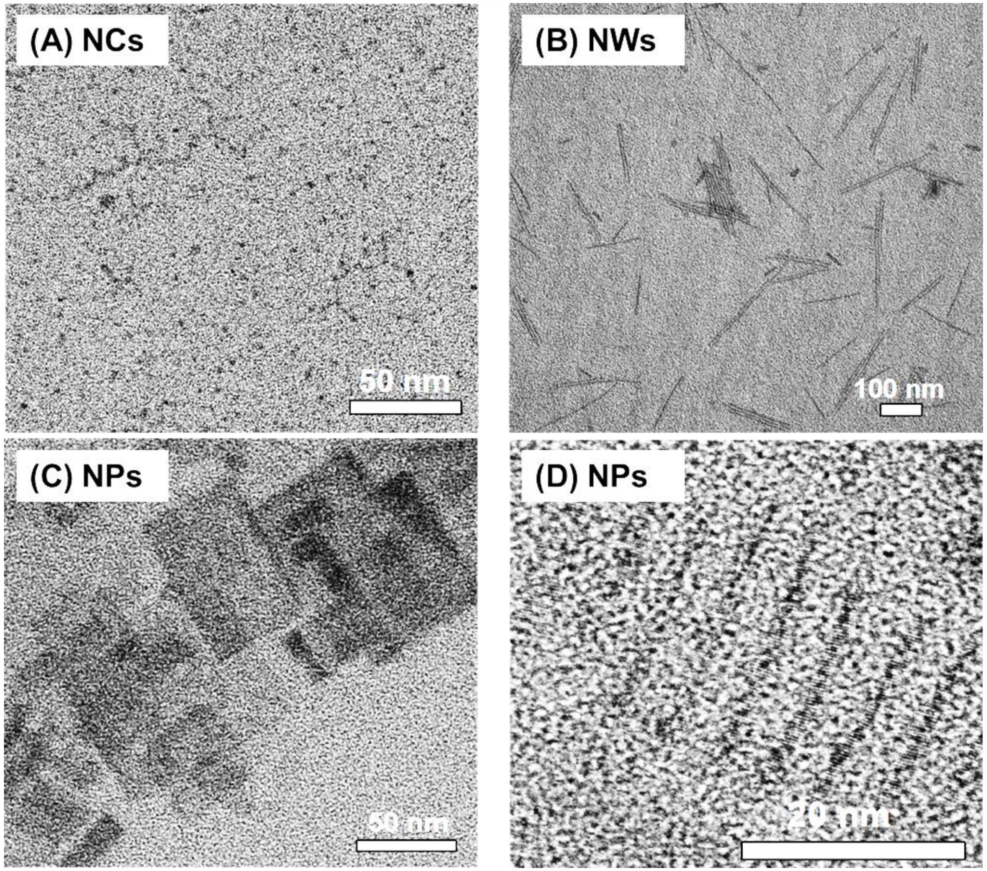
Samples

Transmission Electron Microscope (TEM)

TEM images of NCs, NWs and NPs.
Dimensions:
- NCs: ~2.4 nm,
- NWs: 300 – 900 nm length and ~3.8 nm diameter,
- NPs: 25 – 40 nm edge length.



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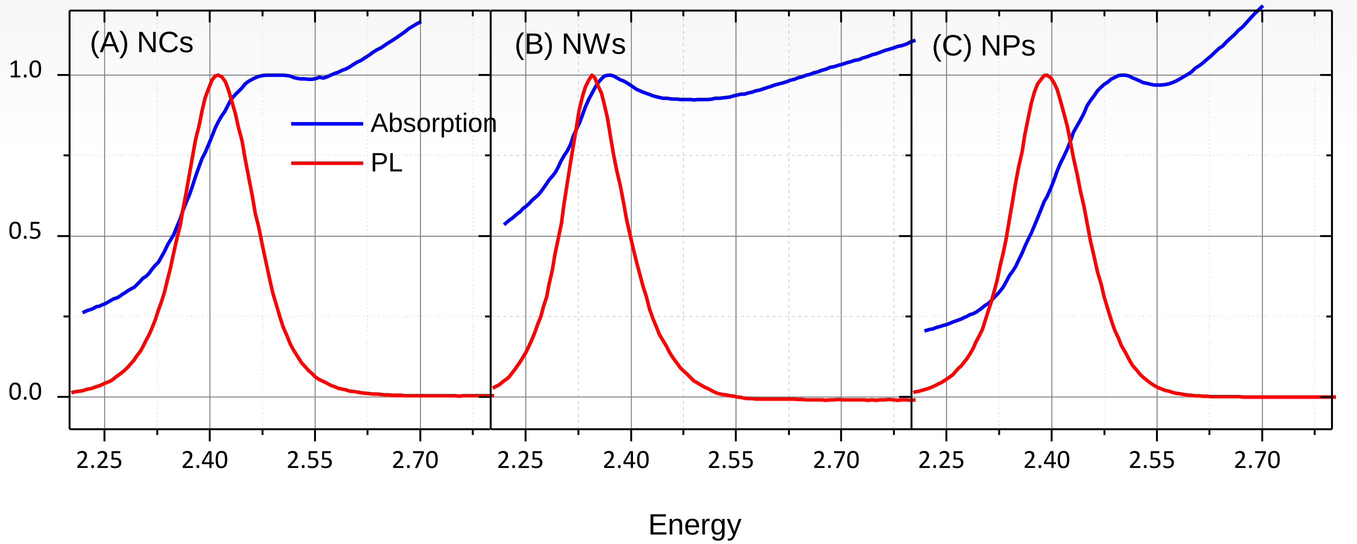
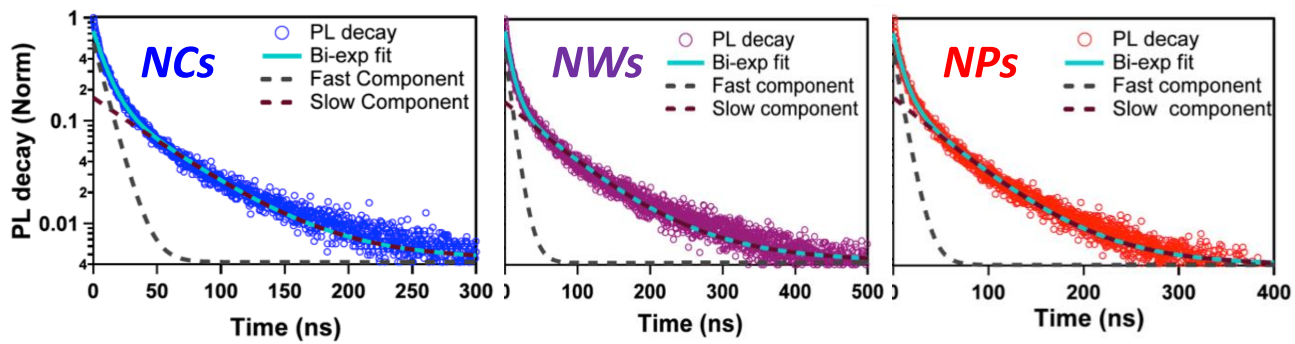
Steady-state absorption & photoluminescence(PL) spectra





	Abs. Peak	PL Peak	Φ_{FL}	radiative life time (ns)	
	(nm)	(nm)	(%)	τ_{fast}	τ_{slow}
NCs	499	513	16 ± 2	9 ± 2	50 ± 5
NWs	522	529	59 ± 7	11 ± 1	89 ± 13
NPs	497	515	44 ± 3	10 ± 1	63 ± 8

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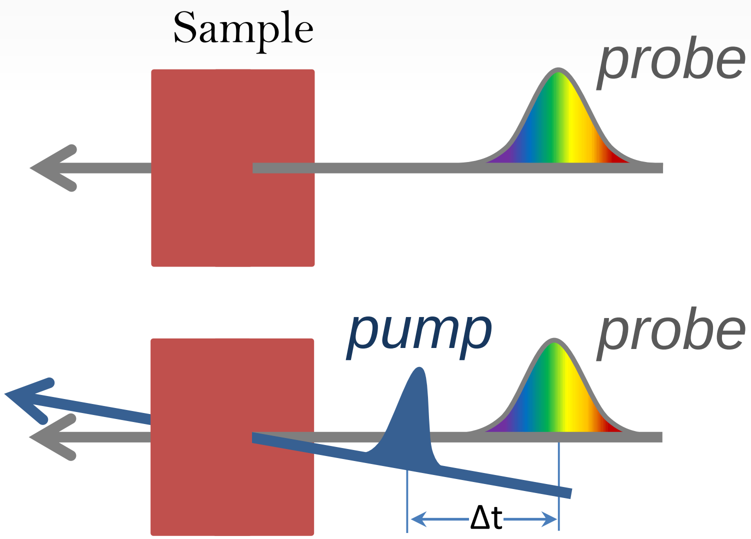
Pump-probe TA spectroscopy experiment, concept

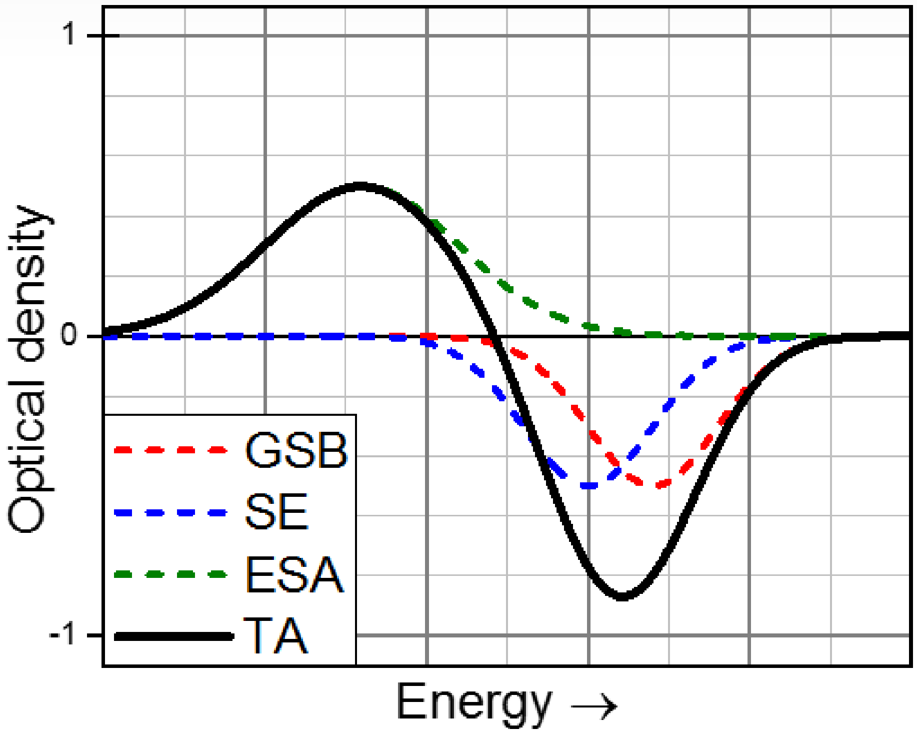


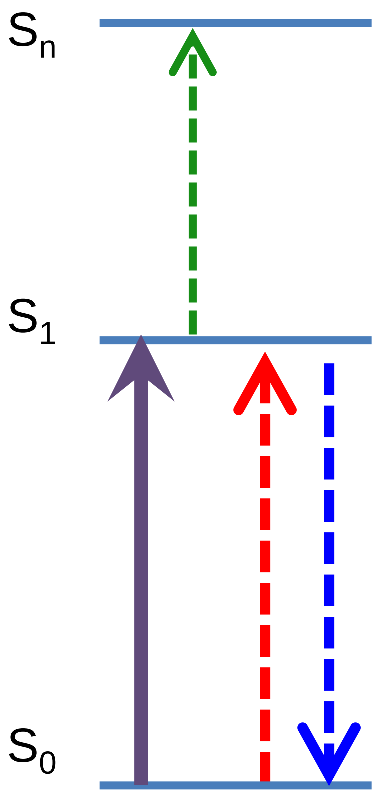
I_0: Unpumped Probe laser transmission

I*: Pumped Probe laser transmission

$$\Delta OD(\Delta t, \lambda) = -\log\left(\frac{I^*(\Delta t, \lambda)}{I_0(\lambda)}\right)$$

Pump-probe TA spectroscopy experiment: possible signal contributions



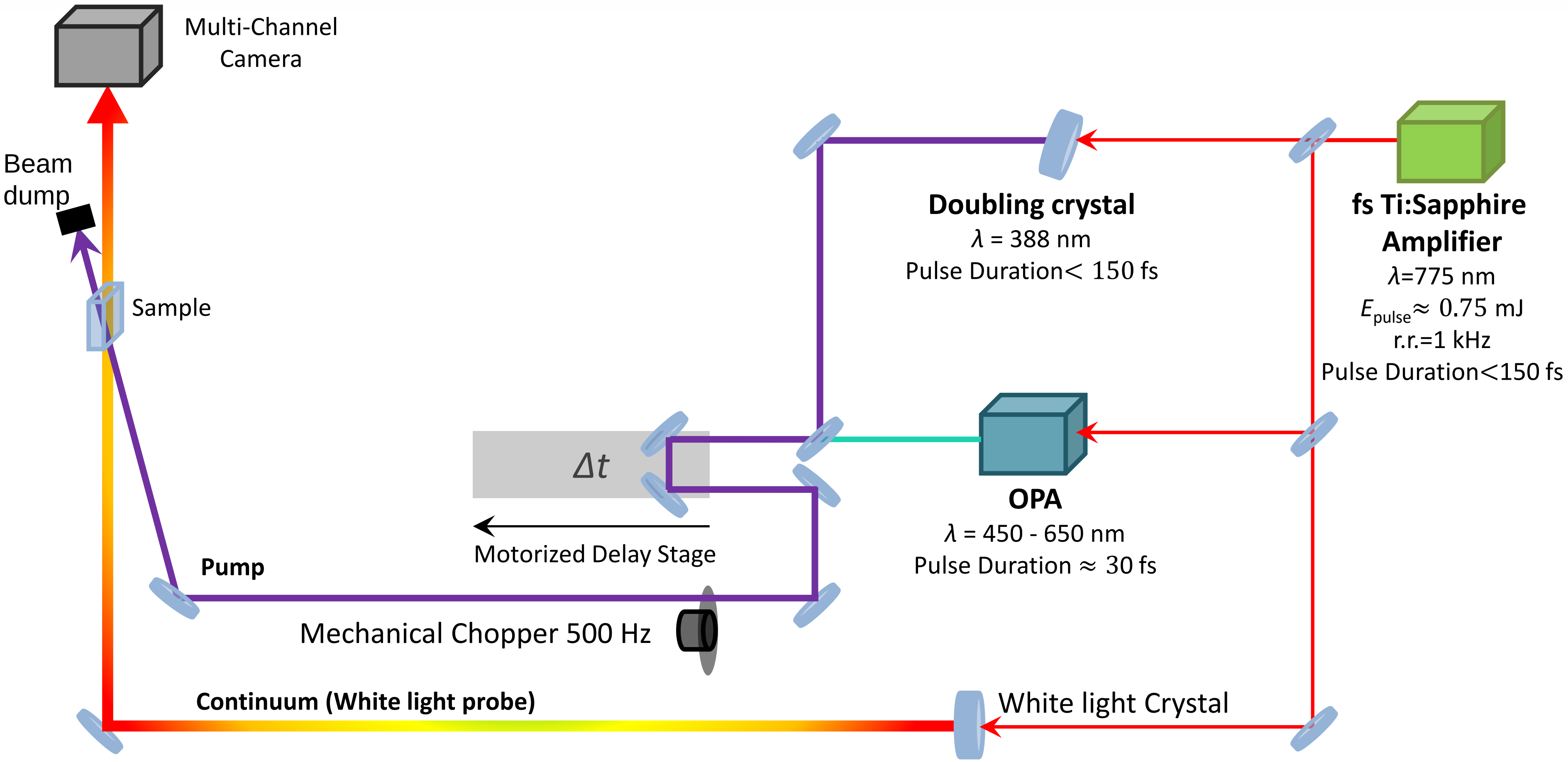


Ground-state bleach (GSB)

Stimulated Emission (SE)

Excited-state absorption (ESA)

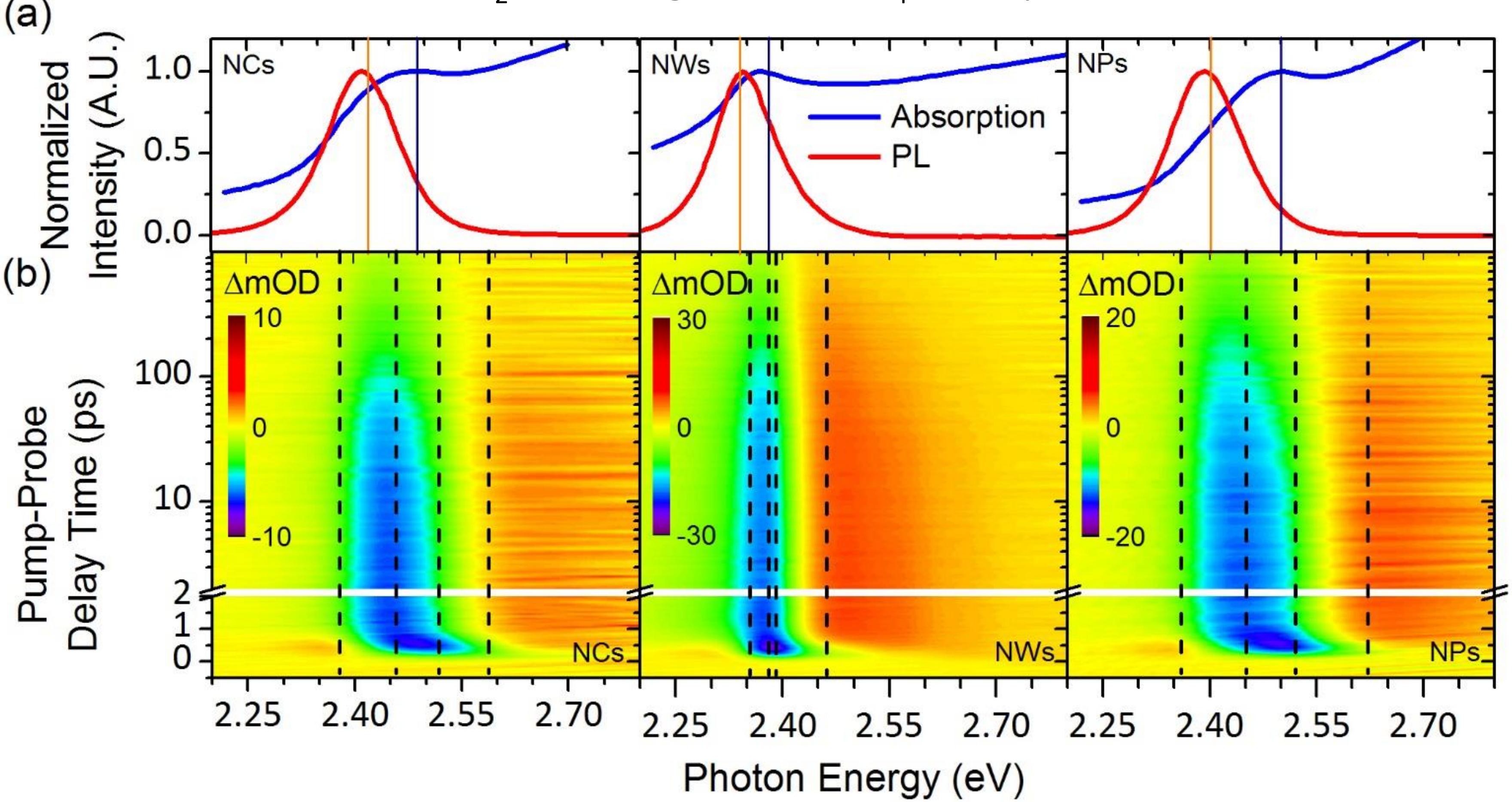
Pump-probe TA spectroscopy experiment: setup



TA Spectra, results

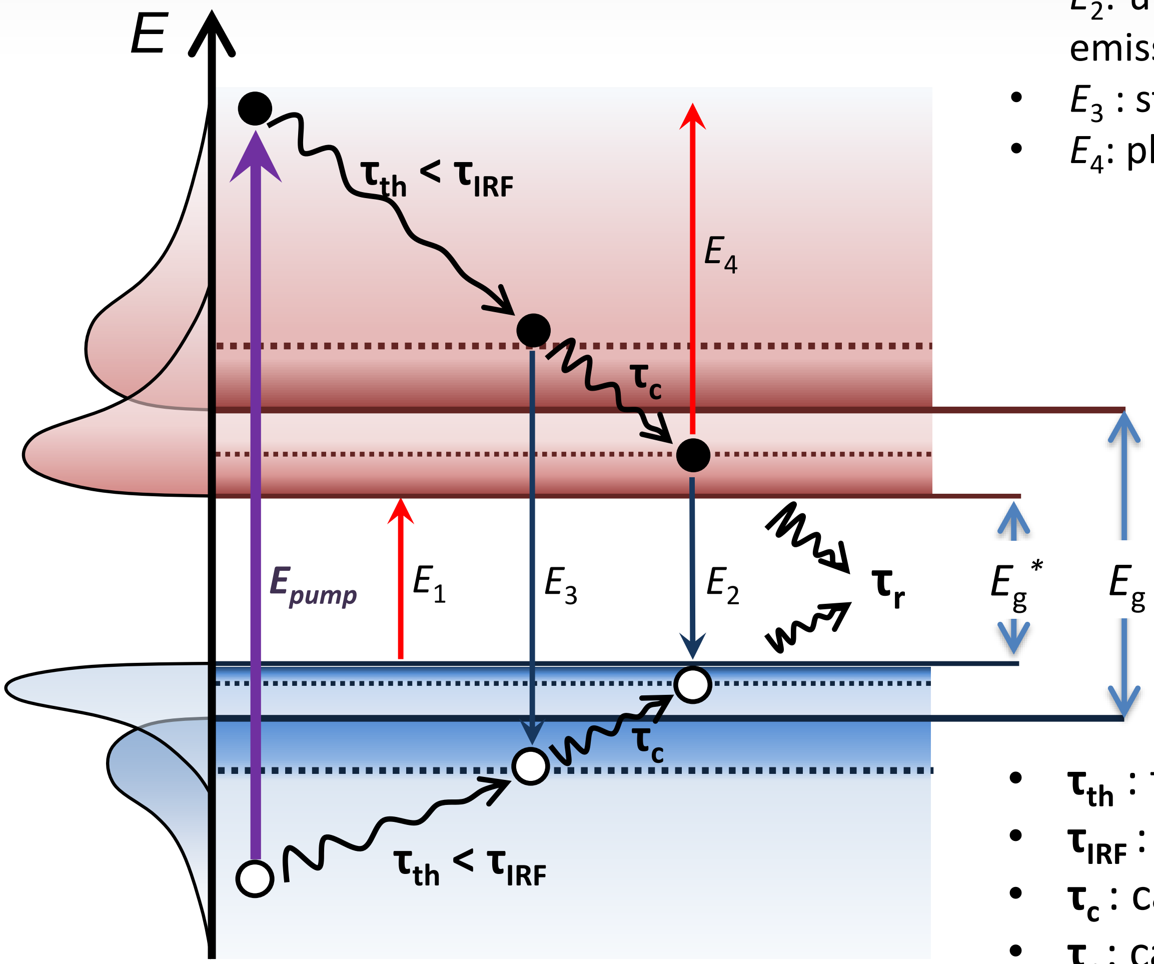
3.2 eV (388 nm) Pump, 20 μJ/cm² Pump Flounce

- E_1 (fast, positive)
- E_2 (slow, negative)
- E_3 (fast, negative)
- E_4 (slow, positive)

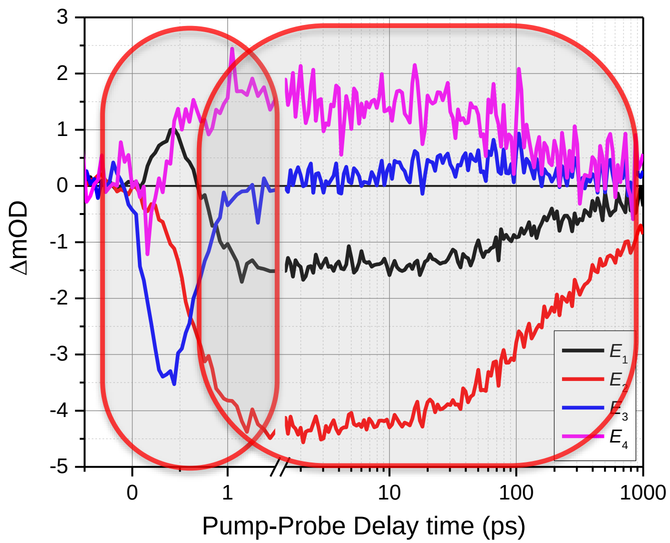


TA Spectra, Results

Suggested Kinetics

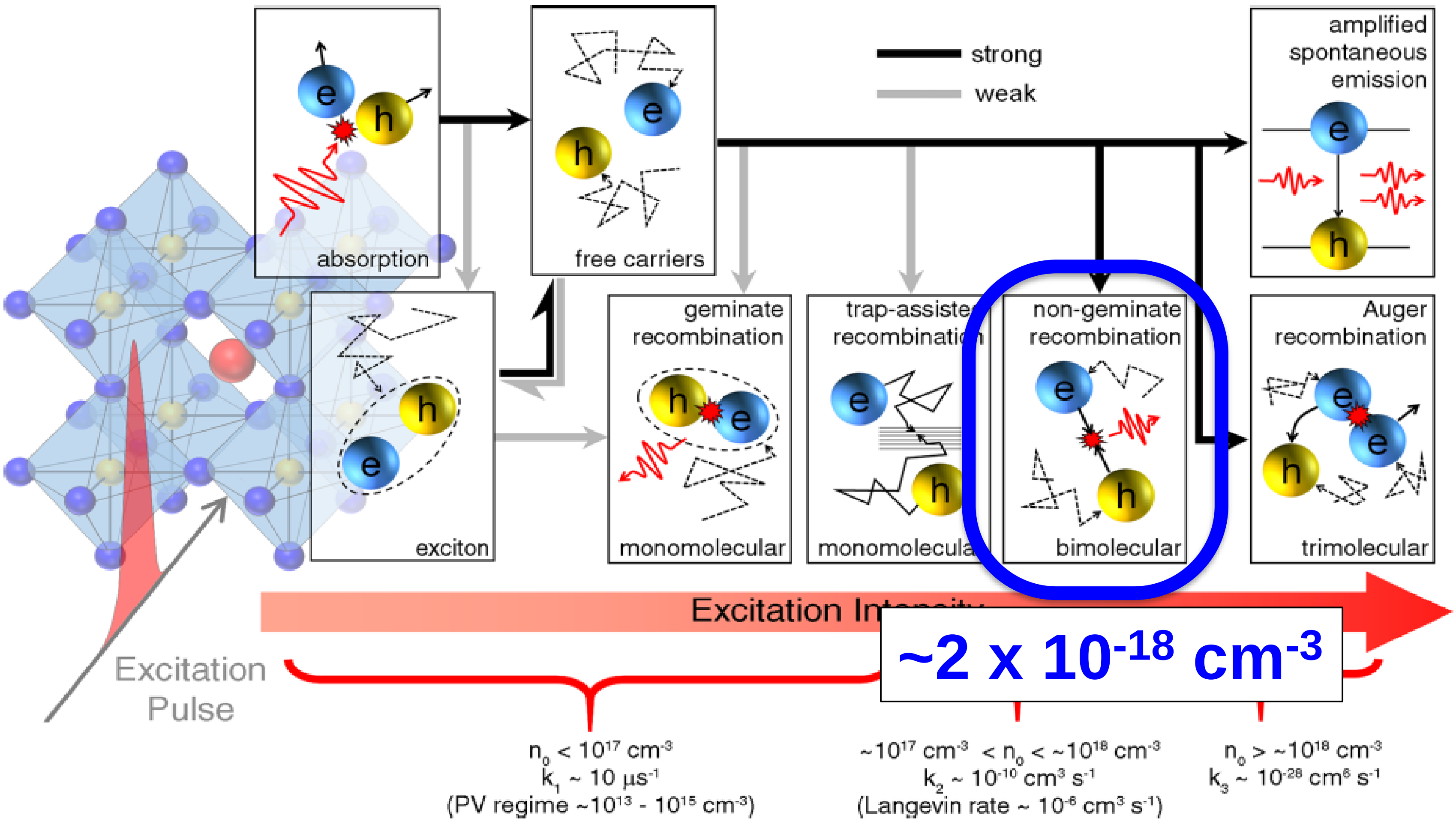


- E_1: photo-induced absorption due to bandgap renormalization,
- E_2: unresolved state filling and stimulated emission (nongemenate recombination),
- E_3 : state filling due to hot carriers,
- E_4: photo-induced intraband absorption.



- τ_{th} : thermalization time
- τ_{IRF} : instrument response time
- τ_c : carrier cooling time
- τ_r : carrier recombination half time

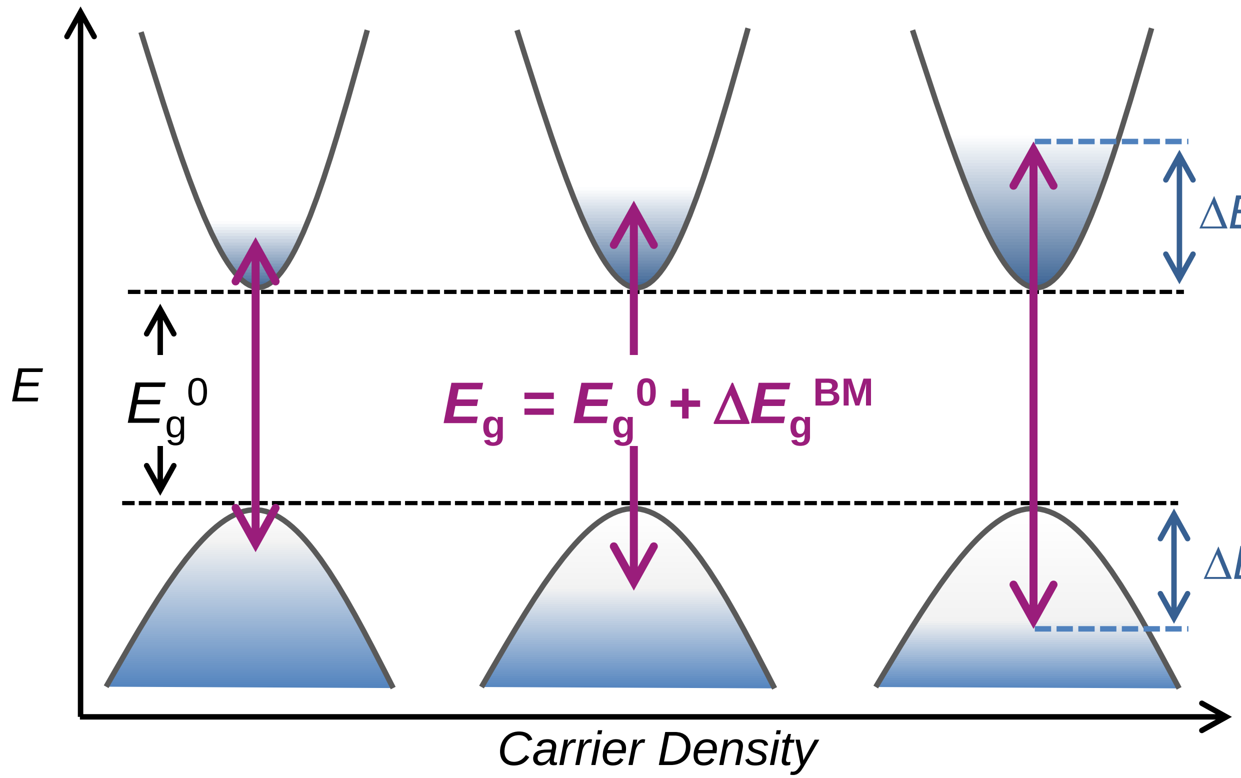
Recombination pathways based on charge carrier density



Acc. Chem. Res. 2016, 49, 294–302

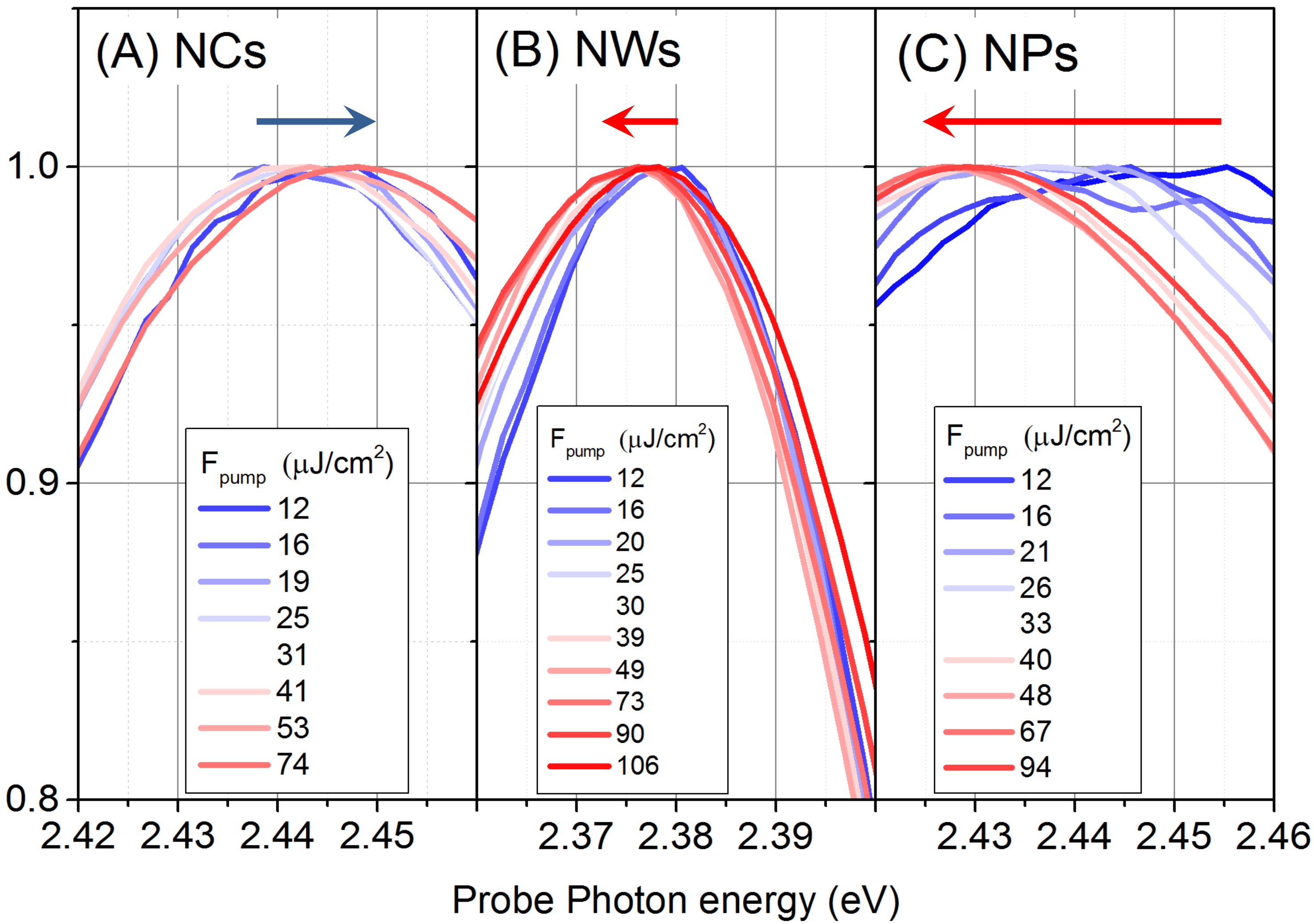
TA Spectra, Results

Pump Fluence Dependency, 3.2 eV (388 nm)



Burstein-Moss effect

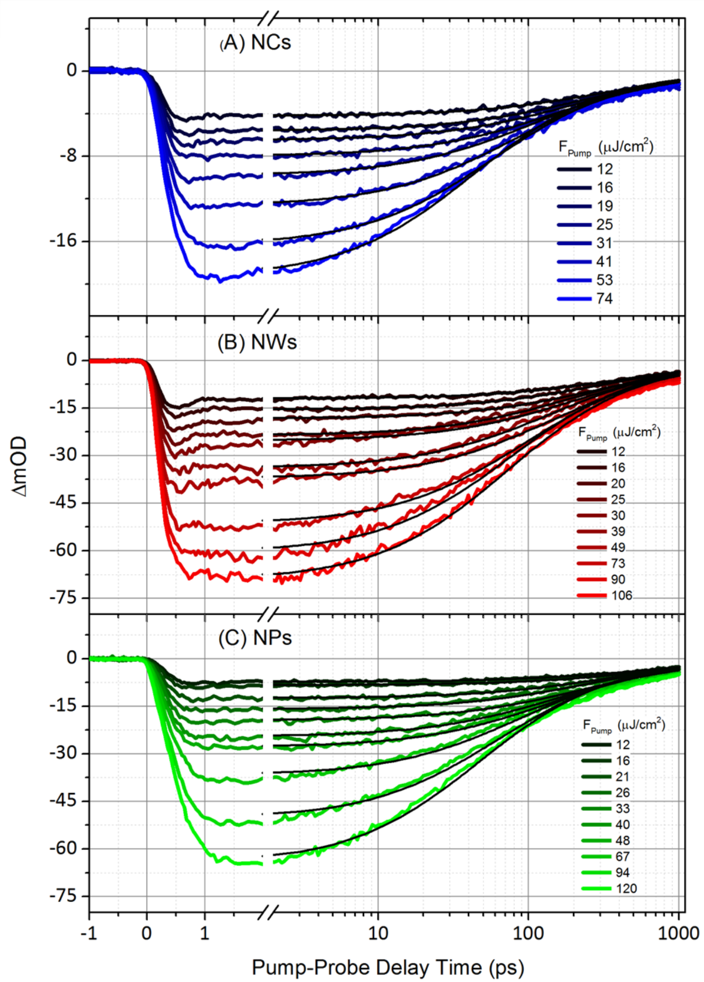
Normalized TA at E_3 (Unresolved SE and GSB)



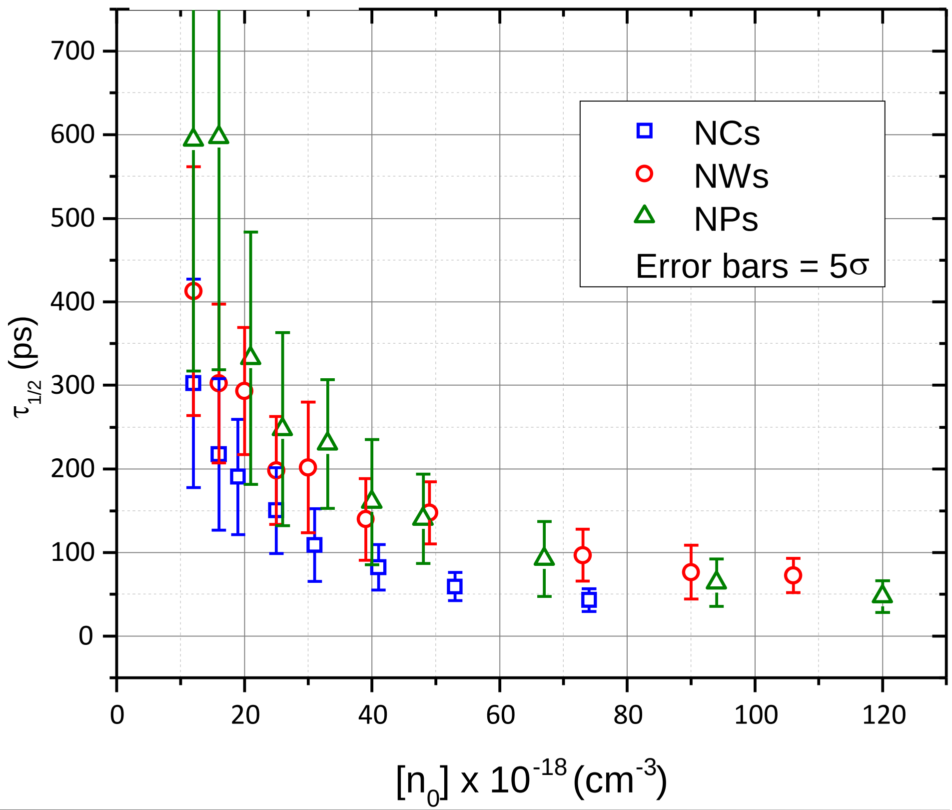
- Cancellation of Burstein-Moss effect and band gap renormalization.

Pump Fluence Dependency, 3.2 eV (388 nm)

Recombination times



$$[n(t)] = \frac{[n_0]}{1 + [n_0] \cdot \frac{t}{\tau_r}}$$



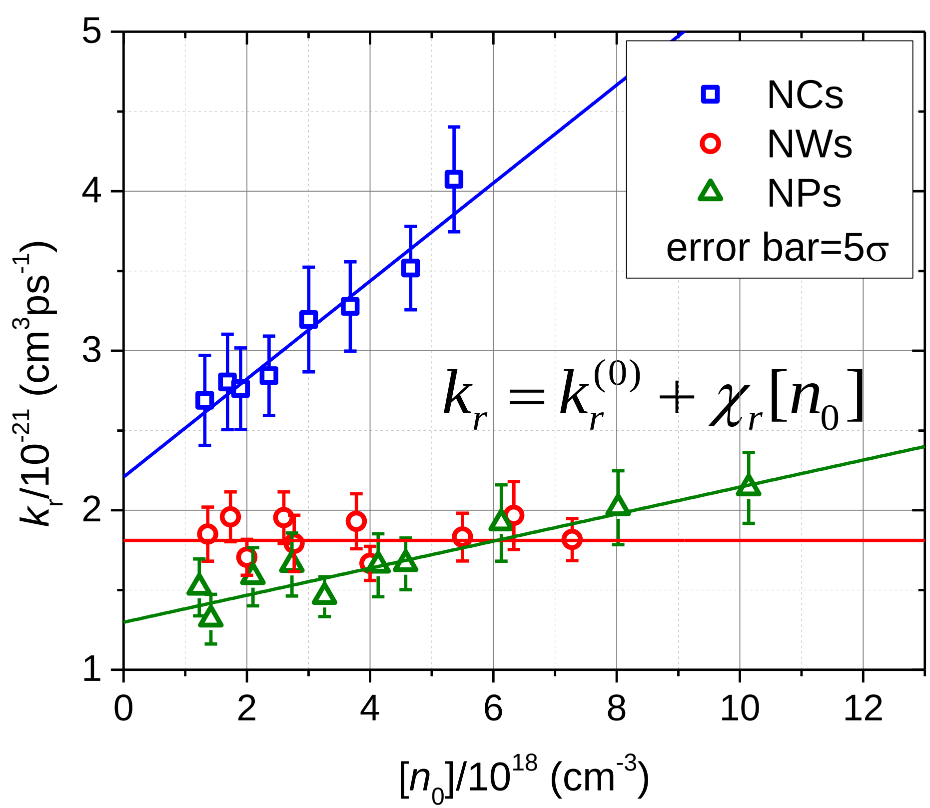
388 nm Pump Flounce Dependency

Recombination Rates

(k_r) of NWs does not dependent on $[n_0]$, while those of NCs and NPs do.

$$k_r = \frac{1}{[n_0] \cdot \tau_r}$$

	$k_r^{(0)}$ (10^{-21} cm^{3}ps^{-1})	χ_r (10^{-30} cm^{6}ps^{-1})
NCs	2.21 (10)	3.07 (31)
NWs	1.81 (4)	0
NPs	1.30 (6)	0.84 (14)



TA Spectra, Results

Global Fitting, results

Decay of E_1 and E_3

$$\Delta OD(t,\hbar\omega) = \left\{ \sum_{i=1,3} A_i(\hbar\omega_i)\cdot e^{-\Delta t/\tau_c} + \sum_{i=2,4} A_i(\hbar\omega_i)\cdot\left[e^{-\Delta t/\tau_c} + \frac{1}{1+{-\Delta t}/{\tau_r}} \right] \right\} \otimes IRF$$

Growth, Decay of E_2 and E_4

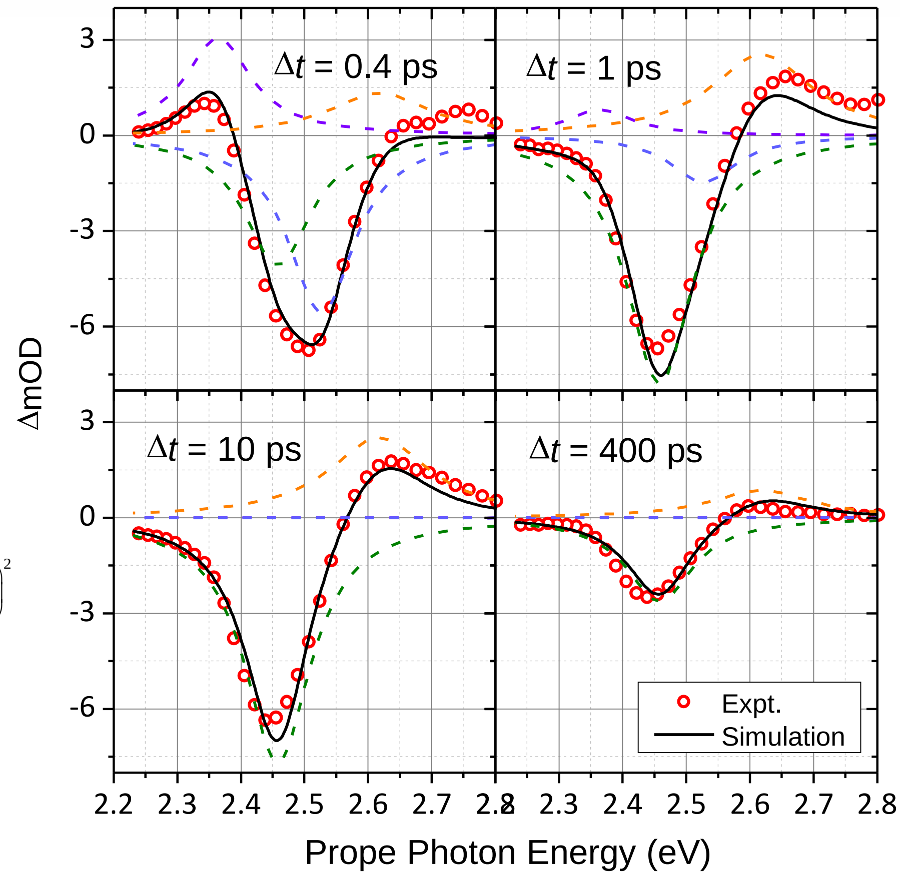
$$A_i(\hbar\omega) = \frac{A_i\gamma_i/(2\pi)}{(\gamma_i/2)^2 + (\omega-\omega_i)^2}$$

Lorentzian line shape used to describe the TA spectra in the frequency domain

$$IRF(t) = \frac{Y_{IRF}}{\sigma_{IRF}\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{t}{\sigma_{IRF}}\right)^2}$$

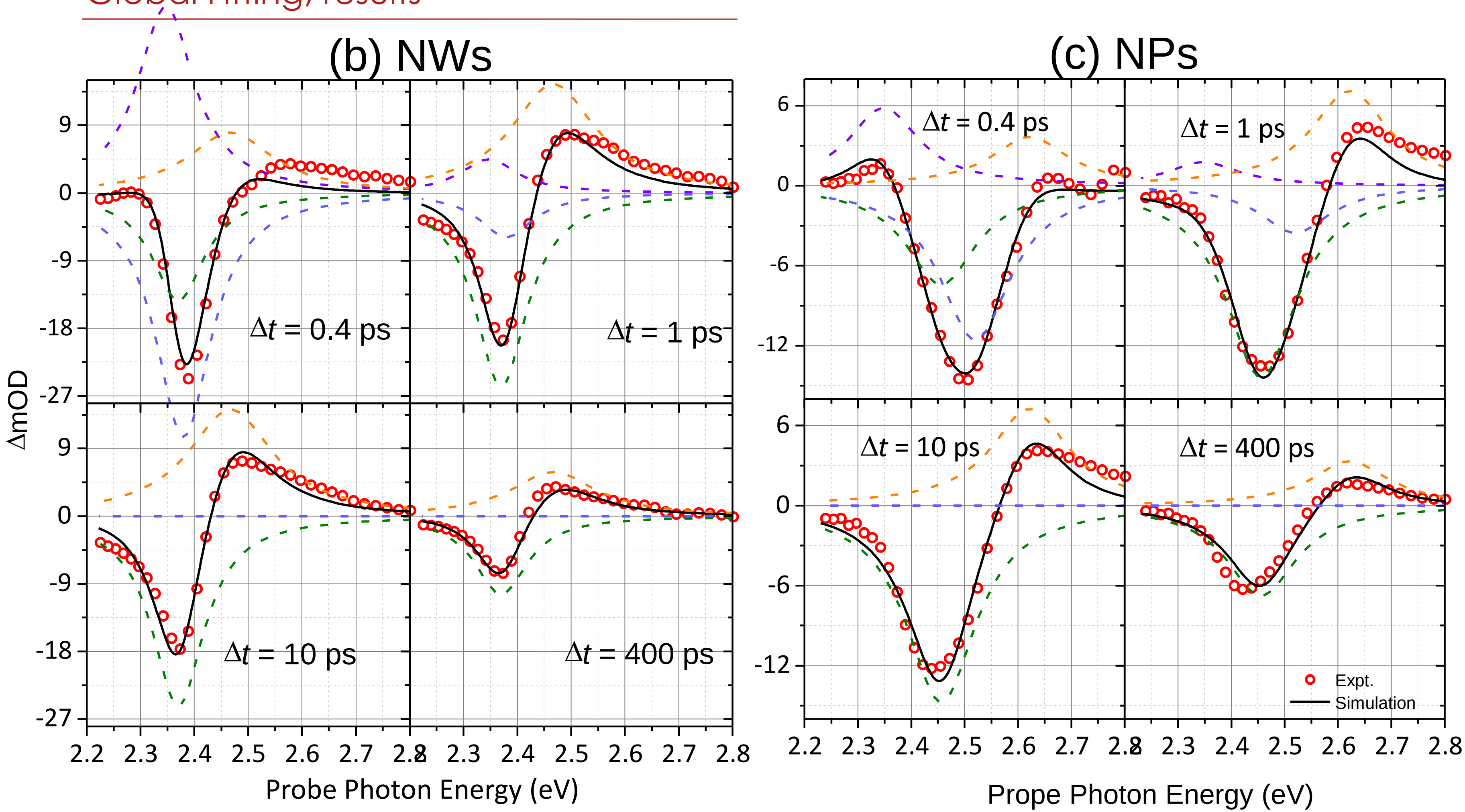
Instrument response function

(a) NCs



TA Spectra, Results

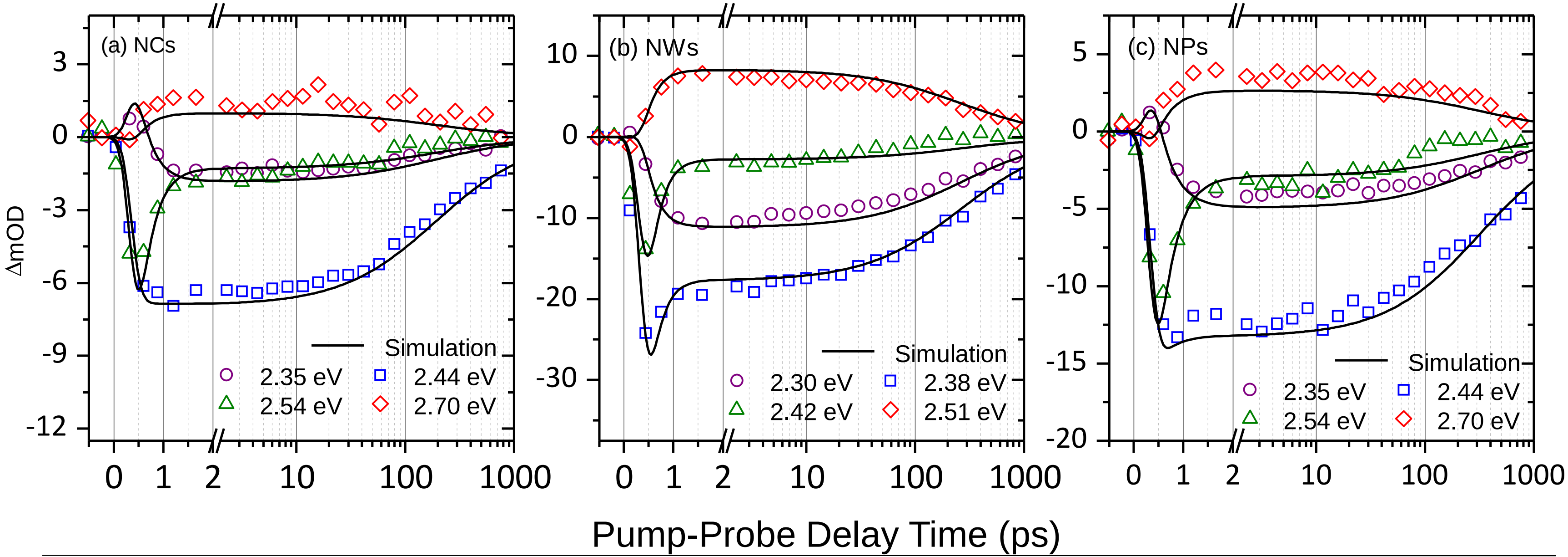
Global Fitting, results



TA Spectra, Results

Global Fitting results, time domain

	$h\nu_1$ (eV)	γ_1 (eV)	$h\nu_2$ (eV)	γ_2 (eV)	$h\nu_3$ (eV)	γ_3 (eV)	$h\nu_4$ (eV)	γ_4 (eV)	τ_c (ps)	$\tau_{1/2,r}$ (ps)
NCs	2.36	0.13	2.46	0.13	2.53	0.13	2.62	0.19	0.28	139
NWs	2.35	0.13	2.37	0.12	2.38	0.13	2.47	0.19	0.23	264
NPs	2.35	0.16	2.46	0.16	2.52	0.16	2.62	0.18	0.34	318



Conclusions

- TA spectra were collected for the three nanostructures: NCS, NWs and NPs. ***Sub-picosecond charge carrier cooling is observed.***
- Decay of the ta signals is best described by a ***second-order reaction dynamics*** and is attributed to ***non-geminate recombination*** of charge carriers.
- The effective rate constants of the NCs and NPs are linearly proportional to the density of the charge carriers with different linearity coefficients, while that of the NWs remains constant.
- Differences between recombination rates of the nanostructures suggest strong ***influence of the quantum confinement*** on the recombination processes.
- Charge carrier thermalization and recombination processes of perovskite nanostructures strongly dependent on their size, shape and morphology ***which can be utilized for improvement of power conversion efficiency.***

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Conn center for renewable energy - University of Louisville