Charge Transport in Perovskite Solar Cells Visualized using Ultrafast Microscopy

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Overview

- Background/Motivation
  - What is a hot carrier?
  - Transient absorption microscopy/spectroscopy
- Utilizing ultra fast microscopy to visualize carrier transport
  - Hot carrier diffusion
- Enhanced carrier diffusion via a hot phonon bottleneck
  - Slow down hot carrier cooling
- Future Work

Why Solar?

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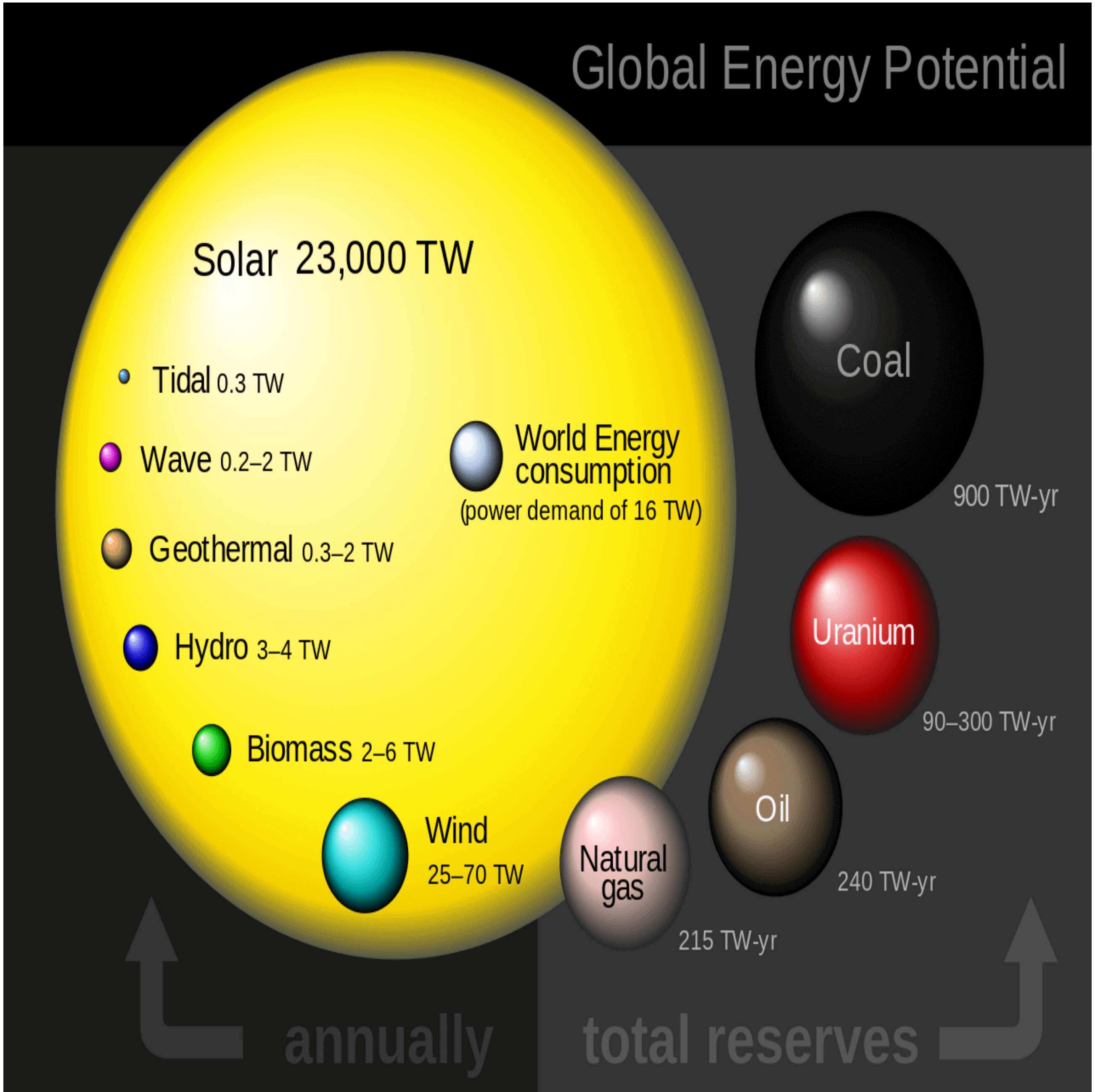
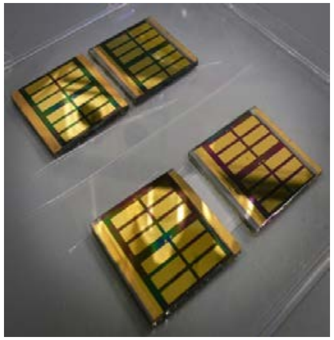


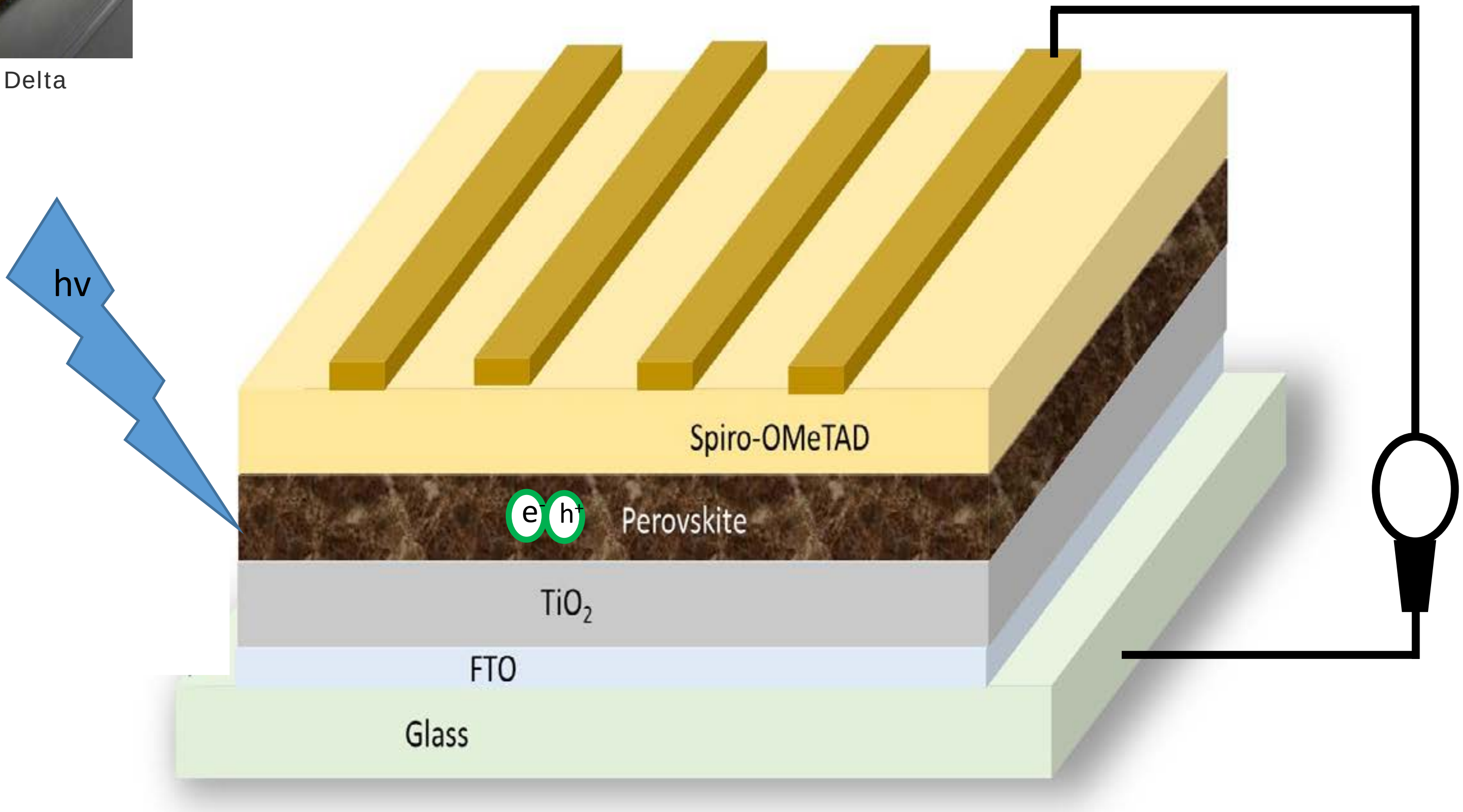
www.revolvesolar.com

How it works



Source: TU Delta

Exciton binding energy < kT at RT



- ~~Charge Separation~~
- Carrier Propagation
- Charge injection/Collection

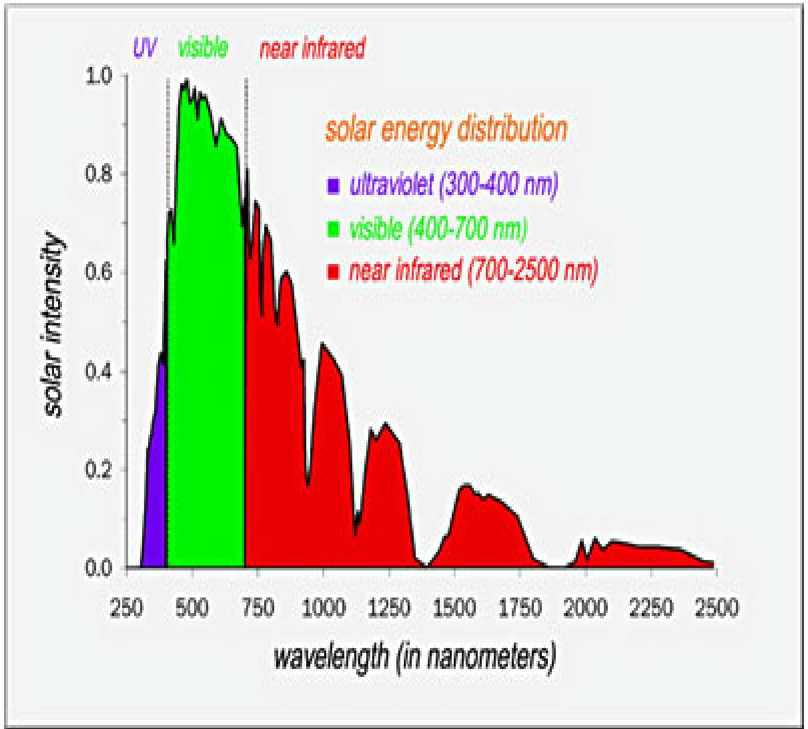
Adapted/modified from UW Clean Energy Institute

Why not?

- Why isn't the sun utilized more?
- Why aren't we making any changes?
- Why doesn't everyone use solar power? ...

Well… we are

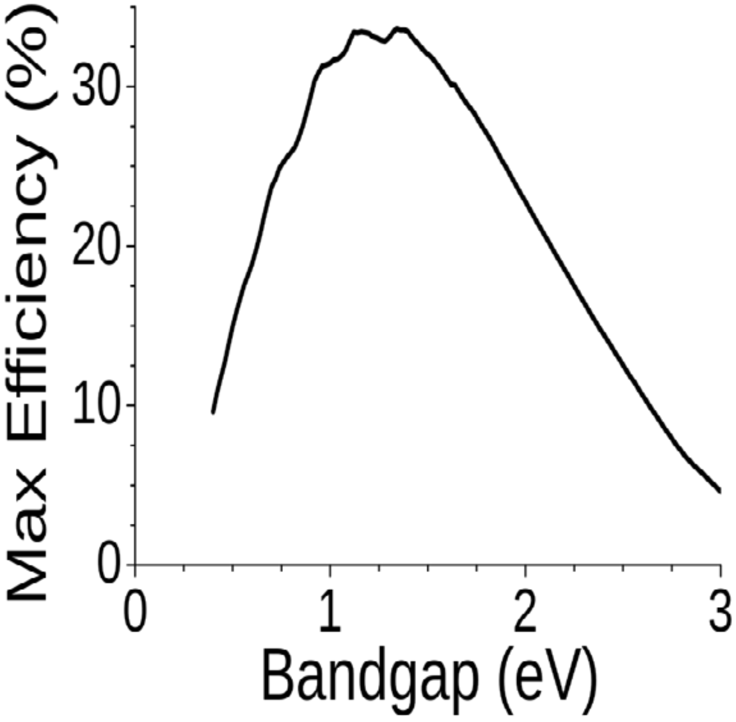
However…



- Highly inefficient => ~ 13-17% Power conversion efficiency
- Expensive to scale up => single crystalline silicon
- Broad spectrum => silicon band gap 1.1 eV (1127 nm)
- Shockley Limit

The Motive: Shockley–Queisser limit

- 1960's
- Maximum theoretical power conversion efficiency for a single junction cell to be 33%
- Losses due to
  - Non-radiative recombination
  - Thermalization
  - Spectral losses
  - Limited mobility



Journal of Applied Physics, Volume 32 (March 1961), pp. 510-519

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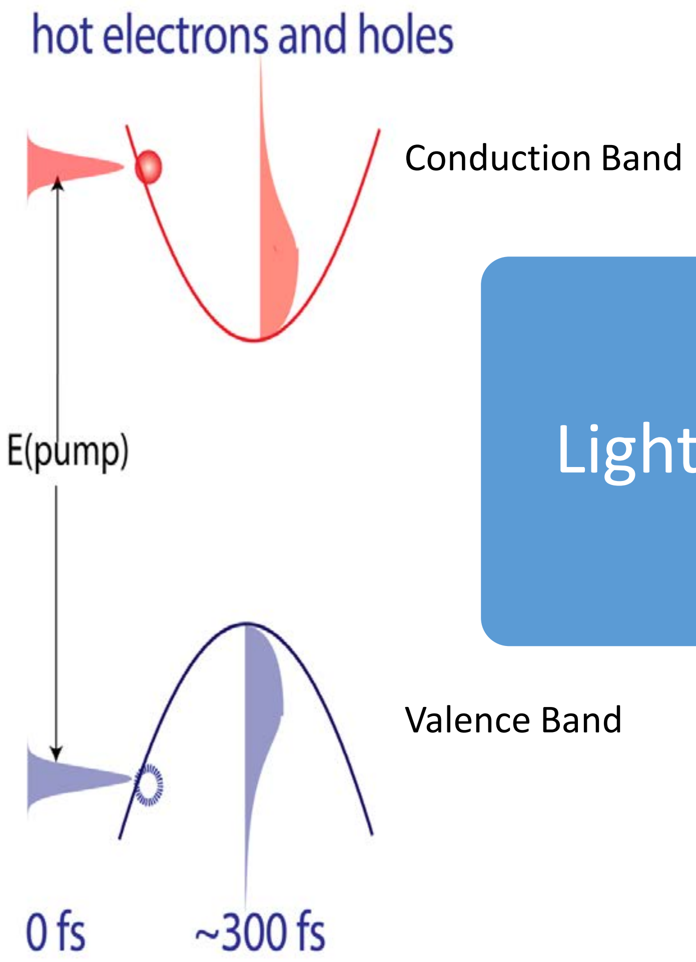
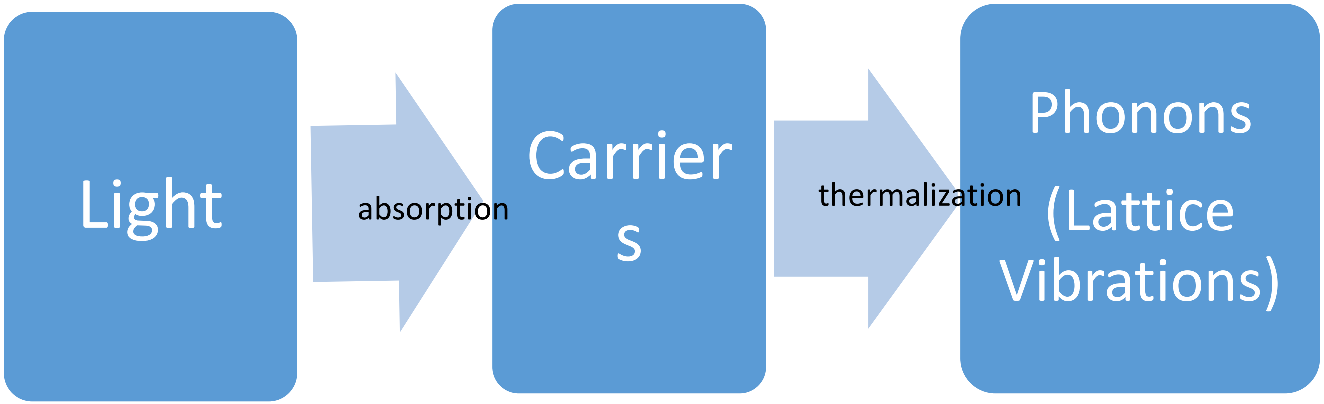
Exceeding the limit

- Tandem cells
- Photon up-conversion
- Hot-carrier extraction
- Singlet Fission

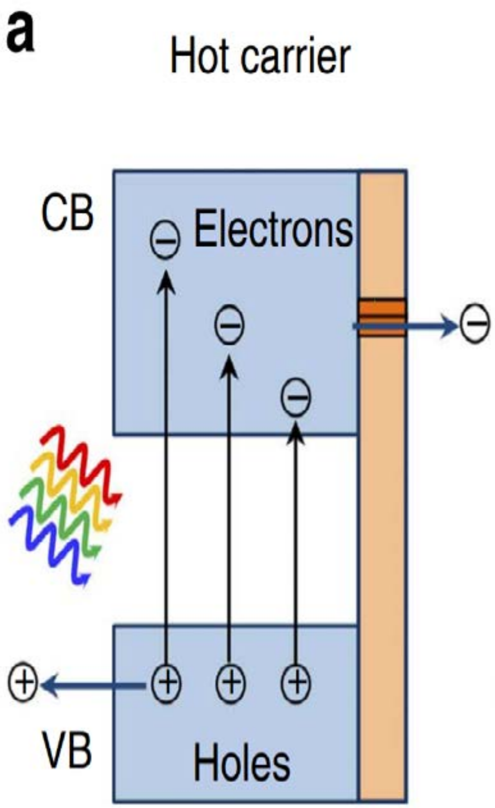
What is a Hot-Carrier





Hot Carrier Extraction

Hot carrier extraction via energy selective contacts



- Highly challenging
- Ultrafast thermalization of hot carriers
  - created by absorption of high-energy photons
- Thermalization leads to heat generation → efficiency loss
- ~ 70% PCE with hot carrier extraction

Saeed et al. Nature Comms. **5**, 4665 (2014)

Challenges of Hot Carrier Cell

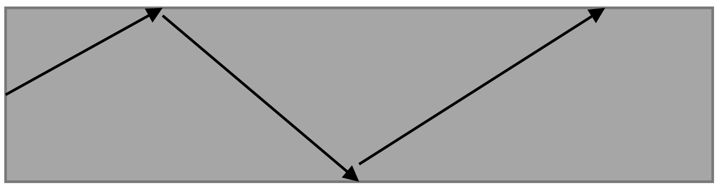
- Need an ideal material that:
  - Allows carriers to propagate further
  - While also living longer
    - Hot carriers in Si have short lifetimes (~100 fs)

- Ultrafast thermalization of hot carriers
  - created by absorption of high-energy photons

Checklist for hot carrier solar cell

- ❑ Lifetime
- ❑ Carrier Transport Velocity

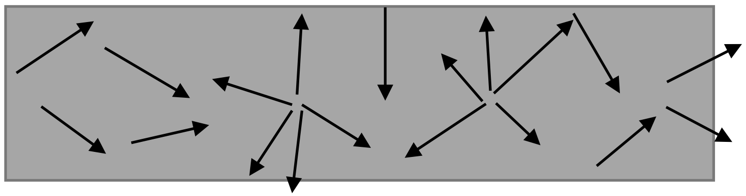
Ballistic vs. Diffusive Transport



Ballistic transport

- Specific trajectory
- Systematic/methodical

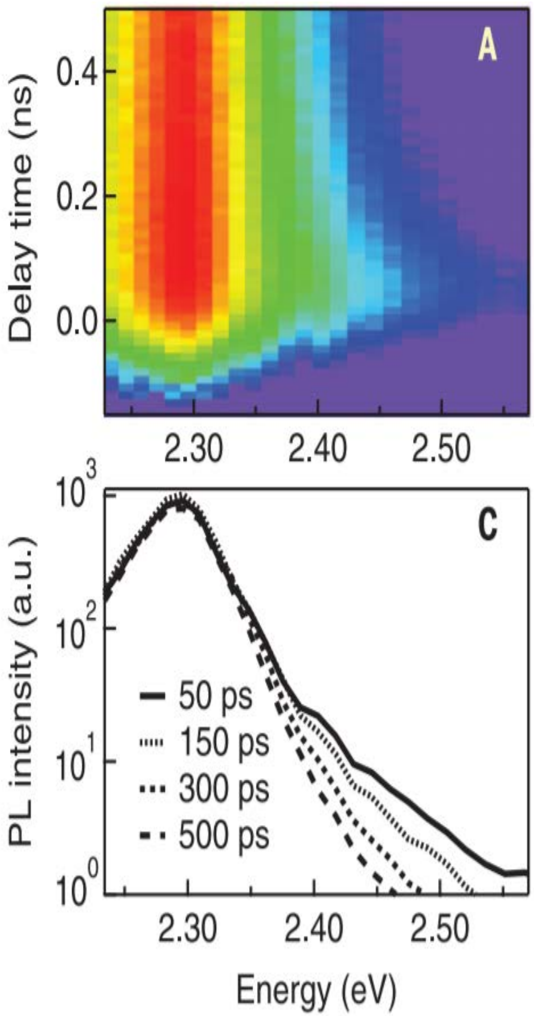
$$K_e = \frac{1}{2} m_{e(h)} v^2$$



Diffusive transport

- Random walk
- Phonon scattering

Potential Candidate: Perovskite

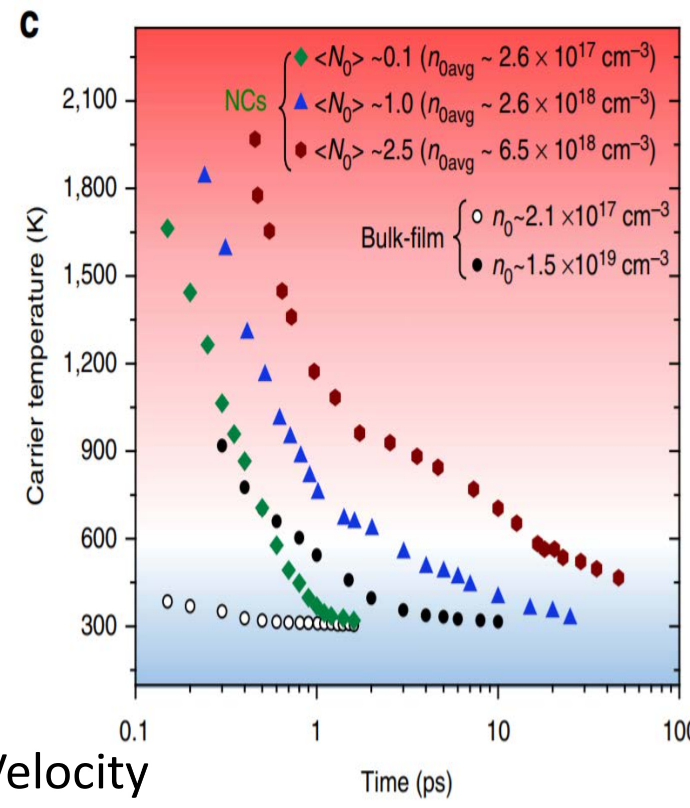


- Slow hot carrier cooling has been shown
  - Takes place on ps time scale (compared to fs)

- Potential candidate for hot carrier solar cell

Checklist for hot carrier solar cell

- ☒ Lifetime
- ☐ Carrier Transport Velocity

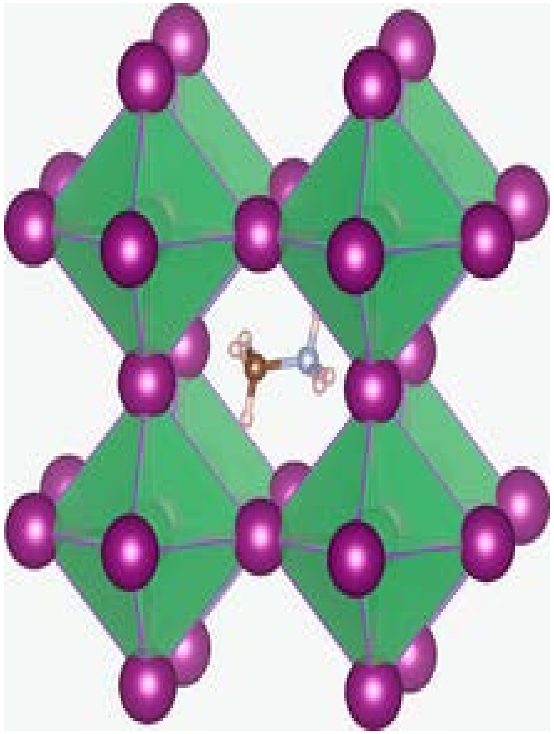


Li et al. NATURE COMMUNICATIONS | MAY 2017 8:14350

Zhu et al. SCIENCE 23 SEPTEMBER 2016 • VOL 353 ISSUE 6306

Perovskite Solar Cells

ABX_3 most commonly Methylammonium lead iodide



A – is the organic cation
- Methyl ammonium ($CH_3NH_3^+$)
- Formamidinium ($CH(NH_2)_2I$)
- Cs^+

B – is the inorganic cation
- Pb
- Sn

X – is the tri-halide
- Cl
- Br
- I
- mixture

Walsh et al. NATURE COMMUNICATIONS | 6:7497 June 2015

Preparing a Perovskite Thin Film

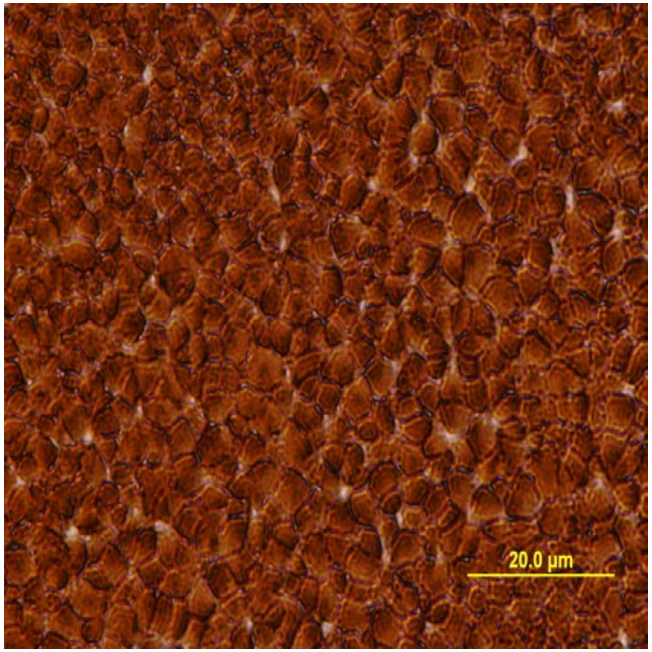
~ 3:1 MAI to PbI_2 (or Cl_2)

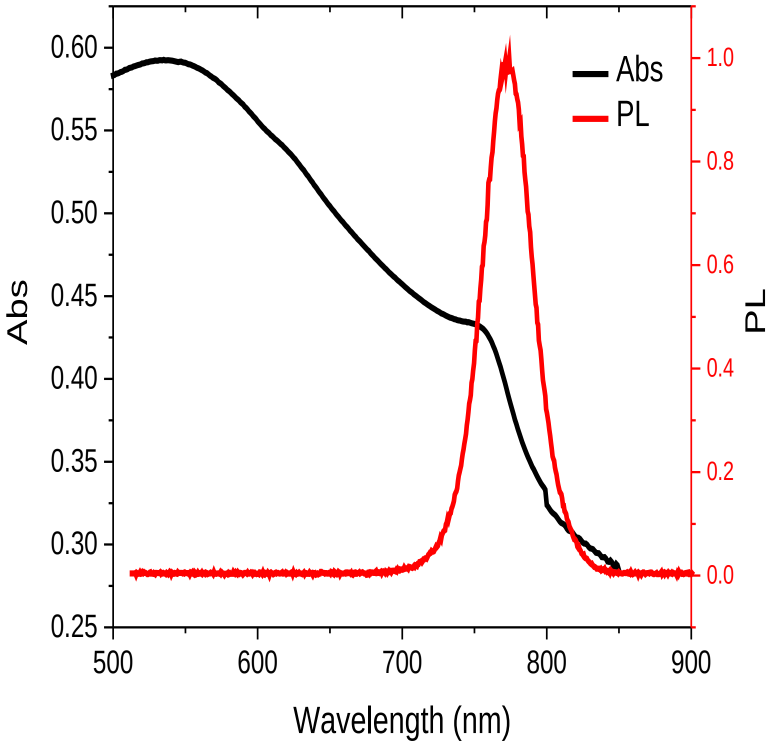
(Filter)

Spin-coat*

Anneal (100 °C)

Seal





*Deposited on a solvent/plasma cleaned substrate

Perovskite Solar Cells

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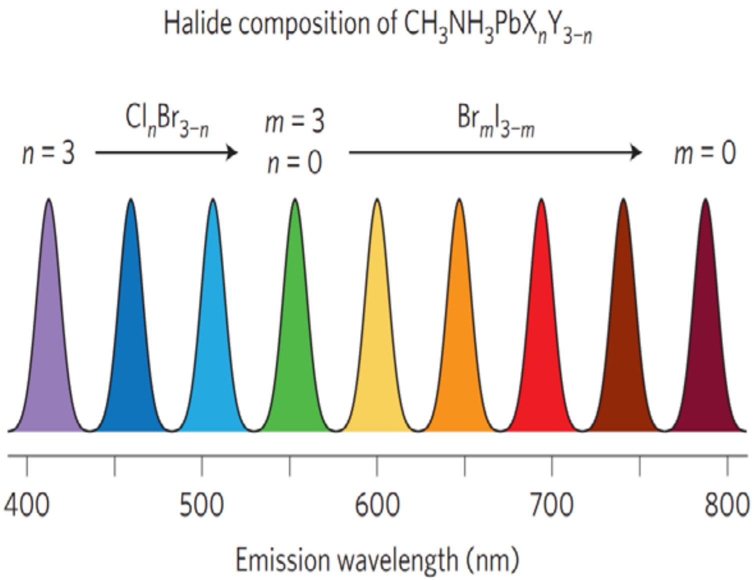
- CHEAP (~ $80 to coat 1000 sq meters at 200 nm thickness)
- Absorption Spectrum (whole visible range)
- Tunable bandgap
- Ease of production
  - "One pot" preparation
  - Spin coating
  - Vapor deposition



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Nature Photonics **10**,295–302 (2016)

Perovskite Solar Cells

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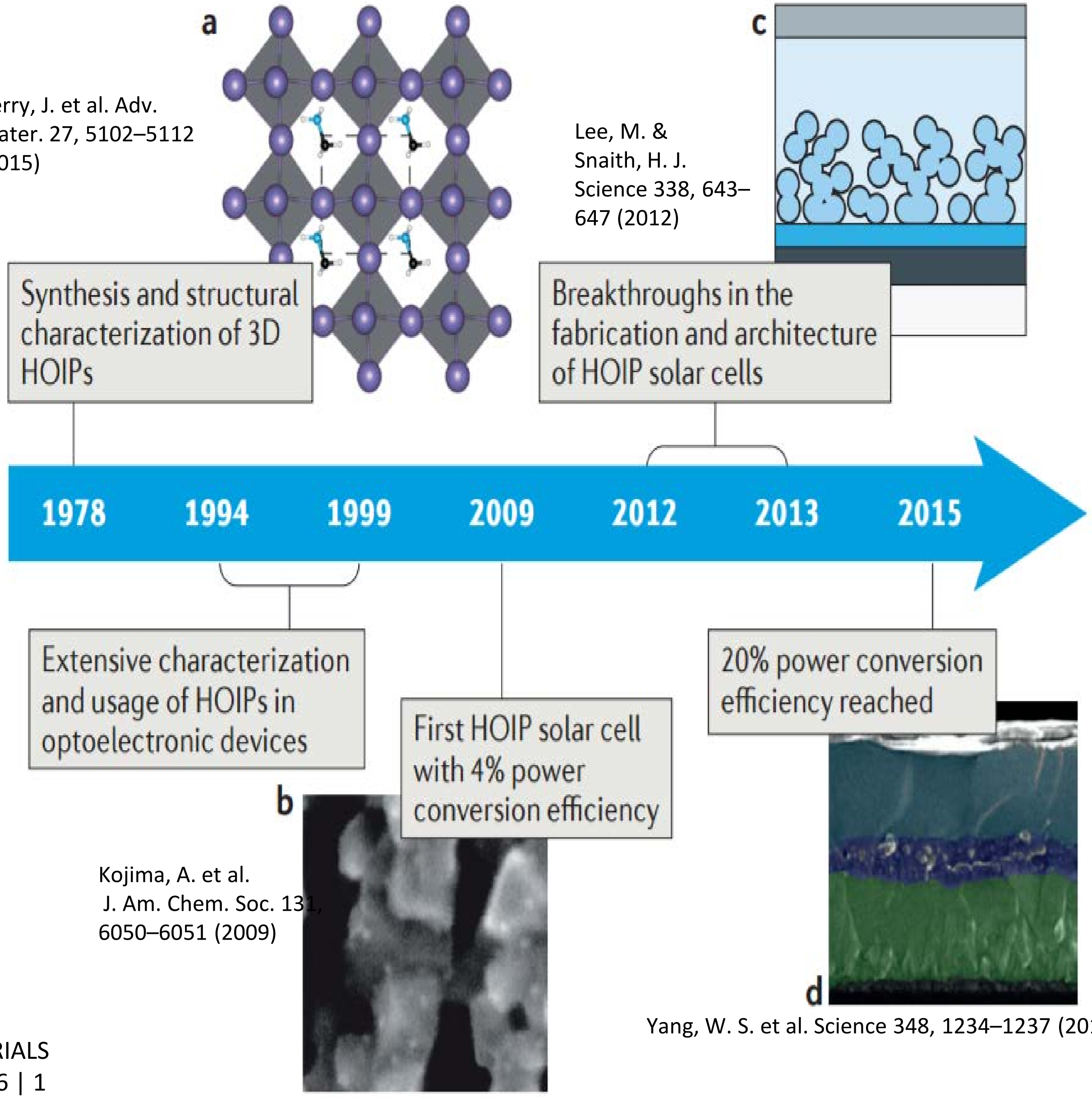

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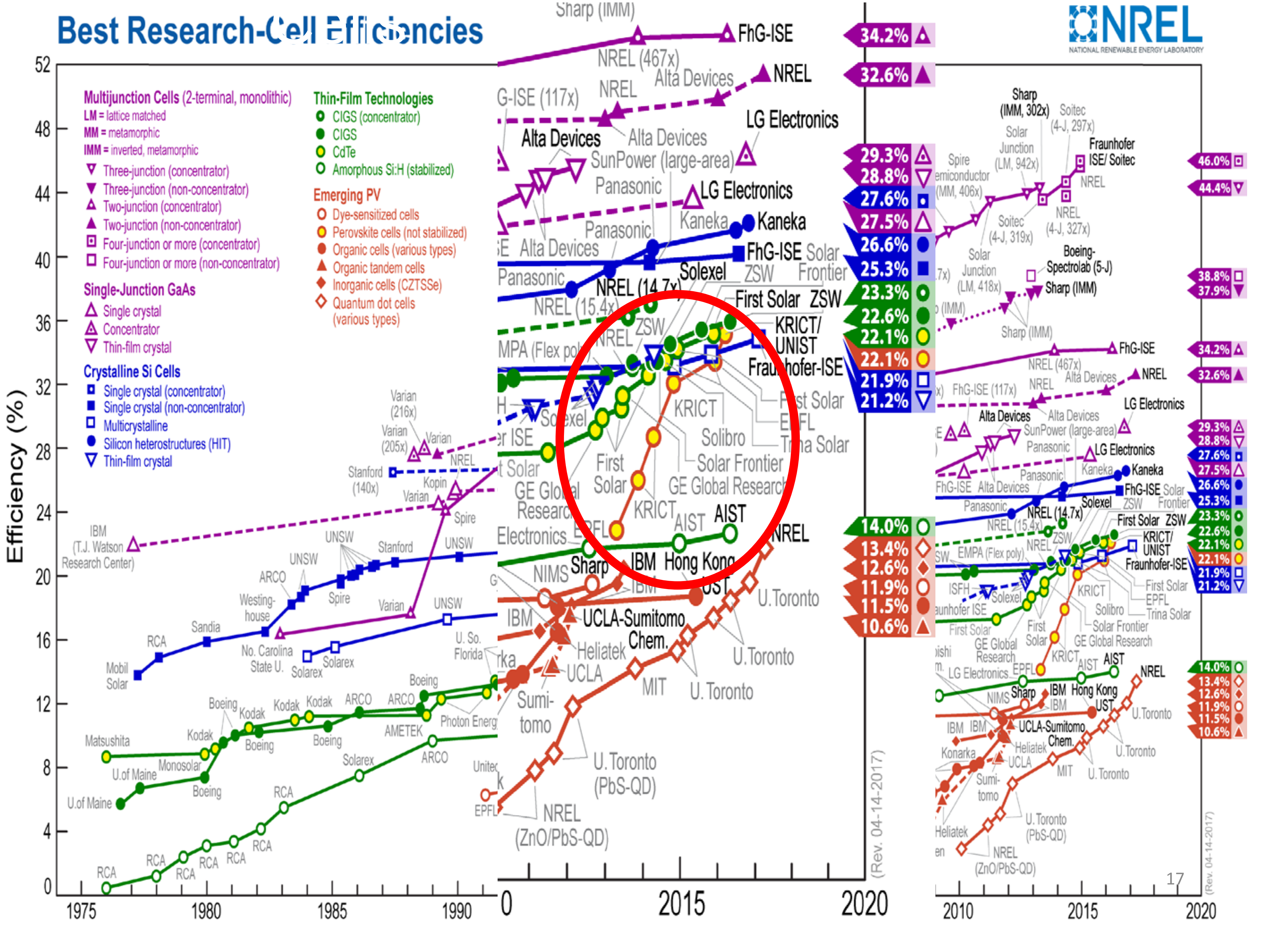
Brenner et al.
NATURE REVIEWS | MATERIALS
VOLUME 1 | JANUARY 2016 | 1

Best Performing Solar



The Technique

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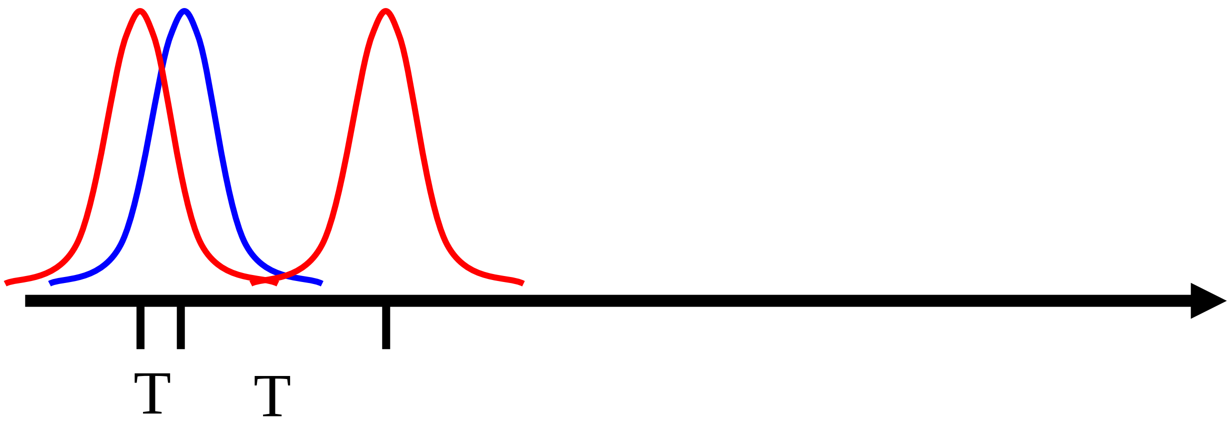
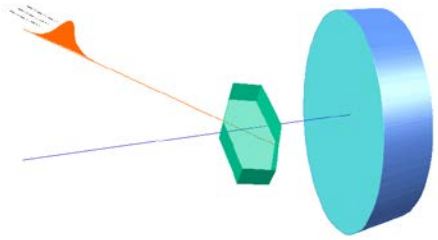
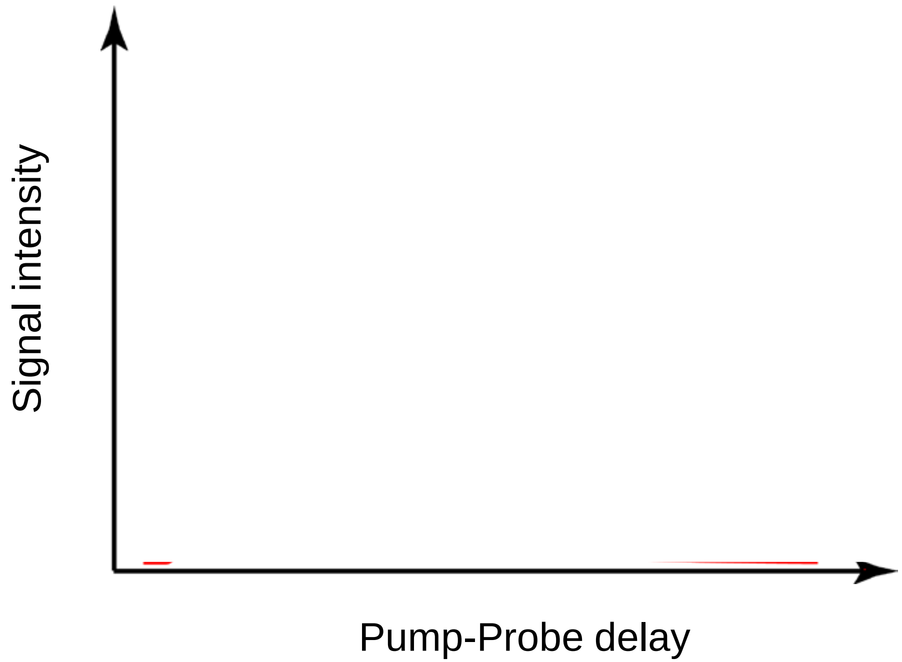
A fast “motion picture” to detect the reaction

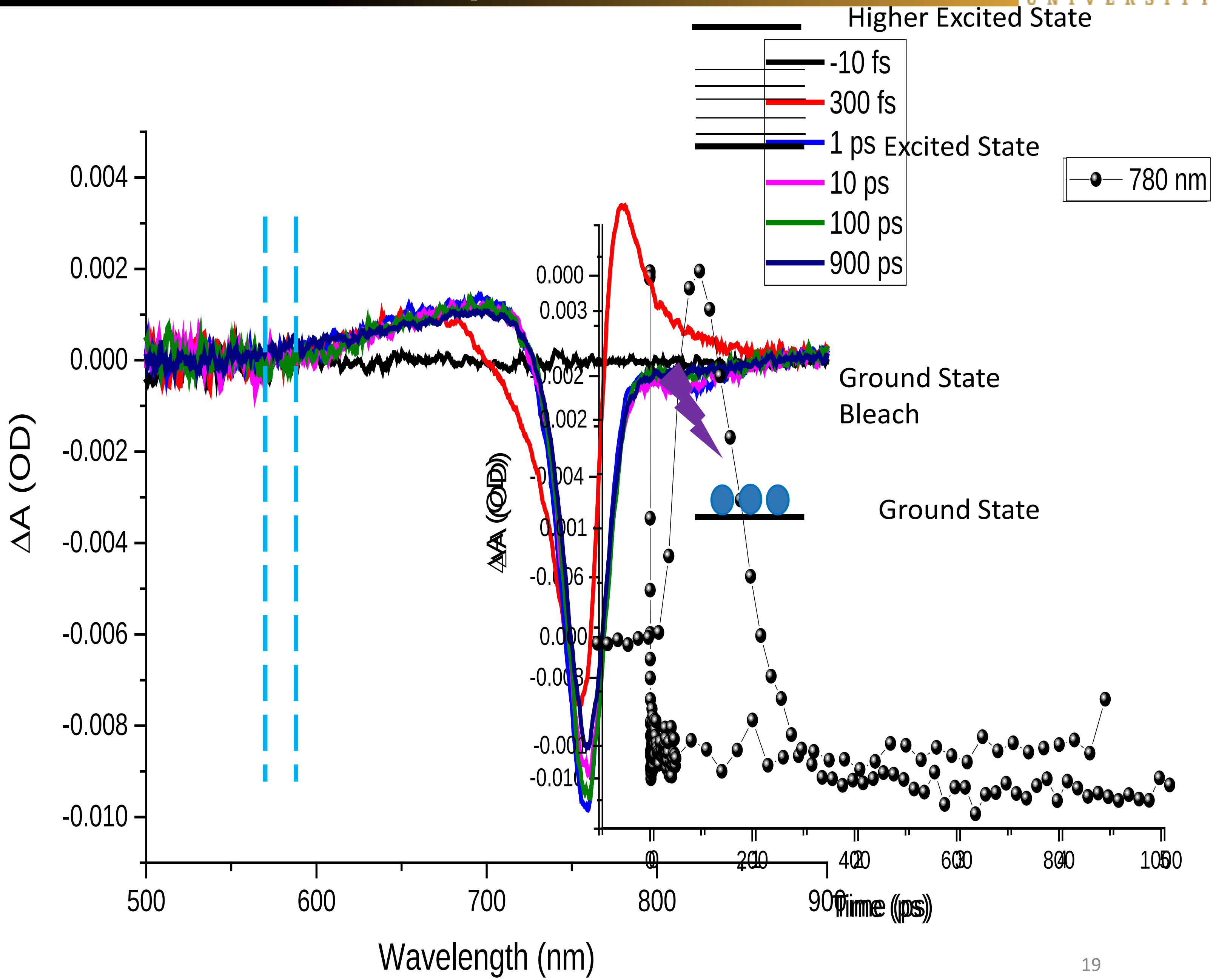






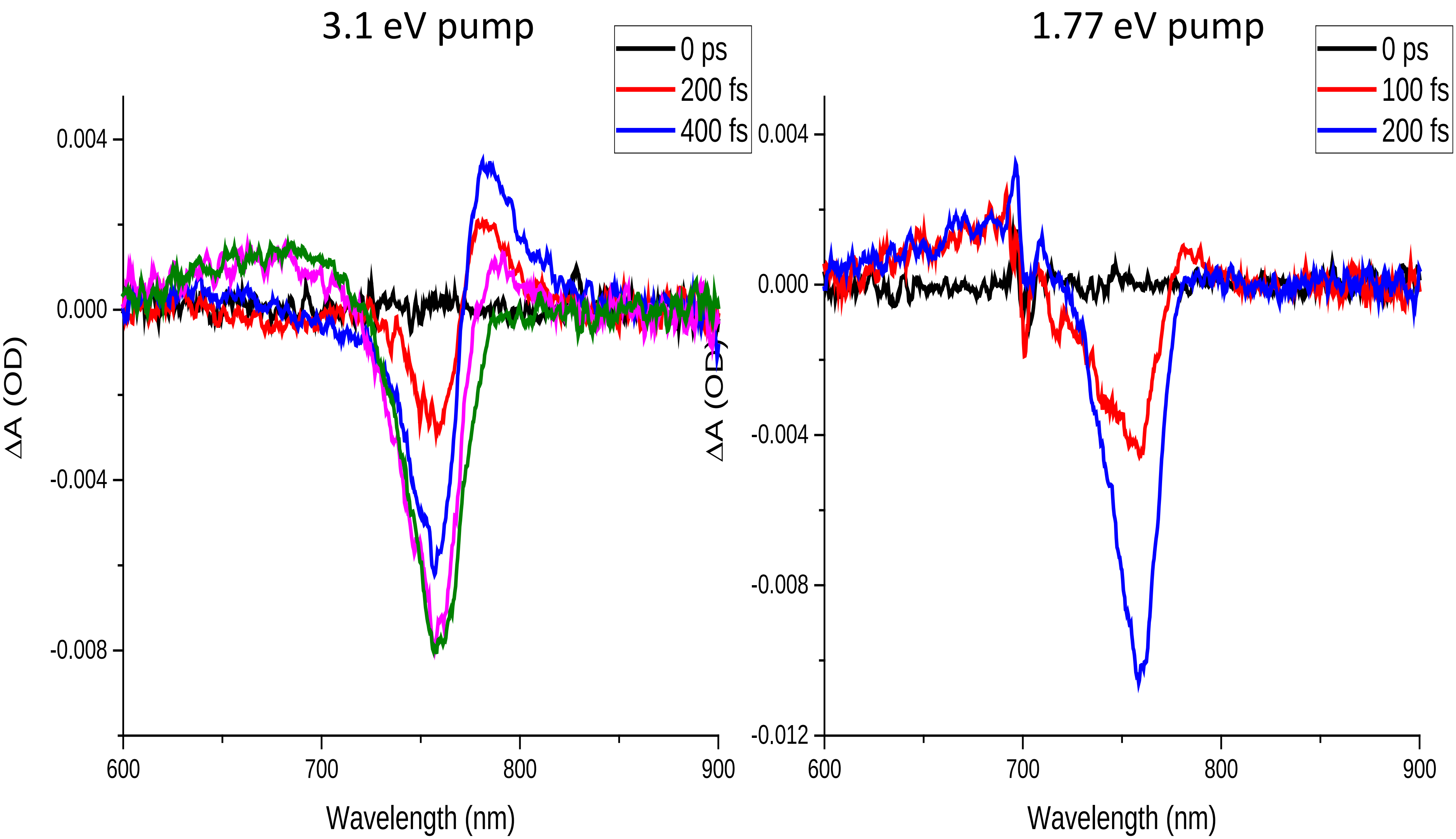
A UV-Vis of the excited states

TA Spectrum

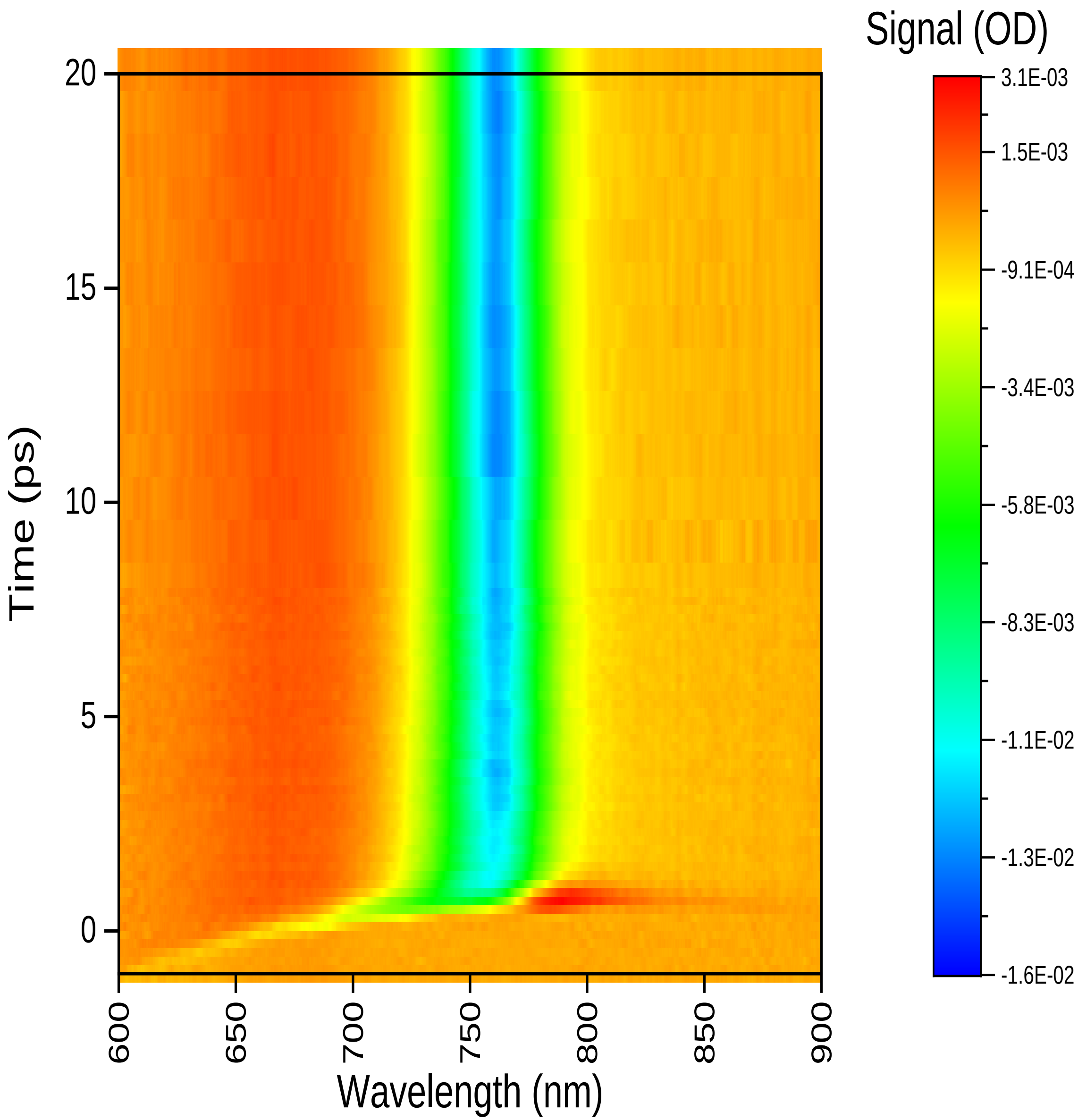


Higher Excited State
-10 fs
300 fs
1 ps
10 ps
100 ps
900 ps
Excited State
780 nm
Ground State Bleach
Ground State
ΔA (OD)
Wavelength (nm)
Time (ps)

3.1 eV vs 1.77 eV Excitation



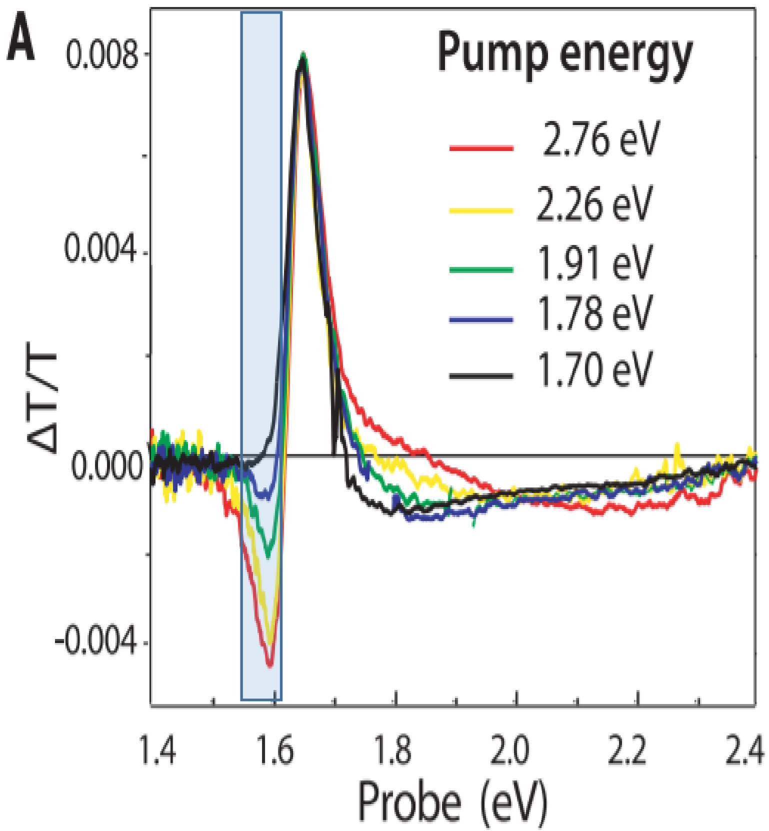
TA Spectrum

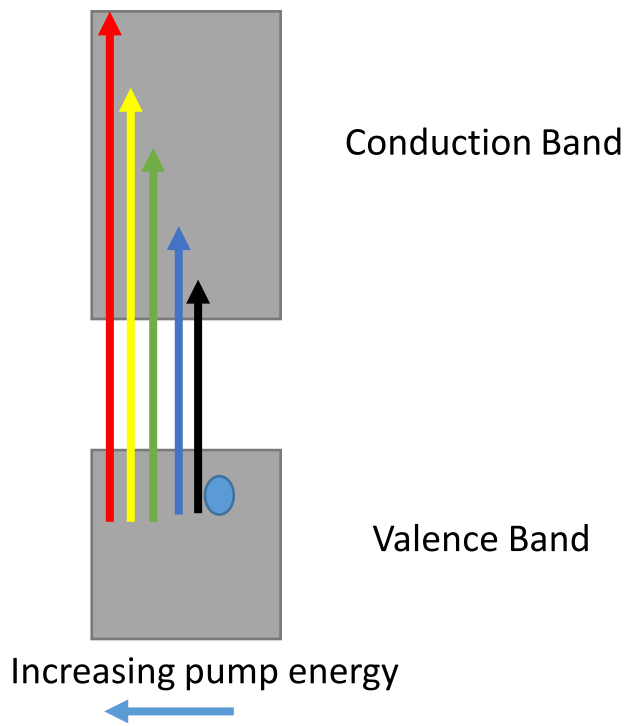


Our TA signal gets compiled into a matrix

Which can allow us to extract out a spectrum at a specific time
Or a decay at a specific wavelength

Pump energy dependence



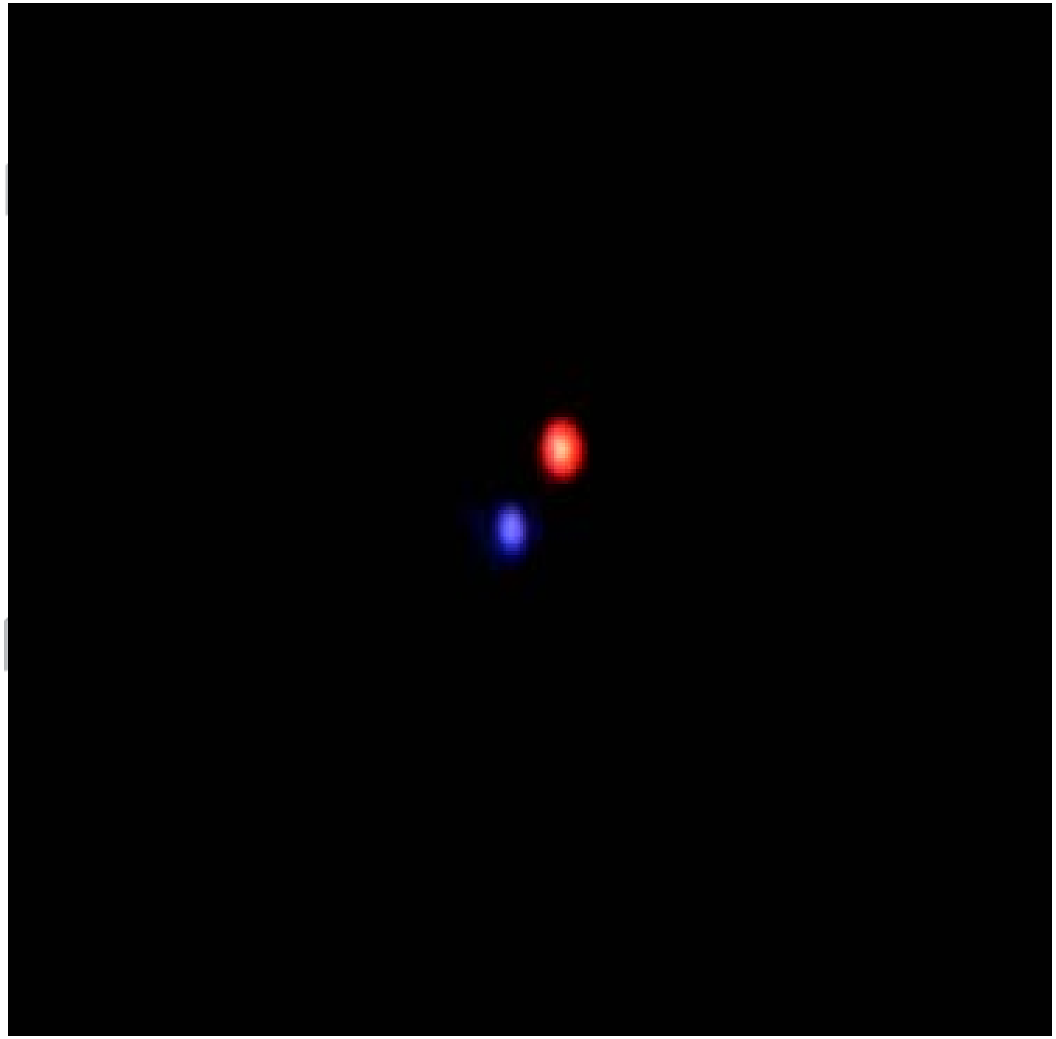


Spectral signatures can be determined

Hot carrier spectral signature at 1.58 eV

Science 356 (6333), 59-62

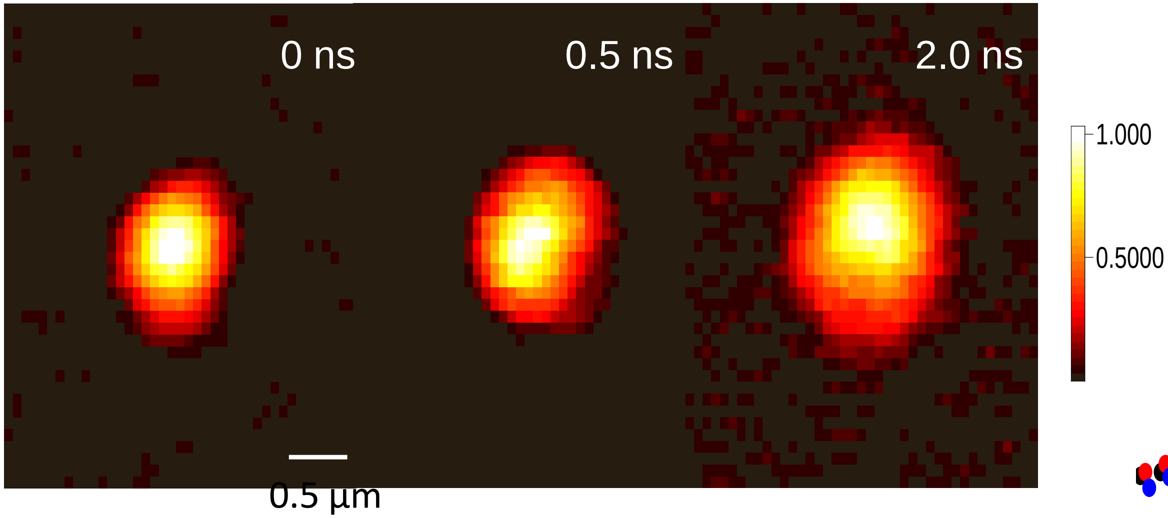
Transient Absorption Microscopy (TAM) setup

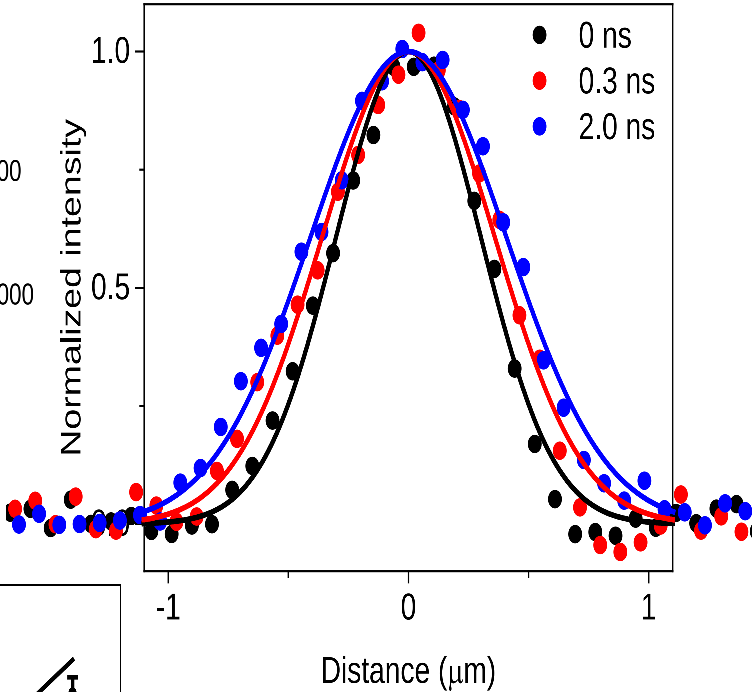


Fixing the pump
Scanning the probe

Temporal resolution: 200 fs
Spatial precision: 50 nm

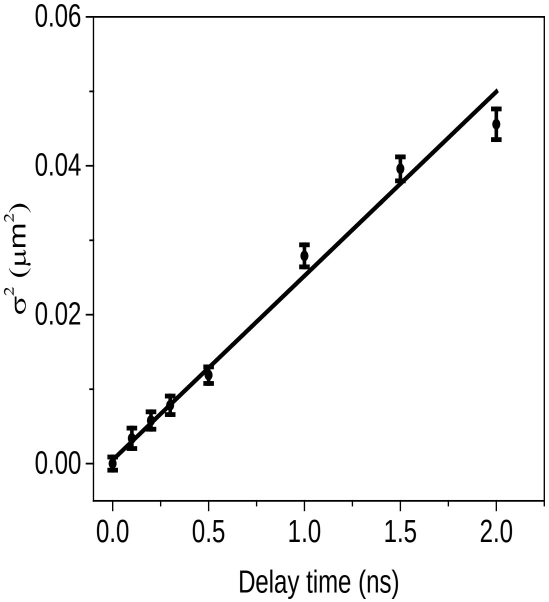
TAM data



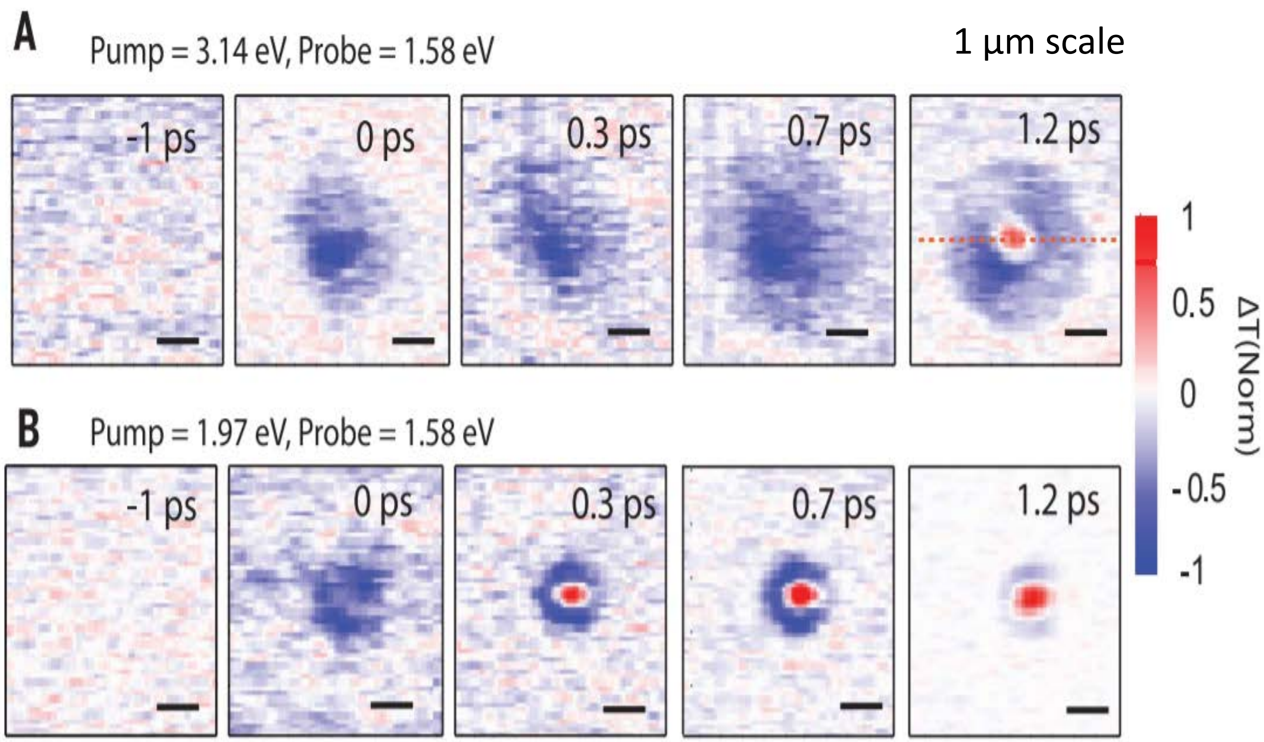


$$\frac{\partial n(x,y,t)}{\partial t} = D\left[\frac{\partial^2 n(x,y,t)}{\partial x^2} + \frac{\partial^2 n(x,y,t)}{\partial y^2}\right]$$

$$\sigma^2_{t,x} = \sigma^2_{0,x} + L^2 = \sigma^2_{0,x} + 2Dt$$



Hot Carrier Transport



- Ballistic velocity of the carriers can be calculated

$$K_e = \frac{1}{2} m_{e(h)} v^2$$

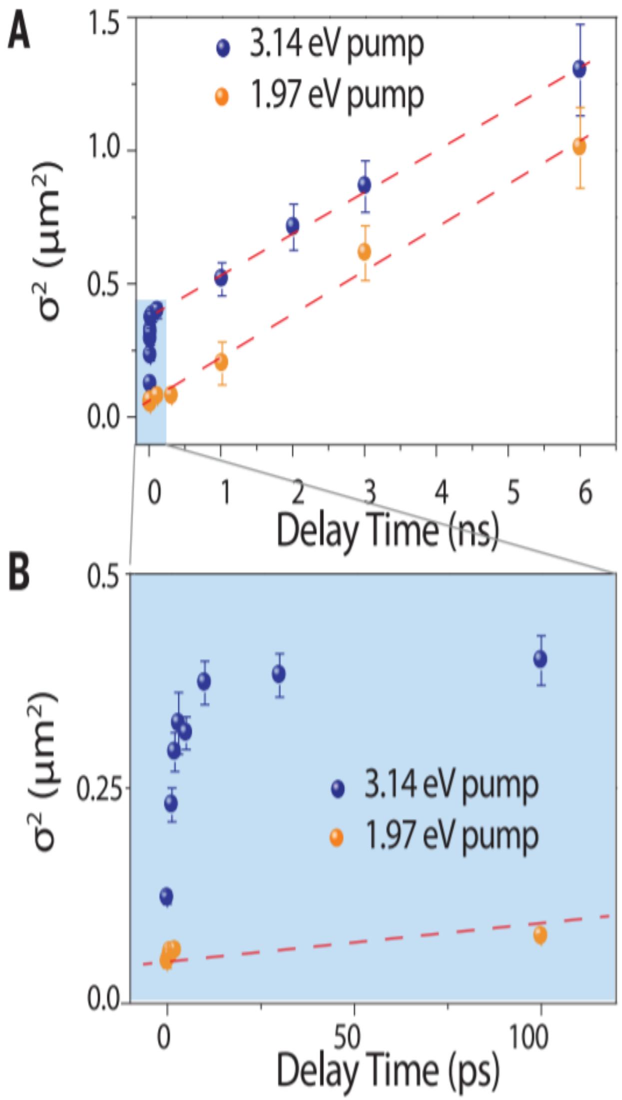
- Effective mass ~ 0.2 m_0
- ~1.6 x 10^6 m/s for 400 nm excitation (theoretical)
- From TAM image: the width expansion gave a velocity of 230 nm/300 fs

  = 0.8 x 10^6 m/s

Science 356 (6333), 59-62

m_0 = 9.11 x 10^{-31} kg

Transport Regimes



- Identical diffusion coefficients on long time scales (> 100 ps)
  - D ~ 0.7 cm^2s^{-1} (@ equilibrium)
  - 450 cm^2s^{-1} (@ 1 ps)

$$\frac{\partial n(x,y,t)}{\partial t} = D\left[\frac{\partial^2 n(x,y,t)}{\partial x^2} + \frac{\partial^2 n(x,y,t)}{\partial y^2}\right]$$

$$\sigma^2_{t,x} = \sigma^2_{0,x} + L^2 = \sigma^2_{0,x} + 2Dt$$

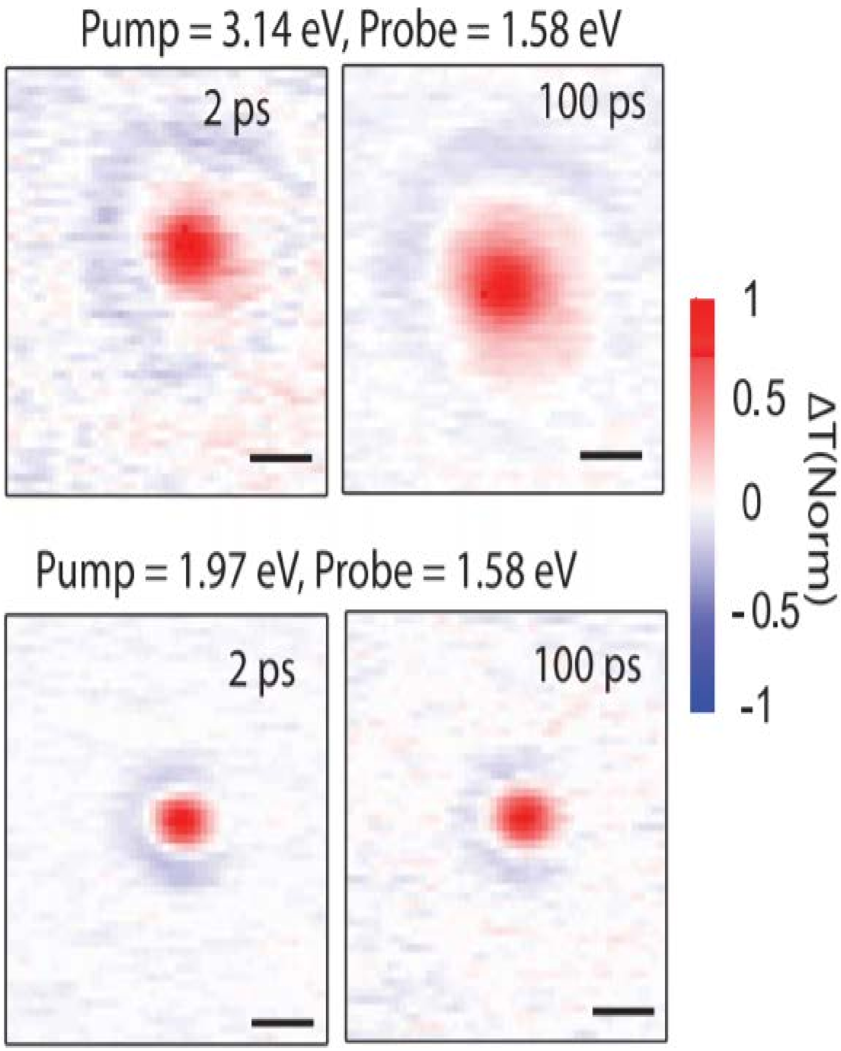
- Hot carriers are seen early time

- Non equilibrium transport that persists over 10's of ps (and ~600 nm)

- Hot electrons are diffusing much quicker

Science 356 (6333), 59-62

Non-equilibrium Transport

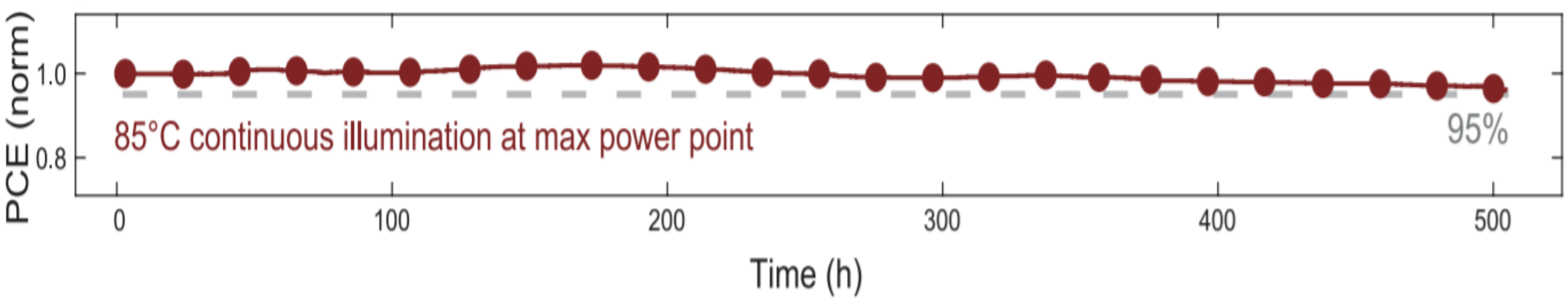


- Comparison between 2 ps and 100 ps time delay
  - At different pump energy
- Higher kinetic energy with hot electrons

Science 356 (6333), 59-62

Enhancing carrier transport

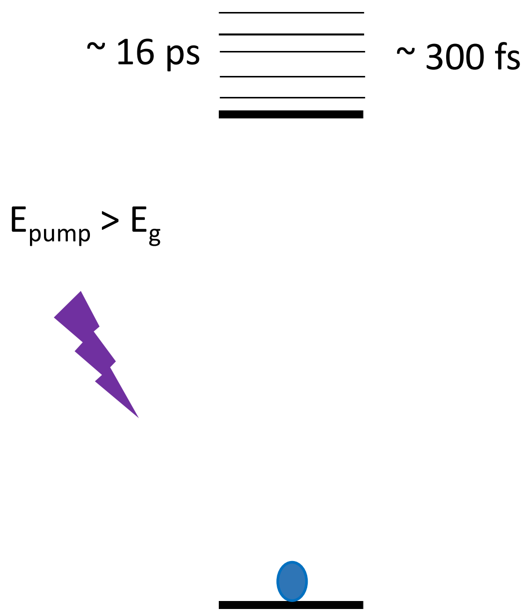
- We chose a special blend of perovskite
  - Provided from MIT
- Has shown to be a champion solar cell performer (~ 22% PCE)
- Increased thermal stabilization



Saliba et al. Science 354 (6309), 206-209

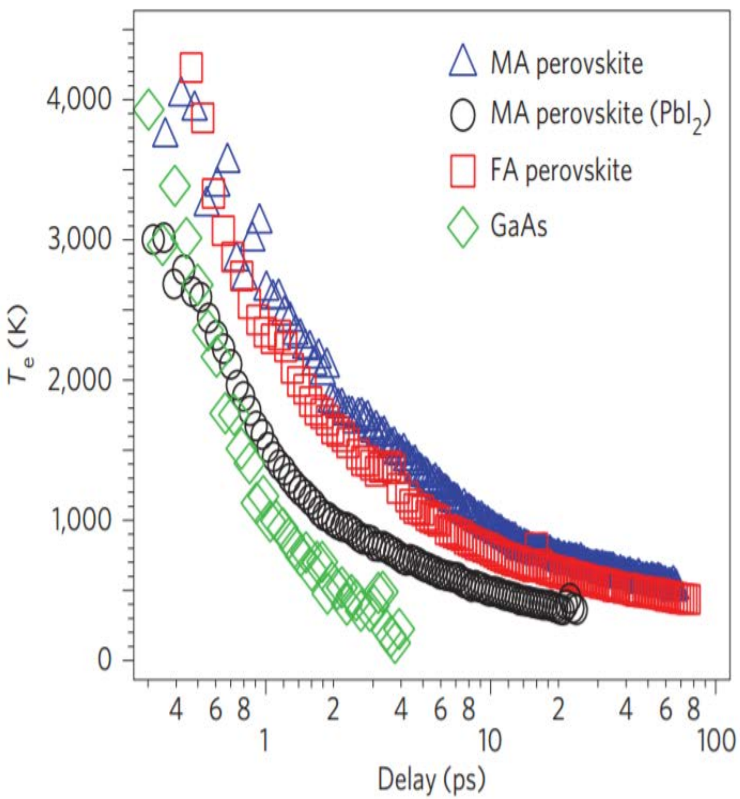
Hot Phonon Effect

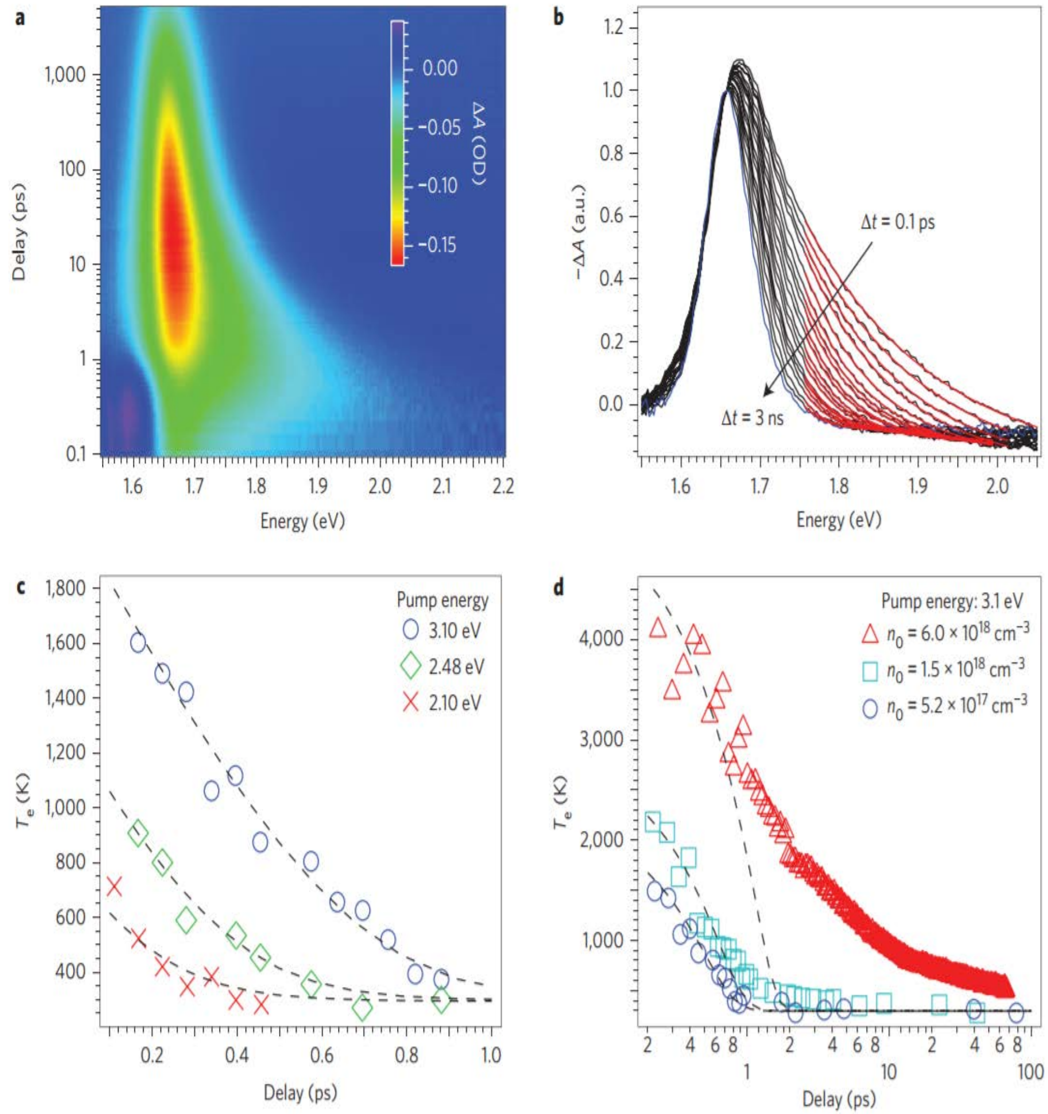
Analogy:
Hot Bathtub



Additional cooling step due to hot phonon

Hot Phonon Effect





$$\Delta A(\hbar\omega) = -A_0(\hbar\omega)\exp\left(\frac{\hbar\omega}{k_B T_e}\right)$$

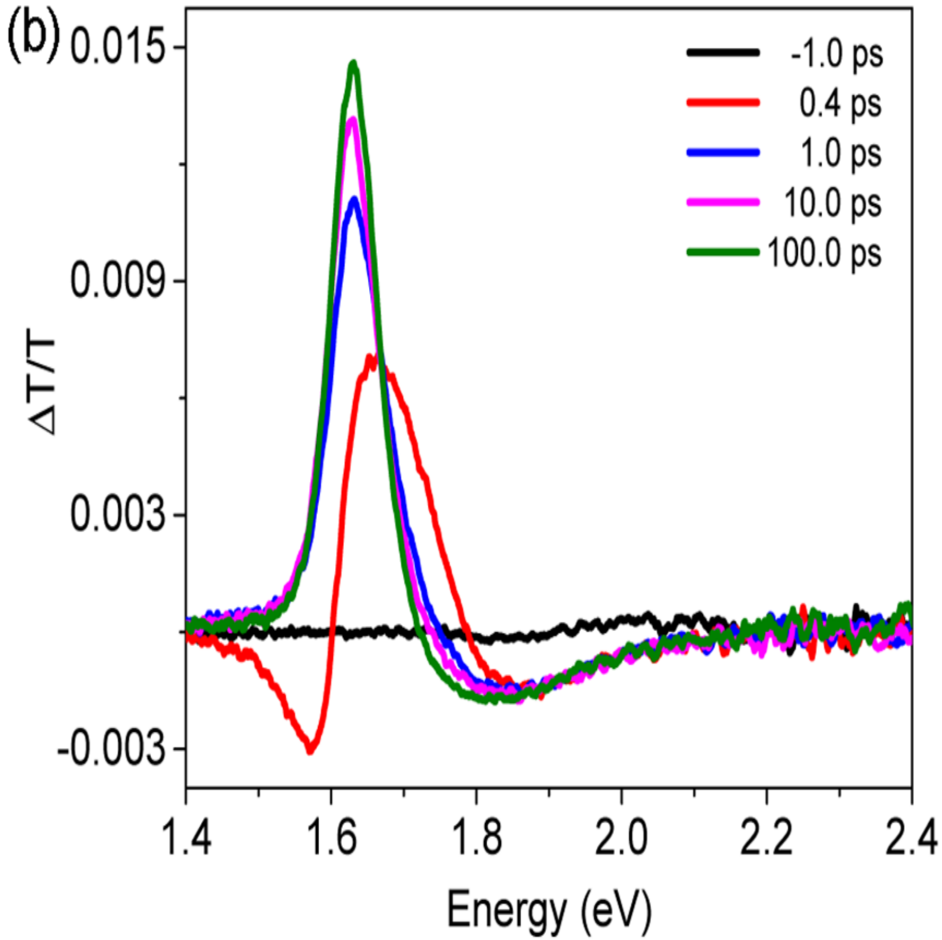
$\Delta A(\hbar\omega)$ is the high energy tail of the bleach

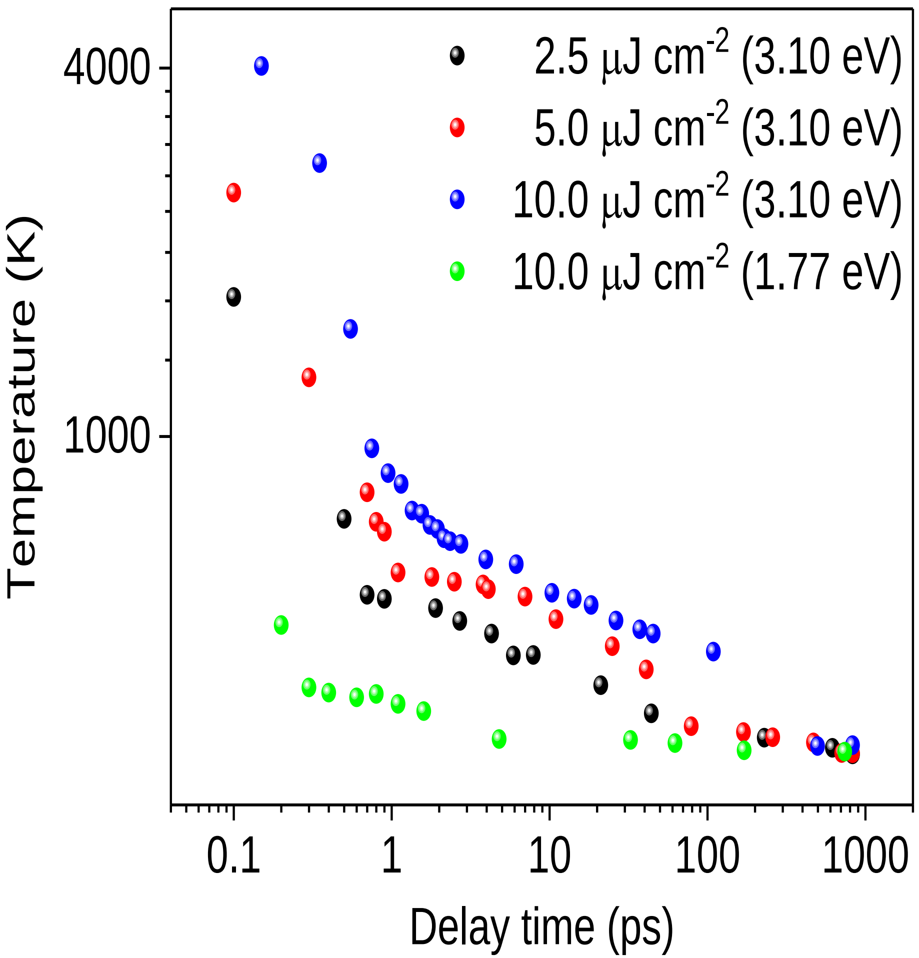
Beard et al. NATURE PHOTONICS | VOL 10 | JANUARY 2016

Hot phonon benefit

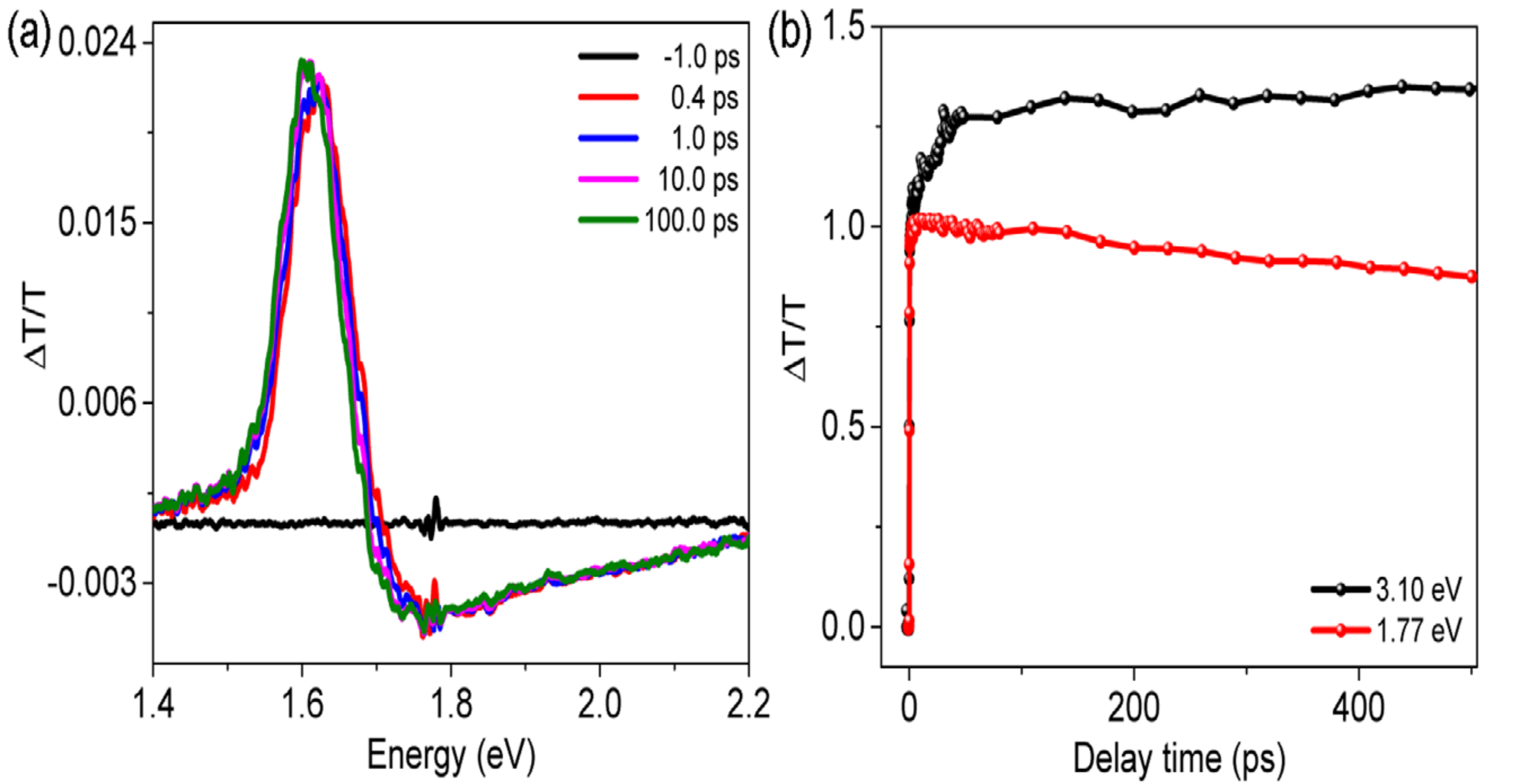
- Excess energy → can be distributed to the lattice in form of phonon
  - Lattice vibrations
- Hot phonon bottle neck can potentially increase the lifetime of hot carriers
  - Slow down the cooling of hot carriers
- Longer lived hot carriers → can diffuse further → collected
  - PCE > 33%?

Observed hot phonon bottleneck

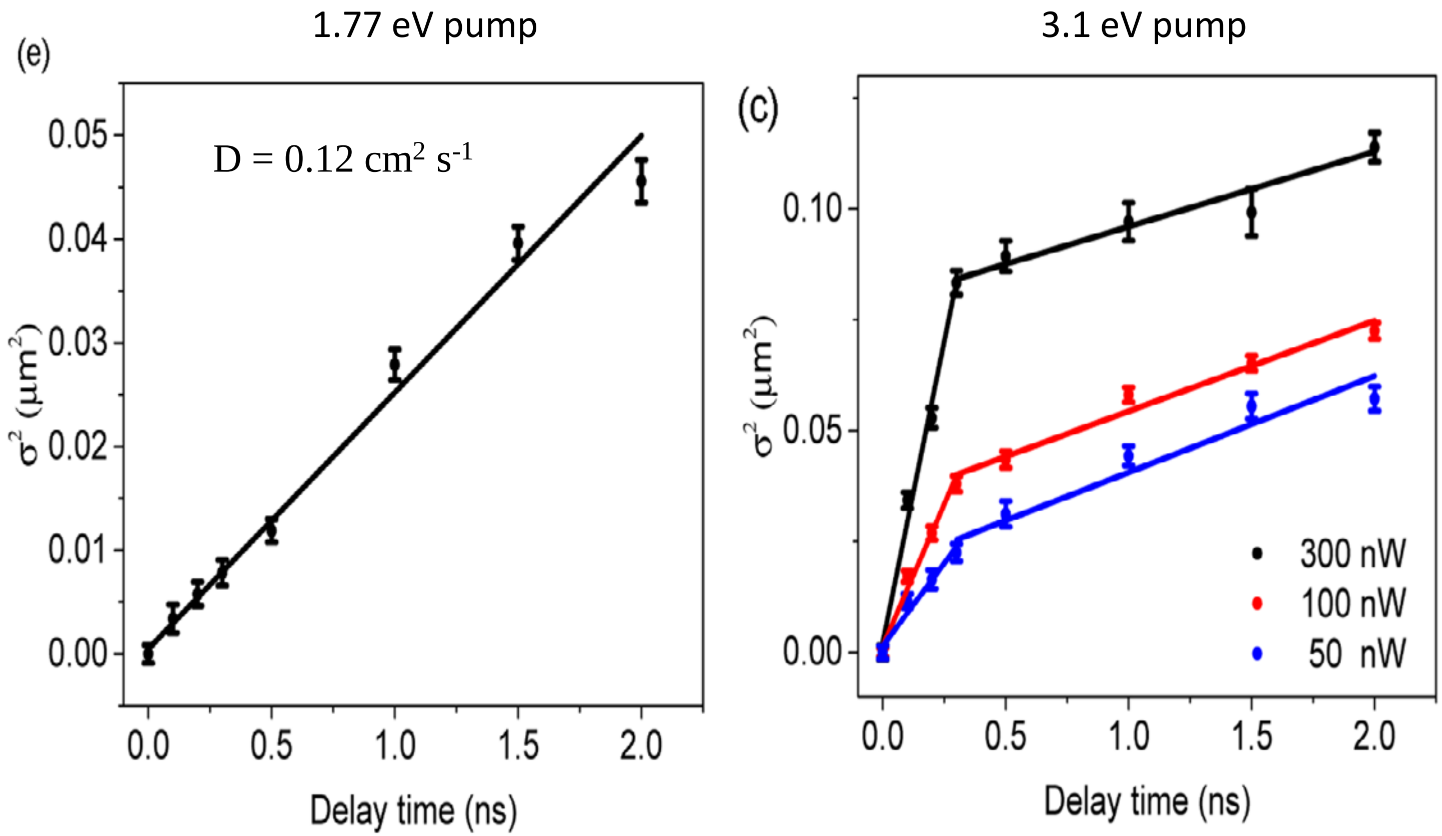




Excitation near band-edge



1.77eV vs 3.1 eV excitation



(First 300 ps) D = 0.37, 0.64 and 1.36 $cm^2\ s^{-1}$
(Later time) D = 0.10, 0.10 and 0.08 $cm^2\ s^{-1}$

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Conclusions

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- Direct visualization of hot carrier transport in perovskite thin films via ultrafast microscopy
  - Quasiballistic hot carrier transport
- Three distinctive regimes:
  - Quasiballisitic transport ~ 230 nm transport
  - Nonequilibrium transport ~ 10s of ps and ~ 600 nm transport
  - Diffusive transport limit (0.7 cm^2s^{-1})
- Observe additional hot carrier cooling step in Rb/Cs incorporated samples
  - Enhanced carrier transport (0.12 cm^2s^{-1} → 1.36 cm^2s^{-1})
  - Hot phonon bottleneck
  - Increasing diffusion constant → PCE?

Future Work

- Elucidate the cation effect in hybrid perovskite (Rb series vs Cs series)

- Unravel the surface/morphological effects on carrier diffusion

- Role of grain boundaries (carrier mobility/carrier lifetime) in polycrystalline perovskite films

Acknowledgments

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- Collaborator
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