Hot Carrier Dynamics in Bulk and 2D Perovskites

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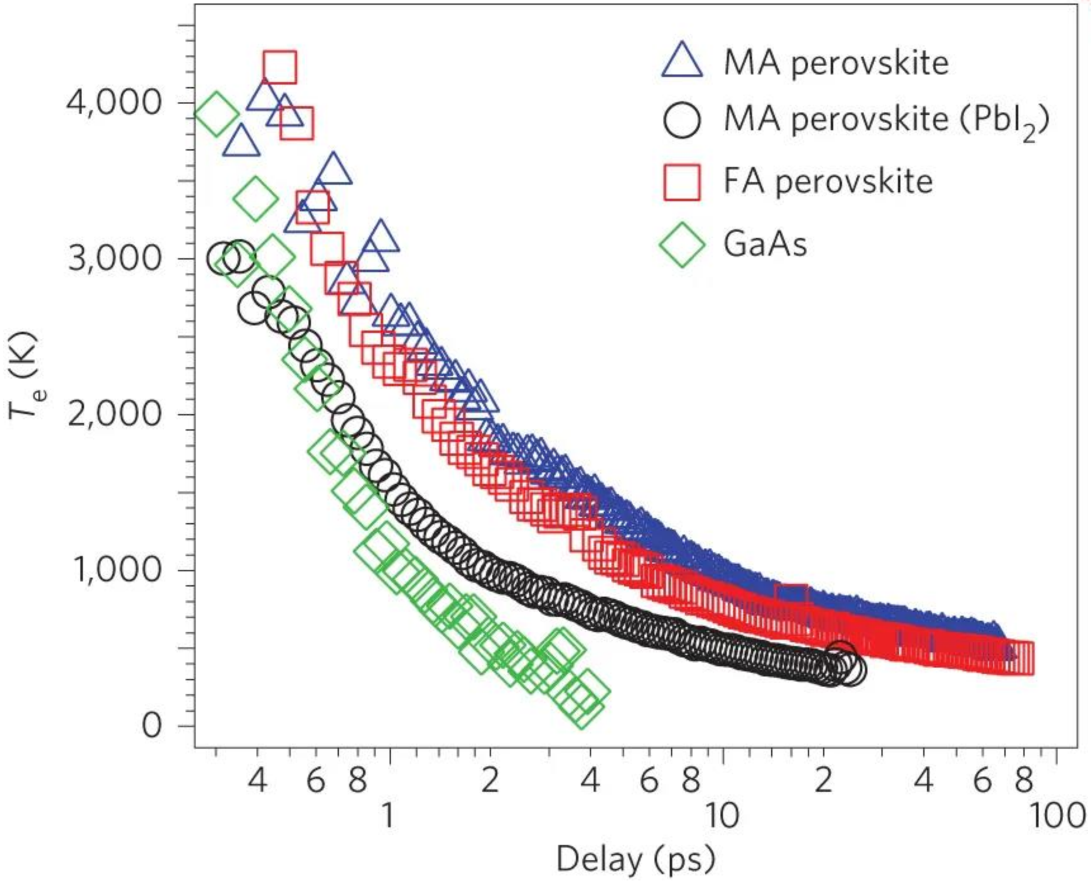
Outline

- Motivation
- Hybrid Organic Perovskites (2D vs 3D)
- Temperature dependent photoluminescence (PL) and transmission
- Exciton dynamics in 2D
- Carrier-phonon interactions in 2D vs 3D
- Conclusions

Motivation

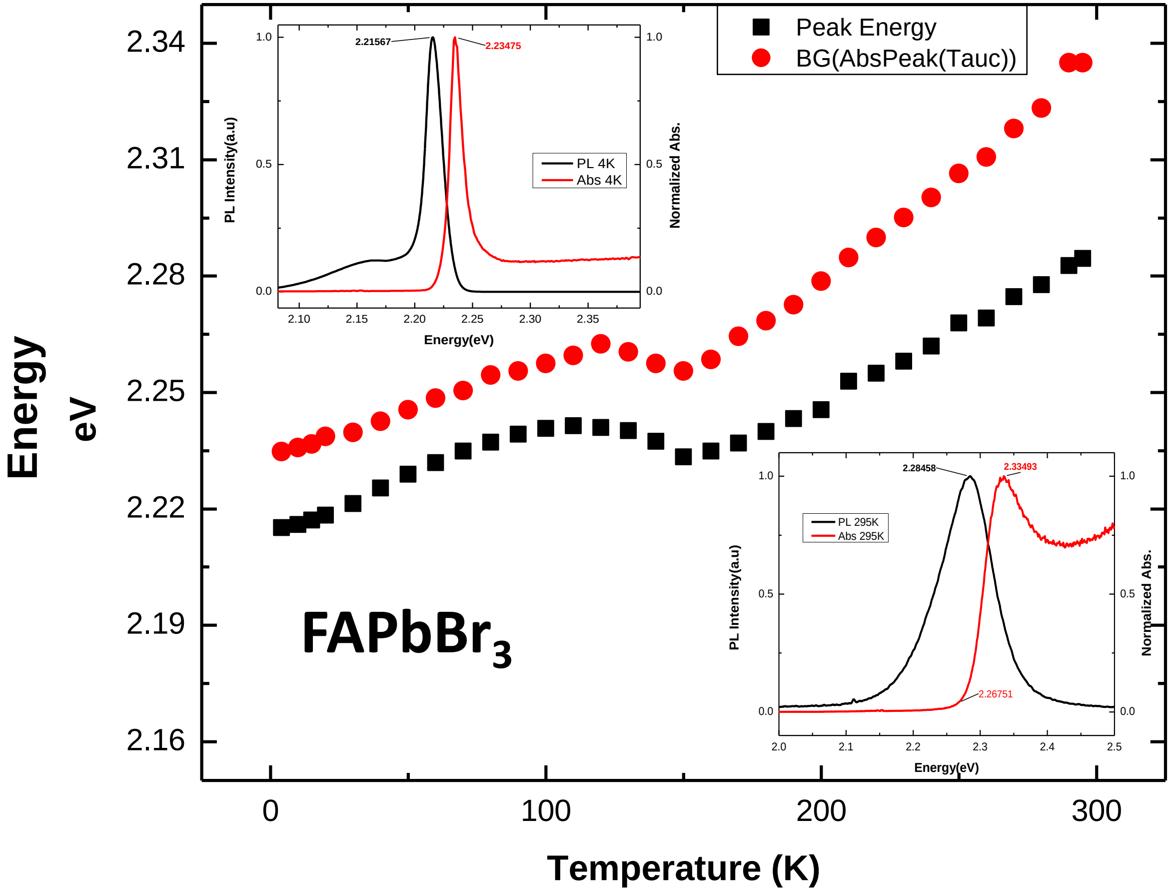
- Sellers group strong background in hot carrier dynamics (III-V)
- Slower apparent thermalization than GaAs
- Slower thermalization at higher temperatures



Y. Y., D.P. O., R.M. F., K. Z., J. van de Lagemaat, J.M. L., M.C. B., *Nature Photonics*, 10 (2015) 53

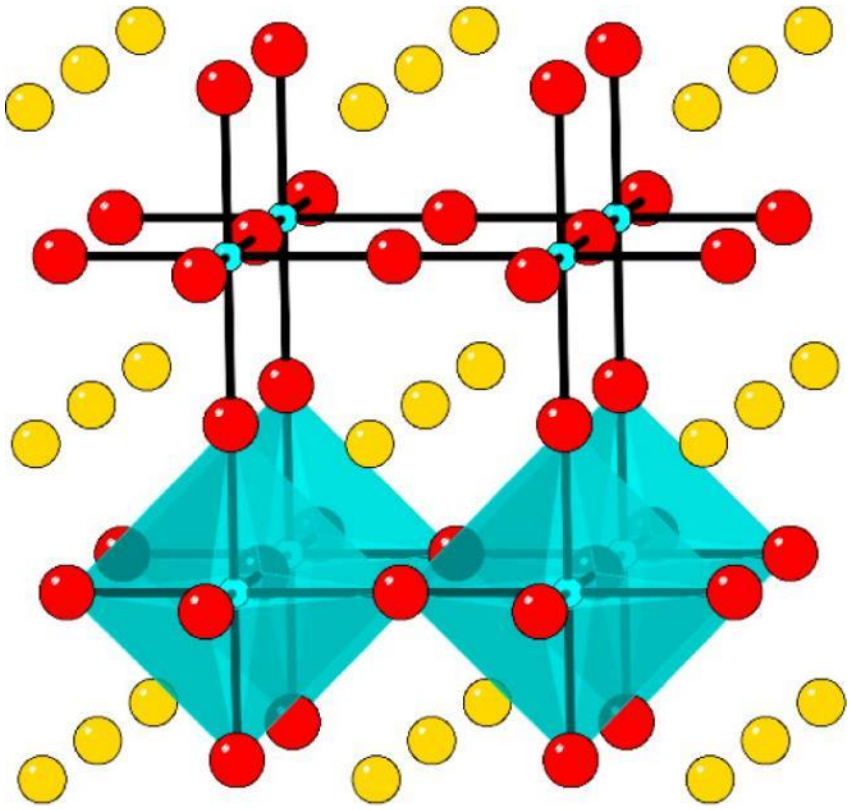
Motivation

- Temperature dependent photoluminescence vs absorbance shows stokes shift
- Carrier dynamics changing



Hybrid Organic Perovskites

- ABX_3 composition
- A=methylammonium, formamidinium, or Cs
- B=Pb or Sn
- X=I, Br, or Cl
- Solution processable
- 23% power conversion efficiency with polycrystalline thin film solar cells
- Increase ionicity I<Br<Cl
- Eg increases with increasing temperature (stabilization of out-of-phase band edge states)



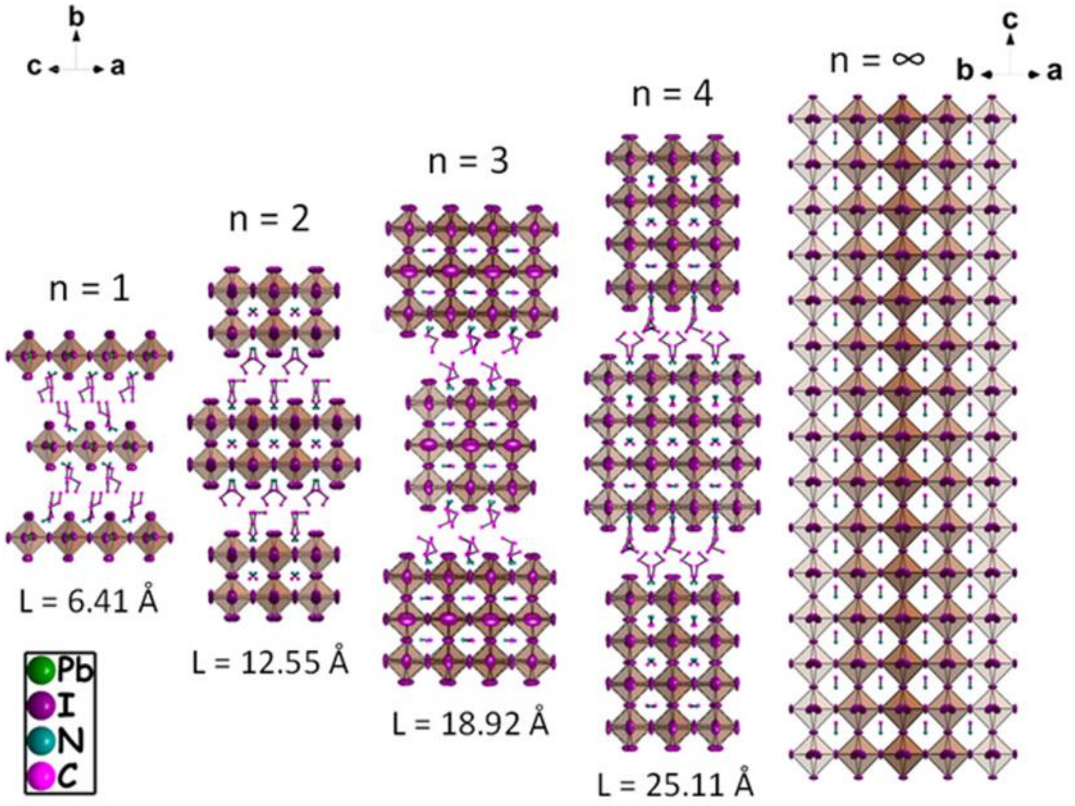
B. Saparov, D.B. Mitzi, *Chem. Rev.,* 2016, 116, 7, 4558-4596

Y. Yang, *et. al.,* Nature Photonics, **10** (2015) 53

Ruddlesden Popper Butylammonium Lead Iodide

$(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$ (Ruddlesden-Popper) films

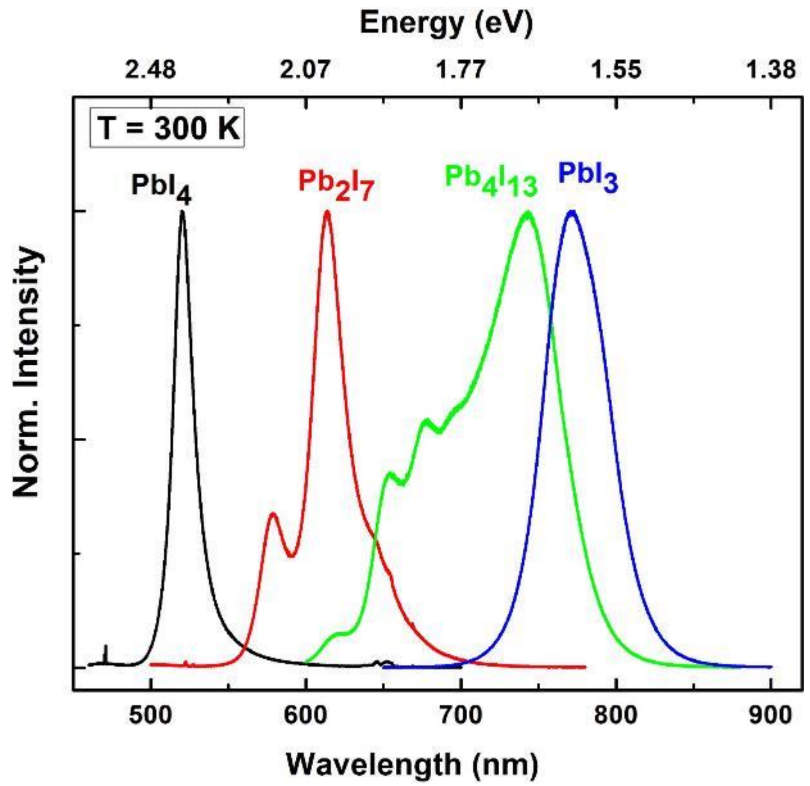
- BA=n-butylammonium
- MA=methylammonium
- Solution processable thin films
- Single inorganic layer (2D) n=1
- Fully 3D perovskite n=∞
- 2D structures high quantum and dielectric confinement



J. Phys. Chem. C 2017, 121, 47, 26566-26574

Temperature Dependent PL

- Increased bandgap and exciton binding energies with increased confinement ($n = \infty \rightarrow 1$)
- 3D: orthorhombic to tetragonal transition at ~130K
- 2D: orthorhombic to orthorhombic phase transition at 280K



2D→3D

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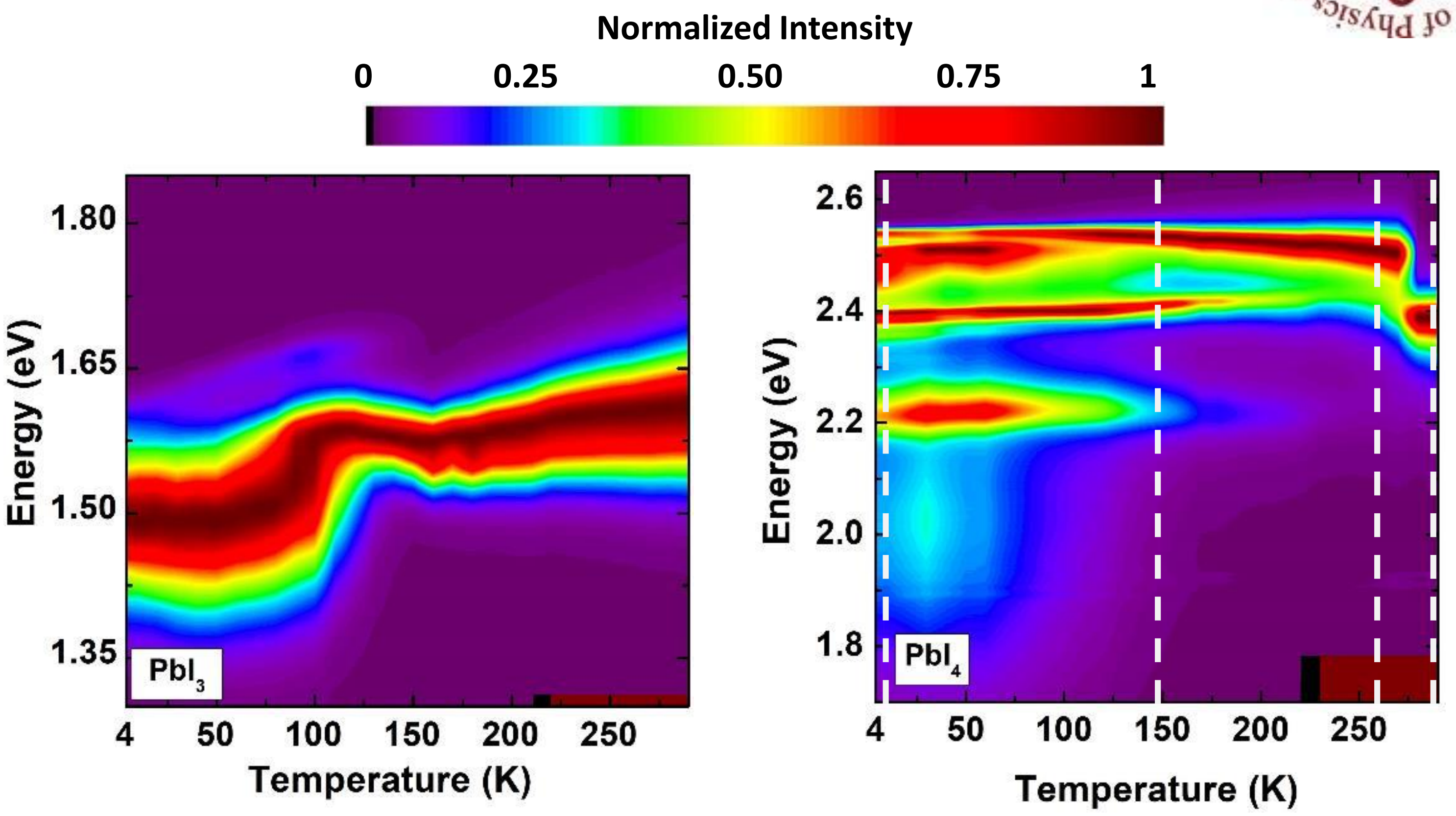


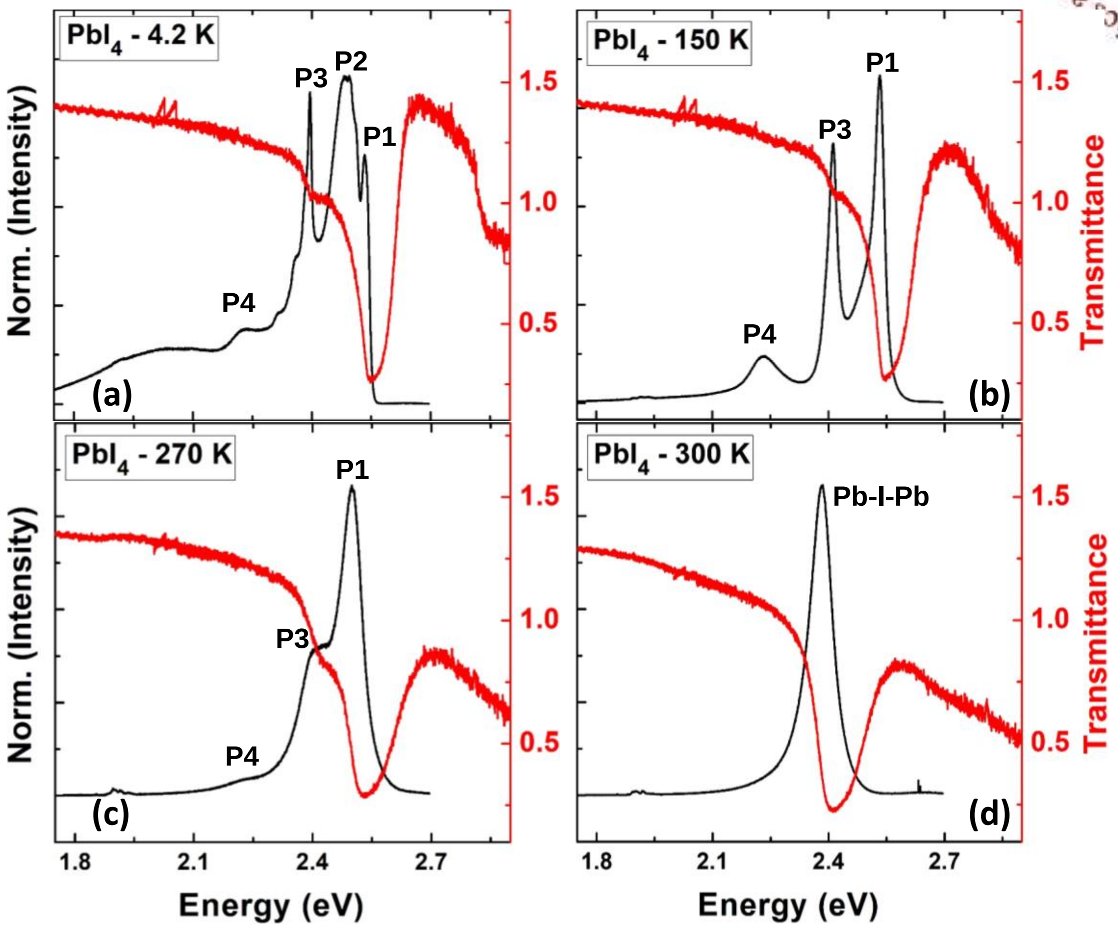
$MAPbI_3$ (3D)

BA_2PbI_4 (2D)

Temperature Dependent PL

$(BA)_2PbI_4$

- Two dominant transitions with strong absorption resonances (P1 and P3)
- Well separated from continuum (2.9 eV)
- Increasing temperature results in broadening and reduced number of peaks due to thermally mediated escape of trapped carriers



Hamidreza Esmaeilpour, Brandon K. Durant, Ian R. Sellers, *paper under review*

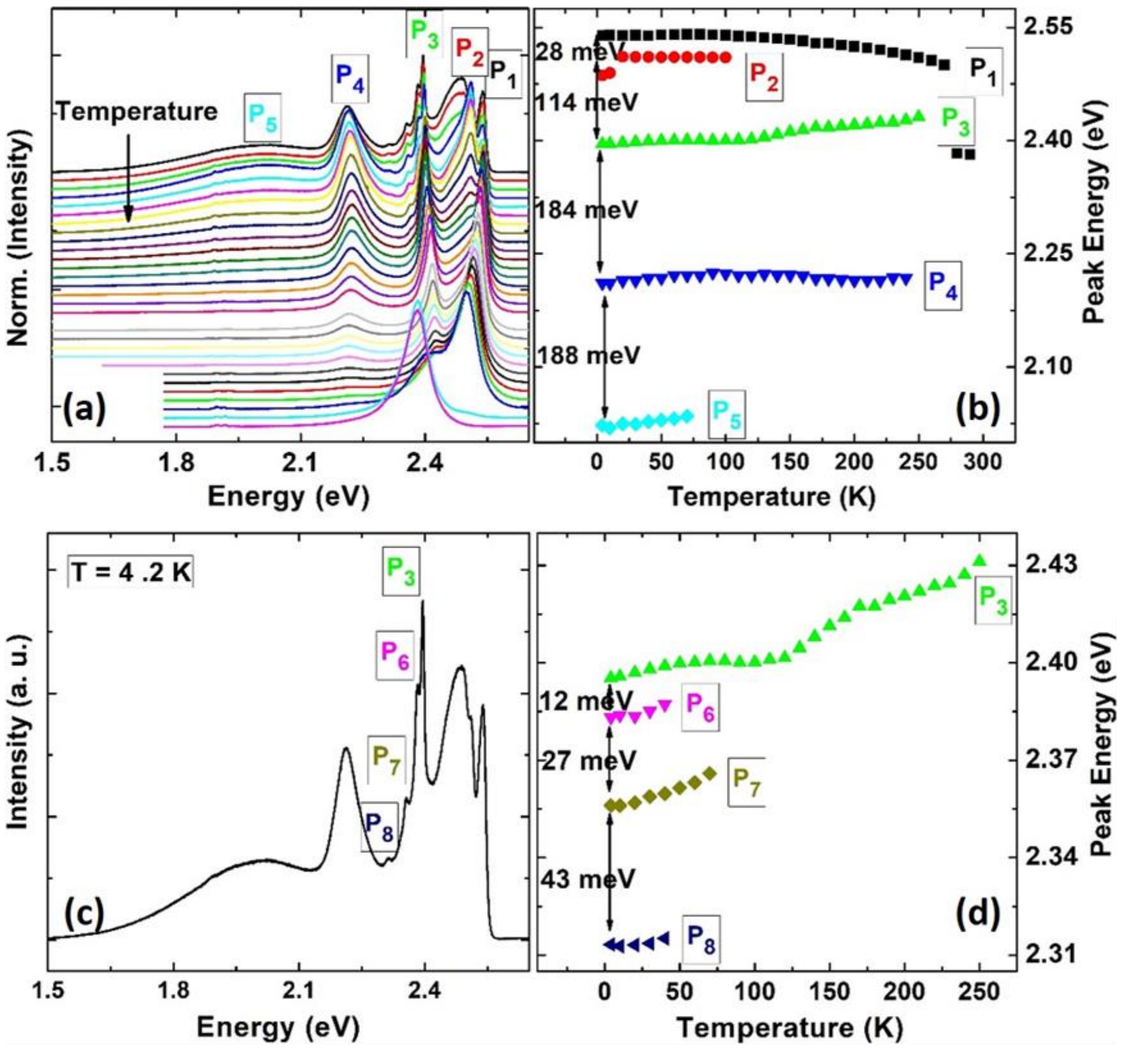
Exciton Dynamics

P3 (2.4 eV at 4.2K)

- 630 meV binding energy (4.2 K)
- LO phonon replicas spaced 12, 27, 43 meV on low energy tail
- More localized
- Lack of phonon broadening with increased temperature

P1

- 2.55 eV (4.2K)
- Closer to continuum by 140 meV
- Strong thermal stability/binding up to 280 K



Exciton Dynamics 2D vs 3D

$$\Gamma_{tot}(T) = \Gamma_0 + \Gamma_{LA}T + \frac{\Gamma_{LO}}{\left[exp\left(\frac{E_{LO}}{k_BT}\right) - 1\right]} + \Gamma_{imp}exp\left(\frac{E_B}{k_BT}\right)$$

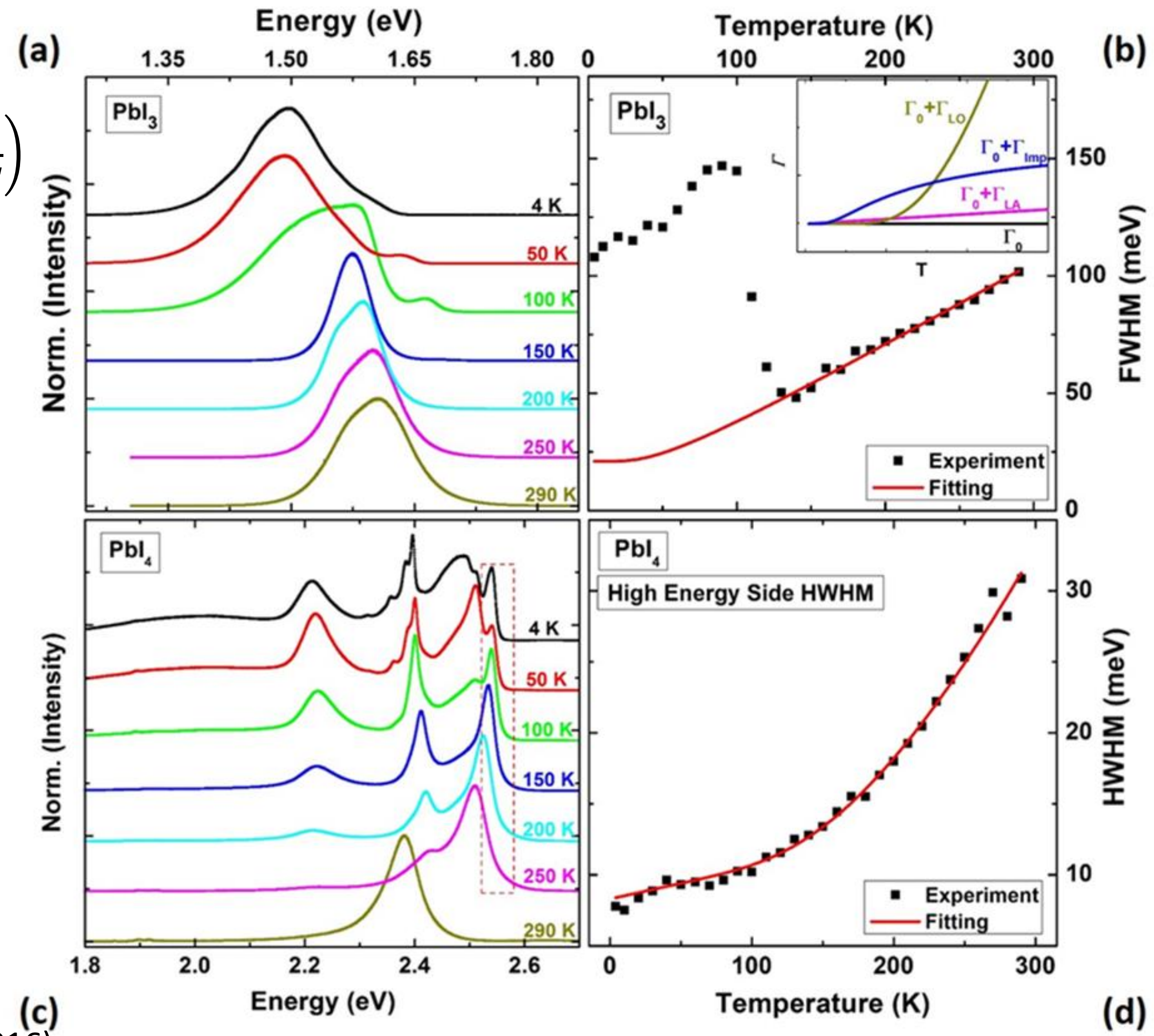
J.V.D. Veliadis, *et. al., Phys Rev B*, **50** (1994) 4463-4469.

$MAPbI_3$

Γ_0 (FWHM) (meV)	E_{LO} (meV)	E_B (meV)	Γ_{LO} (meV)
21	**11.5***	10*	**47.5 ± 1.0**

BA_2PbI_4

Γ_0 (HWHM) (meV)	E_{LO} (meV)	E_B (meV)	Γ_{LO} (meV)
8.3	**57.4 ± 1.1**	490	**148.4 ± 7.1**



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*Wright, A., Verdi, C., Milot, R. et al. *Nat. Commun.* **7**, 11755 (2016)

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E_{LO} Γ_{LO} for 2D 5x and 3x, respectively, compared to 3D

- Stronger carrier-phonon interaction in 2D

P3

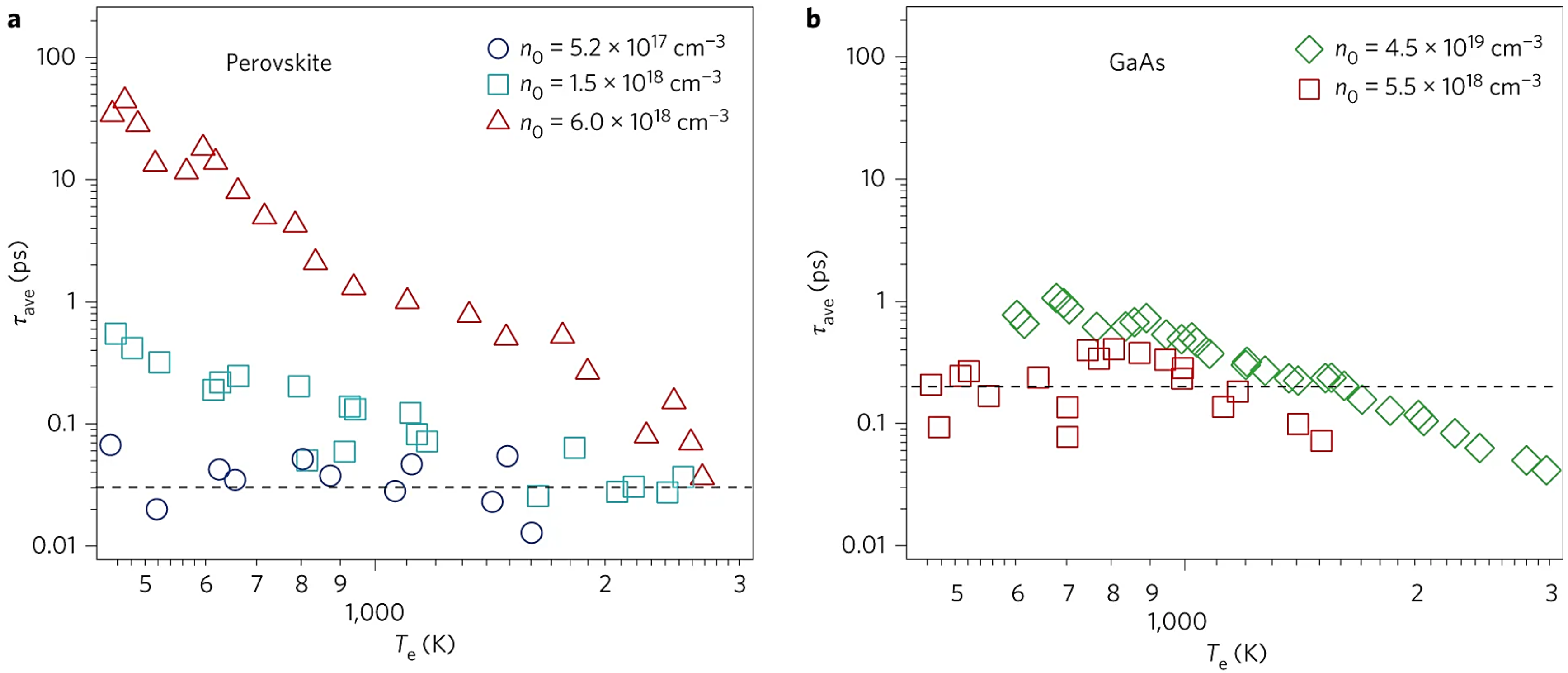
- Strongly bound
- Frenkel-like complex with much lower Fröhlich broadening

P1

- More weakly bound
- Less localized ("freer" carrier)
- Greater Fröhlich broadening
- Large E_{LO} may represent energy of polaron-exciton complex

Hot Carrier Thermalization

- Hot carrier thermalization restricted
- Higher carrier density 3 orders of magnitude increase in phonon emission time constant



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Conclusions

- 2D perovskites show much greater binding energies for multiple exciton transitions
- Highly bound exciton Frenkel-like
- Weakly bound exciton stronger ionic coupling and long-range polarization of the lattice
- Short range variations in structure
- Studies on varying the ionicity of 3D thin films ongoing

Acknowledgements

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