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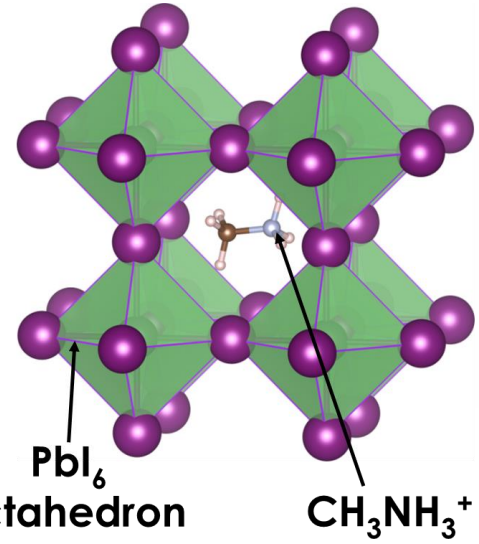
Charge Carrier Dynamics in Hybrid Perovskites: Insights from NAMD Simulations

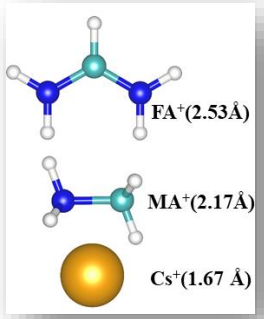
LA-UR-20-21858

Organic-Inorganic Perovskite



Methylammonium lead iodide $CH_3NH_3PbI_3$

A cations

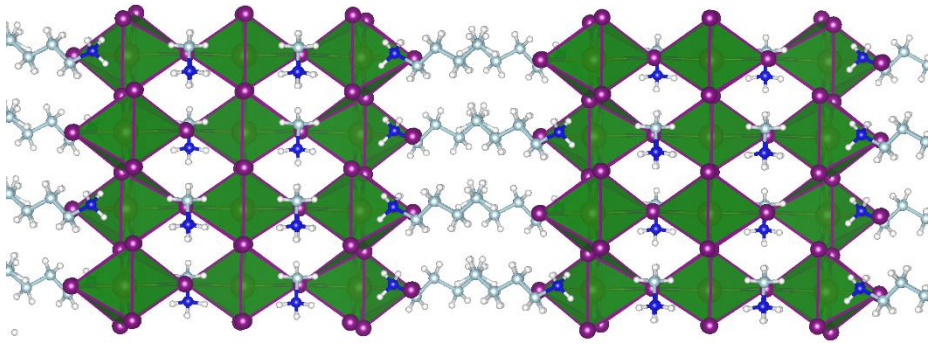


B metals: Pb, Sn

- ❑ Solution processable
- ❑ Strong absorption
- ❑ Excellent charge transport
- ❑ Defect tolerant
- ❑ Tunable Dimensionality

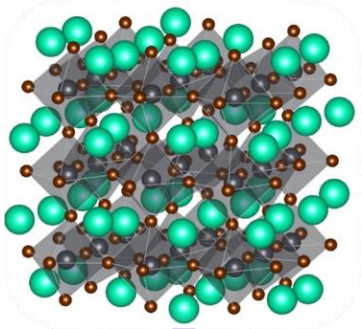
Kojima et al. J. Am. Chem. Soc, **2009**, 131, 6050
Eames et. al. Nature Comm. **2015**, 6, 7497
Lin et al. Science, **2020**, 369, 6499

Layered Perovskites (2D)



Tsai et al. Nature, **2016**, 536, 7616
Shi et al. Nature, **2020**, 580, 614

Quantum Dots (0D)



Raino et al. Nature, **2018**, 563, 671
Swarnkar et al. Angew. Chem., **2015**, 127, 15644

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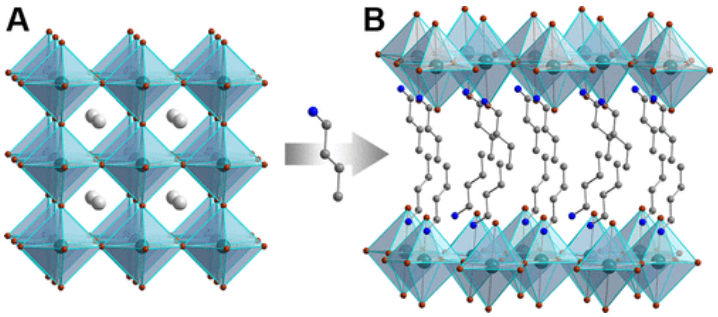
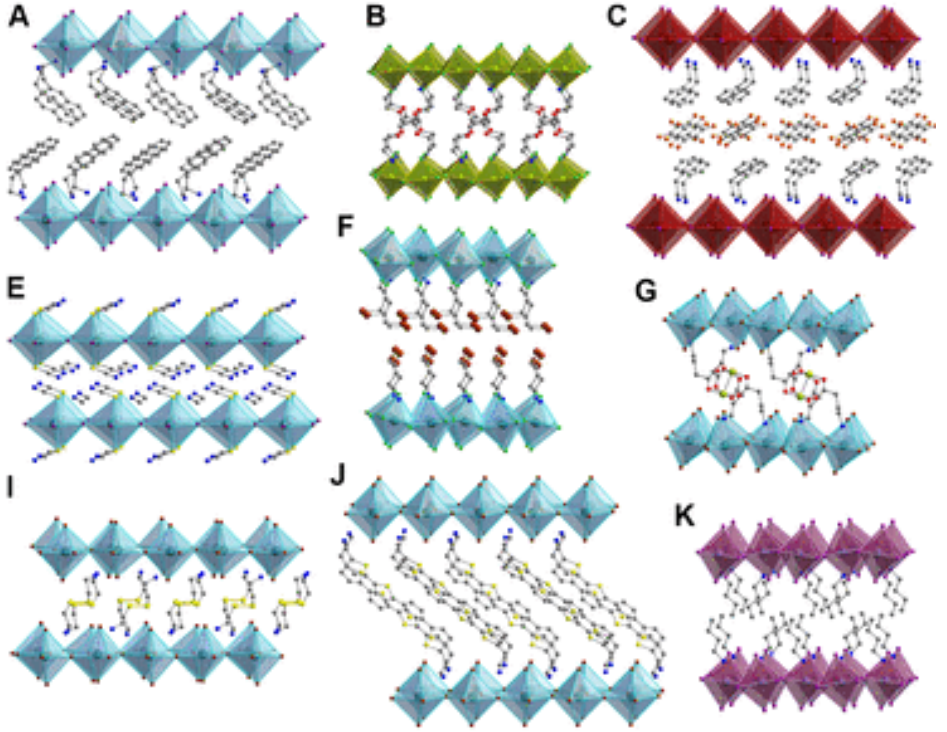
2D-halide perovskites

Conceptual slicing of a 3D-perovskite



- Improved stability
- Higher crystallinity and fewer defects
- Promising light absorption and emission



Wide diversity in crystal structure and emission properties

Grancini *et al. Nat. Rev. Mater.*, **2019**, 4, 4;
Smith *et al. Chem. Rev*, **2019**, 119, 3104

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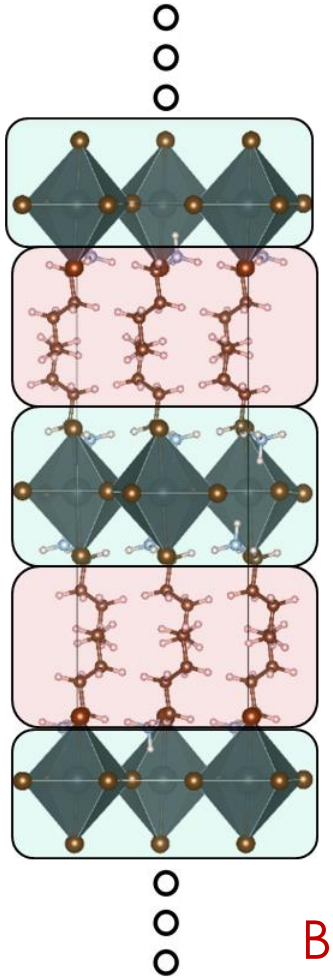
Two-dimensional perovskites for Optoelectronics



B = Pb, Sn
X = Cl, Br, I

Partially known complex nature of **carrier recombination dynamics**

What is the role of spacer cations on the carrier recombination processes ?

Tsai et al. Nature **2016**, 536, 312; Blancon et al. Science **2017**, 355, 1288; Tsai et. al, Science Advances **2020**, 6, 0815

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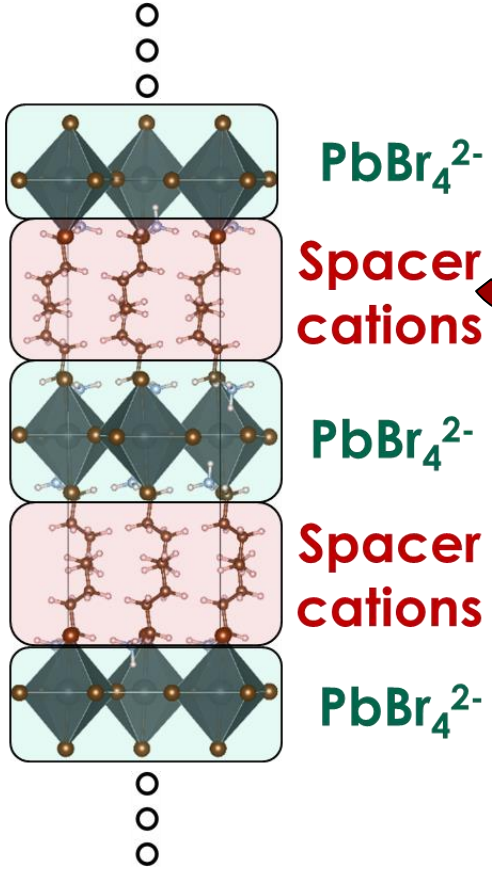
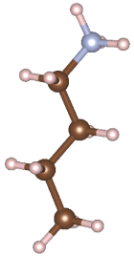
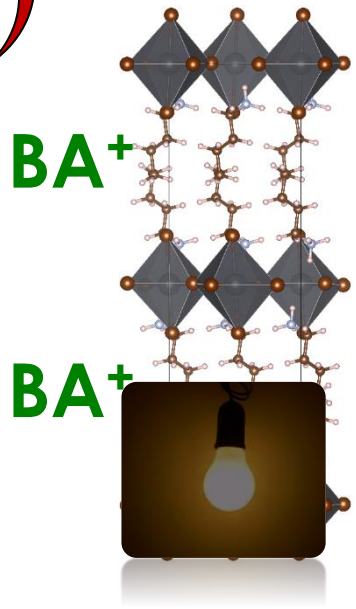
Different Spacer Cations in 2D perovskites



BA (Alkyl chain)





PEA (Benzene ring)

- Well studied and **distinctly different optoelectronic** (LED, detectors) performances
- Similar crystal structure and static electronic properties

Takagi et al. Phys. Rev. B, **2013**, 87, 125421
Gong *et al.* Nature Mater, **2018**, *17, 550*

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Key Questions

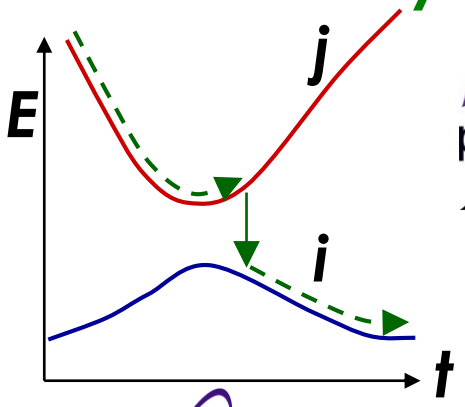
- ❑ How spacer cations impact the electronics?
- ❑ Influences in structural dynamics?
- ❑ What about non-radiative recombination rates?

Methods

Density functional theory & *ab initio* molecular dynamics

- Static Structure and Properties with DFT
- Structural Fluctuations with AIMD

Non-adiabatic molecular dynamics



$$d_{ij} = \left\langle \Phi_i \left| \frac{\partial \Phi_j}{\partial t} \right\rangle \right.$$

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Computational Approach

AIMD (with VASP)

Step 1: Optimize the structure at 0 K

Step 2: Gradually heat the lattice to 300 K

Step 3: Keep the lattice at 300 K and generate the trajectory (NVE ensemble)

Calculate non-adiabatic coupling constants (with VASP)

Step 1: Separate the trajectory in smaller fragments

Step 2: Calculate adiabatic state energies and NA coupling between states

NAMD simulation (with PYXAID)

Calculate the change of state populations over time. Used classical path approximation and decoherence induced surface hopping (DISH).

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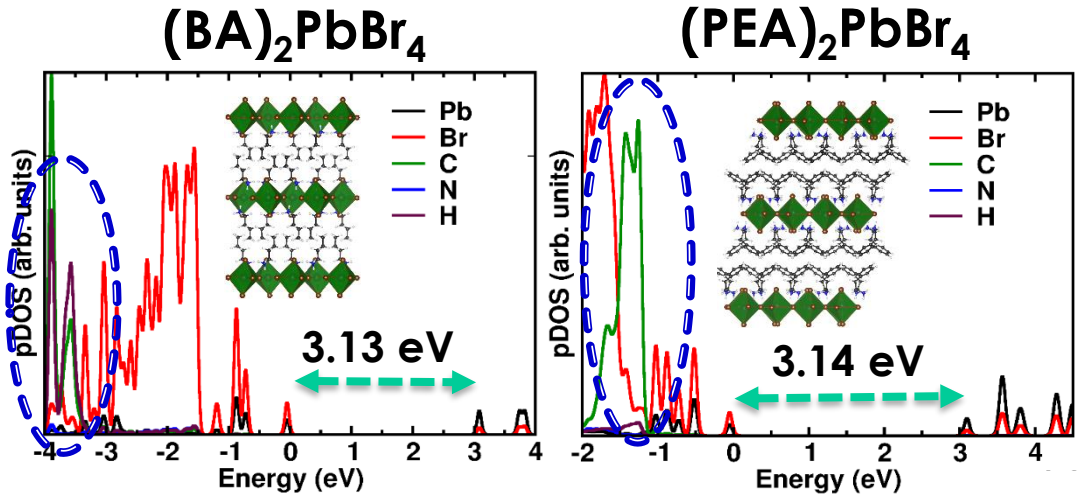
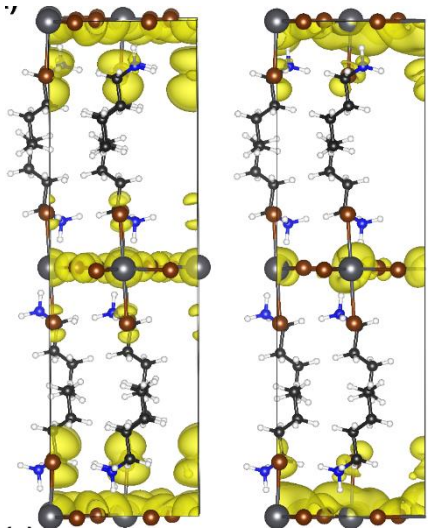
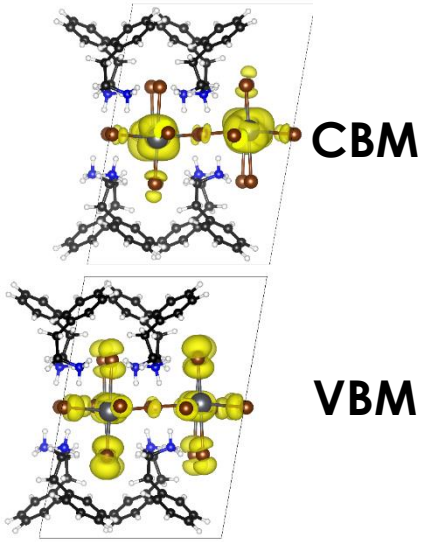
Static Electronic Properties







DFT, 0 K

- Similar band gaps
- Molecular states are well below (>1eV) to band-edges
- PEA states are relatively closer to VBM

Ghosh et al. J. Phys. Chem. Lett, **2020**, 11, 2955

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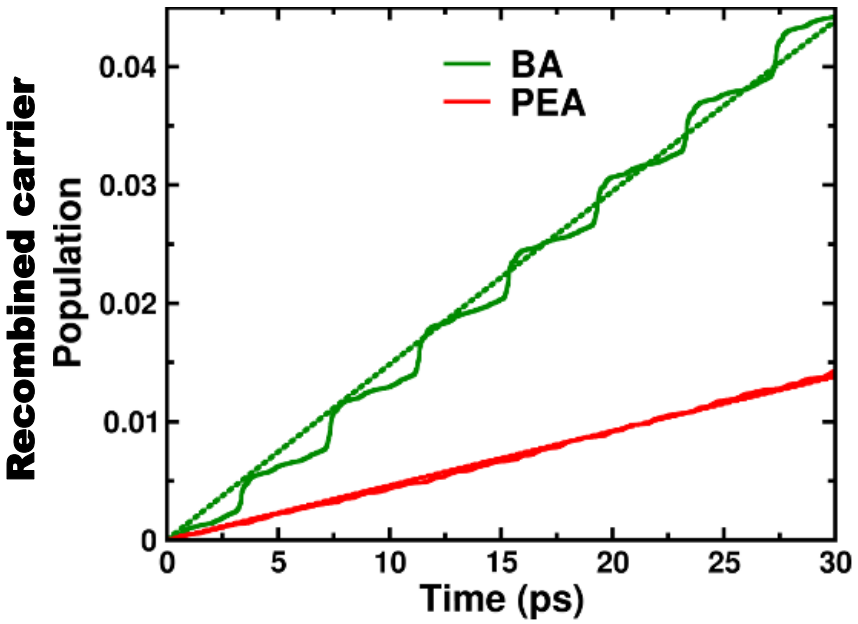
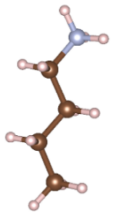
Impact of Spacer Cations on Carrier Dynamics

Population of **electron-hole recombined state** through non-radiative processes (dominant loss mechanism)





$(BA)_2PbBr_4$

$(PEA)_2PbBr_4$

Much faster non-radiative recombination for $(BA)_2PbBr_4$

Ghosh *et al.* J. Phys. Chem. Lett, **2020**, *11, 2955;*
Ghosh *et al.* J. Mater. Chem. A, Just Accepted, **2020**

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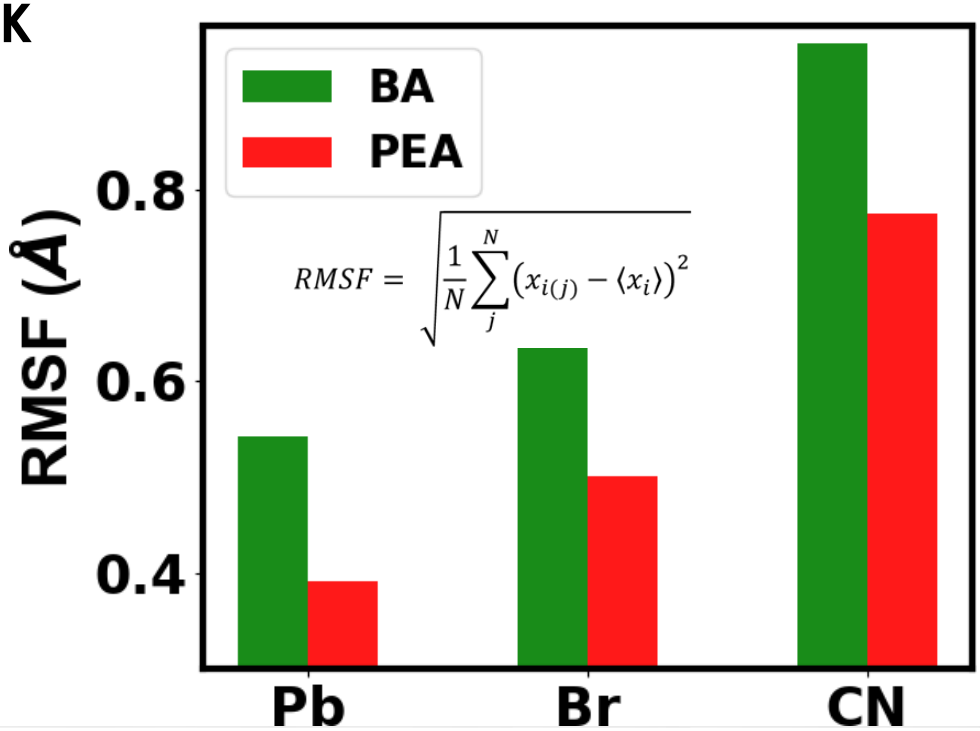
Spacer Cation Dependent Structural Dynamics

AIMD, 300 K



- BA cations make PbBr-layer more dynamic
- $(PEA)_2PbBr_4$ is more rigid; π stacking interactions

Ghosh *et al.* J. Phys. Chem. Lett, **2020**, *11, 2955*

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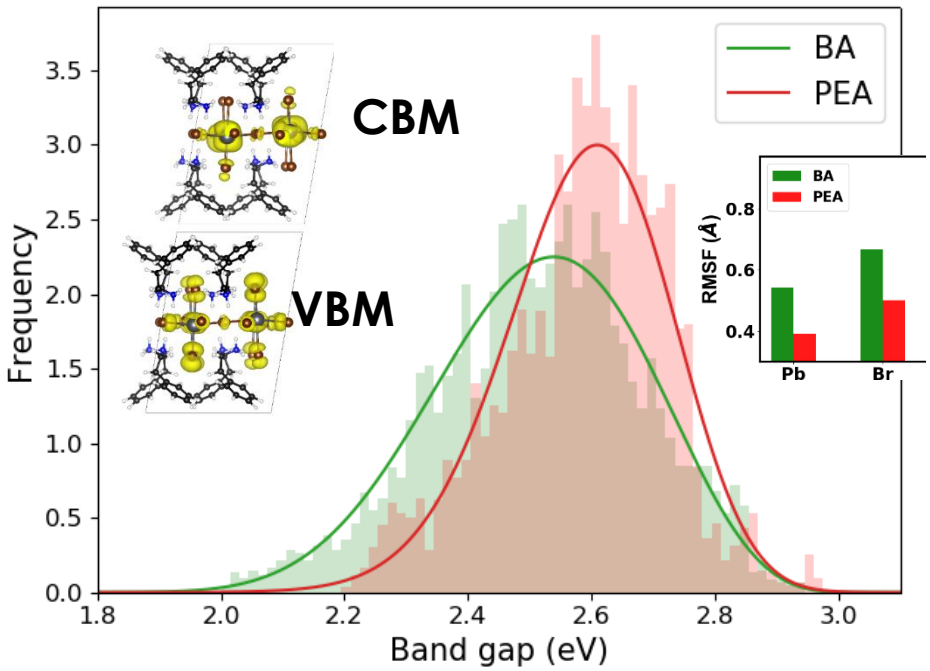
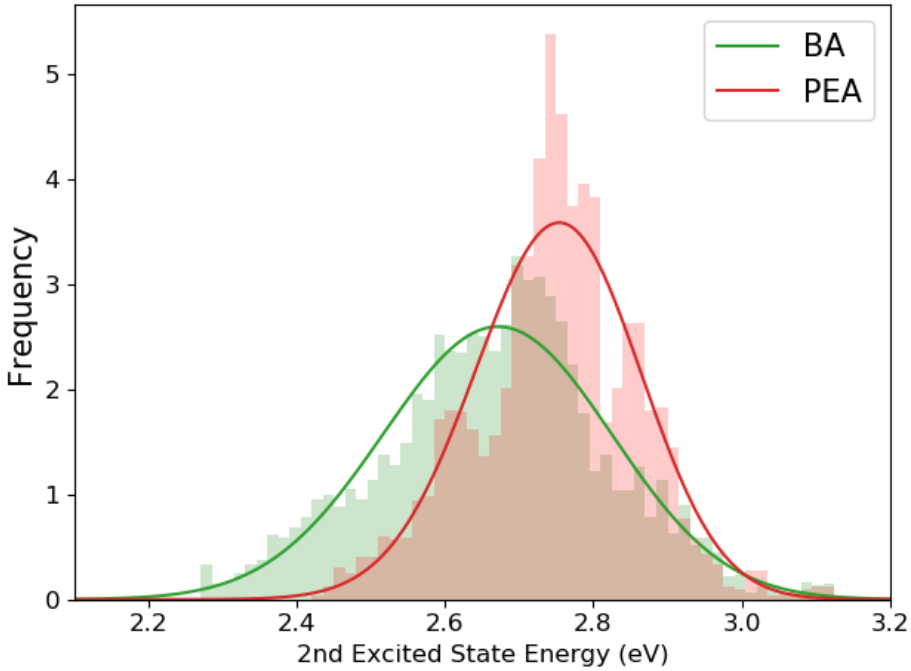
Dynamic Electronic Properties





- Band gaps and excited states fluctuate more for BA-based perovskites
- Strong influence of dynamic structures on the electronic properties

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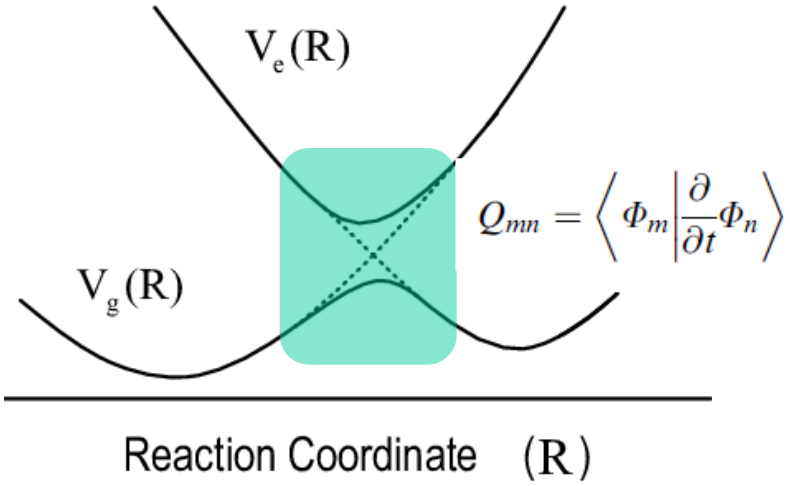
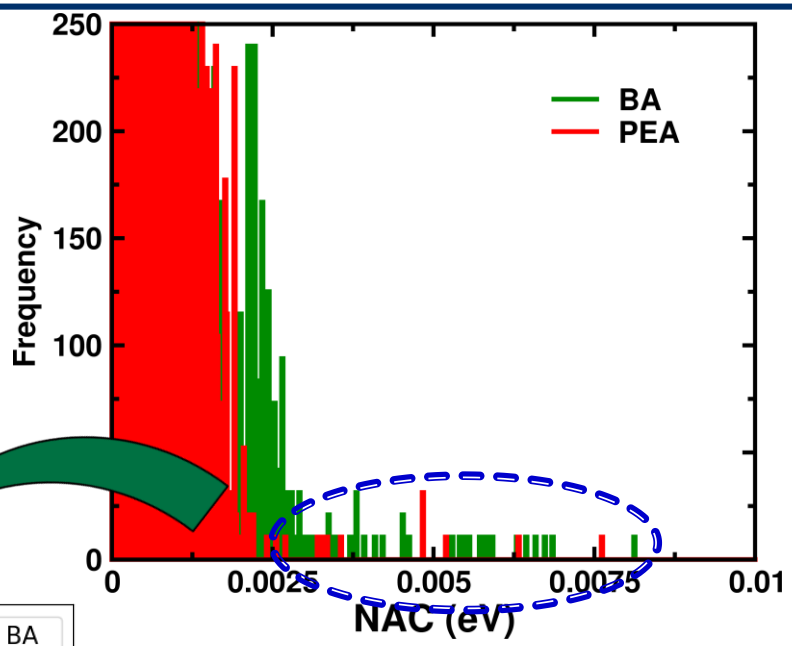
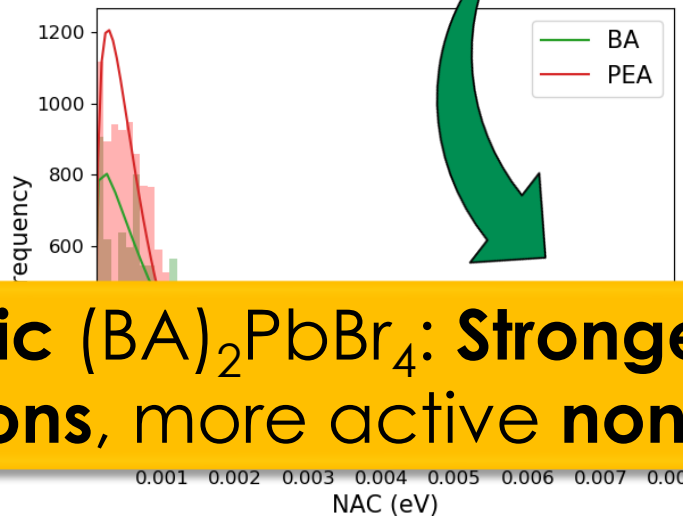
Non-adiabatic Coupling







More number of large NAC values

Dynamic $(BA)_2PbBr_4$: **Stronger electron-phonon interactions**, more active **non-radiative processes**

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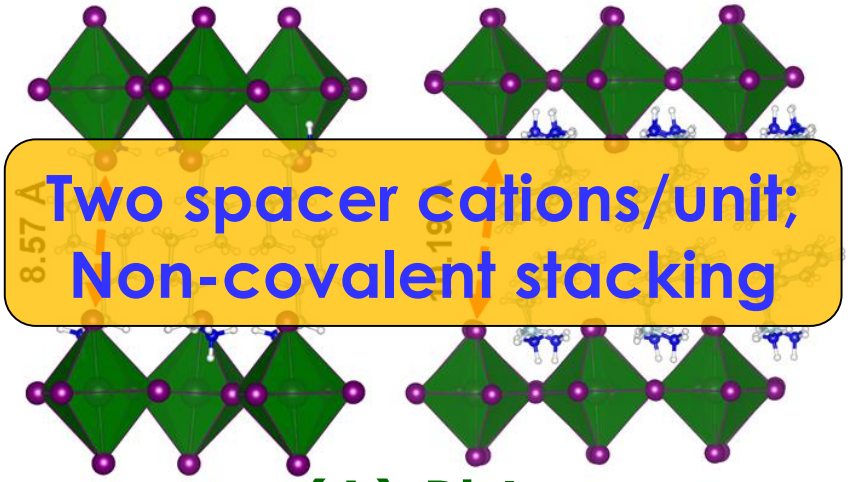
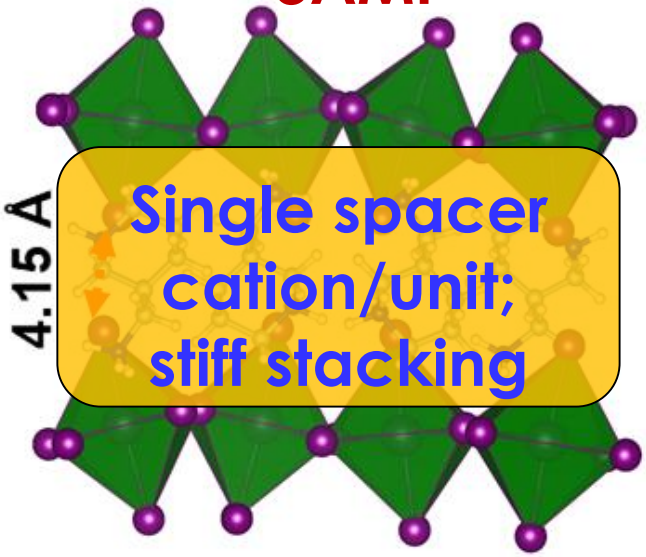
Next Step: *In silico* materials designing for efficient 2D Iodide perovskites

BA^+ PEA^+ $3AMP^{2+}$

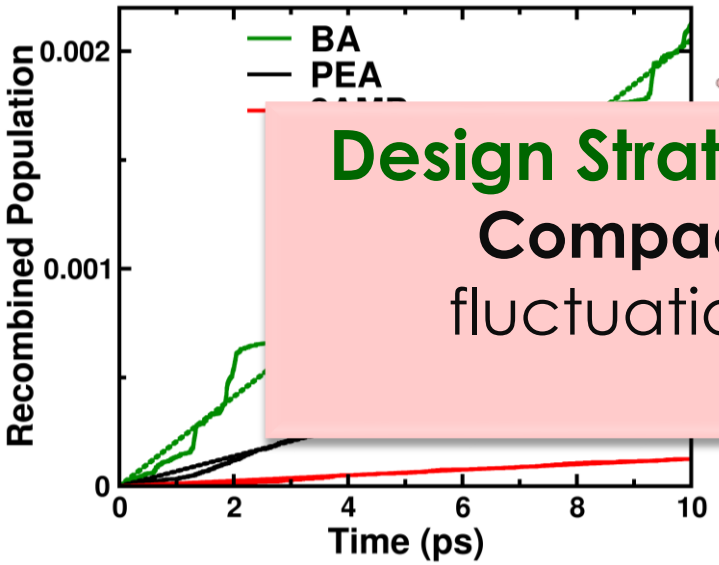


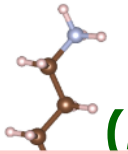
Two spacer cations/unit; Non-covalent stacking



Single spacer cation/unit; stiff stacking

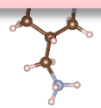
$(A)_2PbI_4$ $(A)PbI_4$





BA (Most dynamic)

Design Strategy for 2D halide perovskites:
Compact the interlayers, mitigated fluctuations; **slower the non-radiative recombination**



3AMP (Stiffest)

Ghosh *et al. Accepted*, J. Mater. Chem. A **2020**

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2D-halide Perovskites for Optoelectronics

- **Dynamic structures** influence the charge **carrier recombination** processes: **Strategic structural modifications** can **mitigate non-radiative losses**

Group & Collaboration

- Dr. Sergei Tretiak and Dr. Amanda Neukirch (LANL)
- Prof. Oleg Prezhdo (USC)and group
- Dr. W. Nei (LANL)