Elucidating the Relationship Between A-Site Mixing and Non-Radiative Carrier Capture

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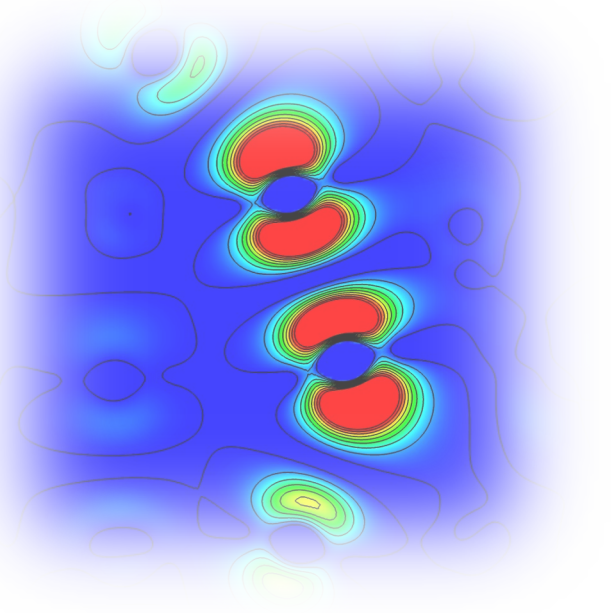
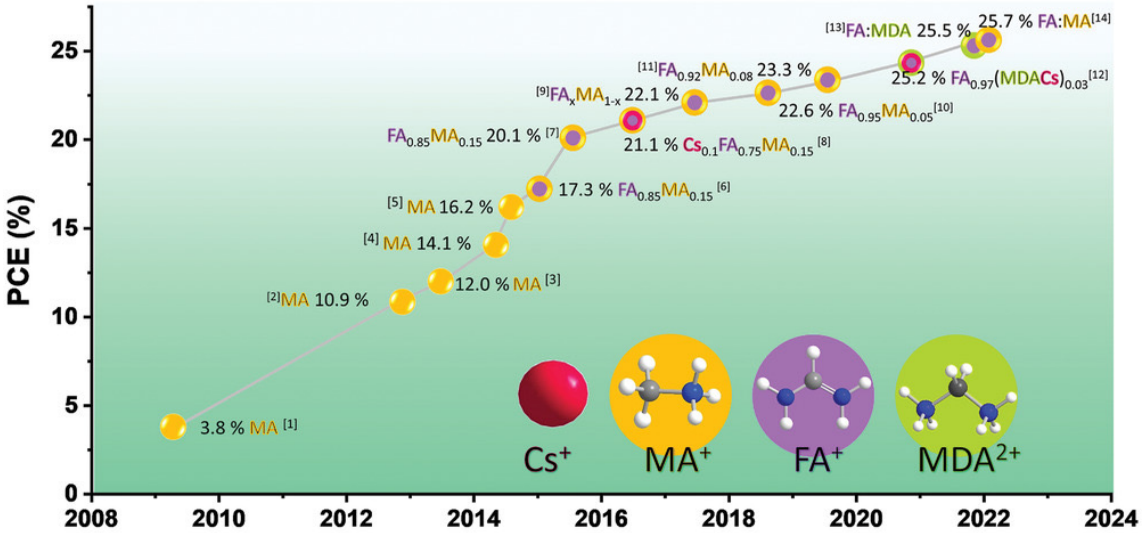


The most stable and efficient ABX_3 perovskite solar cells employ mixed A-site cations

Byranvand *et al., Adv. Optical Mater.* 2022, 10, 2200423

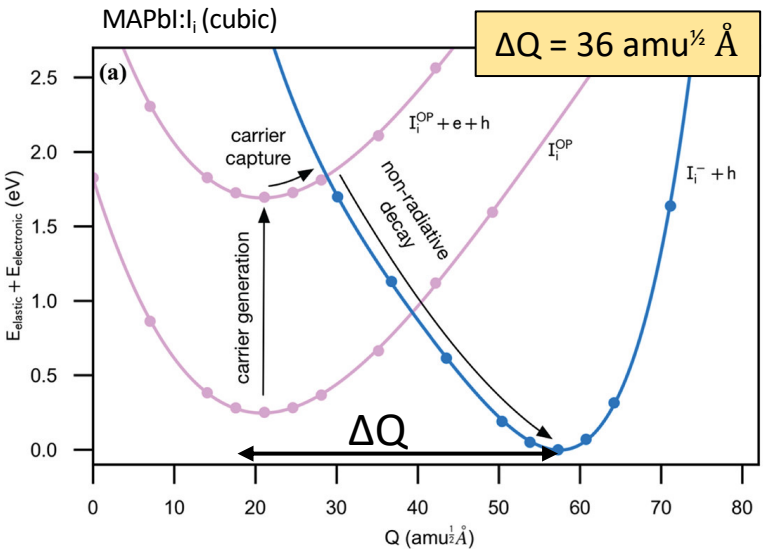


The A-site cation:

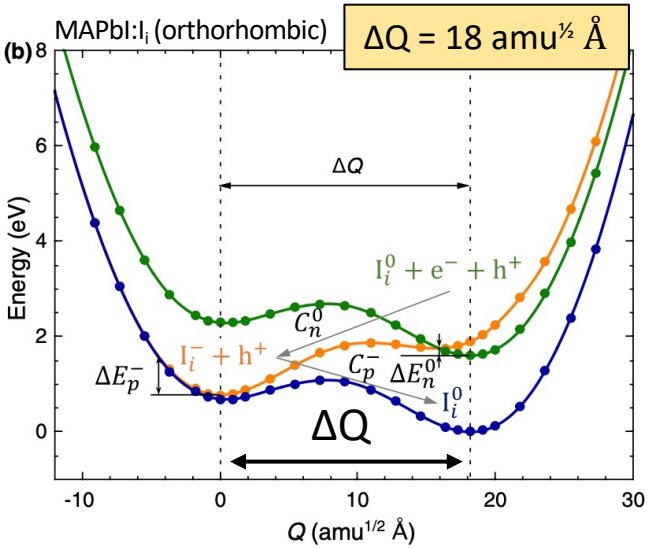
- determines the crystallographic phase
- *directly* affects intrinsic and extrinsic stability
- *indirectly* affects electronic structure at band edge (band gap, effective mass)

The defect physics is highly sensitive to the crystal phase and bulk electronic structure; **the impact of cation mixing on carrier trapping and recombination is not fully understood**

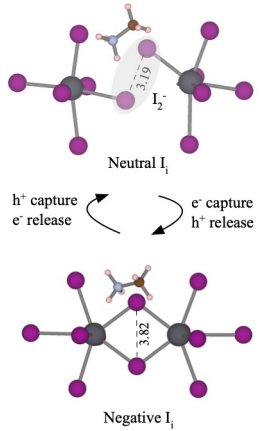
Halide ions form abundant, mobile defects which are active in carrier trapping and recombination



Whalley et al., *J. Am. Chem. Soc.* 2021, 143, 9123−9128



Zhang et al., *Phys. Rev. B* 2020, 101, 140101(R)



cf. DX centre in GaAs
ΔQ = 9 amu^{½} Å

Phys. Rev. B 2019
100, 041202(R)

An easily distorted ('soft') perovskite lattice leads to large lattice relaxation after carrier capture

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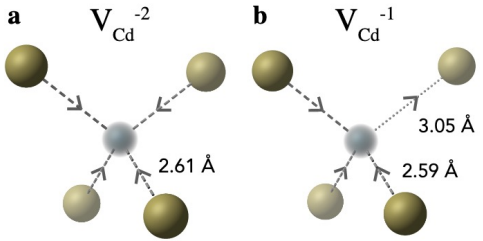
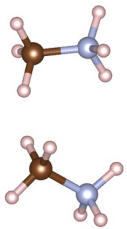
Molecular rotations cannot be described with the standard interpolation methods for inorganic materials

Lattice relaxation corresponds to translational motion in most inorganic systems



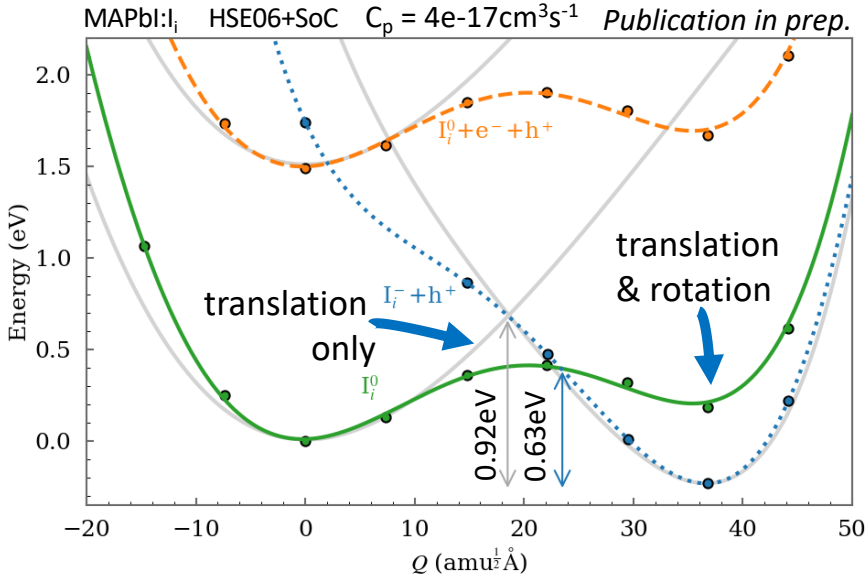
ACS Energy Lett. 2021, 6, 4, 1392–1398

We use the Kabsch algorithm to describe molecular **translations** *and* **rotations**



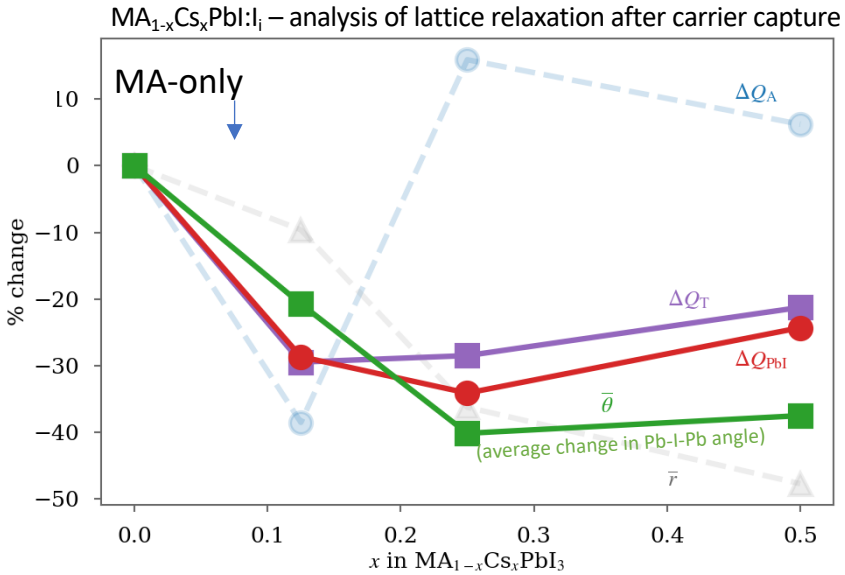
Molecular rotations after carrier capture

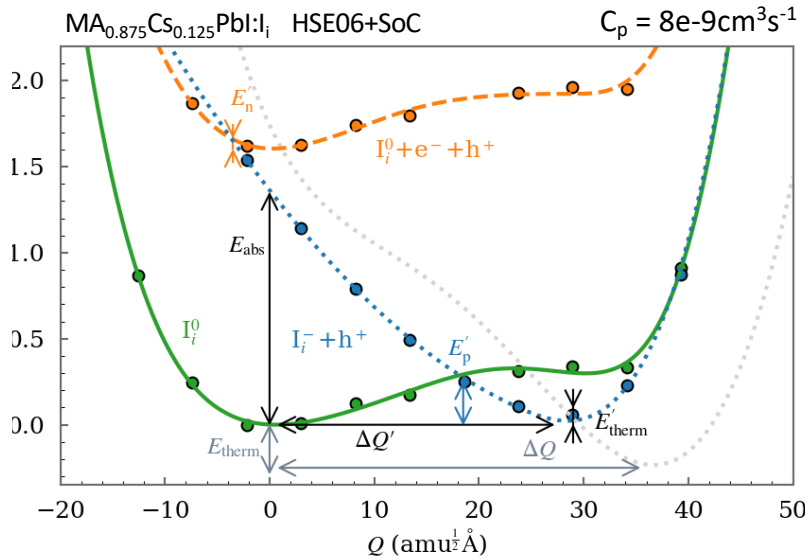
Assumes rigid body motion



Energy is dissipated through rotations of the MA cation, resulting in significant reductions in barrier height. **For accurate predictions we need to consider molecular translations and rotations.**

The iodine interstitial is an active site for carrier capture in $MA_{1-x}Cs_xPbI_3$ for x < 0.5





Publication in prep.

A-site cation mixing in $MA_{1-x}Cs_xPbI_3$ impedes PbI_6 octahedral tilting after carrier capture, **leading to a reduction in ΔQ.**

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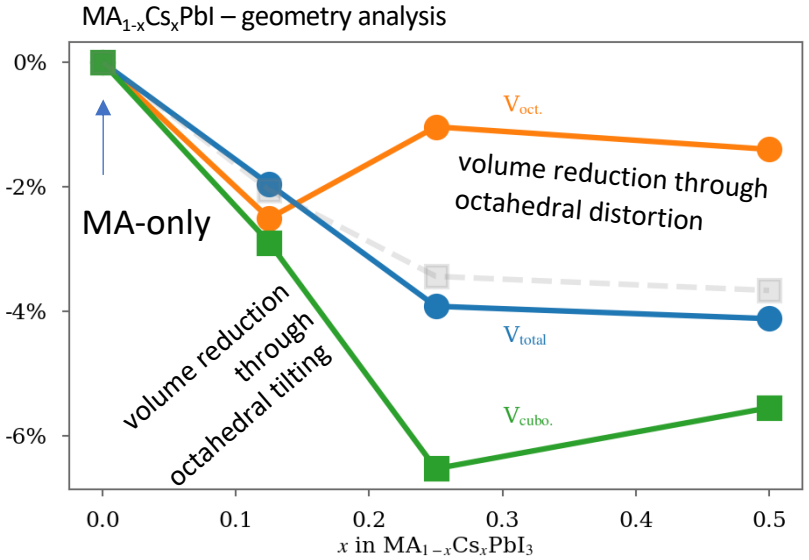
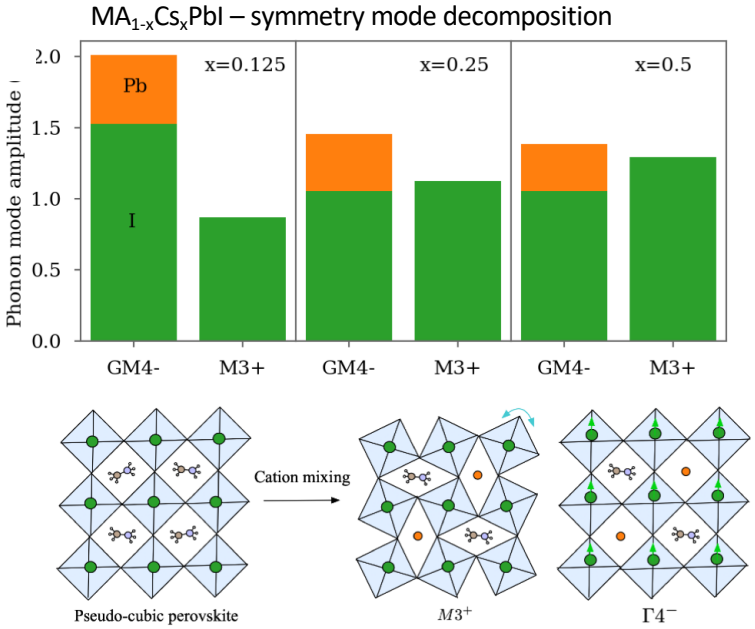
A-cation mixing produces a symmetry-lowering lattice distortion to an orthorhombic-like phase.





Publication in prep.

The reduced steric size of Cs (1.81 Å) compared to MA (2.70 Å) leads to a volume reduction **mediated through condensation of the M3+ octahedral tilting mode.**

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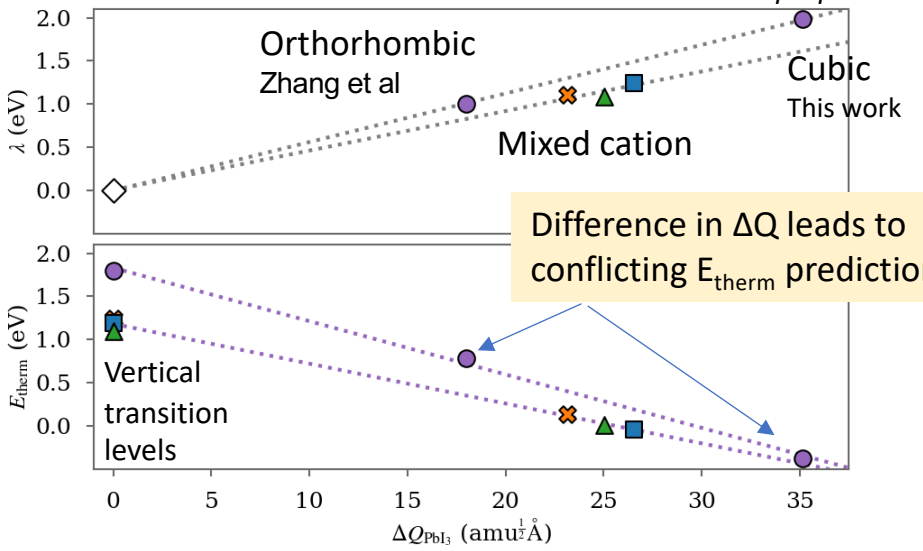
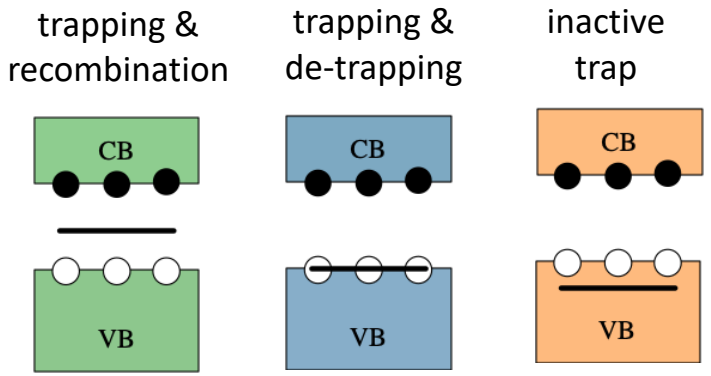
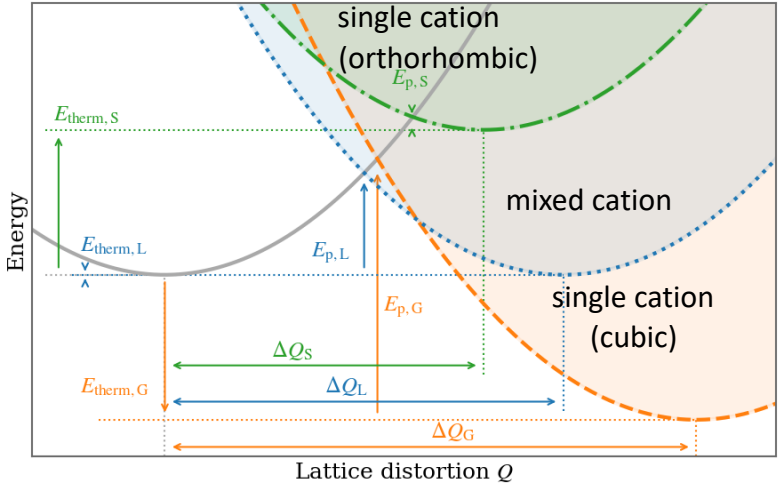
Defect activity is highly sensitive to ΔQ

Publication in prep.



Difference in ΔQ leads to conflicting E_{therm} predictions





Reduced lattice relaxation (ΔQ) leads to a reduced relaxation energy (λ) and increased charge transition level (E_{therm})

Similar behaviour reported with molecular dynamics

Nan et al., *Adv. Energy Mater.* 2018, 8, 1702754
Cohen et al. *J. Phys. Chem. Lett.* 2019, 10, 16, 4490−4498
Wang el al., . *Phys. Chem. Lett.* 2022, 13, 25, 5946−5952

The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity

Summary

- For accurate predictions of capture rates, translations and **rotations** of molecules may need to be considered
- Symmetry lowering leads to a reduction in ΔQ (lattice relaxation after carrier capture). This can be induced by cation mixing.
- ΔQ determines key defect properties: λ, E_{therm} E_b
- The iodine interstitial in $MA_{1-x}Cs_xPbI_3$ can display a wide range of defect activity: inactive acceptor, trapping & de-trapping, recombination site.

Could we use ΔQ to engineer for particular defect properties ?

✅ Control through composition, temperature, particle size, dimension…

❌ Side effects: defect concentration, ion transport, polaron formation…

Thank-you to software developers:
CarrierCapture, ICET (SQS), ISOTROPY, ASE, PIEFACE, Nonrad (EP coupling) , sxdefectalign

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Calculation Details  (software underlined)

- **density functional theory:** as implemented in VASP
- **exchange-correlation:** PBEsol for lattice relaxation, HSE06+SoC (α=0.43) for electronic relaxation evaluated at the gamma-point only (NKRED)
- **basis set:** plane wave with 400eV cutoff
- **SC ionic loop break condition:** all forces < 0.01 eV $Å^{-1}$
- **SC electronic loop break condition:** total energy < 1e-5 eV
- **supercell:** $MAPbI_3$ parent structure is a 192-atom cell
- **k-point sampling:** 2x2x2 gamma-centred Monkhurst Pack mesh
- **disorder:** Cs/MA mixing as special quasi-random structure (SQS) as implemented in ICET
- **interpolation:** Kabsch algorithm implemented in Scipy, with custom ASE-based script (code repo in prep)
- **constraints:** neutral defect occupancies fixed (FERWE/FERDO) during electronic relaxation
- **defect corrections:** Freysoldt, Neugebauer and van de Walle (FNV) method as implemented in sxdefectalign (ε= 22.67)
- **carrier capture rates:** Static coupling theory as implemented in CarrierCapture.jl
- **electron-phonon coupling:** wavefunction overlap analysed with VASP (LWSWQ) and nonrad
- **symmetry mode decomposition:** as implemented in ISODISTORT
- **geometry analysis:** bond lengths & angles with ASE, minimum bounding ellipsoids with PIEFACE
- **convergence testing:** neutral defect formation energies converged to 0.01eV / fu for i) k-point sampling (NKRED=2,1) and ii) supercell size (192,384 atoms). ΔQ converged to 1amu$^{1/2}$Å for supercell size (192,768 atoms).