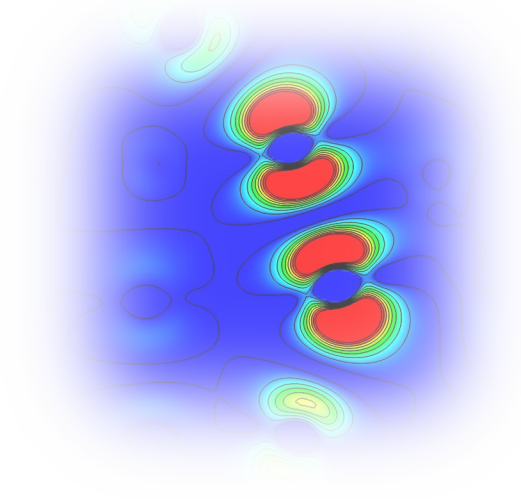
A-site mixing and non-radiative trapping
in hybrid halide perovskites



Dr Lucy Whalley

Vice Chancellor's Fellow, Northumbria University

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Hello!! 👋

- 2015-2019: PhD student in MDG (Perovskites!)
- 2020: Maternity Leave (Robin!)
- 2020-current: Northumbria University (Way aye man!)

My update....("what's occurring?")

- **Teaching**
  - Introductory programming labs (1st year)
  - Computational Physics (2nd year)
  - Quantum optics (don't ask) (3rd year)

nu-cem.github.io/CompPhys/

An Introduction to Computational Physics

Part two: Getting results

- Modelling with ordinary differential equations
- Modelling with partial differential equations

Part three: Getting it out there

- Python scripts and the Unix terminal
- Version control and Github
- Testing and documentation
- Open science and build-your-own website

github.com/lucydot/ChooChoo

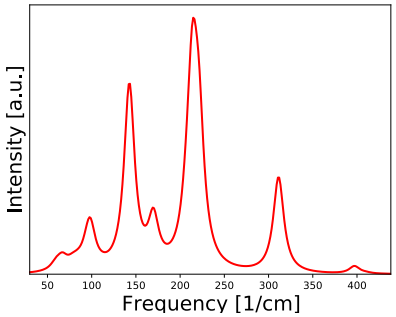
- 📋 Create checklists for your students to work through
- 🔗 Link checklist items to a question bank and/or tutorials
- ❓ Enable students contributions to the question bank
- ☑️ Use student peer-review to decide which questions are published
- 📊 Generate online plots to summarise class progress in real time

My update....

Prakriti Kayastha
BaZrS3

Michael Jones
Experiment/Theory CZTS

- **Research**
  - **Chalcogenide perovskites**
    - Vibrational spectroscopy $BaZrS_3$
    - Thermodynamics (NU-CEM/ThermoPot)
  - **Mixed cation halide perovskites** (more on this later)…
  - **Software**



JOSS
The Journal of Open Source Software

Funding opportunity
Software for research communities
SOLCORE
www.solcore.solar

Effmass

FHI-aims
The ab initio materials simulation package

Interoperability
Reproducibility

ChooChoo! The Checklist Tool

ThermoPot: An ab-initio thermodynamic modelling package

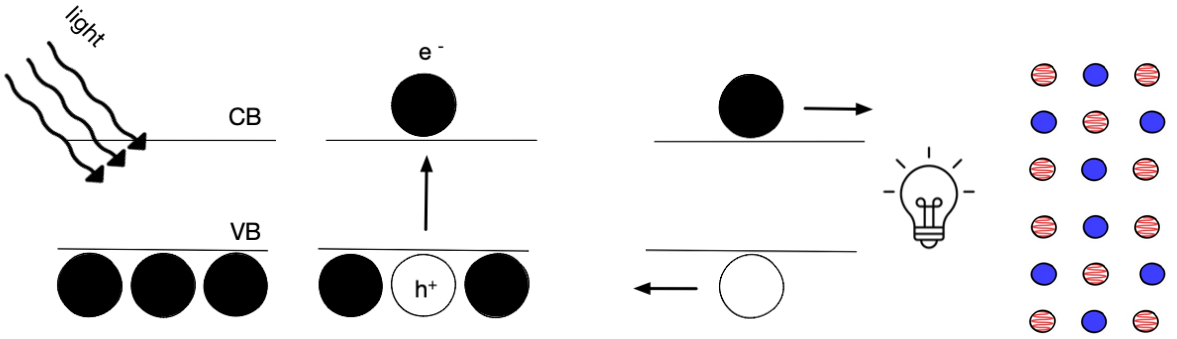
A-site mixing and non-radiative trapping

in hybrid halide perovskites

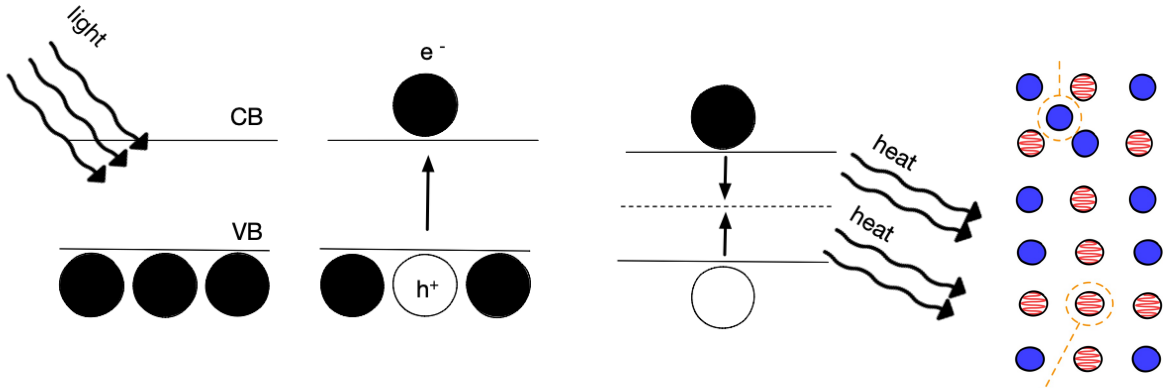
Unpublished results

A-site mixing and non-radiative trapping

in hybrid halide perovskites



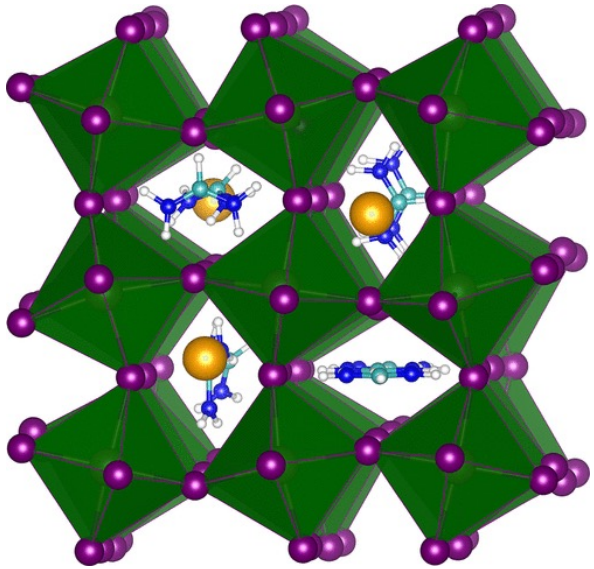
Electron and hole are extracted to the external circuit

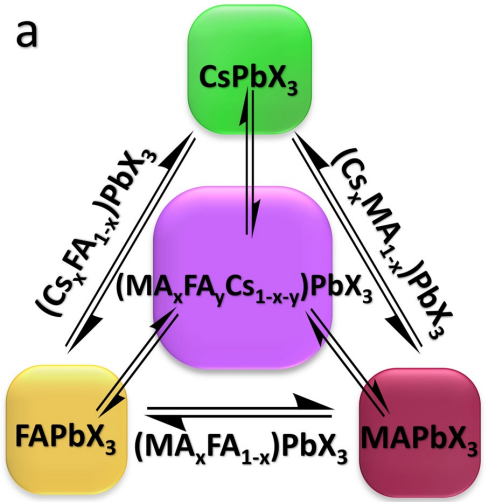


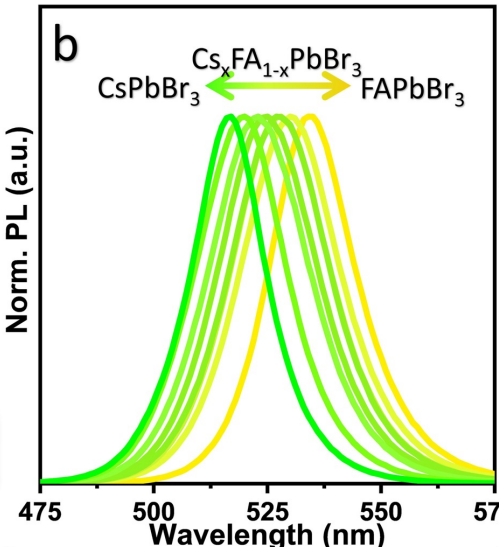
Point defects trap electron and/or hole. Energy lost as heat.

A-site mixing and non-radiative trapping

in hybrid halide perovskites (ABX_3)







Chem. Mater. 2018, 30, 15, 5194–5204

Angew. Chem.Int. Ed.2022,e202205617

Cesium (Cs)–formamidinium (FA)–methylammonium (MA) mixed cation perovskite materials have led to the most **efficient** and **stable** perovskite solar cells reported

A-site cation mixing

composition

What's the connection?

Non-radiative trapping rate

property

A-site cation mixing

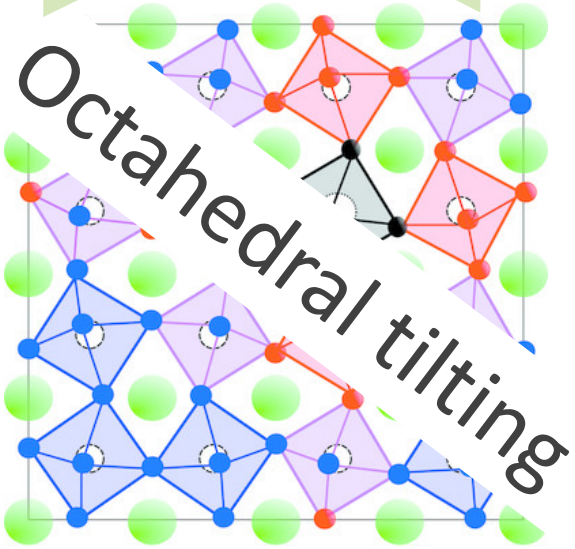
What's the connection?

Non-radiative trapping rate

composition

structure

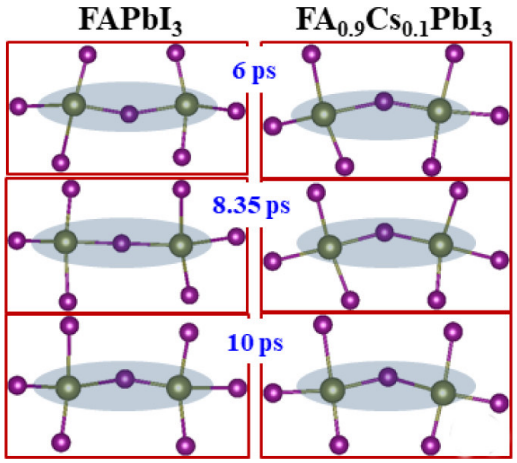
property



A-site cation mixing

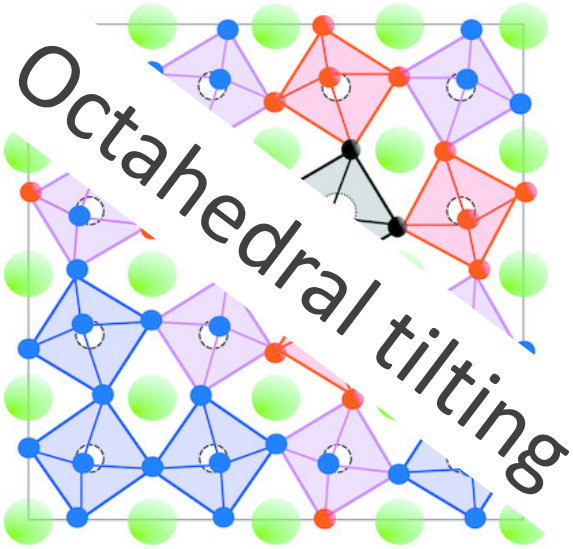
What's the connection?

Non-radiative trapping rate

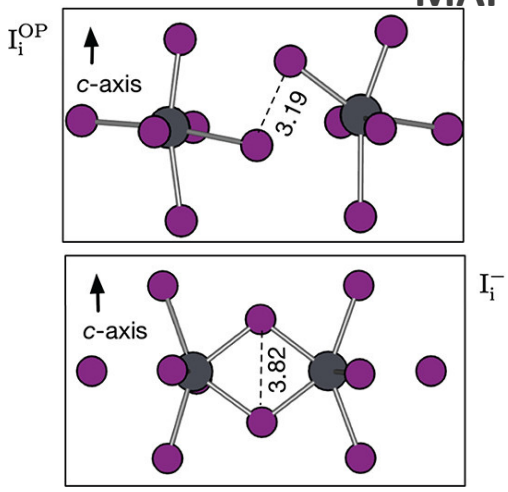


ACS Energy Lett. 2017, 2, 10, 2424-2429

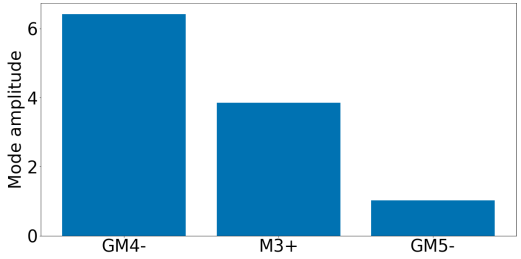
A-site mixing "locks in" tilt patterns



$MAPbI_3$



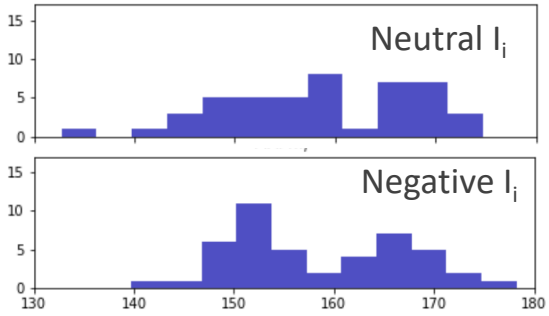
$MA_{0.875}Cs_{0.125}PbI_3$
mode decomposition



volume ⬇️
bandgap ⬆️
Direct E_g at Γ

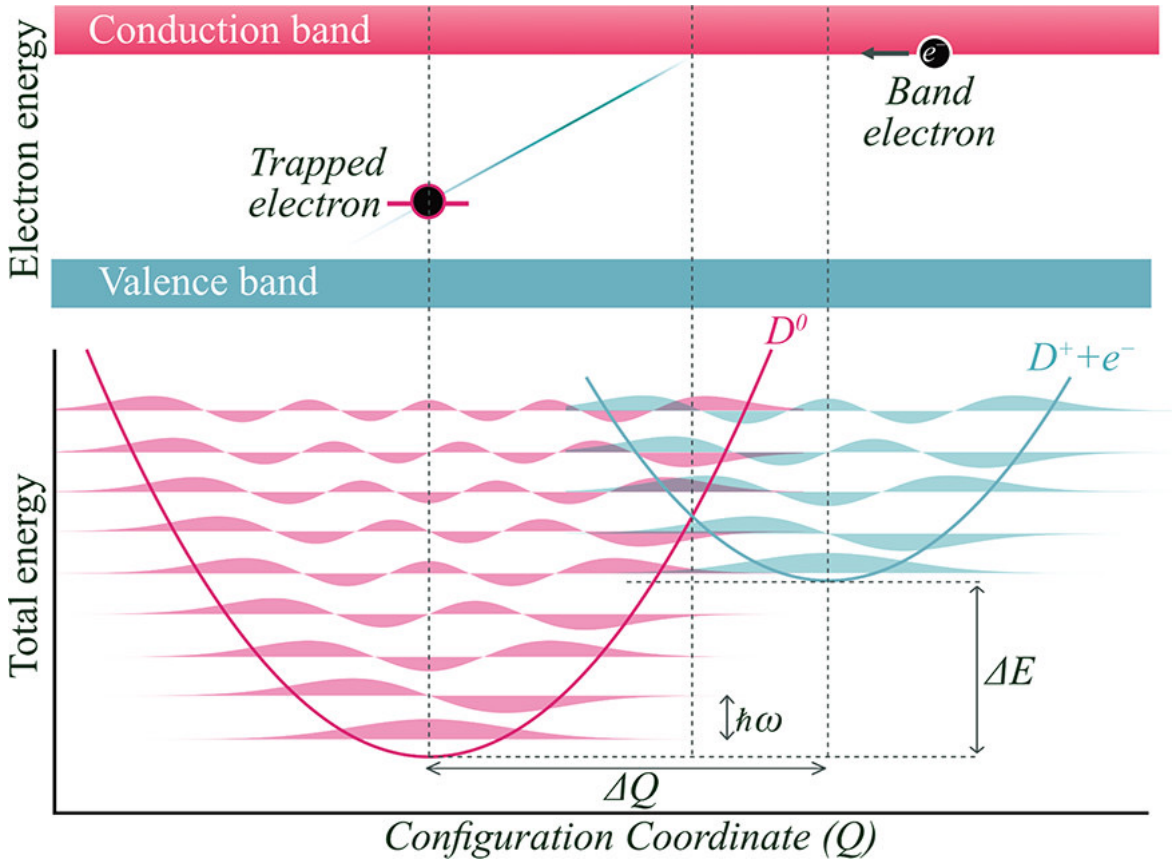
"Tilt relaxation" after carrier capture

Pb-I-Pb angle



J. Am. Chem. Soc. 2021, 143, 24, 9123–9128

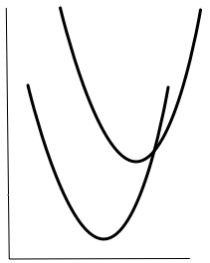
An energy surface is used to describe the change in energy and geometry after charge capture



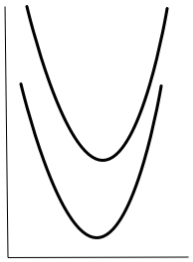
Three key quantities which determine capture rate:

ΔQ, ΔE, $\hbar\omega$

More generally, PES curvature



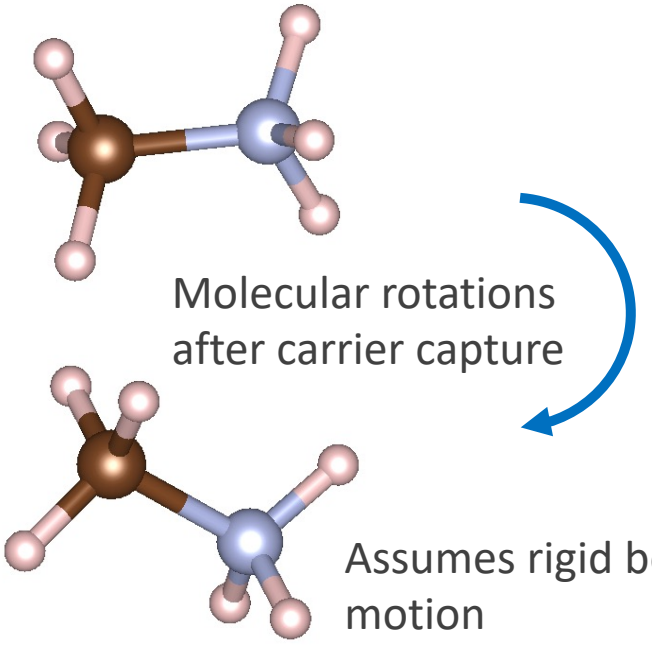
Octahedral tilting



No tilting

Question: Can A-site cation mixing be used to tune octahedral tilting and ΔQ ?

Kabsch interpolation is required to describe molecular rotations accurately



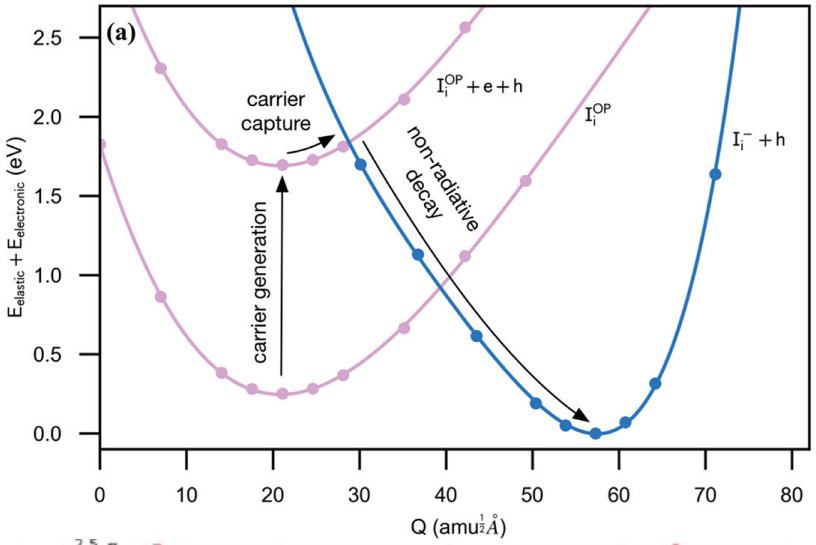
Molecular rotations after carrier capture

Assumes rigid body motion

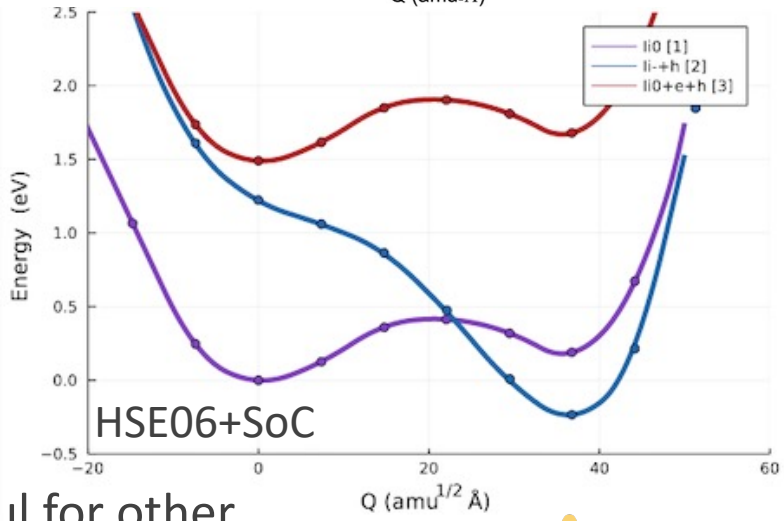
a and **b** are the vector components. Minimise *L(C)* to solve for rotation matrix *C*.

$$L(C) = \frac{1}{2}\sum_{i=1}^{n} w_i \|\mathbf{a}_i - C\mathbf{b}_i\|^2,$$

Iodine interstitial in MAPI



Translation only

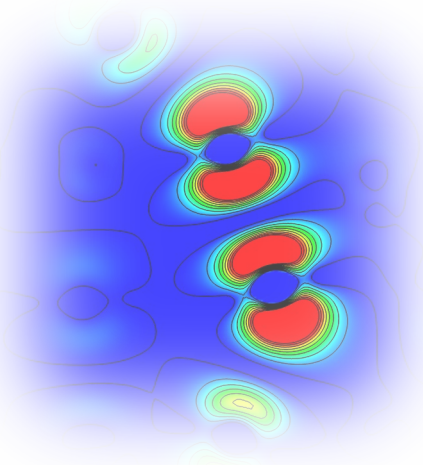


Translation and rotation

Kabsch interpolation may be useful for other systems – ASE-based code in development

Unpublished results

The iodine interstitial defect shows similar behaviour in single and mixed-cation perovskites

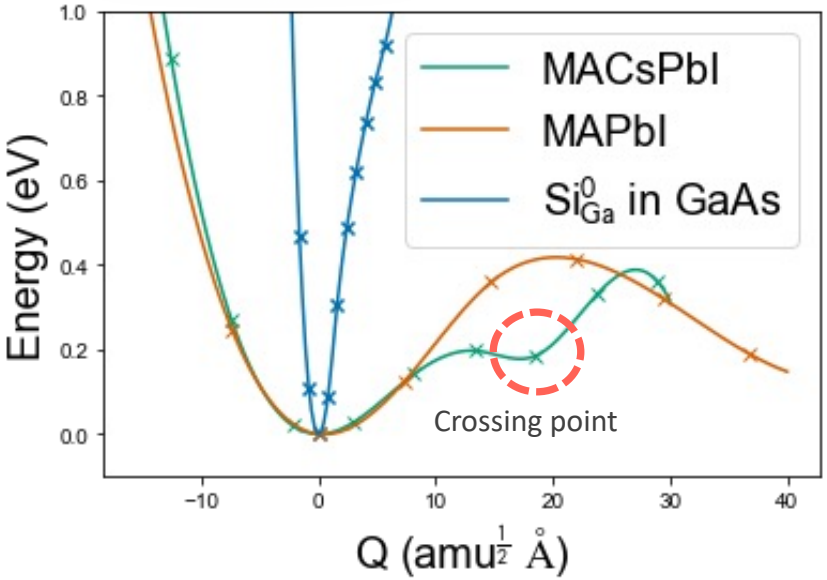


H-centre formed in mixed-cation materials up to a MA:Cs ratio 1:1

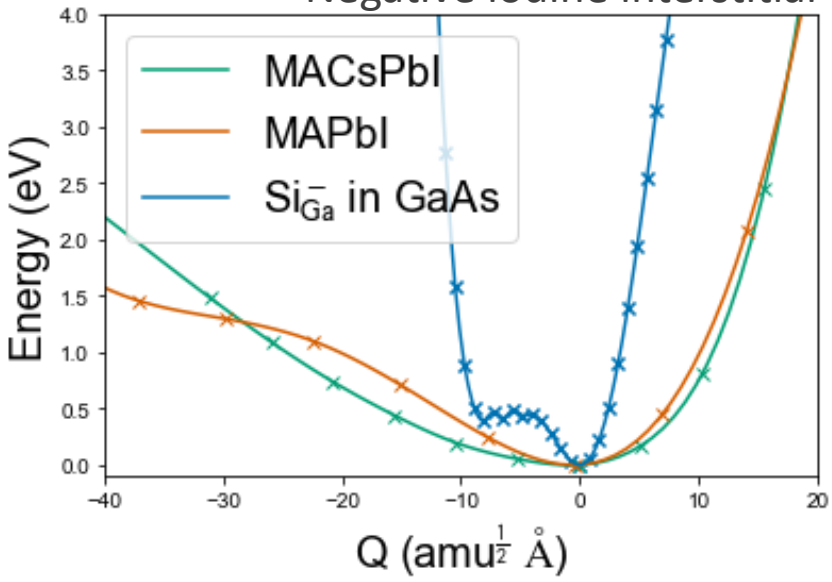
PES shape largely unaffected by mixing.

System	$\hbar\omega$ (meV) neutral	$\hbar\omega$ (meV) negative
Single cation: I_i	5.26	7.06
Mixed cation: I_i	5.26	5.90
DX-centre: Si_{Ga}	34.8	24.5

Neutral iodine interstitial



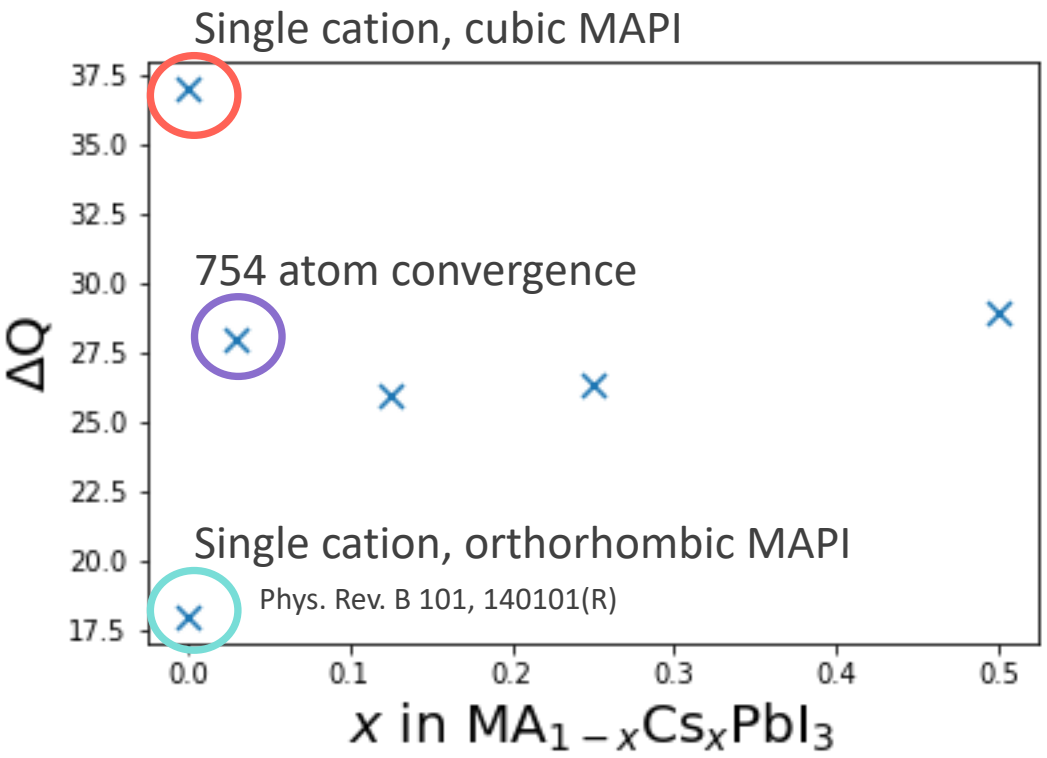
Negative iodine interstitial



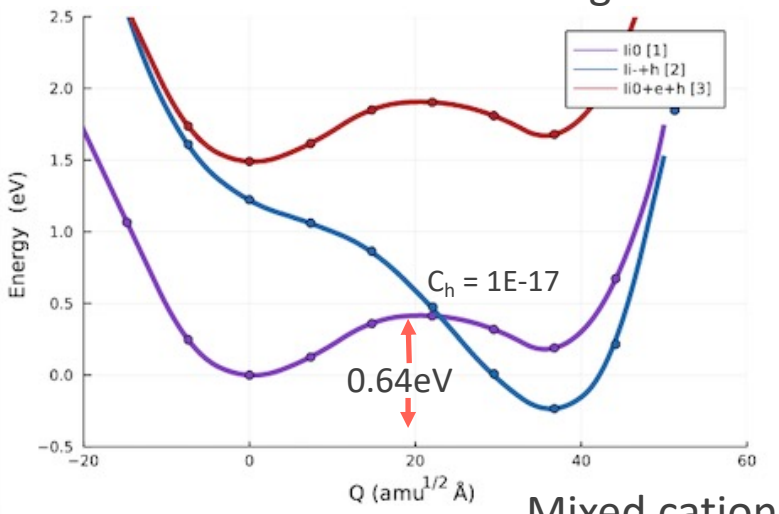
Unpublished results

A-site cation mixing reduces ΔQ, leading to an increase in the electron-hole recombination rate*

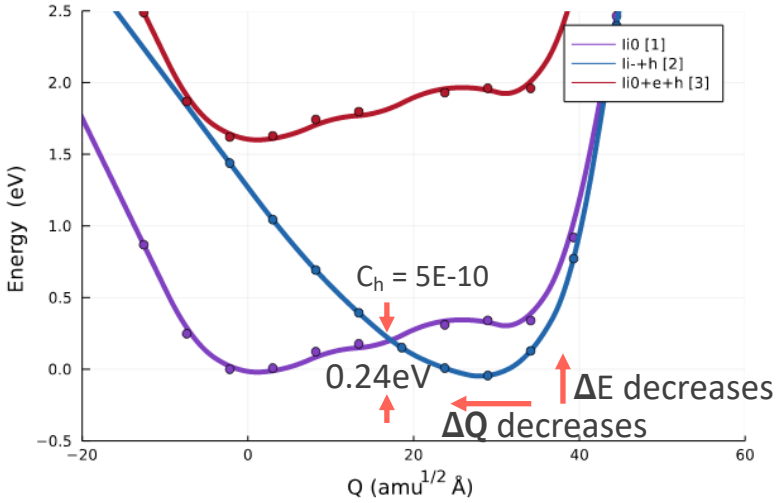
**EP-coupling term tbd*



Single cation



Mixed cation



The results indicate that A-site composition can be used to tune ΔQ and the capture rate at defect sites

Unpublished results

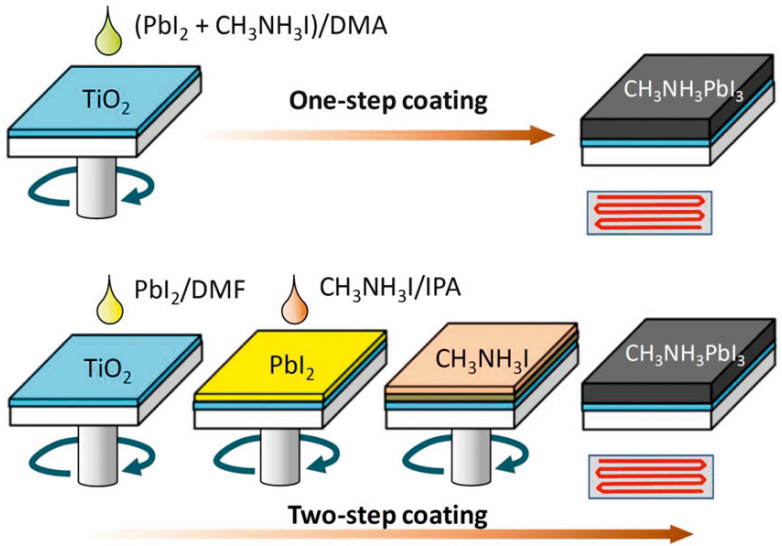
Thank you!!

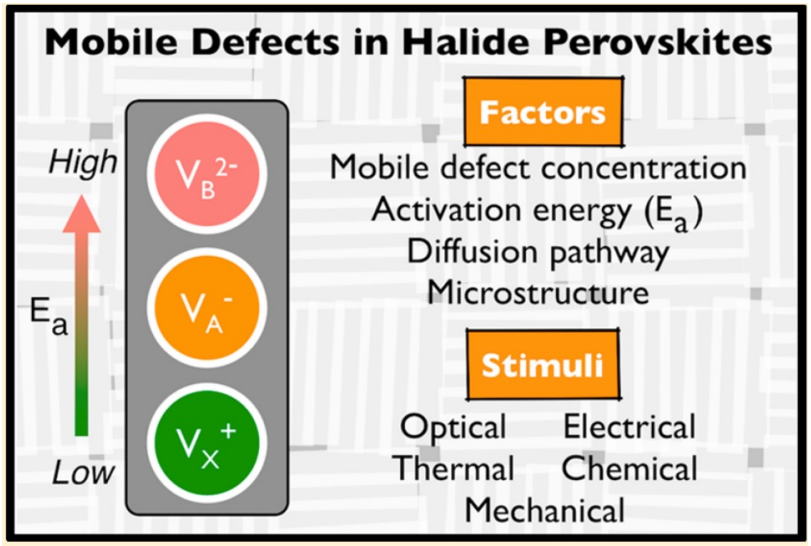
I have learnt a lot from the MDG, and have had a great time doing so

Get in contact -
l.whalley@northumbria.ac.uk

Here’s to the next 10 years

Hybrid halide perovskites have an unusual defect chemistry





High open circuit voltage from solution-processed materials – 1.1V in 2012

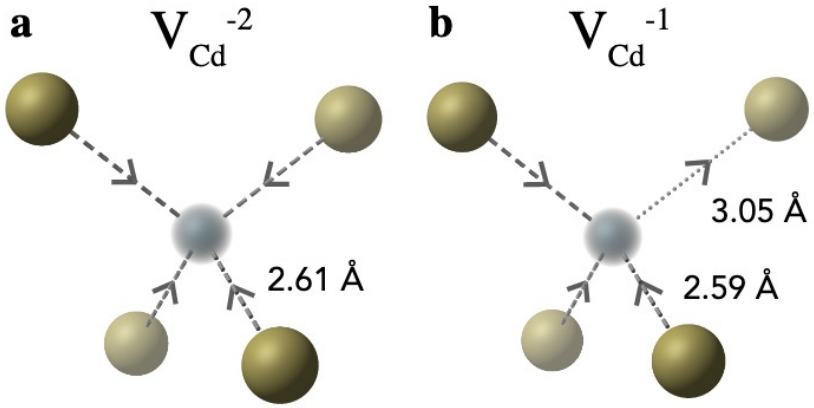
Lee et al. *Science* 2012 338, 6107, 643-647

Dynamic defects that are associated with halide segregation and hysteresis

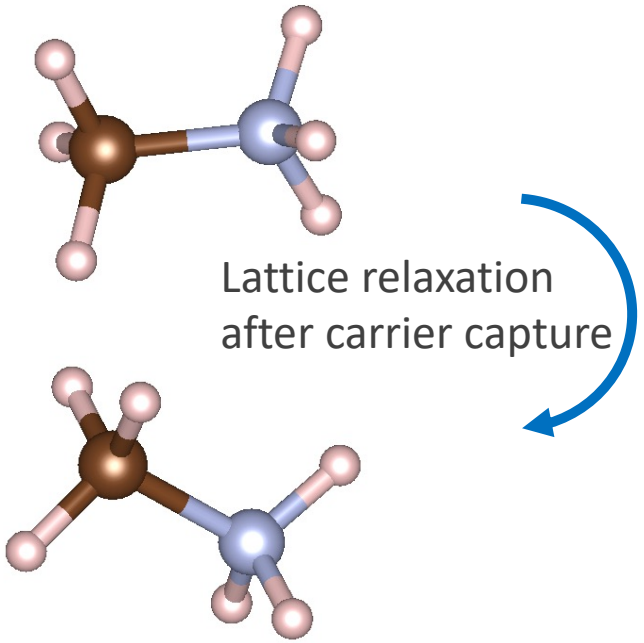
Walsh et al. *ACS Energy Lett.* 2018, 3, 8, 1983–1990

Kabsch interpolation is required to describe molecular rotations accurately

Linear interpolation is adequate for many systems

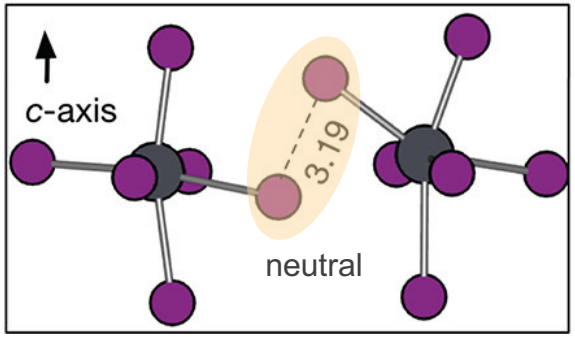


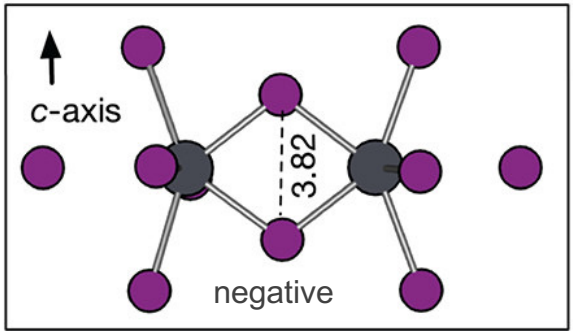
ACS Energy Lett. 2021, 6, 4, 1392–1398

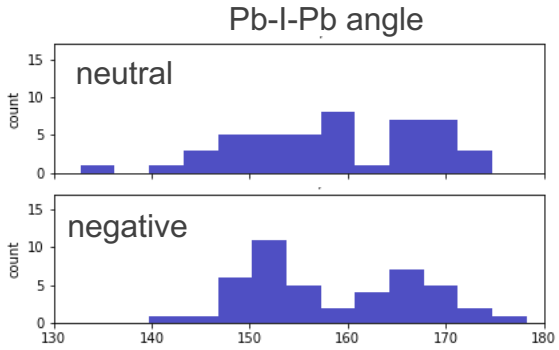


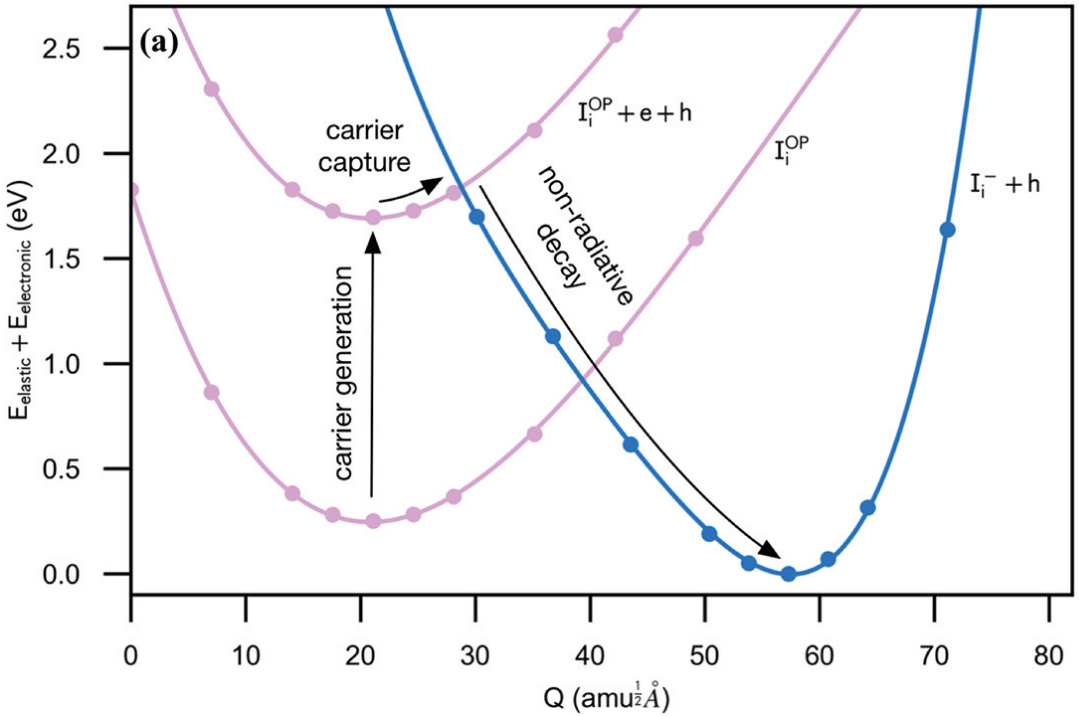
Our results demonstrate the strong electron-phonon coupling that is possible in soft semiconductors

Results for $CH_3NH_3PbI_3$:I_i using DFT (HSE06 +SoC)









	$MAPbI_3$:I_i	GaAs: DX
ΔE (eV)	1.7 [1]	1.7 [2]
ΔQ (amu^{½} Å)	36 [1]	9 [2]
$\hbar\omega$ (meV)	4.7 [1]	10 [3]
$S_{HR} = E/\hbar\omega$	350 [1]	75 [3]

[1] *J. Am. Chem. Soc.* 2021, 143, 9123−9128
[2] *Phys. Rev. B* 2019 100, 041202(R)
[3] *Phys. Rev. B* 1979, 19, 1015

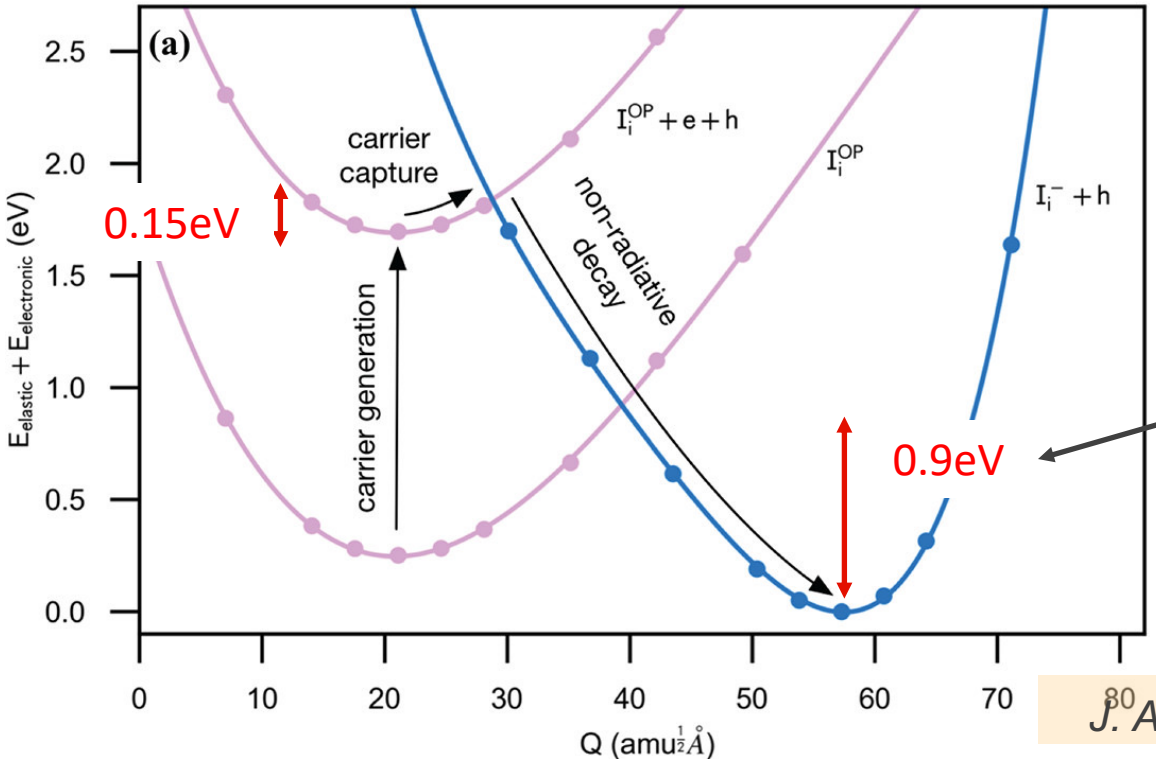
Electron capture at the neutral iodine interstitial is fast, subsequent hole capture is slow

$$C = V\frac{2\pi}{\hbar}gW_{\mathrm{if}}^2\sum_m \Theta_m \sum_n |\langle \chi_{im}|\Delta Q|\chi_{fn}\rangle|^2 \times \delta(\Delta E + m\hbar\omega_{\mathrm{i}} - n\hbar\omega_{\mathrm{f}})$$

Fermi's golden rule is used to give a quantum mechanical prediction of carrier capture coefficient *C*

capture rate = C x trap density x carrier density

Results for $CH_3NH_3PbI_3$:I_i using DFT (HSE06 +SoC)



e- capture rate:
10^{-10}cm^{3}s^{-1}

Radiative recomb. rate:
10^{-10}cm^{3}s^{-1} (*Nat. Comms* 2018, 9 (1), 293)

This asymmetry has been observed in transient photocurrent and absorption spectroscopy (*Energy Environ. Sci.* 2016, 9, 3472-3481) and is one explanation for the observed high open circuit voltages

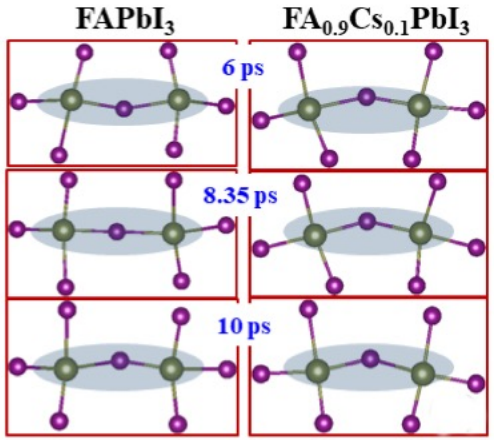
Associated paper

J. Am. Chem. Soc. 2021, 143, 9123−9128

Follow on questions:

Can we translate this result to other systems?

- Mixed A-site cation materials (FA/MA/Cs)
- Grain boundaries

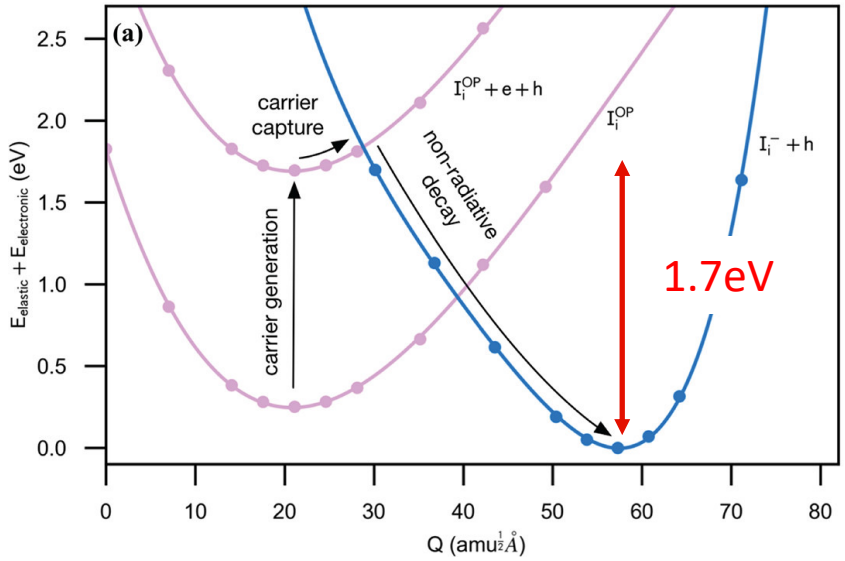


Locked octahedral tilting in mixed A-site cations*:*
ACS Energy Lett. 2017, 2, 2424−2429

Can we connect this result to the observed unusual macroscopic processes?

- halide transport
- Light-induced thermal degradation

  e.g. *J. Mater. Chem. C*, 2019, 7, 9326-9334



Thank you for listening

Dr Lucy Whalley

lucydot.github.io/talks/

l.whalley@northumbria.ac.uk

Associated paper:

J. Am. Chem. Soc. 2021, 143, 24, 9123–9128

Co-authors/collaborators:

Puck van Gerwen, Sunghyun Kim, Jarvist Frost, Samantha Hood, Aron Walsh

Additional picture credits:

Slide 3: https://doi.org/10.1557/mrs.2015.166

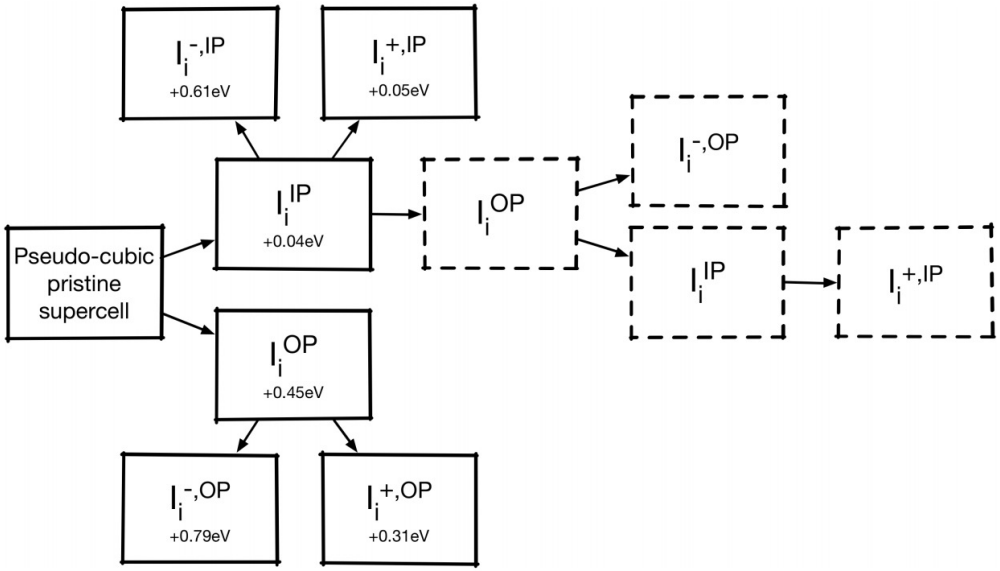
- A-site mixing determines the extent of tilting

- Tilting is associated with charge capture at the iodine interstitial
- What is the relationship between A-site mixing and charge capture?
- Can we use A-site mixing to control the rate of charge capture?
- Prediction: If I mix MA:Cs then I can shift delta Q and adjust the capture rate. The shape and energetics may not be affected in the same way.
- Test prediction/

- Kabsch rotation, SQS structures

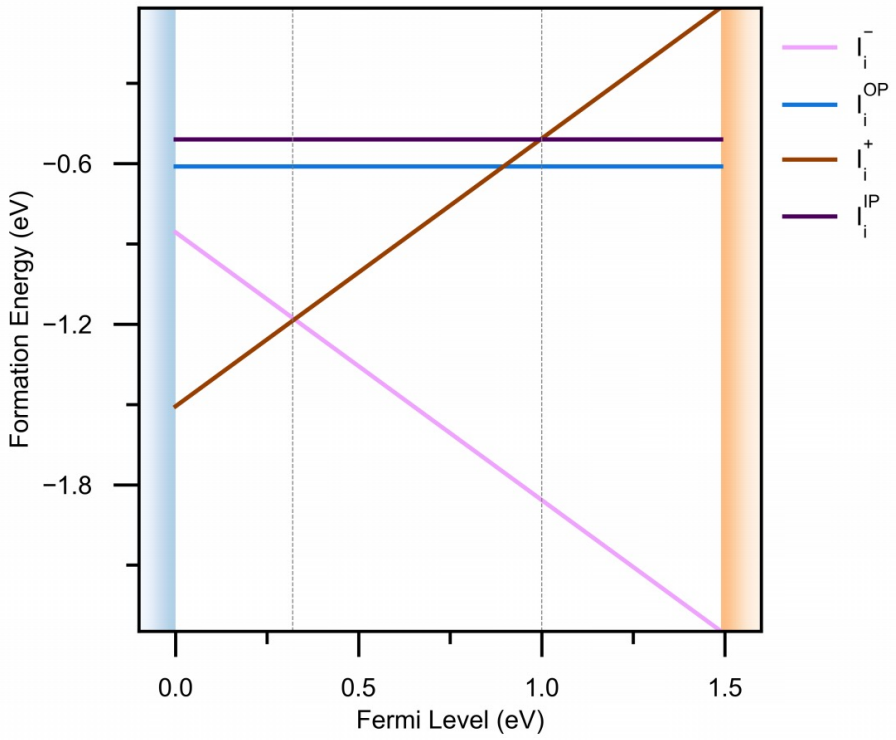
Calculation details

- The underlying electronic structures were calculated using density functional theory (DFT) - plane wave basis set with an energy cutoff of 400 eV.
- Projection operators were optimized in real space with an accuracy of 0.02 meV per atom
- 2 × 2 × 2 gamma centered Monkhorst–Pack mesh was used for the Brillouin zone integration.
- HSE06 functional with spin-orbit coupling for the PES
- PBEsol functional for the electron-phonon coupling term
- The interstitial was placed in a 192-atom pseudocubic supercell.

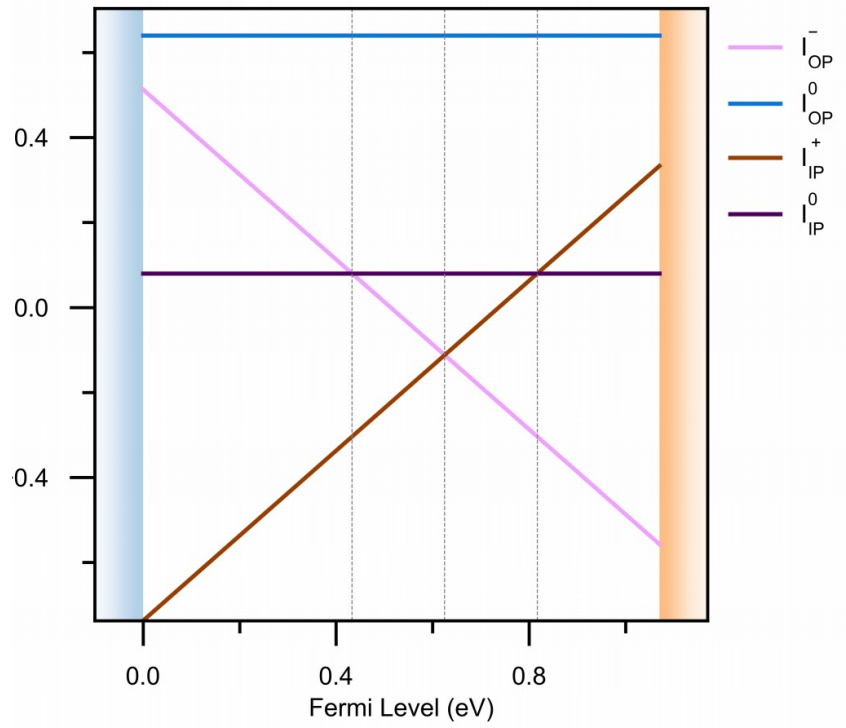


Charge transition levels MAPI:I_i

Ground state defect geometries



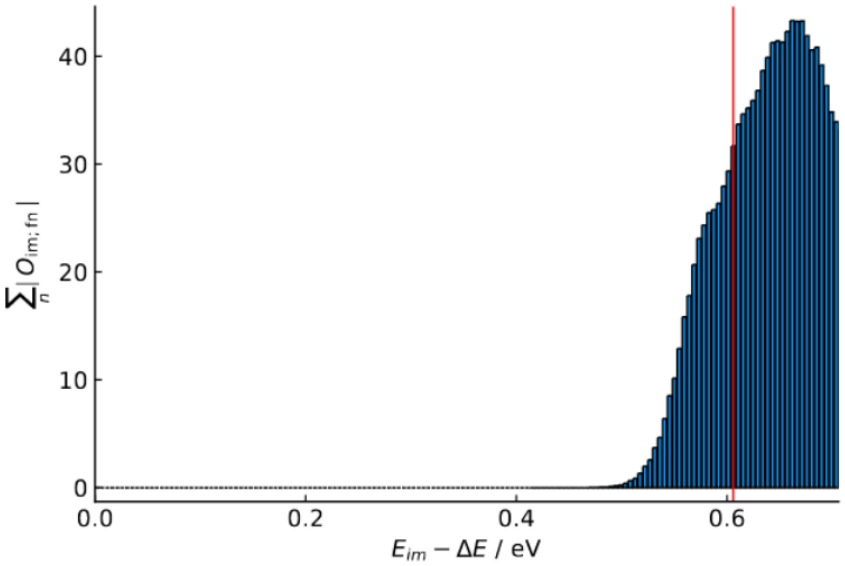
Metastable defects



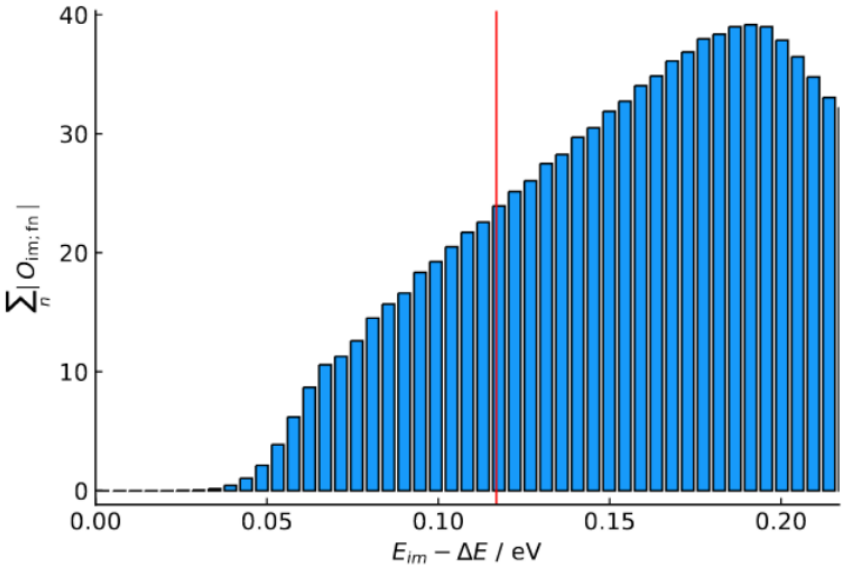
Negative U behaviour, with the neutral defect metastable in equilibrium. The charge transition levels are highly sensitive to the defect geometry and XC functional used.

Quantum tunnelling in MAPI:I_i

harmonic



anharmonic



Electron capture is not fully classical as phonon overlap persists below the classical barrier (red), resulting in significant quantum tunnelling.