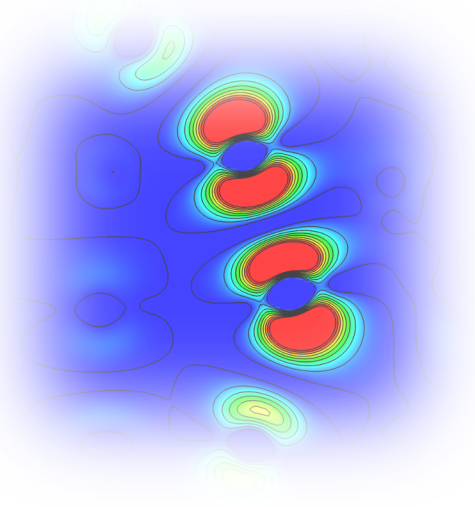
Non-radiative carrier trapping

at the iodine interstitial in hybrid perovskite solar cells



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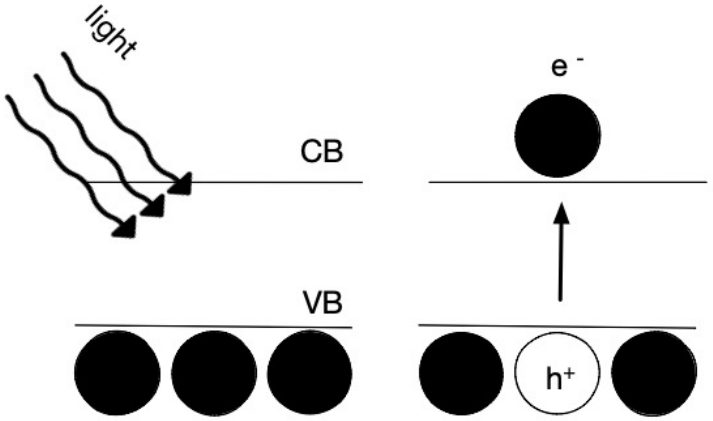
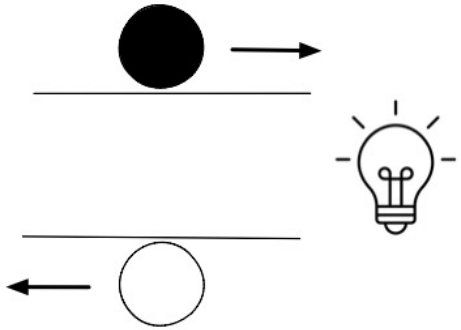
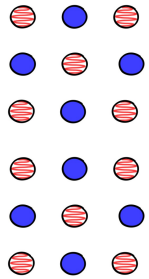
Why is non-radiative carrier trapping important?

In a PV material, a photon excites an electron into the conduction band

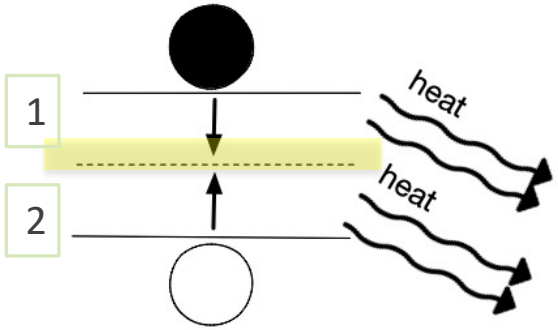




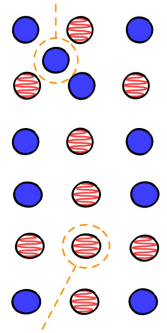
Ideally, the electron and hole are extracted to the external circuit



Shockley-Reed-Hall model: non-radiative recombination is a two-step process – e^- and h^+ trapping required.

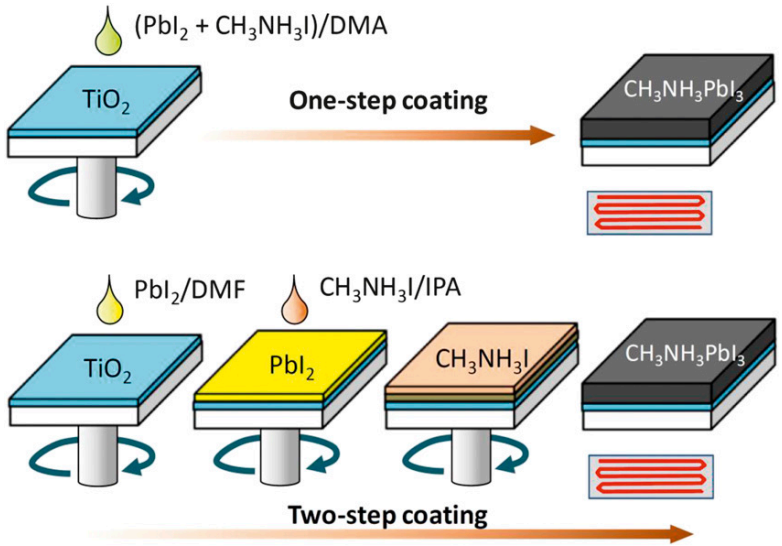


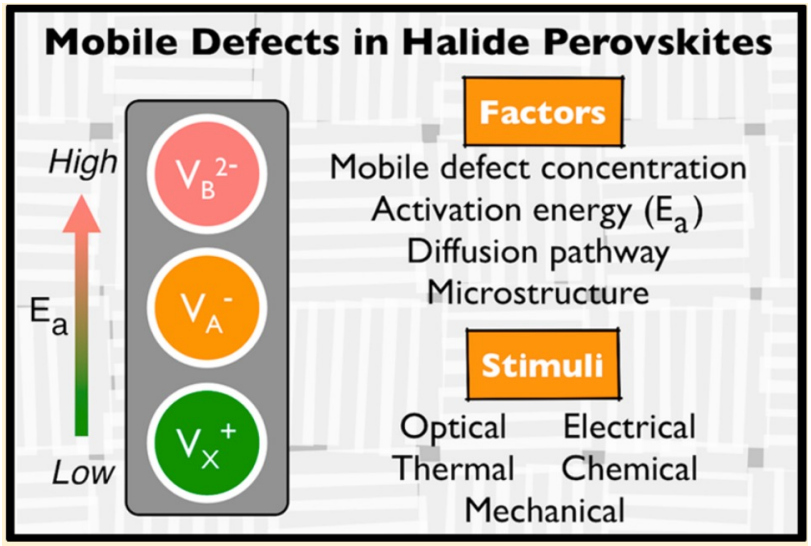
However point defects can introduce electronic trap states in the band gap



Non-radiative recombination: electronic energy is lost as thermal energy, leading to a reduction in open-circuit voltage

Hybrid halide perovskites have an unusual defect chemistry





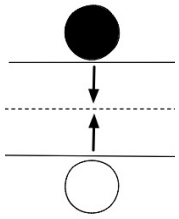
High open circuit voltage from solution-processed materials – 1.1V in 2012

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

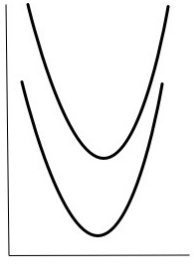
Dynamic defects that are associated with halide segregation and hysteresis

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

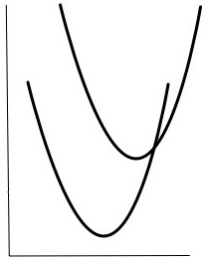
An energy surface is used to describe the change in energy and geometry after charge capture

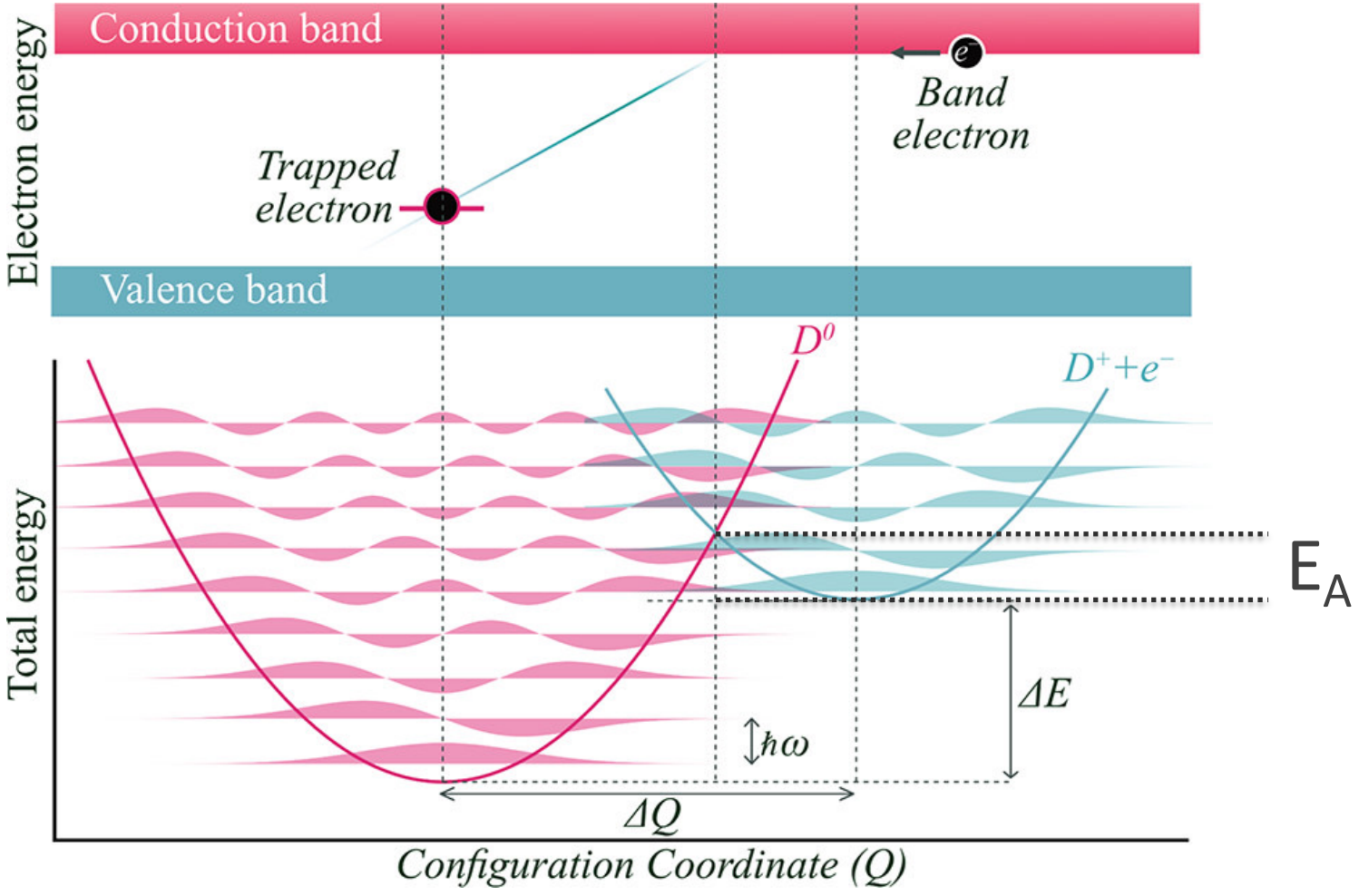


Weak coupling



Intermediate coupling

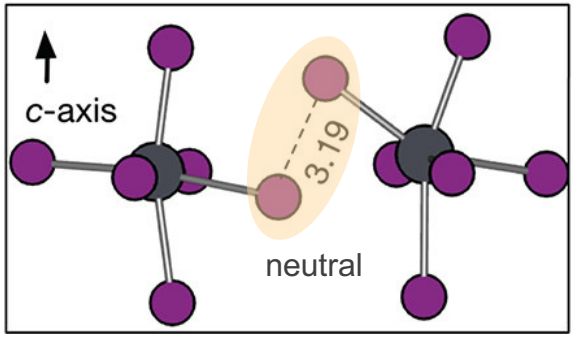


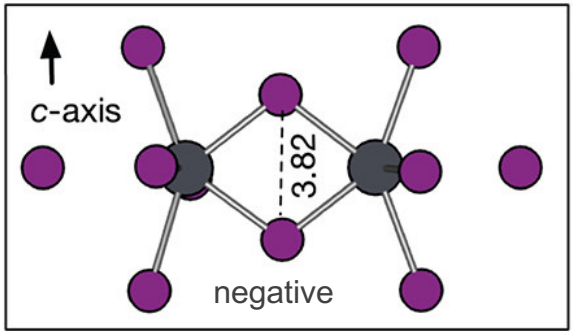


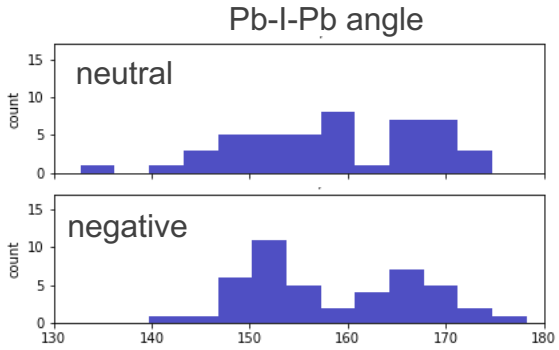
The capture rate is sensitive to E_A, which is determined by ΔQ, ΔE, $\hbar\omega$

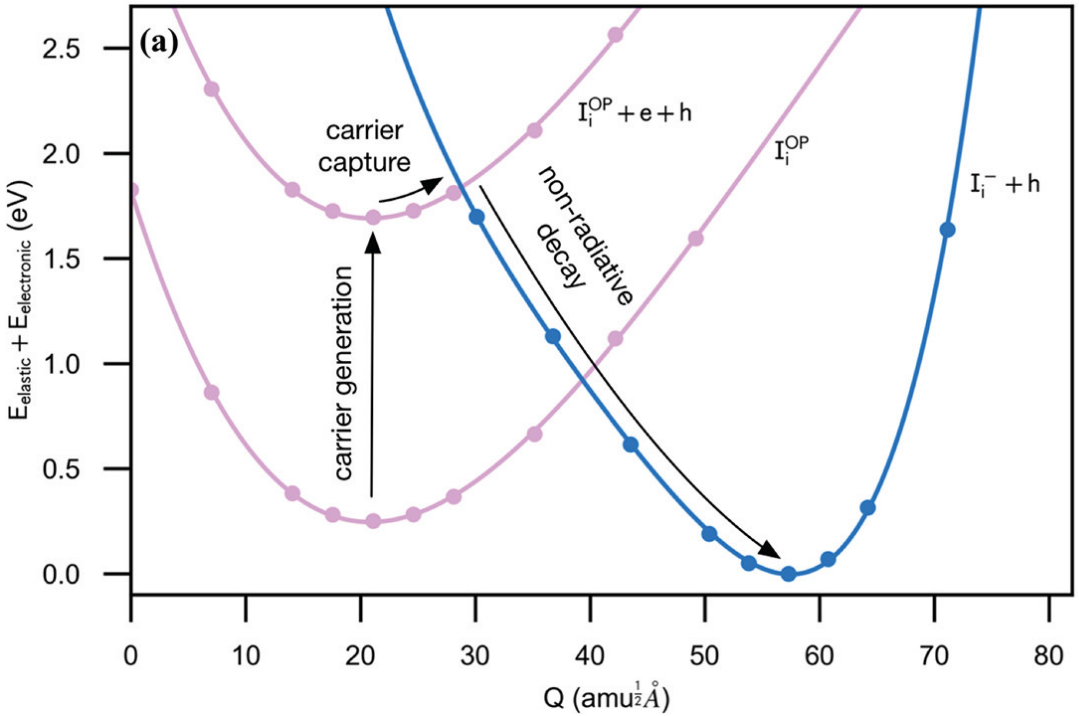
Our results demonstrate the strong electron-phonon coupling that is possible in soft semiconductors

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

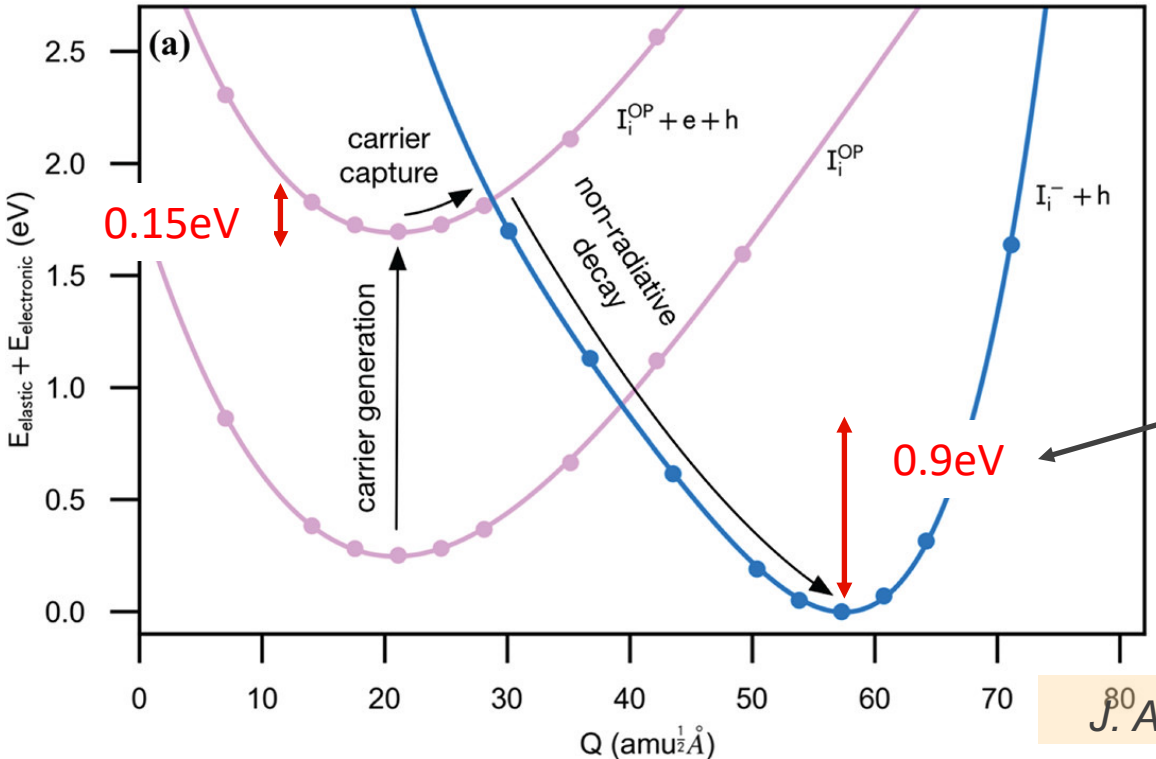
Electron capture at the neutral iodine interstitial is fast, subsequent hole capture is slow

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

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

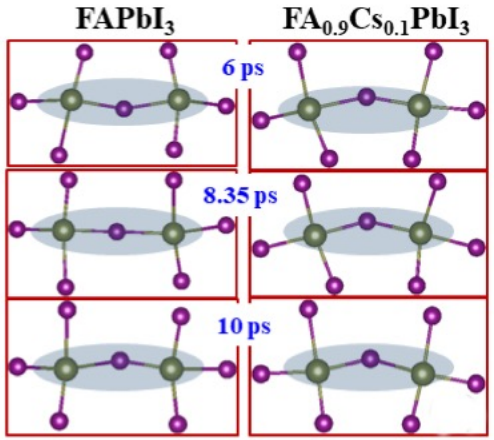
Associated paper

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

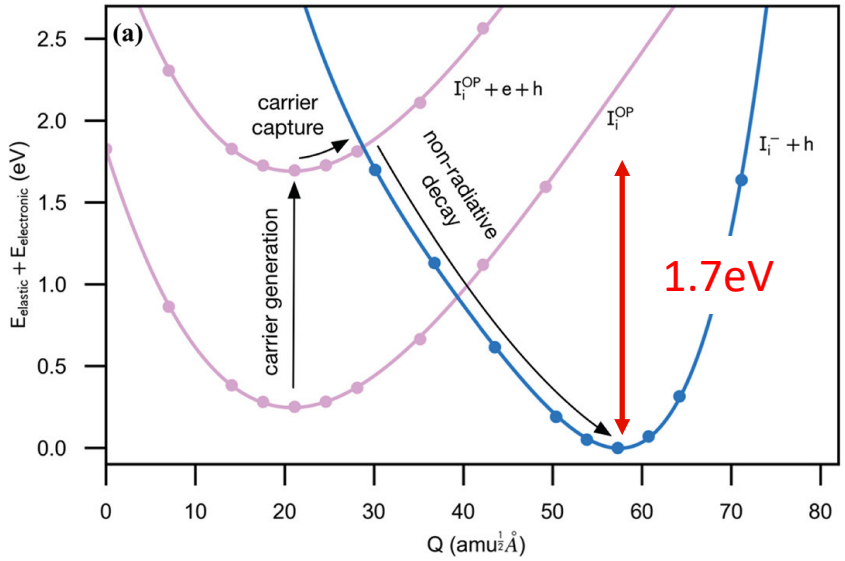


Locked octahedral tilting in mixed A-site cations*:*
ACS Energy Lett. 2017, 2, 2424−2429

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

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Associated paper:

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

Co-authors/collaborators:

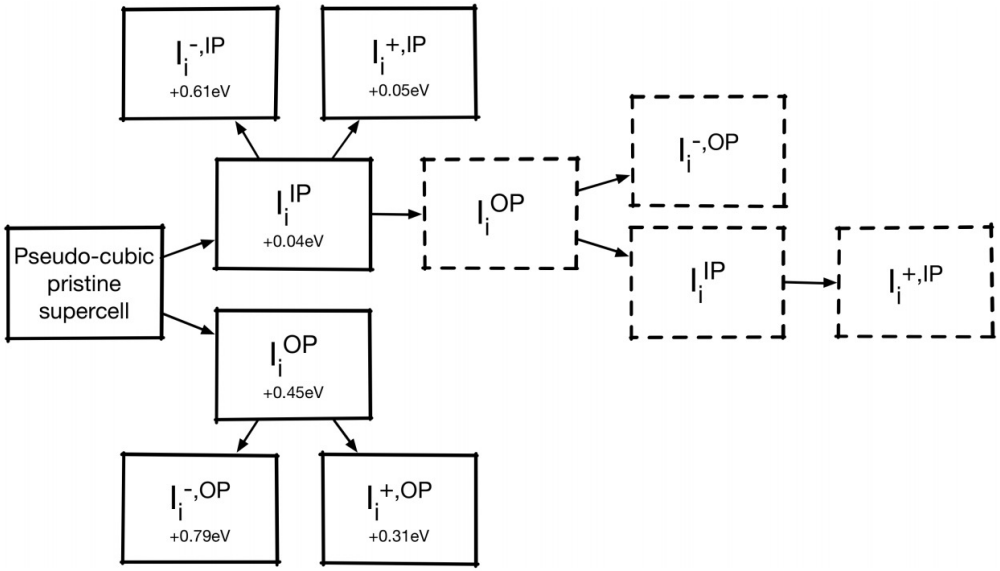
Puck van Gerwen, Sunghyun Kim, Jarvist Frost, Samantha Hood, Aron Walsh

Additional picture credits:

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

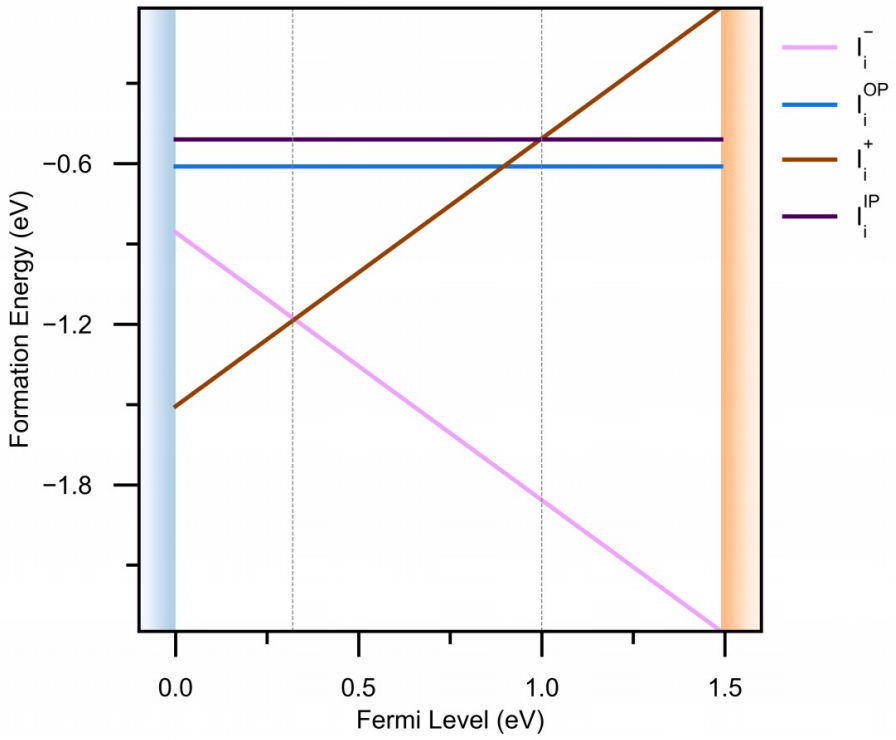
Calculation details

- 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.

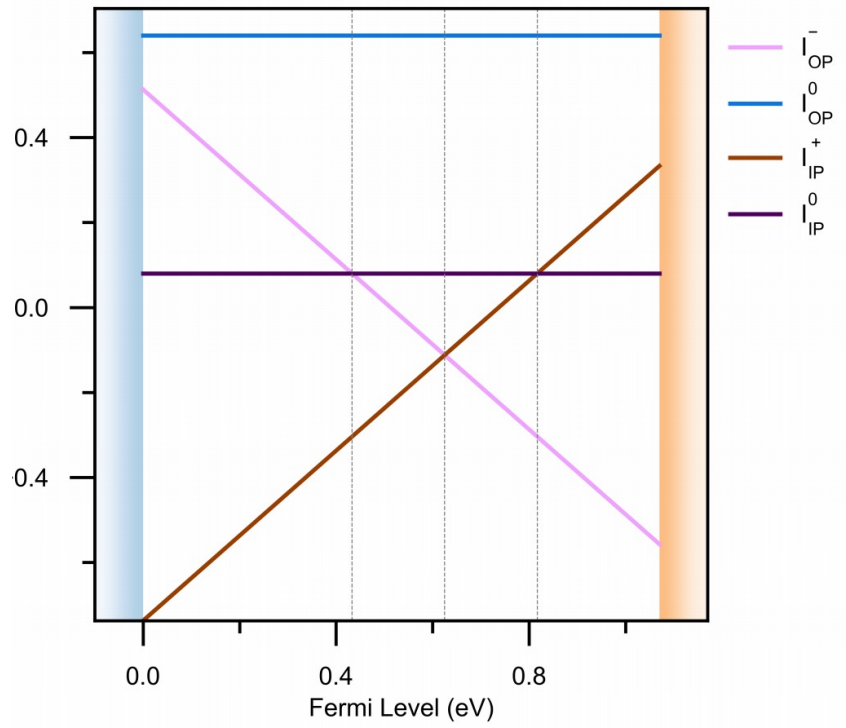


Charge transition levels MAPI:I_i

Ground state defect geometries



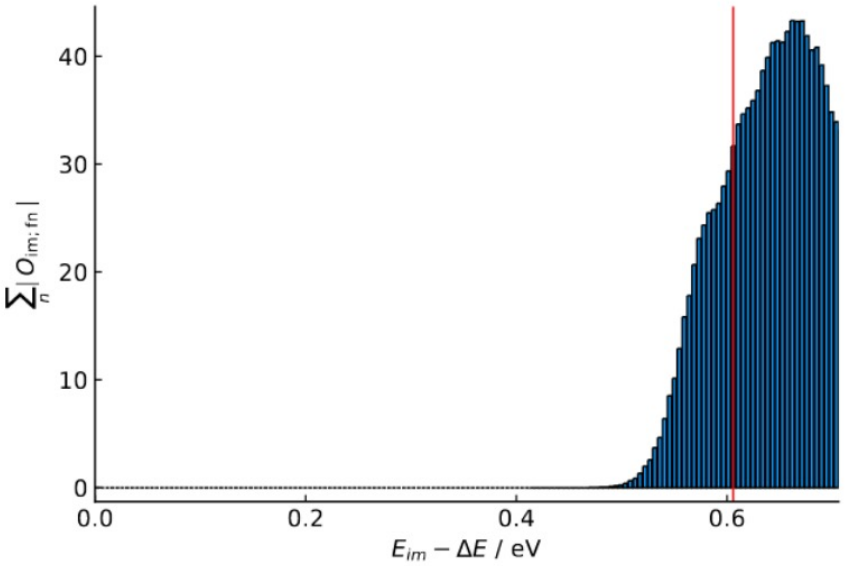
Metastable defects



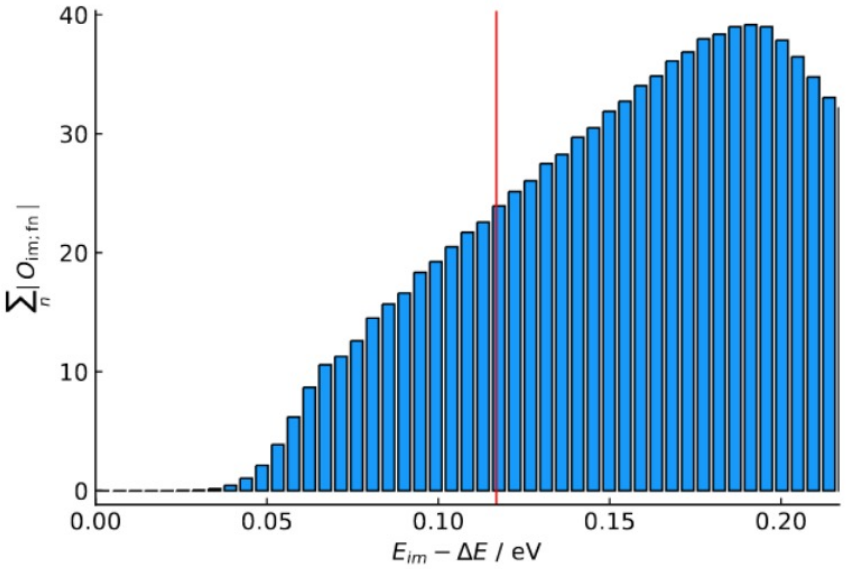
Negative U behaviour, with the neutral defect metastable in equilibrium. The charge transition levels are highly sensitive to the defect geometry and XC functional used.

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.