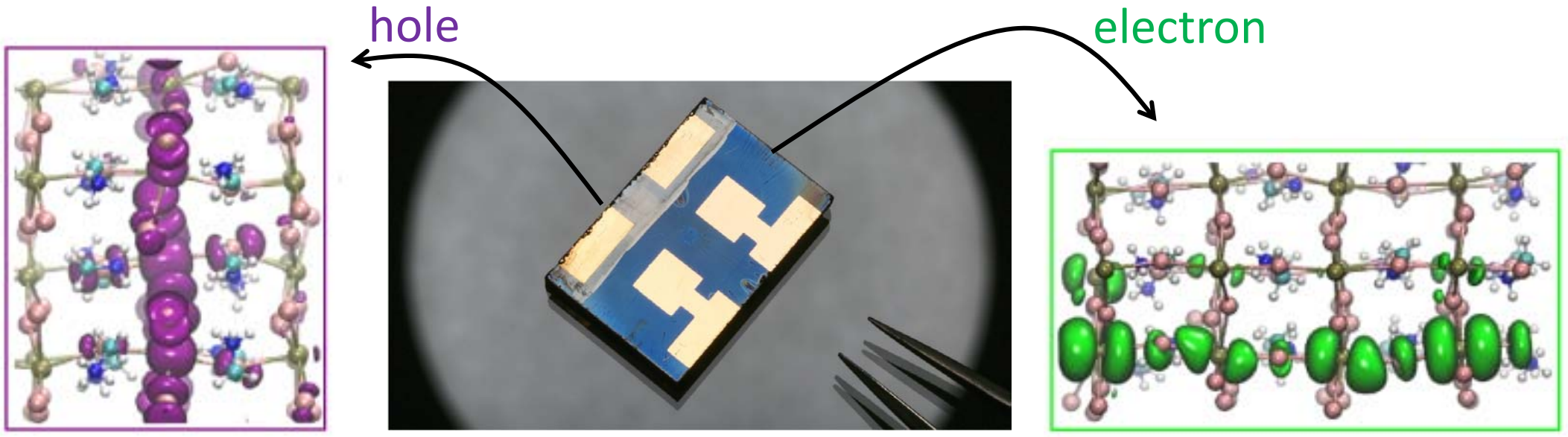
On the electronic properties of metal halide perovskites

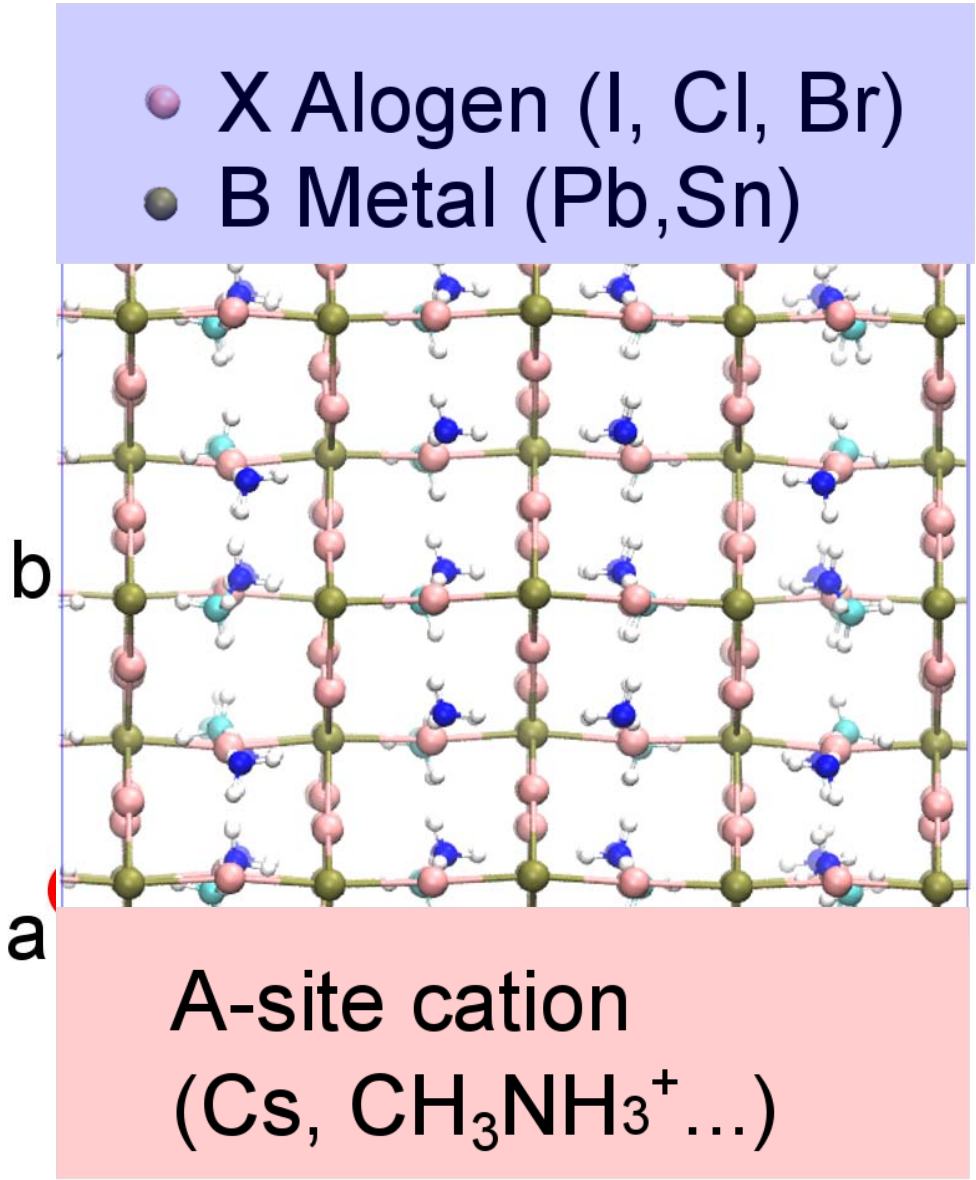
Francesco Ambrosio



DSCTM-CNR YIA2019, Bressanone 30/10/2019

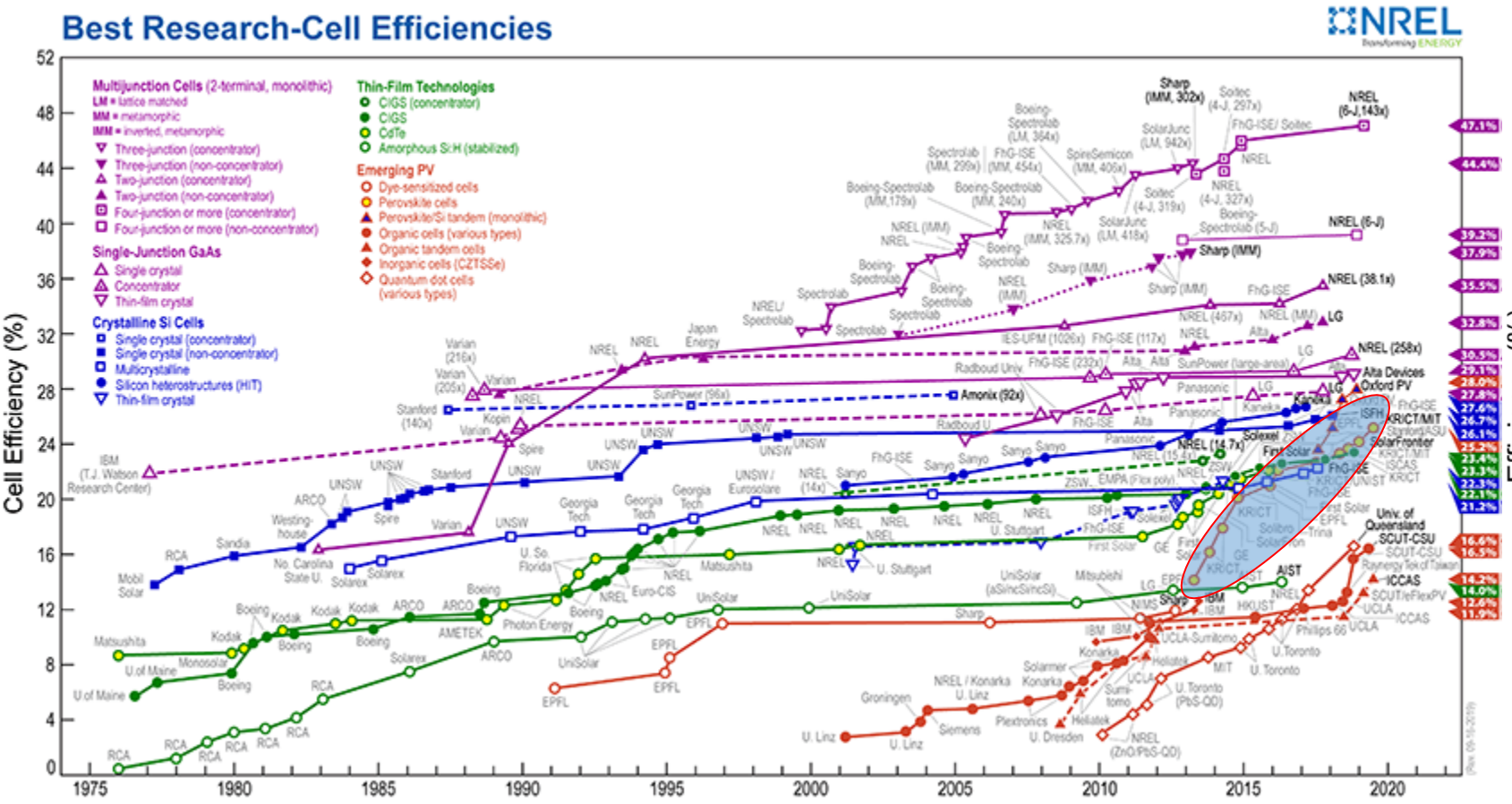
Metal halide perovskite, who art thou?

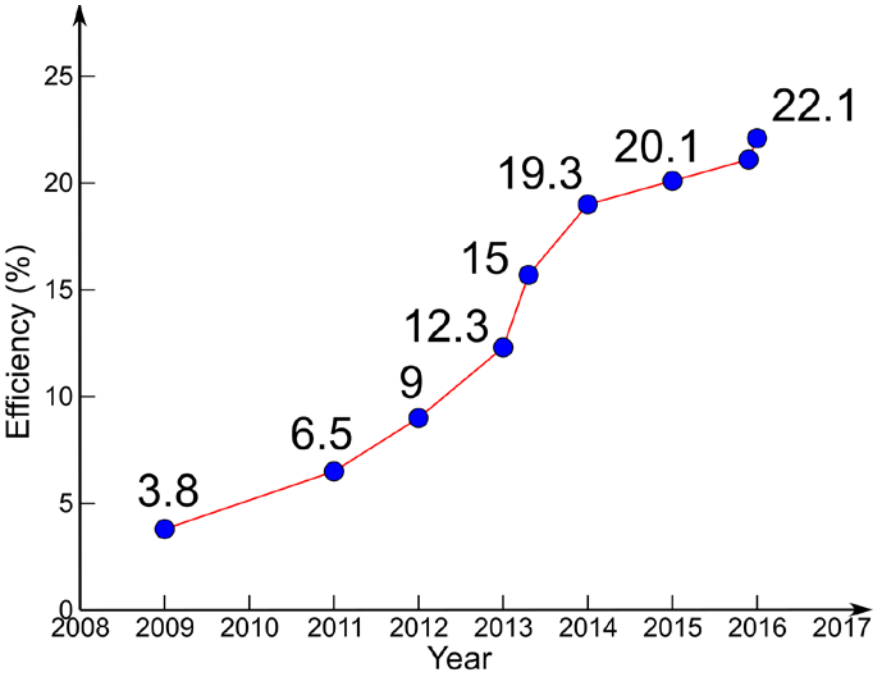
General formula ABX_3



- Easily sinthetized
- Highly tunable electronic properties
- Numerous possible applications

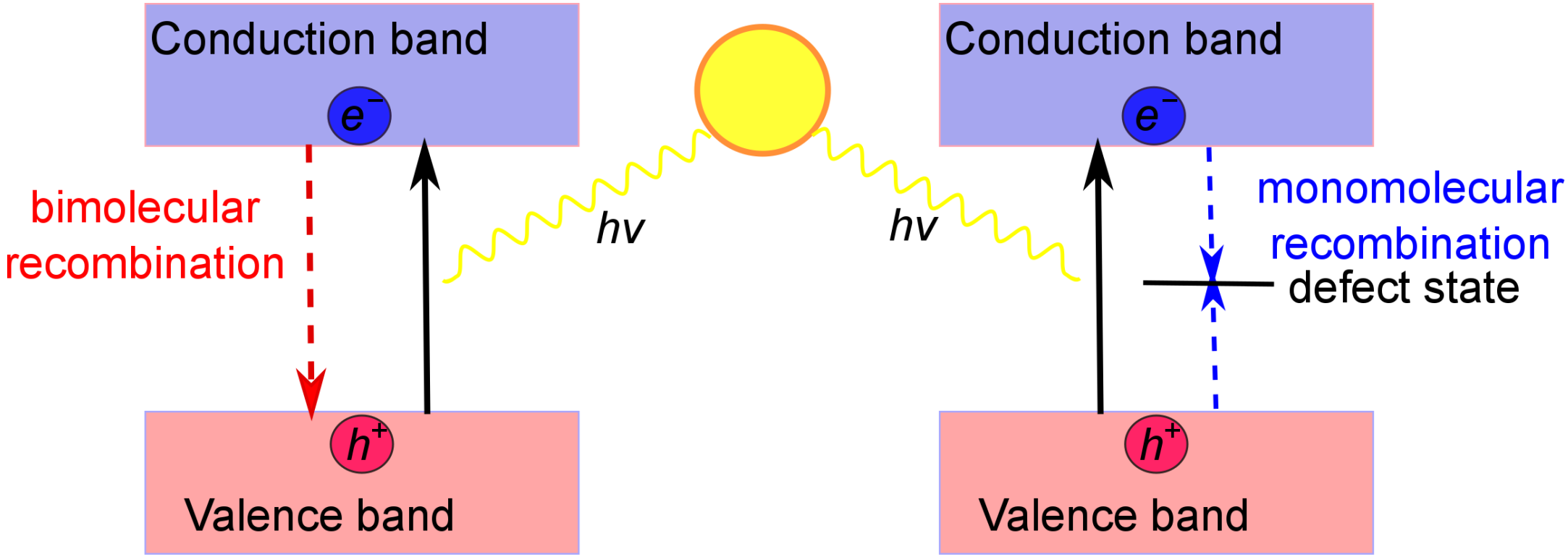
Metal halide perovskites for photovoltaics…why?





First answer: unprecedented growth!

Ok, but again…why? Let's talk about recombination



Both charge loss mechanisms are very slow in MHPs!

Ehm…But why?

Large polarons in metal halide perovskites (?)

2015

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Viewpoint

pubs.acs.org/JPCL

Charge Carriers in Hybrid Organic–Inorganic Lead Halide Perovskites Might Be Protected as Large Polarons

2016

ARTICLE

Received 1 Jun 2015 | Accepted 14 Jun 2016 | Published 1 Aug 2016

DOI: 10.1038/ncomms12253 OPEN

Extended carrier lifetimes and diffusion in hybrid perovskites revealed by Hall effect and photoconductivity measurements

Y. Chen[1,†], H.T. Yi[1], X. Wu[2], R. Haroldson[3], Y.N. Gartstein[3], Y.I. Rodionov[4], K.S. Tikhonov[5], A. Zakhidov[3,4], X.-Y. Zhu[2] & V. Podzorov[1,6]

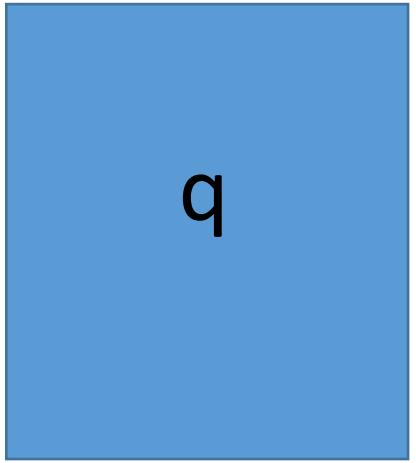
2017

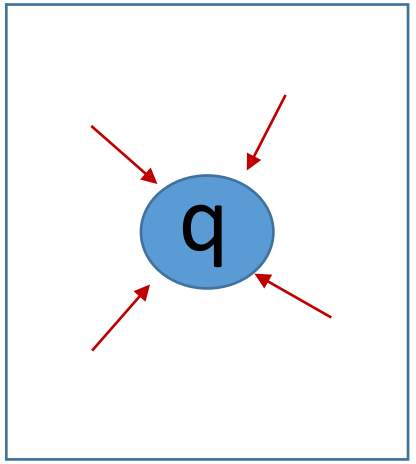
SCIENCE ADVANCES | RESEARCH ARTICLE

MATERIALS SCIENCE

Large polarons in lead halide perovskites

Kiyoshi Miyata,[1] Daniele Meggiolaro,[2,3] M. Tuan Trinh,[1] Prakriti P. Joshi,[1] Edoardo Mosconi,[2,3] Skyler C. Jones,[1] Filippo De Angelis,[2,3]* X.-Y. Zhu[1]*





Meanwhile somewhere else…

Prof. Alfredo Pasquarello

Advanced techniques to simulate polarons in different materials

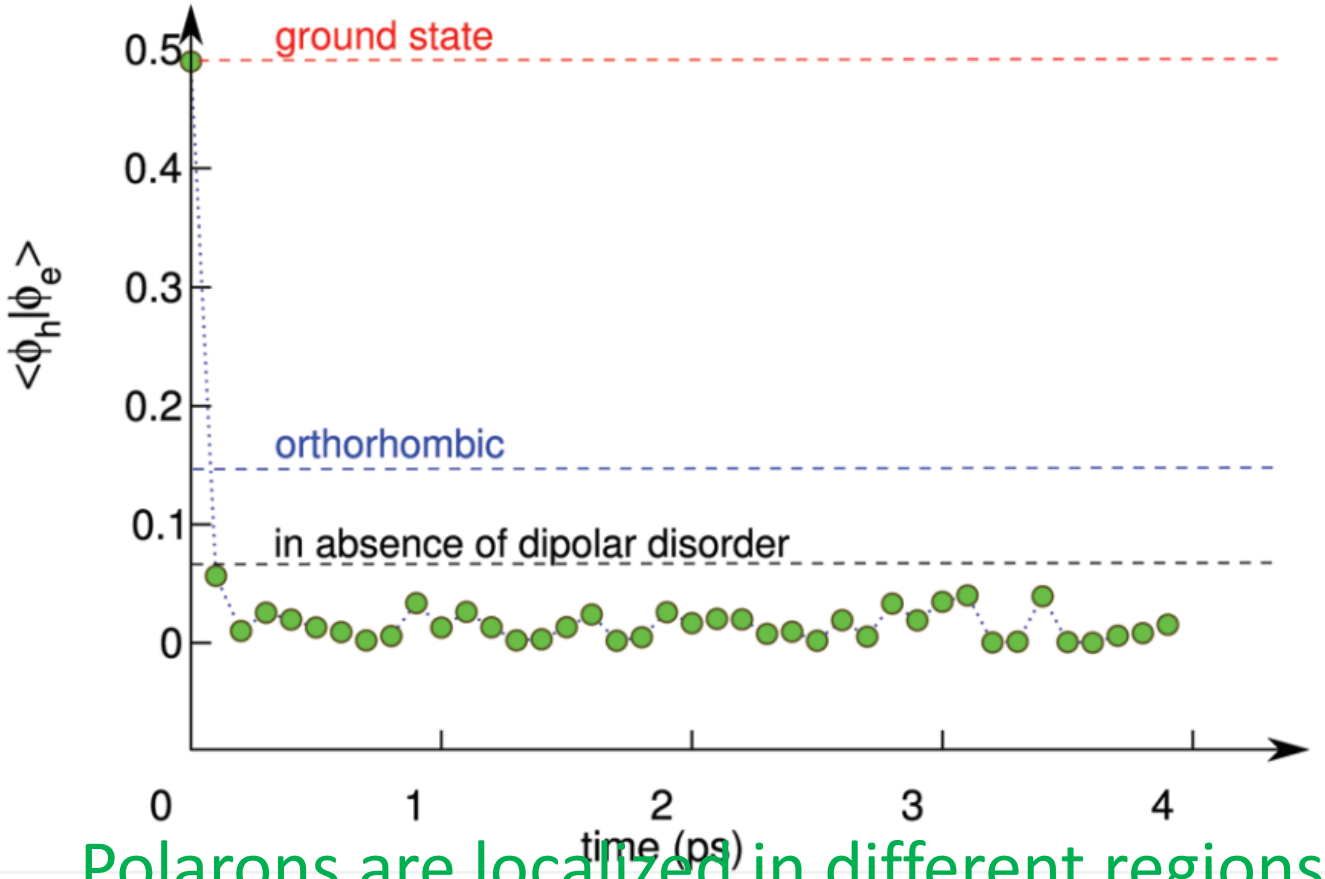
e.g. the solvated electron

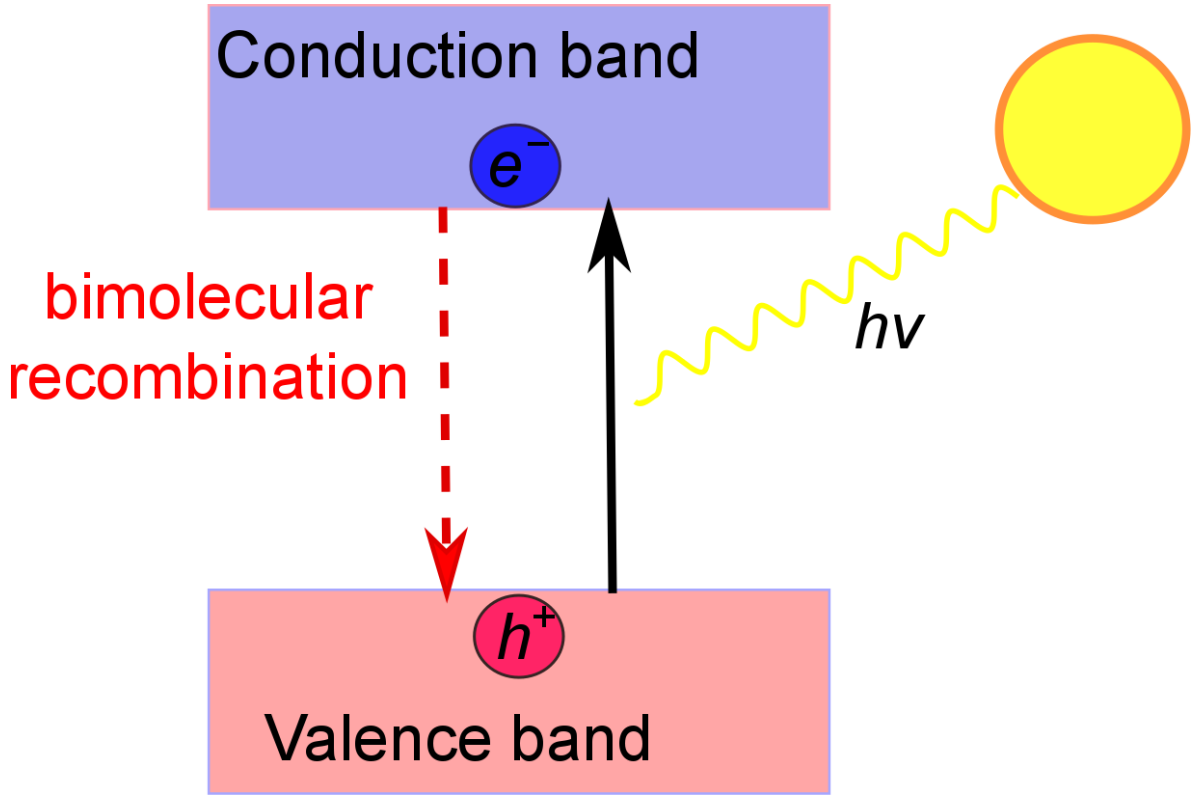
Prof. Filippo De Angelis

Let’s develop these techniques for perovskites!

J. Phys. Chem. Lett. 2017 89 2055-2059

Polarons in $MAPbI_3$ from advanced simulations





Polarons are localized in different regions of the materials following structural distortions in the organic sublattice

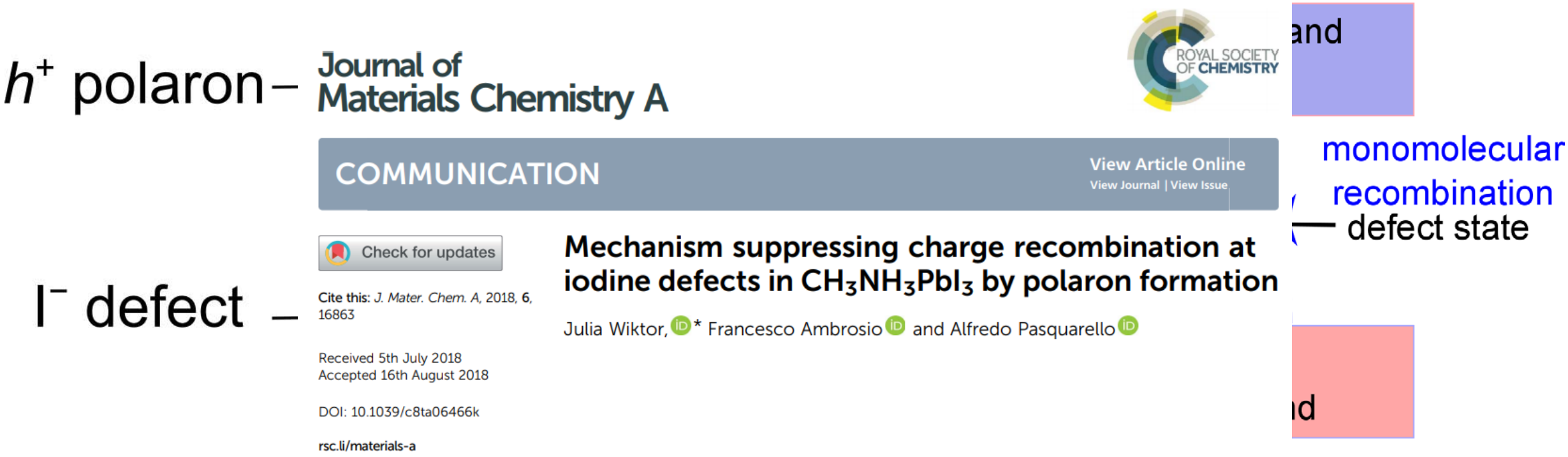
Different spatial localization of the charges reducing bimolecular recombination!

Polarons and the chemistry of Iodine in $MAPbI_3$

MHPs are generally found to be defect-tolerant

But again…why?

Let's consider the typical Iodine interstitial defect in $MAPbI_3$



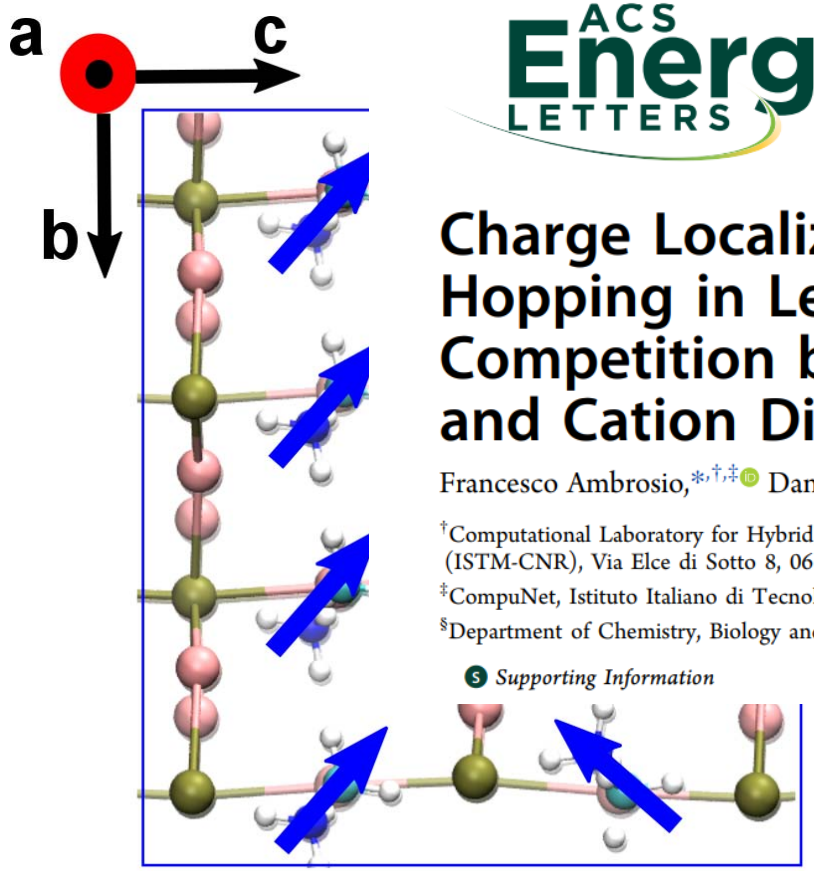
…but the barrier is not enough to explain it!

Reduced interaction between the hole polaron and the interstitial

On the origin of polaron formation and hopping

No A-site cations' dipole field

No polaron!



ACS Energy LETTERS

Cite This: ACS Energy Lett. 2019, 4, 2013–2020

http://pubs.acs.org/journal/aelccp

Charge Localization, Stabilization, and Hopping in Lead Halide Perovskites: Competition between Polaron Stabilization and Cation Disorder

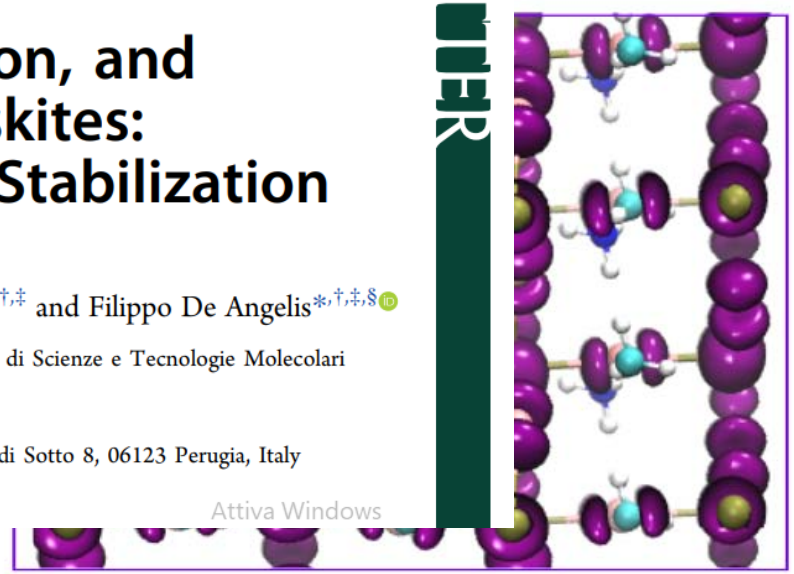
Francesco Ambrosio,*[,†,‡] Daniele Meggiolaro,[†,‡] Edoardo Mosconi,[†,‡] and Filippo De Angelis*[,†,‡,§]

[†]Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), Istituto CNR di Scienze e Tecnologie Molecolari (ISTM-CNR), Via Elce di Sotto 8, 06123 Perugia, Italy

[‡]CompuNet, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

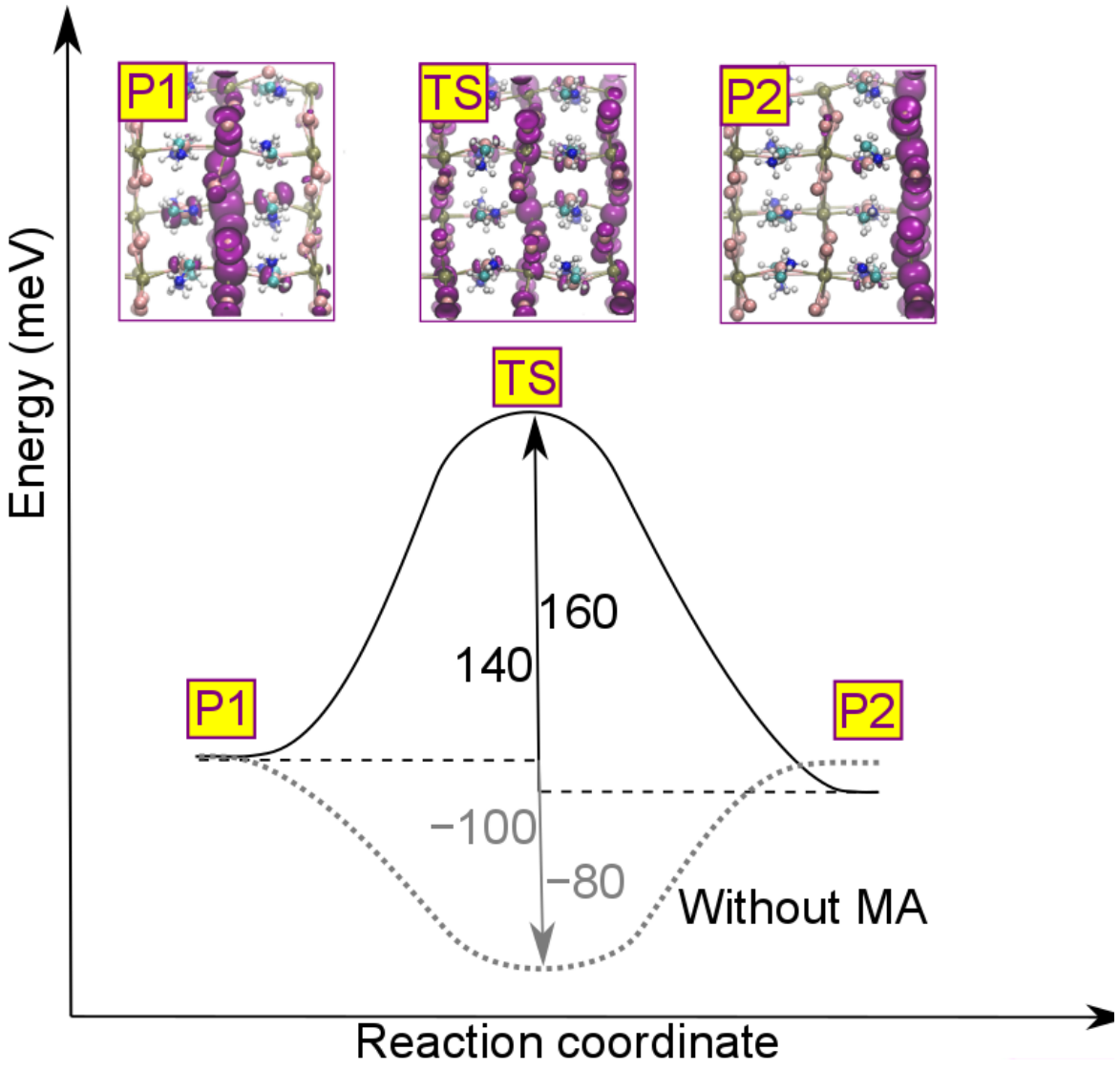
[§]Department of Chemistry, Biology and Biotechnology, University of Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

Supporting Information

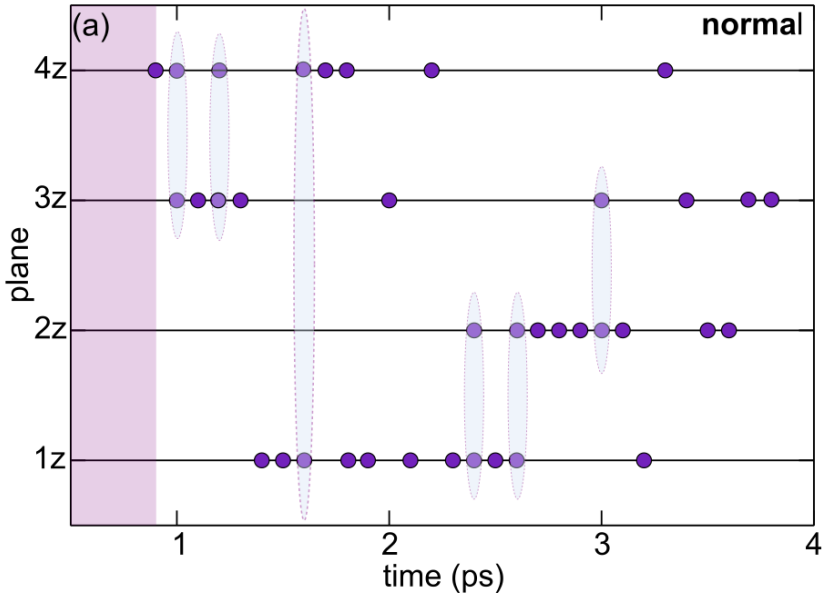


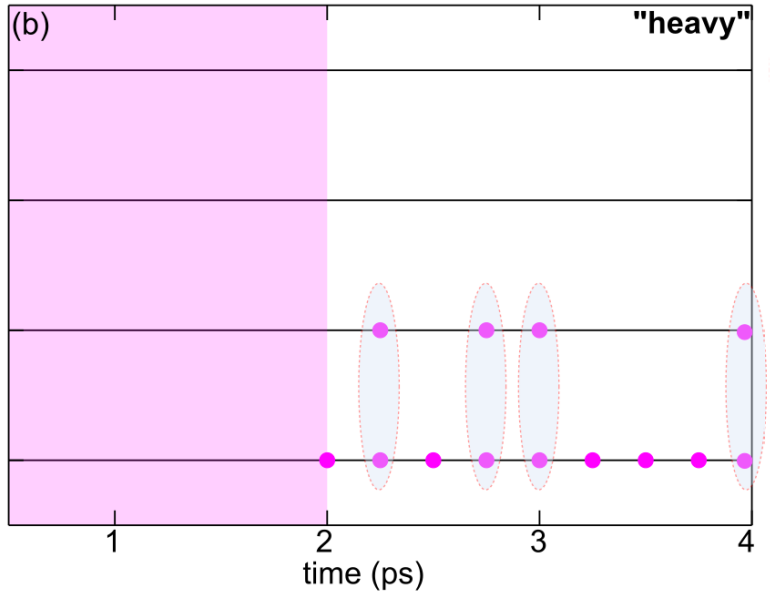
Distortions in the inorganic sub-lattice can form polarons only in presence of a net dipole field of the A-site cations

On the origin of polaron formation and hopping



Barrier is related to MA





The random reorientation of MA cations determines polaron hopping

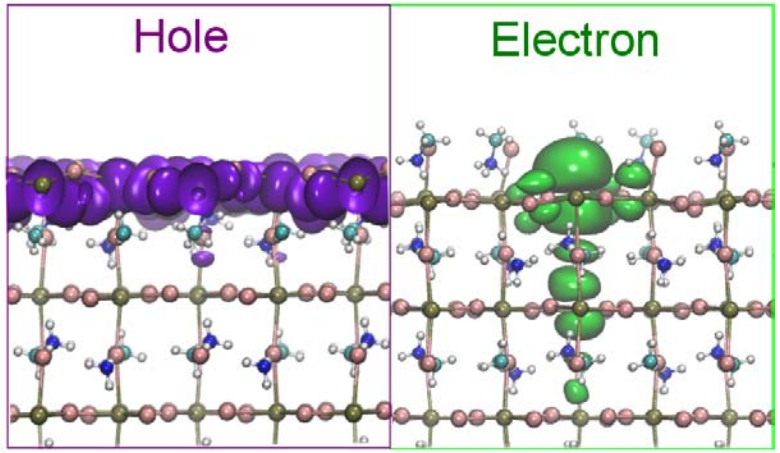
Conclusions and perspective

- Spatial separation of polarons in $MAPbI_3$ explains slow bimolecular and monomolecular recombination.
- Polaron formation is a synergistic process in which distortions in the inorganic sub-lattice are induced by the A-site cations' dipole field.
- Polaron hopping is induced by the random reorientation of A-site cations.

…but what about surfaces?

Charge loss at the surface and interface is one of the main issues for the development of perovskite solar cells

Surface polarons!



Acknowledgements

Prof. Filippo De Angelis

Prof. Alfredo Pasquarello

Dr. Daniele Meggiolaro

Dr. Julia Wiktor

Dr. Edoardo Mosconi

Computational Laboratory for Hybrid and Organic Photovoltaics

Institute of Molecular Science and Technologies (CNR-ISTM)

ISTITUTO ITALIANO DI TECNOLOGIA

EPFL

MARVEL

NATIONAL CENTRE OF COMPETENCE IN RESEARCH

This project has received funding from the Europan Union's Horizon 2020 research and innovation agreement No 764047 of the ESPRESSO project.

…and thank you for your attention!