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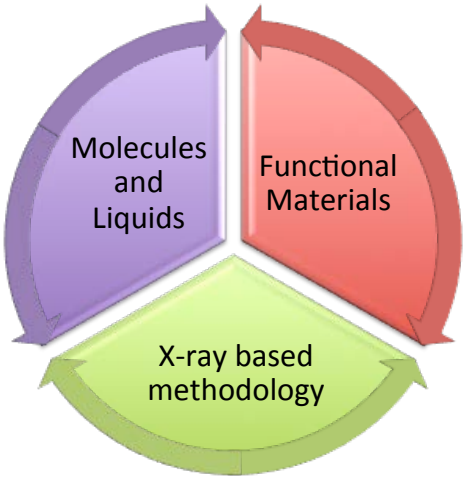
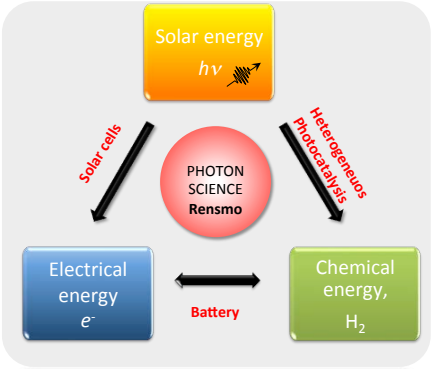
X-ray based spectroscopy for the study of perovskite photovoltaic materials

Håkan Rensmo

Joint French-Swedish school on X-rays and Neutrons techniques for the study of functional materials for energy

Molecular and Condensed Matter Physics





CMD (UU) Erik Johansson, Gerrit Boschloo, Jesper Jacobson,
KTH Ute Cappel, James Gardner , Lichen Sun, Lars Kloo
SU, Michael Odelius
ÅABC (UU) Kristina Edström, Daniel Brndell,
Cambridge: Sam Stranks
EPFL: - Michael Saliba, Anders Hagfeldt
Bessy: Mihaela Gorgoi, UBjL, Föhlish, Ovsyannikov, Giangrisostomi, Bidermane, Leitner,

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- Photoelectron spectroscopy (PES)
- PV materials (Solar Cells)

- EXAMPLES (not all PV materials)
  - Molecular system
  - Crystal system
    - Interface structure
    - Energy Matching
    - Orbital composition
    - Dynamic

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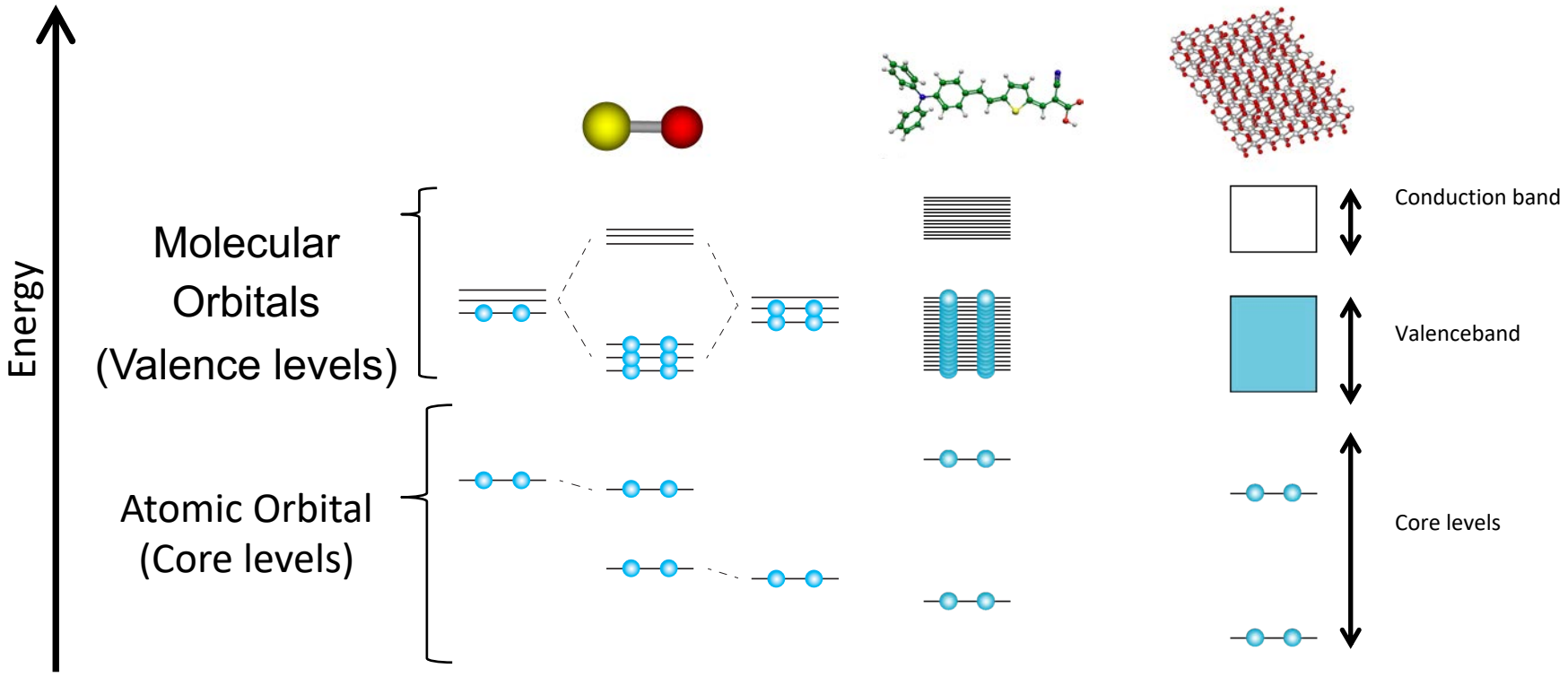
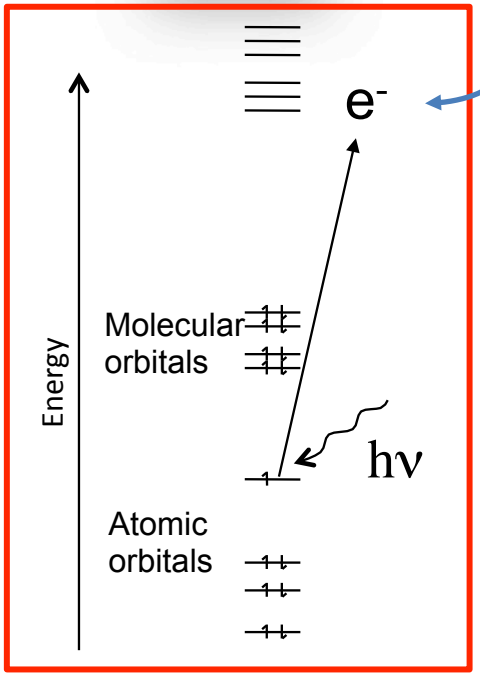
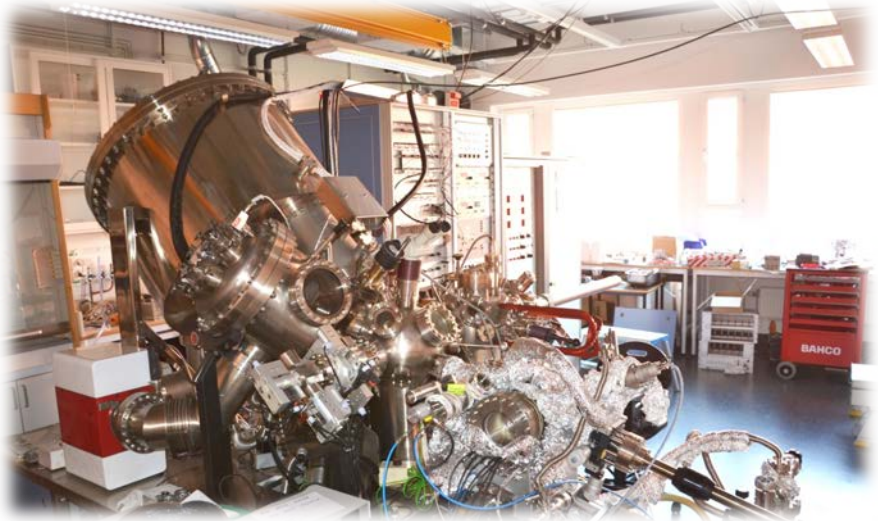
Electronic structure

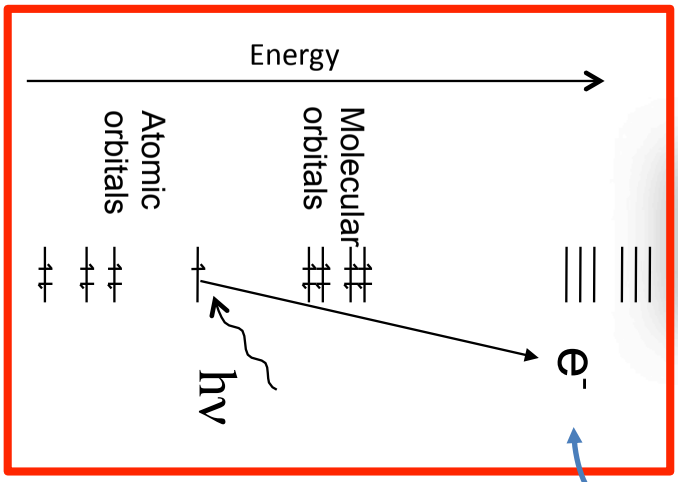


Photoelectron spectroscopy (PES)
XPS,PES,UPS,HAXPES,SOXPES
X-axis



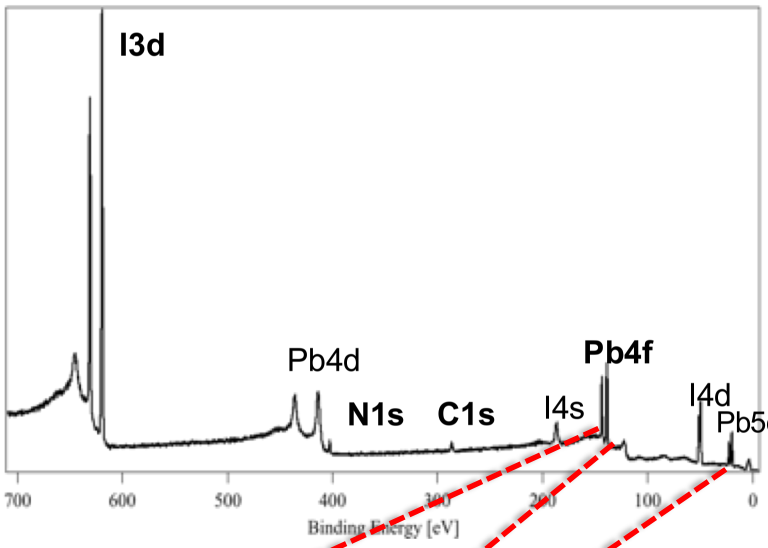


$$E_{binding}=h\nu-E_{kinetic}$$

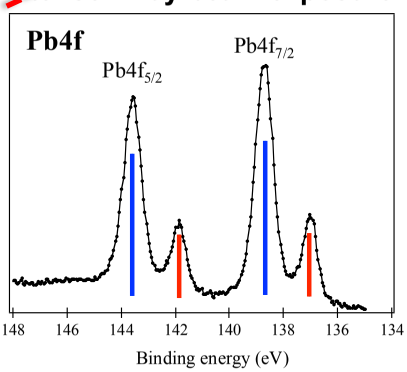


photoelectron

$E_{binding} = h\nu - E_{kinetic}$

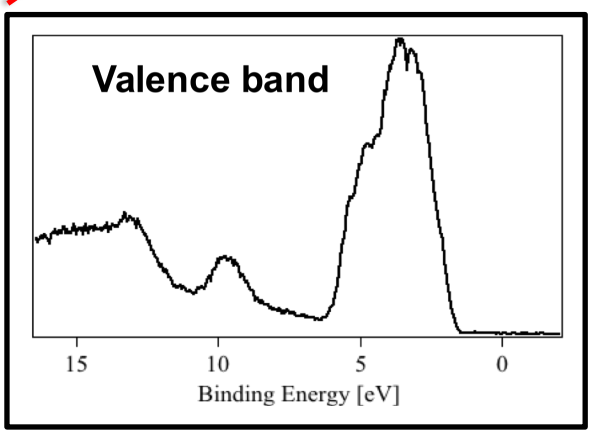


MAPbI$_3$ after heating at 200°C and intense X-ray beam exposure



Pb^{2+}

Pb^{0}



Chemical shifts

PES

X-axis

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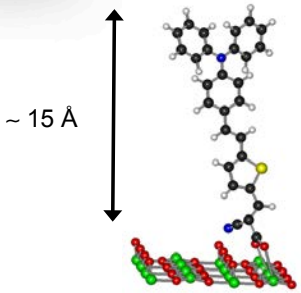
PES, **Y-axis**



$$I_a \propto \rho_a * \mathrm{H} * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$

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PES, **Y-axis**

$$I_a \propto \rho_a * \mathrm{H} * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$

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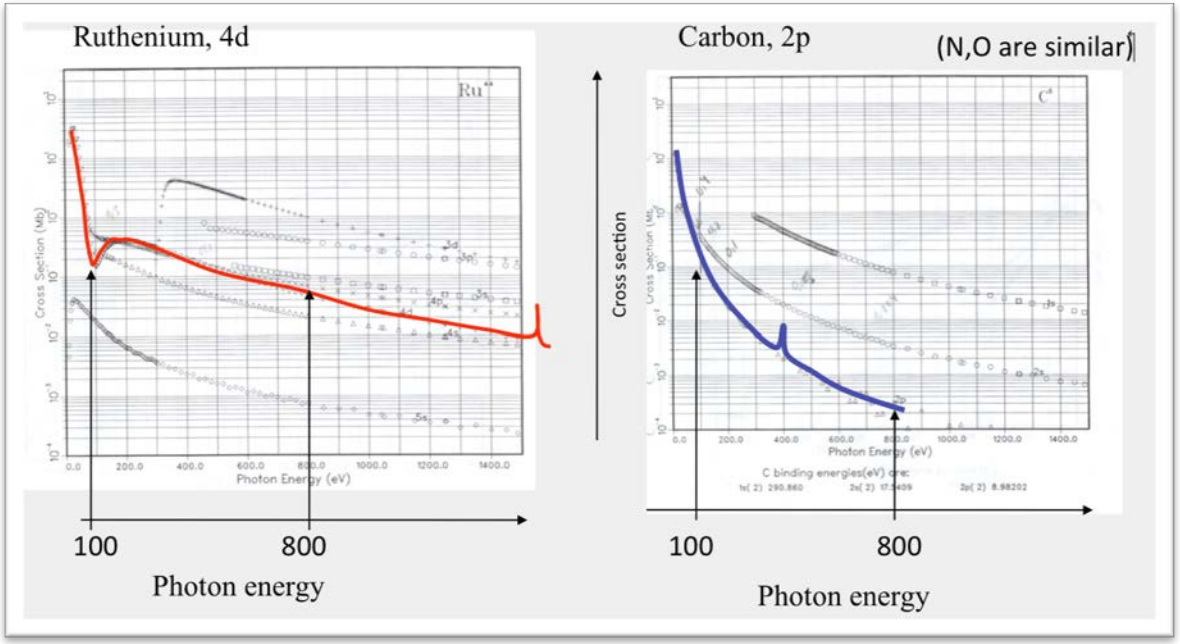
PES, **Y-axis**

$$I_a \propto \rho_a * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$



J. Yeh and I. Lindau, *At. Data Nucl. Data Tables*, 1985, **32**, 1–155

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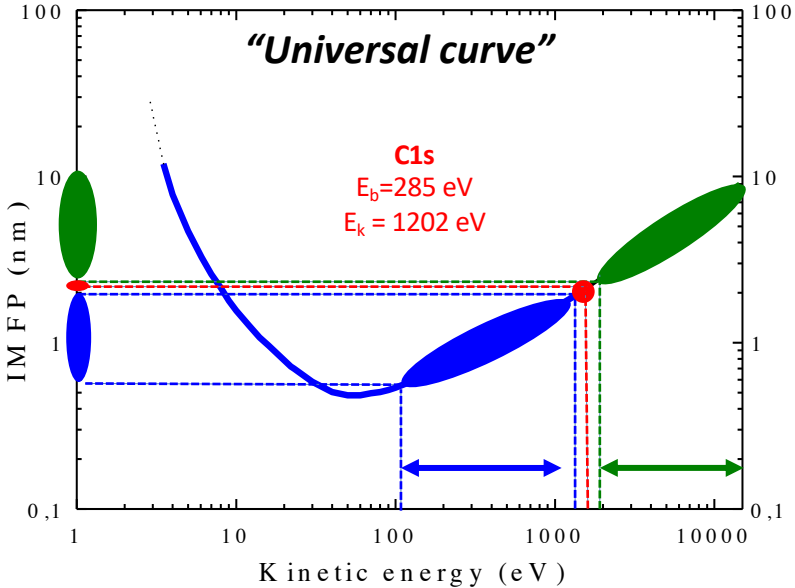
PES, **Y-axis**

”Surface” sensitive

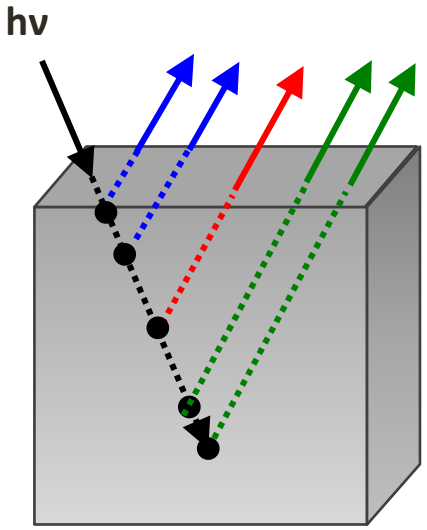
$$I_a \propto \rho_a * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$



Soft X-ray: MAX IV
h ν = 50 - 1500 eV
E_{kin} tunable for each core peak

In-house XPS
hv=1487 eV
E_{kin} fixed for each core peak

Hard x-ray: Bessy II, Soleil, Desy, Dimaond
h ν = 2000 – 10,000 eV
E_{kin} tunable for each core peak



$E_{kin} = hv - E_b$

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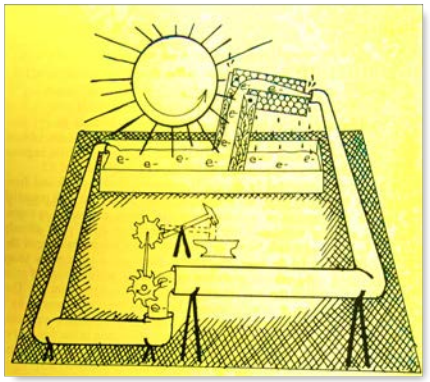
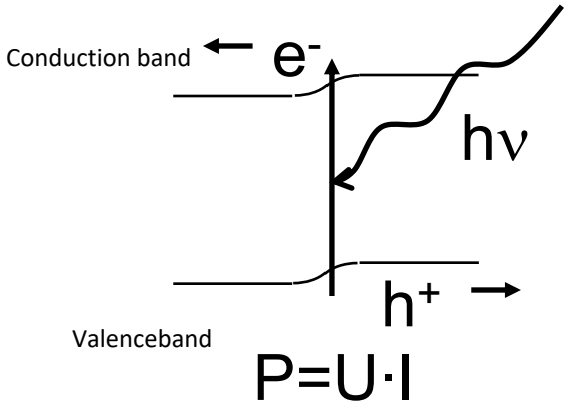
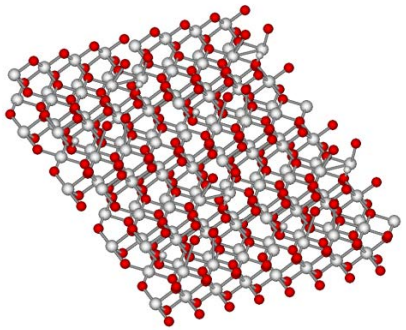
Solar cells (very quickly)

- **Solar cell:** Light ⇒ electrical energy
- Absorb light and separate charges
- Considered expensive (also energy expensive)
- New types
  - Molecular
  - Organic
  - Thin film
  - Perovskite
  - ...







Keyfunction: Light-absorption (electron excitation)
Charge-separation (interface)

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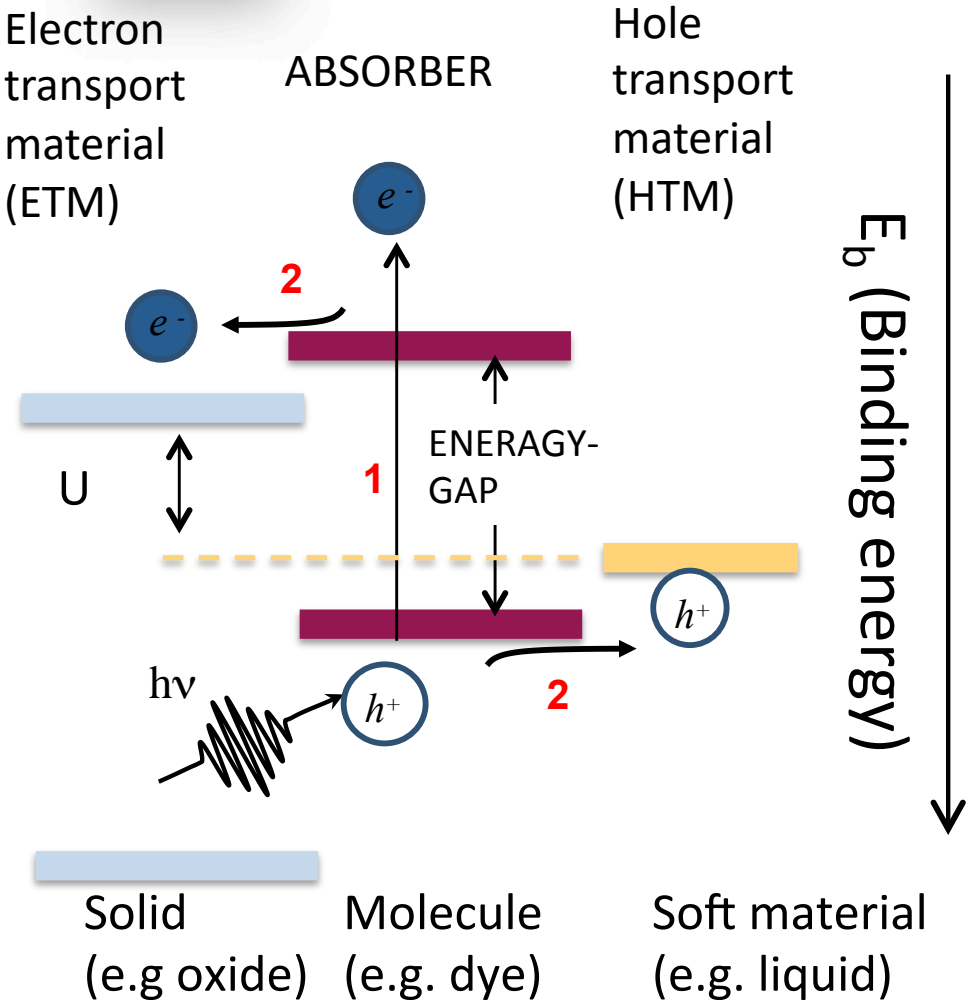
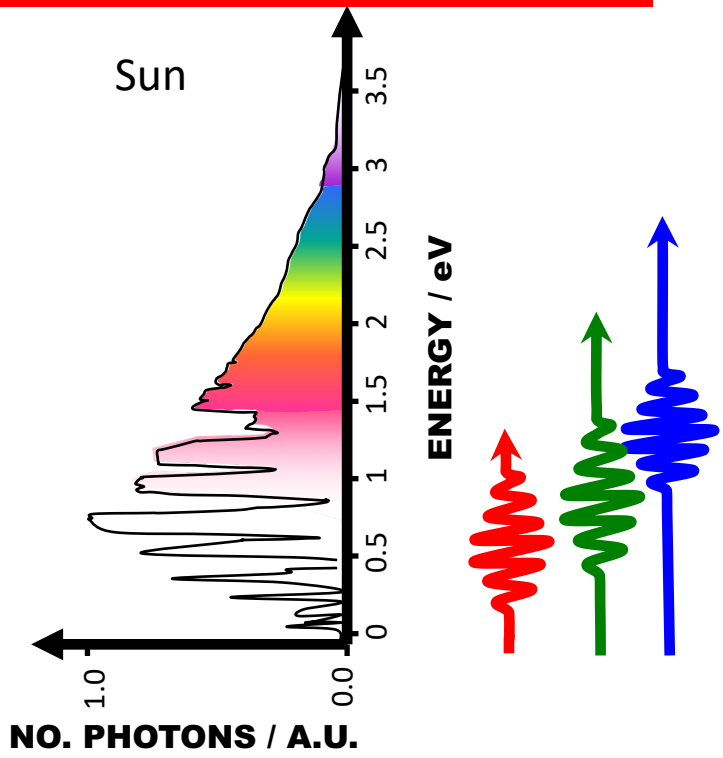


What is the highest efficiency of a solar cell?



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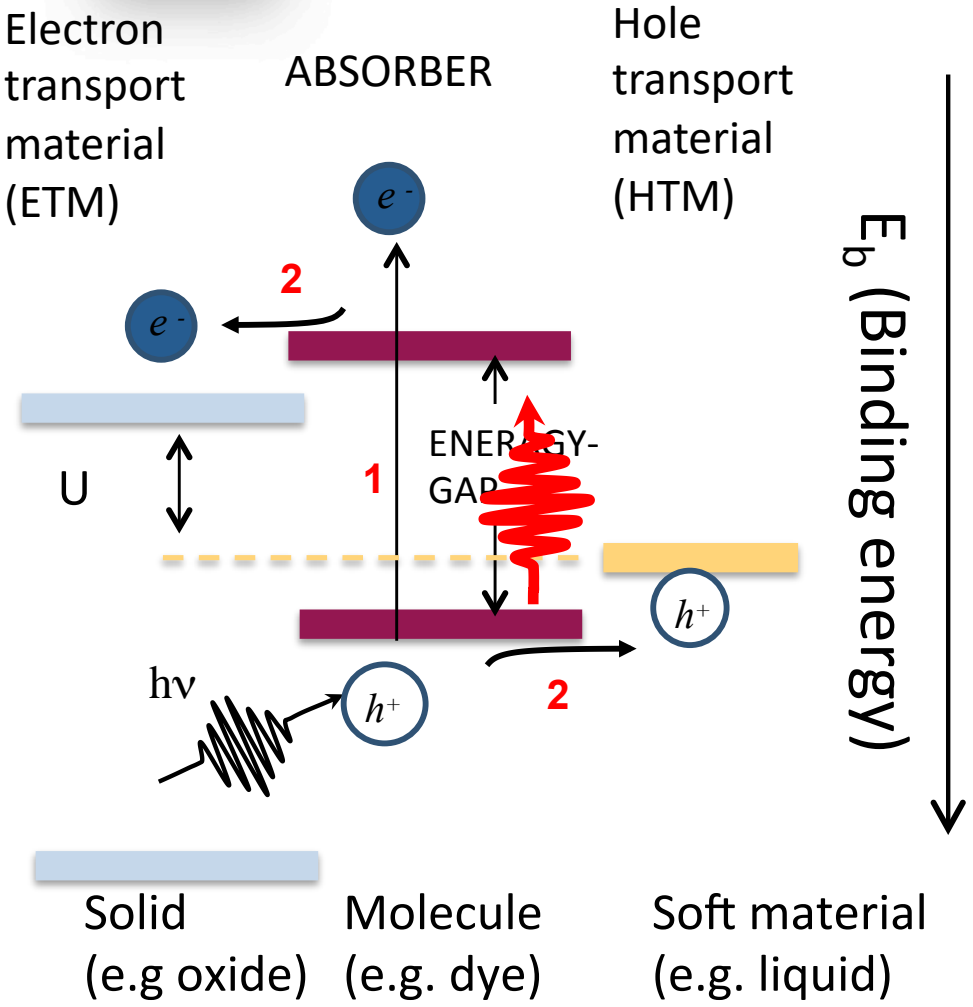
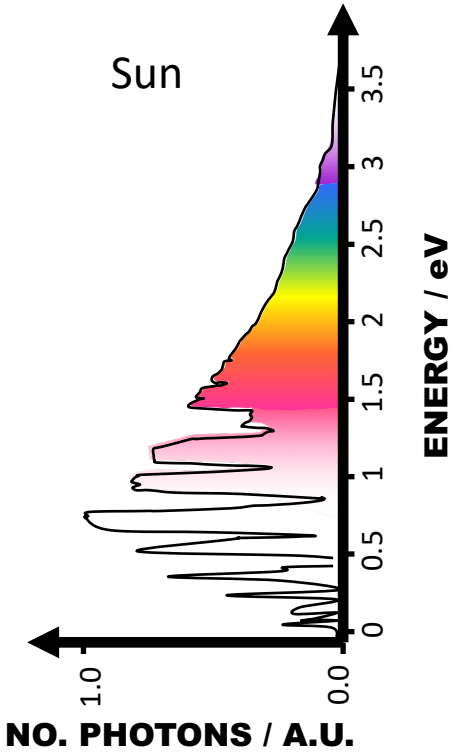
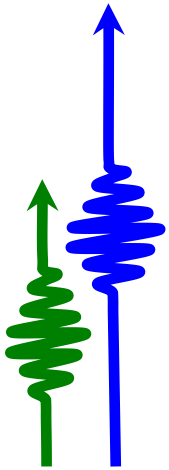
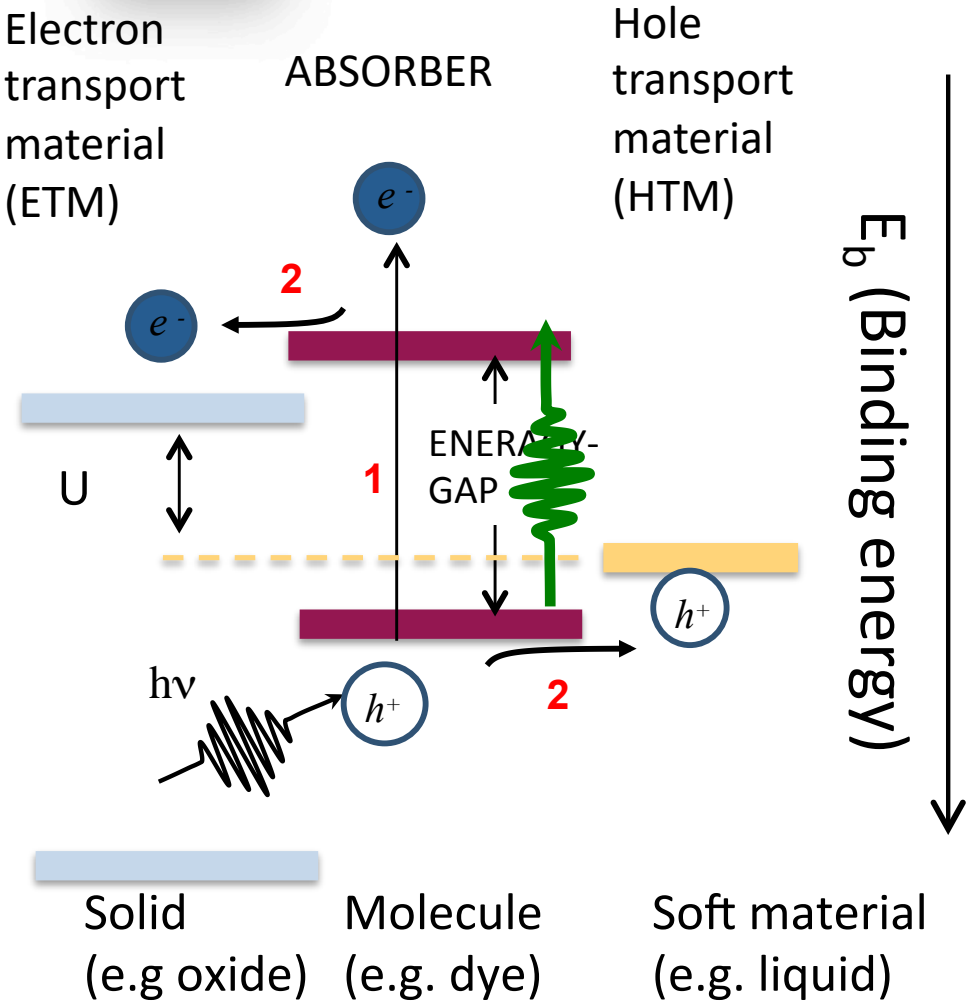
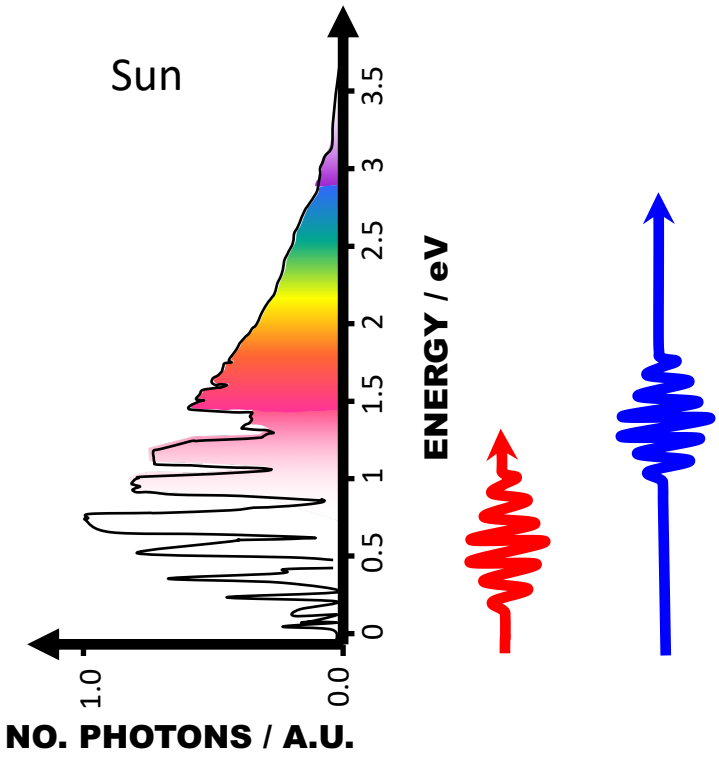







Electron transport material (ETM)
ABSORBER
Hole transport material (HTM)
e^-
2
e^-
U
1
ENERGY-GAP
h^+
hν
h^+
2
E_b (Binding energy)
Solid (e.g oxide)
Molecule (e.g. dye)
Soft material (e.g. liquid)


Sun
ENERGY / eV
0
0.5
1
1.5
2
2.5
3
3.5
1.0
0.0
NO. PHOTONS / A.U.

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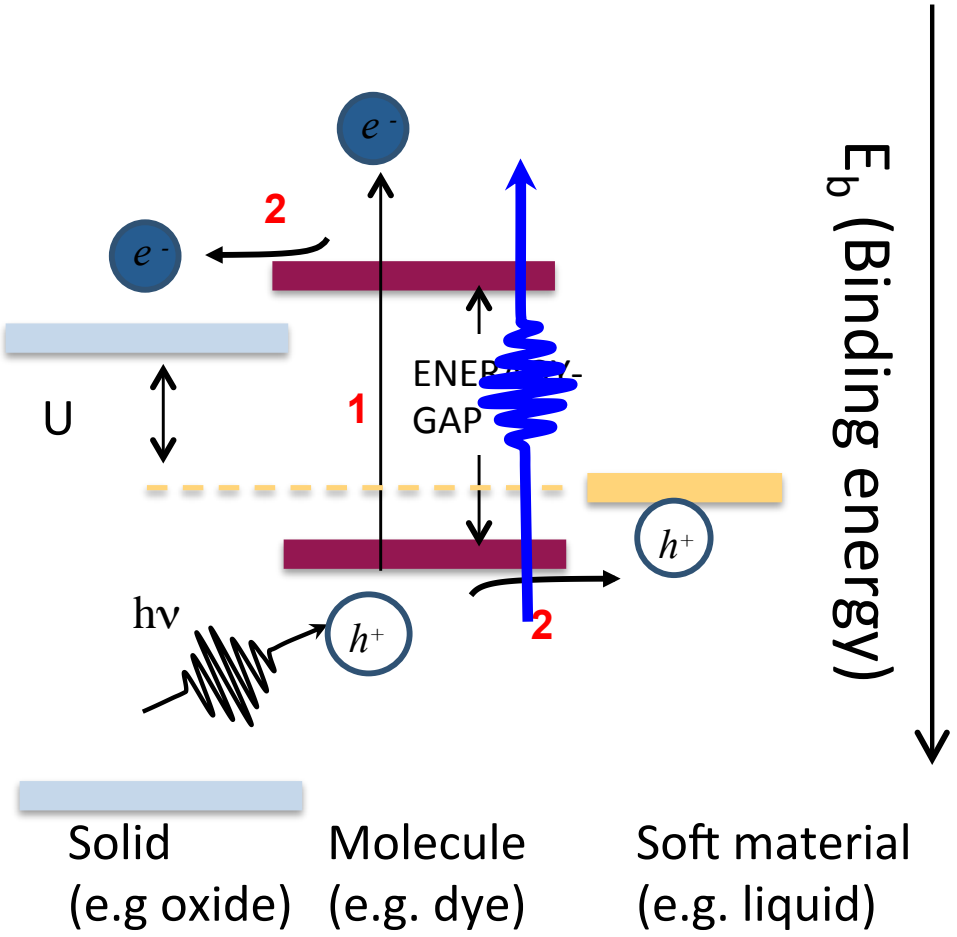
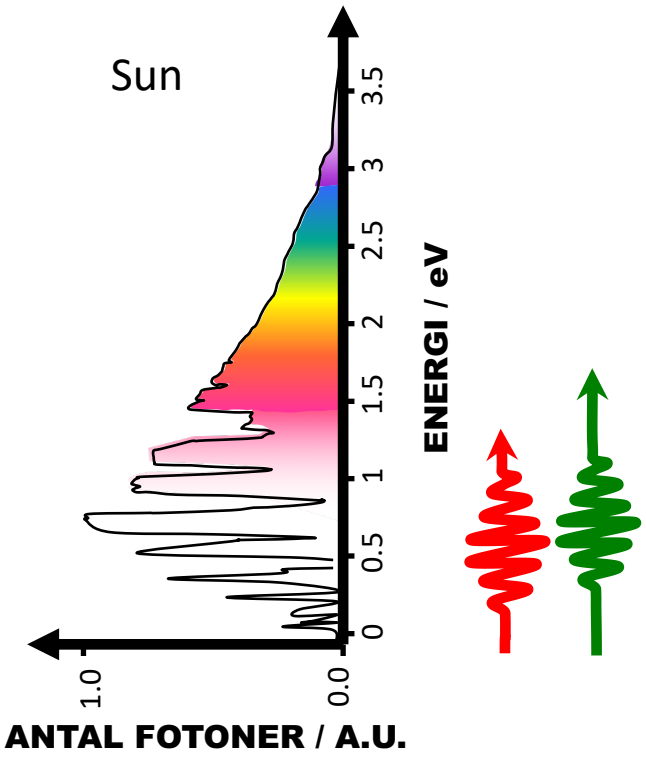
The challenge!!





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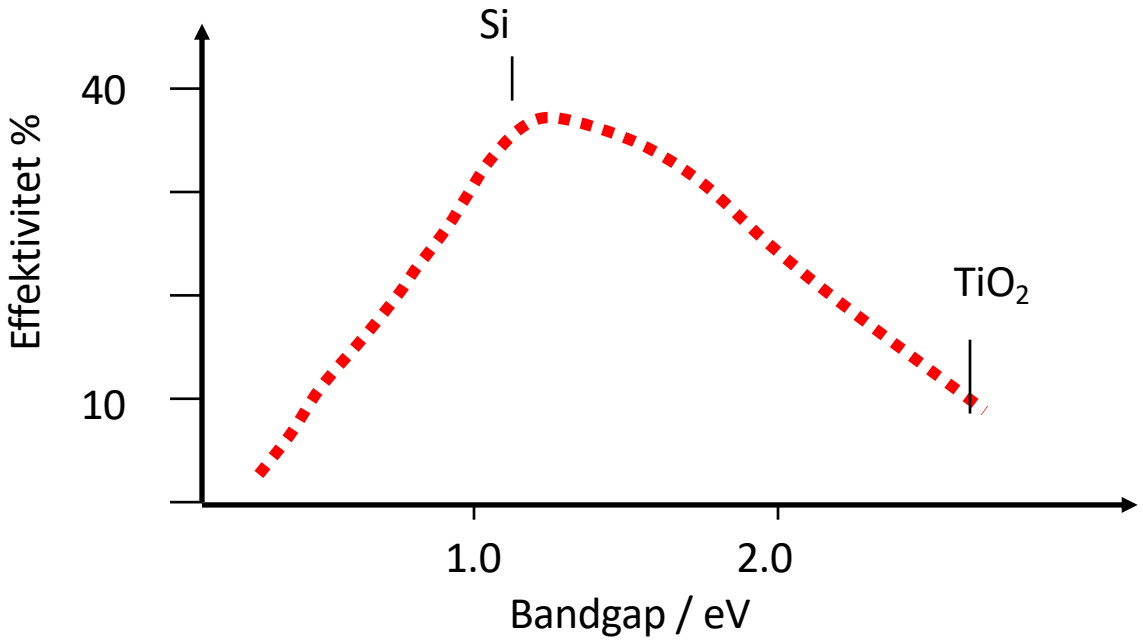
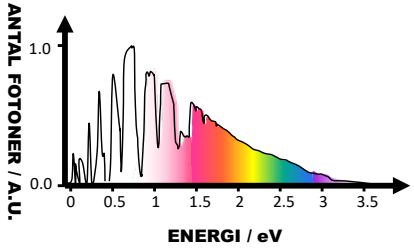
Efficiency

About 34% max for one gap

$$\text{Efficiency} = \frac{(P \times I)_{max}}{\textit{Solar Energy}}$$





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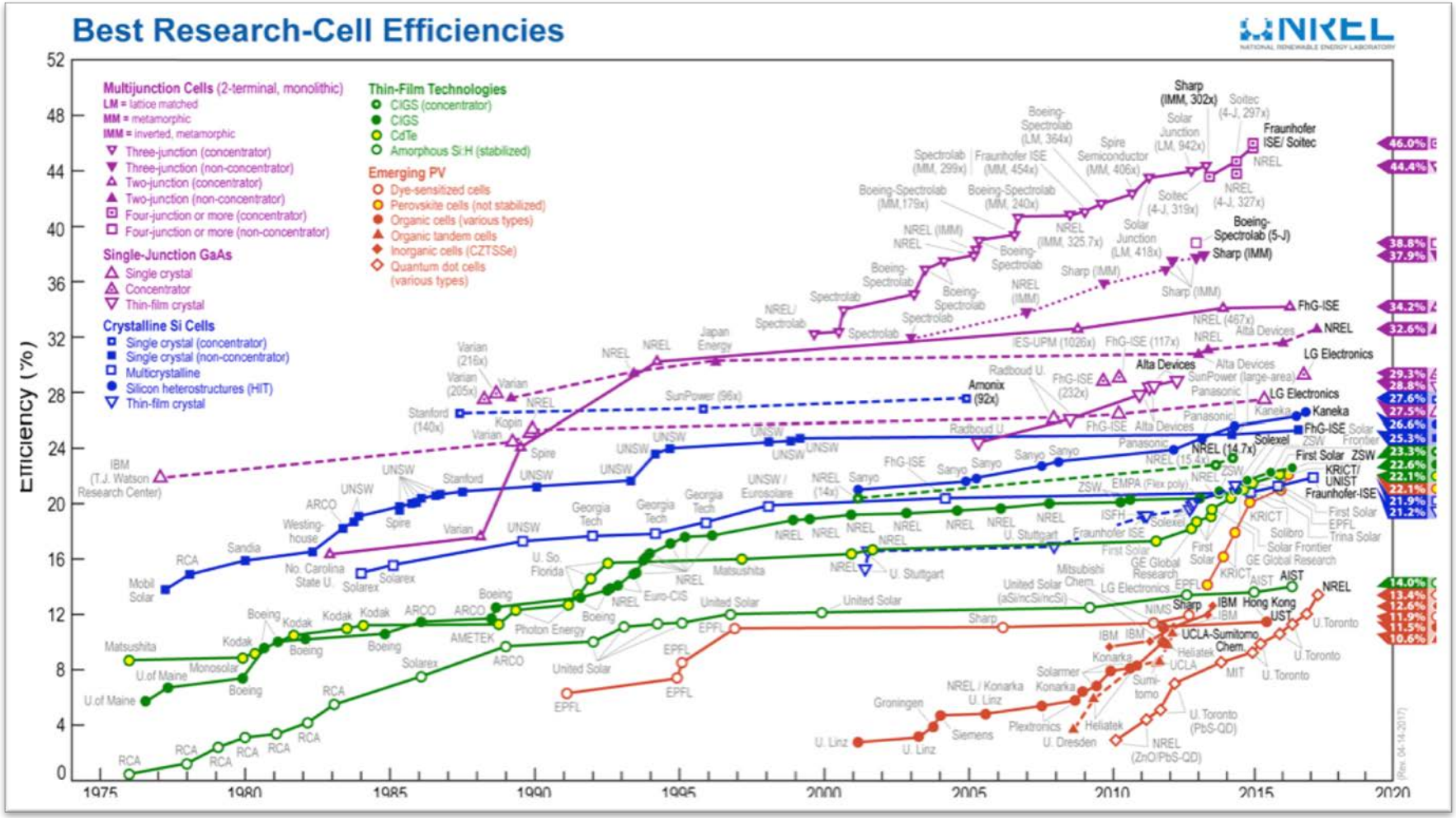

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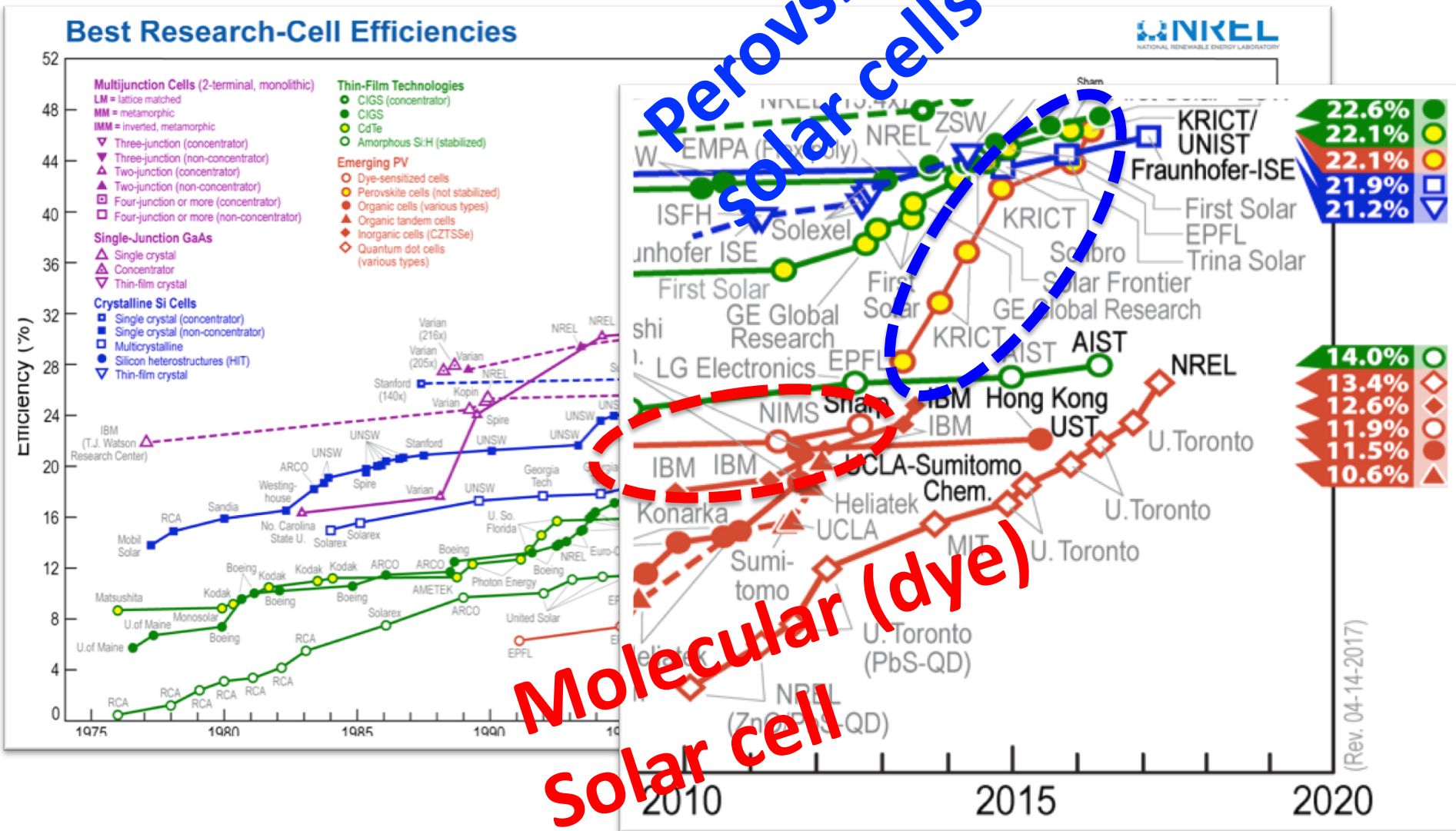
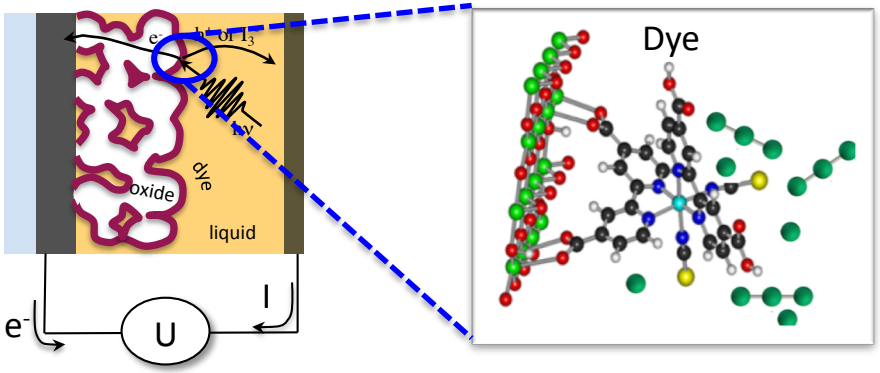
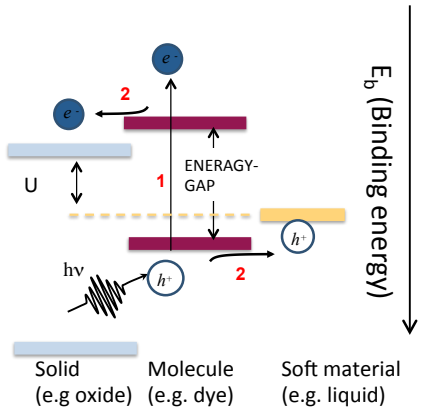
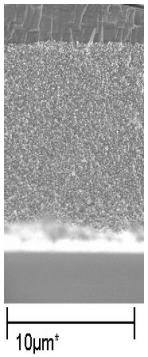


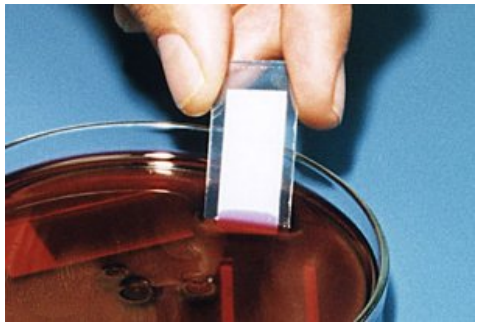
Photoelectron spectroscopy of DSC solar cell materials

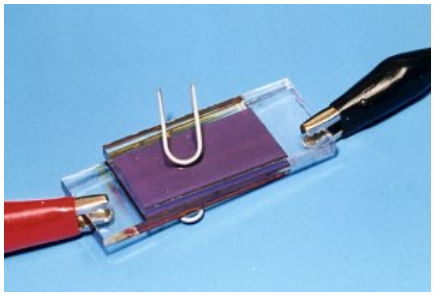
Understand key interfacial processes in conversion











3D design

Interface structure

Electronic structure

Interface structure

Where are the atoms?

Orbital composition

Where are the electrons?

Energy matching

How to facilitate efficient charge transfer

Dynamics

How do electrons and atoms move during the conversion process.

Johansson EMJ; Lindblad R; Siegbahn H; Hagfeldt A; Rensmo H. *Chemphyschem*. 2014;15(6):1006-17

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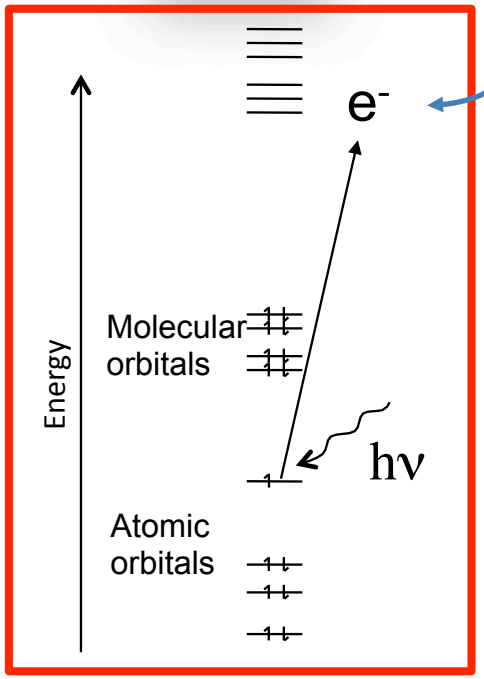
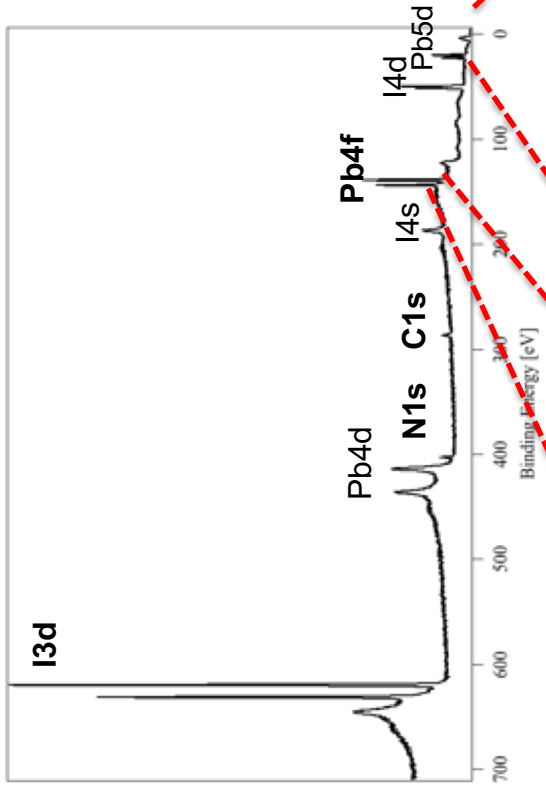
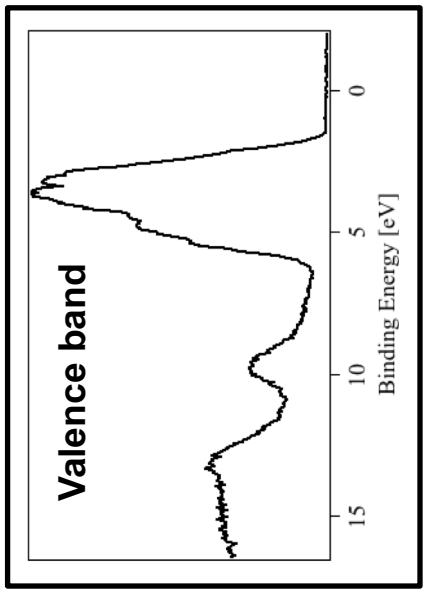
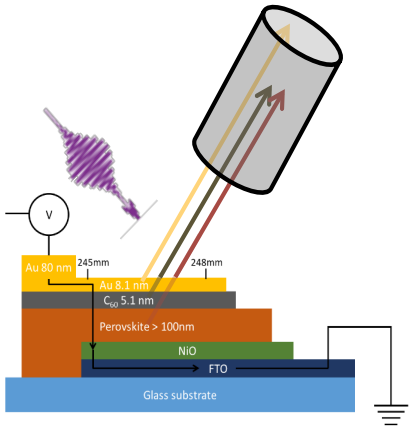
XPS,PES,UPS,HAXPES,SOXPES X-axis



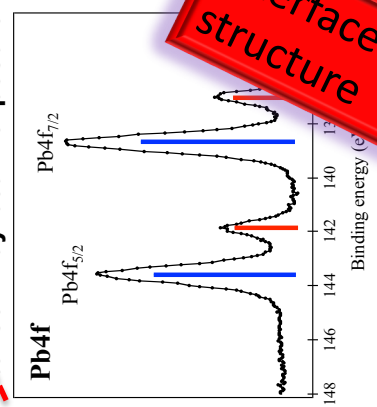






$$E_{binding}=h\nu-E_{kinetic}$$

MAPbI$_3$ after heating at 200°C and intense X-ray beam exposure



Interface structure

Chemical

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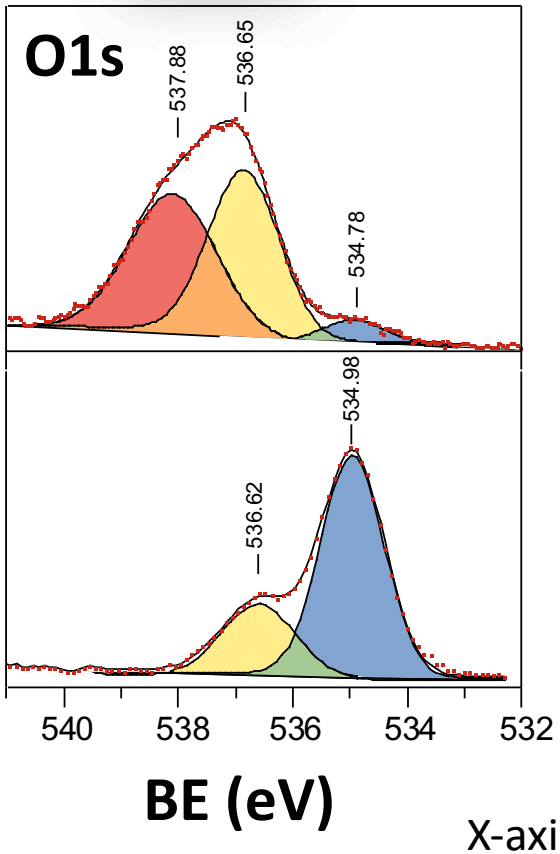
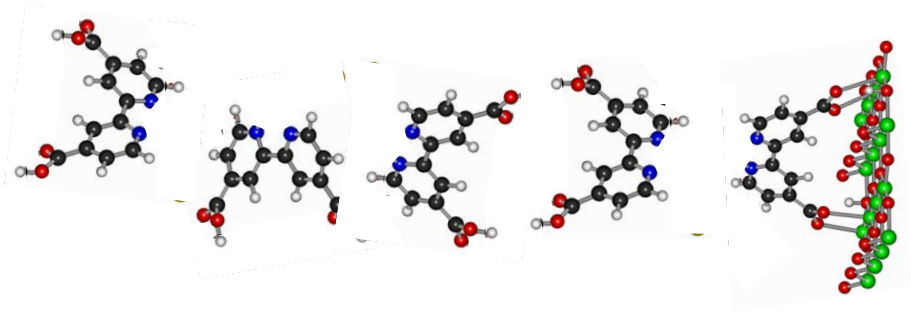
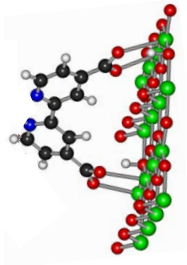
Interface structure

Key interface –
Light to electrical energy conversion using dye molecules





5 monolayers



1 monolayer

Explain?

X-axis

CHEMICAL SHIFT: Depend on the local environment

Y-axis

$$I_a \propto \rho_a * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$

Example 2

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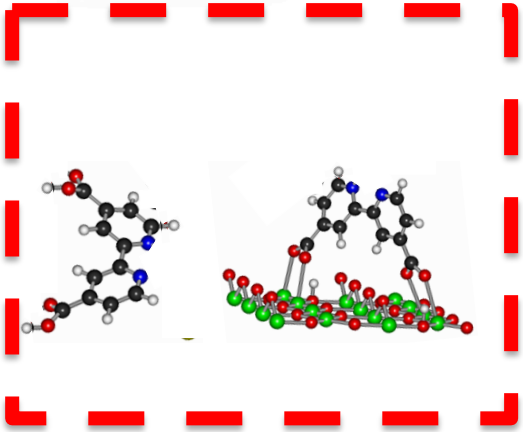
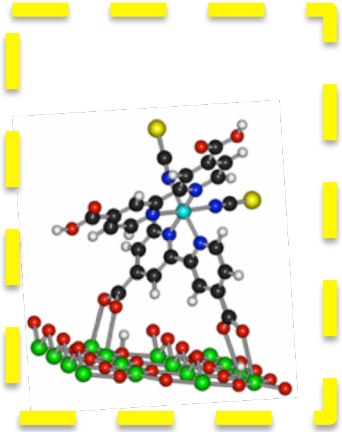
Interface structure

Key interface –
Light to electrical energy conversion using dye molecules

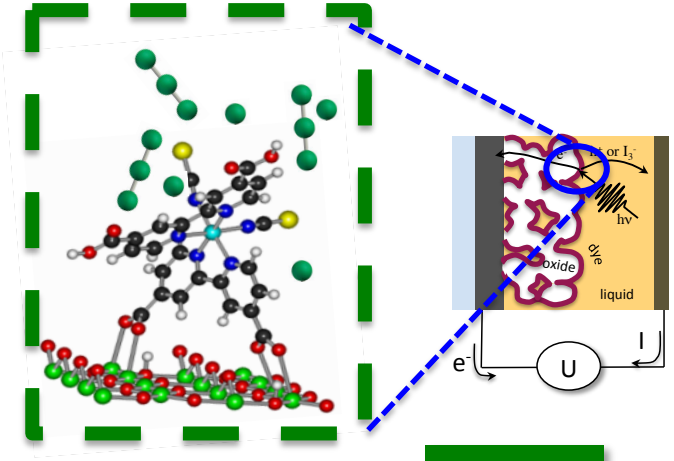
Core levels



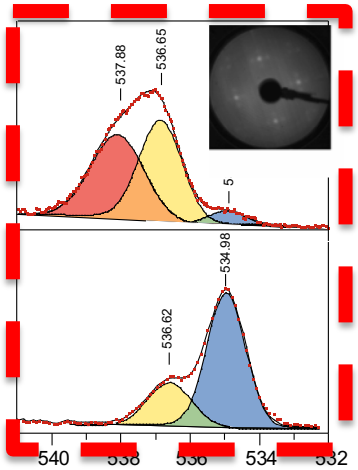
MODEL SYSTEMS

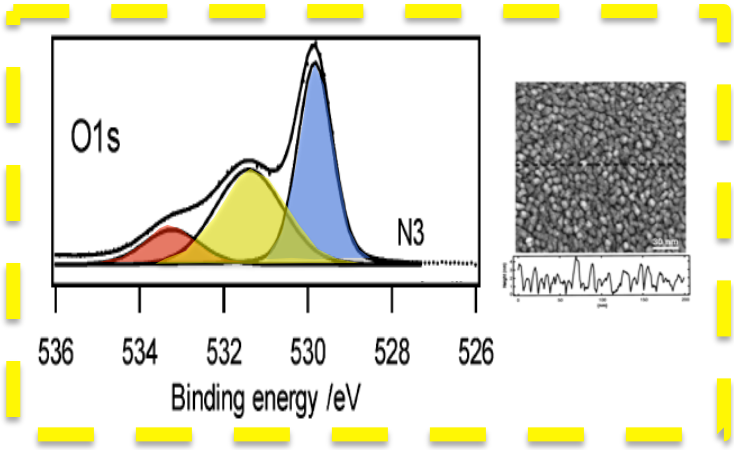


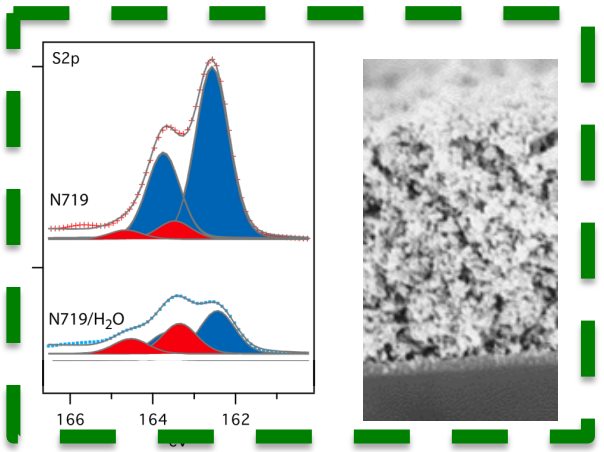
COMPLEX SYSTEMS



REAL SYSTEMS







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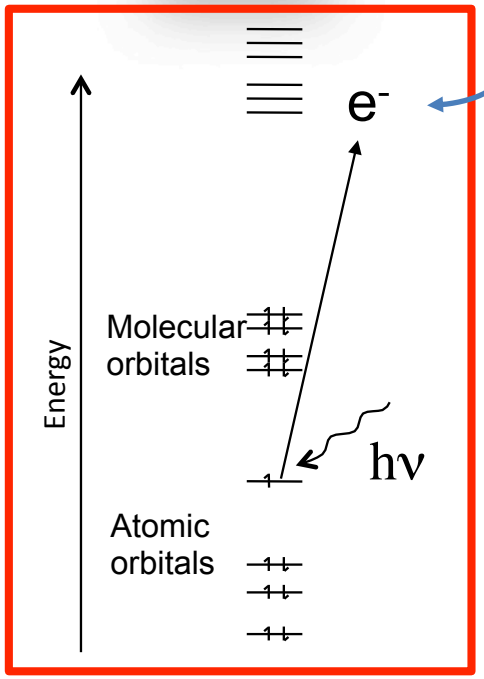
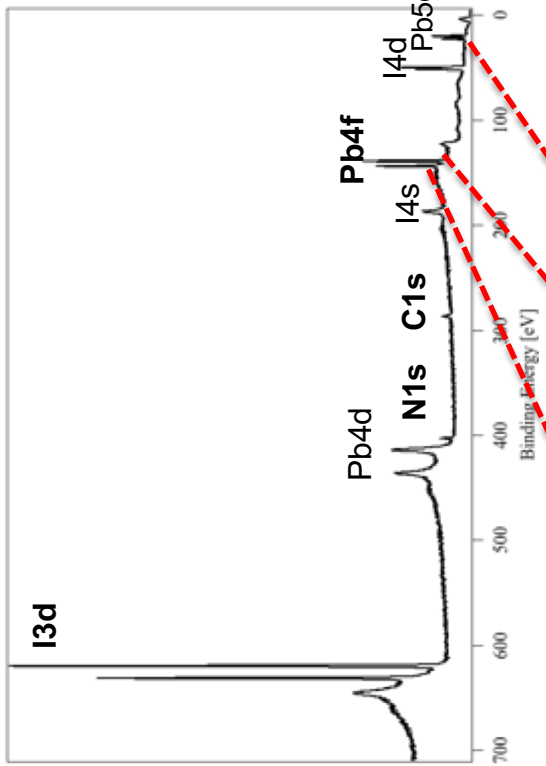
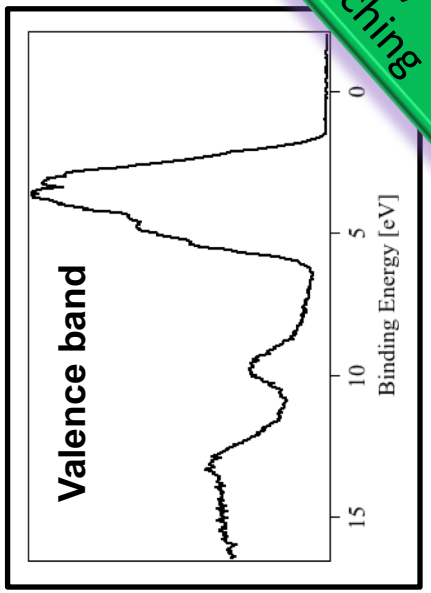
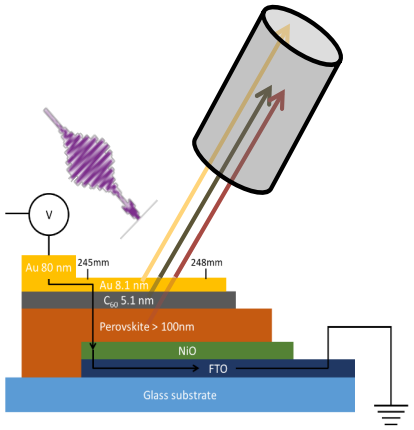
XPS,PES,UPS,HAXPES,SOXPES

Energy matching



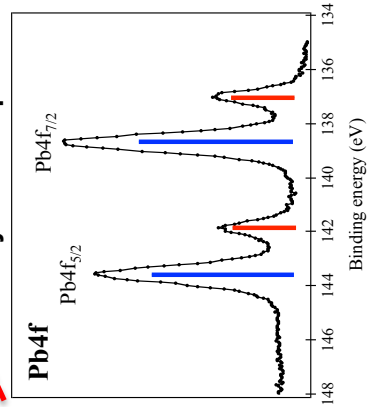






$E_{binding}=h\nu-E_{kinetic}$

MAPbI$_3$ after heating at 200°C and intense X-ray beam exposure



Chemical shifts

Example 2

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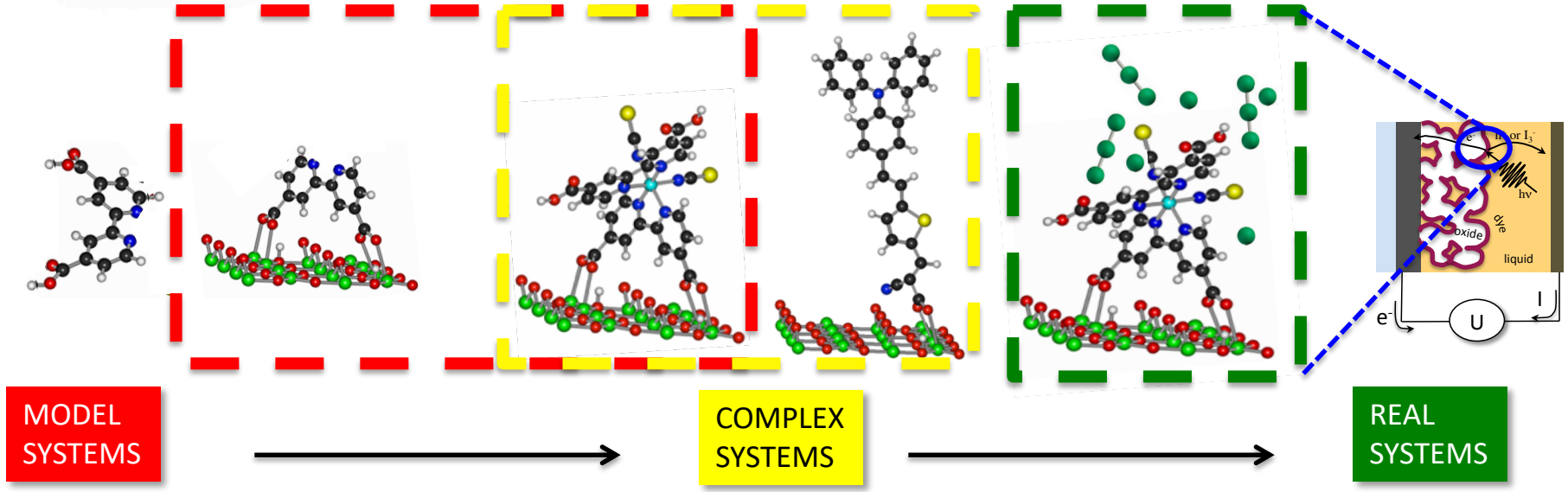
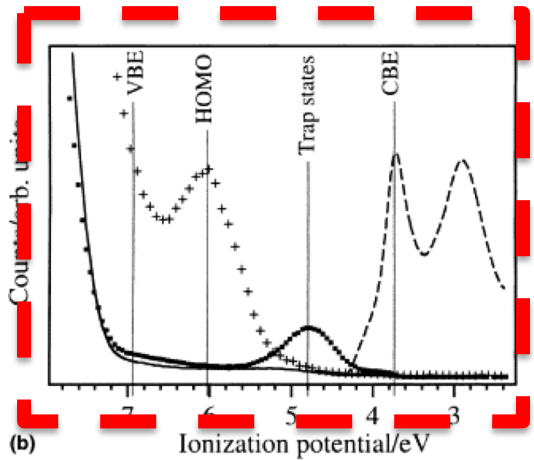
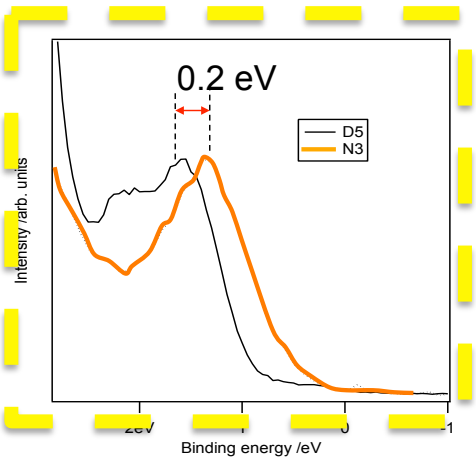
Energy matching

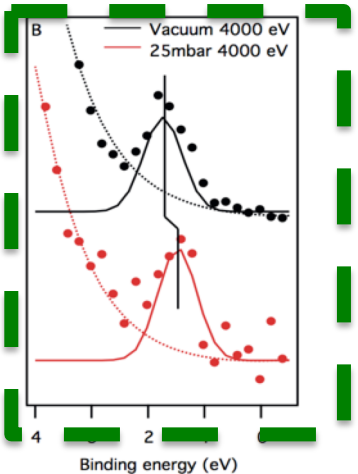
Key interface –
Light to electrical energy conversion using dye molecules

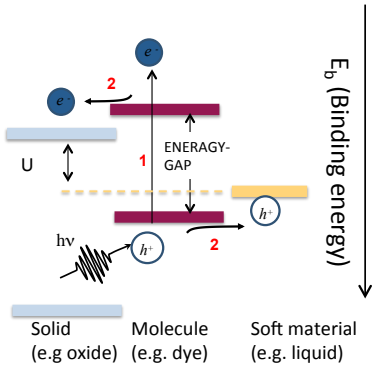
Valence levels











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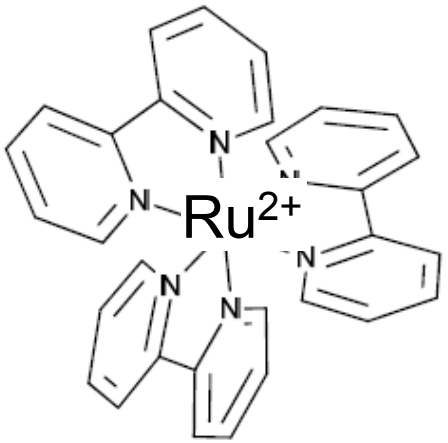
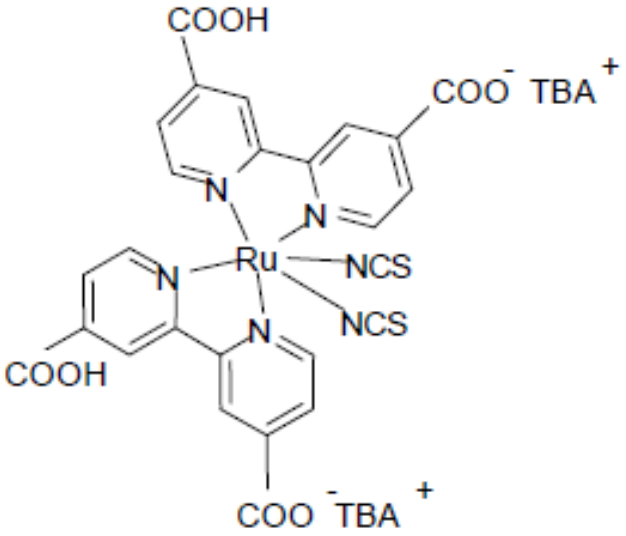
Ru-complexes a molecular example

Orbital composition

$$I_a \propto \rho_a * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$





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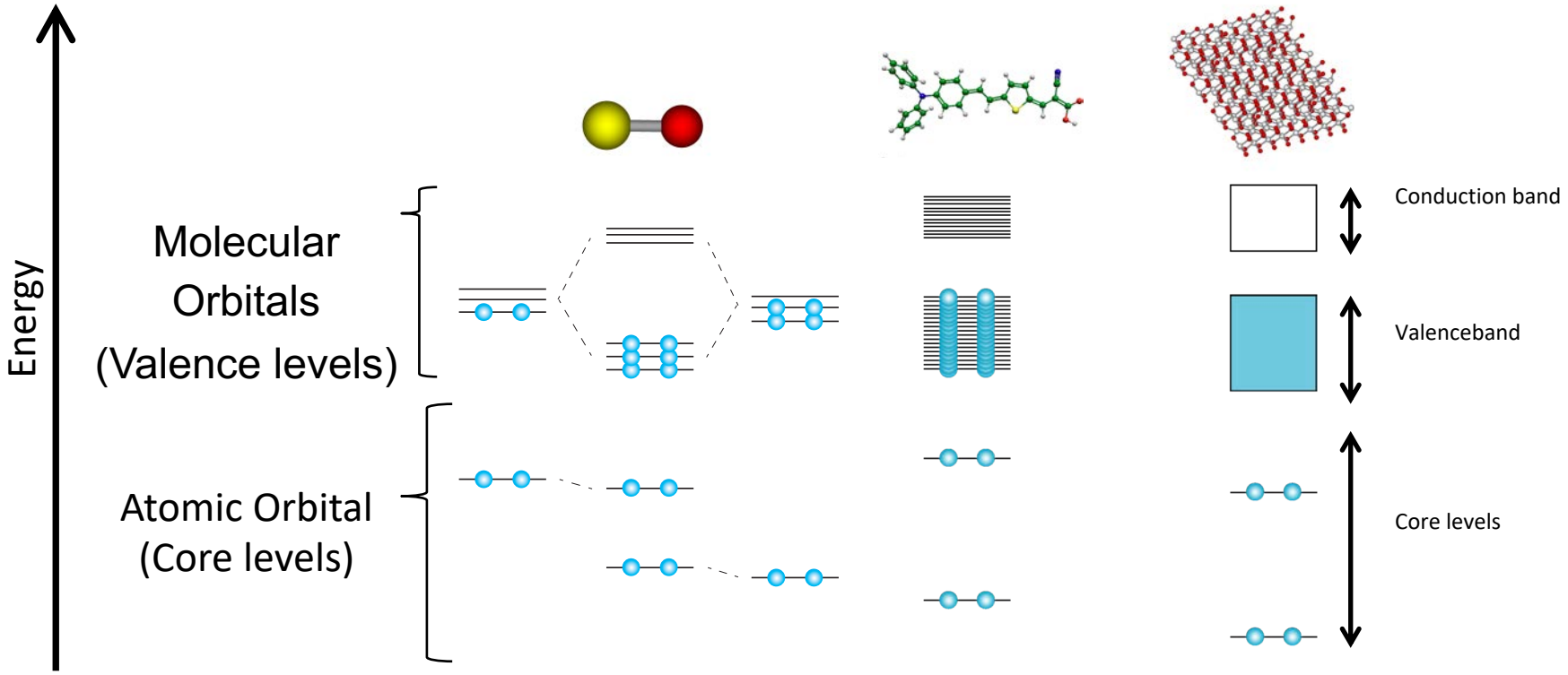
PES measures Partial Density of States (PDOS)

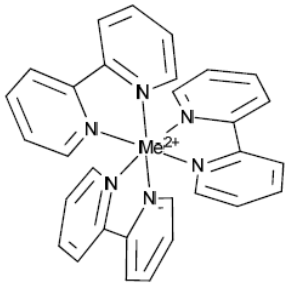
$$I_a \propto \rho_a * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$

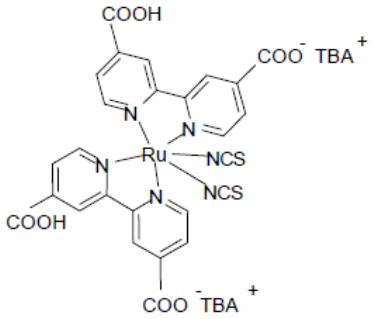


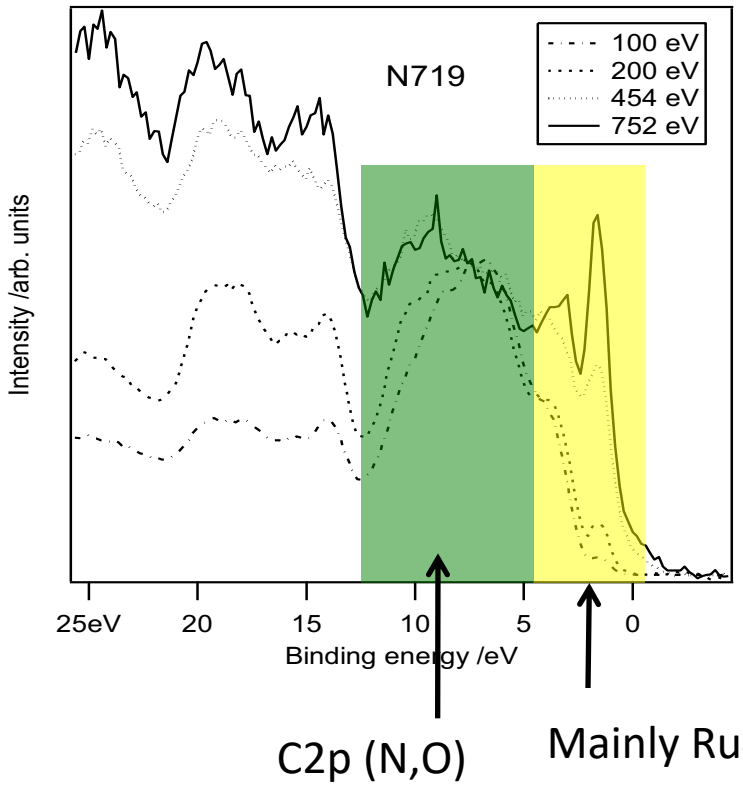
Ru-complexes a molecular example

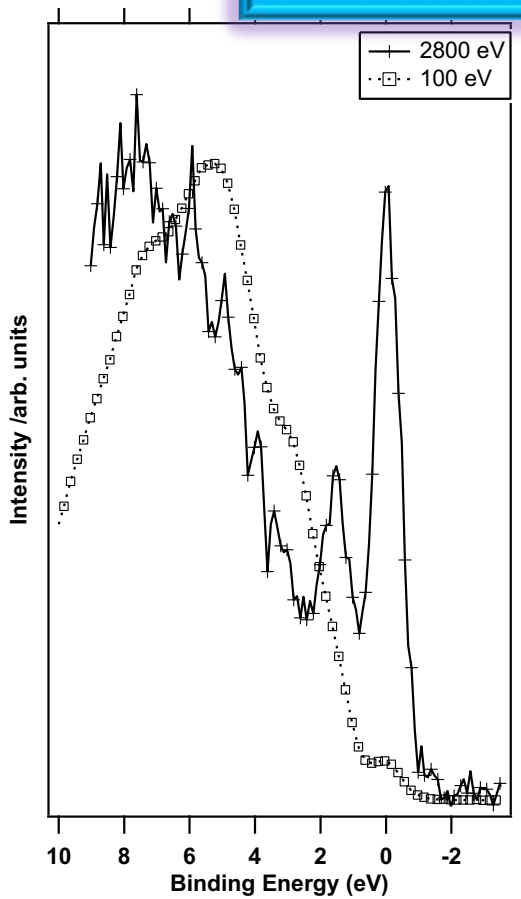
Orbital composition

Multilayer









Cross-section based and resonance techniques (NCS)

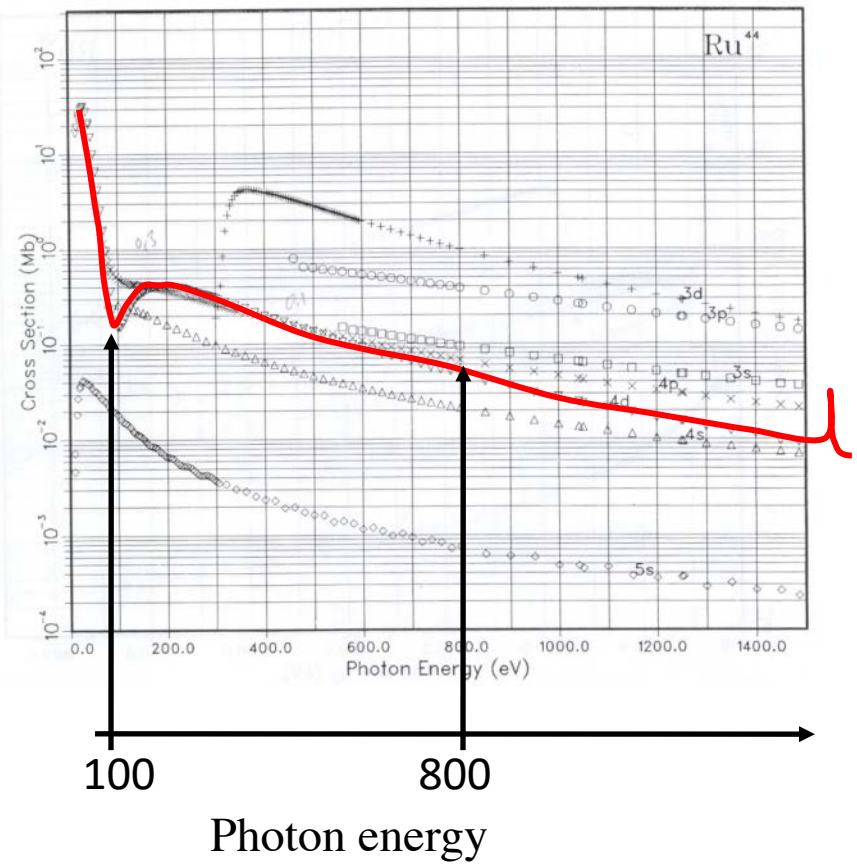
BL 41, BLI 411 and KMC1

Ru-complexes a molecular example

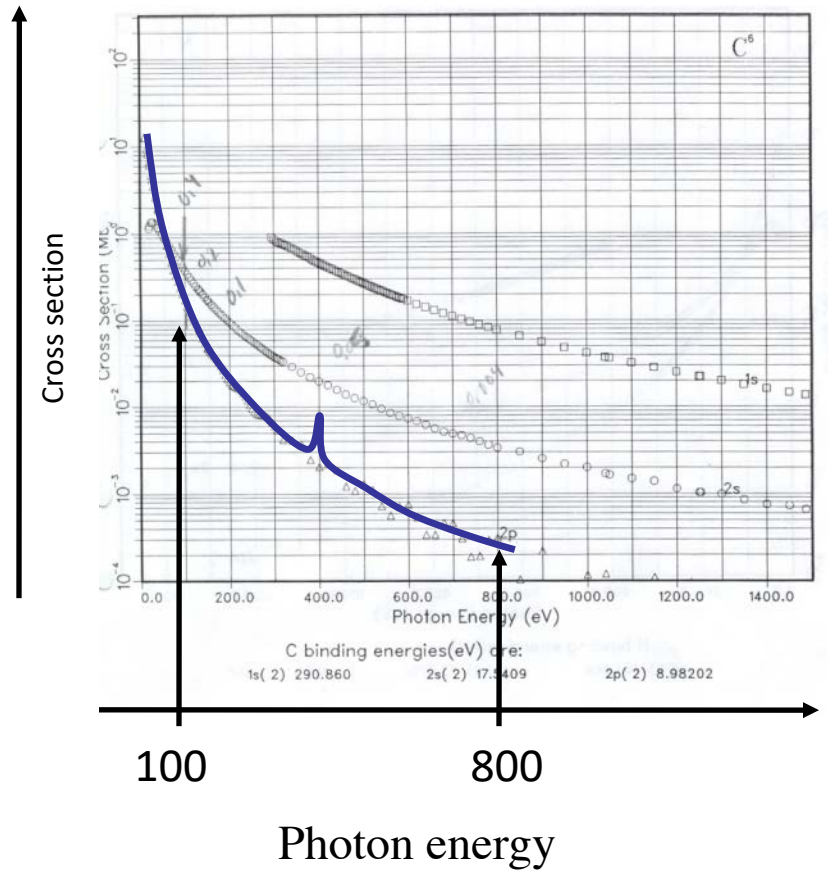
Orbital composition

$$I_a \propto \rho_a * \sigma_a(h\nu,\theta) * exp\,[-z/\Lambda(E_k)]$$

Ruthenium, 4d

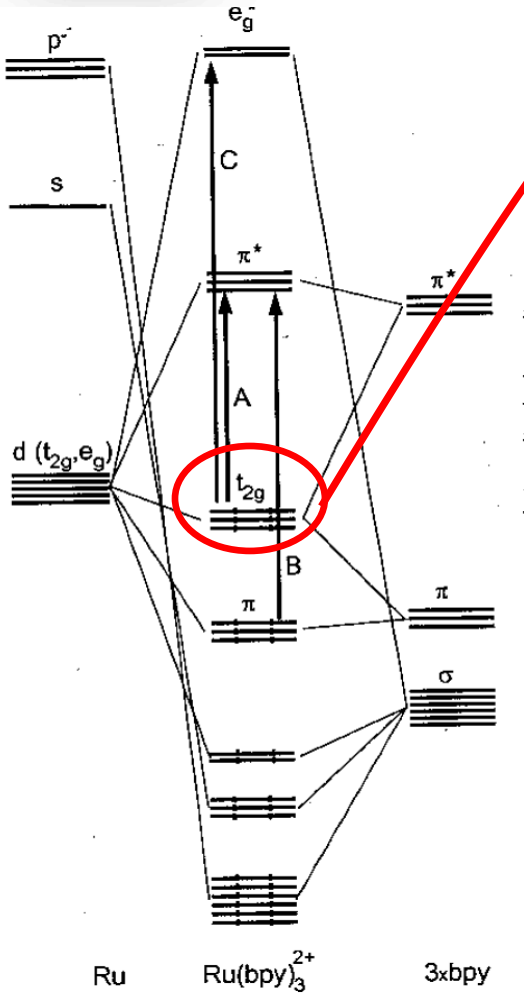


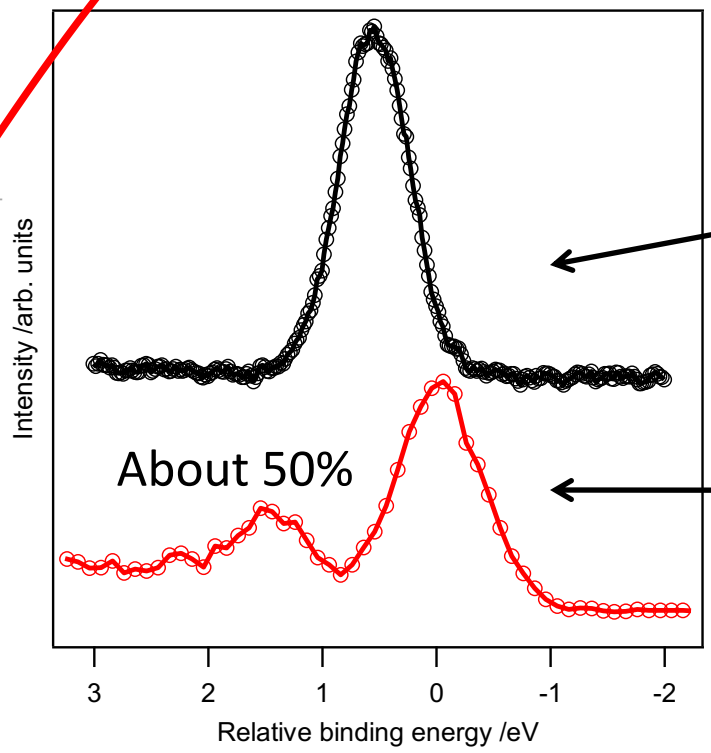
Carbon or Nitrogen, 2p

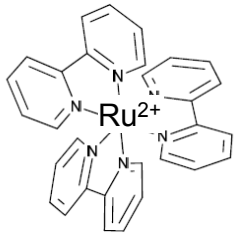


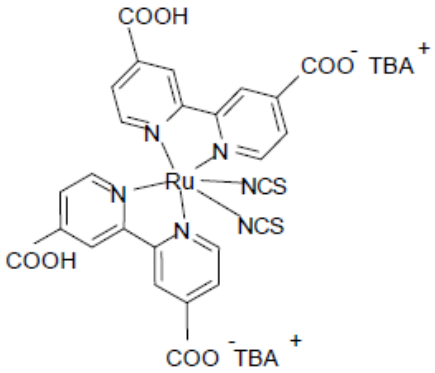
Ru-complexes a molecular example

Orbital composition









Partial DOS of Ru 4d

Valence level at 2800 eV

Example 1

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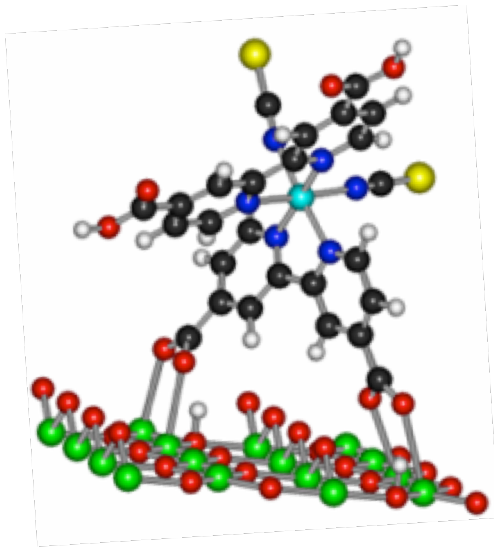
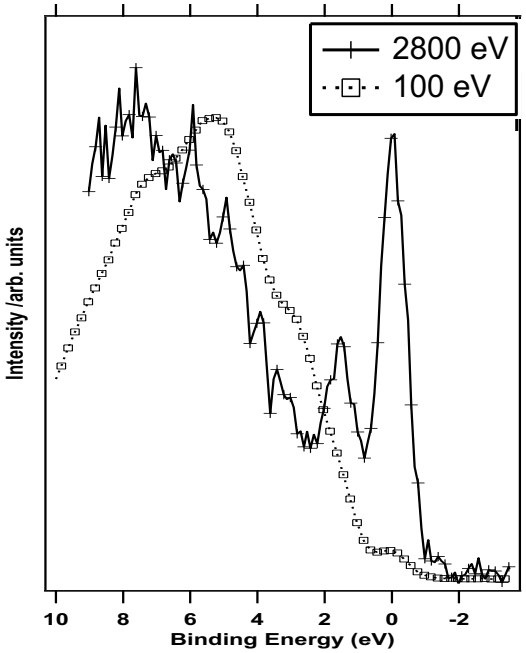
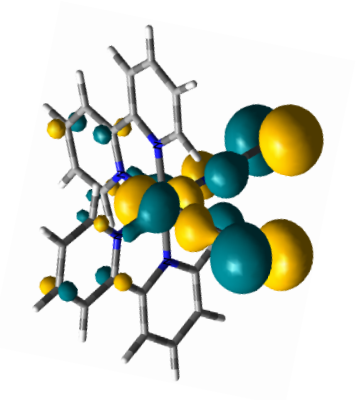
Example on atomic level understanding – Light to electrical energy conversion using dye molecules

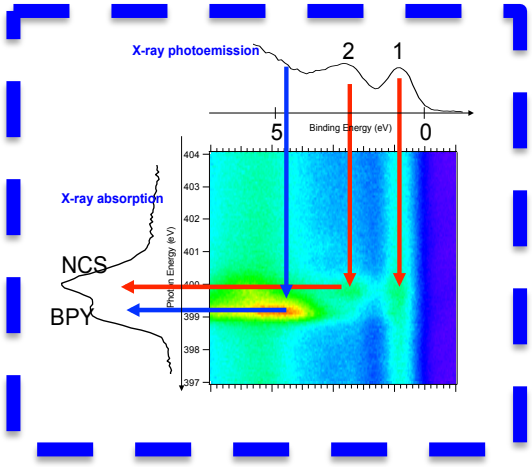
Orbital composition

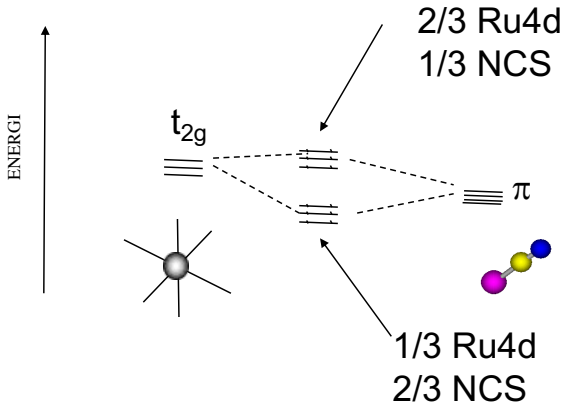






HOMO CHARACTER:
2/3 Ru4d +1/3 NCS p





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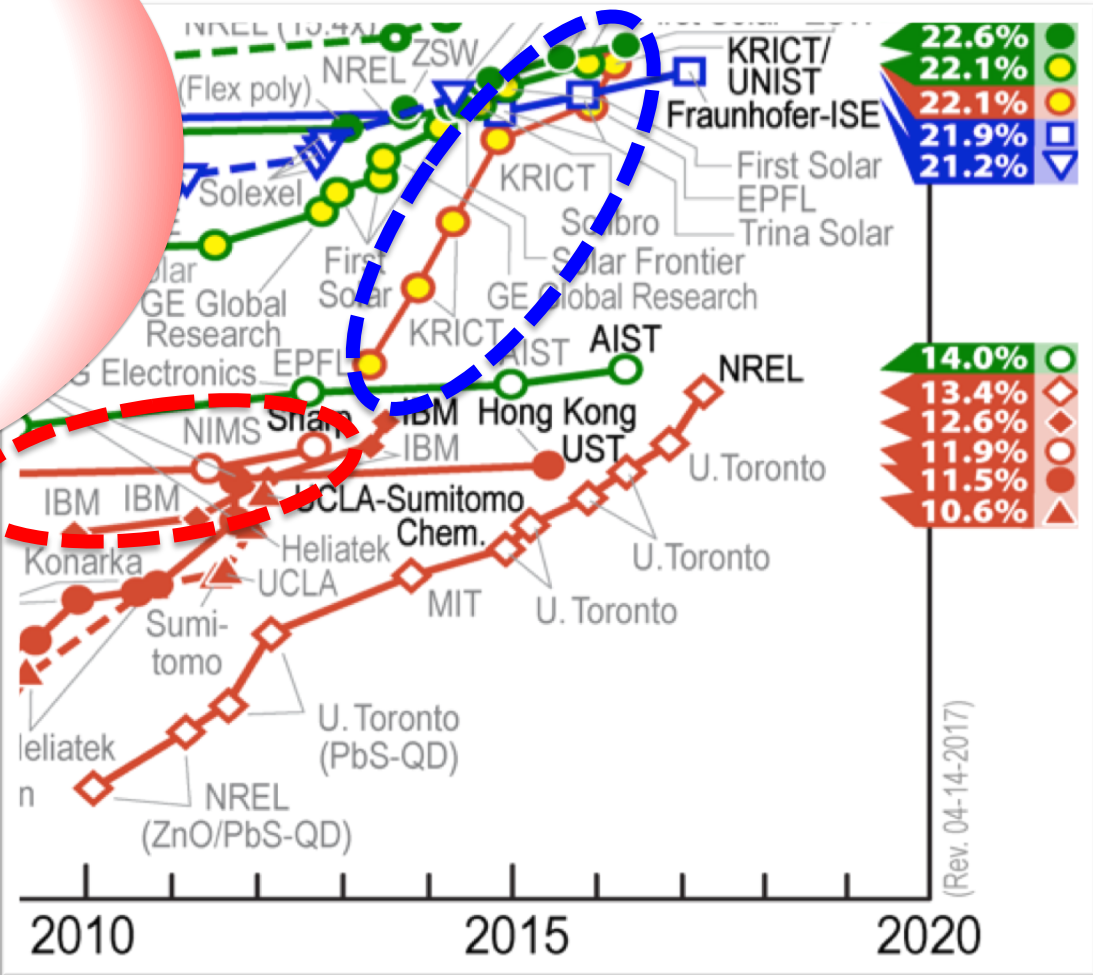
Traditional system

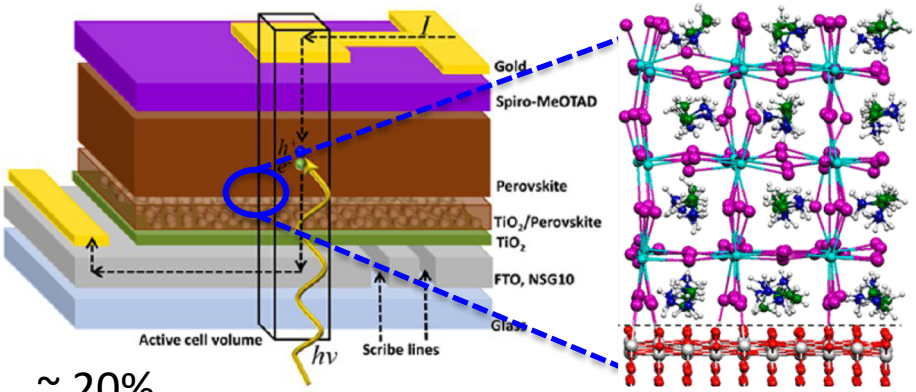
New families of systems

New era in energy research

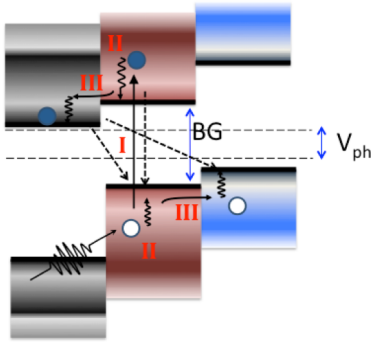


Electron spectroscopy of solar cell materials
Perovskite solar cell materials

Understand key interfacial processes in conversion



~ 20%



Interface structure

Where are the atoms?

Orbital composition

Where are the electrons?

Energy matching

How to facilitate efficient charge transfer

Dynamics

How do electrons and atoms move during the conversion process.

2D/3D design

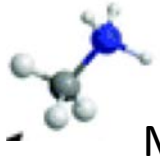
Interface structure

Electronic structure

Goal 1: Explore, at the atomic level, the limitations of conversion due to charge dynamics.
Goal 2: Define design rules for efficient energy conversion. Indoor applications.

Synthesis

Simple: 2 salt solutions, e.g PbI_2 + MAI



MA

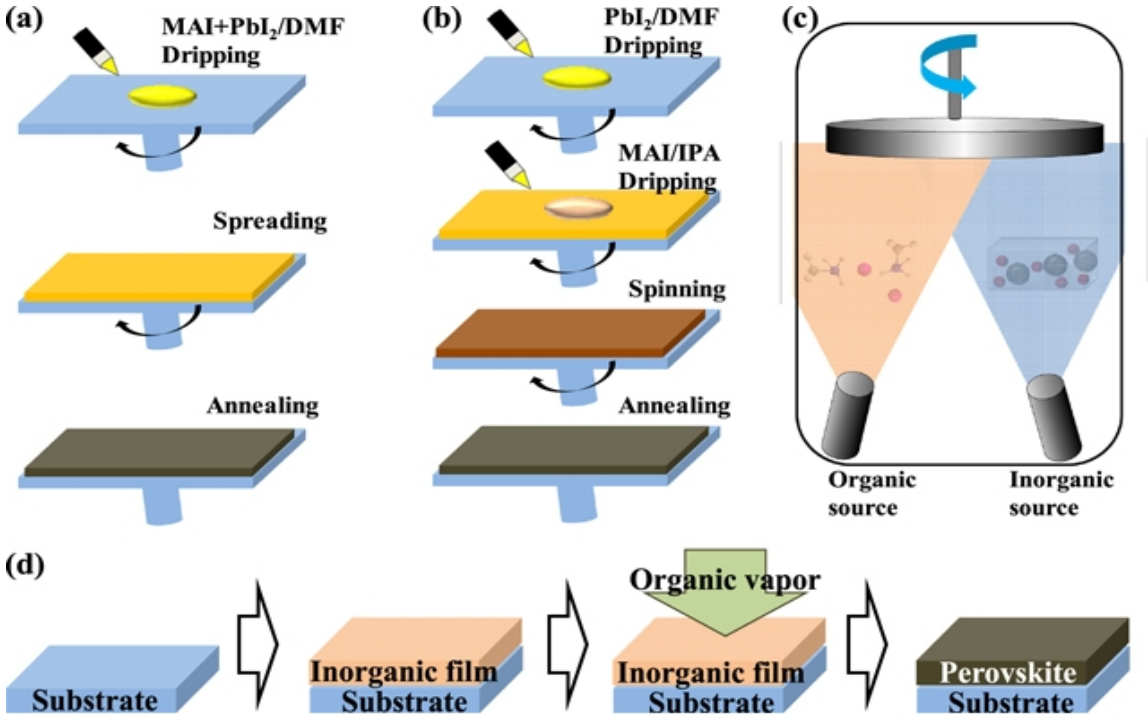


Figure 6 from Recent progress in efficient hybrid lead halide perovskite solar cells
Jin Cui et al 2015 Sci. Technol. Adv. Mater. 16 036004
doi:10.1088/1468-6996/16/3/036004

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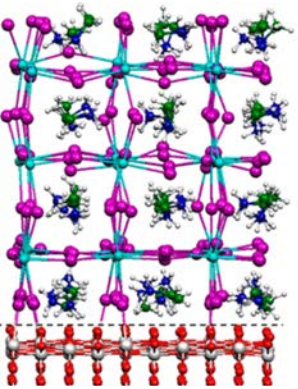
Examples: Lead-based halide perovskite

HAXPES and SOXPES



Time

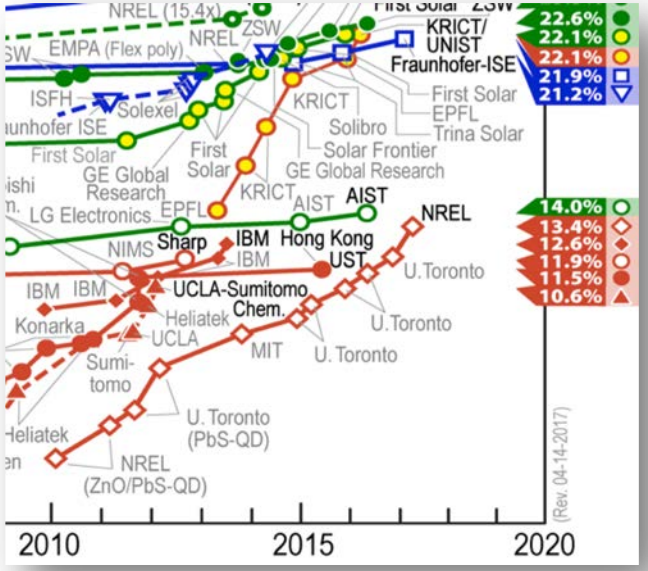
$MAPbI_3$

$MAPb(I_{1-x}Br_x)_x$

$FA_xMA_{1-x}Pb(I_{1-x}Br_x)_3$

Multi cation (K^+, Cs^+, MA^+, FA^+) mixed perovskite

FA MA

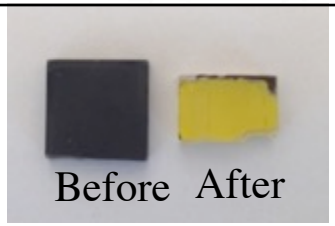


(Also: attempts to replace Pb to Bi, Sn, Sn, Ag)

Degradation, Humidity
$MAPbI_3$

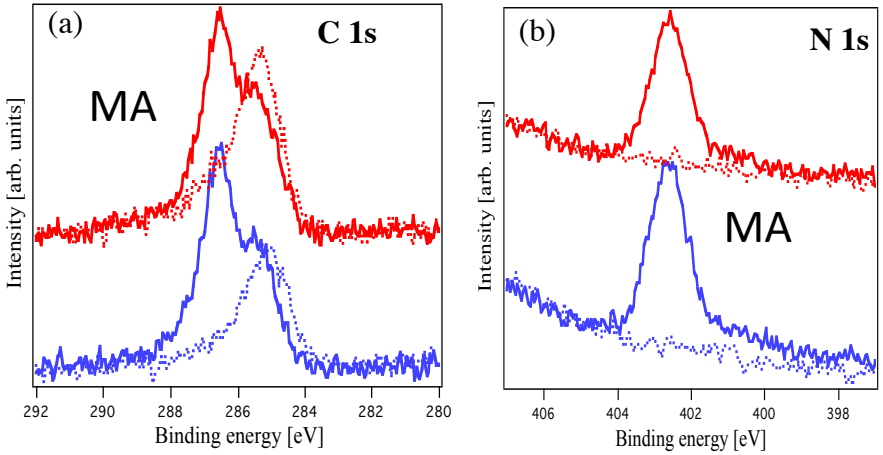
Interface structure

Water exposure



$MAPbI_3$

$MAPbI_{3-x}(Cl_x)$



Exp.	$MAPbI_3$ + H_2O	$MAPbI_{3-x}Cl_x$ + H_2O
I/Pb	1.90	1.91

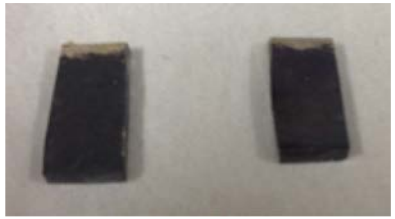
$CH_3 NH_3 PbI_3 \rightarrow PbI_2 + CH3 NH_3I \uparrow$

Philippe et al., *Chem. Mater.* **2015**, *27*, 1720−1731

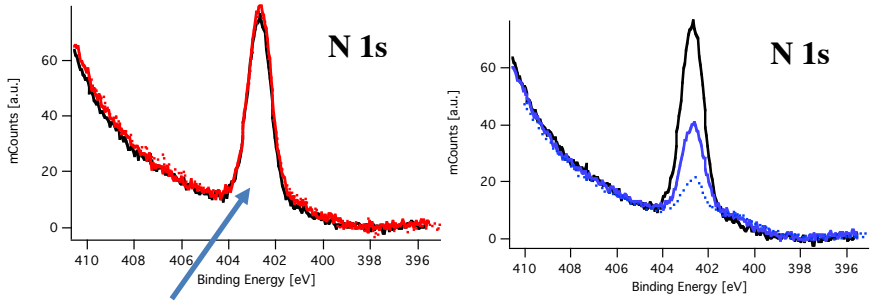
"Long" time storage

$MAPbI_3$ in argon in air (in the dark)

Day 83



Ratio I/Pb	Argon	Air
Day 0	3.09	3.09
Day 45	3.11	2.61
Day 83	3.10	1.98



$CH_3 \mathbf{N}H_3 PbI_3 \rightarrow PbI_2 + CH_3 NH_3I \uparrow$

MAI "leave" the sample

$FA_xMA_{1-x}Pb(I_{1-x}Br_x)_3$

Interface structure

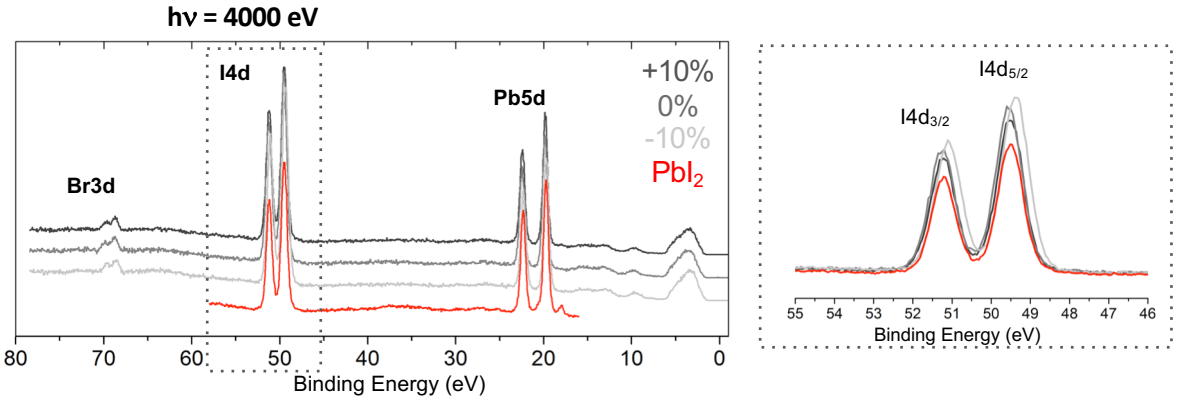
Investigation of a mixed perovskie **($FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$)**

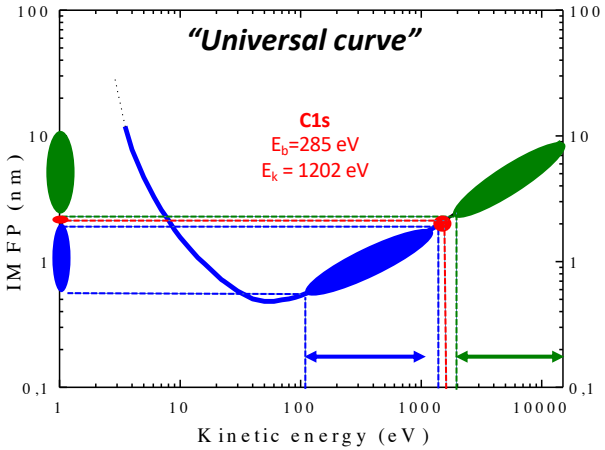
(a) -10% PbI_2

(b) Stoichiometric (0%)

(c) +10% PbI_2

I/Pb ratio of 2.55 is expected





(a) I/Pb intensity ratio

hv [eV]	Probing depth [nm]	-10 %	0	+10 %	PbI_2
4000	18	2.49	2.36	2.28	1.96
2100	11	3.35	3.08	2.90	--
758	5	4.36	4.22	3.82	2.03

Validation of the quantification process with a reference

Jacobsson et al. JACS 2016, 138, 10331−10343

$FA_xMA_{1-x}Pb(I_{1-x}Br_x)_3$

Interface structure

Investigation of a mixed perovskie **($FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$)**

(a) -10% PbI_2

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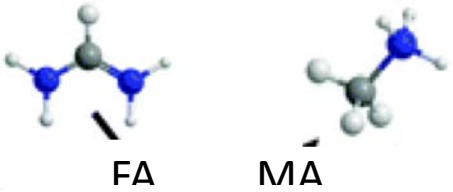
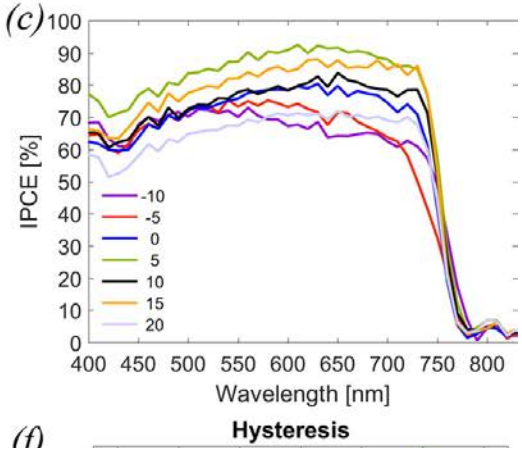


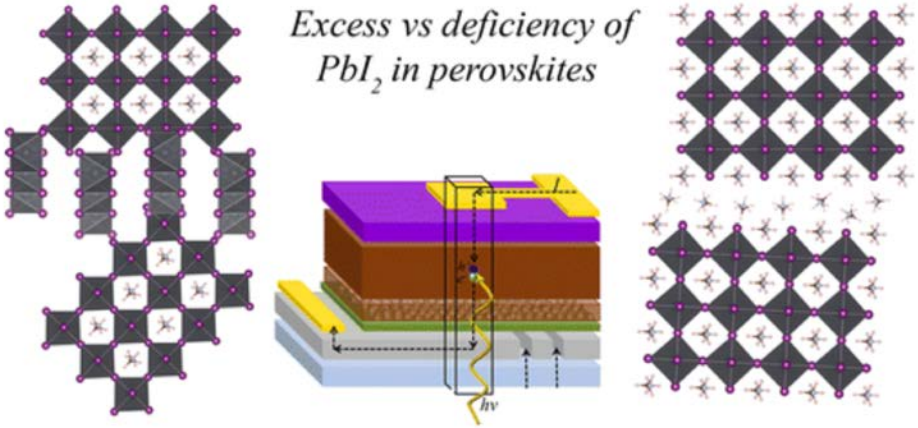
FA MA

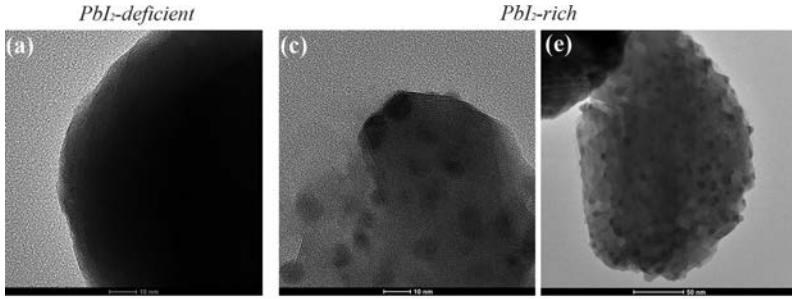
Theo ≈ 2.55

(a) I/Pb intensity ratio					
hv [eV]	Probing depth [nm]	-10 %	0	+10 %	PbI_2
4000	18	2.49	2.36	2.28	1.96
2100	11	3.35	3.08	2.90	--
758	5	4.36	4.22	3.82	2.03

Interpretation of the data







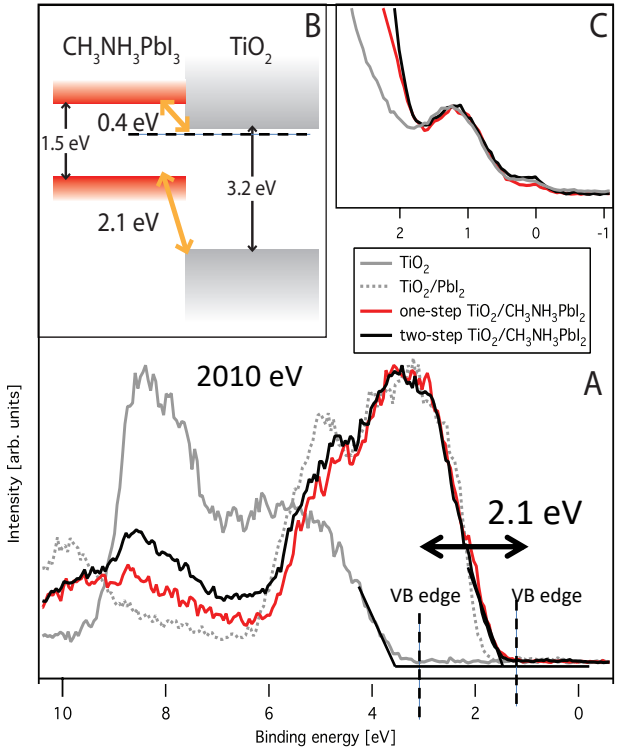
Jacobsson et al. JACS 2016, 138, 10331−10343

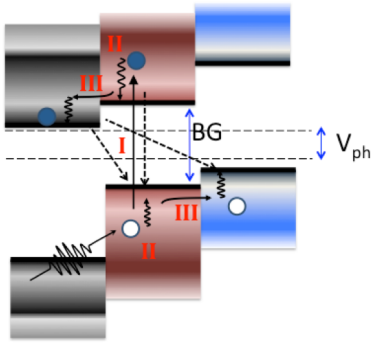
EXCESS PbI_2 FAVOURS PHOTOCURRENT AND EFFIVIENCY (minimize organic layers that prevent charge transport)

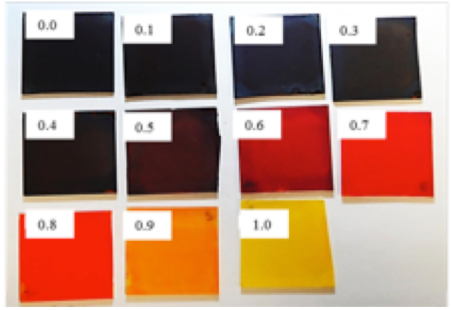
TiO_2/ $CH_3NH_3PbI_3$ band alignment

Energy matching

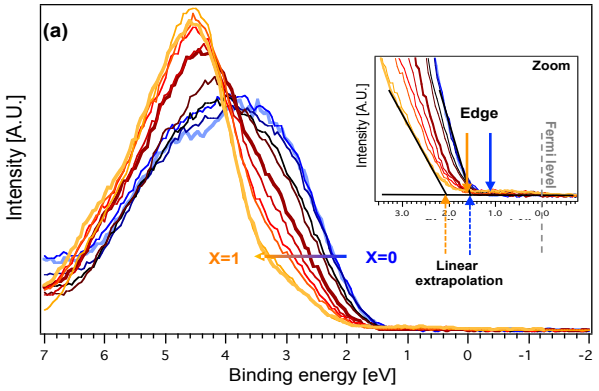
$MAPbI_3$

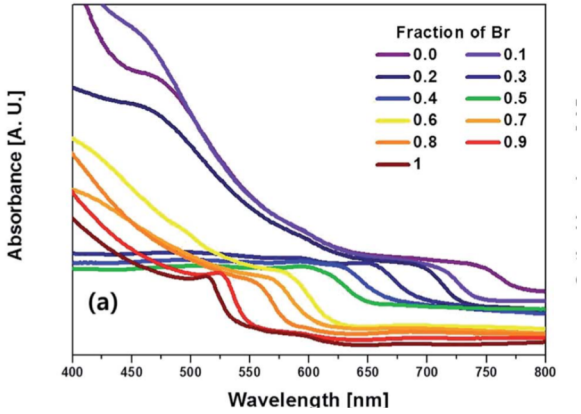






$MAPb(I_{1-x}Br_x)_x$





What can we learn from these measurements???

Lindblad et al. J. Phys. Chem. Lett. 2014, 5, 648–653

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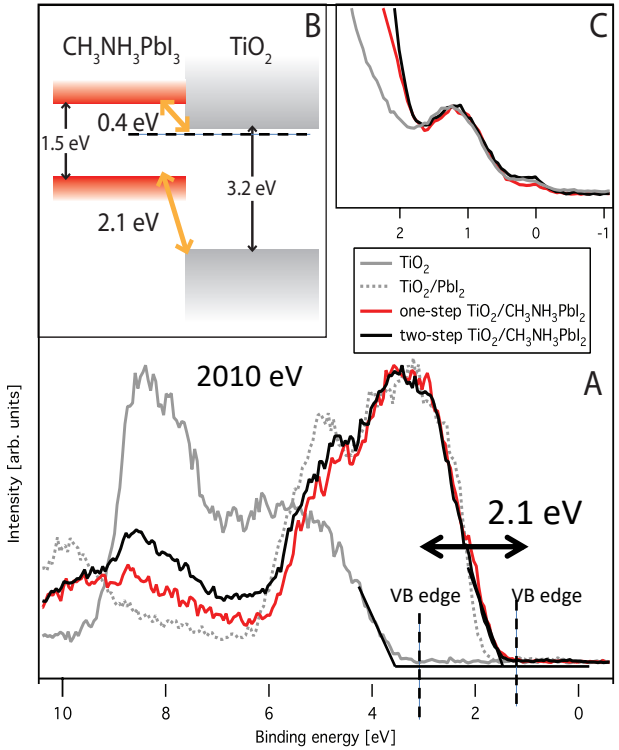
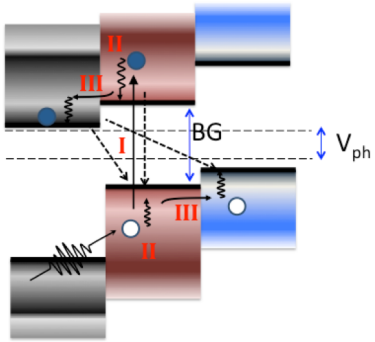
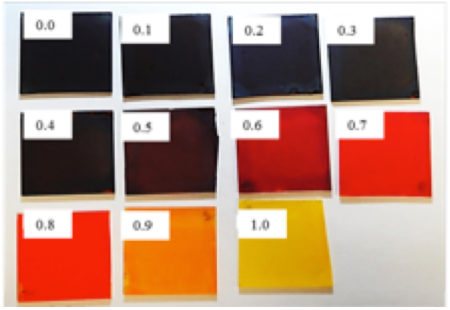
TiO_2/ $CH_3NH_3PbI_3$ band alignment

Energy matching

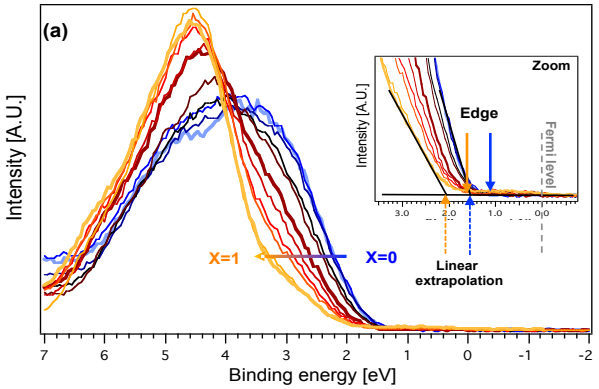
$MAPbI_3$

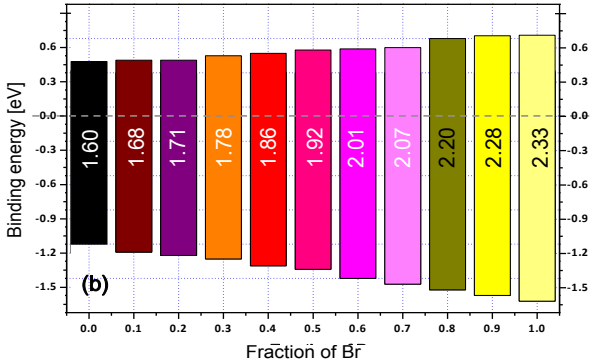






$MAPb(I_{1-x}Br_x)_x$





Lindblad et al. J. Phys. Chem. Lett. 2014, 5, 648–653, J Phys Chem C. 2015;119(4):1818-25

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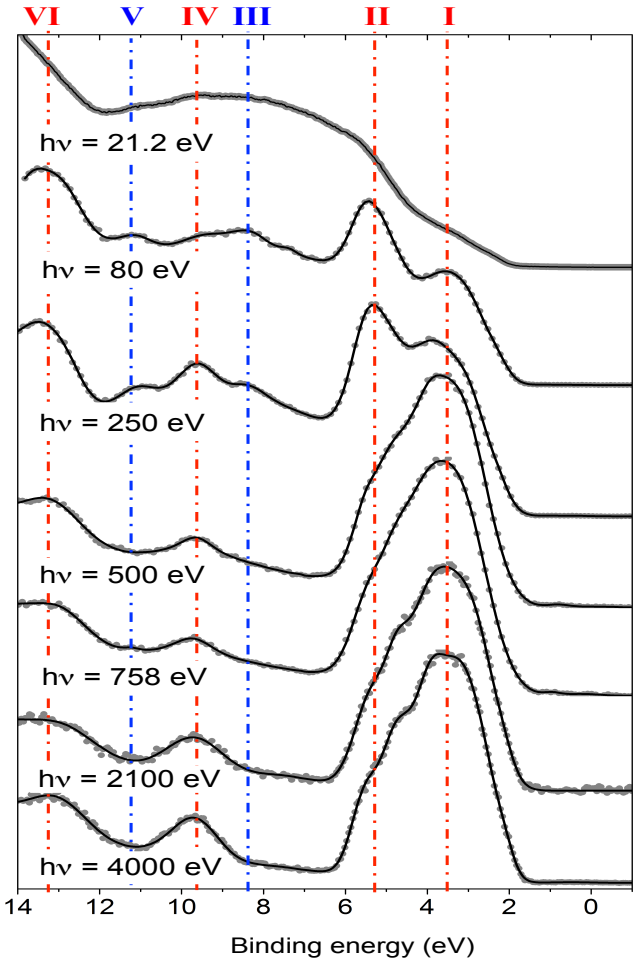
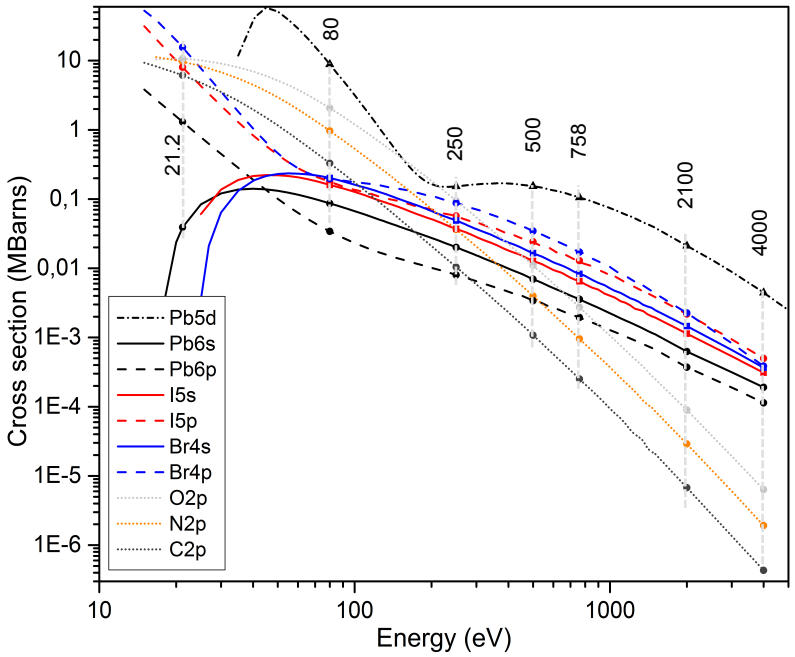
XPS gives Partial DOS (not DOS)

Orbital composition



$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$

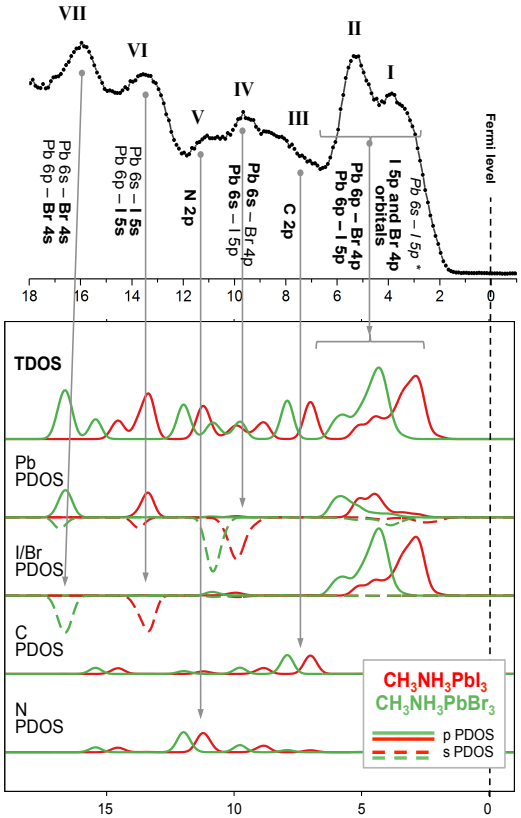


Measurements at high energy mainly measure the PbX_6-unit

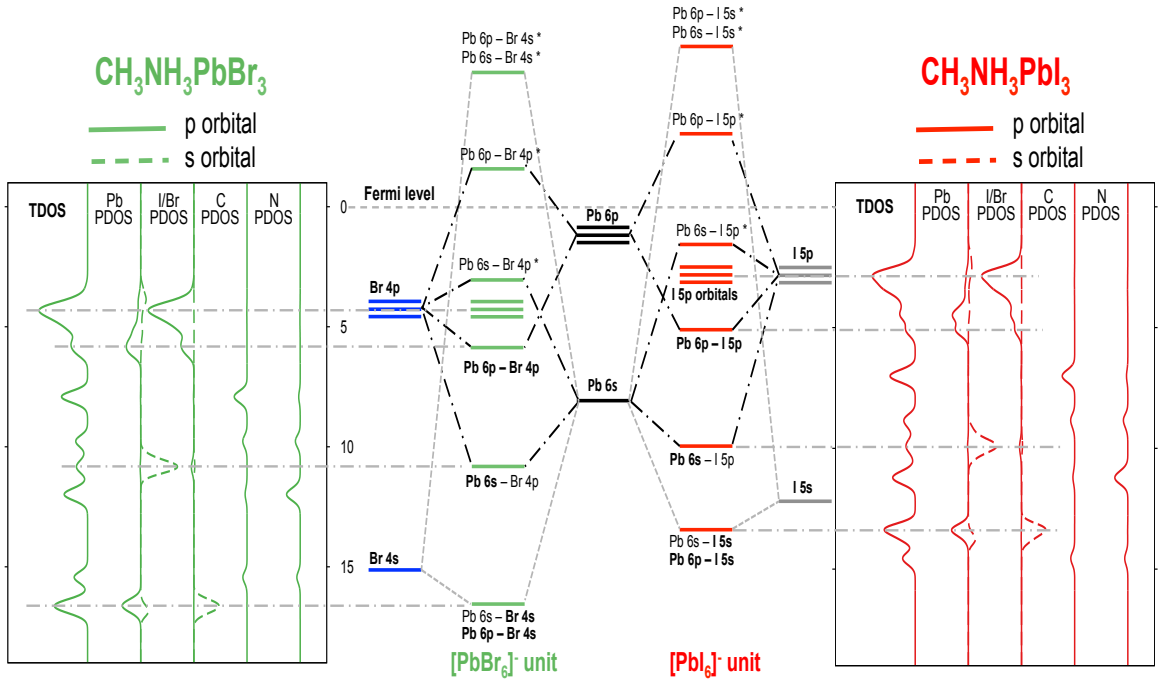
XPS gives Partial DOS (not DOS)

Orbital composition

Odelius (Stockholm University)



$FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$



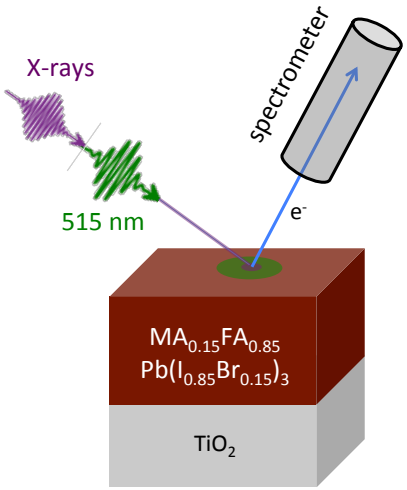
The top of the valence band has Pb6s - I5p (or Br4p) anti - bonding character. Defect tolerant.

Philippe B; et sl. *J Phys Chem C*. **2017**;121(48):26655-66

PES measurements with laser illumination

Dynamics

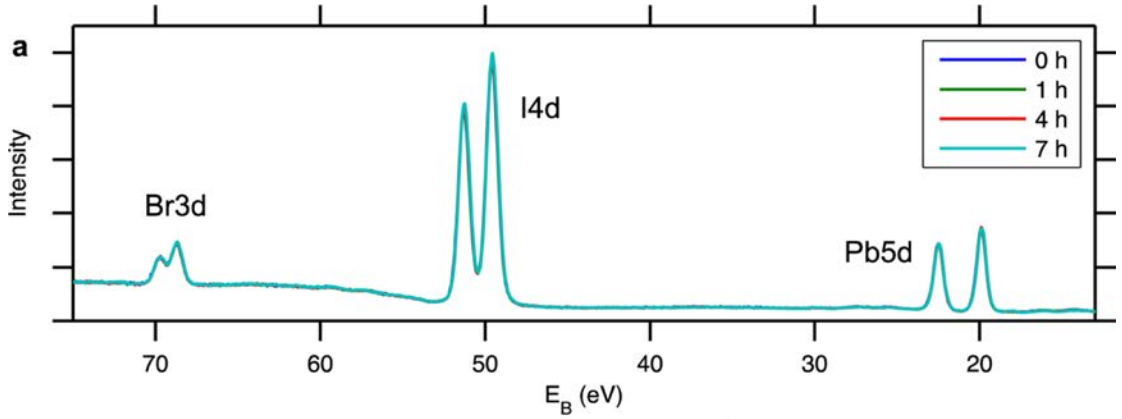
Property	Facility	Technique
EFFICIENT DETECTION	UBjL @ Bessy 2	PES using ArTOF – LowDose-measurements, ps time resolution



515 nm at 1 sun

- X-rays and pump laser on same spot on sample
- Measure spectra using X-rays
- Follow changes induced by laser

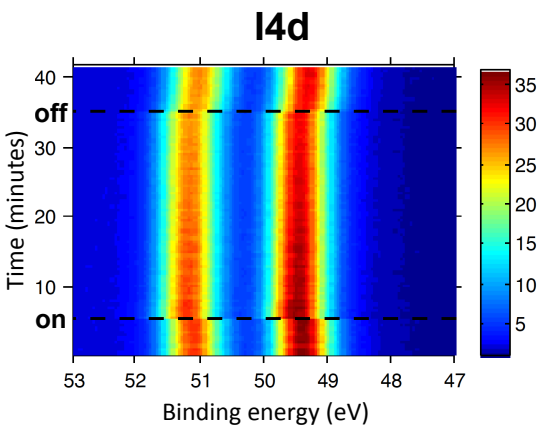
Scienta Omicron

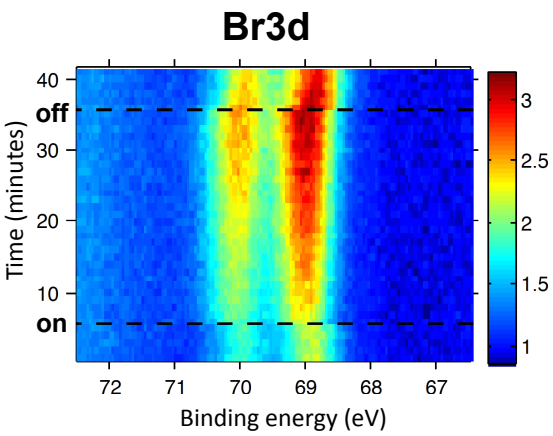


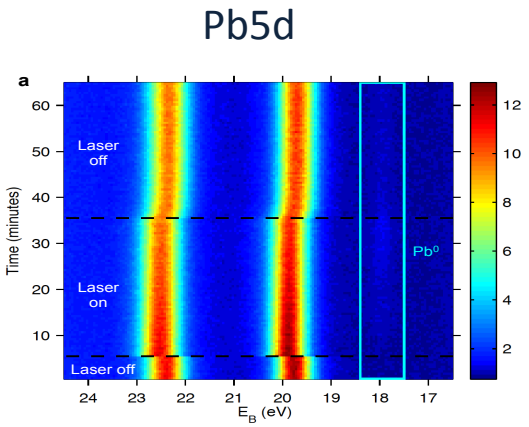
Following moving atoms/charges
Light induced changes

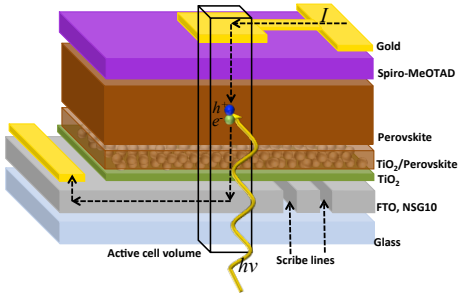
Dynamics

Property	Facility	Technique
EFFICIENT DETECTION	UBjL @ Bessy 2	PES using ArTOF – LowDose-measurements, ps time resolution

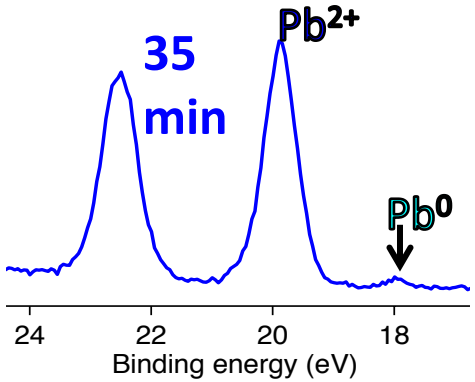








$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$



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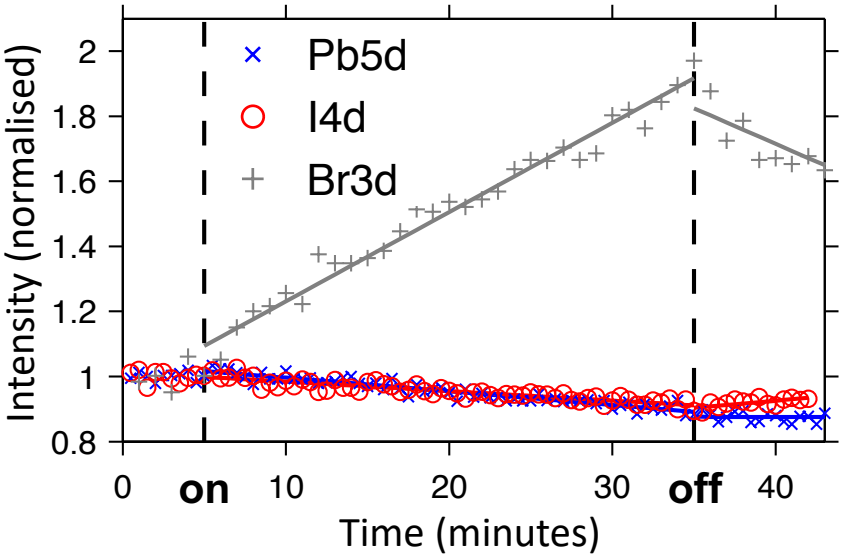
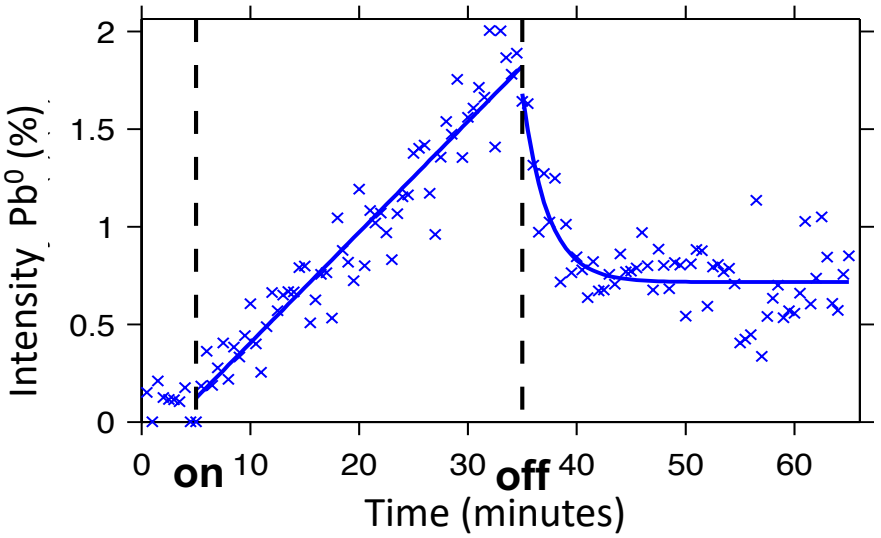
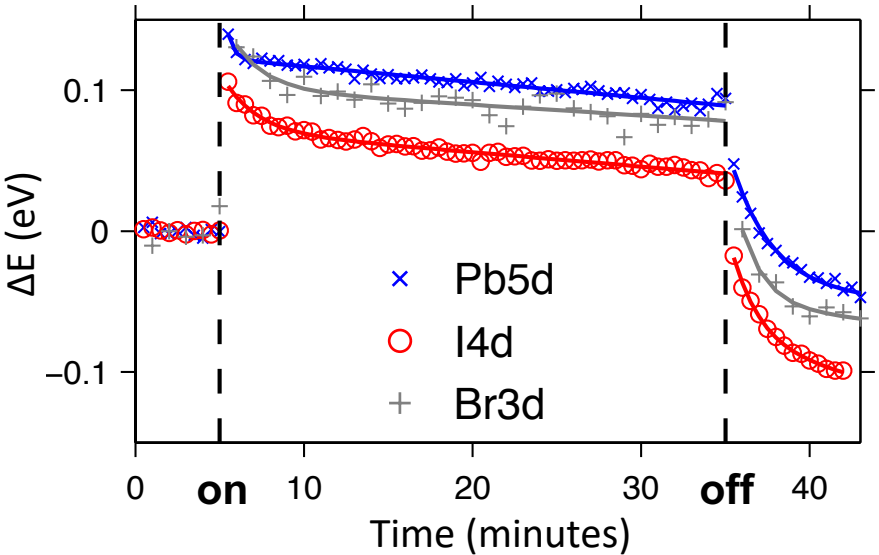
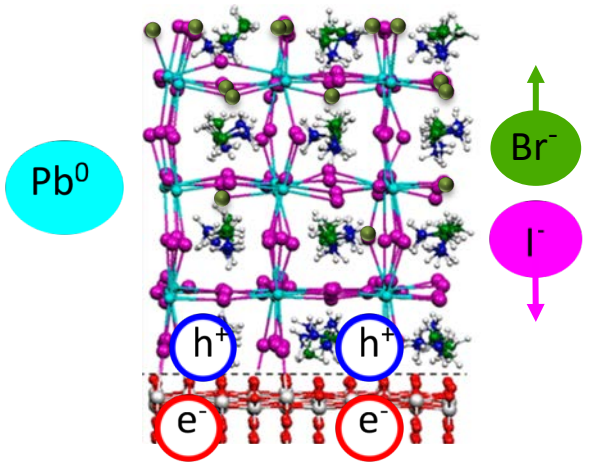
Energy shift, intensity changes and metallic lead

Dynamics







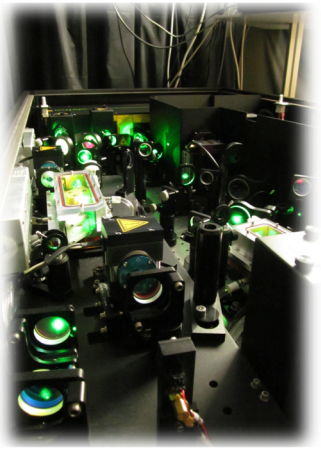


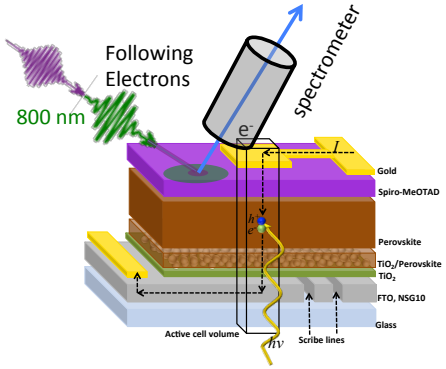
$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$

Following moving electrons

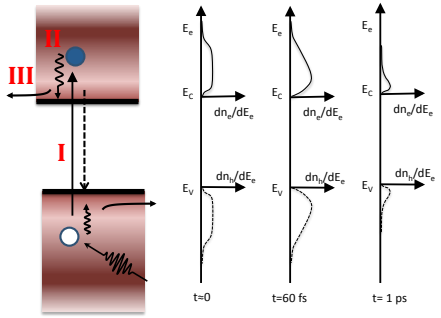
Dynamics

Property	Facility	Technique
TIME RESOLVED	HELIOS (HHG @ UU)	50 fs, 20-70 eV, time-resolved PES and bandmapping





How can one control thermalisation ?



Cappel et al. PCCP, 2016, 18 21921-21929

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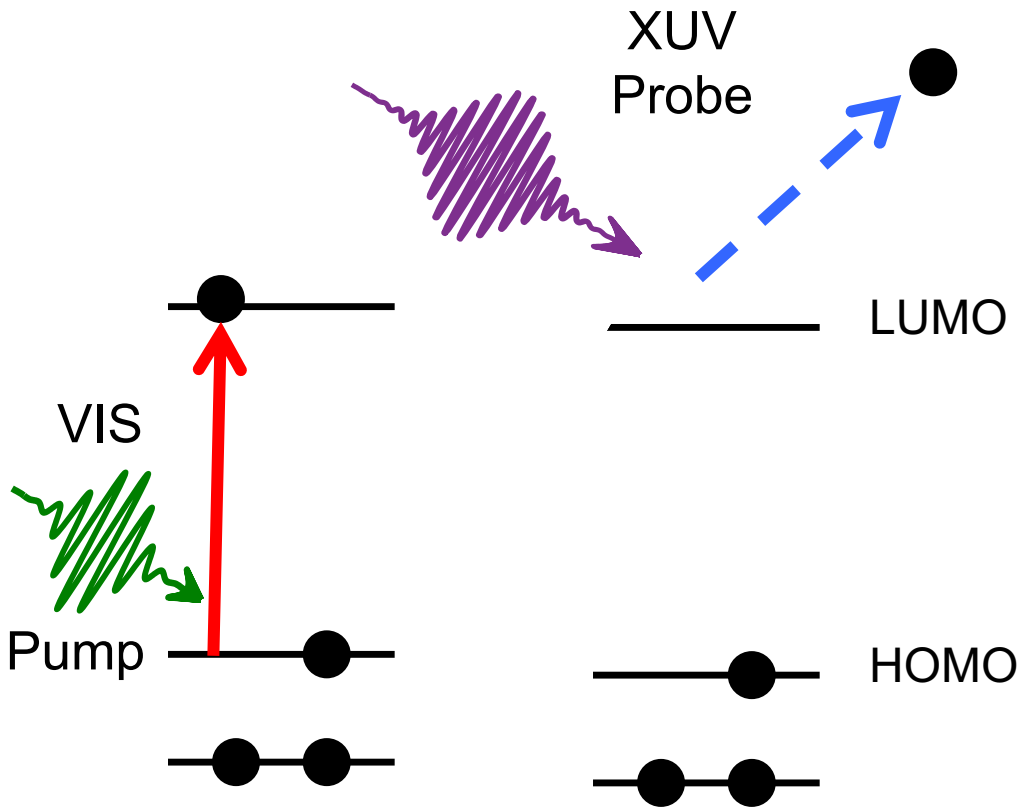
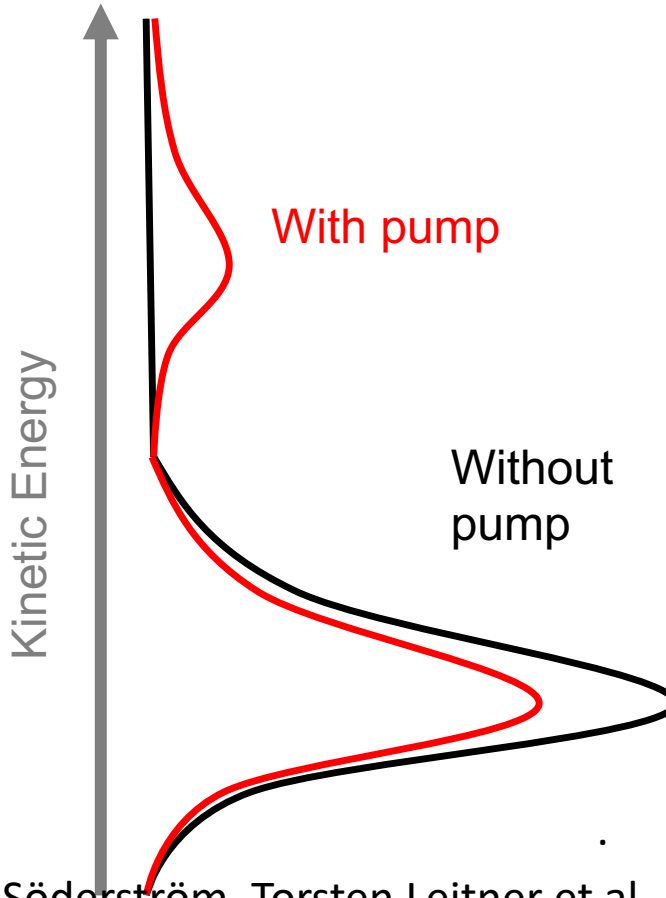
Time-resolved photoelectron spectroscopy

Dynamics





Ute Cappel, Johan Söderström, Torsten Leitner et al.
Ovsyannikov, R. et al., *J. Electron Spectros. Relat. Phenomena* **191,** 92–103 (2013)l.
Terschlüsen, J. A. et al., *Nucl. Instrum. Methods Phys. Res., Sect. A* **768,** 84–88 (2014).

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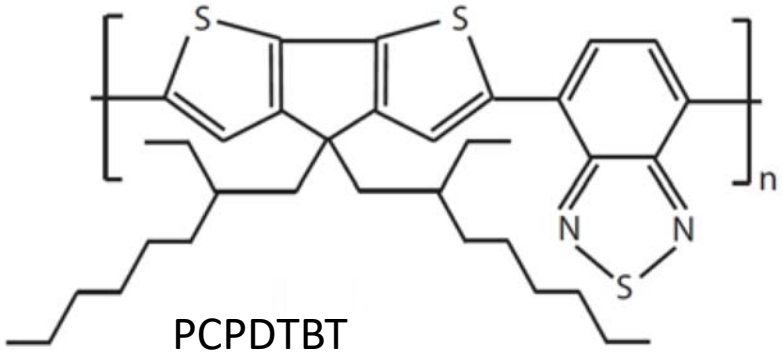
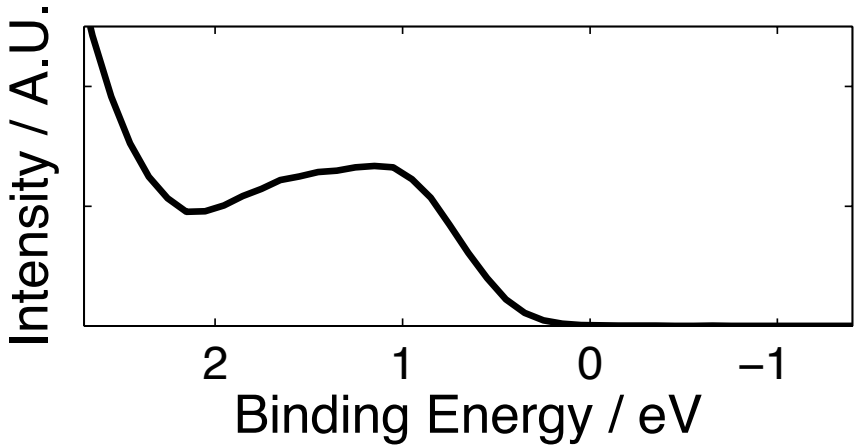
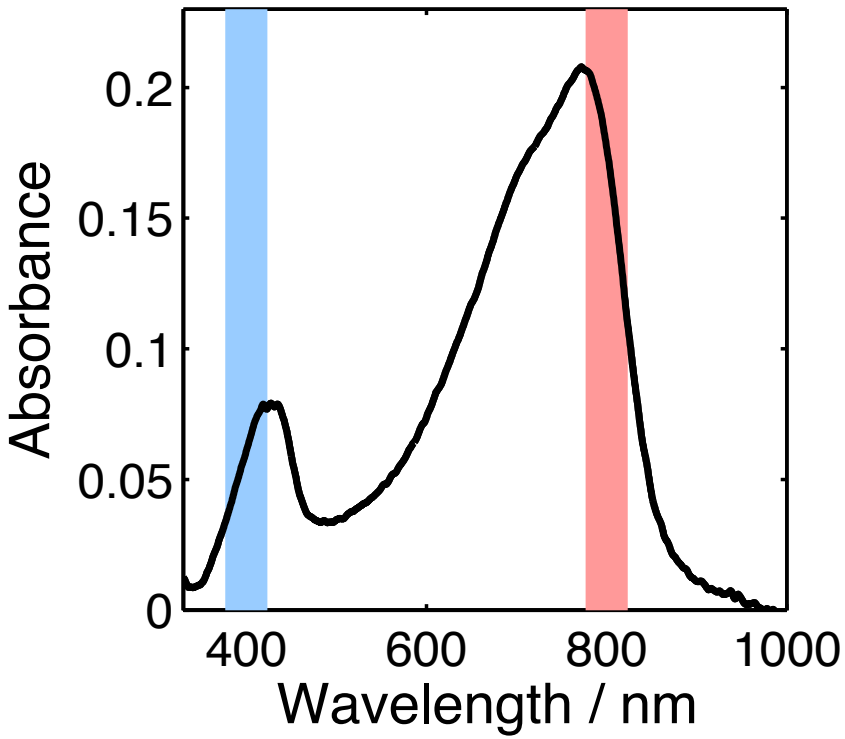
First results

Dynamics



PCPDTBT





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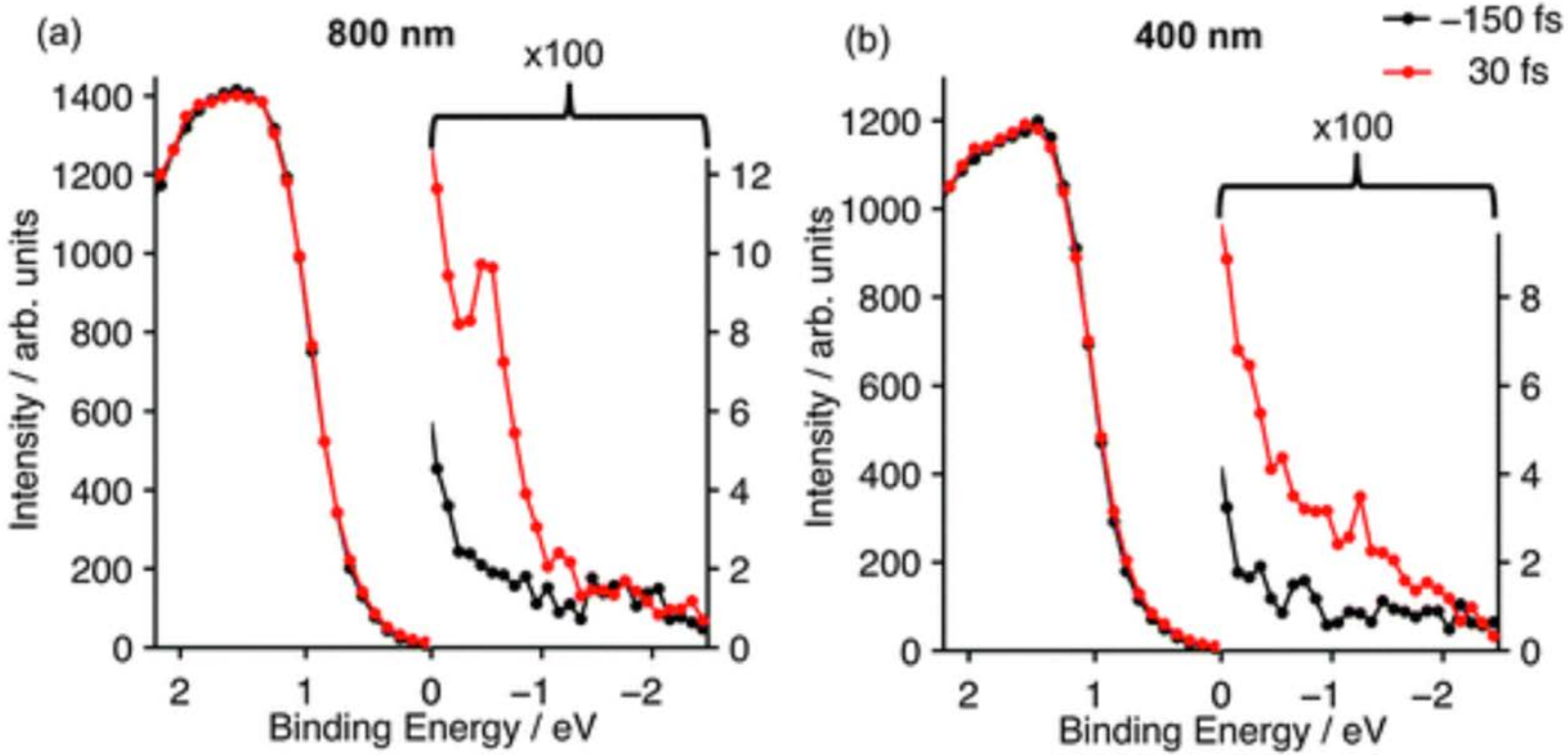
Dynamics



What can we observe?

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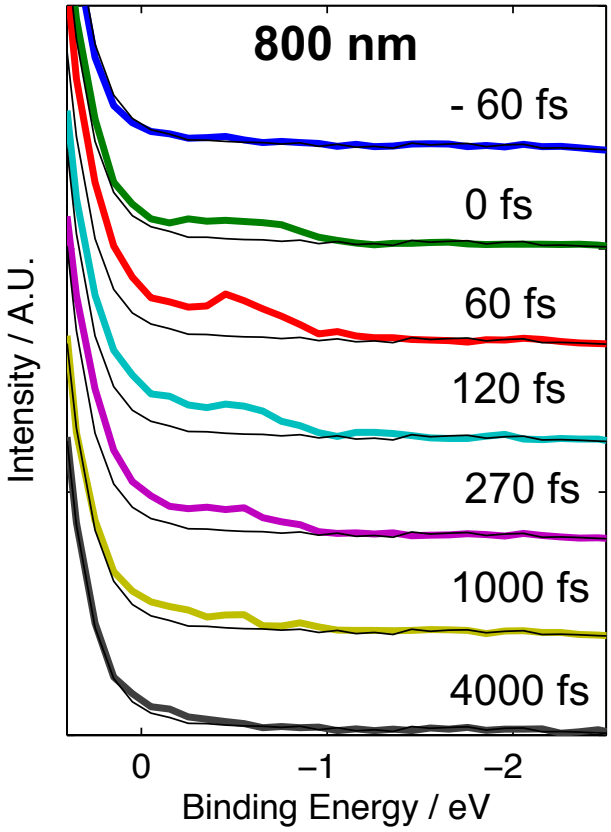
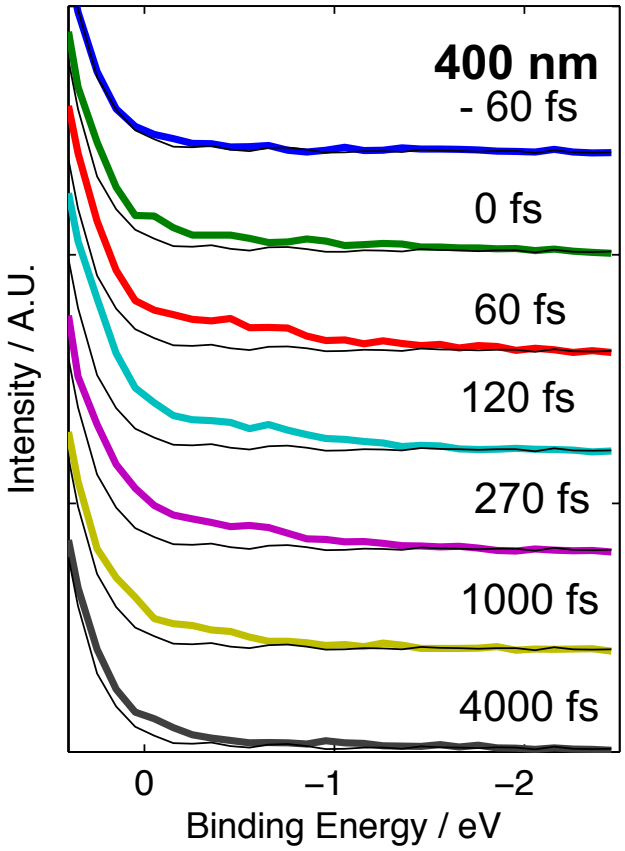
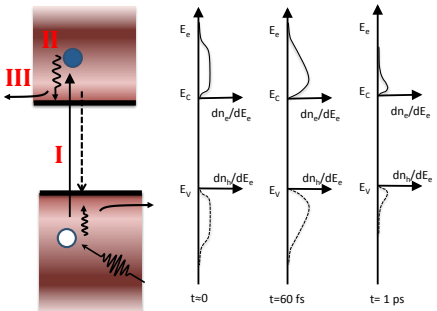
First results

Dynamics

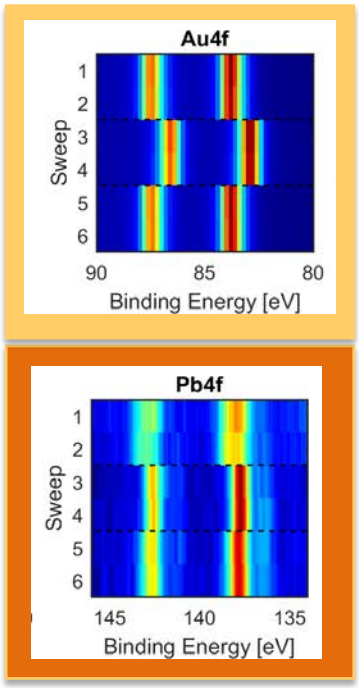


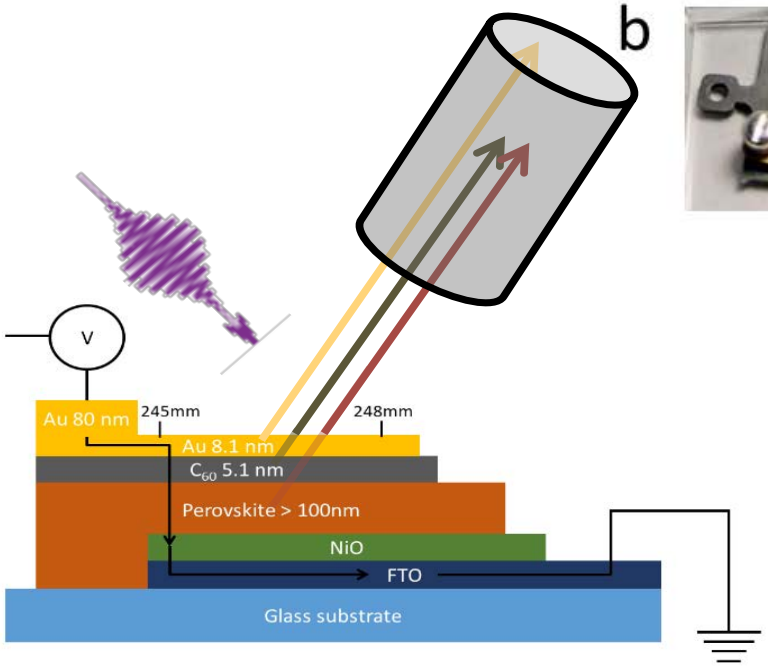




Following moving atoms/charges
Voltage induced changes

Property	Facility	Technique
ENVIRONMENTS I	HAXPES @ BESSY, SOLEIL, DIAMOND, DESY	Real interfaces during operations



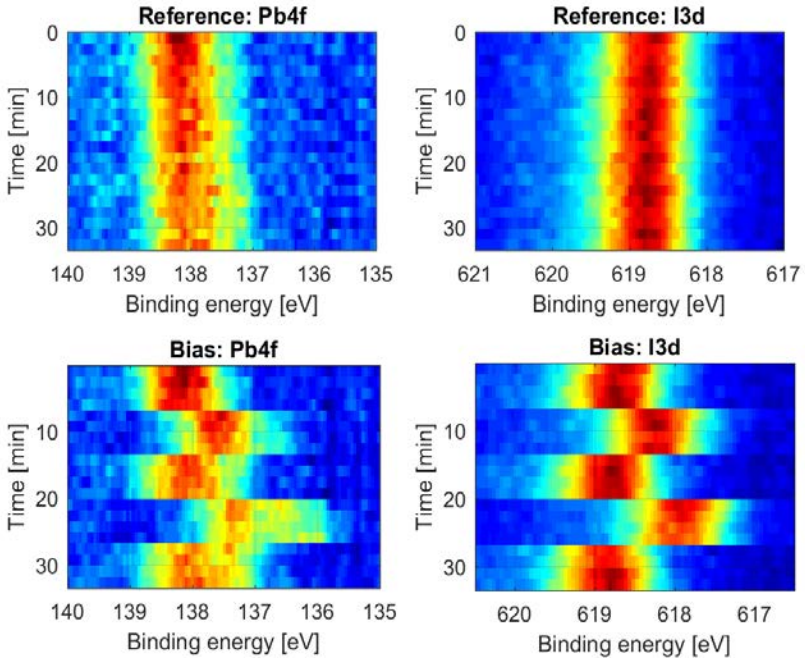


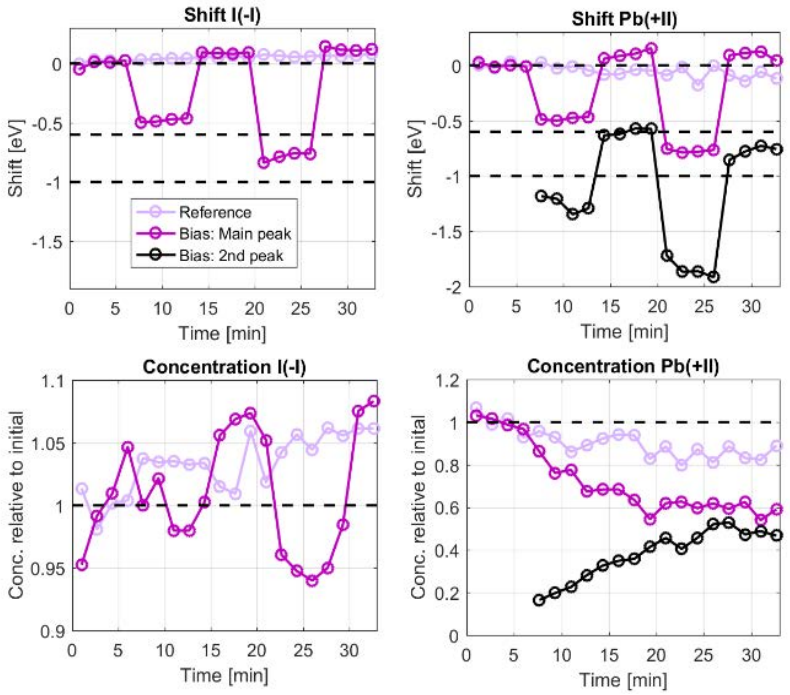
The hard X-ray allow penetration
Through the interface

How is the electric field distributed, what is the role of the electrons/atoms.

Following moving atoms/charges
Voltage induced changes

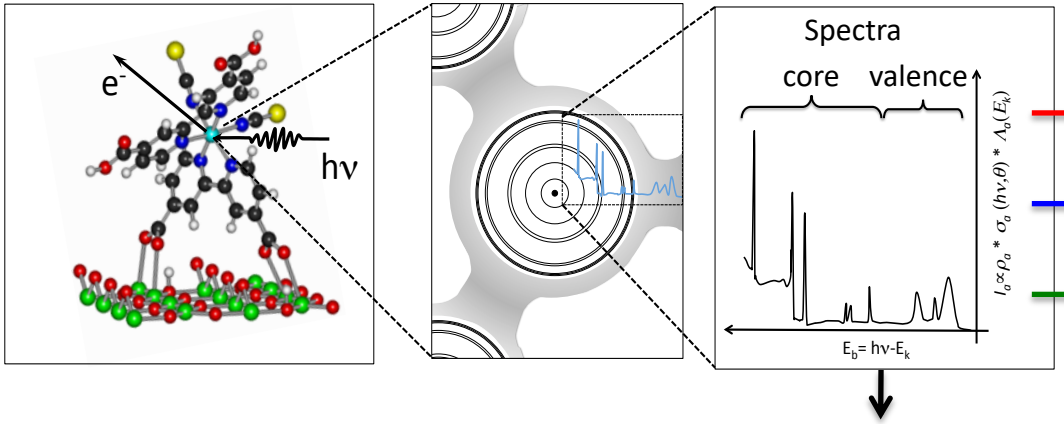
Property	Facility	Technique
ENVIRONMENTS I	HAXPES @ BESSY, SOLEIL, DIAMOND, DESY	Real interfaces during operations





Foundation – X-ray based spectroscopy Methodology development

X-ray based spectroscopy – e.g. Photoelectron spectroscopy



Y-axis:

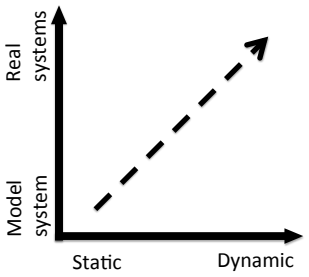
Interface sensitivity in the dimension of 0,3 nm to 10 nm

The character (molecular orbital composition).

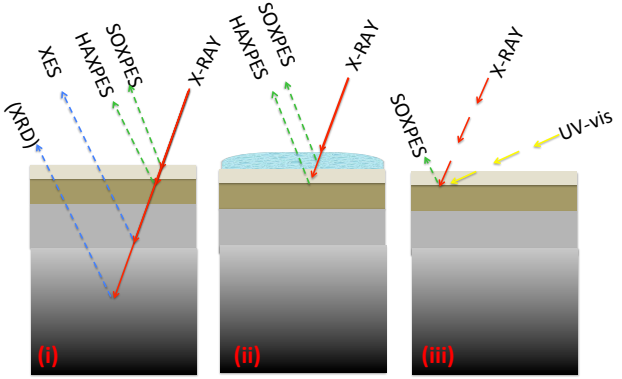
Density and amounts

X-axis: **Energy levels** - **element** and **chemical** sensitivity at an atomic level.

Explore the enormous development of new **sources**



Challenge: relevant samples



Development of new/improved **analytical tools (HAXPES, SOXPES)**

INTERFACES

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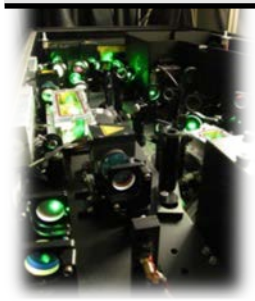
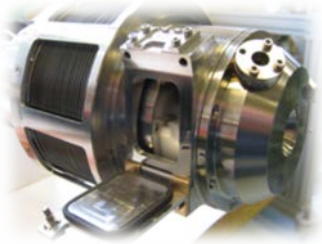
X-ray based methodology

Our main current development projects

Property	Facility	Technique
TIME RESOLVED	HELIOS (HHG @ UU) UBjL @ Bessy 2	50 fs -50 ps, 20-70 eV, time-resolved PES and bandmapping
EFFICIENT DETECTION	UBjL @ Bessy 2	PES using ArTOF – LowDose-measurements, ps time resolution
ENVIRONMENTS I	HAXPES @ BESSY, SOLEIL, DIAMOND, DESY	PES on real buried interfaces during operations. Surface bulk. PDOS.
ENVIRONMENTS II	SPECIES, HIPPIE @ MAX IV	High pressure PES, RIXS on the Li edge
HIGH RESOLUTION	VERITAS @ MAX IV	RIXS > 30 K resolving power



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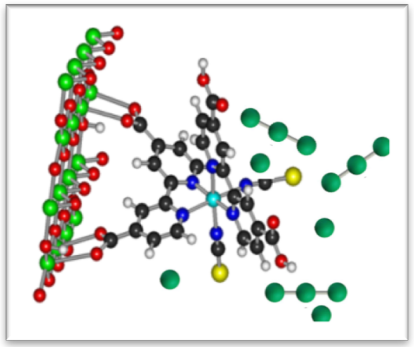
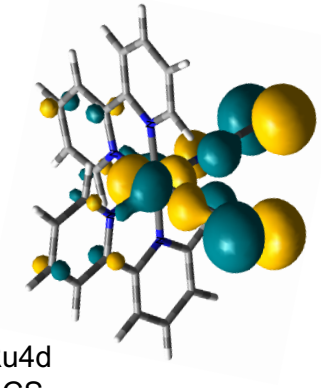
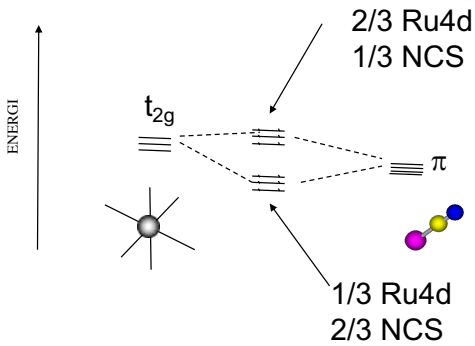
Example on atomic level understanding
Next generation – perovskite solar cells

Interface structure

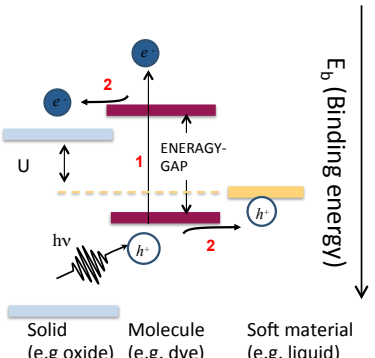


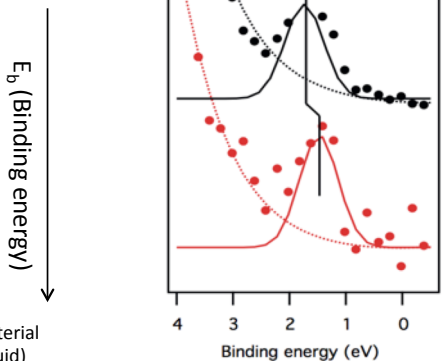
Orbital composition





Energy matching





Dynamics

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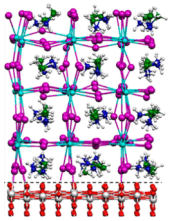
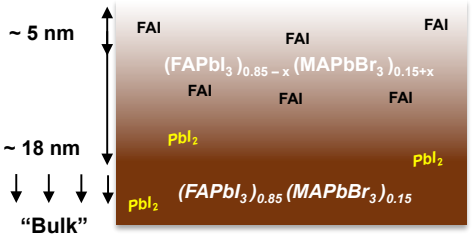
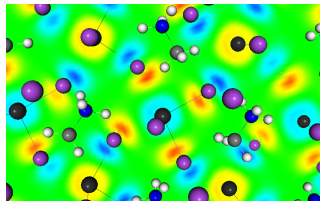
Example on atomic level understanding
Next generation – perovskite solar cells

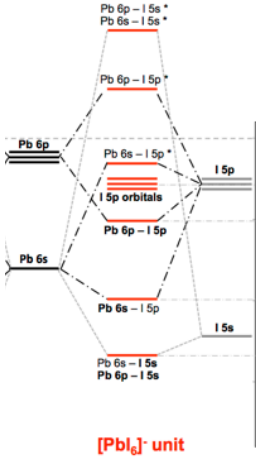
Interface structure



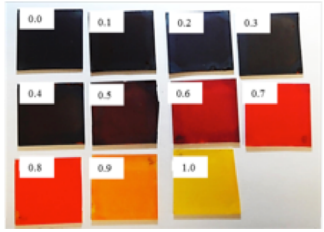


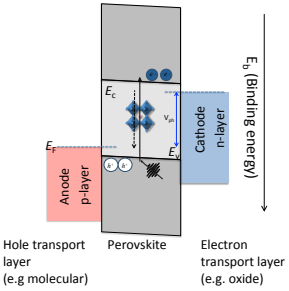
Orbital composition

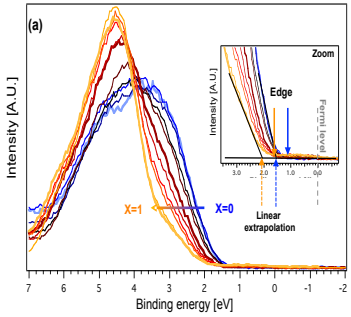




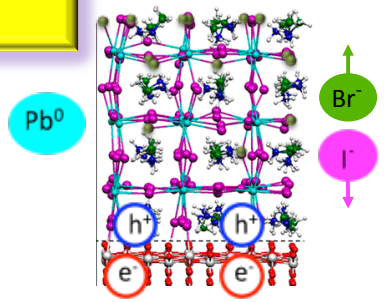
Energy matching







Dynamics



$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$

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