The role of interfaces in perovskite solar cells

Summer School, Khiva

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Content

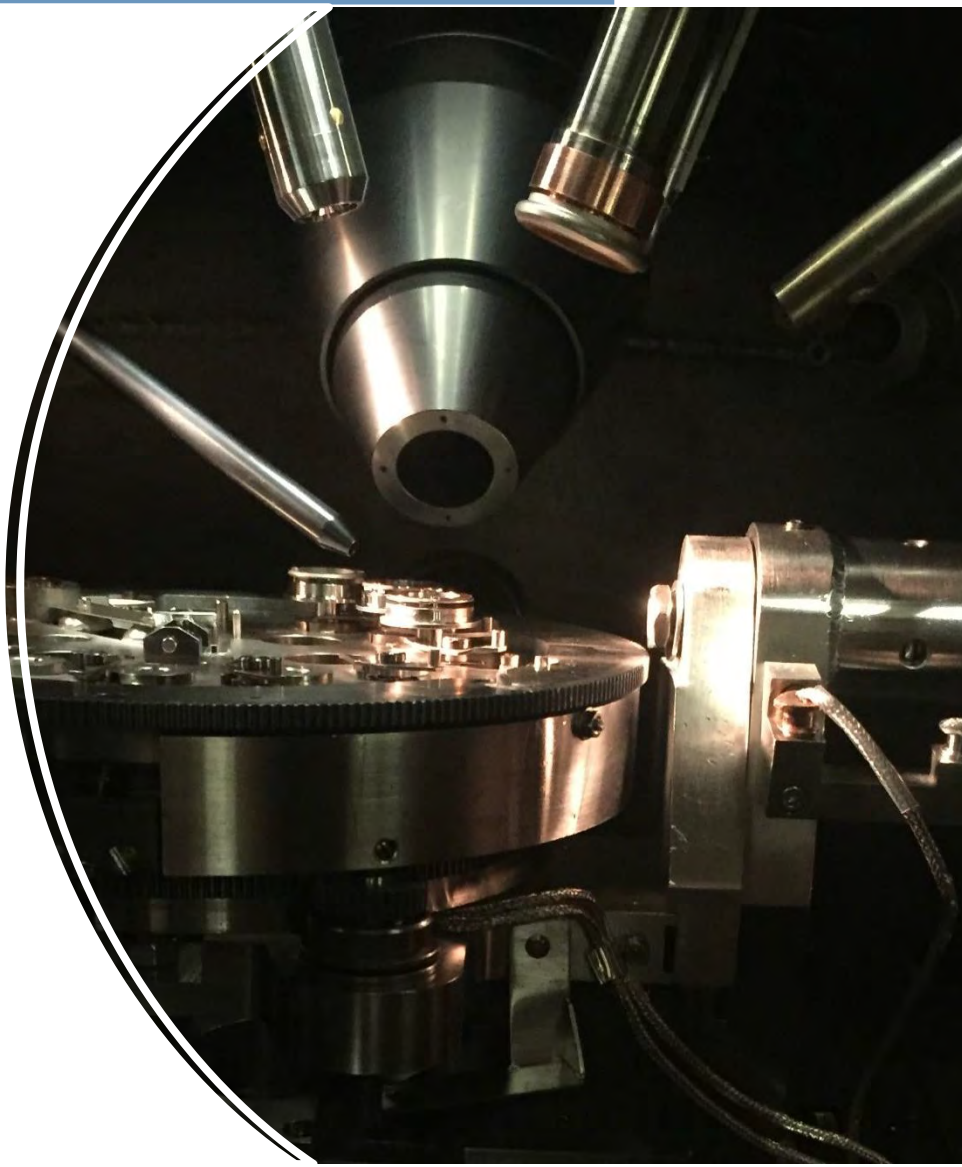
1. Role of interfaces in solar cells

2. Measurement of energy level alignment

3. X-ray photoelectron spectroscopy (XPS)

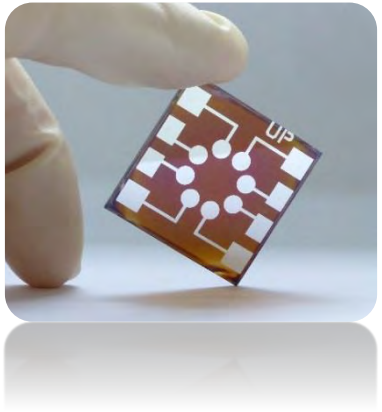
4. Perovskite interfaces measured by XPS

5. Understanding interface chemistry

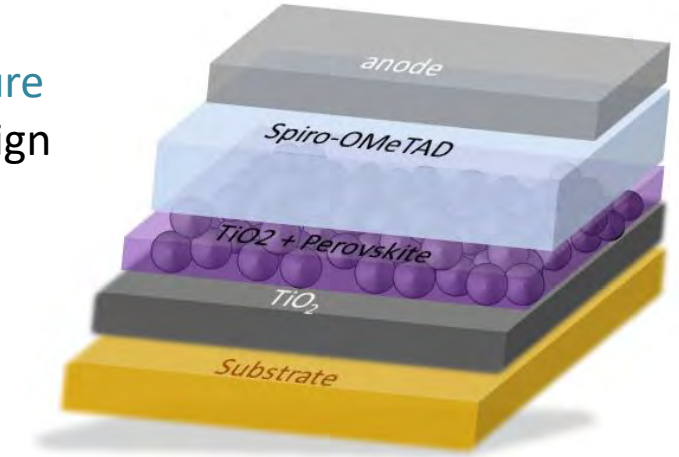


Interfaces in perovskite devices

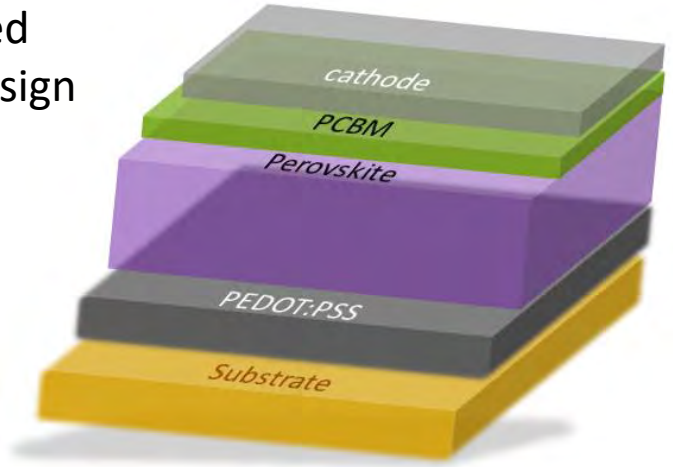
Perovskite solar cells are multilayer devices



1. “Standard” architecture adopted from DSSC design



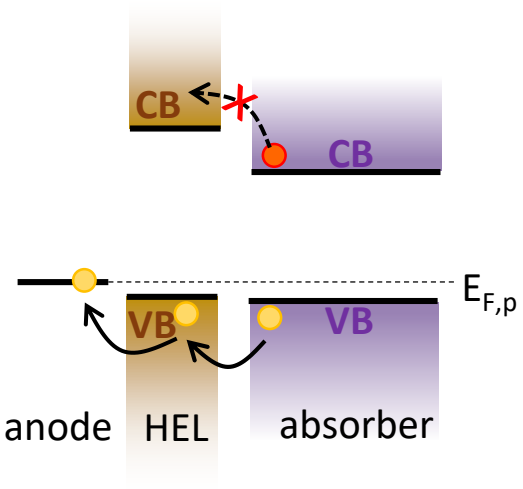
2. Inverted devices adopted from organic solar cells design



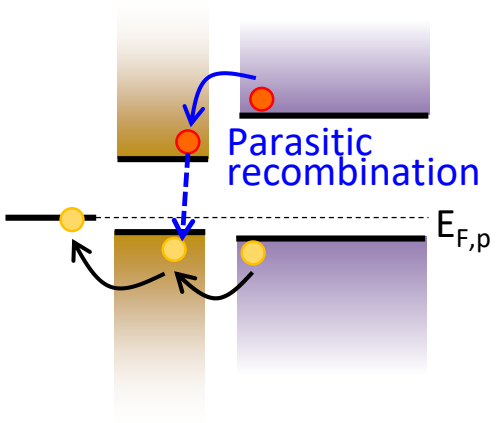
Interfaces play crucial role for efficiency and stability

Interfaces in solar cells

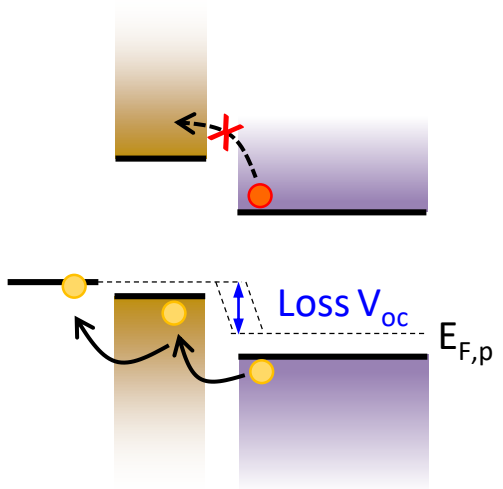
ideal alignment



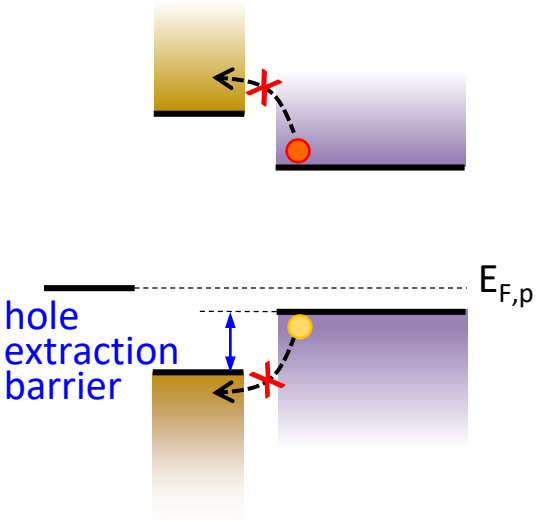
recombination losses

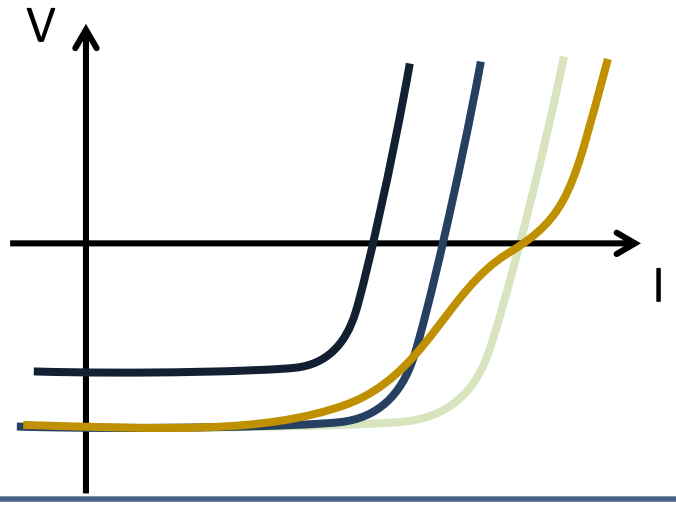


injection barrier = voltage losses



extraction barrier = charge collection losses





Assuming ideal contacts V_{oc} is limited by splitting of quasi Fermi levels and E_g

Extraction barriers, injection barriers, and charge selective contacts effect performance

Image: World Scientific Reference of Hybrid Materials – Vol. 2, Ch. 3 by S. Olthof and T. Riedl (2019)

Literature: effect of barriers in organic solar cells

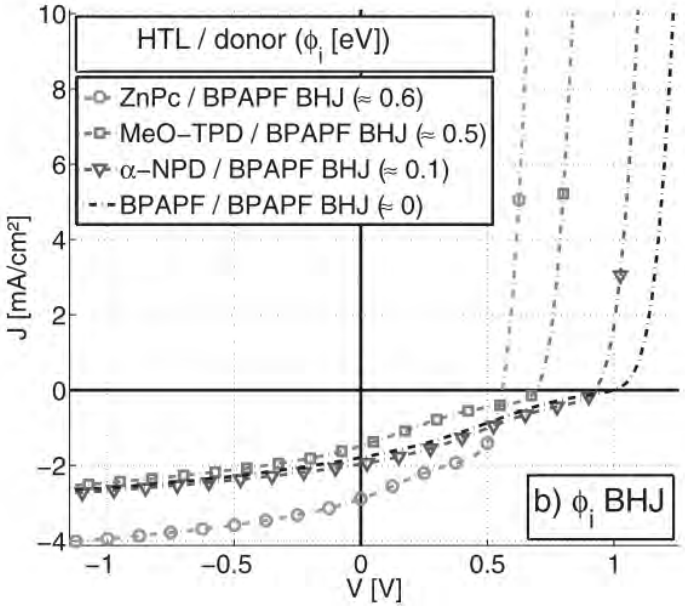
ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de
Materials Views
www.MaterialsViews.com

Influence of Hole-Transport Layers and Donor Materials on Open-Circuit Voltage and Shape of *I–V* Curves of Organic Solar Cells

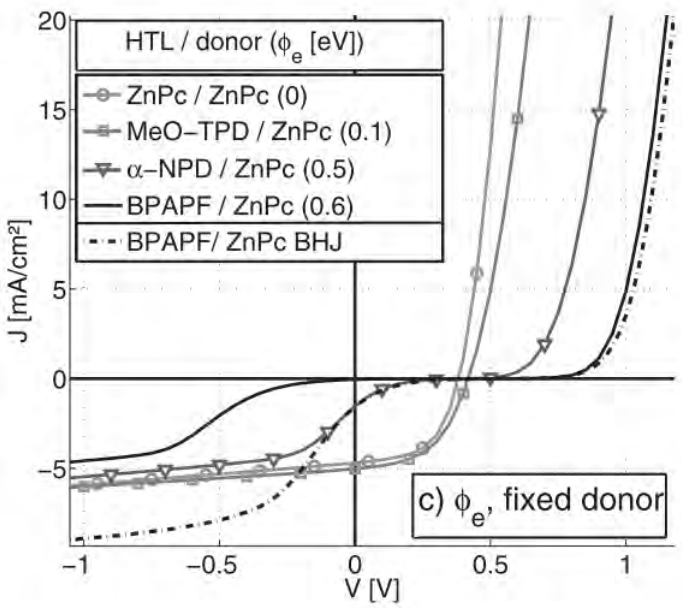
Wolfgang Tress, Karl Leo,* and Moritz Riede*

Experiments: using bulk heterojunction organic semiconductors

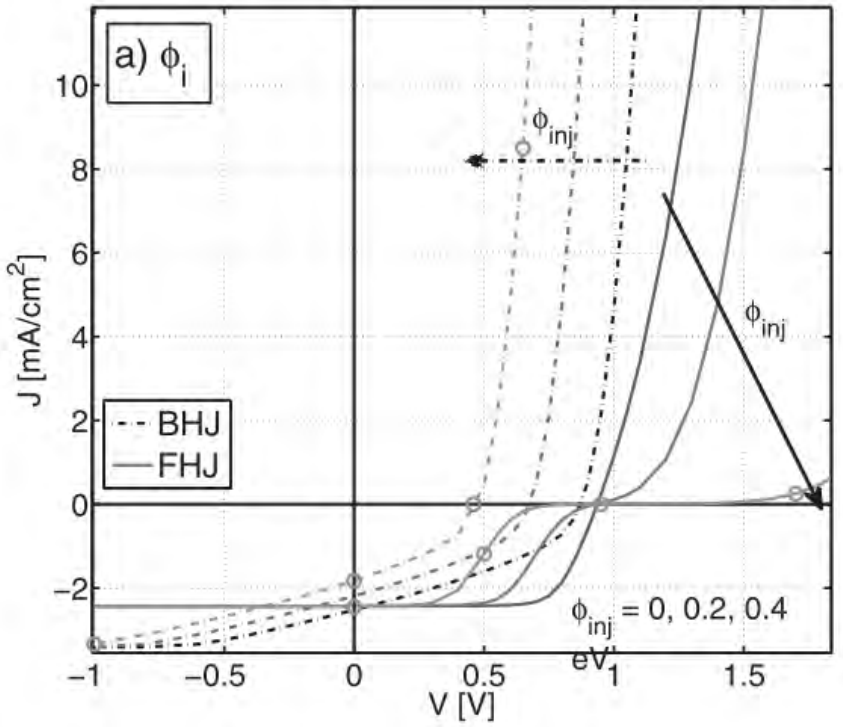
Injection barrier → Loss in V_{oc}



Extraction barrier → Loss in FF



Using drift-diffusion simulations they could reproduce the solar cell behaviors

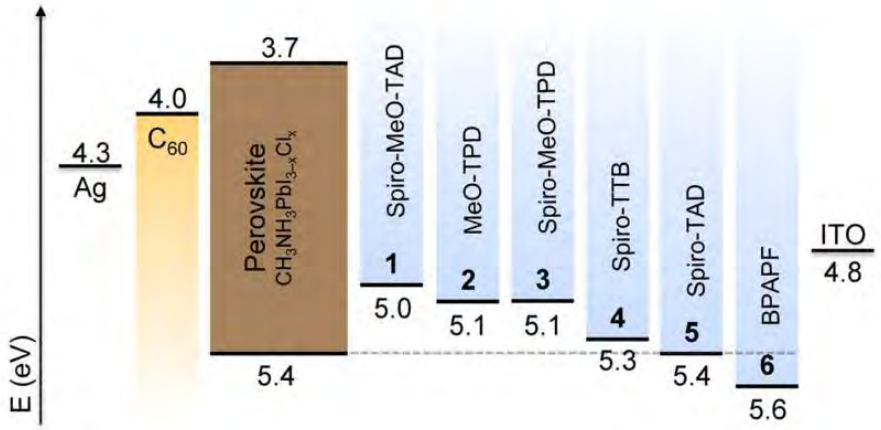


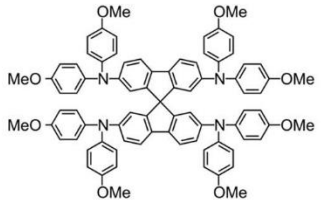
So how does this play out in perovskite solar cells?

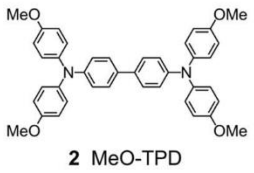
Literature: effect of barriers in perovskite solar cells

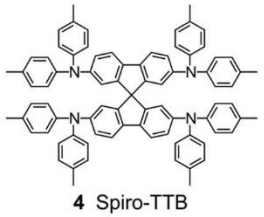
Correlate their ionization potentials with the open-circuit voltage of the device

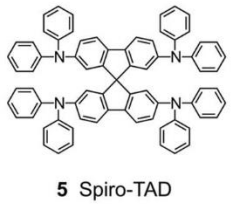
Leo et al., APL mater. 2 0881503 (2014)

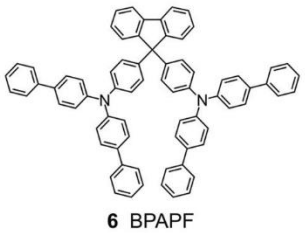


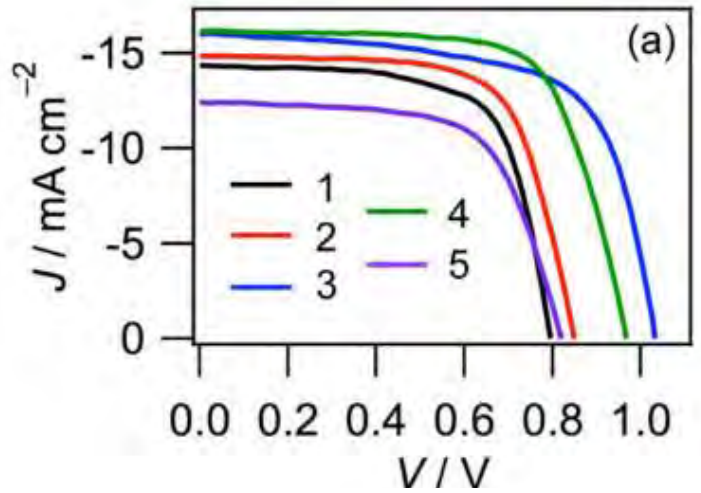




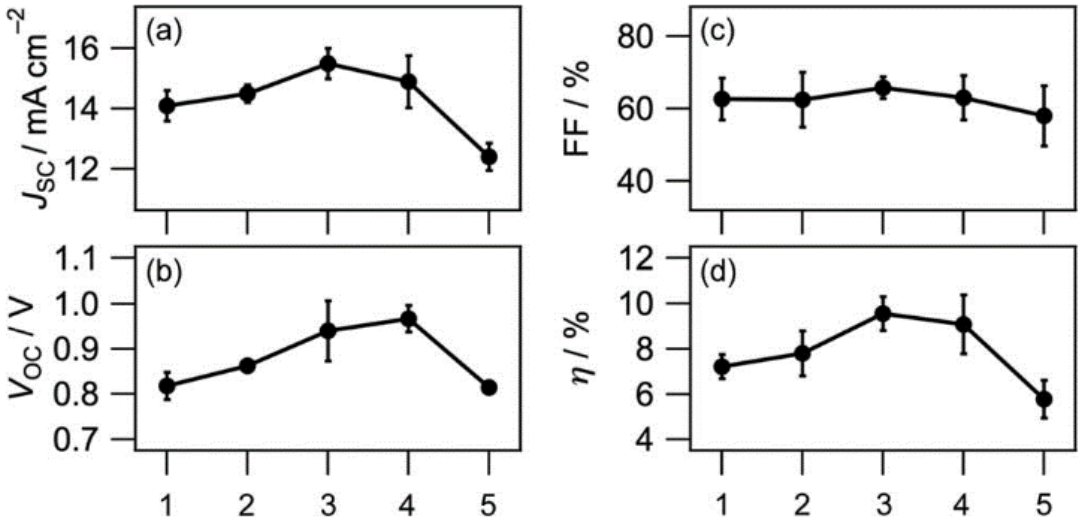








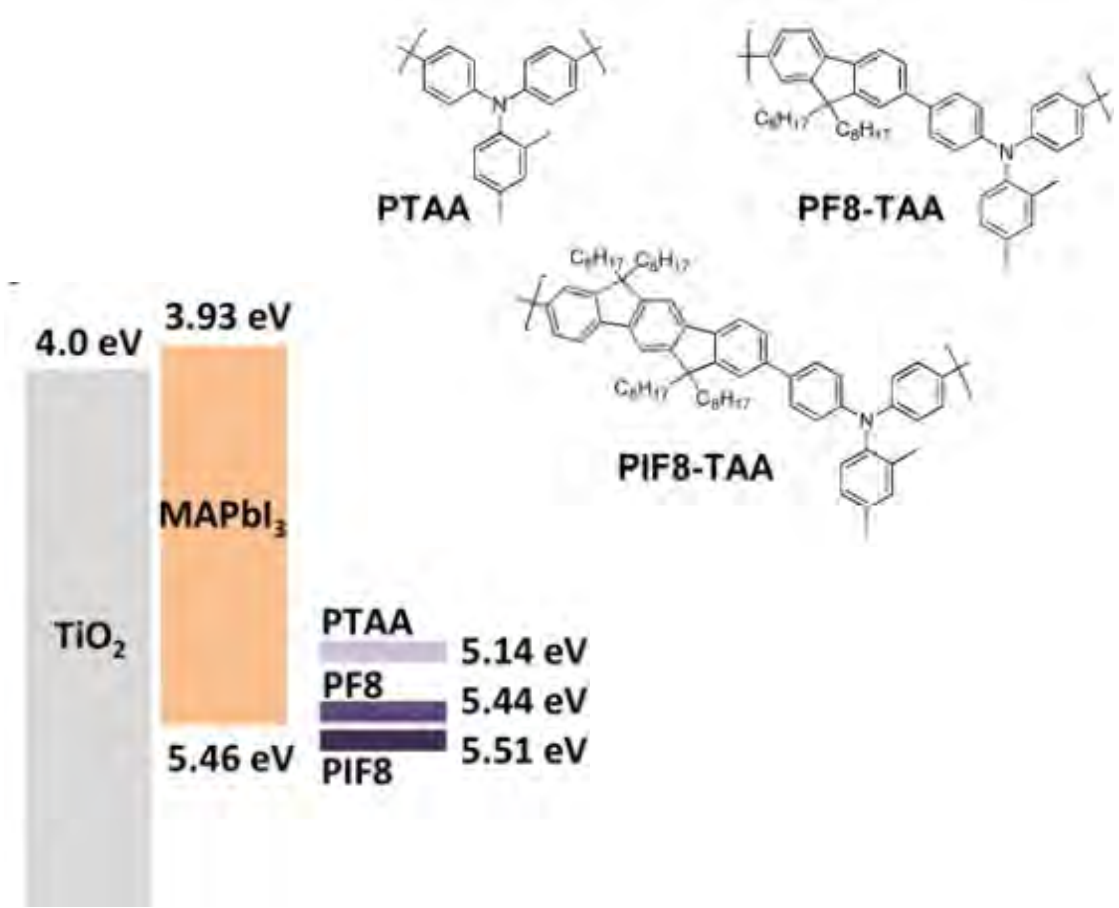
- injection / extraction barriers lead to loss in J_{sc} and V_{oc}

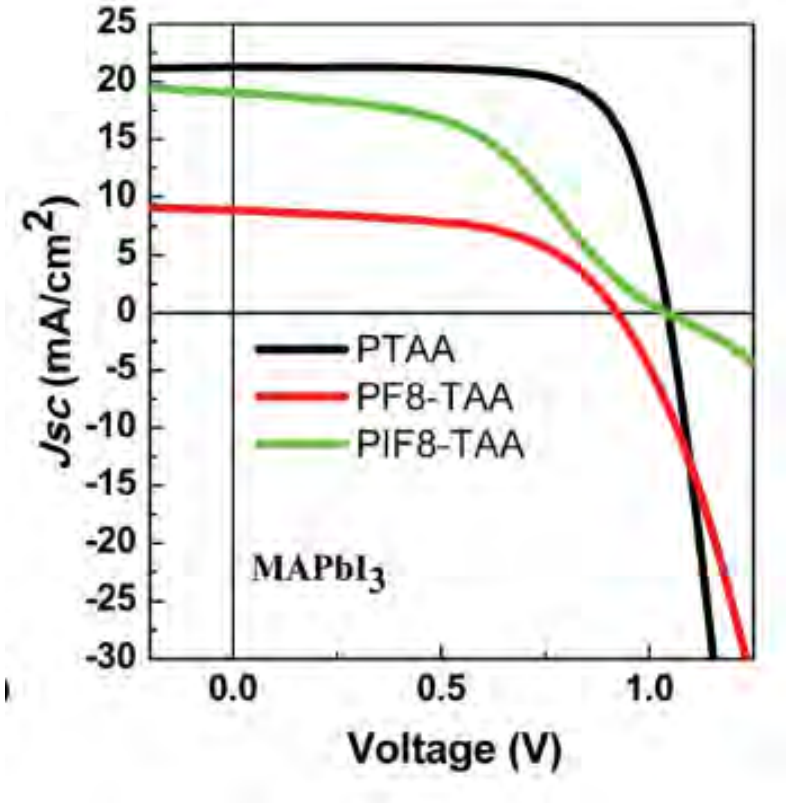


Literature: effect of barriers in perovskite solar cells

Correlate their ionization potentials with the open-circuit voltage of the device

Seok et al., Energy & Env Sci, 7, 2614 (2014)



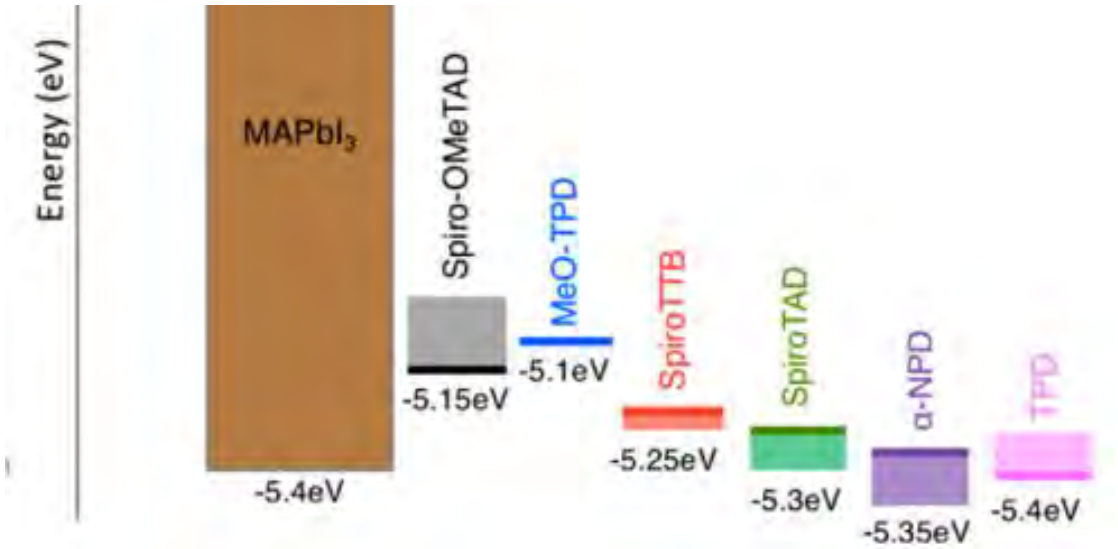


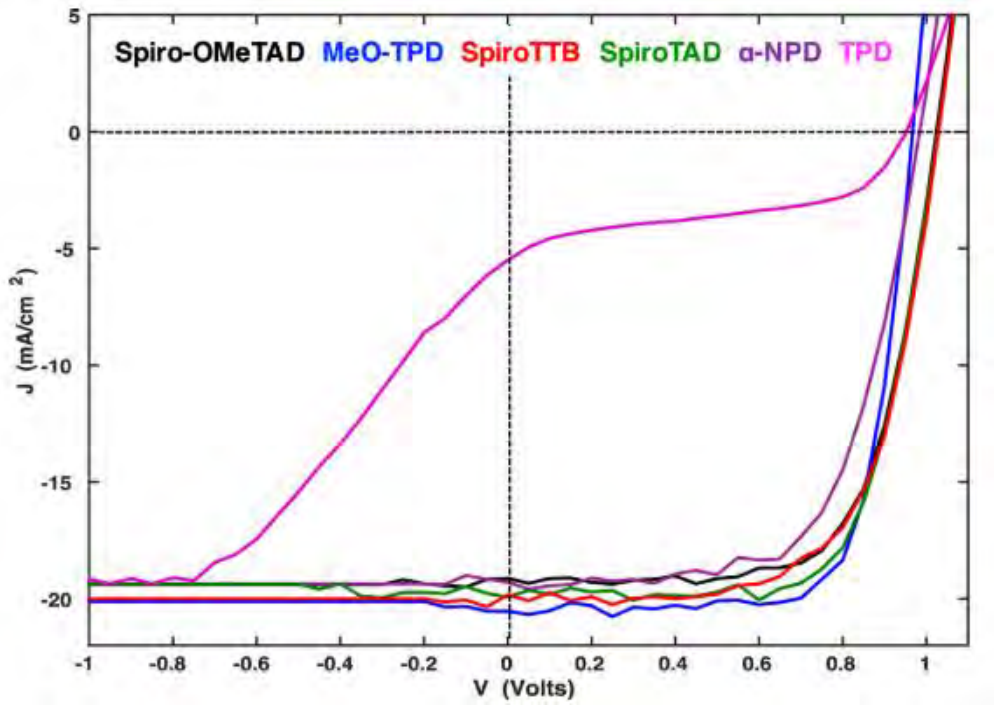
- extraction barrier leads to loss in FF

Literature: effect of barriers in perovskite solar cells

Correlate their ionization potentials with the open-circuit voltage of the device

McGehee et al., ACS Energy Lett, 1, 556 (2016)



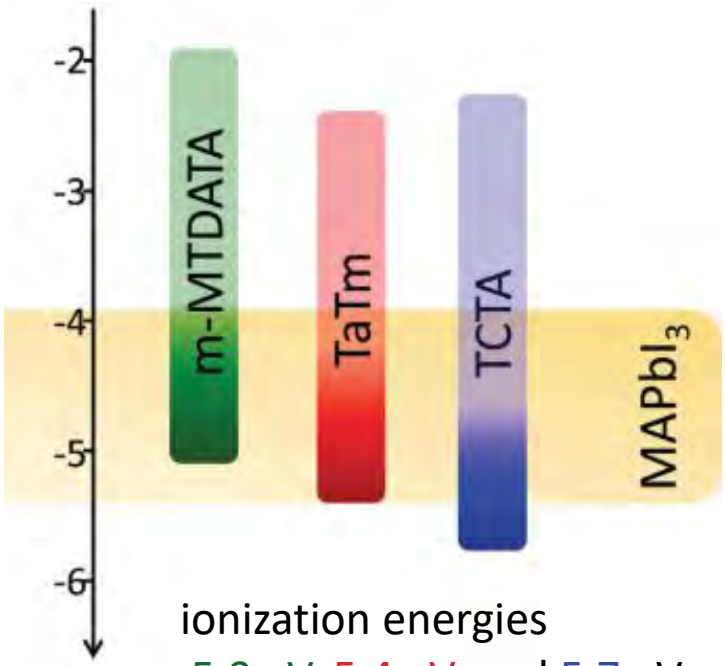


- most devices show similar J_{sc} and V_{oc}
- only for TPD clear extraction barrier – but that does not scale with energy alignemnt

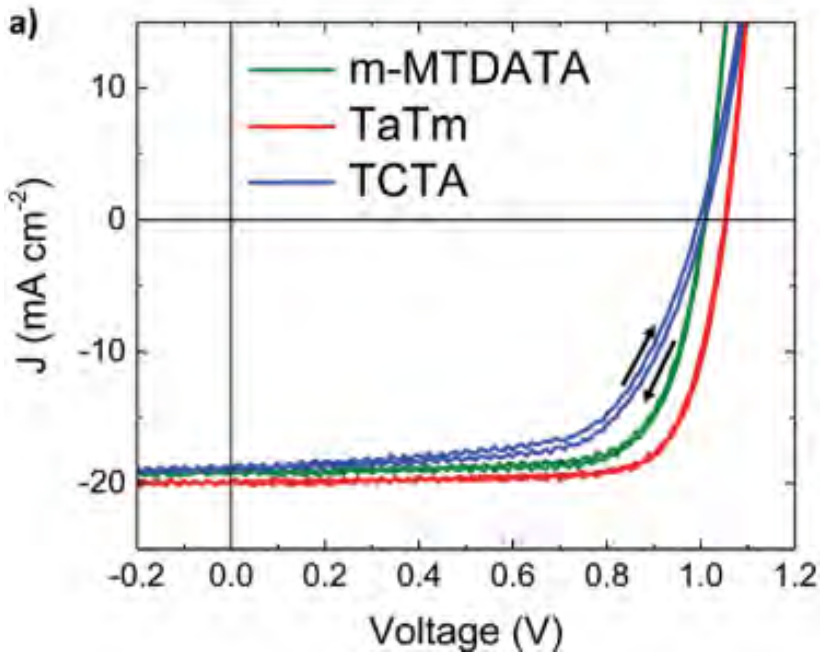
Literature: effect of barriers in perovskite solar cells

Correlate their ionization potentials with the open-circuit voltage of the device

Bolink et al., J Mater Chem C, 7, 523 (2019)



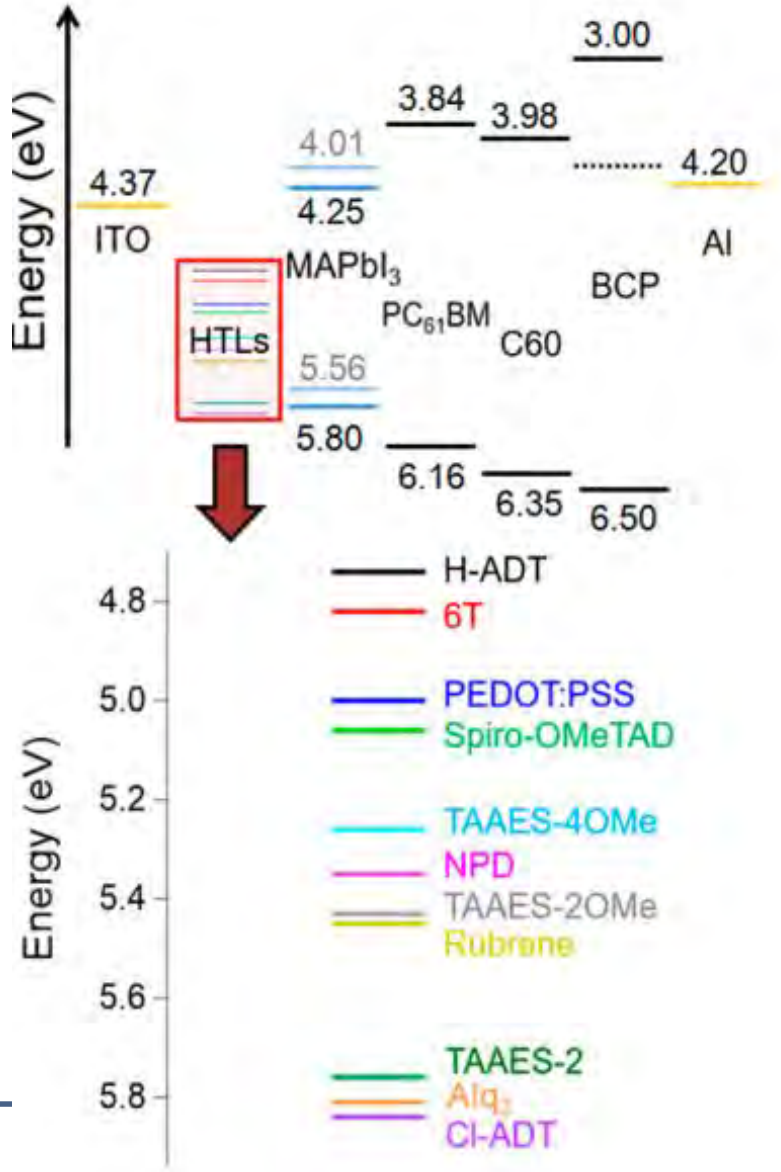
ionization energies
5.0 eV, 5.4 eV, and 5.7 eV



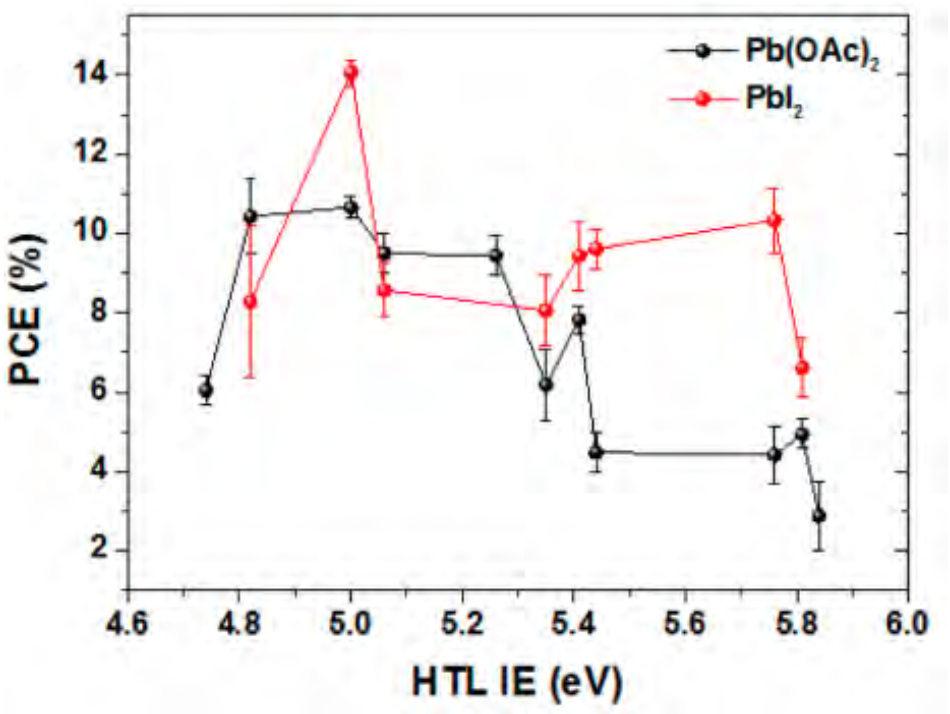
- changes in FF
- but no evidence of a trend

Literature: effect of barriers in perovskite solar cells

Correlate their ionization potentials with the open-circuit voltage of the device



***Park, Graham et al.,* ACS Applied Materials & Interfaces, 10, 15548 (2018)**

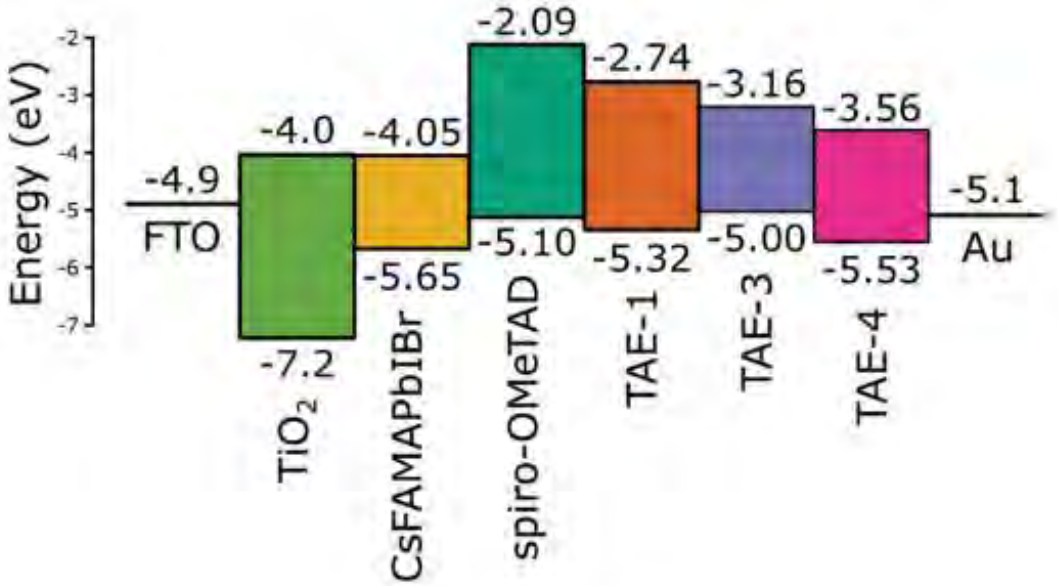


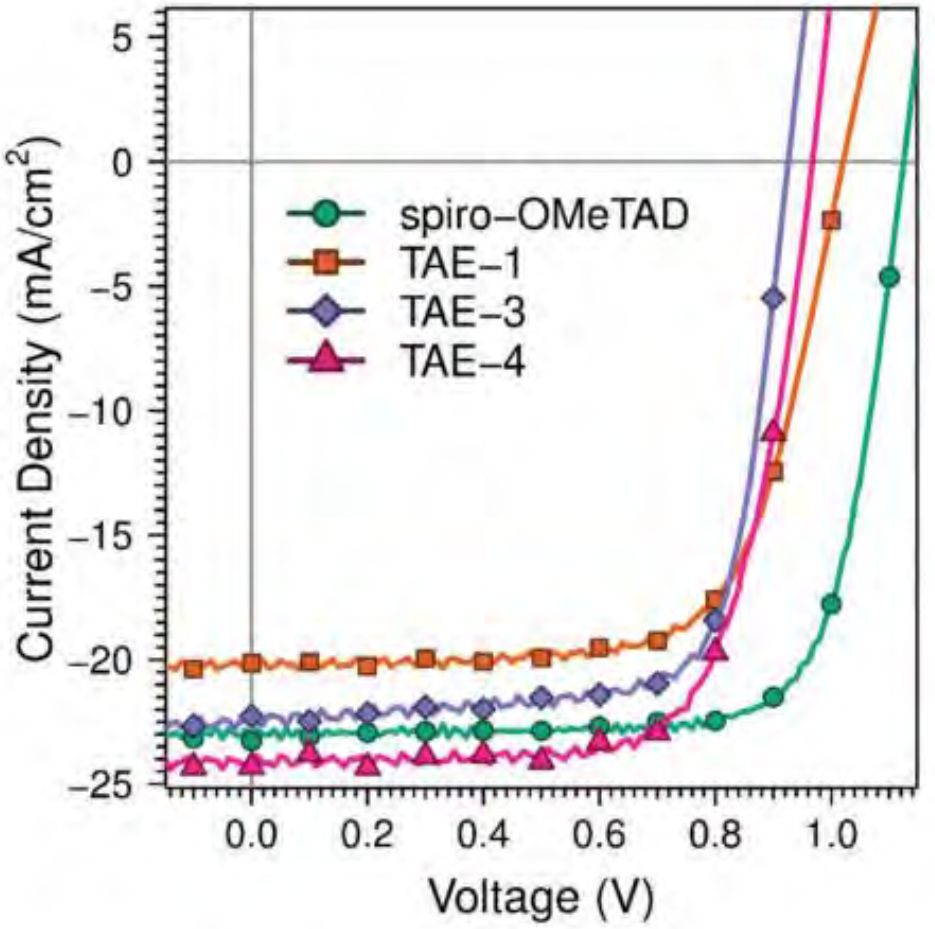
- No significant effect of IE

Literature: effect of barriers in perovskite solar cells

Correlate their ionization potentials with the open-circuit voltage of the device
→ Looking at Br containing perovskites

Gelmetti, Palomares et al., Energy Environ Sci, 12, 1309 (2019)



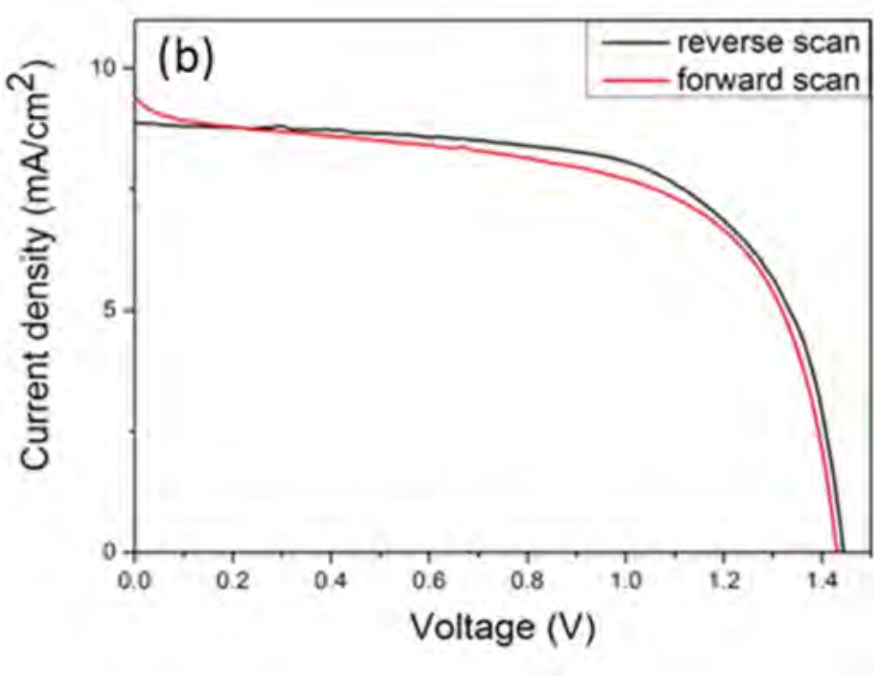


- largest V_{oc} for spiro-OMeTAD, despite large predicted injection barrier

Literature: effect of barriers in perovskite solar cells

Correlate their ionization potentials with the open-circuit voltage of the device
→ Looking at Br containing perovskites

Ho-Baillie / Green et al., J Phys Chem C, 119, 354 (2015)



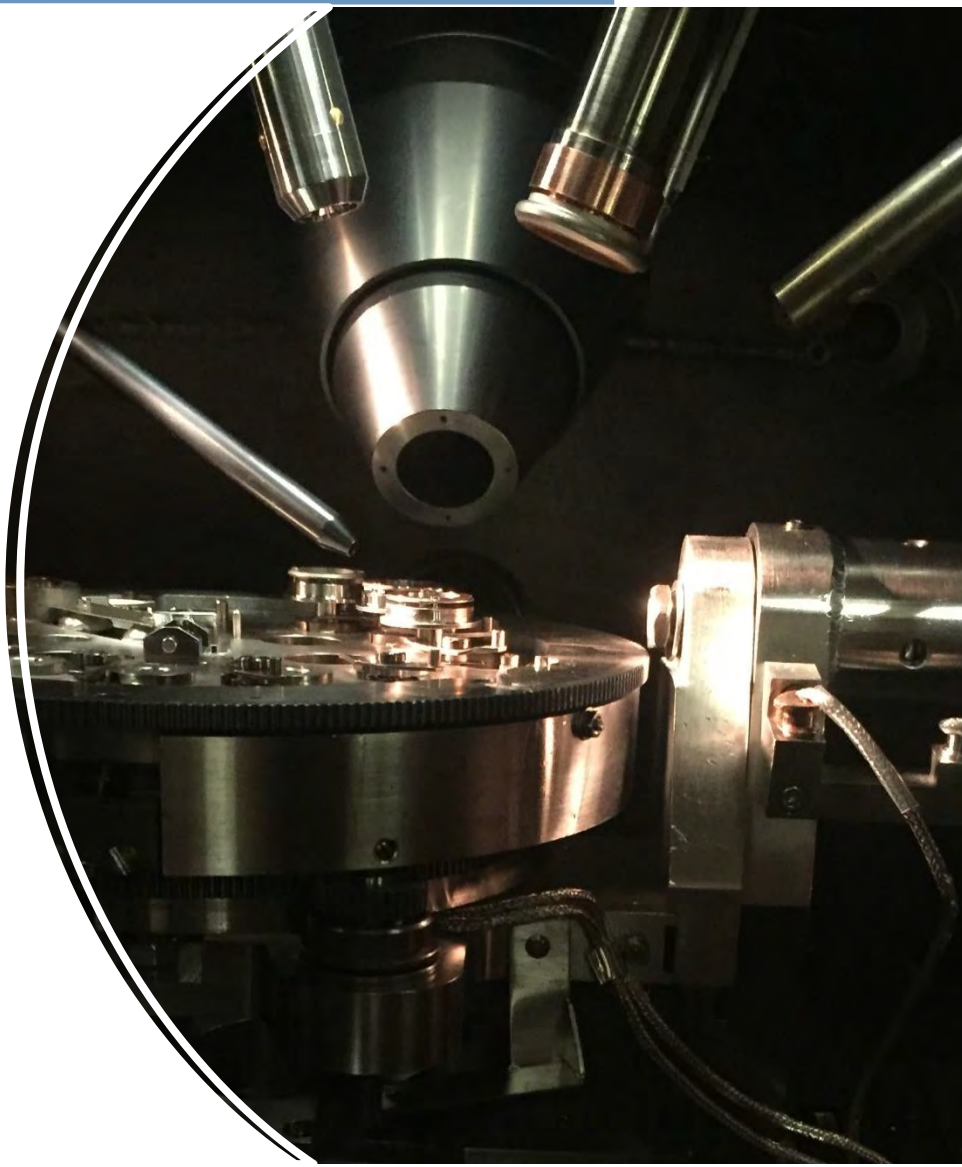
Even for the wide band gap $MAPbBr_3$ spiro-OMeTAD works well!
→ Large V_{oc} achievable

→ Spiro-OMeTAD works well for many of the perovskites
→ IE seems not to matter much

Lets measure anyways…

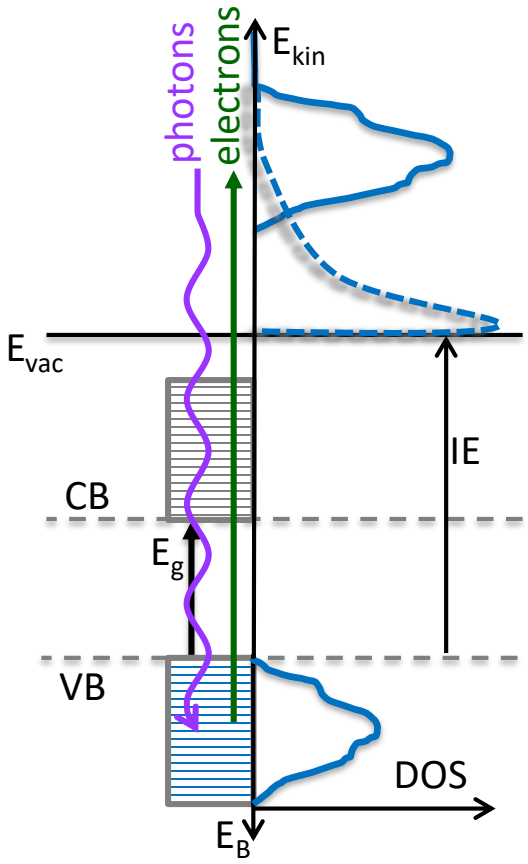
Content

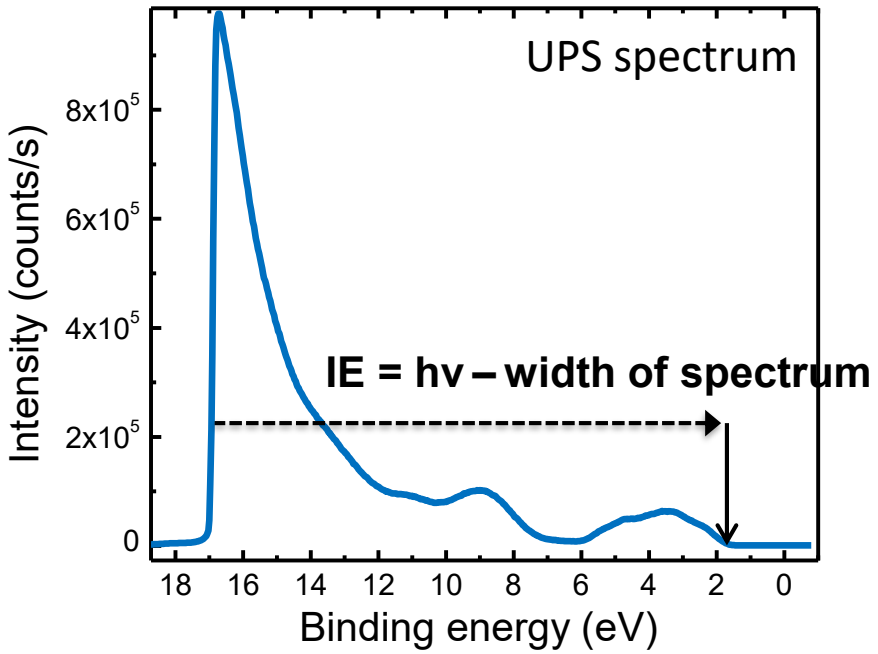
1. Role of interfaces in solar cells
2. **Measurement of energy level alignment**
3. X-ray photoelectron spectroscopy (XPS)
4. Perovskite interfaces measured by XPS
5. Understanding interface chemistry

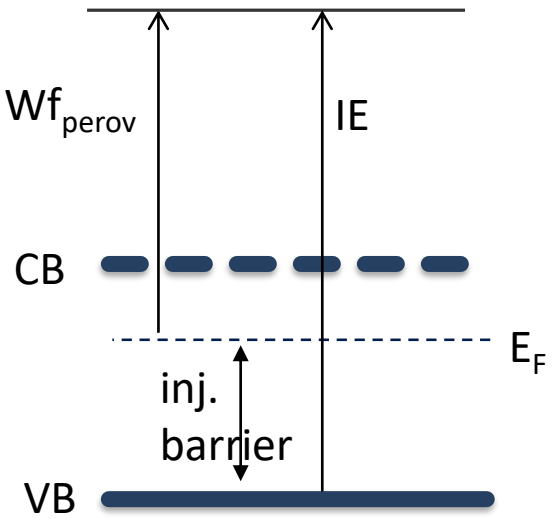


UV photoelectron spectroscopy (UPS)

Measurement of occupied density of states:
UPS: Excitation by UV light, e.g. hv = 21.22eV



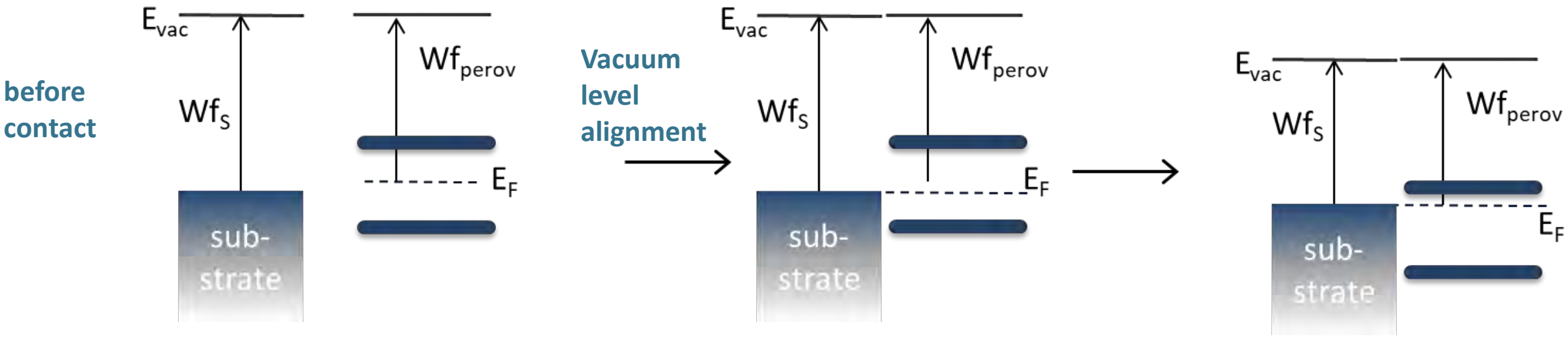




E_{vac}: Vacuum level
IE: Ionization energy

The substrate – perovskite interface

How does the substrate - perovskite interface behave?

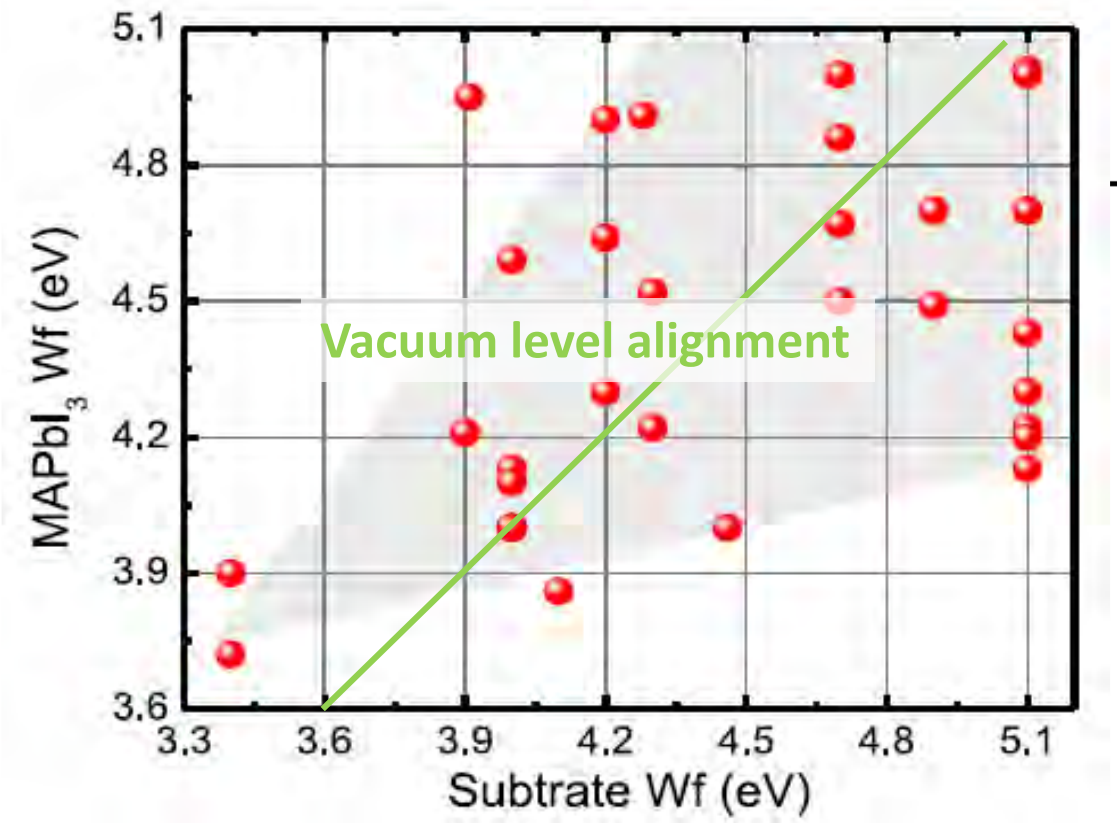


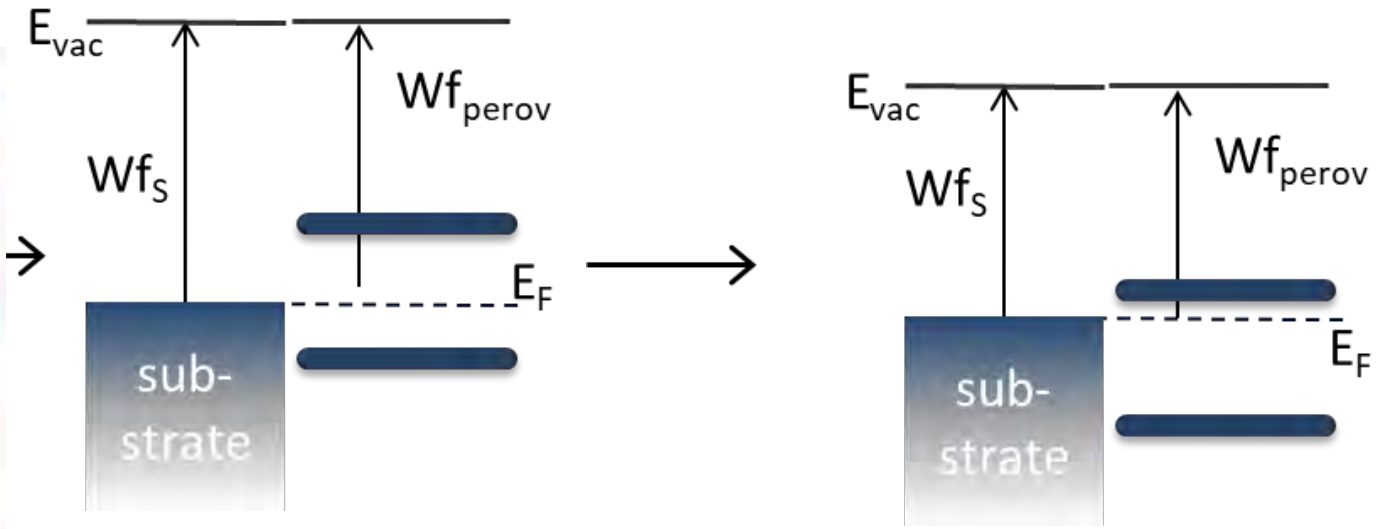
→ this would mean that perovskite Wf can be predicted and tuned by substrate Wf

The substrate – perovskite interface

How does the substrate - perovskite interface behave?

Data collected from literature:





→ this would mean that perovskite Wf can be predicted and tuned by substrate Wf

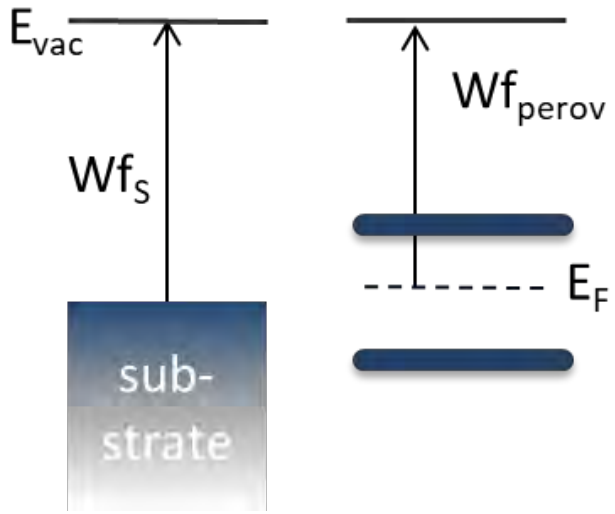
→ literature survey does not show that

S. Olthof, APL Mater. 4, 91502 (2016)

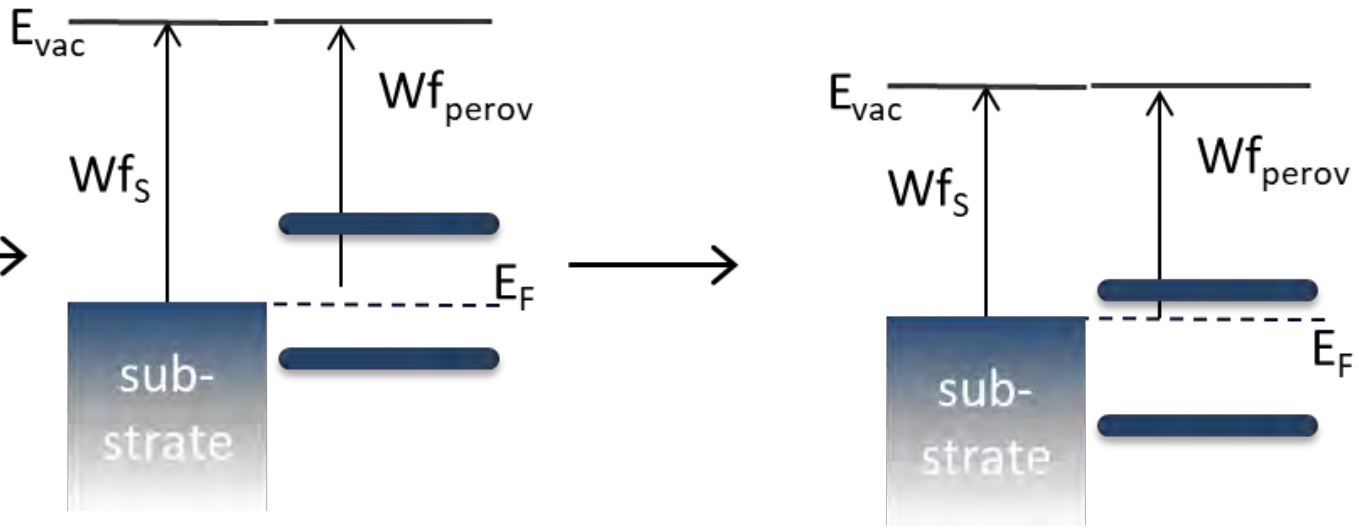
The substrate – perovskite interface

How does the substrate - perovskite interface behave?

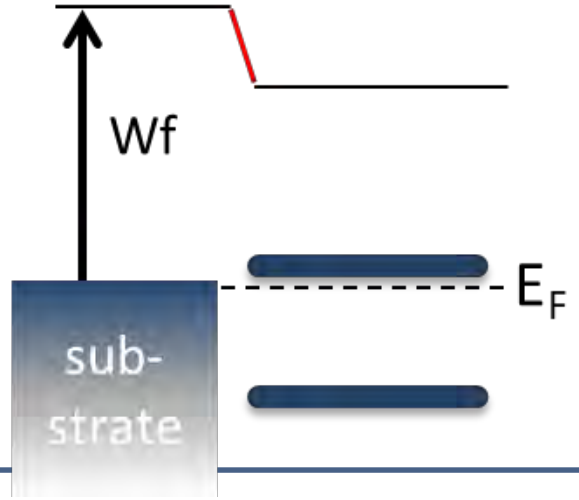
before contact



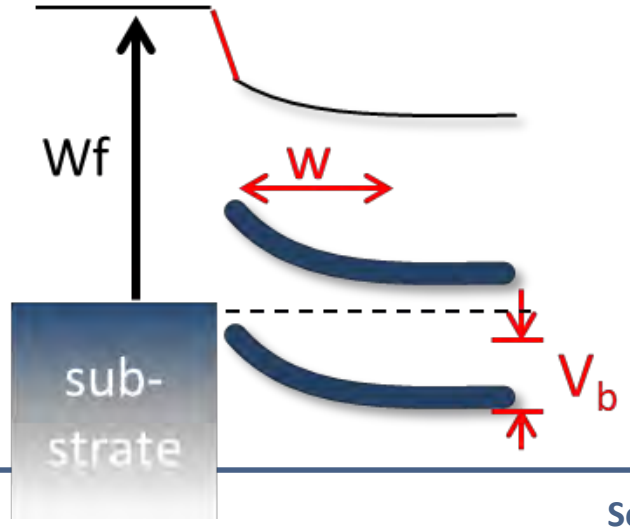
Vacuum level alignment



interface dipoles?



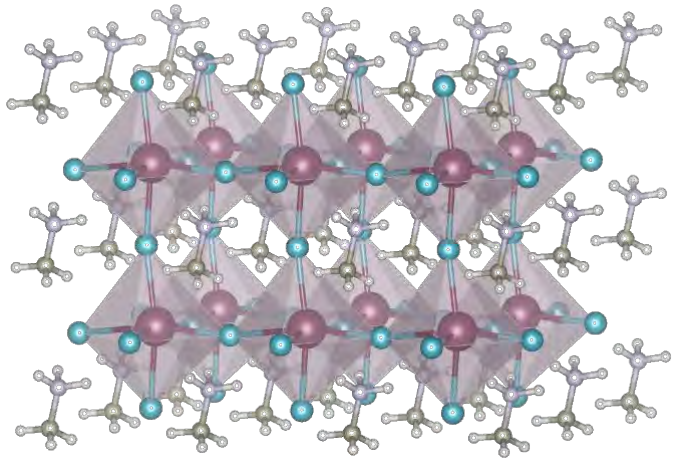
band bending?

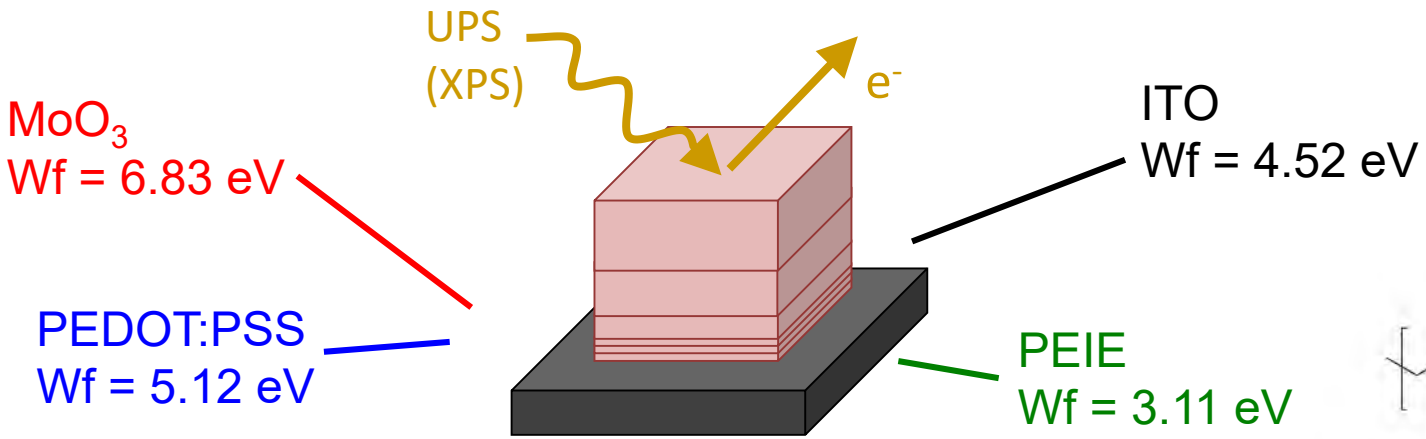


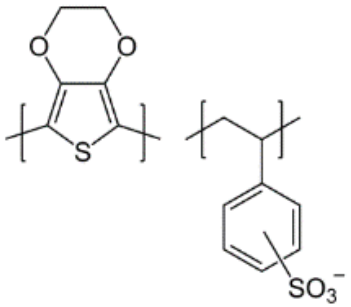
The substrate – perovskite interface

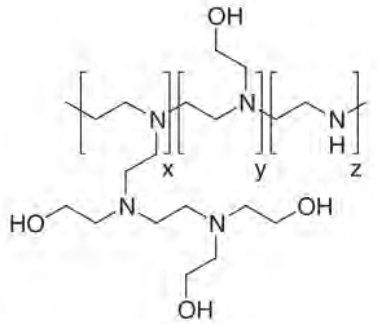
Interface study of:

- **$MAPbI_3$** by *co-evaporation* of PbI_2 and MAI
- on 4 substrates: MoO_3, PEDOT:PSS, ITO, PEIE
- incremental thicknesses 2 Å to 200 nm
- each layer measured by UPS and XPS (in situ)



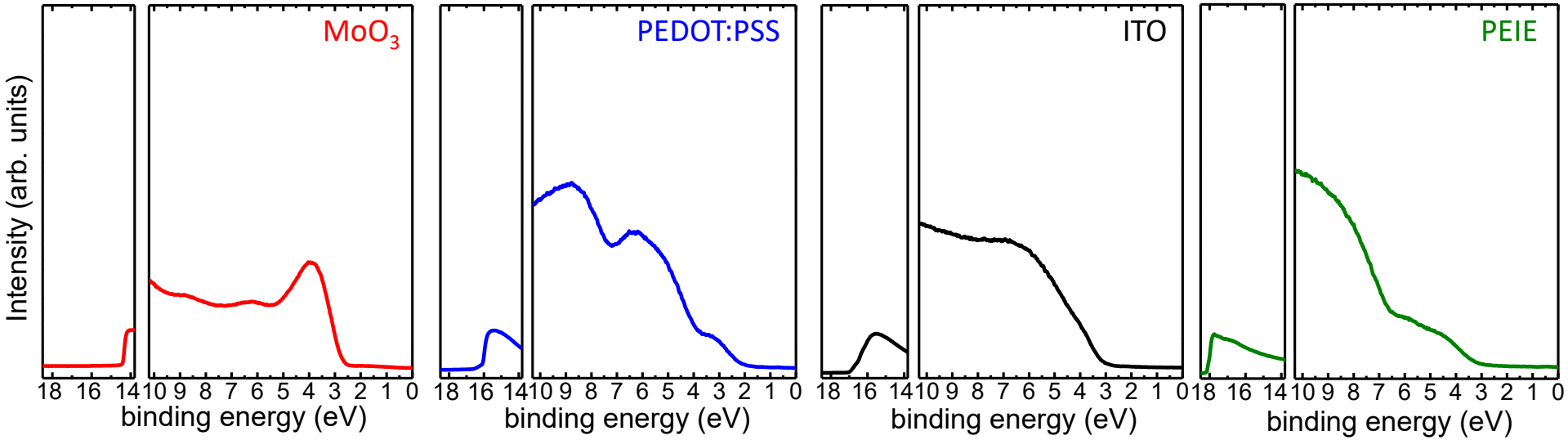






The substrate – perovskite interface: UPS measurement

Interface resolved UPS measurements (d = 0 nm):

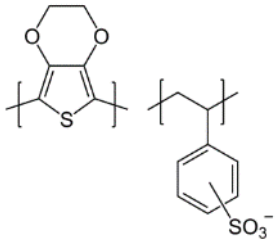


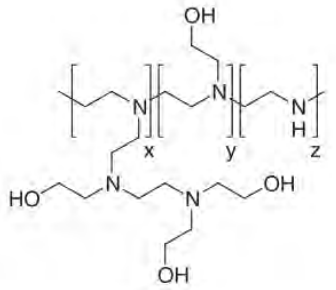
Wf_{substr} = 6.83 eV

Wf_{substr} = 5.12 eV

Wf_{substr} = 4.52 eV

Wf_{substr} = 3.11 eV

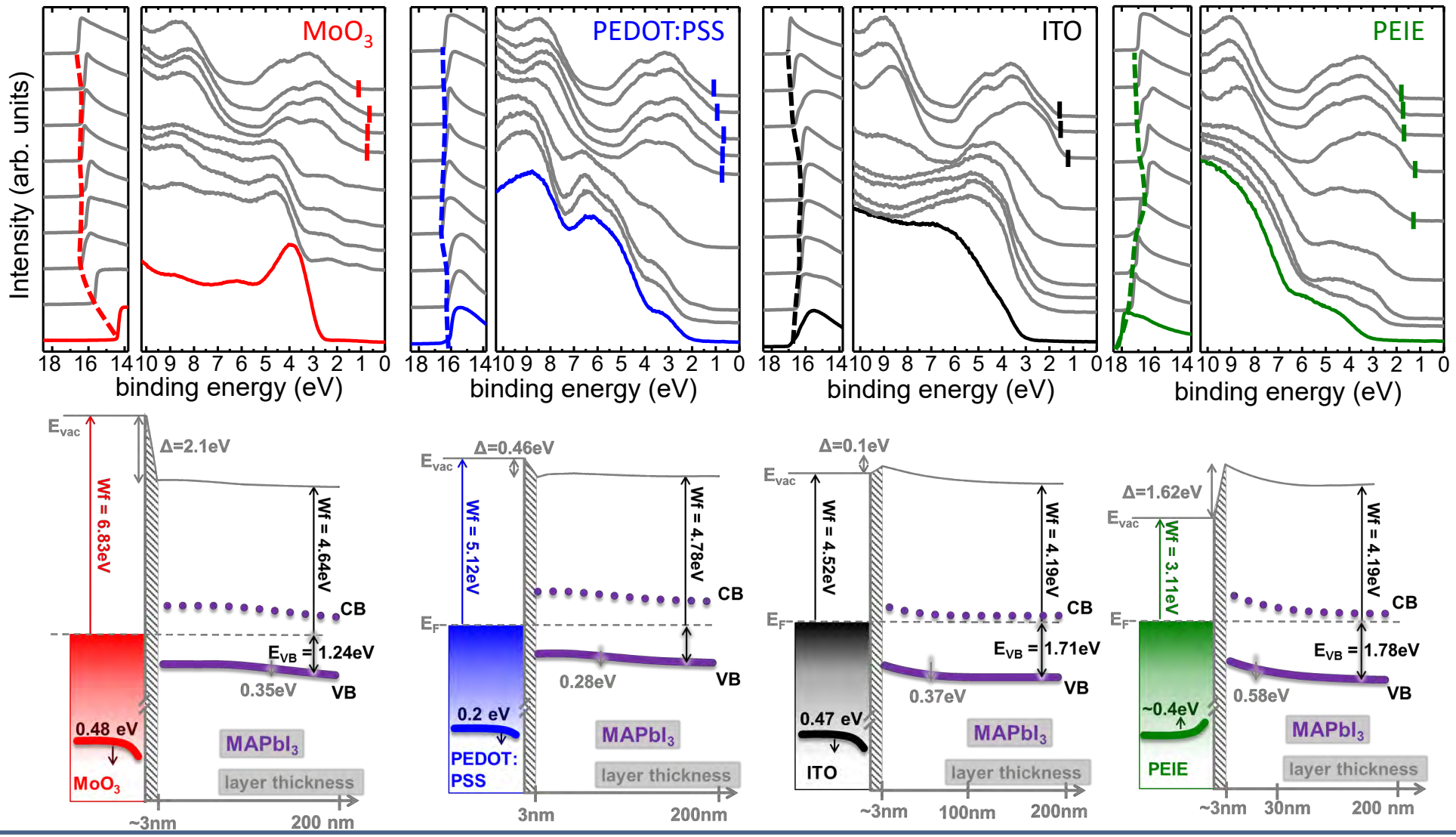




Scientific Reports, 7, 40267 (2017)

The substrate – perovskite interface: UPS measurement

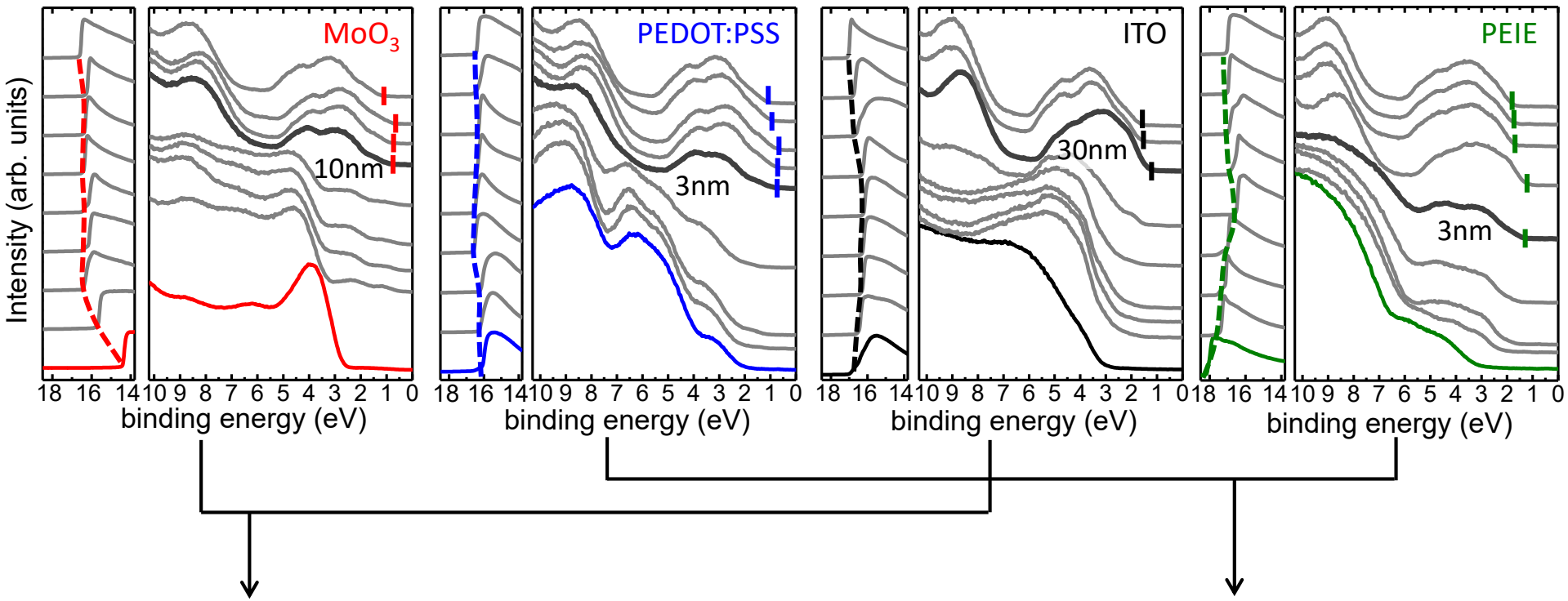
Interface resolved UPS measurements (d = 0, 0.2, 0.5, 1, 3, 10, 30, 100, 200 nm):



Scientific Reports, 7, 40267 (2017)

The substrate – perovskite interface: UPS measurement

Interface resolved UPS measurements (d = 0, 0.2, 0.5, 1, 3, 10, 30, 100, 200 nm):



on metal oxides: perovskite DOS begins to form after 10-30 nm

on organic substrates perovskite DOS begins to form after 3 nm

Why?

Scientific Reports, 7, 40267 (2017)

Content

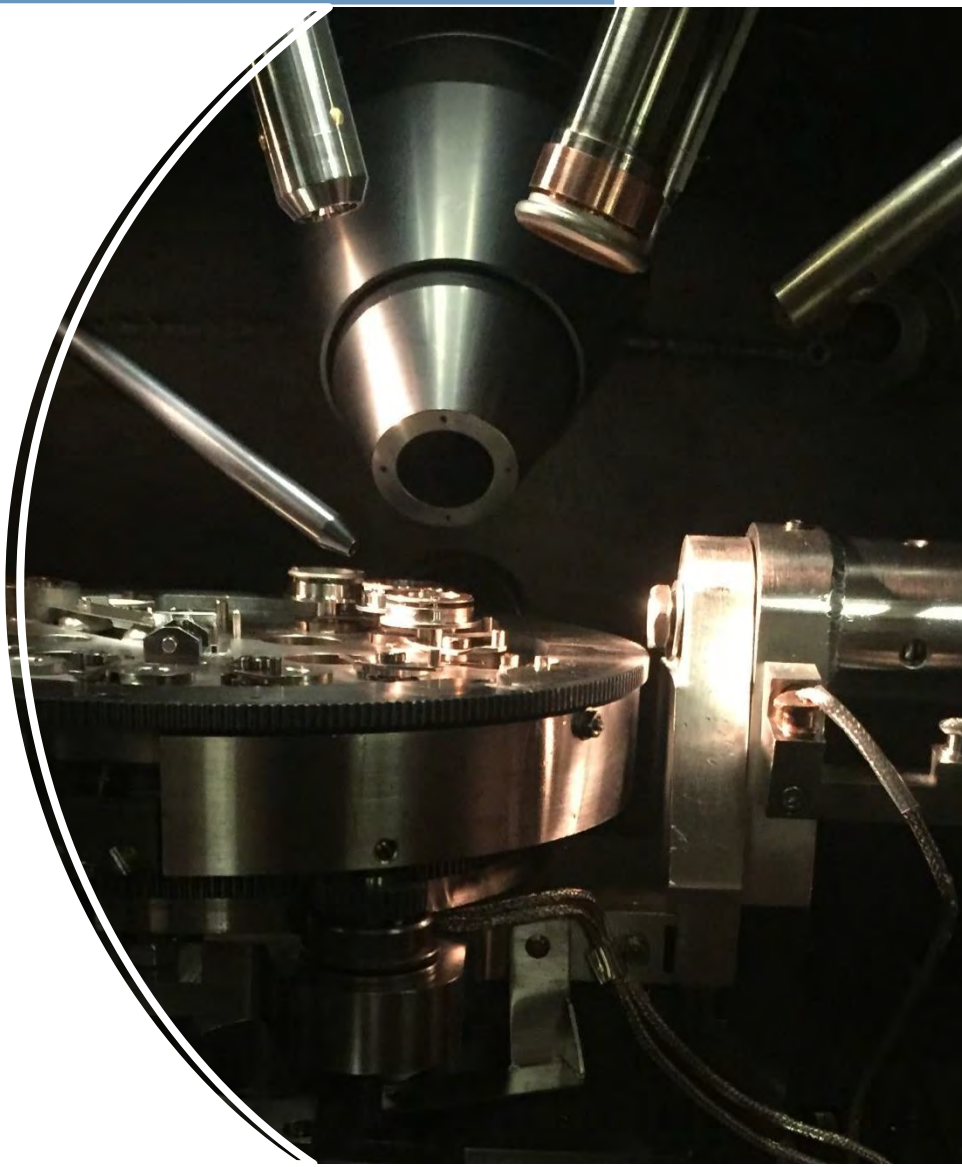
1. Role of interfaces in solar cells

2. Measurement of energy level alignment

3. X-ray photoelectron spectroscopy (XPS)

4. Perovskite interfaces measured by XPS

5. Understanding interface chemistry



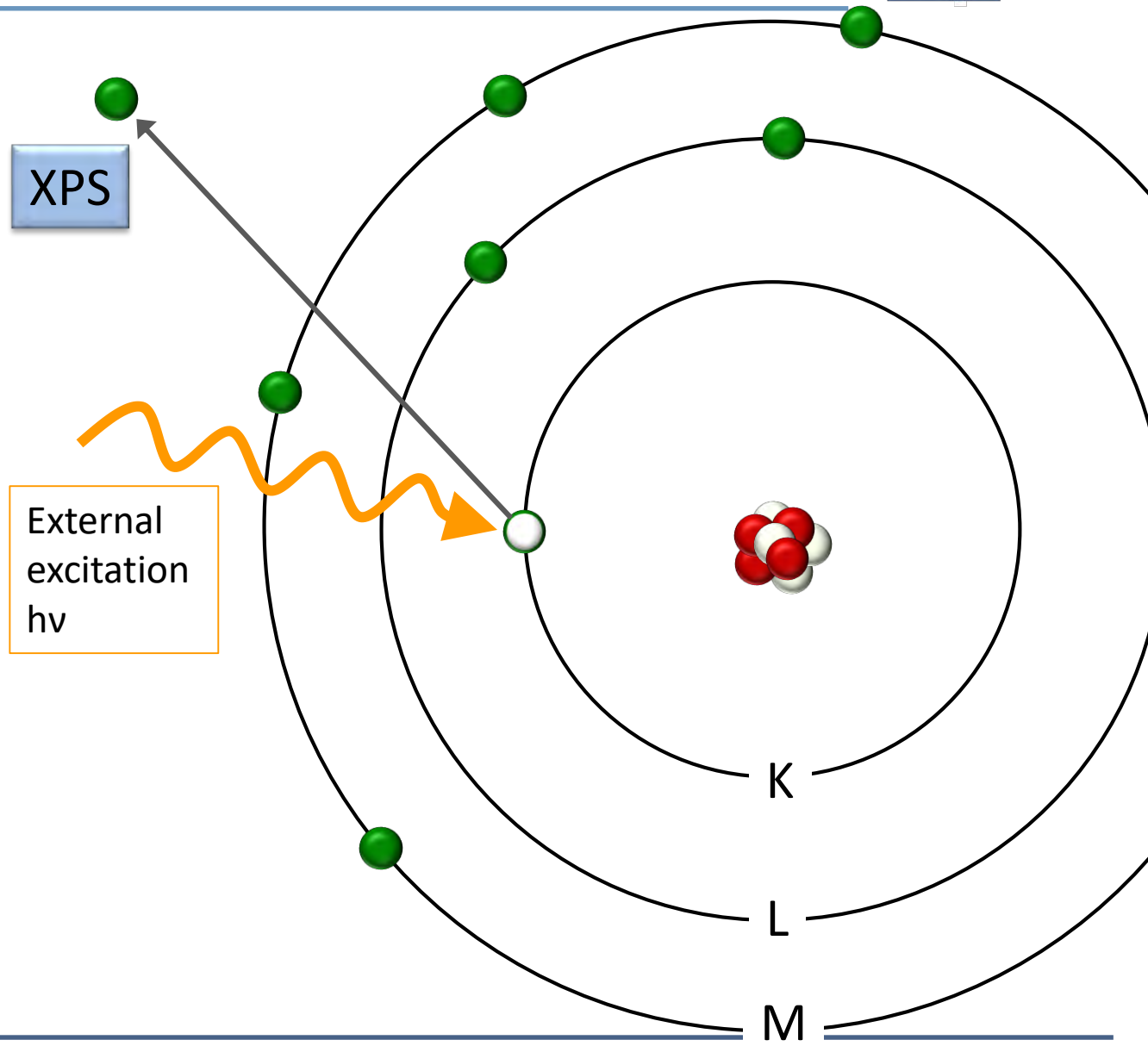
X-ray photoelectron spectroscopy (XPS)

We can learn more about the interface using X-ray photoelectron spectroscopy (XPS)

Tables with characteristic binding energies are used to identify elements

Table 4.2. Binding energies of some elements

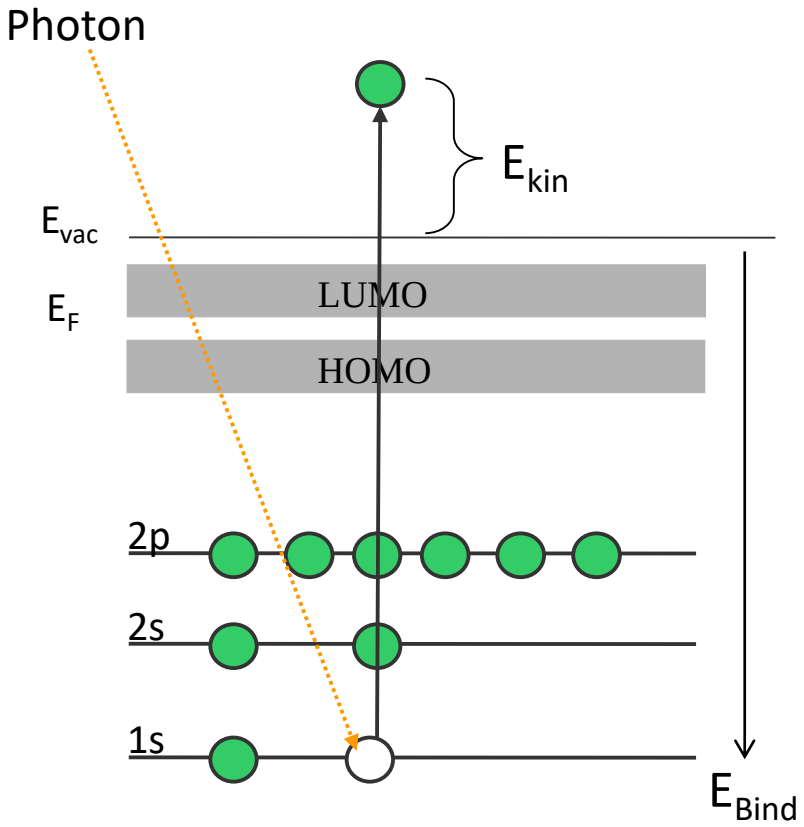
Z	El	$1s_{1/2}$ K	$2s_{1/2}$ L_1	$2p_{1/2}$ L_2	$2p_{3/2}$ L_3	$3s_{1/2}$ M_1	$3p_{1/2}$ M_2	$3p_{1/2}$ M_3	$3d_{3/2}$ M_4	$3d_{5/2}$ M_5
1	H	14								
2	He	25								
3	Li	55								
4	Be	111								
5	B	188			5					
6	C	284			6					
7	N	399			9					
8	O	532	24		7					
9	F	686	31		9					
10	Ne	867	45		18					
11	Na	1072	63		31	1				
12	Mg	1305	89		52	2				
13	Ml	1560	118	74	73	1				
14	Si	1839	149	100	99	8				
15	P	2149	189	136	135	16		10		
16	S	2472	229	165	164	16		8		
17	Cl	2823	270	202	200	18		7		
18	Ar	3202	320	247	245	25		12		
19	K	3608	377	297	294	34		18		
20	Ca	4038	438	350	347	44		26		5



X-ray photoelectron spectroscopy (XPS)

Basic measurement idea same as in UPS:

A photon releases an electron



Sample is illuminated with monochromatic light of specific energy
$E = h\nu$

The kinetic energies of electrons originating from different energy levels will be different – depending on binding energy E_B

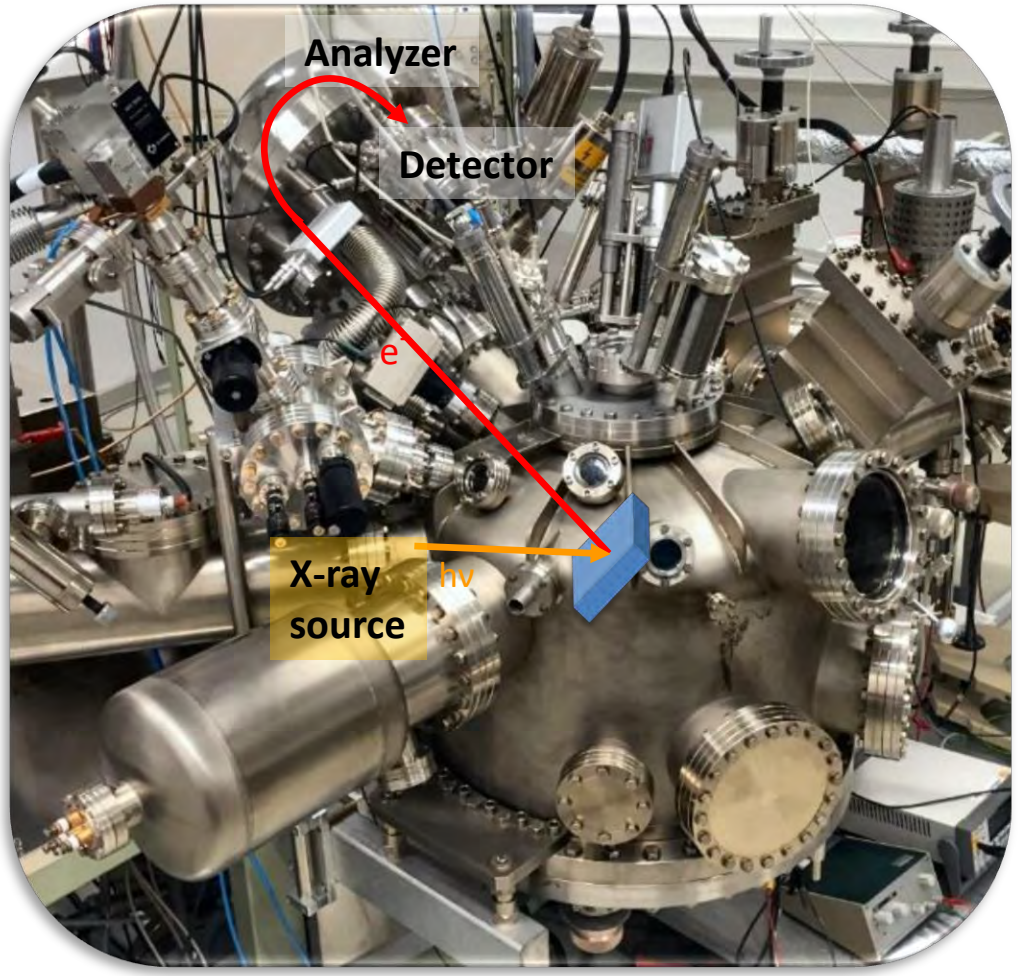
The relation between E_{kin} and E_B is

$$E_{kin} = h\nu - E_B$$

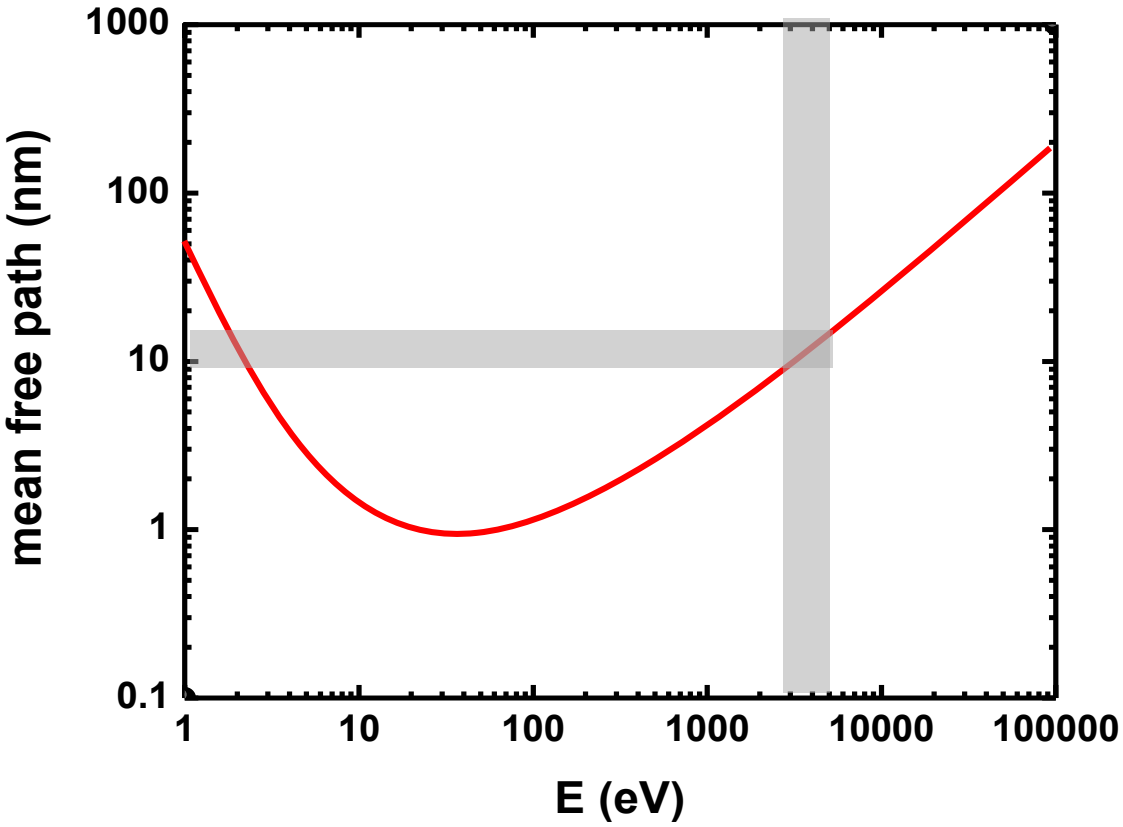
Photon energy of ca. 1-2 keV necessary to excite inner electrons
→ X-rays

X-ray photoelectron spectroscopy (XPS)

Our setup in Cologne



Schematic **mean free path** of an electron in a solid

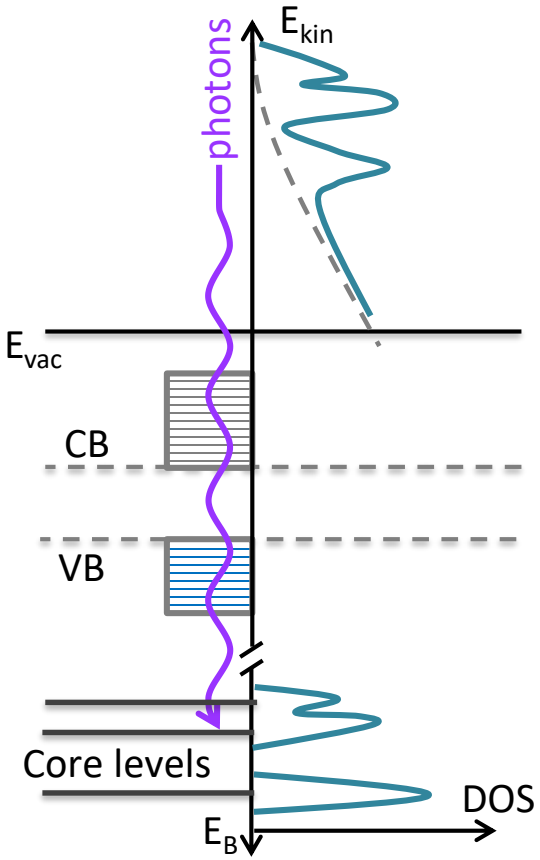


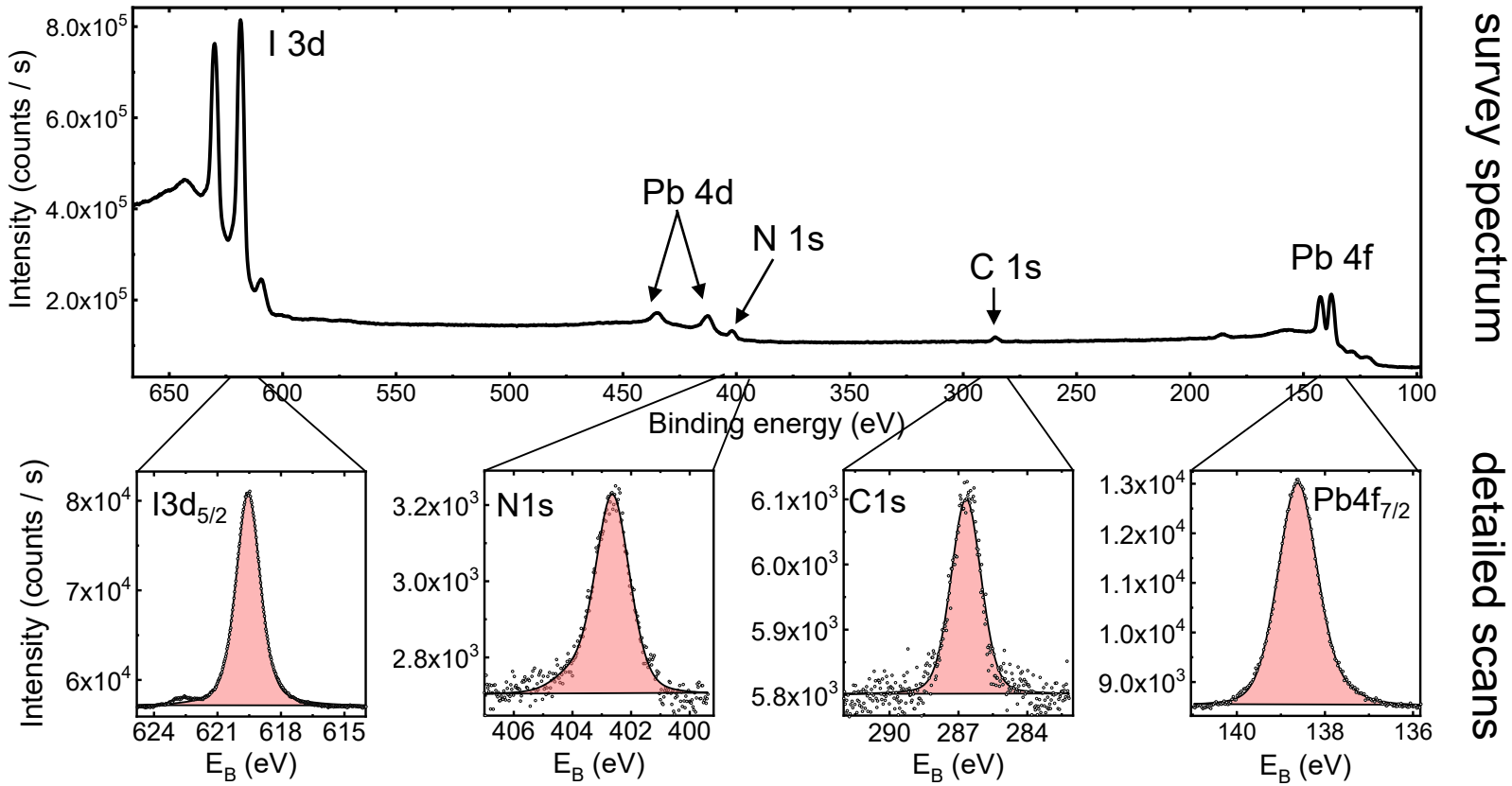
Electrons have energies in the range 1200 -1500 eV
→ ~ 10 nm of surface are only measured

X-ray photoelectron spectroscopy (XPS)

Measure core level states

X-ray photoelectron spectroscopy: Excitation by x-rays, e.g. Mg K_α @ hν = 1253.6 eV



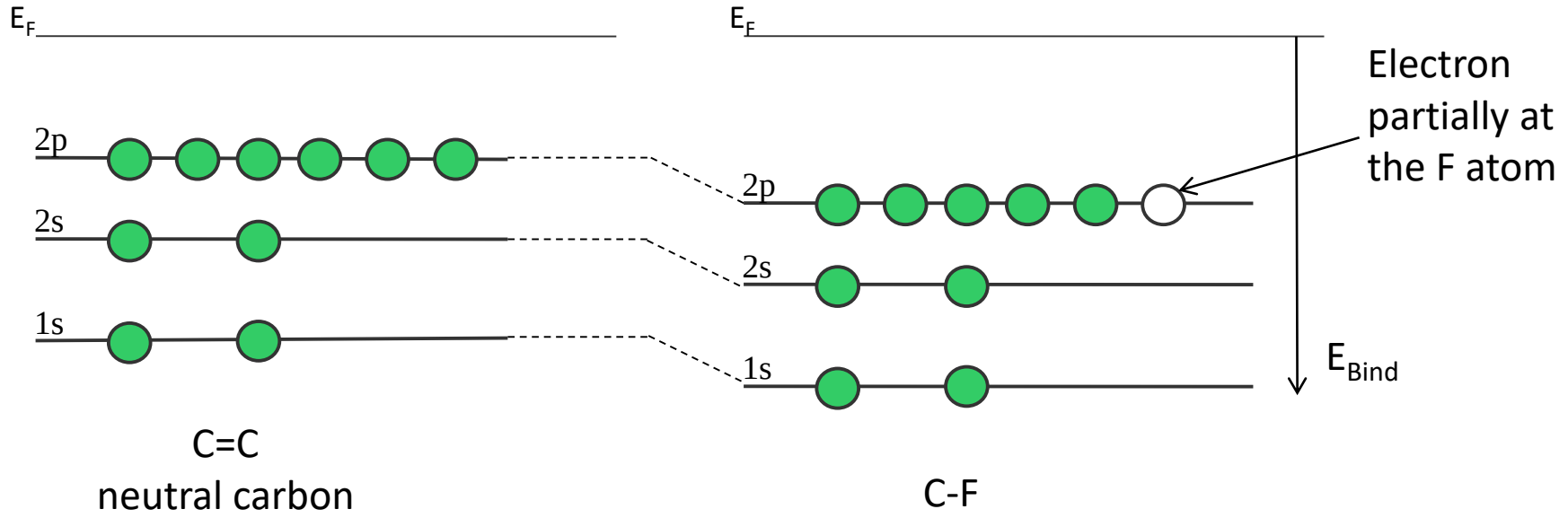


Information on:

- elements present in the film
- element relative concentration (= composition)

X-ray photoelectron spectroscopy (XPS)

Chemical environment of the element has an influence as well



Electronegativity	
C	2.5
N	3.07
O	3.5
S	2.44
F	3.98

F has a higher electronegativity than C

→ Carbon here is slightly more positively charged

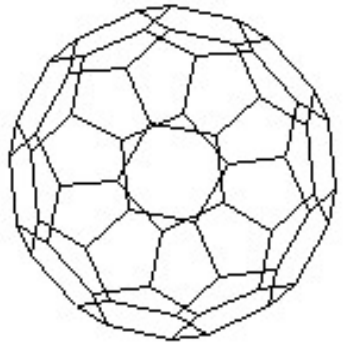
→ Therefore it holds more strongly on to the other e^-

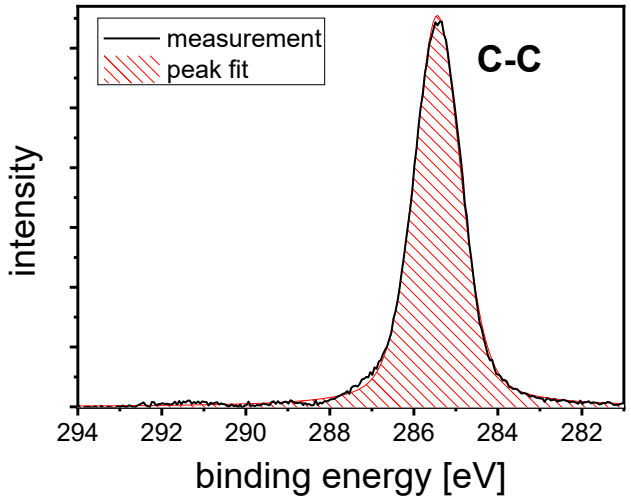
→ E_B increases ↔ E_{kin} becomes smaller

X-ray photoelectron spectroscopy (XPS)

In detailed scans one can see these variations by the appearance of several peaks of the same element
→ this is the **chemical shift**

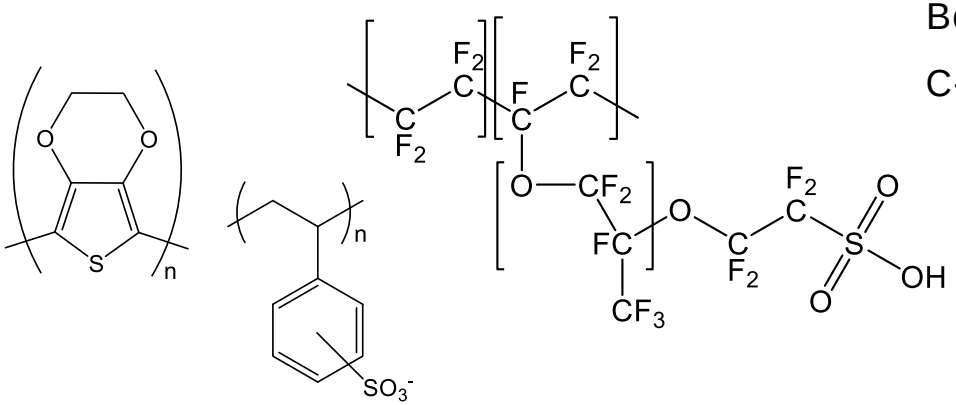
Carbon 1s in C60





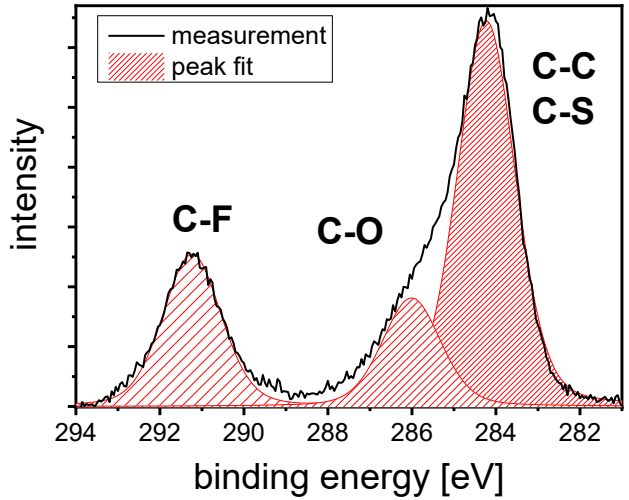
only one binding environment present

PEDOT:PDD + Nafion



Bonds:

C-C, C-H, C-S, C-O, C-F

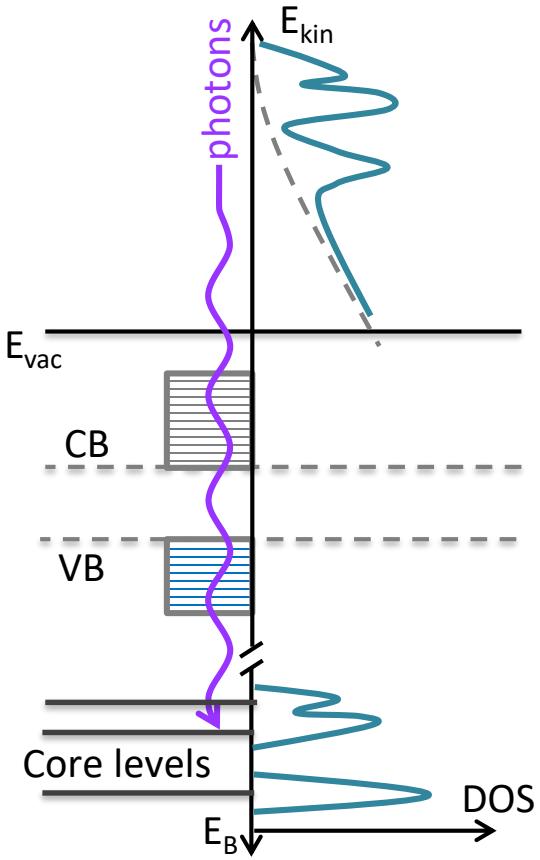


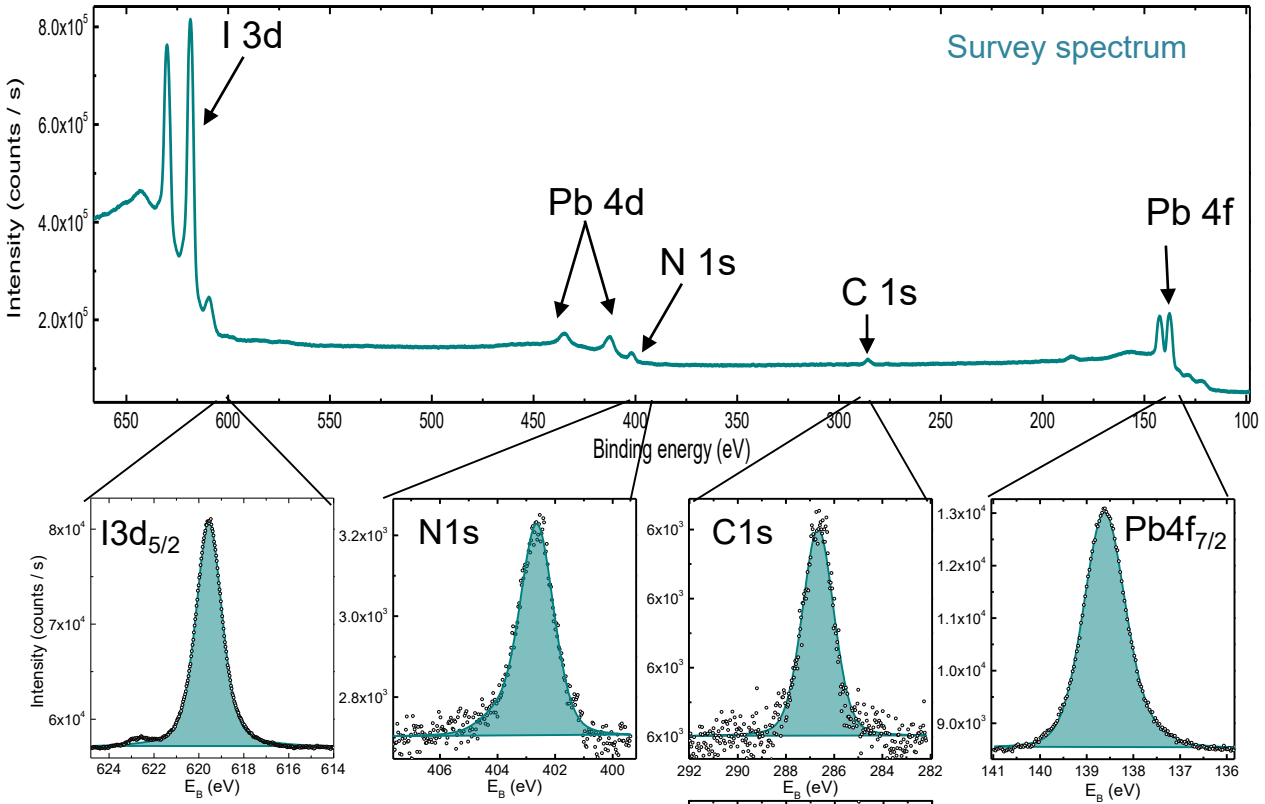
Area under peaks tells us how much of each bond is present

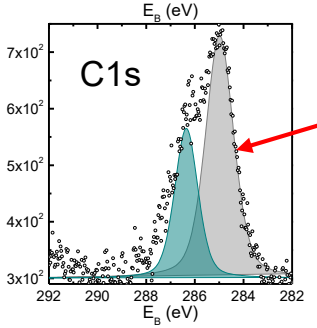
X-ray photoelectron spectroscopy (XPS)

Measure core level states

X-ray photoelectron spectroscopy: Excitation by x-rays, e.g. Mg K_α @ hv = 1253.6 eV







solvent signal

Information on:

- elements present in the film
- element relative concentration (= composition)
- oxidation states

Content

1. Role of interfaces in solar cells

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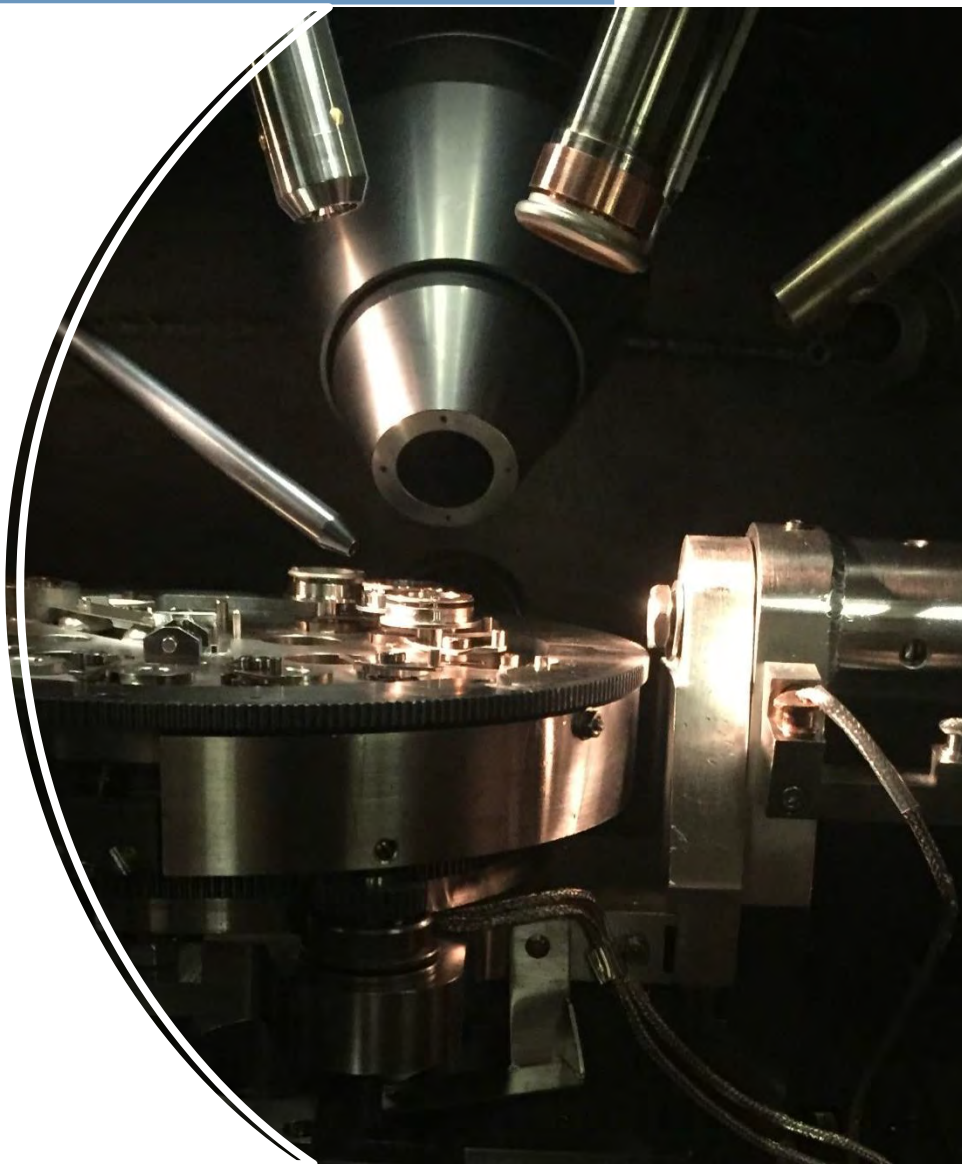
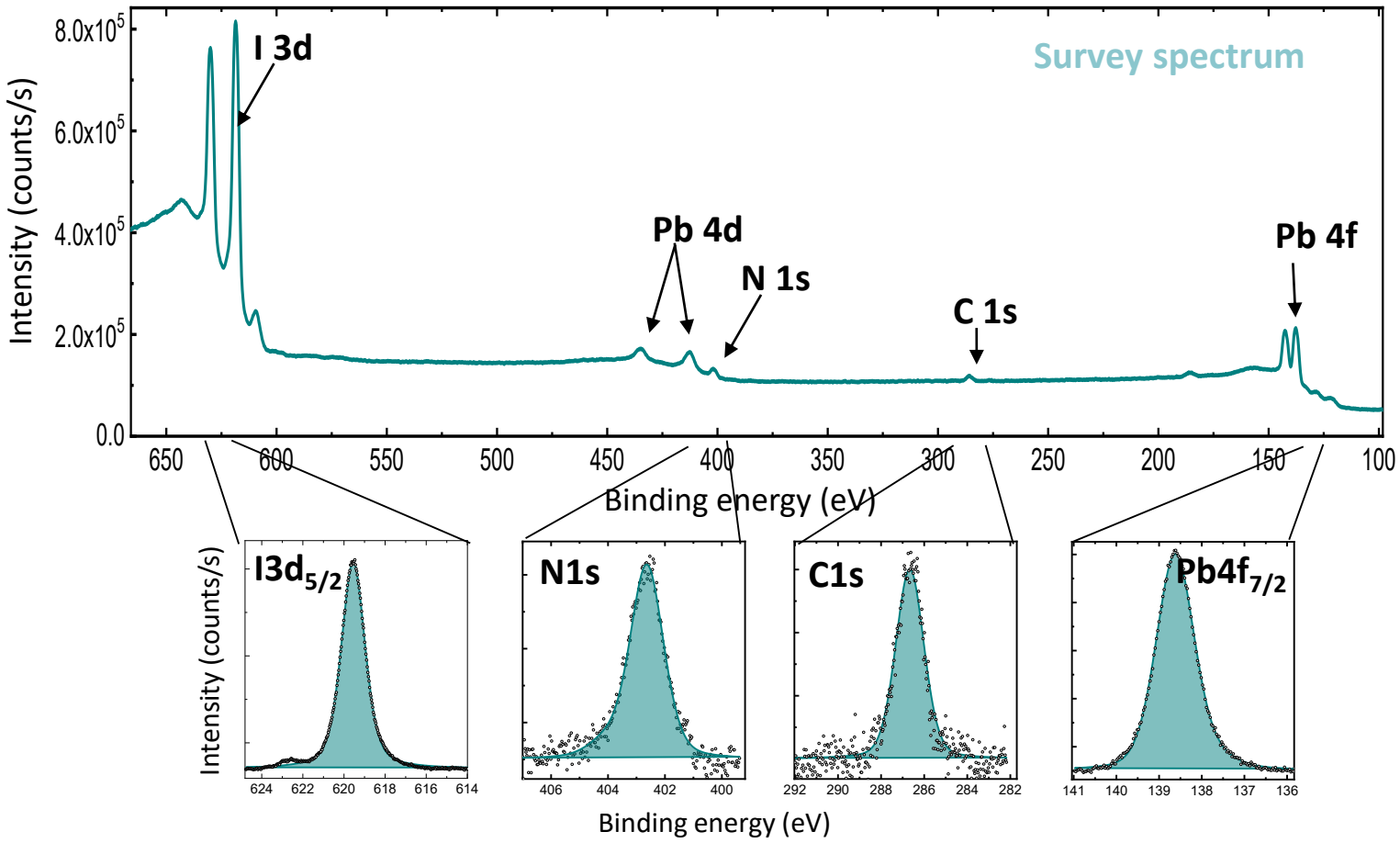
4. **Perovskite interfaces measured by XPS**

5. Understanding interface chemistry



Probing the interface composition by XPS

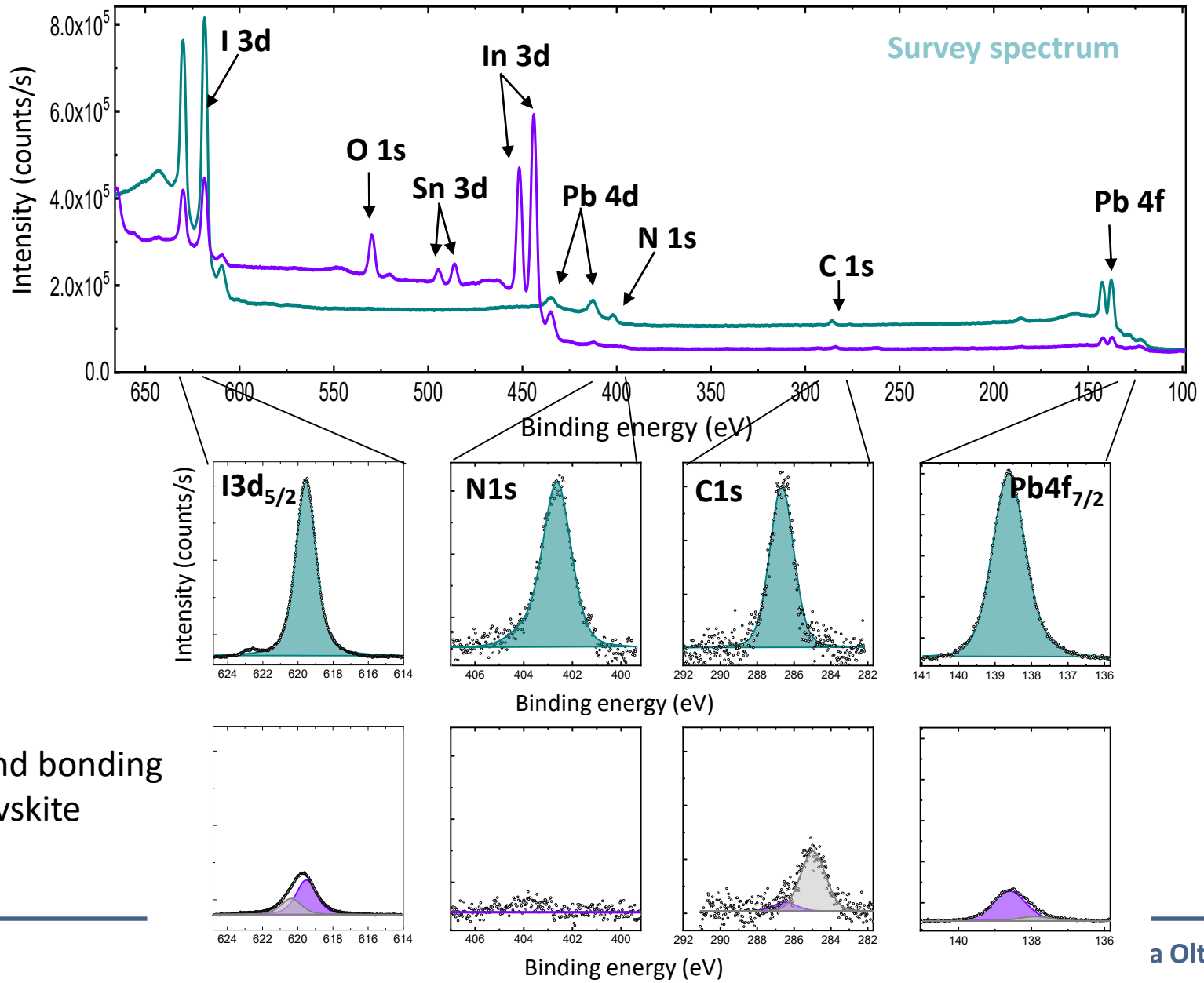
XPS measurement of **thick** $MAPbI_3$ film:



Probing the interface composition by XPS

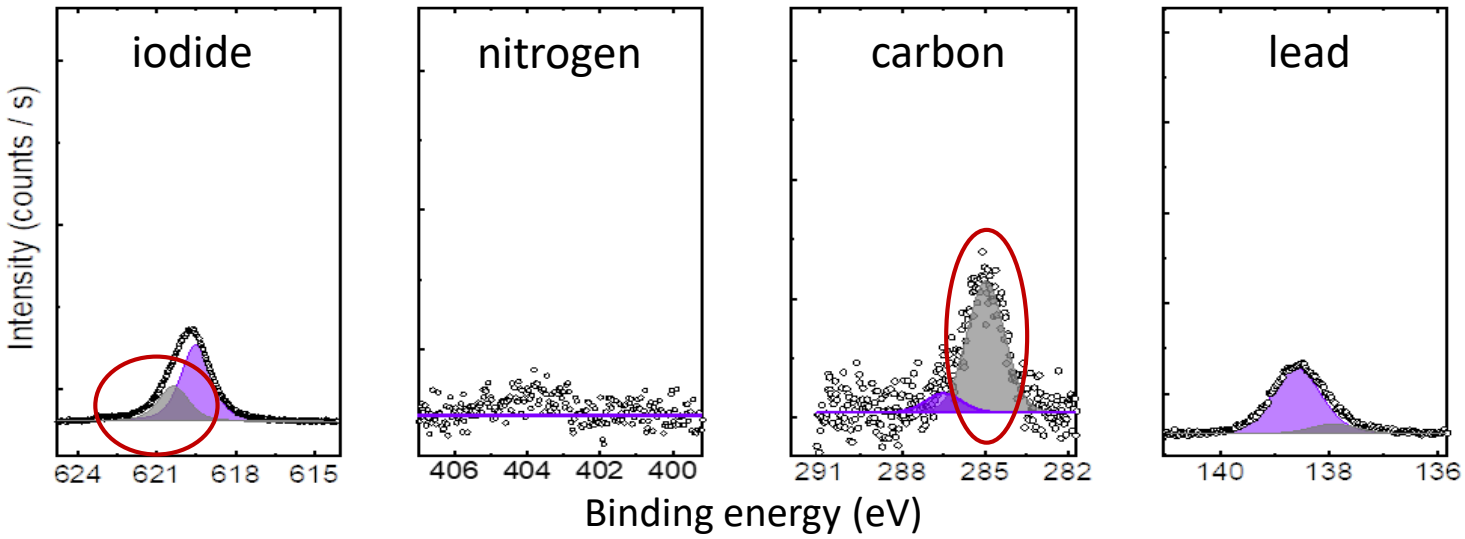
XPS measurement of **thick** $MAPbI_3$ film:

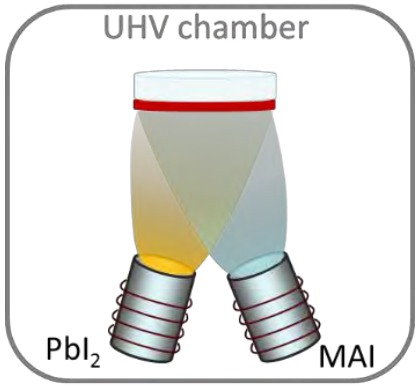
XPS measurement of **thin** $MAPbI_3$ film:



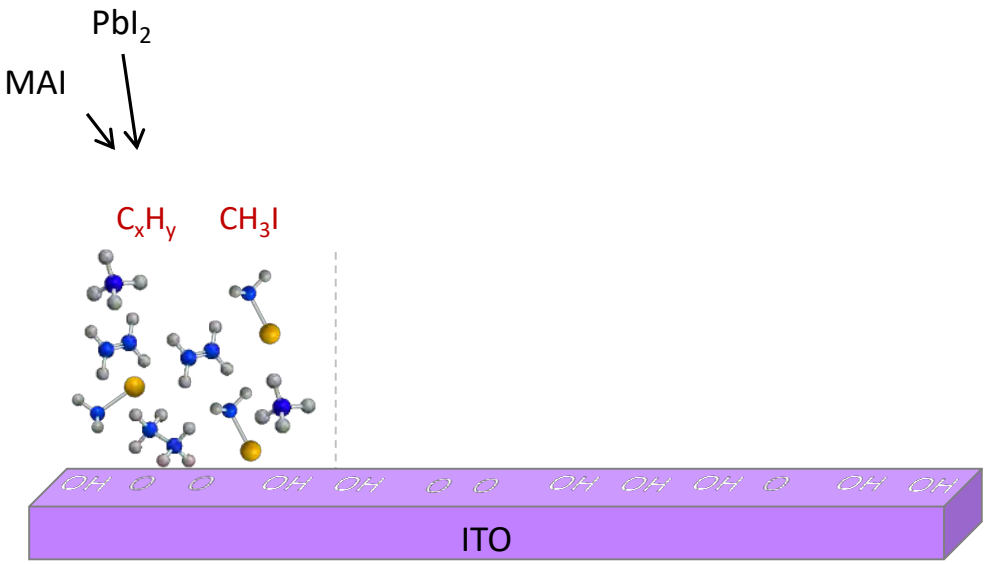
→ changes in intensity and bonding environment reveal perovskite degradation

XPS measurement: ITO – $MAPbI_3$, 3 nm evaporated



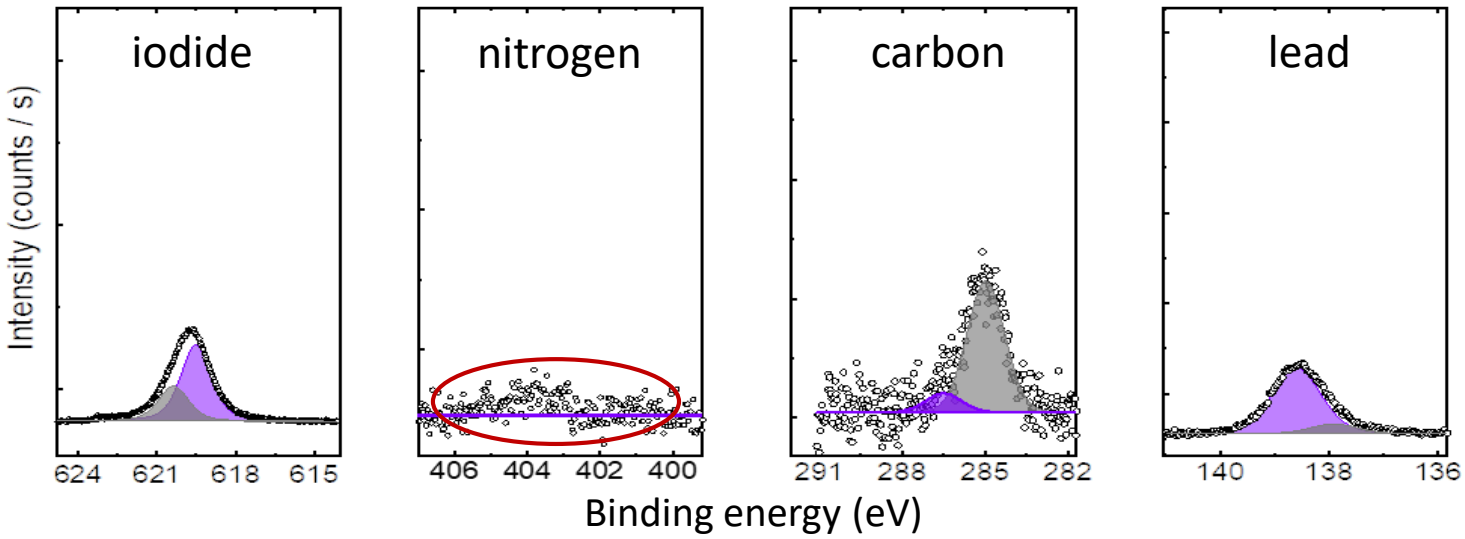


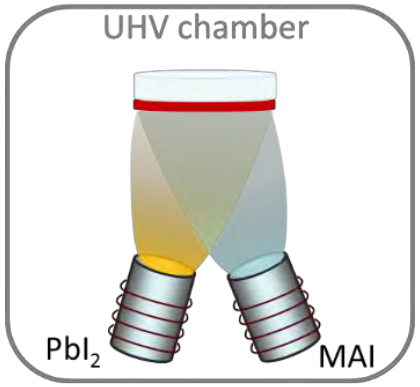
1. More neutral oxidation states of C and I (40%)

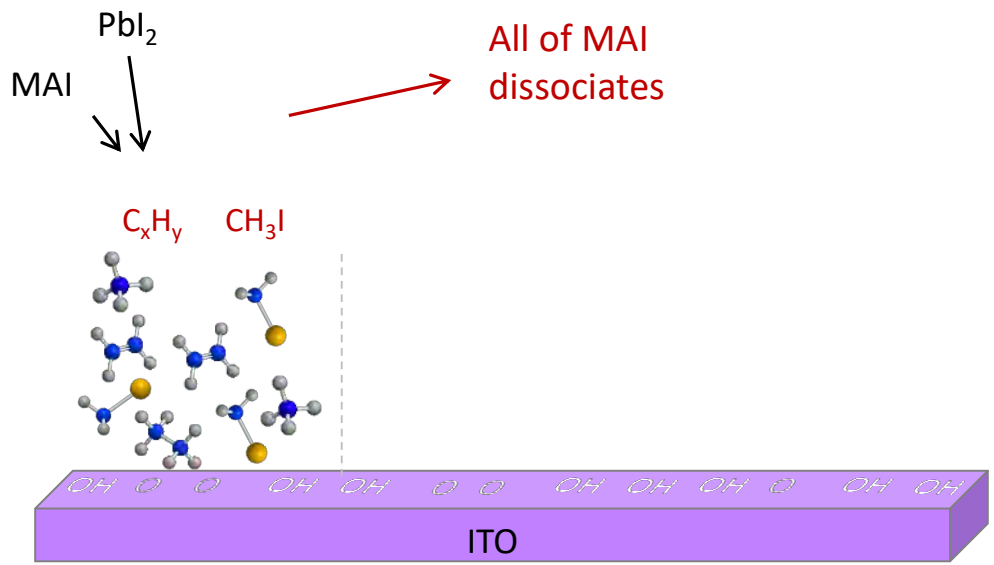


Scientific Reports, 7, 40267 (2017)

XPS measurement: ITO – $MAPbI_3$, 3 nm evaporated



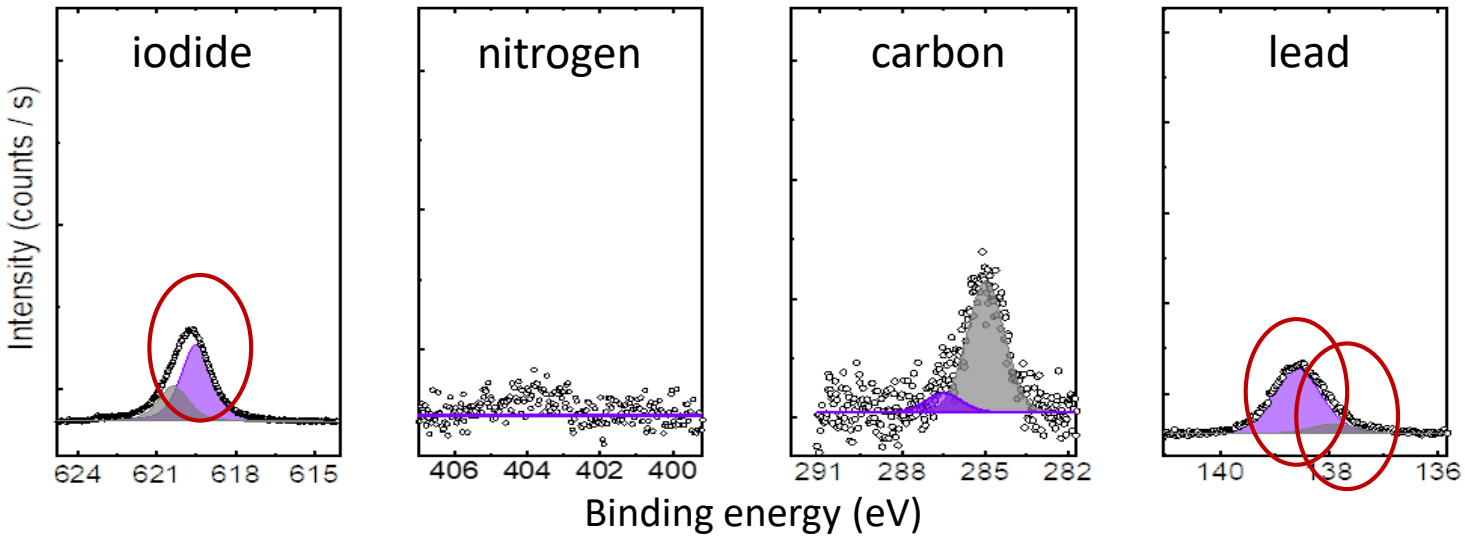


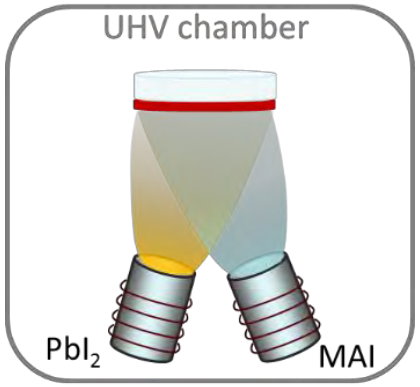


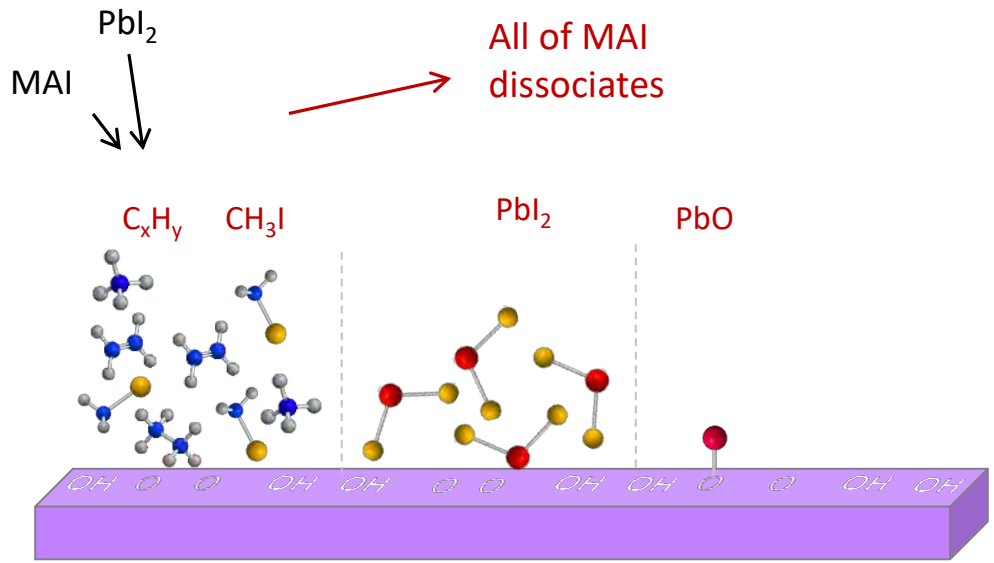
1. More neutral oxidation states of C and I (40%)
2. N is missing

Scientific Reports, 7, 40267 (2017)

XPS measurement: ITO – $MAPbI_3$, 3 nm evaporated







1. More neutral oxidation states of C and I (40%)
2. N is missing
3. Pb present as PbI_2 (11%) / PbO (2%)

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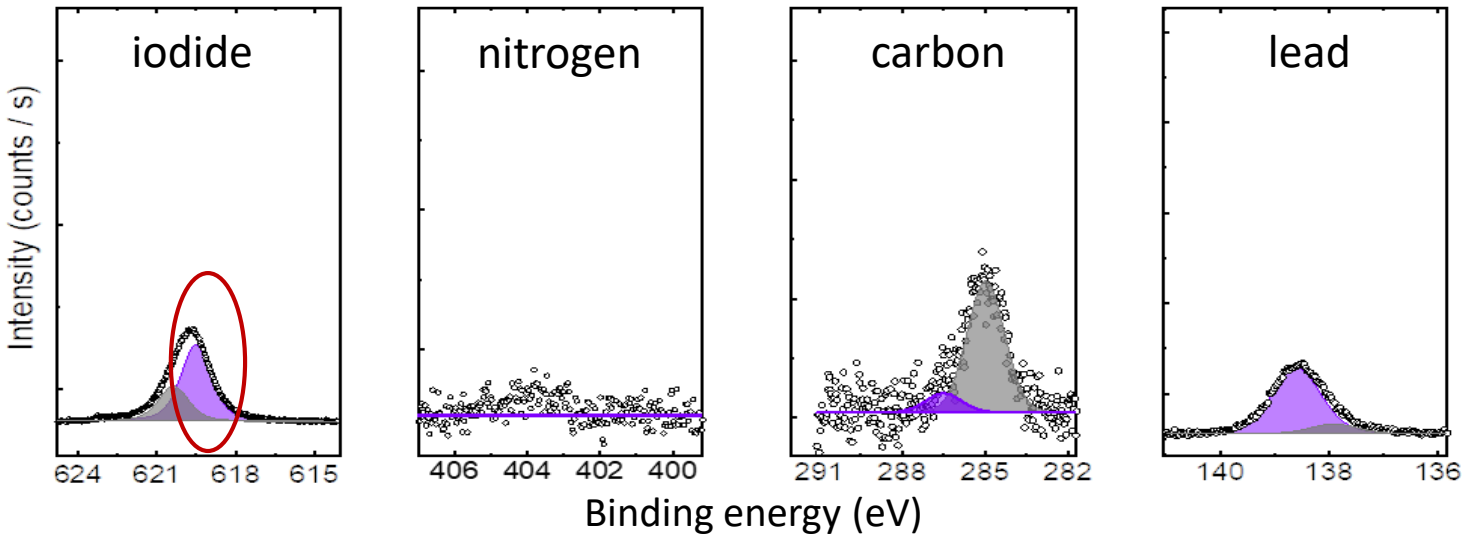
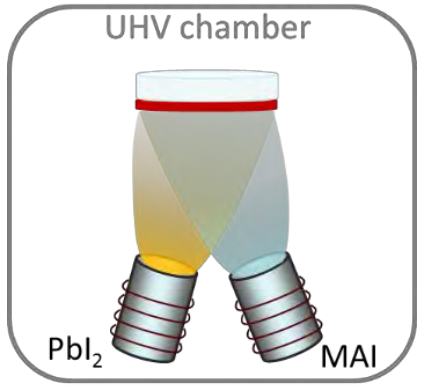
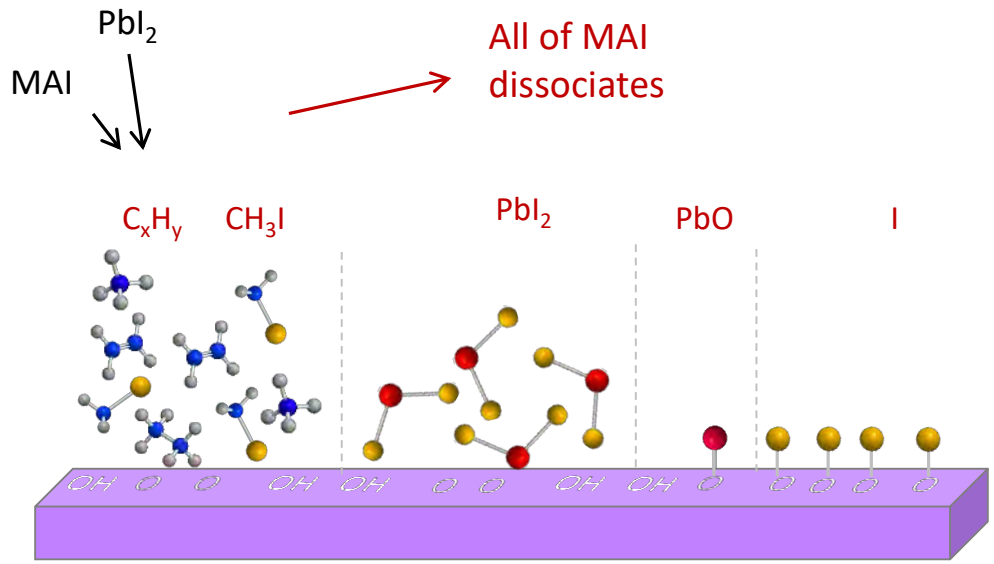
XPS measurement: ITO – $MAPbI_3$, 3 nm evaporated







1. More neutral oxidation states of C and I (40%)
2. N is missing
3. Pb present as PbI_2 (11%) / PbO (2%)
4. Additional I must form surface bonds (31%)

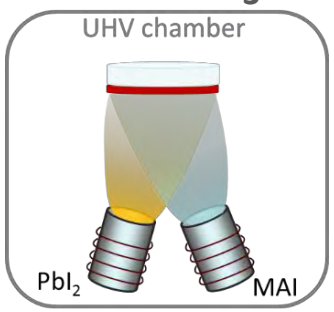
Scientific Reports, 7, 40267 (2017)

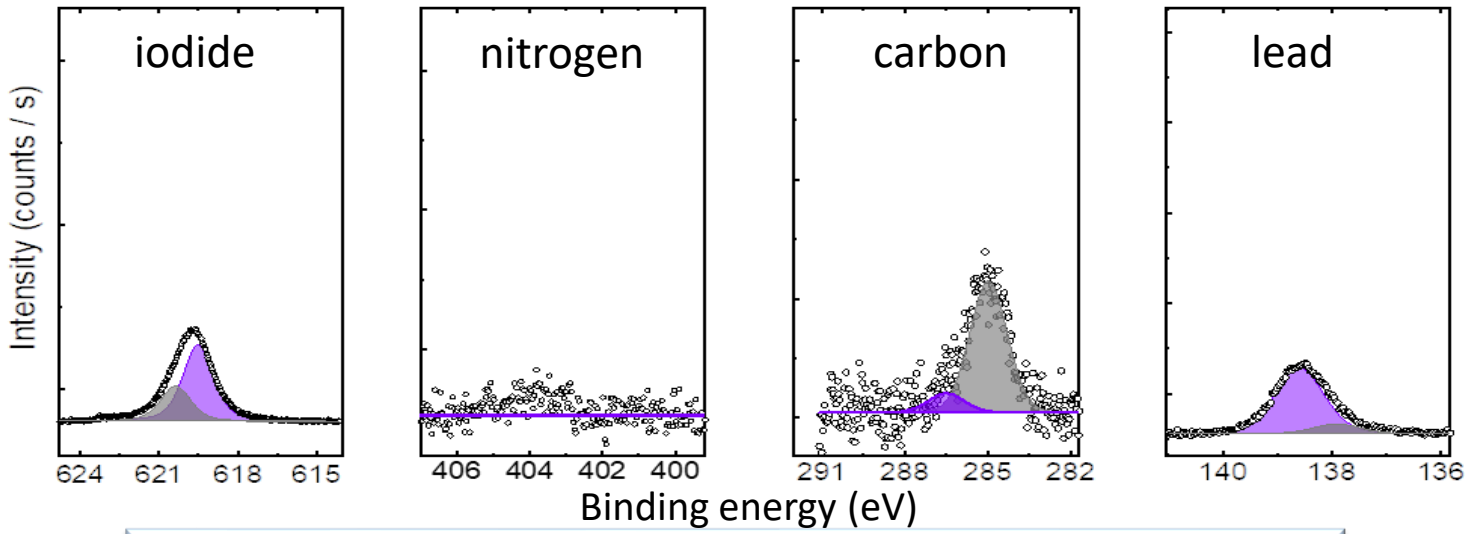
Open Questions

1. Are these results from evaporated layers representative?
2. Do other metal oxides interact similarly?
3. Are different perovskites equally affected?

Comparison $MAPbI_3$ on ITO via evaporation and solution

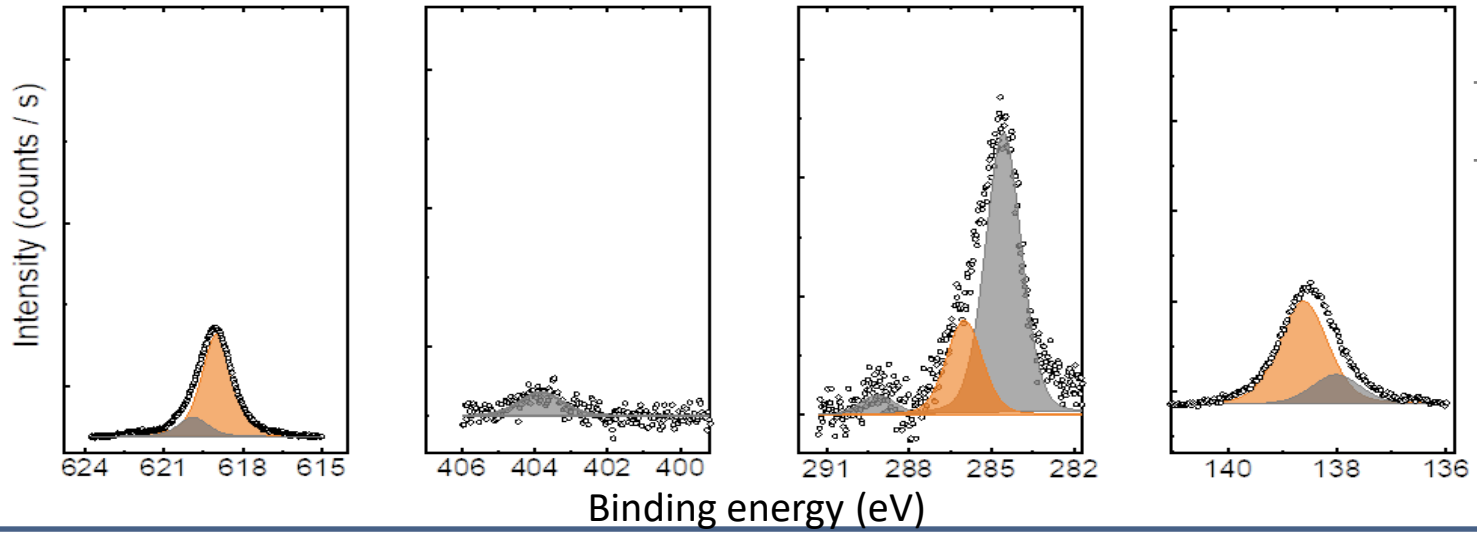
3 nm $MAPbI_3$





Evaporated and solution processed interfaces rather similar

0.01 molar solution



	vacuum	solution
Perovskite	--	--
Hydrocarbons	17%	45%
Methyl iodide	24%	7%
I surface bonds	31%	17%
PbI_2	11%	9%
PbO	2%	3%

Interface of different metal oxides with $MAPbI_3$

ITO[1]

→ Iodide, PbI_2, and hydrocarbons

Organic substrate (PEIE)[1]

→ Perovskite + MAI dissociation products

SnO_x[2]

→ PbI_2

TiO_2[3]

→ PbI_2 and hydrocarbons

ZnO[4]

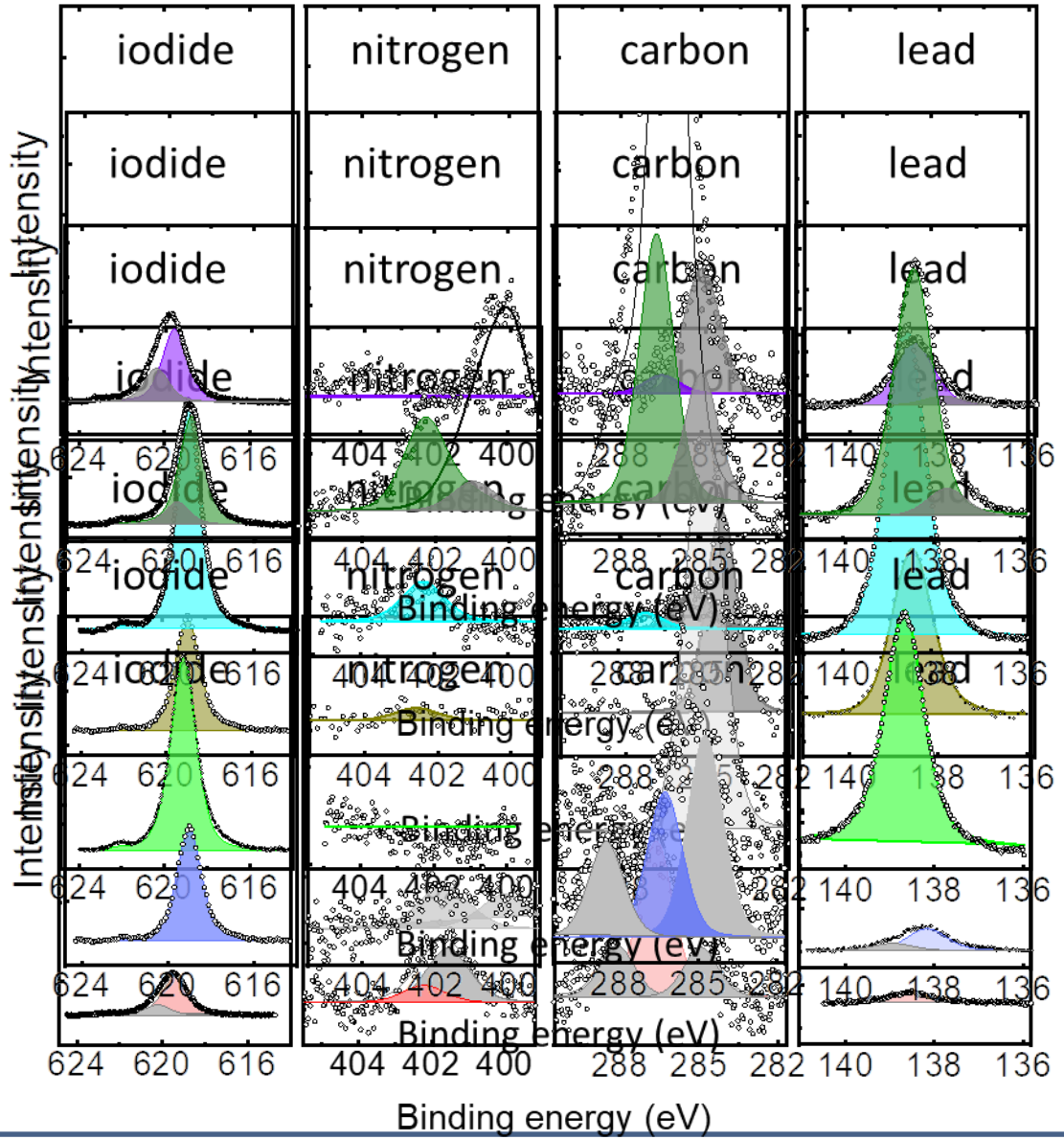
→ PbI_2 and lots hydrocarbons

NiO_x[unpublished]

→ Carbon species and iodide

MoO_3[1]

→ hydrocarbons and amines



[1] Scientific Reports 7, 40267 (2017)
[2] Adv. Mater. 29, 1606656 (2017)
[3] ACS Appl. Mater. Interf. 11 32508 (2019)
[4] Nano Energy 83, 105774 (2020)

Content

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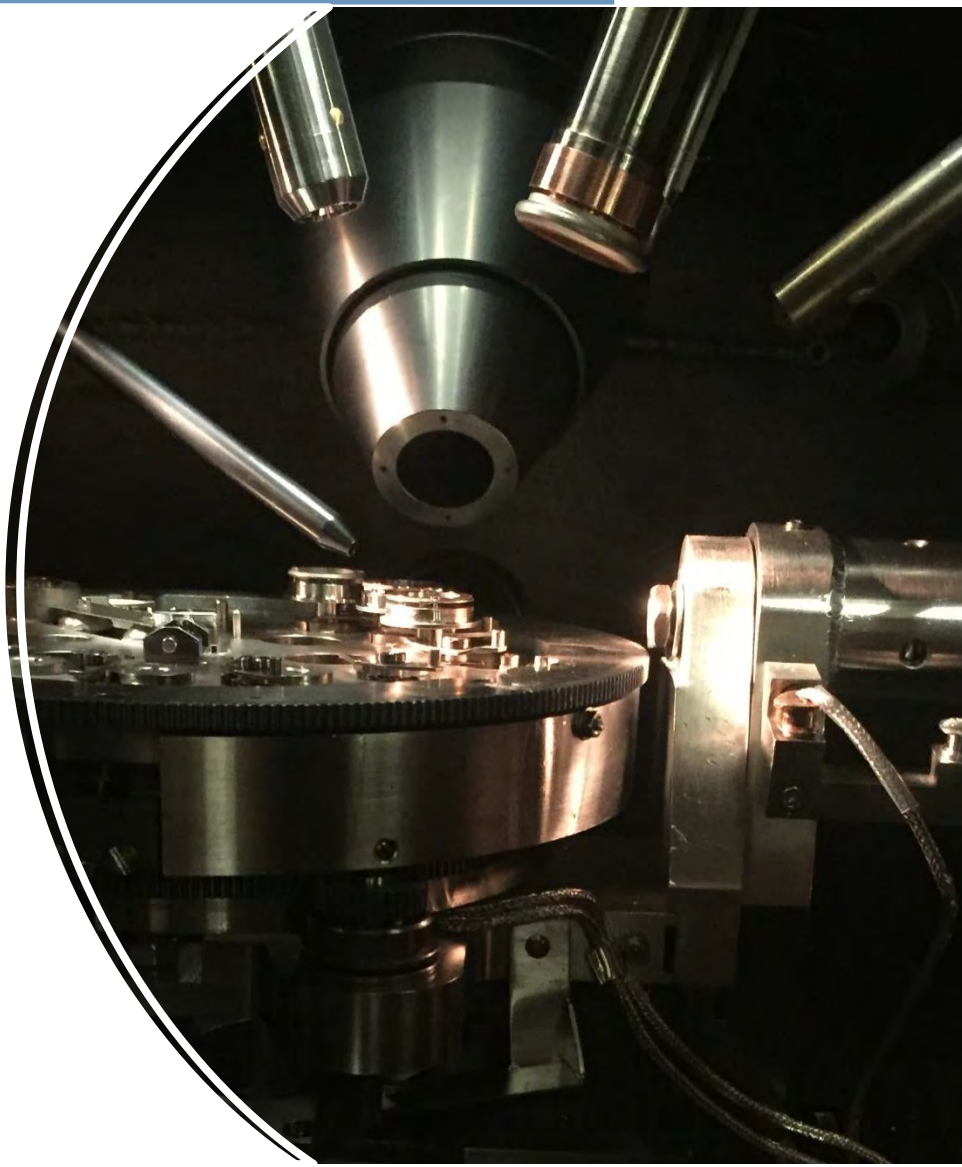


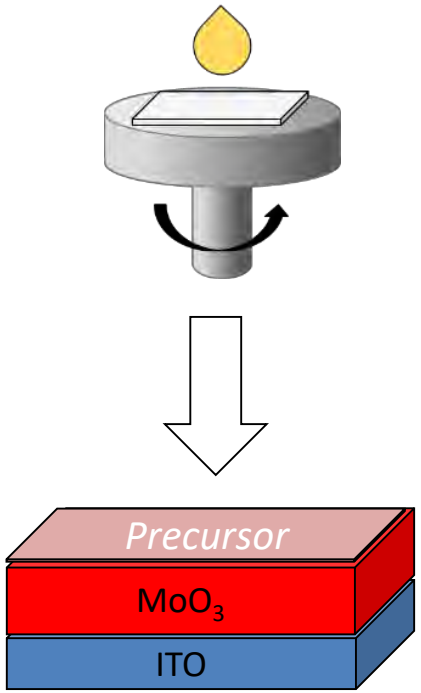
Understanding the reactivity of MoO_3

What triggers the reaction and which component is responsible?

One step back:

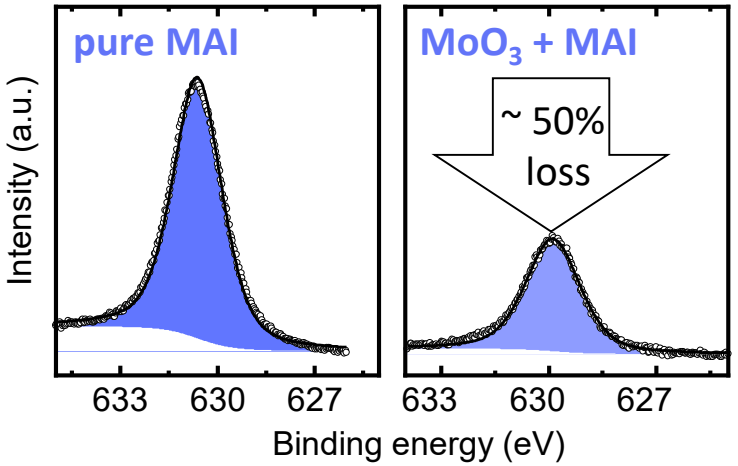
- investigate only the precursors

MAI, FAI, MABr, FABr (0.05M)



Experimental observation for halide species:

Iodide signal



→ at the interface to MoO_3 halide species is missing

ACS Appl. Mater. Interfaces, acsami.1c20847 (2022)

Understanding the reactivity of MoO_3

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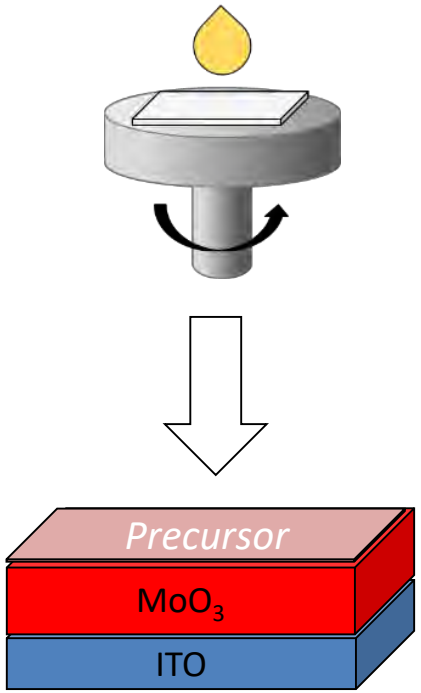

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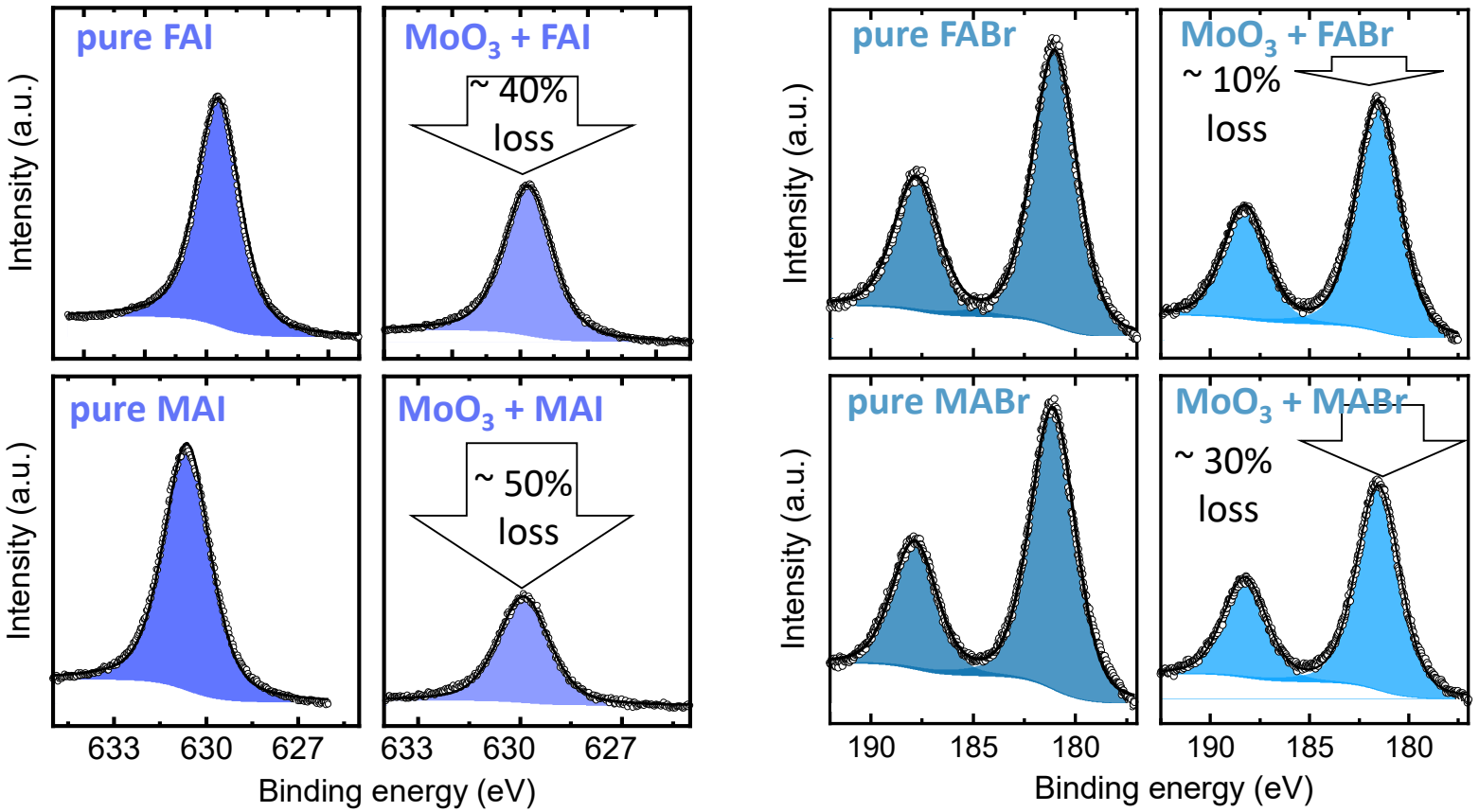


→ at the interface to MoO_3 halide species is missing

ACS Appl. Mater. Interfaces, acsami.1c20847 (2022)

Understanding the reactivity of MoO_3

Assume 4 possible reactions

Reactions for MAX	$CH_3NH_3X \rightarrow HX + CH_3NH_2$	Deprotonation MA^+	A1
	$CH_3NH_3X \rightarrow CH_3X + NH_3$	Dissociation of MA	A2
Reactions for FAX	$CH_5N_2X \rightarrow HX + CH_4N_2$	Deprotonation of FA^+	B1
	$CH_5N_2X \rightarrow NH_4X + HCN$	Dissociation of FA	B2

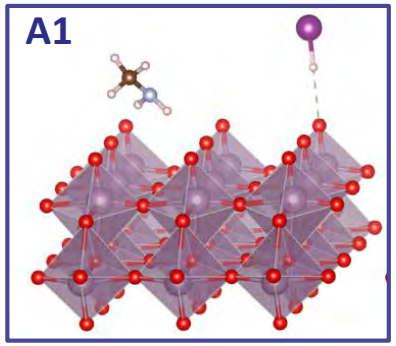
Theory input from TU Eindhoven and U. Twente

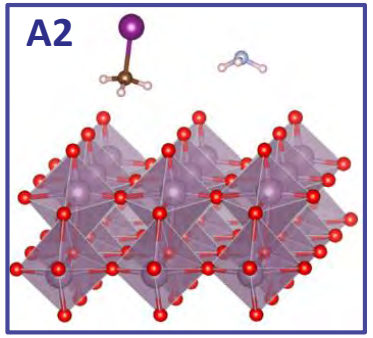

Prof. Shuxia Tao

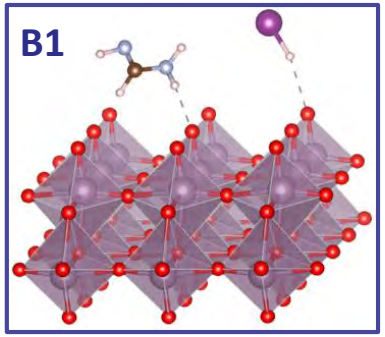

Sofia Apergi

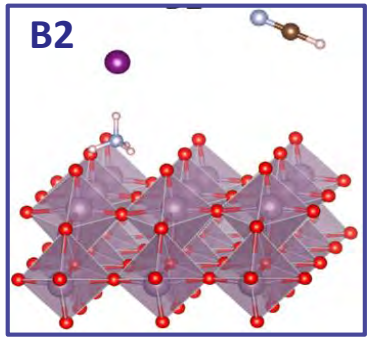

Prof. Geert Brocks

Precursor interaction on pristine surface:









All reaction energies lowered on surface
→ pristine MoO_3 surface stabilizes the precursor molecules

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Understanding the reactivity of MoO_3

Assume 4 possible reactions

Reactions for MAX	$CH_3NH_3X \rightarrow HX + CH_3NH_2$	Deprotonation MA^+	A1
	$CH_3NH_3X \rightarrow CH_3X + NH_3$	Dissociation of MA	A2
Reactions for FAX	$CH_5N_2X \rightarrow HX + CH_4N_2$	Deprotonation of FA^+	B1
	$CH_5N_2X \rightarrow NH_4X + HCN$	Dissociation of FA	B2

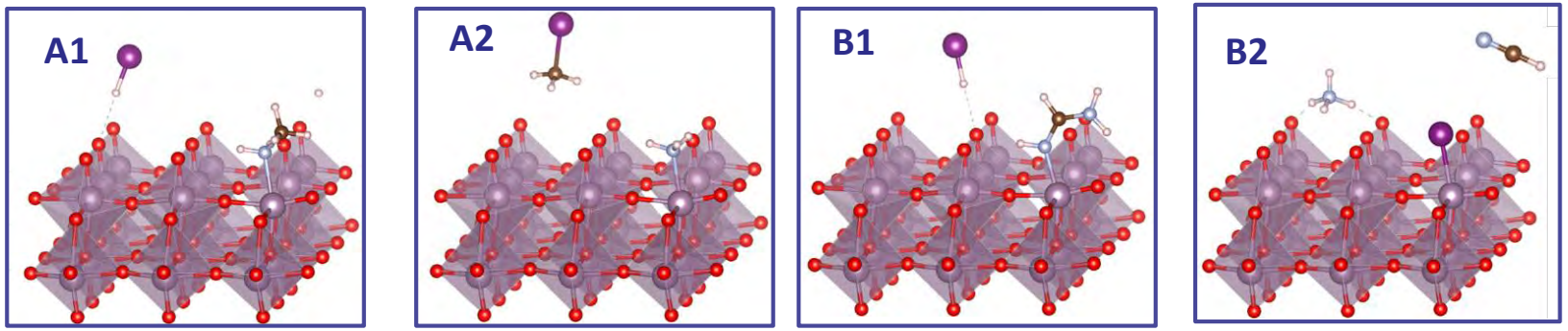
Theory input from TU Eindhoven and U. Twente


Prof. Shuxia Tao


Sofia Apergi


Prof. Geert Brocks

Precursor interaction with **defective surface** (oxygen vacancy):



→ Presence of an O vacancy lowers all reaction energies significantly

→ But no significant difference found between precursors

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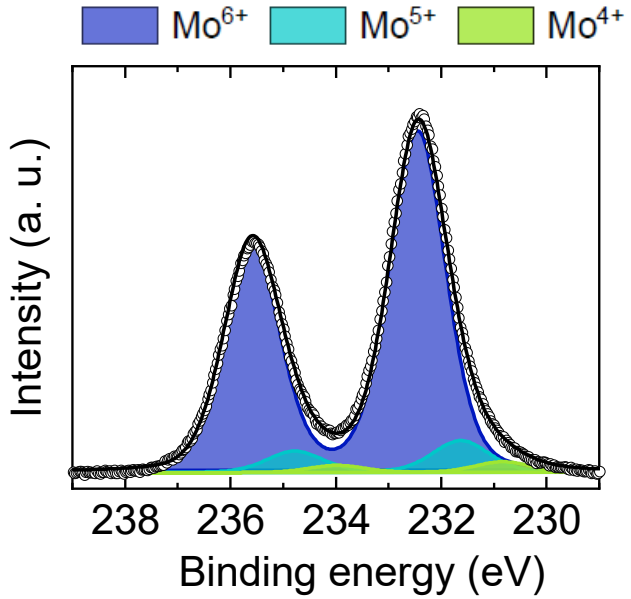
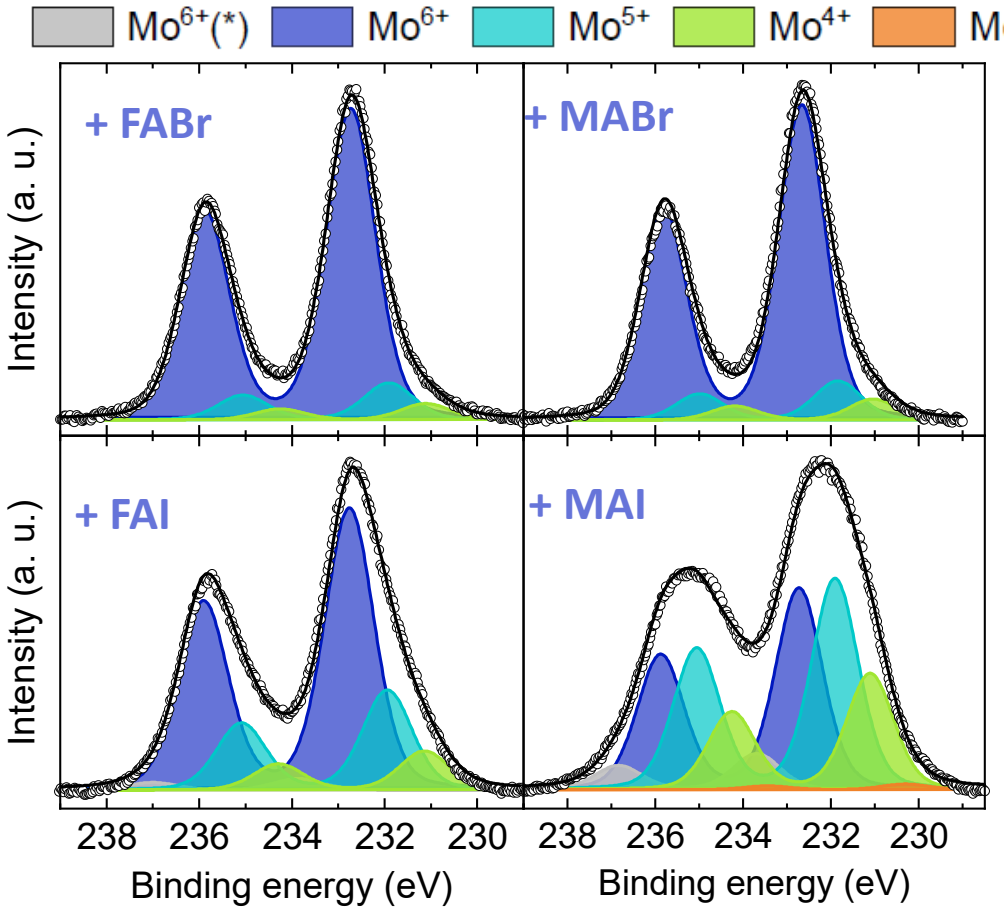
Understanding the reactivity of MoO_3

Indeed, oxygen vacancies are observed experimentally (~4 - 10%)

As prepared MoO_3



Changes in Mo oxidation observed after deposition of precursors:



→ additional Mo oxidation states appear in contact to iodide precursors

→ redox reactions must happen!

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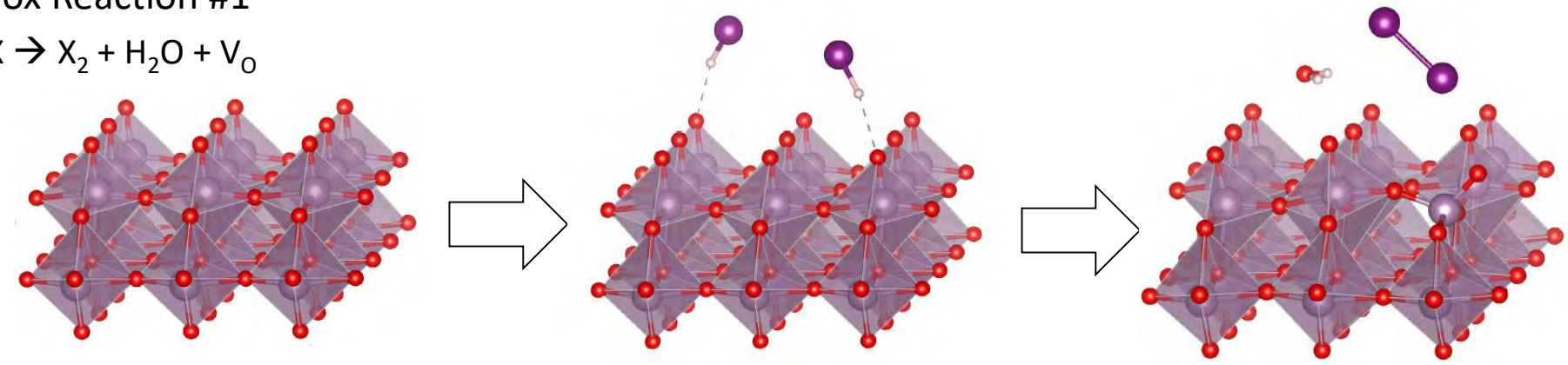
Understanding the reactivity of MoO_3

Redox Reaction #1

2 HX → X_2 + H_2O + V_O

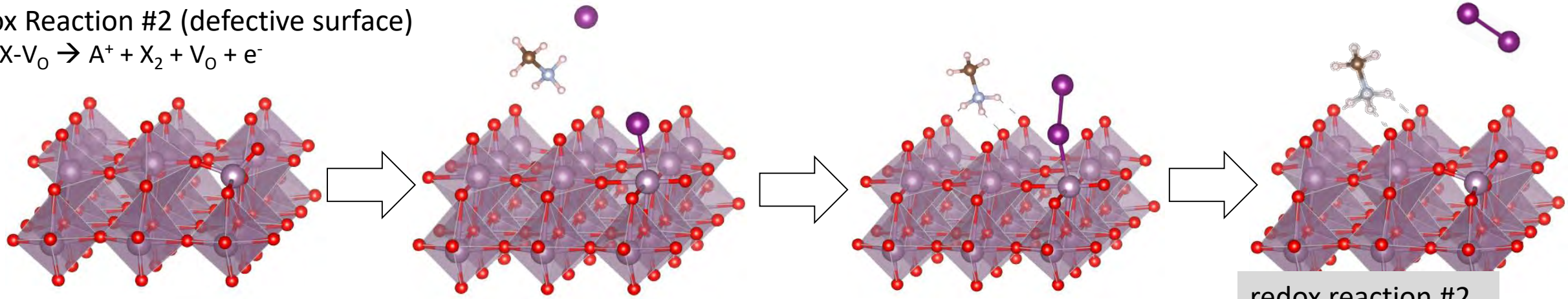


redox reaction #1
only likely for HI

→ reaction creates an O vacancy (V_O)

Redox Reaction #2 (defective surface)

AX + X-V_O → A^+ + X_2 + V_O + e^-



redox reaction #2
only likely for MAI

→ I_2^- forms on surface and is oxidized to I_2
catalytic redox reaction

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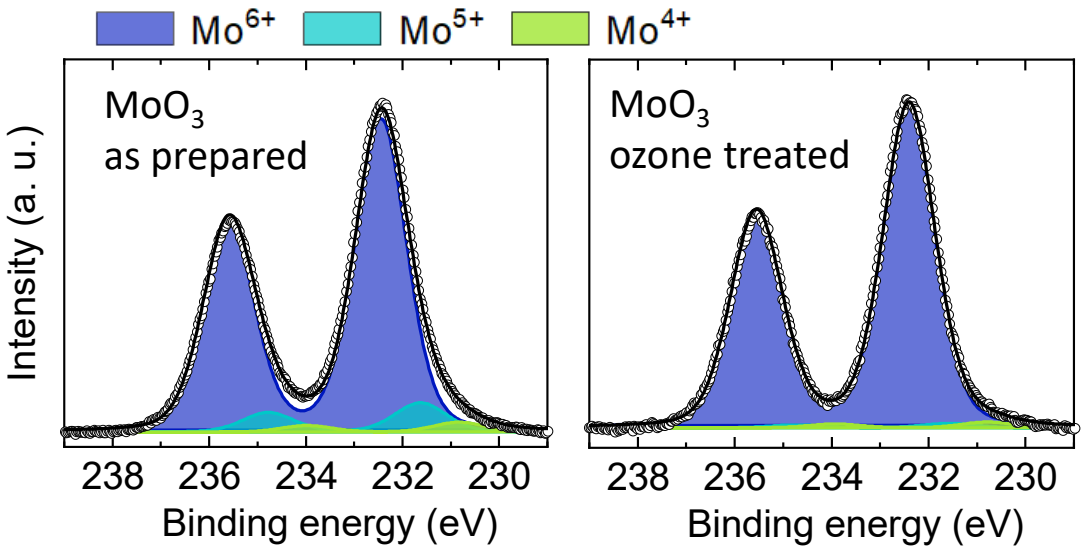
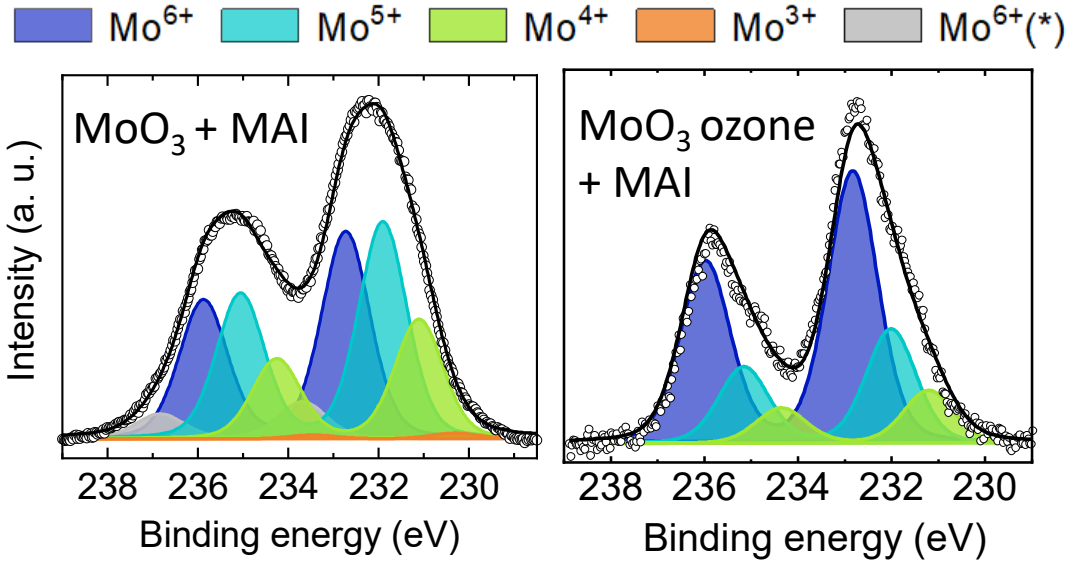
Understanding the reactivity of MoO_3

Can we inhibit degradation by reducing initial defect density?

Ozone treatment of MoO_3



MAI on *as prepared* and ozone treated MoO_3



→ Ozone treatment reduces vacancies by factor ~3

Due to suppression of redox reaction #2 we have

- less reduced Mo species
- no loss in iodide
- for FAI we can suppress redox reaction almost completely

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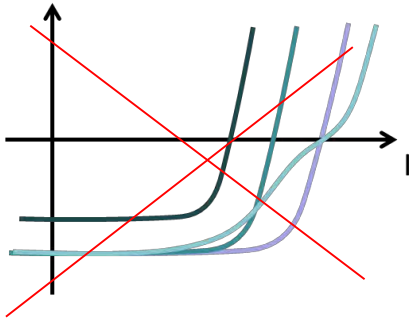
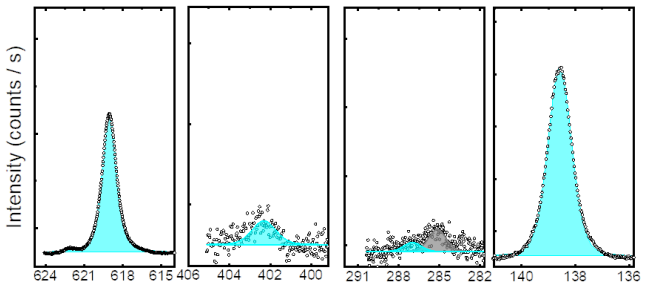
Take home message

Interfaces matter!

… but <u>energetic offsets</u> in perovskite devices are probably less critical

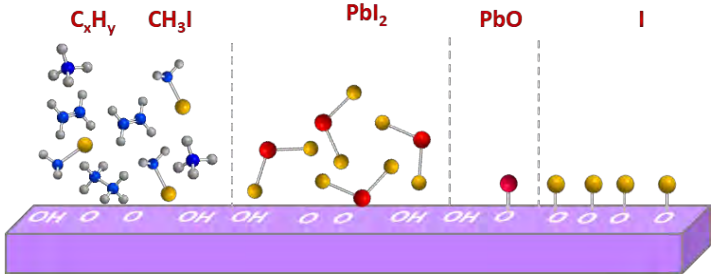




Perovskites tend to strongly interact with metal oxides

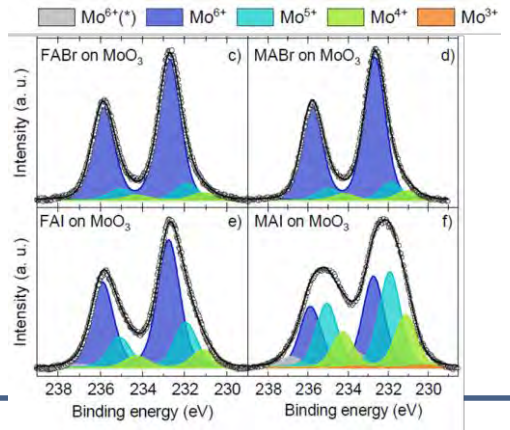
→ much less so with organic surfaces

Interface composition is complex and different for each material



→ hydrocarbons seem detrimental
→ PbI_2 is probably preferred

For MoO_3 the reactivity driven mostly by iodide
→ Br compounds much more stable



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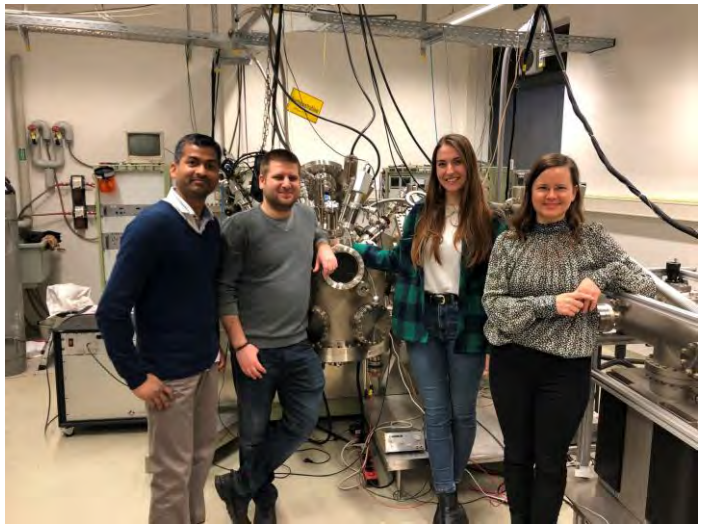

Thank you for your attention

SCALE UP