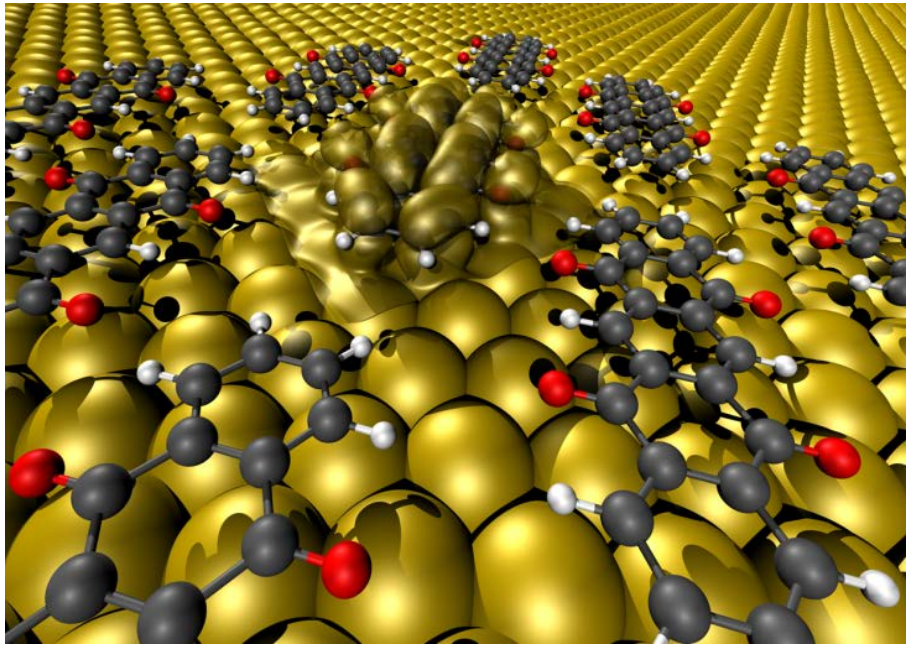
Vertical Adsorption Distances Impact Energetics at Organic-Metal Interfaces

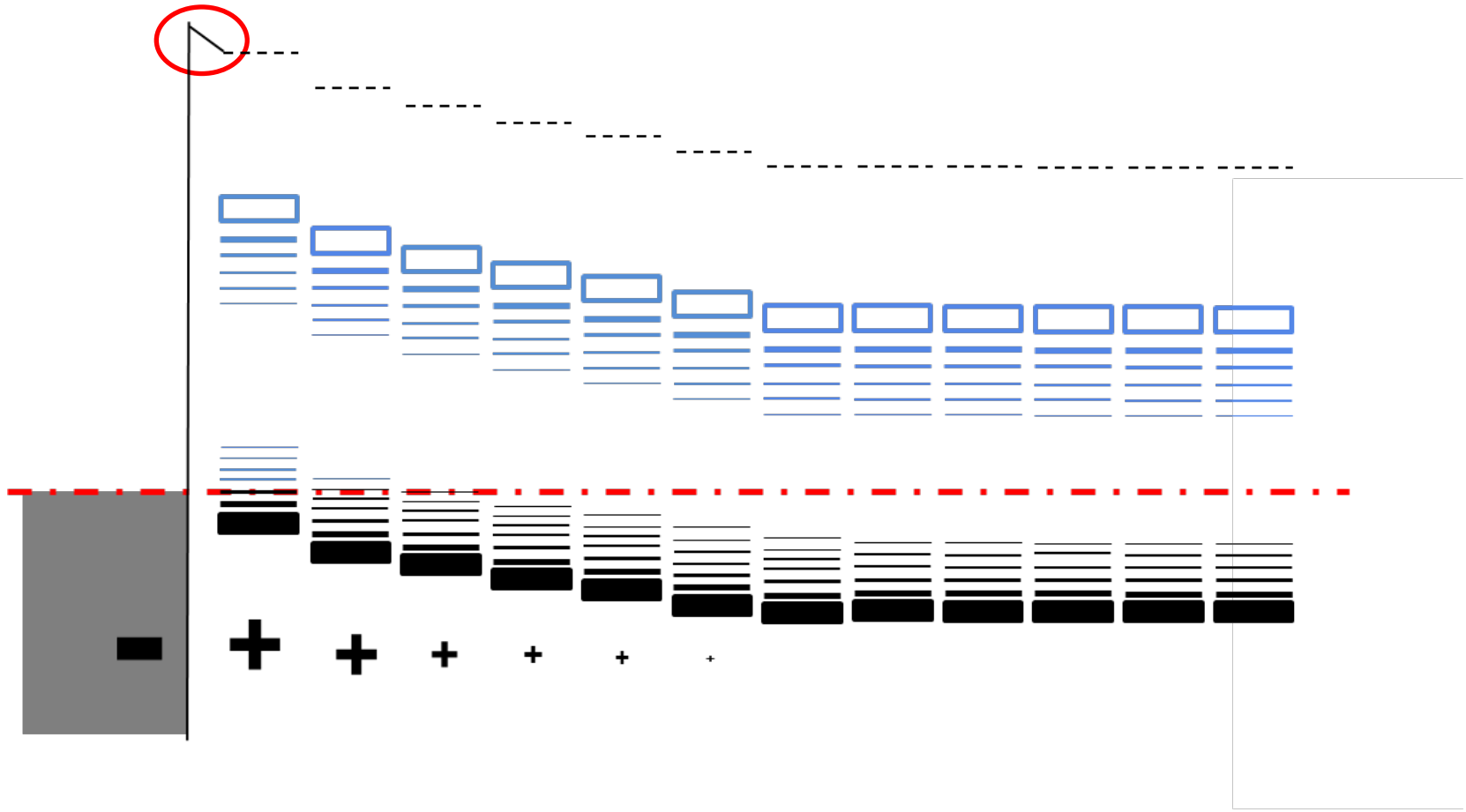


FUNSOM
功能纳米与软物质研究院
Institute of Functional Nano & Soft Materials

Steffen Duhm

蘇州大學
Soochow University

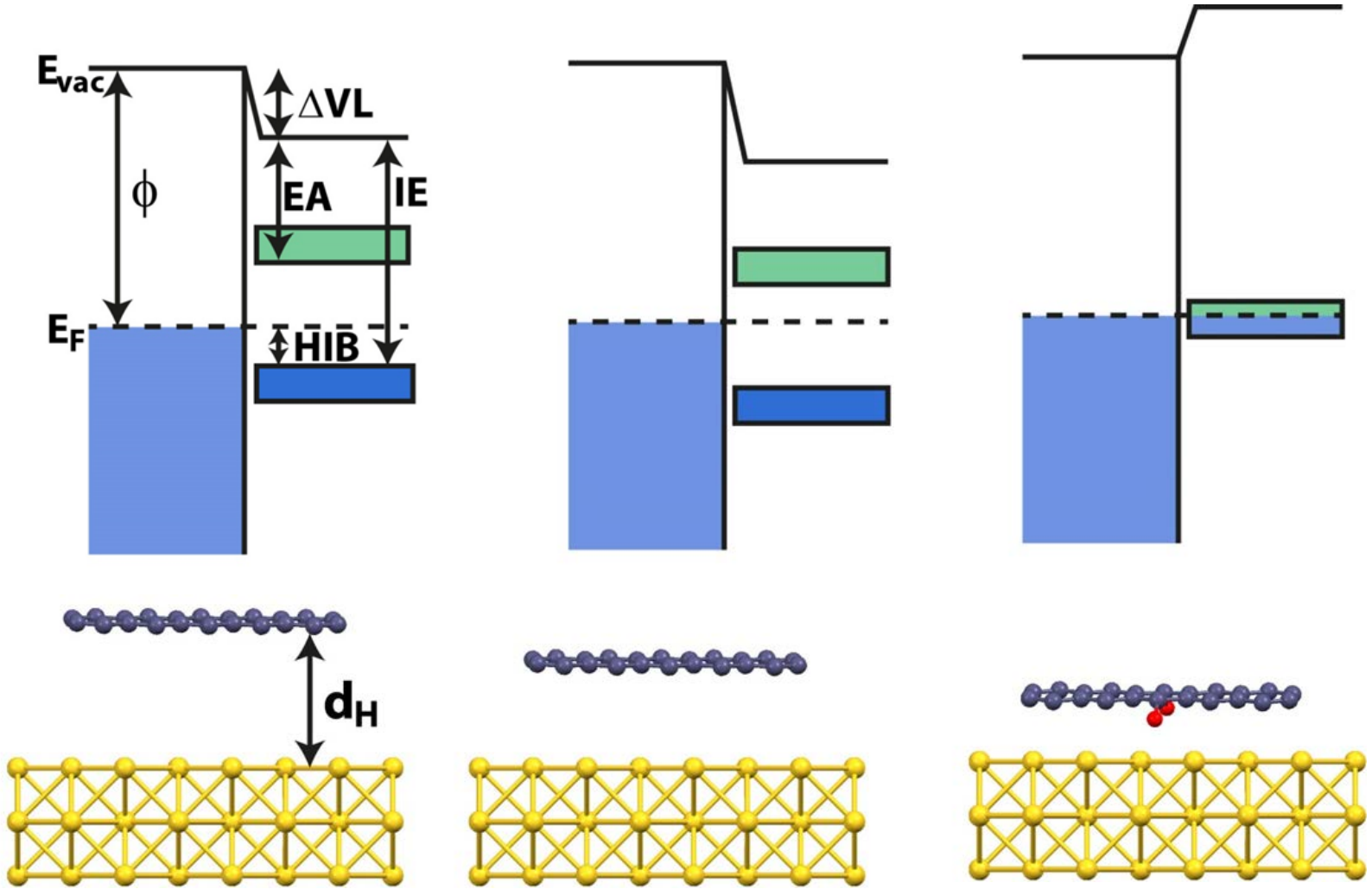
Energy-level alignment



The energy-level alignment at organic-inorganic interfaces is controlled by the density of states of frontier molecular orbitals.

Bussolotti, Kera, Kudo, Kahn, Ueno, *Phys. Rev. Lett.* **110**, 267602 (2013)
and further work by S. Kera, N. Ueno *et al.*

Organic-metal interface energetics

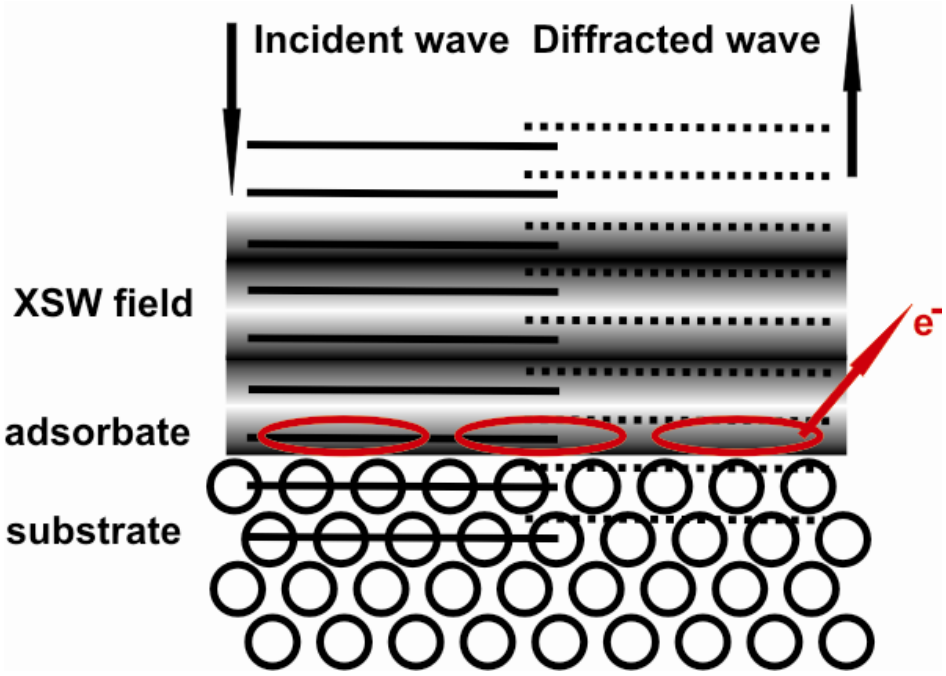


physisorption
ΔVL due to push-back

chemisorption
ΔVL due to coupling

Photoelectron spectroscopy

X-ray standing waves I



With the XSW technique element-specific bonding distances of organic (sub)monolayers on metal single crystals can be determined with high precision.

The photoelectron yield (intensity of XPS signal) of the adsorbate is measured in the standing wave field of incident and diffracted X-ray wave.

$$I(\theta,\mathbf{r}) = \frac{|\mathbf{E_0}+\mathbf{E_H}|^2}{|E_0|^2}$$
$$= \left(1+R(\theta)+2\sqrt{R(\theta)}\cos(\nu(\theta)-\mathbf{H}\cdot\mathbf{r})\right)\times\begin{cases}1 & : \text{ above the surface}\\ \exp(-\mu_z(\theta)z) & : \text{ below the surface}\end{cases}$$

Duhm, Bürker, Hosokai, Gerlach, in "*Electronic Processes in Organic Electronics*" ed. by Ishii, Kudo, Nakayama, Ueno, *Springer Series in Materials Science* **209** (2015)

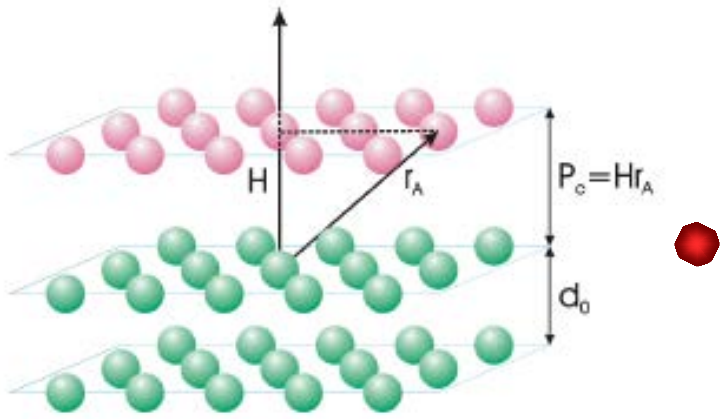
X-ray standing waves II

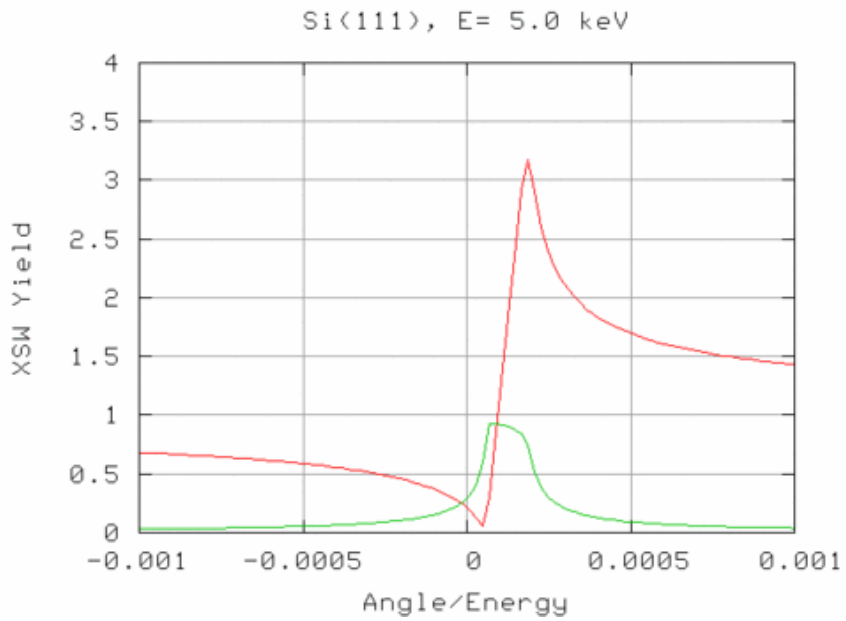
Photoelectron yield from adsorbate (dipole approximation):

$$Y_p(\mathbf{r}) = 1 + R + 2C\sqrt{R} f_H \cos(\nu - 2\pi P_H)$$

- coherent position: P_H
- coherent fraction: $0 < f_H < 1$

$d_H = d_0(n + P_H)$ with n = 0, 1, 2, ...



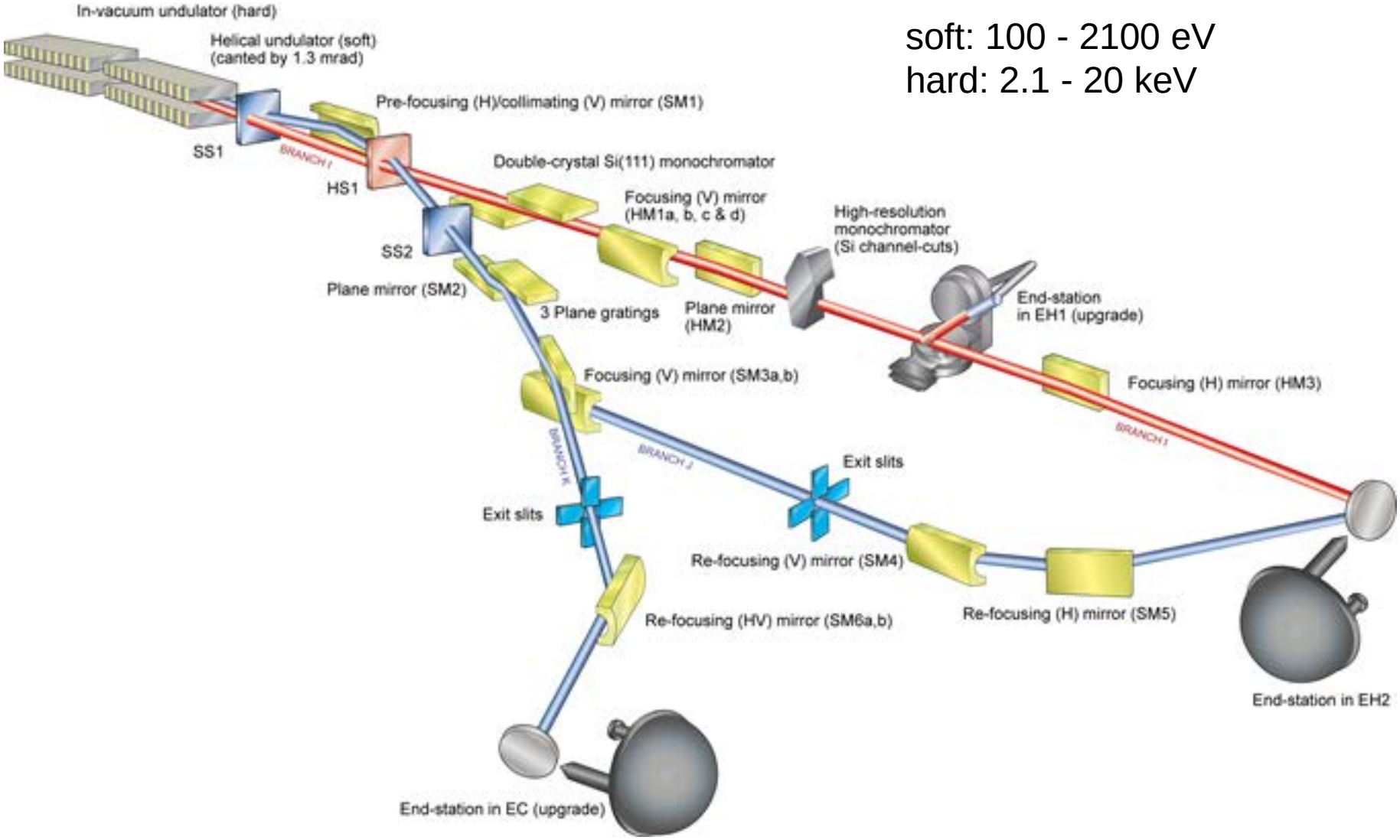


Bragg-energy in normal incidence for Au(111), Ag(111), Cu(111)…: ~3 keV

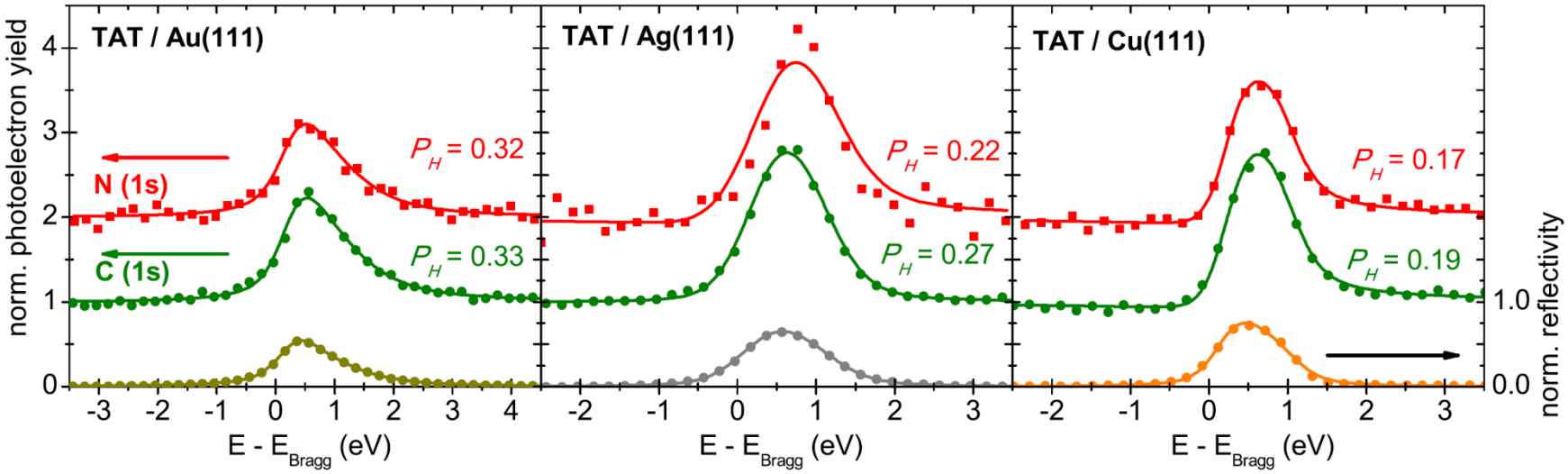
Duhm, Bürker, Hosokai, Gerlach, in "*Electronic Processes in Organic Electronics*" ed. by Ishii, Kudo, Nakayama, Ueno, *Springer Series in Materials Science* **209** (2015)

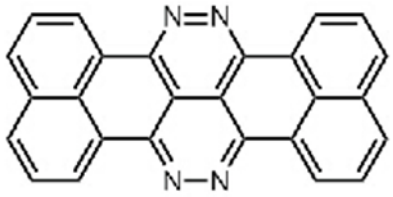
Beamline I09 @ Diamond

soft: 100 - 2100 eV
hard: 2.1 - 20 keV



Bonding distances of tetraazaterrylene

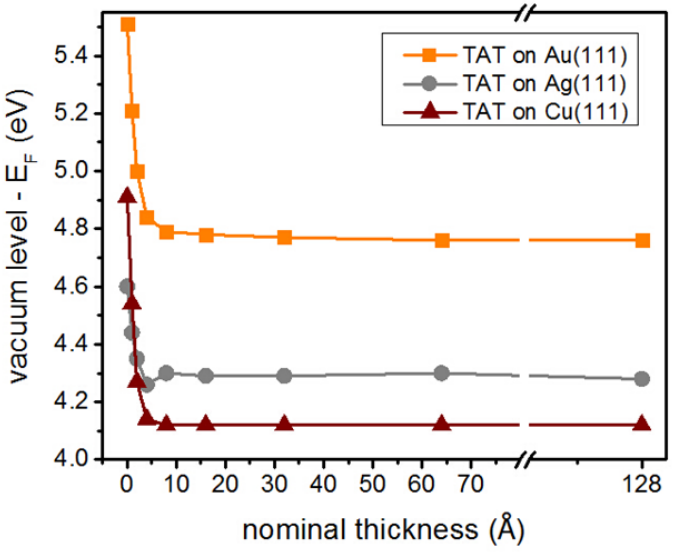


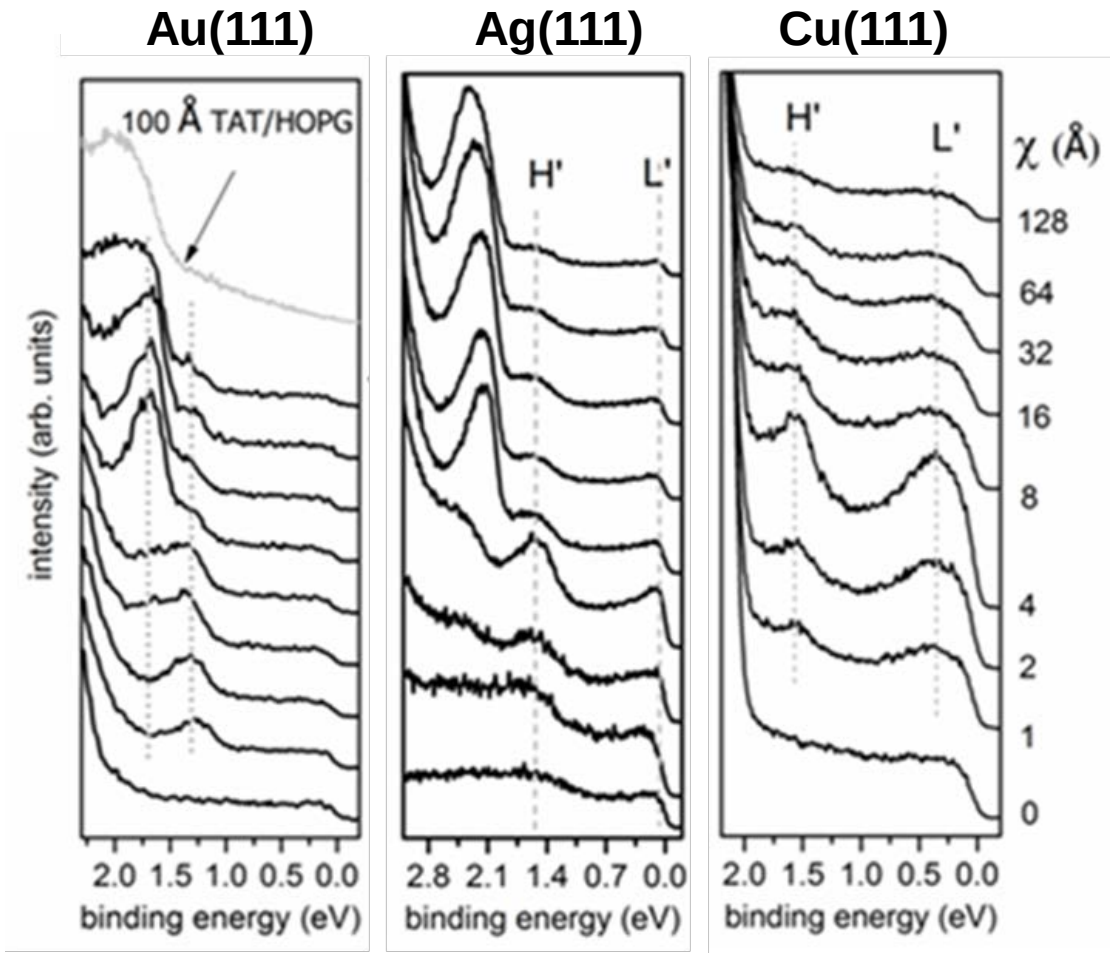


Substrate	Carbon f_H	Carbon P_H	Carbon d_H(Å)	Nitrogen f_H	Nitrogen P_H	Nitrogen d_H(Å)
Au(111)	0.39	0.33	3.06 ± 0.07	0.30	0.32	3.04 ± 0.02
Ag(111)	0.65	0.27	2.99 ± 0.05	0.92[a]	0.22	2.88 ± 0.10
Cu(111)	0.53	0.19	2.48 ± 0.04	0.46	0.17	2.44 ± 0.06

Yang, Franco-Cañellas, Sato, Wang, Wang, Koike, Salzmann, Thakur, Lee, Liu, Kera, Gerlach, Kanai, Fan, Schreiber, Duhm, *Phys. Rev. B* **94**, 155426 (2016)

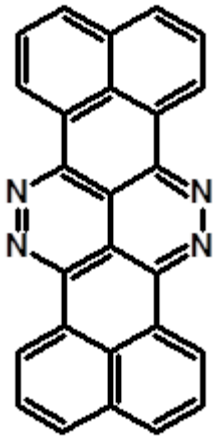
Tetraazaterrylene: UPS

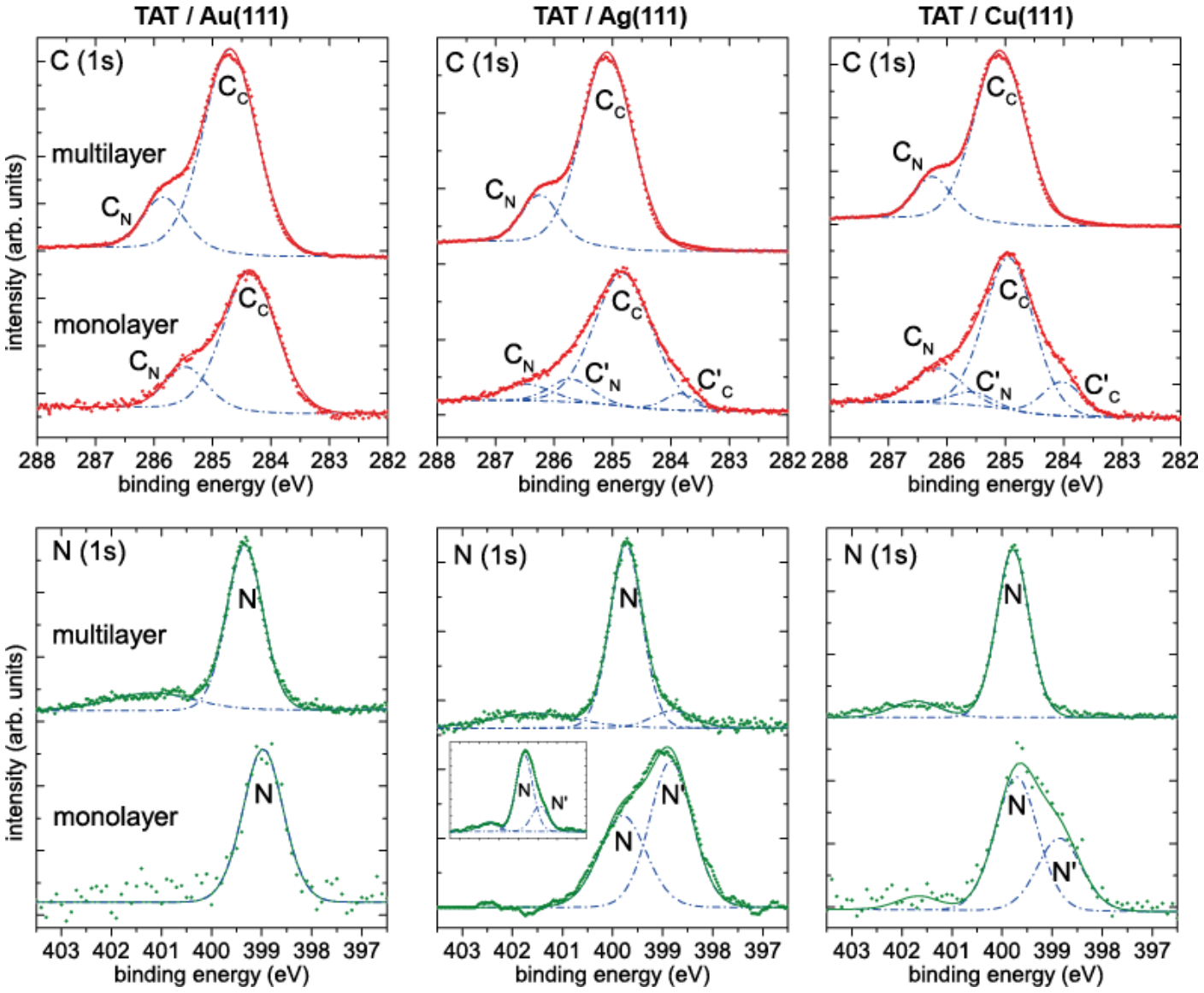




Yang, Franco-Cañellas, Sato, Wang, Wang, Koike, Salzmann, Thakur, Lee, Liu, Kera, Gerlach, Kanai, Fan, Schreiber, Duhm, *Phys. Rev. B* **94**, 155426 (2016)

Tetraazaterrylene: XPS

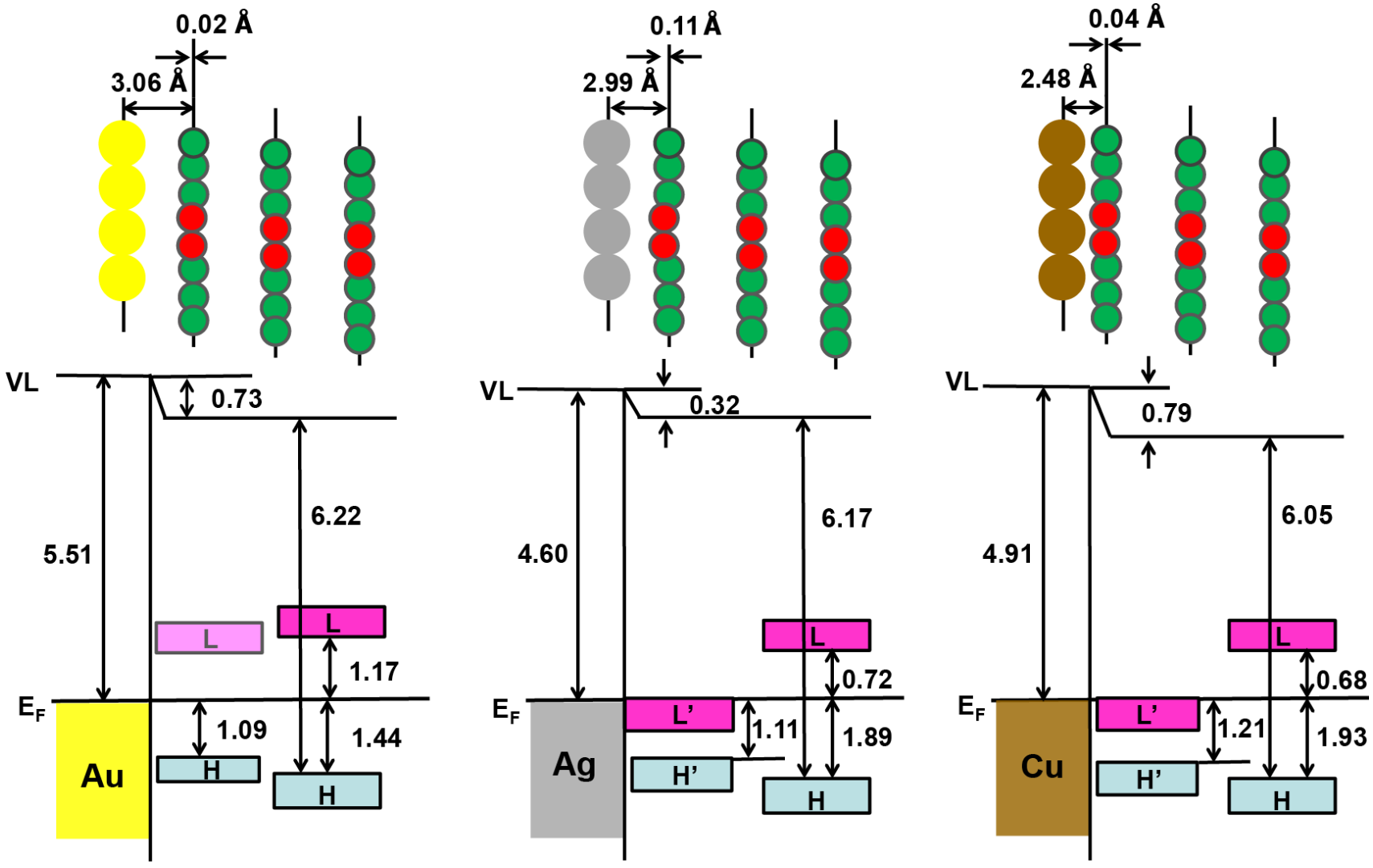




Soochow University

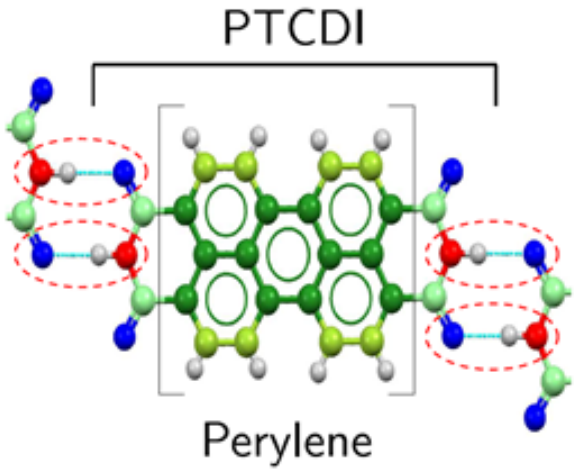
Yang, Franco-Cañellas, Sato, Wang, Wang, Koike, Salzmann, Thakur, Lee, Liu, Kera, Gerlach, Kanai, Fan, Schreiber, Duhm, *Phys. Rev. B* **94**, 155426 (2016)

Tetraazaterrylene: ELA

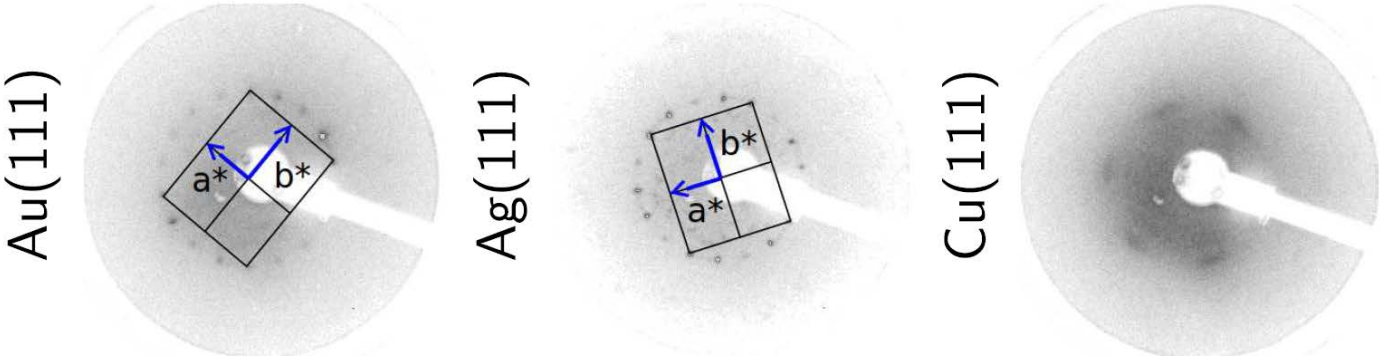


Yang, Franco-Cañellas, Sato, Wang, Wang, Koike, Salzmann, Thakur, Lee, Liu, Kera, Gerlach, Kanai, Fan, Schreiber, Duhm, *Phys. Rev. B* **94**, 155426 (2016)

PTCDI: lateral surface structure



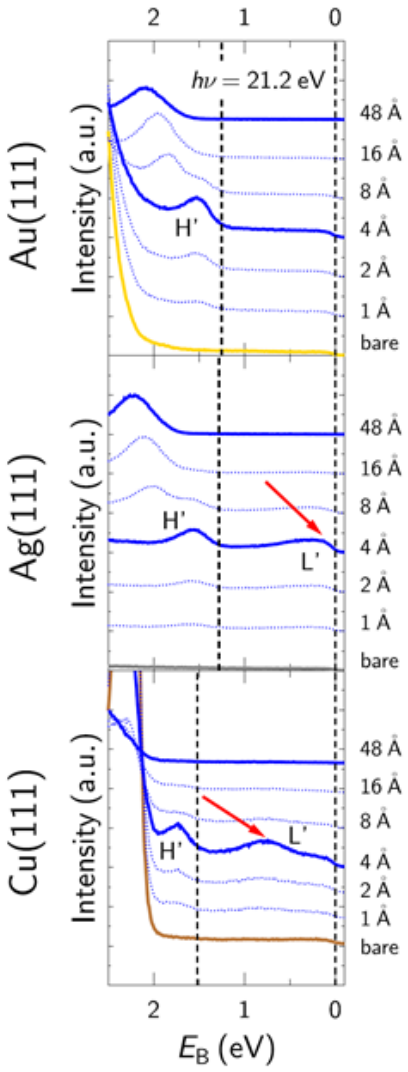
Perylene-3,4,9,10-tetracarboxylic diimide tends to N–H···O hydrogen-bond formation.

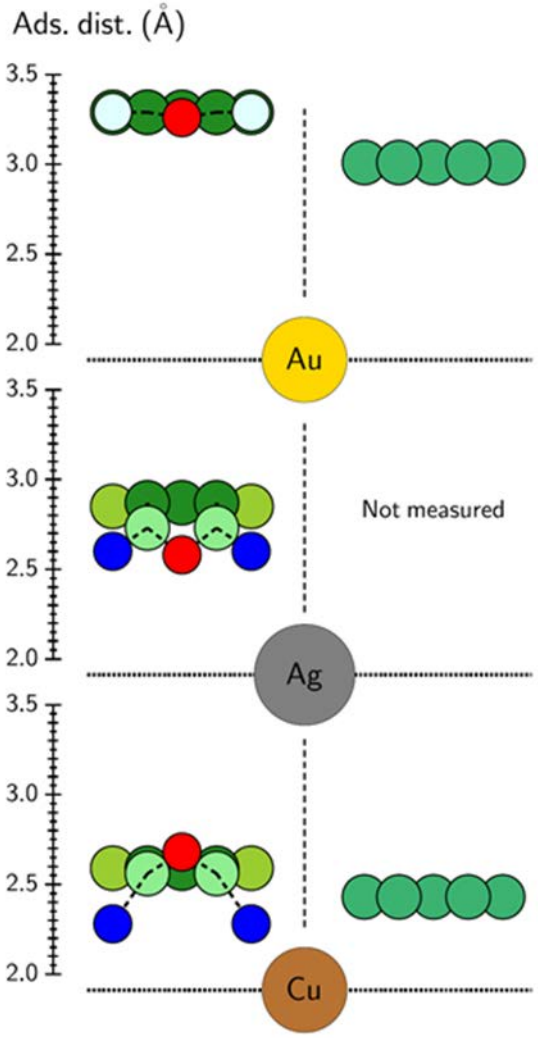


Almost no lateral order in PTCDI monolayers on Cu(111).

Franco-Cañellas, Wang, Broch, Duncan, Thakur, Liu, Kera, Gerlach, Duhm, Schreiber,
Phys. Rev. Materials **1,** 013001 (2017)

PTCDI: UPS and XSW





- physisorption
- large bonding distance

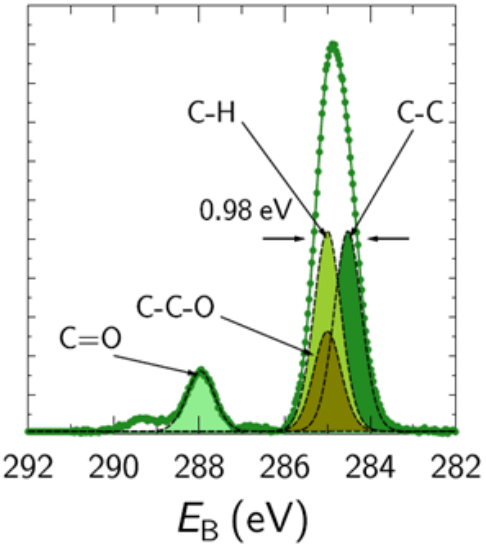
- chemisorption
- O (blue) and N (red) atoms: same bonding distance

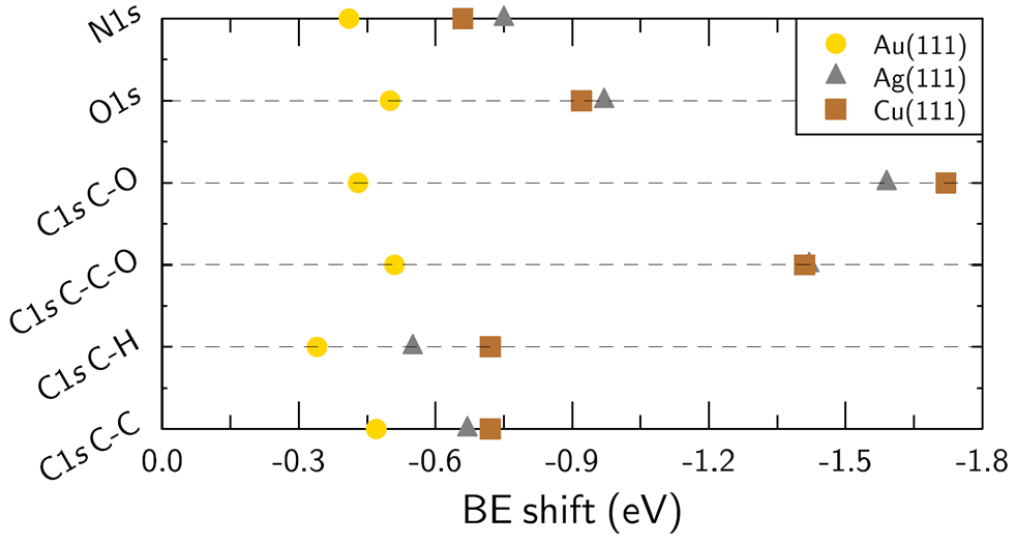
- chemisorption
- O and N atoms: different bonding distances

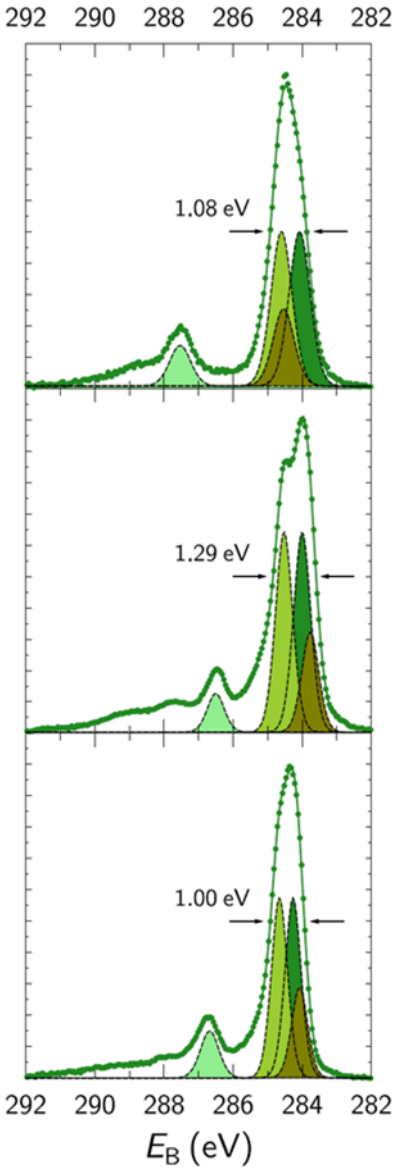
(Adsorption geometry of perylene for comparison.)

Franco-Cañellas, Wang, Broch, Duncan, Thakur, Liu, Kera, Gerlach, Duhm, Schreiber, *Phys. Rev. Materials* **1,** 013001 (2017)

Fingerprints of bonding in core-level spectra







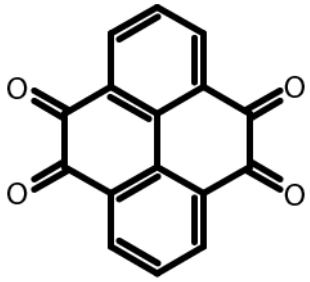
Au(111)

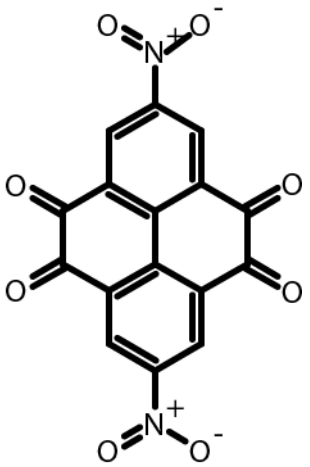
Ag(111)

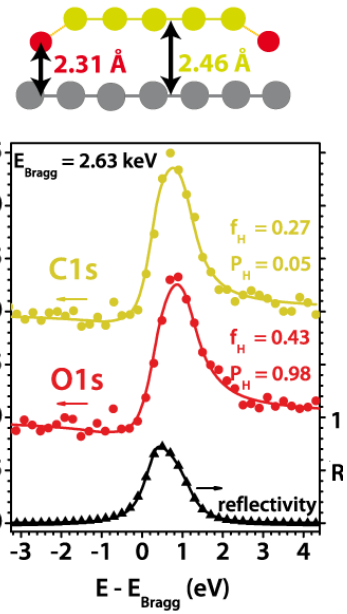
Cu(111)

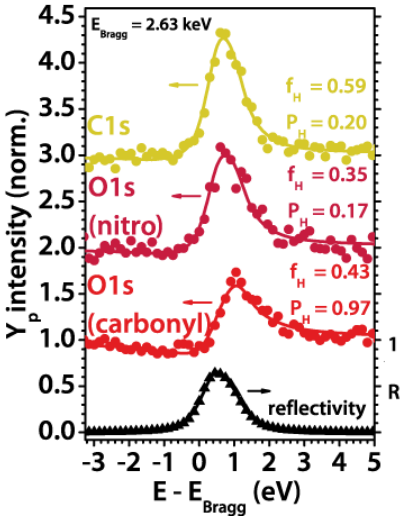
Franco-Cañellas, Wang, Broch, Duncan, Thakur, Liu, Kera, Gerlach, Duhm, Schreiber, *Phys. Rev. Materials* **1,** 013001 (2017)

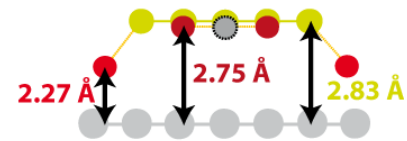
Monstrous work function increase

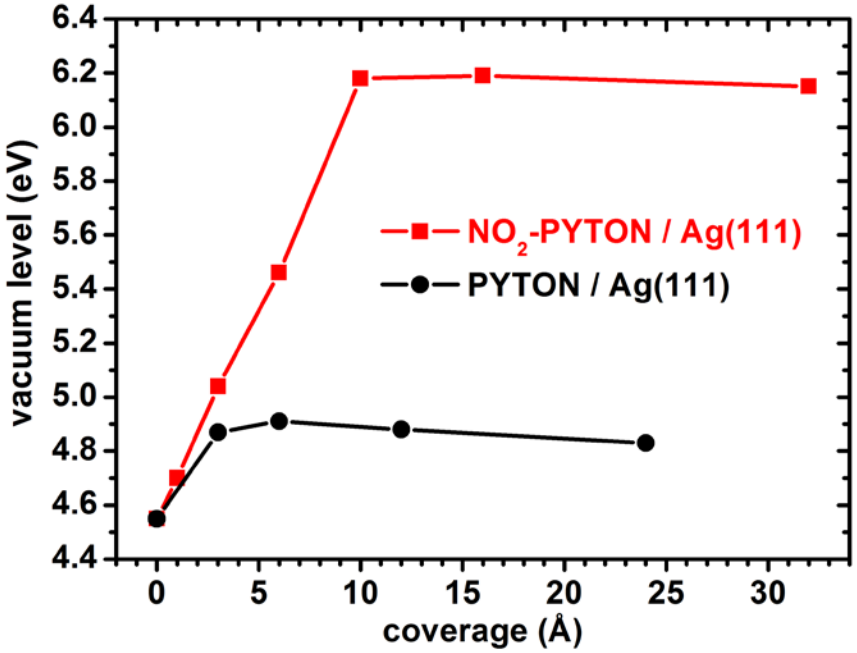








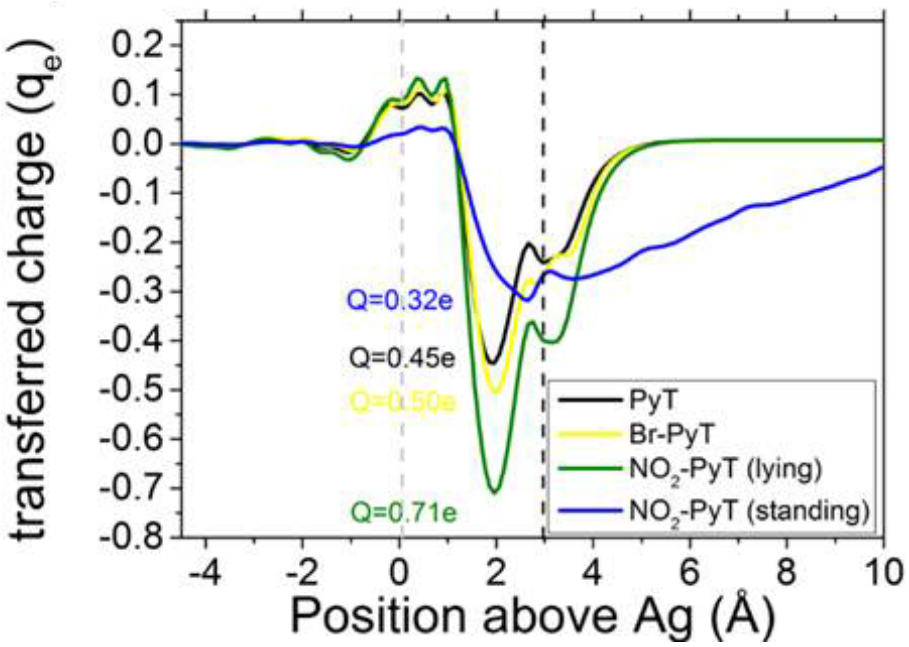


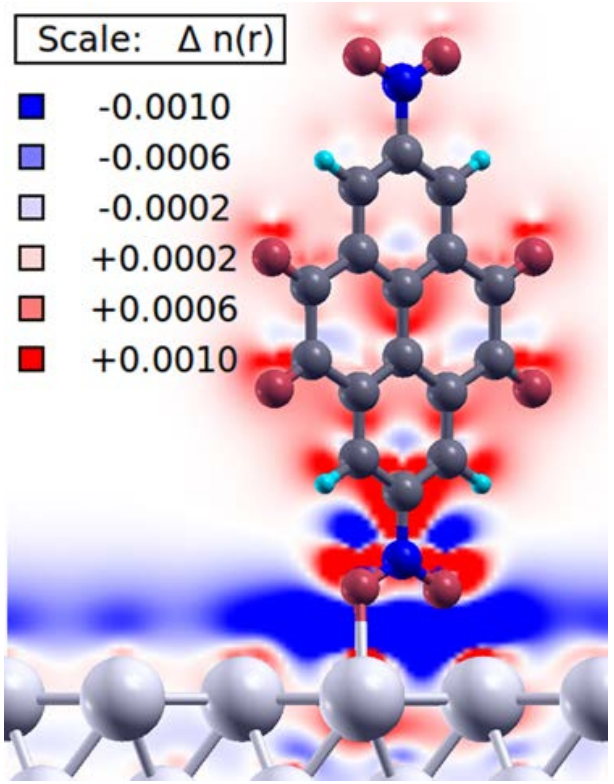


(NO$_2$-)pyrene-tetraone / Ag(111)

Hofmann, Glowatzki, Bürker, Rangger, Bröker, Niederhausen, Hosokai, Salzmann, Blum, Rieger, Vollmer, Rajput, Gerlach, Müllen, Schreiber, Zojer, Koch, Duhm, *J. Phys. Chem. C* in press

Orientational transition



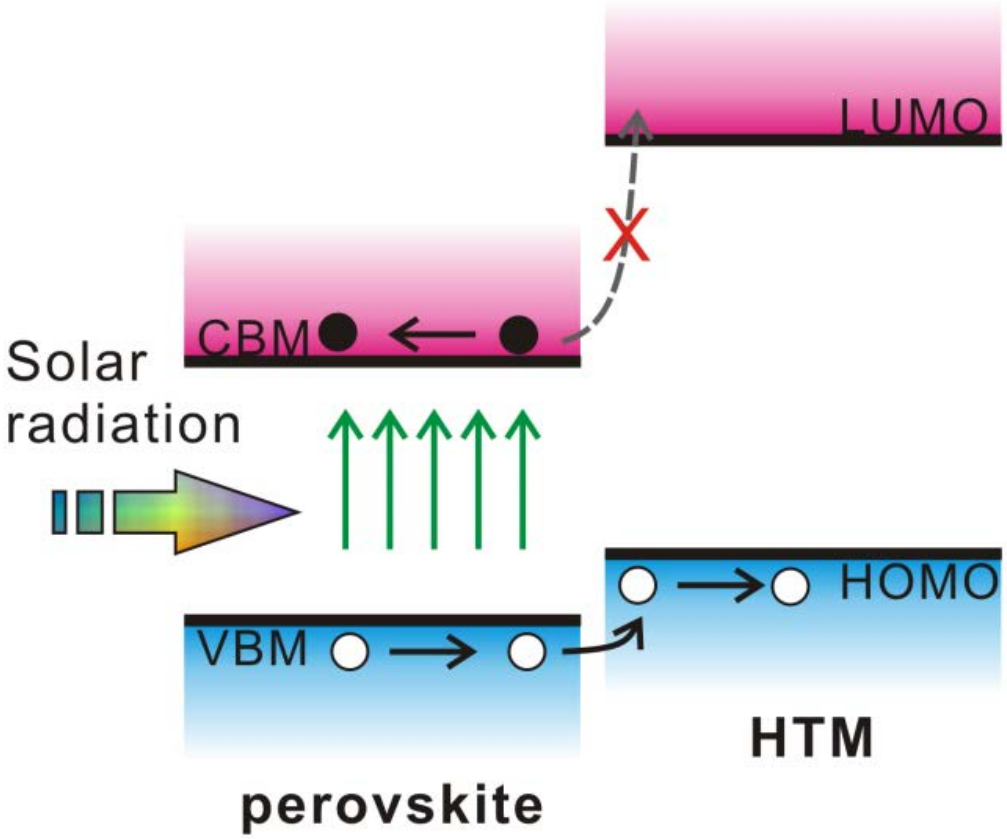


A reorientation from lying to standing NO_2-PYTON in monolayers on Ag(111) decreases the average charge transfer per molecule but increases the work function.

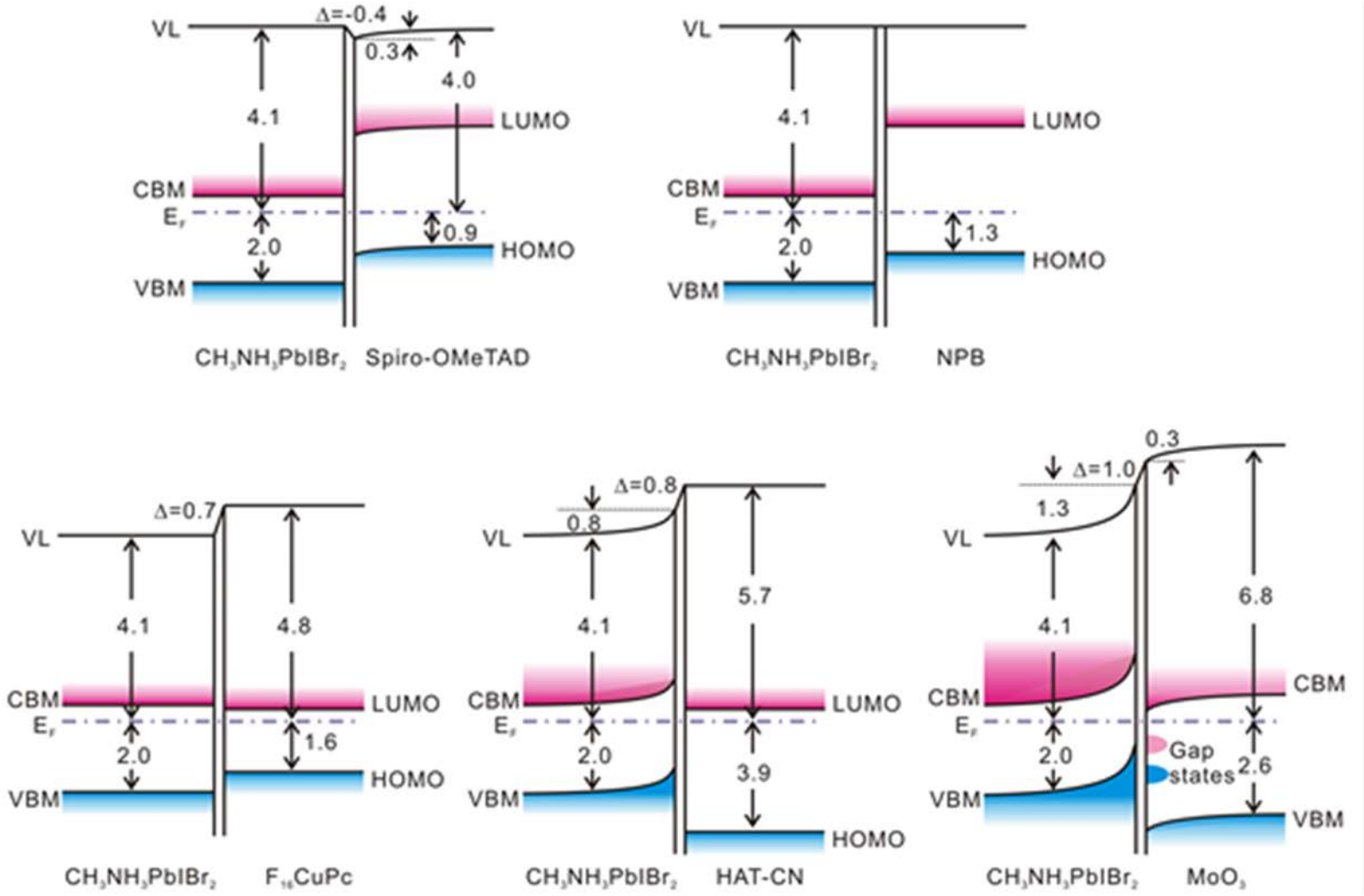
Hofmann, Glowatzki, Bürker, Rangger, Bröker, Niederhausen, Hosokai, Salzmann, Blum, Rieger, Vollmer, Rajput, Gerlach, Müllen, Schreiber, Zojer, Koch, Duhm, *J. Phys. Chem. C* in press

How are these academic interfaces related to Nano and Giga Challenges?

Perovskite solar cell: Energy-level alignment



$CH_3NH_3PbIBr_2$: ELA with OSCs

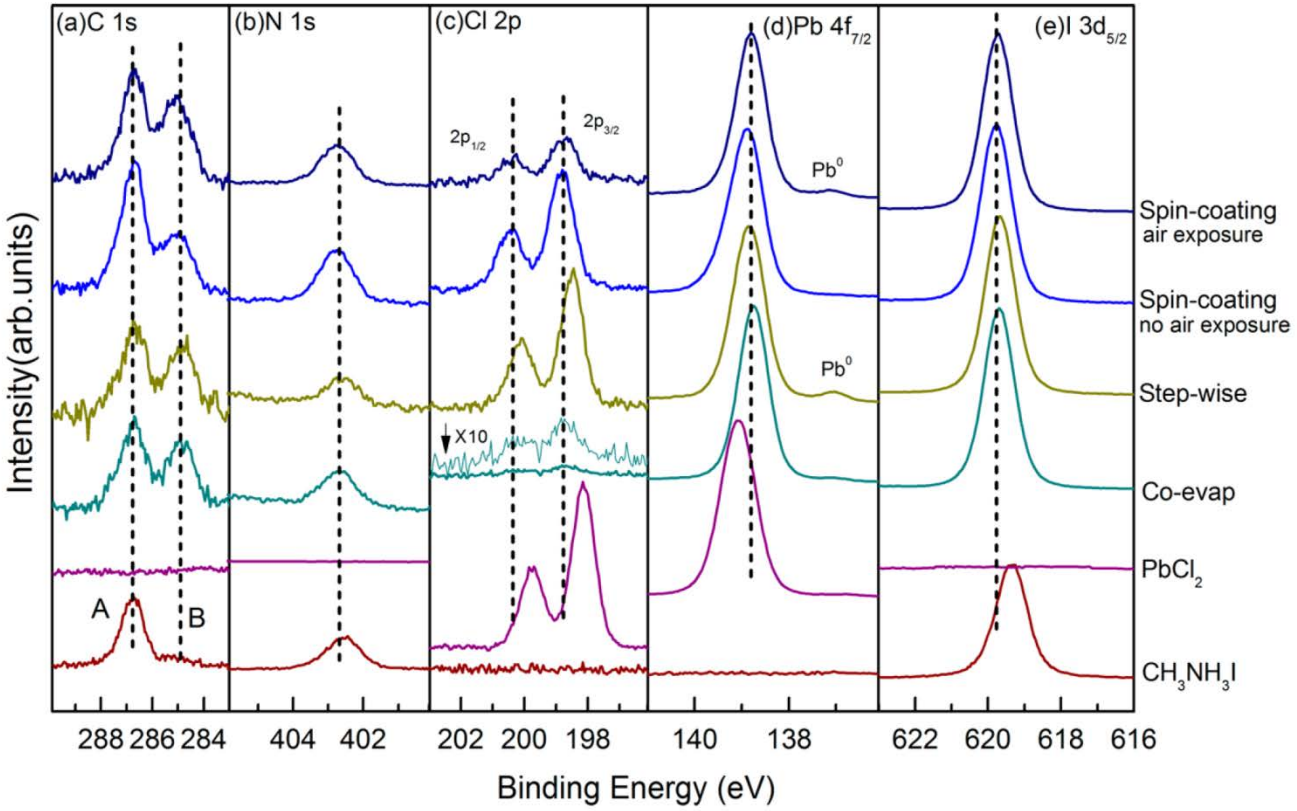


$CH_3NH_3PbIBr_2$ spin-coated on ZnO-coated ITO

Wang, Wang, Shen, Li, Li, Liu, Duhm, Tang, *Adv. Mater. Interfaces* **2**, 1400528 (2015)

Differently fabricated $CH_3NH_3PbI_{3-x}Cl_x$

A: CH_3NH_3
B: CH_3I



C1s, N1s

- same positions
- different relative intensity

➢ cation rearrangement

Cl2p, Pb4f, I3d

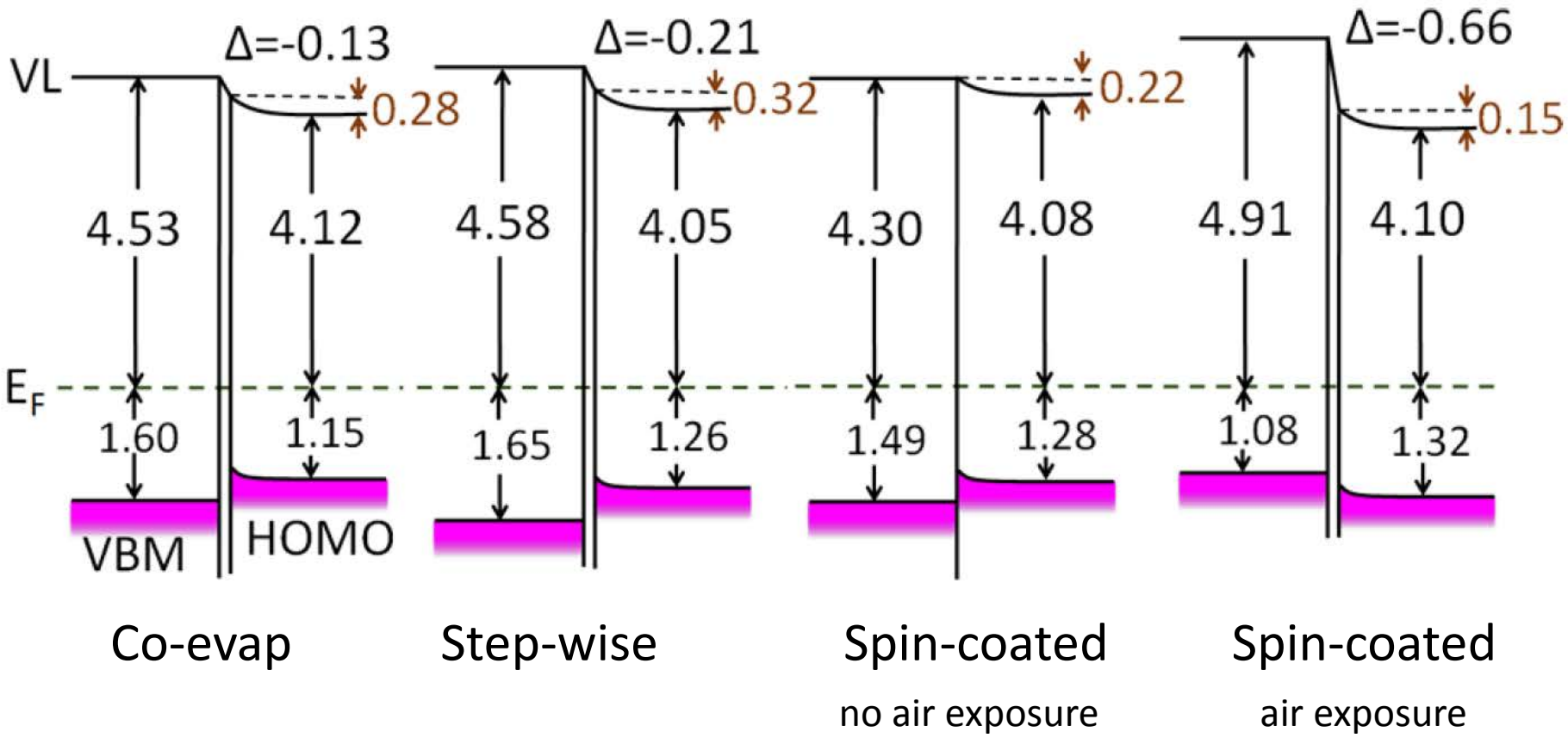
- different positions

➢ interaction between $PbCl_2$ and CH_3NH_3I

➢ step-wise: mixture of perovskite and unreacted $PbCl_2$

Wang, Wu, Hu, Li, Shen, Wang, Liao, Liu, Duhm, *ACS Appl. Mater. Interfaces* **9**, 7859 (2017)

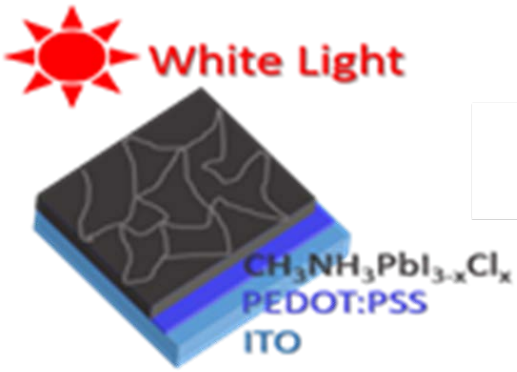
$CH_3NH_3PbI_{3-x}Cl_x$: ELA with NPB

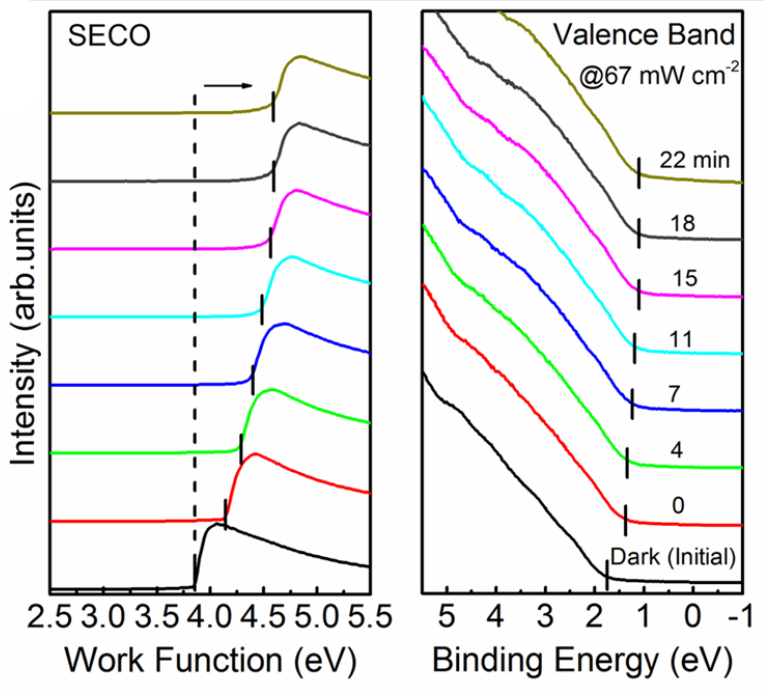


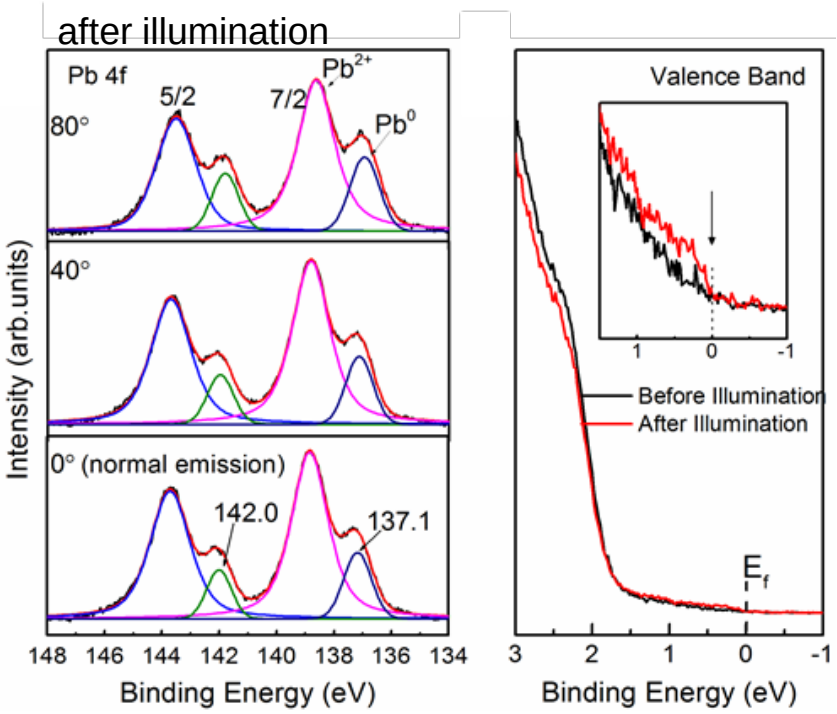
- no band bending on perovskite site.
- almost same band bending on NPB side.
- large interface dipole by air exposure by cation rearrangement.

Wang, Wu, Hu, Li, Shen, Wang, Liao, Liu, Duhm, *ACS Appl. Mater. Interfaces* **9**, 7859 (2017)

Impact of white light illumination (in UHV)



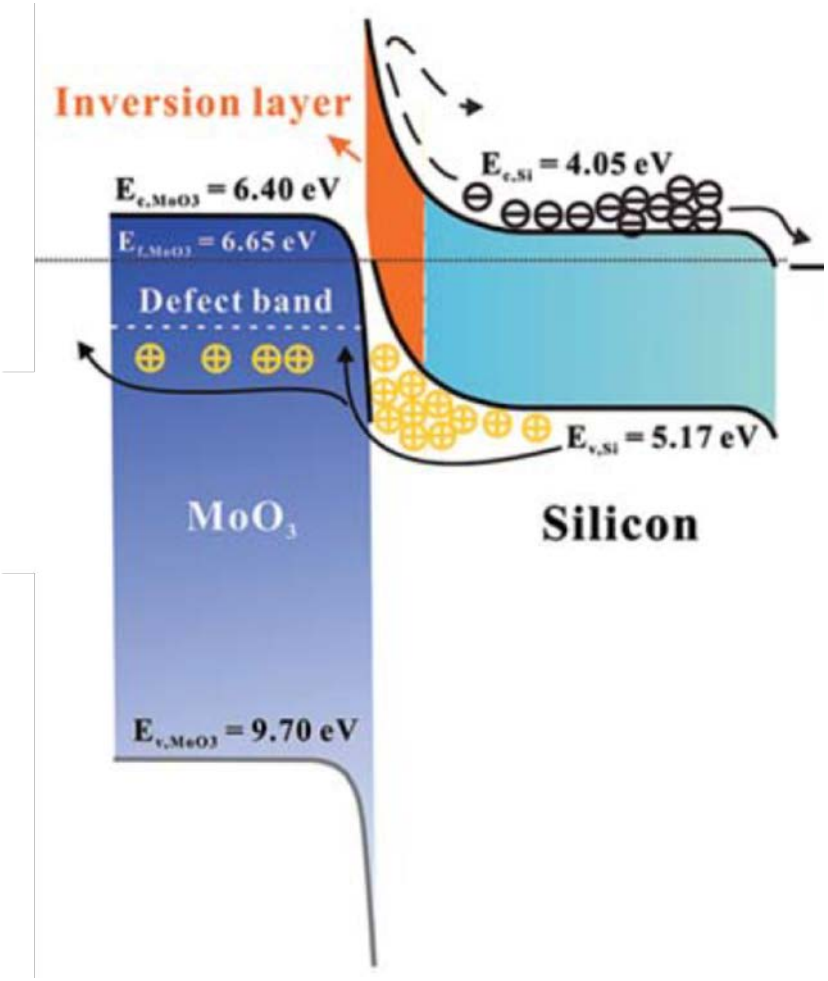




Traps mainly due to metallic lead (Pb^0), which are enriched at the surface.

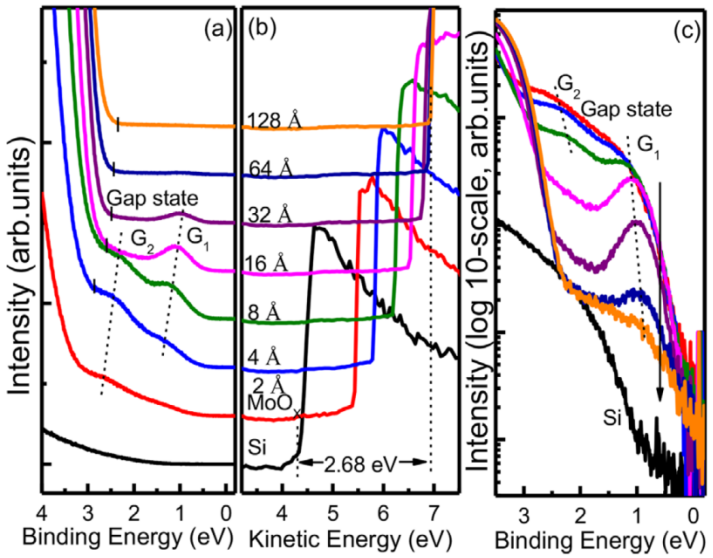
Zu, Amsalem, Salzmann, Wang, Ralaiarisoa, Kowarik, Duhm, Koch,
Adv. Opt. Mater. **5**, 1700139 (2017)

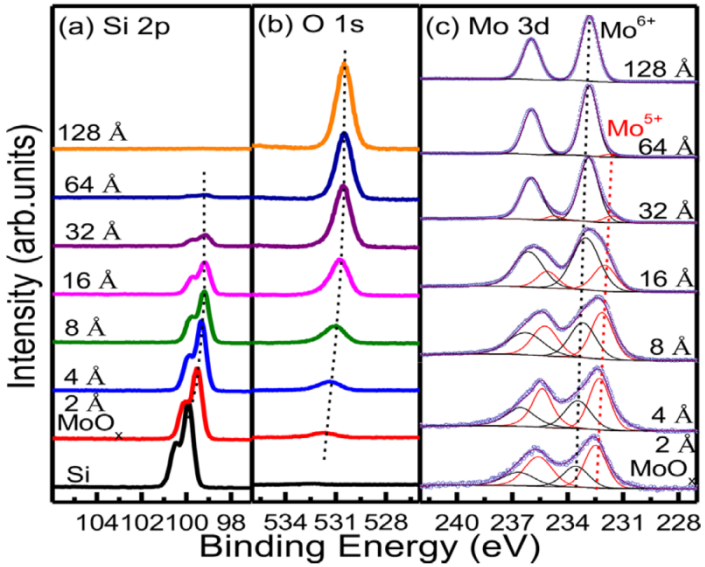
Inversion layers in hybrid devices

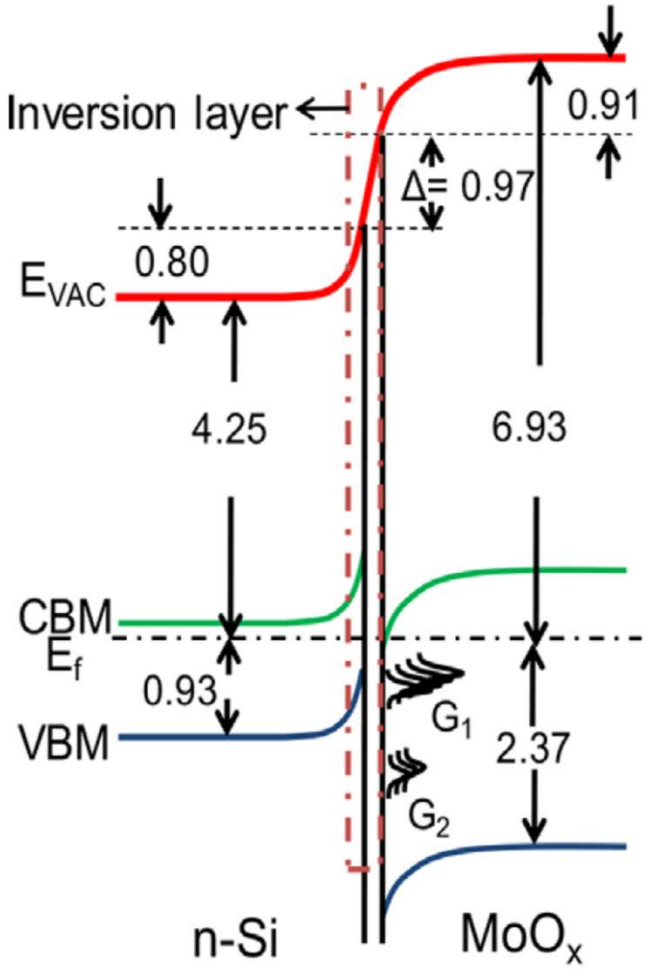


Ding, Zhang, Xia, Wang, Kuang, Duhm, Jie, Zhang, *J. Mater. Chem. A* **5**, 285 (2017)

Inversion layers in n-Si



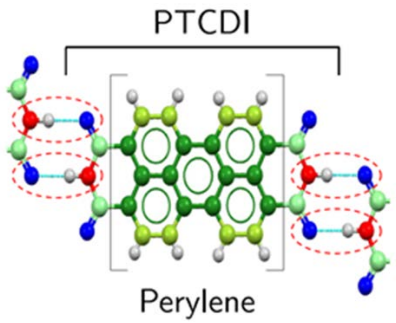


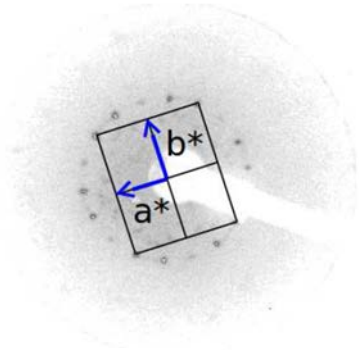


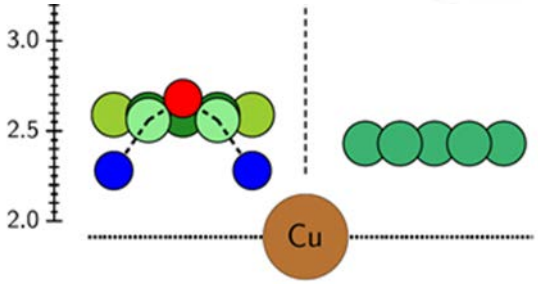
Sun, Wang, Liu, Wu, Zhong, Liu, Wang, Han, Xia, Zou, Song, Koch, Duhm, Sun,
Phys. Status Solidi RRL **11**, 1700107 (2017)

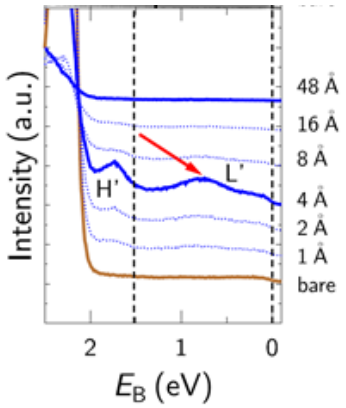
Summary

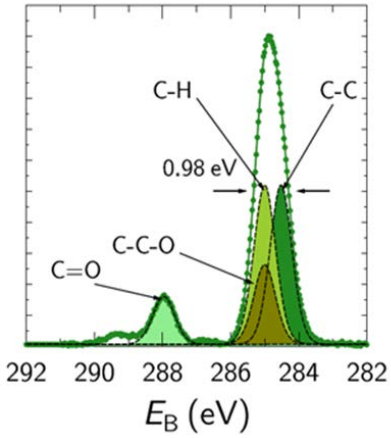
Academic interfaces lead to understanding of device properties.

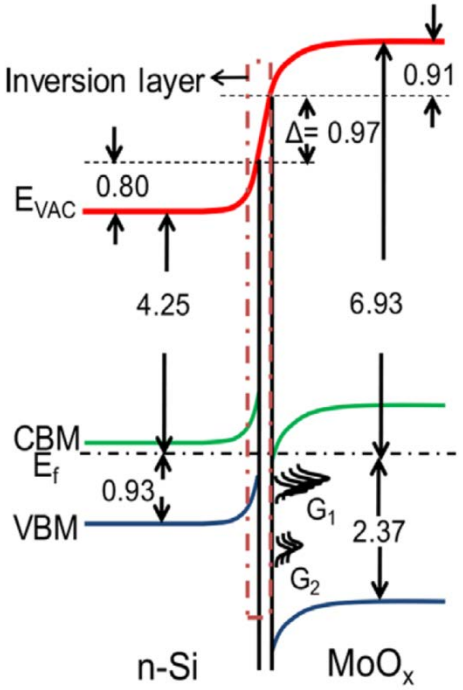












Acknowledgements

Soochow University

Qi Wang
Ao Yang
Rongbin Wang
Lijia Liu

Baoquan Sun
Jiansheng Jie
Jianxin Tang
Jian Fan

Diamond

Tien-Lin Lee

ESRF

Jörg Zegenhagen

Universität Tübingen

Alexander Gerlach
Frank Schreiber

Graz University of Technology

Oliver Hofmann
Egbert Zojer

Institute for Molecular Science

Satoshi Kera