HZB Helmholtz Zentrum Berlin

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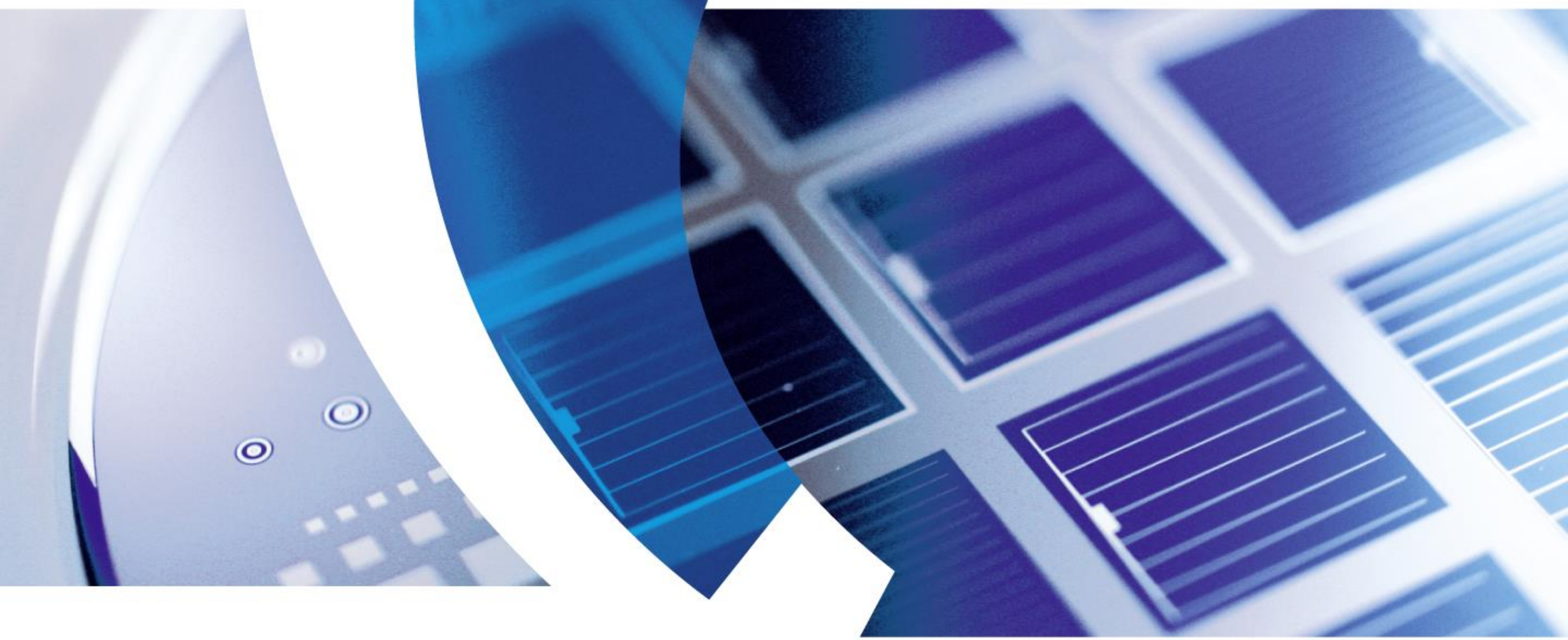

EMIL - Experimental Capabilities of the Energy Materials In-Situ Laboratory

Acknowledgements

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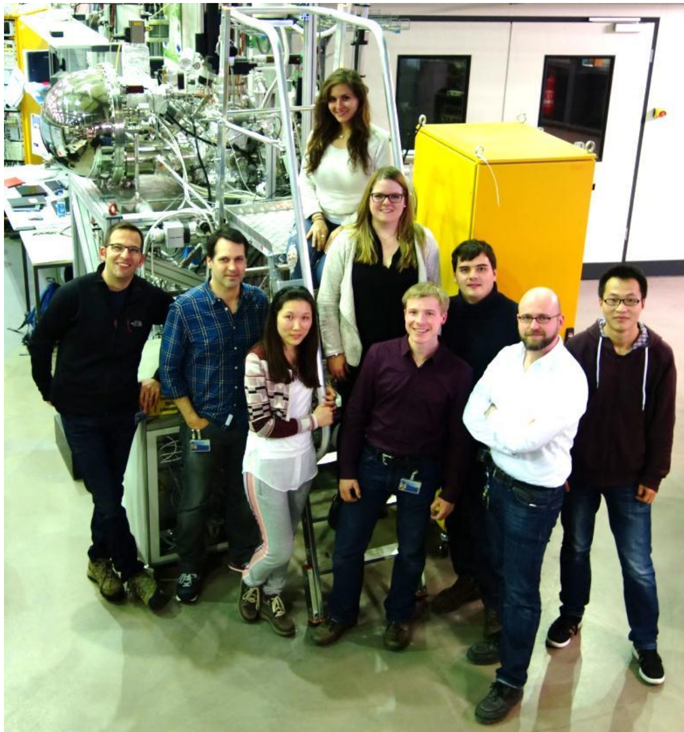


- Dr. Regan G. Wilks
- Dr. Roberto Félix-Duarte
- Dr. Raul Garcia Diez
- **Dr. Evelyn Handick**
- Dr. Xeniya Kozina
- Dr. Thomas Kunze
- (**Dr. David Starr**)
- Ting Xiao
- Penghui Yang
- **Claudia Hartmann**
- Jakob Bombsch
- Andreas Siebert
- Dongyang Liu

HELMHOLTZ | ASSOCIATION

Impuls- und Vernetzungsfonds for support of the
Helmholtz-University Young Investigator Group

Open questions in energy materials research

Chemical/electronic structure?

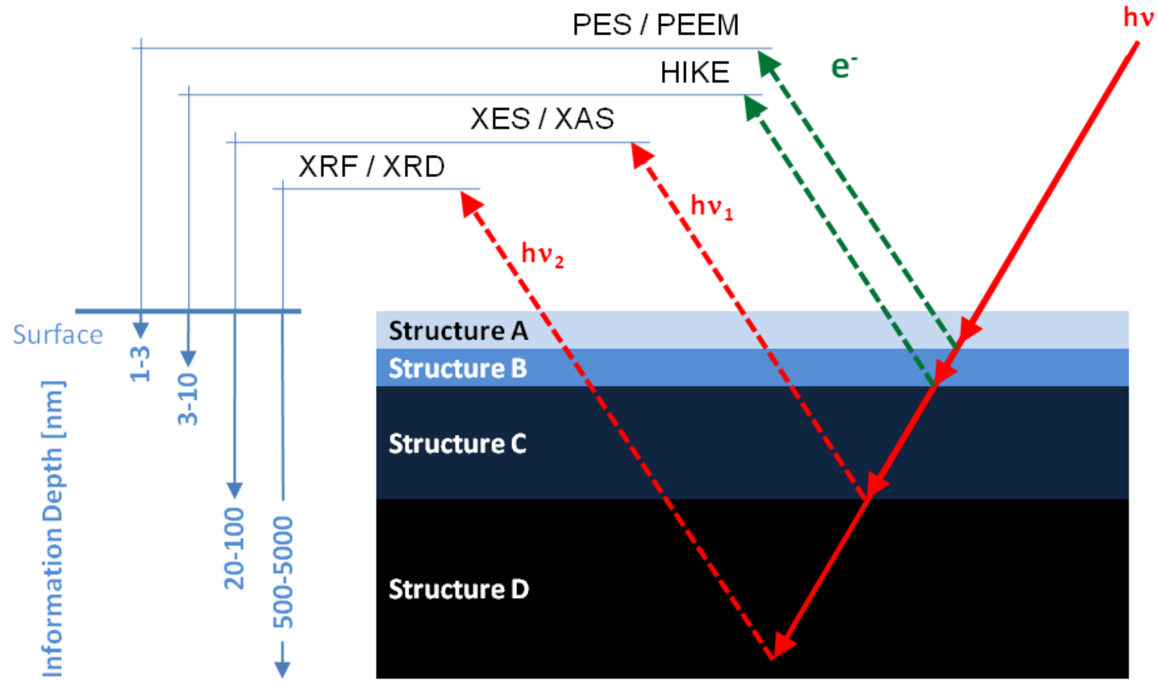
Band alignment?

Compound formation?

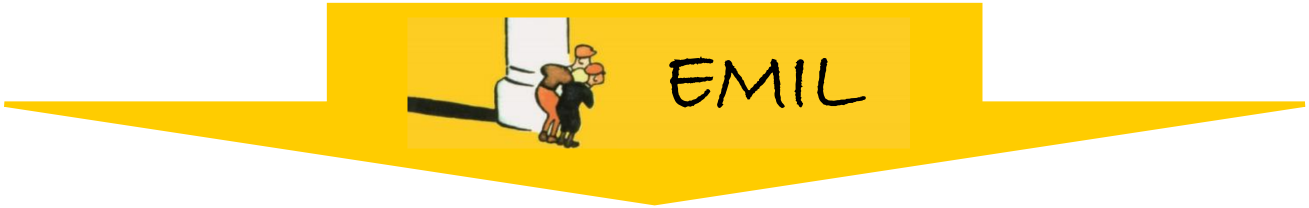
Stability?

Charge carrier separation/transport?

Secondary phases?

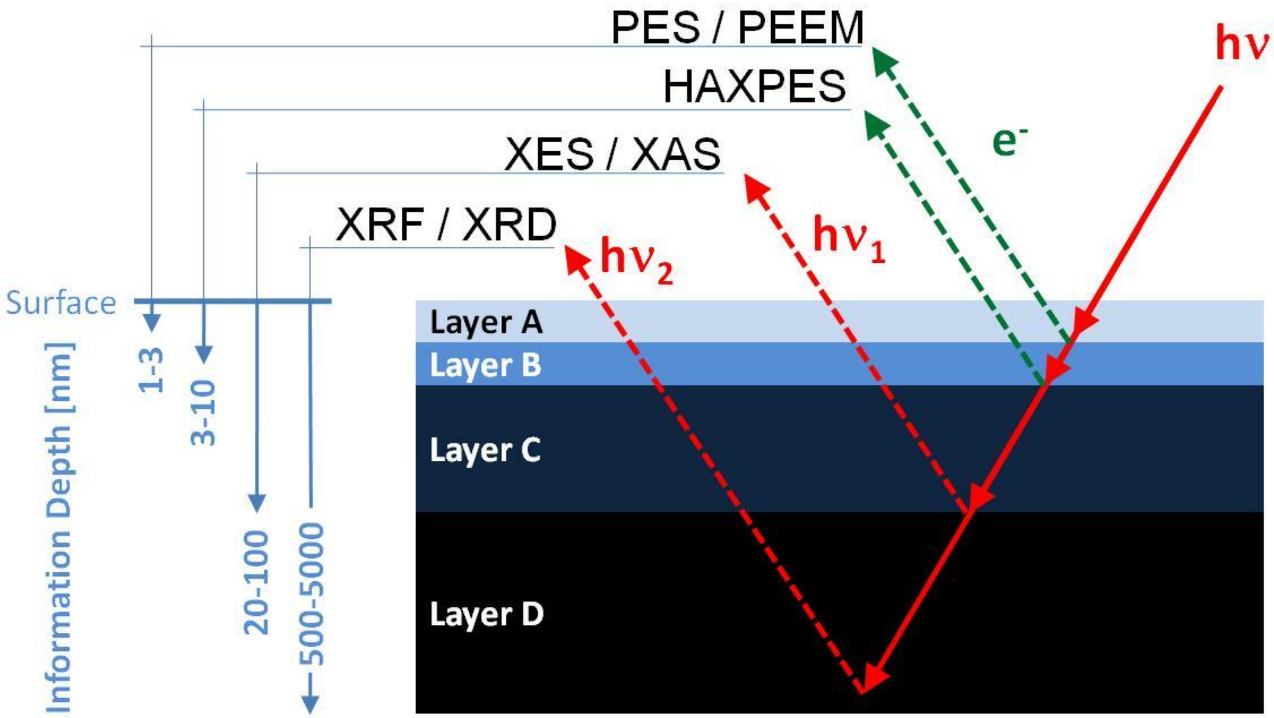


advanced analytics (permanent access & “two color” beamline)
& deposition tools (industry-scale & connected via UHV transfer)



Uniquely suited for tomorrow’s energy materials research!

X-Ray Spectroscopy @EMIL

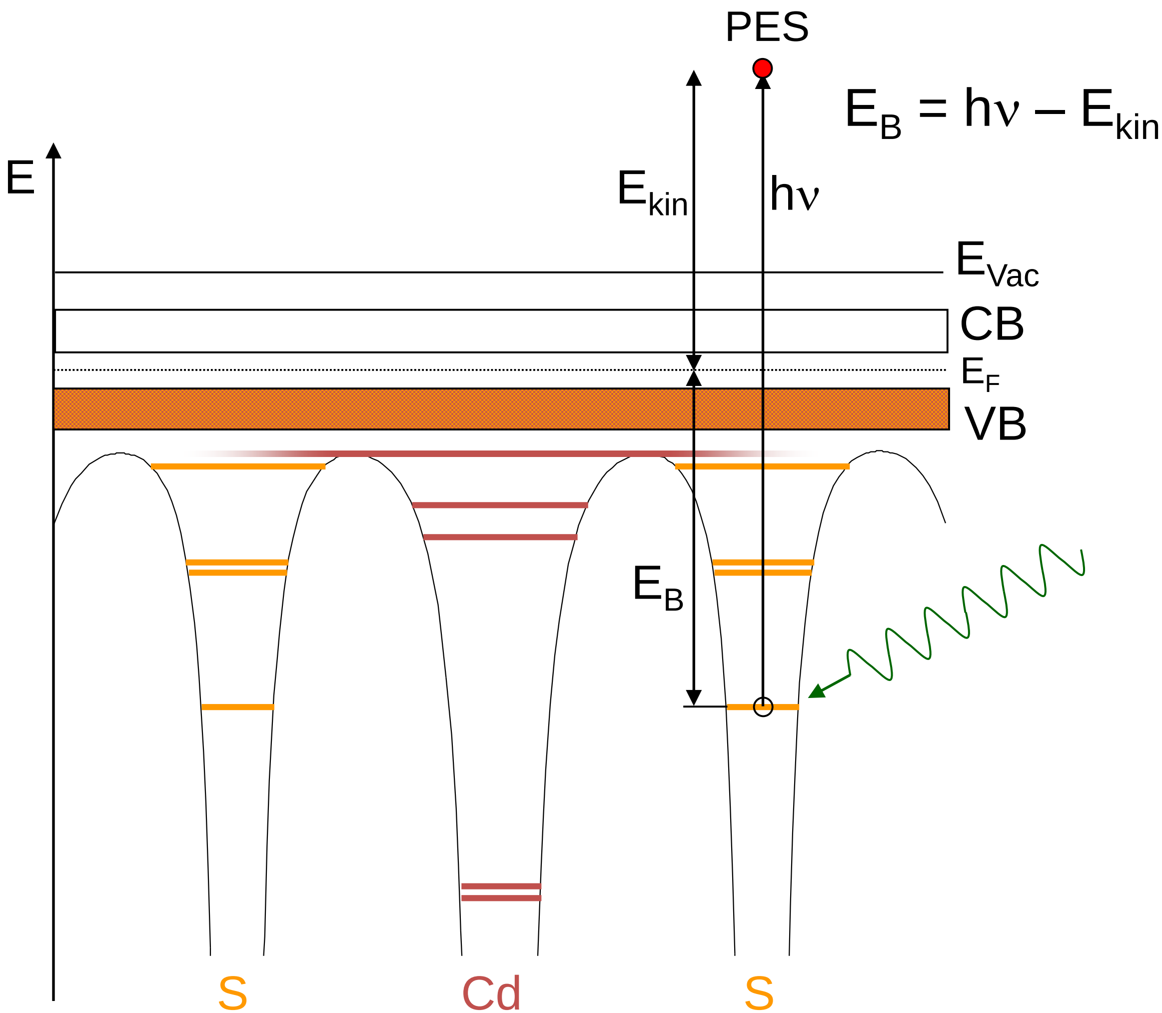


PES – Photoelectron spectroscopy
PEEM – Photoemission electron microscopy
HAXPES – Hard X-ray PES

XES – X-ray emission spectroscopy
XAS –X-ray absorption spec.
XRF – X-ray fluorescence spec.
XRD – X-ray diffraction spec.

Wide X-ray energy range needed (80 eV - 10keV)

Photoelectron Spectroscopy (PES): Principle



<u>X-ray PES (XPS, ESCA) + AES:</u>

$h\nu \sim 100 - 1500$ eV

- Core levels
- Composition of surface
- Chemical species

Courtesy of L. Weinhardt

Experimental Setup

<u>Excitation source:</u>

X-ray tube:

Mg K_α (~1254 eV)

Al K_α (~1486 eV)

UV-lamp:

He I (21.2 eV)

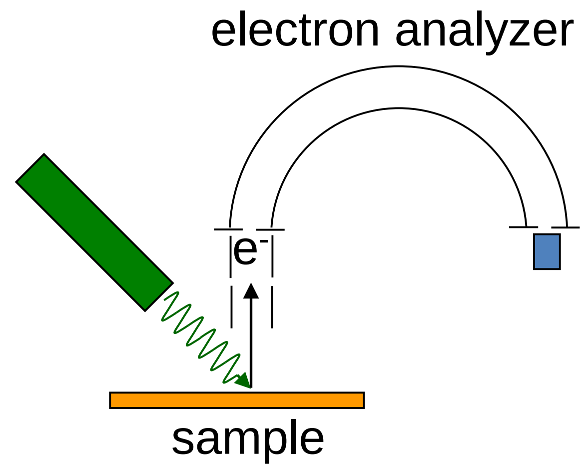
He II (40.8 eV)

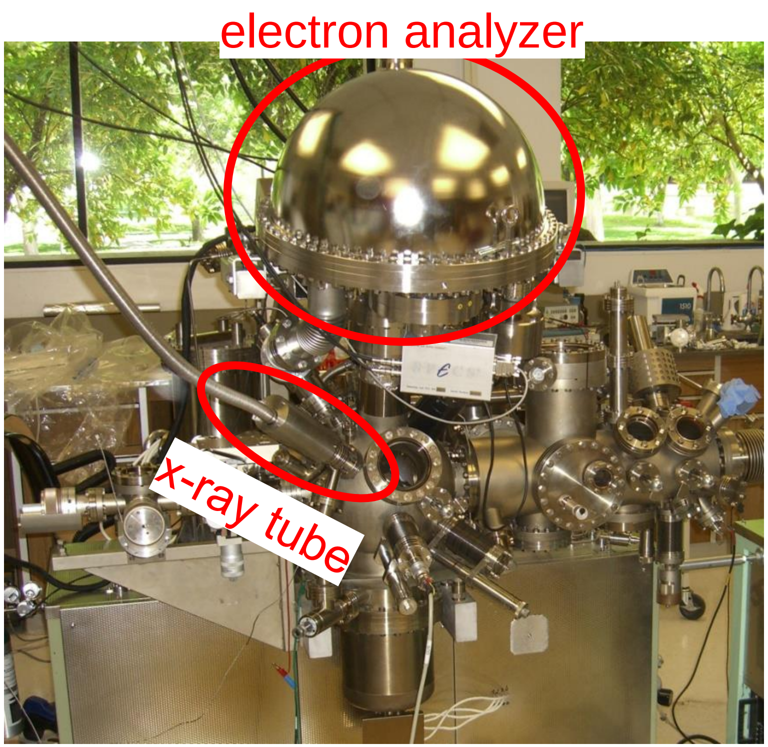
Ne I (16.7 eV)

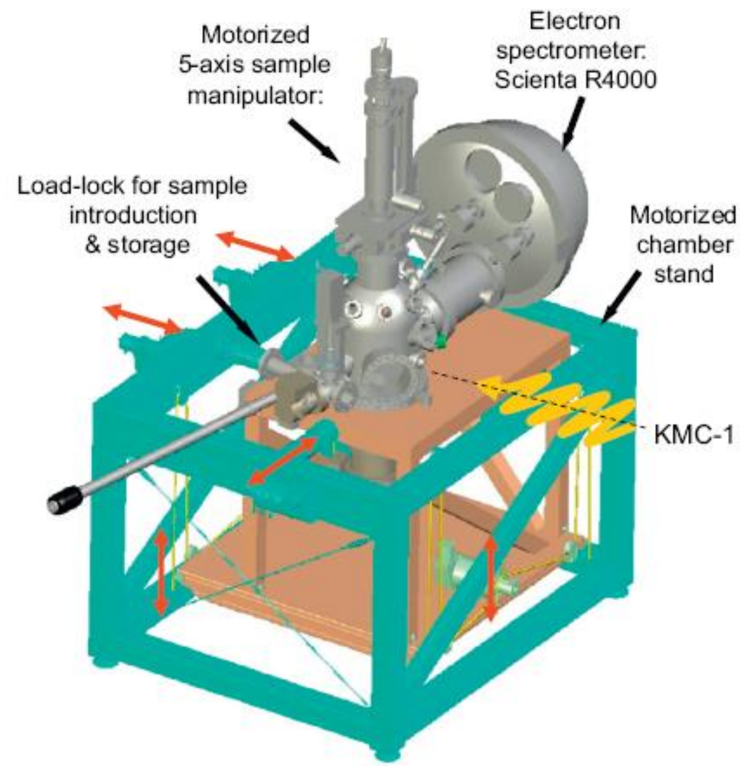
Ar I (11.7 eV)

Synchrotron:

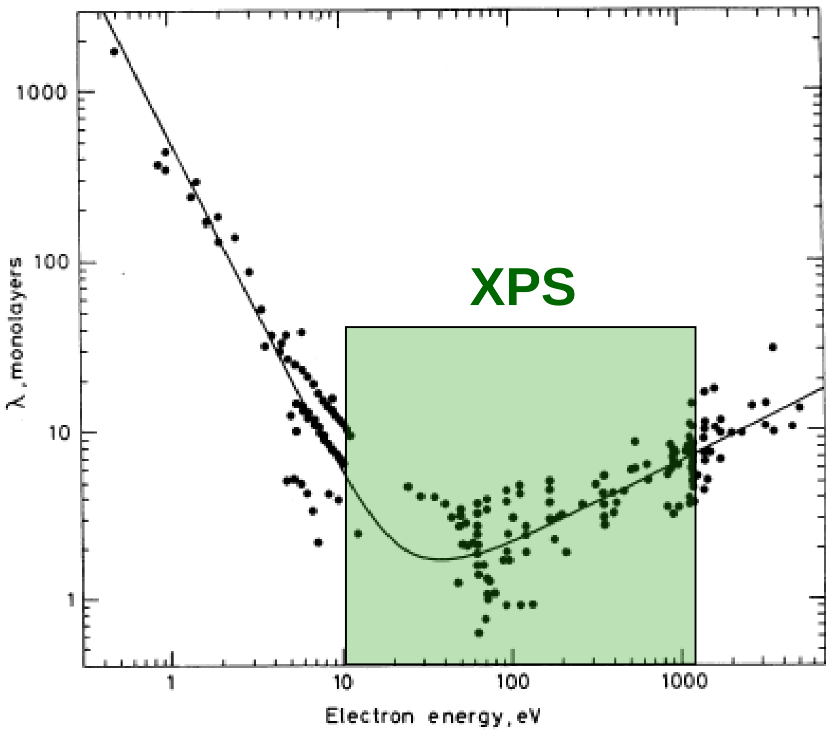
10 - 15.000 eV







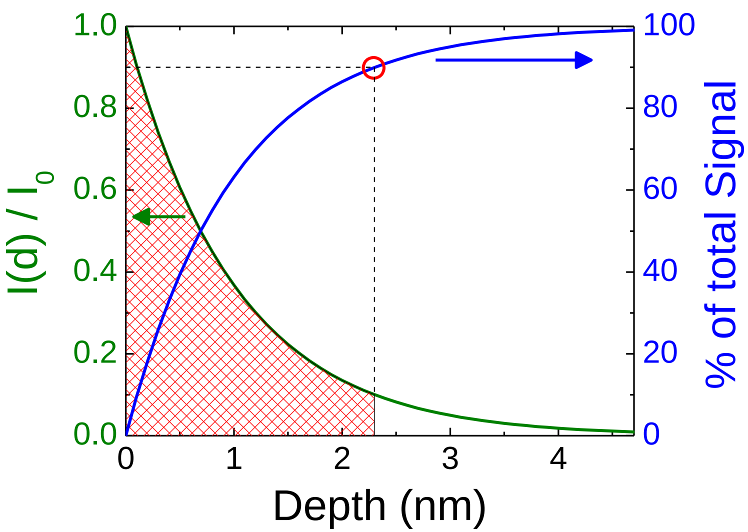
PES: Surface Sensitivity



D. Briggs, M.P. Seah, “Practical Surface Analysis“ (1990)

$$I(d) = I_0 \cdot e^{-d/\lambda}$$

λ: inelastic mean free path

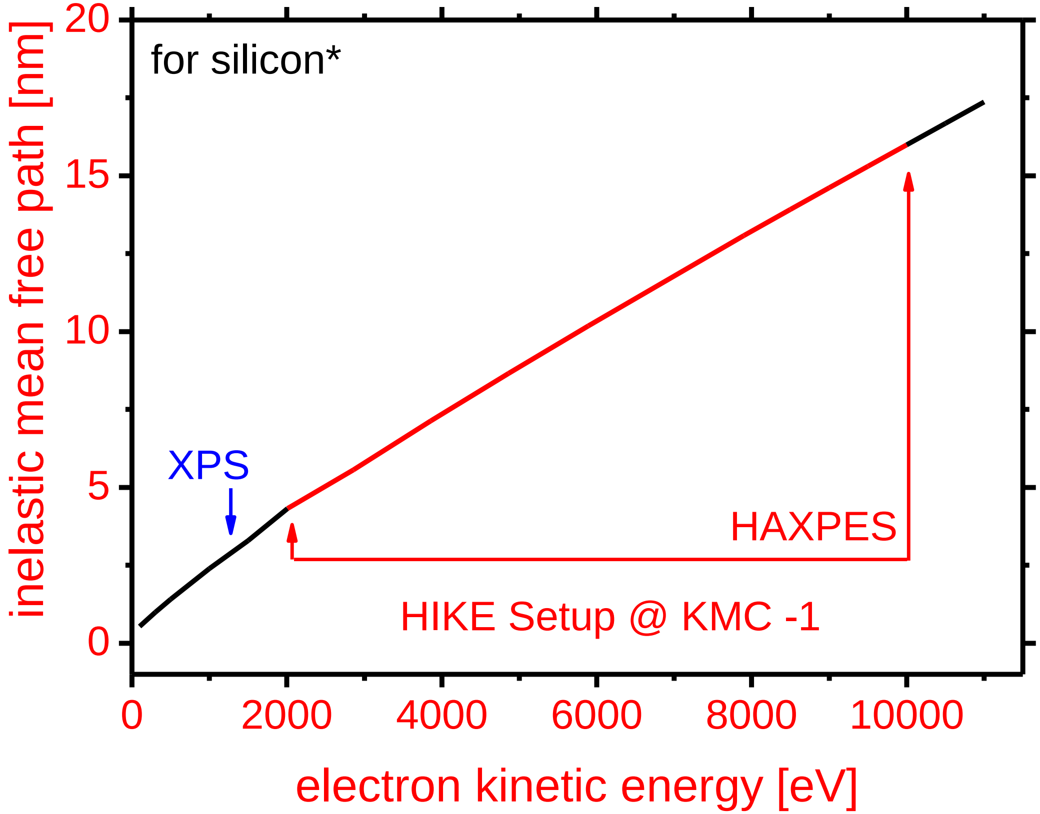


Values can be obtained from:

S. Tanuma et al., Surf. Interf. Anal.,Vol. 21, 165 (1993)
http://www.quases.com/frames/samples_and_downloads.htm

Courtesy of L. Weinhardt

XPS vs. HAXPES: PROBING DEPTH



Probing depth is governed by:

XPS: Inelastic mean free path (a few Å)

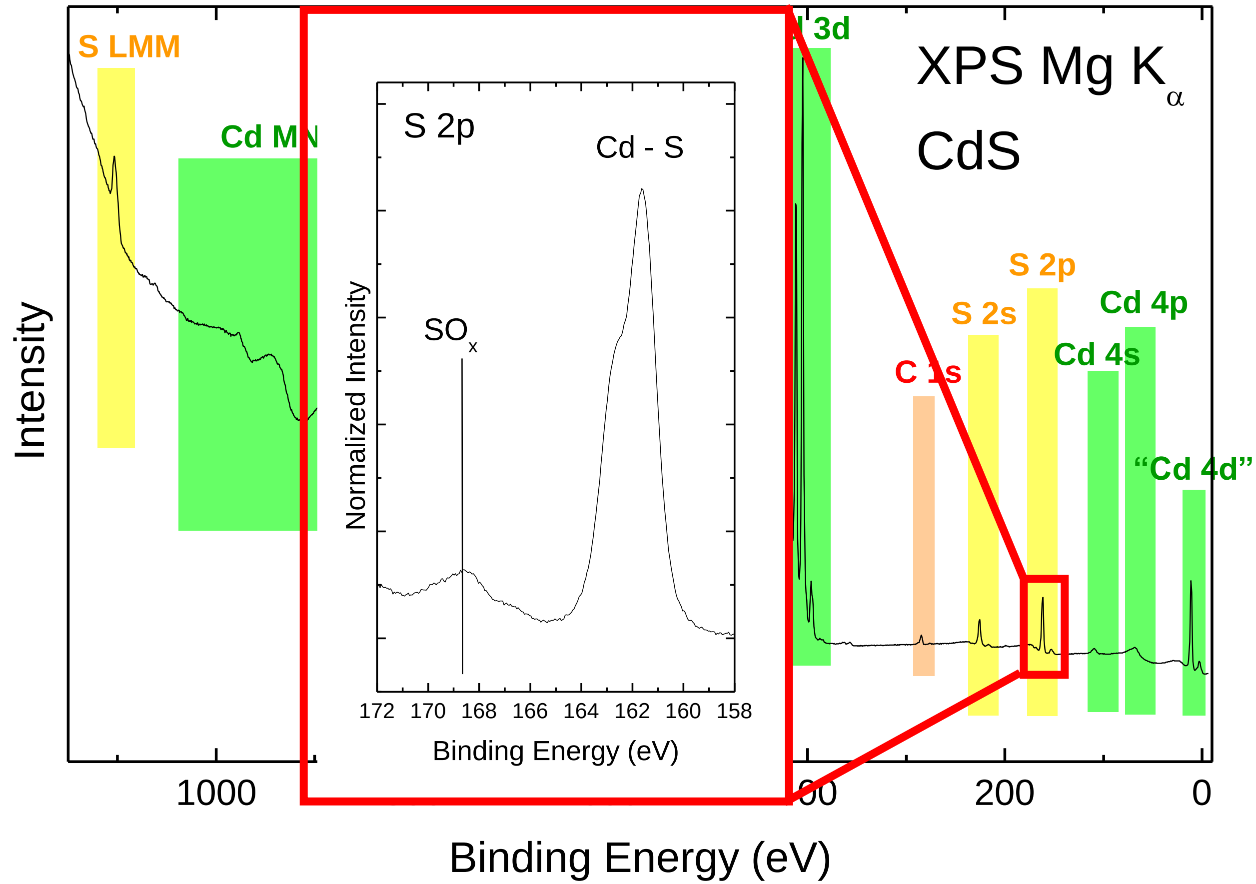
HAXPES: Inelastic mean free path (several nm to a few 10 nm)

according to:

$$I = I_0 \exp(-x/\lambda)$$

*based on
S. Tanuma, C. J. Powell, D. R. Penn, Surf. Interf. Anal. **21**, 165 (1993).

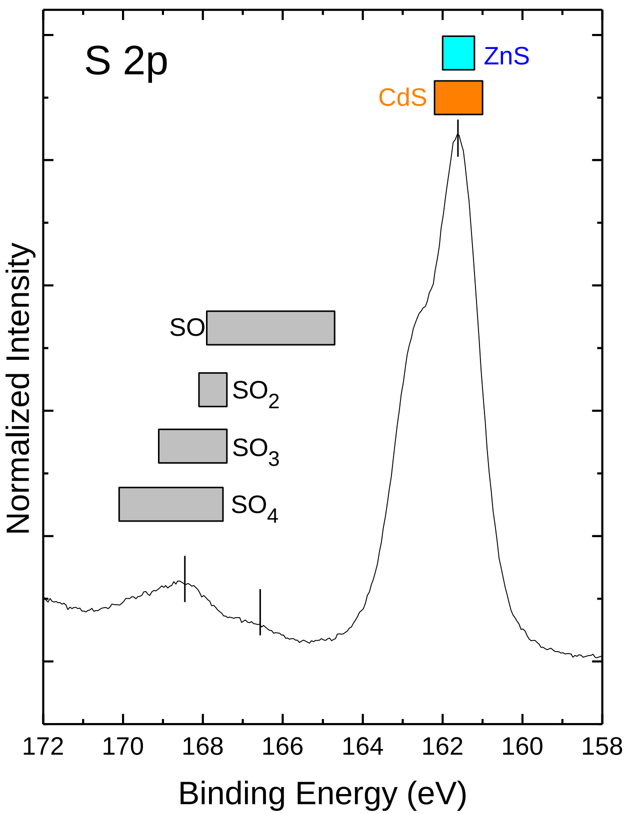
(HA)XP(E)S: Qualitative Information



XPS gives information about elements at surface and chemical compounds (chemical shift)

Courtesy of L. Weinhardt

(HA)XP(E)S (+AES): Chemical shifts



- Energy positions of core levels and Auger lines shift for different chemical compounds
- But: determination of chemical compound typically needs more than just one line position!
- To eliminate effects of band bending and charging the use of the Modified Auger Parameter can be used:

$$\alpha^* = \alpha + h\nu = E_{kin}^{Auger} + E_B^{PES}$$

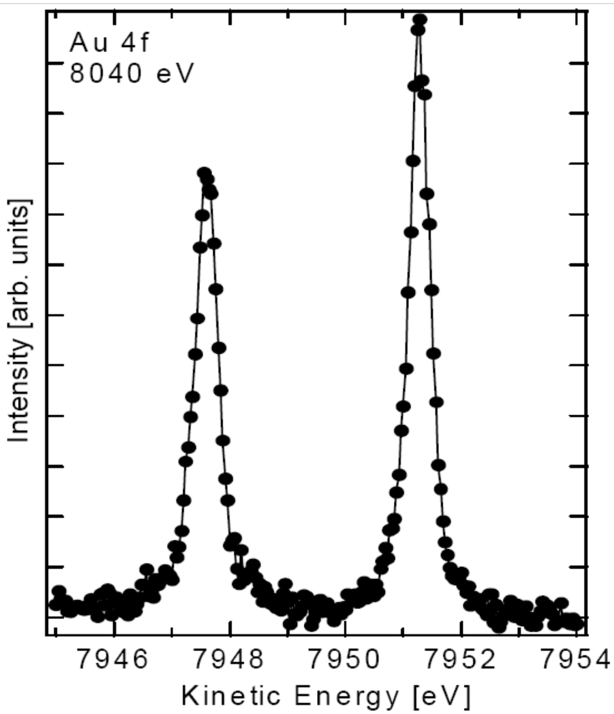
Cd	3d5/2	CdO	404	Click
Cd	3d5/2	CdO	404.2	Click
Cd	3d5/2	CdCr0.3In1.7S4	405.4	Click
Cd	3d5/2	CdCr0.3In1.7S4	405.4	Click
Cd	3d5/2	CdS	405.4	Click
Cd	3d5/2	CdS	405.2	Click
Cd	3d5/2	CdS	405.3	Click
Cd	3d5/2	CdS	405.5	Click
Cd	3d5/2	CdS	405.1	Click
Cd	3d5/2	CdS	405.3	Click
Cd	3d5/2	CdS	405.4	Click
Cd	3d5/2	CdSe	405.3	Click
Cd	3d5/2	CdSe	405	Click
Cd	3d5/2	Ba/Ca/Cd/Sr/in_montmorillonite	406.4	Click

http://srdata.nist.gov/xps/

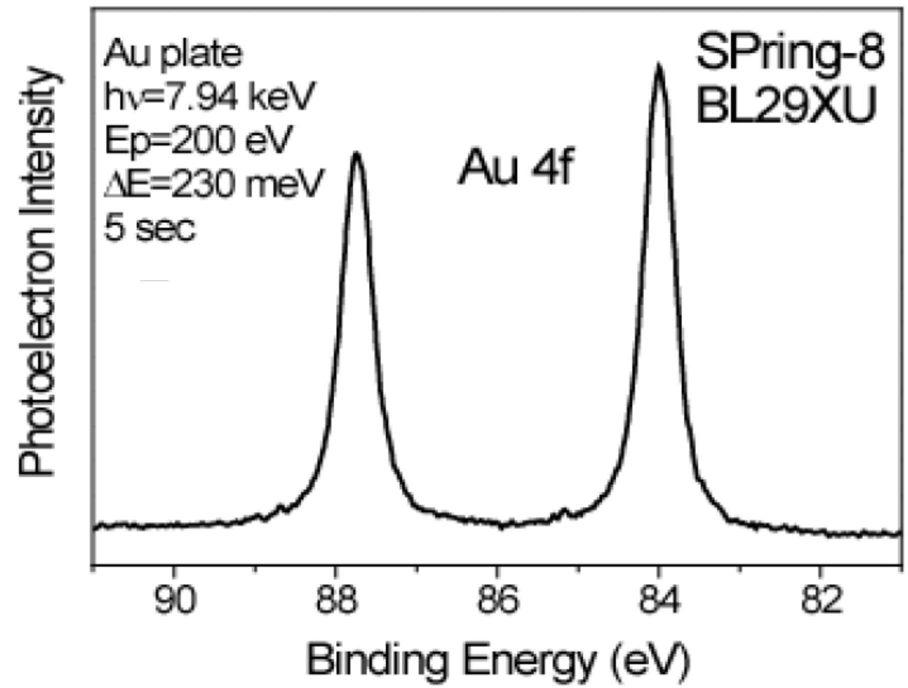
Courtesy of L. Weinhardt

HAXPES: Current state-of-the-art

M. Gorgoi et al, The European Physical Journal **169**, 227 (2009).



Courtesy of Y. Takata



HIKE: 7200s

SPring-8: 5s

- Hard x-ray EMIL beamline (w/ cryogenic undulator) is expected to provide higher flux than current HIKE beamline

XPS: Quantification

Element

Line (e.g. 2p)

Layer thickness

$$I \propto \sigma(Z, N, h\nu) \cdot T(E_{kin}) \cdot L(\gamma, N) \cdot \int_0^d \boxed{c(Z,x)} \cdot e^{-x\cos\theta/\lambda(E_{kin})} dx$$

$\sigma(Z, N, h\nu)$: Photoionization cross section

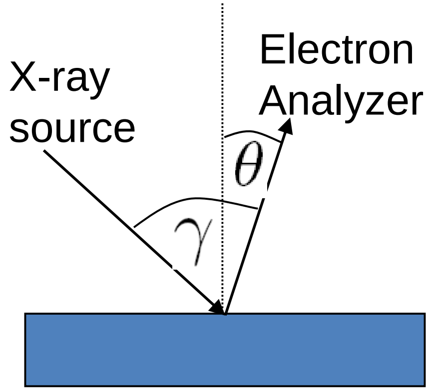
e.g. from Yeh and Lindau, Atomic Data and Nuclear Data Tables **32** (1985)

$T(E_{kin})$: Electron Analyzer Transmission

$L(\gamma, N) = 1 + \frac{1}{2}\beta(N)\left(\frac{3}{2}\sin^2\gamma - 1\right)$: angular asymmetry factor (=1 for "Magic Angle" of 54.7°)

$\lambda(E_{kin})$: inelastic mean free path (of the electrons)

$c(Z, x)$: concentration of element Z



Homogeneous layer, d $\rightarrow \infty$, $\theta = 0$:

$$\frac{c(A)}{c(B)} = \frac{I(A)}{I(B)} \cdot \frac{\sigma_B \cdot T_B \cdot \lambda_B}{\sigma_A \cdot T_A \cdot \lambda_A}$$

XPS: Quantification

Element

Line (e.g. 2p)

Layer thickness

$$I \propto \sigma(Z, N, h\nu) \cdot T(E_{kin}) \cdot L(\gamma, N) \cdot \int_0^d \boxed{c(Z, x)} \cdot e^{-x\cos\theta/\lambda(E_{kin})} dx$$

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J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. **8**, 129 (1976).

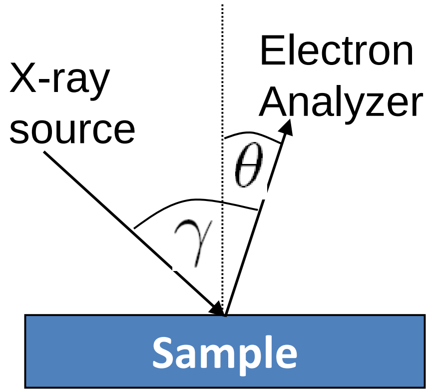
$T(E_{kin})$: Electron Analyzer Transmission

-> similar for similar kinetic energies

$L(\gamma, N) = 1 + \frac{1}{2}\beta(N)\left(\frac{3}{2}\sin^2\gamma - 1\right)$: angular asymmetry factor **(=1 for "Magic Angle" of 54.7°)**

$\lambda(E_{kin})$: inelastic mean free path „IMFP“ (of the electrons)

-> similar for similar kinetic energies



$c(Z, x)$: concentration of element Z

Homogeneous layer, d $\rightarrow \infty$, $\theta = 0$:

$$\boxed{\frac{c(A)}{c(B)} = \frac{I(A)}{I(B)} \cdot \frac{\sigma_B}{\sigma_A}}$$

XPS: Quantification

Element

Line (e.g. 2p)

Layer thickness

$$I \propto \sigma(Z, N, h\nu) \cdot T(E_{kin}) \cdot L(\gamma, N) \cdot \int_0^d c(Z, x) \cdot e^{-x\cos\theta/\lambda(E_{kin})} dx$$

$\sigma(Z, N, h\nu)$: Photoionization cross section

-> same for one photoemission line.

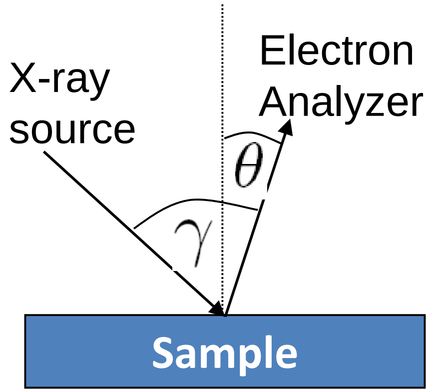
$T(E_{kin})$: Electron Analyzer Transmission

-> same for one photoemission line

$L(\gamma, N) = 1 + \frac{1}{2}\beta(N)\left(\frac{3}{2}\sin^2\gamma - 1\right)$: angular asymmetry factor **-> same for one photoemission line**

$\lambda(E_{kin})$: inelastic mean free path „IMFP“ (of the electrons)

-> same for one photoemission line

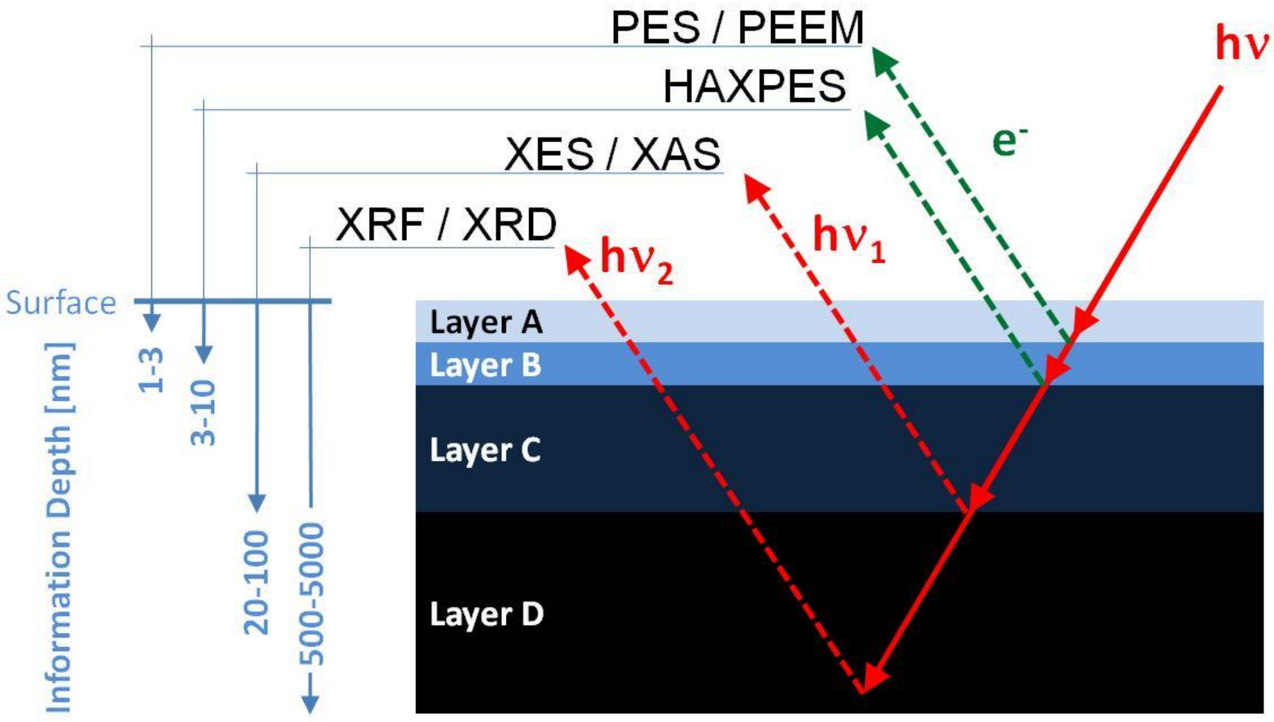


$c(Z, x)$: concentration of element Z

Homogeneous layer, d → ∞, θ = 0 :

$$\frac{c(A)}{c(B)} = \frac{I(A)}{I(B)}$$

X-Ray Spectroscopy @EMIL



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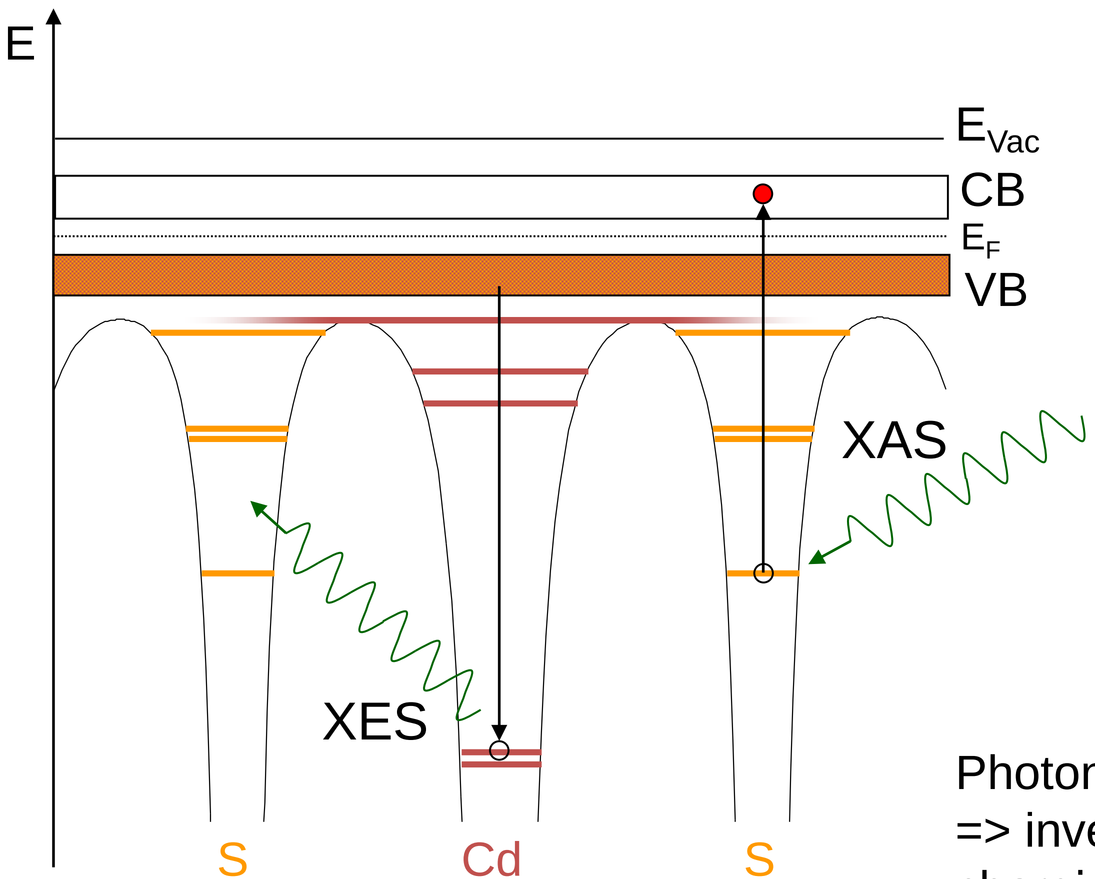
XAS –X-ray absorption spec.
XRF – X-ray fluorescence spec.
XRD – X-ray diffraction spec.

Wide X-ray energy range needed (80 eV - 10keV)

X-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES): Principle



XAS:

- Conduction band from the "perspective of a chosen core hole" (wave function overlap is needed)

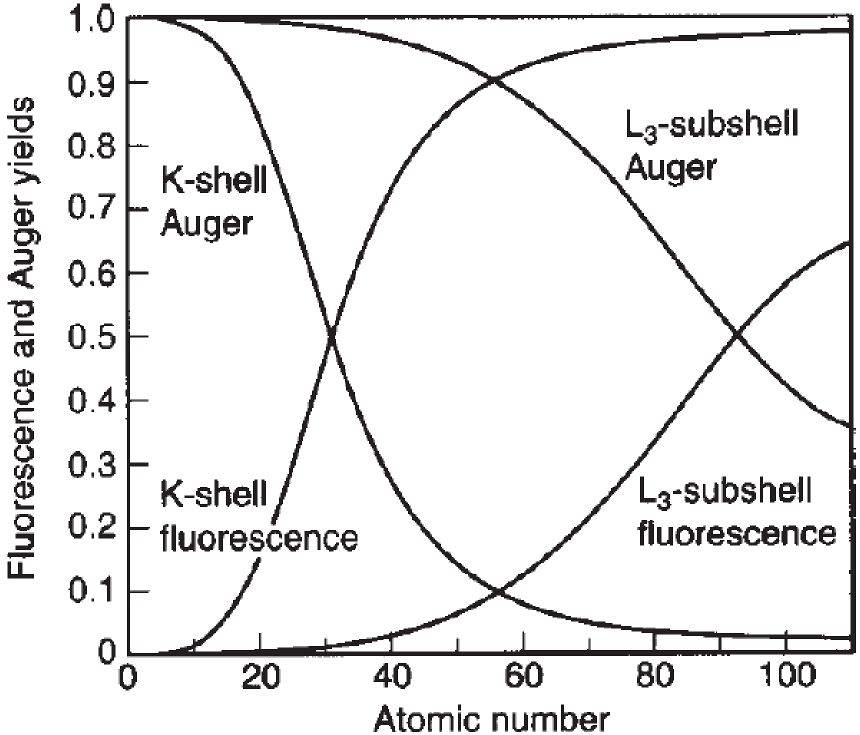
XES:

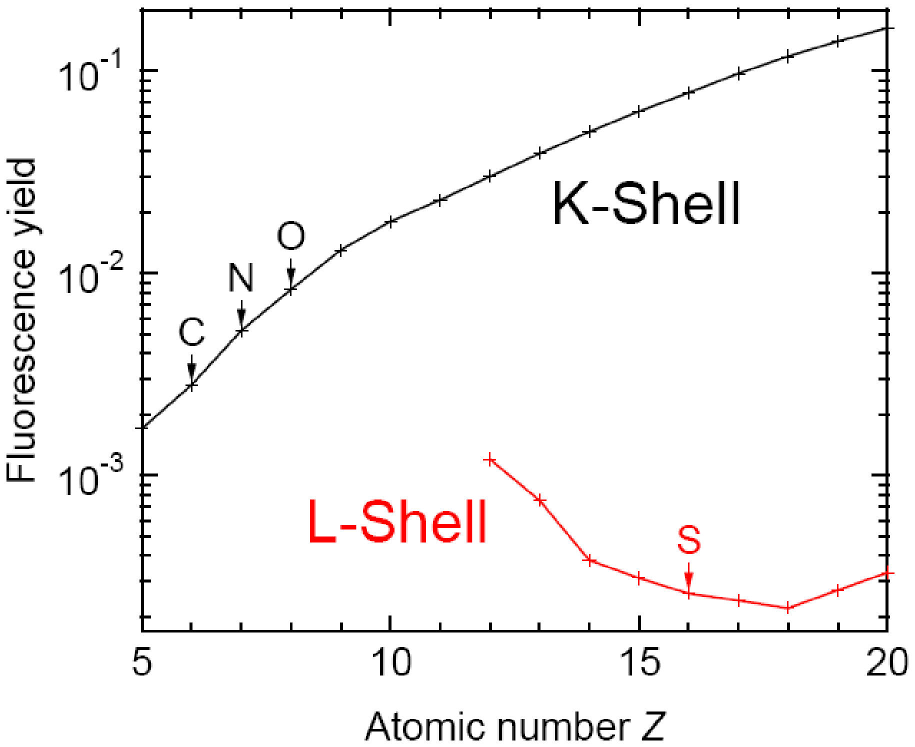
- Valence band and weakly bound core levels from the "perspective of a chosen core hole"

Photon in - photon out techniques
=> investigation of buried interface, charging samples, liquids,…

Courtesy of L. Weinhardt

Fluorescence vs. Auger process





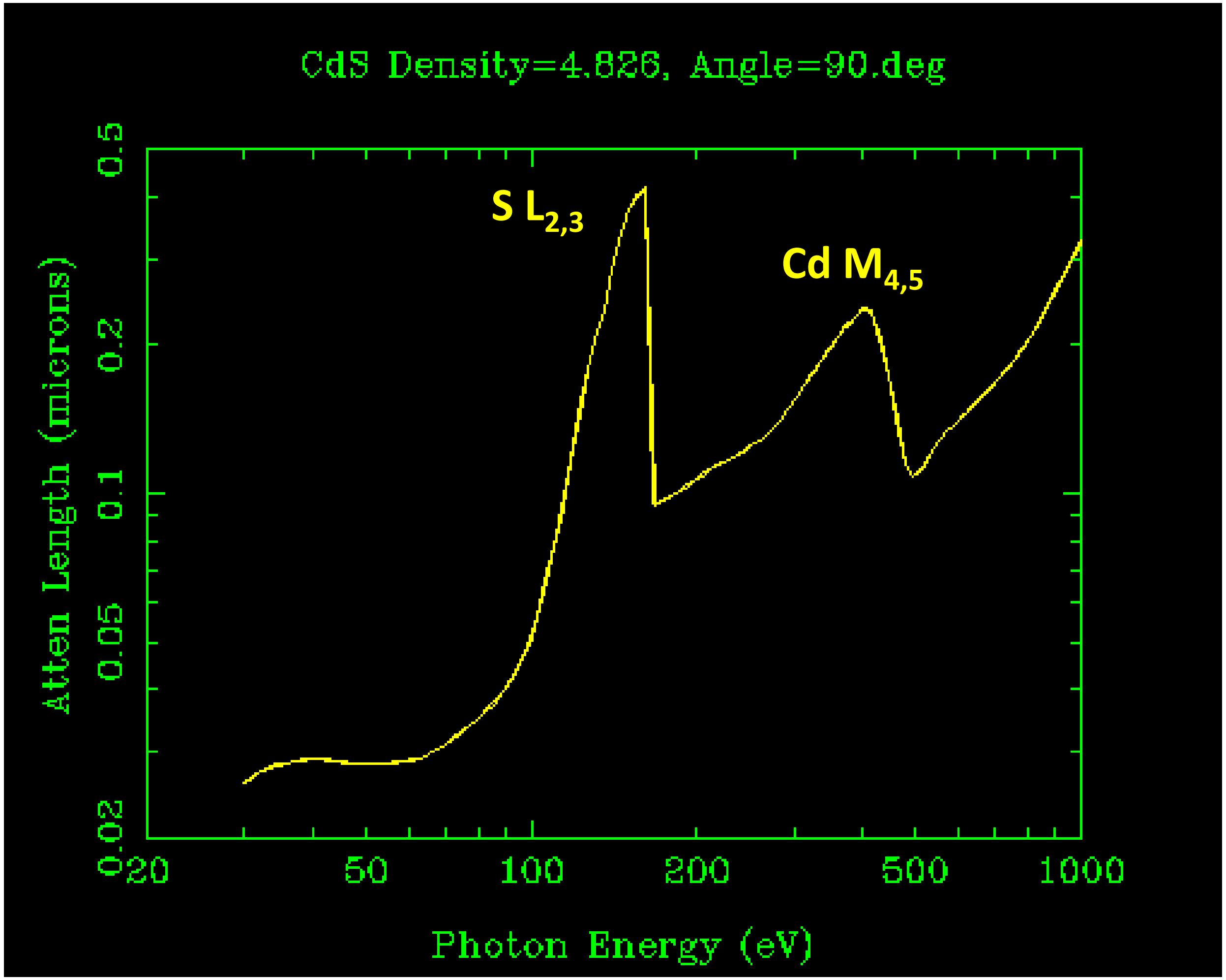
T. Attwood, Soft X-rays and extreme ultraviolet radiation: principles, Cambridge University Press (1999).
M. O. Krause, Atomic radiative and radiationless yields for K-shells and L-shells, J. Phys. Chem. Ref. Data 8, 307 (1979).

Need for high-flux beamline at a 3rd generation synchrotron light source!

Courtesy of L. Weinhardt

XES: Probing depth

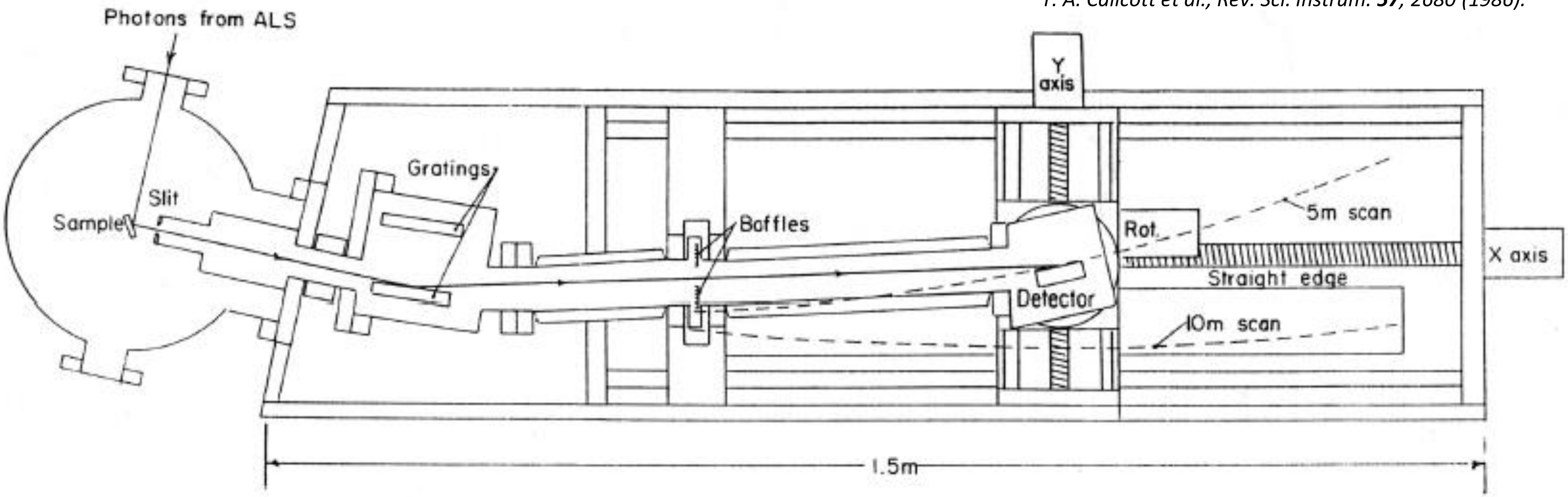
- "photon in - photon out" technique
- More bulk sensitive than photoemission
- Attenuation lengths: some 10 … few 100 nm



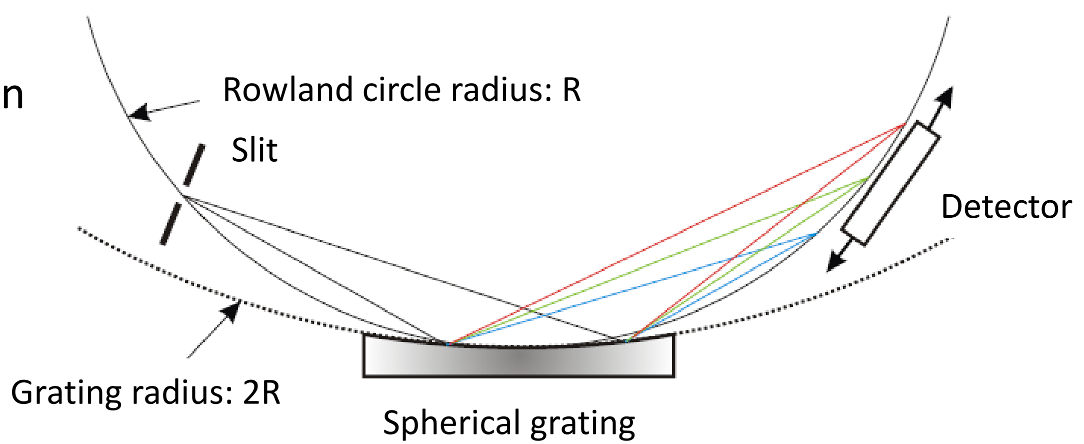
http://www.cxro.lbl.gov/optical_constants/atten2.html

XES & XAS: Experimental setup

T. A. Callcott et al., Rev. Sci. Instrum. ***57****, 2680 (1986).*

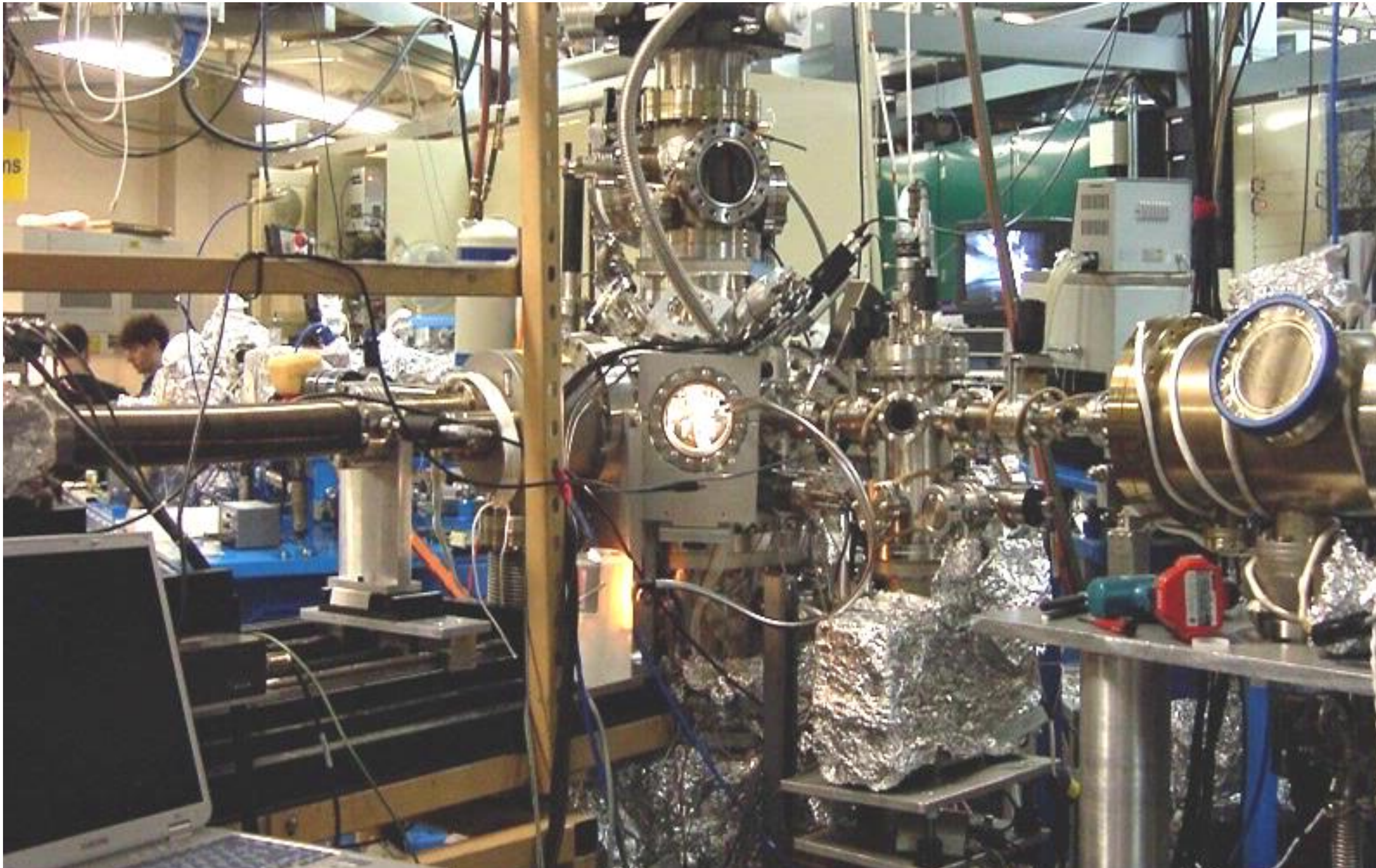


- XES: Grating spectrometer (Rowland geometry) for energy dispersive photon detection
- XAS: Photon/Electron detection
- High-flux beamline at a 3rd generation synchrotron is needed



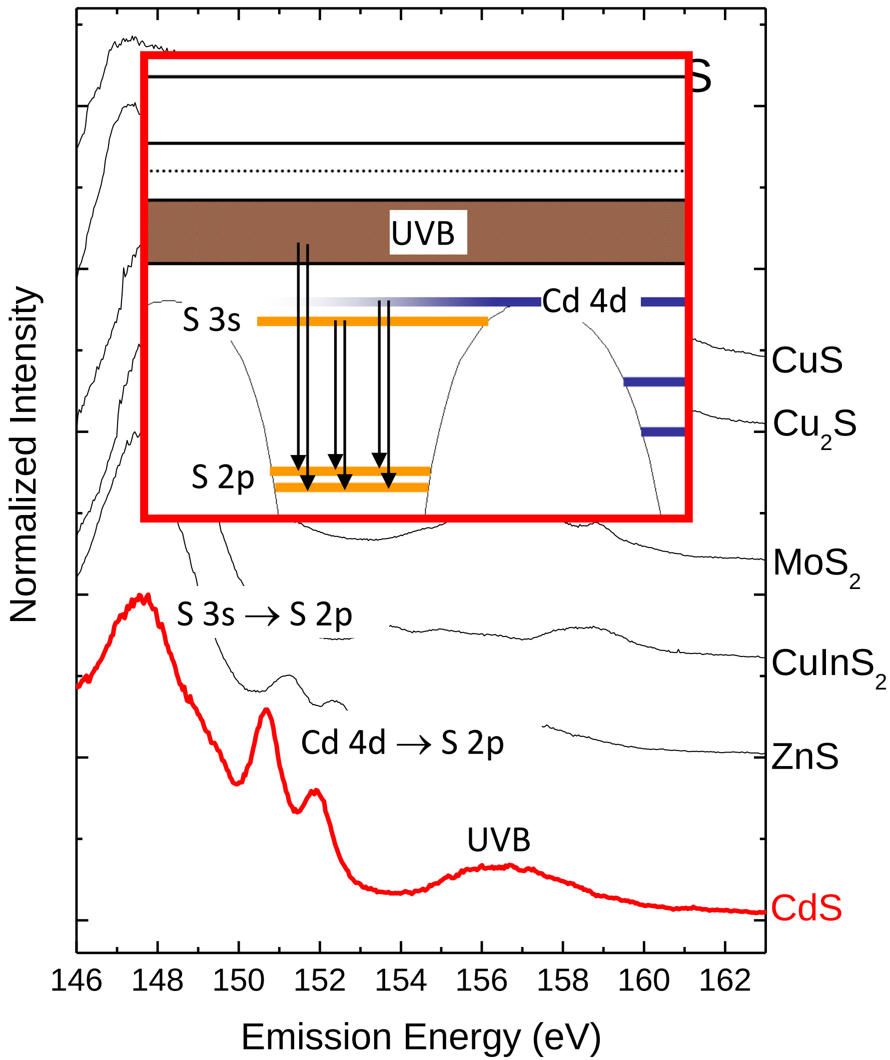
H. A. Rowland, Philos. Mag. ***13****, 469 (1882).*

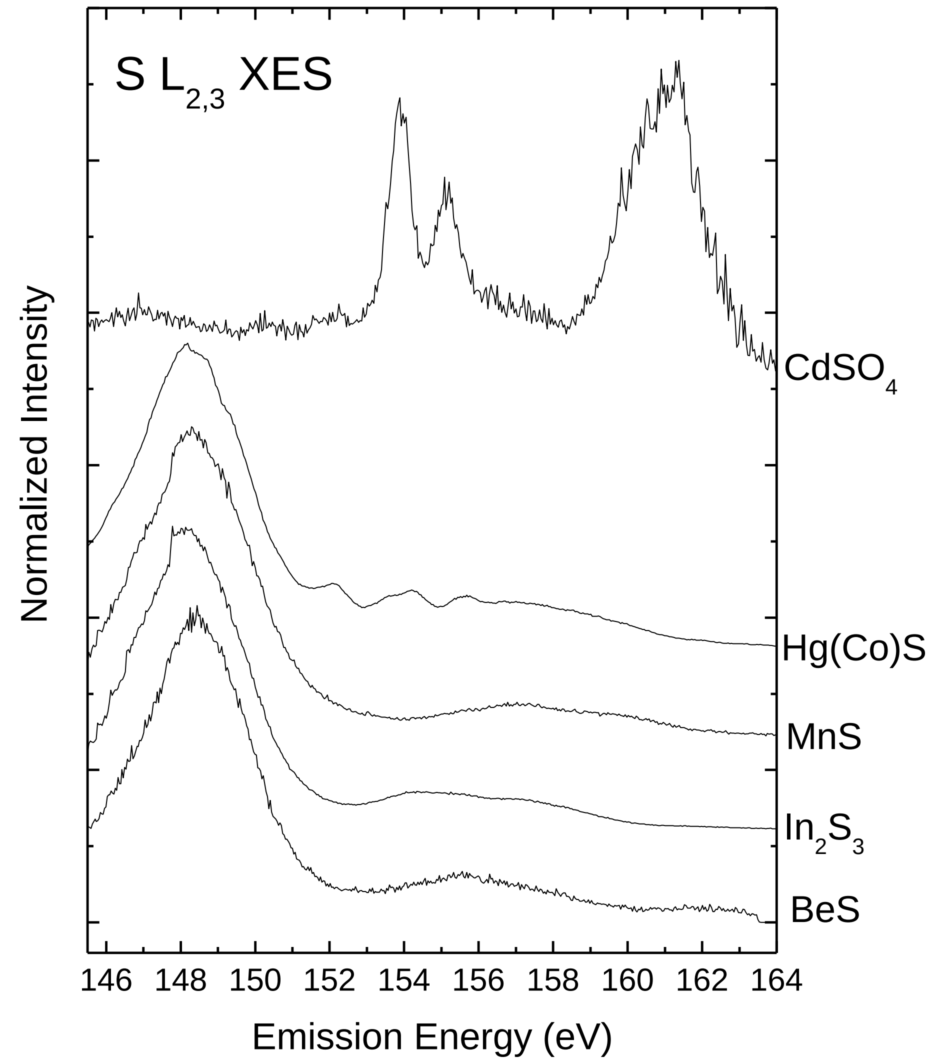
Experimental setup in real life



XES example: S $L_{2,3}$ emission spectrum

„Fingerprint“ approach => identification of different species

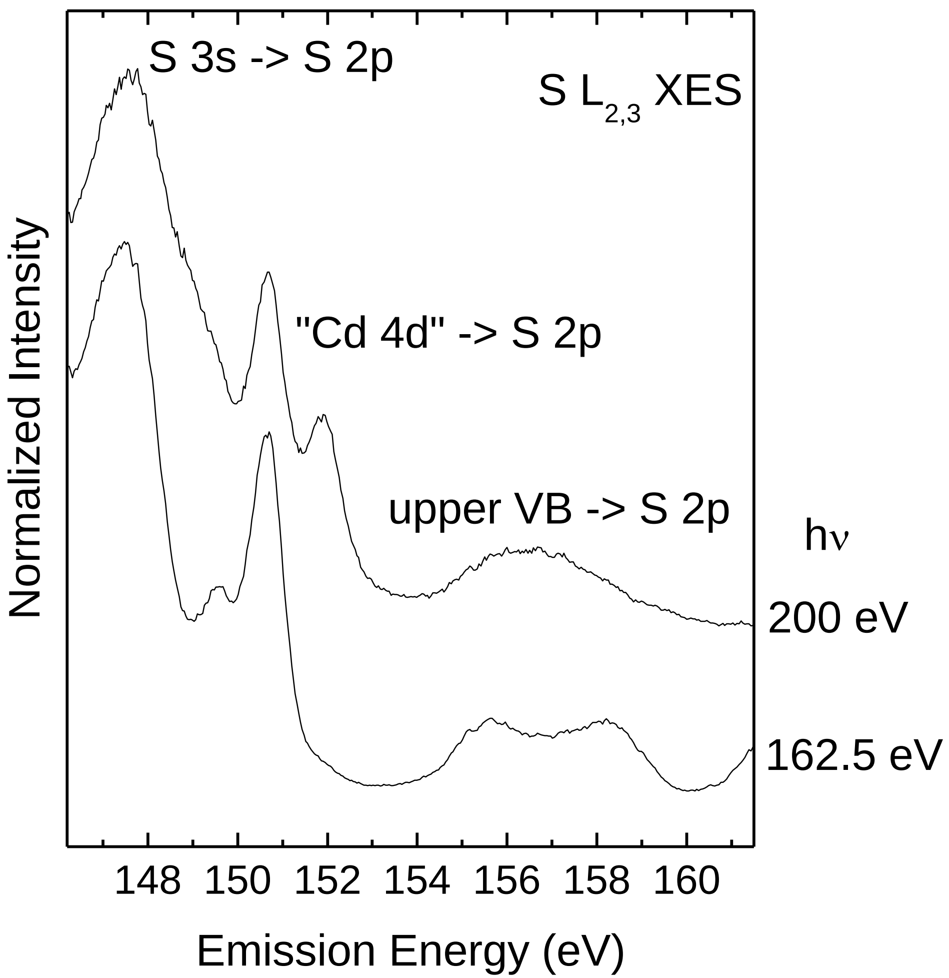




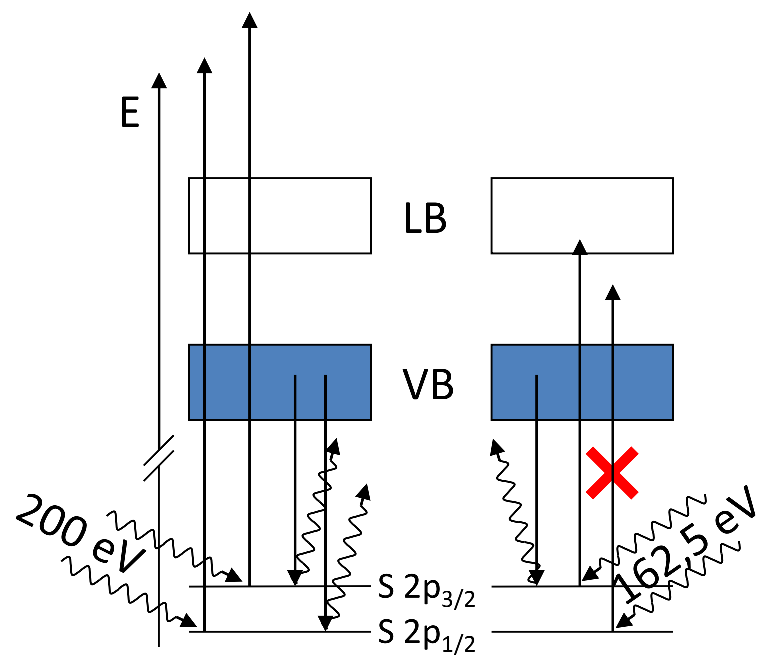
Courtesy of L. Weinhardt

„Resonant“ excitation

*Weinhardt et al., PRB **75**, 165207 (2007).*



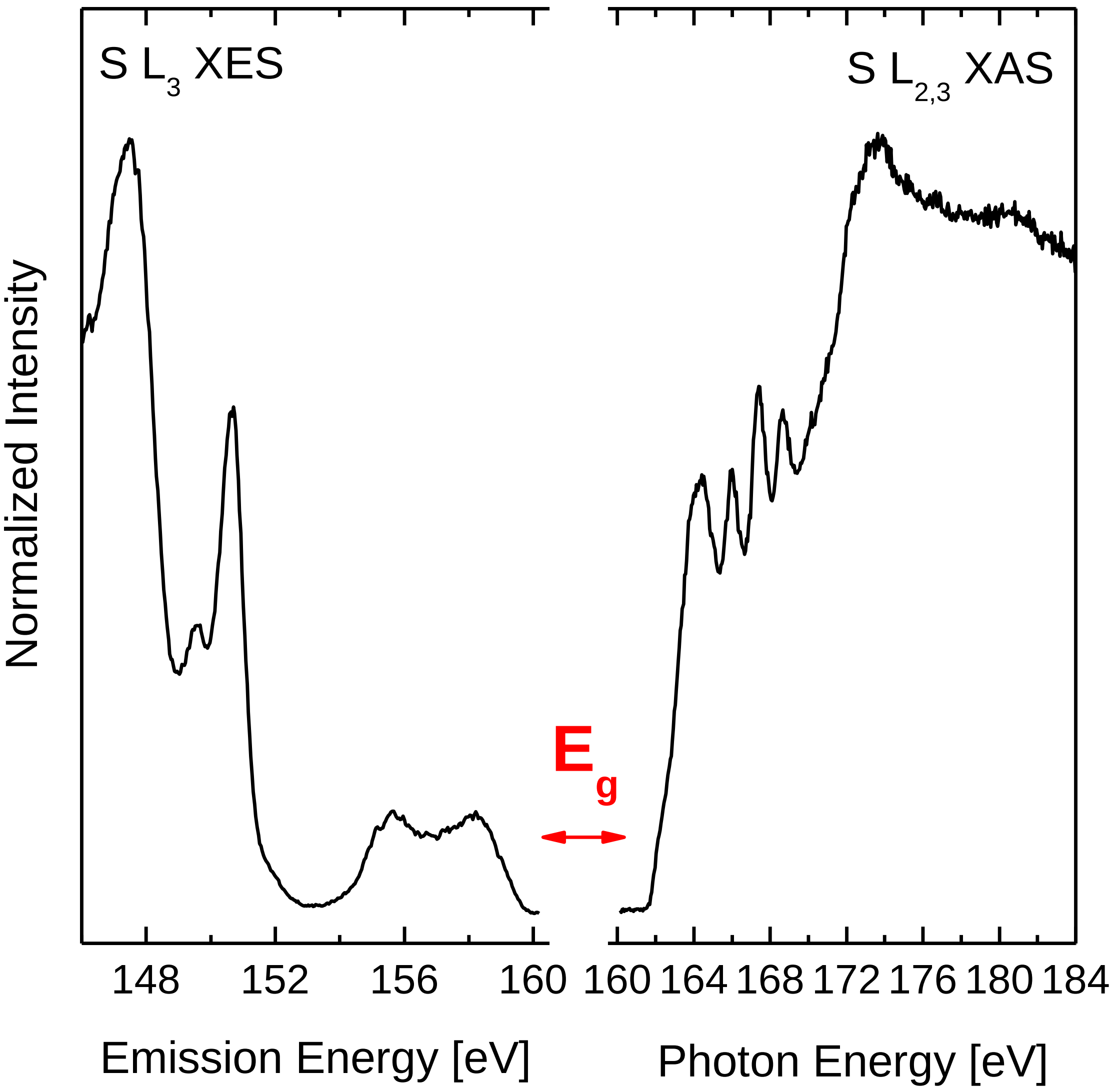
- Wave function overlap between Cd 4d-derived states and S 2p
- L_2 and L_3 contribution to the spectrum can be separated



Courtesy of L. Weinhardt

Combination of XES & XAS spectra

*Weinhardt et al., PRB **75**, 165207 (2007).*



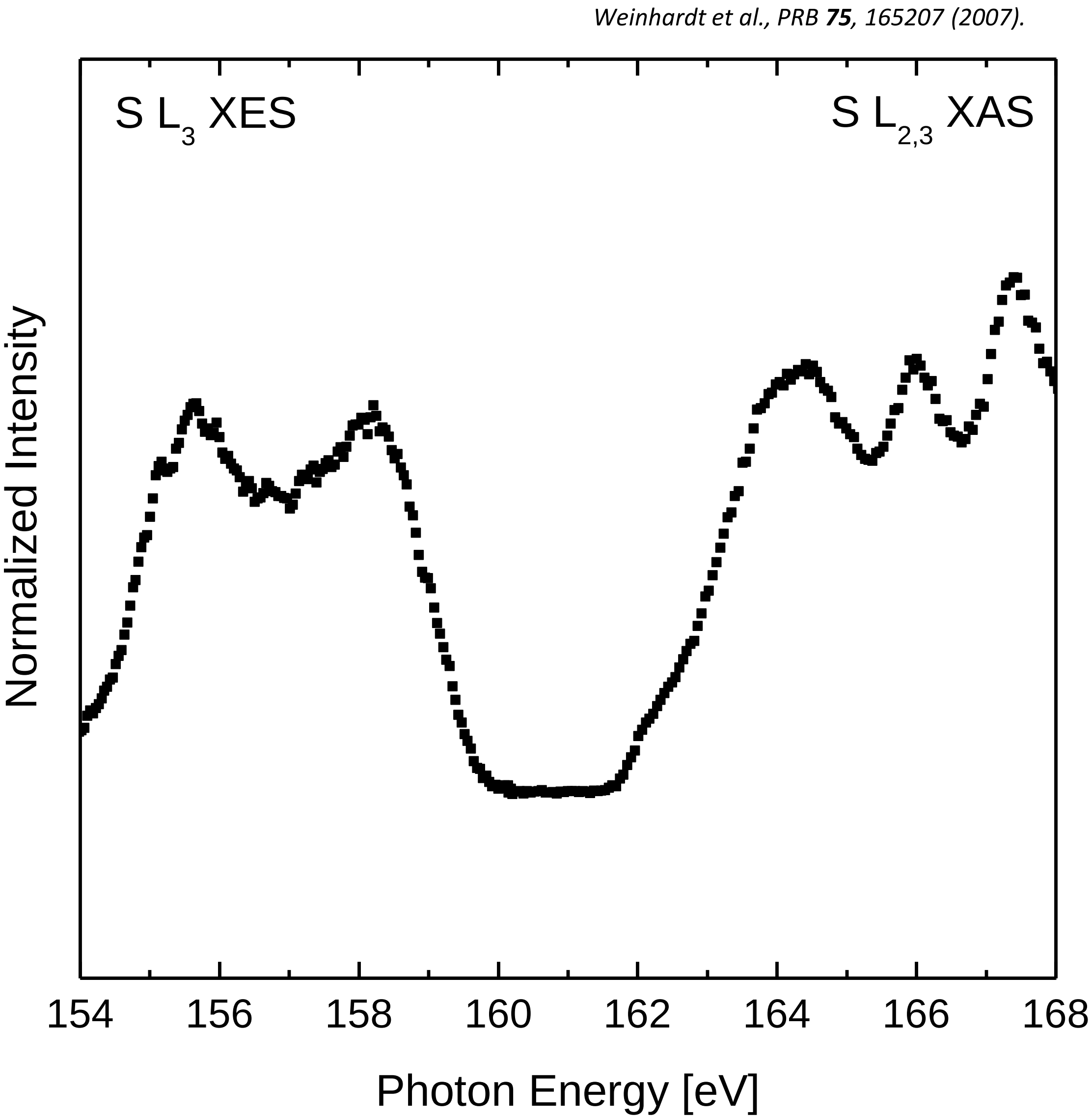
- XES probes occupied states

  => *Onset indicative for VBM*

- XAS probes unoccupied states

  => *Onset indicative for CBM*

Combination of XES & XAS spectra



- XES probes occupied states

  => *Onset indicative for VBM*

- XAS probes unoccupied states

  => *Onset indicative for CBM*

- XES & XAS probe "E_g"

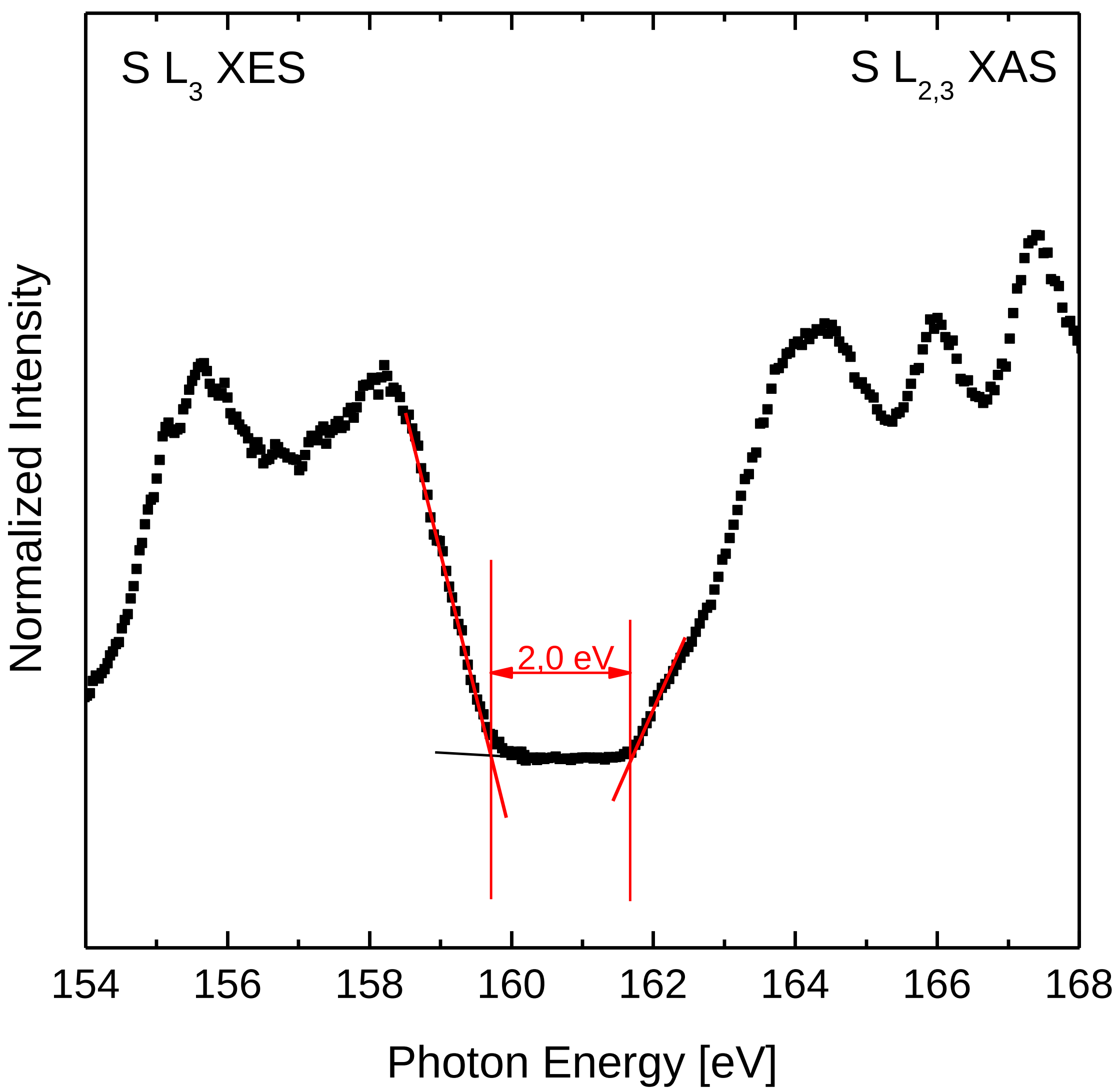
  (experimental uncertainty: ± 0.2 eV)

- Potential existence of core excitonic features in the XAS spectra

"E_g" is lower-bound approximation for the ground state band gap

Combination of XES & XAS spectra

*Weinhardt et al., PRB **75**, 165207 (2007).*



- XES probes occupied states

  => *Onset indicative for VBM*

- XAS probes unoccupied states

  => *Onset indicative for CBM*

- XES & XAS probe "E_g"

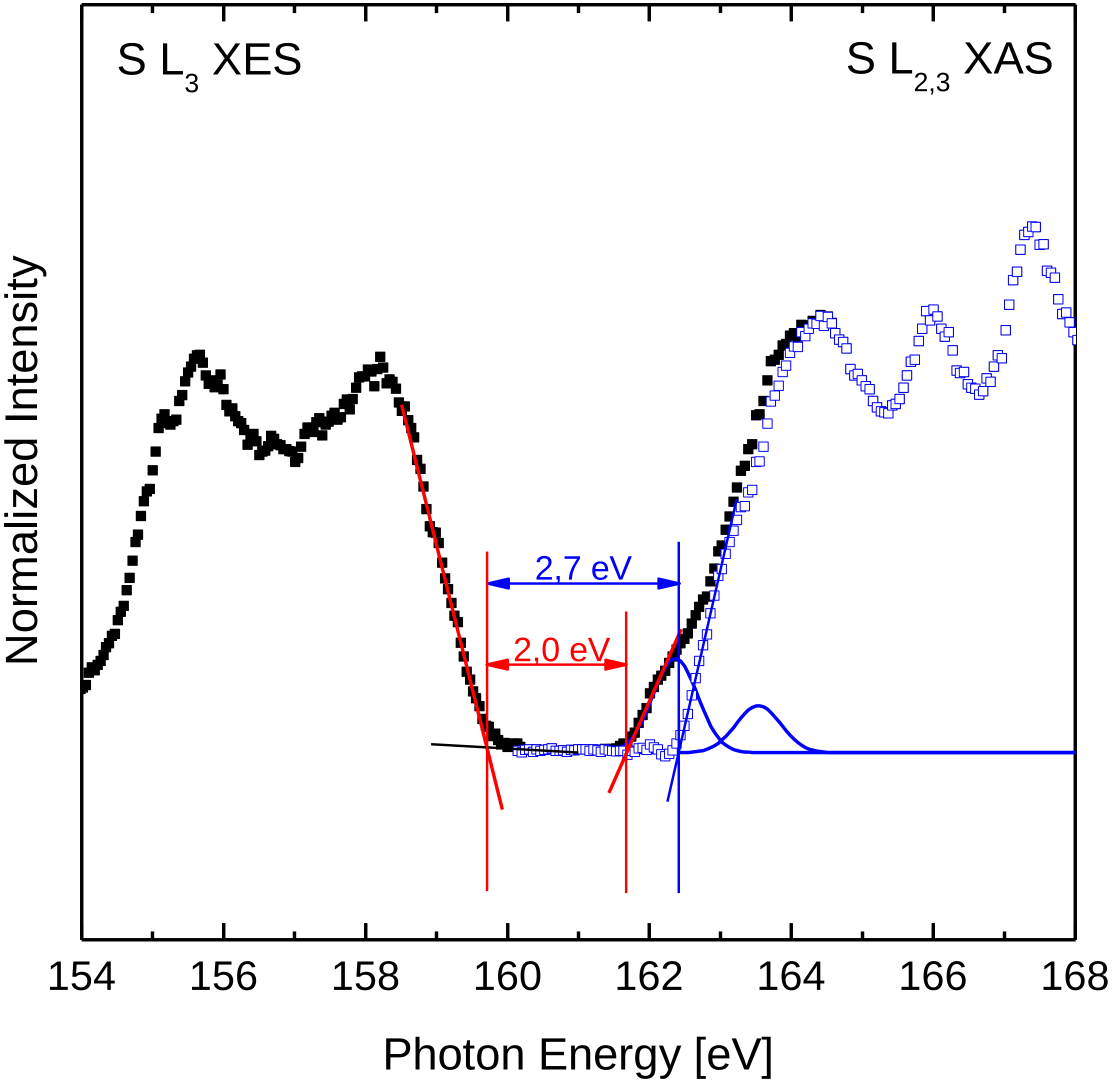
  (experimental uncertainty: ± 0.2 eV)

- Potential existence of core excitonic features in the XAS spectra

"E_g" is lower-bound approximation for the ground state band gap

CdS: Impact of core excitonic feature

*Weinhardt et al., PRB **75**, 165207 (2007).*



E_g (CdS): 2.4 … 2.5 eV

Landolt-Börnstein, Springer (2011)

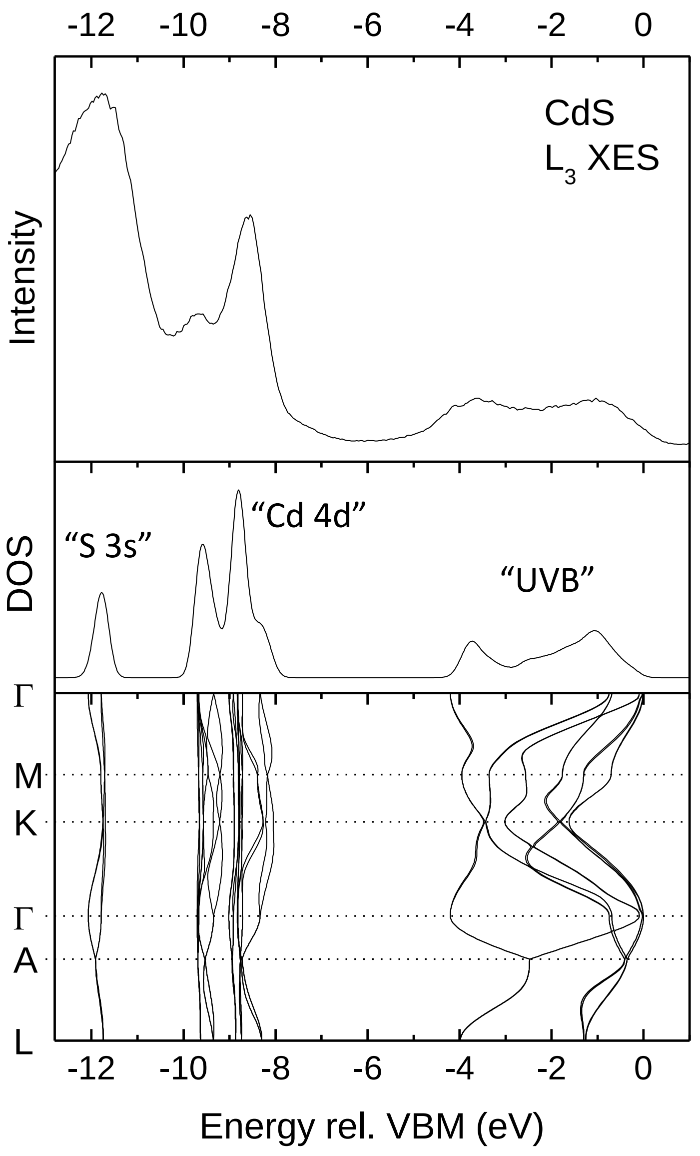
- "E_g" = 2.0 eV
- Taking core exciton into account (Gauss profile):

  => E_g = 2.7 eV

"E_g" is lower-bound approximation for the ground state band gap

Comparison with (validation of) calculated DOS

*Weinhardt et al., PRB **75**, 165207 (2007).*



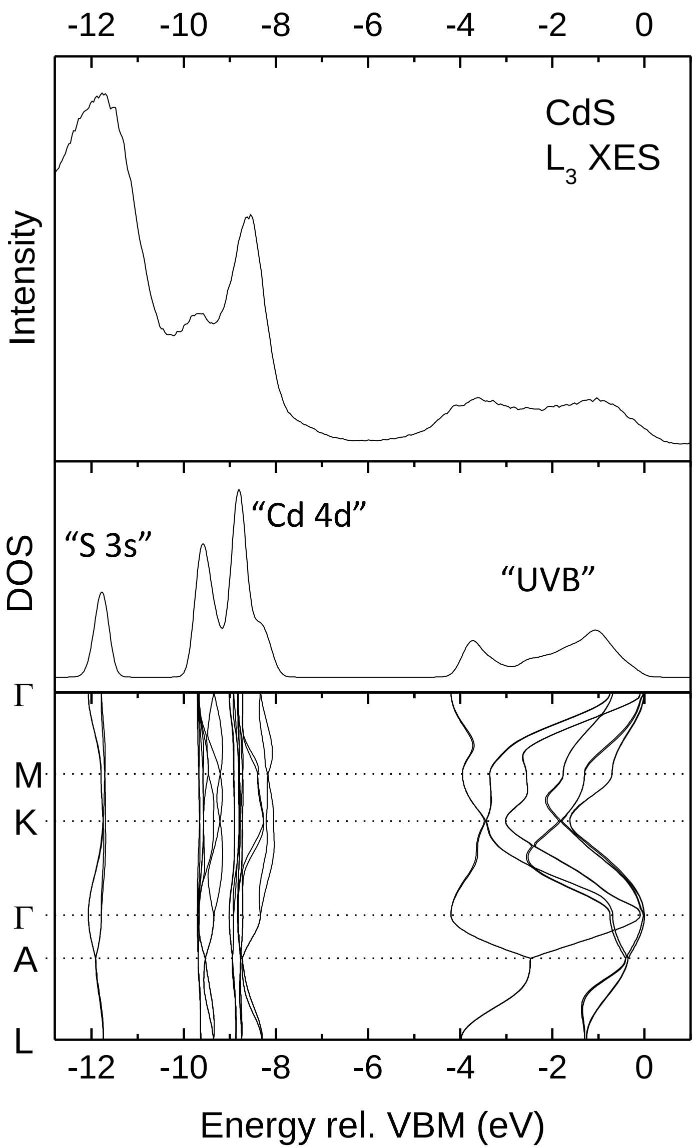
- XES represents (partial) density of states, DOS
- Comparison with calculated DOS useful to

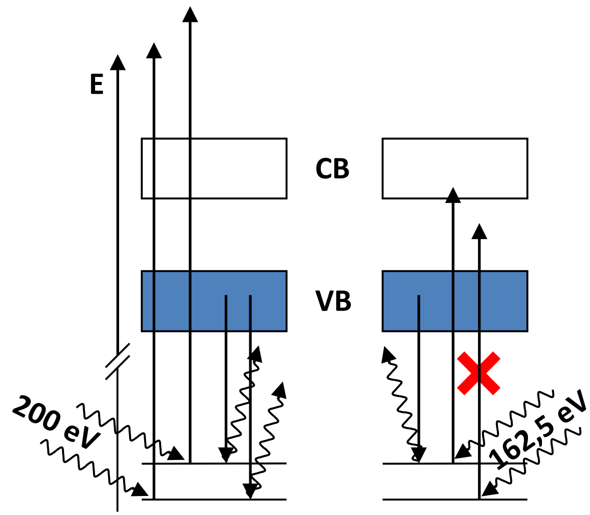
  => identify spectral contributions

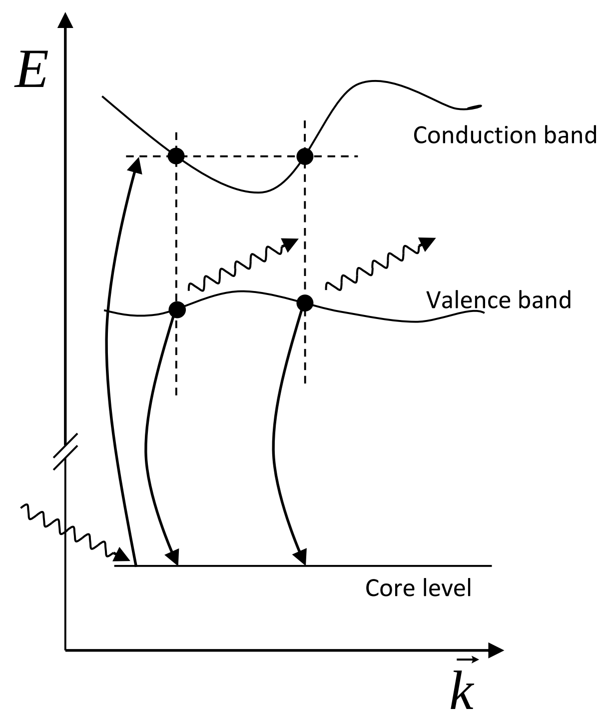
  => validate band structure calculations

„Resonant“ excitation -> RIXS

*Weinhardt et al., PRB **75**, 165207 (2007).*





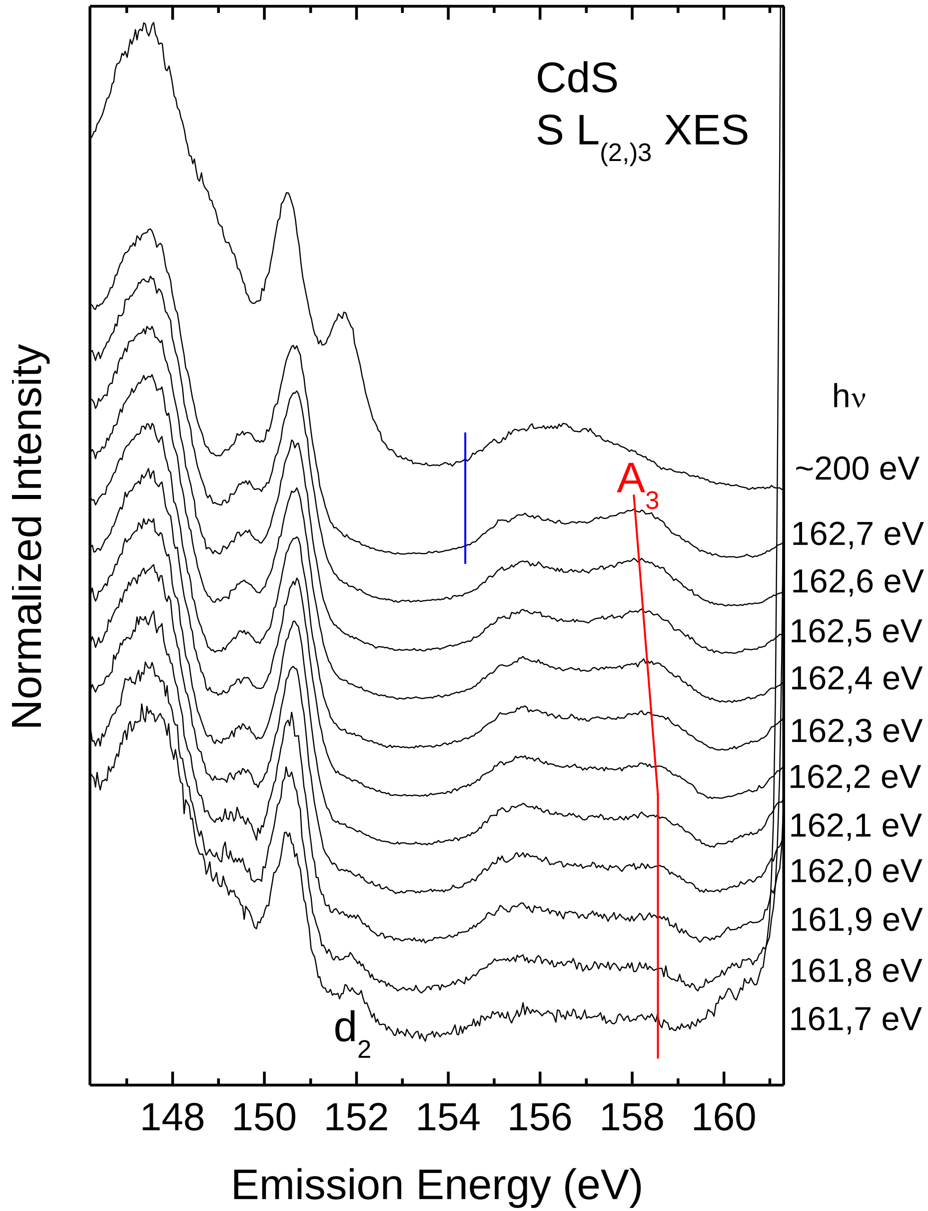


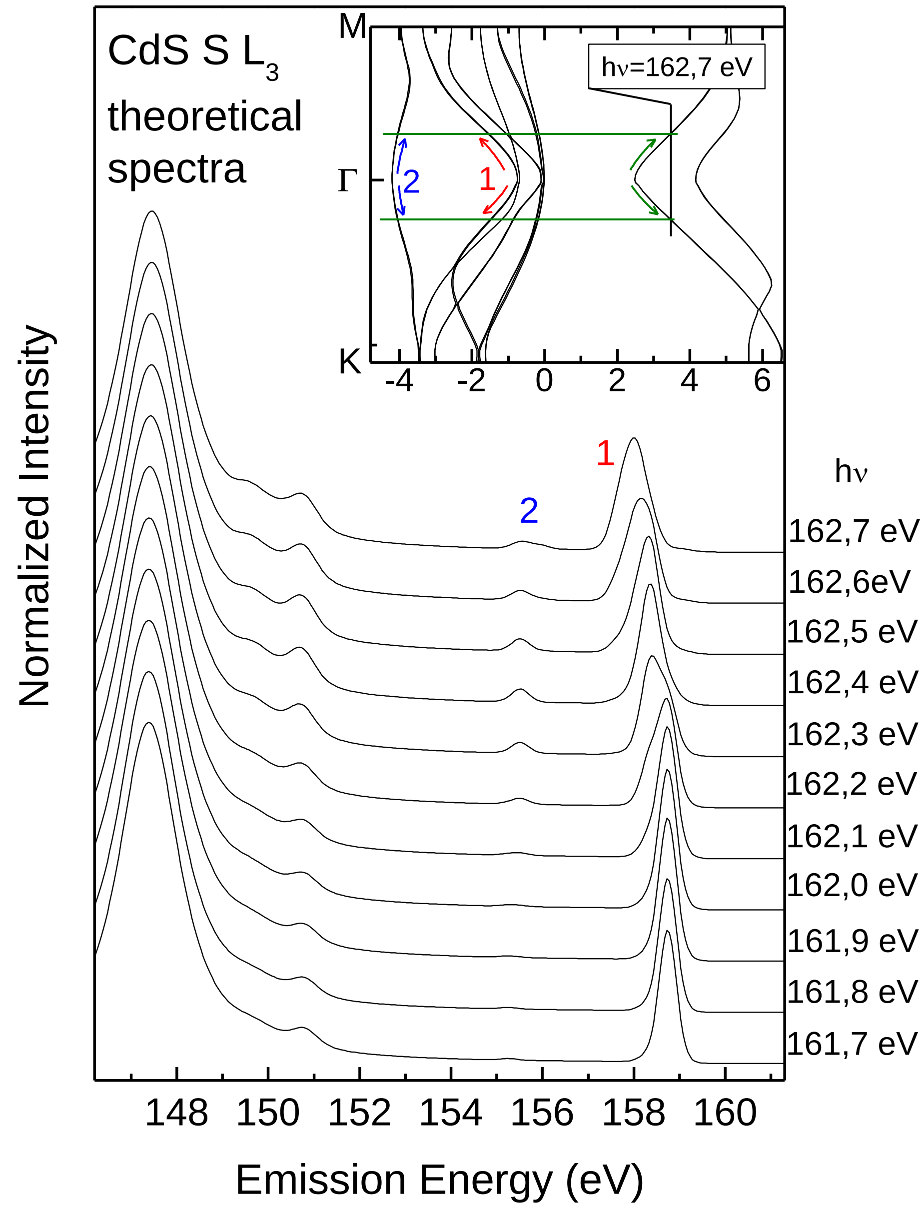
XES => RIXS

(Resonant Inelastic X-ray Scattering)

- Coherent emission, conservation of crystal momentum
- Selection of k vectors only through excitation energy

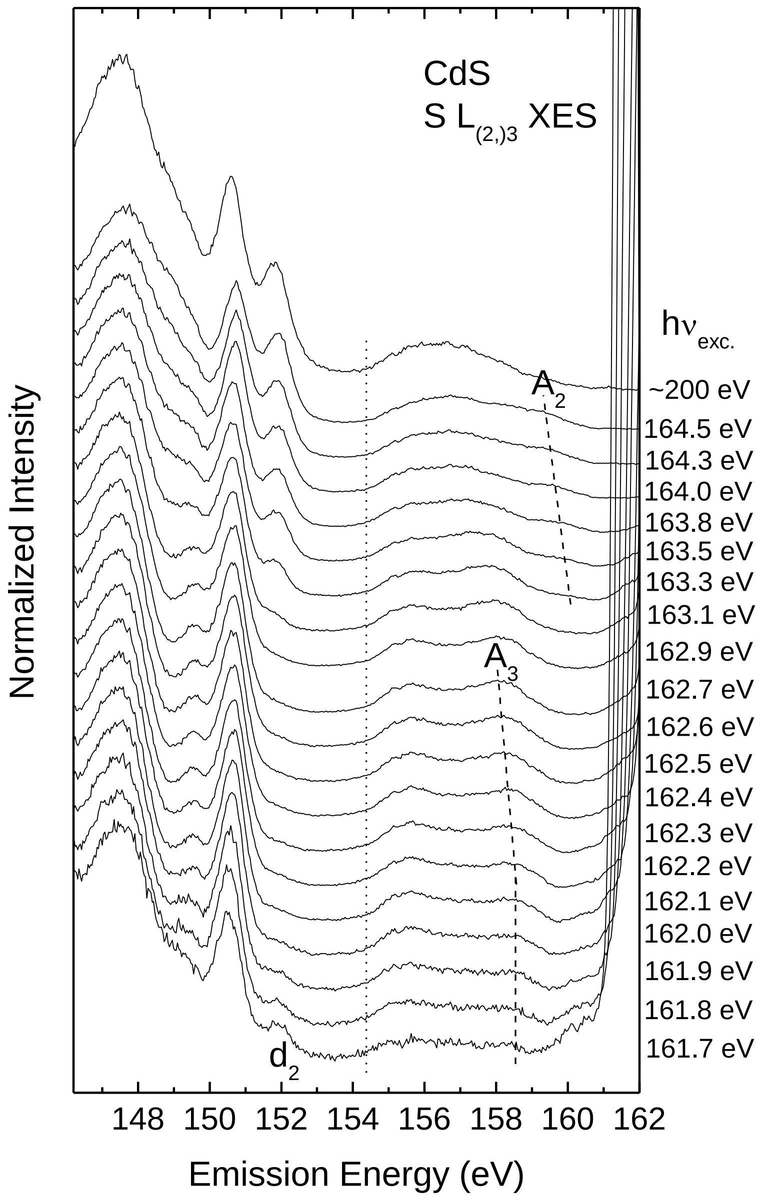
S $L_{2,3}$ RIXS of CdS



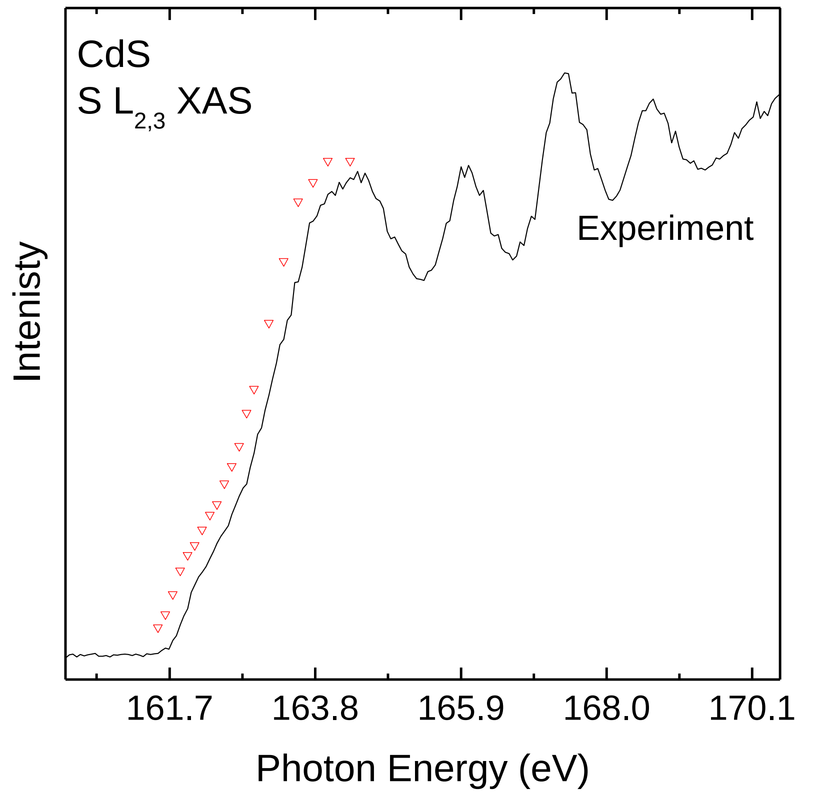


Weinhardt et al., PRB 75, 165207 (2007).

S $L_{2,3}$ RIXS of CdS: Standard approach

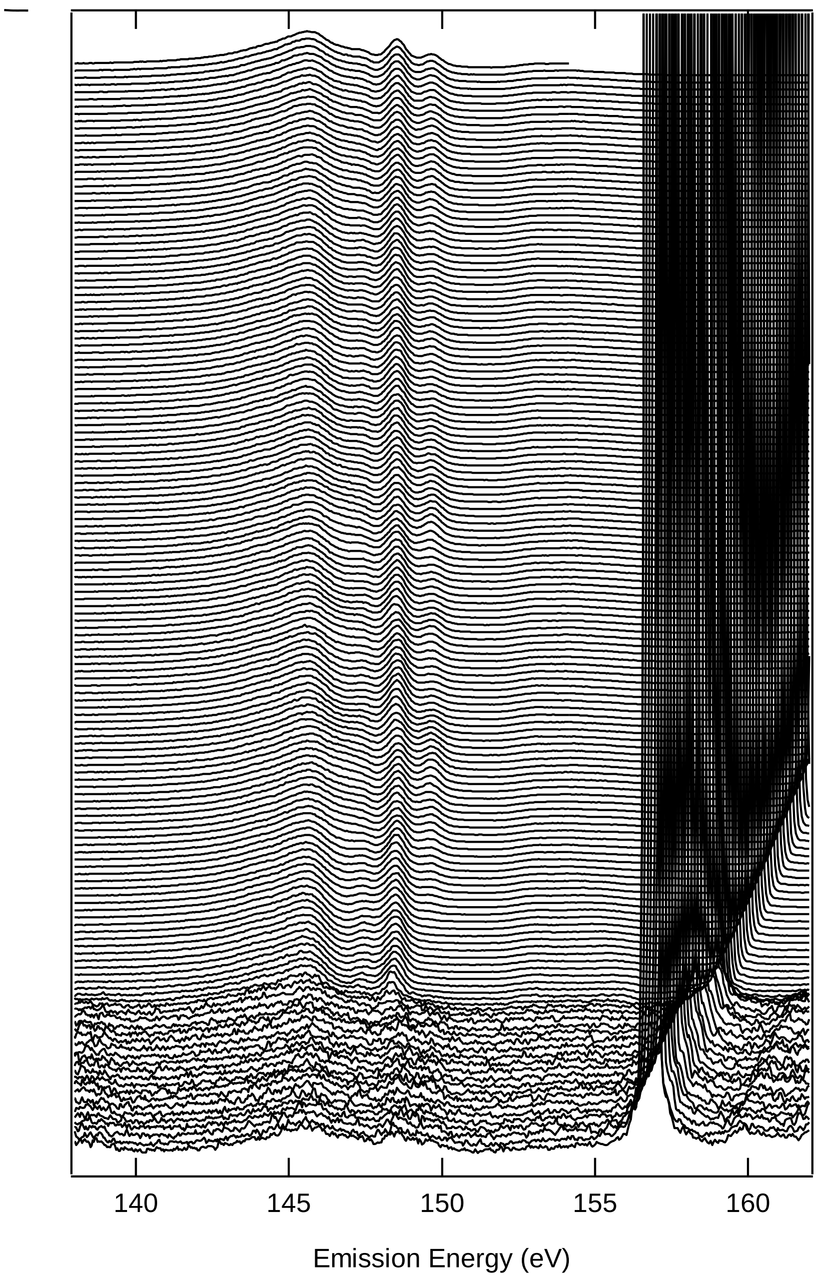


- RIXS spectra measured at a series of energies around the absorption edge
- S $L_{2,3}$ RIXS is tough: ~99.99% Auger
  $\Rightarrow$ approx. 20 hours of measuring time for the complete series

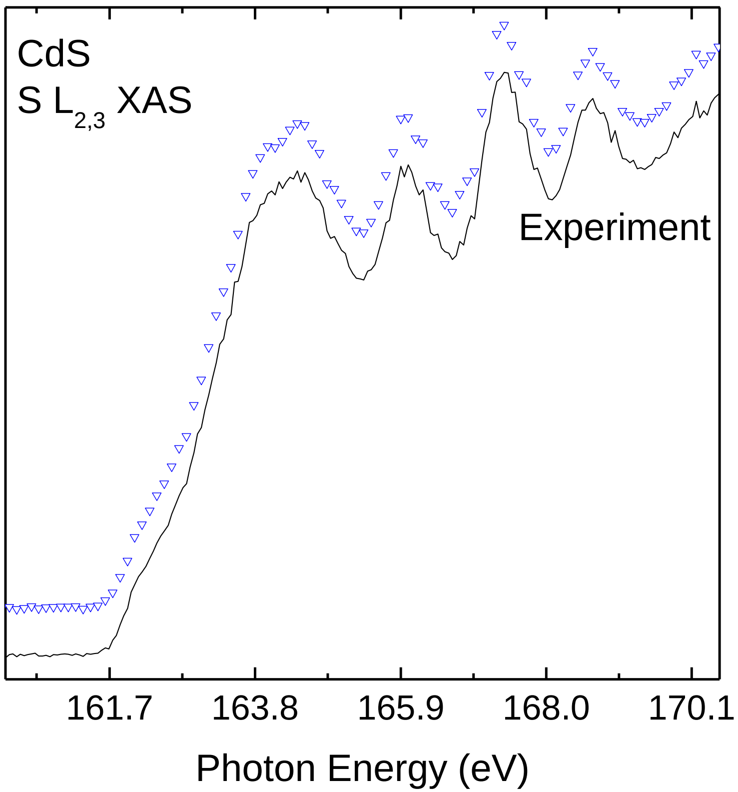


Weinhardt et al., PRB 75, 165207 (2007).

S $L_{2,3}$ RIXS of CdS: New VLS spectrometer

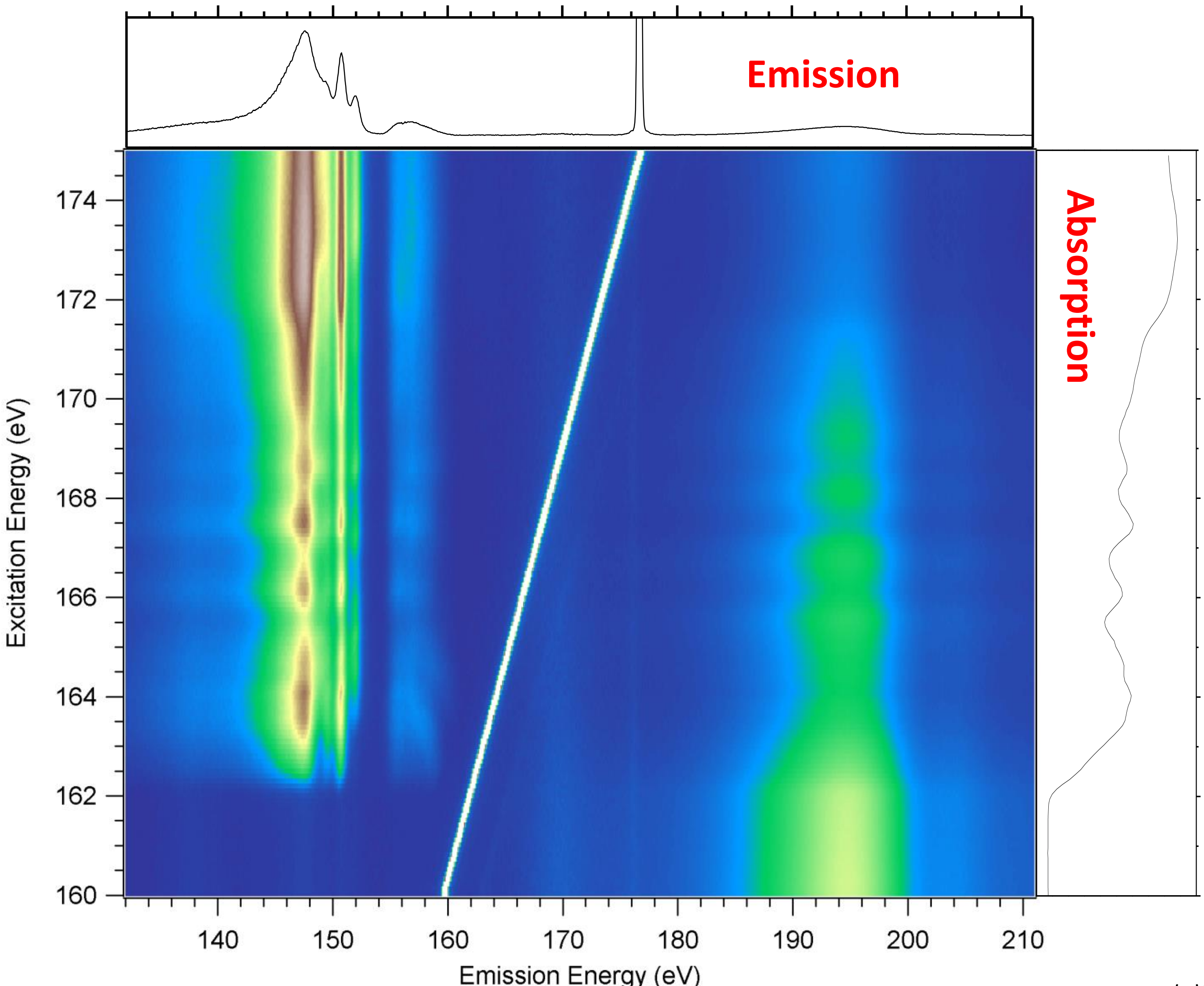


- RIXS spectra measured at every point in the absorption spectrum
- Total measurement time: 33 min



*L. Weinhardt et al., PRB **79**, 165305 (2009).*

S $L_{2,3}$ RIXS of CdS: RIXS map approach

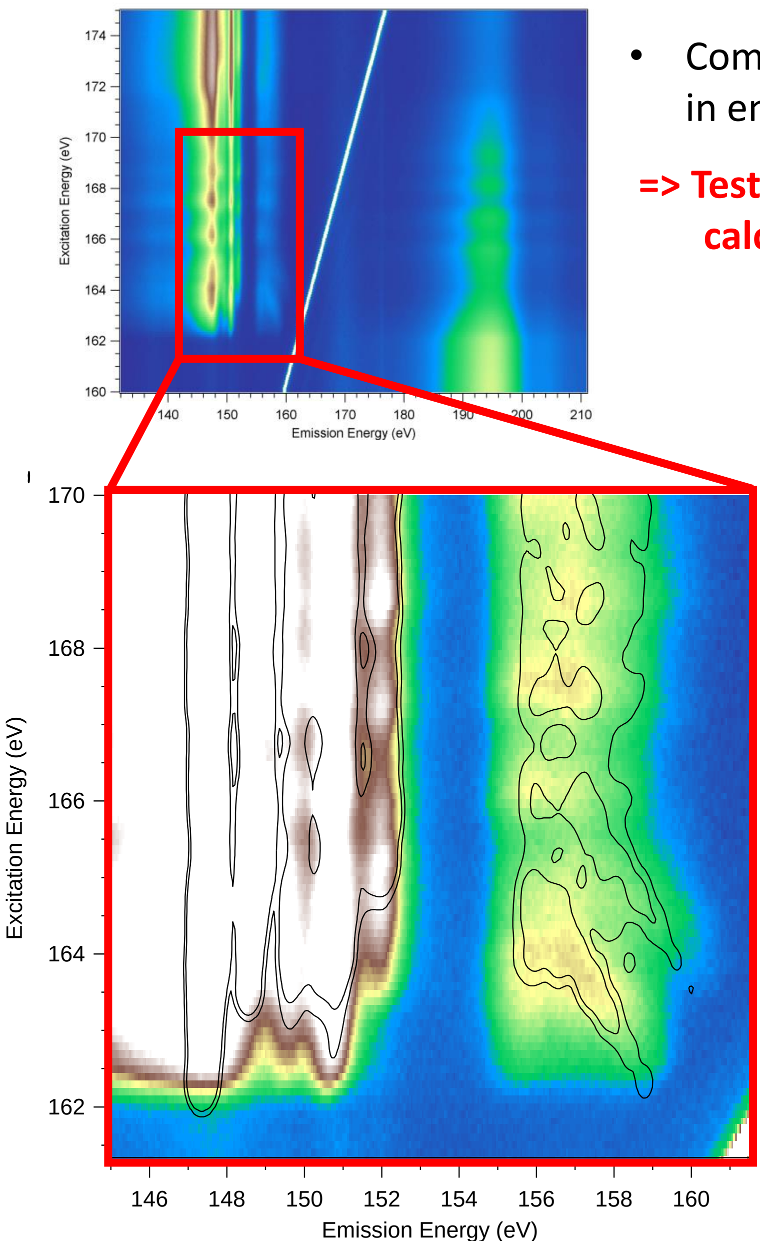


- Simultaneous measurement of RIXS and XAS

=> full electronic structure information

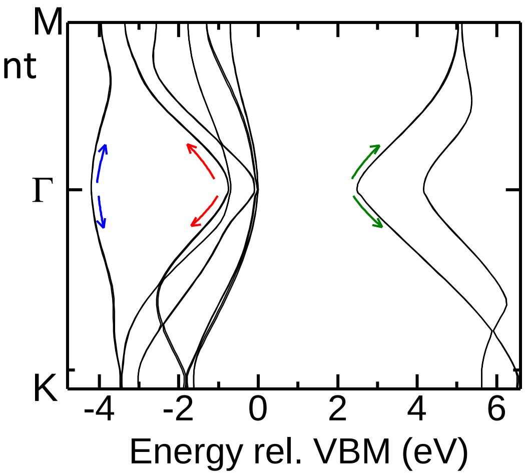
*L. Weinhardt et al., PRB **79**, 165305 (2009).*

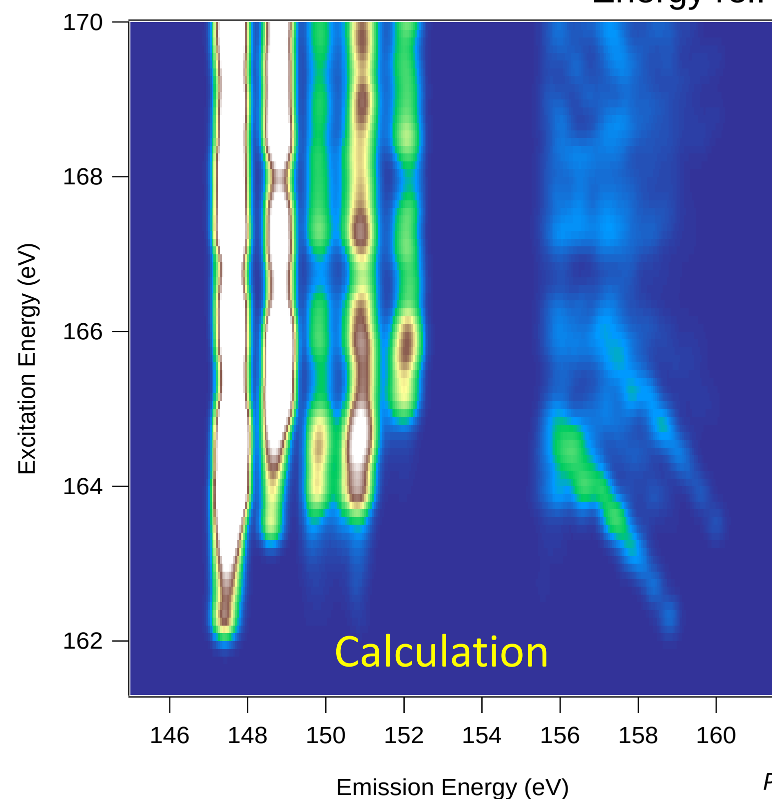
S $L_{2,3}$ RIXS of CdS: Validate theory with experiment



- Comparison of theory and experiment in entire k-space possible

=> Test and validate band structure calculations





L. Weinhardt et al., PRB ***79****, 165305 (2009).*

Research Example: Depth-resolved X-ray spectroscopy of mixed-halide perovskites

D.E. Starr,[1] G. Sadoughi,[2] E. Handick,[1] M. Gorgoi,[1,3] S. Stranks, R.G. Wilks,[1,3] H. Snaith,[2] M. Bär[1,3,4]

1 HZB Helmholtz Zentrum Berlin
2 University of Oxford
3 EMIL
4 b-tu Brandenburgische Technische Universität Cottbus - Senftenberg

Motivation and sample preparation

We have used electron and X-ray based spectroscopies with different information depths to:

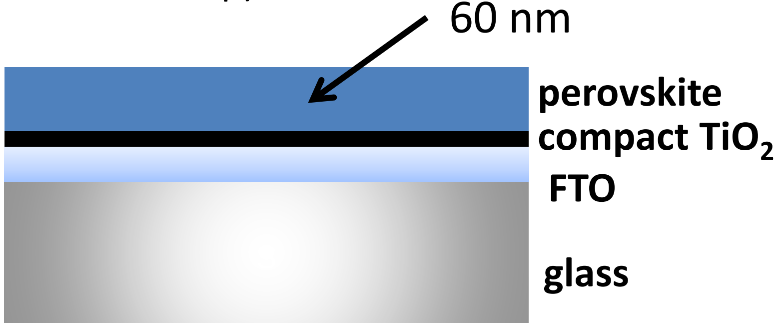
- measure core and valence levels of $CH_3NH_3PbI_{(3-x)}Cl_x/TiO_2$
- correlate the chemical and electronic properties of the *surface* and the *near-surface* region
- monitor the formation of the perovskite *in-situ*

Sample preparation[1]:

$$CH_3NH_3I + PbCl_2 \rightarrow CH_3NH_3PbI_{(3-x)}Cl_x$$

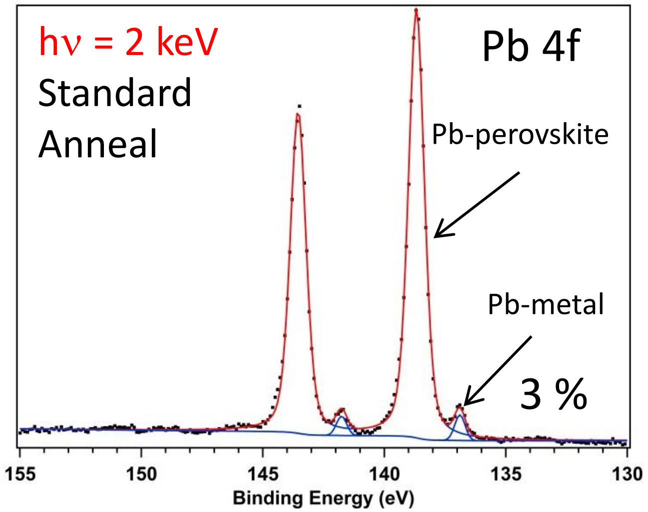
(Samples provided by Prof. Henry Snaith Group)

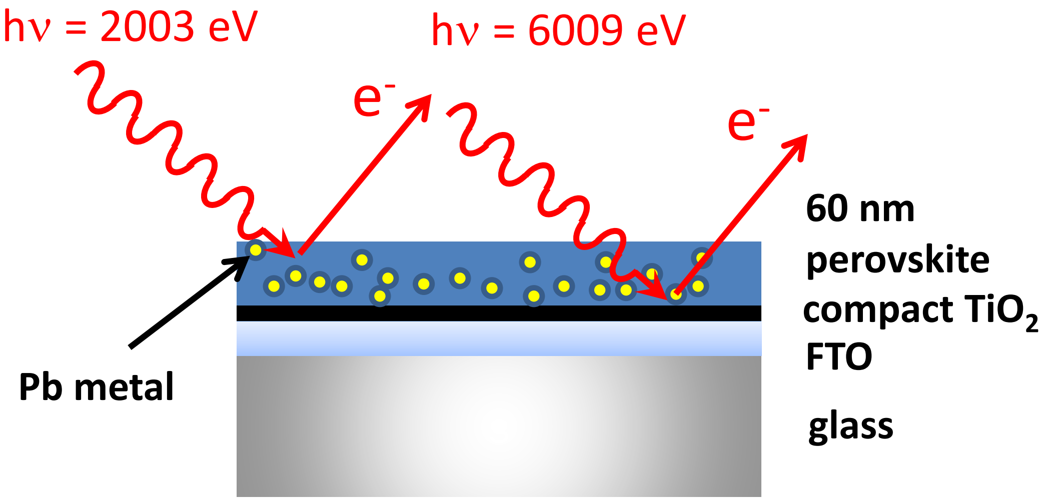
1) Solution of $CH_3NH_3I + PbCl_2$ in DMF spin-coated on compact TiO_2
2) Samples annealed in N_2(g) filled glove box at 90°C for 2h

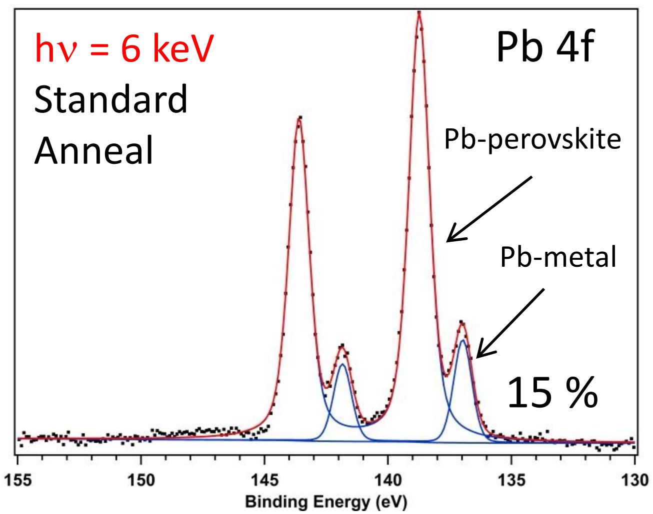


[1]Michael M. Lee *et al.* Science **338**,643 (2012)

Pb 4f spectra: location of metallic Pb





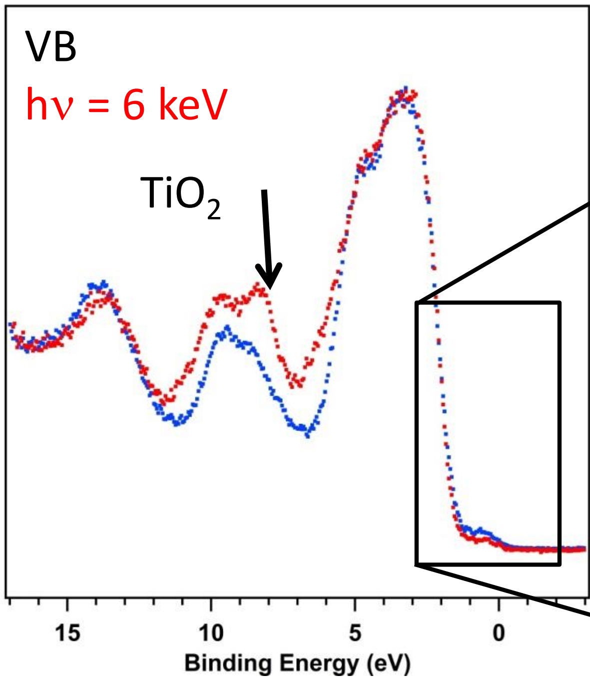


Most (but not all) samples indicate the presence of metallic Pb

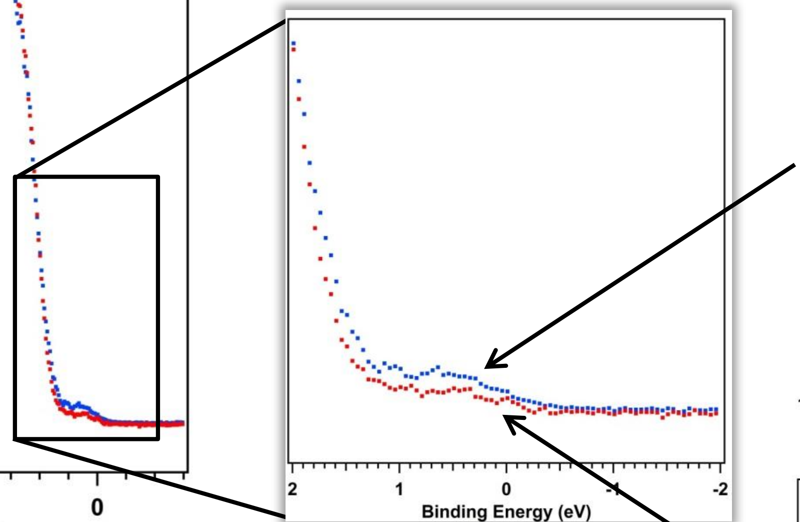
If present, the concentration of metallic Pb is higher deeper beneath the surface

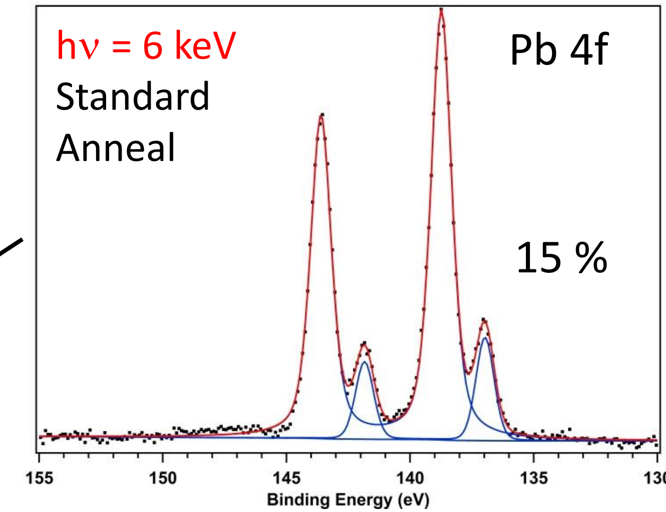
G. Sadoughi, D.E. Starr, E. Handick, S. Stranks, M. Gorgoi, R.G. Wilks, M. Bär, and H. Snaith, ACS Appl. Mat. Interf. doi:10.1021/acsami.5b02237

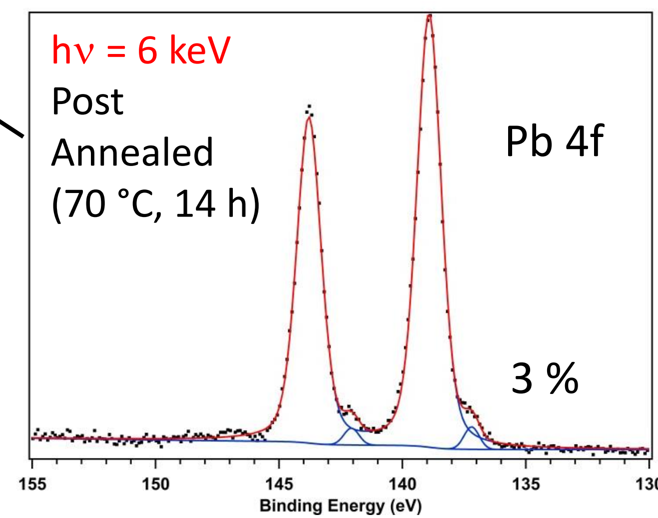
Valence Band Spectra: Metallic Pb



VB spectra 6009 eV



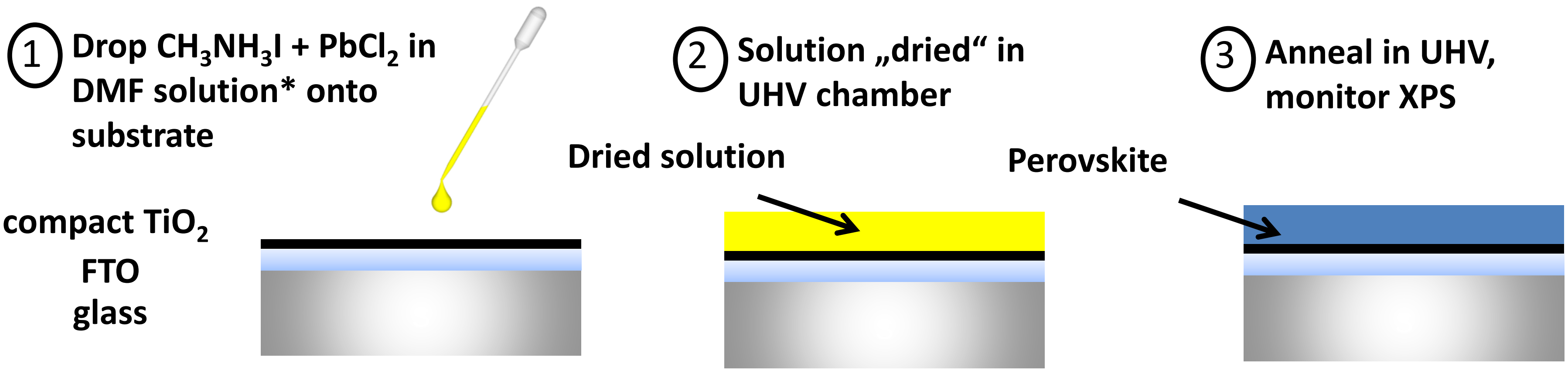


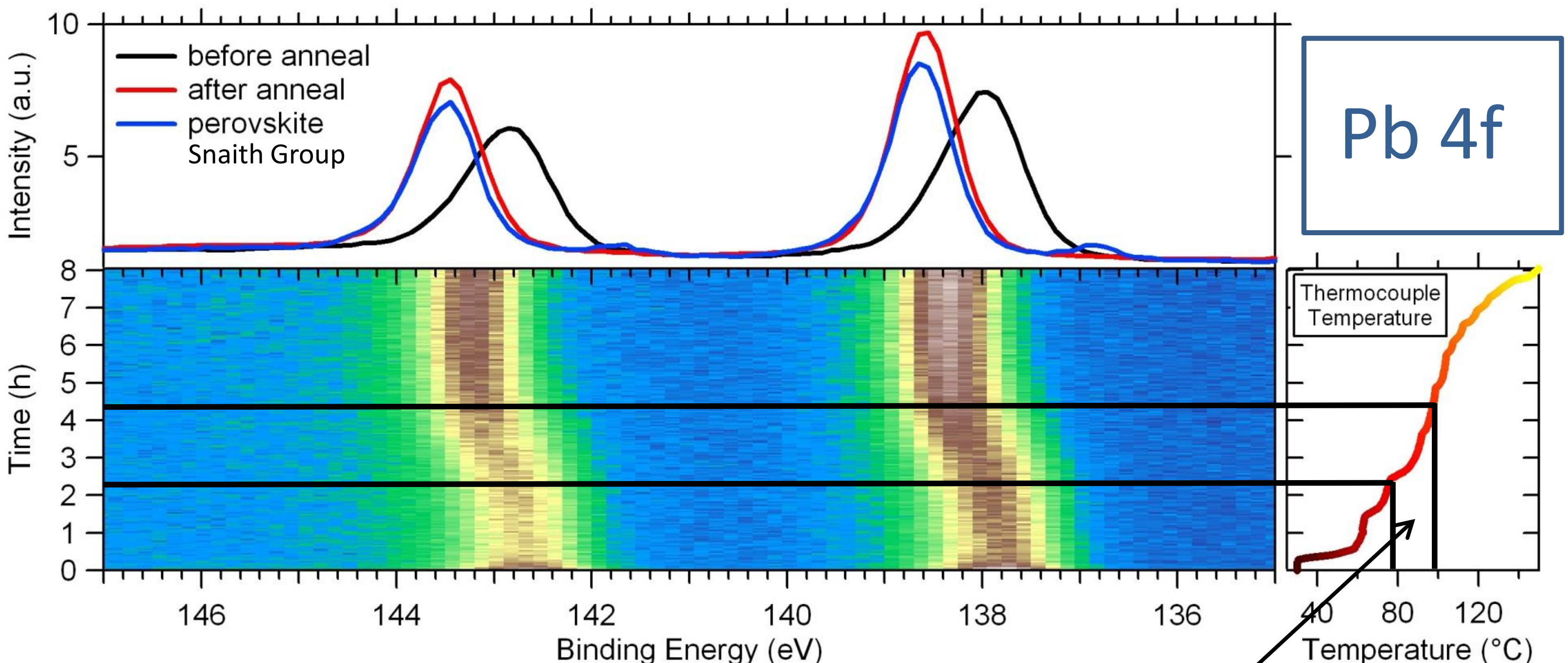


- Amount of metallic Pb correlates with density of occupied states near the Fermi level
- Amount of metallic Pb does not always decrease with annealing
- TiO_2 increase with annealing is likely due to some dewetting of perovskite film

G. Sadoughi, D.E. Starr, E. Handick, S. Stranks, M. Gorgoi, R.G. Wilks, M. Bär, and H. Snaith, ACS Appl. Mat. Interf. doi:10.1021/acsami.5b02237

In-situ perovskite formation in UHV

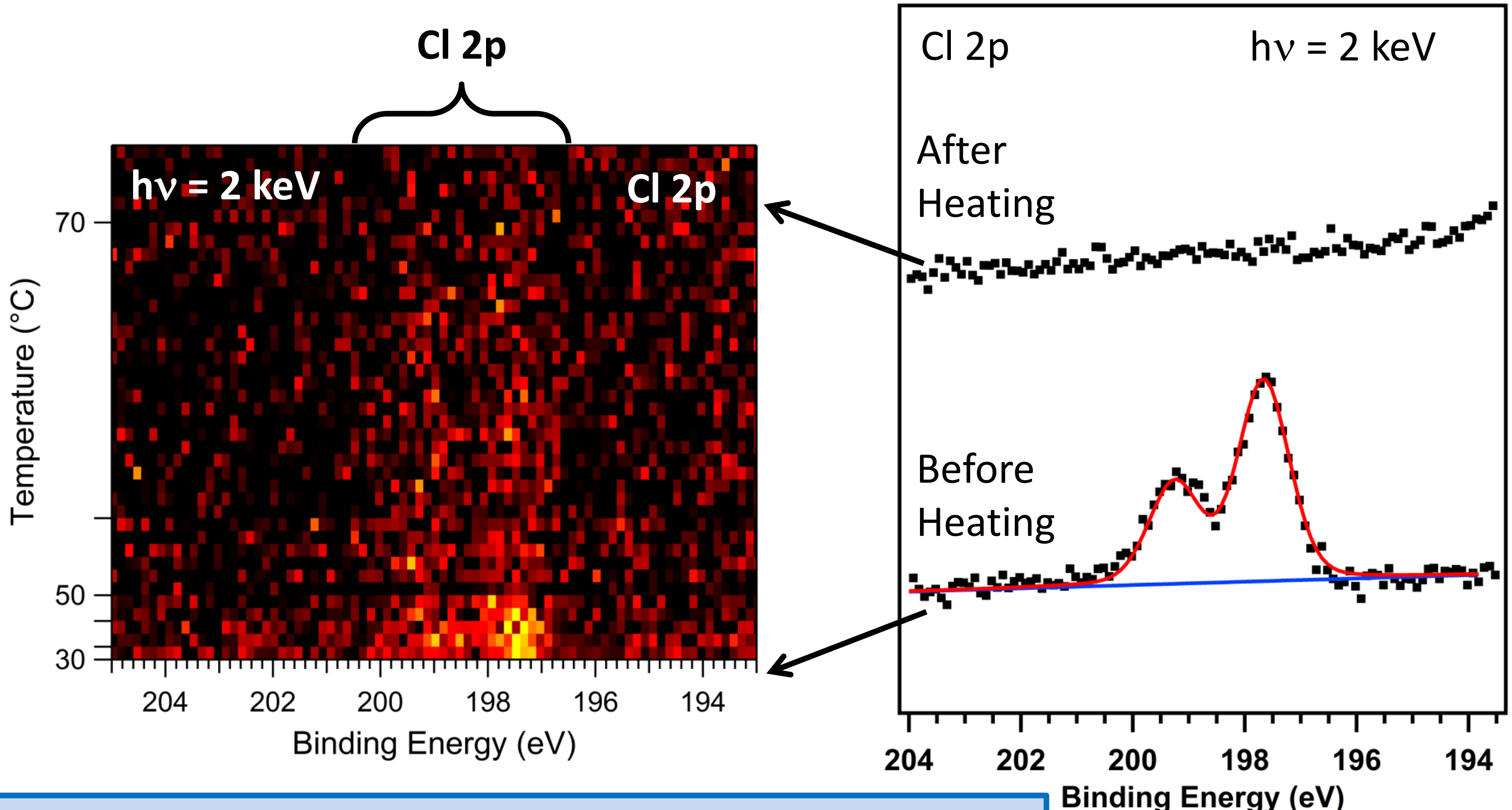




Transition Temperature 80 – 100 °C

*solution prepared @HZB

Depletion of Cl in surface region



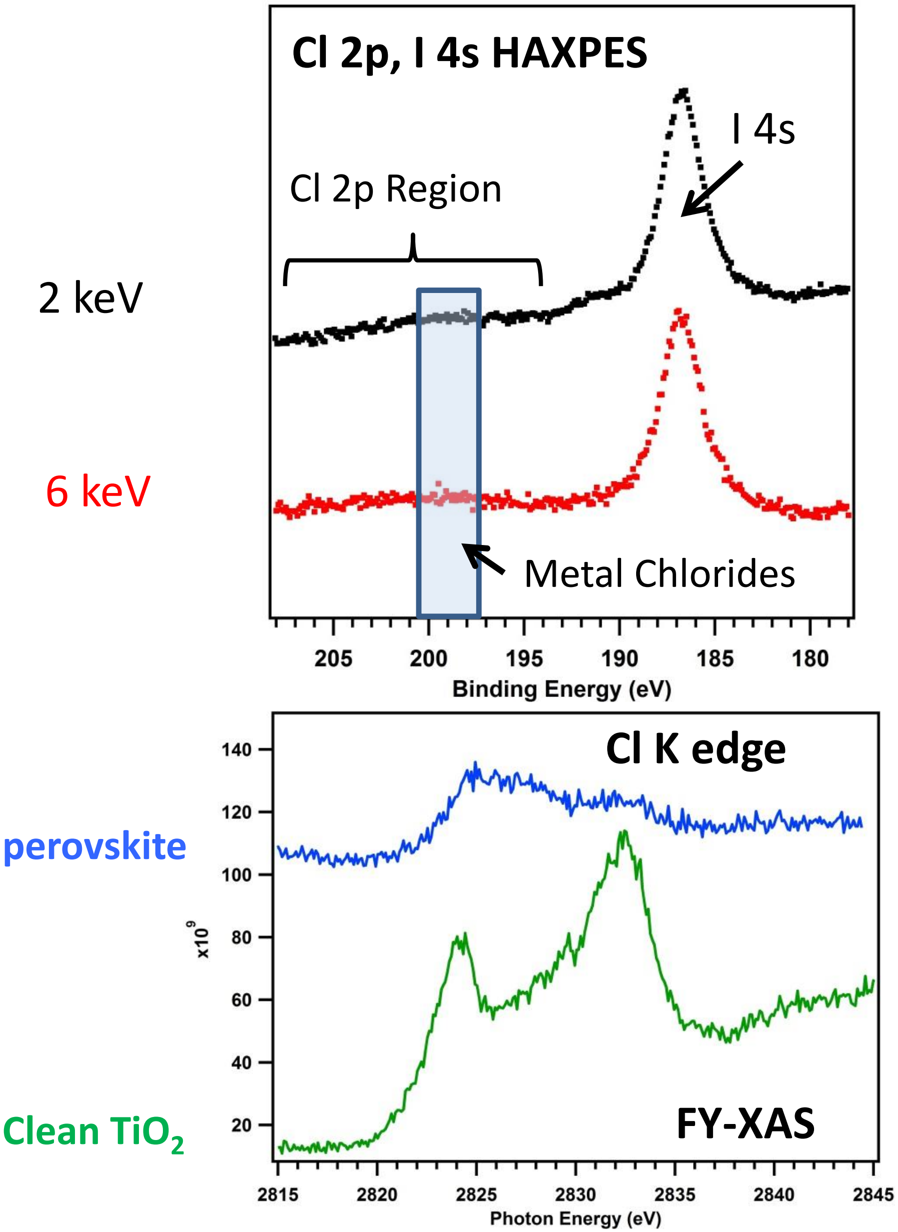
Cl 2p signal decreases drastically at the onset of annealing

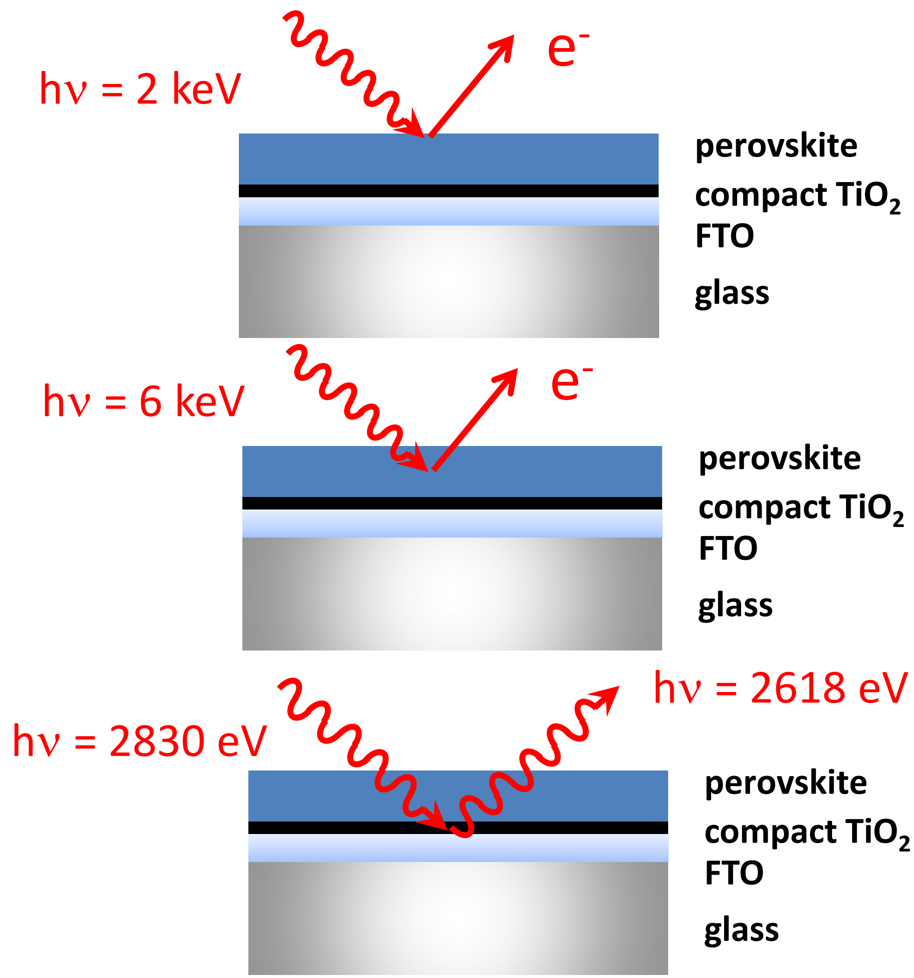
Is depleted in surface region at low temperatures (< 50 °C)

Where does Cl go?

D.E. Starr, G. Sadoughi, E. Handick, R.G. Wilks, J.-H. Alsmeier, L. Köhler, M. Gorgoi, H. Snaith and M. Bär, Energy Environ. Sci. **8** 1609 (2015).

Cl 2p XPS and Cl K edge XAS: Where does the chlorine go?





Cl K edge XAS reveals Cl deep in perovskite

Cl concentration is higher in the bottom half of the 60 nm thick film than near the surface

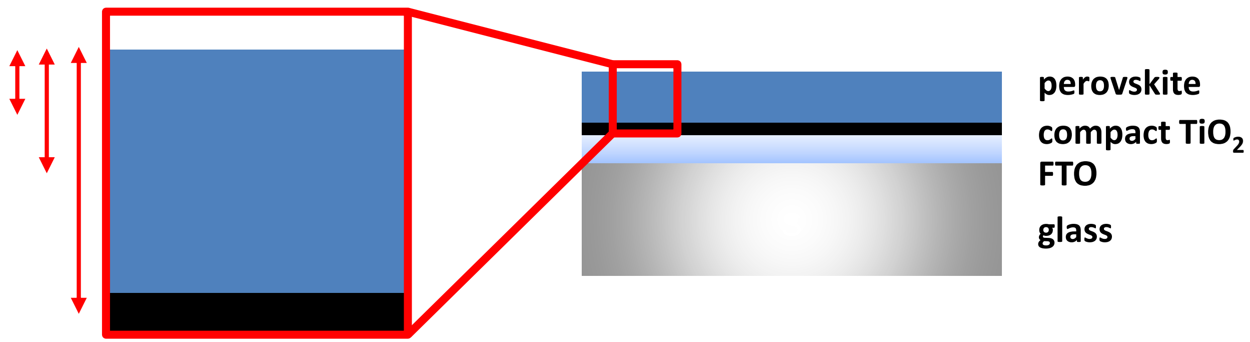
Cl also observed in TiO_2 substrate but different species

D.E. Starr, et al, Energy Environ. Sci. (2015).

Where does the chlorine go?

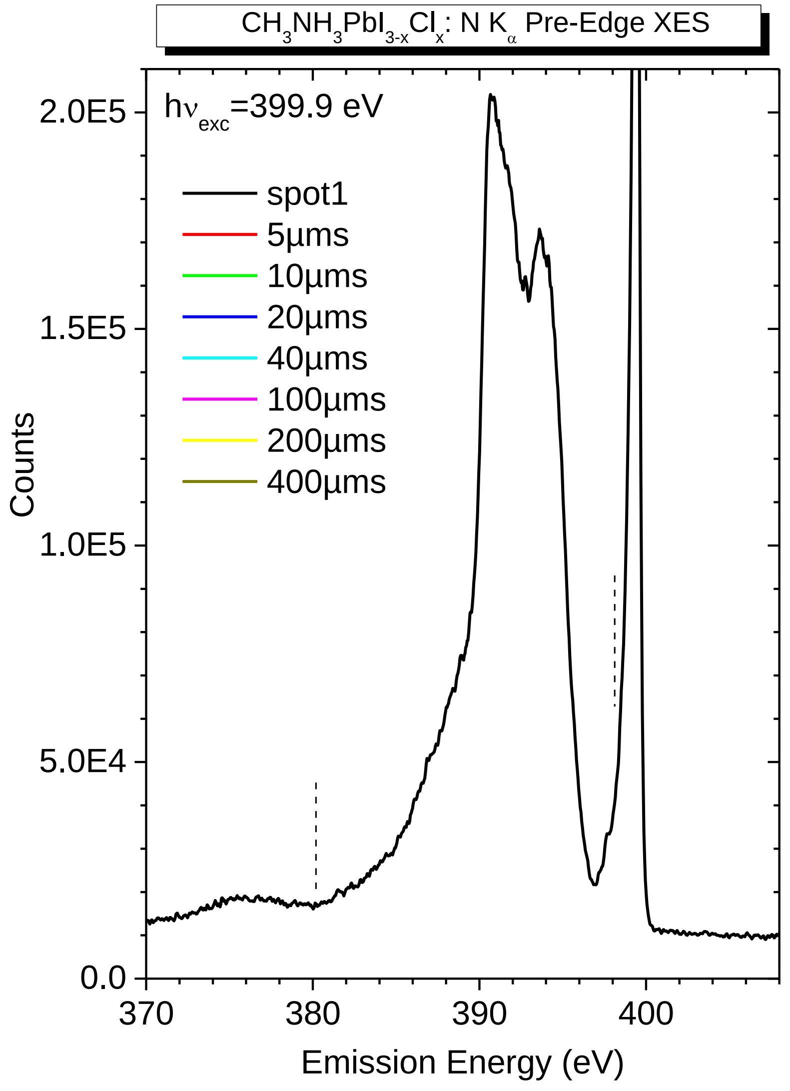
x in $CH_3NH_3PbI_{3-x}Cl_x$

< 0.07 →	10 nm
< 0.40 →	26 nm
≥ 0.40 →	> 26 nm

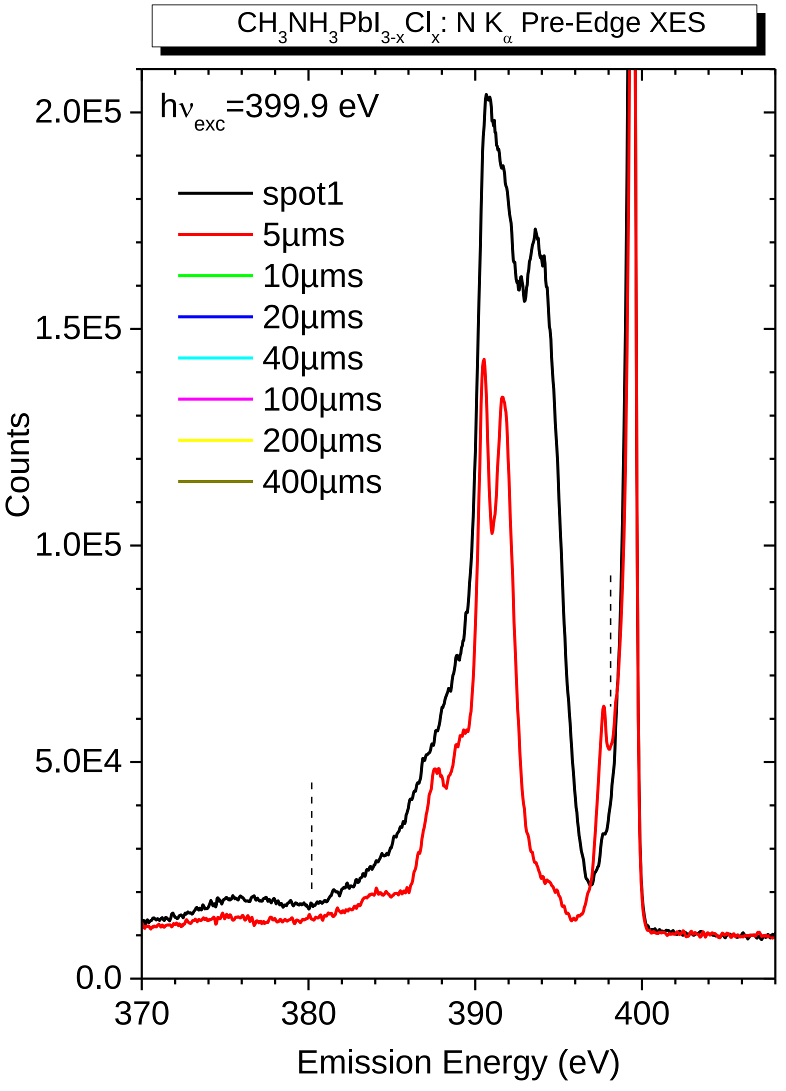


D. Starr et al., Energy Environ. Sci., **2015**,8, 1609.

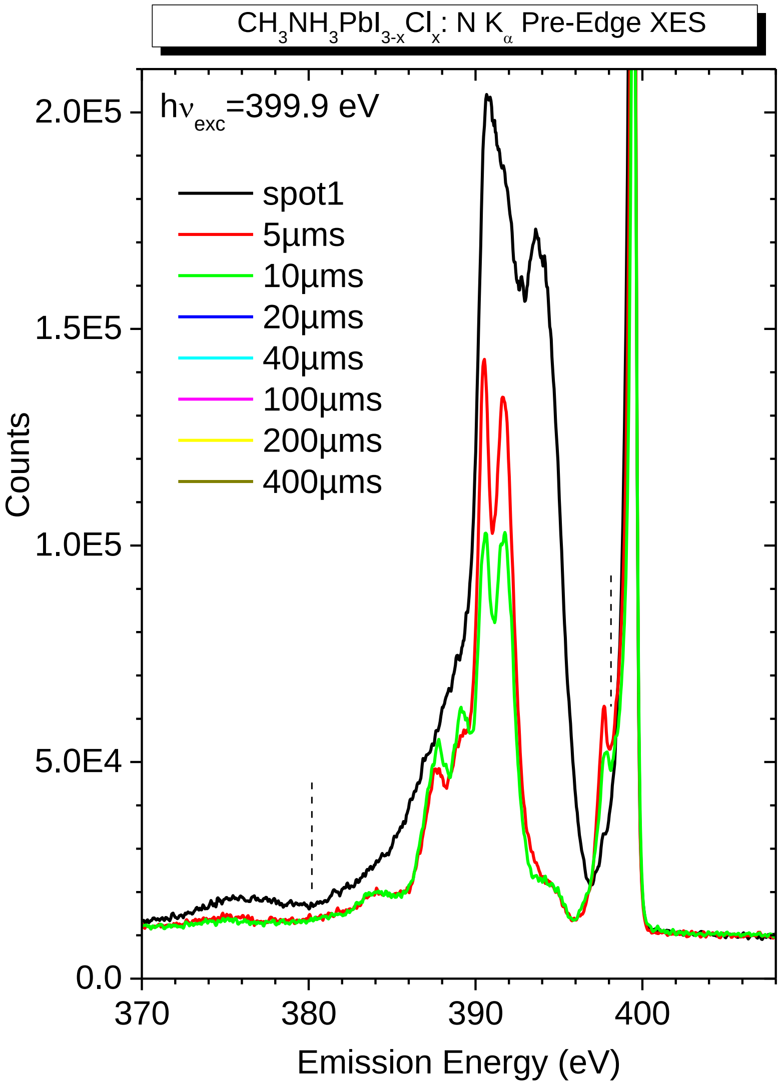
XES: Beamdamage?



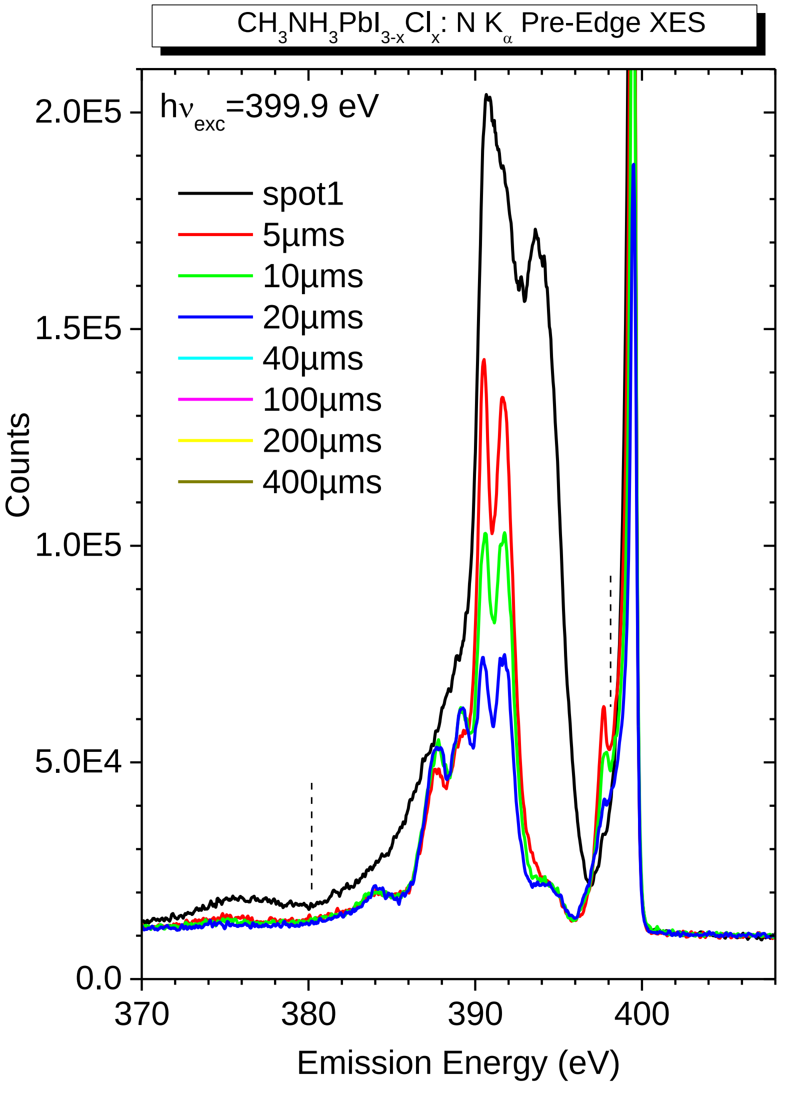
XES: Beamdamage?



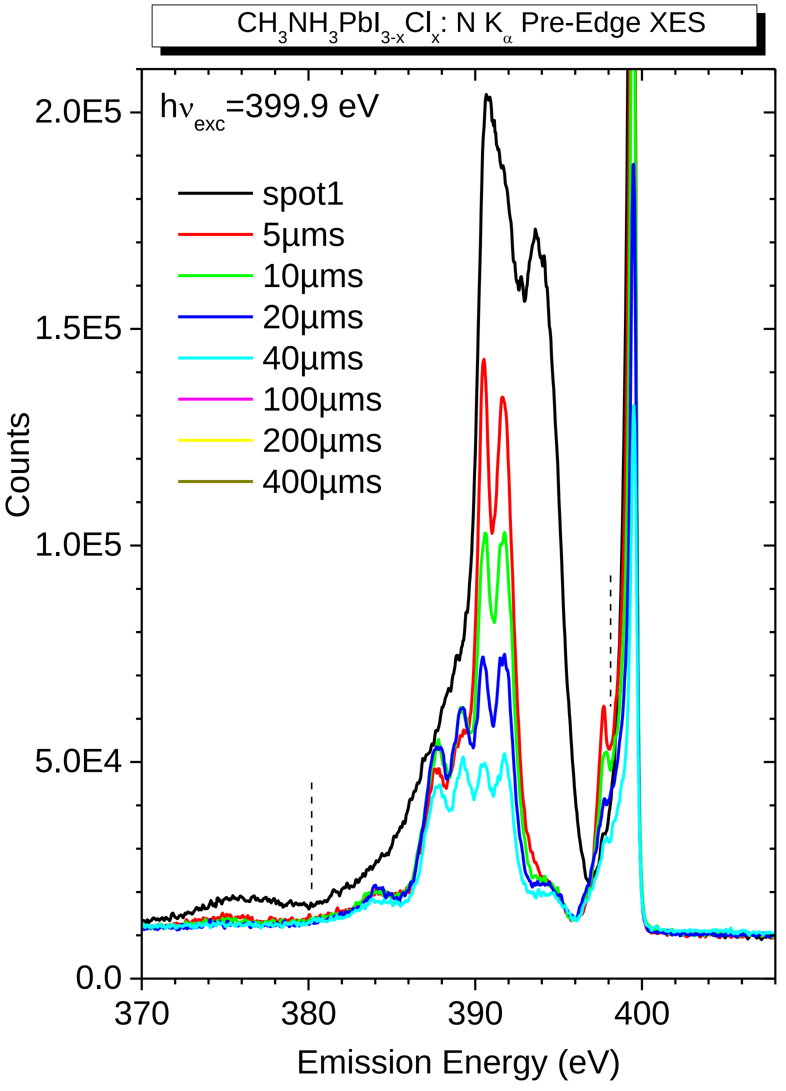
XES: Beamdamage?



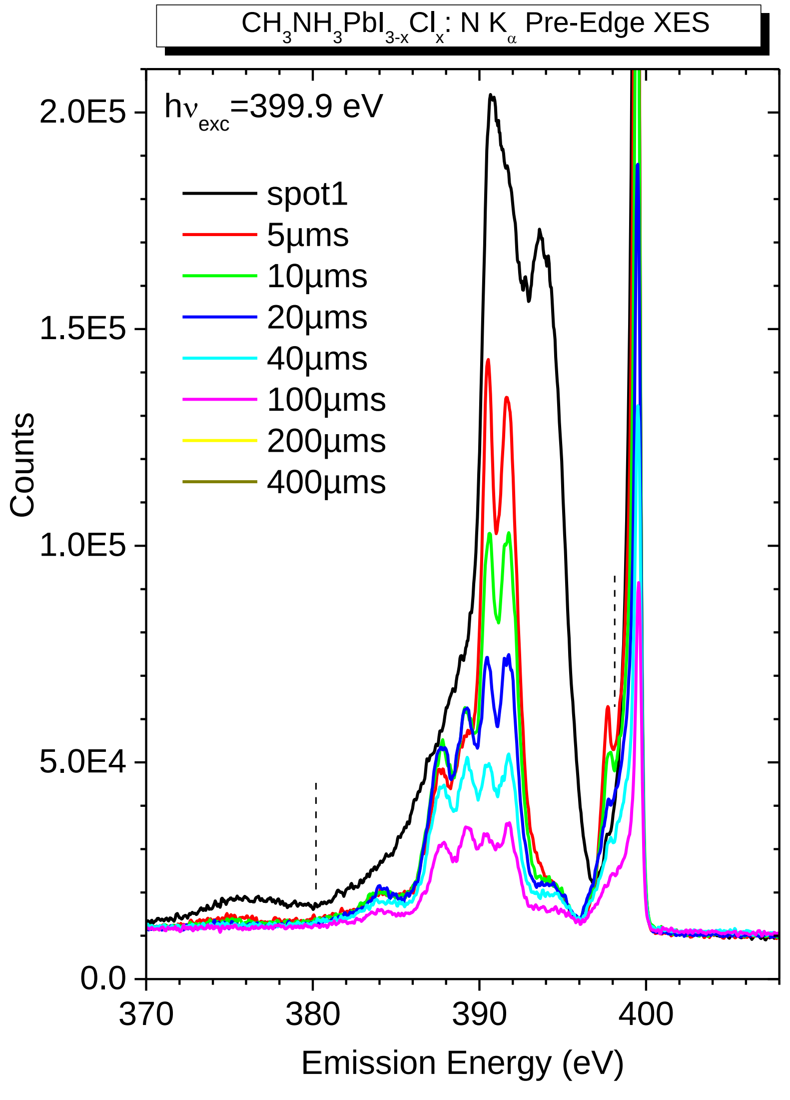
XES: Beamdamage?



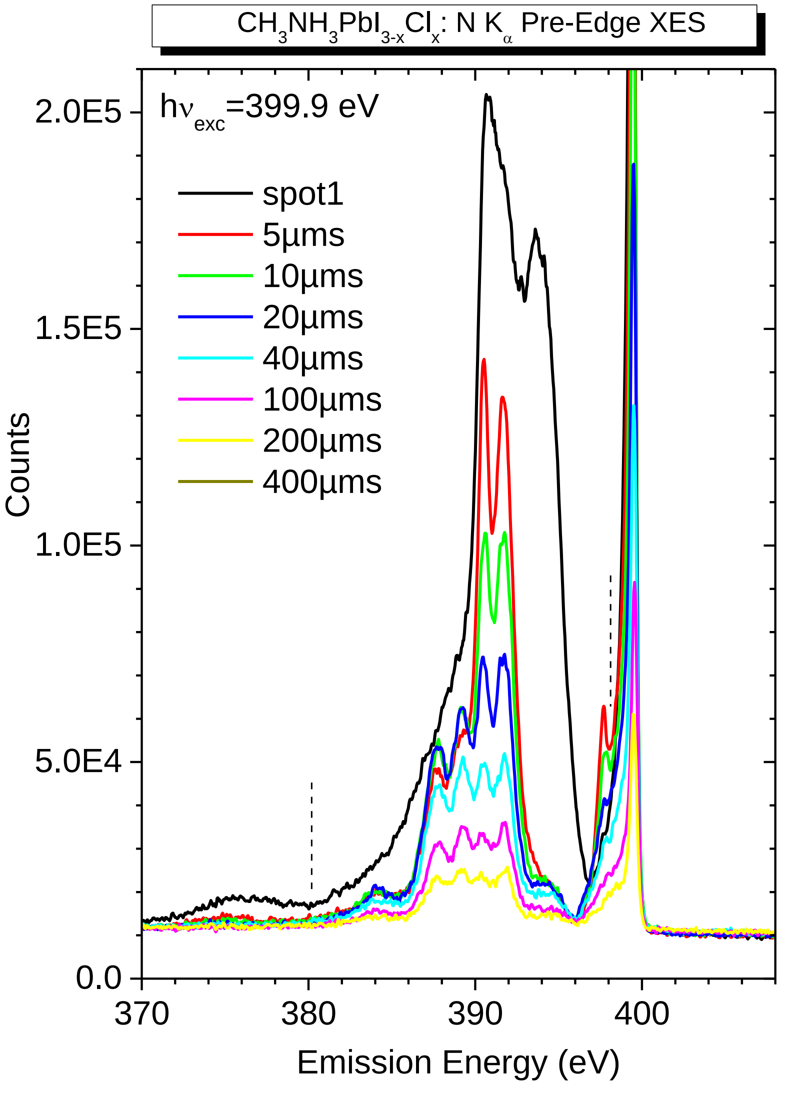
XES: Beamdamage?



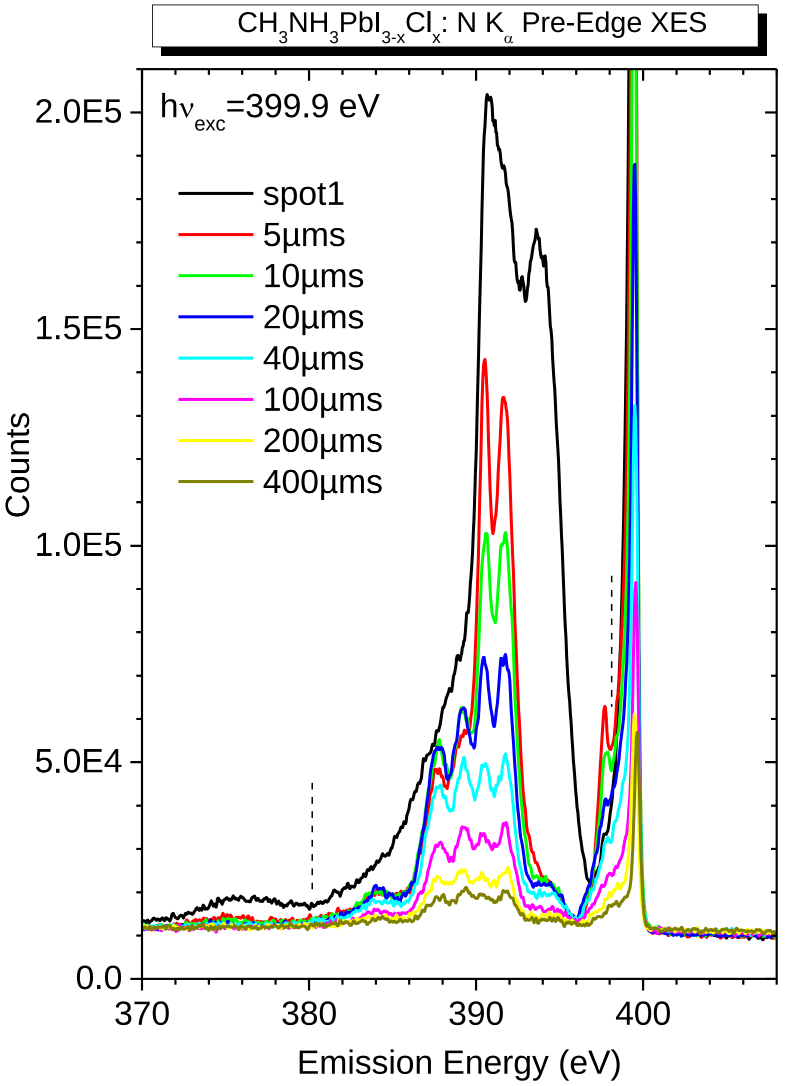
XES: Beamdamage?



XES: Beamdamage?



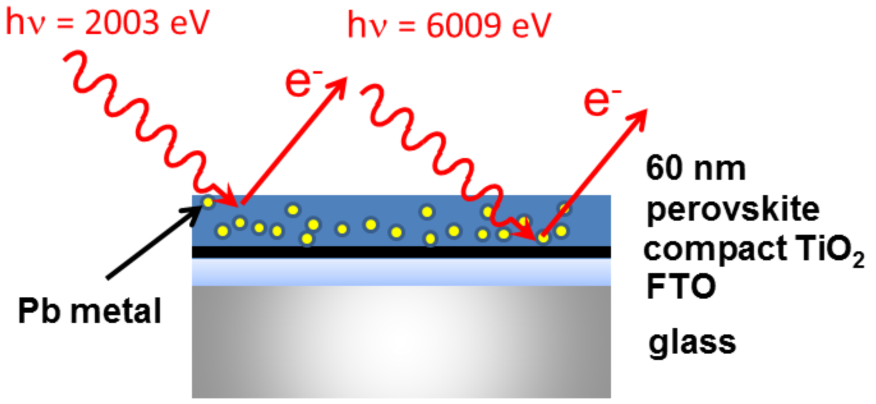
XES: Beamdamage?!!!!!!!!



- N K XES spectra indicate that $CH_3NH_3PbI_{3-x}Cl_x$ is altered in x-ray beam

Summary

- X-ray spectroscopies are well suited to probe the chemical and electronic properties of perovskite-based cell structures
- If observed, metallic Pb increases in its concentration with increasing bulk sensitivity
- No (within the detection limit) Cl is present at the surface of mixed halide perovskites
- Cl concentration increases towards TiO_2 substrate
- Beware of beamdamage



HZB EMIL Helmholtz Zentrum Berlin

ALS

BESSY

SPring-8

The Energy Materials In-situ Laboratory (EMIL) at BESSY II:

SISSY @ EMIL

Energy Materials In-Situ Lab Berlin

Solar Energy Materials In-Situ Spectroscopy at the Synchrotron:

CATalysis Research for Energy Storage (MPG/FHI)

Research alliance between HZB and MPG

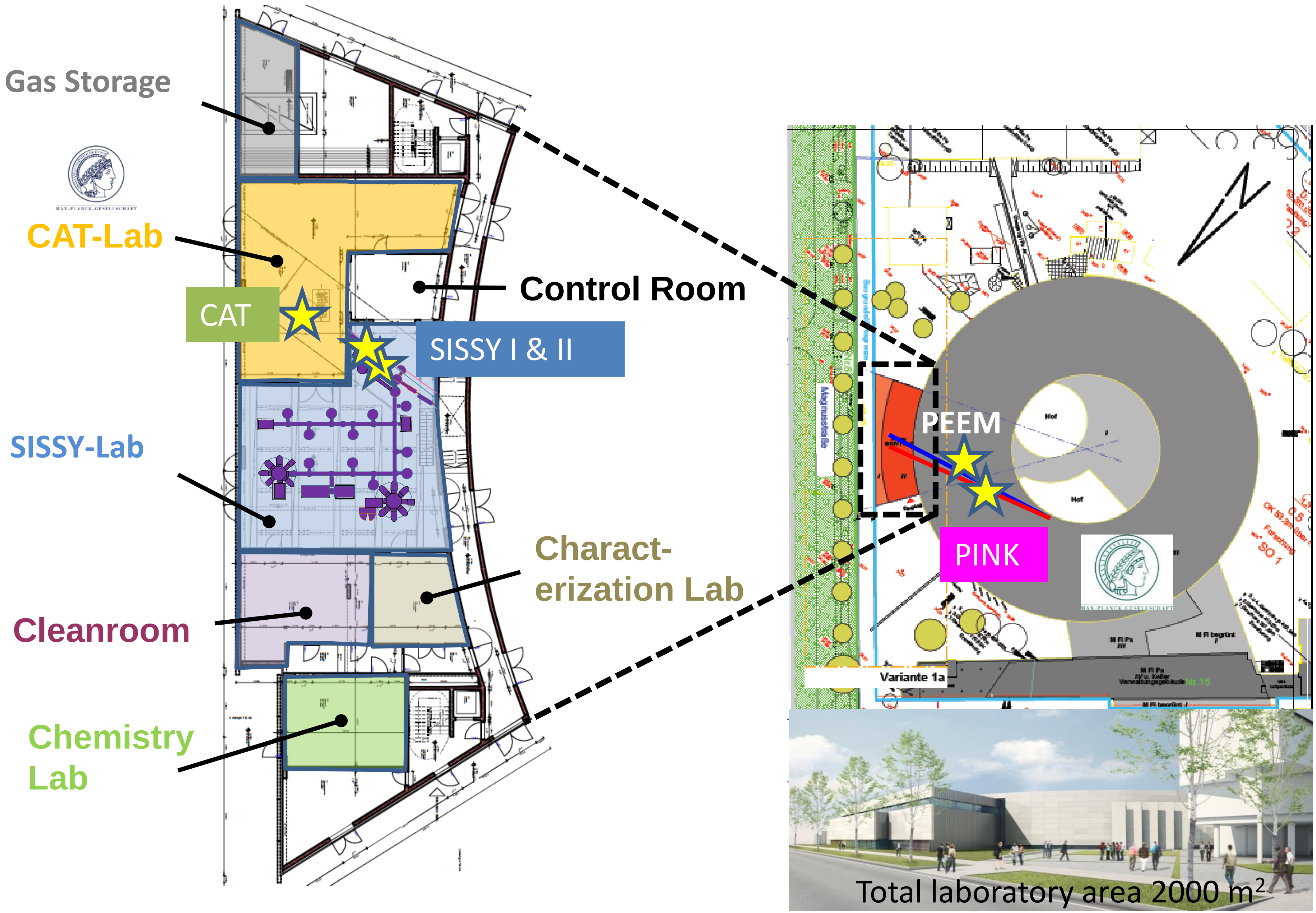
Budget: 26.6 M€ (6.8 M€ HZB, 6.7 M€ MPG, 5.7 M€ BMBF, 7.4 M€ HGF)

Synchrotron-based analytics over large energy range (80 eV – 10 keV)

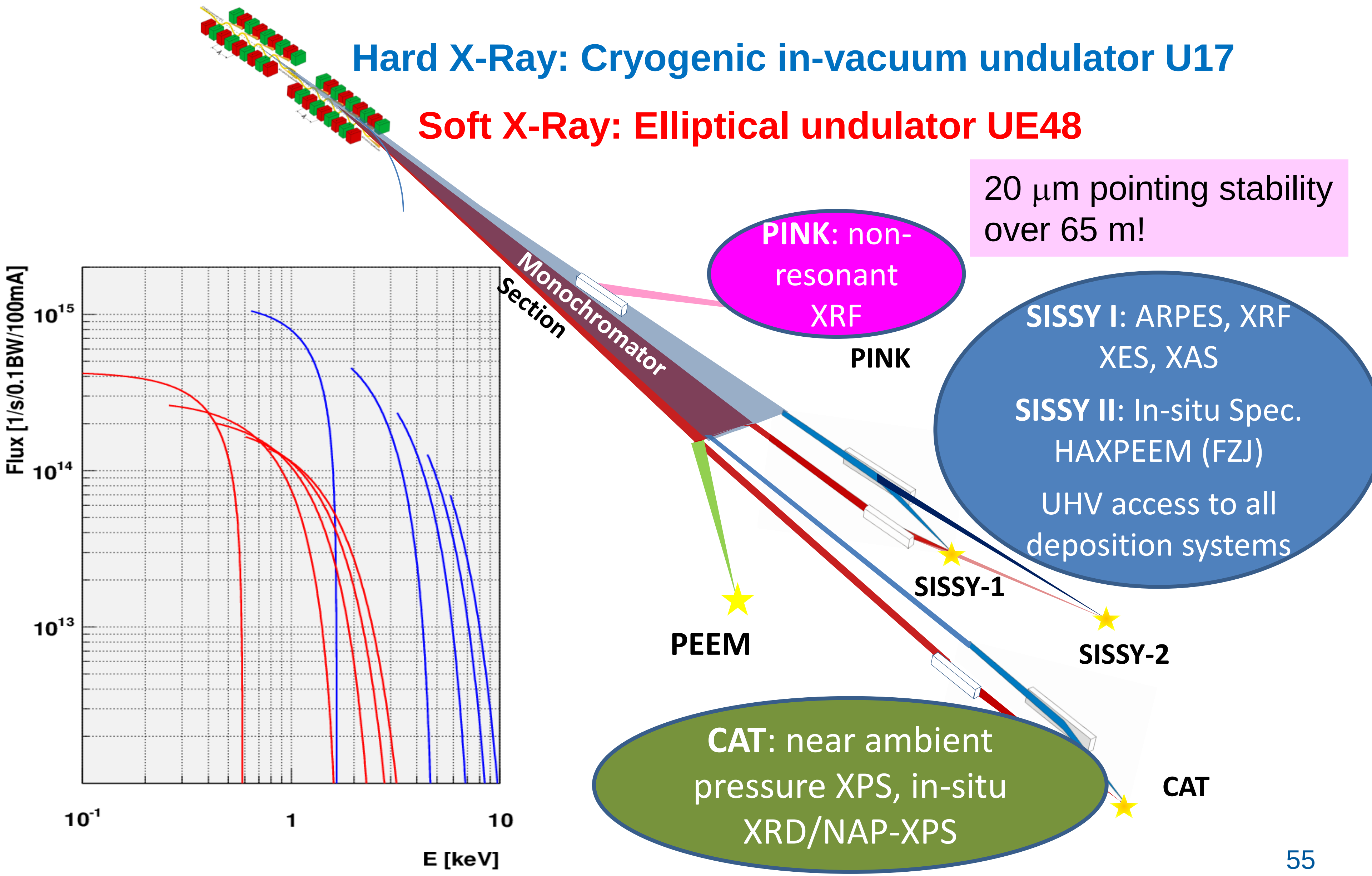
Synthesis and analytics of thin-film materials

In-operando analysis of catalyzers and processes

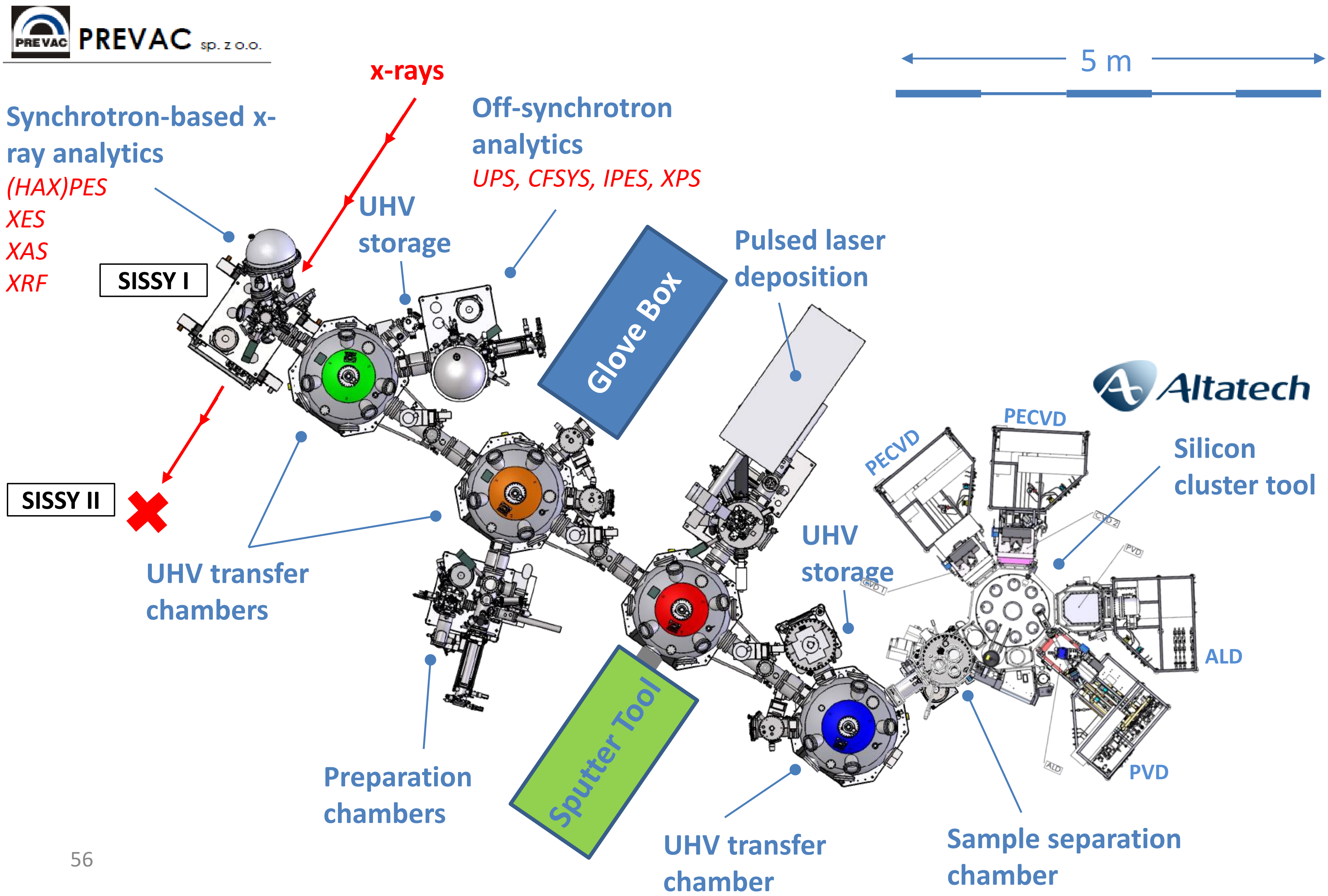
The EMIL Building (2000 qm)



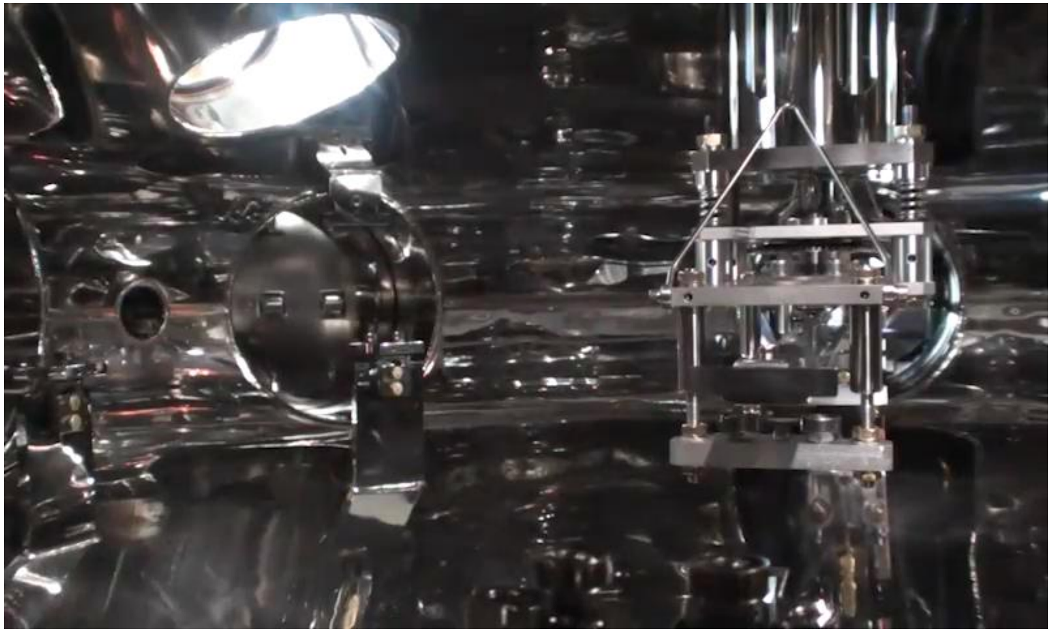
The EMIL beamline (80-10,000 eV)

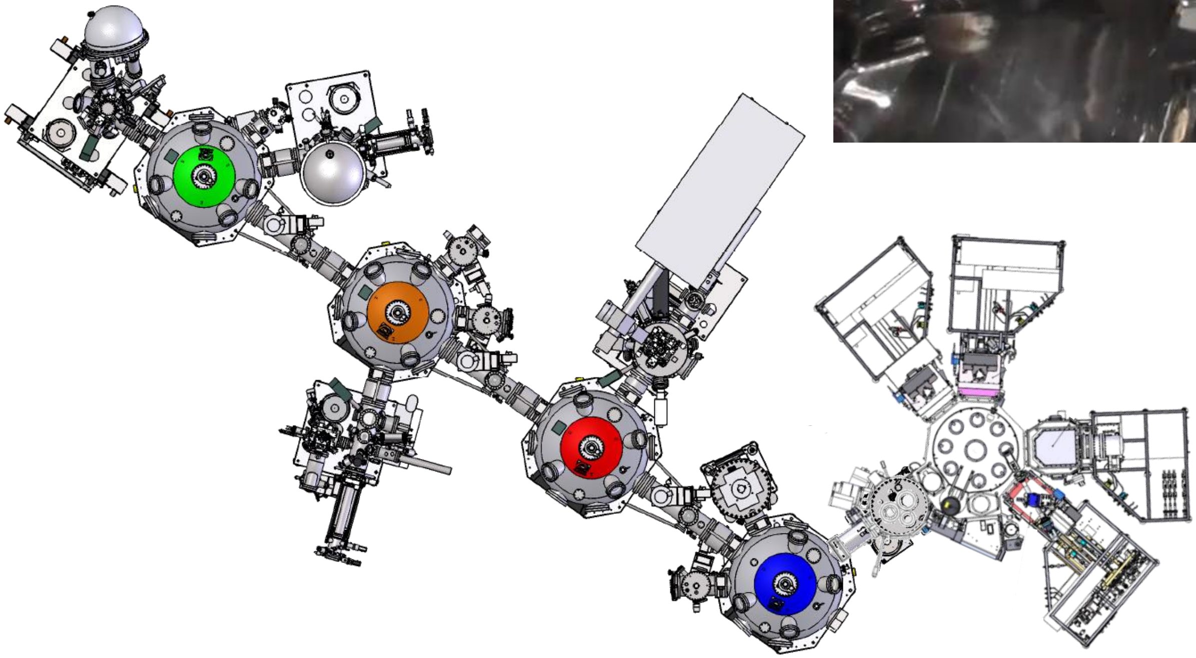


SISSY@EMIL: Analytics, Transfer, Cluster



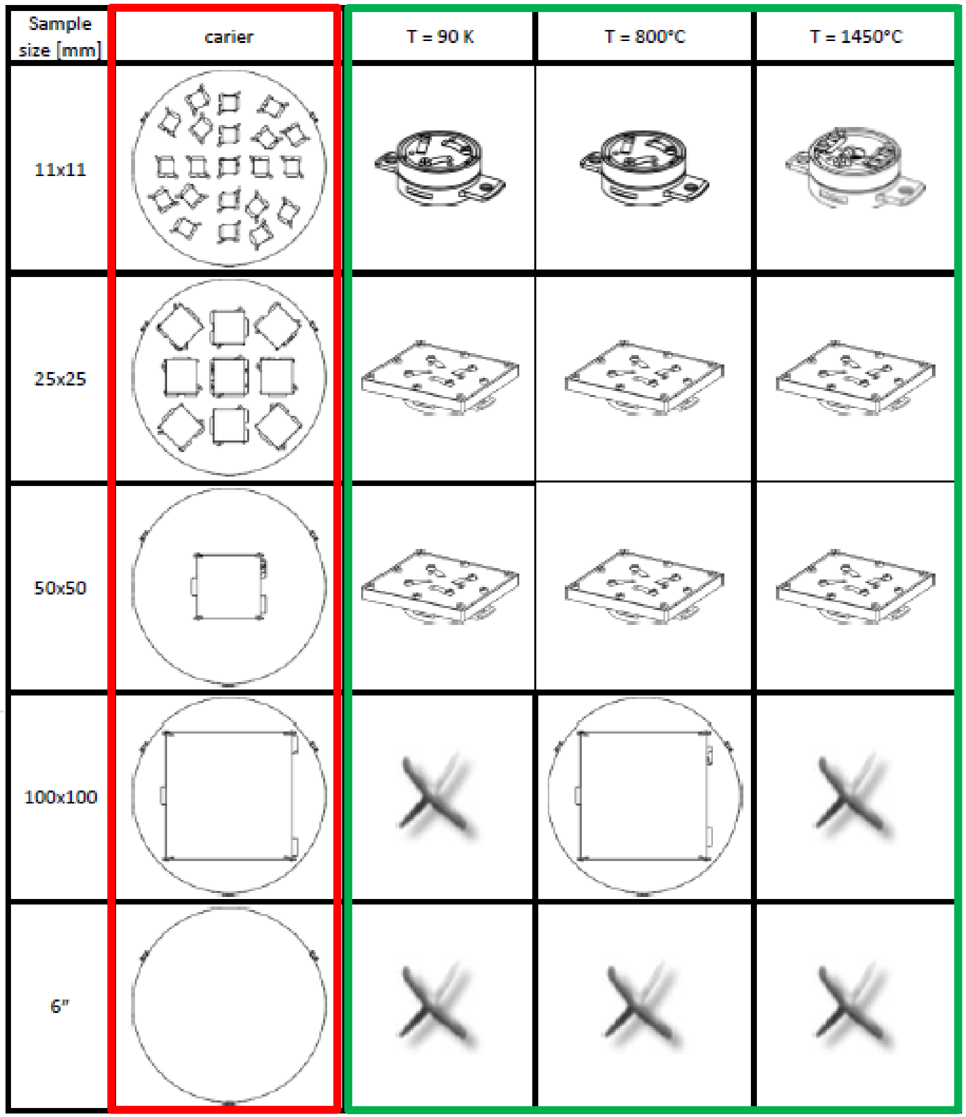
SISSY@EMIL: automated UHV transfer





Sample sizes, holders and adapters

Can be used in Si-deposition system and UHV analytics



T – sample temperature (max. / min.)

Can be used throughout the UHV analytics

EMIL: Advantages for Energy Research

- Unique research environment
  => deposition tools for thin-film materials directly connected to synchrotron analysis without vacuum break (*in situ & in system*)
- (Quasi) permanent access to the synchrotron
  => feedback loop can be established
  => knowledge-driven development of processes, materials, and devices
- Enable the establishment of a world-class international user community and industry collaboration at EMIL
- External User Philosophy
  => Use existing and establish new collaborations with the leading researchers in the world
  => Offer unique characterization and synthesis capabilities at EMIL
  => User support understood rather in form of a collaboration than a service

→ Attractive to researchers from all energy materials communities and beyond…

Acknowledgements: EMIL

K. Lips: Technical Project Head

S. Raoux: Head of Steering Committee, Nanospectroscopy/PEEM

G. Reichardt: Technical Director

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R. Follath, F. Schäfers, S. Hendel, M. Hävecker & team: Beamline optics

R. Keilholz & team, hammeskrause, planungsgruppe M&M: Construction and lab

M. Bär, D. Starr, R.G. Wilks, I. Lauermann, T. Lußky: SISSY analytics

T. Schulze, F. Fenske, O. Gabriel, K. Ellmer, M. Reiche: Deposition tools

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R. v. de Krol, K. Ellmer, K. Harbauer: PLD

Ch. Jung & team: Domino

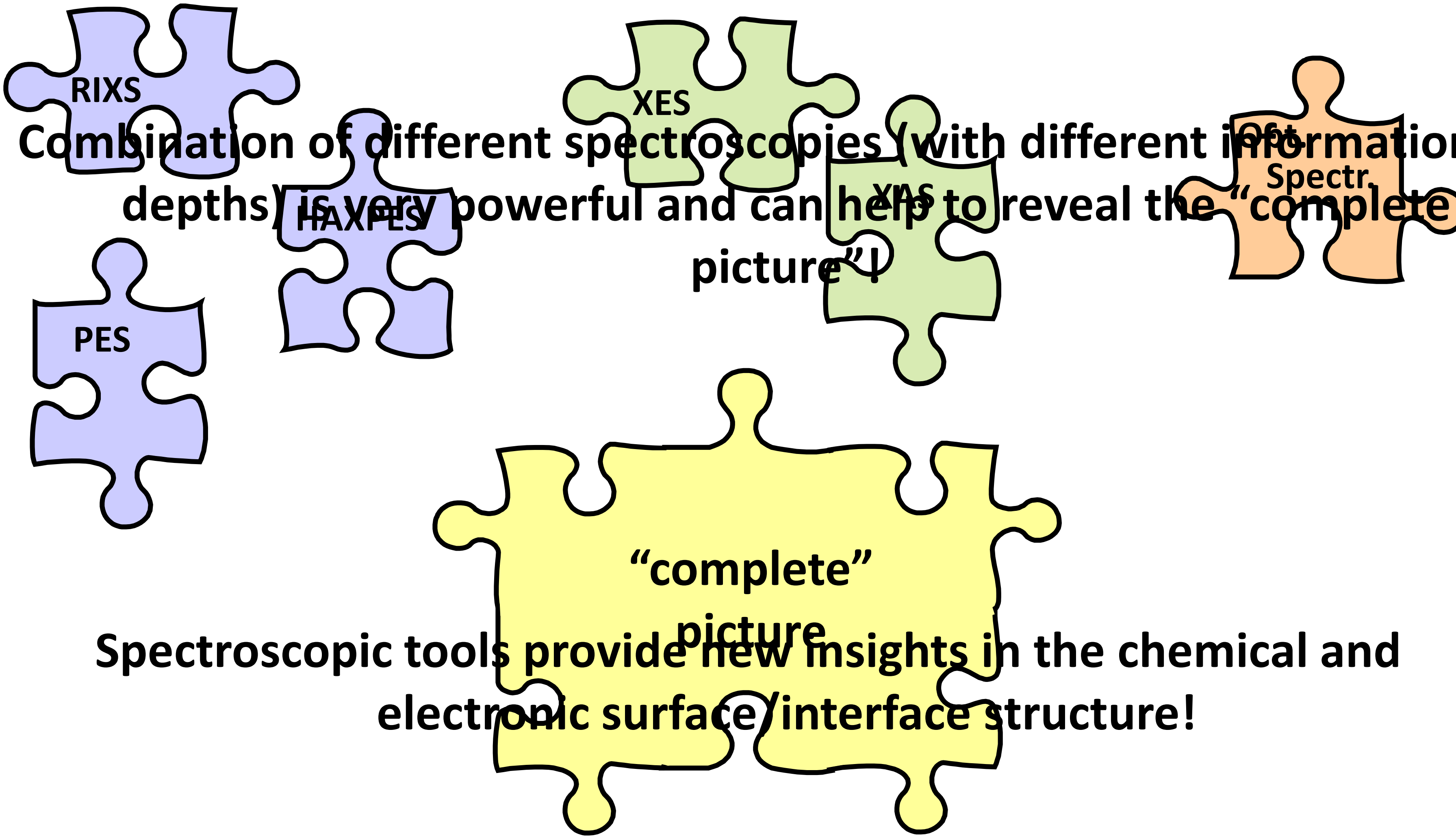
A. Tallarek, J. Proszak: Team assistance

H. Schlender, I. Helms & team: Communication

M. Gorgoi, W. Eberhardt: Discussion and collaboration on HAXPES

B. Rech, R. Schlatmann & team: Renewable Energy Division at HZB

Funding: BMBF, HGF, HZB, MPG



Combination of different spectroscopies (with different information depths) is very powerful and can help to reveal the “complete picture”!

Spectroscopic tools provide new insights in the chemical and electronic surface/interface structure!