Heterogeneous Interfaces Investigated by Photoelectron Spectroscopy

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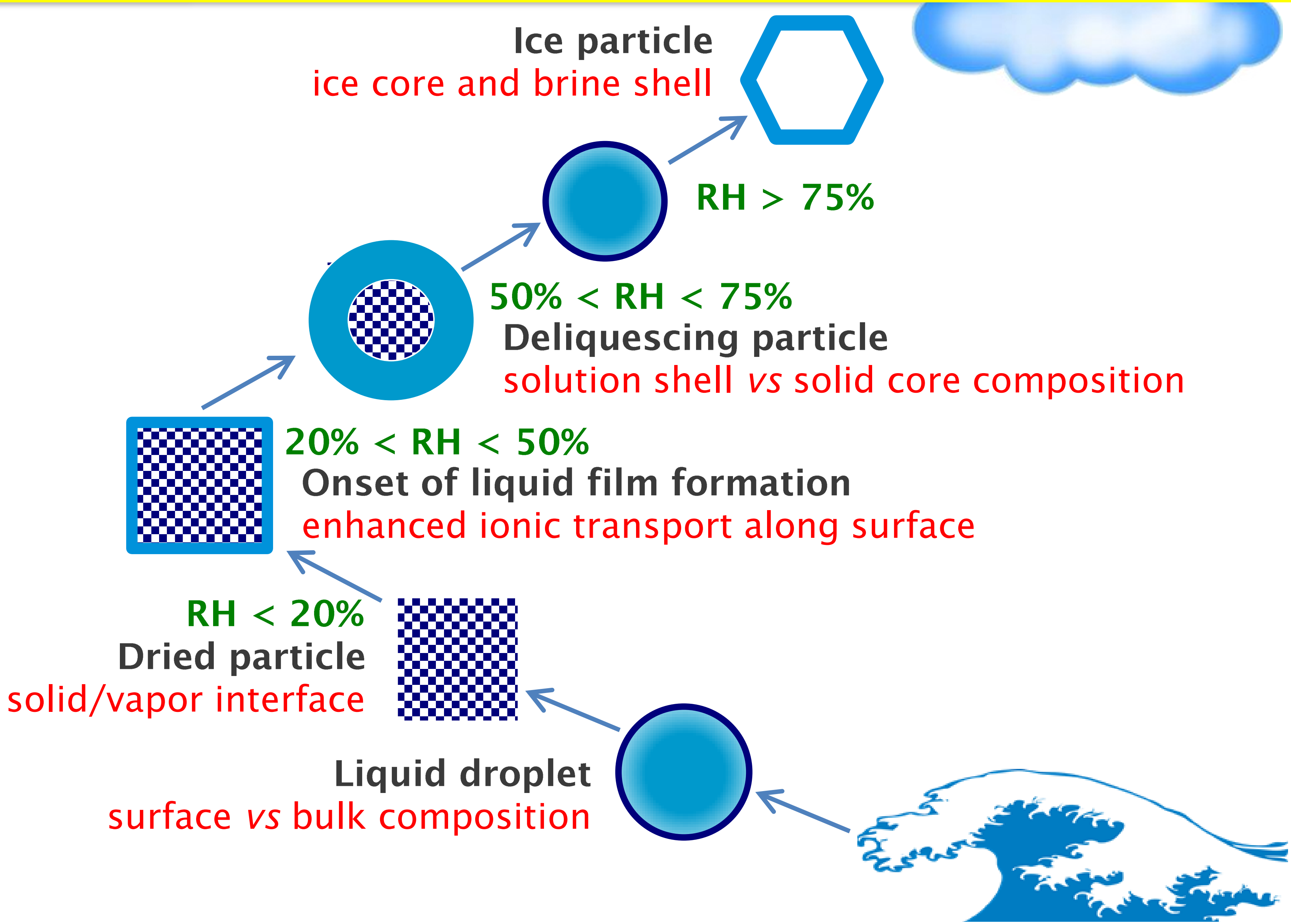
LBNL Interdisciplinary Instrumentation Colloquium
Wednesday, 27 May 2015

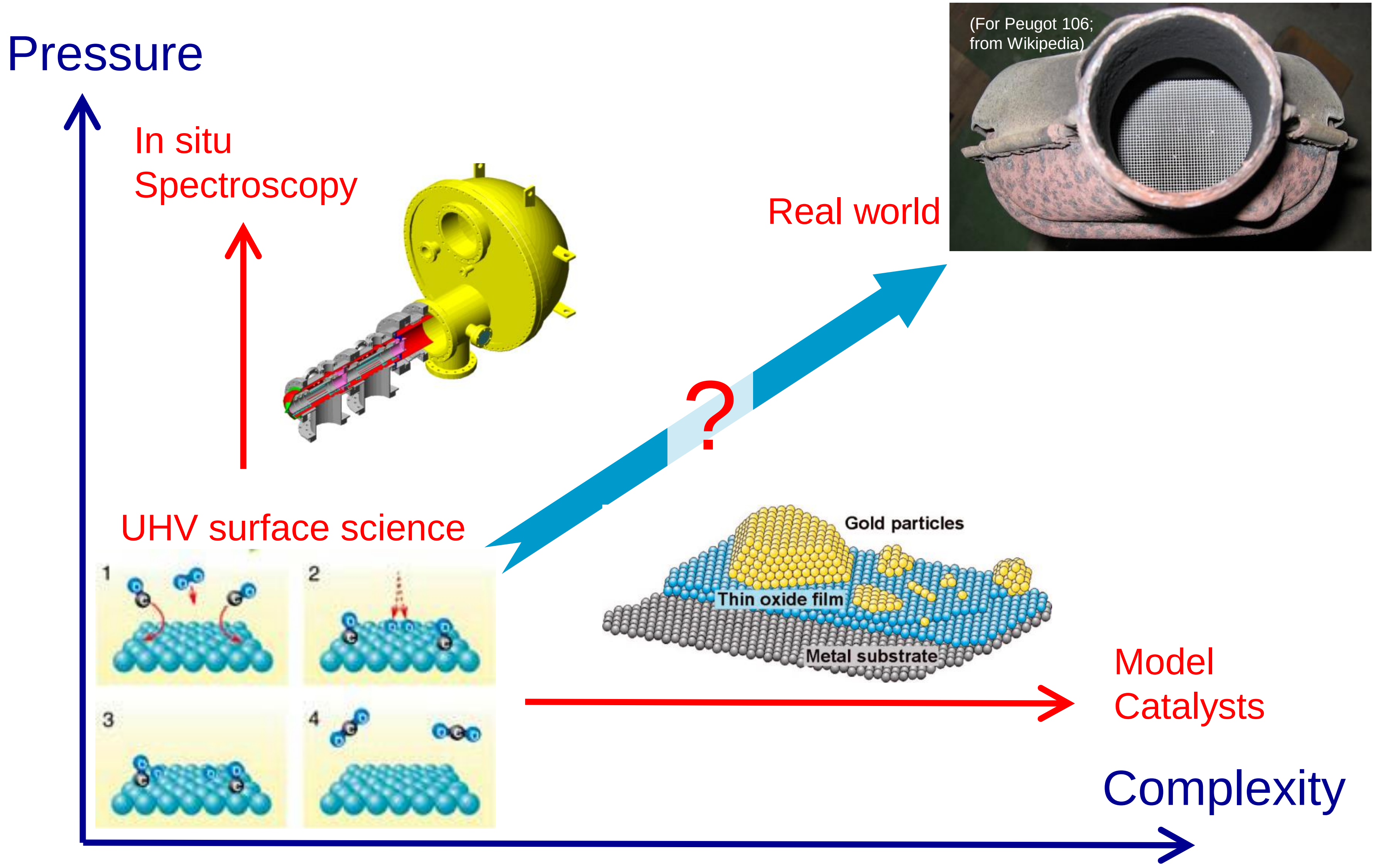
Outline

- Interfaces in the environment and technology: Solid/gas, liquid/gas, solid/liquid, and solid/solid
- Photoemission spectroscopy: Basic technical considerations; Inelastic mean free path in solids and gases
- Studying interfaces under realistic conditions: Ambient pressure and buried interfaces
- Ambient pressure photoemission-instrumentation
- Solid/solid interfaces: Instrumentation and detectors
- Standing wave photoemission
- Application to the solid/liquid interface
- Application to complex oxide interfaces

Complex Interface Chemistry of a Seasalt Aerosol Particle

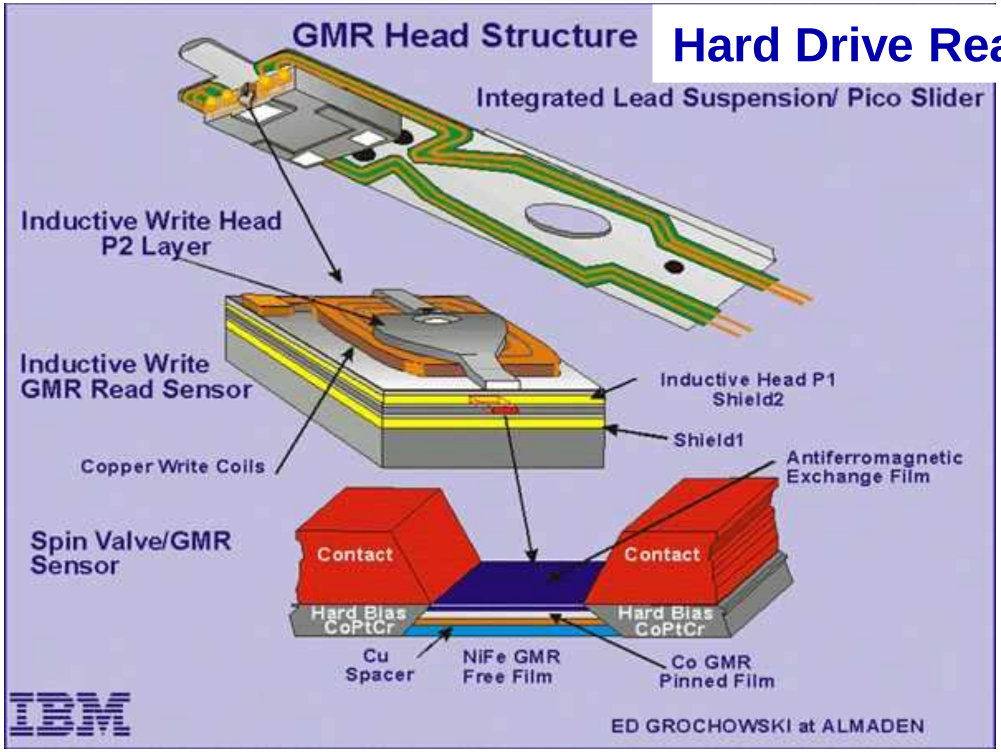


Bridging the Materials and Pressure Gap in Catalysis

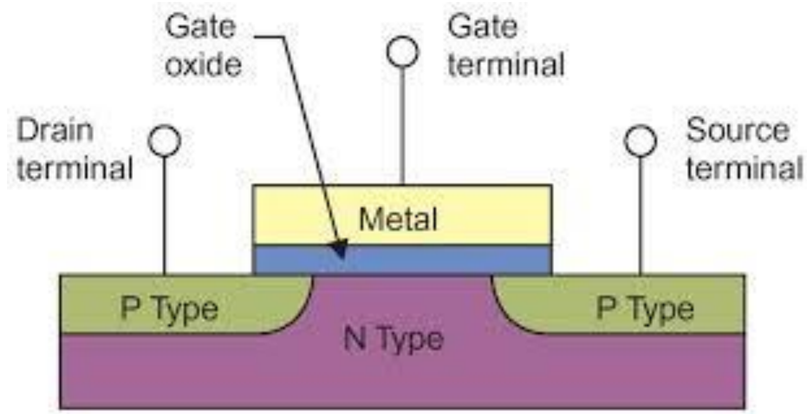


Interfaces in information and energy technology

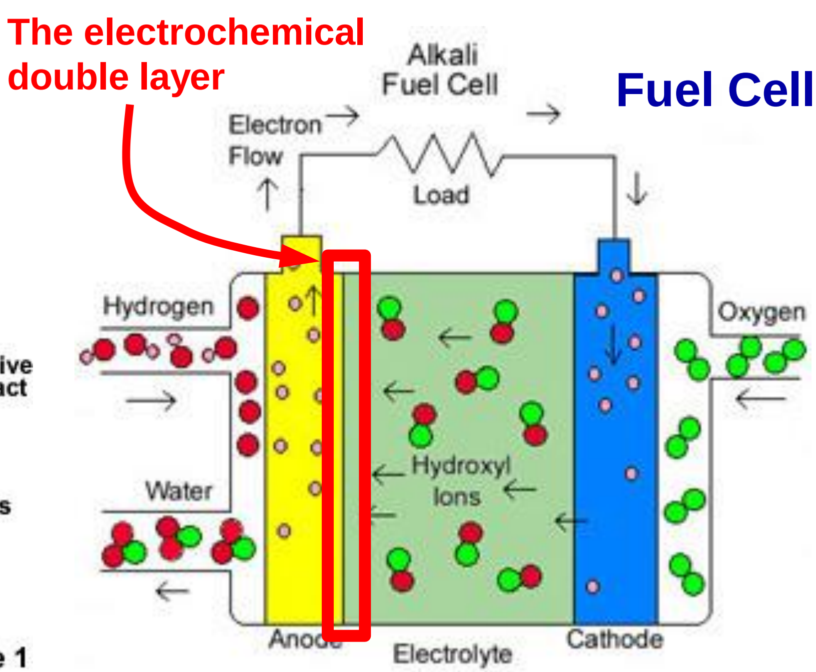
Hard Drive Read Head



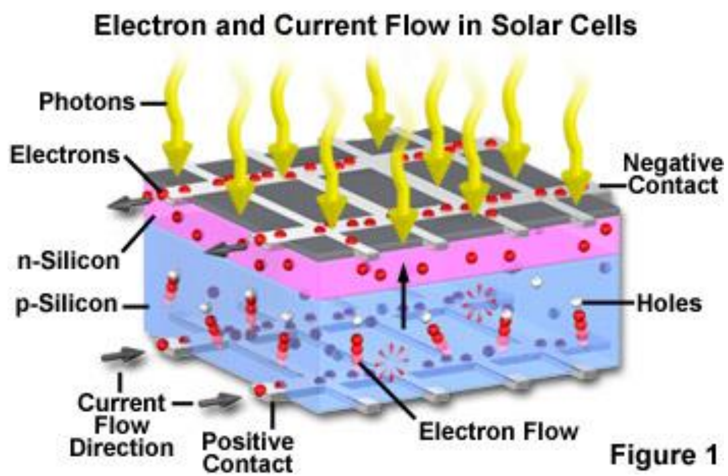
Transistor



Fuel Cell



Photovoltaic Cell



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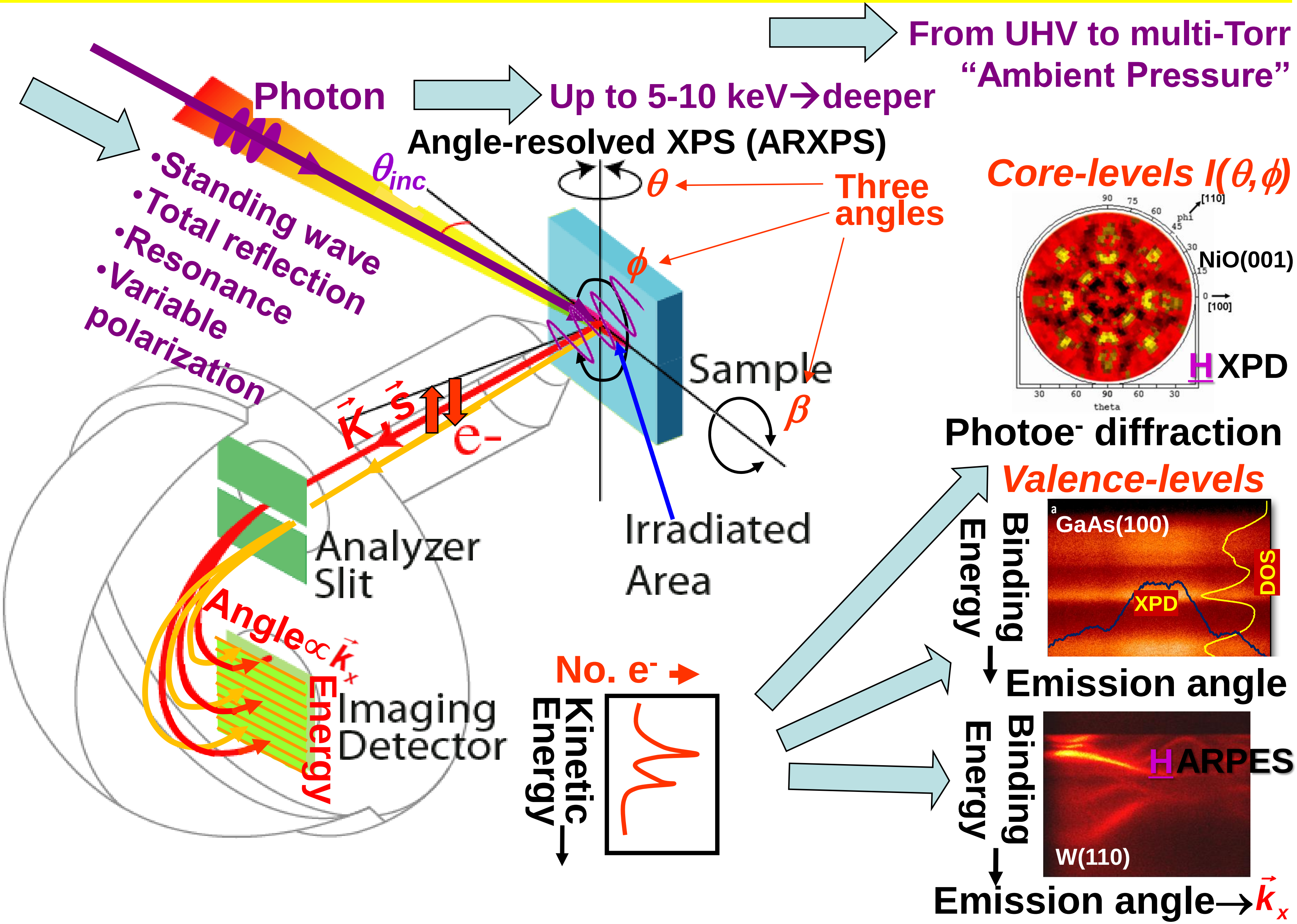
X-ray photoemission: some key elements

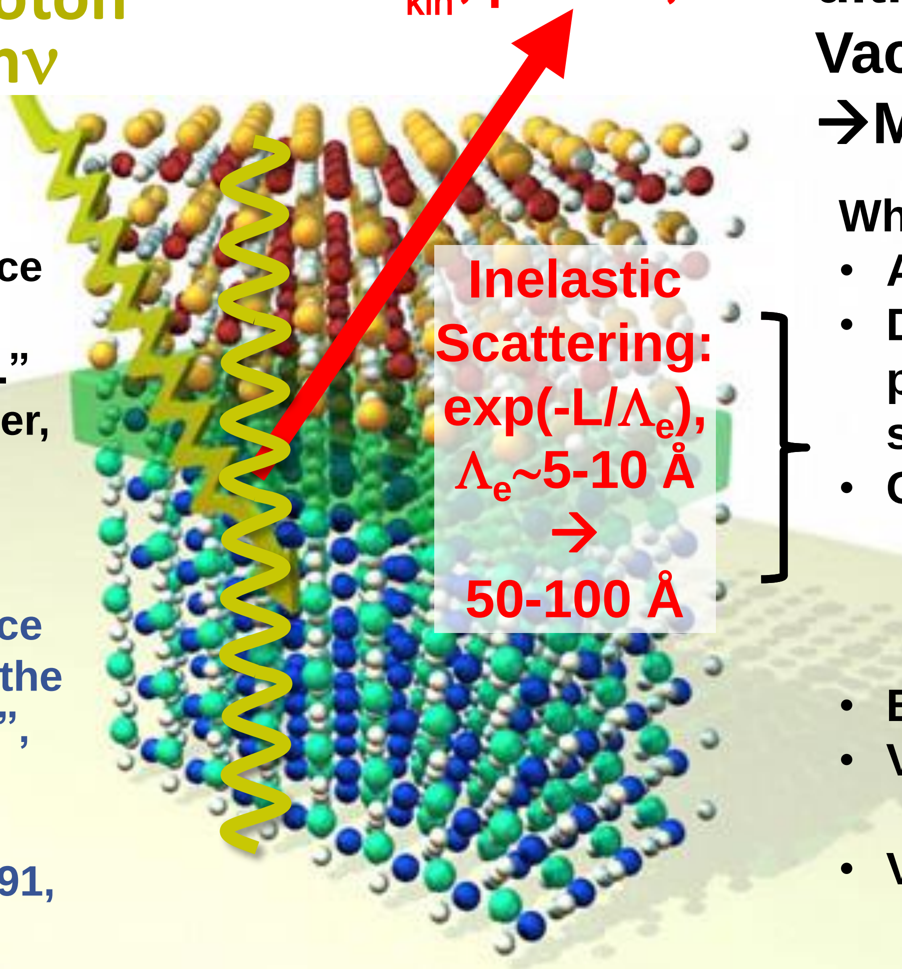


Photoemission from surfaces, complex bulk materials, buried layers, interfaces

Photon
hν

Photoelectron

$E_{kin}, \vec{p} = \hbar\vec{k}, \vec{s}$



"The interface is the device." Kroemer, Nobel, 2000

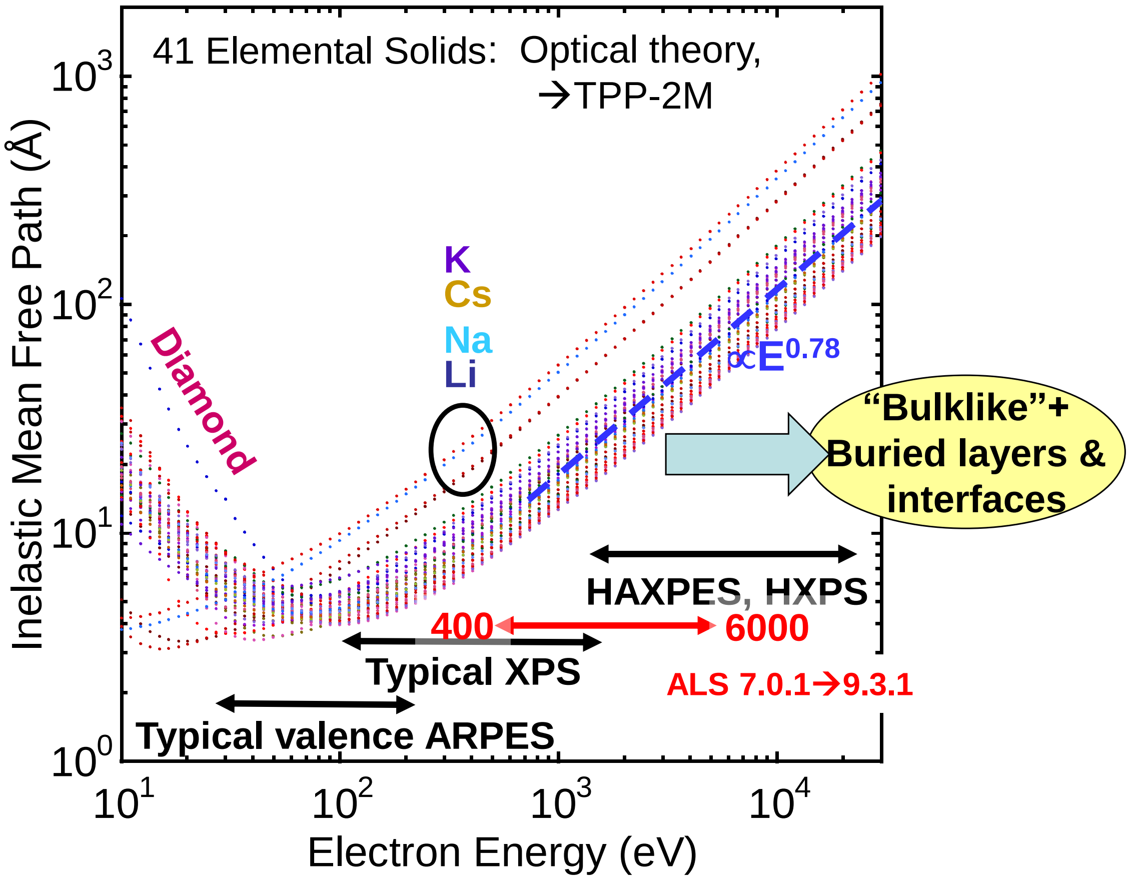
"The interface is still the device", Nat. Mater., <u>11</u>, 91-91, (2012)

Usually ultrahigh Vacuum →Multi-Torr

What do we want to know?

- **Atomic structure, lattice distortions**
- **Depth profiles of composition, optical properties, magnetization, from surface inward, at interfaces**
- **Core-levels→element-specific**
  binding energies, charge states
  electronic configurations,
  magnetic moments/magnetization
- **Band offsets, depth-dependent pot'ls.**
- **Valence-band densities of states**
  bandgaps, behavior near E_F (XPS)
- **Valence-band dispersions, via**
  depth- and angle- resolved
  photoemission (ARPES)

The reasons for higher photon energies

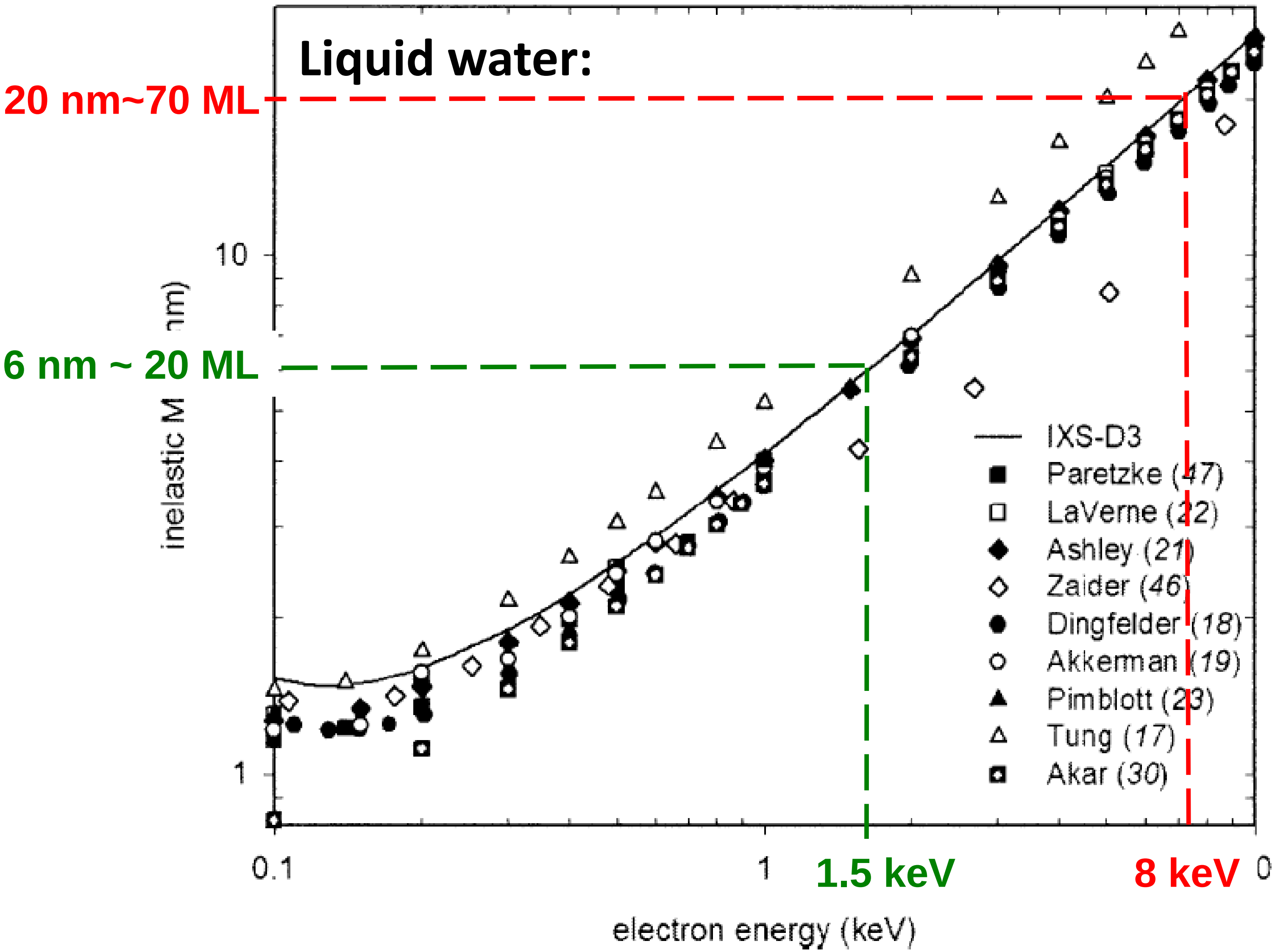


Tanuma, Powell, Penn, Surf. and Interf. Anal. 43, 689 (2011)

- More bulk sensitive spectra: a versatile tool for any new material or multilayer nanostructure
- Broad range of applications to date!: alloys, SC materials, oxides, magnetic devices, PVs, batteries, in operando, ambient pressure,…

- "Recent advances in Hard X-ray Photoelectron Spectroscopy (HAXPES)", Journal of Electron Spectroscopy and Related Phenomena, Volume 190, Part B, Pages 125-314 (October 2013)
- "Some future perspectives in soft- and hard- x-ray photoemission", CSF and S. Nemšák, J. Electron Spect. 195, 409–422 (2014)

Inelastic Mean Free Path of Electrons in Water



Gas-phase water:
IMFP(g) ≈IMFP(ℓ)x ρ(g)/ρ(ℓ)

Can limit pressure if energy is too low

Emfietzoglou & Nikjoo, Rad. Res. 2007.

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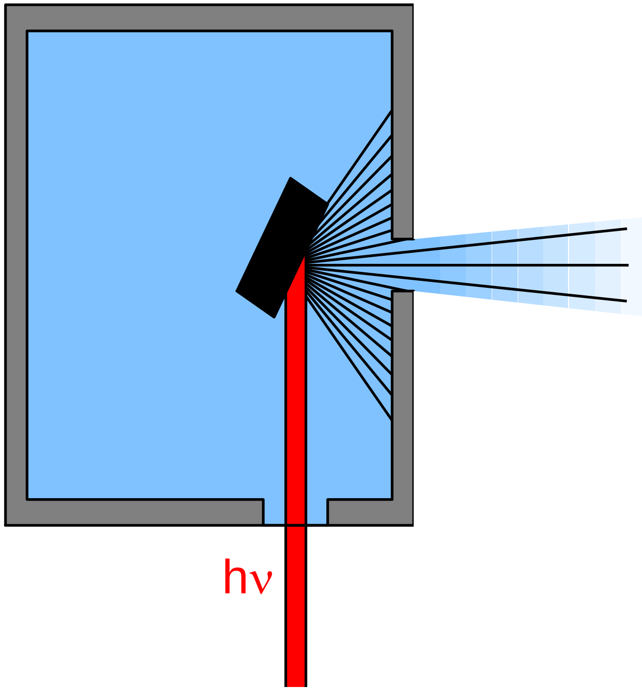
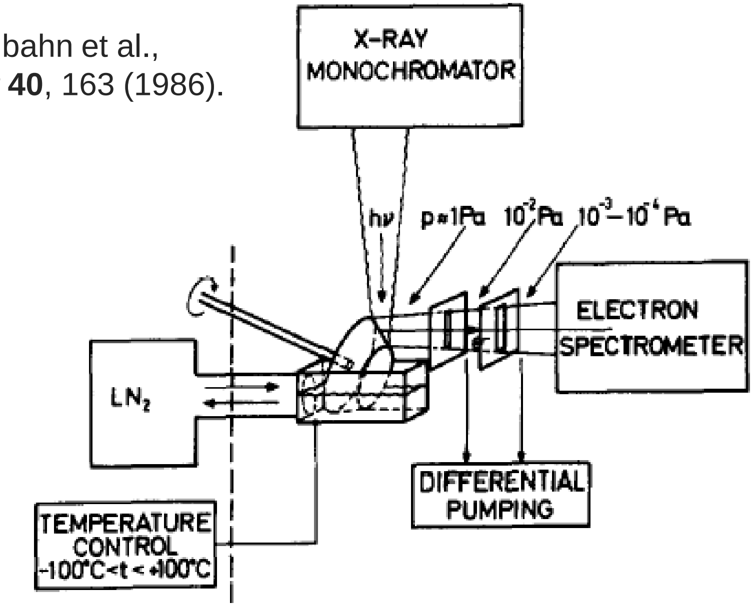
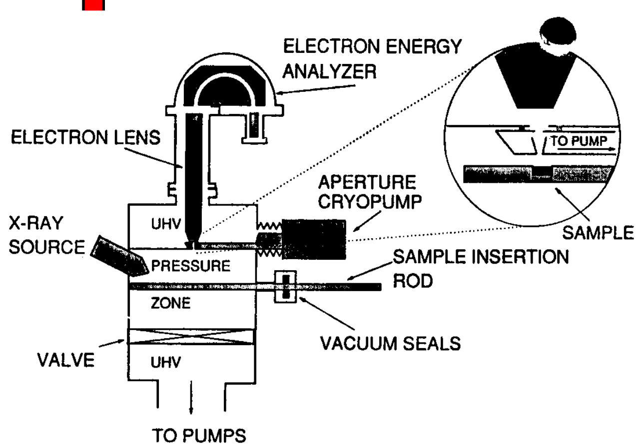
Early Ambient Pressure XPS Designs

H. & K. Siegbahn et al., 1972 ff.

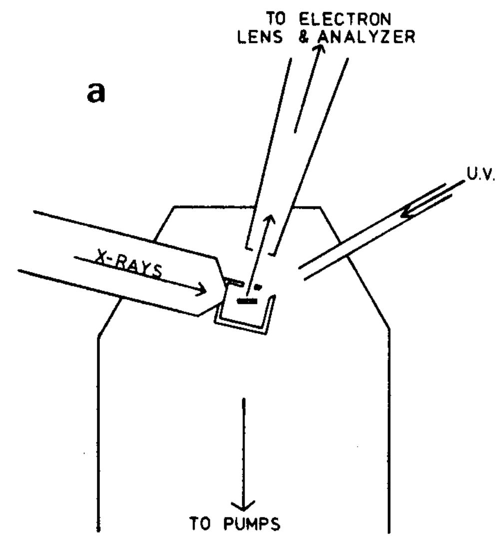


H. Siegbahn et al., *JESRP* **40**, 163 (1986).





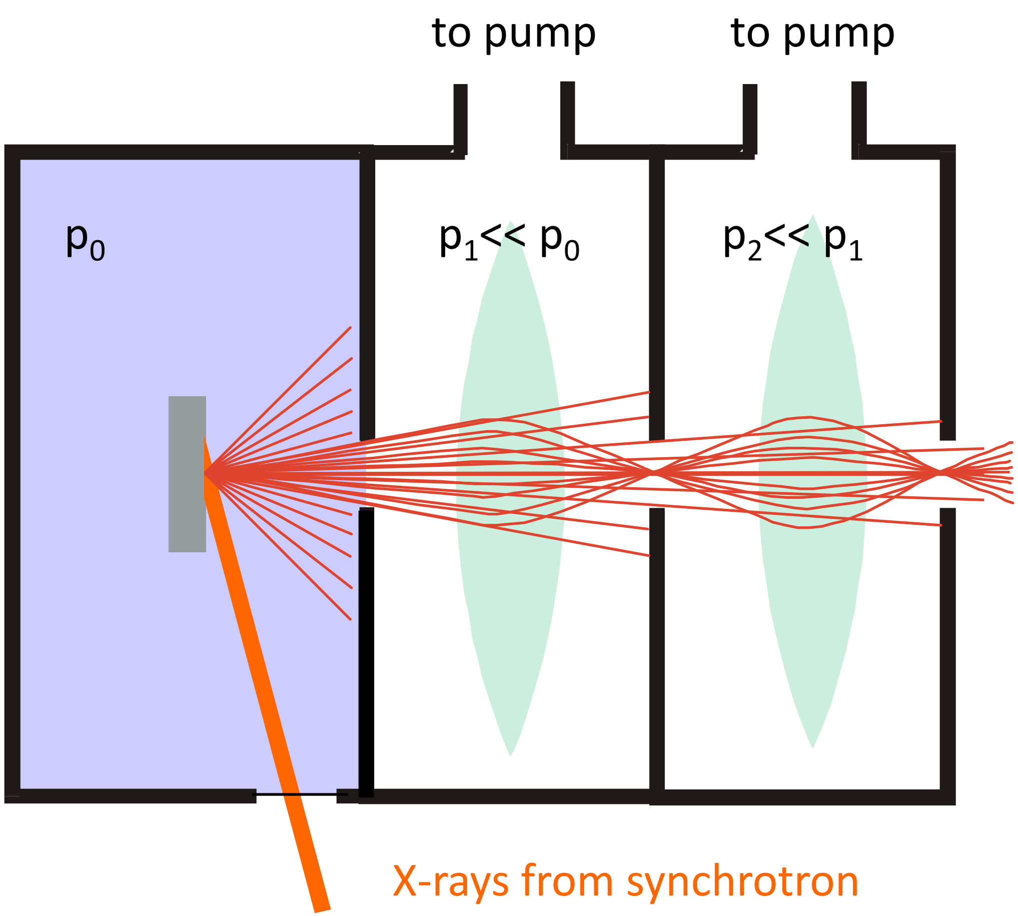
M. Grunze et al., in: *Surface Science of Catalysis (1987).*



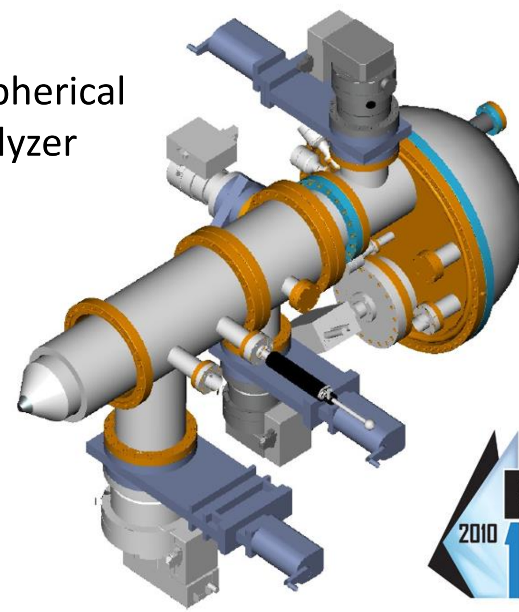
R. Joyner, M.W. Roberts, Surf. Sci. 87, 501 (1979)

LBNL Ambient Pressure XPS Design (~2000)

D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley,
Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.



hemispherical analyzer



LBNL/FHI Berlin/Specs

Measurements at 20 Torr water vapor are now possible (~equilibrium vapor pressure at room temperature)

Ambient Pressure XPS Instruments at Synchrotrons

ALS ADVANCED LIGHT SOURCE
LBNL, Berkeley, CA

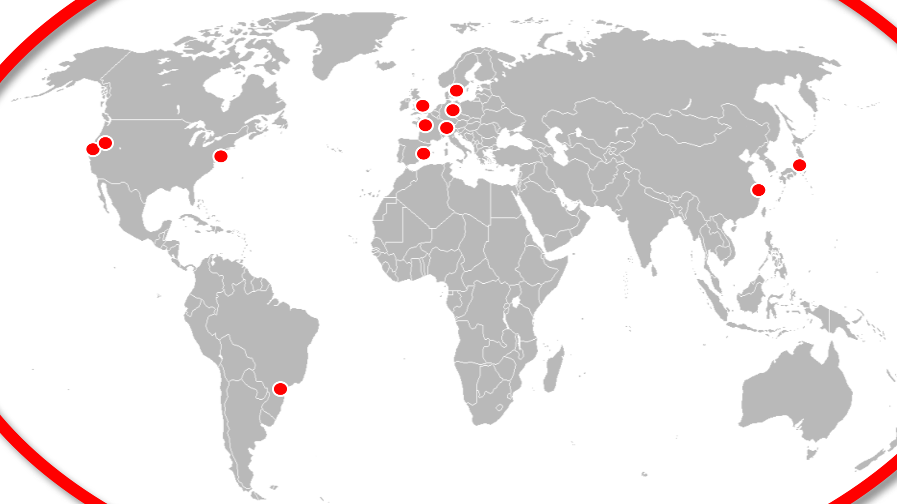
BESSY
Berlin/ Germany

SSRL
SSRL, Stanford, CA

MAX-lab
Lund/Sweden

nsls IR UV X
BNL, Upton, NY

PAUL SCHERRER INSTITUT PSI
Villigen/Switzerland



LNLS
Campinas/Brazil

ALBA Synchrotron Light Facility
Barcelona/Spain

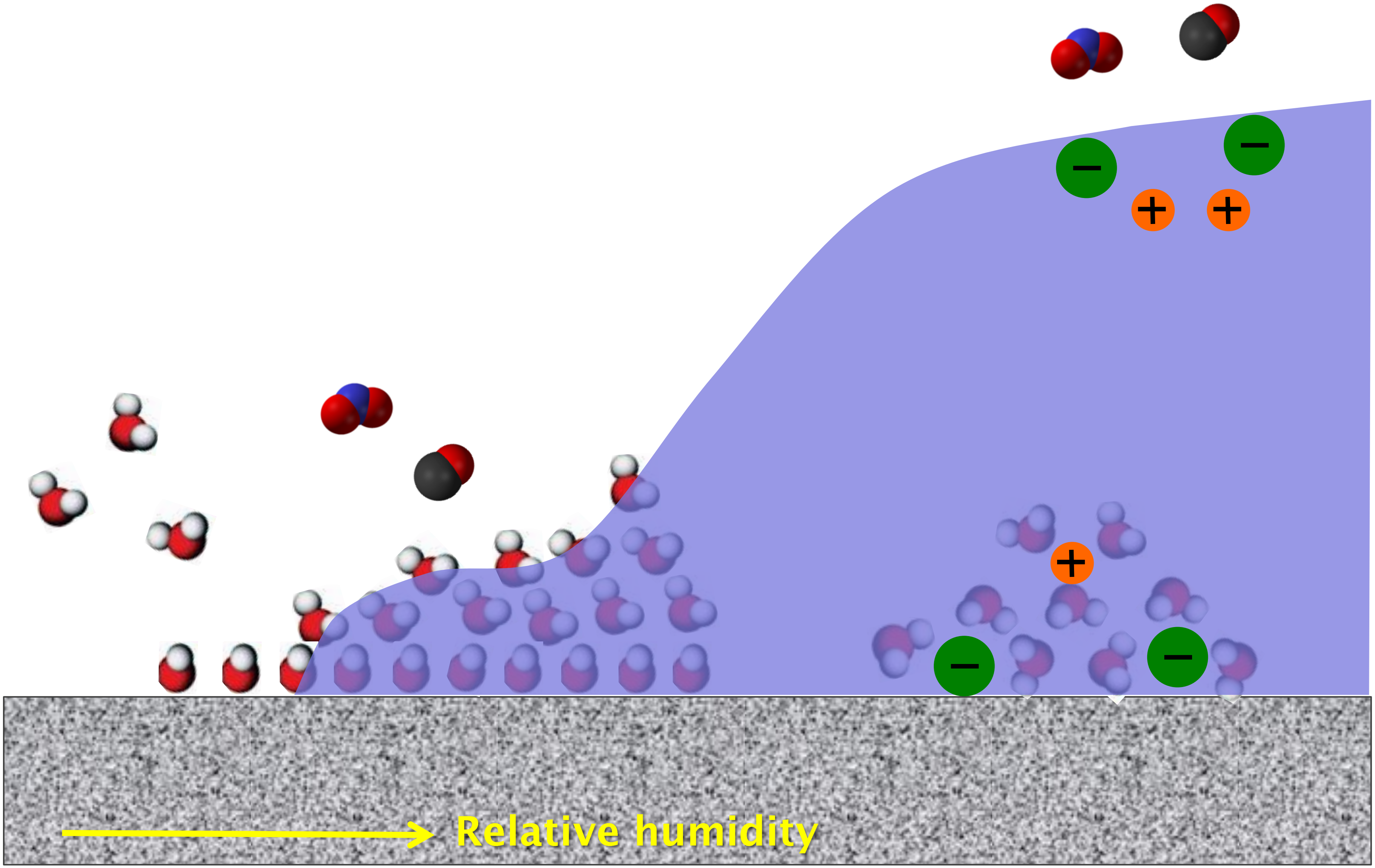
High Energy Accelerator Research Organization (KEK)
Institute of Materials Structure Science (IMSS)
Photon Factory
Tsukuba/Japan

diamond
Oxfordshire/UK

上海同步辐射光源 Shanghai Synchrotron Radiation Facility
Shanghai/China

SOLEIL SYNCHROTRON
Gif-sur-Yvette/France

APXPS for the Investigation of Solid/Vapor, Liquid/Vapor and Solid/Liquid Interfaces



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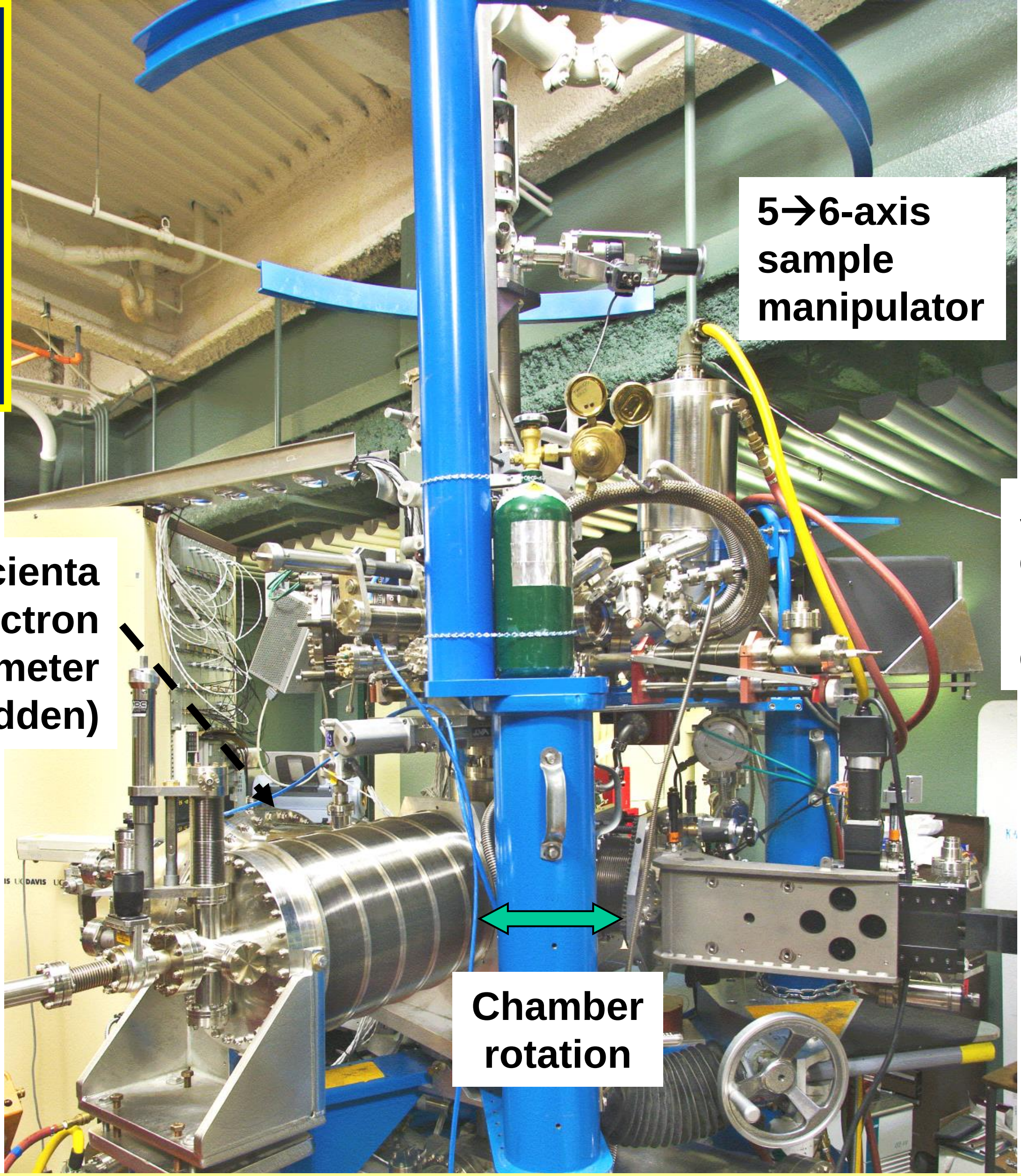
Hard X-ray Photoemission at the Advanced Light Source: The Multi-Technique Spectrometer/ Diffractometer (MTSD)

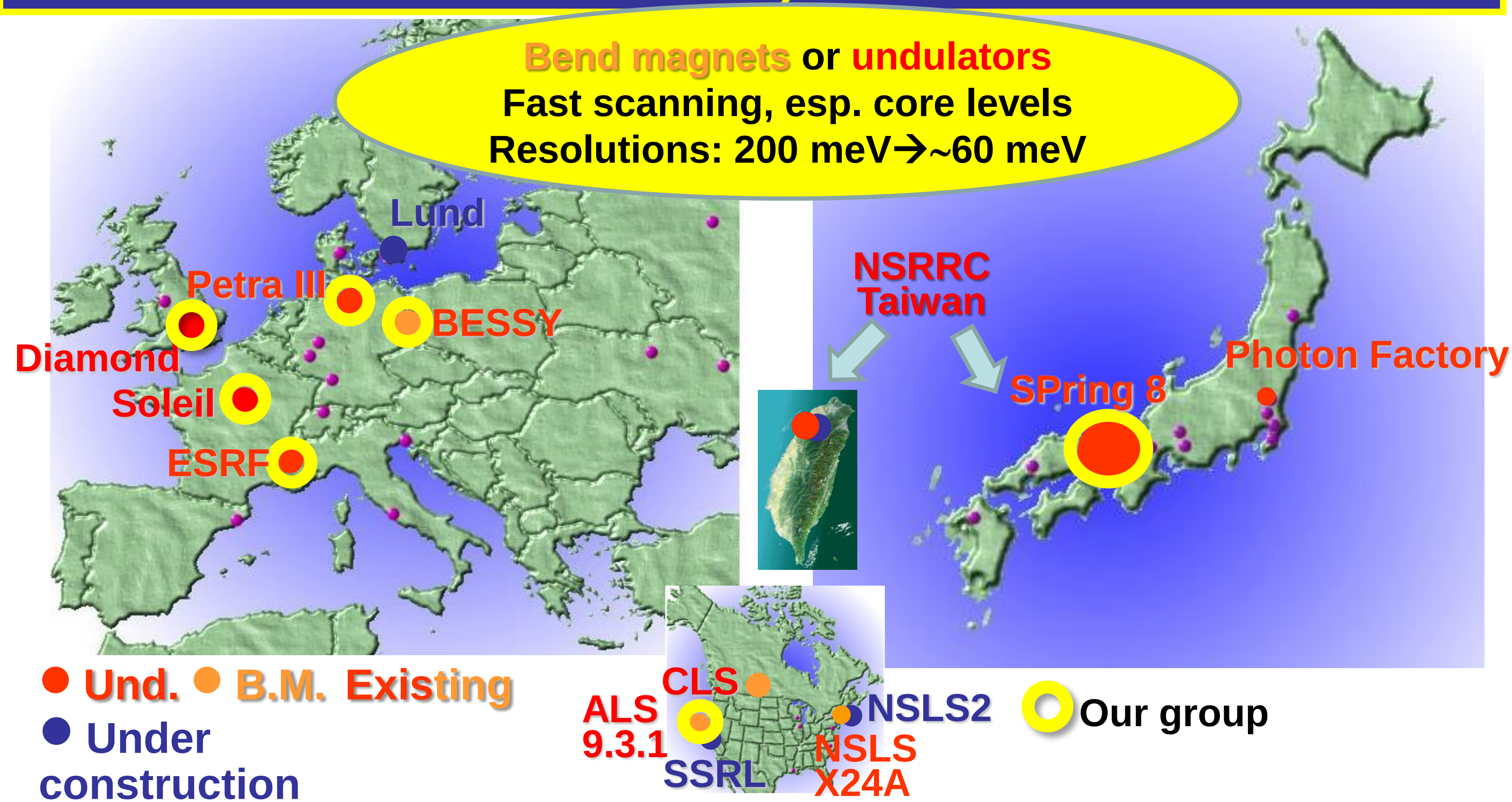
Open to general user program

ALS
BL 9.3.1
hν = 2-5 keV



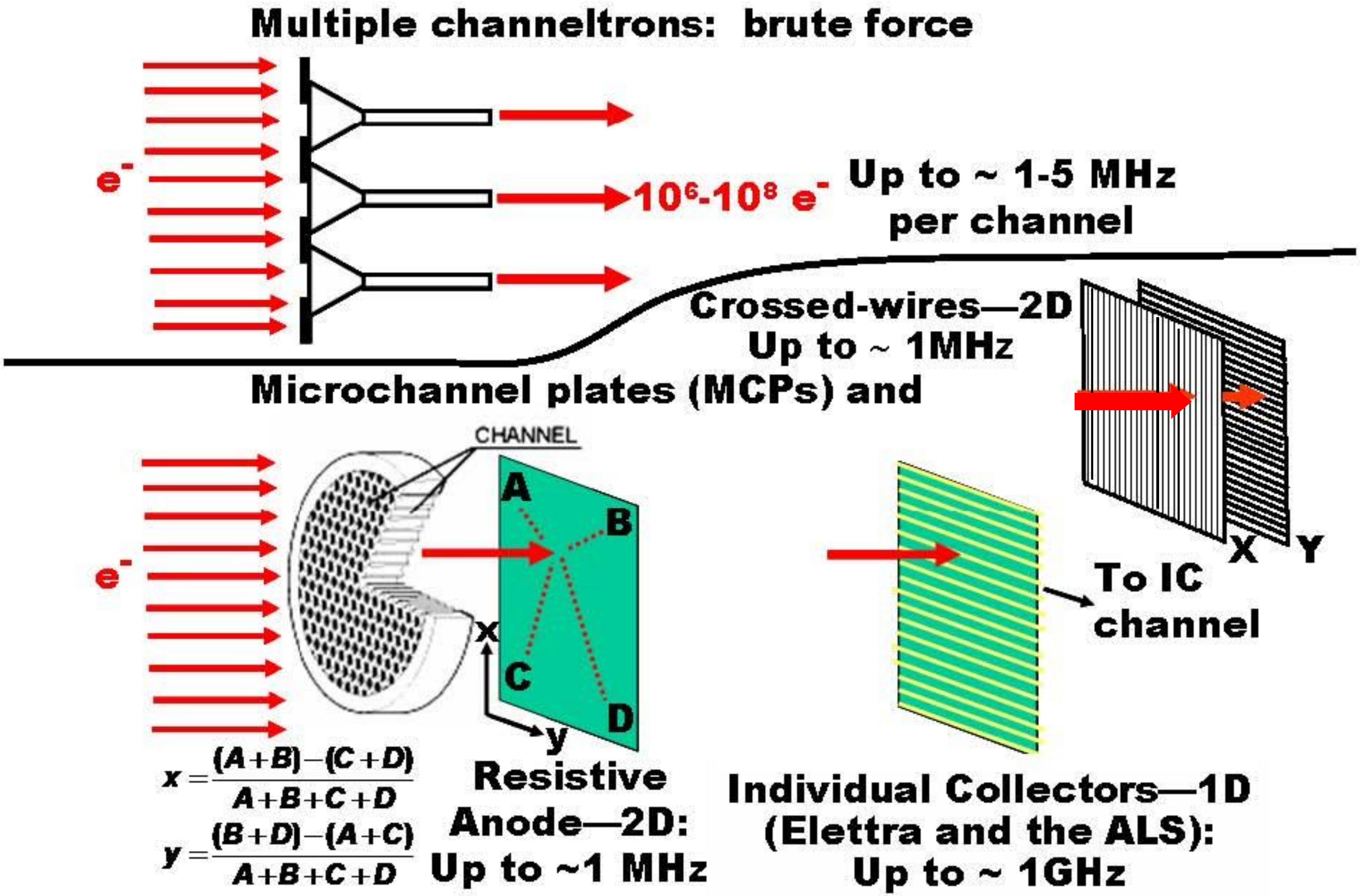
Permits using all relevant spectroscopies on a single sample:
XPS (incl. Al and Mg Kα), HXPS, XPD, XAS, soft XES/RIXS. All details at:
http://www.physics.ucdavis.edu/fadleygroup/Hard.Xray.Photoemission.at.the.ALS.pdf

Hard X-Ray Photoemission (HXPS, HAXPES, HX-PES, HIKE...) in the World

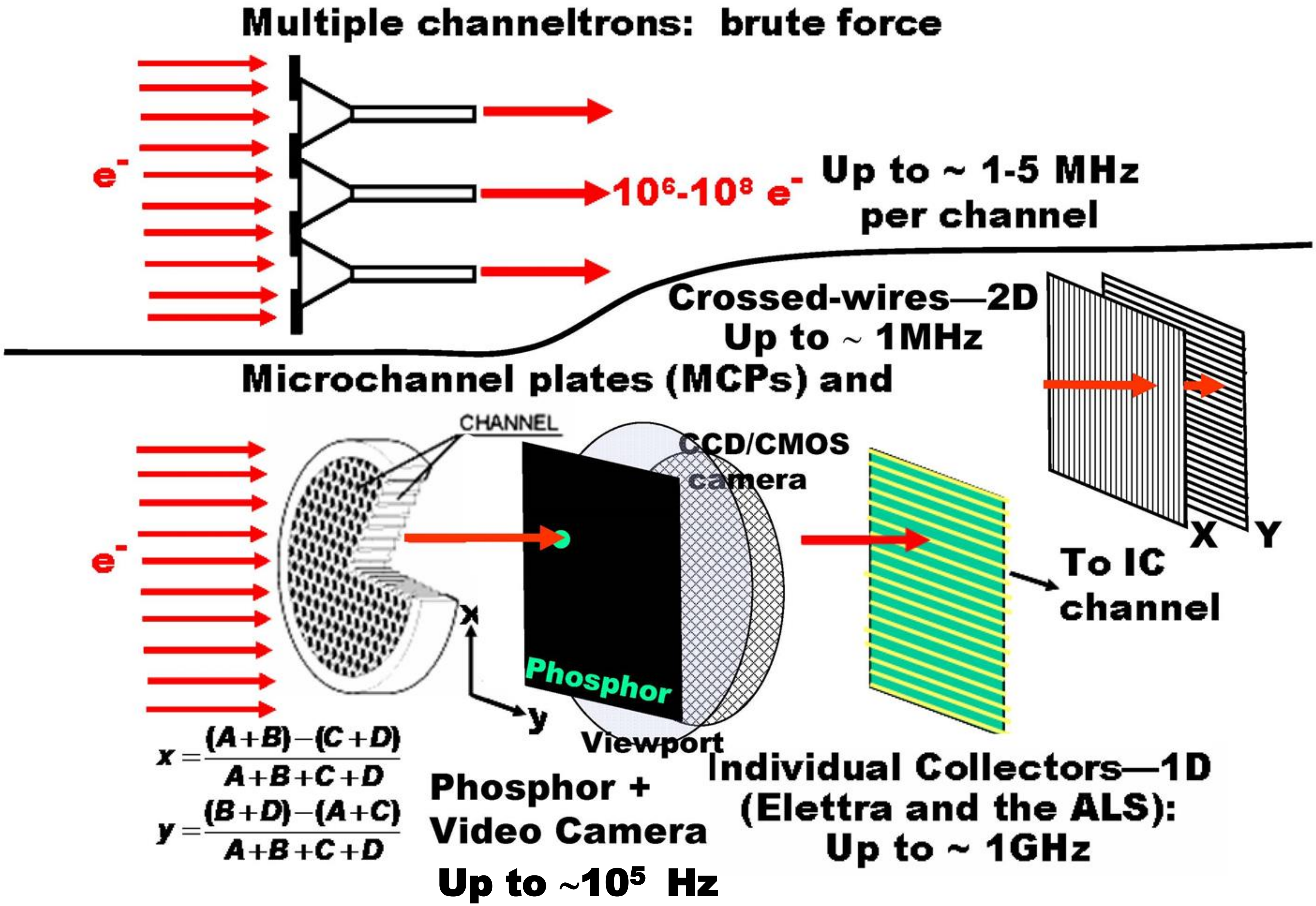


"Recent advances in Hard X-ray Photoelectron Spectroscopy (HAXPES)", Journal of Electron Spectroscopy and Related Phenomena, Volume 190, Part B, Pages 125-314 (October 2013)

Multichannel Electron Detectors for Electron Spectroscopy



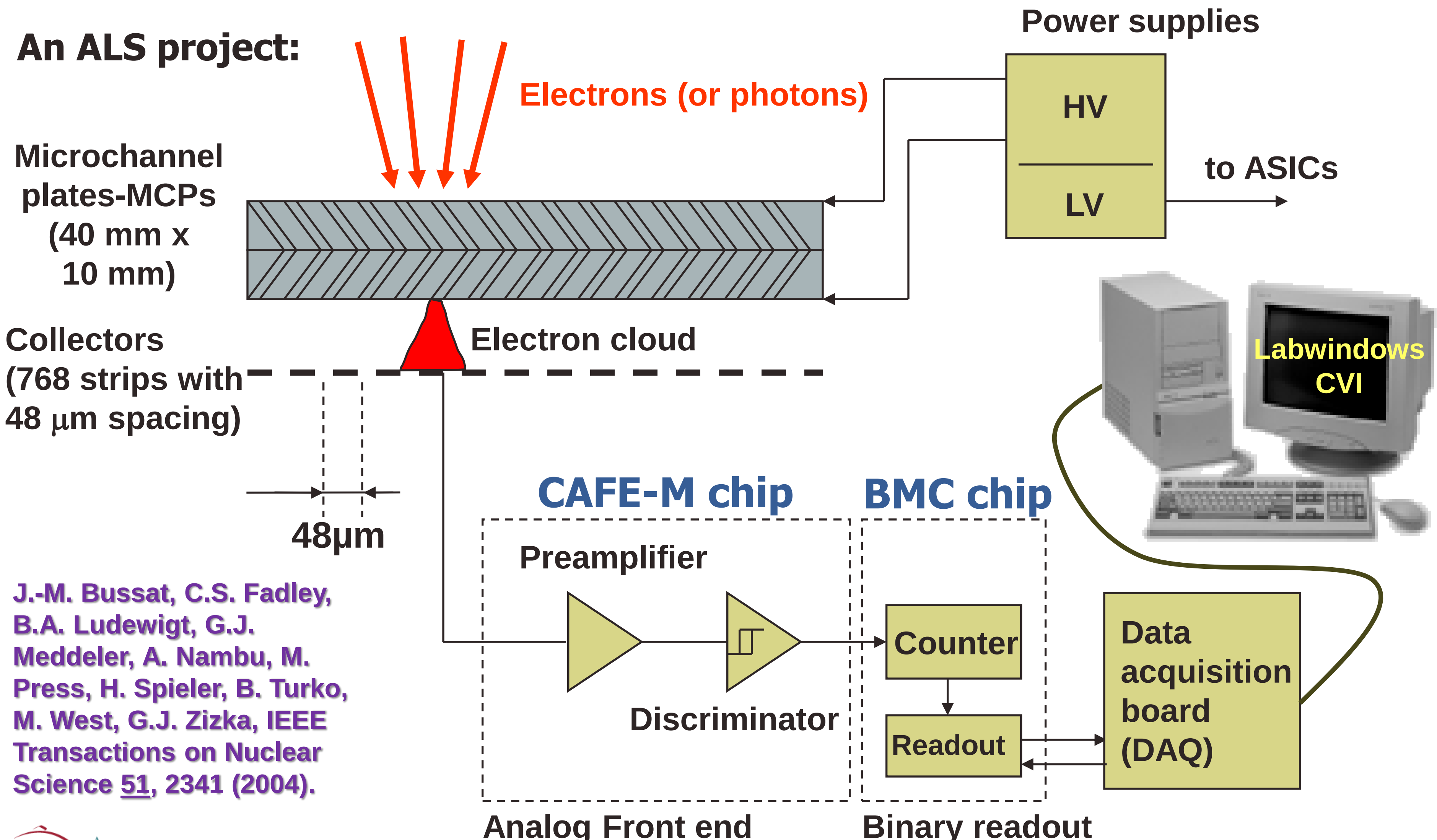
Multichannel Electron Detectors for Electron Spectroscopy



Next Generation Detectors for Electron Spectroscopy

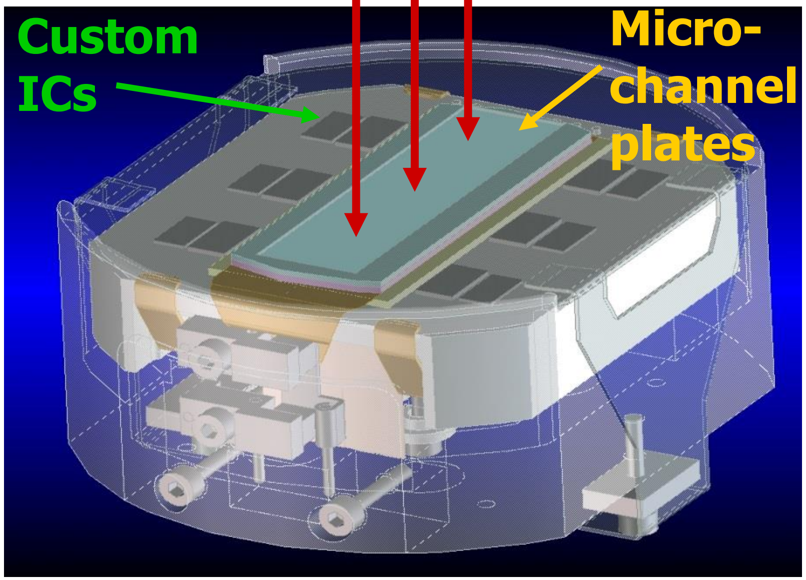
Energy-resolved photoelectrons from a next gen. FEL:
200 GHz at 270 eV to 8 x 109 = 8 GHz at 1200 eV

An ALS project:

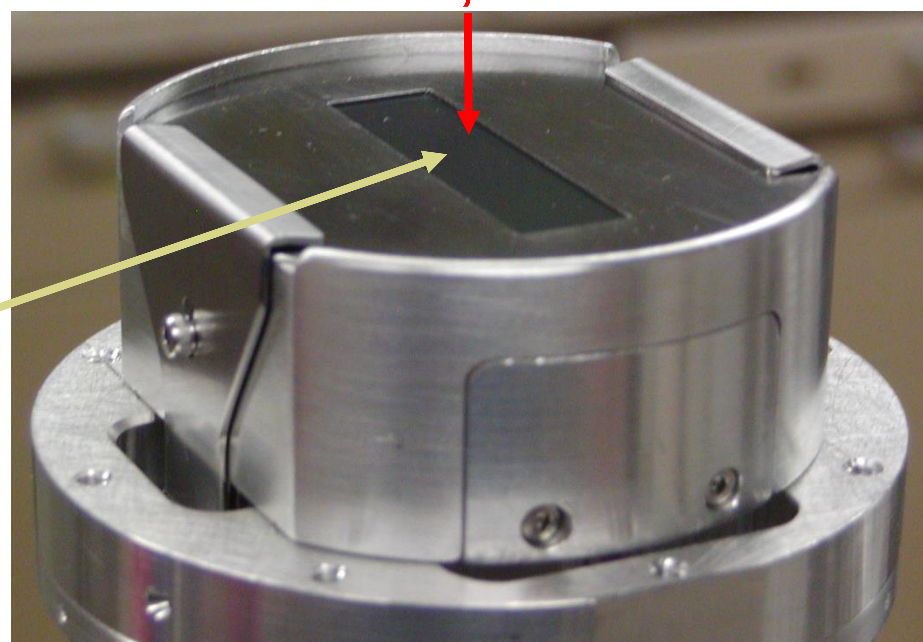


J.-M. Bussat, C.S. Fadley, B.A. Ludewigt, G.J. Meddeler, A. Nambu, M. Press, H. Spieler, B. Turko, M. West, G.J. Zizka, IEEE Transactions on Nuclear Science 51, 2341 (2004).

ALS High-Speed 1D Detector--Project Overview 2003



- ~2 GHz overall linear count-rate→
  100-1000x faster than present detectors
- Position resolution of 75 μ→
  $\Delta E/E \approx 1:10^4$
- Spectral readout in as little as 150 μs→
  time-resolved measurements
- Programmable, robust
- Sized to fit existing spectrometers (Scienta, PHI, ...)

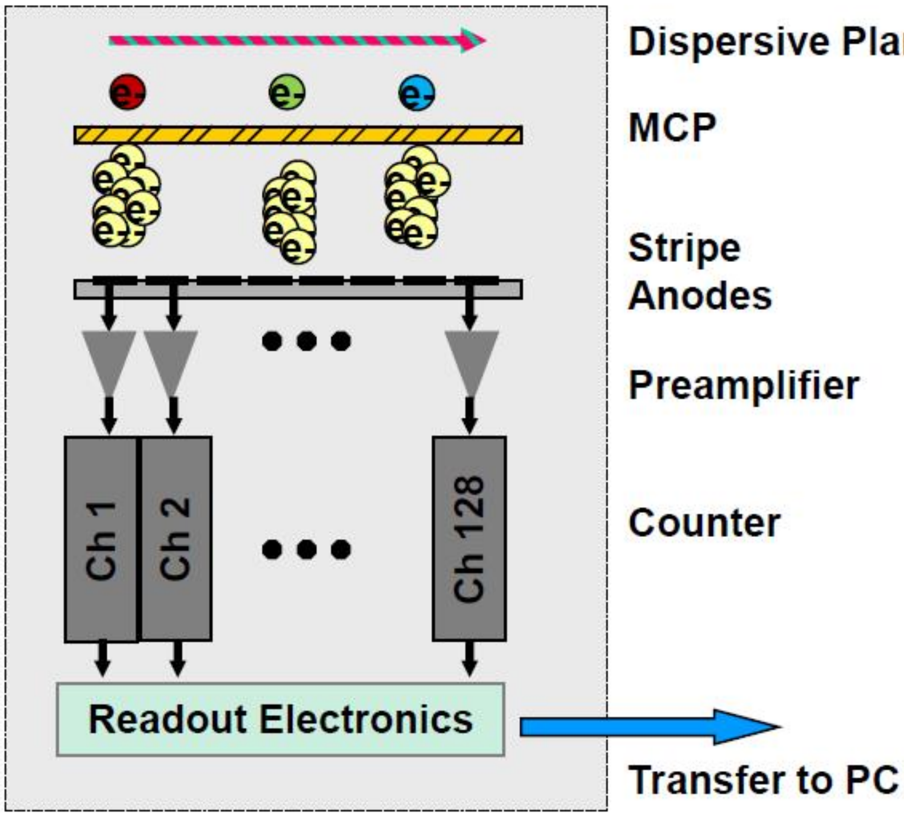


Commercial Product 2011

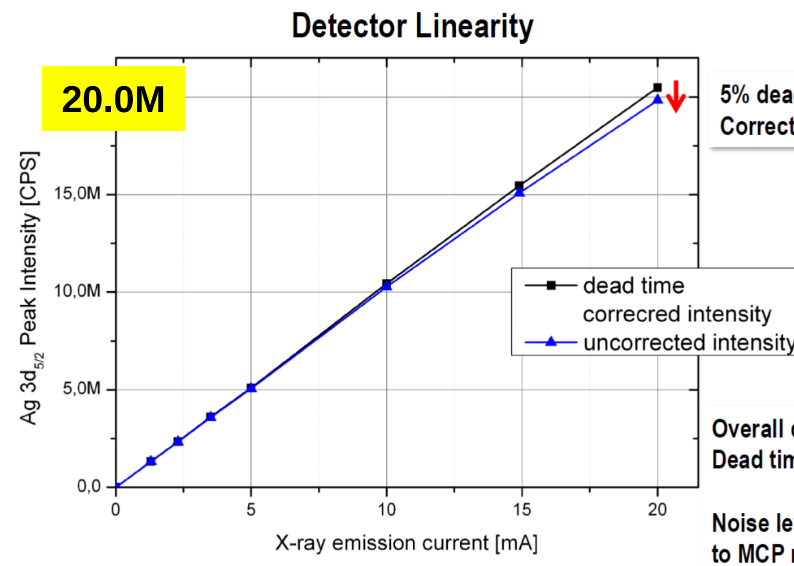
Omicron NanoTechnology

Detector Concept

Multi Channel Detector



Vacuum Side **Air Side**



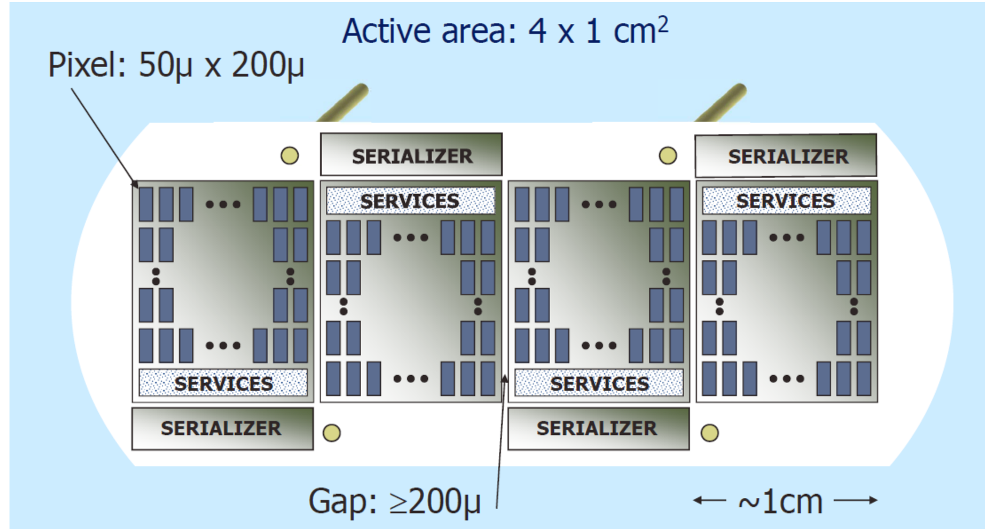
5% dead time Correction @20 MHz

Overall detector Dead time 2.34 ns

Noise level is restricted to MCP noise only

Ideas for the future

2D version of the ALS Detector (2003)



Nm-thinned back illumination of CMOS pixel detector with electrons accelerated to ca. ≥5 keV? (2015)

Nuclear Instruments and Methods in Physics Research A 635 (2011) 69–73

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

Direct detection in Transmission Electron Microscopy with a 5 μm pitch CMOS pixel sensor

Devis Contarato *, Peter Denes, Dionisio Doering, John Joseph, Brad Krieger

Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

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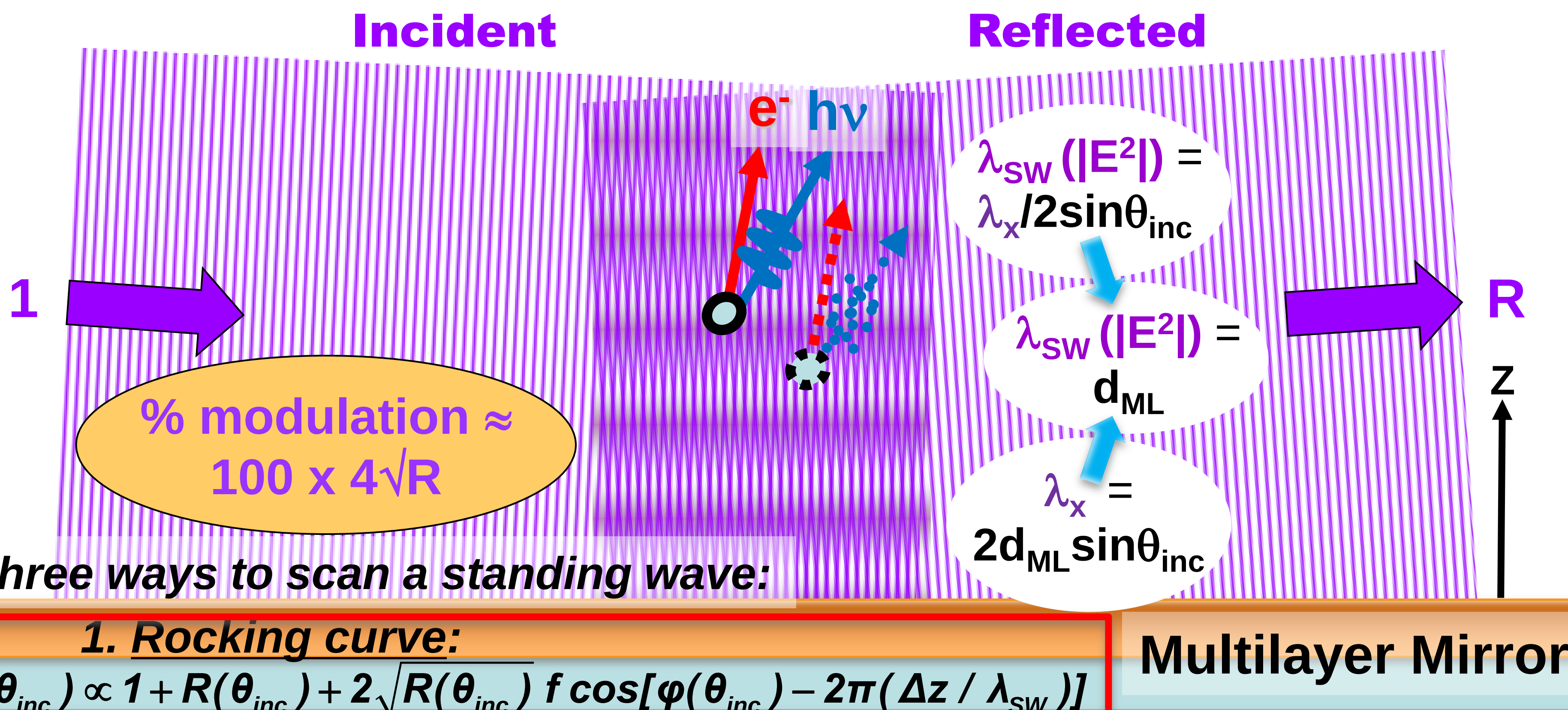
Three ways to scan a standing wave formed in reflection from single-crystal Bragg planes, or a multilayer mirror



Three ways to scan a standing wave:

1. Rocking curve:

$$I(\theta_{inc}) \propto 1 + R(\theta_{inc}) + 2\sqrt{R(\theta_{inc})}\, f \cos[\varphi(\theta_{inc}) - 2\pi(\Delta z / \lambda_{SW})]$$

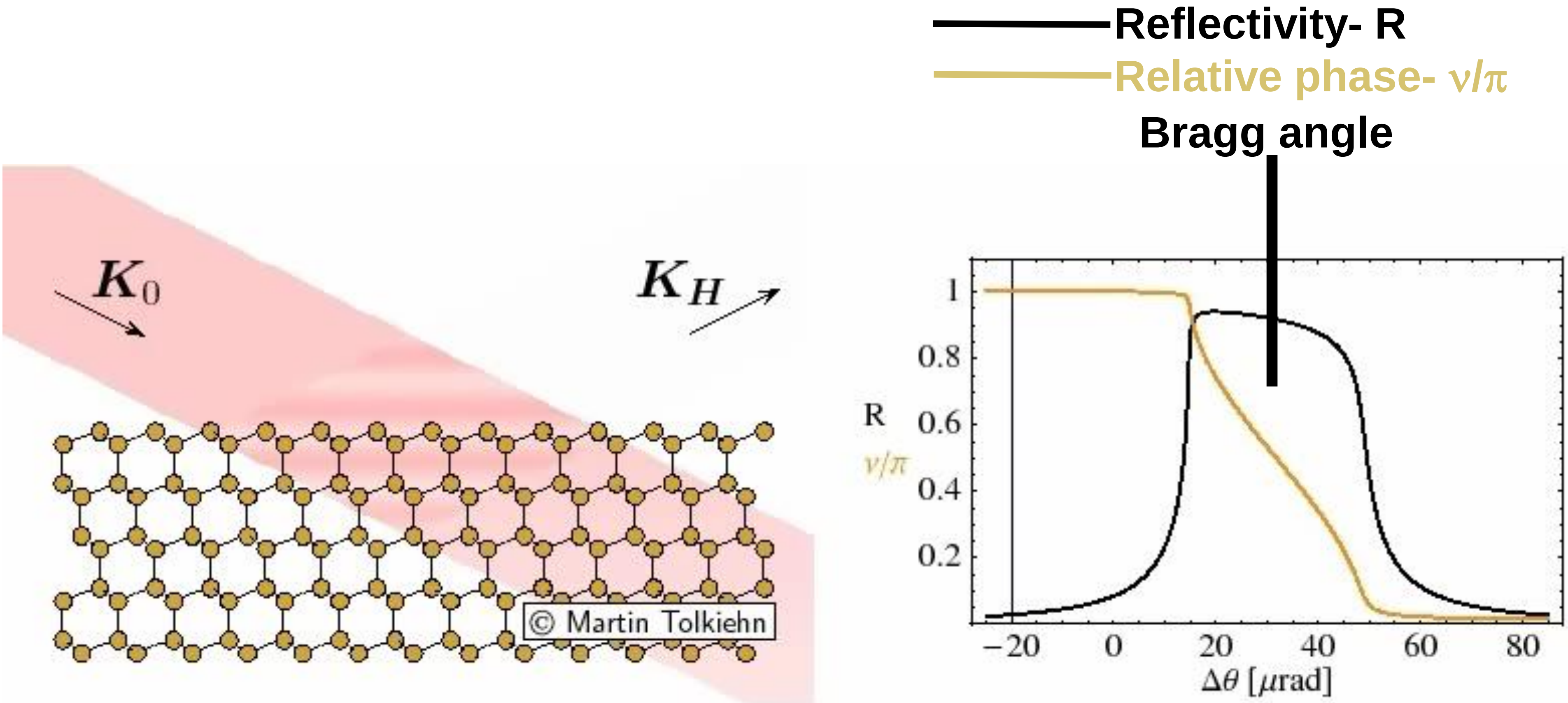
2. Photon energy scan:

$$I(hv) \propto 1 + R(hv) + 2\sqrt{R(hv)}\, f \cos[\varphi(hv) - 2\pi(\Delta z / \lambda_{SW})]$$

with: f = coherent fraction of atoms, $\Delta z / \lambda_{SW}$ = phase of coherent-atom position

3. Phase scan with wedge-shaped sample ("Swedge" method)

Standing Wave Behavior During a Rocking Curve or Photon-Energy Scan

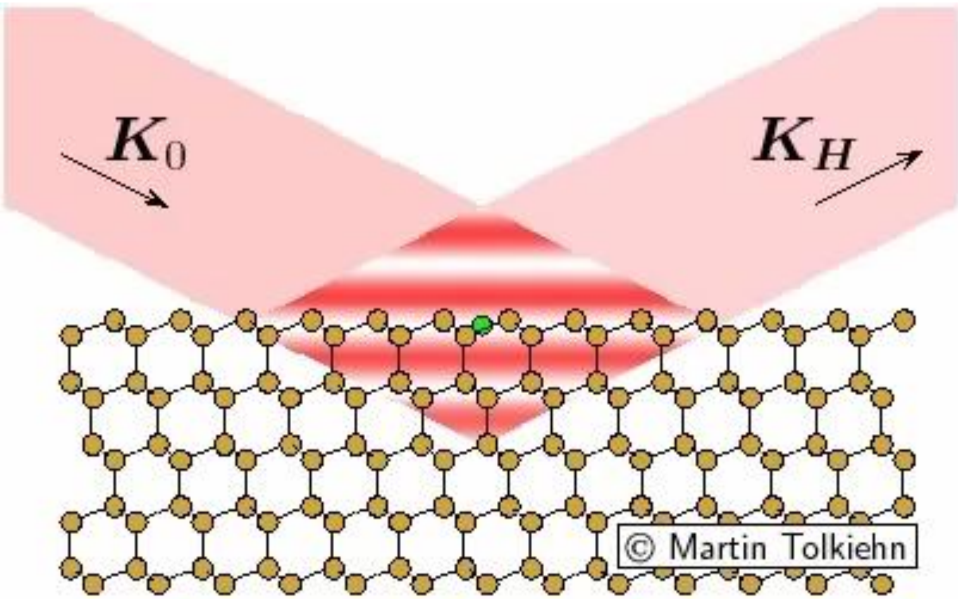


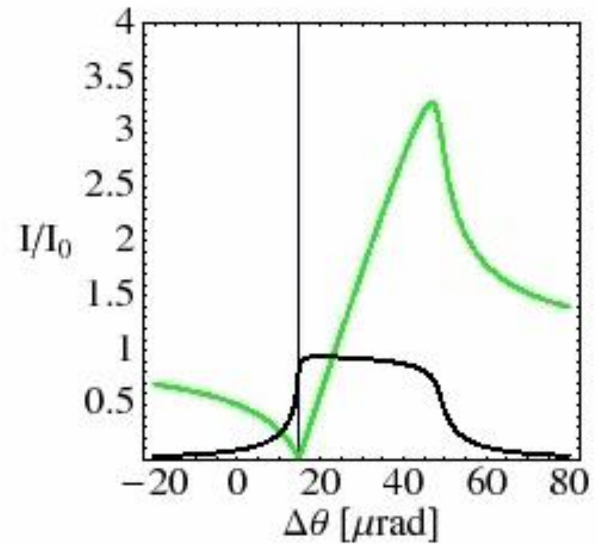
+Same general forms if photon energy is scanned

With thanks to Martin Tolkiehn, Dimitri Novikov, DESY

Form of rocking curve is unique to position of emitter

Intensity vs
atomic position





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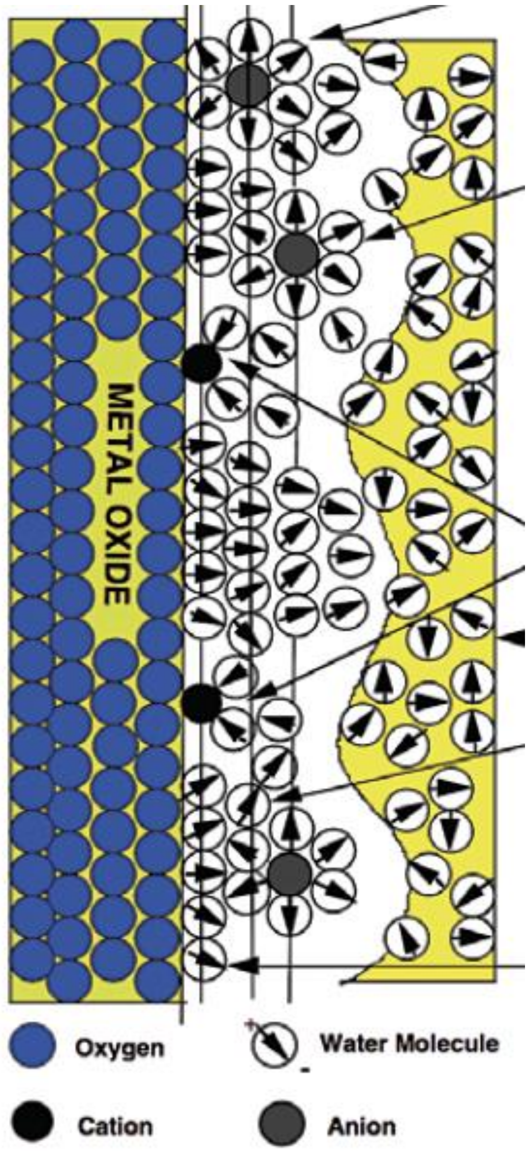
Standing Wave APXPS for Solid/Liquid Interface Studies

G.E. Brown, Geochem. Persp. (2012).



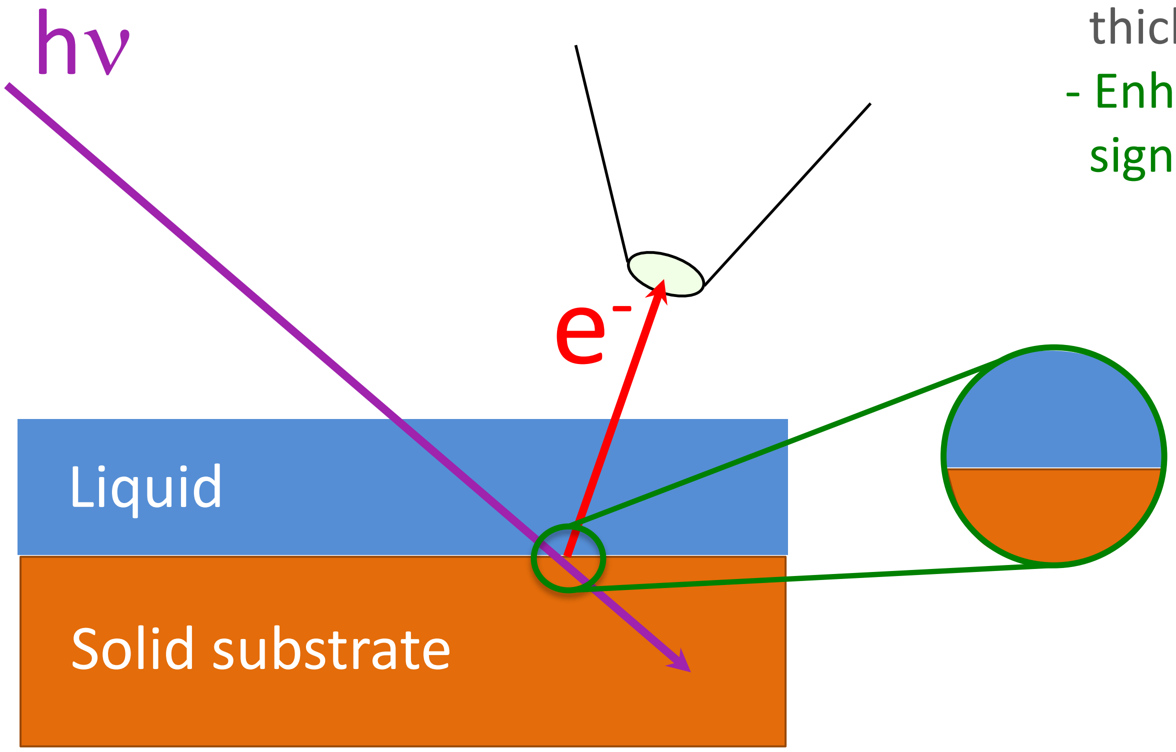
Open questions

- Correlation between chemistry and electrical potentials
- Structure of the electric double layer
- Charge and mass transfer across interfaces.

Relevant research areas

- Electrochemistry
- Corrosion
- Geochemistry
- Catalysis

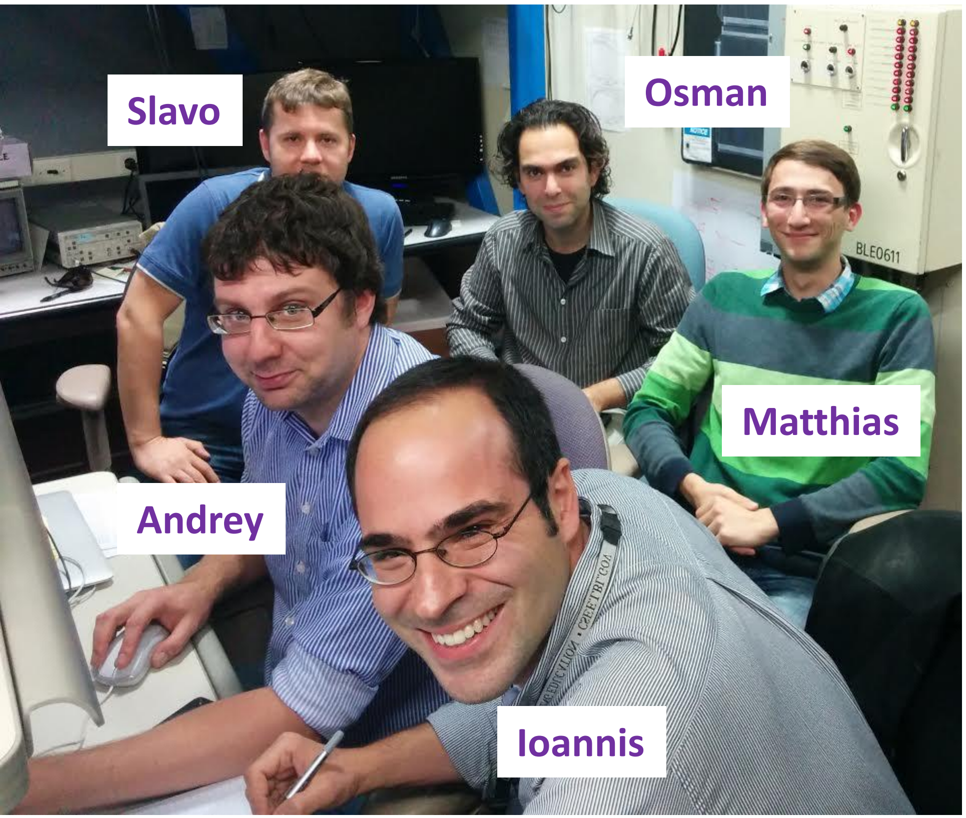
Challenges to Measuring Solid Liquid Interfaces

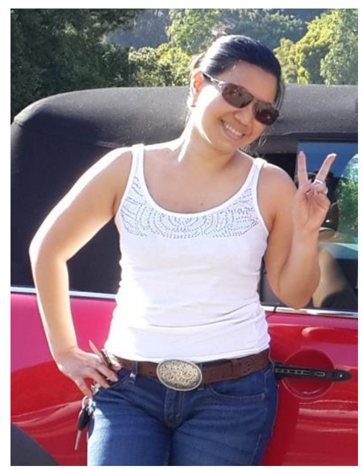


<u>Obstacles:</u>

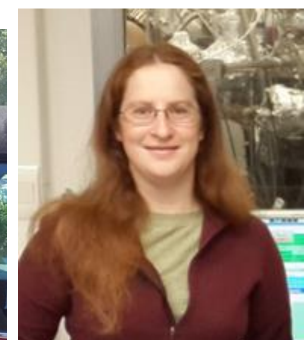
- Preparation of sufficiently thick/thin liquid films.
- Enhancement of interface signal over that of the bulk.

Standing wave photoemission from a liquid-like layer: CsOH and NaOH on Fe_2O_3





Aru



Catherine

Armela

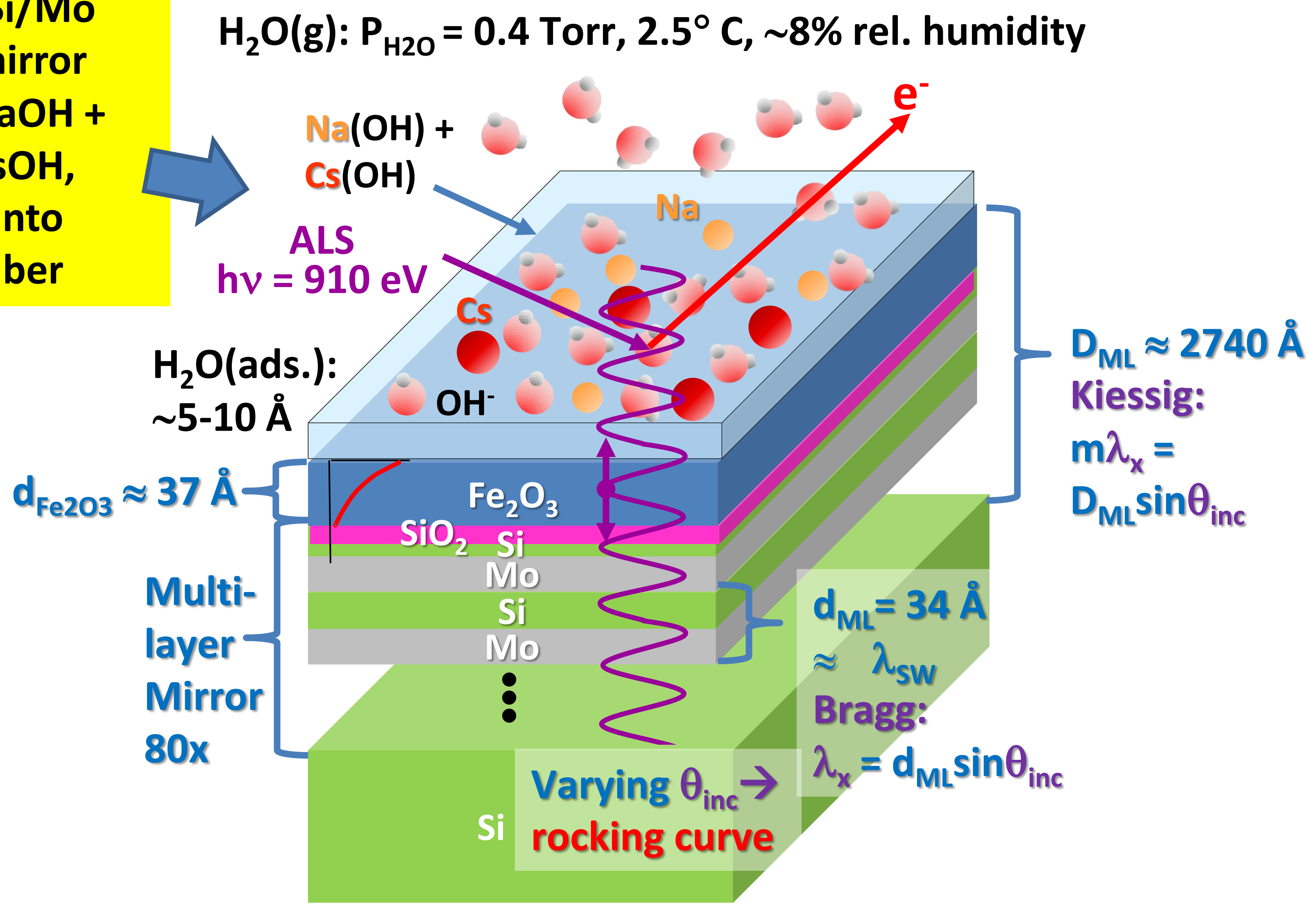
S. Nemšák, A. Shavorskiy, O. Karslioglu, I. Zegkinoglou, A. Rattanachata, C.S. Conlon, P.K. Greene, K. Liu, F. Salmassi, E.M. Gullikson, H. Bluhm, Ch.S. Fadley , Nature Communictions 5, 5441 (2014).

+Samples: Liu Group UCD

+Mirrors: CXRO LBNL

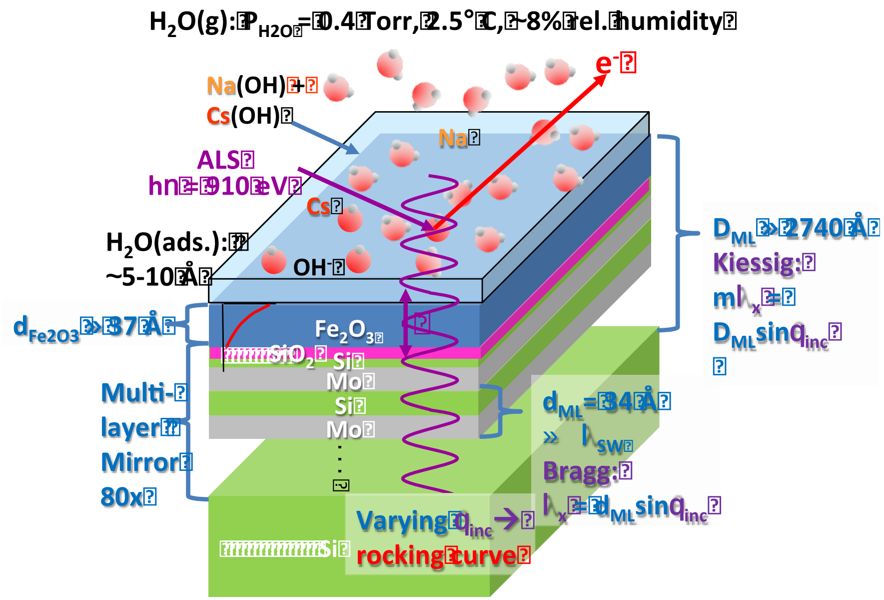
Standing-wave photoemission at the solid-liquid interface: some first experiments at ambient pressure

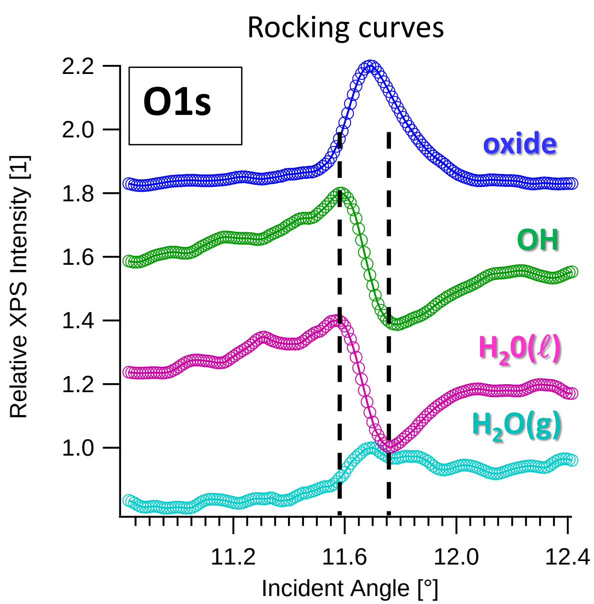
- Fe_2O_3 on Si/Mo multilayer mirror
- ~0.01M NaOH + ~0.01M CsOH, dried in air, into APXPS chamber

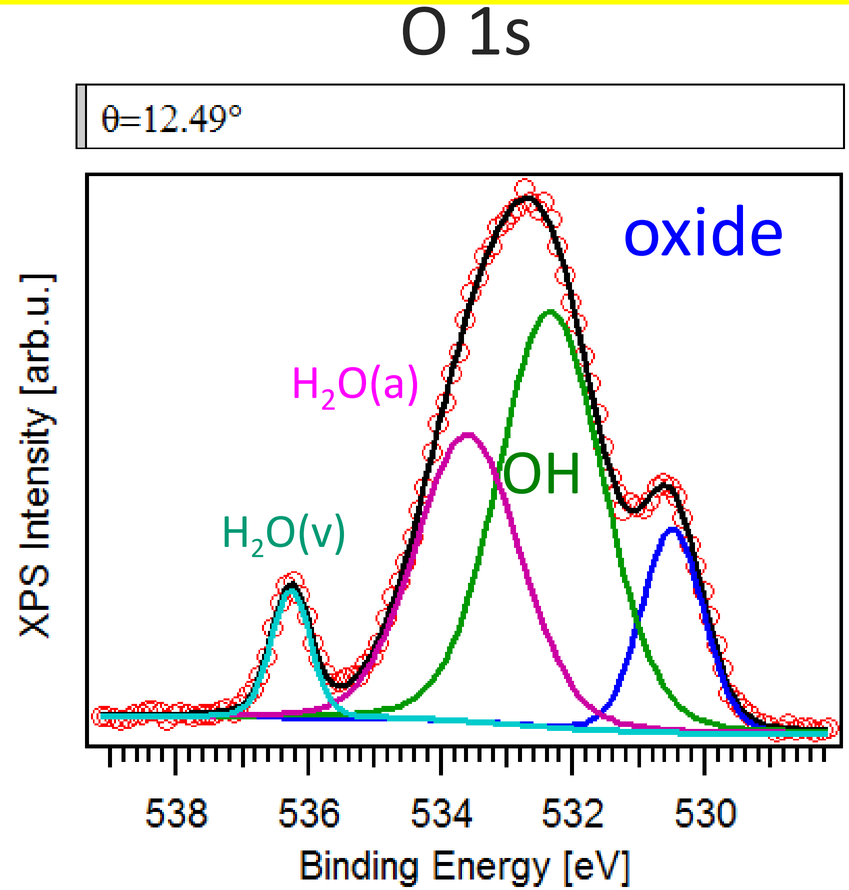


CSD BL 11.0.2 @ ALS

O 1s Rocking Curves

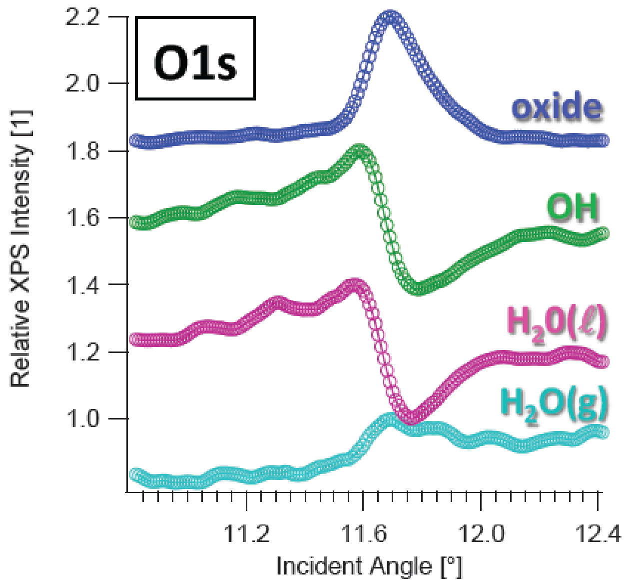


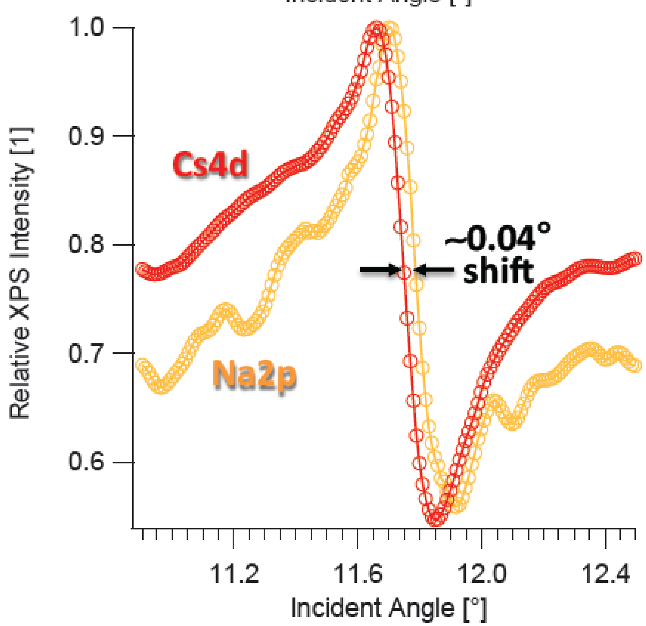


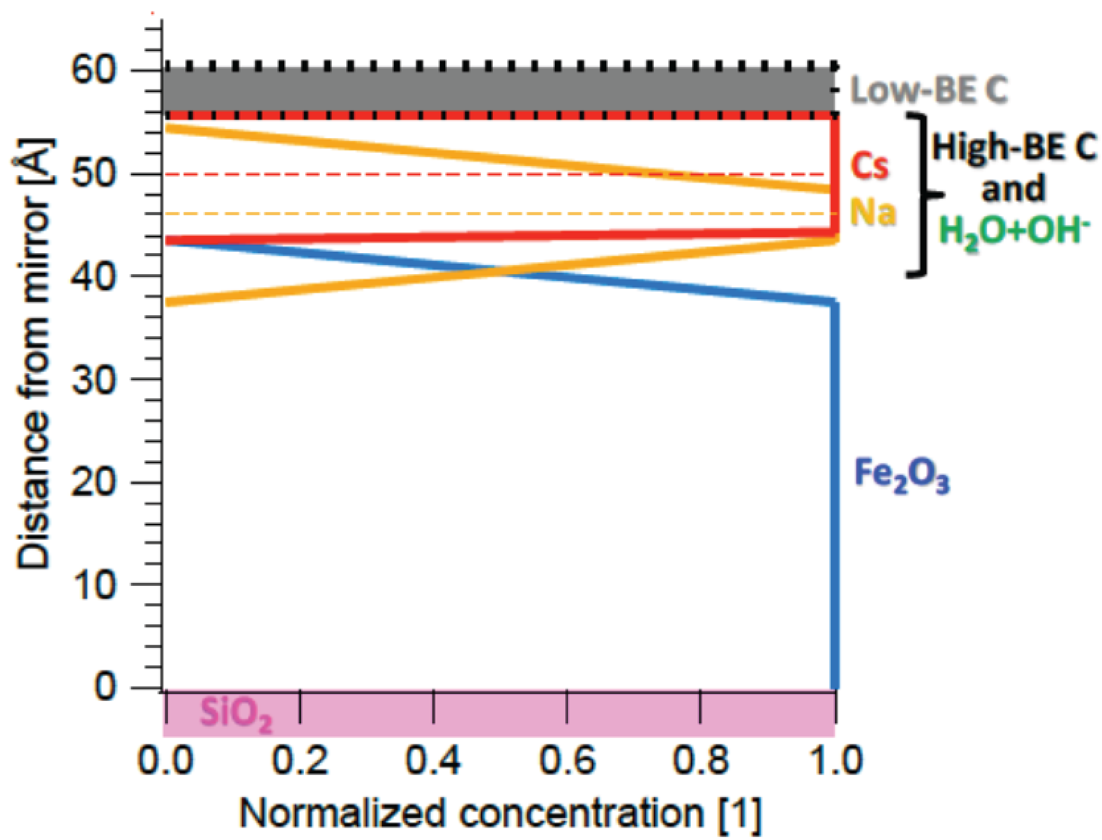


S. Nemšák, A. Shavorskiy, O. Karslioglu, I. Zegkinoglou, A. Rattanachata, C.S. Conlon, P.K. Greene, K. Liu, F. Salmassi, E.M. Gullikson, H. Bluhm, Ch.S. Fadley , Nature Communictions 5, 5441 (2014).

Chemical Speciation at Interface from Standing Wave APXPS







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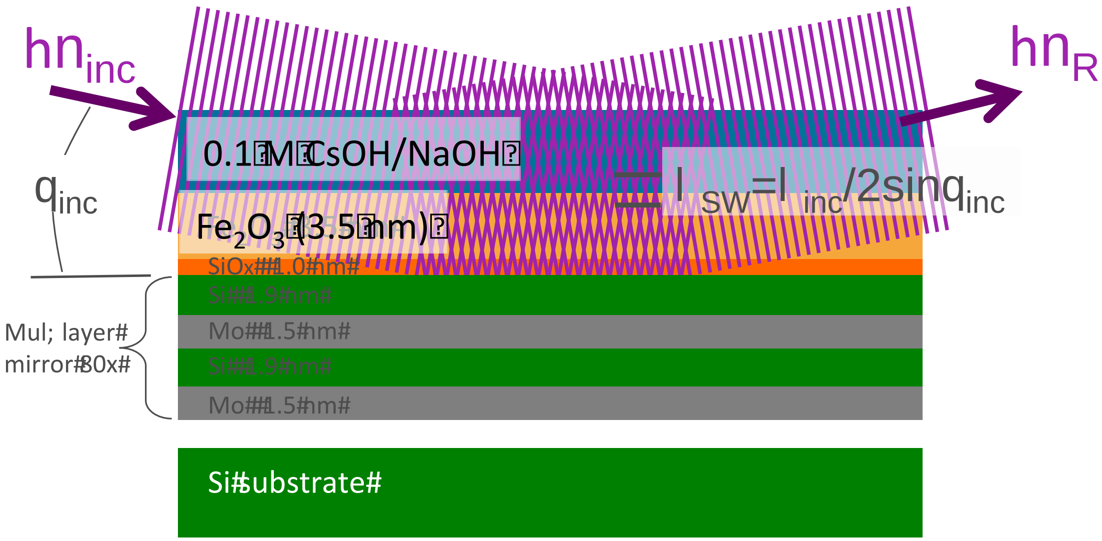
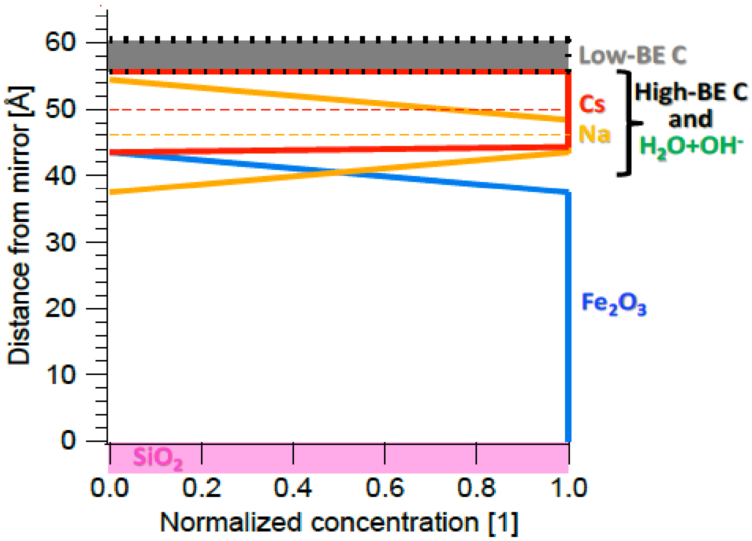
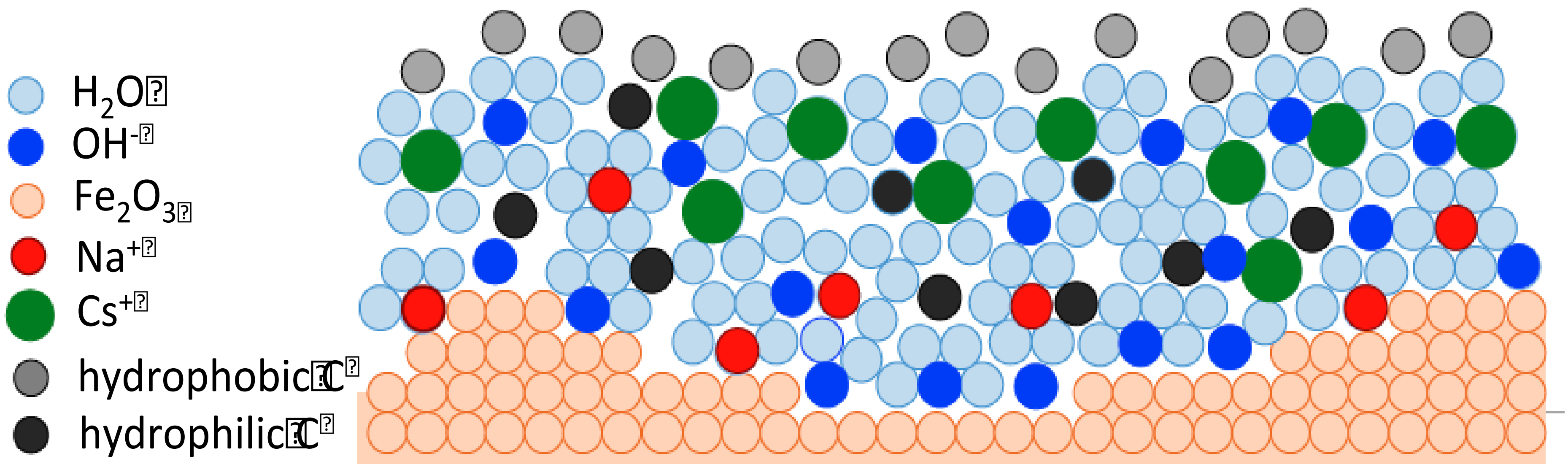
Chemical Speciation at Interface from Standing Wave APXPS

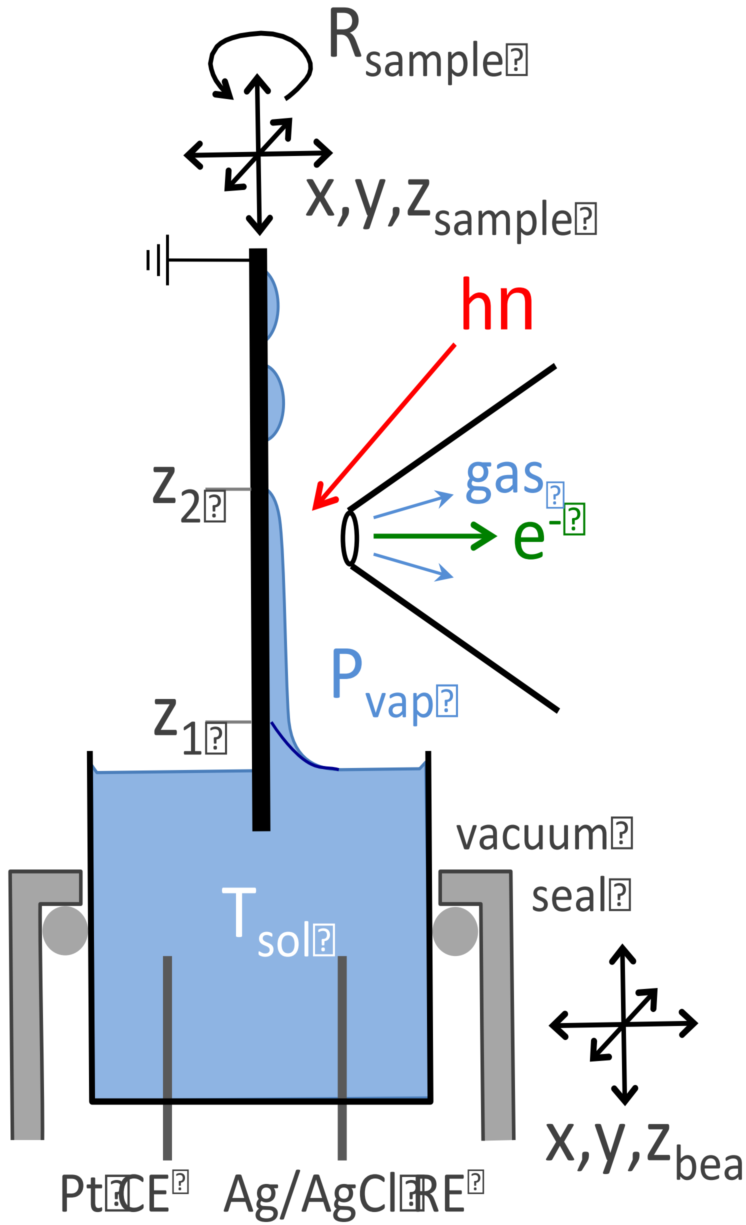


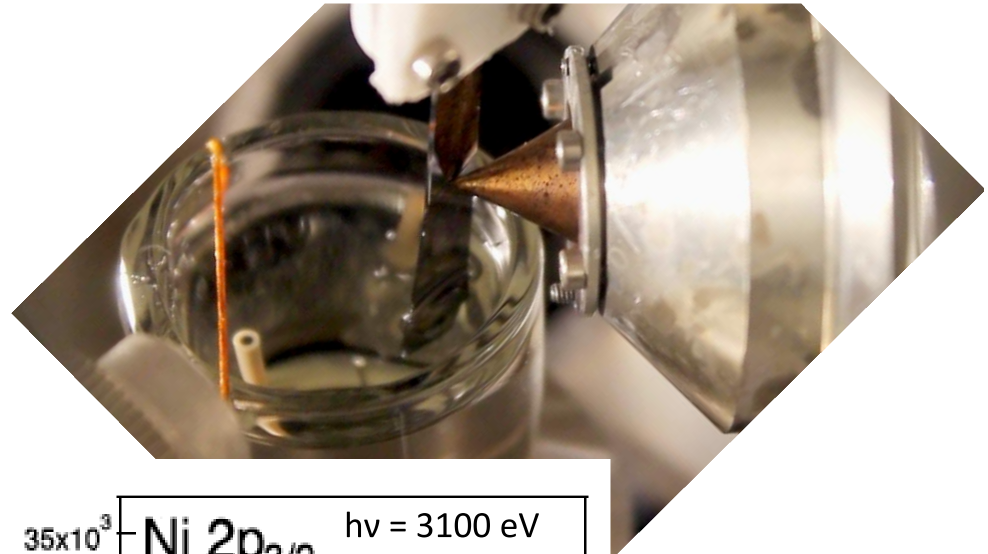


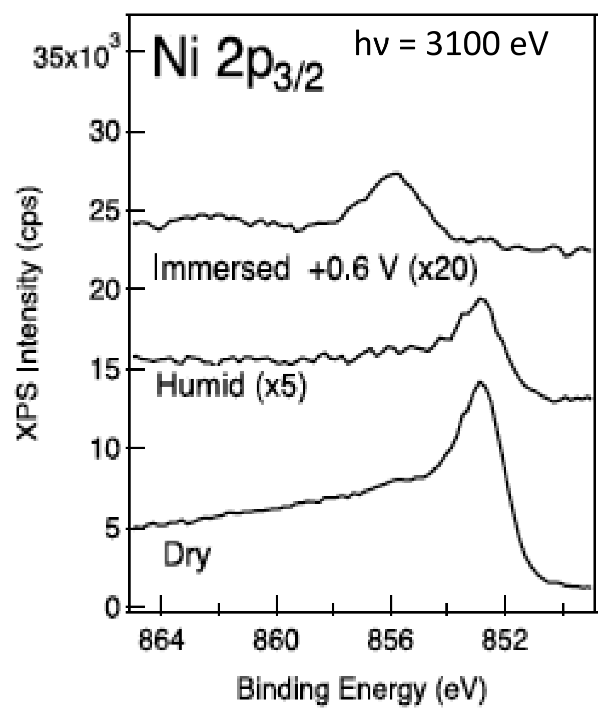


S. Nemšák et al., Nature Communictions 5, 5441 (2014); O. Karslioglu et al., Faraday Discussions (2015).

Preparing Thin Liquid Films Using the "Meniscus Method"







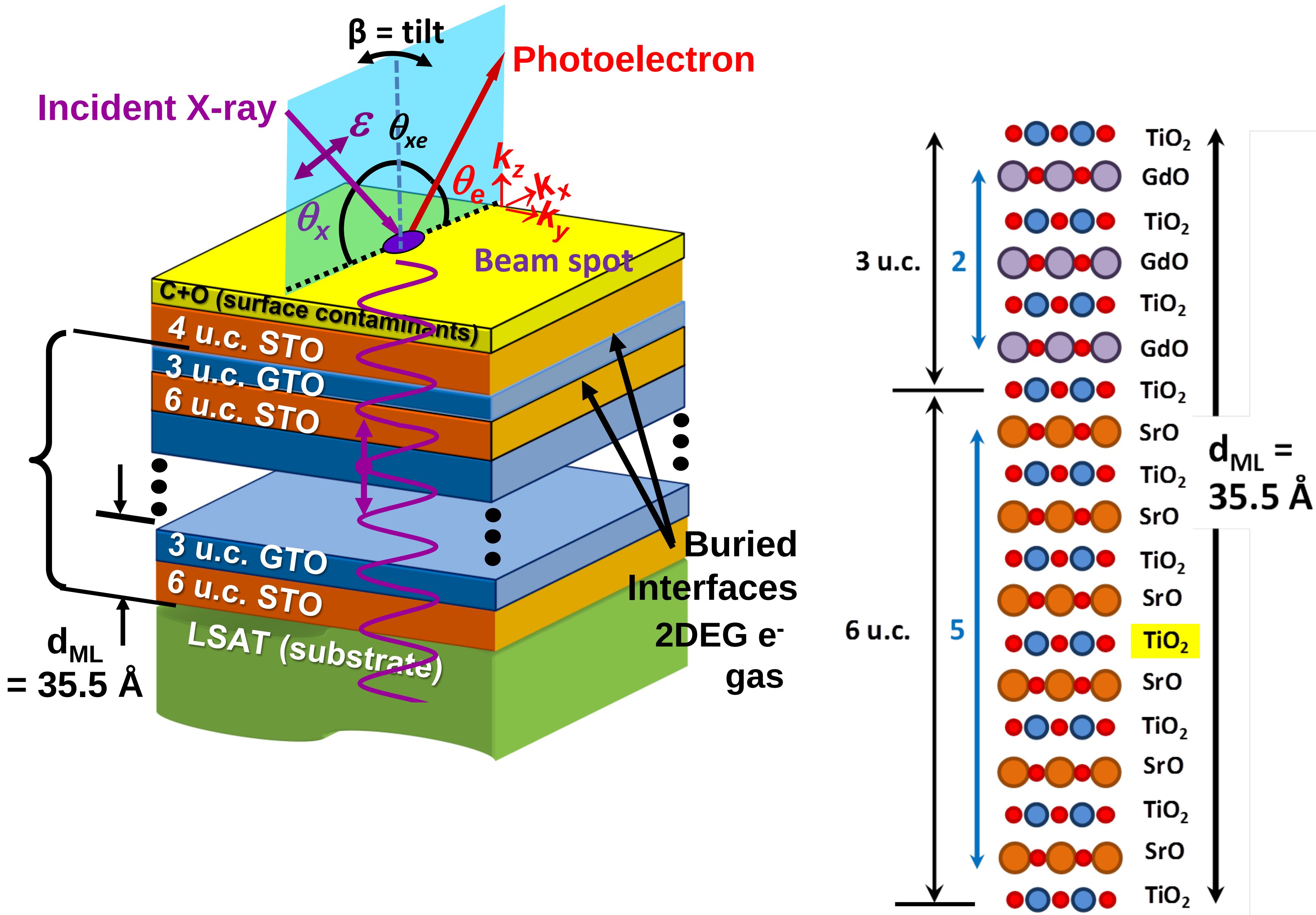
Data taken at beamline 6.0.1.

S. Axnanda et al., Sci. Rep (2015).
O. Karslioglu et al., Faraday Discussions (2015).

Outline

- Interfaces in the environment and technology:
  Solid/gas, liquid/gas, solid/liquid, and solid/solid
- Photoemission spectroscopy: Basic technical considerations; Inelastic mean free path in solids and gases
- Studying interfaces under realistic conditions:
  Ambient pressure and buried interfaces
- Ambient pressure photoemission-instrumentation
- Solid/solid interfaces: Instrumentation and detectors
- Standing wave photoemission
- Application to the solid/liquid interface
- Application to complex oxide interfaces

Multilayer $GdTiO_3/SrTiO_3$



P. Moetakef, S. Stemmer, UCSB

$SrTiO_3/GdTiO_3$
An interface 2D electron gas

S. Nemšák et al., TBP

$SrTiO_3$

- Band insulator (E_g=2.3 eV)
- Low temperature superconductor

$GdTiO_3$

- Mott-Hubbard insulator

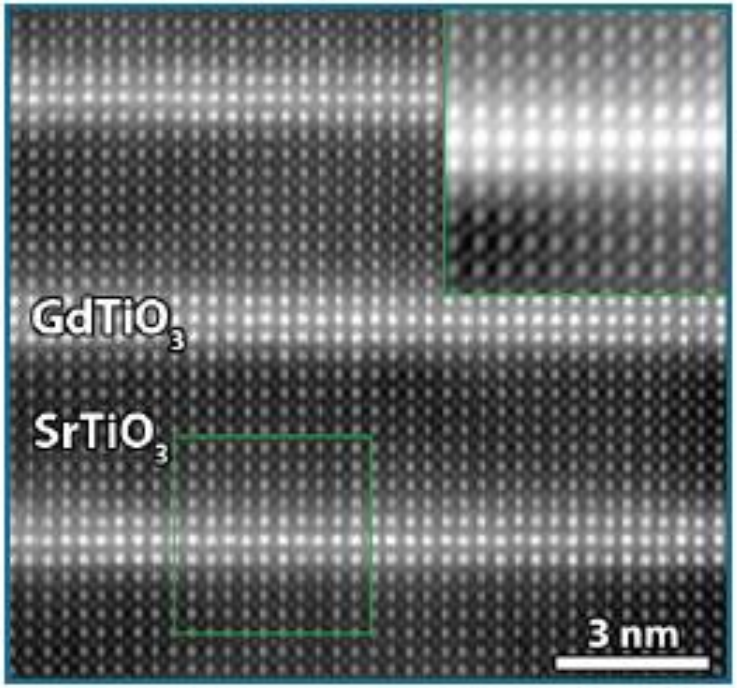
$GdTiO_3/SrTiO_3$ interface

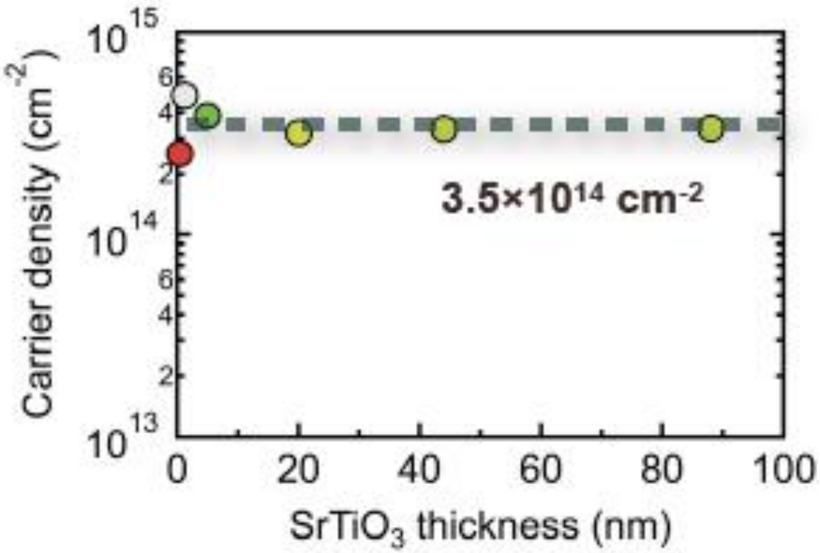
- Two-dimensional electron gas (2DEG) at the interface between two insulators (*Appl. Phys. Lett.* ***99****, 232116, 2011*)
- Sheet carrier density on the order of $3x10^{14}$ cm^{-2}
- Ferromagnetism in the 2DEG at the interface (*Phys. Rev. X* ***2****,021014, 2012*)

Stemmer et al., UCSB

THE UNIVERSITY OF CALIFORNIA DAVIS · BERKELEY LAB · The Advanced Light Source · UCSB · SPring-8 · PAUL SCHERRER INSTITUT PSI · DESY · LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN · Julich Res. Ctr.

The STO/GTO 2D Electron Gas



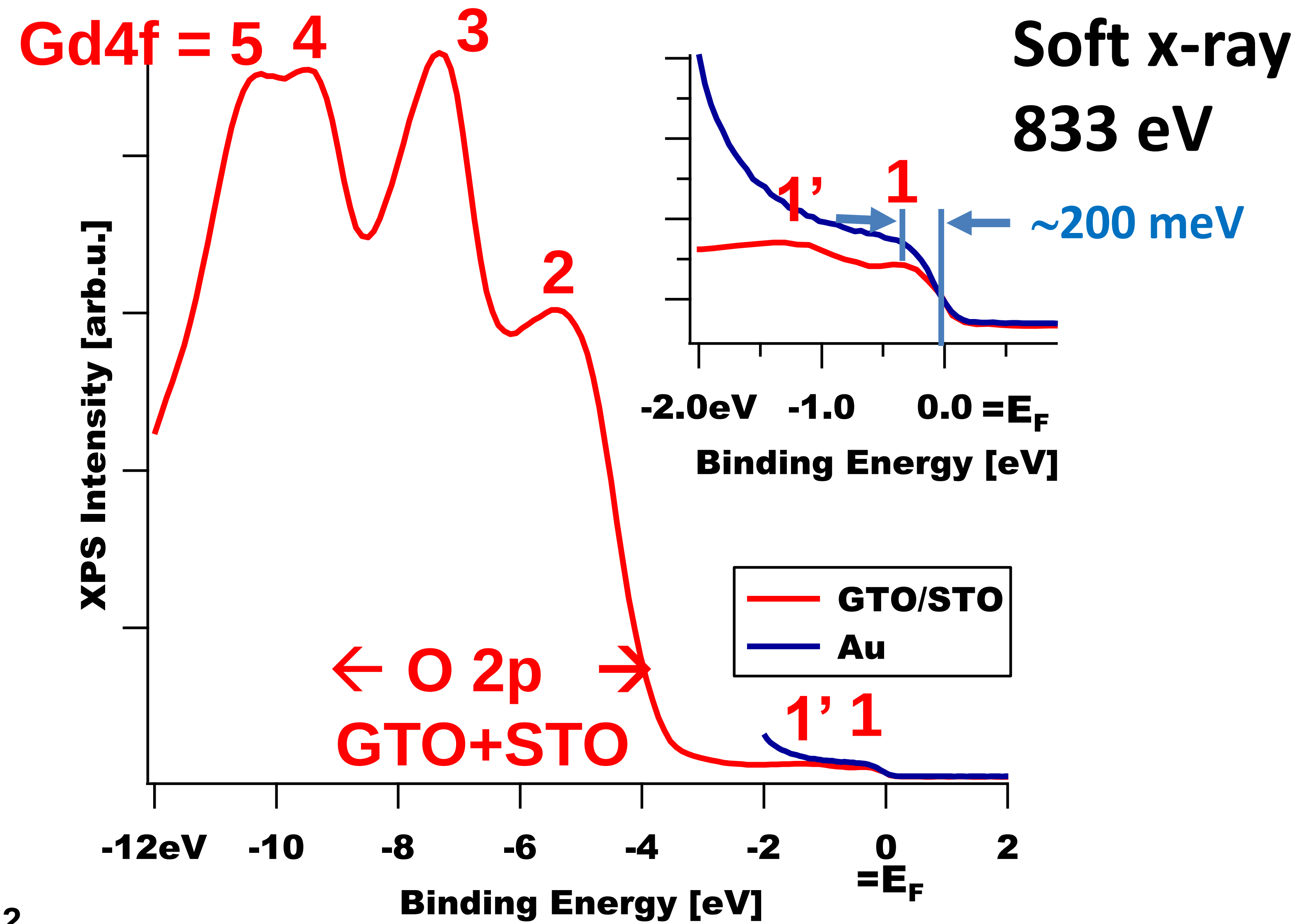


Appl. Phys. Lett. 99, 232116 (2011).

Stemmer et al.

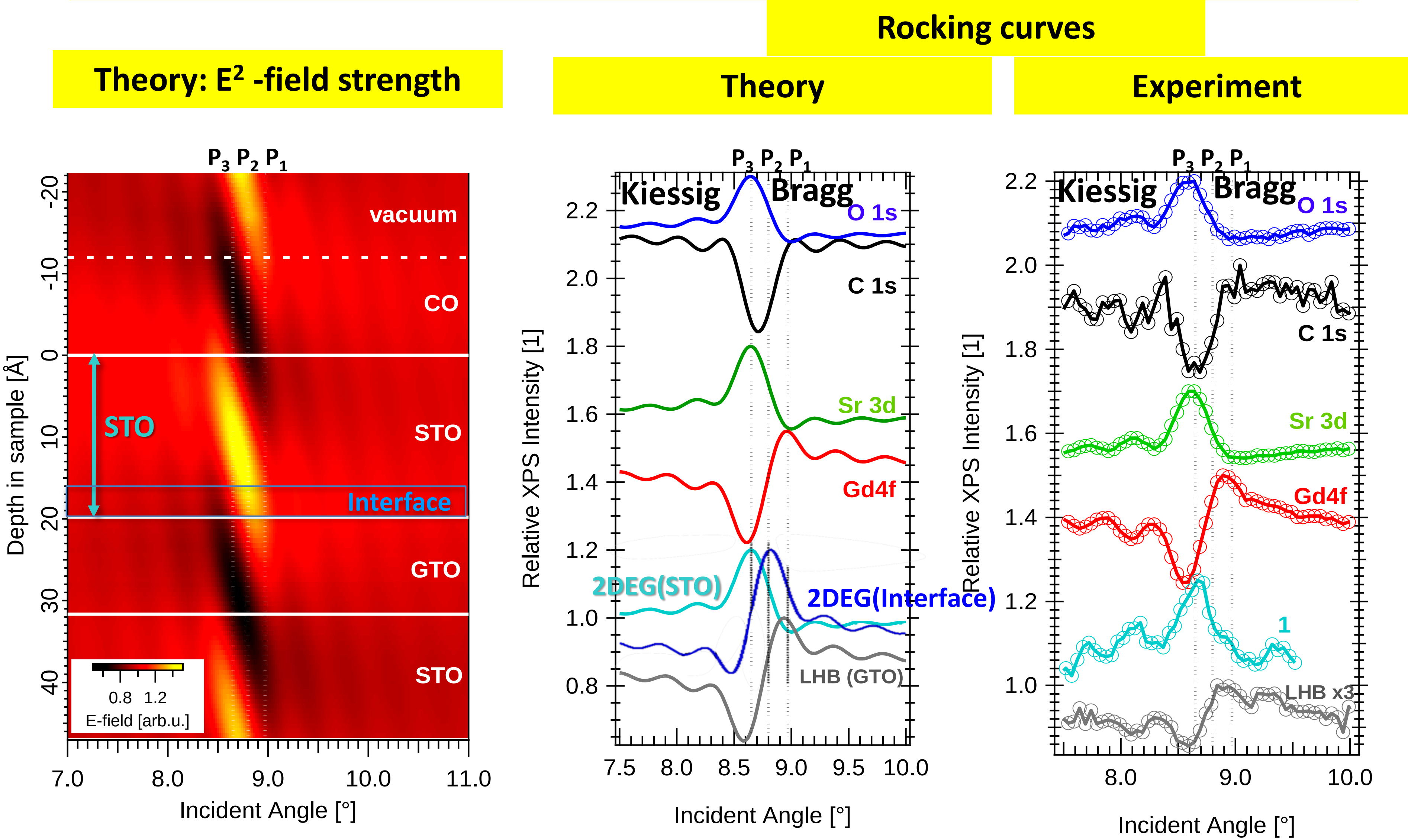
Can we see this 2DEG with standing wave ARPES, including its momentum dispersion and its depth distribution?

GTO/STO multilayer:
Soft x-ray photoemission in the XPS limit @ 833 eV@ 298K
→Matrix-element-weighted densities of states



ALS BL 7.0.2

Theoretical simulations vs. expt.—1187-just above Gd M_5 edge SW emphasizng STO/GTO interface



→Peak 1 = 2DEG & 2DEG occupies the full STO layer

Conclusions: Standing-Wave and Resonant PS and ARPES of $SrTiO_3/GdTiO_3$

- k-resolved bands of GTO LHB and 2DEG, evidence for intermixing of the two
- 2DEG extends through the entire STO layer from standing-wave rocking curve analysis
- Results consistent with 2DEG tunneling subband spacing measurements and tight binding- or LDA + hybrid functional- calculations
- Rocking curve forms very sensitive measure of depth distributions near buried interfaces→future applications to other systems

CSF and S. Nemšák,, J. Electron Spect. , 195, 409–422 (2014):
S. Nemšák, et al., TBP

Summary

- **Photoelectron spectroscopy has developed over the last ~40 years from a vacuum-based technique to measurements at elevated pressures and operating conditions, including buried interfaces**
- **New facilities and instrumentation:**
  - **Differential pumping to permit higher pressures near sample**
  - **Hard x-ray photoelectron spectroscopy: bulk and buried interfaces, higher gas pressures**
  - **Standing-wave excitation to more precisely probe in depth**
- **A development need:**
  - **Detectors with higher efficiency, time resolution and dynamic range up to multi-GHz range**