Take away messages:

what is XPS

e-spectrometer: how it works

HAXPES: probing depth

cross sections

AP-XPS introduction

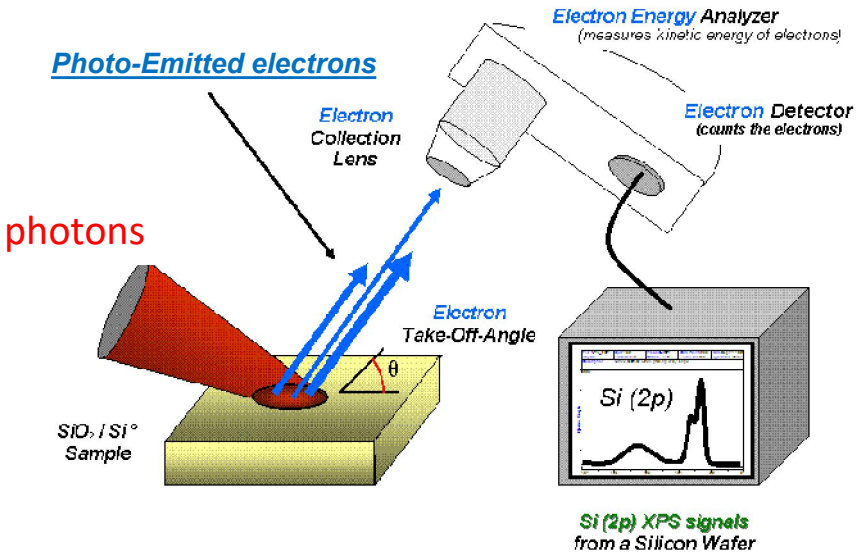
future: AP-HAXPES with membranes

PhotoElectron Spectroscopy (PES)

Photoelectron Spectroscopy (PES) is a widely used technique to investigate the chemical composition of surfaces.

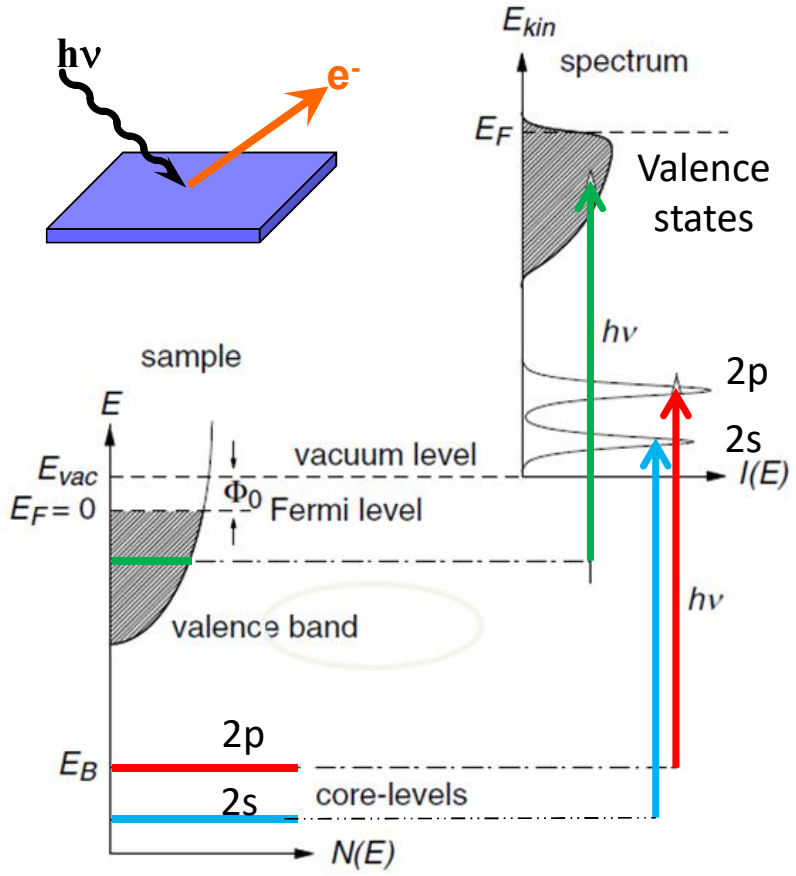
"What is?"	*Elemental composition*
"How much is?"	*Quantitative analysis*

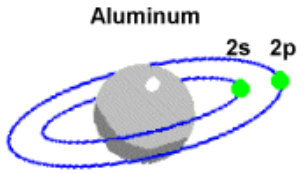
PES can probe many features of the electronic structure, thus providing information useful for the comprehension e.g. of spin/charge transport, magnetic properties, local structural order, etc…

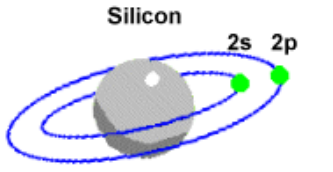


- *Irradiate a solid with monoenergetic UV/X-ray radiation*
- *Analyze the energies of the emitted electrons*

PHOTOELECTRIC EFFECT







$$E_K = h\nu - E_B - \phi_{AN}$$

$h\nu$: photon energy

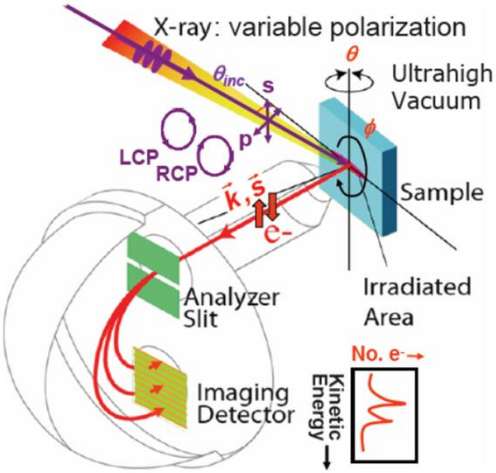
E_B : core level binding energy

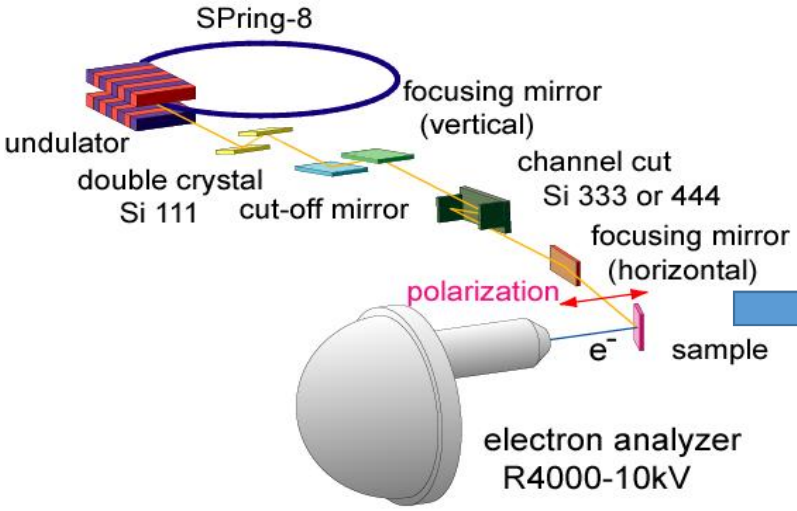
ϕ_{AN}: work function of the electron analyzer

1. H. Hertz, Ann. Physik 31,983 (1887).
2. A. Einstein, Ann. Physik 17,132 (1905). 1921 Nobel Prize in Physics.
3. K. Siegbahn, Et. Al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics.

Exploiting PES features

- ❑ Atomic specie sensitivity
- ❑ Chemical state sensitivity
- ❑ Spin sensitivity
- ❑ Photon Energy and Polarization dependence

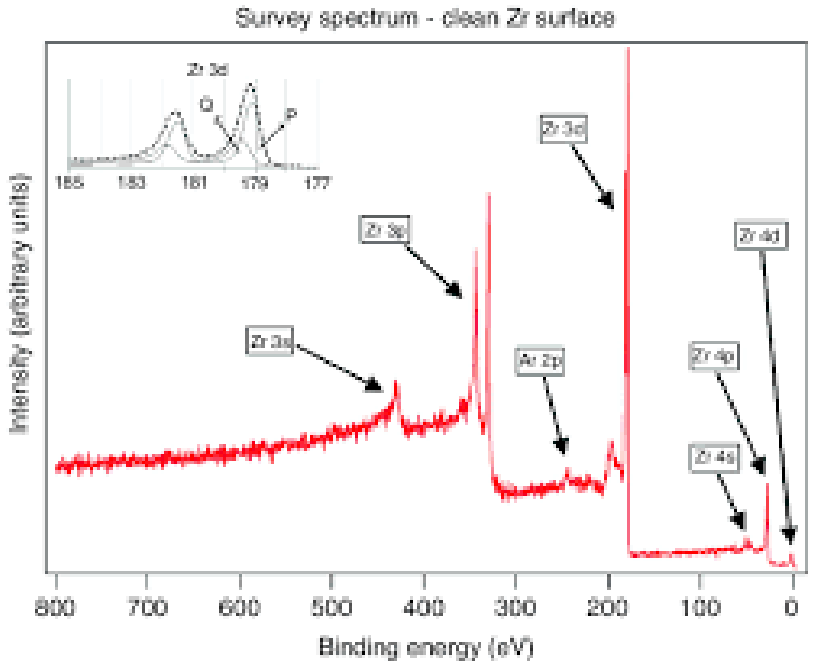




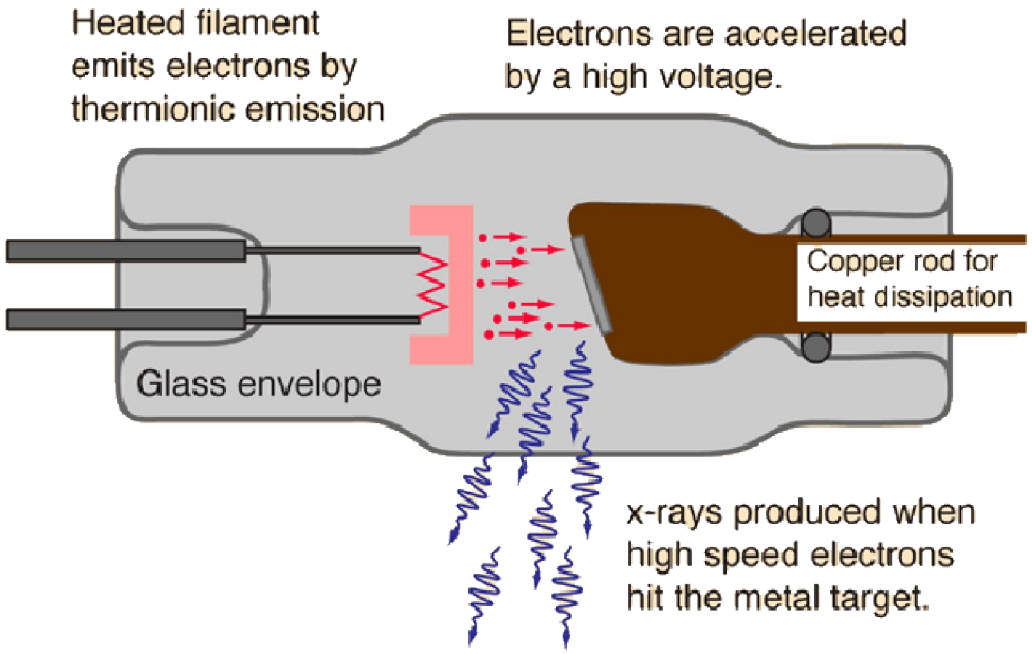
Advantages provided by synchrotron radiation sources

- ✓ Tunability in a very large range
- ✓ Very high intensity
- ✓ Good energy resolution
- ✓ Possibility to have polarized light

True success: chemical analysis with laboratory sources



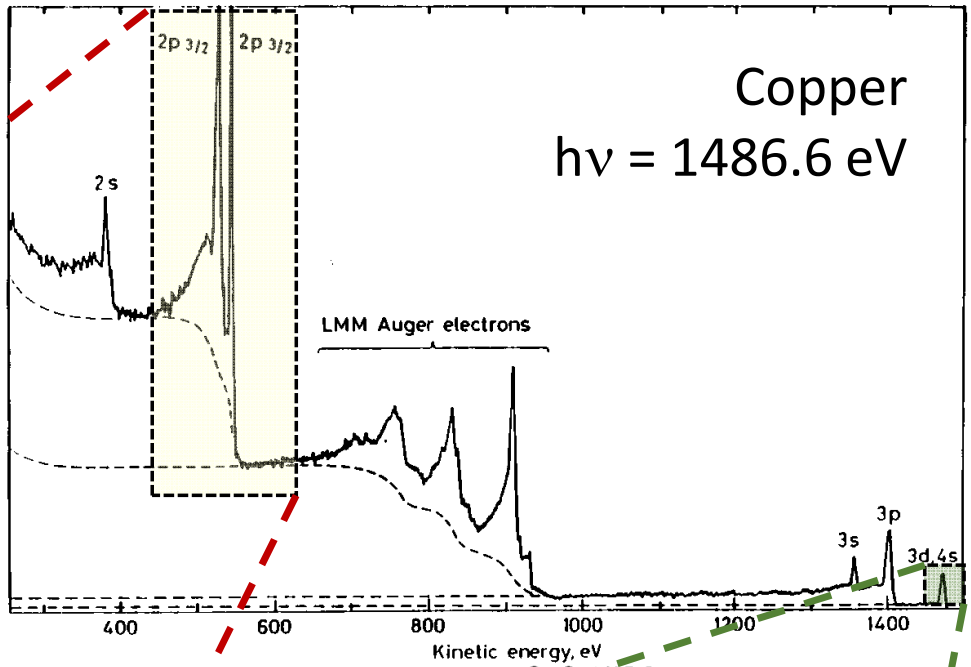
X ray tube



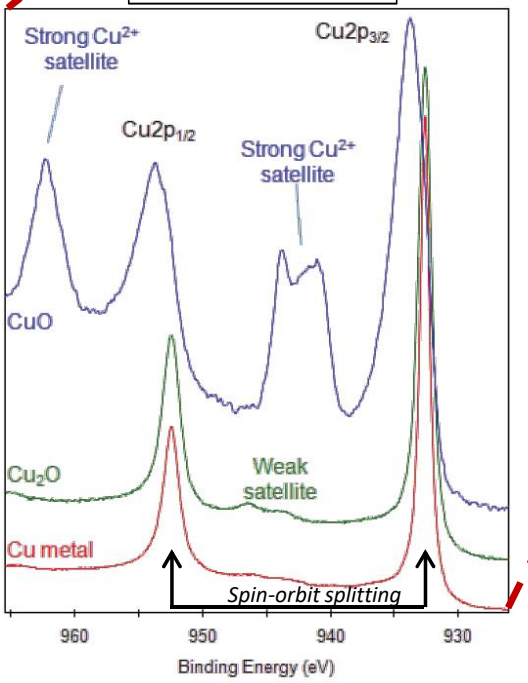
Reference: hanbook of x ray photoemission spectroscopy

CHEMICAL STATE SENSITIVITY

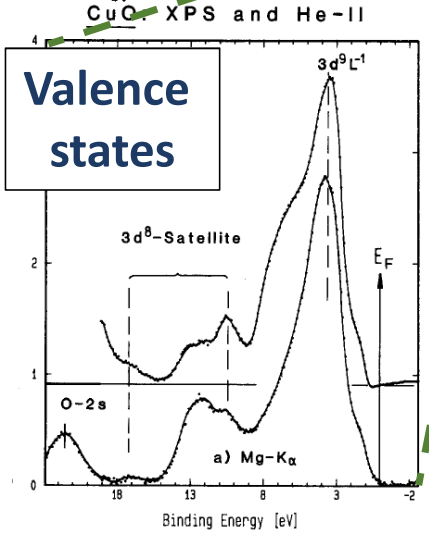
Core level spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).



Core levels

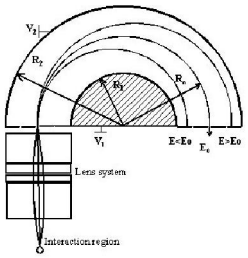


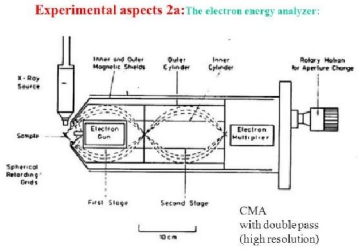
Valence states



Electron energy analysers

Electrostatic energy analyser

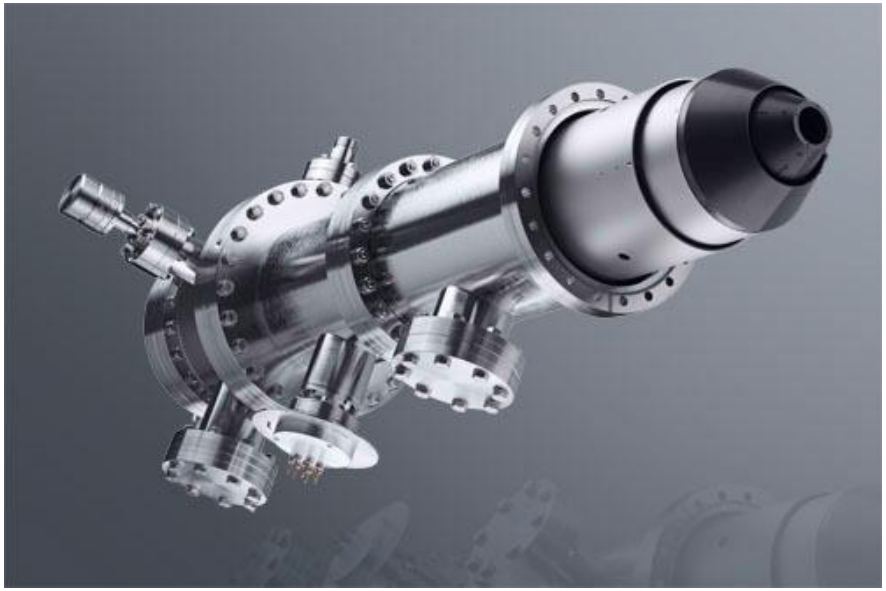




Hemispherical or cilindrical

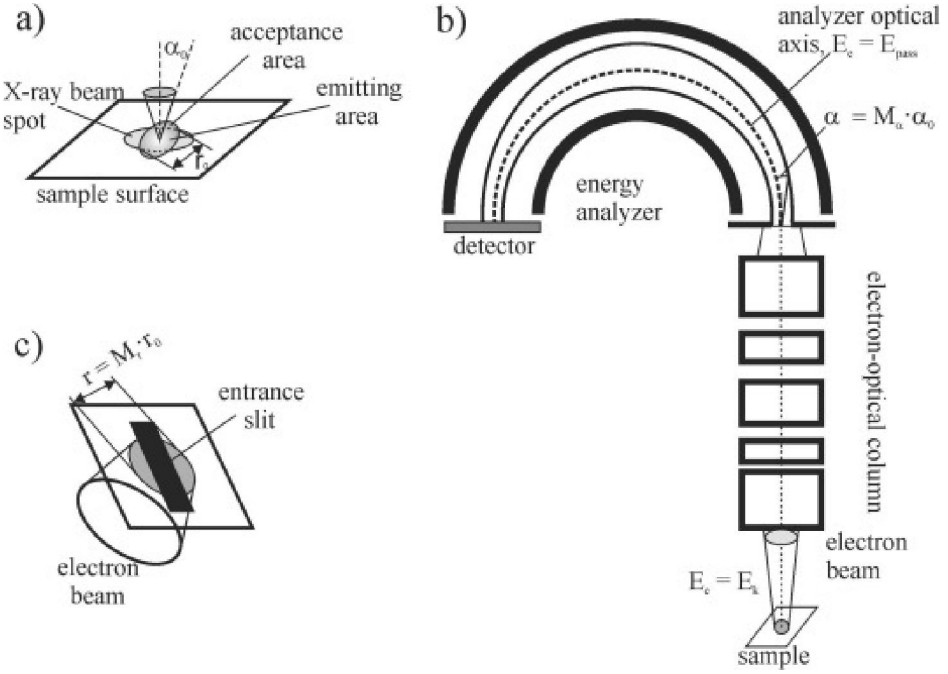
Broad application field with standard and synchrotron sources

Time of flight



Require pulsed sources, special applications:
Time resolved experiment
Angular resolved photoemission

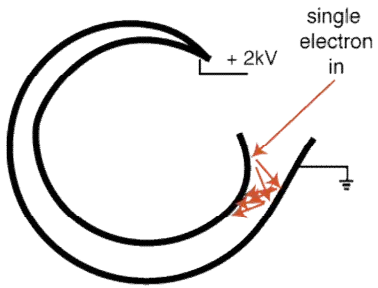
The king of analysers: electrostatic hemispherical analyser



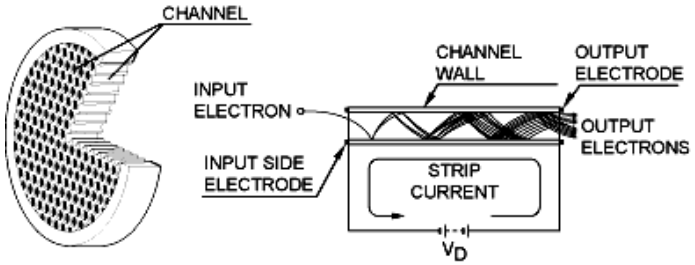
3 parts: input lenses
hemisphers
detectors

Detectors:
electron multipliers

Channeltrons

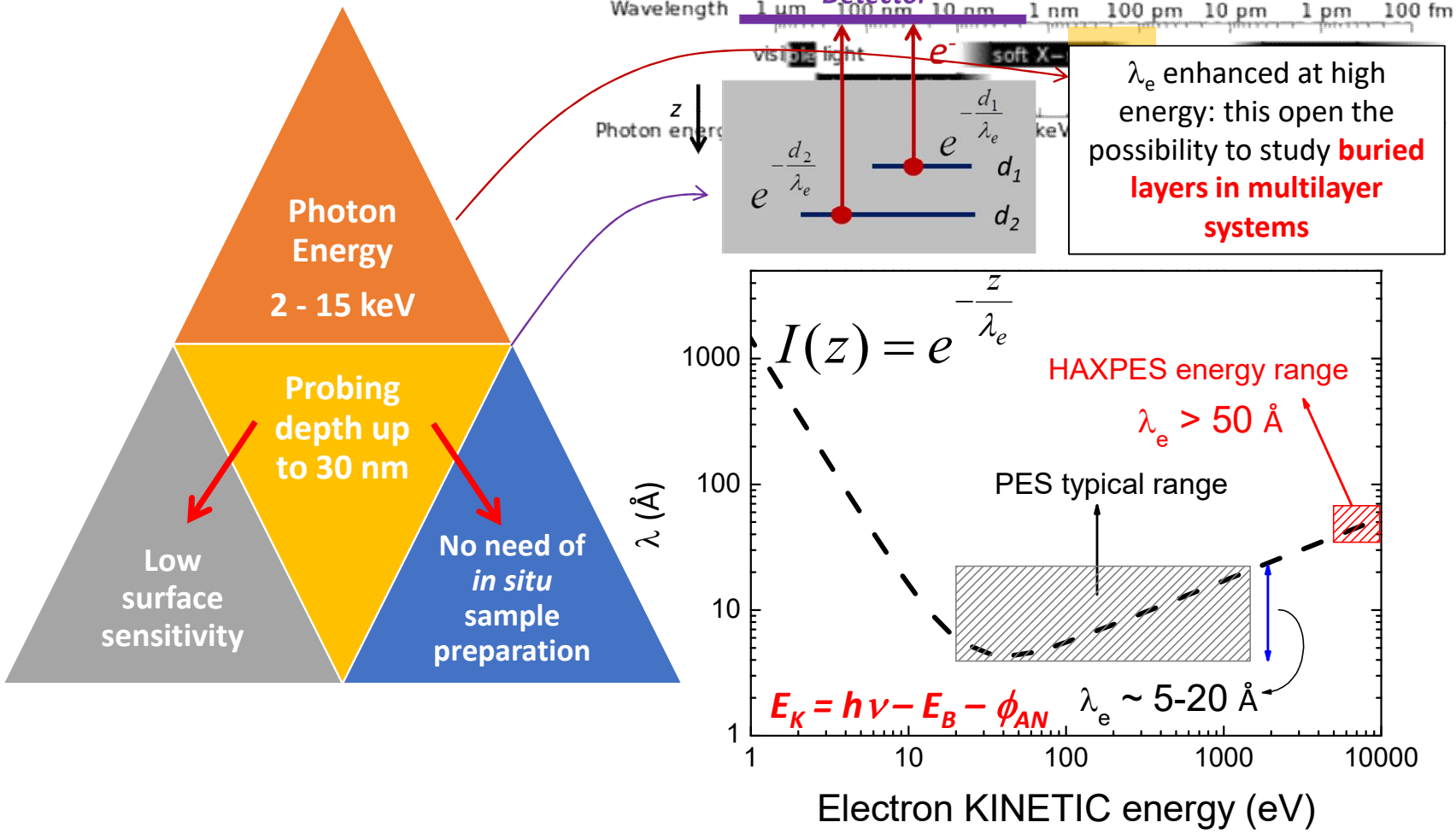


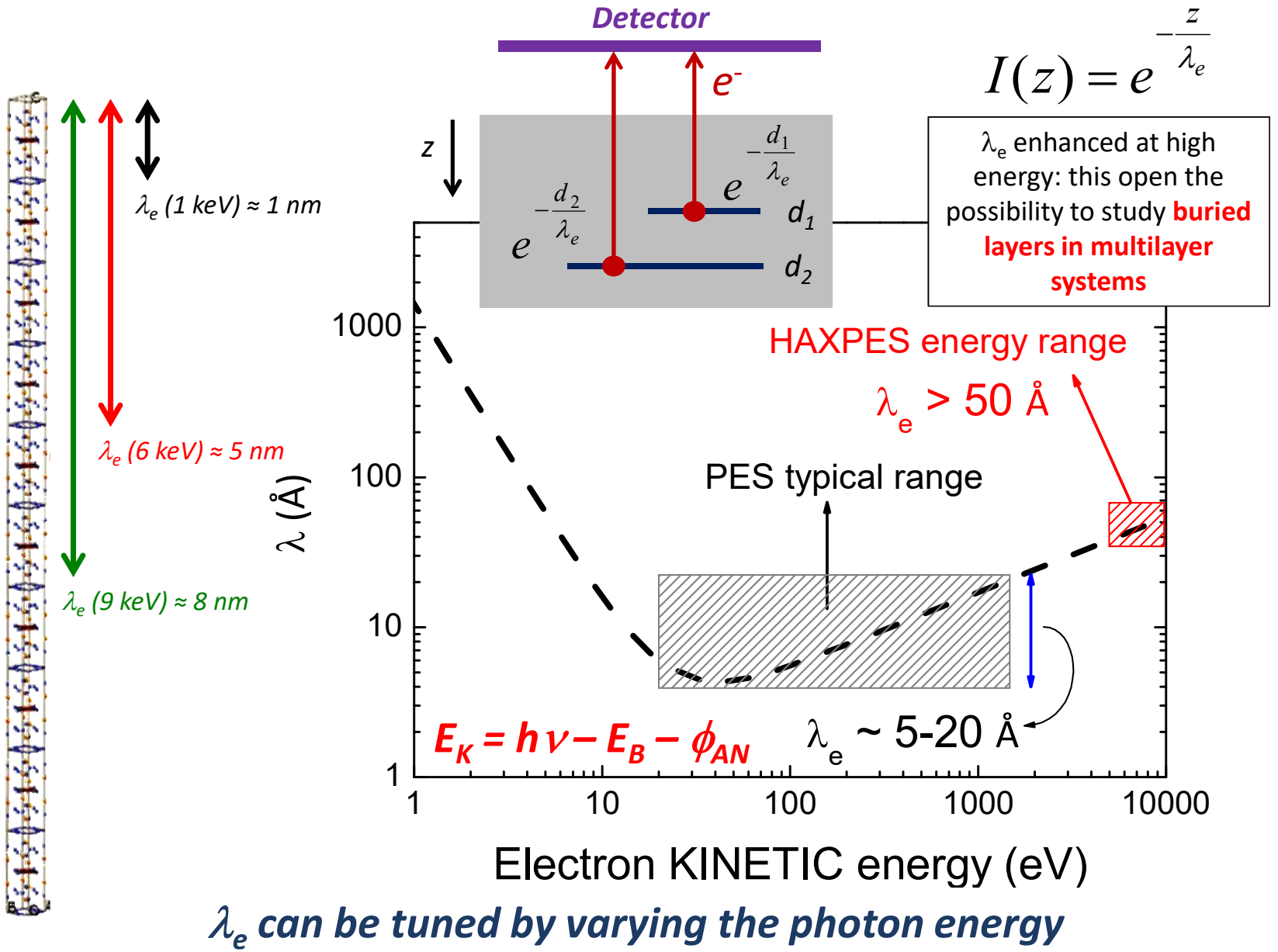
Microchannel plate



Both require vacuum better than 10-6 mbar!!!

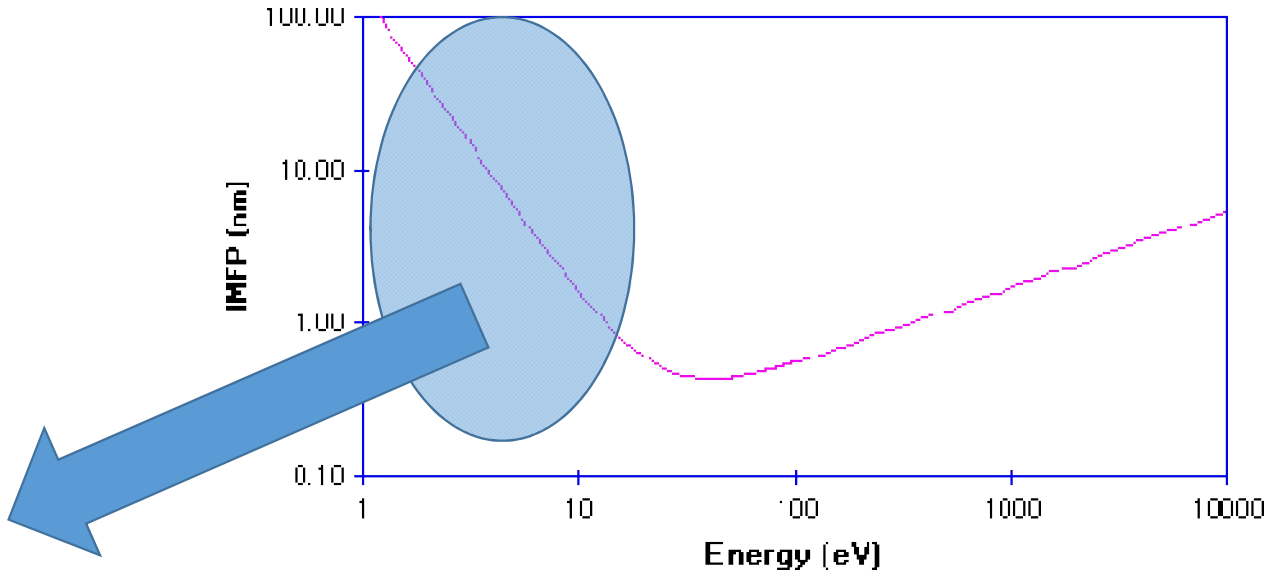
HArd X-ray PhotoElectron Spectroscopy
A tool for looking beneath the surface





λ_e can be tuned by varying the photon energy

parentheses: the universal curve



FAKE!

There are different behaviour below 100eV, not universal

The VOLPE Project

VOLume PhotoEmission from solids with Synchrotron Radiation

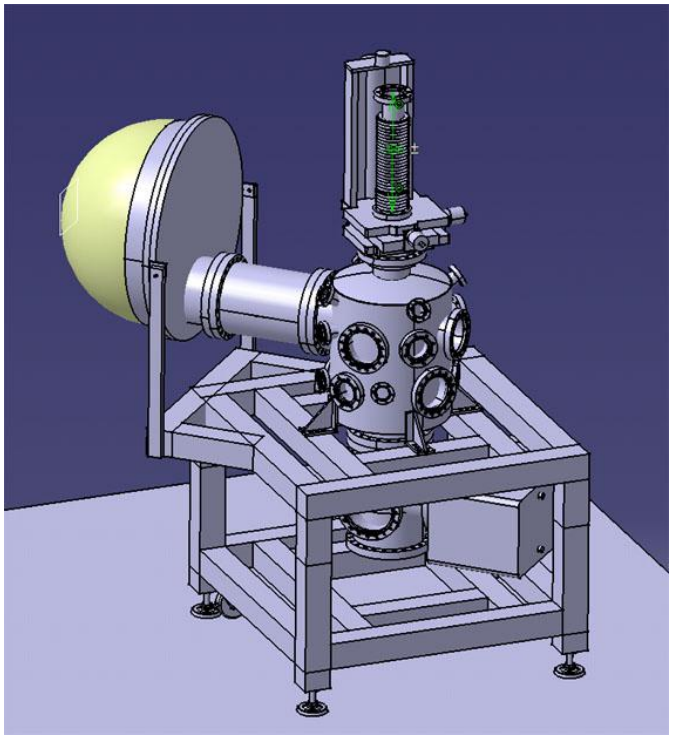
5th Framework RTD European Project - 3 years (2002-2005)

ELETTRA (Trieste), INFM (Rome and Trieste), ESRF (Grenoble), LURE (Paris), EPFL (Lausanne) ,Univ. Neuchatel

OBJECTIVES:
20-40 meV Energy resolution
@ 6-10 keV

1) **High Resolution/High Flux**
   ESRF ID16 beamline
   15-100 meV at 8-10 keV

2) **Dedicated Spectrometer, power supplies and detector**



Challenges:

Power supply stability @HV

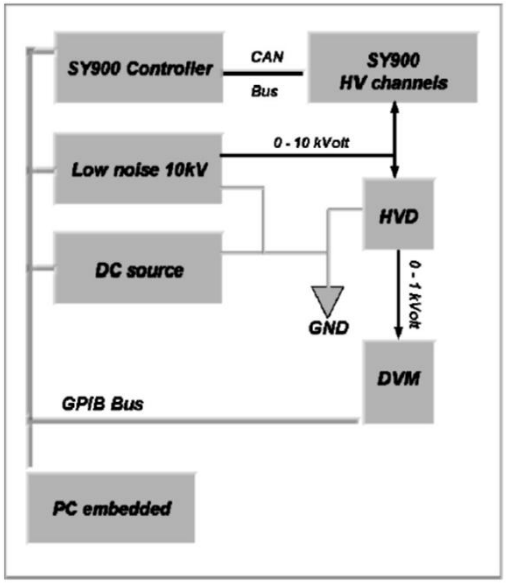


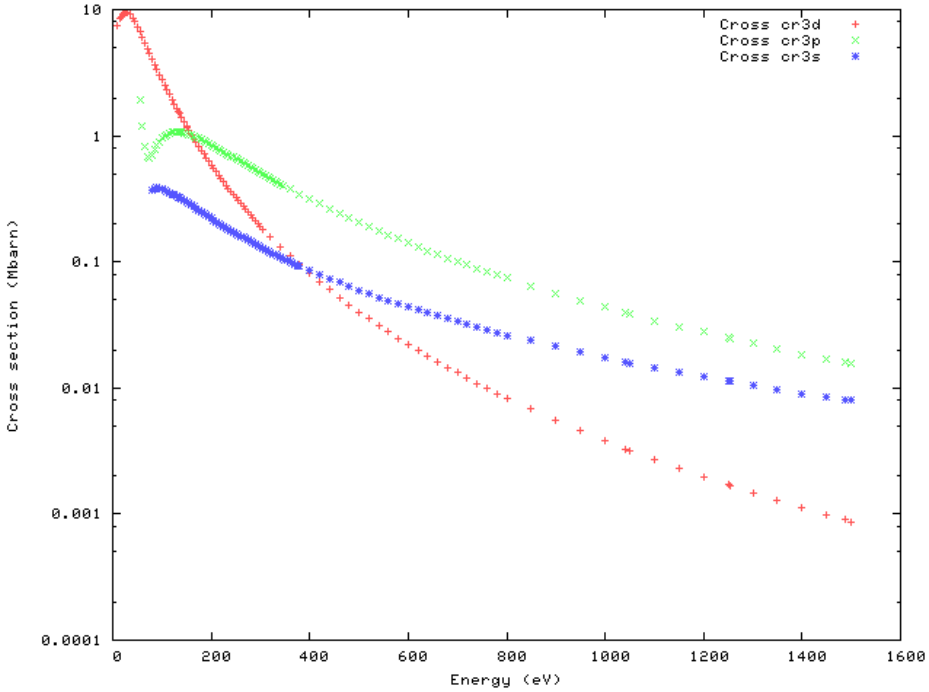
FIG. 5. Block diagram of the power supply system.

Low noise detector:
CROSS SECTION!!!

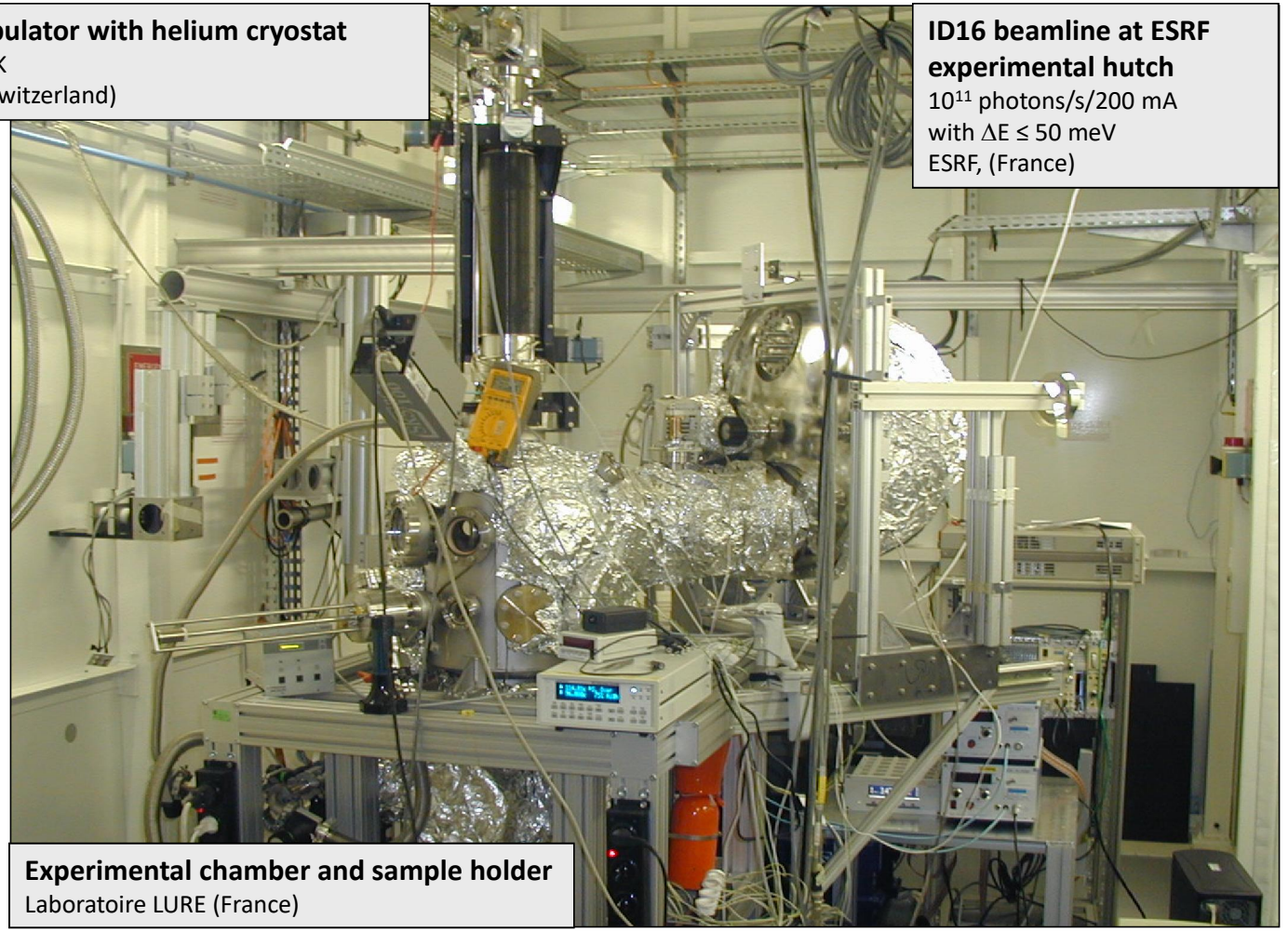
Use the Elettra resource:

https://vuo.elettra.eu/services/elements/WebElements.html

Return to periodic table



VOLPE apparatus at the ID16 beamline of the ESRF



Manipulator with helium cryostat
T < 20 K
EPFL (Switzerland)

ID16 beamline at ESRF experimental hutch
10^{11} photons/s/200 mA
with $\Delta E \leq 50$ meV
ESRF, (France)

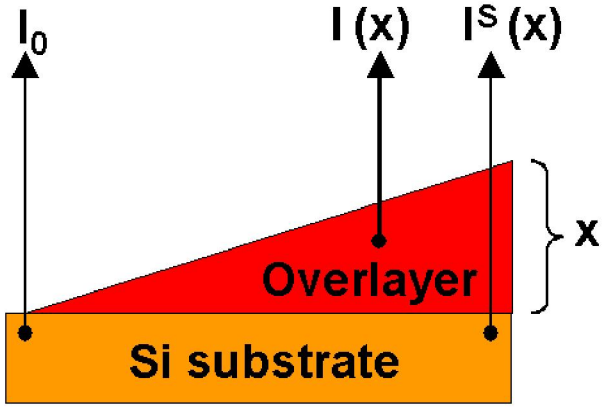
Experimental chamber and sample holder
Laboratoire LURE (France)

P. Torelli et al. RSI 76 023909 (2005)

Estimation of the bulk sensitivity in HAXPES

Bulk sensitivity in PES is typically estimated via measurements of electron effective attenuation length (λ), the thickness of the overlayer that reduces to 1/e the intensity I^S of a core level emission from the substrate.

The "overlayer" experiment:



Overlayer:
Co, Cu, Ge, and Gd_2O_3

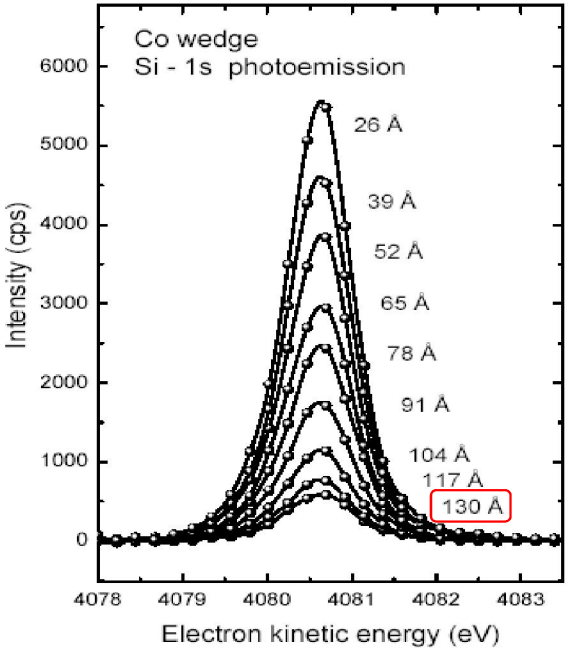
I^0 = intensity from the bare substrate

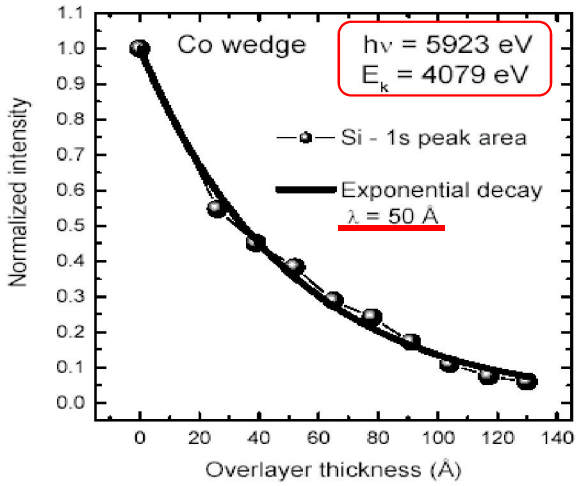
$$I^S(x) = I^0 e^{-\frac{x}{\lambda}}$$

$$I(x) = I^T(1 - e^{-\frac{x}{\lambda}})$$

I^T = intensity for an infinite overlayer

PROBING DEPTH ≈ $3\lambda_e$





M. Sacchi *et al.,* Phys. Rev. B **71**, 155177 (2005)

Bulk vs Surface sensitivity

PRL **100,** 167402 (2008) PHYSICAL REVIEW LETTERS week ending 25 APRIL 2008

Nature of the Band Gap of In_2O_3 Revealed by First-Principles Calculations and X-Ray Spectroscopy

Aron Walsh,[1,*] Juarez L. F. Da Silva,[1] Su-Huai Wei,[1] C. Körber,[2] A. Klein,[2] L. F. J. Piper,[3] Alex DeMasi,[3] Kevin E. Smith,[3] G. Panaccione,[4] P. Torelli,[5] D. J. Payne,[6] A. Bourlange,[6] and R. G. Egdell[6]

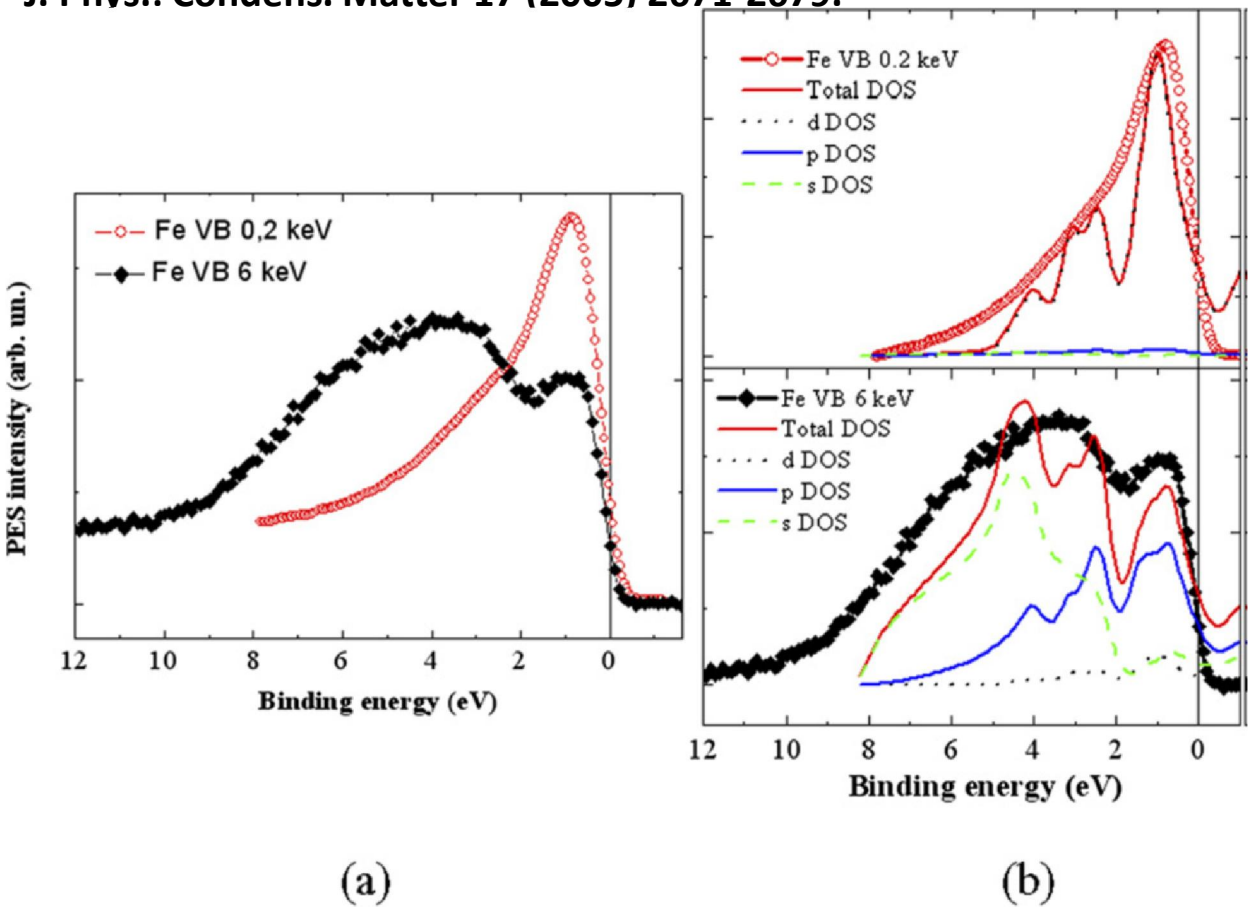
[1]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*
[2]*Darmstadt University of Technology, 64287 Darmstadt, Germany*
[3]*Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, Massachusetts 02215, USA*
[4]*Laboratorio TASC, INFM-CNR, Area Science Park, S.S. 14, Km 163.5, 34012 Trieste, Italy*
[5]*CNR-INFM-S3, Via Campi 213/A, I-41100 Modena, Italy*
[6]*Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, United Kingdom*
(Received 5 November 2007; published 25 April 2008)

Bulk and surface sensitive x-ray spectroscopic techniques are applied in tandem to show that the valence band edge for In_2O_3 is found significantly closer to the bottom of the conduction band than expected on the basis of the widely quoted bulk band gap of 3.75 eV. First-principles theory shows that the upper valence bands of In_2O_3 exhibit a small dispersion and the conduction band minimum is positioned at Γ. However, direct optical transitions give a minimal dipole intensity until 0.8 eV below the valence band maximum. The results set an upper limit on the fundamental band gap of 2.9 eV.

DOI: 10.1103/PhysRevLett.100.167402 PACS numbers: 78.70.En, 73.20.At, 78.20.Bh

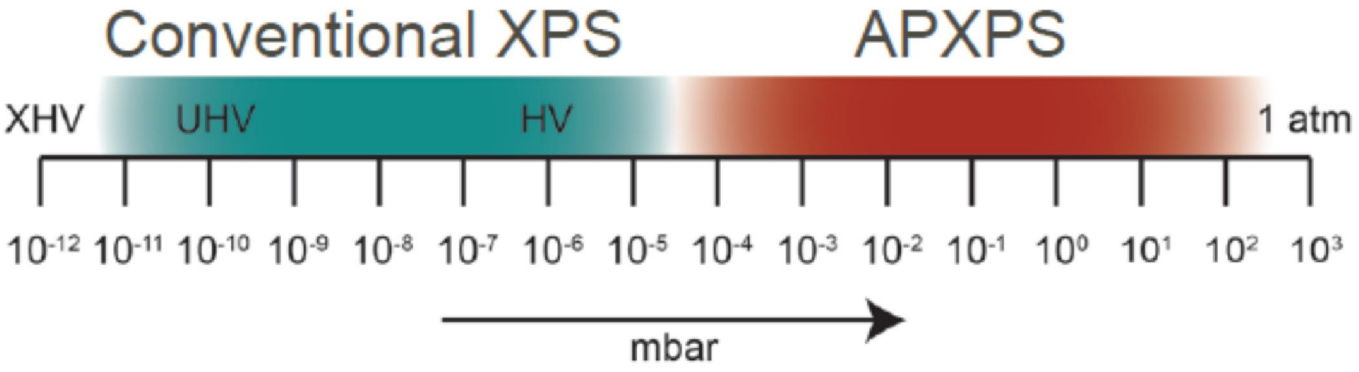
Change in the partial cross section

G. Panaccione, G. Cautero, M. Cautero, A. Fondacaro, M. Grioni, P. Lacovig, G. Monaco, F. Offi, G. Paolicelli, M. Sacchi, N. Stojic, G. Stefani, R. Tommasini and P. Torelli,
"High-energy photoemission in silver: resolving d and sp contributions in valence band spectra",
J. Phys.: Condens. Matter 17 (2005) 2671-2679.



G. Panaccione, F. Offi, M. Sacchi and P. Torelli,
Hard X-ray PhotoEmission Spectroscopy of strongly correlated systems,
Comptes Rendus de Physique 9, 524 (2008)

Ambient pressure XPS



Motivation:
-surface structure may differ from what observed in UHV
-Dynamic effect can play a significant role
-Dynimic processes may be studied
-Material with high vapor pressure can be studied

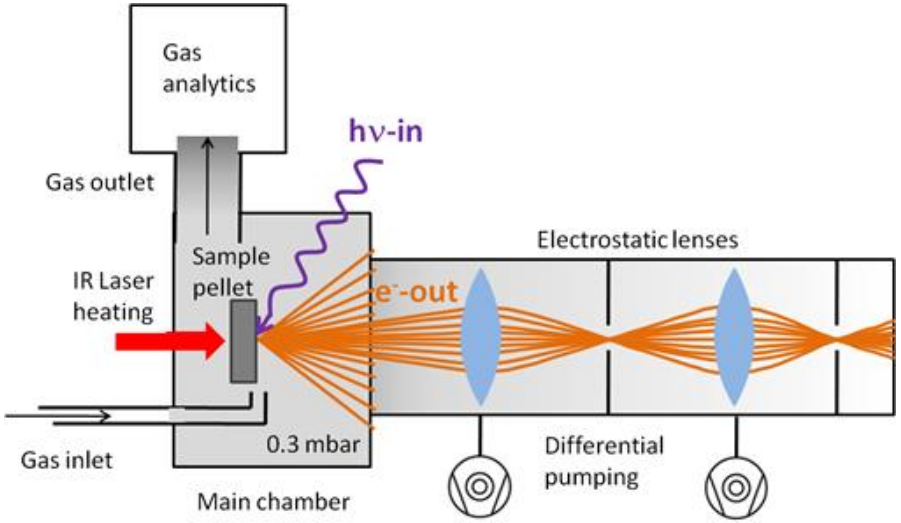
Problems:
1) Electron analyser require UHV

2) Electron escape depth

Analyser for NAP-XPS (a smart solution…)

Several differential pumping stages

Extremely expensive, brute force……



Input lenses focalize electron in small apertures to help differential pumping

Example 1: chemical reactivity @ surfaces

ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

Ambient-Pressure X-ray Photoelectron Spectroscopy Study of Cobalt Foil Model Catalyst under CO, H_2, and Their Mixtures

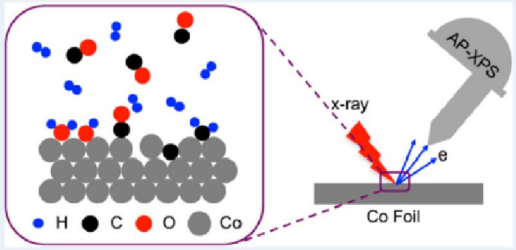
Cheng Hao Wu,[†,‡] Baran Eren,[‡] Hendrik Bluhm,[§] and Miquel B. Salmeron*[,‡,§,∥]

[†]Department of Chemistry and [∥]Department of Materials Science and Engineering, University of California, Berkeley, California 94720, United States

[‡]Materials Sciences Division and [§]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Ambient-pressure X-ray photoelectron spectroscopy (XPS) was used to investigate the reactions of CO, H_2, and their mixtures on Co foils. We found that CO adsorbs molecularly on the clean Co surface and desorbs intact in vacuum with increasing rate until ~90 °C where all CO desorbs in seconds. In equilibrium with 100 mTorr gas, CO dissociates above 120 °C, leaving carbide species on the surface but no oxides, because CO efficiently reduces the oxides at temperatures ~100 °C lower than H_2. Water as impurities or produced by reaction of CO and H_2 efficiently oxidizes Co even at room temperature. Under 97:3 CO/H_2 mixture and with increasing temperatures, the Co surface becomes more oxidized and covered by hydroxyl groups until ~150 °C where surface starts to get reduced, accompanied by carbide accumulation indicative of CO dissociation. A similar trend was observed for 9:1 and 1:1 mixtures, but surface reduction begins at higher temperatures.



KEYWORDS: *catalysis, Fischer−Tropsch synthesis, cobalt, ambient-pressure X-ray photoelectron spectroscopy*

Example 2: solid/liquid interfaces

SCIENTIFIC REPORTS

OPEN

Received: 12 October 2014
Accepted: 09 March 2015
Published: 07 May 2015

Using "Tender" X-ray Ambient Pressure X-Ray Photoelectron Spectroscopy as A Direct Probe of Solid-Liquid Interface

Stephanus Axnanda[1#], Ethan J. Crumlin[1#], Baohua Mao[1,2], Sana Rani[1], Rui Chang[1,2], Patrik G. Karlsson[3], Mårten O. M. Edwards[3], Måns Lundqvist[3], Robert Moberg[3], Phil Ross[4], Zahid Hussain[1] & Zhi Liu[1,2,5]

We report a new method to probe the solid-liquid interface through the use of a thin liquid layer on a solid surface. An ambient pressure XPS (AP-XPS) endstation that is capable of detecting high kinetic energy photoelectrons (7 keV) at a pressure up to 110 Torr has been constructed and commissioned. Additionally, we have deployed a "dip & pull" method to create a stable nanometers-thick aqueous electrolyte on platinum working electrode surface. Combining the newly constructed AP-XPS system, "dip & pull" approach, with a "tender" X-ray synchrotron source (2 keV–7 keV), we are able to access the interface between liquid and solid dense phases with photoelectrons and directly probe important phenomena occurring at the narrow solid-liquid interface region in an electrochemical system. Using this approach, we have performed electrochemical oxidation of the Pt electrode at an oxygen evolution reaction (OER) potential. Under this potential, we observe the formation of both Pt^{2+} and Pt^{4+} interfacial species on the Pt working electrode *in situ*. We believe this thin-film approach and the use of "tender" AP-XPS highlighted in this study is an innovative new approach to probe this key solid-liquid interface region of electrochemistry.

Example 3: the new solution: membranes!

Atmospheric pressure X-ray photoelectron spectroscopy apparatus: Bridging the pressure gap

J. J. Velasco-Vélez,[1,2,a)] V. Pfeifer,[2] M. Hävecker,[1,a)] R. Wang,[3] A. Centeno,[4] A. Zurutuza,[4] G. Algara-Siller,[2] E. Stotz,[2] K. Skorupska,[1] D. Teschner,[2] P. Kube,[2] P. Braeuninger-Weimer,[3] S. Hofmann,[3] R. Schlögl,[1,2] and A. Knop-Gericke[2]

[1]*Department of Heterogeneous Reactions, Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr 45470, Germany*

[2]*Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin 14195, Germany*

[3]*Engineering Department, University of Cambridge, Cambridge CB3 0FA, United Kingdom*

[4]*Graphenea, San Sebastian 20018, Spain*

(Received 1 February 2016; accepted 9 May 2016; published online 25 May 2016)

One of the main goals in catalysis is the characterization of solid/gas interfaces in a reaction environment. The electronic structure and chemical composition of surfaces become heavily influenced by the surrounding environment. However, the lack of surface sensitive techniques that are able to monitor these modifications under high pressure conditions hinders the understanding of such processes. This limitation is known throughout the community as the "pressure gap." We have developed a novel experimental setup that provides chemical information on a molecular level under atmospheric pressure and in presence of reactive gases and at elevated temperatures. This approach is based on separating the vacuum environment from the high-pressure environment by a silicon nitride grid—that contains an array of micrometer-sized holes—coated with a bilayer of graphene. Using this configuration, we have investigated the local electronic structure of catalysts by means of photoelectron spectroscopy and in presence of gases at 1 atm. The reaction products were monitored online by mass spectrometry and gas chromatography. The successful operation of this setup was demonstrated with three different examples: the oxidation/reduction reaction of iridium (noble metal) and copper (transition metal) nanoparticles and with the hydrogenation of propyne on Pd black catalyst (powder). *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4951724]

Take away messages:

XPS basic principles

e-spectrometer: how it works

HAXPES: incresed probing depth

change in relative (s,p,d) cross sections

AP-XPS introduction

future: AP-HAXPES with membranes