Core Level Photoelectron Spectroscopy

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Outline

- *What is core level photoelectron spectroscopy (XPS)?*
- *Instrumentation*
- *XPS Data interpretation*

.....with Synchrotron radiation

- *Examples of Fast XPS*

What is XPS?

XPS X-ray Photoelectron Spectroscopy

or

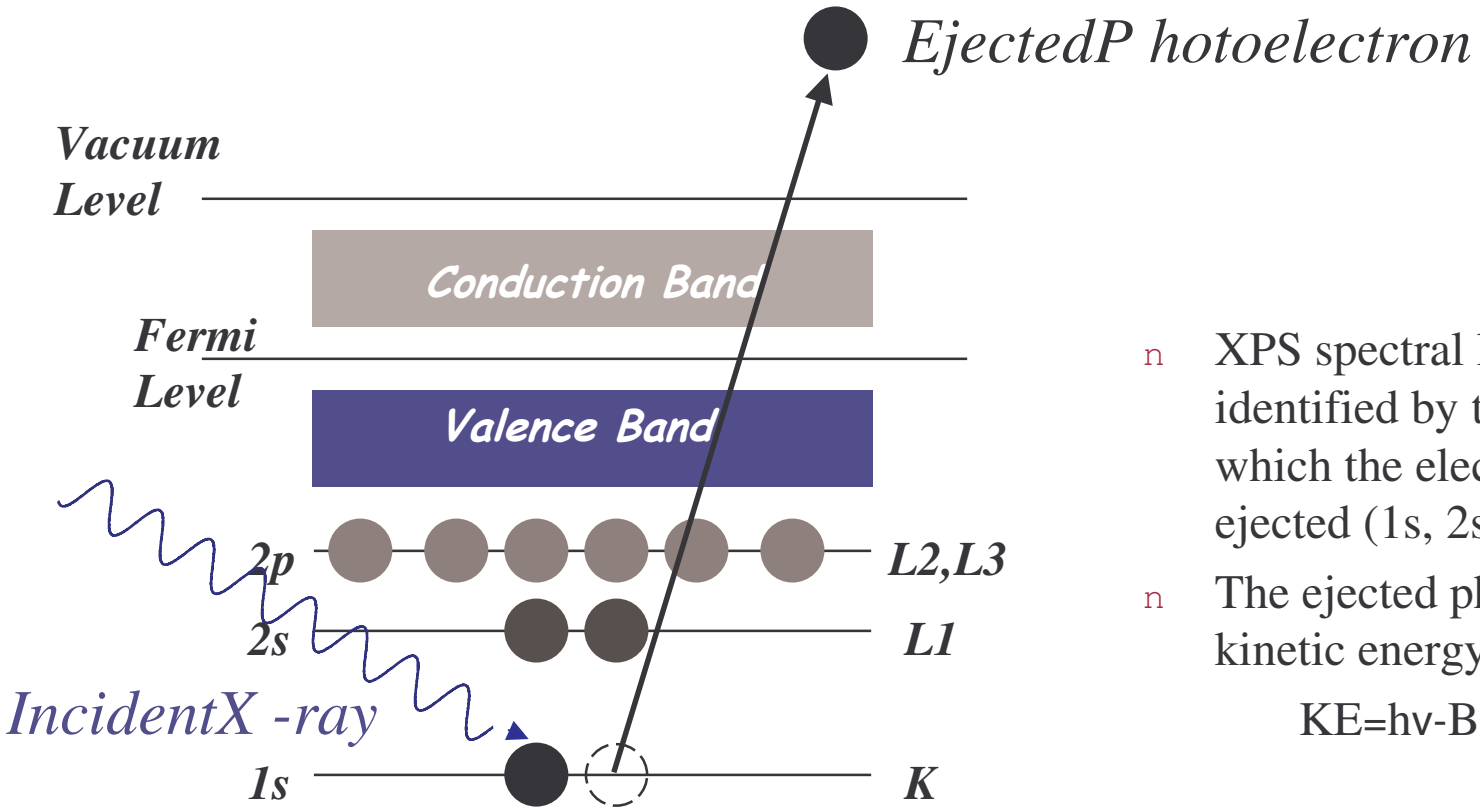
ESCA Electron Spectroscopy for Chemical Analysis

widely used technique to investigate the chemical composition of surfaces.

Based on the Photoelectric effect explained by A. Einstein (1921 Nobel Prize in Physics).

Developed in the mid 60's by the swedish group of K. Siegbahn (1981 Nobel Prize in Physics)

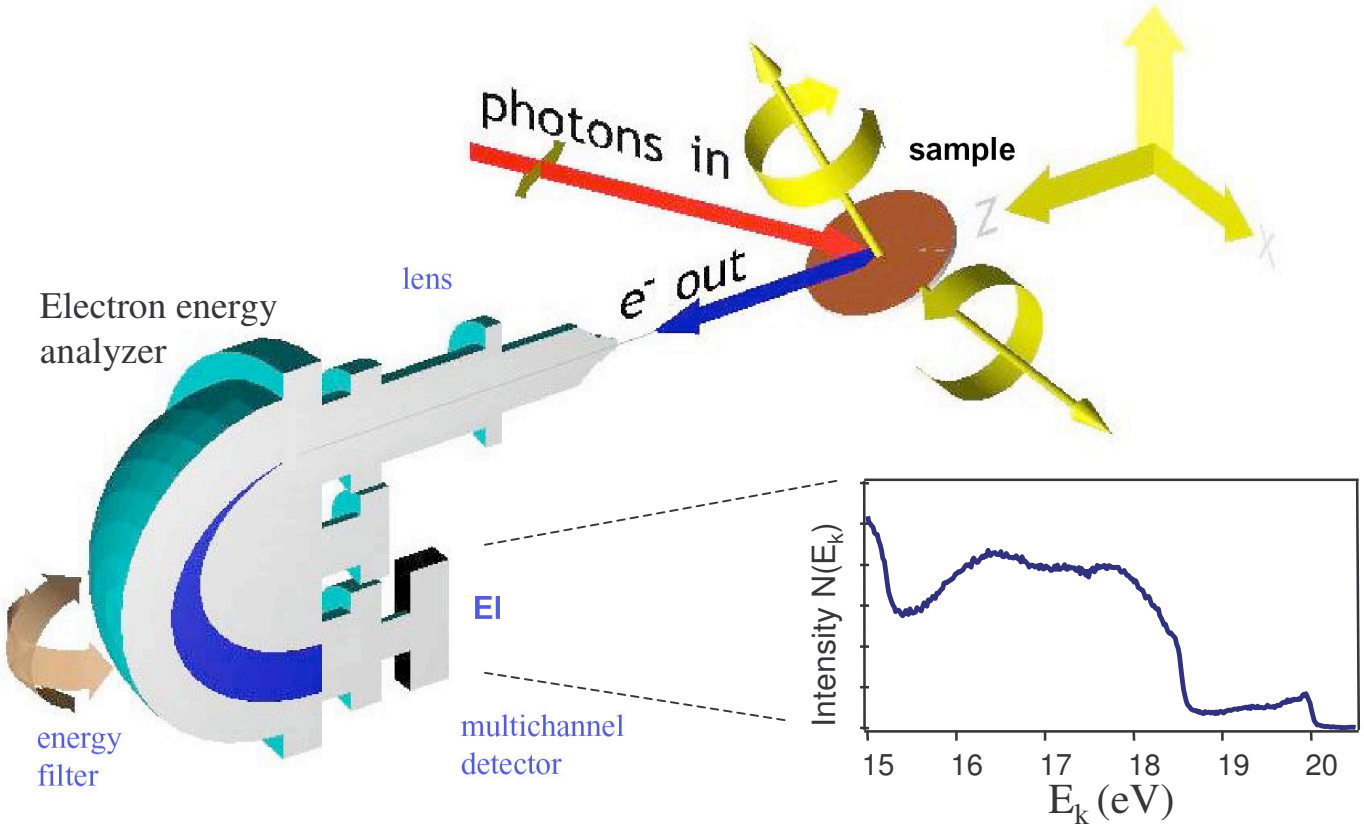
Photoelectric effect



- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:

  $KE = h\nu - BE - \Phi$

Photoemission experiment

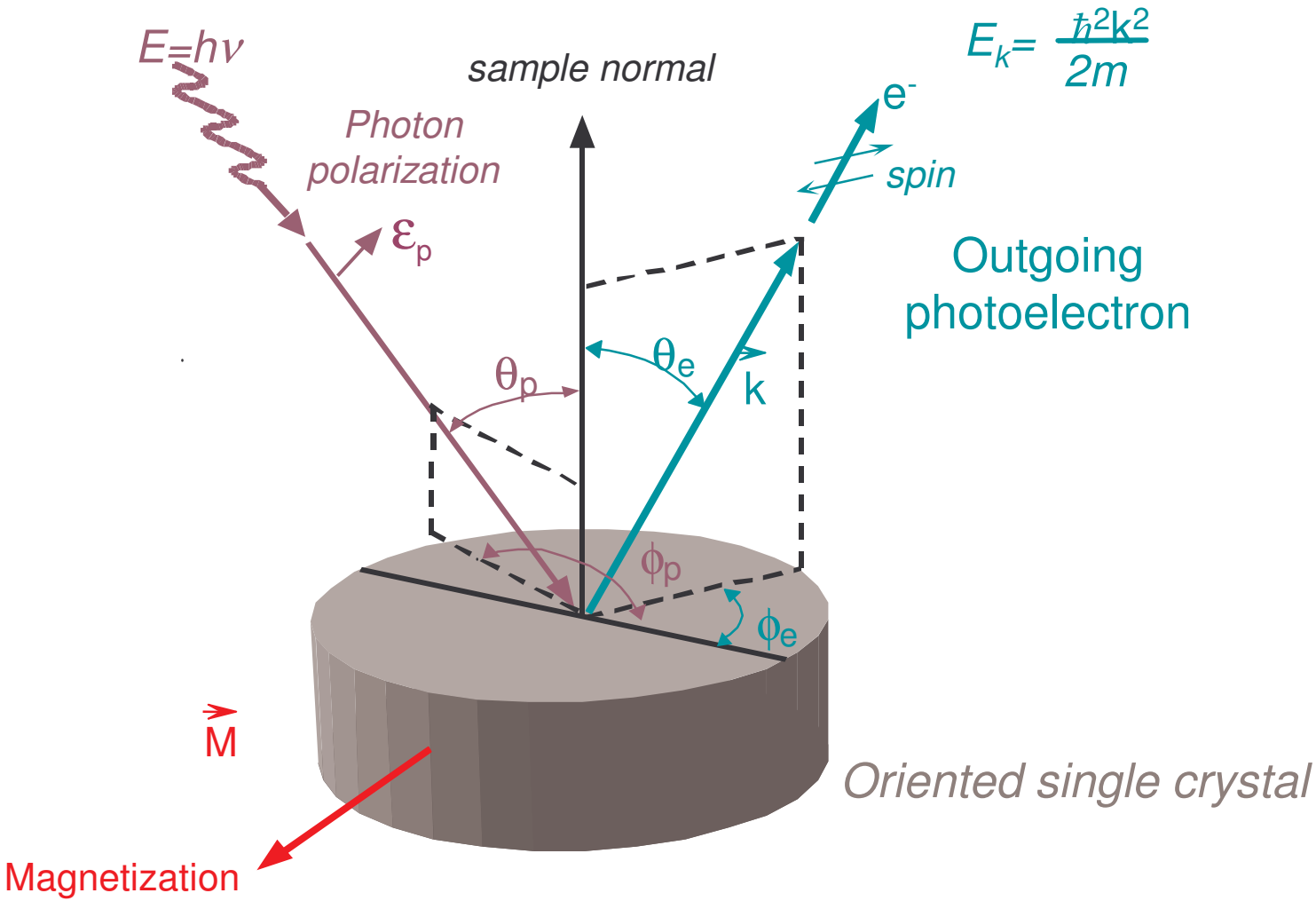


- Photoemission spectroscopy is a (**photon in**) - (**electron out**) experiment

-The kinetic energy of the photoelectrons is measured by an electron energy analyzer.

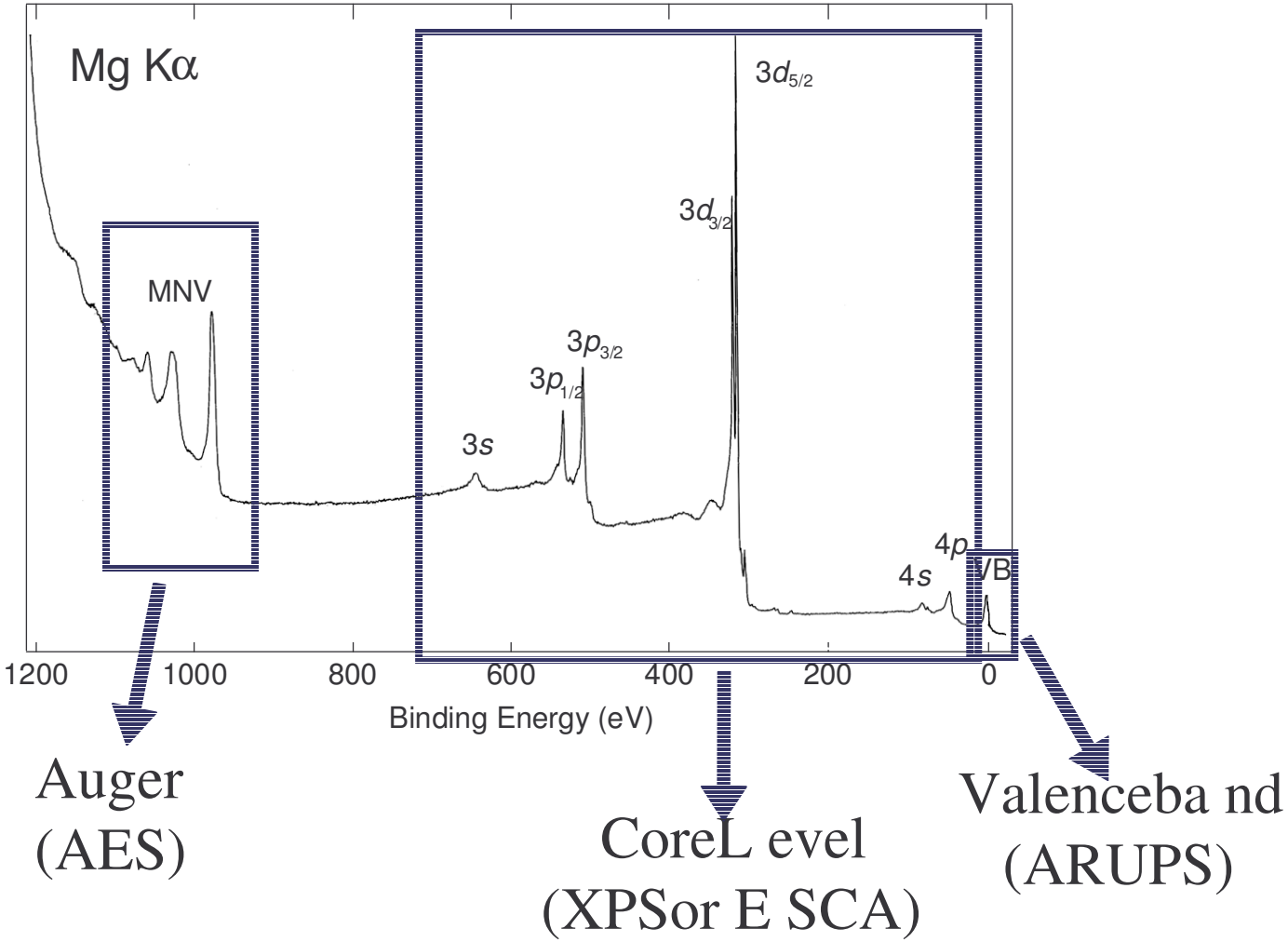
-The number of photoelectrons measured versus their kinetic energy, within the energy and angular windows(resolution)of the analyzer yields a **Photoemission Spectrum** or **Energy Distribution Curve (EDC).**

Photoemission experiment



Photoemission spectrum

Mg Kα hν = 1253.6 eV
Sample : clean Rhodium (Rh)



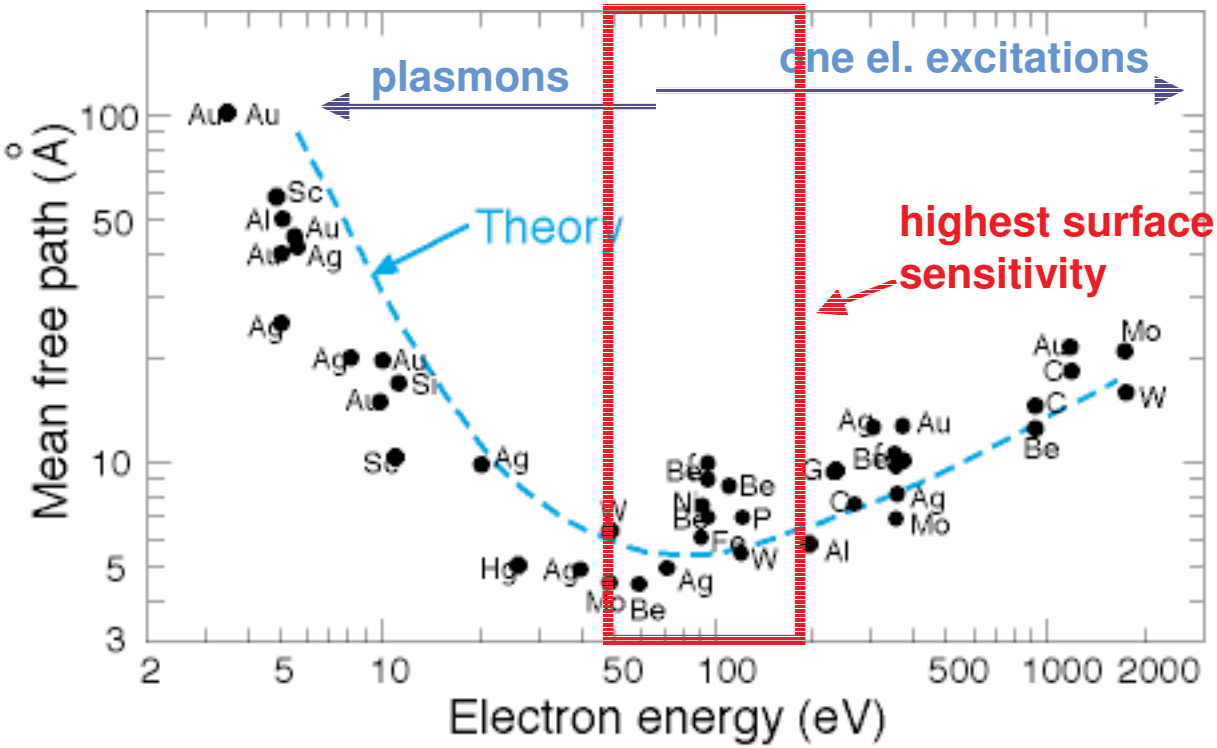
Surface Sensitivity

Loss processes that prevent escape of electrons from solids:

- **Phonons** : collective excitations of atoms 10 meV → 10 eV
- **Plasmons** : collective excitations of electrons 5 eV → 20 eV
- **Interband transitions**

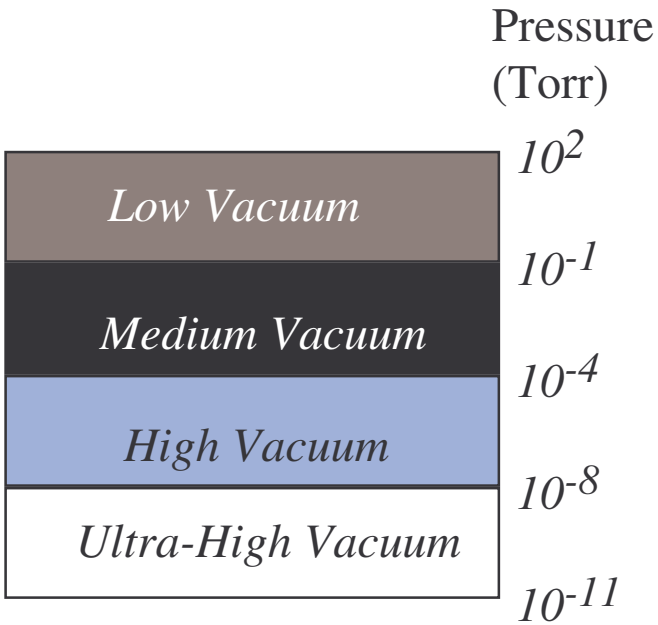
$$I = I_0 e^{-\frac{d}{\lambda}}$$

Universal Curve of Inelastic Mean Free Path λ



Vacuum conditions

Degreeof V acuum

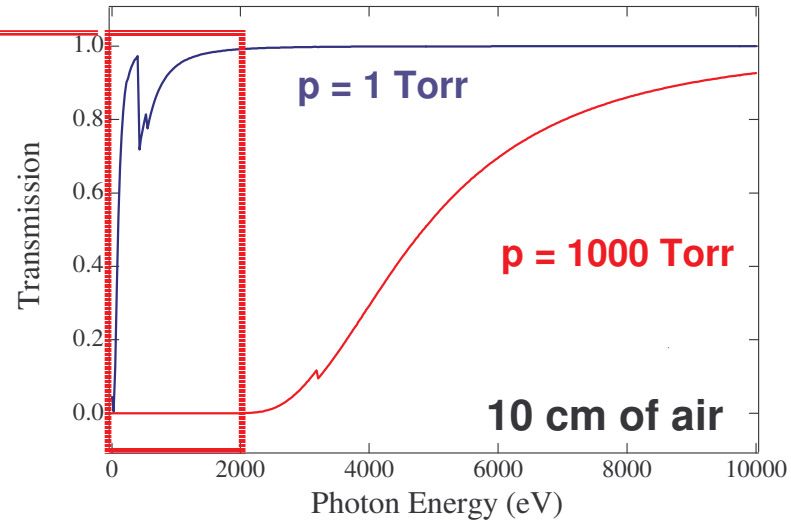


- Increase the mean free path for photons and electrons
- Remove adsorbed gases from the sample.
- Eliminate adsorption of contaminants on the sample.

Vacuum conditions

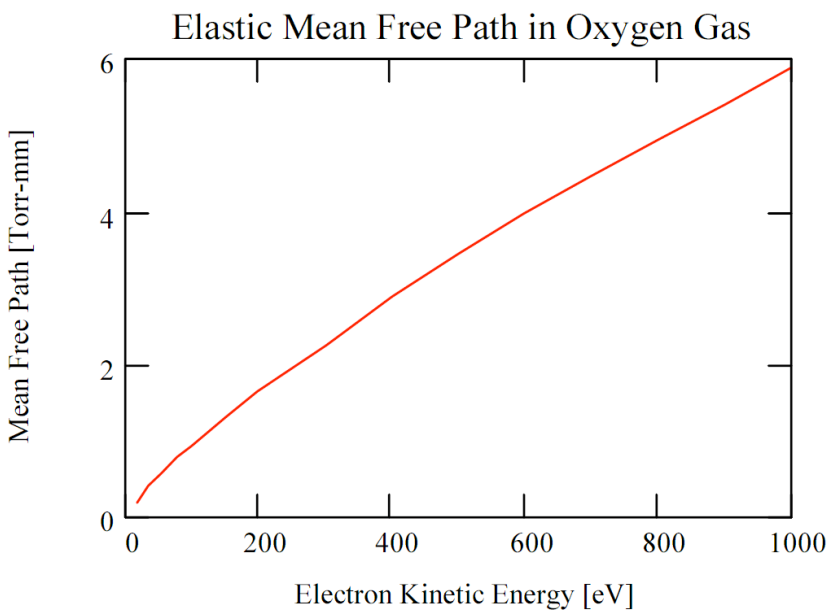
Tipical XPS hν

..... for photons



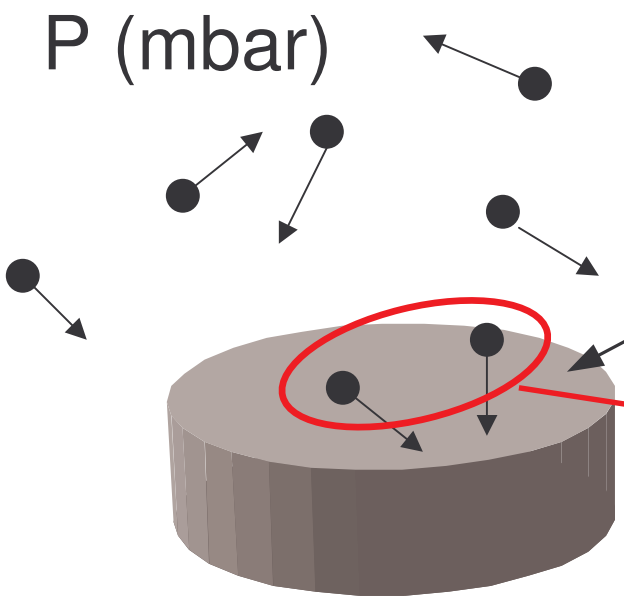
Medium/High Vacuum

..... for electrons



High Vacuum

Ultra High Vacuum (UHV)



$$1ML \sim 1x10^{15} atoms/cm^2$$

$$R = \frac{P}{\sqrt{2\pi MkT}} = \frac{4.567^{22} P_{mbar}}{\sqrt{MT}} cm^{-2}s^{-1}$$

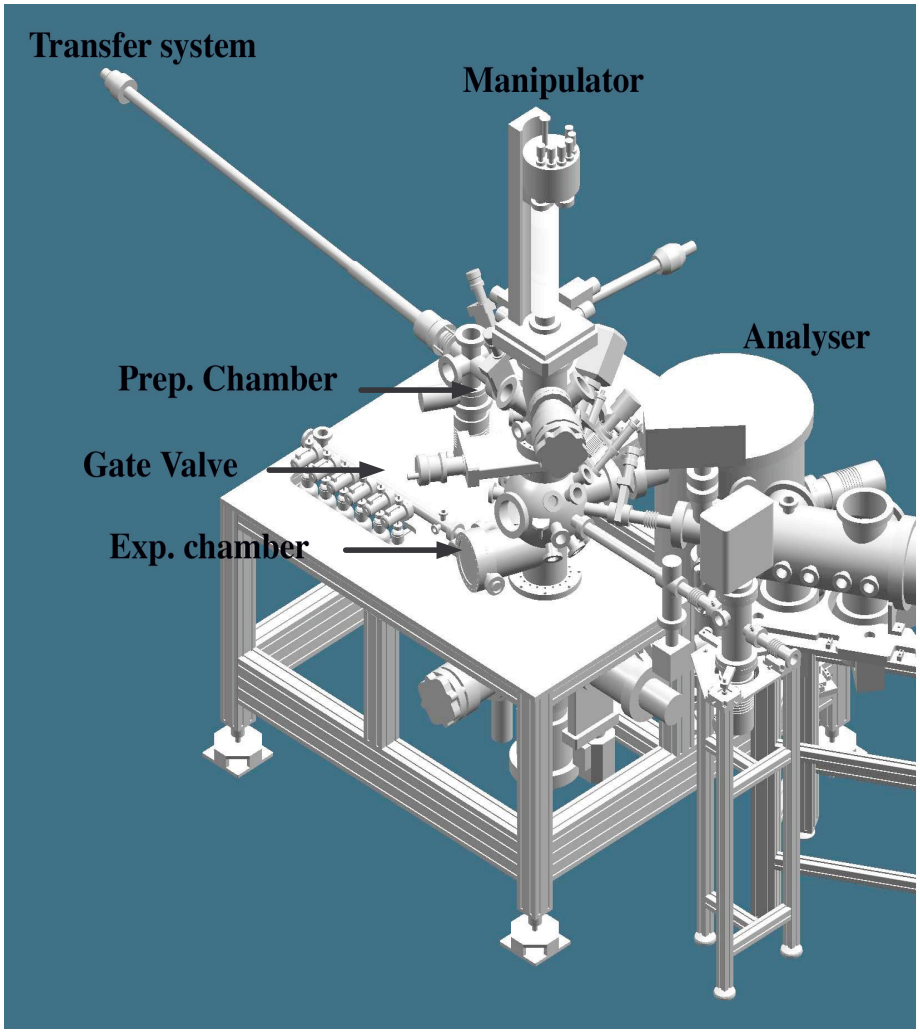
For 10^{-6} mbar of Oxygen (M=32), at T=300K, $R=4.7x10^{14}cm^{-2}s^{-1}$

If every O_2 molecule sticks to the surface of the sample, the latter will stay clean for a second or so

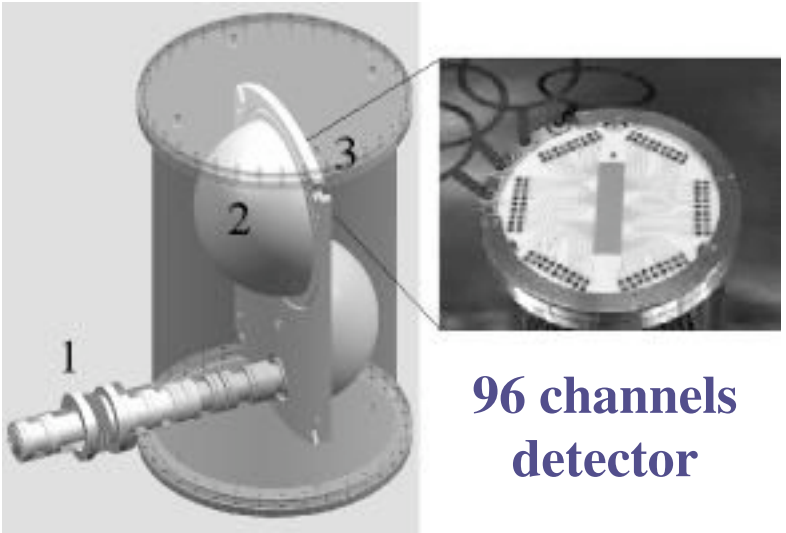
Ultra High Vacuum !!!

UHV experimental set-up

SuperESCA@ELETTRA (photoemission)



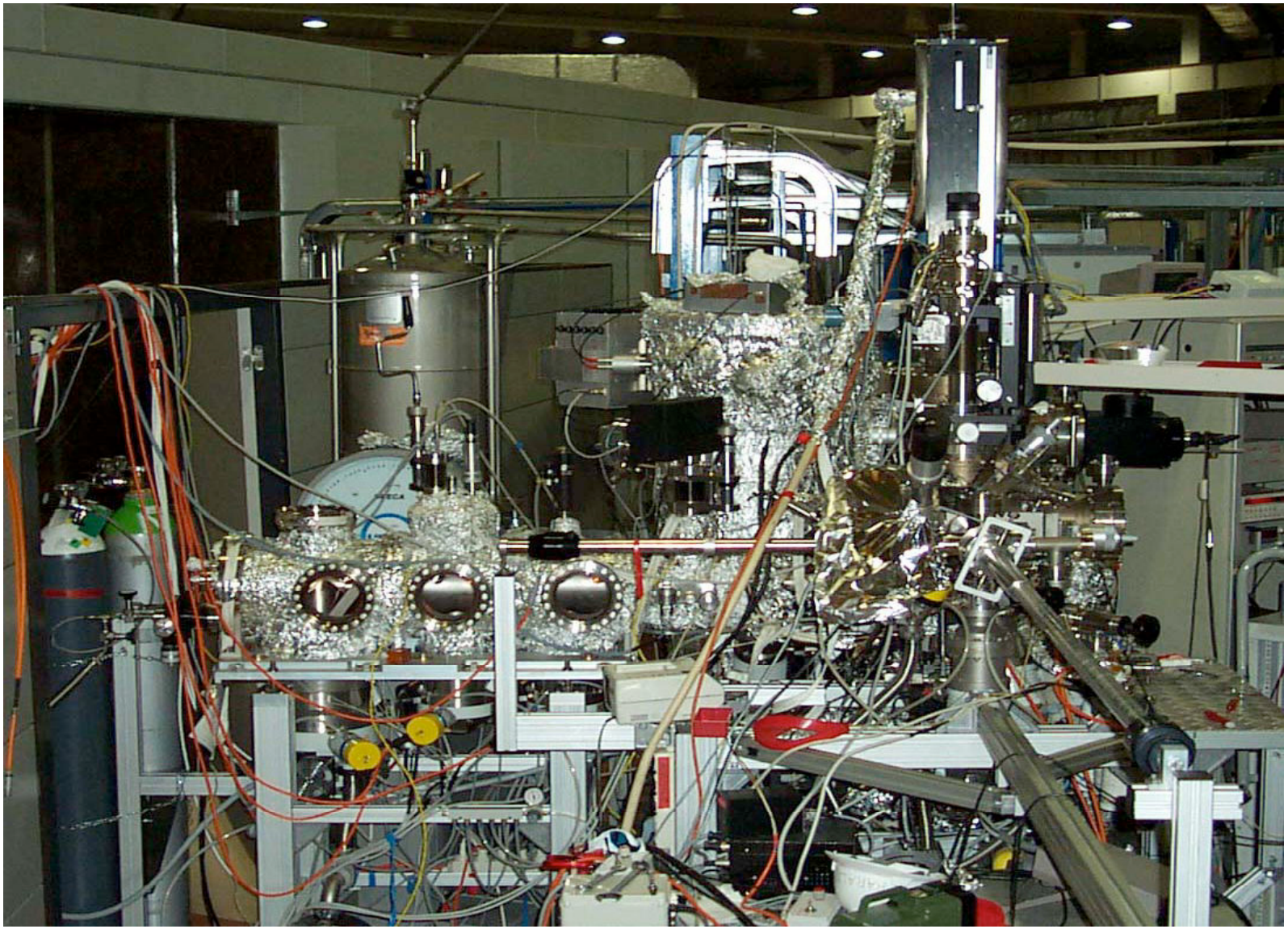
Electron energy analyser



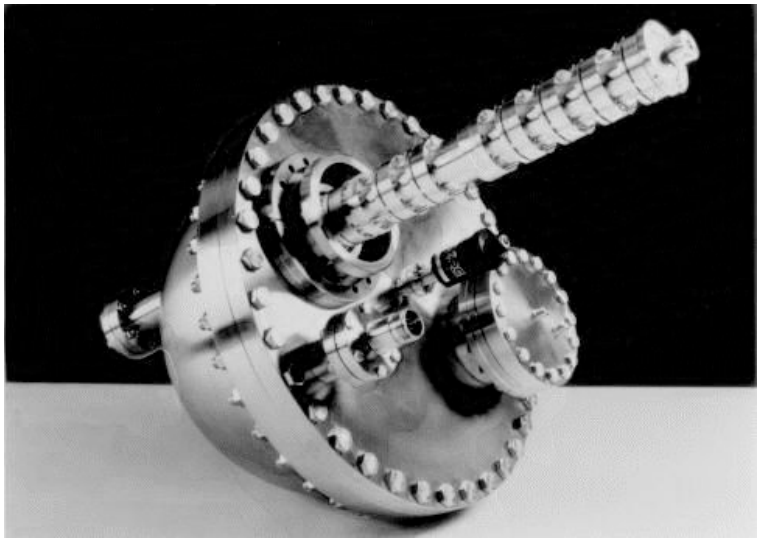
96 channels detector

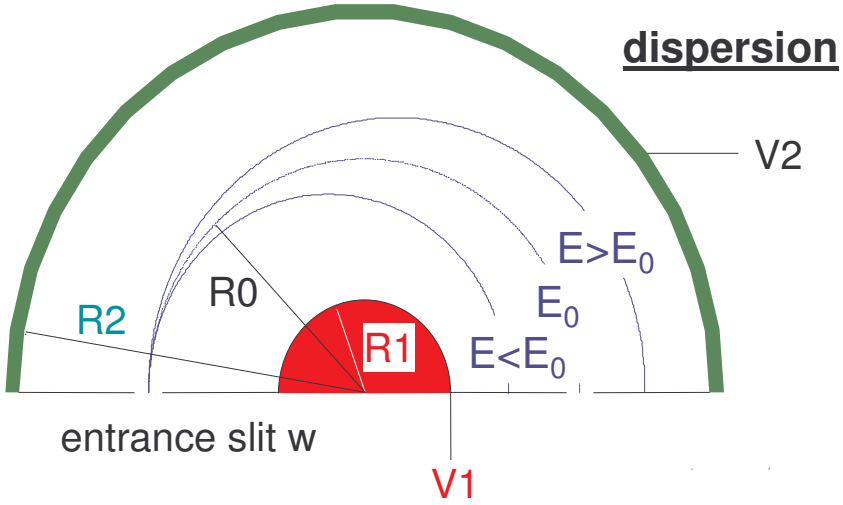
UHV experimental set-up

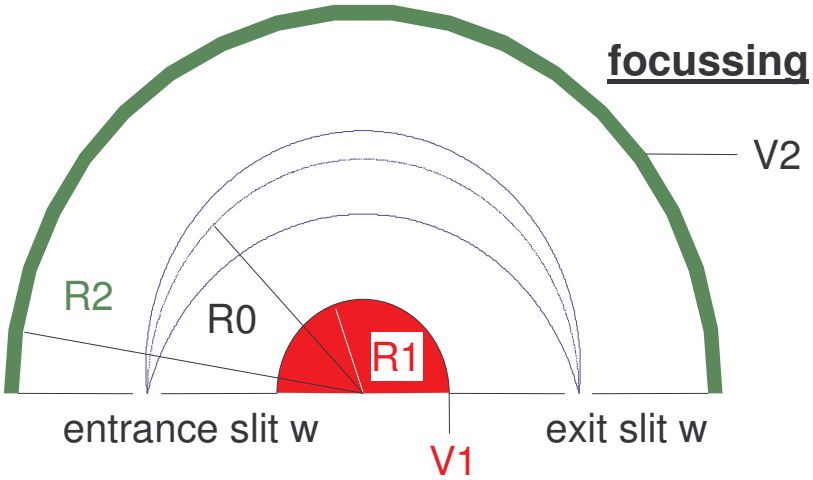
SuperESCA@ELETTRA (photoemission)



Electron Energy Analyser







The pass energy E_0 is the energy at which electrons follow a circular trajectory

$$E_0 = \frac{2(V_2 - V_1)}{R_0}\left(\frac{1}{R_1} - \frac{1}{R_2}\right)^{-1}$$

$$\frac{\Delta E}{E_0} = \frac{w}{2R_0} + \frac{\alpha^2}{4}$$

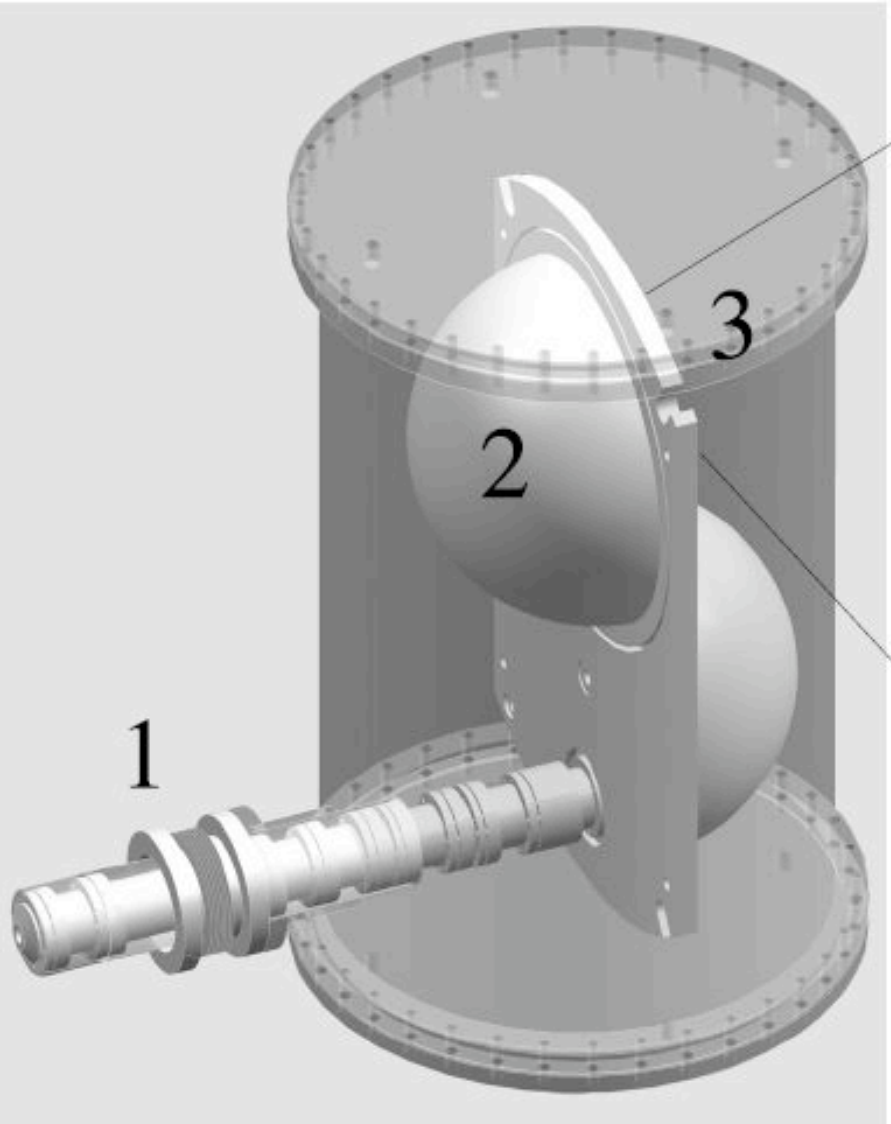
Decreases Pass Energy E_0 or increased R_0

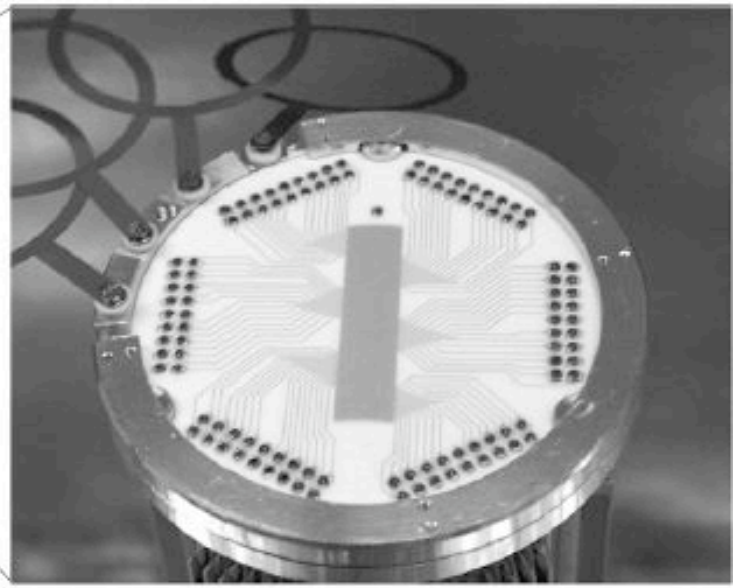
⇓

Higher Energy Resolution

Lens System to:
- -collect electrons at large angles
- -focalize electrons at entrance slit
- -retard electrons at E_0

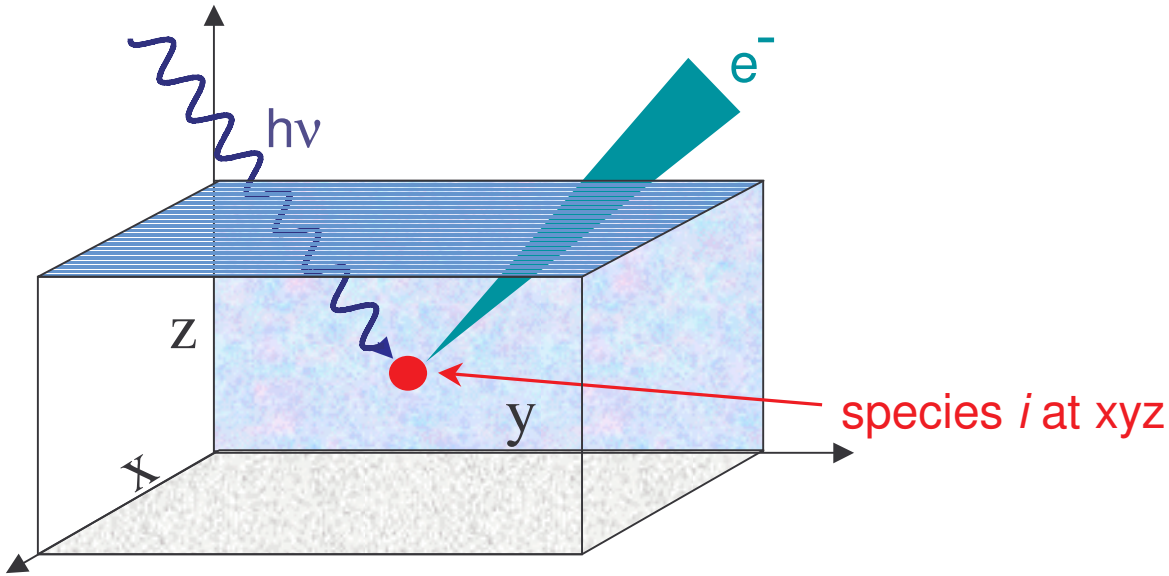
Electron Energy Analyser





Position sensitive detection

Photoemission Intensity



The total photoemission intensity from species *i* is obtained by integrating:

relevant for the choice of photon energy!

$dN_i =$ (nº of atoms of i at xyz)

photon flux at xyz

incoming flux & absorption coefficient

differential cross-section of relevant level of species i

probability of no loss escape of electrons from xyz

electron mean free path

acceptance solid angle of electron energy analyzer

detection efficiency

Incident radiation

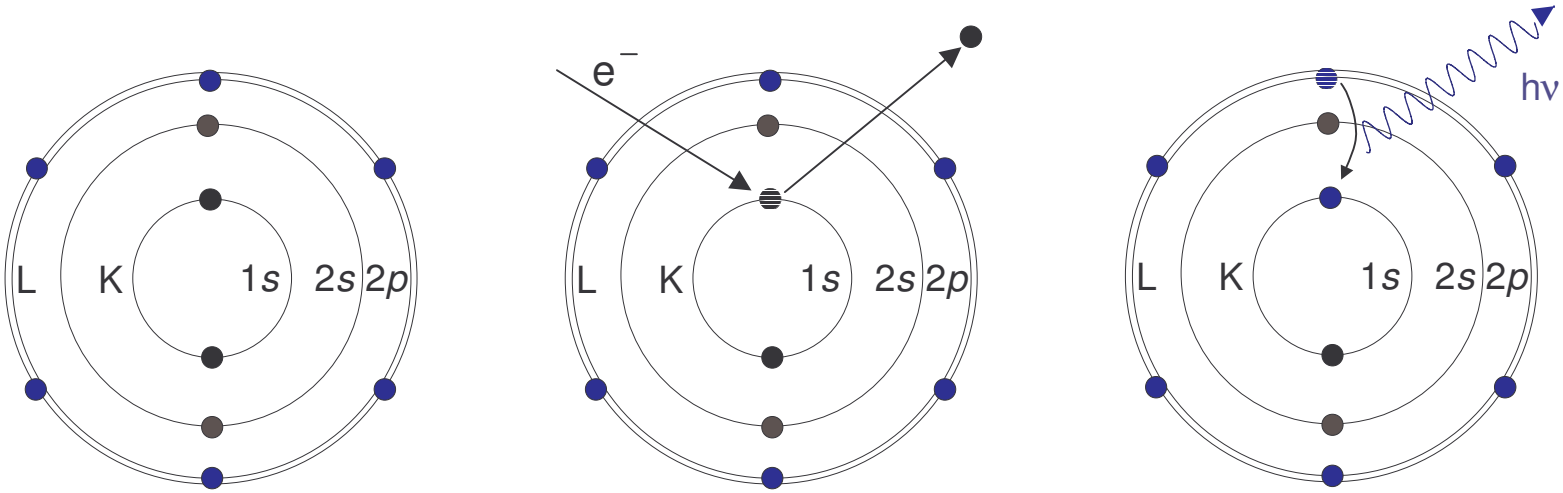
From UV to Soft X-Rays
Energy hν from ~10 to ~1500 eV
or
wavelenght λ from ~ 1240 to ~ 5 Å)

- The laboratory sources use the characteristic emission lines
  - Noble gas discharge (i.e. HeI_{α}=21.2 eV)
  - Emission lines from solid targhets (Al K_{α}= 1486.6 eV Mg K_{α} = 1253.6 eV)

- Synchrotron radiation produced by relativistic electrons moving in a storage ring.

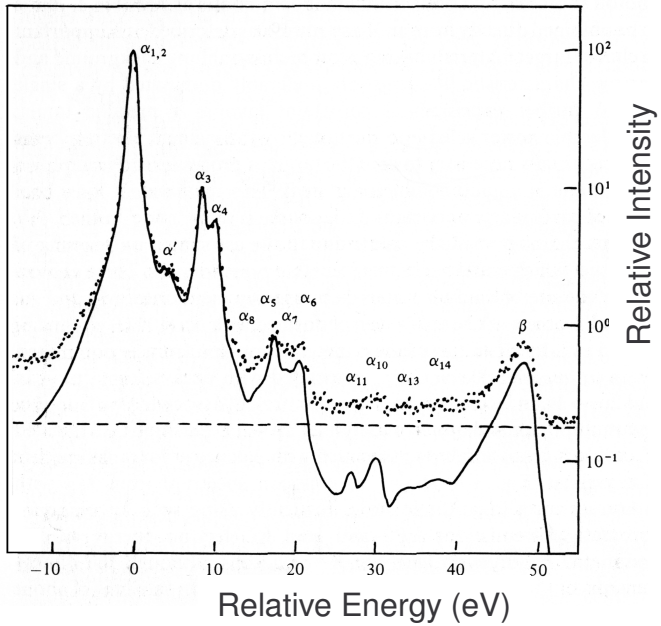
Mg/Al Kα Incident radiation

X-ray emission in source
based on X-ray fluorescence



Mg Kα
hν=1253.6 eV

Al Kα
hν=1486.6 eV



Energy spread
FWHM

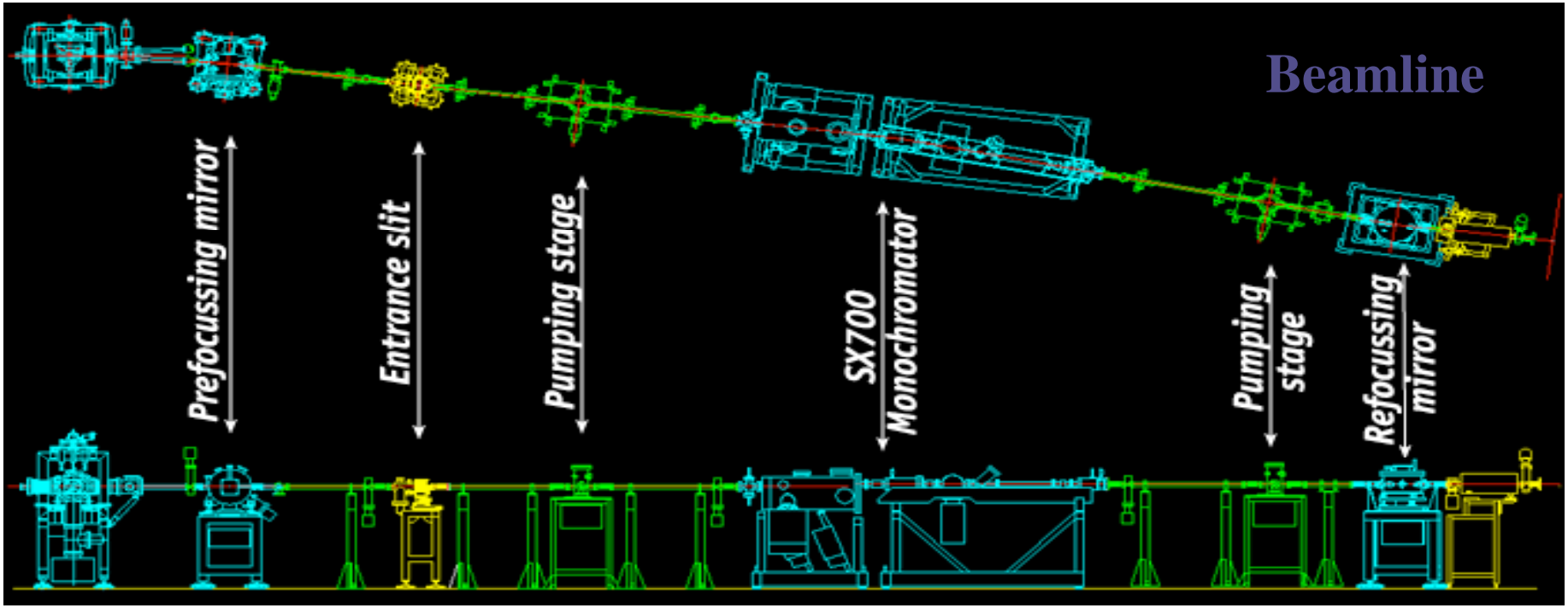
Mg 0.7 eV
Al 0.85 eV

Synchrotron radiation

Electromagnetic radiation emitted by accelerating ultra-relativistic charged particles (mostly electrons) tipically in a storage ring.

- *High intensity and brightness*
- *Very high energy resolution*
- *Tunable photon energy*
- *Polarized radiation*
- *Small photon spots*
- *Temporal structure*

SuperESCA @ ELETTRA



Light source

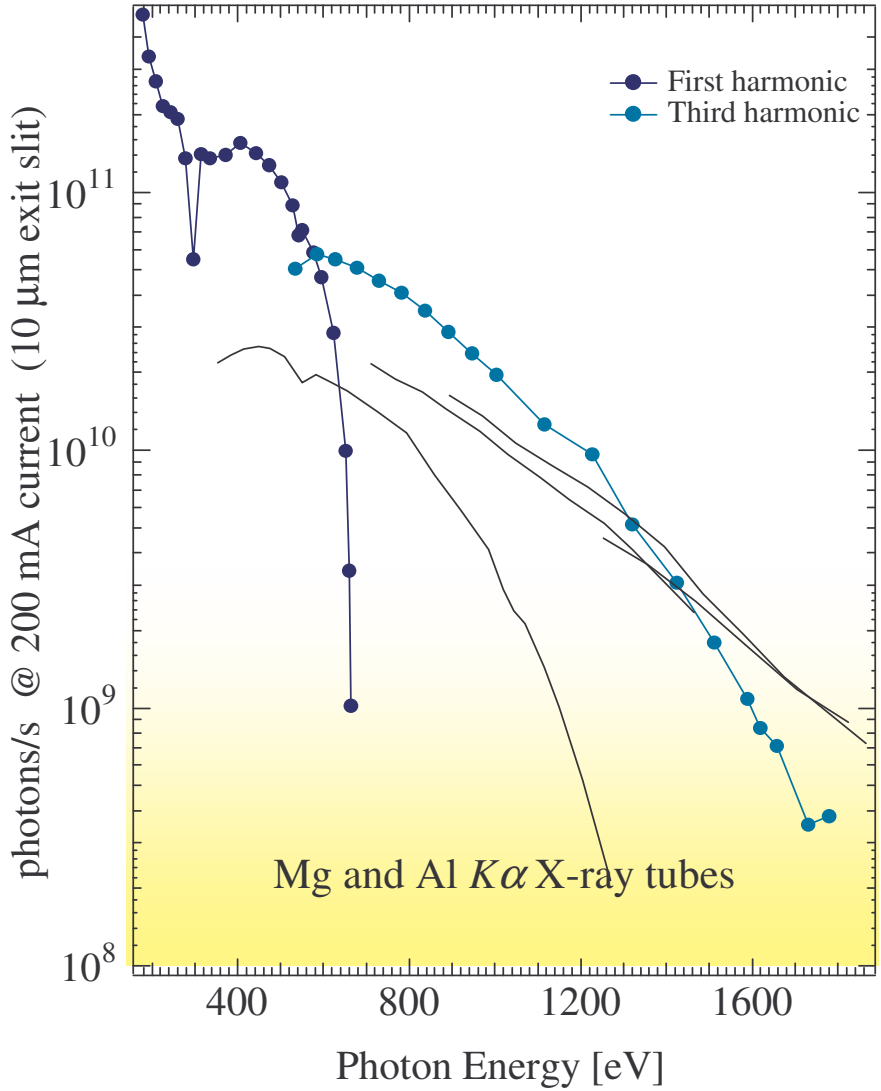
Type	**Undulator** divided in three sections, with 81 periods of 56 mm
Minimum gap	19.5 mm → **hν 85 eV** @ 2 GeV, **hν 125 eV** @ 2.4 GeV
Peak brilliance	10^{15} to 10^{14}photons/sec/0.1%bw/200mA
Max power output	1.9 kW

X-rays at sample

Energy range	**85 ~ 1500 eV**
Energy resolution E/ΔE (10 μm exit slit)	**~ 10^4 at 400 eV ~ $5x10^3$ at 900 eV**
Beam size	100 x Exit slit dimension μm^2
Linearly polarised Photon Flux	> 10^{11} photon/s @ 400 eV

SuperESCA @ ELETTRA

Measured photon flux



Photoemission cross section

Photoemission cross section = Probability per unit time for exciting a system from an initial state Ψ^i to a final state Ψ^f with a photon flux of $1 cm^{-2} s^{-1}$

$$\boldsymbol{Barns} = 10^{-24}\,\boldsymbol{cm}^2$$

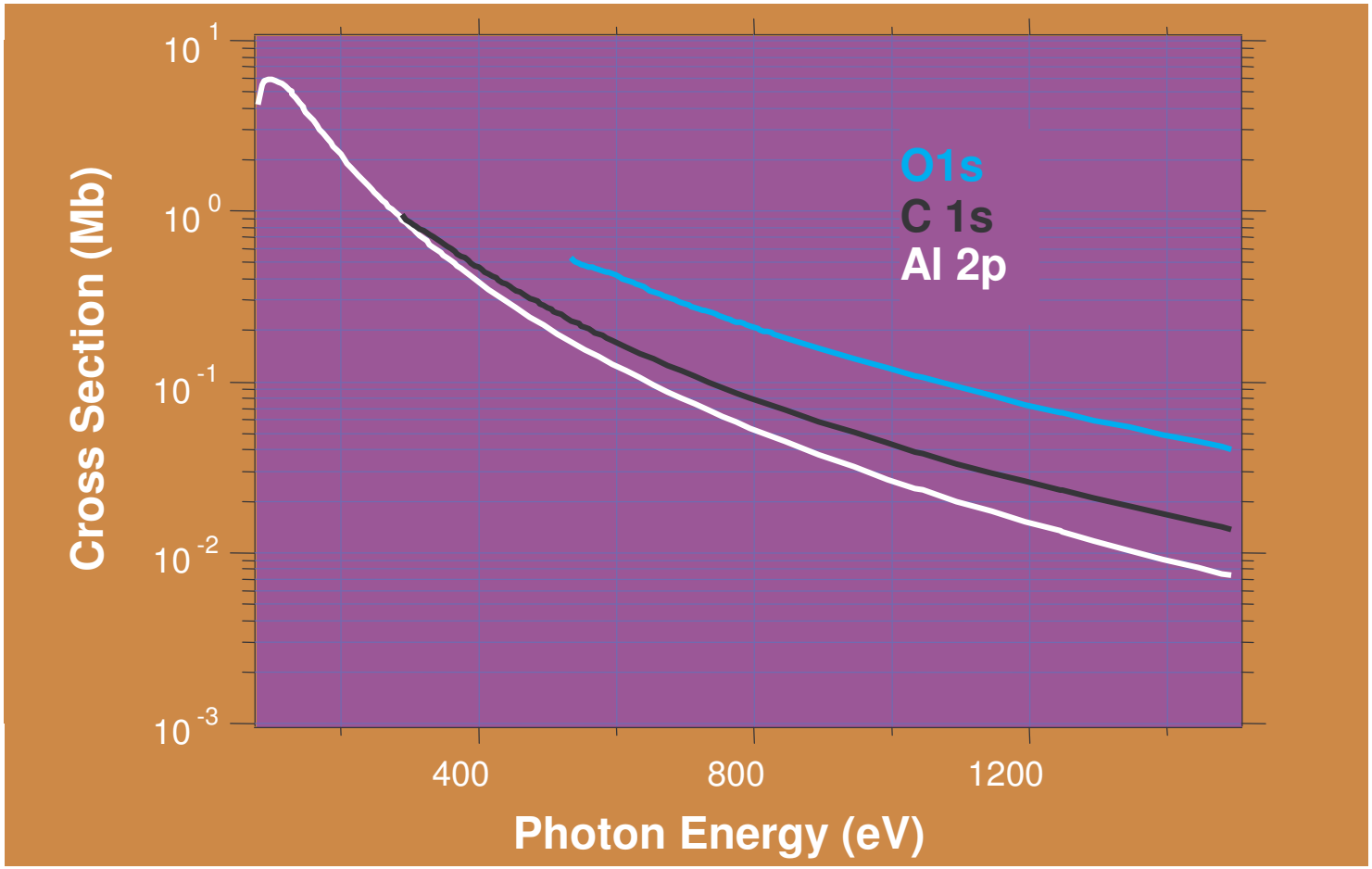
in the case of a solid, one monolayer (ML) contains

$$1ML \sim 1x10^{15}\,atoms/cm^2$$

The cross section of 1 Mb corresponds approximately to **1 photoelectron** emitted from the surface every **1000 incident photons** for 1 monolayer of the species that contribute to the XPS signal.

Photoemission cross section

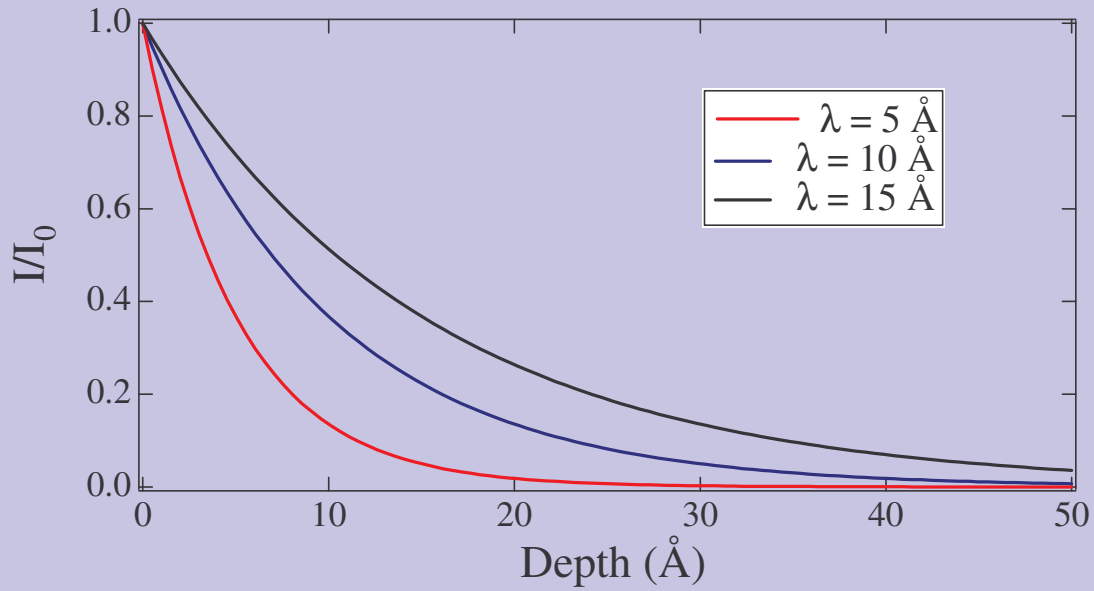
....as a function of the photon energy



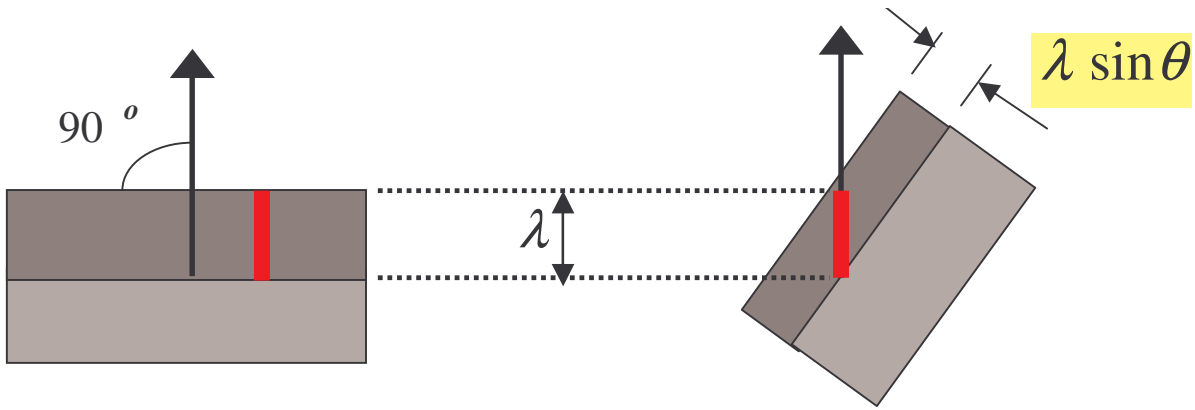
Probing depth

$$I = I_0 e^{-\frac{d}{\lambda}}$$

$$5\breve{A} \le \lambda \le 80\breve{A}$$



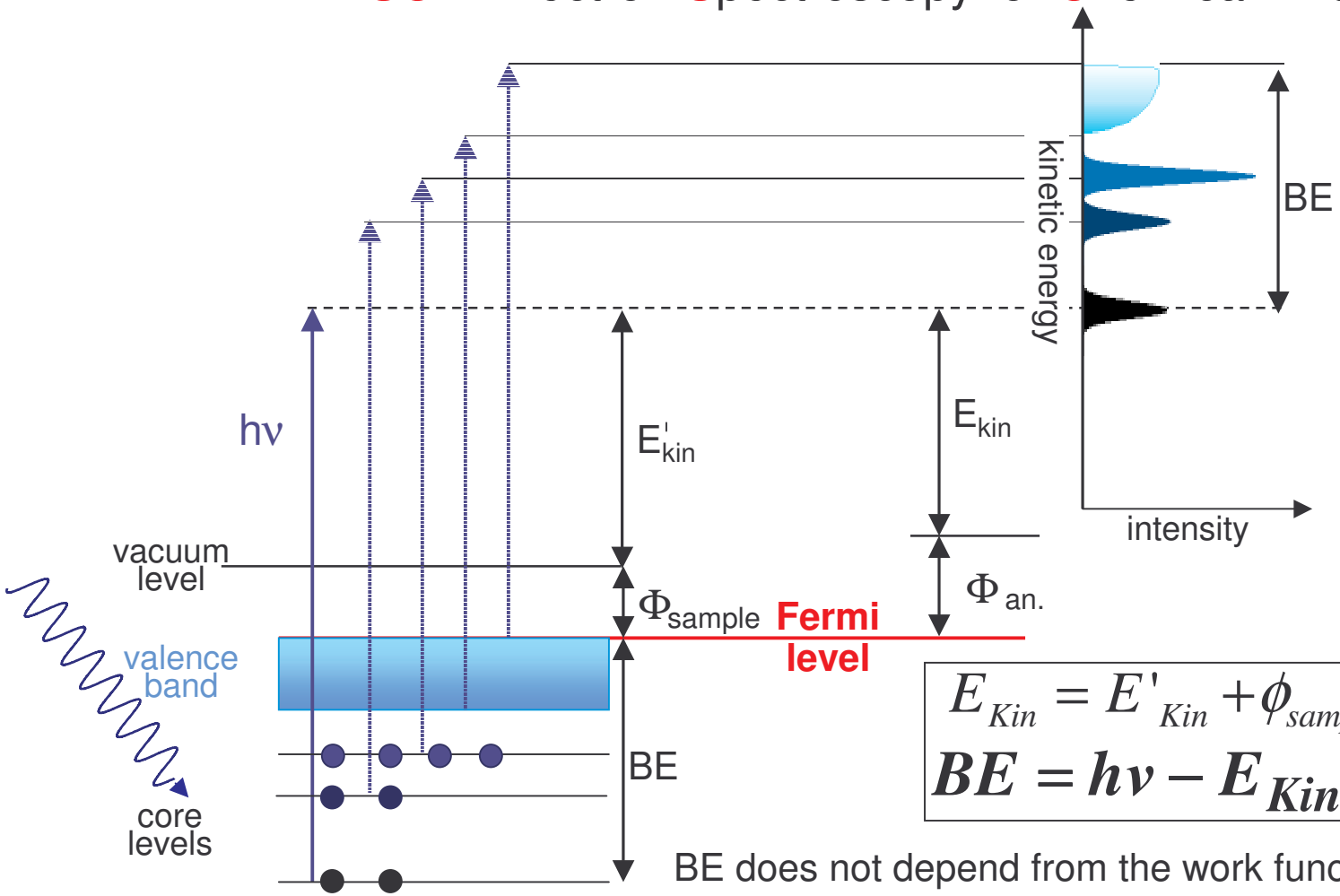
Normal emission vs grazing emission : change of the probing depth



XPS or ESCA

XPS X-ray **P**hotoelectron **S**pectroscopy

ESCA Electron **S**pectroscopy for **C**hemical **A**nalysis



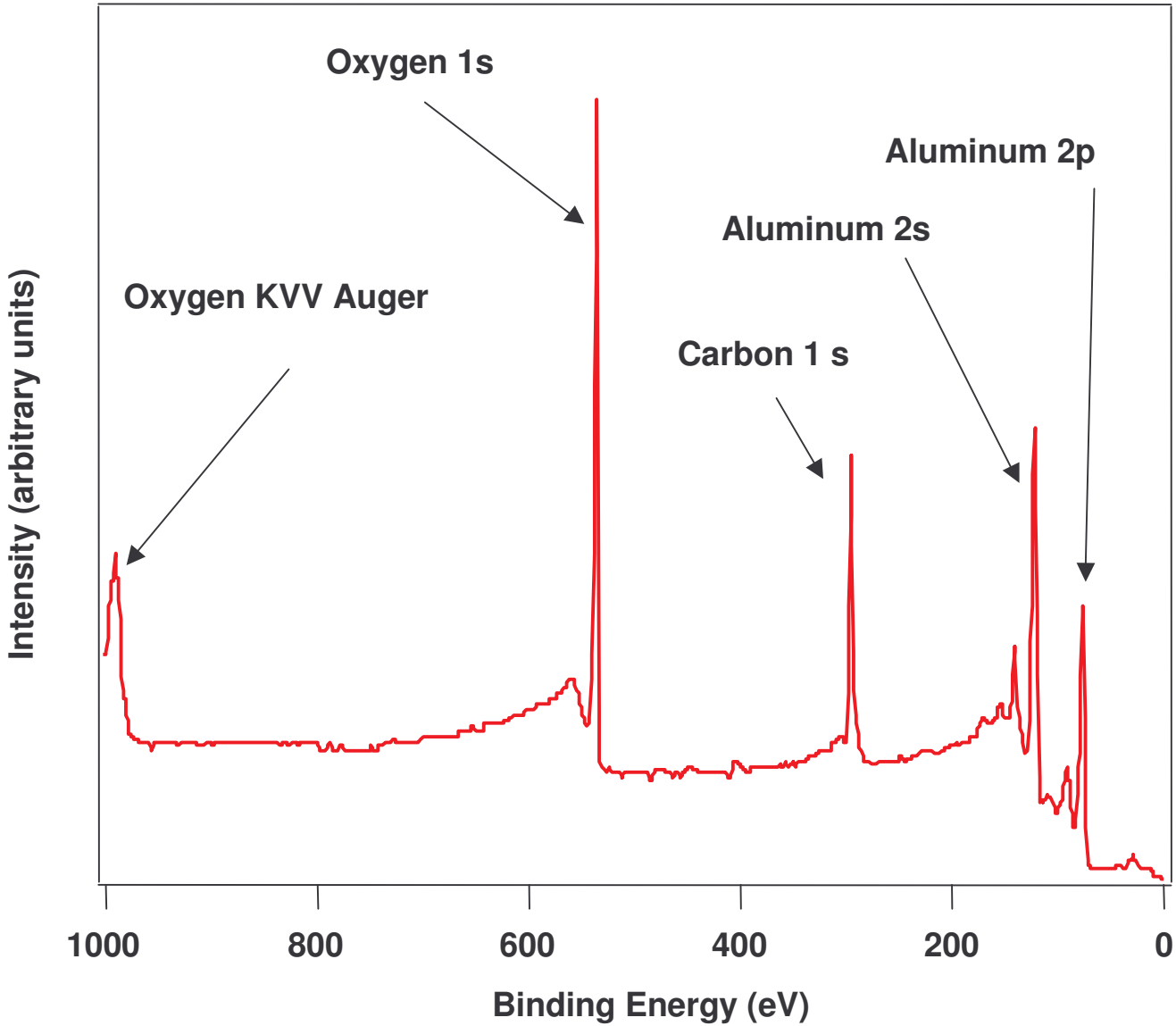
$$E_{Kin} = E'_{Kin} + \phi_{sample} - \phi_{an.}$$

$$BE = h\nu - E_{Kin} - \varphi_{an.}$$

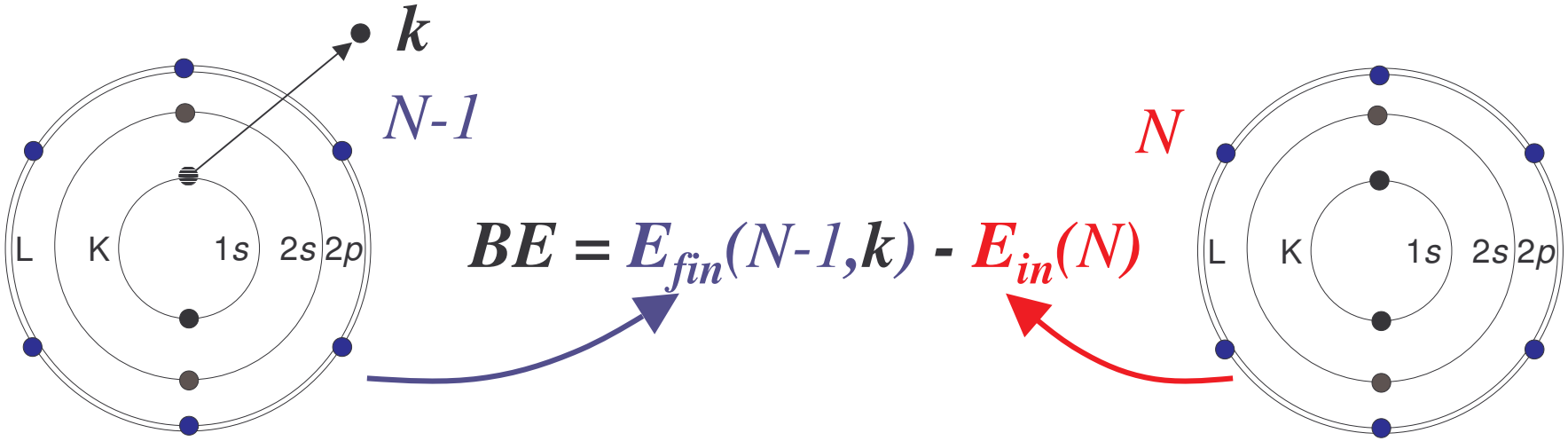
BE does not depend from the work function of the sample ϕ_{sample} but only from that of the analyser $\phi_{an.}$

Each element has unique set of core levels → XPS is element specific

Surface Chemical Analysis



XPS binding energies



Koopman's Theorem

No relaxation of the N-1 electrons after photoemission
Frozen Orbital approximation

$$E_b(k) = -e_k$$

Hartree-Fock orbital energy

Koopman's theorem does not give the right binding energy

Final State Effects

$$E_k = h\nu - E_b + E_a + E_r$$

Koopman (initial state) binding energy

Intraatomic relaxation

Extraatomic relaxation

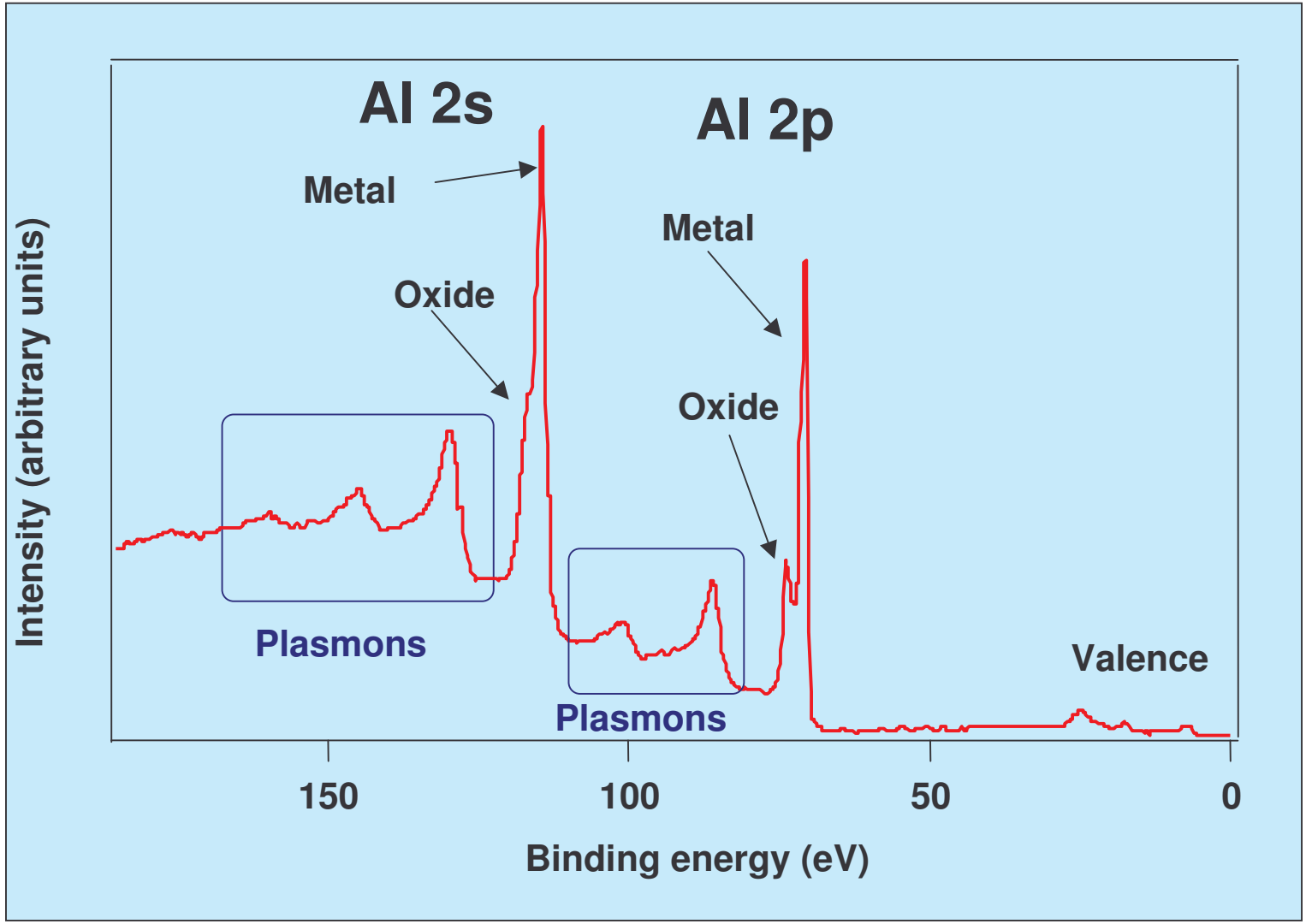
Intrinsic Satellites

There is a finite probability that the ion formed in the photoemission process will be left in an excited state a few electronvolts above the ground state: the kinetic energy of the photoelectrons is then reduced by the energy difference between the ground state and the excited state.

Extrinsic Satellites

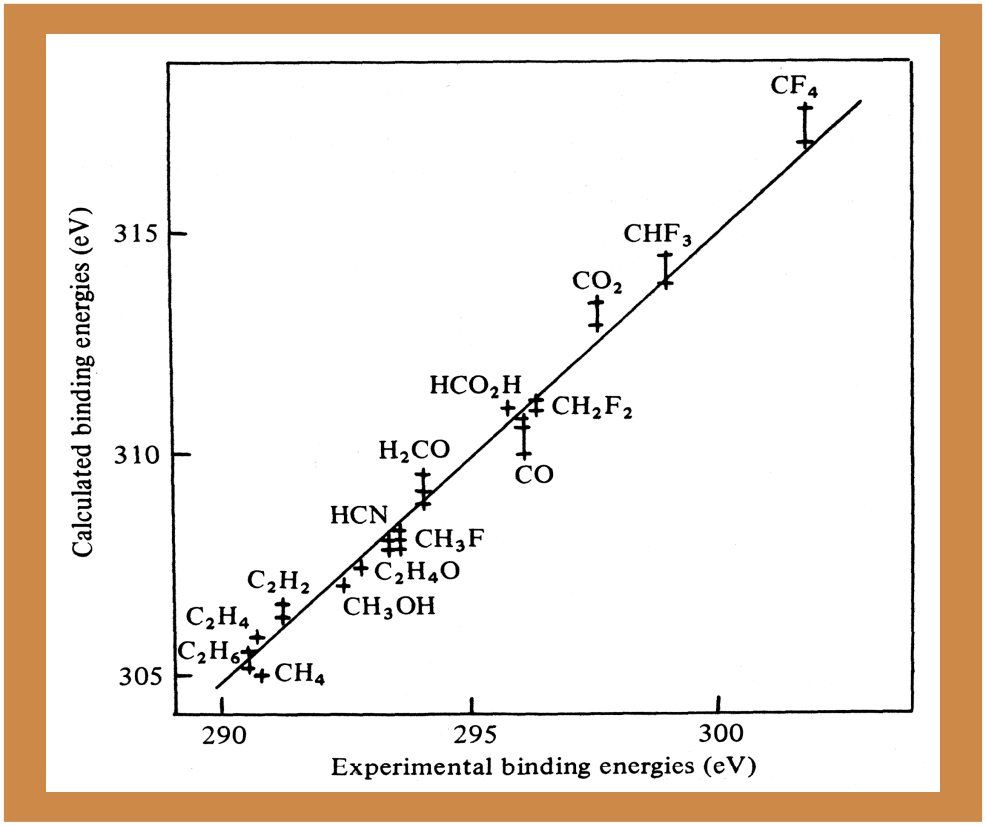
The photoelectrons travelling in the solid interact with other electrons in the surface region of the sample. This gives rise to the excitation of electronic transitions with a corresponding lowering of the kinetic energy of the photoelectron.

Initial and final state effects



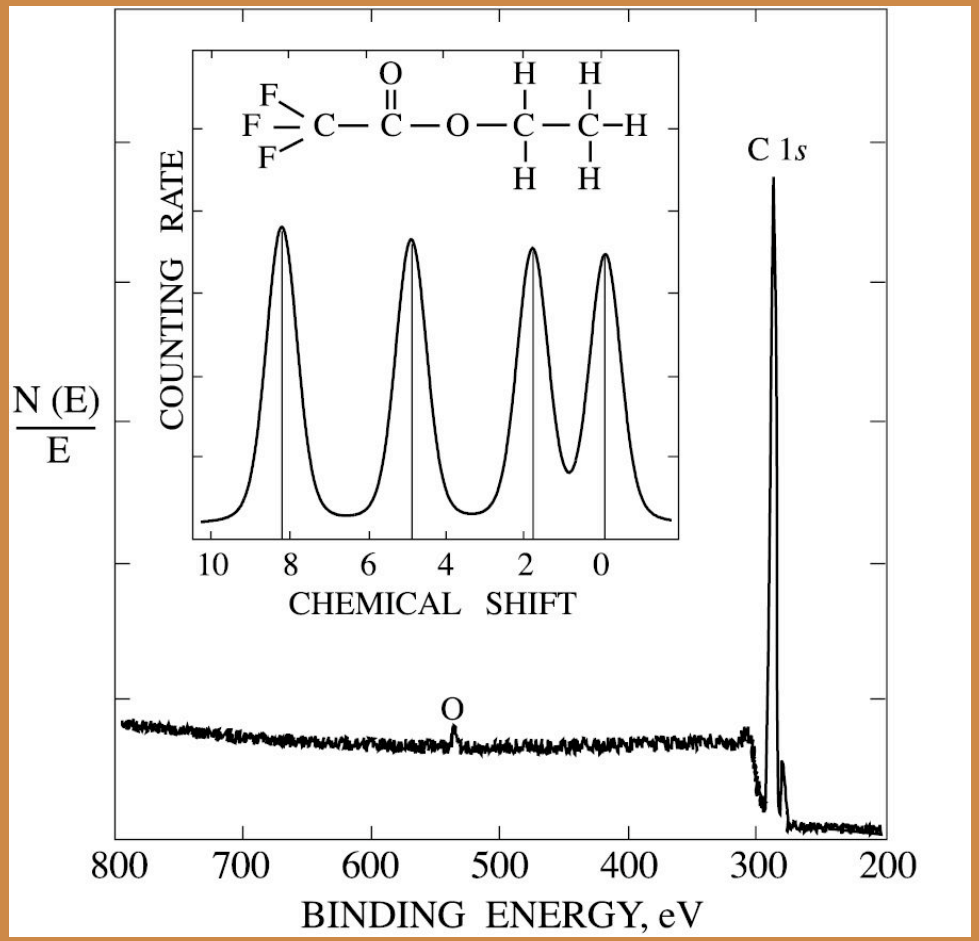
Core level shift

C *1s* Koopman's Theorem BE's for C in a range of molecules
vs
experimental results



Same chemical species C in different environment show a Chemical Shift in the binding energy

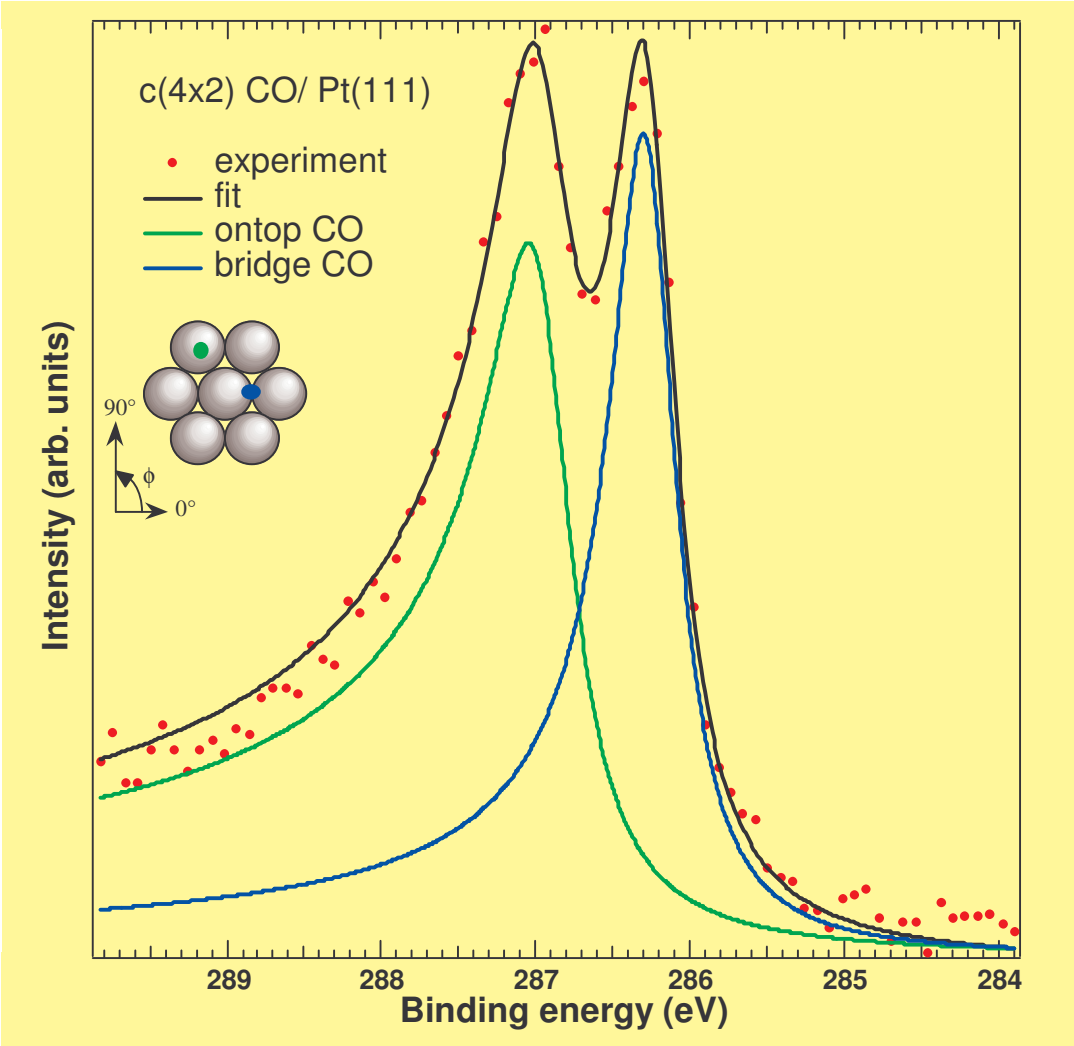
Core level shift



F atoms draw the **C** valence electrons strongly away from the carbon

The C1*s* electrons see an effective increase of nuclear charge = higher BE

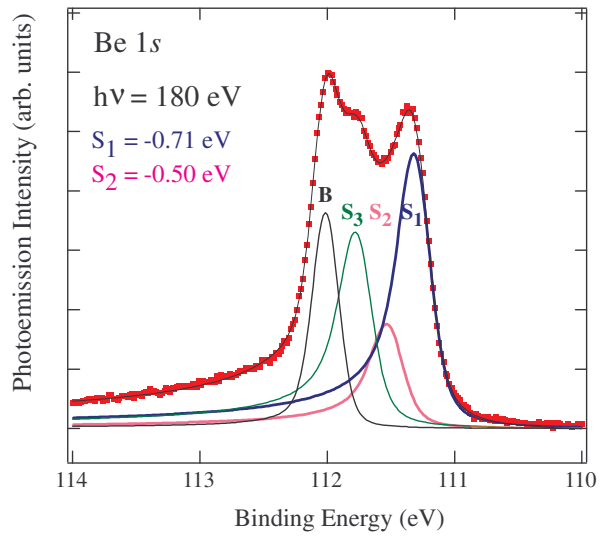
Core level shift



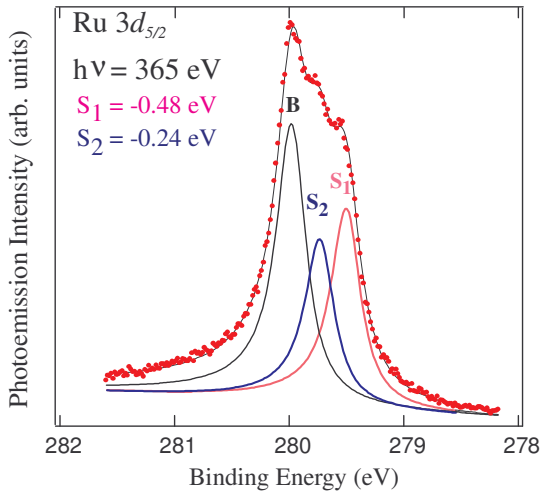
CO molecules sitting in different adsorption sites (ontop and bridge) can be distinguished in the C1s core level spectrum because of a BE shift of ~ **0.8 eV**

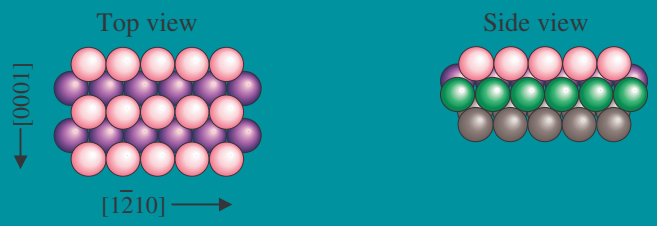
Surface Core level shift

Be(10$\bar{1}$0)

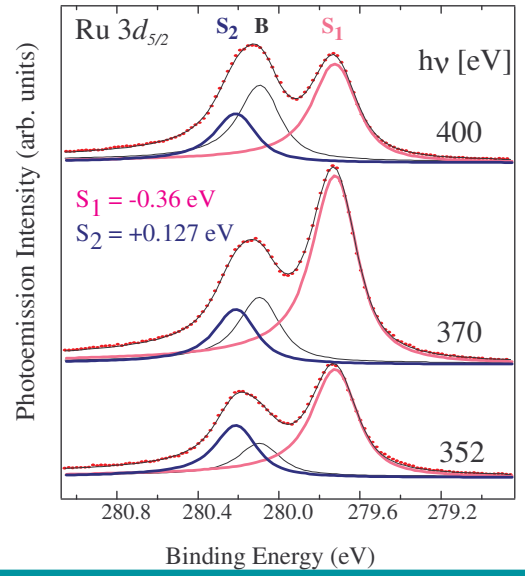


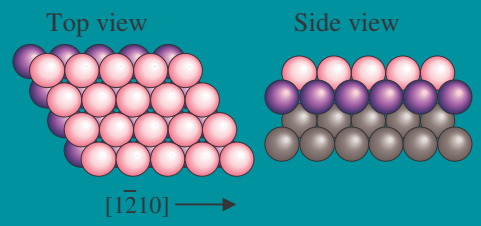
Ru(10$\bar{1}$0)





Ru(0001)

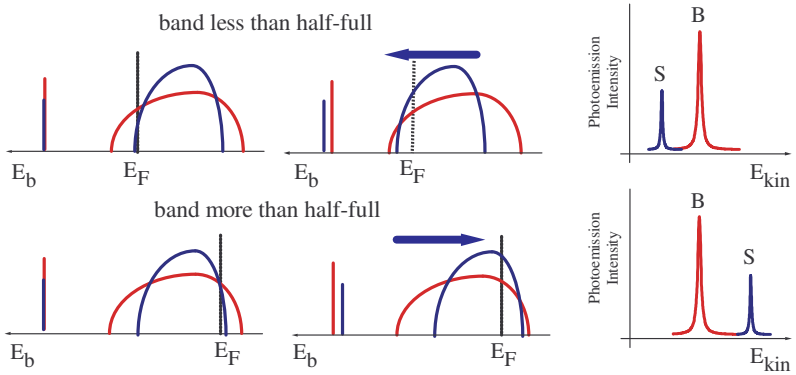




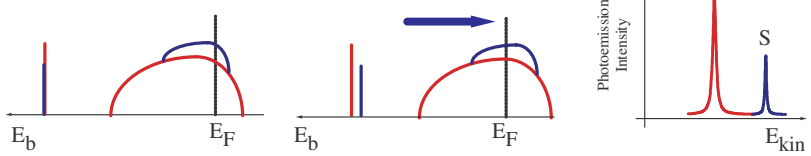
Surface Core level shift

Initial state

- **band narrowing (electrostatic)**



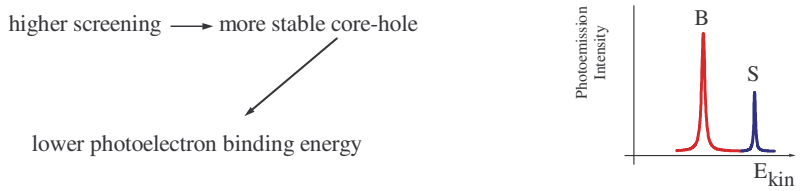
- **surface states (electrostatic)**

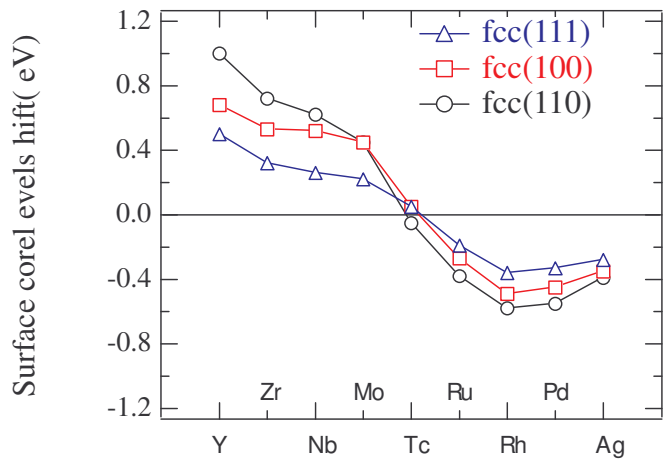


- **change of the exchange-correlation potential**

Final state

- **change of the screening properties at the surface**

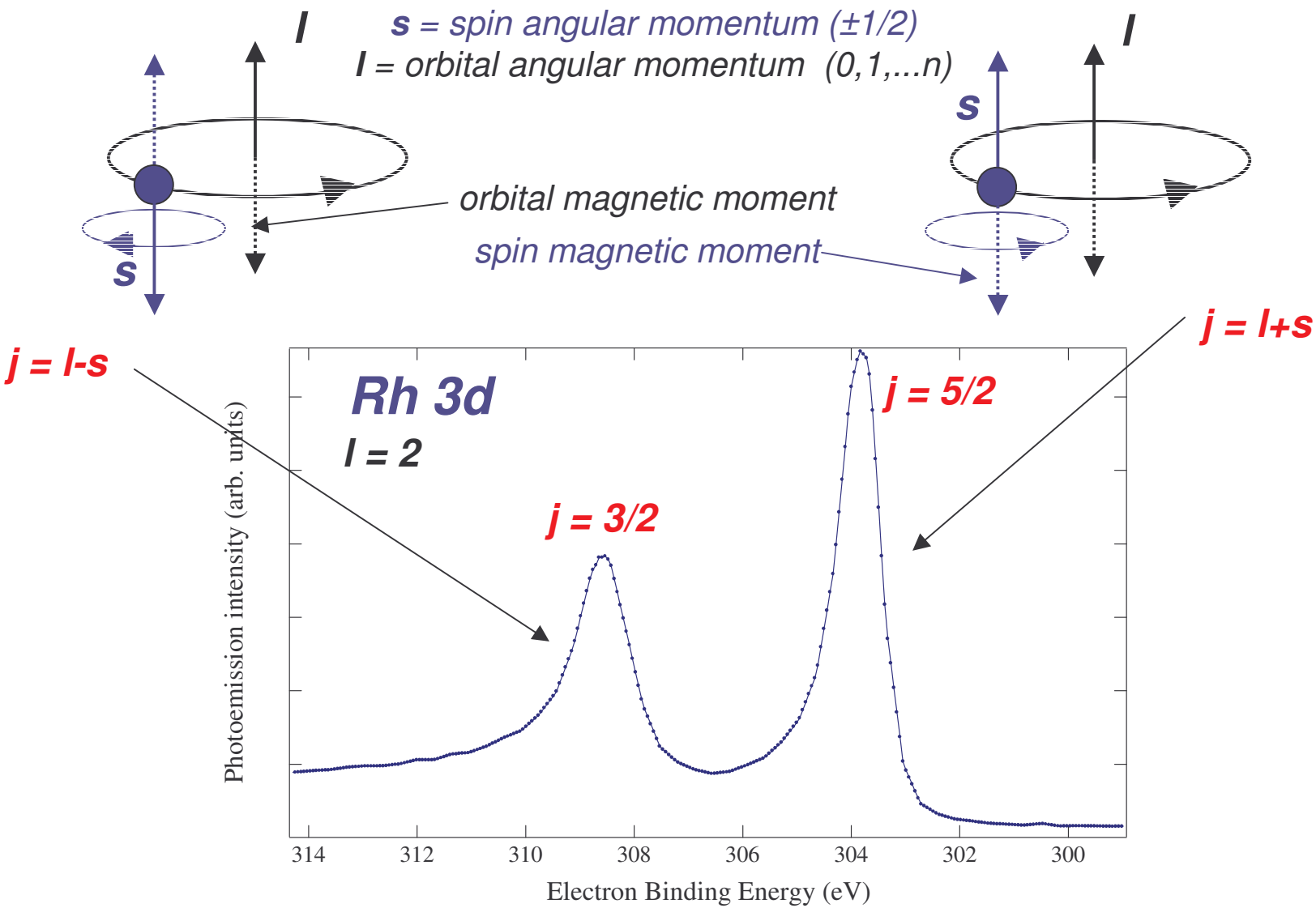




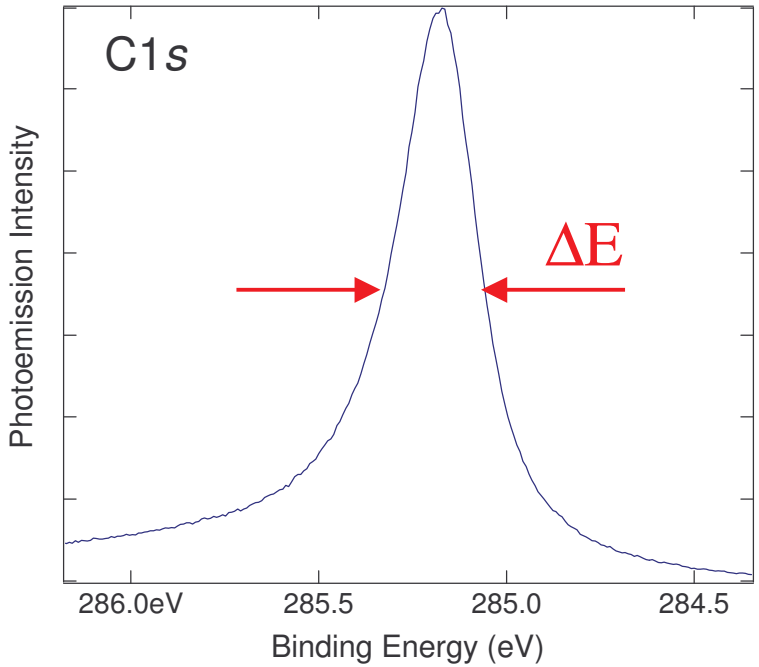
M. Methfessel et al. Surf. Rev. Lett. **2** (1995) 197

Spin Orbit Splitting

Before photoionization the inner shells of an atom (*nlm*) are filled and spin orbit interaction is not taken into account. **After photoionization:**



Linewidth



$$\Delta E = \sqrt{\Delta E_{nat}^2 + \Delta E_{vib}^2 + \Delta E_{in}^2 + \Delta E_{h\nu}^2 + \Delta E_a^2}$$

Natural linewidth

Vibrational effects/phonons

inhomogenities/disorder

Photon energy resolution

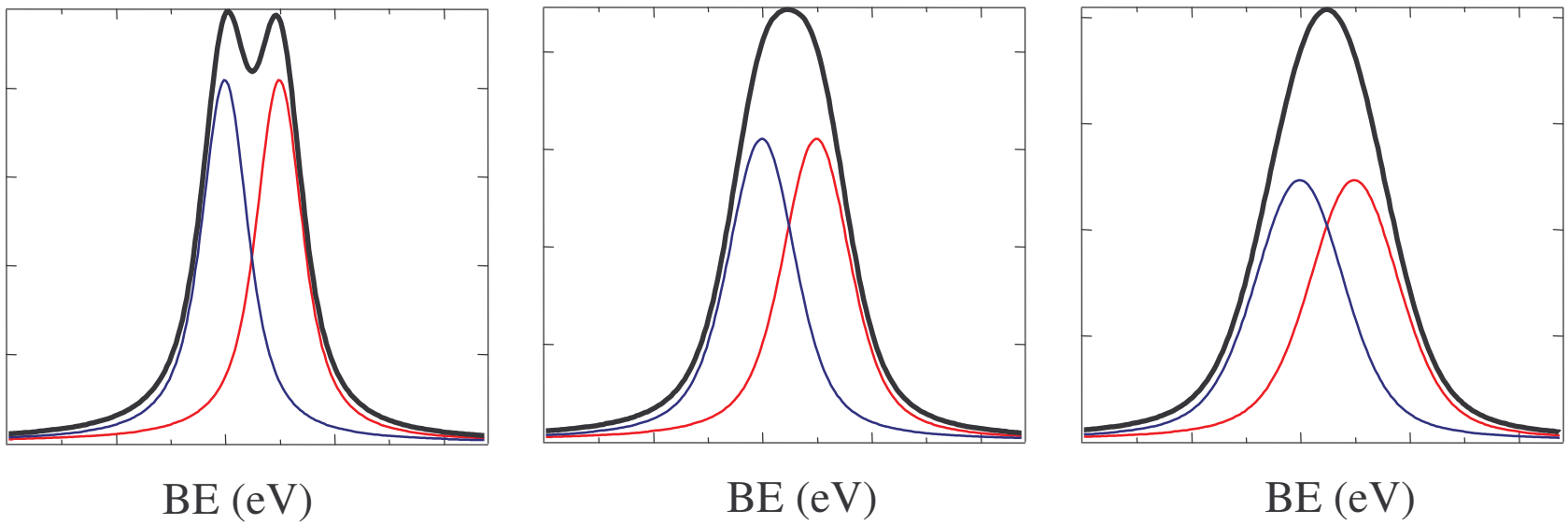
Electron energy analyser resolution

Experimental contributions

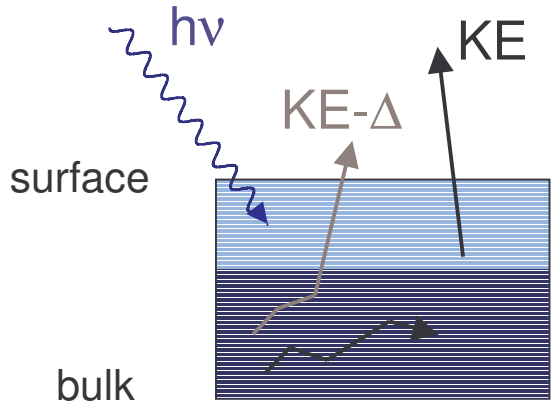
Experimental resolution

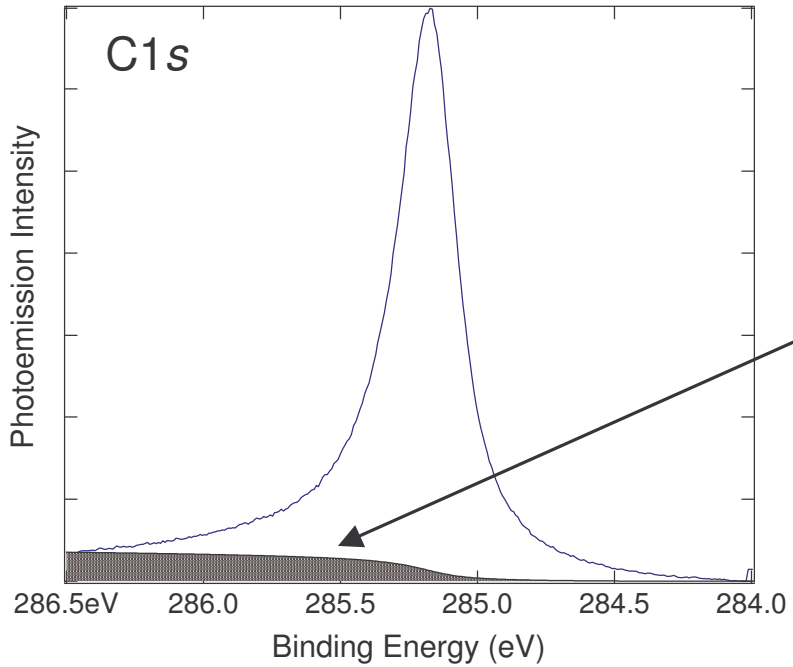
Peak1 and *Peak2* *with naturalw idth150m eV* $\Delta E_{1,2}$ =200 meV

Res =100m eV *Res =200m eV* *Res =300m eV*



Inelastic background





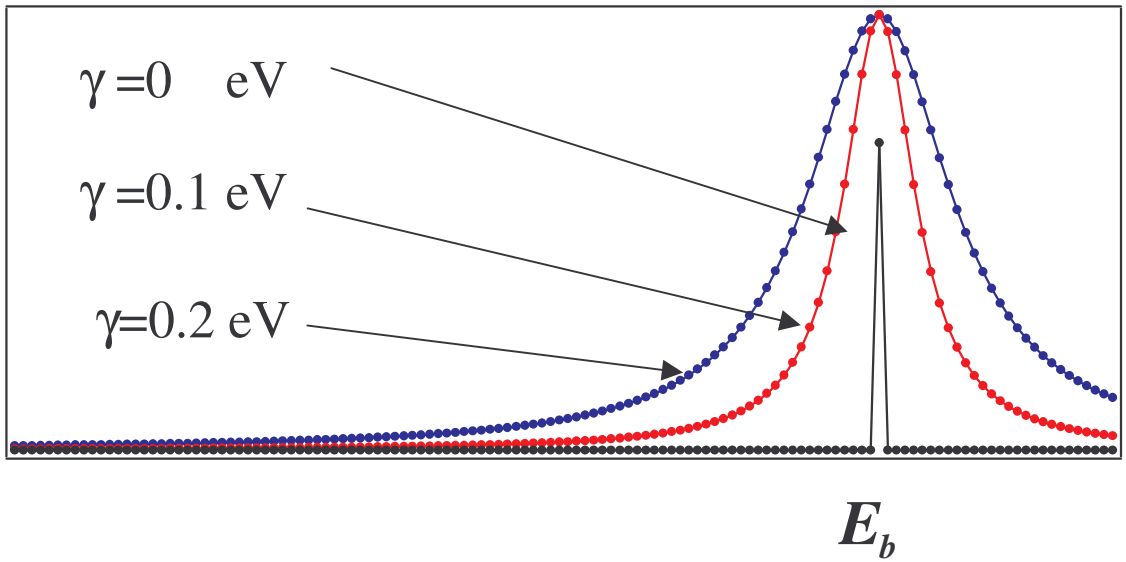
The inelastic background shows up at the **high BE side** of a peak because of inelastic processes

Core-hole lifetime

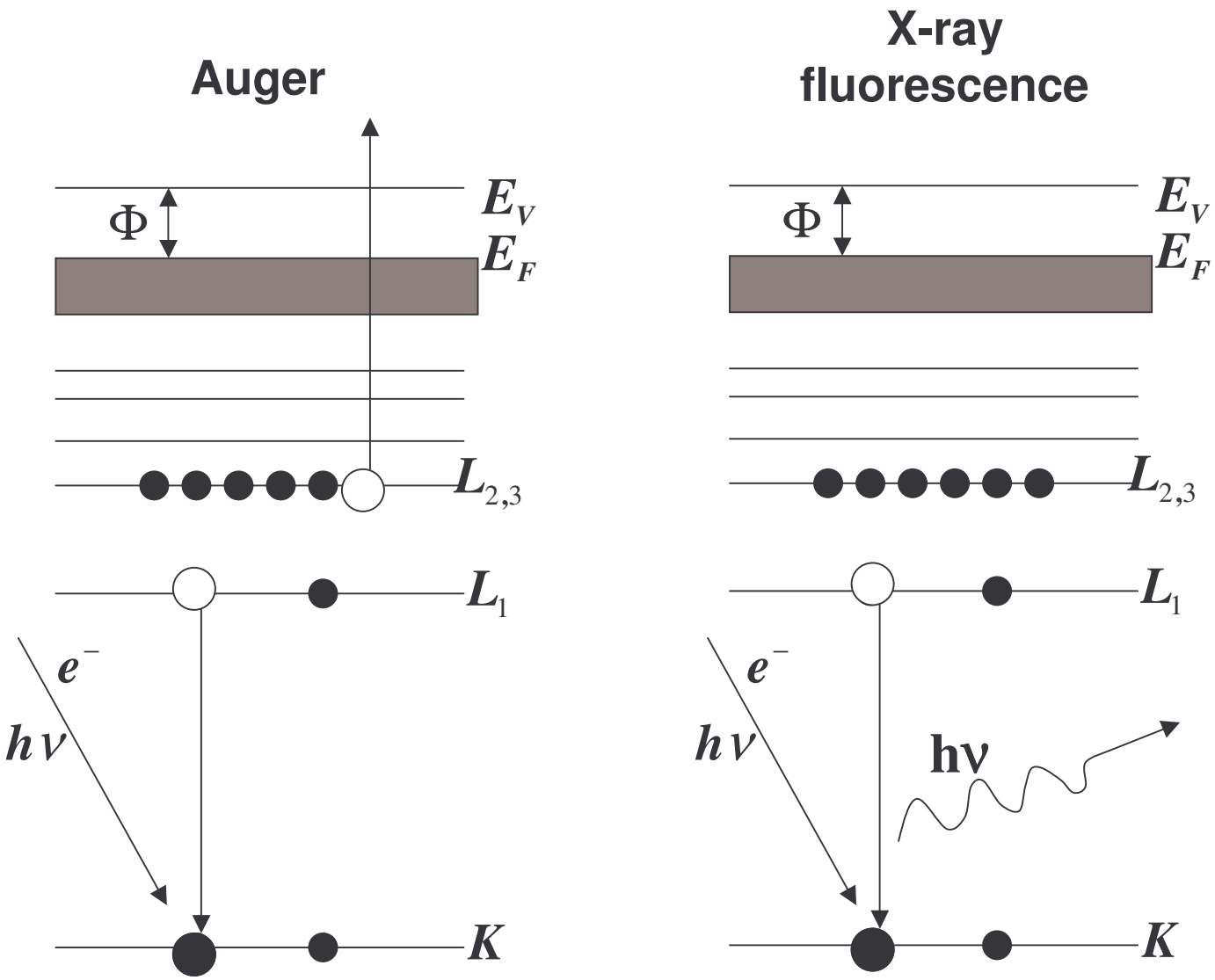
The natural linewidth is directly related to the lifetime of the core-hole created in the photoemission process through the **Heisemberg's Uncertainty Principle**

$$\Gamma(eV) = \frac{\hbar}{\tau(s)} = \frac{4.1\times 10^{-15}}{\tau(s)}$$

$$L = \frac{1}{\pi}\frac{\gamma/2}{\left[(E-E_b)^2 + (\gamma/2)^2\right]}$$



Core-hole decay



electron-hole pairs

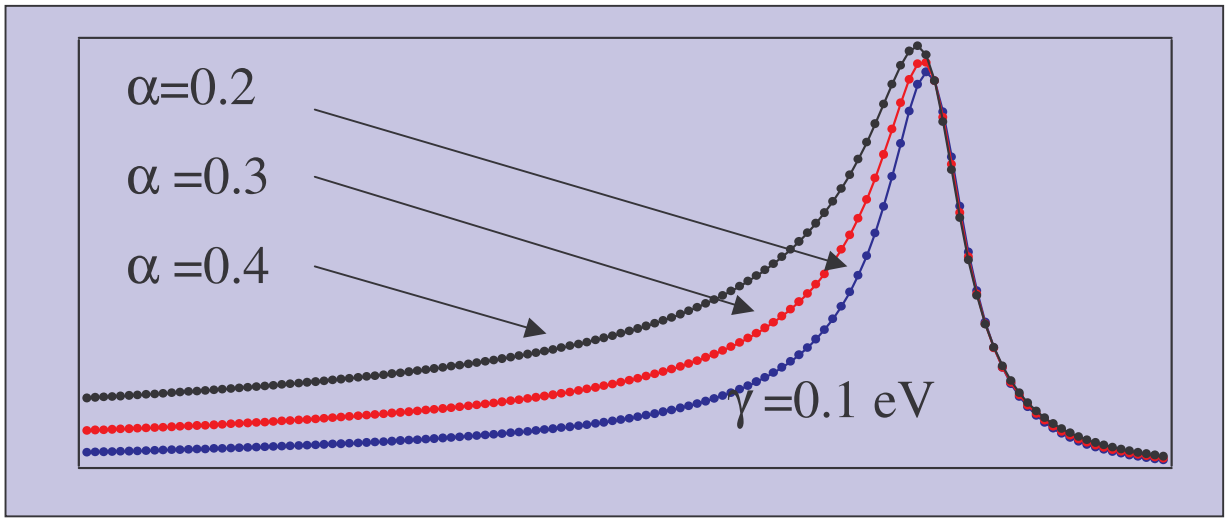
Compared to atoms or molecules, the solids present a continuum of electronic states close to the Fermi level (Density Of States, DOS) where one electron excitations can take place. For metals this gives rise to the creation of **electron-hole pairs** that cause the characteristic asymmetry to the high BE side to the peaks, typical of the **Doniach-Sunjic** lineshape.

$$I(E) = \frac{\cos\left[\frac{\pi\alpha}{2} + (1-\alpha)\tan^{-1}\left(\frac{2E}{\gamma}\right)\right]}{\left[E^2 + \left(\frac{\gamma}{2}\right)^2\right]^{(1-\alpha)/2}}$$

γ=core-hole lifetime

α =asymmetry parameter

Doniach-Sunjic lineshape



Summary

.... Core level Photoelectron Spectroscopy

- is non destructive technique;
- is a surface sensitive technique;
- has unambigous correspondence between chemical species and spectral features;
- is quantitative;
- from the chemical shifts it gives information about the oxidation states and the chemical environment;
- depth information can be gained by changing experimental conditions;
- is applicable for the study of chemical reactions at surfaces because both molecular and atomic adsorbates can be distinguished;
- changes in both adsorbate and substrate can be detected.

with Synchrotron radiation.....

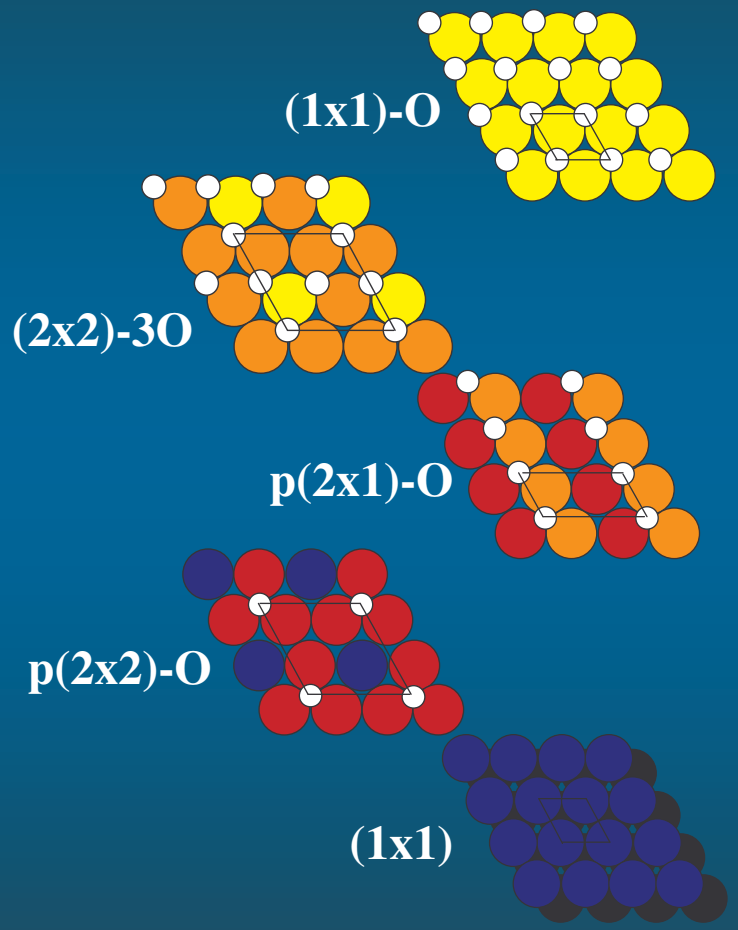
Tunability, Photon flux, Energy resolution available at the same time!!!!!

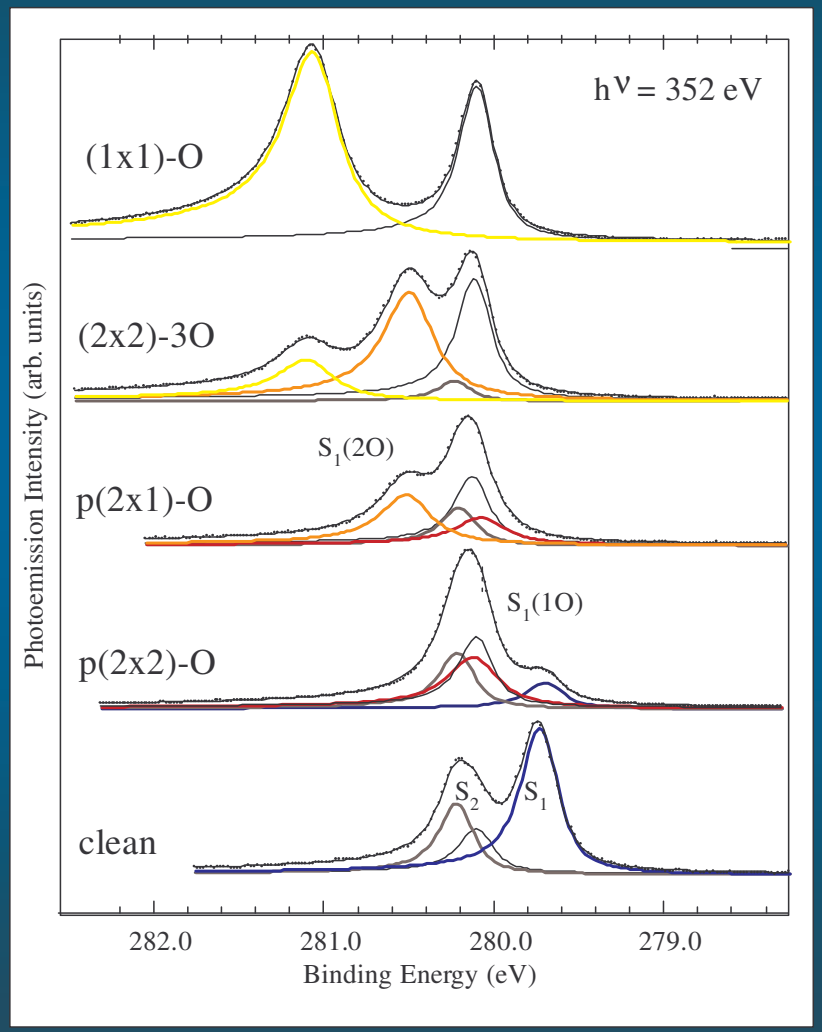
- higher sensitivity to elemental composition (< 0.1 % ML), structural and chemical environment
- higher surface sensitivity
- faster spectra acquisition (below 1 s, to be compared to ~ 30 min with standard X-ray sources)

follow surface time-dependent phenomena in REAL TIME

Fast XPS: some examples

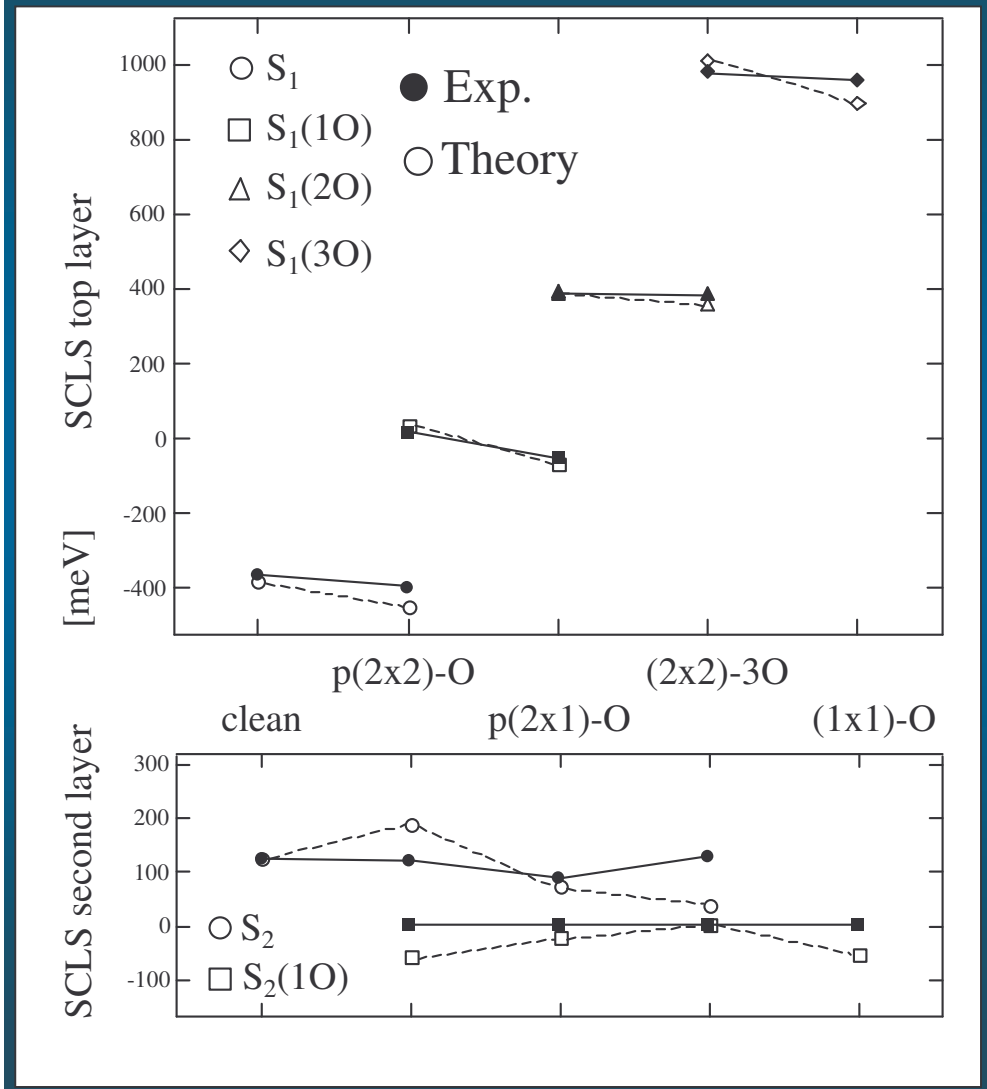
Oxygenad sorptionon R u(0001): *locals urfacec hemicalr eactivity*

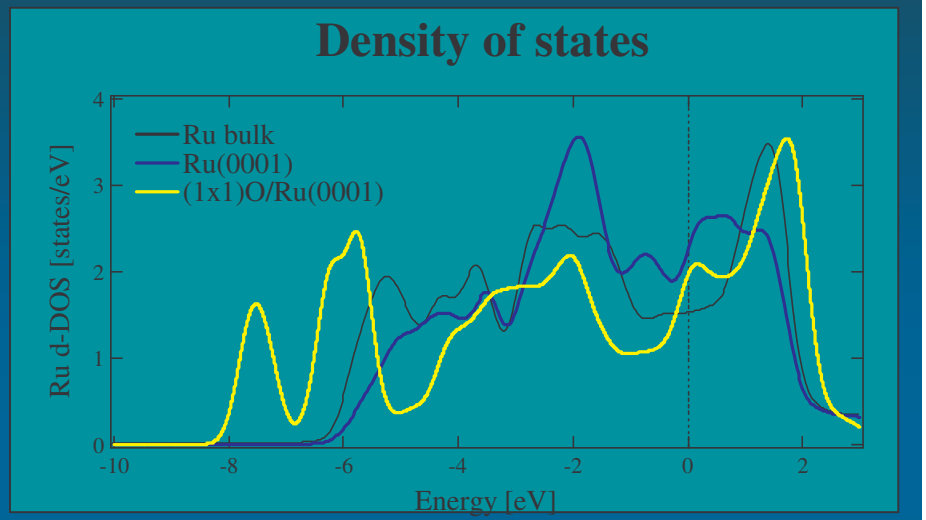




Fast XPS: some examples

Oxygenad sorptionon R u(0001): *locals urfacec hemicalr eactivity*





Formation of bonding and antibonding states widening the band

Almost linear increase of SCLS with O coordination