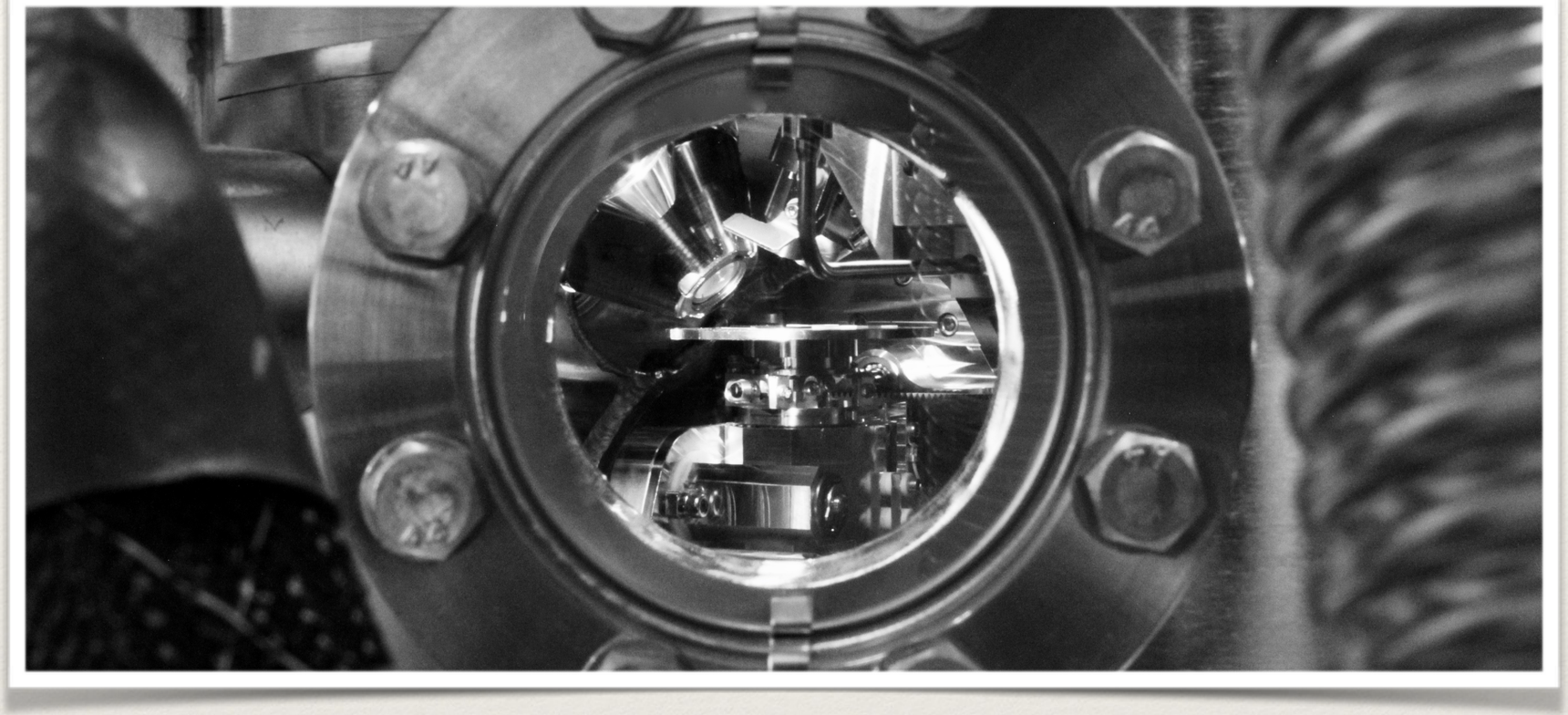


Inside the XPS

Advanced Solid State & Surface Characterization

Pascal Schouwink
Mounir Mensi
Emad Oveisi

Spring term 2025

Surface Characterization

- **Electron spectroscopy, *~6h***
  - X-ray Photoelectron Spectroscopy (XPS)
  - UV Photoelectron Spectroscopy (UPS)
  - Auger Electron Spectroscopy (AES)
- **Force spectroscopy, *~2h***
  - Scanning Tunneling Microscopy (STM)
  - Atomic Force Microscopy (AFM)
- **Vibrational spectroscopy, *~2h***
  - IR
  - Raman
  - SFG
- **Combined techniques, *~2h***
  - Scanning Near-Field Optical Microscopy (SNOM)
  - Tip Enhanced Raman spectroscopy (TERS)

The magnificent library of Uppsala University

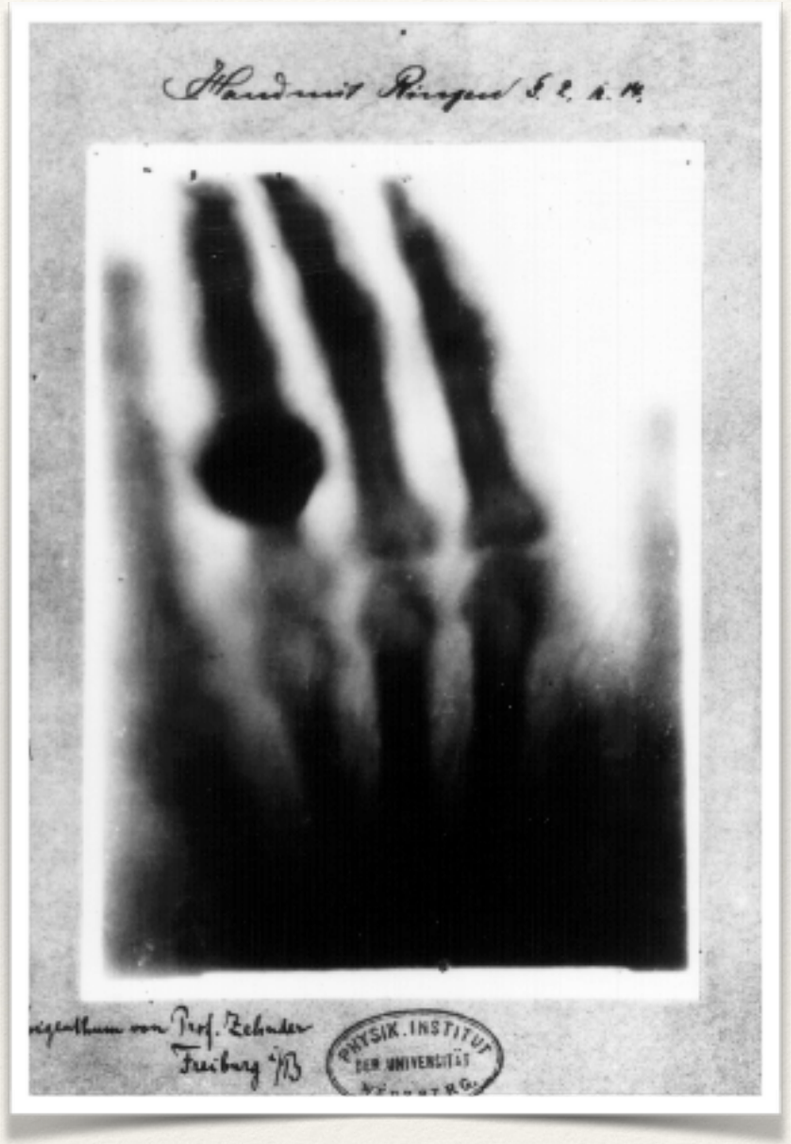
X-ray Photoelectron Spectroscopy

Mounir Mensi
2024/04/17

Course 1

Discovery of X-rays

- In **1895**, **Wilhelm Roentgen,** working on Lenard tubes (~1870), produced and detected electromagnetic radiation known as X-rays or Röntgen rays
- In 1901, Röntgen was awarded the first Nobel Prize in Physics.
- Röntgen donated the monetary prize to his university. Like Pierre Curie, Röntgen refused to take out patents related to his discovery of X-rays, as he wanted "society as a whole to benefit from practical applications of the phenomenon".

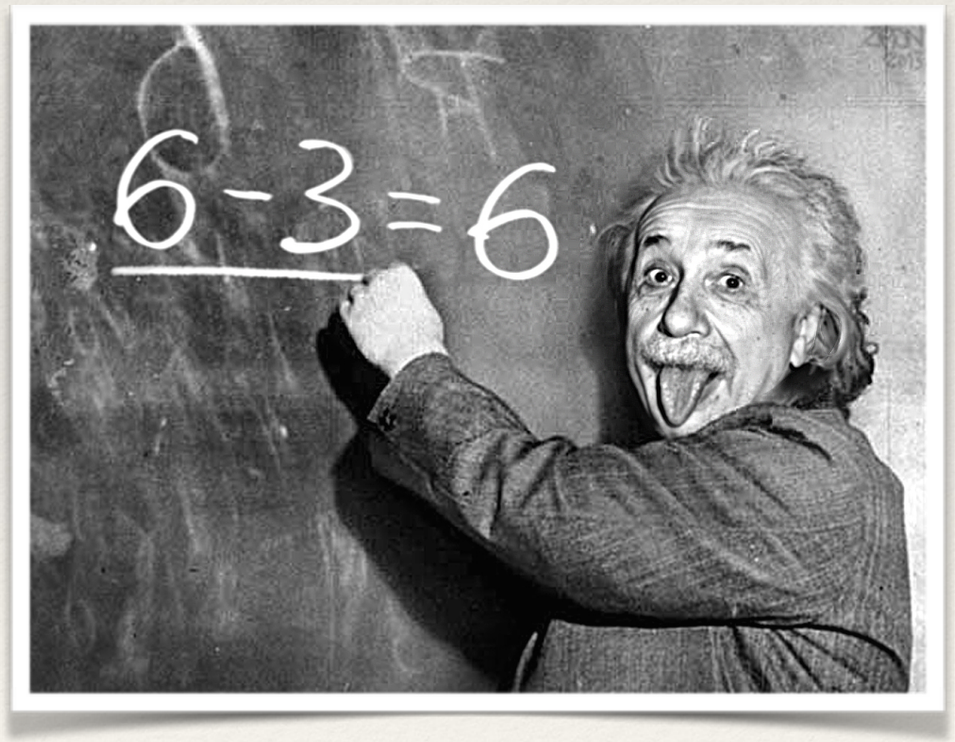


First medical X-ray image: Roentgen's wife hand

The Photoelectric Effect

When certain metals are exposed to light, a stream of ‘particles’, later know as electrons, is emitted from that metal.

First observed by Hertz 1887 [1], understood later by Einstein [2,3], who described the duality of photons

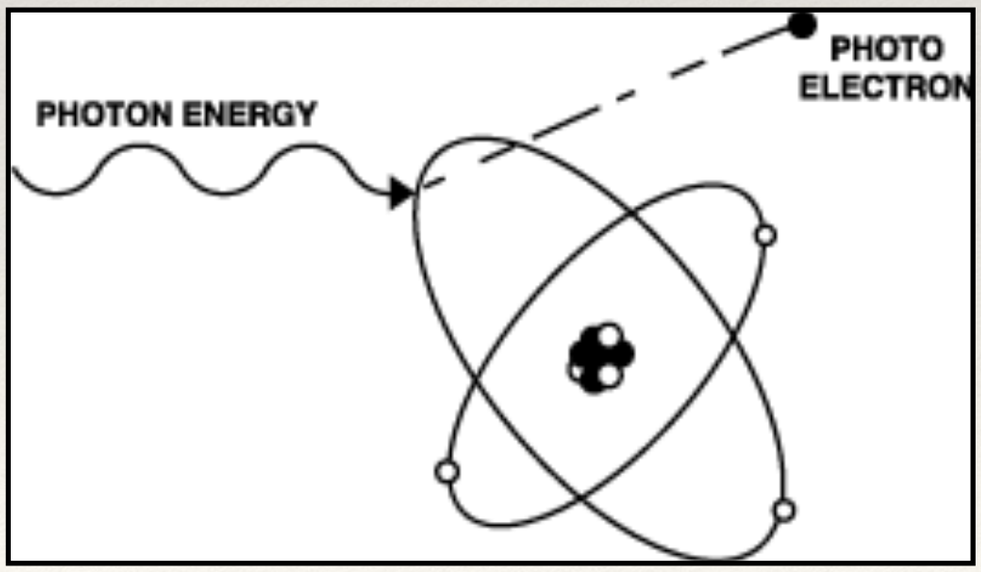


1. H. Hertz, Ann. Physik 31, 983 (1887).
2. A. Einstein, *On a Heuristic Viewpoint Concerning the Production and Transformation of Light*. Ann. Physik 17, 132 (1905)
3. 1921 Nobel Prize in Physics.

Photoelectric effect

The observations couldn't be explained by the light being solely 'a wave':

1. The *number* of electrons emitted by the metal depends on the *intensity* of the light beam applied onto it; the more intense the beam, the higher the number of electrons emitted.
2. The emitted electrons move with greater *speed* if the applied light has a higher *frequency*.
3. **No electron is emitted until the light has a *threshold* frequency, *no matter how intense the light is*.**



Einstein relationship
on the photoelectric effect

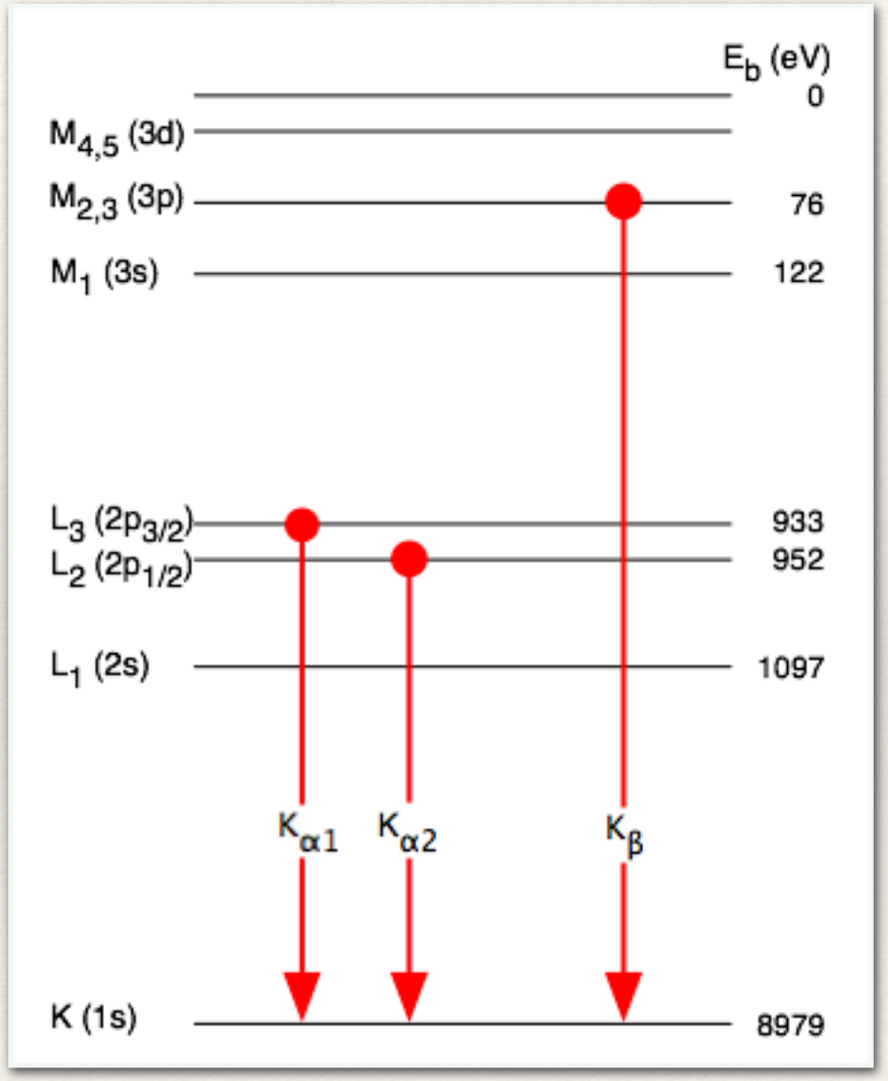
$$E = h\nu - \Phi$$

Siegbahn's Family: Manne Siegbahn

- Siegbahn notation for the X-ray transitions
- Nobel prize in 1924 for his discovery and research in the field of X-ray spectroscopy

Low energy level	High energy level	Siegbahn notation	IUPAC notation
K ($1s^{-1}$)	L_3 ($2p_{3/2}^{-1}$)	$K\alpha_1$	K-L_3
	L_2 ($2p_{1/2}^{-1}$)	$K\alpha_2$	K-L_2
	M_3 ($3p_{3/2}^{-1}$)	$K\beta_1$	K-M_3
	M_2 ($3p_{1/2}^{-1}$)	$K\beta_3$	K-M_2
L_3 ($2p_{3/2}^{-1}$)	M_5 ($3d_{5/2}^{-1}$)	$L\alpha_1$	L_3-M_5
L_3 ($2p_{3/2}^{-1}$)	M_4 ($3d_{3/2}^{-1}$)	$L\alpha_1$	L_3-M_4
M_5 ($3d_{5/2}^{-1}$)	N_7 ($4f_{7/2}^{-1}$)	$M\alpha_1$	M_5-N_7

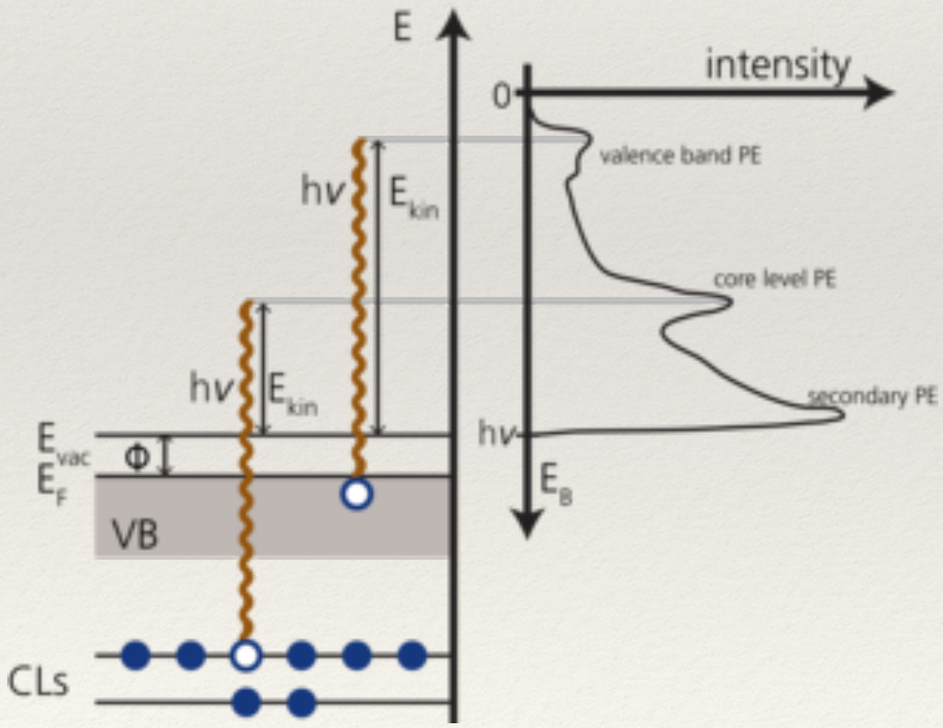
Siegbahn's notation

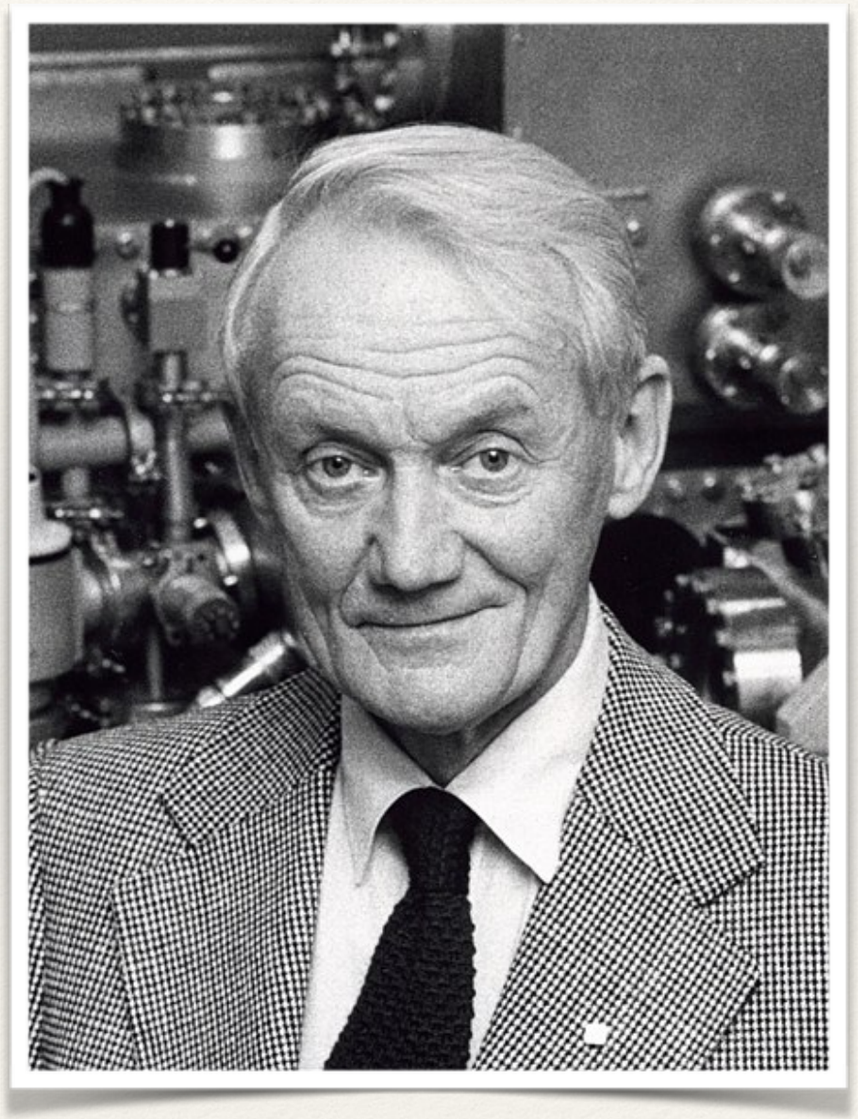


X-ray emission notation

Siegbahn's Family: Kai Siegbahn

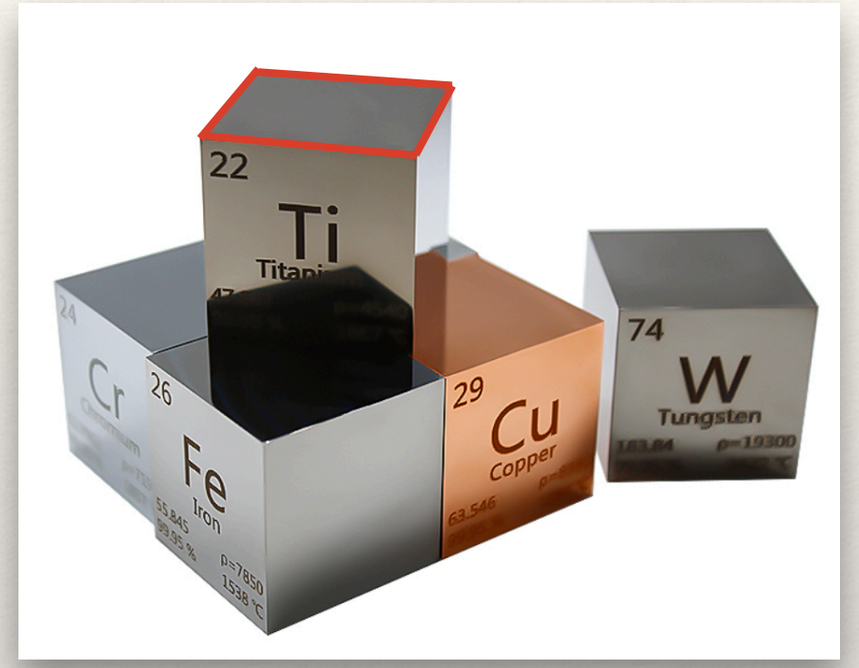
- Invention of the XPS, initially called ESCA [1]
- He further showed that the chemical shift is a linear function of the net charge transfert in chemical bounding
- Nobel prize in 1981 for the invention Electron Spectroscopy for Chemical Analysis (ECSA)





1) K. Siegbahn, Et. Al.,Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics.

The Role of Surfaces and Interfaces



Bulk

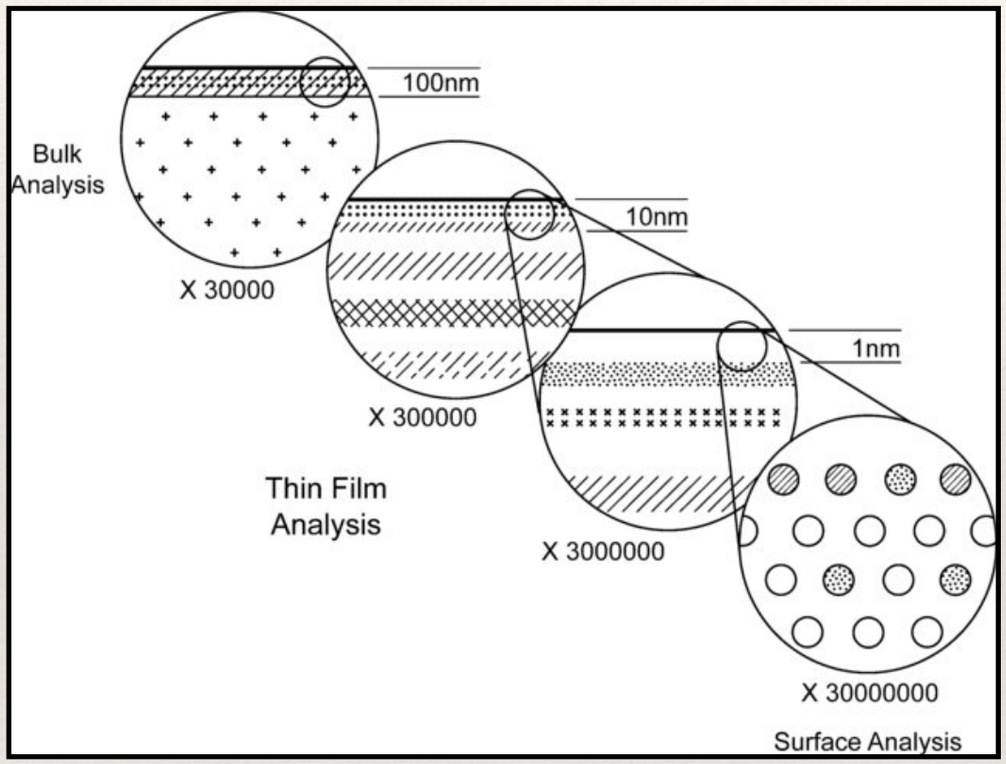
Mostly responsible for: Structural properties, thermal, electrical, magnetic, dielectric, optical, ferroelectric, thermoelectric, etc.

Surface (as defined by an interface)

- **Solid-gas interface:** catalysis, gas exchange, corrosion, -> surface chemistry
- **Solid-solid interface:** electronics, optics, magnetic, bio-chemistry, etc.
- **Friction, tribology, lubrication:** mechanics of surfaces, etc.
- **Growth substrate/surface for growth :** thin films, attachment of molecules, etc.

Every exchange of matter happens at or through an interface (surface)

‘Depth’ of a Surface



Source: Briggs and Seah, 1990

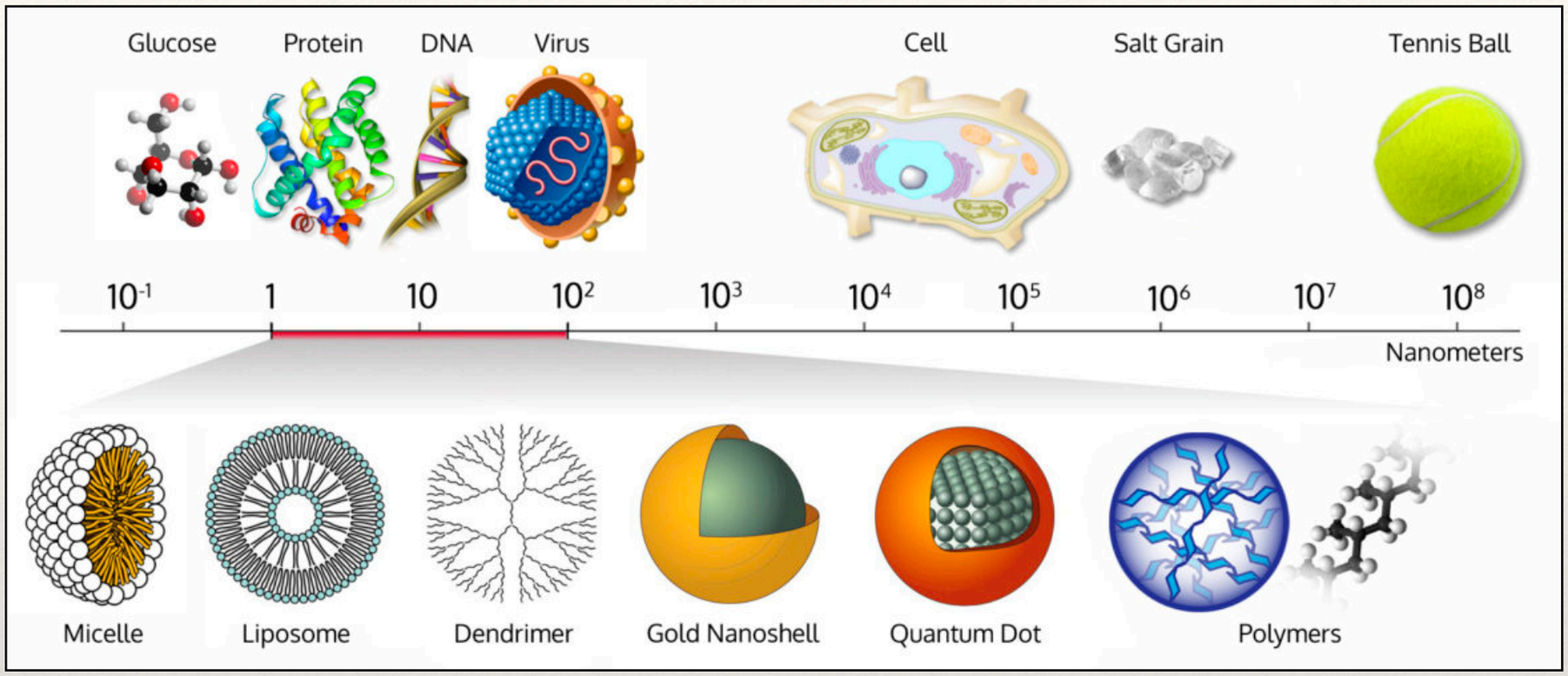
A surface is defined as the topmost atomic layer of a material at an interface. But: **What is the ‘depth' of a surface?**

The « depth » of a surface depends on the phenomena to be studied, or on the limitations of the characterisation method.

Surface analysis techniques explore a depth which depends on the underlying phenomena: *e.g.* energy range, inelastic mean free path, material itself, etc.

The surface defined in relation to XPS and Auger electron spectroscopies is thinner than 10nm, i.e. ~100 atomic layers

Surfaces Towards the Nanoscale



When downscaling to nanometers, properties will change as the surface becomes dominant!

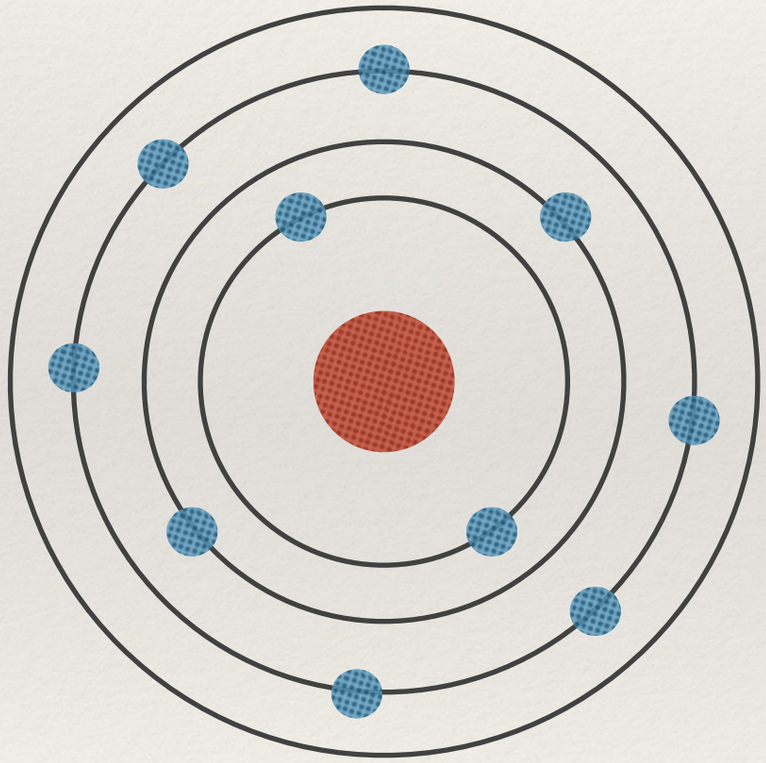
Particle size	0.5nm	1nm	1um
# surface atoms	8	26	5.4E+07
# 'bulk' atoms	1	8	2.7E+10
Fraction of surface	0.89	0.76	0.002

Energy Band Structure of Solids

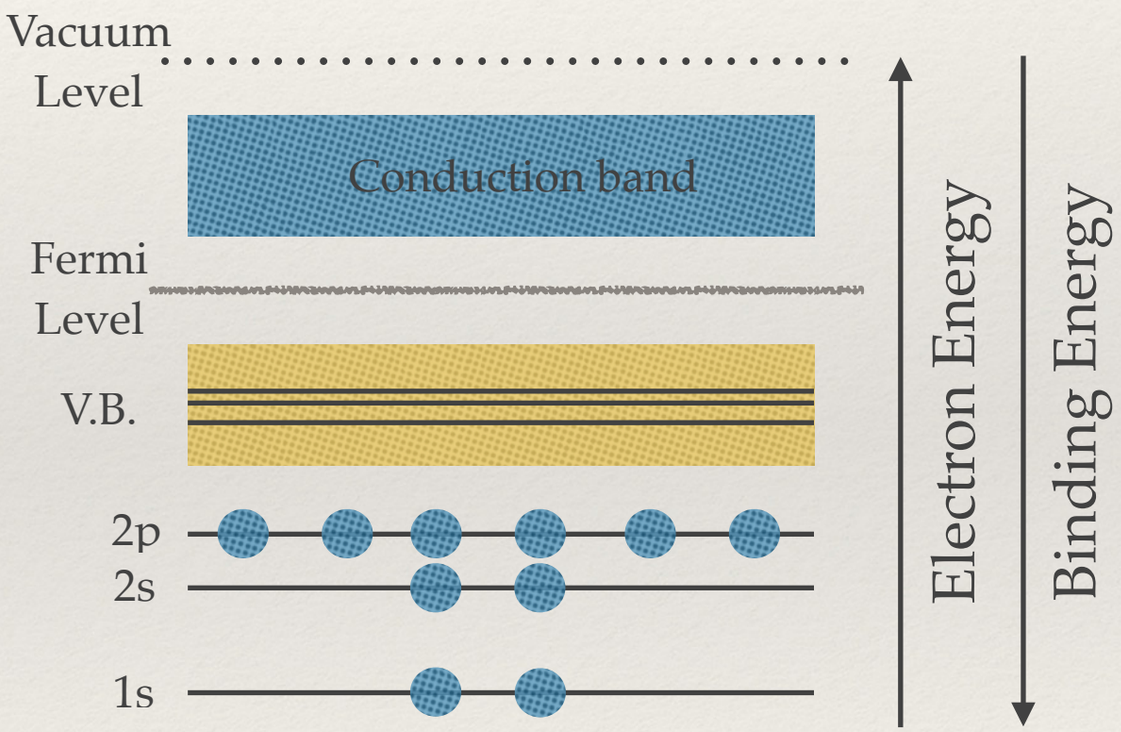
Bohr atomic model

(Useful for didactics)

$1s^2$, $2s^2$, $2p^6$…VE



Energy diagram

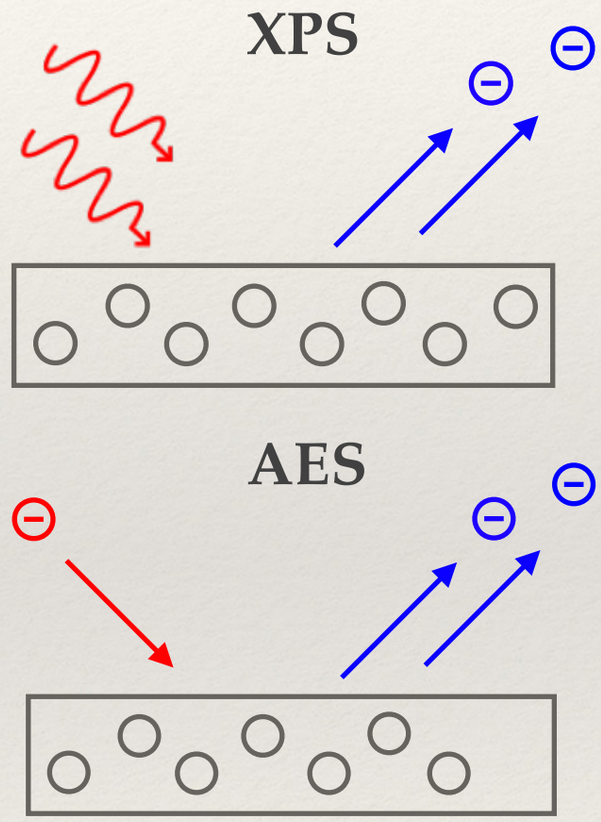


Electrons have energies ‘unique' to each atom:
Finger print of the elemental composition

How to Probe the Electronic Structure?

Traditionally, techniques dedicated to surface characterisation have been subdivided according to the source of exciting radiation:

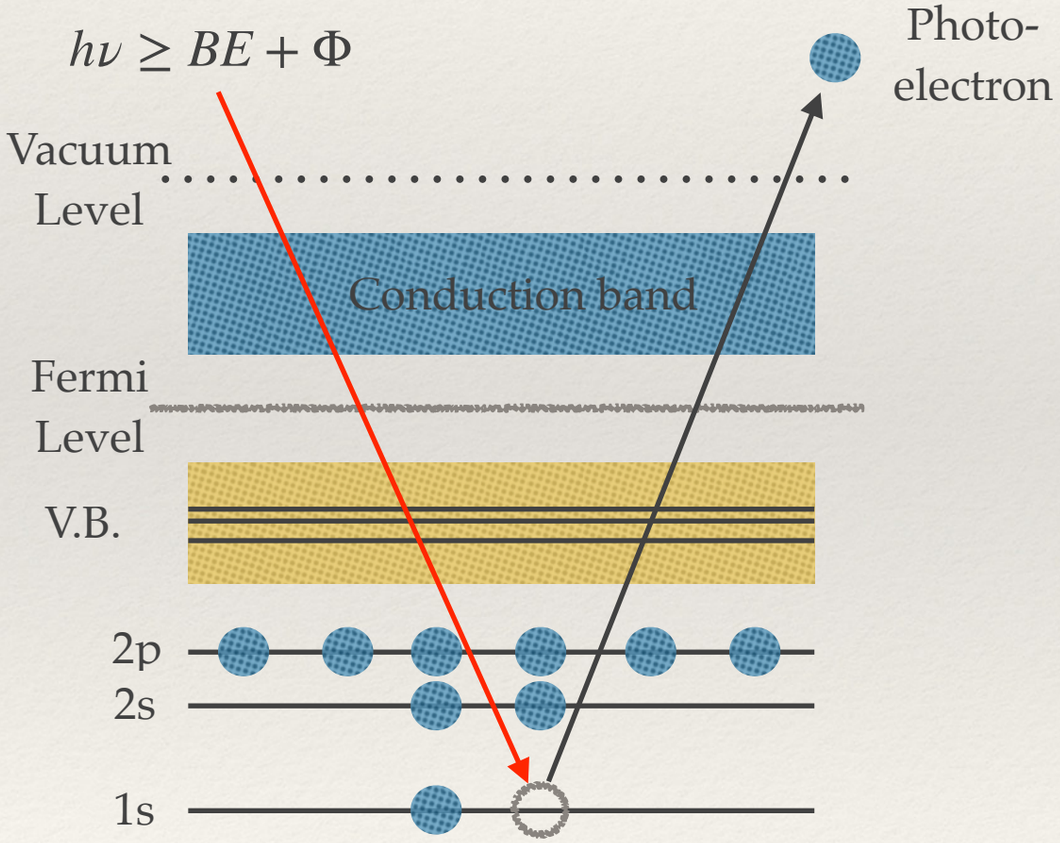
Technique	Source	Detected
XPS	Photons	Electrons
AES	Electrons	Electrons
EDS	Electrons	Photons
SIMS	Ions	Ions
Neutrals S.	Ions	Neutrals



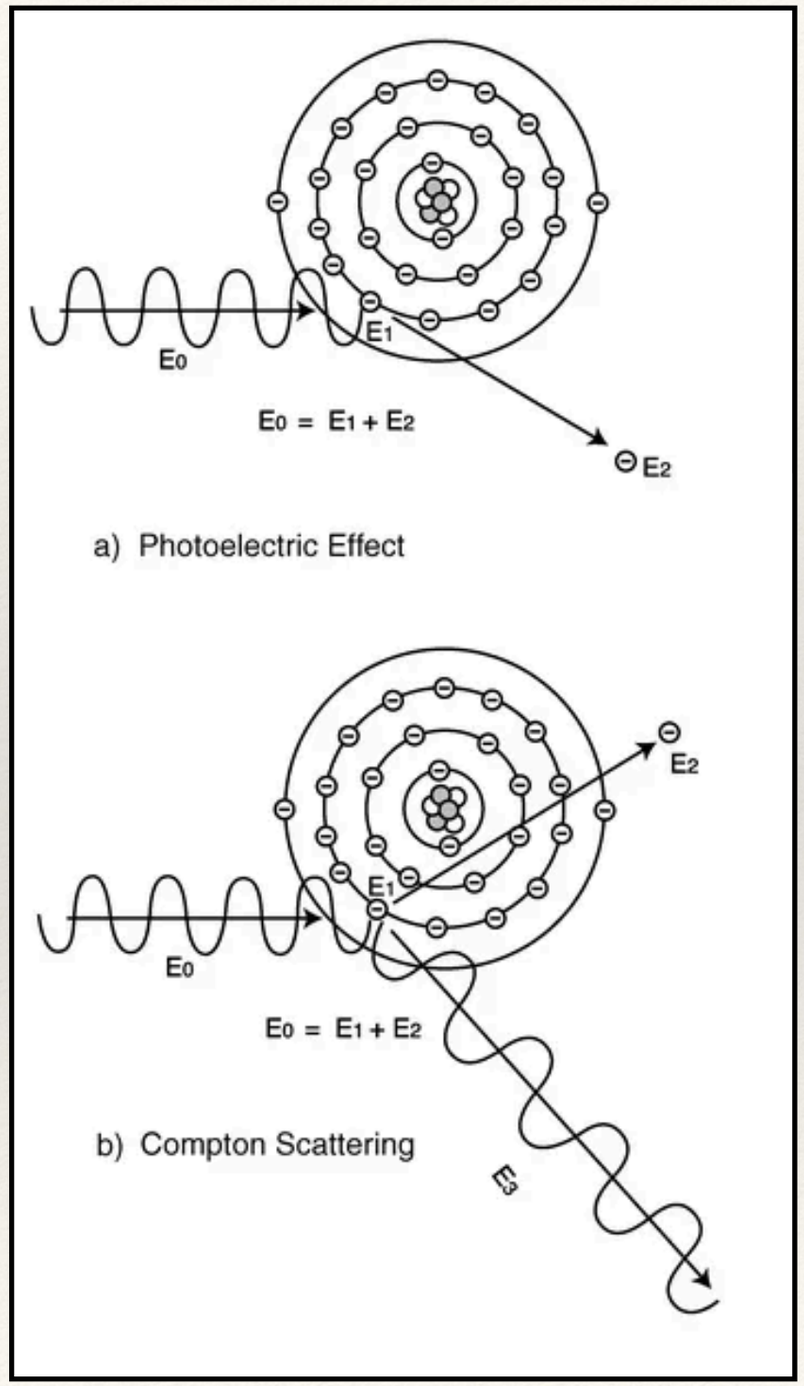
XPS/UPS: By using photo-ionization and energy-dispersive analysis of the emitted photoelectrons, the composition and electronic state of the surface region of a sample can be studied.

X-Ray Interaction with Matter

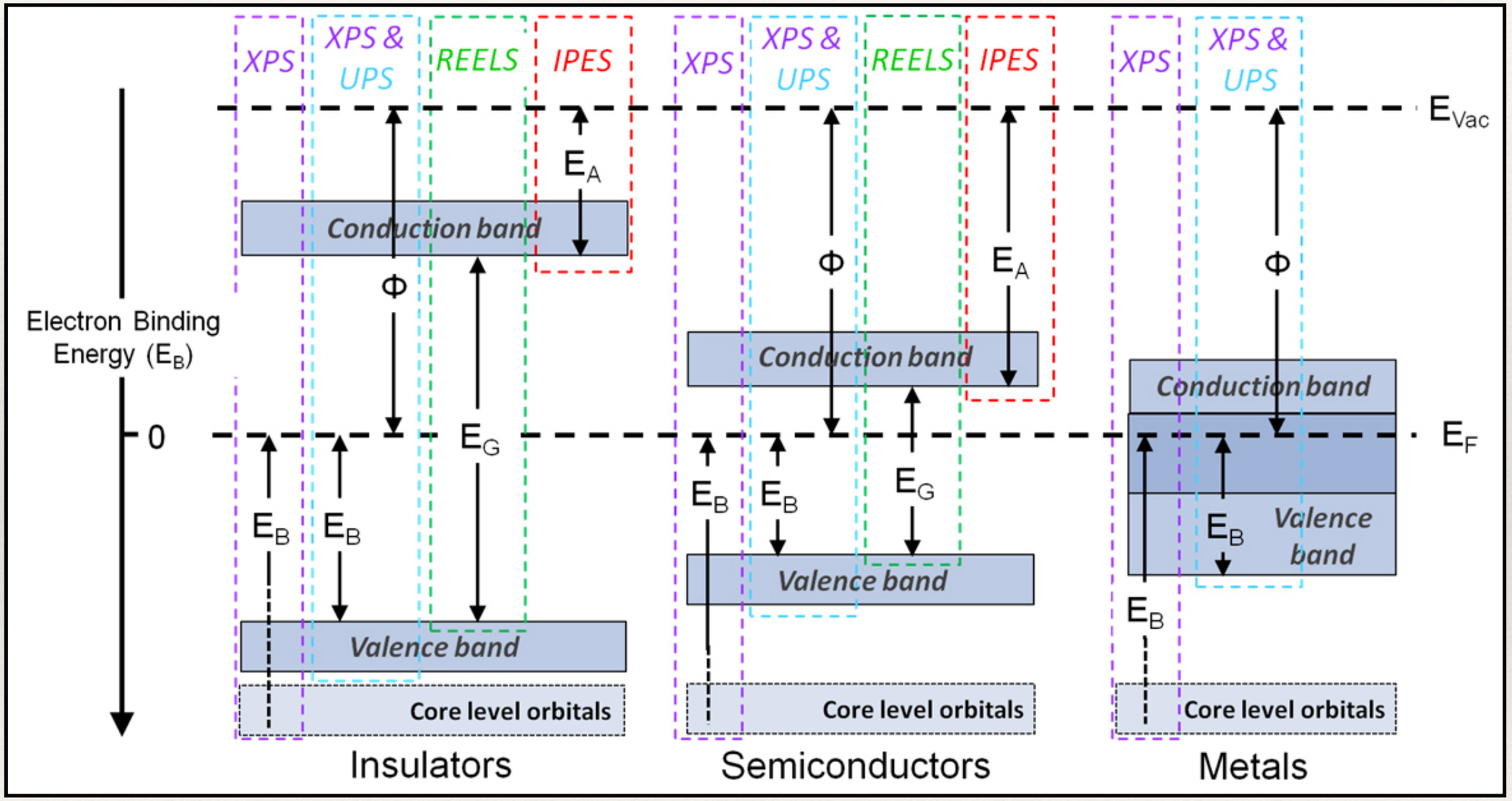
- Photoelectric effect
- Compton scattering



Energy sketch of the photoelectric effect

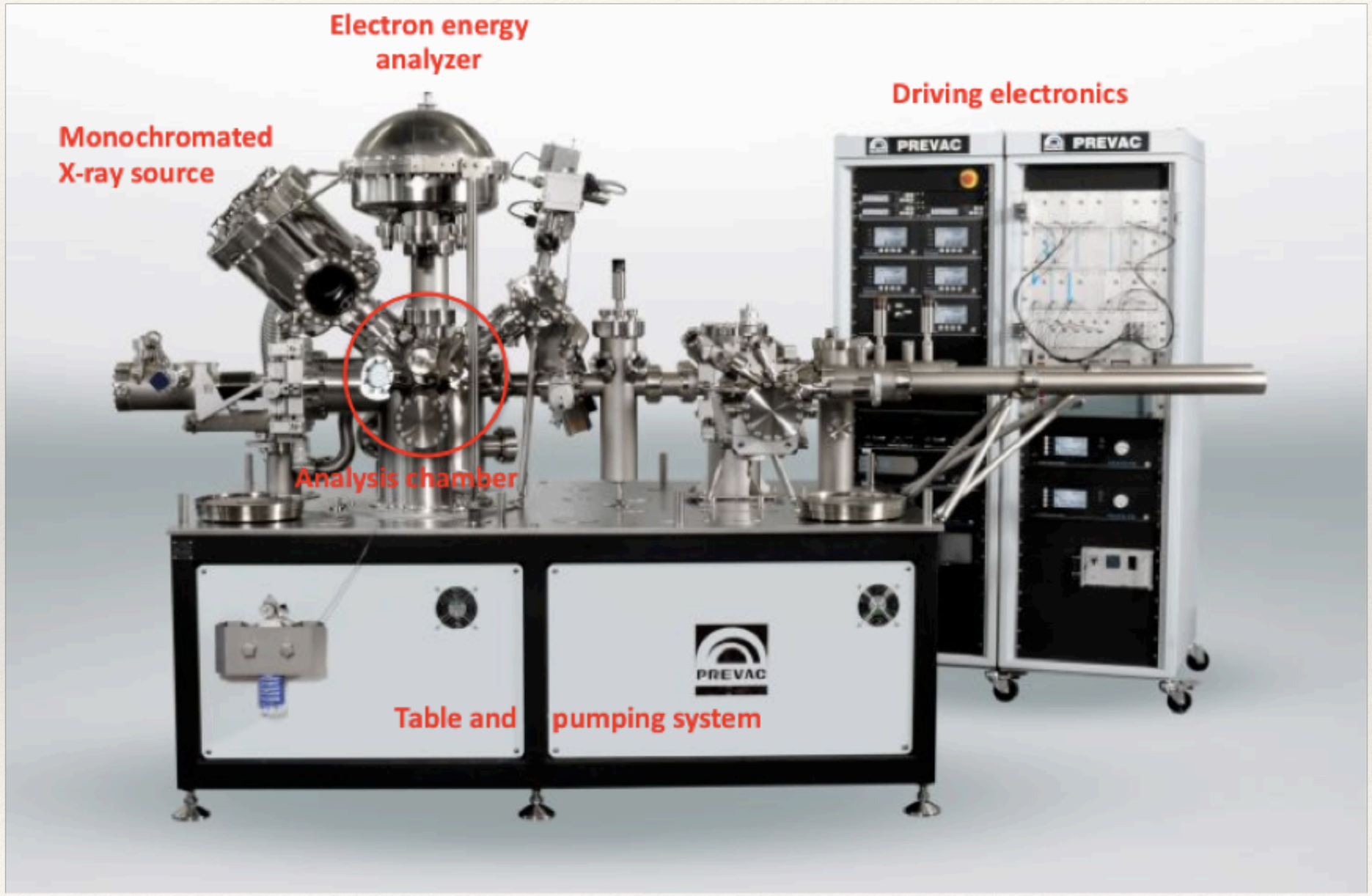


Various Techniques

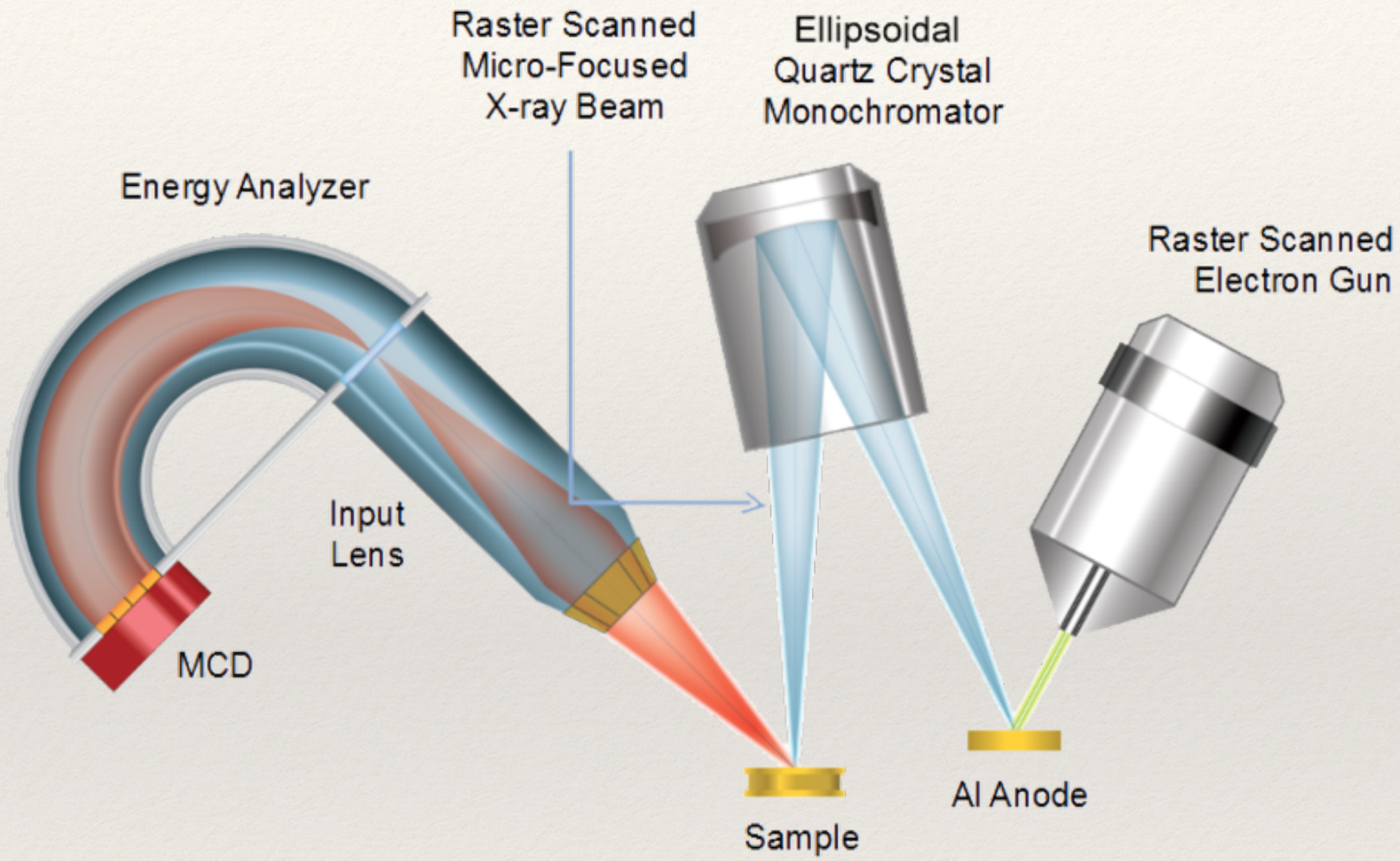


XPS: X-Ray photoelectron spectroscopy, **UPS**: UV photoelectron spectroscopy, **REELS**: reflected electron energy loss spectroscopy, **IPES**: inverse photoemission spectroscopy

XPS Design

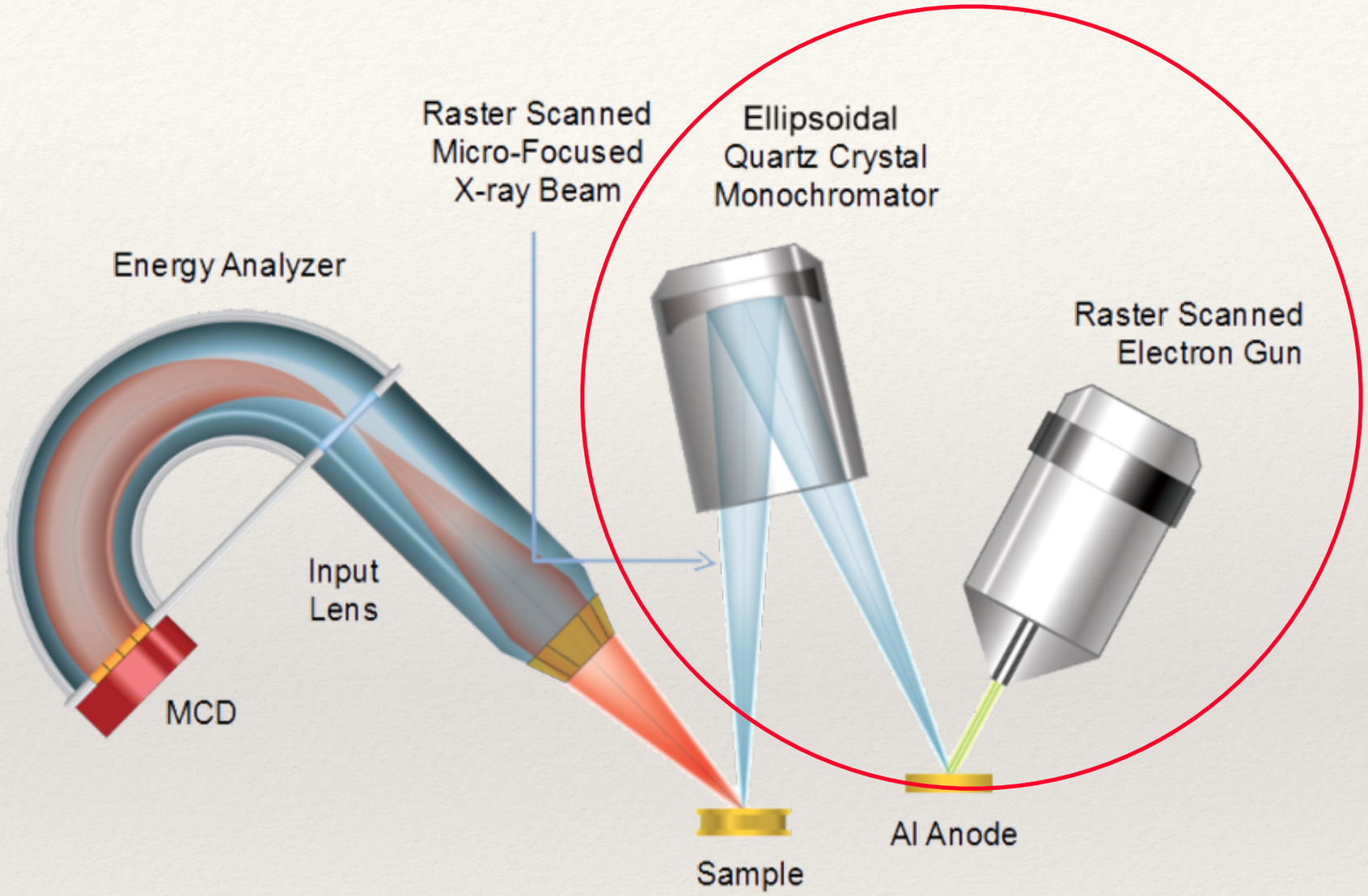

Electron energy analyzer
Monochromated X-ray source
Driving electronics
PREVAC
PREVAC
Analysis chamber
PREVAC
Table and pumping system

XPS Working Principle



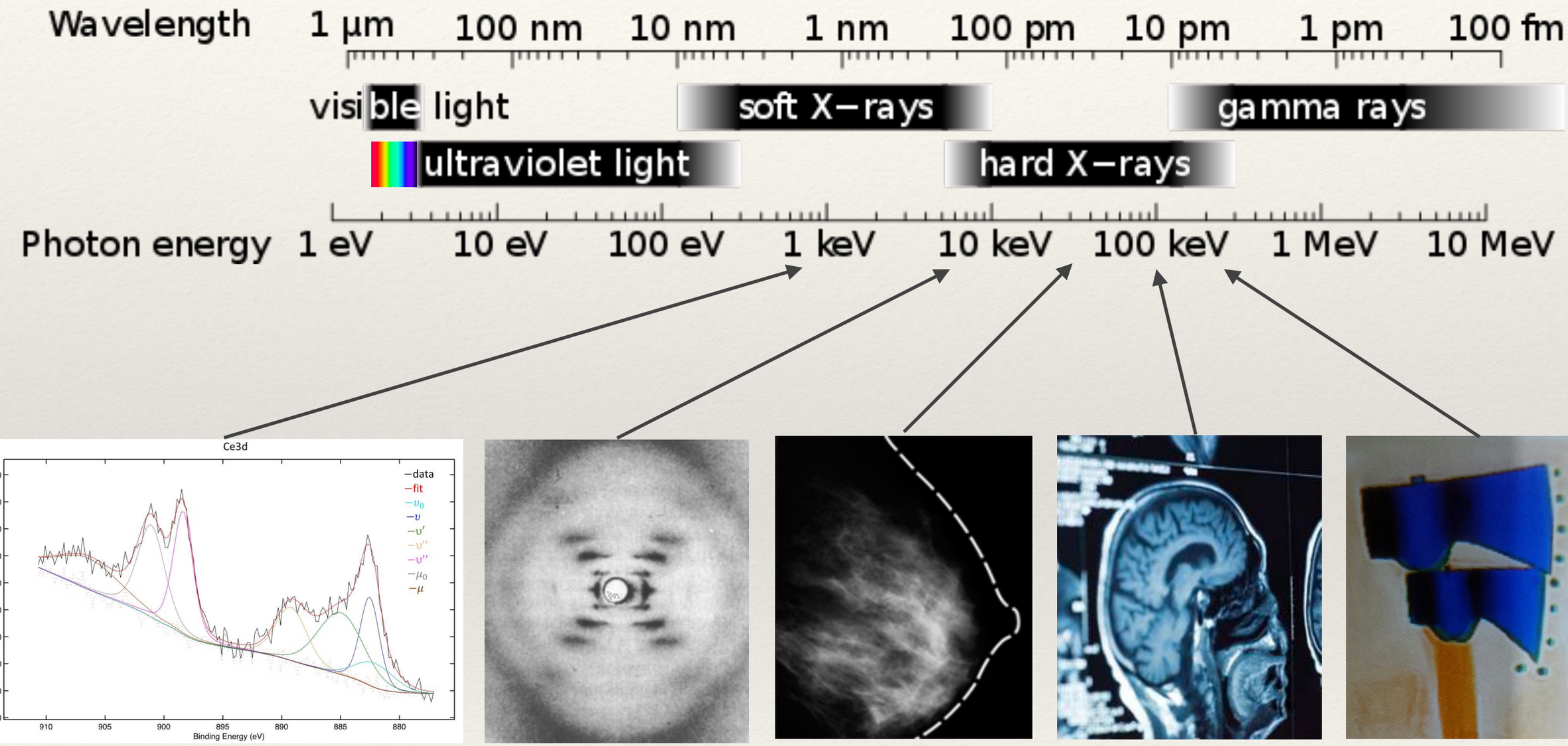
Schematics of the main component of an XPS

X-ray Source



Schematics of the main component of an XPS

X-rays Energy Range



XPS

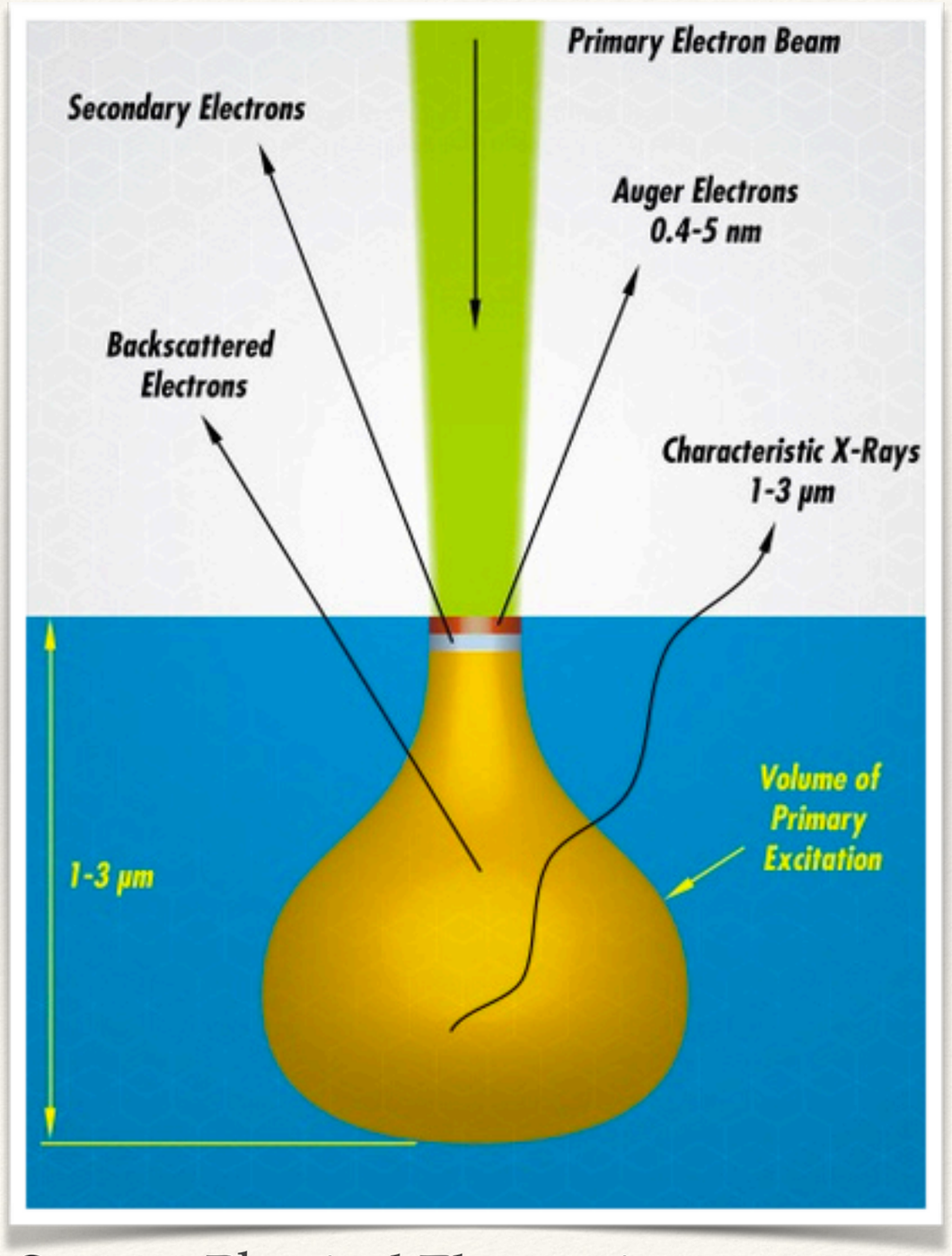
XRD

Mammography

Tomography

Airport Scanning

Generation of X-rays



Source: Physical Electronics

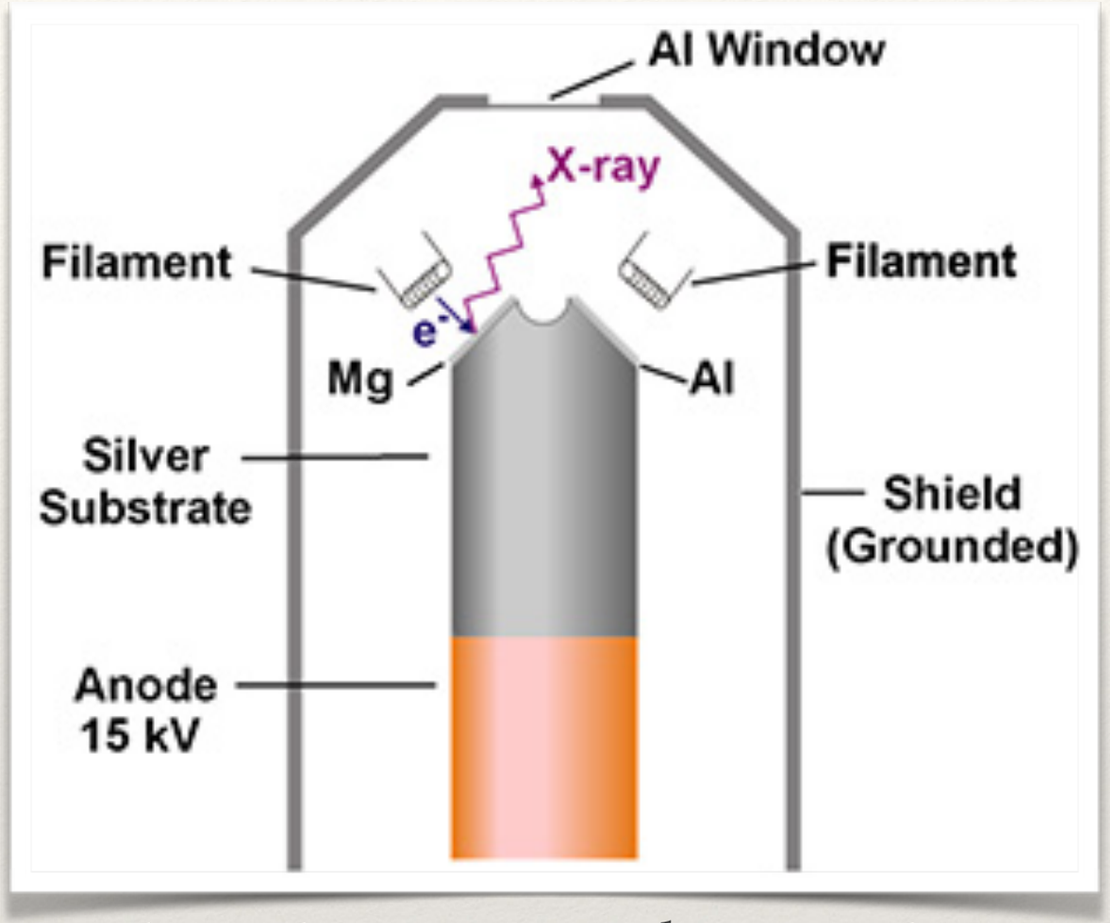
- X-rays are generated by bombarding a metallic anode with high-energy electrons
- The energy of the emitted X-rays depends on the anode material

Transition	Energy eV	FWHM
Mg ka	1253.6	0.70
Al ka	1486.6	0.85
Ag La	2984.2	2.60

Most common anode material

Basic X-ray source

- Thermionic electron emission from a heated up thorium-coated iridium filament (implies vacuum)
- Acceleration of the electrons towards the target (anode)
- Generation of characteristic X-rays…as well as:
  - Brehmstrahlung X-rays
  - Satellites
  - Cross-contamination
  - Ghost-lines



Dual-anode non-monochromated X-ray source. The X-ray source is under vacuum to protect the filment from burning, and the surface of the anode from being contaminated.

Monochromated X-ray Source

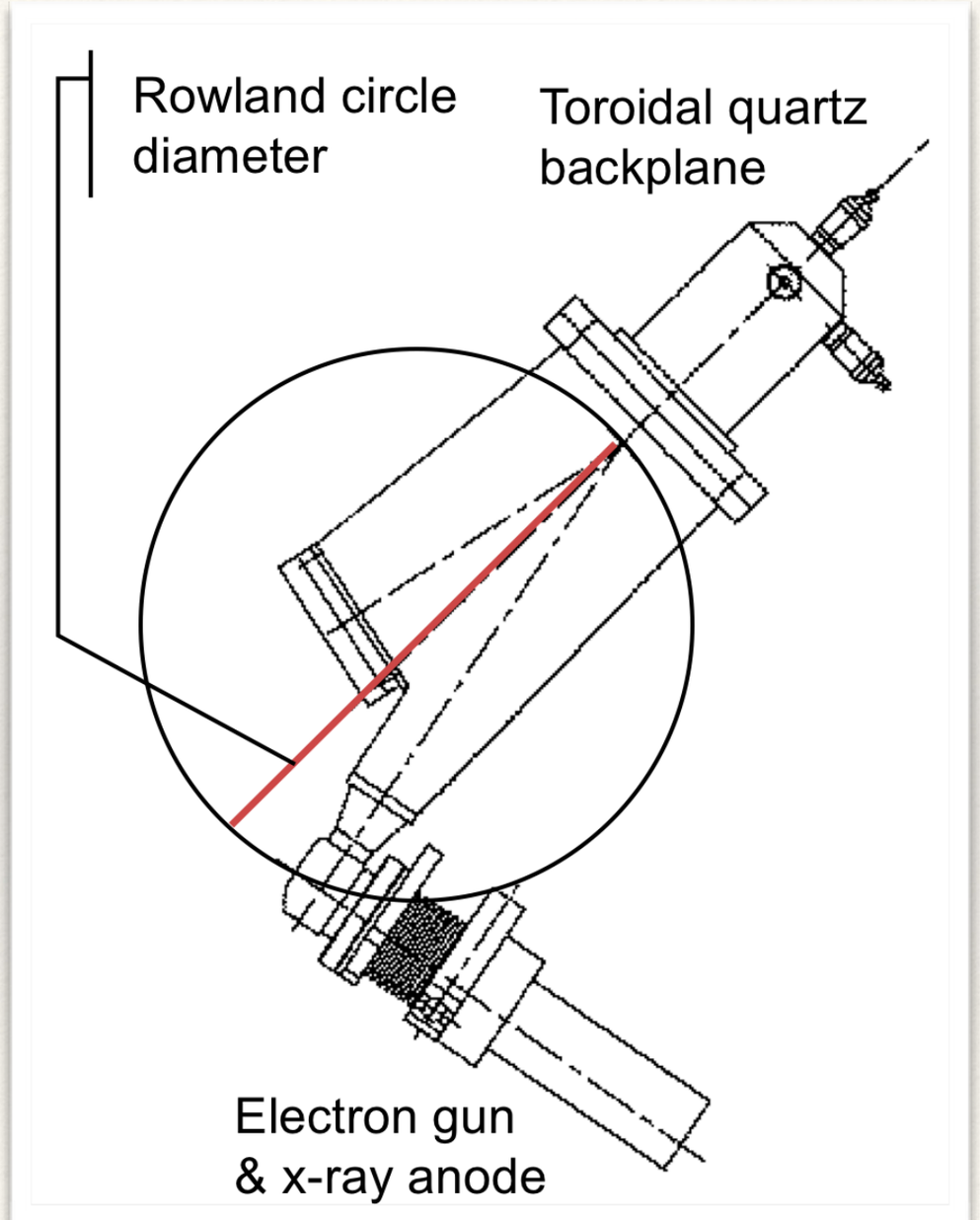
- To limit the problems related to a non-monochromated X-ray source, a monochromator (toroidally bended quartz cristal) is inserted in the X-ray line.
- Most commercial spectrometers use Al Ka as a monochromatic source. A quartz I0$\bar{1}$0 crystal is used to monochromate the X-rays, decreasing the energy spread.

Al Ka; E = 1486.6 eV, Wavelength = 8.3393Å

Conveniently:

Ag La; E = 2984.2 eV, Wavelength = 4.1544Å ~½ Al

2nd order diffraction through the same crystal for Ag La.



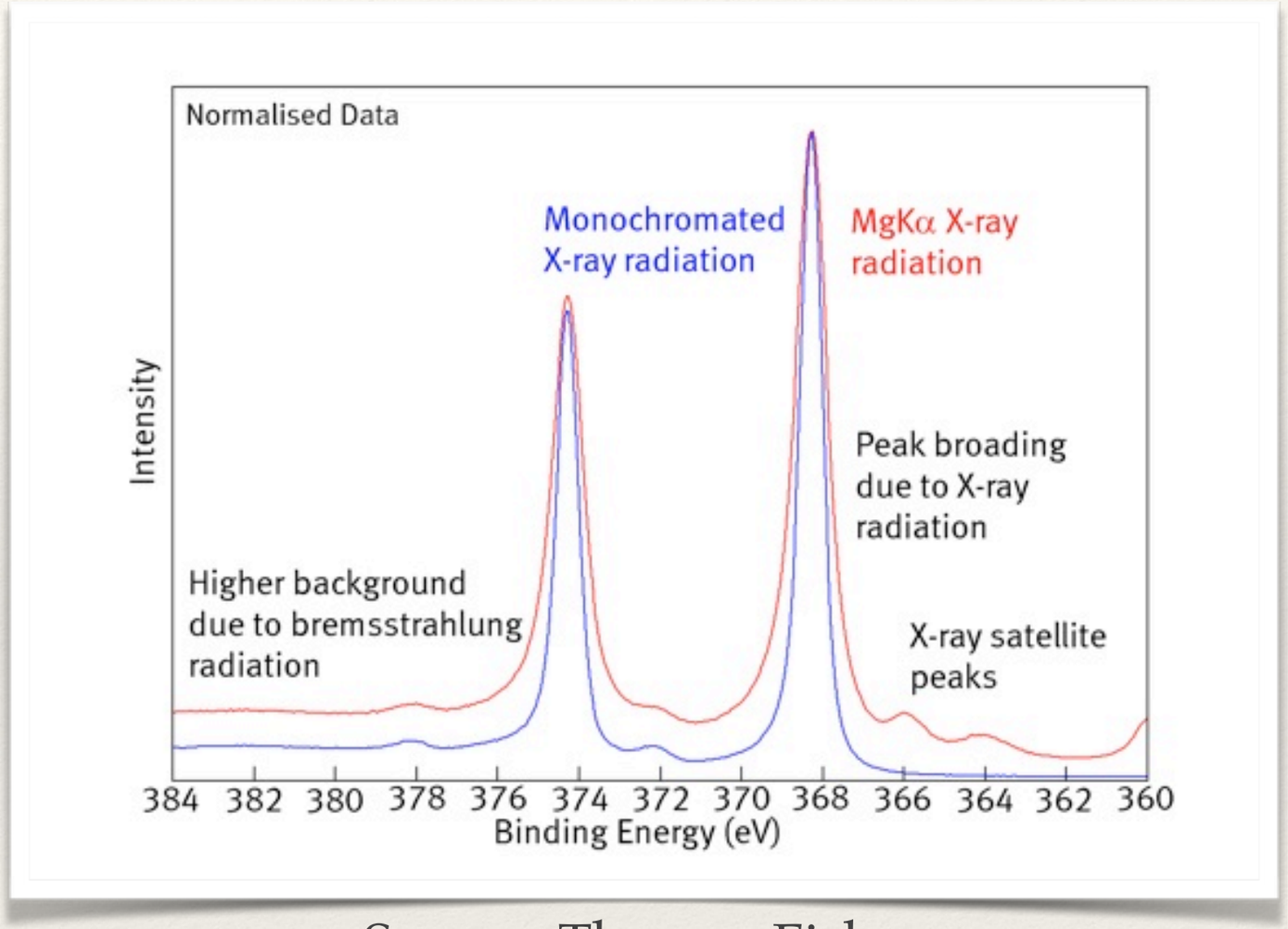
Source: Kratos

Advantages of monochromatic X-ray source

A comparison of the Ag 3d spectra produced with monochromatic and non-monochromatic radiation.

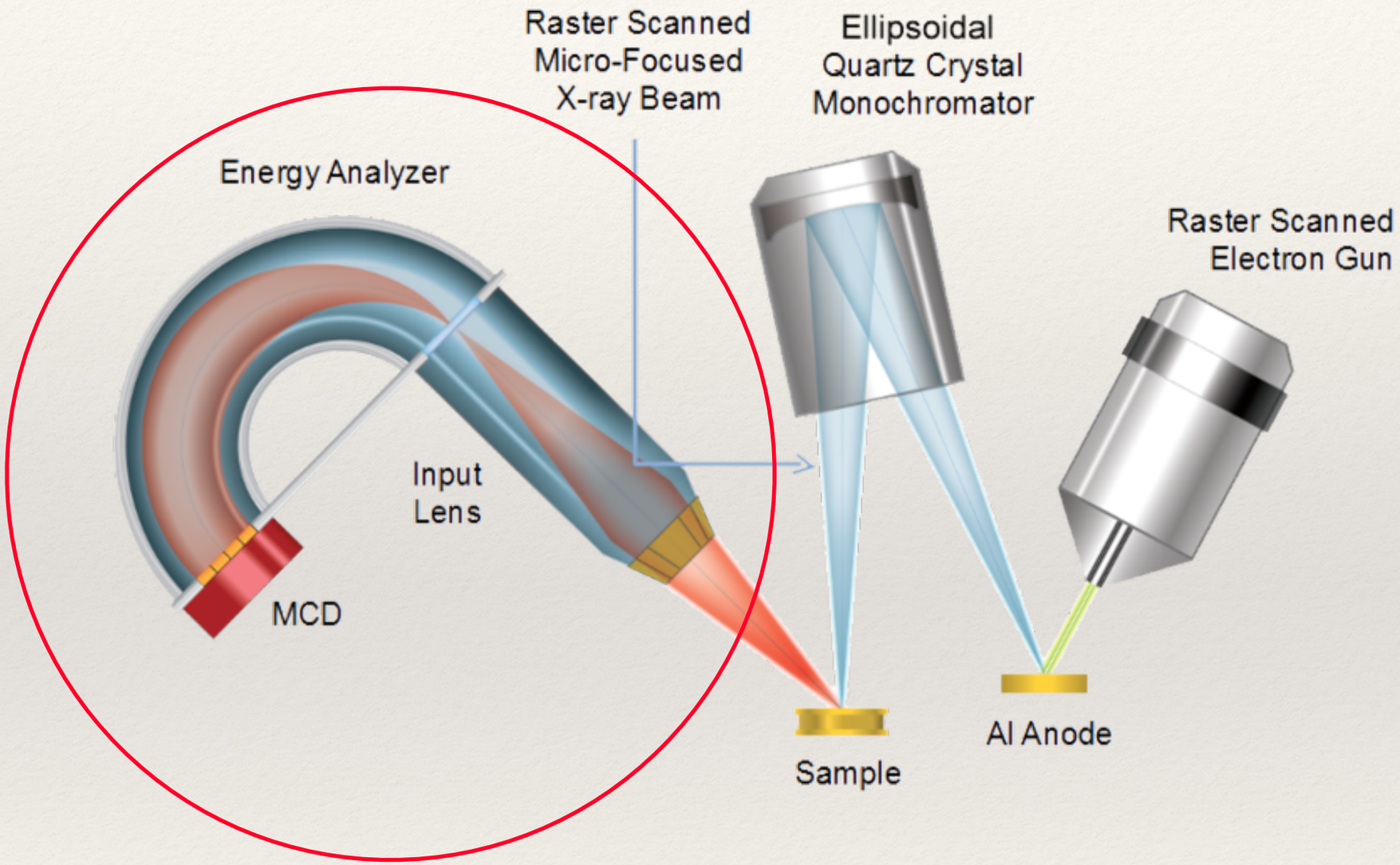
X-rays produced in a twin-anode source have a wide X-ray line width, satellite X-ray peaks and a continuum of background radiation.

Since the line width of the photoelectron peaks are a convolution between the source line width and their intrinsic line width, all of these factors affect the quality of the XPS spectrum.



Source: Thermo-Fisher

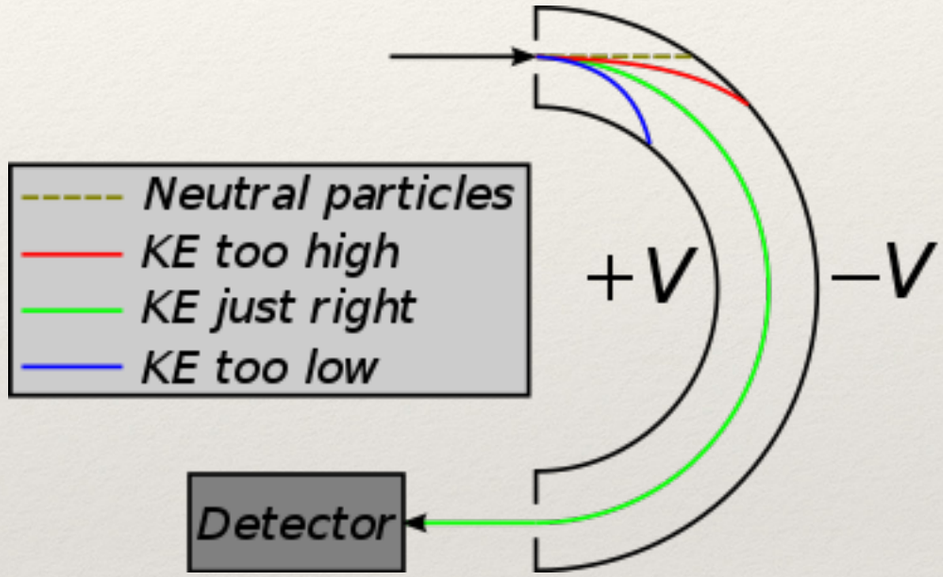
Electron Energy Analyser

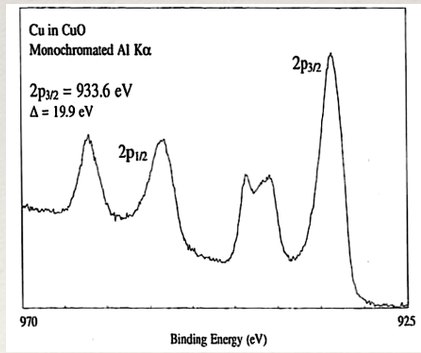


Schematics of the main component of an XPS

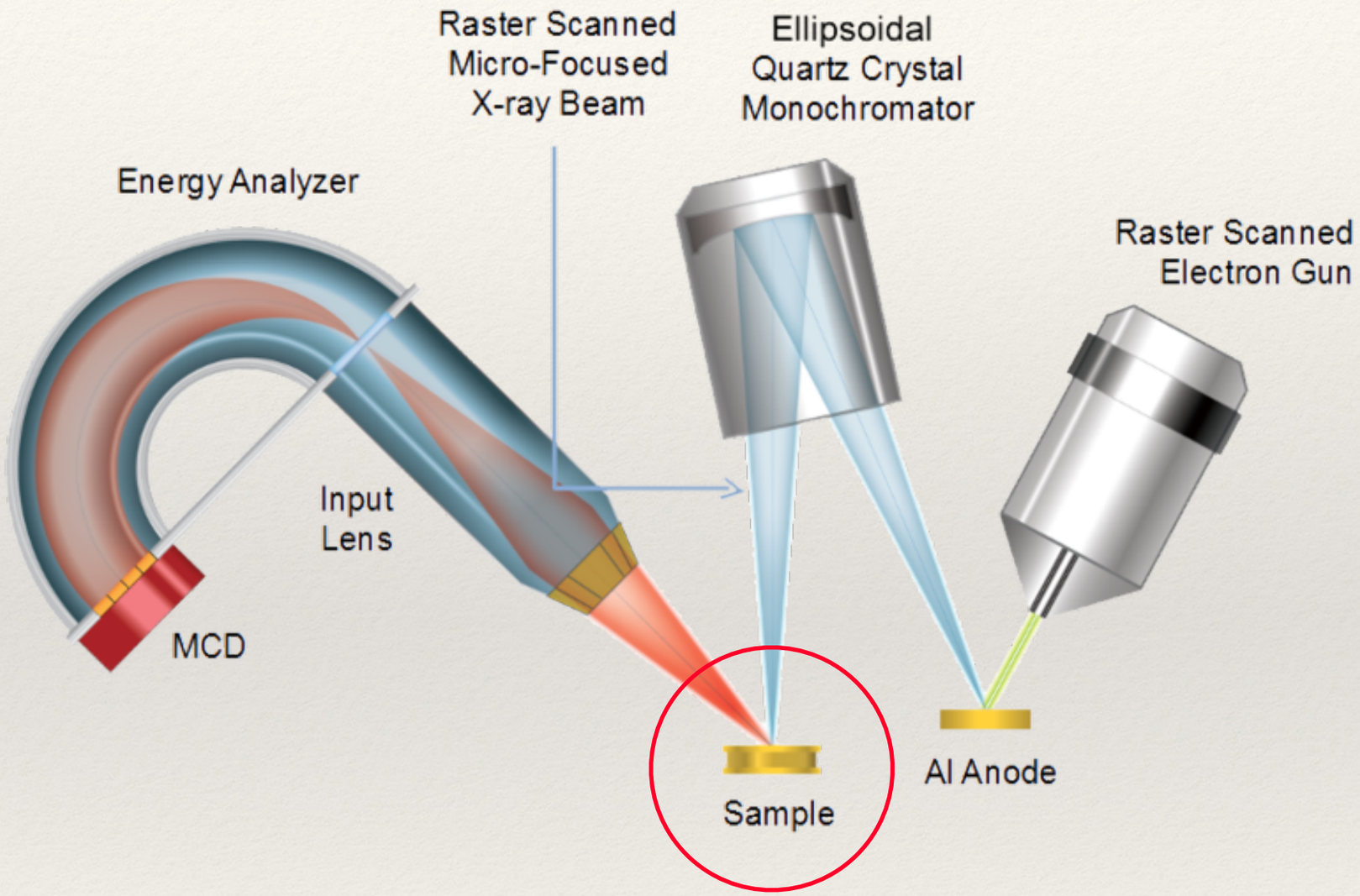
Electron Energy Analyser

- Most electron energy dispersive analysers used for XPS are (hemi-)spherical mirror analyser (SMA)
- A set of electrostatic lenses is placed before the entrance slit of the analyser in order to focus and 'retard' the emitted electrons
- Electron entering the SMA with an energy equal to the pass energy E_0 travel along the mean radius of the SMA and are focused at the exit slit
- Electrons are collected by a multi-channel plate.
- By sweeping the retardation field, a full spectrum is collected



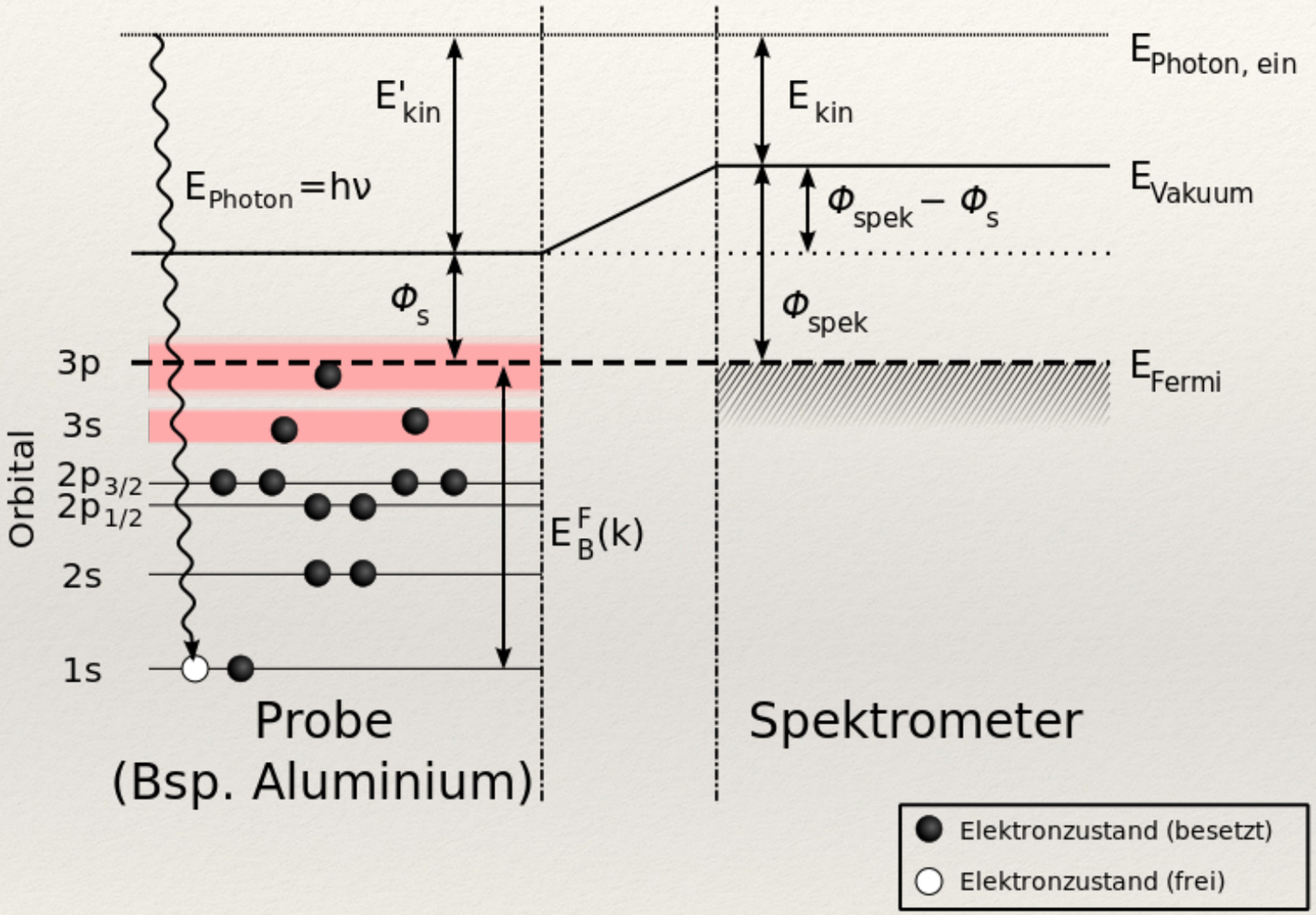


Probing a Sample



Schematics of the main component of an XPS

Energy Referencing



Energy referencing between a conductive sample and the spectrometer. For insulating samples, the Fermi levels are NOT aligned.

- Photoelectrons emission contribute to a positive charging of the sample
- Conductive samples can be grounded to balance the charging effect
- Fermi energies of the metal and the spectrometer are aligned due to electrons transfer until the E_F coincide, i.e.:

$$\mathbf{FL_{spectro} = FL_{sample}}$$

Fermi Level

- By definition, the Fermi level is the thermodynamic work required to add one electron to the body. It represents the top of the electron collection at 0K

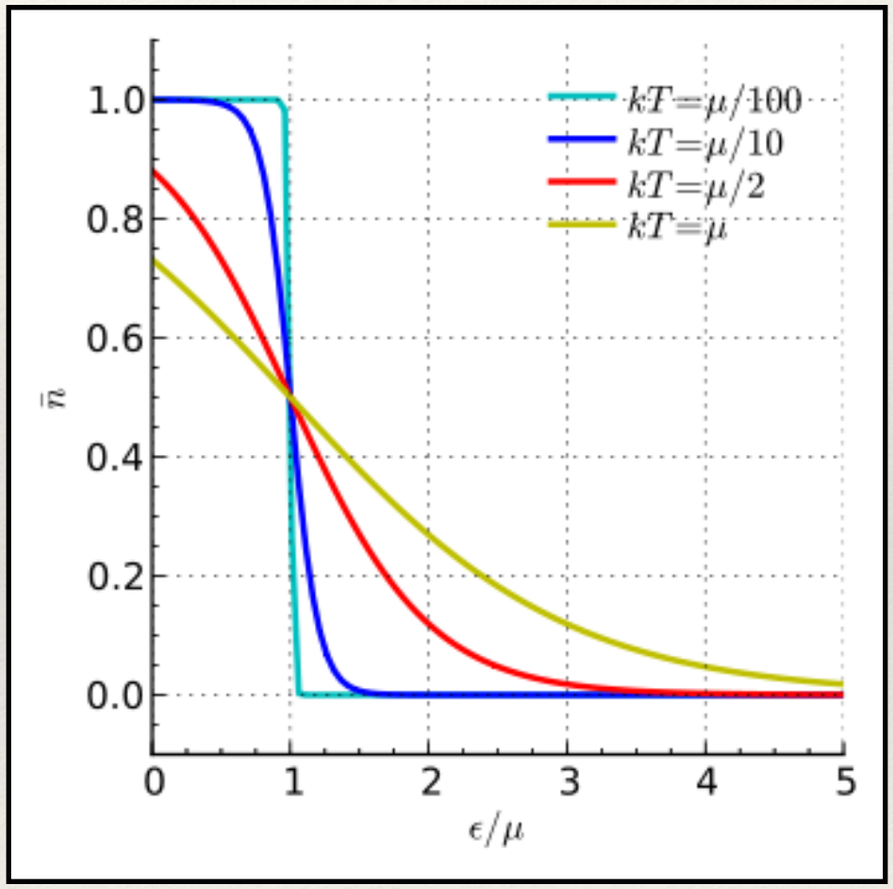
- Fermi-Dirac distribution:

$$f(E) = \frac{1}{e^{[(E-E_f)/k_BT]} + 1}$$

- T=0K: f(E) = 1 for $E<E_f$, 0 for $E>E_f$

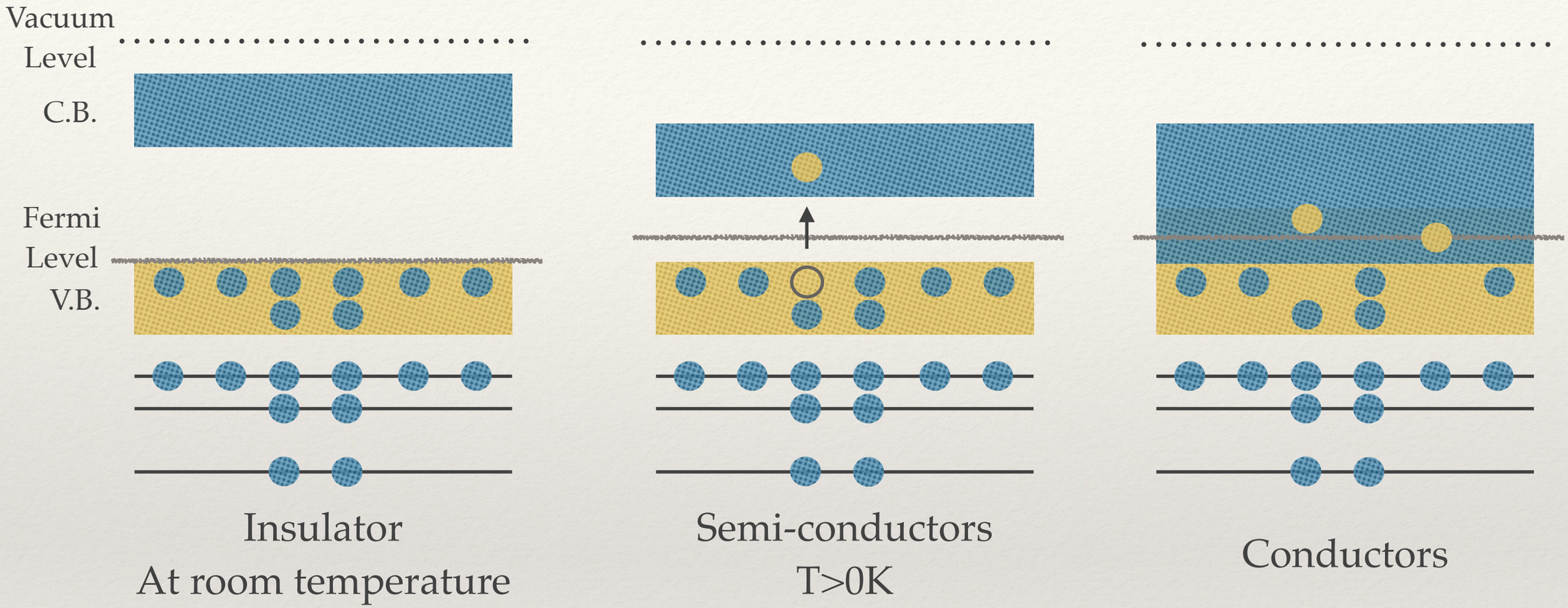
- $k_BT<<E_f$, F(E) = 0.5 for $E=E_f$

  (k_BT = 25meV at 293K)



Fermi-Dirac distribution

Dielectric and Conductive Materials



- From the Fermi-Dirac distribution, at room temperature, electrons do not have enough thermal energy (k_BT~25meV) to populate the CB of insulators, while some populate the CB of semiconductors
- Free electrons, giving rise to conduction, define an equal potential within the material

XPS: an Energy Referenced Technique?

Provided that the Fermi levels are aligned:

$$E_B = h\nu - E_k - \Phi_{spec}$$

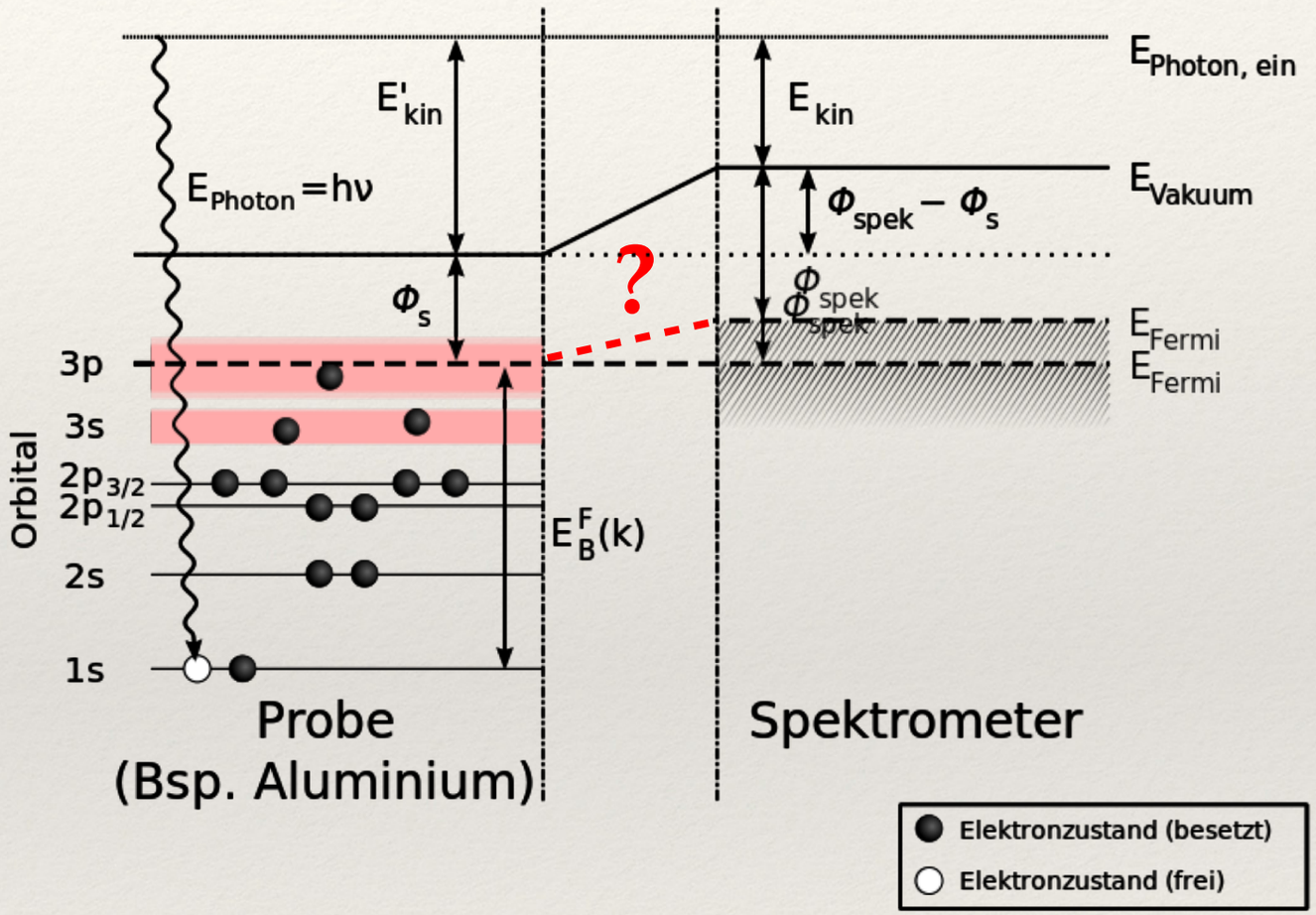
Where E_k is the energy measured

However, charging can never be ruled out

- Dielectrics present challenges

Solutions:

- Referencing, e.g. C-C bound of the C1s line
- Charges compensation ('not possible' for UPS)



Energy referencing between an insulating sample and the spectrometer; Fermi levels are NOT aligned.

Why UHV

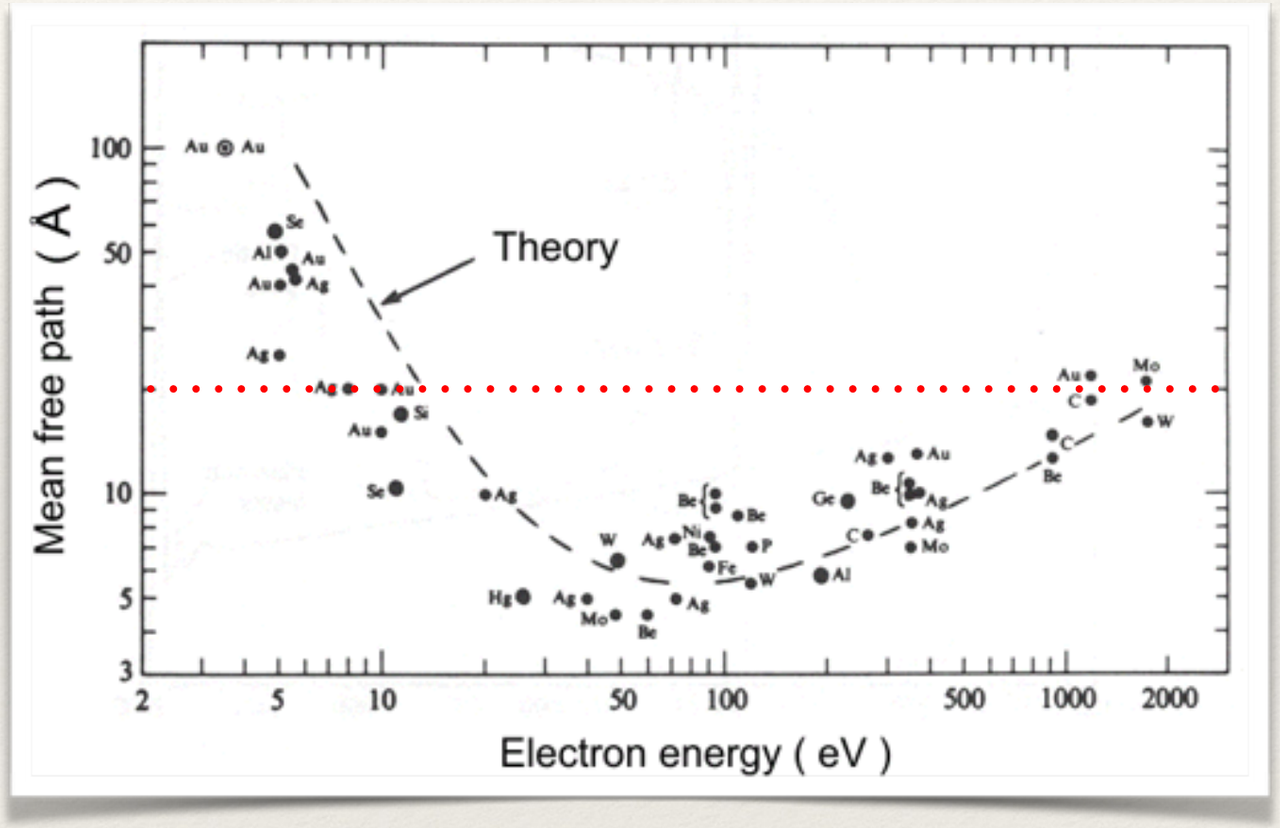
Under UHV, the residual gas is composed mostly of H_2 under UHV (H2O and N2 shortly after sample loading). UHV allows to:

- Desorb the adsorbed species from the sample
- Eliminate further adsorption of contaminant from the surface.
- **Increase the inelastic mean free path of the emitted electrons**

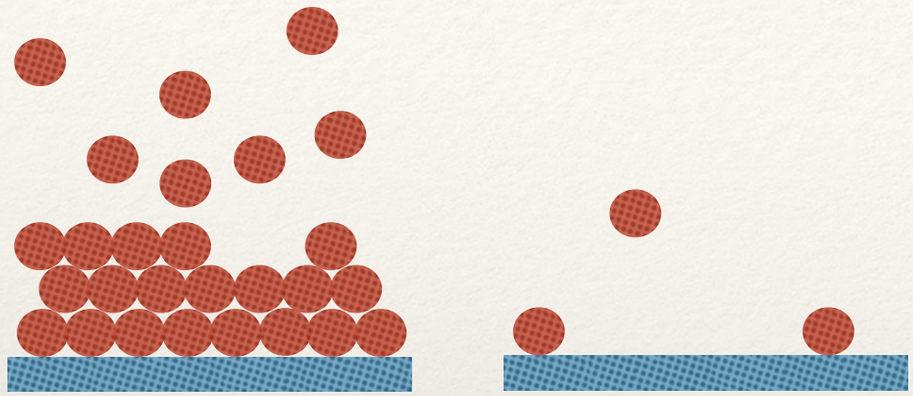
Convention	Pressure Torr	atom / cm^3	
Rough vacuum	1atm - 10^{-3}	$4x10^{13}$	@$4x10^{-3}$ Torr
High vacuum	10^{-3}-10^{-8}	$4x10^{10}$	@$4x10^{-6}$Torr
Ultra high vacuum	10^{-8}-10^{-12}	$4x10^{5}$	@$4x10^{-11}$Torr

Probing Depth and Inelastic Mean Free Path of Electrons

- Inelastic mean free path is dependent on material itself and the electron kinetic energy
- Typical inelastic mean free path is in range of 1-2 nm in the XPS KE range, i.e. few atomic layers
- Hence, XPS is a surface sensitive technique due to the short mean free path of low energy electrons



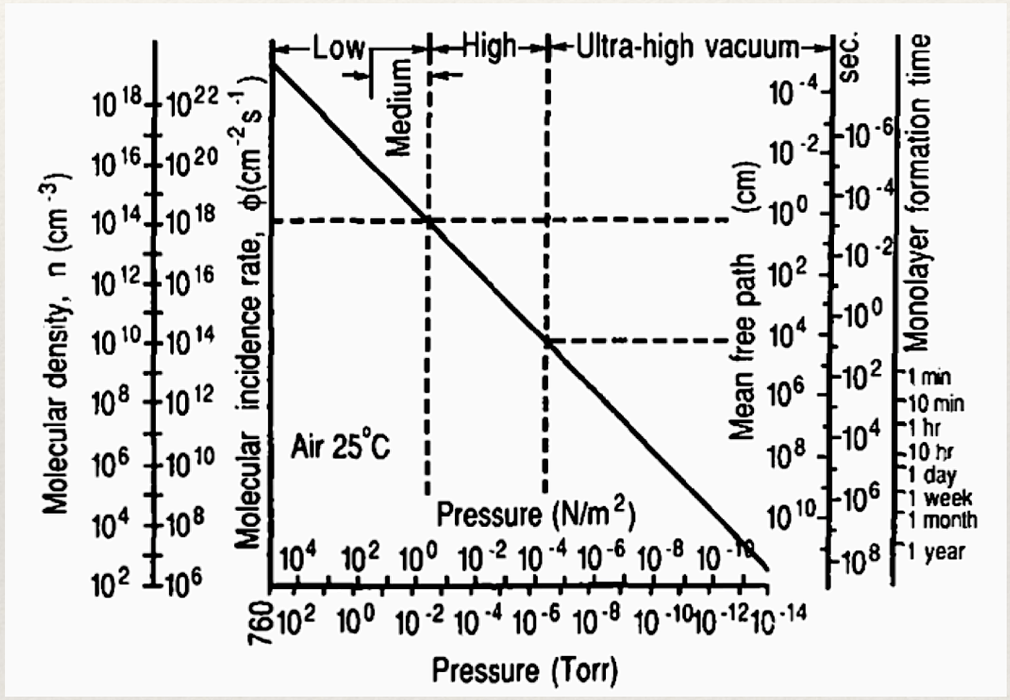
Monolayer formation under UHV



High vacuum
Monolayer formation
in ~seconds

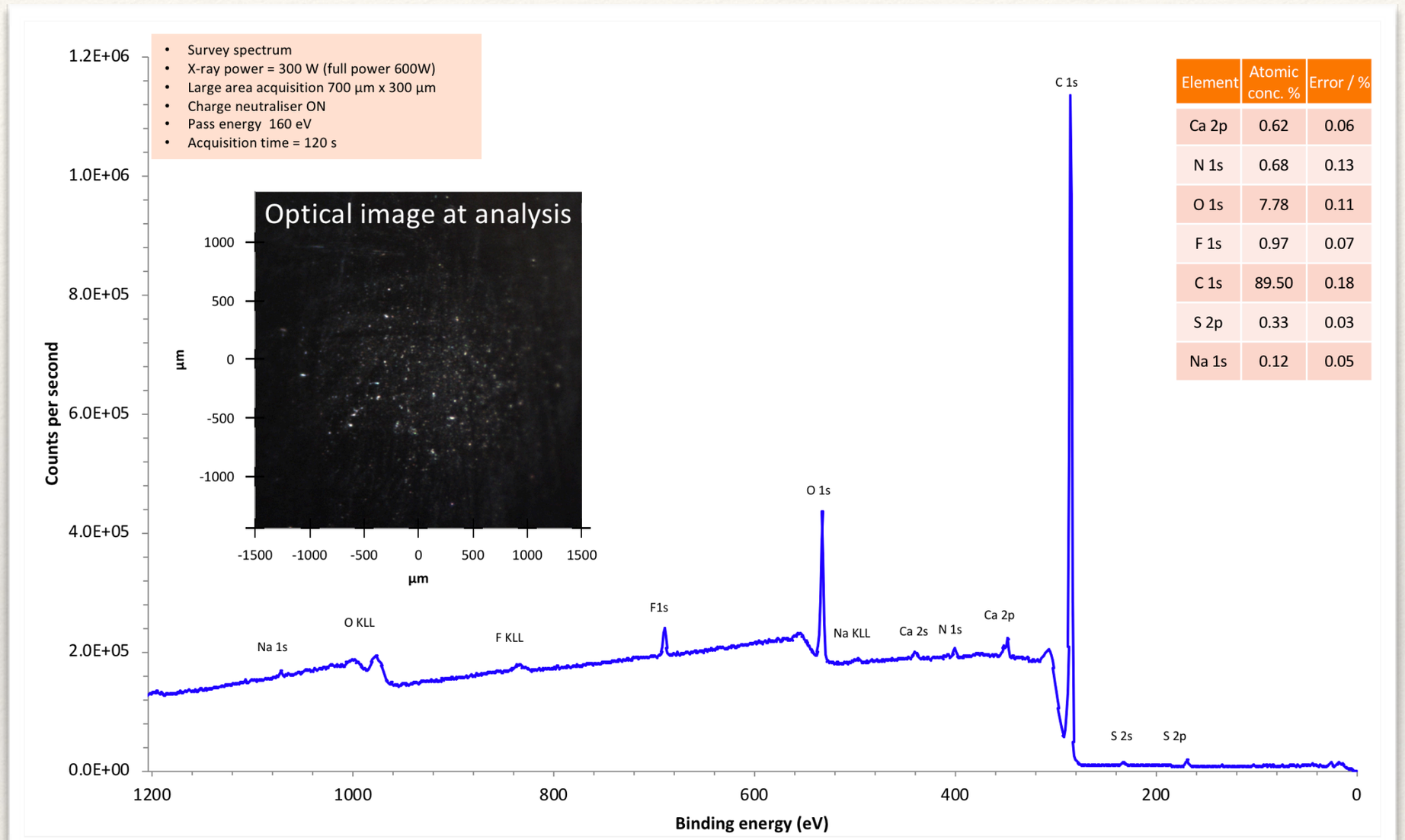
Ultra high vacuum
Monolayer formation
in ~days

Assuming that each molecule hitting the surface adsorbs (sticking coefficient of 1), then the monolayer is formed in seconds under HV and days under UHV Typical Clean metal surfaces have about 10^{15} atoms cm^{-2}.



Source: http://unix.eng.ua.edu/~zhuru/Oring.pdf

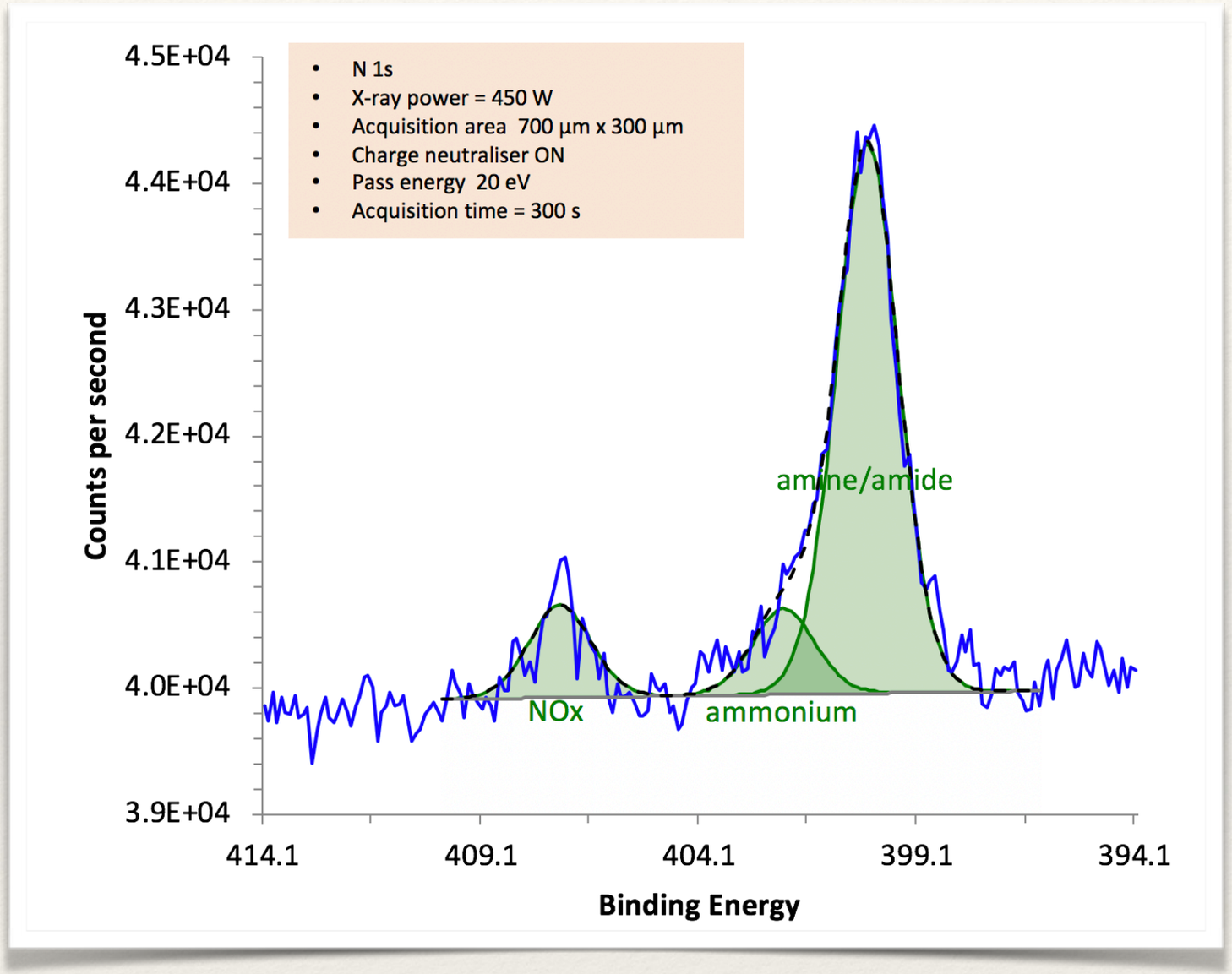
XPS Measurements: Survey



Element	Atomic conc. %	Error / %
Ca 2p	0.62	0.06
N 1s	0.68	0.13
O 1s	7.78	0.11
F 1s	0.97	0.07
C 1s	89.50	0.18
S 2p	0.33	0.03
Na 1s	0.12	0.05

A survey is a spectrum collected over the whole electron kinetic energy range of the instrument. It is then presented the binding energy scale (independant from the X-ray source energy). It allows qualitative evaluation of the surface most important properties as well as quantification

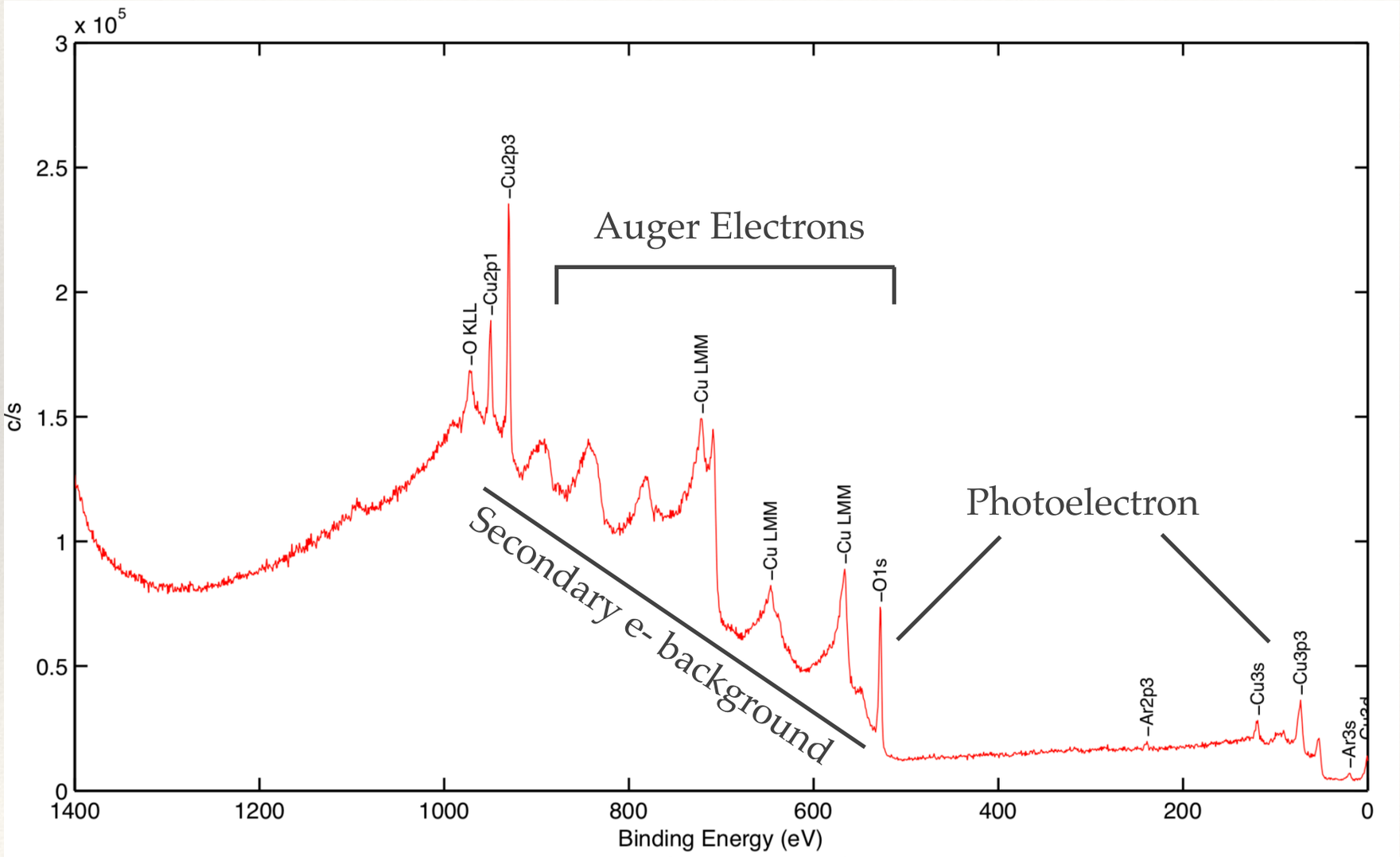
XPS Measurements: Multiplex



A multiplex is a detailed scan of a narrow region of the survey, typically focusing on photoelectron peaks or Auger lines. It allows chemical state identification and quantification

Components of an XPS spectrum

A survey is a spectrum collected over the whole electron kinetic energy range of the instrument. It is presented the binding energy (B.E.) scale, which is independant from the X-ray source energy, and with a reversed abscissa (B.E. increasing from right to left)



Sputter cleaned copper sample showing the presence from Cu, O, Ar

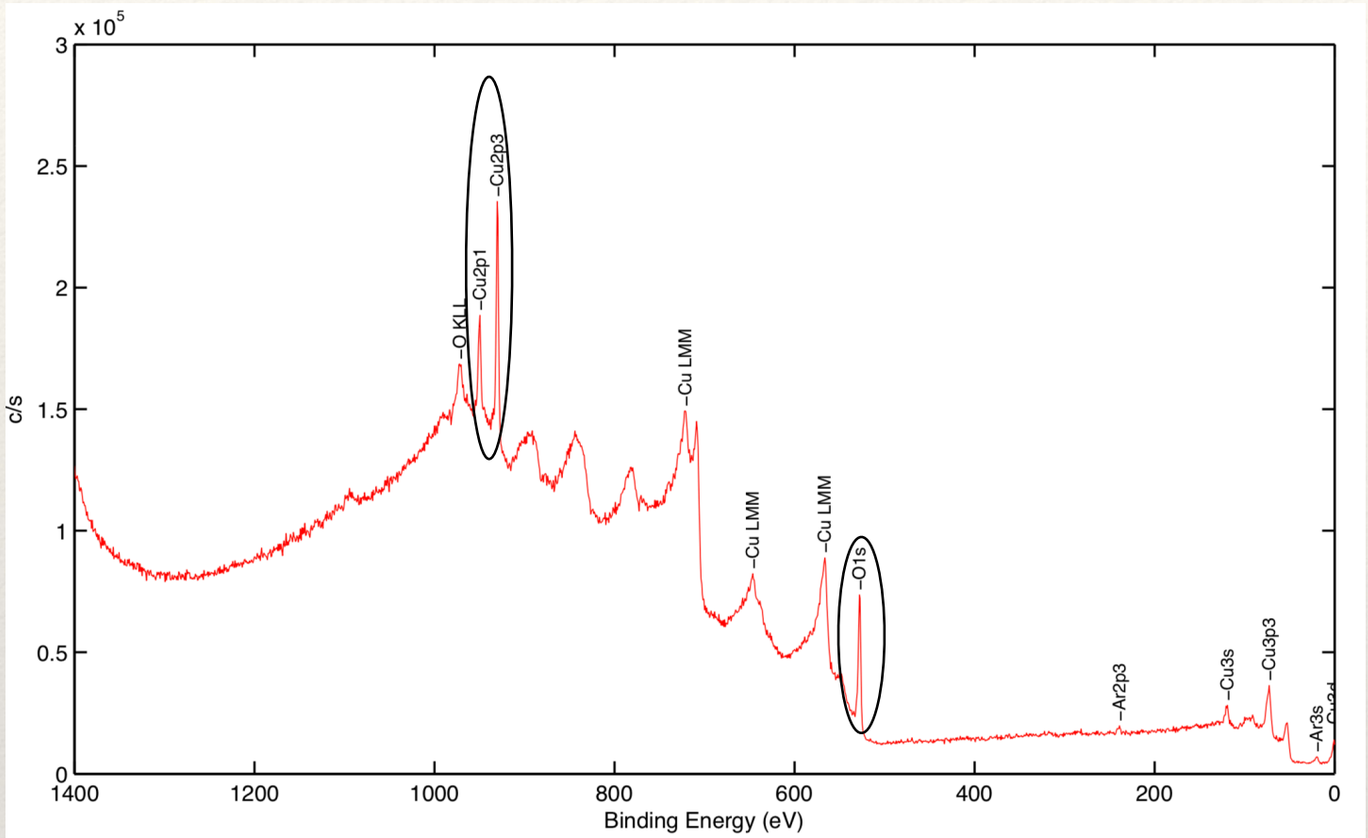
Main contributions

- Photoelectrons
- Auger electrons
- Secondary electrons

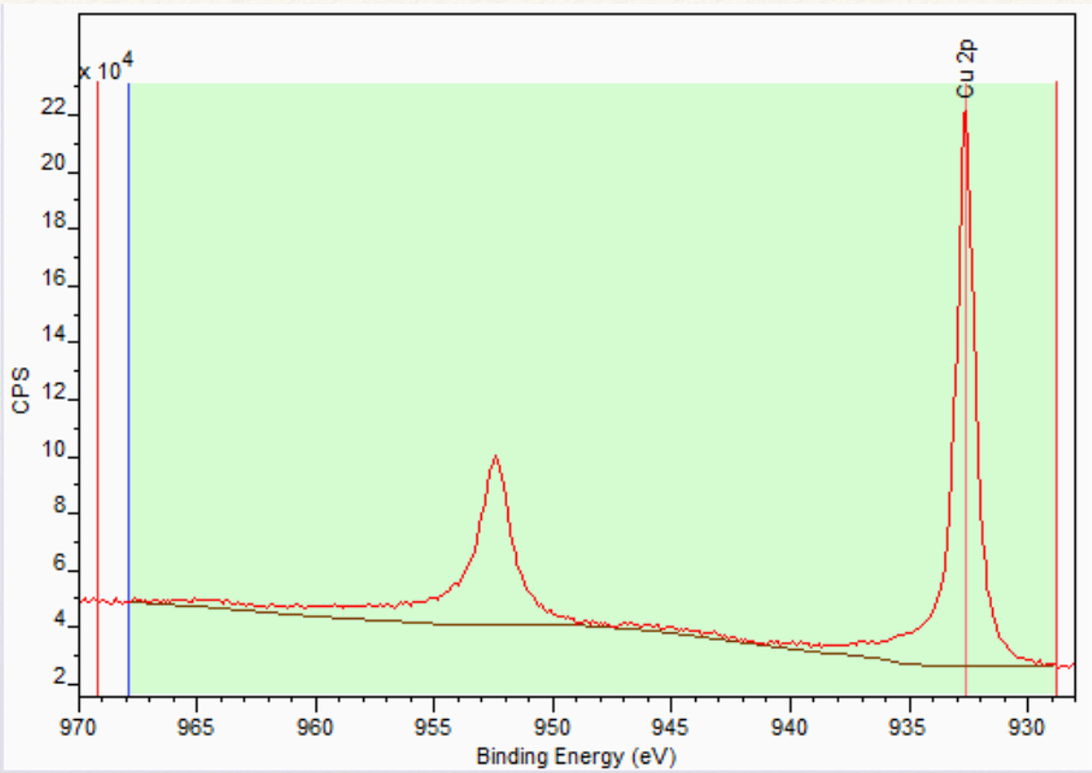
Secondary contributions

- Plasmons losses
- Ghosts
- Satellites

Photoelectron Components



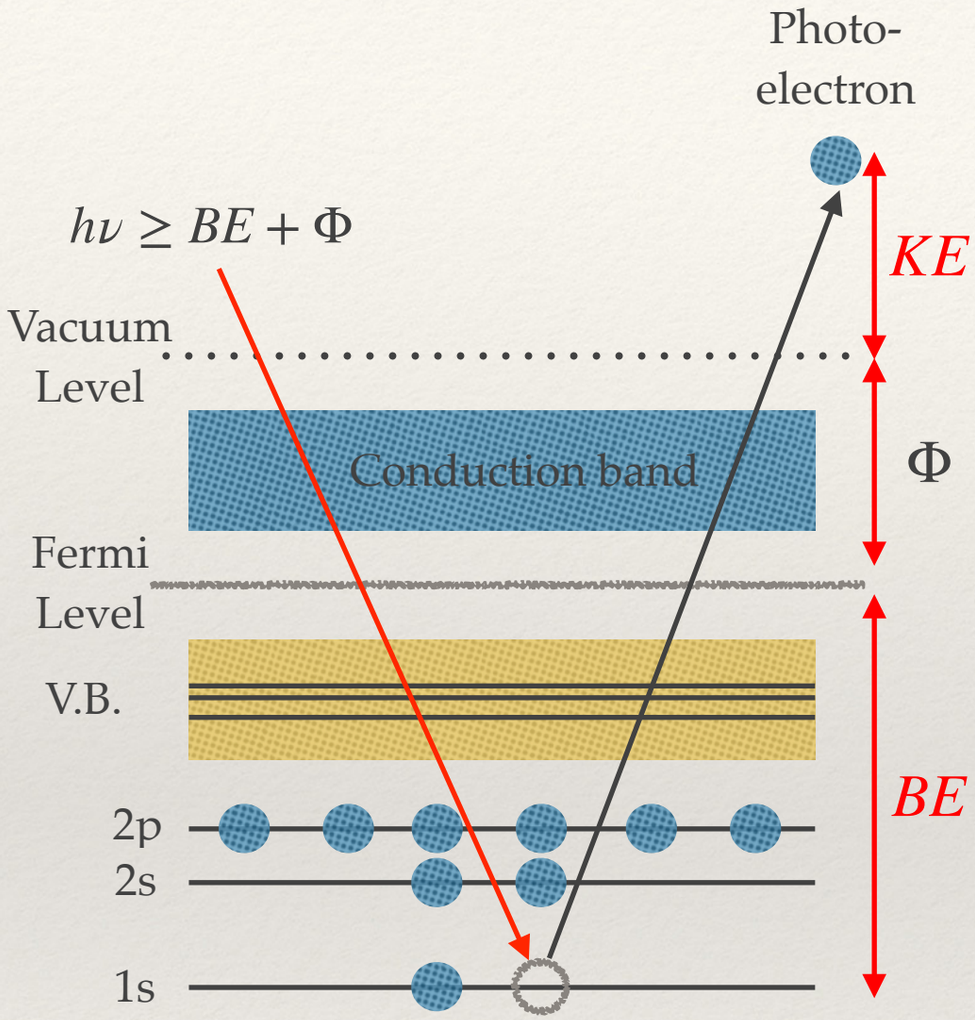
Copper sample showing several photoelectron transitions from Cu, O, Ar



Cu 2p orbital, exhibiting the typical narrow features of PE

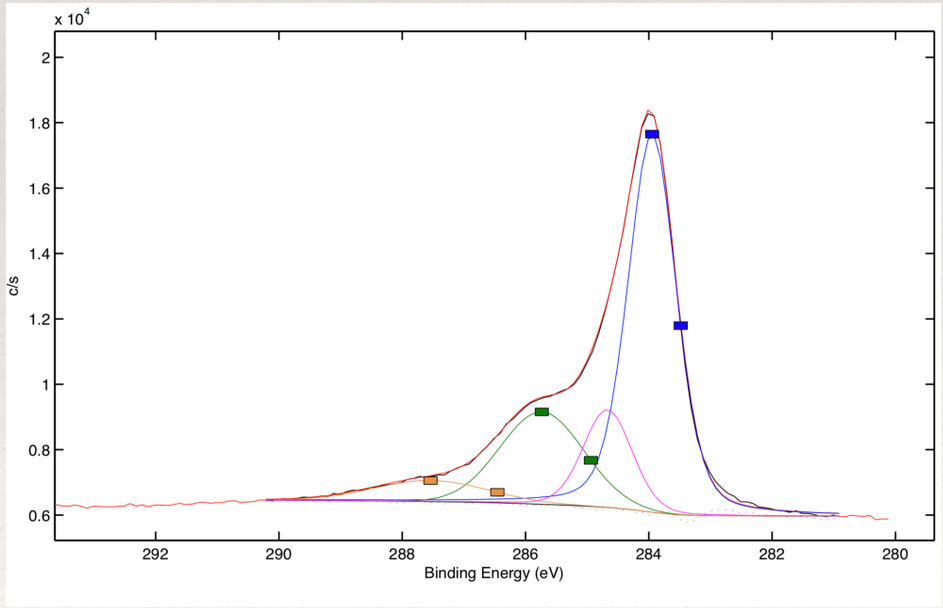
- Sharp peaks, uniquely defined for each atomic orbital
- Peak area allow to calculate the **'relative surface atomic concentration'**
- Sensitivity ~ part per thousand

Photoelectron emission (PEE)



Energy sketch of the photoelectric effect

- Creates sharp peaks in the spectrum, uniquely defined for each atom
- The kinetic energy of the photoelectron depends on the X-ray source, hence the choice of the binding energy scale



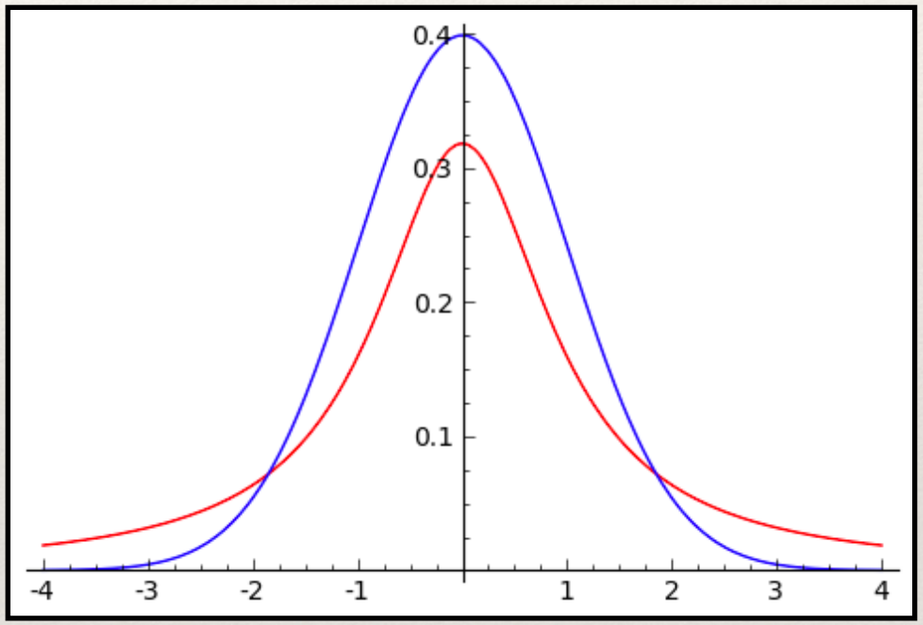
C1s of modified graphene. Courtesy LAS

Photoelectron Linewidth

- The intrinsic energy line width of photoelectrons depends on the lifetime of the core hole state
- From the Heisenberg uncertainty principle:

$$\Delta E \Delta T \geq \frac{\hbar}{4\pi} \Rightarrow \Gamma \geq \frac{2\hbar}{\tau}$$

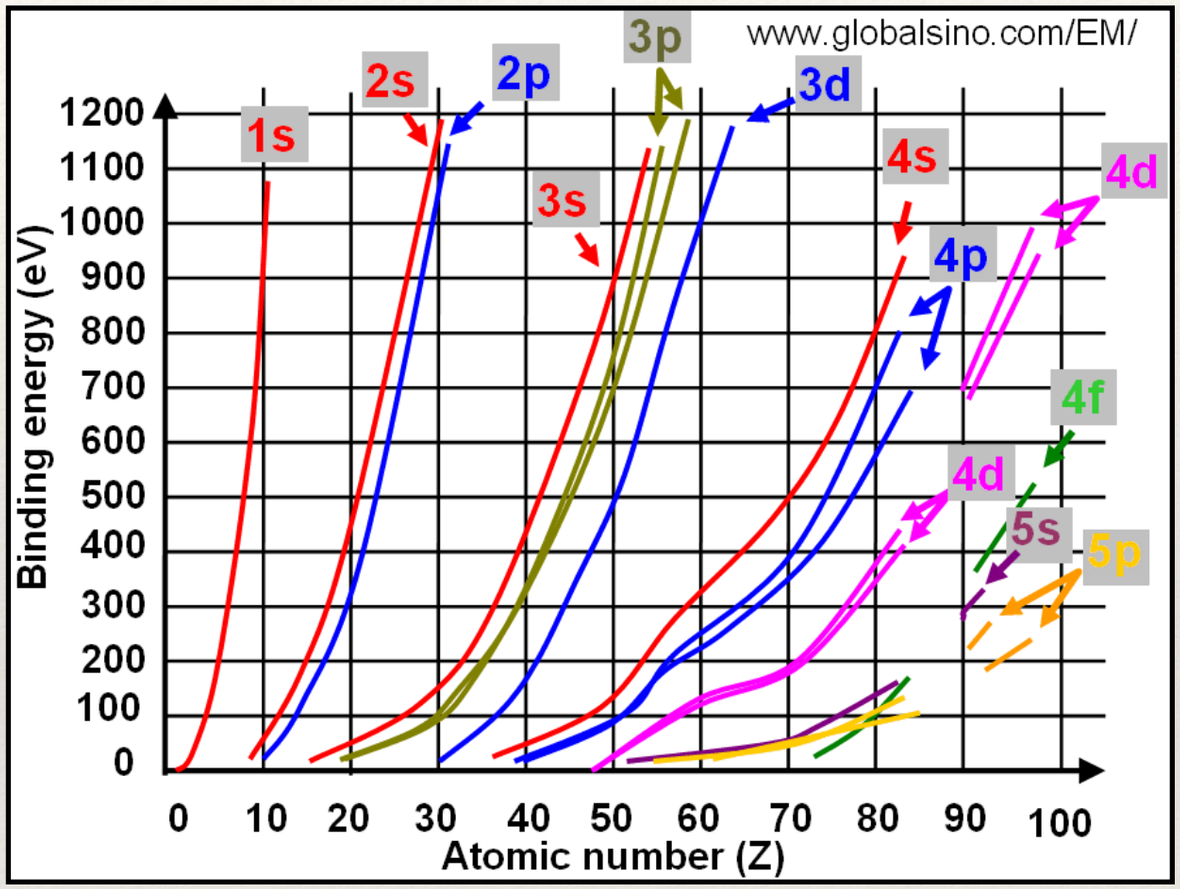
- Lorentzian line shape
- Broadening due to the multitude of decay channels
- Broadening due to phonon excitation (lattice vibrations)
- Inhomogenuous broadening due to chemical shift



Lorentzian (red), Gaussian (blue)

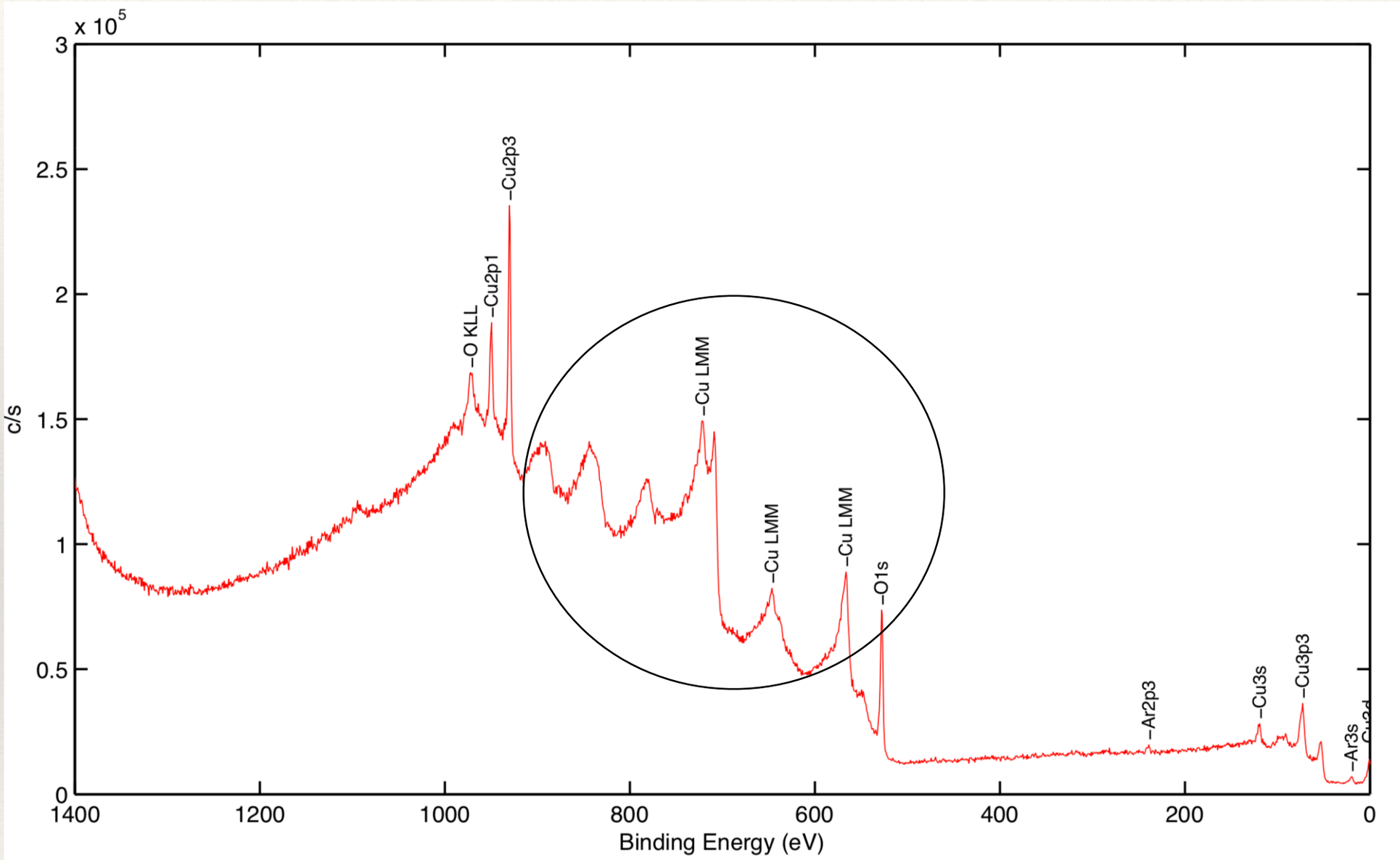
Binding Energy vs Z

- Due to Coulombic attraction between the nucleus and the electronic orbital, the BE increases with Z (for the same line of the periodic table)
- For the same reason the BE remains mostly unaffected by isotopes



Electron binding energy vs atomic number Z, for low binding energies

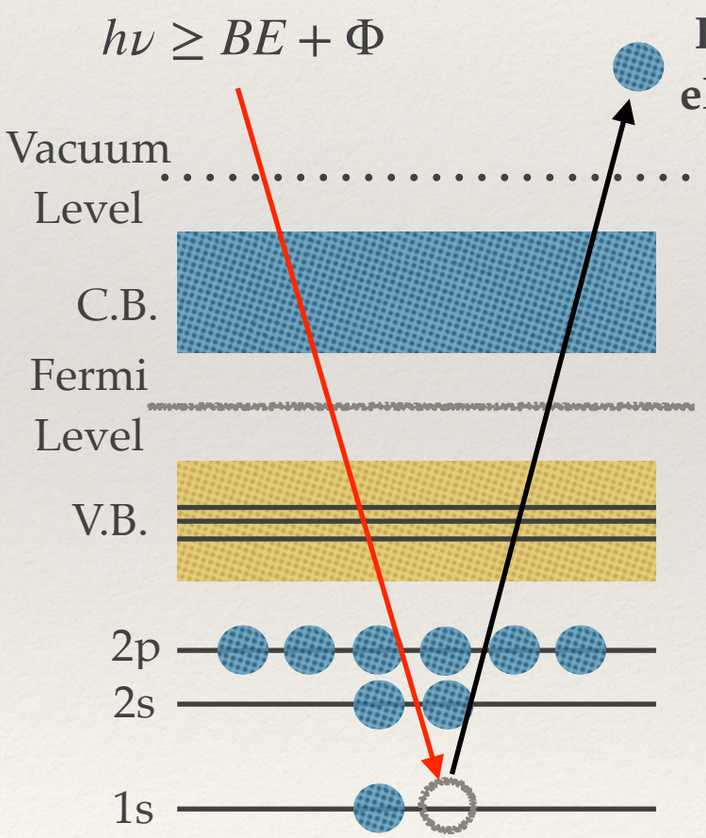
Auger Electrons Components



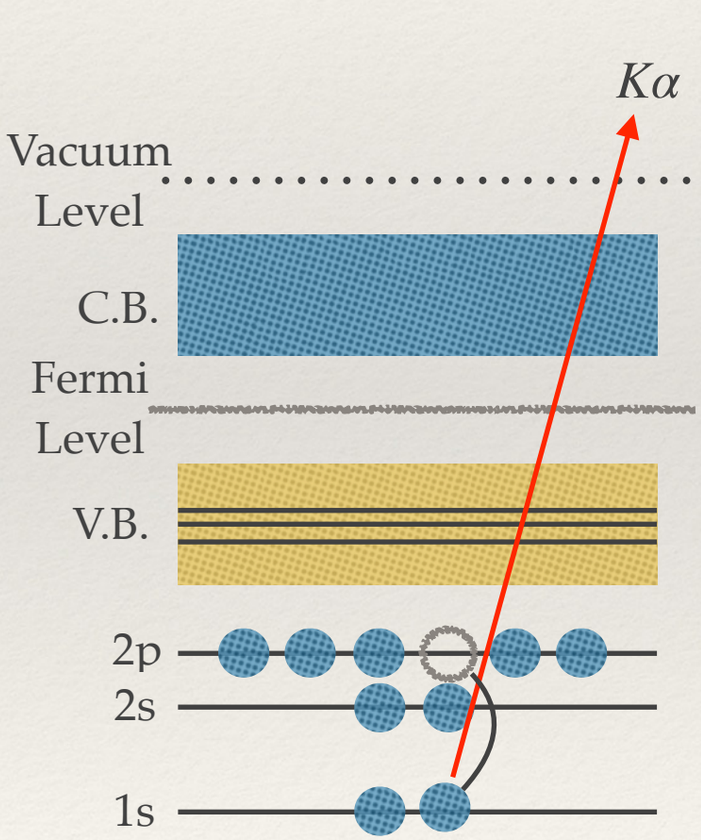
Copper sample showing several X-ray excited Auger transitions lines

Relaxation Paths

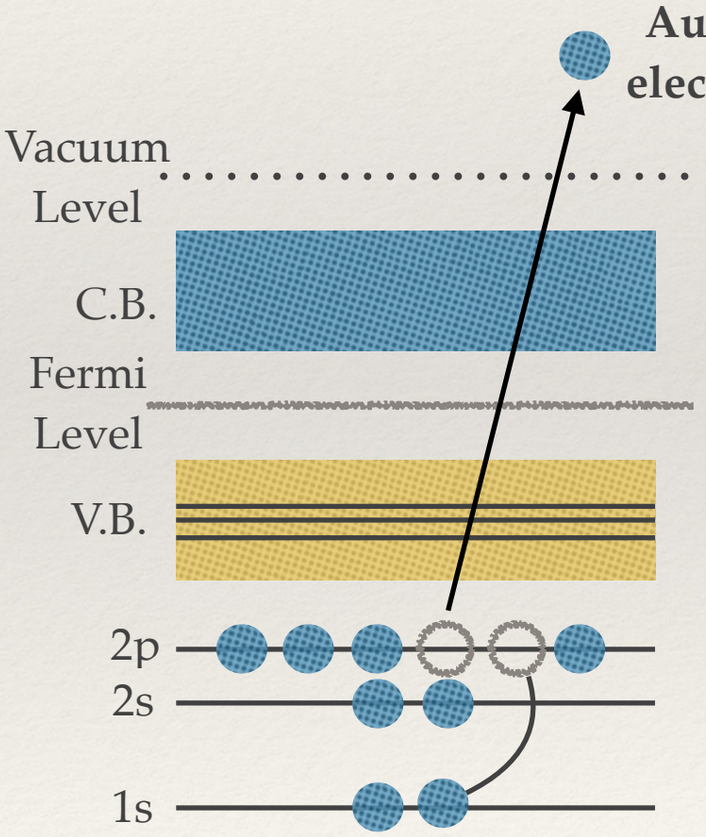
- X-ray induced Auger electron emission is a 3 electrons phenomenon. In a KLL transition:
  - A K level vacancy is created from the emission of a photoelectron (left)
  - An L level electron fills the K level vacancy
  - The released energy is transferred to the L level Auger electron: $E_K = E(K) - E(L_2) - E(L_1)$



Photoelectron Emission



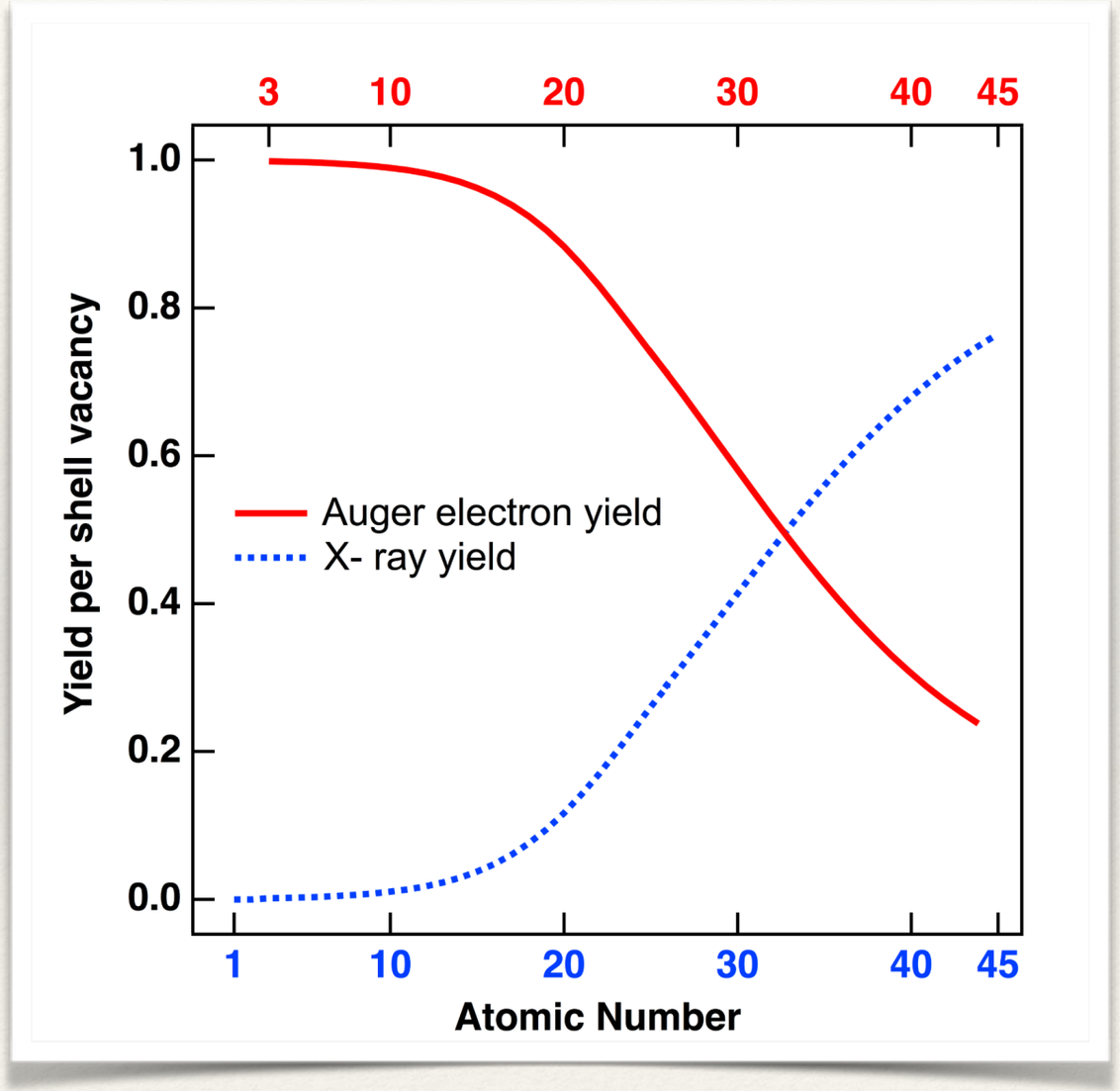
X-Ray relaxation



Auger Relaxation

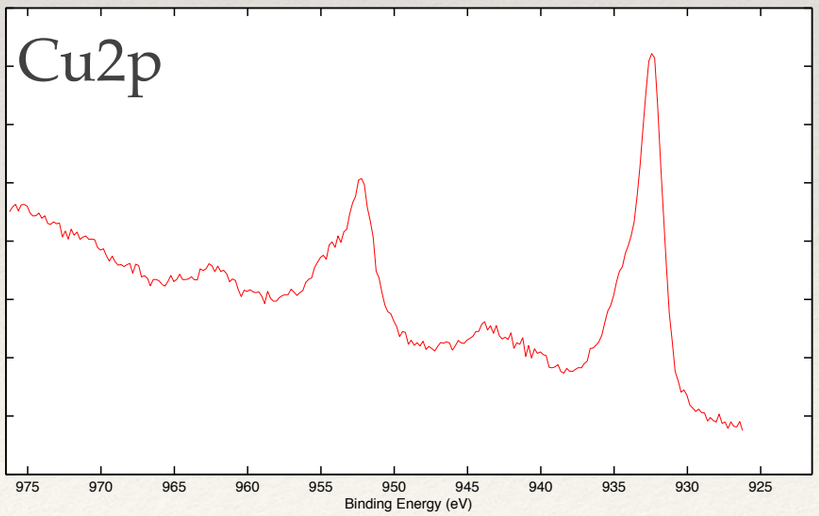
Auger/X-ray Relaxation Probability

- Auger and X-ray relaxation paths are competitive
- For low Z atoms, Auger dominates, while for high Z atoms, X-ray dominates
- Relaxation induced X-ray might generate photoelectrons, and therefore affect the photoelectron spectra by adding so-called ghosts lines

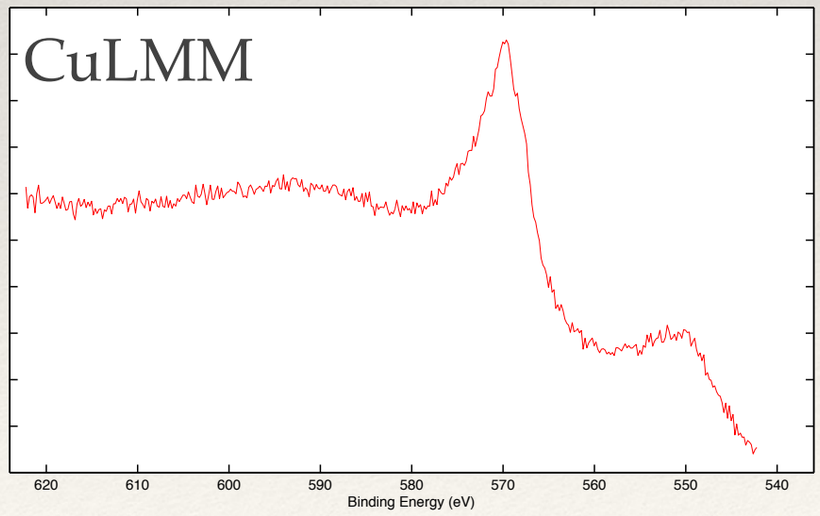


Photoelectrons vs Auger Electrons

- Photoelectron lines depend on the energy of the X-ray source energy: BE independent from source energy
- Auger electrons lines are independent of the energy of the X-ray source: KE independent from source energy
- Therefore, represented on the binding energy scale, photoelectron line position are independent of the source, while Auger line position depend on the source. Changing the source changes the Auger vs photoelectron line relationship!

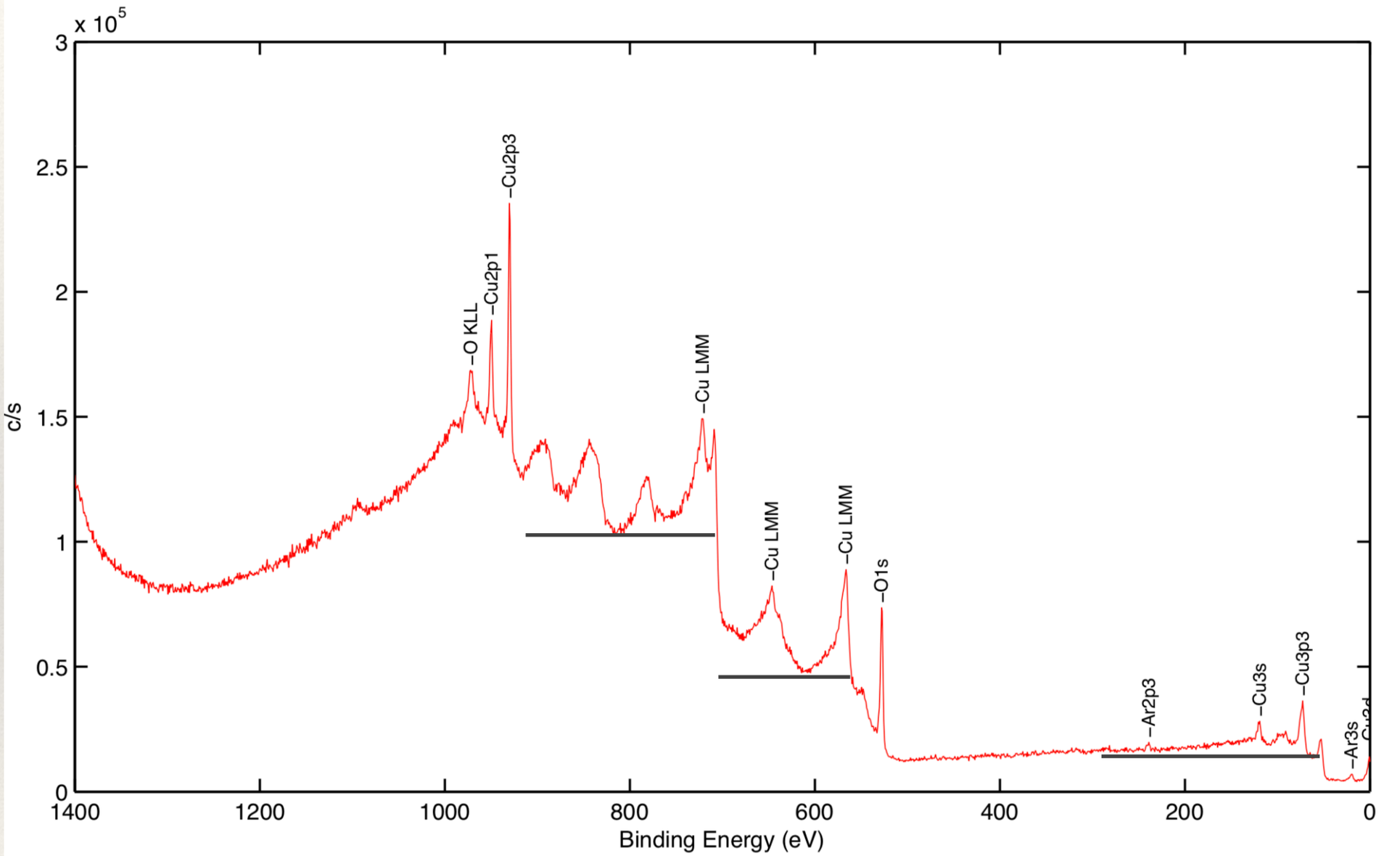


Narrow line feature of PE



Broad line of Auger electrons

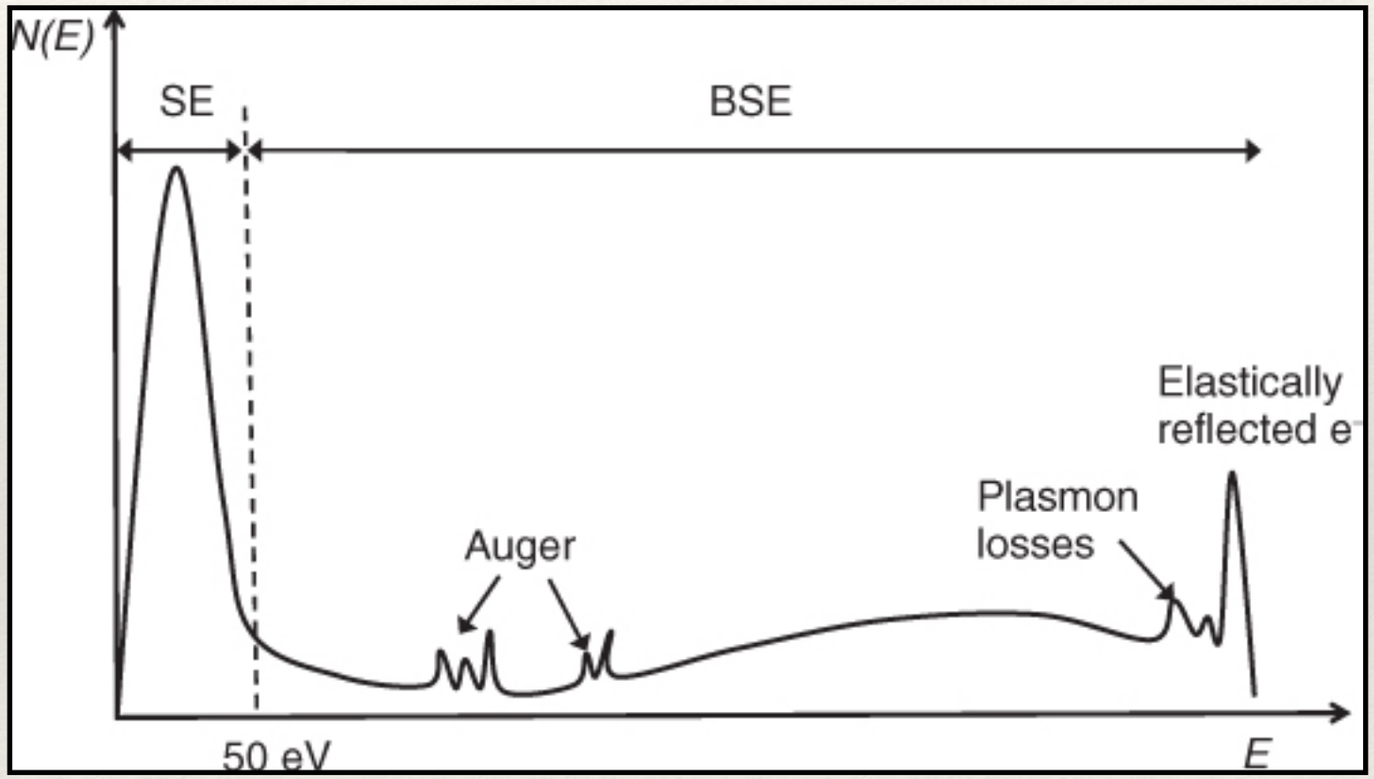
Background from Secondary Electrons



Copper sample showing a pronounced secondary electron background

Secondary Electron Emission

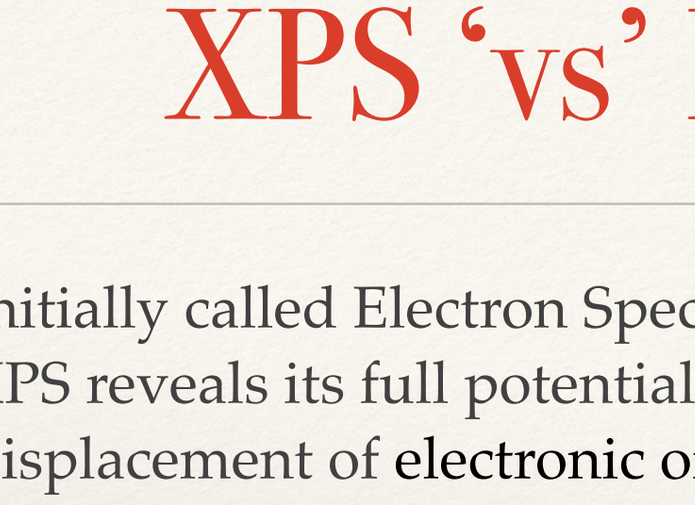
- Most materials undergo a large secondary electron emission yield: SEY>2, i.e. for 1 impinging electron, 2 are emitted
- Energy of 'true' secondary electrons is below 50eV
- Secondary electron form the dominant background in XPS measurement.



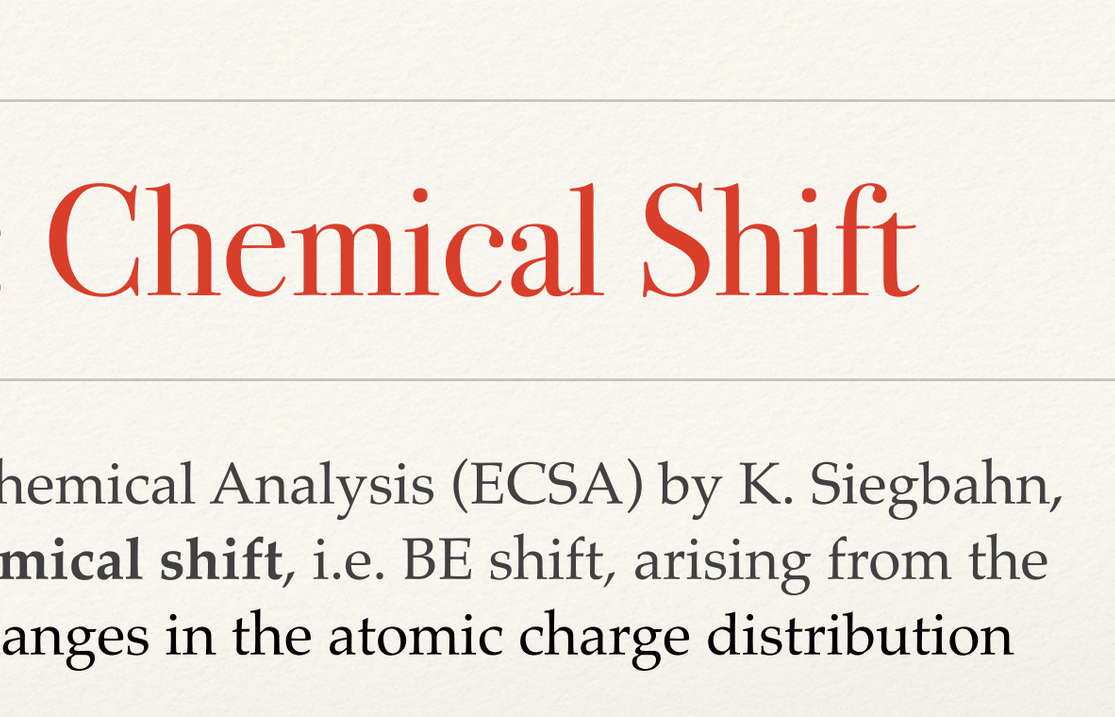
Secondary electron emission energy spectrum

XPS ‘vs’ ESCA: Chemical Shift

- Initially called Electron Spectroscopy for Chemical Analysis (ECSA) by K. Siegbahn, XPS reveals its full potential due to the **chemical shift**, i.e. BE shift, arising from the displacement of electronic orbitals upon changes in the atomic charge distribution
- K. Siegbahn showed that the chemical shift is a linear function of the net charge transfert in chemical bounding



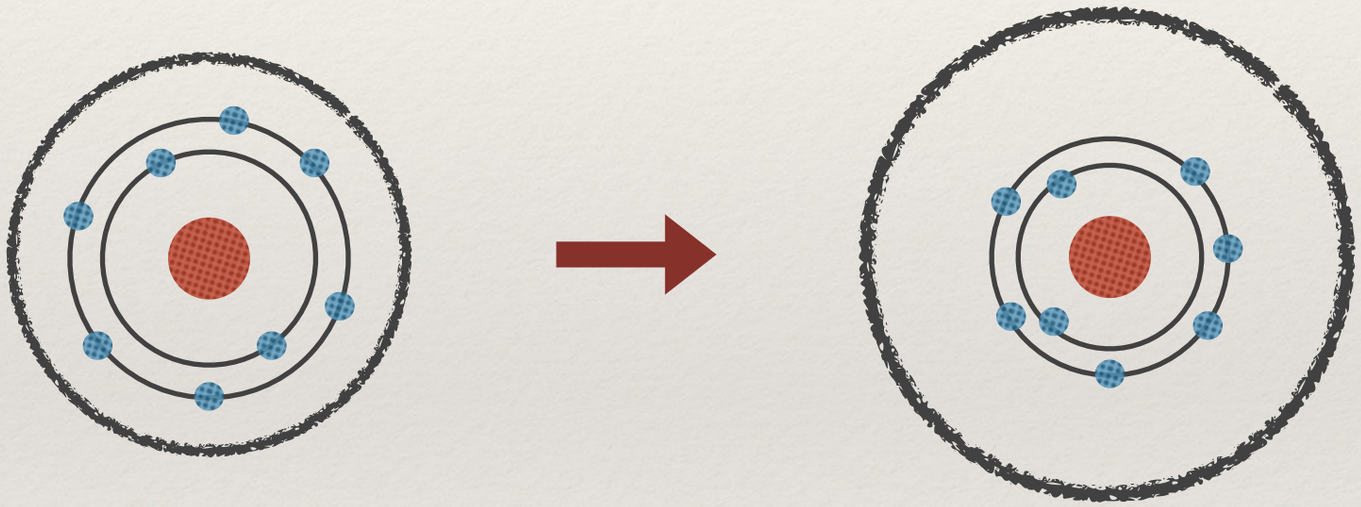
Atomic viewpoint



Energy viewpoint

Binding Energy vs Electronegativity

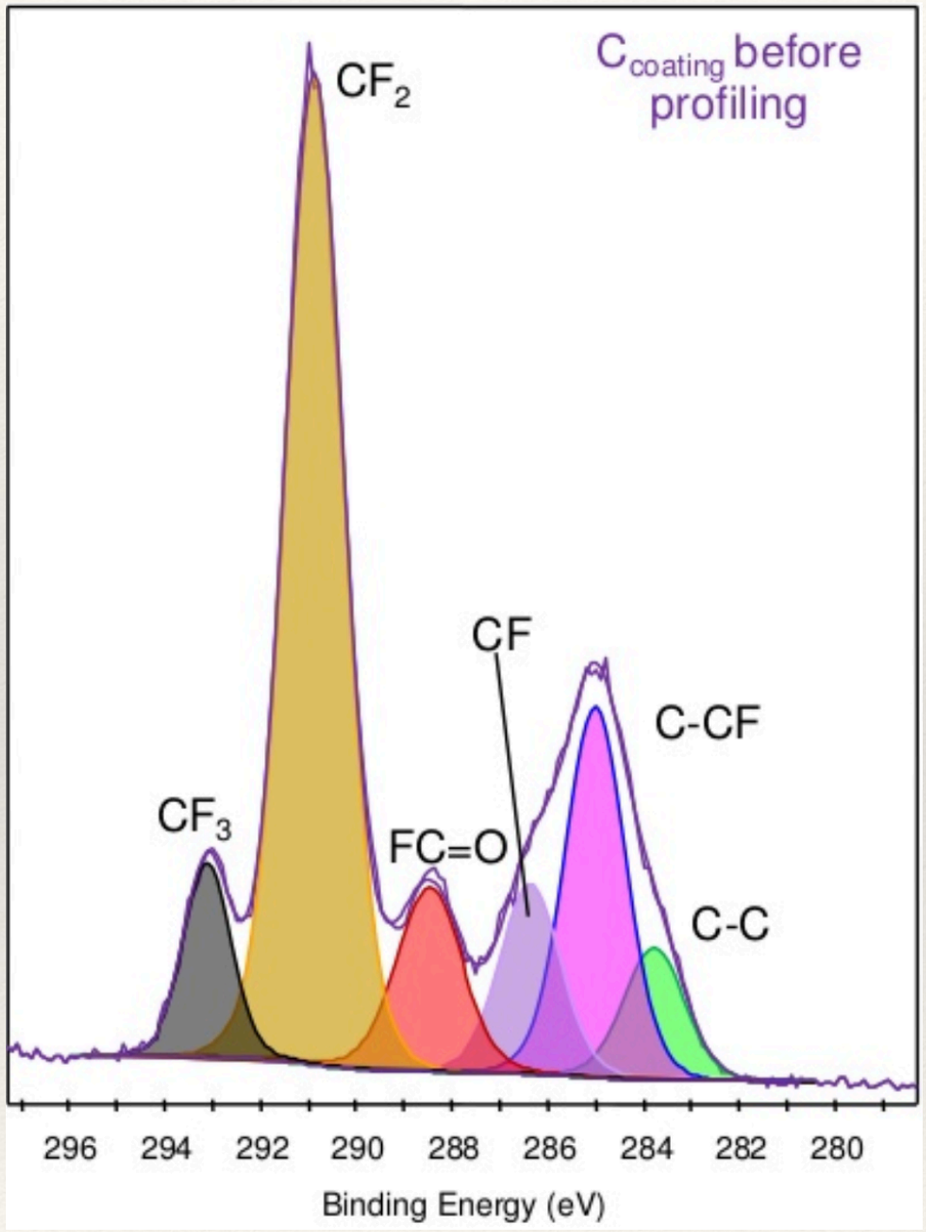
- When a covalent bond is created, electron density is increased at the more electronegative partner.
- The average radius of the valence band of the ‘donor partner’ increases
- Due to a decrease in the valence electrons screening, the core electrons are shifted towards the nucleus, and therefore increasing their binding energy, hence the ‘chemical shift’

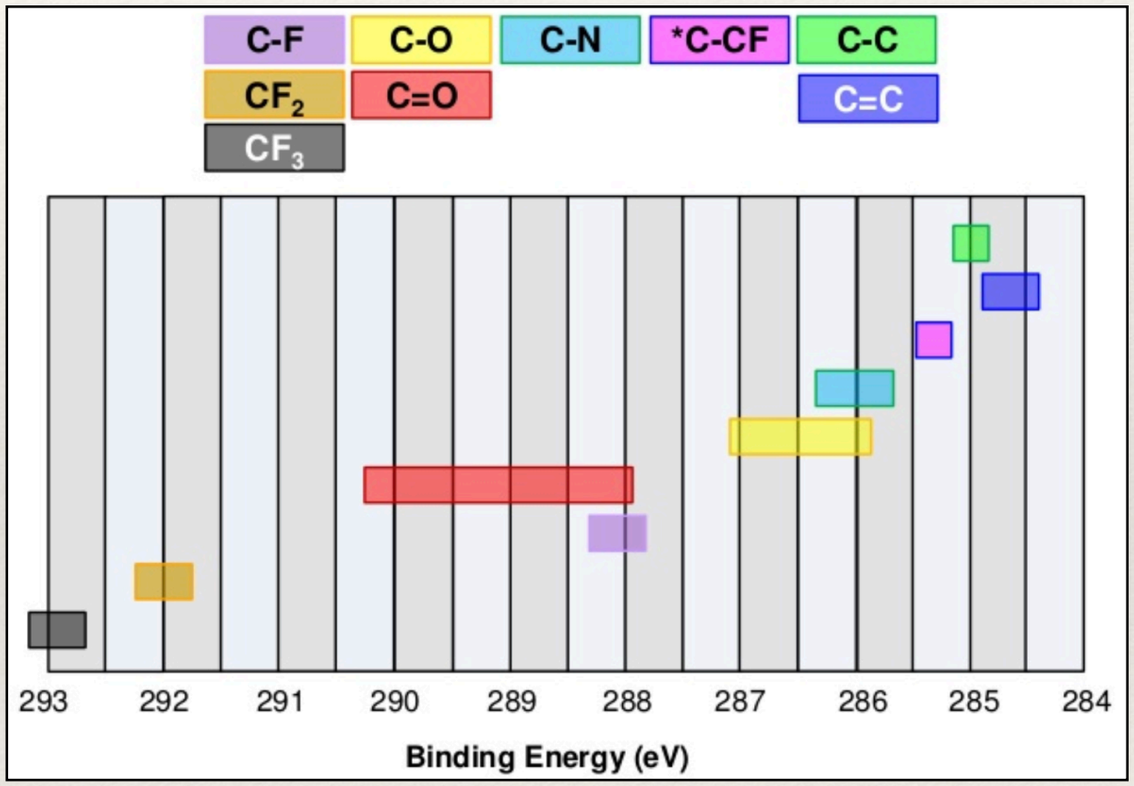


Group		BE eV
hydrocarbon	C-H, C-C	284-285
Amine	C-N	285.6
Alcool	C-O-H, C-O-C	286.5
Cl bound	C-Cl	287.0
F bound	C-F	287.8
Carbonyl	C=O	288.0

Electronegativity

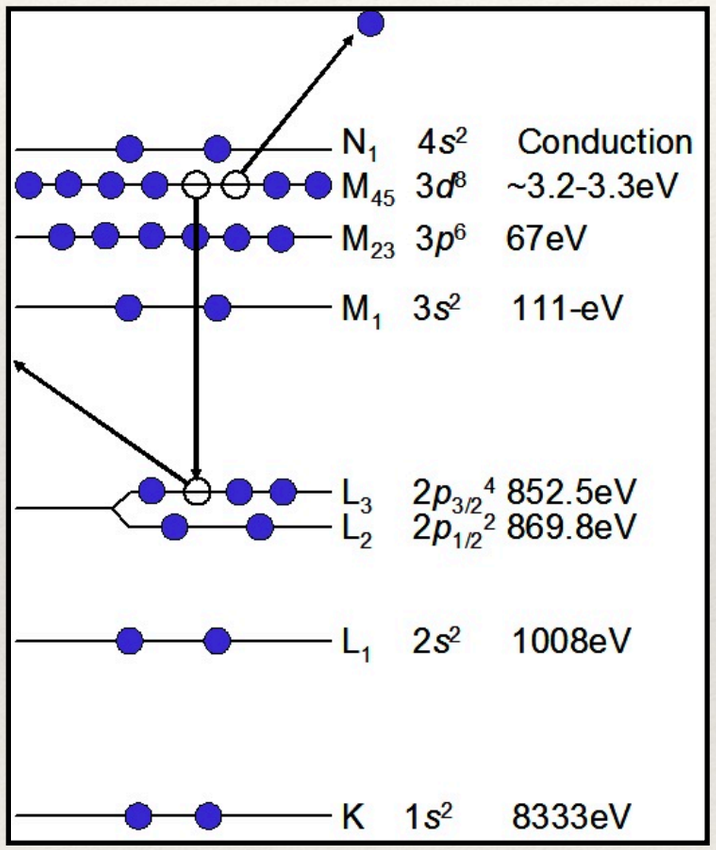
Fluoropolymer C1s line





Source: Thermo-Fisher database

Exercice



Electronic structure of Ni
Source: CasaXPS

Assuming an Al Ka X-ray source (E = 1486.6 eV) and knowing the electronic structure of Ni, sketch its XPS binding energy spectrum *

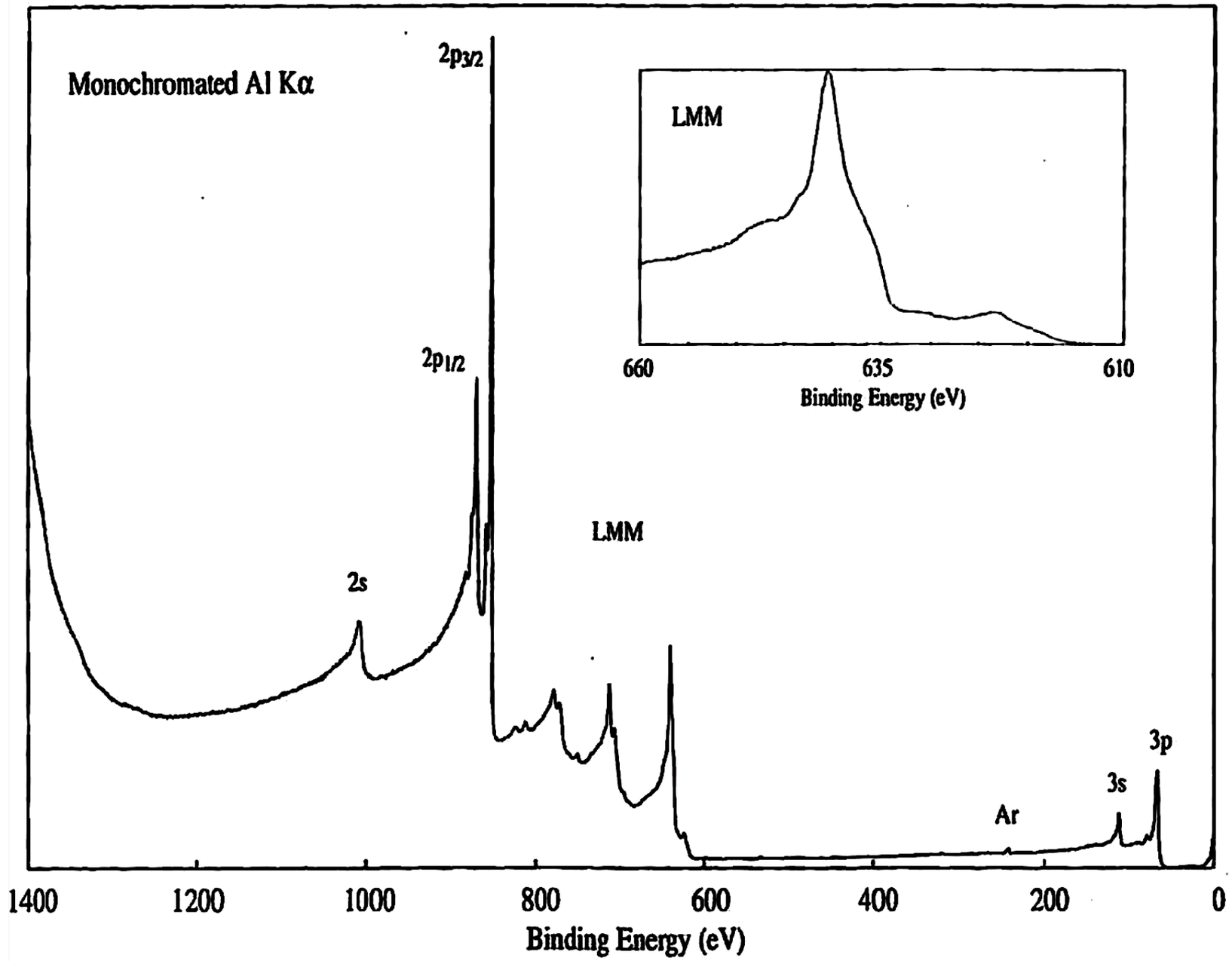
Start with photoelectron lines 2s, 2p, 3s, 3p

- Add the Auger transitions: $L_3M_{23}M_{45}$, $L_2M_{23}M_{45}$, $L_3M_{23}M_{23}$
- Add the secondary electrons background

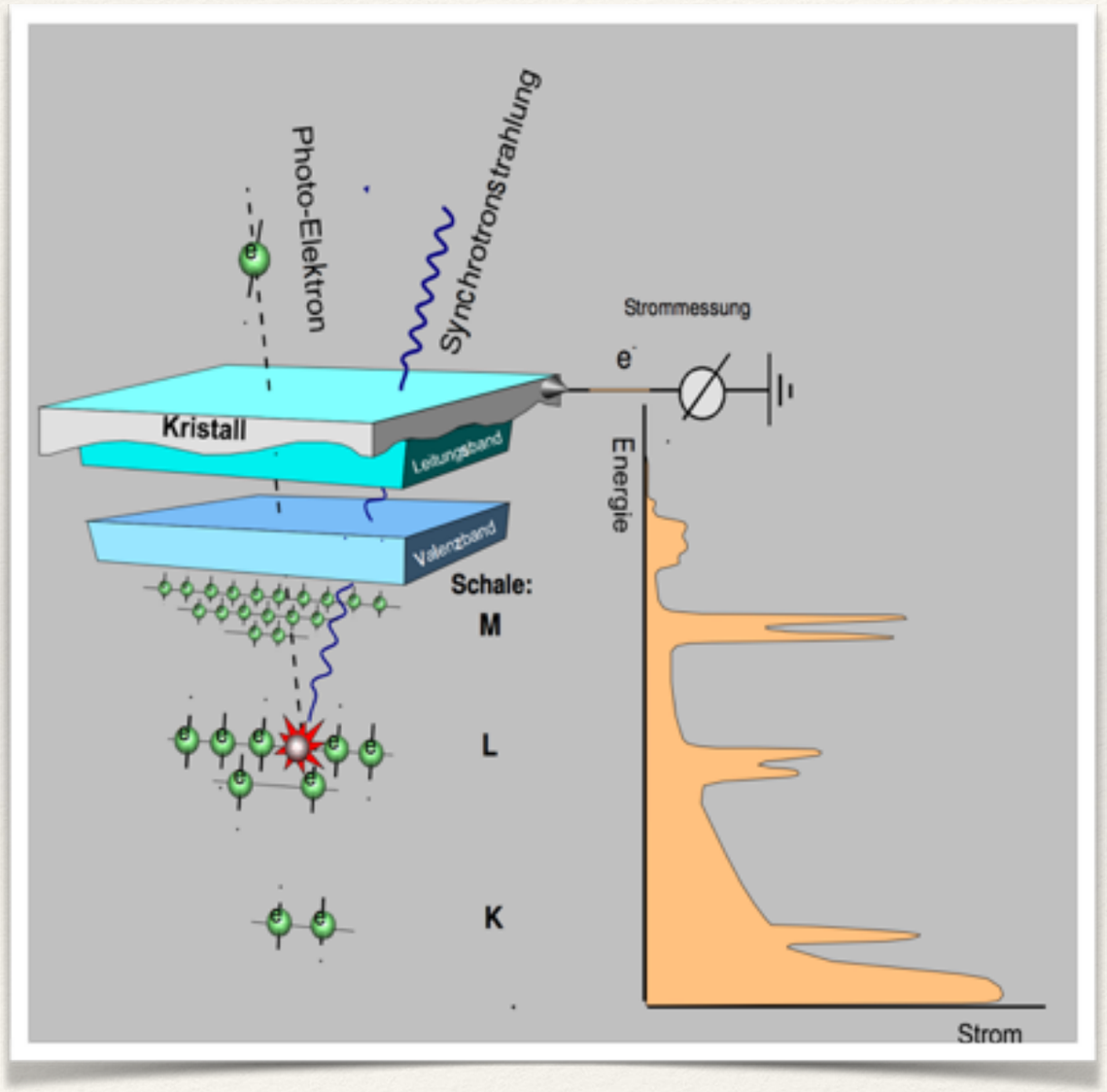
* Reminder: $E_B = h\nu - E_k - \Phi_{spec}$

And neglect the work function (~4.5eV) of the spectrometer

Al Ka XPS Spectrum of Nickel



Conclusion



XPS provides qualitative and quantitative (next course) information regarding the so called surface atomic composition of materials with a probing depth of ~1-5nm and a detection limit in ~ppt.

- Chemical state can be evaluated due to chemical shifts in the BE
- Electronic structure of materials can be retrieved from XPS spectrum and *vice versa*

Thank you!

- **Next course**:
  - Features of photoelectron peaks
  - XPS quantification
  - Depth profiling
  - Angle resolved XPS
  - Study case on surface contamination
- **References**
  - Briggs et al., *Handbook of X-ray and ultraviolet photoelectron spectroscopy*, Wiley, 1977
  - Briggs et al. *Practical surface analysis*, Wiley, 1990
  - Thermo-Fisher XPS webpage:

    https://xpssimplified.com/whatisxps.php