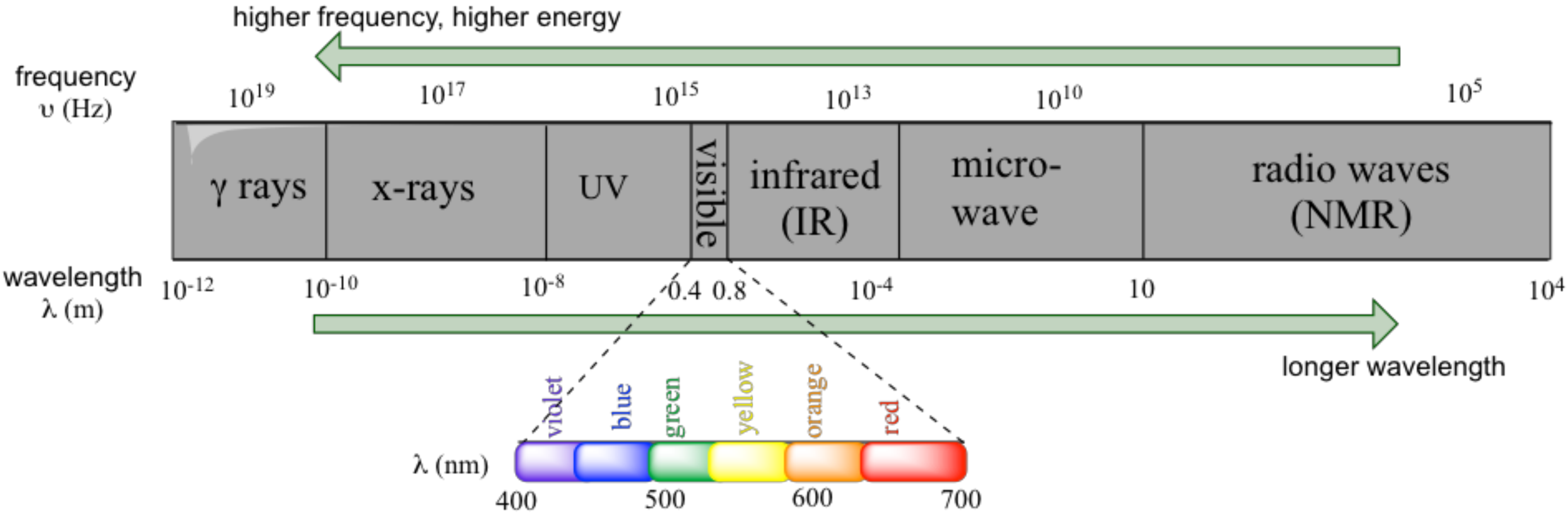
CHPC2

PhD Coursework in Chemistry -Sem I

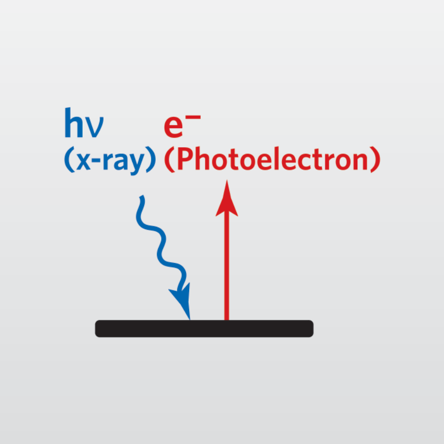
Techniques for Structural Characterization and Material Characterization

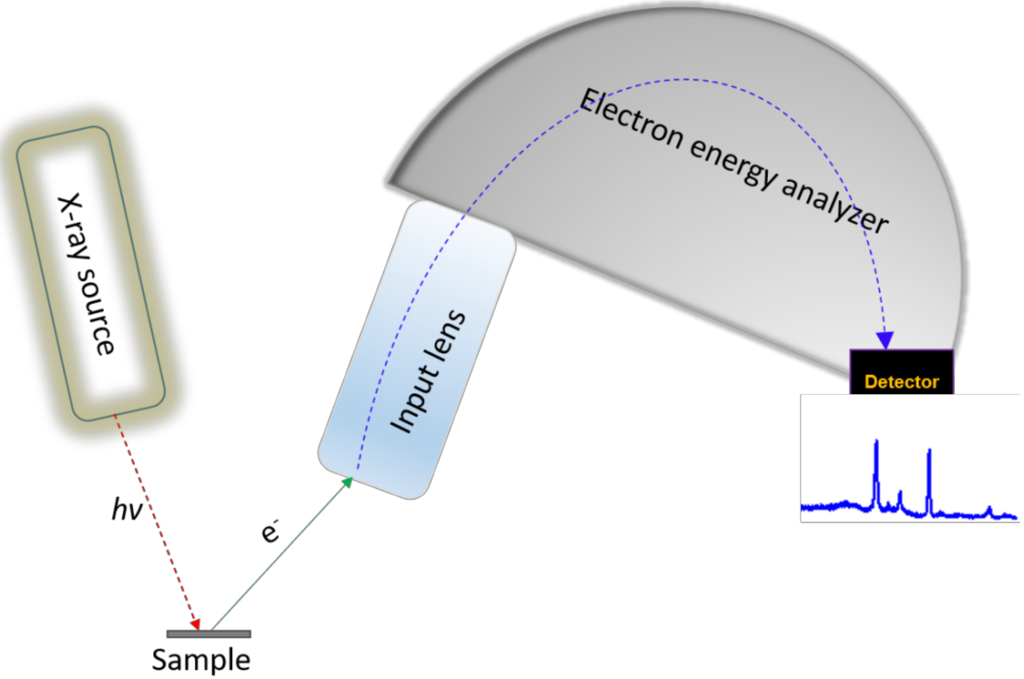
Kanak Roy
kanak.roy@bhu.ac.in

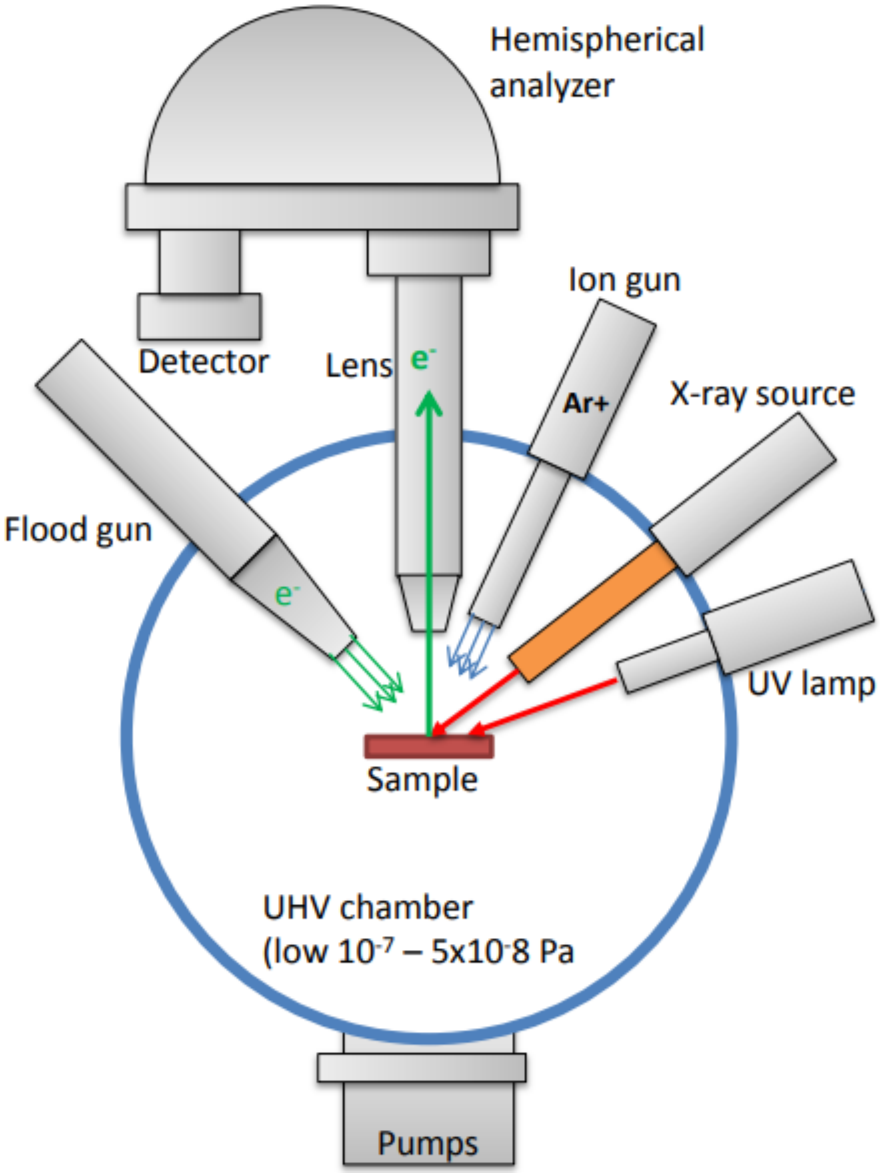
Electromagnetic Radiation



X-ray Photoelectron Spectroscopy (XPS)
UV Photoelectron Spectroscopy (UPS)

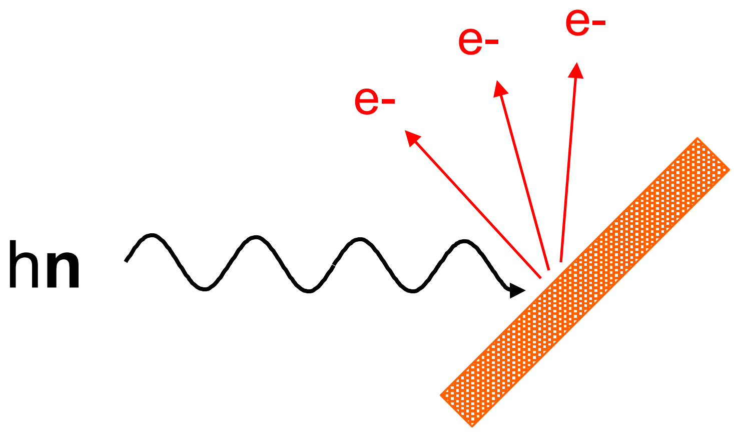


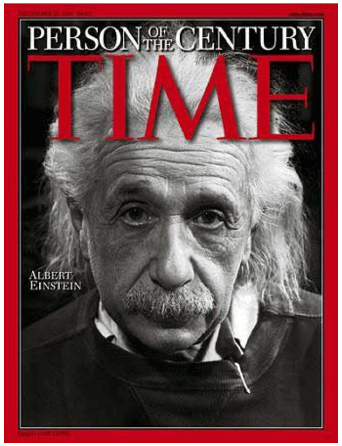



Hemispherical analyzer
Ion gun
Detector
Lens
e$^-$
Ar+
X-ray source
Flood gun
e$^-$
UV lamp
Sample
UHV chamber
(low 10^{-7} – 5x10^{-8} Pa
Pumps

Photoelectric Effect

Ionization occurs when matter interacts with light of sufficient energy (Heinrich Hertz, 1886)
(Einstein, A. Ann. Phys. Leipzig 1905, 17, 132-148.)



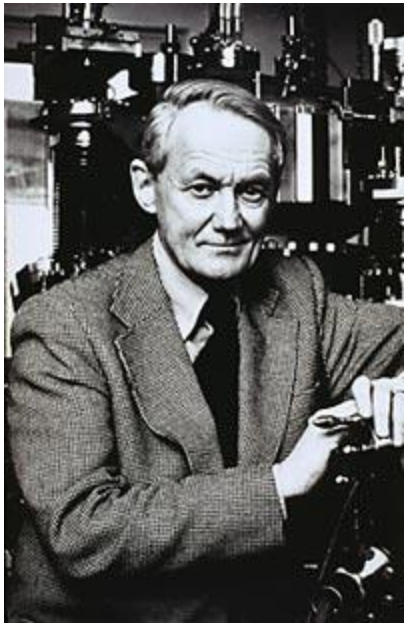


E_{hn} = electron kinetic energy + electron binding energy

Photoelectron spectroscopy uses this phenomenon to study the electronic structure of matter

Kai Seigbahn: Development of X-ray Photoelectron Spectroscopy

C. Nordling E. Sokolowski and K. Siegbahn, *Phys. Rev.* **1957**, *105*, 1676.



Precision Method for Obtaining Absolute Values of Atomic Binding Energies

Carl Nordling, Evelyn Sokolowski, and Kai Siegbahn

Department of Physics, University of Uppsala, Uppsala, Sweden

(Received January 10, 1957)

We have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method

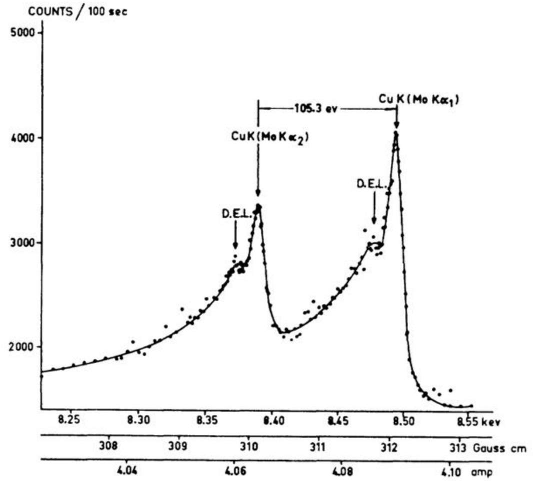
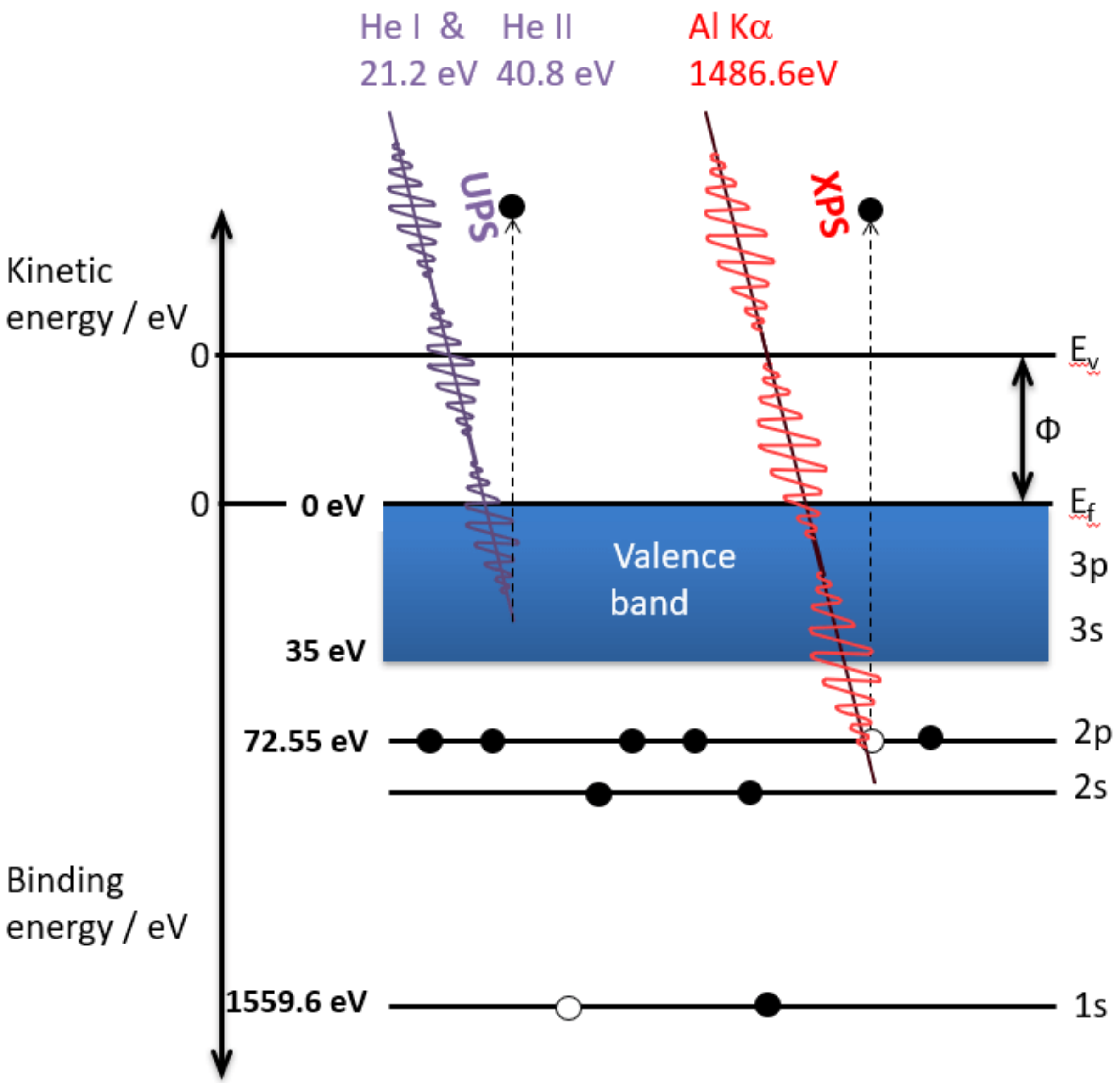


Fig. 1. Lines resulting from photoelectrons expelled from Cu by Mo $K\alpha_1$ and Mo $K\alpha_2$ x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

Nobel Prize in Physics 1981
(His father, Manne Siegbahn, won the Nobel Prize in Physics in 1924 for the development of X-ray spectroscopy)

ESCA **(Electron Spectroscopy for Chemical Analysis)**


He I & He II
21.2 eV 40.8 eV
Al Kα
1486.6eV
UPS
XPS
Kinetic energy / eV
0
0
0 eV
Φ
E_v
E_f
Valence band
3p
3s
35 eV
72.55 eV
2p
2s
Binding energy / eV
1559.6 eV
1s

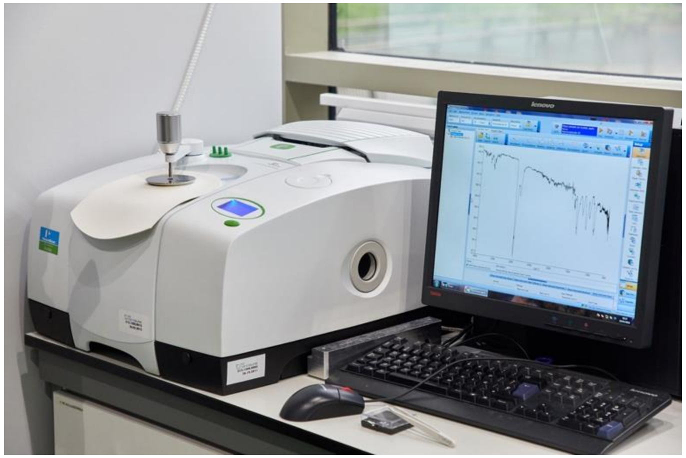
Photoelectron Spectroscopy

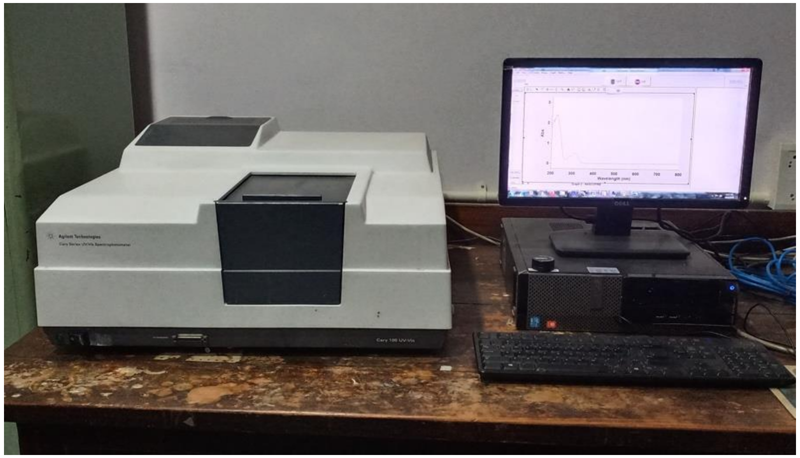
UHV

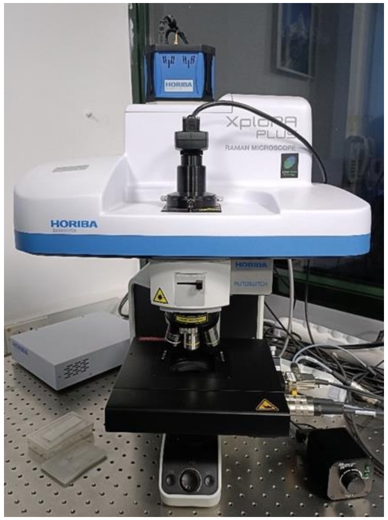
It is traditionally a high vacuum instrument (to prevent attenuation of photoelectrons).

Typically, XPS instruments operate at a pressure of around 10^{-9} mbar.

Molecular Spectroscopy



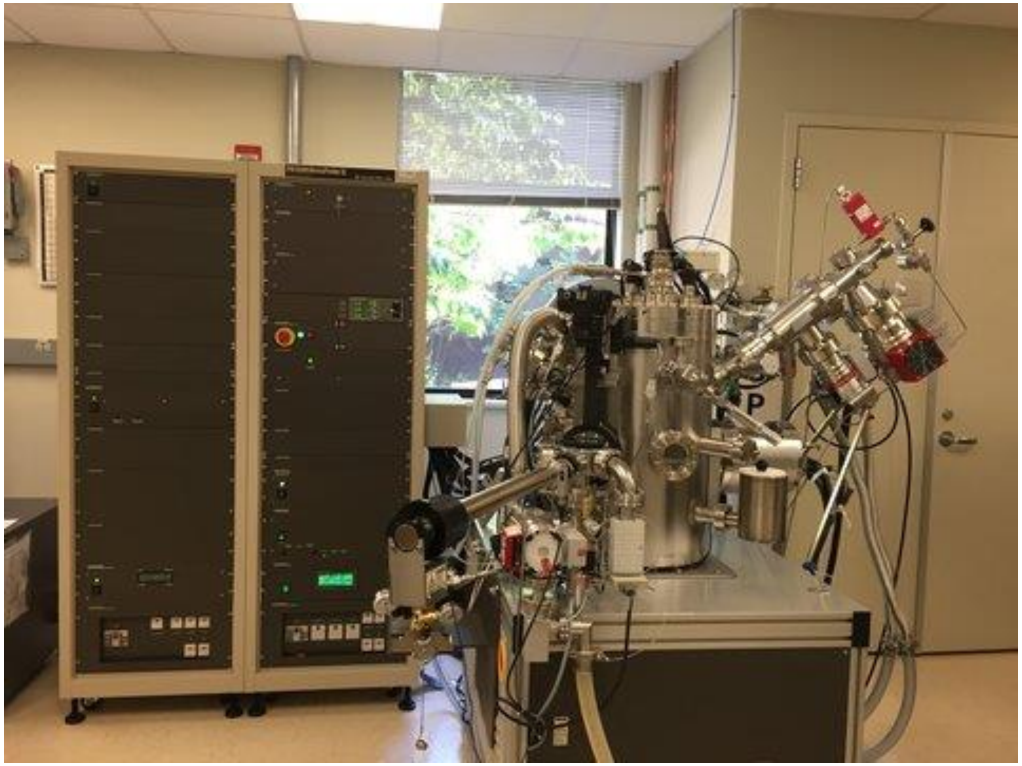




Have you wondered, why IR, UV-Vis, Raman spectrometers are compact in size and relatively low in cost compared to XPS/UPS?

Costs few lakhs to less than a crore.

Photoelectron Spectrometer



Costs 4-6 crores, larger in size.

Historical Timeline

1850s

First spectrophotometer

1880s

First IR

1912

First crystallography

1938

First NMR

1944

First EPR

1957

First PES

What took so long?

- Development of electron kinetic energy analyzers with sufficient resolution to be useful.
- Development of suitable sources of ionizing radiation – vacuum UV, soft X-ray
- Development of electron detectors
- Development of UHV technology

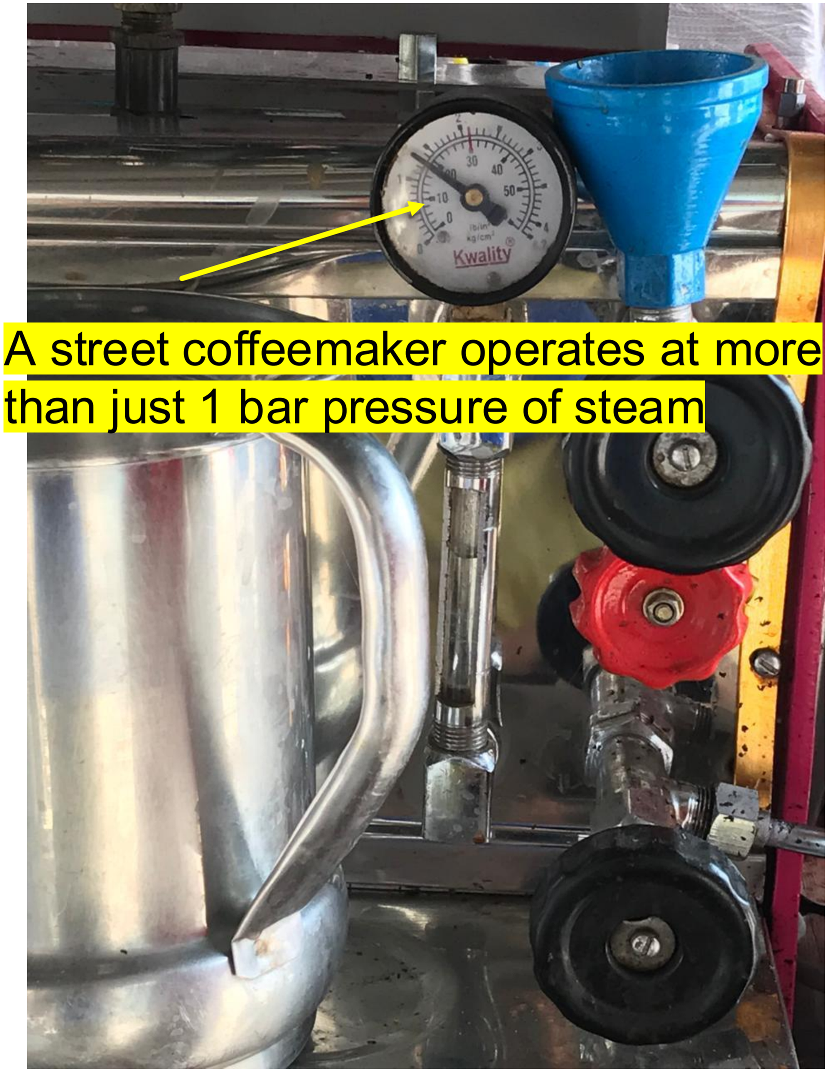
Ultra-high Vacuum : Why we need that?

Why do we need vacuum?

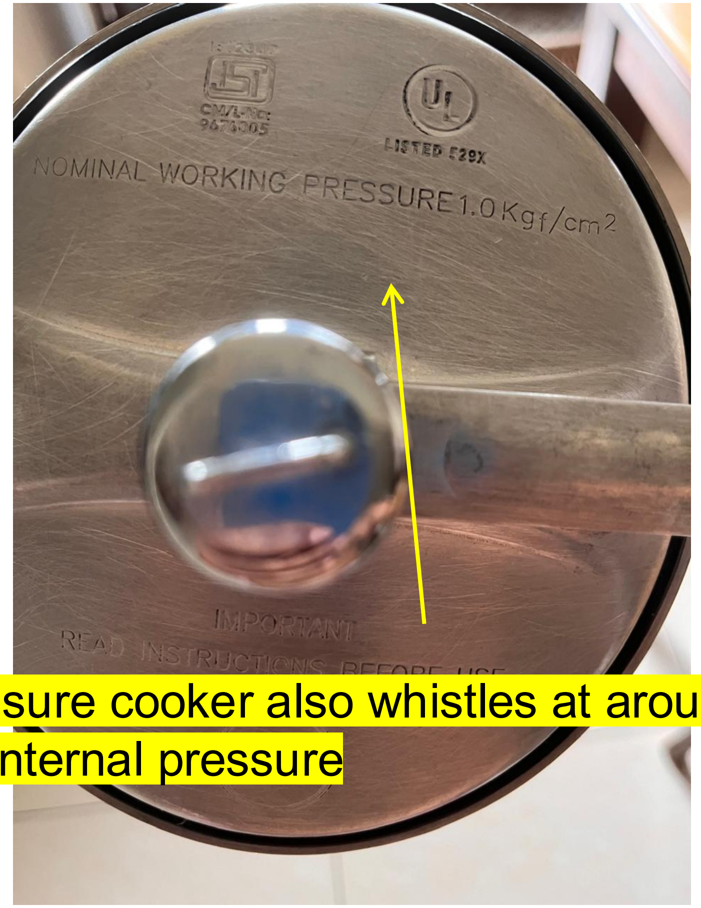
- Low pressure is required for operation of electron detectors

- Pressure must be low enough to allow mean-free-path of electrons through the analyzer

- Ultra-high vacuum is required to lower surface contamination for condensed-phase spectroscopy



A street coffeemaker operates at more than just 1 bar pressure of steam



A pressure cooker also whistles at around 1 bar internal pressure

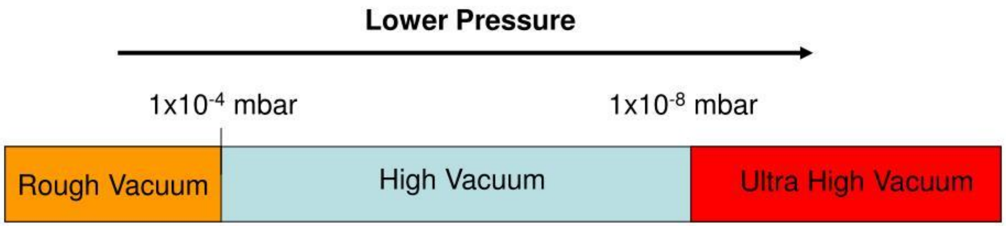
These pressure gauges are relative gauges.

Pressure

1 atmosphere ~ 1 bar ~ 760 mm Hg ~ 760 torr ~ 100,000 Pa

Ion gauges read in mbar i.e. 1×10^{-10} mbar = 1×10^{-13} atm.

Sometimes ion gauges read in torr but ours are set to mbar



Lower Pressure

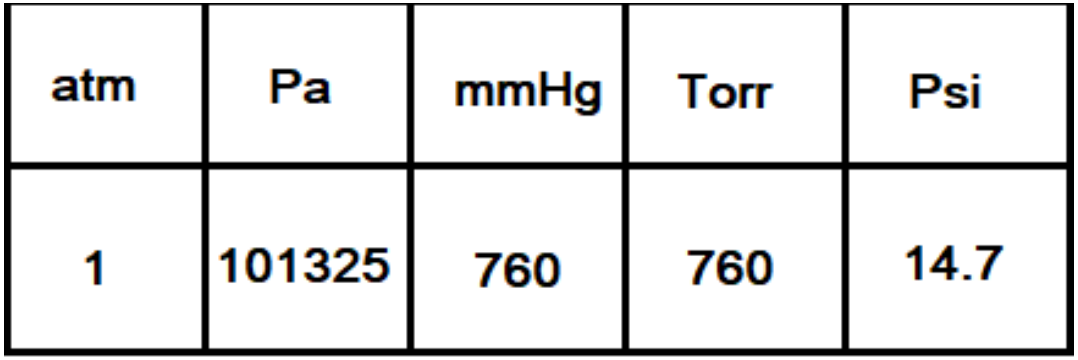
1×10^{-4} mbar

1×10^{-8} mbar

Rough Vacuum

High Vacuum

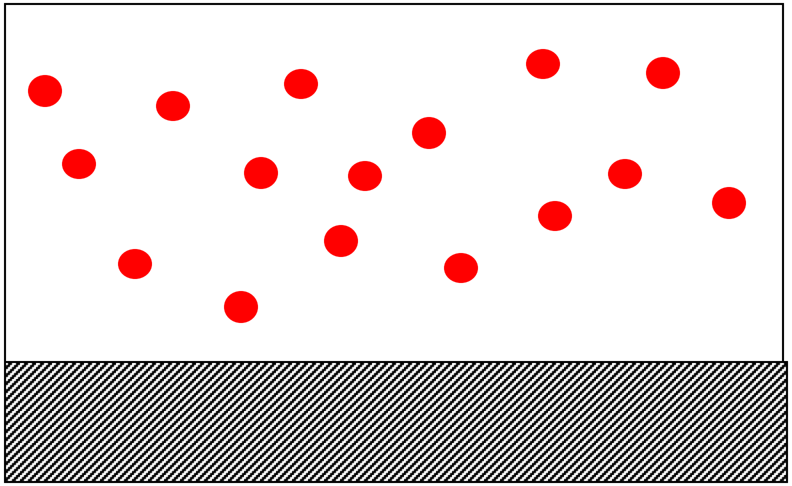
Ultra High Vacuum



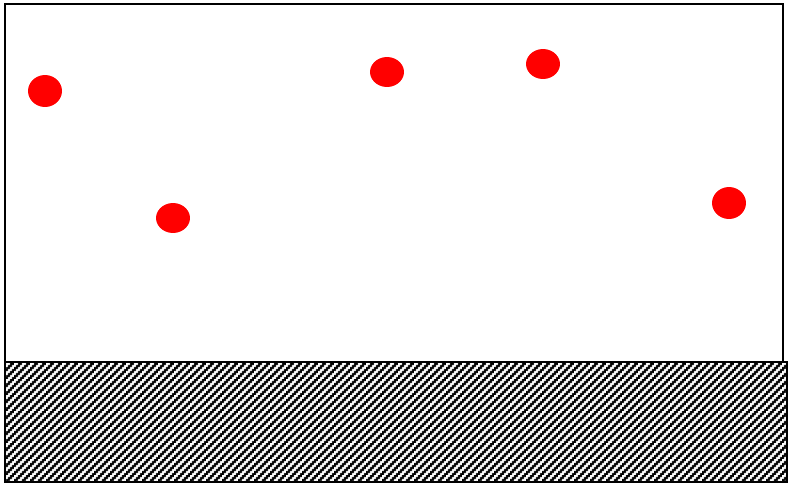
atm	Pa	mmHg	Torr	Psi
1	101325	760	760	14.7

How Low Must Pressure be for a Surface to be "Clean"?

If "sticking coefficient" S = 1
And pressure = 2.5 x 10^{-6} Torr
A monolayer will form in 1 second



Lower pressure to ~ 10^{-9} Torr
A monolayer forms in 1,000 seconds
S is usually <<1



Fundamental Equation of XPS

For solid samples, $\mathbf{h\nu = KE + BE + \phi}$

Incident Photon energy = Kinetic Energy + Binding Energy + **Work Function**

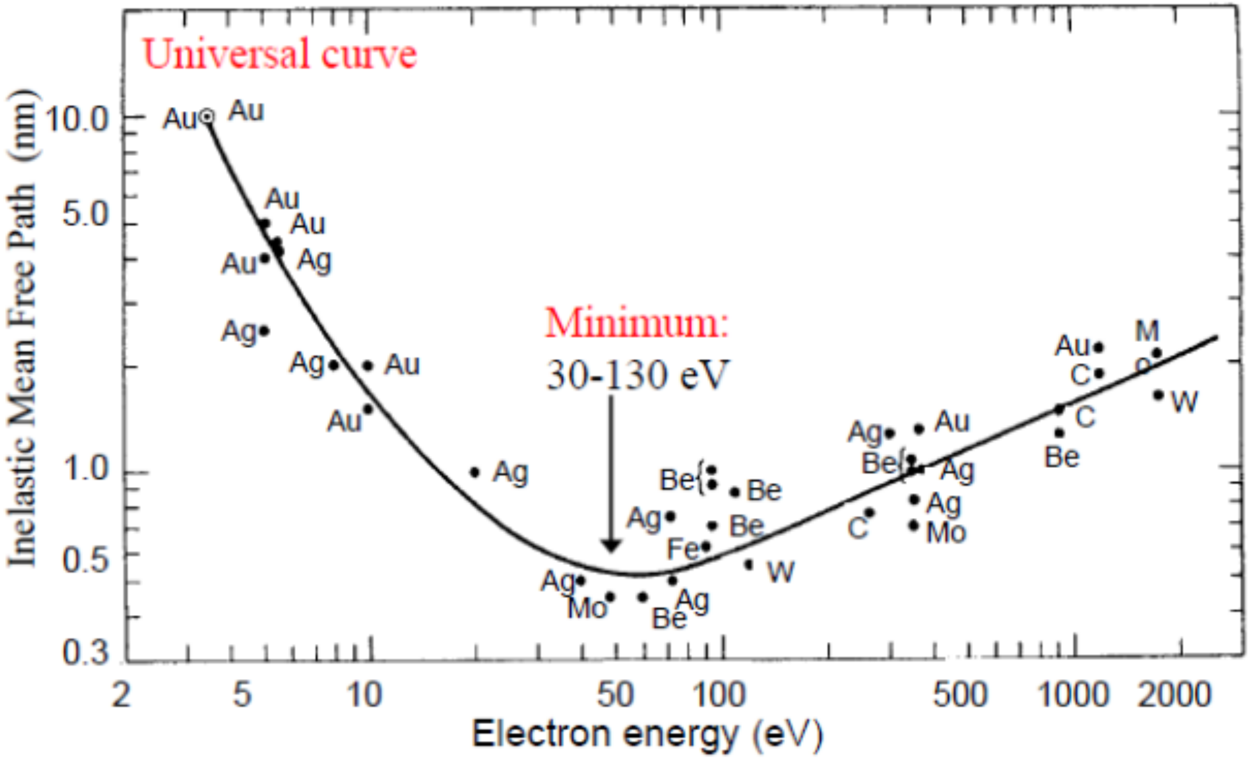
With Al K_α (= 1486.6 eV), C 1s signal (BE=285 eV)

KE = 1486.6 -285 = 1201.6 eV

With Mg K_α (= 1253.7 eV), C 1s signal (BE=285 eV)

KE = 1253.7 -285 = 968.7 eV

Electron inelastic mean free path



Universal curve

Minimum:
30-130 eV

Rule of thumb:

hν=1000 eV

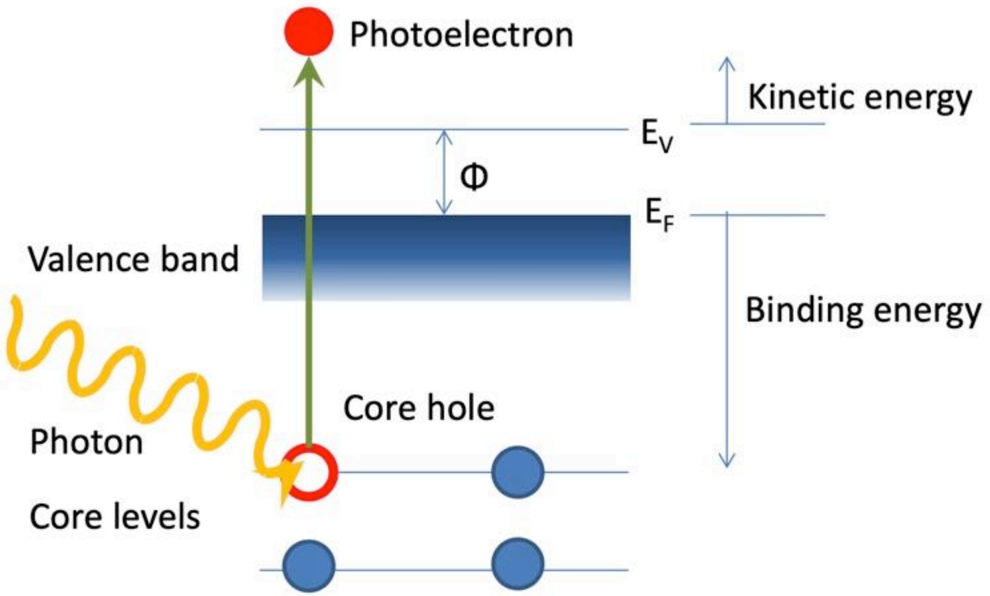
λ_{mfp}:

5-10 Å metals
15-40 Å oxides
15-30 Å polymers

Photoelectron Spectroscopy

Principle

It is based on the photoelectric effect, i.e., emission of electron following excitation of electrons by photons



$KE = h\nu - BE - \Phi$ for a solid

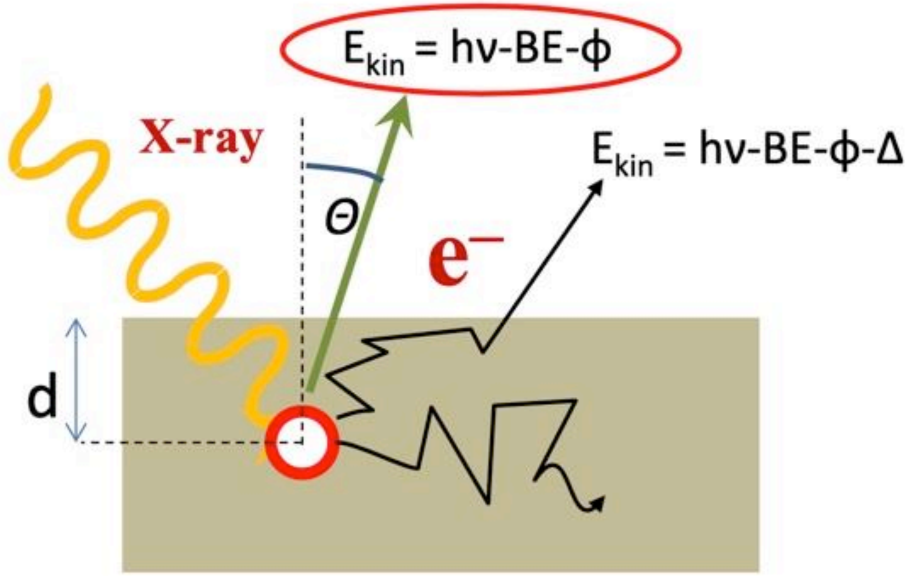
$KE = h\nu - IP$ for a gas

Φ : photoelectric workfunction (4-6 eV)

Photoelectron Spectroscopy

Probed depth

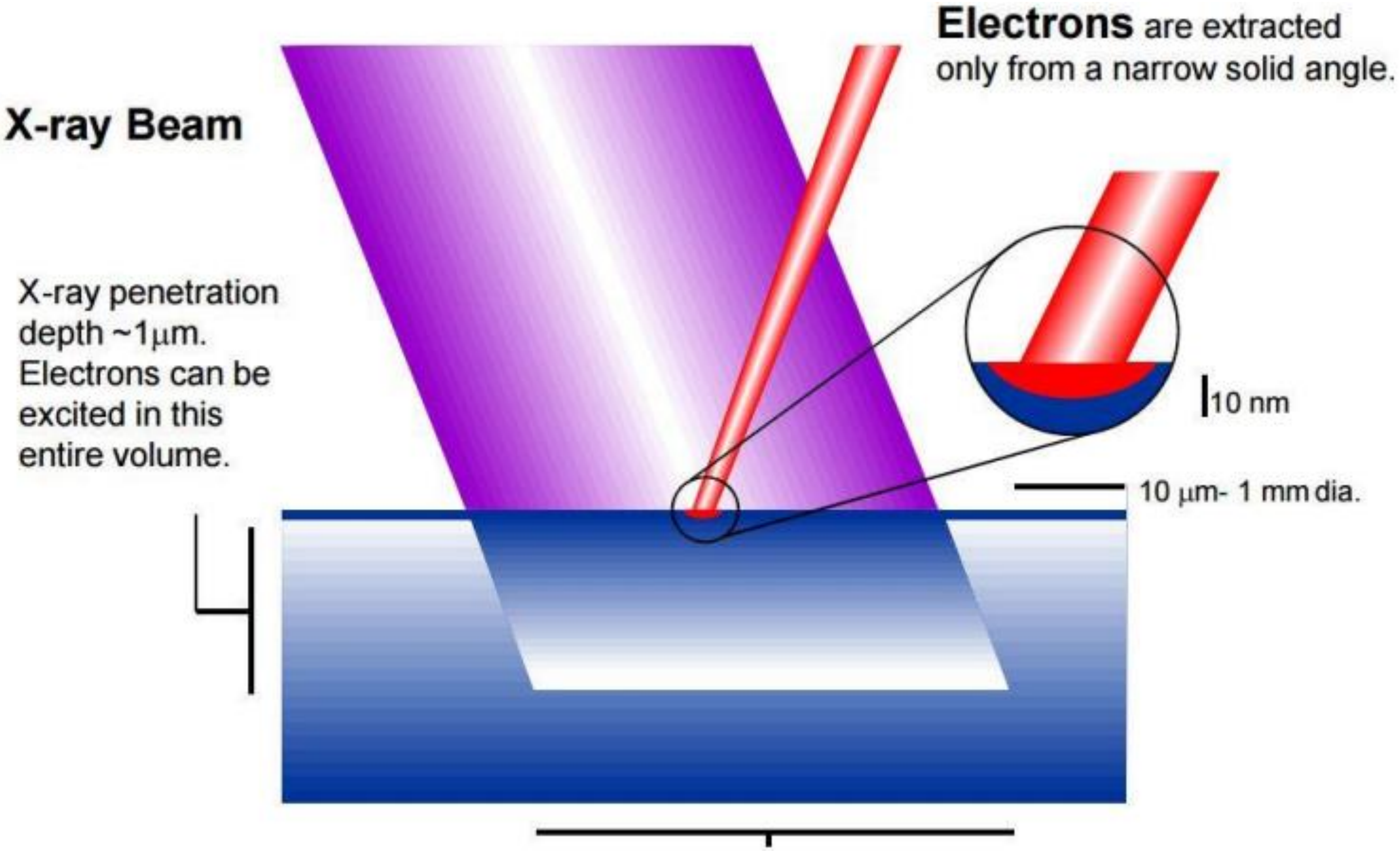
It is surface sensitive because of the low inelastic mean free path of electrons



Contribution of atom in depth d to PE peak:

$$I = I_0 \exp\left(\frac{-d}{\lambda \cos\theta}\right)$$

XPS is a surface sensitive technique

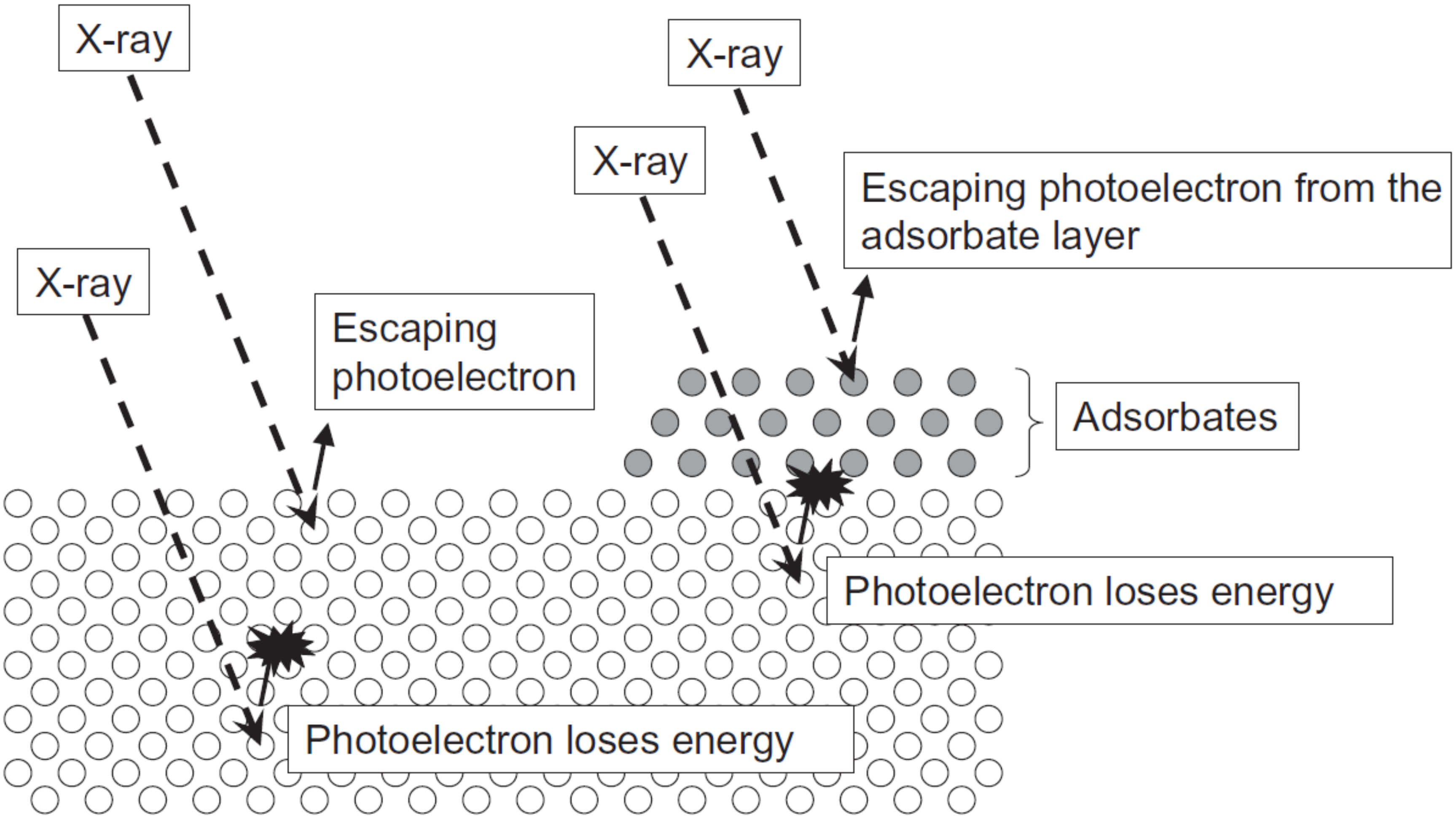


Electrons are extracted only from a narrow solid angle.

X-ray penetration depth ~1µm. Electrons can be excited in this entire volume.

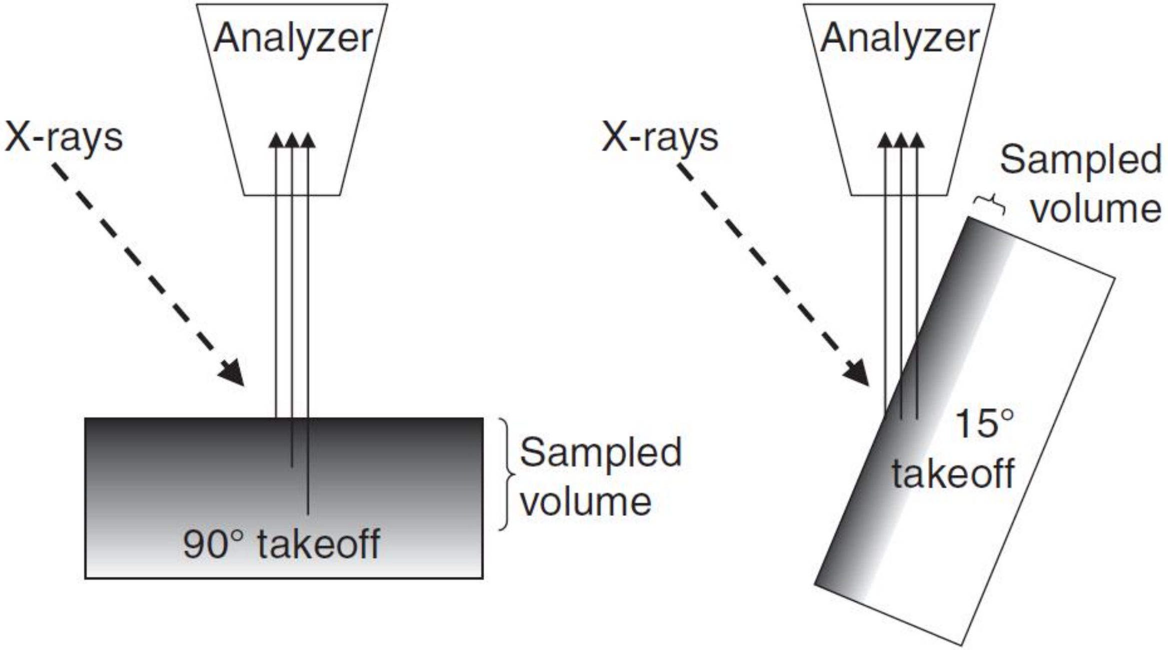
X-ray excitation area ~1 mm-1 cm diameter. Electrons are emitted from this entire area

Penetration Depth Vs. Probed Depth

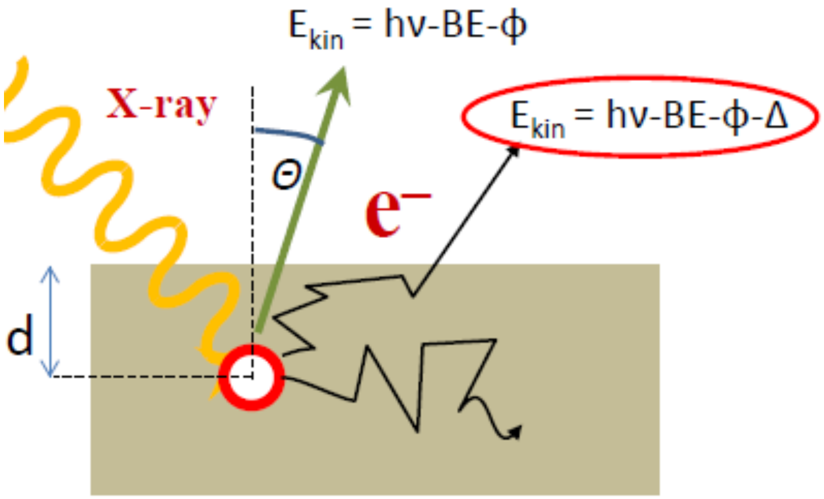


The IMFP (or λ_{IMFP}) : This defines the average distance traveled by an electron of a specific energy within a particular single - layered homogeneous amorphous solid between two successive inelastic scattering events.

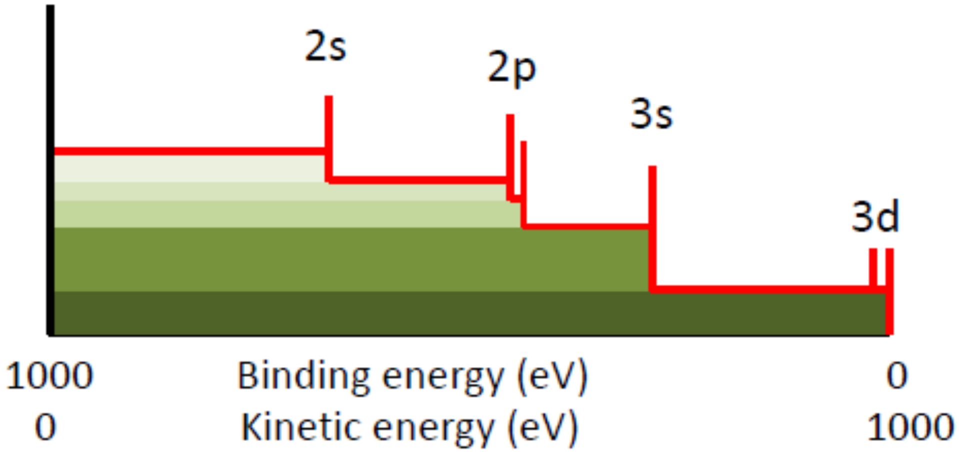
The Sampling Depth (Probed depth) : This equates to the depth from which 95.7% of all photoelectrons emanate. It is equivalent to 3 $\lambda_{IMFP} \cos \Theta$.



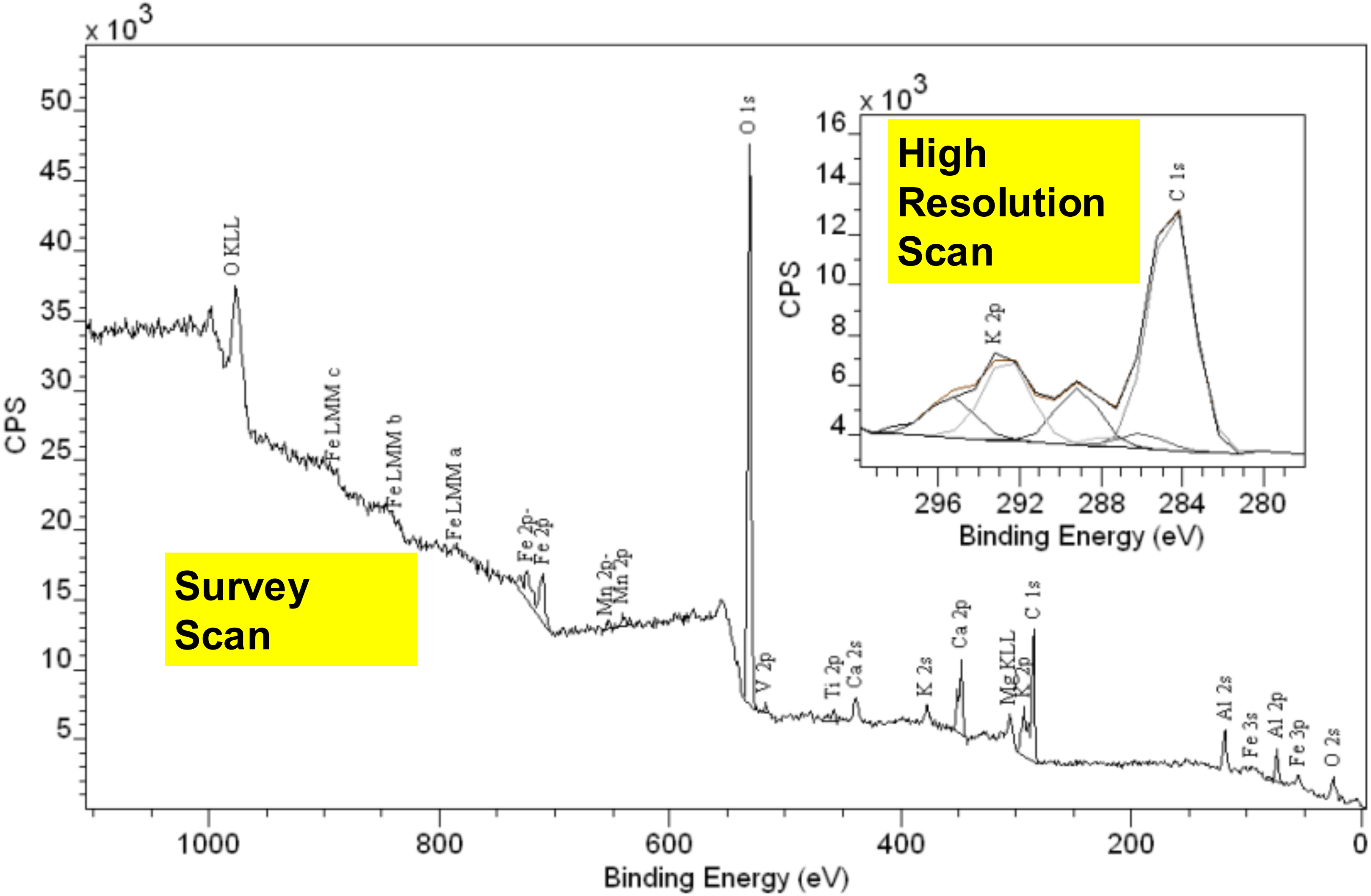
Inelastic background



- Electrons from deeper below the surface loose energy and emerge with reduced KE (increased apparent BE)
- Electrons very deep in surface loose all energy and cannot escape
- XPS spectra show characteristic "stepped" background (intensity of background towards higher BE of photoemission peak is always greater than towards lower BE



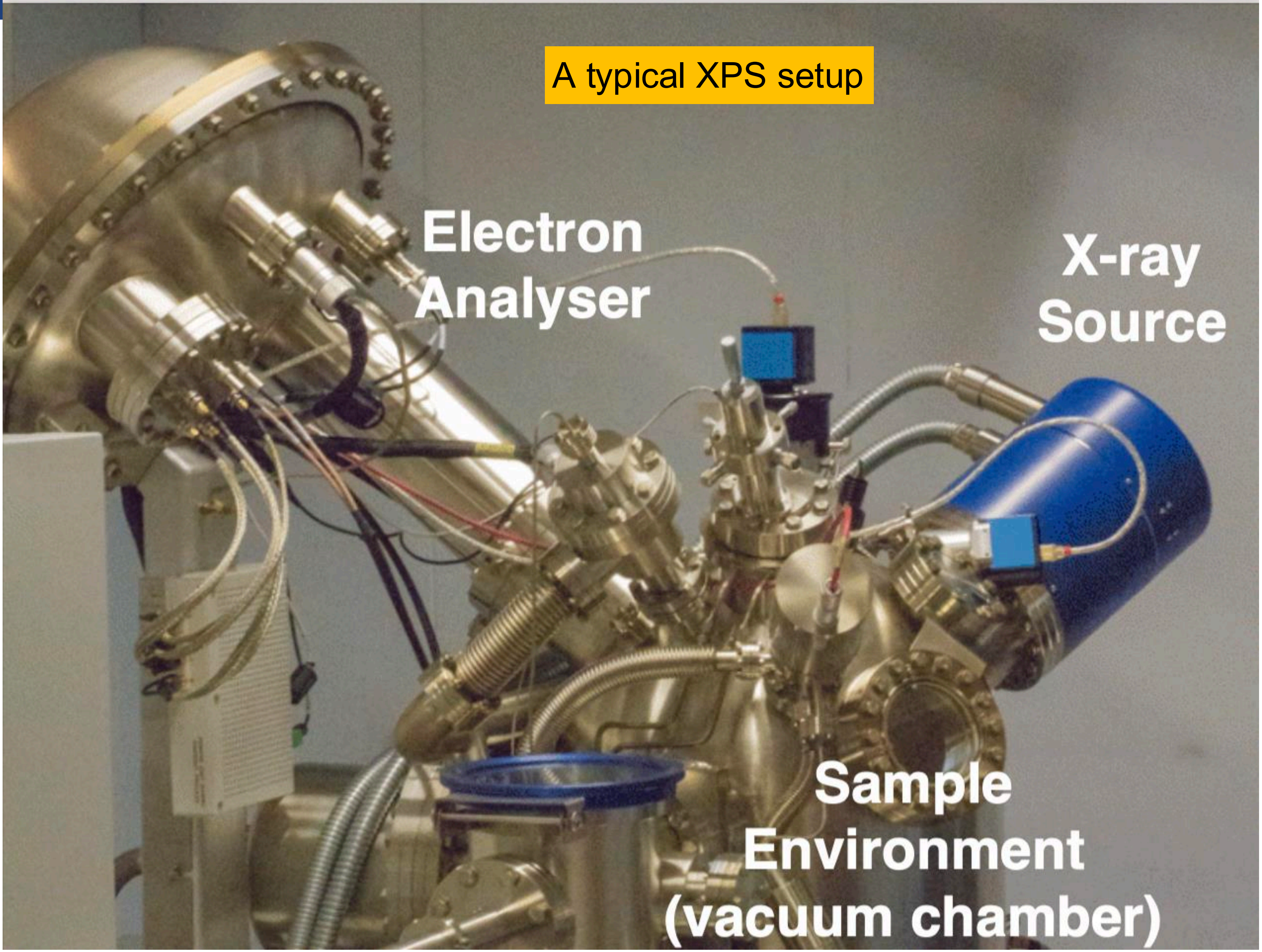
How does a XPS scan look like? For example.

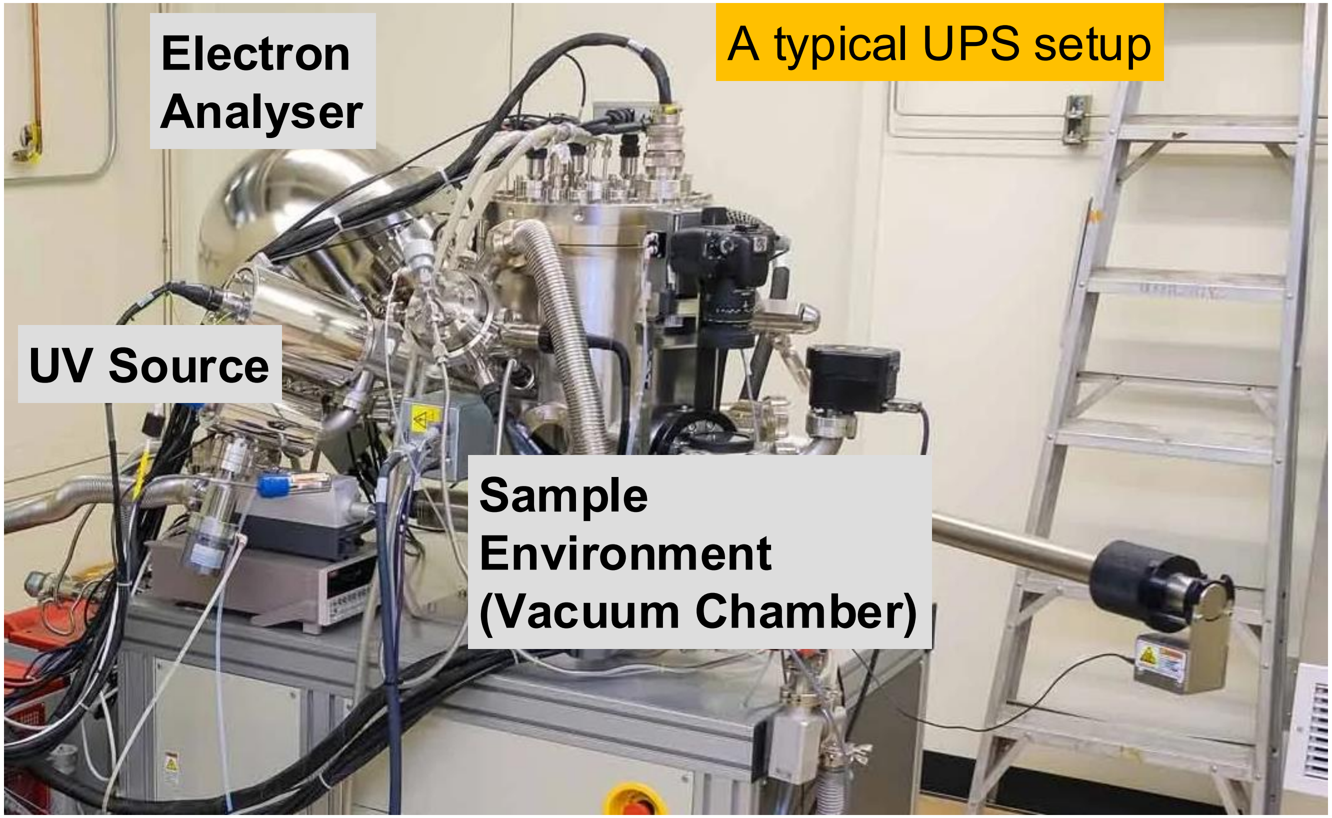


High Resolution Scan

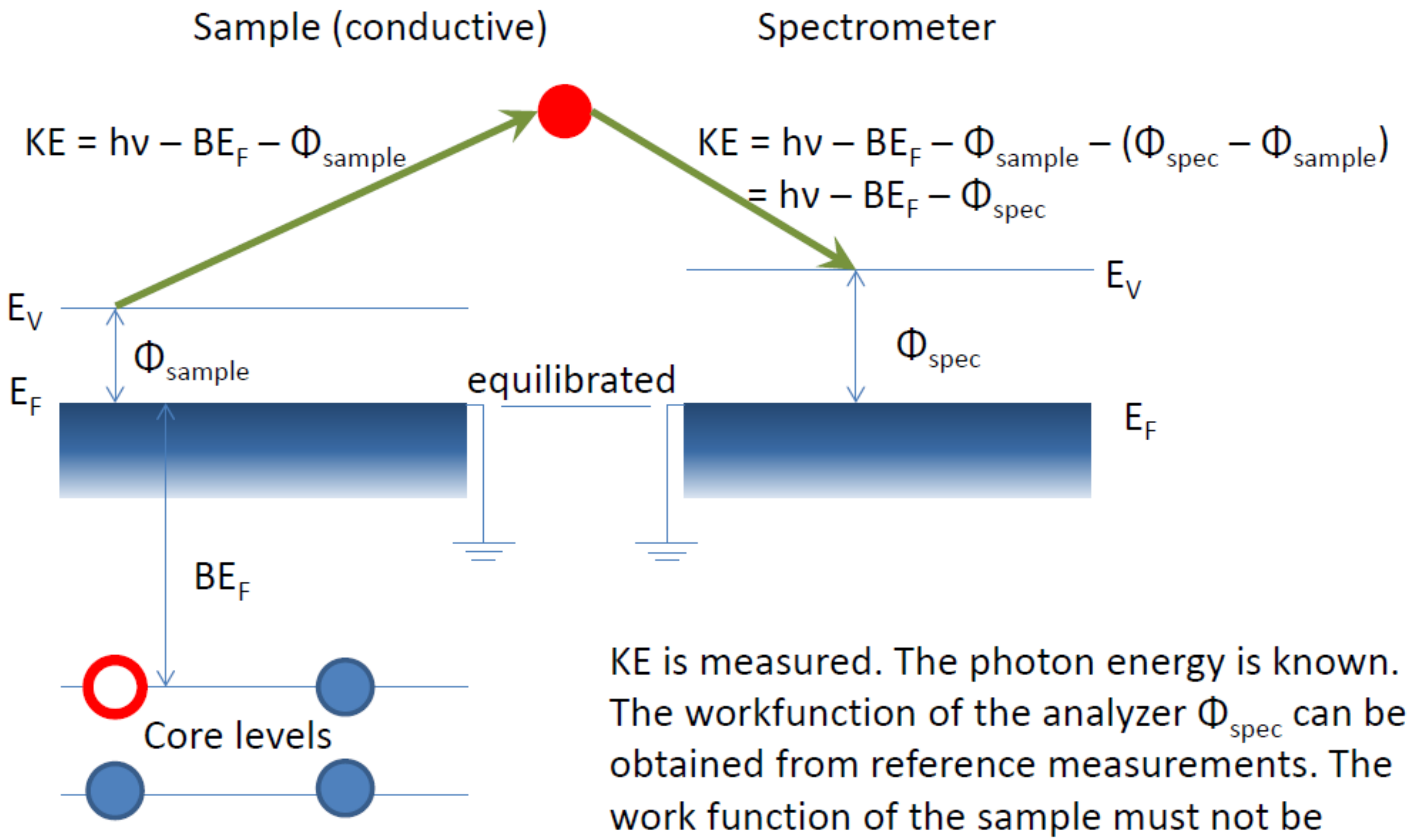
Survey Scan

A typical XPS setup




Electron Analyser
A typical UPS setup
UV Source
Sample Environment (Vacuum Chamber)

How to get the binding energy scale



$$KE = h\nu - BE_F - \Phi_{sample}$$

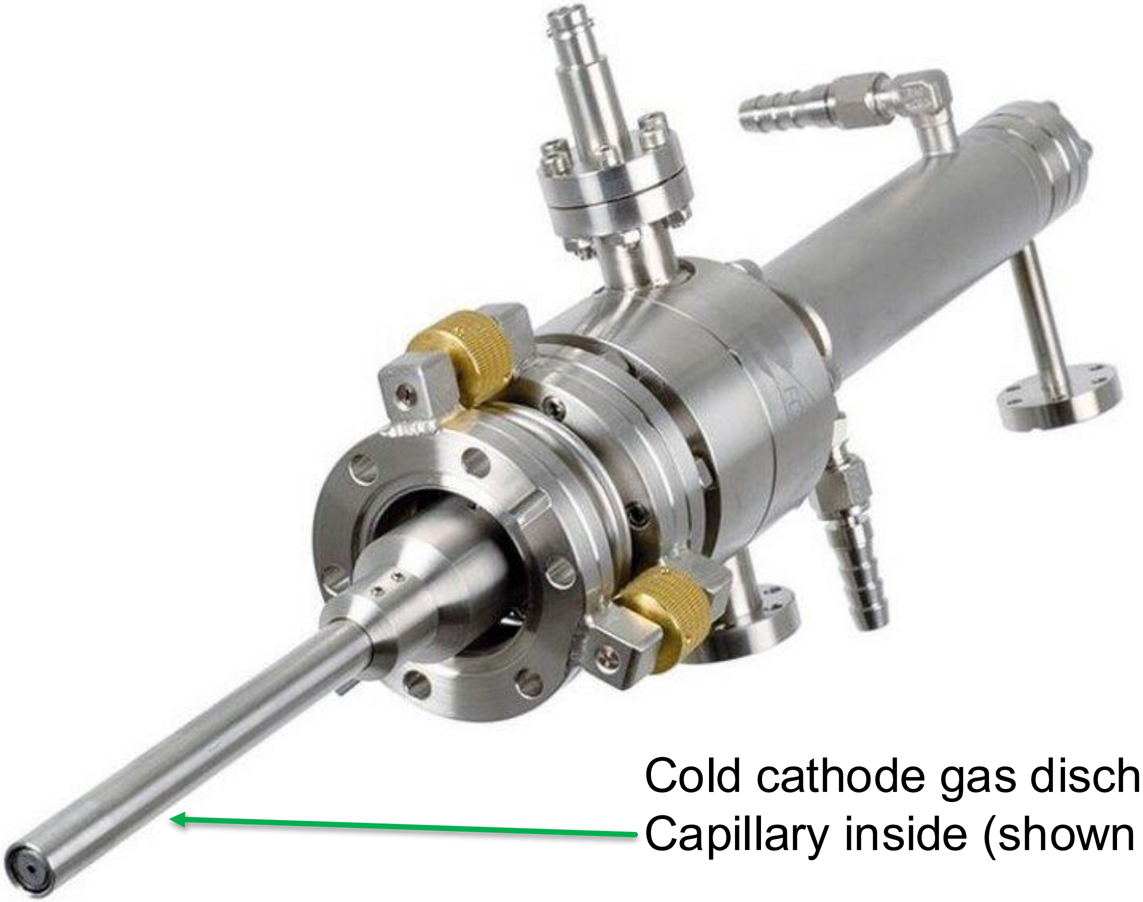
$$KE = h\nu - BE_F - \Phi_{sample} - (\Phi_{spec} - \Phi_{sample})$$
$$= h\nu - BE_F - \Phi_{spec}$$

KE is measured. The photon energy is known. The workfunction of the analyzer Φ_{spec} can be obtained from reference measurements. The work function of the sample must not be known. This procedure leads to a BE scale referenced to E_F.

Laboratory Sources for UPS

Gas discharge VUV sources: ~ 0.005 eV resolution (40 cm^{-1})

He I: 21.2 eV (most common for UPS)
(light emitted from the neutral atoms)
He II: 40.8 eV
(light emitted from the singly ionized atoms)
Ne I: 16.7 eV



Cold cathode gas discharge lamp
Capillary inside (shown below)

Koopmans' Theorem

The binding energy of an electron in state *i* is equal to the negative of the orbital energy of the *ith* state.

$I_i = -\varepsilon_i$

(the ion is represented by (N-1) frozen orbitals)

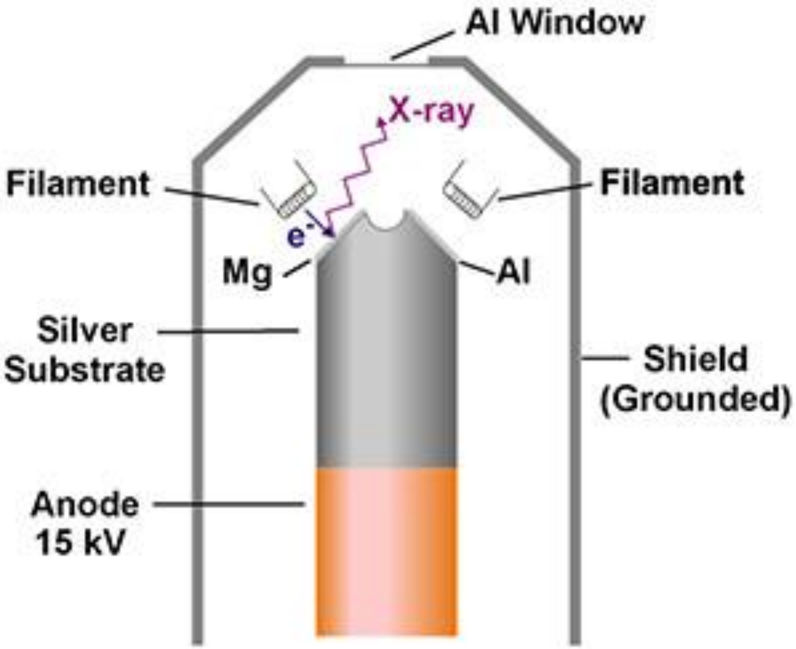
Koopmans' theorem makes possible the identification of calculated orbital energies with ionization potentials.

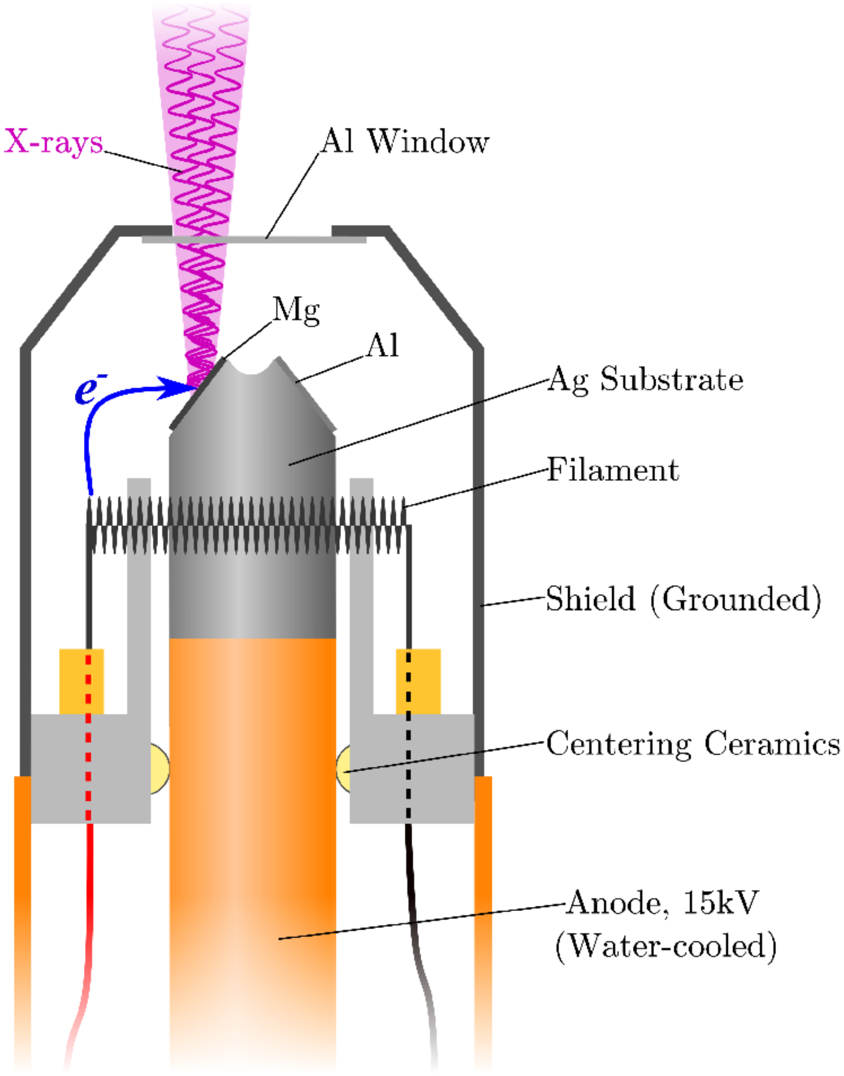
But it does not allow for electronic relaxation

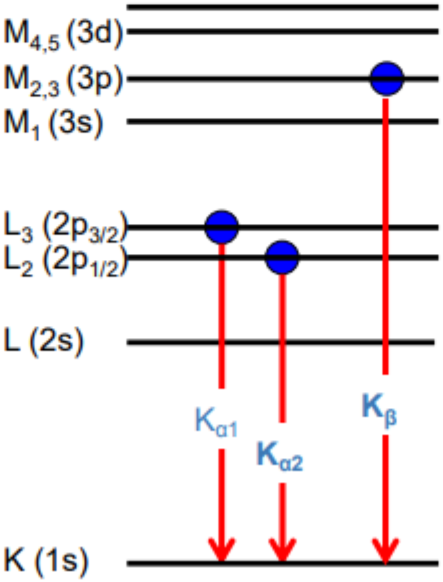
The ionization energy for the removal of electrons from different orbitals in a molecule is given by the energy difference between the initial state of the neutral molecule (in the ground state) and the final state that is the state of the ionized molecule.

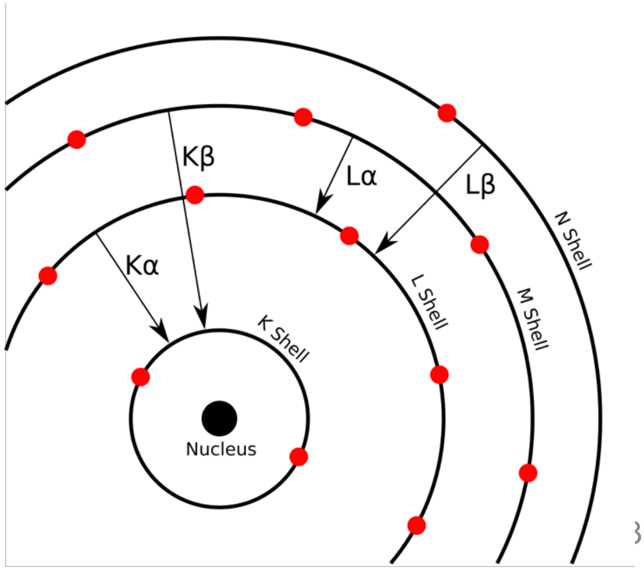
Laboratory Sources for XPS

X-ray lines	Line Energy (eV)	Width (eV)
Mg $K_{\alpha 1,2}$	1253.6	0.70
Al $K_{\alpha 1,2}$	1486.6	0.85




X-rays
Al Window
Mg
Al
e-
Ag Substrate
Filament
Shield (Grounded)
Centering Ceramics
Anode, 15kV
(Water-cooled)

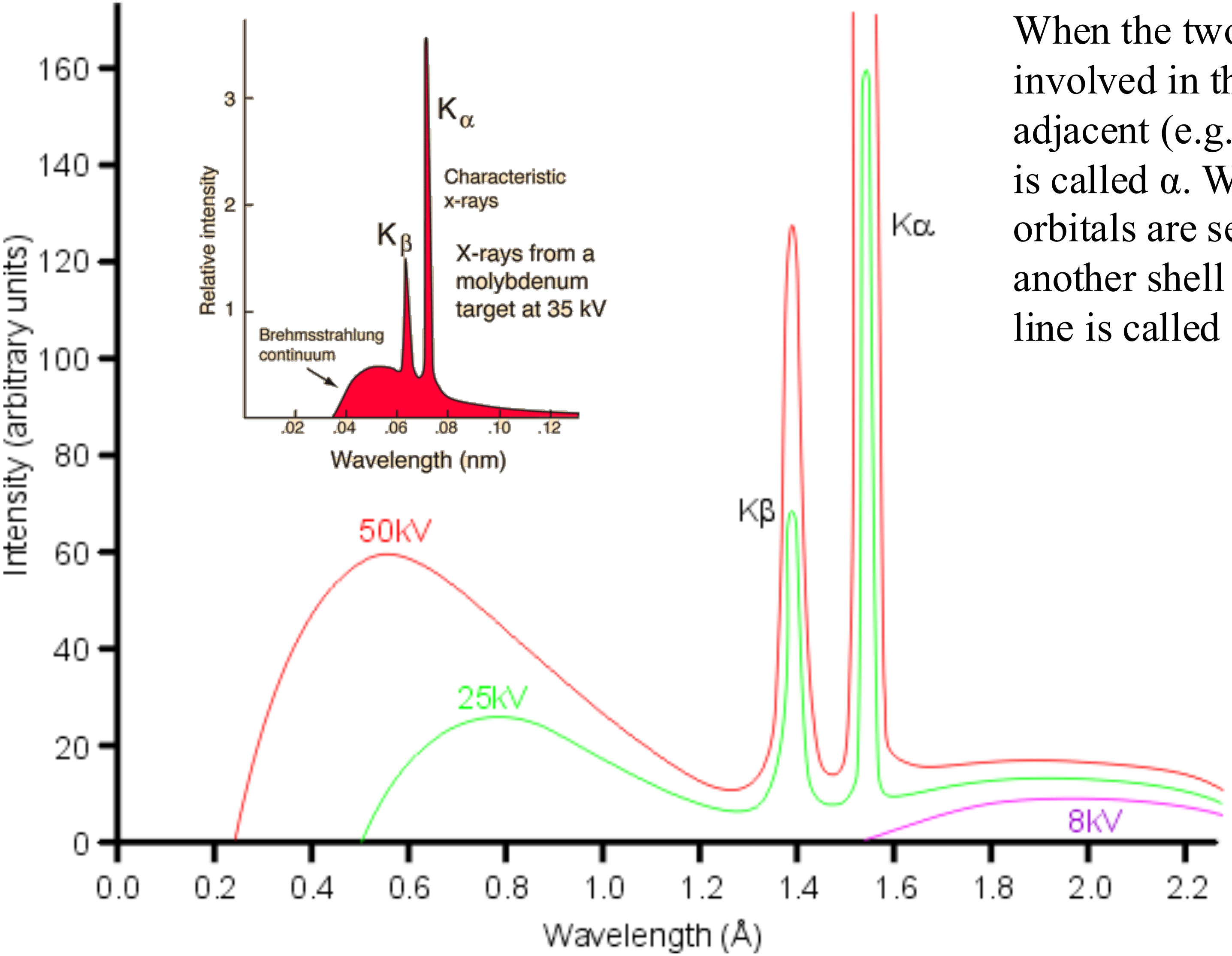

$M_{4,5}$ (3d)
$M_{2,3}$ (3p)
M_1 (3s)
L_3 ($2p_{3/2}$)
L_2 ($2p_{1/2}$)
L (2s)
$K_{\alpha1}$
$K_{\alpha2}$
K_β
K (1s)


Kβ
Lα
Lβ
Kα
N Shell
M Shell
L Shell
K Shell
Nucleus

Notations

Quantum numbers				Atomic notation	X-ray notation
n	ℓ	s	j		
1	0	1/2	1/2	$1s_{1/2}$	K_1
2	0	1/2	1/2	$2s_{1/2}$	L_1
2	1	1/2	1/2	$2p_{1/2}$	L_2
2	1	1/2	3/2	$2p_{3/2}$	L_3
3	0	1/2	1/2	$3s_{1/2}$	M_1
3	1	1/2	1/2	$3p_{1/2}$	M_2
3	1	1/2	3/2	$3p_{3/2}$	M_3
3	2	1/2	3/2	$3d_{3/2}$	M_4
3	2	1/2	5/2	$3d_{5/2}$	M_5

Characteristic X-ray

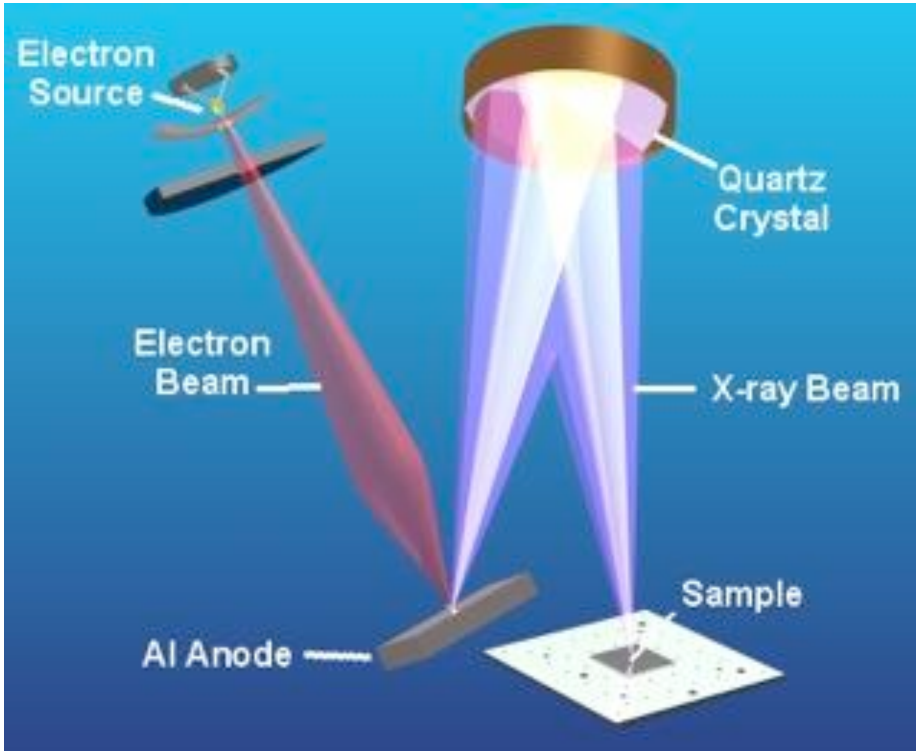


When the two orbitals involved in the transition are adjacent (e.g. 2 → 1), the line is called α. When the two orbitals are separated by another shell (e.g. 3 → 1), the line is called β.

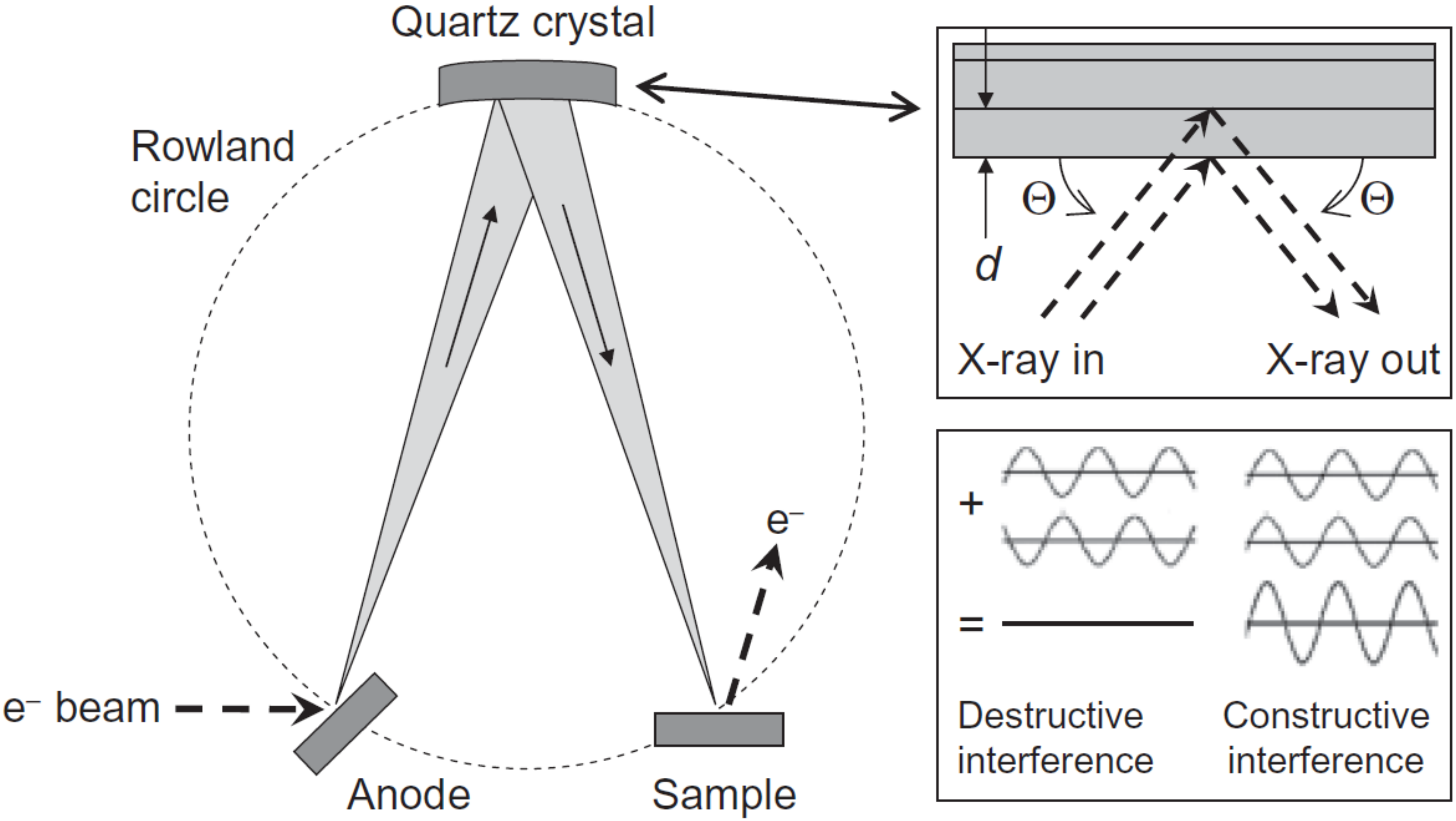
Laboratory Sources XPS

Monochromatic X-ray

Most used is: Al Kα (1486.6 eV)



Arrangement geometry of monochromator

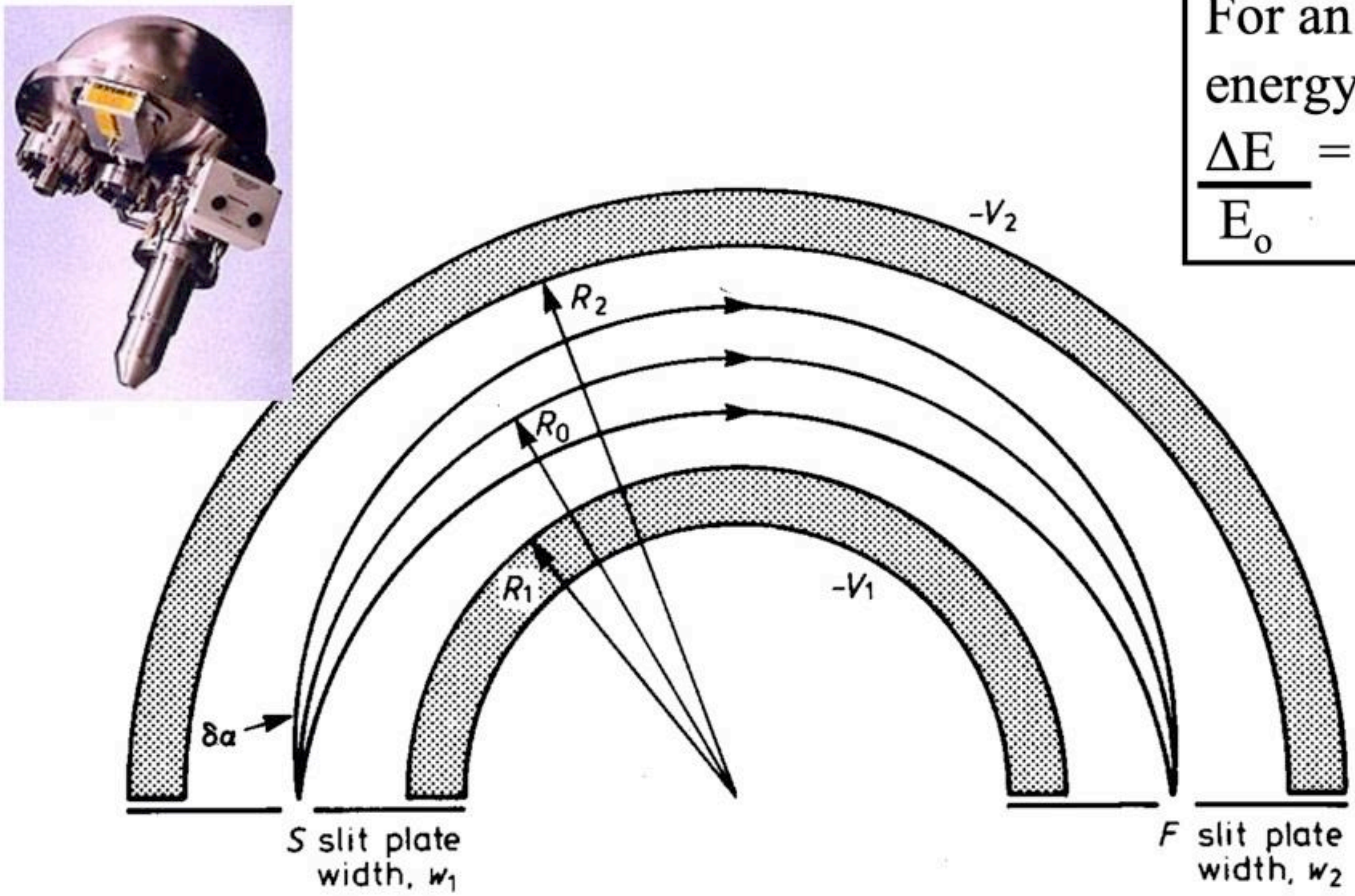


Electron Energy Analyzer

Concentric hemispherical analyzer (CHA)

For an electron of energy E_o at S

$$\frac{\Delta E}{E_o} = 0.63 \frac{\overline{w}_1}{R_o}$$



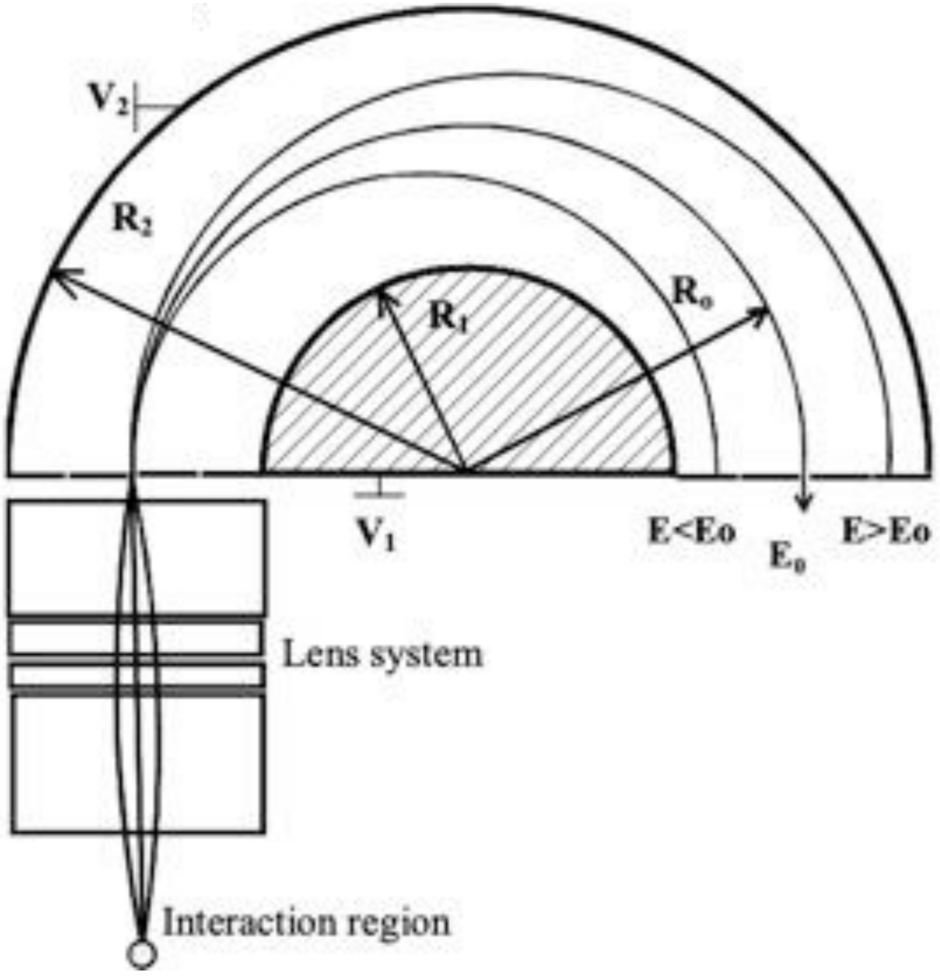
Pass Energies and Transfer Lens

(1) To resolve a 1000 eV electron to ± 0.5 eV would require an analyser with w=1 mm and R=1.2 metres!

Therefore, it is convenient to retard the energy of the incoming electrons so that they have a lower (and constant) energy as they pass through the analyser.

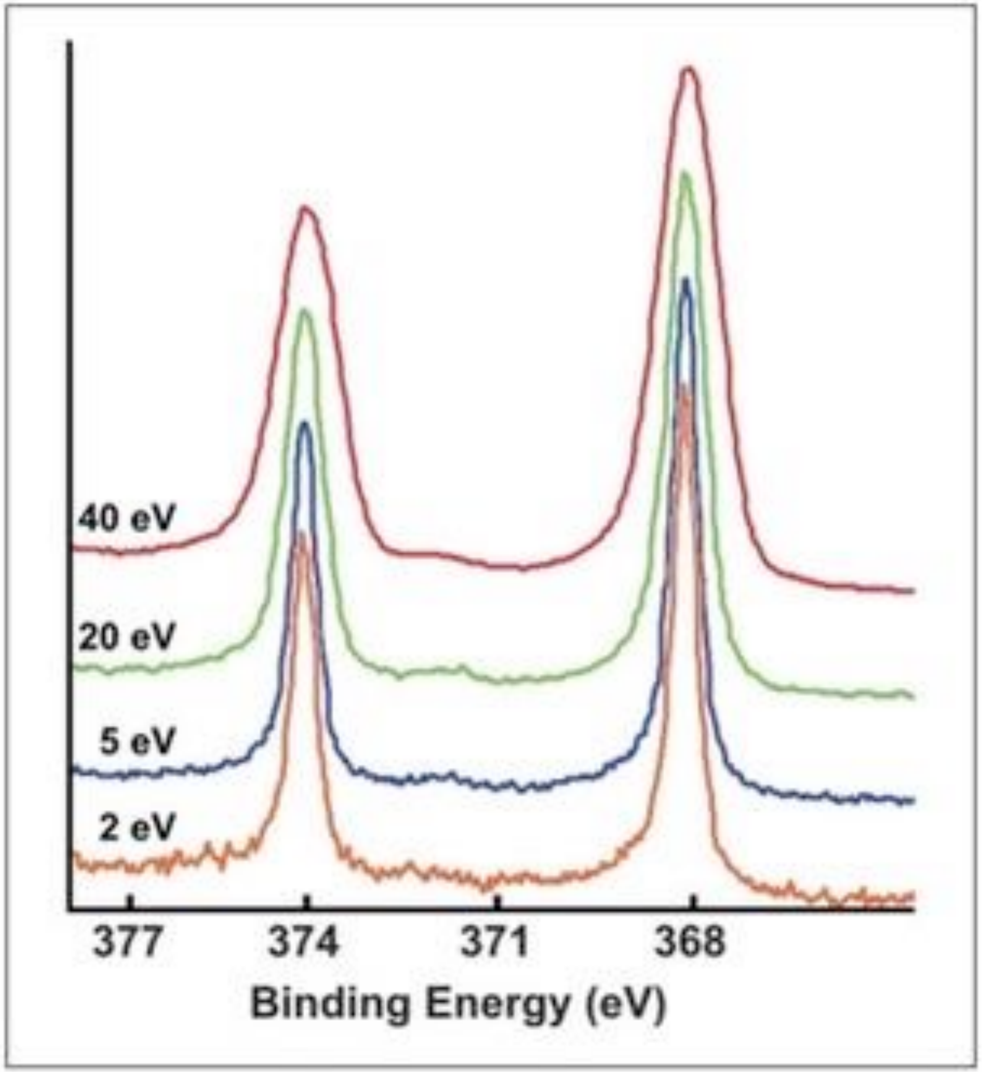
The lens system which retards the electron energy also **focuses** the electrons energy from the sample to increase the throughput.

Concentric Hemispherical Analyzer CHA



- A potential difference between the hemispheres allow only electrons with specific kinetic energies to make it to the electron detector.
- Varying potentials measure different kinetic energies
- Computer calculates binding energy

Pass Energy vs Resolution



Ag 3d spectra
recorded at various
pass energy

With decrease in pass energy, the resolution improves, but intensity decreases.

Photoionization Cross-section

- The probability per unit area, per unit time that a photon of a given energy can be absorbed by an atom to excite the photoelectrons.

\# photons absorbed per unit time

cross-section

$$\sigma(h\nu) = \frac{P(h\nu)}{I(h\nu)}$$

incident photon flux

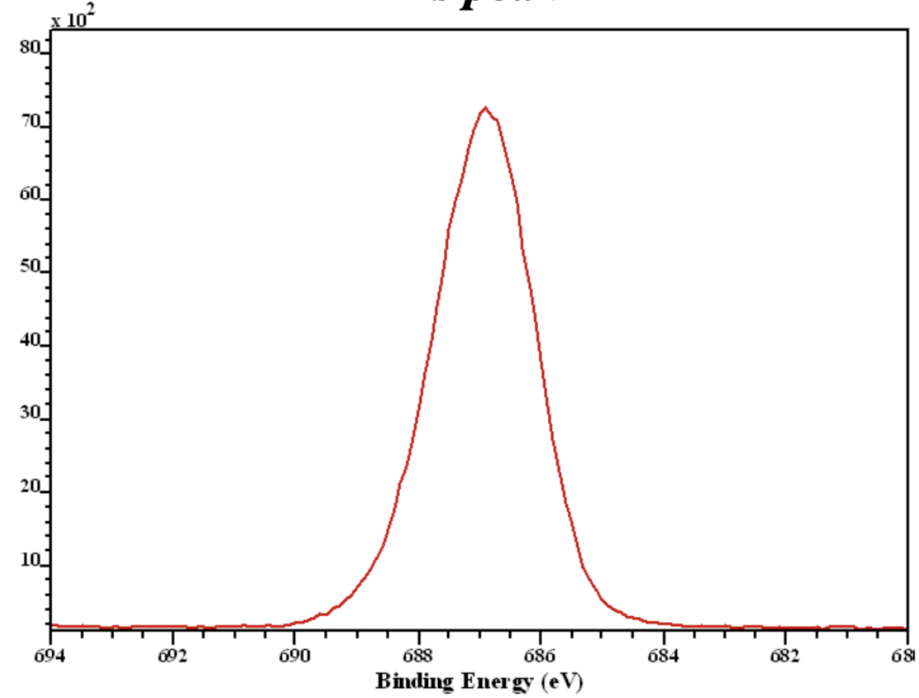
- Unit: barn (10^{-24} cm^2)
  or megabarn (10^{-18} cm^2)

Features in X-ray Photoelectron Spectra

1. Photoemission peaks /Core level
2. Auger peak (due to Auger process)
3. Satellites
4. Plasmon

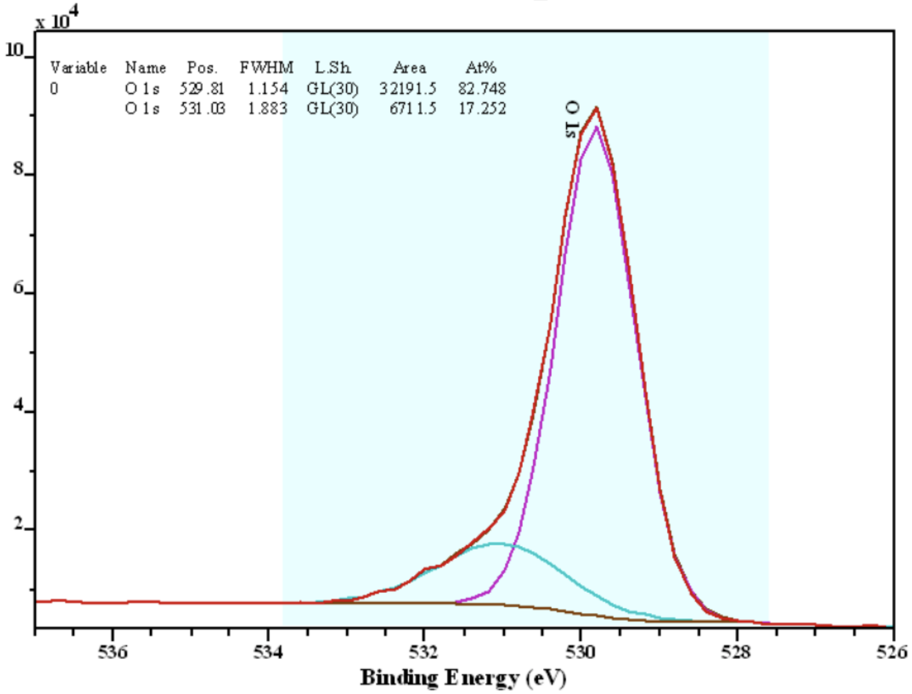
Sharp Peak (core level)

F 1s peak



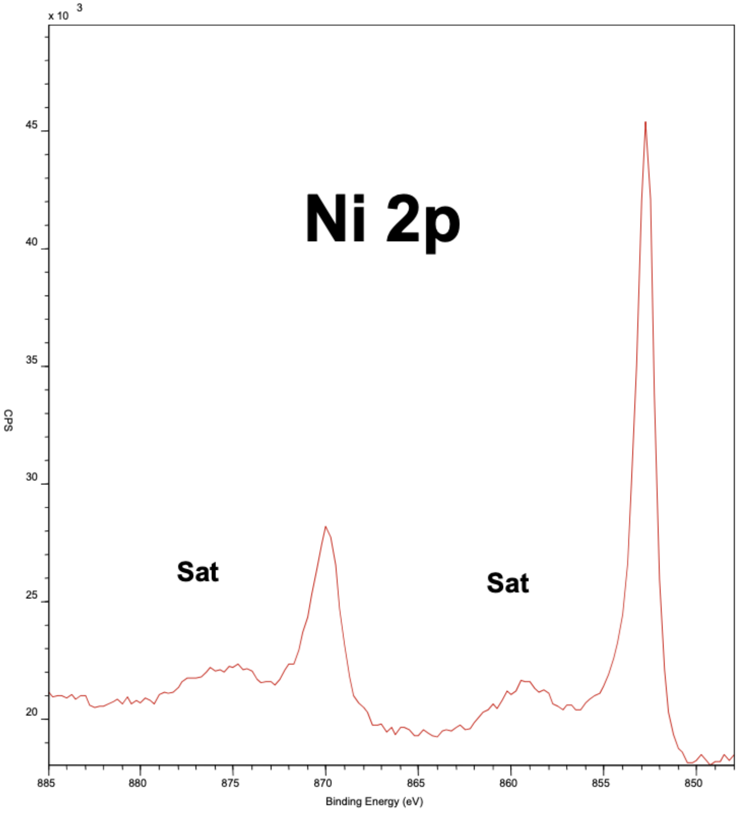
Washington State University--Pullman, WA

O 1s peak

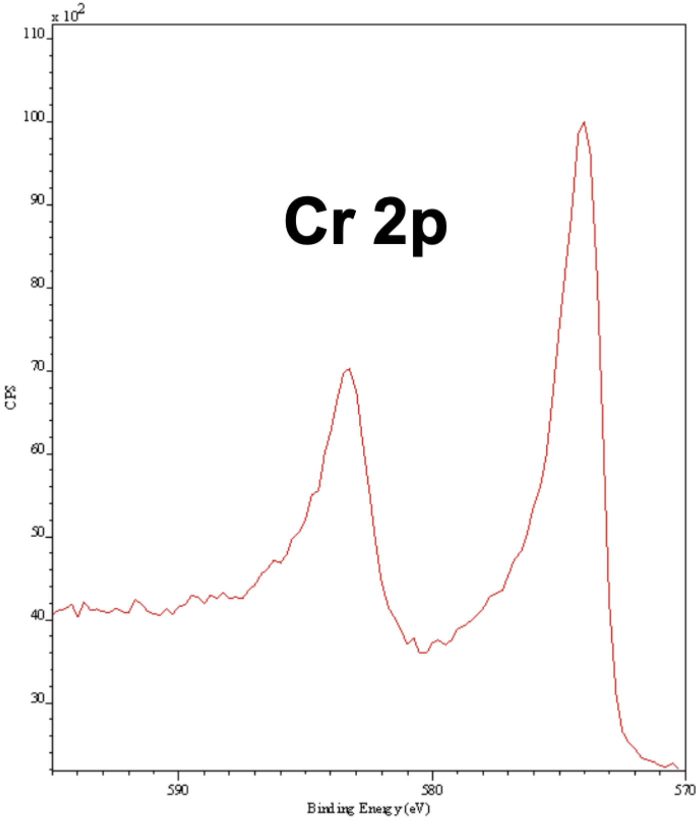


Variable	Name	Pos.	FWHM	L.Sh.	Area	At%
0	O 1s	529.81	1.154	GL(30)	32191.5	82.748
	O 1s	531.03	1.883	GL(30)	6711.5	17.252

Multiplet (Core Level)



Washington State University--Pullman, WA

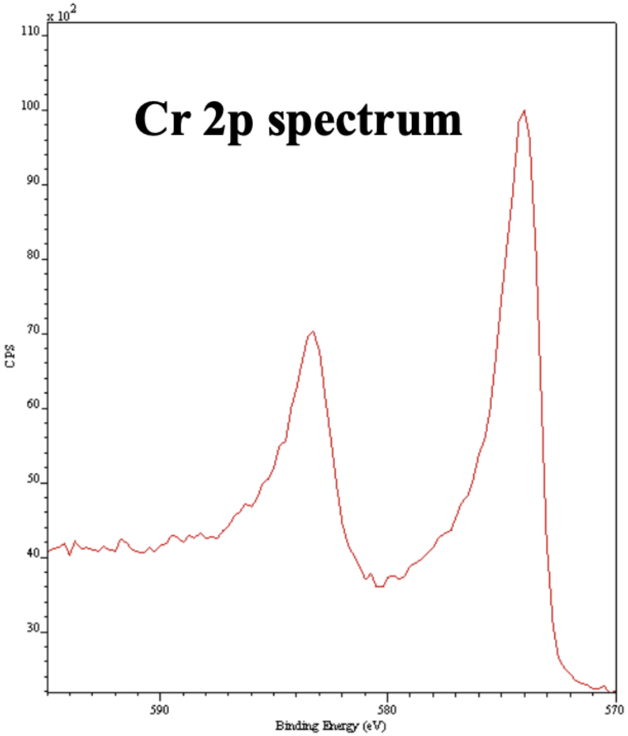


Washington State University--Pullman, WA

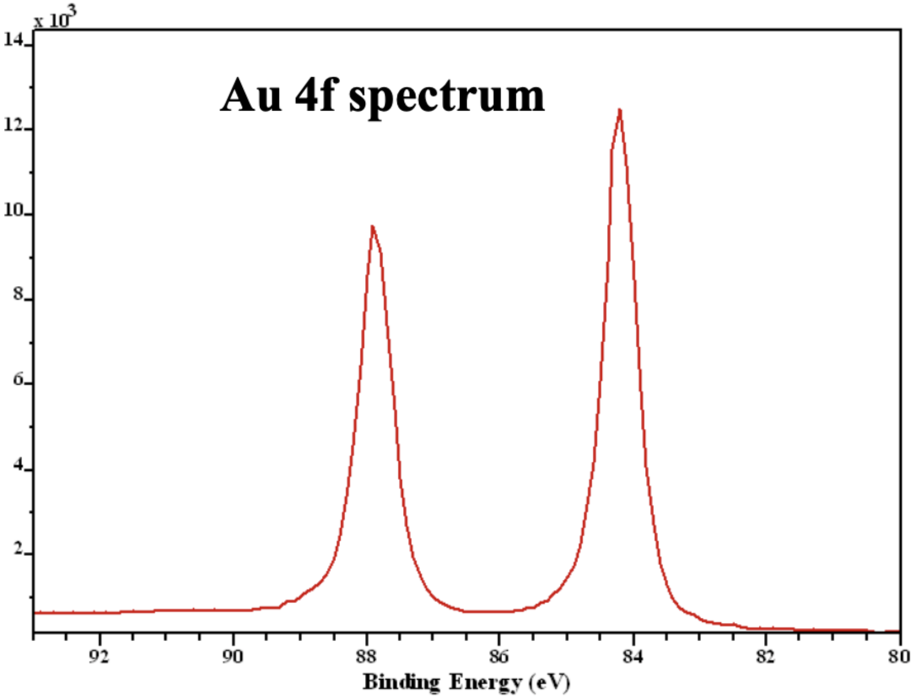
Multiplet splitting occurs when there are unfilled shells containing unpaired electrons. For instance, transition metals with unfilled ***p*** and ***d*** orbitals and rare earths with unfilled ***f*** orbitals all show multiplet splitting.

Intensity ratio is given by **$(2j_- + 1) / (2j_+ + 1)$**

For p orbitals the ratio is given by 2 x 1/2 +1 = 2 ($p_{1/2}$) and 2 x 3/2 +1 = 4 ($p_{3/2}$). Therefore the ratios for *p* orbitals doublet is *1/2*, for *d* orbitals doublet is *4/6 = 2/3*



Ratio = 1/2



Ratio = ??

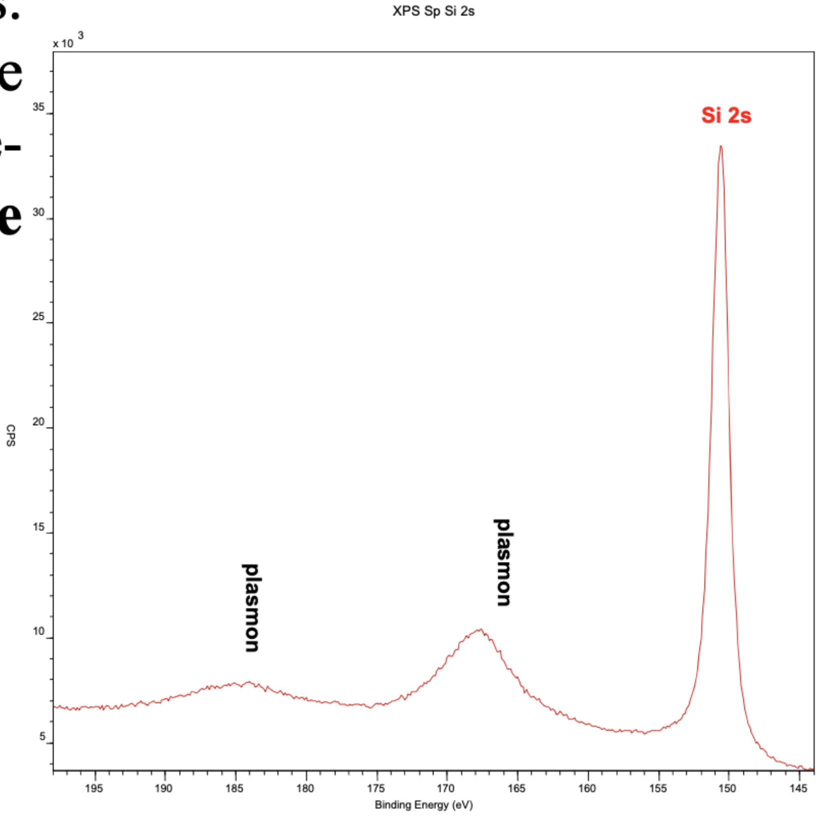
Plasmons

This feature is specific to clean surfaces. The photoelectron excites collective oscillations in the conduction band (free-electron gas), so called Plasmons. (**discrete energy loss**).

The plasmon (bulk) energy is

$$\hbar\omega_p = \hbar\left(\frac{4\pi n e^2}{m}\right)^{1/2}$$

n: e density, e: charge of e,
m: mass of e electron.



Washington State University--Pullman, WA

Surface plasmon: bulk plasmon / 1.414.

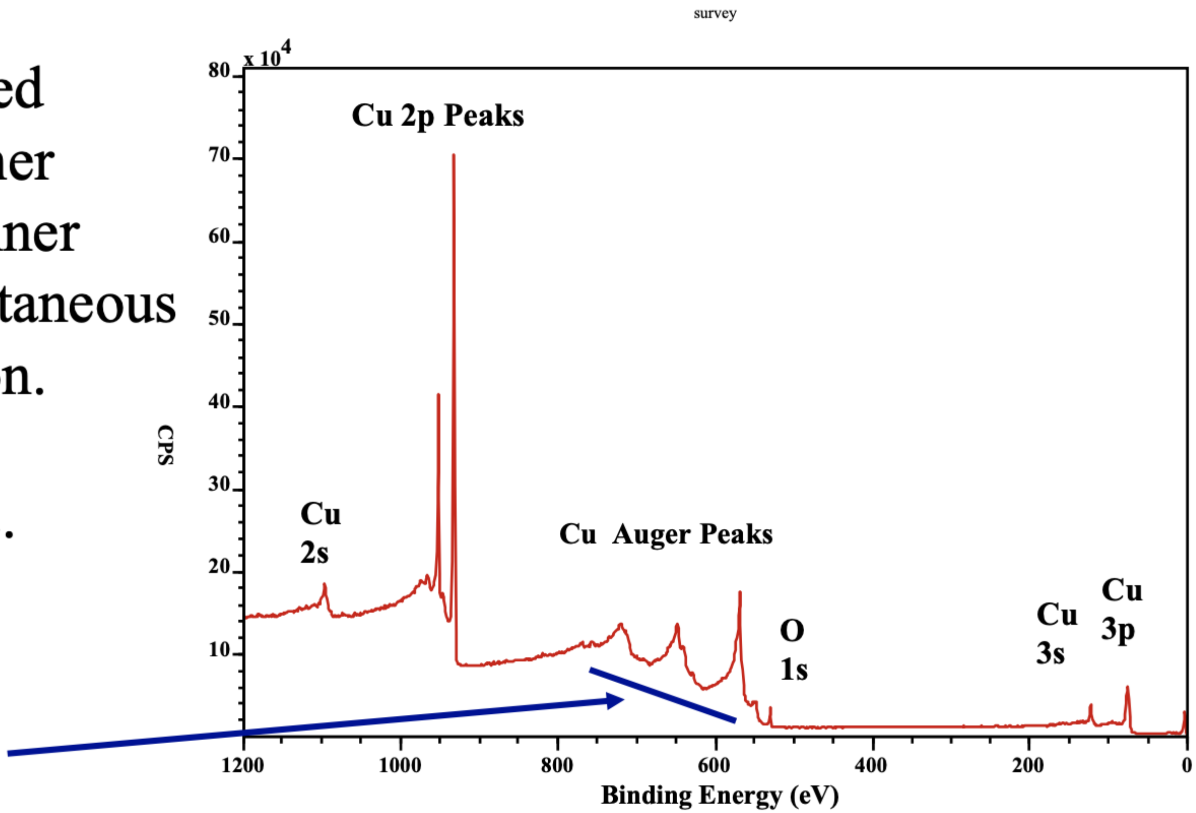
For Al, Mg, Na etc… the energies are 15.3 eV, 10.6 eV and 5.7 eV, respectively.

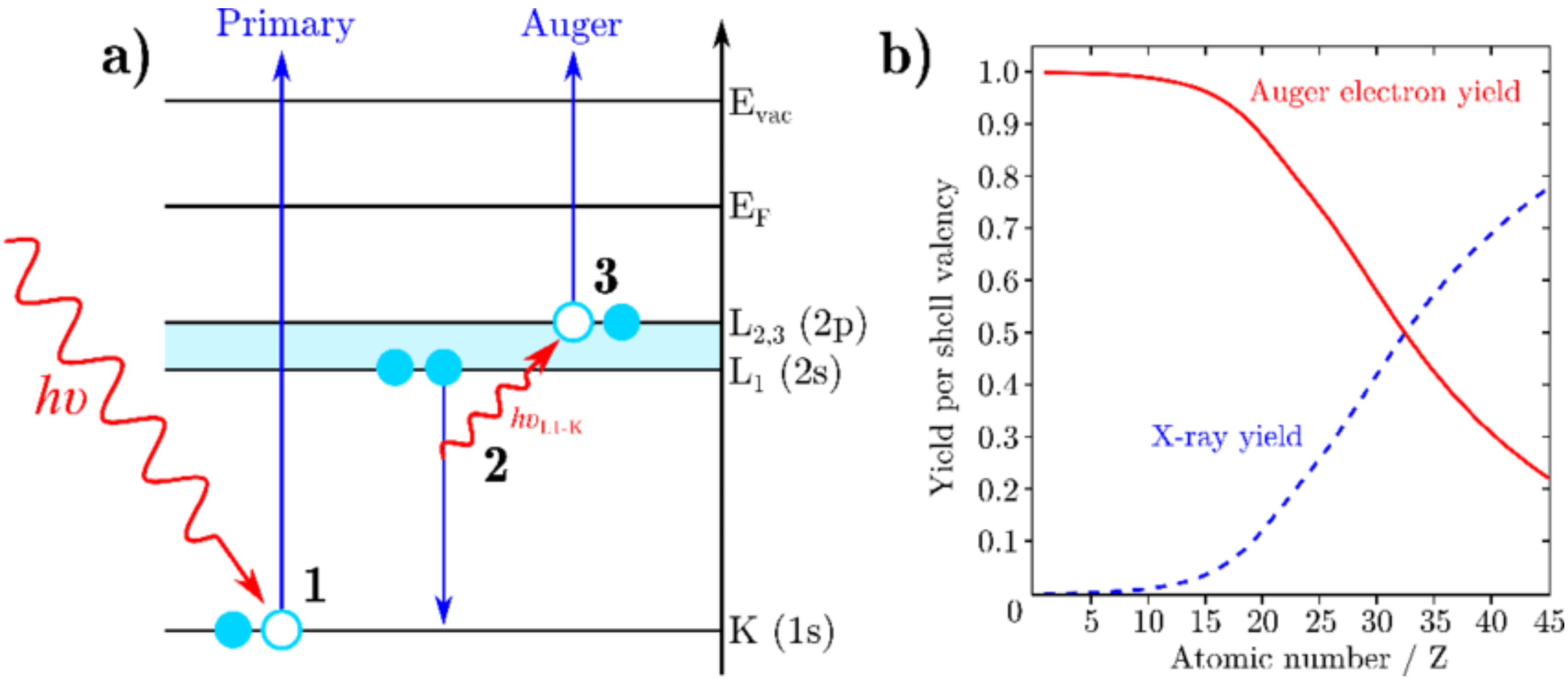
Auger features

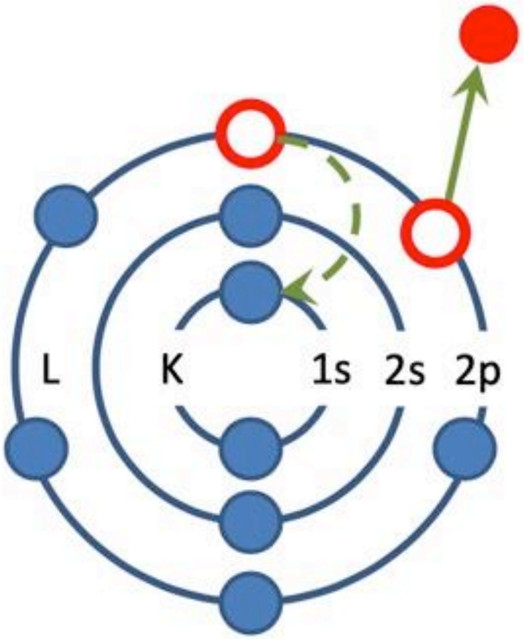
Auger electron emission occurs also when x-rays impinge a sample. Auger electron is initiated by the creation of an ion with an inner shell vacancy. Auger electrons are emitted in the relaxation of the excited ion. An electron from a higher lying energy level fills the inner shell vacancy with the simultaneous emission of an Auger electron.

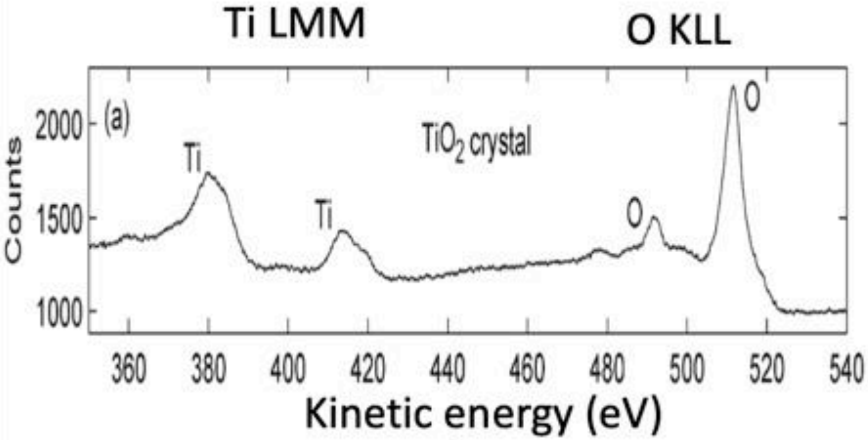
It is a ***three-electron*** process.

3 Distinct Auger Peaks are seen in the data for Copper




a)
Primary
Auger
E_{vac}
E_F
3
$L_{2,3}$ (2p)
L_1 (2s)
$h\upsilon$
$h\upsilon_{L1\text{-}K}$
2
1
K (1s)
b)
Auger electron yield
X-ray yield
Yield per shell valency
Atomic number / Z
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5
10
15
20
25
30
35
40
45





Nomenclature: ABC, with A: level of initial core hole, B: level from which A is filled, C: level from which Auger electron is emitted.
Example: KLL

KE of Auger electrons are independent of incident photon energy: $KE_{ABC} = BE_A - BE_B - BE_{C^*}$.
BE_{C^*} is slightly different from BE_C because of the hole in level B

Satellites

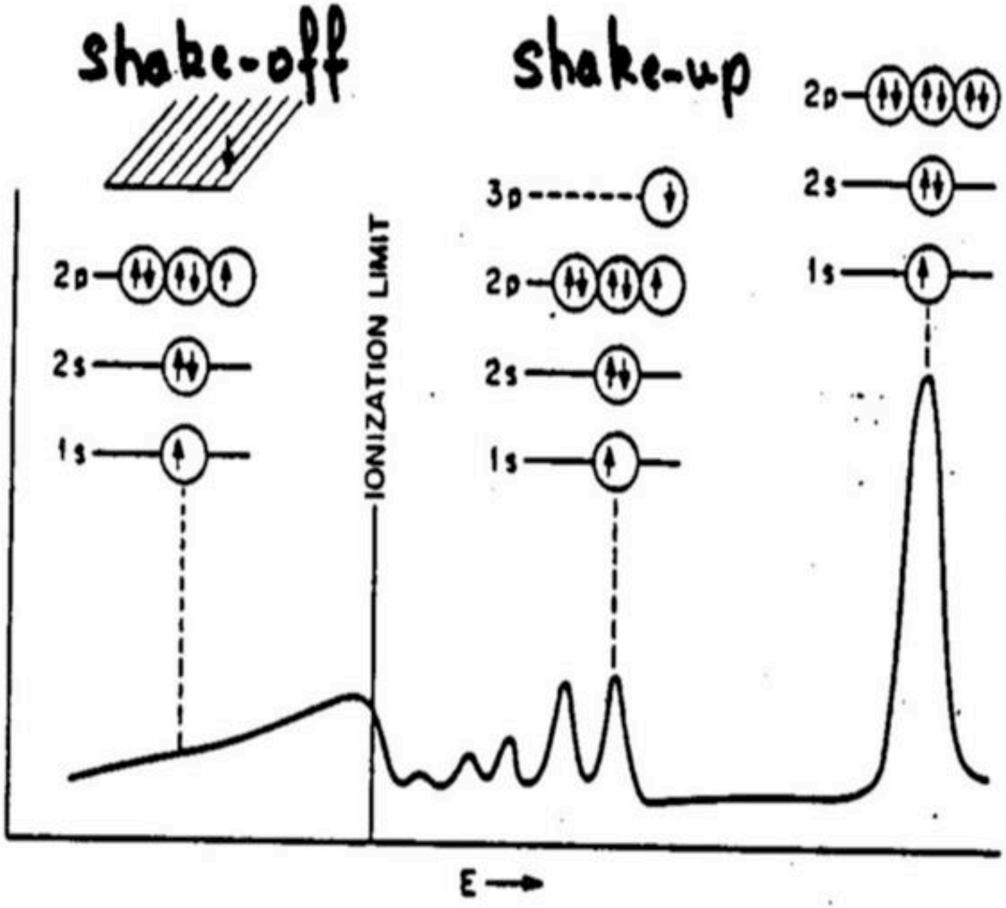
Satellites arise when a core electron is removed by a photoionization. There is a sudden change in the effective charge due to the loss of shielding electrons. (This perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionization).

Two types

Shake-up: The outgoing electron interacts with a valence electron and excites it (shakes it up) to a higher energy level. As a consequence the energy core electron is reduced and a satellite structure appears a few eV below (KE scale) the core level position.

Shake-off: The valence electron is ejected from the ion completely (to the continuum). Appears as a broadening of the core level peak or contribute to the inelastic background.

Shake-up satellites: distinct peaks a few eV below the main line.
Shake-off satellites: broad feature at lower energy w.r.t. to main line.



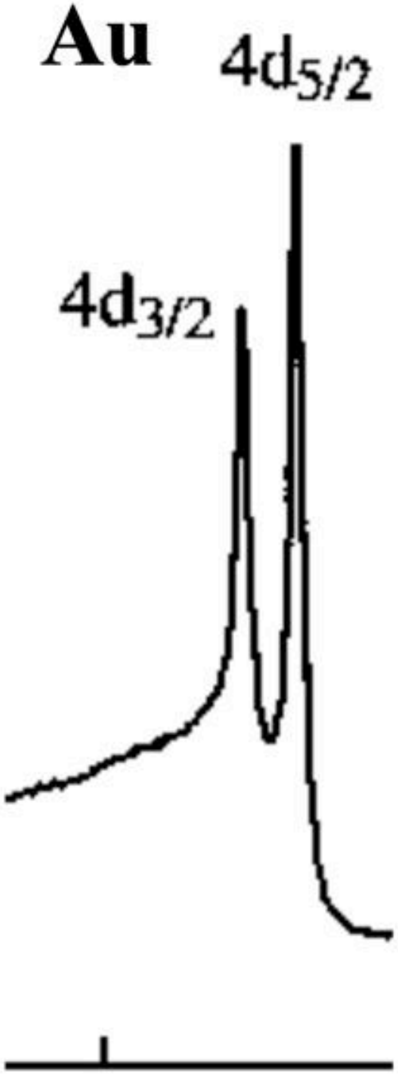
Multiplet splitting

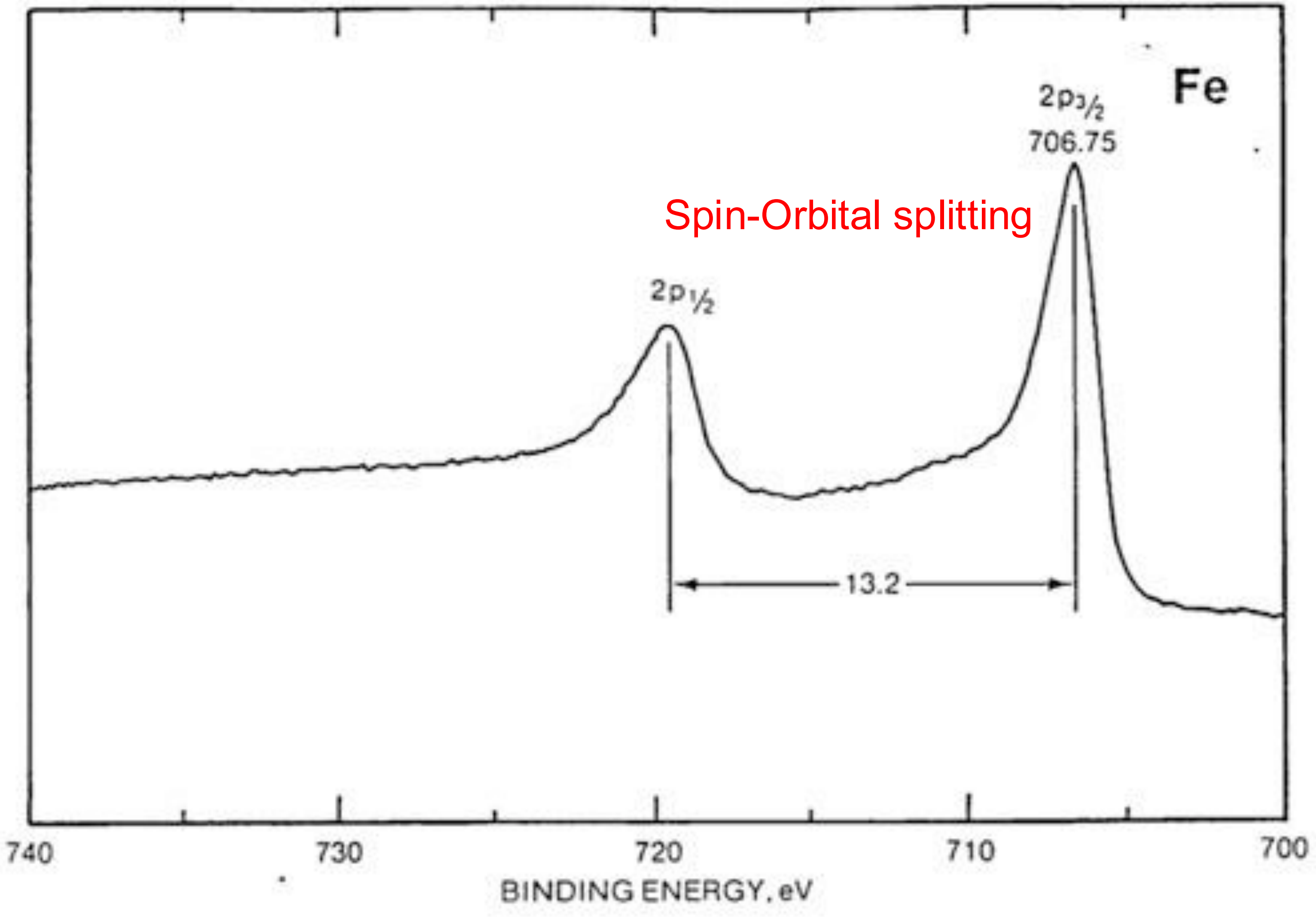
For p, d and f peaks, two peaks are observed.

The separation between the two peaks are named **spin orbital splitting**. The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.

The **peak area ratios** of a core level of an element in different compounds are also nearly the same.

Spin orbital splitting and peak area ratios assist in element identifications.



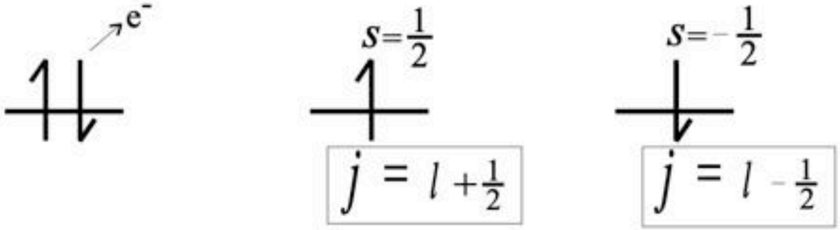


Spin-Orbital splitting

Spin-orbital splitting

Peak Notations

L-S Coupling ($j = l \pm s$)



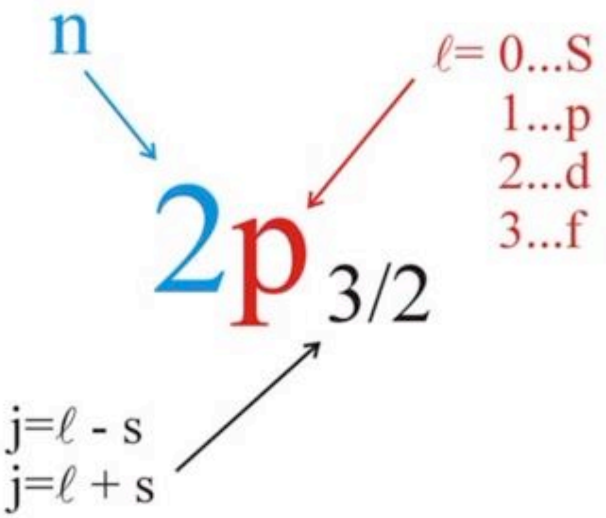
e^-

$s=\frac{1}{2}$

$\boxed{j = l + \frac{1}{2}}$

$s=-\frac{1}{2}$

$\boxed{j = l - \frac{1}{2}}$



n

$2p_{3/2}$

ℓ= 0...S

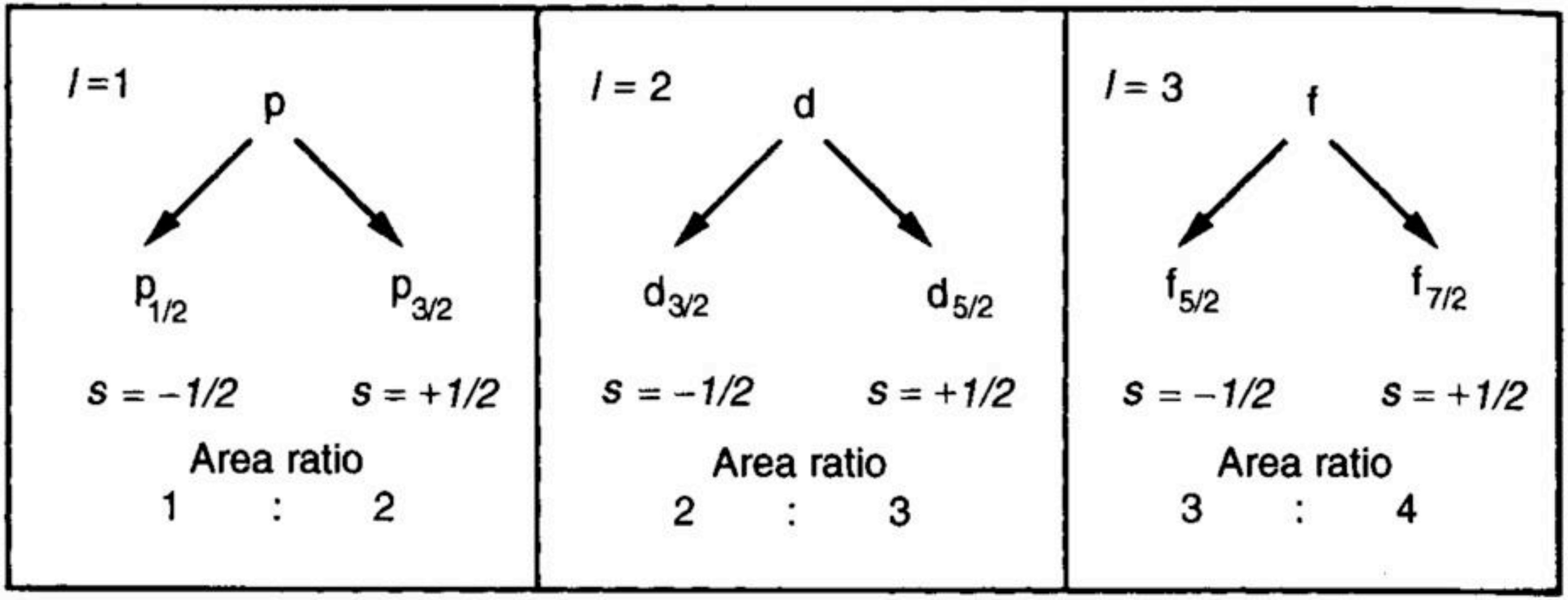
1...p

2...d

3...f

j=ℓ - s

j=ℓ + s



$l=1$

p

$p_{1/2}$ $p_{3/2}$

$s = -1/2$ $s = +1/2$

Area ratio

1 : 2

$l = 2$

d

$d_{3/2}$ $d_{5/2}$

$s = -1/2$ $s = +1/2$

Area ratio

2 : 3

$l = 3$

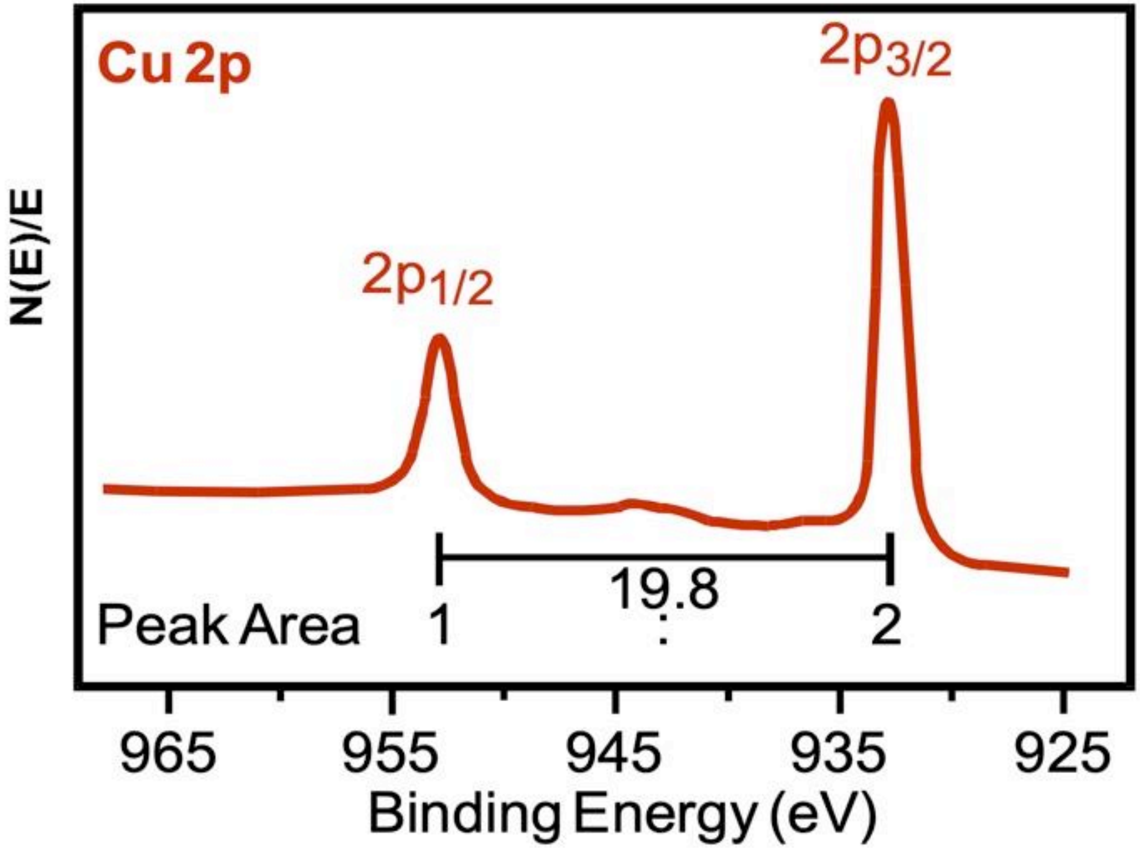
f

$f_{5/2}$ $f_{7/2}$

$s = -1/2$ $s = +1/2$

Area ratio

3 : 4

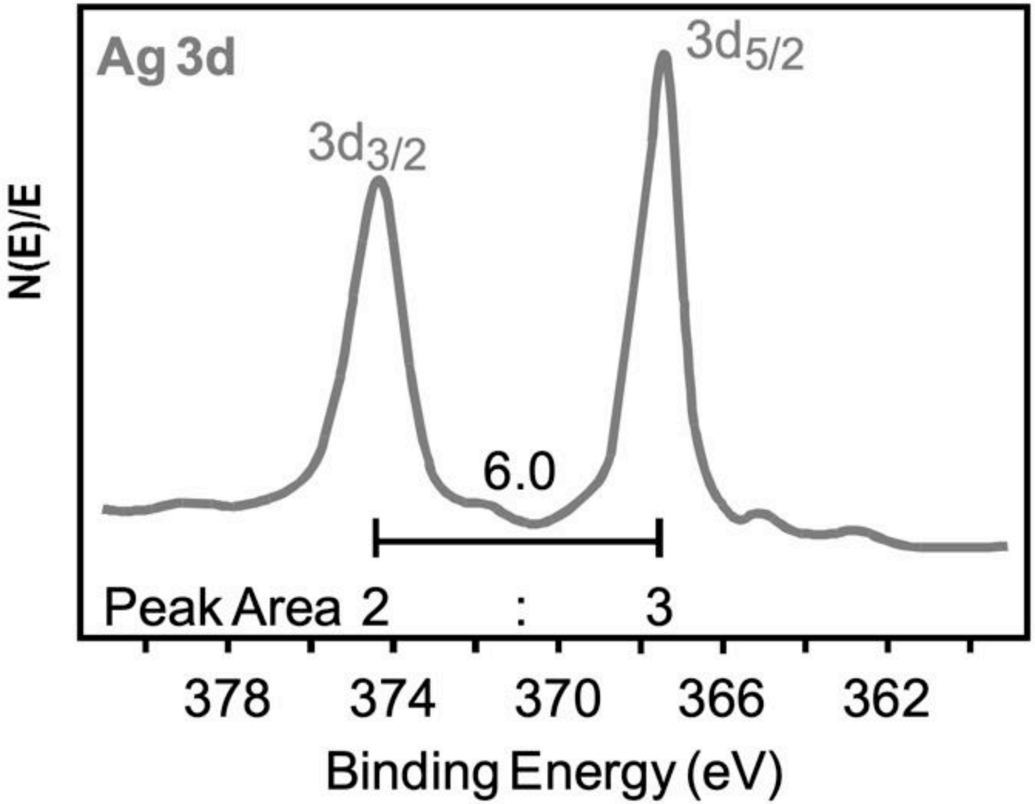


Orbital=p

l=1

s=+/-1/2

ls=1/2,3/2

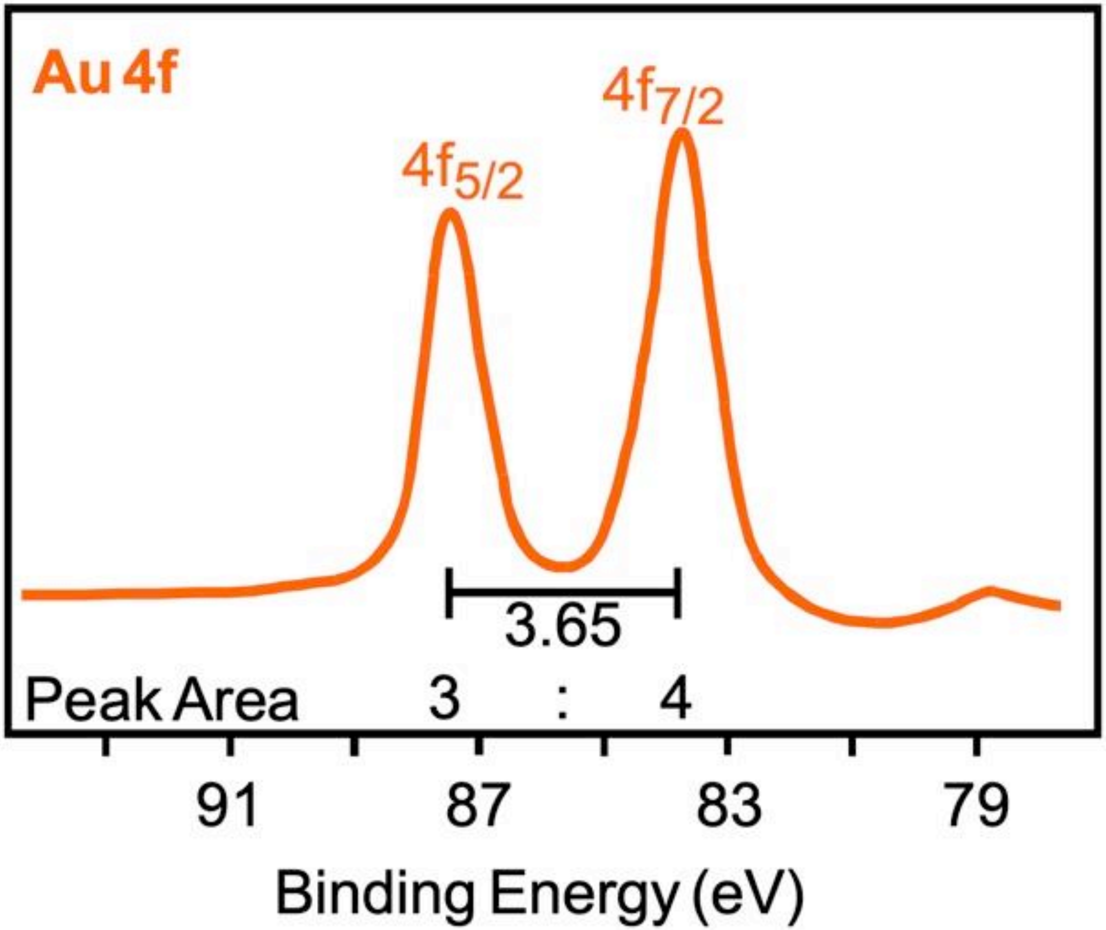


Orbital=d

l=2

s=+/-1/2

ls=3/2,5/2

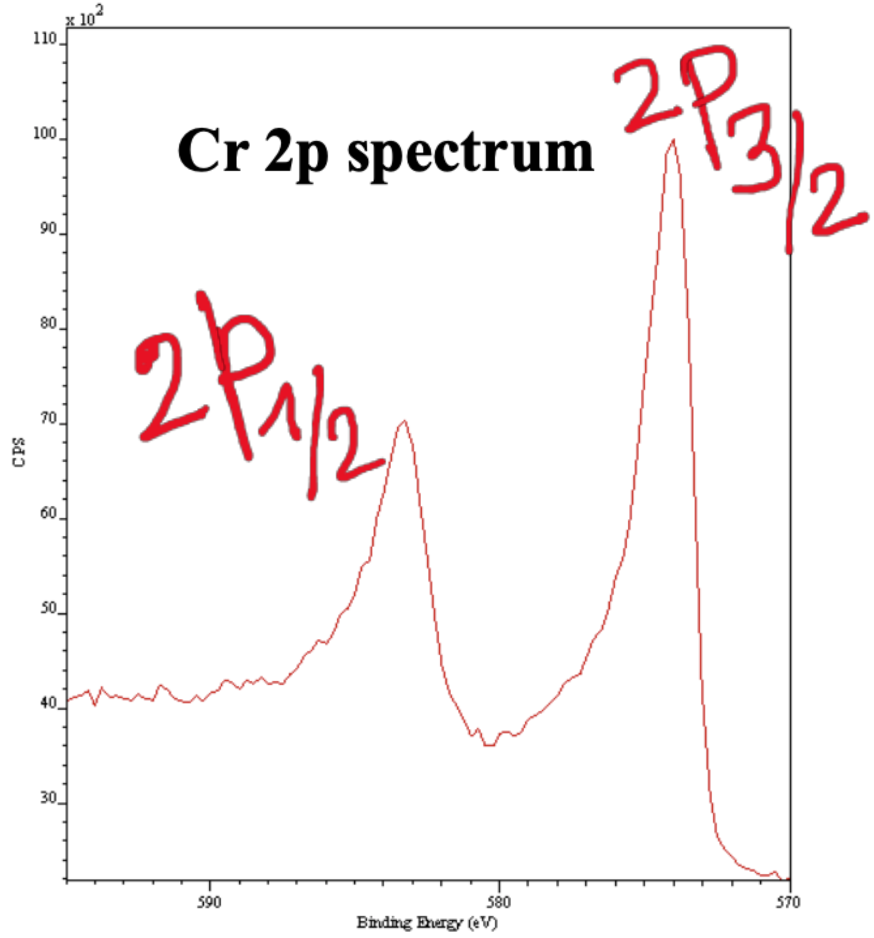


Orbital=f

l=3

s=+/-1/2

ls=5/2,7/2



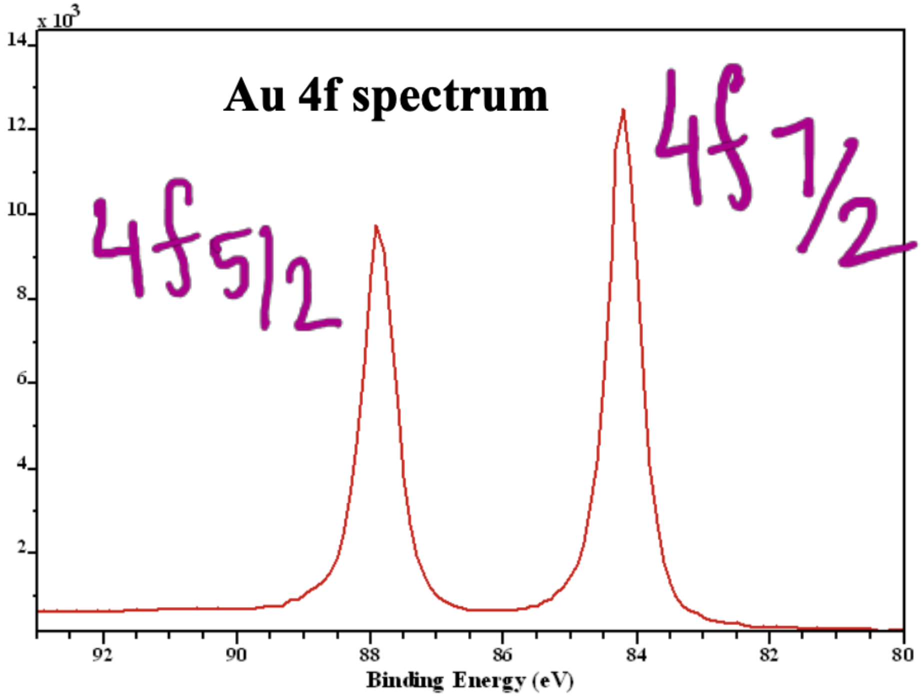
$$(2j_- + 1) : (2j_+ + 1)$$

$$\left[2\times\frac{1}{2}+1\right] : \left[2\times\frac{3}{2}+1\right]$$

$$\Rightarrow 2 : 4$$

$$\Rightarrow 1 : 2$$

Ratio = 1/2



Ratio = ??

$$2\times\frac{5}{2}+1 : 2\times\frac{7}{2}+1$$

$$= 6:8$$

$$= 3:4$$

Applications

Detect elements and their oxidation state

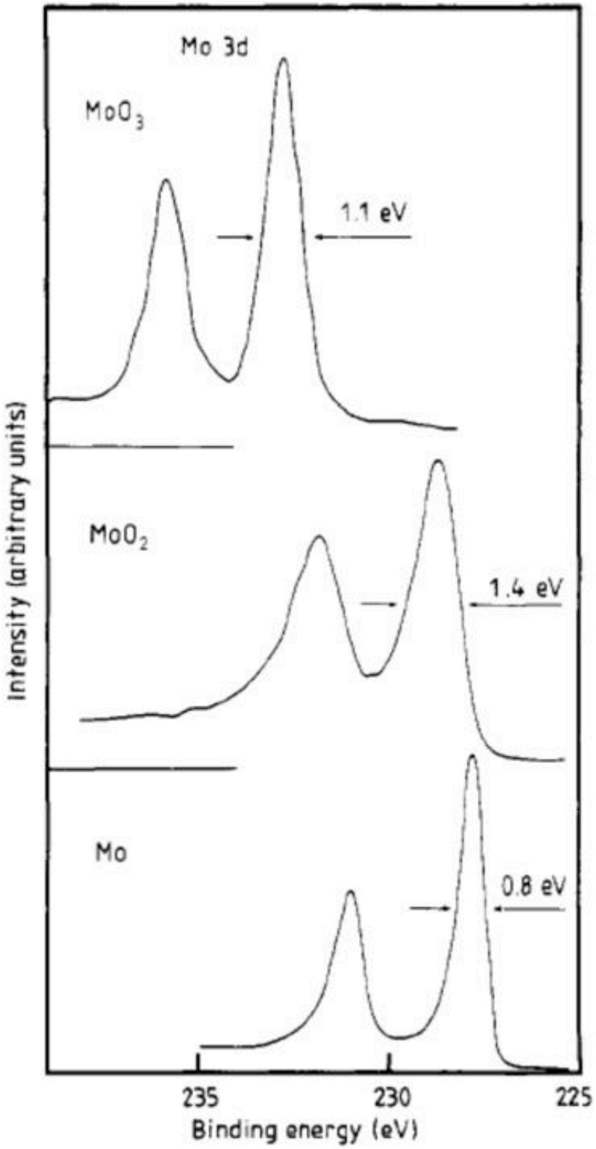
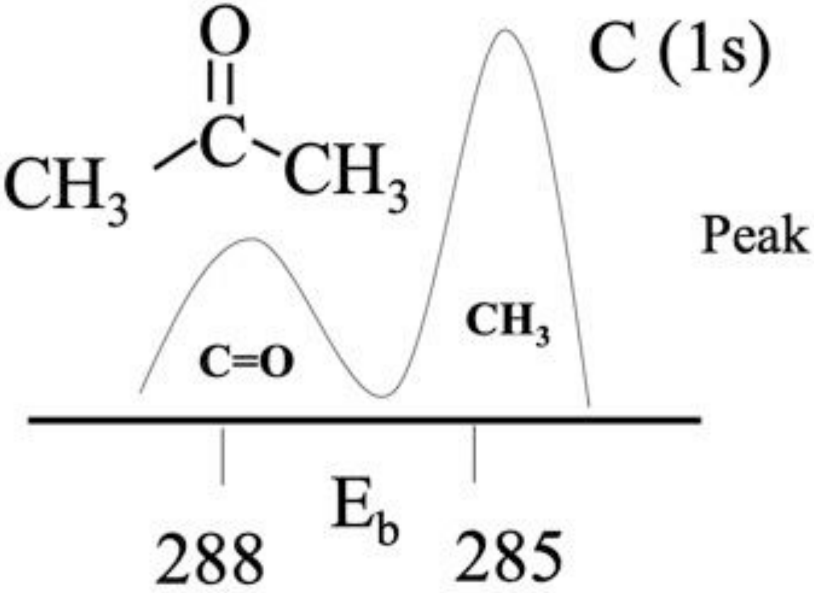
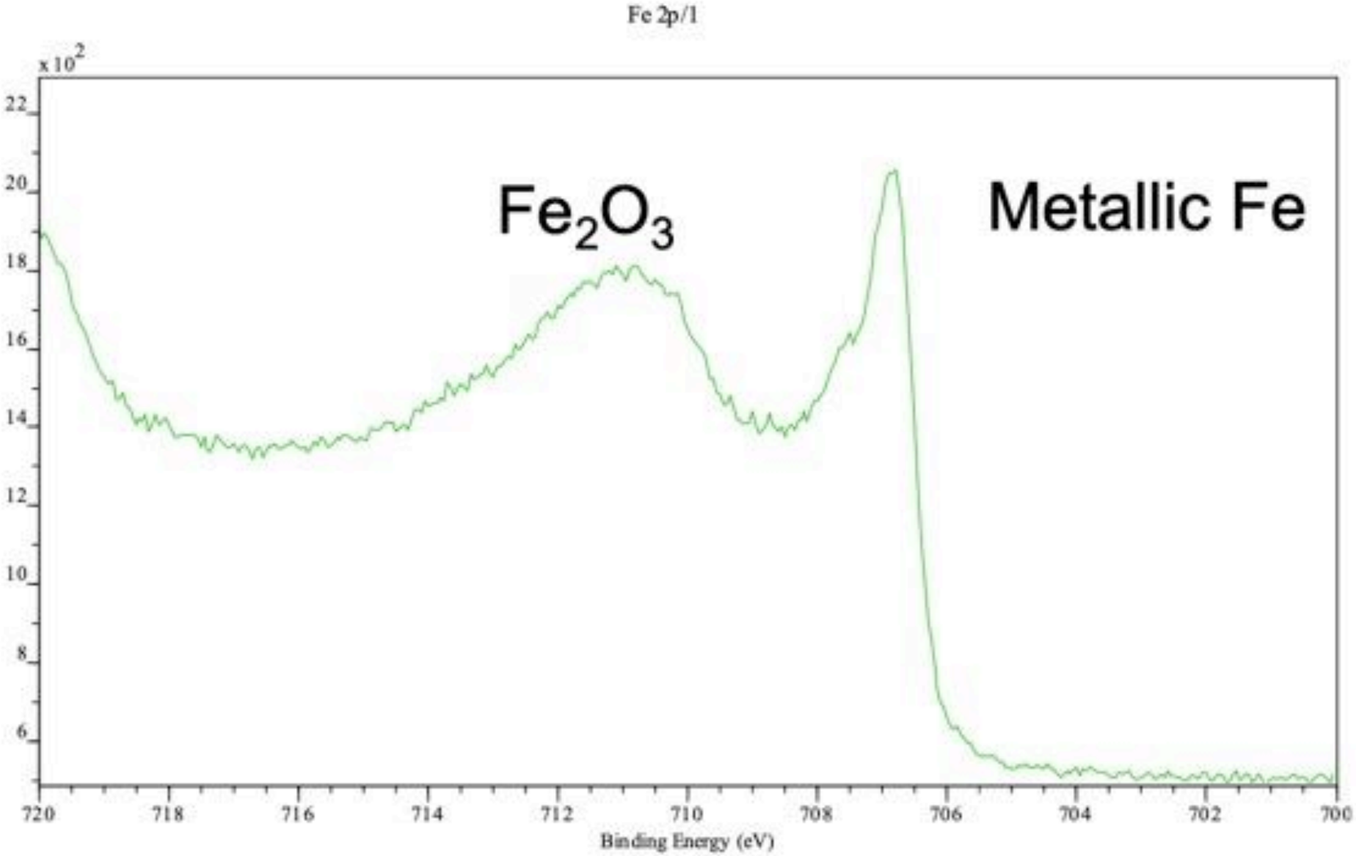


Figure 2. The XPS 3d core level spectra of metallic Mo, MoO_2 and MoO_3.



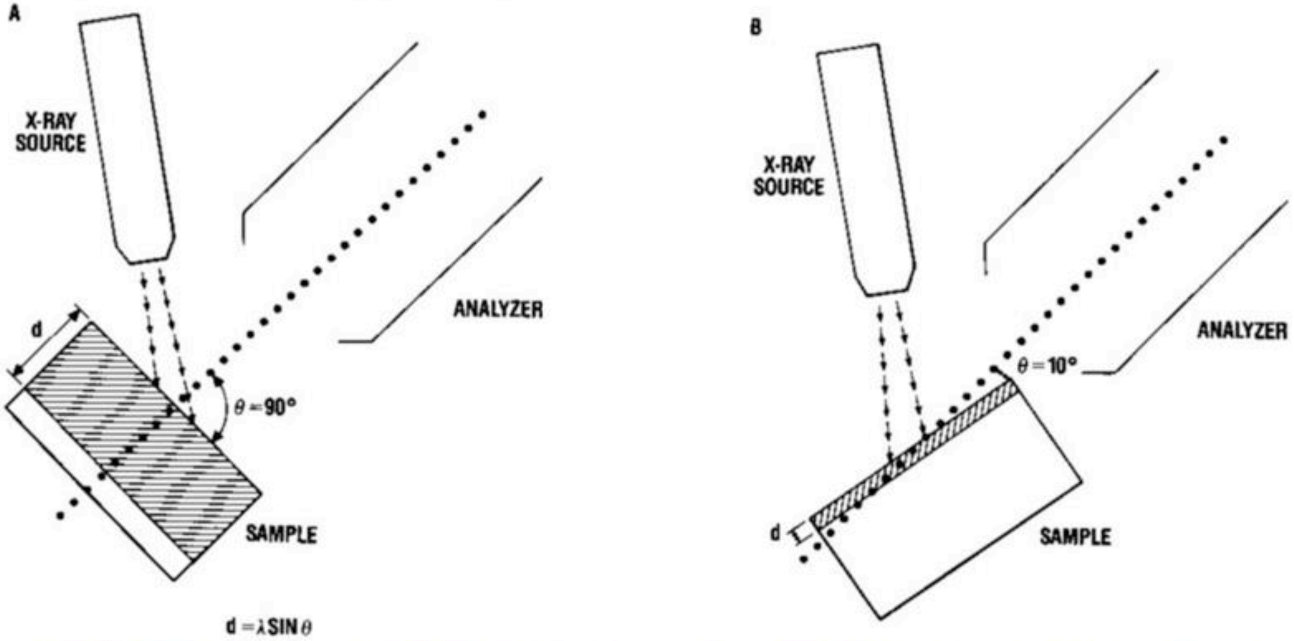
Peak width = 1.1-1.5 eV

Detailed Iron 2p Spectrum of High Purity Iron



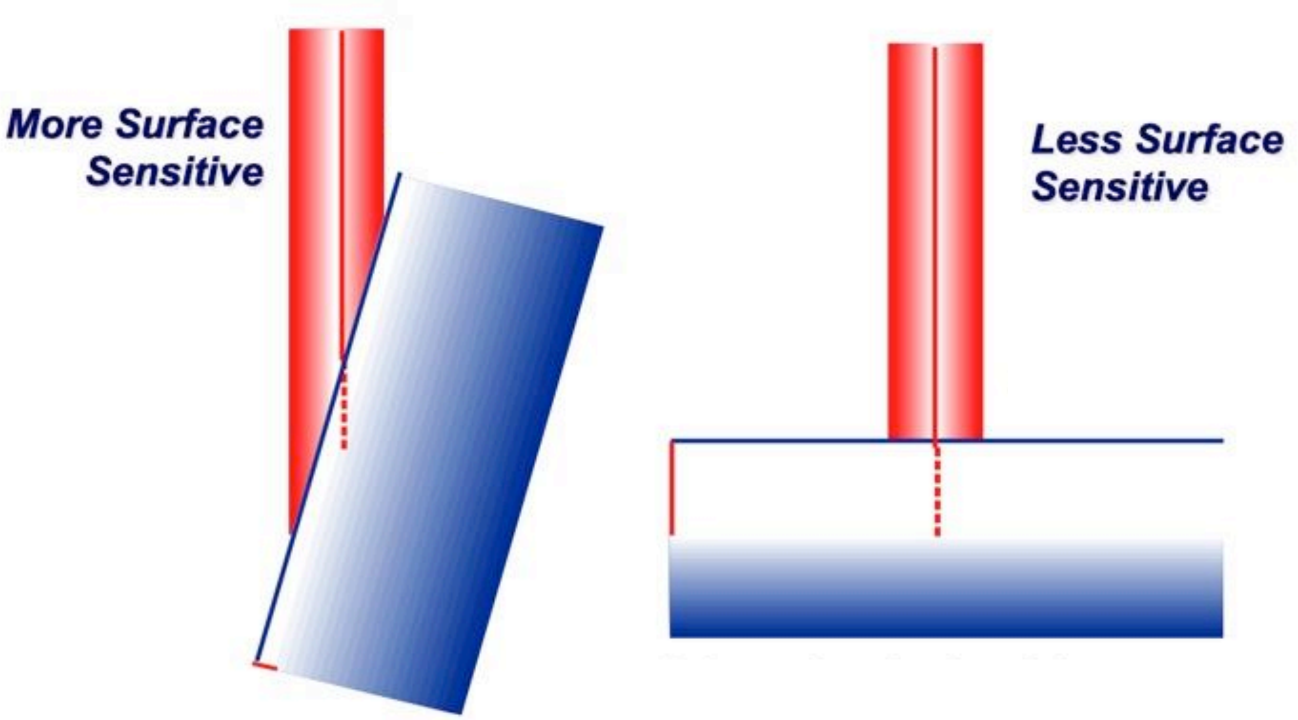
Depth Profiling

The mean free paths (IMFP) are in the range of 5 -100Å falling within 5 –40 Å for inorganic materials. To enhance the surface signal we can vary the photon energy—closer to the attenuation length minimum **or** decrease the angle of electron emission relative to a solid surface.



For example: Au 4f IMFP is about 22Å (d) at angle of 90° using AlKα. The depth (d) probed by XPS becomes about 4-5 Å at angle of 10°.

Probe depth

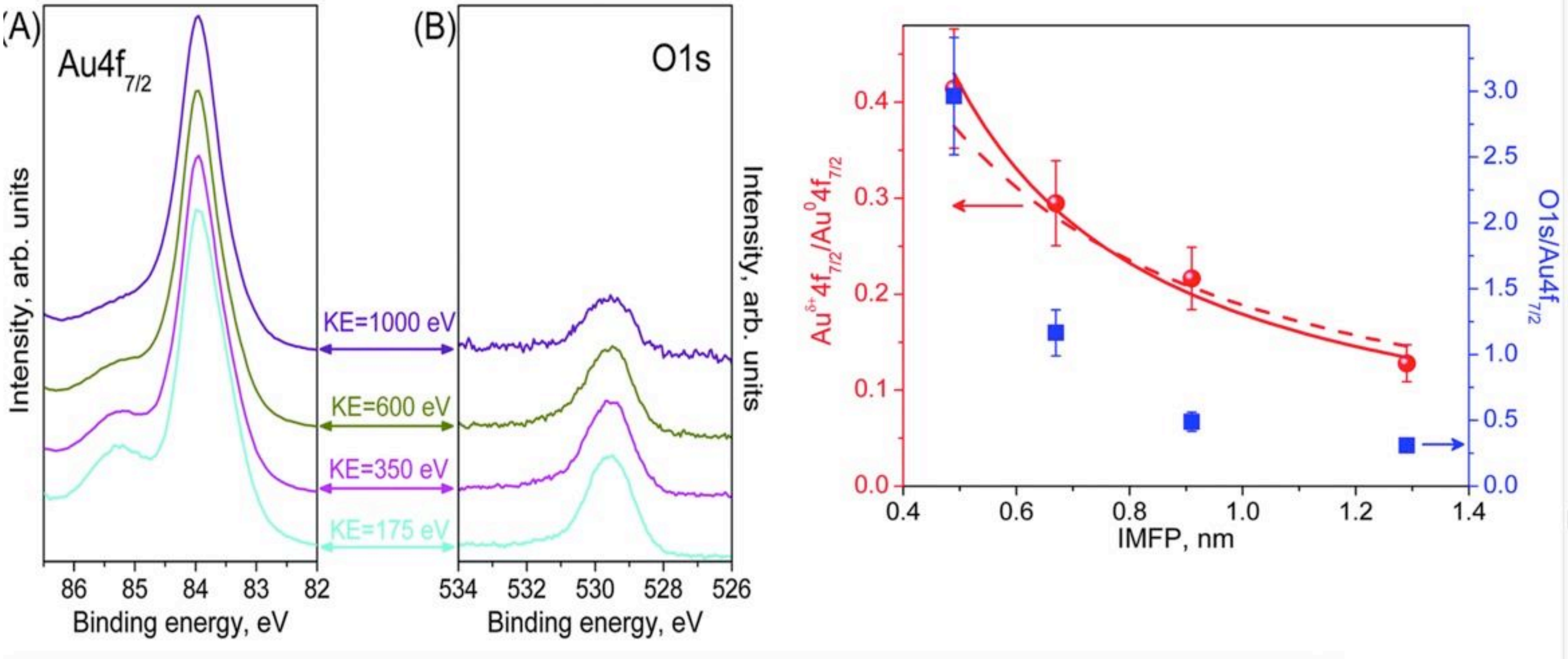


Probe Depth (d) = 3λsinθ

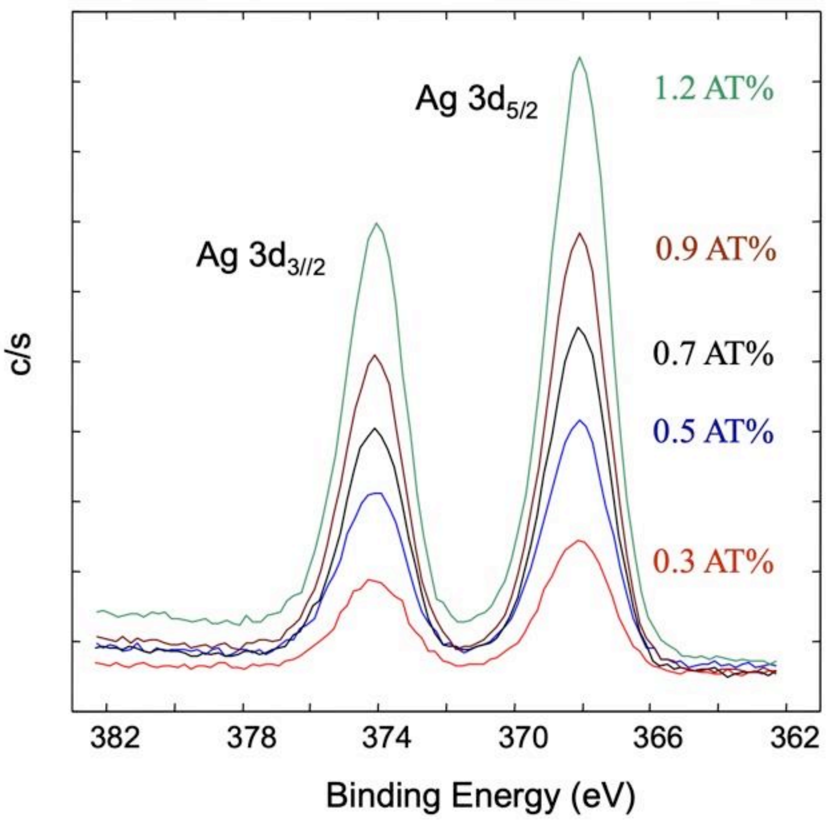
λ= inelastic mean free path

θ=emission angle relative to the surface

Example of Depth Profiling



Relative concentration



Intensity of XPS Signals

Contribution of element A in depth d to photoemission signal

$$I_{\mathrm{A}} = \Phi_{\mathrm{X}} \times c_A(d) \times \sigma_{i,j}(h\nu) \times e^{-\frac{d}{\lambda\cos(\theta)}} \times A_{Analyzer} \times T_{Analyzer}$$

Concentration of element A at depth d

Analyzer transmission

Angular acceptance

Photon flux

Attenuation from depth d at detection angle θ

Subshell ionization cross section

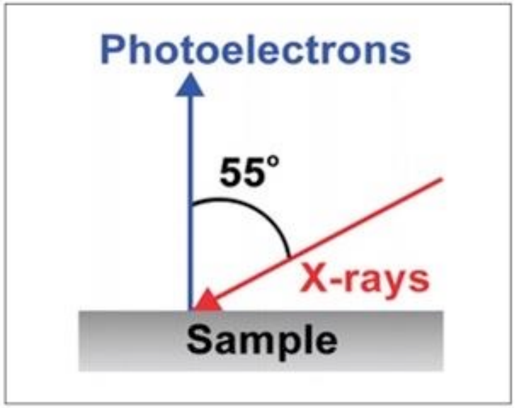
So, if we collect XPS data of same peak with same instrument and same excitation source in different samples, we can directly correlate the intensity with concentration of the element in the samples.

Relative sensitivity factor

$$\frac{n_a}{n_b} = \frac{I_a / S_a}{I_b / S_b}$$

When quantifying XPS spectra, Relative Sensitivity Factors (RSF) are used to scale the measured peak areas so that variations in the peak areas are representative of the amount of material in the sample surface

XPS Geometry



Orbital Angular Symmetry Factor

$$L_A\,(g) = 1 + b_A\,(3\sin^2 g/2 - 1)/2$$

where: g = source-detector angle

b = constant for a given sub-shell and X-ray photon

At 54.7° the 'magic angle'

$$L_A = 1$$

If XPS is operating at around 55 degree (the angle between the source and the detector), the angular distribution correction is not required for calculation of photoionisation cross-section.

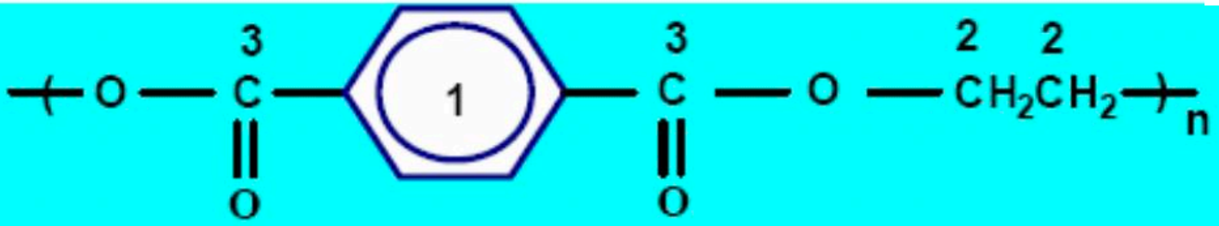
If XPS instrument geometry is not in the magic angle, then a correction (called asymmetry parameter) to the total cross-section has to be considered.

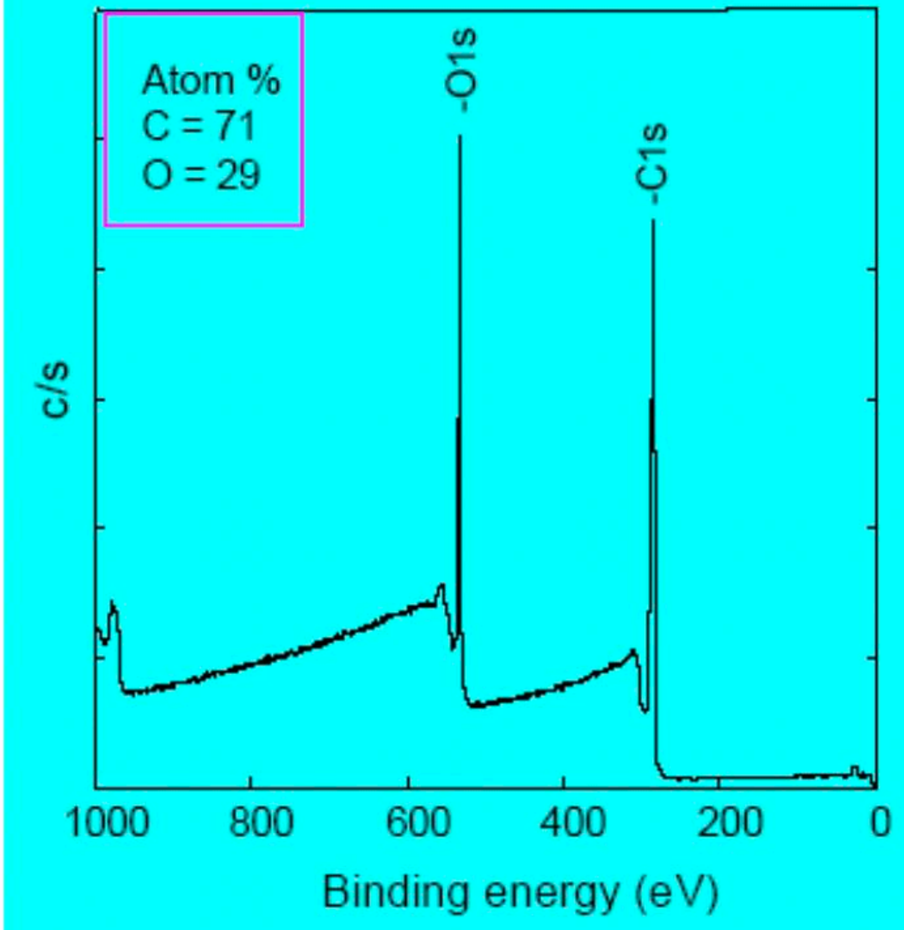
Photoemission intensity

$$\boxed{I(\theta) \propto \frac{\sigma_{total}}{4}[1-\frac{\beta}{4\pi}(3\cos\theta-1)]}$$

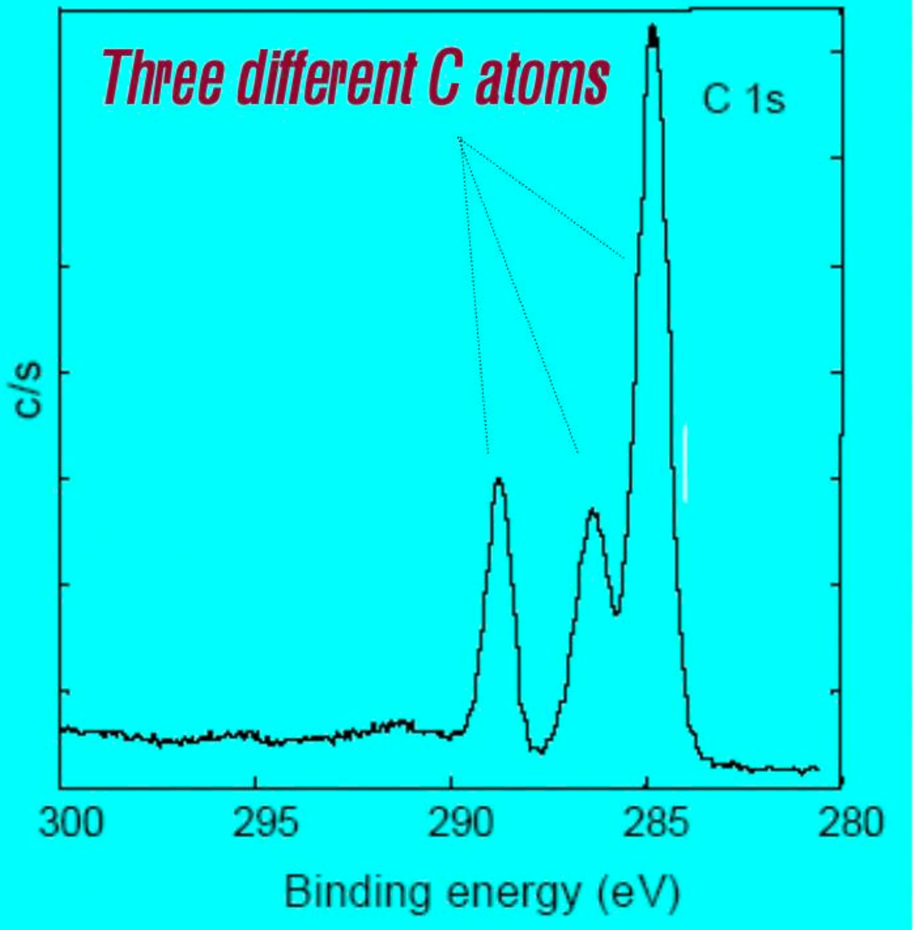
(β: asymmetry parameter, θ: take off angle and σ_{total} the total cross-section)

XPS of Poly(ethylene terephthalate)

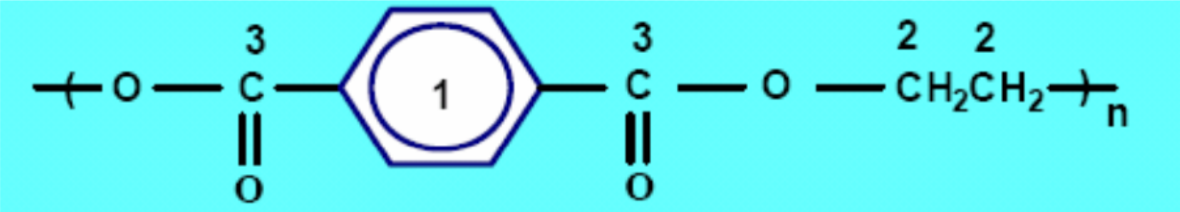




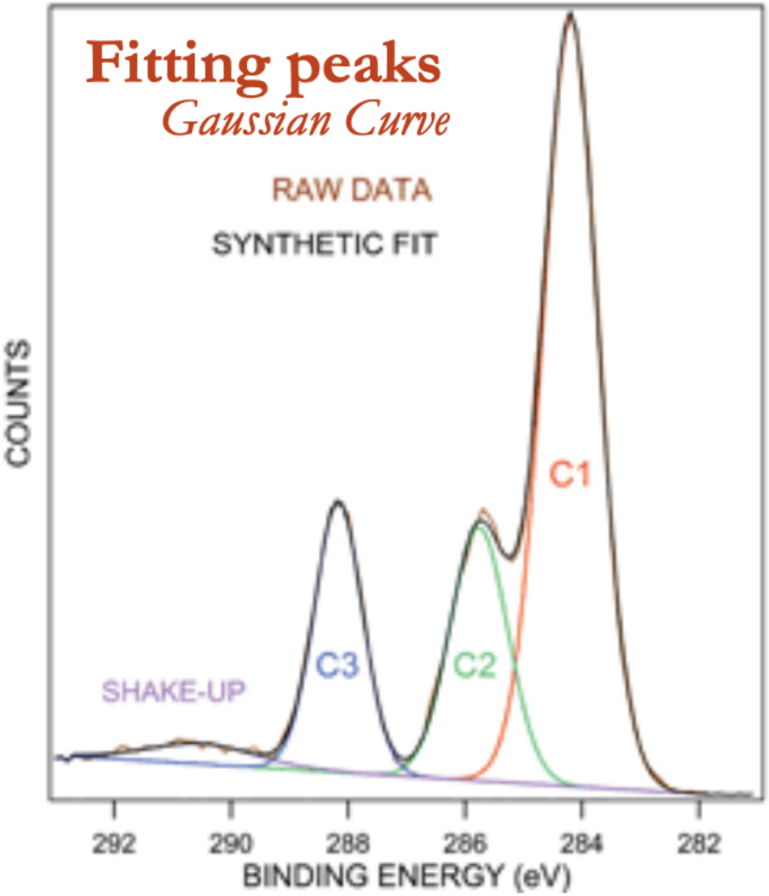
Quantitative elemental information

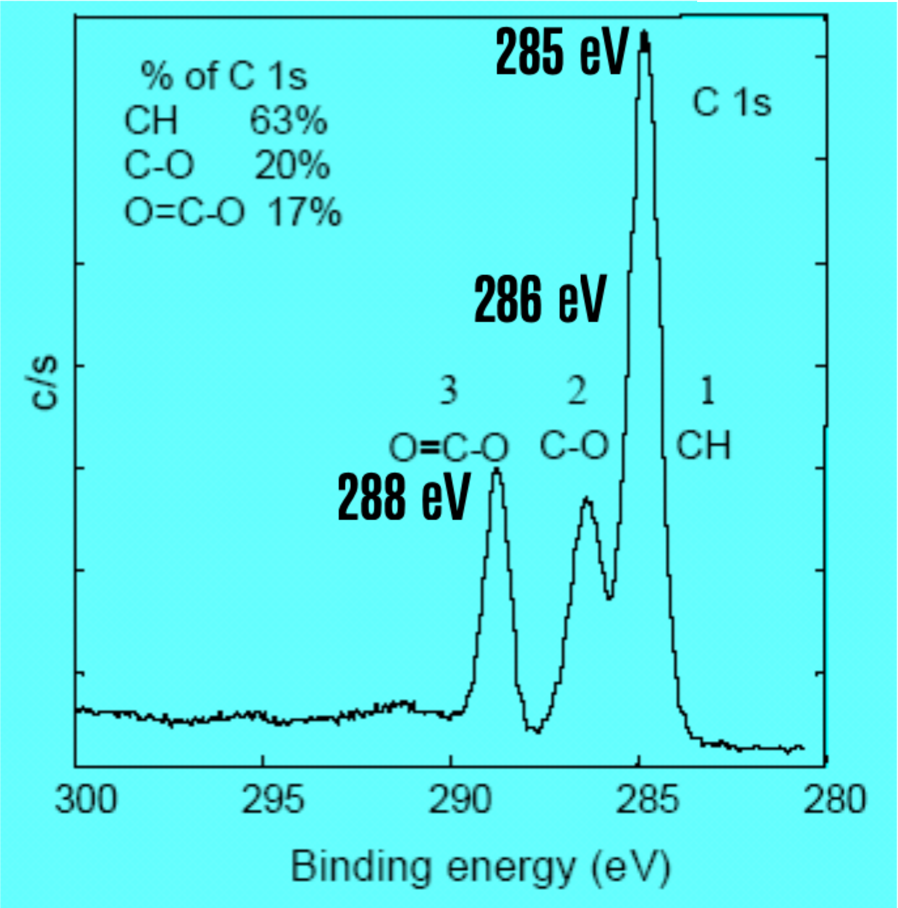


Chemical state information.



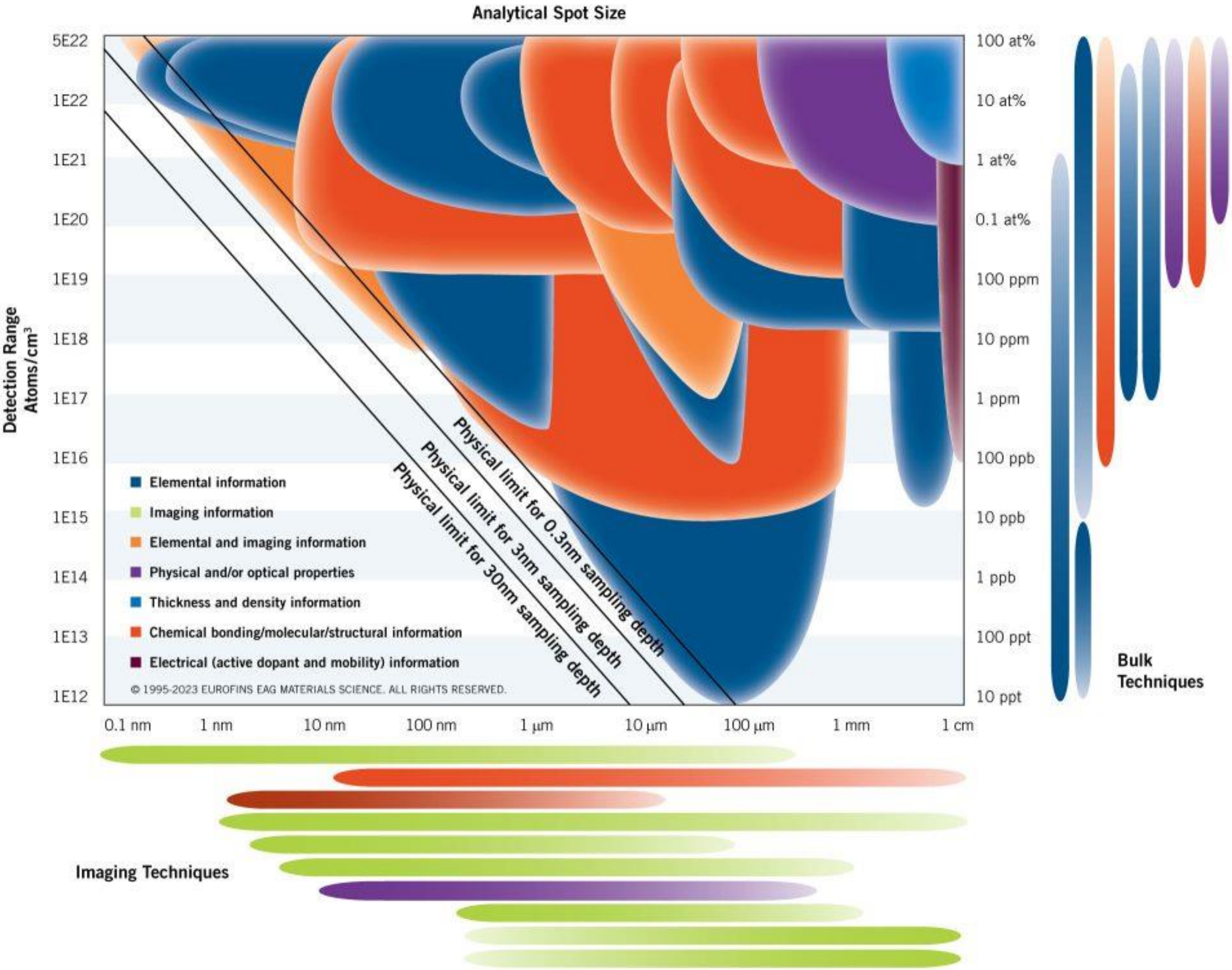
PET CARBON 1S





Chemical state information.

$C1 : C2 : C3 = 3 : 1 : 1$


Analytical Spot Size
Detection Range
Atoms/cm³
5E22
1E22
1E21
1E20
1E19
1E18
1E17
1E16
1E15
1E14
1E13
1E12
100 at%
10 at%
1 at%
0.1 at%
100 ppm
10 ppm
1 ppm
100 ppb
10 ppb
1 ppb
100 ppt
10 ppt
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
Physical limit for 0.3nm sampling depth
Physical limit for 3nm sampling depth
Physical limit for 30nm sampling depth
Elemental information
Imaging information
Elemental and imaging information
Physical and/or optical properties
Thickness and density information
Chemical bonding/molecular/structural information
Electrical (active dopant and mobility) information
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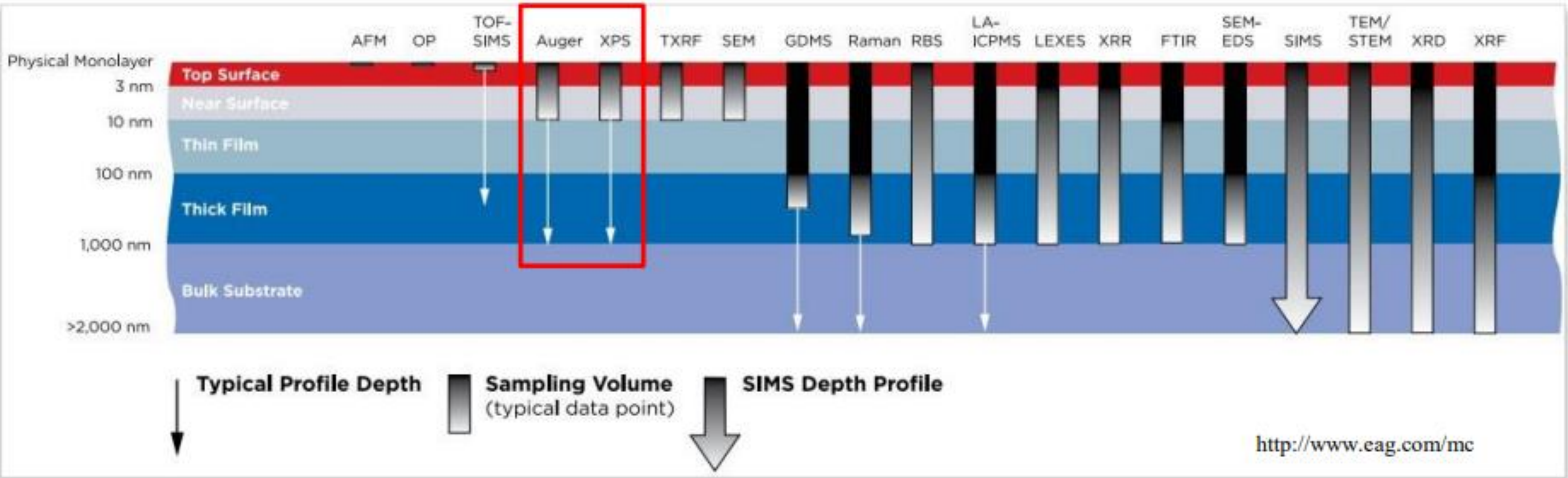
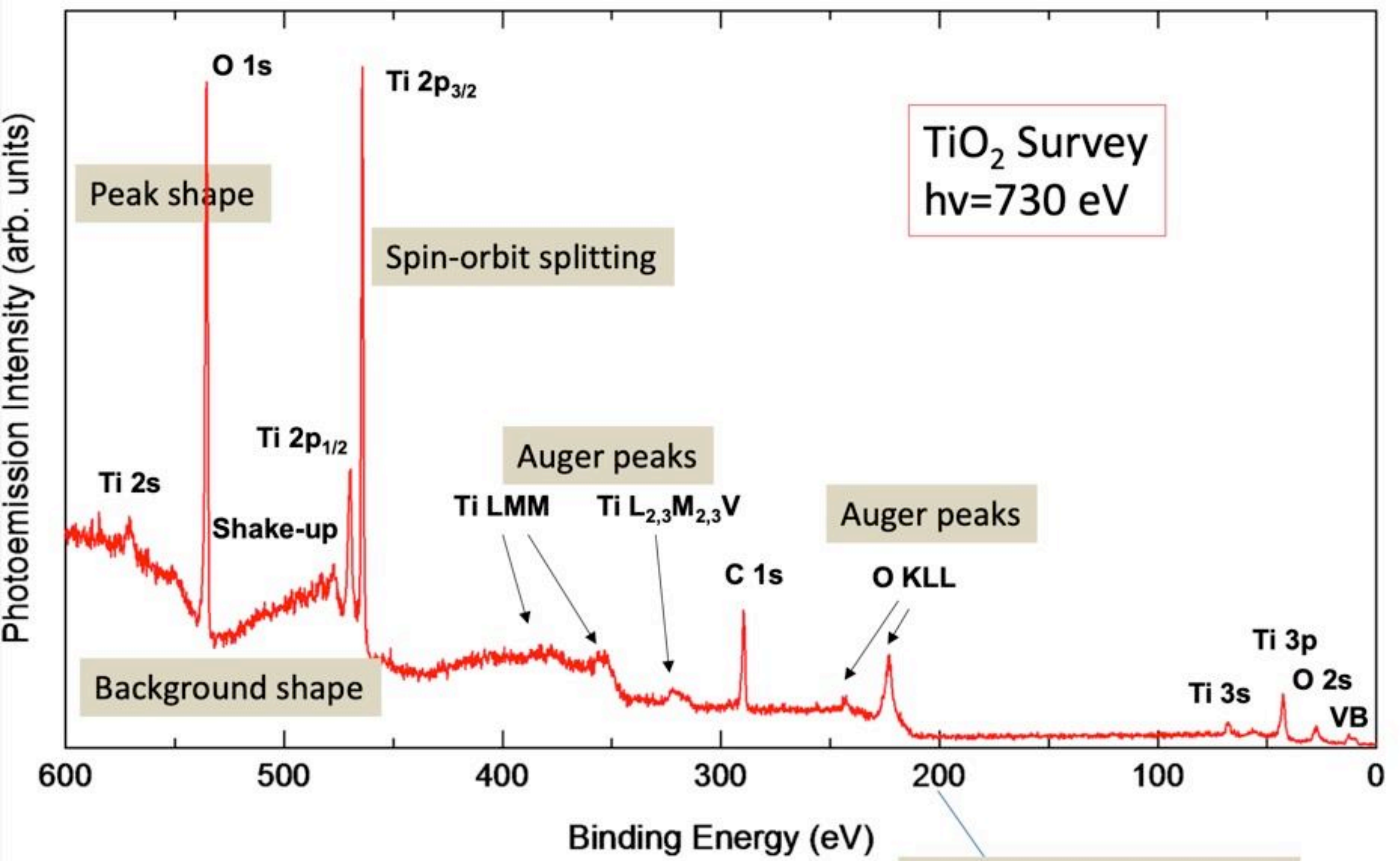
Bulk
Techniques
Imaging Techniques

Typical Analysis Depths for Techniques



http://www.eag.com/mc

XPS Survey Scan



Peak shape

Spin-orbit splitting

Auger peaks

Auger peaks

Background shape