

X-ray Photoelectron Spectroscopy (XPS)

As part of the course 'Characterization of Catalysts and Surfaces'

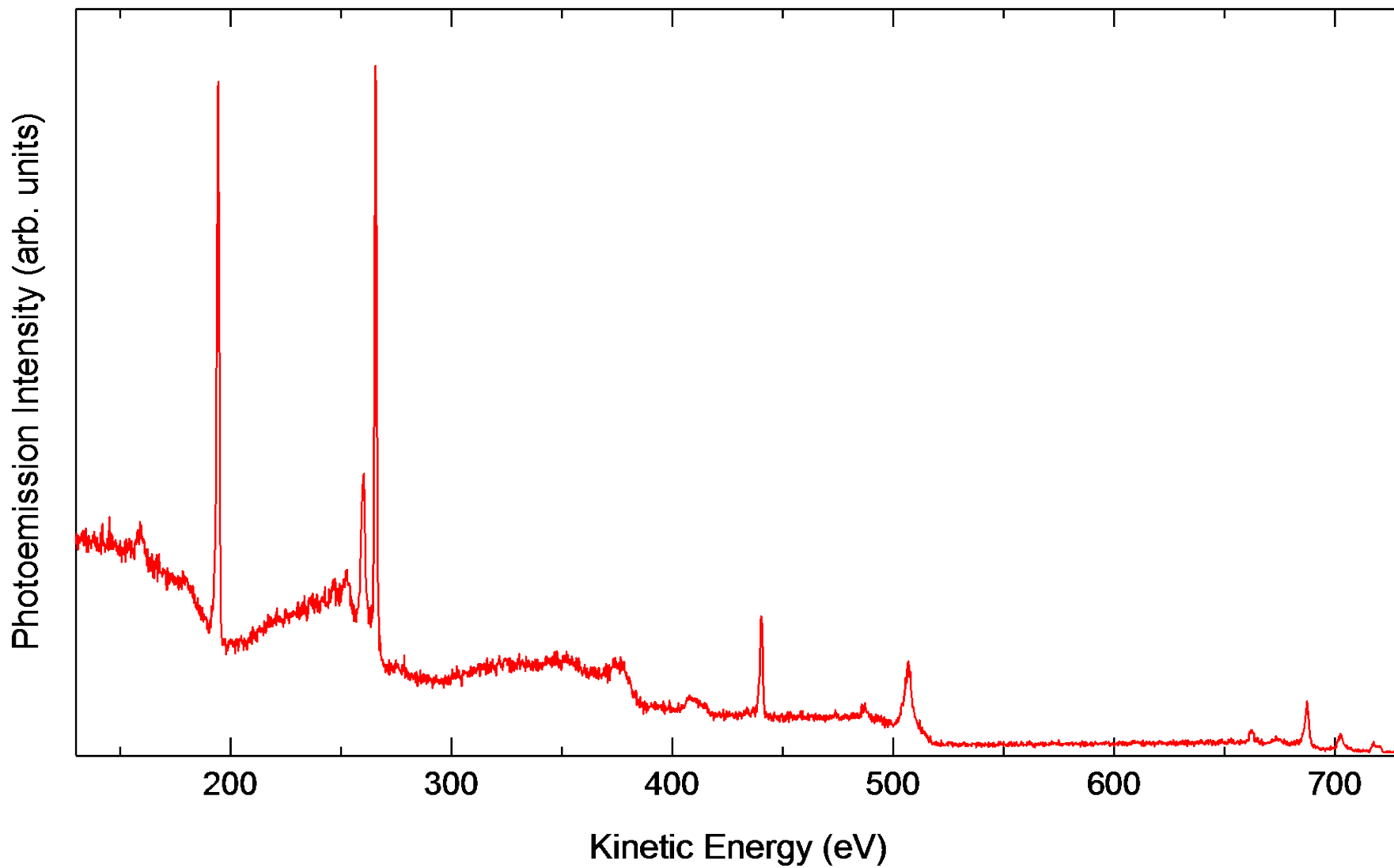
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Resource for further reading: *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, D. Briggs, J.T. Grant, eds., IM Publications and Surface Spectra Ltd., 2003

XPS in a nut-shell

- X-ray photoelectron spectroscopy (XPS) is a classical method for the semiquantitative analysis of surface composition
- It is also referred to as Electron Spectroscopy for Chemical Analysis (ESCA)
- It is based on the photoelectric effect, i.e., emission of electron following excitation of core level electrons by photons
- It is surface sensitive because of the low inelastic mean free path of electrons
- An XPS setup consists of a X-ray source, a sample chamber and an electron analyzer
- XPS requires a monochromatic source of X-rays, i.e., either from a lab based anode or from a synchrotron, with a X-ray monochromator in both cases
- Traditionally, XPS works only in ultrahigh vacuum because of scattering of electrons in gases
- Since recently, XPS can also be performed in the mbar pressure range

This is a photoelectron spectrum of TiO_2

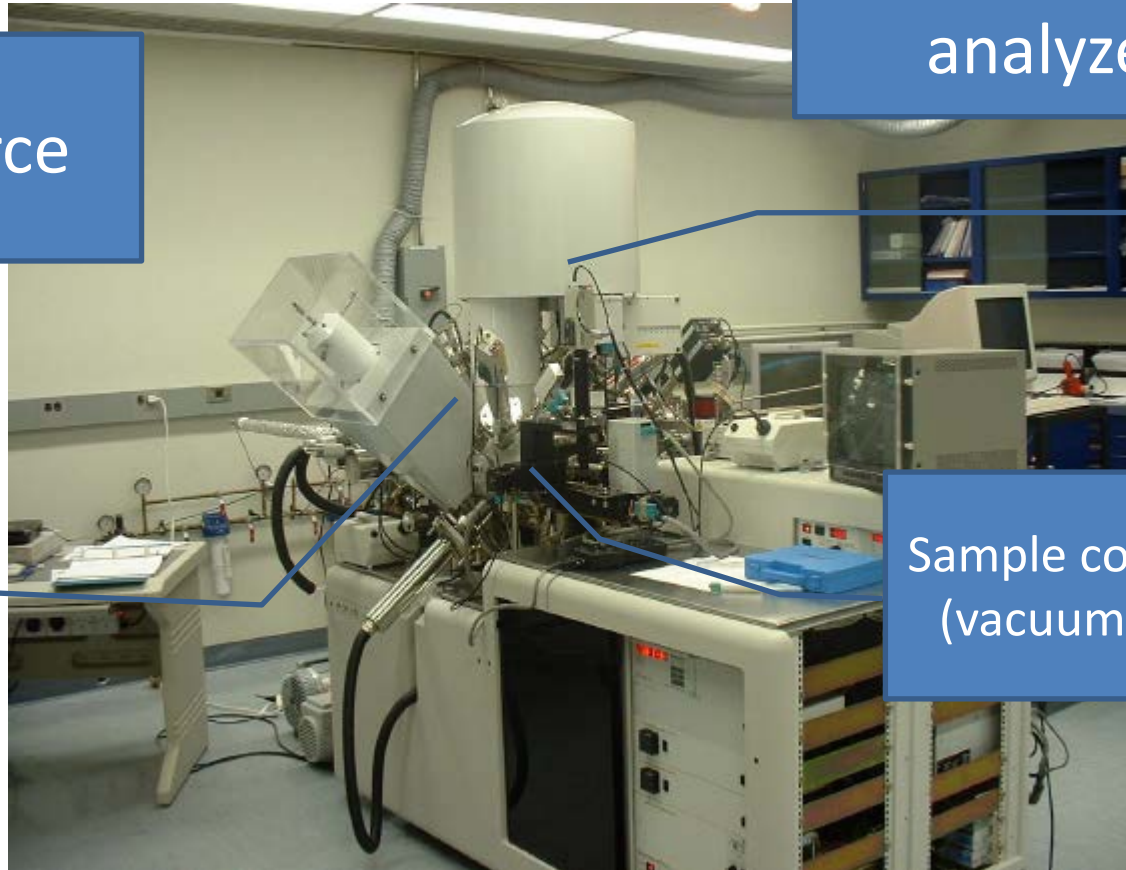


This is a lab based XPS instrument

X-ray source

Electron analyzer

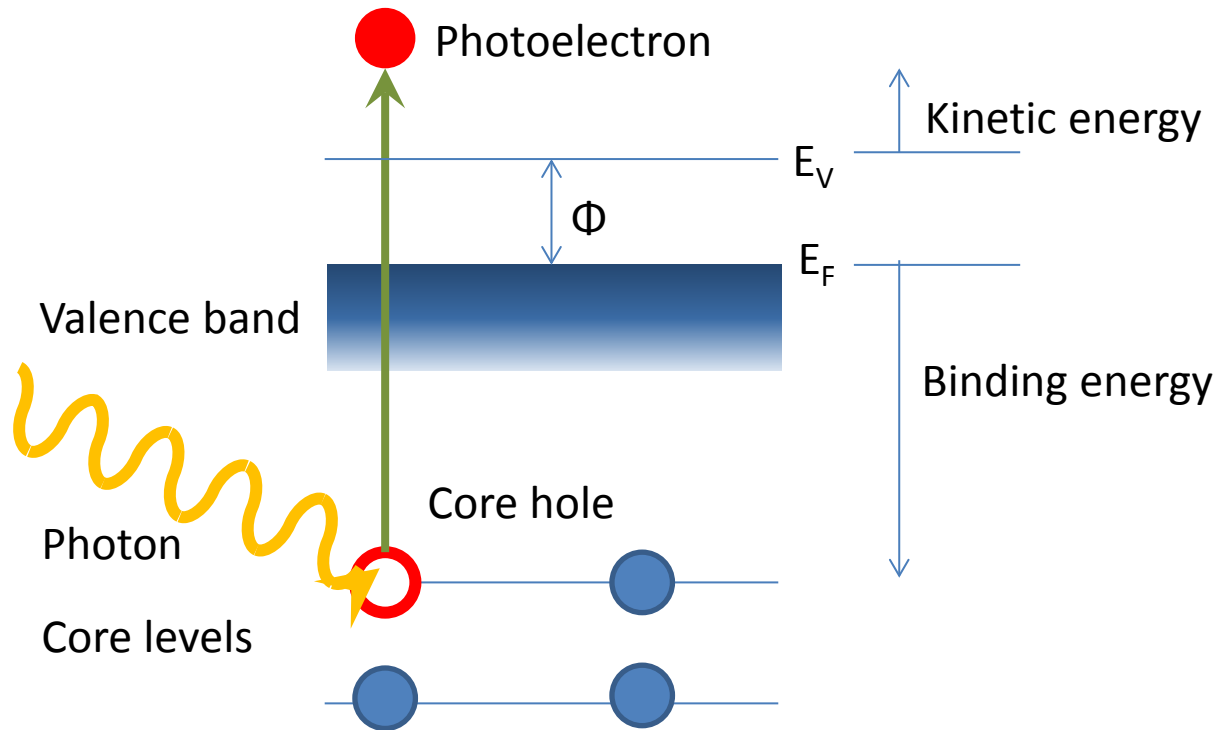
Sample compartment
(vacuum chamber)



Related methods

Method	Particle in	Energy range (eV)	Particle out	Information, electronic level	Technique
Photoemission	Photon	100-10000	Electron	Filled core states	XPS
Photoemission	Photon	0-10 (100)	Electron	Filled valence states	UPS
Inverse photoemission	Electron	100-1000	Photon	Empty states	IPES
Electron energy loss	Electron	10-10000	Electron	Electronic & vibrational transitions	(HR)EELS
Auger	Electron or Photon	10-10000	Electron	Filled states	AES
Absorption/emission	Photon	10-2000	Photon	Electronic transitions, filled states	XRF, XAS, RIXS

The photoemission process

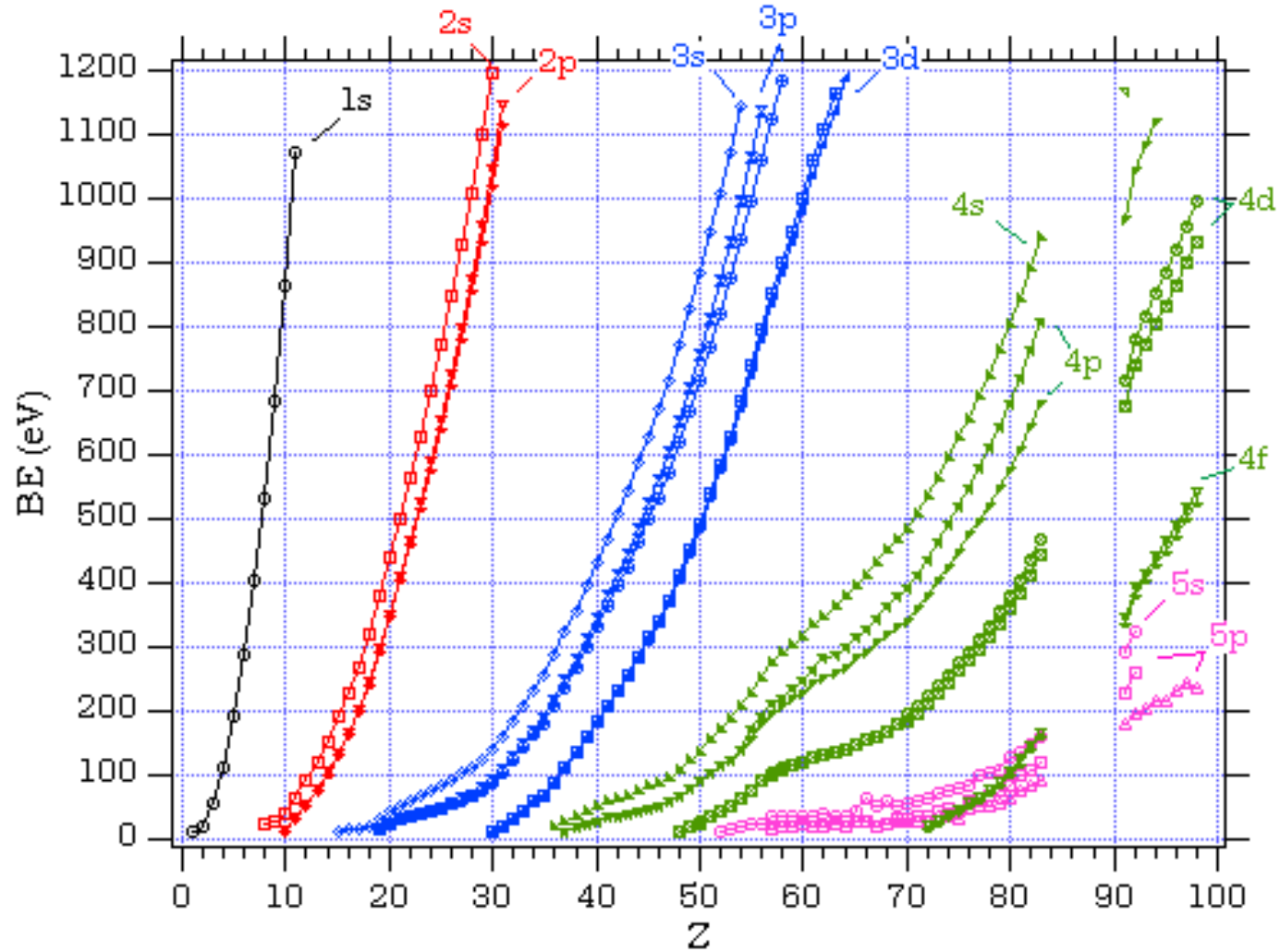


$$KE = h\nu - BE - \Phi \quad \text{for a solid}$$

$$KE = h\nu - IP \quad \text{for a gas}$$

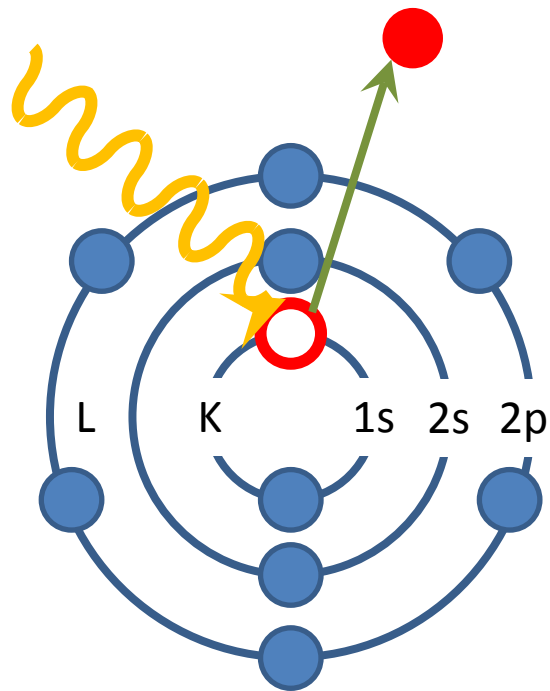
Φ : photoelectric workfunction (4-6 eV)

The binding energy

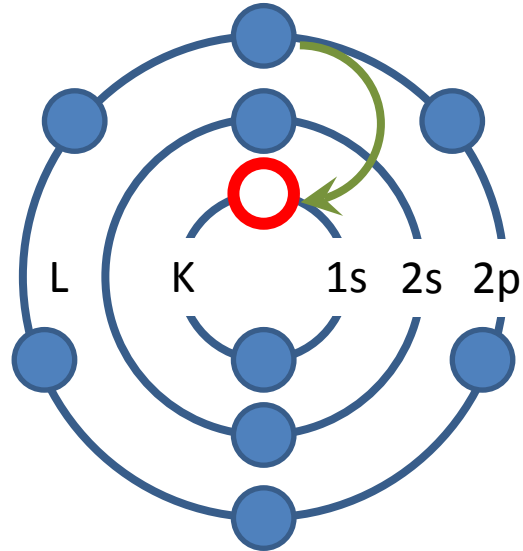


Fate of core hole

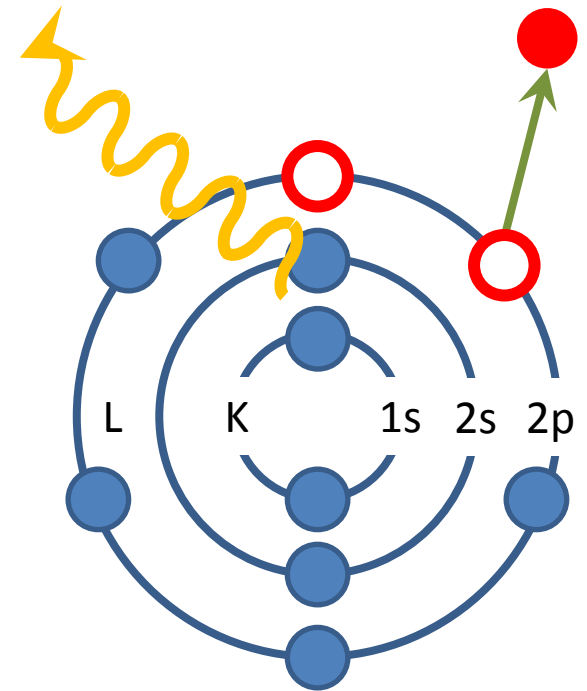
Photoemission



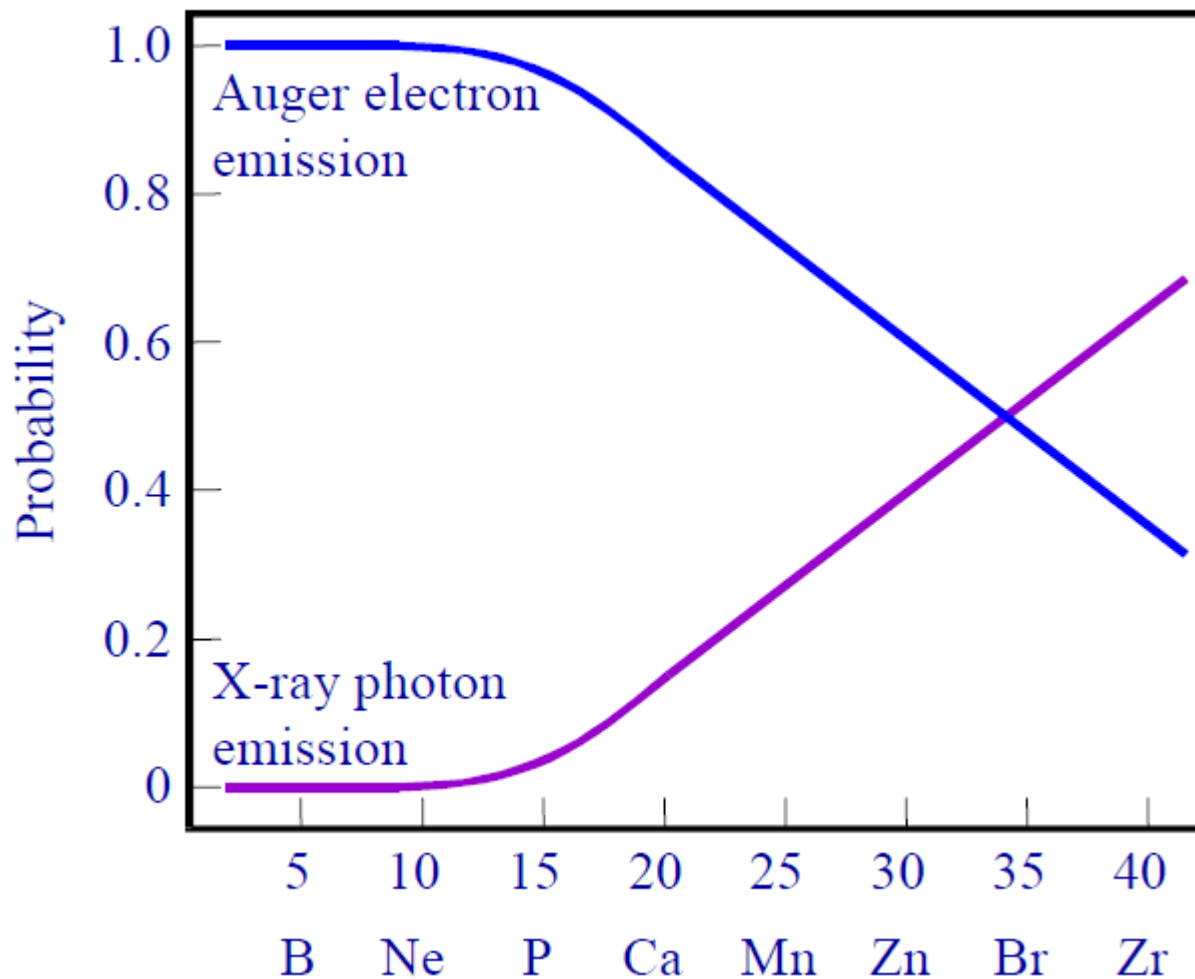
Relaxation



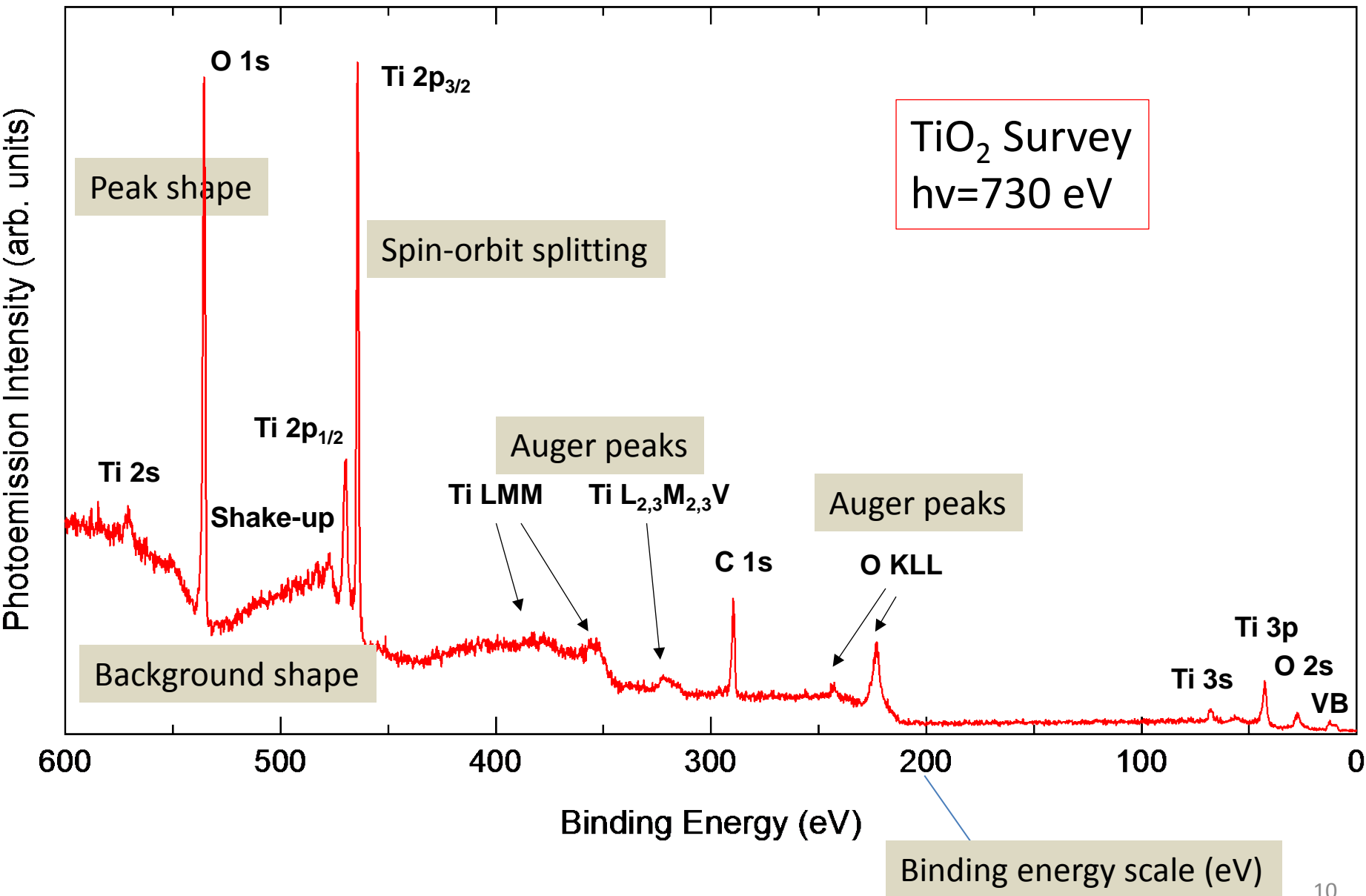
Auger electron emission
Or
X-ray fluorescence



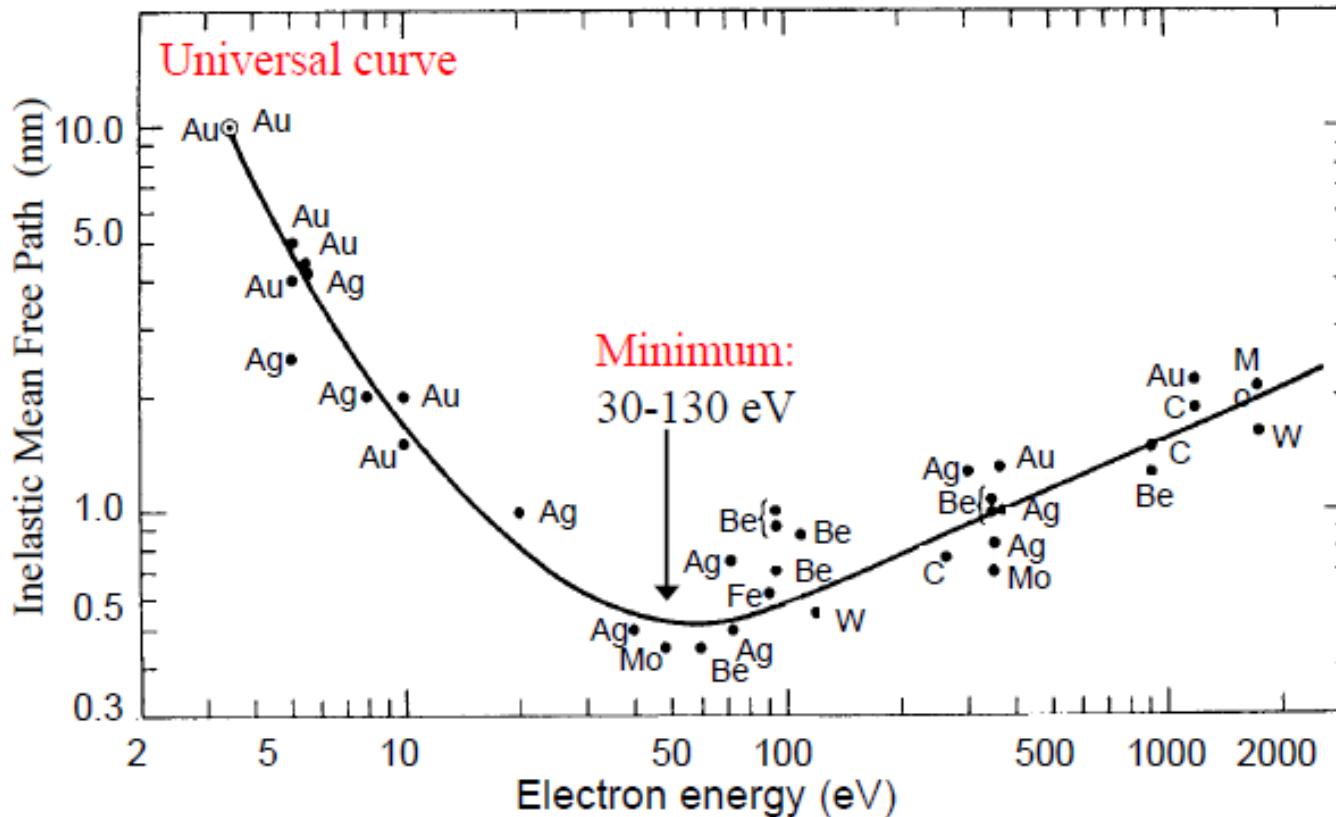
Core hole relaxation: Auger's for low Z – XRF for high Z



A photoelectron spectrum in more detail



Electron inelastic mean free path



Rule of thumb:

$h\nu=1000$ eV

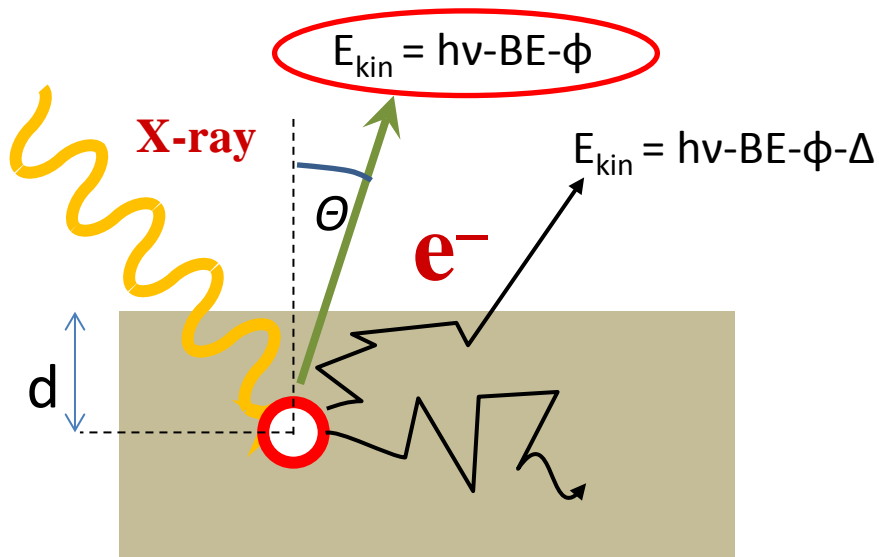
λ_{mfp} :

5-10 Å metals

15-40 Å oxides

15-30 Å polymers

XPS probe depth

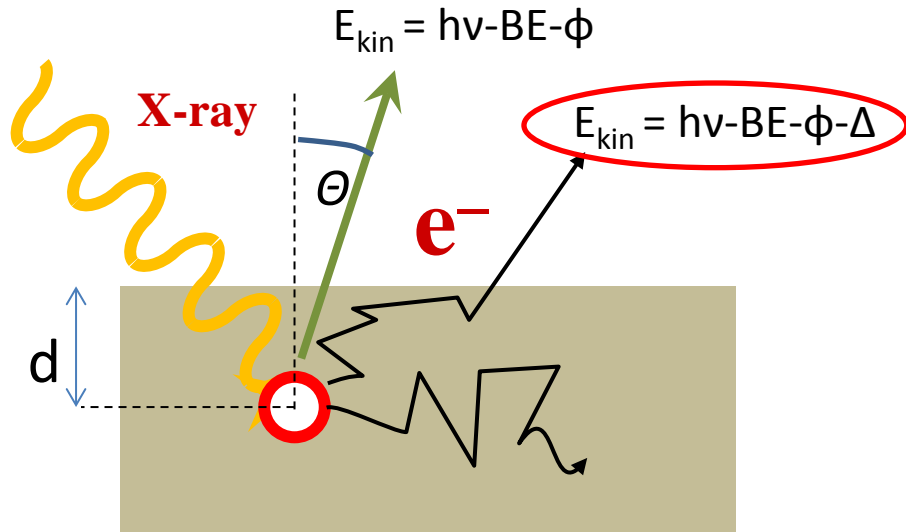


Contribution of atom in depth d to PE peak:

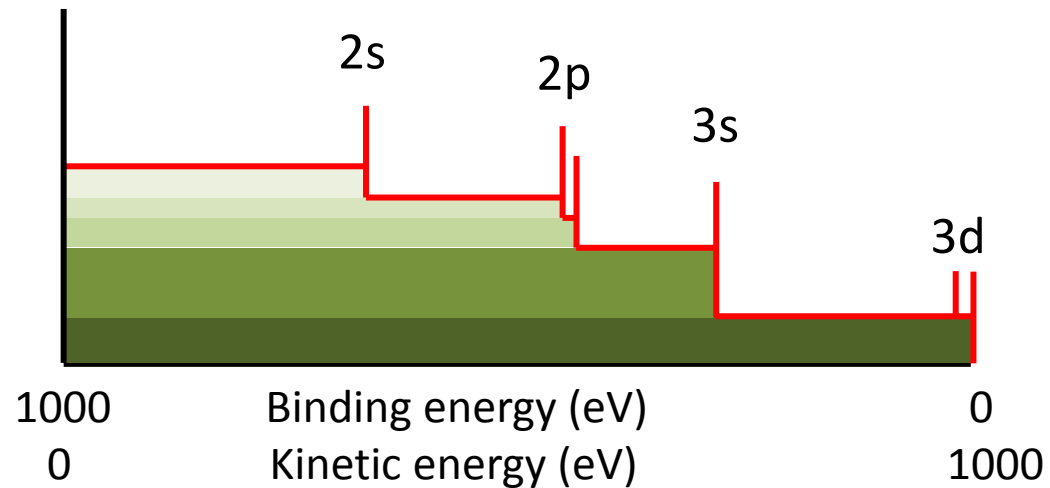
$$I = I_0 \exp\left(\frac{-d}{\lambda \cos \theta}\right)$$

- Only electrons from close to surface can escape without energy loss
- Inelastic mean free path is a strong function of kinetic energy.
- Exponentially decreasing contribution from atoms below the surface to the photoelectron peaks (without loss)
- At close to normal detection angles 95% of the signal comes from atoms within 3λ of the surface
- Molecular scale surface sensitivity
- Probing depth varies with kinetic energy.
- Depth profiles can be obtained by varying the incident photon energy with a tunable X-ray source, i.e., at a synchrotron, or by varying the detection angle

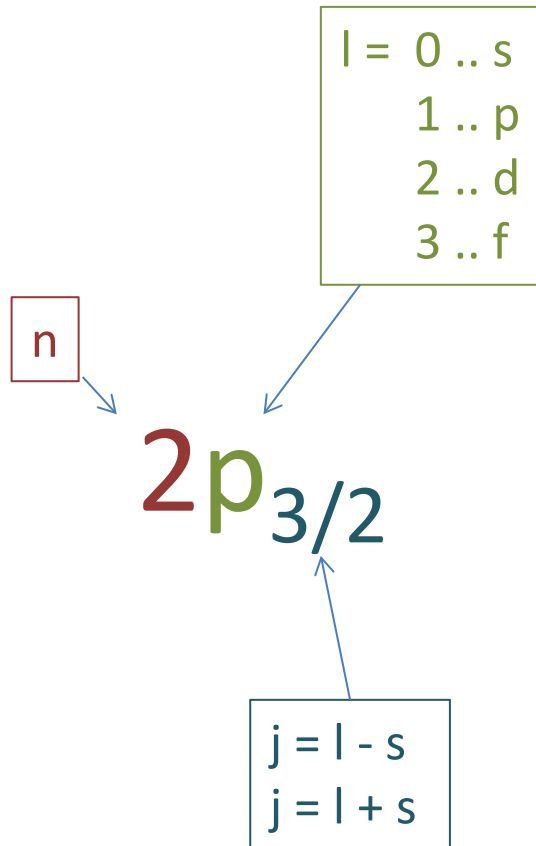
Inelastic background



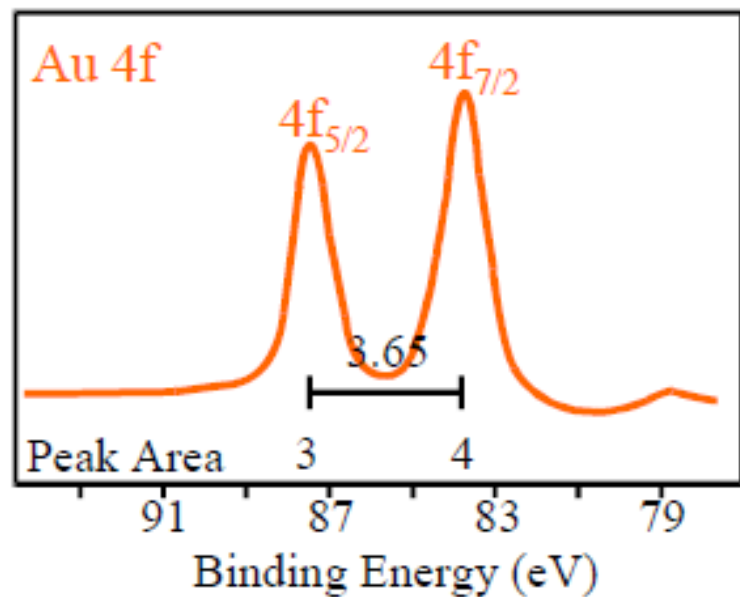
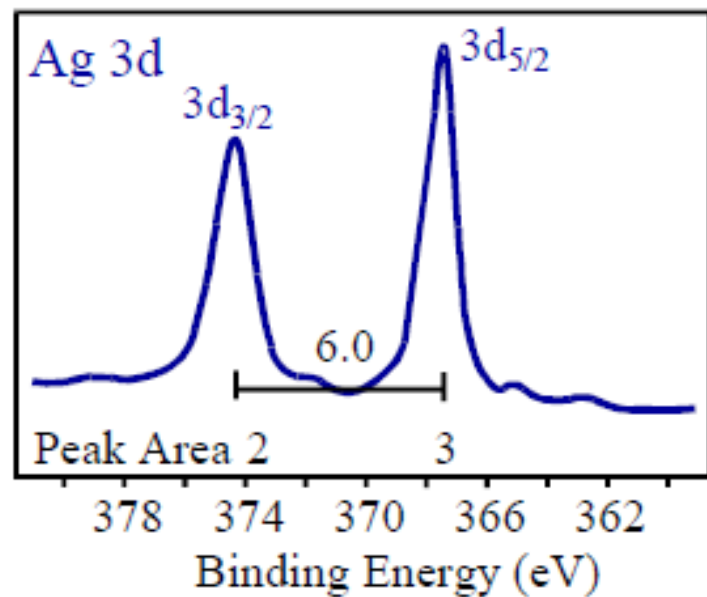
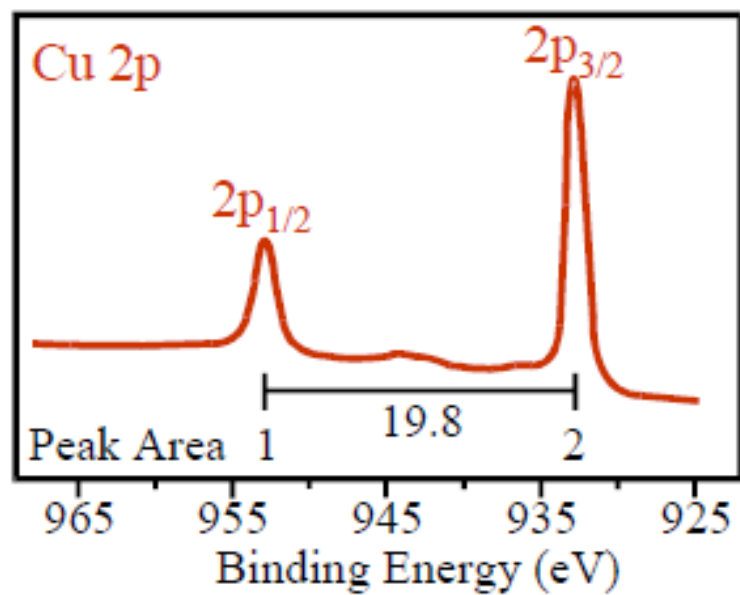
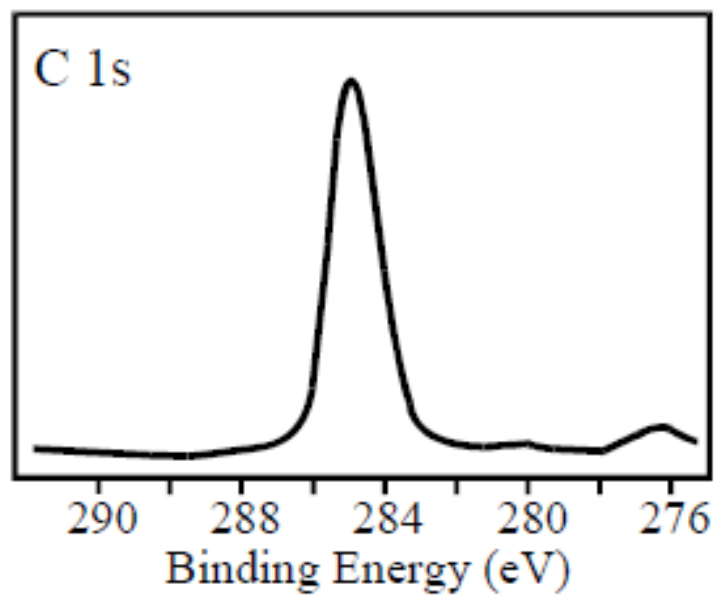
- Electrons from deeper below the surface lose energy and emerge with reduced KE (increased apparent BE)
- Electrons very deep in surface lose all energy and cannot escape
- XPS spectra show characteristic "stepped" background (intensity of background towards higher BE of photoemission peak is always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



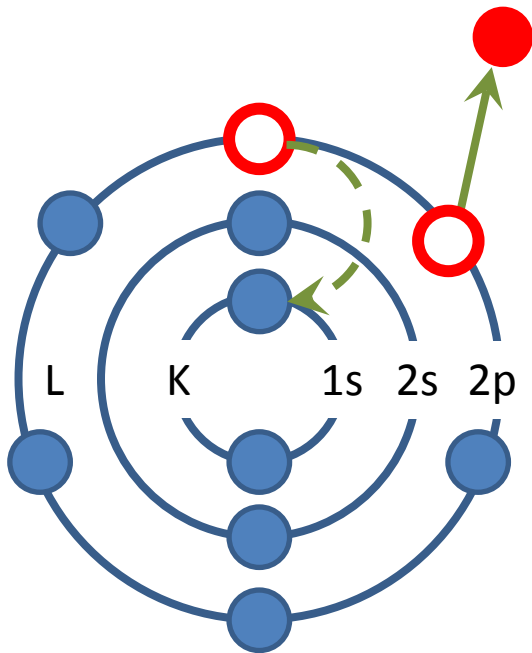
Spin-orbit splitting



- n : principal quantum number
- l : orbital angular momentum quantum number
- s : spin angular momentum quantum number
- $j = |l \pm s|$: total angular momentum quantum number
- For $l = 0$, s levels are singlets, no splitting
- For $l > 0$, p, d, f levels give rise to doublets, because the unpaired electron left in an orbital can have its spin and orbital angular momentum either parallel or anti-parallel
- The degeneracy, $2j+1$, determines how many possibilities exist for parallel or anti-parallel pairing and thus the relative peak ratio of the two doublet components.
- BE of lower j value in doublet is higher (BE $2p_{1/2} >$ BE $2p_{3/2}$)
- Magnitude of spin-orbit splitting increases with Z
- Magnitude of spin-orbit splitting decreases with distance from nucleus (increased nuclear shielding)



Auger peaks



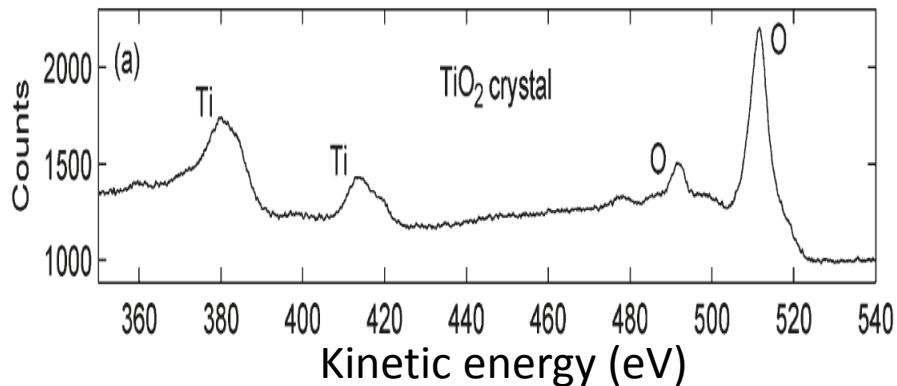
- Result from excess energy of atom during relaxation (after core hole) creation
- always accompany XPS
- broader and more complex structure than photoemission peaks, because of different valence levels involved and secondary effects
- Nomenclature: ABC, with A: level of initial core hole, B: level from 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
- Auger spectra are sensitive to chemistry, because of the involvement of outer shells.

Ti LMM

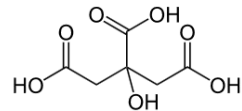
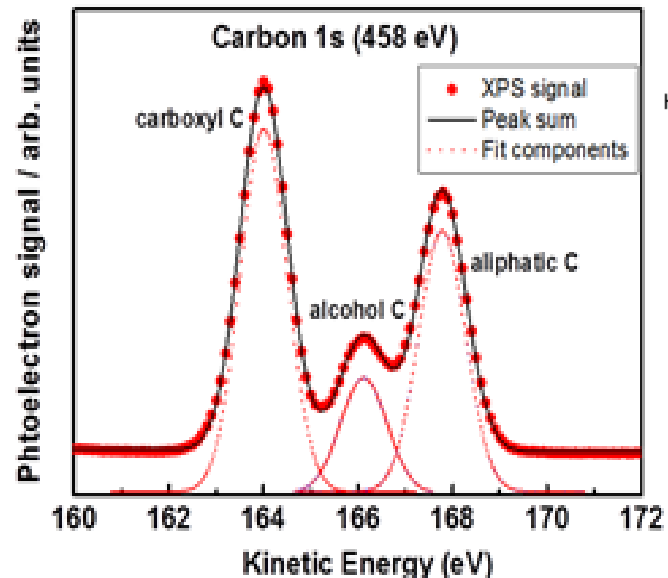
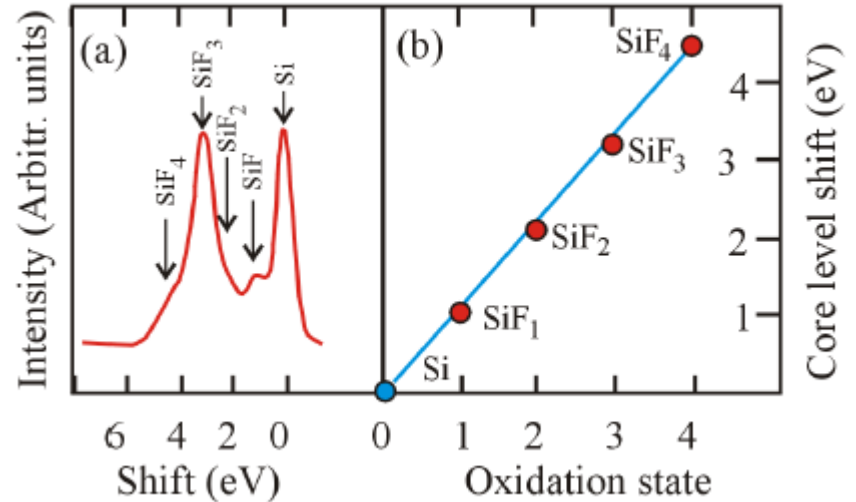
O KLL



Wu et al. 2011

Core level chemical shifts

- Position of orbitals in atom is sensitive to chemical environment of atom
- In gas phase XPS, the differences in core electron ionization energies are directly apparent
- In solids, all core levels for that atom shifted by approx. same amount (<10 eV)
- Chemical shift correlated with *overall charge* on atom (Reduced charge - increased BE)
- number of substituents
 - substituent electronegativity
 - formal oxidation state (unreliable, depending upon ionicity/covalency of bonding)
- Chemical shift analysis is powerful tool for chemical composition, functional group and oxidation state analysis



Citric acid

Further features

- Final state effects
 - Screening and relaxation effects: satellite peaks on low or high BE side
 - Important in transition metal oxides
 - Useful in fingerprinting of complex systems
- Discrete electron structures due to electronic excitations, e.g., (surface) plasmons
- Asymmetric peak shapes in metals due to low energy electron-hole excitations

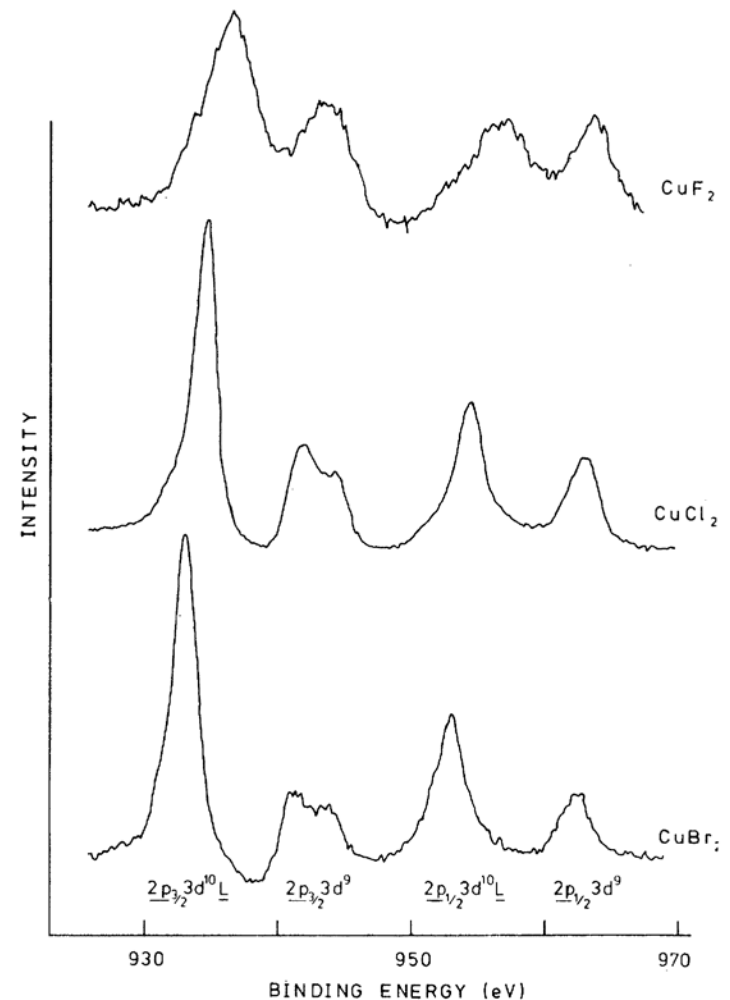


FIG. 1. Cu 2p photoelectron spectra of Cu dihalides. The lines leading to a final state with a ligand hole (L) show a chemical shift.

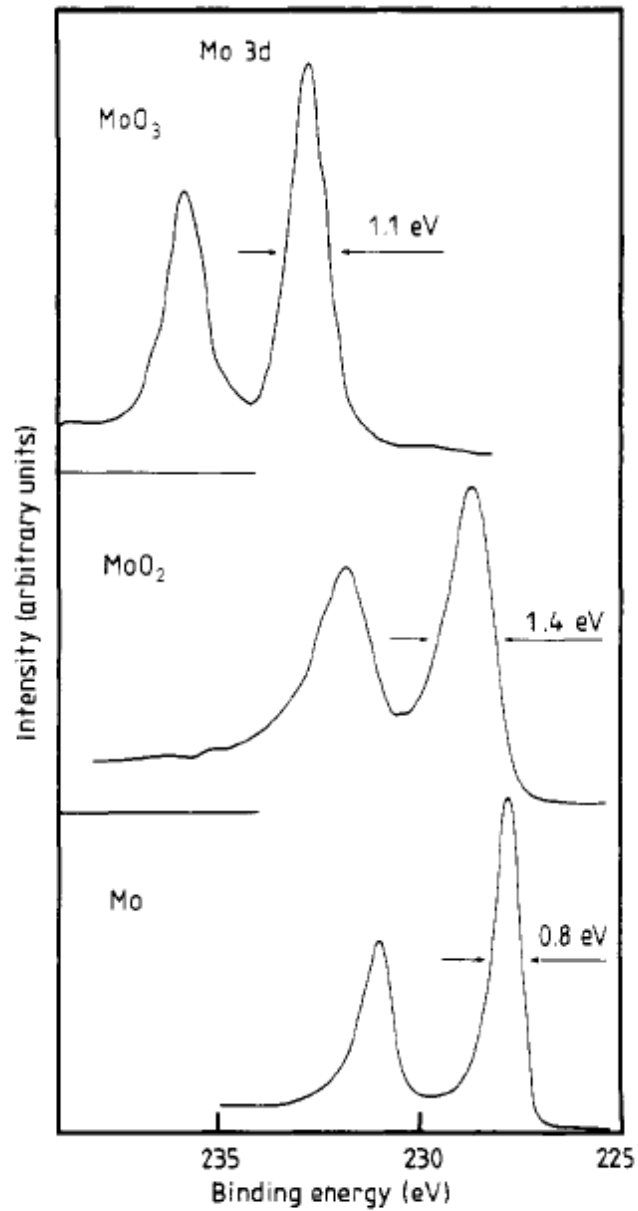


Figure 2. The XPS 3d core level spectra of metallic Mo, MoO₂ and MoO₃.

Werfel and Minni, 1983

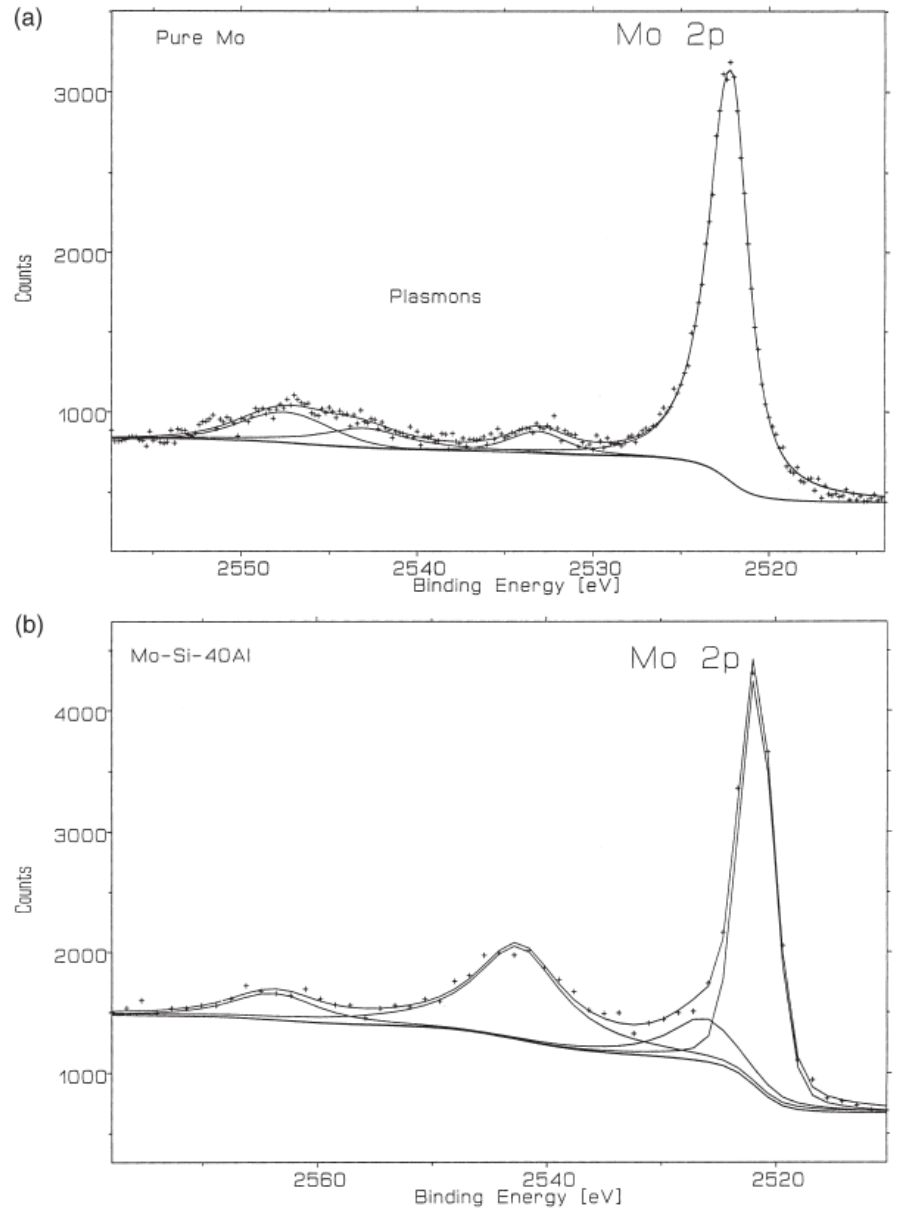


Fig. 7. Plasmons of the Mo 2p_{3/2} peak, (a) from the pure metal standard, and (b) from the MoSi₂+40 at% Al alloy.

Arvantis et al. 2001

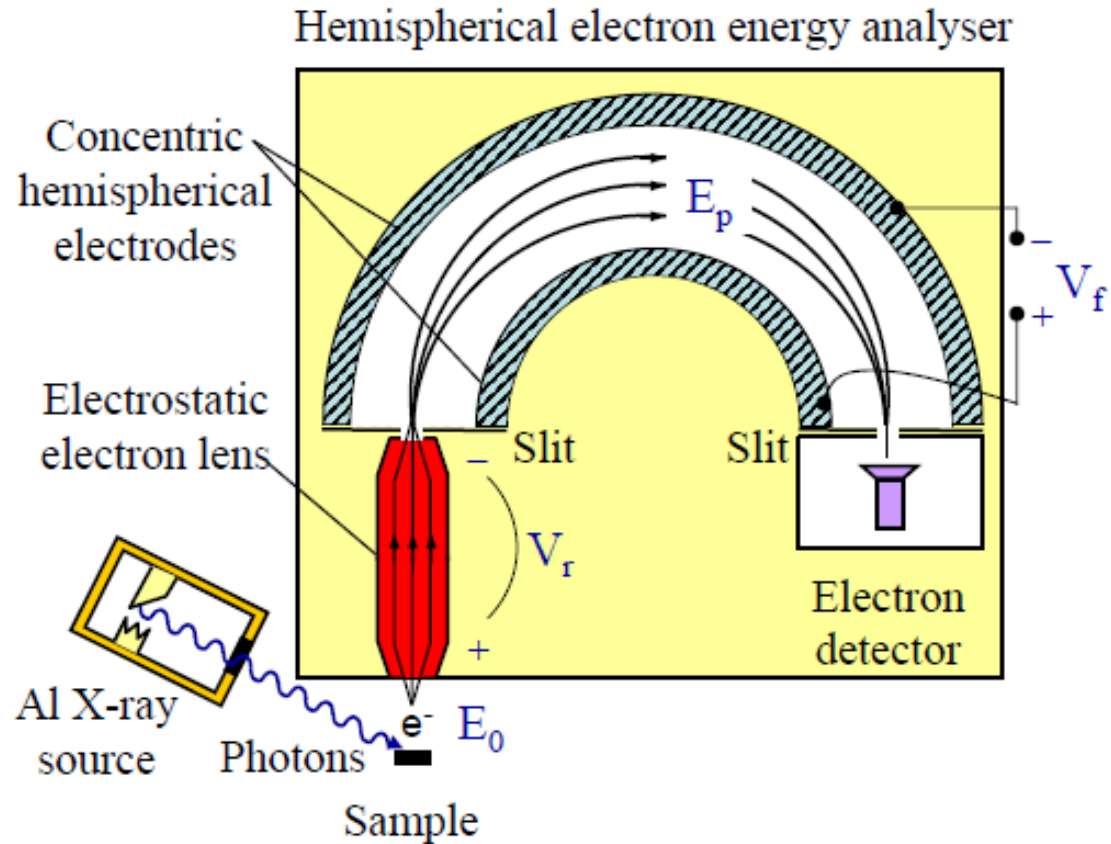
Electron energy analyzer

- Circular orbit of electrons from entrance slit to detector, controlled by inner and outer potential
- Since the resolution, $\Delta E/E$, depends on kinetic energy, an electrostatic lens is used to retard electrons to constant kinetic energy, referred to as pass energy, E_0

$$\frac{\Delta E}{E_0} = \frac{s}{2R_0}$$

s slit width

R_0 radius of electron orbit through hemisphere



Estimation of signal intensities

Contribution of element A in depth d to photoemission signal

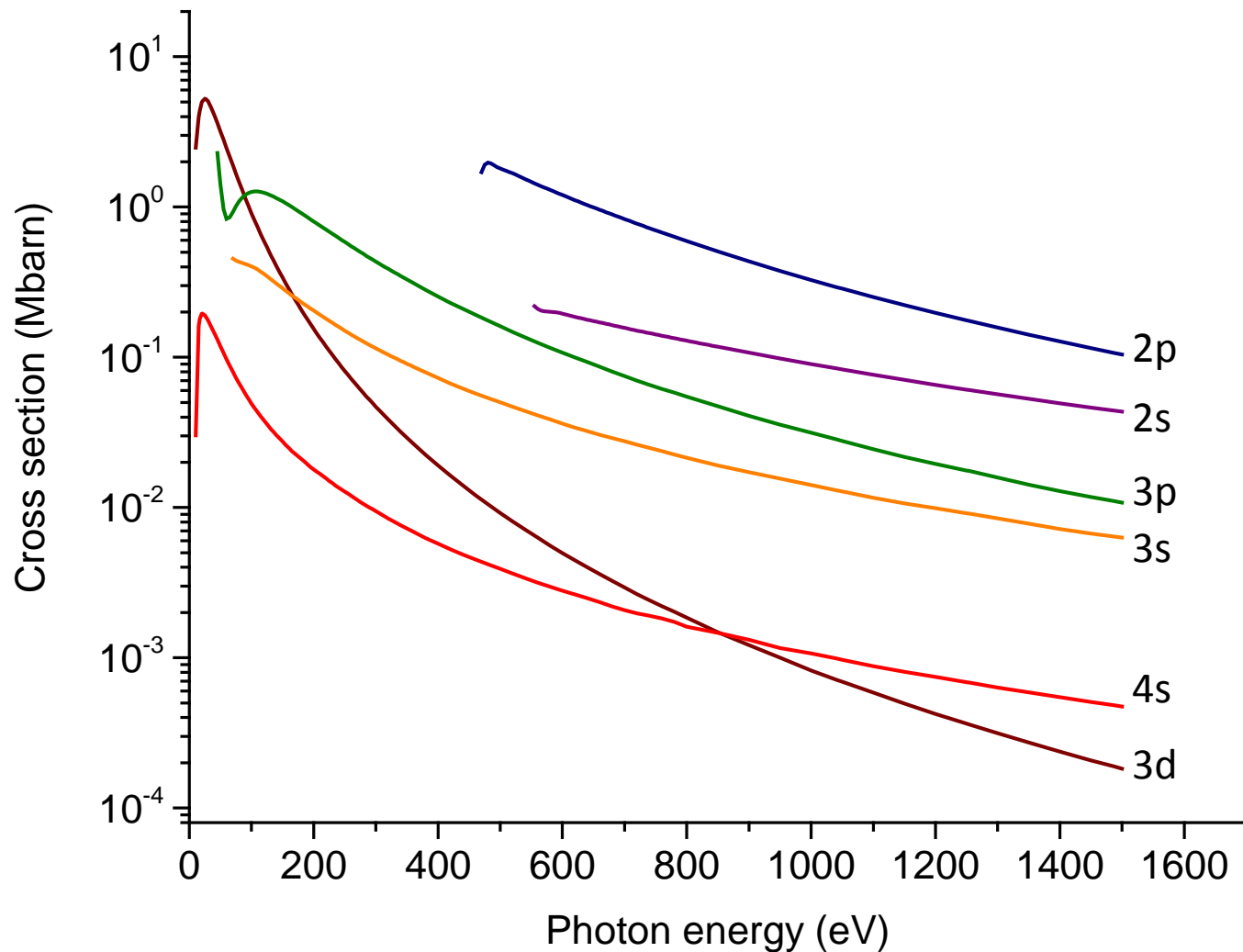
$$I_A = \Phi_X \times c_A(d) \times \sigma_{i,j}(h\nu) \times e^{-\frac{d}{\lambda \cos(\theta)}} \times A_{Analyzer} \times T_{Analyzer}$$

The diagram illustrates the equation for the contribution of element A in depth d to the photoemission signal. The equation is $I_A = \Phi_X \times c_A(d) \times \sigma_{i,j}(h\nu) \times e^{-\frac{d}{\lambda \cos(\theta)}} \times A_{Analyzer} \times T_{Analyzer}$. Each term in the equation is linked by a blue arrow to a corresponding text box:

- Φ_X is linked to "Photon flux".
- $c_A(d)$ is linked to "Concentration of element A at depth d".
- $\sigma_{i,j}(h\nu)$ is linked to "Subshell ionization cross section".
- $e^{-\frac{d}{\lambda \cos(\theta)}}$ is linked to "Attenuation from depth d at detection angle θ ".
- $A_{Analyzer}$ is linked to "Angular acceptance".
- $T_{Analyzer}$ is linked to "Analyzer transmission".

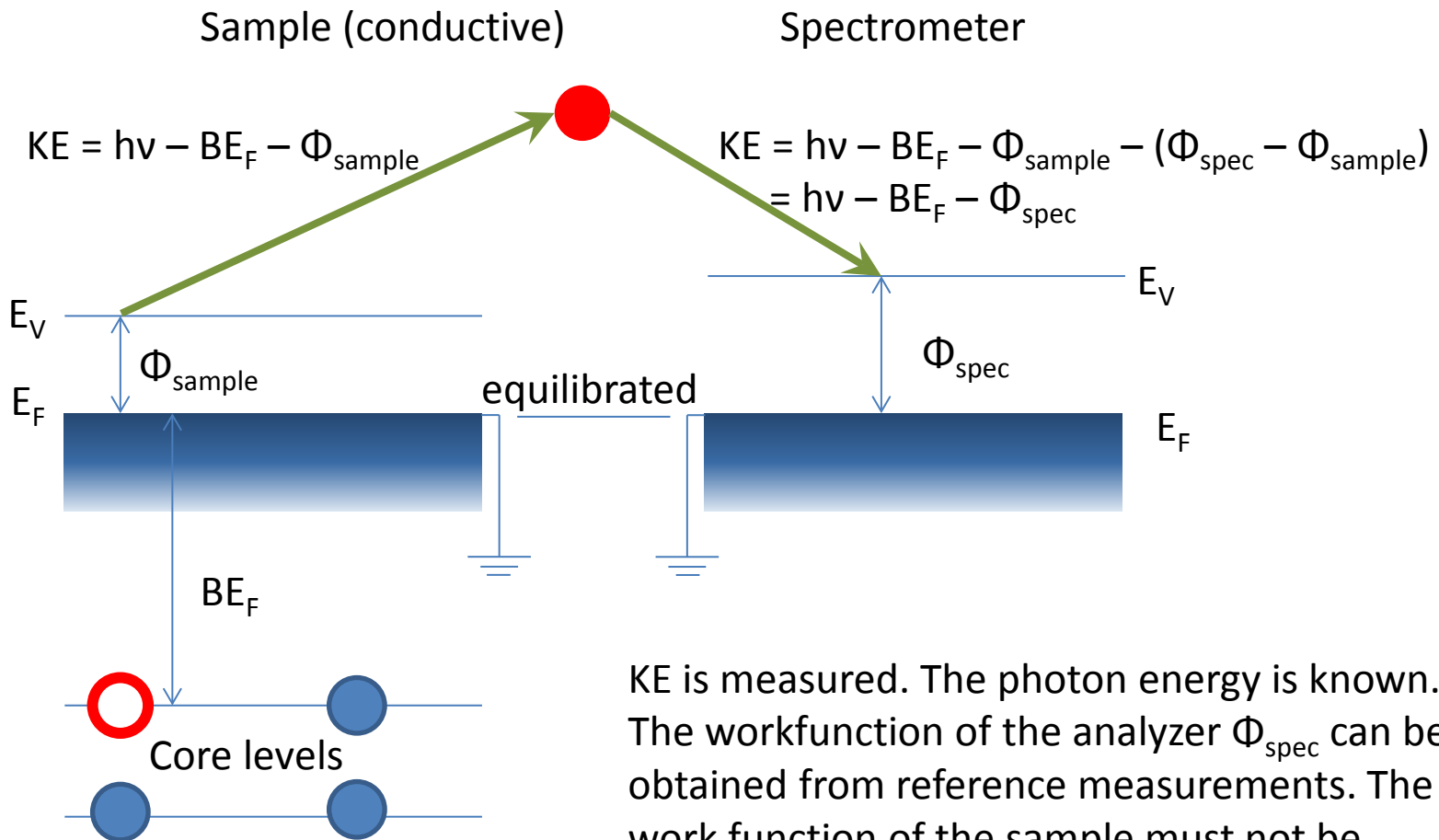
- Cross sections range up to about 10^{-18} cm^2
- $10^{15} \text{ atoms cm}^{-2}$ (equivalent to a monolayer) lead to about 10^{-3} photoelectrons per incident photon
- Typical photon flux: 10^{12} s^{-1} , leads to about 10^9 photoelectrons s^{-1}
- For most elements, sensitivity is in the range of 0.1 to 1 % of a monolayer

Photoionisation cross sections for Ti core levels



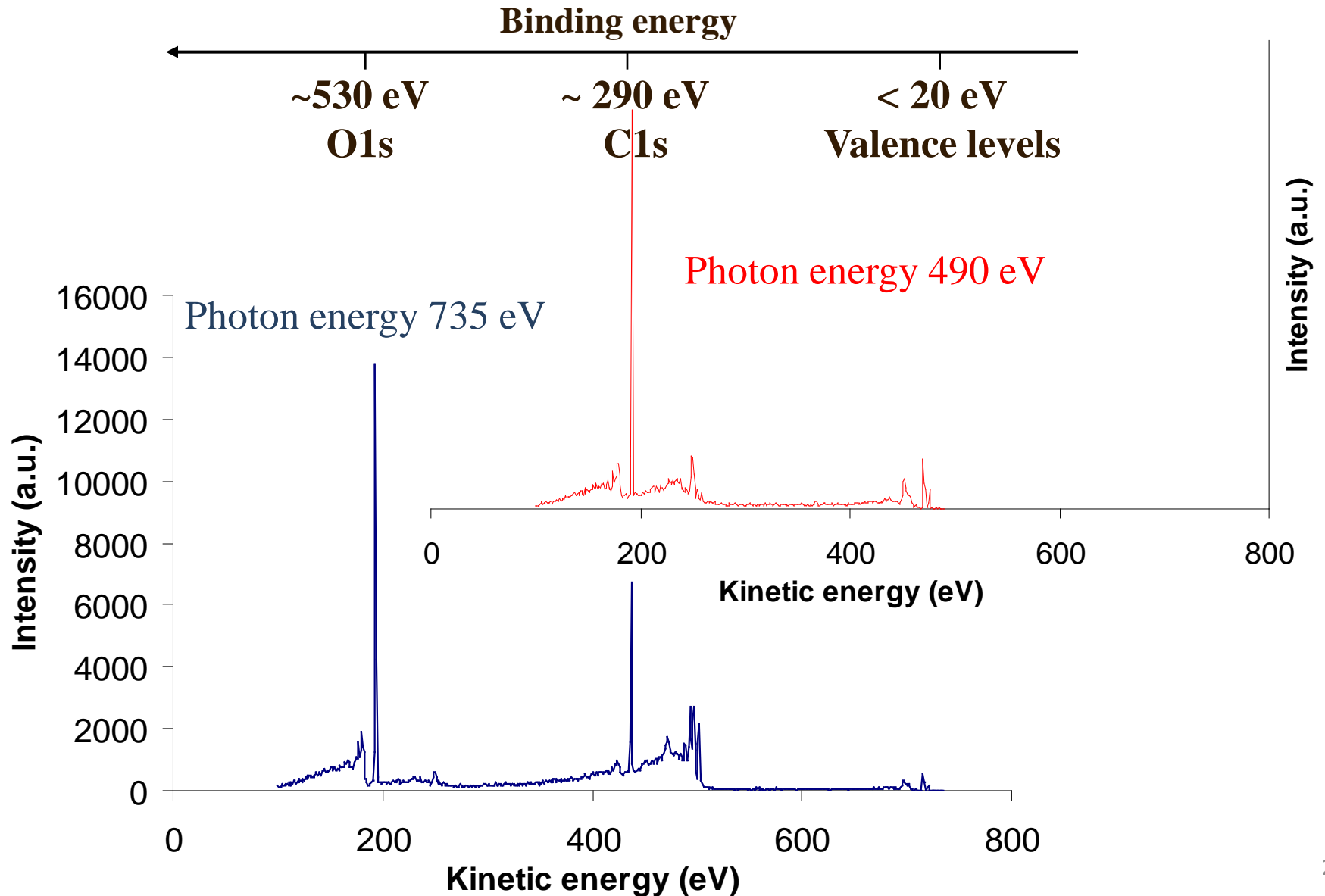
J.J. Yeh, *Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters*, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993, and J.J. Yeh and I.Lindau, *Atomic Data and Nuclear Data Tables*, **32**, 1-155 (1985).

How to get the binding energy scale

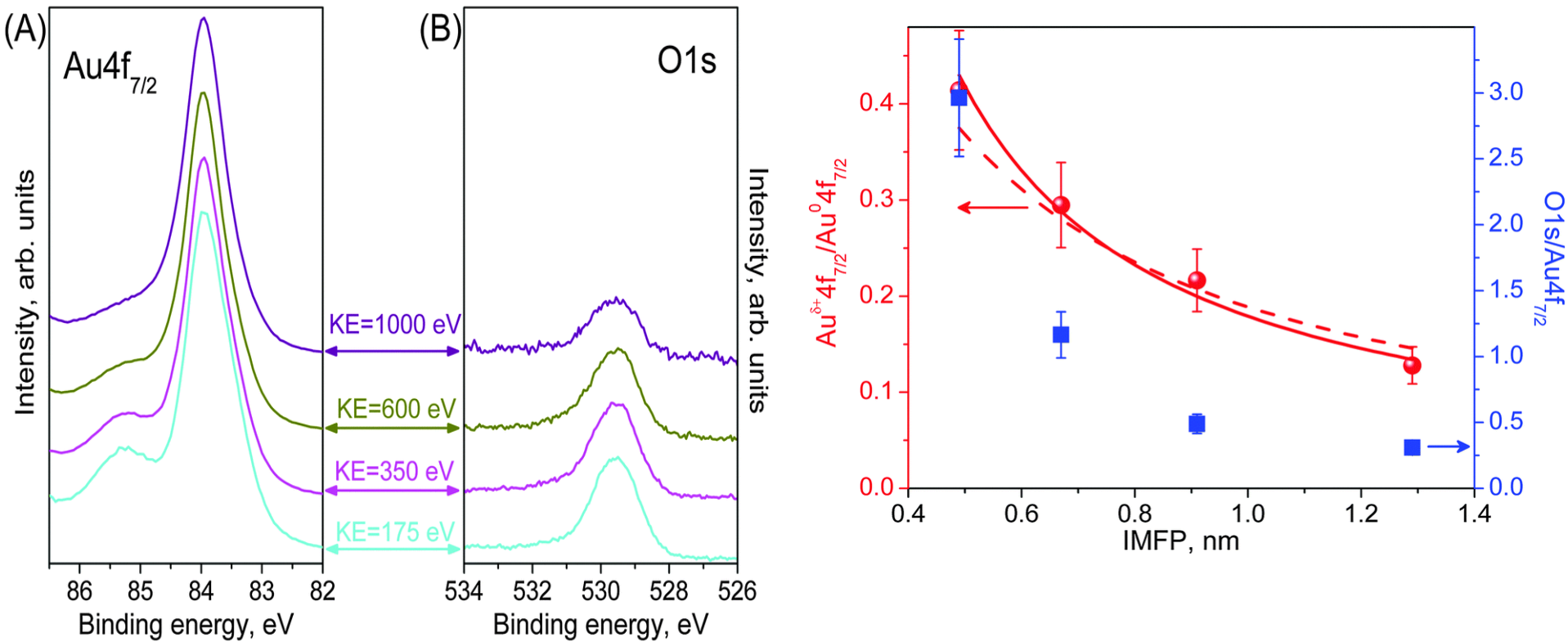


KE is measured. The photon energy is known. The workfunction of the analyzer Φ_{spec} can be obtained from reference measurements. The work function of the sample must not be known. This procedure leads to a BE scale referenced to E_F .

varying KE by changing photon energy

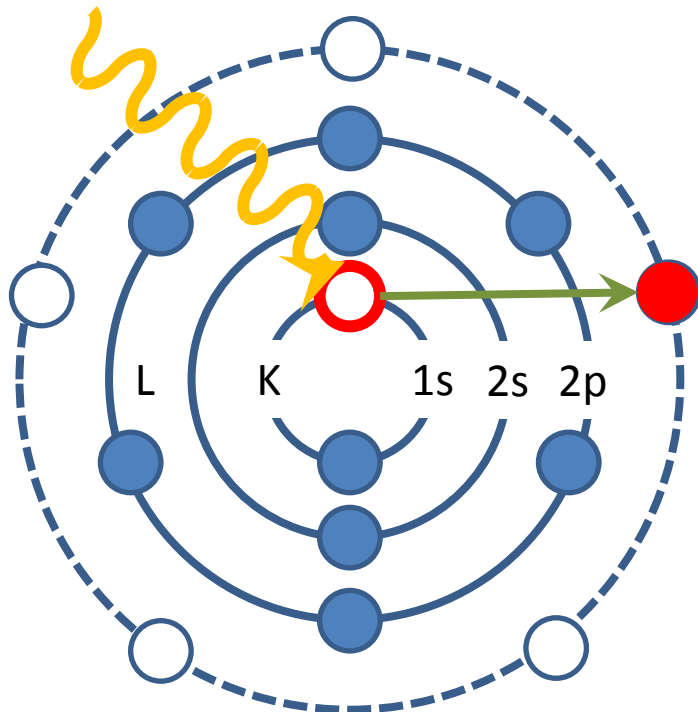


Depth profile

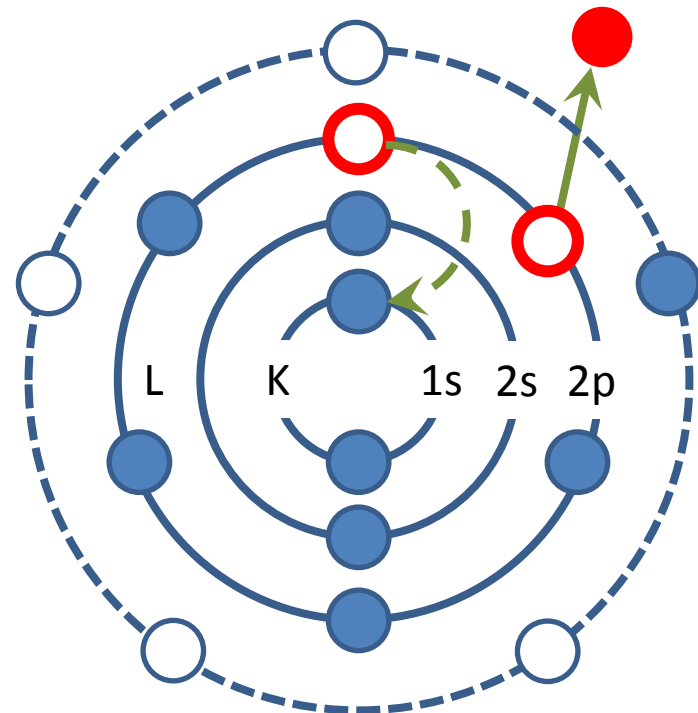


Auger yield NEXAFS

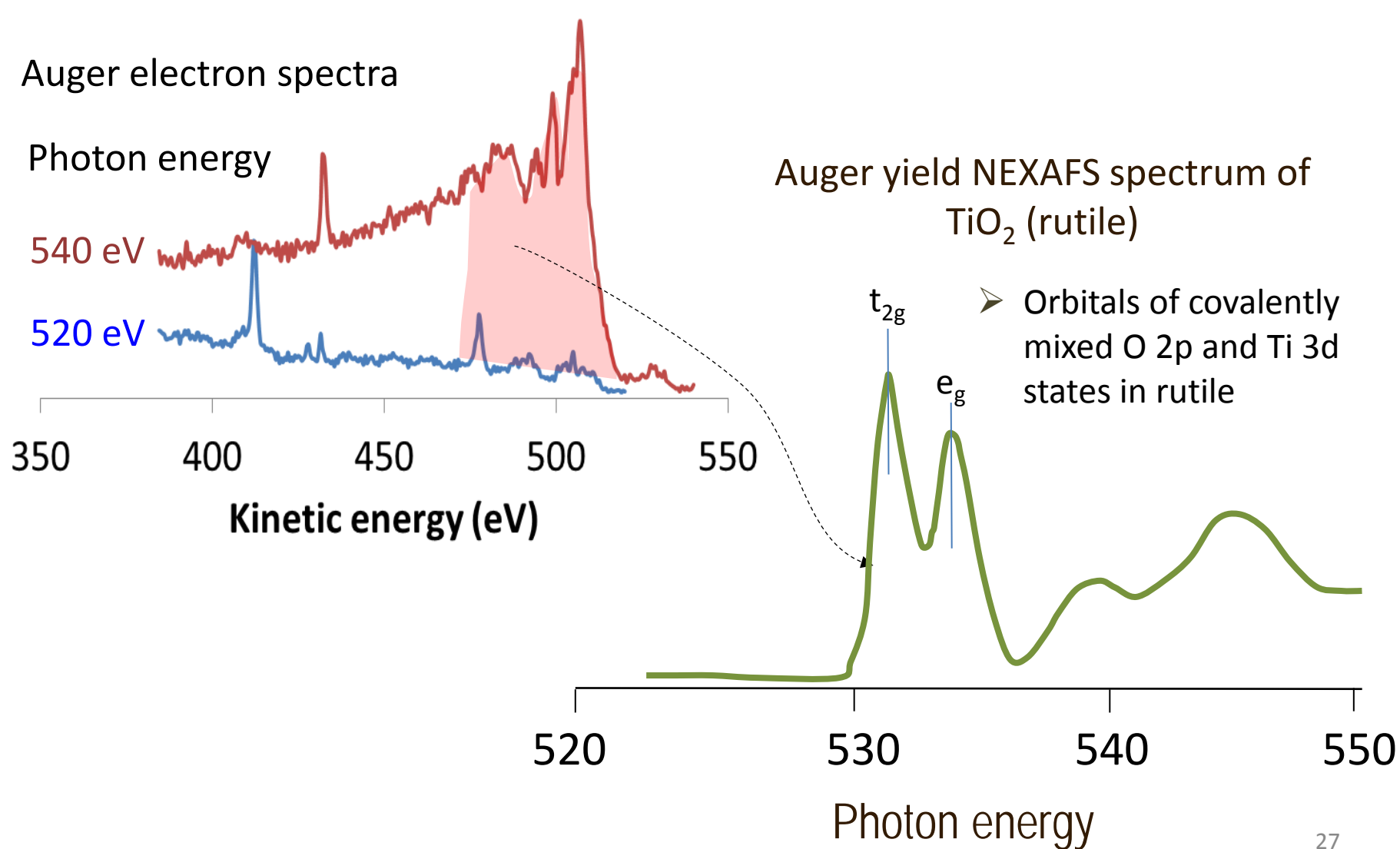
- Excitation into unoccupied molecular orbital (LUMO)
- Resonant absorption



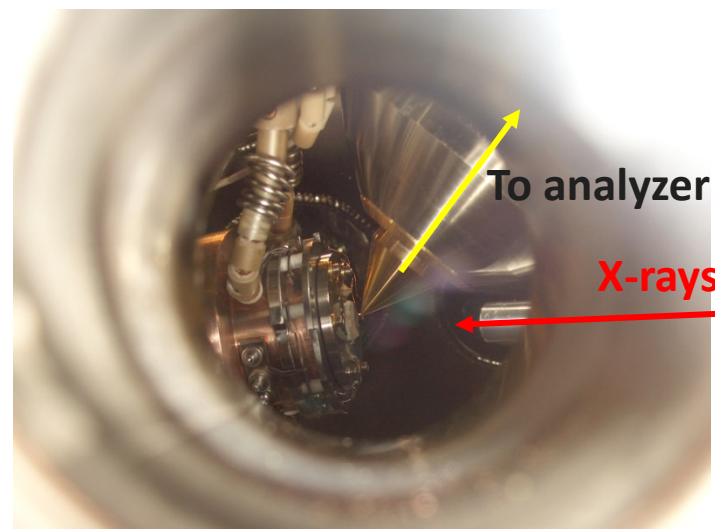
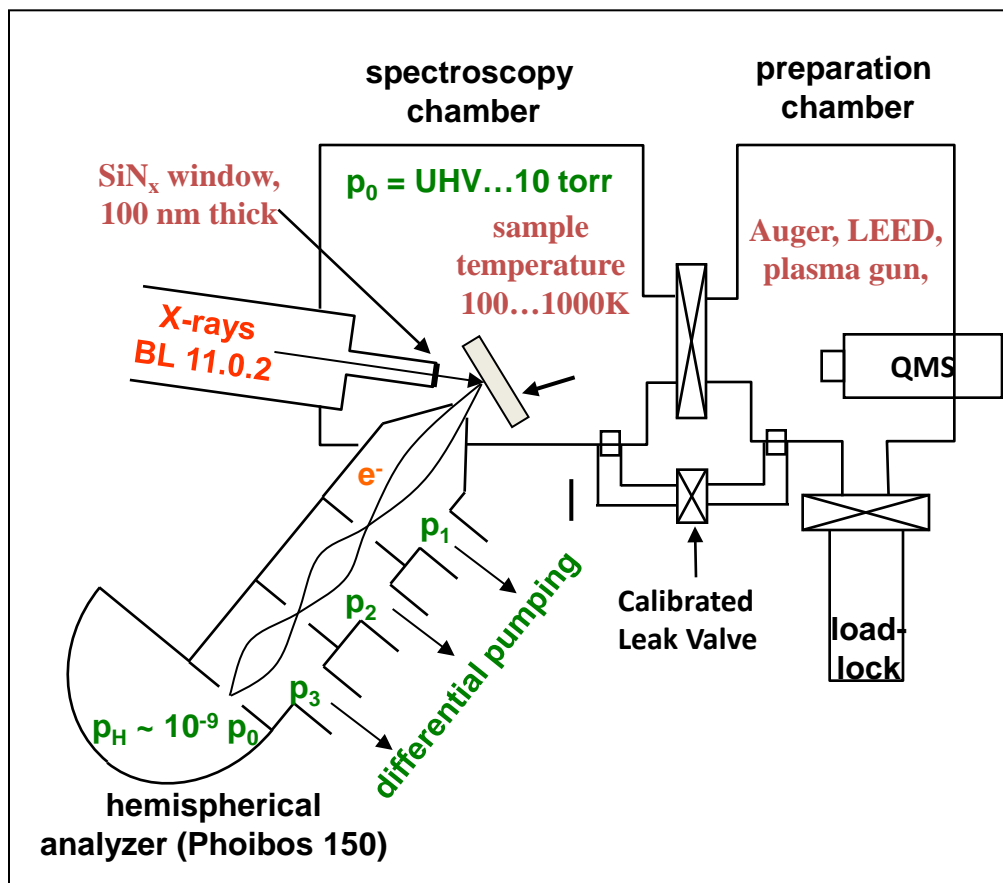
- Auger electron emission following filling of core level
- Auger electron emission intensity scales with rate of initial excitation into LUMO
- Surface sensitive NEXAFS technique



Auger yield NEXAFS

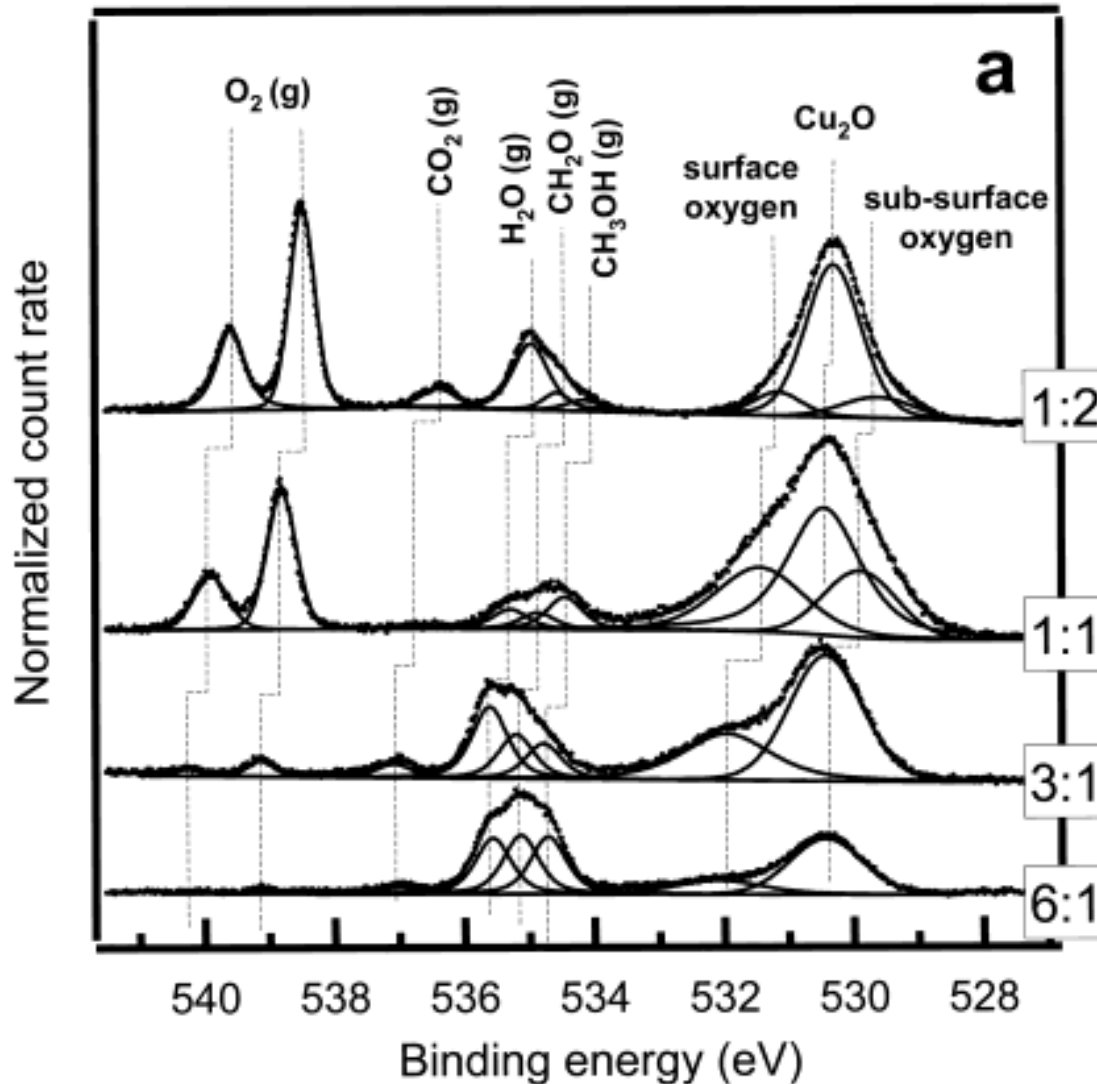


High pressure XPS setup

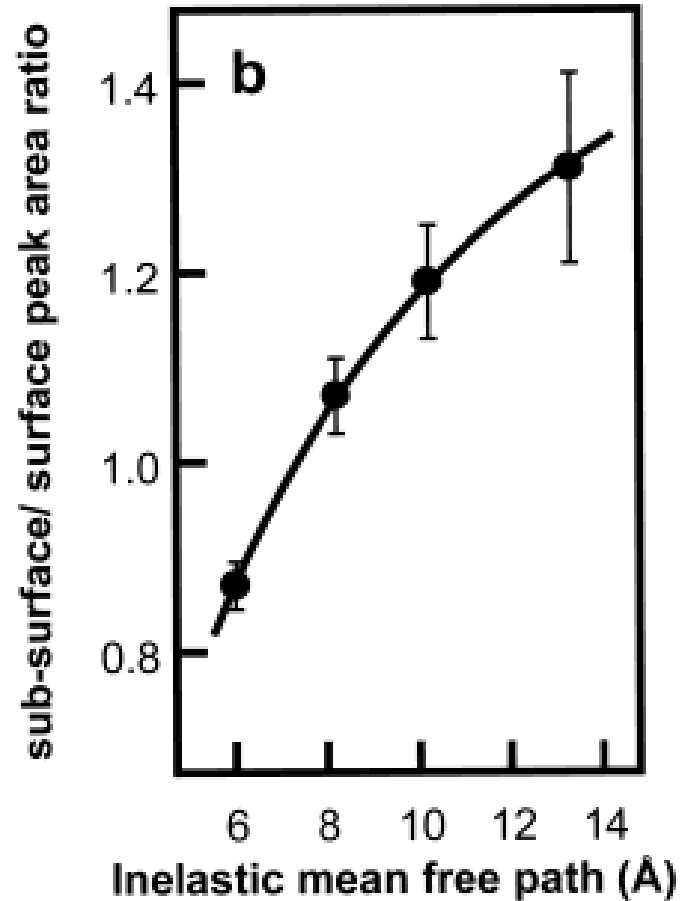
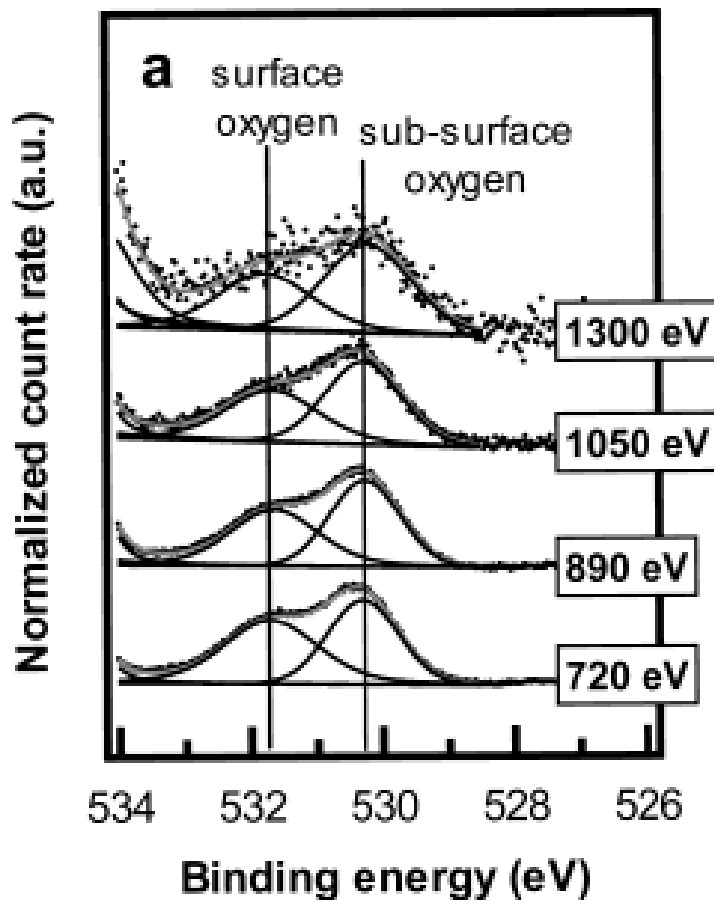


Aperture $\Phi = 0.3 \text{ mm}$

MeOH oxidation on Cu catalyst



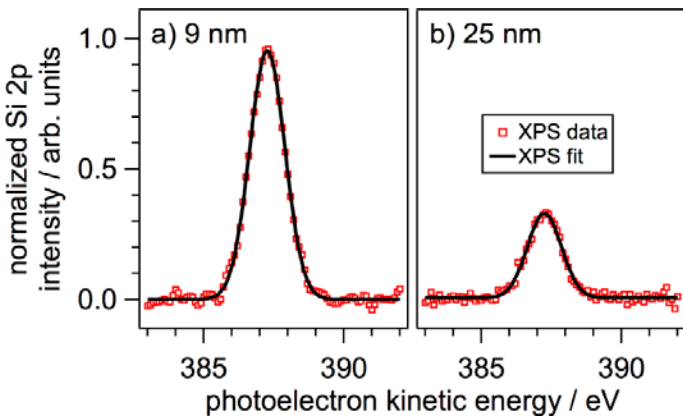
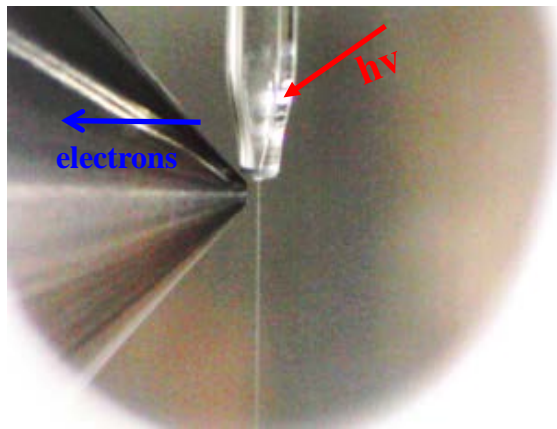
In situ gas and surface characterisation under catalyst operating conditions (400°C, few mbar MeOH, Bluhm et al., 2004)



Identification of sub-surface oxygen species as decisive for catalyst activity

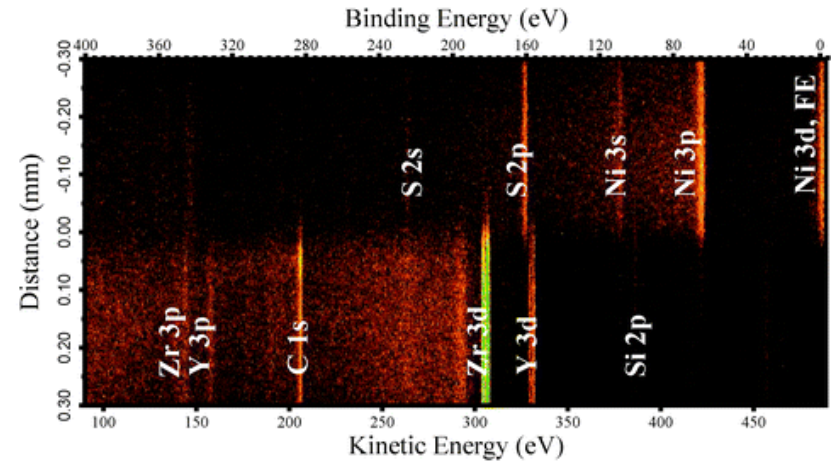
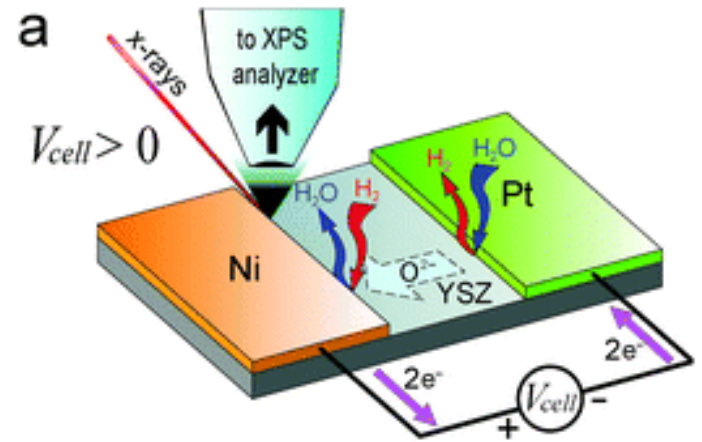
Other XPS developments

Nanoparticles in liquids



Brown et al., Langmuir (2013)

Electrocatalysis



El Gabaly et al. PCCP (2010)