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Data analysis of photoemission data

Some tips for approaching X-ray Photoelectron Spectroscopy
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Luca Bignardi
Department of Physics, University of Trieste and
Nanoscale Materials Lab @Elettra

SCHOOL ON SYNCHROTRON RADIATION “GILBERTO VLAIC”: FUNDAMENTALS, METHODS AND APPLICATIONS

Società Italiana Luce di Sincrotrone

Elettra Sincrotrone Trieste

Outline

With this “tutorial lecture” I would like to give some tips and guidance useful for the analysis and interpretation of photoemission data, focussing mostly on core-level photoelectron spectroscopy.

Specifically, I would like to address these issues, which one faces when dealing XPS spectra:

- What are the features of a spectrum?
- What information can I extract and how?
- What could be some “tricky points” that I have to be aware of?

Photoelectron Spectroscopy

Photoelectron spectroscopy is a Photon IN – Electron OUT technique, relying on the photoelectric effect. One photon gives its entire energy to an electron that goes from a ground to a final state, that can be either bound excited or a free-particle state.

Thus through photoemission we can acquire information about filled electronic states in materials.

The two most common techniques relying on PE effect are:

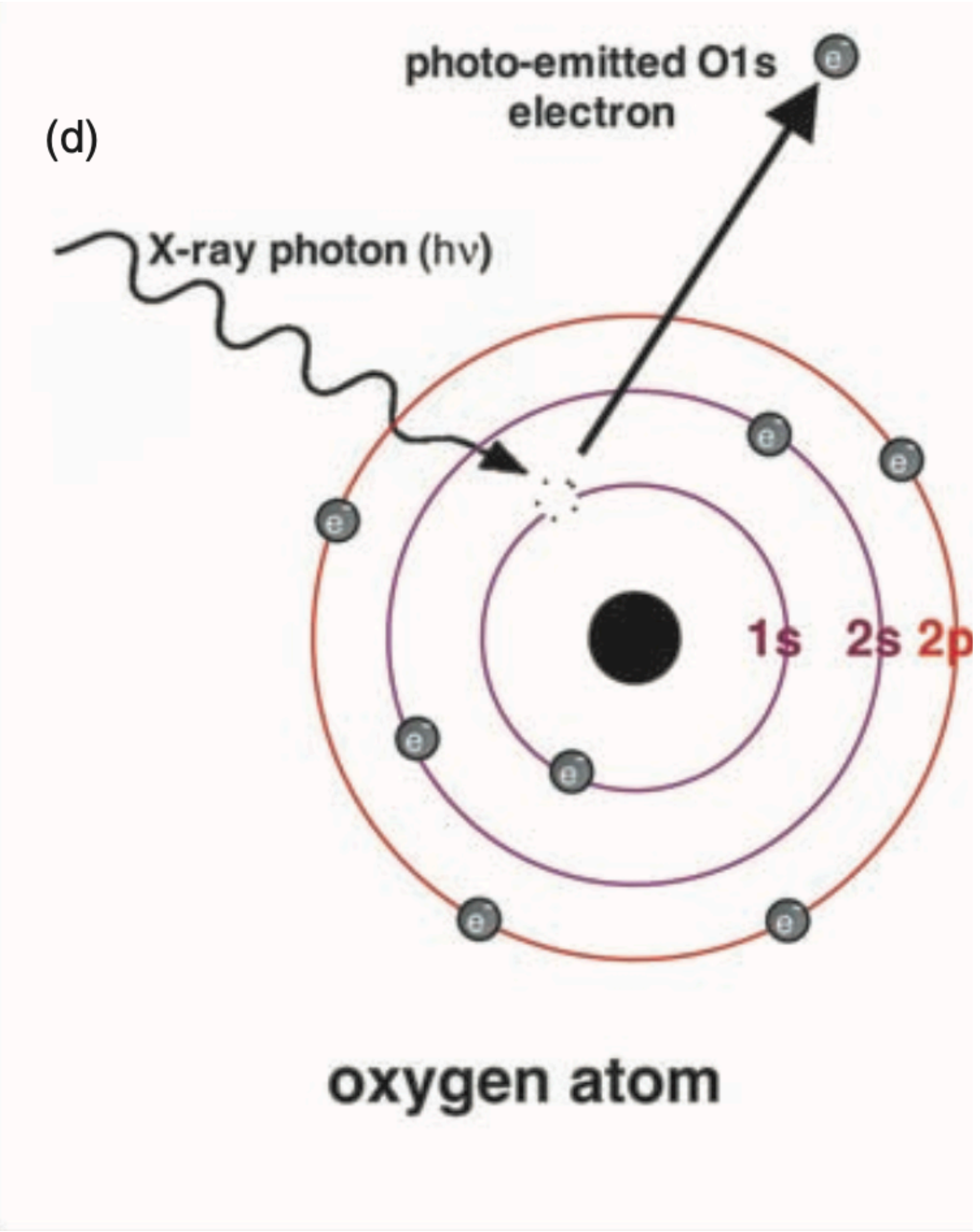
- **X-ray photoelectron spectroscopy:** Probing filled core states, thus compositional analysis, chemical bonds, adsorbates analysis. Also known as **ESCA** (Electron spectroscopy for chemical analysis). Mostly developed by K. Siegbahn from mid ’60s of 20th century.
- **Angle-resolved UV photoelectron spectroscopy:** probing filled valence band states.

Photoemission of Electrons

Assuming we know precisely the energy of the incoming photons, we can write the fundamental Einstein's relation:

$$KE = h\nu - BE$$ (in gas phase)

Incoming photons/electrons may excite electronic transitions in the material. Spectroscopic techniques focus on obtaining information, provided that the excitation process (or its decay) leads to a measurable signal (ejected electron in vacuum).

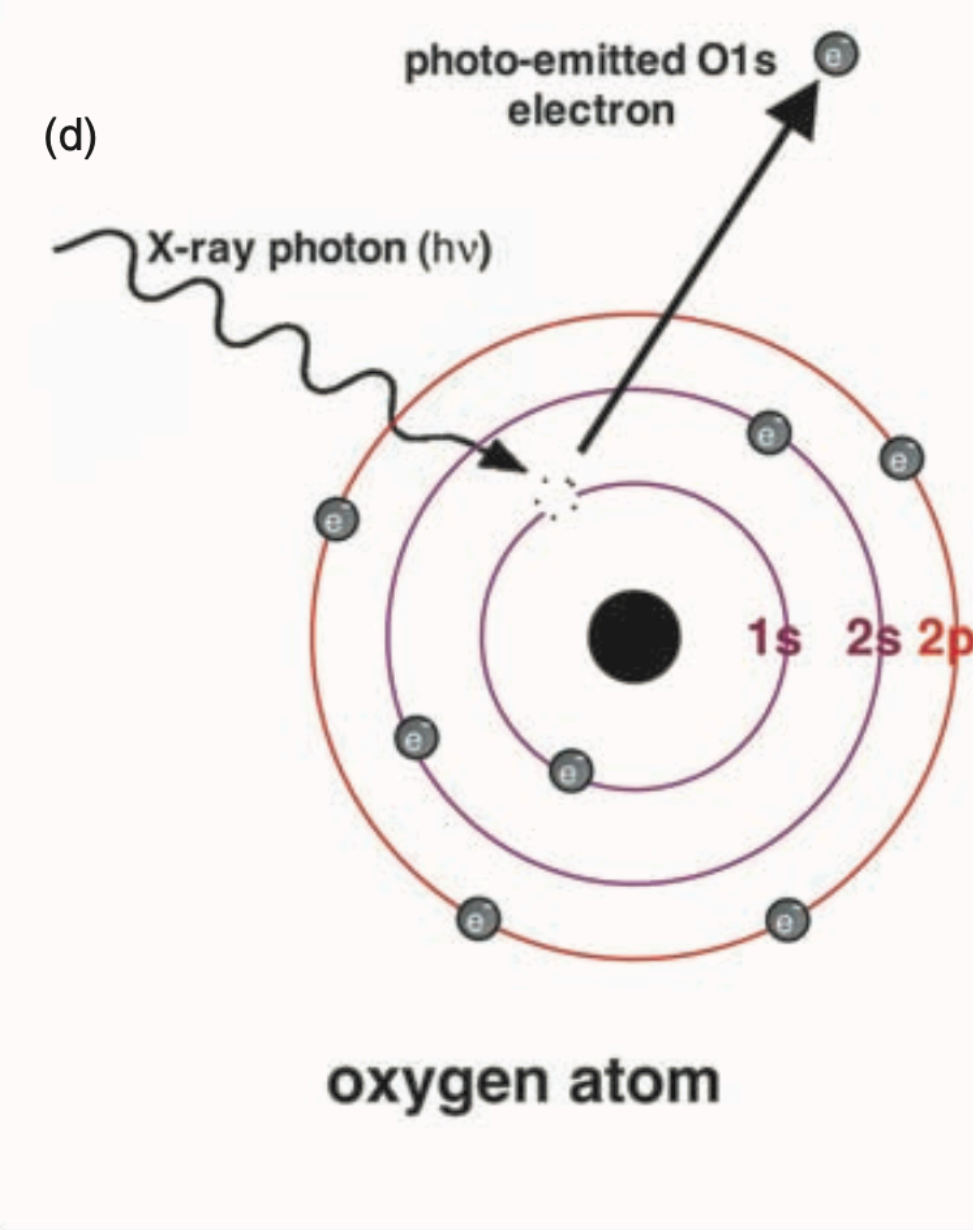


Photoemission of Electrons

(1) no electrons will be ejected from an atom regardless of the illumination intensity unless the frequency of excitation is greater than or equal to a threshold level characteristic for each element (i.e. work function ϕ)

(2) Once the threshold frequency is exceeded, the number of electrons emitted will be proportional to the intensity of the illumination. This is very important when we need to compare spectra!

(3) The kinetic energy (i.e. what we measure) of the emitted electrons is linearly proportional to the energy of the exciting photons.



Photoemission In Solids

We measure the current of photo-emitted electrons corresponding to each energy binning. Strong peaks correspond to the emission from specific electronic core (or Auger) levels. Photoemission in **solids** can be usually described by these three steps:

(1) X-rays interact with the electrons in the atomic shell and photoelectrons (and Auger electrons) are generated.

(2) Part of these electrons move through the solid to the surface and are subject to various scattering processes (those which are inelastically scattered creating the background)

(3) Electrons reaching the surface are emitted in the vacuum (after overcoming the work function threshold)

Analysis of XPS Data

Data analysis and interpretation of XPS data can return a wealth of information about the sample but it may be tricky, since several phenomena are taking place at the same time during electron emission from a solid.

In general we can obtain both *qualitative* and *quantitative* information, but a suitable data processing is required.

However, **there is not always a clear and straightforward way to follow**, but one has to find the best and correct strategy to extract consistent information from the data. There are steps to follow, but there is not a step-by-step procedure that works for each sample you may want to investigate.

XPS Experiment on Solid Samples

- General setup and requirements for XPS: for this spectroscopy we measure the distribution in kinetic energy of the photoelectron current (if any!)

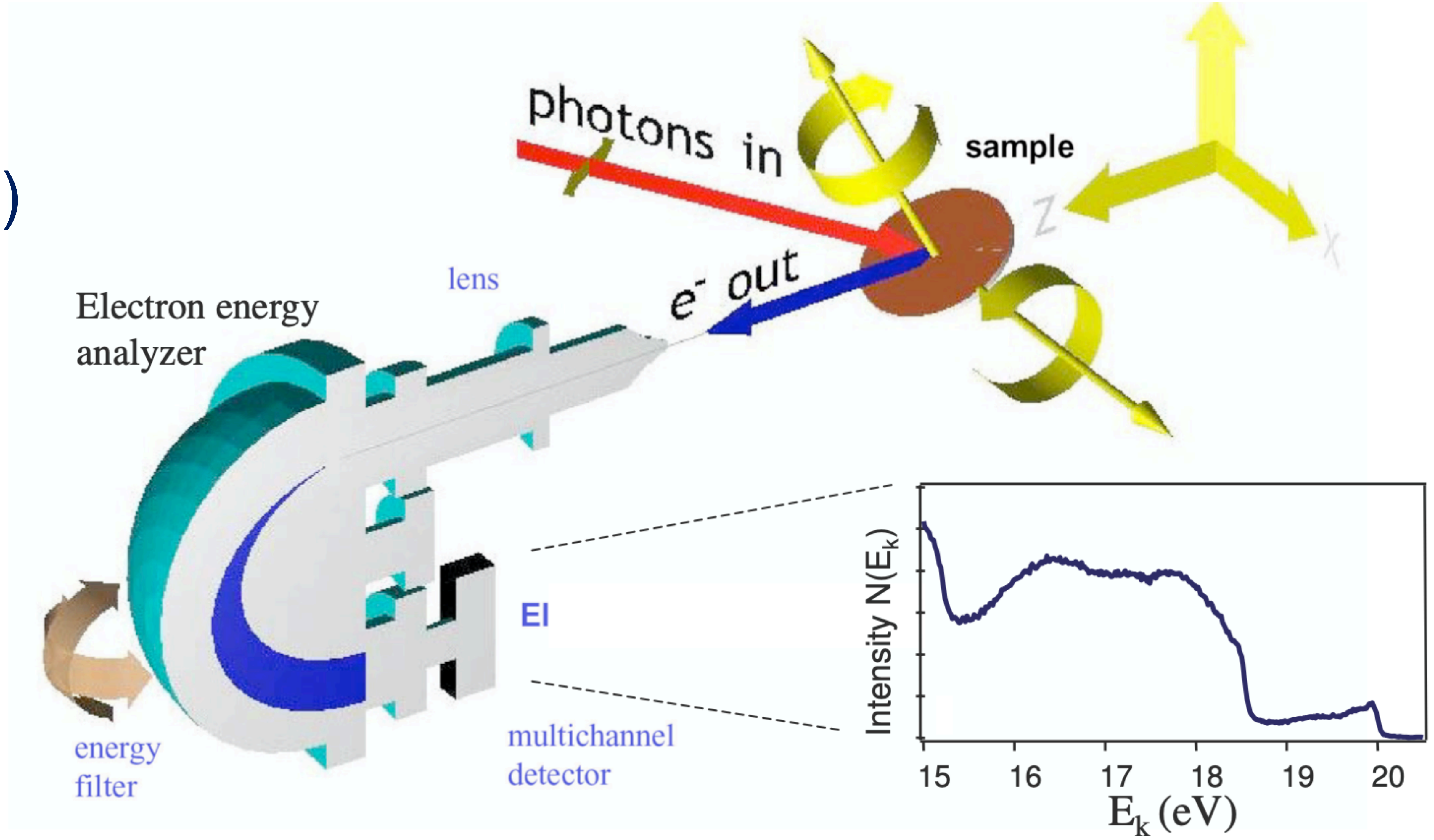
- According to

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

we can extract information about the initial binding energy of the electron.

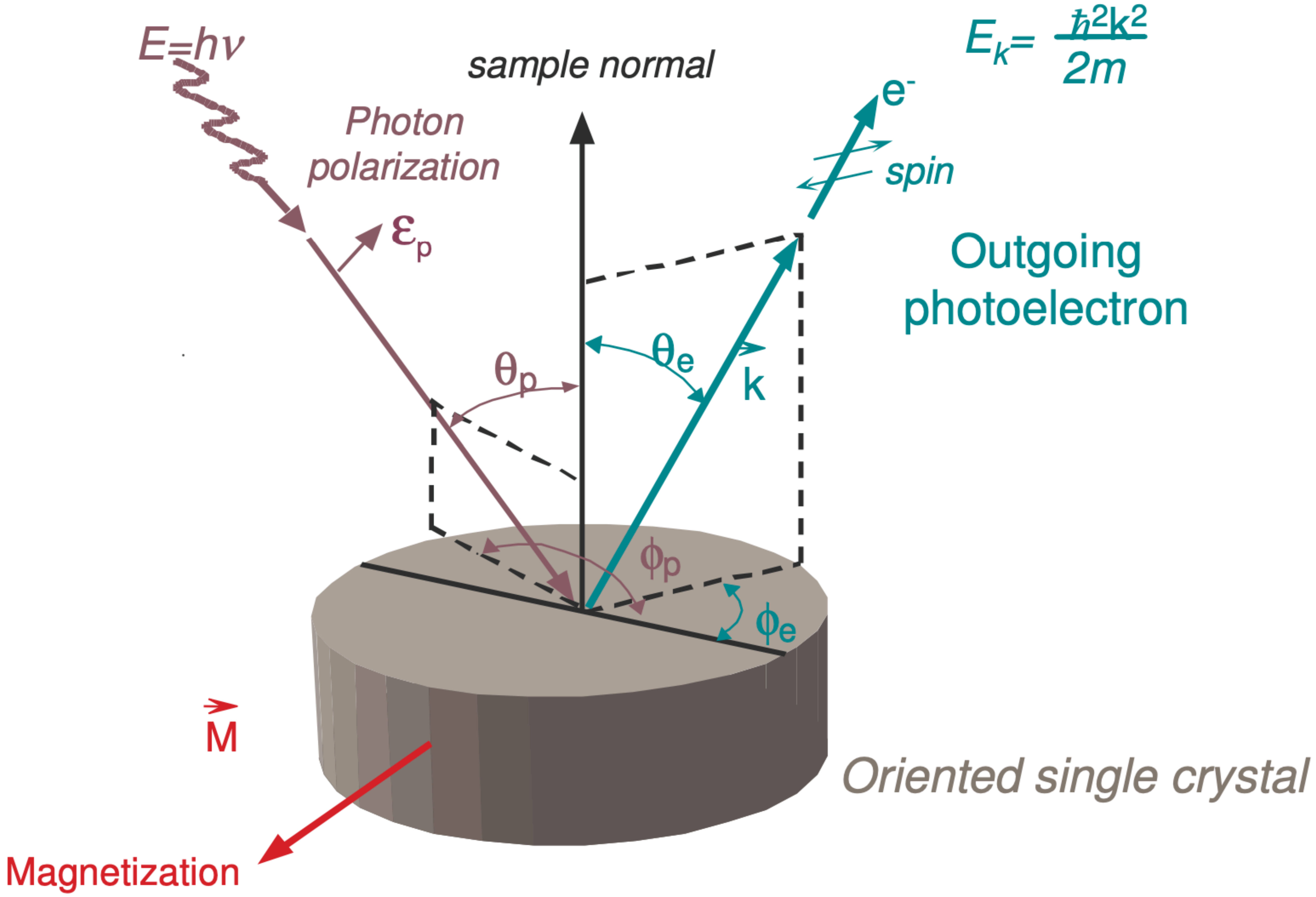
- Monochromatic photon source needed!

- Aim of the experiment: collecting the photoemitted electron current.



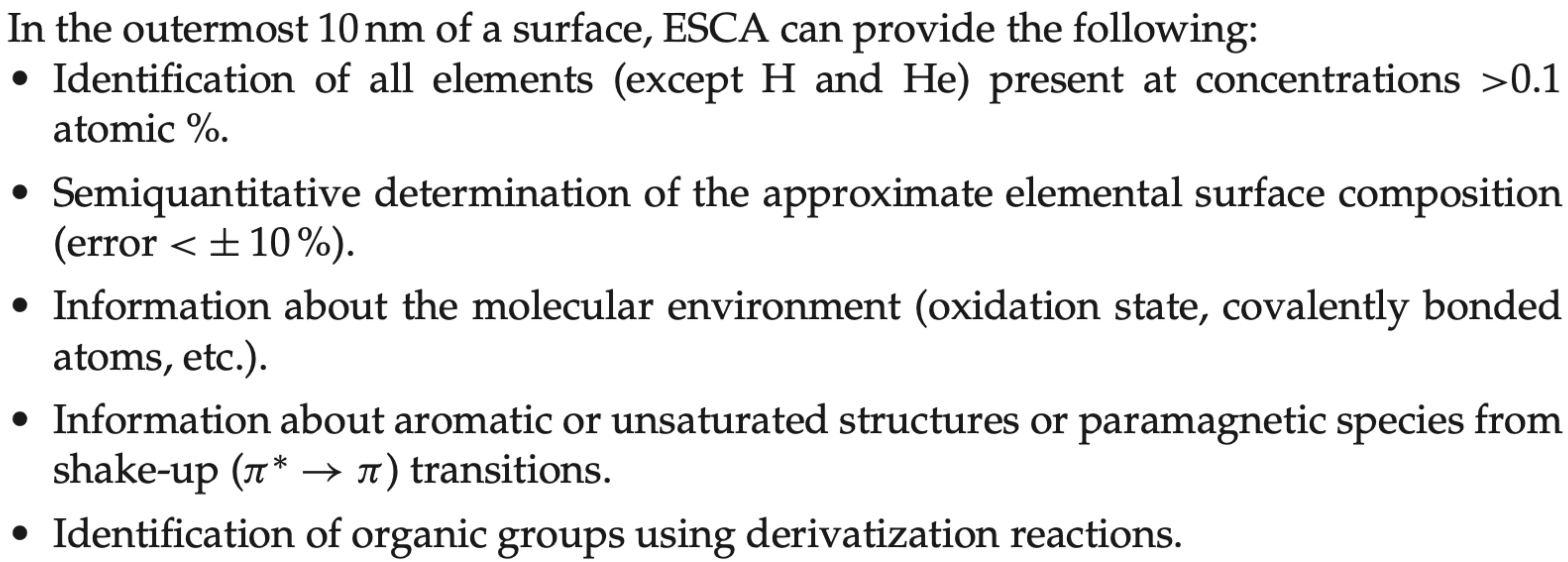
Courtesy: S. Lizzit

XPS Experiment Geometry



Courtesy: S. Lizzit

Information From XPS/ESCA

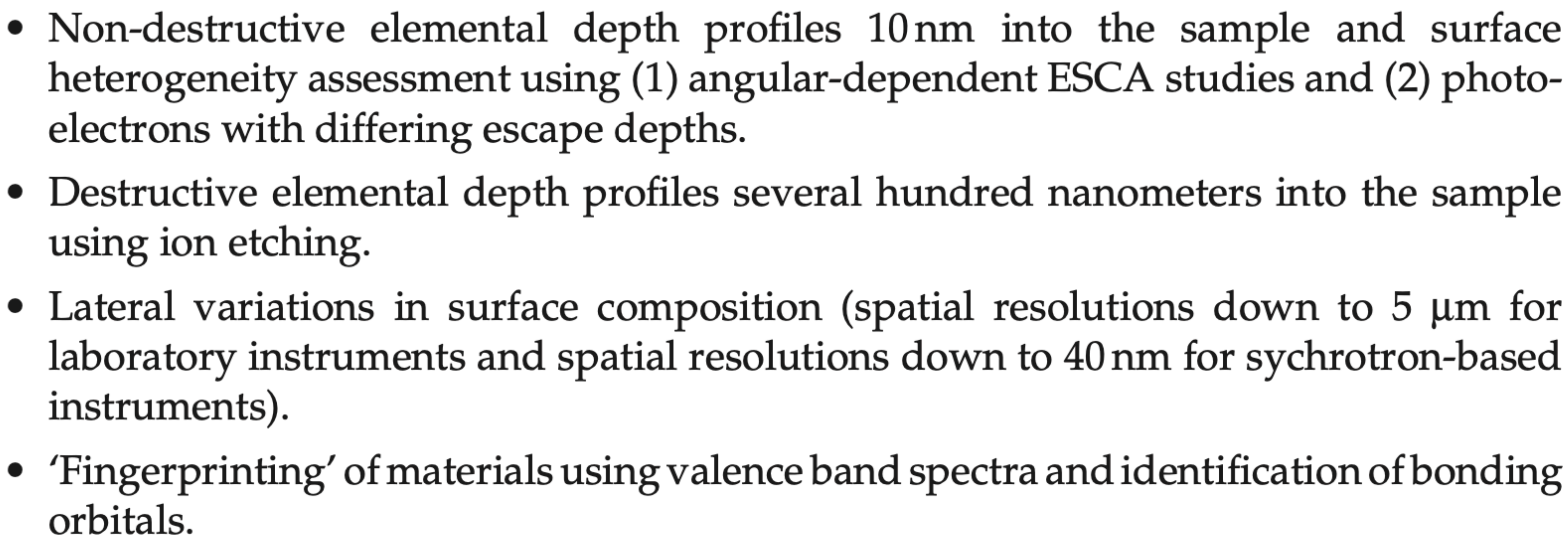


In the outermost 10 nm of a surface, ESCA can provide the following:

- Identification of all elements (except H and He) present at concentrations >0.1 atomic %.
- Semiquantitative determination of the approximate elemental surface composition (error $< \pm 10\,\%$).
- Information about the molecular environment (oxidation state, covalently bonded atoms, etc.).
- Information about aromatic or unsaturated structures or paramagnetic species from shake-up ($\pi^* \rightarrow \pi$) transitions.
- Identification of organic groups using derivatization reactions.

J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

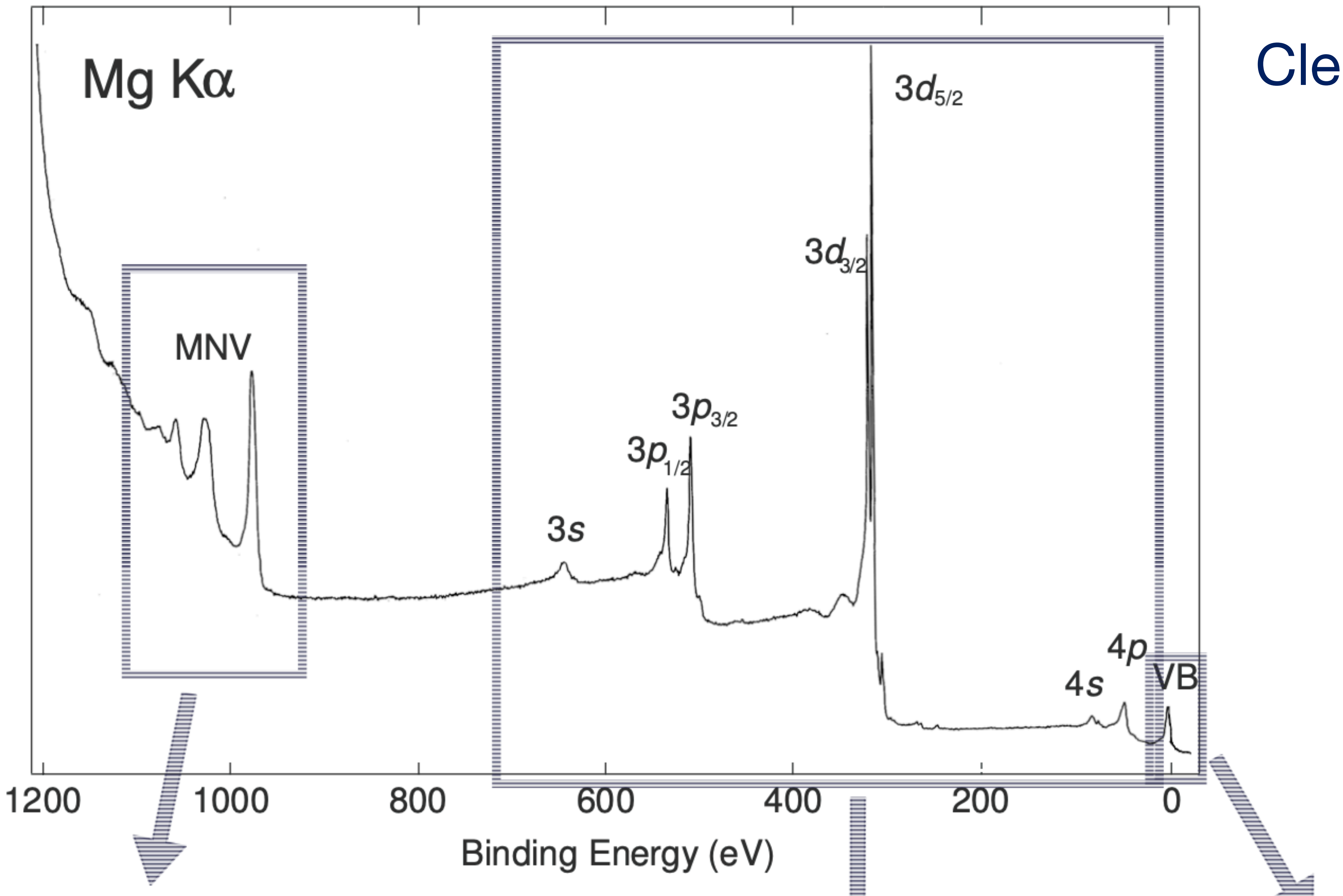
Information From XPS/ESCA



- Non-destructive elemental depth profiles 10 nm into the sample and surface heterogeneity assessment using (1) angular-dependent ESCA studies and (2) photoelectrons with differing escape depths.
- Destructive elemental depth profiles several hundred nanometers into the sample using ion etching.
- Lateral variations in surface composition (spatial resolutions down to 5 µm for laboratory instruments and spatial resolutions down to 40 nm for sychrotron-based instruments).
- ‘Fingerprinting’ of materials using valence band spectra and identification of bonding orbitals.

J. Vickerman, Surface Science, the Principal techniques (Wiley 2009)

A Typical XPS Spectrum



Clean Rh single crystal

Auger Electrons
AES

Core levels
XPS or ESCA

Valence Band
(AR)UPS

The Rich Structure of Photoemission Spectrua

1. Photoemission peaks
   - Narrow
   - Nearly symmetric
   - Shifted by chemistry

2. X-ray satellite peaks
   - Not observed with a monochromatized source.
   - Always the same energy shift from the photoemission peaks

3. Shake-up satellites and shake-off satellites.

4. Photon-induced Auger lines.

5. Inelastic scattering background

6. Valence band features

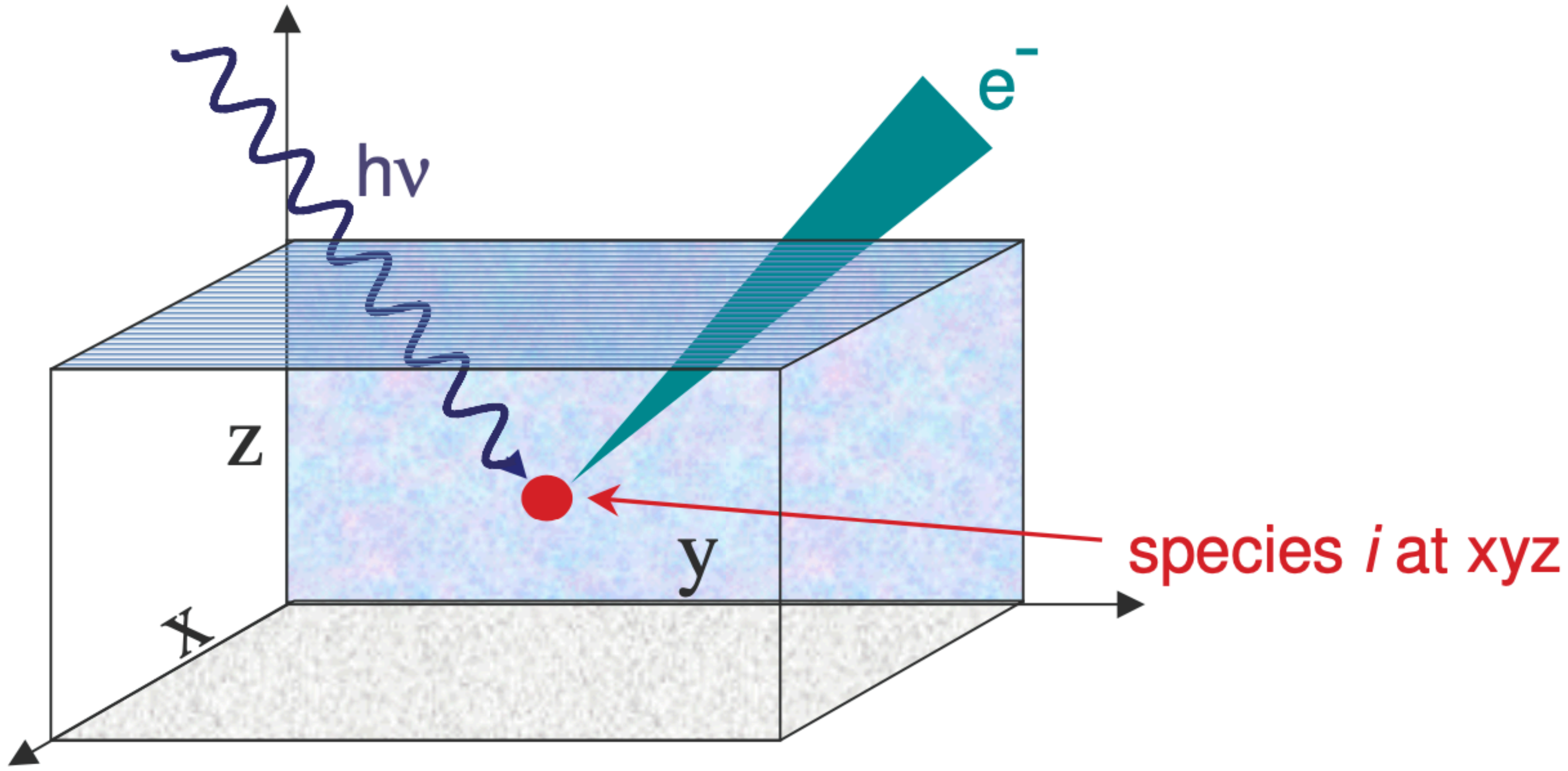
7. Spin–orbit coupling

8. Multiplet splitting

9. Plasmon losses

Photoemission Intensity

Interplay of different factors.



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

- dNi= (number of atoms of *i* at position *xyz*).
- Photon flux at *xyz*.
- 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 and detection efficiency.

Incoming Radiation

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

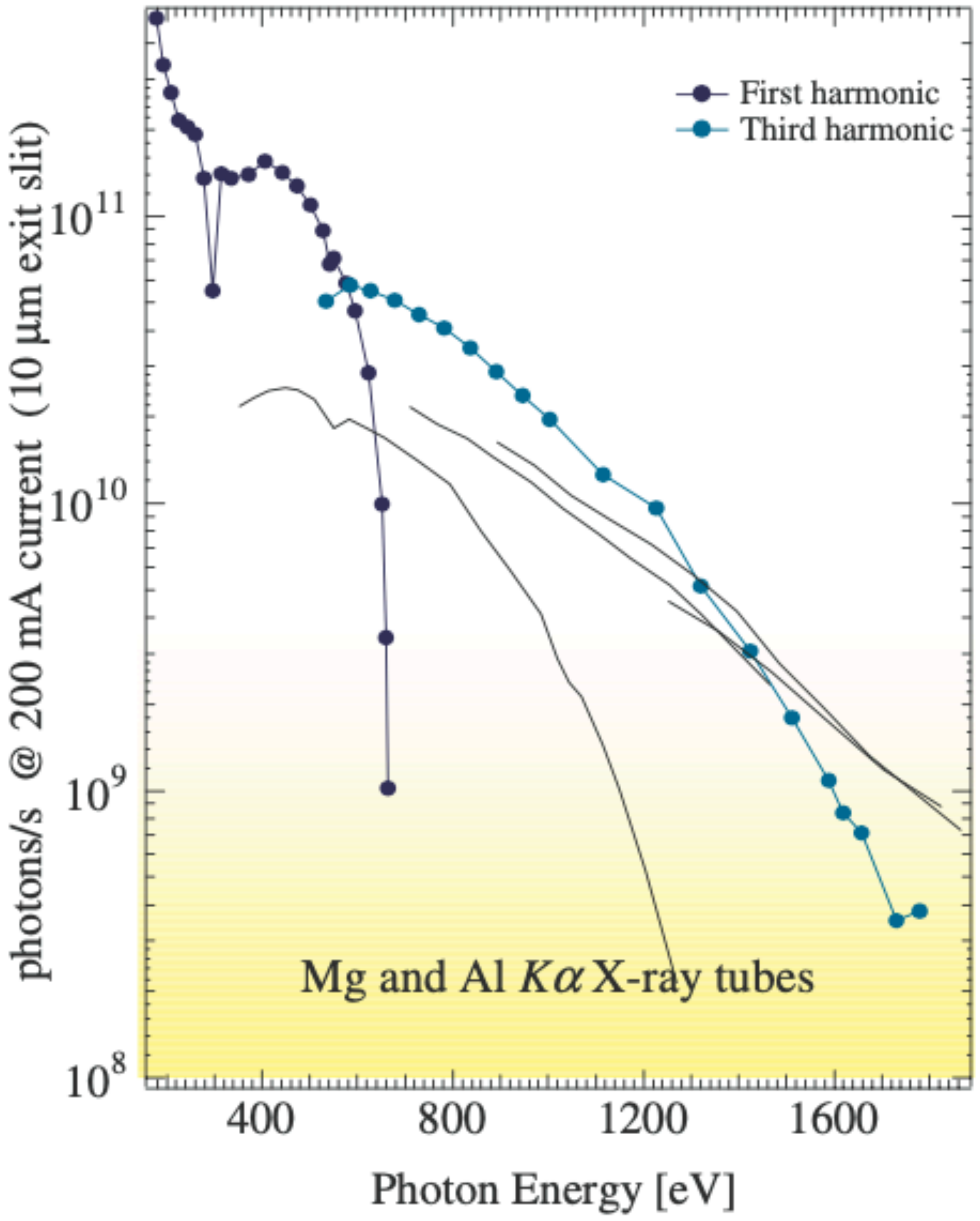
Laboratory sources can generate:

- UV photons (He Iα=21.2 eV), with noble gas discharge sources.
- X-ray photons (Al K_α=1486.6 eV and Mg K_α=1253.6 eV)

Synchrotrons can produce photons with a tunable energy and with much higher brilliance than conventional lab sources.

When comparing spectra, we will need to take into account the photon flux on the sample.

Measured photon flux
at synchrotrons vs conventional sources



Photoemission Cross Section

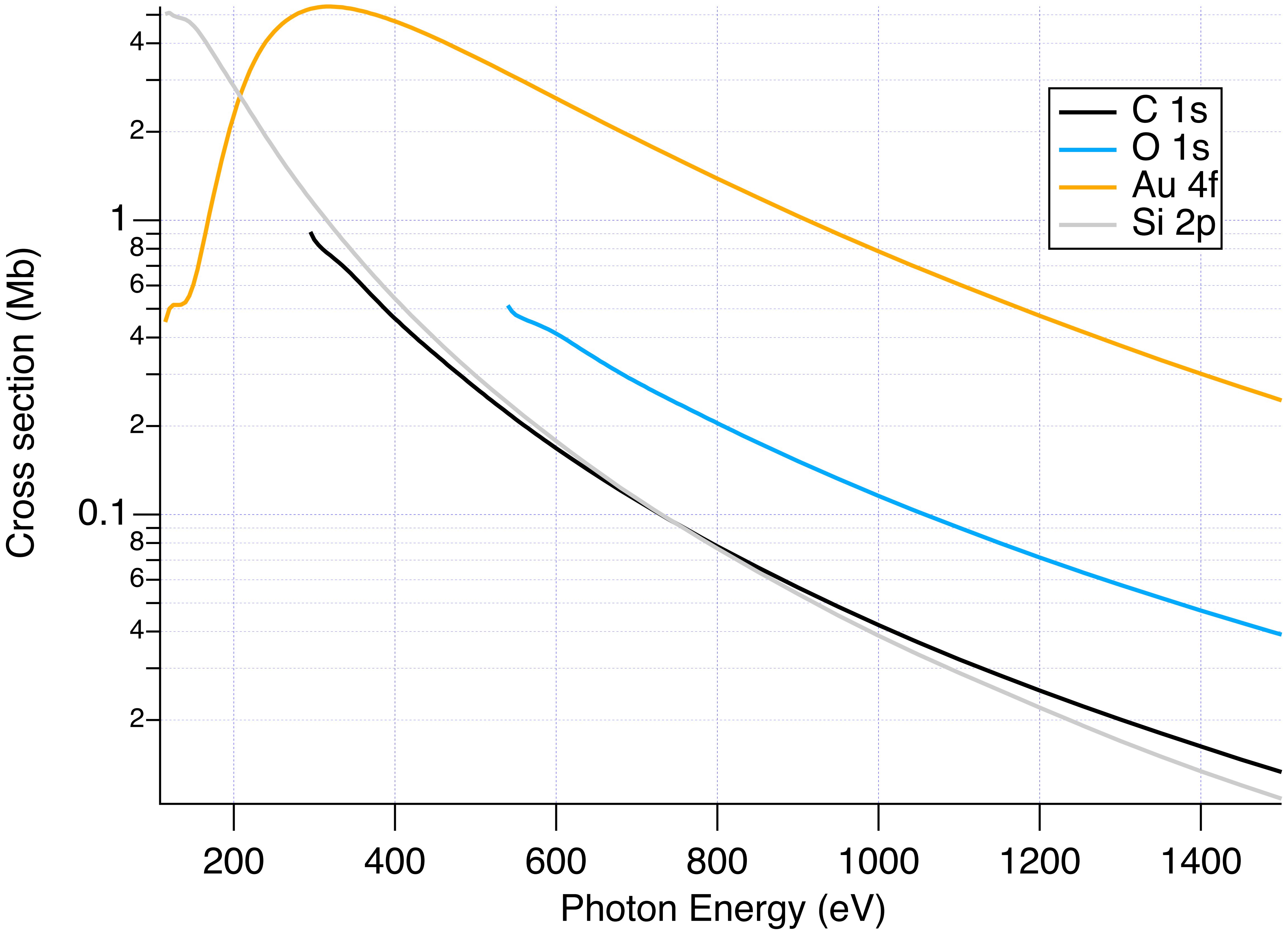
Photoemission cross section= Probability per unit time of exciting the system from an initial state Ψ_i to a final state Ψ_f with a photon flux of 1 cm^{-2} s^{-1}.

We define the **Barns** (unity for the cross section) as $b=10^{-24}$ cm^2

In case of a solid, one monolayer contains ca. 10^{15} atoms/cm^2.

The cross section of 1 Mb corresponds approximately to 1 photoelectron emitted from surface every 1000 incidents photons, for 1 monolayer of the species contributing to the XPS signal.

Photoemission Cross Section



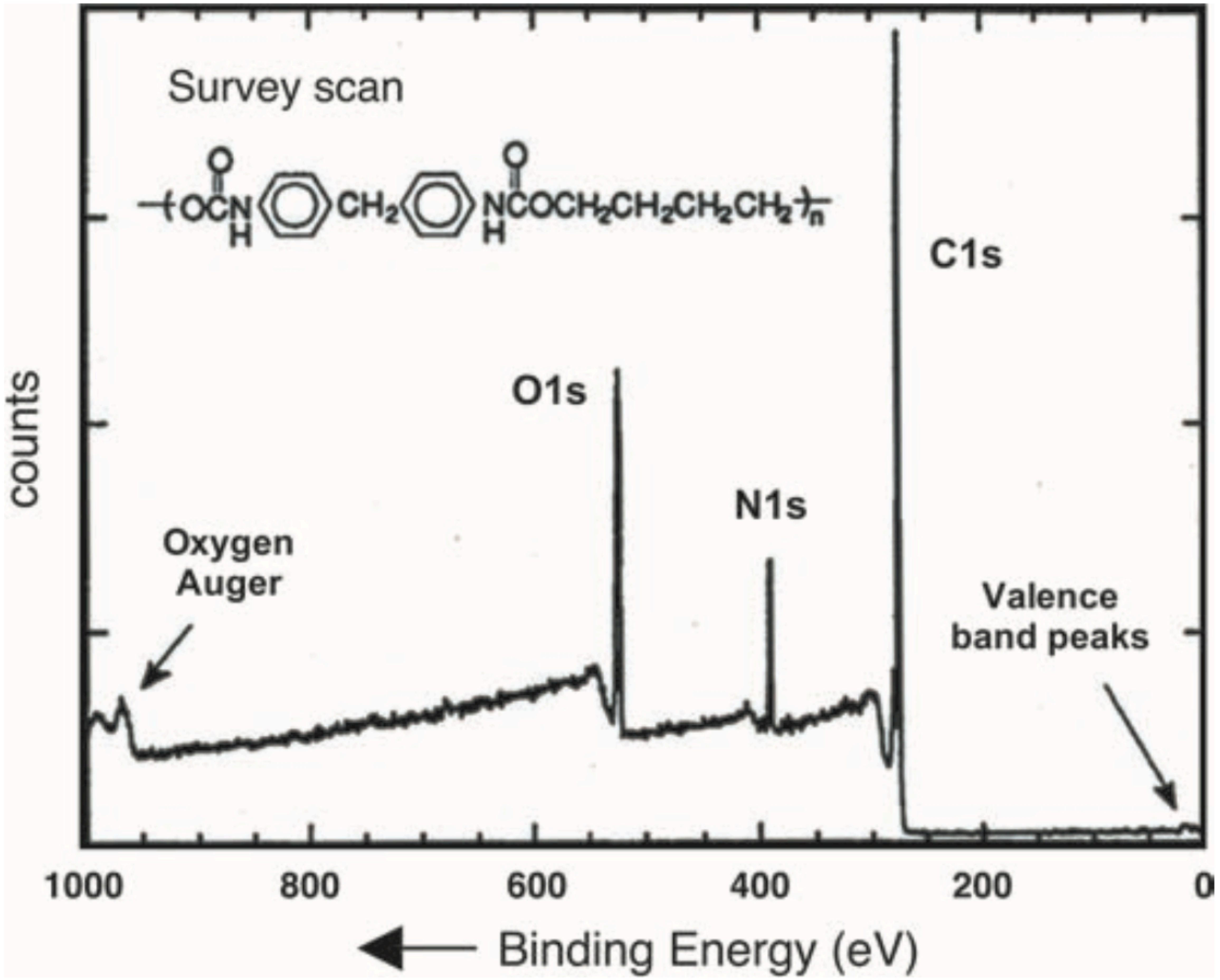
Calculated photoemission cross sectionfor each element and for each emission peak available at https://vuo.elettra.eu/services/elements/WebElements.html. The data are taken from: J.J. Yeh, Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993 and from J.J. Yeh and I. Lindau, Atomic Data and Nuclear Data Tables, 32, 1-155 (1985)

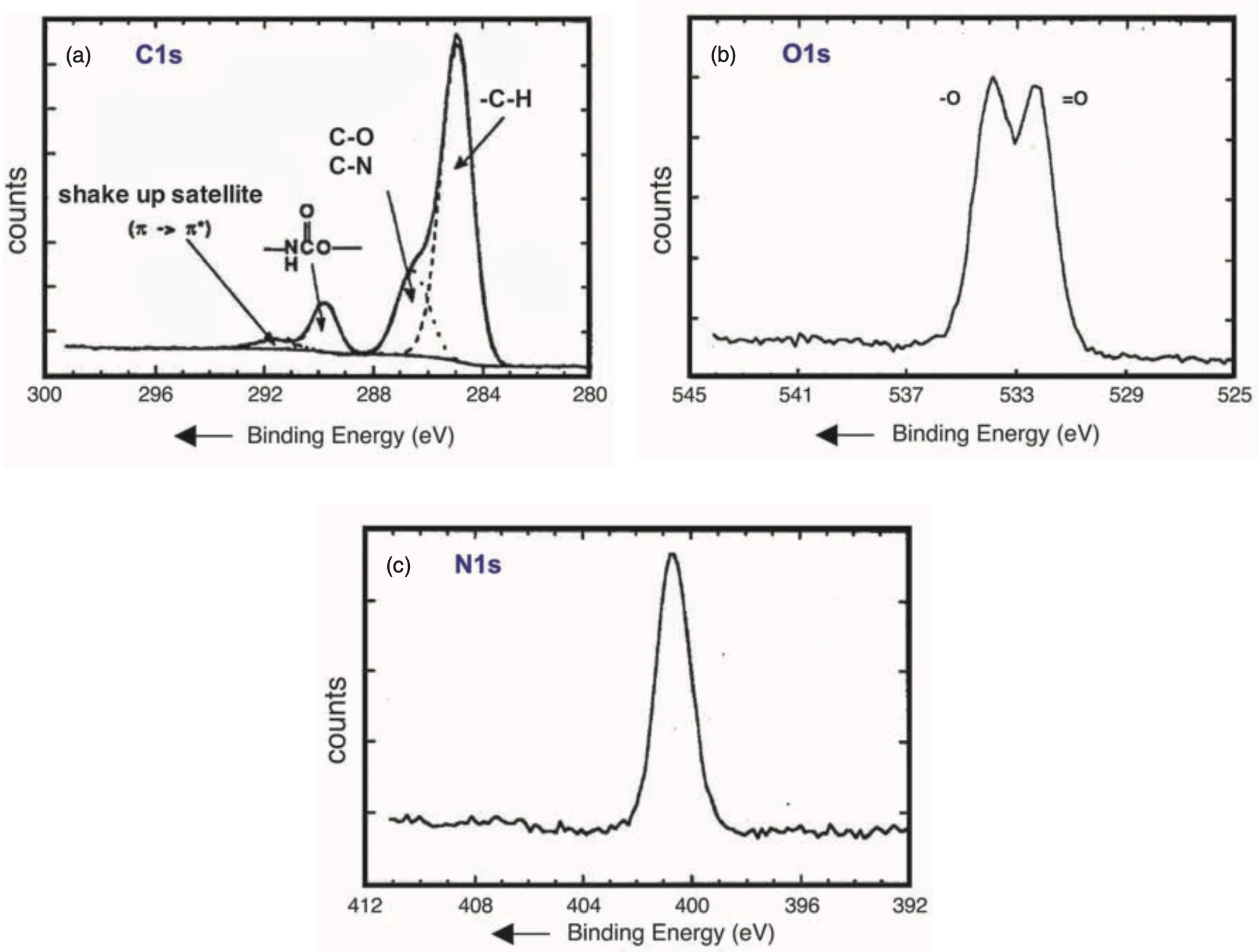
We need to take this value into account when we want to compare spectra!

For example: it is much easier to photoemit electrons from Au 4f than from C 1s with a photon of 400 eV (~10 times higher cross section).
Very important for quantification!

Features in XPS Spectra

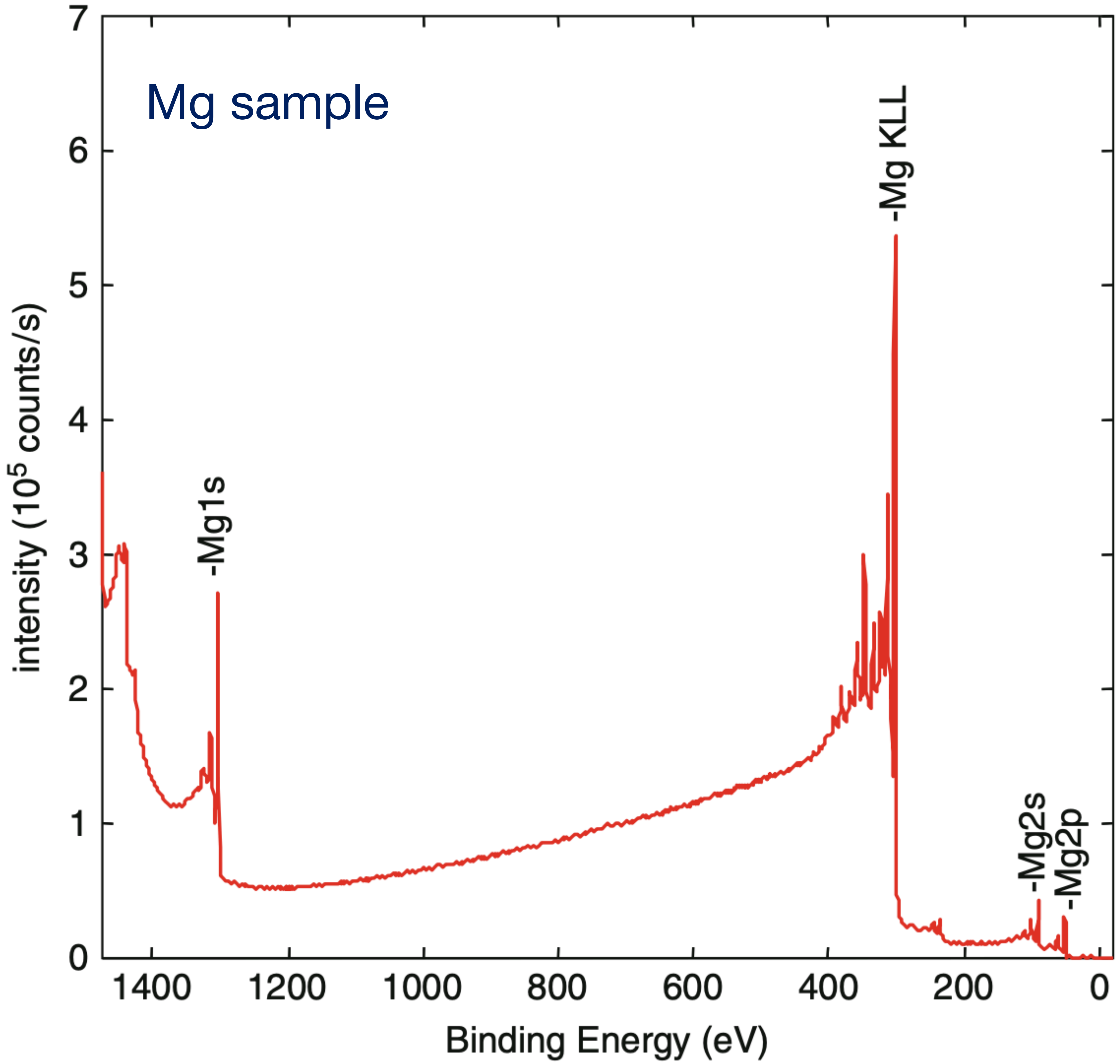
Sample: hard-segment polyurethane



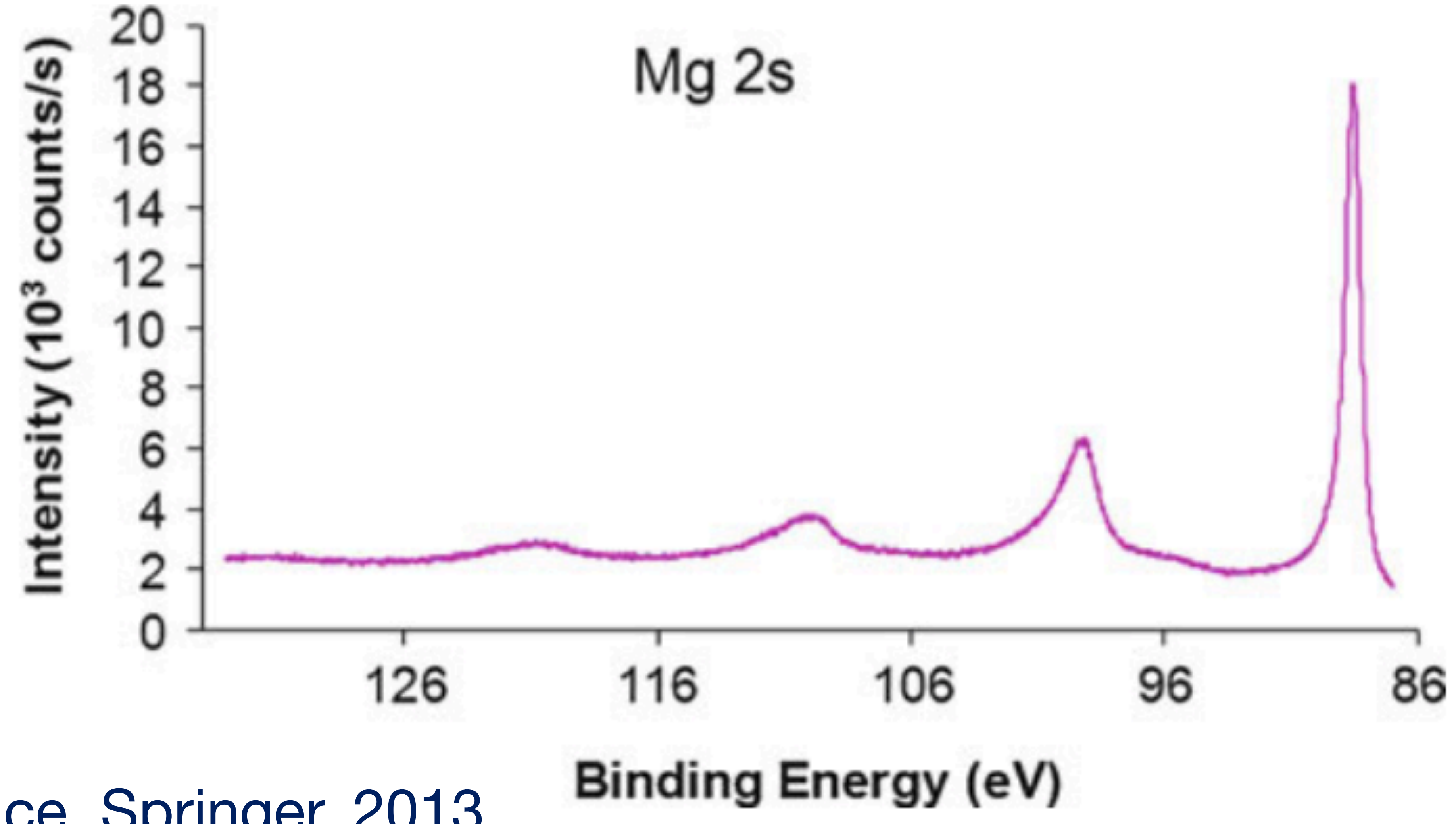


J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

Elemental Identification



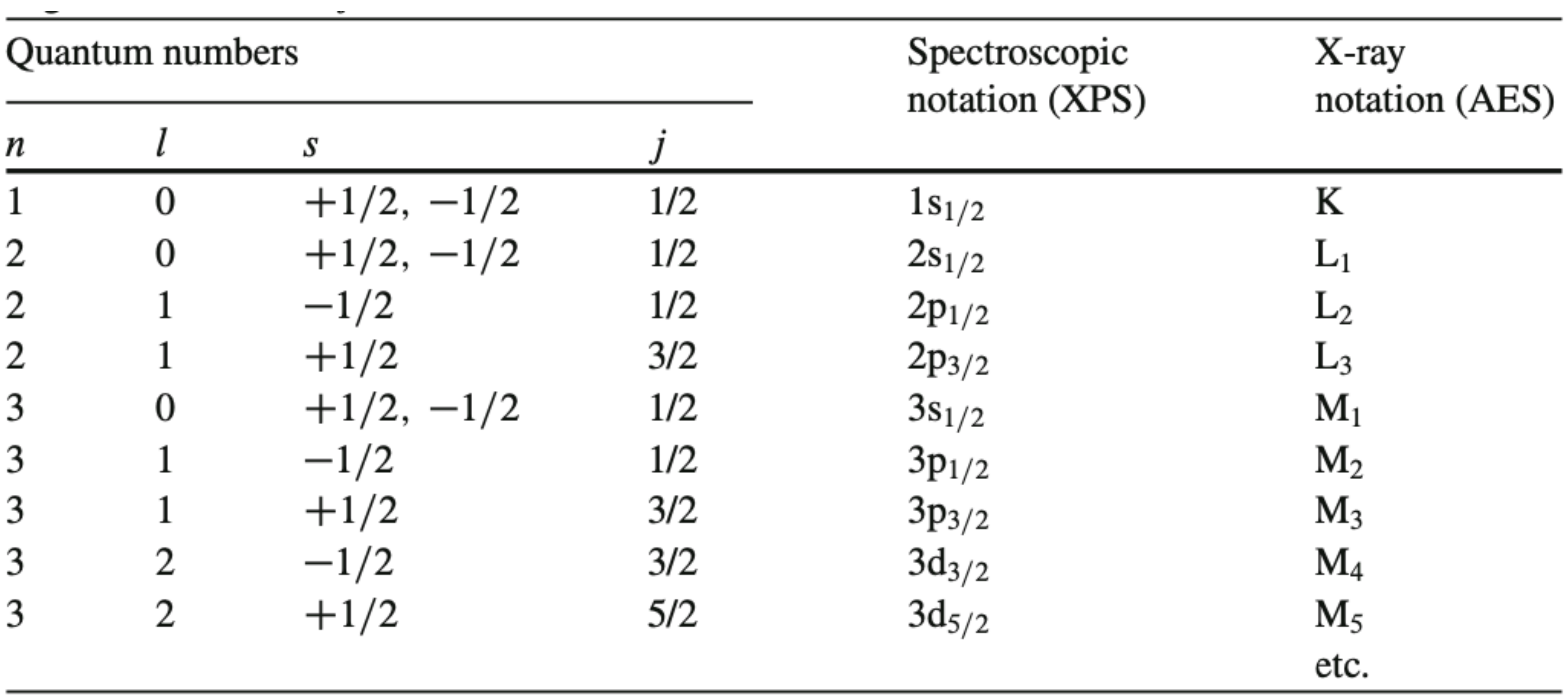
XPS is chemically-selective: we do observe specific emission lines which are different for each chemical element.
Different elements have different electronic state distribution —> different core-level binding energy.



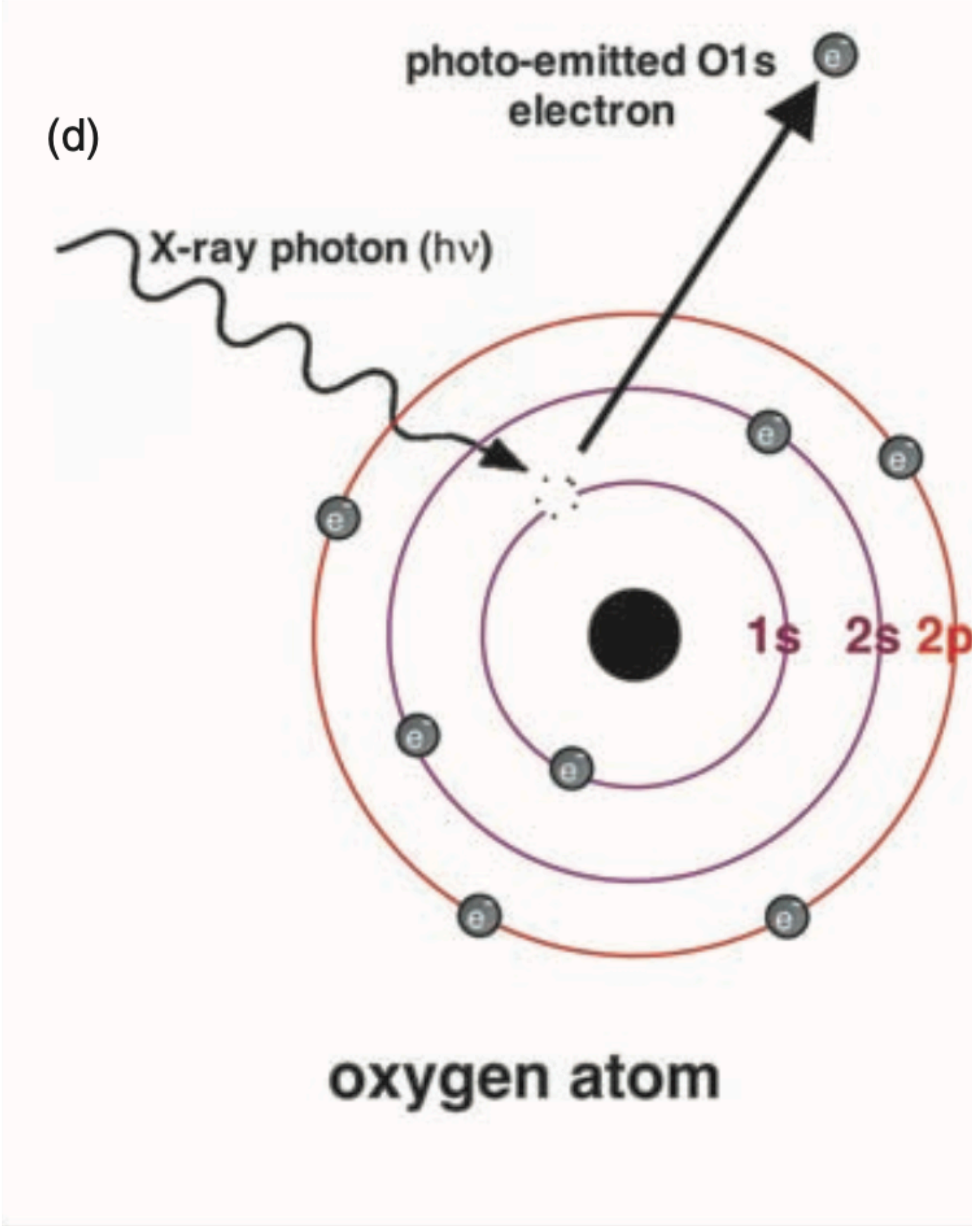
S. Hofmann, Auger- and X-Ray Photoelectron Spectroscopy in Materials Science, Springer, 2013.

Labelling of Initial States

We can label the state from which the electron is emitted.



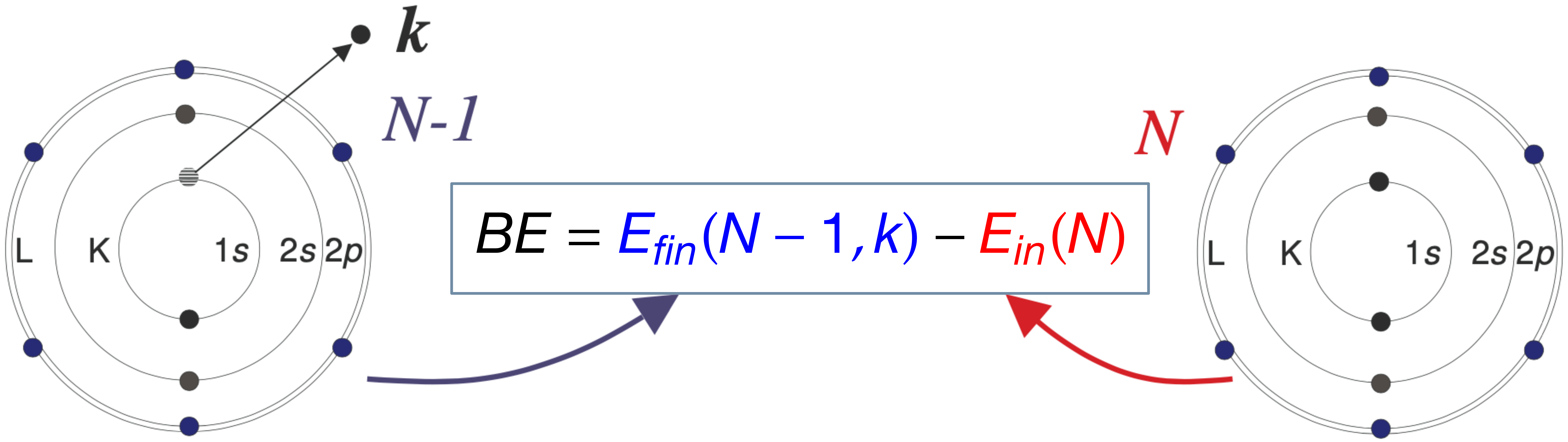
Quantum numbers				Spectroscopic notation (XPS)	X-ray notation (AES)
n	*l*	*s*	*j*		
1	0	+1/2, −1/2	1/2	$1s_{1/2}$	K
2	0	+1/2, −1/2	1/2	$2s_{1/2}$	L_1
2	1	−1/2	1/2	$2p_{1/2}$	L_2
2	1	+1/2	3/2	$2p_{3/2}$	L_3
3	0	+1/2, −1/2	1/2	$3s_{1/2}$	M_1
3	1	−1/2	1/2	$3p_{1/2}$	M_2
3	1	+1/2	3/2	$3p_{3/2}$	M_3
3	2	−1/2	3/2	$3d_{3/2}$	M_4
3	2	+1/2	5/2	$3d_{5/2}$	M_5
					etc.



S. Hofmann, Auger- and X-Ray Photoelectron Spectroscopy in Materials Science, Springer, 2013.

Binding Energy and Chemical Shift

The general concept of the electron binding energy and its relationship to the energy of the incident X-ray and the emitted photoelectron is central in XPS.



$$BE = E_{fin}(N-1,k) - E_{in}(N)$$

Koopman's Theorem

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

$$BE(k) = -\epsilon_k$$

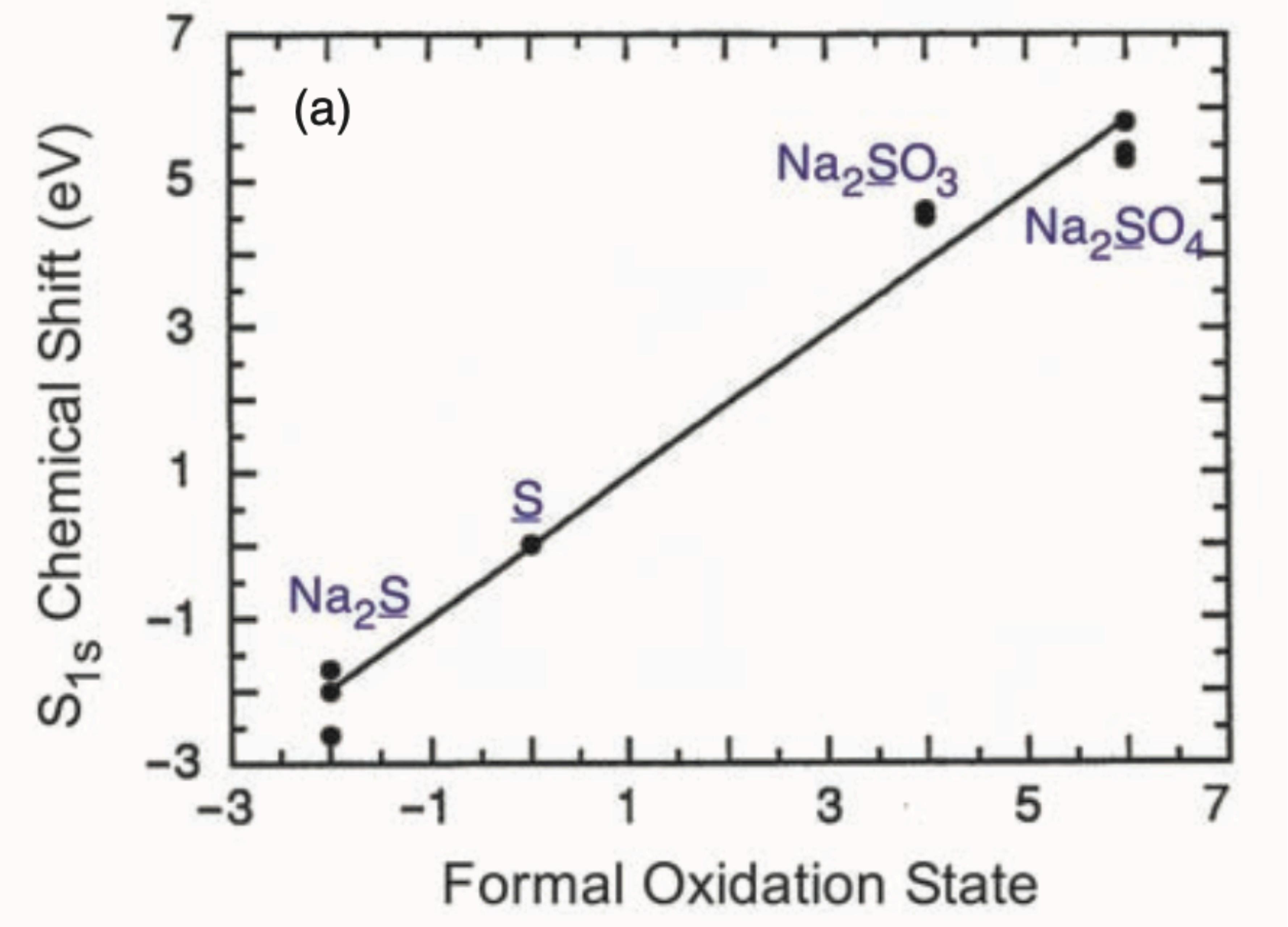
Hartree-Fock orbital energy.
But the value returned is grossly misestimated!

Initial State Effects

The failure of Hartree-Fock calculation in providing the right binding energy for the electrons is due to the frozen-orbital approximation. But other effects need to be taken into account.

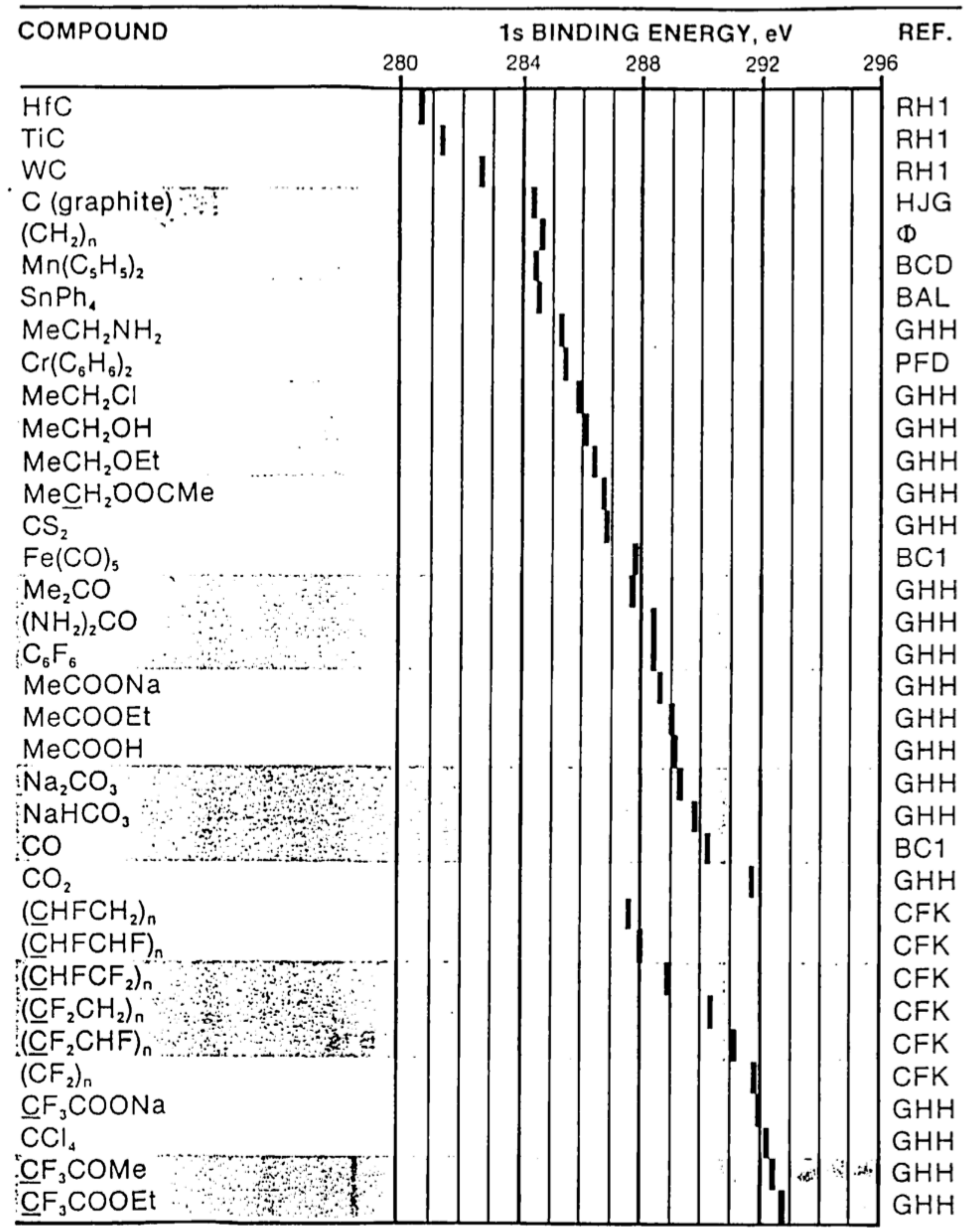
Initial state effects: If the energy of the atom's initial state is changed, for example, by formation of chemical bonds with other atoms, then the *E*$_B$ of electrons in that atom will change.

The change in BE deriving is called the **chemical shift**.



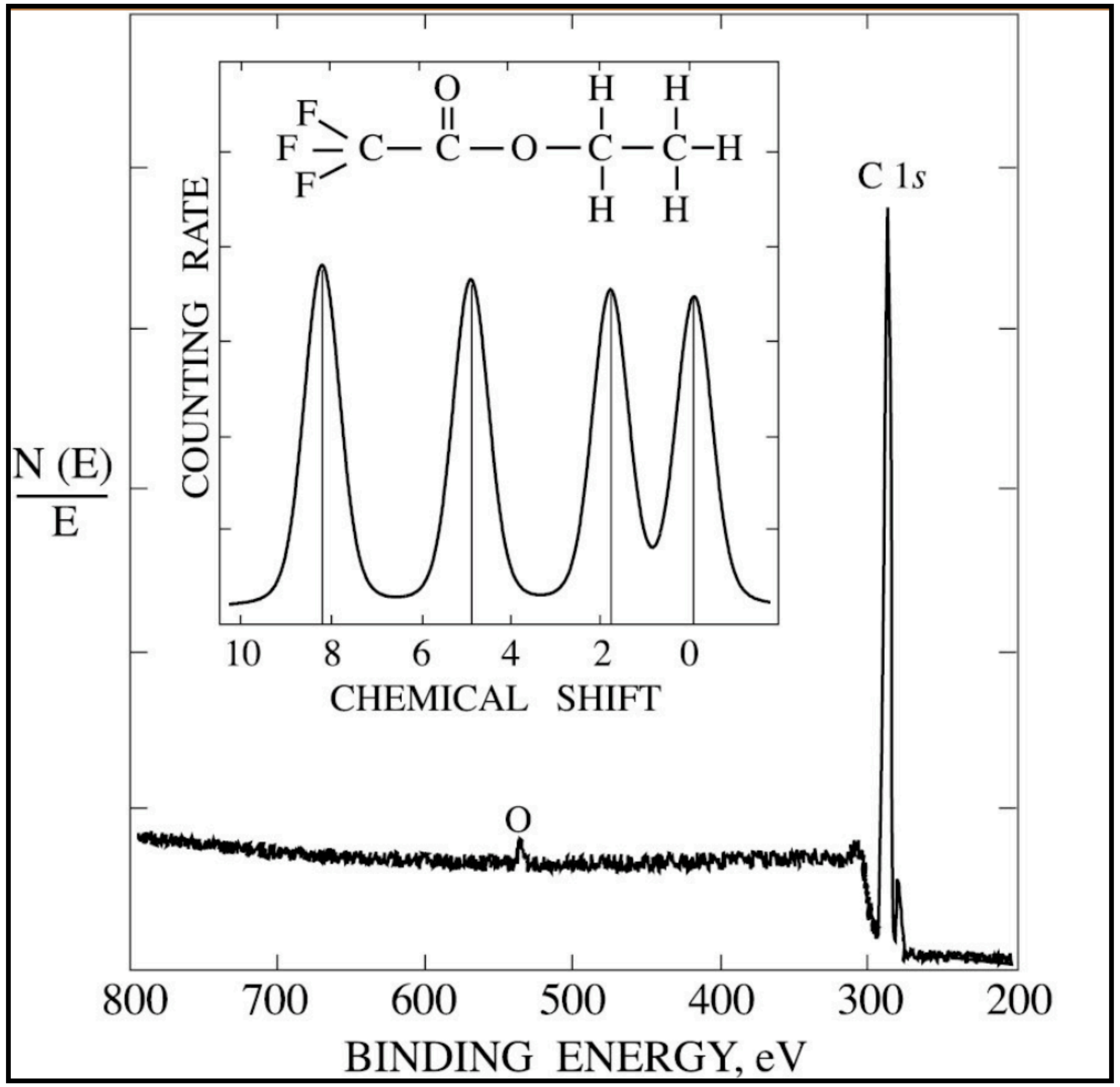
Functional group		Binding energ (eV)
Hydrocarbon	C—H, $\underline{\text{C}}$—C	285.0
Amine	C—N	286.0
Alcohol, ether	$\underline{\text{C}}$—O—H, $\underline{\text{C}}$—O—C	286.5
Cl bound to carbon	$\underline{\text{C}}$—Cl	286.5
F bound to carbon	$\underline{\text{C}}$—F	287.8
Carbonyl	$\underline{\text{C}}$=O	288.0
Amide	N—$\underline{\text{C}}$=O	288.2
Acid, ester	O—$\underline{\text{C}}$=O	289.0
Urea	N—C(=O)—N	289.0
Carbamate (urethane)	O—C(=O)—N	289.6
Carbonate	O—C(=O)—O	290.3
2F bound to carbon	—CH_2CF_2—	290.6
Carbon in PTFE	—CF_2CF_2—	292.0
3F bound to carbon	—CF_3	293–294

Carbon



J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

Chemical Shift in Action

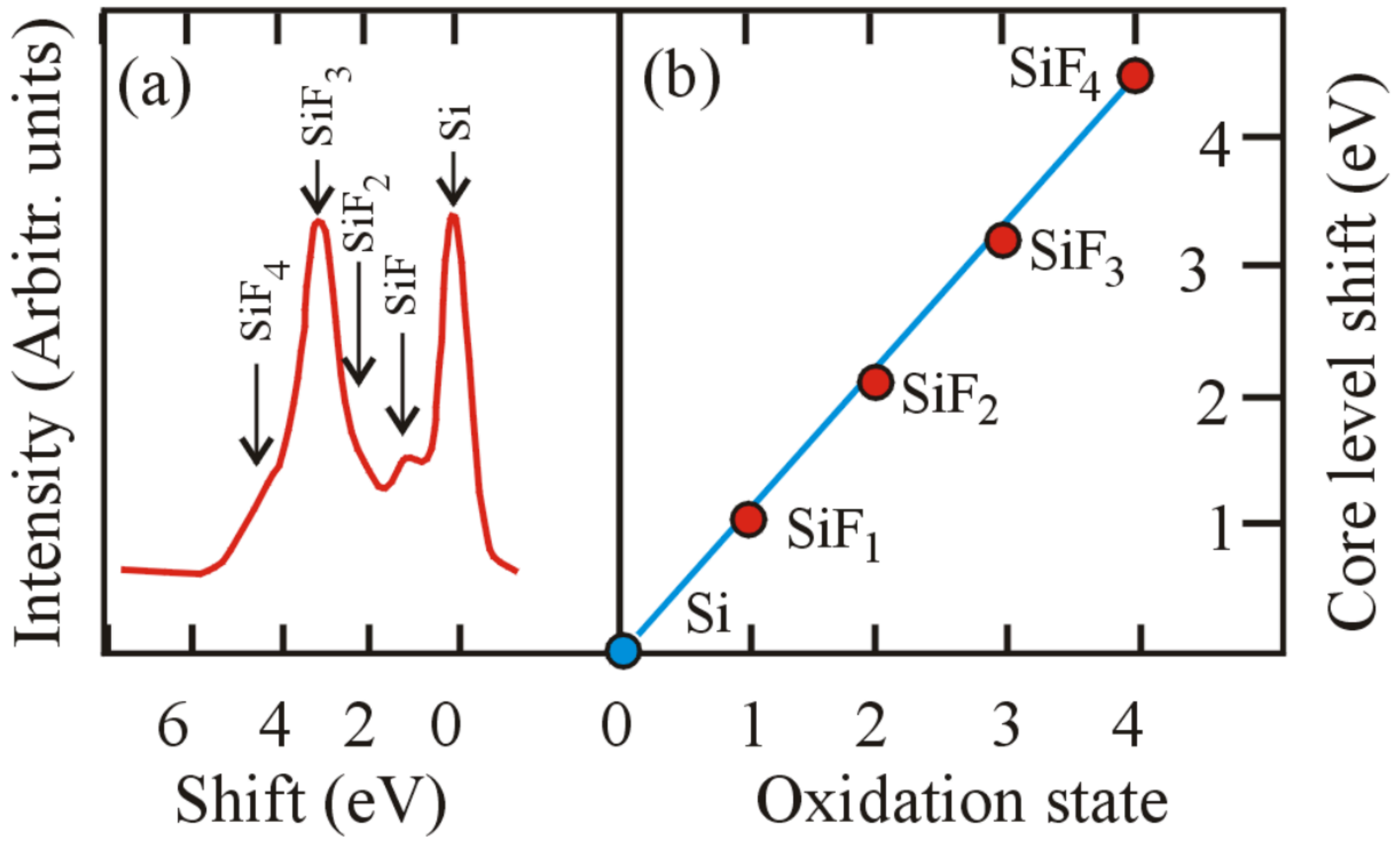


Fluorine atoms draw the C valence electrons strongly away from the carbon nuclei.

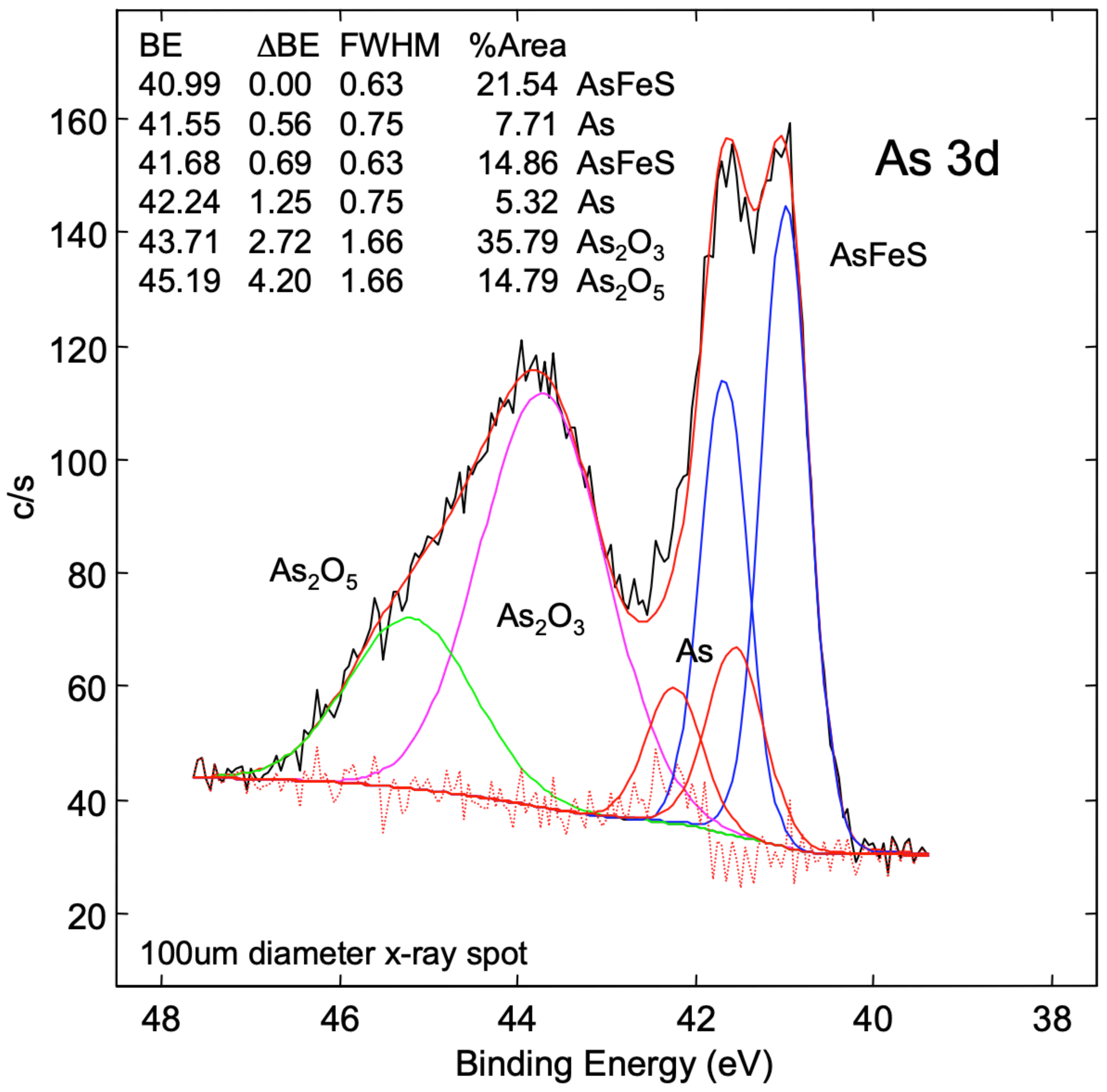
Consequently, the C 1s electrons see an effective increase of nuclear charge, which appears as a higher BE.

Adapted from: U. Gelius, E. Basilier, S. Svensson, T. Bergmark, K. Siegbahn,
J. Elect. Spectr. Rel. Phen. 2, 405 (1973)

Chemical Shift in Action



Different Fluoirine-Silcon compounds, with different oxidation states.



BE	ΔBE	FWHM	%Area	
40.99	0.00	0.63	21.54	AsFeS
41.55	0.56	0.75	7.71	As
41.68	0.69	0.63	14.86	AsFeS
42.24	1.25	0.75	5.32	As
43.71	2.72	1.66	35.79	As_2O_3
45.19	4.20	1.66	14.79	As_2O_5

High-resolution As 3d spectrum of Arsenopyrite

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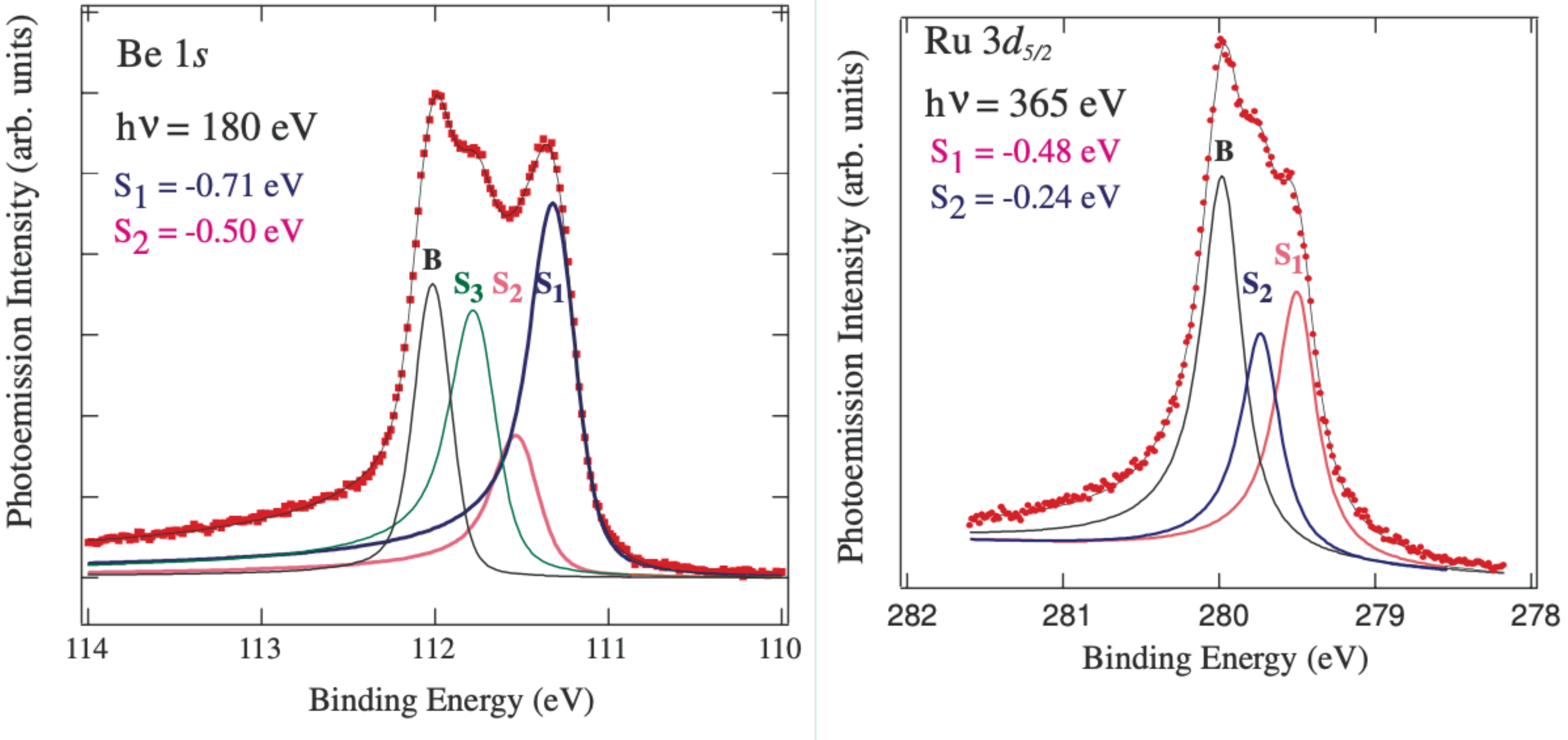
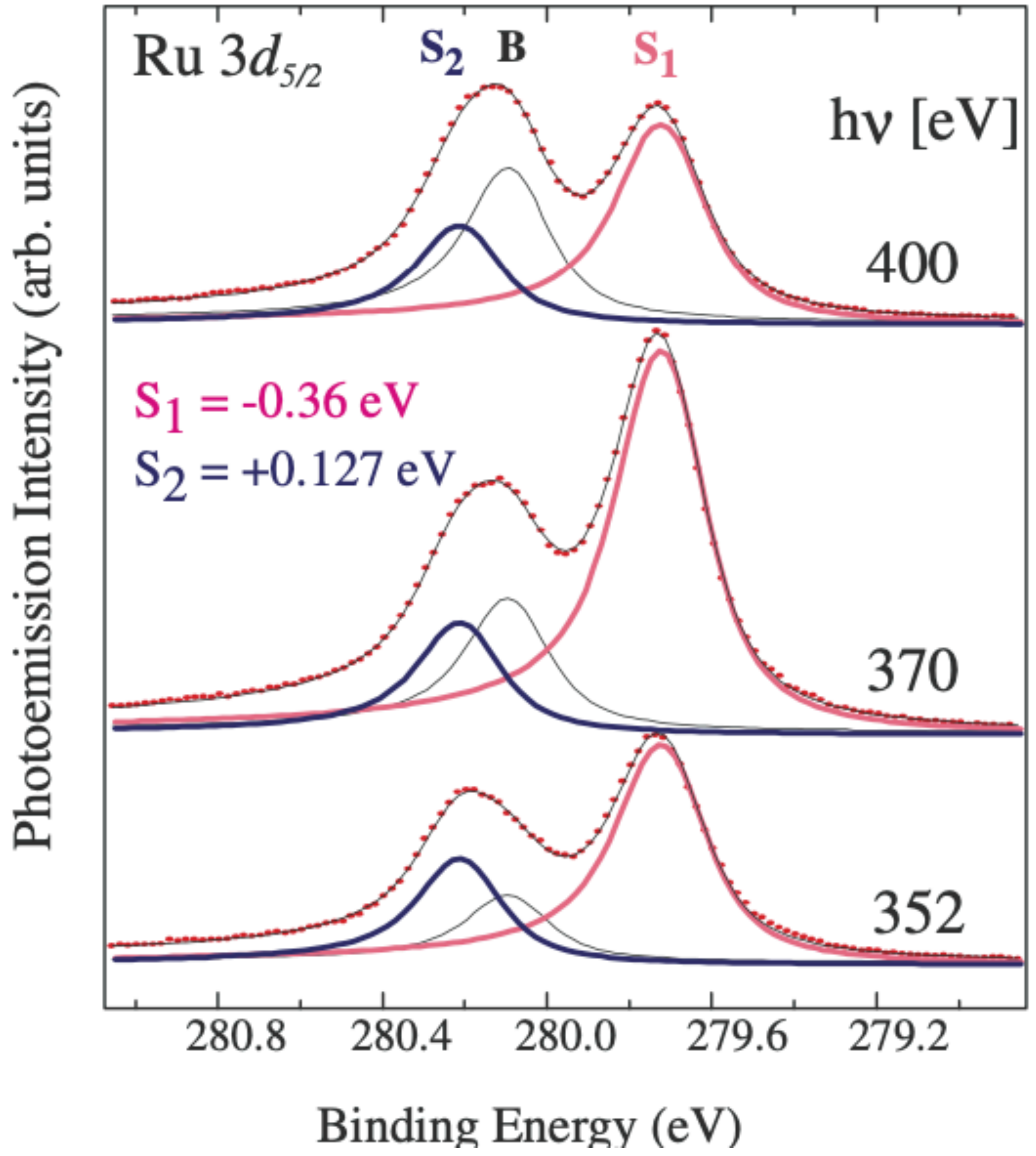
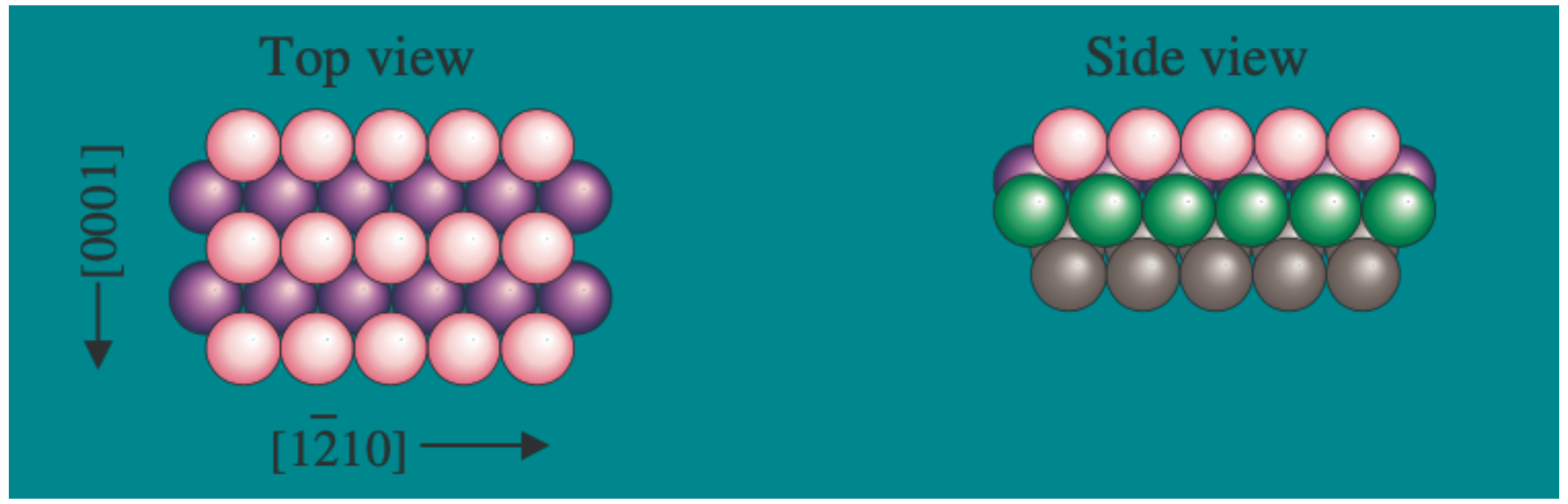
Other Initial State Effects: Surface Core Level Shifts





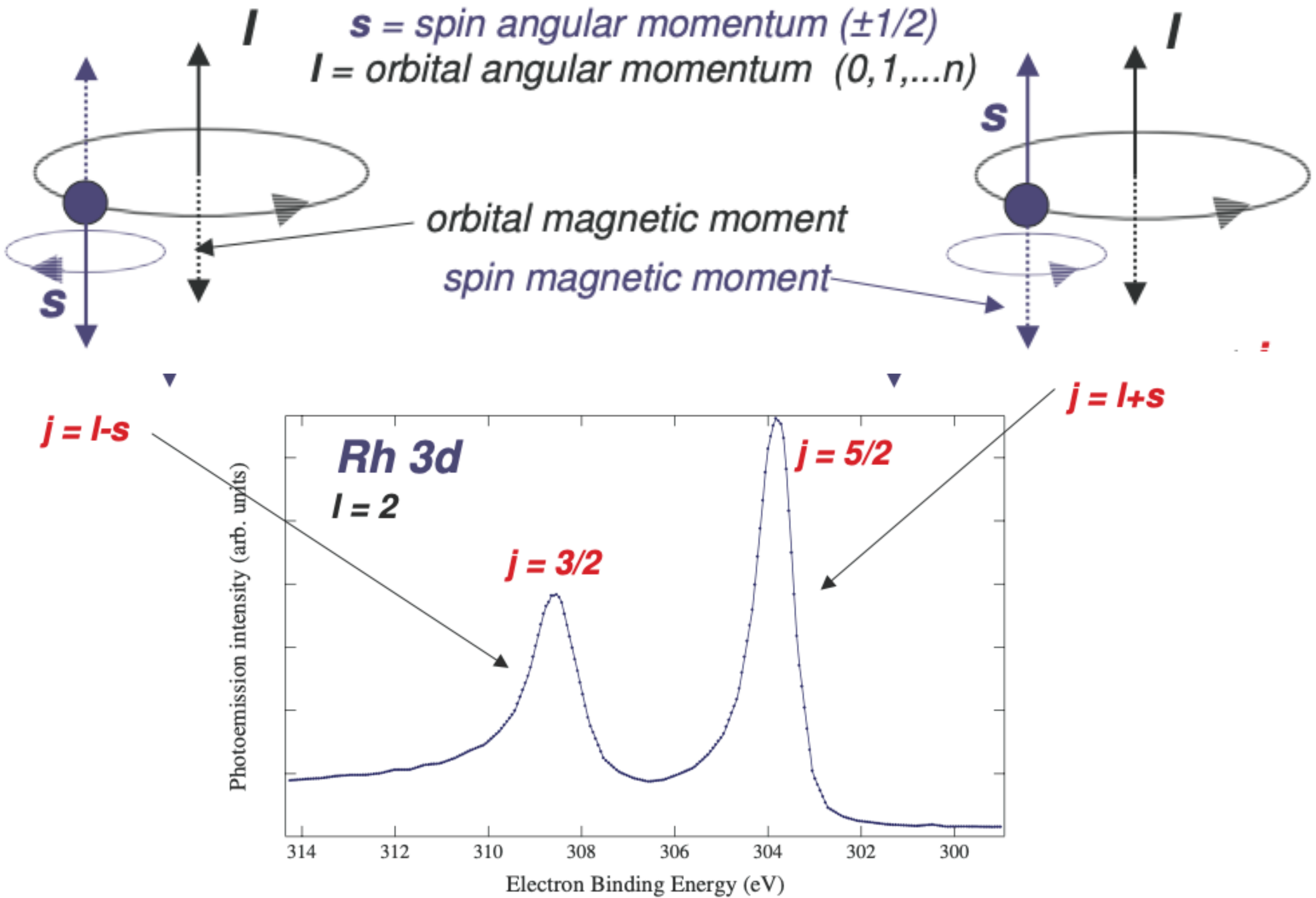


Different photon energy may help to unravel the assignment of peaks.

Courtesy, S. Lizzit.

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 we consider *j=total angular momentum*

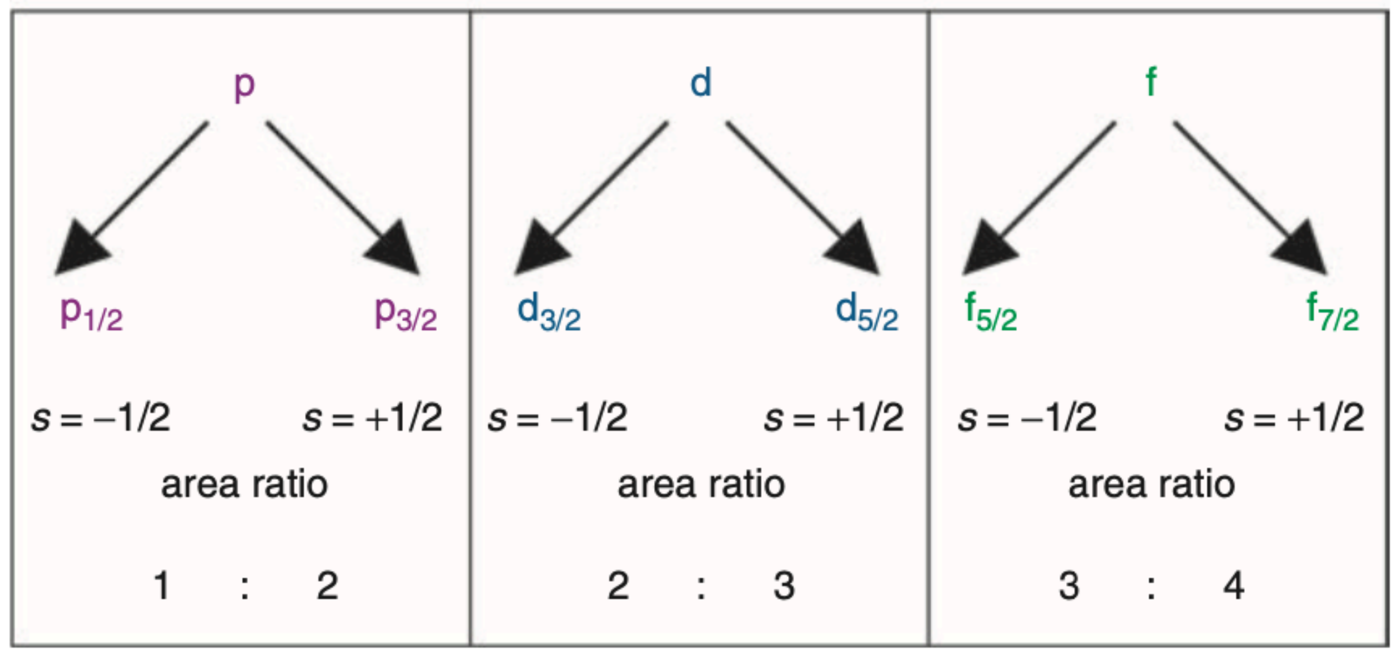


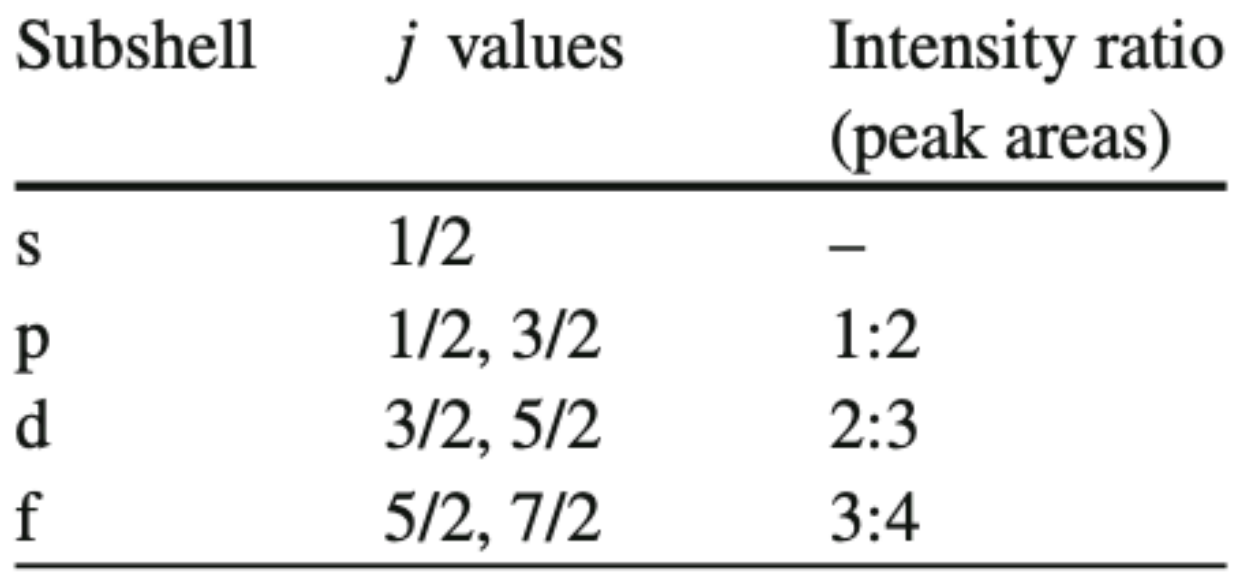
Spin-Orbit Splitting

The energy separation of the two adjacent peaks of the same orbit (same *n*, *l*) increases with atomic number and decreases for the same *n* with higher *l* values.

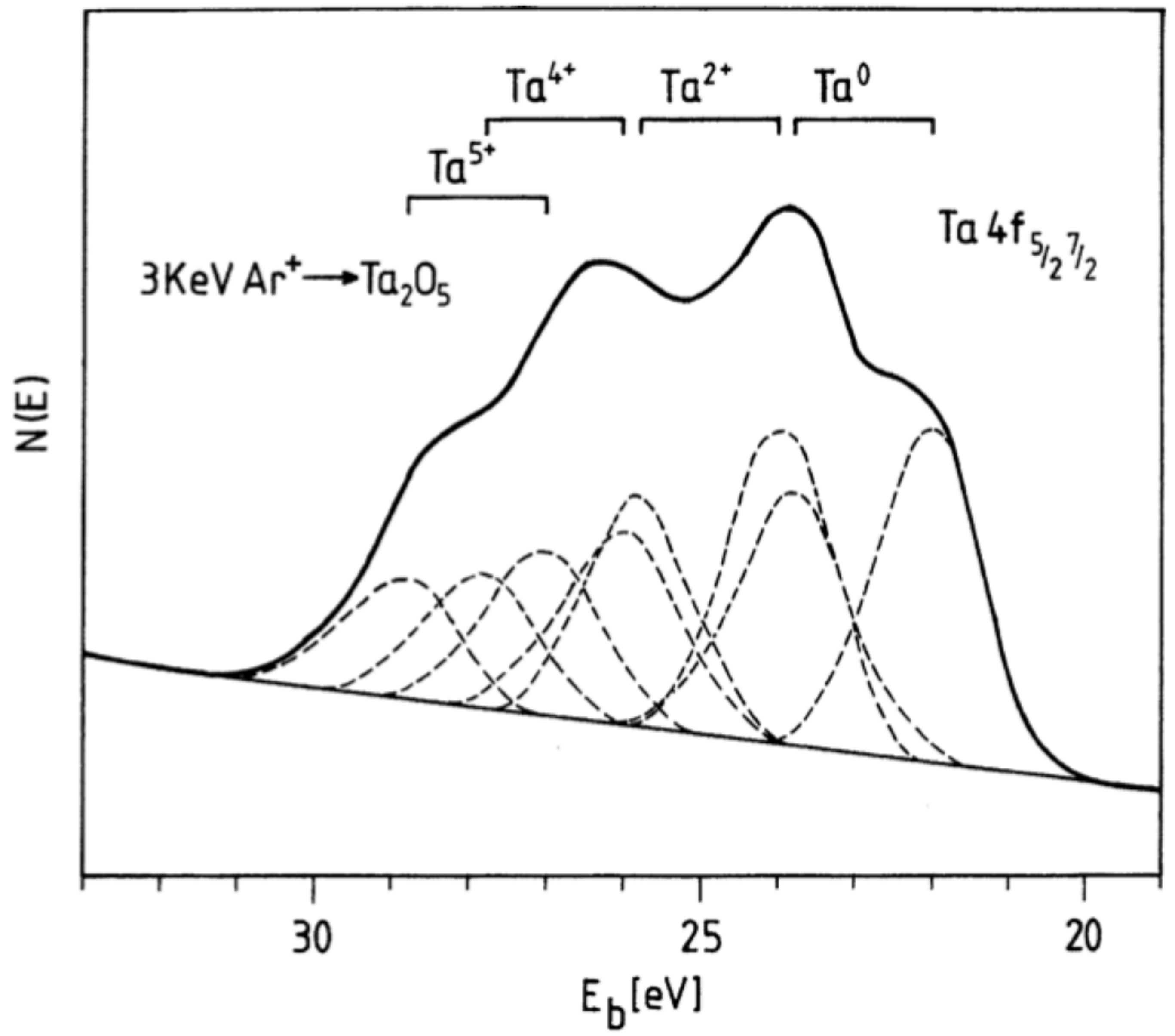
Example: Mg 2p (BE~50 eV) doublet separation is basically zero, while Si 2p shows already a splitting of about 1 eV (Si $2p_{1/2}$=99 eV; Si $2p_{3/2}$=100 eV).

The relative intensities of the doublet peaks are given by the ratio of their degeneracy (2j+1) as in the table:





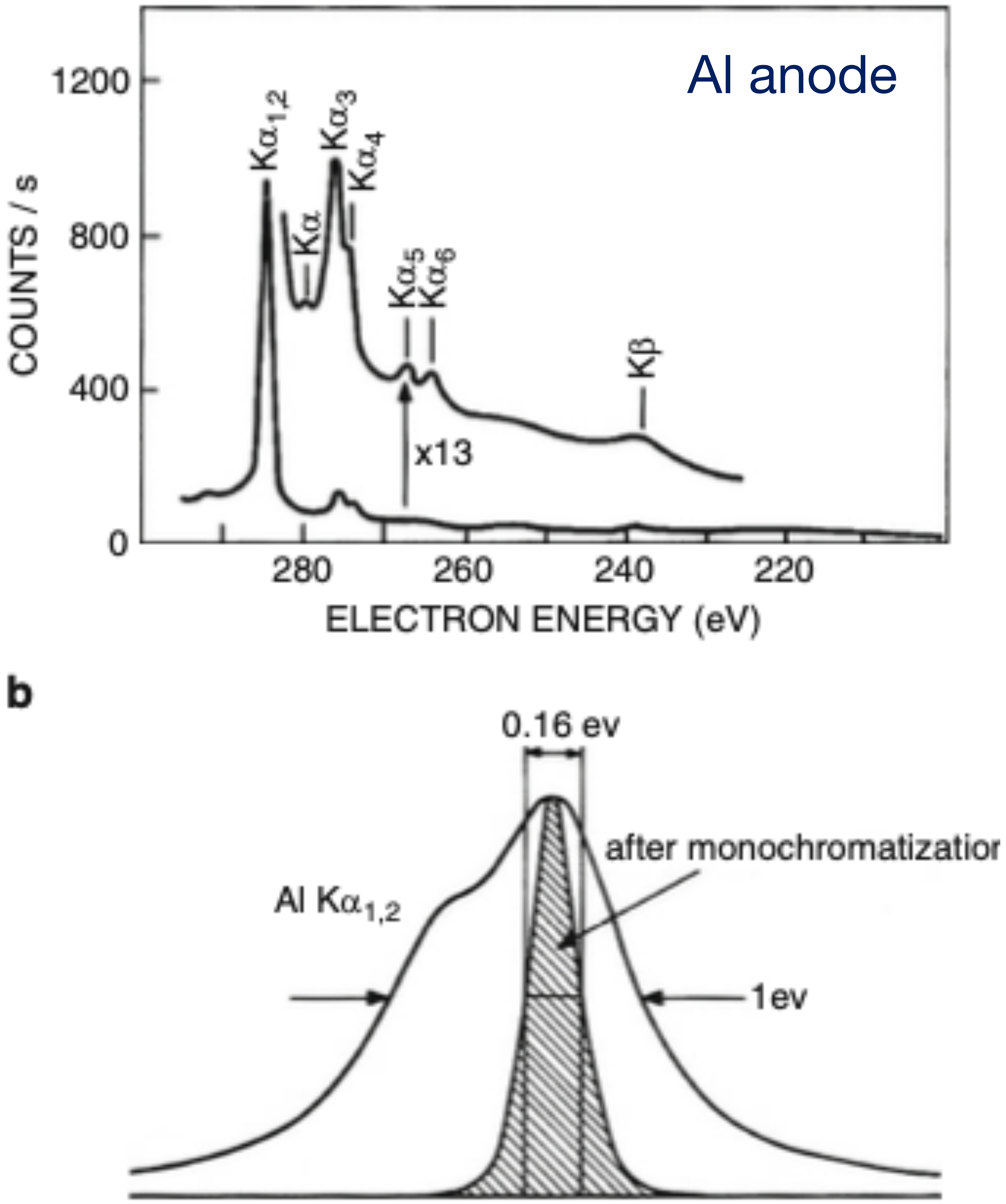
Subshell	*j* values	Intensity ratio (peak areas)
s	1/2	–
p	1/2, 3/2	1:2
d	3/2, 5/2	2:3
f	5/2, 7/2	3:4

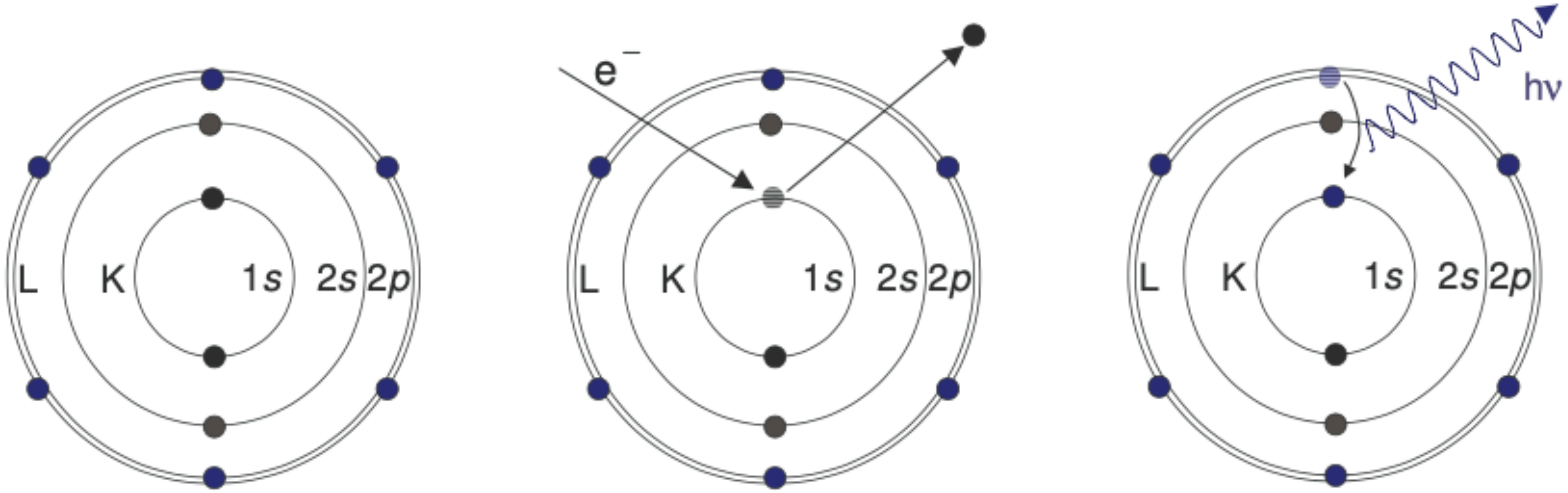


Example of complicated deconvolution with several doublets for different oxidation states (sample: sputtered Ta_2O_5, from S. Hofmann and J.M. Sanz)

Satellite Structures

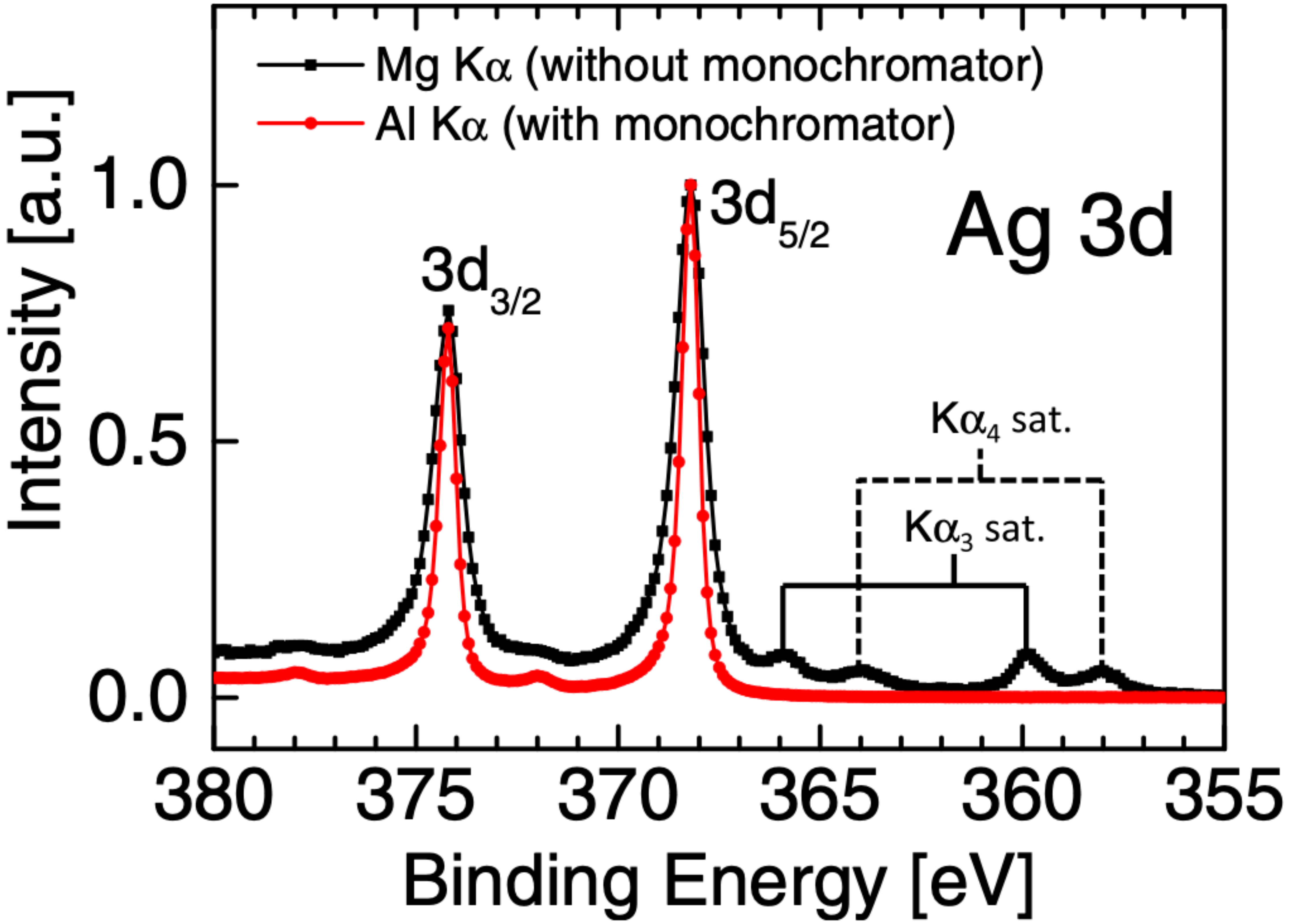
Satellite peaks without monochromator: Satellite peaks from non-monochromatic Mg and Al sources are well known and can be often subtracted. They do not appear with monochromatic radiation (synchrotron or monochromatised lab source).





X-ray production via x-ray fluorescence

Example of Monochromatic vs Non-Monochr. Source



G. Greczynski, L. Hultman, Progr. Mat. Sci. **107**,100591 (2020)

Satellite Structures - Final-State Effects

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.

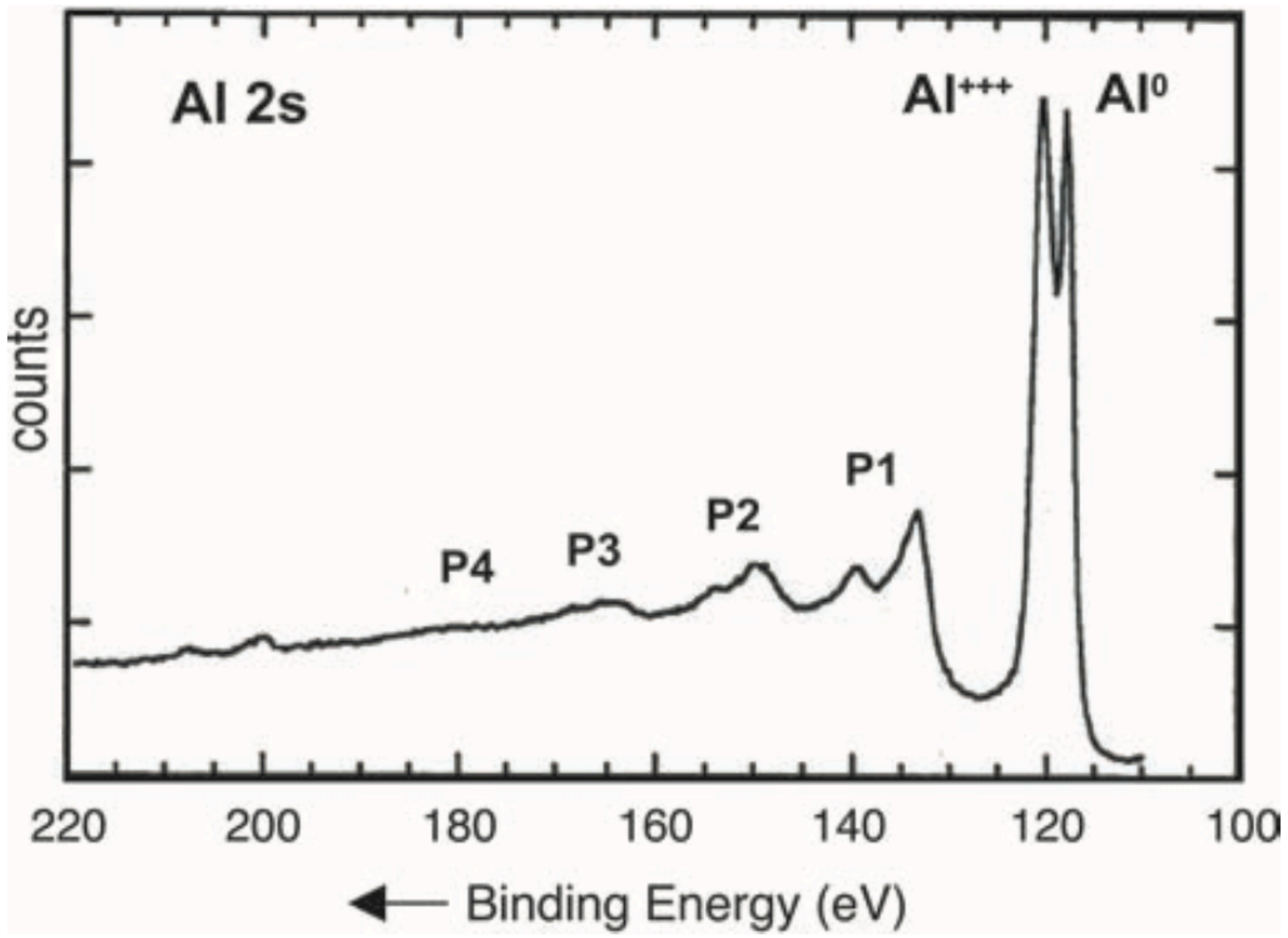
Extrinsic satellites:
The photoelectrons travelling in the solid interact with other electrons in the surface region of the sample. This produces the excitation of electronic transitions with a corresponding lowering of the kinetic energy of the photoelectron.

Final-State Effects - Plasmons

Bulk and surface plasmon peaks are of extrinsic plasmons which have their origin in collective oscillations of an electron gas excited by interactions with electrons of sufficient kinetic energy.

Extrinsic plasmons arise after PE emission and are part of the background (see later, inelastic loss).

Intrinsic plasmons are excited by interaction of the emitted electron with the core hole.

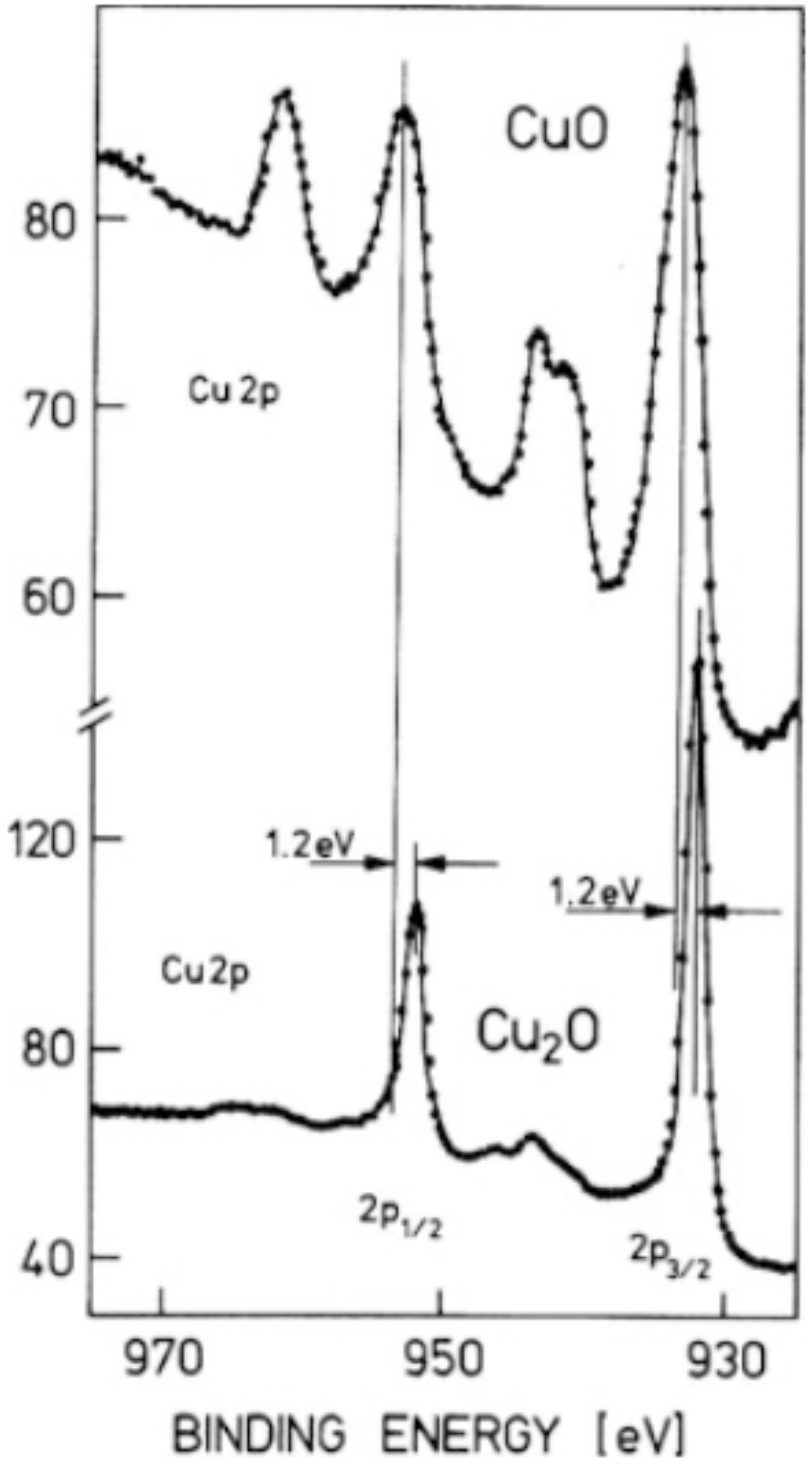


J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

Satellite Structures

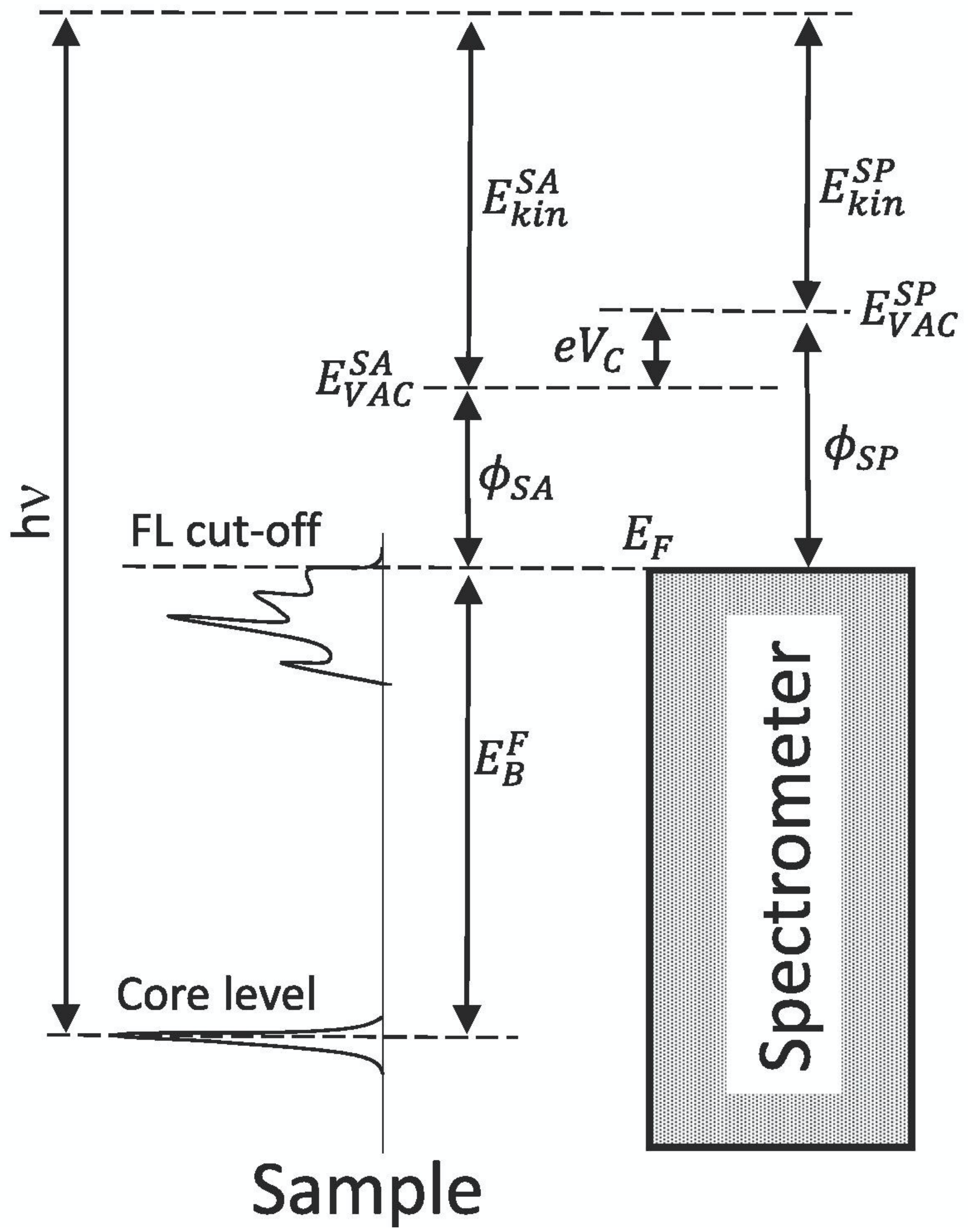
Rearrangement of the electrons after photoemission often results in an excited state a few eV above the ground state.
The photoelectron suffers a loss in kinetic energy of this magnitude that gives rise to a peak at a few eV to the higher binding energy side of the main peak (**shake-up**). In inorganic systems, these satellite peaks can be quite strong, particularly for transition metals and rare earth metals with unpaired electrons in the 3d or 4f shells. Well-known example: CuO and Cu_2O.

Interaction of photoelectrons with valence band electron may cause **shake-off** features. Photoelectrons in metals with high electron density near the Fermi edge may suffer energy losses by excitations in empty states above the Fermi edge. Therefore, instead of discrete losses, a tail on the low kinetic energy



S. Hüfner, Photelectron Spectroscopy, Springer

Referencing Binding Energy (1)



The crucial concept of binding energy is the cornerstone of the XPS process, although we **do not measure** E_B but rather the kinetic energy of emitted electrons.

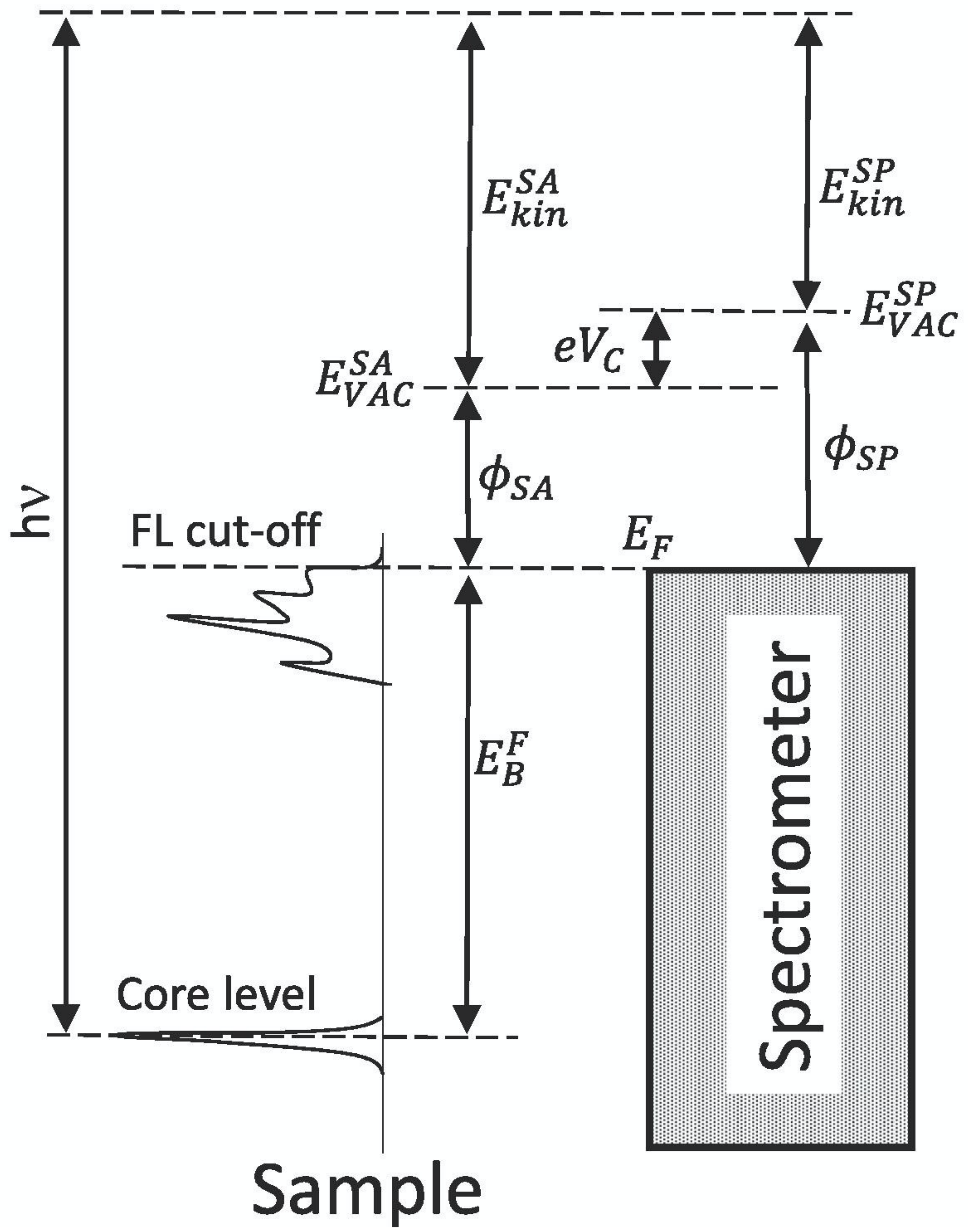
Photoelectrons escaping from the solid surface have to overcome the potential barrier at the surface, the so-called work function ϕ_{SA}, which corresponds to the energy difference between the Fermi level and the vacuum level.

FL appears as a convenient reference level and the electron binding energy is then denoted as E_B^F

$E_K^{SA} = h\nu - E_B^F - \phi_{SA}$ in vacuum.

G. Greczynski, L. Hultman, Progr. Mat. Sci. **107**,100591 (2020)

Referencing Binding Energy (2) - Good Electric Contact

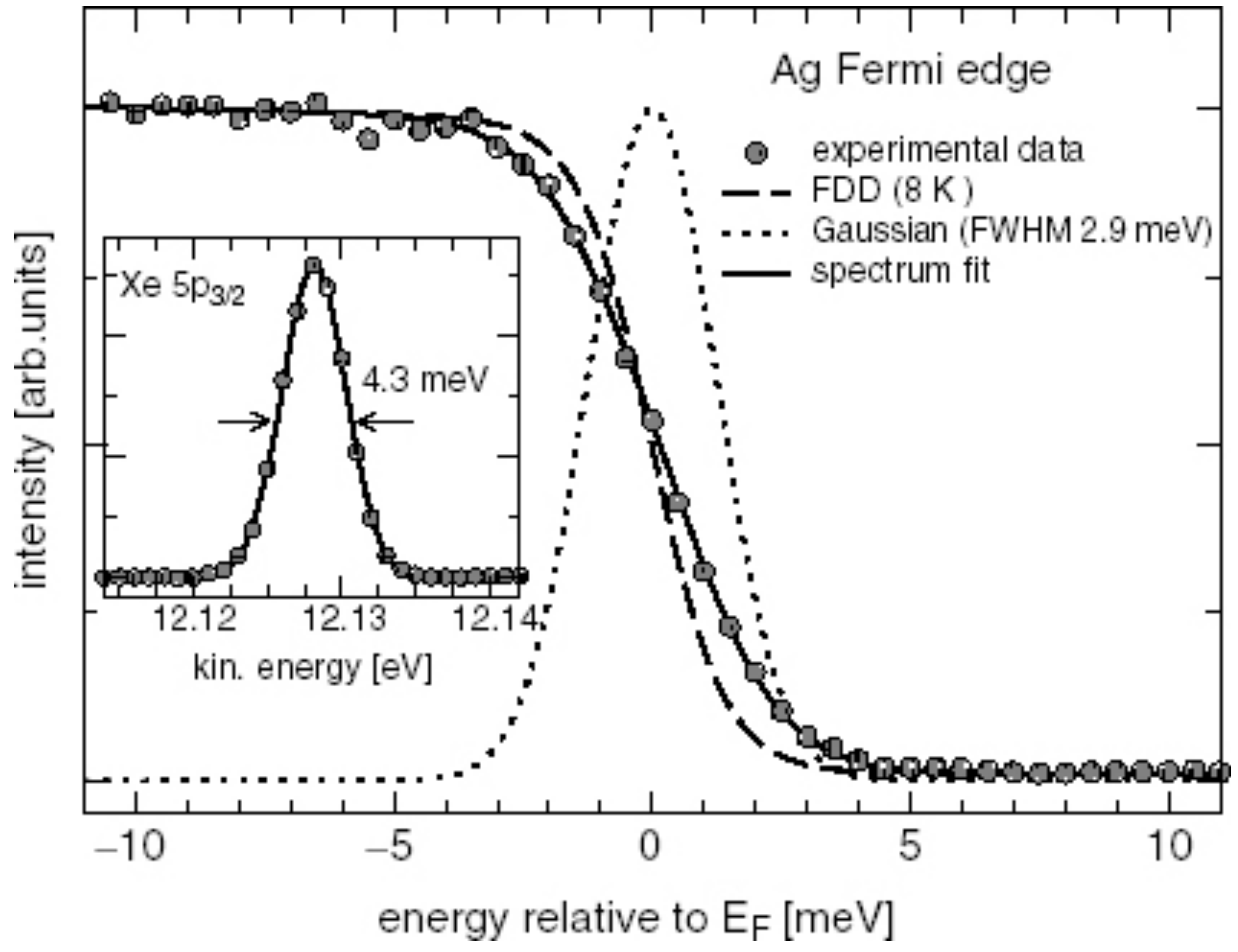


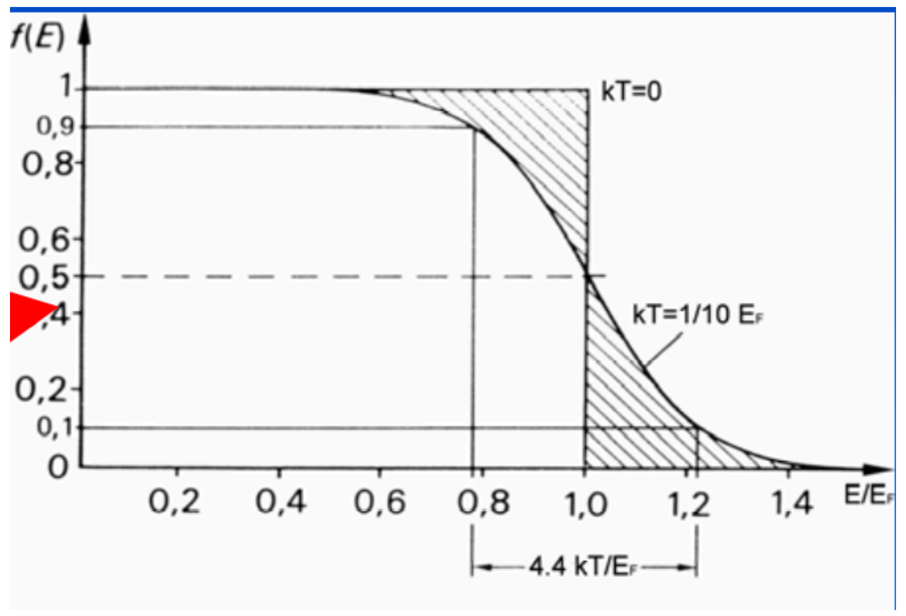
If the sample and the spectrometer are in good electric contact (thus the sample is conductive), there is an alignment of the FL of sample and spectrometer and as a result of negative charge transfer from the sample to the spectrometer characterised by the work function $\phi_{SP} > \phi_{SA}$.

This situation results in a contact potential difference V_C. The initial kinetic energy E_{kin}^{SA} becomes either reduced ($\phi_{SP} > \phi_{SA}$) or increased ($\phi_{SA} > \phi_{SP}$) to the value E_{kin}^{SP} measured at the detector side. Thus, since $E_{kin}^{SA} + \phi_{SA} = E_{kin}^{SP} + \phi_{SP}$ then, we can write: $E_B^F = h\nu - E_{kin}^{SP} - \phi_{SP}$, which is independent from ϕ_{SA}. We just need to to know ϕ_{SP} from calibration.

G. Greczynski, L. Hultman, Progr. Mat. Sci. **107**,100591 (2020)

Referencing Binding Energy (3)





Using lab based sources does not require to constantly check the calibration value for ϕ_{sp}, usually until the system stays in vacuum.

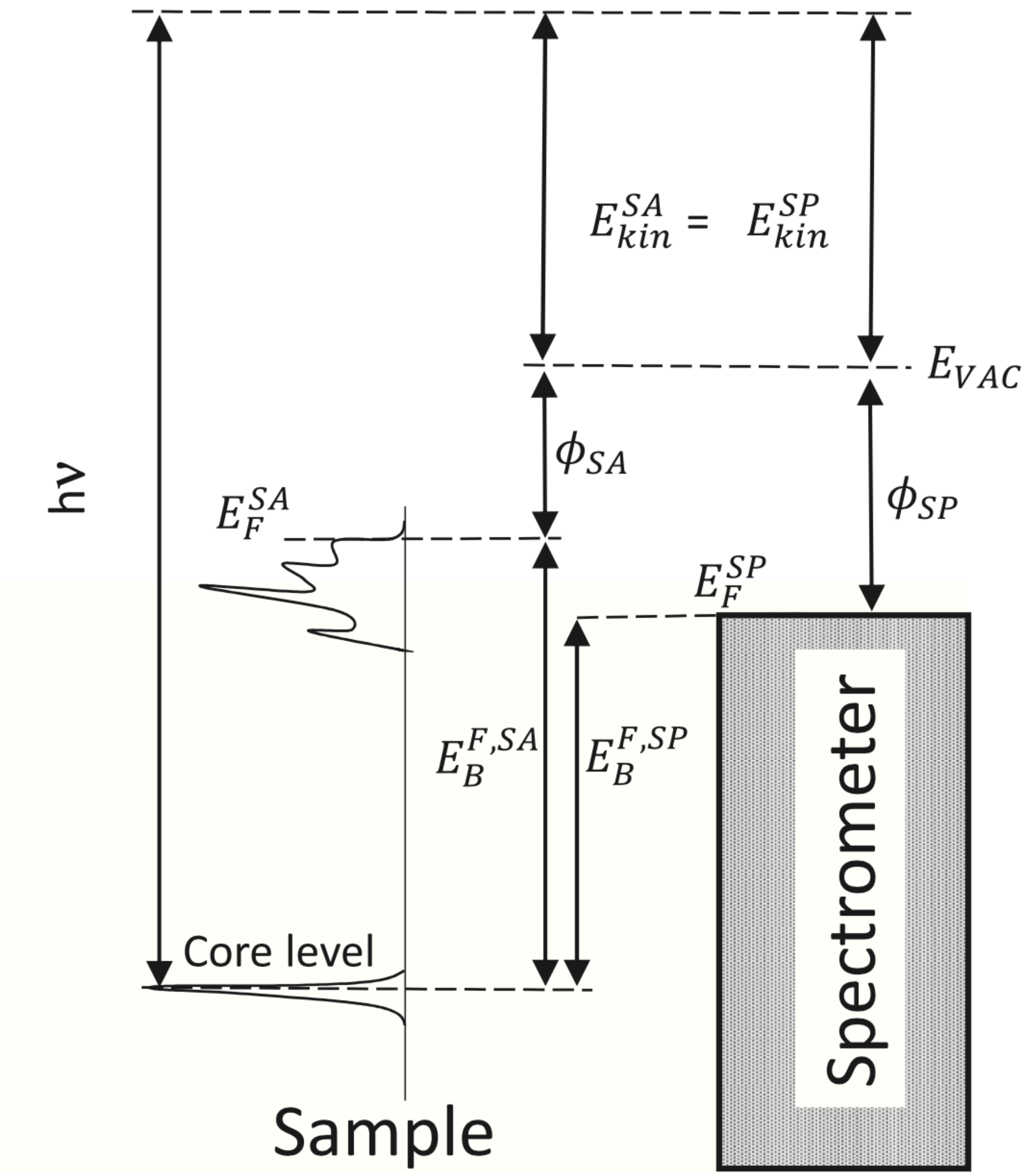
If we tune $h\nu$ often, we can we can have uncertainties in the photon energy. Thus we need to constantly check the BE scale calibration, by measuring the position of the fermi level. We can fit it with the Fermi function

$$F(E) = \left[\exp\left(\frac{E - E_F}{k_B T}\right) + 1\right]^{-1}$$

Plus a gaussian broadening accounting for finite experimental resolution of the spectrometer.

See Rev. Sci. Instrum. 82, 096107 (2011) for a worked example.

Referencing Binding Energy (4)



What if we do not have good contact? The FL are no longer aligned. Plus, we have to compensate the charge getting away from the sample as a photoemission current.

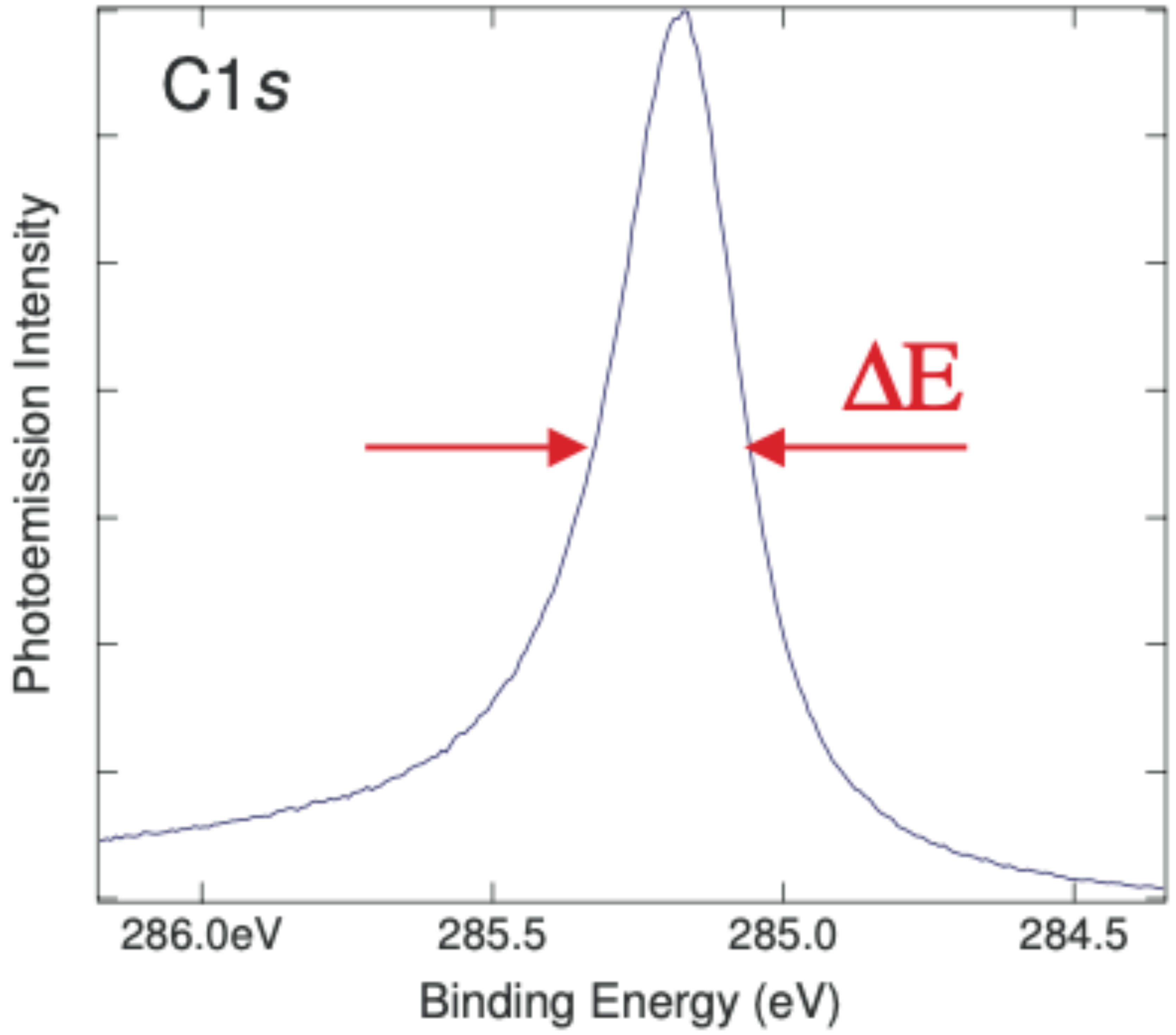
This is accomplished by flooding the sample with a monoenergetic source of low-energy (<20 eV) electrons.

Under these conditions it is best to use an internal reference. For polymer and organic samples, the hydrocarbon component (C—C/C—H) of the C1s peak is typically set to 285.0 eV. For supported catalysts, a major peak of the oxide support (Si2p, Al2p, etc.) is typically used. Decoration with Au nanoparticle is also possible.

G. Greczynski, L. Hultman, Progr. Mat. Sci. **107**,100591 (2020)

Core-Level Line Shape

The Line shape of core level is the result of several concurring factors. The width of the peaks is determined by both experimental contributions and intrinsic factors.



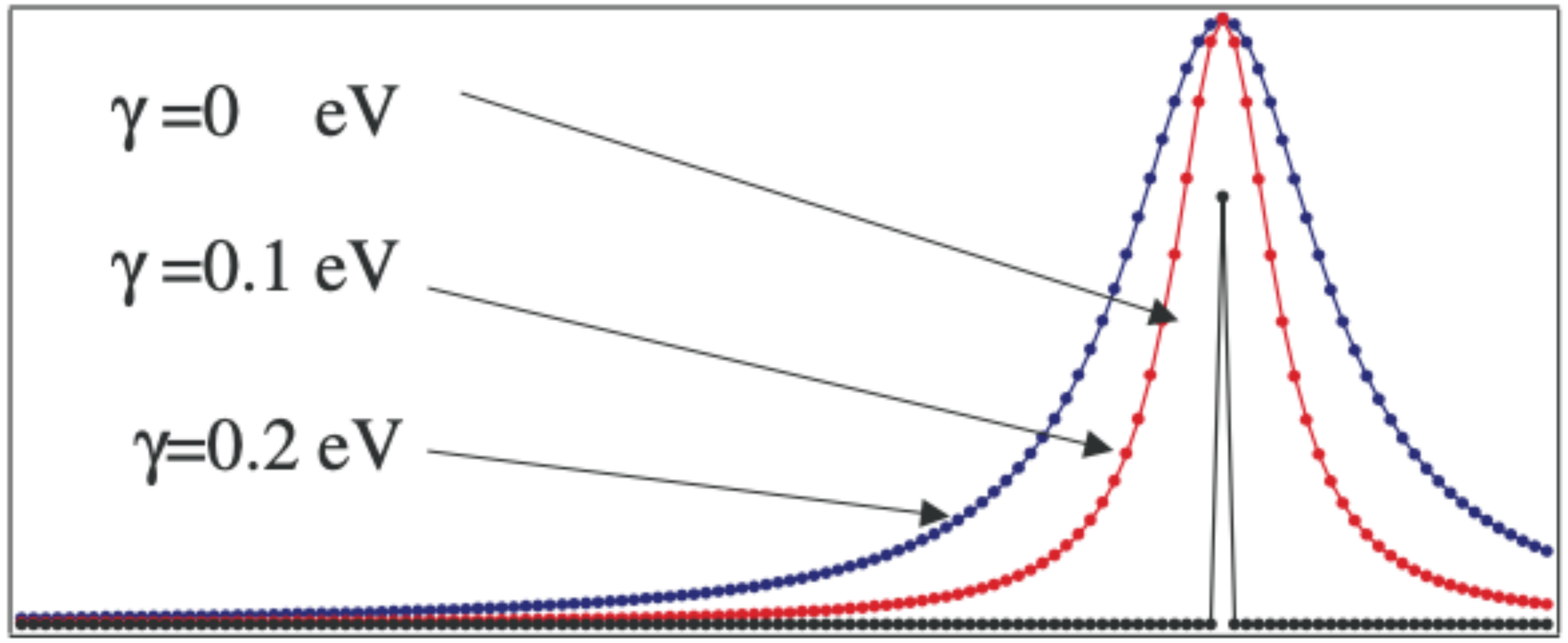
$$\Delta E = \sqrt{\underbrace{\Delta E_{nat}^2}_{\text{Natural linewidth}} + \underbrace{\Delta E_{vib}^2}_{\text{Vibrational effects/phonons}} + \underbrace{\Delta E_{in}^2}_{\text{inhomogenities/disorder}} + \underbrace{\underbrace{\Delta E_{h\nu}^2}_{\text{Photon energy resolution}} + \underbrace{\Delta E_{a}^2}_{\text{Electron energy analyser resolution}}}_{\text{Experimental contributions}}}$$

Line Shapes

The basic lineshape is given by a **Lorentzian** function:

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

The **natural line width** ΔE_0 is determined by the lifetime τ of the core hole state left by photoemission (lifetime broadening) and can be estimated by the uncertainty principle as $\Delta E_0 = \frac{h}{\tau}$. For example a lifetime of 10^{-14} s corresponds to a linewidth of 0.4 eV, as found of the Ag $3d_{5/2}$.



Gaussian-Lorentzian Line Shape

Lorentzian shape is not describing well enough the photoemission from solids. We need to add further contributions to the lineshape, which are generally Gaussian-shaped.

In crystalline materials, atomic vibrations impose a small Gaussian broadening which is temperature dependent. Disorder is also contributing to broadening.

In addition, a Gaussian broadening is caused by the analyzer. This instrumental broadening function is directly given by the resolution of the analyzer. Moreover, we have to take into account the photon resolution, that is the width of the exciting line.

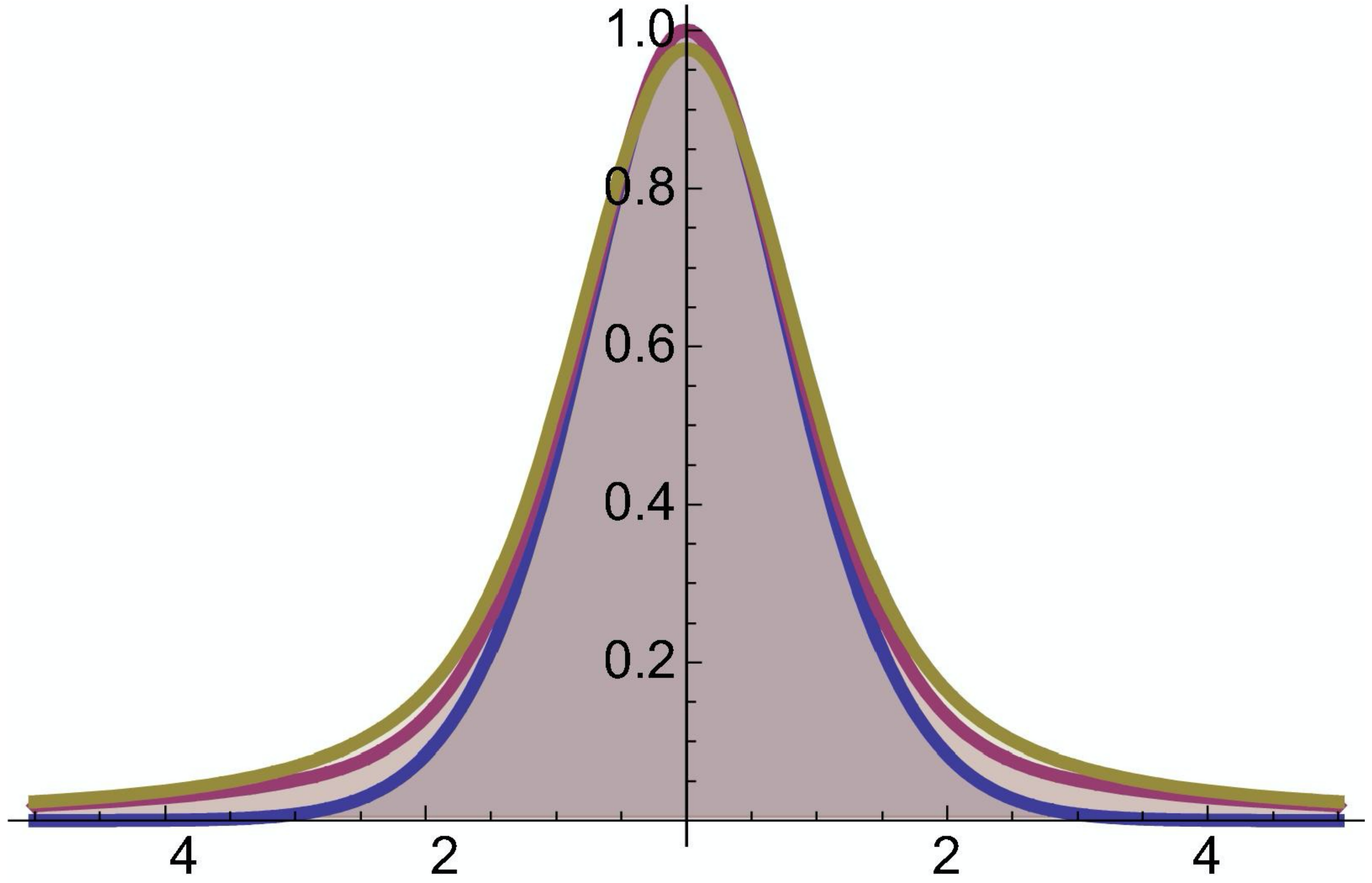
Thus, usually the line shape of an XPS peak is well represented by a combination of both line shape types using a mixed Gaussian–Lorentzian function or, physically more correct, using convolution of a Lorentzian with a Gaussian (Voigt function).

Gaussian Broadening. Voigt Functions

The natural lineshape is however affected by other factors:

- Instrumental broadening
- Photon source bandwidth.
- sample disorder/vibrations.

These contribution are described as gaussian distributions.



GLS function with m = 0.5 (red line), the GLP function with m = 0.5 (blue line), and the Voigt function (yellow line).

Convolution of Gaussian and Lorentzian profiles are called Voigt functions $V(x;\sigma,\gamma) \equiv \int_{-\infty}^{\infty} G(x';\sigma)L(x-x';\gamma)\,dx'$,

These are often approximated as sum:

$$GLS(x;F,E,m,h) = h*(1-m)\exp\left[-4\ln 2\frac{(x-E)^2}{F^2}\right] + \frac{h*m}{\left[1+4\frac{(x-E)^2}{F^2}\right]}$$

or product

$$GLP(x;F,E,m,h) = h*\exp\left[-4\ln 2(1-m)\frac{(x-E)^2}{F^2}\right] * \frac{1}{\left[1+4m\frac{(x-E)^2}{F^2}\right]}$$

with a mixing parameter *m.*

Varun Jain, Mark C. Biesinger, Matthew R. Linford, App. Surf. Sci., **447,** 548-553 (2018)

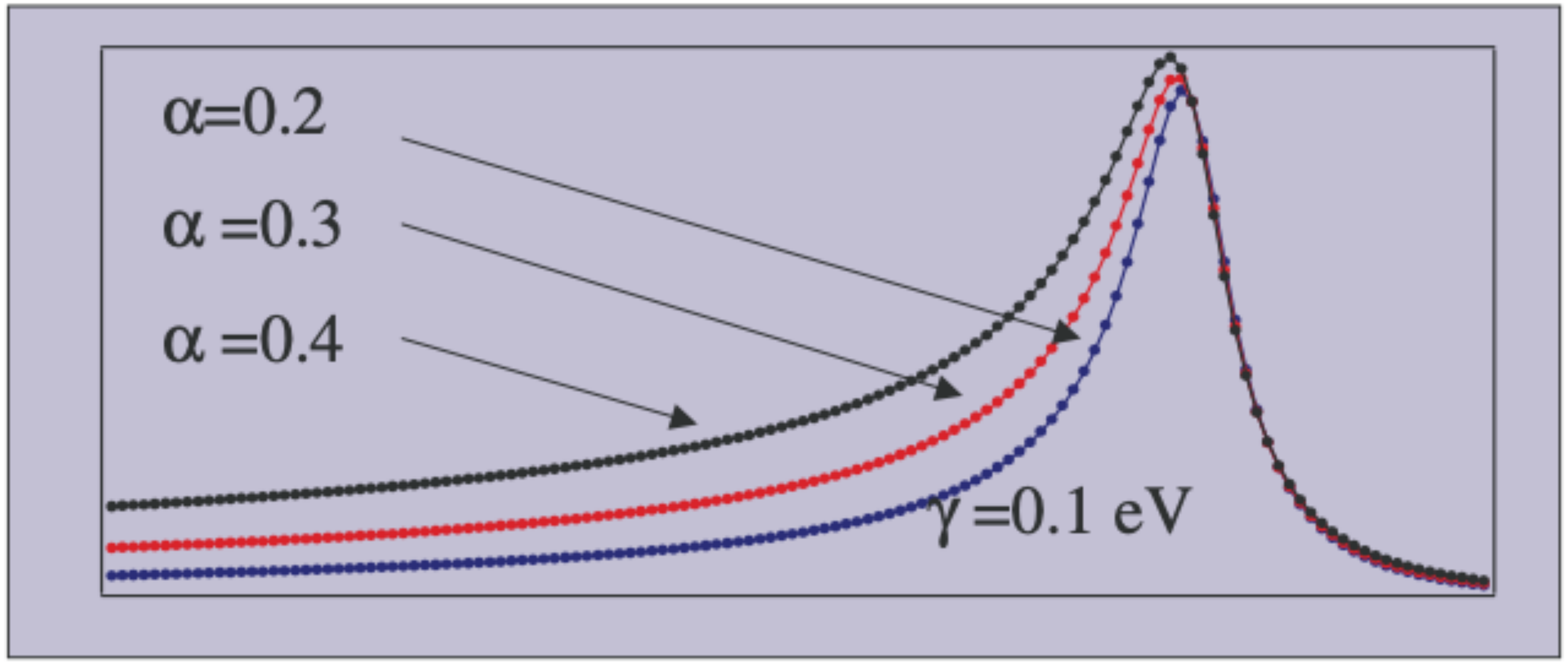
Doniach-Sunjic Line Shape

This is mostly applied when we have XPS in metals. These lines are basically asymmetric Voigt functions, with a tail at high binding energy due to the many-body interactions of the PE with distribution of electrons close to the Fermi edge.

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

γ = core hole lifetime

α = asymmetry parameter

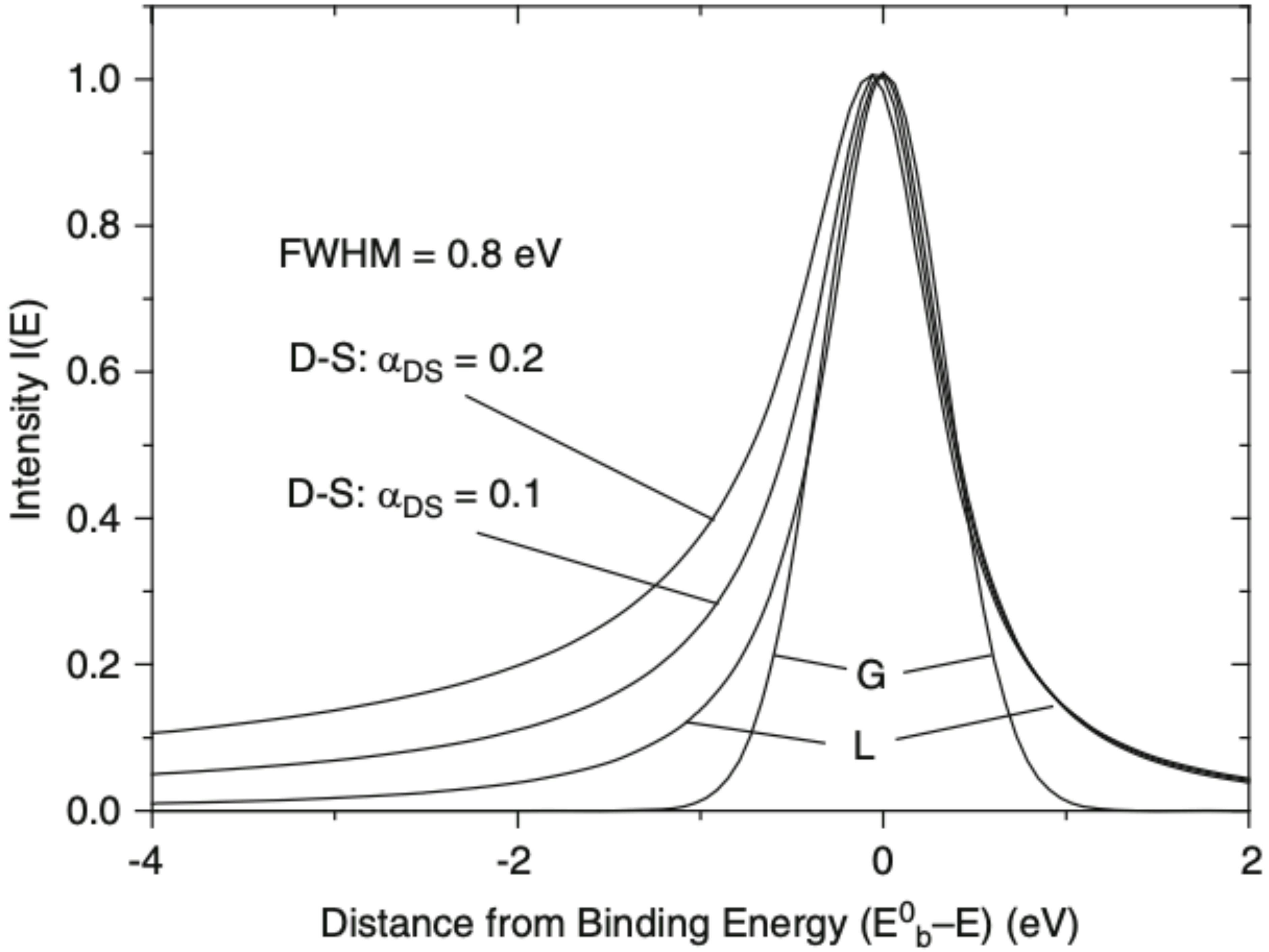


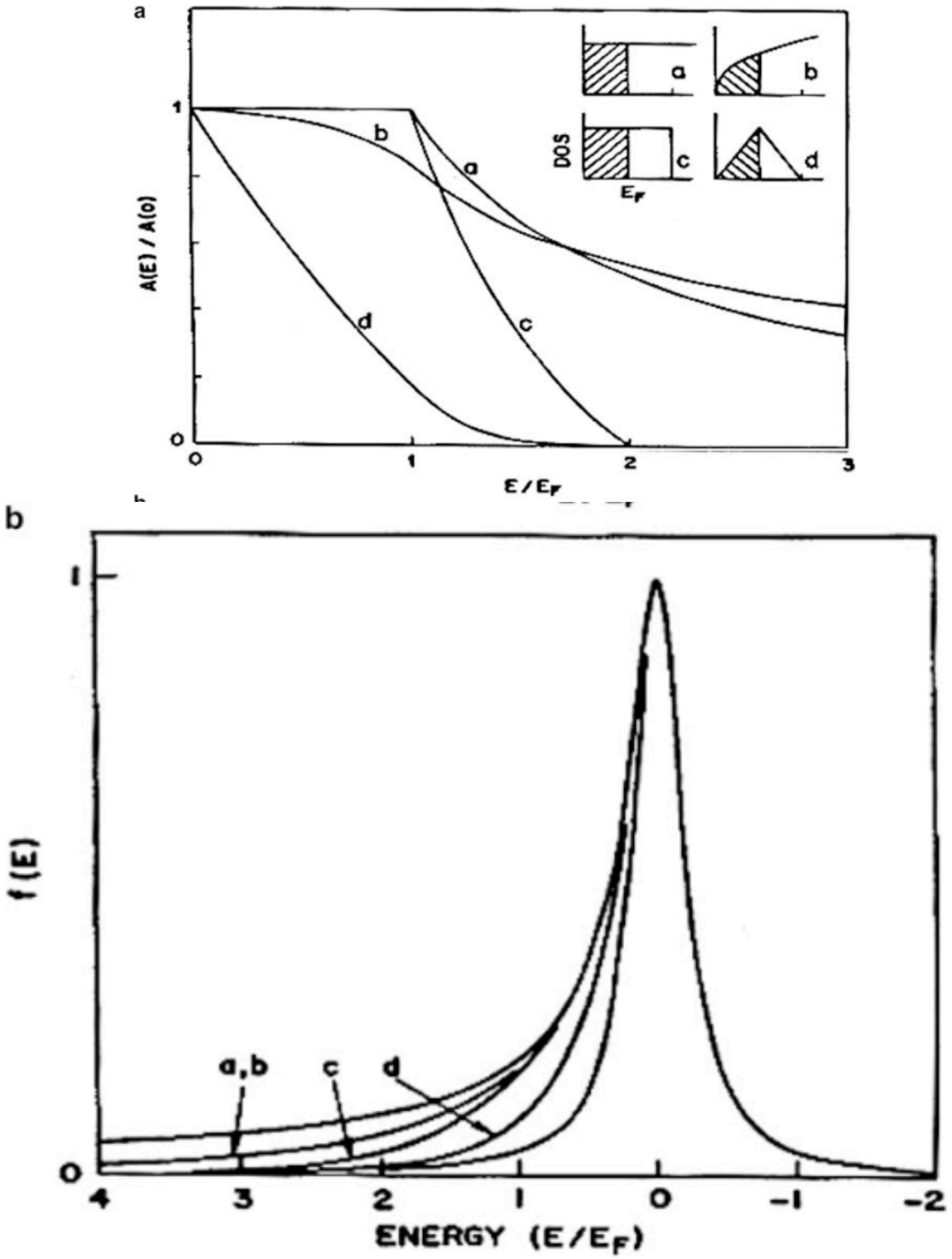
Caution: the integral of this function diverges.
Thus problems in quantification (truncation needed).

S.Doniach, M.Sunjic, J. Phys. C **3**, 285 (1970)

XPS Lineshapes

The shape of the valence band is reflecting the shape of the core levels, via the asymmetry parameter
of the DS curve.





G.K. Wertheim, P.H. Citrin, Fermi Surface Excitations in X-Ray Photoemission Line Shapes from Metals, in *Photoemission in Solids I*, ed. by M. Cardona, L. Ley

Summary on Line-Shapes

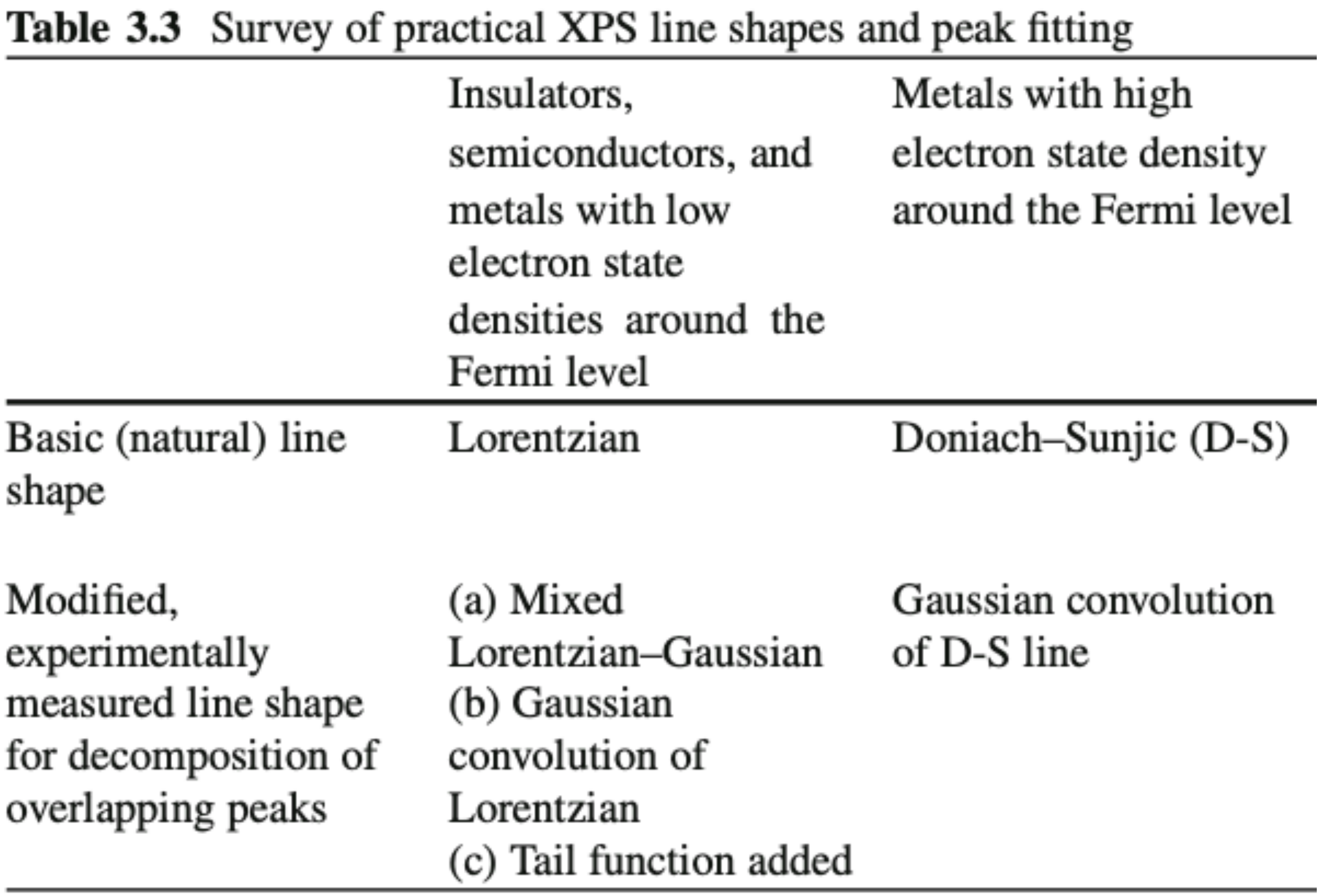


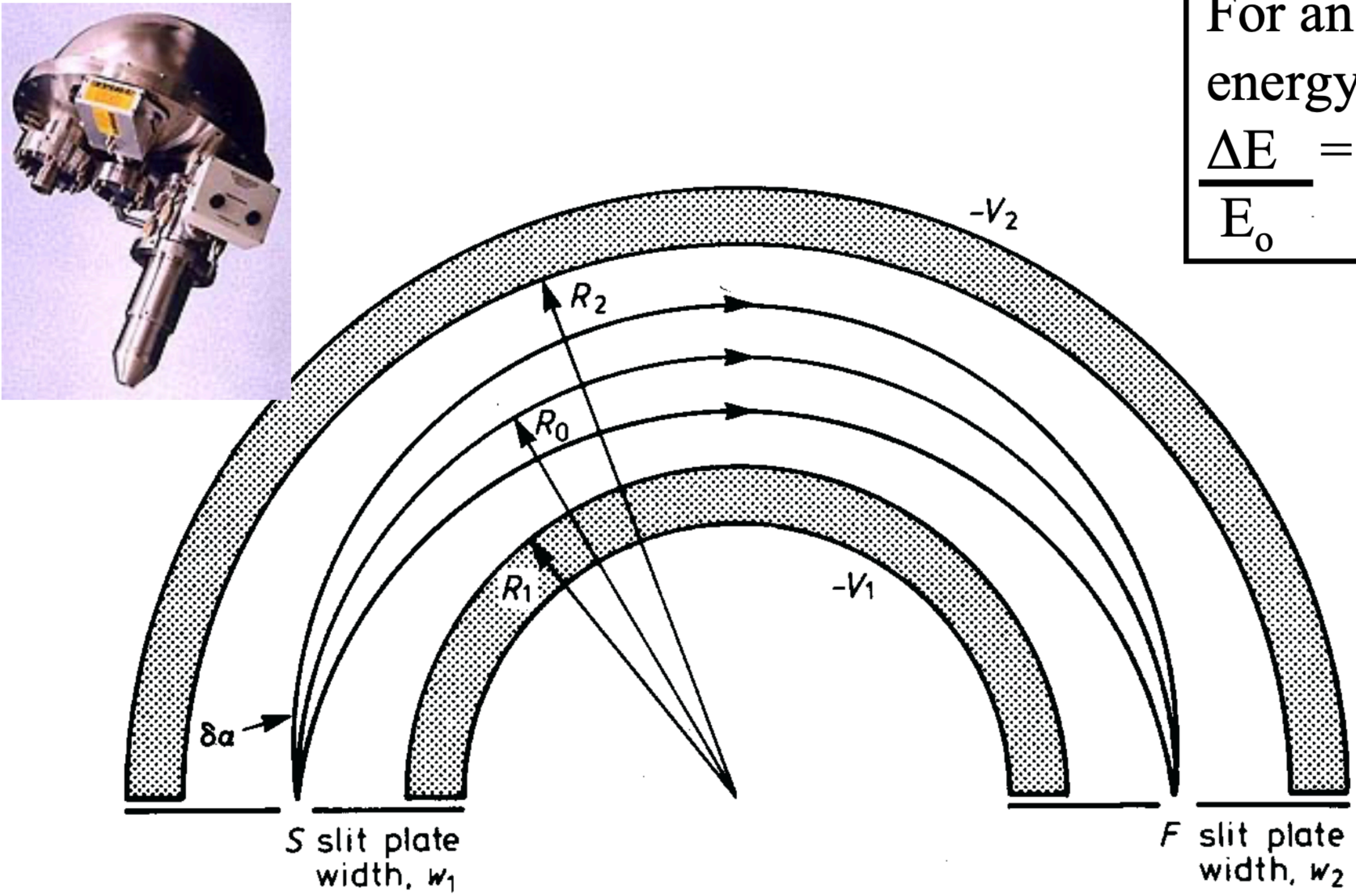
Table 3.3 Survey of practical XPS line shapes and peak fitting

	Insulators, semiconductors, and metals with low electron state densities around the Fermi level	Metals with high electron state density around the Fermi level
Basic (natural) line shape	Lorentzian	Doniach–Sunjic (D-S)
Modified, experimentally measured line shape for decomposition of overlapping peaks	(a) Mixed Lorentzian–Gaussian (b) Gaussian convolution of Lorentzian (c) Tail function added	Gaussian convolution of D-S line

S. Hofmann, Auger- and X-Ray Photoelectron Spectroscopy in Materials Science, Springer, 2013.

Some Words About Instrumentation

Concentric hemispherical analyser (CHA)

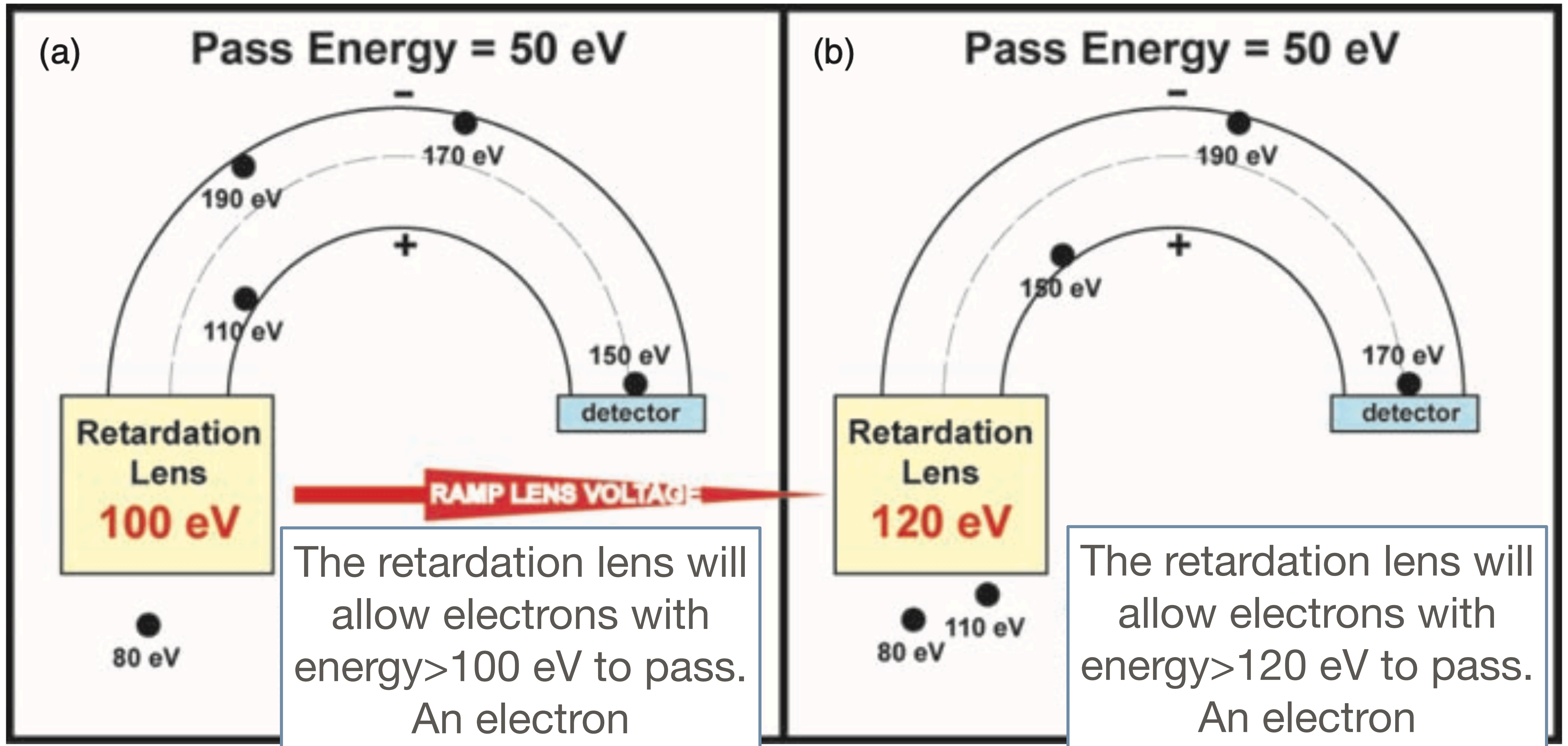


For an electron of energy E_o at S

$$\frac{\Delta E}{E_o} = 0.63\,\frac{\overline{w_1}}{R_o}$$

Pass energy effect: FWHM goes from 1.66—>0.55 eV

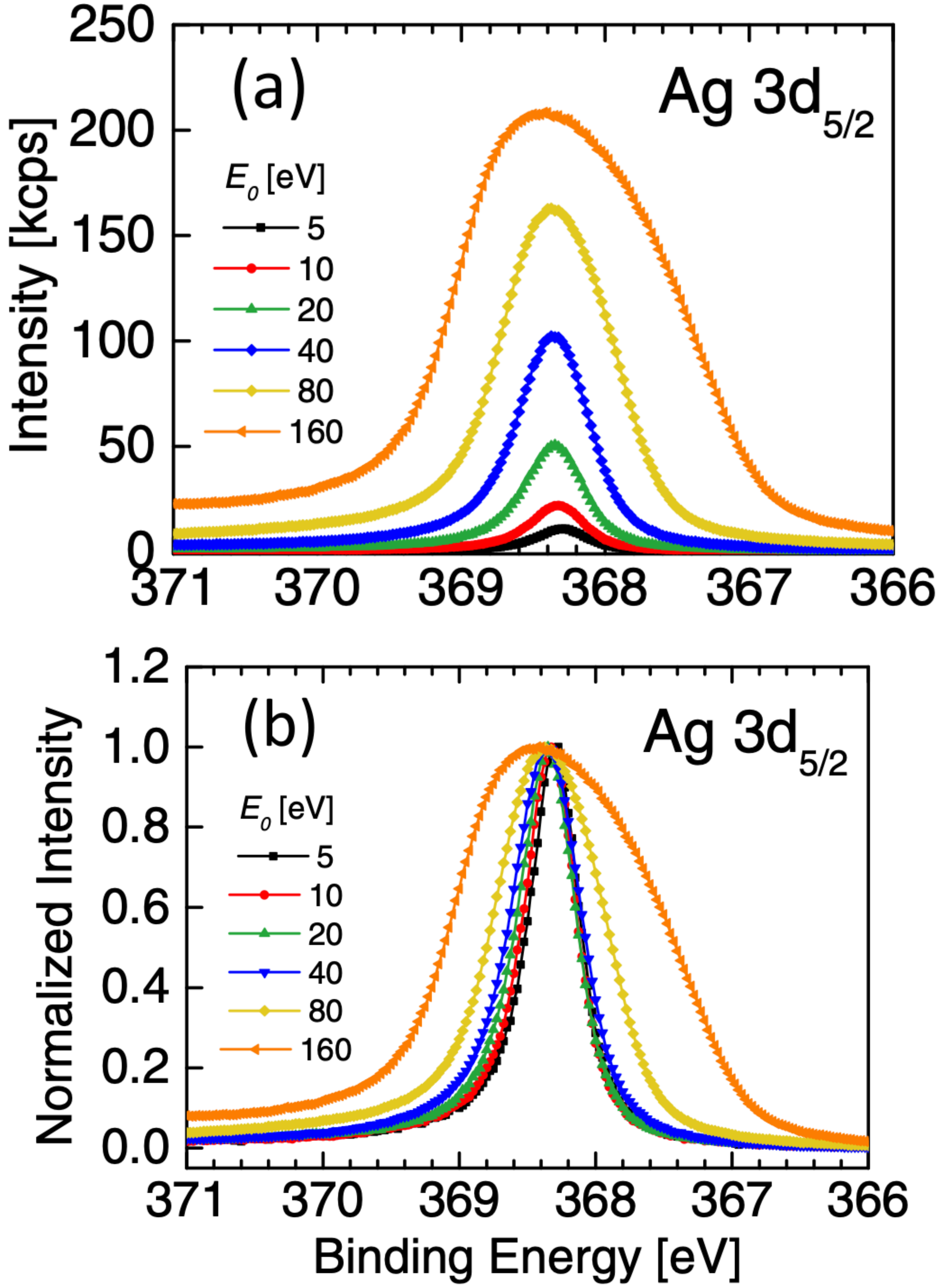
Detectors Effects on Spectra



The retardation lens will allow electrons with energy>100 eV to pass. An electron with 50 eV will satisfy the pass energy requirement of the analyser.

The retardation lens will allow electrons with energy>120 eV to pass. An electron with 50 eV will satisfy the pass energy requirement of the analyser.

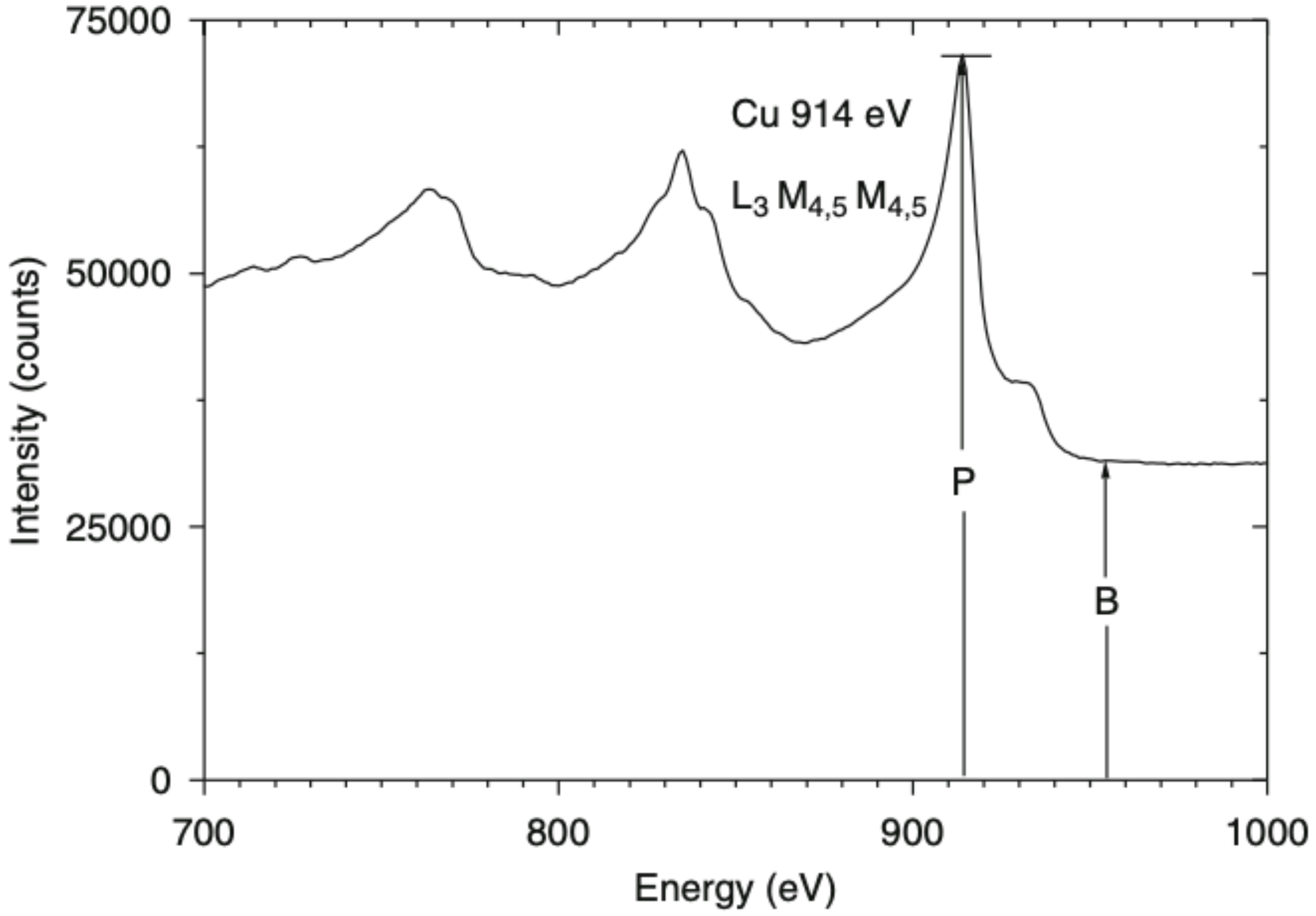
J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)



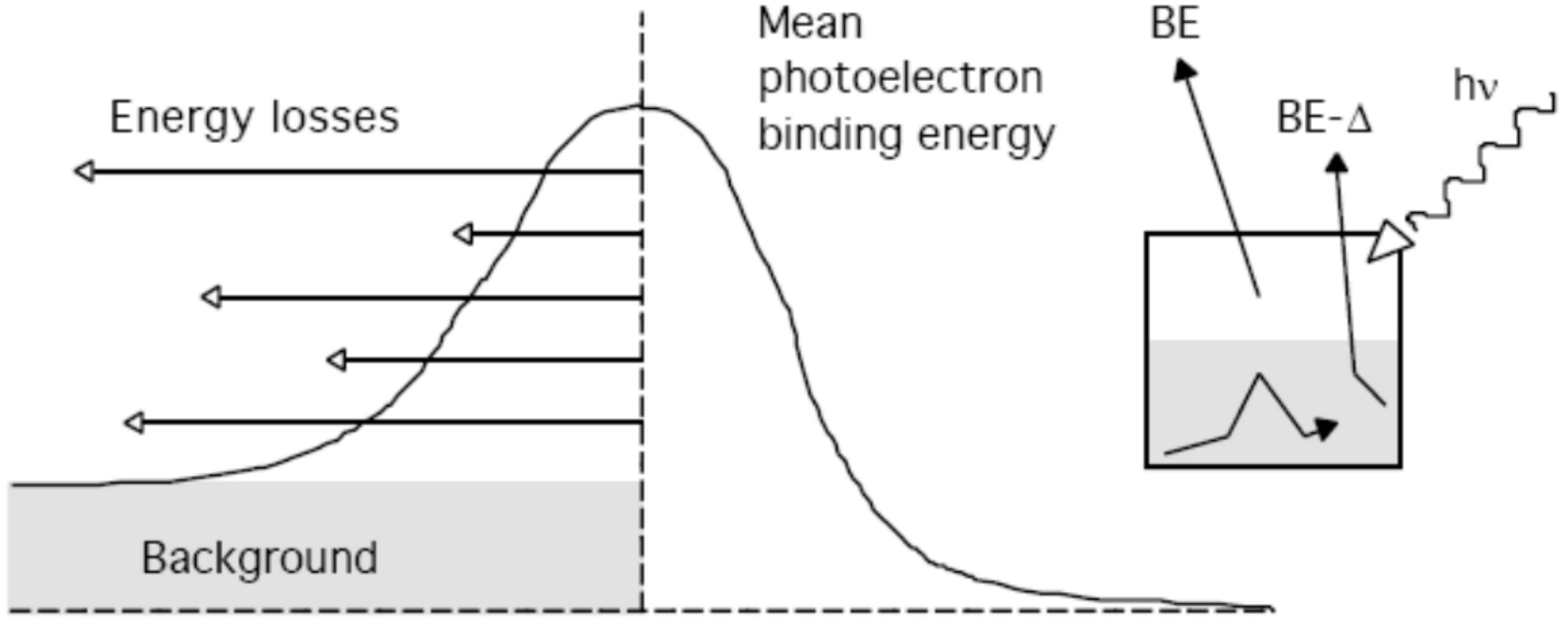
G. Greczynski, L. Hultman, Progr. Mat. Sci. **107**,100591 (2020)

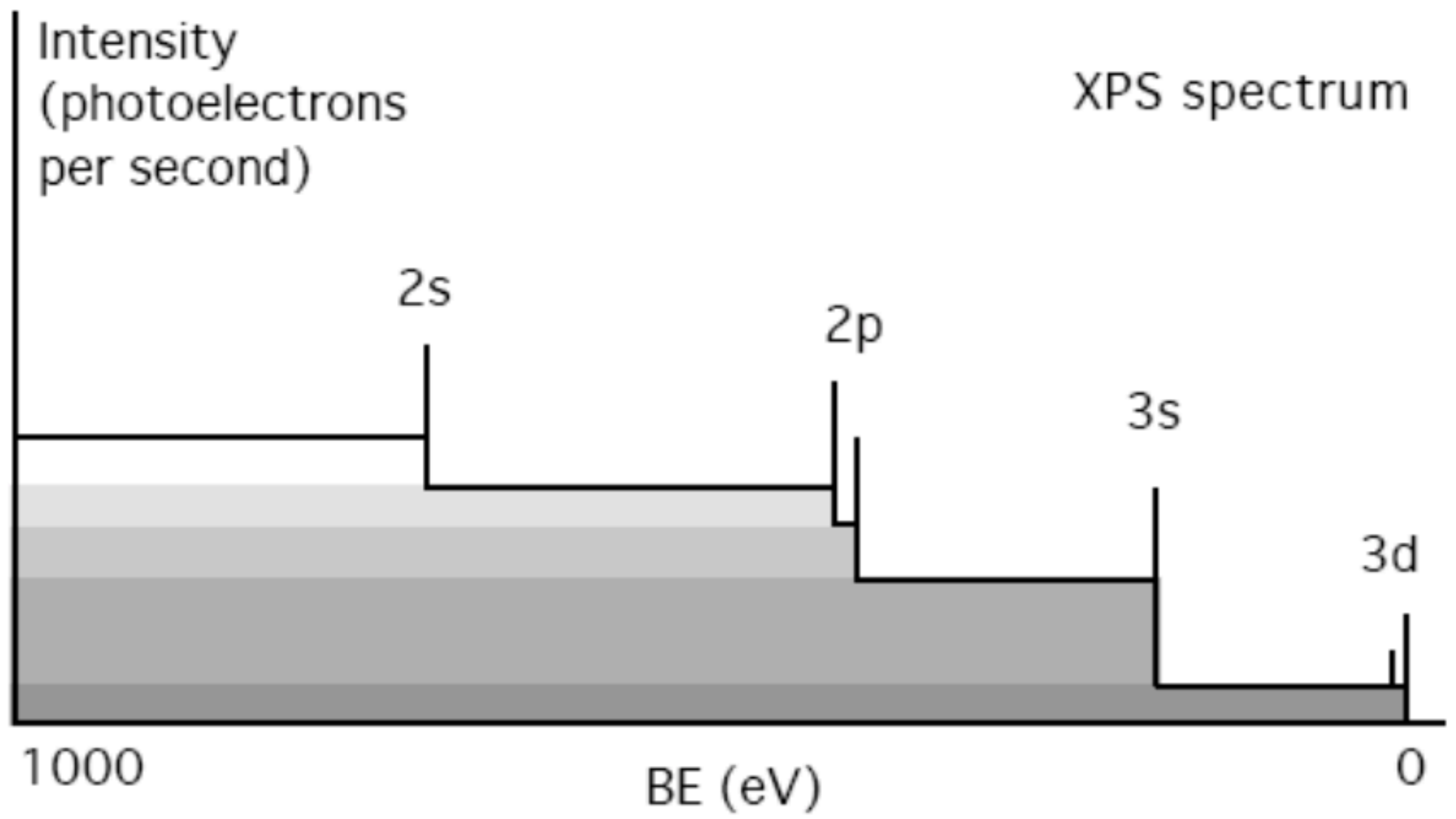
Background in Spectra

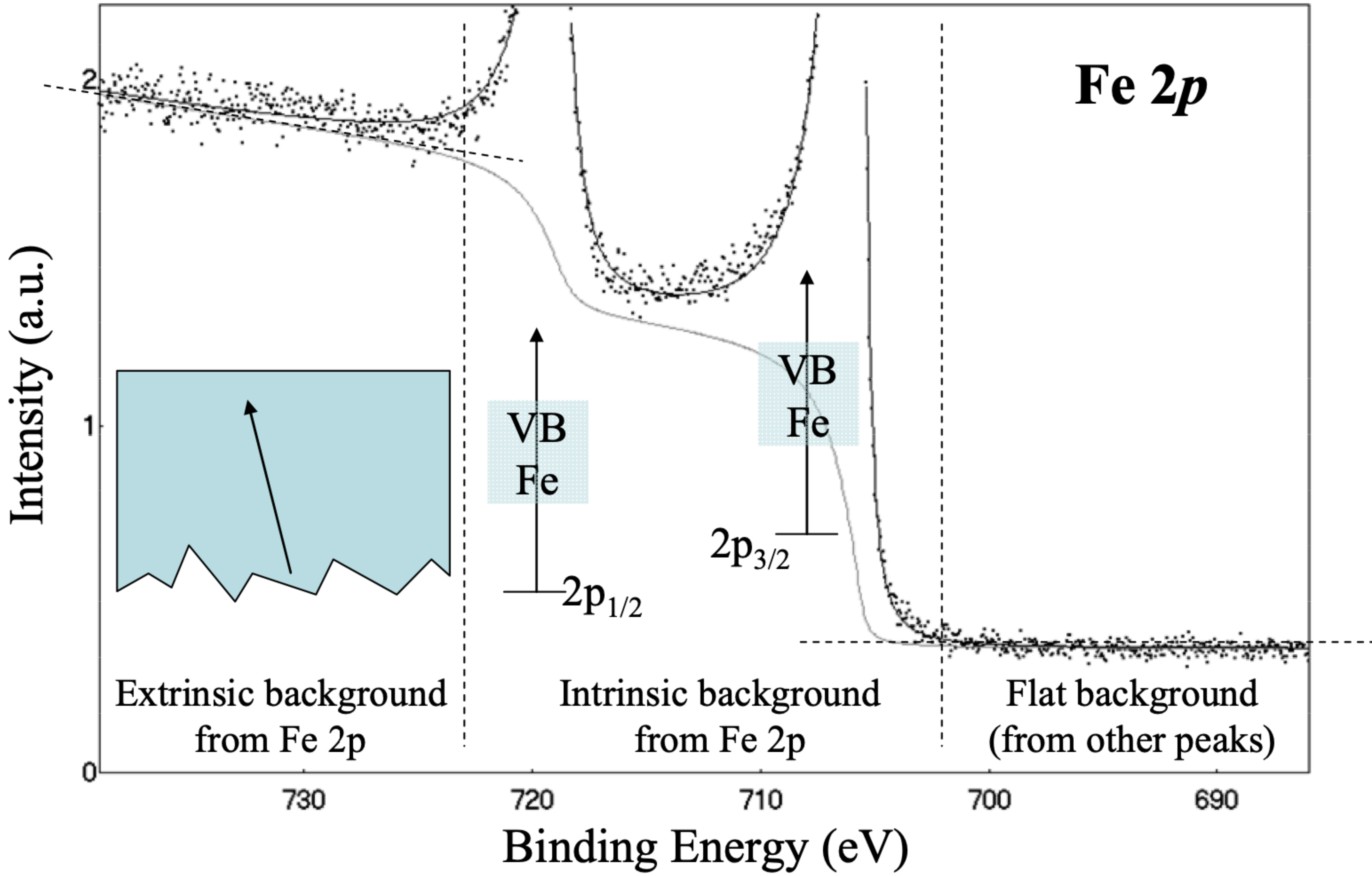
In any spectrum the intensity of a measured peak (P) is sitting on a background intensity (B) that has to be subtracted to give the signal intensity (P–B). For direct, “normal” spectra (usually given by N(E) in XPS), the most simple procedure is to take the peak intensity (or height) (D counts at peak maximum) and subtract the background intensity (D counts measured at higher energy minimum in the vicinity of the peak .



Background in Spectra

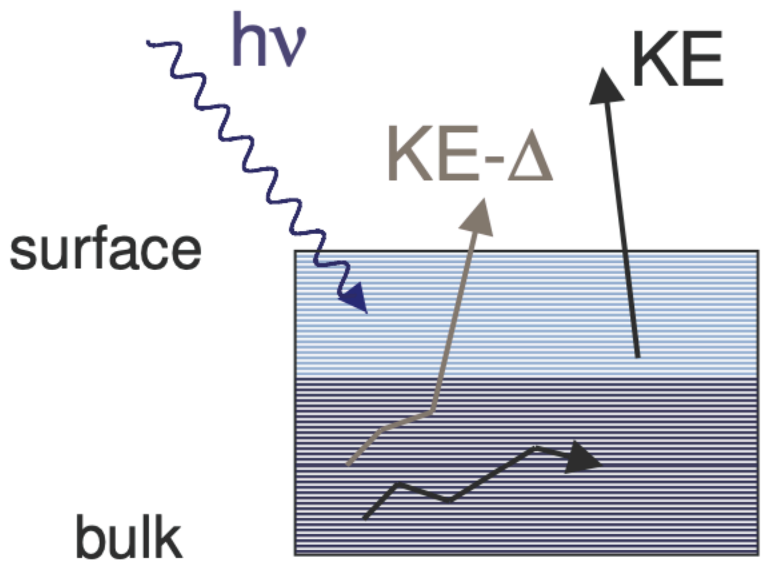


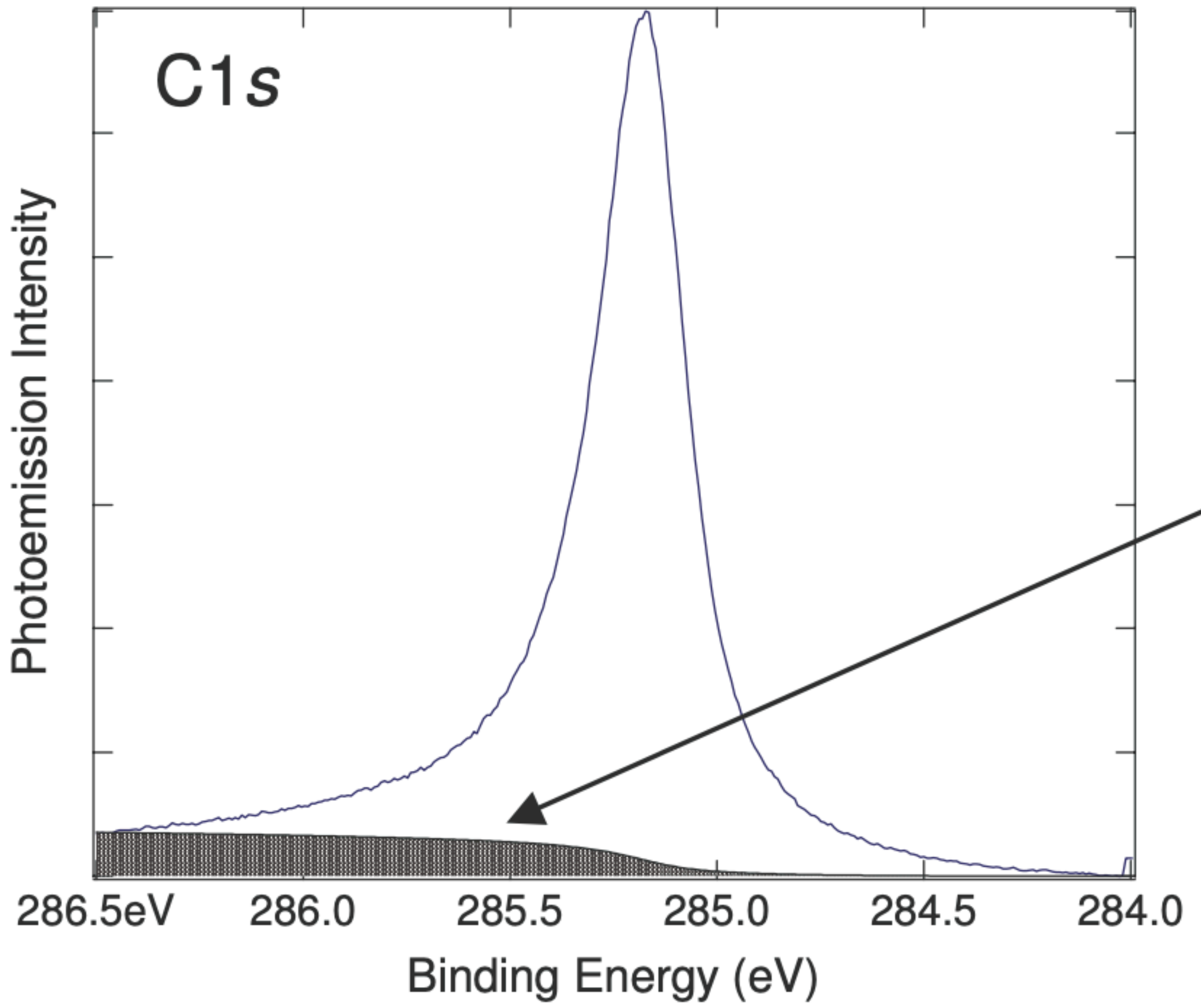




Background of scattered electrons due to limited IMFP Higher for low KE

Background in Spectra





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

Three types of background models are generally used for XPS:

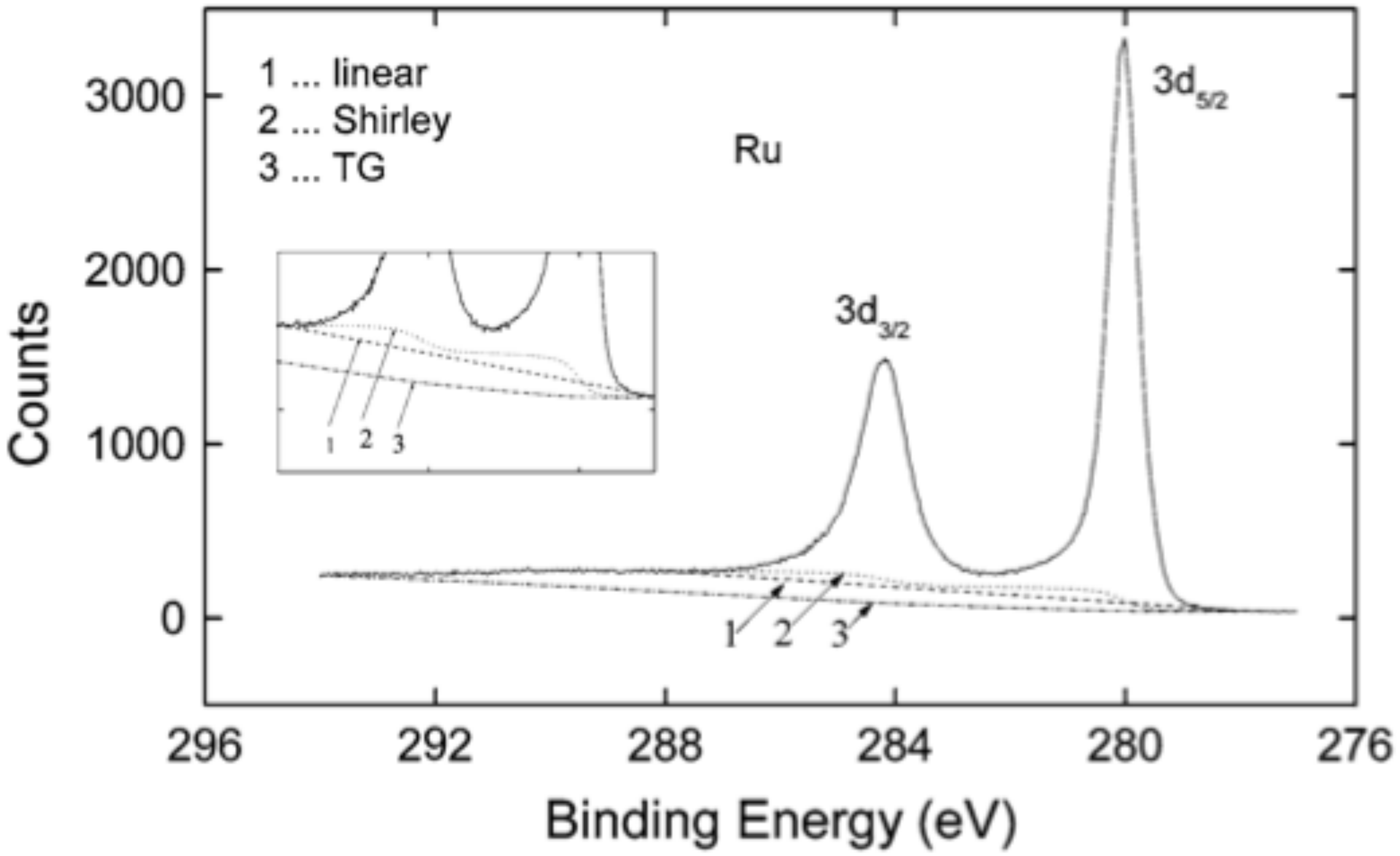
1. Linear background.
2. Integral or Shirley background
3. Tougaard background.

Linear Background

The straight line between the two endpoints of the peak is physically unrealistic but simple and therefore most convenient.

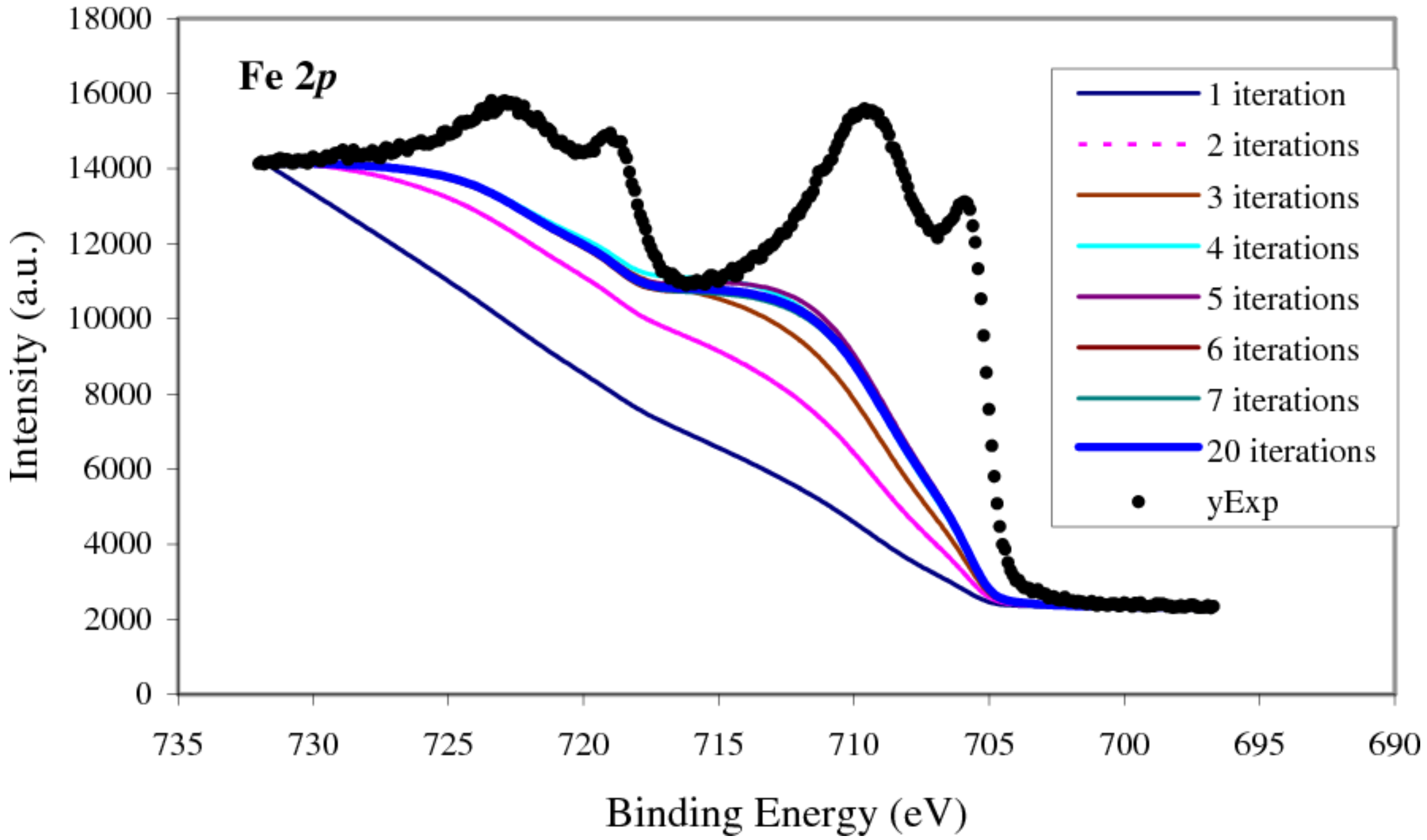
However, it is clear that the physics of background generation is more complicated and that the choice of the endpoint at lower kinetic energy (=higher binding energy) is not well defined.

Therefore, the expected error is larger than for the more refined methods. However, the error is tolerable if the background is relatively small compared to the peak, as in case of XPS signals of surface layers with high kinetic energy.



Shirley Background

The peak spectrum is decomposed in N channels between the peak limiting high kinetic energy and low kinetic energy, which correspond to the lowest binding energy BE_{min} and the highest BE_{max}, respectively. The background intensity B_{i+1} in each channel $i+1$ in the Shirley model is given by a fraction k_s of the signal intensity $(I_i - B_i)$ in the previous channel:



$$B_{i+1} = k_s \sum_{i=0}^{i_{max}} (I_i - B_i)$$

k_s is determined by the condition at BEmax that

$$I(BE_{max}) = B(BE_{max})$$

- D.A.Shirley, Phys. Rev. B 5, 4707 (1972)
- J.Vegh, J.Electron. Spectrosc. Relat. Phenom. 151, 93 (2001)
- H.E. Bishop, Surf. Interface Anal. 3, 272 (1981)

Tougaard Background

The Tougaard background is usually given by

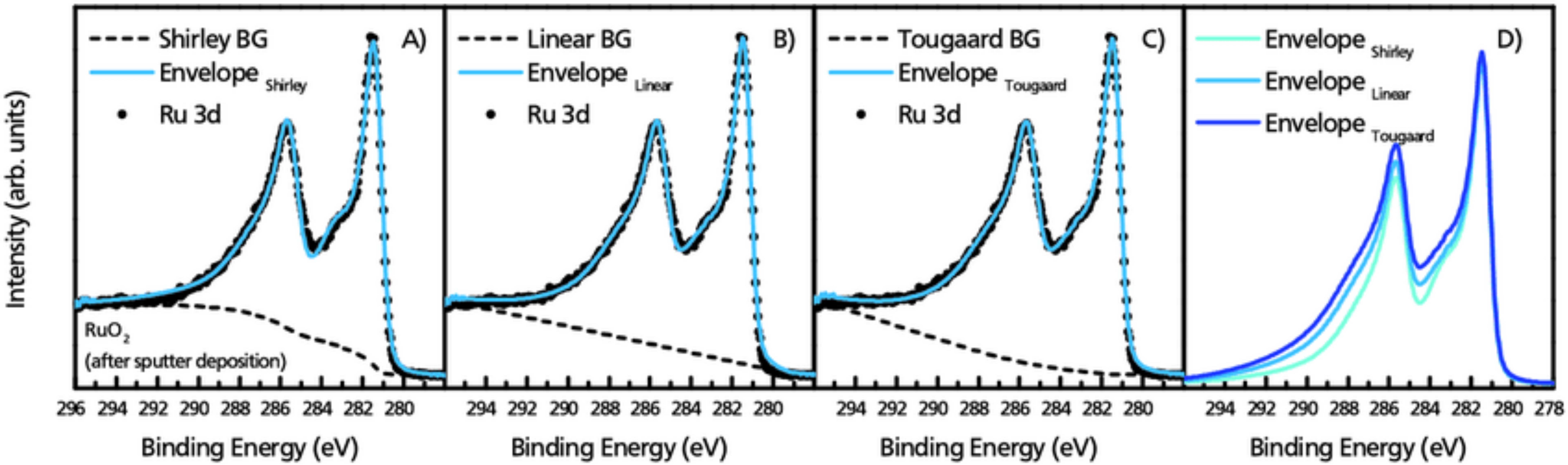
$$B_i = \int_{E^k}^{E^k_{\max}} \frac{B(E' - E)}{\left[C + (E' - E)^2\right]^2} I(E') \mathrm{d}E'$$

where E^k_{max} is the high kinetic energy endpoint where the background is equal to the measured intensity, and B and C are fitting parameters. It was found that a value of B=681.2 eV^2 and of C=355.0 eV^2 gives good results for 59 elements.

The Tougaard background model has a firm physical base because it takes into account the initial energy distribution function and inelastic electron scattering.

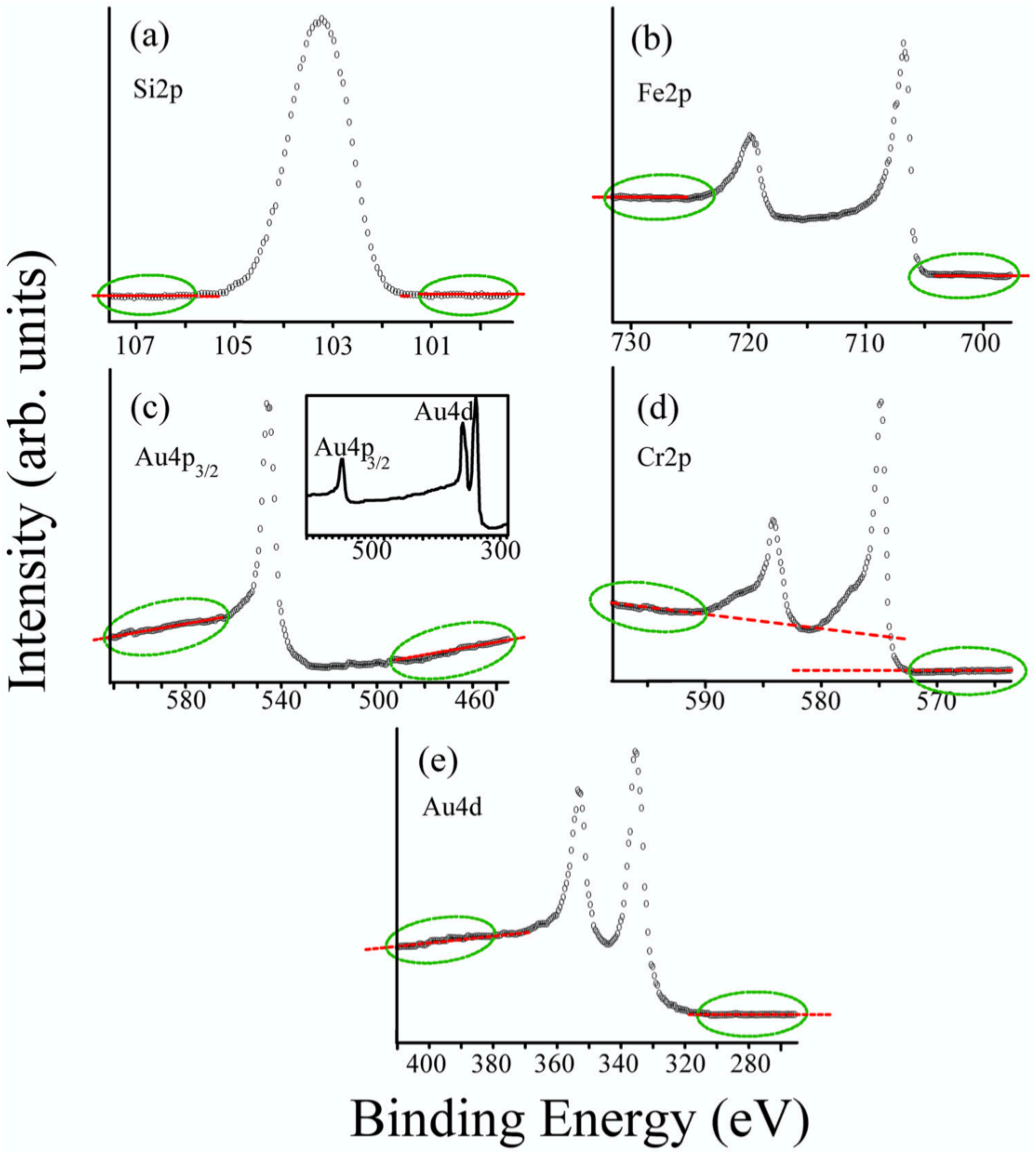
- S. Tougaard, Surf. Sci. 216, 343 (1981)
- S. Tougaard, J. Vac. Sci. Technol. A 14, 1415 (1996)
- M.P.Seah, Surf. Sci. 420,285(1999)

The Different Backgrounds



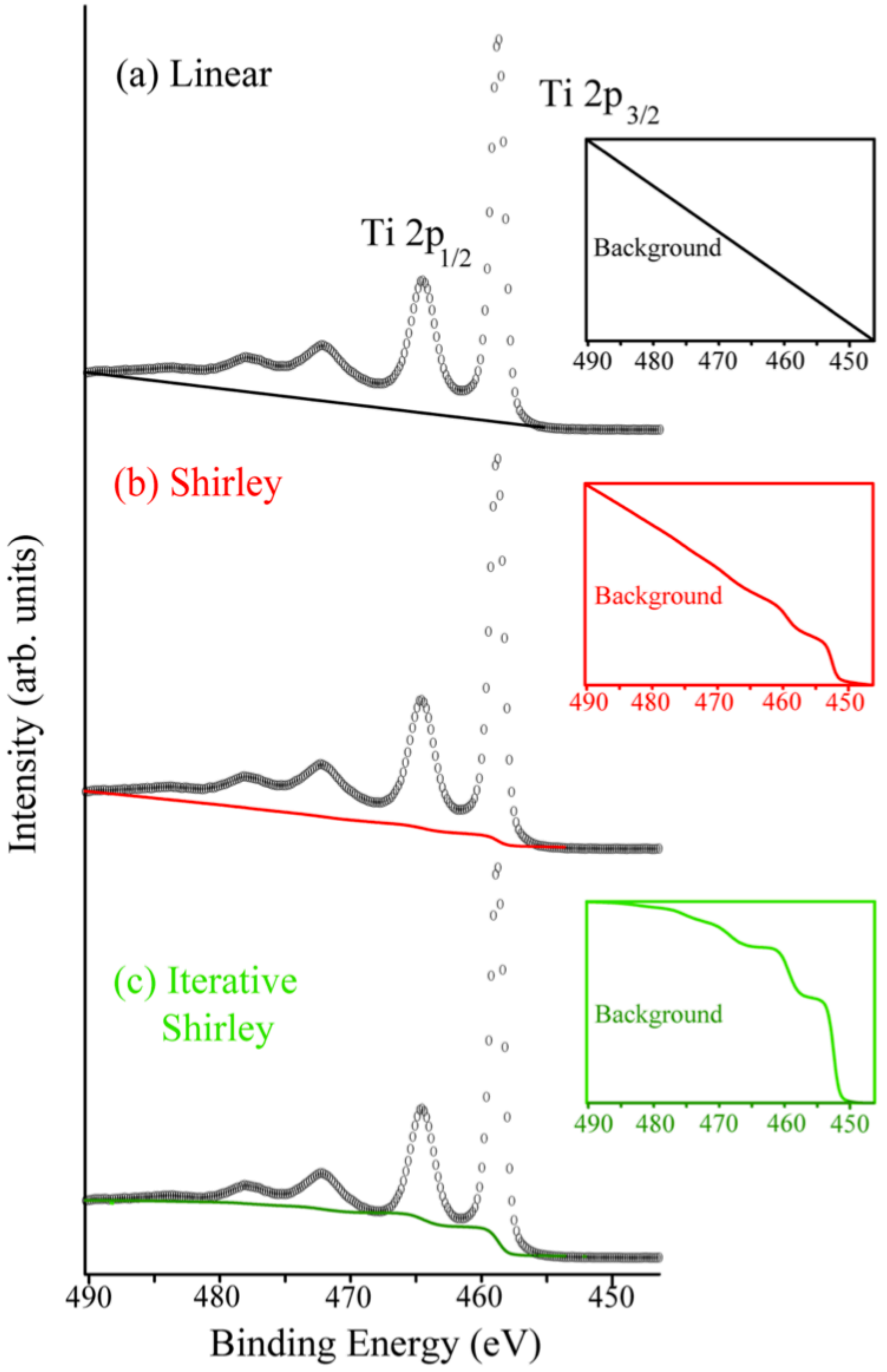
Background removal is a crucial operations especially when dealing with quantification.

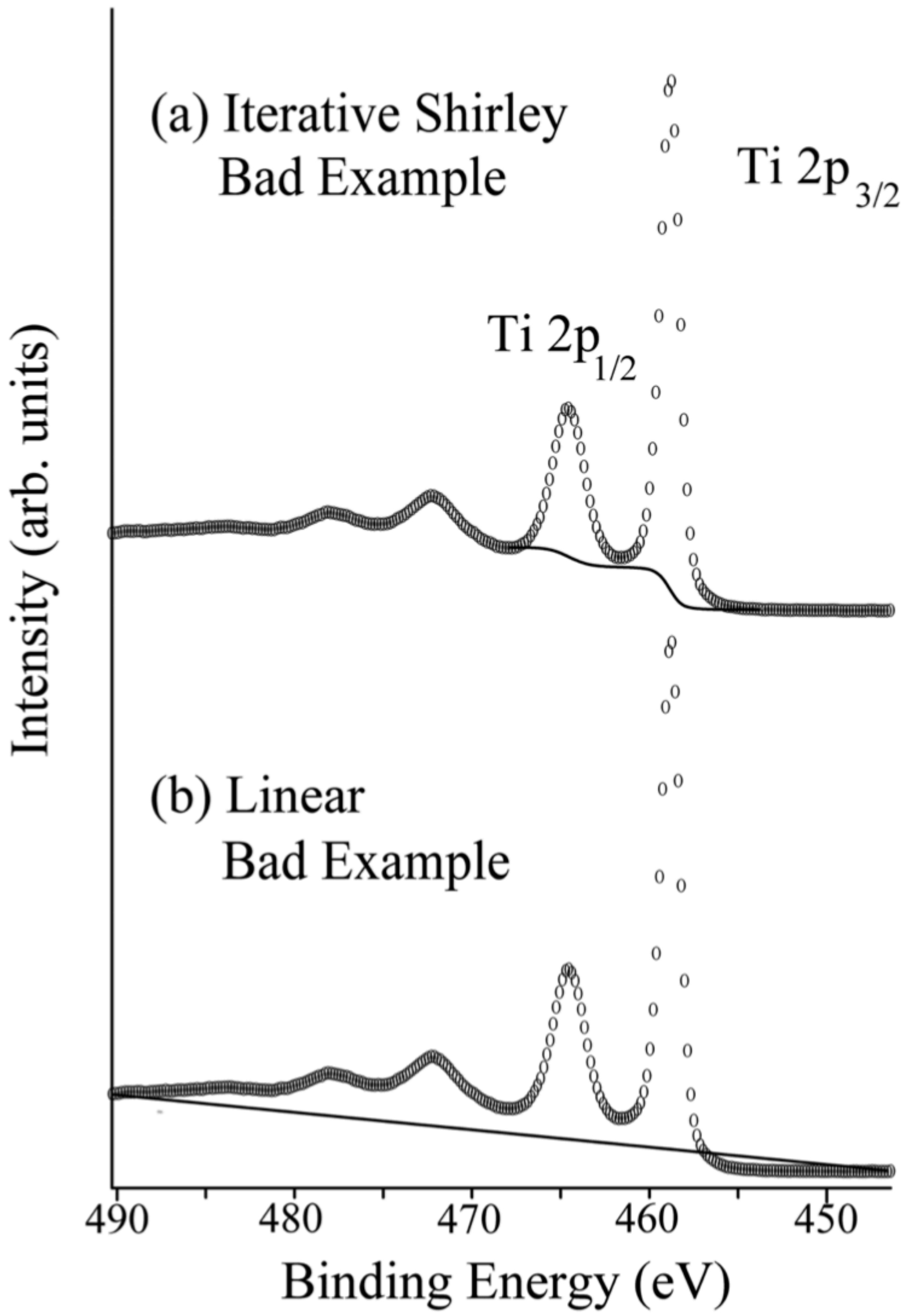
Some Tips About Background



Be sure you acquire an adequate energy window!

J. Vac. Sci. Technol. A **38**, 063203 (2020)





Be sure that the background gets all the signal of interest and does not leave out spectral features.

Peak Fitting - Some Tips

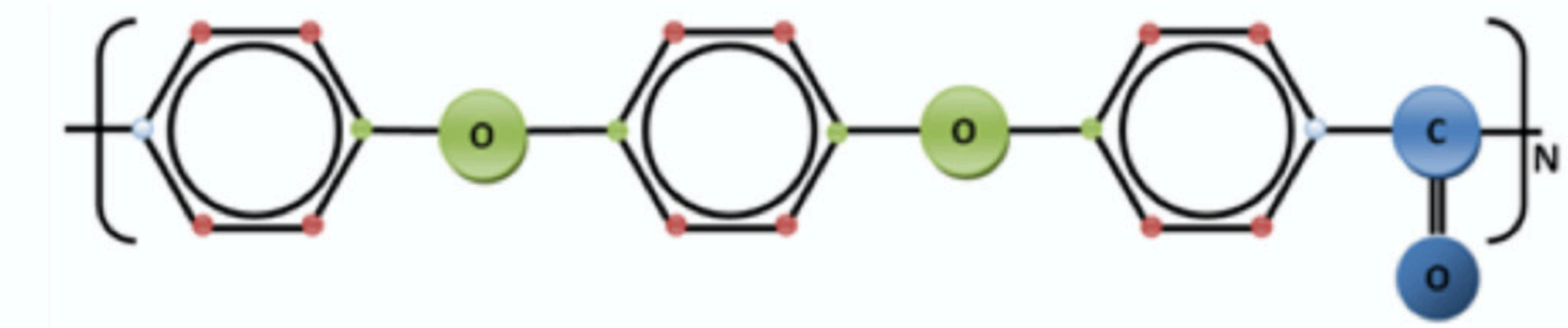
1. Determine number of peaks needed from:
   - Literature.
   - Chemical composition
   - *Common sense (asa Experience).*

2. Quality of the fit: R-factor/Chi-squared (the smaller, the better). Use also residuals.

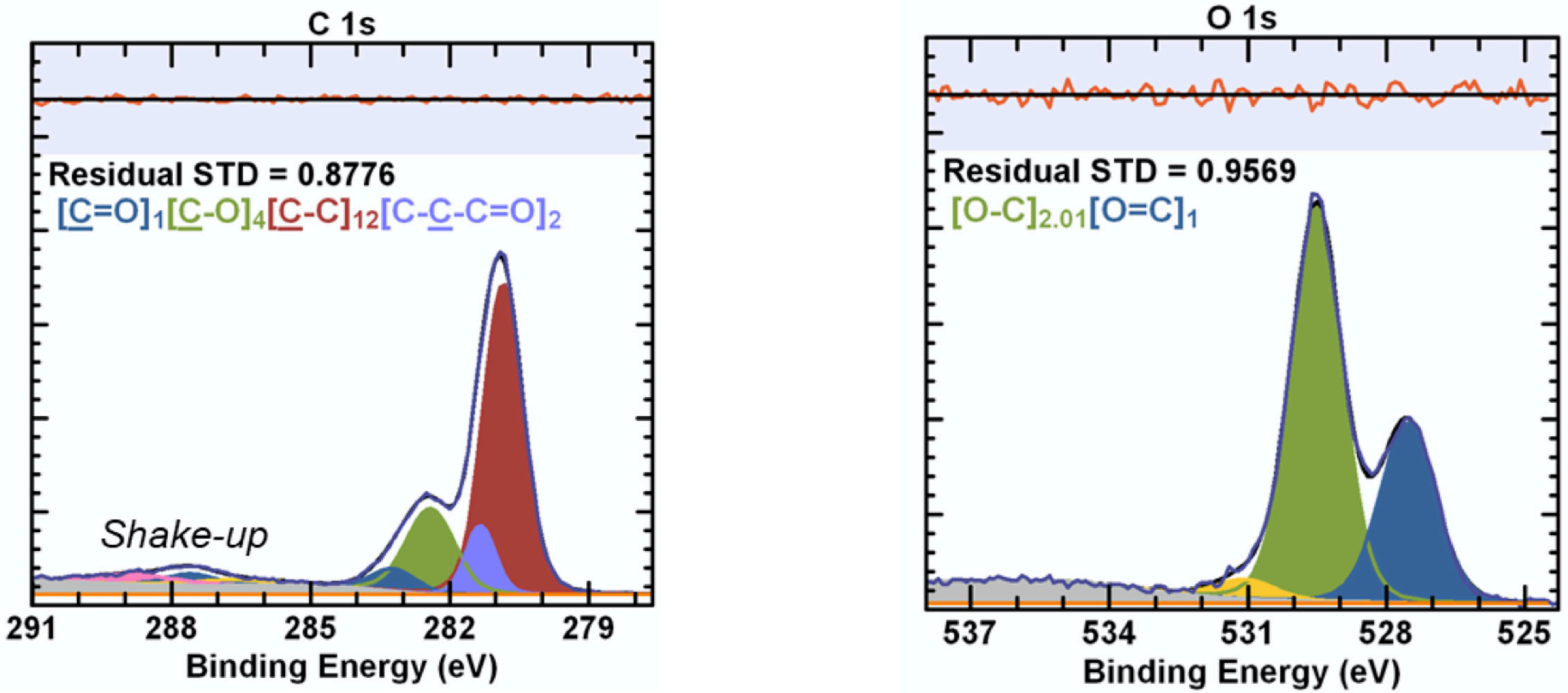
3. Start optimisation of fit with different sets of initial guesses (and peak shapes, motivated), caution to local minima.

4. **As many fit parameters as necessary and as few as possible!** With enough peaks you can fit whatever you want!

Chemical-Shift Identification and Quantification

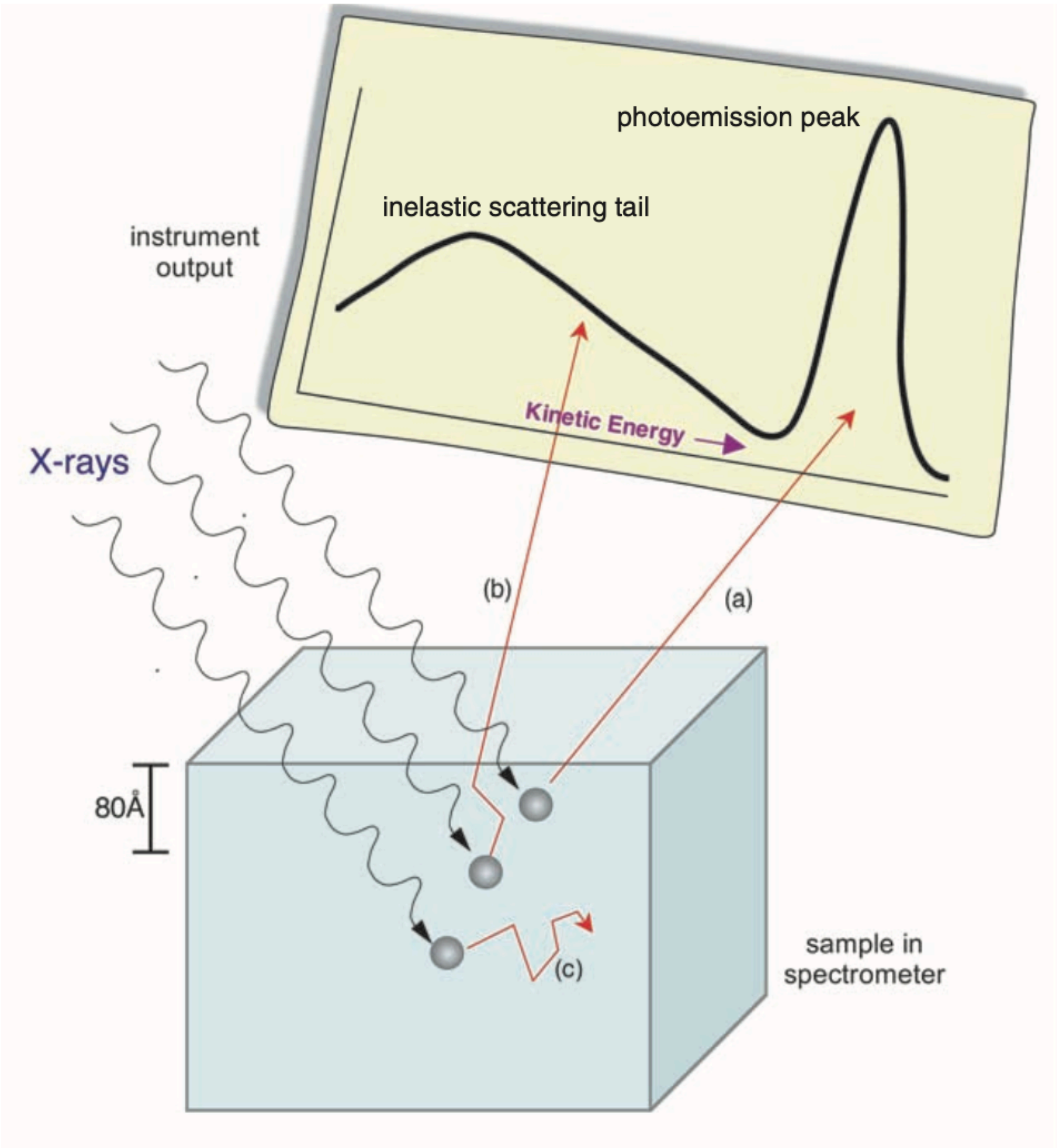


PEEK



J. Vac. Sci. Technol. A 38(6), 061203 (2020)

Probing Depth



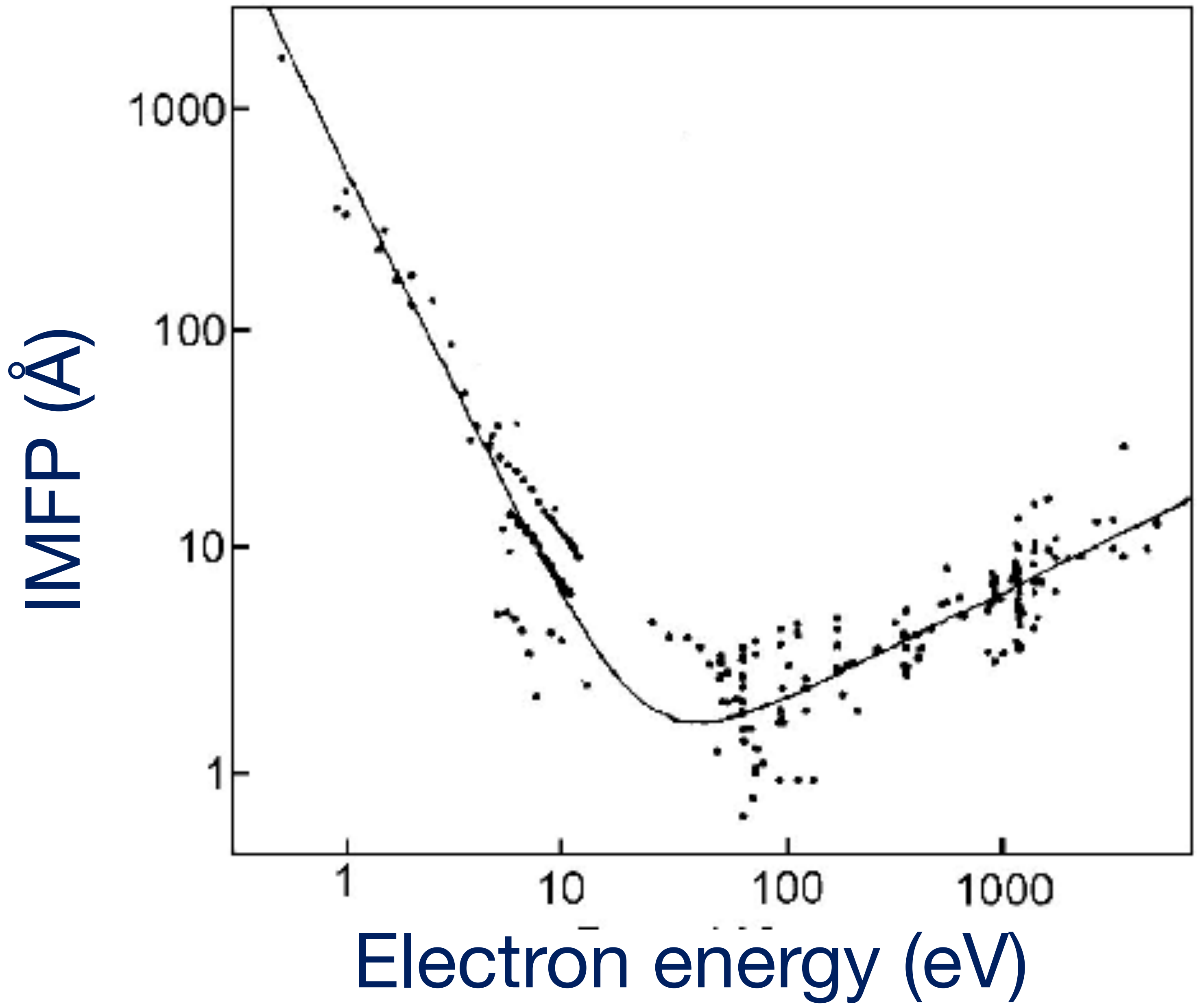
J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

Where do electrons come from? This affects the PE intensity!

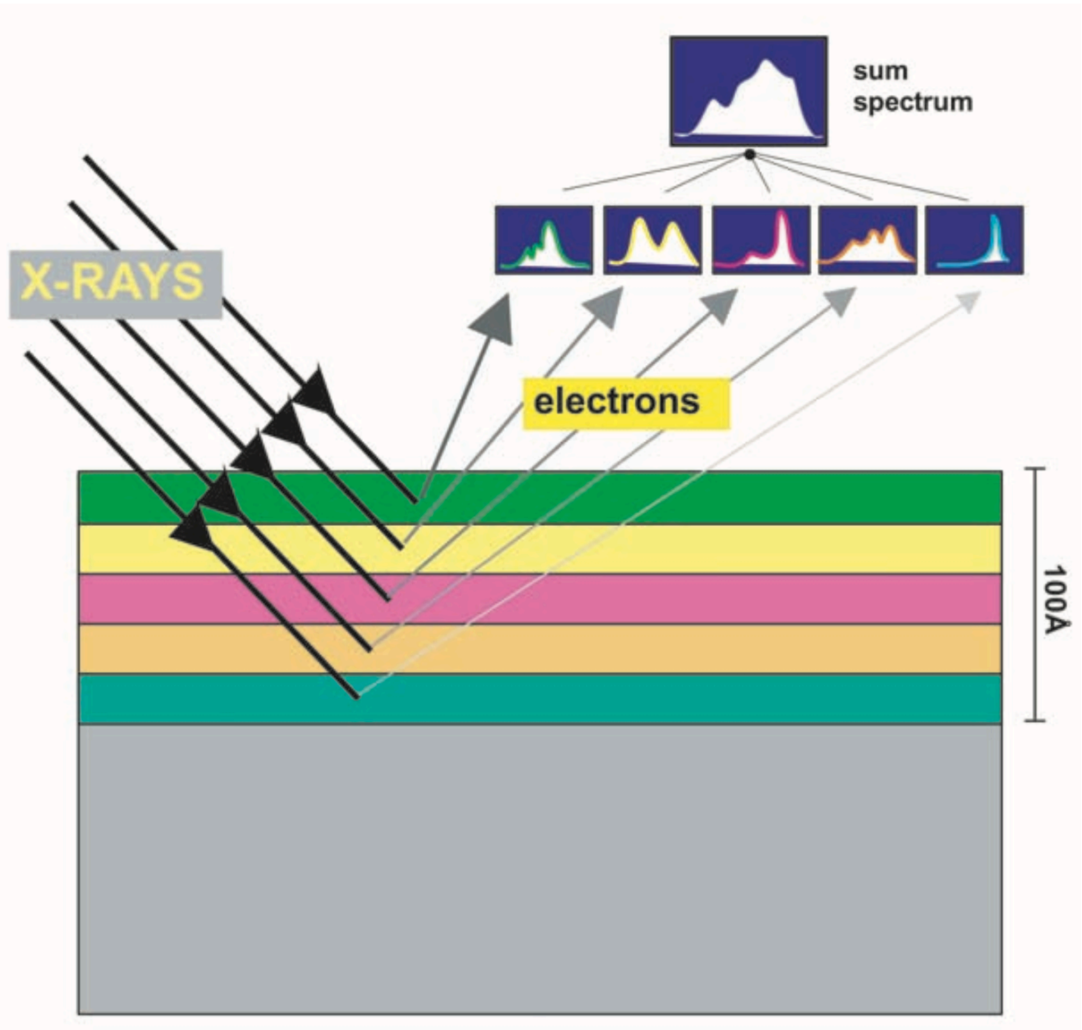
Distance electron can travel in solids depends on:

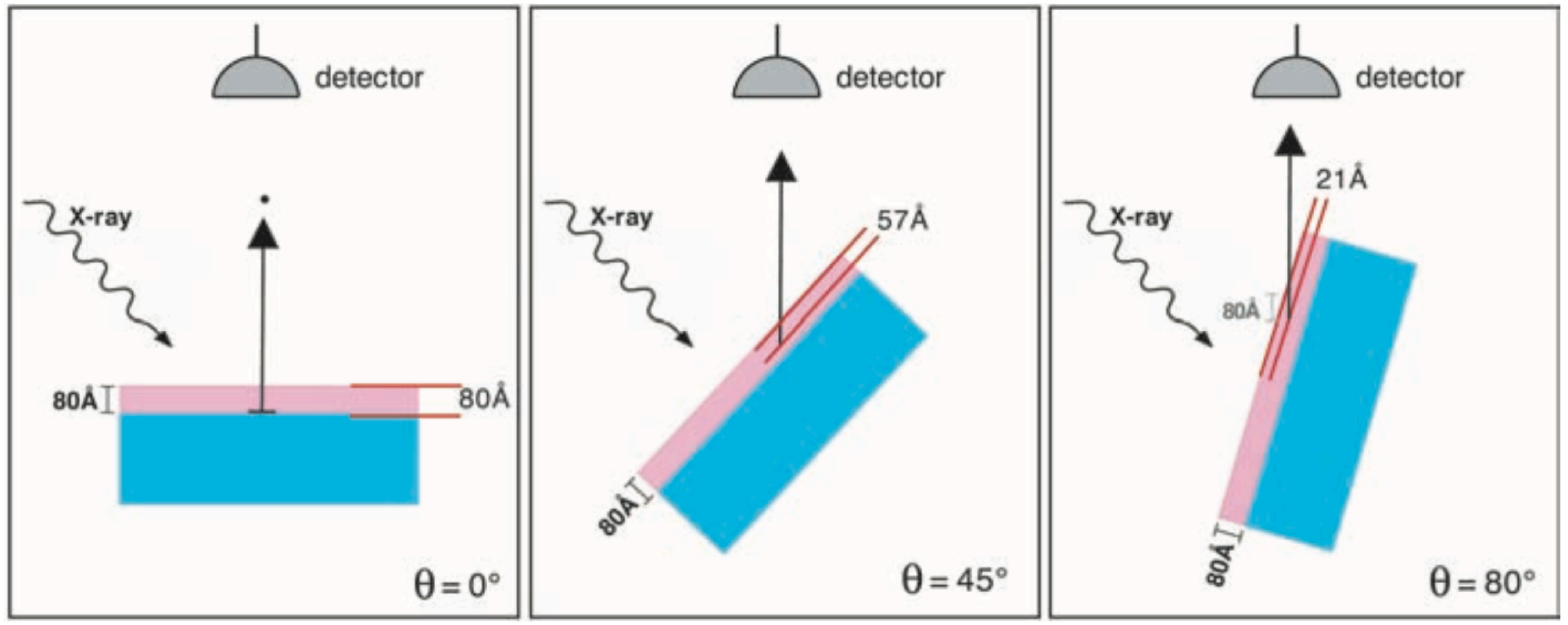
- Material
- Electron kinetic energy.

Measure attenuation of electrons by covering surface with known thickness of element!



Probing Depth





Although ESCA would seem to provide information from a highly surface-localized zone, in fact the surface zone has a finite thickness and often is composed of a vertical composition gradient.

If we estimate that the sampling depth of ESCA is 10nm and the atomic dimensions are 0.3 nm, then the surface region could be composed of ~30 atomic layers.

ESCA spectra are convolutions of the information from each depth within the sampling depth.

Overlayers attenuate the intensities of photoelectrons emitted from deeper layers and so contributions from the underlying layers to the final spectrum will be lower.

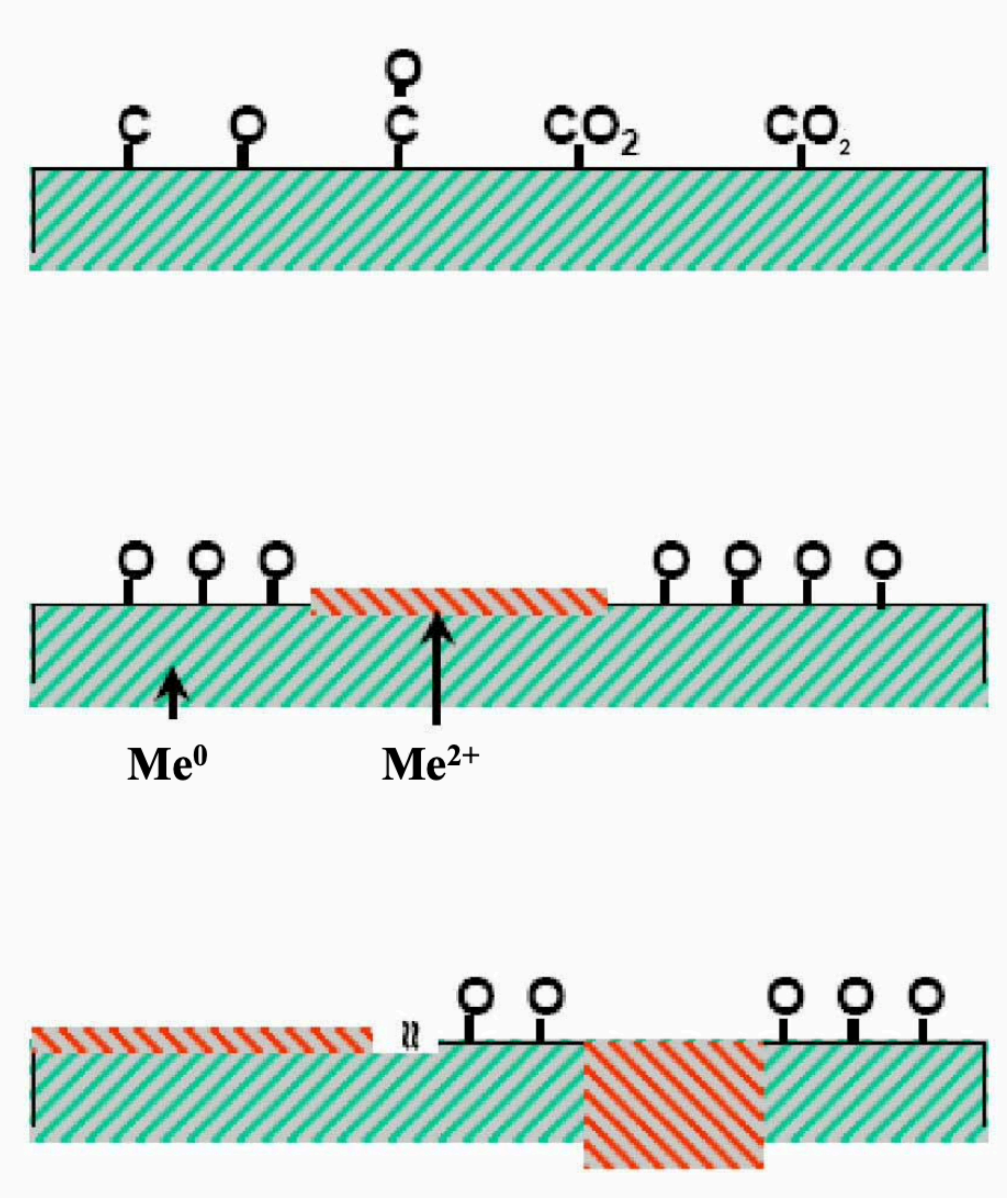
J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

Some Hints on Quantitative Analysis

Extracting information form the measured intensity of the core-level peaks:

Elemental composition

- Species of atoms on the surface
- Concentration of surface atoms
- Vertical distribution:
  - On surface
  - Near the surface



Quantitative Analysis

In general, the measured intensity for each element (peak) is given by:

$$I_x = B \cdot \sigma \cdot \lambda_{tot} \cdot T \cdot n_x$$

B: *all instrumental contributions*
σ: ionisation cross section for given photon energy
λ_{tot}: total escape depth
T: transmission through surface
n_x: atomic density of analysed species in sample

$$\sigma = \sigma_{tot} \cdot f(X, \alpha)$$

with $f(X,\alpha) = 1+(\beta(X)/4)\,(1-3\cos^2\alpha)$

σ_{tot}: total ionisation cross section
f: form function accounting for asymmetry of peak
β: asymmetry parameter
α: angle between photon beam and emitted electron (different for standard x-ray source and synchrotron)
[from J.J. Yeh and I. Lindau, Atomic Data and Nuclear Data Tables, 32, 1-155 (1985)]

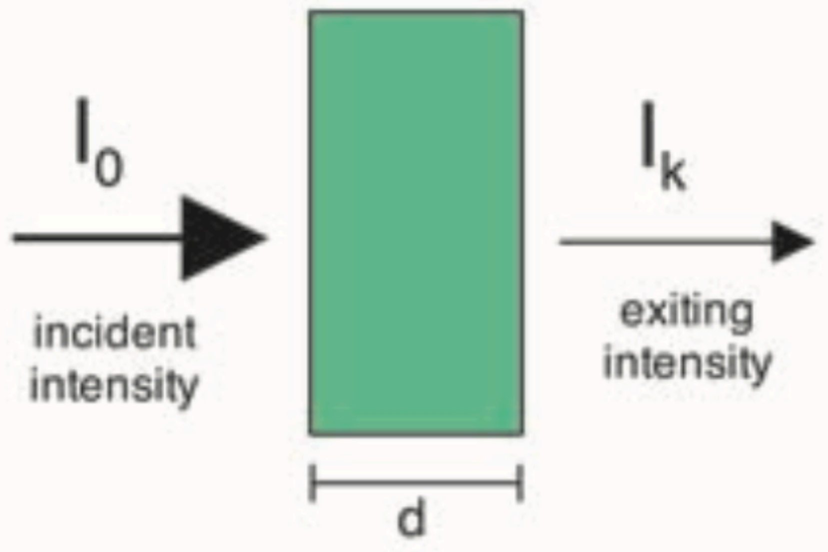
The cross-section changes with photon energy!

$\lambda_{tot} = E(X) \times 1/a[\ln(E(X)-b)$
E: KE of electron
a, b: parameters dependent on dielectric function and concentration of host mater.

In most cases the sample surface is quite heterogeneous. We need *models* to extract an accurate approximation of composition out of spectral intensities

Quantitative Analysis - Beer-Lambert Equation

Transmission

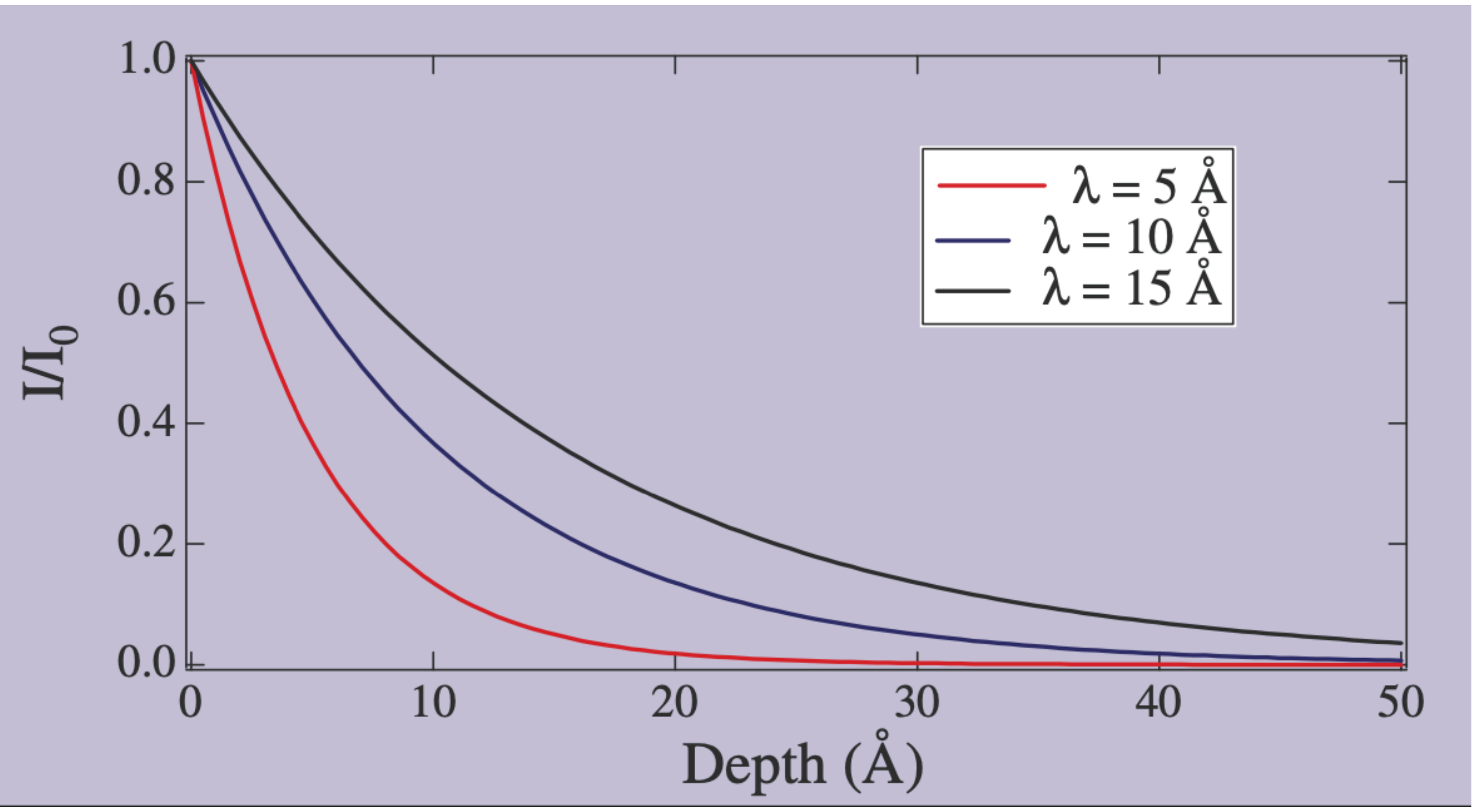


$$I_k = I_0 e^{(-d/\lambda\cos\theta)}$$

λ = inelastic mean free path (an absorption coefficient)

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

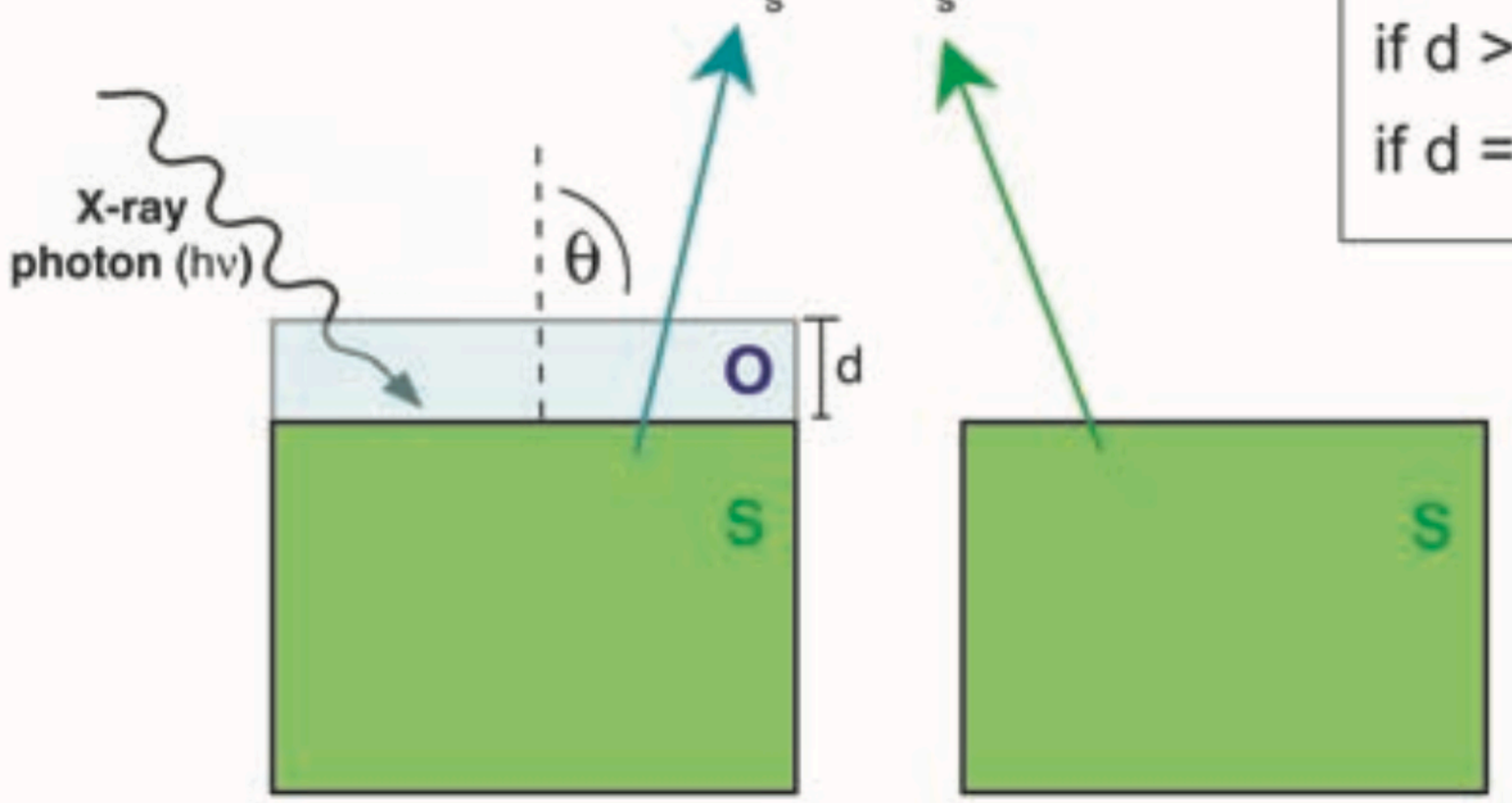
$$5\breve{A} \le \lambda \le 80\breve{A}$$



Emission

overlayer (O) $I_{k_O} = I_{0_O}[1 - e^{(-d/\lambda\cos\theta)}]$

substrate (S) $I_{k_S} = I_{0_S} e^{(-d/\lambda\cos\theta)}$



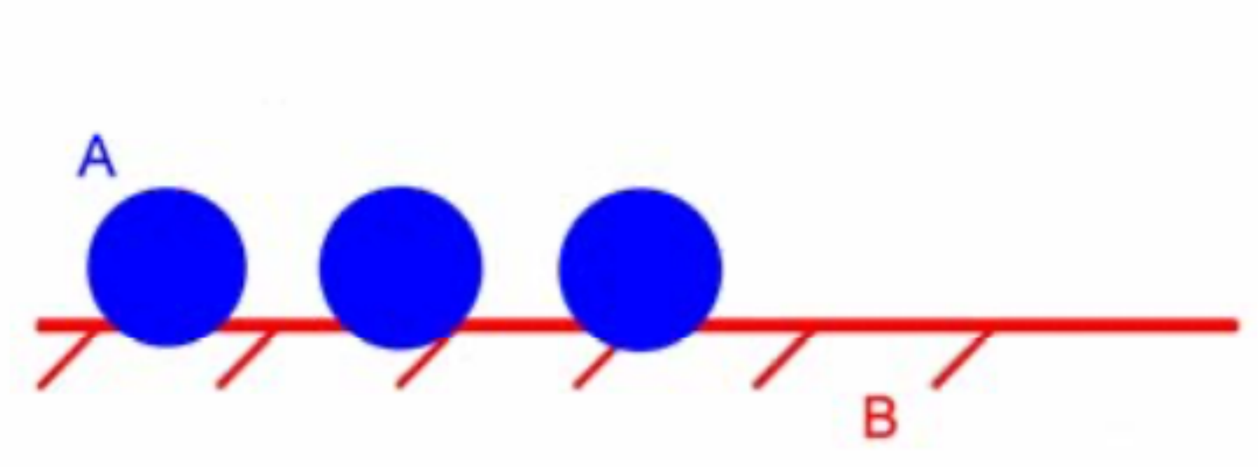
if d >> λ, $I_{kO} = I_{0O}$
if d = λ, $I_{kO} = 0.63 I_{0O}$

When d = 3λ, 95% of the signal comes from d

J. Vickerman, Surface Science, the Principal Techniques (Wiley 2009)

Quantitative Analysis - Example 1

Coverage of A over surface B (adsorbate)



Intensity of A $I_A = I_A^0 \Theta_A$

Intensity of B $I_B = I_B\,\text{(direct)} + I_B\,\text{(attenutated)} = (1-\Theta_A)I_B^0 + I_B^0\Theta_A \exp\left(-\frac{a_A}{\lambda_A \cos\alpha}\right)$

Hence: $I_B = I_B^0\left[1 - \Theta_A + \Theta_A \exp\left(\frac{-a_A}{\lambda_A \cos\alpha}\right)\right]$

Consequently : $\frac{I_A}{I_B} = \frac{I_A^0}{I_B^0}\frac{\Theta_A}{1-\Theta_A\left[1-\exp\left(-\frac{a_A}{\lambda_A}\cos\alpha\right)\right]}$

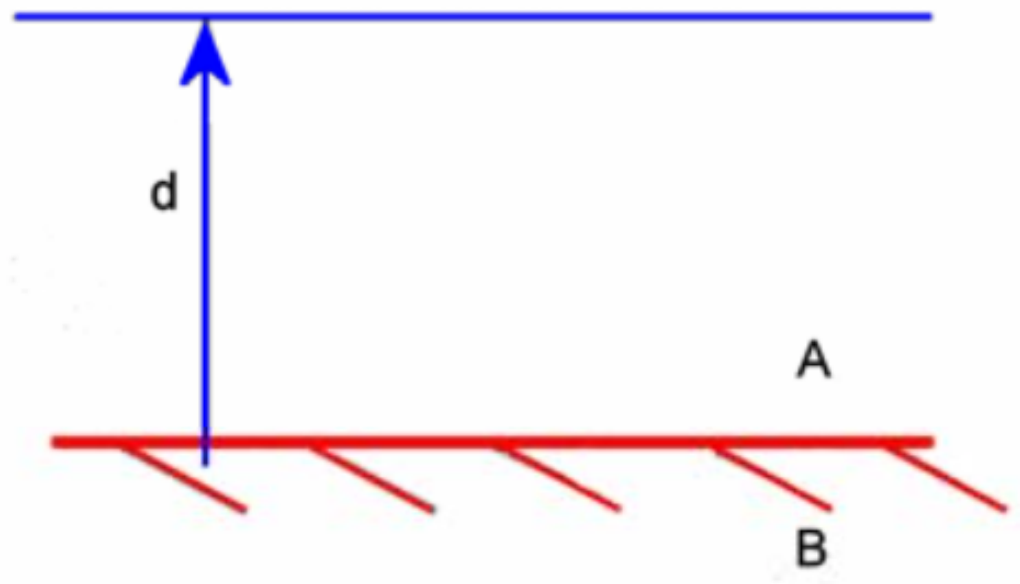
α= angle of electron emission

a_E= average occupancy of A

Θ_A= coverage of A over B

Quantitative Analysis - Example 2

Thin layer of A on B (e.g. oxide)



α= angle of electron emission

Θ_A= coverage of A over B

Intensity of B

$$I_B = I_B^0 \exp\left(-\frac{d_A}{\lambda_A(E_B)}\cos\alpha\right)$$

Hence:

$$I_A = I_A^0\left[1 - \exp\left(-\frac{d_A}{\lambda_A(E_A)}\cos\alpha\right)\right]$$

If $E_A \sim E_B \rightarrow \lambda(E_A) \sim \lambda(E_B)$

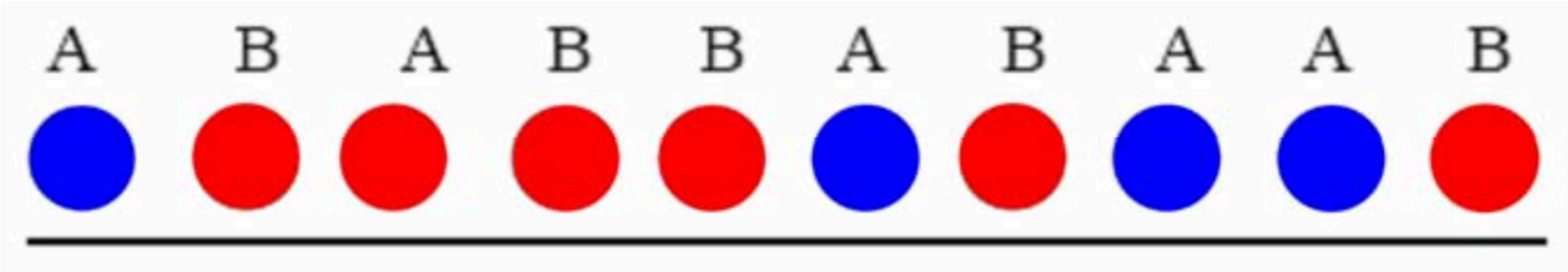
Consequently :

$$\frac{I_A}{I_B} = \frac{I_A^0}{I_B^0}\frac{\left[1 - \exp\left(-\frac{d_A}{\lambda_A(E_A)}\cos\alpha\right)\right]}{\exp\left(-\frac{d_A}{\lambda_A(E_B)}\cos\alpha\right)}$$

$$\boxed{d \sim \frac{\lambda_A}{\cos\alpha}\ln\left[1 + \frac{I_B^0}{I_A^0}\frac{I_A}{I_B}\right]}$$

Quantitative Analysis - Example 3

We have an heterogeneous mixture (e.g. alloy) of A and B.



$$\frac{I_A}{I_B} \cdot \frac{I_B^0}{I_A^0} = \frac{N_A}{N_B} \cdot \frac{N_B^0}{N_A^0} \cdot \frac{\lambda_{AB}(E_A)}{\lambda_{AB}(E_B)} \cdot \frac{\lambda_B(E_B)}{\lambda_A(E_A)}$$

$$\lambda_A = 0.41 \cdot a_A^{1.5} \cdot E_A^{0.5}$$

$$\frac{N_A}{N_B} \cdot \frac{N_B^0}{N_A^0} = \frac{X_A}{X_B} \cdot \left(\frac{a_A}{a_B}\right)^3$$

$$\frac{X_A}{X_B} = \left(\frac{a_B}{a_A}\right)^{1,5} \cdot \frac{I_A / I_A^0}{I_B / I_B^0}$$

a_i = size of an atom of element i calculated using $M_i = \rho_i N_A a_i^3$

$$X_A = \frac{I_A / I_A^\infty}{\sum_{i=1,N} I_i / I_i^\infty}$$

Atomic fraction

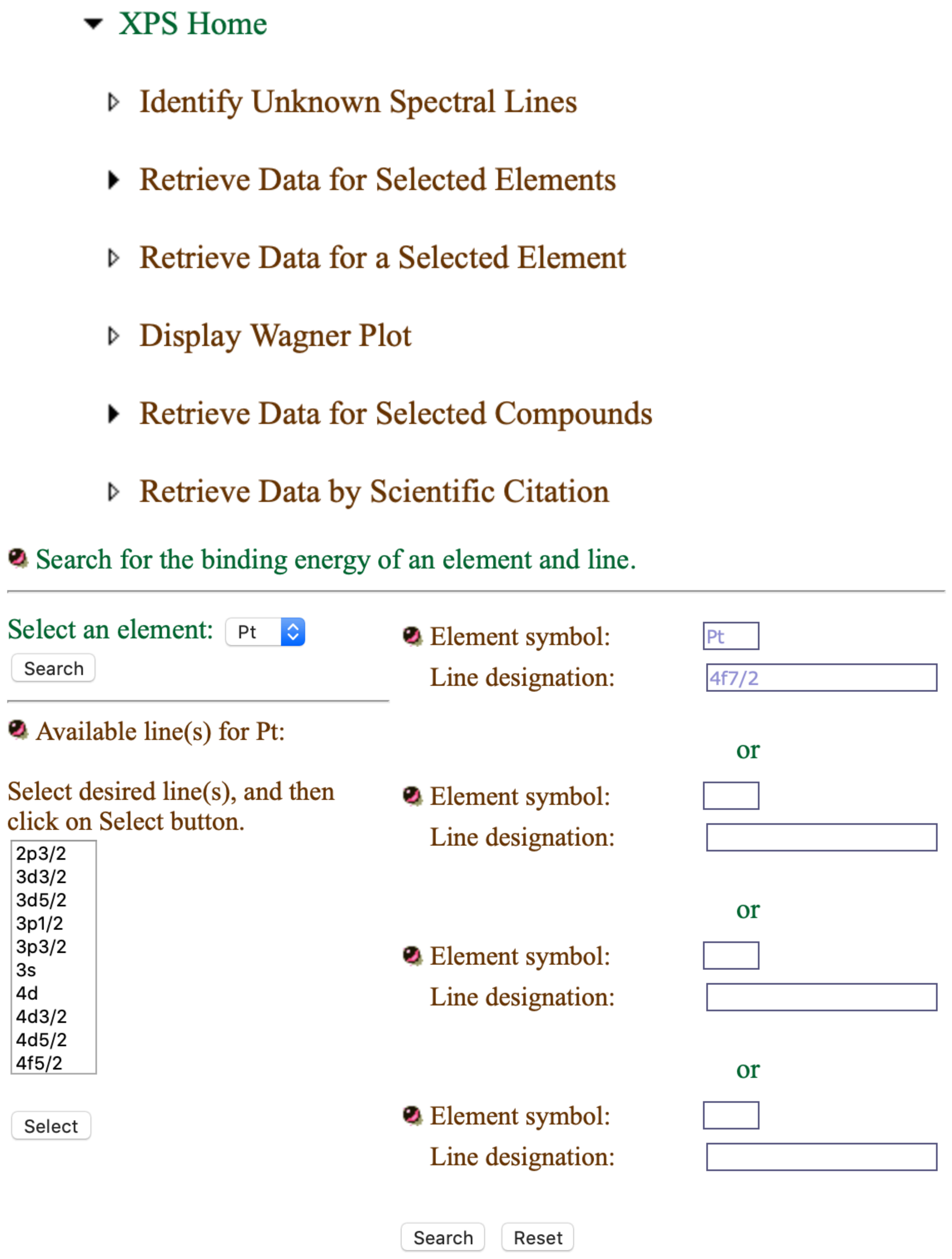
For an accurate review of calculation of λ
J. Vac. Sci. Technol. A 38, 023209 (2020)

Useful Literature

-D. Briggs, M. P. Seah: ***Practical Surface Analysis, Volume 1: Auger and X-Ray Photoelectron Spectroscopy***, John Wiley & Sons, Chichester, 1990
- C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg: ***Handbook of X-Ray Photoelectron Spectroscopy***, Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1979
- H. Lüth: ***Surfaces and Interfaces of Solid Materials***, 3. Auflage, Springer Verlag, Berlin, 1995
- G. Ertl, J. Küppers: ***Low Energy Electrons and Surface Chemistry***, VCH Verlagsgesellschaft, Weinheim, 1985
- K. Siegbahn, C. Nording et al.: ***ESCA Applied to Free Molecules***, North-Holland, Amsterdam, 1971
- M. Cardona, L. Ley: ***Photoemission of Solids***, Topics in Applied Physics, Band 26 und 27, Springer Berlin, 1978
- D. Briggs and J. T. Grant: ***Surface Analysis by Auger and Photoelectron Spectroscopy***, Surface Spectra and IM Publications 2003.
- S. Hofmann, **Auger- and X-Ray Photoelectron Spectroscopy in Materials Science,** Springer, 2013.

Check out the issue of Journal of Vacuum Science and Technology A, vol 38, issue 6 (Dec 2020), which includes several articles on the correct interpretation of XPS spectra, with useful discussion about line shapes, background, quantification.

Useful Database: NIST



Search for the binding energy of an element and line.

Select an element: Pt

Available line(s) for Pt:

Select desired line(s), and then click on Select button.

- 2p3/2
- 3d3/2
- 3d5/2
- 3p1/2
- 3p3/2
- 3s
- 4d
- 4d3/2
- 4d5/2
- 4f5/2

Element symbol: Pt
Line designation: 4f7/2

or

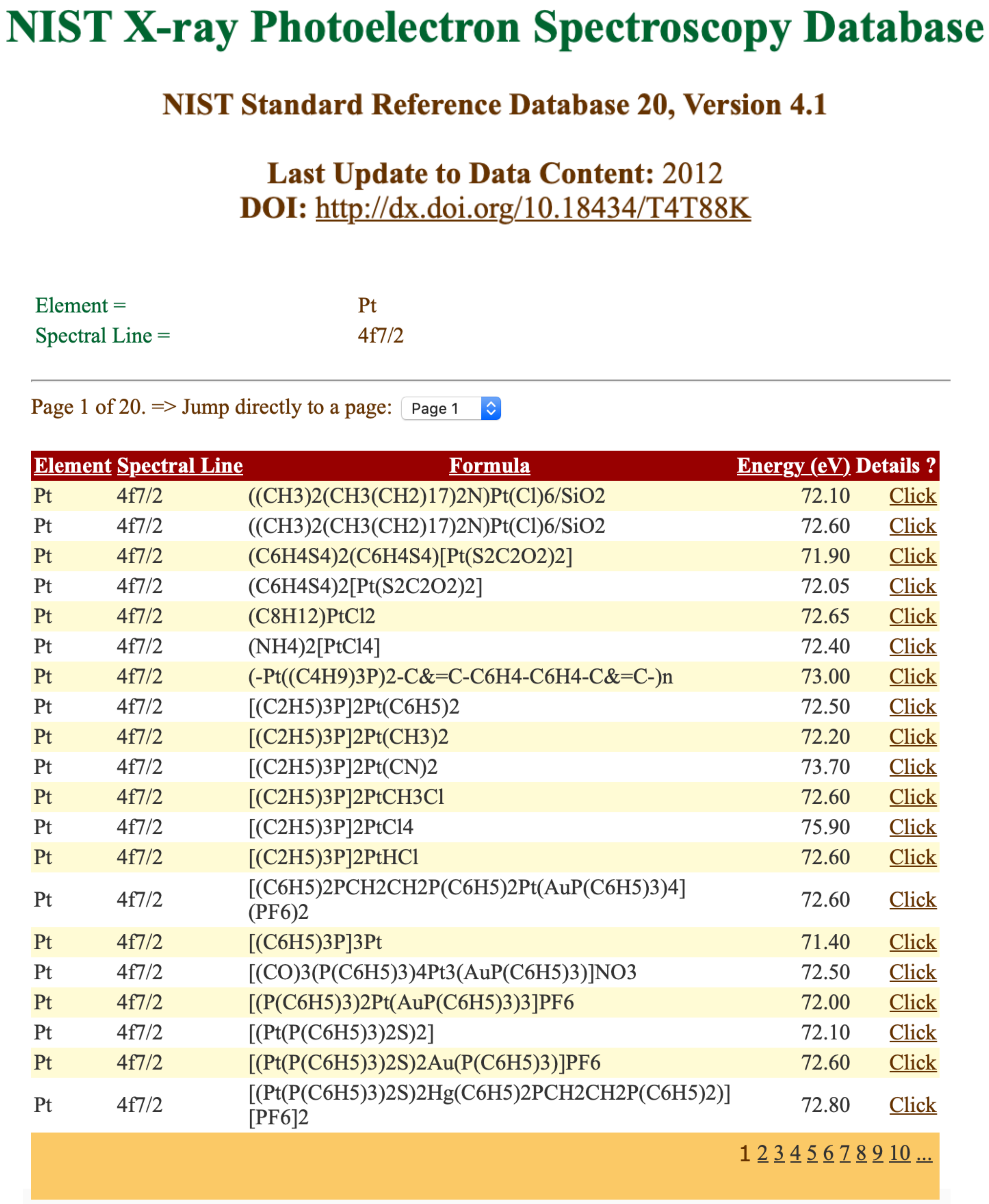
Element symbol:
Line designation:

or

Element symbol:
Line designation:

or

Element symbol:
Line designation:



NIST X-ray Photoelectron Spectroscopy Database

NIST Standard Reference Database 20, Version 4.1

Last Update to Data Content: 2012
DOI: http://dx.doi.org/10.18434/T4T88K

Element = Pt
Spectral Line = 4f7/2

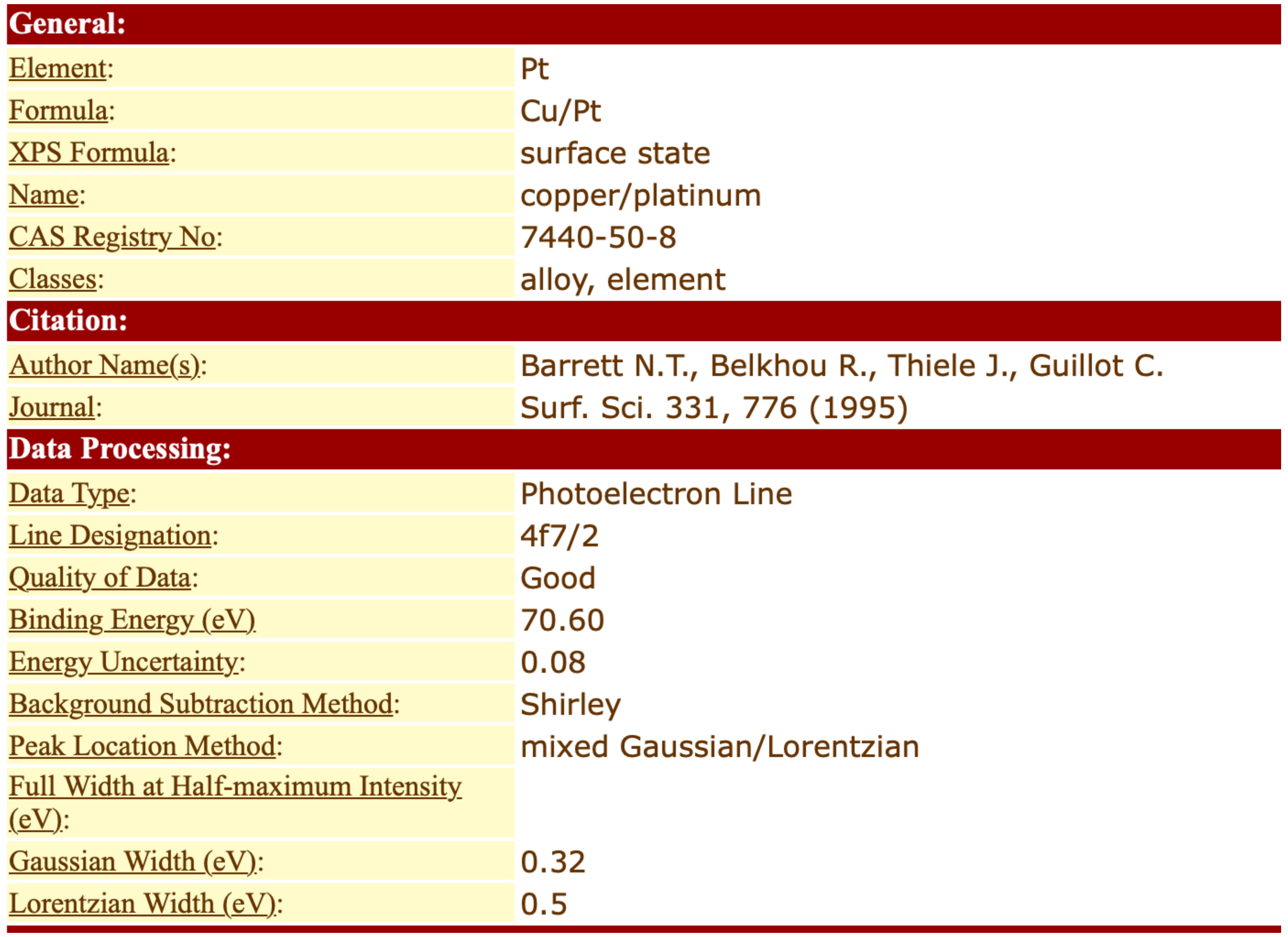
Page 1 of 20. => Jump directly to a page: Page 1

Element	Spectral Line	Formula	Energy (eV)	Details ?
Pt	4f7/2	((CH3)2(CH3(CH2)17)2N)Pt(Cl)6/SiO2	72.10	Click
Pt	4f7/2	((CH3)2(CH3(CH2)17)2N)Pt(Cl)6/SiO2	72.60	Click
Pt	4f7/2	(C6H4S4)2(C6H4S4)[Pt(S2C2O2)2]	71.90	Click
Pt	4f7/2	(C6H4S4)2[Pt(S2C2O2)2]	72.05	Click
Pt	4f7/2	(C8H12)PtCl2	72.65	Click
Pt	4f7/2	(NH4)2[PtCl4]	72.40	Click
Pt	4f7/2	(-Pt((C4H9)3P)2-C&=C-C6H4-C6H4-C&=C-)n	73.00	Click
Pt	4f7/2	[(C2H5)3P]2Pt(C6H5)2	72.50	Click
Pt	4f7/2	[(C2H5)3P]2Pt(CH3)2	72.20	Click
Pt	4f7/2	[(C2H5)3P]2Pt(CN)2	73.70	Click
Pt	4f7/2	[(C2H5)3P]2PtCH3Cl	72.60	Click
Pt	4f7/2	[(C2H5)3P]2PtCl4	75.90	Click
Pt	4f7/2	[(C2H5)3P]2PtHCl	72.60	Click
Pt	4f7/2	[(C6H5)2PCH2CH2P(C6H5)2Pt(AuP(C6H5)3)4](PF6)2	72.60	Click
Pt	4f7/2	[(C6H5)3P]3Pt	71.40	Click
Pt	4f7/2	[(CO)3(P(C6H5)3)4Pt3(AuP(C6H5)3)]NO3	72.50	Click
Pt	4f7/2	[(P(C6H5)3)2Pt(AuP(C6H5)3)3]PF6	72.00	Click
Pt	4f7/2	[(Pt(P(C6H5)3)2S)2]	72.10	Click
Pt	4f7/2	[(Pt(P(C6H5)3)2S)2Au(P(C6H5)3)]PF6	72.60	Click
Pt	4f7/2	[(Pt(P(C6H5)3)2S)2Hg(C6H5)2PCH2CH2P(C6H5)2)][PF6]2	72.80	Click

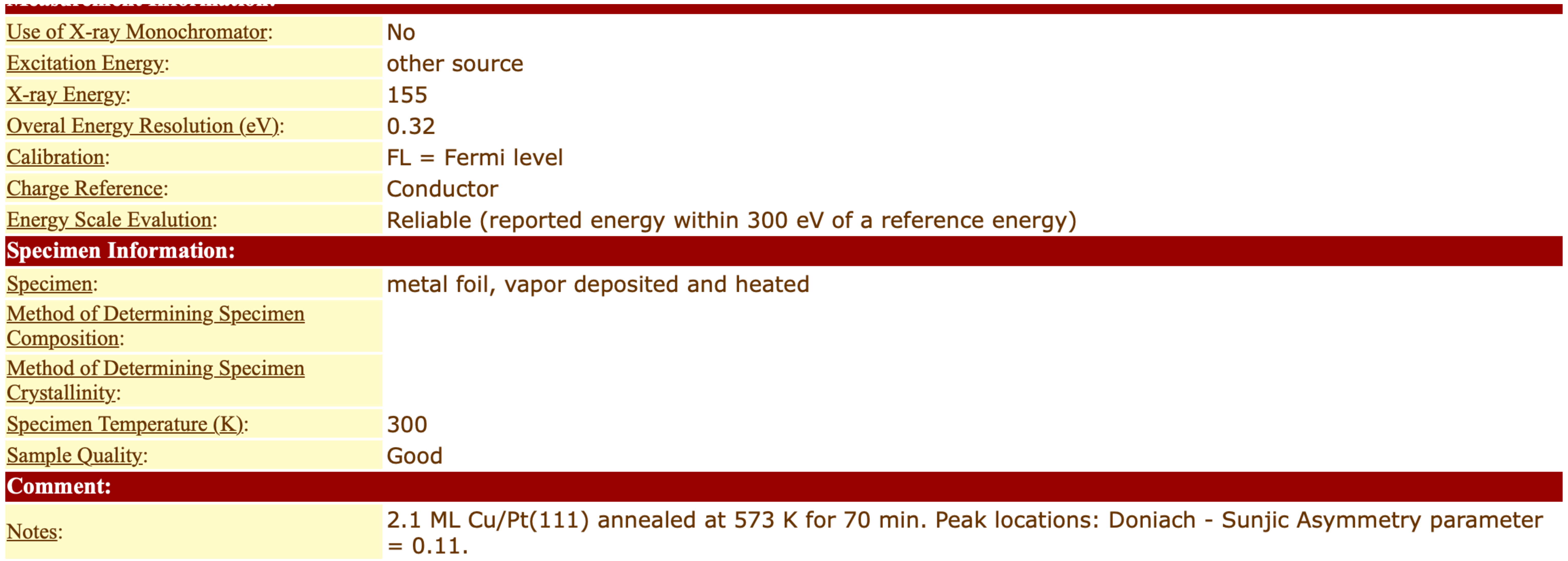
1 2 3 4 5 6 7 8 9 10 ...

Useful Database: NIST

Pt $4f_{7/2}$ in a Cu/Pt sample - 2.1 ML Cu on Pt(111)



General:	
Element:	Pt
Formula:	Cu/Pt
XPS Formula:	surface state
Name:	copper/platinum
CAS Registry No:	7440-50-8
Classes:	alloy, element
Citation:	
Author Name(s):	Barrett N.T., Belkhou R., Thiele J., Guillot C.
Journal:	Surf. Sci. 331, 776 (1995)
Data Processing:	
Data Type:	Photoelectron Line
Line Designation:	4f7/2
Quality of Data:	Good
Binding Energy (eV)	70.60
Energy Uncertainty:	0.08
Background Subtraction Method:	Shirley
Peak Location Method:	mixed Gaussian/Lorentzian
Full Width at Half-maximum Intensity (eV):	
Gaussian Width (eV):	0.32
Lorentzian Width (eV):	0.5



Use of X-ray Monochromator:	No
Excitation Energy:	other source
X-ray Energy:	155
Overal Energy Resolution (eV):	0.32
Calibration:	FL = Fermi level
Charge Reference:	Conductor
Energy Scale Evalution:	Reliable (reported energy within 300 eV of a reference energy)
Specimen Information:	
Specimen:	metal foil, vapor deposited and heated
Method of Determining Specimen Composition:	
Method of Determining Specimen Crystallinity:	
Specimen Temperature (K):	300
Sample Quality:	Good
Comment:	
Notes:	2.1 ML Cu/Pt(111) annealed at 573 K for 70 min. Peak locations: Doniach - Sunjic Asymmetry parameter = 0.11.

In Conclusion

XPS is a very powerful technique and can return a great amount of information about the samples analysed. However interpretation and meaningful analysis of XPS spectra can be extremely difficult and take quite some time.

There are some well-established strategies to analyse XPS data, but there is not just a **single one**. And there is a certain degree of variability depending a lot on instruments and samples measured.

On the other hand, the literature using this technique is quite vast. Thus, one has to combine literature studying and keeping practising, try and error, to finally master the data analysis and interpretation .

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Thank you for your attention!