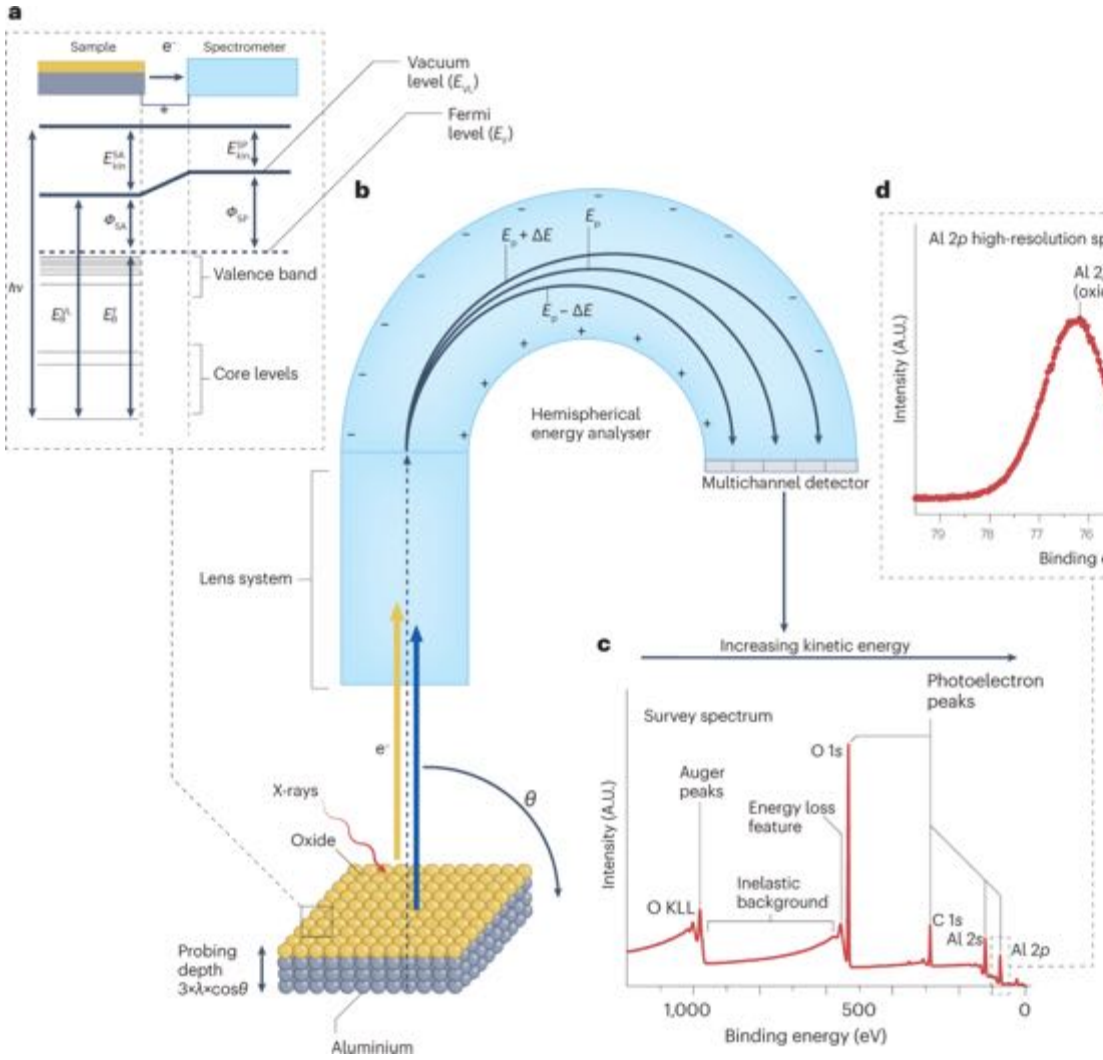
# Near ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS)




**School on Electrocatalysts Functional and In Operando Characterization**
**26. September 2024**
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# Near ambient Pressure X-Ray Photoelectron Spectroscopy

**Content**

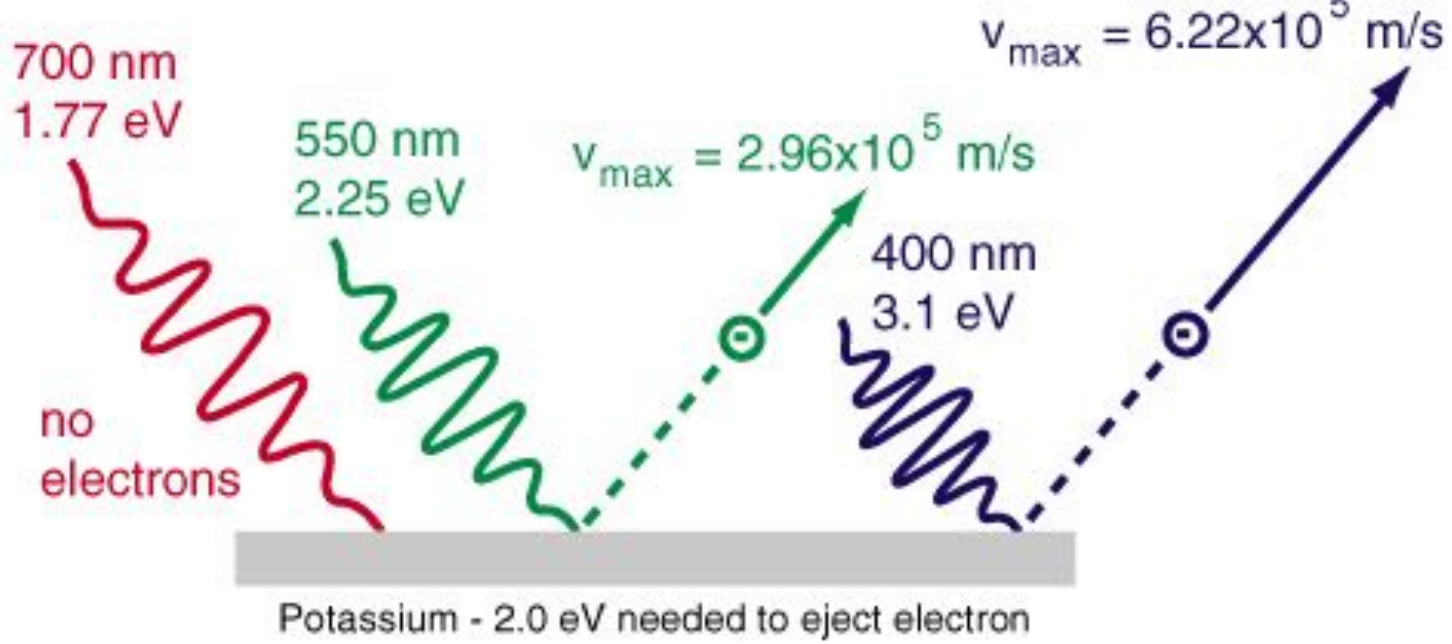
# 1. Photoelectric effect

Electrons leave the metal surface if
condition: E(photon) > frequency threshold ($\nu > \nu_{min.}$)
The remaining photon energy is then transformed into kinetic energy of electrons
A single photon must transmit enough energy to a single electron

$$E_k = h \cdot \nu - E_b$$

*$E_b$ : binding energy of electron*
*$E_k = ½ \cdot m \cdot v^2$, kinetic energy of electron*
*$c = \lambda \cdot \nu$ ..... $c = 3 \cdot 10^8$ m·s$^{-1}$*, photon

Photoelectric effect (potassium)

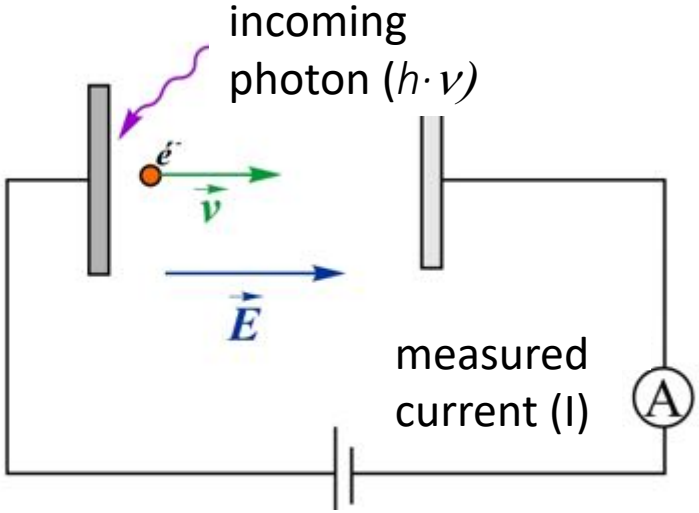


# 1.1. Model for the photoelectric effect

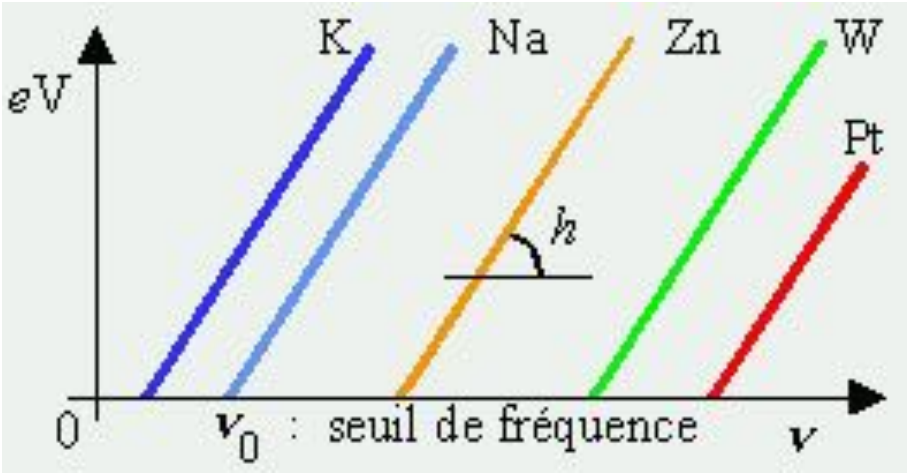
- A photons in a light beam transmit its energy to an electron in the metal atom.
- The excited electron escapes the attraction of the nuclei and leaves the surface of the metal.
- This is an interaction between **a one photon and one electron**.
- The photon's energy ($E_P$) must be greater than a threshold energy ($E_b$). The excess energy is transferred to the electron in the form of kinetic energy ($E_k$).

Albert EINSTEIN
Nobel prize in Physics (1921)

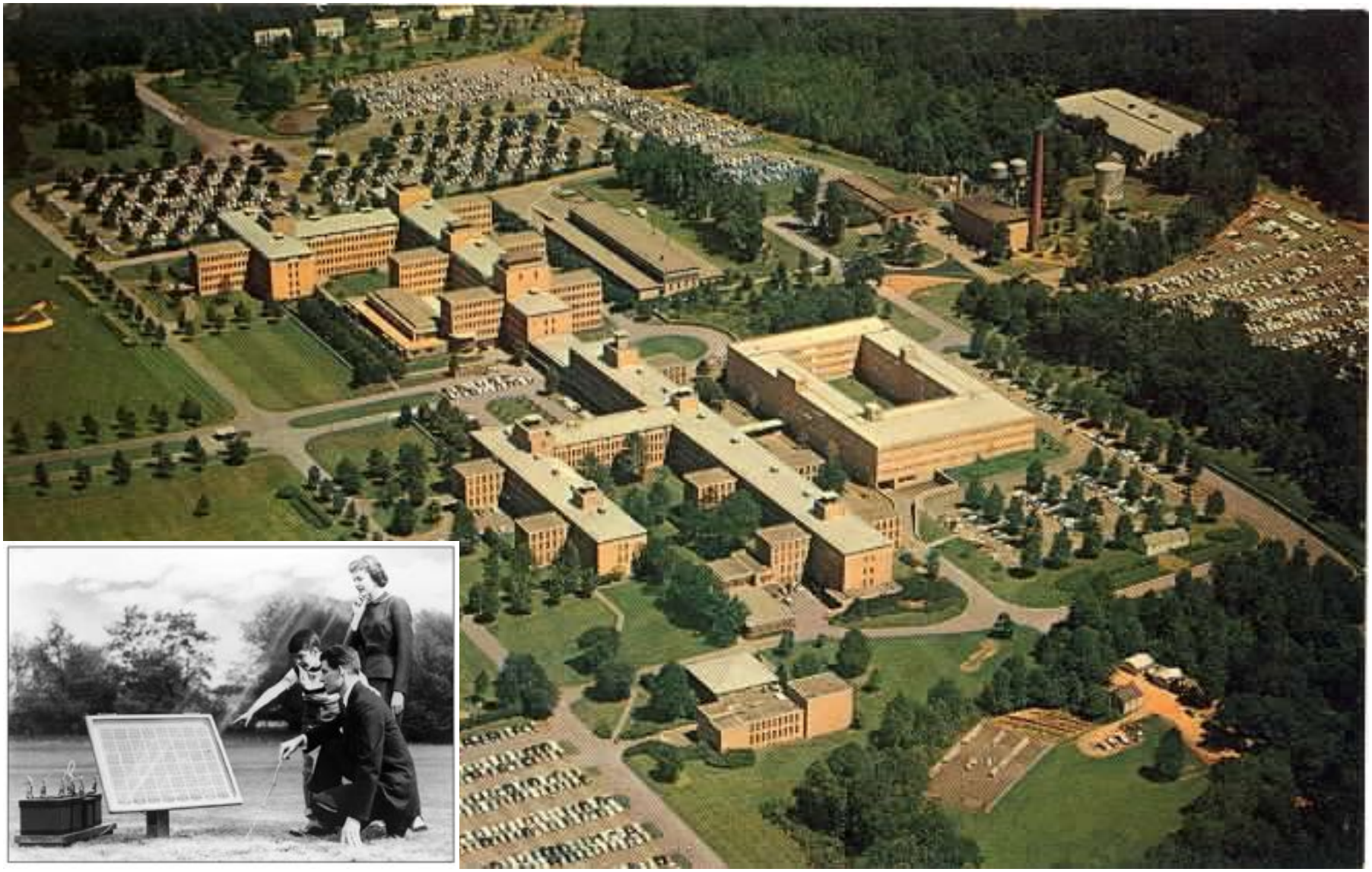
$m_e$ = mass of electron
v = speed of electron
h : constante de Planck = $6.63 \cdot 10^{-34}$ J.s
e : charge of electron $1.60217662 \cdot 10^{-19}$ A·s




$$h \cdot \nu = E_b + E_k \longrightarrow h \cdot \nu = E_b + \tfrac{1}{2} \cdot m \cdot v^2$$



# 1.2. First photovoltaic panel to charge a battery

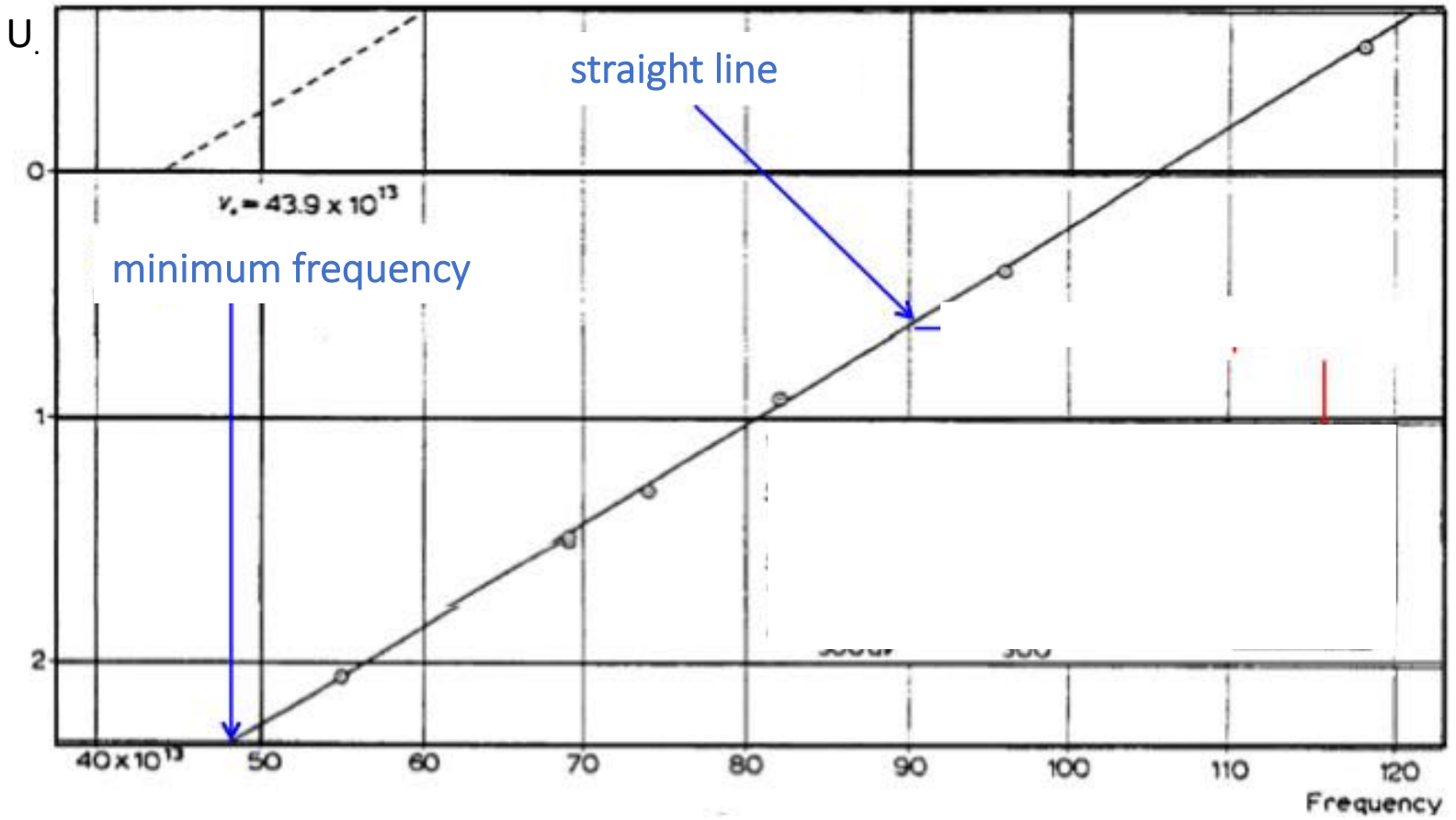


AT&T Bell Laboratories, Murray Hill, NJ, USA, advertisement for first commercial photovoltaic cells (Look magazine, 1956)

# Question

**Photoelectric effect**

1) What is the significance of the minimum frequency?
2) What is the significance of the slope of the straight line?



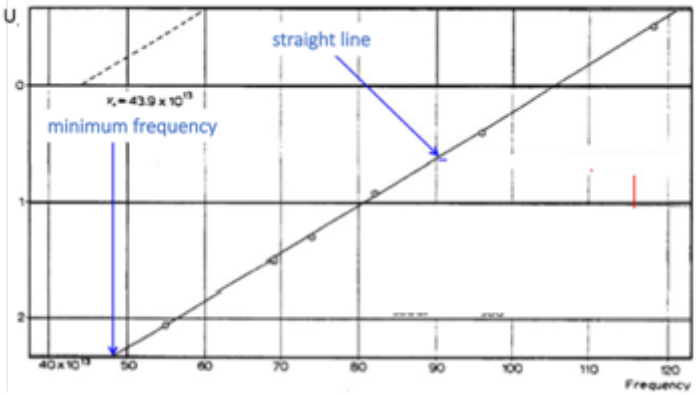
# Answer

## Photoelectric effect

1) What is the significance of the minimum frequency?

$h \cdot \nu_{min.} = E_b \ (E_k = 0)$

2) What is the significance of the slope of the straight line?




$$E_P = \Phi + E_c \longrightarrow h \cdot \nu = \Phi + \frac{1}{2} m_e v^2$$

$$E_P = \Phi + E_c \longrightarrow h \cdot \nu = \Phi + U \cdot e \ (I = 0)$$

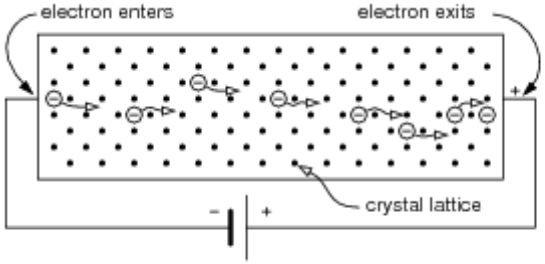
$$U = \frac{h \cdot \nu}{e} - \frac{\Phi}{e}$$

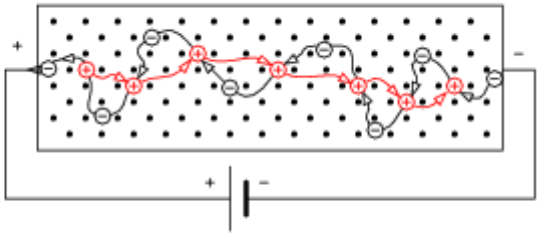
$$\frac{dU}{d\nu} = \frac{h}{e}$$

$$\frac{h}{e} = \frac{6.626069 \cdot 10^{-34} \ Js}{1.60217662 \cdot 10^{-19} \ As} = 4.1357 \cdot 10^{-15} \ Vs$$

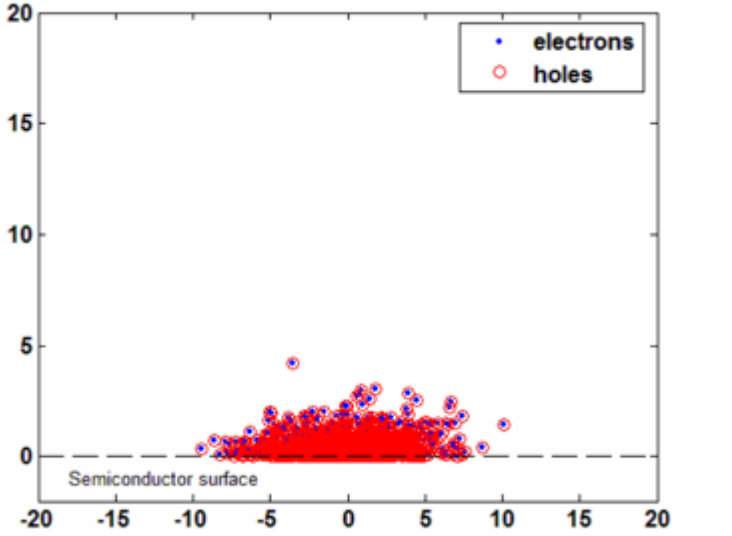
$m_e$ = mass of electron
v = speed of electron
h : constante de Planck = 6.63 $\cdot 10^{-34}$ J.s
e : charge of electron 1.60217662 $\cdot 10^{-19}$ A·s

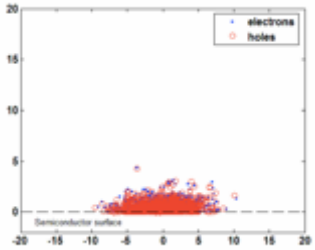
# 1.3. Dember effect

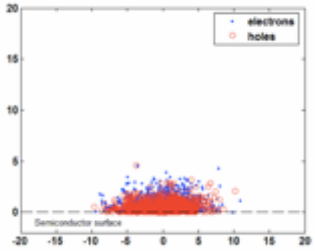


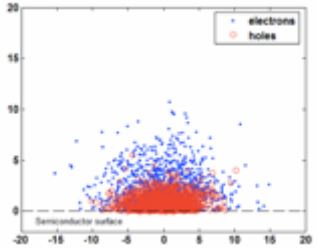



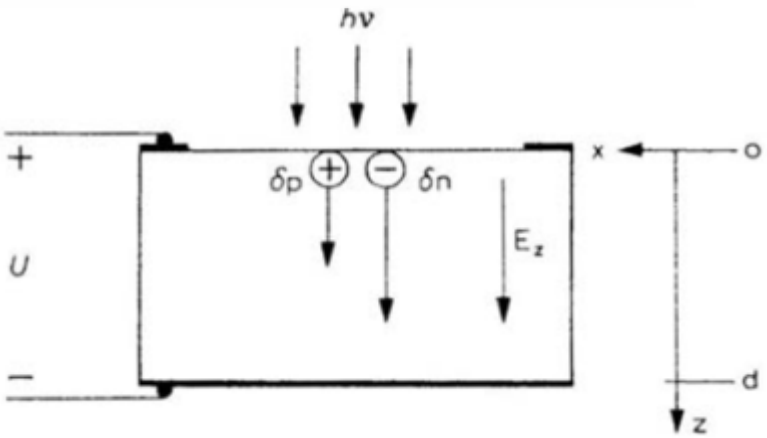
Harry Dember (* 11. Juli 1882 in Leimbach; † 22. März 1943 in New Brunswick, New Jersey

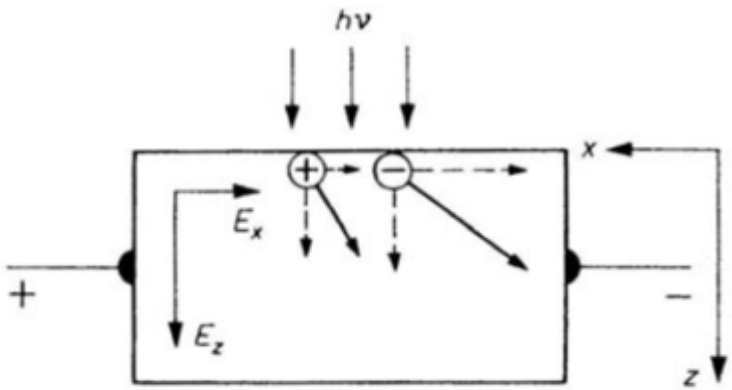






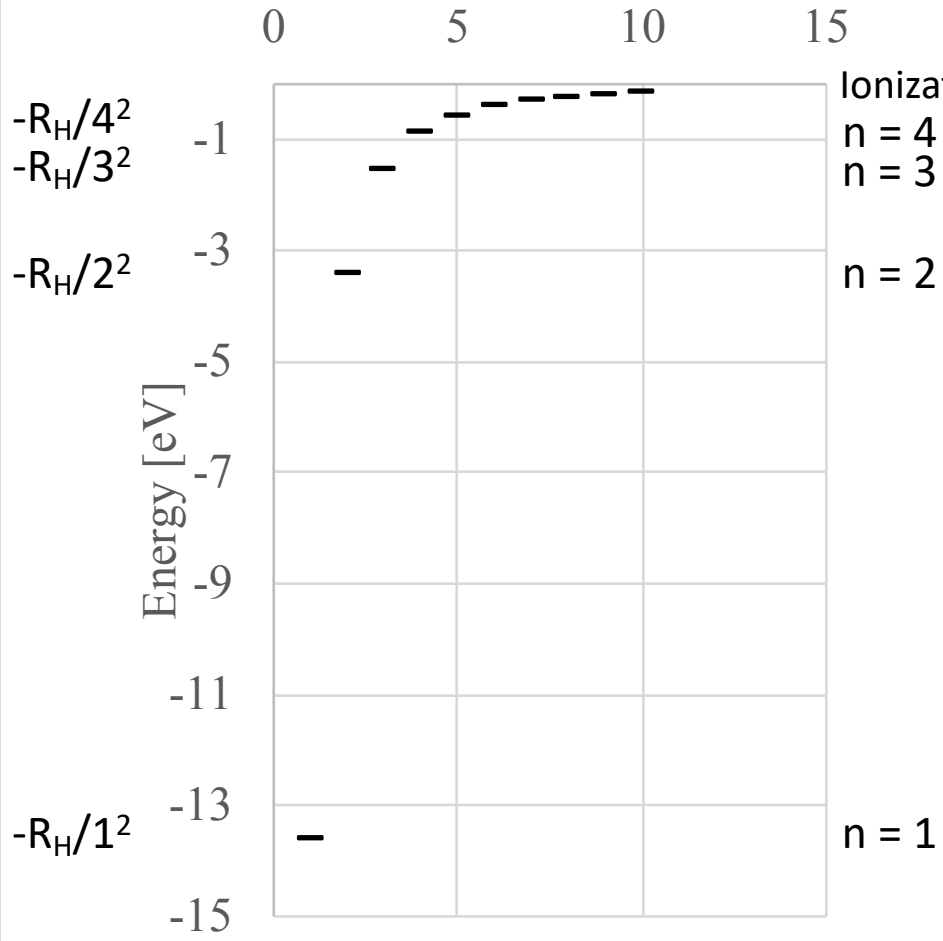


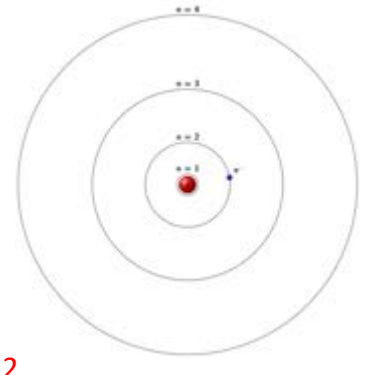
# 2. Bohr model for the hydrogen atom

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}, \quad n = 1, 2, 3 \ldots$$

Niels Bohr
1885- 1962




Ionization: E = 0 for n = infinite



Energy varies with $1/n^2$

$$E_n = -\frac{R_H}{n^2}$$

Minimum energy = -13.6 eV

$R_H = 2.179 \cdot 10^{-18}$ J = 13.6 eV
Rydberg constant

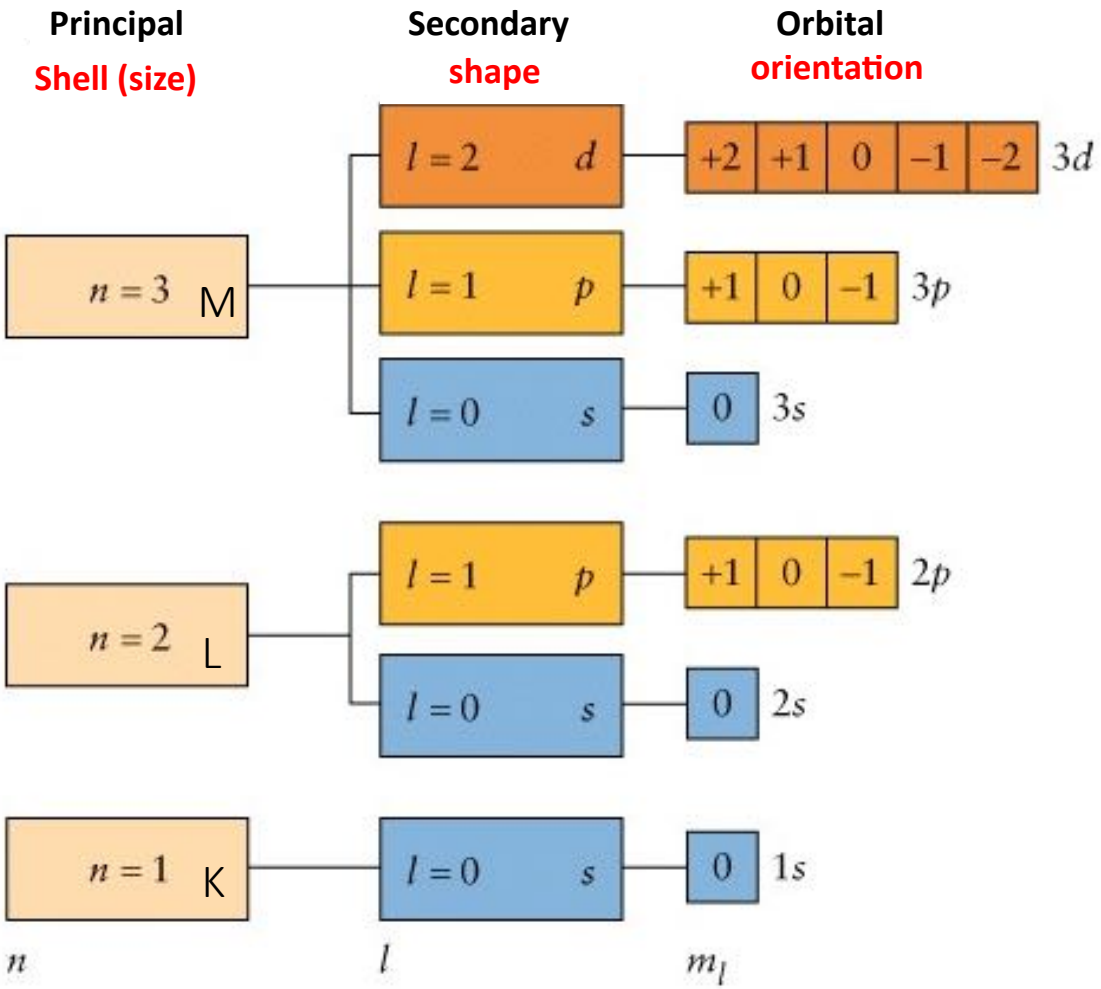
# 2.1. Quantum mechanical model of the atom

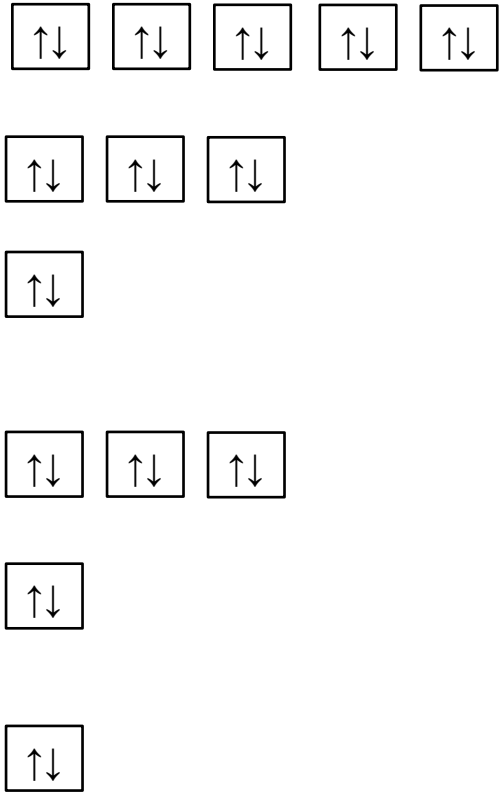
$$\hat{H}\,\psi(r,t) = E\,\psi(r,t)$$

(Ψ = Wave function)

Erwin Schrödinger (1926)

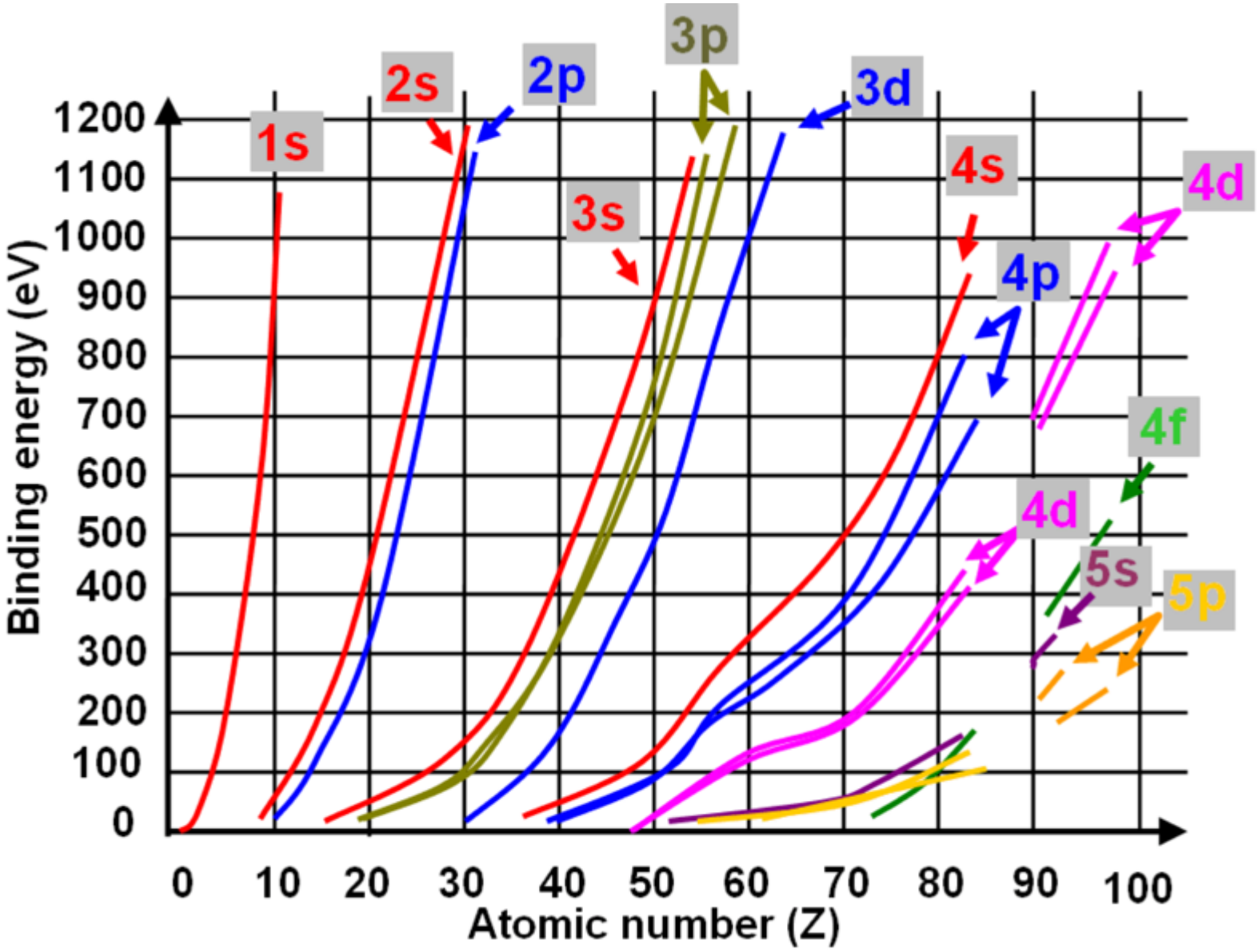
Number of electrons: $2n^2$



Spin $m_s$: ±1/2

# 2.2. Electron binding energy

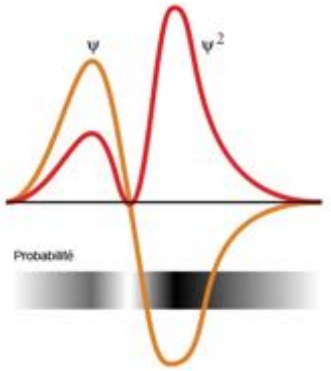



Ref: https://www.globalsino.com/EM/page3959.html

# 2.3. Geometrical representation of the orbitals

Interpretation of Ψ:
$\Psi^2(x)$ electron presence probability density

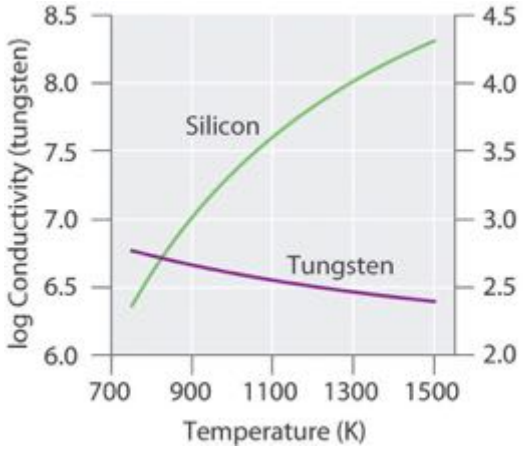
$$P = \int_{x_1}^{x_2} |\Psi(x)|^2 dx$$

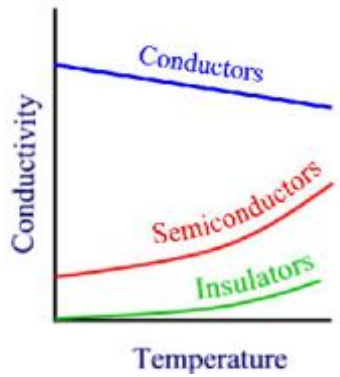


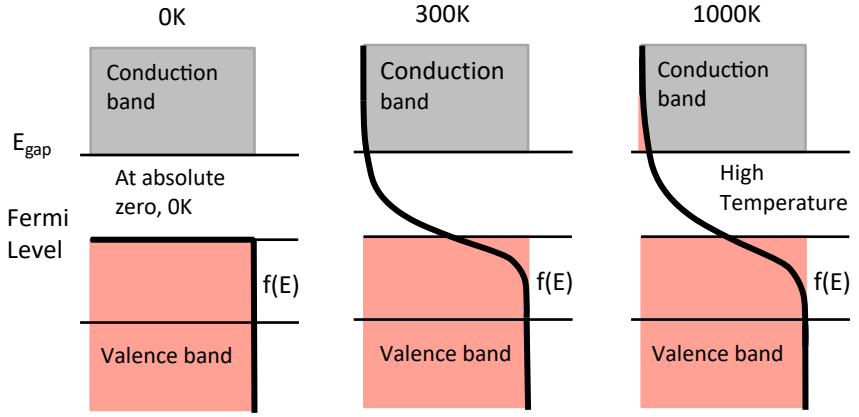

| | s (l=0) | p (l=1) | | | d (l=2) | | | | | f (l=3) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | m=0 | m=0 | m=±1 | | m=0 | m=±1 | | m=±2 | | m=0 | m=±1 | | m=±2 | | m=±3 | |
| | s | $p_z$ | $p_x$ | $p_y$ | $d_{z^2}$ | $d_{xz}$ | $d_{yz}$ | $d_{xy}$ | $d_{x^2-y^2}$ | $f_{z^3}$ | $f_{xz^2}$ | $f_{yz^2}$ | $f_{xyz}$ | $f_{z(x^2-y^2)}$ | $f_{x(x^2-3y^2)}$ | $f_{y(3x^2-y^2)}$ |
| n=1 | | | | | | | | | | | | | | | | |
| n=2 | | | | | | | | | | | | | | | | |
| n=3 | | | | | | | | | | | | | | | | |
| n=4 | | | | | | | | | | | | | | | | |
| n=5 | | | | | | | | | | ... | ... | ... | ... | ... | ... | ... |
| n=6 | | | | | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| n=7 | | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |

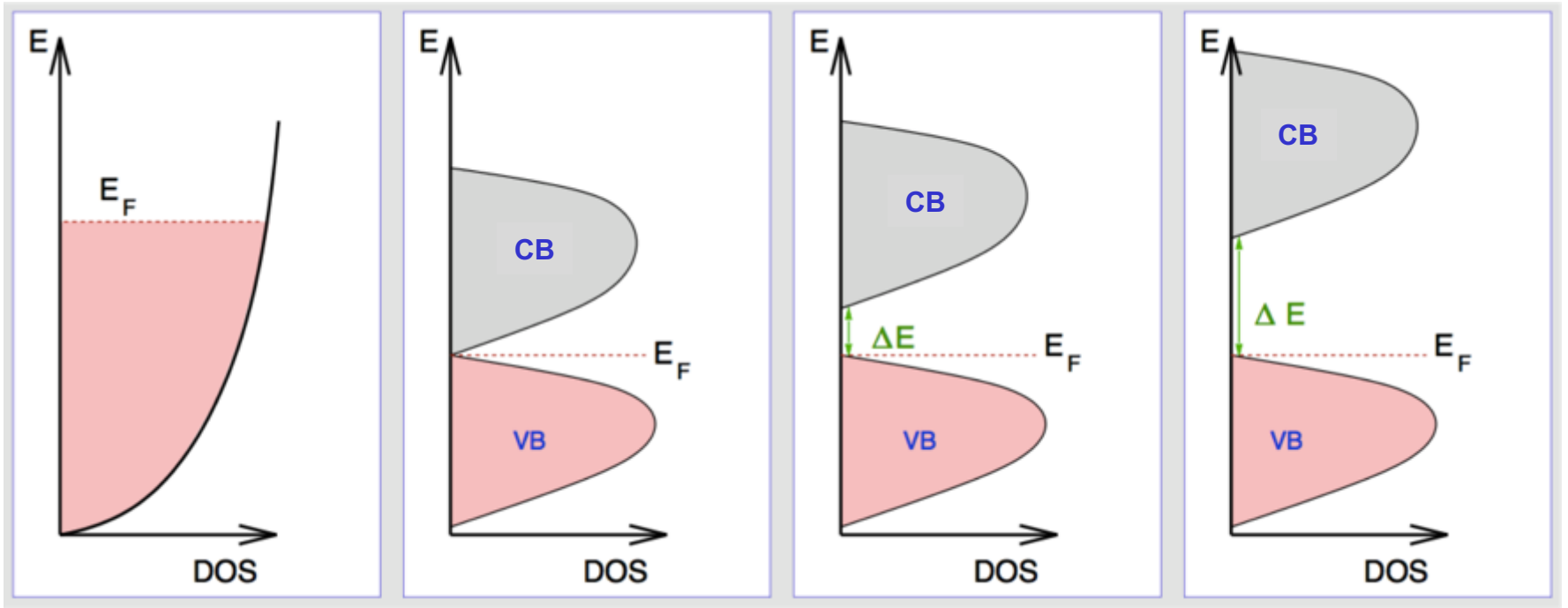
| $n$ | $l$ | $m_l$ | $m_s$ |
|---|---|---|---|
| *principal* | *secondaire* | *magnétique* | *spin* |
| $n \geq 1$ | $0 \leq l \leq n-1$ | $-l \leq m_l \leq l$ | $\pm\frac{1}{2}$ |

# 2.4. Electrons in solids



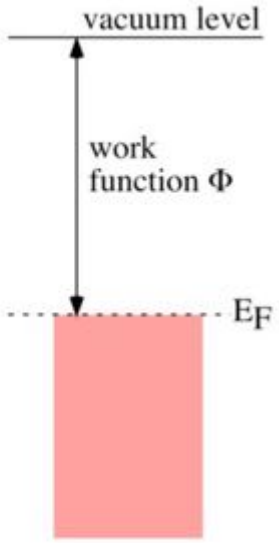



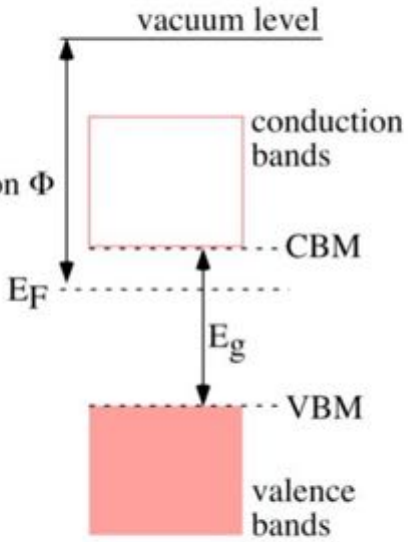

Metal | Half metal | Semiconductor | Insulator

# 3. Photoemmission

## Photoemission energy levels

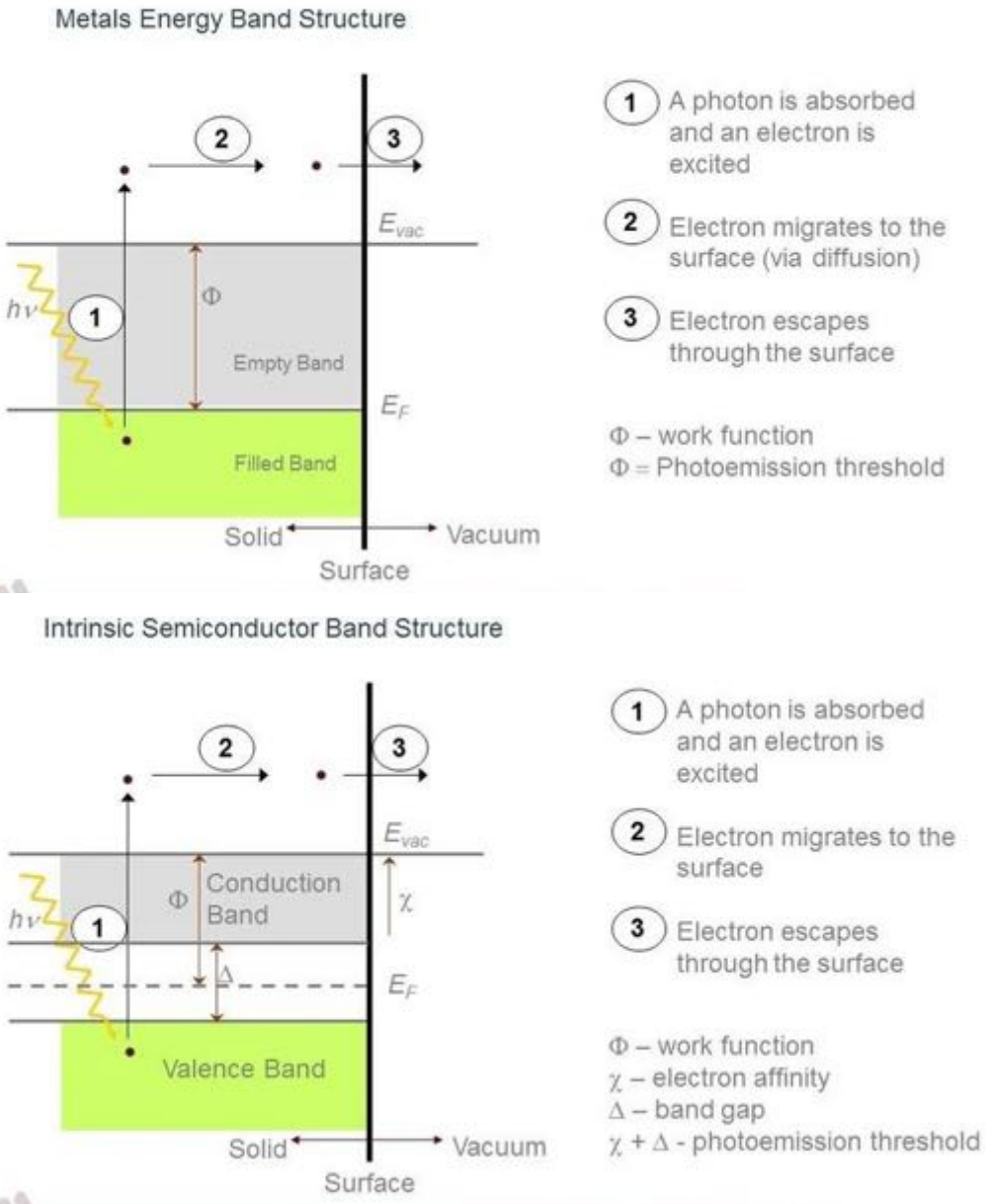



**Metal**

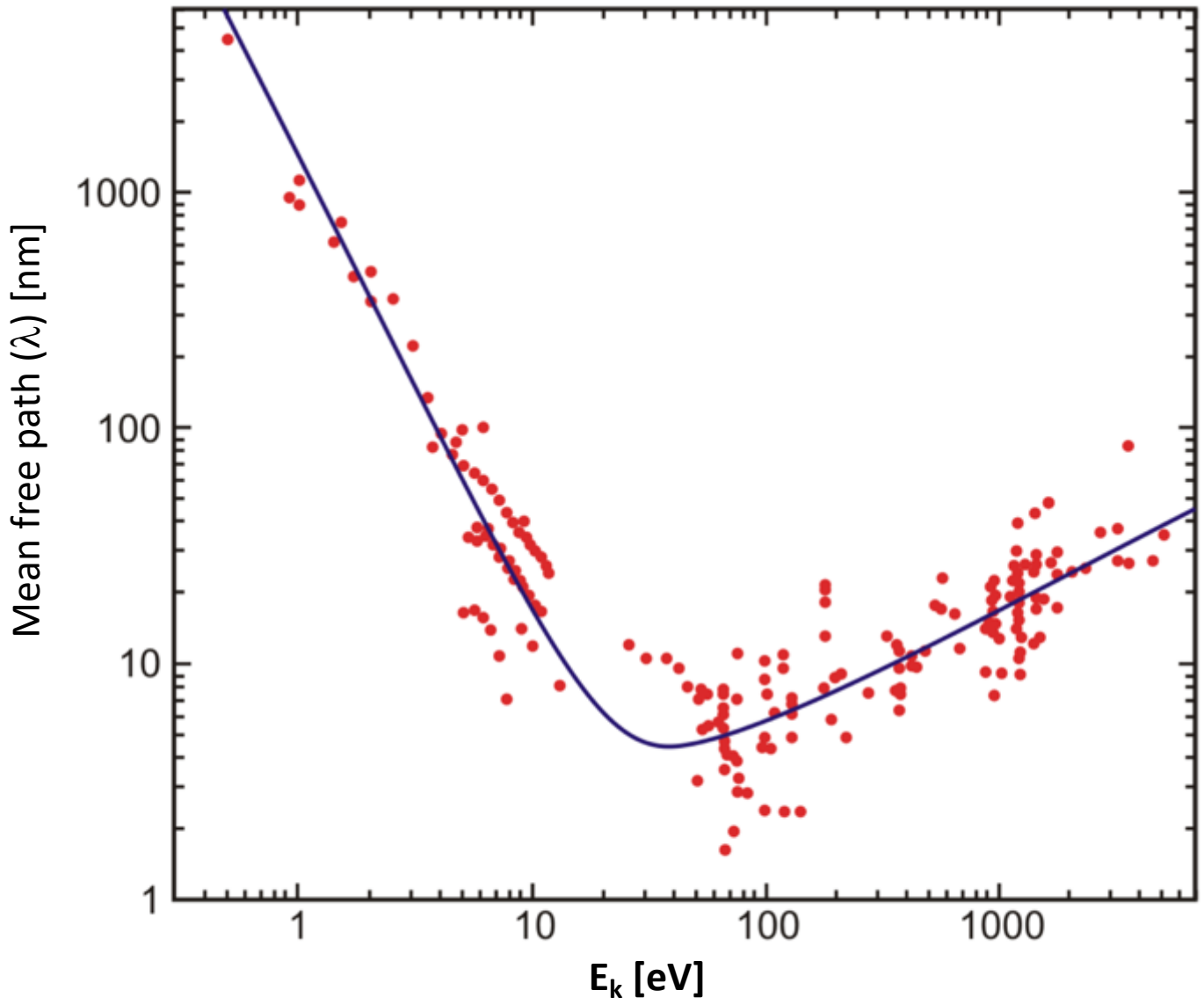



**Semi-conductor**

## Photoemission process – Spicer's 3-step model



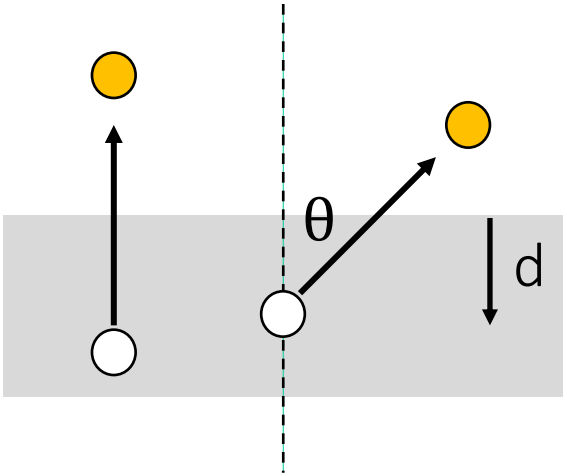
# 3.1. Mean free path of electrons in solids

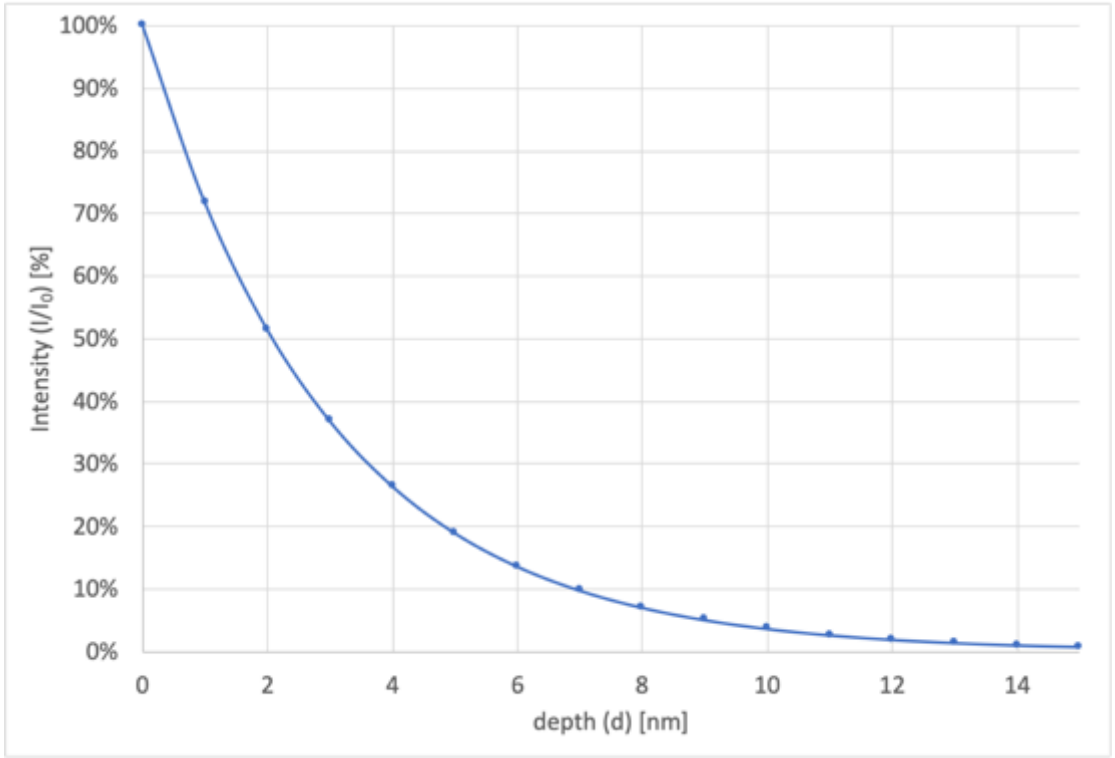



Ref.: Ch. Kittel, Einführung in die Festkörperphysik, Oldenbourg , 1999.

# 3.2. Electron intensity vs. depth

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




Ref.: Ch. Kittel, Einführung in die Festkörperphysik, Oldenbourg , 1999.

# 3.3. Total angular momentum j

| L | symbol | J |
|---|---|---|
| 0 | s | no splitting |
| 1 | p | 1/2, 3/2 |
| 2 | d | 3/2, 5/2 |
| 3 | f | 5/2, 7/2 |

L = orbital angular momentum quantum number

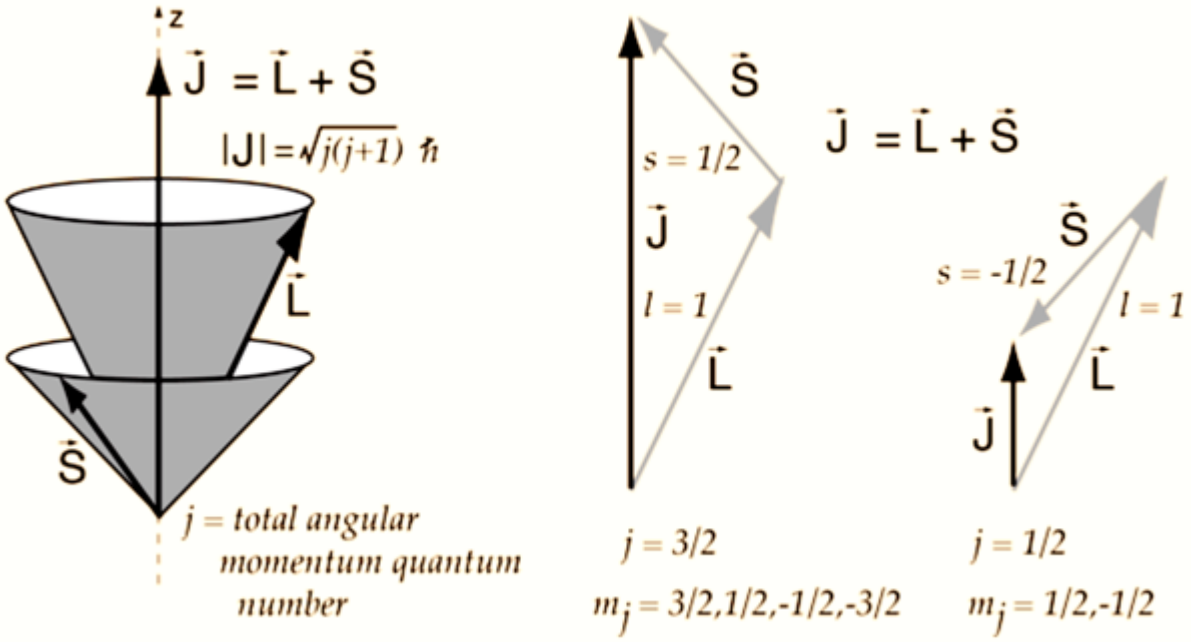
**2p½**

J = total angular momentum quantum number

J = L + S = l ± ½

S = spin quantum number (-½ or +½)

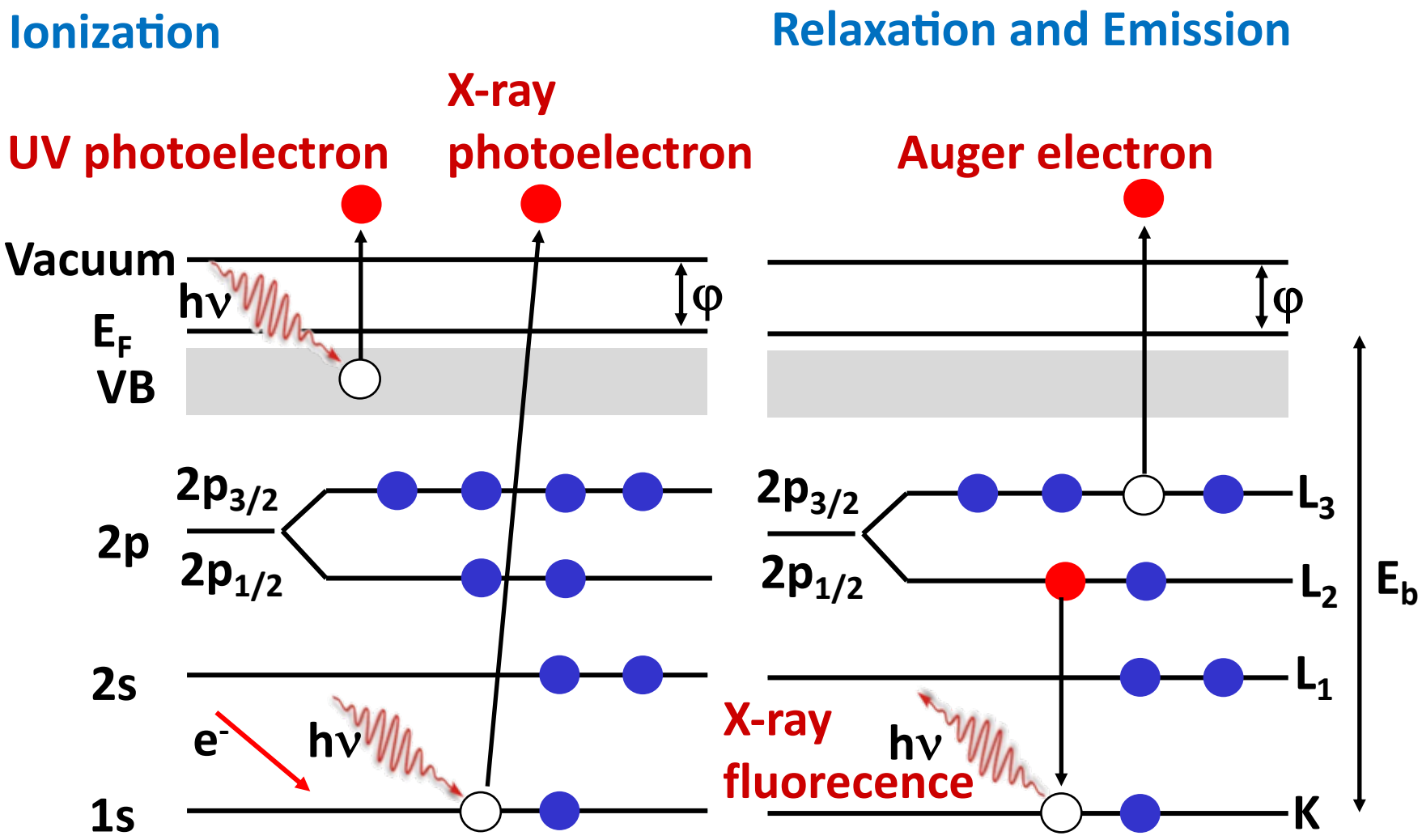
n = principal quantum number (1, 2, 3 .....




When orbital angular momentum L and electron spin angular momentum S are combined to produce the total angular momentum of an atomic electron, the combination process can be visualized in terms of a vector model. Both the orbital and spin angular momentum are seen as precessing about the direction of the total angular momentum J.

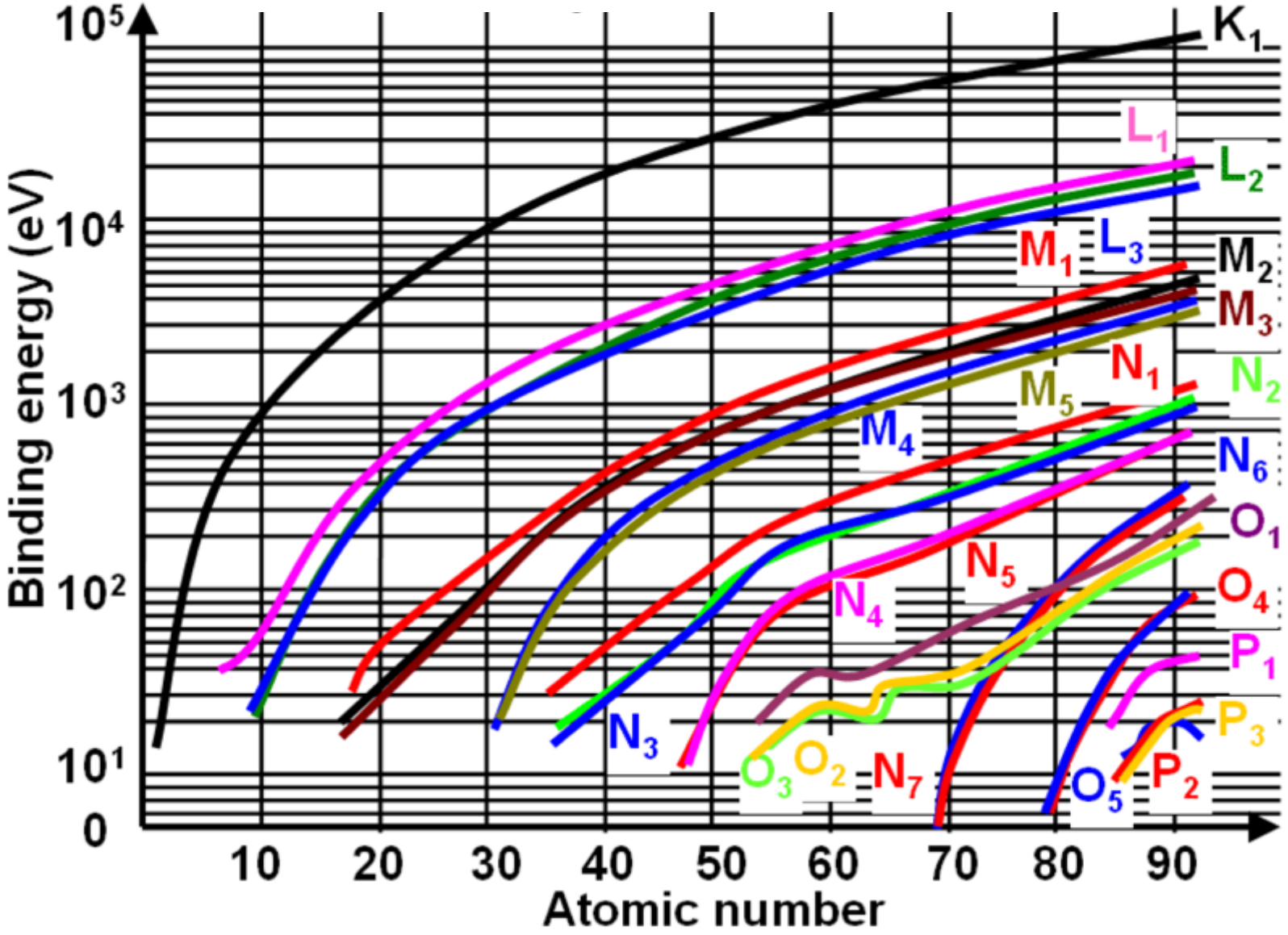
Ref: http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/vecmod.html#c2

# 3.4. Electron emission




Ref: http://www.xpsfitting.com/2009/03/auger-process-and-notation.html, https://ywcmatsci.yale.edu/principle

# 3.5. Electron binding energy




Ref: https://www.globalsino.com/EM/page3959.html

# Question

1) Compare the number of collisions of gas molecules per unit area with the number of surface atoms in the same area?

2) What is the mean free path of an electron in air?

# Answer

## 1) Compare the number of collisions of gas molecules per unit area with the number of surface atoms in the same area?

Calculate the collision frequency per unit area ($Z_w$) for oxygen at 25.0°C and 1.00 bar using equation 27.4.1:

$$z_w = \frac{1}{4}\frac{N}{V}\langle v \rangle$$

**Solution**

N molecules = $N_A$ x $n$, so that

$$\frac{N}{V} = \frac{(N_A)\cdot n}{V} = \frac{(N_A)\cdot P}{R\cdot T}$$

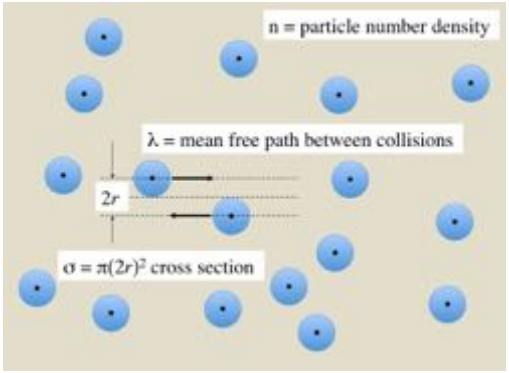
$$\frac{(6.022x10^{23}\ mole^{-1})(1.00\ bar)}{(0.08319\ L\cdot bar\cdot mole^{-1}\cdot K^{-1})(298\ K)} = 2.43\times 10^{22}\ L^{-1} = 2.43\times 10^{25}\ m^{-3}$$

and

$$\langle v \rangle = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8(8.314J\cdot K^{-1}\cdot mol^{-1})(298K)}{\pi\cdot(0.031999\ kg)}\right)^{\frac{1}{2}} = 444\ m\cdot s^{-1}$$

Thus

$$z_w = \frac{1}{4}(2.43\times 10^{25}m^{-3})(444\ m\cdot s^{-1})\left(\frac{1\ m}{100\ cm}\right)^2 = 2.70\times 10^{23}s^{-1}\cdot cm^{-2}$$




surface atoms = $(\rho/M)^{2/3}$
= $2\cdot10^{19}$ atoms/m$^2$ = $2\cdot10^{15}$ atoms/m$^2$

## 2) What is the mean free path (λ) of an electron in air?

The mean free path is $\lambda \approx \frac{1}{n\sigma}$

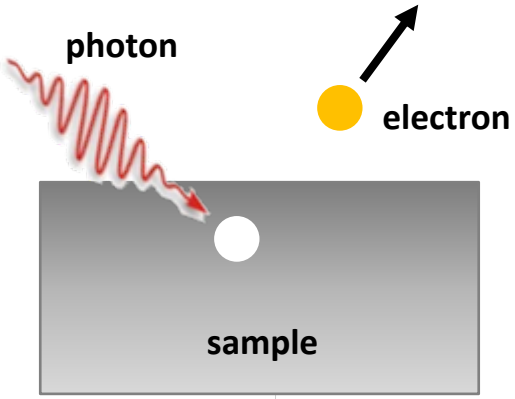
where n is the number density and σ is the collision cross section. $\sigma = \pi(r_{el} + r_{molecule})^2$

$$n = \frac{N}{V} = \frac{P}{k_b T} = 2.45\times 10^{25}\ \mathrm{m}^{-3} \qquad \lambda = \frac{1}{2.45\cdot 10^{25}\pi 2^2 10^{-20}} \approx 3\cdot 10^{-7}\mathrm{m}$$

# 4. Electron Spectroscopy for Chemical Analysis (ESCA)

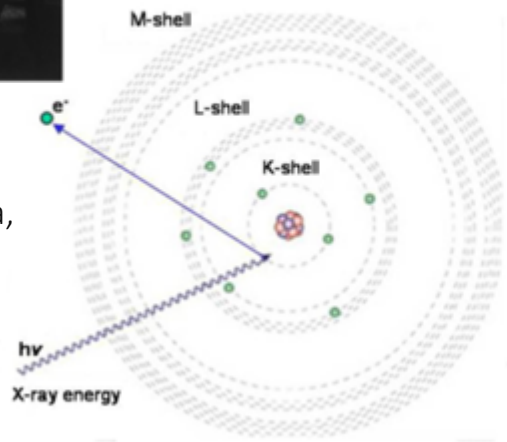
Kai and Manne Siegbahn at the first ESCA spectrometer at the Department of Physics in Uppsala, Sweden.

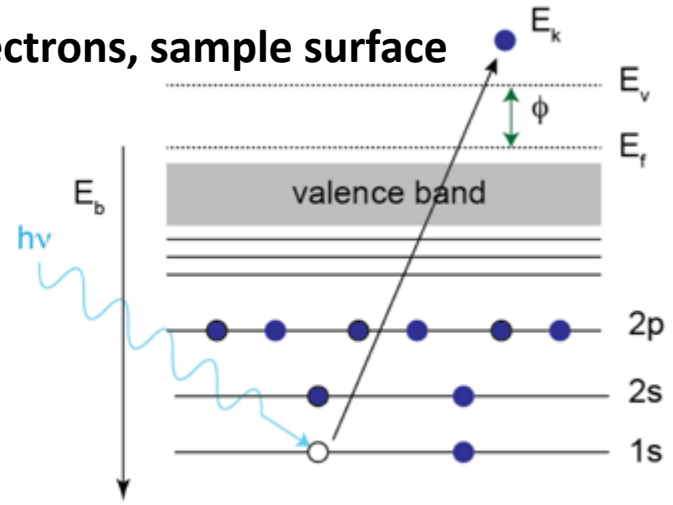
**Energy: element and chemical state**
**Intensity: concentration**
**Angle: location**




Kai Siegbahn
Noble prize 1981

**Ultra high vacuum: electrons, sample surface**

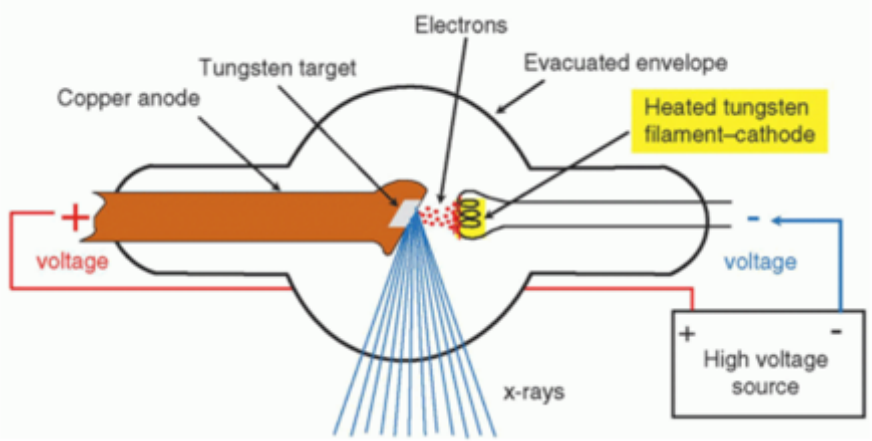


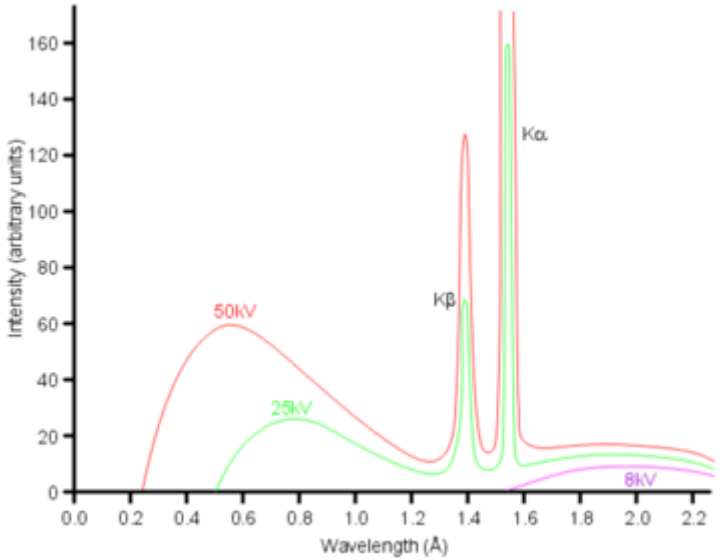

$$E_k = h\nu - E_b - \phi$$

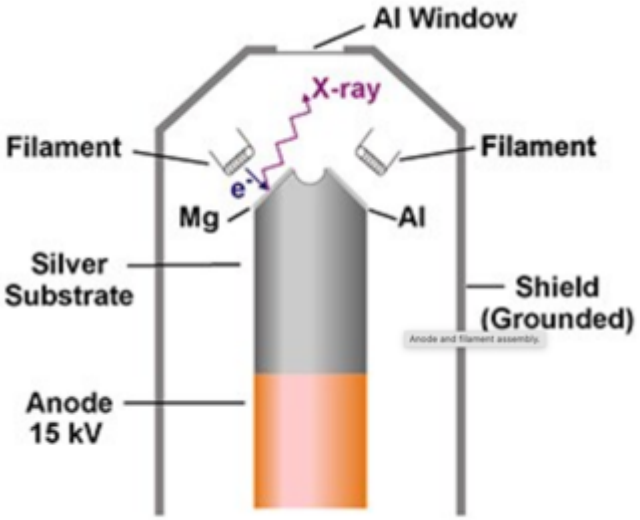
Ref: Grzegorz Greczynski, Richard T. Haasch, Niklas Hellgren, Erik Lewin & Lars Hultman , "X-ray photoelectron spectroscopy of thin films", Nat Rev Methods Primers 3, 40 (2023). https://doi.org/10.1038/s43586-023-00225-y

# 4.1. X-ray Source – X-ray anode ("lab source")




8 keV



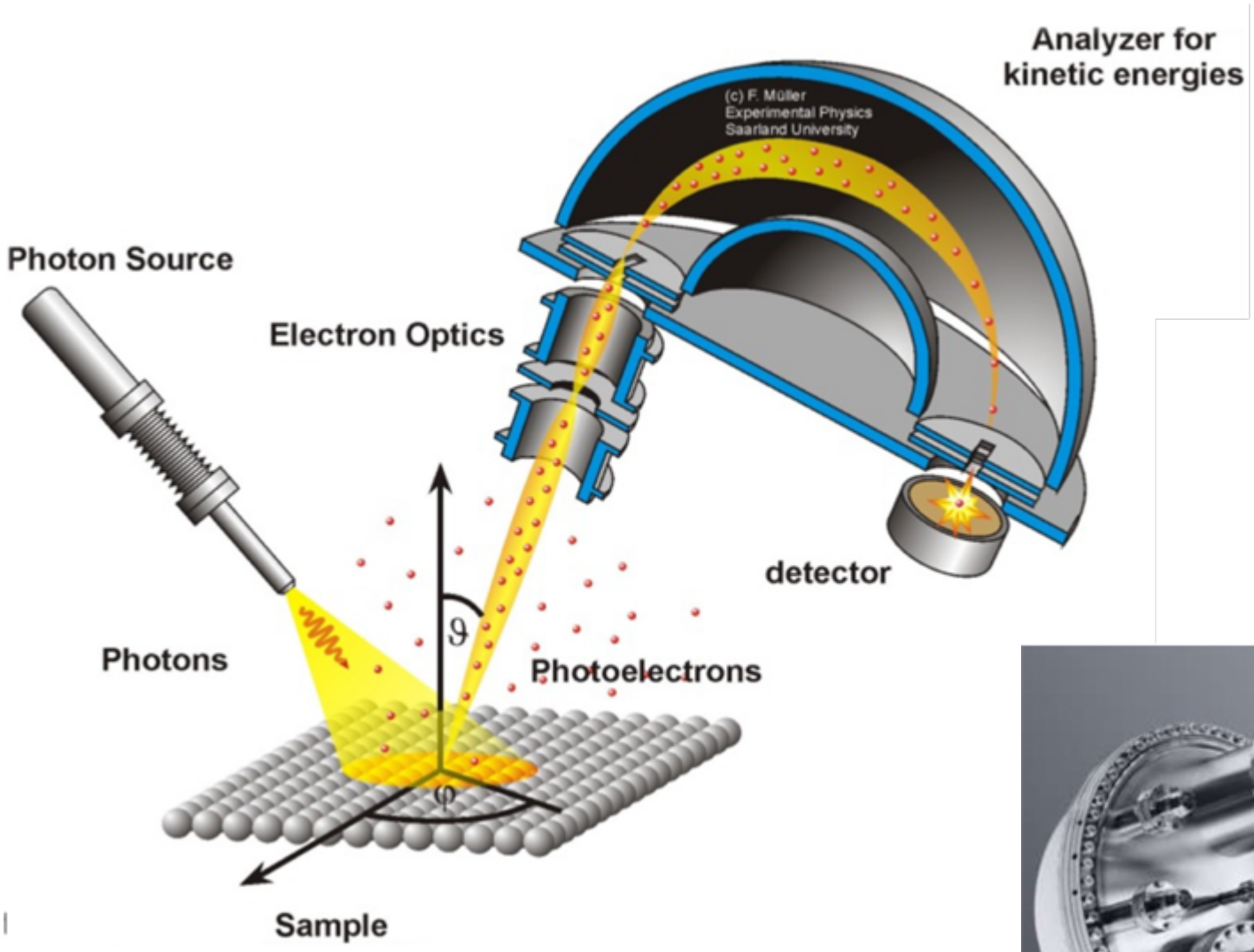

Anode and filament assembly.

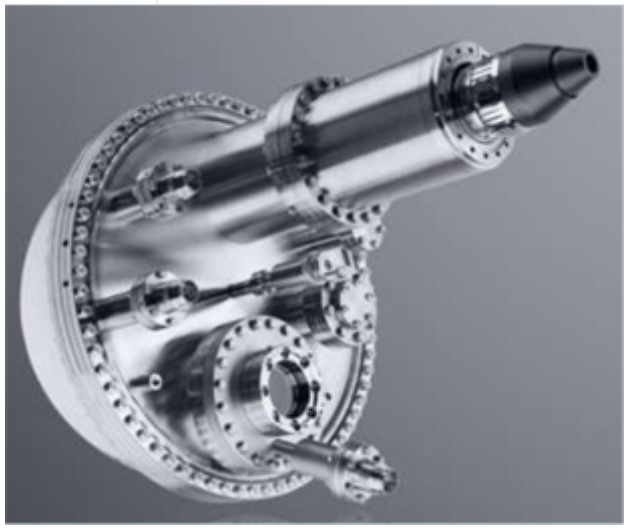
Energy and line widths of available anode materials.

| Anode | Radiation | Photon Energy [eV] | Line Width [eV] |
|---|---|---|---|
| •Mg | •Kα | •1253.6 | •0.7 |
| •Al | •Kα | •1486.6 | •0.85 |
| •Zr | •Lα | •2042.4 | •1.6 |
| •Ag | •Lα | •2984.3 | •2.6 |
| •Ti | •Kα | •4510.9 | •Cr |
| •Cr | •Kα | •5417 | •2.1 |

Ref.: https://www.thermofisher.com/it/en/home/materials-science/learning-center/surface-analysis/x-ray-generation.html; http://pd.chem.ucl.ac.uk/pdnn/inst1/xrays.htm

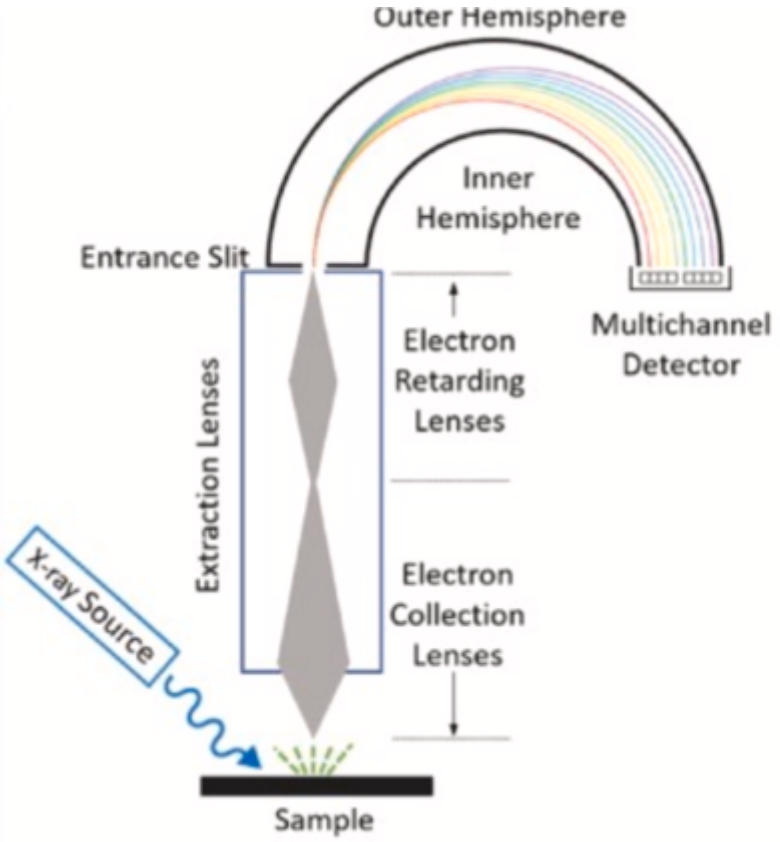
# 4.2. Detecting electrons

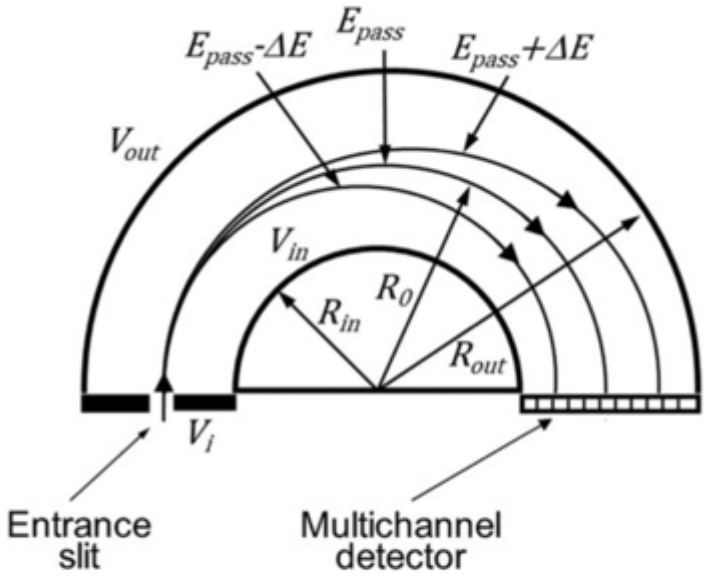


Ref.: F. Müller, Saarland University
https://www.specs-group.com

# 4.3. Hemispherical electron analyzer




$$\Delta E = E_0 \left( \frac{W}{2R} + \frac{\alpha^2}{2} \right)$$

Electrostatic lenses focus electron to the detector
Electron kinetic energy is adjusted to the same pass energy ($E_p$)
To improve resolution:

- lower pass energy
- Decrease slit width

ΔE = energy resolution
$E_0$ = electron energy
W = slit width
R = mean radius
α = acceptance angle

# 4.4. X-ray photoelectron spectroscopy (XPS)

## Sample environment:

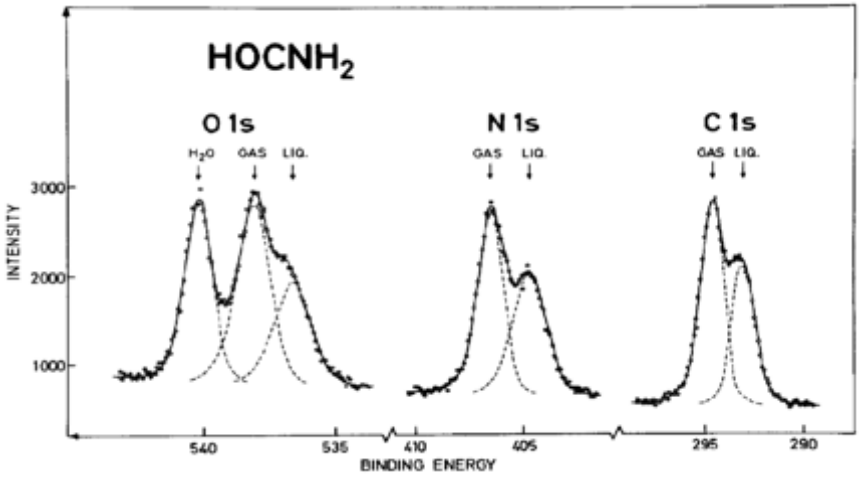
- Electrons need to travel to the detector
- Sample surface needs to remain unchanged during the analysis
- XPS needs ultra-high vacuum chamber ($10^{-8}$ - $10^{-10}$ mbar)

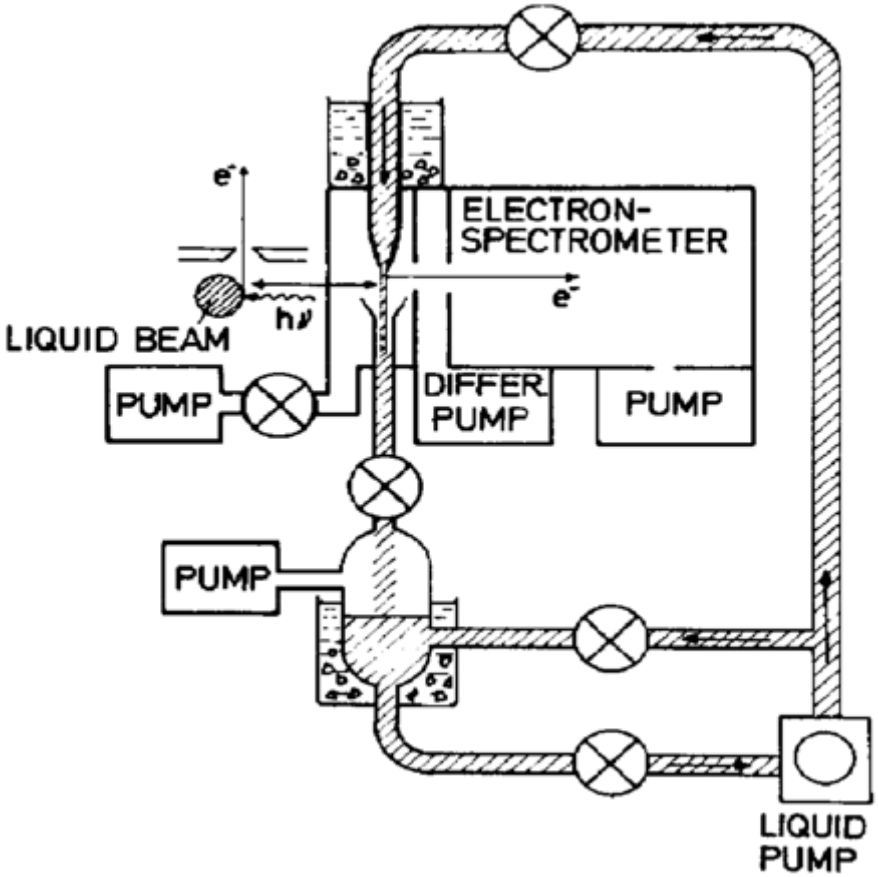
# 4.5. Near ambient pressure XPS (NAP-XPS)

## Real sample environment:

- Electrons need to travel to the detector (UHV)
- Sample surface needs to interact with gas during the analysis
- NAP-XPS needs sample chamber and ultra-high vacuum analyzer

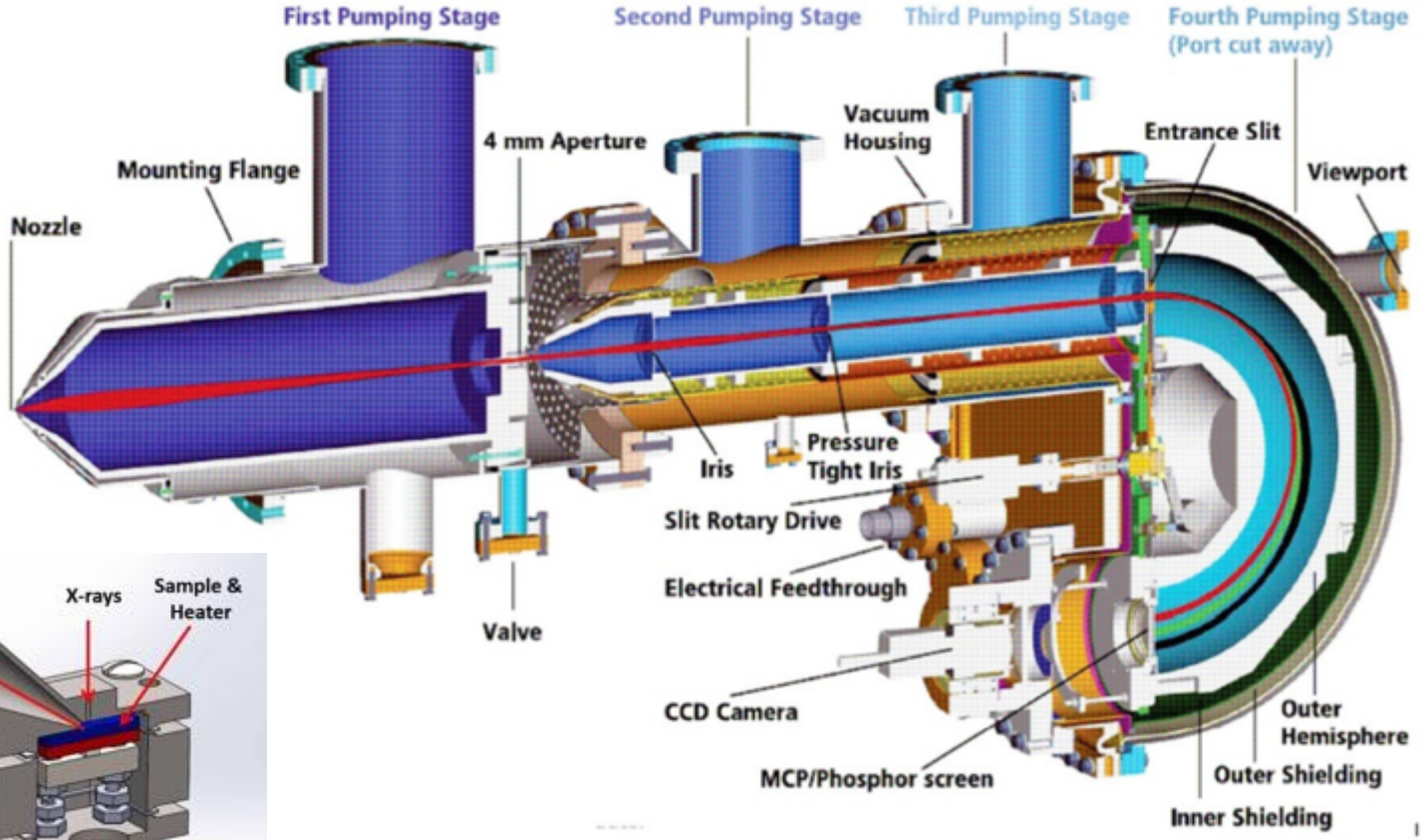
The first AP-XPS instrument was built by Kai Siegbahn's group in the 1970's

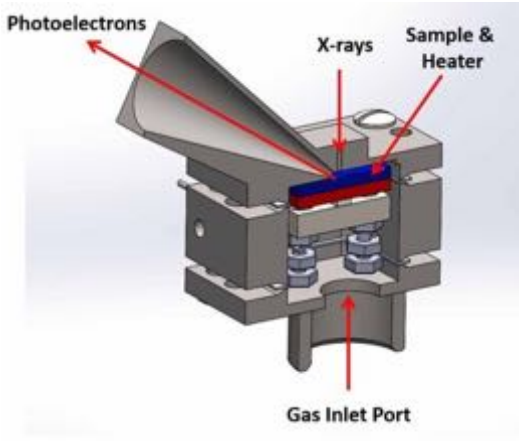



Ref.: Hans Siegbahn and Kai Siegbahn, "ESCA applied to liquids", Journal of Electron Spectroscopy and Related Phenomena, 2:3 (1973), pp. 319- 325

# 4.6. NAP-XPS analyzer

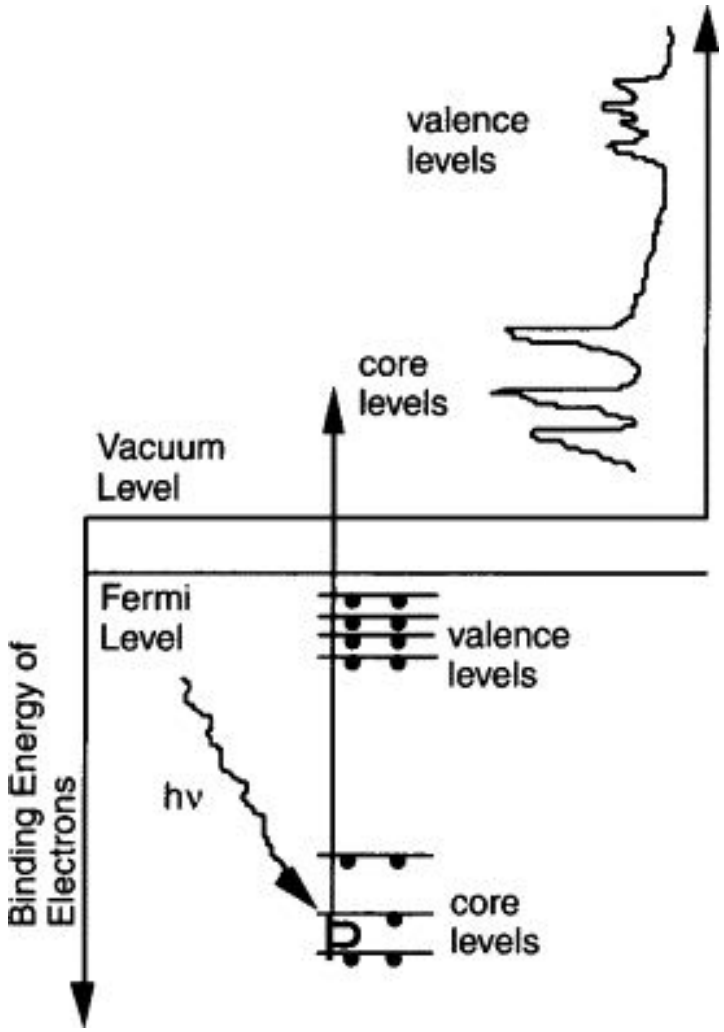



Ref.: Perez-Dieste, V. & Aballe, Lucia & Salvador, Ferrer & Nicolas, Josep & Escudero, Carlos & Milán, A & Pellegrin, Eric. (2013). Near ambient pressure XPS at ALBA. Journal of Physics: Conference Series. 425. 072023. 10.1088/1742-6596/425/7/072023.

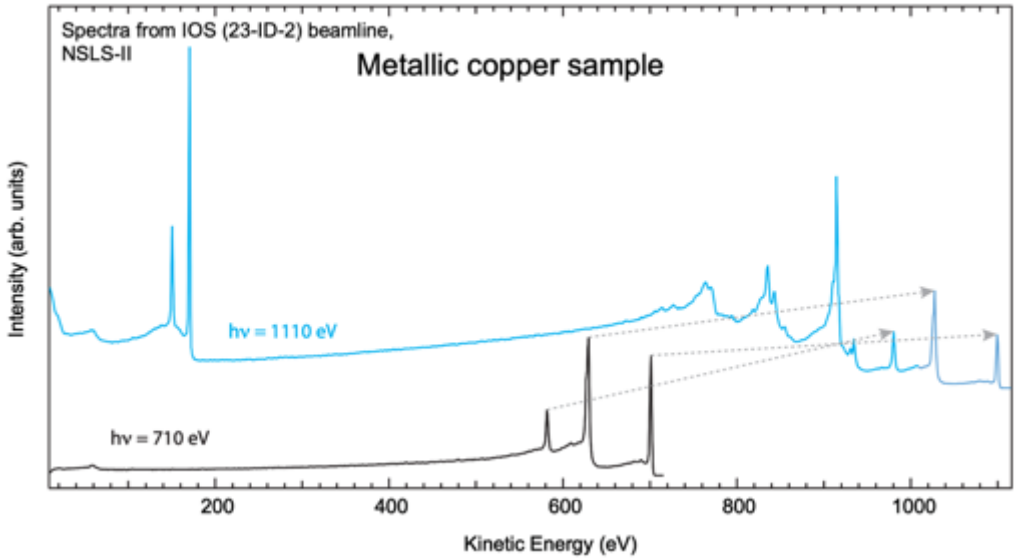
Tomáš Hrbek, Peter Kúš, Miquel Gamón Rodríguez, Vladimír Matolín, Iva Matolínová, "Operando X-ray photoelectron spectroscopy cell for water electrolysis: A complete picture of iridium electronic structure during oxygen evolution reaction", International Journal of Hydrogen Energy, 57, 29 February 2024, Pages 187-197

# 5. Spectroscopy



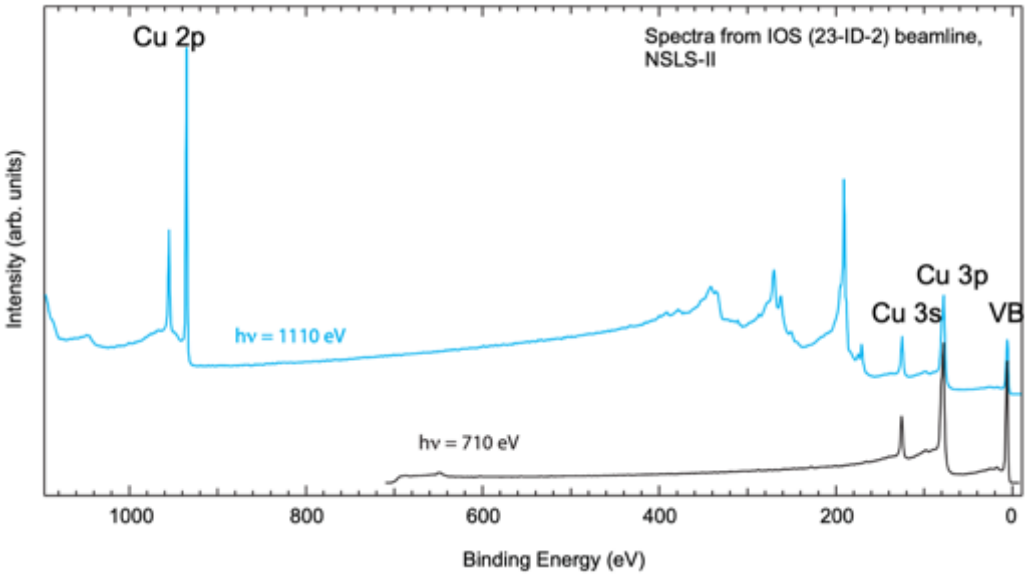

Ref.:
https://www.bnl.gov/nsls2/userguide/lectures/lecture-6-waluyo.pdf

## Measurement: Intensity vs. kin. energy




## Calculation: Intensity vs. binding energy

$$E_b = h\nu - E_k - \phi$$

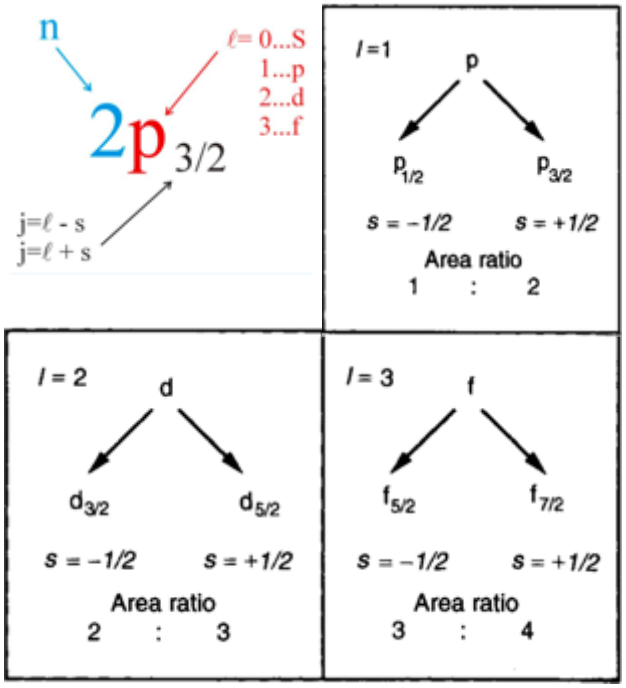


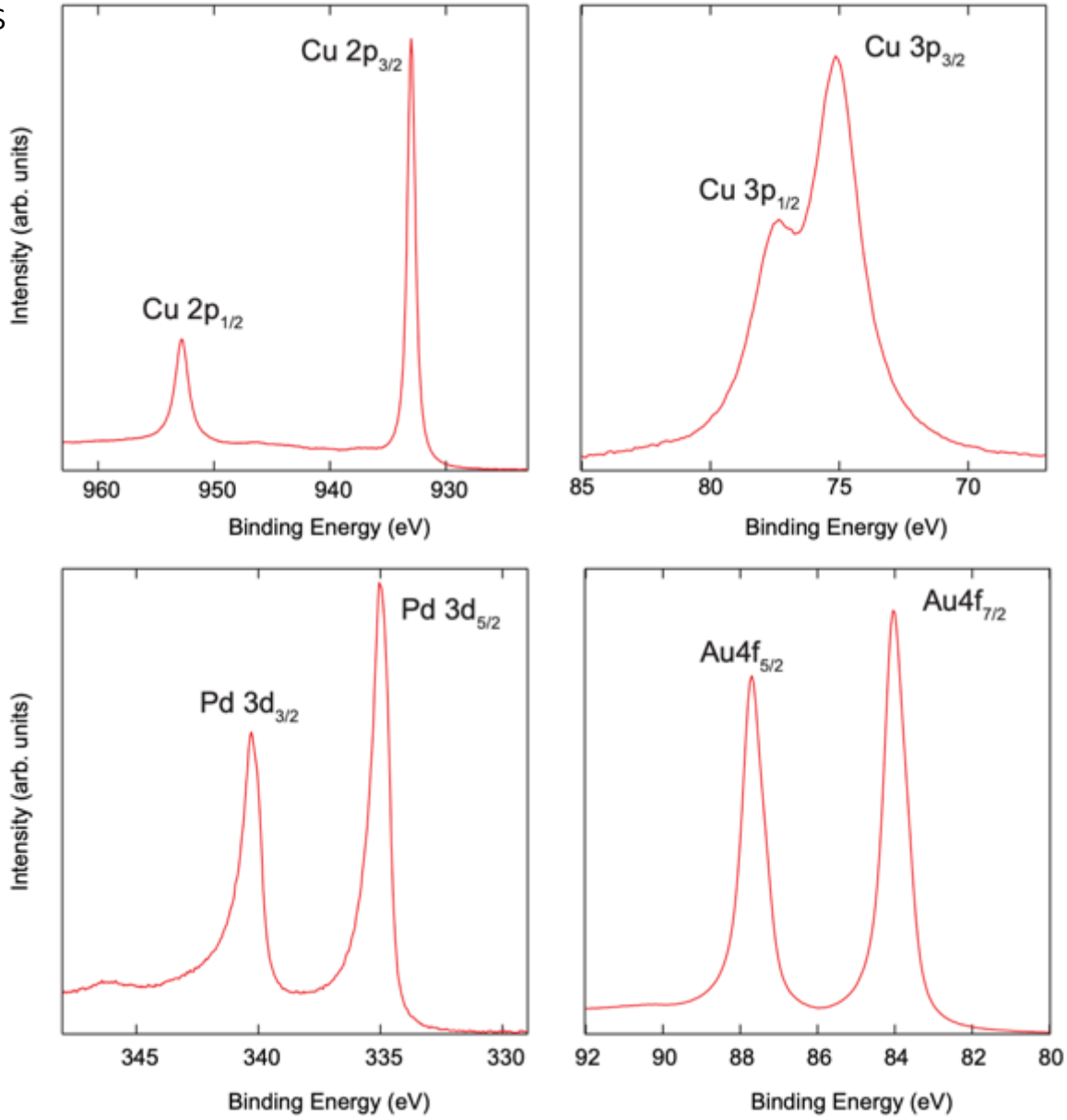
# 5.1. Spin-Orbit peak splitting

Doublets (two peaks) are always observed for p, d, f orbitals

l-s coupling: j = l + s

s = ± ½

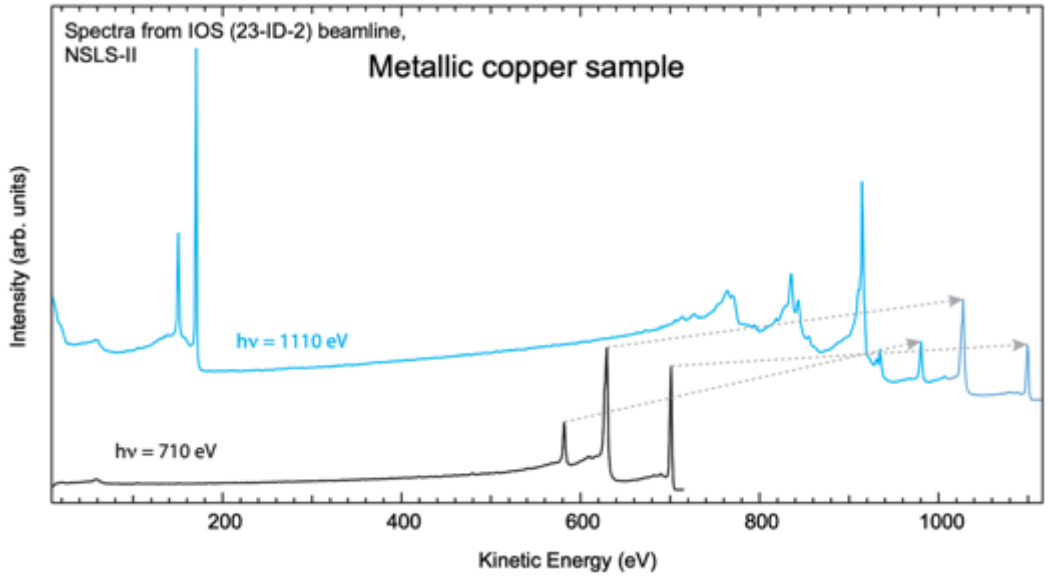



Ref.:
http://www.cityu.edu.hk/phy/appkchu/a
ecture-11-XPS.pdf

# 5.2. Auger peaks

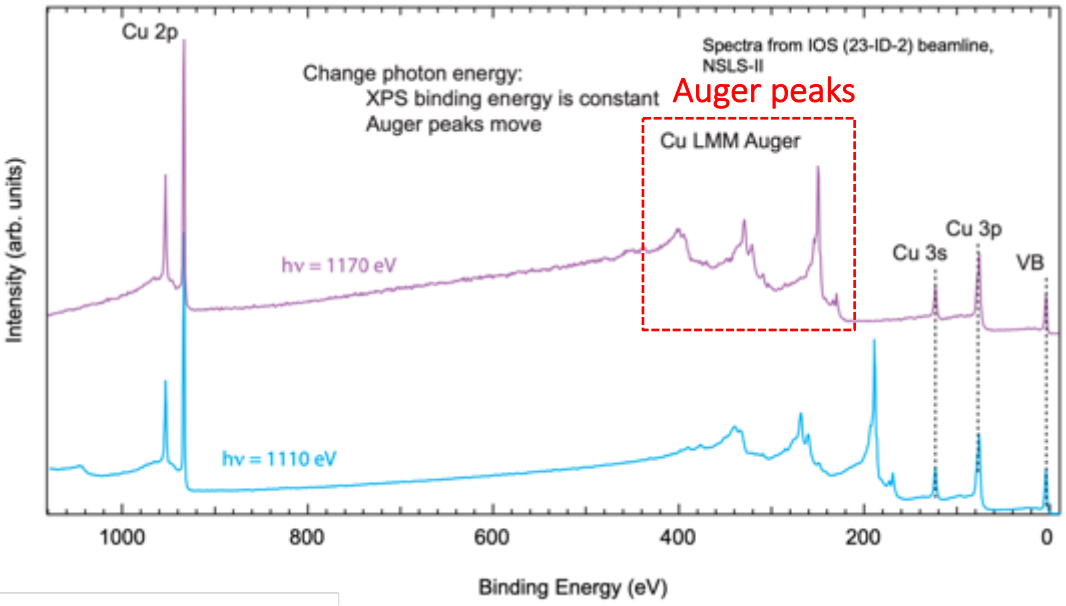
## Measurement: Intensity vs. kin. energy




| Quantum Numbers | | | Level Symbol | Auger Notation | XPS Notation |
|---|---|---|---|---|---|
| $n$ | $\ell$ | $j$ | | | |
| 1 | 0 | 1/2 | $^2S_{1/2}$ | K | $1s_{1/2}$ |
| 2 | 0 | 1/2 | $^2S_{1/2}$ | $L_1$ | $2s_{1/2}$ |
| 2 | 1 | 1/2 | $^2P_{1/2}$ | $L_2$ | $2p_{1/2}$ |
| 2 | 1 | 3/2 | $^2P_{3/2}$ | $L_3$ | $2p_{3/2}$ |
| 3 | 0 | 1/2 | $^2S_{1/2}$ | $M_1$ | $3s_{1/2}$ |
| 3 | 1 | 1/2 | $^2P_{1/2}$ | $M_2$ | $3p_{1/2}$ |
| 3 | 1 | 3/2 | $^2P_{3/2}$ | $M_3$ | $3p_{3/2}$ |
| 3 | 2 | 3/2 | $^2D_{3/2}$ | $M_4$ | $3d_{3/2}$ |
| 3 | 2 | 5/2 | $^2D_{5/2}$ | $M_5$ | $3d_{5/2}$ |

Ref.:
https://www.bnl.gov/nsls2/userguide/lectures/lecture-6-waluyo.pdf

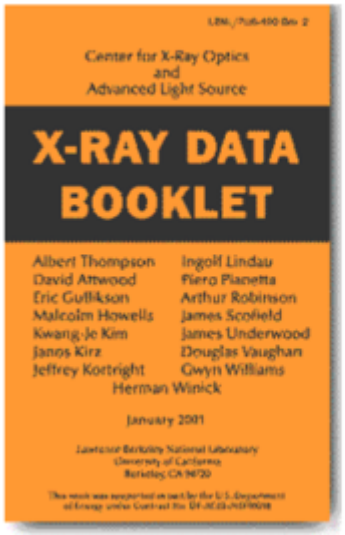
## Intensity vs. binding energy



# 5.3. Electron binding energy

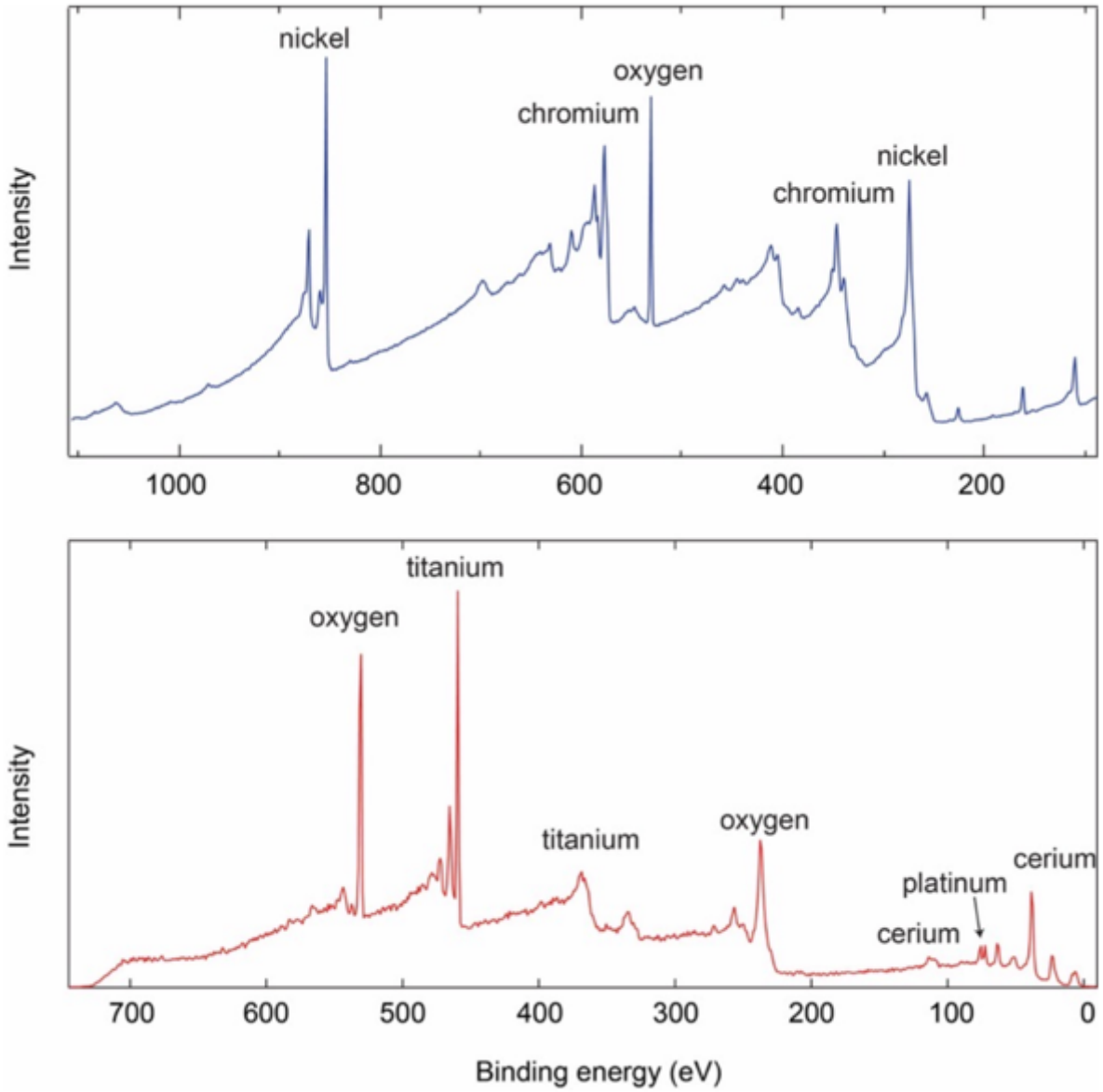
***Table 1-1.*** *Electron binding energies, in electron volts, for the elements in their natural forms.*

| Element | K 1s | $L_1$ 2s | $L_2$ $2p_{1/2}$ | $L_3$ $2p_{3/2}$ | $M_1$ 3s | $M_2$ $3p_{1/2}$ | $M_3$ $3p_{3/2}$ | $M_4$ $3d_{3/2}$ | $M_5$ $3d_{5/2}$ | $N_1$ 4s | $N_2$ $4p_{1/2}$ | $N_3$ $4p_{3/2}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H | 13.6 | | | | | | | | | | | |
| 2 He | 24.6* | | | | | | | | | | | |
| 3 Li | 54.7* | | | | | | | | | | | |
| 4 Be | 111.5* | | | | | | | | | | | |
| 5 B | 188* | | | | | | | | | | | |
| 6 C | 284.2* | | | | | | | | | | | |
| 7 N | 409.9* | 37.3* | | | | | | | | | | |
| 8 O | 543.1* | 41.6* | | | | | | | | | | |
| 9 F | 696.7* | | | | | | | | | | | |
| 10 Ne | 870.2* | 48.5* | 21.7* | 21.6* | | | | | | | | |
| 11 Na | 1070.8† | 63.5† | 30.65 | 30.81 | | | | | | | | |
| 12 Mg | 1303.0† | 88.7 | 49.78 | 49.50 | | | | | | | | |
| 13 Al | 1559.6 | 117.8 | 72.95 | 72.55 | | | | | | | | |
| 14 Si | 1839 | 149.7*b | 99.82 | 99.42 | | | | | | | | |
| 15 P | 2145.5 | 189* | 136* | 135* | | | | | | | | |
| 16 S | 2472 | 230.9 | 163.6* | 162.5* | | | | | | | | |
| 17 Cl | 2822.4 | 270* | 202* | 200* | | | | | | | | |
| 18 Ar | 3205.9* | 326.3* | 250.6† | 248.4* | 29.3* | 15.9* | 15.7* | | | | | |
| 19 K | 3608.4* | 378.6* | 297.3* | 294.6* | 34.8* | 18.3* | 18.3* | | | | | |
| 20 Ca | 4038.5* | 438.4† | 349.7† | 346.2† | 44.3 † | 25.4† | 25.4† | | | | | |
| 21 Sc | 4492 | 498.0* | 403.6* | 398.7* | 51.1* | 28.3* | 28.3* | | | | | |
| 22 Ti | 4966 | 560.9† | 460.2† | 453.8† | 58.7† | 32.6† | 32.6† | | | | | |




Ref.: https://xdb.lbl.gov/Section1/Table_1-1.pdf
From X-ray Data Booklet: https://xdb.lbl.gov

# 5.4. Elemental analysis

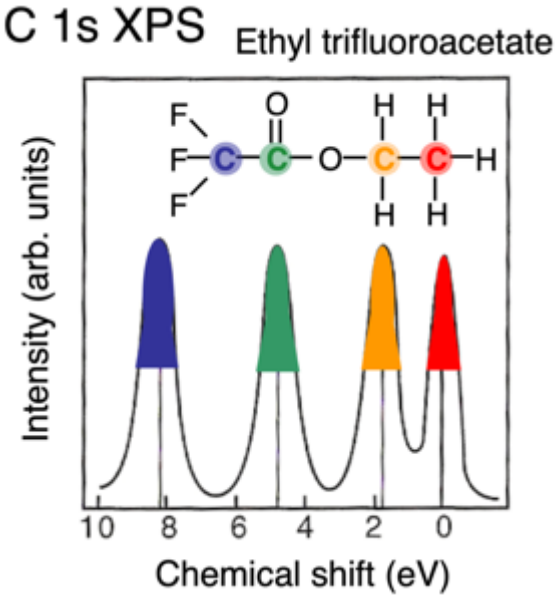



**Nickel-Chromium alloy**
– corrosion resistant material

**$Pt/CeO_2/TiO_2$**
catalyst for methanol production

Ref.: Spectra from IOS (23-ID-2) beamline, NSLS-II

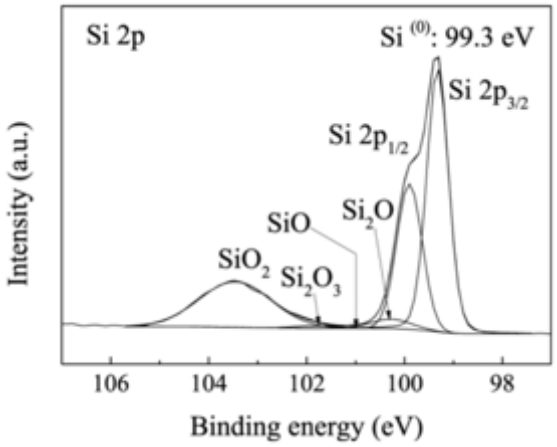
# 5.5. Chemical analysis

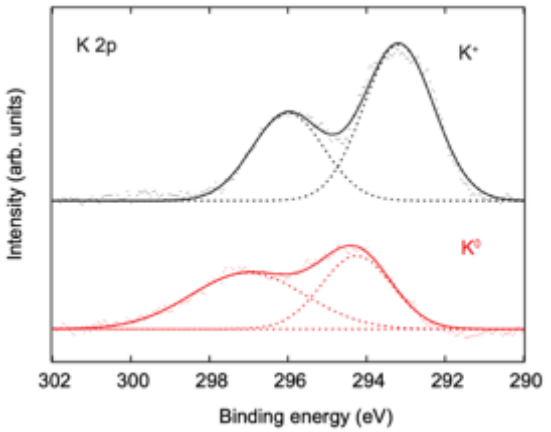



**Binding energy of an electron is affected by the chemical environment of the atom**

- Energy shift can be up to 10 eV
- This makes XPS a powerful tool for chemical analysis
- You can tell the chemical bonding of the probed atom
- Bonding to a more electronegative atom a shift to higher binding energy

In general, higher oxidation state causes a shift to higher binding energy, but... alkali metals behave the opposite way

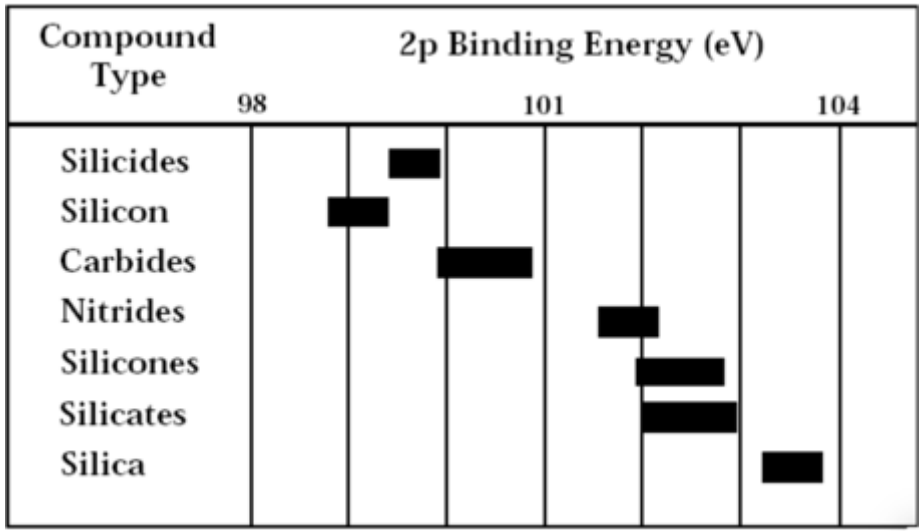


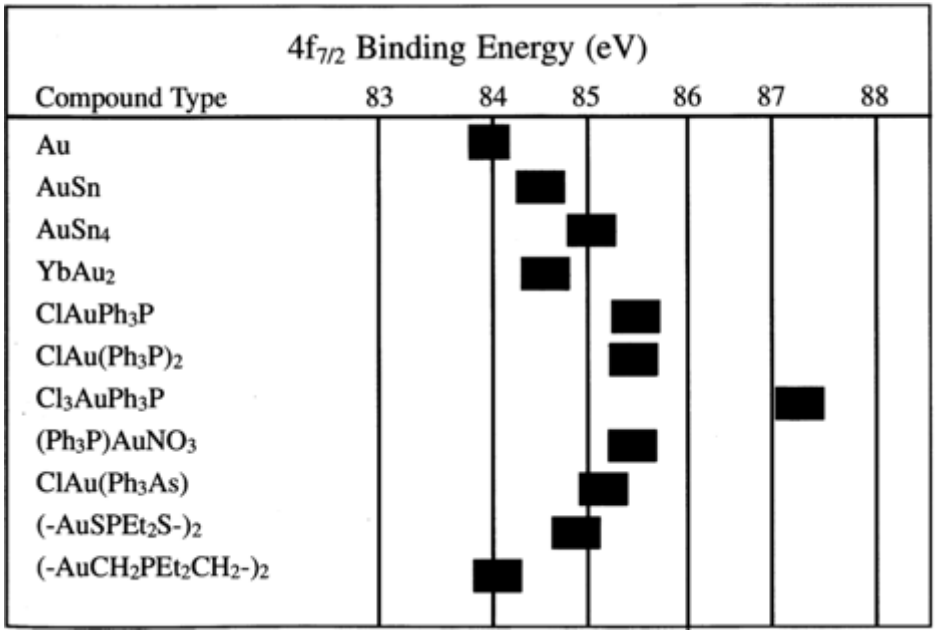

Ref.: K. Siegbahn, J. Electr. Spectrosc. Relat. Phenom., 5, 3 (1974), Zhang et al. IEEE Trans. Instrum. Meas., 66 1297 (2017)

# 5.6. Chemical shifts

## Silicon (si 2p) in compounds



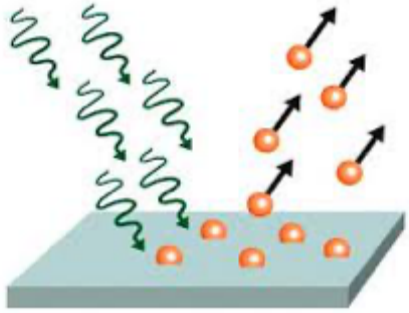

## Gold (Au 4f) in compounds

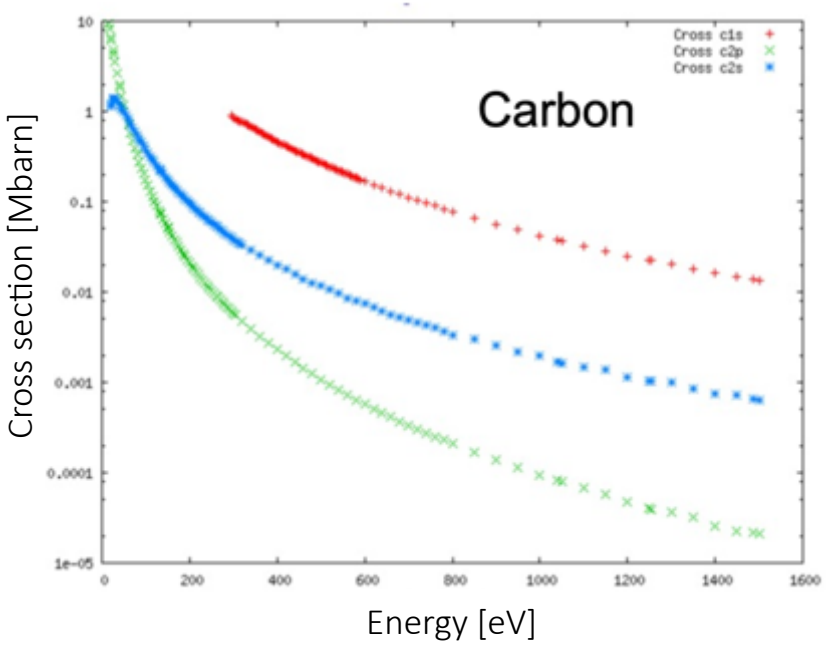


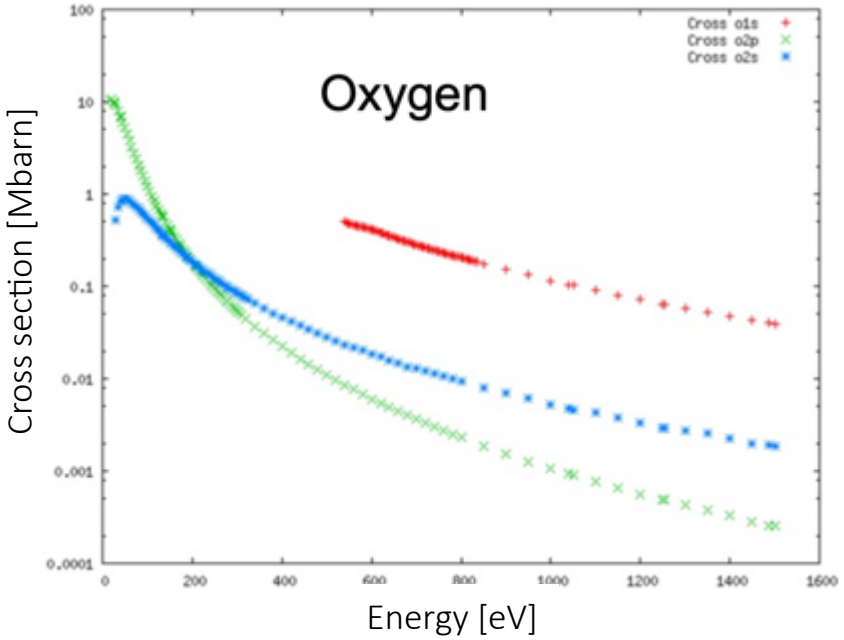

Ref.:
http://www.cityu.edu.hk/phy/appkchu/ap5301/Lecture-11-XPS.pdf

# 5.7. Cross section of photoionization

The photoionization cross section σ(ω) is defined as the probability per unit area that a photon with a particular energy will excite an electron and depends on the photon energy and the element.



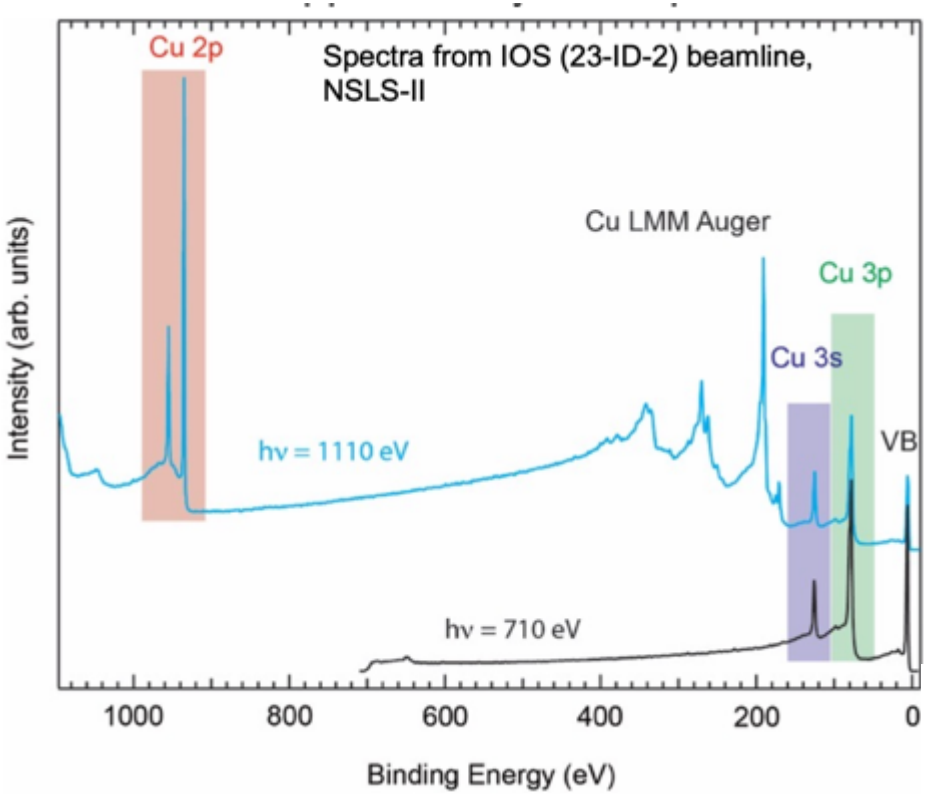


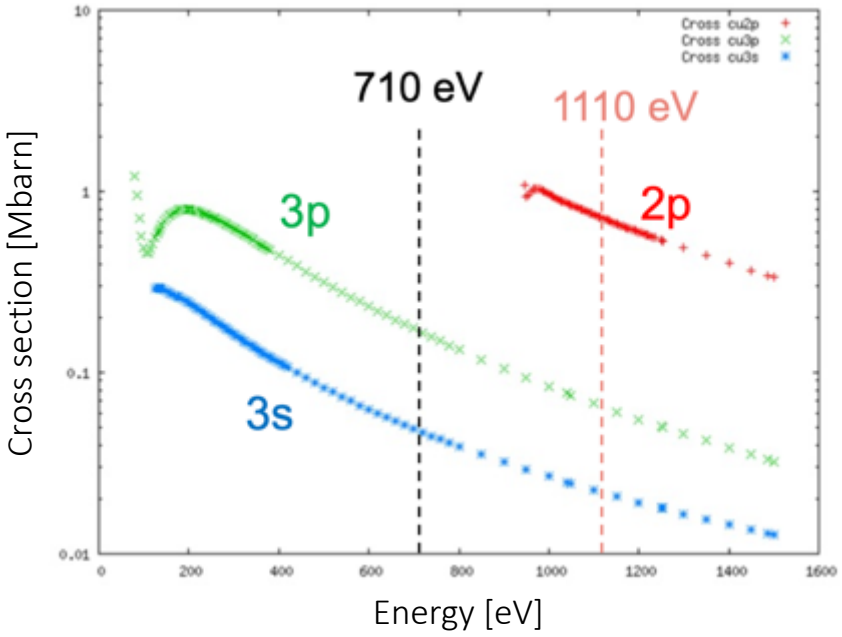




The cross section is measured in barn (symbol: b) is a metrric unit in area equal to $10^{-28}$ $m^2$ (100 $fm^2$).

Ref.: https://vuo.elettra.eu/services/elements/WebElements.html

# 5.8. Cross section of different photoelectrons

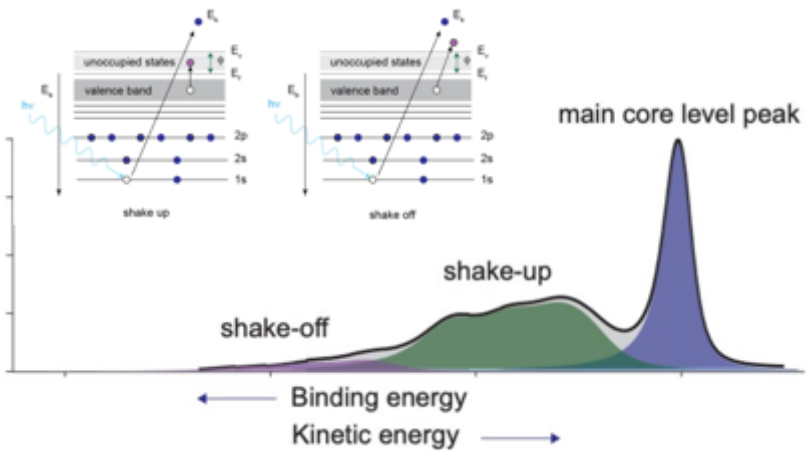


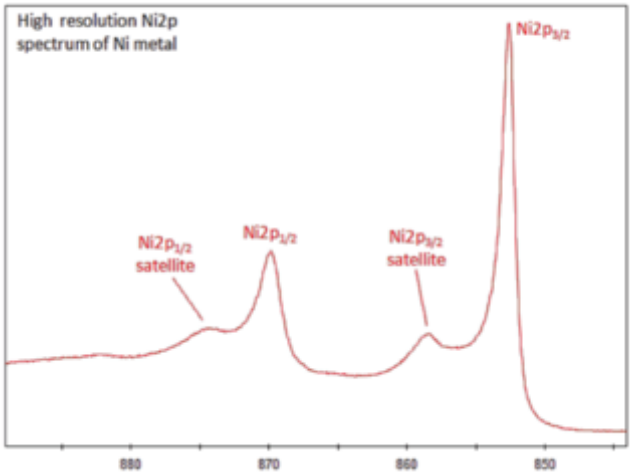

Ref.: https://vuo.elettra.eu/services/elements/WebElements.html

# 6. Other effects influencing the spectrum

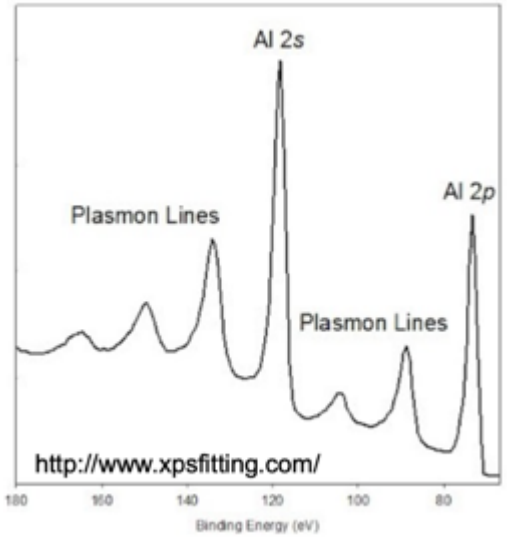
## Shake up and shake off



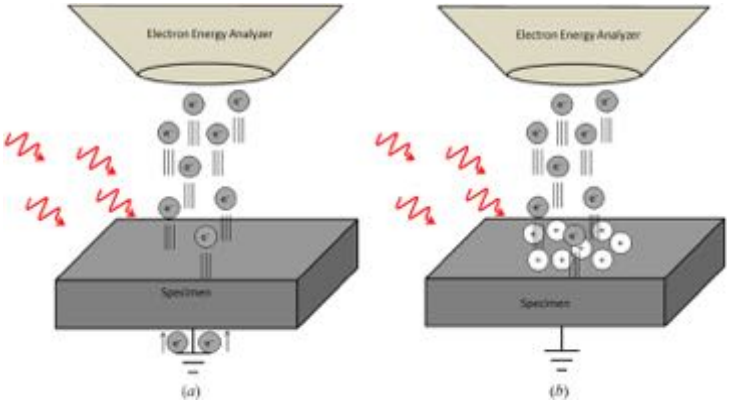

## Multiplet splitting




## Plasmon loss

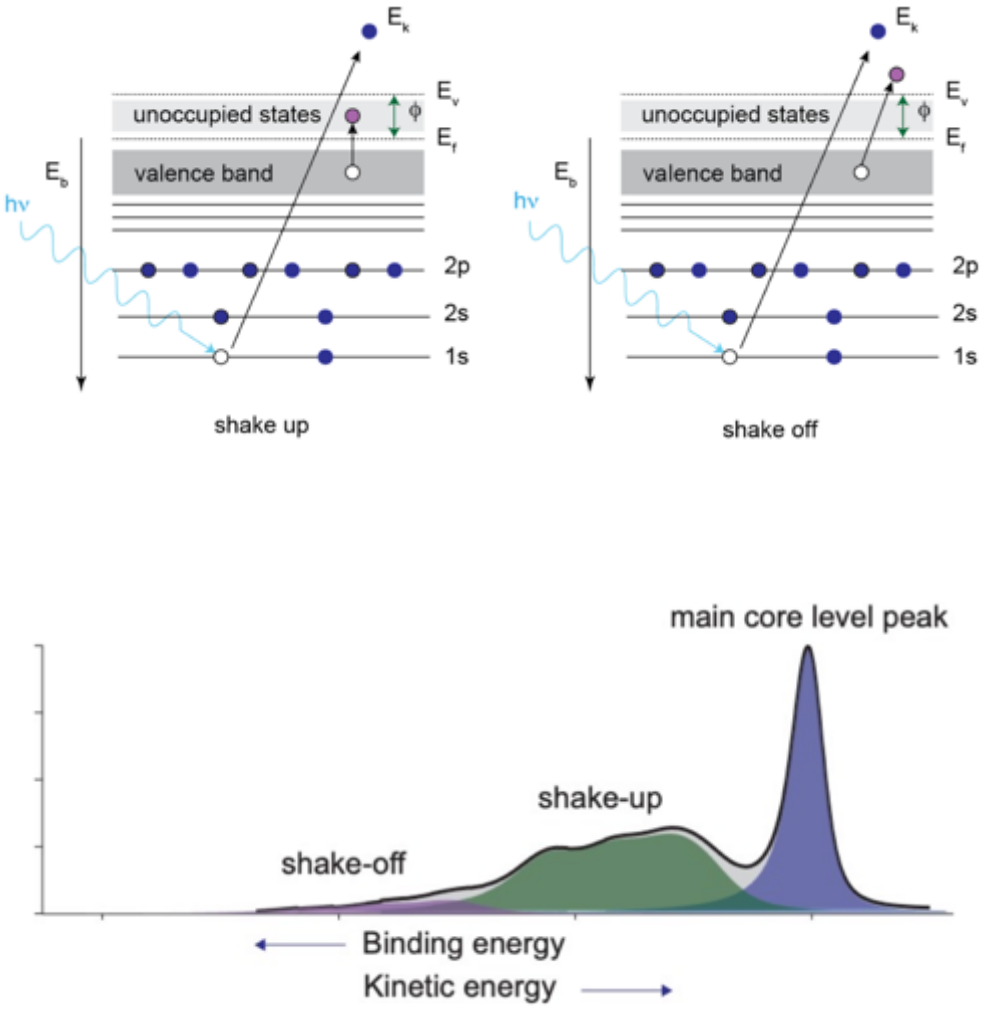


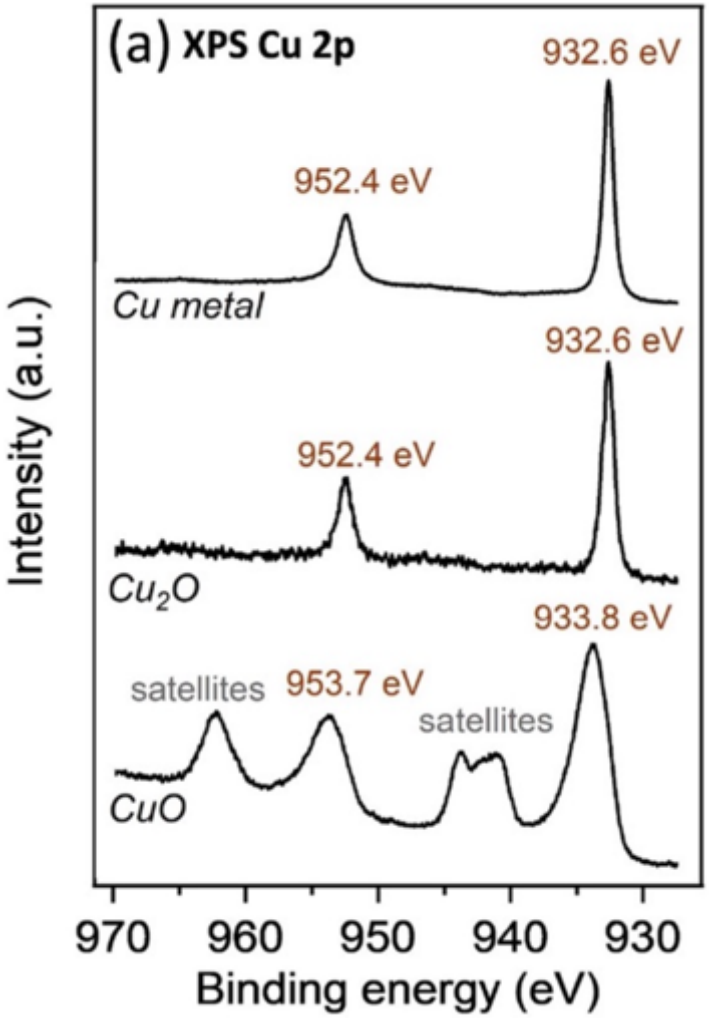

## Charging and charge compensation



# 6.1. Shake up and shake off

**Extra "satellite" peaks appear on the lower kinetic energy (higher binding energy side)**



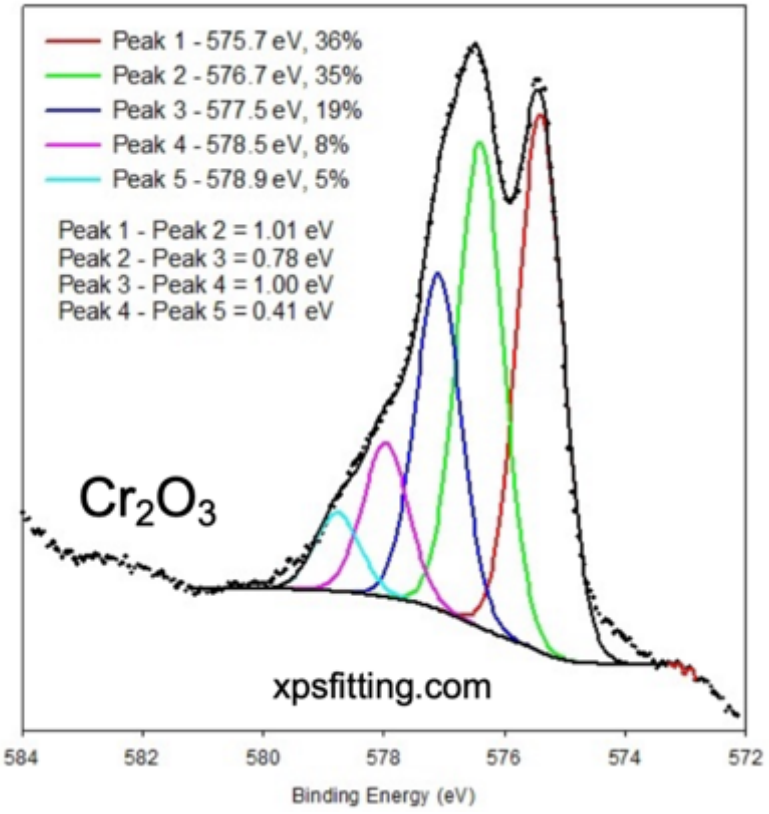



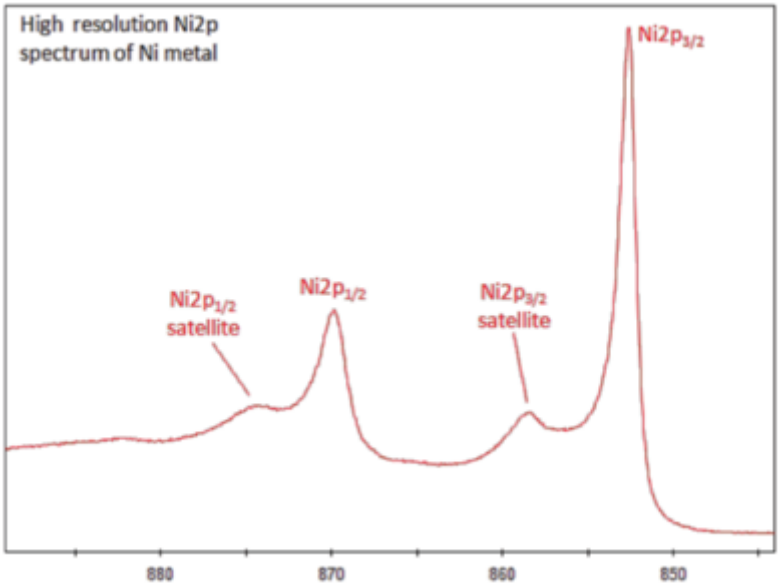

Ref.: Khalakhan et al. J. Elect. Spectrosc. Relat. Phenom. 246, 147027 (2021)

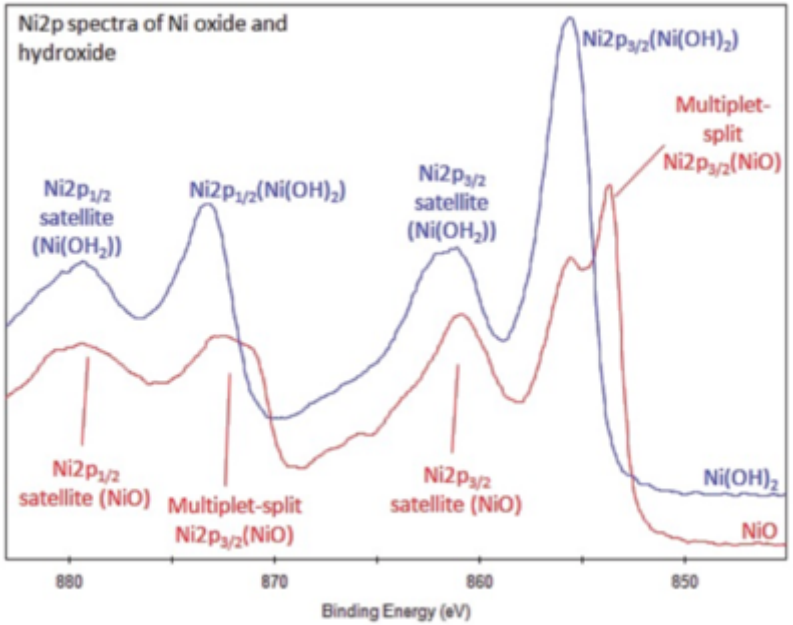
# 6.2. Multiplet splitting

Observed for compounds that have unpaired electrons in the valence band

Unpaired core electron interacts with unpaired valence electron, creating multiple possible final states



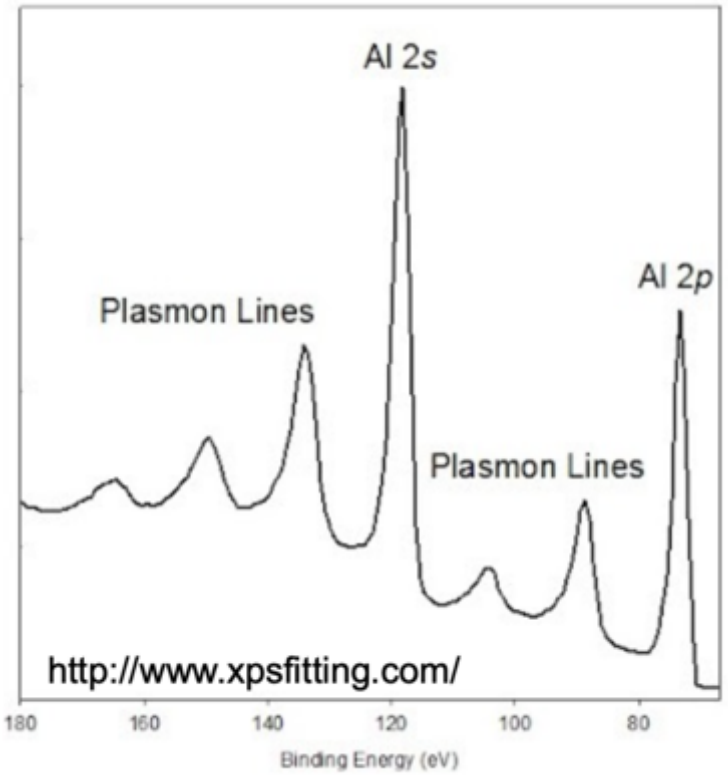

Ref.: https://www.thermofisher.com/it/en/home/materials-science/learning-center/surface-analysis.html

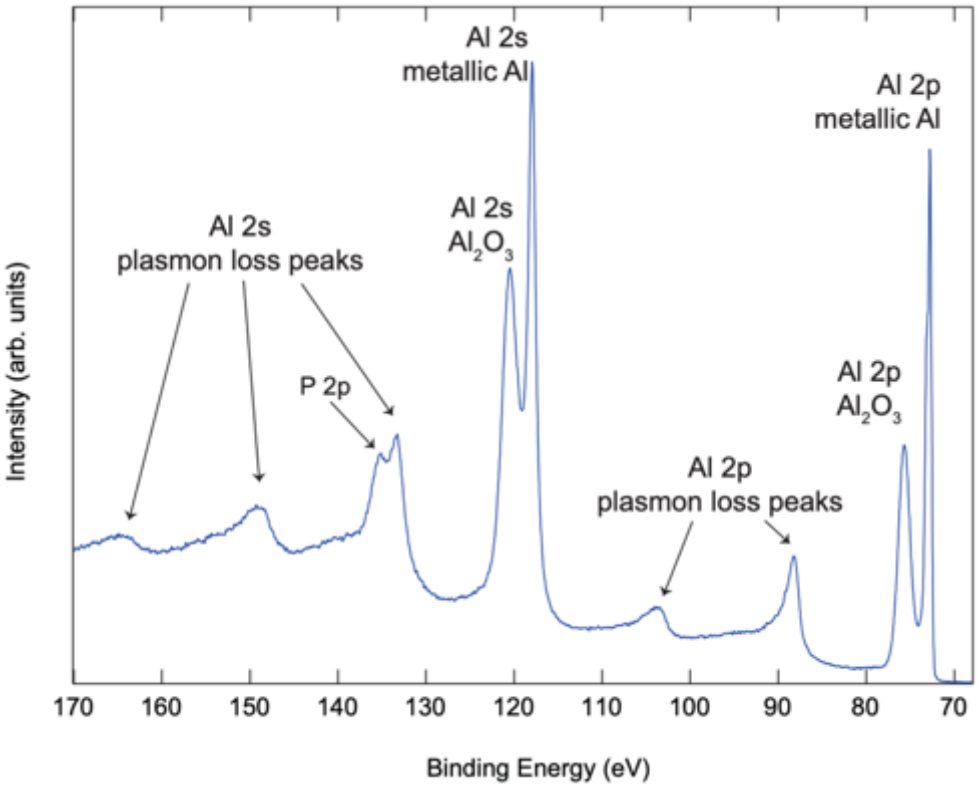
# 6.3. Plasmon loss

Usually observed for metallic surfaces. Outgoing photoelectron excites collective oscillations of electrons in the conduction band.

Photoelectron suffers energy loss and extra peaks appear at low KE/high BE at discrete energy values.

Can be strong for Al, which can interfere with other peaks in the region



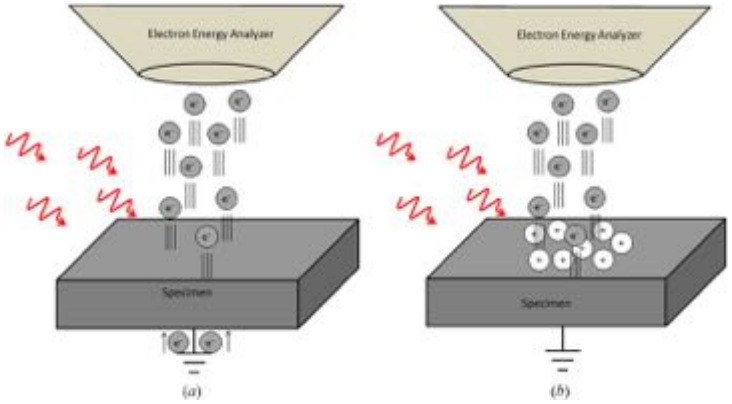



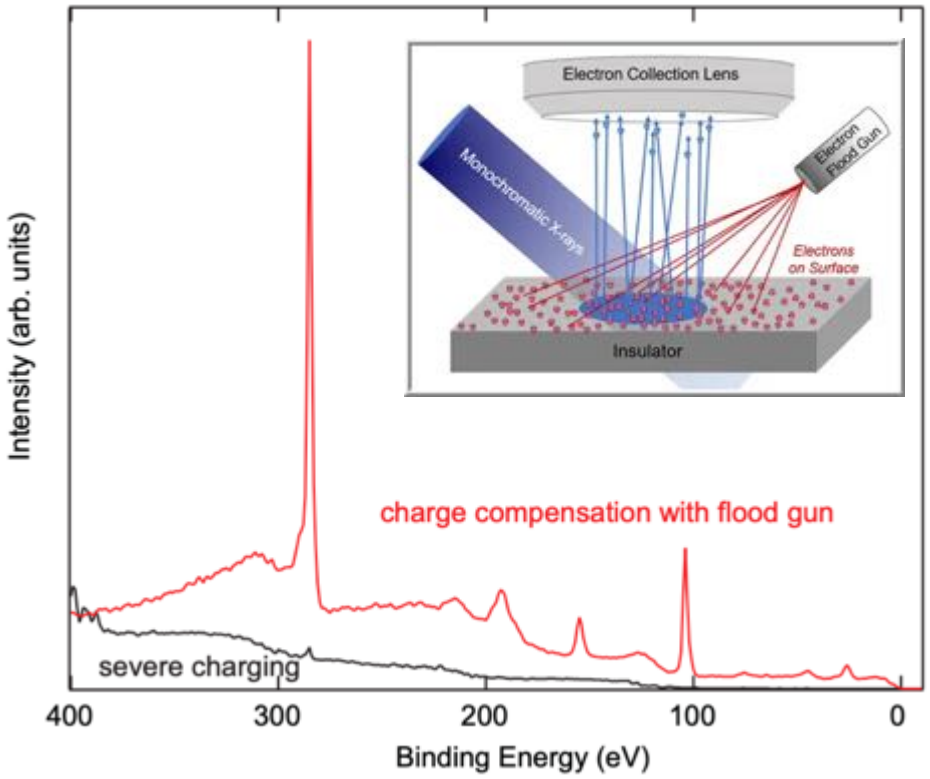

Ref.: https://www.thermofisher.com/it/en/home/materials-science/learning-center/surface-analysis.html

# 6.4. Charging and charge compensation

Photoionization process causes positive charge on the surface

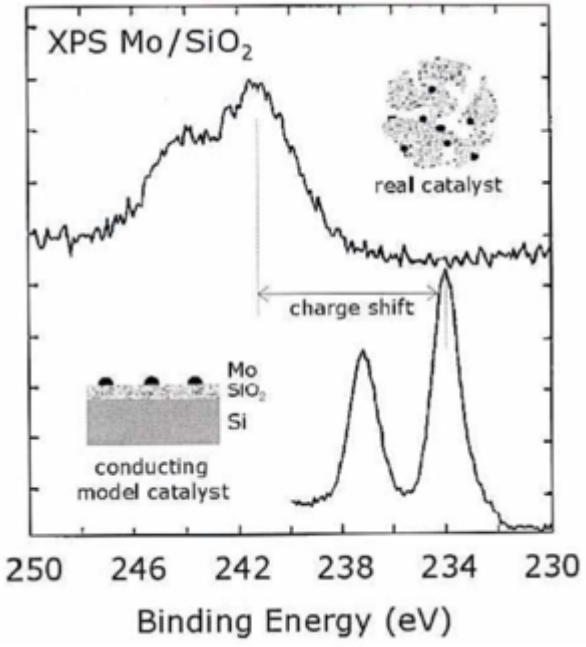
- For grounded electrically conductive samples, the charge is automatically neutralized
- For semi-conductive and insulating samples, the positive charge accumulates, photoelectron kinetic energy decreases
- Effect: shift to higher binding energy, peak broadening, double peaks, sometimes no peaks at all




XPS of Supported Catalysts

• Charge compensation: add electrons back to the sample (use an electron flood gun, or with the presence of ambient gases)

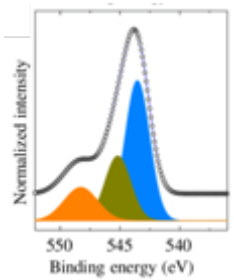



Ref.: https://iopscience.iop.org/book/mono/978-1-6270-5306-8/chapter/bk978-1-6270-5306-8ch4

# 7. Applications

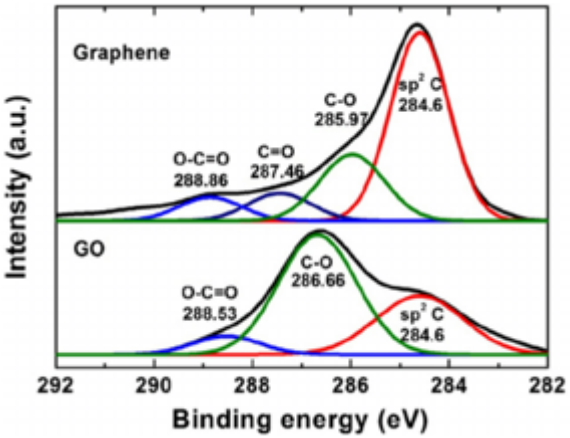
## Quantitative analysis

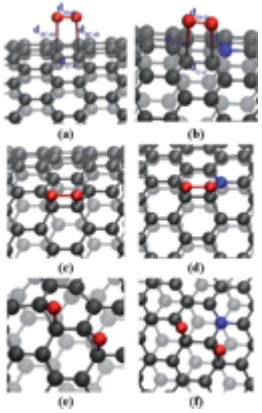
$$I_x = J \cdot c_x \cdot \lambda \cdot \sigma \cdot K$$



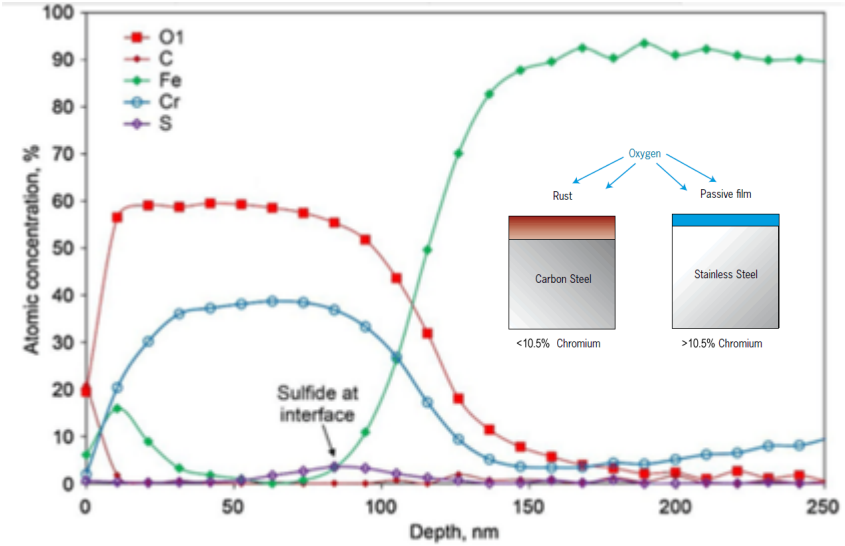

$I_x$ = peak intensity of element x
J = photon flux
$c_x$ = concentration of element x
$\lambda$ = inelastic mean free path
$\sigma$ = photoionization cross-section
K = instrumentation factors

## Chemical state of atoms

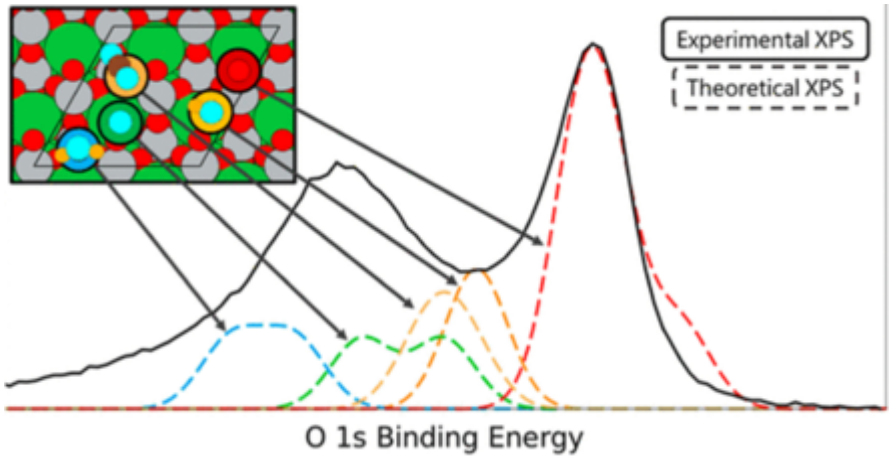


## Chemical composition of materials

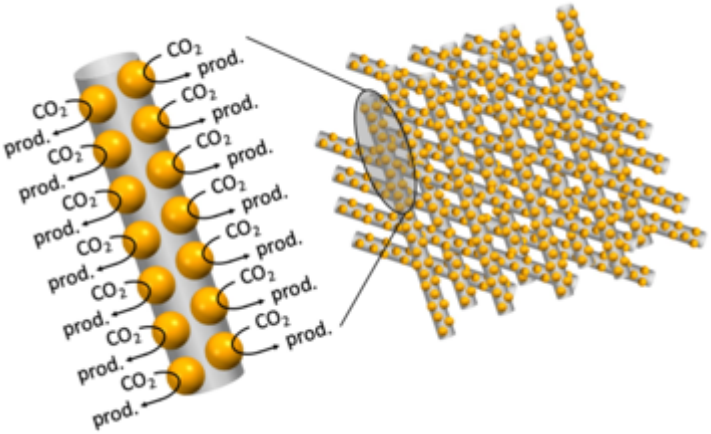



## Ab- and Adsorbents



# 7.1. Electrode surface analysis

Surface analysis before and after electro-reduction revealed that the detachment of citrate capping ligands enhanced the amount of exposed surface gold and concomitantly increased the CO-to-$H_2$ ratio in subsequent $CO_2$ reduction electrocatalysis.



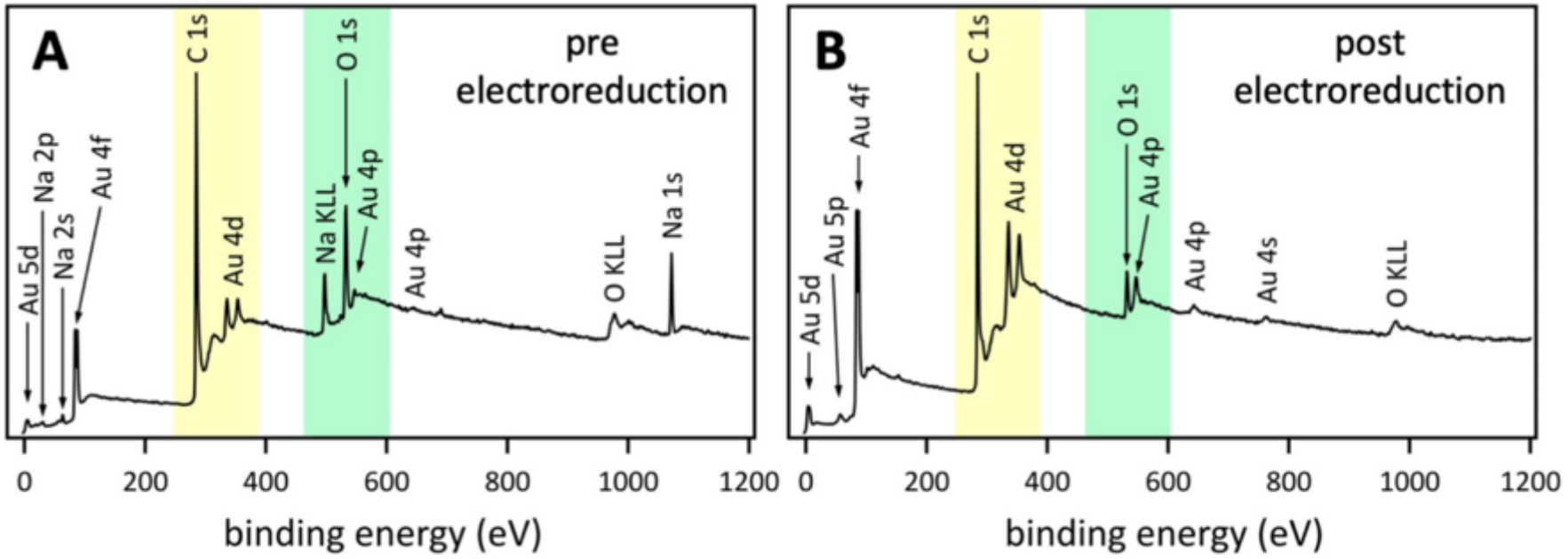
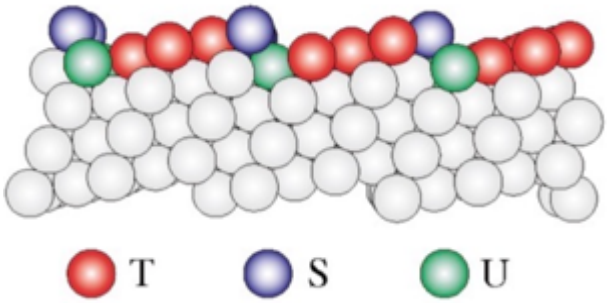



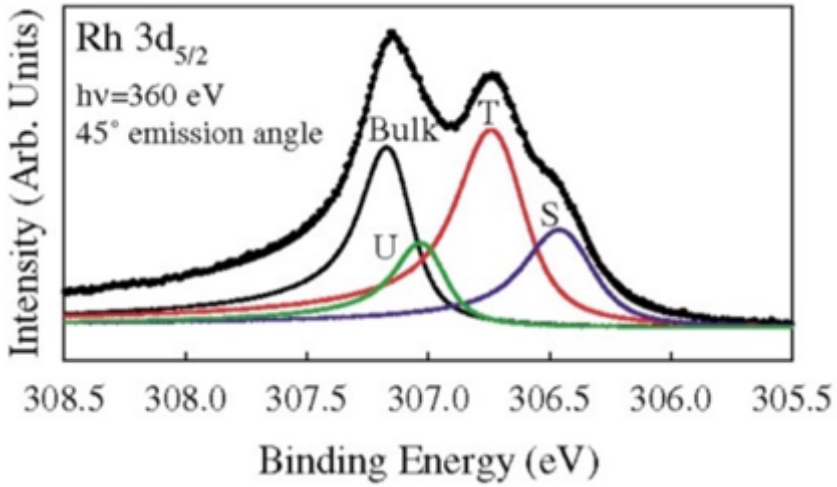

**Fig. 3** Survey XPS data of AuNP–CFP assemblies, collected before (A) and after citrate-removal electroreduction (B). Highlighted in yellow are the C 1s and Au 4d core level regions, which show the surface gold-to-carbon ratio; highlighted in green are the O 1s and Au 4p core level regions, which visualize the surface gold-to-oxygen ratio

Ref.: Ryland C. Forsythe, Connor P. Cox, Madeleine K. Wilsey, Wanqing Yu, Astrid M. Müller, "High Surface Area Assemblies of Gold Nanoparticles on Hydrophilic Carbon Fiber Paper with Ionomer Overlayers for Aqueous $CO_2$ Reduction Electrocatalysis to Clean Syngas", Topics in Catalysis (2024) 67:344–362

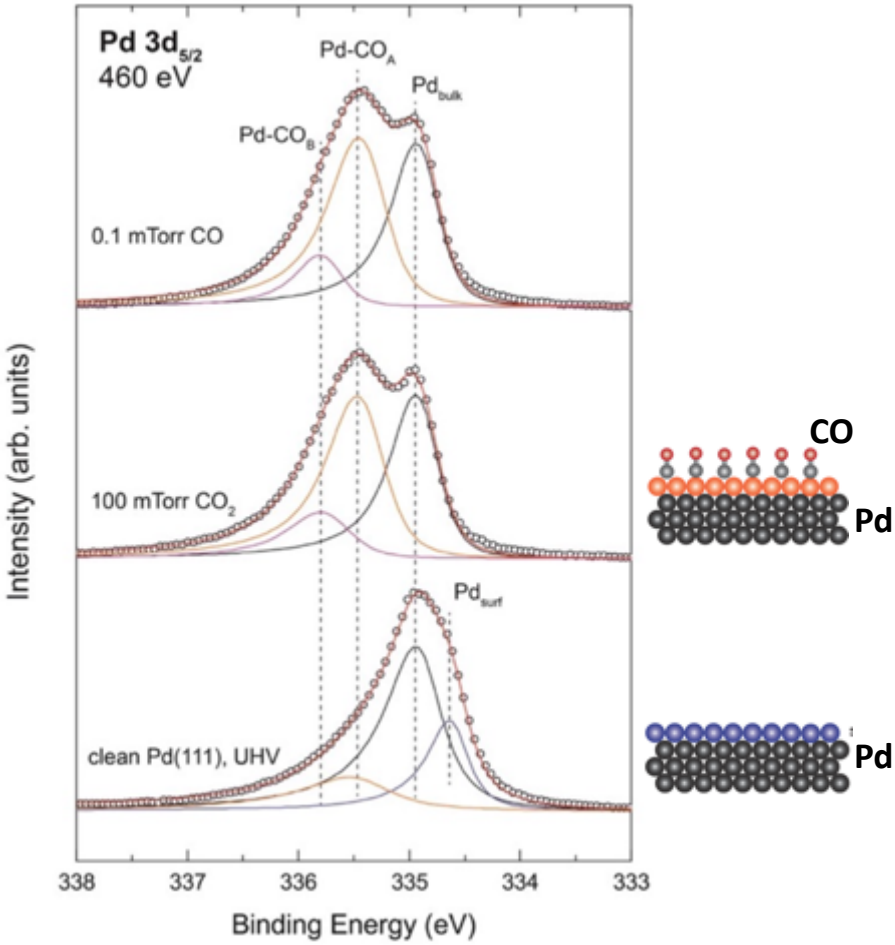
# 7.2. Surface atom core level shift

**Surface atoms of a metal can have distinct binding energy from the bulk atoms**




**Surface peak is shifted by adsorbed molecules**

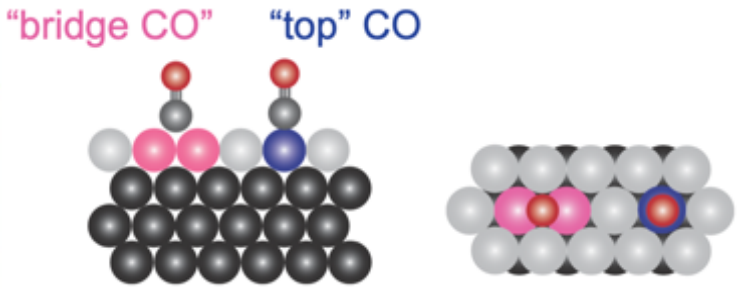


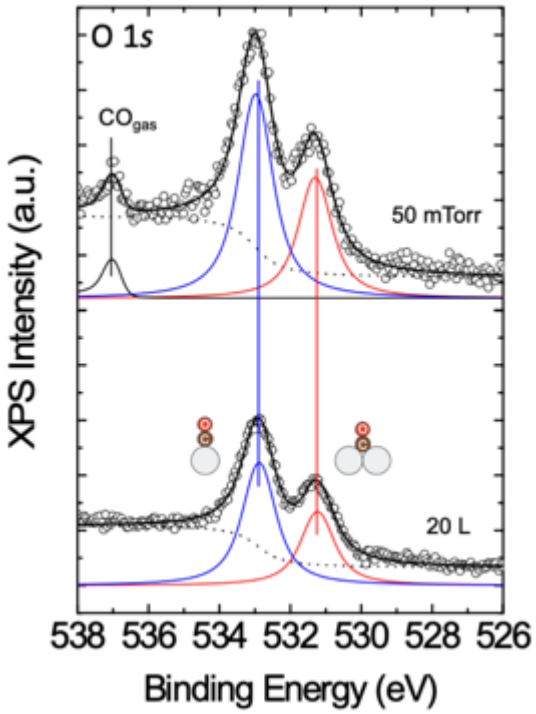

Ref.: Gustafson et al. Phys. Rev. Let. 91, 056102 (2003); Simonovis et al. J. Phys. Chem. C 126, 7870 (2022)

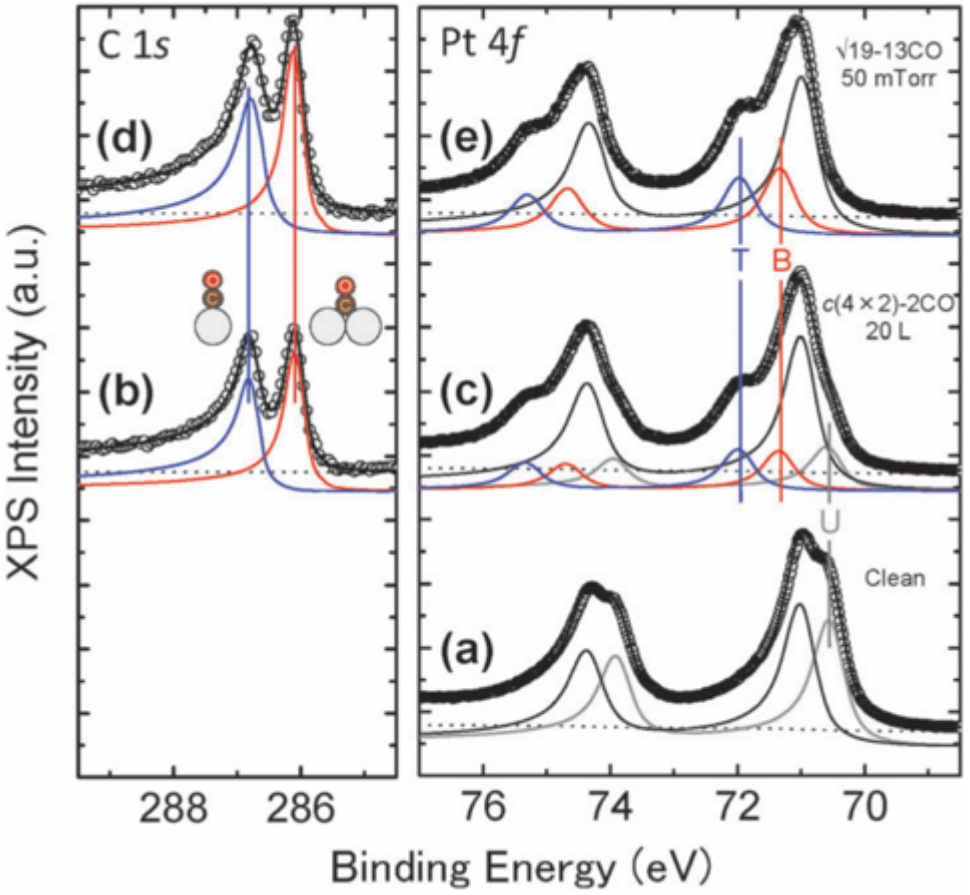
# 7.3. Distinguish different adsorption sites

**Oxygen in CO on bridge (B) and top (T) site**

**Binding of the C to the Pt**



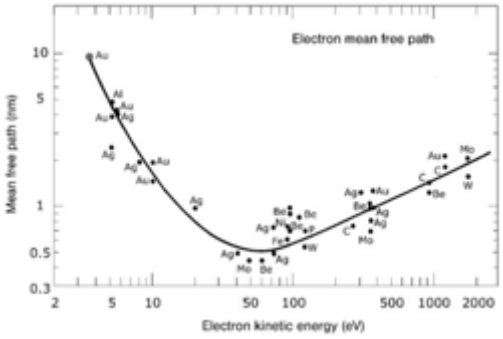



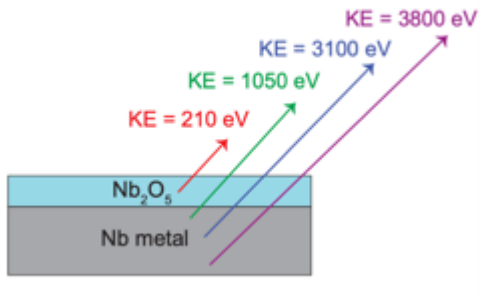



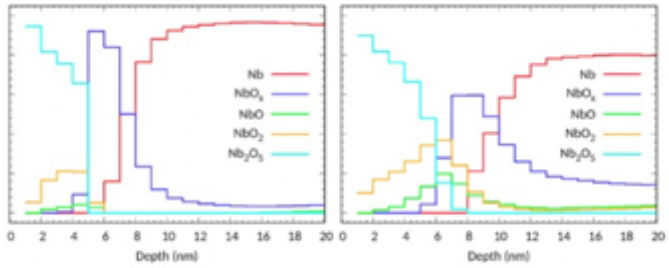

Ref.: Toyoshima et al. Phys. Chem. Chem. Phys. 16, 23564 (2014)

# 7.4. Depth profiling

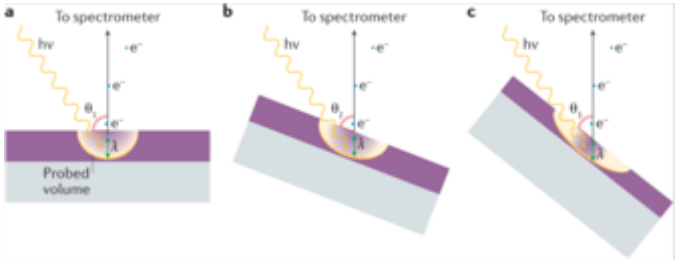
## Change photon energy

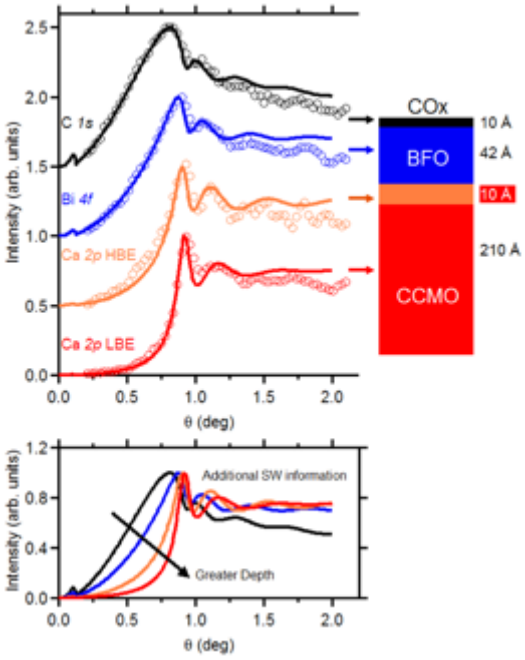


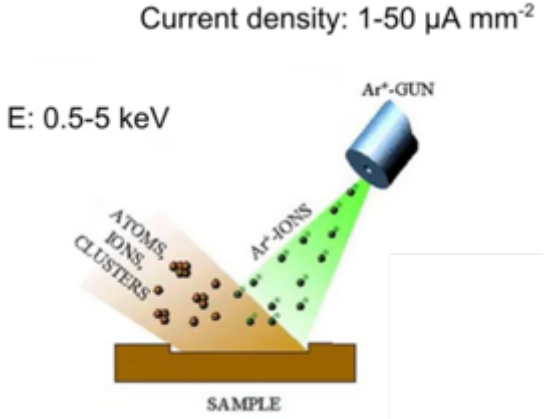



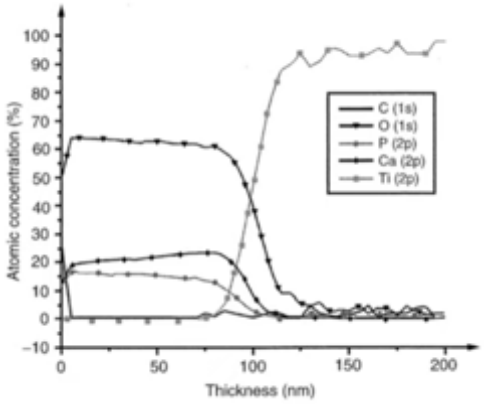

## Change emission angle




## Sputtering




Ref.: Premkumar et al. Commun. Mater. 2, 72 (2021), Di Bernardo, Iolanda "Non-disruptive techniques for depth profiling in photoemission spectroscopy.", Nat Rev Phys 3, 459 (2021).

Surface Science Spectra

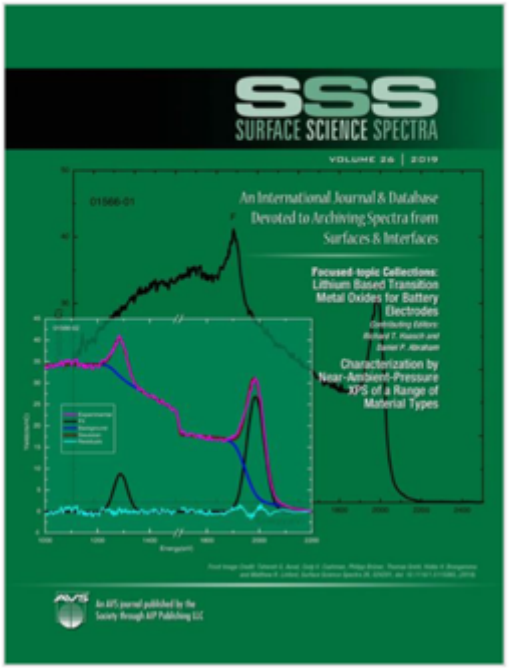
# Introduction to near-ambient pressure x-ray photoelectron spectroscopy characterization of various materials

**Special Collection:** Near-Ambient Pressure x-ray Photoelectron Spectroscopy Characterization of Various Materials

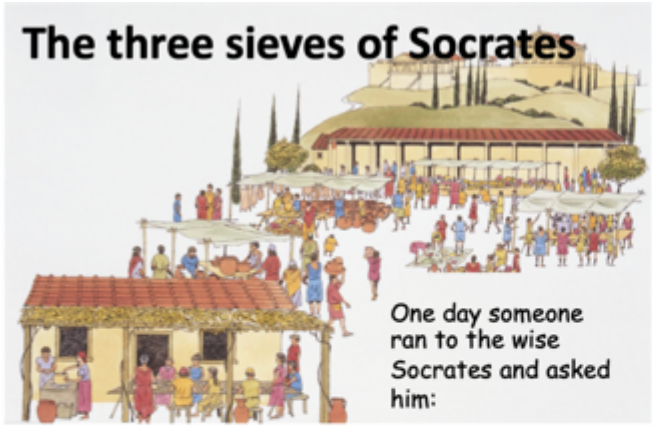
Dhananjay I. Patel; Tuhin Roychowdhury; Varun Jain; Dhruv Shah; Tahereh G. Avval; Shiladitya Chatterjee; Stephan Bahr; Paul Dietrich ; Michael Meyer; Andreas Thißen; Matthew R. Linford

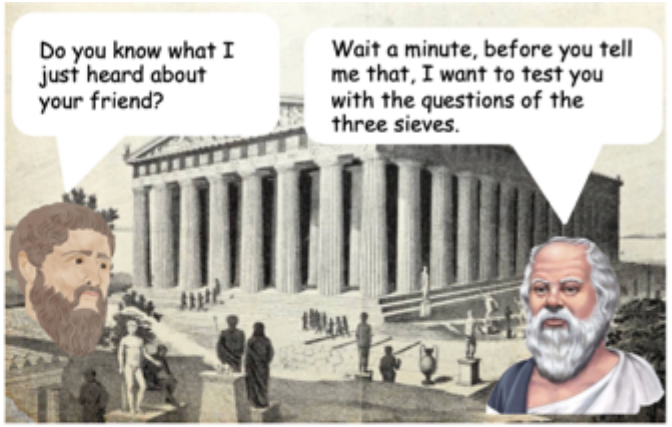
Volume 26, Issue 1

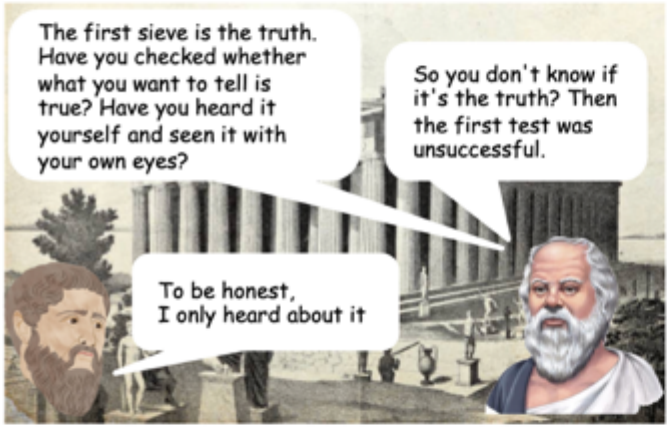
June 2019

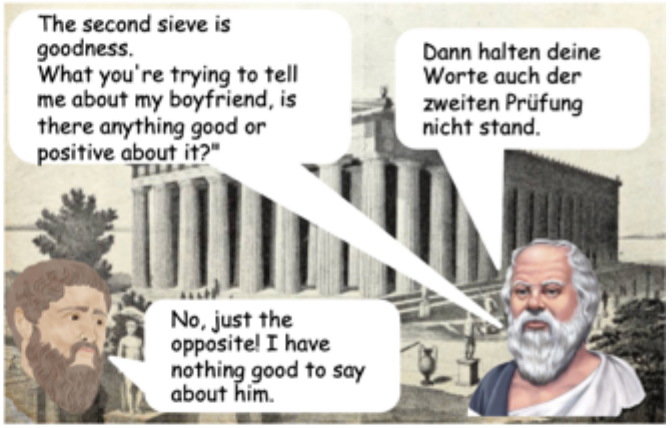


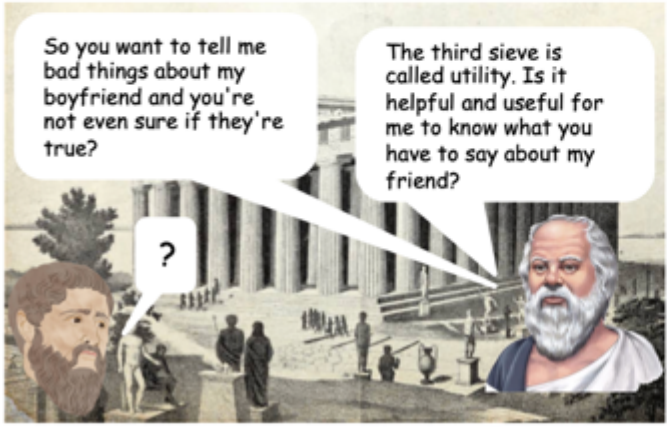

Ref.: https://pubs.aip.org/sss/collection/1638/Near-Ambient-Pressure-x-ray-Photoelectron


The three sieves of Socrates
One day someone ran to the wise Socrates and asked him:


Do you know what I just heard about your friend?
Wait a minute, before you tell me that, I want to test you with the questions of the three sieves.


The first sieve is the truth. Have you checked whether what you want to tell is true? Have you heard it yourself and seen it with your own eyes?
So you don't know if it's the truth? Then the first test was unsuccessful.
To be honest, I only heard about it


The second sieve is goodness. What you're trying to tell me about my boyfriend, is there anything good or positive about it?"
Dann halten deine Worte auch der zweiten Prüfung nicht stand.
No, just the opposite! I have nothing good to say about him.


So you want to tell me bad things about my boyfriend and you're not even sure if they're true?
The third sieve is called utility. Is it helpful and useful for me to know what you have to say about my friend?
?


So if what you are about to tell me is neither true nor good nor useful, I prefer not to know and I advise you to forget it."
No not at all!"

Andreas ZÜTTEL, Prof. Dr.

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