

X-ray Photoelectron Spectroscopy XPS to characterize glassy materials



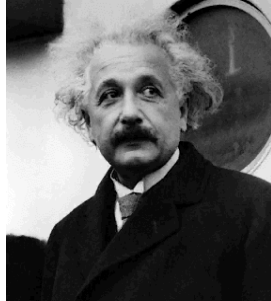
Dominique FOIX

IPREM /Pau University

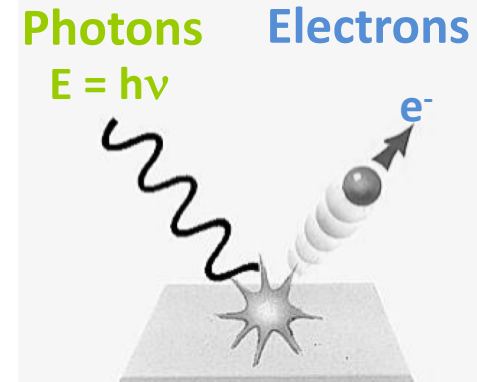
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What is XPS ?

Photoelectric effect presented by R. Hertz in 1887 and explained by A. Einstein in 1905



Nobel Price of Physics
in 1921



XPS or ESCA : Electron Spectroscopy for Chemical Analysis

Analytical tool

Kai SIEGBAHN



Nobel Price of Physics
in 1981

Precision Method for Obtaining Absolute Values of Atomic Binding Energies

CARL NORDLING, EVELYN SOKOLOWSKI, AND KAI SIEGBAHN
Department of Physics, University of Uppsala, Uppsala, Sweden
(Received January 10, 1957)

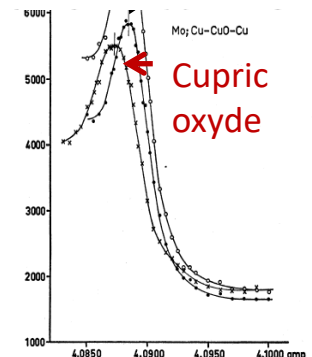
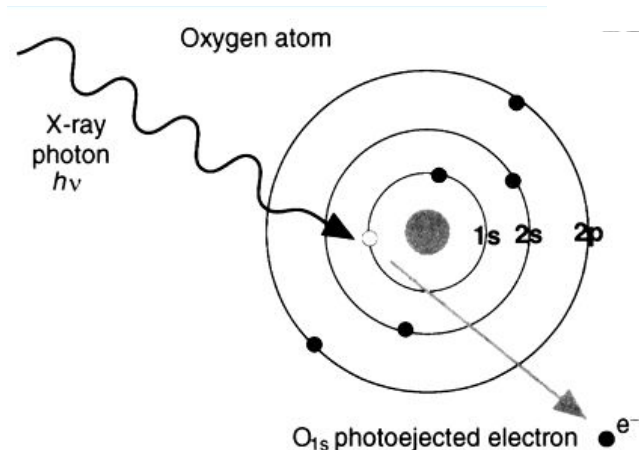
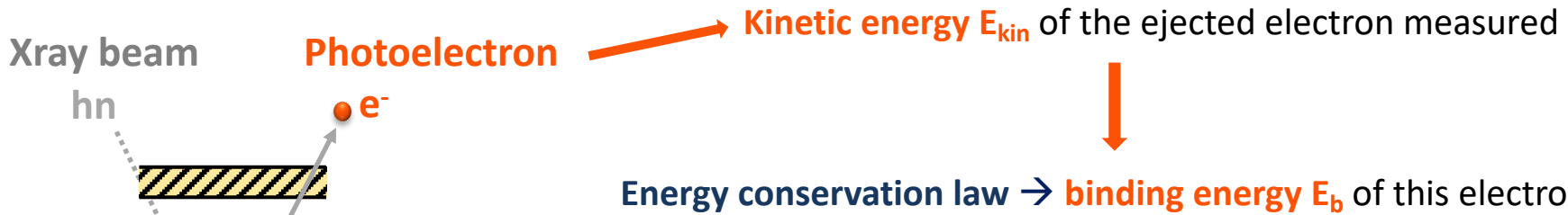


FIG. 1. Cu K (Mo K α) photo-lines. The curves plotted with open and filled circles are the photo-lines of metallic copper.

Binding energy E_b

What is XPS ?



$$E_i(N) + h\nu = E_f(N-1) + E_{kin}$$

$$E_f(N-1) - E_i(N) = h\nu - E_{kin}$$

$$E_b = h\nu - E_{kin}$$

X-ray beam

different energies depending on the anode:

Al $K\alpha \rightarrow 1486.6\text{eV}$

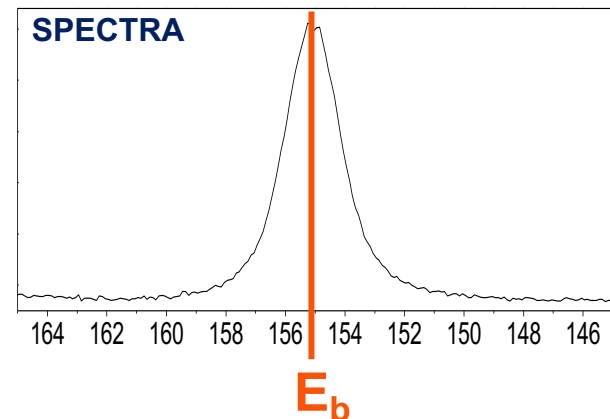
Mg $K\alpha \rightarrow 1253.6\text{eV}$

Ag $L\alpha \rightarrow 2950.6\text{eV}$

Cr $K\alpha \rightarrow 5417\text{eV}$

...

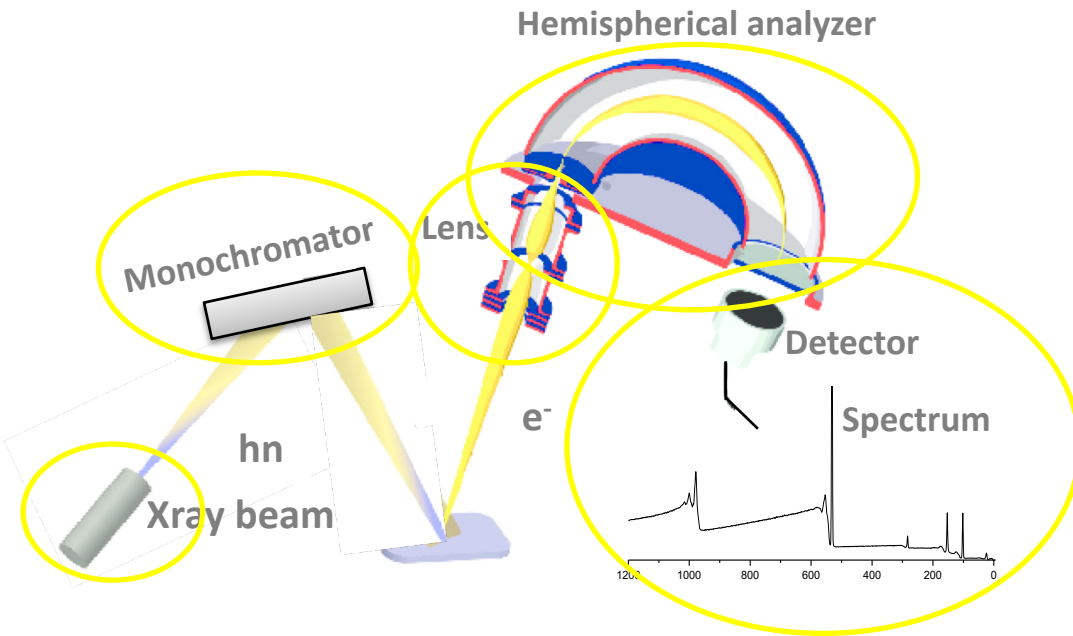
E_b Binding energy (or ionisation potential)
is characteristic of ONE orbital of ONE atom
in ONE environment



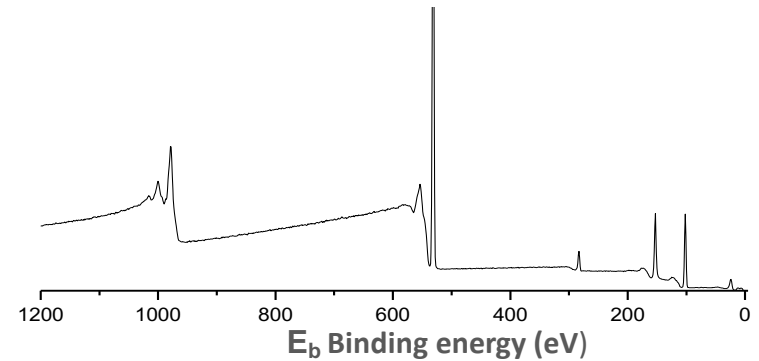
What is XPS ?

XPS spectrometer

XPS spectra are obtained by irradiating a material with a X-rays beam while simultaneously measuring the kinetic energy and number of electrons escaped from material.



Survey spectrum or Wide scan spectrum



Electron intensity as a function of energy

X-ray beam Anode → Monochromator

The photoelectrons are:

- **Ejected** from the sample surface with an KE
- **Focused** and transferred by electromagnetic lenses
- Energy **filtered** by a analyser
- **Detected** and recorded by a counting system



1- What allows XPS ?

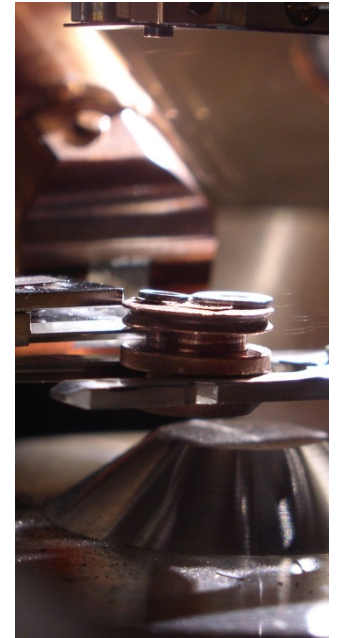
Surface analysis

Atomic Identification

Quantitative analysis

Chemical analysis

2- Equipment



3- XPS to characterize glassy materials



1- What allows XPS ?

Surface analysis

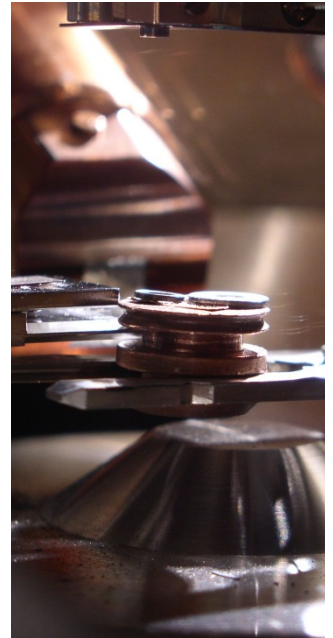
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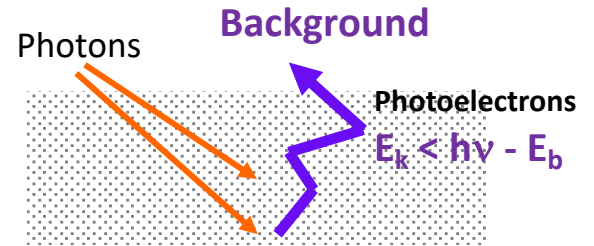
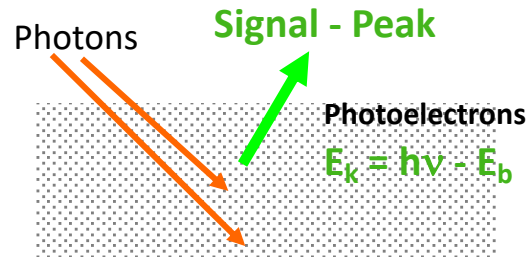
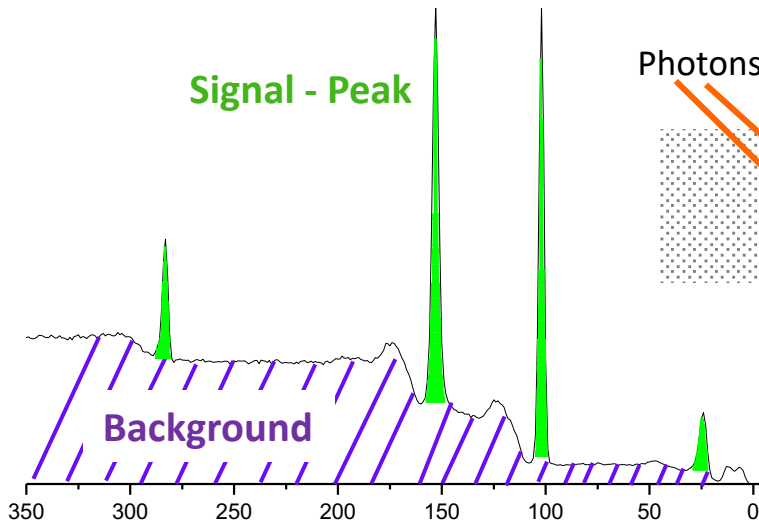
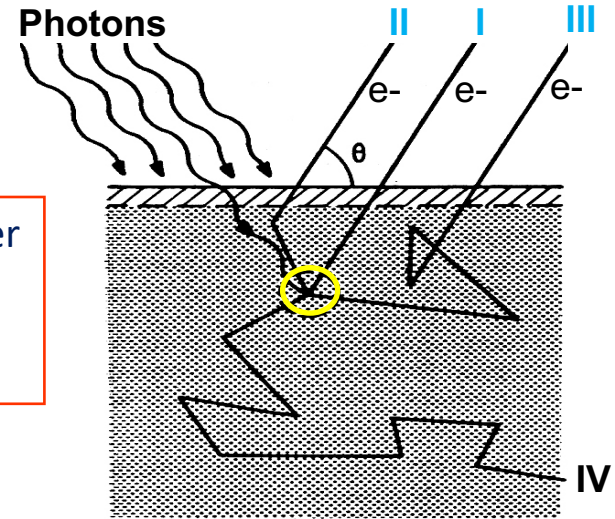


Surface analysis

Interaction process between photoelectrons and solid

3 steps :

- **Absorption** of the photon and creation of a photoelectron
- **Transport** of electrons to the surface
 - I without inelastic scatter
 - II inelastic scatter
 - III many inelastic scatter
- **Escape** of the electrons from surface to the vacuum



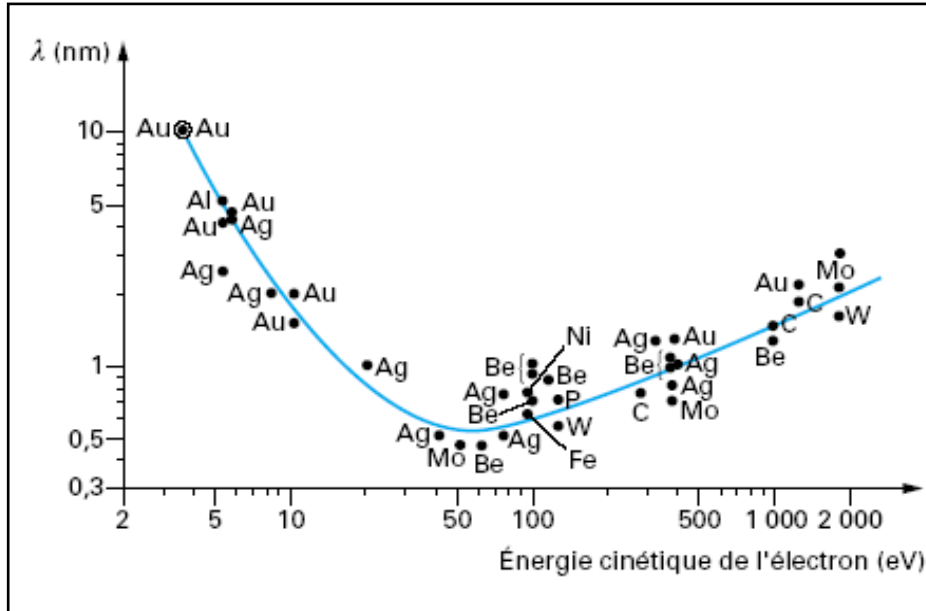
Surface analysis :
depth analysis < 10nm



Not because of the photon beam penetration,
because of the **electron escape without energy loss**

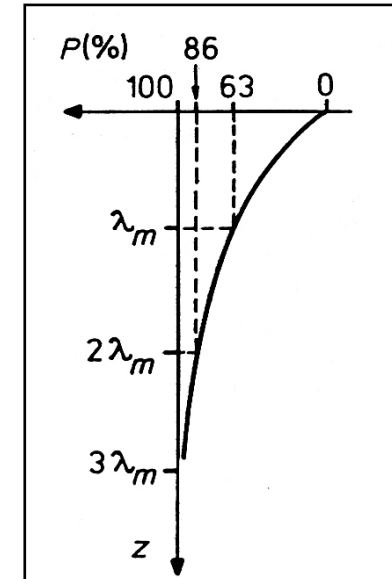
Surface analysis

Inelastic mean free path (λ) =
Average distance between successive inelastic collisions



Mean free path λ depends of:

- electrons kinetic energy
- chemical composition,
- structure and the density



63 % of all photoelectrons will come from within one λ of depth.

The majority of photoelectrons will come from 3λ .

Depth analysis : 5- 10nm



1- What allows XPS ?

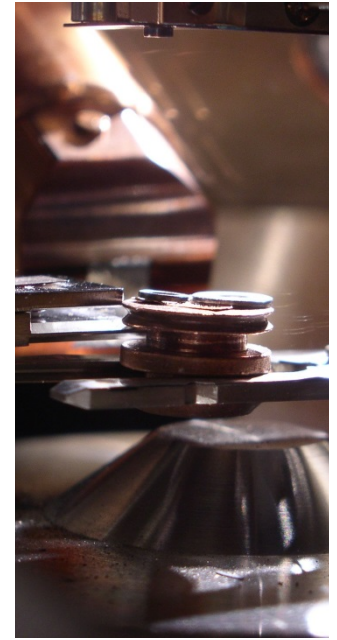
Surface analysis

Atomic Identification

Quantitative analysis

Chemical analysis

2- Equipment



3- XPS to characterize glassy materials

Atomic Identification

All the elements present in the compound are detected except H and He

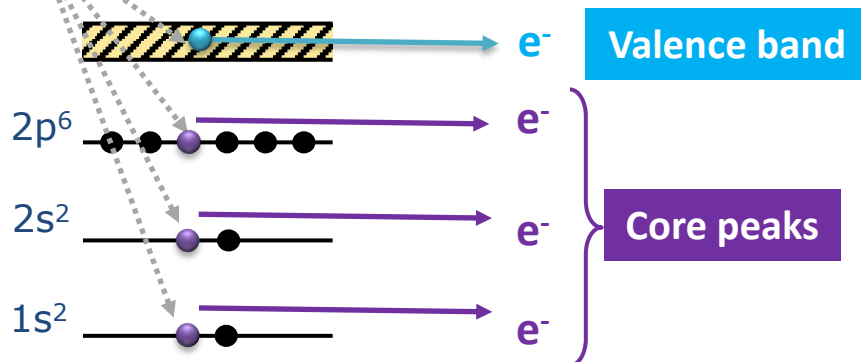
Limit sensibility : around 0.1% (atomic percentage)

For each atom present in the surface, all the orbitals are ionized if :

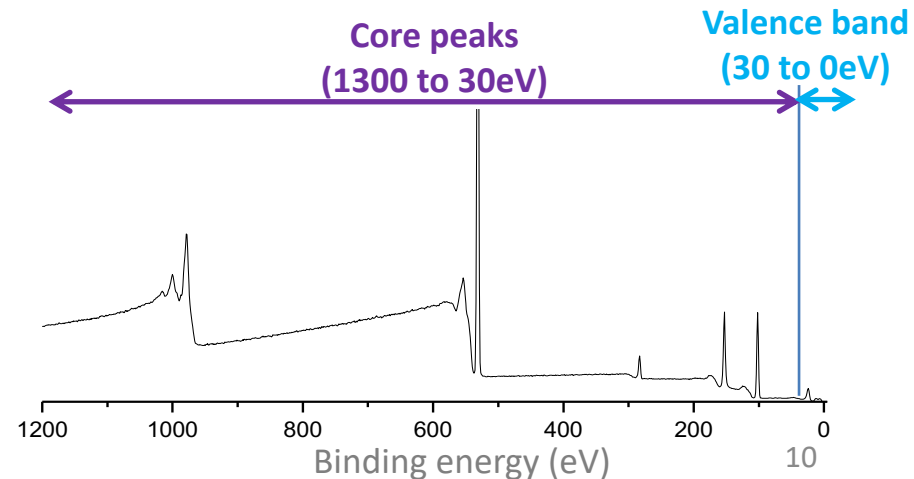
$$E_b < hn$$

A periodic table of elements with color coding by groups. The first two columns (H, He; Li, Be; Na, Mg; K, Ca; Rb, Sr; Cs, Ba; Fr, Ra) are yellow. The next two columns (B, C; Al, Si; Ga, Ge; In, Sn; Tl, Pb) are orange. The next two columns (N, O; P, S; As, Se; Sb, Te; Bi, Po) are green. The next two columns (F, Ne; Cl, Ar; Br, Kr; I, Xe; At, Rn) are blue. The lanthanide and actinide series are shown below the main table, with lanthanides in pink and actinides in purple.

Al $K\alpha$
 $hn = 1486,6 \text{ eV}$



A survey spectrum allows the atoms identification:



Atomic Identification

Valence band

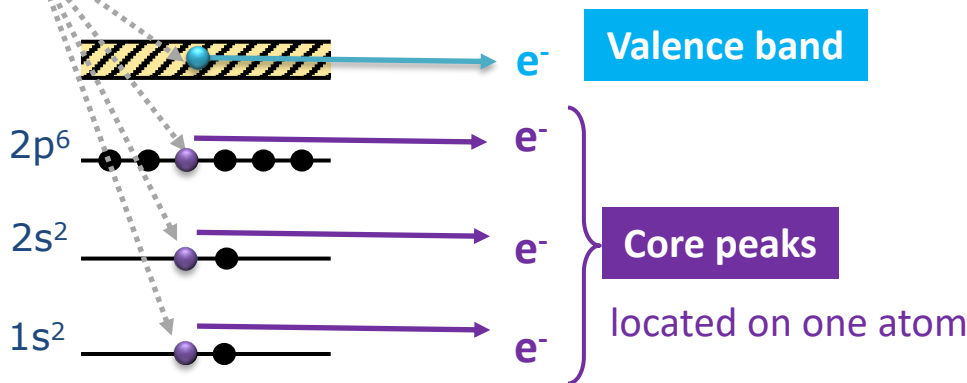
Experimental visualisation of density of states DOS

- highest occupied electronic level (0 à 30eV)
- characteristic of bonds

The intensity are then modulated by photoionization cross-section to be compared to the valence spectra

$$\text{DOS}_{\text{total modulated}} = \sum_{A,o} \sigma_{A,o} * \text{DOS}_{A,o} (E)$$

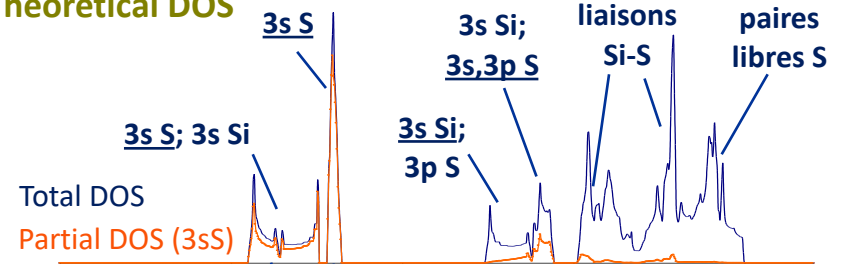
Al K α
 $h\nu = 1486,6 \text{ eV}$



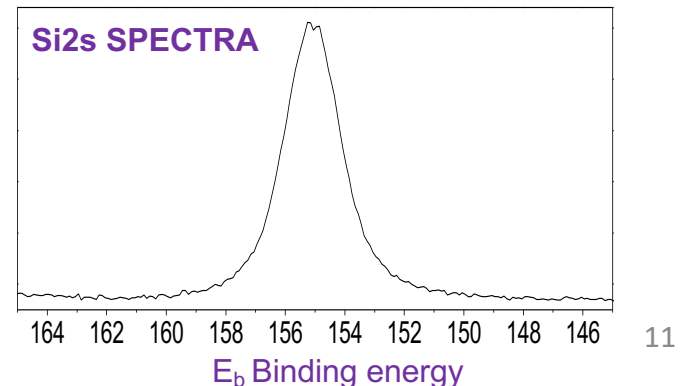
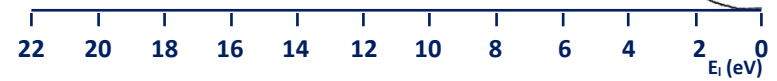
Allow atomic identification

Theoretical calculations allow to simulate DOS

Theoretical DOS



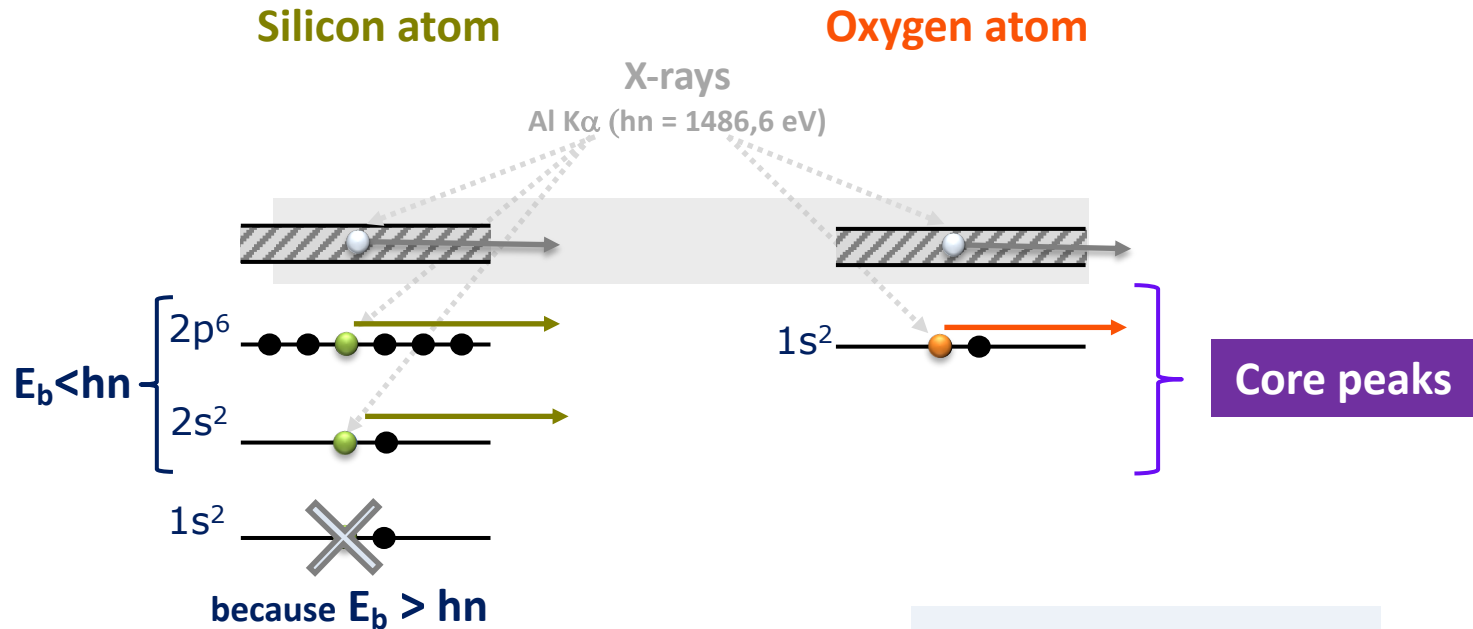
Experimental DOS



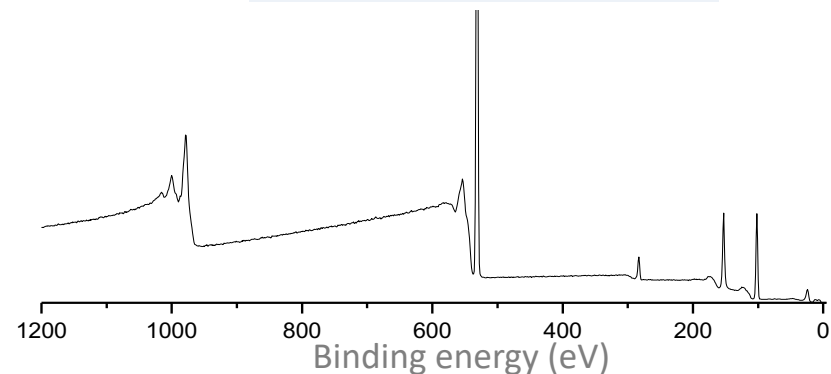
Atomic Identification – Core peaks

Atomic Identification: **Core peaks**

Exemple : SiO_2



Survey spectrum SiO_2



Atomic Identification – Core peaks

The binding energies (eV) are tabulated like in this example:

	1s	2s	2p	3s	3p
Li ₃	55				
Be ₄	111				
B ₅	188		5		
C ₆	285		7		
N ₇	400		9		
O ₈	531	24	7		
F ₉	686	31	9		
Na ₁₁	1072	63	31	1	
Mg ₁₂	1302	89	50	2	
Al ₁₃		118	73	1	
Si ₁₄		153	103	8	3

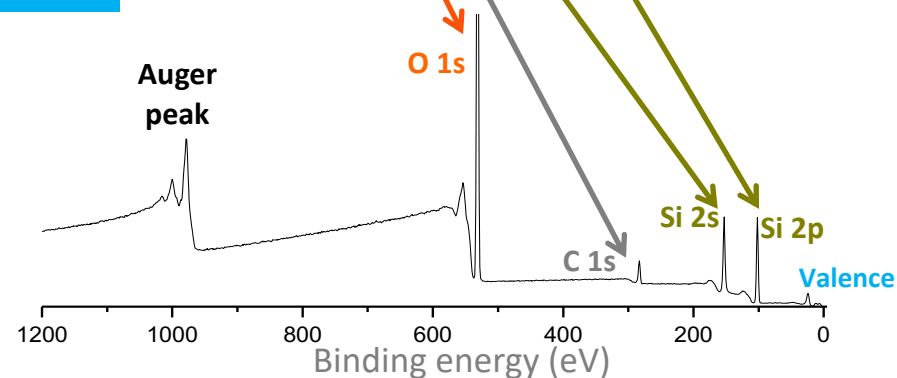
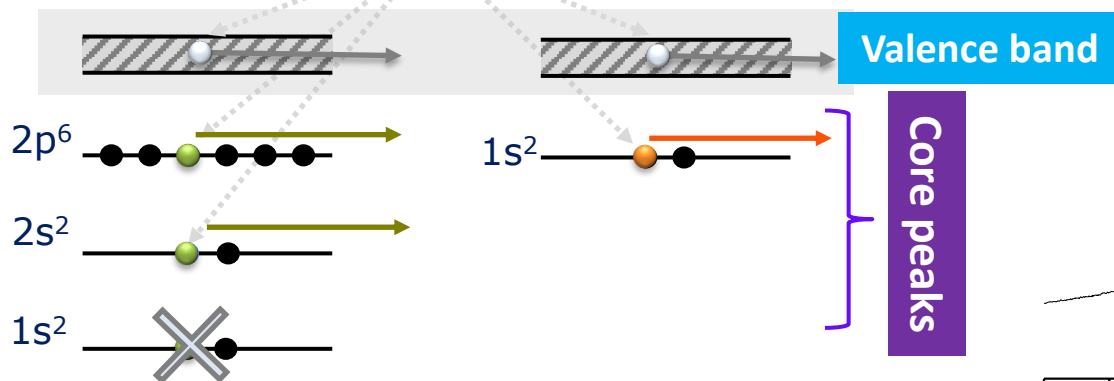
A binding energy (or ionisation potential) is characteristic of ONE orbital from ONE atom

SiO₂

Silicon atom

Oxygen atom

X-rays
Al K α (h ν = 1486,6 eV)



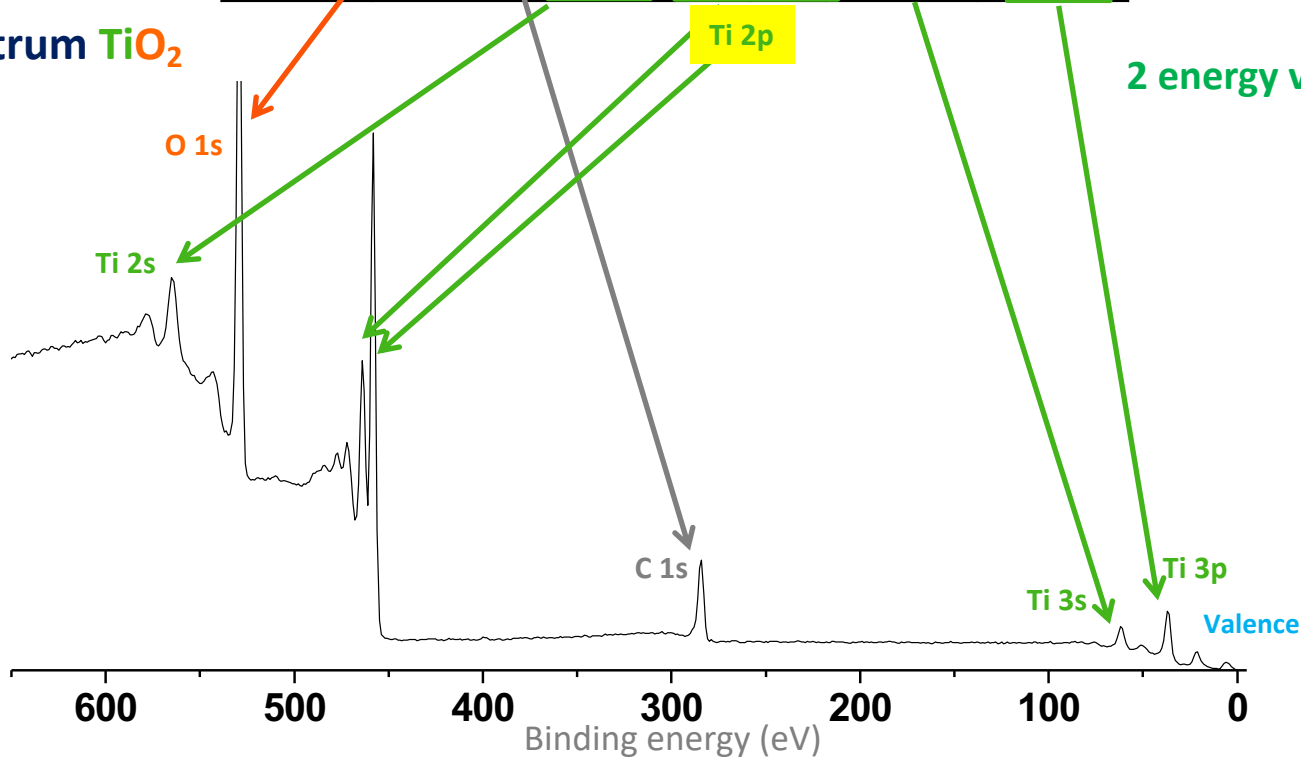
Survey spectrum SiO₂

Atomic Identification – Core peaks

The binding energies (eV) are tabulated like in this exemple:

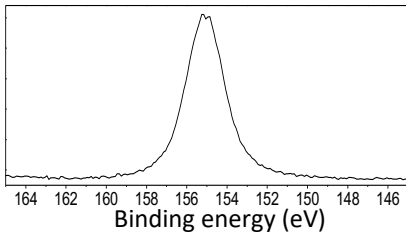
	1s	2s	2p	3s	3p
Li ₃	55				
Be ₄	111				
B ₅	188		5		
C ₆	285		7		
N ₇	400		9		
O ₈	531	24	7		
Ti ₂₂		564	455 461	59	34

Survey spectrum TiO₂

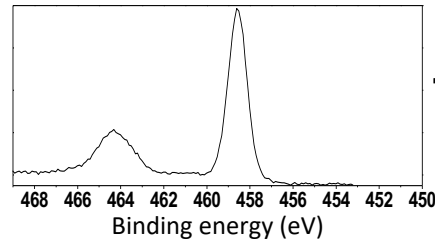


Core Peak : shapes and denomination

For s orbital, **one peak** is observed :



For p, d, f orbitals, **two peaks** are observed :



→ Defining only one kind of atom

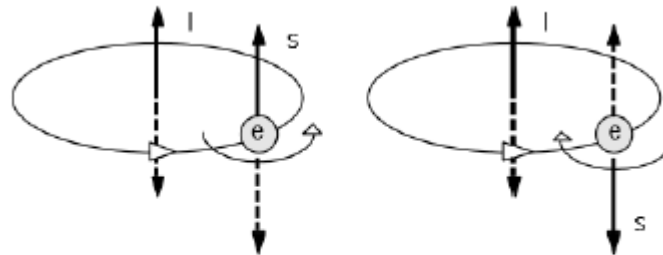
The separation between the two peaks are named **spin orbital splitting**.

This splitting is due to the combination between two characteristics of the photoionized electron:

- its angular momentum l (velocity and radius of the orbit)
- its spin momentum s

Spin-orbit coupling

Coupling between magnetic fields of spin (s) and orbital angular momentum ($l \neq 0$)



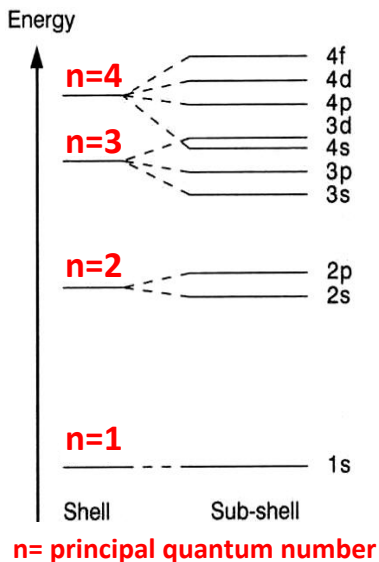
lower BE unfavorable alignment $j = l + s$

favorable alignment **higher BE** $j = l - s$

Depending on the electron movement compared to the orbital movement

Spin-orbit splitting → **Initial state effect**

Core Peak : shapes and denomination

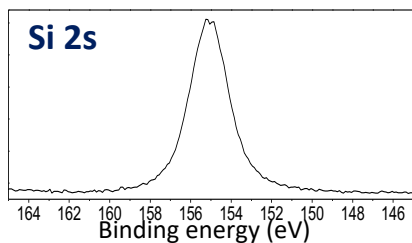


l = orbital angular momentum quantum number	n				j = total angular momentum quantum number $j = l \pm 1/2$	Peaks Area ratio depend on the (2j+1) values
	n=1	n=2	n=3	n=4		
l=0	1s	2s	3s	4s	l=0 → 1/2	l=0 → /
l=1		2p	3p	4p	l=1 → 1/2 3/2	l=1 → 1 : 2
l=2			3d	4d	l=2 → 3/2 5/2	l=2 → 2 : 3
l=3				4f	l=3 → 5/2 7/2	l=3 → 3 : 4

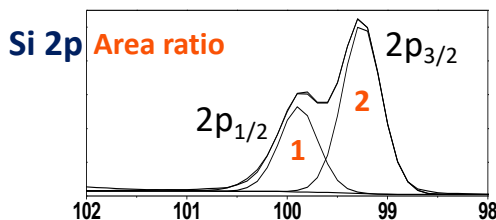
2 peaks, one for each j value

Peak denomination nlj

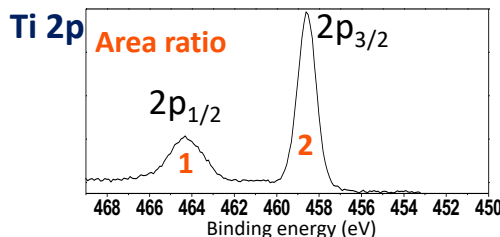
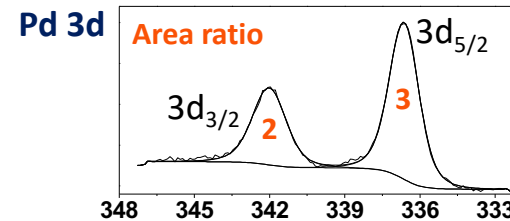
2s



2p_{3/2} - 1/2



3d_{5/2} - 3/2





1- What allows XPS ?

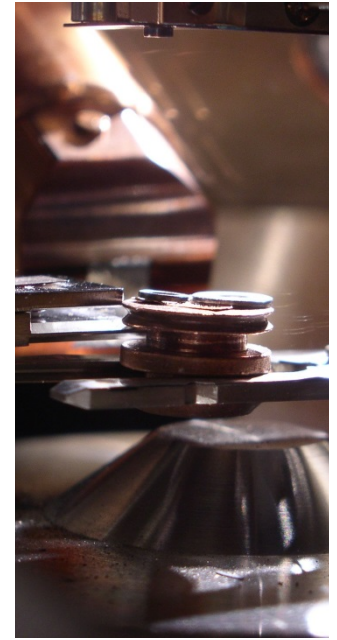
Surface analysis

Atomic Identification

Quantitative analysis

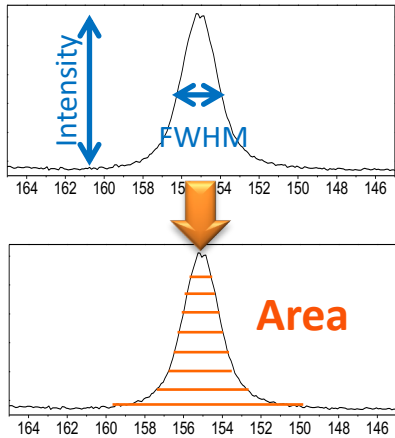
Chemical analysis

2- Equipment



3- XPS to characterize glassy materials

Quantitative analysis



Intensity

Full Width Half Maximum (FWHM)

Area

Depends on

- Spectrometer characteristics
- Sample: element concentration, photoemission cross section ...

The quantification is obtained in atomic percentage, and is not an absolute quantification

Modulated by **Photoionisation cross section σ_{eff}** or **Relative Sensitivity Factors (RSFs)**

Journal of Electron Spectroscopy and Related Phenomena, 8 (1976) 129–137
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HARTREE-SLATER SUBSHELL PHOTOIONIZATION CROSS-SECTIONS
AT 1254 AND 1487 eV

Mg K α

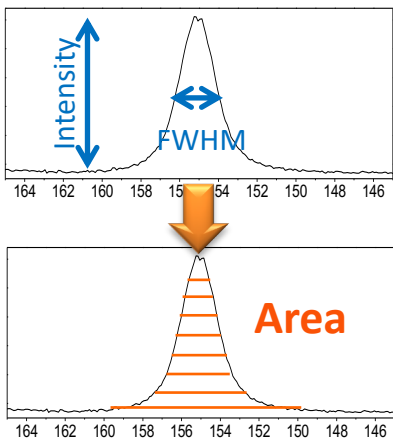
Al K α

J. H. SCOFIELD

Lawrence Livermore Laboratory, University of California, Livermore, California 94550 (U.S.A.)

(First received 27 June 1975; in final form 20 August 1975)

Quantitative analysis



Intensity

Full Width Half Maximum (FWHM)

Area

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Modulated by **Photoionisation cross section σ_{eff}** or **Relative Sensitivity Factors (RSFs)**

Table 2. Photoionization cross sections at 1487 eV in units of the C 1s cross section of 13,600 barns.

Z	Total	1s1/2	2s1/2	2p1/2	2p3/2	3s1/2	3p1/2	3p3/2	3d3/2	3d5/2	4s1/2
H	1	0.0002	0.0002								
He	2	0.0082	0.0082								
Li	3	0.0576	0.0568	0.0008							
Be	4	0.202	0.1947	0.0072							
B	5	0.508	0.486	0.0220	0.0001	0.0001					
C	6	1.05	1.000	0.0477	0.0005	0.0010					
N	7	1.89	1.80	0.0867	0.0022	0.0043					
O	8	3.09	2.93	0.1405	0.0065	0.0128					
F	9	4.68	4.43	0.210	0.0161	0.0317					
Ne	10	6.70	6.30	0.296	0.0347	0.0683					
Na	11	9.14	8.52	0.422	0.0654	0.1287	0.0064				
Mg	12	12.11	11.10	0.575	0.1125	0.221	0.0285				
Al	13	1.35		0.753	0.1811	0.356	0.0535	0.0011	0.0022		
Si	14	1.87		0.955	0.276	0.541	0.0808	0.0047	0.0093		
P	15	2.52		1.18	0.403	0.789	0.1116	0.0124	0.0244		
S	16	3.33		1.43	0.567	1.11	0.1465	0.0262	0.0512		
Cl	17	4.31		1.69	0.775	1.51	0.1852	0.0486	0.0947		
Ar	18	5.49		1.97	1.03	2.01	0.227	0.0821	0.1597		
K	19	6.90		2.27	1.35	2.62	0.286	0.1229	0.239		
Ca	20	8.55		2.59	1.72	3.35	0.351	0.1720	0.335		
Sc	21	10.39		2.91	2.17	4.21	0.411	0.221	0.429	0.0017	0.0025
Ti	22	12.48		3.24	2.69	5.22	0.473	0.276	0.537	0.0055	0.0081
V	23	14.64		3.57	3.29	6.37	0.538	0.339	0.657	0.0125	0.0184
Cr	24	17.43		3.91	3.98	7.69	0.596	0.400	0.773	0.0264	0.0387
Mn	25	20.39		4.23	4.74	9.17	0.674	0.485	0.938	0.0424	0.0622
Fe	26	23.61		4.57	5.60	10.82	0.745	0.569	1.10	0.0694	0.1017
Co	27	27.10		4.88	6.54	12.62	0.818	0.660	1.27	0.1082	0.1582
											0.0069
											0.0268
											0.0314
											0.0355
											0.0394
											0.0497
											0.0497
											0.0529

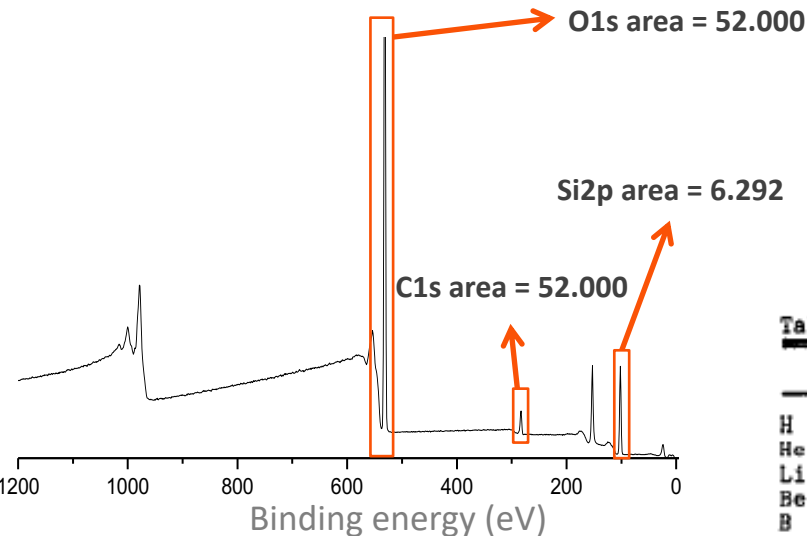
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(First received 27 June 1975; in final form 20 August 1975)

Quantitative analysis

Survey spectrum SiO₂



For quantification :
only ONE orbital for each atom

Quantitative result:

> Without considering cross-section values:

	C	O	Si	SiO₇
Atomic %	4	84	12	

> Considering cross-section values:

Table 2. Photoionization cross sections at 1487 eV in

Z	Total	1s1/2	2s1/2	2p1/2	2p3/2
H	1	0.0002	0.0002		
He	2	0.0082	0.0082		
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Be	4	0.202	0.1947	0.0072	
B	5	0.508	0.486	0.0220	0.0001
C	6	1.05	1.000	0.0477	0.0005
N	7	1.89	1.80	0.0867	0.0022
O	8	3.09	2.93	0.1405	0.0065
F	9	4.68	4.43	0.210	0.0161
Ne	10	6.70	6.30	0.296	0.0347
Na	11	9.14	8.52	0.422	0.0654
Mg	12	12.11	11.10	0.575	0.1125
Al	13	1.35		0.753	0.1811
Si	14	1.87		0.955	0.276 + 0.541

C1s $\sigma_{\text{eff}}=1$

O1s $\sigma_{\text{eff}}=2.93$

Si2p $\sigma_{\text{eff}}=0.817$

	C	O	Si	SiO_{2.4}
Atomic %	7	66	27	

Use of **Relative Sensitivity Factors (RSFs)** to convert the recorded signal to a corrected intensity for use in a **quantification calculation**



1- What allows XPS ?

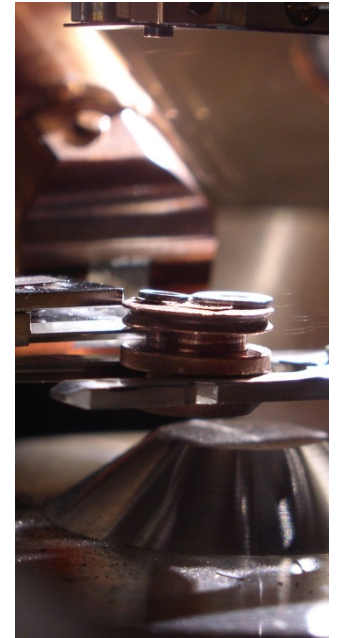
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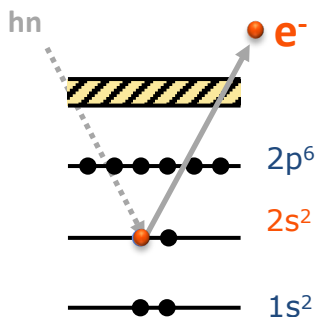
2- Equipment



3- XPS to characterize glassy materials

Core peaks: Binding energy value and shift

Xray beam $h\nu$ → Photoelectron e^- → Kinetic energy E_{kin} of the ejected electron measured



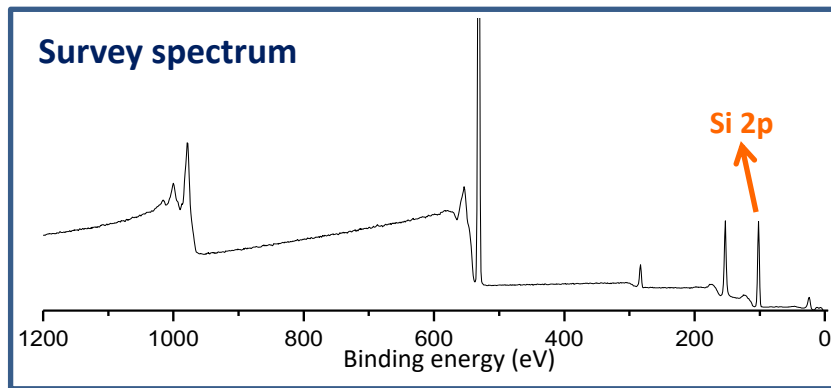
Binding energy E_b of this electron

$$E_b = h\nu - E_{kin}$$

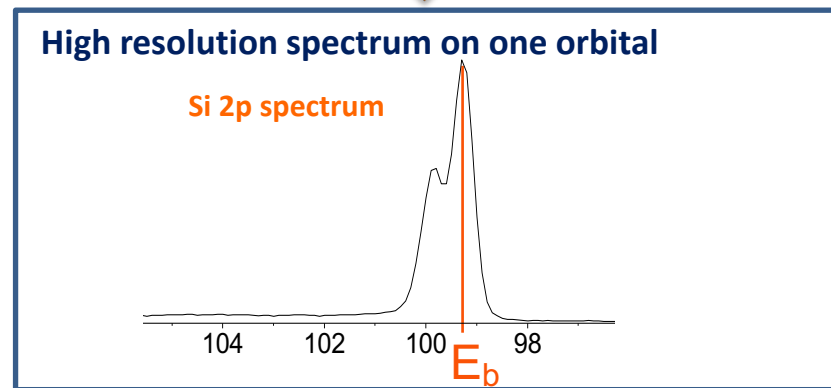
Silicon, Si Atomic Number 14

COMPOUND	2p BINDING ENERGY, eV	REF.
Si	98	Φ
Si	103	CDB
Si	108	MV
Si		HBB
Ph ₄ Si		MV
Ph ₄ Si		NBA
Ph ₄ Si		GCH
Ph ₃ SiSiPh ₃		NBA
Ph ₃ SiSiPh ₃		GCH
Me ₃ SiSiMe ₃		GCH
Me ₃ SiNHSiMe ₃		GCH
Me ₃ SiOSiMe ₃		GCH
Ph ₂ Si(OH) ₂		NBA
Ph ₂ SiOH		NBA
Ph ₂ SiOSiPh ₃		GCH
Et ₃ SiCl		GCH
(Me ₂ SiO) ₅		GCH
(Me ₂ SiO) _n		NBA
Et ₃ SiF		GCH
Et ₂ SiCl ₂		GCH
EtSiCl ₃		GCH
SiI ₄		NBA
Na zeolite silicates		MW, CDB
SiS ₂		MV
SiO ₂		Φ
SiO ₂		NSL
SiO ₂		MV

Handbook of Xray Photoelectron Spectroscopy
Perkin Elmer Edition



Atomic identification

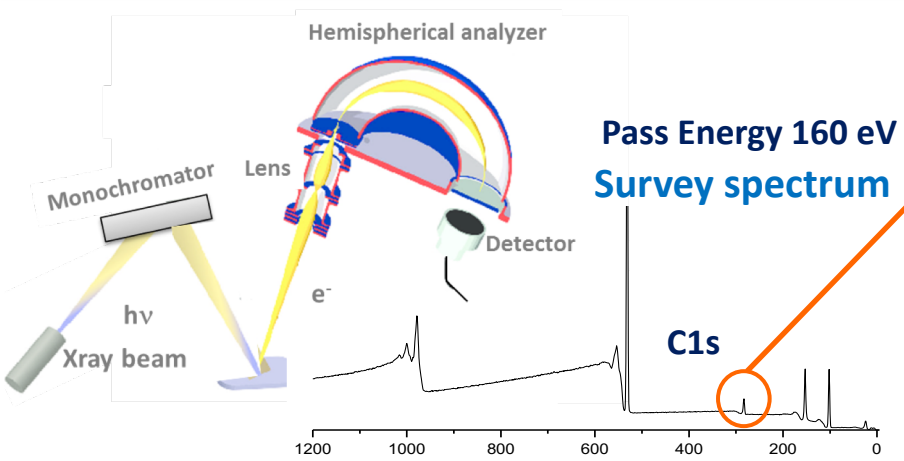


Chemical identification

Binding energy → Position and Shifts

oxydation number, variation in chemical environment, bonds,²²...

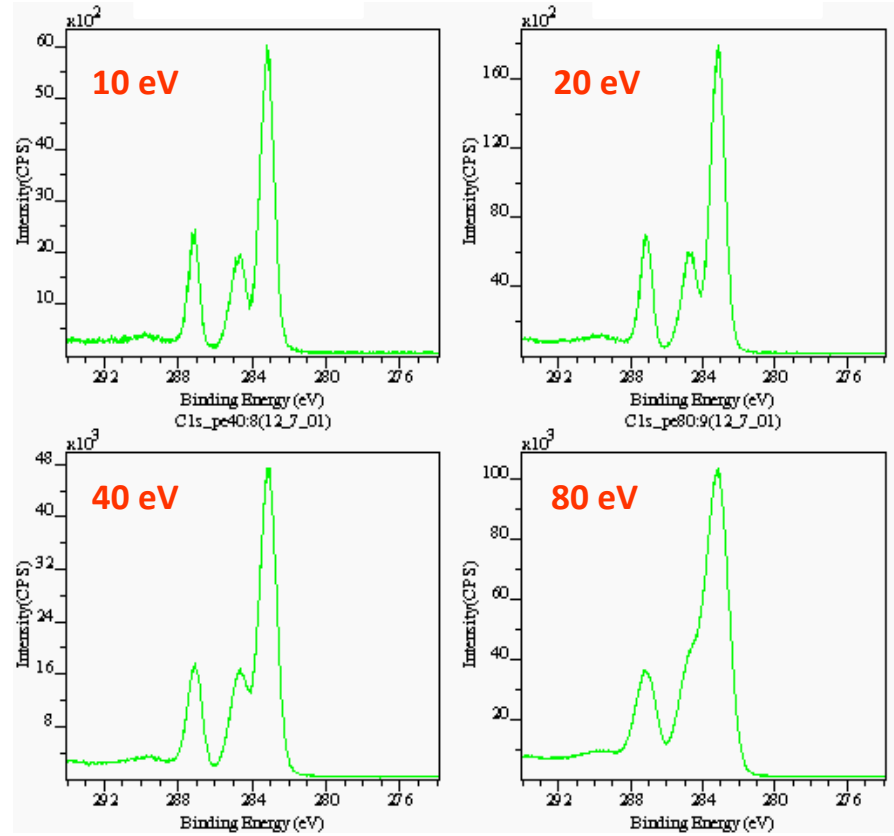
Core peaks : acquisition



Carbon is present. But what is its environment ?

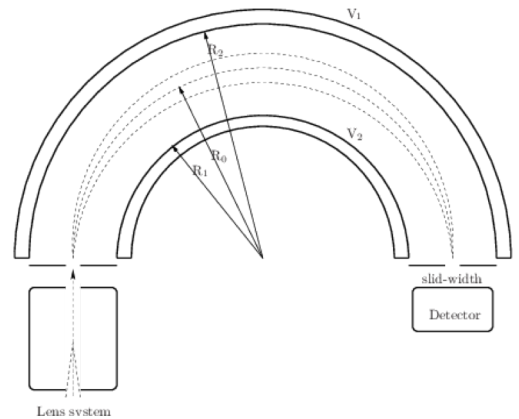
High resolution spectrum C 1s

C1s spectra at different Pass Energies 10-80 eV



Energy resolution depends on Analyzer Pass Energy

The **pass energy** translates the potential difference between inner and outer hemisphere of the analyzer



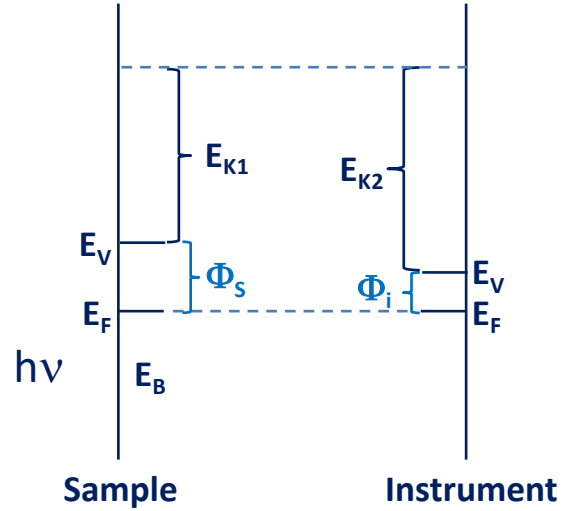
When Pass Energy ↓ → Energetic resolution ↗

Intensity ↓

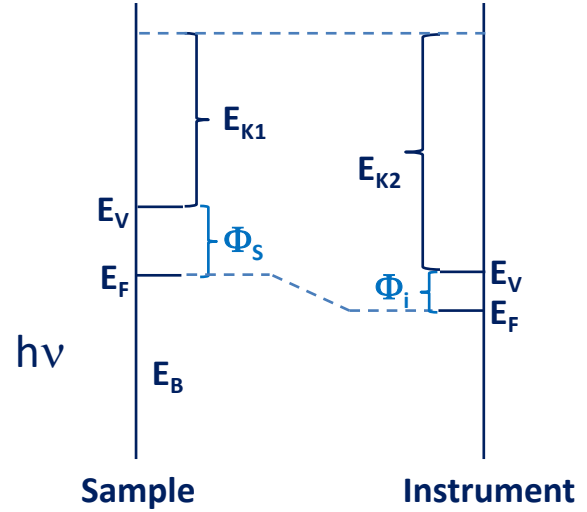
Acquisition time ↗ to reach a good signal/noise ratio

Core peaks : binding energy calibration

For a conducting sample:



For an insulating sample:



Conducting sample in electrical contact with the spectrometer
 → Fermi level equalization

Binding energy calculation: The measured kinetic energy of the photoelectron is influenced by :

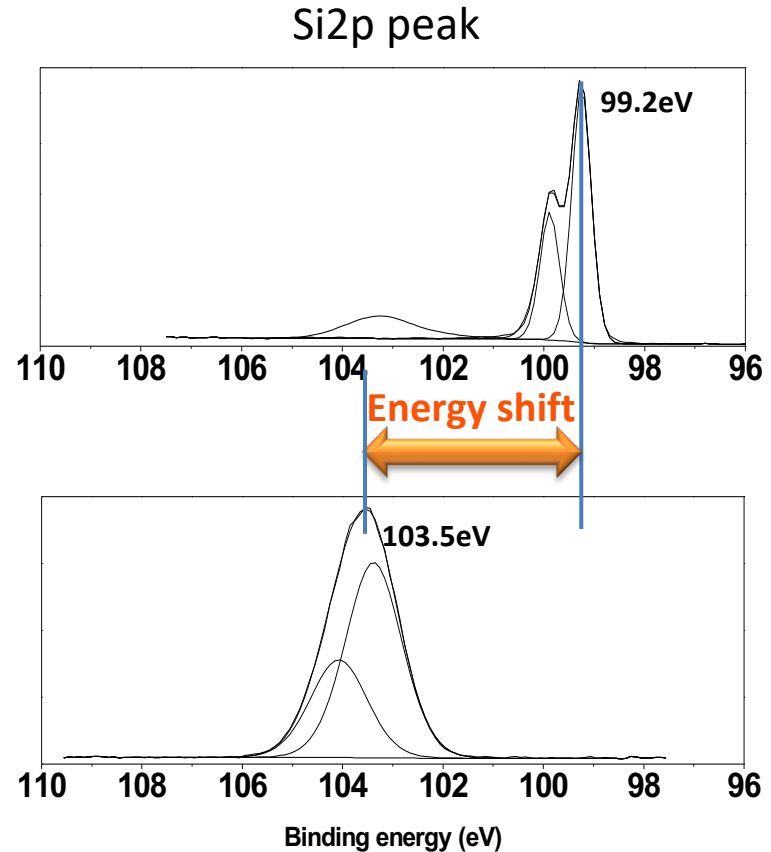
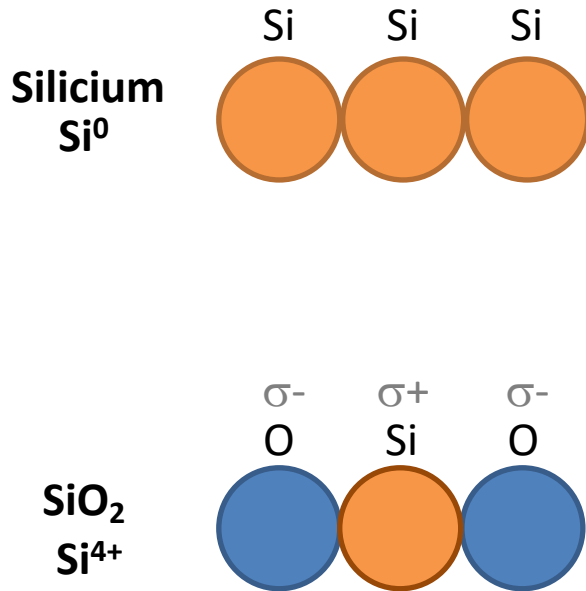
- the work function of the sample: Φ_S
- the work function of the instrument : Φ_i

Internal reference is needed for calibration of all the binding energies of the sample:

Exemples : C1s: 285.0 eV Au4f_{7/2}: 84.0 eV

Chemical characterisation – Binding energy shifts

Change of oxydation degree

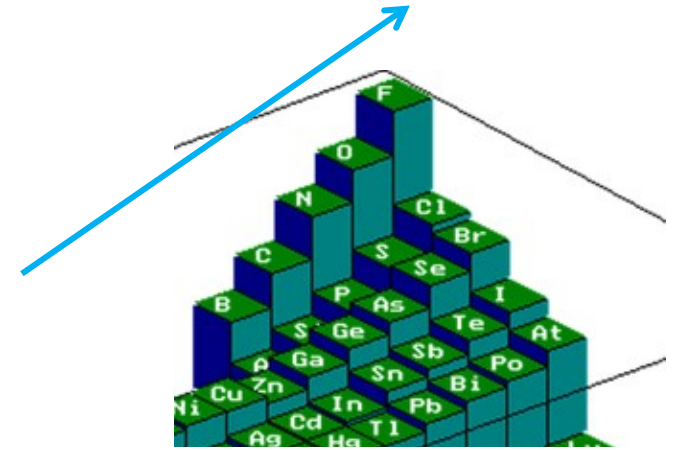
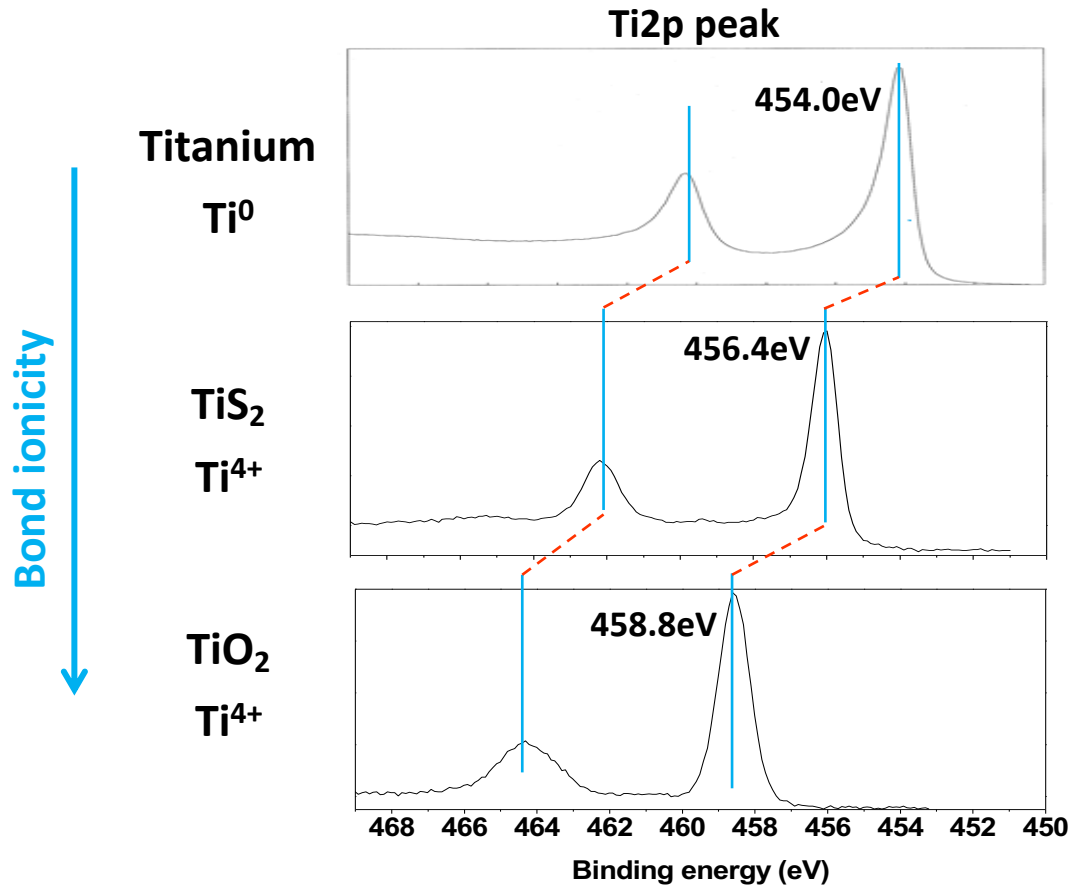


In the bond, the Si valence electrons are attracted by the Oxygen atoms. The oxydation state of the silicium atoms change $\text{Si}^0 \rightarrow \text{Si}^{4+}$.

The remaining Si valence electrons are more attracted by the positive charge of the nucleus, the binding energy is then increasing in the Si-O bond compare to Si neutral.

Chemical characterisation – Binding energy shifts

Change of neighbour characteristic



Electronegativity evolution

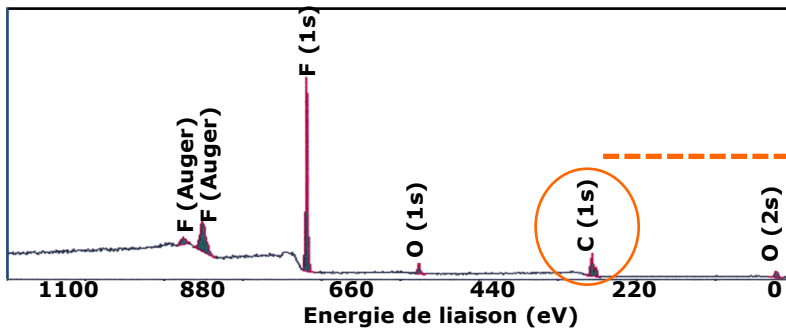
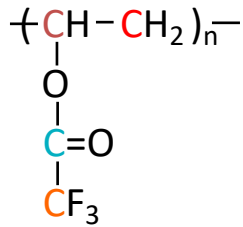
Electronic distribution around the Ti nucleus \neq in TiS_2 and TiO_2 , even if the titanium is referenced in the oxidation number Ti^{4+} in both cases.

Oxygen is more electronegative than sulfur, then the Ti-O bonds is more ionic than Ti-S bonds.

When the electronegativity of the ligand increases, the nucleus feels a depletion in electrons. The remaining electrons are then more attracted by the positive field of the nucleus.

Chemical characterisation – Binding energy shifts

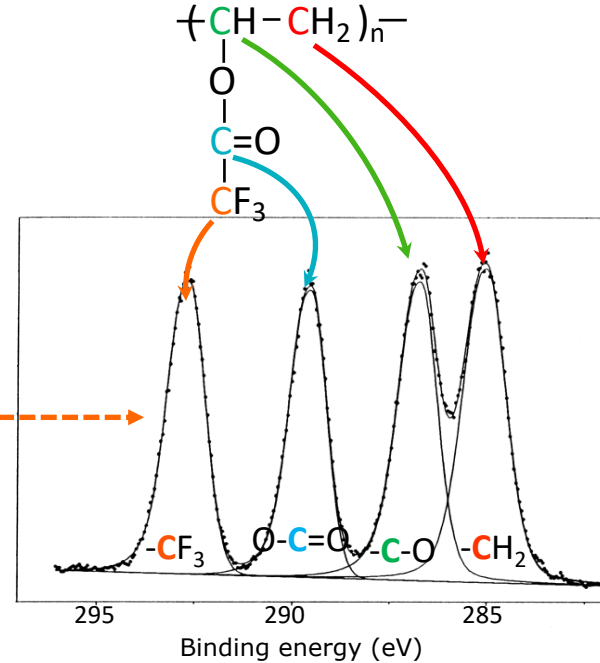
Survey spectrum for this molecule:



Identification of all the atoms present at the surface of the sample

Powerful technique to identify the chemical environments and their proportion

High resolution C1s spectrum



Identification of the 4 different chemical environments for Carbon atoms

4 C1s peaks with same area

The areas can be directly compared because these peaks correspond to the same orbital of the same atom so same cross section σ_{eff}

The binding energy of the C1s peak is changing, depending on the attractivity of the ligand on the carbon electronic cloud.

Chemical characterisation – Other probes

When chemical shift of the principal core peak is not large enough

→ other probes are useful.

“Shake up” satellites

Multiplet splitting

Auger peaks

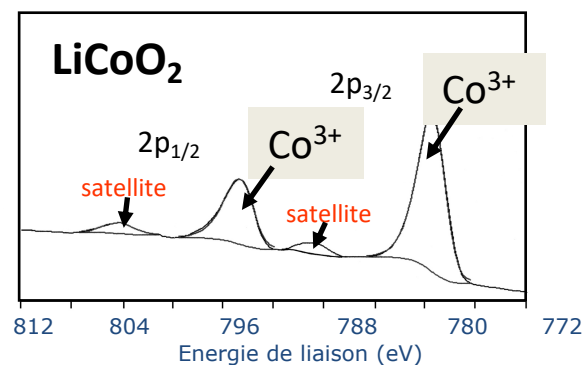
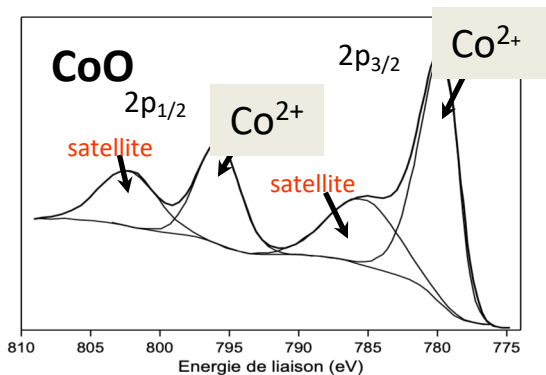
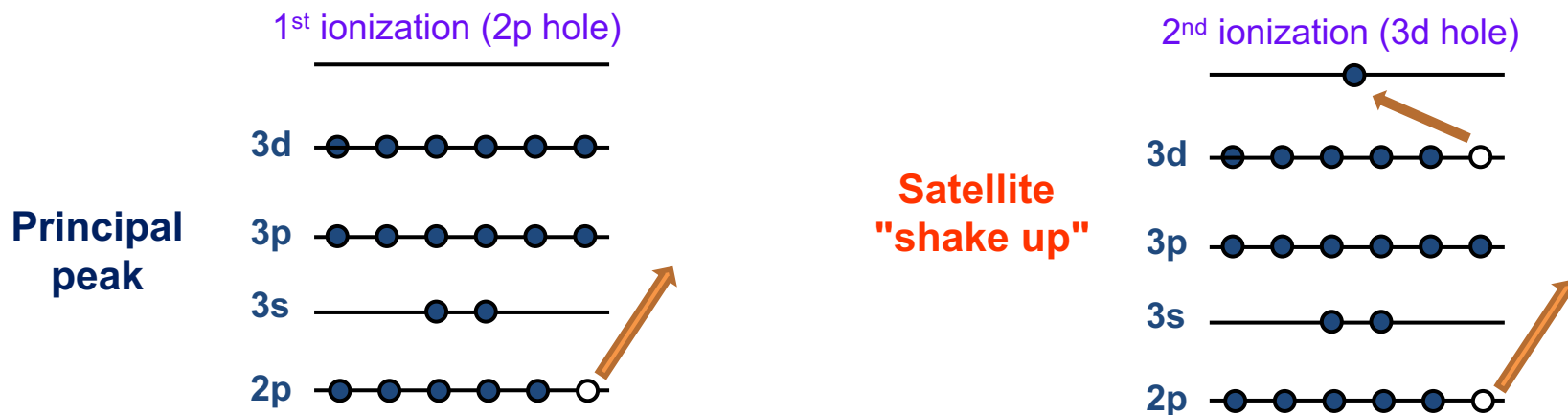
Valence spectra

Chemical characterization - Peaks and satellites

“Shake up” satellites

Multielectronic character of the photoemission

$\text{Co}^{3+} (\text{d}^6)$

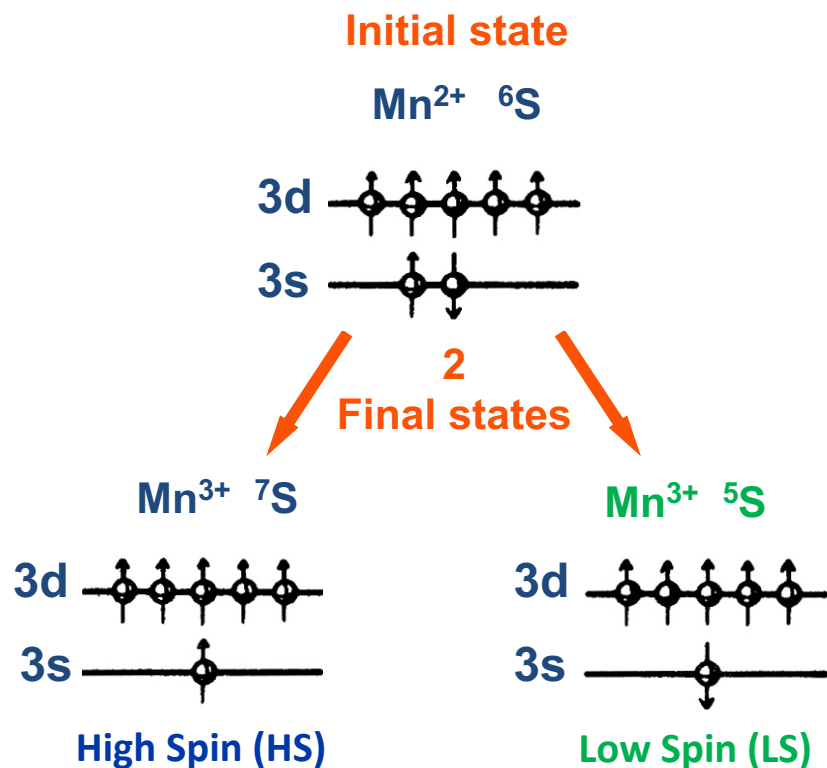


The position and intensity of the satellite can help to elucidate the oxidation degree of the atom.

Chemical characterization - Peaks and satellites

“Multiplet” Structures / Multiplet splitting

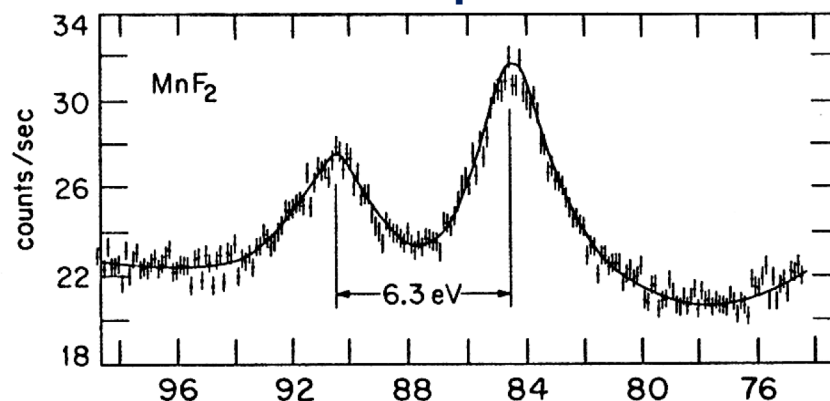
For system with unpaired electrons in valence levels → several final states



B.E. (HS) < B.E. (LS)

MnF_2

Mn3s peak

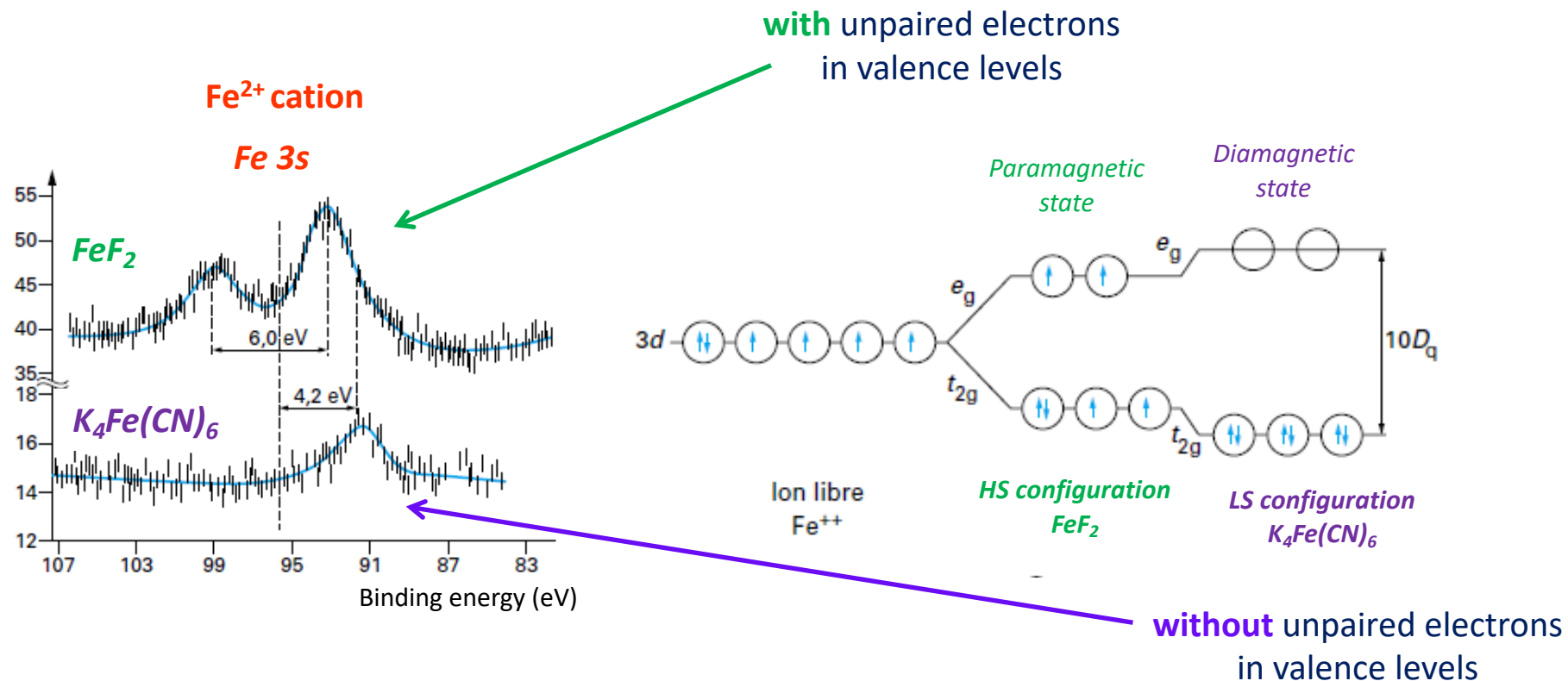


Mn^{2+} : 6.3 eV – Mn^{3+} : 5.5eV – Mn^{4+} : 4.5eV

Strongest multiplet splitting when both levels involved are in the same shell (3s/3p-3d) more than (2p/3p-3d).

Chemical characterization - Peaks and satellites

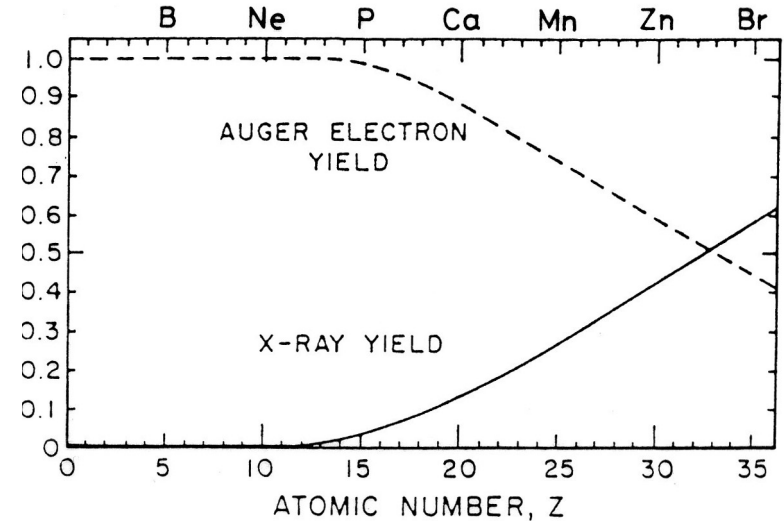
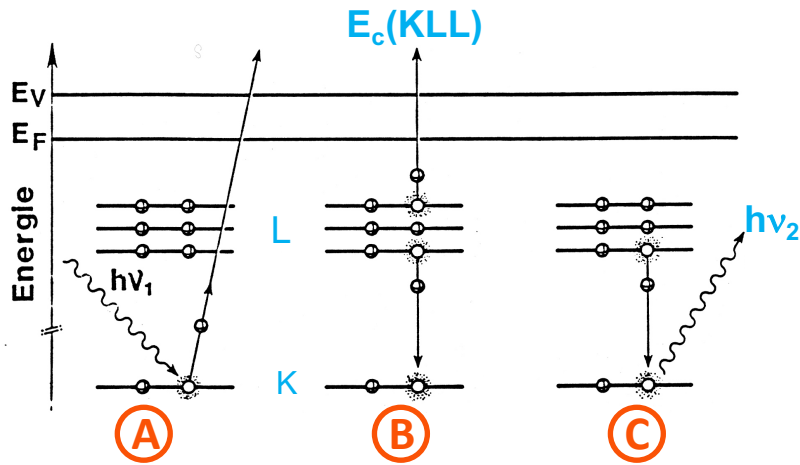
Multiplet splitting



The shape of the peak with or without multiplet splitting can give informations on the electronic valence organization

Chemical characterization – Auger peaks

Relaxation phenomena – Auger process or X-ray fluorescence



Relative probability of Auger emission and X-ray emission depending on the atomic number of atom

(A) : photoionisation ($A + h\nu_1 \rightarrow A^+ + e^-$)

Emission of an XPS core electron => core peak

(B) : desexcitation through Auger effects ($A^+ \rightarrow A^{++} + e^-$)

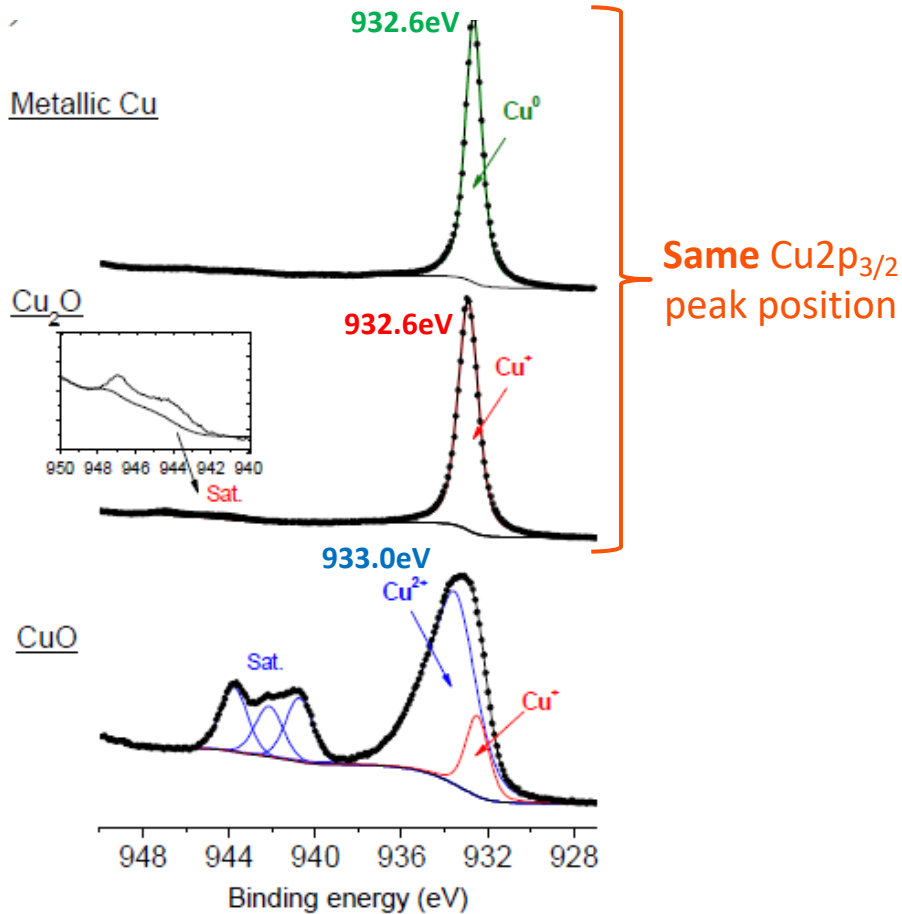
Emission of an Auger electron named: $KL_1L_{2,3}$ => **Auger peak**

(C) : desexcitation through fluorescence X ($A^+ \rightarrow A^+ + h\nu_2$)

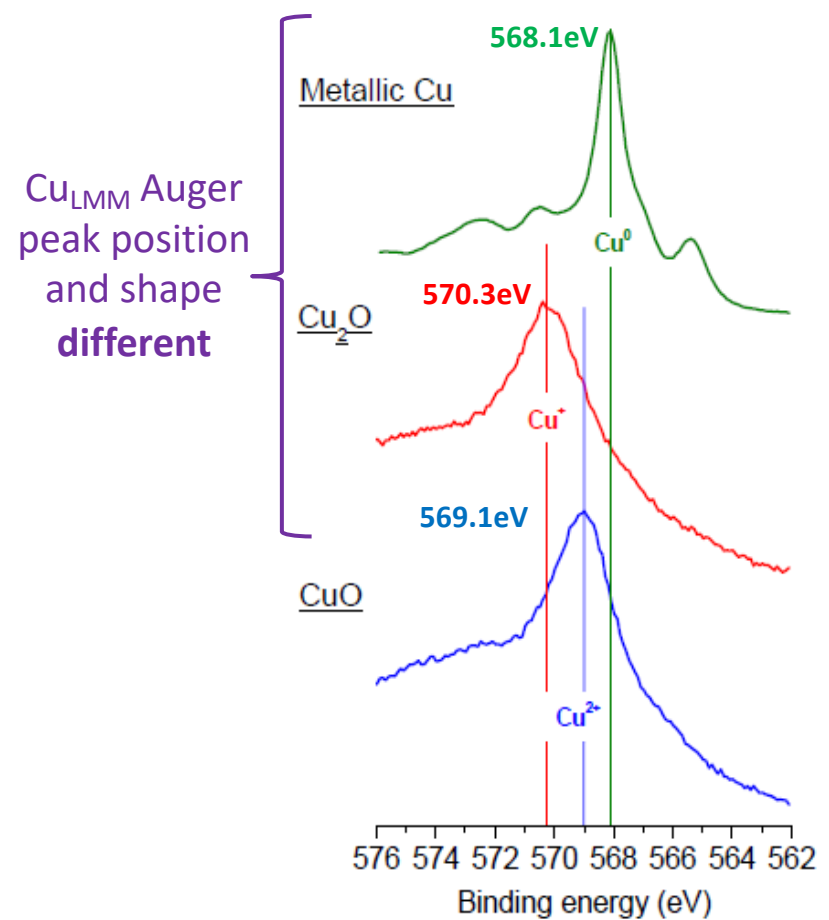
XPS peaks: E_b independant from $h\nu$
 Auger peaks: E_c independant from $h\nu$

Chemical characterization – Auger peaks

Cu 2p_{3/2} core peaks



Cu_{LMM} Auger peaks



A new physical scale is defined: **the Auger parameter α**

$$\alpha = E_{\text{kin KLL}} + E_{\text{b(K)}}$$

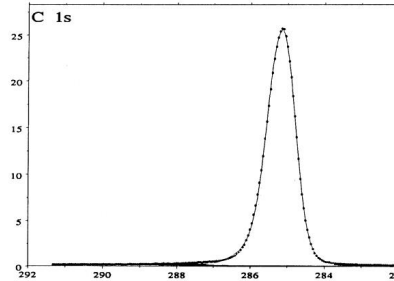
Cu⁰
 $\alpha = 1486,6 - 568,1 + 932,6$
 $\alpha = 1851,1 \text{ eV}$

Cu⁺
 $\alpha = 1486,6 - 570,3 + 932,6$
 $\alpha = 1848,9 \text{ eV}$

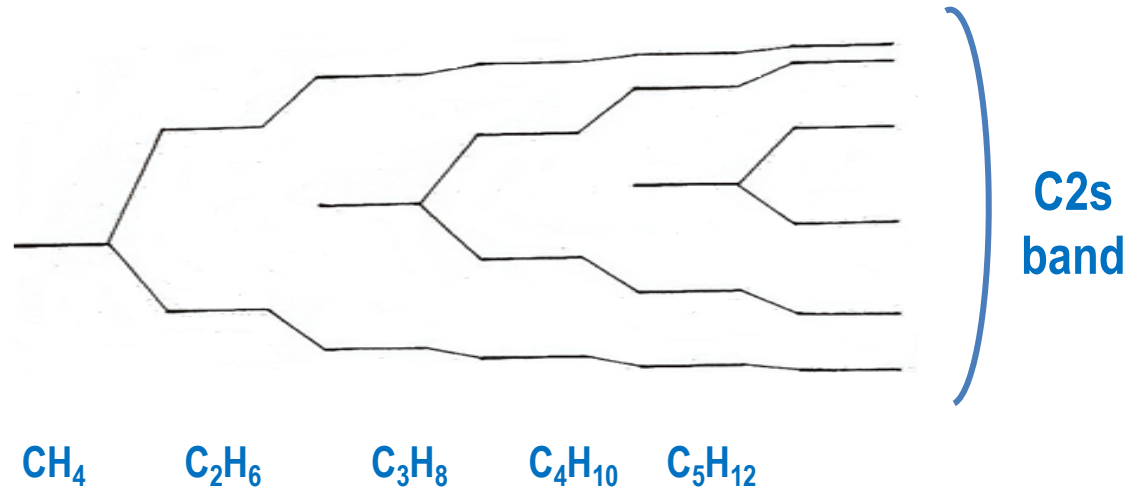
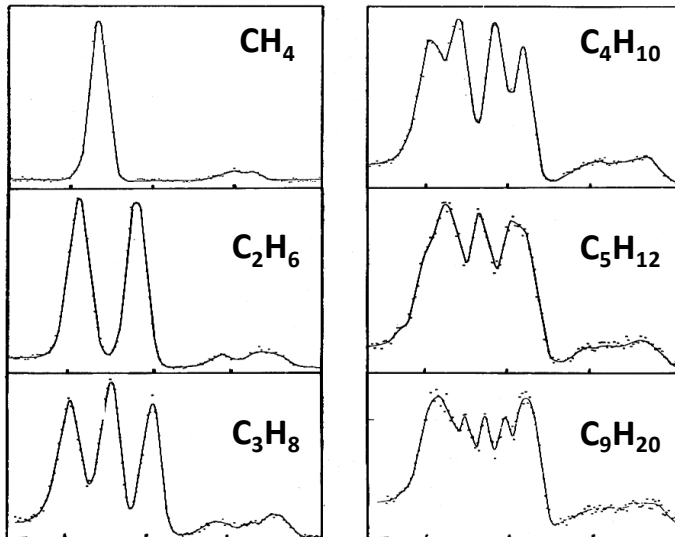
Cu²⁺
 $\alpha = 1486,6 - 569,1 + 933,0$
 $\alpha = 1850,5 \text{ eV}$

Chemical characterisation - Valence spectra

Experimental visualisation of density of states DOS
highest occupied electronic level (0 à 30eV)
characteristic of bonds



Valence spectra of alkanes



Evolution of electronic level
toward a band structure



1- What allows XPS ?

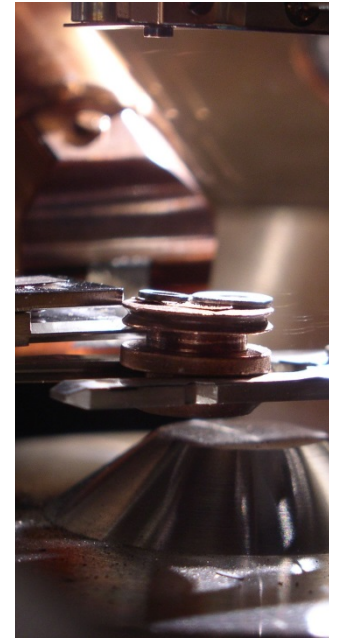
Surface analysis

Atomic Identification

Quantitative analysis

Chemical analysis

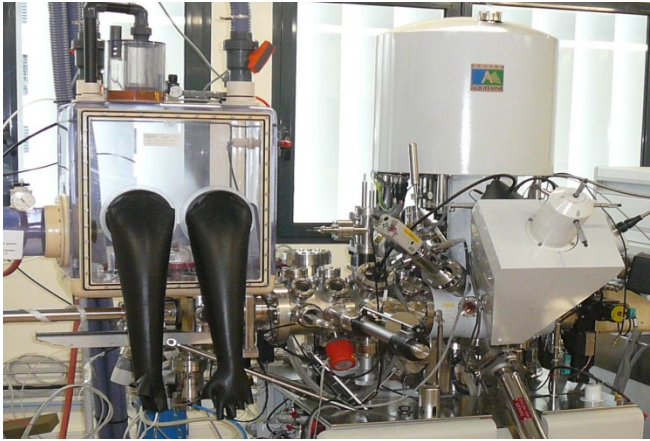
2- Equipment



3- XPS to characterize glassy materials

XPS spectrometer

Kratos – Axis Ultra



THERMO SCIENTIFIC - Escalab 250Xi

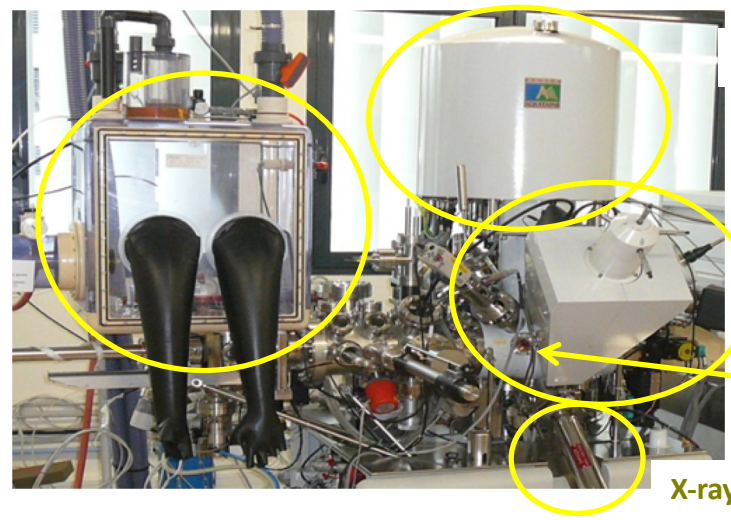


THERMO SCIENTIFIC – K-Alpha



All our spectrometer are directly connected to a glove box in Ar atmosphere

XPS spectrometer



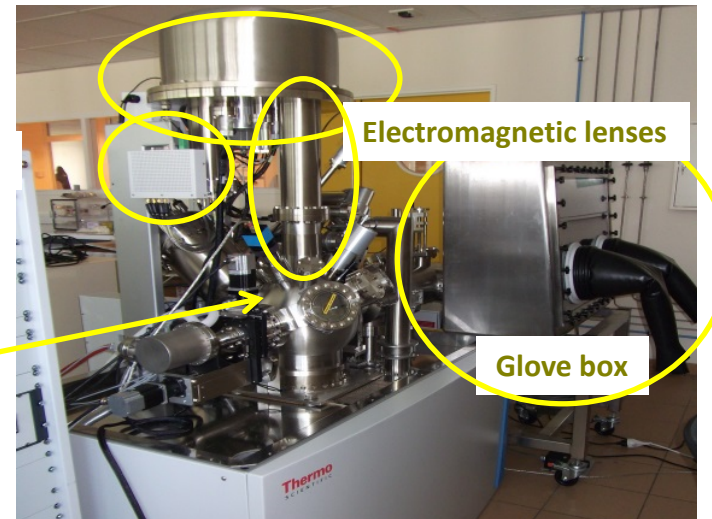
Electron energy analyser

Detection system

Monochromator

Sample

X-ray source

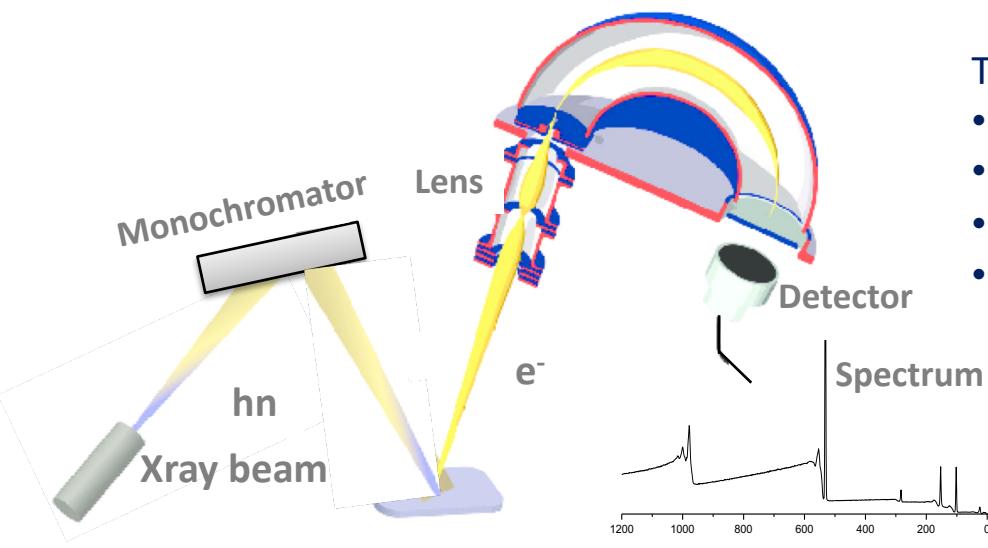


Electromagnetic lenses

Glove box

Vacuum system : many pumps to have an ultra high vacuum in any parts of the system ($\sim 10^{-9}$ mbar)

Hemispherical analyzer



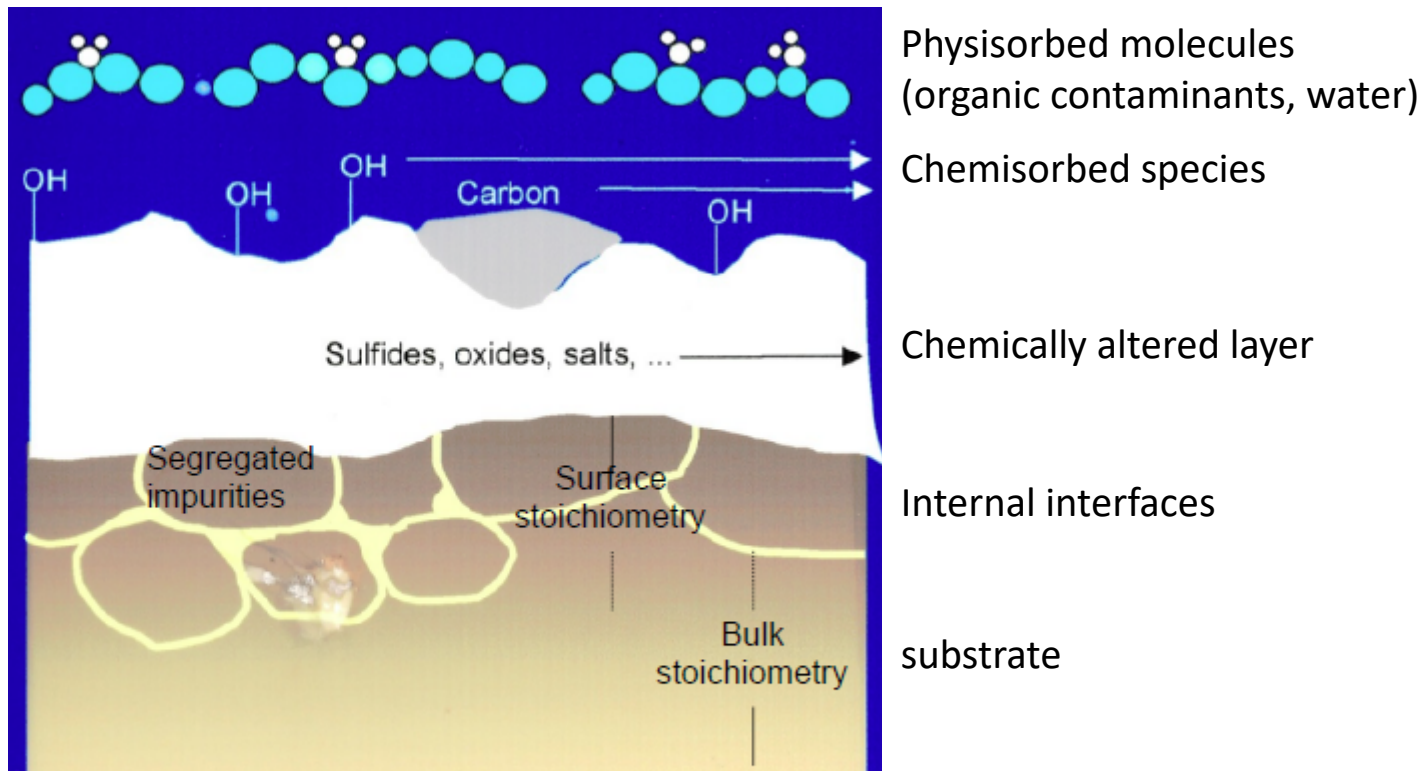
The photoelectrons are:

- **Ejected** from the sample surface with an KE
- **Focused** and transferred by electromagnetic lenses
- Energy **filtered** by a analyser
- **Detected** and recorded by a counting system

XPS spectrometer

Sample preparation – necessity to have a very clean surface

Very sensitive to extreme surface, top atomic layers



XPS spectrometer

Sample Types/ Samples holders

Capable to analyse samples from different nature without any preparation

Solids

- Bulk, thin films, powders, fibers
- Crystallized, amorphous, compact or porous
- Insulating, semiconducting, conducting
- Stable in the UHV chamber

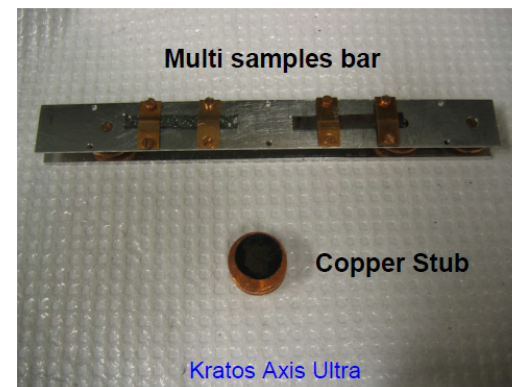
“Cold Analysis” thanks to liquid nitrogen

For materials sensitive to Xray irradiation,
or to freeze Gel / Liquids

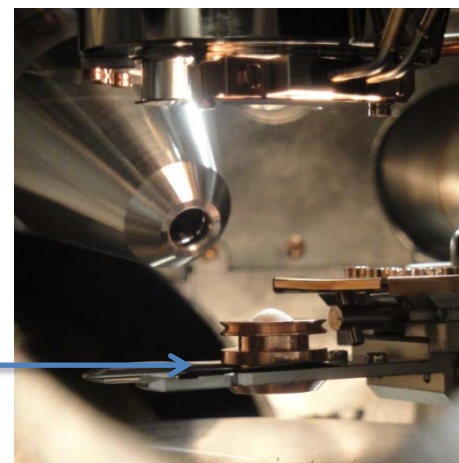
Surface cleaning

Sputter ion sources
In-vacuum fracture
Cross section polisher

Frozen liquid



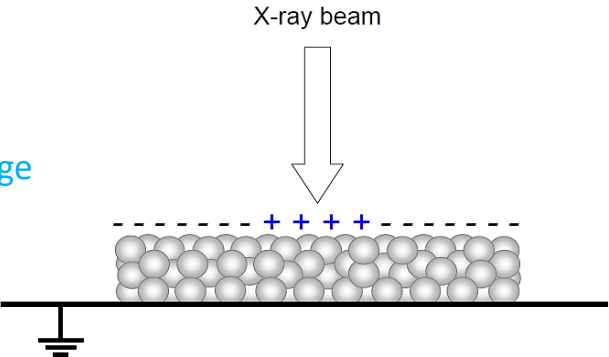
Maintained on the stub or bar with:
- double-sided adhesive tape
- clips



XPS spectrometer - Charge compensation

Why?

Photoemission from an insulating material leads to the build-up of a **positive charge** (insulators cannot dissipate charge generated by photoemission process.)



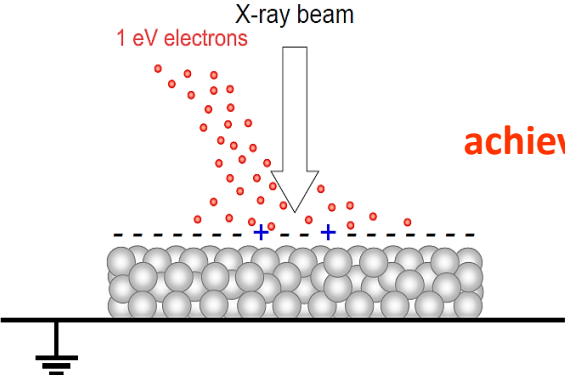
Photoemitted electrons leave local positive charges on the surface

Analysis insulators in XPS presents problems:

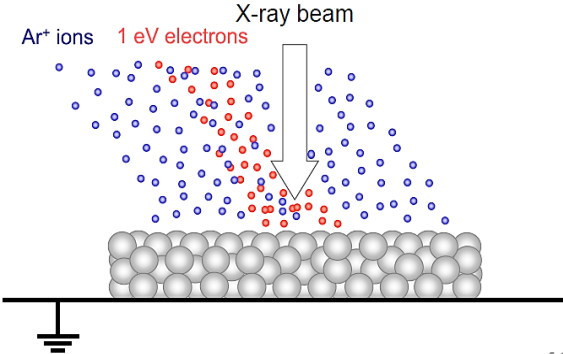
- Spectral peaks are distorted : difficult to **distinguish an artefact from a shift** in energy due to the sample chemistry.
- Apparition of peaks without meaning
- No signal or very shifted

How can we compensate?

An **external source of low-energy electrons** is required in the form of an electron « **flood gun** », to replace emitted electrons



Goal:
achieve a uniform potential surface



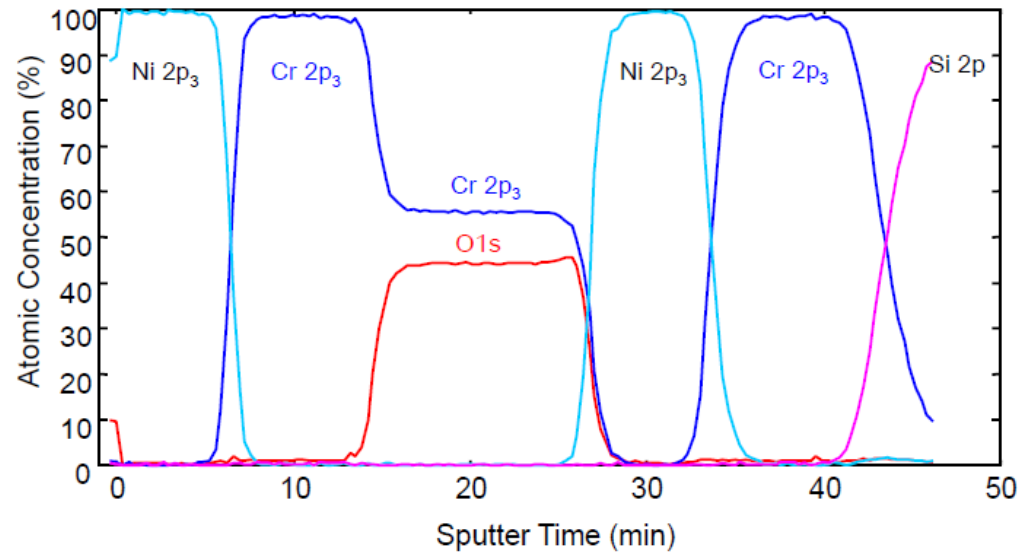
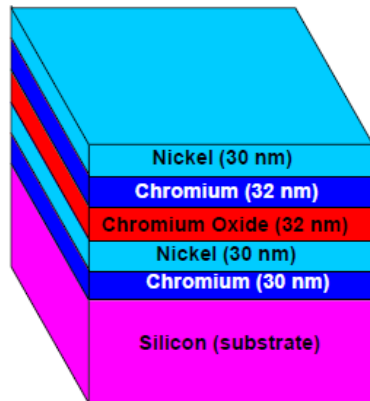
XPS spectrometer – Change depth analysis

Destructive method: Ion etching

Ion mode: monoatomic argon Ar^+ , argon cluster mode Ar_n^+

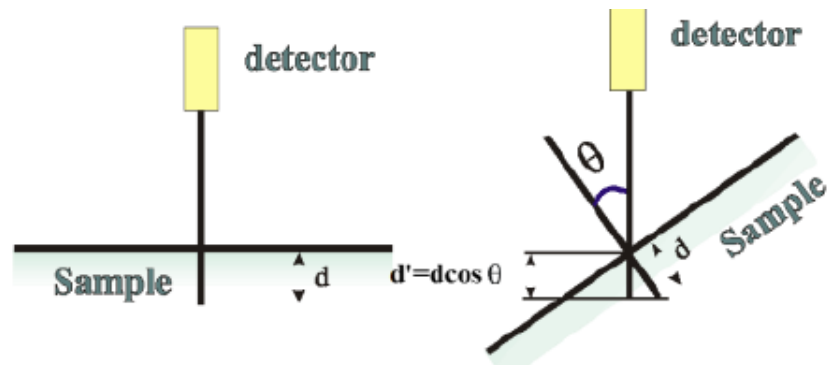
To obtain concentration profile on **depth more than 10 nm**

Sputtering the surface within the spectrometer and use normal mode of XPS (record spectra)



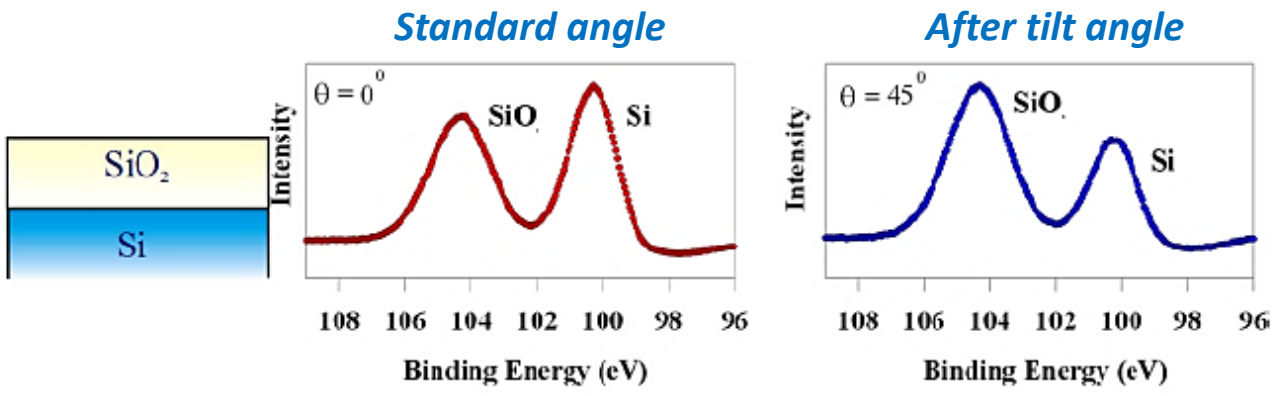
XPS spectrometer – Change depth analysis

Non-destructive method: Variation of analysis angle ARXPS (Angle Resolved XPS)



Analysis depth as a function of detection angle

Si2p spectra



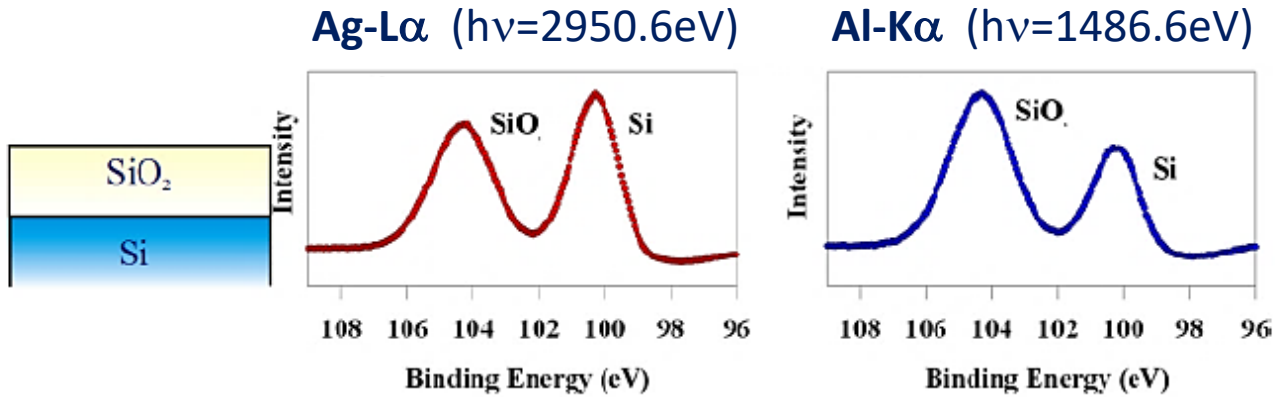
After tilt → exaltation of extreme surface signal : SiO₂ ↗ and Si ↘

XPS spectrometer – Change depth analysis

Non-destructive method: Use of another Xray energy

Possible even in lab with Ag-L α \rightarrow $h\nu=2950.6\text{eV}$

Si2p spectra



With Ag-L α source \rightarrow exaltation of « bulk » signal : SiO₂  and Si 



1- What allows XPS ?

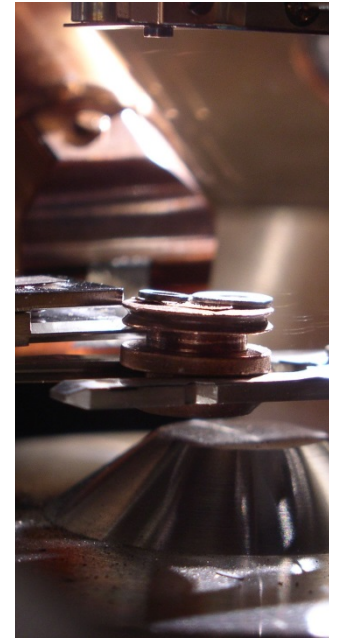
Surface analysis

Atomic Identification

Quantitative analysis

Chemical analysis

2- Equipment



3- XPS to characterize glassy materials

XPS to characterize glassy materials

XPS is sensitive to

short range order,
local structure,
chemical environment of atoms,
electronic distribution ...

Compare to a crystal, a glass doesn't have organization at long range order, and a kind of disorder in bond length, angle values ...

But a glass has well defined short range order and mid-range order (nearest neighbours)

**So XPS is a perfectly suitable tool to characterize
glassy materials as well as crystals**

In glass, disorder exists in bond length, angle...

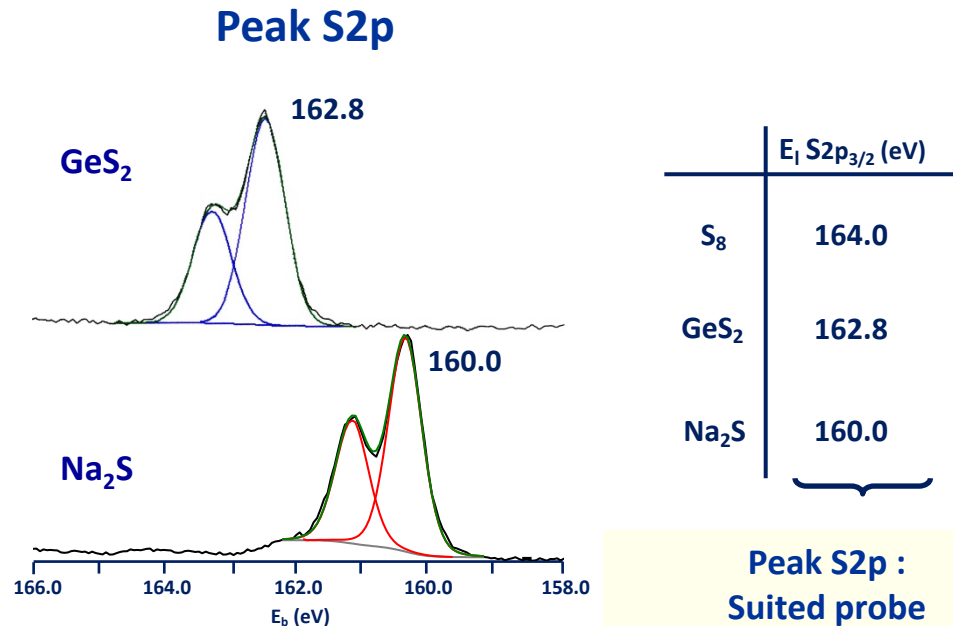


Widening of the peaks compared to the crystal

XPS to characterize glassy materials

Former GeS_2 : covalent bonds

Modifier Na_2S : ionic bonds



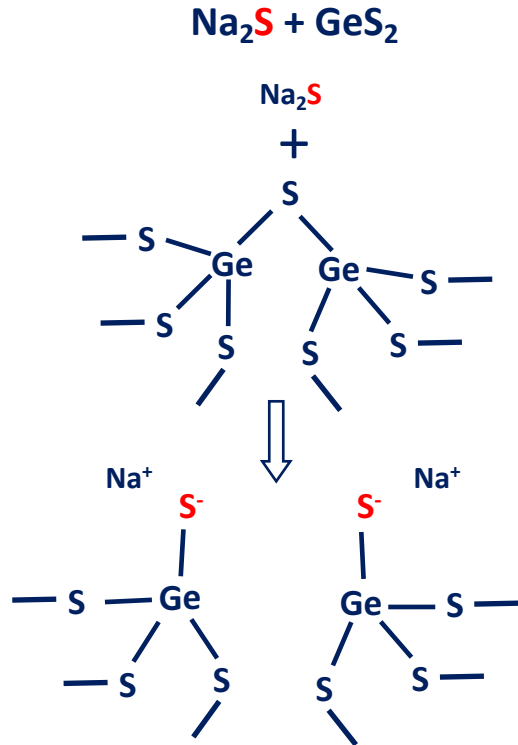
The electronic density around the sulfur is totally different in these two materials because of the bond nature, which is very well translated thanks to the sulfur peak S2p.

Sulfur atoms are more negative in Na_2S , their peak S2p has a lower binding energy compare to GeS_2 .

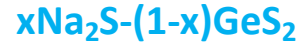
XPS to characterize glassy materials

Influence of the amount of modifier:

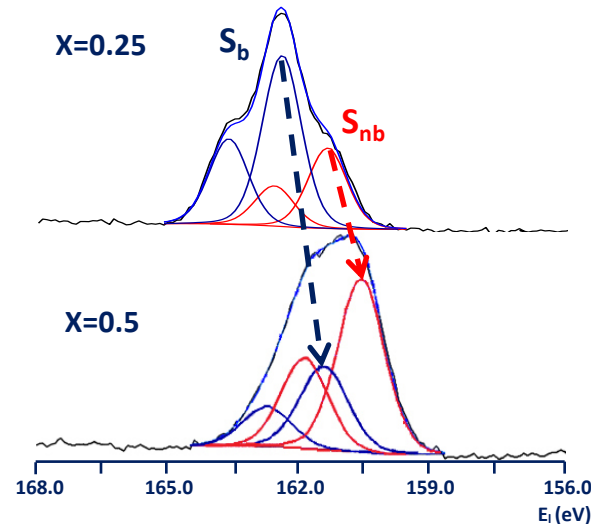
Classical scheme for addition of modifier in former glass



Coexistence of
Bridging sulfur: S_b and
Non-bridging sulfur: S_{nb}



S2p peak



	E_b S2p _{3/2} (eV)	%
X=0.25	S_b 162.5	67%
	S_{nb} 161.5	33%
X=0.5	S_b 161.3	32%
	S_{nb} 160.5	68%

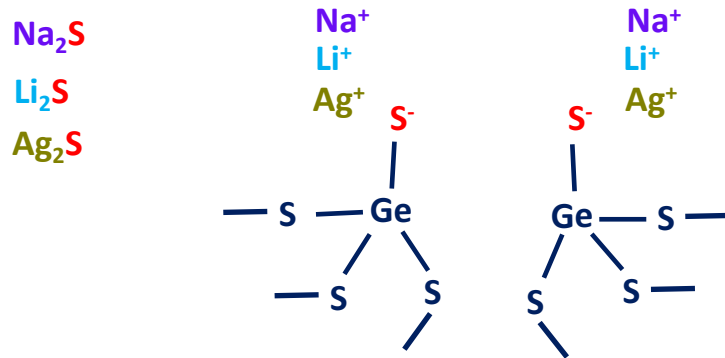
In $x\text{Na}_2\text{S}-(1-x)\text{GeS}_2$, two different environments for sulfur are present. Thanks to the sulfur peak S2p evolution, depending on the **amount of modifier** :

- Evidence of **the evolution of proportion of the two kinds of atom sulfur**.
- Change in the position than in the negative character of sulfur **of the two kinds of atom sulfur**

XPS to characterize glassy materials

Influence of the nature of the modifier cation (x=0.5):

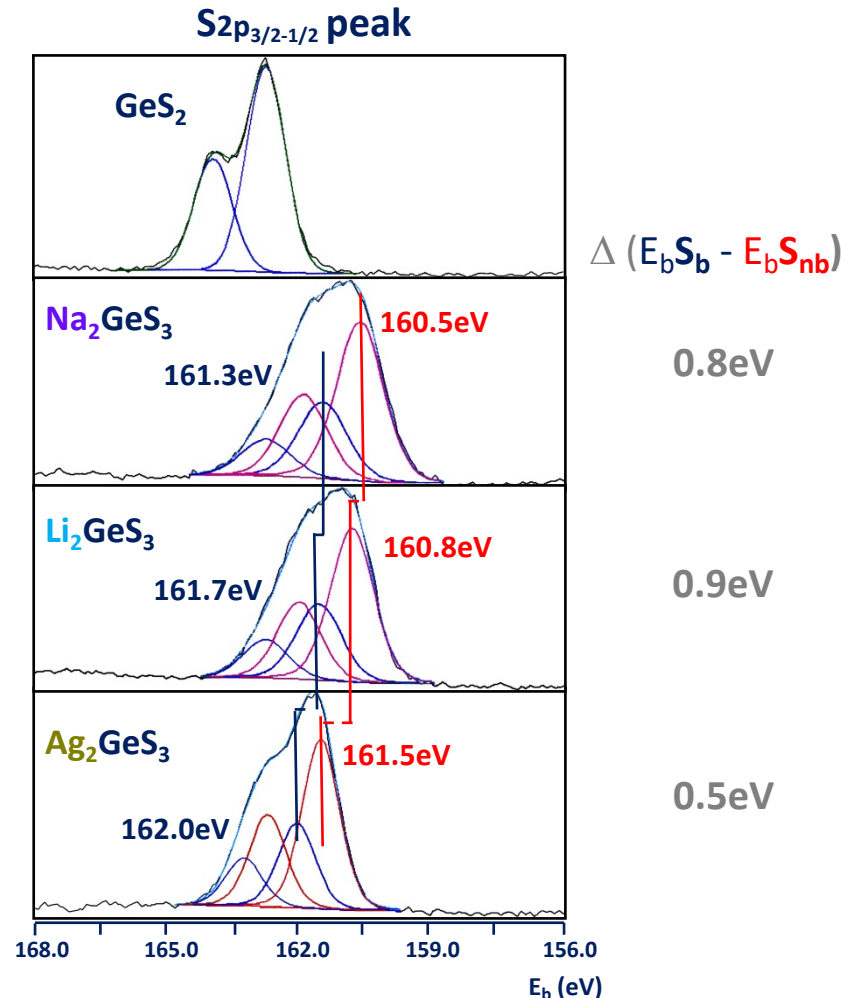
3 natures of glass modifiers:



Coexistence of S_b and S_{nb}

Depending on the nature of the modifier cation, we can observe:

- A binding energy for both bridging and non-bridging sulfurs higher for Ag
- A difference of binding energy between S_b and S_{nb} less important for Ag $\Delta (E_b\text{S}_b - E_b\text{S}_{nb})$



XPS to characterize glassy materials

Influence of the nature of the modifier cation:

Theoretical calculations allow to reach the Mulliken population, informing on the electron population on each atom. The following results were obtained for the charges on bridging (q_{Sb}) and non-bridging (q_{Snb}) sulfurs:

	Mulliken population	
	q_{Sb}	q_{Snb}
Na_2GeS_3	-0,64 to -0,70	-0,86 to -0,87
Li_2GeS_3	-0,63 to -0,69	-0,82 to -0,84
Ag_2GeS_3	-0,62 to -0,66	-0,72 to -0,74

Negative character higher for **Snb** compare to **Sb**

Negative character higher for **Na and Li**, compared to **Ag**, especially for non-bridging sulfurs

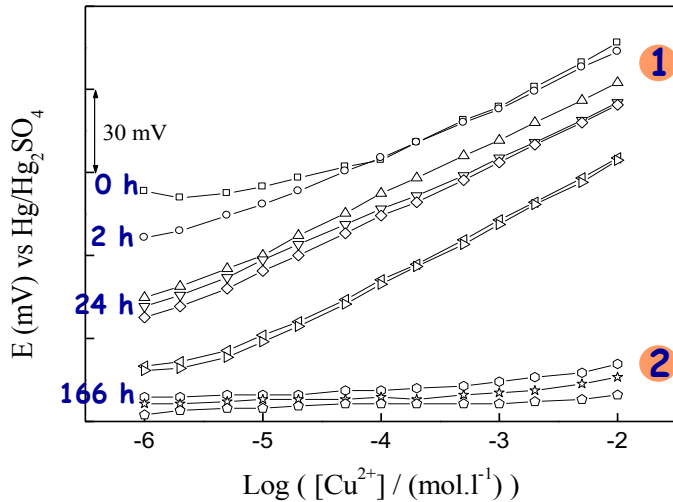
	Mulliken population	XPS results S2p peaks
	$\Delta (q_{Sb} - q_{Snb})$	$\Delta (E_b^{Sb} - E_b^{Snb})$
Na_2GeS_3	0.20eV	0.8eV
Li_2GeS_3	0.17eV	0.9eV
Ag_2GeS_3	0.09eV	0.5eV

XPS shows the importance of the nature of cation modifier on the electronic structure of the glasses.

➔ The interactions between the orbitals of the cations and sulfurs are higher in Ag_2GeS_3 compare to Na_2GeS_3 or Li_2GeS_3 .

XPS to characterize glassy materials

Captors $\text{Cu}_{10}(\text{As}_{0,4}\text{S}_{0,6})_{90}$: mesures potentiométriques



Decrease of the performances after hours of use.
After 166h, no more answer of the system.

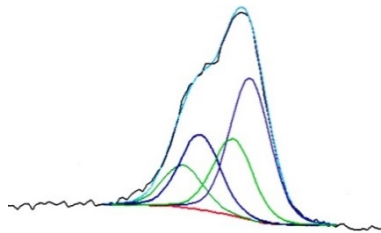
Why ?



XPS analyses to understand the ageing process

S2p

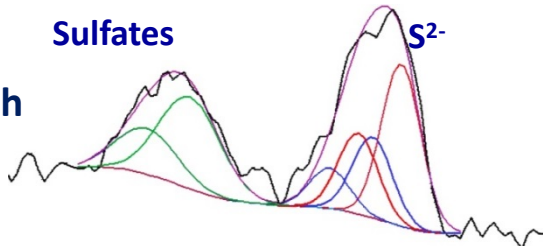
Before



Sulfates

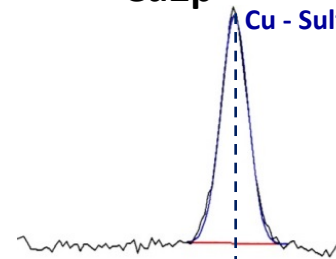
S²⁻

After 166h

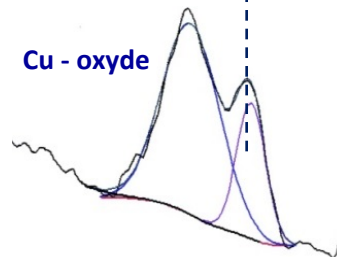


Cu2p

Cu - Sulfur



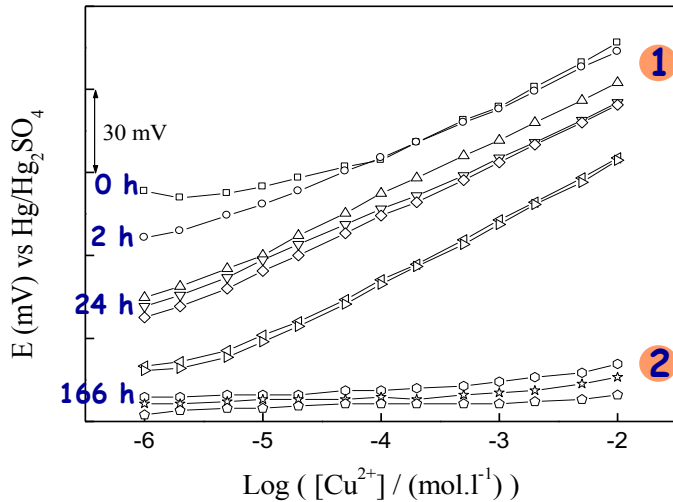
Cu - oxyde



Surface oxidation observed also for the Arsenic peaks.

XPS to characterize glassy materials

Captors $\text{Cu}_{10}(\text{As}_{0,4}\text{S}_{0,6})_{90}$: mesures potentiométriques

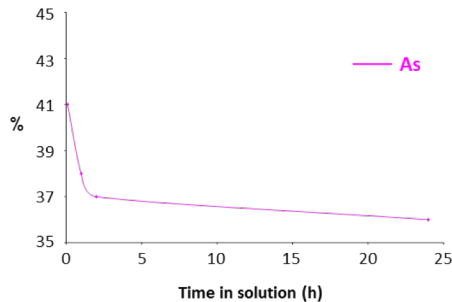


Decrease of the performances after hours of use.
After 166h, no more answer of the system.

Why ?

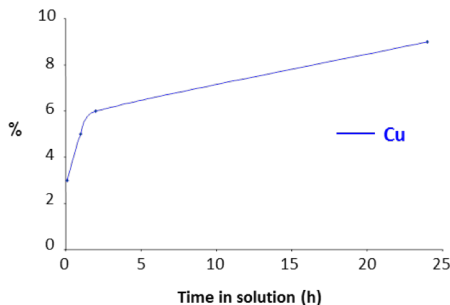


XPS analyses to understand the ageing process



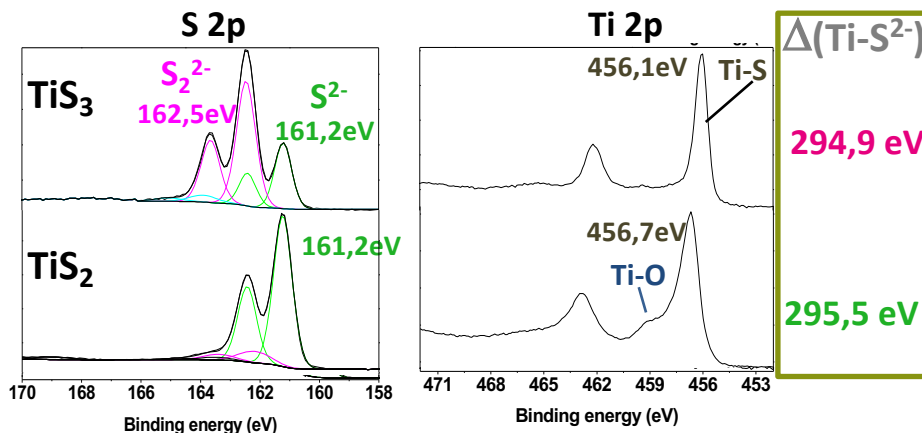
Beside the observed modification of chemical environments,

➡ evolution of the surface composition



➡ Ageing process linked to apparition of modified surface layer

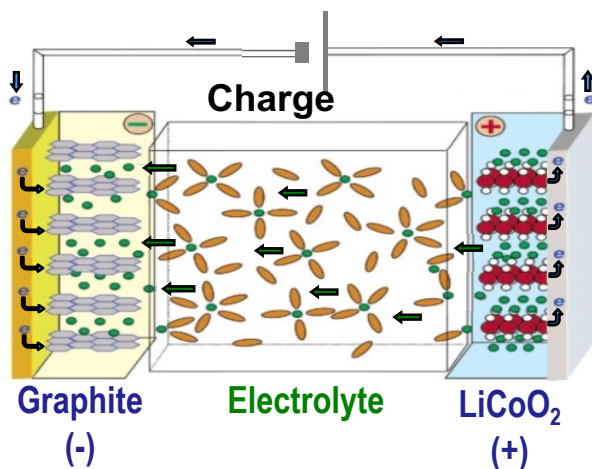
XPS to characterize materials



Ti⁴⁺ in mixed S₂²⁻ / S²⁻ environment : 294,9 eV

Ti⁴⁺ in S²⁻ environment : 295,7 eV

Energy storage : Li-ion battery



During **charge** : Li are leaving from the cathode

→ **oxydation reactions** in cathode material

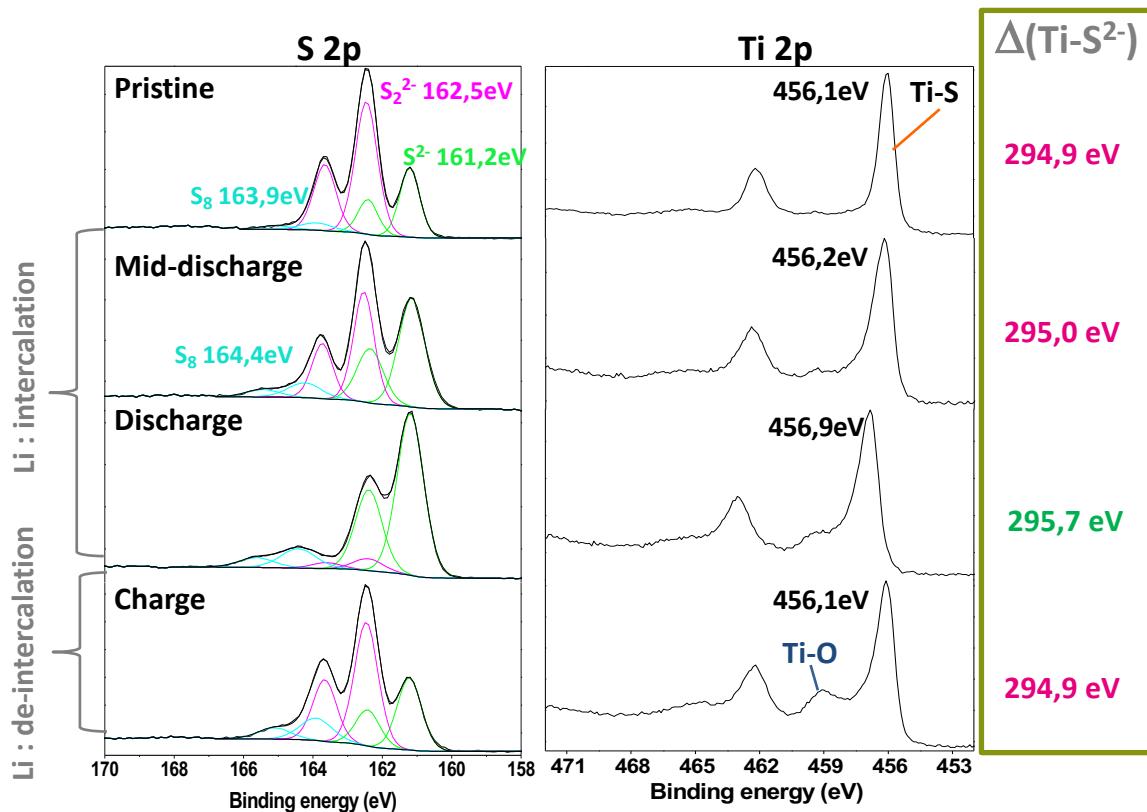
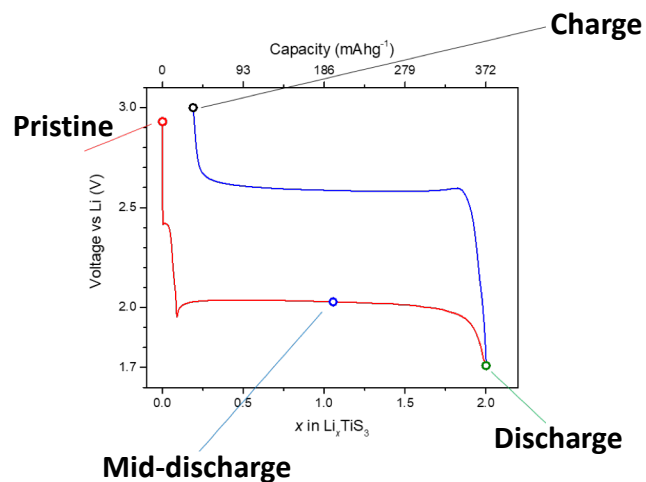
During **discharge** : Li are inserted in the cathode

→ **reduction reactions** in cathode material

XPS : which redox processes allow the Li-intercalation ?

XPS to characterize materials

Electrochemical cycling - TiS_3 is the negative electrode



During the Li-insertion

- the reduction occurs on the anion centers
- the Ti atoms are not the place of reduction in discharge
- the electronic distribution along the Ti-S bond is modified : value of $\Delta(\text{Ti-S}^{2-})$

During the Li-deinsertion ➤ Reversibility of the redox process

Conclusion

As a reminder, X-ray photoelectron spectroscopy technique allows:

Surface analysis (5-10nm)

Detection of all elements except H and He

Quantitative analysis

Qualitative analysis to highlight chemical environment and electronic structure because sensitive to

Oxydation degree
short range order,
local struture,
chemical environment of atoms,
electronic distribution ...



Thank you for your attention

