Photoemission (and angle-resolved photoemission), a tool to probe the electronic structure of materials

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Summary

1. The photoelectric effect – A photoemission experiment
   A photoemission spectrum, experiment, surface sensitivity

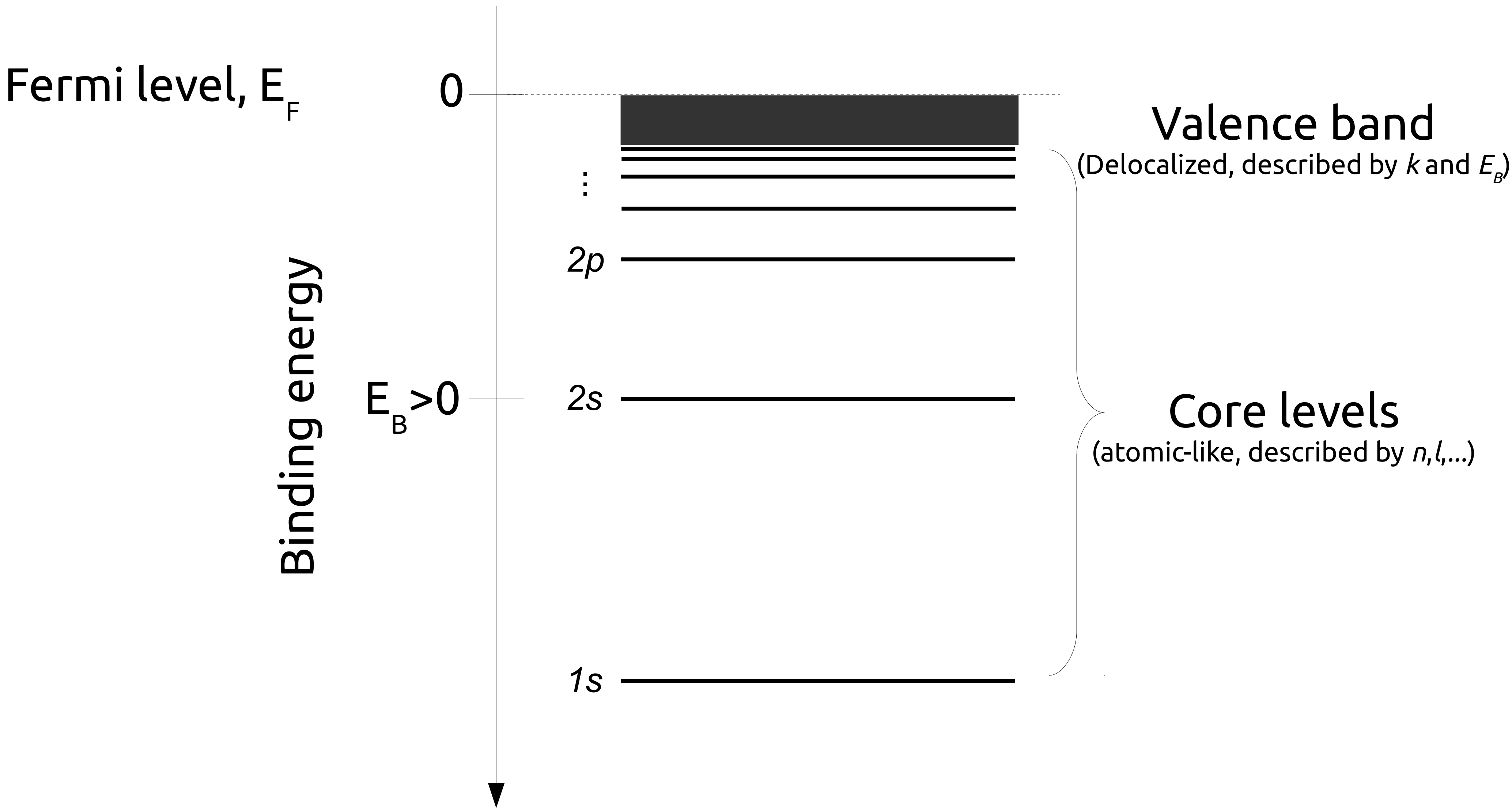
(2. Theoretical background)
   Fermi golden rule and Hamiltonian
   Matrix elements and spectral function

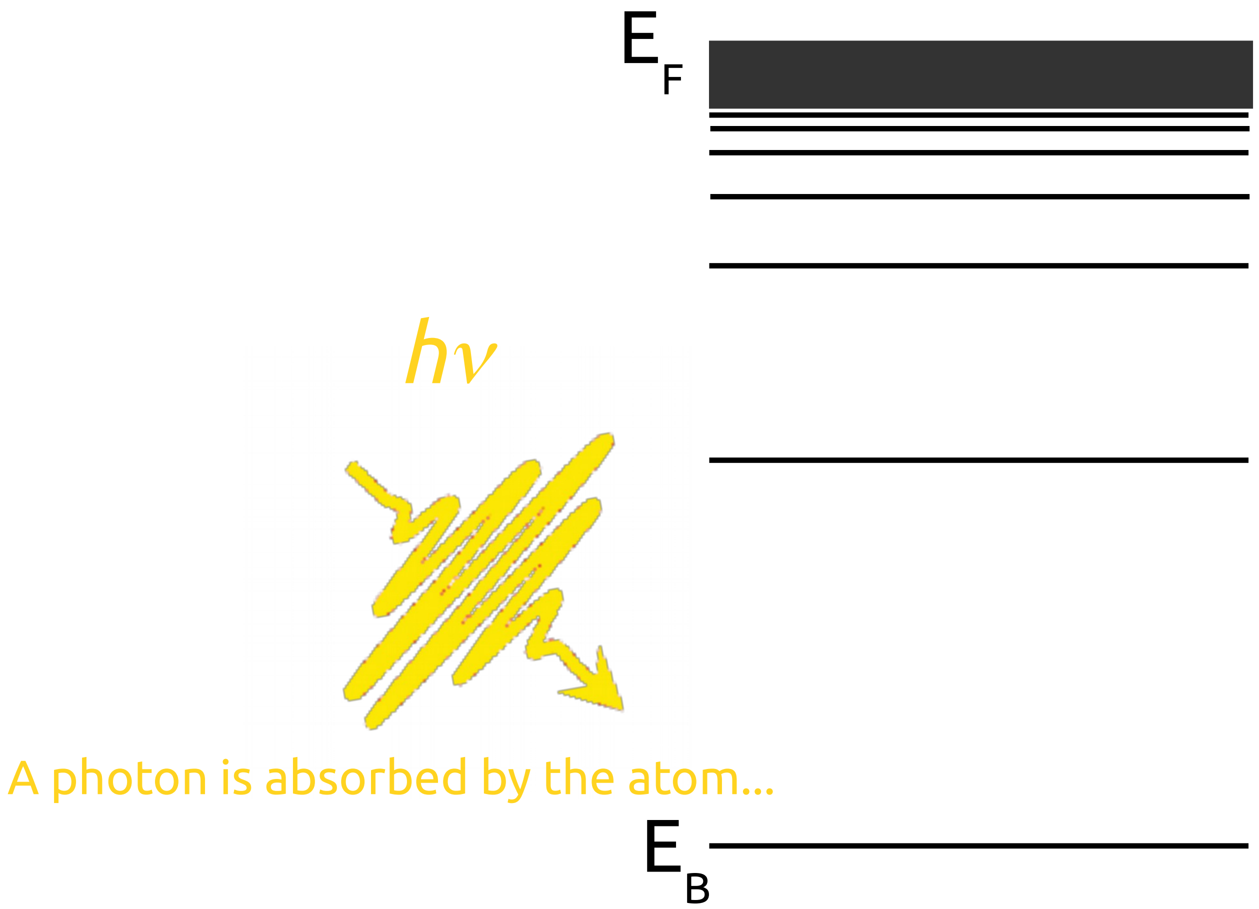
3. Core levels
   Core level shift and ESCA

4. XPS in materials for photovoltaics
   Time-resolved photoemission, electron-hole pair lifetime

(5. Valence band-ARPES)
   Principle, band mapping and Fermi surfaces…

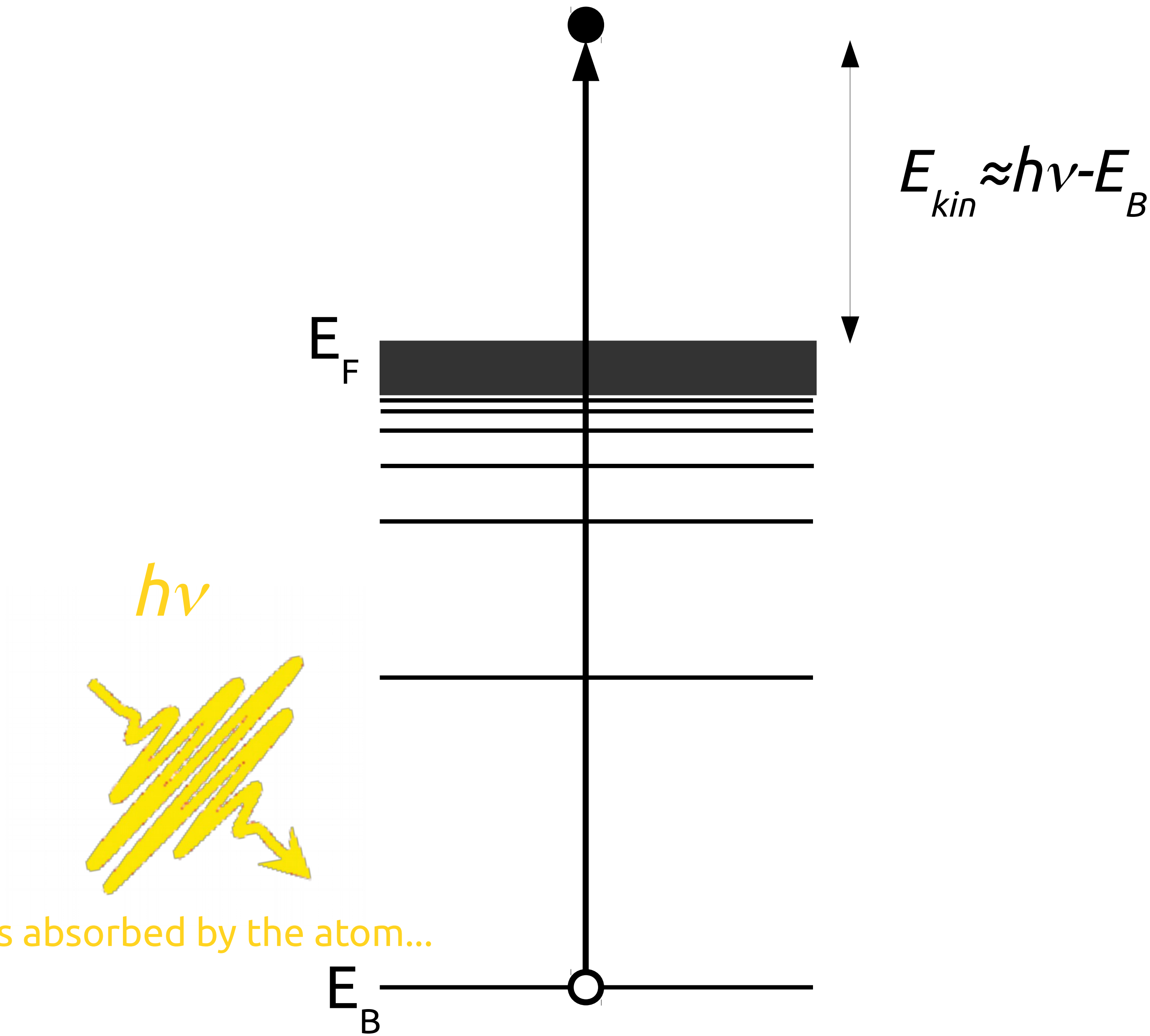
The photoelectric effect : An atom in a solid and its electronic levels



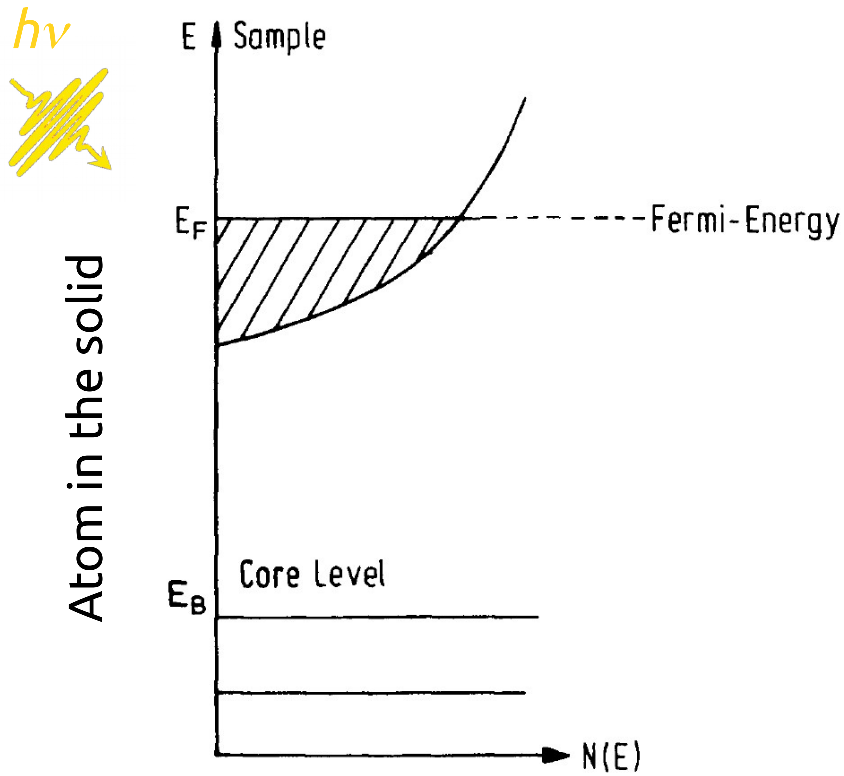

E_F
$h\nu$
A photon is absorbed by the atom...
E_B

The photoelectric effect

...The photon energy is used to eject a photoelectron.

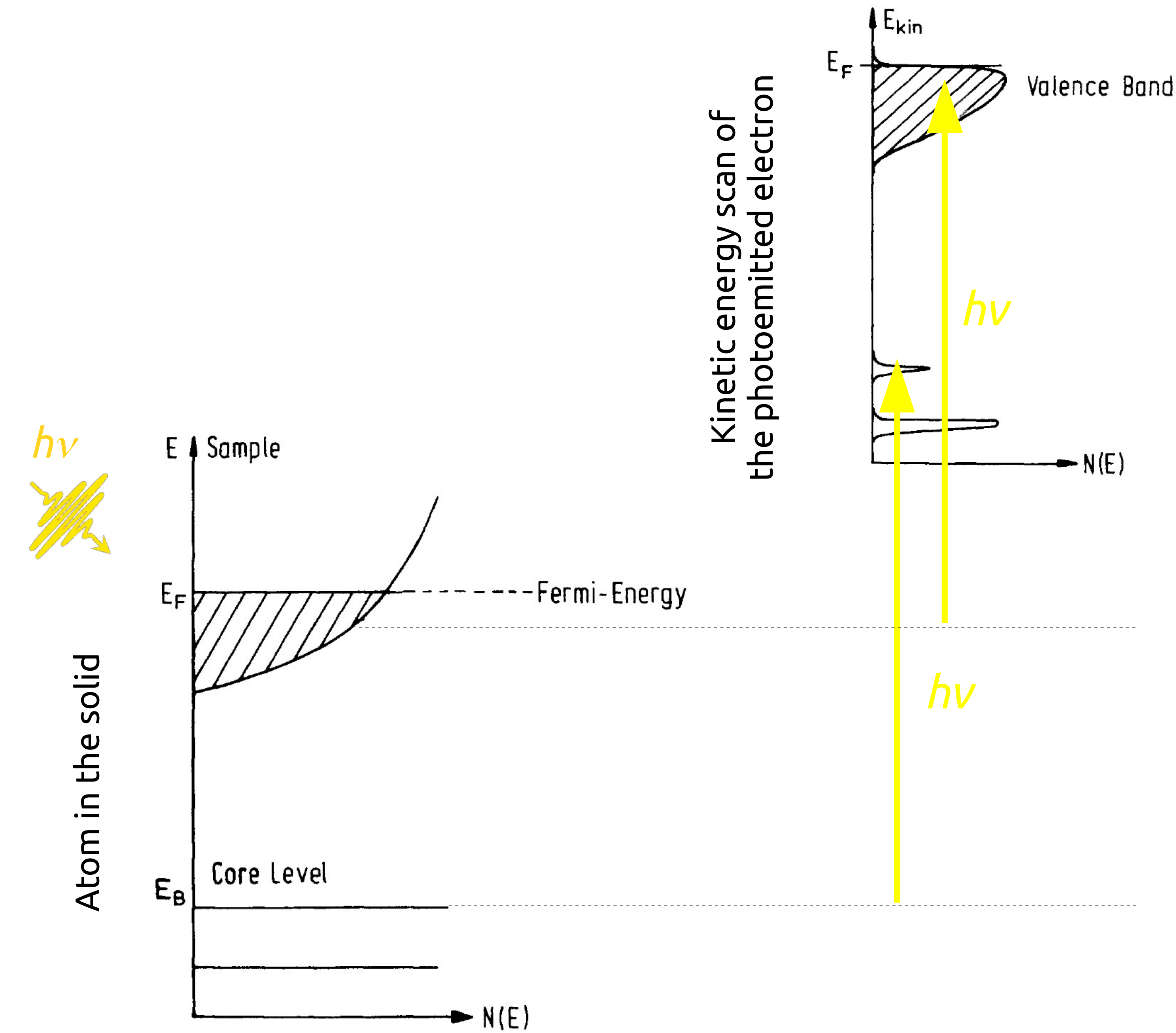


The photoelectric effect : A photoemission experiment



S. Hüfner, Photoelectron Spectroscopy (Springer)

The photoelectric effect : A photoemission experiment



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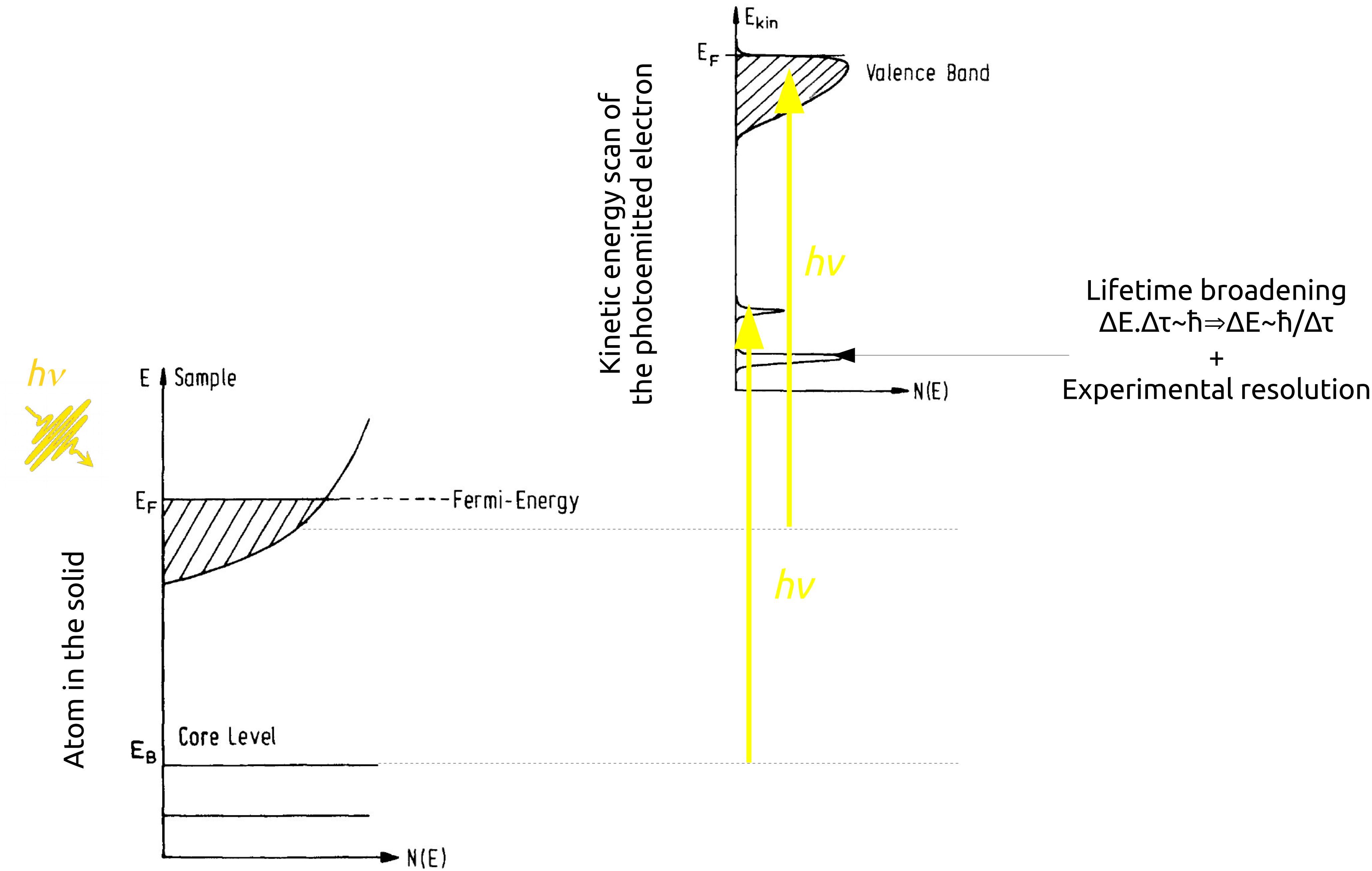
The photoelectric effect : A photoemission experiment



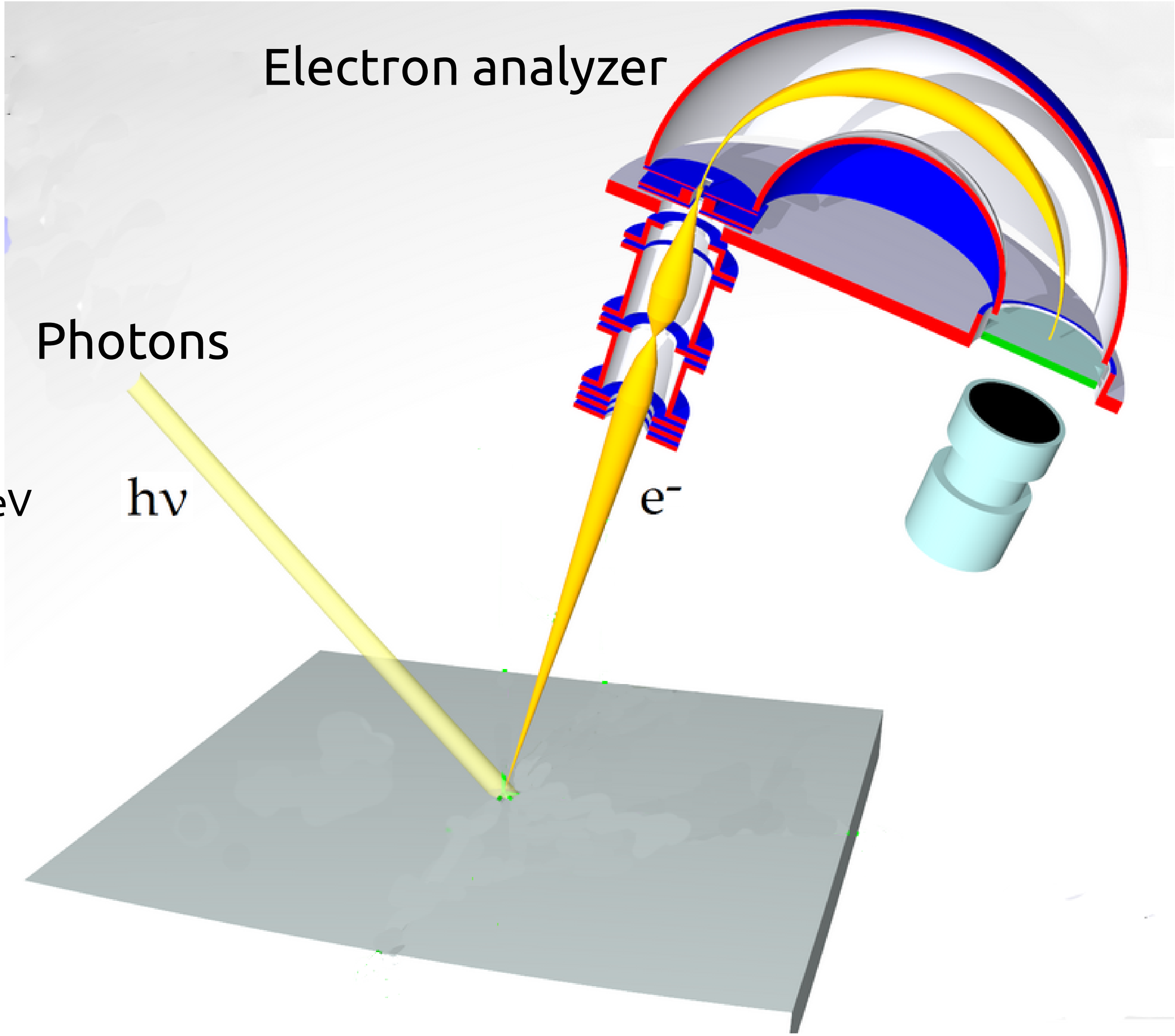
S. Hüfner, Photoelectron Spectroscopy (Springer)

Laser

UV-lamps :
He-Lamp (21.2eV)

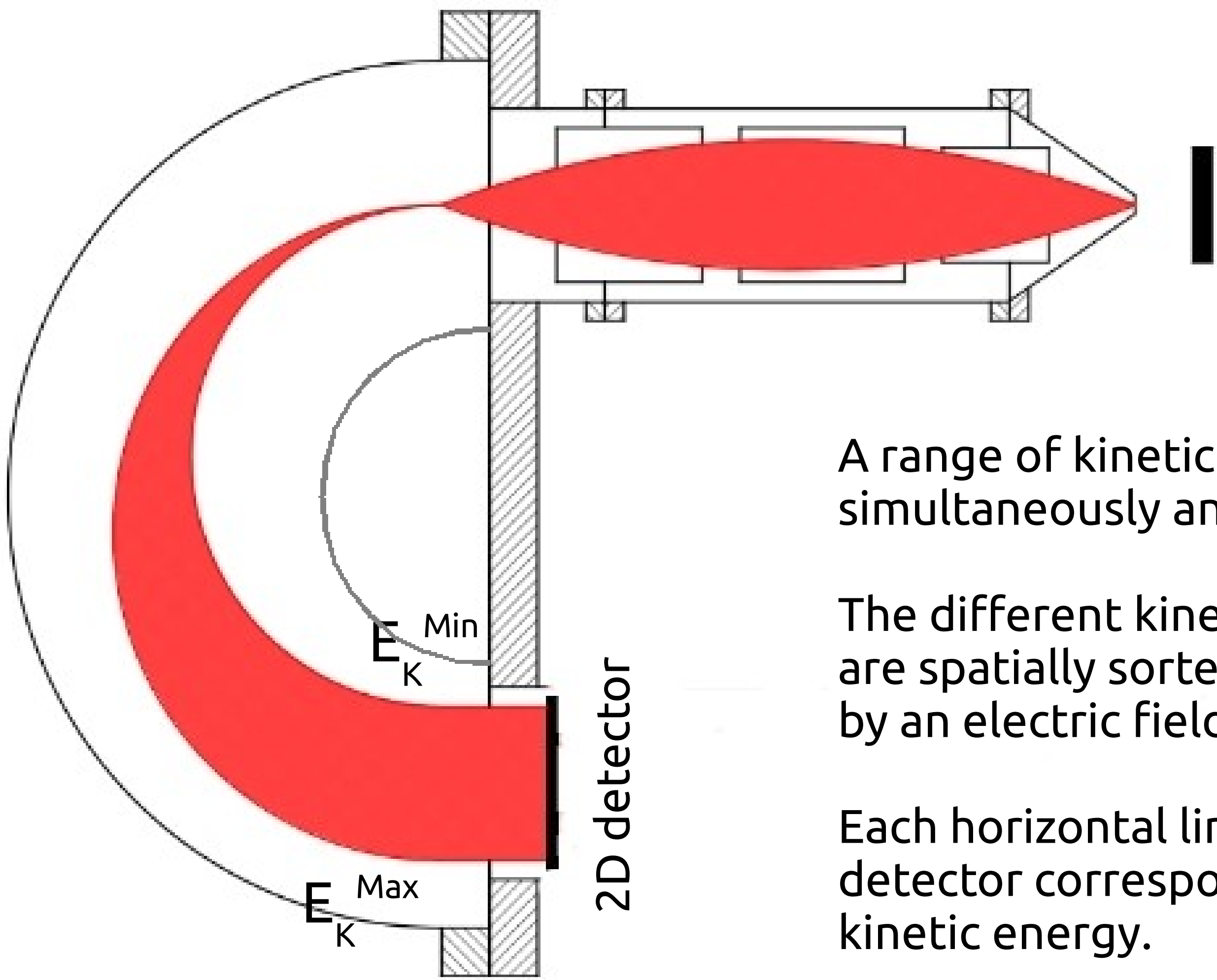
X-ray tubes :
Al-Kα (1486eV)
Mg-Kα (1253.6eV)

SR:
From 10 to 10000eV



http://en.wikipedia.org/wiki/Photoemission_spectroscopy

The photoelectric effect : Hemispherical multichannel electron analyzer

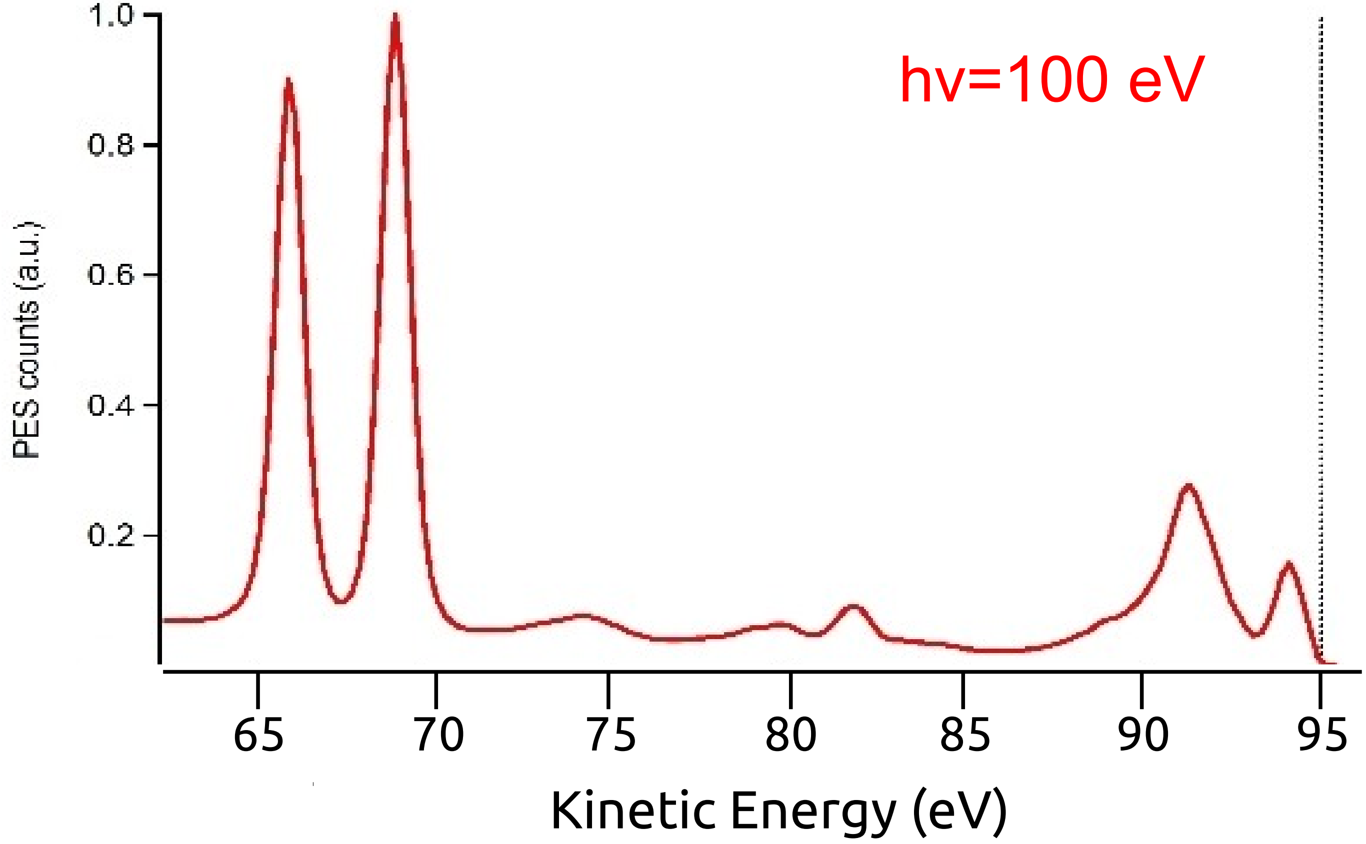


A range of kinetic energies are simultaneously analyzed.

The different kinetic energies are spatially sorted (vertically) by an electric field.

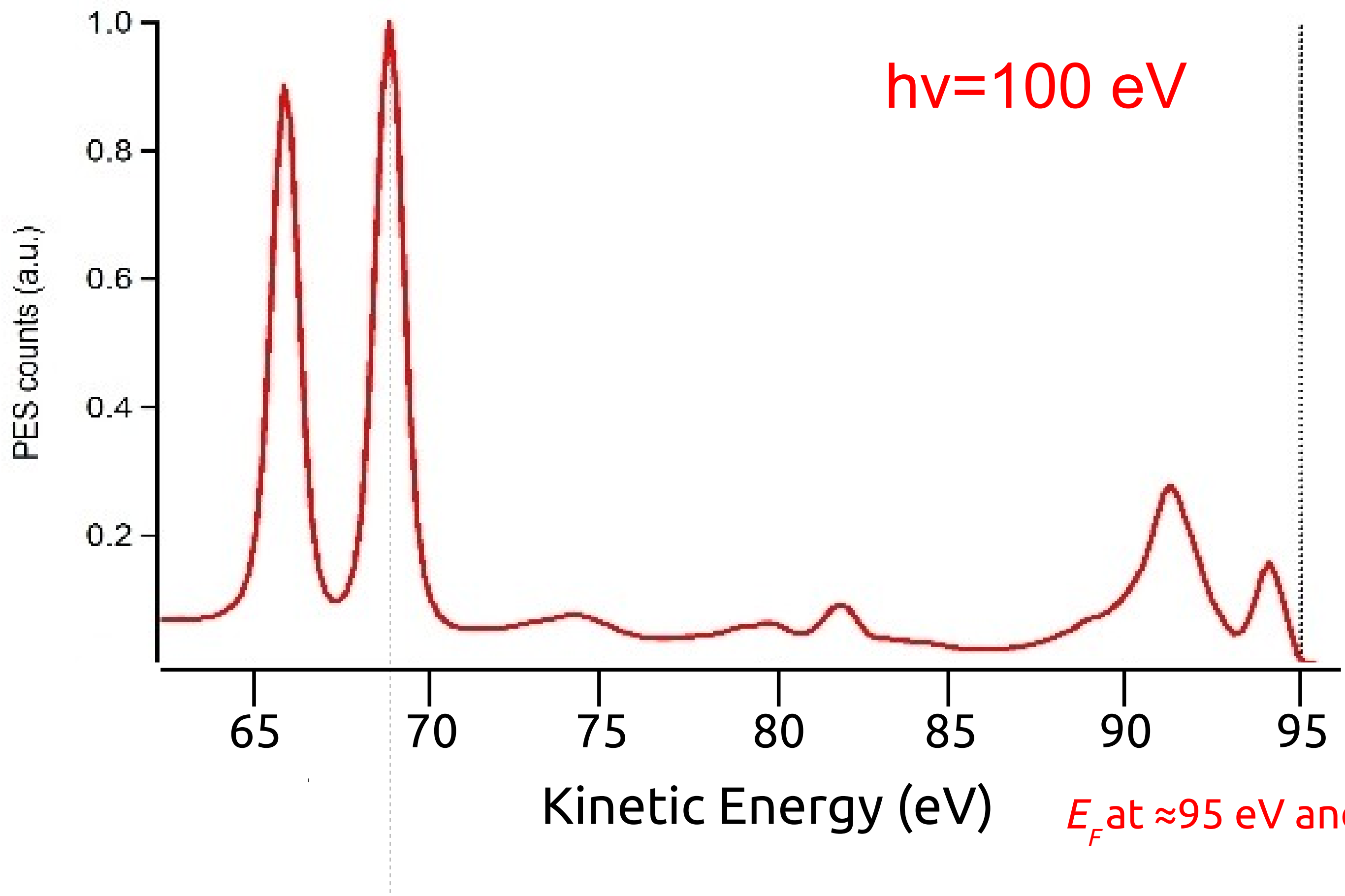
Each horizontal line of the 2D detector corresponds to a kinetic energy.

$[Bi_2Ba_2O_4][CoO_2]$



Nicolaou et al.

$[Bi_2Ba_2O_4][CoO_2]$



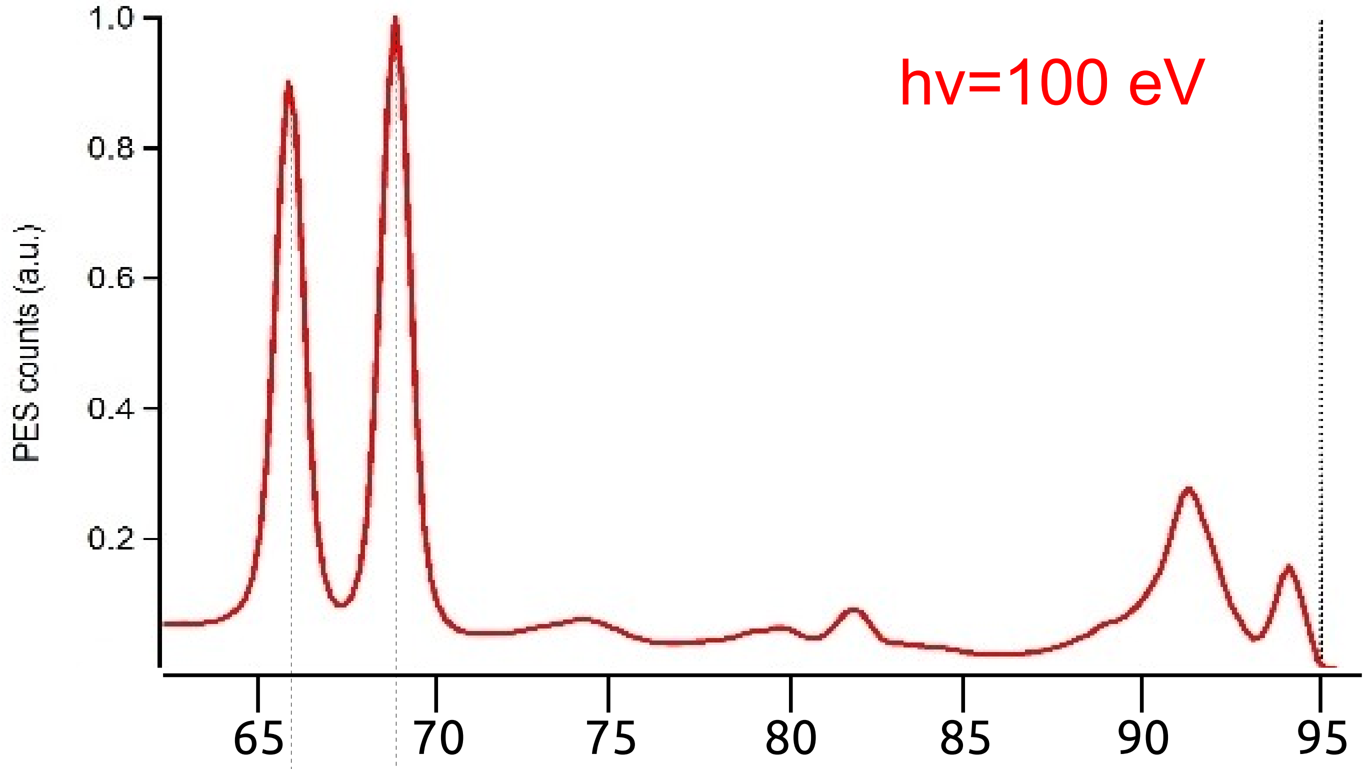
E_F at ≈95 eV and **not** 100 eV !

This is due to the analyzer work function ϕ_{Spect}≈3-5 eV

$E_B = h\nu - E_K - \phi_{Spect}$

Nicolaou et al.

$[Bi_2Ba_2O_4][CoO_2]$



E_{kin}≈66 eV

$E_B \approx h\nu - E_{kin} - \phi_{Spect} \approx 29 eV$

E_{kin}≈68 eV

$E_B \approx h\nu - E_{kin} - \phi_{Spect} \approx 27 eV$

ϕ_{Spect}≈5 eV

E_F at ≈95 eV and **not** 100 eV !

This is due to the analyzer work function ϕ_{Spect}≈3-5 eV

$E_B = h\nu - E_{kin} - \phi_{Spect}$

Nicolaou et al.

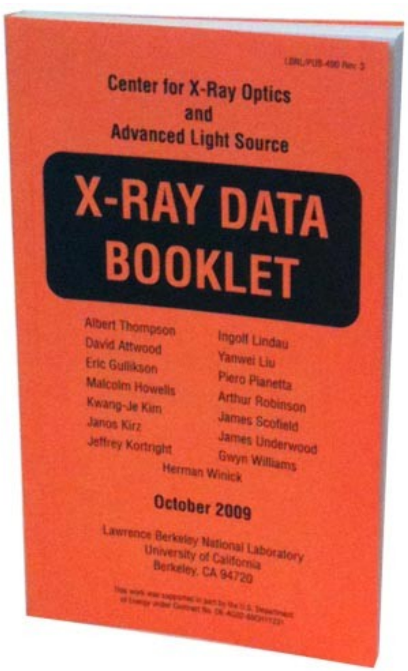
The photoelectric effect : A photoemission experiment (exemple)

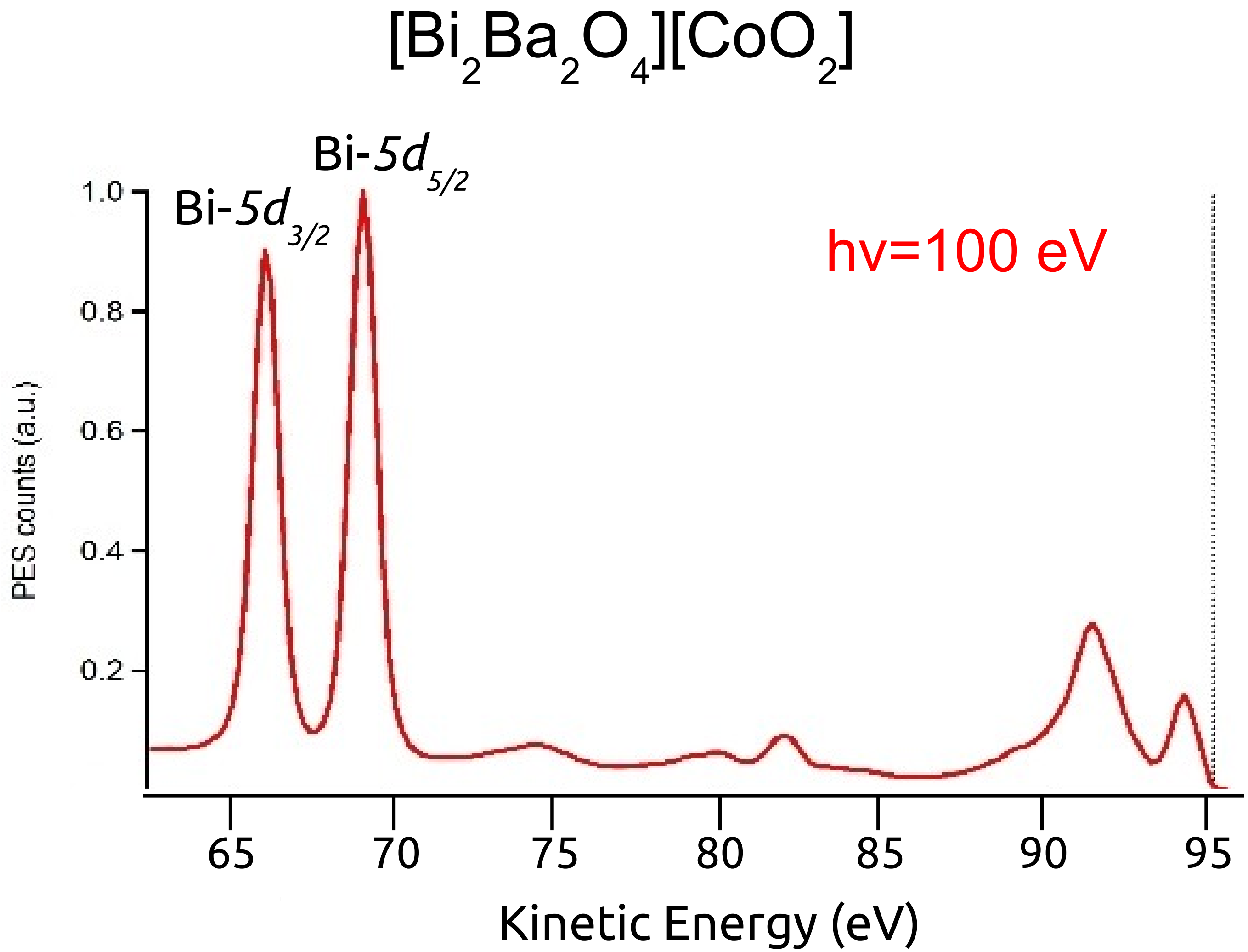
Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$
8 O	543.1*	41.6*					

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 $4p_{3/2}$
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					

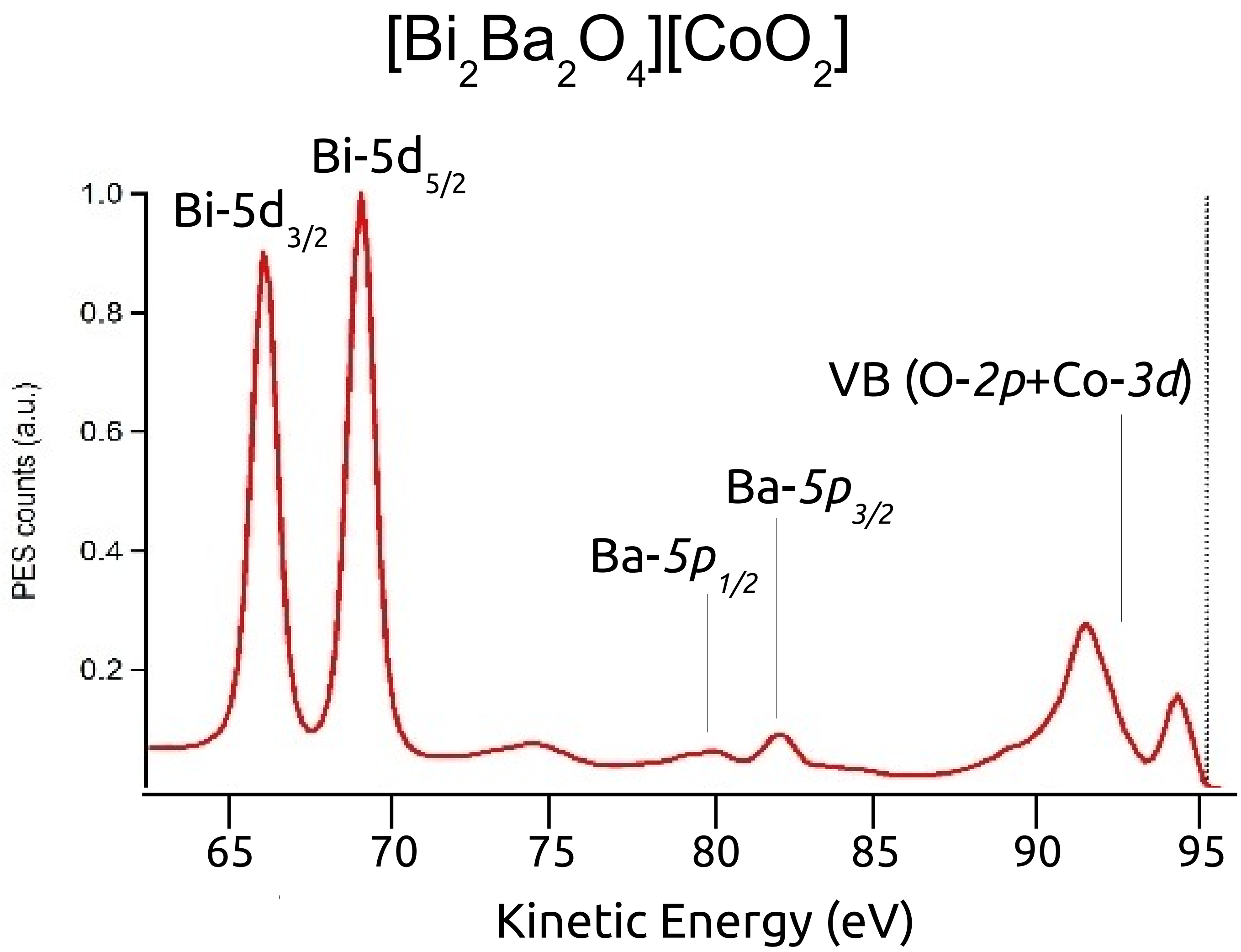
Element	N_4 $4d_{3/2}$	N_5 $4d_{5/2}$	N_6 $4f_{5/2}$	N_7 $4f_{7/2}$	O_1 5s	O_2 $5p_{1/2}$	O_3 $5p_{3/2}$
56 Ba	92.6†	89.9†	—	—	30.3†	17.0†	14.8†

Element	N_4 $4d_{3/2}$	N_5 $4d_{5/2}$	N_6 $4f_{5/2}$	N_7 $4f_{7/2}$	O_1 5s	O_2 $5p_{1/2}$	O_3 $5p_{3/2}$	O_4 $5d_{3/2}$	O_5 $5d_{5/2}$	P_1 6s	P_2 $6p_{1/2}$	P_3 $6p_{3/2}$
83 Bi	464.0†	440.1†	162.3†	157.0†	159.3*b	119.0†	92.6†	26.9†	23.8†			





Nicolaou et al.



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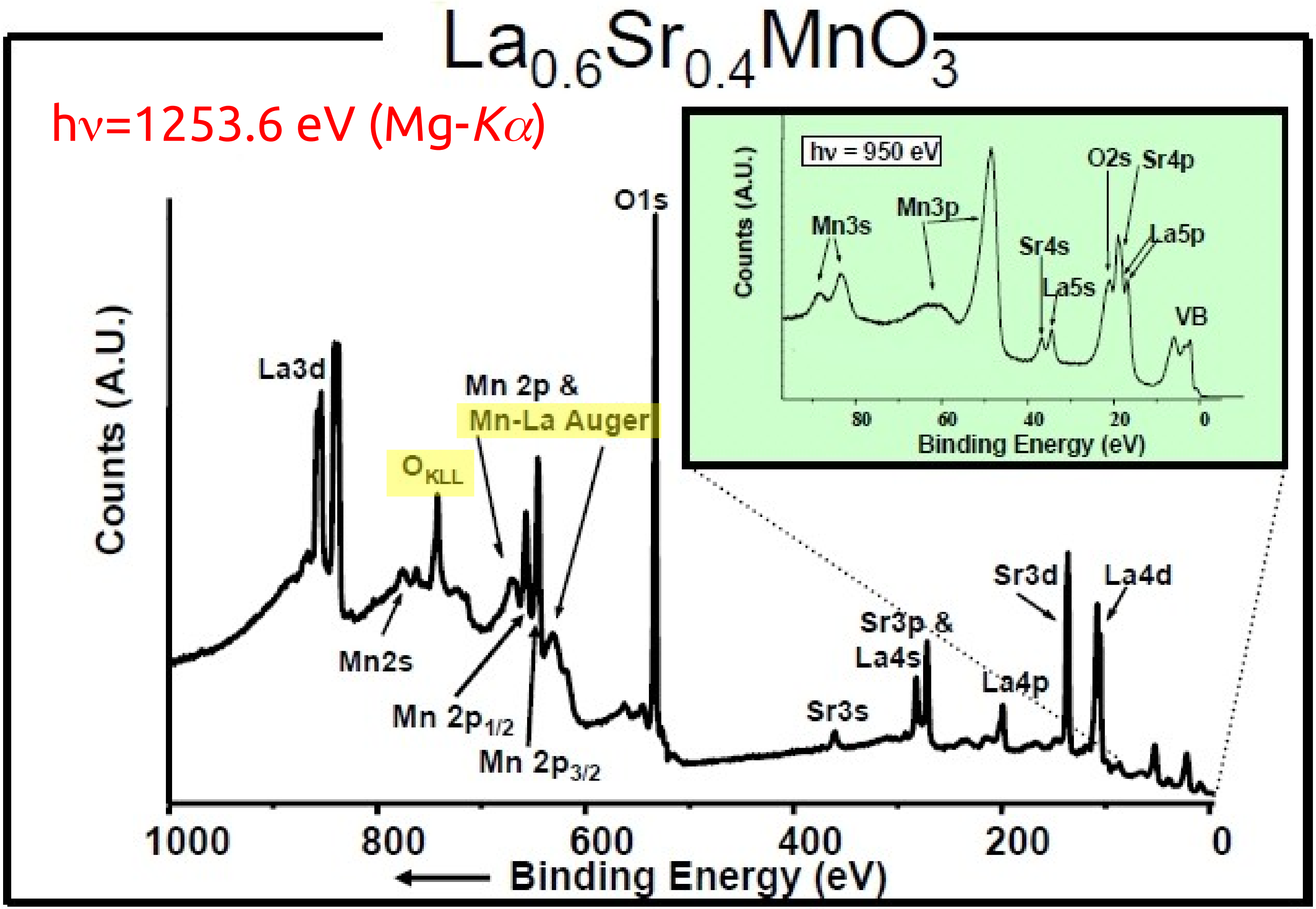
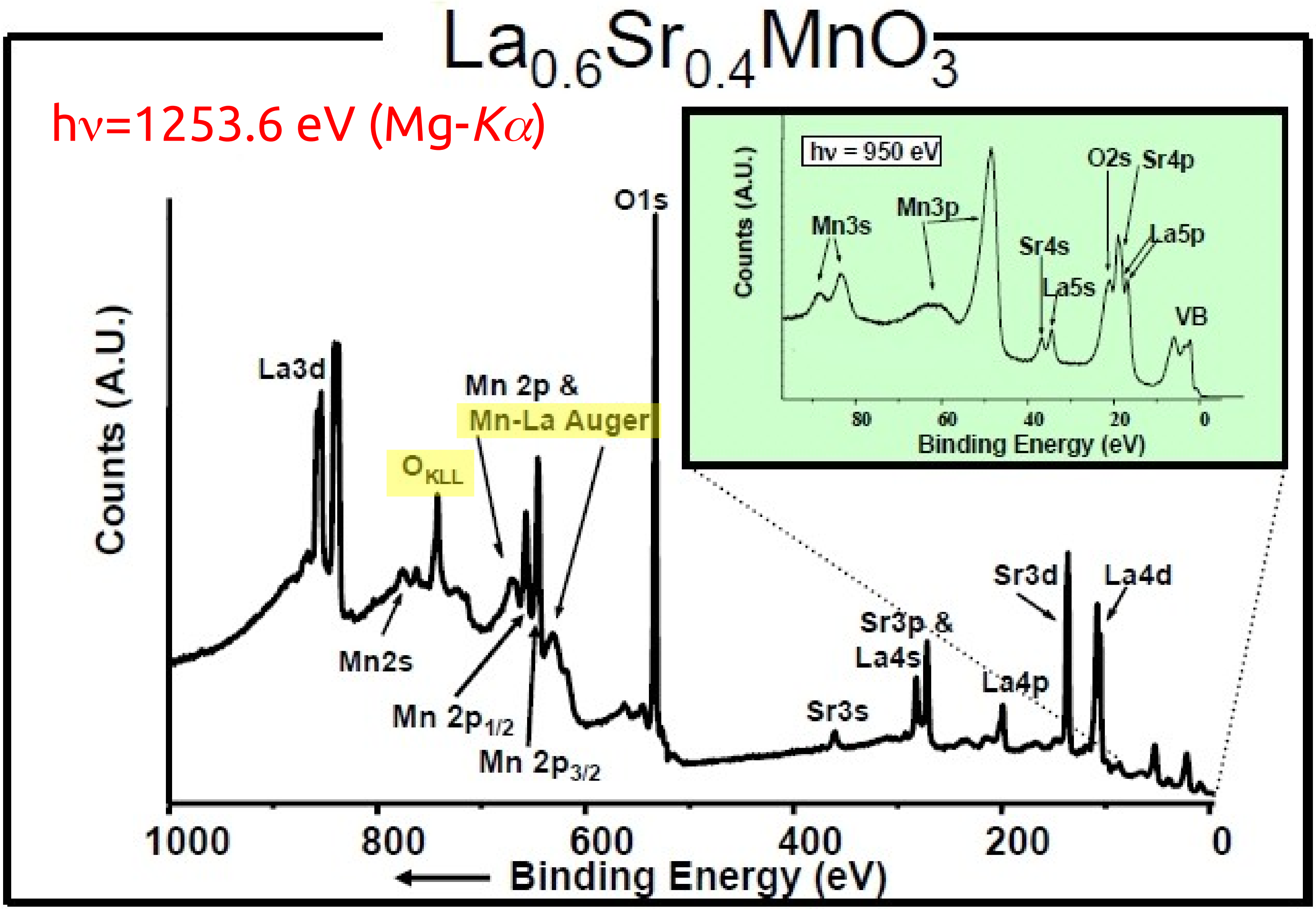
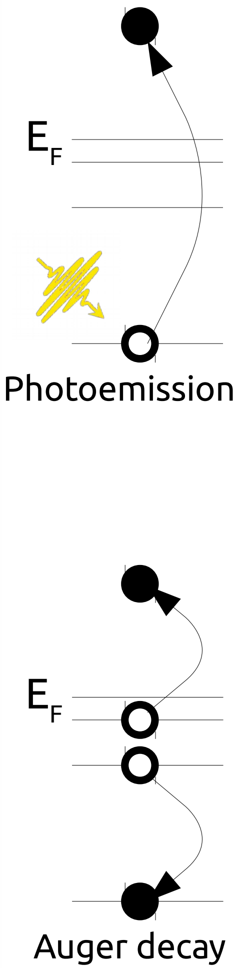


C. S. Fadley et al.





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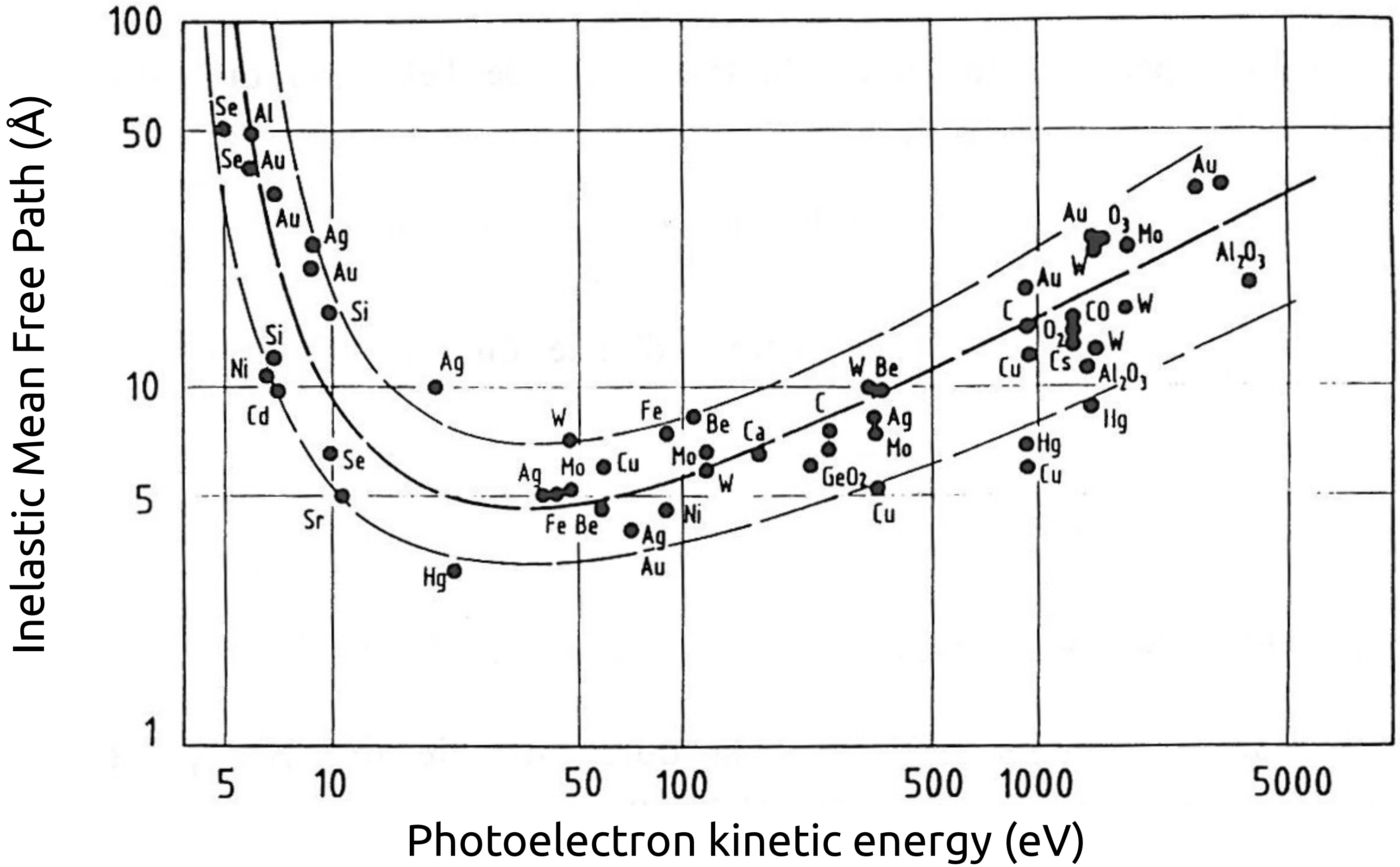


Electron cannot travel far in matter :

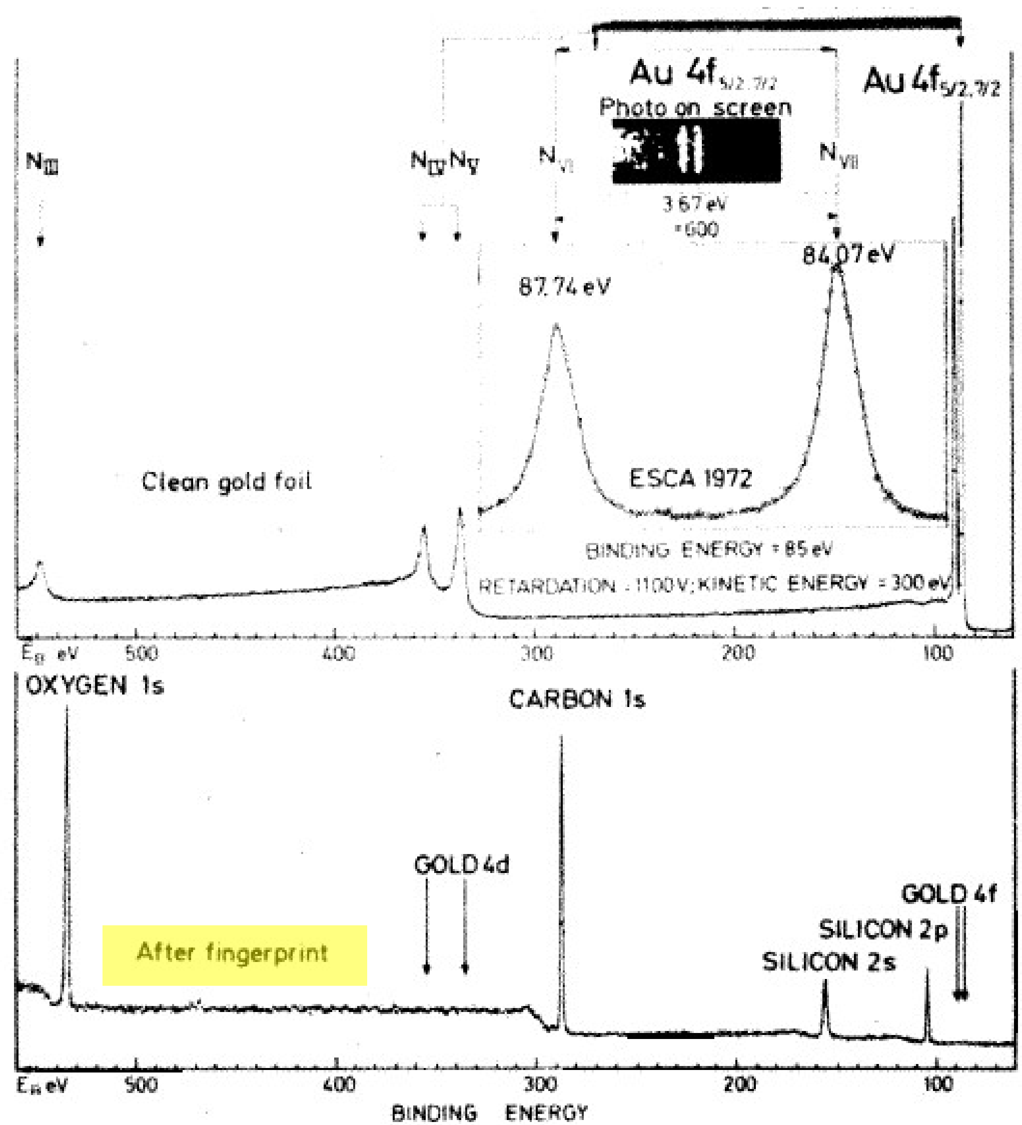
Photoemission is therefore a surface sensitive technique, probing the first atomic planes of the sample.

*M. P. Seah and W. A. Dench, Surf. and Interf. Analysis **1**, 2 (1979)*

The photoelectric effect : Surface sensitivity

According to the idea that the incident light consists of energy quanta with an energy $R\beta\nu/N$, one can picture the production of cathode rays by light as follows. Energy quanta penetrate into a surface layer of the body, and their energy is at least partly transformed into electron kinetic energy. The simplest picture is that a light quantum transfers all of its energy to a single electron; we shall assume that that happens. We must, however, not exclude the possibility that electrons only receive part of the energy from light quanta. An electron obtaining kinetic energy inside the body will have lost part of its kinetic energy when it has reached the surface. Moreover, we must assume that each electron on leaving the body must produce work P, which is characteristic for the body. Electrons which are excited at the surface and at right angles to it will leave the body with the greatest normal velocity.

*A. Einstein, Ann. Physik **17**, 132 (1905)*



K. Siegbahn, Nobel Lecture (1981)

Popular systems in photoemission :

- Surface electronic structure
(surface states, structure of surfaces, surface alloys...)

- Thin films
(Metals, semiconductors, oxides, molecules, « bulk materials » deposited as thin films...)

- 2D or «2D-like» systems
(graphene, dichalcogenides, lamellar systems, cuprates, pnictides, iridates, cobaltates...)

How to study bulk properties with photoemission ?

- Use X-rays (3 to 10 keV)

Theoretical background : The Fermi Golden Rule

$$W_{f,i} \propto \frac{2\pi}{\hbar} |\langle \Psi_f | H | \Psi_i \rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

It gives the probability for the system to go

- from the Ψ_i state
- to the Ψ_f state
- under the action of the hamiltonian H
- The energy difference between Ψ_i and Ψ_f is $\hbar\omega$

Theoretical background : Hamiltonian

The photon electromagnetic field is defined by $\vec{E} = -\frac{\partial \vec{A}}{\partial t}$ and $\vec{B} = \nabla \wedge \vec{A}$

The electron has a kinetic energy $\frac{P^2}{2m}$ and

$\hat{P} = -i\hbar\nabla - qA$ In an electromagnetic field

$\hat{p} = -i\hbar\nabla$ Without electromagnetic field

$$H = \frac{\hat{P}^2}{2m} = \frac{1}{2m}(-i\hbar\nabla - qA)^2$$

$$H = \frac{1}{2m}(-\hbar\nabla)^2 + \frac{q}{2m}(2i\hbar\nabla . A + A^2)$$

Introducing $H_0 = \frac{\hat{p}^2}{2m} = \frac{1}{2m}(-i\hbar\nabla)^2$ and neglecting the A^2 term

$$H = H_0 + \frac{q}{m}(A . p)$$

Ground state (H_0)

Interaction with the photon H_{Int} ($\frac{q}{m}(A . p)$)

The dipole approximation : $\vec{A} \propto \vec{\epsilon}\, e^{i\vec{k}.\vec{r}} \propto \vec{\epsilon}\,(1+i\vec{k}.\vec{r}+\ldots) \simeq \vec{\epsilon}$

ε is the polarisation of the light (direction of the photon electric field)
For low energy photon, the wavelength λ is much larger than the interatomic distance :
ε can be considered as constant.

$$H_{\mathrm{Int}} = \frac{q}{m}(A\,.\,p)$$

Let's express this as a function of *ε* and *r* : • $\vec{A} \propto \vec{\epsilon}$

And using : • $[H,\vec{r}] = \frac{1}{2m}[\vec{p}^{\,2},\vec{r}] = \frac{1}{2m}\vec{p}[\vec{p},\vec{r}] + [\vec{p},\vec{r}]\vec{p} = \frac{-i\hbar}{m}\vec{p}$

$\langle f|\vec{p}|i\rangle \propto \langle f|[\vec{r},H]|i\rangle = (E_i - E_f)\langle f|\vec{r}|i\rangle$

One obtains : $H_{\mathrm{Int}} \propto \vec{A}.\vec{p} \propto \vec{\epsilon}.\vec{r}$

So that finally : $W_{f,i} \propto |\langle \Psi_f|\vec{\epsilon}.\vec{r}|\Psi_i\rangle|^2\, \delta(E_f - E_i - \hbar\omega)$

One electron or multielectronic wave functions ?

Two cases:

The electrons of the atom can be considered as independant
☞ use one-electron wave functions

The emission of one electron influences the other electrons
☞ use multielectronic wave functions

$$W_{Total} = \sum_f W_{f,i} \propto \sum_f |\langle \Psi_f | \vec{\epsilon}.\vec{r} | \Psi_i \rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

$$\Psi_i = \Phi_i \Psi_i(N-1)$$
$$\Psi_f = \Phi_{f,E_k} \Psi_m(N-1)$$

Sudden approximation

Photoelectron decouples from remaining system immediately after photoexcitation, before relaxation sets in.

$$W_{f,i} \propto |\langle \Phi_{f,E_k} | \vec{\epsilon}.\vec{r} | \Phi_i \rangle|^2 \, |\langle \Psi_m(N-1) | \Psi_i(N-1) \rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

$$W_{Total} \propto \sum_f |\langle \Phi_{f,E_k} | \vec{\epsilon}.\vec{r} | \Phi_i \rangle|^2 \sum_m |\langle \Psi_m(N-1) | \Psi_i(N-1) \rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

$$M_{i,f}^2 = |\langle \Phi_{f,E_k} | \vec{\epsilon}.\vec{r} | \Phi_i \rangle|^2$$ Matrix elements

$$A(k,E) = \sum_m |\langle \Psi_m(N-1) | \Psi_i(N-1) \rangle|^2$$ Spectral function

$$W \propto \sum_f M_{i,f}^2 \, A(k,E) \, \delta(E_f - E_i - \hbar\omega)$$

Theoretical background : Matrix element and polarization dependence

- $M_{i,f}{}^2$ describes the interaction with the photon (cross section)
  It also contains the symmetry effects (polarization effects)

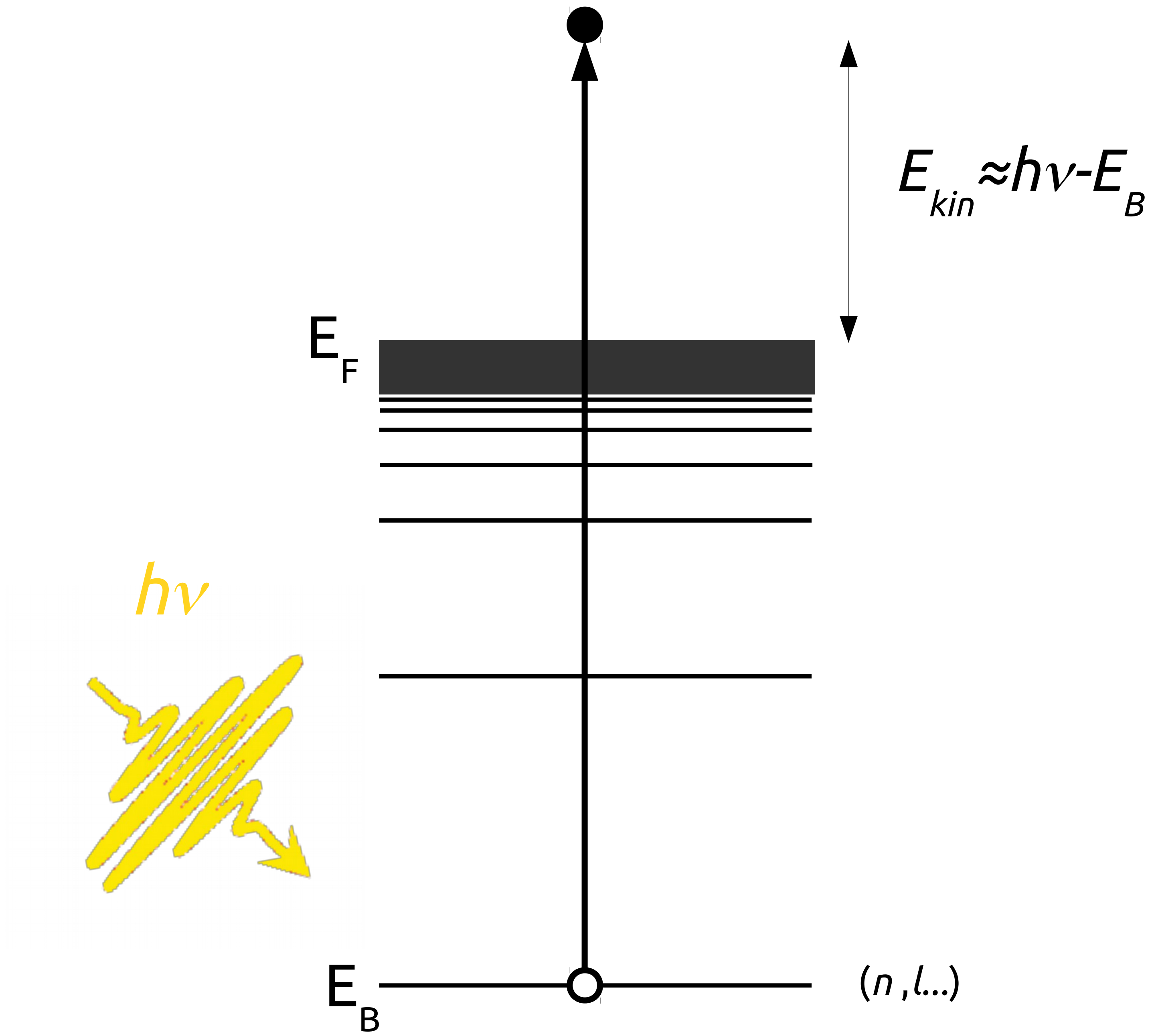
- $$A(k,E)=\sum_m |\langle \Psi_m(N-1)\,|\,\Psi_i(N-1)\rangle|^2$$

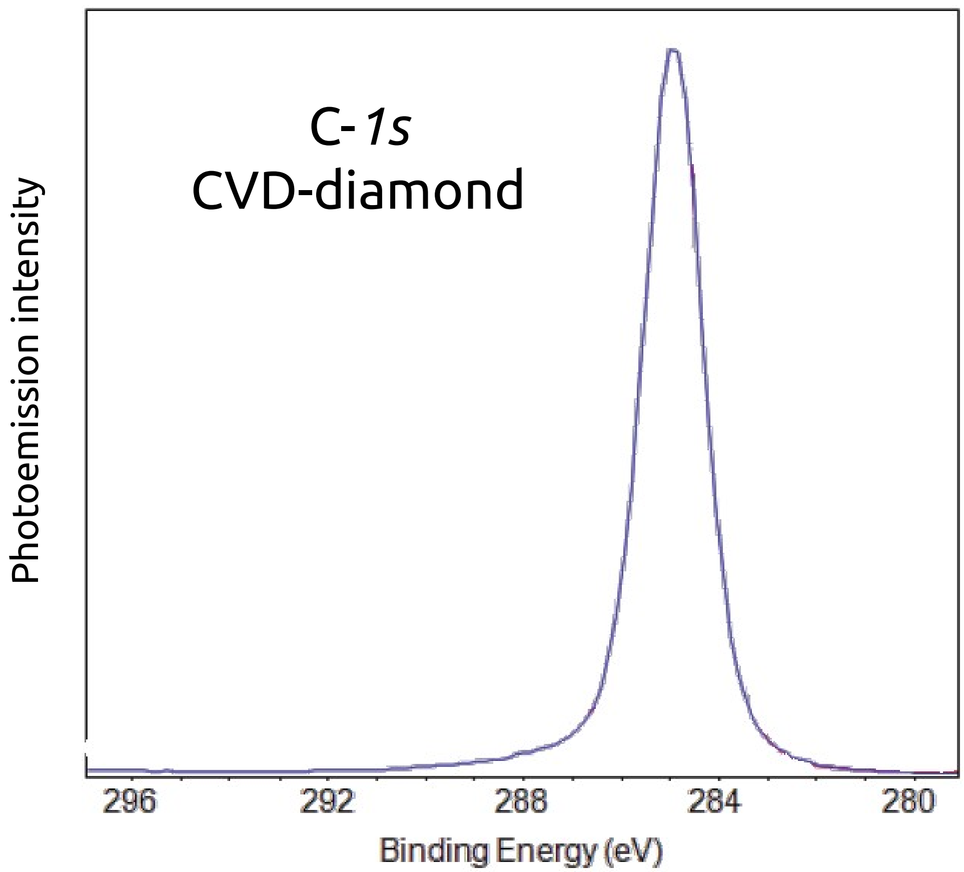
If $|\Psi_m(N\text{-}1)\rangle = |\Psi_i(N\text{-}1)\rangle$
(electrons not perturbed by the core hole: independent electrons)
then $A(k,E)$=1

The spectral function A(k,E) describes

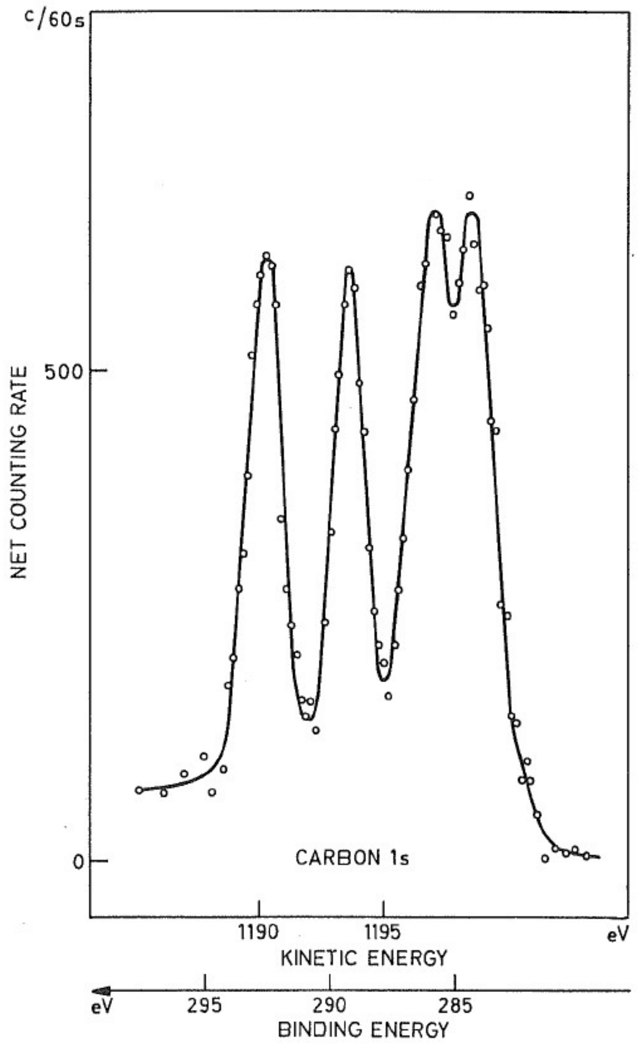
☞Satellites in core level spectroscopy

☞Many body processes in valence states (Electron-electron, electron-phonon,... interactions: correlations)


$E_{kin} \approx h\nu - E_B$
E_F
$h\nu$
E_B
$(n, l\ldots)$

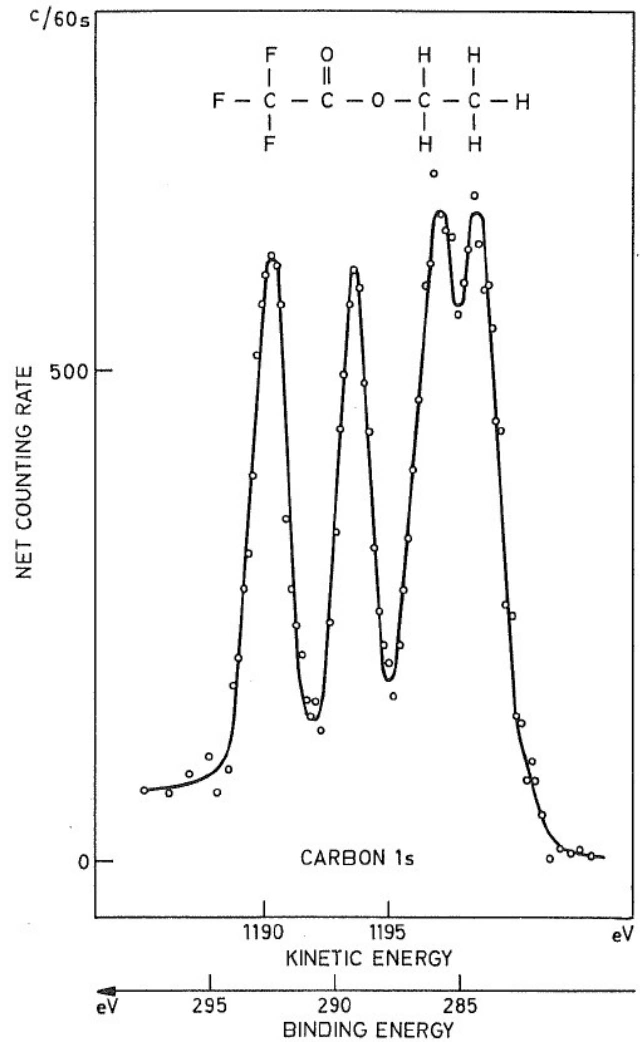


https://xpssimplified.com/elements/carbon.php



C-*1s*
Trifluoroacétate d'ethyle

S.B.M. Hagström, C. Nordling and K. Siegbahn, Z. Physik ***178****, 433 (1964)*

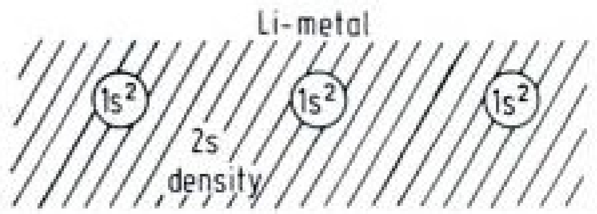


C-*1s*
Trifluoroacétate d'ethyle

Each C-site gives a clear signature in the C-*1s* spectrum

S.B.M. Hagström, C. Nordling and K. Siegbahn, Z. Physik ***178****, 433 (1964)*

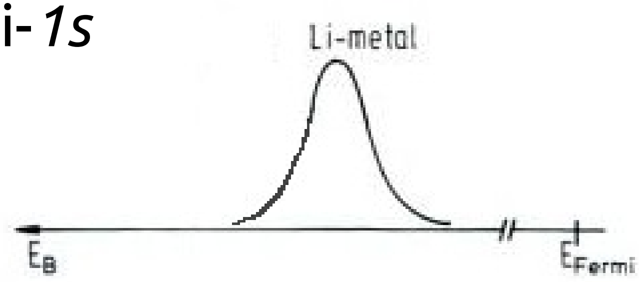
Core levels : Chemical shift in Li-metal and LiO_2



Li : *1s*^{2} *2s*

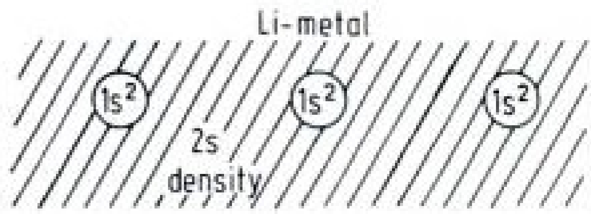
In Li-metal, the *2s* electrons form an electron sea.

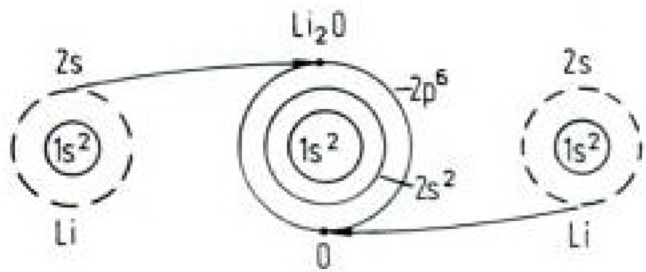
Li-*1s*



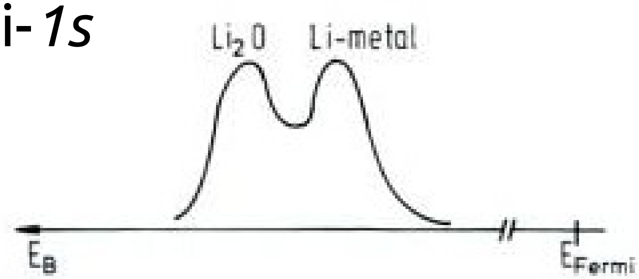
S. Hüfner, Photoelectron Spectroscopy (Springer)

Core levels : Core levels : Chemical shift in Li-metal and LiO_2





Li-*1s*



Li : *1s*^{2} *2s*

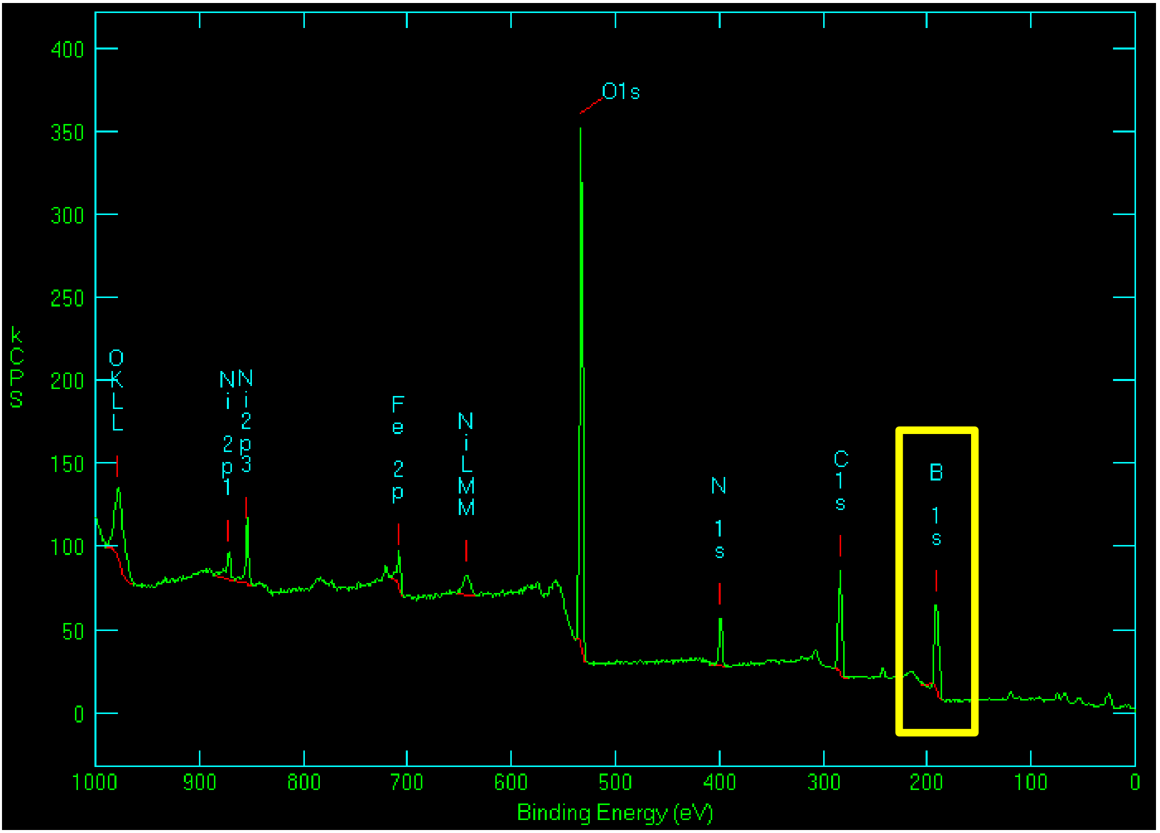
In Li-metal, the *2s* electrons form an electron sea.

In Li-oxide, the *2s* electrons are transferred to O :

- ☞Less electrons on Li-site
- ☞The *1s* electrons feel a stronger attraction from the nucleus.
- ☞E_B(*1s*) increases.

This is the chemical shift

S. Hüfner, Photoelectron Spectroscopy (Springer)

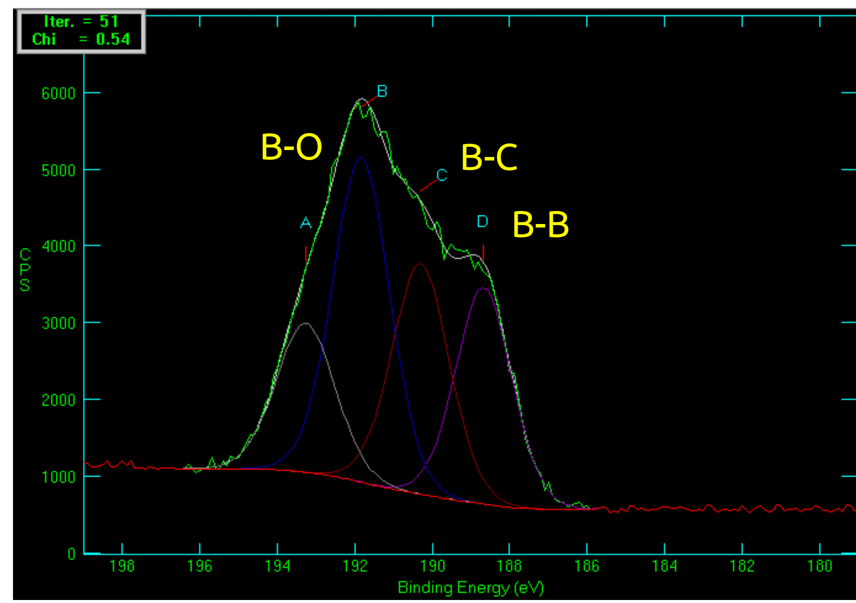


Chemical composition of the material surface...

Peak	SF	[AT]%	Centre	Pk Area	Norm Area
O 1s	2.93	28.7	532.90	84024.2	0.4
N 1s	1.80	4.3	398.50	7500.9	0.1
C 1s	1.00	18.7	283.40	17901.2	0.3
B 1s	0.49	48.4	191.90	22267.2	0.7

...quantitative analysis...

Chemical shifts of the B Core level



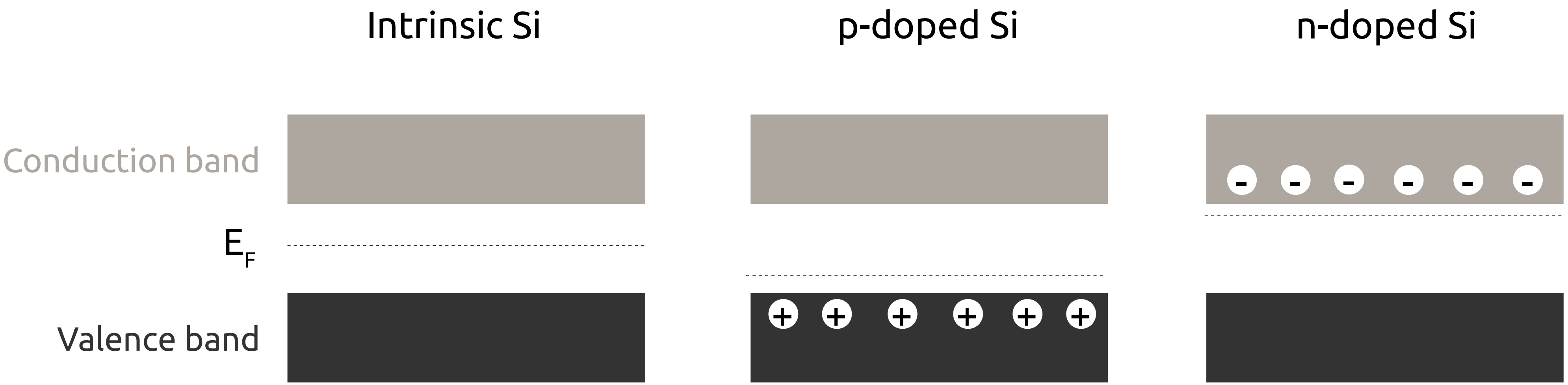
http://goliath.emt.inrs.ca/commerce/xps-tech_fr.html

… and chemical environment of each species.

ESCA : **E**lectron **S**pectroscopy for **C**hemical **A**nalysis

1. Photovoltaics with Si : the p-n junction
2. Sunlight aborbtion and carrier lifetime
3. PbS quantum dots
4. Time resolved photoemission on PbS/ZnO

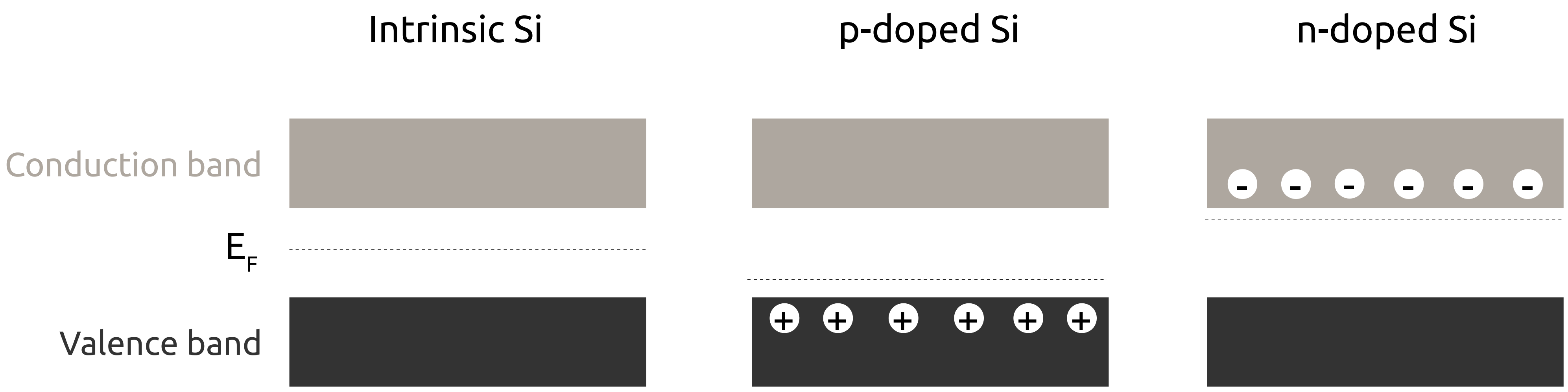
XPS for photovoltaics : Si p-n junction

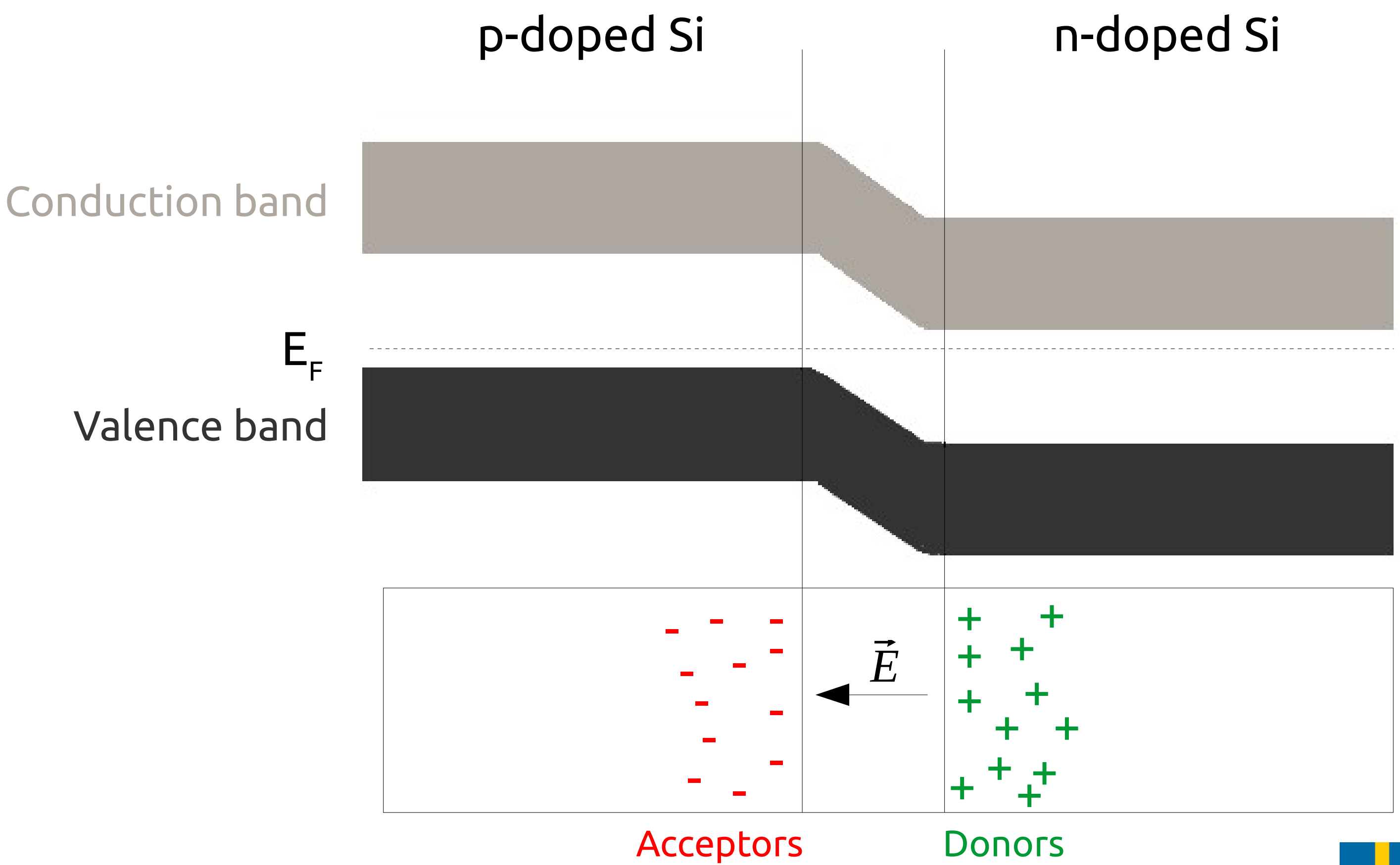


Acceptors (B, Al)
release additional
holes in the structure

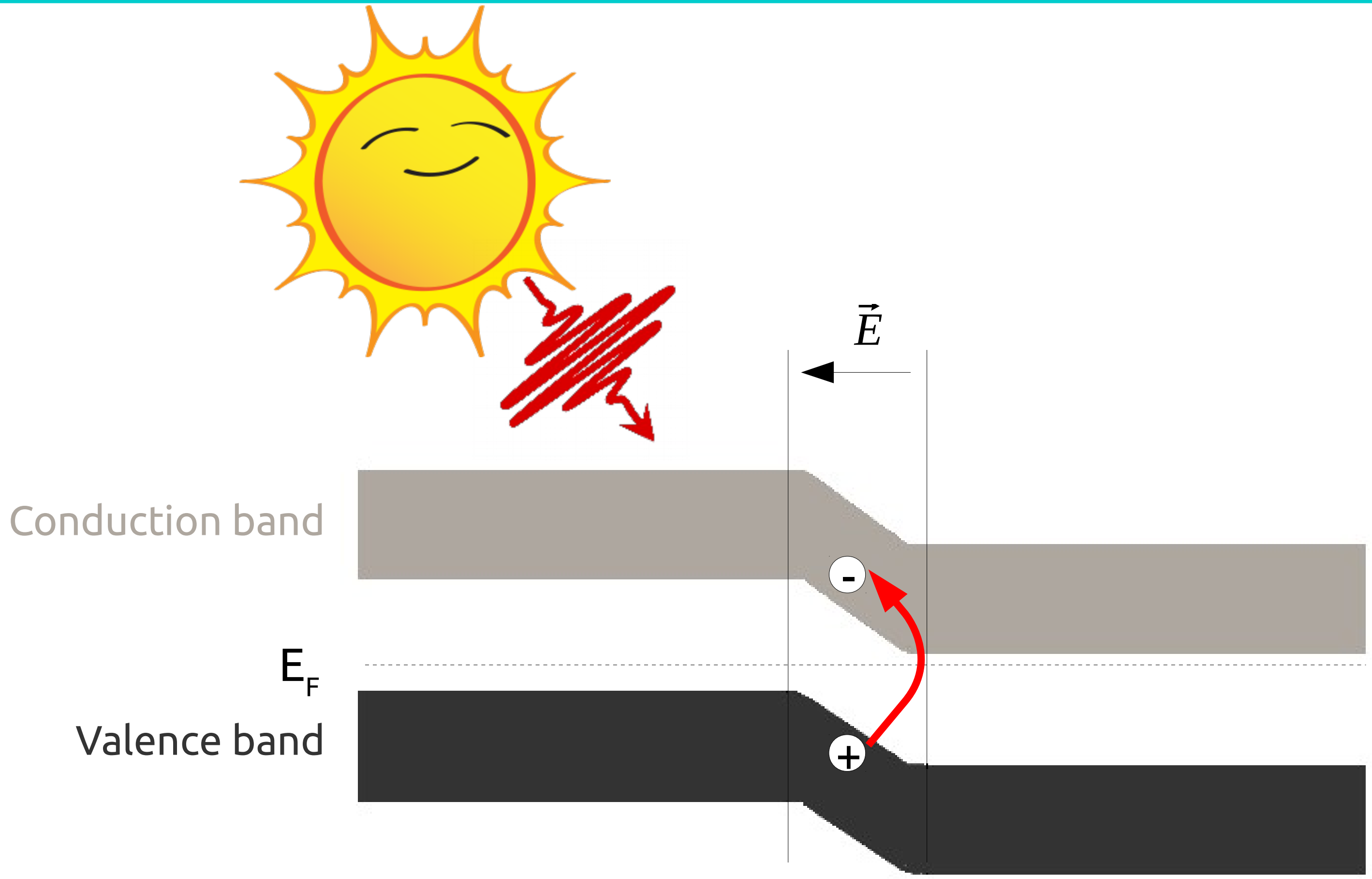
Donors (P, As)
release additional
electrons in the structure

XPS for photovoltaics : Si p-n junction

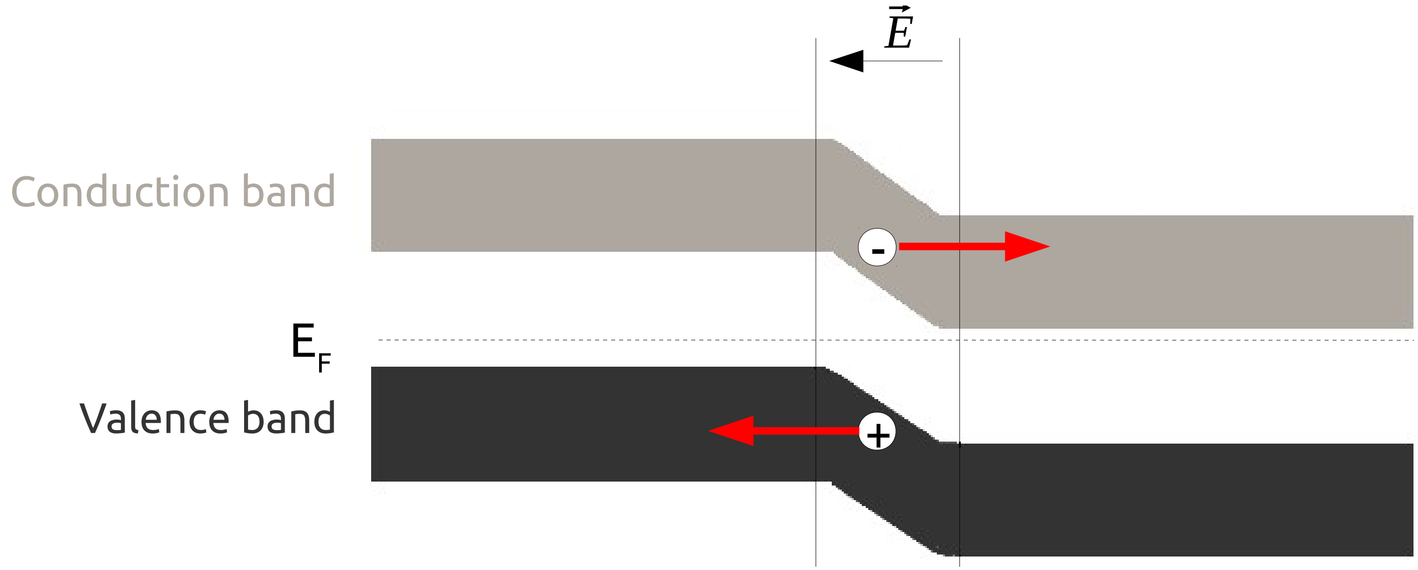




Electrons and holes diffuse through the junction leaving ions behind them thus creating an electric field. This field increases and, at some point, prevents any further diffusion...



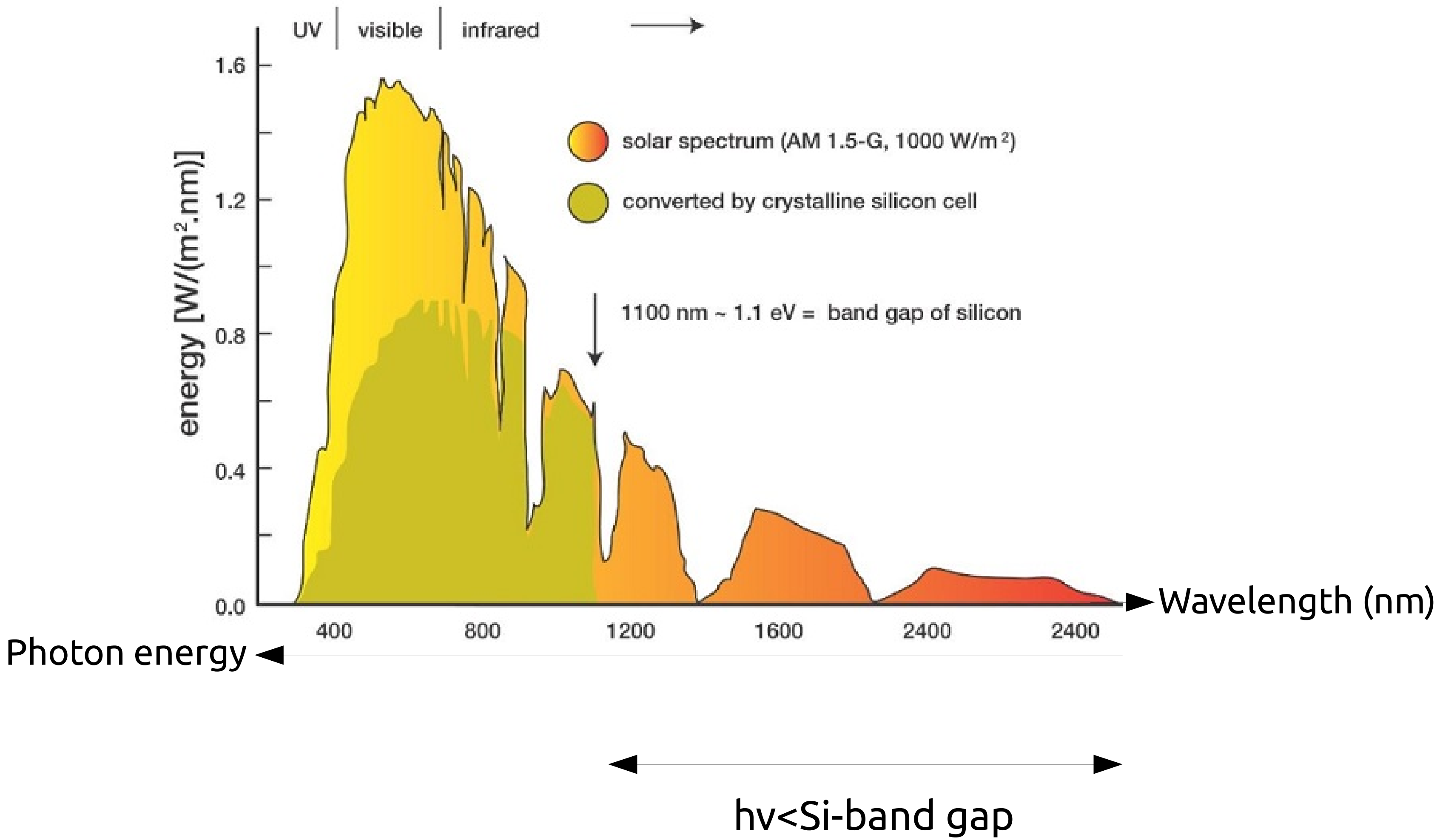
If an electron-hole pair is created by the sunlight...



...it will be separated by the electric field prior to recombination and a current will flow through the device.

- Lifetime of the electron-hole pair must be as large as possible
- Absorption of the sunlight must be optimized (20 % for Si)

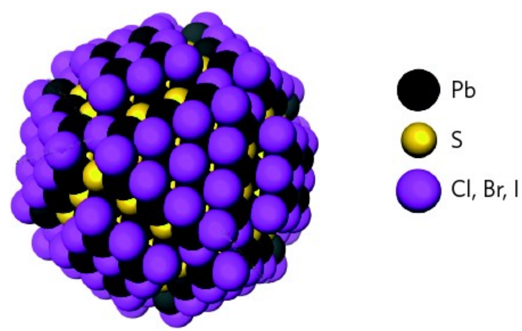
XPS for photovoltaics : Sunlight absorption by Si



There is a cutoff in the absorbed wavelength at the value of the Si-band gap.

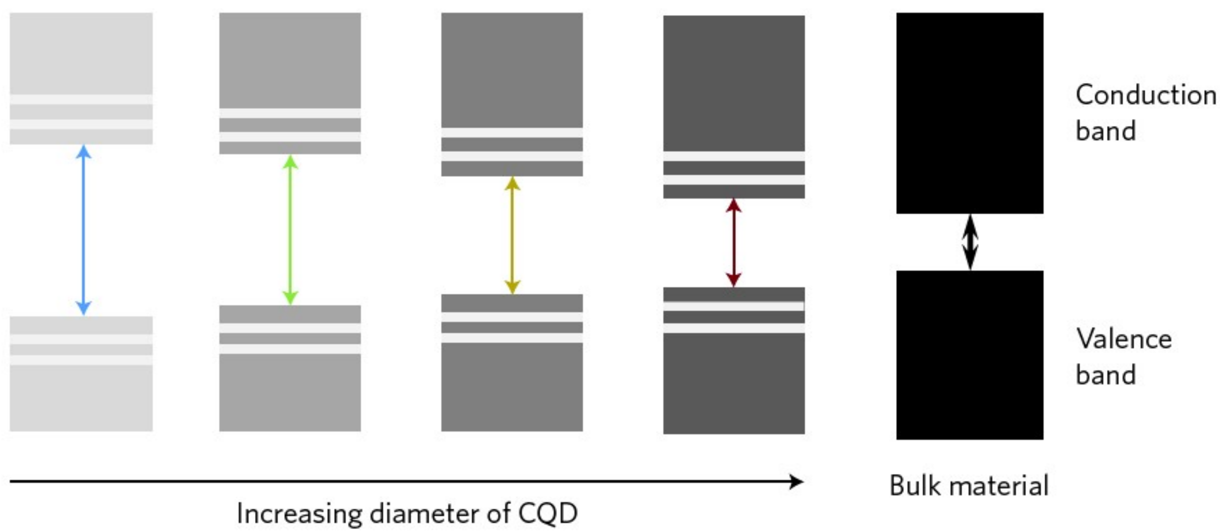
Could we get rid of this cutoff using other materials ?

XPS for photovoltaics : PbS colloidal quantum dots (CQD)



Quantum dots prepared in solution

The surface facets are passivated by forming an Pb-halide

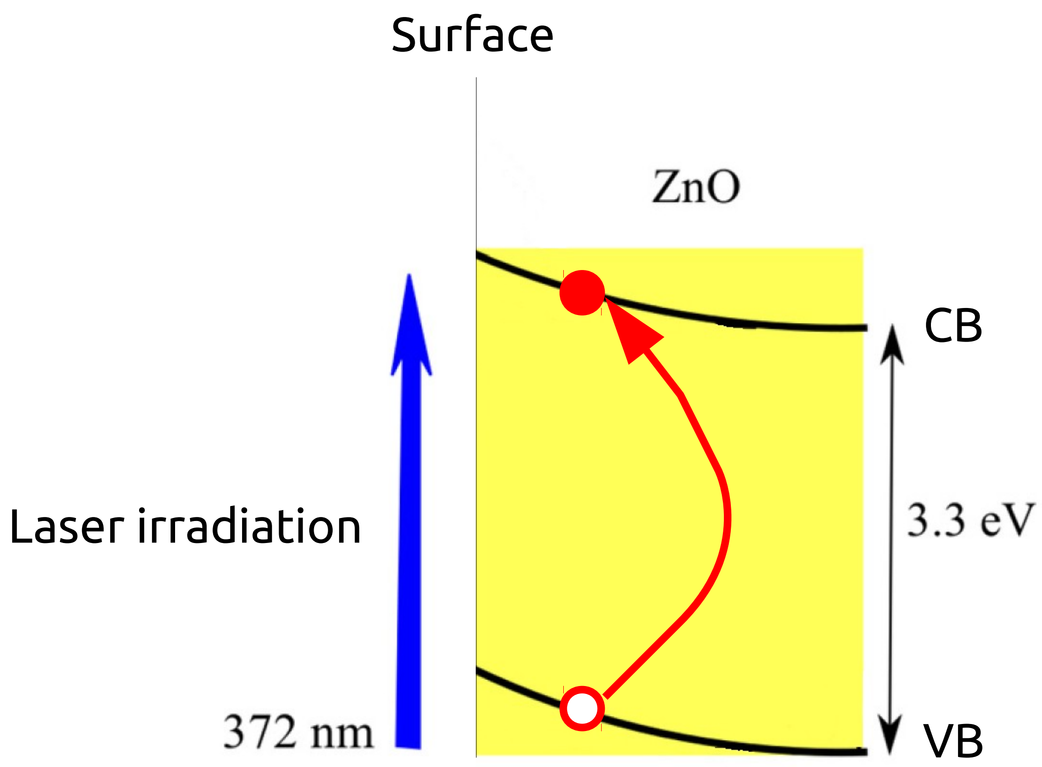


*M. Yuan et al., Nature Energy **1**, 16016 (2016)*

The band gap depends on the QD-size

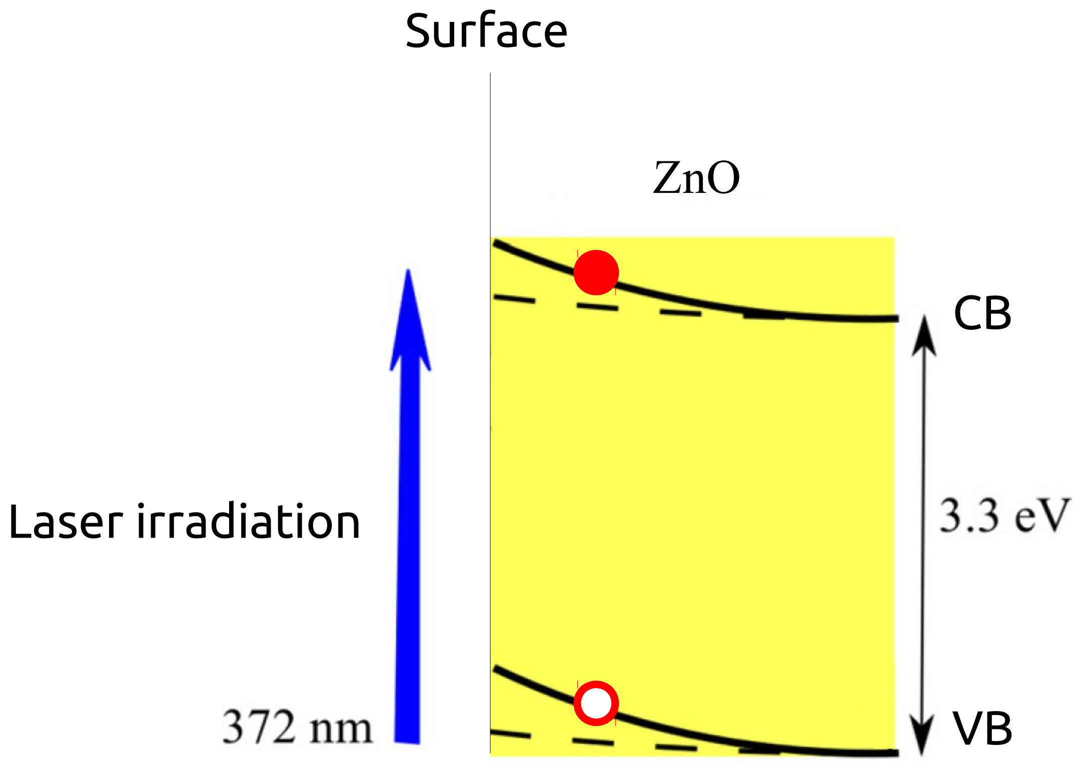
In our exemple, these PbS-QD will be deposited on ZnO.

Let's first see how ZnO behaves under irradiation...



If the laser wavelength is short enough, an electron-hole pair can be created…

B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

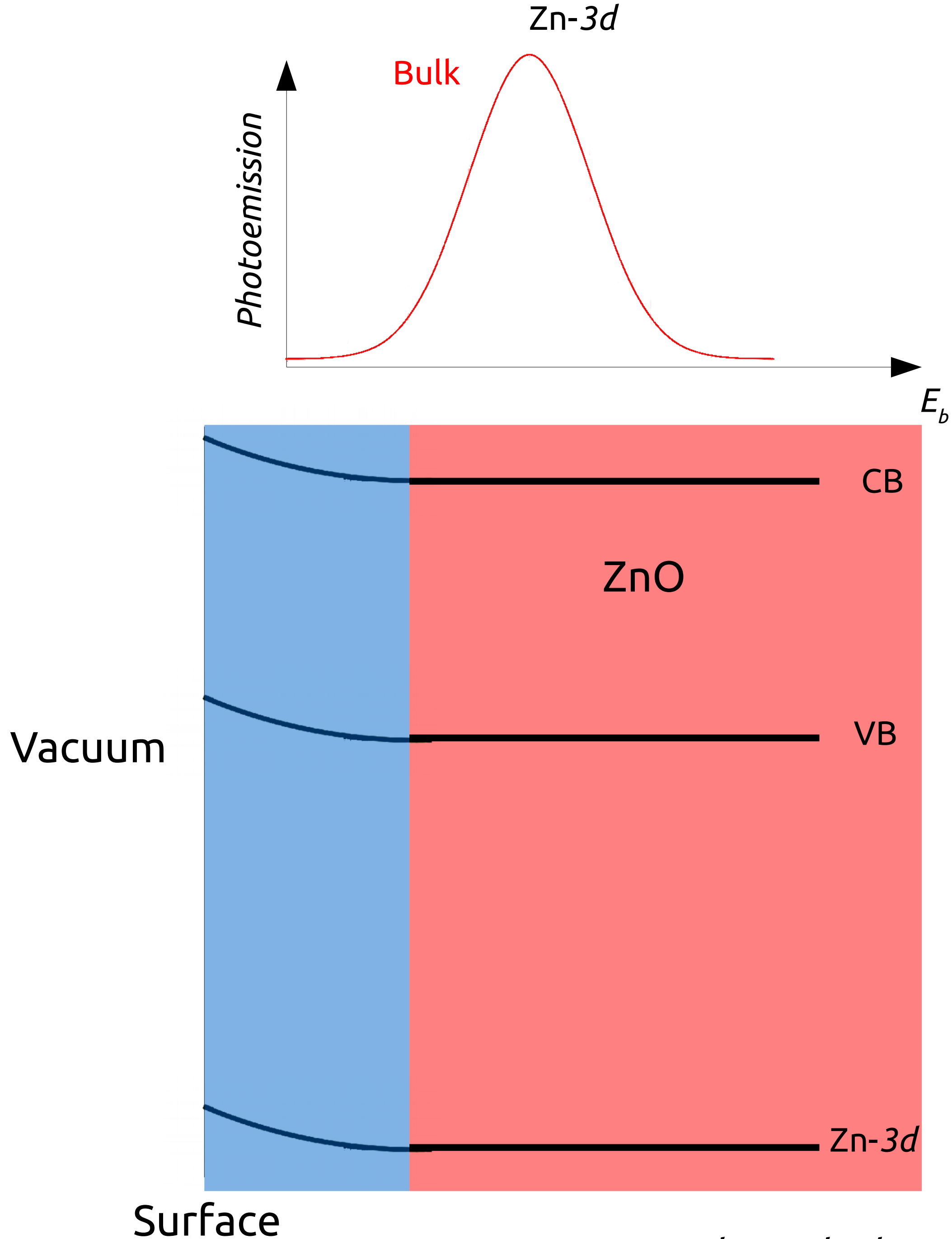


Surface photovoltage : The additional charges due to illumination change the surface potential and flatten the bands.

Can we measure that by photoemission ?

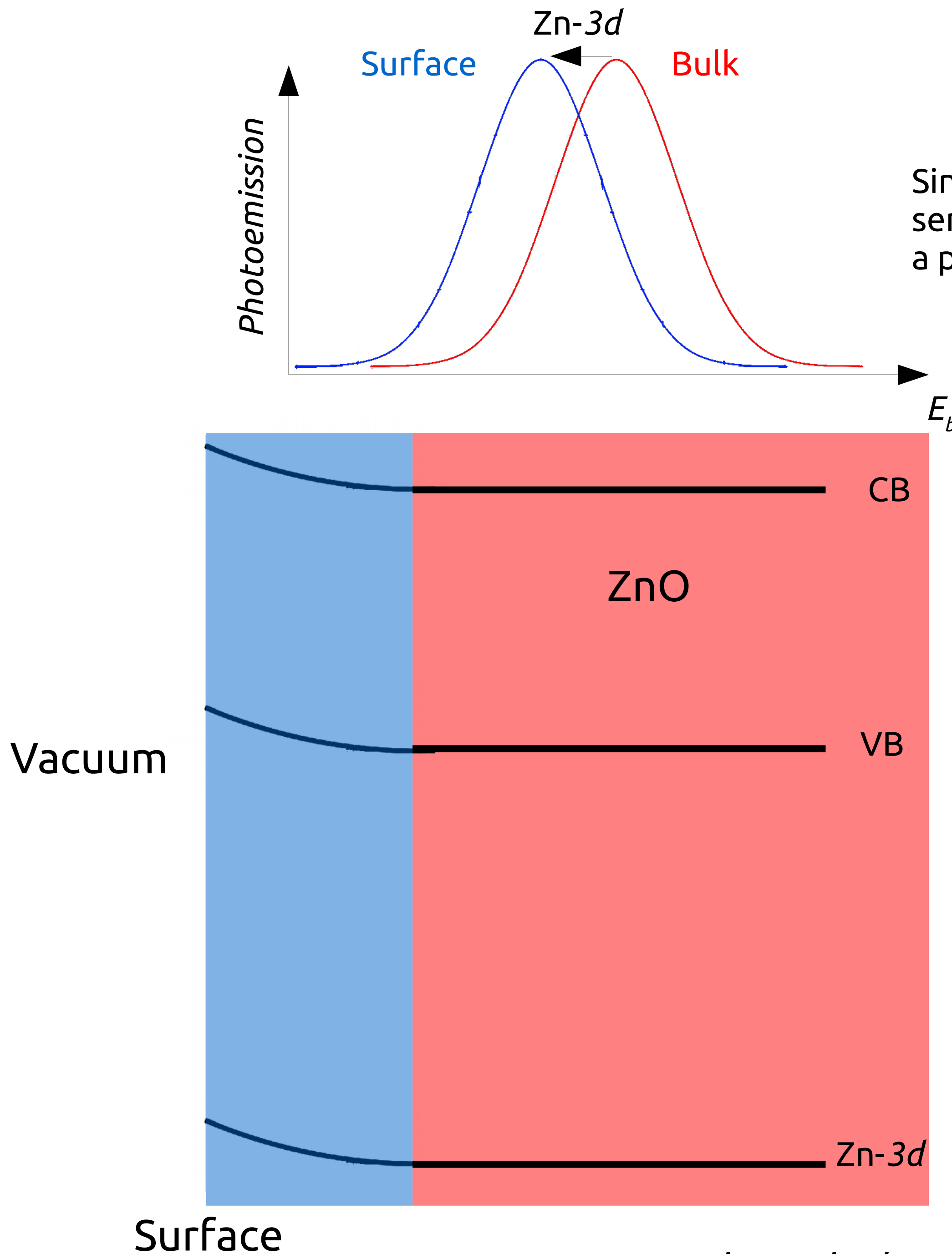
B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

XPS for photovoltaics : Irradiation of ZnO



B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

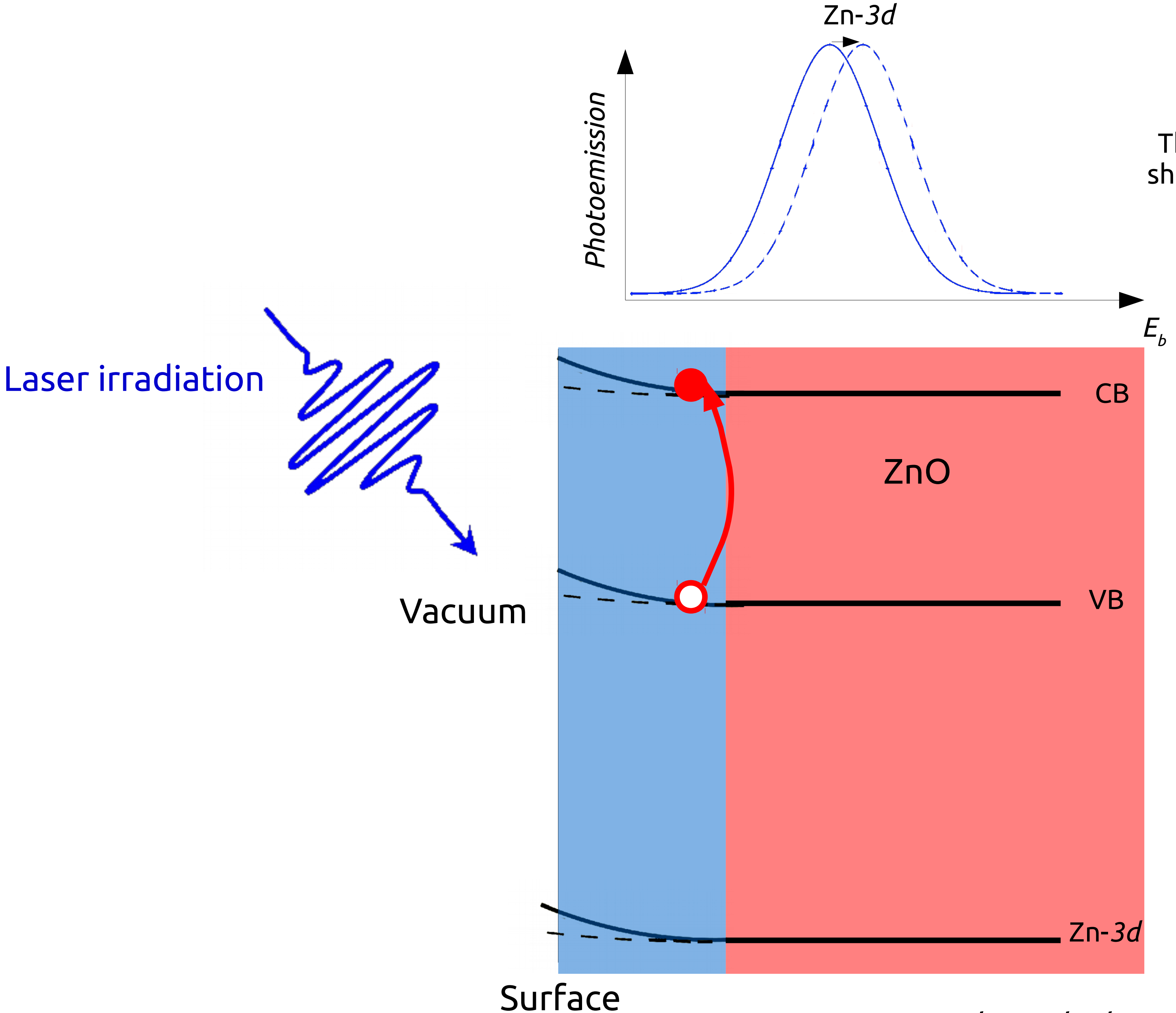
XPS for photovoltaics : Irradiation of ZnO



Since photoemission is surface sensitive, we should rather see a peak shifted to a smaller E_b...

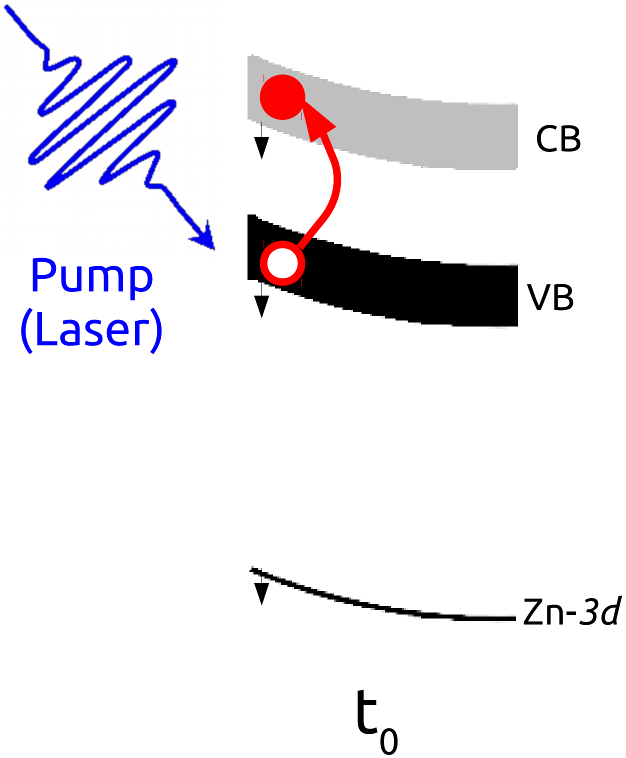
B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

XPS for photovoltaics : Irradiation of ZnO

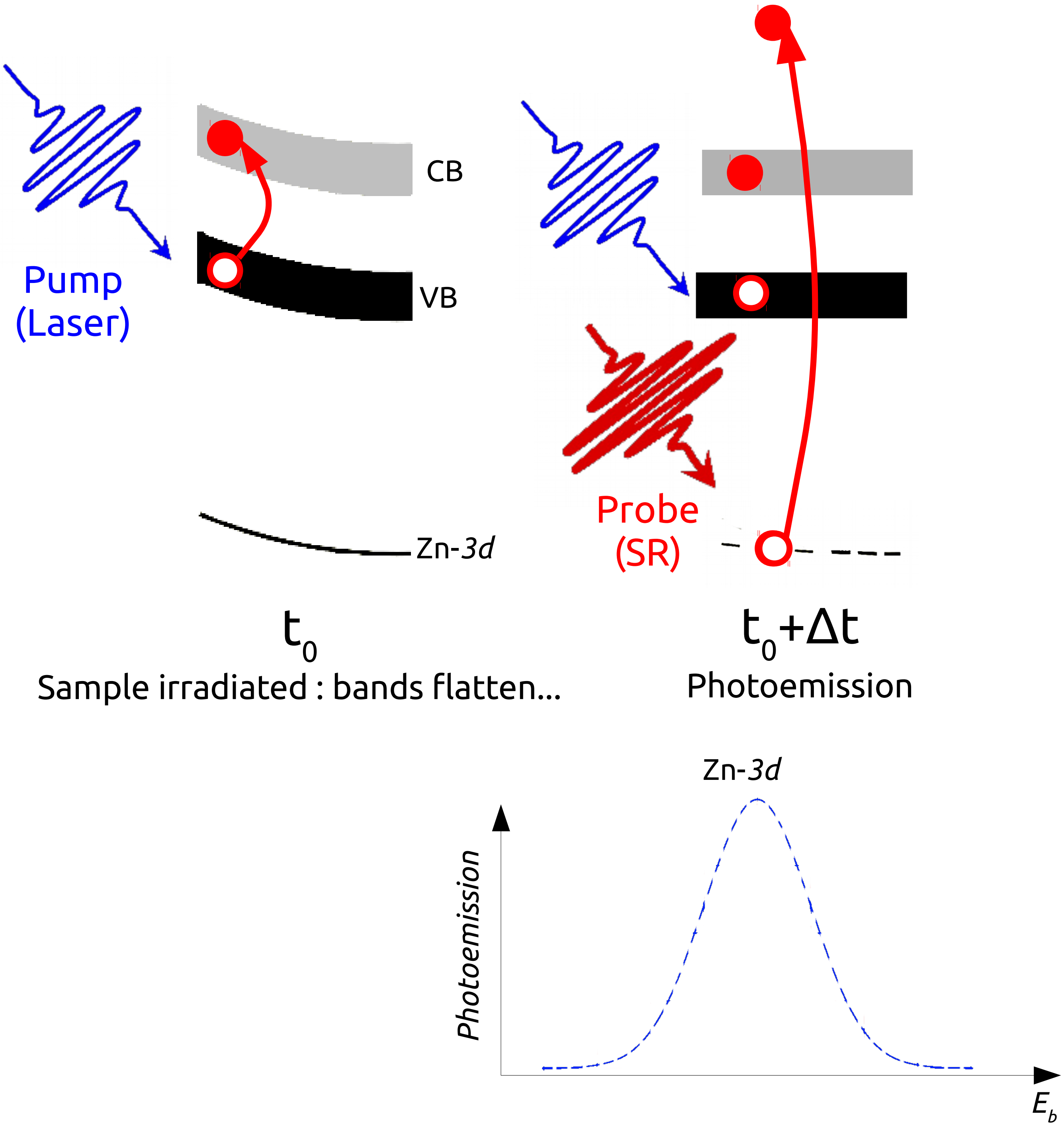


The flattening of the bands should result in a shift of this Zn-*3d* surface peak

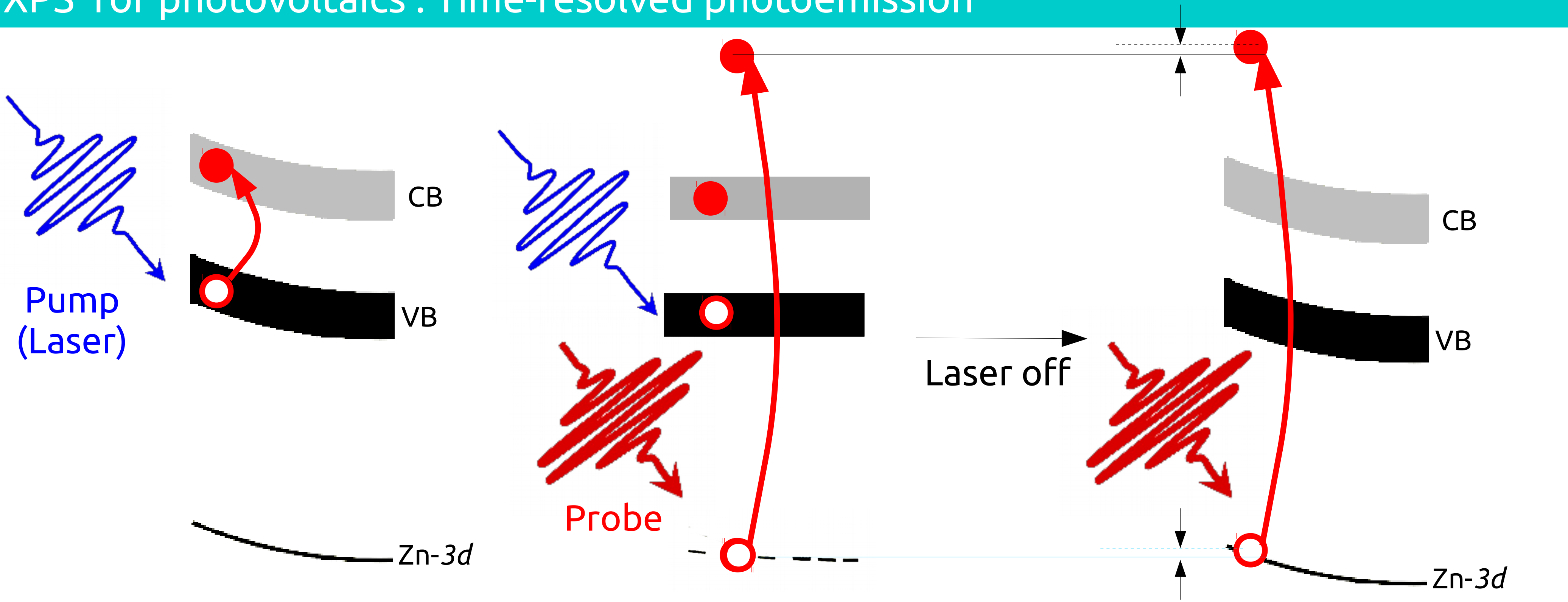
B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*



Sample irradiated : bands flatten...


CB
VB
Pump
(Laser)
Zn-3d
Probe
(SR)
t_0
Sample irradiated : bands flatten...
$t_0+\Delta t$
Photoemission
Zn-3d
Photoemission
E_b

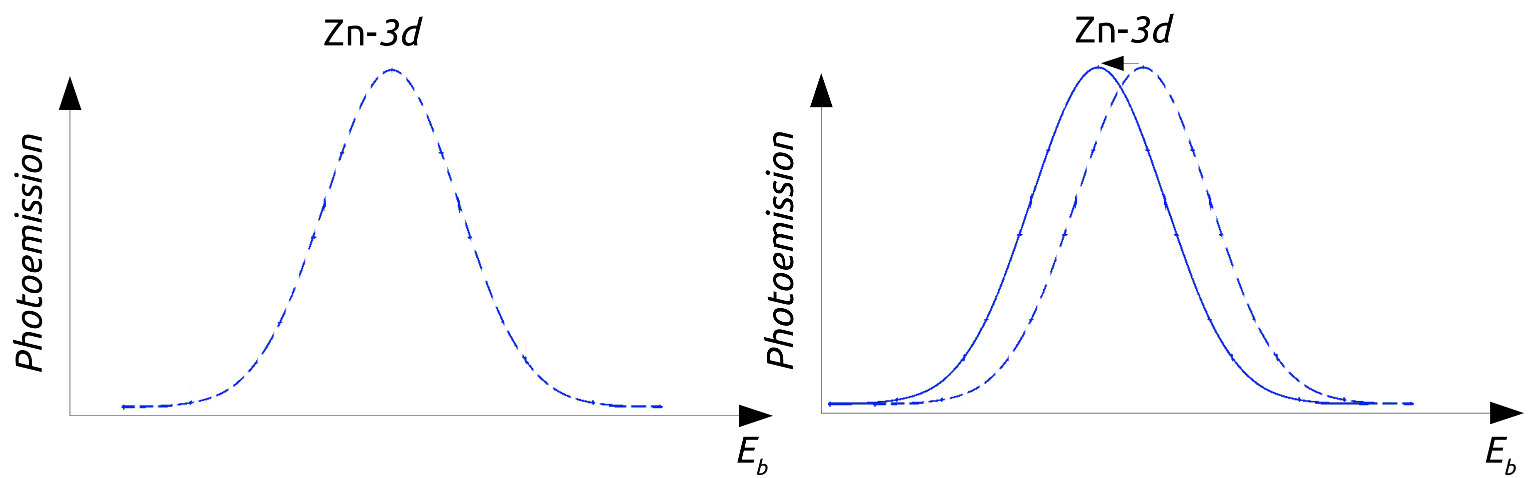
XPS for photovoltaics : Time-resolved photoemission



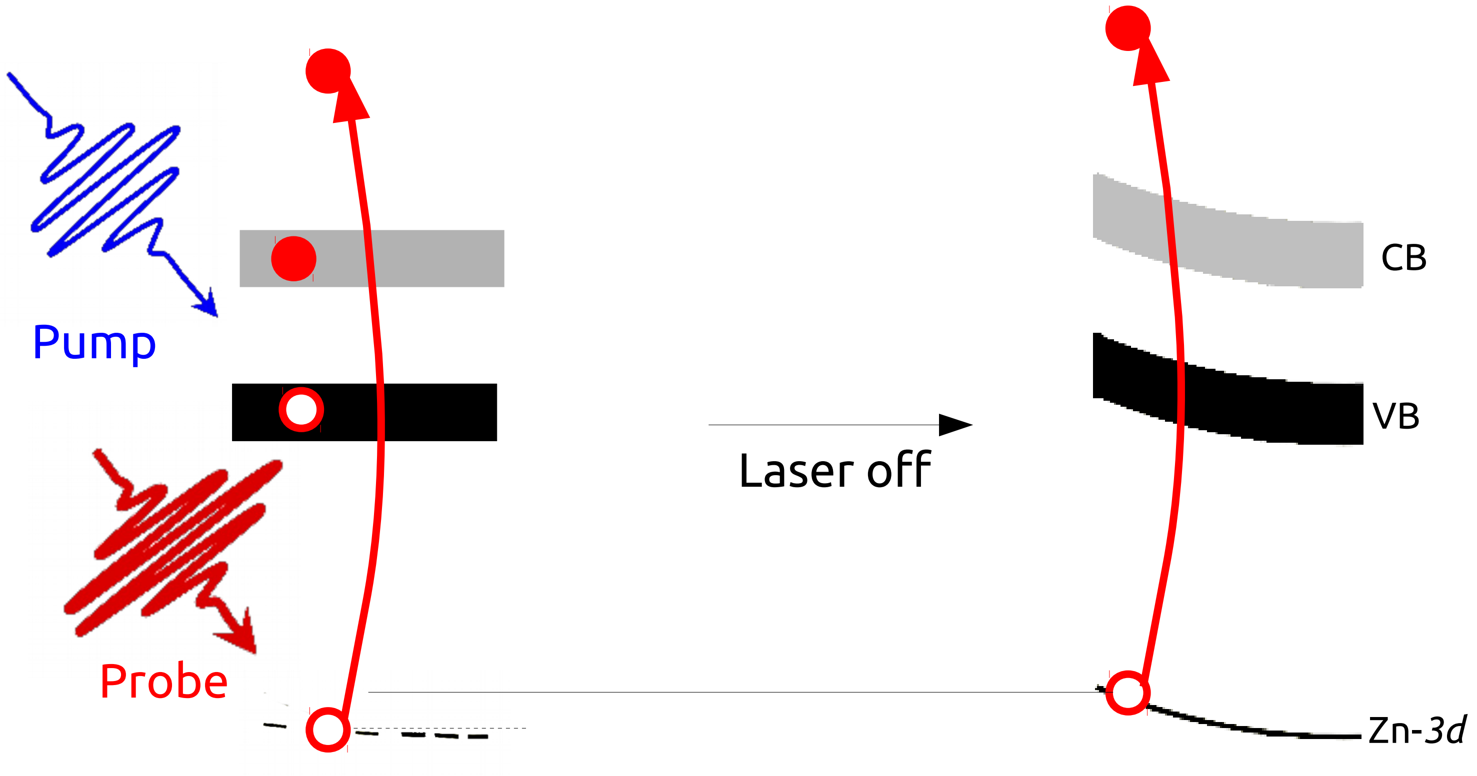
t_0
Sample irradiated : bands flatten...

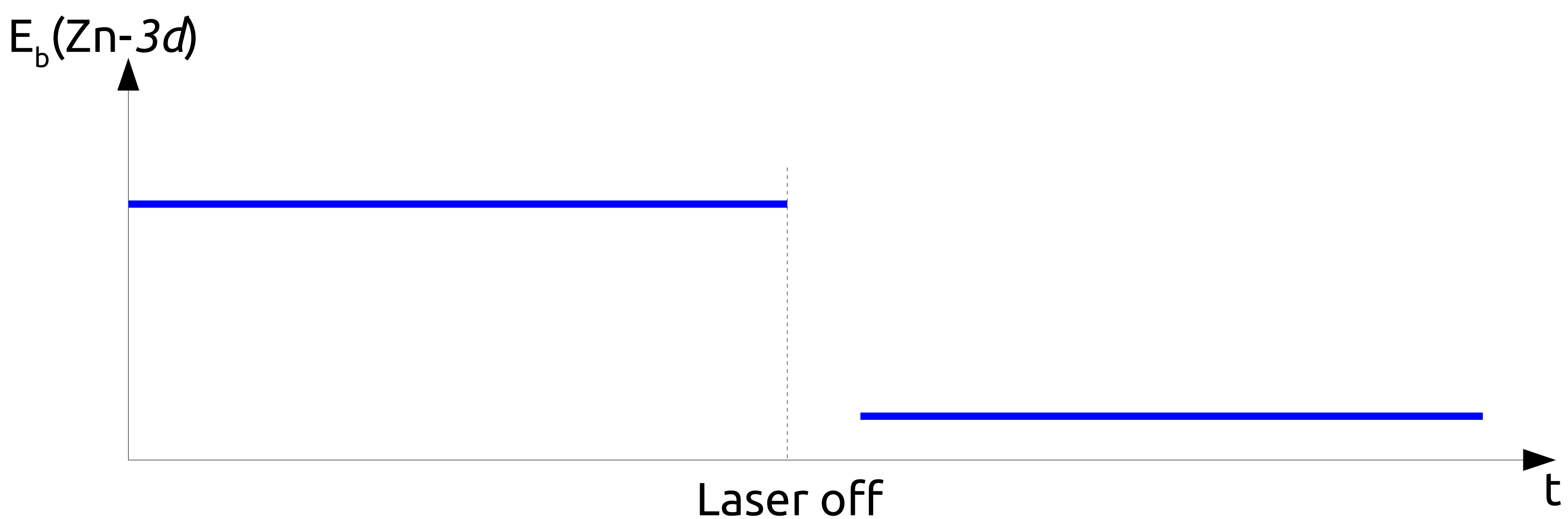
$t_0 + \Delta t$
Photoemission

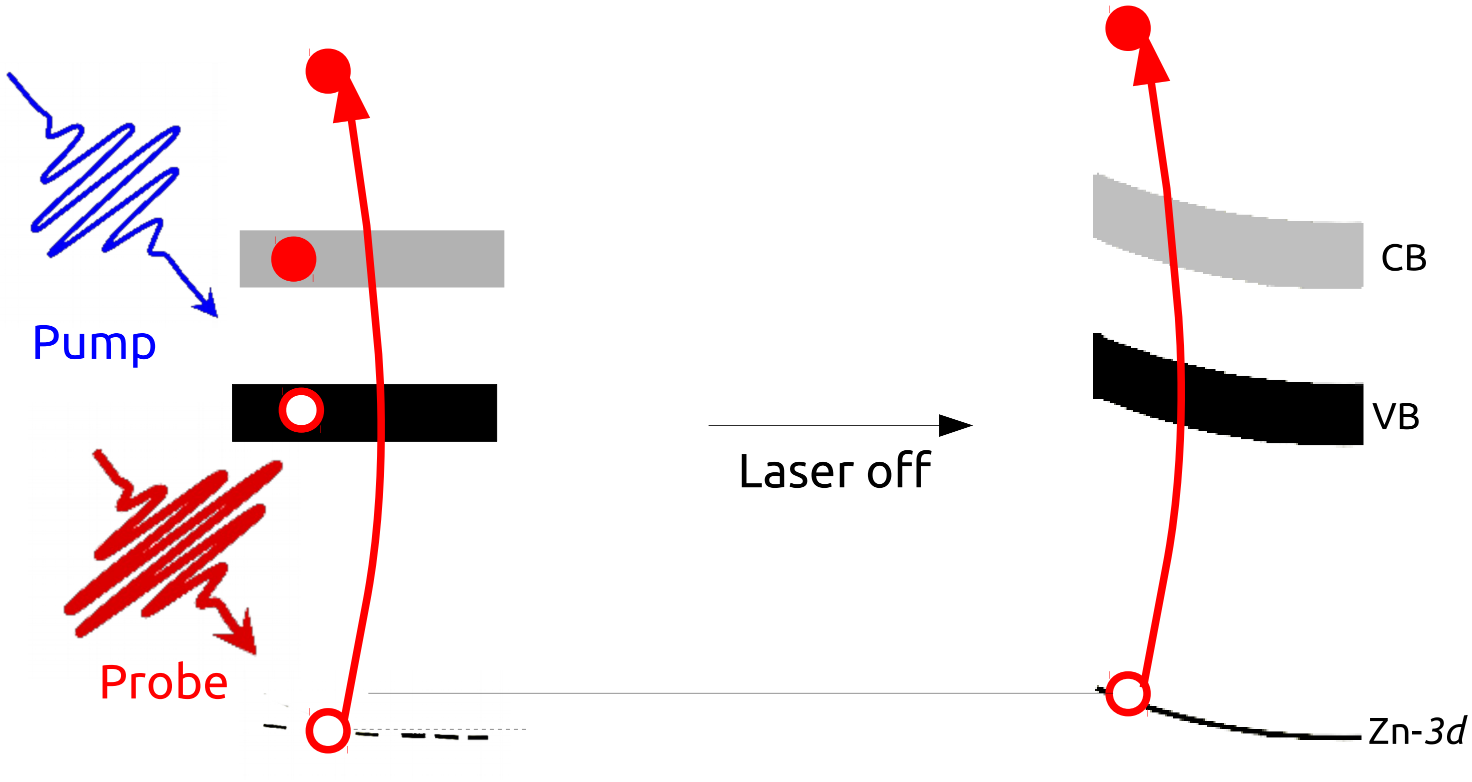
Photoemission with Laser off :
Zn-*3d* shifts to smaller BE

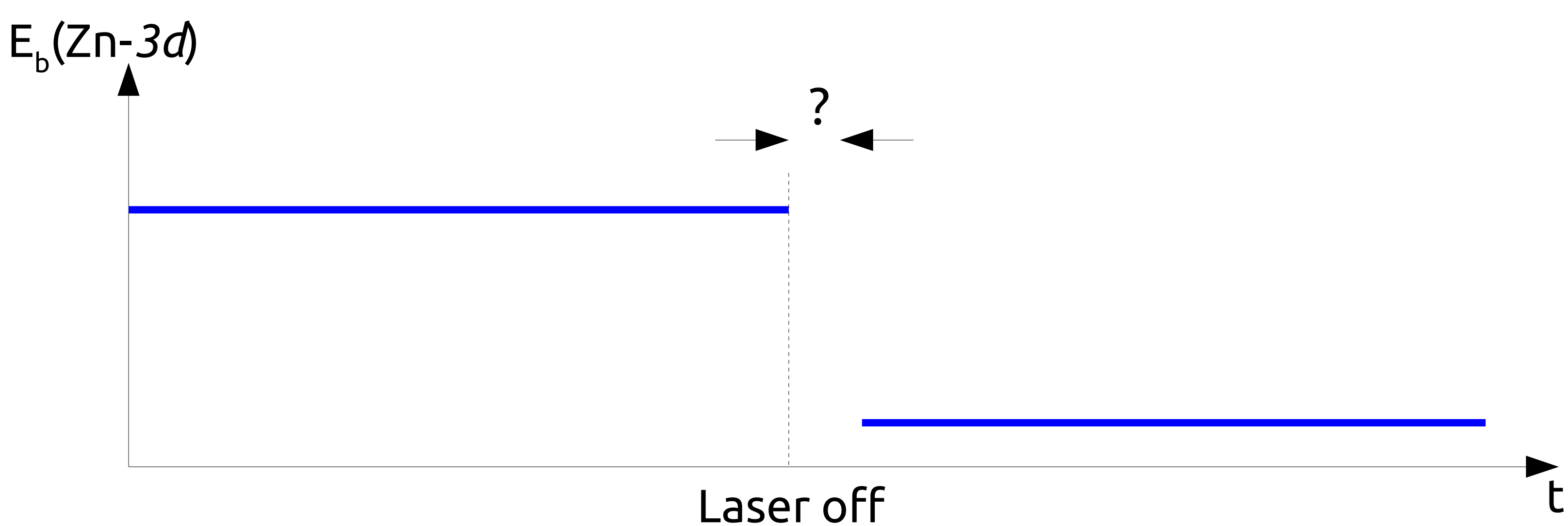


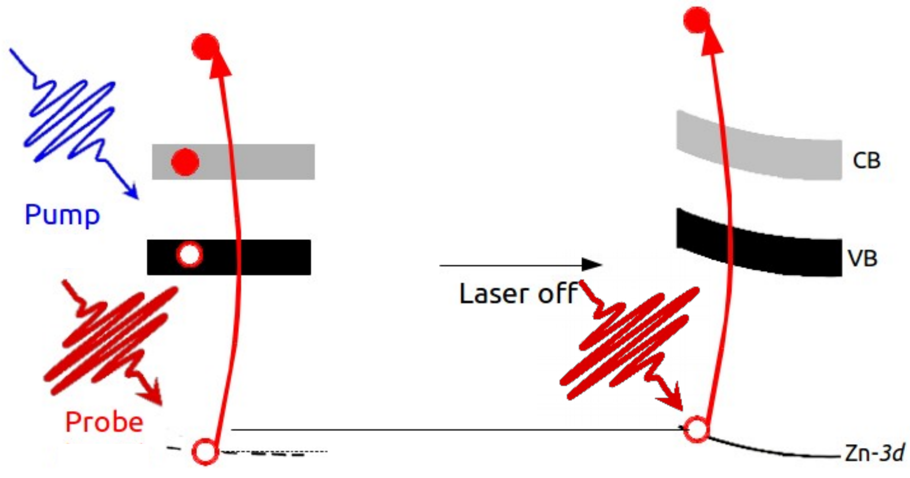
XPS for photovoltaics : Time-resolved photoemission



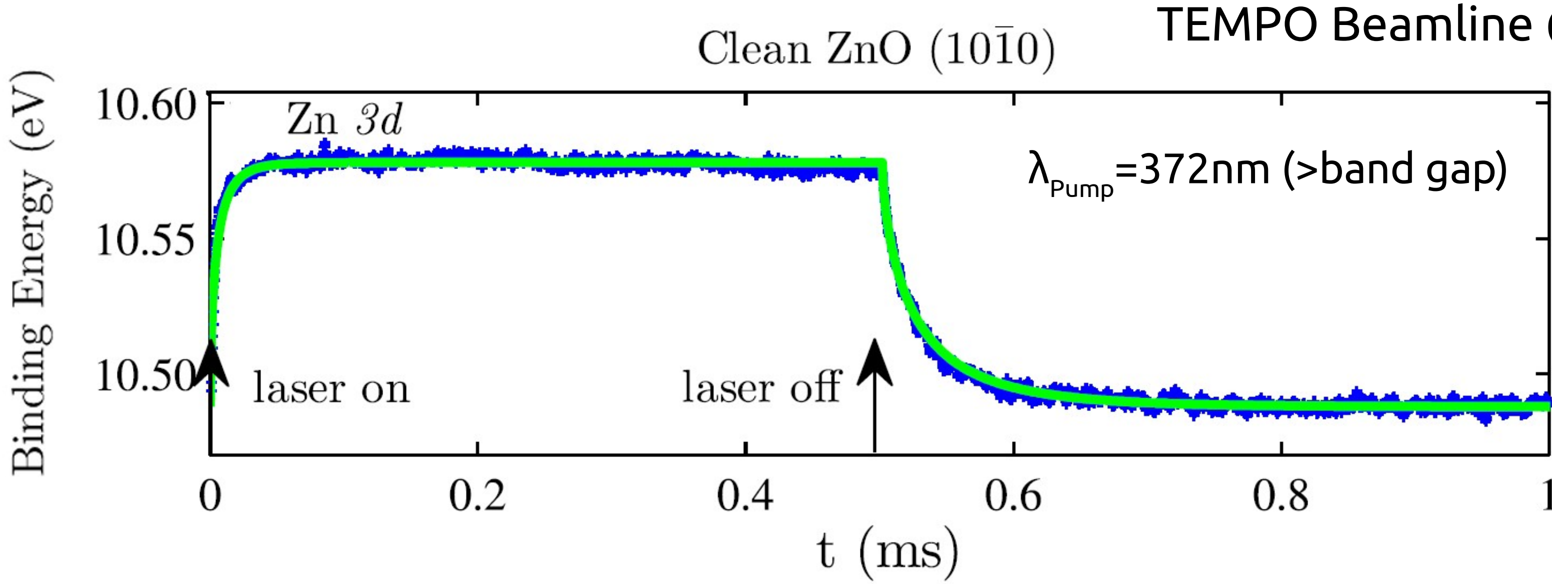



Pump
Probe
Laser off
CB
VB
Zn-3d


Eb(Zn-3d)
?
Laser off
t

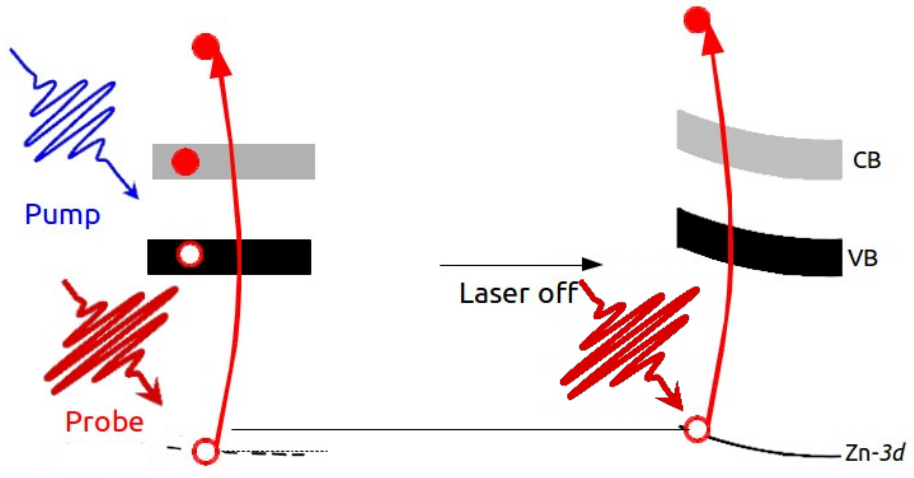


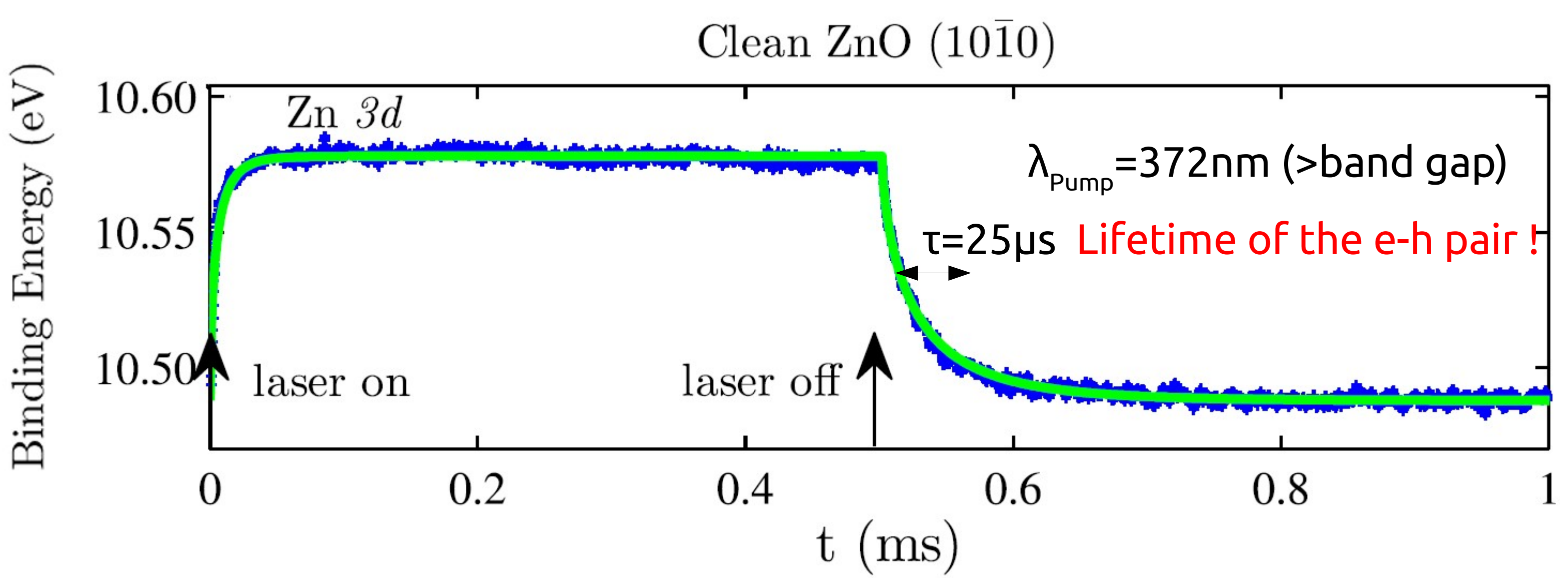
hv=175 eV
1 spectrum/150 ns
TEMPO Beamline @SOLEIL



B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

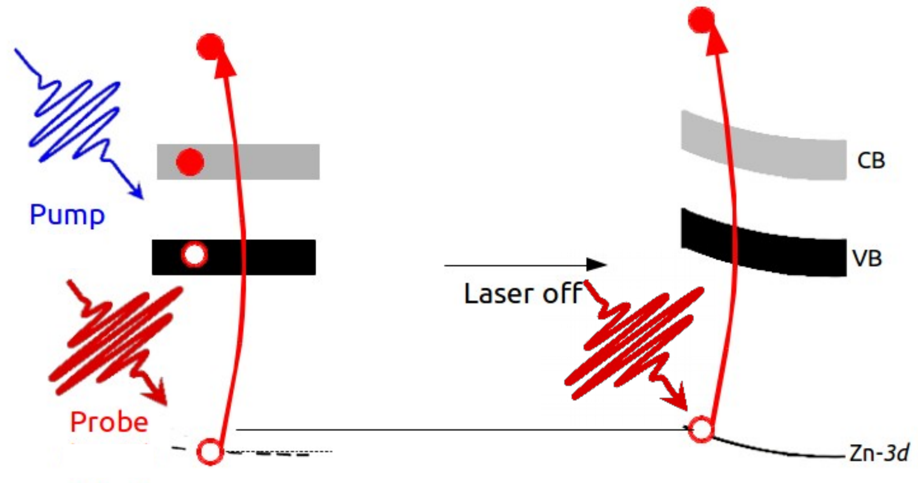
XPS for photovoltaics : Time-resolved photoemission

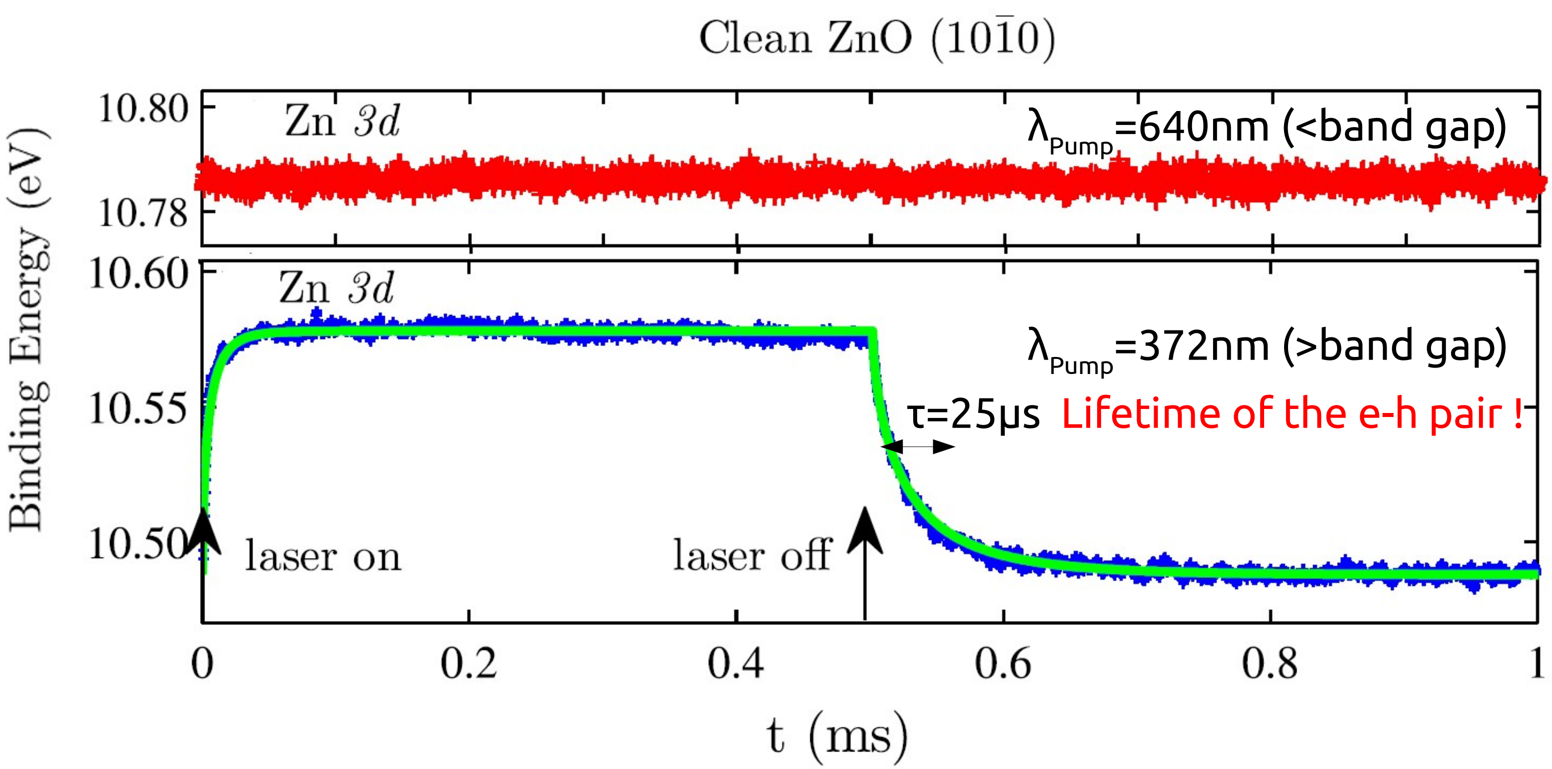




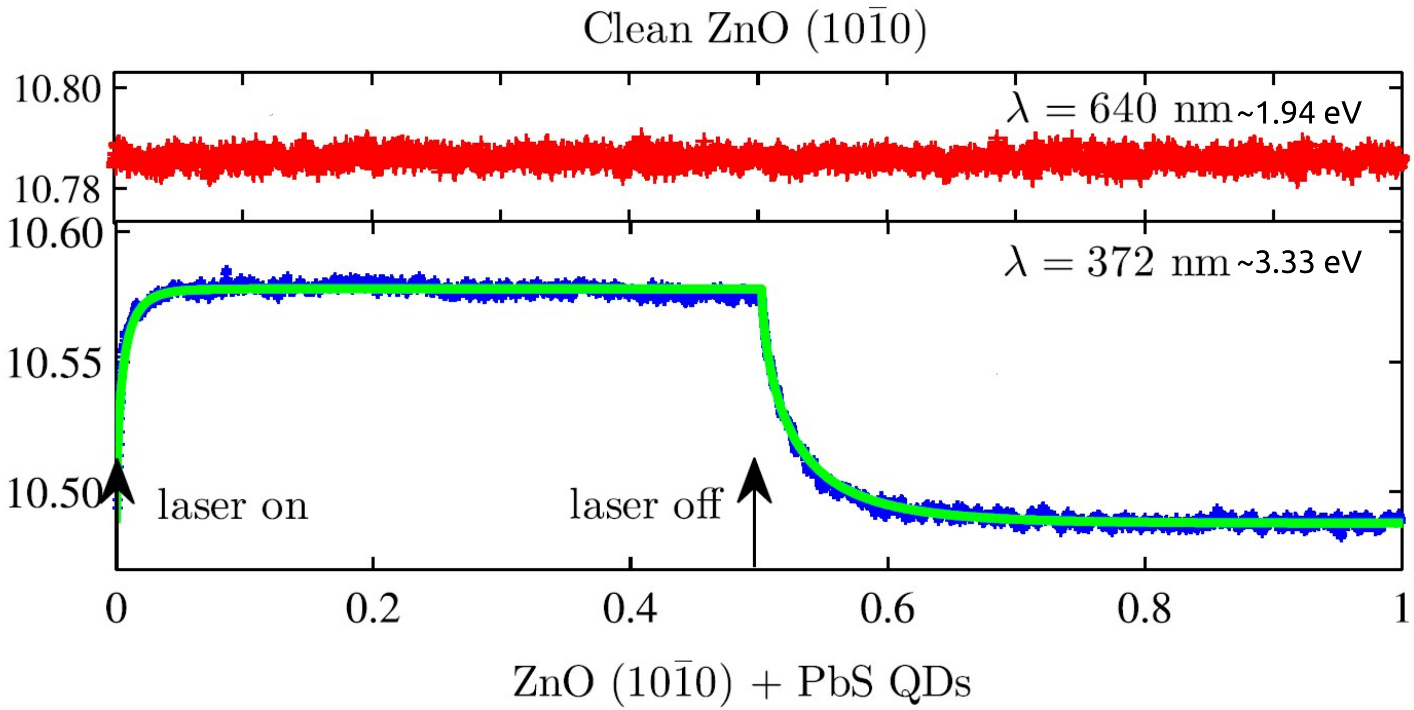
B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

XPS for photovoltaics : Time-resolved photoemission on clean ZnO



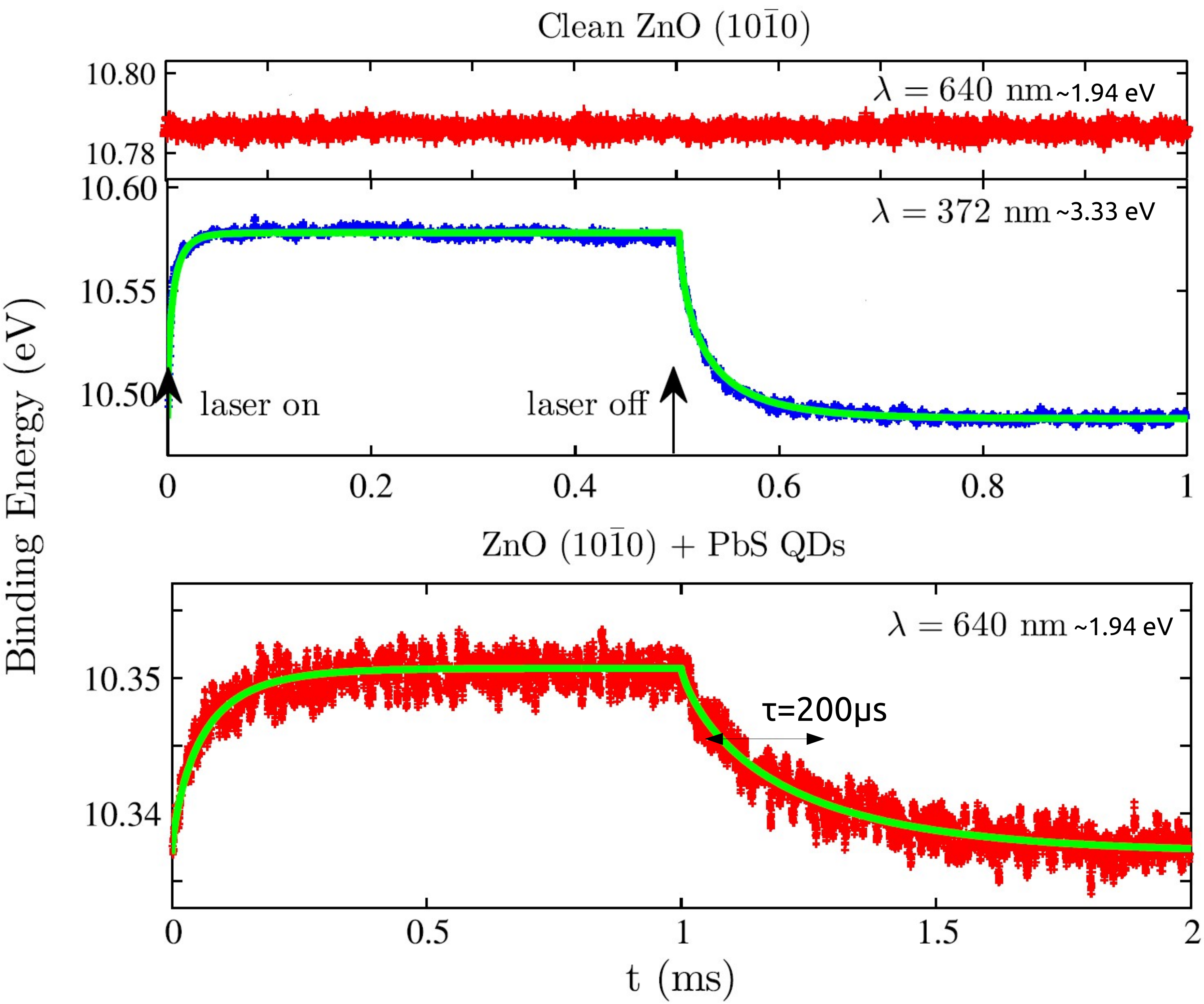


B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*



Let's now add the PbS CQD on ZnO…

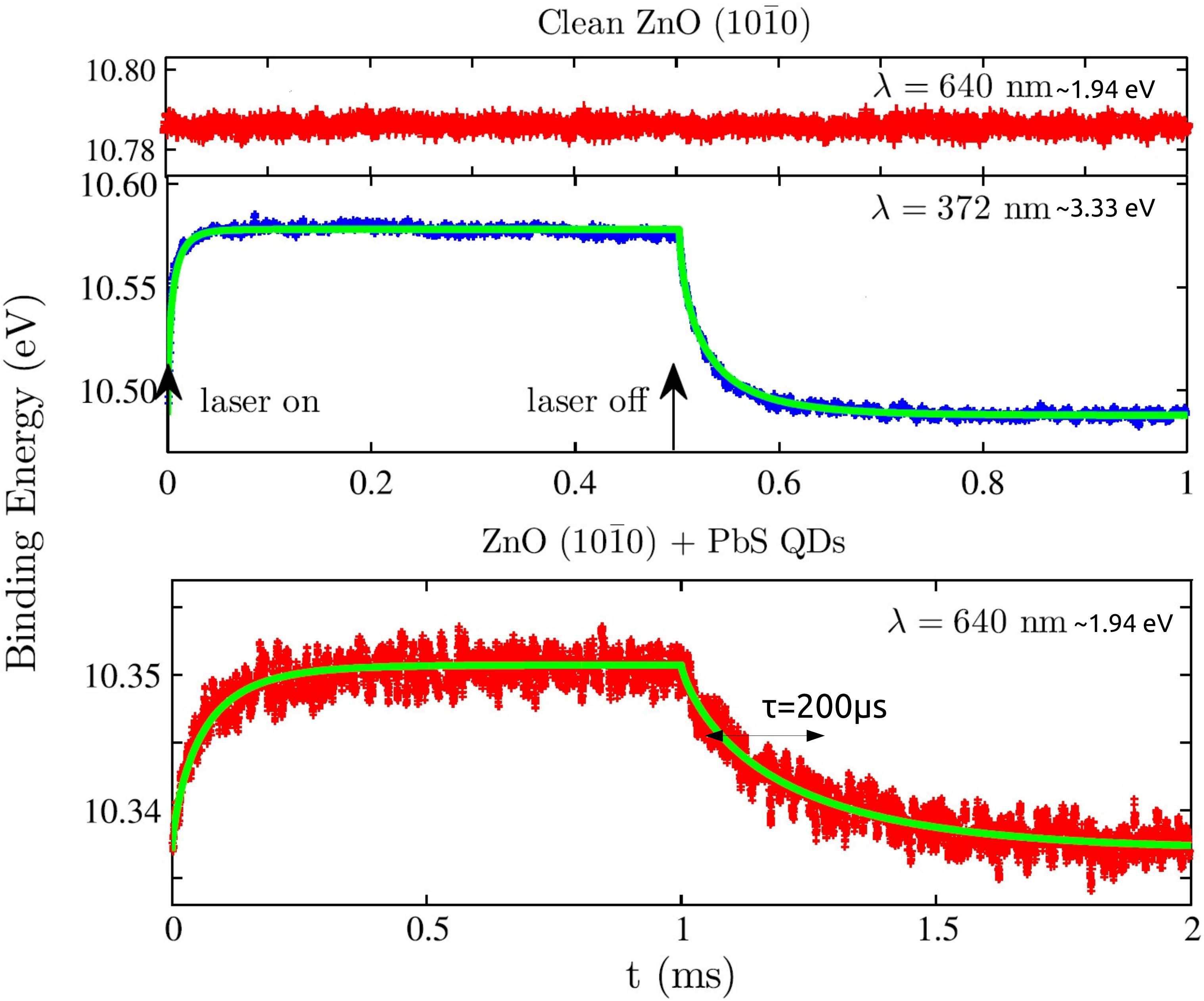
B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

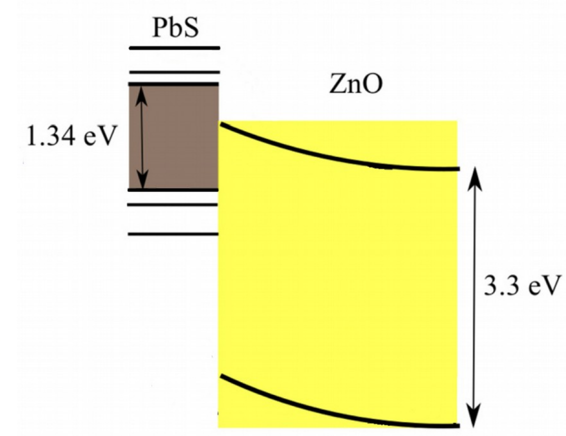


Band bending changes in ZnO for an excitation energy smaller than the band gap !

B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

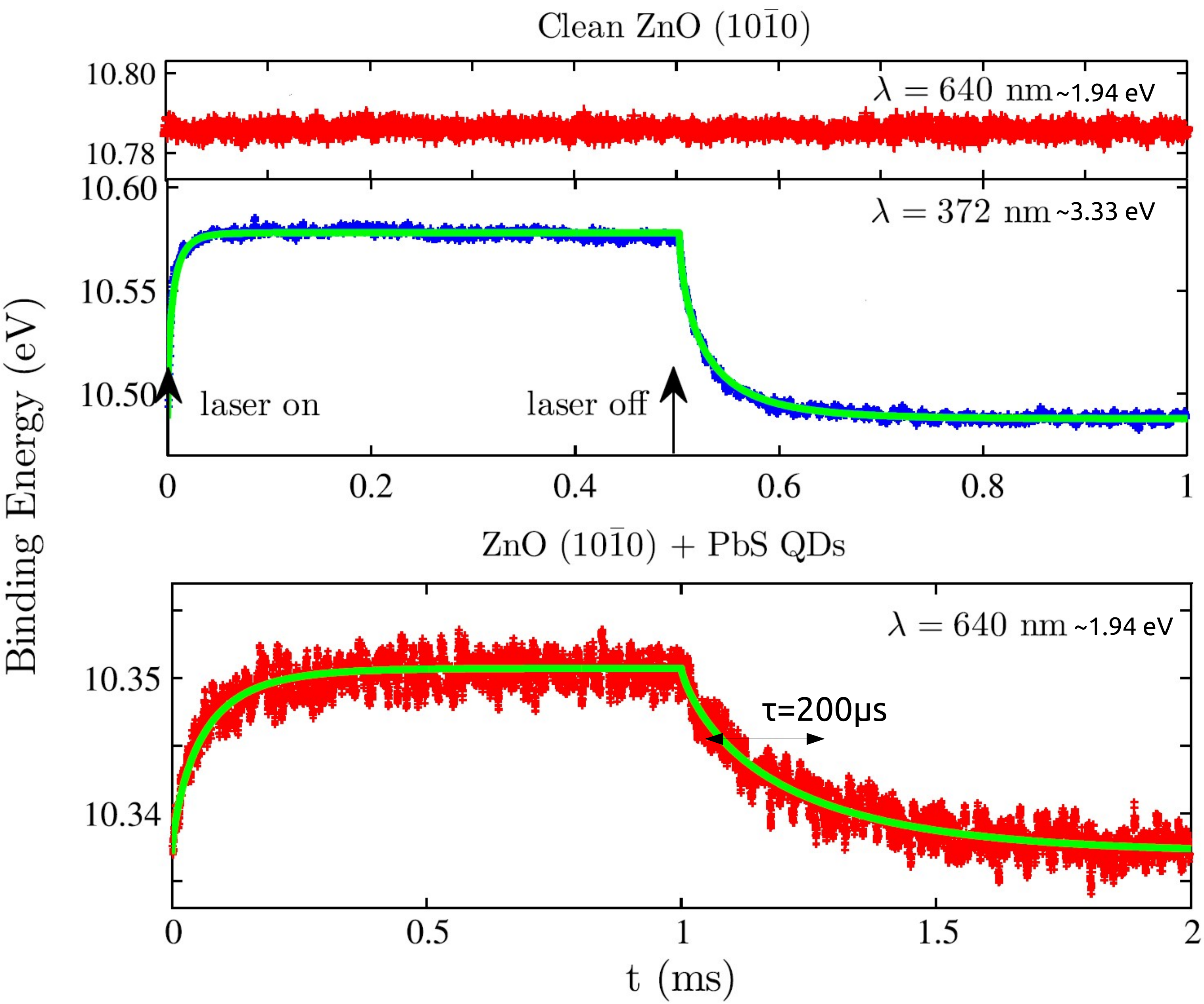
XPS for photovoltaics : Time-resolved photoemission on PbS on ZnO

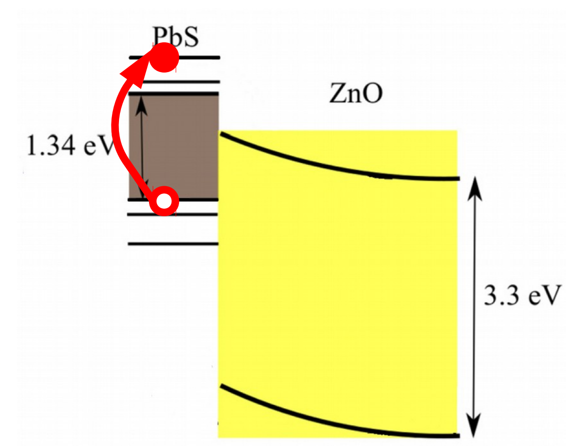




B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

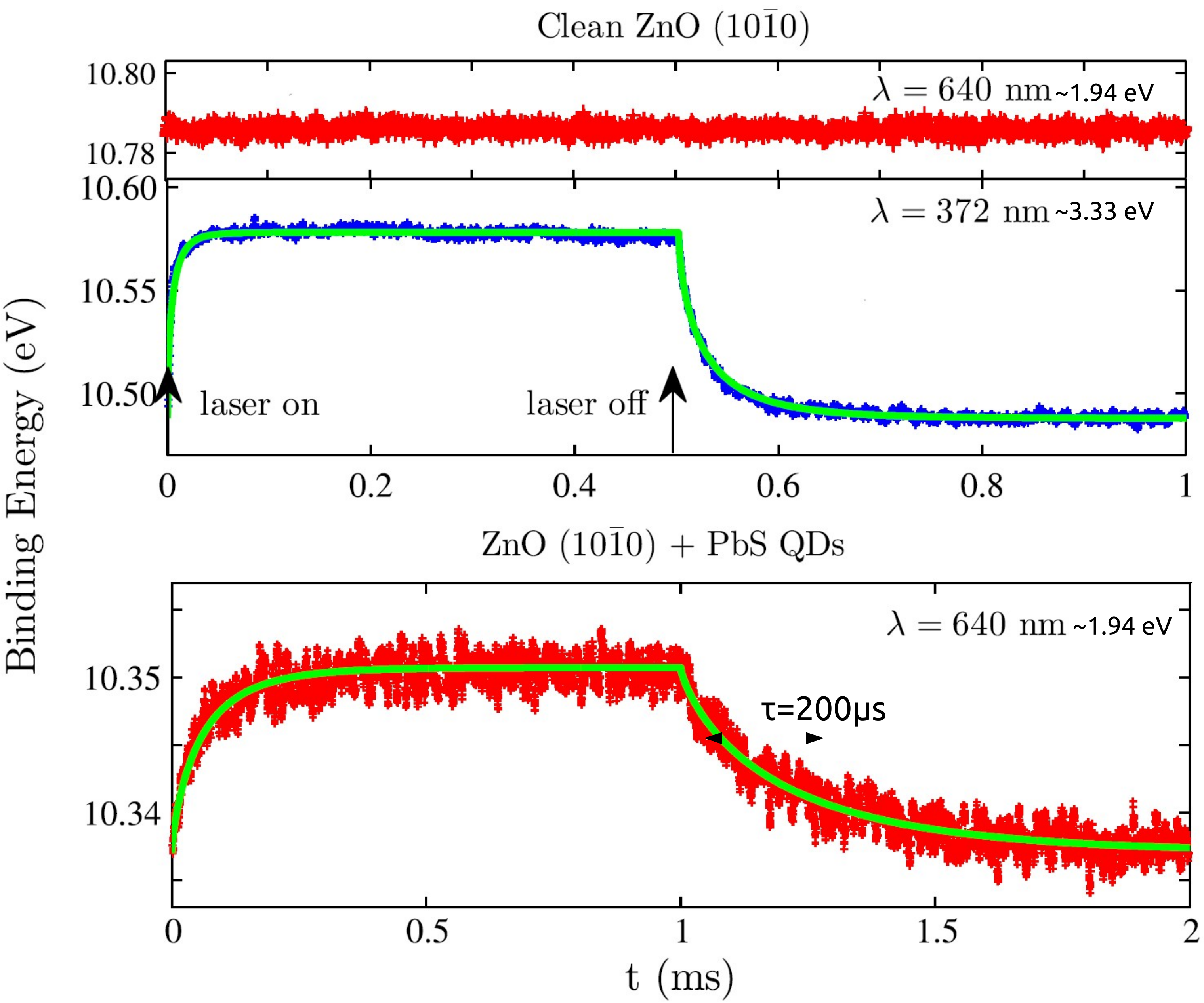
XPS for photovoltaics : Time-resolved photoemission on PbS on ZnO

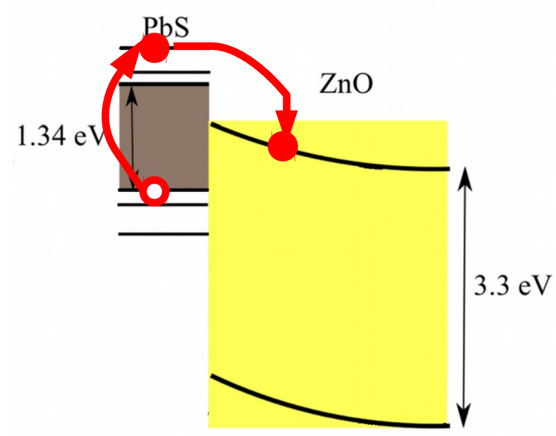




A photoelectron is excited in the PbS-QD...

B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

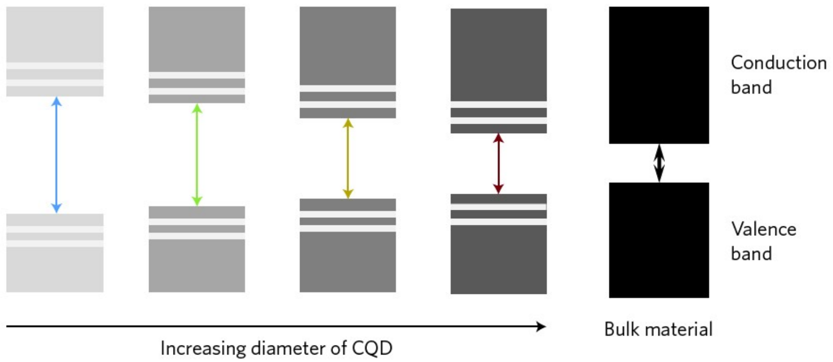




...and transfered to ZnO, changing the band bending.

B. F. Spencer et al., Appl. Phys. Lett. ***108****, 091603 (2016)*

• PbS quantum dots offer the possibility to optimize the sunlight absorption



M. Yuan et al., Nature Energy ***1****, 16016 (2016)*

• Deposited on ZnO, the interface is such that the band bending is smaller and the carrier lifetime is larger. This is a key parameter for a photovoltaic device.

• Lifetime depends on the ZnO conductivity which can be controled by changing the concentration of O-vacancies.

• This lifetime can be measured by time-resolved photoemission. The whole process involved in sunlight absorption was here explained by these measurements.

Conclusions

Photoemission is a very popular technique :

- ☞It gives a picture of the electronic structure of atoms, molecules and solids
- ☞Chemical analysis of surface of materials
- ☞Local chemistry around a selected species (Chemical shift)
- ☞Crystallography (Photoelectron diffraction)
- ☞...Many other things (magnetism, structure, holography, correlations...)

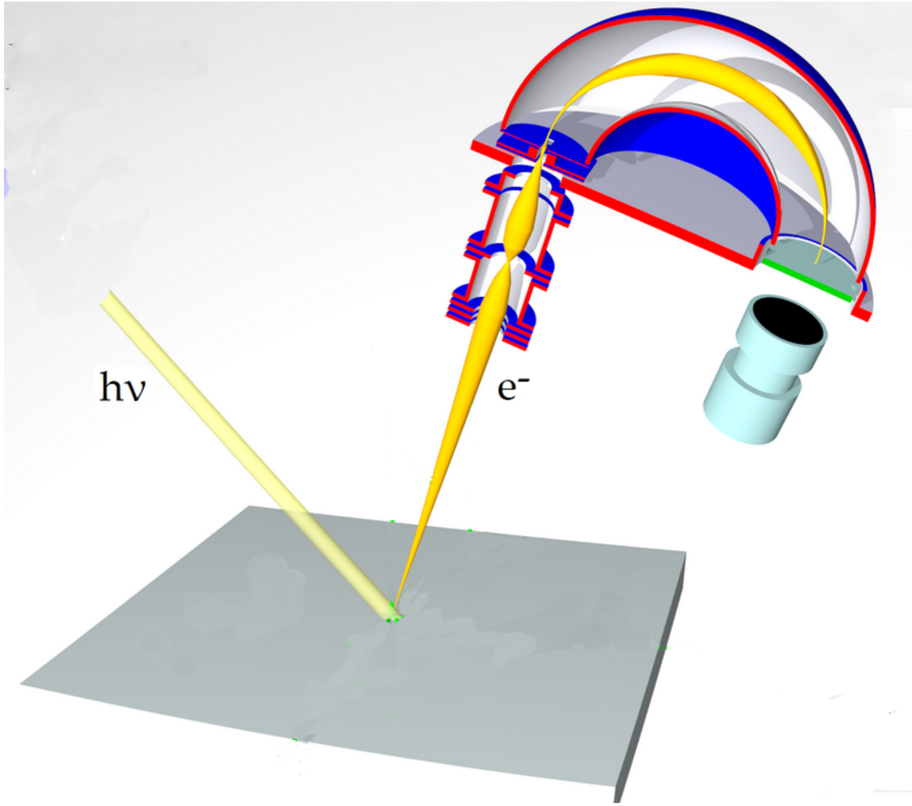
Photoemission : a tool for fondamental research...

☞High T_c superconductors, Graphene, nanoscience, 1D systems, correlations/quasiparticles...

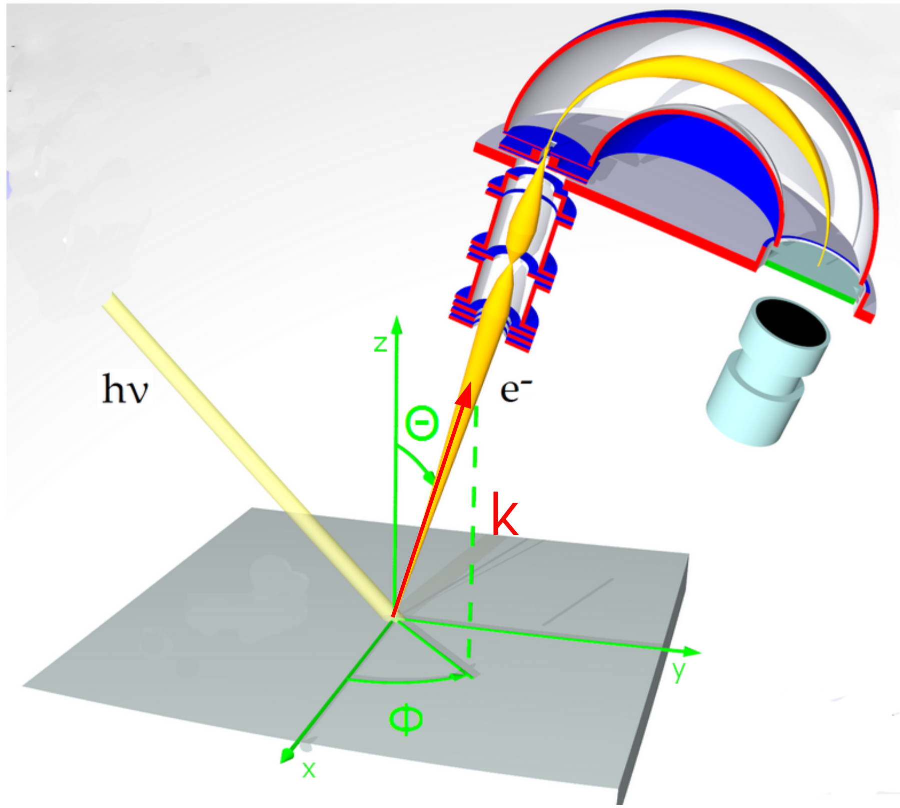
…but also for functionnal materials

☞Materials science for batteries, glass industry, solar cells and other materials for energy...

A photoemission experiment



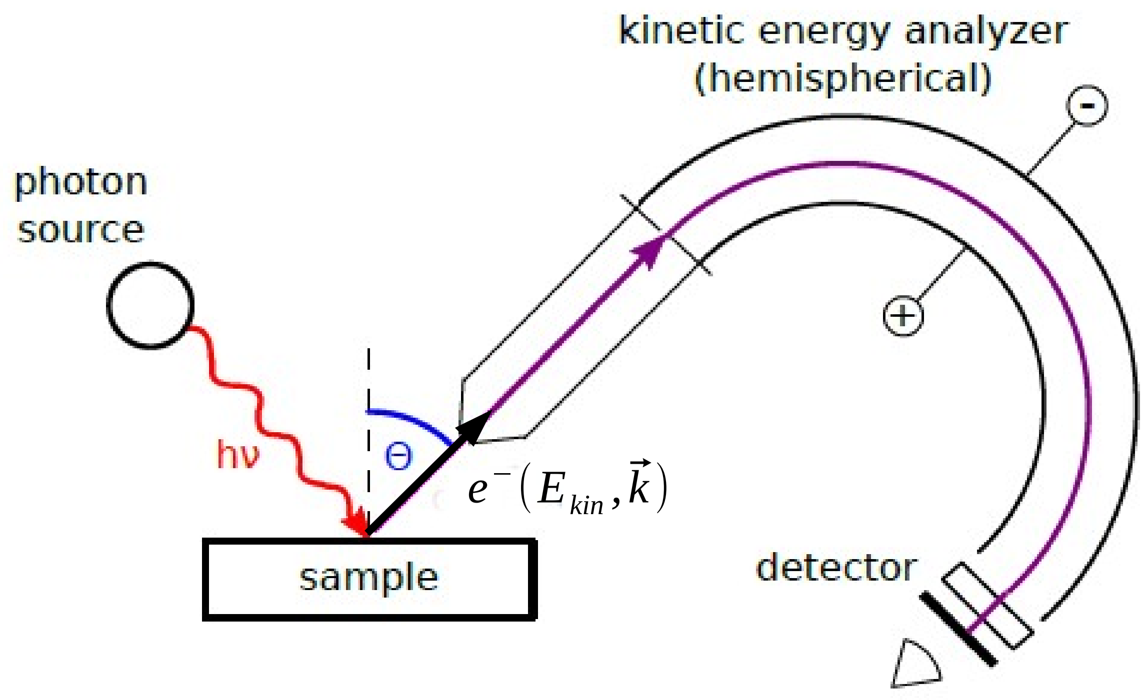
An ARPES experiment



let's assume that, in addition to its kinetic energy, one also measures θ the angle between the photoelectron emission direction (direction of the photoelectron wave vector) and the surface normal.

ARPES

Angle **R**esolved **P**hotoelectron **S**pectroscopy



Conservation laws

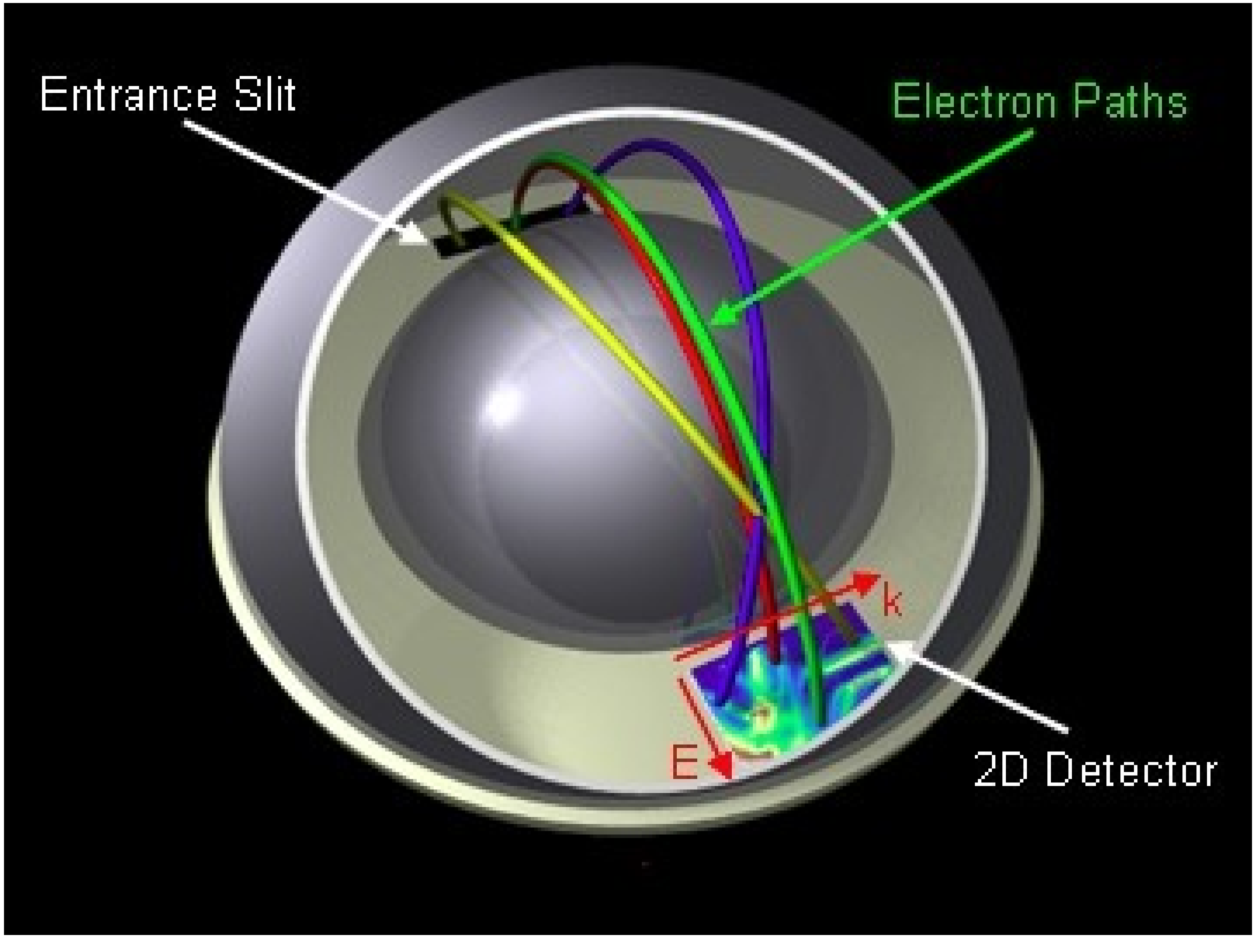
Energy : $E_B \approx h\nu - E_{kin}$

Momentum : $k_{//} = \frac{\sqrt{2mE_{kin}}}{\hbar} \sin(\theta)$

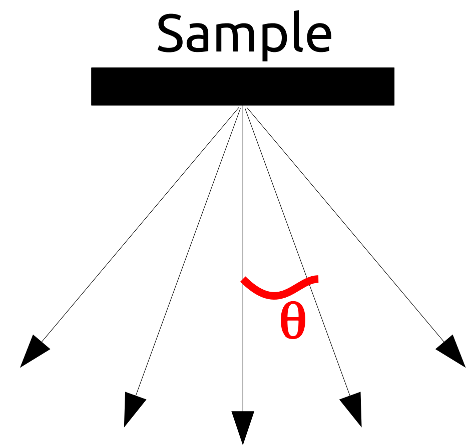
$\text{Momentum}_{\text{Photon}} \ll \text{Momentum}_{\text{Electron}}$

Free electron : $E_K = \frac{\hbar^2 k^2}{2m} \rightarrow |k| = \frac{\sqrt{2mE_K}}{\hbar}$

« Scienta-type » analyzer



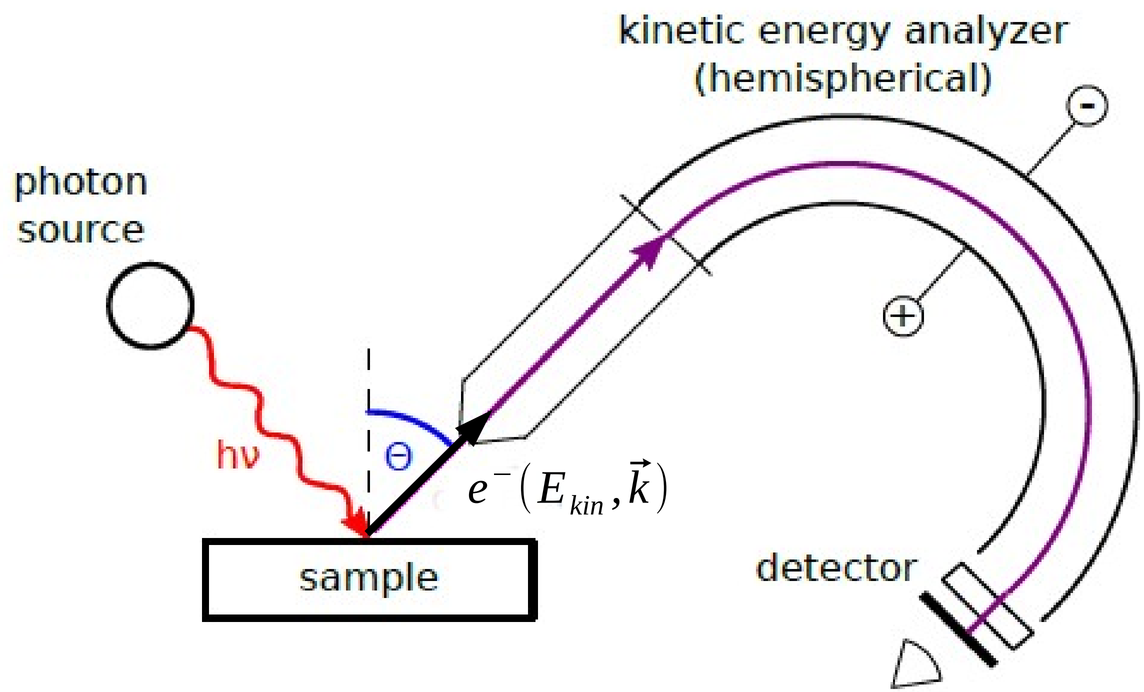
http://arpes.stanford.edu/facilities_ssrl.html

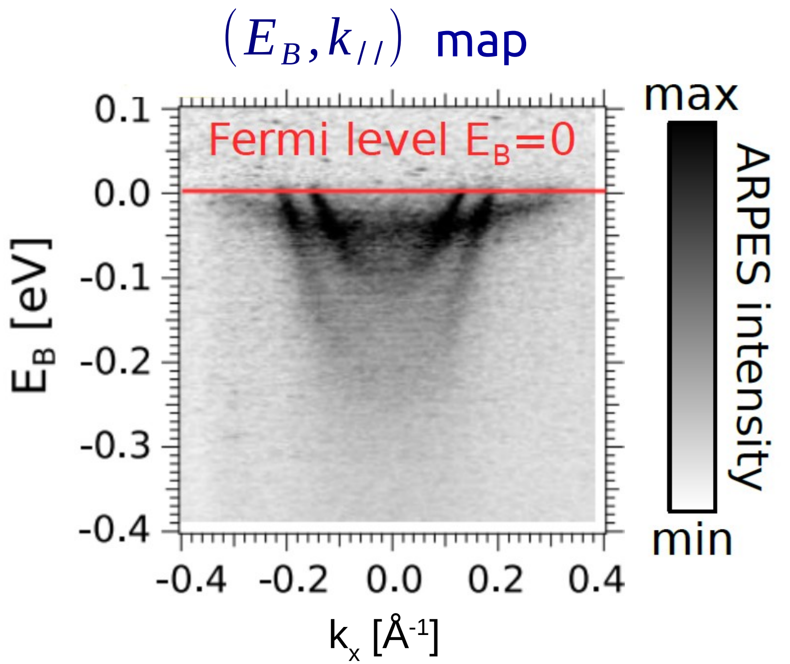


Along the entrance slit, the emission angle θ is conserved.

Finally, the result of a measurement is an image (E_K,θ).

ARPES : Result of a measurement

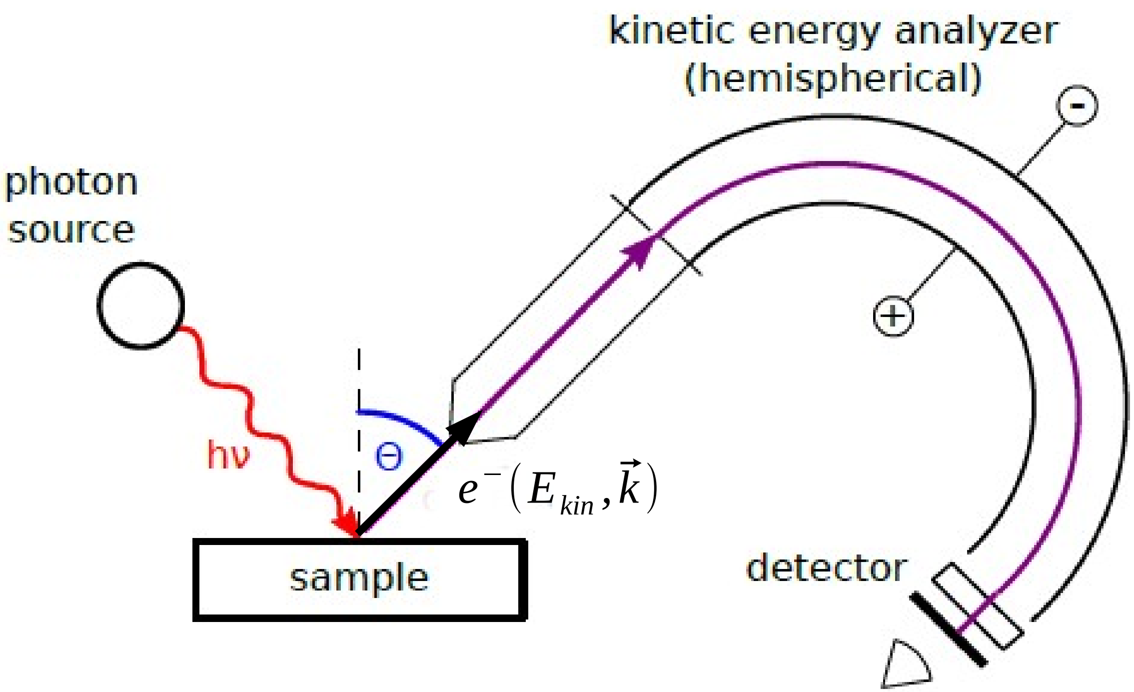


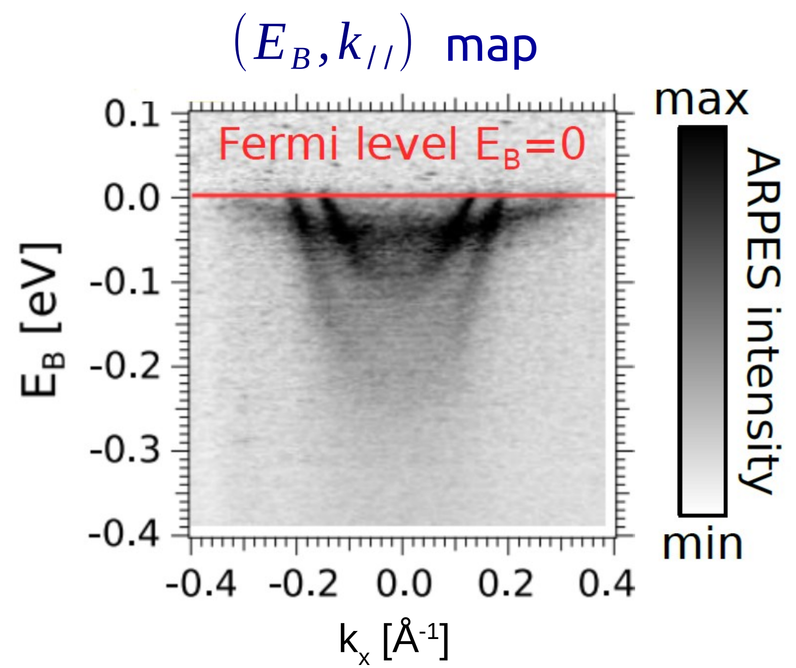


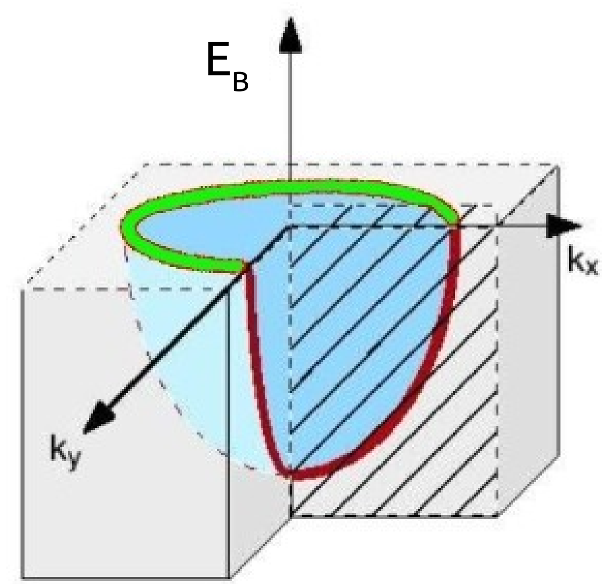
Conservation laws

Energy : $E_B \approx h\nu - E_{kin}$

Momentum : $k_{//} = \frac{\sqrt{2 m E_{kin}}}{\hbar} \sin(\theta)$





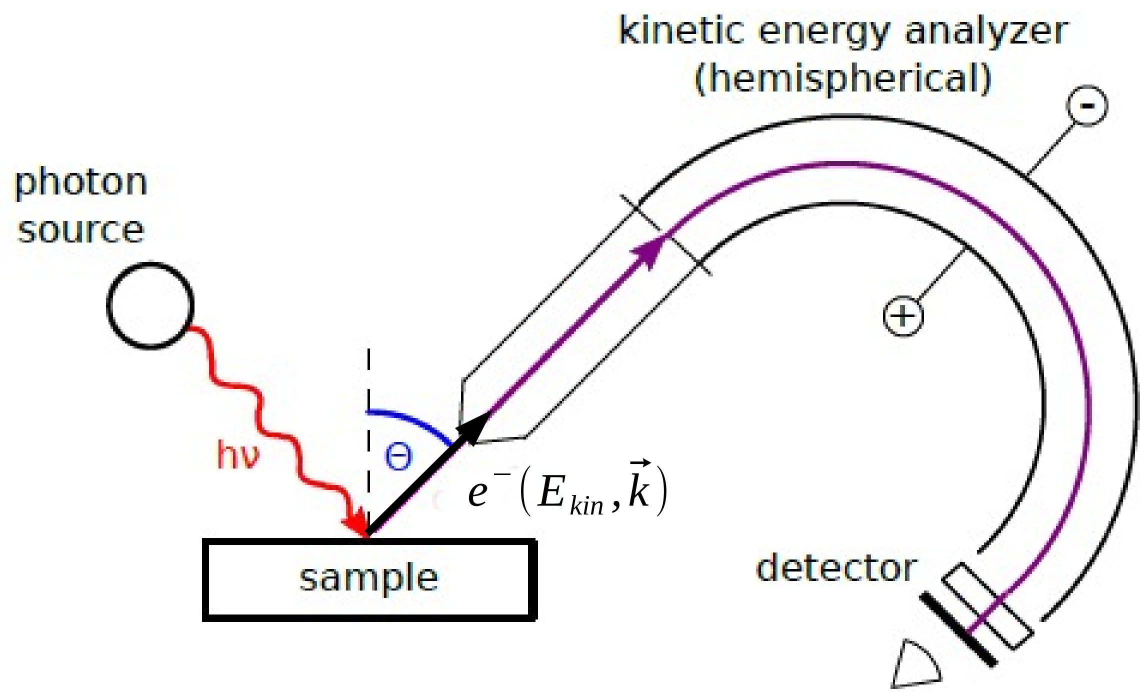


Conservation laws

Energy : $E_B \approx h\nu - E_{kin}$

Momentum : $k_{//} = \frac{\sqrt{2mE_{kin}}}{\hbar} \sin(\theta)$

ARPES : Fermi surface

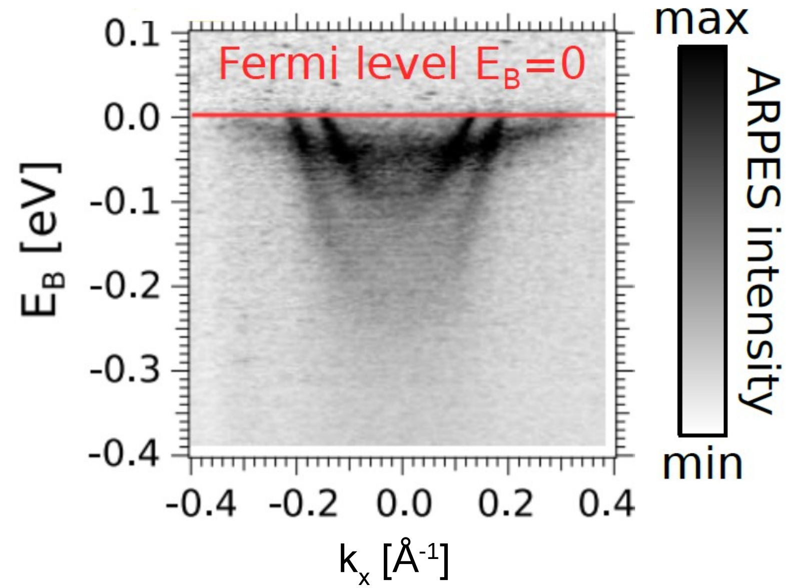


Conservation laws

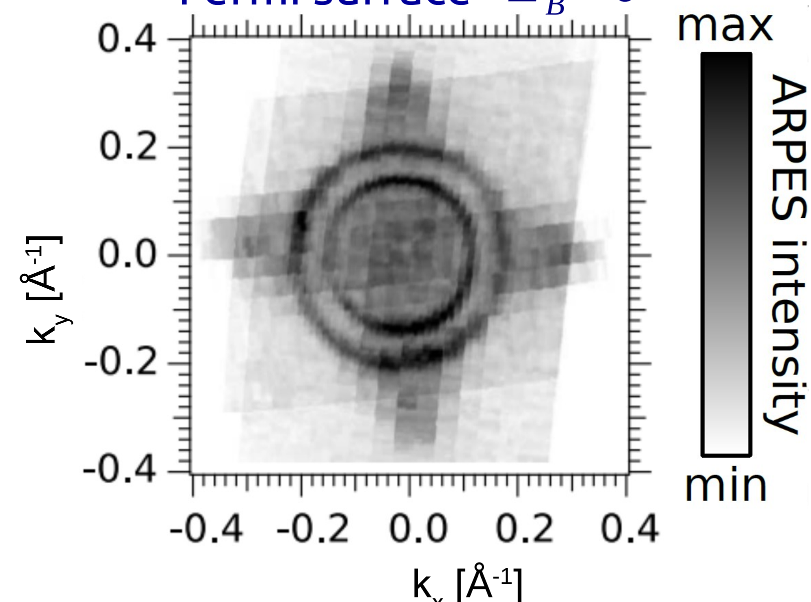
Energy : $E_B \approx h\nu - E_{kin}$

Momentum : $k_{//} = \frac{\sqrt{2mE_{kin}}}{\hbar}\sin(\theta)$

$(E_B, k_{//})$ map



Fermi surface $E_B = 0$



Advantages

- ☞Unique tool for the characterization of the electronique structure
- ☞Easy access to $k_{//}$ → Ideally suited for 2D systems
- ☞Band structure, m*, v_F, charge carriers density, symmetry of the bands…
- ☞Access to correlation effects

Drawbacks

- ☞Surface sensitive → Not easily usuable on a buried interface
  or on truly bulk electronic structure