

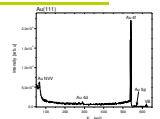


**HELMHOLTZ
ZENTRUM BERLIN**
für Materialien und Energie

Introduction into X-ray and UV Photoelectron Spectroscopy (XPS/UPS)

Introduction to X-ray and UV Photoelectron Spectroscopy (XPS/UPS)

- *What is XPS?*
 - *How can we identify elements and compounds?*
 - *What is UPS?*
 - *What is a work function(Φ)?*
-
- *Examples of investigations using $\Delta\Phi$ /UPS/XPS/HIKE*



What is XPS?

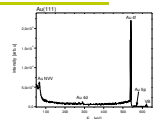
X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces.

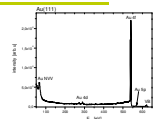
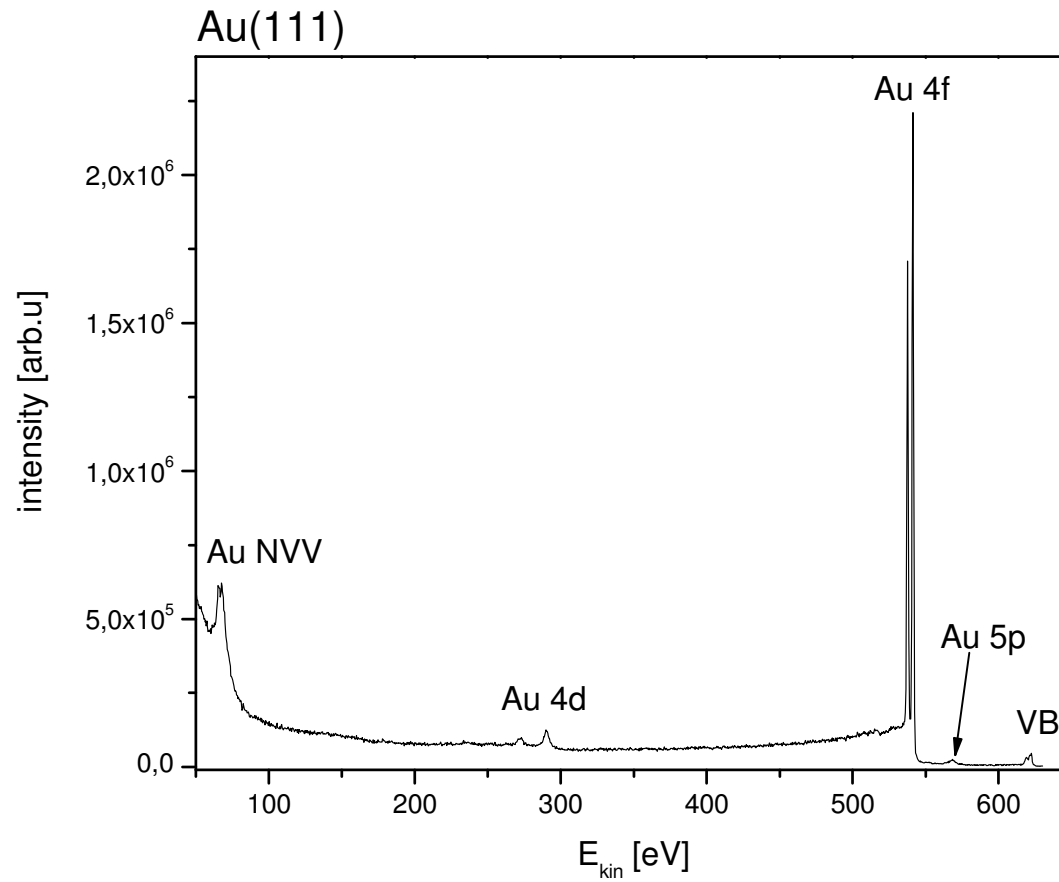
X-ray Photoelectron spectroscopy, based on the photoelectric effect,^{1,2} was developed in the mid-1960's by Kai Siegbahn and his research group at the University of Uppsala, Sweden.³

1. H. Hertz, *Ann. Physik* 31,983 (1887).

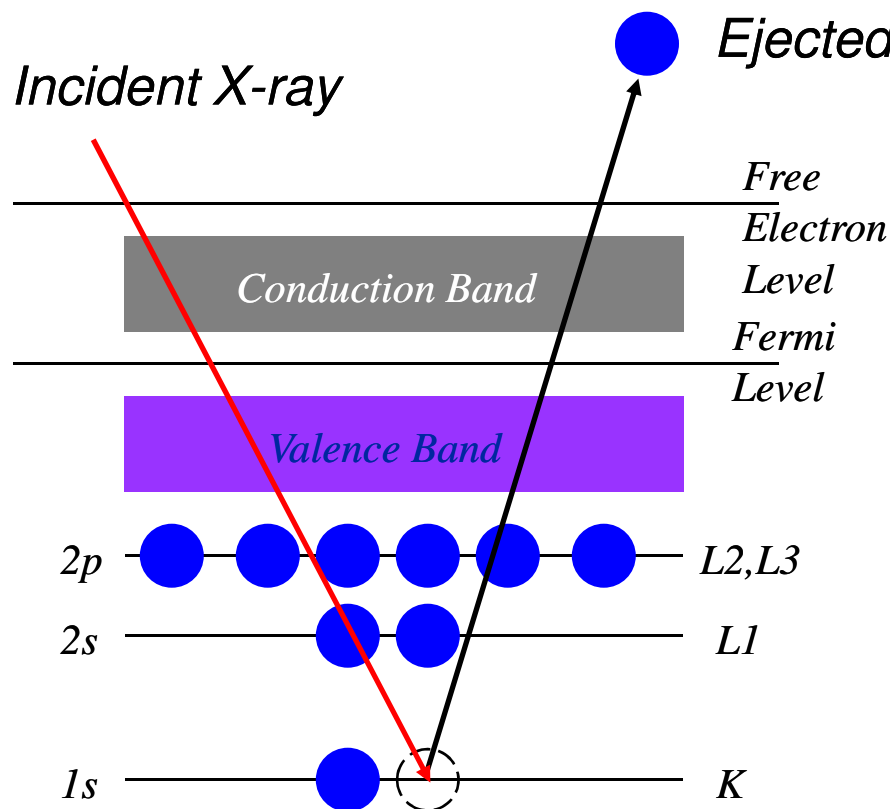
2. A. Einstein, *Ann. Physik* 17,132 (1905). 1921 Nobel Prize in Physics.

3. K. Siegbahn, et. al., *Nova Acta Regiae Soc.Sci., Ser. IV, Vol. 20* (1967). 1981 Nobel Prize in Physics.

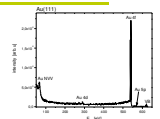




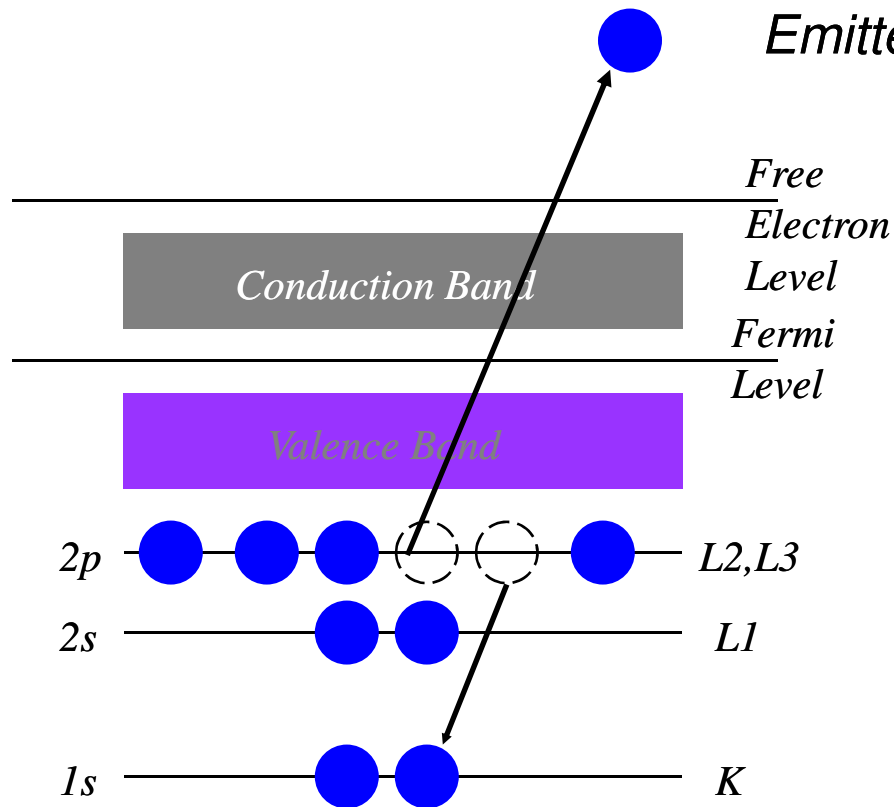
The Photoelectric Process



- XPS spectral lines are identified by the shell from which the electron was ejected (1s, 2s, 2p, etc.).
- The ejected photoelectron has kinetic energy:
 $KE = h\nu - BE - \Phi$
- Following this process, the atom will release energy by the emission of an Auger Electron.

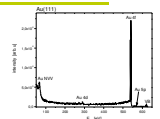


Auger Relation of Core Hole

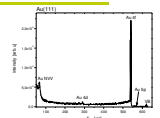
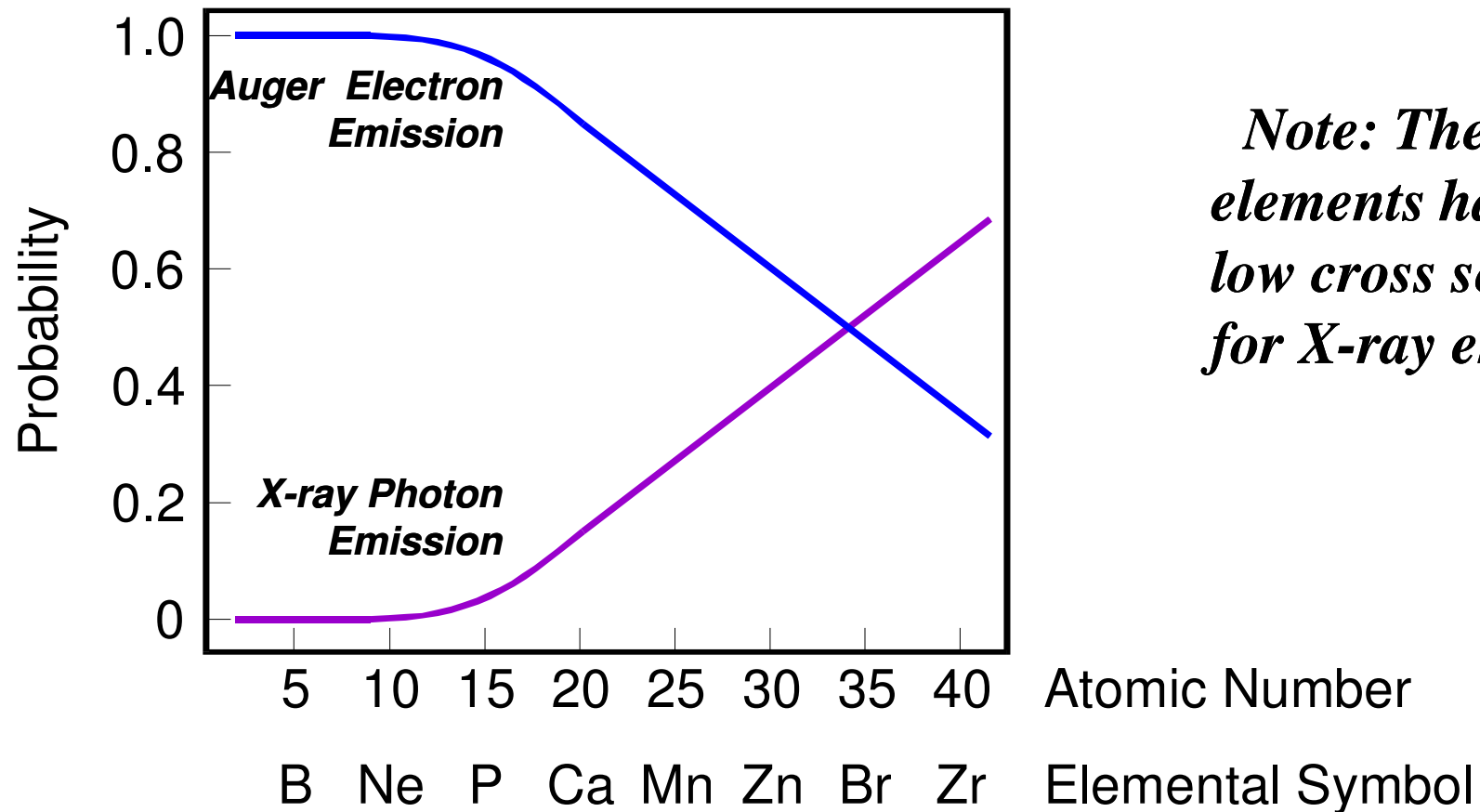


Emitted Auger Electron

- *L electron falls to fill core level vacancy (step 1).*
- *KLL Auger electron emitted to conserve energy released in step 1.*
- *The kinetic energy of the emitted Auger electron is:*
 $KE = E(K) - E(L2) - E(L3).$

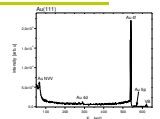


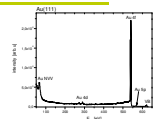
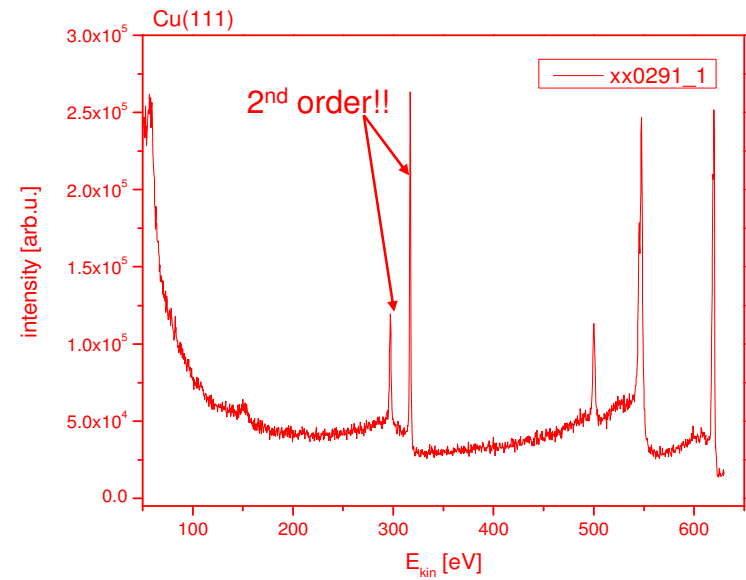
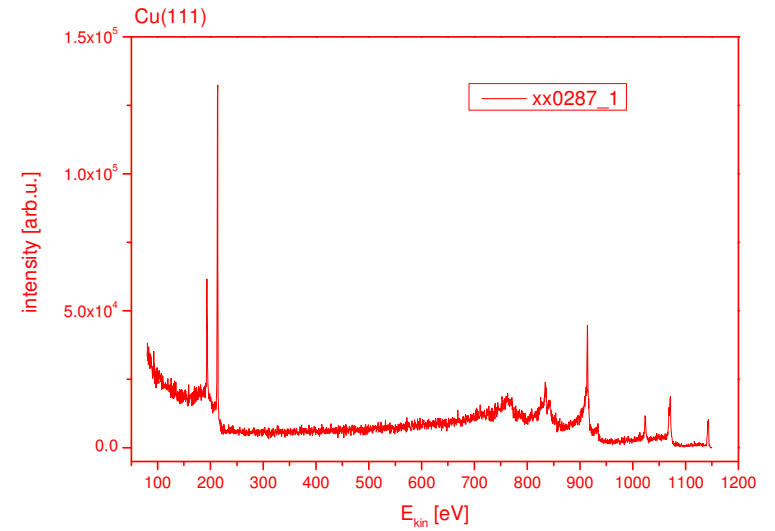
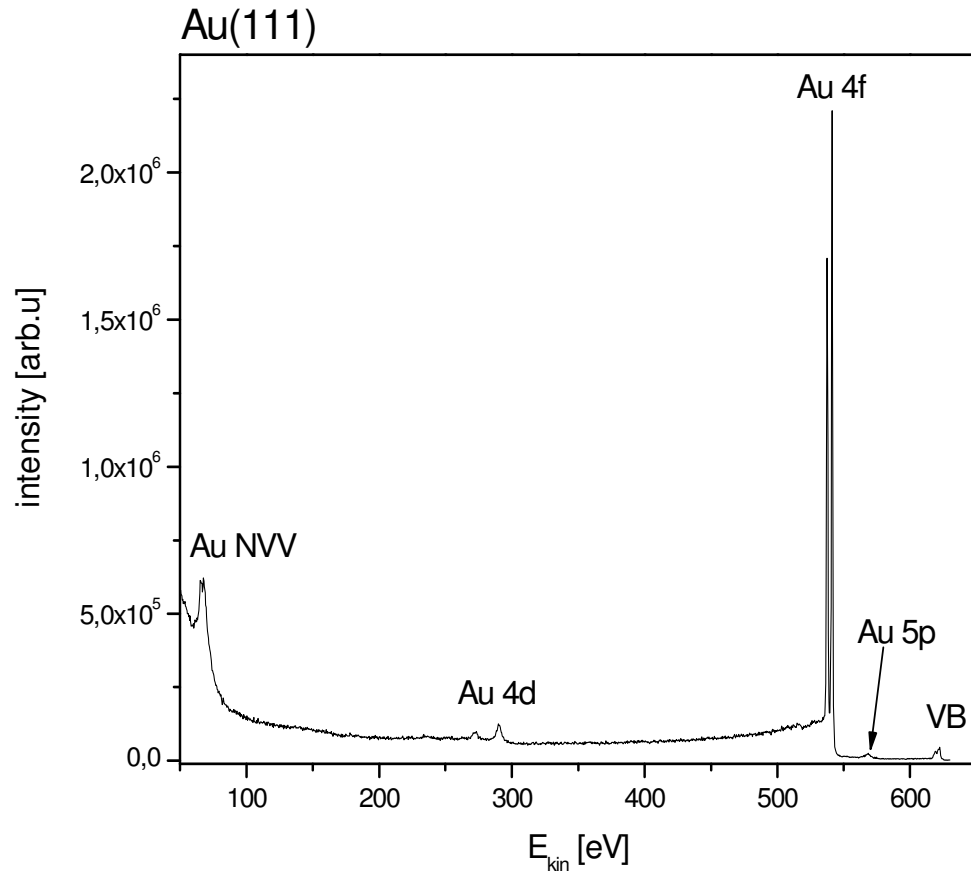
Relative Probabilities of Relaxation of a K Shell Core Hole



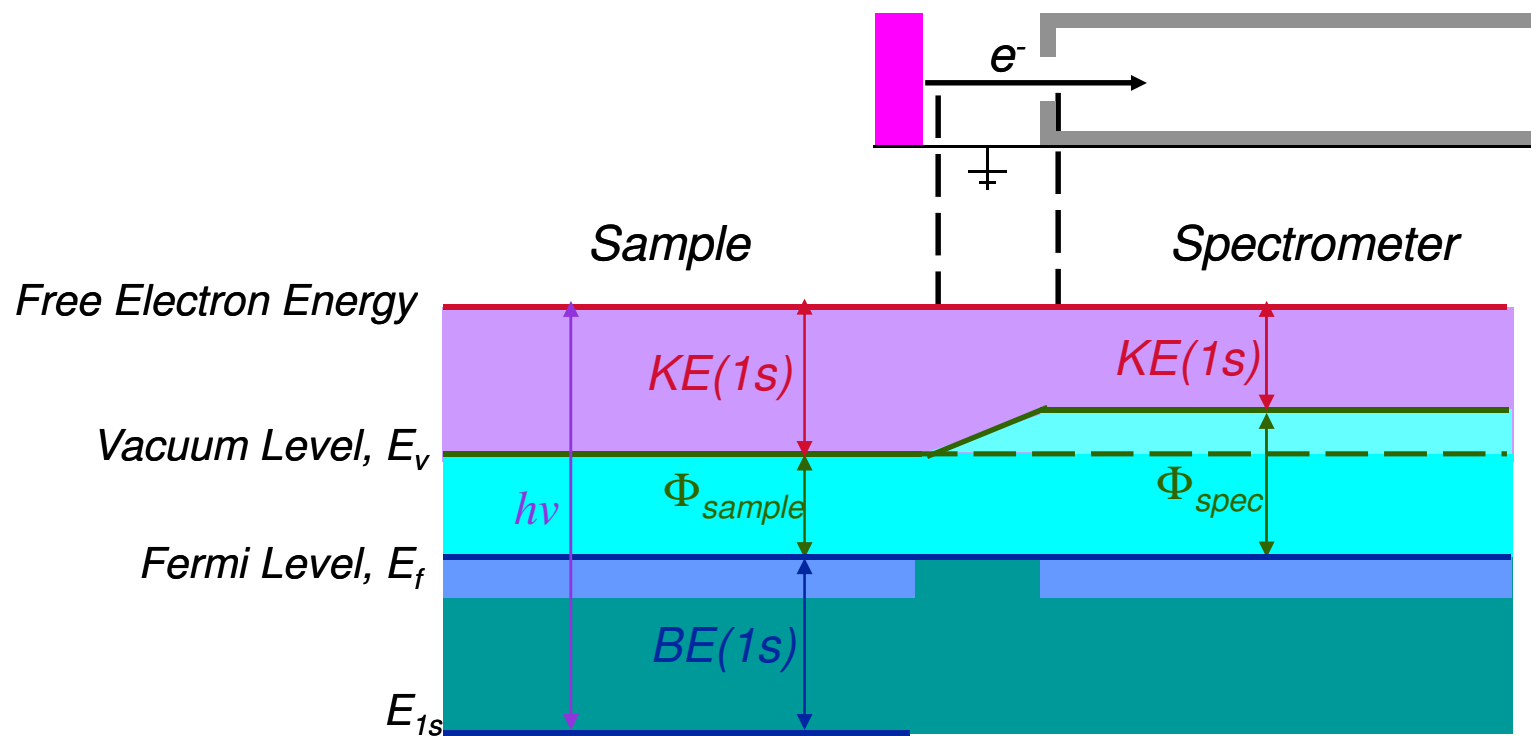
XPS Energy Scale

The XPS instrument measures the kinetic energy of all collected electrons. The electron signal includes contributions from both photoelectron and Auger electron lines.

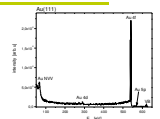




Sample/Spectrometer Energy Level Diagram- Conducting Sample



Because the Fermi levels of the sample and spectrometer are aligned, we only need to know the spectrometer work function, Φ_{spec} , to calculate $BE(1s)$.



XPS Energy Scale - Kinetic energy

$$KE = h\nu - BE - \Phi_{spec}$$

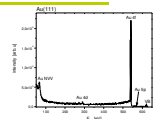
Where: BE = Electron Binding Energy

KE = Electron Kinetic Energy

Φ_{spec} = Spectrometer Work Function

Photoelectron line energies: *Dependent* on photon energy.

Auger electron line energies: *Not Dependent* on photon energy.



XPS Energy Scale- Binding energy

$$BE = h\nu - KE - \Phi_{spec}$$

Where: BE = Electron Binding Energy

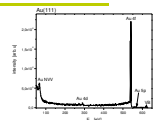
KE = Electron Kinetic Energy

Φ_{spec} = Spectrometer Work Function

Photoelectron line energies: **Not Dependent** on photon energy.

Auger electron line energies: **Dependent** on photon energy.

The binding energy scale was derived to make uniform comparisons of chemical states straight forward.

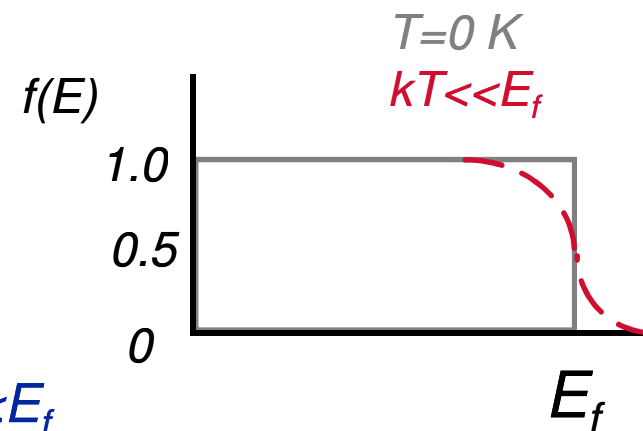


Fermi Level Referencing

Free electrons (those giving rise to conductivity) find an equal potential which is constant throughout the material.

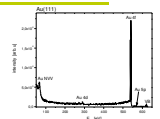
Fermi-Dirac Statistics:

$$f(E) = \frac{1}{\exp[(E-E_f)/kT] + 1}$$

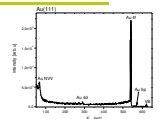
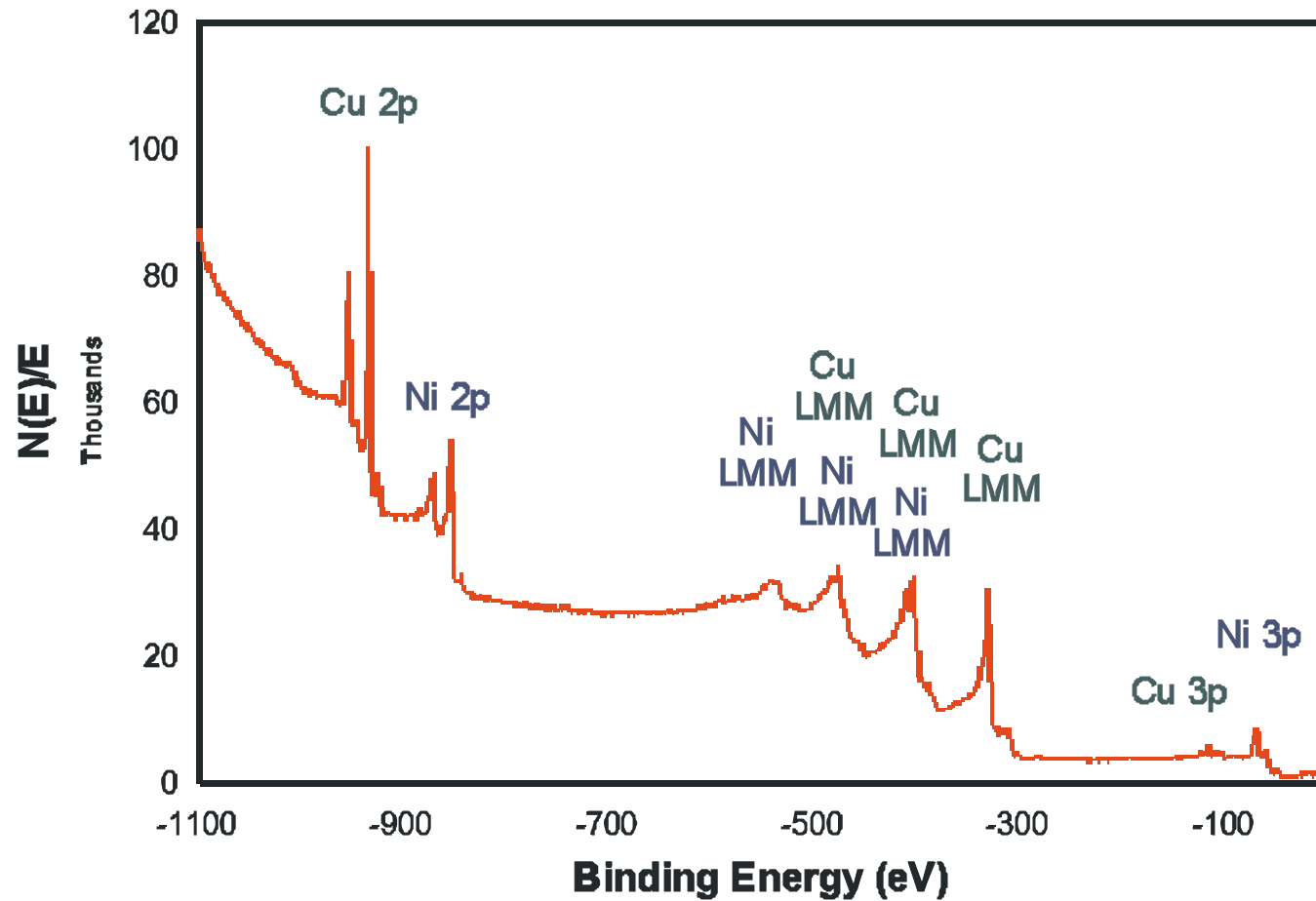


1. At $T=0$ K: $f(E)=1$ for $E < E_f$
 $f(E)=0$ for $E > E_f$

2. At $kT \ll E_f$ (at room temperature $kT=0.025$ eV)
 $f(E)=0.5$ for $E=E_f$



Elemental Shifts



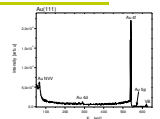
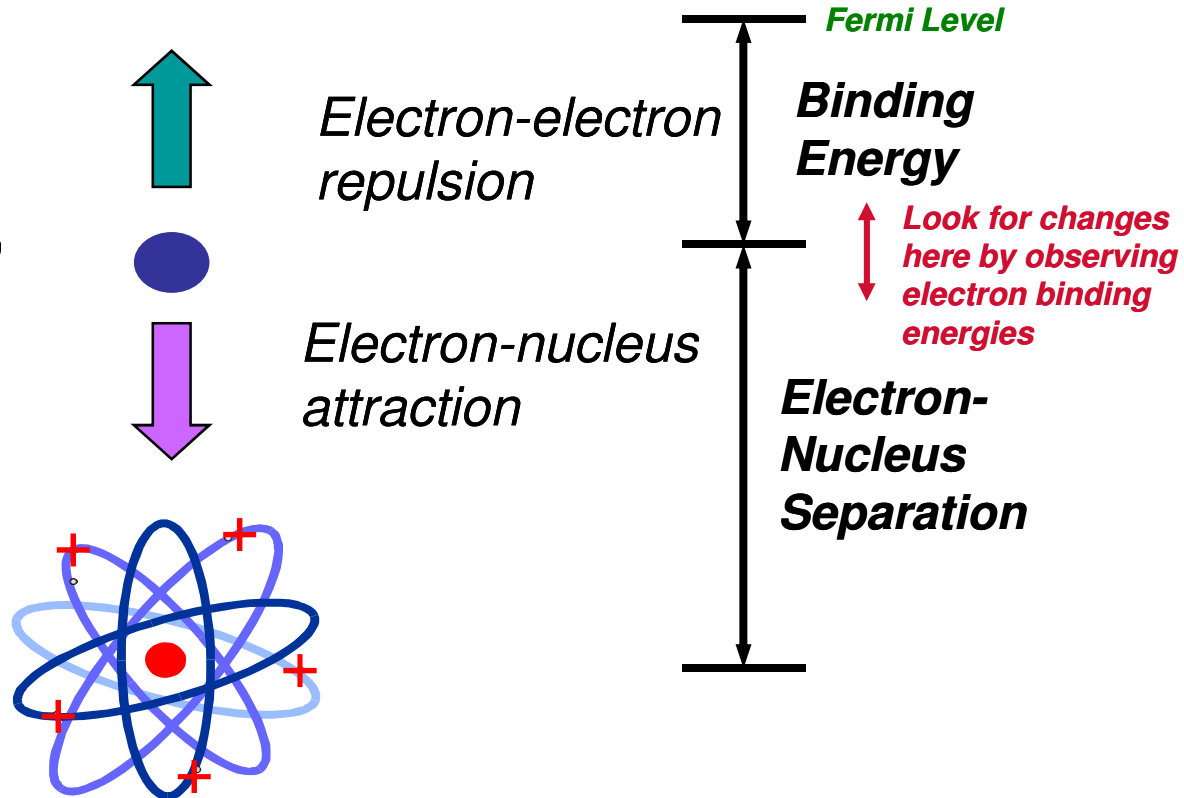
Where do Binding Energy Shifts Come From?

-or How Can We Identify Elements and Compounds?

Pure Element

Electron

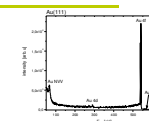
Nucleus



Elemental Shifts

<i>Binding Energy (eV)</i>			
<i>Element</i>	<i>2p_{3/2}</i>	<i>3p</i>	<i>Δ</i>
Fe	707	53	654
Co	778	60	718
Ni	853	67	786
Cu	933	75	858
Zn	1022	89	933

Electron-nucleus attraction helps us identify the elements



The Sudden Approximation

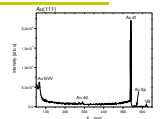
Assumes the remaining orbitals (often called the passive orbitals) are the same in the final state as they were in the initial state (also called the *frozen-orbital approximation*). Under this assumption, the XPS experiment measures the negative Hartree-Fock orbital energy:

Koopman's Binding Energy

$$E_{B,K} \cong -\epsilon_{B,K}$$

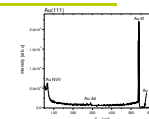
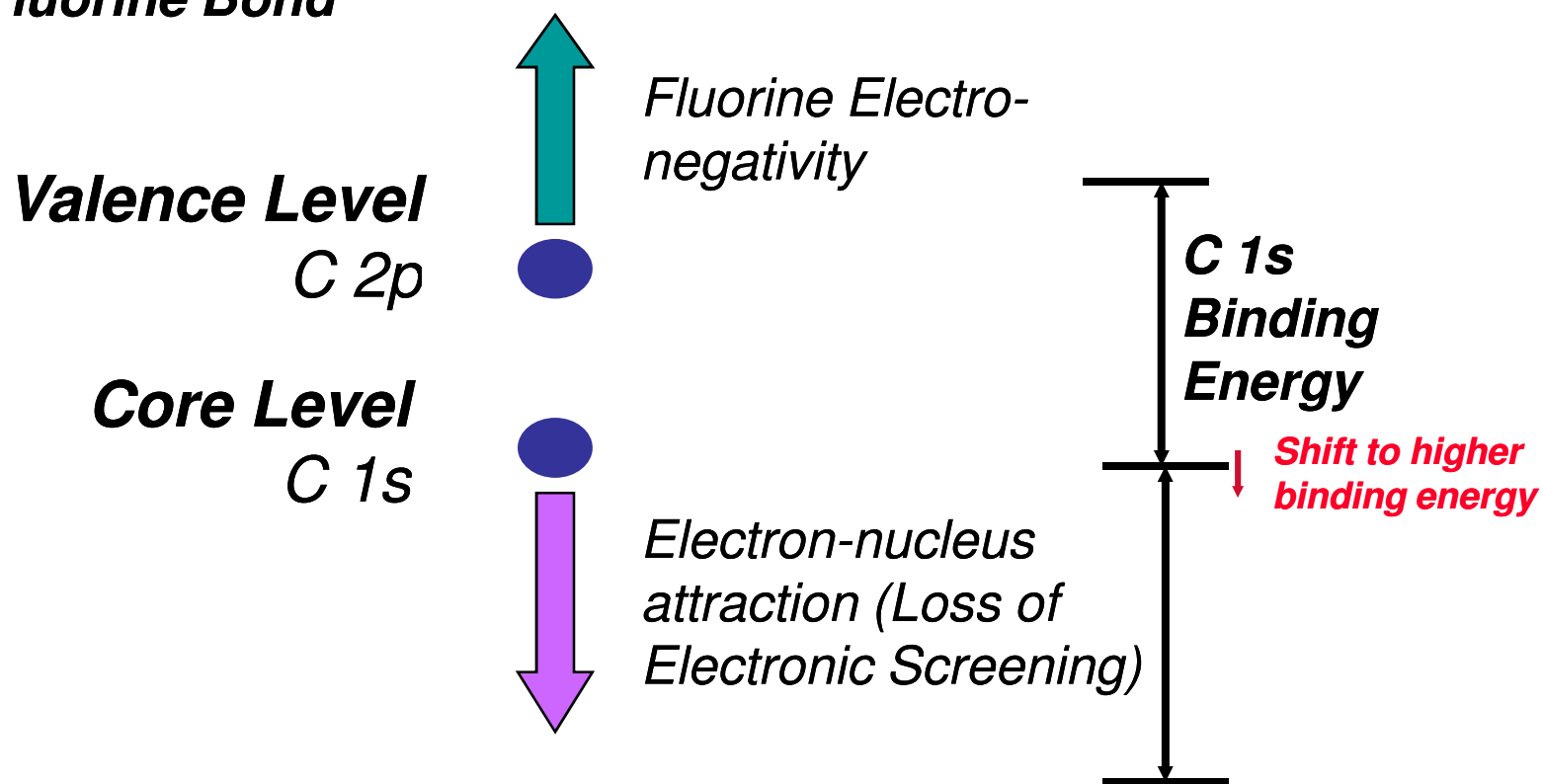
Actual binding energy will represent the readjustment of the N-1 charges to minimize energy (relaxation):

$$E_B = E_f^{N-1} - E_i^N$$



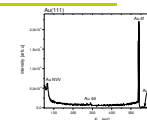
Chemical Shifts - Electronegativity Effects

Carbon-Fluorine Bond

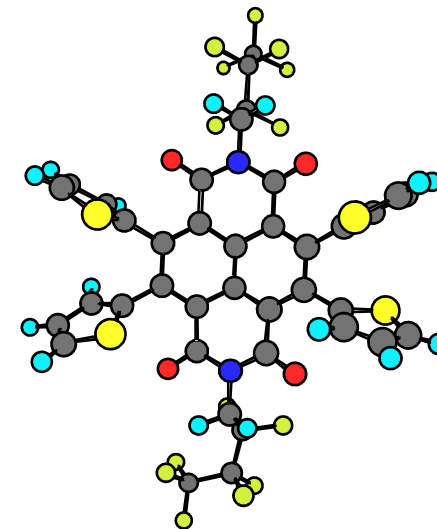
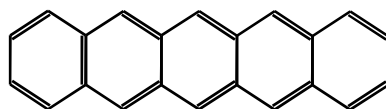
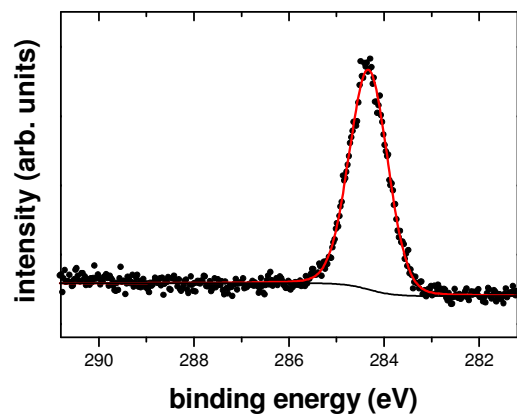


Chemical Shifts- Electronegativity Effects

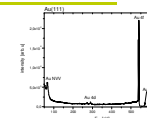
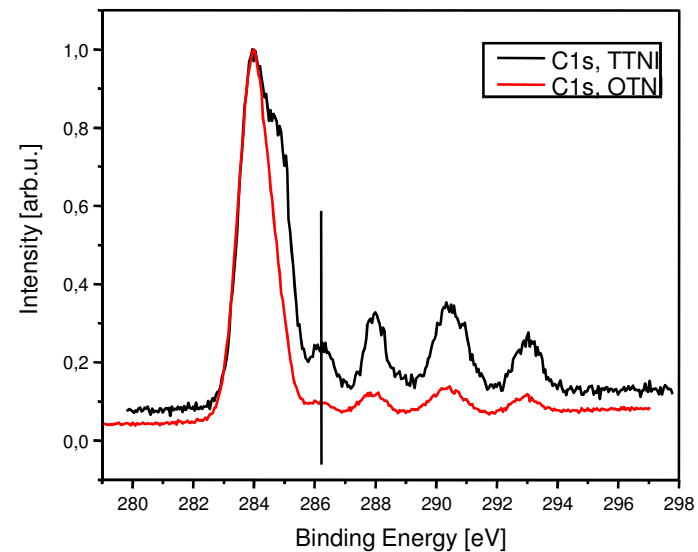
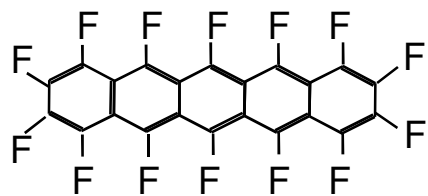
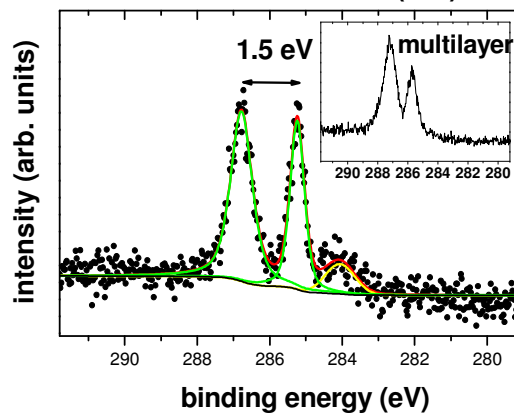
Functional Group		Binding Energy (eV)
<i>hydrocarbon</i>	<u>C</u> -H, <u>C</u> -C	285.0
<i>amine</i>	<u>C</u> -N	286.0
<i>alcohol, ether</i>	<u>C</u> -O-H, <u>C</u> -O-C	286.5
<i>Cl bound to C</i>	<u>C</u> -Cl	286.5
<i>F bound to C</i>	<u>C</u> -F	287.8
<i>carbonyl</i>	<u>C</u> =O	288.0



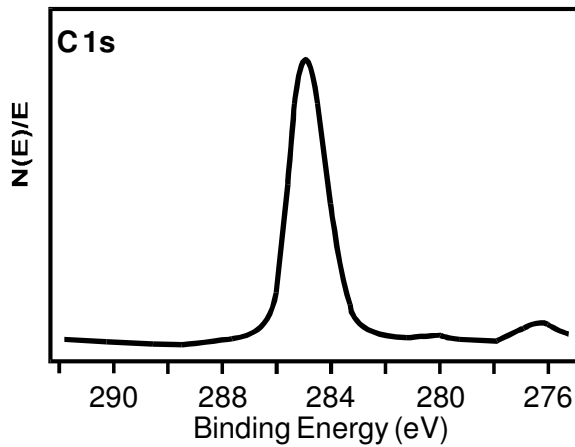
C1s of ca. ML PFN on Au(111)



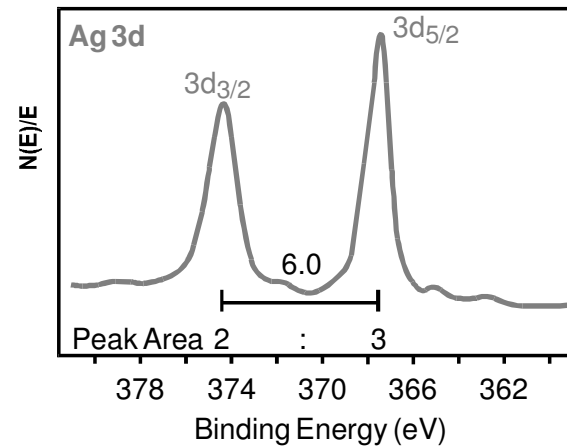
C1s of ca. ML PFP on Au(111)



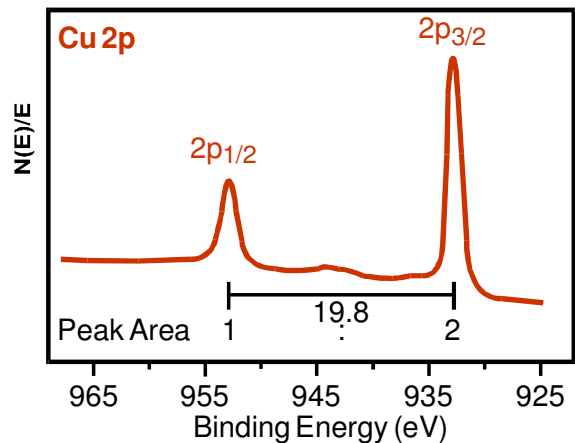
Electronic Effects - Spin-Orbit Coupling



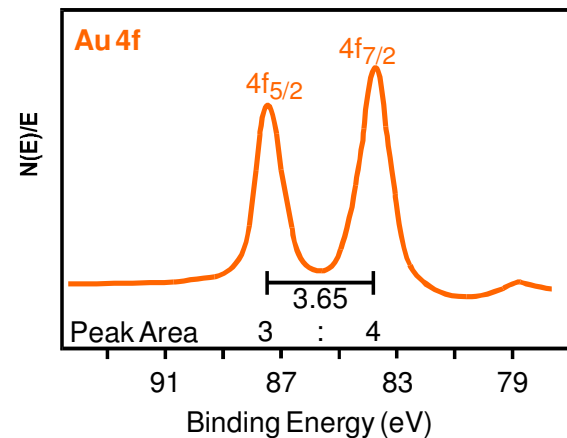
Orbital=s
l=0
s=+/-1/2
ls=1/2



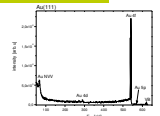
Orbital=d
l=2
s=+/-1/2
ls=3/2,5/2



Orbital=p
l=1
s=+/-1/2
ls=1/2,3/2



Orbital=f
l=3
s=+/-1/2
ls=5/2,7/2



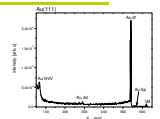
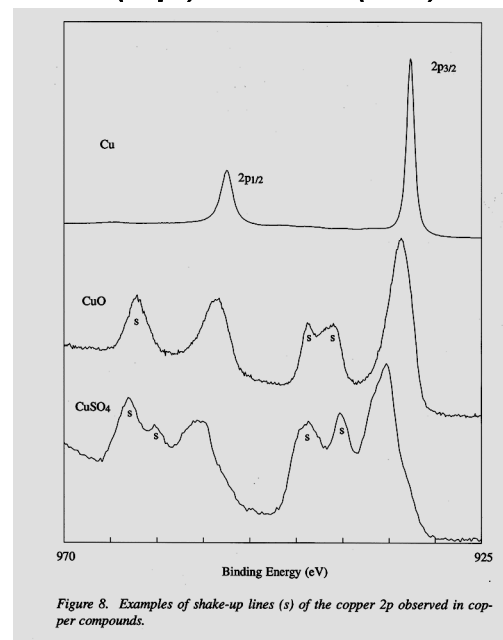
Final State Effects - Shake-up/ Shake-off

Results from energy made available in the relaxation of the final state configuration (due to a loss of the screening effect of the core level electron which underwent photoemission).

Shake-up: Relaxation energy used to excite electrons in valence levels to bound states (monopole excitation).

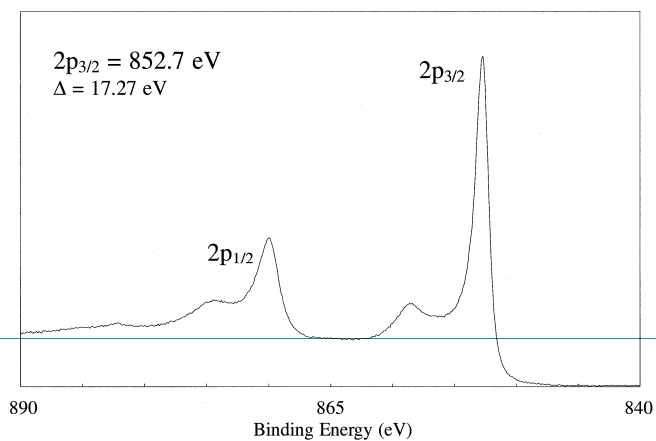
Shake-off: Relaxation energy used to excite electrons in valence levels to unbound states (monopole ionization).

$L(2p) \rightarrow Cu(3d)$

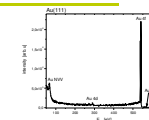
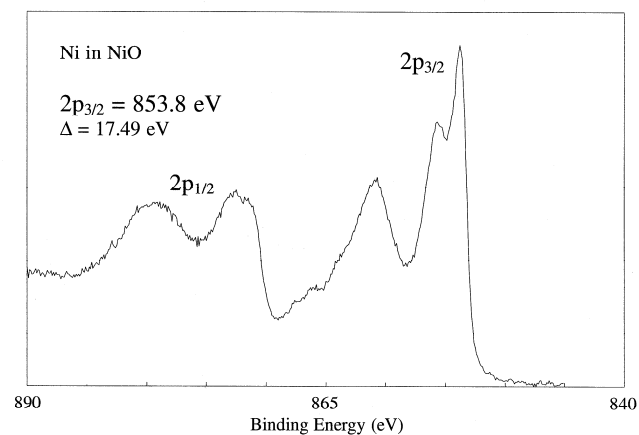


Final State Effects- Shake-up/ Shake-off

Ni Metal



Ni Oxide



Final State Effects- Multiplet Splitting

Following photoelectron emission, the remaining unpaired electron may couple with other unpaired electrons in the atom, resulting in an ion with several possible final state configurations with as many different energies. This produces a line which is split asymmetrically into several components.

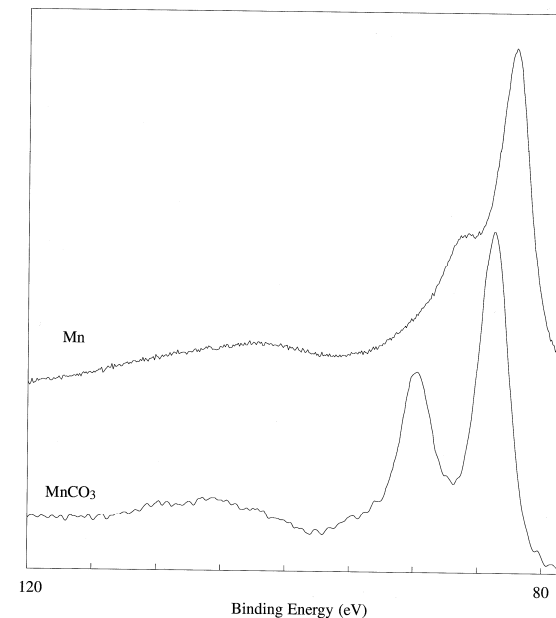
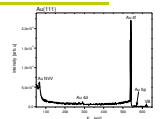
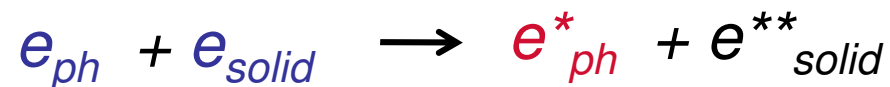


Figure 10. Multiplet splitting of the Mn 3s.

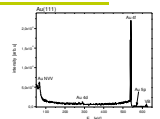


Electron Scattering Effects

Energy Loss Peaks

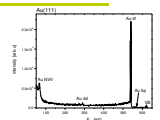
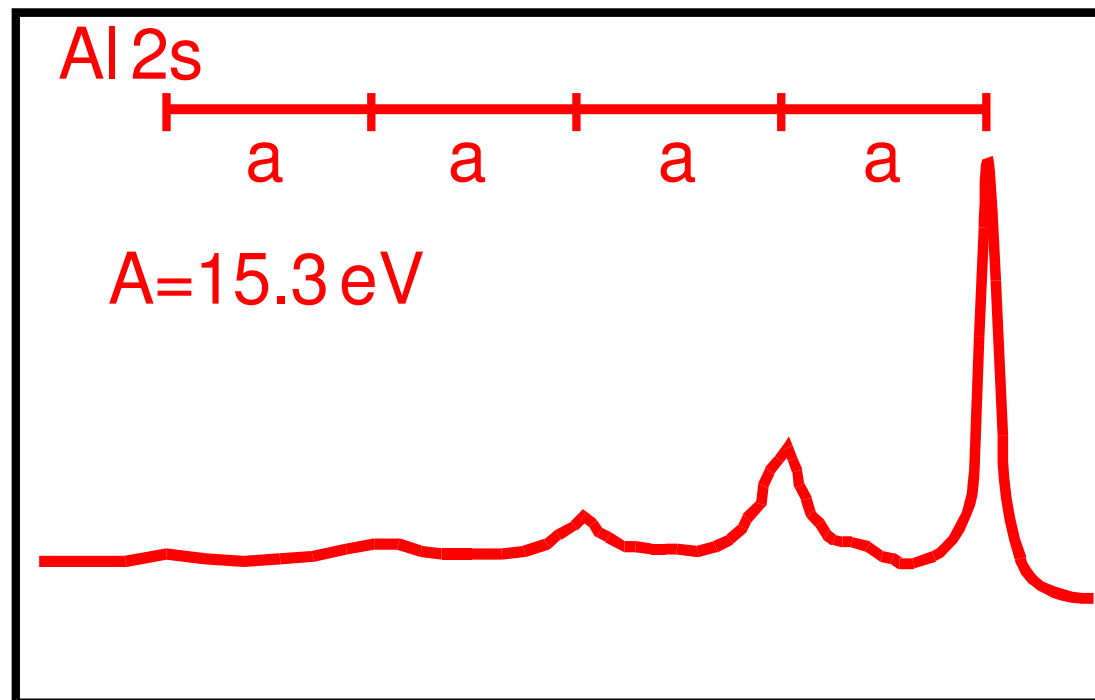


Photoelectrons travelling through the solid can interact with other electrons in the material. These interactions can result in the photoelectron exciting an electronic transition, thus losing some of its energy (inelastic scattering).



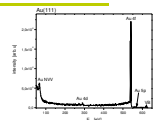
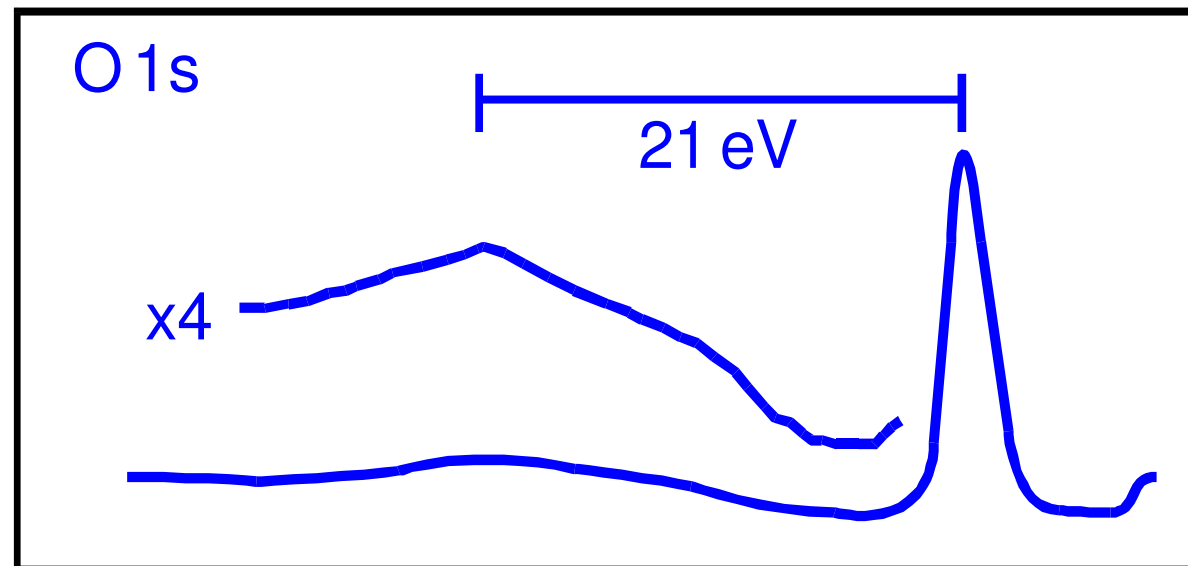
Electron Scattering Effects Plasmon Loss Peak

Metal



Electron Scattering Effects Plasmon Loss Peak

*Insulating
Material*



Quantitative Analysis by XPS

For a Homogeneous sample:

$$I = N\sigma DJL\lambda AT$$

where: $N = \text{atoms/cm}^3$

$\sigma = \text{photoelectric cross-section, cm}^2$

$D = \text{detector efficiency}$

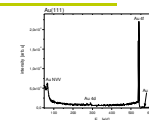
$J = \text{X-ray flux, photon/cm}^2\text{-sec}$

$L = \text{orbital symmetry factor}$

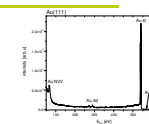
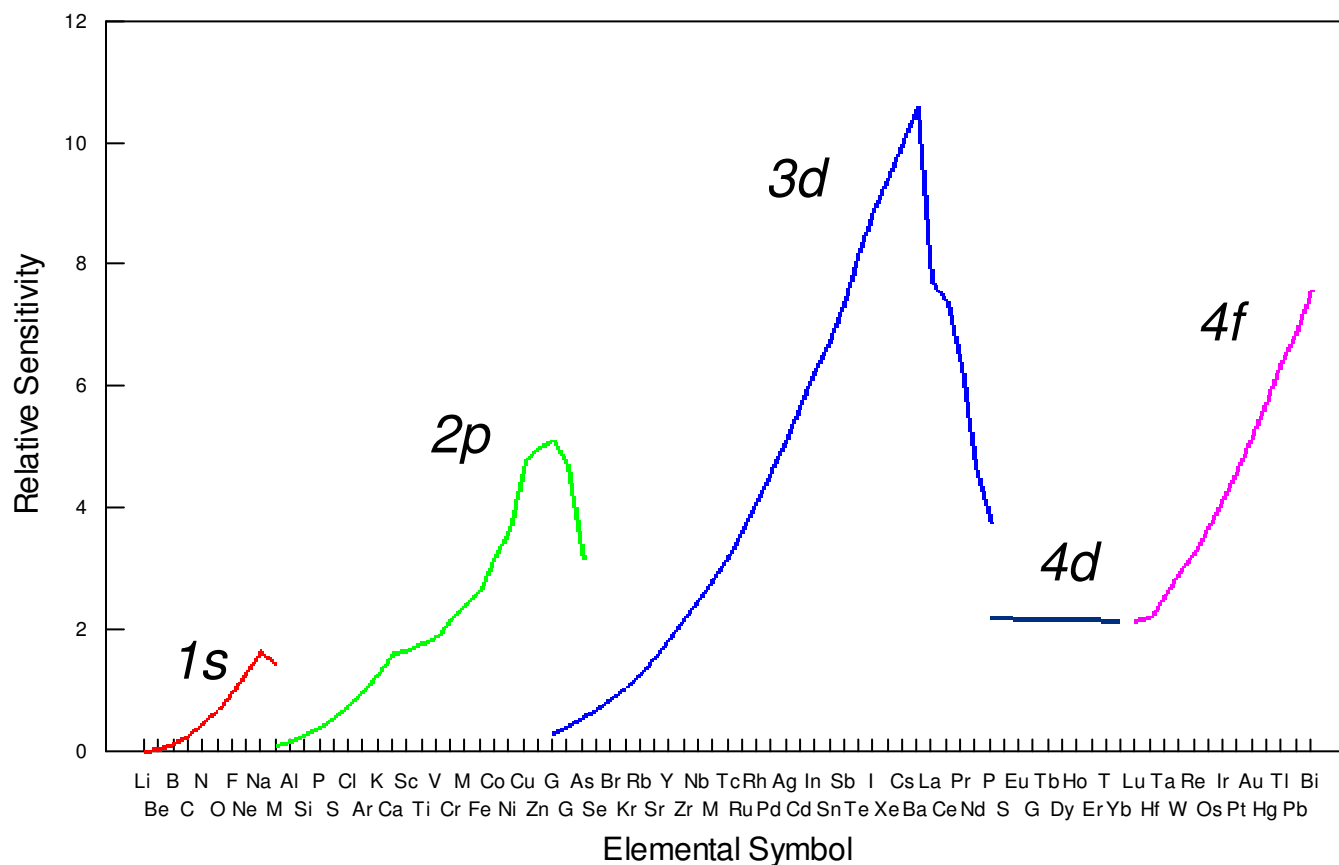
$\lambda = \text{inelastic electron mean-free path, cm}$

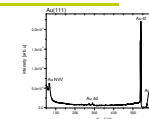
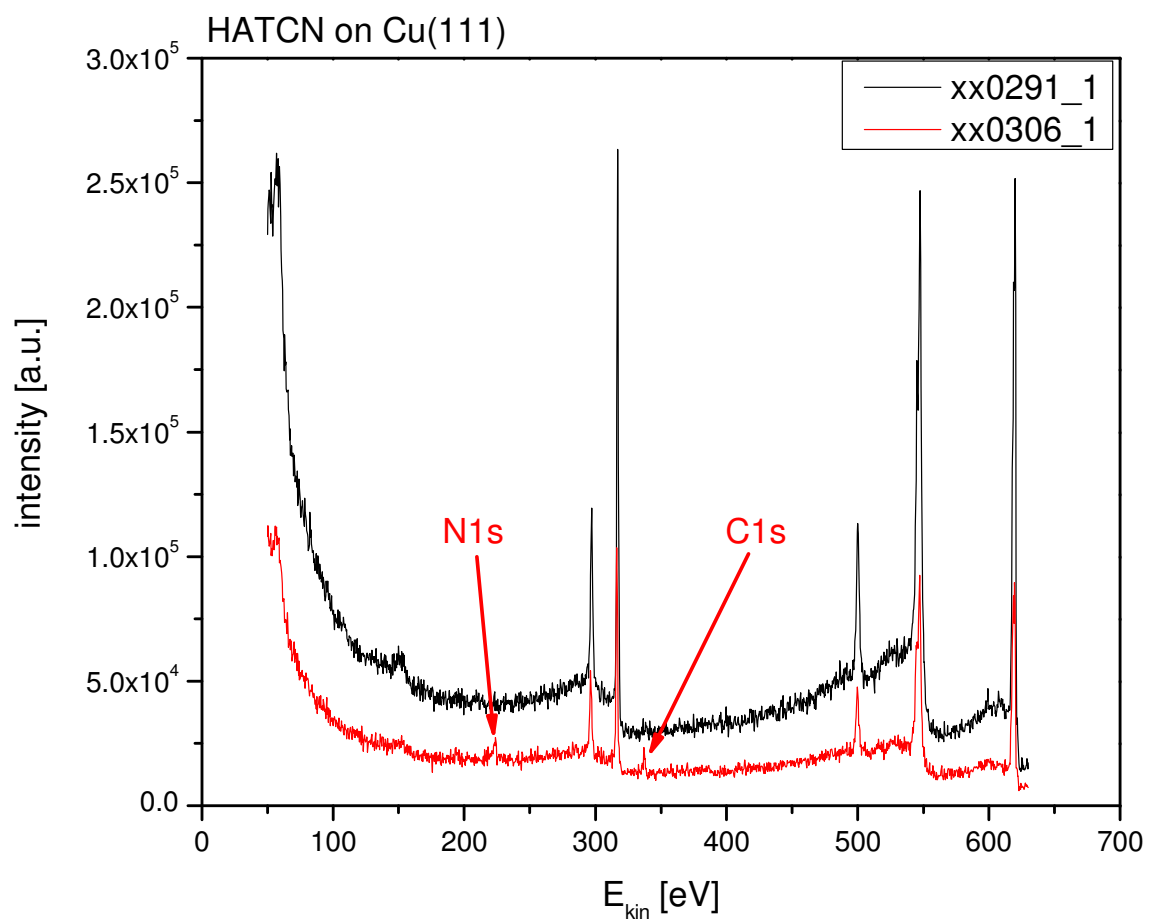
$A = \text{analysis area, cm}^2$

$T = \text{analyzer transmission efficiency}$

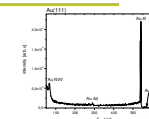
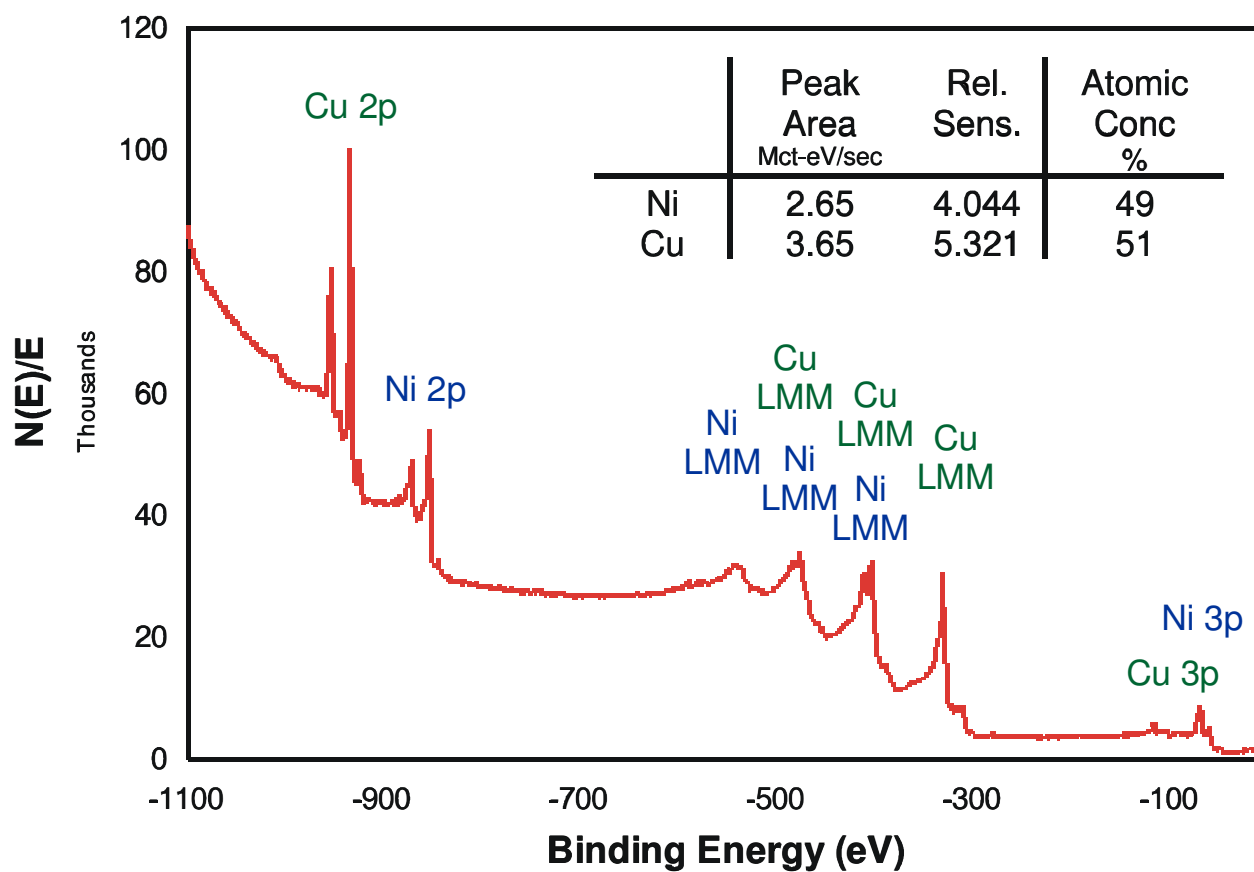


Relative Sensitivities of the Elements

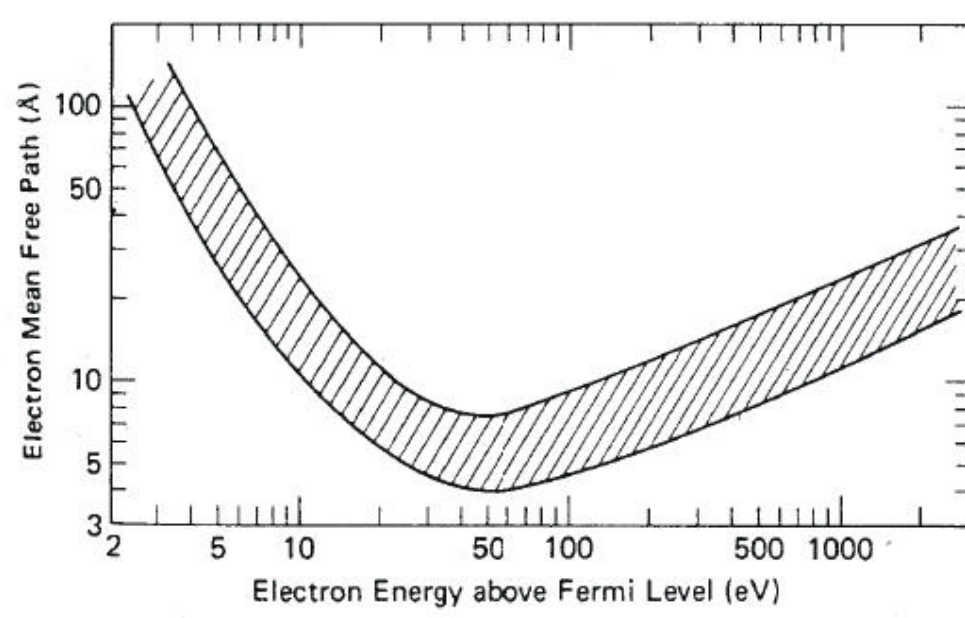




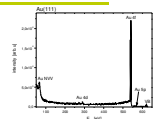
XPS of Copper-Nickel alloy

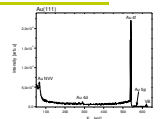
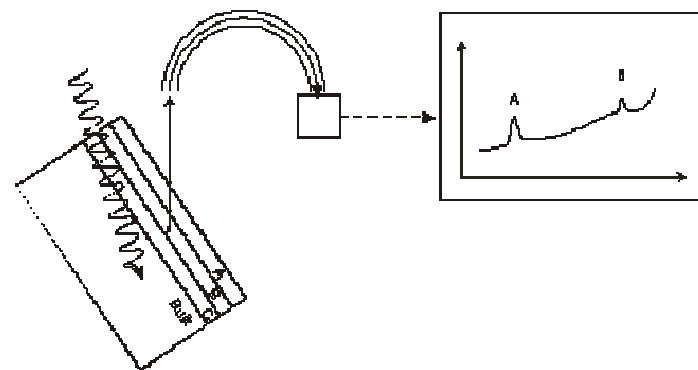
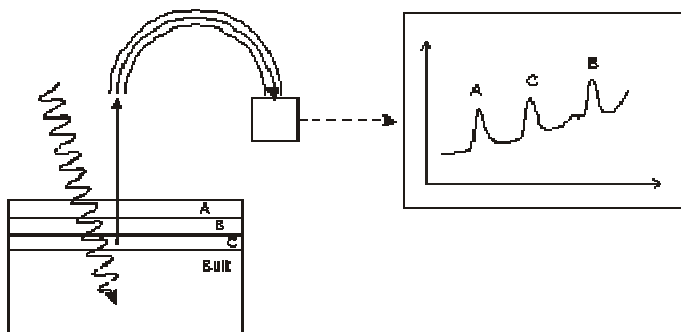
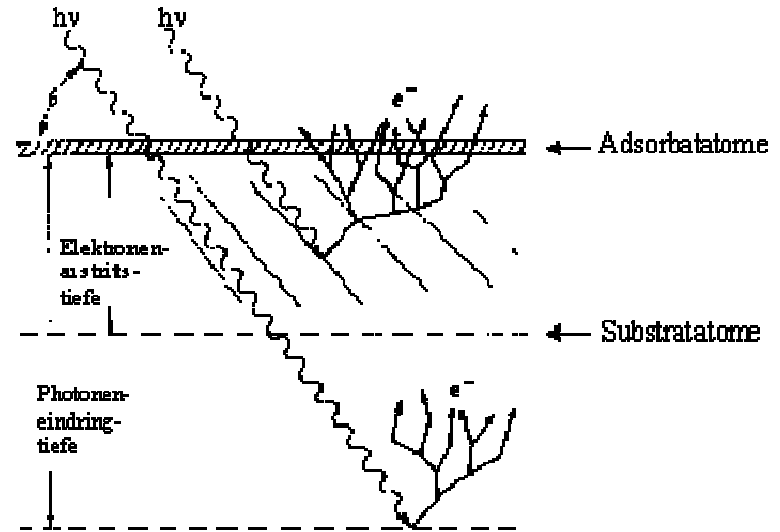
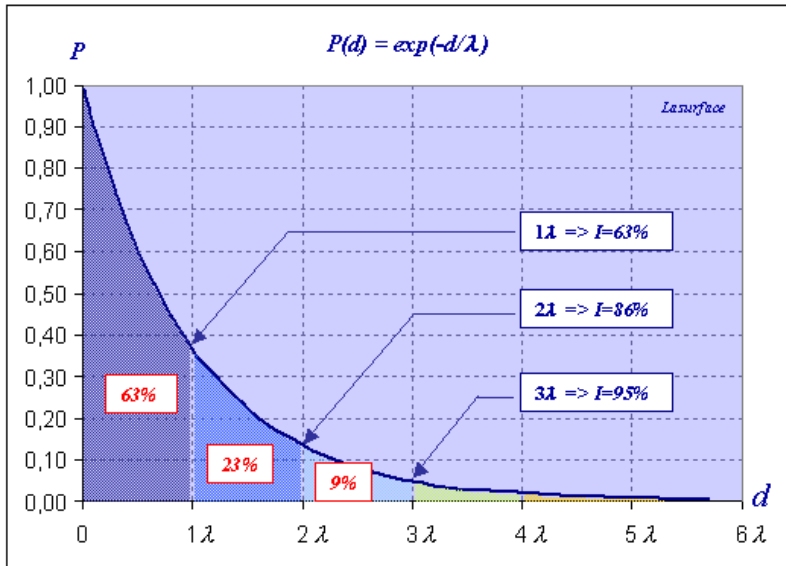


Escape depth – mean free path

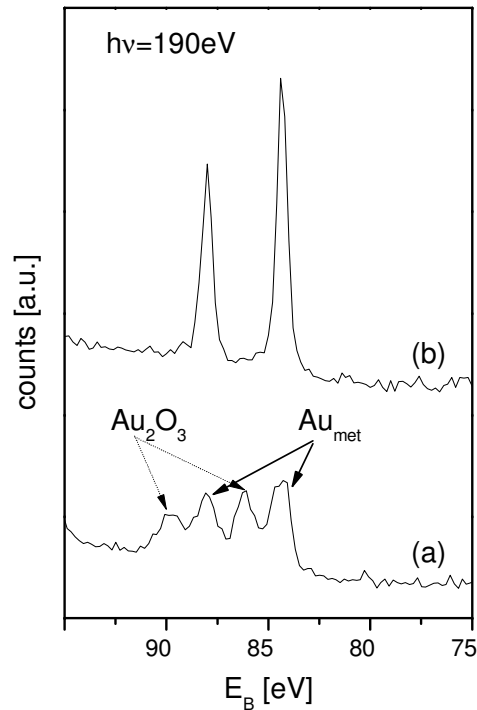


Gezeigt ist die Abhängigkeit der freien Weglänge von Elektronen in Festkörpern in Abhängigkeit von deren kinetischer Energie über dem Fermi-niveau. Der exakte Streumechanismus ist materialabhängig, aber insgesamt folgt der Zusammenhang einer „universellen Kurve“, die hier als Band gezeigt ist. Diese hat ein Minimum bei ca. 50 eV. Zu beachten ist die logarithmische Auftragung an beiden Achsen [87], [88].

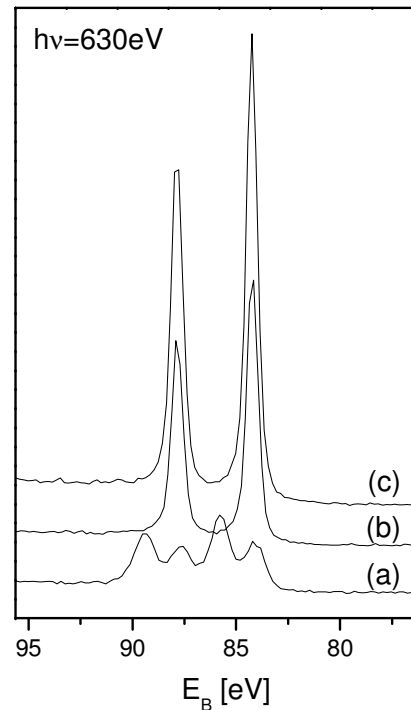




surface sensitive data



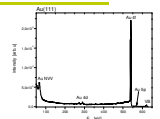
bulk sensitive data



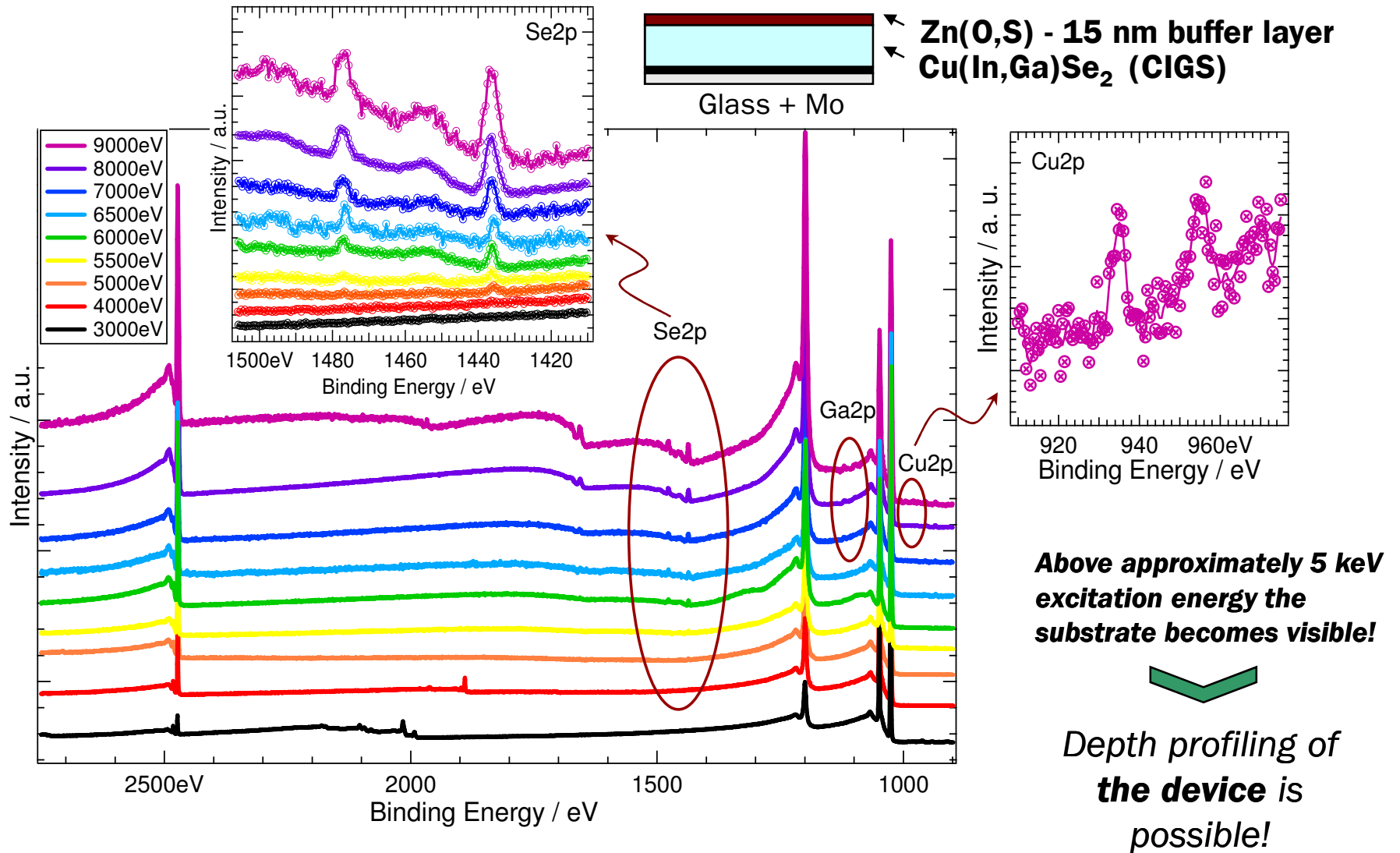
bulk sensitive data:
the oxidic signal exceeds the metallic Au
signal;

surface sensitive data:
metallic signal more intense than oxidic
signal.

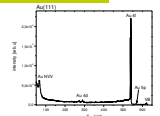
Au_2O_3 : Au 4f 7/2 at 85.7eV binding energy,
Au (metallic) Au 4f at 84eV,
chemical shift = 1.7eV



HIGH KINETIC ENERGY PHOTOELECTRON SPECTROSCOPY (HIKE) on Thin Film Solar Cells

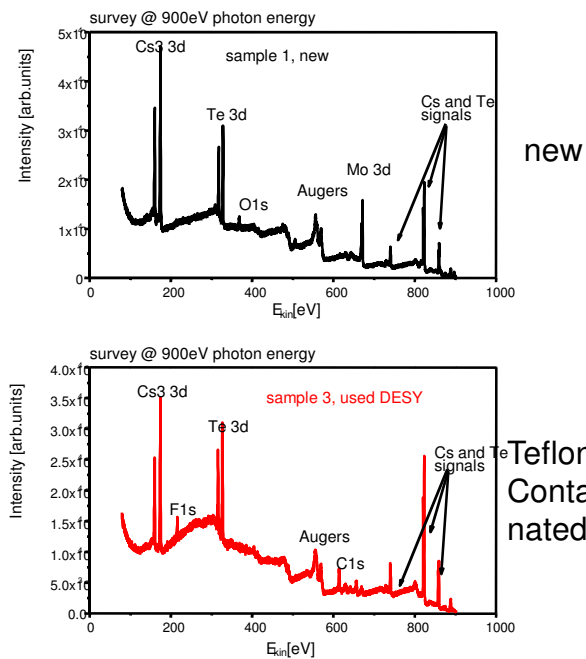


Johansson, Platzer-Björkman, Gorgoi, et al, Rev. Sci. Instrum. 78 (2007) 1.

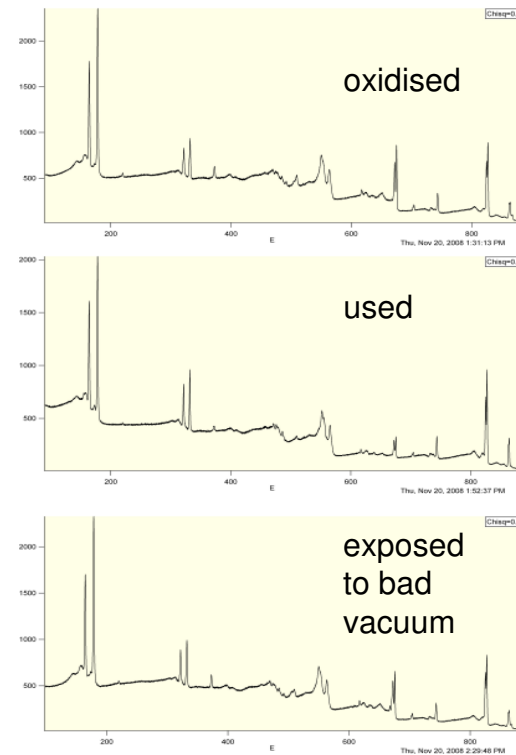


Cs₂Te photocathodes for electron accelerators: new, contaminated, used, oxidised

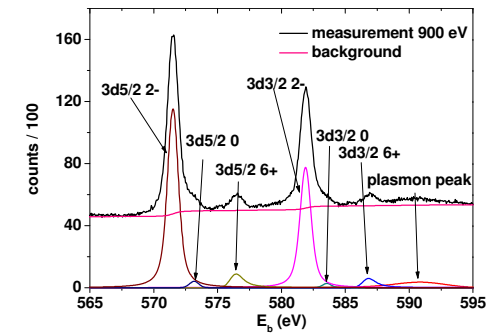
composition



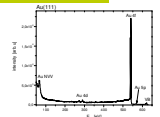
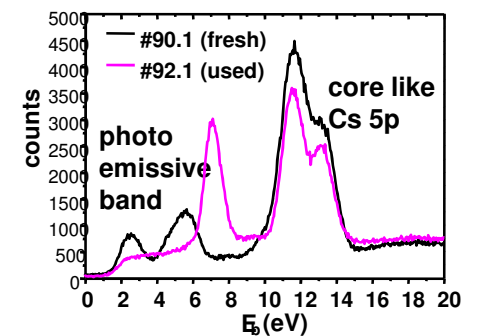
contamination



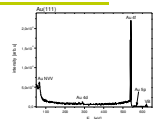
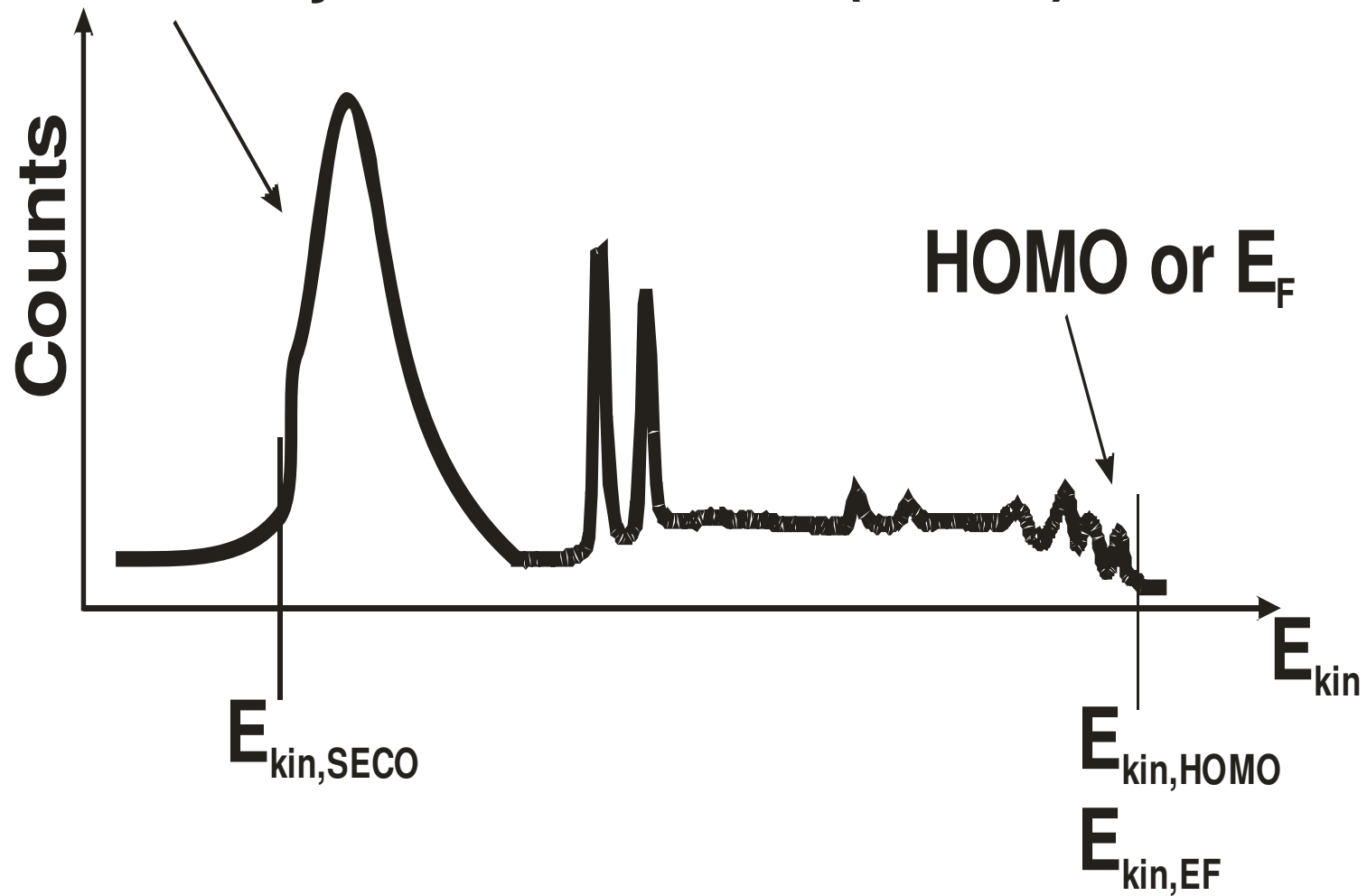
chemical analysis



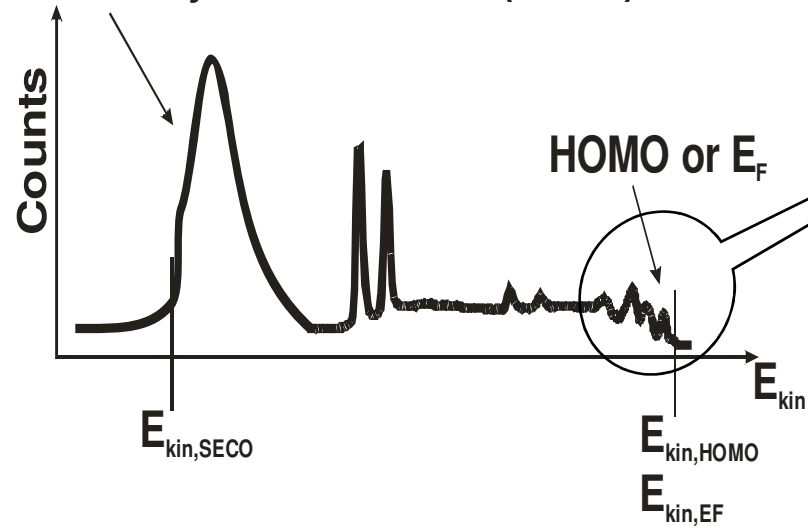
valence bands



Secondary electron cutoff (SECO)

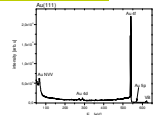
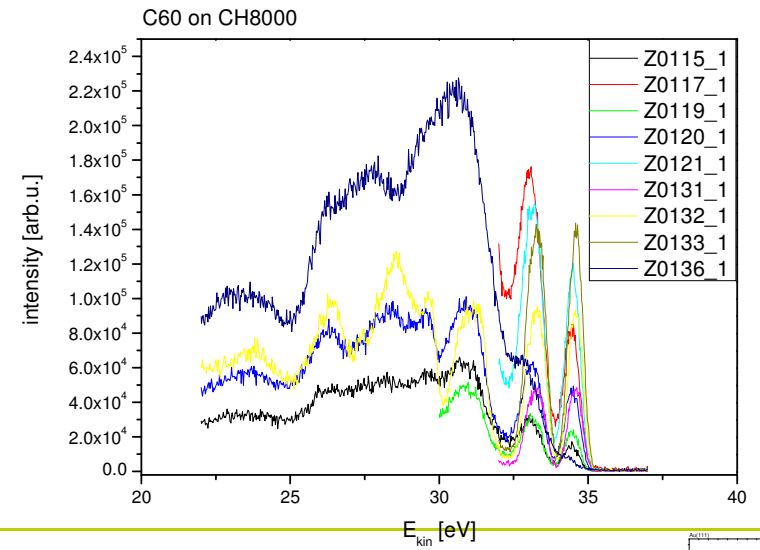


Secondary electron cutoff (SECO)

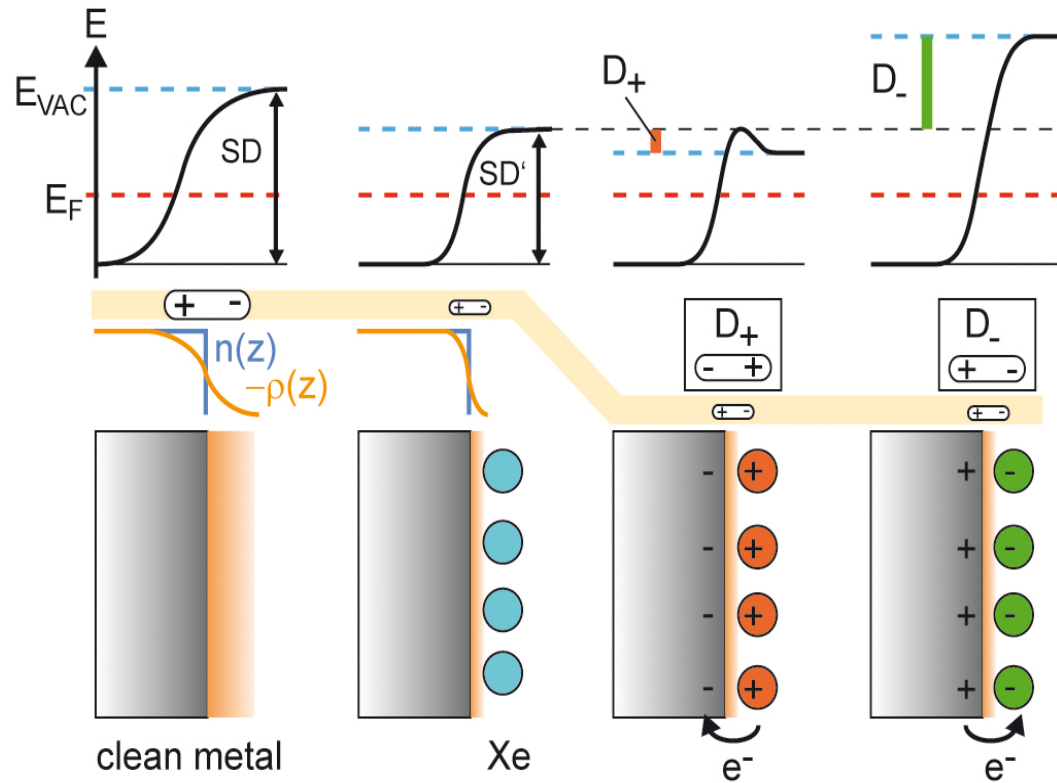
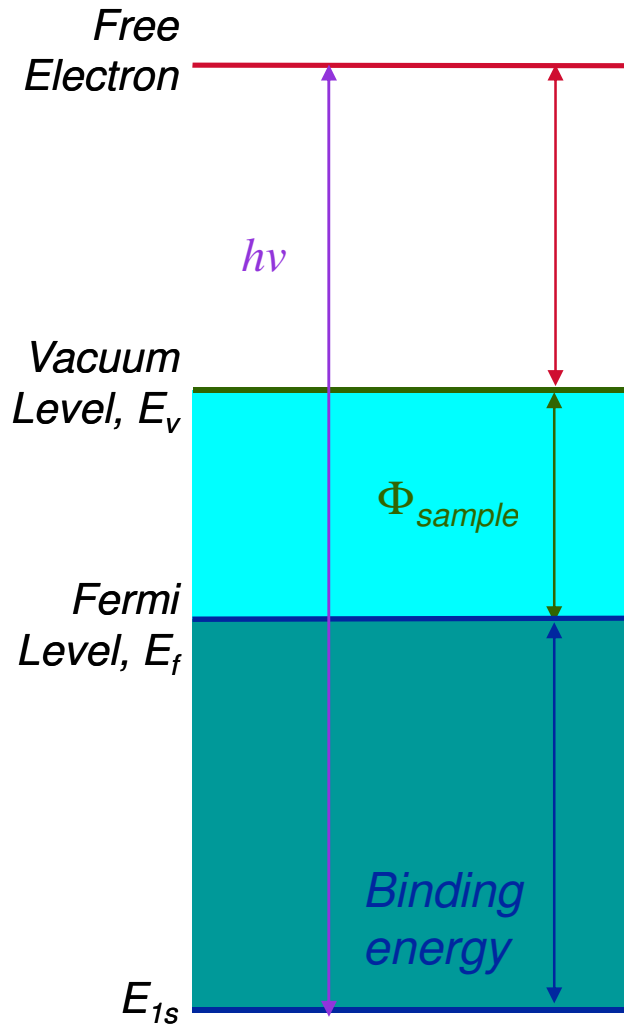


valence states
UPS: valence orbitals
interface states

ionization energy = $h\nu - (E_{kin,HOMO} - E_{kin,SECO})$
 work function = $h\nu - (E_{kin,EF} - E_{kin,SECO})$
 hole injection barrier = $E_{kin,EF} - E_{kin,HOMO}$

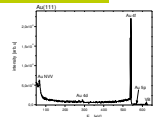


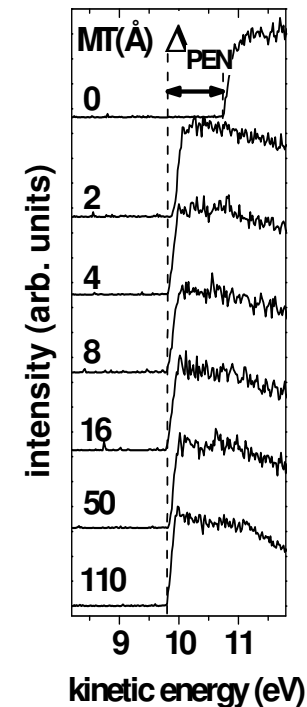
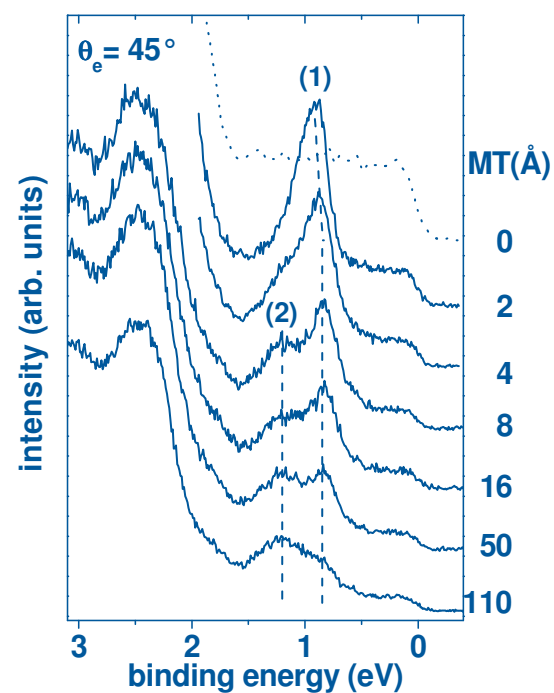
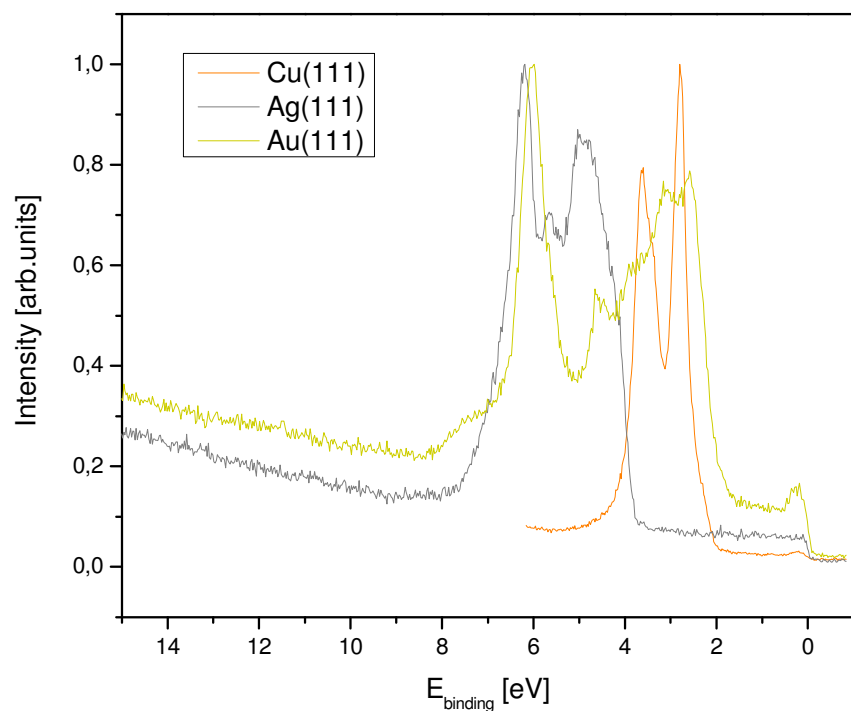
Workfunction



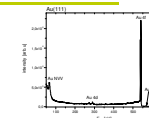
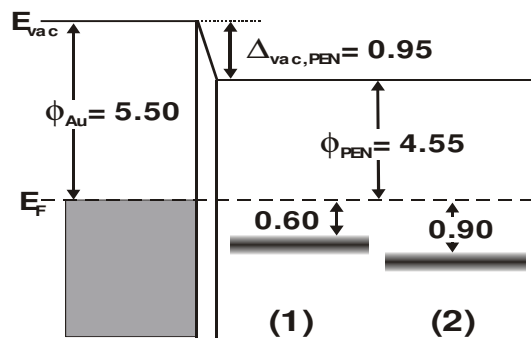
„Push-back“ effect
Charge transfer
Covalent bond formation
Permanent dipoles

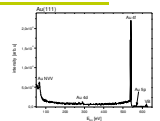
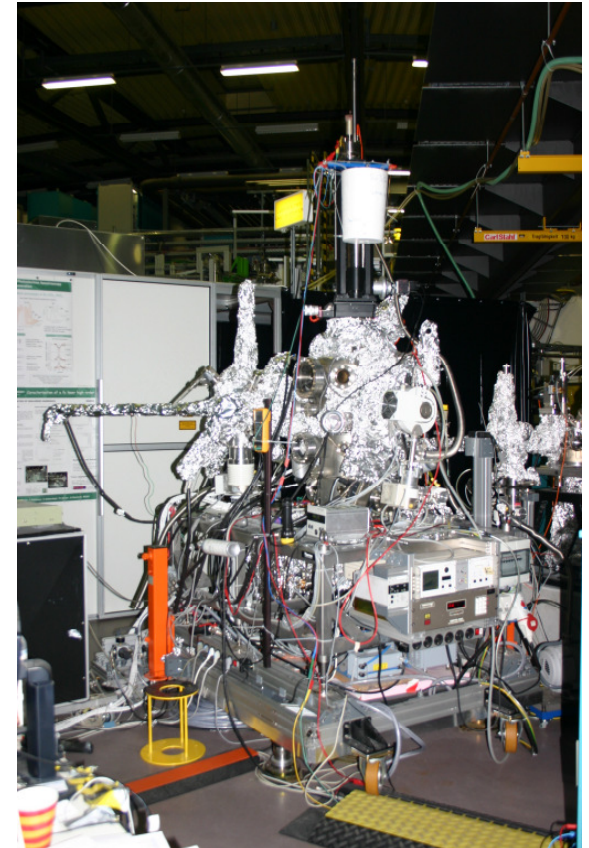
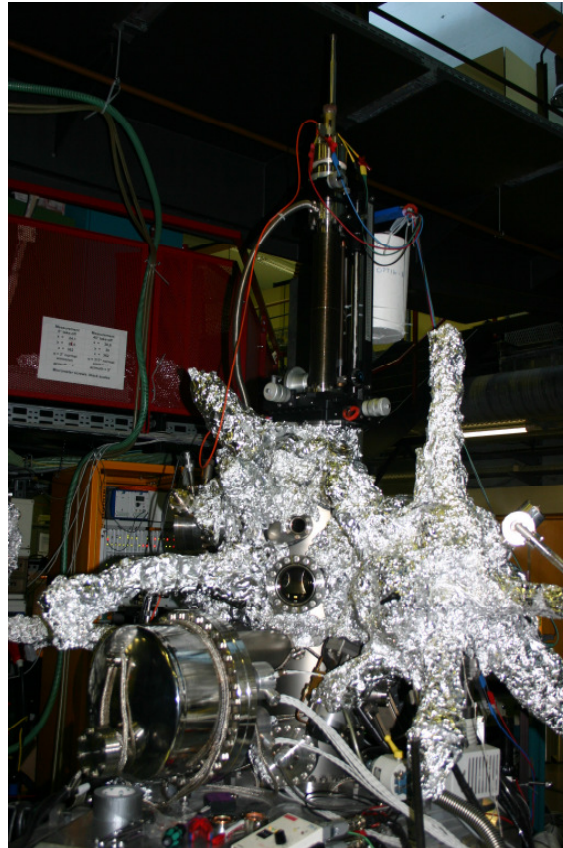
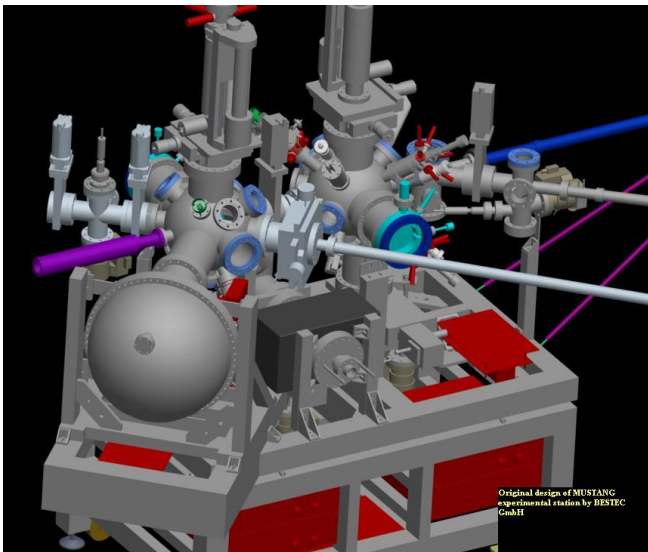
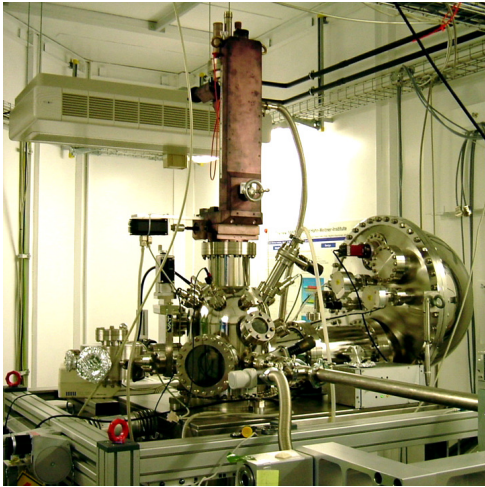
Ishii, Sugiyama, Ito, Seki, *Adv. Mater.* 11, 605 (1999); Kahn, Koch, Gao, *J. Poly. Sci. B* 41, 2529-2548 (2003)





energy level diagrams of
PEN/Au(111)

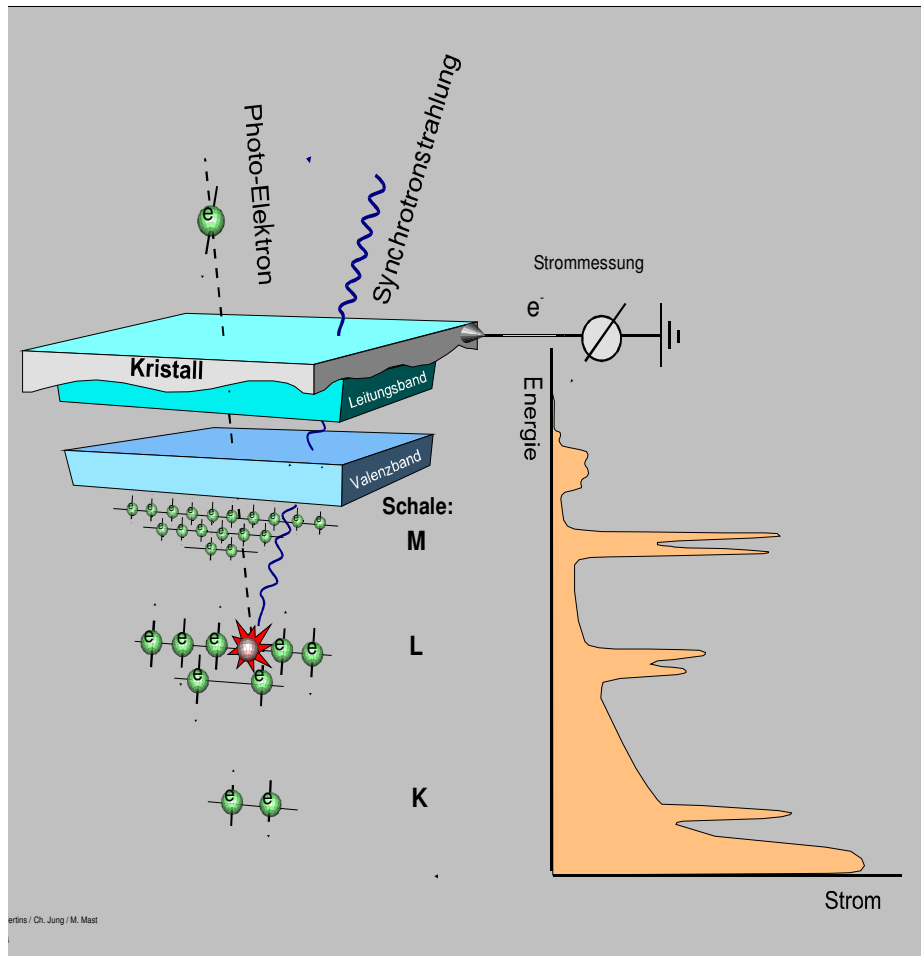




REMINDER

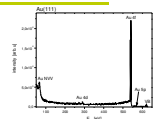
Photoemission provides information on:

- Chemical composition
- Chemical state/reaction
- Electronic state
- Interfaces/interface reactions
- Quantitative analysis
- Depth profiling



ertins / Ch. Jung / M. Mast

12/2011





**HELMHOLTZ
ZENTRUM BERLIN**
für Materialien und Energie

Thank you!