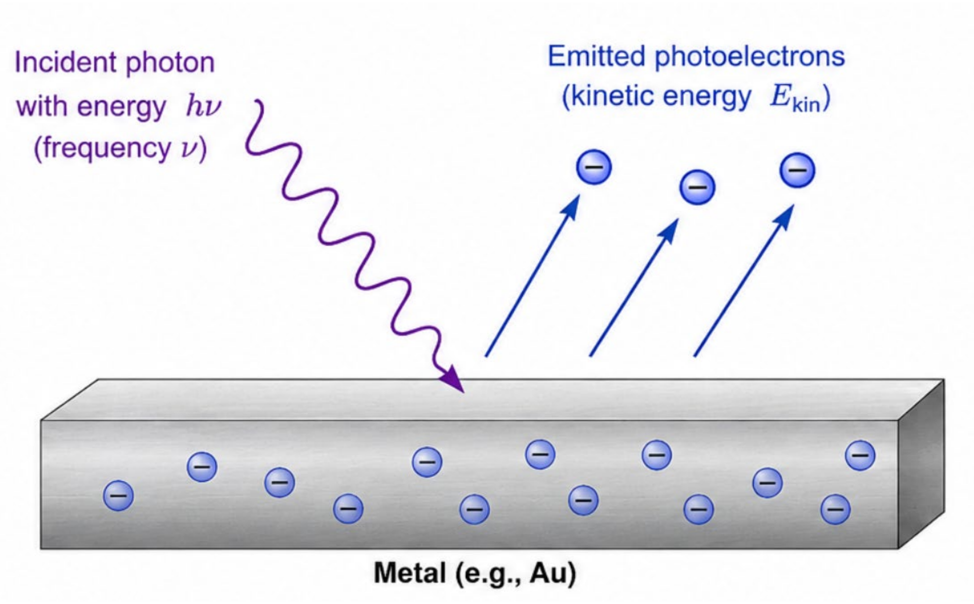
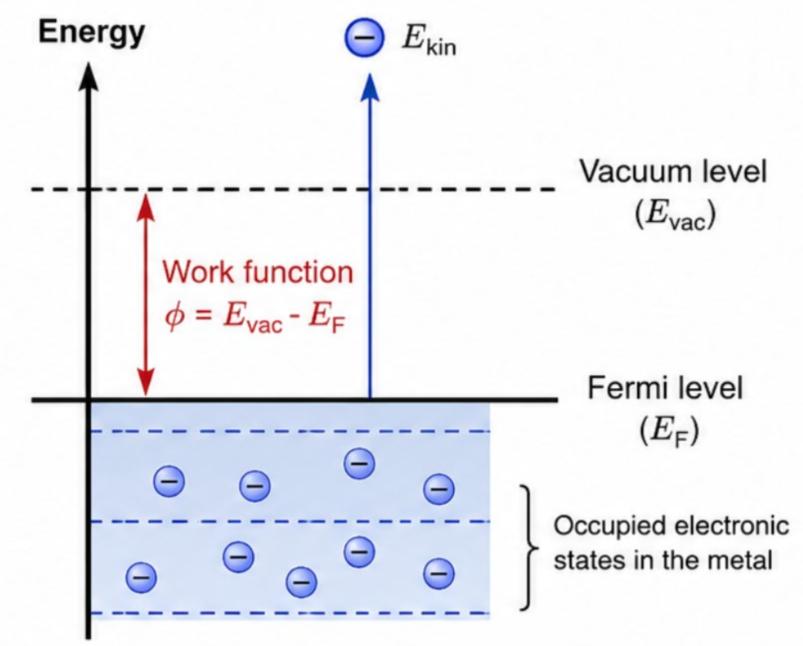
Ultraviolet Photoelectron Spectroscopy (UPS): Principles and Applications

Xinqi Chen, PhD
Research Professor
Department of Mechanical Engineering
NUANCE-Keck-II Manager
Northwestern University
xchen@northwestern.edu

Photoelectric Effect

- Discovered by Hertz and explained by Einstein (1905)
- Photons strike the surface.
- Energy is transferred to electrons.
- Electrons are ejected if photon energy exceeds the binding energy + work function.
- This is the basis of all Photoelectron spectroscopy (PES) techniques.



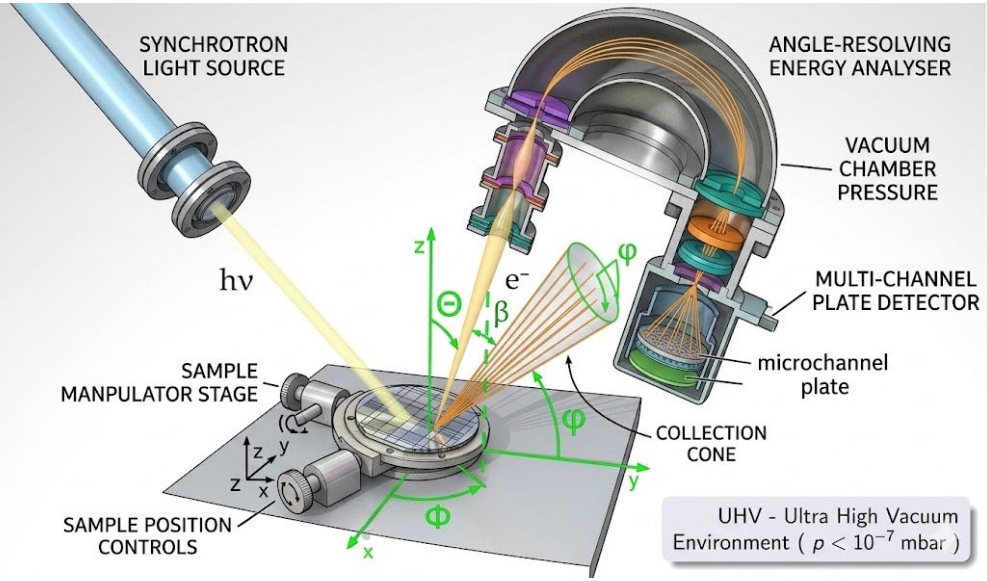


$$h\nu = \phi + E_B + E_K$$

where:

- $h\nu$: photon energy
- ϕ: work function
- $E_{B:}$ binding energy
- E_K :kinetic energy of emitted electron

Photoelectron Spectroscopy (PES)



$E_B = h\nu - \phi - E_K$

where:

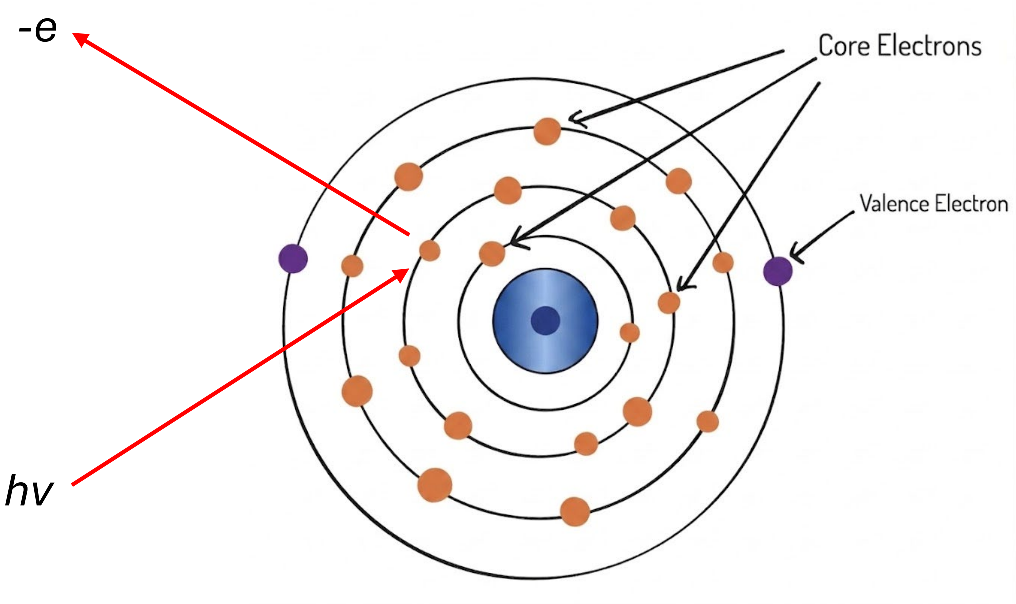
•E_B is electron binding energy inside the material

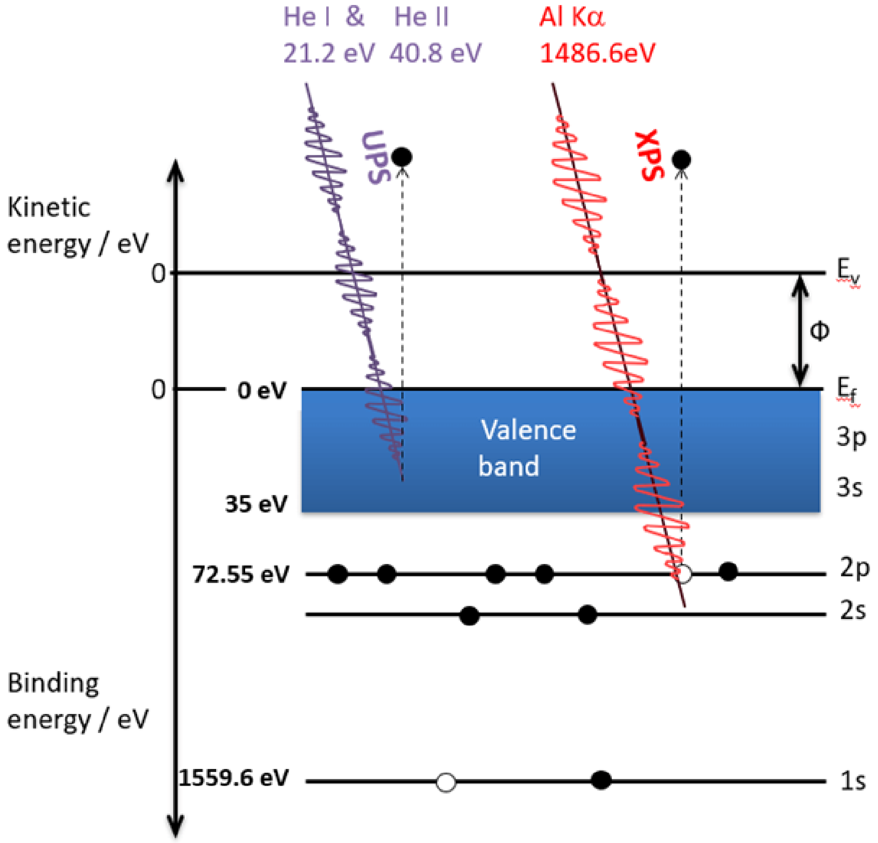
By measuring electron kinetic energies very precisely, you obtain information about:

- **binding energies**
- **valence bands**
- **core levels**
- **chemical states**
- **density of states**
- **work function**
- **electronic structure**

Aspect	**Photoelectric Effect**	**Photoelectron Spectroscopy**
Nature	Physical phenomenon	Analytical technique
Main question	Can light eject electrons?	What are electron energies?
Measurement	Current / threshold	Energy-resolved spectrum
Output	Electron emission	Electronic structure
Energy resolution	Often unnecessary	Critical
Typical purpose	Fundamental physics	Materials characterization

PES (XPS and UPS)

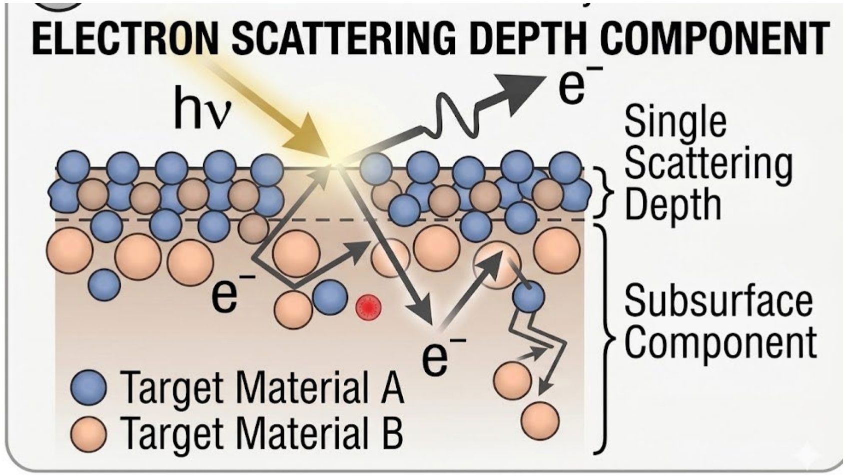


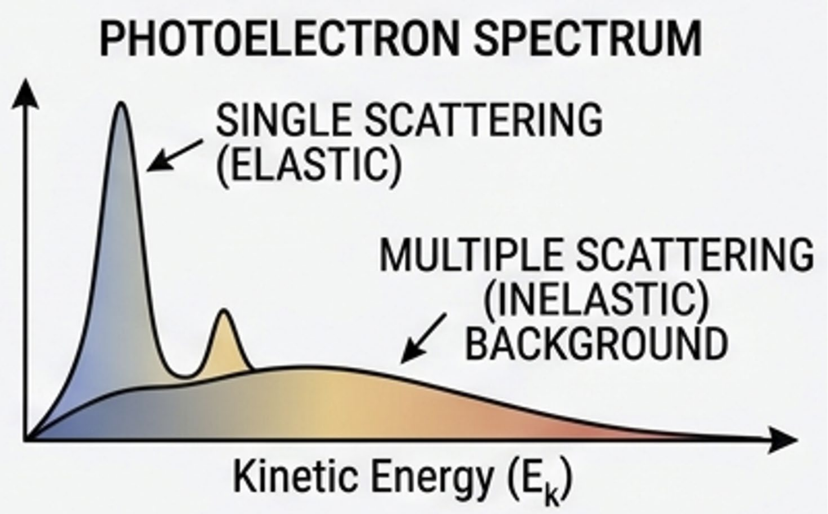


XPS (X-ray): High energy (1000-1500 eV). Probes deep **Core Levels** (e.g., 1s, 2p).

UPS (Ultraviolet): Low energy (10-45 eV). Probes the **Valence Band** and shallow levels.

Electron Scattering





Property	Elastic Scattering	Inelastic Scattering
Kinetic Energy	Conserved (No Loss)	Partially Lost (Transferred)
Spectral Result	Characteristic Peak for Source of Binding information	Secondary Background Source of Spectral Background
Data Value	Elemental/Chemical Identity	Loss of Energy Information
Origin Depth	Very Shallow (< 10nm)	Can originate deeper

Inelastic Mean Free Path (IMFP)

The **inelastic mean free path** (**IMFP**) is an index of how far an electron on average travels through a solid before losing energy.

Why inelastic scattering is critical

Suppose an electron originates from a sharp Au 5d state.
If it escapes without inelastic scattering:

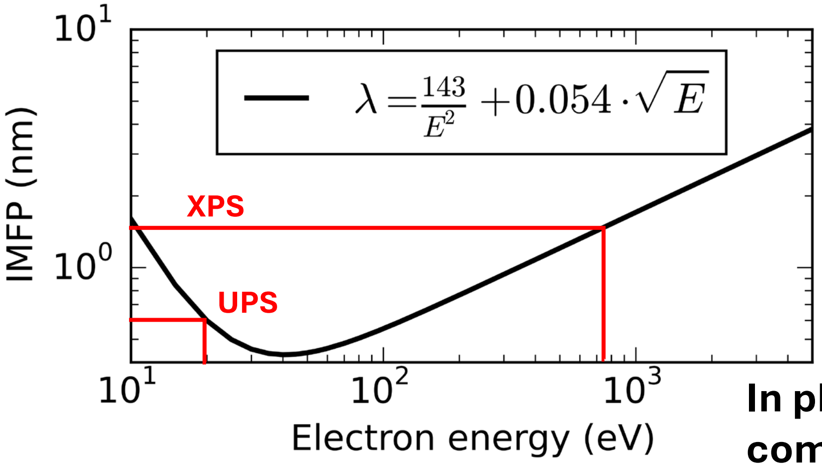
- it contributes to the sharp UPS peaks.

If it loses energy:

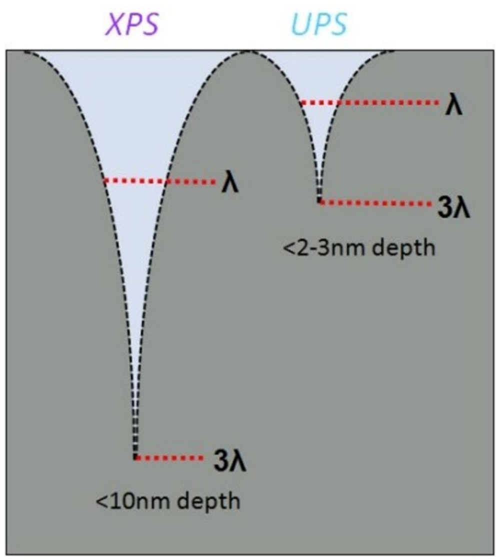
- its original binding-energy information is destroyed
- it becomes part of the secondary electron background.

Therefore:

- useful UPS signal comes mainly from electrons that avoided inelastic collisions.



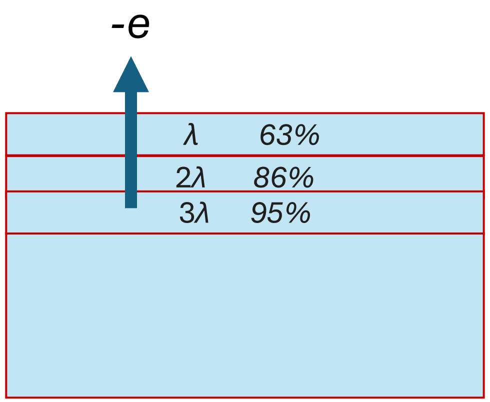
- λ = inelastic mean free path (nm)
- E = electron kinetic energy (eV)



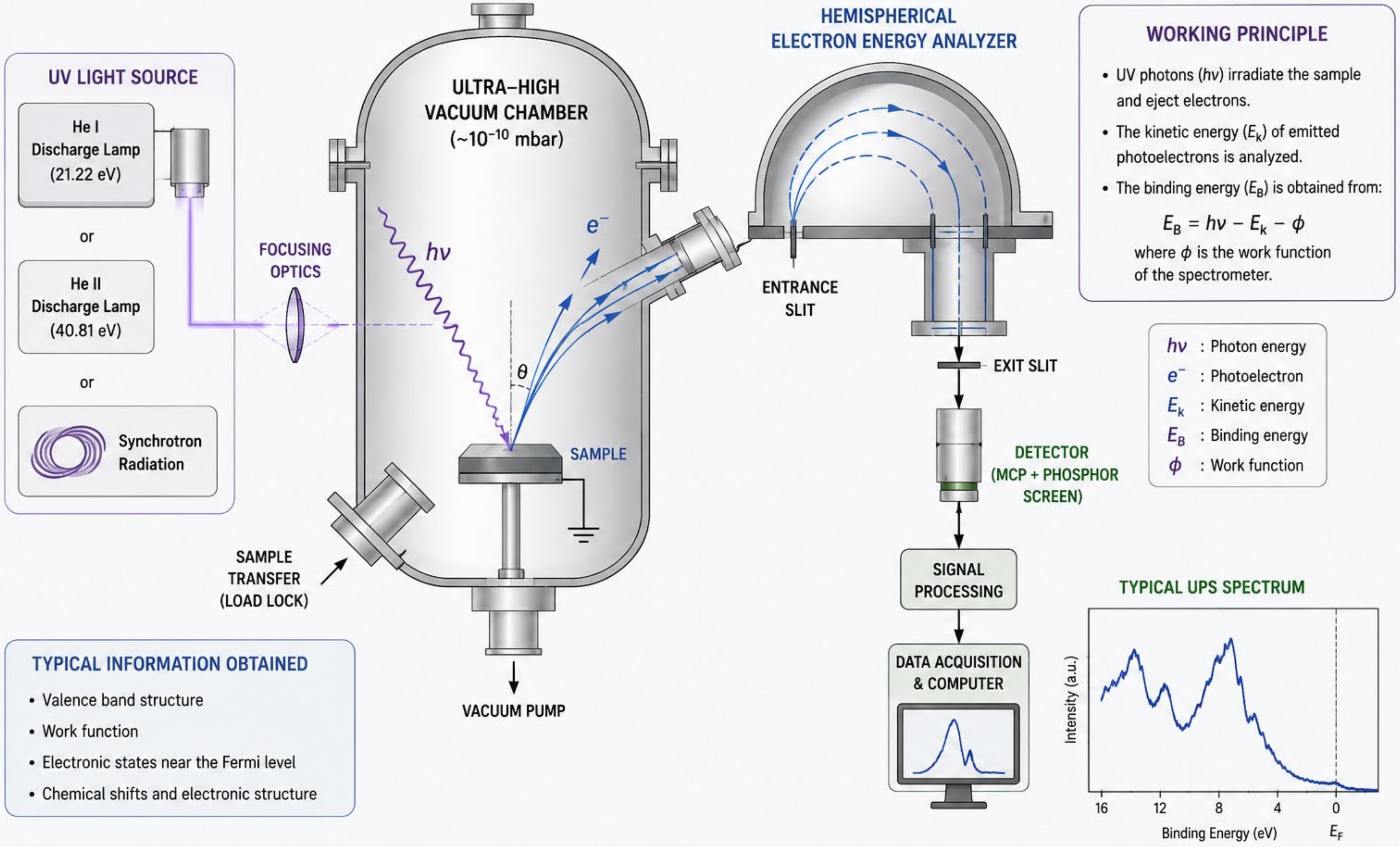
In photoemission, 95% signal comes from 3 λ :

•UPS ≈20 Å probed

•XPS ≈55 Å probed



UPS (ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY)



WORKING PRINCIPLE

- UV photons ($h\nu$) irradiate the sample and eject electrons.
- The kinetic energy (E_k) of emitted photoelectrons is analyzed.
- The binding energy (E_B) is obtained from:

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

where ϕ is the work function of the spectrometer.

$h\nu$: Photon energy
e^- : Photoelectron
E_k : Kinetic energy
E_B : Binding energy
ϕ : Work function

TYPICAL INFORMATION OBTAINED

- Valence band structure
- Work function
- Electronic states near the Fermi level
- Chemical shifts and electronic structure

UV Source

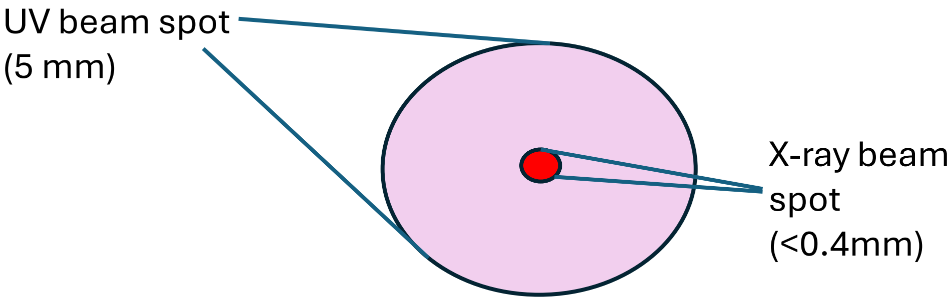
Helium UV Source: He I and He II in UPS

Principle

A helium discharge lamp generates ultraviolet photons when excited helium atoms or ions relax to lower energy states.

Pressure-Tunable Operation

Sources are generated in a cold-cathode capillary discharge. Adjusting gas pressure allows selection: Higher pressure favors He I, while lower pressure optimizes He II yield.



Why Use Two Sources?

He I (21.22 eV)

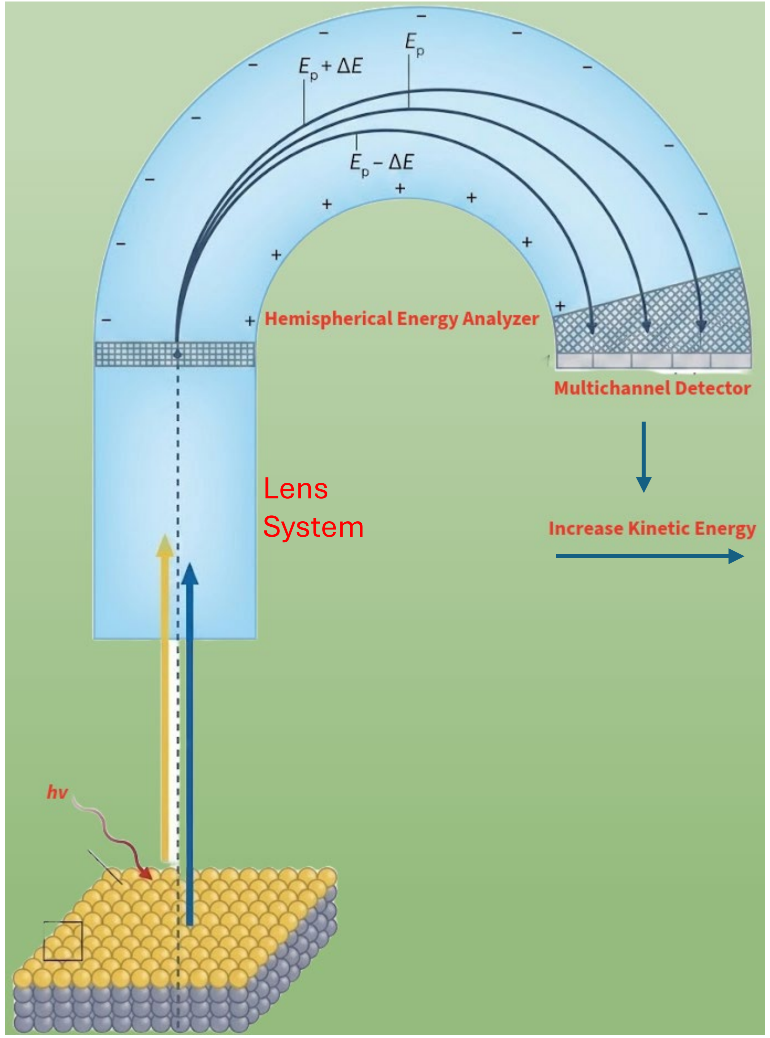
- Higher photoionization cross-section for valence states
- Strong signal intensity
- Standard source for work function and valence band measurements

He II (40.81 eV)

- Higher kinetic energy photoelectrons
- Access to deeper valence levels
- Different orbital sensitivity (especially d- and f-electrons)
- Useful for electronic structure studies

On the Thermo Scientific Nexsa G2 Surface Analysis System, the UPS source uses a He I / He II ultraviolet source and is **not micro-focused** like the X-ray source.

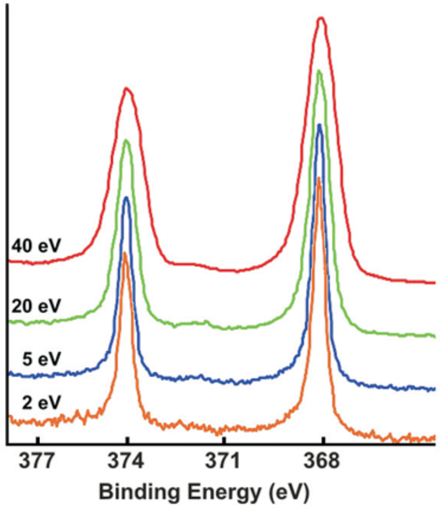
Hemispherical Analyzer



Principle

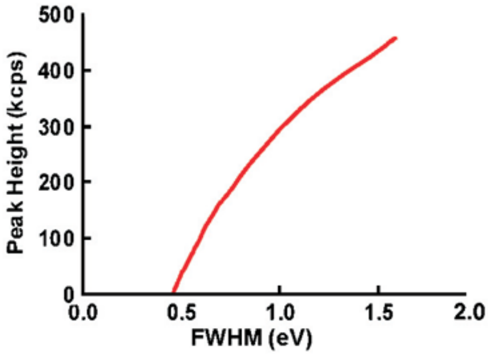
- Electrons with different kinetic energies follow different trajectories in an electric field.
- Only electrons with the selected energy can pass through the analyzer and reach the detector.

Pass energy ∝ Energy resolution



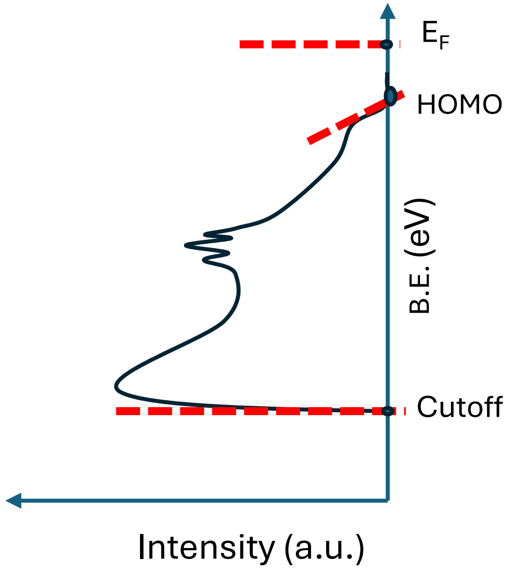
Ag 3d spectra acquired using the XR5 X-ray monochromator

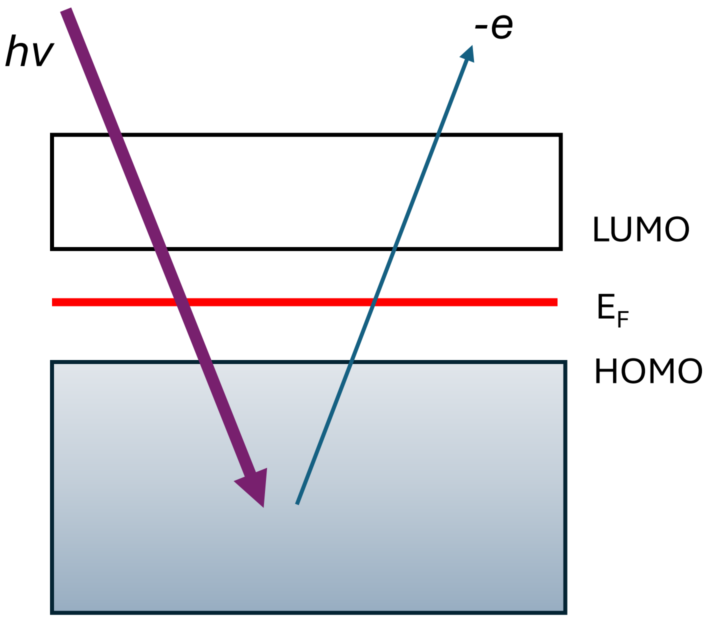
Pass energy 1/ ∝ Peak intensity

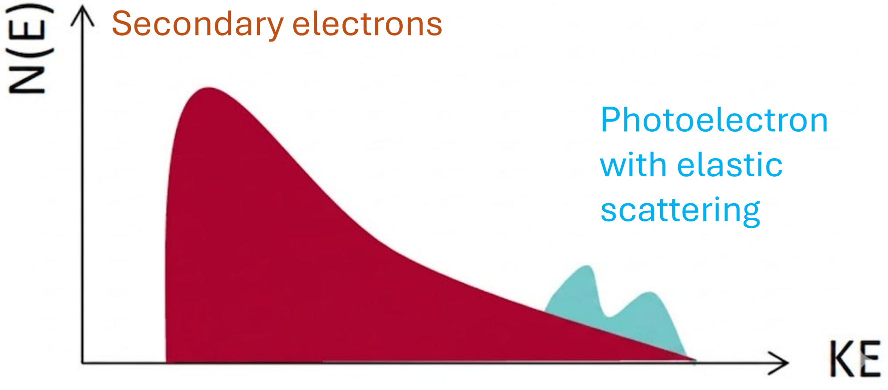


Ag 3d5/2 peak intensity as a function of resolution

UPS Spectrum







HOMO (Highest Occupied Molecular Orbital)

- The onset of the valence-band signal closest to the Fermi level.
- Determined by extrapolating the leading edge of the valence-band feature to the baseline.
- Indicates the energy of the highest occupied electronic state in a semiconductor or organic material.

Secondary Electron Cutoff (SECO)

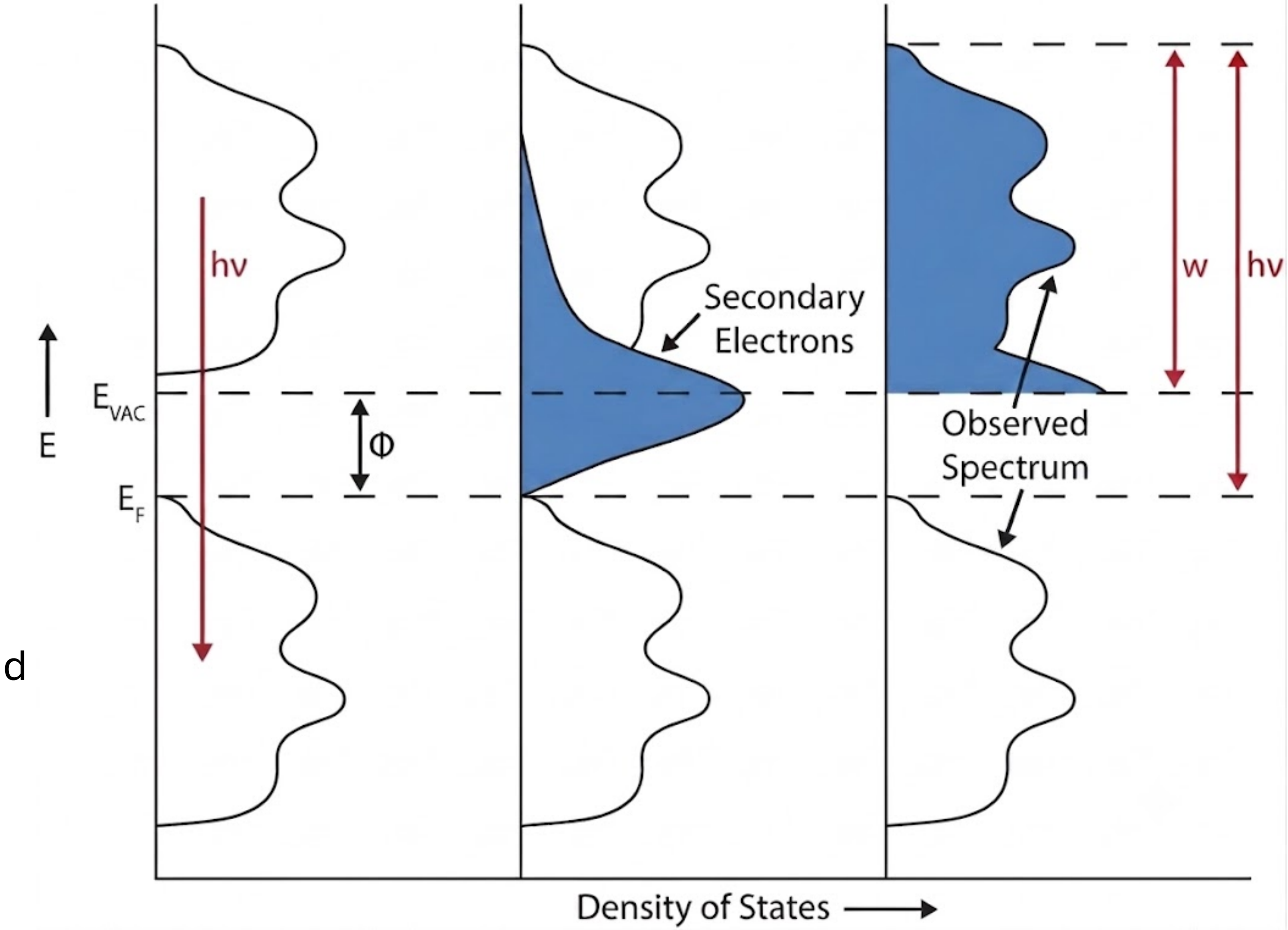
- Located at the **low kinetic energy edge** of the spectrum.
- Corresponds to electrons that barely escape from the sample surface.
- Determined by extrapolating the cutoff edge to the background baseline.

- Photoelectrons that escape without energy loss produce the characteristic UPS peaks;
- Inelastic scattering generates secondary electrons and a broad background signal;
- Photoelectron spectroscopy its strong surface sensitivity.

Illustration of the Processes Leading to a UPS spectrum

Spectrum

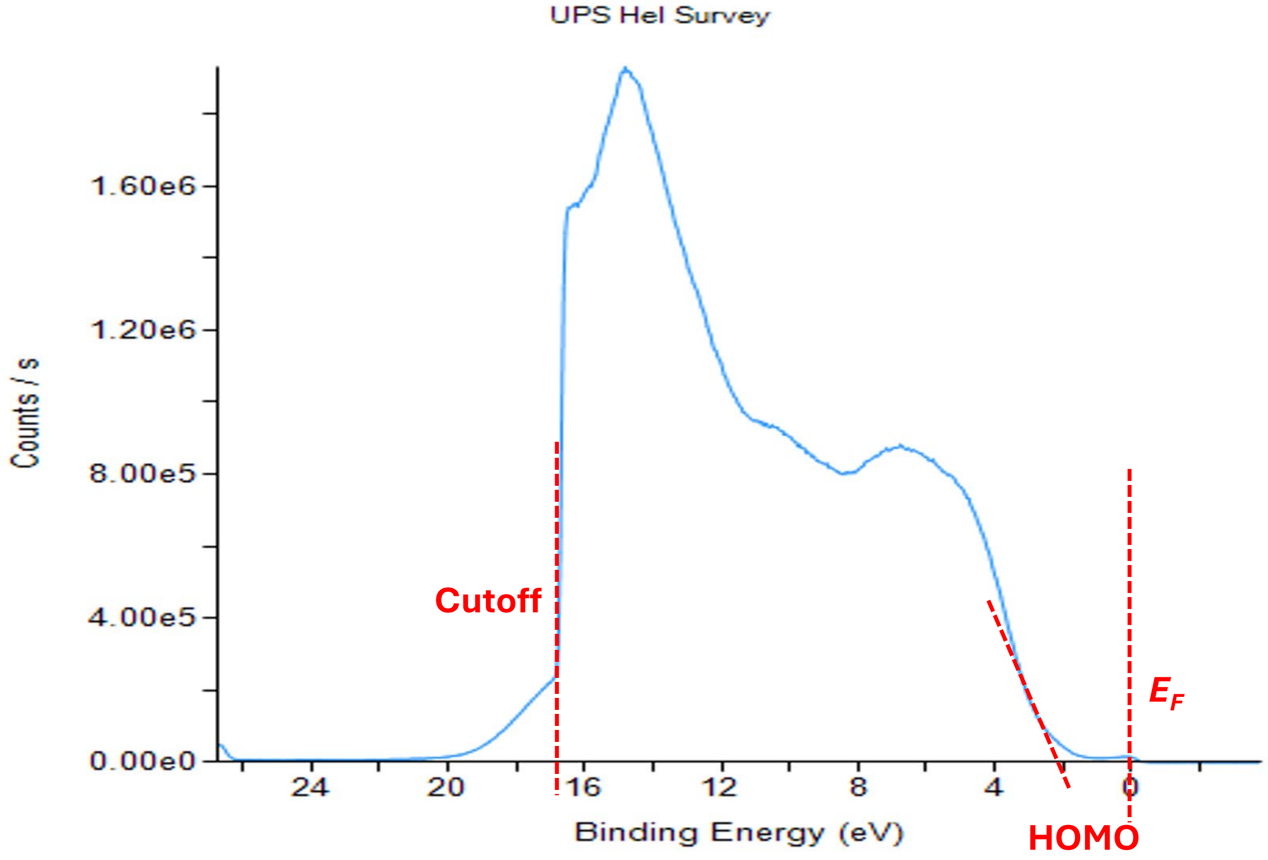
Valance Band



$$hv = w + \phi$$

Applied Surface Science Advances 13 (2023) 10038

UPS Data



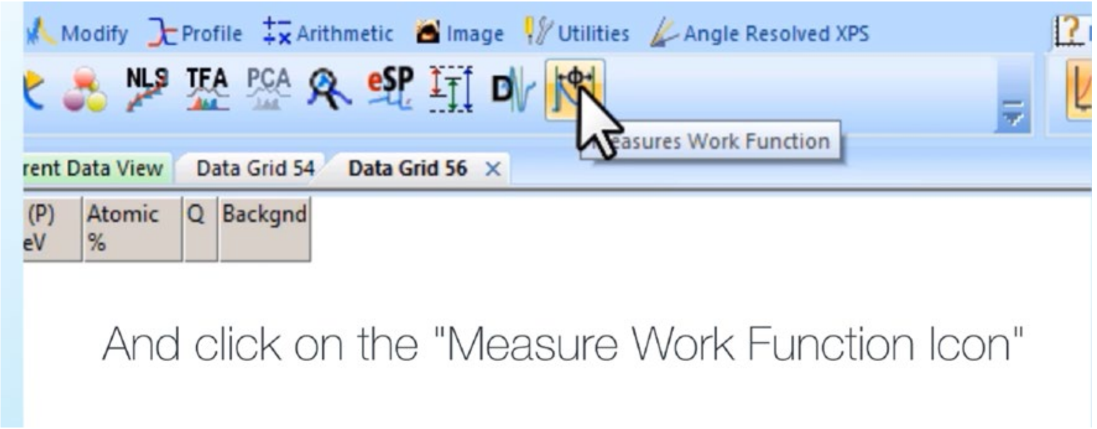
$$\Phi = hv - (E_{cutoff} - E_F)$$

Fermi level = 0 eV

HOMO = 2.1 eV

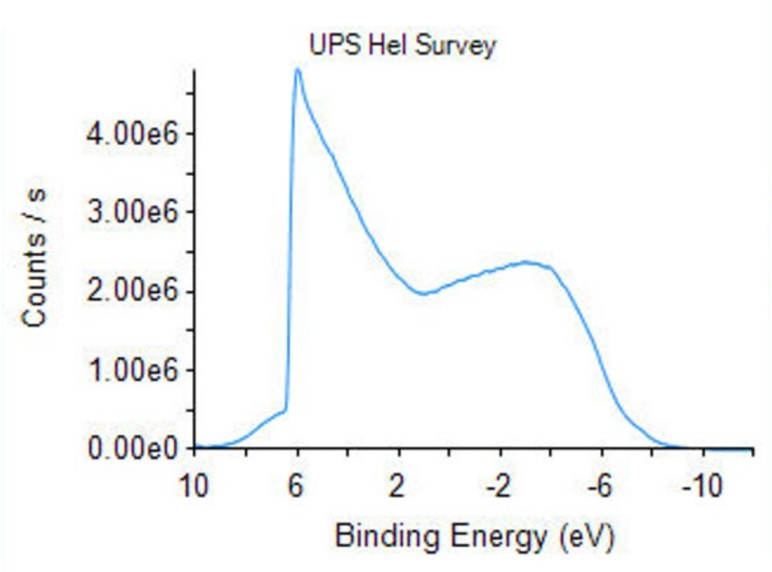
Cutoff = 16.8 eV

Work function = 21.2 eV -16.8eV = 4.4 eV

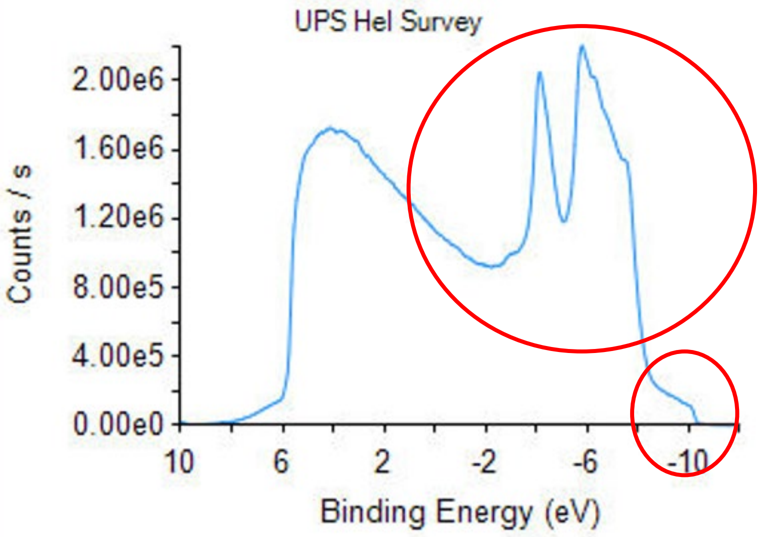


And click on the "Measure Work Function Icon"

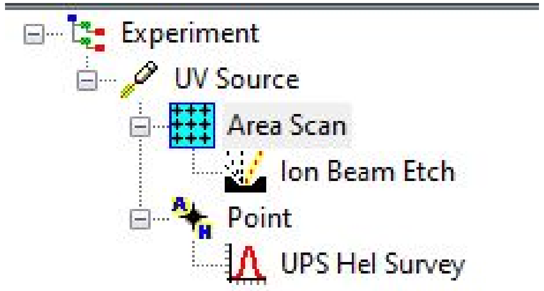
The effect of The Surface Contamination



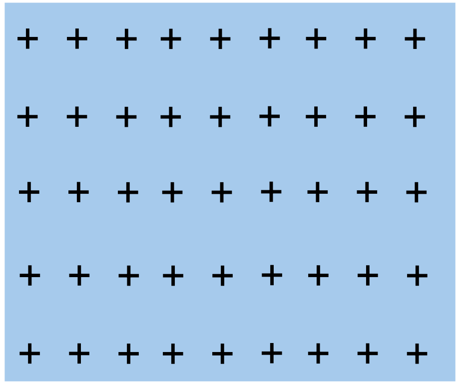
Raw Au surface



Au surface after 30s 3kv high ion etching



Area etching

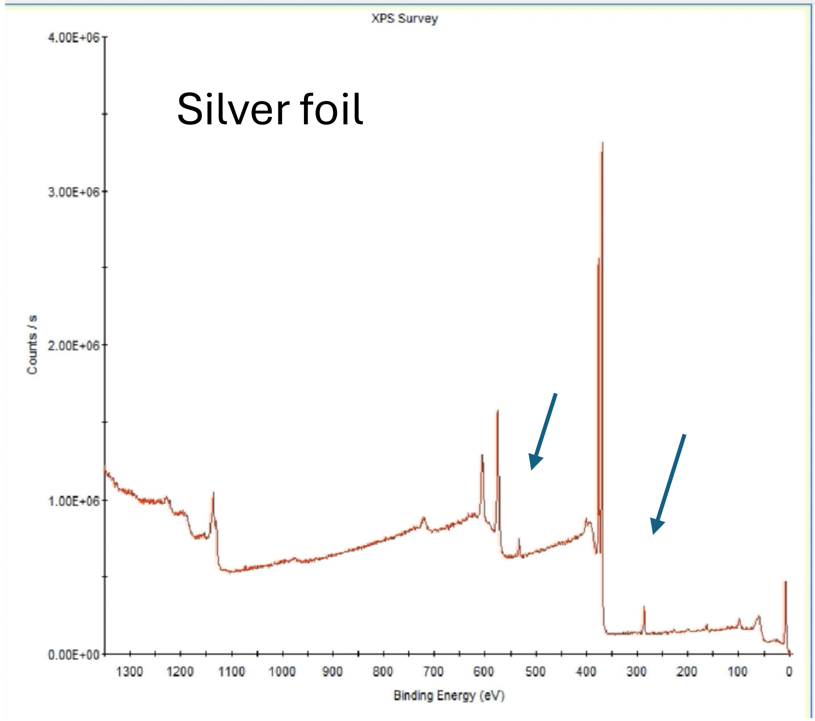


Remove Surface Contamination

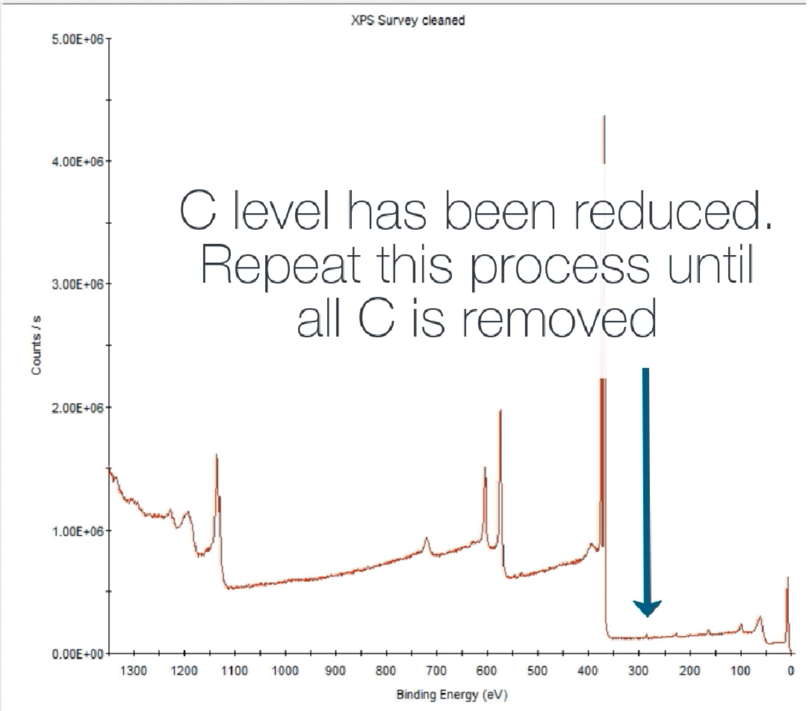
Before we can do UPS we will first need to run some XPS analysis.

This has 3 purposes:

1. Verify that the sample holder is making contact with the stage
2. Find the optimum analysis height
3. Check the level of carbon contamination on the surface



Silver foil

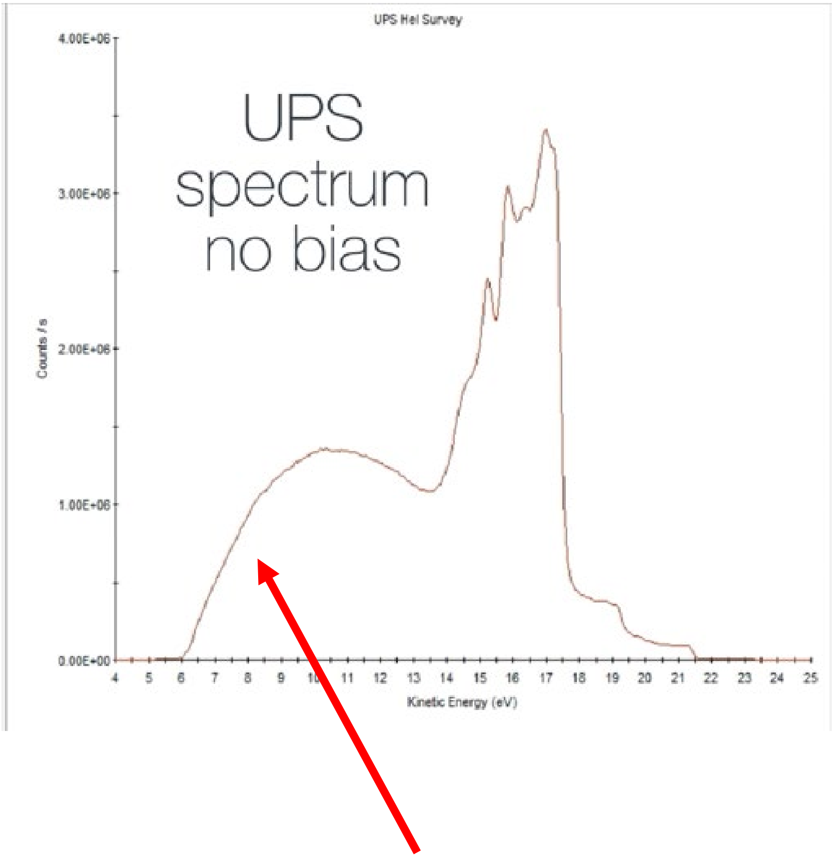


C level has been reduced. Repeat this process until all C is removed

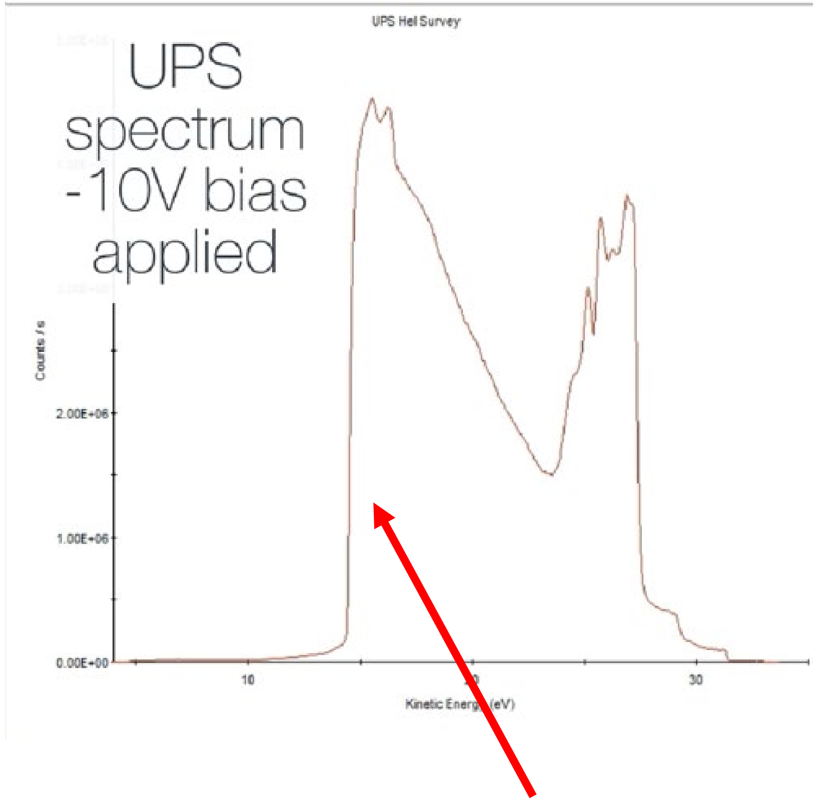
The first few nm of a surface coming from atmospheric environment are composed mostly of O, C.

Sputter cleaning:
High energy (a few keV) Argon ions (Ar^+) impinge to the surface and sputter the topmost atomic layers

Biased UPS



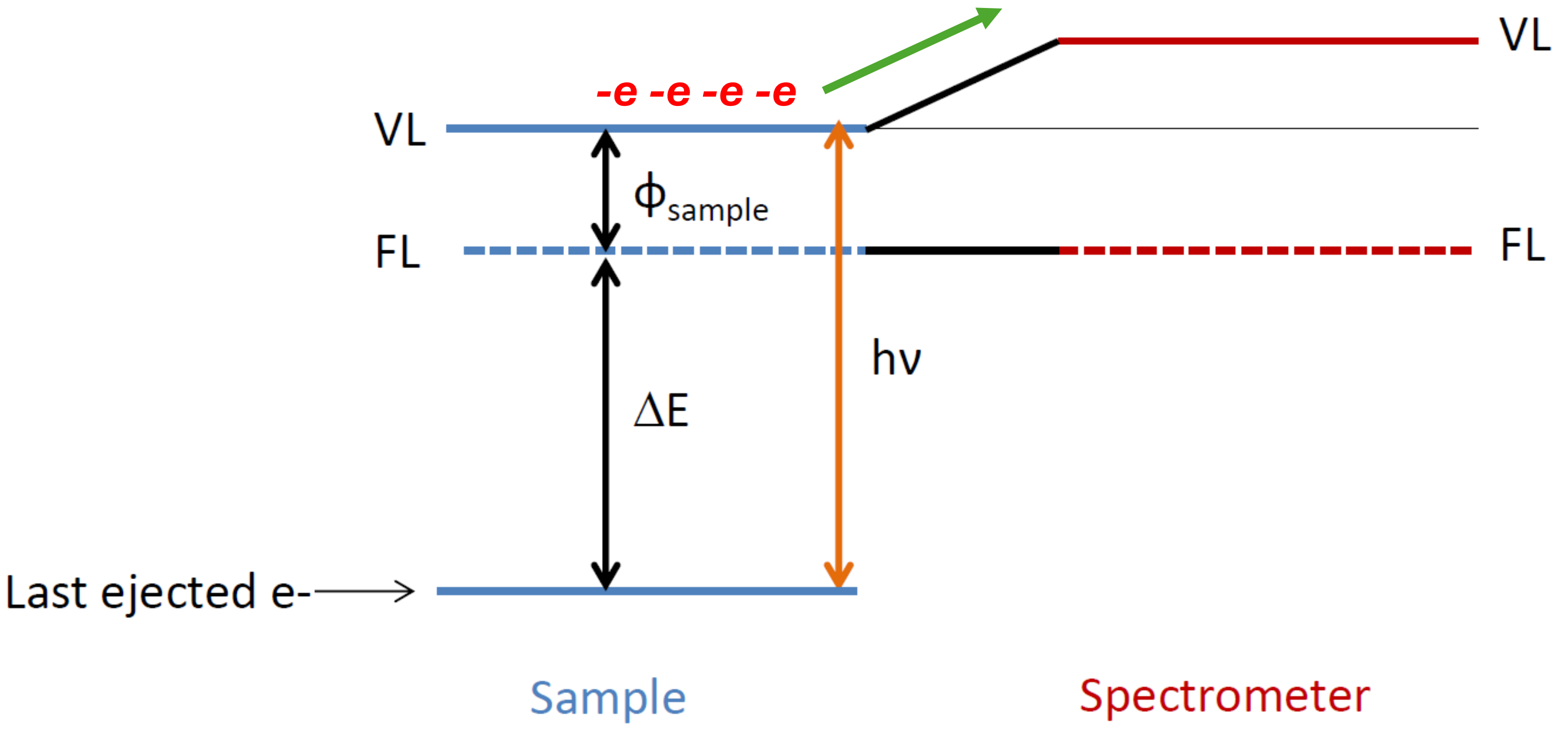
UPS spectrum no bias



UPS spectrum -10V bias applied

With negative bias, the cutoff is sharp and the intensity is high

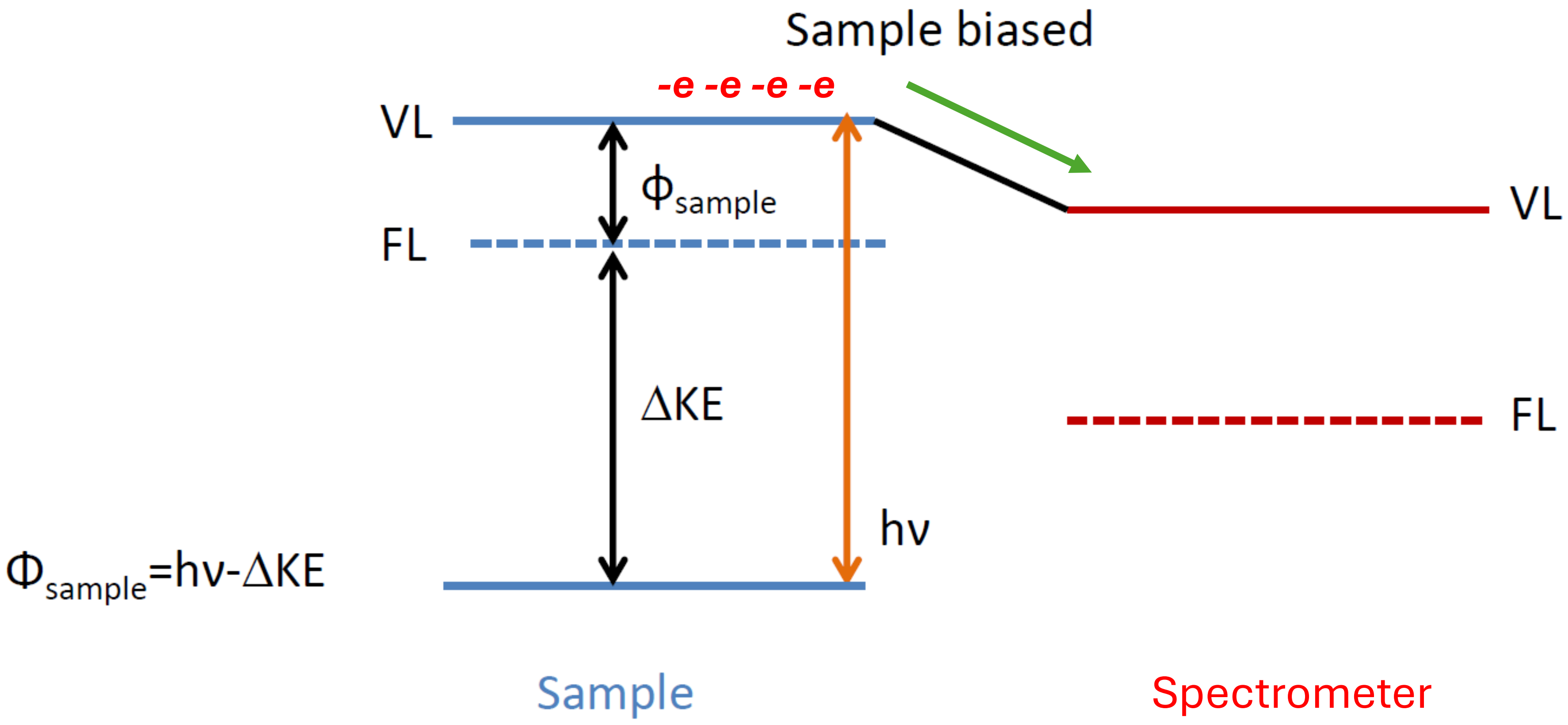
UPS Measurement With No Negative Bias



$$\Phi_{sample}=h\nu-\Delta KE$$

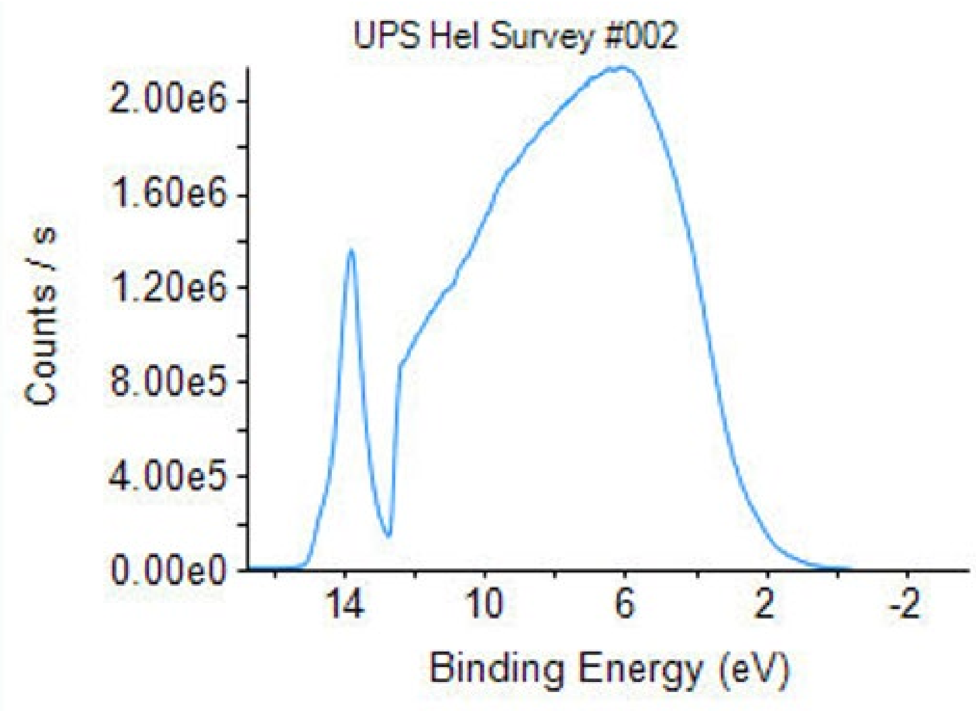
Only e- with a large enough KE can be detected by the spectrometer
Those below the VL of the spectrometer are not detected.

UPS Measurement With Negative Bias

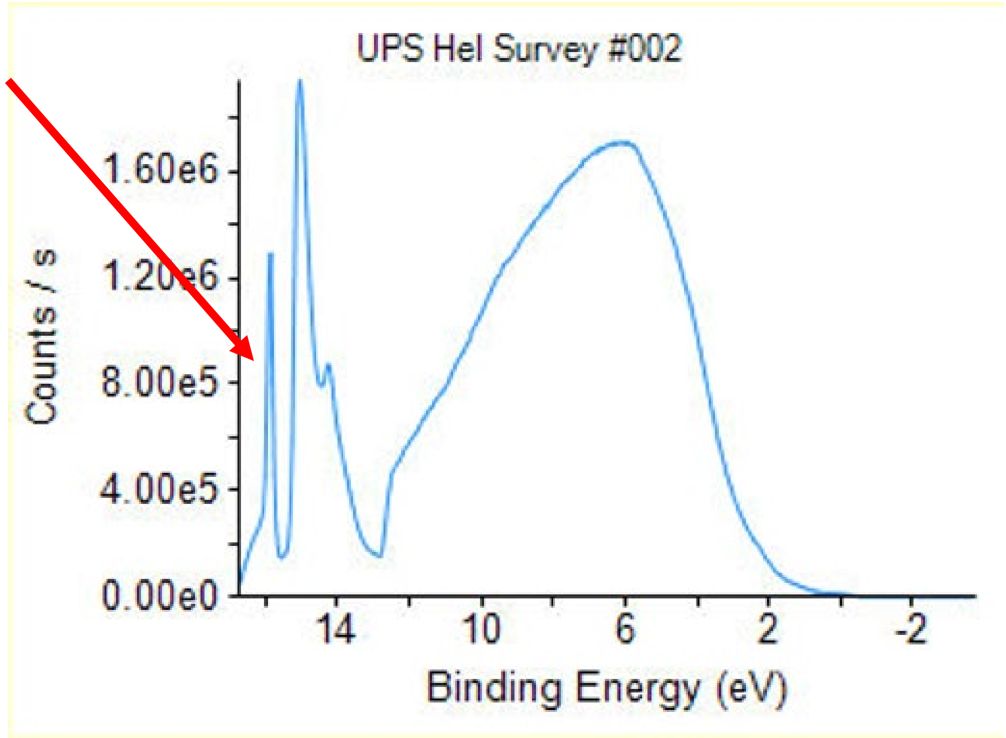


Applying a negative bias to the sample shifts the whole band structure and all the ejected electrons reach the analyzer.

Effect of Charge Compensation



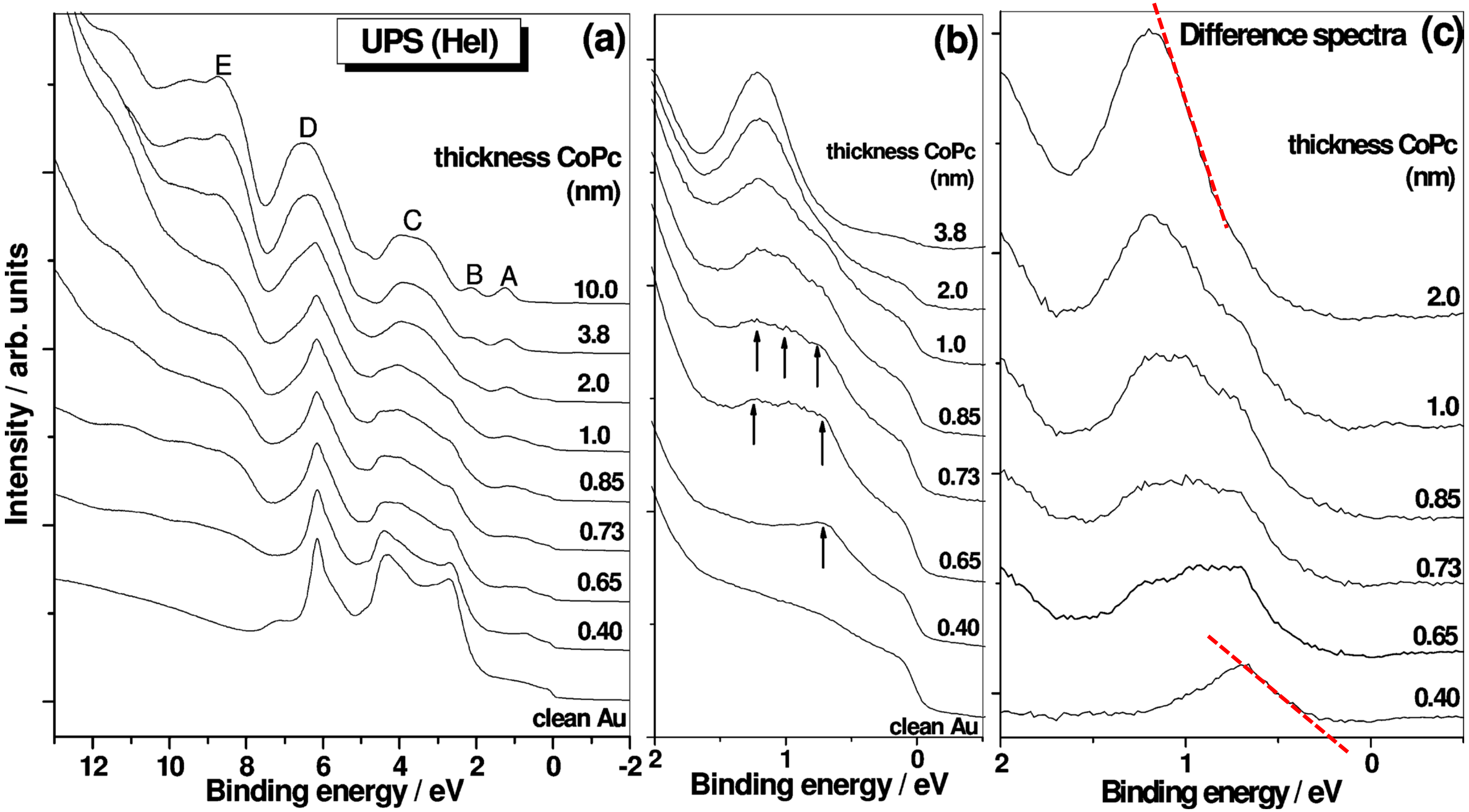
Flood gun is turned off

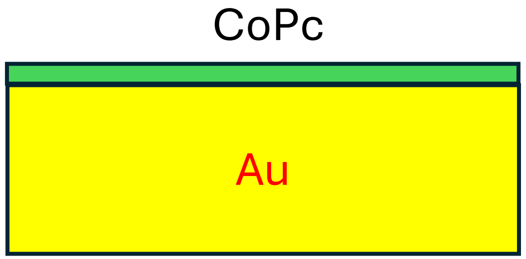


turned on

- Extra peak is from the electron flooding gun. It affects the cutoff accuracy.
- But for insulators like glass and polymer, surface charging heavily shift and distort the spectrum, charge compensation is a compromise method and extra caution about SECO is needed.

Example-1 CoPc/Au





CoPc

Au

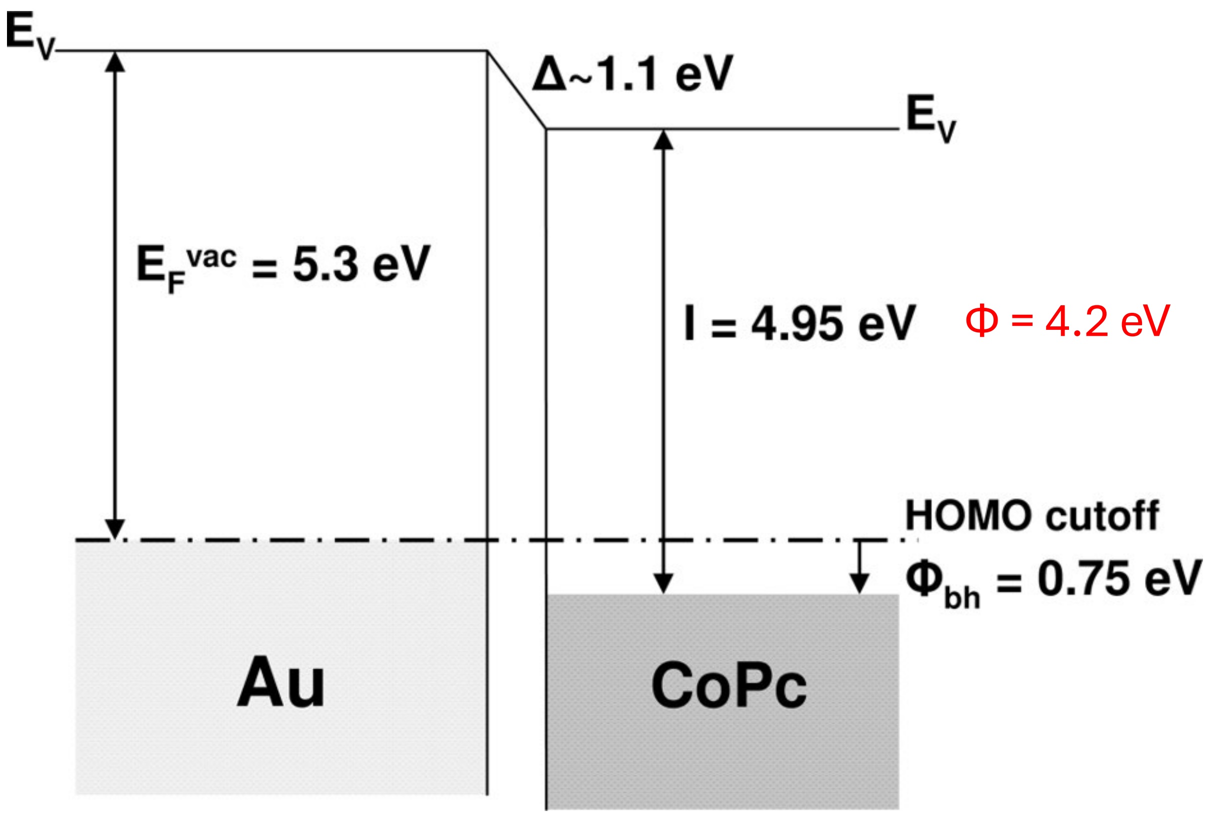
Evolution along the thickness of CoPc film

Zoom-in shows interaction features between the film and substrate

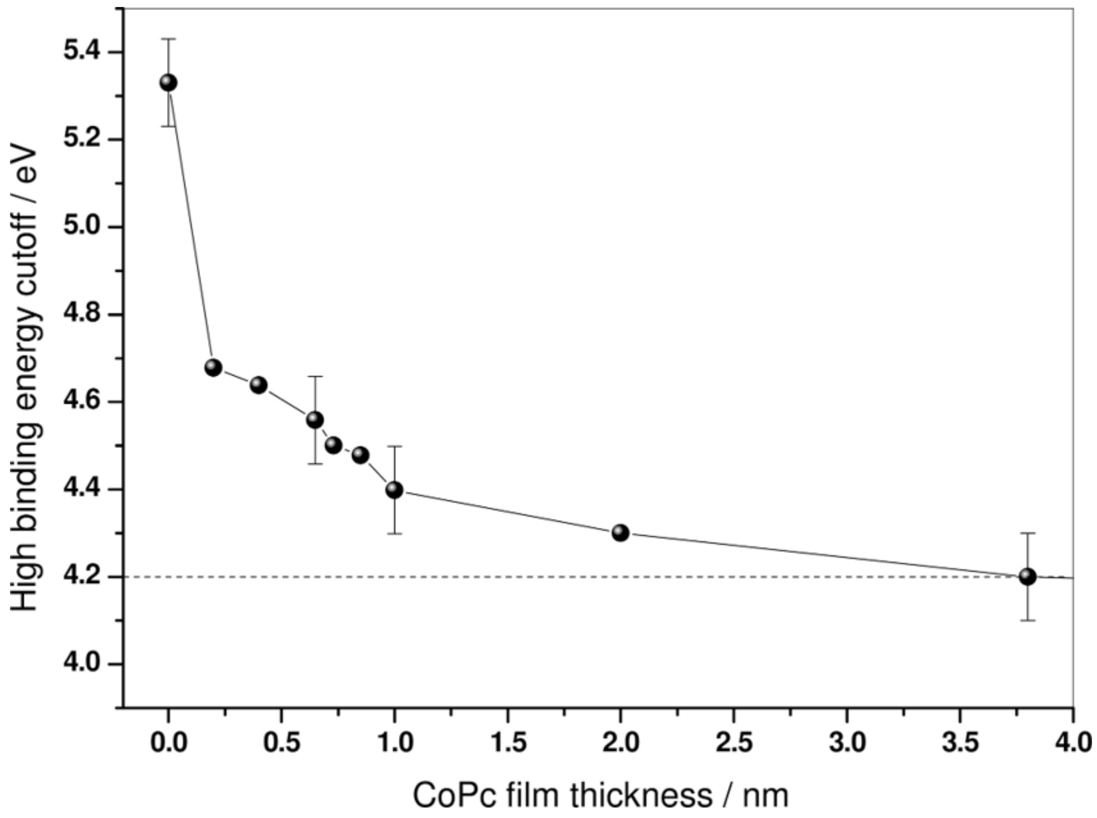
Onset (HOMO)

J. Phys. Chem. C 2010, 114, 41, 17638-17643

Example-1 CoPc/Au



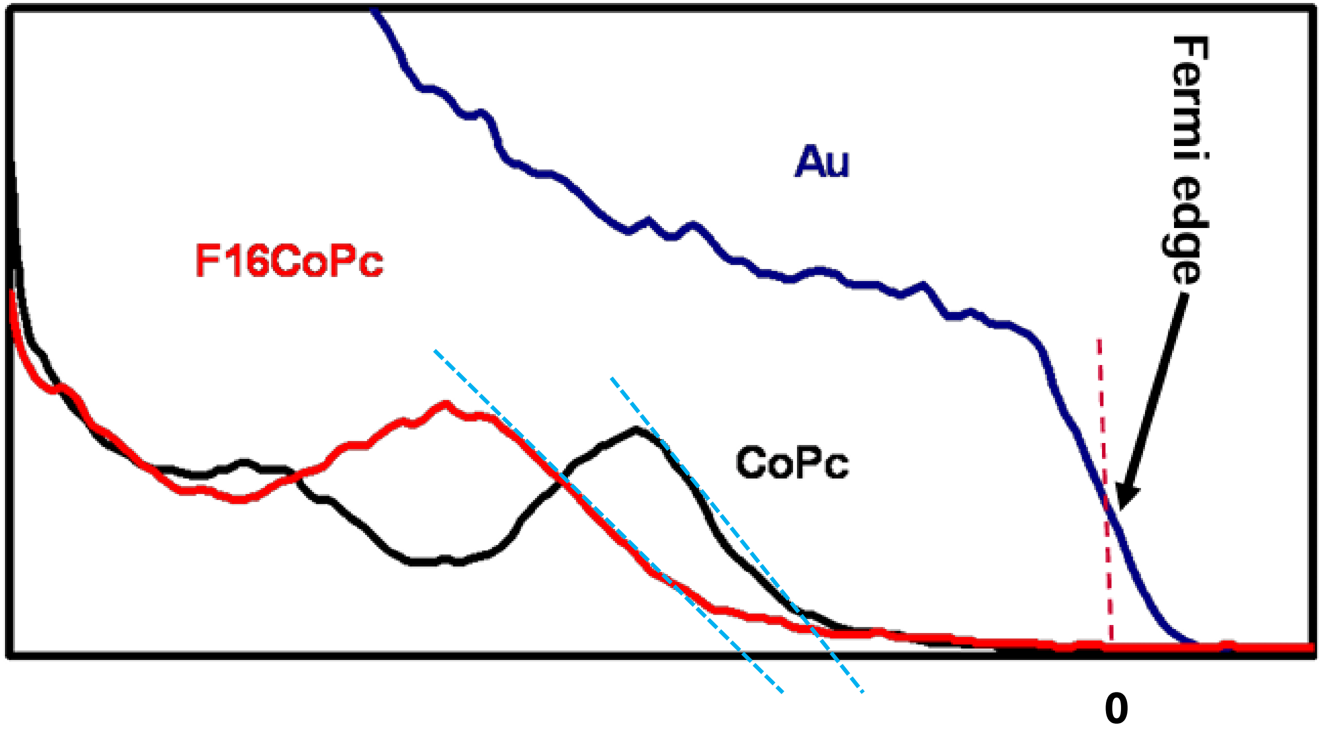
Schematic energy level diagram for the CoPc/Au interface deduced from photoemission measurements.



Variation of the high binding energy cutoff region for the CoPc/poly-Au interface as the organic layer grows thicker.

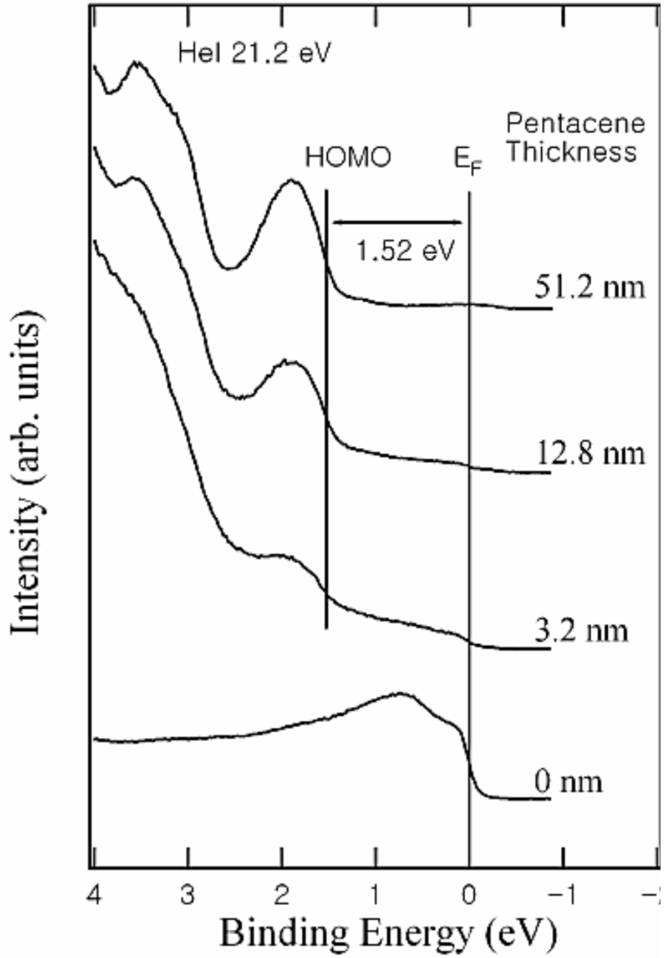
J. Phys. Chem. C 2010, 114, 41, 17638-17643

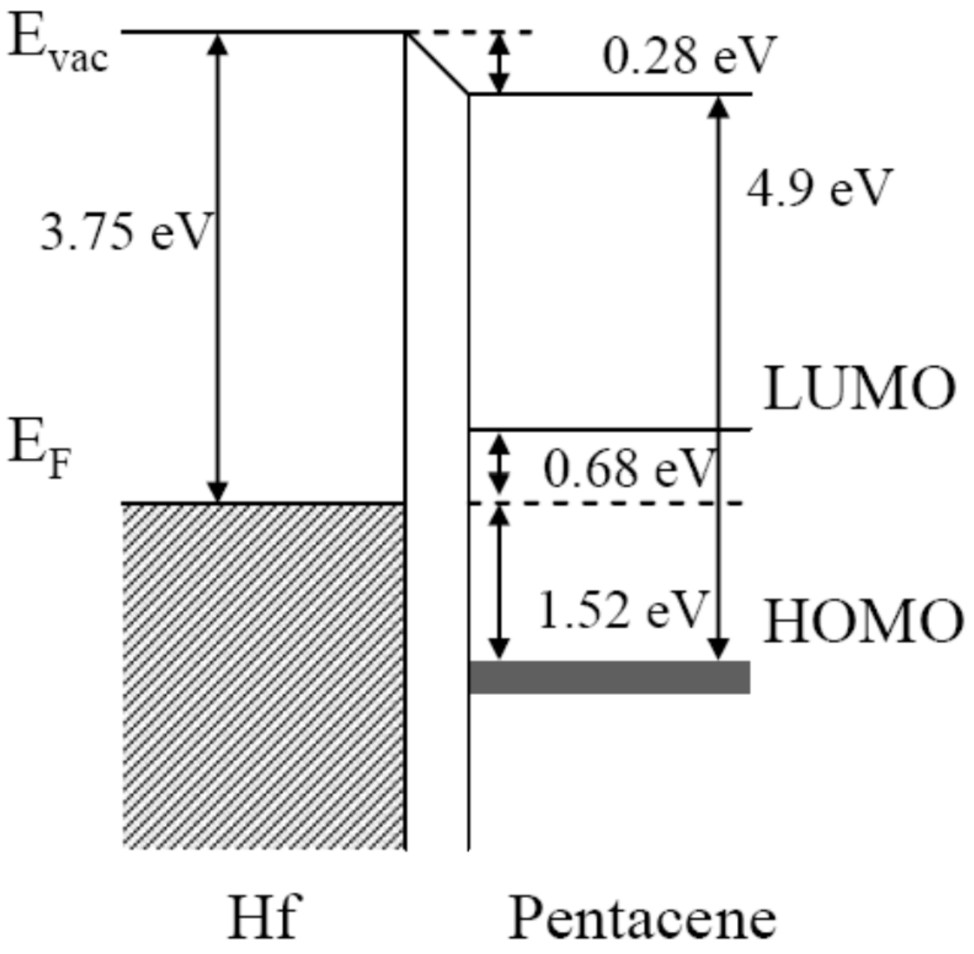
Example-2 CoPc and F16CoPc on Au



- UPS data shows the first ionization energies (HOMO) for CoPc and F16CoPc adsorbed on Au surface.
- A difference of 0.5 eV was measured between CoPc and F16CoPc compounds.
- This is due to the high electro-negativity of fluorine, therefore the electrons are tightly bound → need more energy to escape from the surface.

Exampl-3 Electronic Structure of Pentacene on Hafnium

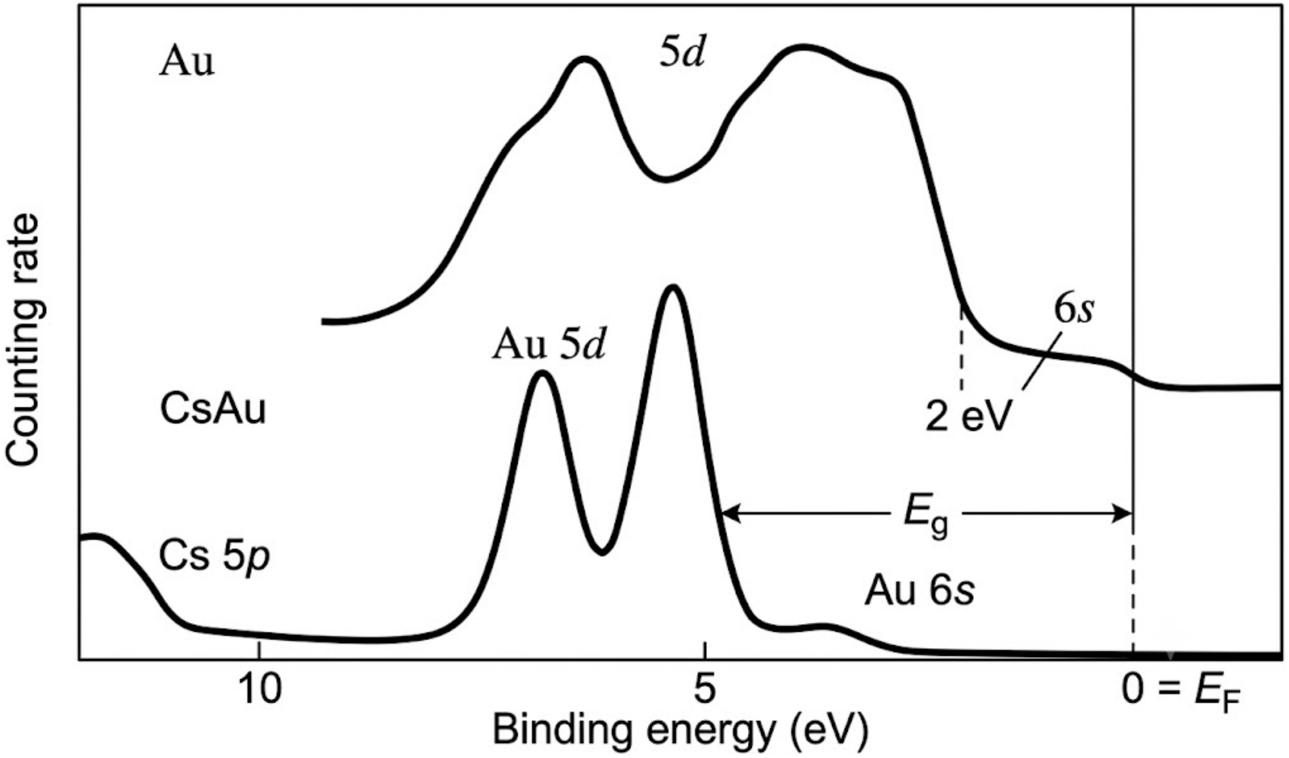




- **Binding Energy Spectra vs. Film Thickness:** The left plot displays UPS data showing the evolution of the HOMO feature as Pentacene thickness increases from 0 nm up to 51.2 nm.
- **Hafnium Work Function:** Measured at 3.75 eV
- **Interface Dipole:** A potential shift of 0.28 eV occurs at the Hf/Pentacene interface.
- HOMO is located 1.52 eV below the Fermi level, while LUMO lies 0.68 eV above Fermi level, indicating a 5.58 eV work function.

J. Korean Phys. Soc. **46**(4), 760 (2005)

Exampl-4 Electronic Structure of Au in Metal and CsAu



- **Metal Au**: The 5d electrons form a broad band between 2-8 eV and the 6s electron is seen between 2eV and the Fermi level. But the 6s band extends to much greater BE, it is strongly hybridized with the 5d band.

- **CsAu**: a red transparent semiconductor with a 2.6 eV band gap (with a large electronegativity), the Au becomes a negative ion with a filled $6s^2$ shell. This results in a $5d^{10}$ shell that is a core like spin-orbit doublet with 1.5 eV splitting, the 6s electrons constitute the VB and lies about 3eV below Fermi level.

A few practicable tips:

- Flush helium gas line
- Ion sputter clean sample surface
- Optimize sample height with X-ray gun
- Apply negative bias
- Check Fermi level with clean Au sample

Summary

What UPS Measures

- Uses ultraviolet photons (He I: 21.22 eV, He II: 40.81 eV) to probe occupied electronic states.
- Highly surface-sensitive technique (~2 nm information depth).
- Provides:
  - Valence band structure
  - HOMO / valence band maximum
  - Secondary electron cutoff (SECO)
  - Work function (Φ)

Key Concepts

- Useful signal originates from electrons that escape without inelastic scattering.
- Hemispherical analyzer measures electron kinetic energy with high resolution.
- Negative sample bias improves SECO measurement accuracy.
- Surface cleanliness and charging control are critical.

Summary - continued

UPS Data Interpretation

- HOMO/VBM → highest occupied electronic states.
- SECO → low kinetic energy cutoff.
- Work function calculated from: $\Phi = h\nu - (E_{cutoff} - E_F)$
- Changes in HOMO position and work function reveal interfacial electronic interactions.

Applications

- Organic semiconductors and OLED materials.
- Metal/organic interfaces.
- Surface modification and treatment studies.
- Electronic structure characterization of functional materials.

Best Practices

- Verify electrical contact with XPS first
- Optimize sample height
- Remove surface contamination when appropriate
- Apply negative bias during UPS measurements
- Check Fermi level calibration using clean Au reference

UPS is a powerful technique for directly probing the occupied electronic structure and surface energetics of materials.

Thank you for your attention!

Questions?