



## X-Ray Photoelectron Spectroscopy (XPS)

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**Electron Spectroscopy for Chemical Analysis (ESCA)** 



• The <u>basic principle</u> of the photoelectric effect was enunciated by Einstein [1] in 1905

#### $\mathbf{E} = \mathbf{h}\mathbf{v}$

There is a threshold in frequency below which light, regardless of intensity, fails to eject electrons from a metallic surface.  $h\nu_c > e\Phi_m$ Where h - Planck constant (6.62 x 10-34 J s),  $\nu$ - frequency (Hz) of the radiation and  $\Phi_m$  work function

• In photoelectron spectroscopy such XPS, Auger and UPS, the photon energies range from 20 -1500 eV (even higher in the case of Auger, up to 10,000eV) much greater than any typical work function values (2-5 eV).

• In these techniques, the kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted electrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyzer and a photoelectron spectrum can thus be recorded.

[1] Eintein A. Ann. Physik 1905, 17, 132.



- By using photo-ionization and energy-dispersive analysis of the emitted photoelectrons the composition and electronic state of the surface region of a sample can be studied.
- Traditionally, these techniques have been subdivided according to the source of exciting radiation into :
- <u>X-ray Photoelectron Spectroscopy</u> (XPS or ESCA) using soft x-ray (200 1500 eV) radiation to examine core-levels.
- <u>Ultraviolet Photoelectron Spectroscopy</u> (UPS) using vacuum UV (10 45 eV) radiation to examine valence levels.
- <u>Auger Electron Spectroscopy</u> (AES or SAM) using energetic electron (1000 10,000 eV) to examine core-levels.
- Synchrotron radiation sources have enabled high resolution studies to be carried out with radiation spanning a much wider and more complete energy range (5 5000+ eV) but such work will remain, a very small minority of all photoelectron studies due to the expense, complexity and limited availability of such sources (Berkeley, Stanford, New York (2), Baton Rouge, Argonne in the US).



#### One way to look at the overall photoelectron process is as follows :

 $\mathbf{A} + h\mathbf{v} = \mathbf{A}^+ + \mathbf{e}^-$ 

1. Conservation of energy then requires that :

 $E(A) + hv = E(A^+) + E(e^-)$  (energy is conserved)

2. Since the energy of the electron is present solely as kinetic energy (KE) this can be rearranged to give the following expression for the KE of the photoelectron :

$$E(e^{-}) = KE(e^{-}) = hv - [E(A^{+}) - E(A)]$$

3. The final term in brackets represents the difference in energy between the ionized and neutral atoms, and is generally called the *binding energy* (BE) of the electron - this then leads to the following commonly quoted equation :

$$\mathbf{KE} = hv - \mathbf{BE}$$







## Energy Diagram



•  $E_b$  (binding energy) is below the conduction band edge.

• Fermi energies of metal and spectrometer coincide (electrons transfer between metal and spectrometer until the  $E_F$  align).

- Contact potential;  $e(\phi \phi_{sp})$ .
- E'<sub>k</sub> :measured kinetic energy.
- $E_b = hv E'_k e\phi_{sp}$  (no need to know the work function of the sample



## X-ray Sources

• Their choice is determined by the energy resolution. Typical materials are Mg and Al.

• A heated filament (cathode) emits electrons which are accelerated toward a solid anode (water cooled) over a potential of the order of 5 -20 kV.

• Holes are formed in the inner levels of the anode atoms by the electron bombardment and are then radioactively filled by transitions from higherlying levels:

 $\frac{\text{Resulting in the emission of X-rays}}{\text{Mg K}\alpha_{1,\,2}} \text{ at } 1253.6 \text{ eV}$  $\text{Al K}\alpha_{1,\,2} \text{ at } 1486.6 \text{ eV}$ 



#### **Typical emission of X-rays**

#### **Typical geometry of an X-ray gun**





Aluminum windows of 10-30  $\mu$ m thick separate the excitation region from the specimen.

Additional x-ray lines (K $\alpha_3$  and K $\alpha_4$ ) and a continuous spectrum (Bremsstrahlung) are produced. Peaks 10 eV above the K $\alpha_{1,2}$ with intensities of 8 % and 4 % of K $\alpha_{1,2}$ and a continuous spectrum contribute to the BG.



## X-ray Sources Available

	X-rays	Energy (eV)	Natural Width (eV)
16 - 14 - 14	Cu Ka	8048	2.5
$ \begin{array}{c c} \hline 12 \\ \hline \\ $	Τί Κα	4511	1.4
A S0 kV   Continuum	Al Ka	1487	0.9
2 0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4	Mg Ka	1254	0.8
λ <sub>min</sub> Wavelength (Å) Continuous and characteristic radiation for copper.	Να Κα	1041	0.7

Kratos and PHI commonly use AlK $\alpha$  and MgK $\alpha$ 



• To remove the unwanted radiation and increase the energy resolution the AlK $\alpha$  is often monochromatized (cut a "slice" from the x-ray energy spectrum, removing both satellites and Bremstrahlung (which increases the BG level).

• <u>*Crystal used*</u> = quartz because can be obtained in near perfect form and can be elastically bent (bending does not affect resolution or reflectivity).



For first order (n =1) diffraction and Al K $\alpha$  X-rays,  $\lambda$  = 8.3 Å for a distance d between planes of about 4 Å and a Bragg angle,  $\theta$  of 78.5°



## **Rowland circle**



The crystal must lie along the circumference of the Rowland circle (focusing circle), Johann focusing geometry.



Analyzers

#### **Dispersive analysis of the kinetic energy spectrum** *n(KE)*

A field is applied between 2 parallel plates, distance s apart. The lower plate has slits a distance r apart (entrance and exit slits). The photoelectrons with kinetic energy KE are transmitted to the detector. By varying  $V_d$  the spectrum of electron kinetic energies can thus be obtained. KE is proportional to V<sub>d</sub> therefore the plot of electron Ionization flux at the detector against V is the chamber photoemission spectrum.

#### The parallel plate electrostatic analyzer









www.Kratos.com

The alternative to dispersive analysis is to discriminate the electron KE by a retarding electric field applied between the target region and the detector. Electrons with  $KE > eV_r$  will reach the detector (a kind of filtration process).



## Spectrometer

Photo ionization process has a rather low absolute probability (10<sup>4</sup> electrons per second, or 10<sup>-15</sup> A) therefore electron multiplier (gain of 10<sup>6</sup>) are used to obtain an accurately measurable current. Newer instruments use channel plates.



#### **Components:**

- 1. Source of radiation
- 2. Ionization Chamber
- 3. Electron energy analyzer
- 4. Electron detector
- 5. High vacuum system software and computer





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The core electron binding energies (BE) of the elements are distinctive



## **Typical High Resolution Spectra**

# *<u>High-resolution</u>* acquisition scans yield information such as

- •Chemical shifts
- •Multiplet structure
- •Satellites
- •Chemical bonding





## Surface Sensitive Technique

- XPS is very surface sensitive because only electrons from the top few atomic layers (mean free path ~1.5 nm) can escape without loss of energy.
- The absorption length of the X-rays is about 100 nm to 1000 nm.



**Universal Curve** 



## AXIS-165 multi-electron spectrometer

### From Kratos analytical Inc.





## Summary

A sample placed in ultra-high vacuum is irradiated with photons of energy (hv); soft x-rays. Atoms on the surface emit electrons (photoelectrons) after direct transfer of energy from the photons to the core-level electron.

This process can be summarized as follows:

- 1. A bound electron adsorbs the photon, converting some of its energy into kinetic energy.
- 2. As the electron leaves the atom some of its energy is used to overcome the Coulomb attraction of the nucleus, reducing its KE by its initial state BE.
- 3. At the same time the outer orbitals readjust, lowering the energy of the final state that is being created and giving this additional energy to the outgoing electron.



## Photoelectric effect





The optical excitation probability is given by the photoionization cross-section  $\sigma(E)$ 

In quantum mechanics  $\sigma(E)$  in a subshell *nl* (*principal and orbital quantum numbers*) is given by

$$\sigma_{n,l}(E) = \frac{4}{3}\pi^2 a_0^2 \alpha [N_{n,l}[E - E_{n,l}] \frac{1}{2l+1}] [lR^2_{E,l-1} + (l+1)R^2_{E,l+1}]$$

 $\alpha$ : fine structure constant 1/137,  $a_0$  Bohr radius (0.05 nm),  $N_{n,l}$ : number of *e* in the subshell,  $E_{n,l}$  the energy of the *nl* electrons, *E*: KE of the ejected electrons.

For n =1 and 1=0 
$$\sigma_{1,0}(E) = \frac{4}{3}\pi^2 a_0^2 \alpha N_{1,0}[E - E_{1,0}]R_{E,0+1}^2$$

The radial dipole matrix elements are

$$R_{E,l\pm 1} = \int_{0}^{\infty} P_{n,l}(r) r P_{E,l\pm 1}(r) dr$$

 $P_{nl}(r)1/r$  and  $P_{E,l \pm l}(r)1/r$  are the radial parts of the single-particle wave functions of the initial (discrete) and final (continuum) states, respectively. For H,  $P_{10}(r)=(1/a_0)^{3/2}2exp(-r/a_0)$ .



<u>Cooper Minimum</u>:  $R_{E,l-1} \ll R_{E,l+1}$ , thus  $R_{E,l+1}$  will give the basic features and the energy dependence of the cross-sections. For a radial wavefunction with nodes,  $R_{E,l+1}$  will go through 0 at a particular energy, giving rise to a minimum in the cross-section  $\sigma$ .

Near photoionization threshold: R  $_{E, 1+1}$  goes through 0 because

1. Final state (emitted) electron wavefunction is largely excluded from the core region

2. Initial state electron wavefunction has most strength, after it goes through a node. As the photon energy increases the final state electron wavefunction begins to "penetrate" the core and the overlap goes to 0 due to the node in the initial state wavefunction.

Reference: Cooper Minima in the Photoemission Spectra of Solids, S.L. Molodtsov et al.





Photoemission intensity

$$I(\theta) \propto \frac{\sigma_{total}}{4} [1 - \frac{\beta}{4\pi} (3\cos\theta - 1)]$$

( $\beta$ : asymmetry parameter,  $\theta$ : take off angle and  $\sigma_{total}$  the total cross-section)

#### **Cooper Minima in the Photoemission Spectra of Solids**

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The energy dependence of photoionization cross sections is a tool frequently used to identify contributions from different atomic states to valence-band photoemission (PE) spectra. Particularly useful is the appearance of phenomena such as Fano resonances [1] or Cooper minima (CM) [2] providing a strong enhancement or decrease of the PE signal from certain states. While the Fano resonance is a many-body effect caused by coupling of the direct PE channel with photoexcitations into localized intermediate states and subsequent autoionization, the CM represents a simple matrix element effect: Due to a node of the initialstate wave functions the transition matrix element into final states with oscillating free-electron-like wave functions becomes canceled. The behavior of the cross section around the CM depends strongly on the shape of the initial-state waves. Atomic calculations by Yeh and Lindau [3] (denoted YL in the following) provide the photoionization cross sections for all elements of the periodic table in a wide range of photon energies. Thereby, not more than one CM is found for any atomic shell considered.



FIG. 2 (color).  $|M_{dd \to (\varepsilon f + \varepsilon p)}^r|^2$  of Pd calculated with our atomic approach for different  $h\nu$  and distances  $r_0$ . The CM are represented by green color (see intensity scale). The white broken line and vertical arrow mark a cut at  $r_0 = 1.52$  Å corresponding to the curve presented at the top of Fig. 1. Results of our atomic approach for  $r_0 > 5$  Å are almost equivalent to those of the atomic YL calculations. The inset shows the radial parts of wave functions for the final  $(\varepsilon f, multiplied with r)$  and (red curve) and the integral (blue curve) of Eq. (2).



## References

- Surface Analysis, The Principal Techniques Edited by John C. Vickerman, John Wiley & Sons (1997).
- •Handbook X-ray and ultraviolet photoelectron spectroscopy, Briggs, Heyden &Son Ltd (1977).
- •Solid State Chemistry: Techniques, A. K. Cheetham and Peter Day, Oxford Science Publication (1987).
- Practical Surface Analysis by D. Briggs and M. P. Seah.

#### Websites:

http://srdata.nist.gov/xps, http://www.xpsdata.com, http://www.lasurface.com, http://www.eaglabs.com