X-ray Photoelectron Spectroscopy for Chemical Analysis

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Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II

Photon Energy: 250 eV to 2000 eV
Pressures up to 5 Torr.
Temperatures up to 900 °C
Capillary tube into Mass Spec.
Who is this guy?
Anibal Boscoboinik - CFN, Brookhaven Lab
Our Playground

Columbia University, Oct 14th 2015. Anibal Boscoboinik - CFN, Brookhaven Lab
What will you learn today?

• X-ray Photoelectron Spectroscopy (XPS)
• Ambient Pressure XPS.

• What you can do with it.
• Some examples.
X-ray Photoelectron Spectroscopy

- Background
Photoelectric Effect

The **photoelectric effect** is the observation that many metals emit **electrons** when **light** shines upon them. (Hertz 1887)

- The energy of the light must exceed certain value for emission of electrons to occur.
- The intensity of the light doesn’t affect the energy of the electrons, but it affects the number of emitted electrons.

In **1905 Albert Einstein** published a paper that explained experimental data from the photoelectric effect as being the result of light energy being carried in discrete quantized packets (**Photon**). → Nobel Prize 1921.

\[ E = h\nu \]
A photon \((E=\hbar\nu)\) is absorbed by an electron.

The electron is emitted from the atom with certain KE.

\[ h\nu = BE + KE \]
Periodicity Table, binding Energies
Binding Energy vs Atomic # vs Electron Configuration

- Atomic Number (Z)
- Binding Energy (eV)
- Electron Configuration (spin-orbit)

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X-ray Photoelectron Spectroscopy

- Background
- Principles
• Karl Manne Georg Siegbahn. **Nobel Prize in Physics** in 1924 "for his discoveries and research in the field of **X-ray spectroscopy**.”

• Kai Manne Börje Siegbahn. **Nobel Prize in Physics** in 1981 “for developing the method of **Electron Spectroscopy for Chemical Analysis** (ESCA), now usually described as **X-ray photoelectron spectroscopy** (XPS)”
Photon (X-ray) Source

Electron Energy Detector

\[ h\nu = BE + KE \]
X-ray Photoelectron Spectroscopy (XPS)

\[ hv = BE + KE \]
\[ h\nu = BE + KE \]
Why is XPS surface sensitive?

X-ray Photoelectron Spectroscopy

- Electrons are extracted only from a narrow solid angle.

- X-ray penetration depth ~1μm. Electrons can be excited in this entire volume.

- X-ray excitation area ~1x1 cm². Electrons are emitted from this entire area.

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\[ h\nu = BE + KE \]
$1s$ binding energies for these elements: B, C, O, Be, F, Li, N

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These elements: B, C, O, Be, F, Li, N
Aluminum Plate

XPS Survey
EV/Step: 1 eV, Time/Step: 50 mSec, Sweeps: 10
Source: Mg Kα, Pass Energy: 100 eV

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William Durrer, Ph.D.
Department of Physics at the University of Texas at El Paso
n = 4 (4\textsuperscript{th} shell),
3 subshells, s, p, d, f

n = 3 (3\textsuperscript{rd} shell),
3 subshells, s, p and d

n = 2 (2\textsuperscript{nd} shell),
2 subshells, s and p

n = 1 (1\textsuperscript{st} shell),
1 subshell, s

Shells and Subshells
Metallic Aluminum

![Graph showing the binding energy spectrum for aluminum, with a peak at 72.65 eV.](image)

**Aluminum Atom**

- **Al**
- **2p**
- **72.65 eV**

**BINDING ENERGY, eV**

86 76 66
Metallic Aluminum

What happens if we oxidize it?

Aluminum Oxide \( \text{Al}_2\text{O}_3 \)

Al

\( \text{O} \)

\( 2\text{[Al]}^{3+} 3\text{[O]}^{2-} \)

2p

72.65 eV

BINDING ENERGY, eV
Oxidation State

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How can you determine the oxide thickness?
"Universal Curve" of inelastic electron mean free paths
Chemical Shift

![Graph showing chemical shift for Al-O and Al-F bonds with percentage values for different Al concentrations]

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### Periodic Table

<table>
<thead>
<tr>
<th>Atomic #</th>
<th>Symbol</th>
<th>Name</th>
<th>Atomic #:</th>
<th>Period</th>
<th>Group</th>
<th>Electronegativity</th>
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<tr>
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<td>Hydrogen</td>
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<td>1</td>
<td>1</td>
<td>2.1</td>
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<tr>
<td>2</td>
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<td>Helium</td>
<td>2</td>
<td>1</td>
<td>18</td>
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<tr>
<td>3</td>
<td>Li</td>
<td>Lithium</td>
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<td>2</td>
<td>1</td>
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<td>Beryllium</td>
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<td>Boron</td>
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<tr>
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<td>C</td>
<td>Carbon</td>
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<td>2</td>
<td>16</td>
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<td>7</td>
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<td>2</td>
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<td>8</td>
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<td>2</td>
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<td>2</td>
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<td>3.9</td>
</tr>
<tr>
<td>10</td>
<td>Ne</td>
<td>Neon</td>
<td>10</td>
<td>2</td>
<td>18</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### Manganese (Mn)
- **Atomic #**: 25
- **Symbol**: Mn
- **Name**: Manganese
- **Atomic #: 55**
- **Period**: 4
- **Group**: 7
- **Electronegativity**: 1.55
- **Electron Affinity**: 8 kJ/mol
- **Heat**: 473 J/kgK
- **Density**: 7470 kg/m³
- **Conductivity**: 7.8 W/mK
- **Modulus**: 120 GPa
- **Melting Point**: 1519 K
- **Boiling Point**: 2334 K
- **Radius**: 161 pm

### CH₃·CH₂·O·CO·Cl

#### Counting Rate

- C 1s
- Cl 2s

#### Binding Energy vs. eV

- 290 eV
- 280 eV
- 270 eV

### CO₂

#### Counting Rate

- 10 eV
- 6 eV
- 4 eV
- 2 eV
- 0 eV = 291.2
XPS tells you

- What elements you have
- How much you have of each of them
- Their oxidation state
- Their coordination to other elements
- How deep they are from the surface
Some fact about XPS

• Surface sensitive
• Traditionally carried out in UHV
• Many relevant systems require higher pressures.
  – Catalysis
  – Environmental and Atmospheric Chemistry
Ambient Pressure XPS
Elevated Pressures

• Developing tools at BNL

1. Ambient Pressure Photoelectron Spectroscopy (AP-PES)
   • AP-XPS & AP-NEXAFS
2. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS)
3. Reactor-Scanning Tunneling Microscopy (r-STM)
Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II

Pressures up to 5 Torr.
Capillary tube into Mass Spec.
AP-XPS

- Differential Pumping
- Refocussing Lenses

Importance of a tightly focused beam

The smaller $z$, the higher $P_0$
What can we use this for?
Catalyst Model System

Simplified version of a commercial catalyst

- allows to disentangle different factors that can potentially affect the chemical reaction.
- used for surface science mechanistic studies

There is a vast set of surface science tools to study model systems:

- Scanning Tunneling Microscopy
- X-ray Photoelectron Spectroscopy
- Etc.
Example using AP-XPS

CO adsorption and dissociation on Ru(0001) at elevated pressures.

David E. Starr, Hendrik Bluhm

Surface Science
Volume 608, 2013, Pages 241–248
Adsorption site on triangular surface

A-top

Bridge

Three-fold
23 L of CO at 300 K

C:Ru 3d$_{5/2}$ ratio (0.088) from the spectrum correlated to known coverage of 0.66 ML

300 K

CO pressure

- 0.5 Torr
- 0.02 Torr
- $10^{-4}$ Torr
- $10^{-6}$ Torr
- UHV

Binding Energy (eV)

- Ru3d$_{3/2}$
- CO

- Ru3d$_{5/2}$ Bulk
- Gas Phase CO
- Ru 3d$_{5/2}$ Inelastically Scattered
- Ru3d$_{5/2}$ SCLS
Unrelaxed

\[ P_{\text{CO}} > 0.01 \text{ Torr} \]

0.66 ML

Relaxed

\[ P_{\text{CO}} > 0.01 \text{ Torr} \]

Further Relaxation

0.83 ML

Ru atom

Adsorbed CO with \( \theta = 0.66 \text{ ML} \)

Additional CO

For \( P \sim 0.01 \text{ Torr} \)
Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II

- Photon Energy: 250 eV to 2000 eV
- Pressures up to 5 Torr.
- Temperatures up to 900 °C
- Capillary tube into Mass Spec.

- We can dose elevated pressures of gases or liquid vapors.
- (only non-corrosive)
Exposure to elevated pressures of $O_2$

$pO_2 = 1 \times 10^{-4}$ Torr

Aluminosilicate Protective Layer

\[ p(\text{O}_2) = 1 \times 10^{-4} \text{ mbar.} \]

cps

300 K
923 K

Ru\(^0\)

Al\(_{0.2}\)Si\(_{0.8}\)O\(_2\)/Ru(0001)

300 K
873 K

Ru\(\text{O}_x\)

Ru(0001)

Ru 3d

T-O-T

O 1s

O-Ru

Ru-CO

Ru(0001)

Useful Resources

Dynamic Periodic Table

• [http://www.ptable.com/#Orbital](http://www.ptable.com/#Orbital)

Useful XPS pages


\[
\lambda = \frac{143}{E^2} + 0.054 \cdot \sqrt{E}
\]
"Universal Curve" of inelastic electron mean free paths