Photoelectron Spectroscopy (PES)

PES spectrum ICl in the gas phase

PES spectrum solid Au
Experiment

Photon energy, polarization, incidence angles

Electron kinetic energy, emission angles, spin polarization
Spectrometers

\[ E_b = h \nu - E_{\text{kin}} \]

measurement of the electron kinetic energy

electrons are dispersed in electric or magnetic fields

hemispherical analyzer
Spectrometer System

Beamline 8.0.1 (ALS) and the Uppsala Surface-Science Endstation

U5 Undulator
Optical Elements
Hemispherical Electron Analyzer

Rotatable Analysis Chamber

Electron Analyser
NEXAFS Detector (not visible)
X-ray Emission Spectrometer

Ion Pump
Background

Electron scattering by transport through solid
Energy losses gives a secondary background

Escape depth of elastic electrons of the order of
5-20 Å

Surface Sensitivity
Energy Scales

Binding energies

- Solids relative to Fermi level
  - Directly from spectrum
- Gases relative to Vacuum level
  - Determined using calibration gases with binding energies obtained from optical measurements
Binding Energies

Ground state picture

Koopmans theorem

\[ E_b = -\varepsilon_b \]

Assuming the remaining electrons inert

Relaxation

Valence electrons change due to electron removal

\[ E_b = -\varepsilon_b + E_{\text{relax}} + E_{\text{corr}} \]

Difference in total energy

\[ E_b = E_{\text{TOT \ Ground}} - E_{\text{TOT \ Final}} \]

total energy of the whole system including all interacting atoms
Chemical Shifts

Chemical shifts of core levels of the same element due to different chemical surroundings
Spin Orbit Splitting

\[ 3p^6 + h\nu \rightarrow 3p^5 \approx (3p)^{-1} \]

Spin and angular momentum interaction \( J = l \pm s \)

For \( l = 1 \) and \( s = +1/2 \) \( J = 3/2 \)

\( s = -1/2 \) \( J = 1/2 \)

Two lines seen in spectrum \( 3p_{3/2} \) and \( 3p_{1/2} \)

Intensities ratio of the two lines given by the population of the orbitals

\( (2J_{3/2} + 1)/(2J_{1/2} + 1) = 4/2 = 2 \)

\( p \) shell \( \rightarrow p_{3/2} \) and \( p_{1/2} \) ratio \( \rightarrow 2:1 \)

\( d \) shell \( \rightarrow d_{5/2} \) and \( d_{3/2} \) ratio \( \rightarrow 3:2 \)

\( f \) shell \( \rightarrow f_{7/2} \) and \( f_{5/2} \) ratio \( \rightarrow 4:3 \)
Open shell interactions

Coupling between open shells

$O_2$ and NO paramagnetic molecules

$\pi$

$\Sigma$

$\Sigma$

$\Sigma$

Open valence 4f shell for trivalent Yb $4f^{13}$

Final state $4f^{12}$

Multiplet splittings
Lifetime broadening

The full width ($\Gamma$) of a spectral line is given by the lifetime ($\tau$) of the final state

$$\Gamma = \frac{\hbar}{\tau}$$

Valence hole states for free atoms no broadening

Lifetime of core hole states is determined by sum of the rate for all decay channels

Auger and fluorescence (X-ray emission)

$$\Gamma = \Gamma_{\text{aug}} + \Gamma_{\text{fluo}}$$
Sudden Approximation

Ionization much faster than motion of electrons

Many different final states

<table>
<thead>
<tr>
<th>INITIAL STATE</th>
<th>(N electrons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>( \Psi_{(N-1)}, \Psi(1) )</td>
</tr>
<tr>
<td>H(N)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FINAL STATES</th>
<th>(N-1 electrons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b) Frozen Orbitals</td>
<td>( \Psi_{(N-1)} )</td>
</tr>
<tr>
<td></td>
<td>( E_k )</td>
</tr>
<tr>
<td></td>
<td>Relaxation Energy</td>
</tr>
</tbody>
</table>

| c) Relaxed Orbitals | \( \Psi_{(N-1)} \) |
|                    | \( \Psi = \sum \xi_i \Psi_i \) |
|                    | \( \xi_i = \langle \Psi | \Psi_i \rangle \) |
|                    | \( E_k = \sum |\xi_i|^2 E_i \) |

He atom

Monopole selection rule

He 1s spectrum

\( r^2\Psi^2(r) \)
Ne 1s Shake up and off spectra
2p—np and 2s—ns excitations
Vibrational Excitations

Born Oppenheimer approximation

$$\psi_{\text{TOT}} = \psi_{\text{electron}} \psi_{\text{nuclear}}$$

Electrons and nuclei move independent of each other

We separate $$\psi_{\text{nuclear}}$$

Adiabatic transition

Excitation takes infinite time, only to lowest vibrational state

Vertical transition

Excitation is sudden, no time, nuclear coordinates are frozen

Diatomic molecule

Different potential energy curves in ground and excited states

Frank Condon Principle (sudden approximation)

$$I = \left| \int \psi_v \psi_{v'}^* d\tau \right|^2$$
Vibrations Valence Levels

Amount of vibrational excitations depends on difference between ground and ionized state potential curves

$N_2$ in the gas phase
Rotational Excitations

Vibrations in $\text{H}_2$

Rotations
Resolution 3meV
Vibrations Core Levels

Core levels are non bonding orbitals
No vibrational excitations expected?
Relaxation in the ionized state
Different potential energy curves

Adsorbed CO on Ni

Chemical shifted components

Methane

CH₄

C1s

292.0 291.5 291.0 290.5

0 500 1000 1500 2000 2500

Counts

Binding Energy (eV)

Intensity (arb. units)

533 532 286.5 285.5

C1s

O1s

hv = 330 eV

vO = 1 for CH stretch

= 700 eV

= 320 eV

C1s photoelectron spectrum of Propyne, CH₃C≡CH
Gas to Solid

Hg gas to solid

Valence levels

Core levels

From orbitals to bands

Hydrocarbons
Angular Distributions

Photoelectrons are ejected along the E-vector

Dipole selections rules

\[ \text{Outgoing waves: } s \rightarrow \varepsilon p, \quad p \rightarrow \varepsilon d, \quad d \rightarrow \varepsilon f, \quad f \rightarrow \varepsilon g \]
Band Structure

Angle resolved photoemission
Photoionization cross sections

Cross sections decreases with increasing photon energy

Resonance in Eu around 4d threshold
Resonant Photoemission

Valence band features resonant enhanced at core level threshold

\[ I = \left| M_{\text{PES}} + M_{\text{Aug}} \right|^2 \]

Constructive and destructive interference of direct photoemission and Auger decay

Fano profile

Auger emission isotropic

Photoemission along E-vector

6 eV  d-band

Ni - L₃

hv (eV)

853.26

× 0.15

852.3

851.8

851.75

850.8

850.7

844.2

Intensity (arb. units.)

Binding Energy (eV)

15  10  5  0

Ni - RPES

× 30

d - band

6 eV satellite

Photon Energy (eV)

800  820  840  860  880  900
Core Level Electron Spectroscopy
Surface Science

Electrons interact strongly with matter

Surface sensitivity

\[ I = I_0 \exp\left(-\frac{d}{\lambda \sin \theta}\right) \]

\[ E_{\text{kin}} = h\nu - E_{\text{bind}} \]

Variation in surface sensitivity with photon energy
Surface Science

Surface and Interfaces exist all around us
This is the way we perceive the world

Solid-Vacuum, Solid-Gas, Solid-Liquid, Liquid-Gas and Solid-Solid, Liquid-Liquid Interfaces
Surface Science
Many important applications

Heterogenous Catalysis
Molecular Environmental Science

Magnetic Storage
Semiconductor Industry
Single Crystal Surfaces

fcc crystal

fcc (100)  fcc (111)  fcc (110)
Core Level Binding Energy

Difference in total energy

\[ E_b = E_{\text{Ground TOT}} - E_{\text{Final TOT}} \]

total energy of the whole system including all interacting atoms

Relaxation
Change of valence electrons
Relaxation

Metallic screening

Electron transfer

When \( N \) (electrons) are \( \cong 10^{23} \)

XPS binding energy is onset for XAS

Image screening or polarization

No mixing of electrons between ionized atom and surroundings

No relationship between XPS and XAS

Chemisorbed C on Ni

Physisorbed \( O_2 \) on graphite
The valence electrons can not approximately distinguish
an extra charge in the core region or in the nucleus.

Core ionized final states

\[ C^*O = NO \]
\[ Ni^* = Cu \]
N$_2$ and CO on Ni(100)

Two different N atoms

1.5 eV binding energy shift

The same ground state for both atoms

\[ E_b = E_{\text{Ground}} - E_{\text{Final}} \]

\[ \Delta E = 1.5 \text{ eV} \]

Difference in Adsorption energies

Similar ground state energy
High resolution XPS of adsorbates

Vibrational effects C-O stretch


High Pressure XPS  A.Nilsson, J. El. Spec. in press
High Pressure XPS

New development of XPS at intermediate pressures
Catalysis, solid/liquid interfaces etc.
Thin films

Electrons interact strongly
Surface Sensitivity
5-20 Å

Dependent on electron kinetic energy

Surface Core Level Shift (SLCS)

$\Delta E = -0.3 \text{ eV}$

$\nu = 125 \text{ eV}$

Ground $\text{TOT}$

Final $\text{TOT}$

$\Delta E$ Surface segregation energy for $Z+1$ impurity in $Z$ metal

We have a lower binding energy for Au at the surface than in bulk for Pt (111)

The more open surfaces have a larger $\Delta E_S$
Adsorbate Induced Shift

N2 is physisorbed on Au
CO is chemisorbed

Pt is segregated to the surface in presence of CO
CO forms stronger bonds to Pt compared to Au
Semiconductor Core Level Shifts

Si 2p Photoelectron Spectrum

Si(100)

Surface reconstruction

Oxidation of Si  Si/SiO₂ interface

Si2p chemical shift due to local charge on Si atom
Electrostatic effects on Shifts

Correlation between local charge on ionized atom and binding energy shifts

Only special cases with ligands with large difference in electronegativity

Do not work for metallic systems

RELAXATION changes the picture

Difference in total energy is the correct approach

Koopmans theorem

Orbital eigenvalue

\[ \Delta E (1s) = \frac{q}{r} + \Sigma \frac{q_i}{r_i} + 1 \]
Photoelectron Diffraction

Forward scattering zero order diffraction
Molecular orientations

For a full structure determination
Energy dependent diffraction together with multiple scattering calculations

Scattering angles at different energies