5. Techniques for Surface Chemical Composition

To obtain a complete description of surface, need elemental or molecular composition in addition to structural information.

Many composition sensitive techniques based on *electron spectroscopy*

- use electrons as incident or detected particle
- exploit surface sensitivity of low energy electrons

5.1 Electron Spectroscopy and Surface Sensitivity

Distance electron can travel in solid depends on (i) material and (ii) electron KE

Measure attenuation of electrons by covering surface with known thickness of element

*Loss processes (inelastic scattering)* reduce KE and can prevent escape from surface:

*Phonon* excitation - collective excitation of atoms in unit cell (0.01-10 eV)

*Plasmon* excitation - collective excitation of electrons (5-20 eV)
Interband transitions, ionization

Measure attenuation lengths for various materials and KE's:

"Universal curve" of electron inelastic mean free path $\lambda$ (IMFP) versus KE (eV)

IMFP is average distance between inelastic collisions (Å)

Minimum $\lambda$ of ~ 5-10 Å for KE ~ 50-100 eV - maximum surface sensitivity
General Classification of Electron Spectroscopic Methods:

<table>
<thead>
<tr>
<th>Method</th>
<th>Particle In</th>
<th>Particle Out</th>
<th>Information</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoemission</td>
<td>Photon</td>
<td>Electron</td>
<td>Filled core states</td>
<td>XPS</td>
</tr>
<tr>
<td>Photoemission</td>
<td>Photon</td>
<td>Electron</td>
<td>Filled valence states</td>
<td>UPS</td>
</tr>
<tr>
<td>Inverse photoemission</td>
<td>Electron</td>
<td>Photon</td>
<td>Empty states</td>
<td>IPES</td>
</tr>
<tr>
<td>Electron energy loss</td>
<td>Electron</td>
<td>Electron</td>
<td>Electronic &amp; vibrational transitions</td>
<td>EELS, HREELS</td>
</tr>
<tr>
<td>Auger</td>
<td>Electron</td>
<td>Electron</td>
<td>Filled states</td>
<td>AES</td>
</tr>
<tr>
<td>Absorption / emission*</td>
<td>Photon</td>
<td>Photon</td>
<td>Electronic transitions, filled states</td>
<td>UV-Vis, XRF</td>
</tr>
</tbody>
</table>

* not normally surface sensitive
5.2 X-ray Photoelectron Spectroscopy (XPS)

also known as electron spectroscopy for chemical analysis (ESCA)

Semi-quantitative technique for determining composition based on the photoelectric effect

5.2.1 The Photoemission Process

\[ KE = h\nu - IP \quad \text{gas} \]
\[ KE = h\nu - BE - \phi \quad \text{solid} \]

Absorption very fast - \(~10^{-16}\) s

Clearly from picture above,

- no photoemission for \( h\nu < \phi \)
- no photoemission from levels with \( BE + \phi > h\nu \)
- \( KE \) of photoelectron increases as \( BE \) decreases
- intensity of photoemission \( \alpha \) intensity of photons
- need monochromatic (x-ray) incident beam
- a range of KE's can be produced if valence band is broad
- since each element has unique set of core levels, KE's can be used to fingerprint element

Binding energy (BE) represents strength of interaction between electron (n, l, m, s) and nuclear charge

- in gases, \( \text{BE} \equiv \text{IP} \ (n, l, m, s) \)
- BE follows energy of levels: \( \text{BE}(1s) > \text{BE}(2s) > \text{BE}(2p) > \text{BE}(3s) \ldots \)
- BE of orbital increases with Z: \( \text{BE}(\text{Na} \ 1s) < \text{BE}(\text{Mg} \ 1s) < \text{BE}(\text{Al} \ 1s) \ldots \)

- BE of orbital not affected by isotopes: \( \text{BE}(^7\text{Li} \ 1s) = \text{BE}(^6\text{Li} \ 1s) \)
What is fate of core hole?

- Auger electron emission - basis of Auger electron spectroscopy (AES)
- X-ray fluorescence
5.2.2 Koopman’s Theorem

The BE of an electron is simply difference between initial state (atom with n electrons) and final state (atom with n-1 electrons (ion) and free photoelectron)

\[
BE = E_\text{final}(n-1) - E_\text{initial}(n)
\]

If no relaxation followed photoemission, BE = - orbital energy which can be calculated from Hartree-Fock

Fig. 3.13 Comparison of experimental XPS C 1s binding energies with those calculated via Koopman’s theorem for C in a range of molecules. Although experimental and theoretical values differ by 15 eV (associated with relaxation effects) the systematic comparison is excellent as indicated by the straight line of unity gradient (after Shirley, 1973).
Measured BE's and calculated orbital energies different by 10-30 eV because of:

- electron rearrangement to shield core hole - the frozen orbital approximation is not accurate
- electron correlation (small)
- relativistic effects (small)

Really, both initial state effects and final state effects affect measured BE

5.3 Primary Structure in XPS

Photemission process often envisaged as three steps

(i) Absorption and ionization (initial state effects)
(ii) Response of atom and creation of photoelectron (final state effects)
(iii) Transport of electron to surface and escape (extrinsic losses)
All can contribute structure to XPS spectrum

5.3.1 Inelastic Background

XPS spectra show characteristic "stepped" background (intensity of background to high BE of photoemission peak is always greater than low BE)

Due to inelastic processes (extrinsic losses) from deep in bulk

Only electrons close to surface can, on average, escape without energy loss

Electrons deeper in surface loose energy and emerge with reduced KE, increased BE

Electrons very deep in surface loose all energy and cannot escape

![Energy losses and Mean photoelectron binding energy diagram](image)

![XPS spectrum diagram](image)
What is probability that electron of kinetic energy KE (and IMFP $\lambda$) will arrive at surface without energy loss?

- what is sampling depth $d$ of photoelectron?

$$I = I_0 \exp\left(-\frac{d}{\lambda \cos \theta}\right)$$

$$\ln\left(\frac{I}{I_0}\right) = -\frac{d}{\lambda \cos \theta}$$

For normal takeoff angle, $\cos \theta = 1$

When $d = \lambda$, - $\ln(I/I_0) = 0.367$ or 63.3 \% of electrons come from within 1 $\lambda$ of surface

When $d = 2 \lambda$, - $\ln(I/I_0) = 0.136$ or 86.4 \% of electrons come from within 2 $\lambda$ of surface

When $d = 3 \lambda$, - $\ln(I/I_0) = 0.050$ or 95.0 \% of electrons come from within 3 $\lambda$ of surface
5.3.2 Spin-Orbit Splitting (SOS)

Spin-orbit splitting is an initial state effect

For any electron in orbital with orbital angular momentum, coupling between magnetic fields of spin (s) and angular momentum (l) occurs

![Diagram showing spin-orbit coupling](image)

**Figure 3.12** Spin–orbit coupling leads to a splitting of the 4f photoemission gold into two subpeaks

Spin-orbit splitting is an initial state effect.

For any electron in orbital with orbital angular momentum, coupling between magnetic fields of spin (s) and angular momentum (l) occurs.
Total angular momentum $j = |l \pm s|$

<table>
<thead>
<tr>
<th>Quantum numbers</th>
<th>Atomic notation</th>
<th>X-ray notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>$l$</td>
<td>$s$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\pm 1/2$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\pm 1/2$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$+ 1/2$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$- 1/2$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\pm 1/2$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$- 1/2$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$+ 1/2$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$- 1/2$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$+ 1/2$</td>
</tr>
</tbody>
</table>

But how many spin-orbit split levels at each $j$ value?

$$\text{Degeneracy} = 2j + 1$$

<table>
<thead>
<tr>
<th>Subshell</th>
<th>$j$ values</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>1/2</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>1/2, 3/2</td>
<td>2, 4 = 1, 2</td>
</tr>
<tr>
<td>d</td>
<td>3/2, 5/2</td>
<td>4, 6 = 2, 3</td>
</tr>
<tr>
<td>f</td>
<td>5/2, 7/2</td>
<td>6, 8 = 3, 4</td>
</tr>
</tbody>
</table>
Observations:

- s orbitals are not spin-orbit split - singlet in XPS
- p, d, f... orbitals are spin-orbit split - doublets in XPS
- BE of lower j value in doublet is higher (BE $2p_{1/2} > BE 2p_{3/2}$)
- Magnitude of spin-orbit splitting increases with Z
- Magnitude of spin-orbit splitting decreases with distance from nucleus (increased nuclear shielding)

5.3.3 Auger Peaks

Result from excess energy of atom during relaxation (after core hole) creation
- always accompany XPS
- broader and more complex structure than photoemission peaks

KE independent of incident $h\nu$

(will discuss in more detail later)

5.3.4 Core Level Chemical Shifts

Position of orbitals in atom is sensitive to chemical environment of atom

In gas phase, can see differences in core electron ionization energies:

![Graph showing core level chemical shifts in CH4, CO2, and CF4](image)

*Fig. 53. The carbon 1s signals in the X-PE spectrum of an approximately equimolar gaseous mixture of CH4, CO2 and CF4. (From Ref. 13.)*
<table>
<thead>
<tr>
<th>1s Ionization</th>
<th>Species</th>
<th>$\Delta$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>IP (BF$_3$ - B$_2$H$_6$)</td>
<td>6.2</td>
</tr>
<tr>
<td>C</td>
<td>IP (CF$_4$ - CH$_4$)</td>
<td>11.1</td>
</tr>
<tr>
<td>N</td>
<td>IP (NF$_3$ - NH$_3$)</td>
<td>7.3</td>
</tr>
<tr>
<td>O</td>
<td>IP (O$_2$ - CH$_3$CHO)</td>
<td>5.5</td>
</tr>
<tr>
<td>F</td>
<td>IP (CF$_4$ - EtF)</td>
<td>3.2</td>
</tr>
<tr>
<td>S</td>
<td>IP (SF$_6$ - SH$_2$)</td>
<td>10.2</td>
</tr>
</tbody>
</table>

In solid all core levels for that atom shifted by approx. same amount (<10 eV)

Chemical shift correlated with *overall charge* on atom (Reduced charge $\rightarrow$ increased BE)

(i) number of substituents

(ii) substituent electronegativity

(iii) formal oxidation state (unreliable depending upon ionicity/covalency of bonding)

![Figure 3.3](image-url)  
*Figure 3.3.* (a) The sulfur 1s chemical shifts, versus formal oxidation state for several inorganic sulfur species. (b) The sulfur 2p binding energy, versus calculated charge for several inorganic and organic sulfur species. Data taken from the results of Siegbahn *et al.* [2]
Usually chemical shifts are thought of as initial state effect (i.e. relaxation processes are similar magnitude in all cases)

Ti $2p_{1/2}$ and $2p_{3/2}$ chemical shift for Ti and Ti$^{4+}$. Charge withdrawn Ti $\rightarrow$ Ti$^{4+}$ so 2p orbital relaxes to higher BE

Note: Spin-orbit splitting is approximately constant - confirming SOS is largely an initial state effect

Chemical shift information very powerful tool for functional group, chemical environment, oxidation state
Table 3.2. Typical C₁₄ binding energies for organic samples

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrocarbon</td>
<td>285.0</td>
</tr>
<tr>
<td>amine</td>
<td>286.0</td>
</tr>
<tr>
<td>alcohol, ether</td>
<td>286.5</td>
</tr>
<tr>
<td>Cl bound to carbon</td>
<td>286.5</td>
</tr>
<tr>
<td>F bound to carbon</td>
<td>287.8</td>
</tr>
<tr>
<td>carboxyl</td>
<td>288.0</td>
</tr>
<tr>
<td>amide</td>
<td>288.2</td>
</tr>
<tr>
<td>acid, ester</td>
<td>289.0</td>
</tr>
<tr>
<td>urea</td>
<td>289.0</td>
</tr>
<tr>
<td>carbamate</td>
<td>289.6</td>
</tr>
<tr>
<td>carbonate</td>
<td>290.3</td>
</tr>
<tr>
<td>2F bound to carbon</td>
<td>290.6</td>
</tr>
<tr>
<td>carbon in PTFE</td>
<td>292.0</td>
</tr>
<tr>
<td>3F bound to carbon</td>
<td>293–294</td>
</tr>
</tbody>
</table>

*The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV, but some (e.g., fluorocarbon samples) can be larger.

Table 3.3. Typical O₁₄ binding energies for organic samples

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbonyl</td>
<td>532.2</td>
</tr>
<tr>
<td>alcohol, ether</td>
<td>532.8</td>
</tr>
<tr>
<td>ester</td>
<td>533.7</td>
</tr>
</tbody>
</table>

*The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV.

5.4 Secondary Structure in XPS

5.4.1 X-ray Satellites

In order to observe sharp photoemission lines in XPS, x-ray source must be monochromatic

X-ray emission in source based on x-ray fluorescence:
$2p_{3/2} \rightarrow 1s$ and $2p_{1/2} \rightarrow 1s$ transitions produce soft x-rays

$K\alpha_{1,2}$ radiation (unresolved doublet)

<table>
<thead>
<tr>
<th>hv (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg 1253.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Al 1486.6</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Same transitions in doubly ionized Mg or Al produce $K\alpha_{3,4}$ lines at $h\nu \sim$ 9-10 eV higher…

$3p \rightarrow 1s$ transitions produce $K\beta$ x-rays

X-ray source is usually unmonochromated so x-ray fluorescence emission lines superimposed on broad background (Bremsstrahlung)
Emission from non-monochromatic x-ray sources produces "ghost" peaks in XPS spectrum at lower BE.

Fig. 4. Partial XP spectra of gold with and without monochromation of the X-rays. Upper spectra with Mg Ka (500 W), lower spectra with monochromatized Al Ka (900 W). Both scans have overall resolution of 0.95 eV f.w.h.m., 0.1 V s⁻¹ scan speed, 0.33 s TC. Count rates are: (a) 10⁴ counts s⁻¹ f.s.d., (c) 3 × 10⁴ counts s⁻¹ f.s.d. (b) and (d) are ×10 sensitivity.
5.4.2 Surface Charging

Electrical insulators cannot dissipate charge generated by photoemission process

Surface picks up excess positive charge - all peaks shift to higher BE

Can be reduced by exposing surface to neutralizing flux of low energy electrons - "flood gun" or "neutralizer"

BUT must have good reference peak

![Graph showing spectral shifts](image)
5.4.3 Final State Effects (Intrinsic Satellites)

Final state effects arise during atom relaxation and creation of photoelectron following core-hole creation.

Koopman's energy never observed because of intra-atomic and interatomic screening by electrons.

Solid relaxation shift

Adiabatic energy never observed because atom doesn't have enough time to fully relax to ground state ionic configuration before photoelectron is created.
Photoelectron is created while ion is in various electronically excited states

\[ \Psi(f) = \Psi(\text{ion}) + \alpha \Psi(1) + \beta \Psi(2) \ldots \]

Energy of electronic excitation not available to departing photoelectron -
satellites at lower KE, higher BE

- excitation of electron to bound state *shake-up satellite*
- excitation of electron to unbound (continuum) state *shake-off satellite*
- excitation of hole state *shake-down satellite* - rare

Longer excited states live more likely to see final state satellites
Shake-up features especially common in transition metal oxides associated with paramagnetic species

![Graph showing examples of shake-up lines observed with the copper 2p spectrum.](image)

**Figure 8.** Examples of shake-up lines observed with the copper 2p spectrum.

Shake-up features especially common in transition metal oxides associated with paramagnetic species

<table>
<thead>
<tr>
<th>Atomic No.</th>
<th>Paramagnetic States</th>
<th>Diamagnetic States</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>Ti⁺², Ti⁺³, V⁺⁵</td>
<td>Ti⁺⁴</td>
</tr>
<tr>
<td>23</td>
<td>V⁺², V⁺³, V⁺⁴</td>
<td>V⁺⁵</td>
</tr>
<tr>
<td>24</td>
<td>Cr⁺², Cr⁺³, Cr⁺⁴, Cr⁺⁵</td>
<td>Cr⁺⁶</td>
</tr>
<tr>
<td>25</td>
<td>Mn⁺², Mn⁺³, Mn⁺⁴, Mn⁺⁵</td>
<td>Mn⁺⁷</td>
</tr>
<tr>
<td>26</td>
<td>Fe⁺², Fe⁺³</td>
<td>K₄Fe(CN)₆, Fe(CO)₆Br₂</td>
</tr>
<tr>
<td>27</td>
<td>Co⁺², Co⁺³</td>
<td>Co₆, Co(NO₃)₂(NH₃)₆, K₃Co(CN)₆, Co(NH₃)₆Cl₃</td>
</tr>
<tr>
<td>28</td>
<td>Ni⁺²</td>
<td>K₂Ni(CN)₆, square planar complexes</td>
</tr>
<tr>
<td>29</td>
<td>Cu⁺²</td>
<td>Cu⁺⁺</td>
</tr>
<tr>
<td>42</td>
<td>Mo⁺⁴, Mo⁺⁵</td>
<td>Mo⁺⁶, MoS₂, K₄Mo(CN)₆</td>
</tr>
<tr>
<td>44</td>
<td>Ru⁺³, Ru⁺⁴, Ru⁺⁵</td>
<td>Ru⁺²</td>
</tr>
<tr>
<td>47</td>
<td>Ag⁺²</td>
<td>Ag⁺⁺</td>
</tr>
<tr>
<td>58</td>
<td>Ce⁺³</td>
<td>Ce⁺⁺</td>
</tr>
<tr>
<td>59-70</td>
<td>Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb compounds</td>
<td>W⁺⁶, WC₂, WC_u, WC, K₄W(CN)₆</td>
</tr>
<tr>
<td>74</td>
<td>W⁺⁴, W⁺⁵</td>
<td>Re⁺⁷, Re₂O₃</td>
</tr>
<tr>
<td>75</td>
<td>Re⁺⁶, Re⁺³, Re⁺⁴, Re⁺⁵, Re⁺⁶, Re⁺⁸</td>
<td>Os⁺², Os⁺⁴, Os⁺⁵</td>
</tr>
<tr>
<td>76</td>
<td>Os⁺¹, Os⁺⁴, Os⁺⁵</td>
<td>Os⁺², Os⁺⁴, Os⁺⁸</td>
</tr>
<tr>
<td>77</td>
<td>U⁺⁴</td>
<td>U⁺³, U⁺⁶</td>
</tr>
<tr>
<td>92</td>
<td>U⁺³, U⁺⁴</td>
<td></td>
</tr>
</tbody>
</table>
Has been used as fingerprint in polymer XPS (termed ESCALOSS by Barr)

5.4.4 Multiplet Splitting

Occasionally see splitting of s orbitals

Occurs with photoemission from closed shell in presence of open shell

\[
\text{ground state } \text{Li}(1s \ 2s^1 2S) \rightarrow \text{Li}^+(1s^1 2s^1 1S) + e^- \text{ final state 1} \\
\rightarrow \text{Li}^+(1s^1 2s^1 3S) + e^- \text{ final state 2}
\]
5.4.5 Extrinsic Satellites

Occur during transport of electron to surface - *discrete loss structure*

Electronic excitation (interband or plasmons (bulk or surface))
Figure 12. Energy loss (plasmon) lines associated with the 2s line of aluminum (a = 15.3 eV; note surface plasmon at b).
Peak asymmetry in metals caused by small energy electron-hole excitations near $E_F$ of metal

"Doniach-Sunjic" line shape

Degree of asymmetry proportional to DOS at $E_F$
5.5 Instrumentation for XPS

Fig. 2.2 Schematic arrangement of a photoelectron spectrometer.

X-ray source, (monochromator), sample, electron energy analyzer (monochromator), electron detector, readout and data processing

5.5.1 X-ray Sources

Twin anode (Mg/Al) source:

Fig. 3. Double-anode X-ray source.
Simple, relatively inexpensive

High flux ($10^{10} - 10^{12}$ photons·s$^{-1}$)

Polychromatic

Beam size ~ 1cm

Monochromatic source:

![Diagram](image)

Fig. 5. X-ray monochromation (Johann approximate focusing geometry).

Diffraction from bent SiO$_2$ crystal - other $\lambda$'s focussed at different points in space
Beam size $\sim 1$ cm to 50 $\mu$m

Eliminates satellites, decreases FWHM of line but flux decreases at least an order of magnitude

5.5.2 Electron Energy Analyzers

Most common type of electrostatic deflection-type analyzer called the *concentric hemispherical analyzer* (CHA) or spherical sector analyzer

![Schematic of concentric hemispherical analyzer](image)

*Figure 2.30 Schematic cross-section of a concentric hemispherical analyser (CHA). Two hemispheres of radii $R_1$ (inner) and $R_2$ (outer) are positioned concentrically. $R_0$ is the radius of the median equipotential surface. Potentials $-V_1$ and $-V_2$ are applied to the inner and outer spheres respectively, with $V_2$ greater than $V_1$. The source $S$ is located in the entrance slit of width $W_1$ and the focus $F$ in the exit slit of width $W_2$. The divergence of an electron entering the analyser from the ideal tangential path is $\Delta \alpha$. The expression for the relationship between the energy of an electron and the difference $V_2 - V_1$ is given by equation (2.21). (Reproduced from Seah\textsuperscript{21} by permission of Cambridge University Press. Crown © reserved)*

Negative potential on two hemispheres $V_2 > V_1$

Potential of mean path through analyzer is

$$V_0 = \frac{V_1 R_1 + V_2 R_2}{2R_0}$$

An electron of kinetic energy $eV = V_0$ will travel a circular orbit through hemispheres at radius $R_0$

Since $R_0$, $R_1$ and $R_2$ are fixed, in principle changing $V_1$ and $V_2$ will allow scanning of electron KE following mean path through hemispheres
Total resolution of instrument is convolution of x-ray source width, natural linewidth of peak, analyzer resolution

\[ FWHM_{\text{total}} = \left( \frac{\text{FWHM}_{\text{x-ray}}}{<0.7-1.0\text{eV}} + \frac{\text{FWHM}_{\text{linewidth}}}{<0.1\text{eV}} + \text{FWHM}_{\text{analyzer}} \right)^{-1/2} \]

Analyzer FWHM is really only one we can control

Resolution defines ability to separate closely spaced photoemission peaks (important for determining chemical shift)

\[ R = \frac{\Delta E}{E} \]

\[ \Delta E \approx \text{FWHM (eV)} \]

\[ E = \text{KE of peak (eV)} \]

But what if we wanted uniform resolution across entire XPS spectrum? Say 0.5 eV FWHM?

At 10 eV KE, \( R = 0.5 / 10 = 0.05 \)

At 1500 eV KE, \( R = 0.5 / 1000 = 0.0005 \)

Easiest way is to retard electrons entering energy analyzer to fixed KE, called the pass energy \( E_0 \), so that fixed resolution applies across entire spectrum

\[ \frac{\Delta E}{E_0} = \frac{s}{2R_0} \]

\( s = \text{mean slit width} \)

Decreased pass energy or increased \( R_0 = \) increased resolution (typical FWHM_{analyzer} 0.1-1.0 eV)

Multi-element electrostatic lens system:

(i) Collects e"s of large angular distribution - larger flux
(ii) focuses e−s at entrance slit

(ii) retards electrons to pass energy

(iv) can "magnify" image of sample for small spot XPS - much easier to look at small spot with analyzer than try to produce focussed x-ray beam

Image spot can be scanned to build up 2-D chemically-resolved "image" of surface - best 5 µm

Basis of photoemission electron microscopy (PEEM) technique

Often coupled with rotating anode x-ray source to increase x-ray flux

![Diagram of a CHA with standard input lens systems for XPS](image)

Figure 2.31 Diagram of a CHA with standard input lens systems for XPS. The lens in this case is simply a transfer lens, which transfers an image of the analysed area on the sample onto the entrance slit to the analyser. Slight magnification is also performed. Removing the sample from close proximity to the entrance slit of the analyser in this way provides much greater working space around the sample. (Reproduced from Coxon et al. by permission of Elsevier Science Publishers)
5.6 Quantitation of XPS

Usefulness of technique depends on

(i) sensitivity (minimum detectable concentration)
(ii) quantitation (accuracy and precision)

5.6.1 Sensitivity

Basic property is probability of subshell ionization

Probability is function of initial and final state wavefunctions

\[ \sigma_{i,j} = A(\text{BE}_i \cdot \text{KE}_j) \cdot \left| \langle \Psi_i | \mu | \Psi_f \rangle \right|^2 \]

where A depends on BE of ionized core level and KE of emerging photoelectron

In effect, \( \sigma_{i,j} \), measures "overlap" of initial and final state wavefunctions

Qualitative picture from radial dependence of \( \Psi_i \) and wavelength of free electron:

---

Fig. 3.21 Radial part of the 2p (Ne) and 3p (Ar) atomic wavefunctions together with the d continuum (final state) wavelengths at zero kinetic energy (i.e. at photoionisation threshold) (after Fano & Cooper, 1968).
Minimum in $\sigma_{ij}$ about 50 eV (KE) above ionization threshold

**Fig. 3.22** Theoretical computation of the Ar 3p atomic photoionisation cross-section by Kennedy and Manson (1972) showing the 'Cooper minimum' around 50 eV above threshold. $L$ and $V$ correspond to the 'length' and 'velocity' forms of the matrix element used in the computation (cf. equation (3.12)). These computations include both d and s final states so that the minimum is not identically zero as it is in the d channel alone.

**Fig. 3.16** Calculated cross-sections for photoemission from occupied levels of the elements for 1.5 keV photons (from Wertheim (1978) based on the calculated value of Scofield, 1976).
Calculations indicate maximum $\sigma_{i,j}$ is $\sim 10^{-18}$ cm$^2$

If 1 ML contains $10^{15}$ atoms·cm$^{-2}$, should get about $10^{-3}$ photoelectron per incident photons ($10^{15} \times 10^{-18}$)

If x-ray source flux is $10^{12}$ photons·s$^{-1}$, should produce about $10^9$ electrons·s$^{-1}$ from 1 ML

For most elements, sensitivity is 0.1-1 % ML (≡ subnanomolar)

Observations:

$\sigma_{i,j}$ for C in CF$_4$, CH$_4$, graphite… is identical

Each subshell has different $\sigma_{i,j}$ - different sensitivity

Low Z elements have low $\sigma_{i,j}$ implies lower sensitivity

5.6.2 Quantitation

Difficult to apply calculated $\sigma_{i,j}$ directly to data (other instrumental parameters need to be included)

$$ I_a = \Phi_{\text{x-ray}}(x,y) \times C_a(x,y,d) \times \sigma_{i,j}(h\nu) \times P_{\text{no-loss}}(\text{material,d}) \times A_{\text{analyzer}} \times T_{\text{analyzer}} $$

$\Phi_{\text{x-ray}} = \text{x-ray flux}$

$C_a = \text{concentration of element a}$

$\sigma_{i,j} = \text{subshell ionization cross-section}$

$P_{\text{no-loss}} = \text{probability of no-loss escape (}\alpha\text{ IMFP)}$

$A_{\text{analyzer}} = \text{angular acceptance of analyzer}$

$T_{\text{analyzer}} = \text{transmission function of analyzer}$
Most analyses use empirical calibration constants (called *atomic sensitivity factors*) derived from standards:

\[ C_a(\bar{x}, \bar{y}, \bar{d}) = \frac{I_{\text{measured}}}{\text{ASF}} \]

<table>
<thead>
<tr>
<th>$Z$</th>
<th>Element</th>
<th>Subshell</th>
<th>ASF (Area)</th>
</tr>
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<tbody>
<tr>
<td>3</td>
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<tr>
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<tr>
<td>15</td>
<td>P</td>
<td>2p</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Note: ASF for H, He very small - undetectable in conventional XPS!

Note: XPS spectrum will show *all* peaks for each element in same ratio

Note: Not all XPS peaks for an element same intensity (in area ratio proportional to ASF's) - choose peak with largest ASF to maximize sensitivity

Note: Sensitivity for each element in a complex mixture will vary
How to measure $I_{measured}$

Accuracy better than 15 % using ASF's

Use of standards measured on same instrument or full expression above accuracy better than 5 %

In both cases, reproducibility (precision) better than 2 %

Must include or correct for (i) x-ray satellites (ii) chemically shifted species (iii) shake-up peaks (iv) plasmon or other losses
5.6.3 Depth Information From XPS

Probability that electrons can escape without losing energy is, on average IMFP, \( \lambda \) where \( d \) is called the sampling depth \( \sim 3 \lambda \) (for 95 % photoelectrons)

For off-normal take-off angle \( \alpha \):

\[
P = \exp\left(-\frac{d}{\lambda \cdot \sin \alpha}\right) \quad P = \frac{I}{I_0}
\]

\[
d = -\ln(P) \cdot \lambda \cdot \sin \alpha
\]

\( d \) decreases by a factor of 4 on going from \( \alpha = 90^\circ \) (normal) to \( 15^\circ \) (grazing)
Figure 3.37 Effect of variation of take-off angle on the Si 2p spectrum from silicon with a passive oxide layer. Note the relative enhancement of the (surface) oxide signal at low angle (measured with respect to the surface). (After Wagner et al.31)

Crude, non-destructive way of "depth profiling"
5.7 Summary

Non-destructive

Quantitative method for elemental composition - relatively straightforward using ASF's

Sensitive ~ 0.1 % ML

Chemical shifts give information about

(i) oxidation states

(ii) chemical environment

Extensive databases of chemical shift information

Sampling depth typically 20-100 Å

Crude depth information by changing take-off angle

BUT

Complex, expensive instrumentation (>\$100,000)

Monochromatic x-ray sources have low flux

Not usually spatially sensitive

Sampling depth varies with electron KE (and material)

Spectra complicated by secondary features

(i) x-ray satellites

(ii) extrinsic losses

(iii) final state effects

Surface charging in insulators shifts BE scale

Cannot detect H, He with good sensitivity