SURFACE STRUCTURE DETERMINATION

We list below some of the more common surface science techniques used for physical structure determination. Following our discussion on LEED, we will briefly discuss two other techniques: Surface EXAFS and STM.

A. Diffraction techniques

- Low Energy Electron Diffraction (LEED)
- Extended X-ray Absorption Fine Structure (EXAFS) and Surface EXAFS
- Electron and Photoelectron Holographies

B. Scattering techniques

- Scanning Electron Microscopy (SEM)
- Transmission Electron Microscopy (TEM)
- Scanning Transmission Electron Microscopy (STEM)

C. Tip-based techniques

- Field Emission Microscopy (FEM)
- Scanning Tunneling Microscopy (STM)
- Atomic Force Microscopy (AFM)

EXAMPLES of Other Techniques

Helium Diffraction
Surface Extended X-ray Absorption Fine Structure (SEXAFS)

We will first introduce the basic principle of EXAFS for bulk analysis. As the
name implies, it has something to do with the “fine” (or small) structure of X-ray absorption cross section.

REF: http://cars9.uchicago.edu/xafs/

- **Photoelectric effect**

EXAFS is caused by photoelectric effect:

\[
\text{hv} + M \rightarrow M^+ + e^-
\]

where we have a photon of the energy \( \text{hv} \) being absorbed completely by the target (e.g. a surface atom or an adsorbate). The photon energy is sufficient to cause an electron bound by the “field” within the target (with a binding/ionization energy of \( \varepsilon_i \)) to be ejected with a kinetic energy K.E. Conservation of energy gives:

\[
\text{hv} = \varepsilon_i + \text{K.E.}
\]

This is the famous Einstein equation (Nobel Prize 1926), which defines the basic principle of photoemission. Experimentally, if we can control the photon energy and determine K.E. of the photoelectron, we can obtain the important information \( \varepsilon_i \). In simple Molecular Orbital theory and if we assume the so-called Koopmans’ theorem, the ionization energy \( \varepsilon_i \) is simply the orbital energy. In the case of solids, this leads to electronic band structure (see later).
Fig. 3.1 Potential energy curves for the molecule AB in its ground state and the corresponding molecular ion AB⁺ in several different ionic states. The Franck-Condon region is between the vertical lines. Photo-electron bands resulting from the various transitions are shown schematically on the right ordinate.
Autoionization

Fig. 3.12. Schematic diagram representing direct and autoionizing transitions of $\text{O}_2$.

Core-shell chemical shifts - ESCA

![Graph showing core-shell chemical shifts for different molecular structures.](image)
• Interference of the photoelectron waves
Suppose that the photon energy is sufficiently high that the absorption of this photon causes ionization of a *core-shell* electron. The photoelectron emits as a spherical wave (from the “emitter” atom), which in turn causes interference effects that depend on the local geometry of the emitter atom and the wavelength. Consequently, this interference modulates the absorption coefficient for the excitation radiation as a function of the photon energy (or wavelength).

If we plot the absorption coefficient as a function of the photon energy for a particular material, we obtain the so-called photoabsorption cross section.

The principle of X-ray absorption spectroscopy is the same as UV absorption spectroscopy. In the latter case, we use UV photon to excite the molecules from the ground electronic state to some excited (bound) electronic state. As the photon energy is increased into the soft X-ray regime, the absorption of the photon can cause not only excitation to discrete excited electronic states of the neutral but also ionization, as discussed above.

Discrete excitations lead to peaks in the absorption spectrum. Ionization leads to the so-called ionization edge and ionization continuum. There are generally two
Single-scattering analysis of EXAFS

The absorption (extinction) coefficient can be written as:

\[ \mu(E) = \mu_0(E) [1 + \chi(E)] \]

where \( \mu_0(E) \) is the atomic-like absorption coefficient (the background) and \( \chi(E) \) is the oscillatory part (the EXAFS modulation caused by the interference effects).

\[ \chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \]

For the special case of ionization of an s-state (i.e. K-edge) and by assuming that
the atoms are point scatterers, it can be shown that:

\[ \chi(k) = \sum_j A_j(k) \sin[2kr_j + \psi_j(k)] \]

\[ k = \sqrt{\frac{2m(h\nu - E_0)}{(h/2\pi)^2}} \]

and \( E_0 \) is the energy of the ionization potential of the s-state. \( A_j(k) \) is a pre-factor that depends on the coordination number (i.e. the number of nearest-neighbour scatterers), the backscattering cross section, a Debye-Waller thermal contribution, a damping factor due to inelastic mean free path, and other kinematic factors. \( r_j \) is the radial distance from the j-th scatterer. \( \psi_j \) is the phase shift related to the potential fields of the emitter and scatterer.

In effect, we can obtain the coordination number from the prefactor \( A_j \) and we can get the radial distance \( r_j \) by an inverse Fourier transform of \( \chi(k) \).
One major difference between LEED and EXAFS is that LEED is sensitive to long range order (i.e. to within the transfer width), while EXAFS and other FS techniques sample only “local” structure (i.e. that of the emitter). In LEED, reflected beams are detected as a consequence of coherent scattering at a periodic array of atoms. In EXAFS, the source is within the array of atoms and interference of a spherical wave causes the modulation. In LEED and XANES, multiple scattering must be considered. (Like EXAFS, XANES also samples local structure but its analysis is considerably more complex and difficult).

EXAMPLES
- Surface EXAFS

In EXAFS, we measure the absorption coefficient of the X ray not just by the surface region but also the rest of the sample (i.e. deeper layers). Although some surface properties can be obtained in systems with a high surface-to-volume ratio (e.g. supported catalysts), we must probe different information in order to be more surface sensitive.

In this case, emission of the Auger electrons associated with the decay of the core hole caused by the X-ray can be recorded. Because of the inelastic mean free path...
imposed by the solid, *only* Auger electrons emitted near the surface region (i.e. within the shallow mean-free-path region of 1-2 nm) can escape without losing any energy.
• **ARPEFS (= Angle-Resolved Photoemission Extended Fine Structure) and Photoelectron Holography**

SEXAFS is a spherically averaged technique, i.e. its intensity comes from emission in all directions. ARPEFS (and photoelectron holography) is in effect an angle-resolved version of SEXAFS and it probes directional specific interference modulations, which can then be recombined to give a more complete (3D) picture of the selvedge.
Simple Analysis: Get the $\chi$ curve and do an inverse Fourier Transform, i.e. follow EXAFS approach.

Quantitative analysis: Assume a structure, apply the scattering theory and perform the calculations, vary the structural parameters and iterate until the residual is minimized, i.e. follow the LEED approach.
NOTE: Both Surface EXAFS and ARPEFS require the use of a tunable wavelength light source – a synchrotron.

REF: Canadian Light Source - http://www.cls.usask.ca/
Advanced Light Source - http://www-als.lbl.gov/
Synchrotron facilities worldwide
“Flower” patterns – photoelectron diffraction

Fig. 3.22: Radial plots of the azimuthal dependence of O 1s photoemission for a Cu(111)/Au(2x2)-2x2 overlayer at a photon energy of 80 eV and 200 eV for the Te 4d level in a Na(100)/Cu(2x2)-2x2 overlayer and from the Na 2p level in a Na(100)/Cu(2x2)-2x2 overlayer. The outer dots are data points while the inner curves are enhanced data points obtained by subtracting the minimum value from all points (after Woodruff et al., 1978).

Fig. 3.21: Radial plots of the azimuthal dependence of adsorbate core level photoemission at photon energies of 80, 90, and 100 eV from the Te 4d level in a Na(100)/Cu(2x2)-2x2 overlayer and from the Na 2p level in a Na(100)/Cu(2x2)-2x2 overlayer. The outer dots are data points while the inner curves are enhanced data points obtained by subtracting the minimum value from all points (after Woodruff et al., 1978).

- Comparison of LEED, EXAFS, and ARPEFS (Photoelectron Diffraction)

\[ \Delta \phi = kr(1 - \cos \theta) + \delta(x - \theta) \]

\[ \Delta \phi = 2kr + \delta(x) + 2\eta_0 \]

PhD: outgoing wave interference

EXAFS: central atom interference