

17.2.1.4 Synchrotron radiation photoelectron spectroscopy (SRPES)

The electron synchrotron is a wide energy range (X-ray to ultraviolet) elliptically polarized continuous radiation source. Several distinct techniques are of significance.

Energy distribution spectroscopy (EDS)

This is the classical fixed energy photoelectron spectroscopy with a continuous choice of excitation. Particularly useful is the ability to work in the extreme vacuum ultraviolet region (50 - 200 eV) where no convenient line sources are available. The technique is sometimes called *Energy Distribution Curve Spectroscopy (EDCS)*. The major application of this spectroscopy is to differentiate between surface and bulk features in the energy distribution spectrum by varying the kinetic energy of the photoelectrons and hence their mean-free-path by changing the photon energy.

Surface barrier induced states and the orientation of adsorbed molecules can be studied by varying the direction of incident s- and p-polarized radiation with respect to the plane of incidence. When combined with angle-resolved detection (ARUPS) details of the symmetry of these surface features can be elucidated.

Magnetized ferromagnetic materials have been shown to emit preferentially electrons of specific spin polarization. This is proving to be a very powerful technique for the study of the d-electron valence band. The combination of this Synchrotron-ARUPS technique with *Spin-Polarized Inverse Photoemission Spectroscopy (SPIPES)* is particularly useful as it permits to measure the density of states of both the occupied and unoccupied parts of the valence band.

Energy Distribution Spectroscopy can also be used to measure the variation of the optical matrix elements with the energy.

Incident: Photons of fixed selected energy 10-1000 eV.

Flux: Medium to low. Angle of incidence: 0-90° (not critical).

Detected: Electrons, 0 eV to within a few eV of incident photon energy. Angle of exit: Polar and azimuthal angles fixed. Polar: 0-90°; Azimuthal: 0-360°.

Spectrum: Photoelectron count rate vs. analysing energy (photoelectron energy).

Total yield spectroscopy or photoelectron yield spectroscopy

This is sometimes referred to as *Photoemission Yield Spectroscopy (PEYS)* and is the measurement of all photoelectrons emitted at a particular photon energy as a function of

that photon energy. Note that if surface states or adsorbates are present they also contribute an absorption coefficient to the total yield. There are three contributions to the total photoelectron yield: primary photoionization, Auger electrons and direct recombination (autoionization) electrons. The structure in the yield curve is directly attributable to the absorption coefficients for each ionization process with some sharp features due to core exciton states, arising from a promoted electron being confined to the vicinity of the core hole by Coulomb coupling with the hole.

Incident: Variable energy photons. Scanned range of 10-100 eV within the overall range 10-1000 eV. Angle of incidence: 0-90° (not critical).

Detected: Electrons. A fixed angle of exit is chosen.

Spectrum: Photoelectron count rate (photoelectron yield) vs. photon energy.

Partial yield spectroscopy (PYS)

The surface sensitivity of the yield spectrum can be varied by selecting those scattered photoelectrons which are within a certain energy interval at emission. This is the *partial yield*. Note that a confusion arises in the use of PYS for *Partial Yield Spectroscopy* as some workers use these initials for *Photoelectron Yield Spectroscopy*. If electrons with an energy distribution independent of the photon energy are selected then the partial yield is proportional to total yield. This measurement has no particular advantage over Total Yield Spectroscopy. If however high kinetic energy electrons whose energy distribution is dependent upon the photon energy are selected, their mean free path and hence escape depth are reduced as the photon energy is increased and so the influence of surface effects on the yield are enhanced. This is *Partial Yield Spectroscopy* or *Partial Photoyield Spectroscopy*. This spectroscopy is similar to *Constant-Final-State Synchrotron Spectroscopy* but in that technique the aim is to investigate the primary excitation electrons not the energy-dependent yield. Closely related to the photoelectron partial yield spectroscopy is *Auger-Electron Partial Yield Spectroscopy (APYS)* in which the yield from a particular Auger process is monitored as the primary photon energy is varied.

Incident: Variable energy photons, a scanned range of 10-100 eV within the overall range 10-1000 eV. Flux: medium to low. Angle: 0-90° (not critical).

Detected: electrons, collected within a selected energy window.

Spectrum: Photoelectron count rate (partial yield) vs. photon energy.

Constant initial state spectroscopy (CISS)

In this technique the energy distribution spectrum of electrons from a specified level in the valence band (i.e., the constant initial state) is recorded as the incident photon energy is

scanned. To achieve this experimentally, the energy difference between the energy analyzer and the incident photons is kept fixed as the photon energy is scanned. Thus, in effect, the initial state of the photoelectrons is fixed while the final state is scanned. The CIS spectrum is thus a mapping of the final states, i.e., the density of unoccupied states.

The initial state is the state of the electron in the surface before irradiation and the final state is the unoccupied state in the conduction band to which the electron is promoted by the photon. This is the first stage of the photoelectron emission process. Confusion arises if the final state is taken to be the continuum state of the photoemitted electron. CISS involve photon energies in the vacuum UV range 10-50 eV.

Incident: Variable energy photons, a scanned range of 5-20 eV, within the overall range of 10-50 eV. The extent of the scanned range is fixed by the final states and its position in the overall range is chosen by the selected initial state. Flux: medium to low. Angle: 0-90° (not critical).

Detected: electrons. The energy difference between the photon energy and the energy analyzer is kept constant. This energy difference corresponds to the energy gap between the selected initial and the final state.

Spectrum: Photoelectron count rate (partial yield) vs. photon energy or photon energy + energy difference (i.e. the final state).

Constant final state spectroscopy (CFSS)

In this technique the energy distribution spectrum of electrons from any initial valence band level which have been promoted to a specified conduction band level (i.e., final state) is recorded as a function of the incident photon energy. In other words, the occupied initial states are scanned into a constant final state. To achieve this experimentally the electron energy analyzer is held at a fixed energy as the photon energy is scanned. The spectra obtained resemble the energy distribution spectra obtained by scanning the analyzer energy at a fixed photon energy. However the weighting of the features in the spectrum is different as the matrix elements are different. The CFS spectrum is a mapping of the initial states, i.e., the density of occupied states.

Incident: variable energy photons; scanned range of 5-20 eV within the overall range of 10-50 eV. The extent of the scanned range is fixed by the extent of the occupied levels of the valence band (the initial state).

Flux: medium to low; angle: 0-90° (not critical).

Detected: electrons. The energy analyzer is held at a fixed energy (i.e., the final state).

Spectrum: Photoelectron count rate (partial yield) vs. photon energy (i.e. the initial state).

Angle resolved synchrotron radiation photoelectron spectroscopy (ARUPS and ARXPS)

There are two techniques for recording angle-resolved spectra. Firstly, the energy distribution spectrum may be recorded at fixed values of emission angle as the photon energy is scanned. Secondly, the energy window of the energy analyzer is fixed on some feature of interest and the polar or azimuthal angle is varied. ARUPS refers to angle-resolved emission from the valence band and ARXPS to emission from core levels particularly in the soft X-ray region.

Incident: Fixed energy photons, within the range 10-1000 eV (elliptically polarized). Flux: medium to low; angle: polar angle within range 0-90° (usually not critical; azimuthal angle not critical).

Detected: photoelectrons, 0 eV to within a few eV of incident energy. Angle of exit: either azimuthal angle fixed and polar angle varied or vice versa (see *Photoelectron diffraction*).

Spectrum: Photoelectron current at stated polar (or azimuthal) angle vs photoelectron energy.

Resonance-enhanced photoelectron spectroscopy

Once the resonant frequency has been found, the photon energy is fixed and the energy distribution spectrum is recorded. This is a particularly powerful technique for investigating the nature of adsorbate bonds. Resonant processes are also observed in clean crystal surfaces.

Incident: Fixed energy photons; photon energy is varied until it is resonant with a bound state-bound state transition from a core level to an unoccupied valence level of a chemisorbed molecule. The photon energy is then fixed. Photon energies are usually in the range 0-20 eV. Angle: 0-90° (not critical).

Detected: electrons (0 eV to within a few eV of the incident photon energy). Angle of exit: fixed.

Spectrum: Photoelectron current at stated polar (or azimuthal) angle vs. photoelectron energy.

Surface extended X-ray absorption fine structure (SEXAFS)

This fine structure technique serves for observation of final state interference effects using Auger yield analysis. Note that 's' at the end of SEXAFS does not denote 'spectroscopy' and that, in consequence, usage which implies 'spectroscopy', e.g.

Partial yield SEXAFS, is inappropriate.

Incident: Variable energy photons.

A scanned range of 50 - several hundred eV within the overall range 50-2000 eV. The scanned range usually commences about 50 eV above the threshold for the selected Auger process. Flux: Medium to low. Angle of incidence not critical.

Detected: Auger electrons with fixed energy at the energy of the electrons from the Auger process.

Spectrum: Auger electron count rate (Auger partial yield) vs. photon energy.