17.7.4 Investigation of surface electronic structure

UV-photoelectron spectroscopy (UPES) See 17.2.1.1.

UPES is the most powerful technique available for probing surface electronic structure. The increased use of synchrotron radiation in photoelectron spectroscopy has blurred the distinction between UPES and XPES. UPES in the laboratory requires a He gas discharge line source which can be operated to maximise the output of either He I (21.2 eV) or He II (40.8 eV) radiation. Using these photon energies it is clear that only valence levels and very shallow core levels are accessible.

Inverse photoelectron spectroscopy (IPS) See 17.2.2.2.

Inverse photoelectron spectroscopy (or inverse photoemission) is often referred to as *Bremsstrahlung Isochromat Spectroscopy* (*BIS*). It is a versatile technique to probe empty electronic states in solids and at clean and adsorbate covered surfaces. For sufficiently low kinetic energy of the primary electrons, inverse photoemission is shown to be applicable to adsorbates too. This allows one to assess directly the unoccupied electronic states of the adsorbate which play an important role in the formation of surface chemical bonds.

Surface Penning ionisation electron spectroscopy (SPIES) See 17.2.6.

When electronically excited, metastable He-atoms (in ^1S or ^3S states) impinge on a clean or adsorbate-covered solid surface, the deexcitation process is accompanied by electron emission. In the Penning ionisation technique, the energy distribution of electrons is measured.

Electronic electron energy loss spectrometry (ELS or EELS) See 17.2.2.1.

Electrons can also induce electronic excitations at the surface of a solid. In a simple experiment of this type a monochromatic beam of electrons of energy up to a few keV is reflected from the surface and subsequently energy analyzed. The excitations appear as characteristic loss peaks in the resulting spectrum. Since the intrinsic width of these loss features is rarely less than ≈ 1 eV, there are no stringent requirements as to the monochromaticity of the incident beam, as in the case of the vibrational EELS. As in photoemission, the inelastic mean free path of the inelastically scattered electrons is such that excitations characteristic of both the surface and the bulk are observed.

The work function (including field emission)

The work function Φ can be defined in terms of the minimum energy $e\Phi$ required to

remove an electron from the highest occupied level of a solid to a specified final state. In terms of thermodynamic quantities, this is the work done to balance the chemical potential μ of an electron in the bulk and the difference $\Delta\Phi$ in electrostatic potential across the surface of the solid, i.e. $e\Phi = e\Delta\Phi - \mu$. The importance of the surface contribution to the work function is shown empirically by the variation in Φ with crystal plane of the same material and by the large changes in Φ that can result from adsorption. Densely packed surface planes of a metal have work functions several 100 meV up to few eV higher than less dense planes. Adsorption also may change Φ by up to several eV.

The work function is a technically important parameter in photoelectric phenomena, thermionic emission and in semiconductor technology (transistors, light emitting diodes, Schottky barriers, etc.). In surface chemical physics it is a useful indicator for surface cleanliness, and permits chemisorption, desorption, and surface reactions to be monitored both as to their extent and rate and on a variety of crystal faces.

For the energy $e\Phi$ to be a minimum, the electron must finally be at rest at the specified final state. The value of Φ may depend on distance from the surface on account of the varying electrostatic potential associated with different crystal surfaces. If a finite crystal is considered and the final position is chosen at an infinitely large distance from the surface, it is then not possible to associate a work function with different crystal faces. In the definition of Φ of a clean monocrystal face, the distance of the electron from the face should be selected to be large enough that the image force is negligible (typically $> 10^{-4}$ cm) but it should be small compared with the size of the face in order to avoid perturbations caused by neighbouring crystal faces.

The most frequently used methods for work function measurements make use of photoemission, field emission or contact potential difference phenomena. See 17.2.12. 17.2.7.