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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY*

A DESCRIPTIVE CLASSIFICATION OF THE ELECTRON SPECTROSCOPIES

(Recommendations 1987)

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A descriptive classification of the electron spectroscopies (Recommendations 1987)

Abstract - The publication supplements an earlier IUPAC publication on electron spectroscopy and is intended to provide a source of reference for those interested in discovering the extent to which one or other of the electron spectroscopies might be of value in a particular area of work. The criterion for inclusion is principally that the use of an energy analyser or monochromator passing selected energies of electrons forms an essential part of the experiment. The different methods are grouped according to the underlying physical process which is involved. Each section is described in detail with all of the sub-divisions which could be discerned as distinctly separate according to the experimental features which are seen to be dominant.

INTRODUCTION

This publication supplements an earlier IUPAC publication on electron spectroscopy and is intended to provide a source of reference for those interested in discovering the extent to which one or other of the electron spectroscopies might be of value in a particular area of work. It has special relevance, however, for those interested in applying electron spectroscopy to structural studies in molecule chemistry and to analytical and structural studies of surfaces.

The criterion for inclusion is principally that the use of an energy analyser or monochromator passing selected energies of electrons forms an essential part of the experiment. The different methods can be grouped according to the underlying physical process which is involved. Each section is described in detail with all of the sub-divisions which could be discerned as distinctly separate according to the experimental features which were seen to be dominant. This coverage is complete up to January 1983.

In general each sub-division is accompanied by one or more references to leading review articles. In some cases, however, where only a few experiments have been reported in a particular area there may well be only one or two original papers to refer to.

In many cases the technique is essentially the same whether the area of work relates to isolated atoms or molecules in the gas phase or to the condensed phases, solid or liquid. Because electrons are weakly penetrating through matter the electron spectroscopies have particular value for the study of surfaces.

For consistency, all energies, whether for free electrons or photons or for excitation levels of atoms, molecules or surfaces, are expressed in electron volts. (1 eV $\approx 1.60219 \times 10^{-19}$ J).

I. THE PHOTOELECTRON EMISSION SPECTROSCOPIES

Photoelectron emission from isolated atoms or molecules in the gas phase is predominantly a direct one-electron emission into the continuum and the electron energy spectrum maps the initially occupied energy levels. Solid state photoemission is a more complex process than this. In the solid state the one-step process is replaced by a three-step process. Firstly, the electron is promoted from its initial state in the valence band or core levels to a final state in the unoccupied conduction band. Then the electron must travel to the surface and finally escape through the surface potential barrier. Thus, surface photoelectron emission is not a direct mapping of the initial density-of-states function, as in the gas phase, but rather the final energy distribution represents a convolution of the initial density-of-states with the density-of-states of the conduction band and some energy-dependent surface escape function.

Some of the energy may appear in simultaneous excitation (a shake-up process) or even further ionization (a shake-off process) instead of all of the energy of the photon being employed in the primary photoionization process. In both of these processes the primary photoelectron has less kinetic energy than expected and in the shake-off process an extra electron appears in the spectrum. The probability of these processes is much less than that of primary photoionization.

A similar process of particular importance for surface studies is resonant enhanced photoemission from a chemisorbed molecule. If the photon energy is varied until it is in resonance with a bound state-bound state transition from a core level of the molecule to an unoccupied valence level then the chemisorbed molecule is left in a highly excited neutral state. This state can then decay by one of three channels:

(a). the promoted electron may escape to the substrate leaving a singly ionized molecule behind. This ionized molecule may then decay by Auger process.

(b). the promoted electron may return to the core hole and the excess energy then ionize an occupied valence level. The energy of this electron is exactly that of an electron excited directly from the occupied valence levels. This is then observed as an enhancement of this line in the spectrum.

(c). an electron from the valence level can fill the core hole and another valence electron is then emitted. This final singly charged excited state is a shake-up state. As the final states in the above processes are different, the three possibilities can be separated by recording the energy distribution spectrum.

The chemical shift. The binding energies of core states observed in molecular and in surface photoemission differ slightly for chemically bound states from those observed in the corresponding free atoms in the gas phase. This binding energy shift is attributed to environmental effects and is thus a chemical shift, varying from one substance to another, and between like atoms in the same molecule.

Initial-state fine-structure. Spin-splitting of electronic states occurs in ferromagnetic materials. This splitting can be investigated by measuring the spin-polarization of the photoelectrons as a function of angle. This technique is known as Spin-Polarized Angle-Resolved Photoelectron Spectroscopy (SPARPES).

Secondary Auger electrons. The secondary Auger electron spectrum resulting from primary core hole creation by photons is considered with the Auger electron spectroscopies (See below).

Final-state effects. In addition to the initial-state effects considered above, final-state effects may also contribute to the observed photoelectron emission: spin-orbit splitting, electron correlation, electron-electron excitation, interference effects and diffraction effects. Final-state effects arise when photoexcited electrons are elastically scattered by surrounding atomic cores and thus reflect the geometry and environment of the source atom through diffraction and interference effects of the de Broglie electron waves. Thus, final-state effects are only significant in experiments in which the incident photon energy is varied.

Interference effects can be observed by monitoring the modulation in the variation of the photoelectron emission cross-section with photon frequency. These effects are the result of interference between the outgoing photoelectron wave and the incoming component of this wave which has been back-scattered from nearest-neighbour atoms. When X-rays are used this effect is known as Extended X-ray Absorption Fine Structure (EXAFS).

Photoelectron diffraction effects are observed in angle resolved spectra. Azimuthal photoelectron diffraction is observed at fixed photon energy and fixed polar angle and normal photoelectron diffraction is observed when the photon energy is varied as some energy-related feature, such as a particular core-ionization, is monitored.

Unlike electron scattering which is non-resonant and in which each electron can be involved in several inelastic processes, photon absorption is a resonant process so the signal-to-background ratio is much improved on similar electron-based spectroscopies, such as Ionization Spectroscopy and the Auger Spectroscopies, which are in other respects comparable. This is the main reason why the fixed photon-frequency photoelectron spectroscopies hold such an important place in surface science.

These fixed photon-frequency spectroscopies are Ultraviolet Photoelectron Spectroscopy (UPES), X-ray Photoelectron Spectroscopy (XPES), XUV Photoelectron Spectroscopy (XUPS, XUVPES) and Gamma-ray Photoelectron Spectroscopy. Gamma-ray Photoelectron Spectroscopy is in fact a rather specialized technique for studying the elemental composition of a surface at depths of up to several hundred nanometres.

The only really effective variable-frequency photon source available, at present, is the electron synchrotron. Thus, variable photon-frequency photoelectron spectroscopy is usually known as Synchrotron-Radiation Photoelectron Spectroscopy (SRPES).

I.1. Ultraviolet Photoelectron Spectroscopy (UPES)

Ultraviolet photoelectron spectroscopy (UPES, UVPES or PES), unfortunately sometimes known as photoemission spectroscopy, (see Note a) is also occasionally referred to as Photoelectron Spectroscopy of the Outer Shell (PESOS).

Experimentally, a fixed frequency resonance light source (10 - 41 eV) and an electron energy analyzer are required. The most commonly employed light sources are Hydrogen Lyα (10.20 eV), Helium I (21.22 eV) and Helium II (40.81 eV). These energies are sufficient to probe all valence electron levels. The observed energy resolution is limited by the analyzer resolution in this spectroscopy and not the light source linewidth. An instrumental energy resolution of 25 → 100 meV is usually adequate for solids, although if chemisorbed species are to be studied there are advantages in using a resolution comparable with gas phase work (∿10 - 25 meV).

Although, as previously mentioned, the photoelectron energy distribution spectrum of surfaces is not a direct mapping of the occupied valence band density of states, it is still possible to interpret the spectrum in this way. UPES, along with Surface Penning Ionization Spectroscopy and Ion Neutralization Spectroscopy, is one of the most chemically-sensitive surface spectroscopies. It is particularly useful for systems with surface layers of different chemical composition to the bulk (e.g. oxide layers) or a chemisorbed surface layer.

Angle-resolved detection adds a new dimension to this spectroscopy. The photoelectron intensity and its energy dependence are measured as a function of the collection angle with respect to some fixed axes. This technique is called Angle-resolved Ultraviolet Photoelectron Spectroscopy (ARUPS, ARPS), Angle-resolved Photoemission Spectroscopy (ARPES or ARP) or Angle-dispersed Electron Spectroscopy (ADES). In contrast UPS without angle discrimination is sometimes referred to as Angle-Integrated Ultraviolet Photoelectron Spectroscopy (AIUPS). However, this usage does not always refer to integration over 2π steradians but often to integration over a considerably more limited range of solid angles. Originally a distinction was drawn between an angle-resolved spectroscopy, in which the photon source and electron detector are fixed in position and the sample, if solid, is rotated, and angle-dispersed spectroscopy, in which the photon source and sample are fixed in position and the electron detector rotated. This distinction, although meaningful, was not strictly applied and has been lost. Most angle-resolved work today involves varying the position of the detector and keeping the sample orientation to the photon beam fixed. Angle-resolved studies are particularly important for systems with a high degree of symmetry.

SUMMARY

NAME: Ultraviolet Photoelectron Spectroscopy

CLASS: Photoelectron Spectroscopies

ACRONYMS: UPES, UVPES, UPS, UVPS, PES

ALTERNATIVE NAMES: Photoelectron Spectroscopy of the Outer Shell (PESOS)

RELATED TECHNIQUES: (Angle-Integrated) Ultraviolet Photoelectron Spectroscopy (AIUPS)
Angle-Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS, ARPES, ARPS, ADES)

INCIDENT: Fixed Energy UV Photons

ENERGY: within the range 4-40 eV

ENERGY RESOLUTION: ∿0.001 eV

INCIDENT PHOTON FLUX: High

Note a. The earlier IUPAC report ('Nomenclature and Spectral Presentation in Electron Spectroscopy resulting from Excitation by Photons: Recommendations 1975' Pure Appl. Chem., 45 (1976) 221-224) notes the possible confusion which this elision from photoelectron to photo- represents since photon emission is so close in appearance and so different in meaning. The use of the term photoemission is therefore discouraged in this context.

BEAM DIAMETER: ∿1 mm-10 mm

ANGLE OF INCIDENCE: within the range 0-85° (not critical)

DETECTED: Electrons

ENERGY RANGE: 0 eV to within a few eV of the incident photon energy

ANALYZER ENERGY RESOLUTION: ∿0.010 - 0.1 eV (typical)

ELECTRON CURRENT AT DETECTOR: ∿10^{-15} - 10^{-9} A

ANGLE OF EXIT: Polar and azimuthal angles fixed.
Polar angle usually in range 10 - 80°
Azimuthal angle not critical

ANGULAR RESOLUTION: not critical in UPS
High (∿3 - 5°) in ARUPS

SPECTRUM:

ORDINATE: Photoelectron Count Rate

ABSCISSA: Analyzing Energy (Photoelectron Energy or Ionization Energy)

SAMPLE: Atomic and molecular gases
Surface of non-volatile liquids and solutions
Single crystals) with or without adsorbed
Polycrystalline materials) layer
Thin conducting films on metal surfaces
Semiconductor surfaces

APPLICATIONS: Valence Structure of Atoms, Molecules, Surfaces and Chemisorbed Species

SELECTED REFERENCES:

(i) 'Ultraviolet Photoelectron Spectroscopy'
J. W. Rabalais
Wiley-Interscience, New York, 1976.

(ii) 'Photoemission and the Electronic Properties of Surfaces'
B. B. Feuerbacher, B. Fitton, R. F. Willis (editors)
Wiley-Interscience, New York, 1978.

(iii) 'Handbook of X-ray and UV Photoelectron Spectroscopy'
D. Briggs (editor)
Heyden, London, 1977.

(iv) 'Electron Emission Spectroscopy'
W. Dekeyer, L. Fiermans, G. Vanderkelen and J. Vennik (editors)
Reidel, Dordrecht, 1973.

(v) 'Photoelectron Spectroscopy of Solids and their Surfaces'
R. H. Williams, G. P. Srivastava, I. T. McGovern
Rep. Prog. Phys., 43 (1980) 1357.

I.2. X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) or Photoemission Spectroscopy (XPES) is also known as Electron Spectroscopy for Chemical Applications (originally Analysis) (ESCA) or, less frequently, as Photoelectron Spectroscopy of the Inner Shell (PESIS). If the photon energy employed is less than 300 eV the technique is sometimes referred to as Soft-X-ray Photoelectron Spectroscopy (SXPS). XUV Photoelectron Spectroscopy (where XUV refers to the extreme vacuum ultraviolet) is sometimes used to refer to PES employing a photon source in the frequency range between the ultraviolet and the X-ray regions.

A fixed-energy X-ray source and an electron energy-analyzer are required. The most common X-ray anodes are magnesium and aluminium with photon energies of 1254 eV and 1487 eV respectively. Other anode materials are sometimes employed with energies ranging from 132 eV (Yttrium) to 4511 eV (Titanium) and 8048 eV (Copper). Dispersive electron energy

analyzers are usually employed. The resolution of the observed spectrum is limited by the linewidth of the X-ray source not the analyzer. For this reason X-ray monochromators are often employed but this can lead to significant reduction in intensity.

The energy resolution of a typical X-ray photoelectron spectrum is $\sim$1 eV with high resolution work (HRXPS) requiring an energy resolution of $\sim$50 eV. The development of high resolution XPS was the basis for the technique of X-ray Photoelectron Diffraction (XPD, XPED). (See Section I.6).

Although angle-resolved measurements are not as important in XPES as in UPES or SRPES, they are useful for discriminating between surface and bulk effects.

The main applications of XPS are based upon its elemental sensitivity, (since the characteristic lines of different elements are often widely separated in relation to their widths) and in addition the chemical shift information. Materials studied range from gases to polymer surfaces and Langmuir-Blodgett films.

SUMMARY

NAME: X-ray Photoelectron Spectroscopy

CLASS: Photoelectron Spectroscopies

ACRONYMS: XPS, XPES

ALTERNATIVE NAMES: Electron Spectroscopy for Chemical Analysis (ESCA)
Photoelectron Spectroscopy of Inner Shell (PESIS)

RELATED TECHNIQUES: X-ray High Resolution Photoelectron Spectroscopy (HRXPS)
Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS)

INCIDENT: Fixed Energy X-ray Photons

ENERGY: within range 1 - 10 keV

ENERGY RESOLUTION: $\sim$0.5 - 1.5 eV (without monochromatisation)
$\sim$0.1 - 0.5 eV (monochromatised)

INCIDENT PHOTON FLUX: Low

BEAM DIAMETER: $\sim$1 - 3mm

ANGLE OF INCIDENCE: within range 70 - 85° (not critical)

DETECTED: Electrons

ENERGY RANGE: 0 eV to within a few eV of incident photon energy

ANALYZER ENERGY RESOLUTION: $\sim$1 eV (XPS, typical)
$\sim$0.1 eV or better (HRXPS, High Resolution)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-15} A

ANGLE OF EXIT: Polar and azimuthal angles fixed
Polar angle usually in the range 10 - 80°
Azimuthal angle not critical in XPS (but see Photoelectron Diffraction)

SPECTRUM:

ORDINATE: Photoelectron Count Rate

ABSCISSA: Analyzing Energy (Photoelectron Energy or Binding Energy)

SAMPLE: Atomic and molecular gases
Single crystals) usually without adsorbed
Polycrystalline materials) layer

Thin conducting films; Langmuir-Blodgett films
Semiconductor surfaces
Polymeric and some dielectric materials
Surfaces of some non-volatile liquids and solutions and some frozen liquids

APPLICATIONS: Elemental Sensitivity and Chemical Shifts

SELECTED REFERENCES:

(i) 'Electron Spectroscopy for Atoms, Molecules and Condensed Matter'
K. Siegbahn
Rev. Modern Phys., 54 (1982) 709.

(ii) 'Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy'
D. Briggs (editor)
Heyden, London, 1977.

(iii) 'Photoelectron and Auger Spectroscopy'
T. A. Carlson
Plenum, New York, 1975.

(iv) 'The Investigation of Polymer Surfaces by Means of ESCA'
D. T. Clark
in 'Polymer Surfaces'.
D. T. Clark and W. J. Feast (editors)
Wiley-Interscience, New York, 1978.

I.3. Gamma-ray (or Depth-Selective) Photoelectron Spectroscopy (DSPES)

This technique is also known as Depth-Selective Photoelectron Spectroscopy (DSPES). It is a rather specialized technique for studying the elemental composition and depth of thin surface layers from several nanometres to several hundred nanometres.

Photoionization is performed with high energy monochromatic γ-radiation, e.g., the 23.8 keV resonance lines of Tm 119.

The experiment is done on a sequence of vacuum evaporated layers on a low γ-ray absorber such as beryllium. A layer of material is vacuum evaporated onto the substrate and the photoelectron spectrum recorded. Then a second layer is deposited and the spectrum recorded again. The difference in the electron count at a given energy then corresponds to the number of electrons generated in the initial layer which have passed through the covering layer. (Note that this conclusion requires identical layers). The thickness of the layers is calibrated by weighing. The attenuation of the photoelectrons is then analyzed in terms of the layer structure. The technique has been applied up to 20 layers (i.e., a thickness of ∿1 μm). The analysis of the resulting attenuated spectra is an adaptation of the more established technique of Depth-Selective Mossbauer Spectroscopy (DSMS). Mixed layers of different materials may be studied.

SUMMARY

NAME: Gamma-Ray Photoelectron Spectroscopy

CLASS: Photoelectron Spectroscopies

ACRONYMS: None

ALTERNATIVE NAMES: Depth-Selective Photoelectron Spectroscopy (DSPES)

INCIDENT: Fixed Frequency γ-Ray Photon

ENERGY: 2.38×10^4 eV (resonance line of Tm 119)

ENERGY RESOLUTION: ∿10 eV

DETECTED: Electron

ENERGY RANGE: $100 - 2.38 \times 10^4$ eV

ANALYZER ENERGY RESOLUTION: ∿10 eV (typical)

SPECTRUM:

ORDINATE: Photoelectron Count Rate

ABSCISSA: Analyzing Energy (Photoelectron Energy)

SAMPLE: Vacuum evaporated layers (several nanometres thick) sequentially deposited on a metallic substrate. Up to 20 layers can be investigated.

APPLICATIONS: Electron Scattering and Surface Effects

SELECTED REFERENCE:

'Depth-Selective Photoelectron Spectroscopy as a Method for Studying Thin Layers'
M. Grozdanov, Tsv. Bonchev, G. Georgiev,
Bulgarian J. Phys. V, 5 (1978) 443.

I.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:

(a). Energy Distribution Spectroscopy

(b). Total Photoelectron Yield Spectroscopy

(c). Partial Photoelectron Yield Spectroscopy

(d). Constant-Initial-State Photoelectron Spectroscopy

(e). Constant-Final-State Photoelectron Spectroscopy

(f). Angle-Resolved Synchrotron-Radiation Photoelectron Spectroscopy

(g). Resonance-Enhanced Photoelectron Spectroscopy

(h). Extended X-ray Absorption-Fine-Structure

(a). 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 the density of states of both the occupied and unoccupied parts of the valence band to be measured.

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

SUMMARY

NAME: Energy Distribution Curve Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: EDCS, EDS

INCIDENT: Photons of Fixed Selected Energy

ENERGY: within range 10 - 1000 eV (but a photon energy in the XUV (50 - 200 eV) is often chosen)

ENERGY RESOLUTION: ~0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: within range 0 - 90° (not critical)

DETECTED: Electrons

ENERGY RANGE: 0 eV to within a few eV of incident photon energy

ANALYZER ENERGY RESOLUTION: ~0.025 - 0.1 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-11} A

ANGLE OF EXIT: Polar and Azimuthal angles fixed
High angular discrimination in angular-resolved experiments (ARUPS, ADES, ARXPS)
Polar: 0 - 90° Azimuthal: 0 - 360°

SPECTRUM:

ORDINATE: Photoelectron Count Rate

ABSCISSA: Analyzing Energy (Photoelectron Energy)

SAMPLE:
Atomic and molecular gases
Single crystals) with or without adsorbed
Polycrystalline materials) layer
Thin conducting films
Semiconductor surfaces

SELECTED REFERENCES:

(i) 'Photoemission and the Electronic Properties of Surfaces'
B. Feuerbacher, B. Fitton, R. F. Willis (editors)
Wiley-Interscience, New York, 1978.

(ii) 'Photoemission Spectroscopy'
B. Feuerbacher, B. Fitton
in 'Electron Spectroscopy for Surface Analysis'
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(iii) 'Synchrotron Radiation: Overview'
C. Kunz
in 'Photoemission in Solids II',
L. Ley and M. Cardona (editors)
Topics in Applied Physics, Volume 27, Springer-Verlag, 1979.

(b). 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. 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.

The total yield can also be recorded as a function of the light polarization angle. This is a measure of the vectorial photoeffect.

However, no electron energy analysis is involved.

SUMMARY

NAME: Total Yield Photoelectron Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYM: PEYS

INCIDENT: Variable Energy Photons

ENERGY RANGE: a scanned range of 10 - 100 eV within the overall range 10 - 1000 eV

ENERGY RESOLUTION: ~0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: within range 0 - 90° (not critical)

DETECTED: Electrons

ENERGY RANGE: 0 eV to within a few eV of incident photon energy

ANALYZER ENERGY RESOLUTION: Not applicable. All electron energies are collected

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-11} A

ANGLE OF EXIT: A fixed angle is chosen (not critical)
Angle-resolved experiments are not relevant

SPECTRUM:

ORDINATE: Photoelectron Count Rate (Photoelectron Yield)

ABSCISSA: Photon Energy

SAMPLE: Atomic and molecular gases
Polycrystalline materials
Thin conducting films
Adsorbed layers on metal substrates

SELECTED REFERENCE:

'Surface Electronic States on NaCl (100) studied with Polarization-Dependent Photoelectron Yield Spectroscopy'
U. Rehder, W. Gudat, R. G. Hayes, C. Kunz
Proceedings 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces (Vienna, 1977) p. 453.

(c). Partial yield spectroscopy. 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 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.

SUMMARY

NAME: Partial Yield Photoelectron Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYM: PYS

ALTERNATIVE NAME: Partial Photoyield Spectroscopy

INCIDENT: Variable Energy Photons

ENERGY RANGE: a scanned range of 10 - 100 eV within the overall range 10 - 1000 eV. The scanned range usually commences at the threshold for the process selected.

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: within range 0 - 90° (not critical)

DETECTED: Electrons

ENERGY: Only electrons within a selected energy window are collected

ANALYZER ENERGY RESOLUTION: ∿0.025 - 0.1 eV (Energy Window)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19} - 10^{-14}$ A

SPECTRUM:

ORDINATE: Photoelectron Count Rate (Partial Yield)

ABSCISSA: Photon Energy

SAMPLE:

Single crystals
Polycrystalline materials
Adsorbed layers on metal substrates
Semiconductor surfaces

SELECTED REFERENCES:

(i) 'Photoemission and the Electronic Properties of Surfaces'
B. Feuerbacher, B. Fitton, R. F. Willis (editors)
Wiley-Interscience, New York, 1978.

(ii) 'Photoemission Spectroscopy'
B. Feuerbacher, B. Fitton
in 'Electron Spectroscopy for Surface Analysis',
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(iii) 'Synchrotron Radiation: Overview'
C. Kunz
in 'Photoemission in Solids II'
L. Ley and M. Cardona (editors)
Topics in Applied Physics, Volume 27, Springer-Verlag, 1979.

(iv) 'Partial Photoyield Study of Adsorbate-Substrate Interactions: O on Al'
R. Z. Bachrach, A. Bianconi, S. A. Flodstrom
Proceedings 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces (Vienna, 1977) p. 1205.

(d,e). Constant-Initial-State Spectroscopy (CISS), Constant-Final-State Spectroscopy (CFSS). (Strictly CIS-UPS and CFS-UPS). In discussing Constant-Initial-State and -Final-State Spectroscopies it may be helpful to stress that 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 previously described. Confusion arises if the final state is taken to be the continuum state of the photoemitted electron. Both CISS and CFSS involve photon energies in the vacuum UV range 10 - 50 eV.

(d). 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.

SUMMARY

NAME: Constant-Initial-State Photoelectron Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: CISS, CIS-UPS

INCIDENT: Variable Energy Photons

ENERGY RANGE: a scanned range of ∿5 - 20 eV within the overall range 10 - 50 eV. The extent of the scanned range is fixed by the final states and its position in the overall range is decided by the selected initial state.

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: within range 0 - 90° (not critical)

DETECTED: Electrons

ENERGY: 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 state (in the valence band) and the lowest unoccupied energy level - the final state.

ANALYZER ENERGY RESOLUTION: ∿0.025 - 0.1 eV (Energy Window)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19} - 10^{-14}$ A

SPECTRUM:

ORDINATE: Photoelectron Count Rate (Partial Yield)

ABSCISSA: Photon Energy

or

Photon Energy + Energy Difference (i.e., The FINAL STATE)

SAMPLE: Single crystals with or without adsorbed layer

SELECTED REFERENCES:

(i) 'Photoemission and the Electronic Properties of Surfaces'
B. Feuerbacher, B. Fitton, R. F. Willis (editors)
Wiley-Interscience, New York, 1978.

(ii) 'Photoemission Spectroscopy'
B. Feuerbacher, B. Fitton
in 'Electron Spectroscopy for Surface Analysis'
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(iii) 'Synchrotron Radiation: Overview'
C. Kunz
in 'Photoemission in Solids II',
L. Ley and M. Cardona (editors)
Topics in Applied Physics, Volume 27, Springer-Verlag, 1979.

(e). 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.

SUMMARY

NAME: Constant-Final-State Photoelectron Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: CFSS, CFS-UPS

INCIDENT: Variable Energy Photons

ENERGY RANGE: a scanned range of ∿5 - 20 eV within the overall range 10 - 50 eV. The extent of the scanned range is fixed by the extent of the occupied levels of the valence band (the Initial States)

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: within range 0 - 90° (not critical)

DETECTED: Electrons

ENERGY: The energy analyzer is held at a fixed energy (i.e., the Final State)

ANALYZER ENERGY RESOLUTION: ∿0.025 - 0.1 eV (Energy Window)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-14} A

SPECTRUM:

ORDINATE: Photoelectron Count Rate (Partial Yield)

ABSCISSA: Photon Energy (i.e., the INITIAL STATE)

SAMPLE: Single crystals with or without adsorbed layer

SELECTED REFERENCES:

(i) 'Photoemission and the Electronic Properties of Surfaces'
B. Feuerbacher, B. Fitton, R. F. Willis (editors)
Wiley-Interscience, New York, 1978.

(ii) 'Photoemission Spectroscopy'
B. Feuerbacher, B. Fitton
in 'Electron Spectroscopy for Surface Analysis',
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(iii) 'Synchrotron Radiation: Overview'
C. Kunz
in 'Photoemission in Solids II',
L. Ley and M. Cardona (editors)
Topics in Applied Physics, Volume 27, Springer-Verlag, 1979.

(f). 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.

SUMMARY

NAME: Angle-Resolved (Synchrotron-Radiation) Photoelectron Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: ARUPS, ARPES, ARXPS

ALTERNATIVE NAME: Angle-Resolved Photoemission (ARP)

INCIDENT: Fixed Energy Photons

ENERGY: within range 10 - 1000 eV (elliptically polarized)

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low

ANGLE OF INCIDENCE: Polar angle within range 0 - 90°
(not usually critical)
Azimuthal angle not critical

DETECTED: Photoelectrons

ENERGY RANGE: 0 eV to within a few eV of incident photon energy

ANALYZER ENERGY RESOLUTION: ∿0.1 - 0.025 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-11} A

ANGLE OF EXIT: either azimuthal angle fixed and polar angle varied (most common) or vice versa (see Photoelectron Diffraction)

ANGULAR RESOLUTION: High (<5°)

SPECTRUM:

ORDINATE: Photoelectron Current at stated polar (or azimuthal) angle

ABSCISSA: Photoelectron Energy (above Fermi Level)

SAMPLE: Atomic and molecular gases
Defined faces of single crystals
Chemisorbed layer

APPLICATIONS: Electronic structure of atoms and molecules
Identification of surface states from bulk states
Symmetry of states

SELECTED REFERENCES:

(i) 'Angle-Resolved Photoemission as a Tool for the Study of Surfaces'
E. W. Plummer and W. Eberhardt
in Advances in Chemical Physics, Volume XLIX,
I. Prigogine and S. A. Rice
John Wiley & Sons, New York, 1982.

(ii) 'Angular Dependent Photoemission'
N. V. Smith
in 'Photoemission in Solids I'
M. Cardona and L. Ley (editors)
Topics in Applied Physics, Volume 26, Springer-Verlag, 1978.

(g). Resonance-enhanced photoelectron spectroscopy. The mechanism of this process has already been discussed. 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 the adsorbate bond. Resonant processes are also observed in clean crystal surfaces.

SUMMARY

NAME: Resonance-Enhanced Photoelectron Spectroscopy

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYM: None

ALTERNATIVE NAME: Resonant Photoelectron Spectroscopy

INCIDENT: Fixed Energy Photons

ENERGY: 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.

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: Within range 0 - 90° (not critical)

DETECTED: Electrons

ENERGY RANGE: 0 eV to within a few eV of the incident photon energy

ANALYZER ENERGY RESOLUTION: ∿0.025 - 0.05 eV

ANGLE OF EXIT: Fixed. Value not critical.

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-15} - 10^{-9}$ A

SPECTRUM:

ORDINATE: Photoelectron Count Rate (showing enhanced resonance lines)

ABSCISSA: Analyzing Energy (Photoelectron Energy)

SAMPLE: Single crystals with/without a chemisorbed monolayer

SELECTED REFERENCES:

(i) 'Observation of Resonant Photoemission in an Adsorbed Molecule'
G. Loubriel, T. Gustafsson, L. I. Johansson and S. J. Oh
Phys. Rev. Lett., 49 (1982) 571.

(ii) 'Surface 4d-4f Photon Absorption and Surface Mixed Valence in Sn Metal'
J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau and S.B.M. Hagstrom
Phys. Rev. Lett., 41 (1978) 1499.

(iii) 'Two-Electron Resonance at the 3p Threshold of Cu and Ni'
M. Iwan, F. J. Himpsel, D. E. Eastman
Phys. Rev. Lett., 43 (1979) 1829.

(h). Extended X-ray absorption-fine-structure (EXAFS, SEXAFS). The mechanism of the process leading to this fine structure has already been discussed (see Note b.). These final state interference effects can be observed in several ways. One can measure the X-ray absorption transmission coefficient, the fluorescent X-ray yield, the Auger electron yield or the yield of a selected range of the inelastically scattered electrons as a function of the photon energy in the X-ray region. EXAFS-like effects (i.e., final state interference structure) are also observed in elastic electron scattering, appearance potential spectroscopy, electron energy loss spectroscopy and angle-resolved ultraviolet photoelectron spectroscopy. The techniques of relevance to electron spectroscopy are Auger yield analysis, known as Surface Extended X-ray Absorption-Fine-Structure (SEXAFS) and Inelastic Electron yield analysis, known as Partial Yield EXAFS. The fine-structure extended to several hundred electron volts above the threshold for the process. Most partial Yield EXAFS and SEXAFS (Auger Partial Yield EXAFS) studies are performed on the structure (oscillations with a period of about 30 eV) starting at ∿50 eV above threshold. Some work has been done on the X-ray Absorption Near-Edge Structure (XANES) and fine-structure (NEXAFS) using photoelectron spectroscopy (< 50 eV from threshold) but direct X-ray absorption is more satisfactory in this region.

Closely related to EXAFS and SEXAFS is Angle-Resolved Photoemission or Photoelectron Extended-Fine-Structure (ARPEFS) from adsorbate core levels. This angle-resolved structure can be Fourier Transformed to give the differences in path-length between the primary (unscattered) photoelectron wave and the substrate-atom-scattered photoelectron wave. Comparison of this data with model calculations gives both the distance and vector direction from the selected atom to nearby substrate atoms.

EXAFS studies are a probe of the local structure and symmetry of the surface. Thus unlike X-ray diffraction (XRD) or Low Energy Electron Diffraction (LEED), EXAFS can be applied to systems which have local structure but not necessarily long range structure, such as non-crystalline materials. In particular, bond lengths and local symmetry may be measured.

SUMMARY

NAME: Surface Extended X-ray Absorption-Fine-Structure

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: SEXAFS, Surface EXAFS

ALTERNATIVE NAME: Auger Partial Yield EXAFS

Note b. Note that 'S' in EXAFS does not denote 'spectroscopy' and that, in consequence, usage which implies 'spectroscopy', e.g., Partial-Yield EXAFS, is inappropriate.

RELATED TECHNIQUE: Angle-Resolved Photoemission or Photoelectron Extended-Fine-Structure (ARPEFS)

INCIDENT: Variable Energy Photons

ENERGY RANGE: 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.

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT PHOTON FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: not critical

DETECTED: Auger Electrons

ENERGY: fixed at the energy of the electrons from the selected Auger process

ANALYZER ENERGY RESOLUTION: ∿0.1 - 0.5 eV (Energy Window)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19} - 10^{-14}$ A

SPECTRUM:

ORDINATE: Auger Electron Count Rate (Auger Partial Yield)

ABSCISSA: Photon Energy

SAMPLE: Single crystals) with or without chemisorbed
Polycrystalline materials) monolayers
Polymeric and glassy materials

SELECTED REFERENCES:

(i) 'Developments in Extended X-ray Absorption Fine Structure Applied to Chemical Systems'
D. R. Sandstrom and F. W. Lytle
Ann. Rev. Phys. Chem., 30 (1979) 215.

(ii) 'EXAFS, Determination of Short Range Order and Local Structures in Materials'
D. C. Koningsberger and R. Prins
Trends Anal. Chem., 1 (1981) 16.

(iii) 'Direct Surface Structure Determination with Photoelectrons'
J. J. Barton, C. C. Bahr, Z. Hussain, S. W. Robey, J. G. Tobin, L. E. Klebanoff and D. A. Shirley
Phys. Rev. Lett., 51 (1983) 272-275.

I.5. Imaging Photoelectron Spectroscopy (SESCA or PESM types)

Two techniques have been reported which permit both the energy analysis (spectroscopy) and spatial analysis (microscopy) of the photoelectrons emitted by a surface. In Scanning Electron Spectroscopy for Chemical Analysis (SESCA) a thin film or slice of specimen is mounted on a thin aluminum foil. An electron beam is then scanned over the back of the foil producing X-rays which pass through the specimen liberating photoelectrons.

In Photoelectron Spectromicroscopy (PESM), on the other hand, no scanning or focussing elements are involved. The whole surface is irradiated from the front and the electron emission mapped by a divergent axially symmetric magnetic field. Both X-ray and ultraviolet radiation can be used in PESM.

(a). Scanning electron spectroscopy for chemical analysis (SESCA). The electron gun provides a primary electron beam of high energy (∿10 keV) and current ($\leq 3 \times 10^{-5}$ A) which is focussed to a spot ($\leq$ 0.5 μm diameter) and scanned across the aluminum foil by electro-

static deflection. The emitted photoelectrons are collected and energy analyzed by a high resolution double pass cylindrical mirror analyzer. The lateral resolution is limited by the foil thickness (about 2 μm) to approximately 15 μm.

SUMMARY

NAME: Scanning Electron Spectroscopy for Chemical Analysis

CLASS: Imaging Photoelectron Spectroscopies

ACRONYM: SESCA

INCIDENT: Fixed Energy Electrons

ENERGY: fixed within range 0.1 - 10 keV

ENERGY RESOLUTION: not critical

INCIDENT ELECTRON CURRENT: $3 \times 10^{-5} - 1 \times 10^{-10}$ A

BEAM DIAMETER: less than 0.5×10^{-6} m

ANGLE OF INCIDENCE: electron beam is scanned across aluminum foil

DETECTED: Photoelectrons

ENERGY RANGE: 0 eV to within a few eV of the X-ray photon energy

ANALYZER ENERGY RESOLUTION: ∿0.05 - 0.5 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-16} - 10^{-19}$ A

ANGLE OF EXIT: normal to surface

SPECTRUM:

ORDINATE: Photoelectron Current

ABSCISSA: Photoelectron Energy (Binding Energy)

SAMPLE: Thin sections of materials (which may be insulating) on thin aluminum foils (∿2 - 6 μm)

APPLICATIONS: Microscopy and imaging

SELECTED REFERENCES:

(i) 'Microanalyse et Microscopie Photoélectroniques: X-Principe et Performances Prévisibles'
J. Casaux
Rev. Phys. Appl., 10 (1975) 263.

(ii) 'SESCA: Scanning Electron Spectroscopy for Chemical Analysis'
C. T. Hovland
Proceedings 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces (Vienna, 1977) p. 2363.

(b). Photoelectron spectromicroscopy (PESM). The whole surface is irradiated with either ultraviolet radiation, soft X-ray radiation, slow metastable atoms or fast atoms. As the emitted photoelectrons travel along the divergent magnetic field lines the conservation of angular momentum (or, more precisely, the conservation of orbital moment) causes the transverse component of the electron's linear momentum to become axial so that when the electron is energy analyzed all the electron's momentum is in the forward (axial) direction. Retarding field energy analysis can be performed with a retarding grid and trochoidal energy analysis with a crossed electric field. The electrons are detected by an electron multiplier or phosphor screen. The lateral resolution is determined by the electron energy and the magnetic field strength and can reach 0.1 μm.

With soft X-rays as image generators elemental mapping can be perfomed and with ultraviolet radiation molecular information maps can be produced by analysis of the valence photoelectron spectrum, (i.e., molecular or chemical mapping).

SUMMARY

NAME: Photoelectron Spectromicroscopy

CLASS: Imaging Photoelectron Spectroscopies

ACRONYM: PESM

INCIDENT: Fixed Energy Photons

ENERGY: fixed within range 4 eV - 10 keV

ENERGY RESOLUTION: ∿0.001 eV (at ∿1 eV energy) to ∿1.5 eV (at 1487 eV)

INCIDENT PHOTON FLUX: High (at 20 eV energy) to low (above 100 eV)

BEAM DIAMETER: 1 - 5 mm

ANGLE OF INCIDENCE: from grazing to ∿80° (not critical)

MAGNETIC FIELD STRENGTH: 1 - 7 tesla

DETECTED: Photoelectrons

ENERGY RANGE: 0 eV to within a few eV of incident photon energy

ANALYZER ENERGY RESOLUTION: ∿0.015 - 0.1 eV

ELECTRON CURRENT AT DETECTOR: can be as high as 10^{-8} A

ANGLE OF EXIT: almost all angles of exit are collected and collimated by magnetic field

SPECTRUM:

ORDINATE: Photoelectron Current

ABSCISSA: Photoelectron Energy

This is an angle-integrated photoelectron spectrum

SAMPLE: Polycrystalline materials
Conducting films
Semiconductor surfaces

APPLICATIONS: Microscopy and imaging, particularly of radiation sensitive materials

SELECTED REFERENCES:

(i) 'Photoelectron Spectromicroscopy'
G. Beamson, H. Q. Porter and D. W. Turner
Nature, 290 (1981) 556.

(ii) 'Soft X-rays and Fast Atoms as Image Generators in Photoelectron Microscopy'
I. R. Plummer, H. Q. Porter, D. W. Turner, A. J. Dixon, K. Gehring, and M. Keenleyside
Nature, 303 (1983) 599-601.

I.6. Photoelectron Diffraction (PD)

Diffraction effects have been observed in angle-resolved photoelectron spectroscopy. This diffraction structure is very similar to that of Low Energy Electron Diffraction (LEED). The term X-ray Photoelectron Diffraction (XPD) is used for diffraction effects observed in an XPS experiment. Two experimental modes have been developed.

In Azimuthal Photoelectron Diffraction (APD) the sample is rotated about the surface normal, thus varying the azimuthal angle, and the energy-selected photoelectron intensity from the selected core level is recorded at a fixed polar angle and at fixed photon energy. This technique was developed initially to probe the azimuthal anisotropy of adsorbate systems. The azimuthal profile is very dependent on both the polar angle selected and the photon energy (i.e., the final state). Most APD experiments to date have involved photoelectrons with low kinetic energies so a synchrotron radiation source is usually employed, although it is not essential.

In Normal Photoelectron Diffraction (NPD) the energy-selected photoelectron intensity from a selected core level emitted normal to the surface is recorded as the photon energy swept through a wide range. A synchrotron radiation source is thus essential for this experiment. The other requirement is that the core level selected has a smoothly varying photoionization cross-section over the range of photon energies. The data recorded are very similar to the I-V curves of the LEED experiment (in fact they are a coherent superposition of several LEED beams).

Undoubtedly Photoelectron Diffraction will be compared with LEED. The experimental requirements of XPD make it unlikely that it will ever be as widely exploited as LEED. The advantages which PD has over LEED may be exploited in particular applications. These advantages are: the essentially non-destructive nature of the photon probe; the fact that the initial state in APD may be easily selected (thus allowing diffraction in an adsorbate - adsorbent system, for example, to be purely adsorbate-specific); and, the fact that, in NPD, the adlayer-substrate separation can be accurately determined, which is not always the case in LEED.

SUMMARY

NAME: Azimuthal Photoelectron Diffraction

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: APD, PD, PED

ALTERNATIVE NAMES: X-ray Photoelectron Diffraction (XPD, XPED)

INCIDENT: Fixed Energy Photons

ENERGY: X-ray region (1 - 2 keV) (often sychrotron radiation)

ENERGY RADIATION: ∿0.1 - 0.5 eV

INCIDENT PHOTON FLUX: Low

BEAM DIAMETER: ∿1 - 3 mm

ANGLE OF INCIDENCE: within range 70 - 85°

DETECTED: Photoelectrons from selected core level

ENERGY: Photoelectrons of low kinetic energy usually selected (< 100 eV)

ANALYZER ENERGY RESOLUTION: ∿ 0.1 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-15} A

ANGLE OF EXIT: Polar angle fixed
Azimuthal angle varied (0 - 360°)
by rotating sample about surface normal

SPECTRUM:

ORDINATE: Photoelectron Current

ABSCISSA: Azimuthal Angle

SAMPLE: Single crystals) with or without adsorbed
Polycrystalline materials) layer

APPLICATIONS: Similar to LEED but less destructive and more surface sensitive

SELECTED REFERENCE:

'Angular-Resolved Ultraviolet Photoemission Spectroscopy and Its Application to the Layer Components $TaSe_2$ and TaS_2'
N. V. Smith and M. M. Traum
Phys. Rev. B, 11 (1975) 2087.

SUMMARY

NAME: Normal Photoelectron Diffraction

CLASS: Synchrotron-Radiation Photoelectron Spectroscopies

ACRONYMS: NPD, PD, PED

ALTERNATIVE NAMES: X-ray Photoelectron Diffraction (XPD, XPED)
Synchrotron Photoelectron Diffraction

INCIDENT: Variable Energy Photons

ENERGY RANGE: ∿200 - 1500 eV (scanned range may be less than this)

ENERGY RESOLUTION: ∿0.1 eV

INCIDENT PHOTON FLUX: Medium to low

ANGLE OF INCIDENCE: within range 45 - 85°

DETECTED: Photoelectron from selected core level

ENERGY RANGE: from ∿0 eV to several hundred eV

ANALYZER ENERGY RESOLUTION: ∿0.1 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19} - 10^{-15}$ A

ANGLE OF EXIT: normal to surface

SPECTRUM:

ORDINATE: Photoelectron Count Rate

ABSCISSA: Incident Photon Energy

SAMPLE: Single crystals) with or without adsorbed
Polycrystalline materials) layer

APPLICATIONS: Similar to LEED but less destructive
Only technique for accurately determining adlayer-substrate separation geometry

SELECTED REFERENCES:

'Photoelectron-Diffraction Measurements of Sulfur and Selenium Adsorbed on Ni (001)'
S. D. Kevan, D. H. Rosenblatt, D. R. Denley, B-C Lu and D. A. Shirley
Phys. Rev. B, 20 (1979) 4133.

II. THE ELECTRON IMPACT SPECTROSCOPIES

The Electron Impact Spectroscopies can be subdivided into Electron Scattering Spectroscopies in which the detected particles are electrons, and Electron-Induced Photon Emission Spectroscopies in which the detected particles are photons.

II.A. The Electron Scattering Spectroscopies

The secondary electron signal produced by a primary electron beam impinging on a surface consists of several contributions. These are: coherent and incoherent elastically scattered electrons, inelastically scattered electrons, primary ionized electrons and Auger electrons.

The coherent and incoherent elastically scattered electrons are the basis of electron diffraction (LEED) and scanning electron microscopy (SEM) respectively. The primary ionized electrons and inelastically scattered electrons are detected and analyzed in the Electron Scattering Spectroscopies. The analysis of the Auger electrons is considered in a later section.

The spectroscopy based on the analysis of the ionized electrons is Ionization Spectroscopy and that based on the analysis of inelastically scattered electrons is Energy Loss Spectroscopy.

The very obvious dissimilarities between these electron induced spectroscopies and the corresponding photon induced spectroscopies arise from the fact that photons can only take part in one resonant absorption process but electrons can take part in many non-resonant scattering processes.

The principle of electron-energy-loss spectroscopy is that a primary electron beam of fixed energy is incident on a surface and the energy distribution of the secondary electrons is recorded. The difference in energy between a primary and a secondary electron corresponds to the energy loss. The major channels by which energy losses can occur are

(a). single valence-band electron excitations to unoccupied states of atoms and molecules and to states above the Fermi level in solids

(b). single core-electron excitations to unoccupied states about the Fermi level

(c). core-electron excitations to exciton states (formed by Coulomb coupling between the core hole and the excited electron)

(d). collective excitation of surface plasmons (oscillatory modes in the conduction electron gas)

(e). collective excitation of bulk plasmons

(f). excitation of surface phonons at clean surfaces

(g). excitation of the localized atomic vibrations in surface complexes formed by chemisorption of atoms or molecules

(h) local electron interference effects on core-ionization probabilities

II.A.1. High Resolution Electron Energy Loss Spectroscopy (HREELS, HEELS)

There are three different energy ranges of the primary electrons employed in electron energy loss spectroscopy. With primary electron energies in the range 4 - 10 eV the technique is Low Electron Energy Loss Spectroscopy (LEELS), also known as High Resolution Electron Energy Loss Spectroscopy (HREELS or HEELS). The primary electron beam is passed through an electron energy monochromator and focussed on the surface. The secondary electrons are collected by an energy analyzer after losing energies of the order of one eV mainly by processes (d), (e) and (g). The spectrum is presented as electron flux versus energy loss. The phonon excitation processes, (d) and (e), provide information on surface relaxation and dielectric behaviour. The chemisorption-dependent processes, (g), provide information on the nature of the adsorbed species, adsorbed states, adsorbed sites, nature of chemisorption bond, electronic rearrangements and reactive intermediates.

Most spectrometers employ thermionic cathodes to deliver a gun current of $\sim 2 \times 10^{-10}$ A at ~ 5 eV. Hemispherical, 127° and cylindrical mirror analyzers have all been used

successfully. Angle-dependent HREELS is now routine and the technique can be combined with LEED and AES.

HREELS has recently been applied to organic solid surfaces. With primary energies of 5 - 40 eV, an energy resolution of ~15 meV and an angular resolution of ~5°, energy losses corresponding to intramolecular vibrations, singlet and triplet excitons and σ electron excitations.

SUMMARY

NAME: High-Resolution Electron Energy Loss Spectroscopy

CLASS: Electron Scattering Spectroscopies

ACRONYMS: HREELS, HEELS

ALTERNATIVE NAME: Low Energy Electron Loss Spectroscopy (LEELS)

INCIDENT: Fixed Energy Electrons

ENERGY: within range 1 - 50 eV (typically 4 - 10 eV)

ENERGY RESOLUTION: ~0.01 - 0.05 eV

INCIDENT ELECTRON CURRENT: ~10^{-10} - 10^{-7} A

BEAM DIAMETER: ~1 - 3 mm

ANGLE OF INCIDENCE: within range 45 - 85°

ANGULAR RESOLUTION: High (1 - 5°)

DETECTED: Scattered Primary Electrons

ENERGY RANGE: Energy loss from 0.02 eV to several eV

ANALYZER ENERGY RESOLUTION: ~0.01 - 0.025 eV

ELECTRON CURRENT AT DETECTOR: ~10^{-3} of incident electron current

ANGLE OF EXIT: near specular (i.e., approximately equal to angle of incidence)

ANGULAR RESOLUTION: High (1 - 5°)

SPECTRUM:

ORDINATE: Electron Current

ABSCISSA: Electron Energy Loss (i.e., Incident Electron Energy - Analyzer Energy)

SAMPLE:

Atomic and molecular gases and beams
Single crystals) with or without adsorbed
Polycrystalline materials) layer
Thin films on metal substrates

APPLICATIONS:

Vibrational spectroscopy gas analysis
Phonon and plasmon excitations of crystal surfaces
Vibrational excitation of adsorbed layer

SELECTED REFERENCES:

(i) 'Resonance in Electron Impact on Diatomic Molecules'
G. J. Schulz
Rev. Modern Phys., 45 (1973) 423.

(ii) 'Electron Energy Loss Spectroscopy and Surface Vibrations'
H. Ibach and D. L. Mills
Academic Press, New York, 1982.

(iii) 'Study of Adsorbed Molecules by Electron Energy Loss Spectroscopy'
C.N.R. Rao, A. Srinivasan, K. Jagannathan
in Int. Rev. Phys. Chem., 1 (1981) 45.

(iv) 'Low Energy Electrons and Surface Chemistry'
G. Ertl and J. Kuppers
Verlag Chemie, Weinheim (1974).

II.A.2. Electron Energy Loss Spectroscopy (EELS, ELS)

With primary electron energies in the range 50 - 200 eV the technique is known as (Electron) Energy Loss Spectroscopy (EELS or ELS), Inelastic Electron Scattering Spectroscopy (IESS) or Characteristic (Energy) Loss Spectroscopy (CLS, CELS or CEELS). Here the major energy losses are through processes (a), (d) and (e) in the range 0 - 20 eV. Electronic excitation processes of atoms and molecules in the gas phase are conveniently studied. The technique is of particular value in the study of optically forbidden singlet-triplet transitions which are allowed under electron impact. The sample receives a collimated beam of electrons usually via a monochromator but in most cases monochromatization is not essential. The secondary electrons are usually collected over a relatively large solid angle and analyzed by a retarding grid structure in the case of solids. The predominant spectral features are the plasmon processes (d) and (e). These sometimes show structure due to the interaction of free-electron plasma oscillations with addition oscillations attributed to adsorbed atom transitions. Plasmon excitations can be studied in more detail by combining EELS with LEED to produce the technique Inelastic Low Energy Electron Diffraction (ILEED). Primary electron energies of 10 - 1000 eV are used.

With higher energy resolution (∿50 meV) surface vibrational modes, process (f), are observed. At the higher primary energies, the loss structure shows features arising from process (a) predominantly.

Energy Loss spectra are often presented as first or second derivatives of the electron current with respect to the energy loss.

A recent extension of EELS is Spin- and Energy-Analyzed Secondary Electron Emission Spectroscopy of ferromagnetic materials. The energy dependence of the spin polarization of low energy (0.5 - 25 eV) secondary electrons when a 500 eV primary beam of electrons is incident on a surface of a ferromagnetic glass. The polarization of the lowest-energy electrons is found to be a measure of the net valence-band spin density. This provides a technique for observing surface magnetic structure with the very high spatial resolution of scanning electron microscopy.

SUMMARY

NAME: Electron Energy Loss Spectroscopy

CLASS: Electron Scattering Spectroscopies

ACRONYMS: EELS, ELS

ALTERNATIVE NAMES: Inelastic Electron Scattering Spectroscopy (IESS)
Characteristic (Energy) Loss Spectroscopy (CLS, CELS)

INCIDENT: Fixed Energy Electrons

ENERGY: within range 50 - 200 eV

ENERGY RESOLUTION: ∿0.5 - 1.0 eV (unmonochromatised)
∿0.025 - 0.050 eV (with monochromatiser)

INCIDENT ELECTRON CURRENT: $\sim 10^{-10} - 10^{-5}$ A

BEAM DIAMETER: ∿1 - 5 mm

ANGLE OF INCIDENCE: within range 30 - 85°

ANGULAR RESOLUTION: High (1 - 3°)

DETECTED: Scattered Primary Electrons

ENERGY RANGE: Energy Losses from 0.005 eV to several eV

ANALYZER ENERGY RESOLUTION: Medium (0.1 - 0.2 eV) to Ultrahigh (0.005 - 0.05 eV)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-3}$ of incident electron current

ANGLE OF EXIT: near specular (i.e., approximately equal to angle of incidence)

ANGULAR RESOLUTION: High (1 - 5°) to Ultrahigh ($\sim 10^{-4}$ rad)

SPECTRUM:

ORDINATE: Electron Current

ABSCISSA: Electron Energy Loss (i.e., Incident Electron Energy - Analyzer Energy)

SAMPLE: Atomic and molecular gases and beams
Single crystals
Polycrystalline materials

SELECTED REFERENCES:

(i) 'Resonance in Electron Impact on Atoms'
G. J. Schulz
Rev. Modern Phys., 45 (1973) 378.

(ii) 'Electron Energy Loss Spectroscopy'
H. Frotzheim
in 'Electron Spectroscopy for Surface Analysis',
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(iii) 'Characteristic Loss Spectroscopy'
J. C. Riviere
in 'Moderne Verfahren de Oberflächenanalyse'
Dechema-Monographien, Band 78, Nr. 1537-1548, p. 83.

(iv) 'Electron Energy Loss Spectroscopy and Surface Vibrations'
H. Ibach and D. L. Mills
Academic Press, New York, 1982.

(v) 'Spin Polarization in Electron Scattering from Surfaces'
D. T. Pierce, R. J. Celotta
Adv. Electron. Electron Phys., 56 (1981) 219.

II.A.3. High Energy Electron Loss Spectroscopy (HEELS)

Higher energy primary electrons (10 - 100 keV) produce electron energy loss more characteristic of the bulk than the surface due to the greater penetration depth of the electrons. Gross structure in the dielectric loss spectrum arises mainly from bulk phonon and plasmon processes. Sharp peaks due to ionization and excitation events are not observed because of the multiple inelastic scattering that the primary electrons undergo before and after the event. However fine structure is observed in the ionization edge steps in the spectrum due to the interference of the electron waves of ionized core electrons backscattered towards the original core hole by near neighbour atoms. This is known as Extended Electron-Energy-Loss Fine Structure (EXELFS) and is equivalent to the Extended X-ray Absorption Fine Structure (EXAFS) associated with the photon absorption electron spectroscopies.

(a). Extended electron-energy-loss fine structure (EXELFS or EELFS). Experiments are performed with a high energy (∿80 keV), sharply focussed (0.3 nm), high current density (∿3 x 10^{-9} A m^{-2}) primary electron beam. This involves fitting a field emission electron gun to a Scanning Transmission Electron Microscope (STEM). The specimen is a thin film (∿10 nm) and the electron energy analyzer monitoring the backscattered electrons has a resolution of 3 - 10 eV. Energy losses for ionization edges are of the order of several hundred volts.

EXELFS provides similar local structural information to EXAFS, such as bond lengths, but has an overall better performance and, of course, does not require a synchrotron. Both EXELFS and EXAFS are particularly appropriate for a wide range of materials, including amorphous materials, and because of the local rather than extended structural information they provide are complementary to Low Energy Electron Diffraction (LEED).

SUMMARY

NAME: Extended Electron-Energy-Loss Fine Structure

CLASS: Electron Scattering Spectroscopies

ACRONYMS: EXELFS, EXELFSS, EELFS, EELFSS

ALTERNATIVE NAME: Surface Extended-Energy-Loss Fine Structure (SEELFS)

INCIDENT: Fixed Energy Electrons

ENERGY: 10 - 80 keV (typically 30 keV)

ENERGY RESOLUTION: not critical

INCIDENT ELECTRON CURRENT: High current density ($\sim$3 x 10^{-9} A m^{-2})

BEAM DIAMETER: $\sim$0.3 nm

ANGLE OF INCIDENCE: approximately normal to surface

DETECTED: Scattered Incident Electrons

ENERGY RANGE: energy loss for ionization $\sim$200 - 4000 eV

ANALYZER ENERGY RESOLUTION: 3 - 10 eV

ANGLE OF EXIT: $\sim$ 45°

SPECTRUM:

ORDINATE: Backscattered Electron Current or its first or second derivative with respect to incident electron energy (Energy Loss Function)

ABSCISSA: Incident Electron Energy

SAMPLE: Thin films
Single crystals
Amorphous materials

APPLICATIONS: Fourier transform of spectrum gives local structure

SELECTED REFERENCE:

'Extended Fine Structure on the Carbon Core Ionization Edge Obtained from Nanometre-Sized Areas with Electron Energy Loss Spectroscopy'
P. E. Batson, A. J. Craven
Phys. Rev. Lett., 42 (1979) 893.

II.A.4. Ionization Spectroscopy (IS)

In Ionization Spectroscopy (IS) a core electron is excited to the Fermi level. The technique is also known as Ionization Loss Spectroscopy (ILS) or Core-Level Characteristic Loss Spectroscopy (CLS). The core electron excitation produces a weak edge (step) in the distribution of backscattered electrons as a function of incident electron energy when the loss energy is equal to the binding energy of the core electron. These weak ionization edges have to be distinguished from the more intense Auger electrons. This is achieved by using the fact that the intensity of electrons scattered after core ionization processes depends on the primary electron energy but the Auger electron signal does not.

There are two methods of recording the characteristic loss spectrum. In the first method, the primary beam energy is modulated by a small alternating voltage. The retarding voltage of a conventional retarding field analyzer is then swept in the usual way. The signal is detected with a lock-in amplifier in phase with the primary modulation to select only features whose energy loss is associated with the primary beam energy change.

In the second method, a cylindrical mirror analyzer of fixed band-pass energy is used. The energy loss features are then swept through this fixed energy window by varying the primary energy.

Primary electron energies in the range 200 - 2000 eV and fairly large primary currents of ∿500 μA are usually employed. For comparison the primary current in Auger electron spectroscopy is ∿20 μA. The core-level characteristic loss spectrum is usually presented as the second derivative of the energy loss function.

The spectrum shows that associated with each core level there is an edge that reflects the density of conduction band states near the Fermi energy. Thus Ionization Spectroscopy provides information complementary to that from X-ray Photoelectron Spectroscopy. There is, however, one important distinction. In a direct excitation spectroscopy, such as XPS, the only limitation to the detail that can be detected in the density of states is instrumental - the resolution of the instrument. In an indirect excitation spectroscopy, such as IS, the localized core electron overlaps only part of the conduction states. The selected core level is a window through which we can view a very local density of states. It is a consequence of the uncertainty principle that a localized view will be fuzzy and this is seen as a broadening introduced by the finite lifetime of the core hole.

SUMMARY

NAME: IONIZATION SPECTROSCOPY

CLASS: Electron Scattering Spectroscopies

ACRONYM: IS

ALTERNATIVE NAMES: Ionization Loss Spectroscopy (ILS)
Core-Level Characteristic Loss Spectroscopy (CLS)

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 250 - 1000 eV

ENERGY RESOLUTION: ∿1 eV

INCIDENT ELECTRON CURRENT: ∿5 x 10^{-4} A

BEAM DIAMETER: ∿3 mm

ANGLE OF INCIDENCE: either ∿0° or 45°

DETECTED: Scattered Incident Electrons

ENERGY: 100 - 500 eV

ANALYZER ENERGY RESOLUTION: ∿1 eV

ELECTRON CURRENT AT DETECTOR: ∿10^{-7} A

ANGLE OF EXIT: not critical (typically ∿45°)

SPECTRUM:

ORDINATE: Second derivative of backscattered electron current with respect to incident electron energy (Energy Loss Function)

ABSCISSA: Incident Electron Energy

SAMPLE: Single crystals
Polycrystalline materials
Semiconductor surfaces

SELECTED REFERENCES:

(i) 'Electron Excited Core Level Spectroscopies'
J. Kirschner
in 'Electron Spectroscopy for Surface Analysis'
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(ii) 'Inner Shell Ionization of Surface Atoms by Electron Impact'
R. L. Gerlach, A. R. DuCharme
Surf. Sci., 29 (1972) 317.

II.A.5. Electron Transmission Spectroscopy (ETS)

Electron Transmission Spectroscopy has been performed on thin films (1 - 10 nm) of organic materials with low energy electrons (0 - 15 eV). The sample is mounted on a stainless steel block at ∿80K. The current to the steel block is recorded as a function of incident electron energy. The transmission spectrum is presented as the first derivative of this current with respect to incident energy versus the incident energy. The spectrum approximately represents the first derivative of the density of states of the vacant conduction bands. The position of onset of the main peak giving the energy of the top of the conduction band. The conduction bands in molecular solids are formed from the free molecule valence levels and additional structure can arise from intermolecular interactions. This is one of the few electron spectroscopies to be applied to molecular crystals.

SUMMARY

NAME: Electron Transmission Spectroscopy

CLASS: Electron Scattering Spectroscopies

ACRONYM: ETS

INCIDENT: Variable Energy Electrons

ENERGY RANGE: ∿0 - 15 eV

ENERGY RESOLUTION: ∿0.1 eV

INCIDENT ELECTRON CURRENT: $\sim 10^{-9}$ - 10^{-5} A

BEAM DIAMETER: 1 - 3 mm

ANGLE OF INCIDENCE: normal to surface

DETECTED: Transmitted Scattered Electrons

ENERGY RANGE: ∿0 - 15 eV

ANALYZER ENERGY RESOLUTION: Not applicable. No energy analysis of transmitted electrons

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-4}$ - 10^{-3} of incident electron current

ANGLE OF EXIT: normal to surface

SPECTRUM:

ORDINATE: First derivative of transmitted electron current with respect to incident electron energy

ABSCISSA: Incident Electron Energy

SAMPLE: Thin films (∿1 - 10 nm) of molecular organic materials mounted on stainless steel block (collector) at ∿80K

SELECTED REFERENCE:

'Conduction Band Structure of Solid n-Alkanes Studied by Electron-Transmission Spectra'
K. Hiraoka and M. Nara
Chem. Phys. Lett., 94 (1983) 589.

II.B. The Electron-induced Photon Emission Spectroscopies

The photon emission spectra produced by primary electron beams impinging on a surface consist of contributions from two distinct mechanisms.

The first of these is decay of the excited core-state by X-ray emission following transitions of valence or core electrons from occupied states to the unoccupied core state. If core-core transitions are involved the technique is X-ray Emission Spectroscopy (XES) (also known as X-ray Fluorescence (XRF)) or Energy-Dispersive (X-ray Analysis) Spectroscopy (EDS) and if valence-core transitions are involved the technique is Valence Band X-ray Emission Spectroscopy (VBXES) or Soft X-ray Emission Spectroscopy (SXES). If these regions are combined for the purpose of elemental analysis this technique is known as Electron Probe Micro Analysis (EPMA).

The second mechanism involves transitions from the free-electron-like states of the incoming electrons, as they are accelerated by the potential inside the surface, to unoccupied states of the surface above its Fermi level with the consequent emission of bremsstrahlung radiation.

At low electron and photon energies, both the energy and direction of the incident beam can be precisely defined. In this regime, both energy and momentum are conserved leading to $\vec{k}$ -selected spectra and the technique is called Inverse Photoemission or Photoelectron Spectroscopy (IPES or IPS) (see Note c.). Angle-resolved Inverse Photoemission studies lead to $\vec{k}$ -resolved Inverse Photoemission Spectroscopy (KRIPES) which can map the $E(k_{11})$ relations in the unoccupied states. This complements Angle-resolved Ultraviolet Photoelectron Spectroscopy (ARUPS) which measures the $E(k_{11})$ relations in the occupied states. Spin-polarized electron sources can be used to study magnetic materials with the technique known as Spin-polarized Inverse Photoemission Spectroscopy (SPIPES).

At higher electron and photon energies the spectrum arises from the $\vec{k}$ -integrated density of states because of thermal and other broadening effects on $\vec{k}$. In this regime the technique is called Bremsstrahlung or Characteristic Isochromat Spectroscopy (BIS). Bremsstrahlung spectra are recorded in the X-ray region (BIS) or ultraviolet region (UVBIS).

Recently, an experiment in momentum-resolved Bremsstrahlung Spectroscopy has been reported. Here as the incident electron energy in an IPES experiment is varied the photon spectrum (as opposed to an isochromat) is recorded. Spectral multiplexing techniques and high photon sensitivity permit photon polarization to be detected. Note that this is a low electron energy ultraviolet photon inverse photoemission experiment NOT the higher energy X-ray continuum Bremsstrahlung spectroscopy.

II.B.1. Inverse Photoemission Spectroscopy (IPS)

Electrons of low energy ($\sim$ few tens of eV) are incident on a clean surface. Ultraviolet Bremsstrahlung radiation intensity at a fixed frequency is recorded. In $\vec{k}$ -resolved Inverse Photoemission Spectroscopy (KRIPES) the isochromat is recorded as a function of angle of incidence of the electron beam. The spectra are usually presented as isochromat intensity versus energy of electron beam above Fermi energy. Unoccupied surface states can be identified as structure in this spectrum arising when the free electron energy, E(k), matches an energy level of the surface. The dipole matrix element for this process is the same as that for the photoelectron emission process. Thus this process is the time reversal of photoelectron emission.

IPES is very surface sensitive. It is a probe of the wave functions of the one-electron surface states and, recently, of the lowest empty orbitals of adsorbate molecules.

Note c. These names though in common usage should ultimately be replaced by the term 'Electron-Induced Photon Emission'.

Spin-polarized Inverse Photoemission Spectroscopy (SPIPES) is a probe of the d-band spin states of magnetic materials. The efficiency of GaAs spin- polarized electron sources have led to the rapid development of this spectroscopy since 1979. It is simpler to perform than the complementary spin-polarized photoelectron emission spectroscopy. The interpretation of IPES is much easier than BIS as in IPES only the initial state is varied but in BIS both initial and final states are varied.

In general polycrystalline samples are preferred as this averages crystal orientation effects so that the true density of states without initial state or angular effects is observed.

SUMMARY

NAME: Inverse Photoemission Spectroscopy

CLASS: Electron-Induced Photon Emission Spectroscopies

ACRONYMS: IPS, IPES

ALTERNATIVE NAME: Ultraviolet Bremsstrahlung Spectroscopy (UVBIS)

RELATED TECHNIQUES: $\vec{k}$-resolved Inverse Photoemission Spectroscopy (KRIPES) (i.e., Angle-resolved IPS)
Spin-polarized Inverse Photoemission Spectroscopy (SPIPES)

INCIDENT: Variable Energy Electrons

ENERGY RANGE: ∿10 - 20 eV, i.e., few tenths of an eV to ∿10 eV above the Fermi Level

ENERGY RESOLUTION: 0.1 - 0.5 eV

INCIDENT ELECTRON CURRENT: $\sim 10^{-7}$ A

BEAM DIAMETER: ∿1 mm

ANGLE OF INCIDENCE: varied from 0 - 30° (IPS)
10 - 20° (fixed in range) in KRIPES and angle-resolved SPIPES

ANGULAR RESOLUTION: High

DETECTED: Fixed Energy Photons

ENERGY: within the range 6 - 10 eV

ANALYZER ENERGY RESOLUTION: 0.4 - 0.7 eV (in most cases resolution is limited to ∿0.7 eV by the Geiger-Muller Detector)

PHOTON FLUX AT DETECTOR: from several hundred counts per second to a few counts per second

ANGLE OF EXIT: not critical (usually about 45°)

ANGULAR RESOLUTION: usually low (10% of maximum 2π steradians) but, if count rates permit, can be improved to ∿6°

SPECTRUM:

ORDINATE: Photon Flux (Isochromat Intensity)

ABSCISSA: Incident Electron Energy (usually presented as Electron Energy above Fermi Level)

SAMPLE: Defined faces of single crystals with or without an adsorbed layer. For SPIPES the crystal must be ferromagnetic.

APPLICATIONS: Investigation of unoccupied electronic surface states and conduction band densities-of-states

SELECTED REFERENCES:

(i) 'New Probe for Unoccupied Bands at Surfaces'
J. B. Pendry
Phys. Rev. Lett., 45 (1980) 1356.

(ii) 'Inverse Photoemission Observation of an Unoccupied Surface State on Pd (111)'
P. D. Johnson and N. V. Smith
Phys. Rev. Lett., 49 (1982) 290.

(iii) 'Empty Orbitals of Adsorbates Determined by Inverse Ultraviolet Photoemission'
F. J. Himpsel and Th. Fauster
Phys. Rev. Lett., 49 (1982) 1583.

(iv) 'Spin-Polarized Inverse Photoelectron Spectroscopy (SPIPES) of Solid Surfaces: Ni (110)'
J. Unguris, A. Seiler, R. J. Celotta, D. T. Pierce, P. D. Johnson and N. V. Smith
Phys. Rev. Lett., 49 (1982) 1047.

II.B.2. Bremsstrahlung Isochromat Spectroscopy (BIS)

In Bremsstrahlung Spectroscopy the spectrum is formed by transitions into the one-electron $\vec{k}$-integrated densities of states. As higher electron and photon energies are employed than in Inverse Photoemission the wave vector $\vec{k}$ is broadened by thermal and other collective factors.

In Bremsstrahlung Isochromat Spectroscopy (BIS), Characteristic Isochromat Spectroscopy (CIS) or X-ray Continuum Isochromat Spectroscopy (XIS) electrons of high energy (1 - 2 keV) are incident on the surface and the photon intensity at constant wavelength is recorded as the electron energy is varied. Usually the photon energy is close (< 50 eV) to the electron energy. Extreme vacuum ($\sim 10^{-12}$ Torr) is essential. Depth resolutions of a few nanometres can be achieved. As the photon energy observed is fixed as the electron energy varies both initial and final states are varied in this spectroscopy.

This technique is used, in conjunction with XPS, to provide the one-electron density of states of f and d levels of transition metals and rare-earth metals. The XPS spectrum gives the filled part of the density of states and the BIS spectrum, if the initial and final states are matched, gives the unoccupied part of the density of states.

Note that the recent technique of momentum-resolved Bremsstrahlung spectroscopy is a low energy inverse photoemission spectroscopy not an X-ray Isochromat Spectroscopy.

SUMMARY

NAME: Bremsstrahlung Isochromat Spectroscopy

CLASS: Electron-Induced Photon Emission Spectroscopies

ACRONYM: BIS

ALTERNATIVE NAMES: X-ray Bremsstrahlung Spectroscopy (XBIS)
Characteristic Isochromat Spectroscopy (CIS)
X-ray Continuum Isochromat Spectroscopy (XIS)

INCIDENT: Variable Energy Electrons

ENERGY RANGE: $\sim$1 - 2 keV

ENERGY RESOLUTION: ~1 eV

DETECTED: Fixed Energy Photons

ENERGY: usually an isochromat energy corresponding to a characteristic X-ray line used in XPS is chosen within the range 1 - 2 keV

ANALYZER ENERGY RESOLUTION: ~0.4 eV

PHOTON FLUX AT DETECTOR: Low (~ few hundred counts per second or less)

SPECTRUM:

ORDINATE: Photon Flux (Isochromat Intensity)

ABSCISSA: Incident Electron Energy

SAMPLE: Single crystal and polycrystalline surfaces of transition metals and rare-earth metals. Usually under UHV conditions without an adsorbed layer.

APPLICATIONS: Measurement of the density-of-states function for the unoccupied part of the d- and f-valence bands of the above samples. Usually presented with the complementary XPS data for the occupied part of the valence band. (For density-of-occupied-states function, from XPS, and the density-of-unoccupied-states function, from BIS, to be complementary the photon energy in the XPS experiment and the isochromat energy in the BIS experiment must be the same).

SELECTED REFERENCES:

(i) 'Study of the 4f Levels in Rare-Earth Metals by High-Energy Spectroscopies'
J. K. Lang, Y. Baer and P. A. Cox
Phys. Rev. Lett., 42 (1978) 74.

(ii) 'Density of Unfilled One-Electron Levels on Elements Vanadium and Iron through Zinc by Means of X-ray Continuum Isochromats'
R. R. Turtle and R. J. Liefeld
Phys. Rev. B, 7 (1973) 3411.

II.B.3. Momentum-resolved Bremsstrahlung Spectroscopy (BS)

This is an Inverse Photoemission Spectroscopy not an X-ray Bremsstrahlung Isochromat Spectroscopy. The confusion in nomenclature is unfortunate.

In Bremsstrahlung Spectroscopy (BS) the incident electron energy is varied and simultaneously a part of the photon spectrum is recorded. Thus, it is not an isochromat spectroscopy. This has been made possible by the recent development of multiplexed ultraviolet photon detectors based on electron microchannel plate multipliers with CsI evaporated on the front face to provide ultraviolet sensitivity. Thus, the energy of the initial state of the electrons can be made constant by scanning, in effect, both electron and photon energy. Bremsstrahlung Spectroscopy is the Inverse Photoemission Constant-Initial-State Spectroscopy corresponding to the Synchrotron-Radiation Constant-Final-State Photoelectron Spectroscopy.

Since the parallel component (relative to the sample surface) of the wave vector of the incoming electron is unchanged in passing through the surface barrier and the momentum of the ultraviolet photon is small with respect to that of the electron, the parallel component of the final state wave vector is known. The polarization of the photon gives additional information about the symmetry of the states involved.

Bremsstrahlung Spectroscopy is very inefficient. The efficiency is $\sim 10^{-8}$ photons per electron in a photon energy interval of 1 eV and over a solid angle of 2π. Angular relationships have not yet been investigated. This is the only one of the electron-photon

spectroscopies to detect the photon polarization and the combination of this feature with a spin-polarized electron source will lead to exciting developments.

SUMMARY

NAME: Momentum-Resolved Bremsstrahlung Spectroscopy

CLASS: Electron-Induced Photon Emission Spectroscopies

ACRONYM: BS

RELATED TECHNIQUE: Angle-Resolved Bremsstrahlung Spectroscopy

INCIDENT: Variable Energy Electrons

ENERGY RANGE: ∿10 - 20 eV (i.e., few tenths of an eV to ∿10 ev above Fermi Level)

ENERGY RESOLUTION: ∿0.25 eV

INCIDENT ELECTRON CURRENT: $\sim 10^{-4}$ A

BEAM DIAMETER: ∿1 mm

ANGLE OF INCIDENCE: within range 0 - 60° (Angle-resolved BS involves varying this angle of incidence)

ANGULAR RESOLUTION: ∿6°

DETECTED: Photons

ENERGY RANGE: 10 - 40 eV (scanned range may be less than this)

ANALYZER ENERGY RESOLUTION: ∿0.3 eV

PHOTON FLUX AT DETECTOR: Low (the selected range of the photon spectrum is recorded simultaneously with a multi-channel detector). Depolarization of the photons is detected.

SPECTRUM:

ORDINATE: Intensity of parallel component of photon wavevector

ABSCISSA: Incident Electron Energy relative to Fermi Level

SAMPLE: Defined face of single crystal or polycrystalline material

APPLICATIONS: Investigation of unoccupied electronic surface states

SELECTED REFERENCE:

'Spectrometer for Momentum-Resolved Bremsstrahlung Spectroscopy'
Th. Fauster, F. J. Himpsel, J. J. Donelon and A. Marx
Rev. Sci. Instrum., 54 (1983) 68.

III. THE APPEARANCE POTENTIAL SPECTROSCOPIES

These are electron spectroscopies based on the principle of measuring the threshold energies for the creation of excited states of matter. They range from inelastic electron tunneling spectroscopy, concerned with the thresholds for the excitation of molecular vibrations at energies less than 500 meV, to the nuclear resonance capture spectroscopies at energies greater than 1 MeV. A particular feature is that no energy analysis of the decay of the excited states is required. It is the energy of the exciting particle that is recorded. The appearance potential spectroscopies used in surface studies all employ differentiation to separate the structure due to threshold excitation from the background of primary and scattered electrons.

The major appearance potential spectroscopies employed in surface studies are Soft X-ray Appearance Potential Spectroscopy (SXAPS), Auger Electron Appearance Potential Spectroscopy (AEAPS), Disappearance Potential Spectroscopy (DAPS), Total Current Spectroscopy (TCS), X-ray Excited Electron Appearance Potential Spectroscopy (XEAPS), Electron (or Extended) Appearance-Potential Fine-Structure Analysis or Spectroscopy (EAPFS, EAPFSS) and Inelastic Electron Tunneling Spectroscopy (IETS). Where Appearance Potential Spectroscopy (APS) is referred to without the particular form being specified it is conventionally assumed that SXAPS is the technique.

III.1. Soft X-ray Appearance Potential Spectroscopy (SXAPS)

In this technique, also known as X-ray Appearance Potential Spectroscopy (XAPS) or Electron excited X-ray Appearance Potential Spectroscopy (EXAPS), core holes are produced by an electron beam incident on the surface. As the energy of this electron beam is increased each threshold for the production of a core hole by electron excitation or ionization is marked by a sudden 'appearance' of soft x-ray fluorescence characteristic of the energy level concerned. These characteristic soft X-rays are superimposed on a large bremsstrahlung background and at each threshold there is a step in the total X-ray flux.

The incident electron energy is usually modulated by adding a sine wave oscillation (usually 6 - 10 kHz) to the accelerating voltage. The X-ray fluorescence is not wavelength analyzed but the total flux is recorded. Although photomulpliers were initially used, the high S/N ratio needed to distinguish the threshold steps from the bremsstrahlung has led to the use of cooled silicon diodes which have a detection efficiency of approximately unity and a lower intrinsic background. Background due to secondary electrons is removed by a negatively biassed grid and bremsstrahlung background is reduced by a thin aluminum foil. Signal-to-noise considerations are still important as the bremsstrahlung yield rises linearly with the energy of the exciting electrons. The modulation signal and the total fluorescence yield signal are input to a lock-in amplifier and the output of this amplifier is differentiated once or twice and plotted against the incident electron energy to give the soft X-ray appearance potential spectrum.

Soft X-rays have energies in the range $\sim$6000 eV down to 100 eV. The electron energies employed in SXAPS are usually less than 1000 eV but may be up to 2000 eV. The main applications of SXAPS are in elemental analysis of metals, semiconductors and insulators. It can also be employed in the study of adsorbed atom - surface atom bonds. SXAPS is the highest energy-resolution appearance potential spectroscopy at the present time.

SUMMARY

NAME: Soft X-ray Appearance Potential Spectroscopy

CLASS: Appearance Potential Spectroscopies

ACRONYMS: SXAPS, XAPS

ALTERNATIVE NAMES: Electron-Excited X-ray Appearance Potential Spectroscopy (EXAPS, EEXAPS)

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 100 - 2000 eV (100 - 100 eV typical)

ENERGY RESOLUTION: $\sim$1 eV

INCIDENT ELECTRON CURRENT: $\sim 10^{-4}$ - 2×10^{-3} A

BEAM DIAMETER: $\sim$10 mm

ANGLE OF INCIDENCE: approximately normal to surface

DETECTED: Soft X-ray Photons

ENERGY: approx. 50 - 1000 eV. No energy analysis.
Total X-ray Flux recorded.

ANALYZER ENERGY RESOLUTION: not applicable. No energy analysis.

ANGLE OF EXIT: almost all photons within the maximum 2π steridians are collected

PHOTON FLUX AT DETECTOR: $\sim 10^{-9}$ of incident electron current

SPECTRUM:

ORDINATE: Total X-ray Flux

ABSCISSA: Primary Electron Energy (Excitation Energy)

SAMPLE: Polycrystalline metal surfaces
Semiconductor surfaces
Insulating materials

APPLICATIONS: Mainly elemental analysis
High surface and analytical sensitivity

SELECTED REFERENCES:

(i) 'Electron-Excited Core Level Spectroscopies'
J. Kirschner
in 'Electron Spectroscopy for Surface Analysis'
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(ii) 'Appearance Potential Spectroscopy and Related Techniques'
A. M. Bradshaw
Surface and Defect Properties of Solids, Volume 3 (1974), Specialist Periodical Reports, Chemical Society, London.

III.2. Auger-Electron Appearance Potential Spectroscopy (AEAPS)

This spectroscopy is also known as Electron-Excited Auger-Electron Appearance Potential Spectroscopy (EAAPS) or Incident Energy Modulation Method Spectroscopy (IEMM).

As in SXAPS, core holes are produced by an electron beam incident on the surface. As the energy of this electron beam is increased the threshold for the production of a core hole by electron excitation or ionization is reached. At the threshold for core hole production there is a sudden 'appearance' or increase in both the X-ray fluorescence yield and secondary electron current. The additional photons and Auger electrons produced at the core hole threshold are isotropically directed unlike the background of quasielastically reflected electrons and inelastically scattered electrons which in the latter case tend to be directed in the forward direction into the bulk of the sample. These soft X-ray photons and Auger electrons can produce further secondary electrons so the secondary electron current is greater after the threshold than before it.

The incident electron energy is modulated as described for SXAPS. A broadband filter is employed to remove the background electrons for the Auger Signal. The modulation and the Auger electron signal are input to a lock-in amplifier and the output, differentiated once or twice, is plotted against excitation energy to give the Auger electron appearance

potential spectrum. In general AEAPS is 10^4 - 10^5 times more sensitive than SXAPS and ~100 times more sensitive than DAPS.

At low energies ($\lesssim$ 100 eV) the technique suffers from artifacts due to diffraction effects. Thus, while SXAPS is usually employed on single crystals or metallic samples, AEAPS is more usually employed on polycrystalline surfaces or films.

SUMMARY

NAME: Auger-Electron Appearance Potential Spectroscopy

CLASS: Appearance Potential Spectroscopies

ACRONYM: AEAPS

ALTERNATIVE NAMES: Incident Energy Modulation Method (IEMM)

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 100 - 2000 eV

ENERGY RESOLUTION: ~1 eV (typically)

INCIDENT ELECTRON CURRENT: ~10^{-4} A

BEAM DIAMETER: ~10 mm

ANGLE OF INCIDENCE: approximately normal to surface

DETECTED: Secondary Auger Electrons

ENERGY: 50 - 1400 eV

ANALYZER ENERGY RESOLUTION: Not applicable. A broad-band energy filter is used to separate the high energy Auger electron signal from the low energy secondary electron signal

ANGLE OF EXIT: usually 2π steradians

ELECTRON CURRENT AT DETECTOR: ~10^{-4} of incident electron energy

SPECTRUM:

ORDINATE: Auger Electron Current

ABSCISSA: Primary Electron Energy (Excitation Energy)

SAMPLE: Polycrystalline metal surfaces
Semiconductor surfaces

APPLICATIONS: Mainly elemental analysis
High surface and analytical sensitivity

SELECTED REFERENCES:

(i) 'Introduction to Surface Spectroscopies'
R. L. Park
Experimental Methods in Catalytic Research, Volume III, (1976) 1,
R. B. Anderson, P. T. Dawson (editors).

(ii) 'Appearance Potential Spectroscopy and Related Techniques'
A. M. Bradshaw
Surface and Defect Properties of Solids, Volume 3 (1974),
Specialist Periodical Reports, Chemical Society, London.

III.3. Disappearance Potential Spectroscopy (DAPS)

As with SXAPS and AEAPS core holes are created by a variable energy electron beam. At the threshold of excitation the electrons in the primary beam, which create the core hole, disappear from the beam. In DAPS it is the attenuation of the primary beam which is studied. As no secondary processes contribute to this attenuation DAPS observes the excitation directly without any interference from the decay processes. The attenuation of the primary beam is small (∿1 in 10^3).

The electron gun in the DAPS experiment must provide a beam of variable energy (50 - 2000 eV) with constant intensity and beam profile. This necessitates an electron optical lens system and a constant emission control circuit for the thermionic cathode. A simple electron energy analyzer is required to select the elastic part of the secondary electron signal. The pass energy of the analyzer must vary with the energy of the primary beam. Cylindrical mirror analyzers or retarding field analyzers with large acceptance angles are usually employed. The large acceptance angle is necessary to minimize diffraction effects and maximise the signal. To enhance the DAPS signal modulation can be applied. This is achieved by modulating (∿0.1 - 1.0 volt at 6-10 kHz) the target potential and the energy of the primary beam.

The applications of DAPS are mainly based on its elemental sensitivity. It is very surface sensitive (1 - 3 atomic layers) and simpler to interpret than other elemental analysis techniques, offering only a few lines per element and no fine structure.

SUMMARY

NAME: Disappearance Potential Spectroscopy

CLASS: Appearance Potential Spectroscopies

ACRONYM: DAPS

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 50 - 2000 eV (modulated with 0.1 - 1.0 volt A.C. at 6 - 10 kHz)

ENERGY RESOLUTION: ∿1 eV or better

INCIDENT ELECTRON CURRENT: ∿10^{-4} A. Incident electron beam current must be stable to 1 in 10^4 or better

BEAM DIAMETER: ∿2 - 10 mm

ANGLE OF INCIDENCE: approximately normal to surface

DETECTED: Attenuation of Primary Electron Beam

ATTENTUATION OF PRIMARY BEAM: ∿1 in 10^3

ELECTRON CURRENT AT DETECTOR: ∿10^{-8} - 10^{-4} A

SPECTRUM:

ORDINATE: Electron Current at Sample (Target Current)

ABSCISSA: Primary Electron Energy (Excitation Energy)

SAMPLE: Polycrystalline metal surfaces
Semiconductor surfaces

APPLICATIONS: Mainly elemental analysis
High surface sensitivity

SELECTED REFERENCES:

(i) 'Electron-Excited Core Level Spectroscopies'
J. Kirschner
in 'Electron Spectroscopy for Surface Analysis'
H. Ibach (editor)
Topics in Current Physics, Volume 4, Springer-Verlag, 1977.

(ii) 'A Novel Electron Spectrometer for Surface Studies'
J. Kirschner and P. Staib
Phys. Lett., 42a (1973) 335.

III.4. Total (or Target) Current Spectroscopy (TCS)

In TCS a beam of low energy electrons varied over the range 0 - 15 eV is incident on the surface and the threshold of secondary electron processes are recorded by monitoring the current to the target rather than by energy analysis of the secondary electrons. TCS is thus similar to DAPS but should not be confused with it. TCS is a very low energy technique and all the secondary electrons originate in the valence band whereas DAPS is a higher energy, core ionization technique. The TCS signal is displayed as a function of increasing energy, starting at zero incident energy. Thus, the low energy part of the spectrum is not influenced by the higher energy loss processes which take place simultaneously and which are observed in some of the other low energy techniques, for example EELS. TCS seems particularly suited to the study of work functions, chemisorption, physisorption and excitons.

SUMMARY

NAME: Total Current Spectroscopy

CLASS: Appearance Potential Spectroscopy

ACRONYM: TCS

ALTERNATIVE NAME: Target Current Spectroscopy

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 0 - 15 eV (modulated at 430 Hz, 0.15 eV)

ENERGY RESOLUTION: $\sim$0.5 eV

INCIDENT ELECTRON CURRENT: $\sim 10^{-4}$ A

ANGLE OF INCIDENCE: normal to surface

DETECTED: Change in Target Electron Current

FRACTIONAL TARGET CURRENT CHANGE: $\sim$1 in 10^{3}

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-8}$ - 10^{-4} A

SPECTRUM:

ORDINATE: First derivative of target current with respect to incident electron energy

ABSCISSA: Incident Electron Energy

SAMPLE: Single crystals) with or without
Polycrystalline materials) adsorbed layer
Semiconductor surface

APPLICATIONS: Study of chemisorption, physisorption and their effect on work functions
Study of excitons

SELECTED REFERENCE:

'Total Current Spectroscopy'
S. A. Komolov
L. T. Chadderton, Surf. Sci., 90 (1979) 359-380.

III.5. X-ray Excited Electron Appearance Potential Spectroscopy (XEAPS)

This is a variable photon energy photoelectron spectroscopy. Monochromatic synchrotron radiation is incident on a surface and the photoelectron yield recorded as the frequency is varied. The XEAP spectrum shows distinct threshold peaks for core ionization processes. The spectrum is similar to, but different from, the SXAP spectrum. The difference in the two spectra arises from the different net charges on the excited species. In XEAPS a neutral atom core electron is excited to above the Fermi level but in SXAPS an excitation of the cation is involved. Thus, there is a slight energy shift, of a few electron volts, in the observed structure in the two spectra.

SUMMARY

NAME: X-ray Excited Electron Appearance Potential Spectroscopy

CLASS: Appearance Potential Spectroscopies

ACRONYM: XEAPS

INCIDENT: Variable Energy Photons

ENERGY RANGE: 100 - 1000 eV (synchrotron radiation)

ENERGY RESOLUTION: ∿0.001 - 0.3 eV (monochromatised, resolution depends on photon energy)

INCIDENT FLUX: Medium to low (depending on photon energy)

ANGLE OF INCIDENCE: not critical

DETECTED: Electrons

ENERGY: approximately 0 eV to within a few eV of photon energy

ANALYZER ENERGY RESOLUTION: Not applicable. Total Photoelectron Yield collected.

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19}$ - 10^{-15} A

SPECTRUM:

ORDINATE: Photoelectron Current (Total Yield)

ABSCISSA: Photon Energy

SAMPLE: Polycrystalline metal surfaces

APPLICATIONS: Elemental analysis
Core ionization effects

SELECTED REFERENCE:

'Electron and X-ray Appearance Potential Spectroscopy'
J. Kanski, P. O. Nilsson
Phys. Scr., 12 (1975) 103.

III.6. Extended (Electron) Appearance Potential Fine-Structure Analysis (EAPFS)

This technique is based on the analysis of the fine structure close to the threshold for the excitation of a core electron by a variable energy electron beam. Thus in terms of experimental technique EAPFS is similar to AEAPS and DAPS, but in terms of analysis of results EAPFS is analagous to the extended structure in X-ray absorption, EXAFS, and that in inelastic electron energy scattering, EXELFS or SEELFS.

The structure results from the interference of the outgoing spherical wave of the scattered electron with the backscattered components from neighbouring atoms. There is an important difference between EAPFS and the other two fine structure analysis techniques, EXAFS and EXELFS. In EAPFS both the incident electron and the ejected core-electron must be accommodated above the Fermi level. Thus, the final state is a two-electron-state. In EXAFS and EXELFS the final state is a one-electron-state.

The fine structure exists several hundred electron volts above the appearance potential but away from the edge the structure becomes masked by the slowly varying elastic background. The spectrum is presented as the second derivative of the elastic electron current with respect to the primary electron energy. The same Fourier transform technique as is used in EXAFS is used to extract the local geometry from the fine structure.

SUMMARY

NAME: Extended (Electron) Appearance Potential Fine-Structure Analysis (or Spectroscopy)

CLASS: Appearance Potential Spectroscopies

ACRONYMS: EAPFS, EAPFSS

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 200 - 2000 eV

ENERGY RESOLUTION: not critical

INCIDENT ELECTRON CURRENT: $\sim 10^{-4}$ A

ANGLE OF INCIDENCE: approximately normal to surface

DETECTED: Elastically Scattered Electrons

ENERGY: same as incident electron energy

ANALYZER ENERGY RESOLUTION: ~ 1 eV

ANGLE OF EXIT: within range 20 - 80° (not critical)

ATTENUATION OF INCIDENT BEAM: ~ 1 in 10^3

SPECTRUM:

ORDINATE: Second derivative of the elastic electron current with respect to the incident electron energy

ABSCISSA: Incident electron energy

SAMPLE:

Single crystals
Polycrystalline materials
Materials with limited structure, e.g. glasses
Thin films
Amorphous materials

APPLICATIONS: Fourier transform of spectrum gives local crystal structure

SELECTED REFERENCE:

'Extended Appearance-Potential Fine-Structure-Analysis: Oxygen on Al(100)'
M. L. den Boer, T. L. Einstein, W. T. Elam, R. L. Park, L. D. Roelofs and G. E. Laramore
Phys. Rev. Lett., 44 (1980) 496.

III.7. Inelastic Electron Tunneling Spectroscopy (IETS)

The tunneling current across a metal-insulator-metal junction does not show normal ohmic behaviour. The overlap between the initial and final many-electron states of the junction may be increased by coupling to vibrational modes of the insulator. This enhances the tunneling probability. When a potential difference is applied across the junction most of the current carrying electrons which tunnel from one metal surface to the other do so elastically. When the junction has a doped insulating layer a few of the electrons, about one in a thousand, interact with the dopant molecules by exciting their vibrational modes. A few of the vibrational modes are those associated with the insulating layer itself. These vibrational modes add a series of inelastic channels for tunneling. As the applied potential difference is increased, the junction current will suddenly increase as each threshold for a vibrational mode is reached. Thus inelastic electron tunneling spectroscopy is a threshold or appearance potential spectroscopy. All vibrational modes may be excited without limitation by selection rules. Both infrared and Raman-active modes are excited together.

The experimental technique measured the junction tunneling current (I) as the applied potential difference (V) is varied from zero to about one volt. In practice an audio frequency modulation voltage is applied to the junction in parallel with the applied potential difference and the tunnel current derivative, $\delta I/\delta V$, is detected with a phase-sensitive lock-in amplifier. This signal is then differentiated to give the second derivative of the tunnel current, $\delta^2 I/\delta V^2$, which is plotted against applied potential difference, V, to give the inelastic electron tunneling spectrum.

The limiting resolution of the IET spectrum is proportional to 5.44 kT. However this resolution can be improved by operating the spectrometer with superconducting metals in the junction at liquid helium temperature. Lead, which superconducts at 7K, is the usual metal chosen. The vibrational frequencies recorded in IETS are slightly shifted due to image-dipole effects in the insulator but these shifts can be calculated. The resolution, at a temperature of 1K, is usually ∿0.001 eV (10 cm^{-1}) over a spectral range of 300 - 400 cm^{-1}.

Applications of IETS in surface science depend on the observation of surface adsorbed dopant molecules. Extra vibrational modes due to surface bonding and the shifting or complete loss of the expected molecular vibrational modes have been observed. Most studies are on small organic or inorganic molecules but the number of studies of larger organic molecules and biological molecules (e.g., DNA, RNA and hemoglobin) is increasing rapidly.

SUMMARY

NAME: Inelastic Electron Tunneling Spectroscopy

CLASS: Appearance Potential Spectroscopies

ACRONYM: IETS

INCIDENT: Variable Energy Electrons

ENERGY RANGE: 0 - 1 eV

ENERGY RESOLUTION: not applicable

INCIDENT ELECTRON CURRENT: ∿1 μA (audio-frequency modulated)

TEMPERATURE: ∿1°K

DETECTED: Tunneling Current

CHANGE IN TUNNELING CURRENT: 1 in 10^5 - 1 in 10^3

ELECTRON CURRENT AT DETECTOR: ∿1 μA (Tunnel Current)

SPECTRAL ENERGY RESOLUTION: ∿0.001 eV

SPECTRUM:

ORDINATE: Second derivative of Tunnel Current (I) with respect to applied Junction Voltage (V) i.e., $\frac{\partial^2 I}{\partial V^2}$

ABSCISSA: Junction Voltage (V)

SAMPLE: Thin insulating layer (which may be doped with a molecular species) in a metal-insulating-metal junction

APPLICATIONS: Vibrational electron-energy-loss spectroscopy of insulating layer and the dopant species

SELECTED REFERENCES:

(i) 'Inelastic Electron Tunneling Spectroscopy'
T. Wolfram
Springer-Verlag, 1978.

(ii) 'Surface Analysis Using Electron Beams'
R. L. Park and M. den Boer
CRC Critical Review in Solid State Sciences, (1976) 275.

(iii) 'Inelastic Electron Tunneling Spectroscopy: A Probe of the Vibrational Structure of Surface Species'
W. H. Weinberg
Ann. Rev. Phys. Chem., 29 (1978) 115.

IV. THE AUGER ELECTRON SPECTROSCOPIES

Auger Electron Spectroscopy measures the energy distribution spectrum of the electrons ('Auger electrons') emitted following the primary ionization of a core energy level. This ionization can result from internal conversion in a radioactive element or from X-ray photoionization, high energy electron ionization or positive-ion ionization (in particular, protons).

Auger Spectroscopy, Auger Emission Spectroscopy, Auger Electron Spectroscopy and Auger Electron Emission Spectroscopy are synonymous terms for the general technique. The most commonly used term is Auger Electron Spectroscopy (AES). The different means of initiating the Auger process define different forms of AES with different spectral characteristics. Thus we have electron-excited, X-ray excited, ion-excited and nuclear Auger Electron Spectroscopies.

Ion Neutralization Spectroscopy (INS) is sometimes classed with Auger Spectroscopy as it involves Auger electron emission. However, we have chosen to classify INS as a particle-induced spectroscopy because of the similarities between the process involved in INS - Auger Neutralization - and those processes involved in the neutral-particle-induced spectroscopies - Auger deexcitation, Resonance Ionization and Resonance Neutralization.

The treatment of the secondary electron signal is common to all forms of AES. The signal is energy analyzed and recorded either at a fixed angle or as a function of angle of emission. The signal is composed of narrow, low intensity, Auger electron peaks superimposed upon an intense smoothly varying background composed of elastically and inelastically scattered primary electrons, core electrons ionized by the primary beam and inelastically scattered Auger electrons. The sharp Auger electron peaks are usually enhanced with respect to the background by electronic differentiation of the secondary electron signal. The Auger electron spectrum is thus $dN(\varepsilon)/d\varepsilon$ displayed as a function of ε where $N(\varepsilon)$ is the energy distribution function.

The energies of the Auger electrons are characteristic of the elements present.

The most common electron energy analyzers employed are the cylindrical mirror analyzer (CMA) and the spherical-grid retarding field analyzer (RFA). Most Auger electron spectrometers employ the higher efficiency CMA but the RFA is still useful in any apparatus which combines AES with LEED. High energy resolution AES requires preretardation of electrons before they enter the CMA as the energy resolution of this analyzer is proportional to the pass energy.

Auger electron spectra are interpreted by comparison with 'standard' spectra from samples of known composition as the spectra are, in general, complex and composed of many lines. Auger electron spectra cannot be calculated accurately from first principles.

The major sources of error in AES are: electron beam or ion beam artifacts and radiation damage, the effects of surface morphology on Auger yields and charging effects in insulators and semiconductors.

The main applications of AES are qualitative and quantitative elemental analysis. All elements except Hydrogen and Helium give Auger electrons, but if many elements are present the spectrum can be very complex. Quantitative work can be complicated by contributions of backscattered electrons to the Auger yield. The absolute detection limit is about 10^{-19} kg in a surface volume of about 10^{-20} m^3. Thin surface layers (<2 nm) can also be analyzed. Depth profiling is possible by removing the surface layers with ion sputtering. Dynamic processes can also be studied, in particular equilibrium surface segregation in alloys. Restrictions are imposed on the materials which can be investigated by their sensitivity to radiation damage and surface charging.

IV.1. Electron-excited Auger Electron Spectroscopy (EAES)

Electron Excited (or Induced or Initiated) Auger Electron Spectroscopy (EEAES or EIAES or EAES) is the most common form of Auger Electron spectroscopy and, if the ionizing source is not obvious from the context, then this technique is assumed by default. Thus electron excited AES is often referred to simply as AES. Two particular forms of EAES are recognized.

High-Lateral-Resolution AES involves a focussed electron beam of small diameter being scanned across a surface to produce Auger electrons from a defined area. This is the Scanning Auger Microprobe (SAM) or High-Resolution AES Probe (AES-probe). If the probe is applied to producing elemental distribution maps of a surface this technique becomes Scanning Auger Microscopy (SAM). If a cold cathode rather than a thermionic cathode, is employed giving a smaller primary electron energy source the technique is called High-Resolution Field Emission AES Probe (FE-AES-probe).

High Energy Resolution AES, on the other hand, involves a fixed electron beam, of larger diameter than that used in probe work, and with some refinements to the energy analyzer and collector affords higher energy resolution than is typical in SAM.

In both the techniques electron beam energies are in the range 1 - 10 keV and current densities in excess of 10 A cm^{-2} are common. Beam currents of up to 1 x 10^{-6} A can be achieved with thermionic cathodes. Beam diameters for high energy resolution AES are commonly 3 - 5 μm but high lateral resolutions of better than 0.3 μm can be achieved with thermionic cathodes and approximately 30 nm with cold cathodes. Further increase in lateral resolution seems to be limited by electron scattering effects which tend to enlarge the Auger analysis spot. The depth resolution of EAES is of the order of 0.4 - 4.0 nm.

Depth-Profiling Auger Electron Spectroscopy involves the addition of argon ion bombardment, for the sequential removal of surface layers by sputtering.

SUMMARY

NAME: (Electron-Excited) Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYMS: AES, AEES, EAES, EEAES, EIAES

INCIDENT: Fixed Energy Electrons

ENERGY: within range 100 eV - 10 keV (typically within range 1000 - 2000 eV)

ENERGY RESOLUTION: not critical

INCIDENT ELECTRON CURRENT: ∿10^{-7} - 5 x 10^{-4} A

BEAM DIAMETER: ∿0.1 - 1 mm

ANGLE OF INCIDENCE: within range 0 - 70°

DETECTED: Secondary Auger Electrons

ENERGY RANGE: 20 - 2000 eV

ANALYZER ENERGY RESOLUTION: ∿1 eV (typical)
∿0.01 eV high resolution

ELECTRON CURRENT AT DETECTOR: ∿10^{-4} of incident electron current (for solids)

ANGLE OF EXIT: Polar angle: 0 - 70°
Azimuthal angle: not critical

SPECTRUM:

ORDINATE: First or second derivative of Secondary Electron Current, $N(E)$, with respect to the Analyzer Energy, E, i.e., $dN(E)/dE$ or $d^2N(E)/dE^2$.

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Atomic and molecular gases
Single crystals) with or without
Polycrystalline materials) adsorbed layer
Semiconductor surfaces

APPLICATIONS: Elemental analysis

SUMMARY

NAME: Scanning Auger Microscopy

CLASS: Auger Electron Spectroscopies

ACRONYM: SAM

ALTERNATIVE NAMES: Scanning Auger (Electron) Microprobe (SAM)
High-Resolution AES Probe (AES-probe)
High-Resolution Field Emission AES Probe (FE-AES-probe)
Electron Microprobe Auger Spectroscopy (EMAS)

RELATED TECHNIQUES: Depth-Profiling Auger Electron Spectroscopy

INCIDENT: Fixed Energy Electrons

ENERGY: within range 2 - 15 keV

ENERGY RESOLUTION: ∿0.5 - 1 eV (not critical)

INCIDENT ELECTRON CURRENT: ∿10^{-10} A (current densities can be in excess of 10 A cm^{-2})

BEAM DIAMETER: ∿0.3 - 5.0 μm (thermionic sources)
∿300 - 30 nm (cold cathode sources)

ANGLE OF INCIDENCE: Electron beam is scanned across surface

DETECTED: Secondary Auger Electrons

ENERGY: a particular Auger electron energy is selected within the energy range 200 - 2000 eV

ANALYZER ENERGY RESOLUTION: ∿1 - 4 eV (typical) although some instruments can operate to ∿0.01 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-4}$ of incident current

ANGLE OF EXIT: ∿0 - 60° (not critical)

ANGULAR RESOLUTION: Large

SPECTRUM: Presented as a map of surface distribution of a particular element

X and Y axes: position coordinates

Z axis: Intensity of first derivative of Auger electron current

SAMPLE: Polycrystalline materials
Semiconductor surfaces

APPLICATIONS: Elemental distributions

SELECTED REFERENCES:

(i) 'Auger Electron Spectroscopy'
S. Hofmann
in Comprehensive Analytical Chemistry, Volume IX (1979),
G. Svehla (editor)
Elsevier, Amsterdam.

(ii) 'High Resolution Auger Spectroscopy of Solids and Surfaces'
J. C. Fuggle
in Electron Spectroscopy: Theory, Techniques and Applications, Volume 4,
C. R. Brundle and A. D. Baker (editors)
Academic Press, New York, 1981.

(iii) 'Surface Analysis Using Charged-Particle Beams'
P. Braun, F. Rudenauer and F. P. Viehbock
Adv. Electron. Electron Phys., 57 (1981) 231.

IV.2. Angle-resolved Auger Electron Spectroscopy (ARAES)

If the Auger electrons, produced as a result of electron ionization of a core level, are collected as a function of their emission angle with respect to the surface the technique is referred to as Angle-Resolved Auger Electron Spectroscopy (ARAES) or Angular-Dependent Auger Spectroscopy (ADAS). This term is applied both to true angular discrimination, in which the electron energy analyzer and collector are moved with respect to the surface, and to the simpler technique in which the portions of the analyzer and collector are fixed and the surface is rotated to vary both the angle of collection and the angle of incidence of the primary radiation or particle beam.

SUMMARY

NAME: Angle-Resolved Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYM: ARAES

INCIDENT: Fixed Energy Electrons

ENERGY: within range 500 - 2000 eV

ENERGY RESOLUTION: ∿1 eV (monochromatised)

INCIDENT ELECTRON CURRENT: $\sim 10^{-7}$ - 10^{-5} A

BEAM DIAMETER: ∿0.1 - 0.5 mm

ANGLE OF INCIDENCE: within range 0 - 70° (must be specified)

DETECTED: Secondary Auger Electrons

ENERGY RANGE: 20 - 2000 eV

ANALYZER ENERGY RESOLUTION: ∿0.050 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-4}$ of incident electron current

ANGLE OF EXIT: Polar angle: 0 - 70°
Azimuthal angle: 0 - 360°

ANGULAR RESOLUTION: ∿1° - 5°

SPECTRUM:

ORDINATE: First or second derivative of Secondary Electron Current, $N(E)$, with respect to the Analyzer Energy, E , i.e., $dN(E)/d$ or $d^2N(E)/dE^2$ at specified polar angle

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Single crystals) with or without
Polycrystalline materials) adsorbed layer
Semiconductor surfaces

APPLICATIONS: Surface specific elemental analysis

SELECTED REFERENCE:

'Theory of Photoemission from Localized Adsorbate Levels'
A. Liebsch
Phys. Rev. B, 13 (1976) 544.

IV.3. Spin-polarized Auger Electron Spectroscopy (SPAES)

The Auger electrons from ferromagnetic elements may be spin polarized. Those Auger electrons which are emitted following CCC processes, in particular the LMM transition, may be spin polarized through the coupling of partly filled inner shells with the net spin of the magnetic 3d electrons. This provides information on the local magnetization, i.e., the average magnetic moment. This important feature being that an Auger transition is both element specific and local in character. Low energy secondary electrons produced by scattering of the primary beam in ferromagnetic solids may also be spin polarized due to spin-orbit coupling in the scattering process. The spectroscopy for studying these spin-polarized Auger electrons is Spin-Polarized Auger Spectroscopy (SPAES).

In SPAES the core hole is produced by electron bombardment with beams up to 3000V striking the surface at a grazing incidence of ∿20°. The secondary electron signal is collected normal to the surface by a Mott detector (of high efficiency with a central electric field for acceleration and focussing) and an electron energy analyzer of constant energy resolution and angular acceptance. A permanent magnet is required to magnetically saturate the sample by aligning the spins parallel to the emitting surface. The polarization due to the spin-orbit coupling in the scattering process can be averaged out by reversing the magnetization direction.

Spin-Polarized Auger Spectroscopy has been applied to the study of ferromagnetics (e.g., the ferromagnetic glass Fe_{83} B_{17}) and it is envisaged that it will prove useful in the

study of magnetic alloys and compounds, where its elemental specificity will prove a useful adjunct to the complementary techniques of spin-analyzed secondary electron emission and spin-polarized photoelectron emission.

SUMMARY

NAME: Spin-Resolved Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYM: SPAES

INCIDENT: Fixed Energy Electrons

ENERGY: within range 1000 - 3000 eV

ENERGY RESOLUTION: not critical

INCIDENT ELECTRON CURRENT: $\sim 10^{-7}$ - 10^{-4} A

BEAM DIAMETER: $\sim$0.1 - 0.5 mm

ANGLE OF INCIDENCE: grazing ($\sim$20°)

DETECTED: Secondary Auger Electrons

ENERGY RANGE: 100 - 2000 eV

ANALYZER ENERGY RESOLUTION: $\sim$0.050 - 0.1 eV

ELECTRON CURRENT AT DETECTOR: Spin-resolved electrons are detected by a Mott detector. These are less than 100% efficient so the detected current may be of the order of 10^{-6} of the incident electron current

ANGLE OF EXIT: Normal to surface

SPECTRUM:

ORDINATE: Secondary Electron Current (or its first derivative)

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Magnetically saturated ferromagnetic materials

APPLICATIONS: Measurement of d-valence band electron spin population

SELECTED REFERENCE:

'Spin-Polarized Auger Spectroscopy from Magnetically Ordered Solids'
M. Landolt, D. Mauri
Phys. Rev. Lett., 49 (1982) 1783.

IV.4. Ion-excited Auger Electron Spectroscopy (IAES)

If the core hole is produced by high energy ion collisions the technique is called Ion-(Excited or Induced or Initiated) Auger Electron Spectroscopy (IAES). Usually heavy ions are employed but Proton-Excited AES (PAES) has also been investigated.

An ion gun producing heavy inert gas ions with kinetic energies in excess of 5 keV and current densities of the order of 100 μA cm^{-2} is required. The lateral resolution is in general poorer than for EAES but the depth resolution is similar to that in EAES.

SUMMARY

NAME: Ion-Excited Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYMS: IAES, IEAES, IIAES

RELATED TECHNIQUES: Proton-Excited Auger Electron Spectroscopy (PAES)
Helium-Excited Auger Electron Spectroscopy (HAES)

INCIDENT: Fixed Energy Ions

ENERGY: within range 1 keV - 10 keV

ENERGY RESOLUTION: not critical

INCIDENT ION CURRENT: $\sim 10^{-7}$ - 10^{-3} A

BEAM DIAMETER: $\sim$0.5 mm - 2.0 mm

ANGLE OF INCIDENCE: within range 20 - 60°

DETECTED: Secondary Auger Electrons

ENERGY RANGE: 100 - 2000 eV

ANALYZER ENERGY RESOLUTION: $\sim$1 eV (typical)

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-9}$ - 10^{-6} A

ANGLE OF EXIT: within range 20 - 90°

SPECTRUM:

ORDINATE: Secondary Electron Current or its first derivative with respect to analyzer energy

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Polycrystalline materials

APPLICATIONS: Elemental analysis

SELECTED REFERENCE:

'Low Energy Electron Spectrometry'
K. D. Sevier
Wiley-Interscience, New York, 1971.

IV.5. Nuclear Auger Electron Spectroscopy (AES, AEES)

In the neighbourhood of an excited or radioactive nucleus the field of the nuclear multipole will act on the core electrons and in some cases the excited nucleus can decay to its ground state by transferring energy to the core electron. This process is called internal conversion. This energy usually exceeds the ionization energy and thus a core hole is formed and Auger electron emission may occur. Nuclear Auger electrons may also be produced by orbital electron capture. These processes do not really constitute a surface electron spectroscopy but are of some importance in considering radiation damage in solids.

SUMMARY

NAME: Nuclear Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYMS: AES, AEES

DETECTED: Secondary Auger Electrons

ENERGY RANGE: 20 - 2000 eV

ANALYZER ENERGY RESOLUTION: 1 - 5 eV

SPECTRUM:

ORDINATE: Secondary Electron Current or its first derivative with respect to analyzer energy

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Naturally radioactive polycrystalline material

APPLICATIONS: Elemental identification

SELECTED REFERENCES:

(i) 'Low Energy Electron Spectrometry'
K. D. Sevier
Wiley-Interscience, New York, 1971.

(ii) 'Internal-Conversion-Electron Spectroscopy'
O. Dragon
Adv. Electron. Electron Phys., 60 (1983) 1.

IV.6. X-ray-excited Auger Electron Spectroscopy (XAES)

Because of the limited flux density of X-ray sources they are seldom employed in Auger electron spectrometers. The importance of the X-ray excited Auger electron spectrum is that it accompanies the photoelectron emission spectrum produced in an X-ray Photoelectron Spectrometer. X-ray (or Photon)-Excited (or Induced or Initiated) Auger Electron Spectroscopy (XAES or XEAES) are synonymous terms.

SUMMARY

NAME: X-ray Excited Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYMS: XAES, XEAES

ALTERNATIVE NAME: Photon (or Photo)-Excited Auger Electron Spectroscopy

INCIDENT: Fixed Energy Photons

ENERGY: within range 1 - 10 keV

ENERGY RESOLUTION: ∿0.5 - 1.5 eV (not critical)

INCIDENT PHOTON FLUX: Low

BEAM DIAMETER: ∿1 - 3 mm

ANGLE OF INCIDENCE: within range 70 - 85°

DETECTED: Auger Electrons

ENERGY RANGE: 50 - 2000 eV

ANALYZER ENERGY RESOLUTION: ∿0.1 - 1.0 eV

ELECTRON CURRENT AT DETECTOR: $\sim 10^{-19} - 10^{-15}$ A

ANGLE OF EXIT: Polar angle: within range 10 - 80°
Azimuthal angle: not critical

SPECTRUM:

ORDINATE: Secondary Electron Current or its first or second derivative with respect to analyzer energy

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Atomic and molecular gases
Single crystals) with or without
Polycrystalline materials) adsorbed layer
Thin conducting films; Langmuir-Blodgett films
Semiconductor surfaces

APPLICATIONS: Some elemental analysis but mainly substrate (and adsorbate) valence band structure

SELECTED REFERENCES:

(i) 'X-ray-excited Auger and Photoelectron Spectroscopy'
P. Weightman
Rep. Prog. Phys., 45 (1982) 753.

(ii) 'High Resolution Auger Spectroscopy of Solids and Surfaces'
J. C. Fuggle
in Electron Spectroscopy: Theory, Techniques, and Applications, Volume 4,
C. R. Brundle and A. D. Baker (editors)
Academic, New York, 1981.

It has been recently shown that Auger processes can be excited by the bremsstrahlung radiation which accompanies the characteristic line radiation from conventional magnesium and aluminum anodes. This has proved useful in studying those Auger transitions inaccessible to the line sources. Anodes with enhanced bremsstrahlung emission have been designed using heavy elements, such as tungsten, or oxide films, such as TiO_2. The technique is known as Continuous X-ray-Induced Auger Electron Spectroscopy (CXAES) or Bremsstrahlung-excited Auger Spectroscopy. One particular application of this technique is in the determination of the Auger parameter for a wide range of transitions and so improve the chemical interpretation of a given X-ray photoelectron spectrum.

SUMMARY

NAME: Continuous (or Continuum) X-ray-Induced Auger Electron Spectroscopy

CLASS: Auger Electron Spectroscopies

ACRONYM: CXAES

ALTERNATIVE NAME: Bremsstrahlung-Excited Auger Electron Spectroscopy

INCIDENT: X-ray Photons

ENERGY: a continuum of 30 - 100 eV between 1 and 2 keV

ENERGY RESOLUTION: Not applicable

INCIDENT PHOTON FLUX: Low

DETECTED: Secondary Auger Electrons

ENERGY RANGE: ∿200 - 4000 eV

ANALYZER ENERGY RANGE: ∿1 eV

ELECTRON CURRENT AT DETECTOR: 10^{-19} - 10^{-15} A

SPECTRUM: ORDINATE: Secondary Electron Current

ABSCISSA: Analyzer Energy (Auger Electron Energy)

SAMPLE: Atomic and molecular gases
Single crystals) with or without
Polycrystalline materials) adsorbed layer
Semiconductor surfaces

APPLICATIONS: Study of wide range of Auger transitions leading to improved interpretation of X-ray Photoelectron spectra

SELECTED REFERENCE:

'Continuous X-ray Induced Auger Electron Spectroscopy'
J. Cazaux and Tran Minh Duc
J. Electron Spectrosc. Relat. Phenom., 31 (1983) 13-23.

V. THE ELECTRON COINCIDENCE SPECTROSCOPIES

In a coincidence spectroscopy two or three particles (electrons, photons or ions) originating from a single event are detected. This event may be an excitation or ionization process initiated by electrons or photons. Sophisticated timing electronics capable of nanosecond resolution and up to three electron energy analyzers are required.

There are three classes of electron coincidence spectroscopy applicable to the gas phase, namely: electron-electron, electron-photon, and electron-ion.

In electron-electron coincidence spectroscopy [(e,2e) spectroscopy] a monochromatic electron beam is incident on atoms or molecules in a gas or a beam. The incident electron ionizes an atom or molecule and the inelastically scattered incident electron and the ionized electron are detected in coincidence.

There are two forms of electron-photon coincidence spectroscopy. The first of these [(e,p) spectroscopy] involves an electron beam incident on an atomic beam. The incident electron excites the atom to a particular electronic energy level which then decays by fluorescent photon emission. The inelastically scattered electron and the photon are detected in coincidence. The second form is photoelectron-photon coincidence spectroscopy in which an ultraviolet photon ionizes a molecule forming one of several electronically excited ionic states which can then decay by fluorescent photon emission. The photon and the photoelectron are then detected in coincidence.

In photoelectron-photoion coincidence spectroscopy (PIPECO) fixed energy photons are incident on a molecular gas. A photoelectron with a selected kinetic energy is detected in coincidence with the corresponding ion (or 'photoion') which is in a known electronic state.

Finally there is the triple coincidence experiment - electron,photon,ion coincidence spectroscopy. A molecular gas is ionized by an electron beam to force an ion in a preselected electronic state. This ion can then decay by fluorescent photon emission. The ion, inelastically scattered electron and the fluorescence photon are then detected in triple coincidence.

SELECTED REFERENCES:

(i) 'Two-Parameter Coincidence Experiments'
M. E. Gellender and A. D. Baker
in 'Electron Spectroscopy: Theory, Techniques and Applications'
Volume 1, Academic Press, New York, 1977.

(ii) '(e,2e) Spectroscopy'
I. E. McCarthy and E. Weigold
Phys. Rep., 27C (1976) 275.

There are two coincidence techniques applicable to solids: Auger electron-photoelectron coincidence and scattered electron-ionized electron coincidence.

In Auger-Electron-Photoelectron Coincidence Spectroscopy (APECS or AEPECS) a core hole is created by photoionization and the photoelectron and subsequent Auger electron are detected and time correlated. Unlike Auger electron spectroscopy, APECS does not require differentiation of the electron signals as the coincidence technique significantly reduces the signal-to-background noise problem. APECS is more surface depth sensitive than either AES or XPS as both electrons involved in the process must escape without energy loss. The observed spectrum is very similar to the Auger electron spectrum but is modified by certain features. For example, there is not satellite structure as the Auger electrons counted must originate from the primary excitation selected. Some of the line broadening effects assoicated with AES are also reduced, in particular that due to the finite lifetime of the core hole. The information in the spectrum is a combination of a one-particle density-of-states, from the photoelectron emission process, and a two-particle density-of-states, from the Auger process.

SELECTED REFERENCE:

'Auger-Photoelectron Coincidence Measurements in Copper'
H. W. Haak, G. A. Sawatzky and T. D. Thomas
Phys. Rev. Lett., 41 (1978) 1825.

In (e,2e) Spectroscopy of surfaces a core hole is created by electron-induced ionization and the time correlation between the inelastically scattered electron and the ionized electron is plotted against the primary electron energy. Preliminary experiments have been performed on films of amorphous carbon, but these experiments had low resolution and low count rates. Once the technical difficulties have been overcome it should be possible to obtain the full four-dimensional (E,k) surface of a solid surface.

SELECTED REFERENCES:

(i) 'On the (e,2e) Reaction in Solids'
N. R. Avery
AIP Conf. Proc. (USA) No. 36 (1977) 195.

(ii) 'Study of Molecular Orbitals by Means of (e,2e) Spectroscopy Oriented Molecules'
R. Camilloni, G. Stefani, R. Fantoni, A. Giardini-Guidoni
J. Electron Spectrosc. Relat. Phenom., 17 (1979) 209.

VI. THE HEAVY-PARTICLE-INDUCED ELECTRON SPECTROSCOPIES

Although fast neutral particles and ions can cause electron emission from a surface, the electron energy distribution involved, probably complex, has not been analysed and developed into an electron spectroscopy.

Low kinetic energy, ground state, neutral molecules can also stimulate electron emission. For example, exoelectron production by oxygen chemisorption on clean nickel and copper surfaces has been investigated. No satisfactory energy analysis of this exoelectron spectrum has been reported. The formation of the chemisorption bond takes place via an excited intermediate state which may then decay to the ground state by the emission of an

electron. However, even if all the energy released by the formation of the chemisorption bond was available to a single electron, very few reactions would release enough energy for subsequent ionization. In the special case of energetic reactions this low-energy, ground-state, neutral-induced exoelectron emission spectroscopy might prove a useful means of monitoring reaction rates.

The only developed electron spectroscopies induced by particles are those involving low kinetic energy atomic ions or metastable atoms incident on the surface. When one or other of these particles approaches a surface several different processes are possible. Which of these dominate is decided by the relative potential energies of the electrons in the particle and the surface. To a first approximation these are purely potential energy processes and the kinetic energy of the incident particle is not important provided it is small.

The particle-surface interaction processes all involve an electron tunneling through the particle-surface potential energy barrier by either a resonant or non-resonant mechanism. 'Resonance' in this context implies that the two energy levels involved, one in the incident particle and one in the surface, have the same potential energy. Non-resonant processes involve two energy levels of different energy. This energy difference will appear as electronic excitation of either the incident particle or the surface states or as an Auger process in the incident particle or surface. The major processes which are of relevance to surface spectroscopy are resonance ionization, resonance neutralization, Auger neutralization and Auger-deexcitation.

In resonance ionization an electron resonantly tunnels from the incident particle to an unoccupied surface valence state of the solid. In resonance neutralization an electron resonantly tunnels from an occupied surface valence state of the solid to the incident particle. Originally these terms were defined specifically for the ionization of incident atoms and the neutralization of incident ions respectively, but the terms have now taken on the wider meanings defined above. In Auger neutralization an incident ion is neutralized by an electron non-resonantly tunneling to neutralize the ion. The excess energy remaining, after the work function has been overcome, ejects an electron from the surface. In Auger-deexcitation an incident neutral particle in an excited metastable state is deexcited on interaction with the surface and the excess energy ejects an electron from the surface.

The electron spectroscopies based on these processes are:

Ion Neutralization Spectroscopy (INS) is an incident-ion electron spectroscopy based on the Auger neutralization process.

Excited-Atom Deexcitation Spectroscopy using Incident Ions is an incident-ion electron spectroscopy based on the consecutive occurrence of the resonance neutralization and Auger-deexcitation processes.

Resonance Ionization Spectroscopy is an incident-metastable-atom electron spectroscopy based on the consecutive occurrence of resonance ionization and Auger neutralization.

Surface Penning-Ionization Electron Spectroscopy (SPIES) is an incident-metastable-atom electron spectroscopy based on the Auger deexcitation process.

Some workers refer to the general technique of using metastable atom sources as Metastable-Quenched Electron Spectroscopy (MQES) reserving the above terms for spectra produced by the specific mechanisms named.

VI.1. Ion Neutralization Spectroscopy (INS)

As slow light ions approach a surface they become polarized and provide a vacant energy level into which a valence electron from the surface can tunnel overcoming the work function. The energy released by this neutralization is taken up by a second valence electron in an Auger-like transition. This process is therefore called Auger Neutralization.

This ionization occurs at or just above the surface. The energy of the emitted electron depends both upon the valence level from which it comes and the level from which the neutralizing electron comes. The energy distribution function reflects the self convolution of the valence band density-of-states and the density-of-states available to the emitted electron. As the emitted Auger electron has to tunnel through the surface barrier to escape, INS is very surface sensitive. In order that Auger neutralization be the major

electron ejection process for the particular system it is necessary to ensure that resonance tunneling processes do not occur. Thus the work function of the surface to be investigated must be greater than the ionization energy of the lowest lying excited state of the ion.

In practice, beams of He^+, Ne^+ or Ar^+ are used. The beam energy is of the order of 5 eV and, as the Auger electrons are of low energy, high-resolution electron energy analysis is required. Ultra-high vacuum conditions are essential because of the high depth resolution of this technique.

The main application of INS is the study of adsorption and desorption phenomena on surfaces. The results are directly comparable with those of Ultraviolet Photoelectron Spectroscopy, UPS, particularly if one-electron processes are involved.

SUMMARY

NAME: Ion Neutralization Spectroscopy

CLASS: Particle-Induced Electron Spectroscopies

ACRONYM: INS

INCIDENT: Ions

SPECIES: Noble gas ions (He^+, Ne^+, Ar^+)

ENERGY: ∿5 - 10 eV (kinetic energy)

ENERGY RESOLUTION: Not applicable

INCIDENT ION CURRENT: Low (∿10^{-10} A)

BEAM DIAMETER: ∿5 mm

ANGLE OF INCIDENCE: not critical (typically within the range 20 -45°)

DETECTED: Electrons

ENERGY RANGE: 0 - 16 eV

ANALYZER ENERGY RESOLUTION: ∿0.1 eV

ELECTRON CURRENT AT DETECTOR: ∿10^{-10} A

ANGLE OF EXIT: not critical (0 - 90°)

SPECTRUM:

ORDINATE: Electron Count Rate

ABSCISSA: Analyzer Energy (Electron Energy)

SAMPLE: Defined faces of single crystals usually with chemisorbed layer

APPLICATIONS: Adsorption and desorption phenomena

SELECTED REFERENCES:

(i) 'The Interrelation of Physics and Mathematics in Ion-Neutralization Spectroscopy'
H. D. Hagstrum and G. E. Becker
Phys. Rev. B, 4 (1971) 4187.

(ii) 'Ion Neutralization Spectroscopy'
H. D. Hagstrum
in Techniques of Metals Research, Volume 6, Part 1, pages 309-335,
R. F. Bunshah (editor)
Wiley, New York, 1972.

VI.2. Excited-atom Deexcitation Spectroscopy Using Incident Ions

If a surface has a sufficiently low work function, incident atomic ions with low kinetic energy (15 eV) can be converted to excited atoms by resonance neutralization. These excited atoms in turn eject electrons by the process of Auger-deexcitation (sometimes called Penning Ionization). Usually He^+ ions are used with kinetic energies of the order of 10 eV. The low work function surface is produced by the adsorption of K^+ ions on a metallic single-crystal surface such as nickel. This process reduces the nickel work function from 5.1 eV to 1.6 eV. The main applications of the technique to date are firstly, to understand the energy considerations involved in the partition between the neutralization and deexcitation processes and secondly, to understand the relative surface sensitivities of ultraviolet photoelectron spectroscopy, UPS, and ion neutralization spectroscopy, INS.

SUMMARY

NAME: Excited-Atom Deexcitation Spectroscopy using Incident Ions

CLASS: Particle-Induced Electron Spectroscopies

ACRONYM: None

INCIDENT: Ions

SPECIES: Noble gas ions (usually He^+)

ENERGY: ∿5 - 10 eV (kinetic energy)

ENERGY RESOLUTION: Not applicable

INCIDENT ION CURRENT: Low (∿10^{-10} A)

BEAM DIAMETER: ∿5 mm

ANGLE OF INCIDENCE: not critical (typically within the range 20 - 45°)

DETECTED: Electrons

ENERGY RANGE: 0 - 16 eV

ANALYZER ENERGY RESOLUTION: ∿0.025 - 0.1 eV

ELECTRON CURRENT AT DETECTOR: ∿10^{-10} A

ANGLE OF EXIT: not critical (0 - 90°)

SPECTRUM:

ORDINATE: Electron Count Rate

ABSCISSA: Analyzer Energy (Electron Energy)

SAMPLE: Specially prepared low work function surfaces of single crystals. The work function is lowered by adsorbing K^+ ions onto the surface.

APPLICATIONS: Fundamental investigation of the nature of the ion neutralization and excited atom deexcitation and the energy considerations involved

SELECTED REFERENCE:

'Excited-Atom Deexcitation Spectroscopy using Incident Ions'
H. D. Hagstrum
Phys. Rev. Lett., 43 (1979) 1050-1053.

The next two techniques employ metastable helium atoms in the states 2^1S_0 and 2^3S_1. These are produced by electron impact on an atom beam from a nozzle. Their kinetic energies are typically 60 meV (300 K). Highly excited helium atoms in Rydberg states and ions are removed from the beam by inhomogeneous electric fields. Measurements show the beam to be approximately 80% He (2^1S_0) and 20% He (2^3S_1). The beam diameter is about 3 mm at the sample surface and the beam flux about 10^8 particles s^{-1}.

VI.3. Resonance Ionization Spectroscopy

Metastable inert gas atoms of thermal kinetic energy (<0.1 eV) are incident on a surface. An electron then tunnels from the excited level of the atom to one of the degenerate unoccupied states of the surface (resonance ionization). This leaves a positive ion at the surface. This ion then decays by the process of Auger neutralization. Firstly, an electron passes from the surface to the ground state of the positive ion to produce a ground state atom. Then the hole created in the valence band is filled by another valence electron. Finally an Auger electron is emitted from the surface valence band. The observed spectrum is a self-convolution of the local density of states of the outermost surface layer. This technique is also called resonance deexcitation of metastable noble-gas atoms. The interpretation of the results is similar to that in Surface Penning Ionization Spectroscopy and will be discussed under that heading.

VI.4. Penning Ionization Spectroscopy (PIS or SPIS)

Metastable helium atoms with thermal kinetic energies (<0.1 eV) enter a gas or are incident on a surface. If the metastable state is sufficiently energetic, in relation to the ionization energies of one or more atomic or molecular orbitals or to the surface work function of a solid, a valence electron is emitted by direct Auger-deexcitation of the metastable atom. For a solid the energy and angular distribution of the Penning electrons is characteristic of the electronic density of states of the valence band and the surface topology. If chemisorbed molecules are present, informations on the symmetries and spatial orientations of the ionized orbitals may be obtained.

The process involved in Penning Ionization Spectroscopy is similar to photoelectron emission but with different selection rules. SPIS can also be compared with Resonance Ionization Spectroscopy and Ion Neutralization Spectroscopy but SPIS is simpler to interpret than either of these as there is no deconvolution of the surface density of states. Compared with ion neutralization and ultraviolet photoelectron emission, resonance ionization and surface Penning ionization are the more surface sensitive as the excitation occurs at the position where the empty incident atom wave function overlaps with the surface wave functions, whereas photoelectron emission, for example, occurs over the entire region covered by the initial state wave function of the photoelectron.

SUMMARY

NAME: 1. Resonance Ionization Spectroscopy
2. Penning Ionization Spectroscopy

CLASS: Particle-Induced Electron Spectroscopies

ACRONYMS: 1. None
2. PIS, PIES, SPIS, SPIES

ALTERNATIVE NAMES: Metastable-Quenched Electron Spectroscopy (MQES)
Metastable (Noble Gas) Deexcitation Spectroscopy (MDS)

INCIDENT: Metastable Atoms

SPECIES: Noble gas atoms (typically He)

ENERGY: Thermal kinetic energy (<0.1 eV)
and,
Metastable state potential energy
(e.g., He^*2^1S = 20.6 eV and He^*2^3S = 19.8 eV)

ENERGY RESOLUTION: Not applicable

INCIDENT ATOM FLUX: Low

BEAM DIAMETER: ∿5 - 8 mm

DETECTED: Electrons

ENERGY RANGE: 0 - ∿20 eV

ANALYZER ENERGY RESOLUTION: ∿0.1 eV

ELECTRON CURRENT AT DETECTOR: ∿10^{-12} - 10^{-10} A

SPECTRUM:

ORDINATE: Electron Count Rate

ABSCISSA: Analyzer Energy (Electron Energy)

SAMPLE: Atomic and molecular gases
Single crystals with or without chemisorbed layer

APPLICATIONS: Electronic structure of atoms and molecules. (In particular unoccupied levels).
Valence band electronic structure of substrate and chemisorbed layer

SELECTED REFERENCES:

(i) 'Penning Ionization'
M. J. Shaw
Contemp. Phys., 15 (1974) 445.

(ii) 'Probing the Local Density of States of Metal Surfaces by Deexcitation of Metastable Nobel Gas Atoms'
W. Sesselmann, H. Conrad, G. Ertl, J. Kuppers, B. Woratschek and H. Haberland
Phys. Rev. Lett., 50 (1983) 446.

(iii) 'V. Cermak Memorial Issue'
J. Electron Spectrosc. Relat. Phenom., 23 (1981).

VII. FIELD EMISSION ELECTRON SPECTROSCOPY (FES)

Field Emission is the emission of electrons from a cold cathode upon application of an intense electric field. An electric field strength of the order of 10^9 Vm^{-1} is required for the electrons to tunnel through the surface barrier. To achieve these field strengths with realistic applied voltages of a few thousand volts the emitting cathode is etched to a very sharp point. This system is the basis of Field Emission Microscopy (FEM) and, with the addition of helium gas, Field Ion Microscopy (FIM). In Field Emission Microscopy however, the information about the surface contained in the electron energy distribution is forfeited in order to retain the spatial information for microscopy. However, if electrons from only a small area of the surface are collected and energy analyzed we have an electron spectroscopy. This is usually known as Field Emission Energy Distribution Spectroscopy (FEEDS) or Field Emission Spectroscopy (FES). Of recent interest is the spin polarization of electrons by tunneling through the spin-dependent surface potential of a ferromagnetic material, This spin dependence occurs because in a ferromagnet, the density of the majority electron spins differs from that of the minority electron spins. This implies that the interaction between a given tunneling electron and the other electrons in the surface (the exchange-correlation interaction) depends on the spin of the tunneling electron. The surface of a ferromagnetic material therefore acts as a spin filter for electrons tunneling through it during field emission. This effect is known as Field-Emitted Electron Spin Polarization (Spectroscopy) (FEESP).

VII.1. Field Emission Energy Distribution Spectroscopy (FEEDS)

The sample is a single crystal, etched to a point (~10^{-7}m in radius). The crystal is at a potential of several kilovolts to an earthed phosphor screen with a small probe hole in it for electrons from a selected spot to pass through. The region of the surface to be analyzed is selected by deflection plates near the cathode. Electrons passing through the probe hole are decelerated by an electron lens system into an electron energy analyzer. The FEED spectrum is displayed as the electron intensity as a function of the difference between the electron energy and the Fermi energy of the surface. The measured energy distribution is the total energy distribution, not as was first thought the normal energy distribution, as the conservation of energy converts the transverse component of the electron momentum at the surface into radial momentum (along the field lines) at the probe hole. One particular advantage of FEED spectroscopy is that it is combined with FE Microscopy so that particular faces of a crystal may be identified and selected before the spectrum is recorded. The FEED spectrum measures the one-dimensional density of surface states.

When an adsorbed species is present the interaction between the adsorbate and the surface substrate leads to a 'virtual adsorbate level' (in fact a very narrow local density of states). This level which is narrow in the isolated adsorbate atom is therefore broadened by the substrate interaction (as the lifetime of an electron in the adsorbate atom is no longer infinite). When an electron tunneling from the substrate has the same energy as a bound state in the adsorbate a resonance will occur which increases the tunneling probability and hence emission current by a factor of 10^2 - 10^5. These resonance features in the spectrum can be used to detect single adsorbed atoms.

There are two substantial limitations to FEED spectroscopy. Firstly, only a limited number of materials can be prepared as single crystals and then etched into suitable emitter geometries. Secondly, the tunneling probability decreases exponentially with increased binding energy in the valence band, so only the first 2 or 3 eV below the Fermi level can be sampled.

SUMMARY

NAME: Field Emission Energy Distribution Spectroscopy

CLASS: Field Emission Electron Spectroscopies

ACRONYMS: FEED, FEEDS, FES

ALTERNATIVE NAME: Field Emission Spectroscopy (FES)

RELATED TECHNIQUE: Field-Emitted Electron Spin Polarization Spectroscopy (FEESP)

ELECTRIC FIELD:

ELECTRIC FIELD STRENGTH: ~10^9 Vm^{-1}

APPLIED VOLTAGE: ~5 - 10 kV

SAMPLE AREA: ~10 - 100 nm

DETECTED: Electrons

ENERGY RANGE: ~2 keV (scanned range of ~10 eV)

ANALYZER ENERGY RESOLUTION: ~0.020 eV

ELECTRON CURRENT AT DETECTOR: 10^{-8} - 10^{-4} A

ANGLE OF EXIT: Forward with a wide spread

ANGULAR RESOLUTION: Very high (5 x 10^{-3} rad)

SPECTRUM:

ORDINATE: Electron Current (Spin-analyzed Electron Current in FEESP)

ABSCISSA: Analyzer Energy (Electron Energy)

SAMPLE: Defined faces of single crystals with or without a chemisorbed layer. FEESP requires a ferromagnetic material.

APPLICATIONS: Analysis of part of the valence band electronic states of a surface and electronic levels of the adsorbate

SELECTED REFERENCES:

(i) 'Field Emission Energy Distribution of Clean Surfaces'
P. Soven, E. W. Plummer and N. Kar
CRC Critical Reviews in Solid State Sciences, 6 (1976) 111-131.

(ii) 'Photoemission and Field Emission Spectroscopy'
E. W. Plummer
in Interactions on Metal Surfaces,
R. Gomer (editor)
Topics in Applied Physics, Volume 4, Springer-Verlag, 1975.

(iii) 'Polarization of Electrons by Tunneling through a Surface Potential'
D. Nagy
Surf. Sci., 90 (1979) 102-108.

VIII. THERMIONIC EMISSION ELECTRON SPECTROSCOPY

Thermionic emission provides information on the energy barrier at the surface of a material, but the emitted electrons represent the tail of the Fermi distribution and thus provide no direct information about energy levels. For this reason there is no electron spectroscopy based on thermionic emission.

INDEX OF SPECTROSCOPIES AND ACRONYMS

The earlier IUPAC report ('Nomenclature and Spectral Presentation in Electron Spectroscopy resulting from excitation by photons: Recommendations 1975', Pure Appl. Chem., 45 (1976) 221-224) discourages the use of acronyms and abbreviations and makes certain recommendations for their usage where unavoidable. In particular, the acronym or abbreviation should not be used in the title of a publication; the first appearance should follow the name of the spectroscopy to which it refers; the letters 'E' and 'S' should always mean 'electron' and 'spectroscopy' or 'spectrum' and where the letter 'S' appears in the acronym or abbreviation to mean 'spectroscopy' or 'spectrum' it should not be followed by the word 'spectroscopy' or 'spectrum'.

The presence of an acronym in this index should not be read as a recommendation for its use.

ADAS	Angular-Dependent Auger Spectroscopy	IV.2
ADES	Angle-Dispersed Electron Spectroscopy	I.1,I.4
AEAPS	Auger Electron Appearance Potential Spectroscopy	III.2
AEES	Auger Electron Emission Spectroscopy	IV
AEPECS	Auger Electron-Photoelectron Coincidence Spectroscopy	V
AES	Auger Electron Spectroscopy, Auger Emission Spectroscopy	IV
AIUPS	Angle-Integrated Ultraviolet Photoelectron Spectroscopy	I.1
APD	Azimuthal Photoelectron Diffraction	I.6
APECS	Auger-Photoelectron Coincidence Spectroscopy	V
APS	Appearance Potential Spectroscopy	III
APYS	Auger-Electron Partial Yield Spectroscopy	I.4.c

ARAES	Angle-Resolved Auger Electron Spectroscopy	IV
ARP	Angle-Resolved Photoemission (Spectroscopy)	I.1,I.4.f
ARPEFS	Angle-Resolved Photoemission (or Photoelectron) Extended Fine Structure (Spectroscopy)	I.4.h
ARPES) ARPS)	Angle-Resolved Photoelectron Spectroscopy	I.1,I.4
ARUPS	Angle-Resolved Ultraviolet Photoelectron Spectroscopy	I.1,I.4.f
ARXPS	Angle-Resolved X-ray Photoelectron Spectroscopy	I.2,I.4.f,I.6
AS	Auger Spectroscopy	IV
BIS	Bremsstrahlung Isochromat Spectroscopy	II.B.2
-	Bremsstrahlung-Induced Auger Electron Spectroscopy	IV.6
BS	Bremsstrahlung Spectroscopy, Momentum-Resolved Bremsstrahlung Spectroscopy	II.B.3
CEELS	Characteristic Electron Energy Loss Spectroscopy	II.A.2
CELS	Characteristic Energy Loss Spectroscopy	II.A.2
CFSS	Constant-Final-State Spectroscopy	I.4.e
CIS	Characteristic Isochromat Spectroscopy	II.B.2
CISS	Constant-Initial-State Spectroscopy	I.4.d
CLS	Characteristic Loss Spectroscopy	II.A.2, II.A.4
-	Core-Level Characteristic Loss Spectroscopy	II.A.4
CXAES	Continuous X-ray-Induced Auger Electron Spectroscopy	IV.6
DAPS	Disappearance Potential Spectroscopy	III.3
DSMS	Depth-Selective Mössbauer Spectroscopy	I.3
DSPES	Depth-Selective Photoelectron Spectroscopy	I.3
e,2e) E2E)	Electron-Electron Coincidence Spectroscopy	V
EAAPS	Electron-Excited Auger-Electron Appearance Potential Spectroscopy	III.2
EAES	Electron Excited Auger Electron Spectroscopy	IV.1
EAPFS) EAPFSS)	Extended (or Electron) Appearance Potential Fine-Structure (Analysis or Spectroscopy)	III.6
EDCS	Energy Distribution Curve Spectroscopy	I.4.a
EDS	Energy Distribution Spectroscopy or Energy-Dispersive (X-ray Analysis) Spectroscopy	I.4a II.B
EEAES	Electron Excited Auger Electron Spectroscopy	IV.1
EELFS	Extended-Energy-Loss Fine-Structure (Spectroscopy)	II.A.3
EELS	Electron Energy Loss Spectroscopy	II.A.2
EEXAPS	Electron Excited X-ray Appearance Potential Spectroscopy	III.1
EIAES	Electron Induced Auger Electron Spectroscopy	IV.1
EIS	Electron Impact Spectroscopy	II.A

ELEED	Elastic Low Energy Electron Diffraction	IV.A.2
ELS	Energy Loss Spectroscopy	II.A
EMAS	Electron Microprobe Auger Spectroscopy	IV.1
EPMA	Electron Probe Microanalysis	II.B
ESCA	Electron Spectroscopy for Chemical Applications (or Analysis)	I.2
ETS	Electron Transmission Spectroscopy or Electron Tunneling Spectroscopy	II.A.5
EXAFS) EXAFSS)	Extended X-ray Absorption Fine-Structure (Spectroscopy)	I.4.h
EXAPS	Electron Excited X-ray Appearance Potential Spectroscopy	III.1
-	Exoelectron Emission Spectroscopy	VI
EXELFS	Extended Electron-Energy-Loss Fine-Structure (Spectroscopy)	II.A.3
-	Excited-Atom Deexcitation Spectroscopy Using Incident Ions	VI.2
FEED) FEEDS)	Field Emission Energy Distribution (Spectroscopy)	VII.1
FEM	Field Emission Microscopy	VII
FES	Field Emission Spectroscopy	VII.1
FEESP	Field-Emitted Electron Spin-Polarization (Spectroscopy)	VII
FIM	Field Ion Microscopy	VII
-	Gamma Ray Photoelectron Spectroscopy	I.3
HAES	He^{+}-Excited Auger Electron Spectroscopy	IV.4
HEELS	High Energy Electron Energy Loss Spectroscopy	II.A.3
HEELS	High Resolution Energy Loss Spectroscopy	II.A.1
HREELS	High Resolution Electron Energy Loss Spectroscopy	II.A.1
HRELS	High Resolution Energy Loss Spectroscopy	II.A.1
HRXPS	High Resolution X-ray Photoelectron Spectroscopy	I.2
IAES	Ion Excited Auger Electron Spectroscopy	IV.4
IEAES	Ion Excited Auger Electron Spectroscopy	IV.4
IEMM	Incident Energy Modulation Method (Spectroscopy)	III.2
IESS	Inelastic Electron Scattering Spectroscopy	II.A.2
IETS	Inelastic Electron Tunneling Spectroscopy	III.7
IIAES	Ion Induced Auger Electron Spectroscopy	IV.4
ILEED	Inelastic Low Energy Electron Diffraction	II.A.2
ILS	Ionization Loss Spectroscopy	II.A.4
INS	Ion Neutralization Spectroscopy	VI.1
IPES	Inverse Photoemission Spectroscopy	II.B.1

IPS	Inverse Photoemission Spectroscopy	II.B.1
IS	Ionization Spectroscopy	II.A.4
-	Isochromat Spectroscopy	II.B.2
KRIPES	$\vec{k}$-resolved Inverse Photoemission Spectroscopy	II.B.1
LEED	Low Energy Electron Diffraction	I.6,II.A
LEELS	Low Energy Electron Loss Spectroscopy	II.A.1
MDS	Metastable (Noble Gas) Deexcitation Spectroscopy	VI.3,VI.4
MQES	Metastable-Quenched Electron Spectroscopy	VI.3,VI.4
NEXAFS	Near-Edge X-ray Absorption Fine-Structure (Spectroscopy)	I.4.h
NPD	Normal Photoelectron Diffraction	I.6
PAES	Proton Induced Auger Electron Spectroscopy	IV.4
-	Partial Yield EXAFS	I.4.h
PD) PED)	Photoelectron Diffraction	I.6
PES	(Ultraviolet) Photoelectron (or Photoemission) Spectroscopy	I.1
PESM	Photoelectron Spectromicroscopy	I.5.b
PEYS	Photoelectron Yield Spectroscopy	I.4.b
PESIS	Photoelectron Spectroscopy of the Inner Shell	I.2
PESOS	Photoelectron Spectroscopy of the Outer Shell	I.1
PIES	Penning Ionization Electron Spectroscopy	VI.4
PIPECO	Photoion-Photoelectron Coincidence Spectroscopy	V
PIS	Penning Ionization Spectroscopy	VI.4
PYS	Partial Yield Spectroscopy	I.4.c
-	Resonance Ionization Spectroscopy	VI.3
-	Resonance-Enhanced Photoelectron Spectroscopy	I.4
-	Resonant Photoelectron Spectroscopy	I.4
SAES	Scanning Auger Electron Spectroscopy	IV.1
SAM	Scanning Auger Microscopy (or Microprobe)	IV.1
-	Secondary Electron Emission Spectroscopy	II.A
SEELFS	Surface Extended-Energy-Loss Fine-Structure (Spectroscopy)	II.A.3
SEM	Scanning Electron Microscopy or Surface Electron Microscopy	II.A
SESCA	Scanning Electron Spectroscopy for Chemical Applications	I.5.a
SEXAFS	Surface Extended X-ray Absorption Fine-Structure (Spectroscopy)	I.4.h
SPAES	Spin Polarized Auger Electron Spectroscopy	IV.3
SPARPES	Spin-Polarized Angle-Resolved Photoelectron Spectroscopy	I.1

SPIES	Surface Penning Ionization Electron Spectroscopy	VI.4
SPIPES	Spin Polarized Inverse Photoemission Spectroscopy	II.B.1
SPIS	Surface Penning Ionization Spectroscopy	VI.4
SPPES	Spin-Polarized Photoelectron Spectroscopy	I.4
SRPES	Synchrotron Radiation Photoelectron Spectroscopy	I.4
STEM	Scanning-Transmission Electron Microscopy	II.A.3.(a)
SXAPS	Soft X-ray Appearance Potential Spectroscopy	III.1
SXES	Soft X-ray Emission Spectroscopy	II.B
SXPS	Soft X-ray Photoelectron Spectroscopy	I.2
TCS	(Total Current Spectroscopy) (Target Current Spectroscopy)	III.4
UPES) UPS) UVPES) UVPS)	Ultraviolet Photoelectron (or Photoemission) Spectroscopy	I.1
UVBIS	Ultraviolet Bremsstrahlung Isochromat Spectroscopy	II.B.1
VBXES	Valence Band (-Core) X-ray Emission Spectroscopy	II.B
XAES	X-ray Excited Auger Electron Spectroscopy	IV.6
XANES	X-ray Absorption Near-Edge Structure (Spectroscopy)	I.4.h
XAPS	X-ray Appearance Potential Spectroscopy	III.1
XBIS	X-ray Bremsstrahlung (Isochromat) Spectroscopy	II.B.2
XEAES	X-ray Excited Auger Electron Sepctroscopy	IV.6
XEAPS	X-ray Excited Electron Appearance Potential Spectroscopy	III.5
XES	X-ray Emission Spectroscopy	II.B
XIAES	X-ray Induced Auger Emission Spectroscopy	IV.6
XIS	X-ray (Continuum) Isochromat Spectroscopy	II.B.2
XPD) XPED	X-ray Photoelectron Diffraction	I.6
XPES) XPS)	X-ray Photoelectron (or Photoemission) Spectroscopy	I.2
XRD	X-ray Diffraction	I.4
XRF	X-ray Fluorescence Spectroscopy	II.B
XUPS) XUVPES)	Photoelectron Spectroscopy in Region Between UV and X-ray	I.2