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A SURVEY OF EXPERIMENTAL TECHNIQUES IN SURFACE CHEMICAL PHYSICS

Prepared for publication by

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A survey of experimental techniques in surface chemical physics

Abstract - The major techniques presently used for characterising solid surfaces are summarized. These techniques include interactions (or release) of photons, electrons and neutral or charged atoms and molecules, and other miscellaneous methods which may be applied to single crystal surfaces or polycrystalline material.

CONTENTS

I. Characterisation of Surface Elemental Composition

1. X-ray photoelectron spectroscopy (XPES)
2. Auger electron spectroscopy (AES)
3. Secondary ion mass spectrometry (SIMS)
4. Laser microprobe mass analysis (LAMMA)
5. Thermal desorption spectroscopy ; Temperature programmed desorption (TPD)

II. Characterisation of Surface Structures

1. Low energy electron diffraction (LEED)
2. Reflection high energy electron diffraction (RHEED)
3. Photoelectron diffraction (PED)
4. X-ray absorption (SEXAFS and NEXAFS)
5. Helium diffraction
6. Ion scattering spectroscopy (ISS)
7. Grazing incidence X-ray diffraction, X-ray standing waves
8. Field ion microscopy (FIM) and related methods
9. Electron microscopy
10. Scanning tunnelling microscopy (STM)
11. Electronically stimulated desorption (ESD)

III. Investigation of Surface Electronic Structure

1. UV photoelectron spectroscopy (UPES)
2. Inverse photoemission (IPES)
3. Penning ionisation spectroscopy (PIS); Metastable deexcitation spectroscopy (MDS)
4. Electronic electron energy loss spectroscopy (ELS or EELS), vacuum UV reflection spectroscopy
5. The work function (incl. field emission)

IV. Characterisation of Vibrational Modes of Adsorbed Species

1. Infrared spectroscopy (IR)
 - 1.1. Infrared transmission spectroscopy
 - 1.2. Diffuse-reflectance infrared spectroscopy (DRIFT)
 - 1.3. Reflection-absorption infrared spectroscopy (RAIRS) and infrared ellipsometric spectroscopy
 - 1.4. Infrared attenuated total reflection spectroscopy (ATR)
 - 1.5. Infrared emission spectroscopy
 - 1.6. Infrared photoacoustic spectroscopy (PAS)
2. Raman spectroscopy, resonance Raman spectroscopy (RRS) and surface enhanced Raman spectroscopy (SERS)
3. Vibrational electron energy loss spectroscopy (EELS or VEELS)
4. Inelastic electron tunnelling spectroscopy (IETS)
5. Inelastic atom scattering
6. Inelastic neutron scattering

V. Miscellaneous Techniques

1. Nuclear magnetic resonance (NMR)
2. Electron spin resonance (ESR)
3. Mößbauer spectroscopy
4. Magnetic methods
5. Neutron diffraction

Appendix: Selected Literature

PREFACE

This Survey is intended to briefly summarize the major techniques of surface chemical physics, including those used in the study of adsorbed species, and gives briefly for each technique the principles on which it is based, associated nomenclature and, where appropriate, representative applications.

Surface chemical physics techniques have burgeoned in number, power and sophistication over the past fifteen years. Indeed, it can be said that there was little direct information available at the molecular level on the composition and electronic structure of solid surfaces in 1970. Many techniques have been introduced or further developed and applied systematically to the study of single crystal surfaces in ultrahigh vacuum environments as well as to the study of adsorbed atoms and molecules on those surfaces. Important advances have been made in the theory of low energy electron diffraction, so that reliance can be placed on carefully documented full surface structures (as opposed to determinations limited to establishing symmetry). The understanding of photoelectron spectroscopy has markedly improved, and its range of applications has been substantially increased by the use of synchrotron radiation (which has also led to the development of the extended X-ray absorption fine structure method). Fourier transform methods have increased the applicability of infrared and magnetic resonance methods to the study of surfaces. High resolution electron energy loss spectroscopy has become particularly important in vibrational studies. The use of ion scattering spectroscopies has increased considerably; the development of static secondary ion mass spectroscopy has been particularly important. This progress in surface chemical physics has been stimulated by the availability of high quality commercial ultrahigh vacuum instrumentation.

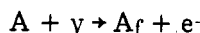
The entries in the Survey are not accompanied by specific literature references; a selection of books and review articles on the various techniques are given in the Appendix. The reader is also referred to the five volumes of "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (eds. D. A. King and D. P. Woodruff) Elsevier, 1982-5 as well as to a new four volume compendium on surface techniques "Methods of Surface Characterisation" (Vol.1, eds. J. T. Yates and T. E. Madey), Plenum Press, 1988.

In the following account the chapters I - IV are mainly, but not exclusively, concerned with techniques for the characterisation of single crystal surfaces and adsorbed layers thereon. Chapter V describes miscellaneous experimental methods which are only suitable for the investigation of large area polycrystalline samples. In general, a particular technique has been included in the chapter where its main area of application lies. Thus, ion scattering falls under "surface structure" and not under "surface elemental composition".

I. CHARACTERISATION OF SURFACE ELEMENTAL COMPOSITION

1. X-ray Photoelectron Spectroscopy (XPS)

This technique (XPS or XPES) is based on the analysis of the kinetic energy distribution of core level photoelectrons produced by irradiation with monochromatic or narrow band characteristic X-rays denoted as γ . Electron Spectroscopy for Chemical Analysis (ESCA) is the original name introduced by Siegbahn and still widely used. The photoionisation, or photoemission, process may be envisaged as



and the kinetic energy E_k of the emitted electron is given by

$$E_k = h\nu - E_b$$

where E_b is the binding energy of the electron, $E_b = E_i - E_f$, where E_f is the energy of the final (generally singly ionised) state A_f and E_i the energy of the initial (neutral) state A of the system. The binding energy E_b of the electron is usually equated with the energy of the corresponding electronic level (orbital energy) in the neutral atom via the frozen orbital approximation (Koopmans' theorem) which ignores the relaxation of the other electrons in the atom or solid during the photoionisation process. The simplest photoelectron spectrum consists, therefore, of discrete peaks, superimposed on a background due to inelastically scattered electrons. The electron binding energies E_b are generally determined with reference to the Fermi level. The usual laboratory photon sources are the $MgK\alpha$ (1253.6 eV) and $AlK\alpha$ (1486.6 eV) lines, although the advantages of performing XPS with monochromatised synchrotron radiation are now becoming apparent. Calibration is usually performed with respect to the C 1s level of carbon (often present as a fortuitous contaminant) at a binding energy of 284.9 eV or to the Au 4f_{7/2} level at 84.0 eV. This latter procedure is of particular use in the case of poorly conducting solid samples where compensation of shifts in the measured E_k due to surface charging effects is necessary.

In addition to the simple process of photoemission consisting of a one-electron transition there is also evidence for multi-electron excitation, manifested as "satellites", in the photoelectron spectrum. Their presence indicates that Koopmans' theorem is only an approximate description.

A frequently observed process is a two-electron transition for which two types can be distinguished depending on whether the second electron is excited to a higher bound state ("shake-up") or to an unbound continuum state ("shake-off"). Both shake-up and shake-off processes require energy that will lower the kinetic energy of the primary photoelectron resulting, therefore, in satellite structure on the low-kinetic energy side of the main (one-electron) photoelectron peak. The satellite structure can be useful to distinguish between different oxidation states of a metal, e.g., Cu^+ and Cu^{2+} .

The value of E_b for a particular photoelectron provides an elemental identification of the atom from which the electron was emitted and is particularly sensitive to the chemical environment through a "chemical shift" effect. This is associated with different atomic environments and is of considerable practical value in XPES. The chemical shifts arise from the sum of two effects, namely, a difference in the relaxation referred to above and a shift in the orbital energy due to the changed chemical environment. Chemical shifts of approximately 1 eV are observed between, for example, the various individual oxidation states of transition metals and also for the O 1s spectra of oxygen when present as $\text{O}^{2-}(\text{a})$, $\text{OH}^-(\text{a})$, and $\text{H}_2\text{O}(\text{a})$ on metal surfaces [(a) denotes an adsorbat species]. There have also been many studies of the difference in binding energy of the atoms at the surface and in the bulk of a solid ("the surface chemical shift").

The low escape depth for photoelectrons in solids means that XPES is a surface sensitive technique, about 20 % of the measured signal intensity (the precise fraction depends on the material and the electron kinetic energy) arising from the outermost atomic layer of the sample. The measured photoelectron intensities can be related to the concentration of emitting atoms in the surface region and a relationship which has been extensively and successfully used, for instance for an adlayer, is the equation

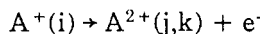
$$\frac{Y_m}{Y_s} = \frac{\mu_m M_m \theta}{N_A \mu_s \rho \lambda \cos \phi}$$

in which θ is the adatom surface coverage, Y_m the integrated photoelectron signal from a particular subshell of the adatom, Y_s the integrated signal from the relevant subshell of the substrate, μ_m and μ_s are the subshell photoionisation cross-sections for the adatom and substrate, M_m and ρ are the molecular weight and density of the substrate, respectively, and λ is the electron escape depth in the substrate for the particular substrate subshell photoelectrons, ϕ is the angle of electron collection with respect to the sample normal and N_A is Avogadro's constant. Various corrections have to be made to the signal intensities; the values of μ and λ are now documented. Extensive use of the above relationship together with comparisons with other methods of estimating surface concentrations suggest an accuracy of up to $\pm 15\%$.

Phenomenologically there is no difference between XPES and ultraviolet photoelectron spectroscopy, or UPES (see section III.1). Since the photon energies in XPES are higher it is clear that photoelectrons can be excited from both core and valence levels. The increasing use of continuously tunable synchrotron radiation (for more fundamental surface studies) has in any case blurred the differences between the two techniques and has led to the sensible suggestion of referring to core level photoelectron spectroscopy and valence level photoelectron spectroscopy. Only the core level variant can be used for quantitative surface analysis.

2. Auger Electron Spectroscopy (AES)

The method is based on the detection of Auger electrons ejected from material as a result of core hole decay following ionisation. An Auger transition for an isolated ion can be represented by



$A^+(i)$ is an ion formed by loss of an electron from a core level i , usually as a result of X-ray irradiation or (more commonly) from bombardment by electrons in the 1 to 2 keV energy range. The Auger process occurs when an electron from a higher level j falls into the level i , and the energy released suffices to eject an electron from a third level k (also higher than i but possibly the same as j). The kinetic energy of an Auger electron emitted during this transition (ijk) is characteristic of the emitting atom. The common notation designates the transition by the atom symbol and the triplet identification. Principal quantum numbers 1, 2, 3... are represented by letters K, L, M... and the total angular momentum $j = \underline{l} + \underline{s}$ by subscripts 1, 2, 3... corresponding to $j = 1/2, 3/2, 5/2$; the subscript is omitted for K electrons as only one is possible. Thus a KL_1L_2 transition starts with a 1s hole in A^+ and finishes with $2p_{1/2}$ and $2p_{3/2}$ holes in A^{2+} . When valence electrons are involved, a notation such as KVV is common, representing in this case a transition in which a 1s vacancy is filled and two vacancies are created in the valence shell.

The electron mean free path λ in a material varies with the kinetic energy E according to the general relation $\lambda = AE^{-2} + BE^{1/2}$ where A and B are material-dependent constants. The escape depth in AES may be equated with λ and varies from 0.4 to 0.8 nm so that the technique is very surface sensitive. Information as to variation in composition with depth can be obtained by exploiting different Auger transitions having different escape depths. With suitable calibration AES can provide quantitative analysis of the surface region. Chemical shifts can also be observed.

Electrons resulting from Auger transitions must be resolved from a high background of other secondary electrons. The sharpness of Auger features makes this feasible particularly when instrumentation is used to measure the derivative spectrum. An Auger transition in such a plot appears as a peak followed by a trough; the voltage at the point of inflection between peak and trough is characteristic of the element and its environment and the peak-to-trough distance is taken as proportional to the surface concentration of that element with the proportionality constant best obtained by standardisation. Sensitivities of the order 0.001 monolayer can be obtained in this way.

It should be emphasised that since the Auger process involves three electrons it is inherently more complex than XPES (a single electron process). Nevertheless it is unquestionably the most frequently used electron spectroscopic technique in surface analysis. By reducing the dimensions of the incident electron beam it is now possible to obtain lateral resolution of less than 50 nm in the scanning Auger electron microscope (SAM). In addition, it is possible to combine its surface sensitivity with ion-etching, so that information on the chemical composition as a function of depth may be obtained. Other variations include making use of photoelectron and Auger peaks to give an "Auger parameter" which has been shown to be sensitive to the oxidation state of a given element. In general, electron-induced Auger spectra do not provide unambiguous information on the nature of adsorbed molecules in view of their sensitivity to electron beam-induced dissociation. However, fingerprint spectra for surface species can be obtained if care is taken in minimising the current in the electron beam with maximisation of the area of incidence. More important for adsorbates from this point of view are photon-induced Auger spectra, where less damage occurs in the layer. Recently, the orientation of molecules on surfaces has been investigated via the angular distribution of Auger electrons excited with synchrotron radiation.

3. Secondary Ion Mass Spectroscopy (SIMS)

The erosion of a solid sample due to bombardment with energetic particles - a phenomenon known as sputtering - is used in this technique for the purpose of surface analysis. The outermost layers are sputtered by the impact of suitable primary ions with energy up to a few keV. The resulting secondary ions, with positive or negative charge are analysed in a mass spectrometer. The relative abundance of sputtered species gives analytical data about the composition of the removed surface layer. SIMS is a very sensitive surface analytical tool. At low primary ion currents surface monolayers may exist for hours before being completely removed (static SIMS). On the other hand SIMS is also capable of elemental depth profile analysis (dynamic SIMS).

The sputtering yield (number of emitted particles per incident particle) depends on the local structure and surface composition of the target material, the incident ion beam and the experimental geometry. It can vary over several orders of magnitude. For ions of medium mass (e.g. Ar⁺) and several keV the sputtering yield normally lies between 0.1 and 20. The bombarding ion transfers energy in collisions to target atoms which recoil with sufficient energy to generate other recoils. Some of these recoils are directed back towards the surface with sufficient energy such that atoms or ions escape from the surface. Thus, the sputtering process involves a complex series of collisions, with energy transfer and angular deflections between many atoms in the solid. In practice, quantitative analysis by SIMS is predominantly carried out by implying empirical sensitivity factors.

The sputtered species are emitted as neutrals (atoms or molecules) in various excited states or as both positive and negative ions, singly and multiply charged. Molecular or cluster ions may reflect nearest neighbour association or, more generally, the structural properties of the sample. The relative proportion of ions and neutrals which are ejected from the surface can vary by orders of magnitude, depending on the surface composition. Usually, adsorbed oxygen greatly enhances the ion yield at a metal surface. With polyatomic targets preferential sputtering of one of the components can change the surface composition. One other complication consists in ion beam mixing, i.e. redistribution of particles in the solid, for instance of a layer structure. For quantitative analyses the sputtering yields, ionisation probabilities and changes in surface composition have to be known.

In "static SIMS" very low primary ion currents at low energies are used to probe the uppermost surface layer. With a 10^{-9} A cm⁻² current density of 2 keV Ar⁺ ions and an emission yield of one secondary particle per incident ion, for instance, it takes 30 minutes to remove 1 % of a monolayer. Thus, although each ion impact damages a small region of the surface the contribution of previously damaged areas of the surface to the secondary ion yield can be neglected.

SIMS has been applied to single crystal surfaces, with or without chemisorbed layers, as well as to polycrystalline samples. Even organic material has been analysed. Instead of noble gas, primary reactive ions (O⁺, CO⁺, etc.) have been used to study surface reactivity. For mechanistic studies the angular dependence of the secondary ion yield as well as the energy distribution of secondary ions have been measured.

For the analysis, the secondary ions first enter an energy filter, normally an electrostatic energy analyser, and are then sampled in a mass spectrometer, for example a quadrupole mass filter. In certain instruments it is possible to scan a primary ion beam of low spot size across the sample for high lateral resolution. There are also imaging devices available which monitor the lateral distribution of the different elements. In another important variation of the technique, secondary neutral mass spectrometry, the yield of neutral particles is measured by ionising the sputtered neutral particles after emission from the solid surface.

4. Laser Microprobe Mass Analysis (LAMMA)

Laser microprobe mass analysis (LAMMA) - also known as laser ionisation mass analysis (LIMA) - has proved to be useful for qualitative analysis of surface or thin film composition. A high-power pulsed laser beam is directed at the surface of the sample under study where it ionises a small fraction of the material. Elemental or molecular ions thus generated, whether positive or negative, are analysed by means of a time-of-flight mass spectrometer with a high transmission coefficient.

The microprobe can be used in the transmission or reflection modes. The transmission mode is used for the study of thin specimens of bulk materials. It allows the qualitative analysis of all solid materials which can be prepared as microparticles, films or thin sections. In the reflection mode, the surface of solid samples can be analysed without any pretreatment. The diameter of the laser impact spot may be as small as $2 \mu\text{m}$. In general, two regimes of ion production are used. Low (under 10^8 W cm^{-2}) power density is used where molecular information is desired; in this case the fraction of emitted species which is ionised is quite small. High (over 10^9 W cm^{-2}) power density is used to obtain elemental compositions; in this case the fraction of emitted species ionised can approach 100 %.

In the same way as the laser microprobe, heavy-ion desorption, induced by nuclear decay of ^{253}Cf , has been applied to thin film analysis.

5. Thermal Desorption Spectroscopy; Temperature Programmed Desorption (TPD)

Thermal desorption consists of the removal of adsorbates from a surface by thermal excitation induced by heating the substrate. The desorbing particles are detected by measuring the pressure increase or more specifically by mass spectrometric determination of desorbing particle fluxes. Desorption processes also have been measured by monitoring the time-dependent surface coverage, for instance from work function data. The thermal desorption ("flash-filament", "flash desorption" or "temperature programmed desorption") method is used to study the surface composition and the binding states of adsorbates, the population of these states, as well as the kinetics of conversion and desorption.

In a particular type of thermal desorption experiment, a gas is allowed to adsorb on a previously cleaned sample, for a controlled exposure at a given temperature. A temperature programme, e.g., linear with time, is then applied to the adsorbent. Desorption of the adsorbate occurs in a continuously pumped chamber and a desorption spectrum (partial pressure of a gas species) is recorded. More generally, a mass spectrometer is used to monitor simultaneously partial pressures of all gas species, evolved as a result of desorption, decomposition, or other surface reactions, as function of time. When the pumping rate is high enough (a condition frequently fulfilled), the number of desorbed gas molecules can be calculated from the area under the desorption curve.

It is usually assumed that the rate of desorption of a surface species from a single binding state, i , (giving a single desorption curve or peak) follows an Arrhenius equation

$$-\frac{dN_i}{dt} = \nu_i (N_i)^{n_i} \exp(-E_i/RT)$$

where E_i is the activation-energy for desorption, ν_i the pre-exponential factor, n_i the reaction order for desorption and N_i the number of molecules in the adsorbed state, i , related to a particular surface area. Values of the desorption rate parameters E_i and n_i can be deduced from the desorption spectra. A fairly good estimate of E_i can be made from the peak-maximum temperature, T_p , if the preexponential term is known. The activation energy for desorption can be determined without assuming a value of the preexponential factor for all orders of reaction by varying the heating rate (β) over a wide range (two orders of magnitude) and plotting $\ln(\beta/T_p^2)$ vs $1/T_p$. Whether a species is adsorbed molecularly or dissociatively can often be inferred from the desorption reaction order n_i , but if the E_i and/or n_i are coverage-dependent, these values cannot be used to define the adsorbed state.

Complex desorption spectra with several overlapping peaks are commonly attributed to multiple binding states, revealing distinct surface sites. Each adsorption state may be therefore treated independently. However, multiple peaks, at least when they are not clearly separated, could also result from induced heterogeneity with increasing coverage, domain growth, and structural transitions in the adsorbate layer, such as might be caused by repulsive lateral interaction between adsorbed species. Recently, it has been observed that even rather simple adsorbate systems (argon/carbon) may display complicated desorption kinetics (e.g. preferential desorption from domain borders).

For surface reactions, temperature programmed desorption (frequently named temperature programmed reaction spectroscopy) has been developed and proven to be a valuable source of reaction kinetic data. Products of a reaction or molecular decomposition which proceeds prior to desorption can be investigated.

The analysis of desorption spectra is seldom unambiguous. Owing to its relative simplicity and great sensitivity, however, thermal desorption is one of the most commonly used techniques to

investigate gas-solid interactions. It is also suitable for the study of displacement reactions, isotope exchange and surface reactions such as thermal decomposition of adsorbed molecules. Thermal desorption is generally used in conjunction with other physical methods providing complementary information on the adsorbed layer. It is of particular value for fundamental studies of chemisorption on clean, structurally well-defined solid surfaces. It has also been successfully applied for the characterisation of less stringently cleaned surfaces containing physisorbed or chemisorbed impurities, e.g. industrial adsorbents and catalysts.

II. CHARACTERISATION OF SURFACE STRUCTURES

1. Low Energy Electron Diffraction (LEED)

In low energy electron diffraction, a monoenergetic (energy typically in the 20 to 200 eV range), collimated beam of electrons impinges on a surface and the diffraction pattern of the elastically scattered electrons is analysed. Because the scattering cross-sections for low energy electrons by atoms is quite large (about 10^{-2} nm², as compared to about 10^{-8} nm² for X-rays) the scattered electrons come chiefly from atoms on or very near to the surface and so carry information concerning the structure in this region.

In the same way as in a bulk crystal, a two-dimensional structure can be characterised by a lattice (the repeat system of the structure) and a motif (the constellation to be repeated). The lattice is characterised by only two vectors \underline{a} and \underline{b} and the single angle α between them such that any point $\underline{r} = n_1 \underline{a} + n_2 \underline{b}$, where n_1 and n_2 are integers, is an equivalent point in the lattice. Starting from an origin, the origin and the termini of the three vectors \underline{a} , \underline{b} , and $\underline{a} + \underline{b}$ furnish four points defining the parallelogram which is the unit cell of the structure. For example, the {100} face of a face-centered cubic metal could be characterised by two vectors of length a_0 with angle 90° and a motif consisting of two atoms at (0, 0) and (1/2, 1/2) in units of a_0 . This is a doubly primitive unit cell for this system; a primitive unit cell with vectors of length $2^{-1/2} a_0$ and angle 90° but rotated 45° with respect to the original set also characterizes the lattice, and in this case the motif is a single atom. Primitive lattice systems are generally preferred choices, and a clean unreconstructed metal surface is usually designated by a symbol for the metal, Miller indices for the crystal face, and the unit cell in terms of the primitive unit cell base vectors, for example Pt{100}(1×1).

Consider a beam of electrons propagating in the +Z direction impacting a two dimensional square (e.g., {100} face-centered cubic crystal) lattice in the $Z = 0$ plane, with unit vector axes parallel to the X and Y axes. Scattering from atoms in this model will lead to constructive interference if $\underline{X}\underline{R}^{-1}$ and $\underline{Y}\underline{R}^{-1}$ are integral multiples of λa_0^{-1} , where λ is the electron wavelength. Because of the two dimensional character of the lattice there is no restriction on $\underline{Z}\underline{R}^{-1}$. Hence constructive interference occurs along a set of "lattice rods" in reciprocal space rather than in a set of points as for the three-dimensional case. A fluorescent hemispherical screen of radius R_s with the sample at its centre will intersect these rods to give a spot pattern independent of the value of R_s . In practice, grids are placed between screen and sample to eliminate inelastically scattered electrons. As in three dimensions, analysis of spot locations establishes the two-dimensional lattice.

Surfaces of interest in surface chemistry are not neat arrays of atoms whose centres all lie in the same plane. For example, the W{100} (1×1) surface will have a square unit cell which can be chosen so that there is a tungsten atom at each corner of it. Because tungsten is body centered cubic, there will also be an atom in the center of the square depressed below the plane of the square, presenting a possible adsorption site. Adsorbed species also contribute three dimensional character. Even on the clean surface the phenomena of relaxation and reconstruction can occur i.e. the arrangement of surface atoms differs from that of the ideally terminated bulk. Finally, the electrons penetrate a few layers into the structure, and hence a very thin slab of sample, rather than a plane of atoms, is responsible for the diffraction pattern observed. This results in a modulation of intensity along the lattice rods of constant intensity that would have resulted from a planar array of scatterers. The modulation appears as a variation in intensity of a given spot (whose position on the screen will vary systematically) as the electron energy, and hence wavelength, is varied. The analysis of spot intensities may permit inference of the motif i.e. the arrangement of the atoms in the unit cell.

A LEED spot pattern defines the two-dimensional lattice, and (importantly) shows that long range order exists on the surface (but neglects short-range structural disorder). LEED is widely used for these purposes. For example, chemisorption of nitrogen on W{100} can lead to a structure at high coverage with the same unit cell vectors as W{100}(1×1) and one nitrogen atom per unit cell; this structure is denoted W{100}(1×1)-N. Nitrogen adsorption can also lead at lower coverage to a structure whose primitive unit cell is defined by two perpendicular vectors rotated 45° with respect to those for the clean surface and longer by a factor $\sqrt{2}$; this structure is designated W{100}($\sqrt{2} \times \sqrt{2}$)R 45° -N. An alternative and more common designation of the same lattice is based on a square centred lattice with vectors in the same direction but twice as long as the base vectors; this alternative designation is denoted W{100}_c(2×2)-N. The unit cell is not primitive. W{100}_c(2×2)-N has half the surface density of nitrogen as W{100}(1×1)-N. The spot pattern does not establish where the nitrogen is located in either case; for example, it could be located on top of a single metal atom, bridging a pair of metal atoms, or in the "hollow" position (interacting with five metal atoms); the location could even be different in the two structures.

Determination of motif by intensity analysis is much more difficult in LEED than in X-ray crystallography. This stems largely from the fact that multiple scattering must be considered in the intensity analysis. The number of crystallographically independent spots available for analysis is also much smaller than commonly used in X-ray diffraction. A LEED structure analysis requires that high resolution intensity-voltage (I - V) plots be obtained for as many independent spots as possible, that these be compared against plots calculated on the basis of a number of assumed surface models, and checking sensitivity of the calculated results to all parameters in the models. Despite these difficulties the number of surface structures determined in this way is now over two hundred, including many adsorbate systems.

2. Reflection High Energy Electron Diffraction (RHEED)

LEED derives its surface sensitivity from the high scattering cross-section for low energy electrons which impinge perpendicular to the surface. RHEED represents an alternative approach: surface specificity is obtained by using higher energy electrons (typically 20 keV) incident at near to grazing incidence. Since the diffracted beams are recorded at grazing exit angles, the overall scattering angle thus remains small giving rise to a sufficiently high elastic scattering cross-section. In the plane of observation the reciprocal lattice rods are not intersected perpendicularly as in LEED but obliquely, giving rise to "streaks" rather than spots. Since there is no complete quantitative theory for RHEED, the method has so far only been used for the determination of surface periodicity. In this respect LEED and RHEED provide identical information for a smooth surface. Since, however, the sample in RHEED must be turned azimuthally to establish the full two-dimensional periodicity, LEED is in fact the simpler technique. On the other hand, RHEED can provide structural information on rough surfaces for which LEED might be ineffective.

3. Photoelectron Diffraction (PED)

Recalling the technique of X-ray photoelectron spectroscopy described in section I.1 we note that the kinetic energy of the photoemitted electron, E_k , is given by the difference between the photon energy and the binding energy of the level concerned. In photoelectron diffraction the photoelectron current from a core level of an adsorbed species is measured as a function of either emission angle or photon energy. The coherent interference between the directly emitted electrons and those elastically scattered from the surrounding, (mainly) substrate atoms means that information is obtainable on the position of the emitting atom relative to the substrate i.e. on the adsorption site.

In the first, and older, variation of the technique the photon energy is fixed so that a laboratory X-ray source (e.g. AlK α) can be used. To eliminate purely atomic photoionisation effects the photon incidence and electron emergence directions are kept constant and the sample is rotated about its surface normal to give a so-called azimuthal or Φ plot. The second alternative approach requires that the incident and emission directions are held constant and the photon energy varied. The scattering variable is thus the photoelectron kinetic energy. Clearly this experiment is only possible at a synchrotron radiation source. The resulting curve (intensity of the core level feature vs. photon energy) is often referred to as a constant initial state (CIS) spectrum and is similar to a LEED I - V plot. There is, however, one important difference. In LEED the initial state is an incident plane wave rather than a localised source of electrons. In PED the localisation is at the point of interest, which means that the method is in principle very sensitive to the adsorption site. An important difference between LEED and photoelectron diffraction (in both variations) is also clear from this discussion: the observation of LEED interferences from an adsorbate requires an ordered overlayer which is not necessary for photoelectron diffraction.

In general, the data analysis in photoelectron diffraction is similar to that in LEED. Model calculations are performed for various possible adsorption sites and geometries and the data compared with experiment. For laboratory experiments with AlK α the photoelectron kinetic energy is normally quite high (> 500 eV) and single scattering calculations suffice. In the CIS experiment most data have so far been collected in the LEED range (50 - 150 eV) where a multiple scattering description is required. Whether full multiple scattering needs to be considered in the kinetic energy range 150 - 500 eV is still the subject of discussion.

As yet, there have been very few adsorbate structural determinations using photoelectron diffraction. Given the new generation of synchrotron radiation sources there are, however, signs that the CIS technique will become a very powerful structural tool, particularly for the investigation of adsorbed molecules.

4. X-ray Absorption (SEXAFS and NEXAFS)

Extended X-ray absorption fine structure (EXAFS) appears in the X-ray absorption spectrum (as a function of photon energy) on the high energy side of an absorption edge. Synchrotron radiation is usually required. The fine structure results from elastically scattered photoelectrons arriving back at the emitting atom and adding coherently to the outgoing wave. This backscattering causes a modulation in the photoionisation cross-section as the photoelectron energy increases and its associated wavelength passes through values which are submultiples of the total distance to and from nearest neighbour atoms. In the surface variant of the technique, Surface-EXAFS or SEXAFS, an electron "yield" is measured which is proportional or nearly proportional to the photoionisation cross-section (or absorption coefficient). The Auger electrons from a particular

adsorbate core level, the complete photoelectron current from the surface (total yield) or a part of it which has been energy-filtered (partial yield) are often used. Most of these electrons have a small escape depth and give a relatively high surface sensitivity. Photoelectron diffraction and photoabsorption (or SEXAFS) are of course related. In the former, the photoelectron current in a particular emission direction is recorded. In the latter, the total photoionisation cross-section is measured which would correspond to collecting the total photoelectron current in 4π solid angle (if this were possible). The photoelectron diffraction effects are entirely averaged out; what remains is the interference between the outgoing wave and the waves backscattered from neighbouring atoms.

SEXAFS has proved particularly successful in determining adsorption sites for atomic adlayers on metal surfaces. As in photoelectron diffraction, no ordered overlayers are necessary. Where LEED and SEXAFS have been applied to the same adsorption systems agreement is good. Data analysis is particularly simple: for energies higher than 50 eV above the edge the EXAFS can be normally described by single scattering. In most cases Fourier transform techniques using known or calculated phase shifts deliver the information on the distance of the emitter atom to the neighbouring substrate atoms. Very often, however, this is not sufficient to determine the adsorption site and a so-called amplitude analysis has to be performed. This entails measuring the amplitude of the SEXAFS modulation for various angles of the polarisation vector relative to the surface.

For the description of the structure in the so-called near-edge region (< 50 eV above the edge), generally referred to as NEXAFS (near edge X-ray absorption fine structure) or XANES (X-ray absorption near edge structure), a multiple scattering calculation is necessary. In the case of adsorbed molecules additional structure occurs in this region due to intramolecular scattering. These resonances tend to dominate the near-edge region although the "substrate NEXAFS" is certainly still present underneath. NEXAFS from adsorbed molecules has acquired particular significance in recent years since it enables molecular orientation to be determined. The strong resonances may be identified with excitations into the anti-bonding molecular orbitals of the system. Because these transitions are subject to dipole selection rules they are polarised, so that the orientation of the molecule can often be determined by suitably varying the direction of the polarisation vector of the incident radiation.

X-ray absorption measurements, both SEXAFS and NEXAFS, have opened up significant new possibilities for adsorbate structure determination and offer a real alternative to LEED. The disadvantage is that such investigations are only possible at synchrotron radiation sources and then only if the appropriate monochromators are available. At present, there are very few monochromators performing satisfactorily in the spectral region of the carbon, nitrogen and oxygen 1s levels.

5. Helium Diffraction

The collision of an atomic beam with a solid surface gives rise to both elastic and inelastic scattering. Since the de Broglie wavelength of a helium atom is of the order of 0.05 nm depending on temperature, elastic collisions are expected to give rise to diffraction phenomena. The repulsive part of the interaction potential between a rare gas atom and a solid arises from the overlap of the electron charge distribution of the surface with that of the incoming atom. Theory shows that a plot of the classical turning point for a scattered He atom corresponds to a constant electron density contour, some tenths of a nm in front of the surface. It is thus clear that He atom diffraction can be used for structural determination of single crystal surfaces. The dimensions of the unit cell can be determined from the angular position of the diffraction peaks, whilst the arrangement of atoms in the unit cell and the resulting surface electronic structure determine their relative intensities. To calculate the intensities of the He diffraction beams a particular structural model is taken and approximated by a periodically modulated hard wall (corrugation function). The model parameters are varied until there is agreement between theory and experiment.

Initially, He diffraction was thought to be observable only on the strongly corrugated surfaces of alkali halide crystals. More recently diffraction patterns have been recorded from both metal and adsorbate-covered metal surfaces. A necessary pre-requisite appears to be a very clean surface and a high degree of order (higher than is necessary for the observation of a LEED pattern). It is still not clear whether the best fit corrugation function - essentially a contour map of surface charge density - also gives atomic positions in a reliable way. A similar problem is encountered with the scanning tunnelling microscope (see section II.9). Note that in LEED scattering occurs at the ion cores so that, given an adequate theoretical description, more precise crystallographic information can be obtained with low energy electrons.

6. Ion Scattering Spectroscopy (ISS)

Ion scattering spectroscopy (ISS) is based on the conservation of energy and momentum during the collision of ions with individual surface atoms. If the initial and final energies and momenta of the projectile are known, the mass of the surface atom from which the ion has been inelastically scattered can be calculated.

If the velocity of the ion is sufficiently high (beam energies of the order of a MeV), the particle penetrates well inside the core of the surface atom. The scattering is then due to the Coulomb

repulsion of two positively charged nuclei (Rutherford backscattering - RBS). At lower ion energies or larger impact parameters (small-angle scattering, higher masses of ions) the incident particle does not completely penetrate through the electron shell and the inner electrons screen the charge of the target atom. This influences the scattering cross section which may decrease by two orders of magnitude for low energy ion scattering (LEIS), i.e. for 1keV He⁺ ions. The penetration depth of high energy ions may reach several microns in Rutherford backscattering, while low energy ions scatter predominantly from the outer surface layer. The surface sensitivity of LEIS is further based on the fact that those ions which penetrate into the solid are readily neutralised and can no longer be detected by the analyser.

Ion scattering is a suitable method for qualitative surface analysis; quantitative data suffer from the uncertainty in scattering cross sections and ion neutralisation probabilities. Experimentally, scattered ion energy distributions are either measured at a fixed or variable angle for instance by using an electrostatic energy analyser. Rutherford backscattering is theoretically well described and provides quantitative data on surface composition and, utilising the so-called channeling and blocking phenomena, surface structure. It is probably the most accurate method of measuring small surface relaxations. This method was recently applied to study surface re-construction and phase transformations as well as lattice dynamics involving enhanced surface vibrations and correlated motions.

7. Grazing incidence X-ray diffraction, X-ray standing waves

X-ray diffraction has always been the most important technique for determining the three-dimensional structure of bulk materials. The main limitations in using it for surface studies have been the lack of surface sensitivity and the low brightness of conventional X-ray sources. By using a grazing incidence geometry, at an angle close to the critical angle for total reflection, however, the penetration depth of the X-rays is minimised and the surface signal enhanced. The use of synchrotron radiation can provide orders of magnitude more brightness, giving substantially more flux per unit area of surface and a strongly collimated beam. The measured Bragg intensities can simply be evaluated with kinematic scattering theory because of the absence of multiple scattering as in LEED. The momentum transfer, and thus the greatest sensitivity to atomic co-ordinates, is in the plane of the surface. A "solved" structure is thus normally the projection of surface and near surface atoms onto the surface plane. In the case of reconstructed semiconductor surfaces this information is sufficiently useful in itself to favour or eliminate a particular model. In the case of adsorbates, however, the vertical distance of the adatom is a crucial parameter. So far there has only been one study involving a low Z adsorbate atom.

X-ray standing wave analysis has also become a viable tool for surface structural studies due to the availability of synchrotron radiation. When an X-ray beam is Bragg diffracted by a perfect crystal, a standing wave field is generated inside the crystal due to the interaction of the coherently related incident and diffracted waves. The nodal and anti-nodal planes of the standing wave field are parallel to and have the same periodicity as the diffraction planes. By varying the angle of incidence it is thus possible to modulate the electric field strength to which an atom at a particular location in the crystal is subjected. If the intensity of a secondary process such as fluorescence is measured, it is then possible to establish the position of the atom relative to the lattice plane. By performing the experiment for more than one lattice plane, the full atomic co-ordinates can be established via triangulation. The fact that the standing wave field extends outside the crystal surface into the vacuum allows adsorbed atoms to be investigated. There have so far been relatively few investigations although the technique is very promising. It is confined at present to high Z atomic adsorbates because of the low fluorescence yield and detection problems associated with lighter atoms such as C, N and O. In addition, a very high degree of crystal perfection is required.

8. Field Ion Microscopy (FIM) and Related Methods

In a high electrostatic field of 20 to 50 V nm⁻¹ atoms or molecules can be field ionised. Field ionisation occurs in front of a nearly hemispherical field emitter tip with an apex radius of ≈ 100 nm, where the required field strength is produced by applying a few kV potential difference against a counter electrode. Field ionisation consists in electron tunnelling from atoms or molecules into empty energy levels above the Fermi energy of the solid. A minimum distance X_c is required (establishing a forbidden ionisation zone) which is determined by the ionisation potential I , the work function ϕ and the field strength E :

$$X_c = \frac{I - \phi}{E}$$

Field desorption and field evaporation are achieved with an even higher electrostatic field strength. They are thermally activated processes.

The field ion microscope (FIM) has the capability of imaging surfaces with high lateral resolution on an atomic scale. An imaging gas (usually noble gas or hydrogen) is ionised near the hemispherical emitter surface, and the ions are accelerated in the high electrostatic field towards a phosphorescent screen or image amplifier, where the image is displayed. Contrast in the field ion image is due to local variations in ion yield, caused by local differences in field strength,

charge penetration into the solid and tunnelling probability (wave overlap). At cryogenic temperatures, the position of individual lattice atoms can be located to better than 0.1 nm precision.

Field ionisation mass spectrometry (FIMS) is concerned with the measurement of the charge to mass ratios of the ions generated at the field emitter surface. Magnetic sector instruments, quadrupole mass filters and time-of-flight devices have been adapted for these investigations. In the atom probe field ion time-of-flight mass spectrometer the individual surface particle from an identifiable atomic position on the surface can be registered. FIM, in combination with the atom probe, has been applied to investigate surface diffusion, surface interaction and cluster formation, site-specific surface reactions, and local surface composition in alloy systems. Field ionisation or field desorption mass spectrometry has also been developed as a sensitive analytical tool to identify high molecular weight compounds, since fragmentation processes are a minor part of these ionisation processes.

Field ion appearance potential spectroscopy involves measurement of the energy distribution of the ions, i.e. the high energy onset in the integral kinetic energy distribution establishes produced by field ionisation, field desorption or field evaporation the minimum energy for the ionisation process. For noble gases, the onset of the energy distribution is determined by the ionisation potential (and the retarder work function). For chemisorbed particles or field evaporated lattice atoms the energy distribution onset is influenced by binding energies. The onset of the energy distribution is field dependent and surface Debye temperatures can be derived from these measurements.

Electron-stimulated field desorption consists of electronic excitation of molecules within the forbidden zone ($X < X_c$) and subsequent acceleration from the equilibrium position of the adsorption site. The cross sections are field dependent and approach gas-phase values (10^{-16} cm²) at high fields.

Pulsed laser field desorption or photon-induced field desorption makes use of an electronic excitation process due to laser photons or synchrotron radiation which initiates field desorption. A time-correlated time-of-flight measurement permits mass to charge determination. In general, the excitation is of a thermal nature, in which the field desorption process is enhanced by a temperature pulse of short duration. In special cases, in particular with synchrotron radiation, quantum effects have been observed with direct photon-induced electronic transitions and subsequent field desorption of electronically excited adparticles.

9. Electron Microscopy

Although a wide variety of diffraction methods and spectroscopic techniques are available for the structural characterisation of surfaces, only direct microscopic methods are able to provide real space information about local inhomogeneities such as surface steps, terraces, domains and defects. Although direct imaging of surfaces with electrons has been somewhat overshadowed by the invention of the scanning tunnelling microscope, considerable progress has been made in recent years in conventional electron microscopy following the belated introduction of ultra high vacuum (UHV) into electron microscopes. In transmission electron microscopy (TEM), very thin samples ("platelets") are required for the observation of surface effects. Small metal crystallites, typically of Au or Ag, evaporated onto thin cleaved MoS₂, MgO or graphite, have so far proved most useful. Surface steps, reconstructions and, at the highest resolution, single atoms have been observed. The most striking application of TEM in this area has probably been in surface profile imaging. If the platelet is thin enough and the surface free of impurities, the image shows the crystal profile. In a microscope capable of atomic resolution (microscopes with 0.2 nm lateral resolution are commercially available) this profile image reveals the projected arrangement of atomic columns along the surface. The direct observation of surface reconstruction on gold crystallites has been possible with this method.

In reflection electron microscopy (REM) the incident electron beam strikes the sample at a grazing angle as in the RHEED experiment referred to in section II.2. The REM image is then formed by passing one of the diffracted beams through the objective aperture of the microscope. The picture obtained is considerably fore-shortened in the incident beam direction depending on angle and beam voltage, thus requiring a careful geometrical analysis to obtain accurate real space information. The best lateral resolution is typically 1 nm but monolayer details such as steps, pits and the emergence of dislocations can be distinguished. Spectacular data have been taken, for instance, on the Si{111} surface. A related and very recent technique is low energy electron microscopy (LEEM) where in a mirror-like geometry the zero order emergent beam is imaged. The lateral resolution is not high but monoatomic steps are clearly observed.

10. Scanning Tunnelling Microscopy (STM)

The scanning tunnelling microscope also probes directly surface structure and electronic properties on the atomic scale. The experimental device consists of a rigid sample holder, with the sample, opposite a sharp tip at a very close distance of a few tenths of a nm. The tip probably contains one or a few protruding lattice atoms. In a usual design it is moved in three mutually perpendicular directions by a tripod of piezoelectric ceramics, with the tip motion typically limited to 1 μ_m in each direction. The sample is transported over large distances (a few millimeters to one micrometer) by a carrier, also operated by piezos or by a cantilever

arrangement. Once the tip and the sample are sufficiently close to each other, a tunnel current can be measured. A "tunnel" voltage of a few millivolts to a few volts is applied between tip and sample. The resulting tunnel current of typically 1-10 nA is recorded either as a function of tunnel voltage or sample distance, or it is used in a feedback loop to control the vertical position of the tip. These modes also indicate the different ways the STM can be operated to detect different surface properties. To record the surface topography, the tunnel current is kept constant while the surface is scanned. The motion of the piezoelectric ceramics then provides a real-space image of the surface. The real-space image, however, needs to be interpreted in terms of surface and tip electronic properties. A resolution of 0.01 nm vertically and 0.2 nm laterally has been achieved. In other modes, the relation between tunnel current and distance (\sim barrier height) or tunnel voltage (\sim density of states) is investigated. In this way an image of the local barrier height (local work function) or of the spatial distribution of electronic states just above or just below the Fermi level (scanning tunnelling spectroscopy - STS) is obtained. This method has promising aspects for surface structural analysis on the atomic scale; for instance, the reconstructed Si {111} (7×7) structure has recently been imaged in real space.

A further new development is the Atomic Force Microscope (AFM), which measures interatomic forces between surface atoms and the apex atoms of a tip with a sensitivity down to 10^{-18} N. The tip - for instance non conducting diamond - is fixed to a conducting cantilever. The bending of the cantilever by the interatomic forces is monitored by the tunnelling current between the cantilever and an oppositely mounted (second) STM tip.

11. Electronically Stimulated Desorption (ESD)

Electron stimulated desorption is the surface analogue of electron impact dissociation or photo-dissociation in free molecules. Ions or neutral species are desorbed from an adsorbate-covered surface as a result of an electronic transition into a repulsive state induced by electron impact (ESD, electron stimulated desorption) or photon absorption (PSD, photon stimulated desorption). The internal bond concerned will then be broken as long as the excitation remains localised. On surfaces the number of channels for energy transfer i.e. for charge delocalisation will be very large so that the desorption cross-sections are in general very small compared to dissociation cross-sections in isolated molecules. They also vary over several orders of magnitude. Although the effect was discovered many years ago there has been renewed interest of late due to the possibilities presented by synchrotron radiation of investigating the primary excitations in some detail. In fact, the technique should really be designated as a probe of electronically excited states at surfaces. Its inclusion at this point is due to the information obtained from the electron stimulated desorption ion angular distribution (ESDIAD). If it is assumed that the desorbing ion leaves the surface along the direction of the ruptured bond, the angular distribution can give some indication of the orientation of the molecule on the surface. For example, ESD of CO bound in a "standing up" configuration on a metal surface will result in a narrow emission cone of O^+ ions in the direction of the surface normal. A display apparatus enables the desorption patterns to be photographed directly. There is still some controversy as to whether the patterns can be so simply interpreted.

III. INVESTIGATION OF SURFACE ELECTRONIC STRUCTURE

1. UV Photoelectron Spectroscopy (UPES)

As already explained in section I.1 the increased use of synchrotron radiation in photoelectron spectroscopy has blurred the distinction between UPES and XPES. UPES in the laboratory requires a He gas discharge line source which can be operated to maximise the output of either He I (21.2 eV) or He II (40.8 eV) radiation. Using these photon energies it is clear that only valence levels and very shallow core levels are accessible. In this section we shall in fact be discussing valence level photoelectron spectroscopy, whilst retaining the abbreviation UPES, and often simply describing the technique as "photoemission". The measured quantities are the same as in the XPES, namely, the kinetic energy and direction (or momentum) of the photoemitted electron. Some of the early UPES work was based on the assumption that the bulk was probed; later (1972) it was established that the technique is surface sensitive due to the relatively low attenuation lengths of the photoelectrons. These aspects still characterize present day UPES studies. Whereas it is possible to use the method to investigate adsorbed atoms and molecules and thus to measure the binding energies (or ionisation energies) of the individual, usually broadened, adsorbate derived levels, it is also possible to use it for bulk band structure studies. The reason is quite straightforward: although UPES is indeed surface sensitive with perhaps 50 % of the elastically scattered photoemitted electrons deriving from the two outermost layers of the substrate, solid state theory has shown that already after two or three layers the electronic structure is essentially identical with that of the infinite three dimensional solid.

Bulk band structure determination is beyond the scope of this Survey. It suffices here to note that such studies generally require an angle resolving photoelectron spectrometer and a continuously variable photon energy. Utilising the property that the parallel component of the photoelectron momentum is conserved as it crosses the interface, it is possible to measure the $E(k)$ dispersion relationship characterising the bulk band structure, providing some procedure is used to determine the perpendicular momentum component, k_{\perp} . Care must be taken when comparison is made with band structure calculations, because these describe the electronic ground state whereas the photoemission spectrum is an excitation spectrum.

UPES studies of clean surfaces also reveal "surface states" which are two-dimensional Bloch states localised in the surface and damped on either side. A gap in the projection of the bulk band structure onto the surface is generally a prerequisite. They are normally recognized by their lack of dispersion with k_{\perp} (i.e. constant binding energy when photon energy is varied) and their sensitivity to contamination. The dispersion with k_{\parallel} can be measured directly because, as mentioned above, parallel momentum is conserved in the photoelectron emission process.

UPES studies of adsorbed atoms and molecules are of two kinds. In the case of ordered overlayers of sufficiently high coverage, the adsorbate orbitals will form two-dimensional Bloch states. The adsorbate band structure, i.e. the dispersion relationship $E(k_{\parallel})$, can then be measured in an angle resolved experiment in the same way as for (intrinsic) surface states. The second application lies in the characterisation of adsorbed molecules or of molecular fragments resulting from a heterogeneous reaction. Having established the identity of the species on the surface (XPES as well as vibrational spectroscopy is useful for this), interest necessarily focusses on structure and bonding. In some cases a qualitative assessment of the spectrum can give an indication as to bonding features. For quantitative work it is necessary to identify the symmetry of all the orbitals, measure their ionisation energies and compare the results with calculation. The selection rules in photoelectron spectroscopy prove most useful in determining level symmetry. For particular experimental geometries (emission direction and orientation of the polarisation vector), emission from a particular level will be allowed or forbidden depending on the point group of the adsorption complex. The latter can only be determined in a separate structural investigation (e.g. with LEED, photoelectron diffraction or SEXAFS). Via Koopmans' theorem measured ionisation energies can be compared with the orbital energies obtained, for example, from cluster calculations. This procedure may be turned around in order to use the technique as a structural tool. If the features in the spectrum are already assigned, which might well be the case if the adsorbed species is only slightly perturbed relative to the free molecule, then the selection rules may be used in certain circumstances to determine the molecular orientation. Because of the additional screening provided by the surface in the $N-1$ final state (N represents the highest occupied initial state), it should be expected that Koopmans' theorem is less good an approximation than in the gas phase. UPES is still, however, the most powerful technique available for probing surface electronic structure.

2. Inverse Photoelectron Spectroscopy (IPES)

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

Monochromatic electrons incident on a metal or semiconductor surface are decelerated and transiently occupy empty electronic states of the system. The emitted Bremsstrahlung photons are then energy selected with a suitable detector or monochromator. If a detector with a fixed energy window, $h\nu$, such as a modified Geiger Müller tube is used, then the spectrum is obtained by varying the electron energy, E_k . For $E_k = h\nu$ the electron is at the Fermi level, E_F , or conduction band minimum in the final state. As E_k is increased and if only photons with energy $h\nu$ are detected, the higher lying unoccupied states above E_F are probed. This experiment is the analogue of photoelectron spectroscopy with a fixed energy laboratory source. If a monochromator is used as a detector (the angular acceptance has to be very high because of the low photon yield), then the experiment becomes analogous to photoelectron spectroscopy with a variable photon energy source.

As in the case of "normal" photoelectron spectroscopy IPES is surface sensitive but at the same time can be used for bulk band structure investigations. In the latter, the direction of the incident electron beam is fixed and, assuming that the parallel component of electron momentum is conserved, is used to define radiative transitions between initial and final bands. To determine the exact point of the transition in the Brillouin zone, i.e. the value of k_{\perp} in the solid, further information is necessary or additional experiments have to be performed, just as in photoemission.

Particularly interesting in recent years has been the application of IPES to the study of the unoccupied states of adsorbed atoms and molecules. Relaxation effects are, however, expected to occur just as in photoemission. Measured are essentially, the affinity energies of the adsorbate-substrate system corresponding to various $N + 1$ states. The energy of an unoccupied level in an adsorbed molecule deriving from a ground state calculation will not necessarily correspond to the difference in energies of the N and $N + 1$ systems. As in photoemission, it is also possible to map out adsorbate-induced bands and to detect intrinsic surface states and resonances associated with the clean surface. Particular attention has recently been paid to the detection of so-called image potential states on metals, where the electron is trapped parallel to the surface in free electron-like states below the vacuum level.

3. Penning Ionisation Spectroscopy (PIS); Metastable Deexcitation Spectroscopy (MDS)

When electronically excited, metastable He-atoms (in $1S$ or $3S$ states) impinge on a clean or adsorbate-covered solid surface, the deexcitation process is accompanied by electron emission. In

the Penning ionisation technique, the energy distribution of electrons is measured. There are two competing processes for electron emission. Firstly the excited He* atoms (excitation energy 20.61 eV (¹S) and 19.82 eV (³S)) can undergo resonance ionisation if their effective ionisation energies are smaller than the work function of the surface. The excitation energy is subsequently dissipated by a two-electron Auger process. This mechanism resembles that of Ion Neutralisation Spectroscopy (INS). The second process, Penning ionisation, consists of an electron transition from the solid surface into the half-empty He 1s orbital state and the simultaneous emission of the 2s electron. This is a quasi-one-electron excitation process which enables identification of occupied electronic levels in the surface.

In contrast to UPES with an escape depth corresponding to several atomic layers, Penning ionisation is a truly surface sensitive method involving only the outermost layer of atoms. In the case of a low local work function or of effective shielding of empty metal states by an adsorbate layer, it is the Penning process that dominates. The experimental spectra of adsorbates resemble those of UPS except that substrate emission is suppressed. This can be of advantage, for example, in the d-band region of transition metals. On the other hand, adsorbate orbitals which are not spatially extended away from the surface tend to have very low cross-sections.

4. Electronic Electron Energy Loss Spectroscopy (ELS or EELS), Vacuum UV Reflection Spectroscopy

Electrons can also induce electronic excitations at the surface of a solid. In a simple experiment of this type a monochromatic beam of electrons of energy up to a few keV is reflected from the surface and subsequently energy analysed. The excitations appear as characteristic loss peaks in the resulting spectrum. Since the intrinsic width of these loss features is rarely less than ~ 1 eV, there are no stringent requirements as to the monochromaticity of the incident beam, as in the case of the vibrational EELS (see Section IV.3). As in photoemission, the inelastic mean free path of the inelastically scattered electrons is such that excitations characteristic of both the surface and the bulk are observed.

Loss features fall into three categories. Firstly, core levels may be ionised leading to features in the loss spectrum corresponding to the excitation of core electrons into unfilled states above the Fermi level. Moreover, there is a fine structure above the threshold which contains, in principle, similar information as SEXAFS. This surface extended energy loss fine structure (SEXELFS) from strongly bound atomic adsorbates has actually been used for structural determinations. Because of the high incident electron current often required, it is doubtful, however, whether the method is of general applicability.

The second type of loss feature which may be observed is due to the collective oscillations of the substrate electrons (plasmons). A plasmon is a quantized oscillation of the electron gas with respect to the positive ion core of the crystal lattice. There are two types: the bulk plasmon with frequency ω_p and the surface plasmon with frequency near $\omega_p/\sqrt{2}$. The surface plasmon is a two-dimensional elementary excitation dispersing only in k_{\parallel} . In a simple equation the (bulk) plasmon energy is related to the square root of the electron density but this applies only to nearly free electron metals. In more complicated systems the presence of interband transitions (see below) strongly influences the plasmon frequency.

Single particle excitation involving valence electrons constitute the third category. Interband transitions characteristic of the bulk band structure. They give rise to structure in the loss spectrum. There is an extensive literature on energy loss and optical spectra of solids and their relation to the bulk dielectric constant. Similarly, discrete, or bound-to-bound, transitions in adsorbates have been studied with this method. In the limit of zero momentum transfer the spectrum should be similar to that obtained with VUV reflection spectroscopy except that symmetry- and spin-forbidden transitions may be allowed. Although this is potentially a method for probing the valence levels of adsorbed species, there is still considerable uncertainty as to the assignment of these transitions even for the simplest case of adsorbed CO. There are only few reports so far on the VUV reflection experiments on adsorbates.

5. The Work Function (Including Field Emission)

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

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

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

The most frequently used methods for work function measurement make use of photoemission, field emission or contact potential difference phenomena. The older, thermionic emission technique is no longer of practical importance. In the photoemission method a photon of energy $h\nu$ strikes a material in which the electron work function is $e\phi$ and an electron can be emitted if $h\nu > e\phi$. Its maximum kinetic energy E_k will be

$$E_k = h\nu - e\phi$$

Hence a plot of maximum kinetic energy against ν should be linear with the zero kinetic energy intercept given by $h\nu_0 = e\phi$. More commonly, the emitted electrons are accelerated to a collector (corrections due to the accelerating field may be needed) and the work function is obtained from the dependence of current density on light frequency according to the Fowler equation.

In the field emission method, the current density i from the tip depends on the field E and work function $e\phi$ according to the Fowler-Nordheim equation

$$\ln i/E^2 = \ln A - 6.83 \times 10^7 \phi^3 s(y)/E$$

with i in amperes/cm², E in volts/cm, ϕ in electron volts. $\ln A$ is a slowly varying function of ϕ and $s(y)$ is an image correction term of the order unity. The work function can be obtained from the slope of a Fowler-Nordheim plot. Probe techniques permit measurements of individual crystal faces of a field emission microscope tip, giving the method considerable versatility. In general, $\Delta\phi$ values obtained from field emission are in agreement with results obtained by other methods on macroscopic crystal planes.

In the contact potential difference method, a parallel plate condenser is essentially formed from two conductors with work functions $e\phi_A$ and $e\phi_B$. If the two plates are connected through an external circuit containing no battery, the electrochemical potentials of the electrons inside the materials will be equal, but there will be a potential difference $\phi_A - \phi_B$ between the positions just outside the materials, and correspondingly the condenser will carry a charge $Q = C(e\phi_A - e\phi_B)$ where C is the condenser capacitance. Hence, if C is varied periodically by periodically varying the distance between the plates, an alternating current will flow in the external circuit, and this can be amplified and measured. A potentiometer can now be used in the external circuit to exactly compensate the work function difference; at this point the alternating current is zero and the potential difference $\phi_A - \phi_B$ is equal to the potentiometer potential difference. This is known as the vibrating capacitor method. Where changes in work function of a given material are to be investigated, for example due to adsorption, it suffices to measure the contact potential difference between the material of interest and a reference material whose work function is known to remain constant. For measuring the work function itself, the work function of the reference material has to be known.

IV. CHARACTERISATION OF VIBRATIONAL MODES OF ADSORBED SPECIES

1. Infrared Spectroscopy (IR)

Infrared vibrational spectra originate in transitions between discrete vibrational energy levels of molecules, energy being absorbed from the incident infrared beam by these transitions. An absorption band is thus manifested as a reduction in the energy transmitted in the absence of the absorbing substance. The frequency of the absorption band can be related to the atomic masses and force constants of the vibrating molecule.

Electromagnetic waves generally penetrate deeply into solids depending on the optical constants of the substrate material and the angle of incidence of electromagnetic waves. The surface sensitivity of the method is limited but adsorbed species can still be identified with efficiency if their frequencies are different from those of the solid substrate. The aim of such investigations is to identify the chemical nature of the surface of adsorbed species, to obtain information on bonding within the adsorbed molecules from characteristic frequencies, and to characterize the nature of the bond between surface and adsorbate. The infrared spectrum may also allow the stereochemical arrangements of atoms in a molecular structure to be deduced since the symmetry of the adsorbed species will determine which vibrational modes are active in the infrared spectrum.

Because of the weakness of many bands from adsorbed species, and the overlapping of spectra from the adsorbate and adsorbent, infrared spectroscopy has become more useful since Fourier transform infrared (FT-IR) spectrometers have appeared with high sensitivity and resolution and the possibility of short measurement times. Computerised subtraction of the absorbance spectra of the adsorbent and the substrate in order to give the spectrum of the adsorbate is also very important.

There are several kinds of IR techniques used in the study of surface chemistry: 1. Infrared transmission; 2. Infrared-diffuse reflectance (DRIFT); 3. Infrared reflection-absorption (RAIRS or IRAS); 4. Infrared attenuated total reflection (ATR); 5. Infrared emission; 6. Infrared photoacoustic spectroscopy (PAS).

1.1 Infrared Transmission Spectroscopy When IR spectroscopy is not otherwise designated this usually refers to the use of the transmission method. The vast majority of infrared studies of adsorbed species to date have been made by this method. In many cases the samples are studied in the form of self-supporting thin but porous discs and the infrared beam passes through the sample to be examined by the spectrometer.

The application of the infrared transmission method in surface studies involving finely-derived adsorbents is often confined to limited spectral regions due primarily to the strong absorption of infrared radiation by the solid adsorbent. Although not all absorption bands belonging to the adsorbed molecules can be recorded, the assignment of structures can often be made on the basis of those that are observable, particularly for organic adsorbates which have high-frequency characteristic absorptions.

This method has been applied very successfully to the study of adsorbed species on materials with a high surface to volume ratio such as metal oxides and finely-dispersed metal catalysts. It can not only be used for identifying the chemical nature of adsorbed species, but also for the quantitative determination of their concentrations and, in particular, for *in-situ* studies of adsorbed species under the relatively high pressures or temperatures applicable to catalytic reactions.

1.2 Diffuse-reflectance Infrared Spectroscopy (DRIFT) This method is often (but not ideally) referred to by the acronym DRIFT (diffuse reflectance infrared spectroscopy by Fourier transform). Although in principle Fourier transform methods are not essential, it is the higher sensitivity of such spectrometers that has enabled diffuse reflectance to be widely used in practice.

The method is particularly useful for investigating adsorbed species on finely-dispersed samples, such as catalysts, which scatter radiation strongly so that transmission measurements of the powder or of pressed discs are very difficult. The incident infrared beam is repeatedly scattered and transmitted by the fine particles so that the collected re-emerging back-scattered radiation has been partially attenuated by absorption resulting from passage through the particles themselves, or through adsorbed layers. In many cases, after scaling of the diffusely reflected spectrum with the help of an algebraic function (the Kubelka-Munk function), the resulting spectrum has a good qualitative resemblance to an absorbance spectrum from the adsorbent/adsorbate system. If the scattering particles exhibit strong selective reflection (associated with intrinsically strong absorption bands, and particularly prevalent with ionic solids) then the penetration of radiation into the particles of the powder in these spectral regions will be reduced relative to scattering. There will then be a relative weakening of the corresponding 'absorption' features in the diffuse-reflectance spectrum arising from the bulk adsorbent, but not from the adsorbed molecules if their frequencies are different from those of the bulk adsorbent. The spectrum of the latter is obtained by subtraction of the diffuse reflectance spectrum of the adsorbent in the absence of adsorbate.

1.3 Reflection-absorption Infrared Spectroscopy (RAIRS) and Infrared Ellipsometric Spectroscopy

Infrared measurements on a highly reflecting surface can give absorption spectra from adsorbed species. The main applications have been to adsorption on metal surfaces which are highly reflecting over large wavenumber ranges. This technique can be applied to polished or evaporated polycrystalline metal films, or to the well-defined surface of a metal single crystal, and the whole range of vibration frequencies (4000 - 100 cm^{-1}) is available. Although the absorptions from a single monolayer of a moderately-sized molecule will necessarily be weak, the higher sensitivity of Fourier transform techniques has helped substantially to obtain acceptable signal/noise. The work on specific faces of metal single crystals is particularly important as it often enables the deduction of the sites of adsorption as well as the nature of the adsorbed species. Polycrystalline metal samples usually give more complex spectra through adsorption on a range of crystal faces.

The polarising properties of a uniaxial planar interface are fully characterised by the ratio of its reflection coefficient for light polarised parallel (p-polarised) to that polarised perpendicular to the plane of incidence (s-polarised). In the latter case, the phase change on reflection is approximately π , so the electric vectors of the incident and reflected light approximately cancel each other and the absorption bands are extremely weak. In the former case, as the incident angle θ increases, the electric vector with the component perpendicular to the surface increases, and infrared absorbance increases for those vibrations of adsorbed molecules whose vibrational dipole

moments have components perpendicular to the surface. On metal surfaces typical angles of incidence of 80 - 89° give a maximum value of reflectance intensity and the reflected beam then gives rise to greatest absorption intensities. When the surface reflectivity is particularly high, a useful increase in sensitivity may also be obtained using multiple reflection.

Two desirable features of the RAIRS technique, not available for example with the alternative electron energy loss technique (see below), are that it has good resolution (1 to 5 cm⁻¹) and is applicable to the study of adsorbed species under the normal pressures at which surface or catalytic reactions can occur.

In infrared ellipsometric spectroscopy a plane polarised beam of monochromatic radiation is allowed to impinge on the interface to be studied. The reflected beam will be elliptically polarised and is returned to plane polarisation by a compensator; the angle of polarisation is determined by setting the analyser to complete extinction. The experimentally-measured quantities are thus the polariser angle and the analyser angle. From these values the phase shift between the parallel and perpendicular components and hence the change in the ratio of their amplitudes and their relative phase changes on reflection can be determined. This is an alternative method of determining the information provided by the reflection-absorption method.

1.4 Infrared Attenuated Total Reflection Spectroscopy (ATR) A light ray passing from a more optical dense medium 1 to a less dense medium 2 will change direction at the interface according to Snells' law,

$$\sin\theta_1/\sin\theta_2 = n_2/n_1$$

where θ_1 and θ_2 are the angles of incidence of the light beam with respect to the normal to the interface between the two media of refractive indices n_2 and n_1 , respectively. It is well known that, when the angle of incidence in the medium with the higher refractive index is greater than a certain value, total internal reflection occurs within that medium. However, the radiation does penetrate into the less-dense medium during reflection by a distance of the order of the wavelength of the radiation, that distance being reduced the higher the angle of incidence within the dense medium. This 'evanescent ray' permits 'sampling' in the close vicinity of the interface in that the reflected beam will be attenuated by absorption in this limited thickness of the less-dense medium. The 'attenuated' total reflection (ATR) spectrum will reproduce the features of a absorption spectrum in a semi-quantitative manner. In favourable cases sensitivity can be increased by the use of multiple internal reflections, so that the spectrum can be obtained of a monolayer adsorbed on the surface of the medium of high refractive index.

The preferred high-refractive-index media which are transparent in the infrared region are KRS 5 (a mixed bromide/iodide of thallium), AgCl or germanium, all of which have refractive indexes greater than 2 throughout most of the infrared region. Germanium is an electric semiconductor and it is possible to use it as an electrode with or without metal coatings.

1.5 Infrared Emission Spectroscopy In a constant-temperature enclosure at equilibrium, Kirchhoff's Law and black body radiation theory requires the absorptance (fractional absorption of radiation) at a particular wavelength, a , to be equal to the emittance, ϵ , where ϵ is the ratio of the energy emitted by the sample at that wavelength to the energy emitted by a black body at the same temperature. Emittance spectra can be measured for samples which are at temperatures other than that of the radiation detector. This indirect method of obtaining information about the absorption spectrum of a compound finds most practical usage for studying films adsorbed on polished metal surfaces.

For incident light, the sum of absorptance a , reflectance, ρ , and transmittance, τ , must add up to unity i.e. $a + \rho + \tau = 1$. A highly reflecting clean metal, with $\rho \approx 1$ will therefore show very small absorptance and hence its emittance will be near zero. Against this near-zero background, an emittance spectrum of an adsorbed layer can be measured and converted into its absorptance equivalent.

Although the amount of energy emitted by a sample at an elevated temperature will be substantially less in absolute amount than that absorbed by the same sample from an incident light-beam provided by a stronger source at much higher temperatures, there are circumstances when the lower signal/noise ratio obtained by the emission method relates well to the limited dynamic range of a spectrometer. This can be particularly the case for Fourier-transform measurements which are otherwise very advantageous. The emission method has also been used to obtain infrared spectra from heated particulate samples, such as working high-temperature catalysts. However, even black body emission sources of moderate temperature only show good signal/noise at the low wavenumber end of the infrared region.

1.6 Infrared Photoacoustic Spectroscopy (PAS) Radiation absorbed by a solid from a modulated infrared light beam in the infrared region is normally efficiently converted into heat by radiationless processes. Such heat pulses arising from radiation absorption by a solid sample can be transmitted to a surrounding gas where they are converted to pulses of pressure. Detection of these pulses by a microphone or piezoelectric transducer at the frequency of modulation of the light beam gives a signal proportional to the energy absorbed. This is the principle of the

photoacoustic spectroscopic method. In a similar manner to diffuse reflectance spectroscopy, photoacoustic spectra can be obtained conveniently from unpeletted powdered solids such as catalysts in contact with a gas phase. Radiation that is reflected or scattered by the sample is not measured in PAS.

The use of Fourier-transform interferometric infrared spectrometers has led to practical applications of the PAS method in the infrared region. By passage of the light beam through the interferometer each wavelength of radiation is modulated at a different frequency by the motion of the mirror moving with uniform velocity. The photoacoustic detector picks up the superimposed signals which can be analysed by the same FT methods as are used for transmission studies. Modulated IR laser sources can alternatively give measurable PAS signals for analysis by dispersion (diffraction-grating) spectrometry. A variation of the photoacoustic technique uses the 'mirage effect' i.e. the modulated pressure waves in the gas phase cause similar deflections of an ancillary visible laser, e.g. He/Ne, whose light beam is directed closely parallel to the surface of the sample. The deflection of the laser beam is a measure of the strength of the absorption by the sample. Both these techniques require the presence of a gas phase over the solid sample.

2. Raman Spectroscopy, Resonance Raman Spectroscopy (RRS) and Surface Enhanced Raman Spectroscopy (SERS)

When a molecule is irradiated by a monochromatic light beam of frequency ν_0 , a small proportion of the scattered (re-emitted) radiation can have different frequencies from ν_0 . The corresponding features ($\nu_0 \pm \nu$) on either side of ν_0 constitute the Raman spectrum, and the frequencies ν are recorded as the Raman frequencies of the sample. For reasons of the Boltzmann factor, $\exp(-h\nu/kT)$, these are stronger on the low frequency side of ν_0 and hence Raman spectra are normally measured in this region. Above about 100 cm^{-1} these features correspond to vibration frequencies in the electronic ground state of the molecule being investigated. Powerful monochromatic gas-phase laser sources in the visible region, such as from Ar^+ or Kr^+ , are normally used. There is a useful complementarity relationship between the infrared and Raman methods of obtaining vibrational spectra, in that features strong in infrared spectra are frequently weak in Raman spectra and vice-versa. Overall, Raman spectra tend to have lower signal/noise than infrared spectra, and some other special problems associated with Raman spectroscopy (such as the excitation of stronger overlapping fluorescence spectra from small amounts of visibly-coloured substances in the form of impurities, or derived from the thermal or photodecomposition of the sample in the laser beam) have reduced the range of applications to adsorption and catalytic phenomena. Nevertheless some good results have been achieved. For example, adsorbents such as SiO_2 and Al_2O_3 , which themselves absorb strongly in the infrared to the detriment of obtaining transmission spectra from adsorbed species, give very weak Raman scattering so that bands from adsorbed species can be detected even in the lower frequency regions of the lattice modes of the oxide. The stronger features of the adsorbate Raman spectra are different from those that are readily identified in the infrared region.

The normal Raman spectrum is obtained when the incident laser frequency does not fall within the electronic absorption band of the sample. When the exciting radiation overlaps the electronic absorption to a limited degree, so as to still avoid the excitation of the more complex fluorescence spectrum involving the energy levels of an upper electronic state, then a Resonance Raman Spectrum (RRS) can be obtained which differs from a normal Raman spectrum by a strong (up to $\times 10^3$) enhancement of intensity of certain of the vibration frequencies compared with the normal Raman spectrum. In such circumstances, much stronger spectra can be obtained from selected adsorbed species. Excitation of these is more readily made by the use of a tuneable laser, usually a dye laser, so that appropriate parts of the electronic absorption band can be irradiated.

Finally, very strongly enhanced Raman spectra (by up to $\times 10^6$) have been obtained from molecules adsorbed on certain rough metal surfaces or on metal colloids. This enhancement is found with relatively few metals (Ag is particularly effective but Au and Cu and, to a lesser extent Pt, have been used) and some adsorbed molecules give much stronger signals than others. The mechanism of this Surface-Enhanced Raman Spectroscopy (SERS) is still a matter for debate. It may involve plasma resonances in the appropriately-sized metal particles, possibly combined with a type of RRS with the adsorbate. With the help of this phenomenon some excellent spectra have been obtained from adsorbed species on the metals mentioned above.

3. Vibrational Electron Energy Loss Spectroscopy (EELS or VEELS)

The vibrational spectra of adsorbed species may also be studied, in some respects very advantageously, by electron energy loss spectroscopy which is based upon excitation of vibrations of adsorbed species by absorption of energy from mono-energetic incident electrons. The vibrational frequency ν , or its wavenumber equivalent, $\underline{\nu}$, is calculated from $\Delta\underline{\epsilon} = h\nu = \frac{h\nu}{c_0}$ where $\Delta\underline{\epsilon}$ is the measured energy loss, and c_0 is the velocity of radiation.

The apparatus for EELS consists of an electron gun, an electron monochromator (energy filter) and an energy analyser. After impinging on the flat solid surface, the energy of the scattered electrons is analysed to determine the electron energy loss associated with the vibrational excitation.

The theory of EELS is not simple, but the interaction of incident electrons through inelastic scattering is classified into 1) dipole scattering and 2) impact scattering. Dipole scattering is due to the long range interaction between the electric field generated by the incoming electron and surface vibrational dipoles of the adsorbed species. The dipoles perpendicular to the surface give the highest scattering intensity in the specular direction, i.e. the direction where the angle of reflection is equal to the angle of incidence. Impact scattering takes place through a short range interaction between the incident electrons and the adsorbed atoms on the surface. Impact scattering occurs over a wide range of angles without any special selectivity and the effect is therefore relatively weak in the specular direction compared with dipolar scattering. Accordingly, by measuring the dependence of the intensity of scattered electrons upon the scattering angle, the spectrum of the adsorbed species can be analysed in more detail. In most cases the stronger features observed at the specular angle can be assigned to the completely symmetrical modes of vibration of the surface complex which have components of dipole changes perpendicular to the surface. Exceptions are the stretching frequencies of CH bonds (and probably other XH bonds) which can give substantial impact-excited features even in the specular direction.

EELS has been mainly applied to obtaining the vibrational spectra of molecules adsorbed on metal single-crystal surfaces. Because the inelastic scattering by the vibrations of the metal atoms itself is weak, and occurs at low energy losses, in effect virtually the whole range of vibrational frequencies of adsorbates are observable by this method. For ionic crystals, spectra of adsorbed species can be obtained in those frequency ranges not dominated by the strong energy losses associated with lattice 'reststrahlen' vibrations of the ionic crystal itself.

For studies over wide frequency ranges, the EELS method can give sensitivities at least one order of magnitude greater than those at present obtainable by reflection-absorption infrared spectroscopy, and the electron spectroscopic method is not confined to observing vibrations with vibrational dipoles perpendicular to the surface. The vibrational EELS method requires the use of high resolution electron spectroscopic techniques (hence the use of the abbreviation HREELS) but it does have much more limited resolution (about 20 to 50 cm^{-1}) in comparison with the infrared method. However, this is not a severe limitation when investigating the spectra of relatively small adsorption complexes which have few vibration frequencies. The much higher sensitivity of the EELS method has enabled many systems to be studied, such as adsorbed hydrocarbons for which, until the advent of FT-IR techniques, there was very limited infrared sensitivity. As with other electron spectroscopies, only very low gas pressures can be used (10^{-9} bar) in the vicinity of the specimen, and this is a disadvantage for studies related to catalytic systems, which often need pressures of several bar.

By increasing the incident electron energy it has recently become possible to observe the collective vibrational phenomena (phonons) associated with clean single crystal surfaces. The surface phonon band structure has now been measured for several metals and the effect of ordered atomic adlayers investigated.

4. Inelastic Electron Tunnelling Spectroscopy (IETS)

Inelastic electron tunnelling spectroscopy is used to measure the vibrational spectrum of molecules adsorbed on an oxide or oxide-supported metal in a metal-oxide-metal sandwich junction. It requires a system of two metals separated by an insulator about 2 nm thick; aluminum-aluminum oxide-lead is a frequently-studied sandwich junction in this application. The adsorbate of interest is adsorbed on the oxide insulator or on metal particles supported by the oxide insulator. At very low temperatures, an electron can cross the junction only by quantum mechanical tunnelling. In the absence of an applied voltage the Fermi levels on both sides of the insulator are the same but no crossing occurs because of a lack of empty state of the same energy within the insulator to receive the crossing electron. The Fermi levels are displaced from each other increasingly as the bias voltage increases. When the voltage increases beyond the point that $e\Delta V = h\nu$, where ν is a vibrational frequency of the adsorbate and ΔV is the bias voltage, additional empty states become available to the crossing electron (i.e. states of energy $e\Delta V$ and of $e\Delta V - h\nu$) so the rate of current, I , increases with voltage increase. AC modulation of the voltage can be exploited with lock-in amplifiers to provide a plot d^2I/dV^2 against ΔV (i.e. against electron energy) in which vibrational modes are displayed as sharp peaks. Resolution is of the order of 10 cm^{-1} . Both Raman- and IR-active vibrational modes can be detected. However vibrational modes constrained by orientation to vibrate parallel to the metal surface are not detected (a fact which can be used to infer orientation).

The method can detect C-H and C-metal modes at submonolayer coverages on oxide-supported metal catalysts. The previous-cited requirement for a metal-oxide-metal sandwich does constitute a disadvantage of the method. If one wishes to study the character of a species adsorbed on alumina it is necessary to deposit a layer of lead on the oxide layer in order to make the measurement. It has to be presumed that this procedure negligibly affects the vibrational properties of the adsorbate/oxide system. Another disadvantage is that the sample has typically to be at liquid helium temperatures in order to give sharp Fermi levels. Under these experimental arrangements it is not possible to change rapidly the adsorbate species of coverage.

5. Inelastic Atom Scattering

Helium atoms which collide with surfaces can undergo inelastic scattering events in which surface phonons are emitted or absorbed. Because the momentum transfer as well as the energy

exchange between the incident atom and the phonon can be directly measured, dispersion relationships can be determined. The energy distribution after scattering from the surface is measured using a pulsed beam and time of flight techniques. It is important for this experiment that a high degree of monochromaticity (i.e. a narrow velocity distribution) is reached in the incident beam. Using suitable jet nozzles a resolution of 1.5 cm^{-1} at a beam energy equivalent to 250 cm^{-1} is possible. Due to the necessarily low beam energies only soft phonon modes are detectable, but, for example, the dispersion of the Rayleigh mode on metal surfaces has been measured. There has also been one investigation of the soft hindered translational modes of an adsorbed molecule. These are not accessible with EELS or infrared reflection-absorption.

6. Inelastic Neutron Scattering (INS)

Using incident neutrons with a continuously varying energy from 5 to 500 meV ($40 - 4000 \text{ cm}^{-1}$) and analysing their loss of energy by time of flight techniques or analysers (crystals or filters), one is in principle able to detect all the excited vibrational modes in a molecule. In this incoherent process, each molecule may be considered as being isolated and the measured intensity of a given mode is proportional to the incoherent cross section of the vibrating atom and to the mass-weighted amplitude of its motion. If a force field has been already proposed from optical data, one is able to recalculate from the neutron spectrum the frequency and the intensity of all the vibrations and thus to check its validity. Conversely, since no selection rules limit the number of observable vibrations, the assignment of bands in a neutron spectrum of an unknown substance can be hazardous.

The main applications of inelastic neutron scattering spectroscopy concern chemisorbed molecules containing protons since the cross section of the H atom is one order of magnitude larger than that of other atoms. Many results concerning the chemisorption of hydrogen on various catalytic metals such as nickel, platinum, palladium or on desulfurisation catalysts like MoS_2 have been obtained. We note that the method is restricted to samples with high surface areas on account of the low scattering cross sections.

V. MISCELLANEOUS TECHNIQUES

1. Nuclear Magnetic Resonance (NMR)

The majority of nuclei have a spin angular momentum, in amounts associated with quantum numbers $I = 1/2, 1, 3/2$ etc. Such nuclei have magnetic moments, and also electric quadrupole moments if $I \geq 1$. They give NMR spectra which are representations of energy absorption as a function of magnetic field strength at a fixed radiation frequency or, vice-versa, as a function of frequency in a fixed magnetic field, B_0 . The magnetic nuclei in question precess about the direction of the applied magnetic field, B_0 , and it is this precession frequency that is measured in the NMR spectrum, thus representing radiative transitions between energy levels in the system. The magnetic field or frequency variation is normally expressed as parts per million (ppm) shift from the value at which a particular nucleus in a standard reference environment gives resonance e.g. in proton NMR, the reference is from protons in tetramethyl silane.

The variation in field or frequency at which absorption occurs for a given type of nucleus reflects variations in the chemical environment of that nucleus. Two factors are particularly important, namely: (a) Electrons around the nucleus provide net diamagnetic shielding, so that the magnetic field experienced by the nucleus is less than the external field B_0 (hence a higher field is required for resonance than would be the case for an unshielded nucleus); variations in this shielding constitute the "chemical shift" effect. (b) The nucleus of interest will usually have in its neighbourhood other nuclei with a magnetic moment, e.g. ^1H , ^{13}C or ^{14}N . Interaction between these nuclei and the protons can occur by two mechanisms, i.e. a direct 'across space' dipolar interaction, or an indirect dipolar interaction transmitted via intervening bonding electrons. Although the first mechanism is much the stronger one, its effects are precisely averaged to zero in non-viscous fluids in which the molecules reorientate rapidly. In such circumstances, it is the weaker electron-mediated interactions that give rise to the well-known fine structure. The latter reflects the different quantized spin states of the adjacent nuclei with respect to the applied magnetic field, B_0 . Thus, a single adjacent spin-1/2 nucleus such as ^1H or ^{13}C , splits the resonance under investigation into a doublet of equal intensity lines, a spin-1 nucleus such as ^{14}N gives a 1:1:1 triplet; and two equivalent spin-1/2 nuclei give a 1:2:1 triplet formed by repeated equal 1:1 doublet splittings etc.

In solids (and for molecules adsorbed on solids) the averaging due to rapid reorientation will not occur, or occur to only a limited extent, in which case the effects of direct dipolar couplings will be present. In addition anisotropic chemical shift effects will also be present in the spectrum in the absence of molecular tumbling. Hence nuclei in polycrystalline or amorphous solid materials (including nuclei in molecules adsorbed on such materials) usually find themselves in a rather broad continuum of magnetic environments leading to absorption peaks many times broader than those obtained in the liquid state, with a corresponding loss of spectral resolution. However, recently-developed NMR techniques (e.g. specially designed multiple pulse regimes to average some dipolar couplings to zero; magic angle spinning (see below) to transform the effective chemical shift tensor into its isotropic average; and cross polarisation techniques to enhance sensitivity) permit the information-rich high-resolution type spectra to be obtained once again. Quantitative information about anisotropies in chemical shifts and dipolar couplings are also derived from such experiments.

On account of its importance, the so-called magic angle spinning (MAS) method will be discussed in some detail. MAS is employed for abundant magnetic nuclei (e.g. ^1H). The method relies on the fact that dipolar interaction is, to first order, proportional to $(1-3 \cos^2 \theta)$, where θ is the angle between the vector connecting the dipoles and the external field. The dipolar interaction therefore vanishes at $\theta = 54^\circ 44'$. Rapid rotation of a powder sample about an axis which makes an angle of $54^\circ 44'$ to the magnetic field direction should then remove dipolar broadening from the spectrum, provided the rotation rate exceeds the magnitude of the broadening (in frequency units). In practice, however, the homonuclear dipolar broadening usually exceeds the highest rotation rates that can be achieved (circa 5000 s^{-1}). An interesting exception is the recently reported observation of ^1H NMR spectra of protons in zeolites. In this case the protons are far enough apart so that MAS at 2500 s^{-1} could remove dipolar broadening sufficiently to allow resolution of two different types of protons in the NMR spectra.

Since the averaging of the anisotropies is much less complete in adsorbed layers than in liquid phases, nuclei exhibiting large shifts are used in such studies in order to attain reasonable resolution in spite of large peak widths. From the isotropic shifts, information can be obtained about e. g. the influence of bonding to adsorption sites, on the electronic structure of the molecules (^{13}C , ^{15}N), protonation reactions in catalysts (^{13}C , ^{15}N), the void structure, ion distribution and pore fillings of zeolites (^{129}Xe), structural details of silicon - aluminates, especially zeolites (^{29}Si , ^{27}Al), acidities of OH groups at the surface of oxides and in zeolites (^1H). A study of the linewidths of the deuteron resonances (^2H , spin $I = 1$) enables the obtaining of surface diffusion coefficients of molecules on mesoporous and non-porous adsorbent particles and intracrystalline diffusion coefficients in zeolites.

Solid state NMR as such is concerned with the study of the anisotropic, angular dependent parts of the internal spin interactions. In this case very broad patterns (10 to 300 kHz) are usually encountered of which the widths and shapes are investigated. Such spectra show up in chemisorption and physisorption systems at low temperatures. Most clearly resolved patterns are obtained with the deuteron (^2H , spin $I = 1$) as the resonant nucleus. The investigation of the shapes and widths of such patterns as a function of temperature yield information on the rotational dynamics of adsorbed molecules and parts of them, the translational dynamics, and under favourable circumstances about the orientation of the adsorbed molecules with respect to the surface. ^1H solid state NMR enables insight to be obtained on the lateral arrangement of molecules on surfaces and in the voids of zeolites. It is foreseeable that with the further improvement of spectrometric technology and the advent of new NMR techniques, solid state NMR will provide a wealth of new information about the bonding and the dynamics of chemisorbed species on surfaces, e. g. metal surfaces of supported catalysts. A great deal of work has already been performed with ^{13}C contained in species chemisorbed on transition metals.

Additional information can be obtained from a consideration of relaxation times. Two important times can be measured. T_1 is the longitudinal or spin-lattice relaxation time which is associated with the return of nuclei excited by absorption of radiation to thermal equilibrium. T_2 , related to the reciprocal of the line-width, is the transverse or spin-spin relaxation time and is associated with loss of phase coherence in the precession of the excited nuclei about the applied magnetic field direction. The transitions between the spin states necessary to bring about relaxation, are provided by the stochastic fluctuations of the anisotropic chemical shifts and the inter- and intramolecular couplings as consequence of the rotational and translational motions of the spin-carrying molecules. The predominant pathways of relaxation are via the dipolar couplings when spin $I = \frac{1}{2}$ and via quadrupolar coupling when spin $I \geq 1$ nuclei are being studied. From the relaxation times very useful information about the microdynamics (rotational and translational) of molecules in adsorbed layers can be obtained over a wide time scale ranging from pico- to microseconds. A fruitful approach to obtain such data is to observe the resonances of both the proton and the deuteron in which cases the relaxation times are determined by the completely different dipolar (^1H) and quadrupolar (^2H) coupling mechanisms.

Under favourable circumstance, NMR can be used, for example, to establish the structure of an adsorbed molecule, to obtain estimates of its mobility, to identify the number of distinct proton acid sites on a catalyst, or to characterize adsorption sites e.g. for carbon monoxide on supported metal catalysts. At present, the overall sensitivity of NMR is still low compared with that of most of the other spectroscopic techniques discussed. In high magnetic fields obtainable with superconducting magnets (7 to 9 tesla [T]) the detection limit is in the order of 10^{18} - 10^{19} resonant spins. This requires a surface area of at least 1 m^2 in a sample volume of about 1 cm^3 . This excludes studies with single crystal surfaces but results can be obtained with finely-divided particles of diameter $1 \mu\text{m}$ or less and non-porous microcrystallites of μm size. Nevertheless, the information that the NMR technique can provide is potentially very valuable and greater sensitivity can be expected in the future.

2. Electron Spin Resonance (ESR)

Electron spin resonance spectroscopy (ESR), also known as electron paramagnetic resonance spectroscopy (EPR), detects unpaired electrons, and, can therefore be applied to systems that are intrinsically paramagnetic, such as organic and inorganic radicals or paramagnetic transition-metal ions and complexes thereof.

Electrons, by virtue of their spin and orbital motions in atoms, give rise to magnetic moments which can interact with a magnetic field. Angular momentum components in the magnetic field

direction are quantized, and associated with magnetic quantum numbers. For example, the orbital magnetic quantum numbers M_l possible for a p electron are 1, 0, and -1 and the spin magnetic quantum numbers M_s are $\pm 1/2$. The magnetic moment associated with these motions is expressed in units of the Bohr magneton $\mu_B = e\hbar/2m_e$, where m_e is the electron mass. In either case, the magnetic moments interact with a magnetic field to produce an energy shift $\Delta E = -\mu \cdot B$ and because the component of μ_B along B may have several quantized values, a corresponding set of energy levels is generated whose separation depends on the magnitude of the field B . Absorption of electromagnetic radiation can lead to promotion of the system from a lower level ϵ_i to a higher level ϵ_j if the frequency ν of the radiation satisfies $h\nu = \epsilon_j - \epsilon_i$. The energy changes associated with μ_B are 9.274×10^{-24} joules per tesla [$J T^{-1}$] and the corresponding frequencies 14×10^9 Hz T^{-1} . Use of the Bohr atom orbital motion model to calculate spin magnetic moments is plainly oversimple, and the resonance condition for spin magnetic moment transitions are $h\nu = g \beta_c B$ where g is the gyromagnetic ratio. For free electrons, $g = 2.0023$ (the Landé g factor) so that resonant frequencies are 28.03×10^9 Hz T^{-1} (free electrons). Electron spin resonance equipment usually is designed to operate in the X-band (9.5×10^9 Hz) or Q-band (35×10^9 Hz) microwave regions. Spectra are commonly obtained at a fixed frequency, with the magnetic field varied to obtain resonance.

The significance of ESR spectroscopy arises because the spin-states of an electron are influenced by the local atomic environment which influences the effective magnetic moment of the electron; since $\mu_c = g \beta_c s$ [s = electron spin], the g -value varies accordingly ("g-factor shift"). It is, therefore, the value of g , which can be determined to a high degree of accuracy, and this is a diagnostic of the paramagnetic species. In surface studies, the electronic g -factor can provide information on the motion of an adsorbed species. Hyperfine splitting into a number of distinct lines can occur when there is interaction between the electron magnetic moment and the magnetic moments of neighbouring magnetic nuclei. The number of lines arising from hyperfine splitting will depend on the number of nuclear spin orientations. It is usual to characterize a species giving rise to an ESR signal from a study of three parameters: (a) the g -tensor for which there is frequently considerable theoretical analysis, available (e.g., for O^-) (b) the shape of the signal and (c) the hyperfine tensor.

3. Mössbauer Spectroscopy

The Mössbauer effect is associated with recoil-free gamma ray resonance absorption. Its principle can be well illustrated by its application to the nucleus $^{57}_{26}Fe$, a case of considerable interest in catalysis. The nucleus $^{57}_{27}Co$ is radioactive, decaying by electron capture to an excited $^{57}_{26}Fe$ nucleus which decays to its ground state by paths involving γ -ray emission. One of these paths results in a γ ray of energy 14.4 keV. If the emitting $^{57}_{26}Fe$ is tightly bound in a lattice, negligible energy is lost in the recoil and the γ -ray line width is extremely small (about 4.6×10^{-9} eV in this case). Were this γ -ray to impact a ground state $^{57}_{26}Fe$ in exactly the same environment as the emitting nucleus, there is a finite probability that it would be absorbed, the resulting excited species re-emitting in a random direction. The process therefore manifests itself as an absorption of part of the energy emitted in the source-absorber direction. Now the source and absorber in general will be in different environments, and hence the transition energies will not be precisely the same but may differ by amounts of the order 10^{-7} eV. This is a small energy, but it is large compared to the emitted γ -ray line width. Emitted and absorbed frequencies can be brought into resonance through the Doppler effect; usually the source is moved towards and away from absorber with controlled velocities up to a few $cm s^{-1}$ (the emitted γ -ray line width in this case corresponds to a velocity of 10^{-2} $cm s^{-1}$) and the Mössbauer absorption spectrum plotted as intensity of transmitted γ -radiation as a function of source velocity. The emitted γ -ray is used as a time marker of the decay; it is not necessary to measure its energy but suffices to distinguish the recoilless event from others in the complex decay of the nucleus. Fluorescence X-rays and electrons resulting from internal conversion may also be used to "mark" the recoilless absorption/emission.

Mössbauer shifts arise chiefly from three origins: (a) The isomer shift results from the interaction of s electrons with the charged nucleus, and is sensitive to the oxidation state of the atom containing the nucleus. (b) The quadrupole splitting results from the interaction between a nucleus with an electric quadrupole and an electric field gradient at the nucleus, and is sensitive to the structure in which the nucleus occurs. (c) The magnetic splitting results from the interaction of the nuclear magnetic dipole with the internal magnetic field; this field can be very large in some metals (e.g., 32 T in metallic iron). While the Mössbauer effect has been observed in about 45 elements, the number of these suitable for Mössbauer spectroscopy is much less, chiefly because radioactive precursors of the gamma ray source nucleus have lifetimes that are too short. Nevertheless, several of these elements or isotopes including ^{57}Fe and ^{119}Sn , are of substantial chemical interest.

Applications of particular interest in surface science include determination of oxidation states and of the number of non-equivalent lattice positions, differentiation between bulk and surface crystal-field environment and inference of numbers of phases present from such observations. Of particular interest is conversion electron Mössbauer spectroscopy where a conversion electron is detected to mark the recoilless event. The electrons are emitted from the near surface region, and counted over as much of the backscattering hemisphere as possible. This geometry allows an increase of the S/N ratio of a few orders of magnitude; a rough depth profile of the surface region can be obtained by electron energy discrimination.

Emission Mössbauer spectroscopy is most surface sensitive, since in this mode the radioactive isotope is deposited directly on the surface as a probe, at concentrations as low as 10^3 of a monolayer.

4. Magnetic Methods

Magnetic methods applied to materials containing transition metals yield information on particle size, surface magnetism, and chemisorption properties.

Particle size determination depends on the fact that a particle of ferromagnetic substance below a certain critical size (30 nm for Ni) consists of a single domain, in a uniform state of magnetisation. It exhibits properties that lie on the borderline between ferromagnetism and paramagnetism (superparamagnetism). Thus, the particle, placed in an external field \underline{B} at temperature \underline{T} , behaves like a single paramagnetic particle, which has a very large magnetic moment $\underline{\mu}$, proportional to the number \underline{n} of atoms in the particle. The Langevin function, \underline{L} , defined by $\underline{L}(\underline{x}) = \coth \underline{x} - 1/\underline{x}$ can be used to describe the magnetic behaviour of the system:

$$\underline{M}/\underline{M}_0 = \underline{L} \left(\frac{n\mu_0 B}{kT} \right)$$

\underline{M} being the magnetisation, \underline{M}_0 the saturation magnetisation and μ_0 the magnetic moment of a metal atom. The average particle size and the particle size distribution curve can be calculated from a plot of \underline{M} as a function of \underline{H} . The advantages of the method are its accuracy (differences of 0.01 nm in diameter are easily detected), its rapidity and its sensitivity (it may easily be applied to samples with a loading as small as 0.1 wt%). It is, however, restricted to ferromagnetic materials. The Néel remanence method can be also applied to estimate the particle size distribution of ferromagnetic catalysts. This method is based on the magnetic relaxation of finely divided ferromagnetic materials.

Magnetic measurements can give indirect information on surface magnetism provided the degree of dispersion of the ferromagnetic material under study is large enough. For instance it has been demonstrated that the Curie point and the saturation magnetisation of pure Ni, proportional to the d-band hole concentration, are almost independent of the degree of dispersion of the metal up to 50%. The result indicates that the magnetic properties of Ni surface atoms are similar to bulk properties, in good agreement with theoretical predictions based on the tight binding approximation. Of particular interest at the moment are adsorbed layers of magnetic material on single crystal surfaces (for instance W{110}-Gd, where detailed information can be obtained on the surface chemical bonds.

Chemisorption on ferromagnetic materials also gives rise to changes of magnetic properties. These effects are similar to those observed when dissolving the element under consideration (e.g. H or C) into the bulk. Changes of saturation magnetisation due to the dissociative chemisorption of hydrogen on nickel, for example, correspond to the cancellation of the magnetism of two Ni atoms. Two surface nickel atoms thus appear involved in the chemisorption of one hydrogen molecule. The method has been extended to other adsorbates (CO, hydrocarbons) and permits calculation of the number of surface Ni atoms involved in the bonding, the so-called "bond number", by comparing the observed decrease of magnetisation per adsorbed molecule with the Ni atom magnetisation.

5. Neutron Diffraction

Neutron scattering is a technique suitable for investigating adsorbed molecules since it probes distances and times which are relevant to surface chemistry. However, elastic scattering cross sections of atoms for neutrons (10^{-10} nm²) are much less than those for low energy electrons (10^{-2} nm²) and even less than those for X-rays (10^{-8} nm²) so neutron scattering studies of surface phenomena are limited to samples with large surface areas.

The study of surfaces by neutron diffraction is complicated by the fact that conceptually one is dealing with scattering from two phases (a substrate phase \underline{S} and an adsorbate phase \underline{A}) each with its own lattice and unit cell, and the two lattices need not be commensurate. Information as to the structure of the adsorbed phase can be obtained under these circumstances if the coherent scattering cross sections of adsorbate and substrate differ sufficiently and if the incoherent scattering cross sections of both are sufficiently low to avoid excessive background scattering. Because of the two lattices involved, the total scattered amplitude \underline{A} is the sum of those due to substrate and adsorbate phases \underline{A}_S and \underline{A}_A , i.e.,

$$\underline{A} = \underline{A}_S + \underline{A}_A$$

in which all terms are complex (to include phase information). The intensity of the scattered beam is:

$$\underline{I} = \underline{A}\underline{A}^* = \underline{A}_S\underline{A}_S^* + \underline{A}_A\underline{A}_A^* + \underline{A}_S\underline{A}_A^* + \underline{A}_A\underline{A}_S^*$$

The first term contains substrate structural information, the second term structural information on the adsorbate (including diameters of two-dimensional crystalline domains and thicknesses of

three-dimensional islands). The last two terms provide the distance between adsorbed layer and substrate and indicate whether adsorbate and substrate structures are commensurate or not.

Most of the early applications of diffraction concerned the physisorption of rare gases on graphite. More recently, studies of chemisorbed molecules on oxides have been performed, where the orientation (normal or parallel) of the molecules with respect to the surface can, in principle, be determined. Neutron diffraction has also solved the problem of the location of organic molecules (C_2D_2 , CD_4) in the pore network of zeolites.

APPENDIX: SELECTED LITERATURE

I. Characterization of Surface Elemental Composition

1. X-ray Photoelectron Spectroscopy

Practical Surface Analysis by Auger- and X-Ray Photoelectron Spectroscopy, eds. D. Briggs and M.P. Seak, Wiley, Chichester (1983).

H. Siegbahn, "Photoelectron Spectroscopy" in: Encyclopedia of Physics, XXXI Corpuscles and Radiation in Matter I, ed. W. Mehlhorn Springer-Verl., Berlin (1987).

2. Auger Electron Spectroscopy

D.E. Ramaker, "Auger Spectroscopy as a Probe of Valence Bonds and Bands" in: Chemistry and Physics of Solid Surfaces IV, eds. R. Vanselow and R. Howe, Springer, Berlin (1982).

Practical Surface Analysis by Auger- and X-Ray Photoelectron Spectroscopy, eds. D. Briggs and M.P. Seak, Wiley, Chichester (1983).

3. Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry, SIMS III, eds. A. Benninghoven, J. Giver, J. Lázlò, M. Riedel and H.N. Werner, Springer-Verl., Berlin (1982).

4. Laser Microprobe Mass Spectrometry

"A Review of the Applications to Solids of the Laser Ion Source" in Mass Spectrometry, R.J. Conzemius and J.M. Capellen, Int. J. Mass Spectrom. Ion Phys. **34**, 197 (1980).

R.D. Macfarlane, "High Energy Heavy-Ion Induced Desorption" in: Ion Formation from Organic Solids, ed. A. Benninghoven, Springer-Verl., Berlin (1983).

5. Thermal Desorption Spectroscopy (TDS)

D. Menzel, "Thermal Desorption" in: Chemistry and Physics of Solid Surfaces IV, eds. R. Vanselow and R. Howe, Springer, Berlin (1982).

R.J. Madix, "The Application of Flash Desorption Spectroscopy to Chemical Reactions on Surfaces: Temperature Programmed Reaction Spectroscopy" in: Chemistry and Physics of Solid Surfaces II, ed. R. Vanselow, CRC Press, Boca Raton/Florida (1979).

II. Characterization of Surface Structure

1. Low Energy Electron Diffraction (LEED)

D. P. Woodruff, "Surface Periodicity, Crystallography and Structure" in: The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, **1**, eds. D. A. King and D. P. Woodruff, Elsevier, Amsterdam (1983).

L. J. Clarke, Surface Crystallography: An Introduction to Low Energy Electron Diffraction, Wiley, Chichester (1985).

G. Ertl and J. Küppers, Low Energy Electrons and Surface Chemistry, Chapter 9, VCH, Weinheim (1985).

Low Energy Electron Diffraction, eds. M. A. Van Hove, W. H. Weinberg, C. - M. Chan, Springer-Verl., Ser. in Surf. Sci. **6**, Heidelberg (1986).

2. Reflection High Energy Electron Diffraction (RHEED)

P. R. Pukite, S. Batra and P. I. Cohen, RHEED and Reflection Electron Imaging of Surfaces, ed. P. K. Larsen, Plenum Press, N. Y. (1988).

3. Photoelectron Diffraction

C. S. Fadley, Angle-Resolved X-ray Photoelectron Spectroscopy, Progr. Surf. Sci. **16**, 275 (1984).

J. J. Barton et al., Adsorbate Geometry Determination by Measurement and Analysis of Angle-Resolved Photoemission Extended Fine Structure, Phys. Rev. B **34**, 3807 (1986).

4. Photoabsorption (SEXAFS and NEXAFS)

EXAFS and Near Edge Structure III Springer Proceedings in Physics **2**, eds. K. O. Hodgson, B. Hedman and J. E. Penner-Hahn, Springer-Verl., Berlin (1984).

X-Ray Absorption: Principles, Applications, Techniques of EXAFS, eds. R. Prins and D. Koningsberger, Wiley, New York (1985).

5. Helium Diffraction

T. Engel, "Determination of Surface Structure Using Atomic Diffraction" in: Chemistry and Physics of Solid Surfaces V, eds. R. Vanselow and R. Howe, Springer-Verl., Berlin (1984).

6. Ion Scattering

W.K. Chu, J.W. Mayer, and M.-A. Nicolet, Backscattering Spectrometry, Academic Press, New York (1978).

J.F. Van der Veen, "Ion Beam Crystallography of Surfaces and Interfaces", Surf. Sci. Reports **5**, 199 (1985).

7. Grazing X-ray Diffraction, X-ray Standing Waves

K. Robinson, "Surface Crystallography" in: Handbook of Synchrotron Radiation 2., ed. E.E. Koch, North Holland, Amsterdam (1987).

8. Field Ion Microscopy and Related Methods

E.W. Müller and T.T. Tsong, Field Ion Microscopy, Principles and Applications, Elsevier, New York (1969).

9. Electron Microscopy

D.J. Smith, "High Resolution Microscopy in Surface Science" in: Chemistry and Physics of Solid Surfaces IV, eds. R. Vanselow and R. Howe, Springer-Verl., Berlin (1986).

10. Scanning Tunnelling Microscopy

R.J. Behm and W. Höslér, "Scanning Tunneling Microscopy" in: Chemistry and Physics of Solid Surfaces VI, eds. R. Vanselow and R. Howe, Springer Ser. in Surf Sci. **5**, Springer-Verl., Berlin (1986).

11. Electronic Stimulated Desorption

"Desorption Induced by Electronic Transitions DIET III", eds. W.R. H. Stolen and M.L. Knotek, Springer Ser. in Surf. Sci. **13**, Springer-Verl., Berlin (1988).

T.E. Madey, Science **234**, 316 (1986).

III. Investigation of Surface Electronic Structure**1. UV Photoelectron Spectroscopy**

Photoemission and the Electronic Properties of Surfaces, eds. B. Feuerbacher, B. Fitton, R.F. Willis, Wiley, Chichester (1978).

E.W. Plummer and W. Eberhardt, "Angle Resolved Photoemission as a Tool for the Study of Surfaces", Adv. Chem. Phys. **49**, 533 (1982).

M. Scheffler and A.M. Bradshaw, "The Electronic Structure of Adsorbed Layers" in: The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis 2, eds. D.A. King and D.P. Woodruff, Elsevier, Amsterdam (1983).

See also previous IUPAC recommendations: Pure & Applied Chem. **45**, 221 (1976); **59**, 1343 (1987).

2. Inverse Photoemission

Th. Fauster and V. Dose, "Inverse Photoemission" in: Chemistry and Physics of Solid Surfaces IV, eds. R. Vanselow and R. Howe, Springer-Verl., Berlin (1986).

N.V. Smith and D.P. Woodruff, "Inverse Photoemission from Metal Surfaces", Progr. Surface Sci. **21**, 295 (1986).

3. Penning Ionisation Spectroscopy

See e.g. W. Sesselmann et al., Surface Sci. **146**, 17 (1984).

4. Electron Energy Loss Spectroscopy (ELS and EELS), Reflection Spectroscopy

G. Ertl and J. Küppers, Low Energy Electrons and Surface Chemistry, Chap. 8, VCH-Verlagsgesellschaft, Weinheim (1985).

H. Raether, "Excitation of Plasmons and Interband Transitions by Electrons" in Springer Tracts in Modern Physics **88**, Springer, Heidelberg (1980).

5. The Work Function (including Field Emission)

J. Hölzl and F.K. Schulte, "Work Function of Metals" in Springer Tracts in Modern Physics, Springer, Berlin (1979).

A.J. Melmed, "Field Emission Microscopy. Trends and Perspectives" in: Chemistry and Physics of Solid Surfaces IV, eds. R. Vanselow and R. Howe, Springer, Berlin (1986).

IV. Characterization of Vibrational Modes of Adsorbed Species**1. Infrared Spectroscopy**

B.E. Hayden, "Reflection-Absorption Infrared Spectroscopy" in: Methods of Surface Characterization, Vol. 4, eds. J.T. Yates and T.E. Madey, Plenum Press, New York (1987).

M.L. Hair, "Transmission IR Spectroscopy for High Surface Area Oxides" in: Vibrational Spectroscopies for Adsorbed Species, eds. A.T. Bell and M.L. Hair, ACS Symposium Series 137, ACS, Washington (1980).

A.T. Bell, "Applications of Fourier Transform IR Spectroscopy to Studies of Adsorbed Species" in: Vibrational Spectroscopies for Adsorbed Species, eds. A.T. Bell and M.L. Hair, ACS Symposium Series 137, ACS, Washington (1980).

N.V. Richardson and N. Sheppard in Vibrational Spectroscopy of Molecules and Surfaces, eds. J. T. Yates, Jr. and T.E. Madey, Plenum Press, New York (1989).

2. Raman Spectroscopy

A. Campion, "Raman Spectroscopy of Adsorbed Molecules" in: Chemistry and Physics of Solid Surfaces IV, eds. R. Vanselow and R. Howe, Springer-Verl., Berlin (1986).

3. Electron Energy Loss Spectroscopy (EELS)

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

4. Inelastic Electron Tunnelling Spectroscopy

D.G. Walmsley, "Inelastic Electron Tunnelling Spectroscopy" in: Vibrational Spectroscopy of Adsorbates, ed. R.F. Willis, Springer Series in Chemical Physics 15, Springer-Verl., Berlin (1980).

5. Inelastic Neutron Scattering

C.J. Wright, "Neutron Scattering Studies, in Vibrational Spectroscopy of Adsorbates", ed. R.F. Willis, Springer Series in Chemical Physics 15, Springer-Verl., Berlin (1980).

V. Miscellaneous Techniques

1. Nuclear Magnetic Resonance (NMR)

R.F. Howe, "Magnetic Resonance in Surface Science" in: Chemistry and Physics of Solid Surfaces V, eds. R. Vanselow and R. Howe, Springer-Verl., Berlin (1984).

2. Electron Spin Resonance (ESR) Spectroscopy

H. Lundsford, "Surface Analysis by Means of Magnetic Resonance Techniques" in: Chemistry and Physics of Solid Surfaces, Vol. 1, eds R. Vanselow and S.Y. Tong, CRC Press, Cleveland, (1977).

3. Mössbauer Spectroscopy

B.J. Tatarchuk and J.A. Dumesic, "Mössbauer Spectroscopy: Application to Surface and Catalytic Phenomena" in: Chemistry and Physics of Solid Surfaces V, eds R. Vanselow and R. Howe, Springer Series in Chemical Physics 35, Springer-Verl., Berlin (1980).

4. Magnetic Methods

W. Selwood, Chemisorption and Magnetization, Academic Press, New York (1975).

VI. IUPAC Green Book

Quantities, Units and Symbols in Physical Chemistry, eds I. Mill, T. Cvitaš, K. Homann, N. Kallay and K. Kuchitsu, Blackwell Scientific Publ., Oxford (1988).