17.7.5 Characterisation of vibrational modes of adsorbed species

Infrared spectroscopy (IR) See Ch.10.

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.

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*).

Infrared transmission spectroscopy

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. When IR spectroscopy is not otherwise designated this usually refers to the use of the transmission method.

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 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 absorbent, 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.

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.

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 ratios.

The polarising properties of an 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 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 analyzer to complete extinction. The experimentally-measured quantities are thus the polariser angle and the analyzer 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.

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 Snell's 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 more 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 an 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.

Infrared Emission Spectroscopy

In a constant-temperature enclosure at equilibrium, Kirchoff's Law and black body radiation theory requires the absorptance (fractional absorption of radiation) at a particular wavelength, α, 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 α, reflectance, ρ, and transmittance, τ, must add up to unity i.e. $\alpha + \rho + \tau = 1$. 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, and 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 adsorbed 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.

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 pulse 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.

Raman Spectroscopy (RS) See Ch.10.

When a molecule is irradiated by a monochromatic light beam of frequency v_0, a small proportion of the scattered (re-emitted) radiation can have frequencies different from v_0. The corresponding features ($v_0 + v$) on either side of v_0 constitute the Raman spectrum, and the frequencies v are recorded as the Raman frequencies of the sample. For reasons of the Boltzmann factor, exp (hv/kT), these are stronger on the low frequency side of v_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 amount of visibly-coloured substance 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.

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 $x10^3$) enhancement of intensity of certain 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 $x10^6$) 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) too and some adsorbed molecules give much stronger signals than others. The mechanism of the _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.

Vibrational electron energy loss spectroscopy (EELS) See 17.2.2.1.

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

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.

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; aluminium-aluminium 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 states 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 previous-cited requirement for a metal-oxide-metal sandwich constitutes a disadvantage of the method. Another disadvantage is that the sample typically has to be at liquid helium temperatures in order to give sharp Fermi levels. Under these experimental arrangements it is not possible to rapidly change the adsorbate species of coverage.

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 measured directly, dispersion relationships can be determined. The energy distribution after scattering from the surface is measured using a pulsed beam and time of flight techniques.

Inelastic neutron scattering

Using incident neutrons with a continuously varying energy from 5 to 500 meV (40-4000 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.