17.7.6 Miscellaneous techniques

Nuclear magnetic resonance (NMR) spectroscopy See also Ch.14.2.

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 electrical 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 NMR spectra represent 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 tetramethylsilane.

The variation in field or frequency at which energy 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, 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.

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.

The magic angle spinning (MAS) method employed for abundant magnetic nuclei (e.g. ^{1}H) 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 $\Theta = 54°44^\wedge$. Rapid rotation of a powder sample about an axis which makes an angle of $54°44^\wedge$ 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}).

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.

Electron paramagnetic resonance (EPR) spectroscopy See also Ch.14.3.

Electron paramagnetic resonance (EPR) spectroscopy, also known as electron spin resonance (ESR) spectroscopy, 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. 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 v of the radiation satisfies $hv = \varepsilon_j - \varepsilon_i$. The energy changes associated with μ_B are 9.274x10^{-24} joules per tesla [J T^{-1}] and the corresponding frequencies 14x10^9 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 $hv = g \beta_e B$ where g is the gyromagnetic ratio. For free electrons, $g = 2.0023$ (the Landé g factor) so that resonant frequencies are 28.03x10^9 Hz T^{-1} (free electrons). Electron spin resonance equipment is usually 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. 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.

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 $_{26}^{57}$Fe, a case of considerable interest in catalysis. The nucleus $_{27}^{57}$Co is radioactive, decaying by electron capture to an excited $_{26}^{57}$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 $_{26}^{57}$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 $_{26}^{57}$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 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 mainly 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).

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 number 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.

Magnetic methods See also Ch.14.3.

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 magnetisitation. It exhibits properties that lie on the borderline between ferromagnetism and paramagnetism (superparamagnetism). Thus, the particle, placed in an external field B at temperature T, behaves like a single paramagnetic particle, which has a very large magnetic moment μ, proportional to the number n of atoms in the particle. The *Langevin function*, L, defined by $L(x) = \coth x - 1/x$ can be used to describe the magnetic behaviour of the system:

$$M/M_0 = L\left(\frac{n\mu_0 B}{kT}\right)$$

M being the magnetisation, 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 M as a function of 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 measurement can give indirect information on surface magnetism provided the degree of dispersion of the ferromagnetic material under study is large enough.

Neutron diffraction

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 S and an adsorbate phase 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 A is the sum of those due to substrate and adsorbate phases A_S and A_A, i.e.,

$$A = A_S + A_A$$

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

$$I = AA^* = A_SA_S^* + A_AA_A^* + A_SA_A^* + A_AA_S^*$$

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.

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} nm^2) are much less than those for low energy electrons (10^{-2} nm^2) and even less than those for X-rays (10^{-8} nm^2) so neutron scattering studies of surface phenomena are limited to samples with large surface areas.