

1 THEORETICAL FUNDAMENTALS AND EXPERIMENTAL CONSIDERATIONS OF THE SPECTROSCOPIC METHODS USED IN SURFACE CHEMISTRY

Three principal types of problems may be distinguished in the application of molecular spectroscopic techniques in surface chemistry, namely (i) the characterization of the surface, (ii) the estimation of the type and structures of surface compounds, and (iii) the obtaining of information required to understand the mechanisms of the processes proceeding on the surface of a solid. The first problem requires the determination of the types and properties of surface centers, which are dependent on the structure and morphology of the solid. The second and third problems concern adsorption processes and involve the study of the following: (i) the structures and properties of the surface compounds forming at different surface centers, (ii) reaction intermediates, and (iii) the directions of their transformations to the products. During recent years, the situation in this area has greatly improved, and different spectroscopic methods are now available for these studies.

The general principles of all of the techniques is the interaction between the incident radiation or particle beam and the specimen and the following analysis of both the nature and energy of the beam after such interaction. The energy regions involved in the different spectral methods involving electromagnetic radiation are represented in Figure 1.1, while Table 1.1 summarizes some of the essential characteristics of the various techniques.

It is clear today that any progress in the field of surface chemistry is impossible without the application of such modern methods of molecular spectroscopy as UV–Vis spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, electron energy loss spectroscopy, (EELS) including high-resolution electron energy loss spectroscopy (HREELS), and neutron spectroscopy.

The main feature of these methods is that they are nondestructive analytical methods, because the electromagnetic (radiation) or particle beams which are used, disturb the investigated system insignificantly. This is why such vibration techniques in different electromagnetic variants, such as transmission, reflectance and emission, or the low-energy electron loss spectroscopies, are very widely used nowadays.

1.1 Electronic spectroscopy

Electronic spectroscopy (ES) is normally concerned with the valence electronic transitions between molecular orbitals. The transmissions between the electronic levels (Figure 1.2) are

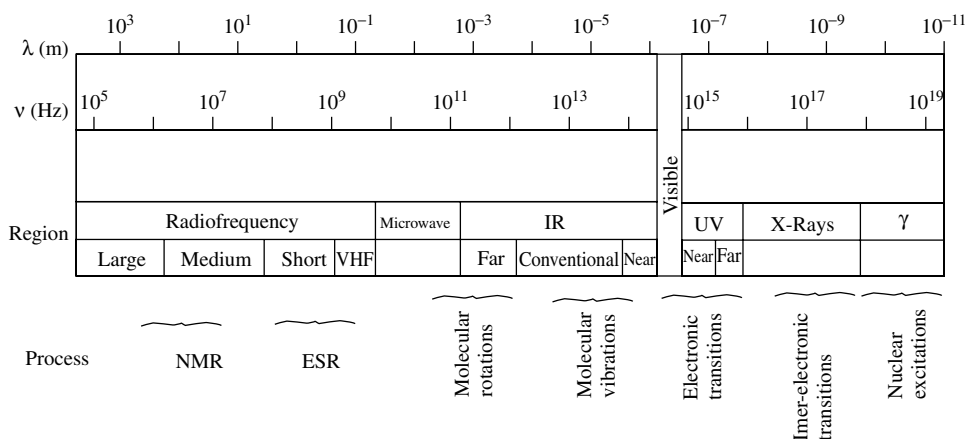


Figure 1.1. The regions of the electromagnetic spectrum, classified according to the experimental techniques employed and the molecular information that can be obtained.

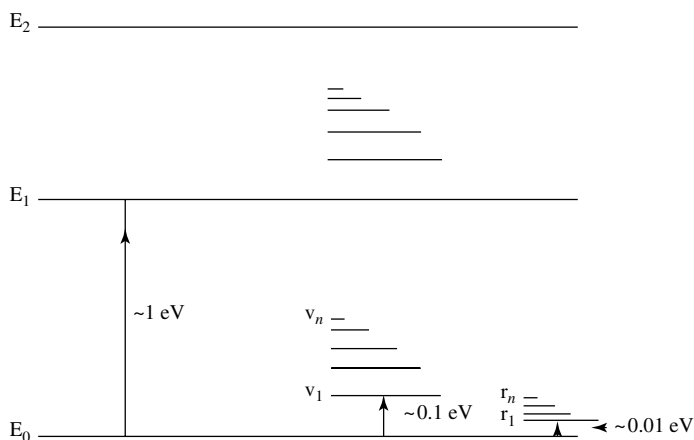


Figure 1.2. Scheme of energy levels: E, electronic; v, vibrational; r, rotational.

located in the range of the electromagnetic spectrum ($50\,000\text{--}3000\text{ cm}^{-1}$) – this is the basis of UV–Vis spectroscopy. The energies associated with the electronic ‘jumps’ are large enough to *provoke* vibrations of the molecule, and the transitions are thereby broadened [6, 8–10, 33, 116].

Light in the UV–Vis region of the electromagnetic spectrum can be used to study the electronic transitions of the substrates. According to the nature of the electronic jumps, the electronic transitions found in organic and inorganic chemistry can be classified into several groups: (i) $d \rightarrow d$ transitions (Figure 1.3(a)), (ii) charge transfers, (iii) $\pi \rightarrow \pi^*$ transitions (Figure 1.3(b)), and (iv) $n \rightarrow \pi^*$ (Figure 1.3(b)). In the far-UV range are found other transitions, e.g. ($n \rightarrow \sigma^*$) and ($\sigma \rightarrow \sigma^*$) (Figure 1.3(b)). Charge transfers occur due to electron transfers from an occupied orbital localized on a donor to an unoccupied orbital of an acceptor. In organic systems, these transitions are between electron acceptors and electron donors and produce the absorption bands in the UV and visible regions of the spectra with $\epsilon \sim 10^3\text{--}10^6$ (see below). In inorganic systems, the charge-transfer phenomena are of two types, involving an electron

Table 1.1. Comparative characteristics of the different spectral methods used in surface chemistry.

Characteristic	Technique									
	Molecular spectroscopy				Resonance spectroscopy			Surface studies		
	IR, PAS	Raman	UV-Vis	EPR	NMR	Mössbauer	Neutron spectroscopy	XPS	AFS	SIMS
Thickness analyzed	mm	mm	mm	mm	mm	100 μm	0.1 mm	20–50 \AA	10–20 \AA	2–3 \AA
Area analyzed	cm^2	μm^2	cm^2	cm^3	cm^2	cm^2	mm^2	cm^2	cm^2	cm^2
Sample degradation	No	Possible	No	No	No	No	Possible	Possible	Possible	No
Sample preparation	Easy	Easy	Easy	Easy	Easy	Easy	Difficult	Easy	Easy	Easy
Quantitative measurements	Possible	difficult	Possible	Yes	Yes	Yes	Yes	Yes	Possible	Possible
Gaseous atmosphere	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Difficult	Difficult	No
Temperature range ($^{\circ}\text{C}$)	–196 to 500	–196 to 500	–196 to 500	–269 to 1000	–196 to 200	–269 to 400	–269 to 800	–180 to 600	–180 to 600	Ambient
Information obtained	Functional groups; adsorbing species	Functional groups; adsorbing species	Degree of oxidation; ion symmetry; adsorbing species	Paramagnetic species; degree of oxidation; symmetry	Functional groups	Degree of oxidation; symmetry of environment	Adsorbing species; atomic structure	Degree of oxidation; surface composition	Surface composition	Surface composition

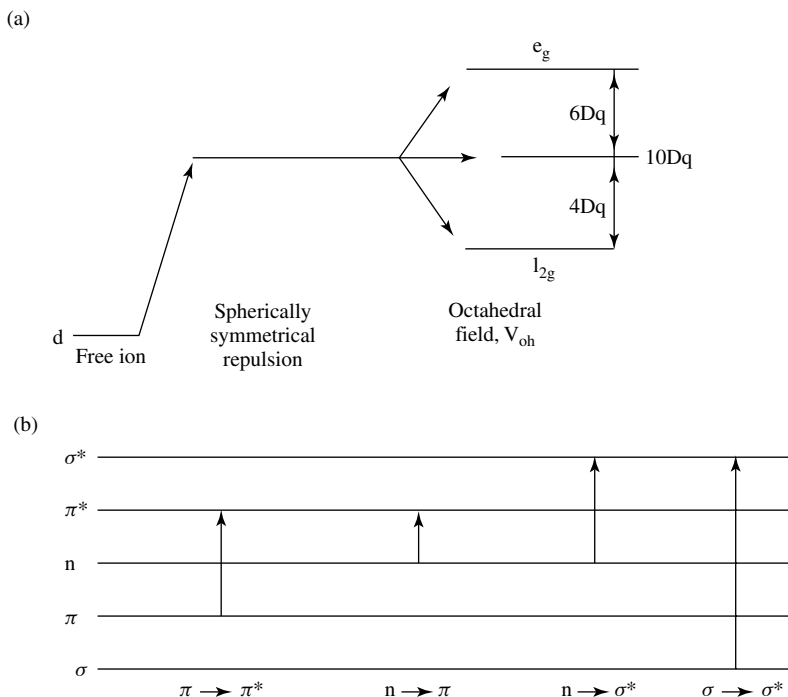


Figure 1.3. Schemes of electron transfers: (a) $d \rightarrow d$ electron transitions in an octahedral field; (b) relative energies of electronic transitions between different types of orbitals typical of organic molecules (σ , π and n).

transfer in different directions: (i) from an orbital mainly localized on the metal to that mainly localized on the ligand ($M \rightarrow L$), and (ii) in the opposite direction ($L \rightarrow M$). The energies of these transitions is higher than that for $d \rightarrow d$ transitions, and accordingly the absorption bands are in the UV region of the spectra ($\varepsilon \sim 10^3\text{--}10^6$). Optical spectra can be directly obtained by either internal or external reflection-absorption techniques (reflectance spectroscopy).

1.1.1 TRANSMISSION SPECTRA

The transmitted light of intensity I is related to the incident light intensity I_0 by the *transmittance*, T , given by I/I_0 ($0 < T < 1$). For thin samples, the transmittance can be related to the concentration of the absorber (c) and the thickness of the sample (l) by the Lambert–Beer law, as follows:

$$T(\nu) = \exp(-\varepsilon lc) \quad (1.1)$$

where ε is known as the *molar absorption coefficient* ($\text{cm}^2 \text{mol}^{-1}$). The *optical density* or *absorbance*, $A(= \log(I/I_0))$ is also used frequently. It is often preferable to use this parameter in the integral form (A), as follows:

$$A = \int_{\nu_1}^{\nu_2} A(\nu) d\nu = \int_{\nu_1}^{\nu_2} \ln[I_0(\nu)/I(\nu)] d\nu \quad (1.2)$$

UV–Vis spectroscopy is distinguished by a fairly high sensitivity. In particular, the intensity of the absorption for allowed one-electron $d \rightarrow d$ transitions is characterized by a molar absorption coefficient of the order of ~ 1 –100. The ε value is significantly lower for complexes with a high symmetry and is much greater in the case of the bands characteristic of the charge transfer in the complex.

1.1.2 DIFFUSE REFLECTION SPECTRA

In surface chemistry, the UV–Vis spectroscopic method is usually used in its diffuse reflection modification. The radiation reflected from a powdered crystalline surface consists of two components, i.e. (i) that reflected from the surface without any transmission (mirror or specular reflection), and (ii) that absorbed into the material and which then reappears at the surface after multiple scattering. Modern spectrometers minimize the first component, and the term ‘reflectance’ is thus used for diffusely reflected radiation [25, 117].

Since only a part of the diffuse radiation is returned to the detector, measurement of the diffused intensity is difficult. For this purpose, a special integrative sphere (Table 1.2), coated inside with a highly reflecting layer, such as MgO or BaSO₄, is used. Such a sphere increases the part of the diffused intensity that reaches the detector (30–50 %). Spectra are recorded ‘in ratio’ with a sample which has similar diffusion characteristics to the sample under investigation, but without any absorption losses.

The evaluation of the intensities of diffuse reflectance spectra is based on the theory of Kubelka and Munk. The reflectance is given by $R = I/I_0$ ($0 < R < 1$). For a nontransparent thick layer, R is called R_∞ and the ratioed $R'_\infty = R_\infty(\text{sample})/R_\infty(\text{standard})$. The quantity $\log(1/R')$ is known as the *apparent absorbance* and is not strictly proportional to the concentration of the absorbing species [117]. To calculate the Kubelka–Munk function, the measurable reflectance R'_∞ can be used as follows:

$$F(R'_\infty) = (1 - R'_\infty)^2 / 2R'_\infty \quad (1.3)$$

This quantity, for a layer of infinite thickness, has been related to the parameters K and S ($F(R'_\infty) = K/S$), which are themselves linked to the absorption (K) and the reflection–diffusion (S is a scattering coefficient). The theoretical base, as well as the conditions of application of the Kubelka–Munk function, has been discussed in detail elsewhere [25, 117].

Electronic spectroscopy may be used to determine the local symmetry and oxidation state of a transition metal, and thus it is a sensitive probe for the type of site in which such an ion exists. The applicability of this method is not limited to transition-metal-containing systems. It can be also used to measure the electronic spectra of adsorbed molecules and to obtain direct information about the excited and ground states of such species.

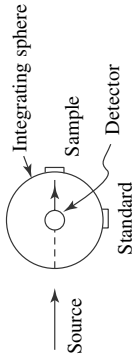
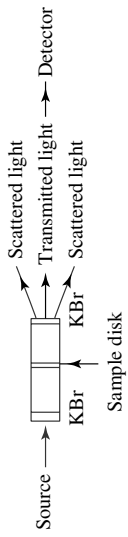
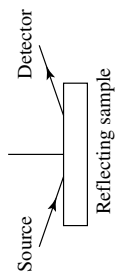
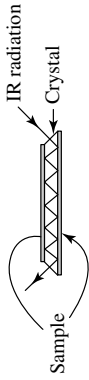
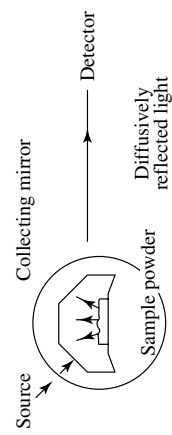
There are no problems in constructing a cell for electron spectroscopy since quartz is fully transparent to UV–Vis radiation. Some types of cells used to study the UV–Vis spectra of cations in oxide systems and adsorbed molecules are described in the literature [25, 117].

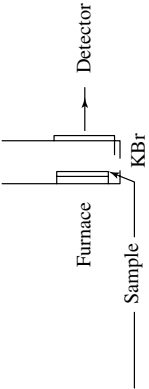
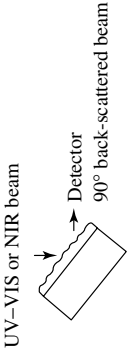
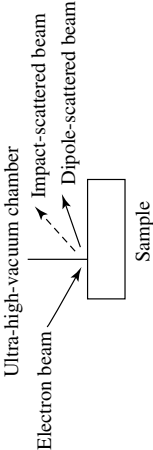
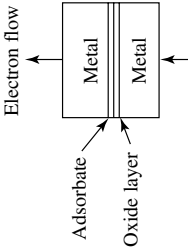
1.2 Vibrational spectroscopy

Vibrations in molecules are excited by absorption (infrared spectroscopy (IRS) or by scattering (Raman spectroscopy) of photons, electrons (electron energy loss spectroscopy (EELS)) or neutrons (inelastic neutron scattering (INS)).

Since the bands in the spectra are observed at specific frequencies, it follows that the rotational, vibrational and electronic motions leading to electrical dipole changes must occur at specific frequencies. A classical model gives considerable information concerning the existence of vibrational

Table 1.2. Basic experimental principles and applications of the different spectral methods used for surface chemistry analysis.

Method	Common scheme	Thickness analyzed	Quantitative measurements	Information obtained
UV-Vis		mm	Possible	Ion symmetry; adsorbing species; degree of oxidation
Transmission IR		mm	Possible	Adsorbed species; surface active sites; functional groups
Reflection IR (RAIRS)		mm	Possible	Adsorbed species; surface active sites; functional groups
ATR		mm	Possible	Adsorbed species; surface active sites; functional groups
Diffuse reflection (DRIRS)		mm	Possible	Adsorbed species; surface active sites; functional groups

Emission IR		mm	Possible	Adsorbed species; surface active sites; functional groups
Raman		mm	Possible, but with difficulties	Functional groups; adsorbed sites; surface structure; bulk structure; structure of adsorbed species
EELS		μm	—	Metal–ligand bonds; phase transitions; chemical structure
IETS		μm	Possible, but with difficulties	Vibrational spectra of minute quantities of materials

frequencies of atoms within the molecules, but allows us to explain the existence of rotational frequencies only if the electronic motions occur at the same frequencies.

The vibration of a diatomic molecule can be reduced to the motion of a single particle of reduced mass μ_m . In this model, the problems are simplified by considering that the diatomic molecule can be analogous to the harmonic oscillator (Figure 1.4), in which two masses (m_1 and m_2) are joined by a perfect spring of length r_0 . A restoring force f is directly proportional to the distance r , as follows:

$$f = -kr = \mu_m(d^2r/dt^2) \quad (1.4)$$

where k is known as the harmonic force constant, and is a function of the potential energy U in accordance with Hooke's law:

$$f = -dU/dr = -kr \quad (1.5)$$

Integration of this equation leads to the following parabolic relationship see (Figure 1.4(a)):

$$U = 1/2kr^2 \quad (1.6)$$

For diatomic molecules A–B, r represents the displacement of the atoms from the equilibrium separation r_0 . A small displacement of one of the masses relative to the other will cause the system to vibrate as a simple harmonic oscillator with a frequency given by the following:

$$\nu_0 = (1/2\pi)\sqrt{k/\mu_m} \quad (1.7)$$

where μ_m is the reduced mass of the system. At the assignment of the frequencies observed in the infrared spectra, this relationship is often used in conjunction with isotopic exchange, in particular deuterio exchange, as follows:

$$\nu_{X-H}/\nu_{X-D} = \sqrt{2} = 2m_x/(2 + m_x) \quad (1.8)$$

where m_x is the mass of the X atom. This ratio is 1.37 for OH–OD and NH–ND, and 1.36 for CH–CD (i.e. ca. $\sqrt{2}$).

According to quantum theory, the energy of the molecule is given in terms of a series of discrete energy levels, E_0 , E_1^v , E_2^v , etc. (see Figure 1.2), and each discrete molecule must exist at one or other of these levels. The frequency of absorption or emission of radiation for a transmission between the levels with energies E_0 and E_1 is given by the following:

$$\nu = (E_1 - E_0)/h \quad (1.9)$$

where h is the Planck constant.

From the Schrödinger wave equation, the total energy of vibration is as follows:

$$E_{\text{vib}} = h\nu(v + 1/2) \quad (1.10)$$

where ν is the frequency of vibration of the oscillator and v is the vibrational quantum number. For any transition between quantized levels in which $v' \pm v'' = 1$.

$$\Delta E = h\nu \quad (1.11)$$

The differences between two levels arise directly as a result of the quantum-mechanical derivation of Equation (1.10). For the simple quantum-mechanical model, the presence of combination bands and overtones in the spectrum is forbidden, because such bands involve jumps between

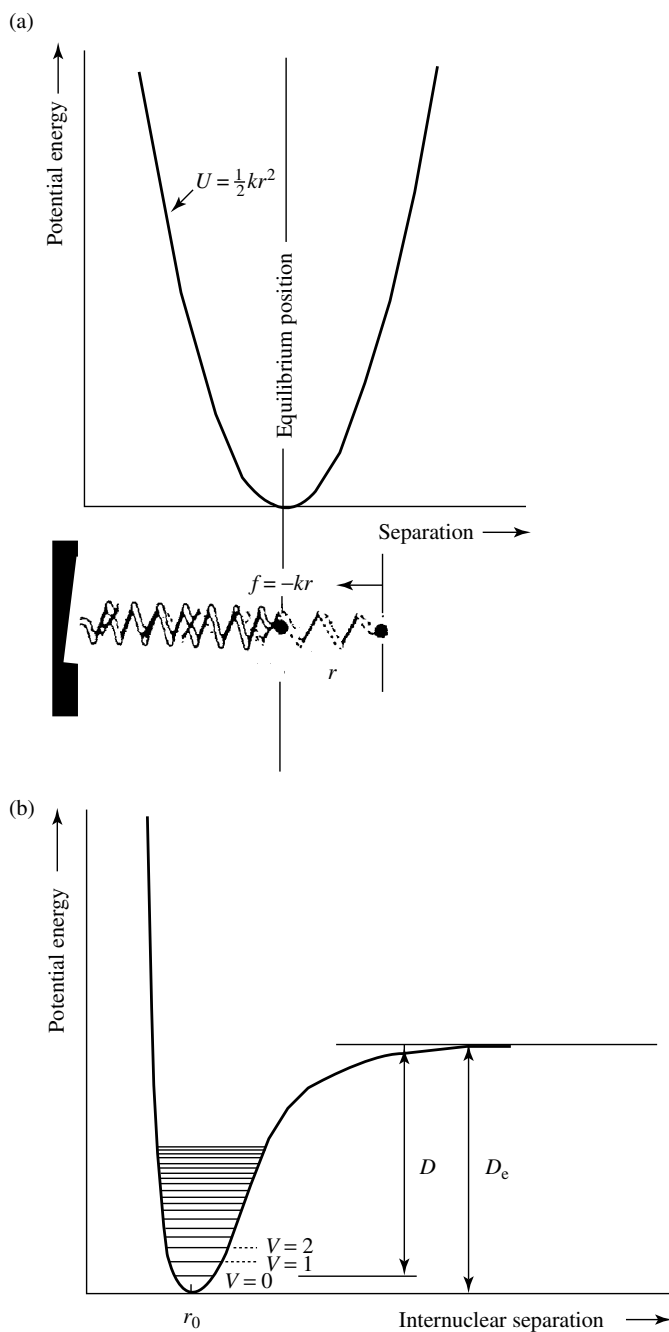


Figure 1.4. Potential-energy functions for (a) a mass and spring system obeying Hooke's law, and (b) a real diatomic molecule with a dissociation energy D_e and equilibrium bond length r_e (where r_0 represents the first energy level).

several different quantum levels. There are no such stringent rules in the case of an anharmonic oscillator, where overtone and combination bands can appear, often weakly in the spectra, according to the following:

$$E_{\text{vib}} = h\nu(v + 1/2) - x_e(v + 1/2)^2 \quad (1.12)$$

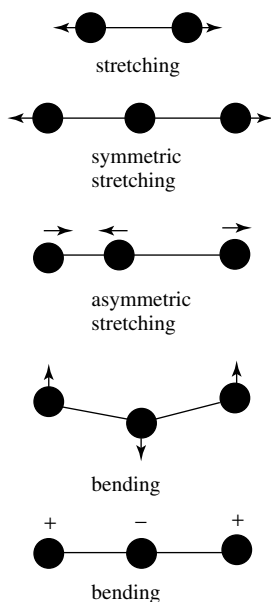
where x_e is the anharmonicity constant. Introduction of this parameter leads to the potential curve shown in Figure 1.4(b).

The movements of the atoms in a molecule during vibration can be approximately classified into two groups, i.e. (i) bond stretching, and (ii) angle deformations. For an N -atomic molecule, the number of fundamental vibrations is $3N - 6$ for a nonlinear and $3N - 5$ for a linear molecule. There are four types of vibrations, i.e. ν , δ , γ , and τ (Figure 1.5). Generally, the frequencies of these vibrations decrease in the order $\nu > \delta > \gamma > \tau$.

All molecules can be classified into a limited number of symmetry groups, which obey the rules of group theory. A knowledge of the symmetry group of a molecule allows the determination of the symmetry classes of the $3N - 6$ normal modes of vibration and their activities in IR and Raman spectroscopies.

Assignment of the bands in the spectrum to particular types of vibrations is an important stage and is based, as a rule, on *group-characteristic* (of limited dependence on the nearest molecular environment) modes. Calculations based on vibrational theory are used for more accurate assignment [4, 14–16]. These calculations show that there are no strictly characteristic vibrational modes; frequencies of many group vibrations are coupled and make certain contributions to each other. A vibration with a minimum contribution from other vibrations is known as a *group characteristic*. Usually, interpretations of the spectra of adsorbate–adsorbent systems are made by the

(a) Linear molecules



(b) Non-linear molecules

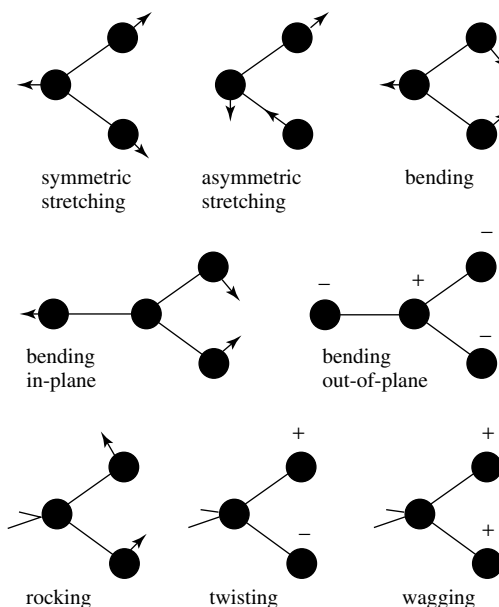


Figure 1.5. Fundamental modes of vibration of (a) linear, and (b) nonlinear molecules.

comparison with the spectra of bulk compounds or fragments isolated in a matrix. However, in this way only certain types of compound can be identified. Calculations of the vibrational spectra of individual surface species based on the modeling of the potential function of the molecule (vibrations in the force constants of the potential function) are useful for interpreting changes in vibrational frequencies and their reactions to changes in the force field of molecules subjected to the influence of a highly nonuniform field at an adsorbent surface [19, 118].

Several forms of vibrational spectroscopy are now in routine use, i.e. (i) transmission infrared, (ii) Raman, (iii) diffuse reflection, (iv) reflection–absorption infrared, and (v) electron energy loss, but in the study of surfaces none has found wider application than infrared spectroscopy.

1.2.1 INFRARED SPECTROSCOPY

The infrared (IR) region corresponds to the energies of the vibrations and rotations of molecules. If a molecule is subjected to IR radiation whose frequency is equal to that of one of its oscillators, this oscillator will resonate and absorb part of the radiation. The absorption (emission) intensity is given by the transition probability between the ground and excited states. Not all vibrations are observed—only those transitions corresponding to vibrations with variation of the dipole moment are active in IRS. The intensity of the infrared band is proportional to the square of the change in dipole moment. The principles of this method have been presented in numerous books and reviews [1–5, 11–16, 119–123] and are summarized in Table 1.2.

In the study of processes occurring on surfaces, transmission, reflectance, emission and diffuse reflection infrared spectroscopies are used.

Transmission spectroscopy

A common infrared transmission spectrum is obtained as a result of the direct transmission of an infrared beam through a sample when the following conditions apply: $\Delta\nu = +1$ ($\partial\mu/\partial Q$)₀ $\neq 0$, where μ is the dipole moment, and Q is a normal coordinate. As in UV–Vis spectroscopy, the spectrometer records the transmission, $T(= I/I_0 = \exp(-kl))$, the intensity of which can be found from the Lambert–Beer law (Equation (1.1)). The sensitivity of this method is determined by both the characteristics of the radiation detector and by the absorption coefficient of the medium. Approximately a 10-fold gain in sensitivity can be achieved by the use of the Fourier transform (FT) technique [1, 120].

To study the spectra of bulk oxides, dilution in either KBr (down to 400 cm^{−1}) or CsI (down to 200 cm^{−1}), or polyethylene disks are used. If the sample is stable in air and does not react with KBr or CsI, these are the methods most often used. However, if any interactions take place, then the techniques of attenuated total (internal) reflection (ATR) or emission spectroscopies have to be used.

For both cases, in order to obtain a typical transmission IR spectrum from oxides in the region of surface vibrations (in this case, the thickness of the corresponding sample is ten times more, as a minimum, than that of the corresponding samples prepared in an immersion media), the sample has to allow at least a partial transmission, preferably 10 % or more, of the IR beam. Scattering of the radiation by the particles can be another factor which leads to low transmission. The transparency is improved when the oxide particle sizes are small relative to the radiation wavelength. Scattering may be significantly reduced by the use of pressed disks or highly dispersed samples (particles size less than 1 μm). The latter can be prepared in two different ways, i.e. (i) sedimentation of the dissolved sample from an inert solvent or from air onto a transparent window, or (ii) by using an electrical field [42]. When a material is pressed into a thin flat self-supported disk, the scattering, which takes place during the transmission of the IR radiation through the sample, can be substantially reduced. In general, such a disk should be from one to a few tenths of a millimeter in thickness and have a density between 10 and 100 mg cm^{−2}

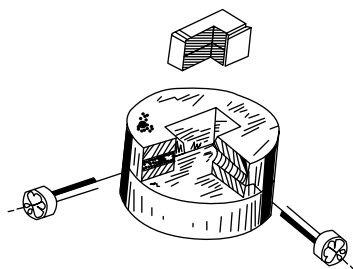


Figure 1.6. A typical mold used for compressing self-supported pellets of adsorbent in infrared studies.

in order to give good transmission in the infrared and also to have good mechanical properties. It is better to press the samples in a demountable mold (Figure 1.6) [19, 42], which then allows adjustment of the lateral pressure on the compressed sample by means of a number of screws and plates, in order to prevent cracking of the thin disk and to facilitate its removal from the mold. Preparation of such thin samples, especially from transition-metal oxides or zeolites, is truly ‘an art’. If the solids are not transparent or cannot be molded as disks and hence have to be handled as powders, the following methods can be useful: (i) the use of a grating; (ii) a (powder) technique in which the powder is finely pulverized, sifted, and then spread out on an IR-transparent disk (such as KBr, CaF_2 or a silicon single crystal) and, if this covering is stable, then covered by a second disk; (iii) dilution of the sample in a compound that is transparent and inert to the reaction being studied (e.g. SiO_2 and Al_2O_3); (iv) the use of special cells. The problem of sample preparation is minimized in the case of diffuse reflection spectroscopy [25, 61, 122–124].

To record the infrared spectra of adsorbed molecules, special vacuum cells are used – these are available in many different and widely variable types, depending on the system being studied [18–21, 23–26, 28–35, 42, 44–46, 63, 64]. Ideally, these cells should be designed so that the sample can be heated up to 1273 K, and cooled to liquid nitrogen temperature, to adsorb/desorb both gases and vapors at different temperatures, be able to maintain a high vacuum, and to record the spectra of adsorbed molecules without exposing the pellet (disk) to the air. The main problem here is achieving an hermetic sealing of the ‘windows’ (plates) which are transparent in the IR (Table 1.3 [42, 119, 125–127]). Frequently, such a sealing is made by the use of different cements and glues with low vapor pressures, or alternatively by using O-rings and flanges.

There are two types of cells used for recording infrared spectra under high vacuum over a wide temperature range: (i) a cell, large in length, which gives the possibility of separating a heater from the region of the sealed windows, i.e. where the recording of spectra and the heating of the sample are carried out in different parts of the cell or if a static sample is heated, a cooling of the windows is required (see, for example, a cell design resulting from the work of this present author (Figure 1.7) [42, 128]); (ii) a cell with a very short optical pass (<10 mm), and thus the absorption spectrum is not affected by the gaseous-phase molecules, even at high pressures (Figure 1.8(b)) [42]. As a rule, in the second type of cell (Figure 1.7(a); Figure 1.8(a)) a sample has to be moved to the heating zone, which is far from the site of hermetic sealing. The necessity to move the sample is a disadvantage of such cells because of the possibility of irreproducible measurements. It should be noted that in order to measure the temperature of a sample with a thermocouple, direct contact of the latter with the sample and contact of the sample with a furnace are needed. For this purpose, special samples holders, in which the samples are situated on the heated walls (Figure 1.9), are used. If heating of the sample is only by radiation, the measured temperatures of the sample in vacuum and in the presence of gas may be significantly different and thus can lead to errors. Several designs of cells used in adsorption studies have

Table 1.3. Various optical materials used for lenses and windows in infrared studies.

Material	Low-energy cutoff (cm^{-1})	Comments
Sapphire	>1600	High mechanical strength; inert; connected with metal; hard; expensive
Quartz	>2500	Good for high-temperature work and in the overtone region; insoluble; easy to work in fused form
LiF	>1200	Good dispersion in the near-IR region; easily scratches
MgF ₂	1400	Strong; chemically durable
CaF ₂	1200	Inert to most chemicals; tends to be costly; slightly soluble; good from 73–373 K
MgO	>1200	Hard and costly; can be sealed to a high-expansion glass
Silicon	1100	Inert; insoluble; connected with glass; not transparent at high temperatures
NaF	1000	Slightly hygroscopic
BaF ₂	900	Hard; expensive
ZnS	714	Good up to 1073 K; strong; chemically durable
NaCl	600	Slightly hygroscopic; cheap; easily worked
KCl	550	Slightly hygroscopic; cheap
AgCl	500	Photosensitive; can corrode metals
ZnSe	500	Good up to 573 K; soluble in acids
KBr	350	Hygroscopic; easily scratched; used as powder for pressed-disk technique
CsBr	250	Very hard; expensive
KRS-5	250	Very soluble; expensive; toxic; deforms under pressure
CsI	180	Very hard; expensive

been reviewed by Little [18], Kiselev and Lygin [19], Delgass *et al.* [25], Shchekochikhin and Davydov [42], Bell [119, 127], and Basu, Ballinger, Yates *et al.* [128a], as well as in numerous original studies.

The best materials for windows directly connected to glass are silicon, MgO and AgCl, while sapphire is the best material for connection to metals (see Table 1.3). Quartz cells, which are usually routinely used in the visible and UV regions of the spectrum, can also be employed in the infrared region, but only above 2000 cm^{-1} . A very convenient cell is one with silicon single crystal windows (Figure 1.8(a)) but, unfortunately, this cannot be used at temperature higher than 473 K because of the reduced transparency of the silicon single crystal as a result of internal electron transfer mechanisms.

There are several types of cells of minimized volume, used in order to record spectra under dynamic conditions (e.g. at high temperatures during catalytic transformations – so-called *in situ* conditions – see, for example, Figures 1.7(b) and 1.10). A simple flow-cell-reactor made from metal [42] or quartz [64, 65] practically without any ‘free volume’, has been proposed (Figures 1.7(b) and 1.11). The main part of such a cell is a reactor made from metal or quartz. Both the reactor and windows (CaF₂, BaF₂, ZnS or ZnSe) are polished and clamped to each

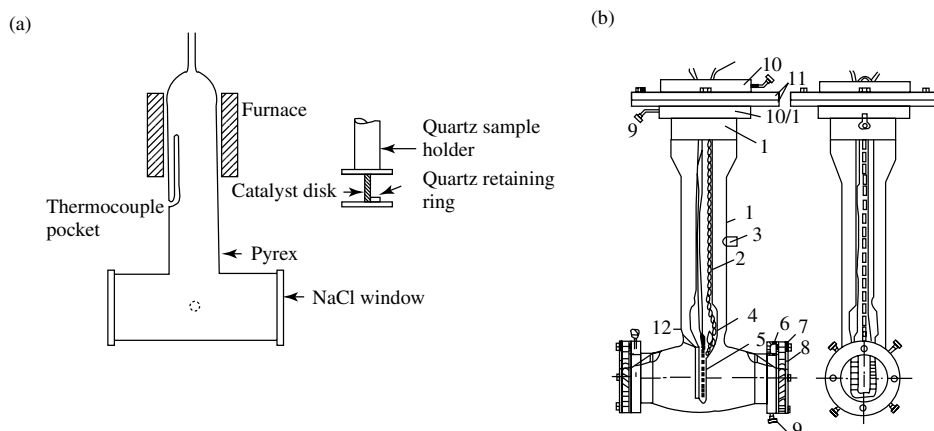


Figure 1.7. Schematics of cell-reactors used for studying the spectra of adsorbed molecules at (a) room, and (b) high temperatures: 1, cell body; 2, sample holder; 3, evacuation port; 4, case for thermocouple; 5, container for heater; 6, 10, cooling channels; 7, 11, flanged connectors; 8, windows; 9, connectors; 12, sample pocket.

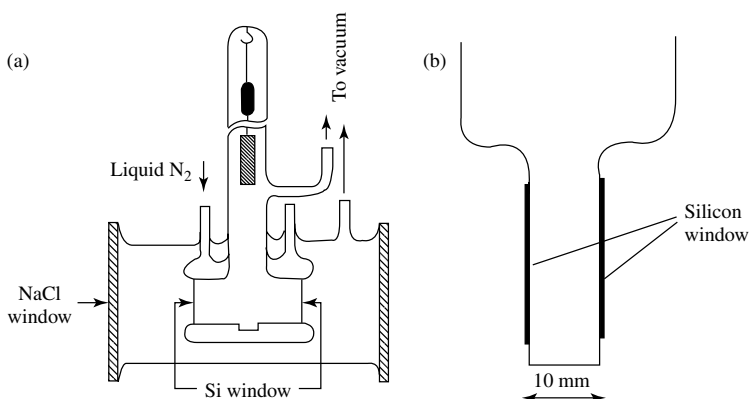


Figure 1.8. Schematics of vacuum cells with silicon windows: (a) for low-temperature investigations; (b) with a short optical path.

other [64, 65]. Connections between the cell body and the windows is achieved by using iridium or gold foils, or with Teflon [42]. The Graseby Specac company now produces standard *in situ* high-temperature cells for temperature ranges up to 773 K, as well as high temperature and pressure cells.

Emission spectroscopy

Methodological difficulties in the study of surface species caused by strong scattering or absorption of infrared light by the adsorbing sample can be eliminated if emission spectra are recorded [1, 25, 35]. This method, however, is less frequently used since the intensities of the emission bands are quite low, except at higher temperatures. Emission spectra are usually produced by heating the sample above 473 K (Figure 1.12) [129] and are the most appropriate in cases where

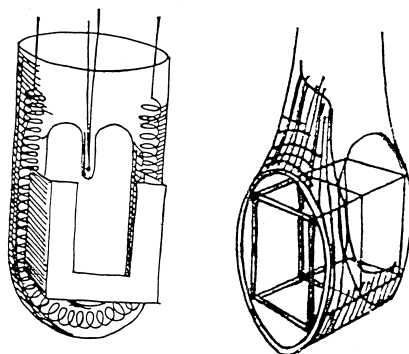


Figure 1.9. Schematics of types of sample holder.

reactions proceed on surfaces at high temperatures (see Table 1.2). The spectrum is obtained by measuring the ratio of the emitted radiation at any wavelength to that emitted by a perfect ‘black body’ at the same wavelength and temperature. According to the Kirchhoff law, $\varepsilon_v = a_v$, where a_v is the absorbance (fractional absorption) of the substance. It follows from the Lambert–Beer law that emission of a thick nonopaque emitter will approach that of a black body, so the ideal sample to record an emission spectrum is a thin layer supported on a near perfect reflector such as a metal.

The basic equation for quantitative measurements is as follows

$$\varepsilon + r + t = 1 \quad (1.13)$$

where r and t are the reflectance and transmittance coefficients of the substance, respectively. It follows from this that for an opaque sample ($t \sim 0$), $c = 1 - r$, and thus selected peaks in the reflection spectra will be recorded as minima in the emission spectra.

In principle, emission spectra can be recorded by employing any one of the cells described above for use in transmission spectroscopy, including the cell-reactor design for recording spectra *in situ* (see Figure 1.11) in which the sample in the infrared beam is heated (see Table 1.2).

The high sensitivity of the FTIR technique has significantly increased the possibilities for emission spectroscopy, and this can now be used to study the structure of solid surfaces, molecules adsorbed on the surfaces of different substances, formation of oxide films, etc. More details of the application of this method are available in a number of references [1, 25, 31, 64].

Reflection spectroscopy

Numerous oxide systems exist as opaque powdered samples from which light is reflected and not transmitted. Reflected radiation, in this case, consists of two components: the specular component reflected from the surface without transmission (mirror or specular reflection), and the diffuse component which is absorbed into the sample and reappears at the surface after multiple scattering [2, 9, 130]. The various forms of reflection spectroscopy (see Table 1.2) are less frequently used than the transmission methods, although they do have some important specific uses. In principal, the best way of obtaining absorbance and reflectance mode information from flat samples is by reflection spectroscopy (which gives signals that depend on these two related variables), in which the data is then analyzed by use of the Kramer–Kronig equation.

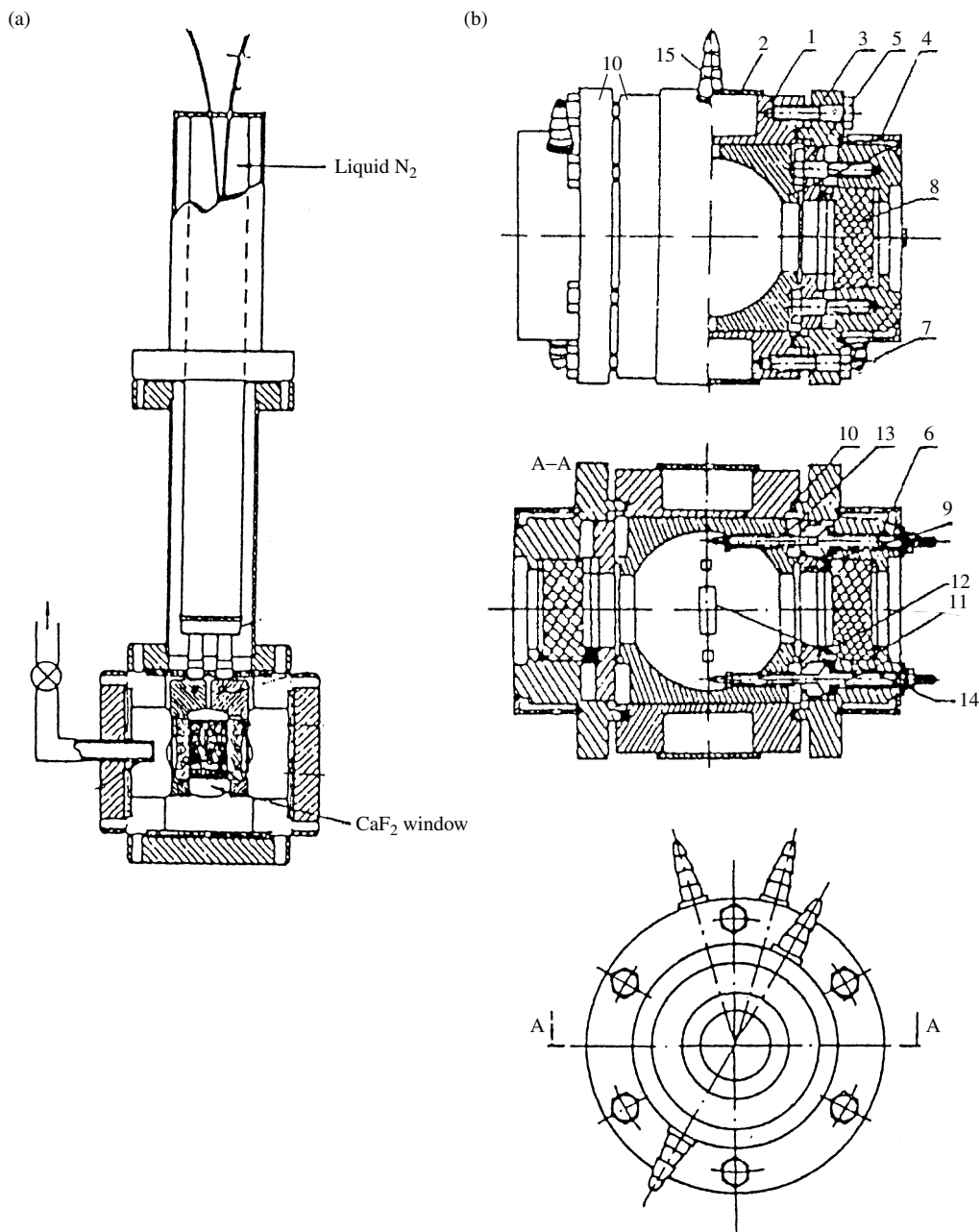


Figure 1.10. Schematics of cell-reactors used to study *in situ* spectra at (a) low temperatures [128c]. Reprinted with permission from Basu, P., Ballinger, T. H. and Yates, J. T., Jr, *Rev. Sci. Instrum.*, **59**, 1321–1327 (1988), American Institute of Physics, and (b) high temperatures and high pressures: 1, body of the cell; 2, 4, 6, cooling channels; 3, window holder; 5, 7, bolts; 15, water connectors; 8, window; 9, leads for heater and thermocouples; 10, flange seal between cell and window holder; 11, 12, O-ring seals; 13, insulating tube; 14, sample holder.

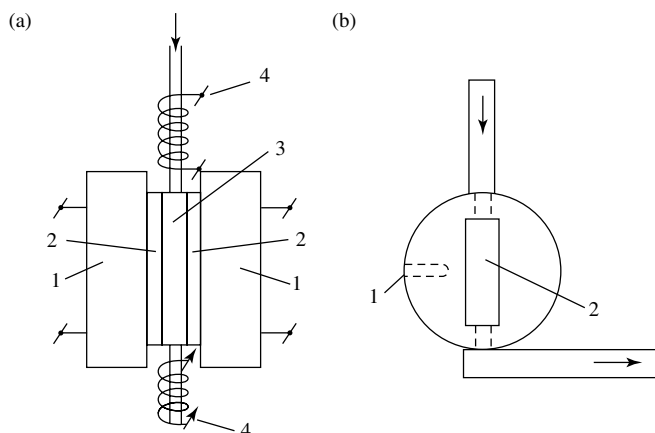


Figure 1.11. Schematics of a flow-cell-reactor of minimal volume: (a) 1, heater; 2, window; 3, reactor; 4, auxiliary heaters; (b): 1, thermocouple pocket; 2, sample position [64]. Reprinted from *Catal. Today*, **25**, Matushak, V. A. and Krylov, O. V., 'In situ IR spectroscopy of intermediates in heterogeneous oxidative catalysis', 1–88, copyright (1996), with permission from Elsevier Science.

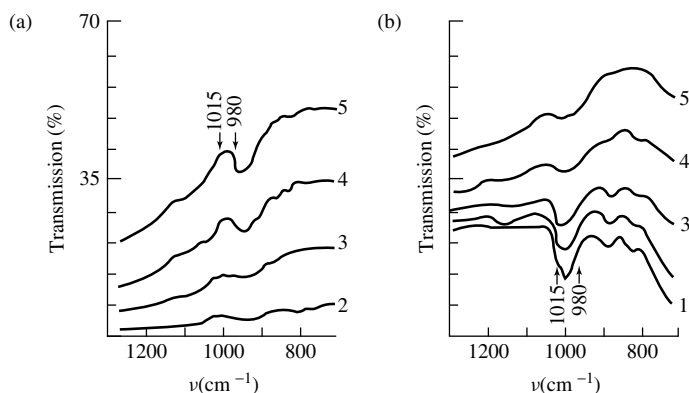


Figure 1.12. Infrared (a) emission, and (b) absorption spectra of oxygen adsorbed at 673 K on chromium oxide, recorded at (1) 345, (2) 373, (3) 473, (4) 573, and (5) 673 K.

Mirror reflection (reflection–absorption IR spectroscopy – RAIRS)

As was predicted by Greenler [131] and then experimentally verified later [132–135], a good metal reflector gives rise to maximum absorption from a monolayer near grazing incidence as a result of the phase shift between the incident and reflected waves which combine to form a standing wave mode approximately normal to the surface. The trade-off between the high incident electric fields at the surface and the number of reflections leads to an optimum value for the latter (see Table 1.2). It is often possible to use only one reflection without any loss of sensitivity if the optimal angle (88°) of the beam incidence is chosen [131].

Internal reflection spectroscopy (attenuated total reflection – ATR)

This technique is elementary to the more usual external reflection spectroscopy. In this case, the infrared radiation approaches the solid–gas interface via the solid phase [2, 9, 25, 136]. The

radiation is totally reflected back into the solid if the angle of incidence exceeds a critical angle when the absorbing molecules are absent. The incident and reflected waves superimpose and form a standing nonpropagating electric field (see Table 1.2). The sample, prepared as a very fine powder in order to maximize optical contact, is dispersed on one of the two faces of a KRS (TlBr + TlI) single crystal, which has a high refractive index. The IR beam enters via the input side of the crystal, leading to n reflections on the two faces. A small part of the light is adsorbed by the sample at each reflection [136]. This method can be used to obtain the spectra of adsorbed species [130–137].

Diffuse reflection infrared spectroscopy (DRIRS)

In this technique, diffuse scattered radiation is collected by the sphere or an ellipsoidal mirror and focused on the detector (see Table 1.2), with the infrared absorption spectrum being described by the Kubelka–Munk function (Equation (1.3) above) [19, 25, 35, 61, 122–124, 137]. The relationship between the intensity of the band due to an adsorbed substance and its concentration is as follows:

$$F(R) = I[(1/(R - R_{\infty}))] = 2\epsilon c/S \quad (1.14)$$

This equation assumes that the scattering coefficient S is wavelength-independent (which is not the case line in regions of very low absorption).

Theoretical studies indicate that diffuse reflection spectroscopy is more sensitive than transmission spectroscopy if the effectively scattering components are investigated. However, reflection spectroscopy has not been used in the IR region until fairly recently because of the insufficient sensitivity of infrared detectors, and the great difficulty in constructing integration spheres for collecting diffuse radiation in this region. The sensitivity problem was overcome by the development of FTIR spectroscopy. In addition, this method allows the direct investigation of powdered materials contained in cells of small volume. Therefore, it has significantly simplified sample preparation, as well as pretreatment techniques and the obtaining of the spectra, particular at low temperatures.

In order to obtain diffuse reflectance spectra, various commercial attachments (for example, the Harrick or Spectra-Tech Collector, which is more convenient for adjustment) and *in situ* cell-reactors [1], including chambers for high-temperature, pressure or vacuum work, are now available. An interesting variation of this technique which uses an additional internal source of radiation has been proposed by Kazansky and coworkers [124]. For measurements in the near-infrared region, thin-walled quartz ampoules have been used as IR cells, while in the mid-infrared range, CaF_2 or BaF_2 windows are preferred.

1.2.2 PHOTOACOUSTIC SPECTROSCOPY

If radiation is absorbed by a sample in a closed cell, it is converted into heat and the temperature of the sample increases. This is so-called *photothermic effect*. If the sample is irradiated with a modulated IR beam, the photothermic effect in turn periodically heats a gas in contact with the sample in the boundary layer, $2\pi/a_g$, where $1/a_g$ is the thermal diffusion length of the gas. The energy is hence transferred to the gas phase as modulated pressure changes. The modulation of the gas pressure can be detected by a microphone and amplifier. Blank and Wakelfield [138] showed that for absorbing compounds the photoacoustic signal is proportional to the absorbance, and thus a photoacoustic spectrum is similar to an absorption spectrum, except that the thickness of the layer giving rise to the acoustical output increases with the wavelength of the incident radiation.

An advantage of this method is the possibility of investigating surface species without any special preparation of the sample being required. Photoacoustic spectroscopy (PAS) is well suited

to the study of turbid media, including liquids, solids and gases, and suitable equipment is now commercially available [25, 125].

1.2.3 RAMAN SPECTROSCOPY

The *Raman effect* is based on the inelastic scattering of electromagnetic radiation due to its interaction with molecular vibrations or rotations (see Table 1.2). Raman spectra are recorded as a function of the wavenumber of inelastically scattered light which results from the excitation of vibrations in molecular and crystalline materials. Because the shifts in the frequency of the scattered radiation are usually in discrete vibrational quanta, this technique provides the same kind of detailed molecular structural information that can be obtained from infrared absorption, except for the differing relative intensity relationships between the vibrational features. The excitation source is a single monochromatic line of a continuous gas laser in the visible or UV region. In Raman spectroscopy, the optics employed in optical microscopy can be used for measurement of samples down to a few μm in size [5, 12, 15, 139–146].

When the molecule recovers its energy after an elastic collision process, the emerging photon has its former energy ($h\nu_0$), but its direction or angular momentum can be changed. This is known as the *Rayleigh effect*. If the energy of the molecule is changed to E_n , corresponding to a new quantum state, the collision is inelastic, and the emitted photon has a different frequency, as follows:

$$h\nu = h\nu_0 - (E_n - E_0) = h\nu_0 - h\nu_n \quad (1.15)$$

where ν_n is the frequency of a vibrational or rotational energy of the E_n level. In the so-called Raman Stokes scattering, the molecules receive extra energy from the photons and the frequency of the latter is decreased (Figure 1.13). Sometimes the molecule may be in an excited state and during the collision process can lose energy and return to the ground state. The energy of the emitted photon in this case is then greater:

$$h\nu = h\nu_0 + h\nu_n \quad (1.16)$$

This is known as Raman anti-Stokes scattering (Figure 1.13). For a particular situation such a peak has much lower intensity than the Stokes one, because the proportion of vibrationally excited molecules is usually small according to the Boltzmann distribution. The difference between the energies of the incident ($h\nu_0$) and emitted ($h\nu_n$) photons depends only on the vibrational and rotational energy levels of the molecules and not on the wavelengths or frequencies of the exciting radiation.

As in infrared spectroscopy, some vibrations are also forbidden in Raman spectroscopy. Only vibrations which change the polarizability of a molecule are Raman-active. Usually, this requires that the molecule changes its shape. From quantum-mechanical theory, it is possible to conclude that for harmonic vibrations Raman scattering occurs only if the following conditions apply:

$$\Delta\nu = \pm 1 \quad (1.17)$$

$$(\partial\alpha/\partial Q)_0 \neq 0 \quad (1.18)$$

where α is the polarizability, and Q is a normal coordinate. According to the selection rules, Raman spectroscopy is complementary to infrared spectroscopy since the vibrations forbidden in an IR spectrum are often active in the corresponding Raman spectrum, and vice versa. This is strictly the case for the vibrations of centrosymmetric molecules.

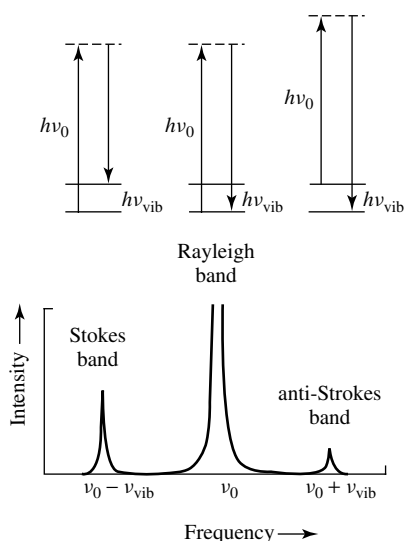


Figure 1.13. The energy-level transitions and spectral features in the Raman effect.

Raman spectroscopy is sensitive to molecular and crystal structure. Applications include chemical fingerprinting, examination of single grains in ceramics and rocks, single crystal measurements, aqueous solution investigations, identification of compounds in bubbles and fluid inclusions, and investigations of structure and strain states in polycrystalline ceramics, glasses, fibers, gels, and thin and thick films. It should be noted, however, that a significant disadvantage of the Raman technique is the small scattering cross-section, as the majority of the intensity is in the Rayleigh scattering mode which is much stronger than the Stokes bands.

The development of intense and monochromatic lasers has significantly increased the number of applications of Raman spectroscopy for the study of the surface chemistry of metal oxides [5, 25, 34, 35, 40, 41, 141–143, 145]. However, even so, a significant limitation for the application of Raman spectroscopy to the study of surfaces can be the superposed strongest fluorescence from the sample itself or from any impurities that might be present. The exciting and scattered frequencies are close together and are in the visible range. Thus, there is generally no problem of cell transparency whatever the material of the cell (silica, quartz, glass or Pyrex), or whichever diffused radiation is observed. There are no difficulties in the use of pressure cells and cells able to withstand very low or very high temperatures. In addition, there is no need for any special preparation of the samples. Powders, liquids, crystals, and even metallic surfaces, can all be studied. A strong point of its application in surface chemistry research is the fact that this technique is highly suitable for *in situ* studies. Even commercial flow-cell reactors have been constructed to study catalytic and adsorption phenomena *in situ*. More widely Raman spectroscopy is used to study the surface layers of supported oxides [104, 105] since the spectral lines of the oxides normally used as supports do not appear in the regions which are characteristic of the fundamental vibrations of the oxides themselves. Linkam Scientific Instruments Ltd and Wotton Scientific are two companies which now commercially produce simple and convenient *in situ* Raman cells. In the latter cell, the sample can be rotated, which thus reduces the heating of the sample by the laser beam radiation.

Despite some advantages (a wider spectral range than for infra red, easier sample preparation, etc.), there are several problems that limit the use of Raman spectroscopy [145], including the following:

1. The intensities of diffused Raman lines of adsorbed species are low and in some cases detection is not possible.
2. Fluorescence of ultra-low level traces of impurities can be so significant that the Raman scattered radiation can no longer be observed.
3. The local heating of the sample by the laser beam can be significant enough to modify or even destroy the sample.

Fortunately, technical progress over the last few years has overcome most of these difficulties. Thus, *resonance* Raman spectroscopy has solved the problem of the intensities of the Raman bands, pulsed lasers reduce fluorescence, cooling of the sample avoids heating and consequent desorption of the adsorbed species, while sample rotation allows different ‘parts’ of the sample to be examined, thus overcoming local heating problems.

Surface-enhanced Raman spectroscopy

This is a modification of the Raman technique which is used in surface chemistry to study molecules adsorbed on metal surfaces [24, 34, 147, 148]. A large number of mechanisms have been postulated in order to explain the very large enhancement process – of the order of up to 10^6 . These include electronic resonance phenomena similar to those observed in ‘standard’ Raman Spectroscopy (RS), based on the surface complexes and surface plasmons activated by the surface process resulting from electrochemical oxidation–reduction cycles [34], and cold deposition of the metal from the vapor state. Restrictions of this otherwise very attractive technique are the limited number of metal systems for which the surface-enhancement phenomena on is observed (silver, copper and gold) and the necessity for special pretreatment of the system under investigation.

Different aspects of the theory, experimental techniques and applications of the Raman effect are analyzed in detail elsewhere [25, 35, 141, 146].

1.3 Electron energy loss spectroscopy

In this method, a beam of mono-energetic, low-energy electrons (commonly with energies of 2–10 eV) falls on a surface and excites the lattice vibrations of the substrate, molecular vibrations of the adsorbed species and even electronic transitions [29, 122, 149–154]. The energy loss of the scattering electrons is described by the following:

$$E = E_0 - h\nu \quad (1.19)$$

where E is the energy of the scattered electron, E_0 is the energy of the incident electrons, h is the Planck constant, and ν is the frequency of the excited vibration.

A primary mechanism by which electrons lose some of their energy to the vibrational modes of an adsorbate is a long-range interaction between the electric field of the incoming electron and the dynamic dipole of the adsorbate [28, 29, 137, 151]. The inelastic collision electrons are mostly forward-scattered and appear close to the specular direction (see Table 1.2). Because of the dipole nature of this interaction, the same selection rule that applies to RAIRS is applicable, as follows:

$$(\partial\mu_{\perp}/\partial Q)_0 \neq 0 \quad (1.20)$$

i.e. only the vibrational modes of the adsorbate with a component of their associated dynamic dipole moment perpendicular to the surface are observable in electron energy loss spectroscopy (EELS). This limits the identification of modes in an EELS spectrum, but in the case when such

a mode can be identified, allows us to obtain information about the geometry and symmetry of the surface complex [137].

While the dipole mechanism of EELS is the most important, it is not the only mechanism of inelastic scattering. A second excitation mechanism, i.e. (impact scattering, involves a short-range interaction between the electron and the molecule which scatters the electrons over a wide range of angles (see Table 1.2). By this mechanism, all vibrations may be excited – not only the dipole-active ones. Similarly to Raman spectroscopy, the electron may take an amount of energy, $h\nu$, away from the excited molecules and leave the surface with an energy equal to $E_0 + h\nu$.

A strong point of EELS is that it detects losses in a very broad energy range from infrared to electronic transitions at several electronvolts. There are no difficulties with EELS in detecting vibrations in the range between 50 and 800 cm^{-1} , which are accessible only with difficulty in RAIRS studies.

There are three main requirements which EELS spectrometers have to satisfy: (i) the primary electrons should be mono-energetic, with as little spread in energy as possible, preferably by only a few meV; (ii) the energies of the scattered electrons should be measured with an accuracy of 1 meV or better; (iii) the low-energy electrons must effectively be shielded from magnetic fields [35]. A comparison of EELS with RAIRS on a number of points has been made by Niemantsverdriet [35]. Although, in principle, EELS can provide more information about the vibrational frequencies of modes involving atoms of the adsorbate or the surface of the adsorbent when compared with optical spectroscopies, its practical use is limited at present by the relatively poor resolution of EEL spectra (10–30 cm^{-1}) and the necessity for flat samples. It is principally used, as for RAIRS, to study monolayers on single crystal metal surfaces.

1.4 Inelastic electron tunneling spectroscopy

The inelastic electron tunneling spectroscopy (IETS) technique involves an electron tunneling between two metal electrodes separated by a thin oxide-based intermediate layer which constitutes the sample [155–159]. Inelastic electron tunneling (IET) junctions are prepared as follows: (i) a thin (ca. 1000 Å) metal film is evaporated onto a clean insulating substrate under vacuum (ca. 10^{-6} Torr); (ii) the film is oxidized by glow discharge anodization or by exposure to air or oxygen; (iii) the oxide is doped with the material of interest; (iv) the junctions are then completed by evaporating a counter-electrode through a second metal mask [158]. If adsorption is on the high-area oxide itself or on metal particles supported on the oxide, the loss processes in the tunneling electrons increase, corresponding to the vibrational quanta of the adsorbed species, and both IR- and Raman-active modes of vibration can be observed in this case.

Several different approaches have been presented in the literature concerning theoretical treatments of the IETS intensities, starting from the first published by Scalapino and Marcus and based on the modification of the tunneling potential barrier by a simple molecular dipole potential.

IETS is a very sensitive technique for obtaining the vibrational spectra of monolayer or sub-monolayer coverages of molecular layers at the oxide interface region of metal–insulator–metal tunneling junctions, has good resolution and a wide spectral range, is sensitive to all surface vibrations, and can be used on oxide and oxide-supported metal systems. IETS can also give information on the orientation of the molecules toward the surface. However, there are marked disadvantages, (i) i.e. the necessity to use a counter-electrode, (ii) spectra must be recorded at low (usually liquid helium) temperatures, and (iii) single crystal metal surfaces cannot be used. Nevertheless, IETS can be useful in catalytic and adsorption investigations on model oxide and supported metal systems.

1.5 Inelastic neutron scattering spectroscopy

This method is based on analysis of the energy distribution among neutrons, which are inelastically scattered by the chemical species under investigation. From a poly-energetic source, the energy dispersion of the scattering beam is limited by Bragg reflection from a single crystal operating as a diffraction monochromator located before the sample. In the case of a pulsed neutron beam, analysis of the energies is obtained by measuring the times of arrival at the detector by the scattered neutrons [155, 160–163]. There are no selection rules for inelastic neutron scattering spectroscopy (INSS), so all vibrational transitions are active in principle. However, their intensities depend on the INS cross-section and amplitudes of all of the atoms involved in the corresponding vibrational mode. Such cross-sections are characteristic of each element and do not depend on their chemical environments. However, there is a particularly high sensitivity to vibrations involving the moving of hydrogen atoms; The hydrogen (H) nucleon has a high cross-section, while the deuterium (D) nucleon has a low one. The INS technique can be used to determine the orientations and positions of the adsorbed molecules, as well as the strength and location of the forces bonding a particular molecule to a surface [161].

1.6 Other vibrational spectroscopies

1.6.1 INFRARED ELLIPSOMETRIC SPECTROSCOPY

Reflectance ellipsometry is concerned with the measurement of the polarizing properties of an interface, i.e. with measurement of $\tan \psi$ and Δ (ψ and Δ denoting the angles) or of the complex function R_p/R_s (values of the reflection coefficients, corresponding to the incident and reflected (complex) amplitudes for the p and s electric vectors, respectively) for the ‘clean’ and covered surface. From the following equation, defining the ellipsometric reflectance absorbance as:

$$A_e = \log_{10}(|R_p/R_s|^2 / |R_p/R_s|^2) \quad (1.21)$$

it follows that:

$$A_e = A_p - A_s \quad (1.22)$$

This is the fundamental equation connecting ellipsometric reflection spectroscopy with photometric reflection spectroscopy. If the substrate is metallic, $A_e \approx A_p$, and so photometric and ellipsometric spectroscopies will yield the same absorption spectrum. Further details of the theory of this method can be found elsewhere [164, 165].

1.6.2 SURFACE ELECTROMAGNETIC WAVE SPECTROSCOPY

This technique has recently received considerable attention [166]. Surface electromagnetic waves (SEWs) are surface waves in the sense that the electric and magnetic fields decay exponentially as one moves away from the surface, either into the metal or into a vacuum (Figure 1.14).

SEW spectroscopy provides the possibility of researching the vibrational spectra of adsorbed molecules, the processes of surface reconstruction, corrosion processes, and determination of the optical constants for adsorbed layers and supported thin films, as well as for the metal surface

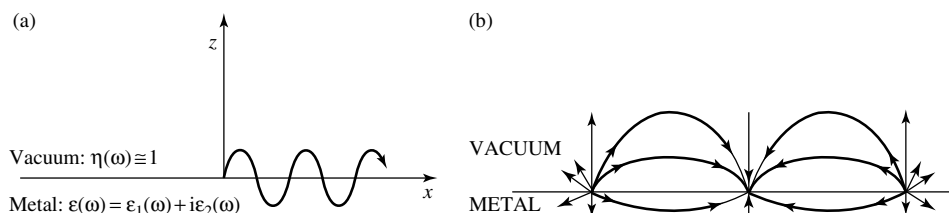


Figure 1.14. Schematic representations of (a) the coordinate systems for surface electromagnetic waves on a metal–vacuum interface, and (b) the electric field associated with a surface electromagnetic wave.

itself. The SEWS technique does not require ultra-high vacuum and can be carried out in the presence of reactant gases. It is a simpler method than ellipsometry for monolayer and sub-monolayer coverages. SEW spectroscopy has also been used to study oxide surfaces [167, 168].

1.7 *In situ* measurements

In studying the chemical transformations which take place during the interaction between a molecule and a solid surface it is very important to record the spectra under conditions (temperature, pressure, contact time, etc.) which are similar to those at which the process proceeds, in either steady-state or unsteady-state conditions in the case of catalytic reactions [21, 30, 129]. In parallel with the spectral registration, by using special cells it is possible to measure the catalytic

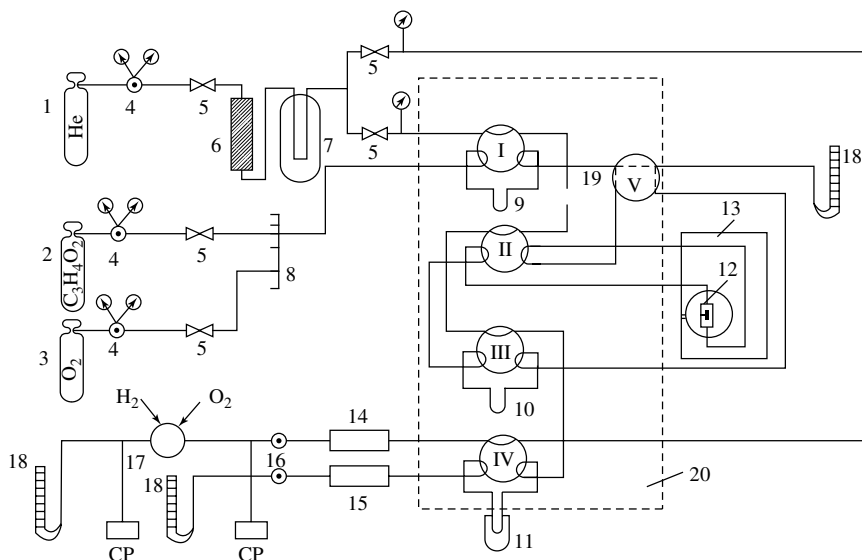


Figure 1.15. Schematic diagram of an experimental installation for studying the IR spectra of adsorbed molecules: 1, 2, 3, vessels with He, reaction mixture and O₂, respectively; 4, flow regulator; 5, stop valve; 6, 7, columns with molecular sieves to purify He from H₂O and O₂; 8, distribution 'comb' for gas mixtures; 9, dosing loop; 10, sampling loop to take samples for analysis from a flowing mixture; 11, freezing trap for reaction products; 12, cell-reactor; 13, cell compartment of IR spectrometer; 14, column with 'Porapak-Q'; 15, column with molecular sieves; 16, catharometers; 17, flame-ionization detector; 18, rheometers; 19, syringe sampler; 20, thermal case; I–IV, 6-port metal valves; V, 4-port valve; CP, control potentiometer.

activities of the samples. Several types of such apparatus have been described (see, for example, [169–171]). In catalytic measurements involving the simultaneous recording of infrared spectra, Davydov and coworkers [30, 129, 172], using a pulsed or flow catalytic cell-reactor combined with catalytic equipment (Figure 1.15), have determined the rates of transformation of a number of different surface species.

In principle, it is possible, by using infrared techniques, to study the kinetics of numerous different processes and transformations of surface complexes (so-called spectro-kinetic measurements). Unfortunately, the practical application of infrared spectroscopy to such studies was until recently very limited. This is because of a number of disadvantages of this approach, such as its certain method restrictions and the limited range of temperatures over which it is possible to take spectra. The ready, availability of FTIR techniques and of equipment for high-temperature IRS has now significantly increased the potential of this method for studying the kinetics of surface reactions (rates, rate constants and activation energies for separate stages).

Two different cases can be identified when the kinetics of surface reactions are being studied: (i) direct determination of the relationships between an absorbance for a characteristic band and the reaction times of complexes which are intermediates or products; (ii) indirect determination of the reaction rates on the basis of the interaction between the adsorbed molecule and surface center being reduced during the conversion of intermediates. In the second case, the adsorption rate should be much higher than that of the reaction rate. Such applications have been described in literature [172–175].

1.8 Quantitative measurements

The determination of the surface complexes concentrations is based on the use of the Beer–Lambert law for the separate bands. The extinction coefficient is determined in accordance with the Beer–Lambert law. For the adsorption of complexes, the following parameters are used: $\varepsilon = AS_{\text{pellet}}/C_s G$, where G is the sample weight(g), S_{pellet} is the sample area (cm²) and C_s is the concentration of the adsorbed probe ($\mu\text{mol g}^{-1}$). Alternatively, in integral form, $A = 10^{-3} A_0 C_s \rho$, where $A = \int \log(T_0/T) d\nu$, is the integrated absorption coefficient of the band observed (cm⁻¹), A_0 is the integral absorption coefficient of the band when the adsorbate concentration is equal to 1 $\mu\text{mol g}^{-1}$, and ρ is the amount of the catalyst per cm² of the light flux profile (in mg). In the latter case, potential mistakes in the determination of A_0 are reduced and there is no necessity to measure the geometrical thickness of the pellet.

Several factors influence the accuracy of such measurements: (i) the possibility of using the Lambert–Beer law for analyzing the infrared spectra of surface compounds; (ii) the influence of the changes in optical characteristics of the investigated systems during the interaction; (iii) the ranges over which absorptions change; (iv) conditions for the registration of kinetic curves. In the case when the Lambert–Beer law can be used, it is possible to obtain the relationships between the strength of a particular absorption band and both the time and pressure of the component in the gas phase. The relationship of the absorbance of the band of the surface compound to its concentration can be found by a comparison of infrared and adsorption (desorption) measurements. The values of the extinction coefficients of the most intense bands allow an estimation of the sensitivity of the method for particular surface compounds (for further details, see [20, 30]). By using the relationship between the change in concentrations of the surface compounds and the temperature it is possible to estimate the heat of adsorption [176].

The reliability of the spectral interpretations can be improved by a combination of the results obtained from molecular spectroscopy with those available from other physical techniques, in particular thermodesorption spectroscopy with analysis of the products (TDS), and ESR and NMR spectroscopies.

