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Catalysis Today 27 (1996) 323–352

CATALYSIS TODAY

The use of vibrational spectroscopies in studies of heterogeneous catalysis by metal oxides: an introduction

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Abstract

The fundamentals of the different IR spectroscopic techniques (transmission/absorption, total reflection, diffuse reflectance, emission, phothermal and surface vibrational sum frequency generation techniques) and of other vibrational spectroscopic techniques (Raman, EELS, IETS, INS and IAS) are very briefly outlined in view of their use in the field of the studies of oxide heterogeneous catalysts. Some less usual applications of IR and Raman techniques to oxide catalysis are also briefly reviewed.

Keywords: Vibrational spectroscopy; Metal oxides

1. Background and historical perspective

Any chemical species containing more than one atom, i.e., polyatomic molecules, molecular ions, molecular radicals and any crystal, can be described in terms of atomic positions, bond lengths and bond angles. However, it has been recognized long ago that actually any atom vibrates around its equilibrium position in any condition, giving rise to more or less complex vibrational modes. At absolute zero all polyatomic chemical species lye at the vibrational ground state. However, they can undergo vibrational excitation so they can occupy higher energy vibrational states. The energy difference between the nearest vibrational states lye in the medium and far infrared ranges, generally defined by the wavenumber limits 4000–400 cm^{-1} ($0.496 > E > 0.0496$ eV, medium IR) and 400–10 cm^{-1} ($0.0496 > E > 1.24\ 10^{-3}$ eV, far infrared, FIR).

The simplest way to cause vibrational excitation is to allow the chemical species to absorb an energy quantum from an electromagnetic radiation of appropriate energy so giving rise to a vibrational transition from the ground state to an excited vibrational state. Thus, the analysis of the quanta that are actually absorbed by a polyatomic chemical species and those that are not absorbed (so they can be transmitted) gives information on the vibrational structure of this species and, consequently, on its chemical and geometric structure. These are the fundamentals of the *transmission/absorption infrared spectroscopy*, developed in the last decades of the nineteenth century and in the very first years of our century (as historically reviewed in [1]) and has become one of the most widely used techniques for chemical analysis.

Successively, it has also been recognized that other infrared techniques (reflection, emission and photothermal techniques) can be applied and

SSDI 0920-5861(95)00160

that infrared spectroscopy only gives a partial information on the vibrational structure of any polyatomic species. In fact, selection rules apply to the IR light absorption phenomena so that only vibrational modes that are associated to changes in the molecular dipolar moment can be directly excited.

Another vibrational technique has been developed later, based on the so-called Raman effect, recognized by Raman in 1928 [2]. He showed that if a monochromatic high energy radiation (UV, visible or near IR) interacts with a chemical species the scattered light is no more monochromatic, but it can contain photons whose energy is produced by the sum or the subtraction of the original radiation energy with some vibrational transition energies of the chemical species. Interestingly, owing to the different selection rules for the Raman effect, the Raman-active modes do not correspond to IR-active modes in centrosymmetric chemical species and only partly correspond (generally) for non-centrosymmetric species. Thus, Raman spectroscopy is in most cases almost complementary with respect to IR spectroscopy.

It seems that the very first application of IR spectroscopy to the surfaces of oxide materials was reported in 1937 by Buswell et al. [3], concerning water adsorbed in montmorillonite. In the forties and fifties Terenin and its pupils at the Leningrad University showed that this technique can be applied widely to molecules adsorbed on solid materials, including metal oxides [4]. In fact most metal oxides only absorb radiation in the low-energy IR region (below 1000 cm^{-1}) while most gaseous or volatile molecules absorb strongly also in the higher energy IR region (4000–1000 cm^{-1}). However, adsorption on solids causes vibrational perturbation of the adsorbate (if adsorbed as such) or can definitely produce a chemical reaction and the spectroscopic detection and discussion of these phenomena gives information on the adsorption or interaction modes. Eventually, data are obtained both on the chemical structure of the metal oxide surface and on the perturbation mode of the adsorbate.

The use of infrared spectroscopy to catalysis and surface chemistry was later developed in the fifties by Eischens et al. at Texaco laboratories (Beacon, New York [5]) in USA and by Sheppard and Yates at the Cambridge University [6] in the UK. Since then, interest for IR spectroscopic techniques in the fields of the surface chemistry and catalysis grown progressively not only in the academia but in the industry as well, as demonstrated not only by the work of Eischens and Pliskin at Texaco [5], but also, among others, by the work of Peri and Hannan at Amoco first published in the early sixties [7] and, later, by several other industrial research groups. The infrared techniques underwent in the eighties a great improvement with the development of Fourier transform instruments, commercialized at the end of seventies.

The application of Raman spectroscopy to molecules adsorbed on metal oxides has been pioneered in the late sixties by Hendra and Loader [8] but did not rise very wide utilization until now. The use of this technique can result in a great expansion in the nineties by the commercialization of Fourier transform Raman instruments. A particular case is the application of Raman spectroscopy to molecules adsorbed on rough surfaces of some particular metals (Cu, Ag, etc.) due to the so-called SERS effect (surface enhanced Raman spectroscopy) recognized as a particular magnification effect on the intensity of Raman peaks in 1977 [9]. Early attempts to use this technique for the characterization of supported oxide catalysts were considered to be unsuccessful [10] but after the works of Brown et al. [11] and Knözinger and Jeziorowski [12] this technique became widely utilized for the characterization of this kind of catalysts, like shown in this issue by Wachs.

Meanwhile, other techniques have been developed to obtain information on the vibrational structure of chemical species. The electron energy loss spectroscopy (EELS) technique was first proposed by Probst and Piper in 1967 [13] but underwent a decisive development by the work of Froitzheim and Ibach in the seventies [14]. However, its application was at first limited to the investigation of metal single crystal surfaces. The application of this technique to adsorption on metal oxide single crystals started more recently [15] but is now under promising development.

The appearance of the inelastic electron tunnelling spectroscopy (IETS) technique also dates in the middle of sixties [16] but this technique was mainly developed in the seventies: it implies the observation of surface species adsorbed on oxide surfaces placed in between two metal electrodes (like for instance $Al/AlO_x/Pb$ junctions). So it is essentially devoted since its nascence to surface chemistry studies on metal oxides like alumina and magnesia.

Inelastic neutron scattering (INS) spectroscopy was applied first in the middle of seventies by several groups [17] to investigate the vibrational spectrum of hydrogen adsorbed on Ni, Pd and Pt bulk metals. At the end of the seventies, some papers concerning INS of hydrocarbons in zeolites appeared [18]. Its first application to hydrogen adsorbed on a metal oxide (ZnO) dates, to our knowledge, to 1984 [19].

The atom inelastic scattering spectroscopy technique has been also proposed as a surface vibrational technique in the early eighties [20] and is focusing increasing attention of surface chemists and physicists in very recent years.

Starting from the late fifties, vibrational techniques (with the predominance of the simplest one, infrared spectroscopy) became a common and very widely used tool in any academic and industrial laboratory involved in heterogeneous catalysis research. The development and use of the infrared techniques in the field of heterogeneous catalysis and (in particular) in the field of surface chemistry and catalysis over metal oxides produced a number of monographs devoted to the use of vibrational techniques [21–24,169] or specifically to IR spectroscopy [25–29], Raman spectroscopic methods [30–32], EELS [33–35] and IETS [36,37] in surface and interface chemistry. Similarly, review papers have been published in the last two decades on the use of IR spectroscopy [38–48], Raman spectroscopic methods [49–54], EELS [55] and INS [56–58] in surface and interface chemistry. A very recent book on spectroscopic methods in catalysis should also be noticed [59].

On the other hand, vibrational techniques are very widely used nowadays and further developments are expected in the near future. The authors of the present issue of Catalysis Today want to give their contribution to a first step of this further development with the presentation of some reviews focused at some particular non-exhaustive topics thought to be of wide interest in laboratories working in the field of heterogeneous catalysis and surface chemistry.

2. The vibrational spectra and their interpretation

The total degrees of freedom associated to a chemical species containing N atoms are $3N$. If this chemical species is a molecule in the gaseous state, 3 of these degrees of freedom are associated to its translations and other 3 to its rotations, so that, in the most general case, 6 modes are associated to 'external' modes and $3N-6$ degrees of freedom are associated to 'internal' vibrational modes. However, if the molecule is a linear one, only 2 degrees of freedom are associated to rotations. Thus, in this particular case the degrees of freedom associated to vibrations are $3N-5$.

If the group of atoms considered here is in the solid state it is not free to translate and rotate. The 6 (or 5) degrees of freedom associated to external modes give rise to lattice vibrations ('frustrated translations and rotations') and acoustic modes. When a non-molecular solid is considered (like an ionic or a covalent solid) to count the fundamental vibrational modes the N atoms present in the smallest (primitive) Bravais cell must be taken into account. They give rise to $3N$ total degrees of freedom, 3 of which give rise to translational modes of the cell as a whole, these are the acoustic modes. Thus, the vibrational degrees of freedom are, in this case, $3N-3$.

The analysis of the symmetry of the chemical species under study (i.e., the point group of a molecule and the space and factor group of a crystal [60]), according to the site symmetry of every atom, allows to determine the irreducible representation of the total modes and, after the subtraction of the translational and rotational modes (the acoustic modes of the crystals), the irreducible representation of the vibrational (or 'optical') modes can be obtained. This means that the number of vibrational modes belonging to the symmetry species associated to the molecular or crystal symmetry can be counted, taking into account that they can be non-degenerate, doubly or triply degenerate (in the most common case). Consequently, the number of active modes can be counted, according to the symmetry selection rules of the different techniques. If the chemical species under study is relatively simple, it can not be difficult to identify the movements associated to every vibrational mode of a given symmetry. In any case, lattice or molecular dynamics calculation can give rise to this information.

However, it is well-known that a 'group approximation' can be most frequently used so that every vibrational mode (that is in principle due to motions of the chemical species as a whole) can be attributed to the movements of small groups of atoms. Thus, it is possible to 'dissect' the chemical species under study in 'pieces' and to consider separately the vibrations of groups of a few atoms (like the functional groups in organic compounds). This makes the interpretation of the vibrational spectra of polyatomic molecules by far easier.

In the case of solids spectra, the polar phonons (those that are IR active, see below (Section 3.1)) split into two components, the transverse mode (TO) and the longitudinal mode (LO). This is because the electric field associated to the transverse wave is zero while that associated to the longitudinal wave is not zero so that the coupling of these modes with the associated electric fields gives rise to $\nu_{LO} > \nu_{TO}$. This makes more complex the interpretation of the IR spectra of solid materials like metal oxides.

A treatment analogous to that outlined above for forecasting and interpreting the IR spectra of molecules and of solids can be done for surface species or, better, for the surface complexes produced by adsorption. A rigorous treatment has been reported by Sheppard and coworkers [61,62] with application to adsorbed species on metal single crystal surfaces, whose surface atom array can be determined rather precisely. For dispersed surfaces, like oxide powders, the surface structure is frequently assumed on the basis of the structure of some crystal planes expected to constitute the predominantly exposed faces. However, recent high-resolution transmission electron microscopic studies showed that the exposed faces on microcrystal powders, e.g., of chromia, do not correspond to those assumed to be preferential before [63]. As it will be shown by Zecchina in this issue, the observation of the surface species upon progressive sintering of the powder allows to discriminate between adsorption complexes located in extended faces and in surface defects like edges and corners. The uncertainty in the real surface structures of oxide powders, evidenced in this issue in the review on catalytic aluminas by Morterra, makes difficult to elaborate definite structural models for surface complexes on real high-area catalysts.

3. The vibrational spectroscopic techniques and their applicability to the surface chemistry of metal oxide catalysts

The vibrational spectrum (i.e., the collection of the energies associated to the vibrational transitions) of every polyatomic chemical species can be primarily obtained 'directly' by measuring the 'quality' of the radiations that are absorbed or emitted upon these transitions. This is the so-called IR spectroscopy, that can be performed with different experimental setups. However, due to the existence of selection rules, the vibrational spectrum obtained using IR spectroscopies is generally only a partial one, because several vibrational modes are infrared inactive.

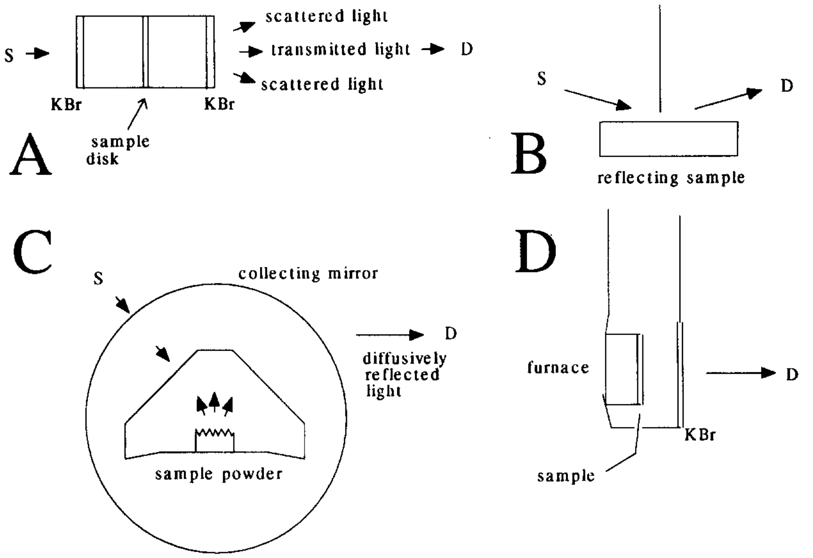


Fig. 1. Scheme for IR spectroscopies: **A**: transmission/absorption IR; **B**: total reflection and IRRAS; **C**: diffuse reflectance IR; **D**: emission IR. S: source; D: detector.

Another way to obtain part or all the vibrational spectrum of a chemical species is to look at the inelastic scattering of beams other than IR radiation. In other words, when such beams are scattered by a polyatomic species part of them lose (or gain) energy due to the interaction with the vibrational states of the matter. The vibrational spectrum is obtained by measuring the difference between the energies of the incident beam and of its small fraction that is inelastically scattered. If the incident particles are relatively high energy photons (UV, visible or near infrared photons) we are dealing with Raman spectroscopy. Both IR and Raman spectroscopy are nowadays largely used in the field of surface chemistry of oxidic catalytic materials. Thus, in the next chapters of this issue the use and the utility of these techniques will be deeply demonstrated.

Alternatively, the inelastic scattering of particles other than photons can also be used to obtain the vibrational spectrum: they can be electrons, and the corresponding techniques are EELS or IETS, following two different experimental setups. Finally, the incident particles can be neutrons and this gives rise to the INS spectroscopy, or atoms and this gives rise to atom scattering spectroscopy. In the next sections of this introduction we will briefly review the use of these techniques in the field of the surface chemistry of metal oxides.

3.1. Infrared spectroscopic techniques

As already remarked, a variety of IR techniques have been and can be used in order to have information on the surface chemistry of different solids. In Fig. 1 the setups for the most common IR techniques are schematized. However, some of them have particular application on metals or semiconductor surfaces or have only limited application. In the field of characterization of metal oxide catalysts two techniques largely predominate, i.e., the transmission/absorption and the diffuse reflection techniques. In any case, it seems interesting to very briefly summarize also the characteristics of other IR techniques and the reasons of their more limited application.

When an incident electromagnetic radiation interacts with a sample, the light may essentially be absorbed, reflected and transmitted. From the conservation of energy it follows

$$I_0 = I_R + I_T + I_A \tag{1}$$

where I_0, I_R, I_T and I_A are the intensities of the incident, reflected, transmitted and absorbed radiation, respectively. By dividing Eq. (1) per I_0 we obtain

$$R+T+A=1 \tag{2}$$

where $R=I_R/I_0$, $T=I_T/I_0$ and $A=I_A/I_0$ are the apparent reflectivity, transmittivity and absorptivity (absorbance), respectively. The 'true' reflectance and transmittance are defined when $T=0$ and $R=0$, respectively.

In any IR technique, two selection rules are valid. They can be schematically simplified as follows:

$$\Delta v=\pm 1 \tag{3}$$

$$\left(\frac{\partial \mu}{\partial Q}\right)_0 \neq 0 \tag{4}$$

Eq. (3), where v is the vibrational quantum number, means that only transitions between nearest vibrational states can directly occur in the case of the harmonic oscillator. This condition, however, is relaxed in the case of anharmonic oscillators, so that not only fundamentals but also overtones and combination modes can be sometimes observed, although weak. Eq. (4) indicates that only vibrational modes that are associated to a change in the dipole moment μ of the molecule upon the atomic displacement (Q is the normal coordinate) different from zero can be directly excited. According to the Lambert–Beer law:

$$A=-\log_{10} I_T/I_0=\varepsilon c l \tag{5}$$

the absorbance A linearly depends on the molar concentration of the absorbing species c, through the molar absorption coefficient ε and the sample pathlength l. This relation (valid in non-scattering media) is the base for quantitative analysis performed through IR spectroscopies.

On the other hand, the absorbance at a particular wavelength also depends from the population of the corresponding vibrational states. According to the Boltzman's law:

$$N_i/N_0=g_i/g_0 e^{-\Delta E/kT} \tag{6}$$

where N_i's are the state populations, g_i's are the state multiplicities, ΔE is the energy difference between the states and k is the Boltzmann's constant. ΔE's for fundamental vibrational transitions fall in the IR region so that the population of the first excited states is very small at room temperature (rt) and lower than the population of the ground state even at 1000 K. This means that only transitions originating from the ground state can be ordinarily excited at rt or relatively low temperature.

Since the commercialization of Fourier transform IR spectrometers, instruments allowing short recording times (one to few min at most) and high resolution (0.5–4 cm^{-1}), adjustable to obtain the desired signal-to-noise ratio in dependence of the sample properties, are easily available at moderate costs. These performances fulfill the requirements for studies of surface species over oxide catalysts in relation to the intrinsic linewidth of the adsorbates modes (few cm^{-1}) and the optical properties of the samples (see below for the different experimental setups).

3.1.1. Transmission/absorption infrared spectroscopy

This technique has been originally applied by the pioneers of the IR technique in catalysis and is still today perhaps the most widely used. It implies the preparation of the catalyst sample in the form of a self-supporting disk (most frequently obtained by pressing) of the pure catalyst powder (with no binding materials in order to avoid contamination during heat treatments). Moreover, it is necessary that this sample is at least in some ranges of the IR spectrum nonopaque to the radiation. This excludes the application of this technique with excessively conductor materials, like bulk metals and metallic-like oxides (like for example Fe_3O_4, RuO_2, $LaNiO_3$, etc.). On the other hand, the use of insulator metal oxides with excessively high particle size (greater than a micron) is also excluded because in this case the IR radiation, although not absorbed, can be almost totally scattered by the sample. When a radiation interacts with a layer constituted of N particles per unit volume, its intensity decreases exponentially with the sample thickness x following the law:

$$I_T = I_0 e^{-\varphi x} = I_0 e^{-N\sigma x} \tag{7}$$

so that an apparent absorbance A' can be defined for an absorbing and scattering medium:

$$A' = -\log_{10} I_T/I_0 = 0.43\, N\sigma x = 0.43\, N(\varepsilon' + s)x$$

$$= A + 0.43\, Nsx = A + S' \tag{8}$$

where φ is the linear attenuation coefficient and σ is the linear attenuation coefficient of one particle. σ contains a component due to absorption, ε', and a component due to scattering, s. So that, the apparent absorbance is composed by the true absorbance A added to the component due to the light scattering S'. This simplified approach is similar to that by Henry [64] who proposed for the component dependent from scattering the following expression:

$$S' = kxd(n-1)^2/\lambda^2 \tag{9}$$

where k is a constant independent from λ but dependent on the particle arrangement, d is the particle diameter and n is the refraction index of the material. On the other hand, according to the Rayleigh theory, S' would depend on the third power of the particle diameter (so linearly on the particle volume) and on the fourth power of the radiation frequency ν. The effect of scattering on the IR transmission spectra of powder samples has been studied by Lejeune and Duyckaerts [65] who showed that if the particle diameter is sufficiently small (definitely smaller than the IR wavelength), the scattering of the IR radiation is very small. Thus, finally, the apparent absorbance of a pressed disk of a powder depends on its own absorptivity, on the disk thickness and density, on the particle size and on the wavelength.

In any case, the disk of a material that is not excessively absorbing and scattering should also be sufficiently thin to limit scattering to a fraction of incident photons as small as possible. This is also sometimes a problem, because it is not infrequent to find powders very refractory to pressing. Moreover, to have high signal-to-noise ratios for absorption bands associated to surface species, high-surface area samples are useful. On the other hand, samples with no more than 1 m^2/g can also be studied, if sufficiently transmitting, with FT-IR spectrometers, in case by increasing the scanning time to some minutes. On the other hand, many catalytic materials do not give any problem of sample preparation (like most pure insulating or weakly semiconducting oxides in the form of highly dispersed powders, like aluminas, silicas, magnesias, titanias, zirconias, chromias, iron oxides, vanadium oxide, etc., as well as many mixed oxides like spinels, perovskites, ilmenites, etc.).

In Fig. 2 the IR spectra of an oxide catalytic material are shown, in the forms of the pure powder pressed disk and of a KBr pressed disk. As usual, the pure powder disk is opaque in the region where the skeletal absorptions of the oxide occur, most frequently in the region below 1200–1000 cm^{-1} down to near 400–200 cm^{-1}. On the other hand, above the skeletal region, the ‘apparent absorption’ depends mainly on scattering, that increases with increasing frequency. Thus, there is a ‘transmission window’, more or less large, available to detect the absorptions of the surface species. It is not infrequent that for a given sample the higher wavenumber IR region is not available too, because there the light scattering approaches to be total.

To have an idea of the complex effect of particle morphology on the usefulness of catalytic materials for transmission/absorption IR spectroscopy, the experimental spectra of the pressed disks of two different TiO_2 commercial samples are compared in Fig. 3. They are the most transmitting we were able to prepare with these materials. Sample (a) is actually a mixture of nearly 20% rutile and 80% anatase with crystal size of 160 A (230 A for the rutile particles) as measured from XRD line broadening, nearly 300 A estimated from TEM and from the experimental surface area (50 m^2/g). The scattering is very small and the scattering baseline is apparently linear, like also for the Ba-β-Al_2O_3 sample of Fig. 1. In the case of sample (b) (anatase with traces of brookite) the

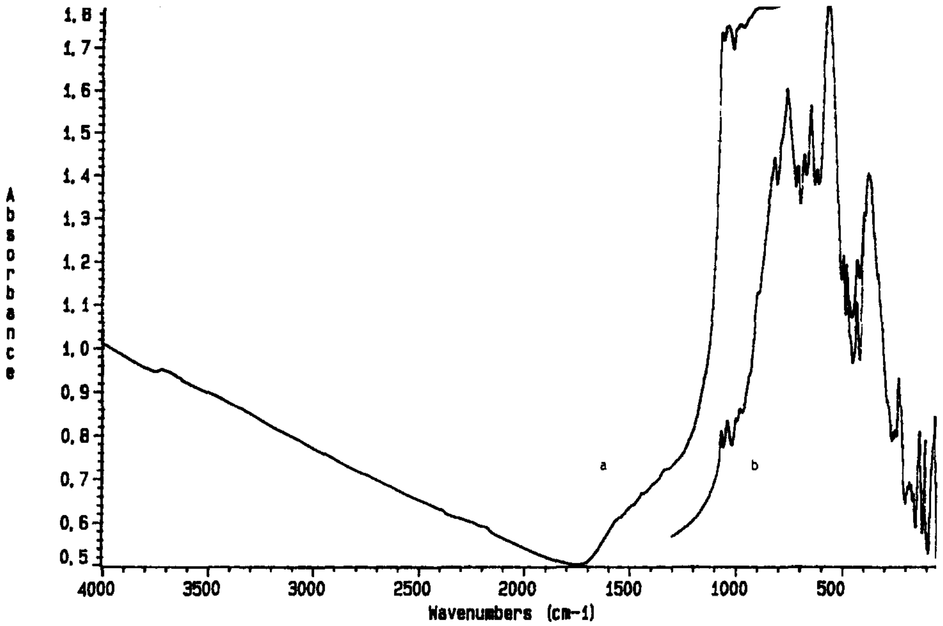


Fig. 2. FT-IR transmission/absorption spectra of a Ba-β-alumina sample: (a) pressed disk of the pure powder, outgassed at 773 K; (b) pressed disk in KBr (absorbance scale of sample (a)).

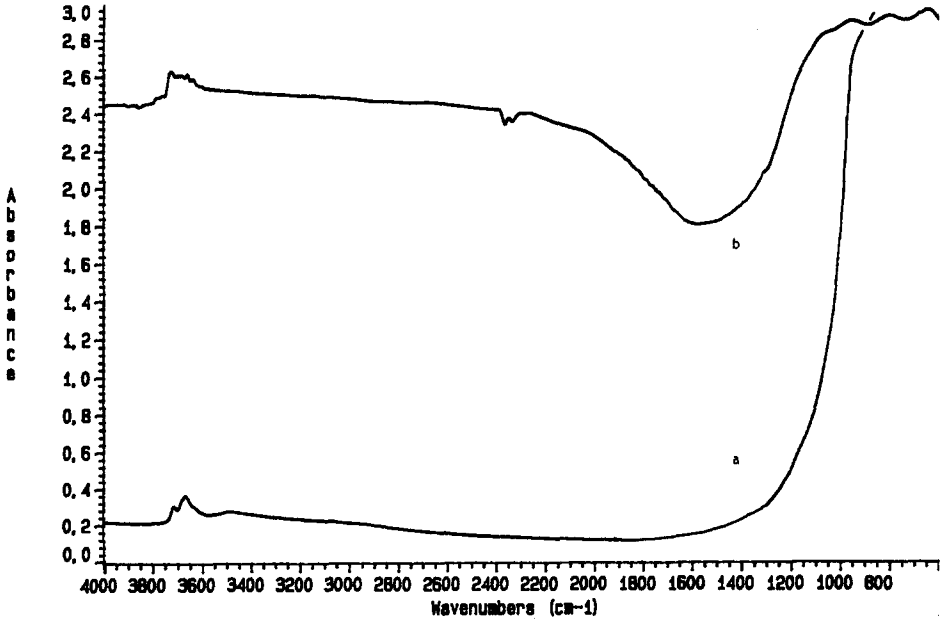


Fig. 3. FT-IR transmission/absorption spectra of two different powder samples of TiO_2 (pure powder pressed disks) both outgassed at 673 K: (a) 80% anatase, 20% rutile, 50 m^2/g, non-porous; (b) anatase with traces of brookite, 115 m^2/g, microporous.

scattering is much higher and the scattering baseline is clearly not linear in the range 4000–1500 cm^{-1} but it fitted very well with a fourth power curve in ν (so that scattering depends from λ^{-4}, as forecasted by Lord Rayleigh's theory). This is in spite the crystal size of this material, measured by XRD line broadening, is less than 100 Å. TEM and surface area measurements (120 m^2/g) give rise to particle size values near 100 Å too, but TEM micrographs show that the particles are very inhomogeneous. It is evident that, in spite of the high surface area and small particle size of the this

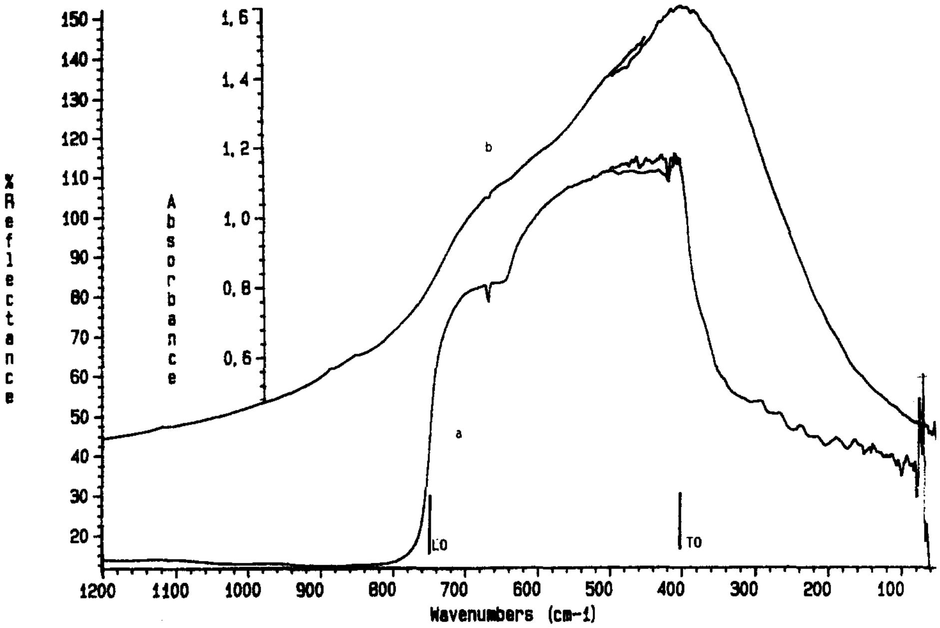


Fig. 4. FT-IR reflectance spectrum of a MgO monocrystal (angle of incidence = 26.5°, face [001]) (a) and FT-IR transmission/absorption spectrum of an high-area MgO powder (KBr and polyethylene disks) (b).

sample, it is very difficult to prepare by pressing an highly transparent disk, mainly because of the refractory behavior of this powder to the compression. In any case the above data confirm the dependency of the scattering from the fourth power of the frequency, that approaches to linear when scattering is low because of the very sharp thickness of the pressed disk samples.

Thus, the sample preparation is the more stringent limit of this IR technique. This difficulty can occur in studies of real catalysts. In some cases (when the use of real catalyst powders for transmission studies is actually excluded, and it rarely occurs) these studies can be made using 'model catalysts', i.e., powders with composition similar to real catalysts but with higher surface areas, smaller particle sizes and smaller amounts of conducting components in order to have better performances relatively to the IR analysis. Sometimes this is obtained by supporting the active catalyst phases over high-area highly transmittant powders, hoping that they are inactive in the experiment conditions (and this generally is not true).

Another important limit of this technique concerns the opacity of the pressed disks used for adsorption experiments in their skeletal region. This is because these samples are 'bulk' samples and because skeletal absorption bands are very broad in part due to the splitting of any IR-active (polar) crystal vibrational mode into the longitudinal mode (LO) and the transverse mode (TO). This is shown in Fig. 4 and briefly discussed in the next section for MgO and is also shown for TiO_2-anatase in Fig. 9. In the case of highly divided powder samples this splitting results essentially in the broadening of the skeletal bands as well as in an apparent increased complexity of the spectrum. So the IR skeletal absorptions are so intense and continuous in the case of pressed disks of pure powders to cut any transmission in the skeletal region (Fig. 2 and Fig. 3, below 1000 cm^{-1}). Thus, generally, the available spectral region is from 4000 cm^{-1} (the usual high-frequency limit of commercial grating and FT-IR spectrometers) to the so-called cut-off limit that depends on the particular material under study. As for example, for silica and silica-containing samples (including zeolites) this limit falls near 1200 cm^{-1}, for aluminas and titanias it falls near 1000 cm^{-1} while for heavy ion containing metal oxides it can fall low as 600 cm^{-1}.

Above the cut-off limit, however, overtone or combination bands of skeletal vibrations can also sometimes occur (see region 1700–1200 cm^{-1} in Fig. 2) but, although frequently intense in the pressed disk spectra of covalent oxides, they are generally not so intense to obscure the spectral region. It is sometimes also possible to work at lower frequencies (i.e., below the skeletal absorptions) or in some windows in the skeletal region (like in the case of silica). At very low frequencies (like in the far IR) the investigation needs the use of cells and of spectrometer's optical elements (beam splitter) built up with appropriate materials (like pure silicon, polyethylene or Mylar) transparent in this region, instead of the usual alkali-halide materials used for working in the 4000–400 cm^{-1} range.

Finally, with the transmission/absorption technique applied to high surface area oxides it is possible to detect absorptions related to surface species covering very small fractions of the surface (1 % and far less) but this limit increases by decreasing the surface area of the powder. The role of sites placed on surface defects in the spectra of adsorbed species on metal oxides will be shown by Zecchina later on in this issue.

3.1.2. Infrared reflection spectroscopic techniques (IRAS, ATR, CIR, SEWS)

According to the laws of optics the light can not only be transmitted, absorbed or scattered but it can also be reflected. When an incident radiation interacts (from the vacuum) with a flat surface, the 'reflectance' of the parallel and perpendicular polarized light (with respect to the incidence plane), $R_{\parallel}$ and $R_{\perp}$, are given by the relations:

$$R_{\parallel}=\left[\frac{\varepsilon\cos\theta-\sqrt{\varepsilon-\sin^2\theta}}{\varepsilon\cos\theta+\sqrt{\varepsilon-\sin^2\theta}}\right]^2 \tag{10}$$

$$R_{\perp}=\left[\frac{\cos\theta-\sqrt{\varepsilon-\sin^2\theta}}{\cos\theta+\sqrt{\varepsilon+\sin^2\theta}}\right]^2 \tag{11}$$

where ε is the complex dielectric constant of the material (supposed to be isotropic) and θ is the incidence angle. From these relations it results that the reflected light is essentially polarized perpendicular (in fact $R_{\perp}$ is large while $R_{\parallel}$ has a minimum for $0<\theta<90$). When $\theta=0$, converting $\varepsilon=(n-ik)^2$, we obtain:

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2} \tag{12}$$

where n and k are the real and imaginary parts of the absolute index of refraction. For conducting materials, like metals, the refraction index is totally imaginary, that means that $n=0$. So that $R=1$ at any frequency, so the radiation is totally reflected. This is a case of 'total' or 'specular' reflection.

For insulating or weakly semiconducting materials, like most metal oxides, $k=0$ and n is nearly constant (i.e., the index of refraction is real) in the entire IR spectrum except near the absorption frequencies, i.e., for $\nu>\nu_{\mathrm{LO}}$ and $\nu<\nu_{\mathrm{TO}}$. This means that out of the skeletal region, metal oxide surfaces only weakly reflect the radiation, being R the smaller the greater is n. However, for $\nu_{\mathrm{LO}}>\nu>\nu_{\mathrm{TO}}$, the index of refraction is imaginary and $k>0$ goes through a maximum. This means that near the skeletal absorption region, R again becomes $\cong 1$, i.e., the skeletal vibrations of metal oxides correspond not only to absorbed radiation in transmission experiments but also to reflected radiations in the reflection experiments (reststrahlen effect). Thus, the specular reflectance for insulating materials like most metal oxides both in the form of monocrystals [66] and in the form of sintered pellets [67] is frequently the basis for the best determination of the skeletal spectrum.

In Fig. 4 the reflection spectrum of a MgO monocrystal is reported and is compared with the transmission/absorption spectrum of a MgO powder. MgO (periclase) has the rock-salt structure (space group $\mathrm{Fm3m}\equiv\mathrm{O}_{\mathrm{h}}^{5}$, with $Z=4$ and with one formula unit only in the smallest Bravais cell). The six degrees of freedom associated to the two atoms in the primitive cell give rise to a triply degenerate acoustical mode and to a triply degenerate optical mode. In fact, the irreducible representation for the optical modes is:

$$\Gamma_{\mathrm{opt}} = F_{1u}(\mathrm{IR}) \tag{13}$$

Thus, the rock-salt-type compounds like MgO are Raman-silent (as the fundamentals are concerned) and only show one IR-active fundamental mode. The transverse optical mode (TO), quoted for MgO at 401 cm^{-1} (see Fig. 4a), corresponds to the lower frequency limit of the reflectance band while the longitudinal mode (LO) corresponds to the higher-energy limit of the reflectance and is quoted at 718 cm^{-1} for MgO (see Fig. 4a). For $\nu_{\mathrm{LO}} > \nu > \nu_{\mathrm{TO}}$ the reflectance is strong and almost constant, while out of these limits the reflectance is zero. The transmission/absorption IR spectrum of the MgO powder shows the maximum slightly above ν_{TO} (407 cm^{-1} in our spectrum of a polyethylene disk) and a shoulder near ν_{LO}. Other components arise from particles with different morphologies [68] although it has been shown that the microcrystal powder spectrum of MgO is also affected by surface relaxation [69]. In any case, it is evident that for insulating materials like MgO the reflection is limited to the skeletal region and that the reflected light cannot be easily utilized to investigate adsorbed species.

The total reflection of an IR incident light at any wavelength from a surface can occur in two cases: (i) if the beam arises from a transmitting medium and is incident on the surface of a conducting material; (ii) the beam arises and is incident on transmitting media but the medium from which the beam arises has higher refraction index than that where the beam is incident and the incidence angle bypasses the limit for refraction.

In the first case, it has been recognized that if molecules are adsorbed over the surface of a metal, only part of the grazing incident radiation is reflected, part being absorbed strongly by the adsorbed species. This absorption is greatly increased if the incident radiation is polarized parallel to the metal surface. This is the so-called infrared reflection absorption spectroscopy (IRRAS) that, mainly after the work of Greenler [70] and Pritchard [71] is applied widely to surface studies on metal surfaces. In this conditions, an additional selection rule apply:

$$\left(\frac{\partial \mu_{\perp}}{\partial Q}\right)_0 \neq 0 \tag{14}$$

that means that only the adsorbate vibrations associated to a change in the dipole moment perpendicular to the crystal surface are detectable. However, as already said, this technique cannot be applied to the adsorption on metal oxide surfaces because they are generally insulating or semiconducting. On the other hand, the total reflection technique can be applied to detect layers over metal surfaces (i.e., the skeletal bands of oxide layers) and this is a widely applied technique in the corrosion and electrochemical research [72], colloid chemistry [73] and coating technology [74].

The second case refers to the ''internal reflection spectroscopy'' that is utilized in the so-called attenuated multiple total internal reflection technique (ATR) [75] where an absorbing layer is deposed on one or two external surfaces of a prism. The light penetrates the prism from a free surface and is multiply reflected by the other faces. During the reflection part of the light penetrates the external layer and is absorbed by it. Thus, in the case of the internal reflection techniques the reflectance is given by the following relation:

$$R = 1 - A = 1 - \varepsilon c d \tag{15}$$

where d is the thickness of the layer penetrated by the radiation, c the molar concentration of the absorbing species in that layer and ε is the molar absorption coefficient of that species. This technique found application in the case of several bulk solids (like polymers [76]) and electronic devices, like those constituted by silica layers on silicon [77,78]. This technique can also be applied to metal layers at the interface with a solution and in this case the signal can be surface enhanced [79]. This technique is of wide interest in the fields of electrochemistry [80] and colloid chemistry [29]. An interesting variation of this technique is the so-called cylindrical internal reflection technique (CIR) invented by Wilks [81] and developed by other authors [82,83]. In this case an hydrogel slurry can be analyzed using cylindrical crystals immersed in it where an IR radiation is transmitted and multiply reflected at the internal surface. This technique could be successfully applied at heterogeneous catalytic systems at the water-solid interface or in stages of catalyst preparation (e.g., zeolite syntheses).

Another interesting variant of total reflection technique is the so-called surface electromagnetic wave spectroscopy (SEWS) that consists in the generation of a surface plasmon on a substrate by the frustrated total internal reflection in a prism located few microns from the surface. This plasmon is decoupled by a second prism. Some interesting data have been reported recently with this technique concerning surface modes on alumina [84].

3.1.3. *Diffuse reflectance infrared (DRIFT)*

In recent years, the use of IR spectroscopy in the diffuse reflectance mode is grown strongly, also because of the commercialization of appropriate attachments and cells. This technique is particularly attractive because it does not need particular efforts in the sample preparation (the powder is simply deposed in a sample holder). Moreover, this technique, in contrast to the above transmission technique, takes advantage of light scattering so being very useful for samples that, in spite of an high surface area and a substantial non-conducting character, scatter so much IR light because of a too high particle size. This can occur with very porous materials.

This technique implies the collection, with appropriate collecting mirrors (integration sphere), of the radiation scattered by the sample. Obviously, most photons are essentially simply scattered while those corresponding to the energies of vibrational transitions are more or less absorbed. The interpretation of the diffuse reflectance spectra is based on the phenomenological theory of Kubelka and Munk [85–87] who defined the so-called Kubelka–Munk (K–M) function as follows:

$$f(R_\infty) = (1 - R_\infty)^2 / 2R_\infty = k/s \qquad (16)$$

where R_∞ is the reflectance of an 'infinitely thick' layer and may in practice be substituted by $R_\infty - R'_\infty$ (i.e., by the reflectance spectrum from which the reflectance of a reference transparent material like KBr has been subtracted). The K–M function depends linearly from the absorption coefficient k (that can be stated as $k = 2{,}303\varepsilon c$, where ε is the molar absorption coefficient and c is the molar concentration) and, inversely, from the scattering factor s. Obviously, the greater the absorption coefficient and the smaller the scattering, the higher the K–M function.

More realistic and complex theories have been developed later [88–90] according to the quite complex nature of the phenomena involved in the diffuse reflectance of light. Experimental studies [91–93] showed that this technique, that takes advantage from the light scattering, is positively affected by the factors that negatively affect the transmission techniques (as discussed above). These factors are the particle size, granulometric distribution and index of refraction and have an important role when particle size is near the wavelength of the IR radiation. The DRIFT spectra of adsorbed species have also been the object of theoretical investigations [94].

One important problem in diffuse reflectance measurement is to be able to cancel the specular reflectance by the sample, that generates 'negative' bands in the DRIFT spectrum, so causing apparent shifts in the true absorption bands. This is obtained by using appropriate cell designs in commercial DRIFT attachments [95].

The advantages of diffuse reflectance technique over the transmission/absorption technique in the field of the surface chemistry of oxides are the following:

(i) easier sampling; (ii) applicability to powders which scatter too much for the transmission/absorption technique, supposed the surface area is sufficiently high to detect surface vibrations with a sufficiently high signal-to-noise ratio; (iii) slightly lower sensitivity to bulk conduction phenomena because of a higher surface-to-bulk sensitivity ratio. In Fig. 5 the DRIFT spectrum of a commercial catalyst (a ZnO-Cr_2O_3 high-temper-

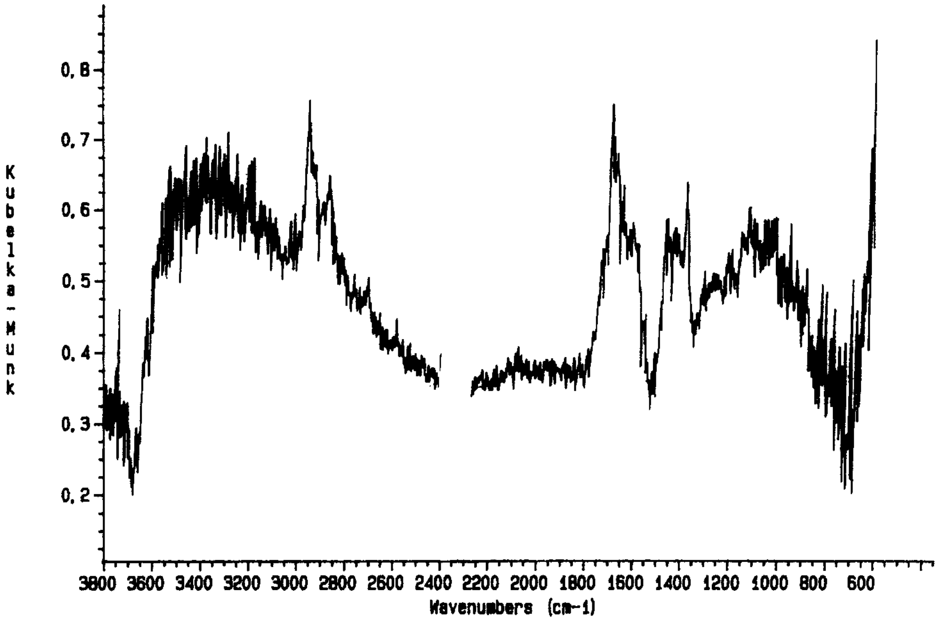


Fig. 5. Diffuse reflectance FT-IR spectrum of a commercial $ZnO–Cr_2O_3$ catalyst after adsorption of $n\text{-}C_3H_7CHO$ (see bands in the C–H and C=O stretching regions)

ature methanol synthesis catalyst) upon adsorption experiment is shown. We were unable to prepare a transmitting disk available for transmission/absorption IR study with this catalytic material. In effect, for general purposes (adsorption studies on relatively small-crystal-size powders) the only advantage of the DR technique is the first one, in the opinion of this author, with the disadvantages of: (i) less easy optical setting up; (ii) needing to work in flow rather than in vacuum (mainly because the sample is not pressed and powders fly in vacuum and because of a more difficult evacuation of the cell due to their design and size) with a consequent frequently more difficult sample activation.

The spectra of adsorbed and surface species obtained by using the transmission and the diffuse reflectance techniques are very similar in quality, as resolution, signal-to-noise ratio and sensitivity, as demonstrated among others, in Ref. [96], where the same catalytic materials have been investigated with the two different techniques in different laboratories. In Fig. 6 the spectra of the probe molecule pyridine adsorbed on the same catalytic materials, as recorded in two different laboratories with the transmission/absorption and with the diffuse reflectance techniques, respectively, are compared. They are in effect closely comparable in quality. For the use of the two techniques for mechanistic studies, see our next chapter in this issue for a discussion.

3.1.4. Infrared emission spectroscopy (IRES)

According to the Kirchoff's law,

$$E = I_{em}/I_b = A \tag{17}$$

the emissivity E (i.e., the ratio of the light emitted by the sample I_{em} with respect to that emitted by a black-body at the same temperature, I_b) is equal to the absorptivity or absorbance A. This value is proportional to the fourth power of the temperature difference between the emitting sample and the detector (Stefan's law). This implies that emissivity is sufficiently strong at relatively high temperatures to have a good signal-to-noise (s/n) ratio in a large part of the IR spectrum. In fact, the black body emission at $T < 1000$ K shows its maximum in the medium IR region. According to Koenig [76] the emission spectra of polymers can be taken above 70°C with sufficiently good s/n ratios in the range 1800–450 cm^{-1} (out of this range the s/n ratio is very high). As pointed out

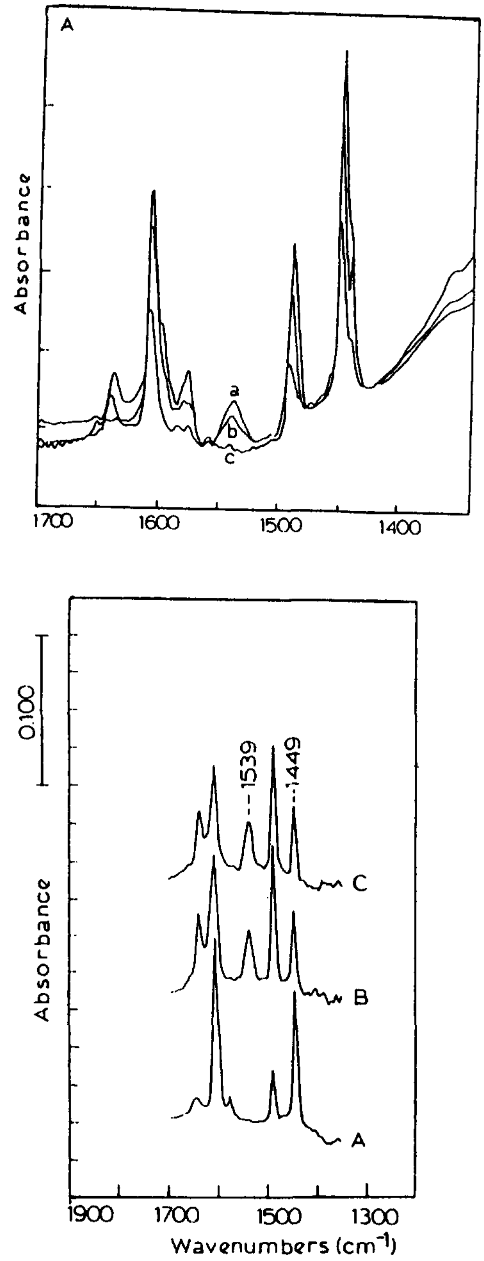


Fig. 6. Comparison of the spectra of pyridine adsorbed on TiO_2 (a and A), 1% V_2O_5–TiO_2 (b and B) and 8% V_2O_5–TiO_2 (c and C) catalysts obtained by two different laboratories using transmission/absorption FT-IR (above) and diffuse reflectance FT-IR (below) Reprinted from ref. [93].

by Griffiths et al. [97] temperatures well above 500°C are needed to have sufficiently good *s*/*n* ratio in the CH stretching region near 3000 cm^{-1}.

A number of problems are related to the use of emission IR spectroscopy. One of them arises from the existence of temperature gradients that can cause self-absorption of the emitted radiation by the colder parts of the sample itself. Moreover, perturbations can be created by reflections and emission by the cell elements. These problems, however, can be in part overcome so that IRE spectra can be successfully recorded and are largely used, e.g., in the field of polymer chemistry [76]. The use of IRES in the field of surface chemistry and catalysis is less extensive, but offers very interesting examples, like reviewed recently by Sullivan et al. [98]. These authors reported several examples of emission spectra of oxide catalysts and of adsorbates on supported metals and cite in their review at least eleven papers concerning metal oxide surfaces. However, in several cases the IRE technique has been used to show the spectra of the oxide itself and of its reduction or of its formation by metal oxidation. Less frequently, spectra of the adsorbed species on metal oxides have been reported with this technique, like for toluene on different oxides [99], carbonates on vanadia [100], methanol on molybdena [101] and the $CO+NH_3$ reaction on magnesia [102].

According to Sullivan et al. [98] the IRES technique should be competitive with the other more popular techniques for IR surface analysis, like the transmission and the diffuse reflectance technique. Some of the advantages of this technique are the very easy sample preparation, their applicability at temperatures near to those of catalytic reactions (150–400°C), the possibility to detect the bands of the adsorbates in the skeletal region of the sample and simultaneously to the detection of them (so allowing the control on the state of the catalyst).

3.1.5. Photoacustic and photothermal beam deflection infrared spectroscopies (PAS and PBDS)

When an IR beam is incident on a solid surface it can be absorbed in part and this leads to its conversion into heat. If the beam is modulated (as in any interferometers like those of FT-IR instruments) and the solid is in contact with a gas (air, He, Ar, etc.) its conversion to heat gives rise to

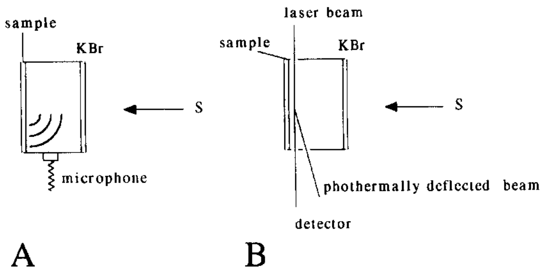


Fig. 7. Scheme for PA (A) and PBD (B) spectroscopies. S: source.

an acoustic signal. In fact, the periodic temperature rise so obtained causes a periodic modulation of the gas pressure in the cell that can be detected by a sensitive microphone. This acoustic signal will be the more intense the stronger is the absorption at a particular wavelength. It is interesting to remark that reflected or scattered light do not cause the photoacustic signal. However, absorbed light by the gases do it. The photoacustic effect, discovered as early as in 1880 by Bell [103], could be successfully applied essentially only after the work of Rosencwaig and Gersho [104] in 1976. The main limits of this technique applied to surface chemistry and catalysis [105,106] are that (i) it needs a gaseous atmosphere; (ii) the cell needs a microphone just near the sample (Fig. 7) so that the sample cannot be heated and activated conveniently; (iii) the *s*/*n* ratio is intrinsically low [97]. On the other hand, the photothermal effect is much more efficient for species in the vapor phase than for bulk and surface species. This makes necessary the use of monatomic non-absorbing gases (He, Ar, etc.) and makes the detection of species weakly adsorbed on solids only in equilibrium with the absorbing gas (like, e.g., CO on oxides) difficult. Finally, the photoacoustic spectrometry is not exactly a surface spectroscopy, because the penetration of the thermal effect is always significant, although it depends on the scan speed. Thus, only when the surface-to-bulk ratio is very high, the *s*/*n* ratio is sufficiently good.

The PAS technique found successful application in the fields of polymer science [76] as well as in the field of surface carbon and coal characterization [107]. In the field of heterogeneous catalysis some interesting data have been reported, e.g., for pyridine adsorption on acidic catalysts [106] but it does not seem to be competitive with transmission and diffuse-reflectance techniques except in a few cases when very opaque materials are studied, like sulphided HDS catalysts [106]. Interesting spectra have also been reported in the case of heteroplyacids and their salts and of molecules adsorbed on them [108].

An alternative photothermal technique is the so-called photothermal beam deflection spectroscopy [PBDS], based on the so-called 'mirage' effect first reported by Boccarra et al. [109] and developed in the IR region by M.J.D. Low and coworkers [110]. In this case, the periodic temperature rise caused by the absorption of the modulated IR radiation (i.e., the photothermal effect) is detected optically because it causes the periodic deflection of a laser beam passing close to the surface of the solid sample (Fig. 7). The PBDS technique has some advantages over the PAS technique because of its lower limits in sample dimensions but it has disadvantages because of the critical geometric set-up. Like PAS, PBDS can have advantages with respect to traditional IR technique for the detection of surface vibrations in very opaque materials. This resulted in their application to carbons and coals [107]. The application of the PBDS technique to catalysis has been very limited, up to now.

3.1.6. Surface vibrational sum frequency generation technique (SFG)

This is a very recent technique [111] that can be applied to both metals and insulating oxide materials. This technique is based on the physical phenomenon that implies the generation, when two beams with different frequencies interact on a surface, of a new radiation whose frequency is the sum of the incident ones. Thus, mixing a tunable IR laser with a visible laser over a surface where molecules are adsorbed, the surface generated sum frequency signal is modified when the IR radiation is absorbed by the adsorbate. Using polarized laser beams, information on the orientation of the adsorbed molecule can be obtained.

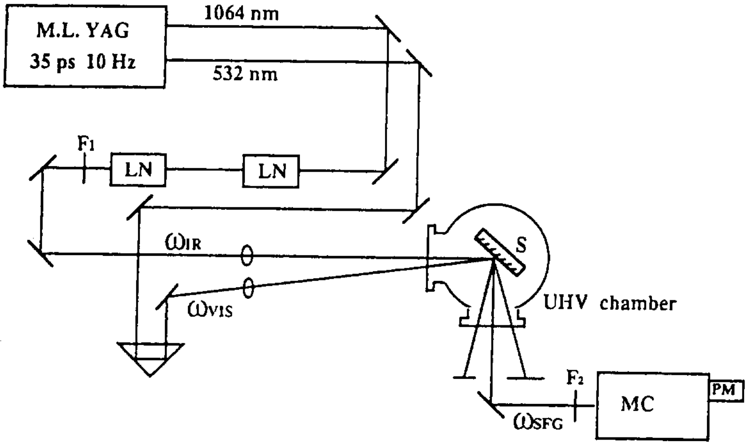
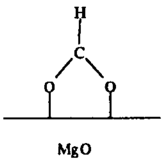


Fig. 8. Scheme of the SFG apparatus (taken with permission from ref. [112]).

Several applications of this new technique are now appearing among which some related to adsorbed species on metal oxides. As for example, Yamamoto et al. [112] observed a band from the spectrum of the formate ion adsorbed on the [001] MgO monocrystal surface. The experimental setup used by these authors is schematized in Fig. 8. In Table 1 the position of the bands recorded with different techniques for formate ions over MgO surfaces are compared together with those reported for the salt $(HCO_2)_2Mg$. Yamamoto at al. [112] were able to conclude

Table 1
Wavenumber (cm^{-1}) and assignment of the bands of formate ions adsorbed on MgO surfaces

HCOOH adsorbed on MgO					
	$(HCO_2)_2Mg$ Nujol mulls	Powder	Single crystal [100] face	Single crystal [100] face	Plasma-grown layer on Mg
Assign. technique →	IR	FT-IR[a]	SFG	EELS	IETS
$\nu_{as}COO^- + \delta CH$		2930		2950	2976
νCH	2907	2885	2870		2815
		2870			
$\nu_s COO^- + \delta CH$		2770			2709
		2735			
$\nu_{as}COO^-$	1603	1630		1634	1575
		1605			
δCH	1404	1395			
	1391	1383			
	1385			1349	1348
$\nu_s COO^-$	1374	1370			
	1366	1340			
γCH	1081	1085		1094	1046
$rCOO^-$	761	masked			
$\nu Mg–O$					236
Ref.	[113,114]	[114,115]	[112]	[116]	[117]

[a] Transmission/absorption technique.

from their SFG experiments that formate ions stand perpendicular to the surface with rather broad distribution width of tilt angle $\theta = 0 \pm 30°$.

Also remarkable is the recent work of Maechlung et al. [118] who studied Langmuir–Blodgett films of organic compounds over iron oxide layers on Fe with this technique.

3.2. Raman spectroscopy

The Raman effect is based on the inelastic scattering of an electromagnetic radiation due to their interaction with molecular vibrations. When the radiation irradiates a sample part of photons are scattered due to the dipole moments induced through the static polarizability of the electrons. This is the Rayleigh or elastic scattering. However, a small part of the photons are scattered through the modulation of the polarizability by electronic, vibrational or rotational motion leading to Raman or inelastic scattering.

Using a simple classical model it is easy to demonstrate [119] that when a chemical species is irradiated at the frequency ν_0 and its polarizability is modulated at the vibrational frequency ν_1, the time dependence of the induced dipole moment μ is given by

$$\begin{aligned}\mu(t) &= \alpha_0 E_0 \cos 2\pi\nu_0 t \\ &+ 1/2\left(\frac{\partial\alpha}{\partial Q}\right)_0 Q_0 E_0 \cos 2\pi(\nu_0+\nu_1)t \\ &+ 1/2\left(\frac{\partial\alpha}{\partial Q}\right)_0 Q_0 E_0 \cos 2\pi(\nu_0-\nu_1)t \qquad (18)\end{aligned}$$

where α is the polarizability that is a function of the normal coordinate Q in a Taylor's series:

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q + 1/2\left(\frac{\partial^2\alpha}{\partial Q}\right)_0 Q^2 + \ldots \qquad (19)$$

with α_0 = the static polarizability and E_0 = the amplitude of the radiation. The three terms in Eq. (18) correspond to the Rayleigh scattering (with $\nu = \nu_0$), to the anti-Stokes Raman scattering (with $\nu = \nu_0 + \nu_1$) and to the Stokes Raman scattering (with $\nu = \nu_0 - \nu_1$). From a quantum-mechanical treatment it is possible to rationalize why anti-Stokes Raman scattering is by far weaker than Stokes Raman scattering, in particular for high frequency modes [119].

It is possible to conclude that Raman scattering occurs only if:

$$\Delta v = \pm 1 \qquad (20)$$

$$\left(\frac{\partial\alpha}{\partial Q}\right)_0 \neq 0 \qquad (21)$$

that mean that also in Raman spectroscopy only transitions between nearest levels and associated to changes in the polarizability α upon motion are allowed for an harmonic oscillator. The first selection rule is relaxed for anharmonic oscillators. Group theory shows that for centrosymmetric chemical species Raman-active modes are IR inactive and vice-versa. This is the so-called 'mutual-exclusion rule'. Other modes can be both IR and Raman inactive. For non-centrosymmetric molecular species, also modes that are both IR and Raman active occur.

The Raman scattering process is inherently weak (only a small fraction of photons are inelastically scattered, like 10^{-6}) and this limit is expected to be even more important for surface species. The intensity of the Raman signal of adsorbed species can be enhanced by the so-called SERS effect (surface enhanced Raman scattering) that is however limited to rough surfaces of few highly reflective metals [30–32].

The FT-IR and FT-Raman skeletal spectra of a TiO_2-anatase sample are compared in Fig. 9. This shows that Raman spectroscopy is a very useful technique for the bulk characterization of some oxide catalysts (other, like amorphous silica and transitional aluminas give weak very broad diffractions). Moreover, Raman spectroscopy offers rather high spectral resolution, and high spacial resolution allowing microspectroscopy. Details on the use of Raman spectroscopy in the field of the surface chemistry of the oxide catalysts can be found later on in this issue in the review of Wachs.

On the other hand, Fig. 9 shows that Raman spectroscopy of species adsorbed on metal oxides

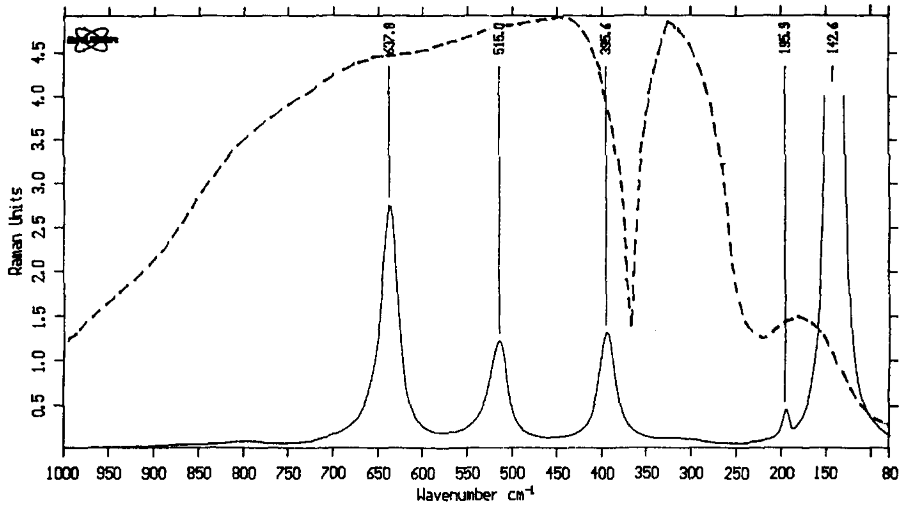


Fig. 9. FT-IR transmission/absorption (KBr disk, broken line) and FT-Raman spectrum (full line) of a commercial TiO_2-anatase powder (10 m^2/g).

should offer advantages over IR spectroscopy because of the relatively weak Raman scattering intensity from the skeletal vibrations of ionic oxides and (generally) the absence of TO–LO splitting, allowing the inspection of the far infrared region (that is instead strongly absorbed by metal oxides).

However, laser Raman spectroscopy of adsorbed species suffers from the draw-back associated with the high energy beam involved, that can cause (photo)chemical transformation of the adsorbate on the oxide surface under measurement. As for example, polymerization of benzene over TiO2-rutile was observed under the 457.9 nm Ar ion laser excitation line [170]. Accordingly, Raman spectra of very stable species like pyridine over metal oxides and zeolites have been studied since the work of Hendra et al. [171] and represent alternative and somehow complementary methods with respect to the analogous IR spectroscopic experiments for the characterization of the surface acidity of catalysts. Some data on this respect have been summarized recently in the Stencel's book [32]. Ammonia is another molecule whose stability allows its adsorption to be investigated with success. The recent work of Went et al. [172] that investigated by laser Raman spectroscopy the adsorption and the transformation of ammonia over catalysts active for the $NO+NH_3$ reaction is remarkable. Another remarkable success was the characterization of the adsorbed allyl species from propylene over ZnO with Raman spectroscopy [173].

In any case, the Raman spectra of many other molecules like CO, nitriles and hydrocarbons adsorbed on oxides and zeolites have also been recorded [32]. The problems concerning the reactivity of the adsorbed molecules under the beam can be greatly reduced with the use of Fourier transform Raman instruments, that work with NIR laser beams (Nd-YAG lasers, 1064 nm) as shown by the more recent data by Hendra et al. [174] and others. It should however be remarked that FT-Raman instruments give additional problems related to the emission of the IR light from the sample [175].

3.3. Electron energy loss spectroscopy (EELS)

EELS consists in the inelastic forward scattering of low energy electrons (commonly 2–10 eV) by adsorbed species at surfaces that causes a loss of their energy and their appearance close to the specular direction (Fig. 10) [33–35]. The primary mechanism of this inelastic collision is through a long-range interaction between the electric field of the incoming electron and the dynamic

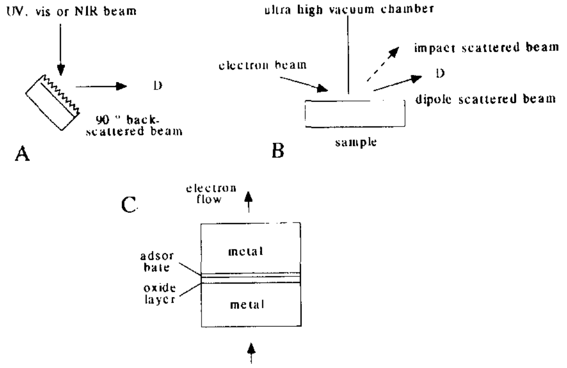


Fig. 10. Scheme for Raman (A), EELS (B) and IETS (C) spectroscopies.

dipole of the adsorbate [120] and this implies the following stringent selection rule

$$\left(\frac{\partial \mu_{\perp}}{\partial Q}\right)_0 \neq 0 \tag{22}$$

i.e., only the vibrational modes of the adsorbate with a component of their associated dynamic dipole moment perpendicular to the surface are observable (i.e., the same selection rule as for IRRAS). This can make difficult the identification of the mode responsible for an EELS peak but, if this mode is identified, allows stringent information on the geometry and symmetry of the surface complex [61]. Another scattering mechanism, the so-called 'impact scattering' can also be active and it gives rise to less stringent and more complex selection rules. This scattering is not confined to the forward direction and this implies that it is best observed away from the specular direction where the primary dipole-driven losses are weaker.

The main limits of the EELS technique in view of its use in catalysis research are the follows: (i) very expensive apparatuses; (ii) only high vacuum ambient; (iii) rather low resolution (down to 1 meV, equivalent to 8 cm^{-1}, at most [35]); (iv) limited applicability to samples different from single crystals. The advantages are: (i) very informative on the structure of the surface species; (ii) high spectral range ($>100\,cm^{-1}$); (iii) good sensitivity; (iv) small sample dimensions.

Most EELS experimental work has been focused on adsorbate-covered single crystal metal surfaces. In fact, two main difficulties arise when insulating substrates are used. The first one is the appearance of very strong losses due to surface optical phonons that are by far more intense than those due to the vibrational transitions of the adsorbed species. The surface phonons on metal oxides have been detected by EELS on several oxide monocrystal surfaces after the work of Ibach on ZnO [121], but their losses need to be eliminated to detect the surface species. For this purpose a Fourier spectral deconvolution method has been developed [15] and appeared to be very practical [122]. Alternatively, high-energy beams (like 46 eV [123]) can be used instead of the low energy beams most commonly employed. A more complex problem is common to all techniques implying high energy beams with insulating materials: they become electrostatically charged under such beams. This problem was solved by Thiry et al. [124] who proposed the irradiation of the samples with the defocused beam of a second electron gun. These methods allow the successful detection of adsorbed species on monocrystals of metal oxides, shown by several papers published in recent years [117,122].

In Table 1 the position of the EELS peaks of formate ions on MgO [100] monocrystal faces are compared with those that have been found with other techniques on similar systems. The lower complexity of the EELS spectra with respect to those measured by FT-IR on MgO powders reflects in part the higher resolution of IR with respect to EELS measurements but also the, by far, higher complexity of a high-area powder surface with respect to a monocrystal surface. EELS spectra show strong the C–H stretching and stronger ν_sCOO^- mode with respect to the $\nu_{as}COO^-$ mode, while the δCH mode is not detectable. On the contrary, IR spectra have a weak νCH, $\nu_{as}COO^-$ stronger than ν_sCOO^- and δCH well evident. This confirms the above cited selection rule for EELS also for insulating surfaces, where the modes associated to dipole moment variations perpendicular to the reflecting face (νCH and ν_sCOO^-) are strong while those associated to dipole moment variations mainly parallel to the reflecting face ($\nu_{as}COO^-$ and δCH) are weak or absent at all. The observed spectra agree with the conclusion that formate species stand vertical on the MgO surface, as also concluded from SFG studies (see above). This emphasizes how more precise the information is arising from EELS on the geometry of the surface complexes with respect to those arise from IR of powder.

3.4. Inelastic electron tunnelling spectroscopy (IETS)

IETS is performed by measuring the current-voltage characteristics of a metal-insulator-adsorbate-metal tunnelling sandwich (Fig. 10) [36,37]. The tunnel current flowing when a potential difference is applied is mostly due to elastic tunnelling but an additional inelastic tunnelling process occurs due to the interaction of the electrons with the vibrational states of the adsorbate. The current versus voltage (I vs. V) has a kink when its energy is such that:

$$eV_{\min} = h\nu \qquad (23)$$

where ν is a vibrational frequency of the adsorbate. This kink corresponds to a step in the dI/dV vs. V curve and a peak in the second derivative curve d^2I/dV^2 vs. V. In general the curve d^2V/dI^2 vs. V, that has bands in the same position as the curve d^2I/dV^2 vs. V, is actually measured.

This technique is generally performed over oxide layers grown over the 'bottom' sandwich electrodes, the 'top' electrode being most frequently constituted by a Pb layer deposed from vapor phase. So that the preparation of the sample favors oxide layers of oxidizable metals like alumina and magnesia that, in fact, are most frequently studied. As for the adsorbates, in generally rather heavy organic compounds have been studied. However, also lighter molecules like CO and acetylene as well inorganic complexes [117,125,126] have been investigated. Also phonons of the metal and of the oxides as well as of surface hydroxy-groups can be observed. Finally, the nature of the 'top' metal electrode can also affect the position and shape of the bands of the adsorbate on the 'bottom' oxide [125,127].

In principle, the entire 0–4000 cm^{-1} wavenumber range can be investigated with a resolution most commonly in the range 10–30 cm^{-1}, although resolution up to 2 cm^{-1} could also be achieved at very low temperatures (liquid He). No selection rules apply so that all vibrational transitions of the adsorbate are IETS-active. On the other hand, some intensity dependence is found on orientation of the molecule. The position of the observed IETS bands of formate ions observed on a MgO layer grown over Mg are compared with those observed by IR over MgO powder and by EELS and SFG over monocrystals in Table 1. Also IETS spectra, like in EELS spectra for single crystals, show very intense the νCH and ν_sCOO^- 'perpendicular' modes while $\nu_{as}COO^-$ is weak and δCH is not resolved from ν_sCOO^-. However, also the γCH mode (out-of-plane bending) is very strong, in spite of being a 'parallel' mode and a further very strong band is observed at 236 cm^{-1}. We assigned it to a Mg–O stretching in Table 1 in contrast to Walmsley that assigned it to the CO_2^- rocking [117]. The further use of IETS in catalysis is limited due to the limited kinds of oxide samples that can be investigated and to the measurements conditions that are far from those of interest in catalysis. However, the absence of selection rules can allow this technique to complete the picture of the vibrational spectrum for particular systems.

3.5. Inelastic neutron scattering spectroscopy (INS or NSS)

The INS technique [128] consists in the analysis of the energy distribution among neutrons inelastically scattered by the chemical species under study, generally in a dispersed form like in the form of powders. If the instruments operates with a polychromatic continuous neutron source (from a fission nuclear reactor), the dispersion of the scattered beam is obtained before the sample by Bragg reflection from a single crystal operating as a diffraction monochromator.

On the contrary, if the instrument works with a pulse neutron beam (spallation source) the energy analysis is obtained by using the time-of-flight technique, i.e., measuring the time of arrival to the detector spent by scattered neutrons through the source-sample-detector way.

The INS technique has, obviously, many disadvantages with respect to the much easier IR technique essentially associated to the availability of a neutron beam source, to the complexity of the neutron energy dispersion and of the neutron detection. Moreover, the measurement resolution is much smaller (near 2% of the energy transfer, that means 20 cm^{-1} at 1000 cm^{-1}) and to increase s/n ratio the spectra are usually recorded at very low temperature.

In principle, there is a great advantage of INS with respect to both IR and Raman spectroscopies, related to the fact that there are not selection rules, so all vibrational transitions are in principle INS-active. However, the intensity of the INS peaks depends on the INS cross-section of all the atoms involved in the corresponding vibrational mode. This cross-section is characteristic of each element and does not depend from its chemical environment and is at least 40 times greater for hydrogen than for any other element. Thus, the peaks associated to modes that involve hydrogen motions dominate the spectra while those that do not involve hydrogen can be so weak to become undetectable.

Thus, it is evident that INS spectra are particularly useful for the detection of vibrational transitions involving adsorbed hydrogen and hydroxy-groups. This is in particular true for the vibrational transitions associated to adsorbed hydrocarbons and hydroxyls on zeolites [57] and of hydrogen adsorbed on and absorbed species in metallic catalysts (that, when unsupported, cannot be studied by IR and Raman) as well as hydride species on oxide and sulphide catalysts [58,129–131]: in the last cases, these absorptions not infrequently fall in the region below 1000 cm^{-1} where also metal–oxygen and metal sulphur skeletal vibrations fall and dominate IR and Raman spectra. On the contrary, skeletal vibrations of oxides and sulphides are very weak, if any, in INS spectra so that those involving hydrogen can be detected easily.

3.6. *Inelastic atom scattering spectroscopy (ASS)*

As already remarked, also an atom beam can be inelastically scattered so giving rise to the detection of a vibrational spectrum. The application of this technique, in particular using He (inelastic helium scattering or helium atom scattering spectroscopy) is a recent one, but interest for it is rapidly growing. Several papers appeared about its application to metal surfaces [24] but studies on ionic insulators are also beginning to appear, like the studies of surface phonons on NiO [132,133] and of external vibrational modes of CO_2 adsorbed on NaCl crystals [134]. This technique seems to be particularly useful for the detection of low-frequency vibrational modes (below 100 cm^{-1}), although its deep limitation is just that it is limited only mainly to this range.

4. Less usual applications of vibrational spectroscopies to metal oxide catalysts

The most widespread applications of IR and Raman spectroscopies to metal oxide catalysts will be reviewed in the next chapters of this issue. We would like to briefly summarize here some other topic that will be not covered in detail but that is of interest in the field of catalysis.

4.1. *Solid state characterization of amorphous and crystalline metal oxide catalysts by vibrational spectroscopies*

As already cited, the vibrational spectra are characteristic of the structure of a crystalline non-conducting oxide, from two respects: (i) the dimensions and symmetry of the unit cell; (ii) the strength and the nature of the element–oxygen bond. In this sense, vibrational spectroscopies are more informative than the mostly utilized solid state technique, i.e., X-ray diffraction, that only gives information on geometry (although more precise and straightforward).

The complete determination of the 'true' vibrational spectrum of a crystalline oxide can be done by using single crystal reflection IR measurements together with single crystal Raman measurements [66,119]. On the other hand, as shown above, some solids, including several metal oxides, due to symmetry reasons have not first-order Raman activity, only rather weak overtones or harmonic modes being Raman active. This is the case, for example, for solids with the salt-rock-type structures (like, among others, the oxides MgO, CaO, SrO and BaO, see Eq. (13)), truly cubic perovskites (like $SrTiO_3$) and ReO_3 – type structures that, in fact, do not show any Raman active fundamental. In these cases, however, strong IR spectra are recorded (see Fig. 4 for MgO).

On the other hand, catalysts are generally in the form of powders. The Raman spectra of crystalline metal oxides (in general of crystalline solids), in particular when the unit cell is centrosymmetric, are generally not strongly perturbed when powders instead of single crystals are used; in fact, in these cases the position of Raman peaks recorded using powders in generally do not shift significantly with respect to those measured on single crystals. Only small effects on peak width are observed [135].

When IR powder spectra are concerned the picture is different. This also occurs also for Raman spectra of crystalline powders with non-centrosymmetric unit cell, where some Raman-active modes are also IR active. This is the case, for example, for ferroelectric materials, like tetragonal $BaTiO_3$. In fact, all IR-active modes undergo the so-called TO–LO splitting, i.e., they actually split in a transverse and a longitudinal component, that can be well distinguished by reflectance monocrystal measurements. For this reason, IR spectra of powders (and to some extent also Raman spectra of non-centrosymmetric structures) differ from the single-crystal spectra and are very sensitive to the morphology of the powder samples. In fact, the actually observed IR bands for perfectly monosized and monoshaped powders do correspond neither to TO's nor to LO's but are centered in between, in dependence on the sample shape and size. Moreover, on powders where different powder morphologies are present, the sum of their different spectra is actually observed [136,137].

Data on the phonon spectrum of metal oxides can be obtained on monocrystals also using EELS spectroscopy, that allows the detection of surface phonon and multiphonon modes [15,121–124]. INS could also give rise to the detection of phonon modes of oxides but the observed peaks are generally weak. In any case, INS has been used to investigate the low frequency soft modes in ferroelectric and incipient ferroelectric materials [119], investigated also by Raman spectroscopy [138]. Phonon spectra can also be observed in the IETS spectra, where LO modes can have stronger intensities than TO modes [117,125,126]. Interestingly, the IETS [117], IRAS [119] and SEWS [84] spectra of aluminas are similar, showing a main band near 950 cm^{-1} that is weak, if any, in the transmission IR spectra and in Raman spectra.

On the other hand, vibrational spectroscopies (even performed on powders) can give information additional to XRD on the true structure of crystalline powders. As for example, it has been shown recently using Raman spectroscopy that the α-$FeCrO_3$ mixed oxide (an active oxy-dehydrogenation catalyst), that appears to be a disordered corundum-type solid solution to XRD (due to the nearly equivalent X-ray scattering factor of Cr^{3+} and Fe^{3+}), can actually have at least partly an ordered superstructure, being likely isostructural with ilmenite [139]. Similarly, Raman spectroscopy allowed to determine that high-area $BaTiO_3$, that is cubic to XRD analysis and is not ferroelectric, is 'microscopically' certainly distorted like in the tetragonal ferroelectric low-area material [140]. A third example is the determination of the state of Ti in titanium silicalites, that can be obtained with clarity using IR and Raman spectroscopy [141,142].

Finally, vibrational spectroscopies are almost unique for the characterization of non-crystalline

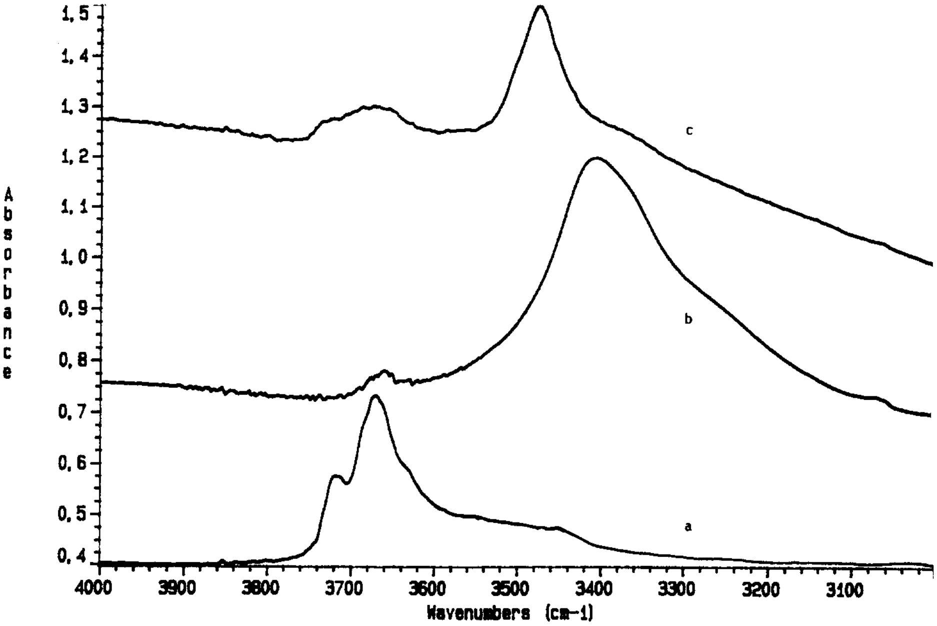


Fig. 11. FT-IR spectra of OH groups of (a) TiO_2 (anatase), (b) cubic $SrTiO_3$ and (c) 'pseudocubic' $BaTiO_3$.

solids (like silicas and silica-aluminas). The IR spectra show that Al^{3+} in amorphous alumina is octahedrally coordinated so explaining why amorphous aluminas are not as acidic as transitional aluminas where Al^{3+} ions in a unsaturated tetrahedral coordination sphere constitute the acidic sites [143] and that boron in amorphous alumina-boria is trigonally coordinated [144], while it can be tetrahedrally coordinated in part in crystalline alumina-borias [145]. Finally, IR and Raman spectroscopies also detect structures that have not long-range order, like the so-called 'monolayers', as shown by Wachs in the Chapter 5 in this issue.

Vibrational spectroscopies allow also the detection and the characterization of defects on both amorphous and crystalline materials, that can have crucial role in catalysis. In Fig. 11 the spectra of the perovskites $BaTiO_3$ and $SrTiO_3$ are compared, in the OH stretching region, with that of a TiO_2 sample. Internal OH groups in perovskites are evidenced by strong bands in the 3500-3400 cm^{-1} region in the IR spectrum (but they are also detectable by Raman [140]). The detection of such internal OH's (not present usually in oxides including TiO_2 and ilmenite-type titanates) by vibrational spectroscopies allows the investigation of hydrogen diffusion in perovskites [146,147]. Raman spectroscopy has been utilized to detect and characterize the hydrolyzed defects in Ti-silicalite, thought to be involved in the activation of hydrogen peroxide [148], and to investigate the nature of the defects in amorphous and vitreous silicas [149].

As already remarked, a disadvantage of IR spectroscopy when used to detect adsorbed species over oxides is that the skeletal region for the pressed disks samples is totally obscured. For this reason, it is not possible to monitor the state of bulk during the experiment. However, in several cases overtone bands are observable at higher frequency and, due to their intrinsic lower intensity, their behavior during experiment can be followed and analyzed. This behavior is typical of rather covalent and reducible oxides like, among others, V_2O_5 and vanadyl-phosphate catalysts. As shown in Fig. 12 the overtone spectrum of vanadia (region 2200-1000 cm^{-1}) is strongly changed when it interacts with and is reduced by propene. The spectroscopic features of the adsorbed species are simultaneously detected. Also in the case of other catalysts like vanadyl-phosphates, molybdena and molybdates, tungsta and tungstates and

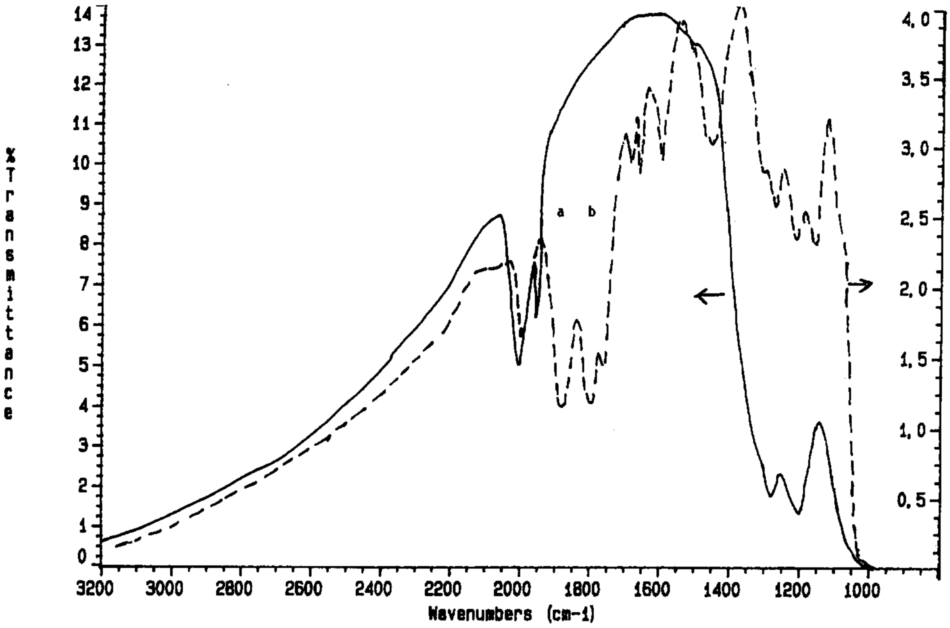


Fig. 12. FT-IR spectra of a pure V_2O_5 pressed disk after outgassing at 573 K (a) and after oxidation of propylene on it at 573 K (b). Sharp bands at 1703, 1690 and 1620 cm^{-1} are due to C=O and C=C stretchings of adsorbed acrolein and acetone.

also metal sulphates, the analysis of the behavior of the overtone region allows us to monitor the state of the catalyst bulk upon adsorption as well as upon a catalytic reaction, investigated in situ [150,151]. The same phenomena have been observed using IR emission spectroscopy [152], working in the fundamental skeletal region (see above). However, with this technique the detection of the adsorbed species is more difficult.

4.2. Electronic transitions and the vibrational spectra

Most transition metal oxides can easily be non-stoichiometric, either due to oxygen excess (p-type semiconductors) or due to oxygen defect (n-type semiconductors). In these cases, broad absorptions can be observed in the IR region, certainly non-associated to vibrational transitions but arising from either localized or delocalized electronic transitions. These features, although quite complex to be interpreted and explained with clarity, give information on the state of the oxide. This topic will be briefly discussed later on in a next chapter of this issue, where its relevance to oxidation catalysis will be emphasized. Interesting observation on the state of semiconducting materials like ZnO and TiO_2 and of metal-semiconducting interfaces, like Cu/ZnO, Pt/ZnO and $RuTiO_2$, have been reported by Boccuzzi et al. and can have important applications not only in the field of heterogeneous catalysis [153] but also in that of sensor technology [154].

Electronic transitions can also affect deeply the Raman spectra of oxide materials. As for example, the Raman spectrum of TiO_2 rutile is completely cancelled after a very weak reduction [155] while the intensity of the Raman pattern of anatase in V_2O_5-TiO_2 catalysts strongly depends on the V_2O_5 content [156,96]. It has been shown by Waters [157] that this effect can be due to the absorption of the incident light by the surface vanadium complexes so that the scattered light is strongly diminished. However, on V_2O_5-WO_3-TiO_2 catalysts for De-NO_xing a very complex behavior of the anatase Raman peak intensity and the appearance of broad scatterings is observed,

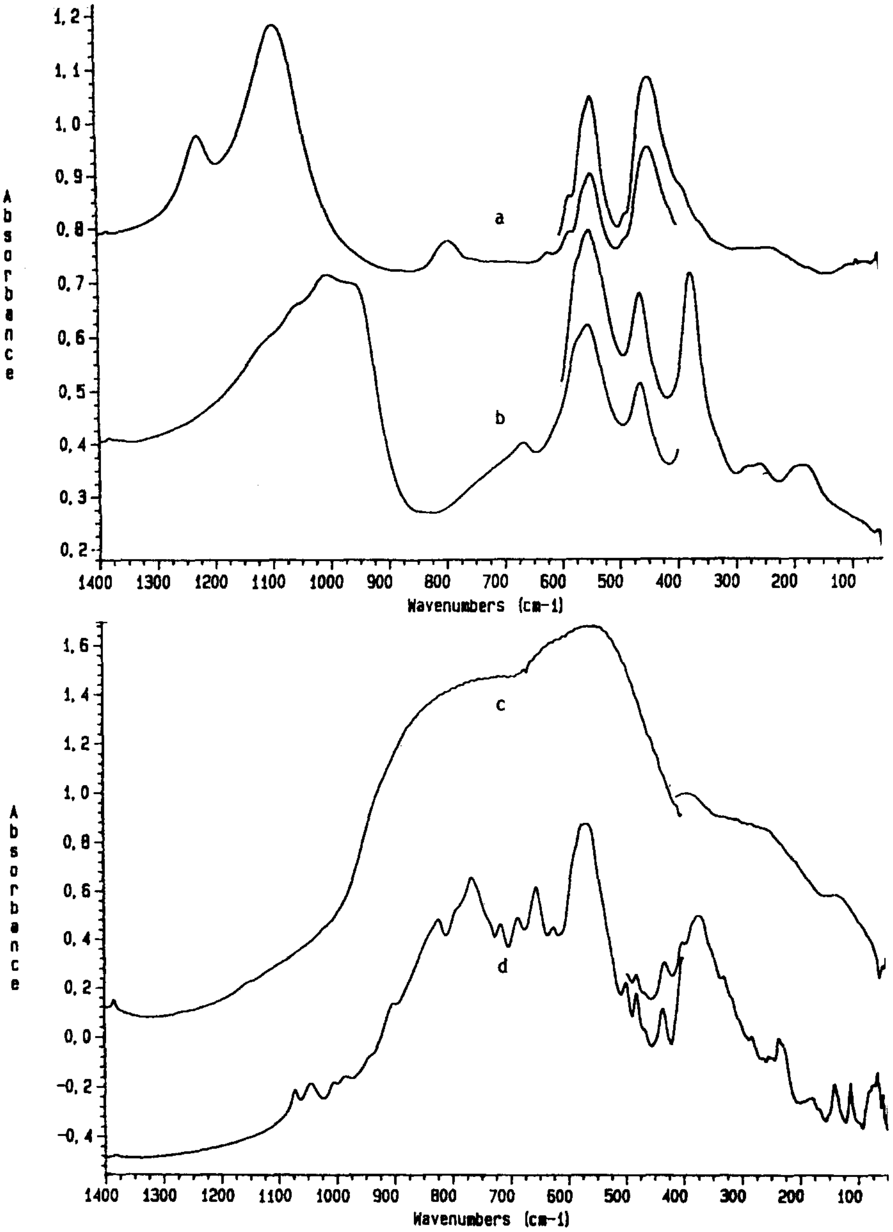


Fig. 13. Skeletal infrared spectra of the zeolites H-ZSM-5 (a); Na-A (b); and of γ-Al_2O_3 (c) and Ba-β-Al_2O_3 (d). Region 4000–400 cm^{-1}: KBr disks; region 500–50 cm^{-1}: polyethylene disks.

that likely imply electronic transitions between the different catalyst components [158].

4.3. Vibrational spectra of surface species in the far infrared (FIR) and in the near infrared (NIR) regions

The most usual wavenumber range of IR spectrometers is 4000–400 cm^{-1} (medium infrared region, MIR). The lower limit is mainly due to the use of optical elements (beam splitter in the FT-IR spectrometers) built up of KBr, that absorbs below 400 cm^{-1}. The use of polyethylene as the optical material allows to shift this limit down to 20 cm^{-1} and less. However, the s/n ratio in this region is generally lower than for MIR, due to lower emissivity from the sources and lower detectivity by detectors. Raman, EELS, IETS, INS and IAS have also low-frequency limit associated to the breadth of the incident line band.

On the other hand, the inspection of the very far infrared region is not always very informative, except in some cases that can be interest for heterogeneous catalysis. In this region fall the soft modes of ferroelectric materials [138] that strongly shift down by lowering the temperature. However, in the FIR region also fall the oxygen–cation vibrational modes for highly uncoordinated and/or highly weighted cations, like for cage cations in cation exchanged zeolites [159,160] and for mobile cations of cation-conducting β-aluminas [161,162]. In Fig. 13 the FIR spectra of a non-exchanged zeolite (H-ZSM-5) and of a cation exchanged zeolite (Na-*X*) of a γ-alumina and of a β-alumina are reported, showing the bands associated to the vibrations of the low-coordination cations. In the case of cation-exchanged zeolites, these bands are perturbed by adsorption, so that the detection of these perturbations can give information on the surface chemistry and catalysis of these systems [163]. In the same region modes involving OH groups in zeolites also fall, well detectable by INS measurements [57].

Most metal oxides do not present any band below the cut-off region due to the skeletal vibrations so that in this region too the spectra of the adsorbed species could be detected. However, also most adsorbates do not show any strong band in the very far infrared region. Studies of the adsorbed species in the far infrared have been published, showing only broad bands likely associated to hydrogen bonds and/or surface-adsorbate modes. The torsional modes of surface silanol groups on silica have been characterized [164]. Raman spectra of oxides supported on oxides show bands in the FIR region, useful to determine the nature of the supported oxide species, as reported by Wachs, in this issue (Chapter 5). Similar absorptions can also be found by FIR experiments [165].

Studies of adsorbed and surface species on metal oxides can be extended above the limit of 4000 cm^{-1}, i.e., in the near infrared (NIR). In this region rather intense absorptions can be easily observed using the diffuse reflectance technique, that takes advantage of the severe scattering occurring in the high-frequency region. These absorptions are associated to overtone and combination modes of the surface hydroxy groups. Investigation on silicas [166], aluminas [167] and zeolites [168] in the NIR region in the presence or in the absence of adsorbates have been performed and have been correlated with the results of MIR experiments.

5. Conclusions

The brief summary reported here would allow to somehow complete the picture on the actual and potential use of vibrational spectroscopies in the field of heterogeneous catalysis by metal oxides. In the next chapters in this issue some topics of greater relevance will be covered in detail by experts in the particular fields. It is evident that, although IR spectroscopy is nowadays a routine technique in any catalysis laboratory, by the use of this technique and of other perhaps more sophisticated vibrational techniques like those briefly reviewed here, there is room for detailed investigation of any particular system, as well as for high-level fundamental studies concerning the metal oxide surfacial phenomena. It appears that vibrational spectroscopy had, and will have further in the near future, a very prominent role in the development of surface chemistry as a scientific discipline.

Acknowledgements

cm The author gratefully acknowledges the suggestions of Prof. U. Valbusa (University of Genova).

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