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Chapter 16
Vibrational spectroscopy

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1 INTRODUCTION

Understanding surface electrochemical processes, including those that take place at fuel cell electrodes, requires knowledge of data regarding both the composition and the structure of the electrode surface and their role in the electrochemical reactivity. Many surface characterization techniques have been developed over recent decades but just a few of them can be applied under electrochemical conditions. Among them, scanning tunneling microscopy (STM) and surface X-ray scattering (SXS) techniques can provide structural information both on the electrode surface and the presence of ordered adsorbate adlayers. On the other hand, vibrational spectroscopy techniques have been classically used to gain insight on the chemical composition of a given system. Infrared (IR) spectroscopy is probably the most popular among these techniques, and has been used for the characterization of both bulk phases and interphases via transmission or reflection experiments, respectively. In this way, particular groups of atoms can be identified through their characteristic group frequencies in the IR spectra. In the case of adsorbate species, the corresponding spectra are also determined by chemical factors such as the bonding configuration, the coordination of the substrate atoms and local chemical environment, including vicinal molecules of the same or different species.

The application of IR spectroscopy to electrochemical systems has the absorption of radiation from the solvent as the main problem. To minimize this problem, IR spectroscopy experiments were first performed by using the internal reflection configuration. However, this approach has additional difficulties related to the preparation and stability of thin film electrodes. In fact, surface enhanced Raman scattering (SERS), that also provides vibrational information for adsorbed species, was the vibrational technique first applied under external reflection conditions for the study of adsorbate layers at electrode surfaces. Absorption from the solvent is not a problem in this case since the frequency of the exciting beam lies in the visible range. Later, Bewick et al. were the first to demonstrate the feasibility of in situ infrared reflection/absorption spectroscopy (external reflection or IRRAS) experiments with a thin layer cell. In the following two decades, IR spectroscopy techniques have become very popular among surface electrochemists. Information derived from the IR spectra deals with the composition and structure of the interphase, including both adsorbed and solution species, and their dependence with the electrode potential. Structural aspects of electrochemical processes have been thoroughly studied spectroscopically by using single crystal electrodes in external reflection experiments, whereas internal reflection experiments with thin film electrodes have regained interest for kinetic studies.

In this chapter, we review both fundamental and experimental aspects of IR spectroscopy techniques in connection with their application to the in situ characterization of the electrode/solution interphase. Recent developments in the field and a selected number of applications are discussed in this paper, which joins a long list of review papers on this topic previously published by various authors. As a related topic, the reader is also referred to a number of papers reviewing the application of IR spectroscopy to
the characterization of solid surfaces at the metal/gas and metal/vacuum interfaces.[4, 21–23]

2 FUNDAMENTALS

2.1 External versus internal reflection experiments at the metal/solution interface

When compared with analogous solid/gas experiments, the main problem for the application of IR spectroscopy to the characterization of the electrode/solution interphase comes from the fact that the solution side of the interphase has to be probed in some extent and strong absorption from the solvent may occur. This point determines the experimental conditions to be used, which are based either on the attenuated total reflection (ATR) (internal reflection) or on the reflection–absorption (external reflection) configurations.[8, 13, 14, 24]

In internal reflection experiments, a window of a transparent material with a high refraction index is used as internal reflection element. In the so-called Kretschmann configuration, the window is used also as a substrate for the deposition of a thin metal film. The IR beam reaches the metal surface from the window, being largely reflected at the window/metal interface. However, an evanescent wave passes through the metal and interacts with species at (or close to) the metal/solution interface (Figure 1a). In the case of external reflection experiments, the IR beam is reflected at the metal/solution interface from the solution side (Figure 1b). Obviously, both the incident and the reflected beam have to cross the IR transparent window and the solution layer between the window and the electrode surface. At the same time, the thickness of the solution layer has to be low enough (a few microns) to limit the loss in the intensity of the IR radiation due to absorption from the solvent (normally water). So, a thin-layer configuration is currently used, with the electrode surface being pushed against the window.

A third configuration, known as the Otto configuration, combines internal reflection elements and a thin-layer configuration (Figure 1c). Obviously, the thickness of the solution layer between the electrode and the window has to be necessarily small in this case so that the evanescent wave can reach the electrode surface.

Different problems and advantages are associated with each of the configurations described above. First, the IR beam probes both the electrode surface and a solution layer in contact with it. The thickness of this solution layer is minimal when working with the Kretschmann configuration and, thus, absorption from the solvent is also lower. Conversely, the whole thin layer of solution between the working electrode and the IR window is probed in the external reflection and Otto configurations. This could be an advantage if one is also interested in detecting the generation (or consumption) of solution species. However, one has to take into account that the thin layer is diffusionally decoupled from the rest of the working solution. Thus, species consumed (or formed) at the electrode surface cannot be easily replaced from (or diffused to) the bulk solution. As a result of this situation, absorption bands related to processes taking place at the electrode surface have often their counterpart corresponding to processes in the solution side of the electrode/solution interface. In this way, the IR spectra may also reflect changes in the concentration of IR active species, the solution pH or ionic migration processes.[25–27] Finally, problems associated with mass transport together with a high resistivity (and thus a high time constant) of the thin layer cells make this configuration unsuitable for kinetic studies. These studies are better performed with the Kretschmann configuration, for which mass transport is not impeded. At the same time, enhancement of IR absorption can take place for adsorbates at thin metal films,[14] thus lowering their detection limit. However, thin films are often unstable and, with a few exceptions, their surfaces are ill-defined from a crystallographic point of view. That is why most IR studies dealing with structural aspects of the electrode/solution interphase...
are carried out with bulk single crystals in a thin layer configuration.\cite{11, 13, 15, 17, 18}

## 2.2 Regular reflection theory

When a parallel beam of electromagnetic radiation is reflected at the surface separating a solid material from a homogeneous isotropic phase, two limiting cases can occur. The first one concerns regular (specular) reflection from a polished (smooth) surface, whereas the second case concerns diffuse reflection from an ideal matt surface. In this section, the characteristics of the regular reflected radiation and its dependence on the optical properties of the adsorbate and substrate, the angle of incidence and the polarization state of the incident radiation are summarized. The reader is referred, among others, to Refs. [8, 9, 23, 28–30] for a complete treatment of this topic.

The instantaneous magnitude of the oscillating electric field vector $\vec{E}$ is obtained from the time-dependent solution of Maxwell’s equation:

$$\vec{E} = \vec{E}^0 e^{i(ut - \vec{K} \cdot \vec{r})}$$

(1)

In this expression $E^0$ is the wave amplitude, $\omega$ is the angular frequency of the wave, $\vec{r}$ is the position vector referred to an arbitrary reference coordinate system and $\vec{K}$ is the wave vector, which is given by

$$K = |\vec{K}| = \frac{\omega}{v} = \frac{2\pi n}{\lambda}, \quad n^2 = \varepsilon \mu$$

(2)

where $v$ is the phase velocity in the medium, $n$ is the refractive index, $\varepsilon$ is the dielectric constant and $\mu$ is the magnetic permeability of the material. If the medium is absorbing $n$ becomes complex, $n = n - ik$, and the radiation propagates as an exponentially damped wave according to

$$\vec{E} = \vec{E}^0 e^{i(ut - \vec{K} \cdot \vec{r})} e^{-\gamma r}$$

(3)

where $\gamma = |\gamma| = 2\pi k/\lambda$ and $k$ is the extinction coefficient.

In the absorbing medium

$$\hat{n}^2 = \varepsilon' - i\varepsilon'', \quad \varepsilon' = n^2 - \frac{k^2}{\mu}, \quad \varepsilon'' = \frac{2nk}{\mu}$$

(4)

Let us consider first the reflection of obliquely incident radiation at the interface between two contiguous phases $j$ and $l$ (Figure 2a). The reflectivity of this interface, $R_{jl}$, also called reflectance, is defined by

$$R_{jl} = |r_{jl}|^2 = r_{jl} r_{jl}^* = \frac{E'_{jl}}{E_j}$$

(5)

where $r_{jl}$ is the Fresnel reflection coefficient of this interface, which is defined as the ratio of the complex amplitudes of the electric field vectors of the reflected and incident waves. For an incident beam linearly polarized in a plane perpendicularly to the plane of incidence (i.e., parallel to the metal surface), the so-called s-polarized radiation, the Fresnel reflection coefficient, $r_{\perp,jl}$, is given by

$$r_{\perp,jl} = \frac{\mu_j \xi_j - \mu_j \xi_l}{\mu_j \xi_j + \mu_j \xi_l}, \quad \xi_j = \hat{n} \cos \psi_j$$

(6)

where $\psi_j$ stands for the angle of incidence that is real if phase $j$ is the transparent ambient phase. If the phase $l$ is the absorbing one and the phase $j$ does not absorb, then $r_{\perp,jl} \to -1$ and according to equation (5), $E'_{\perp,jl} \to -E'_{\parallel,jl}$. So a phase change, $\delta''_j$, that approach $\pi$ radians occurs (Figure 3). In addition, the ratio of the mean-square net electric field in the phase $j$ to that of the incident plane

![Figure 2. Schematic representation of the electric-field vectors for an external reflection experiment with a (a) two-phase and (b) three-phase system.](image)

![Figure 3. Phase shift for s-polarized ($\delta_\perp$) and p-polarized ($\delta_\parallel$) light reflected from a metal surface. (Reproduced from Greenler (1966)\cite{28} with permission from the American Institute of Physics.)](image)
wave in this phase for s-polarized radiation is given by

\[ \frac{\langle (E_{ij})^2 \rangle}{\langle (E_{ij})^2 \rangle} = (1 + R_{ij}) + 2R_{ij}^{1/2} \cos \left[ \delta_i + 4\pi \left( \frac{z}{\lambda} \right) \xi_j \right] \]

(7)

From the above expression, if \( R_{ij} \to 1 \) and \( \delta_i \to \pi \) then, at the reflecting surface (\( z = 0 \)), \( E_{ij} \to 0 \) and within a distance comparable with the wavelength of the incident radiation \( E_{ij} \) will remain very small (Figure 4).

On the other hand, the Fresnel reflection coefficient for the so-called p-polarized radiation (parallel to the incidence plane) can be calculated as follows:

\[ r_{ij} = \frac{\hat{e}_i \hat{e}_j - \hat{e}_j \hat{e}_i}{\hat{e}_i \hat{e}_j + \hat{e}_j \hat{e}_i} \]

(8)

As \( \hat{e} \) depends on the square of \( \hat{n} \) while \( \xi \) does it on \( \hat{n} \), \( r_{ij} \to 1 \) when \( n_i \) increases; consequently, \( E_{ij} \to E_{ij} \) and \( \delta_i \). Thus, no phase change occurs in this case. In general, as shown in Figure 3, the phase changes for p-polarized component at a given interface, \( \delta_i \), is a function of the angle of incidence, and varies from nearly \( 0^\circ \) at normal incidence to \( 180^\circ \) at grazing incidence. For this type of polarization, the ratio of the mean-square net electric field in the phase \( j \) to that the incident plane wave in this phase, along the \( x \) and \( z \) axes, are now given by the following expressions:

\[ \frac{\langle (E_{ij})^2 \rangle}{\langle (E_{ij})^2 \rangle} = \cos^2 \theta_i \left[ (1 + R_{ij}) \right] - 2R_{ij}^{1/2} \cos \left[ \delta_i + 4\pi \left( \frac{z}{\lambda} \right) \xi_j \right] \]

(9)

\[ \frac{\langle (E_{ij})^2 \rangle}{\langle (E_{ij})^2 \rangle} = \sin^2 \theta_i \left[ (1 + R_{ij}) \right] + 2R_{ij}^{1/2} \cos \left[ \delta_i + 4\pi \left( \frac{z}{\lambda} \right) \xi_j \right] \]

(10)

If \( R_{ij} \to 1 \) and \( \delta_i \to 0 \), then, at \( z = 0 \),

\[ \frac{\langle (E_{ij})^2 \rangle}{\langle (E_{ij})^2 \rangle} \to 0 \text{ but } \frac{\langle (E_{ij})^2 \rangle}{\langle (E_{ij})^2 \rangle} \to 4 \sin^2 \theta_i \]

(11)

On the other hand, the Fresnel reflection coefficient for the so-called p-polarized radiation (parallel to the incidence plane) can be calculated as follows:

\[ r_{ij} = \frac{\hat{e}_j \hat{e}_i - \hat{e}_i \hat{e}_j}{\hat{e}_j \hat{e}_i + \hat{e}_i \hat{e}_j} \]

(12)

From the discussion above, we conclude that the conditions for high surface sensitivity on a high reflectivity surface are large angles of incidence and p-polarized light. Moreover, it is clear that only p-polarized radiation can significantly interact with the adsorbate. This conclusion points out the necessity of considering an additional surface selection rule to the well-known selection rules for electric dipole transitions for an adsorbate on a highly reflectivity surface (such as a metal electrode, for example). This point is discussed again in Section 2.4.

For a thin film of thickness, \( d \), that is much less than the incident wavelength, \( \lambda \), (linear approximation theory), and considering that \( R_{im} = R(d) \) and \( R_{jm} = R(0) \), we can write for p-polarized radiation:

\[ \frac{R(d)}{R(0)} = 1 + \frac{8\pi n_j \cos \phi_j d}{\lambda} \times \text{Im} \left( \frac{\mu_j \hat{e}_m \cos^2 \phi_j - \mu_m \hat{e}_j \cos^2 \phi_m}{\mu_j \hat{e}_m \cos^2 \phi_j - \mu_m \hat{e}_j \cos^2 \phi_m} \right) \]

(13)

It is very difficult to measure absolute reflectivities \( R(d) \) and \( R(0) \) separately. However, the ratio \( R(d)/R(0) \) can be measured accurately due to the cancellation of unknown factors. In any case, it is more convenient to calculate the normalized reflectance, defined as

\[ \frac{\Delta R}{R} = \frac{R(d) - R(0)}{R(0)} \]

(14)
which is related to the absorbance variation $\Delta A$. For very small values of the normalized reflectance, which usually is the case for most of the adsorbed layers, equation (14) equals $-\Delta A$. In the optical frequency range $\mu_j = \mu_i = \mu_m = 1$ and the normalized reflectance for p-polarized obliquely incident radiation can be obtained from

$$
\frac{\Delta R}{R} = \frac{8\pi n_j \cos \varphi_j d}{\lambda} \text{Im}\left\{ \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_j^2 - \varepsilon_m^2} \right\} \times \left[ \frac{1 - (\varepsilon_i/\varepsilon_m)(\varepsilon_i + \varepsilon_m) \sin^2 \varphi_j}{1 - (1/\varepsilon_m)(\varepsilon_j + \varepsilon_m) \sin^2 \varphi_j} \right]
$$

(15)

For weakly absorbing films on a metallic substrate $\varepsilon_m \gg \varepsilon_i$, and equation (15) becomes

$$
\frac{\Delta R}{R} = -\left( \frac{4 \sin^2 \varphi_j \sec \varphi_j n_j \varepsilon_j}{n_i^3} \right) (d \alpha_l)
$$

(16)

where $\alpha_l = 4\pi k_j/\lambda$.

Equation (16) can be compared with Lambert–Beer’s law for transmission experiments. In this respect, the first term can be considered as an amplification factor since it can be larger than unity for high angles on incidence. Note also that this expression is independent of the optical constants and reflectivity of the substrate, so the reflectivity change is determined largely by the optical properties of the absorbing film. In the case of (sub)monolayers films, $d$ has to be considered as an effective thickness that would be proportional to the adsorbate coverage.[30] Finally, it has to be pointed out that the reflectivity changes calculated from equation (16) are usually very small (about $10^{-7}$).

The three-phase model described here can be directly used to optimize external reflection experiments in the case of adsorbed layers at the metal/vacuum or metal/gas interphases. Obviously, the situation at the metal/solution interphase is more complex. Calculations of the normalized reflectance, $\Delta R/R$, for p-polarized radiation have been carried out for a multilayer model including the presence of a thin layer of an absorbing bulk solution and the IR window.[31, 32] Faguy and Fawcett[31] found $\Delta R/R$ maximum for incidence angles near the critical angle at the window/water interface, this angle being around 70° in the case of the CaF$_2$/water interface. Lower optimum angles, around 60°, are found in the case of the CaF$_2$/D$_2$O interface.[32]

For very small values of the normalized reflectance, which usually is the case for the most adsorbed layers, further information about the orientation of adsorbate can be obtained from the magnitudes of the normalized reflectance for the p- and s-polarized incident radiation.[32]

\[
\int (\Delta A)_{\|} dy = \frac{(E_{\|})^2}{(E_{\perp})^2} - 3 \cos^2 \phi \frac{(E_{\parallel=0})^2}{(E_{\perp})^2} \tag{17}
\]

In this equation, $\Delta A$ is the absorbance variation, $\langle E_{\|}^2(z) \rangle$ and $\langle E_{\perp}^2(z) \rangle$ are the time and $z$ averaged mean square field within the thin layer for s- and p-polarized radiation, $\langle E_{\parallel=0}^2(z = 0) \rangle$ is the time-averaged mean square field at the electrode surface and $\phi$ is the angle between the direction of the transition dipole for the adsorbate and the direction of the field of the p-polarized incident radiation. The latter angle can be considered a good approximation to the tilt angle ($90^\circ - \theta$). In order to determine the tilt angle for a given adsorbate, the average fields $\langle E_{\|}^2(z) \rangle$, $\langle E_{\perp}^2(z) \rangle$ and $\langle E_{\parallel=0}^2(z = 0) \rangle$ have to be calculated from a three-phase model including the IR window, the thin layer and the metal electrode.[32]

### 2.3 Internal reflection

Internal reflection is produced when the light approaches the interface from the denser medium (Figure 5a). For a complete description of this topic see Refs. [5, 33]. If the incidence angle is equal to the critical angle, $\varphi_c$, defined as $\varphi_c = \sin^{-1} n_{21}$, the reflectivities for perpendicular and parallel polarized light become 100% ($n_{21}$ stands for the refractive index ratio, $n_{2}/n_{1}$ and $n_1$ is the refractive index of the denser medium). This situation is called total internal reflection. In this case, standing wave amplitudes established near a totally reflecting interface show a sinusoidal dependence of the electric field amplitude on the distance from the surface in the denser medium, and an exponential dependence, $E = E_0 e^{-z \gamma}$, in the rarer medium ($z$ is the distance from surface) (Figure 5b). The damped wave is termed the evanescent wave. The decay coefficient $\gamma$ depends on $\varphi$ and $n_{21}$, and the inverse of $\gamma$ is the depth of penetration, $d_p$, that is the distance required for the electric field amplitude to fall to $e^{-1}$ of its value at the surface (a few hundred angstroms). The depth of penetration can be calculated by

$$
d_p = \frac{\lambda}{2\pi n_1 (\sin^2 \varphi - n_{21}^2)^{1/2}} \quad (\varphi > \varphi_c) \tag{18}
$$

The depth of penetration is proportional to the wavelength of radiation in the denser medium, and at a fixed angle it is larger for $n_{21} \to 1$. On the other hand, when $\varphi \to \varphi_c$ then $d_p \to \infty$. 
In the presence of an adsorbed layer, the evanescent wave is attenuated by layer’s absorbance. This is the so-called ATR. A linear approximation can be considered when the absorption loss does not exceed 10%. In this case, a simple expression for the strength of interaction as a function of an effective film thickness, $d_e$, is obtained. The reflectivity of bulk materials for these thin films, $R$, is given by $R = 1 - \alpha d_e$ where $\alpha$ is the absorption coefficient and $d_e$ is the effective layer thickness (the product of both parameters stands for the reflection loss per reflection). If multiple, $N$, reflections occur, and $(\alpha d_e) \ll 1$:

$$d_e = \frac{1 - R^N}{N\alpha}$$

and if the thickness of the rarer medium, $d$, is much greater than the penetration depth, $d_p$, the effective thickness can be calculated from the following equation:

$$d_e = \frac{n_{21}E_0^2d_p}{2\cos \varphi}$$

and the strength of coupling of the evanescent wave to the absorbing rarer medium increase with $\varphi$. Since $d_p$ is proportional to wavelength, then $d_e$ also increases with it, so in internal reflection the absorption bands at the longer wavelength are relatively stronger in intensity. Additionally, the stronger absorption on the long wavelength side of a band also causes a distortion of the band (as compared to its shape in transmission experiments). These phenomena do not take place either for very thin films of thickness $d \ll d_p$ or for low absorptions in bulk materials, for which $E_0$ can be considered as constant and $d_p$ can be substituted by $d$ in equation (20).

As discussed above, internal reflection experiments can be performed at the metal/solution interphase either with the Kretschmann or with the Otto configurations (see Section 2.1). In the latter case, calculation of the normalized mean-squared electric field intensities showed that optimum intensity is achieved for angles slightly above the critical angle and water phase thickness below 2 µm.[24, 34] On the other hand, adsorbates on thin metals films (Kretschmann configuration) can exhibit hugely strong IR absorption.[14] This surface enhancement is at the origin of the so-called surface enhanced infrared absorption (SEIRA) spectroscopy technique. The enhancement is only significant for the chemisorbed first layer (it diminishes within a few nanometers from the surface) and is strongly dependent on the island structure of the metal film, which is determined by the film thickness and the deposition rate. The fact that SEIRA spectroscopy has the same surface selection rule as reflection absorption spectroscopy can be explained by assuming that the electric field is normal to the local surface of metal islands.[14] Similarities between SEIRA spectroscopy and SERS enhancement mechanisms have been pointed out. In this way, the enhancement of the electric field at the film surface due to the exaltation of localized plasmons of the metal particles has been proposed (electromagnetic mechanism). Additional chemical effects have been suggested to contribute also to the SEIRA phenomenon.[14]
2.4 Selection rules and vibrational frequency shifts

The dominant interaction between long-wavelength radiation and molecules is of dipole character, so only transitions involving vibrational states coupled by a dipole operator will be observable (selection rules for electric dipole transitions). The electric dipole transition probability between the $\Psi_i$ and $\Psi_j$ states is given by $P_{ij} = \langle \Psi_i | \mu | \Psi_j \rangle$. Since the dipole moment can be resolved into three spatial components, $P_{ij}$ will be different from zero if any one of the three component integrals ($P_{ij}^x$, $P_{ij}^y$, $P_{ij}^z$) is nonzero. Using symmetry arguments and group theory, this condition is satisfied when the symmetry representation of any one of the three component integrals of $P_{ij}$ contains the totally symmetric representation.

However, an additional surface selection rule for an adsorbate on a metal electrode surface must be considered according to the results in Section 2.2. Since $\Psi_i$ is usually the vibrational ground state (totally symmetric state) and defining the surface normal as the $z$ direction, the additional imposition of the surface selection rule for metals implies that $\Psi_j$ must transform as $z$. Thus, only vibrations with $P_{ij}^z$ component nonzero will be dipole allowed. This result has several consequences from an experimen- tal point of view. First, the signal-to-noise ratio in the spectra of adsorbed species is increased by working with $p$-polarized light. Second, changes in the spectra collected with $s$- and $p$-polarized radiation can be envisaged as a tool to distinguish between surface and solution species in spectro-electrochemical experiments with the external reflection configuration. Since solution species are randomly oriented in the solution layer probed by the IR beam, the corresponding bands should be observed both with $p$- and $s$-polarized light. In contrast, bands for the vibrational modes of adsorbed species that fulfill the surface selection rule (i.e., with a nonzero component of the dipole moment perpendicular to the electrode surface) will not be observed with $s$-polarized light. However, this criterion must be handled with care since the changes of the reflectance of $s$- and $p$-polarized light at a given wavenumber as a function of the thickness of the solution layer depends on the angle of incidence and the wavenumber of the incident radiation itself. In this way, $s$-polarized light could be much less sensitive to solution species than $p$-polarized light when working at high angles of incidence. In addition, the polarization plane for the incident linearly polarized radiation can be slightly rotated from that provided by the polarizer due to the spectro-electrochemical optics (including reflections at the air/window and window/solution interfaces).

Another point to be considered here is the relation between the vibrational modes of a given adsorbate and those corresponding to the isolated molecule. When an $N$-atom species is adsorbed on a solid it contributes with $3N$ extra kinetic freedom degrees to the overall system. Among them, the translational freedom degrees of the isolated molecule have to be converted into new vibrational modes involving the vibration of the adsorbate against the surface. Whether the remaining $3N - 6$ (or $3N - 5$) internal vibrational modes of the adsorbate are perturbed with respect to the internal modes of the isolated molecule depends on the strength of the interaction with the surface. This perturbation will be minimal if physisorption is produced. On the other hand, when chemisorption takes place, significant changes in the frequencies in some or in all the internal vibration modes of the adsorbate may occur as a consequence of major rearrangements of the bonding pattern. In a first approximation, the chemical factor, which results from the bonding configuration, the coordination of the substrate atoms and the local chemical environment (including coadsorbed species, and the influence of the same neighboring molecules at finite coverage, $\theta$) determines the sensitivity of the IR spectra to the metal substrate. In the same way, additional contributions to this frequency shift are related to the interaction of the adsorbed dipole with its surface image and the mechanical renormalization upon adsorption.

As a general rule, singleton frequencies ($\nu_0$) on metals (vibration frequencies of adsorbates for $\theta \rightarrow 0$) are always shifted towards lower wavelength values than the corresponding in gas phase. On the other hand, it is experimentally found that the vibrational frequencies of the adsorbate are always function of the coverage, even when no change in the adsorbate configuration occurs. Two contributions to the frequency shift with respect to the singleton frequency, $\Delta \nu (\theta)$, can be distinguished: the vibrational coupling between adsorbed species, $\Delta \nu_{\text{bb}} (\theta)$, and the static shift, $\Delta \nu_{\text{ss}} (\theta)$. Since only molecules of the same identity (i.e., the same vibrational frequency) couple strongly, coupling and static contributions can be experimentally resolved by using isotopic mixtures, providing information about the nature of the chemisorption bond as well as the adsorbate interactions. The extent of the coupling among dipoles depends on the molecular polarizability along the direction of the vibration, the coverage, the lattice sum and the dipole orientation. The contribution of the static shift results from the chemical contributions (adsorbate–metal bonding) and the static dipole. Coverage changes can produce changes in the electronic density distribution between adsorbate and metal. This would imply modifications of the vibrational frequencies of both internal and adsorbate–metal modes. Several explanations have been proposed in the frame of molecular orbital theory that.
involves changes in the extent of backdonation from the metal to the unoccupied 2π* orbital of adsorbed CO.[35–37]

2.5 Natural halfwidths and intensities

Chemical bonding and dipole image not only produce shifts in the frequency values but also influence the halfwidth, line shape and intensities of adsorbate vibrational bands.[6, 21, 22] There are two kinds of mechanisms that account for band broadening: the homogeneous and the inhomogeneous mechanisms. The first one can be due, according to the uncertainty principle, to a shortening of the lifetime of the vibrationally excited state (decay due to energy dissipation). If electron–hole pairs are created the oscillator can interact with them, and the lifetime of the vibrational excited state diminishes due to the periodic charge fluctuation. In addition, if the frequency of the oscillator lies near some substrate phonon transition, coupling with surface phonons could produce. Another process, called dephasing (i.e., decay of the temporal correlations of the oscillations due to impulsive elastic collisions, which induces a phase shift) can be claimed to explain temperature dependent broadening of internal modes.

On the other hand, a spatial nonuniform distribution of interacting oscillators and the occupation of nonequivalent adsorption sites produce a lack of order in the adsorbate overlayer. An inhomogeneity in the distribution of the oscillator frequencies measured produces the inhomogeneous line broadening. In addition, an asymmetry in the line shape can be observed when the spectral resolution is adequate. A variety of band shapes can be expected depending on whether a random occupation or an island formation on surface metal occurs. If both adsorbate islands and lattice gas regions are present on the metal surface, two overlapping or separate bands could be registered.

Experiments clearly show that the intensity of an adsorbate bands strongly depends on the adsorbate coverage. In Section 2.2 we approached this problem within the three-phase model by relating the effective thickness appearing in equation (16) with the adsorbate coverage of a (sub)monolayer film. From a microscopic point of view, a linear relation between the integrated absorption intensity and the adsorbate coverage can be expected in the absence of adsorbate–adsorbate interactions. This behavior is predicted from the theoretical treatment developed by Persson[38] which considered the interaction between the dipole moment of the adsorbed molecule and the electric field at the metal surface. Even if absolute coverages cannot be calculated from the integrated intensity of an adsorbate band alone, the latter can be used to monitor changes in the adsorbate coverage from a semi-quantitative point of view. However, it has to be kept in mind that the adsorbate–dipole interaction with the substrate and with the neighboring adsorbate molecules, at finite coverage, influences the magnitude of the integrated intensity, and may give rise to nonlinear intensity-coverage plots. Furthermore, coupling between juxtaposed oscillators having distinct frequencies can also take place with a significant intensity transfer from the low- to the high-frequency band.[39] This phenomenon is characteristic of dense layers of adsorbates with relatively high vibrational polarizabilities.[39] Under these conditions, relative coverages calculated from the ratio between the high- and low-frequency integrated band intensities could be overestimated.

2.6 Band position shift with the electrode potential

Changes in the frequencies of the vibrational bands in the spectra of adsorbates at the electrode/solution interphase are often observed when the electrode potential is varied. The frequency change induced by the potential is usually called the Stark-tuning rate. Two mechanisms have been proposed in order to explain this experimental fact.[40, 41] The first is based on the electronic transfer between the molecular orbitals of the adsorbate and the substrate. The second is based on the presence of strong electric fields across the double layer and their effects on the molecular polarizability.

In the electronic transfer mechanism, filled adsorbate orbitals of adequate symmetry can transfer electrons to empty metal orbitals through σ-overlap. Next, an electronic transfer from filled d-orbitals of the metal to empty π* adsorbate antibonding orbitals (back-donation) can occur. Depending on the relative importance of the π*-bonding and σ-bonding interactions, the frequency of the adsorbate vibrational mode will decrease or increase with respect to solution species. On the other hand, if the electrode potential is made more negative, the back donation is reinforced and the adsorbate metal bond weakened, so the frequency will be shifted to lower values. On the contrary, when the electrode potential is made more positive, the adsorbate metal bond is straightened and the frequency will be shifted to higher values. New insight on the Stark-tuning behavior is achieved from quantum-chemical calculations, by using the density functional theory and finite cluster approach, to compute energy and vibrational properties of CO and NO adsorbed on hexagonal Pt-group metal surfaces as a function of the external interfacial field.[42–44] It is found that the field-dependent νM–CO behavior has different components, with π-bonding mainly responsible for the blue-shift of νM–CO and the decrease of the metal–CO bond length, this effect being
offset increasingly toward more negative electrode potentials due to the contribution of σ-bonding and steric repulsion.

The electric field mechanism is based on the changes of the molecular polarizability under the influence of a strong electric field that is present across the electrochemical double layer. This is usually known as the electrochemical Stark effect. According to the Gouy–Chapman–Stern model, very high electric fields (near $10^9 \text{ V m}^{-1}$) are predicted to exist. Changes in the vibrational frequency can be expected from the interaction of this field with the dipole moment of the adsorbate. Lambert[41] has proposed a theoretical treatment based on the perturbation of the energy potential function of the adsorbate by the electric field. This perturbation results in a modification of the curvature of the energy potential function, and so a change in the frequency of the adsorbate mode will occur. On the other hand, this large value of the electric field, $E$, can produce significant effects on adsorbates in which large polarizability changes with bond distance exist. If a large component of the polarizability derivative, $\partial \alpha / \partial Q_k$, lies in the normal direction to the surface and the electric field is increased in its magnitude, the band intensity can be enhanced. It is due to the contribution of an additional induced component to the transition dipole matrix element, $P_{ij}$, (the intensity of a transition is proportional to the square of this magnitude) as shown by:

$$P_{ij} = \left\langle \Psi_i \left| \frac{\partial \mu}{\partial Q_k} Q_k \Psi_j \right| \right\rangle + \left\langle \Psi_i \left| \frac{\partial \alpha}{\partial Q_k} Q_k \Psi_j \right| \right\rangle E$$

(21)

As in the Raman scattering, the existence of a gradient of polarizability can favored the observation of transitions, which are forbidden by the surface selection rule (induction of a dipole moment component in the direction of the field on permanent dipoles, which are parallel to the electrode surface).

3 EXPERIMENTAL ASPECTS

3.1 Experimental set up and cell design

Typical optical arrangements used for in situ IR spectroscopy experiments are shown in Figure 6. Mirrors are used to direct the IR beam to the electrode surface at a given angle of incidence (see below). The reflected beam is then collected and directed to the detector. The number and characteristics of the folding mirrors vary from one design to another.[8, 26, 34] Reducing the number of mirrors down to two diminishes both reflection losses and changes in the polarization plane of the incident beam. A static linear polarizer is used in linear polarization experiments (Figure 6a), whereas a polarizer and a photoelastic modulator are employed in polarization modulation experiments (Figure 6b). In both cases, either a dispersive or a Fourier transform (FT) spectrometer can be employed. The latter has several advantages over conventional grating spectrometers,[46] including higher energy throughput and accuracy in frequency determination. Higher speed in data collection is also achieved since a wide spectral range can be explored at the same time. This point facilitates greatly the accumulation and averaging of spectra collected under the same experimental conditions in order to increase the signal-to-noise ratio. Finally, it has to be noted that, except for potential or polarization modulation experiments, the optical path of the IR beam has to be purged in order to eliminate CO$_2$ and water vapor. This can be achieved either by maintaining a small overpressure of dried air (or nitrogen) or by applying a gentle vacuum.
Many different designs have been reported in the literature for thin-layer external reflection spectro–electrochemical cells. Figure 7 shows a sketch of a typical glass cell designed for thin layer external reflection experiments, which is based on the cell previously reported by Iwasita et al. Most of the elements of this thin layer cell are common with those of cells used in internal reflection experiments performed with the Otto configuration. A window of a material transparent to the IR radiation is attached at the bottom of the cell. A teflon joint is used to prevent leakage between the window and the cell. The cell has entries for the reference and counter electrodes as well as for gases and solution. The latter allow the dosing and replacing of the solution containing a given substance while controlling the electrode potential. The working electrode surface is placed in a special teflon holder at the end of a glass plunger which can be adapted to samples of different shapes and sizes.

In the optical configuration sketched in Figure 6(a), the spectro–electrochemical cell is placed in a vertical configuration, at the top of the reflectance accessory, and out of the spectrometer chamber. In this way, all the steps in the experimental procedure, including the replacement of the working electrode and its alignment prior to the collection of the spectra, can be done without losing the purge in the spectrometer chamber. In addition, keeping the cell vertical facilitates the use of the dipping technique for the recording of cyclic voltammograms. The latter can be used to determine the cleanliness and surface order of the oriented surface. Once these two aspects have been checked, the electrode surface, which must be as parallel as possible to inner side of the window, is pushed against the window to form a thin layer of solution.

Various materials and shapes have been used for the window by the different authors. Calcium fluoride is probably the most popular window material in external reflection experiments due to its chemical stability. Severe IR absorption takes place at wavenumbers lower than 1100 cm\(^{-1}\) especially for prismatic (thick) windows. In some other cases, barium fluoride can be employed since it allows the study of the spectral region between 1100 and 800 cm\(^{-1}\). However, this material is more soluble in water than calcium fluoride and special care has to be taken when working in sulfuric acid solutions due to the formation of barium sulfate. Regarding the shape of window, either flat or beveled windows can be used to work at fixed angle of incidence. In the first case, refraction at the air/window interface determines the angle of incidence at the electrode/solution and, consequently, the intensity of the electric field at the electrode surface. For a flat CaF\(_2\), the maximum angle at the electrode surface is ca. 50° far from grazing incidence. Higher angles are achieved working at normal incidence with prismatic windows beveled at 60°. Both hemispherical and hemicylindrical windows allow the possibility of varying the angle of incidence. In addition, it has to be noted that hemispherical and hemicylindrical elements of high refraction index can be used to collimate the IR beam in ATR experiments, thus correcting the dispersion in the focusing beam of most transmission spectrometers and achieving an exact angle of incidence. This point has been taken into account when designing the optical layout and the spectro–electrochemical in Refs. 34, 47.

Mass transport problems in thin layer cells can be solved by using special windows, which allow the collection of spectra under hydrodynamic flow conditions. In this respect, Roth and Weaver have proposed the use of a CaF\(_2\) window featuring a central small hole into which a 0.7 mm platinum tube was epoxyed. These authors showed that flowing the working solution through the thin layer in concentric fashion eliminates solution bands in the IR spectra since it is possible to maintain a constant composition of the thin layer irrespective of the processes taking place at the electrode surface. Some other authors have reported different designs of flow cells for spectro–electrochemical experiments. Nichols and Bewick have designed a flow cell where the working electrode had a 0.5 mm hole drilled at its center and hydrostatic pressure was applied from an elevated reservoir containing the test electrolyte. Suction was applied through the working electrode in order to maintain a constant flow.
rate. A more sophisticated design has been proposed by Roe et al.\textsuperscript{[51]}

In a series of recent papers, several groups have described the use of temperature controlled cells for in situ IR spectro–electrochemical experiments.\textsuperscript{[52–55]} In the cell designed by Korzeniewski’s group,\textsuperscript{[52, 53]} sensing and heating elements are located in the working electrode (Figure 8) whereas the cell, constructed from standard glass components and equipped with a trapezoidal calcium fluoride window, is insulated by aluminum housing (Figure 9). On the other hand, Christensen’s group in Newcastle used a jacketed cell heated (or cooled) by water and mounted in special plates that can be either heated resistively (temperatures above ambient) or cooled by flowing a coolant through inner channels (temperatures below ambient).\textsuperscript{[54]}

Spectro–electrochemical cells employed for internal reflection experiments with the Kretschmann configuration are similar to those described above for external reflection except for the working electrode, which in the former case is a thin metal layer deposited on the window surface. At the same time, total reflection conditions require the use of windows of high refraction index materials such as zinc selenide, germanium or silicon. Osawa et al. used typically a 20 nm thick film of gold evaporated on a hemicylindrical silicon prism.\textsuperscript{[14]} The electric contact with the working electrode can be achieved through a thin copper lead placed between the teflon joint and the prism. Multiple reflections at the electrode surface, which can enhance the signal-to-noise ratio, could be obtained by using trapezoidal prisms.\textsuperscript{[8, 12, 56]} However, a single reflection can be enough to reach a good signal-to-noise ratio when surface-enhanced IR absorption takes place at the electrode surface.

3.2 Sampling techniques and data processing

One of the main problems of in situ IR experiments under electrochemical conditions is related with the strong attenuation of the IR intensity reaching the electrode surface due to absorption from the solvent. Moreover, a very low number of adsorbed molecules is sampled by the IR beam in comparison with transmission experiments. The first problem is that the single beam spectra obtained at a given potential in an external reflection experiment are dominated by features corresponding to the vibrational modes of the solvent even with a thin layer configuration.\textsuperscript{[17]} In this way, strong bands at ca. 3500 and 1650 cm\textsuperscript{−1} appear in the spectra obtained for aqueous solutions corresponding to the O–H stretching and bending modes, respectively.\textsuperscript{[57]} This is also the case in internal reflection experiments except for the intensity of these bands, which are much lower than in the case of external reflection experiments since the thickness of the solution layer probed by the IR beam is also lower. In order to reduce the contribution of solvent absorption to background of the spectra, potential difference techniques are usually applied. The simplest approach consists of collecting spectra at two different potentials and calculating the resulting potential difference spectrum either as changes in reflectivity at a given wavenumber

$$\frac{\Delta R}{R} = \frac{R_2(\nu) - R_1(\nu)}{R_1(\nu)} \quad (22)$$

or as

$$-\log\left(\frac{R_2(\nu)}{R_1(\nu)}\right) \quad (23)$$

where the subscripts 2 and 1 refer to the sample and reference potentials, respectively. Absorption bands will appear in the potential difference spectrum if either the concentration or vibrational frequency of a given species changes with the electrode potential. In the latter case, which is typical for adsorbed species in their potential range of stability, bipolar bands are observed. Absolute bands appear in the spectra associated with changes in the concentration of the corresponding species, either adsorbed or in solution. According to equation (22) negative-going bands (decrease in reflectivity) would correspond to species which exist at higher concentration at the sample than at the reference potential. Conversely, positive-going bands (increase in reflectivity) correspond to species existing at higher concentrations at the reference than at the sample potentials. The opposite behavior holds if spectra are calculated in absorbance units according to equation (23). It has to be noted that, even if potential difference spectra are calculated, background shifts often take place in the spectral region of strong absorption of the solvent.
Figure 9. Cell assembly for IR spectro–electrochemical measurements at above ambient temperatures. (a) Glass chamber with optical window attached. (b) Glass chamber mounted in an insulated housing. (Reproduced from Kardash et al. (1999)[53] with permission from Elsevier Science.)

Thus, uncompensated solvent bands may appear that disturb the spectra for species that absorb in the same frequency region. To avoid this effect in the case of experiments in aqueous solutions, water can be replaced by deuterium oxide for which the O–D stretching and bending modes absorb radiation at around 2500 and 1200 cm$^{-1}$, respectively.[57]

The signal-to-noise ratio in potential difference spectra of adsorbed layers is related both to the surface concentration and the extinction coefficient of adsorbed molecules and is often very low. This situation can be improved by averaging spectra collected under the same experimental conditions. This can be easily done in experiments performed with a FT spectrometer by accumulating a large number of interferograms at each potential (the signal-to-noise ratio is proportional to the square root of the number of interferograms). However, this approach has several problems related to the time needed to collect each single beam spectrum. First of all, it limits the possibility of collecting time-resolved data in potential step experiments. A second problem related with the accumulation of a large number of interferograms is that of the consumption of the species in the thin layer cavity when an irreversible reaction takes place at either the sample or reference potentials. Reaction products out of the thin layer can also diffuse out of the thin layer cavity, giving rise to changes in their concentration during collection of
the spectra. Finally, background shifts and CO₂ and water vapor absorption in the spectrometer chamber takes place when a long period of time elapses between the collection of the sample and reference spectra. This latter problem can be overcome when working with reversible systems for which the stationary concentration for a given species at (or near) the electrode surface depends only on the electrode potential. Then the potential step experiments can be repeated many times and a low number of interferograms collected at each potential. Finally, they are co-added to obtain the single beam spectrum at each potential. This is the so-called subtractively normalized interfacial FT IR spectroscopy technique (SNIFTIRS).

In addition to the average of a large number of spectra, other techniques are useful for increasing the signal-to-noise ratio in the spectra of adsorbed species, based on the modulation of either the potential (electrochemically modulated IR spectroscopy (EMIRS)) or of the polarization of the IR beam (polarization modulationIRRAS (PM-IRRAS)). In the case of EMIRS,[8, 19] the electrode potential is modulated at a given frequency, \( \omega_c \), (close to 10 Hz) between two potentials chosen to induce reversible changes either in the coverage or in frequency of a given mode of the adsorbed species. Spectra are collected with a dispersive spectrometer and a thin-layer configuration is used. Synchronous analysis at the frequency \( \omega_c \) allows the discrimination of unmodulated information coming from species other than the adsorbate. In this respect, no purging of the optical path is needed. Because of the modulation of the electrode potential, which is maintained as the spectral range is slowly scanned, irreversible processes cannot be studied with EMIRS. Most of the data obtained with this technique concerns adsorbed CO in its range of stability. Hence bipolar bands appear in the corresponding EMIRS spectra.

PM-IRRAS experiments take advantage of the surface selection rule to discriminate absorption from surface and bulk species. In this way, the photoelastic modulator is used to alternate the state of polarization of the IR beam from s- (parallel to the electrode surface) to p- (normal to the electrode surface) polarization.[8, 20, 58] After demodulation of the reflected beam, the spectra are plotted as the ratio \((I_p - I_s)/(I_p + I_s)\), where \(I_p\) and \(I_s\) stand for the intensities of the reflected p- and s-polarized radiation, respectively. As in the case of EMIRS, polarization modulation experiments discriminate between absorption from adsorbed and bulk (in the solution or gas phases) species. In addition, spectra with absolute bands are obtained at a single electrode potential allowing quantitative estimations from intensity of the bands. However, both the wavelength-dependent response of the photoelastic modulator and the differences in the regions sampled by s- and p-polarized radiation in spectro-electrochemical external reflection experiments give rise to contributions to the spectra background. These contributions often have to be corrected by making a ratio of spectra collected at two different electrode potentials. PM-IRRAS experiments can be performed either with a dispersive or with a FT spectrometer.[8, 20, 58] In the latter case, the use of a lock-in amplifier to demodulate the signal detector limits the velocity of the moving mirror of the Michelson interferometer, thus limiting its stability and the signal averaging capability of the spectrometer.[59] The use of real-time sampling electronics has been shown to avoid this limitation.[59]

As discussed above, kinetic measurements can be carried out with a FT spectrometer. The highest temporal resolution is determined by the time needed to collect one interferogram, which is limited by the mechanical stability of the moving mirror, and can be as low as 10–20 ms for a rapid scan interferometer at 16 cm⁻¹. To go below the millisecond regime a step-scan interferometer is needed to replace the constant linear scan of the moving mirror in conventional interferometers by a step-by-step change of the optical retardation.[60] Step-scan experiments can be performed in the so-called frequency and time domains.[60] In the first case, one of the mirrors is dithered at a fixed frequency to provide a modulation of the IR beam (phase modulation). In the time-domain, data are collected with both mirrors being completely stopped. The system is perturbed at each optical retardation (for example, by a potential step in the case of an electrochemical system) and the signal at the detector is measured as function of time. Then, the system is driven back to the initial state (reference potential) and the perturbation is applied at the next retardation value. The signal measured at a given time for the different optical retardation values is used to reconstruct the interferogram associated with this value of time. Time-resolved spectra are then computed by FT of these interferograms. Obviously, the studied system has to be reversible in order to have the same response for every one of the potential steps applied at each optical retardation. Time resolution in this kind of experiment is limited by the response of the a/d converter and the detector rise time and could be in the range of several tenths of nanoseconds. Osaka’s group at Hokkaido University reported the first time domain step-scan experiments with an electrochemical system.[64, 61–63] They performed experiments with a Kretschmann configuration in order to attain a low time constant, which cannot be achieved in external reflection experiments. Moreover, enhancement of the IR absorption under SEIRA spectroscopy conditions help in reducing the number of interferograms needed to have a good signal-to-noise ratio. This point is also crucial since the time needed to collect one interferogram at each time value during the step scan experiment is about 10 min at a resolution of 16 cm⁻¹.
Step-scan experiments in the frequency domain have also been reported for electrochemical systems.\cite{64,65} As a first application, the phase modulation introduced by the step scan interferometer can be used to remove the cross-talk between the frequency and the potential modulation in FT-EMIRS experiments, as first shown by Budevska and Griffith.\cite{64} In these experiments, the electrode potential is sinusoidally modulated at a given frequency, and in-phase and quadrature spectra are measured with a lock-in amplifier. With the same tactics, Ataka et al.\cite{65} applied potential-modulated step-scan FTIR spectroscopy to the study of electrode kinetics of very fast reactions (below the time constant of the cell). From the analysis of the spectra collected at various modulation frequencies, they obtained kinetic and dynamic information in a similar way as it is done in impedance spectroscopy. The method is applied by the authors to the study of the charge transfer reaction at a gold electrode surface covered by a self-assembled monolayer of 4-mercaptopyridine.

Another technique introduced by Osawa’s group for the spectroscopic characterization of electrochemical systems is the two-dimensional correlation analysis of time (or potential) dependent IR spectra (2D-IR spectroscopy).\cite{14} Two-dimensional spectra are generated by a cross relation analysis of dynamic fluctuations induced by an external perturbation (e.g., the electrode potential for an electrolytic system). Following the generalized 2D-IR spectroscopy formalism proposed by Noda,\cite{66} the correlation intensity between two arbitrary wavenumbers $\nu_1$ and $\nu_2$ is given by

$$\phi(\nu_1, \nu_2) + i \psi(\nu_1, \nu_2) = \frac{1}{\pi T} \int_0^\infty \tilde{Y}_1(\omega) \tilde{Y}_2(\omega) d\omega$$

where $\tilde{Y}_1(\omega)$ and $\tilde{Y}_2(\omega)$ represent, respectively, the FT of the dynamic spectra at wavenumbers $\nu_1$ and $\nu_2$. The latter is calculated as the difference between the time dependent and the average spectrum in the time interval explored.

The real and imaginary components of the correlation function, $\phi$ ($\nu_1, \nu_2$) and $\psi$ ($\nu_1, \nu_2$), are referred to as the synchronous and asynchronous correlation, respectively. Synchronous and asynchronous two-dimensional correlation spectra are constructed by plotting $\phi$ ($\nu_1, \nu_2$) and $\psi$ ($\nu_1, \nu_2$) over a spectral plane defined by $\nu_1$ and $\nu_2$. The synchronous spectrum characterizes the coherence of dynamic fluctuation of IR signal measured at two different wavenumbers. If the variations of the two IR signals are similar to each other, cross peaks appear at coordinates ($\nu_1$, $\nu_2$) and ($\nu_2$, $\nu_1$). Conversely, peaks appear in the asynchronous spectrum if the IR signals vary at different rates and/or phases. Finally, the sign of the synchronous and asynchronous peaks are related with the relative direction and the temporal relationships between the intensity fluctuations at $\nu_1$ and $\nu_2$.

4 APPLICATIONS

Many examples can be found in the literature regarding the application of IR spectroscopy to the in situ characterization of the electrode/solution interphase.\cite{8–20} Most of them are related to: (i) the spectroscopic characterization of adlayers of strongly bonded adsorbates, such as carbon monoxide and nitric oxide; (ii) the spectroscopic study of the reversible anion (and water) adsorption–desorption processes; (iii) the study of the adsorption and electrocatalytic oxidation of small organic molecules. Here we will review a limited number of these examples. The reader is also referred to the ensemble of excellent review papers previously published\cite{8–20} to complete the picture presented here, especially in the case of anion adsorption at single crystal electrode surfaces.\cite{11,12,17}

4.1 Strongly bonded adsorbates at single crystal electrode surfaces: carbon monoxide and nitric oxide

Carbon monoxide is probably one of the most studied adsorbates under electrochemical conditions. CO adlayers are strongly bonded at the surface of platinum-group metals, being stable in a wide potential range. These adlayers can be easily characterized from the spectroscopic point of view due to its relatively strong absorption in the IR region. Well-defined C–O stretching spectra are obtained, which are strongly sensitive to both the structure and composition of the electrode surface.\cite{18,67} Additional interest for the study of the CO adlayers comes from the observation that adsorbed CO is often one of the species formed upon adsorption and/or electrooxidation of many small organic molecules, including those that has been envisaged as fuel for fuel cells.\cite{8,15,17}

Figure 10 shows results of a typical spectro–electrochemical experiment performed with a CO-covered Pt(111) electrode.\cite{68} Voltammograms in this figure correspond to the flame annealed surface before (a) and after (b) dosing CO at 0.10 V followed by argon purging to remove dissolved CO. After the oxidation of the CO adlayer (c), the initial state of the surface is recovered (d). According to these results, spectra for the CO-covered surface can be obtained at potentials below 0.60–0.70 V and a proper reference spectrum must be recorded at potentials around 0.90 V. In this way, spectrum for the CO adlayer at 0.10 V is reported in Figure 10. Note that changes in reflectivity are plotted as a function of the wavenumber, according to equation (22). Thus, positive- and negative-going bands correspond to species predominating at the reference and sample potentials, respectively. In this way, the positive-going band at 2344 cm$^{-1}$ corresponds to the asymmetric
O–C–O stretching of the CO$_2$ molecules formed upon CO oxidation at the reference potential and remain in the thin layer cavity. The intensity of this band can be considered as proportional to the CO coverage as far as diffusion of CO$_2$ molecules out of this thin layer is negligible during the time needed to collect the reference spectrum (true for large electrodes and short collection times). Negative-going bands at 2063 and 1782 cm$^{-1}$ correspond to the adsorbed CO molecules at the sample potential. Similar features have been reported by different authors for the saturated CO adlayers formed at low potentials on the Pt(111) electrode surface.\cite{67, 69–71} The observed bands can be ascribed tentatively to the C–O stretching of atop and three-fold hollow CO molecules on the basis of the comparison between the observed frequencies and data available for carbonyl compounds. This classical approach, which involves the determination of the local adsorption site from the internal vibrational mode of a diatomic adsorbate, has to be used with caution since it has been shown to lead to wrong conclusions in several adsorbate–metal systems.\cite{72}

However, the aforementioned assignments were later confirmed from density functional theory (DFT) cluster model calculations.\cite{43, 44}

The IR spectra obtained for the CO-saturated Pt(111) electrode are sensitive to small changes in the adsorbate coverage related to changes in the electrode potential and/or to the presence of CO in the working solution. Figure 11 shows two sets of spectra collected for a CO-covered electrode in a CO-saturated (A) and a CO-free (B) solution. Since these spectra are plotted in absorbance units (equation (23)), absorbate bands are now positive-going. Subtle differences between the spectra at 0.10 V in these two series regard the frequency of the bands, which appear at slightly higher wavenumbers in the presence of dissolved CO, and the intensity of the three-fold hollow band. In situ STM\cite{70} and XRD\cite{73} measurements have shown that the CO molecules form a compressed (2 × 2)-3CO adlayer at the Pt(111) electrode surface in this potential range. As the potential is stepped positively, the (2 × 2)-3CO adlayer disappears, this process being triggered by the oxidation of a small fraction of the adsorbed CO adlayer.\cite{73} The range of stability of the (2 × 2)-3CO adlayer is slightly wider in the presence of dissolved CO.\cite{73} Figure 11(b) shows that, in the CO-free solution, the three-fold hollow band is replaced at 0.50 V by a new band at 1845 cm$^{-1}$ that can be related to bridging CO molecules.\cite{43} This change can be considered a consequence of the transformation of the (2 × 2)-3CO structure.\cite{70, 71} Despite the controversy about the existence of an ordered CO structure when bridge bonded CO is detected, it seems clear that the three-fold hollow band can be taken as diagnostic of the ordered (2 × 2)-3CO structure.\cite{71} At this point one could try to connect the fraction of CO molecules occupying either atop or three-fold hollow sites in this surface structure with the relative intensities of the corresponding adsorbate bands in Figures 10 and 11. However, this kind of quantitative analysis has to be done with caution due to coupling-induced intensity transfer from the lower- to the higher-frequency band. This effect greatly distinguishes the ratio
of the integrated intensities of these two bands (2 : 1) from the 1 : 2 site occupancy deduced from the real space surface structure.[39, 70]

Figure 11(a) shows also the effect of the electrode potential on the spectra for adsorbed CO in the range between 0.10 and 0.50 V. In the presence of dissolved CO, CO coverage remains constant in this potential range. Both atop and three-fold hollow bands are shifted towards higher wavenumbers with an average slope of 25 and 45 cm$^{-1}$ V$^{-1}$. Recent DFT calculations have confirmed that this behavior is mainly related to changes in the back-donation of the electronic density of the metal to the 2\pi$^*$ molecular orbital of adsorbed CO\[^{42, 44}\] (see Section 2.6). At the same time, DFT analysis shows that increasing back-donation at higher electrode potentials favors an increase in the CO coordination,\[^{44}\] which is consistent with experimental observation of the (2 × 2)-3CO structure with three-fold hollow CO.

Nitric oxide adlayers can be formed at platinum electrodes and the corresponding spectra obtained in a similar way to that described above for adsorbed CO.\[^{18, 74, 75}\] Differences between these two adsorbates are related to the conditions for the formation and stability of the adlayer. Saturated NO adlayers can be formed by immersing the platinum electrode surface at open circuit in either a NO-saturated or an acidic solution of nitrite. The resulting adlayer survives after rinsing the sample with ultrapure water and is stable under electrochemical conditions between 0.50 and 0.90 V as reflected by curve (a) in Figure 12(a) for a NO-covered Pt(100) electrode. The NO adlayer can be reductively stripped from the electrode surface (curve b) and the clean surface recovered (curve c). From this behavior it is clear that the spectra collected between 0.50 and 0.90 V can be referred to the single beam spectrum obtained at 0.10 V. The inset in Figure 12(a) shows the spectrum obtained at 0.50 V. The frequency of the negative-going band around 1611 cm$^{-1}$ is in the typical region for the N–O stretching mode of NO adsorbed at a Pt(100) surface under ultrahigh vacuum (UHV) conditions.\[^{76}\] On the other hand, the positive-going

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Figure 12. (a) Voltammetric profiles obtained in a 0.1 M HClO$_4$ solution after the formation of a saturated NO adlayer on a Pt(100) electrode surface. The inset shows the spectrum obtained for such adlayer at 0.5 V (100 interferograms were collected at 8 cm$^{-1}$). (Reproduced from Climent et al. (1999)\[^{73}\] by courtesy of Marcel Dekker Inc. (b) Spectra collected for the NO-saturated Pt(100) electrode at different electrode potentials (same conditions as in (a) except for the test solution that was prepared in deuterium oxide). Reproduced from Rodes et al. (1998)\[^{74}\] with permission from Elsevier Science.)
The American Institute of Physics.

Coverage effects on the spectra of adsorbed species can be observed in Figure 13(a, b), which report series of coverage-dependent spectra of NO adsorbed on Pt(100) and Pt(111), respectively. Surface coverages ranging from zero to saturation were obtained by increasing the dosing time from the NO-containing solution. In the first case, a single adsorbate band is observed in the N–O stretching region between 1590 and 1630 cm$^{-1}$ at all coverage range. This band is blue-shifted as the NO coverage increases, due mainly to dipole–dipole coupling. In the case of the NO-covered Pt(111) electrode, coverage effects are more complex. The spectrum at the lowest coverage in Figure 13(b) shows two adsorbate bands at 1666 and 1440 cm$^{-1}$. Increasing NO coverage gives rise to the increase of the relative intensity of the high wavenumber feature, which is shifted towards higher wavenumbers. At saturation, a single band is observed at 1680 cm$^{-1}$. This behavior is similar to that observed under UHV conditions and could be explained as due to a change in the bonding site of adsorbed NO, namely from bridging to atop sites as NO coverage increases. However, both experimental data and DFT calculations support the idea that three-fold hollow sites are preferentially occupied by adsorbed NO in the whole coverage range.

In the preceding example, we have discussed the spectra for a single adsorbate on well-ordered metal substrates. However, the spectra for adsorbates such as carbon monoxide or nitric oxide can provide indirect information about the composition and/or the structure of the topmost layer of a given substrate in more complex situations. A good example of molecularly intermixed layers are those formed by co-adsorbed NO and CO molecules on different transition metal electrode surfaces. These adlayers can be formed by displacing NO molecules from saturated NO adlayers exposed to diluted CO solutions. Figure 14 shows two sets of spectra showing the effect of selectively removing one of the adsorbates. In the initial state, the spectra for the mixed CO + NO adlayer show bands in the ranges 2060–2035 and 1830–1860 cm$^{-1}$ for atop and bridge bonded CO together with a band between 1580 and 1612 cm$^{-1}$ corresponding to adsorbed NO. Oxidative stripping of adsorbed CO gives rise to the removal of the C–O stretching bands and an increase of the intensity of the N–O stretching band. Assuming that NO coverage remains constant, this latter observation indicates that the N–O stretching absorbance is partially suppressed in the CO + NO adlayer by intensity transfer to the C–O stretching modes at higher wavenumbers. This provides strong support to the idea that the CO + NO adlayer is largely intermixed. The same conclusion can be derived from spectra (B) in Figure 14, showing the effect of the reductive stripping of adsorbed NO from the mixed layer. From these spectra it is clearly seen that the presence of co-adsorbed
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Figure 14. Representative IR spectra for mixed CO–NO adlayers on ordered Pt(100) at 0.5 V SHE, showing the effect of: (a) the electrooxidative removal of CO for $X_{\text{NO}} \sim 0.25$, and (b) electroreductive removal of NO for $X_{\text{CO}} \sim 0.3$. (Reproduced from Tang et al. (1999) [82] with permission from Elsevier Science.)

NO gives rise to a significant increase in the atop to bridging ratio for adsorbed CO.

Another set of interesting examples involves the use of the CO molecule as a surface probe for the spectroscopic characterization of metal substrates modified by foreign adatoms. Chang and Weaver [83] have found that the presence of bismuth leads to a selective blocking of the bridge sites as witnessed by the disappearance of the C–O stretching band at 1830 cm$^{-1}$. This observation is consistent with the presence of bismuth atoms intermixed with the adsorbed CO layer. The spectra of adsorbed CO have also been used to gain information about the growing mode of palladium on a platinum substrate. As a difference with the previous example, CO adsorbs both on palladium and platinum atoms when dosed on a Pt(111) electrode partially covered with palladium atoms. Figure 15 shows a series of C–O stretching spectra for CO-saturated palladium-covered Pt(111) electrodes at different palladium coverages. Experimental conditions to generate the palladium layers are...
similar to those employed by Inukai and Ito,\textsuperscript{[84]} except for the absence of palladium ions in the working solution when CO is dosed. The spectrum at the bottom in Figure 15 correspond to the bare Pt(111) surface and shows the typical bands at 2066 and 1781 cm$^{-1}$. The deposition of increasing amounts of palladium gives rise to a new band in the spectra of adsorbed CO at ca. 1900 cm$^{-1}$, which increases with palladium coverage. This feature can be assigned to the C–O stretching of CO molecules adsorbed at palladium atoms. As this new feature increases, the intensity of the bands at 2066 and 1781 cm$^{-1}$ decrease. However, these bands are observed even at high palladium coverages at nearly the same frequency as for the palladium-free surface. In addition, the C–O stretching spectra for the palladium-covered electrode shows the same potential dependence as in the case of the uncovered Pt(111) surface, with the band at 1781 cm$^{-1}$ being replaced by a band at ca. 1840 cm$^{-1}$ at potentials above 0.50 V. These observations can be understood by assuming that palladium islands are formed on the Pt(111) substrate in such a way that they coexist with relatively wide uncovered platinum domains at intermediate palladium coverages.

4.2 Carbon monoxide at nanoparticles and films

Carbon monoxide can be envisaged as a surface probe for substrates other than flat and well-ordered samples. Nanoparticles\textsuperscript{[85–88]} and thin films\textsuperscript{[89–93]} have been also spectroscopically characterized under electrochemical conditions by analysing the corresponding in situ spectra in the C–O stretching region. Friedrich et al.\textsuperscript{[86]} have studied platinum nanoparticles deposited on gold electrodes and found size-dependent vibrational spectra for these CO-covered particles that can be used in some way to characterize the size distribution in a given sample. The size of the platinum particles in freshly prepared samples was found to be around 3 nm from transmission electron microscopy analysis. The authors compared the spectra for a freshly prepared sample saturated with adsorbed CO (Figure 16a) with that obtained with an aged sample for which particles with sizes around 2.2 and 8.5 nm were detected (Figure 16b). Differences between the spectra obtained for two kinds of samples are evident only at low particle coverage. In this way, the C–O stretching spectra in Figure 16(b) show two bands around 2013 and 2046 cm$^{-1}$, the latter being absent.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectra.png}
\caption{IR spectra of the C–O stretching region for CO adsorbed on Pt particles at different particle coverages and with (a) homogeneous and (b) inhomogeneous size distribution. Spectra were collected at (a) 0.08 and (b) 0.1 V RHE. (Reproduced from Friedrich et al. (1998)\textsuperscript{[86]} with permission from Elsevier Science.)}
\end{figure}
in the spectra obtained for a homogeneous sample. These two bands can be ascribed to linearly bonded CO adsorbed on the small and large particles, respectively. On the other hand, the differences in the spectra obtained at different particle coverage could be understood by invoking the effect of dipole–dipole interactions between CO molecules adsorbed at neighboring particles, which would increases as particle coverage increases. However, the authors concluded from their analysis that both dipole field interactions and the effect of the coordination of the platinum sites are too weak to explain the frequency shift with respect to CO bonded on a polycrystalline platinum electrode as well as the observed platinum coverage effect. Thus, they postulate the existence of chemical effects implying an increased back-donation into the CO $2\pi^*$ orbital in the case of the smaller particles. Marked particle-coverage effects could be due to particle–substrate interactions.

Results have also been reported for CO adsorbed on thin film electrodes. In the corresponding experiments, advantage is taken of some enhancement effect of the IR absorption that makes the spectra more sensitive to the presence of adsorbed species. Thin films of evaporated[14, 92] or sputtered[93] metals deposited onto a transparent germanium or silicon prisms have been used in ATR experiments using the Kretschmann configuration. Figure 17 shows spectra obtained at different electrode potentials in a CO-saturated solution for a gold film as evaporated. STM experiments have shown that the thin film electrode consisted of islands of 50–80 nm in diameter whose surface is constructed with wide (111) terraces separated by steps.[94] The corresponding cyclic voltammograms are similar to those reported in the same electrolyte for well-ordered Au(111) surfaces.[94, 95] STM imaging shows also flame annealing increases the order and preferential orientation of the gold crystallites.[92] The spectra in Figure 17 show a main C–O stretching band at 2110–2136 cm$^{-1}$ and small bands at 2020–2045 and 1925–1975 cm$^{-1}$ (for the flame-annealed sample) that vanishes at potentials 0.20 V when adsorbed CO is oxidized. The authors assigned these bands to linearly bonded CO. On the other hand, the spectra for the flame-annealed film showed an additional band in the range 1925–1975 that has been ascribed to bridge bonded CO.[92] Besides the sensitivity of the C–O stretching spectra to the surface order, the main observation from the spectra in Figure 17 is the high intensity of the main absorption band. This feature is ca. 20 times more intense than the bands typically reported for CO adsorbed on gold in external reflection experiments.

A different approach when working with thin films has been followed by Sun et al. who prepared electrodeposited thin films of platinum-group metals[89, 96] and alloys[97] on glassy carbon substrates and collected spectra for adsorbed CO as well as for other adsorbates in a external reflection configuration. The authors observed abnormal IR effects consisting of enhancement of IR absorption as well as inversion and broadening of the IR bands. Figure 18 allows the comparison between the IR spectrum of adsorbed CO on a massive platinum electrode (a) and that corresponding to CO adsorbed on a platinum film deposited on a glassy carbon electrode (b). Both spectra were obtained following the same experimental procedure, i.e., a single beam
spectrum collected for the CO-covered surface that collected after the oxidative stripping of the adsorbed layer was referred to. As expected, a positive-going band is observed in both cases at 2344 cm$^{-1}$ corresponding to carbon dioxide formed at the reference potential. Regarding adsorbed CO, a negative-going band appears in the CO stretching region in the spectrum for the massive platinum electrode. However, the bands observed in this frequency region for the platinum film, including a small band below 1900 cm$^{-1}$, are positive-going and much more intense than in the previous case. Similar behavior is observed for palladium, rhodium, and ruthenium films. The authors observed potential-dependent adsorbate bands that appear in the frequency region characteristic of each metal but always inverted with respect to the expected decrease in reflectance for an adsorbate present at the sample potential. This behavior, which was related by the authors to the layered structure of the crystallites formed by electrodeposition, was found to depend on the thickness of the metal layer in the case of ruthenium films with a maximum enhancement around 86 nm.

Abnormal effects (namely, enhanced IR absorption and/or anomalous bipolar bands in the potential-difference spectra) have also been observed in the external reflection spectra of CO adsorbed on metal films and nanoparticles deposited on glassy carbon or metal electrode substrates. Ortiz et al. have reported the spectra for CO adsorbed at iridium films electrodeposited at glassy carbon electrodes. They pointed out that the anomalous bipolar bands first reported by Christensen et al., indicating higher reflectance for the CO-covered electrode, can be understood on the basis of well-known reflectance laws. In this way, the authors recall that adsorption of ca. a monolayer of a strong absorber on the surface of a moderately reflecting substrate can increase the reflectivity of the latter. On the other hand, Bjerke et al. have shown that the abnormal behavior in the spectra of CO adsorbed on platinitized platinum electrodes increased as the deposition time increased. These authors have demonstrated that both the enhancement of the IR absorption and the distortion of the CO peaks in the spectra of CO-covered platinum film deposited on a platinum substrate can be simulated by using the Bergman representation to calculate the effective dielectric function for such a film. They assumed that the platinum film is formed by islands and that percolation between the platinum islands grows with increasing deposition times.

4.3 Water and anion adsorption

This section is devoted to one of the applications of SEIRA spectroscopy to the characterization of electrochemical interfaces, namely the study of water and anion co-adsorption at metal film electrodes. In the previous section we illustrated one of the important features of SEIRA spectroscopy experiments, that is, the enhanced sensitivity with respect to external reflection experiments. This is an important characteristic of the SEIRA spectroscopy experiments, but not the only one. As we have already mentioned, a thin layer of solution (much thinner than in the case of the external reflection experiments) is probed by the IR beam in the internal reflection configuration. Furthermore, enhancement in IR absorption decays as the distance from the surface increases. Thus, SEIRA spectroscopy is especially suitable for the study of water adsorption at the electrode surface. Osaka et al. reported the SEIRA spectra for a gold film in perchloric and sulfuric acid solutions. Figure 19 shows a series of potential-dependent spectra obtained in a sulfuric acid solution. These spectra are referred to that obtained at a potential low enough to assure a negligible anion adsorption. A positive-going band appearing in the range 1155–1195 cm$^{-1}$ at potentials higher than 0.50 V correspond to the S–O stretching of adsorbed sulfate anions, of which surface concentration increases with the electrode potential. Positive and negative-going bands which can be assigned to the O–H stretching ($\nu_{\text{OH}}$) and H–O–H bending ($\delta_{\text{OH}}$) modes of water, respectively appear around 3500 and 1650 cm$^{-1}$. These water bands change clearly at a potential around 0.50 V, which is close to the potential of zero charge (pzc) of the Au(111) electrode surface in the working solution employed. These changes affect both the sign and the frequency of the bands. In this way, changes in absorption in the $\nu_{\text{OH}}$ region gives rise to a negative-going at ca. 3505 cm$^{-1}$ for potentials below 0.50 V whereas it appears to give a positive-going band at 3480 cm$^{-1}$ at higher potentials. At the same time, negative-going bands are observed at 1616 cm$^{-1}$ in the $\delta_{\text{OH}}$ region at potentials below the pzc that becomes a positive-going band at 1654 cm$^{-1}$ at higher potentials. An additional negative-going band appears at 1730 cm$^{-1}$ that can be assigned to the doubly degenerated H–O–H bending mode of hydronium cations.

More information about the potential-dependent co-adsorption of water and anions can be obtained from two-dimensional correlation spectra calculated from the potential-difference spectrum discussed above. This information concerns, for example, the detection of absorption bands that are either too weak or ill-resolved in the potential-dependent IR spectra. In this way, a close inspection of the spectra reported in Figure 19 indicates that the absorption band observed at potentials above the pzc in the $\nu_{\text{OH}}$ region is rather asymmetric, suggesting the existence of some contribution at ca. 3200 cm$^{-1}$. The cross peaks at (3505, ~3200) and (~3200, 3505) in the
corresponding asynchronous 2D-IR correlation spectrum for the potential region between 0 and 0.80 V shown in Figure 20(a) confirms the existence of a broad \( \nu_{\text{OH}} \) absorption band at ca. 3200 cm\(^{-1}\). This frequency range is typical of the O–H stretching of ice\(^{[57]}\) thus indicating the existence of an ice-like structure for interfacial water. The same conclusion was derived from the spectra obtained in perchloric acid solutions.\(^{[95]}\) Figure 20(b) shows the synchronous correlation spectrum constructed from spectra between 0.80 and 1.20 V in Figure 19. This spectrum shows that the band at 1654 cm\(^{-1}\) changes synchronously with the sulfate band at 1180 cm\(^{-1}\), indicating also that water molecules (and not hydronium cations) are incorporated in the anion layer at potentials above the pzc. The synchronous

![Figure 19](image1.png)

**Figure 19.** Series of potential-dependent IR spectra for a thin film Au(111) electrode in a 0.1 M H\(_2\)SO\(_4\). The spectrum collected at 0 V RHE was used as the reference. The inset shows the spectrum at 0.48 V. (Reproduced with permission from Ataka and Osawa (1998)\(^{[94]}\) © American Chemical Society.)

![Figure 20](image2.png)

**Figure 20.** Asynchronous (a) and synchronous (b) 2D-IR spectra constructed from the spectra reported in Figure 19 between (a) 0 and 0.8 V and (b) 0.8 and 1.2 V. (Reproduced with permission from Ataka and Osawa (1998)\(^{[94]}\) © American Chemical Society.)
two-dimensional correlation spectrum in Figure 20(b) also shows the presence of a band at 955 cm\(^{-1}\), which also changes synchronously with the sulfate band at 1180 cm\(^{-1}\), and can be ascribed to the totally symmetric \(\nu_1\) mode of adsorbed sulfate.

The information derived from the spectra in Figures 19 and 20 can be related with the potential-dependent reorientation of water molecules around the pzc.\(^{[94]}\) At potentials below the pzc, water molecules seem to be adsorbed with their two hydrogen atoms closer to the electrode surface, thus diminishing the extent of hydrogen bonding with water molecules in solution. This fact implies a lowering of the \(\delta_{OH}\) frequency and an increase of the \(\nu_{OH}\) frequency. At potentials above the pzc, hydrogen atoms of adsorbed water are oriented towards the solution and hydrogen bonding takes place to form an ice-like structure. Adsorption sulfate anions form additional hydrogen bonds with co-adsorbed water giving rise to an increase in the intensity of water bands due to the orientation of the water dipole along the surface normal. The change in the orientation of water molecules (from H-down to O-down) around the pzc has also been invoked by Iwasita and Xia\(^{[98]}\) to explain potential-dependent changes in the \(\nu_{OH}\) and \(\delta_{OH}\) regions of the external reflection spectra obtained for the Pt(111) electrode in a perchloric acid solution.

Finally, a third advantage of the SEIRA is the feasibility of time-resolved experiments due to the lower time constant of the cell (around 1 ms\(^{[65]}\)) when compared to that in the external reflectance experiments. As discussed in Section 3.2, a step-scan interferometer is needed to go below the sub-millisecond time scale. The kinetics of several fast reactions have been studied by Osawa et al. with this approach including the reduction of heptil viologen on a silver film\(^{[61]}\) and the adsorption of fumaric acid on gold.\(^{[92]}\) In a recent paper, the same authors reported the study of the kinetics of copper desorption from gold in sulfuric acid solutions.\(^{[63]}\) Copper adsorption on Au(111) electrodes takes place with the consecutive formation of a disordered phase, a honeycomb \((\sqrt{3} \times \sqrt{3})\) phase, formed 2/3 of a monolayer of copper atoms and 1/3 of monolayer of sulfate anions, and, finally, a \((1 \times 1)\) phase. The adsorption of sulfate anions can be easily detected by the presence of the corresponding S–O stretching band the frequency of which is sensitive to the presence of co-adsorbed copper atoms and also to the local environment given by each adsorbed phase. The authors used the time-dependence of the S–O stretching band of adsorbed sulfate to study the kinetics of the desorption process of the \((\sqrt{3} \times \sqrt{3})\) phase during a potential step from 0.1 to 0.3 V saturated calomel electrode (SCE). The series of spectra in Figure 21 shows how the intensity of the absorption band at 1214 cm\(^{-1}\) for adsorbed sulfate diminishes during the removal of the \((\sqrt{3} \times \sqrt{3})\) phase. This desorption process is paralleled by the desorption of water molecules hydrogen-bonded to sulfate anions as witnessed by the absorption band at 1645 cm\(^{-1}\). The change in the integrated intensity of the S–O stretching band can be compared in Figure 22 with the corresponding current transient measured during the potential step. The latter can be decomposed in two processes, noted I and II in the figure, corresponding to a random and a nucleation-and-growth desorption process, respectively. If we assume the proportionality between the intensity of the S–O stretching band and the sulfate coverage, the time-dependent behavior of the former clearly indicates that process (I) is related to sulfate desorption.

Figure 21. Series of time-resolved IR spectra of sulfate adsorbed on the thin film Au(111) electrode. The spectra were collected with a resolution of 1 ms during the potential step from 0.1 to 0.3 V SCE in a 0.1 M H\(_2\)SO\(_4\) + 1 mM CuSO\(_4\) solution. (Reproduced from Ataka et al. (2000)\(^{[63]}\) with permission from Elsevier Science.)
4.4 Organic molecules

Many spectroscopic studies have been carried out on the adsorption and electrooxidation of small organic molecules such as formic acid, methanol and other related C<sub>1</sub> and C<sub>2</sub> compounds.<sup>[8, 12, 15, 17]</sup> Here we will focus on the electrooxidation of ethanol at platinum single crystal electrodes in order to show how IR spectra can be used for the detection of both adsorbed and solution intermediates. Figure 23(a–c) shows results obtained by Xia <i>et al.</i><sup>[99]</sup> for a Pt(100) electrode surface immersed in a 0.1 M CH<sub>3</sub>CH<sub>2</sub>OH + 0.1 M HClO<sub>4</sub> solution. Spectra in Figure 23(b) are referred to the single beam collected at 0.05 V just after contacting the working solution at this electrode potential for which no irreversible process takes place in the ethanol-containing solution. Increasing the electrode potential gives rise to different absorption bands in the corresponding spectra. Bands appearing at 2055 and 1866 cm<sup>−1</sup> correspond to atop and bridge bonded CO<sup>[67]</sup> whereas the band at 2341 cm<sup>−1</sup> can be assigned undoubt- edly to the asymmetric stretching of dissolved CO<sub>2</sub>. The intensities of these three bands are plotted in Figure 23(c).
Vibrational spectroscopy

as a function of the electrode potential. It can be concluded first that CO is formed in the same potential range where a pre-peak is observed in the corresponding voltammogram (Figure 23a). Second, the ratio between atop and bridge CO increases as the electrode potential is raised up to 0.50 V. The onset of the CO₂ production at this electrode potential fits with the decrease of the bands for adsorbed CO. Finally, the maximum production of CO₂ is observed at 0.80 V, coincidently the main oxidation peak observed in the cyclic voltammogram. Other adsorbed and solution species can be detected from the spectra reported in Figure 23(b). Bands appearing at 1712 and 1282 cm⁻¹ at potentials higher than 0.65 V can be ascribed to the formation of acetic acid. The band at 1407 cm⁻¹ corresponds to adsorbed acetate anions coming from acetic acid.

From the data discussed above, it can be concluded that two reaction pathways operates in the oxidation of ethanol at platinum electrodes. A direct oxidation pathway leads to the formation of acetic acid (and adsorbed acetate) whereas an alternative pathway involves the cleavage of the C–C bond to form adsorbed CO, which is further oxidized to carbon dioxide. Shin et al.[100] used isotopic labelling of the alcohol and methyl groups to decide which group is at the origin of the species detected as a function of the electrode potential. The spectra obtained for the Pt(111) electrode surface in the presence of ¹³CH₃¹²CH₂OH and ¹²CH₃¹³CH₂OH are reported in Figures 24 and 25. The spectra in Figure 23(a) for the C–O stretching region show that adsorbed CO in the low potential region comes mainly from the oxidation of the alcohol group. At potentials above 0.1 V SCE, the dominance of the ¹²C–O stretching band (appearing between 2000 and 2050 cm⁻¹) irrespective of the labeled group can be explained by the effect of dipole coupling when a relatively high CO coverage is attained. Under these conditions, intensity transfer from the ¹³C–O stretching appearing between 1960 and 2000 cm⁻¹ is expected. The spectral range analyzed during the oxidation of the labeled ethanol molecules is extended to the frequency region between 2500 and 1200 cm⁻¹ in the spectra reported in Figure 25, thus allowing the monitoring of the formation of carbon dioxide and adsorbed acetate anions. The frequency shift of the band observed

![Figure 24](image-url)  
**Figure 24.** IR spectra of CO formed during reaction of (a) ¹³CH₃¹²CH₂OH and (b) ¹²CH₃¹³CH₂OH at a Pt(111) electrode. Solutions contain 4 mM ethanol in 0.1 M HClO₄. Spectra were obtained while the potential was stepped in sequence from an initial value of −0.25 V SCE and the reference spectrum was recorded at 0.6 V. Spectral resolution is 4 cm⁻¹. (Reproduced from Shin et al. (1996)[100] with permission from Elsevier Science.)

![Figure 25](image-url)  
**Figure 25.** IR spectra of species formed during reaction of (a) ¹³CH₃¹²CH₂OH and (b) ¹²CH₃¹³CH₂OH at a Pt(111) electrode. The spectrum recorded at −0.25 V was used as the background. Other parameters are the same as in Figure 24. (Reproduced from Shin et al. (1996)[100] with permission from Elsevier Science.)
at 1406 cm\(^{-1}\) in the presence of \(^{13}\)CH\(_2\)\(^{12}\)CH\(_2\)OH down to 1387 cm\(^{-1}\) in the presence of \(^{12}\)CH\(_3\)\(^{13}\)CH\(_2\)OH is consistent with the assignment of these features to the symmetric O–C–O stretching of adsorbed acetate. The spectra in Figure 25 also shows that the asymmetric O–C–O–C stretching region appears earliest in the potential excursion when the methyl group is labeled with \(^{13}\)C atoms. This observation indicates that carbon dioxide is formed preferentially from the alcohol group, especially in the low potential region.

5 CONCLUSIONS AND PROSPECTS

In situ IR experiments can provide chemical and structural information about the electrode/solution interphase. Chemical information is related with the identification of both adsorbed and solution species, including intermediates and reaction products in electrocatalytic processes. On the other hand, structural information obtained from the spectra obtained for adsorbed species, which is related with the structure-sensitive character of the substrate–adsorbate and adsorbate–adsorbate interactions that determine the number and frequency of the adsorbate bands in the spectra. In some cases, including chemically modified surfaces, nanoparticles and films, an adsorbed molecule such as CO or NO can be envisaged as a probe to characterize the underlying electrode substrate. Obviously, the structural aspects in the IR spectra are better interpreted when experiments are performed with well-ordered single crystal electrode surfaces and parallel structural information about the existence of ordered adsorbate layers is also available from in situ STM or SXS experiments carried out under the same experimental conditions. Also related to interpretation of the IR spectra, new quantum-mechanical insights on the field-dependent chemisorption and on the intramolecular and metal–adsorbate stretching frequencies of adsorbate molecules are provided by DFT calculations.\(^{[42–44]}\)

At this point, it is worth recalling here two approaches that have been proven useful for the analysis of IR data obtained for the electrode/solution interphase. First of all, these data can be compared with those obtained either from IR experiments in different environments or from other vibrational techniques that can also be applied under electrochemical conditions. The first approach has been fruitfully explored by Weaver’s group at Purdue University by comparing in situ IR spectra for a given adsorbate–substrate system with data available for the same system under UHV conditions.\(^{[18, 101]}\) Modeling of the electrode/solution interphase has also been reported by dosing interfacial components onto clean metal surfaces under UHV conditions.\(^{[102]}\) Vibrational spectra for adsorbates at the electrode surface can also be obtained in situ by performing sum frequency generation (SFG)\(^{[103]}\) or SERS\(^{[104–106]}\) experiments. These vibrational techniques are intrinsically surface-selective and provide absolute bands at a given potential in such a way that potential-difference tactics are not necessary. In addition, SERS experiments give access to the far-IR region down to ca. 200 cm\(^{-1}\). This allows the study of metal–adsorbate vibrations, which cannot be observed with conventional IR experiments due to the low energy of standard IR sources. The use of synchrotron radiation is a promising alternative to overcoming this problem.\(^{[107]}\) Both SFG and SERS experiments have their own limitations from an experimental point of view. In the case of SFG, the use of an IR beam gives rise to the same problem of solvent absorption. Thus, a thin-layer configuration has to be used in external reflection experiments. Furthermore, the heating of the sample and the availability of tuned IR lasers in a wide frequency range are also problematic. Regarding SERS, the main drawback comes from the fact that surface enhanced scattering, which initially seemed to be limited to the so-called coinage metals (silver, gold and copper), is related to significant surface roughness factors. In this respect, it has to be mentioned that SERS can be applied for the study of molecules adsorbed on thin metal films electrodeposited at roughened gold substrates.\(^{[104, 105]}\) Nevertheless, the use of confocal Raman spectroscopy allows not only the collection of Raman spectra for adsorbates at moderately roughened transition metal electrodes,\(^{[106]}\) but also the study of different metal nanorod arrays applying a probe molecule strategy.\(^{[108]}\) Also, by employing a STM tip in order to achieve local electromagnetic field enhancement, the very weak surface enhancement at smooth metal surfaces can be surmounted.\(^{[109]}\)

Finally, we have to mention that ongoing experimental developments are continuously opening the field of application of IR spectroscopy in the study of electrochemical systems. In this way, the use of step-scan interferometry in combination with internal-reflection optics is allowing time-resolved spectroscopic studies of fast electrode processes.\(^{[14]}\) The study of temperature effects on adsorption and reactivity at electrode surfaces can also be envisaged now that proper cell designs allowing the control of the temperature of the electrode surface are available.\(^{[52–55]}\)

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