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Spectroscopic methods for the study of inter-phase zones under reaction conditions

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Abstract

Vibrational spectroscopy methods offer a number of possibilities to investigate the most different aspects of chemical interactions between solids and gases or liquids. The investigations can be performed to provide kinetic or dynamic information. Here we present a synthetic picture of the issue selecting and describing transmittance, reflectance, scattering and emission experiments performed in extremely different reaction conditions. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

High-temperature–high-pressure (HTHP) interactions between surfaces and gases or liquids originate an extremely anisotropic and dynamic environment where a series of reaction intermediates at steady state participate to the main repeating loop of a catalytic cycle and where molecular environments are repeatedly constructed and destructed generating periodical spatio-temporal evolutions.

The attempts to understand HTHP reaction environments examining simplified model situations using single crystal surfaces at low surface coverage have unveiled many aspects of this chemistry. However these attempts have also disclosed that HTHP inter-phase environments present unique features that are not reproduced in other experimental situations.

Some photons are able to penetrate this thin and unstable inter-phase matter, re-emerging with signs of its structural, electronic and chemical properties. Among these photons there are the ones of infrared and visible light. A number of experiments are possible and an arbitrary selection will be very briefly presented to span the range of the known possibilities and to suggest a creative manner to face the study of inter-phase regions and of catalytic phenomena.

This text does not want to be a review in the field; its main aim is to stimulate curiosity towards the spectroscopic approach in the study of catalytic phenomena. Hints on the theory, on the details of the spectroscopic methods and on the experimental results are reported; however a number of references are also given and the curious reader could find there more satisfaction. Each of the experimental techniques here mentioned could absorb the energy of an experimentalist for a number of years, however the approach to the investigation of inter-phase phenomena also demands an eclectic mind which could select and adapt the spectroscopic tools to look at the surface phenomena from different angles.

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Surface-sensitive techniques here summoned include IR external reflection and internal reflection spectroscopy, IR diffuse reflectance spectroscopy and Raman spectroscopy.

External reflection spectroscopies measure the light absorption phenomena on highly reflecting metal surfaces and the spectroscopic experiments are often performed under low pressure conditions. However some applications also include the study of the HTHP chemistry produced at the electrode–electrolyte interphase.

Internal reflection spectroscopies utilize an internal reflection element (IRE) in which the electromagnetic field of a propagating radiation wave is almost completely confined. The IRE can be realized with different materials and with very different shapes and is immersed in the environment to be studied. The electromagnetic field propagating through the IRE generates an evanescent field which penetrates for very short distances ($\approx 1\ \mu$) the surrounding medium allowing measurements of light absorption at interphases.

Diffuse reflectance IR Fourier transform (DRIFT) spectroscopy can investigate on HTHP inter-phase environments generated at the surface of polycrystalline sample placed inside flowing reaction environments in conditions in which inter and intra-particle diffusional limitations are avoided. The phenomenological treatment of Kubelka–Munk of the scattering phenomena and of spectrometers which utilize interferometers to modulate the incident IR radiation allows this kind of experiments inside reaction chambers where temperatures up to 900°C and pressures up to 5.0 MPa are reached. These spectroscopic experiments can be easily combined with mass spectrometry measurements of the reaction products allowing for parallelism between kinetic measurements based on reactant conversion and selectivities with inter-phase absorption features.

In conclusion a paragraph which reports on some of the possibilities of Raman spectroscopies which are also surface-sensitive techniques, is included. Examples of HTHP experiments performed to study the solid–gas interfaces originated by contacting powdered polycrystalline materials and gaseous environment will be given. Experimental solution in which the laser beam impinging on the samples can be periodically moved to avoid photochemical reactions and overheating of the surface will be also mentioned. The possibilities of surface enhanced Raman spectroscopy (SERS) will be briefly discussed in Section 6 and an extreme example of its application will be given.

2. External reflection spectroscopy and inter-phase studies

The reactivity occurring at smoothed metal layer surfaces can be examined with external reflection spectroscopy. Fig. 1 shows the reflection basic geometry of an infrared reflection absorption spectroscopic (IRAS) experiment. Referring to the figure the incident beam impinges the surface with an angle ϕ relative to the surface normal generating an incident plane; on the same plane lies the reflected beam.

The electric field experienced by molecules adsorbed on the metal has peculiar features which are determined by the interactions with the metal electrons. The theoretical treatments which describe the phenomena involved in IRAS usually resolve the electric field vector into components in the incident plane (P polarized) and perpendicular to the incident plane (S polarized) [1]. The theories indicate the way with which experiments must be attempted and the following three general statements are defined: (a) only radiations with a component parallel to the metal surface (p polarization) interact with adsorbed species and only vibration with a dipole moment perpendicular to the surface can be excited, (b) the incident

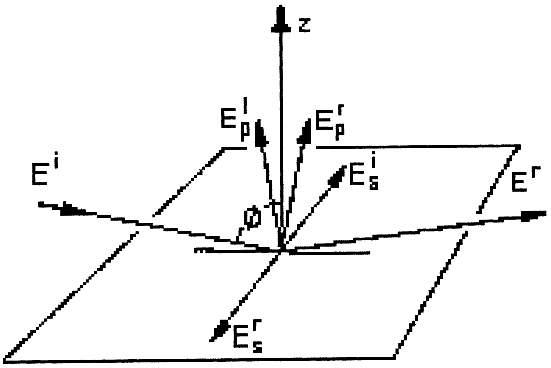

Fig. 1. The reflection geometry showing the s and p components of the electric fields of incident (E′) and reflected (E′) radiation.

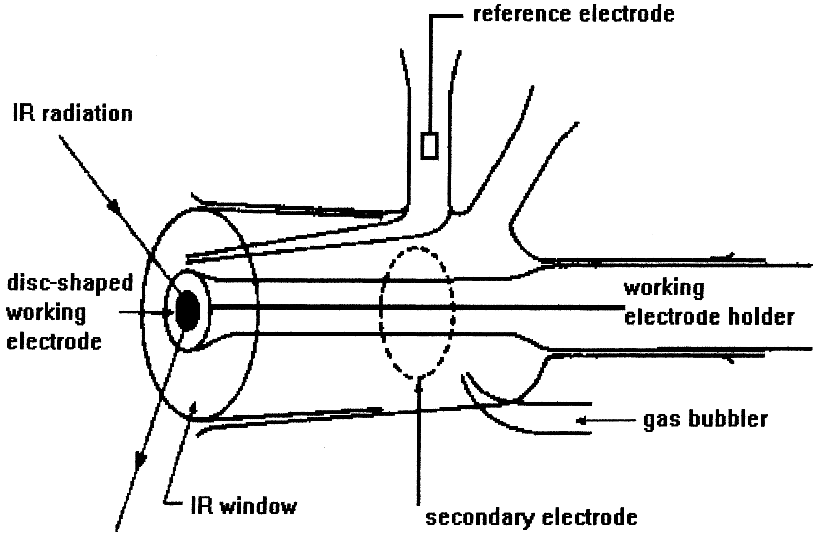

Fig. 2. Scheme of a cell for IRAS measurements during electrocatalytic reactions.

light should be reflected at the metal surface at grazing incidence, and (c) the most reflecting metal surfaces will yield the highest absorbances.

Indications coming from IRAS are related to geometry of adsorption, modification of electronic structure at increasing coverage, intermolecular interactions (ordering, island formation). The main historical activities performed with IRAS have been devoted to the study of CO adsorption on metal single crystals under UHV conditions and are described in a number of reviews and articles [2,3]. Studies which are more directly related to the chemistry of HPHT inter-phases have been performed during solid–liquid interactions between electrodes constituted by thin smoothed metal surfaces and electrolyte solutions containing reactive molecules. Due to the low amount of adsorbed species the deleterious influence of liquid or gaseous phase adsorption need to be minimized with thin layer electrochemical cells (see Fig. 2).

With this device IRAS has been performed while the electrochemical reactions were proceeding [4]. The electrocatalytic oxidations of small molecules such as CH_3OH, HCHO, HCOOH have been investigated with these means enlightening the changes in the absorption bands with the potential difference infrared technique [5]. This technique produces bipolar bands and allows to follow the extent of the reaction by modulating the electrode potential, respectively, from negative to positive potential. During the study of the electrocatalytic oxidations above mentioned the shift of C–O stretching bands maxima assigned to adsorbed CO_2 and to adsorbed CO has been related to charge distribution variation between the metal and the adsorbed molecules and indirectly to reaction rates. The major problems which limit the possibility of extending the range of experimental conditions are related to the very low amount of absorbing species. Spectra are produced at the metal surfaces due to very small changes in absorbance, typically from 10^{-2} to 10^{-6}. These small perturbations are difficult to analyze at high temperatures (at increasing temperature a band broadening is produced and the number of surface oscillators stabilized enough to be detected is reduced) and high pressures (due to the absorbance of the gaseous or liquid media). High intensity sources such as synchrotrons can in principle enhance the sensitivity but their application to this study has not been yet extensively attempted.

3. Experimental approaches to the inter-phase study with internal reflection spectroscopy (IRS)

Newton [6] observed that an ''evanescent field'' was produced in a lower index of refraction medium in

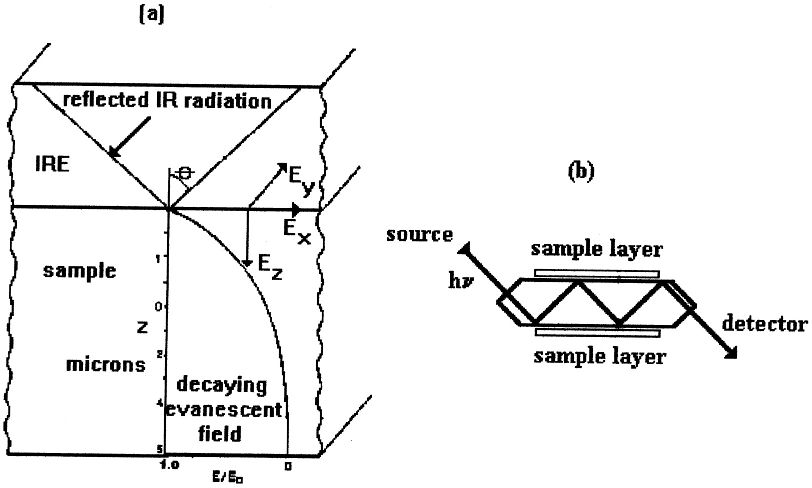

Fig. 3. Representation of the basic IRS experiment. The IR radiation propagates through the IRE and the evanescent field penetrates the rarer sample medium and decays exponentially with distance from the IRE/sample interface.

contact with a higher index refraction medium in which a propagating wave of radiation undergoes total internal reflection. The exploitation of this phenomenon for the production of absorption spectra begun in 1960 [7] and after the initial experimental and theoretical observation a number of applications were developed [8].

The basics of the IRS experiment are represented in Fig. 3. The IR radiation propagates through an internal reflection element (IRE) which have a very high index of refraction compared with the index of refraction of the surrounding medium in which an evanescent field is generated. This evanescent field decays exponentially with the distance from the IRE/surrounding medium interface and becomes very weak after 1–2 μm.

A variety of experimental configuration can be used to study the inter-phases with IRS [9]. In some cases the sample adsorbant has been fabricated into an IRE and exposed to the interaction with a liquid or a gaseous phase in HTHP conditions. IRE made of alumina has been used to study chemisorption of various molecules since 1970 [10]. In other experimental configurations the solid is deposited as a very thin film on the IRE such that its thickness is less than the penetration of the evanescent field. The IRE/adsorbant combination is then subjected to a flow of reactant. This experimental approach has been successful for the study of adsorption of gases on metal films [11]. In another way solid–gas or liquid–gas inter-phases are studied by equilibrating the adsorbant with the adsorbate and bringing in contact the surface of the adsorbant with the IRE [12]. Again the IRS can be used for the study of electrode solution inter-phases and these studies can be divided into two classes: those employing an IRE which also serves as an electrode [13] and those using a film coated on an IRE (the so called optically transparent thin layer electrode) [14]. Coated IRE include metal or metal oxide films on various substrates.

4. Diffuse reflectance spectroscopy of HTHP inter-phases

The first IR trasmittance studies on physisorption and chemisorption on porous glasses, silica gels and on silica supported metals were published, respectively, in 1940s [15] and 1950s [16]. Since then an enormous number of solid–gas interactions and surface reactions have been examined with transmittance IR spectroscopy in which solid particles are pressed into coherent, but still porous, discs that can be placed in the radiation beam. A number of reviews can be found on these works and some of them are mentioned in [17]. However although the relatively small pores in

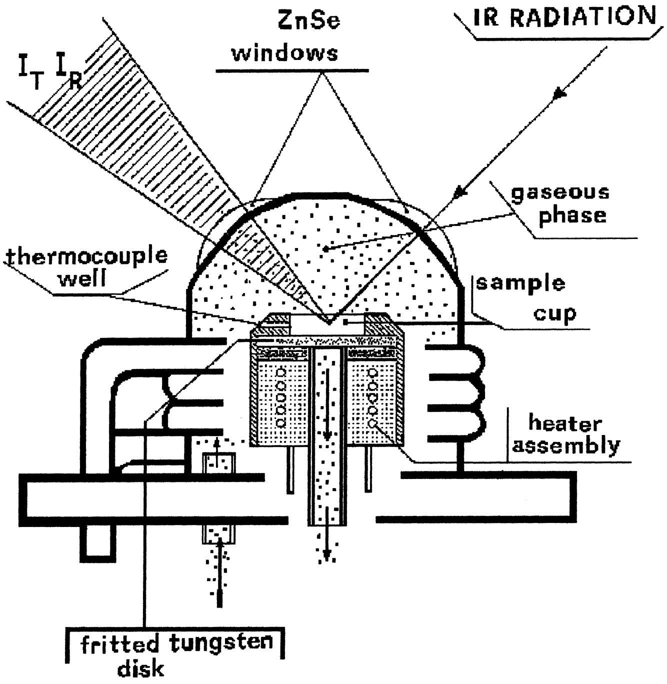

Fig. 4. Scheme of a catalytic reaction chamber equipped for HTHP DRIFT spectroscopy.

the disk allow contact between a gaseous reagent and the surface, when kinetic measurements are made to determine which surface species is catalytically active, it often turns out that for faster reactions, it is the diffusion of the reactant/products into or out of the pores which determine the reaction rate rather than the reaction at the surface. The use of Fourier transform techniques in conjunction with interferometry enabled new sampling methods in which inter and intra-particle diffusional limitations of molecules can be greatly reduced and in the great part of cases almost completely eliminated. Diffuse reflectance Fourier transform spectroscopy [18] does not require a compression of a powder into a self-supporting disk. It is sufficient to place the sample in a shallow cup exposed to an incident IR radiation beam which undergoes reflection, refraction and absorption before re-emerging at the sample surface. The diffusively reflected radiation is then collected by an elliptical mirror and focalized onto a detector. The interpretation of the diffuse-reflectance spectra is based on the phenomenological theory developed by Kubelka and Munk [19] which is a general treatment of beam-matter interaction seen as an extension of the Lambert–Beer treatment. What is relevant to this discussion is that DRIFT signals specific for molecular environments produced at inter-phases can be extracted from spectra collected in very drastic reaction conditions.

Fig. 4 shows the schematic of a DRIFT cell in which the powdered solid materials are deposited onto a fritted tungsten disc inside a heater. Gaseous flowing atmospheres can be admitted into these kinds of cell at pressures up to 5.0 MPa and temperatures up to 900°C. Reactant gases flow through the solid powders into the output line. This can be easily linked with a quadrupole mass spectrometer in order to have a contemporaneous indication on reaction products and inter-phase characteristics. A number of reactions including the very fast partial oxidation of natural gas have been examined with these methods [20].

5. Raman spectroscopy of HPHT inter-phases

The Raman effect – inelastic light scattering by molecular vibrations – is inherently weak (only one photon in a million is Raman scattered) and 10 years ago the possibility to apply Raman spectroscopy to the study of inter-phase regions would have been considered hardly feasible. The introduction of multichannel detectors [21], of a number of lasers in the UV, visible and near-IR region, the discovery of the surface enhancement effect of Raman signals (SERS) [22,23], the combination of near-IR laser excitation of Raman signals together with Fourier transform methods [24] have widened the horizons of the experimental situations that can be examined. Indeed the Raman experiment has been used as a direct structural probe to study inter-phase regions spanning from UHV conditions into HPHT conditions.

Briefly we mention that the widespread multichannel detectors compared to single channel detectors allow for a decrease in the acquisition time by a factor of 10^2 and for signal enhancement of a factor between 10^2 and 10^3. Instead the SERS effect discovery is not related to technical solutions which concern the spectrometer or the laser sources but to a physico-chemical effect first experimentally enlightened by Fleischman et al. [25]. A number of theoretical works have been published to discuss this experimental event. The electromagnetic theories [26] (EM) ascribe the giant enhancement to the presence of large electromagnetic fields produced by excitations of conduction electron resonances in the metal substrate. The chemical theories consider a charge transfer mechanism (CT) and assert that enhanced cross sections arise from the participation of adsorption-induced resonances [27]. We address the reader interested in technical solutions and theoretical works concerning Raman spectroscopy to the literature reviews mentioned in [28]. Here we mention a selection of few examples concerning HTHP experiments which could be performed by using the above mentioned technical solution and the SERS effect.

Solid–gas interaction between oxidic species and reactive molecules have been often studied [29] and interactions of gaseous reactants with zeolites have been particularly examined [30]. However to my knowledge the more drastic reaction environment successfully investigated had been the one generated at the surface of Ba and Mg mixed oxides, during catalytic partial oxidation of methane at 800°C and 1 atm [31]. An experimental solution often adopted to avoid overheating of inter-phase zone consists of an arrangement of rotating mirrors which avoid that the laser beam remains focalized on the same area for a long time [32] (see Fig. 5).

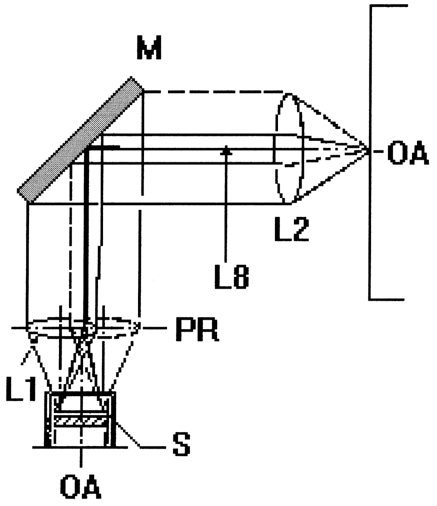

Fig. 5. Rotating lens system: LB – laser beam, OA – optical axis, M – plane mirror, L1 – condenser lens, L2 – telescope lens, S – sample surface, and PR – plane rotation.

SERS is now a well-established technique and is extremely selective for obtaining vibrational spectra at inter-phases. Interferences from bulk atmospheres or condensed phases are completely avoided [33]; only the Raman scattering of species which are formed at the inter-phases are affected by the giant surface enhancement. Although the choice of SERS active substrate is mainly restricted to silver, gold and copper other transition metal and other surfaces can be examined by depositing them as thin films on these metals [34]. In addition the combination of multichannel detectors and of SERS effect can provide a sensitive mean of following high pressure heterogeneous process in real time [35]. As already mentioned the SER effect is large on silver, gold and copper; however also other metals and Pt in particular have shown their ability to enhance surface electromagnetic fields. Fig. 6 shows the schematic of an electrochemical cell which has been used to collect SERS signals of Pt–O bonds generated onto a porous Pt electrode in the 100–200 cm^{-1} range at 350°C. The electrode was deposited on yttria stabilized zirconia (YSZ) which is an oxygen ion conductor. The signals appeared only after applying a small positive anodic current to the cell, i.e. pumping oxygen ions into a Pt electrode (see Fig. 7).

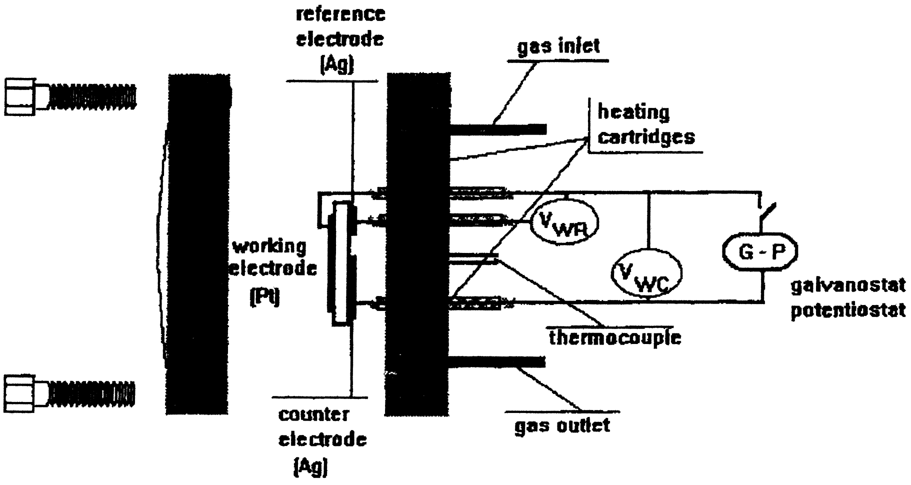

Fig. 6. Scheme of the cell for laser Raman experiments at the surface of a thin layer in a solid electrolite system.

These signals showed a transient behavior and followed the migration of the oxygen species from the metal solid-electrolyte gas three phase boundary zone onto the porous Pt electrode [36]. The experiment was defined to investigate on electrocatalytic reactions in which reaction rates can be changed up to a factor of 500 greater than the rate $I/2F$ (where I is the cell current) of the ions transport to or from the metal electrodes [37].

6. Conclusions

Till now I have discussed how the IR and Raman spectroscopies are employed in the investigation of HTHP inter-phases; however what I still have to say is something on the kind of information and how the information can be used to understand catalytic phenomena.

IR or a Raman signals inform the spectroscopist about the origin of a molecular bond about the structure of a molecular environment and about charge distributions. However, as already mentioned, the inter-phase zone contains a number of chemical species and many of them are inter-converting one into the other during a catalytic reaction. Fortunately the vibrational spectroscopies have intrinsic time constants which are below the life time of the most stable reaction intermediates (indeed ultrafast IR spectroscopy allows the observation of extremely short-lived intermediates and even species at the transition states [38]) and in principle the band width should be sufficiently sharp to allow assignments to individual molecular features. Temperature broadening and anisotropy of the reaction environment complicate the things but in some lucky cases, some of the reaction intermediates could be observed with simple experiments even in complex reaction environments [39].

Moreover a description of transition states and of the dynamics of catalytic phenomena can also be approached with IR emission spectroscopy; [40] with experiments not properly performed in HTHP conditions, but with molecular beams of reactants produced in "well known" quantum states and with high internal energy content. These reactant beams are collided with the catalytic surfaces and transformed into reaction products which desorb in translational and rotovibrational excited states from which decay emitting IR quantized radiation. The rotovibrational spectra which are originated through this process contain information of transition states and allow the dynamic descriptions of catalytic reactions. Dynamic descriptions deal with microscopic forces (bond length, bond angles, charge distributions, etc.) which persist between reacting species throughout the interaction. These forces can be constructed by quantum-mechanics as gradients on a potential energy hypersurface (PES). The state-to-state cross sections in PES are a measure of reaction probability and estimated on the

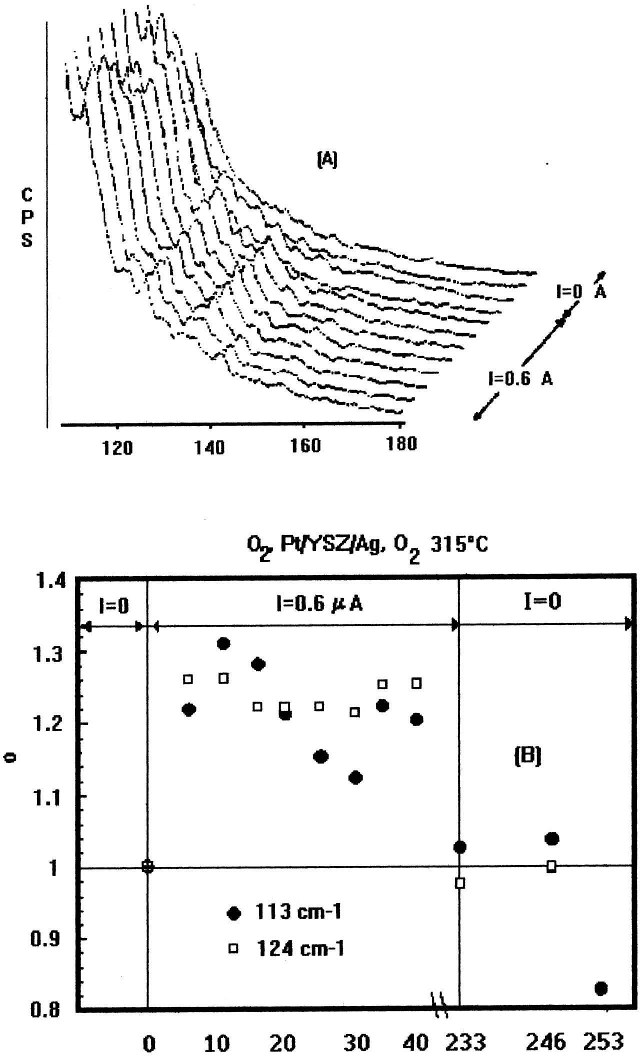

Fig. 7. (a) Sequence of spectra showing the temporal evolution of the Raman bands during a transient between I=0 and I=0.6 μA, and (b) normalized variations of the bands at 113 and 125 cm^{-1} under open and closed circuit conditions.

basis of theoretical and calculation procedures. IR emission spectrocopy indications are often the only way to evaluate the structure of the calculated PES and are a direct way to promote the development of theoretical understanding of reacting matter at interphases providing links between calculation and the experimental nature of the studied phenomena. Spectroscopic approach can hence provide a common field of verification for fundamental theories and can stimulate cooperation between theoretical and experimental chemists.

I conclude by saying that, being an applied scientist, the application of spectroscopic studies has satisfied in many occasion the need of understanding and promoted my capacity to define starting points for innovative catalytic technologies.

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