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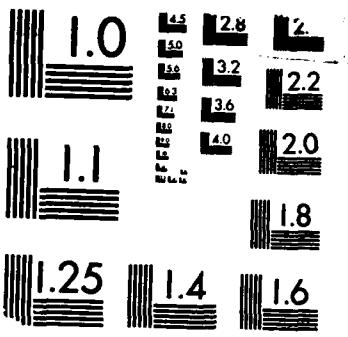

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In Situ Infrared Spectroelectrochemistry

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By

Stanley Pons
J. Foley

Prepared for Publication in

Analytical Chemistry

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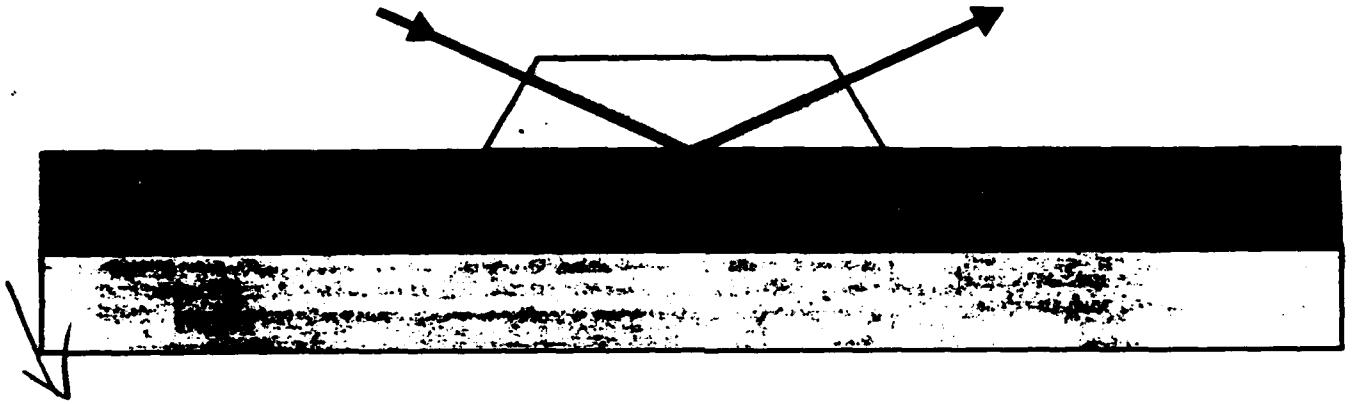
In Situ Infrared Spectroelectrochemistry



In situ infrared (IR) spectroelectrochemistry has become a viable experimental technique only within about the past five years, but it has already proved to be an important addition to the small number of in situ spectroelectrochemical methods currently in use (electron spin resonance spectrometry, ellipsometry, UV–visible spectrometry, resonance Raman, and surface-enhanced Raman spectrometry). The technique has found two broad areas of application.

- *Adsorption on electrodes.* In situ IR spectra can give information about the identity and molecular structure of adsorbed species and about the orientation and bonding of these species to the electrode surface.
- *Electrode reactions.* In situ IR spectra can conveniently be used to identify reactants, products, and intermediates of electrode reactions, both on the electrode surface and in solution. Species on the electrode surface can be distinguished from species in solution by varying the polarization state of the incident light.

In this article we will consider particularly the problems involved in obtaining IR spectra at the electrode–electrolyte interface and how such problems are overcome by cell design and signal-processing techniques. We will also discuss how the spectra are affected by the nature of the electromagnetic electric fields near an electrode surface and the additional information about surface species that can be gained from this phenomenon. Finally, some examples of applications of IR spectroelectrochemistry will be given. We start with some general points about IR radiation and its absorption by molecules, which are pertinent to much of the following discussion.

If a molecule is to absorb IR radiation, two conditions have to be met. First, there must be an electromagnetic electric field where the molecule is situated, oscillating at the same frequency as a vibration of the molecule. The probability of absorption of radiation is proportional to the square of the strength of this field. Second, during the vibration of the molecule there must be a change in dipole moment with a component in the same direction as the electric field vector (the direction of oscillation of the field). The mechanism of absorption involves interaction between the oscillating dipole moment and the oscillating electric field.

A beam of light incident on a plane surface (such as an electrode) can be considered to be made up of two components, s-polarized light, which has its electric field vector oriented perpendicular to the plane of incidence (and therefore parallel to the surface) and p-polarized light, which has its electric field vector oriented parallel to the plane of incidence (and therefore with components both parallel to and perpendicular to the surface). Either s-polarized light or p-polarized light can be selected, if desired, by placing an appropriately oriented optical polarizer in the path of the beam.

Experimental problems

There are two major problems in measuring IR spectra of species at the electrode–electrolyte interface. The other in situ spectroelectrochemical techniques do not share these difficulties to the same extent and were consequently developed earlier. One problem, which occurs whenever IR radiation is passed through a solution, is absorption of most of the radiation by the bulk solvent. This is especially serious if the solvent is water, which absorbs strongly throughout most of the mid-IR region. The other problem is one of sensitivity. The number of molecules under study is usually very small (less than a surface monolayer in some experiments), while conventional IR sources are weak and IR detec-

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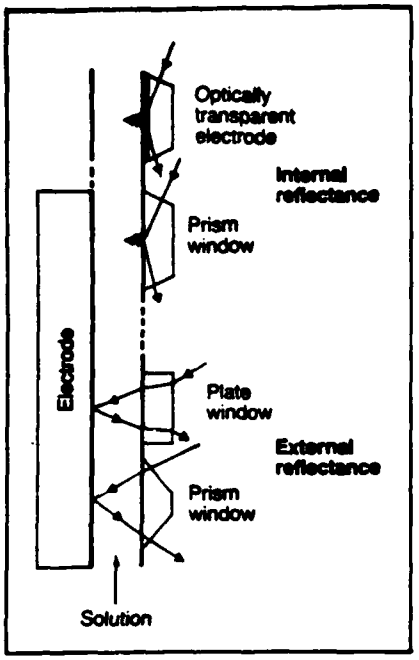

Figure 1. Optical geometries for internal- and external-reflection spectroelectrochemistry

tors are very noisy. This usually means that the total amount of radiation absorbed by the species of interest is small compared with the detector noise.

Internal and external reflection

The most important factor in the design of an IR spectroelectrochemical cell is minimization of absorption of the incident IR radiation by the solvent. To achieve this, ideal electrochemical behavior has to be sacrificed. Two optical approaches have been used—internal reflection and external reflection.

The older method is attenuated total reflection (ATR) (*1–3*). In this method the light is passed through the cell at an angle such that it undergoes total internal reflection at the electrode–solution interface (Figure 1). The electric field of internally reflected light penetrates a short distance across the interface, its intensity falling off exponentially with distance into the solution. The depth of penetration of this "evanescent wave," which is a function of the wavelength of the radiation, is greatest at the critical angle and decreases to about one-tenth of the wavelength of the light at angles well above the critical angle. This means that the internally reflected radiation can be absorbed by species on the solution side of the interface, but only by species either adsorbed on the electrode or in solution within a micrometer or so of the electrode. Thus the bulk of solution does not contribute to the total absorbance.

This type of experiment puts quite stringent demands on the electrode material, which must both conduct electricity and transmit IR light. Because good conductors are also good IR absorbers, a compromise between these properties has to be reached. Early workers used germanium, which is an IR-transparent semiconductor. More recently, very thin films of metal (Au, Pt, or Fe) deposited onto IR-transparent substrates have been used. Near the critical angle, and if the solution is not too absorbing, the electric field in the solution adjacent to the electrode can be several times greater than the electric field in the incident beam. This enhancement is greater for the latter type of electrode than for the former. Both single-reflection and multiple-reflection arrangements have been designed.

The more common way of reducing solvent absorption is to use external reflection in a thin-layer cell (Figure 1). In external reflection one end of the cell is an IR-transparent window. The IR beam passes through this window and through the solution, is specularly reflected from a polished electrode surface, and travels back through the solution and the window to a detector. The electrode is positioned very close to the window so that only a very thin layer of solution is sandwiched between them. The working electrode is a disk sealed into the end of an insulating cylinder, which can be moved inside a syringe barrel oriented perpendicular to the window (Figure 2). For the IR spectroscopic experiments the electrode is pushed forward until it makes contact with the window, forming a thin-layer cell with solution thickness of 1–100 μm.

The material for the IR-transparent window is chosen primarily for high transmission and insolubility in the solvent. Windows have been made from calcium fluoride, silicon, silica, Irtran 2, Irtran 4, and zinc selenide. Two shapes have been used—flat and prismatic. Prismatic windows allow the beam to strike the electrode at

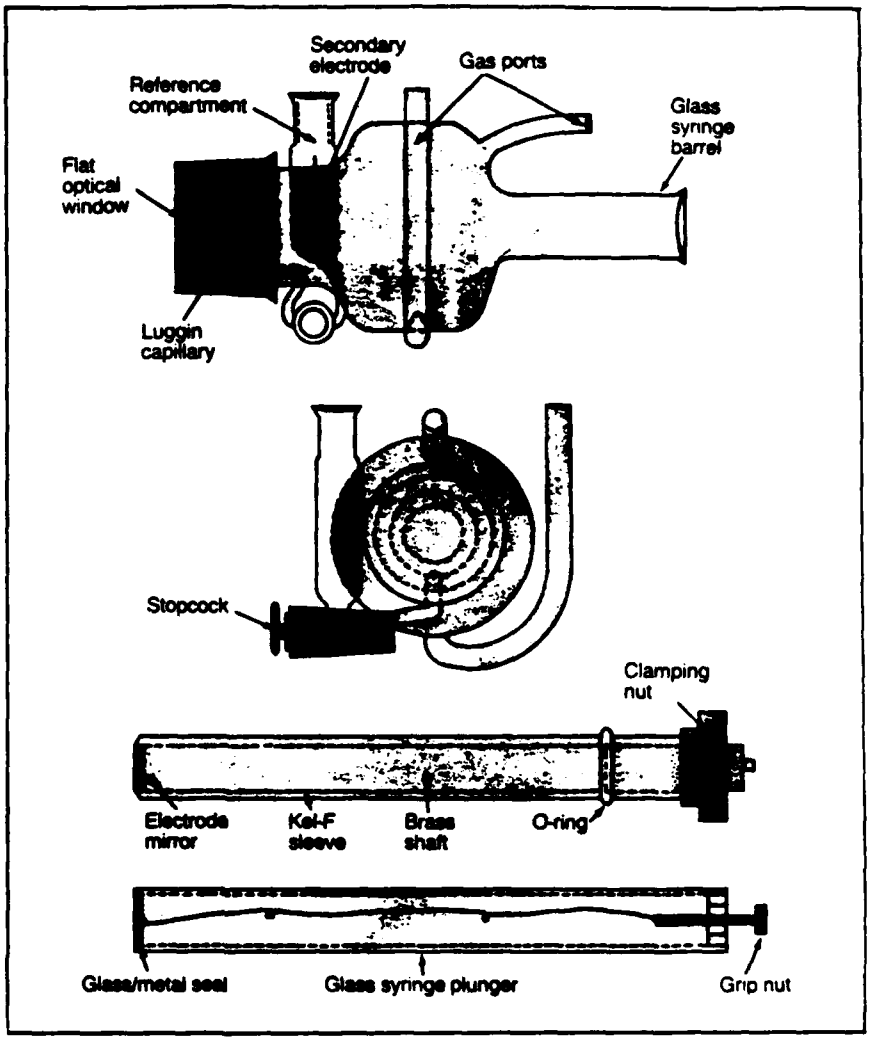

Figure 2. Typical external-reflection spectroelectrochemical cell

The top two drawings are side and end-on views of the cell. Either of the two mirror electrode assemblies at the bottom fits into the glass syringe barrel. The mirror is pushed forward until flat against the optical window

more glancing angles, which increases the sensitivity for adsorbed species. Also, if the incident beam is normal to the edge of the window, nearly equal amounts of s- and p-polarized light enter the cell, which is important if the difference in absorption of the two polarizations is to be used to distinguish surface species from solution species. Flat windows preferentially transmit p-polarized light.

The electrode material has to be able to specularly reflect IR radiation. Polished disks of Pt, Rh, Au, Ag, Pd, Fe, C, and p-type CdTe have all been used. However, even if the electrode does not reflect (as seems to be the case for carbon electrodes in contact with some aqueous solutions), it is still possible to obtain spectra of solution-free species by using a prismatic IR-transparent window with angles of incidence where internal reflection occurs at the window–solution interface (Figure 1).

IR spectroelectrochemical cells usually use the potentiostated three-electrode arrangement. However, both the ATR and external-reflection configurations suffer from unusually high resistances in the current path. In an ATR cell the high resistance is in the working electrode itself, which must have low conductivity if it is to transmit IR light. In an external-reflection cell the thin layer of solution between the working electrode and the window has the high resistance. The result is that when current flows the electrode potential differs by an amount iR from the value controlled by the potentiostat, and this difference increases across the electrode as the resistance in the current path does. Furthermore, the response of the cell to a change in potential is slow because the RC time constant for charging the double-layer capacitance is high.

Signal processing

Signal-processing techniques in in situ IR spectroelectrochemistry serve two purposes—to remove the spectrum of the bulk solvent, which would otherwise swamp out the spectrum of adsorbed or electrogenerated species, and to enhance the very low S/N ratios encountered in these experiments.

The first goal is nearly always achieved by potential modulation. The electrode potential is changed from a value E_1 where the reflectance is R_1 to a value E_2 where the reflectance, R_2, is different. The quantity measured is a function of

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

and spectra are usually presented as plots of $\Delta R/R$ vs. wavenumber $\bar{\nu}$. Thus the spectrum is a *difference* spectrum, which shows only changes in reflectance caused by the change in potential. The spectra of the bulk solution, atmosphere, etc., generally do not change with potential and are canceled out in the subtraction. Note that spectra are also sometimes plotted as

$$\% \text{ transmittance} = 100\left(\frac{R_2}{R_1}\right) = 100\left(\frac{\Delta R}{R} + 1\right)$$

$$\text{or absorbance} = -\log_{10}\left(\frac{R_2}{R_1}\right) = -\log_{10}\left(\frac{\Delta R}{R} + 1\right)$$

against wavenumber.

A change in potential can cause a change in the reflectance for any of several reasons, including changes in the number and bonding of species adsorbed on the electrode, migration of ions into or out of the optical path, electron transfer reactions that form or destroy films on the electrode surface, and electron transfer reactions that form or consume species in solution.

Several approaches to increasing the S/N ratio are in use, depending particularly on whether a dispersive or a Fourier transform IR (FT-IR) spectrometer is used. With a dispersive instrument the variation of reflectance with potential is measured at constant wavenumber, whereas with an FT-IR instrument the variation of reflectance with wavenumber is measured at constant potential. Use of a dispersive spectrometer therefore implies an ac potential program, whereas either dc or ac potential programs can be used with an FT-IR spectrometer.

When using a dispersive instrument the most common method is to modulate the electrode potential between E_1 and E_2 with a square wave (or sine wave) of about 10-Hz frequency, while changing the wavelength of the light very slowly. The signal from the IR detector then consists of a dc component, $R(\bar{\nu})$, a small ac component, $\Delta R(\bar{\nu})$, at the same frequency as the potential modulation, and noise over a wide range of frequencies. This signal is fed into a lock-in amplifier which picks out only that component of the signal at the same frequency as the alternating potential. This provides a direct measure of ΔR at each wavenumber and very effectively removes noise at other frequencies. For further discrimination against noise, the output of the lock-in amplifier can be stored in a computer, and a number of spectra can be signal averaged. The number required with modern commercially available instruments is quite small. S/N is increased with the square root of the number of signal-averaged spectra. The background spectrum $R(\bar{\nu})$ is obtained by mechanically chopping the beam and using the lock-in amplifier to pick out the component of the detector signal at the chopping frequency. This spectrum is also stored in the computer, and $\Delta R/R(\bar{\nu})$ can then be calculated. When this method is used in an external-reflection experiment, it is known as electrochemically modulated IR spectroscopy (EMIRS) (*4–6*).

Another approach that has been used with a dispersive instrument is linear potential-sweep IR reflectance spectroscopy (LPSIRS) (*7*). In this case, at each wavenumber the potential is swept rapidly over the required range. The time-varying output of the detector, which is a measure of reflectance as a function of potential at constant wavenumber, is stored in a computer. Several of these sweeps can be signal averaged to increase the S/N. The experiment is carried out at several different wavenumbers, and a series of spectra of reflectance against wavenumber at constant potential is reconstructed from the data. One potential is taken as the reference potential, E_1, and the spectrum at this potential, $R_1(\bar{\nu})$, is divided into each of the other difference spectra to give $R_2(\bar{\nu})/R_1(\bar{\nu})$, which can be converted to $\Delta R/R(\bar{\nu})$.

FT-IR spectrometers are being used in increasing numbers for IR spectroelectrochemical experiments because of their very high throughput and because of their ability to acquire large numbers of spectra rapidly, which follows from the simultaneous sampling of the entire range of wavelengths. In an FT-IR spectroelectrochemical experiment the electrode potential is modulated between E_1 and E_2. At each potential a large enough number of interferograms are added to give the desired S/N, and the two resulting single-beam spectra are ratioed to give the difference spectrum $R_2(\bar{\nu})/R_1(\bar{\nu})$. S/N is proportional to the square root of the number of interferograms collected. The potential–time program may be either a simple potential step from E_1 to E_2 or a square wave of frequency low enough that an integer number of interferograms can be collected during the period that the potential is held at each value. The square wave program reduces the effects of long-term drift in the spectrometer output but is not highly suitable for very complicated or chemically irreversible processes. When used with an external-reflection cell, this method is known as subtractively normalized interfacial FT-IR spectroscopy (SNIFTIRS) (*4, 5, 8, 9*).

A variation of the SNIFTIRS method is polarization-modulation or FT-IRRAS (FT-IR reflection–absorption spectroscopy) (*10*). A photoelastic modulator is used to modulate the

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state of the light between s- and p-polarization at a frequency of about 70 kHz, depending on the photoelastic modulator, which is much higher than the modulation frequencies of the interferogram. A lock-in amplifier is used to pick out the component of the detector response at the same frequency as the polarization modulation, and the output of the lock-in amplifier is Fourier transformed to give a spectrum that is the difference between the spectrum from the p-polarized light and the spectrum from the s-polarized light. For a distance of about one-quarter wavelength of the light from the electrode surface, s-polarized light is absorbed less than p-polarized light. Therefore the polarization modulation difference spectrum is the spectrum of a region about 1 μm thick adjacent to the electrode surface, which is about the thickness of the thin layer of solution between the electrode and window. To remove the spectrum of the solvent it is necessary to carry out the experiment at two potentials and ratio the spectra, as in a SNIFTIRS experiment. The main advantage of this technique is probably the increased sensitivity from the additional phase-sensitive detection stage.

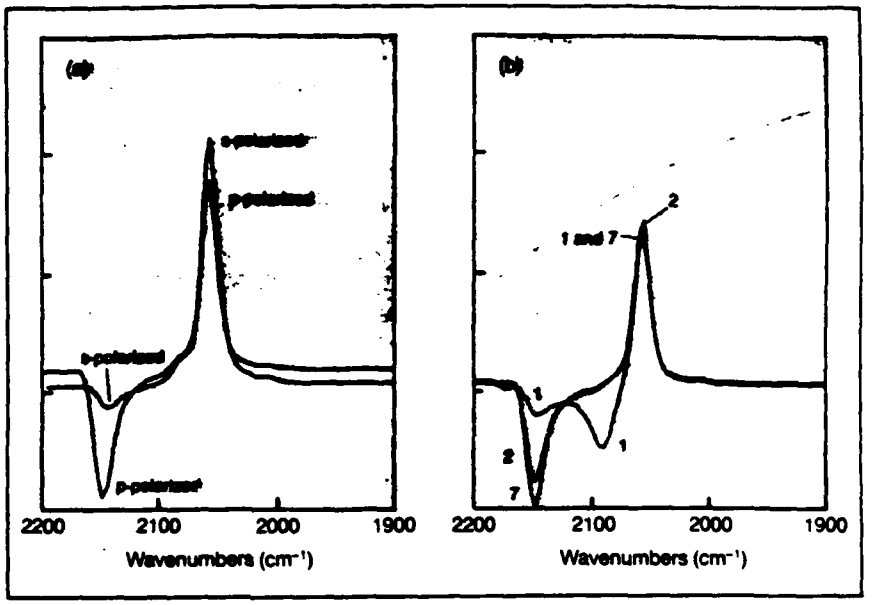

Figure 3. Difference SNIFTIRS spectra of the SCN^- system in acetonitrile at a silver electrode between −0.7 and +0.4 V vs. Ag/Ag^+ reference using (a) p- and s-polarized radiation, (b) p-polarized radiation at 1 min, 2 min, and 7 min after potential pulse
Vertical scales are 2×10^{-1} $\Delta R/R$ per division

Reflection spectroscopy of surface species

In an ATR experiment the electric fields of both s-polarized and p-polarized light penetrate the interface. At the critical angle the evanescent wave from p-polarized light has only a strong electric field perpendicular to the surface, whereas the evanescent wave from s-polarized light has only a weak electric field parallel to the surface. It has been pointed out (*1*) that differences in absorption of the two polarization states by an adsorbed molecule could be used to determine its orientation, but no experimental demonstrations using this technique have appeared. At other angles of incidence p-polarized light gives rise also to a weak electric field parallel to the surface. In general, therefore, p-polarized light interacts more strongly with absorbing species than does s-polarized light, and ATR experiments use either unpolarized or p-polarized radiation.

The situation is more interesting in an external-reflection experiment. Upon specular reflection at a metal surface, s-polarized light undergoes a phase shift of close to 180° at all angles of incidence, and so the incident and reflected beams interfere destructively. Therefore, the electric field of s-polarized light has zero intensity close to the surface, and species near the surface cannot absorb s-polarized light. On the other hand, p-polarized light undergoes smaller phase shifts upon reflection, and there is a finite component of the electric field at the surface, but only in a direction normal to the surface. The strength of this electric field increases with angle of incidence, being zero at normal incidence and reaching a maximum close to glancing incidence. High angles of incidence are therefore advantageous if the spectra of adsorbed species are to be observed.

Two important and useful consequences follow from the presence at the surface of electromagnetic electric fields only normal to the surface and only arising from p-polarized radiation. First, species on the electrode surface can be distinguished from species in solution because species in solution can absorb both s-polarized and p-polarized light, whereas species on, or close to, the surface can absorb only p-polarized light. Second, IR radiation can interact only with those modes of vibration of an adsorbed molecule that have a component perpendicular to the surface of the change in dipole moment with normal coordinate. (This is the surface selection rule [*11*].)

Therefore, information about the orientation of an adsorbed molecule can be obtained by noting which of its modes of vibration are IR active and which are forbidden by the surface selection rule. To take a simple example, the C ≡ O stretching vibration of an adsorbed CO molecule will give an external reflection IR spectrum with p-polarized light if the C ≡ O bond is perpendicular to the surface, but not if the C ≡ O bond is parallel to the surface. At no orientation will the molecule absorb s-polarized radiation. Recent results, however, indicate that orientation data for very polarizable molecules deduced from the surface selection rule should be treated with caution. There is a very high electrostatic electric field (10^6–10^8 V cm^{-1}) at the electrode–electrolyte interface, normal to the electrode surface, which can induce a dipole moment normal to the surface in a sufficiently polarizable adsorbed molecule. Even though the permanent dipole of such a molecule may be oscillating parallel to the surface during a vibration (or even if there is no change in permanent dipole moment at all), the induced dipole moment can oscillate normal to the surface at the vibrational frequency, providing a mechanism for absorption of IR radiation (*12*). Bands observed from flat-adsorbed TCNE radical anion and acrylonitrile have been attributed to this effect.

Applications to electrode reactions

FT-IR spectrometers have been used more often than dispersive spectrometers to obtain spectra of the reactants and products of electrode reactions. There are some disadvantages to using dispersive instruments for these applications because of the ac potential programs that must be used. The short time scale of the ac experiment allows relatively little reaction to take place during each cycle, so changes in reflectance are small. If a chemically irreversible reaction is taking place in a thin-layer cell then all of the reactant in the thin layer may be consumed within the first few cycles of the potential, and no change in reflectance will be seen in the remainder of the spectrum. If the reaction mecha-

nism is complicated, a complicated time-averaged mixture of species close to the electrode may be obtained, making the spectra difficult to interpret.

External-reflection methods seem to be superior to internal-reflection methods in the study of electrode reactions. External reflection uses a thin-layer cell, where bulk electrolyses of solution species can be quickly and conveniently carried out and the IR spectra of reactants and products obtained in a nearly ideal double-beam experiment. Spectra of intermediates can also be obtained if they are stable on the time scale of an FT-IR spectrum. Species on the electrode surface can be distinguished from species in solution by changing the polarization state of the radiation or noting potential-dependent band positions.

We use as an example anodic processes that take place at a silver electrode in acetonitrile solutions of thiocyanate ion, SCN^- (*13*). Cyclic voltammetry shows two oxidation waves, the first characteristic of a reversible reaction with reactant and product in solution, the second characteristic of a surface process. SNIFTIRS spectra were taken with a single potential step from E_1 to E_2. A step from a potential where no reaction occurs to a potential in the first wave gives a product absorbing at 2092 cm^{-1}, shown to be a solution-soluble species by its absorption of both s-polarized and p-polarized light, and thought to be the complex $Ag(SCN)^-_2$. Figure 3a shows the spectrum obtained in a potential step experiment from a potential where no reaction occurs to a potential just past the second voltammetric wave. The sign convention for $\Delta R/R$ has bands due to absorption by reactants at the base potential pointing up ($\Delta R/R > 0$) and bands due to products pointing down ($\Delta R/R < 0$). It can be seen that a solution-soluble species absorbing at 2056 cm^{-1}, which is presumably SCN^-, is converted to a species that absorbs only p-polarized light at 2141 cm^{-1}. This surface product is thought to be a film of AgSCN. Figure 3b shows spectra taken with the same potentials as in 3a (this time using only p-polarized light) with the spectra at the more positive potential taken at various time intervals after the potential step. This shows that SCN^- (at 2056 cm^{-1}) is initially converted to $Ag(SCN)_2^-$ (at 2092 cm^{-1}), which later forms AgSCN on the surface (at 2141 cm^{-1}). The reactions can therefore be written

First wave:

$$Ag(s) + 2SCN^- \rightleftharpoons Ag(SCN)_2^- + e^-$$

Second wave:

$$Ag(s) + 2SCN^- \rightleftharpoons Ag(SCN)_2^- + e^-$$

$$Ag(SCN)_2^- + Ag(s) \rightleftharpoons 2AgSCN(s) + e^-$$

The most successful use of the ATR method has been in the study of polymer films on electrodes, where very high concentrations of absorbing species exist close to the electrode surface. A system that has been studied by FT-ATR is poly(3-methylthiophene) on a thin film of gold (*3*). Trnsitions between the semiconducting neutral species and the highly conducting oxidized state were clearly indicated in the IR spectra.

Thin layers of iron on germanium were used by the same workers to study the oxidation products of iron in alkaline media.

Applications to surface studies

All IR spectroelectrochemical studies of adsorbed species have been carried out by external-reflection methods. EMIRS has so far proved to be the most sensitive of these methods, but because of the ac potential program used, EMIRS spectra are also the most difficult to interpret.

A particularly interesting EMIRS study was carried out on the oxidation of methanol on platinum in aqueous acid solutions (*14*). The spectrum obtained by modulating between two potentials where methanol is adsorbed is shown in Figure 4. Bands pointing up ($\Delta R/R > 0$) correspond to species present at the more negative potential. There is a weak band at 1850 cm^{-1}, attributed to CO adsorbed in a site where it is bridge bonded to three platinum atoms, and a strong bipolar band at about 2050 cm^{-1}, attributed to linearly adsorbed CO (i.e., bonded to one Pt atom). The bipolar nature of this band is caused by a shift in band position to more positive wavenumbers as the electrode potential is made more positive. This shift is most probably the result of strengthening of the C ≡ O bond by withdrawal of electrons from the C ≡ O antibonding π^* orbitals when the electrode is made more positive.

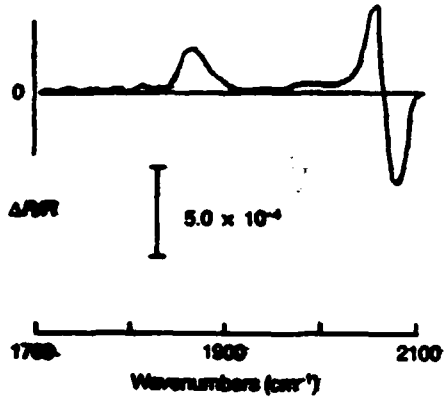

Figure 4. Difference EMIRS spectrum for methanol adsorbed on a platinum electrode from 1 M H_2SO_4 solution
Modulation +0.05 to +0.45 V (vs. NHE) at 8.4 Hz

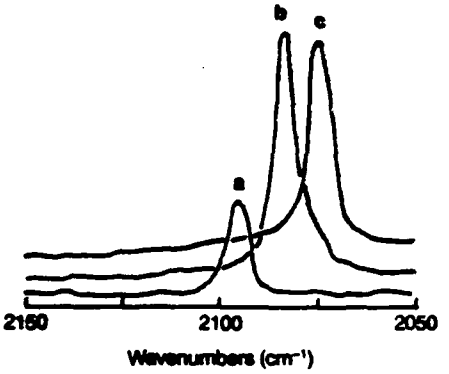

Figure 5. FT-IRRAS spectra of CO adsorbed on a platinum electrode from 1 M $HClO_4$ solution
These are difference spectra taken between 0.8 V and (a) 0.675 V, (b) 0.4 V, and (c) 0.0 V (vs. NHE). The maximum absorbance is $\sim 5 \times 10^{-2}$

Because of its importance in catalysis and because it has a very intense band at a frequency well away from the regions of strong water absorption, linearly adsorbed CO has been studied a great deal. Figure 5 shows FT-IRRAS spectra of CO adsorbed on Pt in 1 M $HClO_4$ (*15*). For all of the spectra the reference potential E_1 = 0.8 V, where no CO is adsorbed. The shift of band position to higher wavenumber with increasing positive potential can easily be seen, together with a decrease in intensity at higher potentials due to oxidation to CO_2 of some of the adsorbed CO.

An example of the use of the surface selection rule to predict the orientation of an adsorbed molecule is provided by the case of *p*-difluorobenzene adsorption on Pt from aqueous acid solution (*16*). This molecule has 13 IR-active normal modes, of which 10 (the b_{1u} and b_{2u} modes) have dipole changes in the plane of the aromatic ring, and three (the b_{1u} modes) have dipole changes perpendicular to the plane of the ring. If the molecule is adsorbed flat, only the b_{1u} modes should be seen, whereas if it is adsorbed edgewise only the b_{1u} and b_{2u} modes should be seen. At intermediate ("skew") orientations all modes should be seen. SNIFTIRS spectra with modulation between a potential where p-difluorobenzene is adsorbed and a potential where it is not adsorbed show, at concentrations less than 0.8 mM, two bands due to the ad-

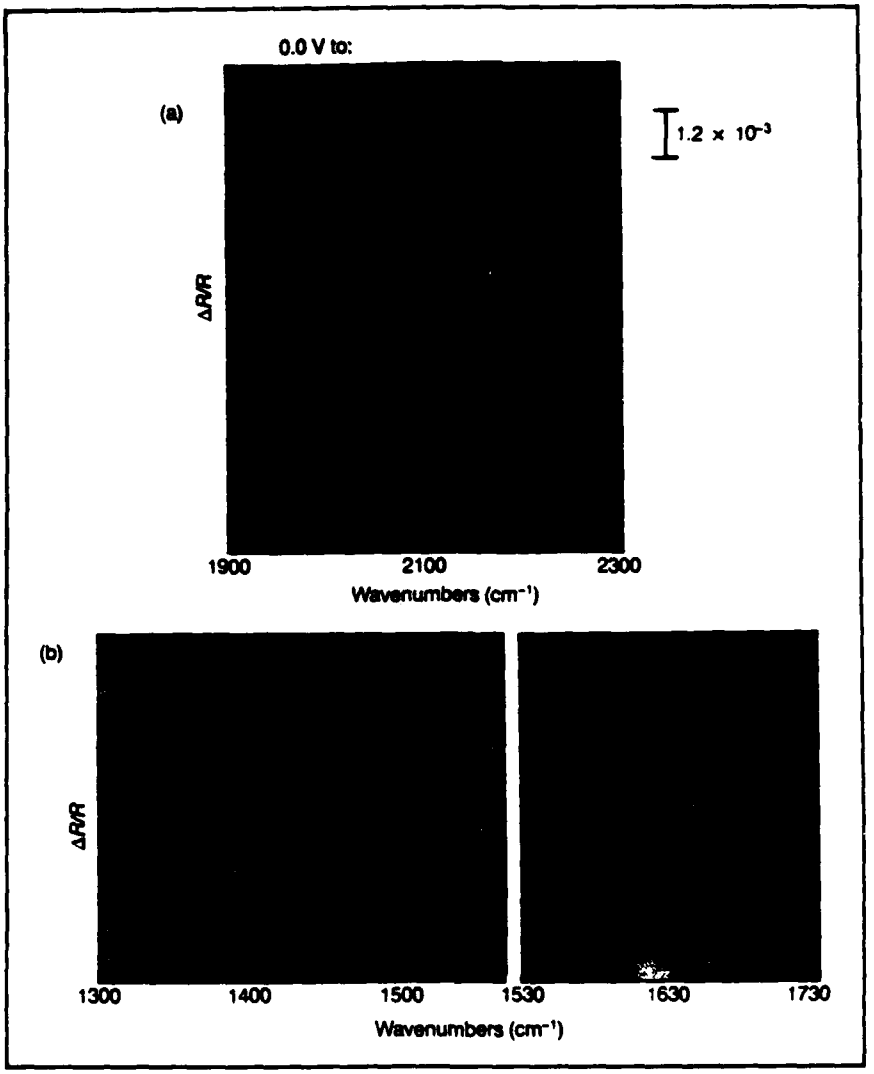

Figure 6. EMIRS difference spectra for adsorption of benzonitrile on a gold electrode from H_2SO_4 solution

Modulation at 8.5 Hz. (a) C ≡ N stretch region, voltage limits as indicated vs. SCE. (b) Ring mode region, voltage limits 0 to 1.1 V vs. SCE

sorbed species corresponding to two of the three b_{1u} modes. At concentrations above 0.8 mM, bands due to all of the modes appear. Therefore, at solution concentrations below 0.8 mM, *p*-difluorobenzene is adsorbed flat on the electrode, but a transition to skew orientation takes place at higher solution concentrations.

In addition, benzonitrile and acrylonitrile adsorbed on gold electrodes from aqueous acid solutions are examples of systems in which the surface selection rule is respectively successful and unsuccessful in predicting the orientations of adsorbed molecules (*17*).

Figure 6 shows EMIRS spectra taken in a solution of benzonitrile (0.02 M) and H_2SO_4 (1 M) at a gold electrode. Modulation from a fixed base potential to more positive potentials gives a negative-going band at about 2250 cm^{-1}, which shifts to higher wavenumber with increasing positive potential. The sign of the band and the potential dependence of its intensity indicate increasing adsorption of benzonitrile with increasing positive potential, until at very positive potentials formation of gold oxide and oxidation of benzonitrile take place. There can also be seen a very small positive-going band at 2229 cm^{-1} arising from solution-free benzonitrile, which is depleted at the positive modulation limit because of its adsorption onto the electrode. In other regions of the spectrum there are two negative-going bands at 1480 cm^{-1} and 1595 cm^{-1}, corresponding to A_1 benzene ring modes, and a weak positive-going band at 1448 cm^{-1}, corresponding to a B_1 ring mode. These observations are all consistent with benzonitrile adsorbed perpendicular to the surface and bonded to the surface through the N atom. Bonding through the N atom might be expected to involve donation of electrons from the slightly antibonding nitrogen lone pair orbital to

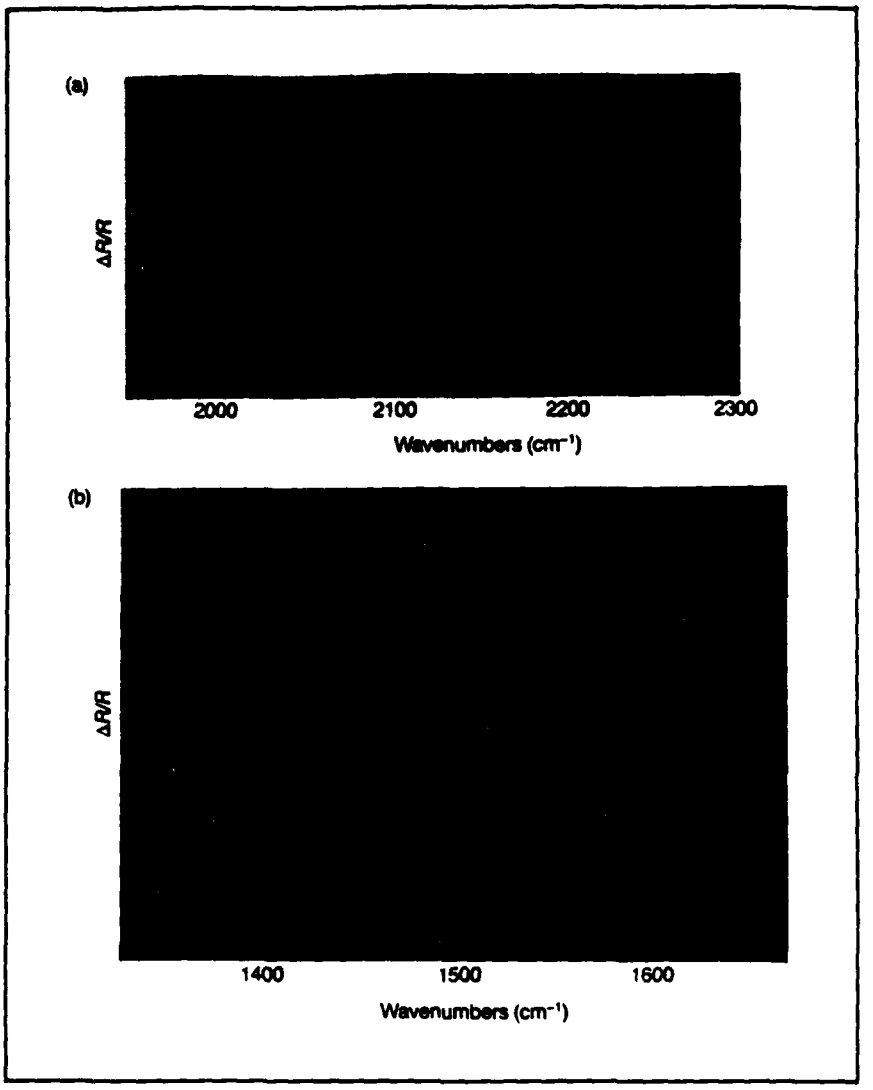

Figure 7. EMIRS difference spectra of acrylonitrile adsorbed on a gold electrode in (a) the C ≡ N stretch and (b) the C = C stretch regions
Modulation from 0.05 to 1.0 V vs. SCE at 8.5 Hz

empty metal orbitals and back donation of electrons from filled metal orbitals to empty benzonitrile π^* orbitals. For both bonding mechanisms, a shift of the electrode potential to more positive values would strengthen the C ≡ N bond and would shift the C ≡ N stretch mode to higher wavenumber, as observed. The surface selection rule also predicts orientation of the C ≡ N bond normal to the surface, because a strong C ≡ N stretch band and bands from A_1 ring modes are observed.

An EMIRS spectrum from a solution of acrylonitrile (0.05 M) and H_2SO_4 (1 M) at a gold electrode is shown in Figure 7. Modulation to a more positive potential gives positive-going bands at about 2130 cm^{-1} and 1520 cm^{-1}, with potential-dependent frequencies and intensities. These bands are assigned to C ≡ N and C = C stretching vibrations, respectively, but occur about 100 cm^{-1} lower in frequency than the corresponding bands of solution-free acrylonitrile. This is evidence that the molecule is adsorbed flat, where it would probably be bonded to the electrode by donation of acrylonitrile π-bonding electrons to empty orbitals on the metal and by back donation of electrons from filled metal d-orbitals to empty acrylonitrile π^* orbitals. In this case, the C ≡ N and C = C bonds would be weakened by adsorption, and the C ≡ N and C = C stretch modes of the adsorbed molecule would be at lower wavenumbers than the corresponding modes of the solution-free molecule. Flat orientation of the adsorbed molecule is not predicted by a simple application of the surface selection rule, because C ≡ N and C = C bands are observed. However, these bands are very weak, and the C = C band is stronger than the C ≡ N band, whereas the opposite is the case for the free molecule. The most likely explanation for the appearance of these bands is the pres-

ence normal to the surface of a molecular dipole moment induced by the high electric field across the double layer. As the molecule vibrates, this dipole can oscillate normal to the surface and interact with the electric field of p-polarized IR radiation.

It is clear that IR spectroelectrochemistry can provide valuable insight into the vibrational structure of surface-bound and solution-soluble intermediates. Extending the technique to the far-IR to observe metal–adsorbate structure and use of the technique for surface dynamics studies are likely short-term extensions of the technique.

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