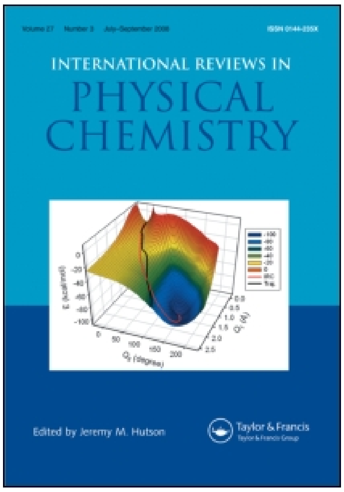

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

Infrared and molecular beam studies of chemical reactions on solid surfaces

Francisco Zaera

To cite this Article Zaera, Francisco(2002) 'Infrared and molecular beam studies of chemical reactions on solid surfaces', International Reviews in Physical Chemistry, 21: 3, 433 — 471
To link to this Article: DOI: 10.1080/01442350210156033
URL: http://dx.doi.org/10.1080/01442350210156033

INT. REVIEWS IN PHYSICAL CHEMISTRY, 2002
VOL. 21, NO. 3, 433–471

Infrared and molecular beam studies of chemical reactions on solid surfaces*

FRANCISCO ZAERA†
Department of Chemistry, University of California, Riverside, Riverside, CA 92521, USA

The experimental technology available to surface scientists has improved enormously over the last few decades, and most properties of solid surfaces can now be characterized in great detail. In particular, extensive knowledge has been accumulated on the structure, composition, and electronic and dynamic behaviour of many metal, semiconductor and ionic surfaces. Great progress has also been made in the use of those techniques to widen our understanding of surfaces physics, surface bonding and adsorption. The field of surface chemical kinetics, on the other hand, has been advanced to a lesser degree. Here we describe the approach taken in our laboratory to study the kinetics of the reactions followed by molecules adsorbed on solid surfaces, in particular those relevant to heterogeneous catalysis. Special emphasis is placed on describing the use of infrared spectroscopy for the characterization of surface intermediates and molecular beams for the measurement of reaction rates. Some examples of results from those studies are provided, and a few ideas for future directions in this field are proposed.

Contents

---

*Invited article.

† Email: francisco.zaera@ucr.edu

International Reviews in Physical Chemistry ISSN 0144–235X print/ISSN 1366–591X online © 200? Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/01442350210156033

1. Introduction

The chemistry of solid surfaces is at the heart of many fields of fundamental and practical applications such as tribology, electrochemistry, polymer science, corrosion, semiconductor device manufacturing, coatings development for mechanical, optical and electronic applications, and prosthetics. Among those, the surface chemistry of heterogeneous catalysis has received special attention, perhaps because the business of catalysis adds up to about $10 billion worldwide and produces goods worth approximately a quarter of the world's gross domestic product (Martino 2000). Indeed, more than 80% of the industrial chemical processes in use nowadays rely on one or more catalytic reactions (Thayer 1992). A number of those, including oil refining, petrochemical processing and the manufacturing of commodity chemicals, are already well established (Thomas and Thomas 1967, Gates *et al.* 1979). However, many others, such as the clean manufacturing of specific pharmaceuticals, especially optically active ones, and the abatement of pollutants, still represent unresolved challenges which require the development of entirely new chemistry (Blaser 2000, Farrauto and Heck 2000).

The initial advances in catalysis were often made serendipitously. More recently, however, catalyst design has been greatly aided by the advent of new surface-sensitive analytical techniques. Basic surface-science studies in particular have laid the bases for understanding the interfacial chemistry underlying heterogeneous catalytic processes (Somorjai 1994). Unfortunately, in spite of the progress made in this area so far, research on the microscopic details of catalysis is still a young field with many unanswered questions. Also, a strong connection is lacking between the knowledge derived from basic surface-science studies and the development of new and better catalytic processes of practical importance. Much more work is required to fulfil the promise of surface science to develop a systematic approach for the design of catalysts from first principles.

The success of catalysis is based on its ability to improve the kinetics of desirable chemical processes. Specifically, a catalyst accelerates chemical reactions by opening alternative mechanisms with lower activation barriers (Laidler 1987). In fact, over the years, the emphasis in catalysis has shifted away from increasing overall activity and toward the design of more selective processes. As the reactions involved become more complex, the issue of driving desirable pathways selectively takes centre stage, because high selectivity toward specific product(s) implies the consumption of less reactants, the minimization of the need for expensive and difficult separation processes, and the reduction in the production of polluting byproducts.

The issue of selectivity adds to the demand for an accurate picture of the chemistry that takes place on solid surfaces, because the selective production of particular compounds in catalysis can be significantly altered by subtle changes in the properties of the catalyst and/or the conditions of the reaction. In terms of kinetics, what matters for selectivity is not so much the absolute height of the activation barrier toward a desirable pathway, but its relative value with respect to those of other undesirable side steps (Zaera 2002b). Changes in the difference between the activation barriers of two competing reactions of a few kcal mol^{-1}, a small fraction of the absolute magnitude of each barrier, can lead to a switch in selectivity from one product to the other. The ability to predict those changes is still in the future.

We in our laboratory have focused on the characterization of the kinetics of chemical reactions on solid surfaces relevant to heterogeneous catalysis (Zaera *et al.* 1986, Zaera and Somorjai 1988, Zaera 1992, 1994, 1995, 1998, 2001a, 2002a–e). Our emphasis has been on the understanding of the kinetics of elementary processes occurring at solid interfaces. Two aspects of this problem have captured our special attention: the identification of surface intermediates, and the measurement of kinetic parameters for the rates of conversion of those species. We have relied on a combination of surface-sensitive techniques for these studies, but have depended heavily on the use of infrared (IR) spectroscopy for the first task and on molecular beams to advance the second. In this review we elaborate on the advantages of using those techniques for the investigation of surface catalytic reactions. Emphasis is given to the work performed in our laboratory, but references are also made to key advances by other researchers.

2. Infrared spectroscopy

IR absorption spectroscopy was one of the first and has been one of the most used techniques for the characterization of adsorbates on solid surfaces. Besides the well-developed instrumentation available for it, the fact that the energy of the IR photons fall in the range of molecular vibrations makes IR spectroscopy one of the most specific, and thus most informative, experimental probes for chemical characterization. For one, vibrational frequencies can be easily identified with specific localized vibrational groups within a given molecule. Molecular vibrations also depend strongly on the local environment in which the probed moiety is placed (Nakamoto 1978, Socrates 1994). These properties allow for the determination of specific chemical properties in adsorbates. In addition, the use of IR spectroscopy was greatly enhanced by the development of Fourier-transform spectrometers in the early 1970s, an event that brought about an enormous improvement in performance in terms of sensitivity, acquisition time, dynamic range and ease of data processing (spectra ratioing in particular) over conventional scanning apparatus (Griffiths and de Haseth 1986). It could be said that it was this advancement what made the extension of IR spectroscopy to surface studies feasible.

2.1. *Supported catalysts*

Several experimental approaches have been developed for the utilization of IR spectroscopy in surface studies. They include transmission, diffuse reflectance, reflection–absorption, attenuated total reflectance (ATR) and emission detection. From those, transmission absorption IR spectroscopy is the oldest and most widely used for the study of supported catalysts. The transmission IR approach was pioneered by Terenin and coworkers, who used it to study porous glasses (Yaroslavskii and Terenin 1949), and extended soon afterwards by Eischens and others for the characterization of the chemisorption of catalytically relevant species over supported metals (Eischens *et al.* 1954). The early work in this area has been already beautifully reviewed in the literature (Little 1966, Hair 1967).

Extensive studies have been carried out since on the characterization of many adsorbed reactants, simple molecules such as carbon and nitrogen oxides (Blyholder 1968, Bell 1984) as well as hydrocarbons and other complex species (Sheppard and de la Cruz 1996, 1998). A number of experimental set-ups have also been developed over the years for these studies (Yates and Madey 1987). Thanks to the localized nature of surface bonds (Hoffmann 1988, Zaera 1995), IR spectroscopy has proven quite useful for the detection and identification of many surface intermediates on heterogeneous supported catalysts. Transmission absorption IR spectroscopy is still used often for catalytic studies to this date.

The most straightforward procedure for the use of IR spectroscopy in the study of surface reactions is via the acquisition of spectra for adsorbed species as a function of temperature. These experiments often lead to the identification of surface intermediates of relevance to catalysis. As an example, figure 1 displays a set of

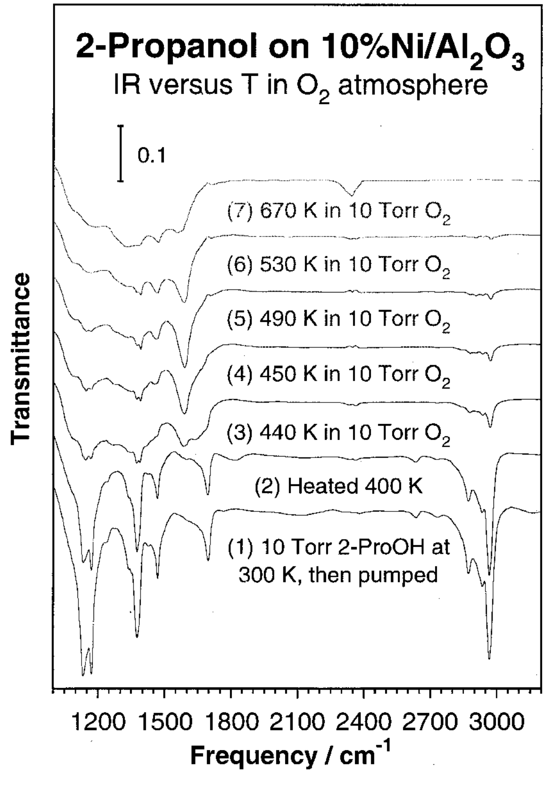

Figure 1. Transmission IR absorption spectra for the oxidation of 2-propanol on a 10% Ni catalyst supported on alumina after sequential exposure to 10 Torr of the alcohol and 10 Torr of oxygen. Data are shown here as a function of the temperature of the sample and reactor. A change in the nature of the adsorbed species is seen about 440 K, from molecular adsorption to a new species, most likely acetone bonded to the metal surface. Experiments such as these allow for the identification of potential surface intermediates during catalysis.

transmission IR spectra obtained in our laboratory for the thermal chemistry of 2-propanol on a 10% nickel catalyst supported on alumina in the presence of gas-phase oxygen (Ali and Zaera 2002b). The main goal of this project has been to identify the conditions that favour dehydrogenation over dehydration during the catalytic partial oxidation of alcohols. In this particular example, it can be clearly seen that oxidized nickel samples favour the former pathway. Specifically, the low-temperature data, characteristic of the 2-propanol reactant, evolve between 440 and 450 K to yield significantly different spectra. The new high-temperature traces are dominated by absorption bands around 1378, 1472 and 1590 cm^{-1}, which can be easily assigned to the symmetric and asymmetric methyl deformations and to the carbonyl stretching modes of acetone respectively. Interestingly, additional vibrational modes associated with acetate surface species were detected under certain conditions. The chemistry seen in these IR studies has proven consistent with the results from kinetic work on the same system (Zaera *et al.* 1999, Ali and Zaera 2002a). Similar experiments can be carried out *in situ* during catalysis, since it is often easy to discriminate between signals from gas-phase and adsorbed species, either because of their different frequencies, or because they behave differently as the conditions of the reaction are varied.

2.2. *Diffuse reflectance*

An alternative to the transmission arrangement for IR absorption spectroscopy studies of powder samples is diffuse reflectance IR Fourier-transform spectroscopy (DRIFTS) (Willey 1976). The development of efficient optics to collect the diffuse reflected radiation from samples illuminated with a focused IR beam has greatly advanced this technique, and several cell designs are available commercially for this endeavor (Griffiths and de Haseth 1986, Drochner *et al.* 2000, Schubert *et al.* 2001). DRIFTS offers several advantages over the conventional transmission arrangement. First, loose powders can be used without the need to press them into pellets, thus avoiding any sample distortions due to severe physical treatments. This allows for better exposures of the surface to adsorbates, and avoids losses in the high-frequency range due to light scattering. Second, band intensities in the DRIFTS mode can be several times more intense than in the transmission mode, possibly because of the potential multiple internal reflection of the light in the vicinity of the surface before its emergence towards the detector. Last, DRIFTS is better for opaque samples than transmission IR spectroscopy, although the diffuse reflectance may still be low in spectral regions where the absorptivity of the substrate is high. On the negative side, the reproducibility of DRIFTS intensities is poor because of variations in scattering coefficients with cell geometry and sample loading procedure. Furthermore, diffuse reflectance suffers from the same key limitation in transmission IR, namely it requires high-surface-area samples, and therefore provides average spectra from many types of surface local ensembles and adsorption sites. The use of DRIFTS for the characterization of catalytic surfaces has taken some time to develop, but has advanced considerably in recent years (Blitz and Augustine 1994, Busca 1996).

2.3. *Titration of catalytic sites*

Another approach commonly used to characterize the surface of catalysts with either transmission or diffuse reflectance IR absorption spectroscopies is via the use of appropriate probes as titrants of specific surface sites. Carbon monoxide is by far the most widely employed molecule for this purpose, because its C–O stretching

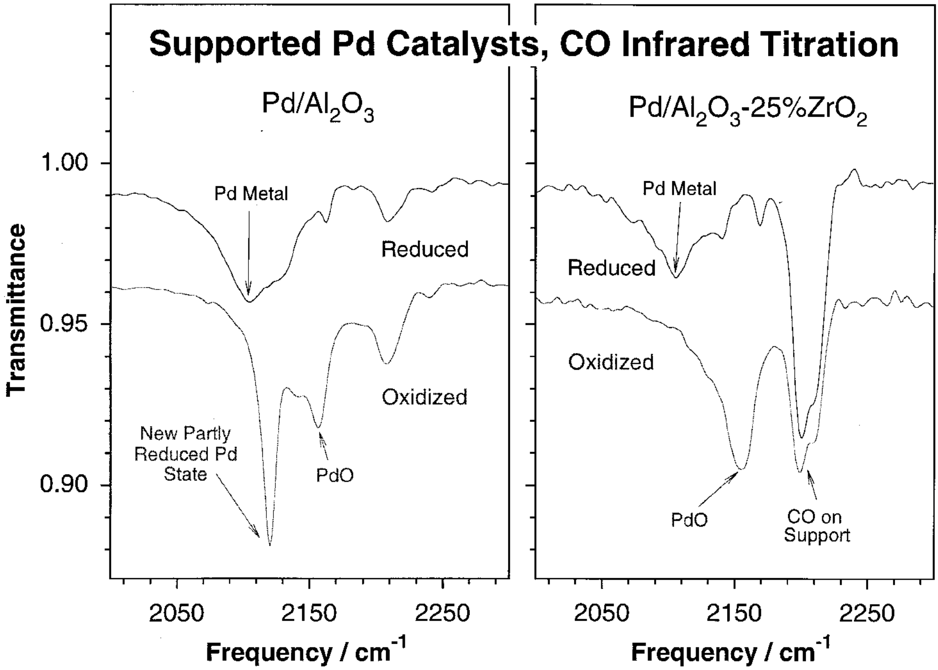

Figure 2. CO titration IR characterization of palladium catalysts supported on high-surface-area supports, on sol–gel prepared alumina (left) and 25% zirconia–75% alumina (right) materials. Carbon monoxide is adsorbed at 150 K on catalysts previously treated at 700 K with either hydrogen (reduced samples, top traces) or oxygen (oxidized samples, bottom traces). The fact that the vibrational stretching frequency of the C–O bond is highly sensitive to the electronic details of the adsorption renders these spectra quite useful for the determination of the nature of the catalytic sites. In this case, the incomplete reduction of the reduced samples is indicated by the features about 2140 and 2170 cm^{-1} that accompany the main Pd metal feature at 2100 cm^{-1} in both top traces. Perhaps more importantly, the differences between the two bottom spectra point to the potential role of zirconia as a stabilizer of palladium oxide particles.

frequency is highly dependent on the details of its coordination on the surface (Xu *et al.* 1994). Figure 2 displays a few transmission spectra obtained by us illustrative of this principle, in this case for the characterization of palladium supported catalysts developed for nitrogen oxide reduction processes (Tiznado *et al.* 2002). The question addressed here is the role that zirconia additives have in stabilizing new palladium phases on alumina. It can be seen that, in both cases (with and without zirconia), the metal can be reduced almost completely by heating in hydrogen atmospheres: the main C–O stretching frequency of adsorbed carbon monoxide is observed around 2110 cm^{-1}, a value characteristic of atop adsorption on metallic Pd (Lee *et al.* 1984, Ryndin *et al.* 1990). Nevertheless, the observation of additional bands about 2140 and 2170 cm^{-1} is indicative of incomplete reduction (the peaks above 2200 cm^{-1} are due to adsorption on the support). More interesting is the fact that, while oxidation of the palladium supported on alumina–zirconia leads to the appearance of only one CO IR band about 2155 cm^{-1} (from PdO) (Okuhara *et al.* 1997, Schmal *et al.* 1999), the same treatment on pure alumina leaves new partly reduced sites, as indicated by the IR peak at about 2120 cm^{-1}. One role of the zirconia additive appears to be to favour the completely oxidized phase of the catalyst.

In spite of the wide use of transmission and diffuse reflectance IR spectroscopies in catalysis, it should be said that the their general application to catalytic problems faces some significant limitations, in particular the need for high-surface-area solids (which usually have quite heterogeneous and ill-characterized surfaces) and the restricted range of frequencies available away from the regions where the solids absorb (below $1300\,cm^{-1}$ for silica, $1050\,cm^{-1}$ for alumina, $1200\,cm^{-1}$ for titania, $800\,cm^{-1}$ for magnesia).

2.4. *Low-surface-area model catalysts*

As mentioned above, the localized nature of the interaction of adsorbates with catalytic sites makes the IR characterization of heterogeneous systems possible. Because local bonding geometries may be similar even if the adsorption takes place on catalyst particles with vastly different structures, the vibrational features of a given adsorbate on a supported catalyst often display frequencies that are quite close in value. Therefore, specific absorption bands can still be easily identified in the IR spectra of most species bound to heterogeneous surfaces. On the other hand, small variations in local environment lead to the broadening of those IR absorption spectral features. Consequently, it is particularly difficult to investigate subtle electronic or geometrical differences among similar catalytic sites within heterogeneous supported catalysts. It is therefore highly desirable to also carry out experiments on well-defined model surfaces such as those of single crystals, annealed foils or films, even if such experiments bring about a number of new technical difficulties, in particular the small number of sites that can be probed on such surfaces. Two main arrangements have been developed to perform infrared spectroscopy studies on small samples, namely, reflection-absorption (RAIRS) and ATR, which work best for opaque and transparent substrates respectively.

RAIRS has become by far the method of choice for the study of adsorbates on well-characterized metal samples, including single crystals. The first attempt to obtain spectra from adlayers on bulk metal samples was that of Pickering and Eckstrom, who in 1959 looked at the adsorption of carbon monoxide and hydrogen on metal films by using a multiple-reflection technique with an incoming beam at close to normal incidence to the surface (Pickering and Eckstrom 1959). It soon became clear that better spectra could be obtained by illuminating the sample at glancing incidence angles instead (Francis and Ellison 1959). It was also learned that the gain from using multiple reflection was not worth the complications connected with the required experimental setup. In fact, the optimum number of reflections was determined to be between 3 and 10, and even then the increase in signal was calculated to amount to only about 30–50% of that from a single reflection (Hollins and Pritchard 1985).

The theory for the reflection of IR radiation from metal surfaces was later developed by Greenler, who proved that only the p-polarized component of the incident beam is capable of strong interaction with adsorbates on metals. In fact, the interference between the p components of the incident and reflected rays was shown to lead to the creation of a strong standing field at the surface which can yield an intensity enhancement of a factor of up to 25 compared with that from the s-polarized photons (Greenler 1966). Many surface scientists have since taken advantage of these properties to perform reflection–absorption measurements of monolayers on solid metals (Bradshaw 1982, Hoffmann 1983, Chabal 1988, Zaera 2001b). The initial RAIRS experiments were carried out with molecules with large dynamic dipole moments such as CO (in order to take advantage of their large absorption cross-sections), but more recent Fourier transform IR (FTIR) developments have led to the possibility of detecting submonolayer quantities of species such as hydrocarbons with much weaker signals on single crystals of less than 1 cm^2 area. Our group in particular has reported numerous studies on the characterization of hydrocarbons on metals (Zaera *et al.* 1990b, Zaera and Hoffmann 1991, Hoffmann *et al.* 1992, Jenks *et al.* 1992, Zaera 1992, Jenks *et al.* 1993, Zaera 1994, Zaera and Bernstein 1994, Janssens and Zaera 1996, Zaera *et al.* 1996, Gleason *et al.* 1998, Zaera *et al.* 1998, de Jesús and Zaera 1999a, French and Zaera 1999, Chrysostomou *et al.* 2000, Jenks *et al.* 2000, Zaera and Chrysostomou 2000a, Chrysostomou *et al.* 2001, Chrysostomou and Zaera 2001, Kubota and Zaera 2001, Zaera *et al.* 2001a, Janssens and Zaera 2002a, b) as well as on other systems (Zaera 1991, Zaera *et al.* 1997).

2.5. *Reactivity studies*

An example of the application of RAIRS to the study of surface reactions is provided in figure 3. There, the chemistry of acrolein on a Pt(111) single-crystal surface was probed as a function of annealing temperature (de Jesús and Zaera 1999a, b). It was determined that the main thermal decomposition path for the unsaturated aldehyde was the expected decarbonylation to carbon monoxide and the corresponding olefin (ethylene). Notice in particular the appearance of new C–O stretching frequencies at 1811 and 2055 cm^{-1} above 280 K, values characteristic of bridged and atop coordinations for the carbon monoxide molecule respectively (Shigeishi and King 1976, Zaera *et al.* 1997). Moreover, the peaks at 1124 and 1341 cm^{-1} correspond to the C–C stretching and methyl symmetric deformation modes of ethylidyne, the surface species that forms on heating ethylene above room temperature (Skinner *et al.* 1981, Zaera *et al.* 1996). The spectra in our data set are displayed as differences between consecutive annealing traces in order to highlight the chemical changes that occur on the surface versus temperature.

RAIRS has been particularly useful in surface-science studies of bond-forming reactions. Figure 4 displays data corresponding to the formation of C–O bonds between adsorbed alkyl moieties and surface oxygen (Gleason and Zaera 1997a, b, Zaera *et al.* 1999, 2001a). In this case, 2-propyl iodide was used as a precursor for 2-propyl groups on an oxygen-pretreated Ni(100) surface (Zaera 1992, Zaera 2001a, 2002c, e). The metal was predosed with a combination of oxygen and water in order to produce hydroxyl groups as well, since it was found in our previous work that such species can enhance the reactivity of hydrocarbons toward partial oxidation pathways (Zaera *et al.* 1999, Ali and Zaera, 2001a, 2002b). The thermal evolution of this system is evidenced by the changes in the IR spectra. At low (100 K) temperatures, molecular propyl iodide adsorption is manifested not only by the appearance of a series of peaks at approximately 1012, 1080, 1140, 1194, 1367, 1387, 1450, 2860, 2910, 2955 and 2962 cm^{-1} but also by their relative intensities. By 200 K, the C–I bond is broken, and a new surface 2-propyl moiety is formed. The main spectral changes seen at that stage are in the relative intensities of the adsorption bands, but clear shifts in the 1012 and 2962 cm^{-1} features (to 1015 and 2958 cm^{-1} respectively) are observed as well. The most exciting result is observed after annealing the sample at 300 K, after oxygen atoms are inserted into the metal–

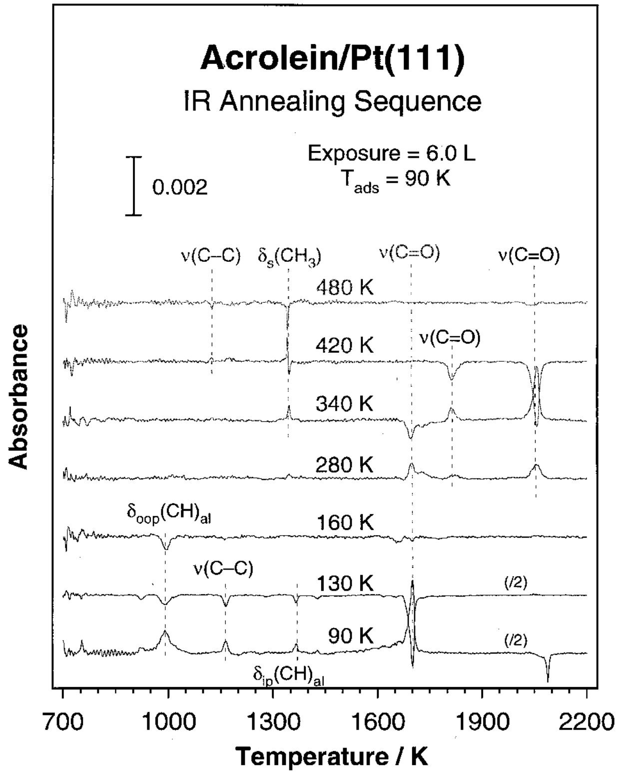

Figure 3. RAIRS for 6.0 L of acrolein adsorbed on Pt(111) at 90 K after annealing to the indicated temperatures. The spectra for the given temperatures were ratioed against those obtained for the one immediately preceding them in order to highlight the changes that the sample incurs between the two *T* values: positive peaks represent the appearance of new species, while negative ones correspond to disappearing intermediates. After molecular desorption from the multilayer and the monolayer at 130 and 160 K respectively, a series of surface species are identified by the spectra: (1) CO, which starts to form at 280 K and desorbs by 420 K; (2) ethylidyne, produced by thermal activation of chemisorbed ethylene, which appears below 340 K and decomposes by 480 K; (3) a species produced at 280 K and consumed by 340 K, which has been proposed to be either ketene or an acrolein dimer.

carbon bond and 2-propoxide intermediates are formed. Notice in particular the development of the C–O bond stretching mode about 1096 cm^{-1}. Additional experiments indicated that this alkoxide species later dehydrogenates at the β position to yield acetone (Gleason and Zaera 1997b).

2.6. *Determination of bonding interactions*

Because of the high sensitivity of molecular vibrations to variations in electronic bond structure, IR spectroscopy is also ideally suited for the characterization of the nature of the interaction between adsorbates and surfaces. This is exemplified in figure 5, which displays two IR spectra obtained for propylene adsorbed on a Pt(111) single-crystal surface as a function of coverage (Zaera and Chrysostomou 2000a). At low (submonolayer) coverages, propylene rehybridizes upon adsorption on the platinum surface, so the electronic density associated with the double character of

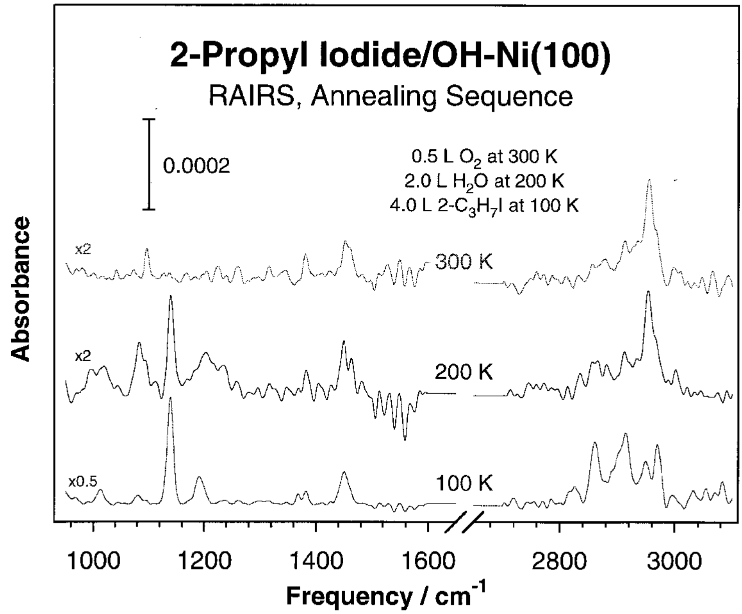

Figure 4. RAIR spectra for 4.0 L of 2-iodopropane adsorbed on a hydroxide-covered (0.5 L of O_2 at 300 K plus 2.0 L of H_2O at 200 K) Ni(100) surface. The 2-propyl iodide, used as a precursor for the formation of 2-propyl surface groups, was dosed at 90 K. Data are shown for the surface species obtained after annealing to different temperatures in order to highlight the chemical changes that occur. Of particular importance is the peak around 1090–1096 cm^{-1} seen after heating to 300 K, which corresponds to the stretching mode of the C–O bond in surface propoxide: the appearance of that vibrational band is indicative of the formation of a new bond via the insertion of an oxygen atom into a metal–carbon bond.

the carbon–carbon bond is transferred into the formation of two platinum–carbon single bonds. This electronic rearrangement, typical of unsaturated bonds adsorbed on transition metals, leads to significant changes in most of the vibrational modes of the molecule (Stuve and Madix 1985, Zaera 1995, 1996, 1998). In the example depicted in figure 5, the resulting di-σ-bonded propylene is characterized by IR peaks at 1014, 1037, 1088, 1438, 2883 and 2916 cm^{-1}. At high coverages, by contrast, new sharp features appear around 989, 1453 and 1680 cm^{-1}. Those are easily assigned to the methylene twisting, methyl asymmetric deformation, and C=C stretching modes of molecular propylene. Bonding in this case is via the donation of electronic density from the π bond of the molecule into the empty d orbitals of the metal. Additional peaks are also observed at 2939, 2963, 2978, 2995, 3066 and 3080 cm^{-1} for the C–H stretches of the methyl and methylene moieties of molecular propylene weakly bound to a second layer.

2.7. *Bonding geometries*

As stated before, Greenler established that the absorption of IR radiation by surfaces displays a strong polarization dependence (Greenler 1966, Hoffmann *et al.* 1995). This property adds some nice possibilities to the use of IR spectroscopy in surface science (Zaera 2001b). In particular, it leads to the so-called surface selection rule, which states that, on metals, only vibrational modes with dynamic dipole

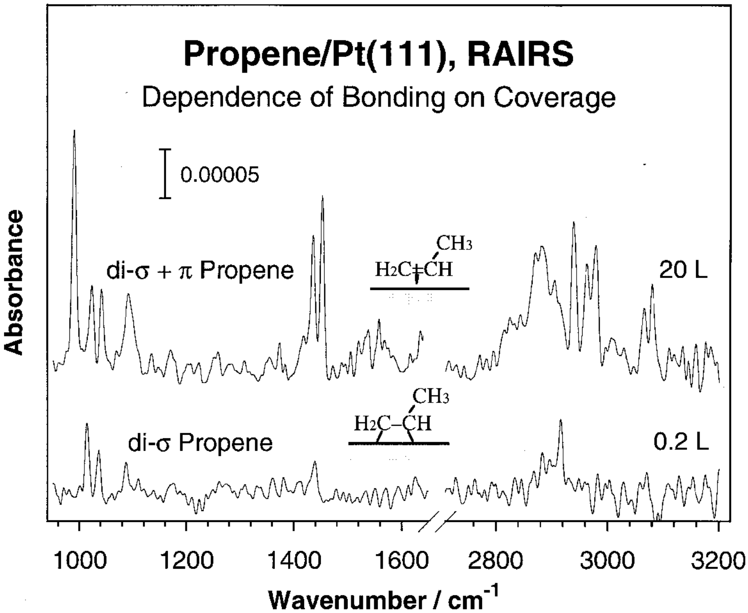

Figure 5. RAIRS data for propylene dosed on Pt(111) at 90 K for two extreme initial exposures. At least four different adsorption states were identified in this series, namely, a V-shaped di-σ state below 0.4 L, a second di-σ species with a horizontal C=C bond up to 1.0 L, a flat-lying π-bonded second layer between 1.0 and 5.0 L and a more weakly adsorbed propylidyne state beyond 5.0 L. In this figure, particular emphasis was placed on contrasting the spectra for the di-σ and π types of bonding in order to highlight the usefulness of IR spectroscopy for the study of different interactions between the adsorbate and the surface.

moments with components perpendicular to the surface plane can be detected by RAIRS (Bradshaw 1982, Hoffmann 1983, Chabal 1988, Fan and Trenary 1994, Zaera 2001b). This rule may in some instances limit the usefulness of the reflection technique for adsorbate identification because of the reduction in the number of modes visible in the IR spectra, but more often becomes an advantage thanks to the simplification of the data. Furthermore, it allows for the relative intensities of different vibrational modes to be used to estimate the orientation of the surface moieties. This has been particularly useful in the study of self-assembled and Langmuir–Blodgett monolayers, where RAIRS data have been unique in providing information on the orientation of the hydrocarbon chains (Parikh and Allara 1992). We have used RAIRS extensively in the study of adsorbed hydrocarbons, and have determined that a collective change in adsorption geometry occurs often for alkyl chains (including those in alkyl halides and in alcohols) on metal single crystals as the surface coverage is increased past the half-monolayer (Zaera *et al.* 1990a, b, Zaera and Hoffmann 1991, Hoffmann *et al.* 1992, Zaera 1992, Jenks *et al.* 1993, Gleason *et al.* 1998, de Jesús and Zaera 1999a, Chrysostomou *et al.* 2000, Jenks *et al.* 2000).

Figure 6 provides a striking example of how changes in adsorption geometry can lead to significant differences in the resulting IR spectra. The case presented there is that of the adsorption of ethylene on two copper single-crystal surfaces. On Cu(111), only one vibrational feature is prominent in the spectral range displayed, that of the

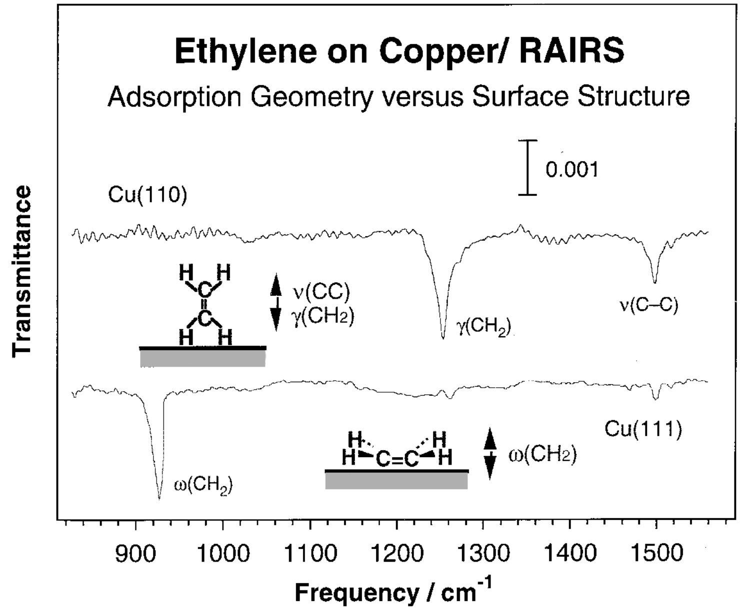

Figure 6. RAIRS traces for ethylene adsorbed on Cu(110) and Cu(111) single-crystal surfaces. Three vibrational modes are seen in those spectra: the out-of-plane CH_2 deformation at 910 cm^{-1}, the in-plane (scissors) CH_2 deformation at 1261 cm^{-1}, and the C–C stretching at 1522 cm^{-1}. The key observation here is the fact that the relative intensities of the three bands within each spectrum are dramatically different. On the basis of the surface selection rule that applies to RAIRS on metals, those changes can be traced back to changes in adsorption geometry. It was determined that while the molecular plane of ethylene is oriented parallel to the surface on Cu(111), it stands up in a perpendicular configuration on Cu(110).

out-of-plane deformation of the CH_2 groups about 903 cm^{-1} (McCash 1990). Since the dynamic dipole of that mode is oriented perpendicularly to the plane of the molecule, this means that ethylene adsorbs flat on Cu(111) surfaces. Such adsorption geometry is in fact the most common bonding configuration of olefins on metals (Zaera 1995, Sheppard and de la Cruz 1996, Zaera 2001a), and is also seen on Cu(100) (Nyberg *et al.* 1982). On Cu(110), on the other hand, the predominant features of the IR spectrum are centred at 1261 and 1522 cm^{-1} and correspond to the in-plane methylene scissoring and C–C stretching modes; no signal at all is detected for the deformation reported on Cu(111) (Jenks *et al.* 1992). The interpretation of these results is straightforward: ethylene on Cu(110) adopts a unique configuration with the main axis oriented perpendicularly to the surface.

2.8. *RAIRS sensitivity and spectral range*

One of the main shortcomings of RAIRS is its sensitivity. Studies on low-surface-area surfaces offer an intrinsic limitation in connection with this. In particular, by illuminating a 1 cm^2 single-crystal sample, it is only possible to probe up to 10^{14}–10^{15} adsorbates. Fortunately, the use of Fourier transform spectrometers, together with recent improvements in the associated detector and electronic technology, has made these experiments viable. Because FTIR is a non-zero-background technique (that is, full intensity is measured when there is no absorption from the adsorbates), the detection limit is usually defined by the absolute noise level of the spectra. These days, typical noise levels in vacuum RAIRS experiments (with ~5 min acquisition time) are of the order of $(1–2) \times 10^{-5}$ absorbance units. When working with molecules with strong dynamic dipoles such as CO, NO and PF_3, which display IR absorption peaks on the order of 10^{-2} absorbance units for a monolayer, it is possible to detect coverages well below 1% of saturation (Liang and Trenary 1988, Zaera *et al.* 1997). With adsorbed hydrocarbons, on the other hand, low-coverage studies are much more difficult, because most of their vibrational modes have absorption cross-sections 1 or 2 orders of magnitude lower than those seen with other simple molecules (Zaera *et al.* 1990b). There are some exceptions, however; witness, for instance, the high intensity of the methyl umbrella mode in ethylidyne (Malik *et al.* 1987, Zaera *et al.* 1996). Also, the adsorption of hydrocarbons with longer carbon chains sometimes leads to stronger signals (Zaera and Chrysostomou 2000a).

Another common issue related to the use of RAIRS is its limited spectral range. Typical mid-IR experiments can easily cover frequencies between 800 and 4000 cm^{-1}, but slow molecular deformations and metal–adsorbate stretches are much more difficult to detect. The low end of this range can be extended somewhat by changing detectors (commonly, by using a wide-band instead of a narrow-band cadmium-mercury-telluride detector), but this normally comes at the expense of an increase in noise level. In fact, when only vibrations above about 1900 cm^{-1} are important, it is better to use an indium antimonide (InSb) detector instead (Zaera *et al.* 1990b). Nevertheless, by carefully choosing detectors and optical elements, it is possible to probe metal–adsorbate stretches in the 400–600 cm^{-1} region (Malik and Trenary 1989). The use of synchrotron sources can also help in this endeavour (Hirschmug 1992).

In surface-science studies on single crystals and under ultrahigh vacuum conditions, vibrational spectra is often acquired by using high-resolution electron energy loss spectroscopy (HREELS) (Ibach and Mills 1982). Because of their different limitations, HREELS and RAIRS are often complementary techniques. HREELS is usually more sensitive than RAIRS and can easily probe vibrations down to the 200–300 cm^{-1} range. On the other hand, even the best HREELS instruments cannot achieve resolutions better than ~10 cm^{-1}, and more typical values range from 50 to 100 cm^{-1}. This is to be compared with the less than 1 cm^{-1} resolution possible with most commercial IR spectrometers. The lack of resolution of HREELS is a particularly severe limitation when studying complex molecules such as hydrocarbons, because of the difficulty in separating the many vibrational modes of those species in those spectra. Also, RAIRS follows more straightforward selection rules than HREELS, and spectra can usually be acquired faster. Finally, being an optical technique, RAIRS can be used in non-vacuum environments, as discussed in more detail next.

2.9. *Non-vacuum conditions*

The anisotropic nature of the absorption of light by chemisorbed species as a function of polarization direction can also be used to discriminate between adsorbates and gas- or liquid-phase molecules. This is of crucial importance for catalysis, because it makes RAIRS one of the few surface-sensitive techniques useful for *in situ* characterization of adsorbates under realistic catalytic conditions. A number of arrangements have been developed in the past for this purpose, most of them based on the idea of recording IR spectra using p-to-s polarized light intensity ratios (Dowrey and Marcott 1982, Ishida *et al.* 1987, Hoffmann *et al.* 1989, Barner *et al.* 1991). Since on metals adsorbates only absorb the p-polarized component of the IR beam incident on the surface (Greenler 1966), the p-to-s spectral ratio provides absorbance information exclusively for surface species (the signals from the homogeneous media cancel out). Thanks to these developments, it has been possible to obtain RAIRS data on species chemisorbed on single-crystal metals *in situ* under realistic catalytic conditions (Hoffmann and Weisel 1993, Bandara *et al.* 1997), even in electrochemical cells (Bewick and Pons 1985).

The most popular techniques for signal discrimination between adsorbates and molecules in homogeneous media rely on the use of photoelastic modulators (PMAs) (Bewick *et al.* 1980, Golden 1985, Griffiths and de Haseth 1986, Barner *et al.* 1991). Unfortunately, PMAs usually need to be tuned around a specific vibrational frequency, since their behaviour varies sinusoidally with photon energy. This makes them impractical for the acquisition of IR spectra in a broad range of frequencies, a key requirement for many experiments involving complex molecules with large numbers of vibrational modes. In order to overcome this difficulty, we in our laboratory have developed an alternative arrangement based on the static mixing of the two beams originating from cube-corner interferometers (Hoffmann *et al.* 1989). The arrangement used by us is shown schematically in figure 7, and typical data illustrating its performance are reported in figure 8. Our set-up takes advantage of the fact that the two signals exiting the beam splitter of most Fourier-transform interferometers are 180° out of phase. By using a recombining polarizer, the two

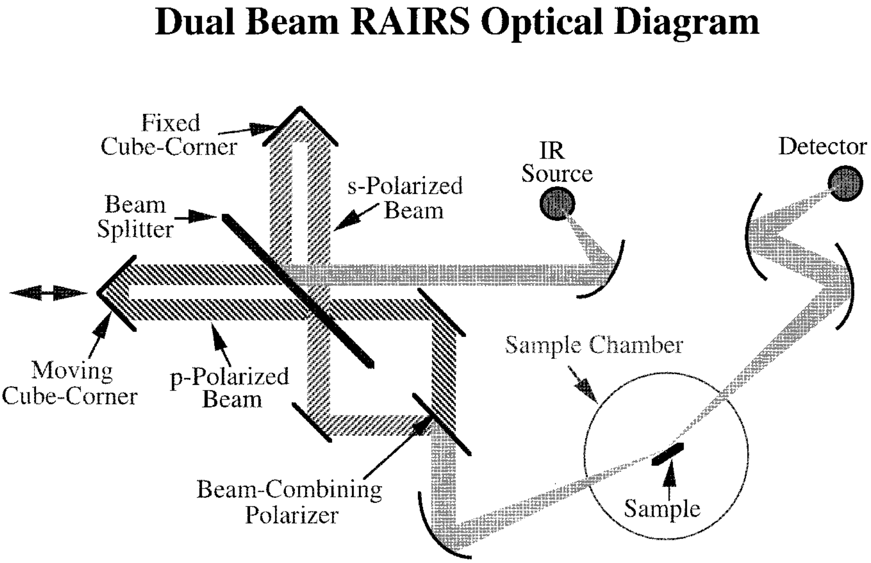

Figure 7. Schematic representation of the static dual-beam FTIR spectroscopy set-up developed in our laboratory to discriminate between molecules in gas or liquid phases and adsorbates on solid surfaces. Both beams out of a cube-corner FTIR interferometer (hatched lines) are added by using a recombining polarizer. Given that the two beams are 180 out of phase, their recombination usually leads to a DC signal, but since they are also polarized at right angles from each other, a residual signal due to the preferential absorption of p-polarized light by species chemisorbed on the surface is detected.

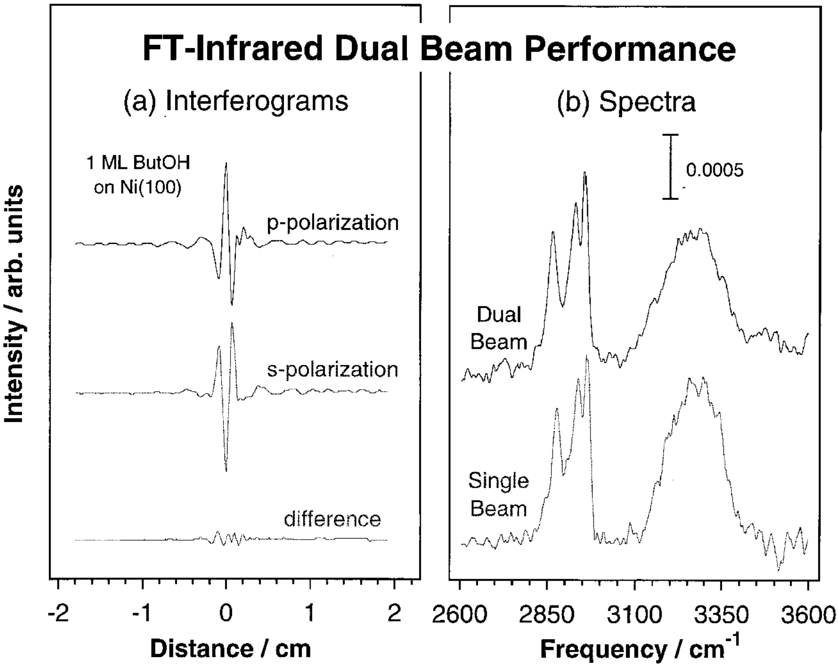

Figure 8. Representative data from experiments using the dual-beam FTIR spectroscopy set-up shown in figure 7. The left panel displays the raw interferograms obtained from each of the beams exiting the beam splitter of the interferometer (the hatched lines in figure 7). Notice the 180° out-of-phase displacement of the two (s- and p-polarized) single-beam traces and also the small residual interferogram seen for the combined beam (left panel, bottom trace) corresponding to the absorption of the p-polarized IR radiation by the molecules on the surface. The right panel contrasts the spectra obtained by Fourier transformation of an interferogram obtained with a regular single beam against that from our dual-beam arrangement for the case of one monolayer of *n*-butanol on Ni(100). Comparable spectra are obtained in both cases. The advantage of the dual-beam approach is that spectra can be acquired in non-vacuum conditions such as those present during catalysis.

beams can be added such that they are also perpendicularly polarized with respect to each other. The different polarization directions of those two components do not affect their behaviour through isotropic media, so they cancel each other out, but when the added beam is reflected off surface species, a difference corresponding to the selective absorption of the p-polarized component is seen. The net result is a small residual interferogram resulting from absorption by the chemisorbed molecules, which can then be Fourier transformed to obtain the IR spectra of those species (figure 8).

The effectiveness of using IR polarized light to characterize adsorbed species selectively is illustrated by our recent results from studies on the chemisorption of cinchonidine on platinum surfaces (Kubota and Zaera 2001, Kubota *et al.* 2002). Our interest in this system derives from the observation that some chiral molecules can be used to impart enantioselectivity to heterogeneous catalysts (Baiker and Blaser 1997). Specifically, the hydrogenation of α-keto esters on supported platinum can be performed with a high degree of enantioselectivity if the catalyst is modified with cinchona alkaloids (Orito *et al.* 1979, LeBlond *et al.* 1999). It has been

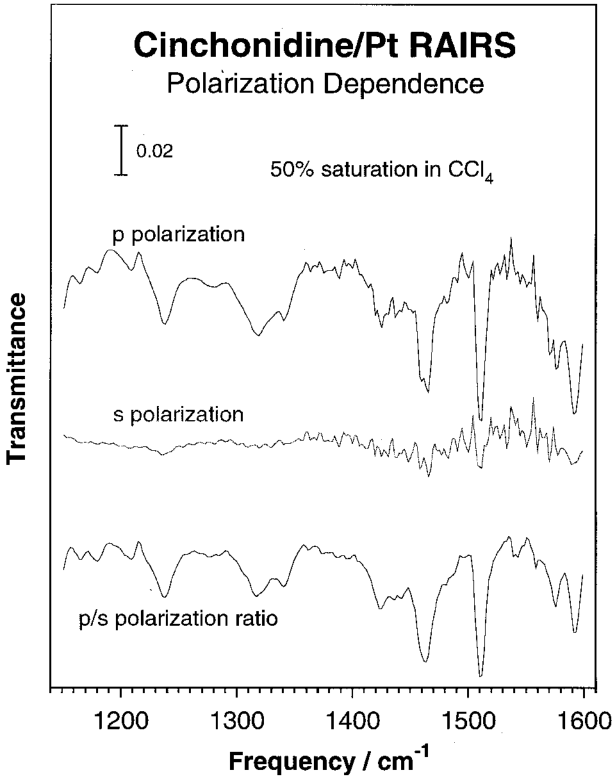

Figure 9. RAIRS traces for cinchonidine adsorbed from a carbon tetrachloride solution onto a platinum foil, taken *in situ* by using a liquid cell equipped with appropriate IR optics. The two top traces correspond to the data recorded by using p- and s-polarized radiation. Notice that significant absorption bands are observed only in the spectrum acquired using p-polarized light, because the IR absorption surface selection rule indicates that the electrical field of the s-polarized light at the surface is equal to zero. Thanks to this, it can be established that the vibrational modes seen in the bottom trace, the one corresponding to the p-to-s ratio, correspond to adsorbed species exclusively. Adsorption geometries can then be determined by further analysis of the relative intensities of those bands.

speculated that both the yields and the enantioselectivity excess ratios in those -keto ester catalytic hydrogenations can be optimized by tuning the adsorption geometry of the aromatic ring of the cinchona modifier (Bond *et al.* 1991). We have proven that such a hypothesis can be tested directly by RAIRS. First, the feasibility of using RAIRS for the characterization of the adsorption of cinchonidine from a liquid (CCl_4) solution was indicated by data such as those in figure 9 (Kubota *et al.* 2002). As explained above, since the molecules on the surface absorb only p-polarized light, the ratio of the p-to-s spectra produces a trace with bands exclusively associated with the adsorbed cinchona. It was found in our studies that the initial concentration of the modifier in the carbon tetrachloride solution controls its adsorption geometry on the platinum surface and, with that, the performance of the catalyst (Kubota and Zaera 2001). Three distinct regimes were seen as a function of that concentration, namely, no adsorption from solutions below 5% of saturation, a flat geometry for concentrations between 5% and 20% and a tilted configuration above 20%. The interesting observation from our study is the fact that the adsorption geometry changes identified by IR correlate nicely with the activity and selectivity variations reported for a similar system (LeBlond *et al.* 1999): it is when the aromatic ring of the cinchonidine adsorbs in a flat geometry on the surface that the selectivity of this system is optimized (Kubota and Zaera 2001).

2.10. *Other infrared spectroscopy approaches*

An alternative to RAIRS for the characterization of small flat surfaces is ATR. The basis for ATR was introduced in 1960 by Harrick, who demonstrated that for transparent substrates absorption spectra of adsorbed layers could be obtained using internal reflection (Harrick 1960). By cutting the sample in a trapezoidal shape, the IR beam can be made to enter through one end, bounce internally a number of times from the flat parallel edges, and exit out the other end without any losses, leading to high adsorption coefficients for the species adsorbed on the external surfaces of the plate (Chabal 1988).

In the past, ATR has been used primarily in connection with the characterization of semiconductor surfaces. For instance, McCombe *et al.* reported some pioneering work on the characterization of intersubband optical transitions in silicon metal–oxide–semiconductor field-effect transistors using this approach (McCombe *et al.* 1979). Significant experimental difficulties need to be resolved before ATR becomes widely used in catalytic studies. Nevertheless, there have already been a few reports in this area (Awatani *et al.* 1998, Ferri and Buergi 2001, McQuillan 2001). One particularly interesting extension to the use of multiple internal reflection for the characterization of non-transparent samples was discussed by Bermudez, who suggested that the sensitivity to adsorbates in IR reflection spectroscopy can be enhanced by burying a metal layer beneath the surface of a dielectric material (Bermudez 1992). This approach could be easily extended to the study of catalytic model systems.

There have been a few other experimental set-ups developed for the IR characterization of surfaces. Both tunable IR lasers (Hoffmann *et al.* 1986, Wragg *et al.* 1988) and synchrotrons (Hirschmug 1992) have been used as alternative sources in IR reflection absorption spectroscopy. Absorption spectra may only be obtained in a limited range of frequencies this way, and the data acquisition is slowed down by the loss of the Fourier-transform advantage. On the other hand, high-resolution data can be easily obtained, and kinetics can be easily followed in the microsecond time domain (Borguet and Dai 1990). Another approach is photo-acoustic spectroscopy (PAS) or, more generally, photothermal IR spectroscopy. This relies on temperature fluctuations caused by radiating the sample with a modulated monochromatic beam: the acoustic pressure wave created in the gas layer adjacent to the solid by the adsorption of light is measured as a function of photon wavelength in order to determine the absorption spectra (Griffiths and de Haseth 1986). It has sometimes been thought that PAS is more surface sensitive than DRIFTS, but in fact that depends on the specific optical and thermal properties of the material being studied. In emission spectrometry, the IR radiation emitted by the sample is directly collected and analysed. The detection of the (non-monochromatized) IR radiation from thin films has recently being combined with molecular beam techniques to perform differential microcalorimetric measurements on adsorption processes (Borroni-Bird and King 1991). Finally, the sample itself can be used as the detector of IR radiation. None of these techniques has found much use in surface studies to date.

3. Molecular beams

Concurrently with our focus on the use of IR spectroscopy for the characterization of surface intermediates, we have also developed a programme for the use of molecular beams to obtain kinetic information on surface reactions of catalytic importance. Molecular beams are ideally suited for the study of surface kinetics on model systems, because they allow for great control of the parameters that define the conditions of the reaction. For one, collimation defines the directionality of the beam with respect to the surface plane. If supersonic expansion is used, additional control can be exerted on the energy of the reactants, both on their kinetic energy and on the energies of the different internal degrees of freedom. Finally, the details of the outgoing reactants can be characterized by angle-resolved, time-of-flight and spectroscopy-based detection. Kinetic experiments with molecular beams can be easily carried out isothermally and, in some cases, isosterically as well.

Molecular beams have been used extensively for the characterization of the physical properties of surfaces. For instance, helium diffraction experiments have been employed to probe surface ordering (Engel and Rieder 1982). Helium and hydrogen atom scattering can also be used to map out gas-surface potential energy surfaces (Barker and Auerbach 1985). Measurement on the inelastic scattering of atoms provides a direct method to interrogate surface vibrational properties (Toennies 1982, Farias and Rieder 1998). The dynamics of many surface processes can be investigated with molecular beams (Cardillo 1994, Tully 2000). Since much work has already been published on these applications, our attention here will focus on the use of molecular beams for the characterization of chemical kinetics.

There has also been some pioneering molecular beam work reported for the study of simple reactions on single-crystal surfaces. In particular, the use of modulation in conjunction with lock-in detection has been used to determine the dynamics of a number of surface reactions (Schwarz and Madix 1968, Engel and Ertl 1978). Time-resolved molecular beam experiments have also helped in differentiating between Langmuir–Hinshelwood and Eley–Rideal mechanisms (Ertl and Kueppers 1971) and in separating mass transport from chemical conversion steps (Chang and Weinberg 1977). Isotopic labelling has been used to determine the role of steps in catalysis as well (Salmeron *et al.* 1977). Unfortunately, most of the past work on surface reactions with molecular beams has been performed using supersonic expansions, and the high energies of the molecules from those sources impinging on the surface make the extrapolation of the results to realistic catalytic conditions less than straightforward. Low-energy or effusive beams are perhaps more appropriate for the emulation of catalytic processes. Below we discuss this issue in more detail, and describe some of the chemical kinetic information extracted from some recent molecular beam work reported by us and others.

3.1. *Molecular activation*

One of the areas of surface chemistry where molecular beam work has contributed greatly is the activation of stable molecules by surfaces. In particular, extensive work has been performed to elucidate the mechanism of alkane activation by metals. It has been concluded that the promotion of C–H bond-scission steps in alkanes by metal surfaces may occur either directly on collision of the incoming gas molecule with the solid or via the formation of weakly adsorbed intermediates trapped on the substrate (Rettner *et al.* 1985, Ceyer *et al.* 1987). It has also been shown that the critical factor for alkane activation is the efficiency with which energy is transferred from the translational and internal degrees of freedom of the gas molecules to the particular C–H bond to be broken; the energy stored by the surface is often of little importance for this process (Rettner *et al.* 1985, Ceyer *et al.* 1987, Hamza and Madix 1987). It has been reported that it is the normal component of the translational energy of the alkane that is important for the C–H bond-breaking step (McMaster and Madix 1992, Verhoef *et al.* 1994), and Stewart and Ehrlich revealed that the vibrational modes of the incoming molecules are the most likely to provide energy for the dissociation of methane (Stewart and Ehrlich 1975).

Direct alkane activation may occur via a tunneling mechanism (Yang and Whitten 1992), at least at the high kinetic energies associated with supersonic beam experiments. Alkane sticking probabilities often increase monotonically with increasing kinetic energy, not in a stepwise fashion at a given threshold energy value as expected if the kinetics were dominated by an activation barrier. Also, the observed shifts in the translational energy needed to activate CH_4 vs. CD_4 (or C_2H_6 vs. C_2D_6) are usually on the order of $5\,\mathrm{kcal\,mol^{-1}}$, much larger than the differences in the zero-point energy due to isotopic substitution (Verhoef *et al.* 1994). On the other hand, the energy and angle dependences of the sticking coefficient of methane observed on some metals may be explained by a classical model based on the microscopic reverse of the reductive elimination of methyl with hydrogen (Ukraintsev and Harrison 1994). Furthermore, other molecular beam work has provided evidence for a precursor-mediated alkane activation mechanism. The trapping probability of ethane on Ir(110)-(1 × 2), for instance, shows only a weak dependence on the angle of incidence of the beam, suggesting that the momentum of the incoming molecules is rapidly transferred to the surface (Mullins and Weinberg 1990). In some cases, the dissociation of alkanes is also assisted by a reverse energy transfer from the surface to the molecule. On both platinum and rhodium, for example, the sticking probability of methane displays an Arrhenius temperature dependence in the limit of low kinetic energy, with an activation energy between 5 and $10\,\mathrm{kcal\,mol^{-1}}$ (Luntz and Bethune 1989).

Unfortunately, supersonic beams probe only a small fraction of the gas molecules in typical catalytic mixtures, those at the high-energy tail of the Boltzmann distribution. Consequently, the probability of alkane activation under normal catalytic conditions by the same direct collision processes observed in molecular beam experiments is predicted to be quite low (Hanley *et al.* 1991). Additional complications arise from the fact that the mechanism of activation may change with varying incident energy. In fact, recent studies with low-energy beams have indicated that the probability of dissociation for methane on platinum decreases with increasing incoming kinetic energy, a result that is counterintuitive and that has yet to be properly explained (Reeves *et al.* 2001).

3.2. *Sticking probabilities*

Molecular beam work has also helped significantly in developing an understanding of the kinetics of adsorption (Doyen 1987, Engel 1987, Bowker 1997). From the kinetic point of view, adsorption is often described in terms of sticking coefficients, that is, in terms of the probability for a molecule impinging on a surface

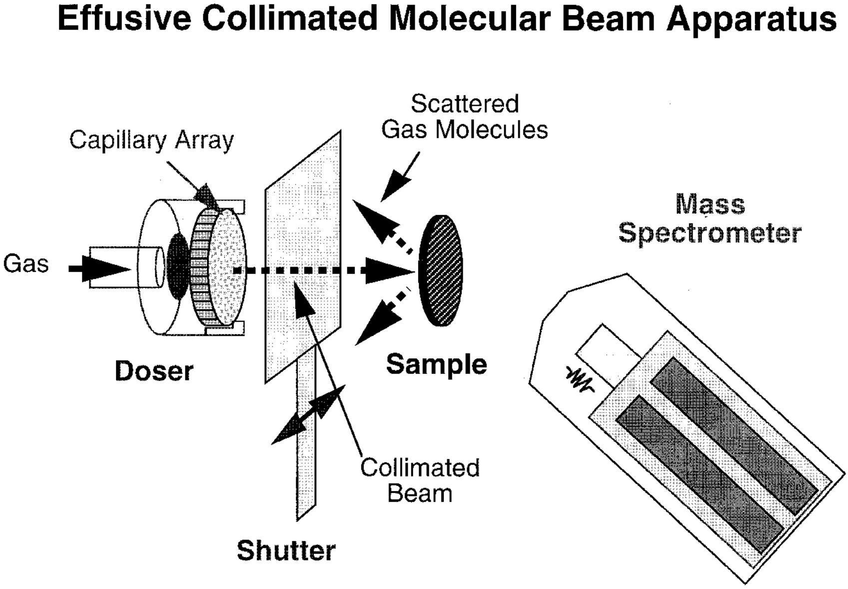

Figure 10. Schematic representation of the effusive molecular beam experimental instrumentation used for the kinetic measurements described in this review. Our set-up consists of a capillary array doser used to produce collimated beams, a shutter, and a mass spectrometer, used for the detection of gas molecules desorbing from the surface. The surface, typically a 1 cm diameter single crystal, is placed within 1 cm of the front face of the doser, which is bigger (~1.3 cm) to ensure that the sample only intercepts the central (and homogeneous) portion of the beam. The mass spectrometer is placed out of the line of sight of both sample and doser in order to integrate over any angular profile of the desorption process.

to adsorb instead of scattering back into the gas phase. These sticking probabilities have commonly been measured by a method pioneered simultaneously by King and Wells (1972) and Madey (1972) which relies on reflectivity measurements of molecular beams directed at solid surfaces. Further details on how this method works are provided later in this section. It has been found from studies using the King and Wells technique that initial sticking coefficients (s_0) on clean surfaces are often quite high, close to unity, but that they can also be very low (10^{-10} or lower), in particular with saturated hydrocarbons (as mentioned above), or when adsorbing on oxides or other covalent solids (Somorjai 1981, Zaera 2001a).

As indicated above, supersonic beams allow for the control of the energetics of the reacting molecules but typically produce molecules with energies several times higher than those found in regular gas reaction mixtures. In order to obtain more realistic kinetic parameters in terms of catalysis, we in our laboratory have developed a variation of the King and Wells methods that uses effusive collimated beams instead (Liu *et al.* 1995, Zaera and Gopinath 2000b, Zaera 2002a). A schematic representation of our instrument is provided in figure 10. A collimated beam of the gas of interest is generated by a capillary array and directed towards the sample while the partial pressure of the gaseous environment is recorded with a non-line-of-sight mass spectrometer. A shutter is placed between the doser and the sample in order to control the time of direct exposure of the surface to the beam. The size of the beam and position of the sample are chosen so that the single crystal only intercepts about 15–25% of the total gas flux in order to ensure a homogeneous beam profile across the surface (Liu *et al.* 1995, Guevremont *et al.* 2000).

3.3. *Adsorption kinetics*

In its most straightforward application, the molecular beam set-up described above can be used to measure adsorption probabilities. An example of this is provided in figure 11 for the case of the adsorption of carbon monoxide on a Pt(111) single-crystal surface (Liu *et al.* 1995). Notice that these experiments provide information not only on initial sticking probabilities (on the clean surface) but also on the evolution of those probabilities as a function of coverage. This allows for a comparison with known models for adsorption, such as simple Langmuir isotherms or precursor-mediated kinetics (Kisliuk 1957, Morris *et al.* 1984). We have in the past performed Monte Carlo simulations to explore these ideas in detail (Nordmeyer and Zaera 1992).

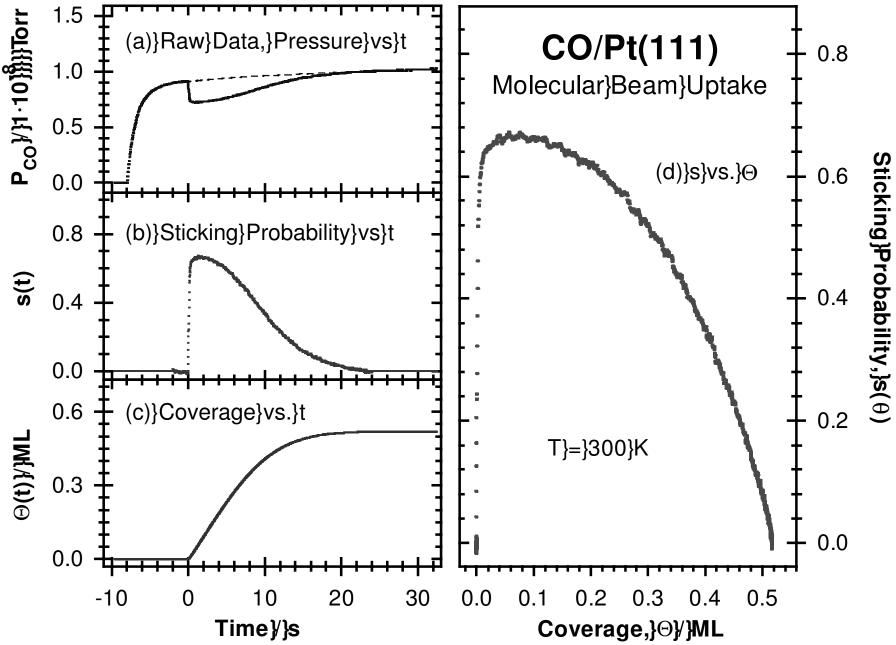

Figure 11. Typical kinetic data from experiments using the molecular beam arrangement shown in figure 10. This case corresponds to the uptake of carbon monoxide on a Pt(111) surface at 300 K. (*a*) Raw data, in the form of CO partial pressure (P_{CO}) vs. elapsed time. The beam is turned on at $t = -8$ s, but the shutter is kept in place at that time in order to avoid direct exposure of the crystal to the beam. The observed rise in signal corresponds to the increase in pressure due to CO scattering off the intercepting flag. The flag is then removed at $t = 0$ s, at which point the partial pressure of CO drops because of its removal from the gas phase via adsorption on the surface. Finally, P_{CO} returns asymptotically to the value before the flag is removed as the platinum surface becomes saturated with CO. (*b*) Plot of the CO sticking probability (s) vs. time, calculated directly from the data in the first panel after appropriate calibration. (*c*) CO surface coverage (Θ) vs. time, obtained by integration of the temporal evolution of the sticking coefficient. (*d*) Sticking probability vs. coverage for CO adsorption on Pt(111) at 300 K, obtained by combining the data in (*b*) and (*c*).

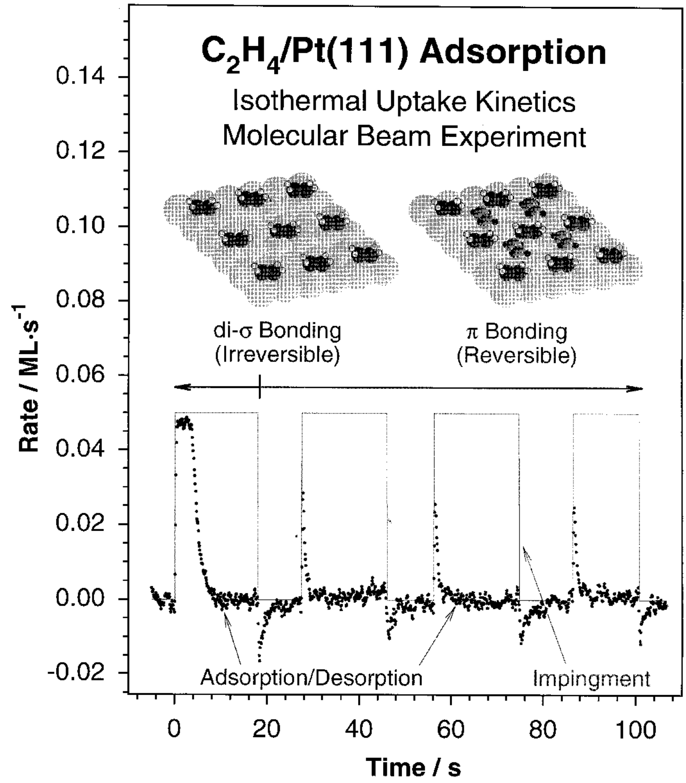

Figure 12. Isothermal kinetic data for the uptake of ethylene on Pt(111) at 270 K obtained with our molecular beam set-up. The initial adsorption of ethylene seen within the first 20 s of the experiment, associated with strongly bonded di-σ ethylene, is followed by an additional reversible adsorption of weakly (π) bonded olefin, as manifested by the spikes observed right after blocking and unblocking of the beam. It was determined that the weakly bonded ethylene is the one relevant to catalytic hydrogenation reactions. This example illustrates how molecular beams can be used to follow the kinetics of reversible surface reactions under both isothermal and isosteric conditions.

Molecular beam techniques can also be used to follow the transient kinetic behaviour of adsorption systems around equilibrium. Ideally, kinetic measurements should be performed under both isothermal and isosteric conditions in order to separate the effects exerted by temperature and coverage on the overall kinetics of reaction. Figure 12 illustrates how transient adsorption–desorption kinetics can be evaluated in the case of ethylene adsorption on Pt(111) (Zaera *et al.* 1996, Öfner and Zaera 1997, Zaera 2002b, c, e,). Our interest in this system stems from the significant differences in the mechanism of catalytic hydrogenation identified between model vacuum conditions and more realistic atmospheric pressures. It has become clear that, in systems involving double bonds, the very nature of the adsorbate–substrate interaction changes with increasing coverage, so two distinct types of adsorption modes develop: a strongly di-σ interaction on clean surfaces, and a more weakly π bonding after the surface is covered with other adsorbates (Zaera and Chrysostomou 2000a, b). The second mode of adsorption is of particular significance to hydro-

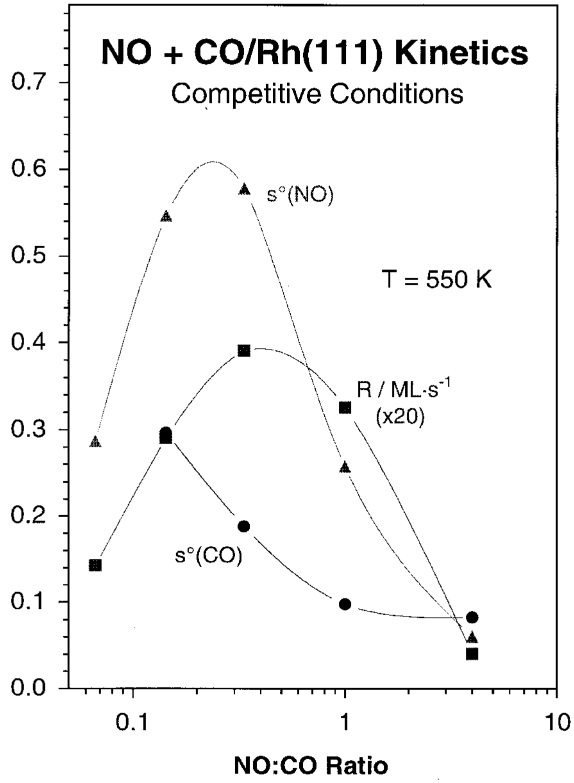

Figure 13. Changes in sticking coefficients for carbon monoxide and nitrogen monoxide on Rh(111) and in the rate of conversion of NO + CO mixture as a function of the composition (the NO:CO ratio) of the premixed molecular beam used in the experiments. These data correspond to a surface temperature of 550 K. A nice general correlation was observed between the adsorption probabilities of CO and NO and the rates of the overall NO + CO conversion to molecular nitrogen and carbon dioxide. It is worth highlighting that the sticking coefficients reported here are associated with competitive adsorption conditions, where both CO and NO molecules impinge simultaneously on the surface. It is clear that each gas exerts a detectable effect on the adsorption probability of the other.

genation catalysis, because the catalytic metal surfaces become covered with carbonaceous species immediately after exposure to the reaction mixture (Zaera and Somorjai 1984, Wieckowski *et al.* 1985, Zaera and Somorjai 1988, Zaera 2002c). Our molecular beam kinetic work on the ethylene/Pt(111) system has revealed that it is the weakly bonded π olefins, those that adsorb reversibly according to the data in figure 12, the ones that intervene directly in the hydrogenation process (Öfner and Zaera 1997).

Catalysis often involves two or more reactants. Accordingly, the kinetics of adsorption of catalytic reactants needs to be determined under competitive conditions. This is easily accomplished by using mixed molecular beams (Liu *et al.* 1996, Gopinath and Zaera 1999). It is important to realize that the kinetics of adsorption of a given reactant can be deeply affected by competition with other adsorbates (Zaera 2001a). A direct observation of this is reported in figure 13 for the case of the reaction between nitrogen monoxide and carbon monoxide on an Rh(111) single-crystal surface (Gopinath and Zaera 2000). NO reduction is a critical step in the catalytic conversion of polluting gases from the exhaust of automobiles and power plants that, to date, can only be performed efficiently by expensive rhodium-based catalysts (Shelef and Graham 1994, Farrauto and Heck 2000). Our work in this area focuses on trying to determine the kinetic reasons behind the unique performance of rhodium for this process (Zaera and Gopinath 2000b, 2001). We have found that the rate of reaction between NO and CO can be optimized by using gas mixtures which yield equal coverages of both reactants on the surface. The data in figure 13 indicate that such conditions are defined, at least in part, by the changes in sticking coefficients of both reactants as a function of the composition of the reaction mixture (Gopinath and Zaera 2000).

3.4. *Surface reactions*

In many instances, chemical adsorption is immediately followed by surface reaction. The kinetics of reactive adsorption can also be studied with molecular beams, in particular when the products desorb from the surface (and can be detected in the gas phase). Examples of this include our work on the decomposition of nitrogen oxide on rhodium surfaces, a reaction that leads to the desorption of molecular nitrogen (Aryafar and Zaera 1998), and on the conversion of ethylene to ethylidyne over platinum (Öfner and Zaera 1997). Typical data for the latter system are provided in figure 14 to highlight some of the potential complexities of research in these types of problems. Notice in particular that ethylidyne ($Pt{\equiv}C{-}CH_3$) formation is detected only indirectly, via the desorption of molecular hydrogen. Several steps are involved in that process (Zaera 1996, Zaera and French 1999), including a 1,2-H shift in ethylene to form an ethylidene ($Pt{=}CH{-}CH_3$) intermediate (Zaera 1998) and subsequent fast α-H elimination (Janssens and Zaera 1996) and H–H recombination (Christmann *et al.* 1976) reactions. Therefore, caution should be exerted when analysing the molecular beam H_2 desorption kinetic data from this system (Zaera *et al.* 1988, Janssens and Zaera 1995). The one thing that is clear is the fact that the delay between the adsorption of ethylene and the production of hydrogen is indicative of the need for the build-up of a critical C_2H_4 coverage before other reactions can take place. Also, a small amount of ethane is formed simultaneously during the decomposition of ethylene to ethylidyne, although the yield of that product is low enough not to affect the kinetics of the latter reaction in any significant way.

The production of both hydrogen and ethane seen in figure 14 is transient, because the clean Pt(111) is poisoned by the ethylidyne byproduct that builds up on that surface with ethylene exposure time. A similar behaviour is observed in the case of the conversion of nitrogen monoxide on rhodium, the reason there being the blocking of sites by the deposition of atomic surface oxygen (Aryafar and Zaera 1998). Nevertheless, other reactions can be sustained catalytically under appropriate conditions, so many turnovers can be carried out without any loss of activity (as in real catalytic systems). For instance, NO reduction can be made catalytic by adding a reducing agent to the reaction mixture. As an example of this, figure 15 shows typical molecular beam data for the steady-state conversion of NO with CO on an Rh(111) single crystal (Gopinath and Zaera 1999, Zaera and Gopinath 2000b). When the impingement of the reactive beam is interrupted in that case, step-like changes are seen in the partial pressures of the reactants and products corresponding to changes

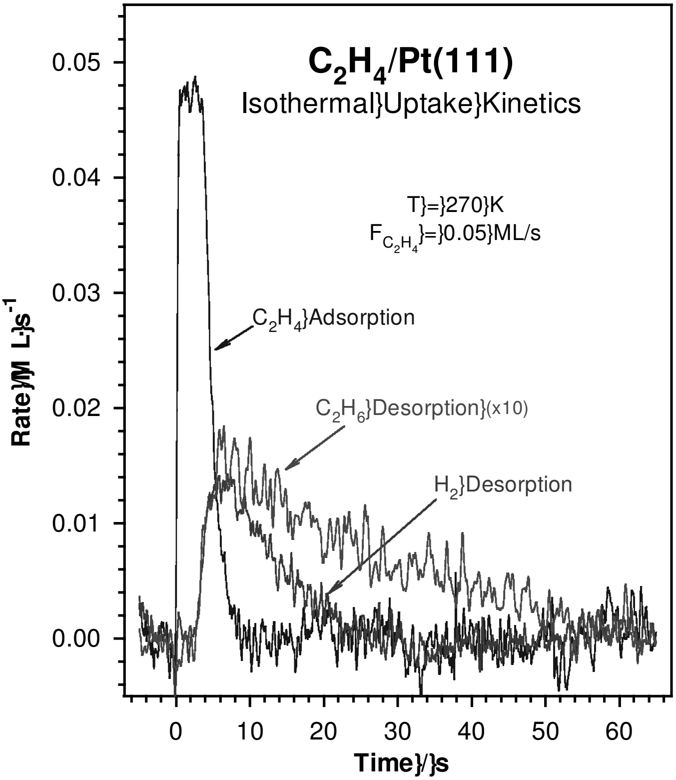

Figure 14. Typical isothermal kinetic raw data for the conversion of ethylene on Pt(111) at 270 K. The rates of ethylene consumption, hydrogenation to ethane and ethylidyne formation were measured as a function of time by following the mass spectrometer signals for 25, 30 and 2 amu, respectively, after calibration and correction for cracking interferences in the mass spectrometer. Notice in particular the delay in hydrogen and ethane production, indicative of complex surface kinetics. These data can be used to extract kinetic parameters for the reactions that ethylene follows after adsorption on the platinum surface.

in the steady-state rate of the reaction. These changes are reversible, so restoration of the exposure of the crystal to the molecular beam results in the recuperation of the signals seen before the beam was blocked. Also, the transient response right after the blocking and unblocking of the beam provides some insight into the mechanism of reaction. In the example of figure 15, for instance, the slow response of the $^{15}N_2$ trace to the beam perturbations indicates that molecular nitrogen production is involved in the rate-limiting step of the NO reduction process.

The kinetics of bimolecular reactions can be probed with molecular beams in at least three different ways. Perhaps the most direct of those is the use of beams with premixed reactants, as in the case of the example in figure 15 (Liu *et al.* 1996, Gopinath and Zaera 1999). In fact, this approach is not limited to just two reactants; witness, for instance, our recent work with $NO + CO + O_2$ mixtures (Gopinath and Zaera 2001). Alternatively, it is possible first to adsorb one of the reactants and then to follow the temporal evolution of the appropriate species as the predosed surface is exposed to a molecular beam of the second reactant. We have used this arrangement

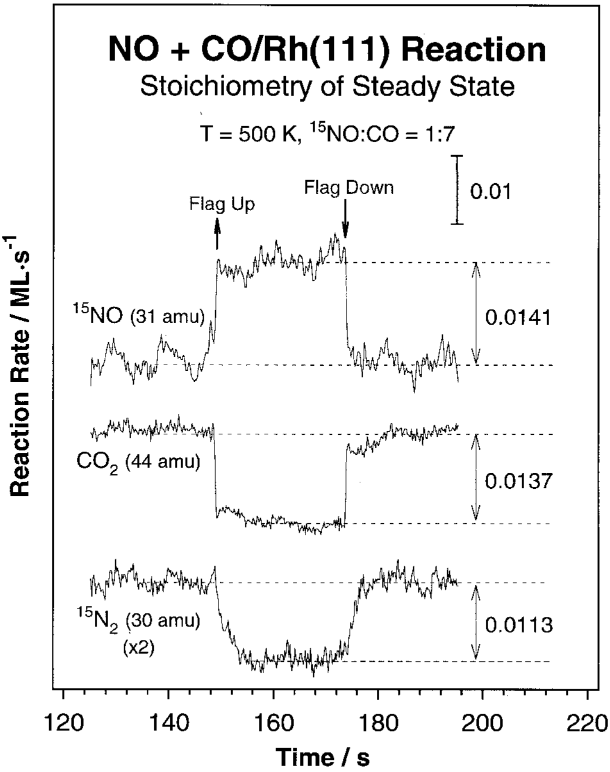

Figure 15. Time evolution of the reaction rates for the uptake of ^{15}NO and for the production of $^{15}N_2$ and CO_2 in the steady-state regime of the conversion of a $^{15}NO + CO$ mixture ($^{15}NO:CO = 1:7$) on an Rh(111) single-crystal surface heated to 500 K. The catalytic nature of the reaction was checked by temporarily blocking the reaction mixture beam (between $t = 148$ and 176 s) in order to measure the net changes in the partial pressures of the appropriate species induced by the surface reaction. Step-like changes are seen in the traces for the temporal evolution of ^{15}NO and CO_2, which, after calibration, were converted to the corresponding steady-state rates. The signal for molecular nitrogen production, on the other hand, responds more slowly to the perturbations of the beam, indicating that nitrogen production is involved in the rate-limiting step of the overall reaction. The behaviour shown here can be repeated indefinitely, even after many turnovers. These data also show how the steady-state rate of NO adsorption is equal, within experimental error, to that of CO_2 production and to twice the N_2 production, a result that corroborates the stoichiometry of the reaction as $NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$.

to investigate both the oxidation of carbon monoxide (figure 16) (Zaera *et al.* 1997) and the hydrogenation of ethylene (Öfner and Zaera 1997). The pre-adsorption method is limited by design to the study of transient behaviour, since the reaction stops once the first reactant is fully consumed, but can nevertheless offer additional and complementary information to that from experiments with mixed beams. Finally, a pure one-component molecular beam can be used to control the kinetics of the reaction being studied while a constant pressure of the second gas is maintained in the background. This technique is in many ways similar to the first, except that it may offer more flexibility for transient kinetic measurements after small perturbations from steady-state conditions.

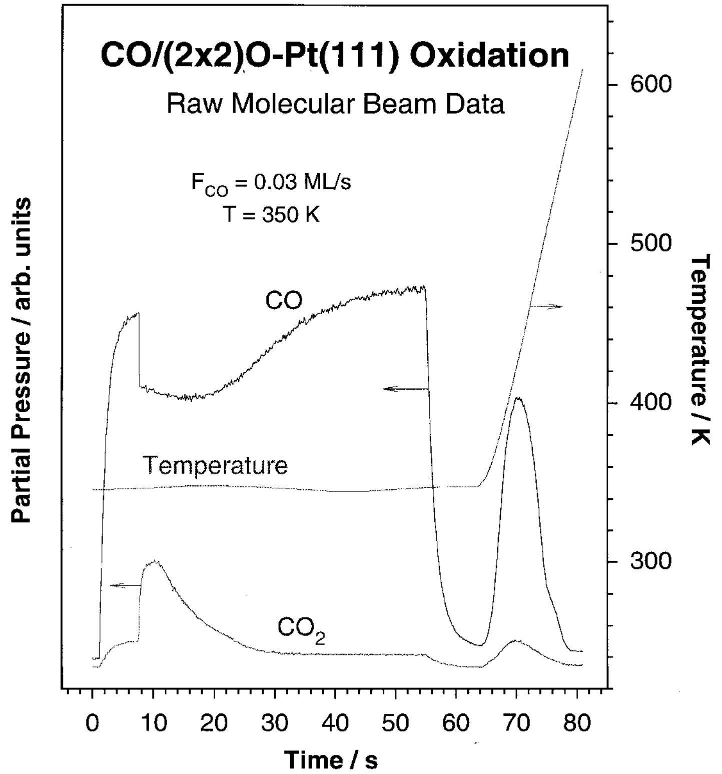

Figure 16. Typical isothermal kinetic raw data for the oxidation of carbon monoxide on a Pt(111) single-crystal surface. In these experiments, an effusive directional CO molecular beam ($F_{CO} = 0.03\,\mathrm{ML\,s^{-1}}$) is directed onto a platinum surface predosed with oxygen (to saturation of the ordered p(2×2) layer). The crystal is then kept at a constant ($T = 350\,\mathrm{K}$) temperature while the partial pressures for both CO and CO_2 are followed as a function of time. Oxidation is detected for approximately 20 s after the start of the exposure of the surface to the CO beam, but then stops when the reactive oxygen on the surface is consumed. The adsorption of additional carbon monoxide at that point is indicated by the extended time period before the partial pressure of CO reaches its steady-state value ($t \sim 50\,\mathrm{s}$). Finally, the beam is blocked and the temperature is ramped to acquire standard temperature-programmed desorption (TPD) spectra from the resulting surface. Notice in particular the desorption of a small amount of CO_2, indicative that not all the predosed oxygen reacts at 350 K.

3.5. *Isotope labelling*

In order to obtain additional information on the mechanism of surface reactions, molecular beam experiments can be complemented with isotope labelling. Isotopic substitution is a well established method in many fields of chemistry, and has been used extensively in surface science as well (Zaera and Somorjai 1985, Zaera 1990, Janssens and Zaera 1995, Janssens *et al.* 1998, Zaera and French 1999, Chrysostomou *et al.* 2001). In the case of surface kinetics, isotope substitutions can lead to significant variations in reaction rates (Gland *et al.* 1988, Zaera *et al.* 1988) and even induce a change in reaction mechanism (Janssens *et al.* 1997). Nevertheless, in molecular beam work, isotope labelling has primarily been used to

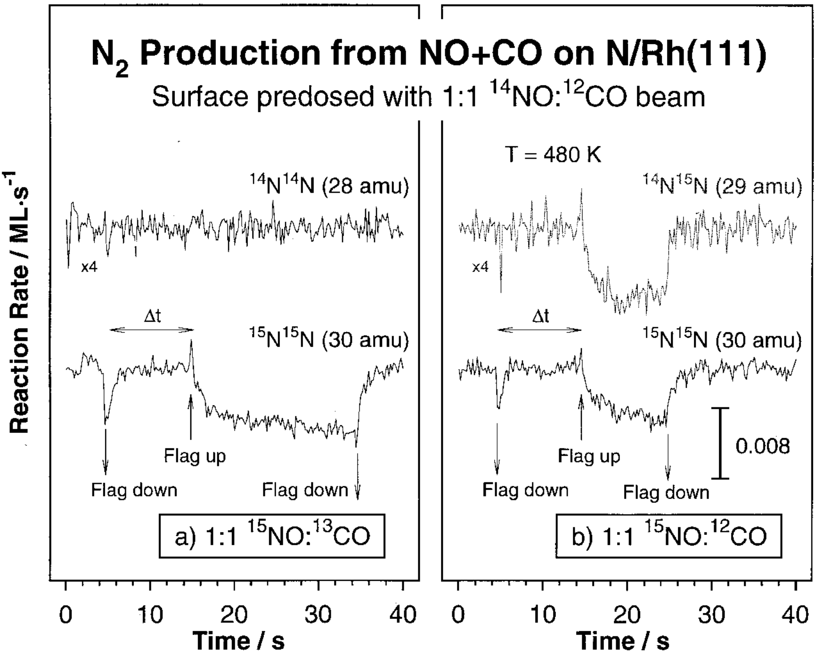

Figure 17. Typical raw data (after background subtraction) from the second half of two different isotope switching experiments for the conversion of NO with CO on Rh(111) ($T = 480$ K, NO:CO = 1:1). The first 250 s of these kinetic runs (the first half, not shown here) were carried out by using a $^{14}NO + ^{12}CO$ beam. After that, the first beam was replaced with a similar mixture of either $^{15}NO + ^{13}CO$ (left) or $^{15}NO + ^{12}CO$ (right). The steady-state rates of formation of the three possible N_2 isotopologsmes as a function of the time delay (Δt) after the isotope switching is indicated by the pressure drops at the first flag-up points of those traces, at $t = 15$ s in this case. While changes in the rates for $^{14}N^{15}N$ and $^{15}N^{15}N$ production are easily seen, no $^{14}N^{14}N$ formation is observed at all, indicating that at least one incoming NO molecule is always involved in the formation of molecular nitrogen. Experiments such as these are very useful in kinetic studies of surface species during catalysis.

keep track of the fate of specific atoms. An early example of this was provided by Somorjai and colleagues in their study of the dissociation of hydrogen on stepped platinum surfaces (Salmeron *et al.* 1977). Our work on the conversion of ethylene on platinum also illustrates how deuterium labelling can help to track the source of the needed hydrogen atoms (Zaera *et al.* 1996, Öfner and Zaera 1997).

Deuterium is the most common isotopic substitution used in surface chemistry experiments, but other atoms, such as carbon (with ^{13}C, or even ^{14}C), nitrogen (with ^{15}N) and oxygen (with ^{18}O), can be labelled this way as well. Also, information can be extracted from both transient and steady-state measurements using isotopes. In fact, isotopic switching experiments, where a reaction mixture is replaced during steady state by an identical but isotope-labelled beam, offer a common and powerful approach for obtaining information about the kinetics of surface reactions. To illustrate this point, in figure 17 we show raw data from the second half of isotope switching experiments with NO + CO mixtures on Rh(111) (Zaera and Gopinath 1999, 2000a). In this case, the rhodium surface was initially covered with a steady-state concentration of ^{14}N via long doses with a ^{14}NO:^{12}CO beam. After that, the original $^{14}NO + ^{12}CO$ beam was rapidly replaced with an identical beam of either a $^{15}NO + ^{13}CO$ or a $^{15}NO + ^{12}CO$ mixture. Figure 17 displays the temporal evolution of the mass spectrometer signals for the different isotopomers of the molecular nitrogen that desorbs afterwards ($t = 0$ s was set as the time at which the new beam is turned on). Those results indicate that replacement of surface ^{14}N by ^{15}N on switching the isotopic nitrogen label in the NO (from ^{14}NO to ^{15}NO) occurs via the exclusive formation of $^{14}N^{15}N$, since no $^{14}N^{14}N$ was ever detected. The conclusion is that the mechanism for molecular nitrogen production is likely to involve the formation of an N–NO intermediate.

3.6. *Post-mortem analysis of the surface*

Finally, the nature and concentration of the species present on the surface during steady-state molecular beam experiments can be determined by surface analysis after (or even during) reaction. One easy way to do this is by ramping the surface temperature and detecting the desorbing species by mass spectrometry, as done in TPD experiments (Redhead 1962, King 1975, Menzel 1975). We have used this approach extensively in our studies on the conversion of NO with CO on Rh(111) (Gopinath and Zaera 1999, Zaera and Gopinath 1999). Post-mortem TPD data have been particularly useful in that case, because they have offered a quantitative measure of the amount of atomic nitrogen present on the surface during the steady-state conversion of NO + CO mixtures. It was found that the surface coverage of that atomic nitrogen could be accounted for by the delay in nitrogen production observed during the transient right after the clean surface is exposed to the reaction beam (Gopinath and Zaera 2000). Our results also indicate that a critical coverage of nitrogen needs to build up on the surface before the steady-state conversion of NO can occur (Zaera and Gopinath 1999, Gopinath and Zaera 2000).

A number of variations can be applied to the TPD analysis described above. For instance, desorption of species left behind after reaction can be carried out isothermally instead of by ramping the temperature at a linear rate in order to obtain more detailed information on the kinetics of reaction of the adsorbed intermediates. In our work on the reduction of nitrogen monoxide, isothermal measurements of the rates of recombination of adsorbed nitrogen atoms allowed us to compare them with those of NO reduction to determine the role of the first reaction in the mechanism of the second (Zaera and Gopinath 2002). Also, adsorbed species that do not desorb by themselves on heating of the surface can be removed via their titration with a second probe molecule. An excellent example of this approach is given by the quantitative removal of residual oxygen with co-adsorbed carbon monoxide. We have used CO titrations to determine the amount of atomic oxygen present during both NO reduction (Gopinath and Zaera 1999) and CO oxidation (Zaera *et al.* 1997) processes. The results in the latter case turned out to be quite interesting, because it was found that not all the surface oxygen reacts with the incoming CO molecules, in spite of the fact that they all sit in identical sites at the start of the reaction (figure 16) (Xu *et al.* 1996). One possible explanation for such an observation is that nearby oxygen atoms weaken the adsorption energy of CO, thus enhancing its reactivity (Zaera 2002a). In fact, it was determined that when the oxygen is adsorbed in islands on the Pt(111) surface, the CO oxidation rate is up to 4

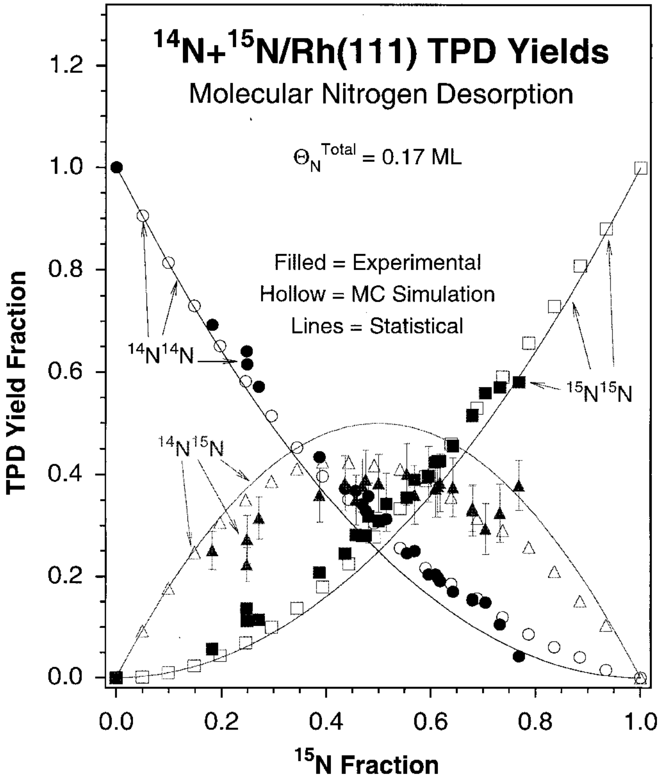

Figure 18. $^{14}N^{14}N$, $^{14}N^{15}N$, and $^{15}N^{15}N$ TPD yield fractions as a function of the fraction of ^{15}N within the total atomic nitrogen present on the surface of an Rh(111) single crystal after the isotope switching experiments with NO + CO mixtures described in figure 17. The filled symbols correspond to the experimental data, obtained by integration of TPD traces recorded after steady-state molecular beam experiments. The open symbols correspond to results from Monte Carlo simulations starting with hexagonal islands containing 61 atoms (5 layers) each and by assuming surface diffusion. The lines correspond to the yields expected on statistical grounds. This example illustrates how island formation and other inhomogeneities in the distribution of adsorbates, which complicate the kinetic picture of surface reactions, can be probed by combining isotope labelling and post-mortem surface analysis.

times faster than when the same number of oxygen surface atoms are randomly distributed on the metal surface (Xu *et al.* 1996).

Isotope labelling can also be combined with TPD surface characterization to learn more about the nature of the reactive surface. In the case of NO reduction, this combination has led us to a better understanding of the role of adsorbed atomic nitrogen in the overall kinetics of conversion. Figure 18 displays some key results from that study. Isotope labelling experiments were performed by exposing ^{14}N-dosed surfaces to $^{15}NO + CO$ gas mixtures for varying times, in the same way as in the work reported in figure 17. The main observation from the subsequent TPD data in figure 18 is that they point to a non-statistical distribution of isotopes in the resulting molecular nitrogen, the yield of the mixed $^{14}N^{15}N$ isotopomer being significantly lower than that expected by assuming random atomic nitrogen recombination (Zaera and Gopinath 2000b, 2001). Monte Carlo simulations were used to explain the observed isotopic distributions in terms of the formation of islands with the nitrogen isotopes distributed in a layered structure, the ^{14}N atoms in a core surrounded by a ^{15}N outer shell (Bustos *et al.* 2001, Zaera *et al.* 2001b).

4. Concluding remarks

In this review we have presented an overview of the key features of our experimental approach to the study of the kinetics of surface reaction on model surfaces. As mentioned above, the proposal of viable mechanisms for surface reactions, in particular those associated with heterogeneous catalysis, requires the detection and characterization of relevant surface intermediates as well as the reliable measurement of reaction rates for elementary steps under controlled conditions. Although our surface-science studies have traditionally been based on the use of multiple techniques, we have emphasized the use of IR spectroscopy for the first task and of molecular beams for the second.

IR spectroscopy is by no means the only way to study surface intermediates. In fact, we believe that only by combining results from several techniques is it possible to get a reasonable picture of the state of reactive surfaces. Nevertheless, IR absorption offers a number of unique features that distinguishes it from other analytical probes. First, it is particularly sensitive to small changes in chemical composition, structure and configuration in adsorbed molecules. This is particularly critical in studies with complex molecules such as hydrocarbons. Second, it is non-intrusive, so it does not affect chemical reactions, and therefore can be used continuously for *in situ* monitoring of reactive surfaces. Third (related to the previous point), being an optical technique, it is ideally suited both for studies in non-vacuum environments and to characterize more realistic samples such as supported catalysts. IR spectroscopy is expected to play an increasing role in surface science as more *in situ* studies on catalytic systems are attempted (Zaera 2001b).

Some IR-based techniques are already widely used in the catalysis community. Certainly, transmission IR spectroscopy has been one of the standard probes used in the study of adsorbates on supported catalysts, and diffuse reflectance has been gaining more popularity in recent years as well. Reflection–absorption arrangements are now commonplace in many surface-science laboratories for studies with single crystals and other model surfaces. However, attenuated reflection has not yet been exploited to its fullest potential. Also, RAIRS reports under non-vacuum are only now starting to appear in the literature. The use of laser and synchrotron sources for IR studies may have limited uses, but may still be employed for specific kinetic experiments. Finally, the continuing development of Fourier-transform technology promises the extension of IR spectroscopy to time-resolved measurements for kinetics. To date, this has only been done in a few cases, usually for reactions that take seconds or more to occur (Moshin *et al.* 1989, Erley *et al.* 1994, Janssens *et al.* 1998, Libuda *et al.* 2001), but the advent of step scanners augurs the availability of time resolutions in the 10^{-8} s range or better in the near future (Johnson *et al.* 1993).

There are other alternatives to IR spectroscopy in terms of optical characterization of surfaces. A number of laser-based techniques are available as well, including Raman and second-harmonic generation (SHG) and sum-frequency generation

(SFG). While regular Raman has been employed primarily for the characterization of high-surface-area solids (Stencel 1990, Vuurman and Wachs 1992), surface-enhanced Raman has found some applications in studies of model system (Pemberton *et al.* 1992, Campion and Kambhampati 1998). Also, ultraviolet Raman has recently been advanced for the study of dark samples (Stair and Li 1997). SHG typically probes electronic transitions, and is therefore mostly used as a way to measure changes in work function or localized electrostatic surface potentials (Shen 1989). Because of the nature of the excitations involved, SHG is not very chemically sensitive and therefore offers limited flexibility for the study of chemical systems. SFG, on the other hand, does provide vibrational information, and therefore is more directly applicable to complex kinetic problems (Shen 1994). There are a number of interesting publications available in the literature already dealing with the application of these techniques to catalytic problems (Williams *et al.* 1996, Hirose *et al.* 1999, Somorjai *et al.* 1999), and even for the characterization of liquid interfaces (Eisenthal 1996, Watry *et al.* 2001). In general, IR, Raman and SFG can offer complementary information on a given system.

In terms of rate measurements, one of the main issues for the future is, in our opinion, the ability to perform them isothermally. Ideally, kinetic measurements should be carried out isosterically as well, but that requires the reaction under study to be reversible (Peterlinz *et al.* 1991, Kevan 1998). It is in isothermal studies of kinetic processes that the use of molecular beams improves on the more established temperature-programmed approach. The continuous heating of the surface in the latter experiments leads to simultaneous changes in surface temperature and surface concentrations, and the interdependence between those parameters in not easy to separate. The difficulties in extracting kinetic parameters from TPD experiments has been recognized for a number of years (Goymour and King 1973, Yates and Goodman 1980, Steininger *et al.* 1982), in particular because surface reactions seldom follow simple rate laws (Zaera 2002a). Desorption measurements can be performed isothermally, but this has, to date, been reported only for a handful of cases (DeAngelis and Anton 1992, Zaera and Gopinath 2002).

One limitation of molecular beams is the low molecular flows that can be reached with the present technology. So far, molecular beam kinetic studies have been carried out under vacuum, and only for high probability reactions such as CO oxidation or NO reduction (Zaera 2001a). Other processes, even facile reactions such as olefin hydrogenations, are difficult to sustain in a catalytic regime with molecular beams. This is because they have relatively low reaction probabilities, and because those depend not only on the beam composition but also on the beam total flux (Zaera 2001a, 2002b, c). To address this difficulty, it is necessary to develop high-flux molecular beam sources. Some preliminary work from our laboratory, some of which is summarized in figure 19, shows some promise in this direction (Guevremont *et al.* 2000). In particular, it was found that, as the pressure of the source is increased beyond the transition from the molecular to the viscous flow regime, the conductance of the beam source (a capillary tube) increases with increasing backing pressures. This means that the total beam flux grows at a faster rate than expected, as the square of the backing pressure in some cases. In addition, the directionality of the beam appears to improve as well: notice the increase in peaking factor seen in figure 19 at atmospheric backing pressures. There is still the issue of high gas loads, but that may be resolved by using pulsed beams with low duty cycles.

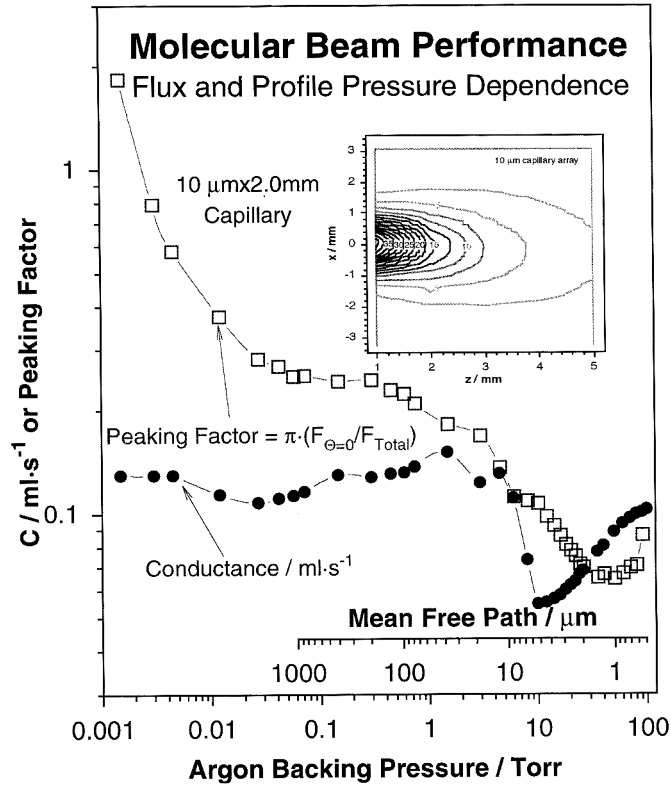

Figure 19. Conductance and peaking factor for beams produced by a 10 μm diameter capillary as a function of backing pressure. The conductance remains constant in the molecular flow regime and drops at pressures between 5 and 10 Torr but increases again in the viscous flow regime. Moreover, the peaking factor, a measure of collimation, also improves somewhat after reaching a minimum about 50 Torr. The inset shows the actual spatial distribution of the gas beam generated by the 10 μm diameter capillary, highlighting again the peaked nature of the resulting beam. These results show the promise of using capillary sources to emulate atmospheric pressures locally on catalytic surfaces embedded in vacuum environments.

An alternative to molecular beams for the study of low-probability and demanding reactions is the use of small, nanolitre-sized, reactors. This way, a small volume of the reaction mixture can be brought close to the surface of model samples such as single crystals while maintaining a clean vacuum surrounding. The idea behind the design of these nano-reactors is to bring a high-flux beam of reactants to the surface via a narrow ($\phi \sim 0.01$ mm) capillary tube and to trap the molecules in a nanolitre-size volume defined by a second outer tube, also used to collect the gases for mass spectrometry detection. By bringing the whole assembly within a few microns of the surface, the load of gases into the ultra-high-vacuum environment is minimized. To the best of our knowledge, no nano-reactors of this sort have been developed yet, but related designs used in the fast screening of potential catalysts by combinatorial methods (Cong *et al.* 1999, Orschel *et al.* 1999, Weinberg *et al.* 1999) support the feasibility of this approach.

Finally, it would be particularly powerful to combine kinetic and spectroscopic methods for the study of the kinetics of surface reactions. It is conceivable to combine pulsed molecular beams with *in situ* optical spectroscopies for the characterization of the chemistry of weakly adsorbed transient intermediates. Time resolution is an added possibility in those experiments; witness, for instance, the recent use of rapid-scan IR spectroscopy for the study of the reaction of ammonia with oxygen on a platinum surface (Kim *et al.* 2000). Techniques such as rapid-scan or step-scanning IR or Raman spectroscopies could be used in kinetic studies under high pressures.

Acknowledgements

Funding for the preparation of this manuscript has been provided by grants from the National Science Foundation and the Department of Energy.

References

ALI, A. H., and ZAERA, F., 2002a, *J. mol. Catal.* A, **177**, 215.
ALI, A. H., and ZAERA, F., 2002b, to be published.
ARYAFAR, M., and ZAERA, F., 1998, *J. Catal.*, **175**, 316.
AWATANI, T., DOBSON, K. D., MCQUILLAN, A. J., OHTANI, B., and UOSAKI, K., 1998, *Chem. Lett.*, 849.
BAIKER, A., and BLASER, H. U., 1997, in *Handbook of Hetrogeneous Catalysis*, Vol. 4, edited by G. Ertl, H. Knözinger and J. Weitkamp (Weinheim: VCH), p. 2422.
BANDARA, A., KUBOTA, J., WADA, A., DOMEN, K., and HIROSE, C., 1997, *J. phys. Chem.* B, **101**, 361.
BARKER, J. A., and AUERBACH, D. J., 1985, *Surf. Sci. Rep.*, **4**, 1.
BARNER, B. J., GREEN, M. J., SÁEZ, E. I., and CORN, R. M., 1991, *Anal. Chem.*, **63**, 55.
BELL, A. T., 1984, in *Chemistry and Physics of Solid Surfaces V*, Springer Series in Chemical Physics, Vol. 35, edited by R. Vanselow and R. Howe (Berlin: Springer), p. 23.
BERMUDEZ, V. M., 1992, *J. Vac. Sci. Technol.* A, **10**, 152.
BEWICK, A., and PONS, S., 1985, in *Advances in Infrared and Raman Spectroscopy*, Vol. 12, edited by R. J. H. Clark and R. E. Hester (New York: Wiley Heyden), p. 1.
BEWICK, A., KUNIMATSU, K., and PONS, B. S., 1980, *Electrochim. Acta*, **25**, 465.
BLASER, H. U., 2000, *Catal. Today*, **60**, 161.
BLITZ, J. P., and AUGUSTINE, S. M., 1994, *Spectroscopy (Eugene, Oreg.)*, **9**, 28.
BLYHOLDER, G., 1968, in *Experimental Methods in Catalytic research*, edited by R. B. Anderson (New York: Academic Press), p. 323.
BOND, G., MEHEUX, P. A., IBBOTSON, A., and WELLS, P. B., 1991, *Catal. Today*, **10**, 371.
BORGUET, E., and DAI, H. L., 1990, *J. Electron Spectrosc. relat. Phenom.*, **54–55**, 573.
BORRONI-BIRD, C. E., and KING, D. A., 1991, *Rev. sci. Instrum.*, **62**, 2177.
BOWKER, M., 1997, *Appl. Catal.* A, **160**, 89.
BRADSHAW, A. M., 1982, *Appl. Surf. Sci.*, **11/12**, 712.
BUSCA, G., 1996, *Catal. Today*, **27**, 323.
BUSTOS, V., GOPINATH, C. S., UÑAC, R., ZAERA, F., and ZGRABLICH, G., 2001, *J. chem. Phys.*, **114**, 10927.
CAMPION, A., and KAMBHAMPATI, P., 1998, *Chem. Soc. Rev.*, **27**, 241.
CARDILLO, M. J., 1994, *Surf. Sci.*, **299–300**, 277.
CEYER, S. T., BECKERLE, J. D., LEE, M. B., TANG, S. L., YANG, Q. Y., and HINES, M. A., 1987, *J. Vac. Sci. Technol.* A, **5**, 501.
CHABAL, Y. J., 1988, *Surf. Sci. Rep.*, **8**, 211.
CHANG, H. C., and WEINBERG, W. H., 1977, *Surf. Sci.*, **65**, 153.
CHRISTMANN, K., ERTL, G., and PIGNET, T., 1976, *Surf. Sci.*, **54**, 365.
CHRYSOSTOMOU, D., and ZAERA, F., 2001, *J. phys. Chem.* B, **105**, 1003.
CHRYSOSTOMOU, D., FRENCH, C., and ZAERA, F., 2000, *Catal. Lett.*, **69**, 117.
CHRYSOSTOMOU, D., CHOU, A., and ZAERA, F., 2001, *J. phys. Chem.* B, **105**, 5968.

Cong, P., Doolen, R. D., Fan, Q., Giaquinta, D. M., Guan, S., McFarland, E. W., Poojary, D. M., Self, K., Turner, H. W., and Weinberg, W. H., 1999, *Angew. Chem., Int. Edn. Engl.*, **38**, 484.

De Jesús, J. C., and Zaera, F., 1999a, *Surf. Sci.*, **430**, 99.

De Jesús, J. C., and Zaera, F., 1999b, *J. mol. Catal.* A, **138**, 327.

Deangelis, M. A., and Anton, A. B., 1992, *J. Vac. Sci. Technol.* A, **10**, 3507.

Dowrey, A. E., and Marcott, C., 1982, *Appl. Spectrosc.*, **36**, 414.

Doyen, G., 1987, *Top. Curr. Phys.*, **43**, 301.

Drochner, A., Fehlings, M., Krauss, K., and Vogel, H., 2000, *Chem. eng. Technol.*, **23**, 319.

Eischens, R. P., Pliskin, W. A., and Francis, S. A., 1954, *J. chem. Phys.*, **22**, 1986.

Eisenthal, K. B., 1996, *Chem. Rev.*, **96**, 1343.

Engel, T., 1987, in *Kinetics of Interface Reactions: Proceedings of a Workshop on Interface Phenomena, Campobello Island, Canada, 24–27 September 1986*. Springer Series in Surface Science, Vol. 8, edited by M. Grunze and H. J. Kreuzer (Berlin: Springer), p. 195.

Engel, T., and Ertl, G., 1978, *J. chem. Phys.*, **69**, 1267.

Engel, T., and Rieder, K. H., 1982, in *Structural Studies of Surfaces*, Springer Tracts in Modern Physics, Vol. 91), edited (Berlin: Springer), p. 55.

Erley, W., Li, Y., Land, D. P., and Hemminger, J. C., 1994, *Surf. Sci.*, **103**, 177.

Ertl, G., and Kueppers, D., 1971, *Ber. Bunsenges. phys. Chem.*, **75**, 1017.

Fan, J., and Trenary, M., 1994, *Langmuir*, **10**, 3649.

Farias, D., and Rieder, K.-H., 1998, *Rep. Prog. Phys.*, **61**, 1575.

Farrauto, R. J., and Heck, R. M., 2000, *Catal. Today*, **55**, 179.

Ferri, D., and Buergi, T., 2001, *J. Am. Chem. Soc.*, **123**, 12074.

Francis, S. A., and Ellison, A. H., 1959, *J. Opt. Soc. Am.*, **49**, 131.

French, C., and Zaera, F., 1999, *Chem. Phys. Lett.*, **309**, 321.

Gates, B. C., Katzer, J. R., and Schuit, G. C. A., 1979, *Chemistry of Catalytic Processes* (New York: McGraw-Hill).

Gland, J. L., Zaera, F., Fischer, D. A., Carr, R. G., and Kollin, E. B., 1988, *Chem. Phys. Lett.*, **151**, 227.

Gleason, N. R., and Zaera, F., 1997a, in *Proceedings of 3rd World Congress on Oxidation catalysis, San Diego, CA, 21–26 September 1997*, Elsevier Studies in Surface Science and Catalysis Series, Vol. 110, edited by R. K. Grasselli, S. T. Oyama, A. M. Gaffney and J. E. Lyons (Amsterdam: Elsevier), p. 235.

Gleason, N. R., and Zaera, F., 1997b, *J. Catal.*, **169**, 365.

Gleason, N. R., Jenks, C. J., French, C. R., Bent, B. E., and Zaera, F., 1998, *Surf. Sci.*, **405**, 238.

Golden, W. G., 1985, in *Fourier Transform Infrared Spectroscopy*, Vol. 4, edited by J. R. ferraro and L. J. Basile (Orlando, FL: Academic), p. 315.

Gopinath, C. S., and Zaera, F., 1999, *J. Catal.*, **186**, 387.

Gopinath, C. S., and Zaera, F., 2000, *J. phys. Chem.* B, **104**, 3194.

Gopinath, C. S., and Zaera, F., 2001, *J. Catal.*, **200**, 270.

Goymour, C. G., and King, D. A., 1973, *J. Chem. Soc. Faraday Trans. I*, **69**, 749.

Greenler, R. G., 1966, *J. chem. Phys.*, **44**, 310.

Griffiths, P. R., and De Haseth, J. A., 1986, *Fourier Transform Infrared Spectrometry* (New York: Wiley).

Guevremont, J. M., Sheldon, S., and Zaera, F., 2000, *Rev. sci. Instrum.*, **71**, 3869.

Hair, M. L., 1967, *Infrared Spectroscopy in Surface Chemistry* (New York: Dekker).

Hamza, A. V., and Madix, R. J., 1987, *Surf. Sci.*, **179**, 25.

Hanley, L., Xu, Z., and Yates, J. T., Jr., 1991, *Surf. Sci.*, **248**, 1265.

Harrick, N. J., 1960, *Phys. Rev. Lett.*, **4**, 224.

Hirose, C., Bandara, A., Katano, S., Kubota, J., Wada, A., and Domen, K., 1999, *Appl. Phys.* B, **68**, 559.

Hirschmug, C., 1992, *Nucl. Instrum. Methods Phys. Res.* A, **319**, 245.

Hoffmann, F. M., 1983, *Surf. Sci. Rep.*, **3**, 107.

Hoffmann, F. M., and Weisel, M. D., 1993, *J. Vac. Sci. Technol.* A, **11**, 1957.

Hoffmann, F. M., Levinos, N. J., Perry, B. N., and Rabinowitz, P., 1986, *Phys. Rev.* B, **33**, 4309.

Hoffmann, H., Wright, N. A., Zaera, F., and Griffiths, P. R., 1989, *Talanta*, **36**, 125.

Hoffmann, H., Griffiths, P. R., and Zaera, F., 1992, *Surf. Sci.*, **262**, 141.

Hoffmann, H., Mayer, U., Brunner, H., and Krischanitz, A., 1995, *J. mol. Struct.*, **349**, 305.

Hoffmann, R., 1988, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* (New York: VCH).

Hollins, P., and Pritchard, J., 1985, *Prog. Surf. Sci.*, **19**, 275.

Ibach, H., and Mills, D. L., 1982, *Electron Energy Loss Spectroscopy and Surface Vibrations* (New York: Academic Press).

Ishida, H., Ishino, Y., Buijs, H., Tripp, C., and Dignam, M. J., 1987, *Appl. Spectrosc.*, **41**, 1288.

Janssens, T. V. W., and Zaera, F., 1995, *Surf. Sci.*, **344**, 77.

Janssens, T. V. W., and Zaera, F., 1996, *J. Phys. Chem.*, **100**, 14118.

Janssens, T. V. W., and Zaera, F., 2002a, *J. Catal.*, submitted.

Janssens, T. V. W., and Zaera, F., 2002b, *Surf. Sci.*, **501**, 1.

Janssens, T. V. W., Jin, G., and Zaera, F., 1997, *J. Am. Chem. Soc.*, **119**, 1169.

Janssens, T. V. W., Stone, D., Hemminger, J. C., and Zaera, F., 1998, *J. Catal.*, **177**, 284.

Jenks, C. J., Bent, B. E., Bernstein, N., and Zaera, F., 1992, *Surf. Sci.*, **277**, L89.

Jenks, C. J., Bent, B. E., Bernstein, N., and Zaera, F., 1993, *J. Am. Chem. Soc.*, **115**, 308.

Jenks, C. J., Bent, B. E., Bernstein, N., and Zaera, F., 2000, *J. Phys. Chem.* B, **104**, 3008.

Johnson, T. J., Simon, A., Weil, J. M., and Harris, G. W., 1993, *Appl. Spectrosc.*, **47**, 1376.

Kevan, S. D., 1998, *J. mol. Catal.* A, **131**, 19.

Kim, M., Pratt, S. J., and King, D. A., 2000, *J. Am. Chem. Soc.*, **122**, 2409.

King, D. A., 1975, *Surf. Sci.*, **47**, 384.

King, D. A., and Wells, M. G., 1972, *Surf. Sci.*, **29**, 454.

Kisliuk, P., 1957, *J. Phys. Chem. Solids*, **3**, 95.

Kubota, J., and Zaera, F., 2001, *J. Am. Chem. Soc.*, **123**, 11115.

Kubota, J., Morton, T. H., and Zaera, F., 2002, to be published.

Laidler, K. J., 1987, *Chemical Kinetics*, 3rd edn. (New York: Harper & Row).

Leblond, C., Wang, J., Liu, J., Andrews, A. T., and Sun, Y. K., 1999, *J. Am. Chem. Soc.*, **121**, 4920.

Lee, B. Y., Inoue, Y., and Yasumori, I., 1984, *Bull. Chem. Soc. Jpn.*, **57**, 1283.

Liang, S., and Trenary, M., 1988, *J. chem. Phys.*, **89**, 3323.

Libuda, J., Meusel, I., Hoffmann, J., Hartmann, J., Piccolo, L., Henry, C. R., and Freund, H. J., 2001, *J. chem. Phys.*, **114**, 4669.

Little, L. H., 1966, *Infrared Spectra of Adsorbed Species* (New York: Academic Press).

Liu, J., Xu, M., Nordmeyer, T., and Zaera, F., 1995, *J. phys. Chem.*, **99**, 6167.

Liu, J., Xu, M., and Zaera, F., 1996, *Catal. Lett.*, **37**, 9.

Luntz, A. C., and Bethune, D. S., 1989, *J. chem. Phys.*, **90**, 1274.

Madey, T. E., 1972, *Surf. Sci.*, **33**, 355.

Malik, I. J., and Trenary, M., 1989, *Surf. Sci.*, **214**, 1237.

Malik, I. J., Brubaker, M. E., and Trenary, M., 1987, *J. Electron Spectrosc. relat. Phenom.*, **45**, 57.

Martino, G., 2000, in *Proceedings of 12th International Congress on Catalysis, Studies in Surface Science and Catalysis Series, Vol. 130*, edited by A. Corma, F. V. Melo, S. Mendioroz and J. L. G. Fierro (Amsterdam: Elsevier), p. 83.

McCash, E. M., 1990, *Vacuum*, **40**, 423.

McCombe, B. D., Holm, R. T., and Schafer, D. E., 1979, *Solid State Commun.*, **32**, 603.

McMaster, M. C., and Madix, R. J., 1992, *Surf. Sci.*, **275**, 265.

McQuillan, A. J., 2001, *Adv. Mater.*, **13**, 1034.

Menzel, D., 1975, in *Interactions on Metal Surfaces*, edited by R. Gomer (New York: Springer), p. 102.

Morris, M. A., Bowker, M., and King, D. A., 1984, in *Comprehensive Chemical Kinetics*, Vol. 19 (*Simple Processes at the Gas–Solid Interface*), edited by C. H. Bamford, C. F. H. Tipper and R. G. Compton (Amsterdam: Elsevier), p. 1.

Moshin, S. B., Trenary, M., and Robota, H. J., 1989, *Chem. Phys. Lett.*, **154**, 511.

Mullins, C. B., and Weinberg, W. H., 1990, *J. Chem. Phys.*, **92**, 3986.

Nakamoto, K., 1978, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn. (New York: Wiley-interscience).

Nordmeyer, T., and Zaera, F., 1992, *J. chem. Phys.*, **97**, 9345.

Nyberg, C., Tengstaal, C. G., Andersson, S., and Holmes, M. W., 1982, *Chem. Phys. Lett.*, **87**, 87.

Öfner, H., and Zaera, F., 1997, *J. phys. Chem.*, **101**, 396.

Okuhara, T., Hasada, Y., and Misono, M., 1997, *Catal. Today*, **35**, 83.

Orito, Y., Imai, S., and Niwa, S., 1979, *Nippon Kagaku Kaishi*, 1118.

Orschel, M., Klein, J., Schmidt, H. W., and Maier, W. F., 1999, *Angew. Chem., Int. Edn. Engl.*, **38**, 2791.

Parikh, A. N., and Allara, D. L., 1992, *J. chem. Phys.*, **96**, 927.

Pemberton, J. E., Bryant, M. A., Sobocinski, R. L., and Joa, S. L., 1992, *J. phys. Chem.*, **96**, 3776.

Peterlinz, K. A., Curtiss, T. J., and Sibener, S. J., 1991, *J. chem. Phys.*, **95**, 6972.

Pickering, H. L., and Eckstrom, H. C., 1959, *J. phys. Chem.*, **63**, 512.

Redhead, P. A., 1962, *Vacuum*, **12**, 203.

Reeves, C. T., Seets, D. C., and Mullins, C. B., 2001, *J. mol. Catal.* A, **167**, 207.

Rettner, C. T., Pfnür, H. E., and Auerbach, D. J., 1985, *Phys. Rev. Lett.*, **54**, 2716.

Ryndin, Y. A., Alekseev, O. S., Paukstis, E., Kalinkin, A. V., and Kochubei, D. I., 1990, *Appl. Catal.*, **63**, 51.

Salmeron, M., Gale, R. J., and Somorjai, G. A., 1977, *J. chem. Phys.*, **67**, 5324.

Schmal, M., Baldanza, M. A. S., and Vannice, M. A., 1999, *J. Catal.*, **185**, 138.

Schubert, M. M., Haring, T. P., Brath, G., Gasteiger, H. A., and Behm, R. J., 2001, *Appl Spectrosc.*, **55**, 1537.

Schwarz, J. A., and Madix, R. J., 1968, *J. Catal.*, **12**, 140.

Shelef, M., and Graham, G. W., 1994, *Catal. Rev.—Sci. Eng.*, **36**, 433.

Shen, Y. R., 1989, *Annu. Rev. phys. Chem.*, **40**, 327.

Shen, Y. R., 1994, *Surf. Sci.*, **300**, 551.

Sheppard, N., and De La Cruz, C., 1996, *Adv. Catal.*, **41**, 1.

Sheppard, N., and De La Cruz, C., 1998, *Adv. Catal.*, **42**, 181.

Shigeishi, R. A., and King, D. A., 1976, *Surf. Sci.*, **58**, 379.

Skinner, P., Howard, M. W., Oxton, I. A., Kettle, S. F. A., Powell, D. B., and Sheppard, N., 1981, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1203.

Socrates, G., 1994, *Infrared Characteristic Group Frequencies: Tables and Charts*, 2nd edn. (Chichester: Wiley).

Somorjai, G. A., 1981, *Chemistry in Two Dimensions: Surfaces* (Ithaca, NY: Cornell University Press).

Somorjai, G. A., 1994, *Introduction to Surface Chemistry and Catalysis* (New York: Wiley).

Somorjai, G. A., Su, X. C., McCrea, K. R., and Rider, K. B., 1999, *Top. Catal.*, **8**, 23.

Stair, P. C., and Li, C., 1997, *J. Vac. Sci. Technol.* A, **15**, 1679.

Steininger, H., Lehwald, S., and Ibach, H., 1982, *Surf. Sci.*, **123**, 264.

Stencel, J. M., 1990, *Raman Spectroscopy for Catalysis*, Van Nostrand Reinhold Catalysis Series, edited by B. Davis (New York: Van Nostrand Reinhold).

Stewart, C. N., and Ehrlich, G., 1975, *J. chem. Phys.*, **62**, 4672.

Stuve, E. M., and Madix, R. J., 1985, *J. phys. Chem.*, **89**, 3183.

Thayer, A. M., 1992, *Chem. eng. News*, **9 March**, 27.

Thomas, J. M., and Thomas, W. J., 1967, *Introduction to the Principles of Heterogeneous Catalysis* (London: Academic Press).

Tiznado, H., Fuentes, S., and Zaera, F., 2002, to be published.

Toennies, J. P., 1982, in *Dynamics of Gas–Surface Interaction: Proceedings of the International School on Material Science and Technology, Erice, Italy, 1–15 July, 1981, Springer Series in Chemical Physics, Vol. 21*, edited by G. Benedek and U. Valbusa (Berlin: Springer), p. 208.

Tully, J. C., 2000, *Annu. Rev. phys. Chem.*, **51**, 153.

Ukraintsev, V. A., and Harrison, I., 1994, *J. chem. Phys.*, **101**, 1564.

Verhoef, R. W., Kelly, D., Mullins, C. B., and Weinberg, W. H., 1994, *Surf. Sci.*, **311**, 196.

Vuurman, M. A., and Wachs, I. E., 1992, *J. phys. Chem.*, **96**, 5008.

Watry, M. R., Brown, M. G., and Richmond, G. L., 2001, *Appl. Spectrosc.*, **55**, 321A.

Weinberg, W. H., McFarland, E. W., Cong, P., and Guan, S., 1999, US Patent 5,959,297.

Wieckowski, A., Rosasco, S. D., Salaita, G. N., Hubbard, A., Bent, B. E., Zaera, F., Godbey, D., and Somorjai, G. A., 1985, *J. Am. Chem. Soc.*, **107**, 5910.

Willey, R. R., 1976, *Appl. Spectrosc.*, **30**, 593.

Williams, C. T., Tolia, A. A., Chan, H. Y. H., Takoudis, C. G., and Weaver, M. J., 1996, *J. Catal.*, **163**, 63.

Wragg, J. L., White, H. W., and Sutcu, L. F., 1988, *Phys. Rev.* B, **37**, 2508.

Xu, M., Liu, J., and Zaera, F., 1996, *J. chem. Phys.*, **104**, 8825.

Xu, X. P., Chen, P. J., and Goodman, D. W., 1994, *J. phys. Chem.*, **98**, 9242.

Yang, H., and Whitten, J. L., 1992, *J. chem. Phys.*, **96**, 5529.

Yaroslavskii, N. G., and Terenin, A. N., 1949, *Dok. Akad. Nauk SSSR,* **66**, 885.

Yates, J. T., Jr., and Goodman, D. W., 1980, *J. chem. Phys.*, **73**, 5371.

Yates, J. T., Jr., and Madey, T. E. (Editors), 1987, *Vibrational Spectroscopy of Molecules on Surfaces*, Methods of Surface Characterization, Vol. 1 (New York: Plenum), p. 468.

Zaera, F., 1990, *J. phys. Chem.*, **94**, 8350.

Zaera, F., 1991, *Surf. Sci.*, **255**, 280.

Zaera, F., 1992, *Acc. chem. Res.*, **25**, 260.

Zaera, F., 1994, *J. mol. Catal.*, **86**, 221.

Zaera, F., 1995, *Chem. Rev.*, **95**, 2651.

Zaera, F., 1996, *Langmuir*, **12**, 88.

Zaera, F., 1998, *Isr. J. Chem.*, **38**, 293.

Zaera, F., 2001a, *Prog. Surf. Sci.*, **69**, 1.

Zaera, F., 2001b, in *Encyclopedia of Chemical Physics and Physical Chemistry*, Vol. 2, edited by J. H. Moore and N. D. Spencer (Philadelphia, PA: IOP Publishing), p. 1563.

Zaera, F., 2002a, *Acc. chem. Res.*, **35**, 129.

Zaera, F., 2002b, *J. phys. Chem.* B, **106**, 4043.

Zaera, F., 2002c, *Appl. Catal.*, **229**, 75.

Zaera, F., 2002d, *Surf. Sci.*, **500**, 947.

Zaera, F., 2002e, *Mol. Phys.*, in press.

Zaera, F., and Bernstein, N., 1994, *J. Am. Chem. Soc.*, **116**, 4881.

Zaera, F., and Chrysostomou, D., 2000a, *Surf. Sci.*, **457**, 71.

Zaera, F., and Chrysostomou, D., 2000b, *Surf. Sci.*, **457**, 89.

Zaera, F., and French, C. R., 1999, *J. Am. Chem. Soc.*, **121**, 2236.

Zaera, F., and Gopinath, C. S., 1999, *J. chem. Phys.*, **111**, 8088.

Zaera, F., and Gopinath, C. S., 2000a, *Chem. Phys. Lett.*, **332**, 209.

Zaera, F., and Gopinath, C. S., 2000b, in *Studies in Surface Science and Catalysis Series*, Vol. 130 (*Proceedings of 12th International Congression Catalysis, Granada, Spain, 9–14 July 2000*), edited (Amsterdam: Elsevier), p. 1295.

Zaera, F., and Gopinath, C. S., 2001, *J. mol. Catal.* A, **167**, 23.

Zaera, F., and Gopinath, C. S., 2002, *J. chem. Phys.*, **116**, 1128.

Zaera, F., and Hoffmann, H., 1991, *J. phys. Chem.*, **95**, 6297.

Zaera, F., and Somorjai, G. A., 1984, *J. Am. Chem. Soc.*, **106**, 2288.

Zaera, F., and Somorjai, G. A., 1985, *J. phys. Chem.*, **89**, 3211.

Zaera, F., and Somorjai, G. A., 1988, in *Hydrogen Effects in Catalysis: Fundamentals and Practical Applications*, edited by Z. Paál and P. G. Menon (New York: Dekker), p. 425.

Zaera, F., Gellman, A. J., and Somorjai, G. A., 1986, *Acc. chem. Res.*, **19**, 24.

Zaera, F., Fischer, D. A., Carr, R. G., Kollin, E. B., and Gland, J. L., 1988, in *Electrochemical Surface Science: Molecular Phenomena at Electrode Surfaces*, ACS Symposium Series, Vol. 378, edited by M. P. Soriaga (Washington, DC: ACS Books), p. 131.

Zaera, F., Hoffmann, H., and Griffiths, P. R., 1990a, *J. Electron Spectrosc. relat. Phenom.*, **54/55**, 705.

Zaera, F., Hoffmann, H., and Griffiths, P. R., 1990b, *Vacuum*, **41**, 735.

Zaera, F., Janssens, T. V. W., and Öfner, H., 1996, *Surf. Sci.*, **368**, 371.

Zaera, F., Liu, J., and Xu, M., 1997, *J. chem. Phys.*, **106**, 4204.

Zaera, F., Tjandra, S., and Janssens, T. V. W., 1998, *Langmuir*, **14**, 1320.

Zaera, F., Gleason, N. R., Klingenberg, B., and Ali, A. H., 1999, *J. mol. Catal.* A, **146**, 13.

Zaera, F., Guevremont, J. M., and Gleason, N. R., 2001a, *J. phys. Chem.* B, **105**, 2257.

Zaera, F., Wehner, S., Gopinath, C. S., Sales, J. L., Gargiulo, V., and Zgrablich, G., 2001b, *J. phys. Chem.* B, **105**, 7771.