

The influence of surface defects on the infrared spectra of adsorbed species

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NORTH-HOLLAND

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Defect sites on a surface frequently give rise to small wavenumber shifts in the infrared spectrum of an adsorbed species. When this effect is combined with the influence of dipolar coupling interactions, serious distortions can occur in the spectra and may lead to erroneous interpretations, particularly in spectra from supported catalysts and other relatively poorly defined substrates. The problem is especially acute in the case of carbon monoxide, the molecule most commonly employed as a probe of substrate morphology. The influence of defect sites is shown to have a major effect on the interpretation of spectra from the CO/Cu and CO/Pt adsorption systems, and its relevance to other substrates and adsorbates is discussed.

1. Introduction

In the investigation of surfaces, infrared spectroscopy is employed in two distinct and complementary roles. The first of these is its use to determine the chemical nature of the adsorbed species. Many thousands of papers describing such applications have been published, mainly concerned with supported catalysts and other relatively ill-defined surfaces, but supplemented in increasing numbers since the early 1970s by studies on atomically clean single-crystal surfaces, in which infrared spectroscopy has frequently been used in combination with other surface-sensitive techniques. Two earlier reviews in this series have described the forms of infrared spectroscopy applicable to well-defined surfaces, and have discussed some of the results obtained [1,2]. An area of considerable current interest is the correlation of results from single crystals with those from supported catalysts, an application likely to become of major importance in identifying surface intermediates and elucidating the mechanisms of catalytic reactions. To facilitate such comparisons, in recent years experimental facilities have been developed which permit in-situ infrared studies at high pressure on a well-defined surface prepared and characterised under UHV conditions, thus exploiting the unique ability of the technique to bridge the “pressure gap” between the vacuum conditions required for most surface spectroscopies and the super-atmospheric pressures of commercial catalytic processes [3–6].

The second application of infrared spectroscopy is its use to characterise not the adsorbate, but the substrate, by observing the spectrum of some adsorbed probe molecule. Again, the earliest studies were necessarily confined to relatively poorly characterised surfaces, but investigations using single crystals were first carried out in the early 1970s, and these have since become a major area of surface science. In such studies of substrate morphology, it has been found easier to draw correlations between catalyst and single-crystal surfaces than is the case when attempting, for example, to ascertain the chemical identity of a catalytic intermediate, mainly because difficulties attributable to different pressure regimes do not arise. Infrared spectroscopy has risen to considerable importance in the study of supported catalysts, where it is one of the few techniques capable of establishing structural information under operating conditions.

By far the most widely employed probe molecule for such studies, at least when they are carried out on metal substrates, is carbon monoxide. (On oxide surfaces, nitric oxide is also very frequently used as a probe [7], but the complexity of its spectrum and its possible chemical interactions have restricted its application on metals. However, see sections 2.1 and 4.1.) The reasons for the predominance of carbon monoxide in infrared applications include those which make it a favourite molecule of surface science in general, chiefly its ease of handling and its huge importance as an industrial feedstock, but there are two others specific to vibrational spectroscopies. The first of these is the very high absorption coefficient associated with the C–O stretching mode, which makes it a particularly easy molecule to study. This factor was of overwhelming significance in the early days of surface infrared spectroscopy, when sensitivity was a major problem, particularly in the study of low-area samples: subsequent advances in instrumentation, however, have largely eliminated these difficulties, and investigation of much more weakly absorbing species at sub-monolayer coverages is now more or less routine. The second factor, which is still of great relevance, is the sensitivity of the molecule’s vibrational frequency to the manner in which it is bonded to the substrate.

The reasons for this sensitivity are well known; carbon monoxide is the classic example of a π -acid ligand that exhibits synergic bonding [8]. Its interaction with a metal surface involves a

combination of electron donation from the 5σ orbital of the molecule, together with acceptance of metal electrons into the initially empty 2π orbital. With respect to the C–O bond of the adsorbed molecule, the 5σ orbital is weakly anti-bonding, the 2π more strongly so. Consequently, the vibrational frequency of this bond is sensitive to the balance of dative and back-bonding effects, which depend not only on the chemical identity of the adsorbate, but also on details of the bonding geometry. In surface and catalytic chemistry, the best known example of this effect is the correlation found between the vibrational frequency of the molecule and the number of metal atoms to which it is bonded. As Sheppard and Nguyen [9] have discussed in detail, linearly bonded carbon monoxide molecules are associated with wavenumbers in the approximate range $2000\text{--}2130\text{ cm}^{-1}$, doubly-bridged with the $1880\text{--}2000\text{ cm}^{-1}$ region, and multiply-bridged with that below 1880 cm^{-1} .

More recently, experimental studies have been made of carbon monoxide adsorption on various single-crystal surfaces of high Miller index. From such studies it has been found that the vibrational frequency of an adsorbed molecule depends not only on the number of metal surface atoms to which it is bonded, but also on the coordination number of those atoms within the surface. The wavenumber changes involved are much smaller than those noted above, being typically $10\text{--}20\text{ cm}^{-1}$, but the effect still has important consequences for the interpretation of spectra, particularly those from less well-defined surfaces, such as supported catalysts. This is because catalyst surfaces, in contrast to the low-index single-crystal surfaces usually examined in surface science experiments, often exhibit a relatively high proportion of low-coordination sites, associated with edges and defects on small particles. Since these sites are likely to exhibit very different chemical reactivity from high-coordination sites (and, indeed, are in many cases believed to be dominant in catalytic activity), monitoring their presence can provide valuable information about the catalyst.

However, interpretation of spectra from surfaces which contain defects is complicated by another effect that has also been extensively studied on single-crystal substrates. This is the dipolar interaction which serves to couple the vibration of individual molecules within an adlayer. One consequence of this coupling is that the spectrum of an adlayer containing two or more species of similar vibrational frequency is distorted by intensity shifts between bands. Under conditions which arise rather often in practice, this distortion may become so massive that serious errors will occur if coupling effects are not recognised when interpreting the spectra. This problem is particularly severe for species which absorb infrared radiation strongly: we have already noted that carbon monoxide is the archetype of such species.

In this review, we shall consider the influence that surface defects have on the infrared spectra of adsorbed species, with particular emphasis on the probe molecules used to characterise metal catalysts (principally carbon monoxide, but with some discussion of other molecules with current or potential applications as probe species). Section 2 discusses the physical principles necessary to understand spectra from such surfaces. Experimental results from various adsorption systems, involving both single-crystal substrates and supported catalysts, are considered in sections 3 and 4. We conclude with a discussion of possible future applications.

2. Physical principles

In this section, we shall consider the two physical factors that govern the appearance of infrared spectra from surfaces containing defects and similar low-coordination sites: firstly,

Table 1

Principal band observed in the infrared spectrum of carbon monoxide adsorbed at low coverage on copper and platinum single-crystal surfaces

Surface	$\tilde{\nu}$ (cm ⁻¹)	Reference
Cu(111)	2077	[10]
Cu(100)	2078	[11]
Cu(110)	2088	[12]
Cu(16,15,0)	2106	[13]
Cu(211)	2109	[14]
Cu(311)	2109	[14]
Cu(755)	2111	[14]
Pt(111)	2089	[15]
Pt(100)	2062	[16]
Pt(110)	2079	[17]
Pt(432)	2072	[18]
Pt(533)	2067	[18]
Pt(12,11,10)	2059	[19]
Pt(28,27,26)	2059	[19]

the influence of such sites on the vibrational frequency of adsorbed carbon monoxide (and related species), and secondly the effects of coupling interactions within the adsorbed layer.

2.1. Wavenumber shifts at defect sites

It is instructive to apply the bonding concepts which were introduced in the preceding section to the example of carbon monoxide bonded to different types of surface atom. In general, we anticipate that the molecule will be bound more strongly to defect sites (which are coordinatively unsaturated) than to normal, terrace ones. Where bonding primarily involves donation from the 5σ orbital, this stronger bonding will result in lower occupation of this orbital, and an increase in the vibrational frequency. Conversely, when a substantial degree of back-donation into the $2\pi^*$ orbital occurs, the dominant effect will be increased occupation of this strongly anti-bonding orbital, with a consequent reduction in vibrational frequency.

This model, while based on very simple and qualitative ideas, correctly describes the behaviour of the two CO/metal systems that have been most extensively investigated to date. These metals, copper and platinum, show opposing traits which seem to reflect the differences in bonding. As we shall see in detail in section 3, on copper, a metal for which donation from the 5σ orbital is believed to predominate, carbon monoxide molecules bound to defects exhibit a vibrational frequency approximately 20 cm⁻¹ higher than those bound to terrace sites, while the reverse situation obtains on platinum, where π back-donation prevails. Indeed, as table 1 indicates, increasing unsaturation of surface atoms is in general associated with a frequency increase on copper, and a decrease on platinum. The other carbon monoxide adsorption systems that have been studied, while not so comprehensively investigated, show behaviour which can apparently be rationalised in the same way.

The model can also be extended to other adsorbates. The dinitrogen molecule is isoelectronic with carbon monoxide, but is generally far less reactive. The differences in chemisorptive behaviour between the two species have been discussed by de Paola et al. [20,21], who infer that π back-donation does not occur to any significant extent with nitrogen, a conclusion

in agreement with the findings of coordination chemistry (ref. [8], p. 334). Although the homonuclear nature of dinitrogen ensures that the orbitals involved in its bonding are rather different from those of carbon monoxide, the predicted consequence of this absence of back-bonding is that N_2 /metal systems should in general behave like CO/Cu ; i.e. defect sites should give rise to higher frequencies. This is supported by experimental studies of nitrogen adsorption on low-index single-crystal surfaces of nickel [22–24] and ruthenium [21], where bands or shoulders attributed to defects have been observed on the high-frequency side of the principal band.

Nitric oxide has a similar electronic configuration to carbon monoxide, but contains an additional electron in the $2\pi^*$ orbital. The energy of this orbital is close to that of many metal d-orbitals, facilitating π back-bonding. One might anticipate, therefore, that nitric oxide would behave like carbon monoxide bound to platinum, and that bonding to defect sites would lead to a rise in the frequency of the N–O stretching vibration. While this is broadly the case, the situation is complicated by the fact that nitric oxide may adopt a variety of bonding configurations, and interconversion of these is often facile. The analogue of linearly bonded carbon monoxide is one in which the nitric oxide molecule is formally regarded as donating three electrons, and has an M–N–O bond angle of 160° – 180° . This contrasts with the “bent” configuration (M–N–O angle in the range 120° – 140°) in which nitric oxide is formally a one-electron donor, while doubly- and triply-bridging species also occur. Dimerisation of nitric oxide to give the hyponitrite (O–N–N–O) ligand is a well-established phenomenon in coordination chemistry [25], and has frequently been invoked as an explanation of spectra from surfaces. Naturally, each of these different structures gives rise to a range of vibrational frequencies, and there is some overlap between these ranges: spectroscopic evidence from adsorbed nitric oxide is accordingly much more difficult to interpret than that from carbon monoxide. Specific examples of nitric oxide spectra will be given in section 4.1.

2.2. Coupling interactions within adlayers

The phenomenon of dipole coupling has been described at some length in reviews published quite recently [26,27], and discussion here will accordingly concentrate only on those principles and effects which are of direct relevance to spectra from surfaces exhibiting defects or other anomalous adsorption sites.

The mechanism by which the vibrational motions of the individual molecules within an adsorbed layer become coupled together was first considered by Hamaker, Francis and Eischens (HFE) [28], drawing on the work of Decius in solid-state spectroscopy [29]. In this earliest treatment, the oscillating molecules were assumed to interact via their through-space dipolar fields: subsequent refinements have included explicit consideration of the role of the metal in modifying this field [30], of electronic polarization effects [30,31], and of changes in the effective absorption coefficient of the adsorbate [32,33]. HFE originally expressed the potential energy of a planar array of N parallel dipoles as the sum of simple pairwise dipole–dipole interactions, each proportional to the product of the instantaneous dipoles of the two interacting molecules, and to the inverse cube of their separation. In terms of the normal coordinates Q_i of the dipoles, their dipole moments μ_i and intermolecular spacing R_{ij} , this yields:

$$2V = \sum_{i=1}^N \lambda_i Q_i^2 + 2 \sum_{i>j=1}^N (\partial\mu_i/\partial Q_i) Q_i R_{ij}^{-3} Q_j (\partial\mu_j/\partial Q_j), \quad (1)$$

where $\lambda_i = 4\pi^2 c^2 \Omega_i^2$, and Ω_i is the wavenumber of an isolated adsorbed molecule (usually referred to as a “singleton”). Eq. (1) can be rendered more compactly in matrix notation as:

$$2V = \mathbf{Q}' \boldsymbol{\lambda} \mathbf{Q} + \boldsymbol{\mu}' \mathbf{S} \boldsymbol{\mu}, \quad (2)$$

where $S_{ij} = R_{ij}^{-3}$ except when i equals j , in which case $S_{ij} = 0$. The normal modes of vibration were then found by solving the secular equation (2).

The modifications subsequently introduced to the HFE model [30–33] change eq. (2) to the following form:

$$2V = \mathbf{Q}' \boldsymbol{\lambda} \mathbf{Q} + \boldsymbol{\mu}' \mathbf{S} (\mathbf{E} + \boldsymbol{\alpha}_e \mathbf{S})^{-1} \boldsymbol{\mu}, \quad (3)$$

where

$$S_{ij} = \begin{cases} R_{ij}^{-3} + (R_{ij}^2 + 4d^2)^{-3/2} - 12d^2 (R_{ij}^2 + 4d^2)^{-5/2} & (i \neq j), \\ -\frac{1}{4}d^{-3} & (i = j). \end{cases} \quad (4)$$

Here, \mathbf{E} is the $N \times N$ identity matrix, $\boldsymbol{\alpha}_e$ the electronic polarizability tensor, and d the distance between the centre of the adsorbed dipole and the classical image plane. The additional terms in the dipole matrix \mathbf{S} account for the influence of the metal, treated as a classical conductor. (S_{ii} accordingly represents the interaction between a dipole and its own classical image.) Electronic polarization is accounted for by the term $(\mathbf{E} + \boldsymbol{\alpha}_e \mathbf{S})^{-1}$ in eq. (3).

(We note in passing that an alternative, but entirely equivalent, expression is obtained if the self-image interaction term (i.e. S_{ii}) is not considered explicitly, but rather in terms of a modified polarizability which includes the self-image [33].)

Solution of eq. (3) for the case where all the adsorbed molecules are identical indicates two observable effects in the infrared spectrum – a shift of the absorption band to higher frequency, and a reduction in the effective molecular absorption coefficient as the number of interacting molecules increases. Both of these have been confirmed by experiment, and analysis of the dipole-induced frequency shift has been the chief concern in most studies of coupling. A third effect, however, arises when the adlayer consists of more than one species. (Different “species” are here distinguished by their having different singleton frequencies.) There is then a characteristic transfer of intensity from the band due to the lower-frequency species to that of its high-frequency counterpart. The magnitude of this intensity shift depends on the dynamic dipole of the adsorbed species (which also governs the absorption intensity), being greatest for strongly absorbing molecules such as carbon monoxide. It also depends on the adsorbate density and the frequency separation between the species, small separations giving rise to the largest shifts. In the case of carbon monoxide, coupling effects are small when the bands are more than 100 cm^{-1} apart, and usually quite negligible when the separation exceeds 200 cm^{-1} . Since linear and bridge-bonded carbon monoxide species generally exhibit wavenumber separations of at least 100 cm^{-1} , coupling between these species is unlikely to affect spectra very significantly. However, the separation between bands arising from terrace sites and from defects are such that they can produce very strong effects indeed.

To illustrate the physical basis for this intensity shift, it is useful to solve eq. (3) for a very simple model system. Fig. 1 illustrates the solution for a system consisting of just seven carbon monoxide molecules: six of these have identical vibrational wavenumbers of 2100 cm^{-1} , while the final, central molecule has a slightly higher one (2115 cm^{-1}). Nearest-neighbour separations are taken to be 4.0 \AA , and the intermolecular parameters on which the interaction depends are those appropriate for carbon monoxide adsorbed on the Cu(111) surface [32,34].

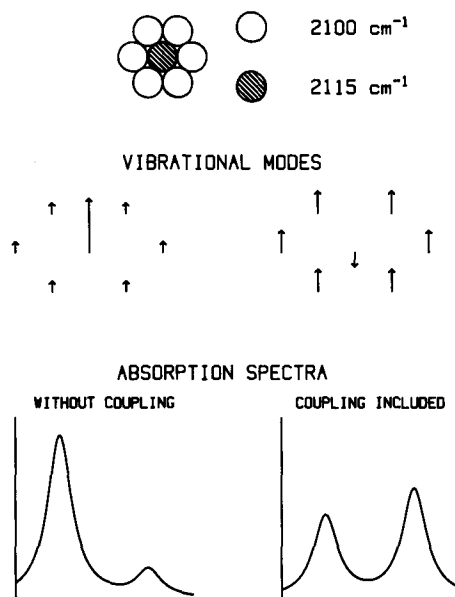


Fig. 1. Influence of dipolar coupling on the infrared absorption spectrum of the 7-molecule island shown. (In the spectra, wavenumber increases from left to right.)

(Unless indicated otherwise, these parameters will be used in all calculations. Parameters for carbon monoxide adsorbed on other substrates have been found to be slightly different, but not sufficiently so to alter any of the general conclusions presented here.) Two strongly infrared-active modes arise. The first is dominated by the central molecule and accordingly has a frequency close to 2115 cm^{-1} , while the second mainly involves the peripheral molecules and appears at lower frequency. However, in the first mode, all the molecules oscillate in phase, so that their dipole moment changes interfere constructively, yielding an enhanced absorption intensity, whereas the second mode exhibits partial destructive interference and an accordingly reduced intensity. Quantitatively, the intensity gained by the first mode is exactly equal to that lost by the second, so the phenomenon can properly be considered as an intensity transfer. The net result is that the high-frequency band is actually slightly stronger than the low-frequency one, instead of being only one-sixth as intense, as would have been expected in the absence of coupling interactions.

The magnitude of the shift increases as the number of interacting molecules rises, and, for a constant number of molecules, as the intermolecular separation decreases. This is illustrated in fig. 2, which shows spectra for a fixed number of molecules (127) belonging to the two species considered in the previous example, randomly arranged in a hexagonal array which is progressively reduced in size. At the lowest adsorbate densities the molecules are essentially uncoupled and there is no intensity shift. By the time the adsorbate density has reached $10^{14}\text{ molecules cm}^{-2}$, however, the transfer is quite significant, and it then quickly reaches the point at which the low-frequency band becomes difficult to discern.

Fig. 2 also demonstrates other effects arising from coupling. The frequency shift of the high-frequency band is very evident, as is the progressive fall in absorption intensity due to depolarization effects. The highest coverage spectra also show a marked shoulder on the low-frequency side of the band. These arise from edge effects; molecules at the edge of the

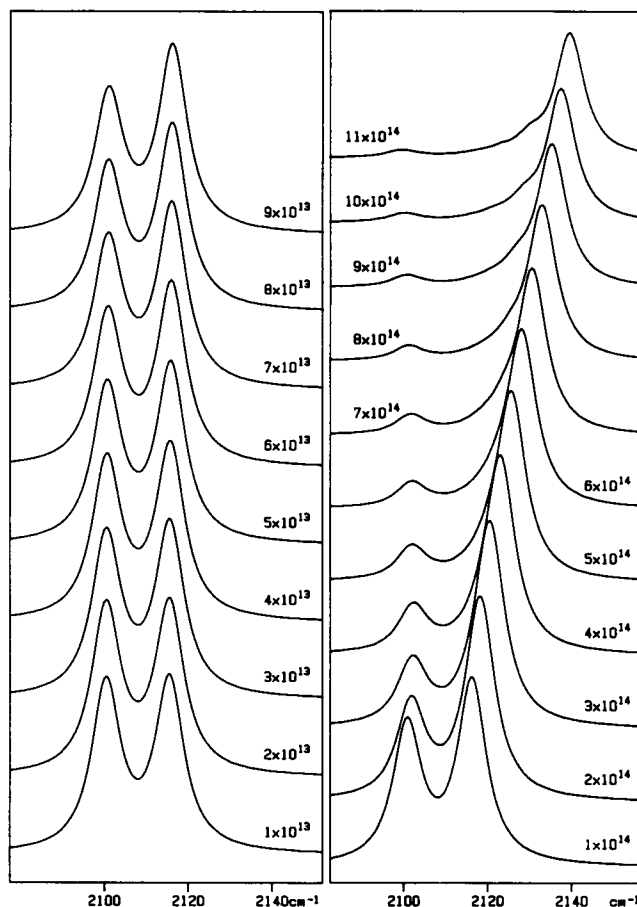


Fig. 2. Calculated spectra as a function of adsorbate density (indicated: molecules cm^{-2}) for islands consisting of an equimolar mixture of the species shown in fig. 1.

cluster experience a dipolar interaction which differs from that of the central molecules, yielding a slightly lower vibrational frequency. We note also that the dipolar model employed here assumes point dipoles. At high densities ($\geq 6 \times 10^{14}$ molecules cm^{-2}), this approximation begins to break down, and the model consistently underestimates coupling effects [32]. The intensity shifts predicted should therefore be taken as a lower bound to those which would be observed in a real system.

At sufficiently high densities, the shift of intensity becomes so large that even a small proportion of the higher-frequency species is likely to dominate the spectrum. This is illustrated in fig. 3, in which spectra are shown for an extended adlayer at a constant high coverage. In every case, the species having a singleton wavenumber of 2100 cm^{-1} constitutes the overwhelming majority of the adsorbed molecules, but a small proportion of molecules having a higher frequency are then introduced. The intensity transfer to the high-frequency band is so great that the high-frequency band becomes the more intense when only 4% of the high-frequency species is present, and by the time this proportion has reached 10%, the low-frequency band has virtually disappeared, even though the species from which it derives still constitutes 90% of the adlayer.

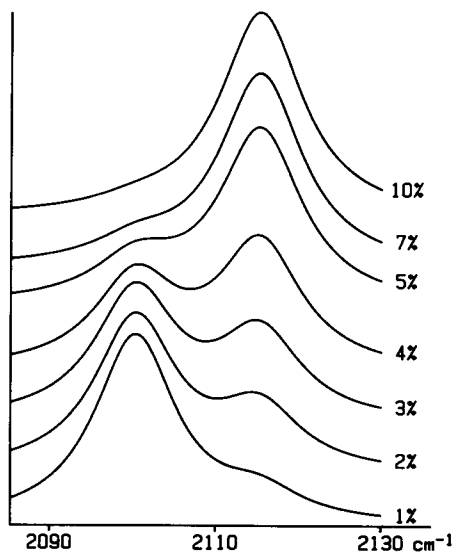


Fig. 3. Calculated spectra for an extended adlayer containing a small percentage (indicated) of the higher-frequency species. Adsorbate density is $1.1 \times 10^{15} \text{ cm}^{-2}$ in each case.

As the proportion of the high-frequency species increases from zero, fig. 3 indicates that initially the spectrum changes very rapidly. However, at quite a low percentage of this species (one easily attained on catalyst surfaces), the high-frequency band comes to dominate the spectrum, and thereafter subsequent changes are slight. It is clear therefore that surfaces of profoundly different morphology may give rise to essentially identical spectra. Misinterpretation of such results is accordingly very likely to occur unless explicit account is taken of coupling effects, which has not normally been the case in analyzing spectra. We shall now examine the implications of this for some specific adsorption systems.

3. Applications to carbon monoxide adsorption

As already noted, carbon monoxide has been overwhelmingly the most widely used infrared probe molecule. In studies related to defects, copper and platinum have been investigated quite extensively, and will be discussed in some detail below. Both metals show a preference for bonding carbon monoxide in the linear configuration [9]. On platinum, molecules are usually observed in bridge sites only after the density of linear species has reached approximately $4 \times 10^{14} \text{ molecules cm}^{-2}$ [15], while on copper bridge-bonding is seen only very near to saturation coverage [10,35,36]. In neither case has the bridge species yet been found relevant to studies of defects, and so it will not be considered further.

Other metals, which have been studied in much less detail, will be considered in section 3.3.

3.1. CO on copper

3.1.1. Supported catalysts and polycrystalline films

Transmission infrared spectroscopy of carbon monoxide adsorbed on supported copper catalysts was first reported by Eischens, Pliskin and Francis [37], and many subsequent studies

Table 2

Wavenumbers of the infrared band in selected transmission spectra of CO adsorbed on supported copper

Support	T^a (K)	$\tilde{\nu}$ (cm^{-1})	Reference
Silica	298	2120	[37]
Silica	298	2100	[38,39]
Silica	113	2110	[40]
Silica	298	2103	[14]
Silica	298	2129	[41]
Silica	298	2099	[42]
Alumina	298	2100	[39]
Alumina	298	2110	[40]
Alumina	298	2108	[14]
Magnesia	298	2081	[14]

^a) Adsorption temperature. Literature reports of "room temperature" are taken to refer to 298 K.

have confirmed their finding of a single absorption band close to 2100 cm^{-1} (table 2). It is now generally acknowledged that the higher-frequency bands (with wavenumbers greater than about 2110 cm^{-1}) are characteristic of imperfectly reduced catalysts (see section 3.1.4), although de Jong et al. have argued that such bands may also be produced by well-reduced particles of unusual morphology [41]. Even on fully reduced catalysts, however, the band is usually above 2100 cm^{-1} , with just two exceptions in the table. The first of these, only marginally below 2100 cm^{-1} , was obtained by Zecchina et al. from a catalyst which had been reduced at high temperature (973 K) in order to sinter the copper particles [42]; the second, with a band at 2081 cm^{-1} , comes from a catalyst supported on magnesium oxide, a substrate which is known to promote the epitaxial growth of metal films with low Miller index orientations [14]. We shall return to these examples in section 3.1.3.

As fig. 4 illustrates, the infrared band on supported copper catalysts shifts scarcely at all with coverage, and similar behaviour has been found with all copper surfaces studied, whether single-crystal or polycrystalline. This is surprising in view of the comments made about dipole

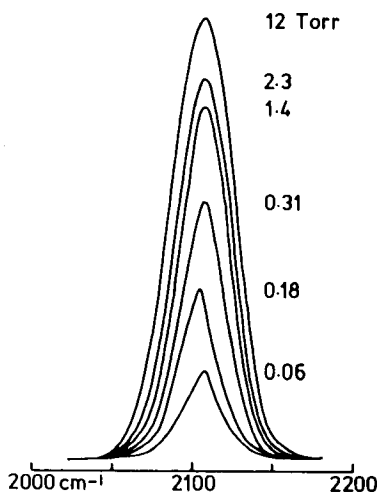


Fig. 4. Transmission spectrum of CO adsorbed on $\text{Cu}/\text{Al}_2\text{O}_3$ at room temperature and the pressures indicated. (Reprinted with permission from ref. [48]: copyright 1980 American Chemical Society.)

Table 3

Wavenumbers of the CO band in reflection-absorption infrared spectra from evaporated copper films

Substrate	<i>T</i> (K)	$\tilde{\nu}$ (cm ⁻¹)	Reference
Glass	298	2105	[44]
Glass	298	2102	[14]
Glass	298	2102	[45]
Glass	77	2105	[43]
Ta foil	298	2105	[46]
Oxidised Al	298	2106	[14]
Oxidised Mg	298	2082	[14]
Ru(001)	85 ^{a)}	2098	[47]
Ru(001)	85 ^{b)}	2075	[47]

^{a)} Film deposited and maintained at 85 K.^{b)} Annealed at 650 K.

coupling effects in section 2.2: one would ordinarily expect the band to move to higher frequency as the coverage was increased. However, it has been shown on a range of copper single crystals [12,13,33,34] that the dipolar shift is almost precisely countered by an opposing “chemical” shift which tends to reduce the frequency as the coverage rises. This chemical shift reflects a change in the bonding of carbon monoxide as a function of coverage, which may be associated with changes in the relative importance of σ - and π -bonding [34,43]. For our present purposes, the chief significance of the near constancy of the band position is that it simplifies comparison of different surfaces, since allowance does not have to be made for the possibility that different coverages may be involved.

Spectra from films of copper prepared by evaporation onto various substrates (table 3) are similar to those from supported catalysts, except that bands above 2110 cm⁻¹ are not observed, supporting the earlier assertion that such bands are due to imperfectly reduced copper. Once again, bands in the range 2100–2110 cm⁻¹ are the norm, lower wavenumbers being reported only from films evaporated onto substrates likely to promote epitaxial growth of low-index surfaces (fig. 5).

3.1.2. Single-crystal substrates

The first application of the then newly developed RAIRS (reflection-absorption infrared spectroscopy) technique to single-crystal substrates was the study of carbon monoxide adsorption on copper(100) reported by Chesters, Pritchard and Sims in 1970 [11], which was soon followed by work on the (111) surface [43]. As has already been noted, the bands found in the spectra from these surfaces were in the region around 2080 cm⁻¹, well below the values obtained from most polycrystalline samples.

The question naturally arose, therefore, as to whether catalyst particles and polycrystalline films could be modelled by single-crystal surfaces. This problem was addressed by Pritchard, Catterick and Gupta in a 1975 paper which is remarkable both for its comprehensiveness and for the new ideas it introduced [14]. Spectra from a variety of polycrystalline samples were compared with those from six different single-crystal planes – the three low-index faces and the stepped surfaces whose spectra are shown in fig. 6.

The stepped surfaces did indeed display the high-frequency bands found with catalysts and evaporated films: fig. 7 compares the spectrum of a polycrystalline film with those from all six crystal faces. The most striking feature of this comparison is that the spectrum from the polycrystalline surface appears to show virtually no contribution from the low-index faces; as

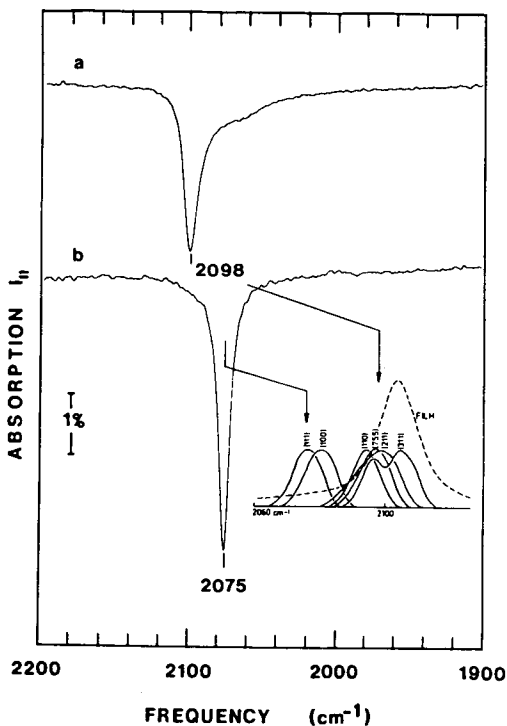


Fig. 5. RAIR spectrum of CO adsorbed on a Cu multilayer ($\theta_{\text{Cu}} = 8$) on Ru(001): (a) as deposited at 85 K; (b) after annealing to 650 K. The inset shows how these compare with spectra from different Cu single-crystal faces (see fig. 7). After Hoffmann and Paul [47].

Pritchard et al. noted, the (100) and (111) planes were “conspicuous by their absence”. Even though the surface energy of copper is known to be highly isotropic [49], the almost complete absence of spectroscopic features characteristic of the low-index planes was surprising. This comment applies to the spectra from some of the high-index single-crystal surfaces themselves. The (755) surface, for example, consists of terraces six atoms wide and of (111) structure, separated by monatomic steps. It is clear that at saturation coverage the majority of adsorbed carbon monoxide molecules must be in a local environment closely similar to that which they would experience on a perfect (111) surface, but this fact is not reflected in the spectrum.

Retrospectively, this is easy to rationalize. The molecules adsorbed at step sites, while constituting a small proportion of the total adsorbate, have a higher vibrational frequency than the majority, terrace species. Coupling interactions then ensure that intensity is transferred from the low-frequency band to the higher one, so that the latter becomes much the more intense, even though it is associated with the minority species. Since the significance of coupling effects in adsorbate spectra was not realised until the late 1970s or early 1980s, however, this explanation was not at first evident. Even after the theoretical basis of coupling had been established, full appreciation of the extent to which intensity transfers could modify spectra only arose as the result of a fortunate error.

This occurred when a further study of carbon monoxide adsorption on copper(110) was undertaken, and the spectra shown in fig. 8 were obtained. It can be seen that at all stages the most intense feature of the spectrum is a band near 2105 cm^{-1} , with a second, weaker band

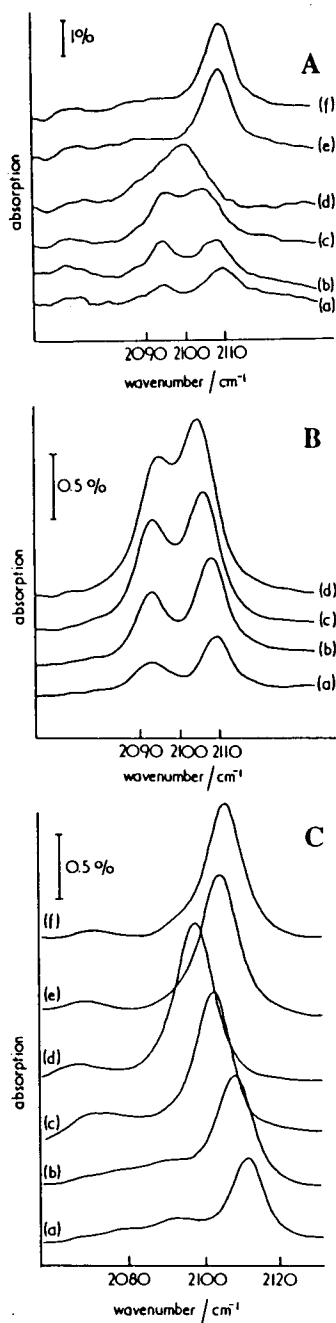


Fig. 6. RAIR spectra as a function of coverage for CO adsorbed on (A) Cu(211), (B) Cu(311) and (C) Cu(755). After Pritchard et al. [14].

about 15 cm^{-1} below it. In an earlier investigation, the same two bands had been seen, but the low-frequency one was then significantly the more intense [50]. In an attempt to discover the origin of this discrepancy, the orientation of the crystal was carefully checked, and found

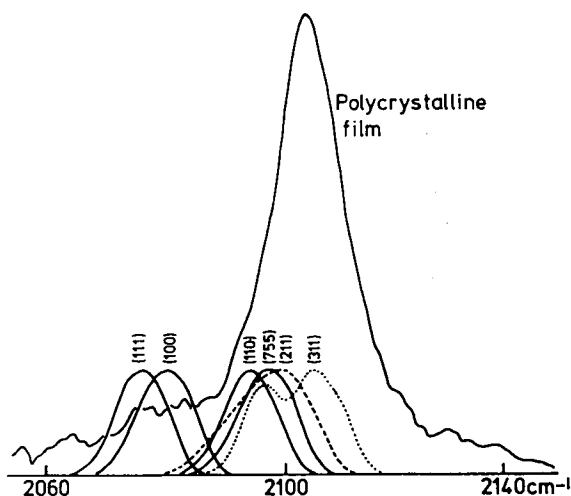


Fig. 7. Comparison of the IR spectrum of CO adsorbed on a polycrystalline Cu film with bands observed on single-crystal surfaces. (Reprinted with permission from ref. [48]: copyright 1980 American Chemical Society.)

to be 1.9° away from the true (110) plane. The surface was thus more accurately described as (16,15,0), having the structure shown in fig. 9, a series of terraces sixteen atoms wide with a local (110) structure, separated by monatomic steps.

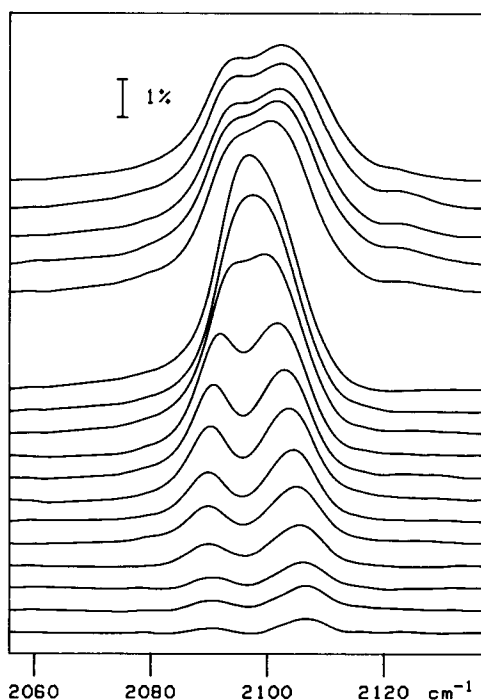


Fig. 8. RAIR spectra as a function of coverage for CO adsorbed on a surface vicinal to Cu(110).

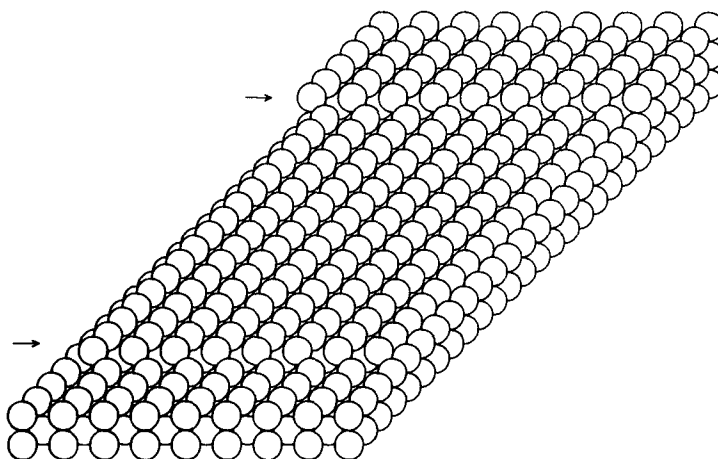


Fig. 9. Cu(16,15,0) surface: arrows indicate step edges.

The explanation for the spectra in fig. 8 is then as follows. Initial adsorption occurs mainly onto the more reactive step sites, which yield a higher vibrational frequency; at very low coverages, therefore, the high-frequency carbon monoxide species is actually in the majority. The step sites quickly saturate, however, and molecules bound to terrace sites become the more common. In the absence of any intermolecular interaction the lower-frequency band would accordingly come to dominate the spectrum. The intensity transfer produced by dipolar coupling, however, ensures that the high-frequency band remains the more intense at *all* coverages, even though it is very much a minority species at saturation.

This explanation is subject to experimental verification. Since the intensity of the high-frequency band at high coverages is believed to be mainly due to coupling interactions, it should be possible to reduce this intensity by reducing the coupling. This can be done without changing the coverage by using isotopic mixtures. Consider for example an adlayer consisting of a mixture of ^{12}CO and ^{13}CO , with the heavier isotope forming a substantial majority of the total. Both step and terrace sites will be occupied by molecules of both isotopic species. Now, a ^{12}CO molecule bonded to a step site will not be able to interact strongly with other ^{12}CO s on terrace sites, since the isotopic dilution ensures that the partial coverage of ^{12}CO is low. The coverage of ^{13}CO (both step and terrace species) will of course be much higher, but the frequency separation between the two isotopes is quite large (47 cm^{-1} in the gas phase), so coupling interactions and intensity transfers will be much reduced. Accordingly, the model predicts that in such an isotopic mixture the relative intensity of the high-frequency component of the ^{12}CO doublet should be very much less than in the single isotope case.

Experimental confirmation of this is shown in fig. 10. To understand the mixed isotope spectra fully, it is necessary to consider two additional factors not mentioned above. Firstly, when coupling effects are reduced by isotopic dilution, the balance between coupling and chemical shifts noted in the previous section no longer applies, and the bands move to lower frequency as the coverage increases. This downward shift naturally becomes greater as the degree of isotopic dilution increases. Secondly, there is some coupling between isotopically different species. Were the frequency separation between ^{12}CO and ^{13}CO to remain at its gas-phase value, intensity transfers would be slight, but the downward chemical shift just mentioned causes the separation to decrease in the case of a mixture dilute in ^{12}CO , sometimes to the point where intensity transfer reduces the ^{13}CO bands almost to zero.

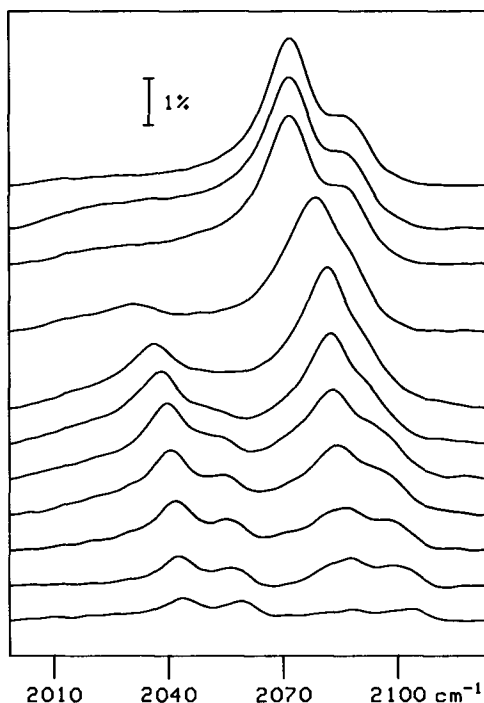


Fig. 10. Mixed isotope RAIR spectra from CO on Cu(16,15,0). ($^{12}\text{CO} : ^{13}\text{CO}$ ratio of 25:75.)

Despite these complications, it is clear that the spectra in fig. 10 do show the predicted effects – at high coverages the intensity of the high-frequency component of the ^{12}CO doublet is much reduced by isotopic dilution, indicating that molecules adsorbed at steps are a minority species. This qualitative assessment of the spectra is confirmed by a full analysis in which the effects described in the preceding paragraph are considered quantitatively.

3.1.3. Mixed isotope study of catalyst spectra

In the light of the results obtained from the copper(16,15,0) surface, there is an evident explanation for the high-frequency bands which are almost always observed in studies of carbon monoxide adsorbed on polycrystalline surfaces. Because molecules adsorbed at defect sites exhibit a higher frequency than those at terrace sites, they will come to dominate the spectrum whenever they are present to any significant extent. Even though the particles in copper catalysts tend to be quite large (typically 100–500 Å), they will still contain a sufficient number of edge sites for these to dominate the spectrum once coupling effects have taken their toll. Similarly, surfaces which are structurally close to low-index single-crystal planes but contain a few percent of their atoms in step or defect sites will yield spectra dominated by the latter. Only when surfaces grow under conditions which permit exceptionally good epitaxial deposition will spectra characteristic of low-index planes appear, as the entries in tables 2 and 3 indicate.

Once again, the presence of terrace site molecules on a surface whose spectrum is otherwise dominated by higher-frequency defect sites can be demonstrated using isotopic mixtures. Fig. 11 shows spectra from a supported copper catalyst recorded using both natural carbon monoxide and an isotopic mixture dilute in ^{12}CO . To ensure narrow line-widths which

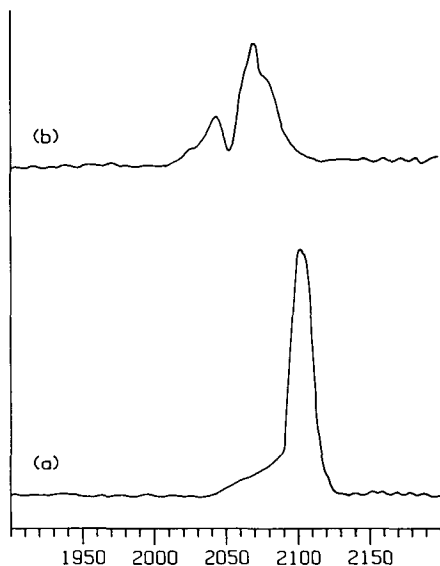


Fig. 11. Transmission spectra from a Cu/SiO₂ catalyst: (a) natural CO; (b) ¹²CO:¹³CO ratio of 24:76.

facilitate analysis of the spectrum, the catalyst was prepared from copper nitrate impregnated onto silica at high salt concentration (giving a catalyst containing 17% w/w metal), and using a reduction temperature of 700°C to encourage sintering of the copper into large particles, following the procedure described by Zecchina et al. [42]. The single isotope spectrum shows the usual single peak in the C–O stretching region, but this splits into a partially resolved doublet in the spectrum of the isotopically dilute mixture, indicating the presence of two distinct adsorption sites, with the low-frequency component now clearly the more intense [51].

3.1.4. Partially oxidised surfaces

The occurrence of bands above 2110 cm⁻¹ on imperfectly reduced catalysts has already been mentioned. The usual observation is of a band in the 2115 to 2130 cm⁻¹ range, but on heavily oxidised samples, or supported CuO, the main band usually occurs around 2140 cm⁻¹, sometimes with an additional feature near 2200 cm⁻¹ [52–55]. The significance of these figures for our present discussion is that they lie just above the wavenumber range found for clean copper, so that, as with defects, a small percentage of molecules adsorbed on sites influenced by oxygen will give rise to abnormally strong infrared bands as a result of coupling.

Adsorption on oxidised single-crystal surfaces has been little studied. However, in one infrared study on an oxidised (111) surface [56], the growth of a doublet band with components initially at 2100 and 2117 cm⁻¹ was noted. That the components of this doublet arose from molecules adsorbed at different types of site was established from an investigation into the temperature dependence of the spectrum (fig. 12), and from mixed isotope studies, which also indicated that the species were in sufficiently close proximity for strong coupling interactions to occur. Oxidised Cu(110) surfaces gave similar spectra, but with an additional band near 2140 cm⁻¹. A weak feature in the same position was observed on the oxidised (111) surface at high coverages, but was shown to derive almost all its intensity from coupling effects: it was accordingly attributed to defect sites.

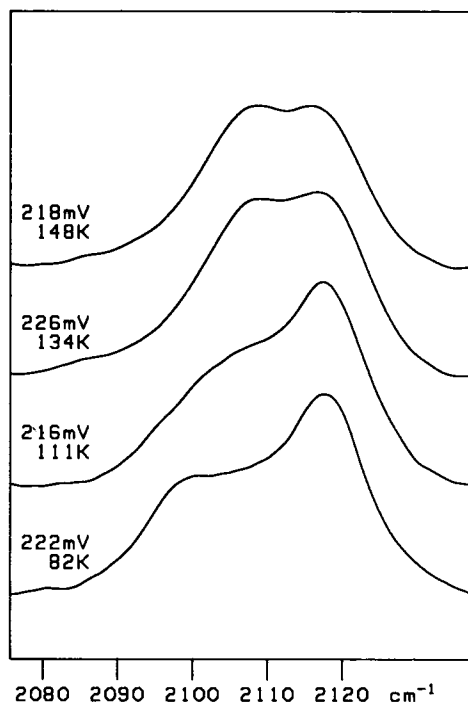


Fig. 12. Spectra of natural CO adsorbed on the $\text{Cu}(111)\text{-O}_{\frac{1}{2}}$ surface at constant coverage (as indicated by surface potential) but varying temperature.

3.2. CO on platinum

Platinum, like copper, shows a preference for linear sites in its adsorption of carbon monoxide. However, the different balance between σ - and π -bonding shown by the two metals, which was discussed in section 2.1, results in defect and other low-coordination sites on platinum giving rise to lower C–O stretching frequencies than those found at terrace sites. Consequently, the effect of coupling interactions is rather different from that observed on copper, where the opposite situation prevails. On platinum, at low coverages a band due to defect species appears at relatively low frequency, followed at higher coverage by a band due to molecules on terrace sites which lies approximately 20 cm^{-1} above the first. Dipolar interactions transfer intensity from the defect band to the terrace one, so the absorption peak moves to higher frequency as coverage increases. This has led to two types of error in interpreting the spectrum. Firstly, on both supported catalysts and extended substrates, this shift in frequency has been interpreted as a dipolar effect acting on a single adsorbed species. Secondly, the relatively small size of the metal particles in supported platinum catalysts means that a high proportion of the adsorption sites occur at edges and defects: intensity transfers may however prevent the detection of molecules adsorbed at these sites if terrace sites are also occupied.

In the following discussion, our chief concern will be the correlation of catalyst data with results from single crystals characterised under UHV conditions; we shall accordingly not consider the results, often of high quality, which have been obtained in recent years from platinum electrodes in electrochemical cells (see ref. [57] and references therein).

3.2.1. Single-crystal substrates

Early infrared studies of adsorption on platinum single crystals were plagued by problems arising from the fact that in many cases true monocrystals were not employed, but rather polycrystalline foils thermally processed to expose Pt(111) facets preferentially. While such samples frequently gave excellent LEED patterns, their defect concentration was usually sufficient to produce very misleading infrared results. Accordingly, in this section we shall be concerned only with true monocrystals, reserving studies of oriented foils for the next. We shall also concentrate on Pt(111) and surfaces vicinal to it, which have been the subject of the great majority of studies to date.

The first investigation of a true single crystal was that of Horn and Pritchard [58] on platinum(111). At an adsorption temperature of 80 K, a band first appeared at 2090 cm^{-1} and shifted smoothly to 2101 cm^{-1} with increasing coverage. At 295 K, the band appeared at 2082 cm^{-1} and shifted to 2089 cm^{-1} . However, at the lowest coverages in the room-temperature study, a band was observed at 2065 cm^{-1} but disappeared as the main band grew in: on the basis of later studies, this band can be confidently assigned to defects.

Subsequent RAIRS studies, performed with relatively low-resolution dispersive instruments, largely confirmed Horn and Pritchard's findings, although there was considerable variability in the reported intensity of the low-frequency band [59–63]. Proof that a band in this position could arise as a result of adsorption onto low-coordination sites was established by Bradshaw and co-workers [18,64–66] in their studies of the Pt(533) and Pt(432) surfaces. These surfaces are each about 15° away from the (111), in the $[\bar{1}01]$ and $[\bar{1}12]$ zones, respectively, and have the alternative designations of Pt(s)- $[(4(111) \times (100))]$ and Pt(s)- $[4(111) \times (3\bar{1}\bar{1})]$. Both consist of (111) terraces four atoms wide separated by monatomic steps: in the case of the (533) surface these steps are straight, but on the (432) they are jagged ("kinked"). Accordingly, the (533) surface has 25% of its exposed atoms coordinated to 7 nearest neighbours (cf. 9 neighbours for the terrace atoms), while the (432) has 14% in 8-coordinate sites and the same proportion in 6-coordinate. One reason for studying these crystals was to establish a basis for interpreting spectra from supported catalysts, since in idealised models of catalyst particles as semi-regular and truncated polyhedra [67,68], surface sites similar in structure to these steps and kinks are prevalent (fig. 13).

Correlation of thermal desorption and infrared results showed that the step and kink sites were the first to be occupied when adsorption took place at 90 K, and that they gave rise to bands at 2067 and 2072 cm^{-1} , respectively, in the low-coverage limit. This lowering of the frequency compared with terrace sites is, of course, in accord with the model outlined in section 2.1, although the fact that the frequency at steps is a little lower than that at kinks is perhaps surprising. (However, see the discussion on the investigation by Reutt-Robey et al. below.) At higher coverages, a band due to terrace molecules appeared above 2080 cm^{-1} : as the coverage increased coupling effects shifted this to above 2090 cm^{-1} , while transferring intensity into it from the lower-frequency band. At intermediate coverages, the doublet structure was well resolved on Pt(533), but imperfectly so on Pt(432), probably because of the relatively low instrumental resolution.

In the mid-1980s, introduction of Fourier transform instruments into RAIRS led to considerable improvements in resolution and sensitivity, as Chesters [69] has described. Such improvements enabled Tüshaus et al. [15] to investigate the behaviour of a nearly perfect Pt(111) crystal at very low coverages, where the influence of the small concentration of defects could be examined. Fig. 14A shows the evolution of the spectrum for a sample dosed to $\theta = 0.01$ at 93 K and then warmed and re-cooled. Initial adsorption is almost entirely into terrace sites, with only a very weak defect band being observed at 2065 cm^{-1} , suggesting that

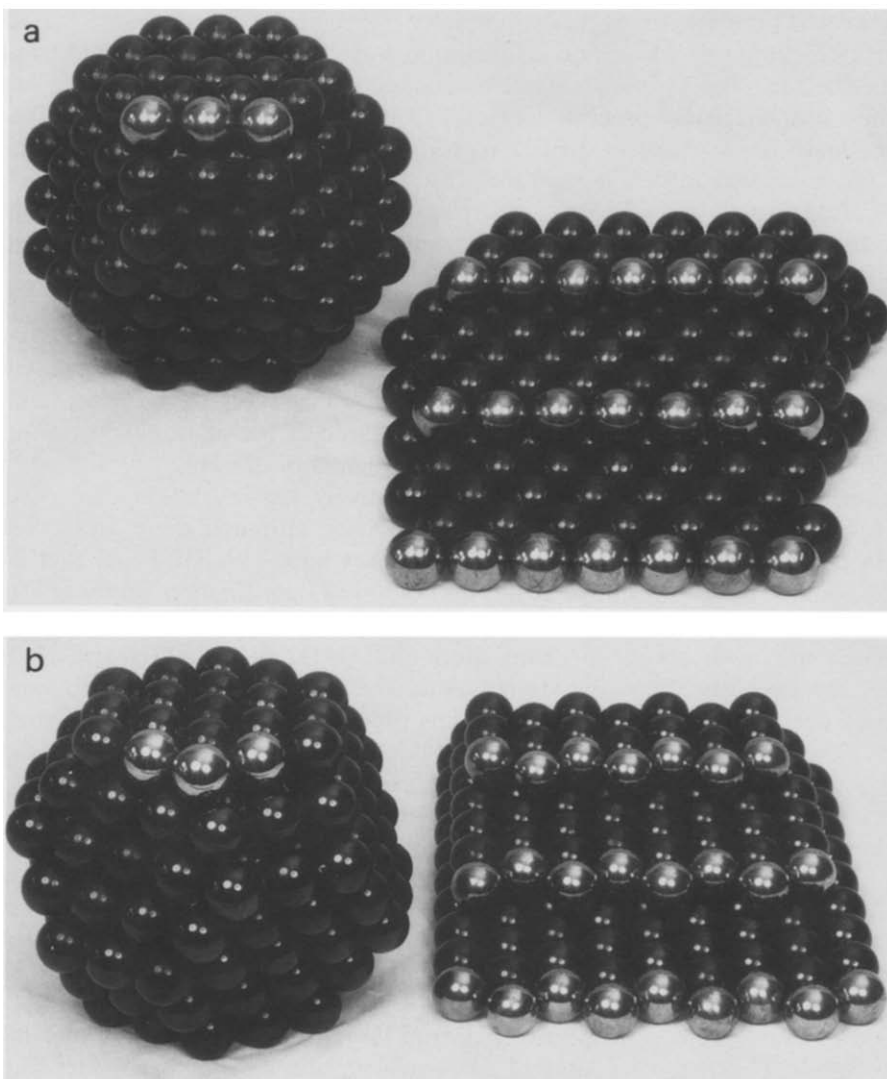


Fig. 13. Models of the (a) Pt(533) and (b) Pt(432) surfaces, illustrating the similarity of the step atom sites to the edge sites on polyhedral particles.

the molecules have insufficient mobility to migrate to their preferred sites at this temperature. Warming causes a progressive shift of intensity into the defect band, which also exhibits a small change in frequency, until at 346 K a band at 2068 cm^{-1} dominates, with only a weak shoulder to higher frequency. The defect band remains dominant during subsequent cooling. Fig. 14B demonstrates similar behaviour at a slightly higher coverage. When the coverage was increased substantially the defect band was, as expected, lost as a result of coupling with the terrace band; it could not be detected above $\theta = 0.2$.

A detailed study of the diffusion from terrace to defect sites was performed by Reutt-Robey et al. in a elegant experiment which is likely to be the forerunner of many kinetic investiga-

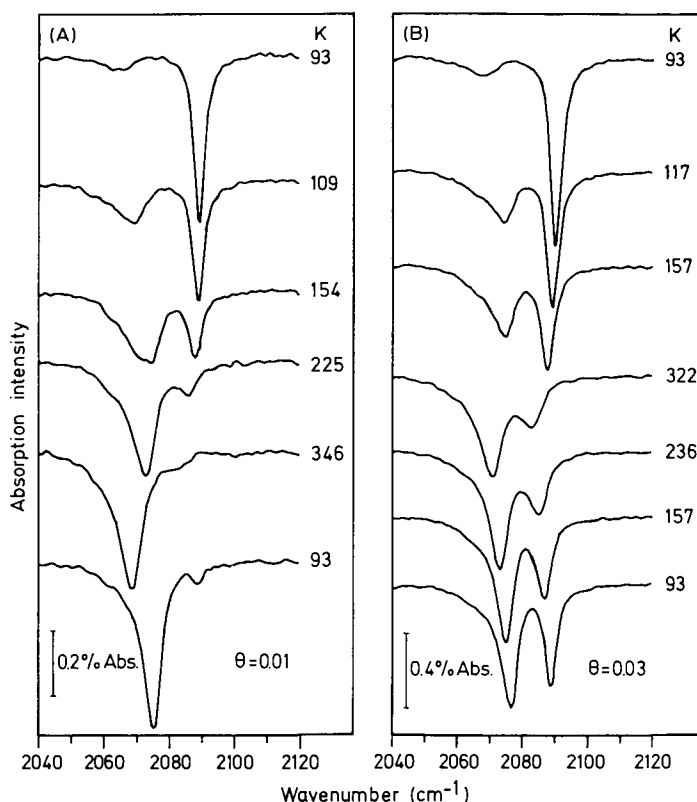


Fig. 14. Thermal evolution of low-coverage CO/Pt(111) spectra. Temporal sequence runs from top to bottom in each case.

tions by infrared spectroscopy [19,70,71]. In this experiment, the surface was first dosed very rapidly (in 600–700 μ s) using a pulsed supersonic molecular beam source, and its infrared spectrum then recorded as a function of time using a fast-scanning FT-IR spectrometer. This enabled surface changes occurring on time scales between 5 ms and several tens of minutes to be monitored. Diffusion from terrace to step sites on the Pt(12,11,10) and Pt(28,27,26) surfaces was studied; as their Miller indices suggest, these surfaces both exhibit kink steps with the same structure as those found on Pt(432), but with terrace widths of 12 and 28 atoms, respectively. The infrared band characteristic of the kink sites was found to occur at 2059 cm^{-1} , significantly below that reported for the Pt(432) surface and more in line with what one might expect by comparison with the Pt(111) and Pt(533) surfaces. The diffusion rate was measured over the temperature range 105–195 K on the Pt(28,27,26) surface (a range over which the rate increases by almost five orders of magnitude), and for the range 117–158 K on Pt(12,11,10). The data for both surfaces was found to be well described by a model for site-to-site hopping on the terraces with an activation barrier of $17 \pm 3 \text{ kJ mol}^{-1}$ and a pre-exponential factor given by $\log(A/\text{s}^{-1}) = 9.2^{+1.2}_{-2.2}$.

3.2.2. {111}-oriented Pt foils

As was mentioned in the introduction to the preceding section, many of the earlier studies of carbon monoxide adsorption on surfaces which were nominally platinum(111) were in fact

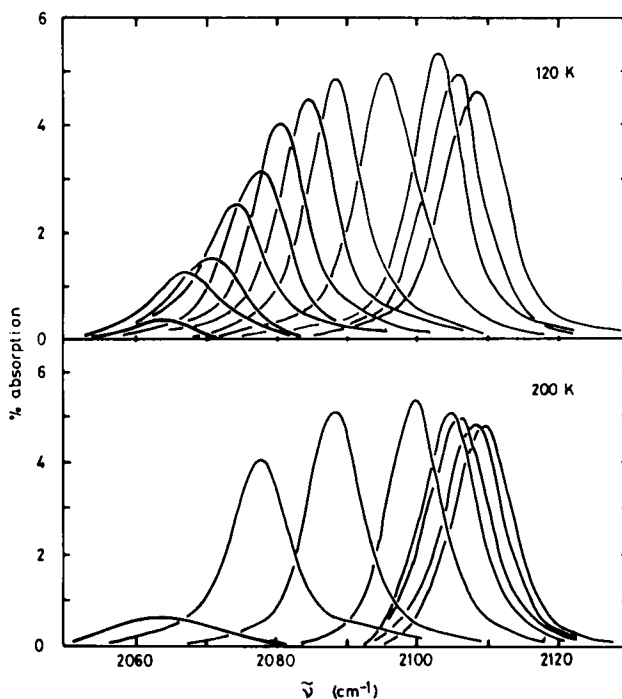


Fig. 15. Development of infrared spectrum with exposure on a {111}-oriented Pt foil at two adsorption temperatures [72].

carried out using polycrystalline foils thermally processed to expose {111} facets [72–79]. (Typically, re-crystallisation and cleaning would be accomplished by heating in 10^{-6} to 10^{-5} Torr of oxygen for a period of hours or days, followed by an extended anneal at 1200 to 1500°C.) While the resulting surface generally gave LEED and thermal desorption results which were in good agreement with those from true Pt(111) monocrystals, it is now clear that the density of defects was sufficient to change the infrared spectrum markedly. This caused a great deal of confusion at the time, but the results are of considerable use to us now in evaluating the influence of defects. Since the surface cleanness of the samples was generally good, they serve as examples of chemically well-defined surfaces with relatively high defect densities, which are of great help in the interpretation of spectra from catalysts, to be considered in the next section.

The first study on an oriented foil under UHV conditions was that of Shigeishi and King [72], who combined infrared spectroscopy with thermal desorption measurements. They observed, for a range of adsorption temperatures between 120 and 300 K, that a band appeared initially at 2065 cm^{-1} and shifted with increasing coverage, apparently smoothly, to 2101 cm^{-1} at an adsorbate density of $7 \times 10^{14}\text{ molecules cm}^{-2}$ (fig. 15).

This behaviour was confirmed by Crossley and King [73], who also performed the prototype of an ingenious experiment designed to determine the origin of the frequency shift. As the discussion concerned with fig. 10 in section 3.1.2 has already indicated, frequency shifts may be due to real changes in chemical bonding as a function of coverage, to dipolar coupling effects, or to a combination of both. By recording spectra from $^{12}\text{CO}/^{13}\text{CO}$ mixtures, the dipolar effect can be reduced in a controlled fashion, while leaving the chemical shift

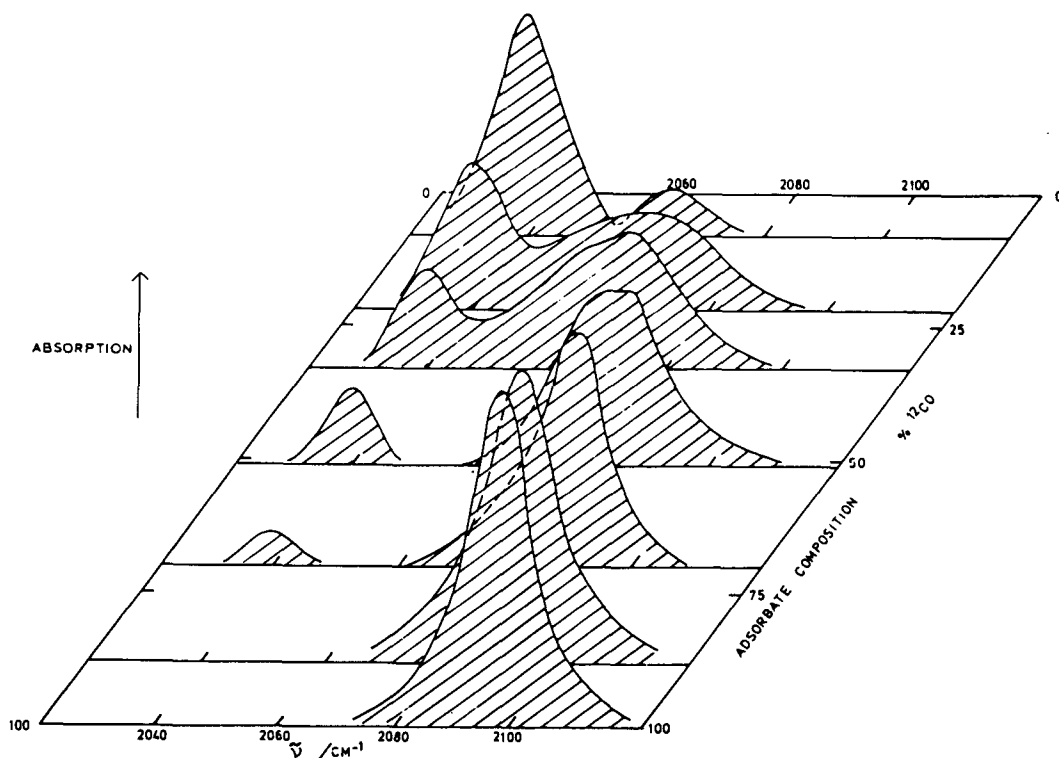


Fig. 16. Spectra of $^{12}\text{CO}/^{13}\text{CO}$ mixtures at constant coverage on a {111}-oriented Pt foil [73]. Resolution: 15 cm^{-1} .

unchanged. Thus, by comparing the wavenumber of the band due to, say, ^{12}CO in the single isotope spectrum with that of the same band in a $^{12}\text{CO}/^{13}\text{CO}$ mixture very dilute in the lighter isotope, the coupling shift at a particular coverage can be measured. Any difference between this value and the total shift from zero coverage must then be due to the chemical shift. Spectra for a range of isotopic compositions at constant (saturation) coverage are shown in fig. 16. These show the ^{12}CO band shifting down as the proportion of the isotope is reduced, and in the limit of isotopic dilution it lies very close to its position in the low-coverage single isotope spectrum. Accordingly, the entire shift was attributed to coupling, with no chemical component.

Similar results were obtained by other investigators using dispersive spectrometers. However, Baker and Chesters [79], in one of the first studies to employ modern Fourier transform instruments, showed that the situation was more complicated. Their spectra (fig. 17) clearly indicate that, instead of a single band shifting smoothly, there is a doublet at intermediate coverages, with components too close together to have been properly resolved by the dispersive spectrometers. In the light of subsequent single-crystal investigations the attribution of the low- and high-frequency bands to defect and terrace sites is evident.

Crossley and King's mixed isotope experiment, however, needs a little more explanation, since the results depend on a rather complicated balance of intensity transfers. Fig. 18 illustrates the coupling effects expected at high coverage for a mixed overlayer (molecules on both defects and terrace sites) both for a single isotope and in the case of extreme isotopic dilution. In the pure isotope, the high-frequency band, which is in any case likely to belong to

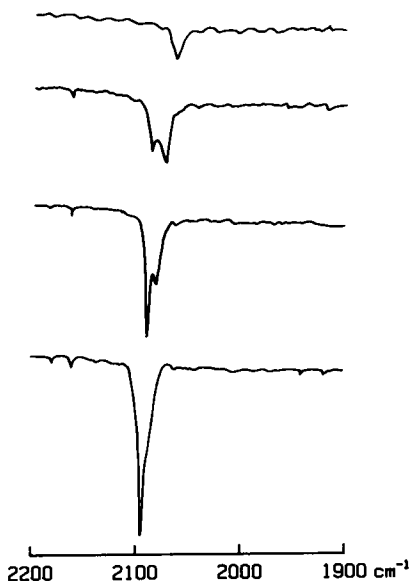


Fig. 17. High-resolution (2 cm^{-1}) spectra of CO on a {111}-oriented Pt film. After Baker and Chesters [79].

the majority species, gains intensity from its low-frequency counterpart, which consequently diminishes almost to zero: the spectrum is accordingly dominated by terrace site molecules. With the dilute isotopic mixture, however, the low-frequency component of the ^{12}CO doublet is only weakly coupled to its high-frequency counterpart, since there are very few ^{12}CO

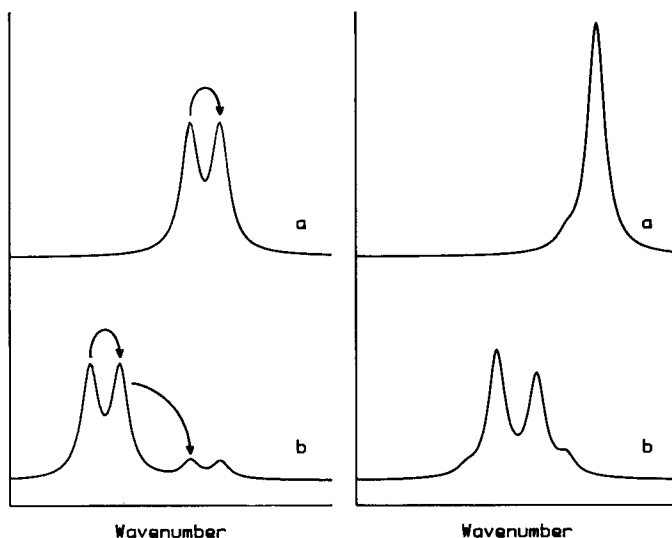


Fig. 18. Influence of a high density of defects on spectra from a {111}-oriented Pt foil: (a) pure ^{12}CO ; (b) a dilute $^{12}\text{CO}/^{13}\text{CO}$ mixture. Left-hand traces exclude coupling effects, while right-hand ones include them. Major intensity transfers are indicated [80].

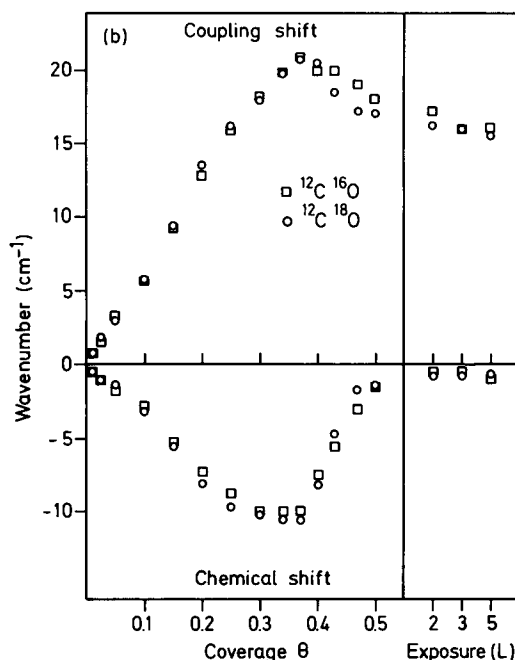


Fig. 19. Coupling and chemical shifts as a function of coverage on Pt(111).

molecules present on either type of site, but it is strongly coupled to the high-frequency component of the ¹³CO doublet, from which it gains intensity. (Not only is the high frequency, terrace, ¹³CO the most abundant species on the surface, but the frequency shift arising from dipole coupling moves its absorption band closer to that of the low-frequency ¹²CO species, enhancing the intensity transfer.) Under these conditions, therefore, the ¹²CO doublet is dominated by the contribution from molecules on defect sites. The apparent frequency shift in going from the dilute isotope to the pure one is accordingly the sum of two separate components – the true coupling shift which the experiment is designed to measure, plus the frequency difference between terrace and defect sites. The experiment therefore seriously overestimates the coupling shift.

Two pieces of evidence point to the above being the correct explanation for Crossley and King's experiment. First, coupling and chemical shifts have been measured on an almost defect-free Pt(111) crystal [15]. As fig. 19 indicates, the shifts both exhibit a maximum as a function of coverage: under the conditions employed in ref. [73], the chemical shift should have been close to zero (as was indeed observed), but the coupling shift should have been barely half the reported 35 cm⁻¹. Second, at isotopic compositions between the extremes illustrated in fig. 18, the balance of intensity transfers should allow both components of the ¹²CO band to attain comparable intensity, so that an incipient doublet structure would be observed even at relatively poor resolution: such an effect can be discerned (by an observer possessing the incomparable advantage of hindsight!) in the experimental spectra of fig. 16.

3.2.3. Supported catalysts and polycrystalline films

The infrared spectrum of carbon monoxide adsorbed on supported platinum has been studied particularly extensively. A comprehensive and critical review of the literature up to

1977 has been given by Sheppard and Nguyen [9]. The spectra obtained in most subsequent investigations fall into patterns of behaviour identified in this review, apart from a number of studies in which zeolite supports were used. These produce very small catalyst particles (typically of the order of 10 Å or less [81,82]), and are characterised by rather low C–O stretching frequencies ($\bar{\nu}$ in the 2000 to 2060 cm^{-1} range [83]). Bands at similar frequency occur in spectra reported from colloidal platinum particles [84].

On larger particles, usually supported on silica or alumina, a band is normally observed between 2070 and 2090 cm^{-1} at high coverage. These frequencies are a little lower than those found on the Pt(111) surface at saturation, where a value closer to 2100 cm^{-1} is the norm [15]. Some of this disparity may be due to smaller coupling-induced frequency shifts on catalyst particles, since the small facets limit the size of the adlayer and hence of the dipole sum (S of eq. (3) of section 2.2). However, the dipolar interaction is of fairly short range (falling off as R^{-3}), so the difference in the coupling shift between large and small particles is not expected to be very great [85]. The remaining discrepancy may be due to the particles having a more open surface structure, or to the bonding on small particles being rather different from that on extended substrates. (We note that supported platinum catalysts generally exhibit smaller particle size ranges than the copper catalysts considered in sections 3.1.1 and 3.1.3.) Whatever the reason, it is generally observed that larger particle sizes are associated with higher wavenumbers; for example, Dalla Betta [86,87] found bands centred at 2077 and 2093 cm^{-1} for carbon monoxide adsorbed on catalyst particles of 10 and 120 Å, respectively. In a very recent study using a variety of supported platinum catalysts, Kappers and van der Maas [88] have reported a correlation between the wavenumber of adsorbed carbon monoxide and the coordination number of the adsorbate atom. As with copper, bands above about 2110 cm^{-1} are usually attributed to partially oxidised catalysts [89].

At low coverages on well-reduced catalysts, a band is normally seen near 2050 cm^{-1} . The change in wavenumber on going from low to high coverage has often been interpreted as a continuous shift of a single band, but it is clear that in many, if not all, cases two distinct species are involved. From catalysts on both silica and alumina supports, a doublet structure in the band has been observed [80,90,91], and the relative intensities of the components of this vary with the details of catalyst preparation, as well as with coverage. By analogy with single-crystal surfaces, it seems very likely that adsorption initially occurs on defect sites yielding low vibrational frequencies, with later adsorption populating higher-frequency terrace sites which eventually come to dominate the spectrum through coupling effects. The catalyst spectra themselves provide further intrinsic evidence for the presence of defects. Thus, Primet [92] observed that the low-frequency band could be preferentially populated by heating in a closed system, and that the position of the band was then essentially independent of coverage: the absence of a shift with coverage due to dipolar coupling implies that the molecules occupy widely separated sites. Bartók et al. [90] found that the molecules in the low-frequency band appeared to exhibit a higher molecular infrared absorption coefficient: this could again be indicative of the molecules being isolated, and therefore subject to weaker depolarization effects, or it might be due to the field enhancement at defects which is predicted to increase absorption intensity [93].

In the very first application of dipole coupling concepts to adlayers, Hammaker, Francis and Eischens [28] carried out mixed isotope studies of carbon monoxide adsorbed on silica-supported platinum. On the basis of their results, they attributed the entire shift observed on this catalyst to coupling effects, but the probable occurrence of two distinct binding sites is suggested by comparison with the studies on {111}-oriented foils which were described in the previous section. Quantitative interpretation of similar spectra from an

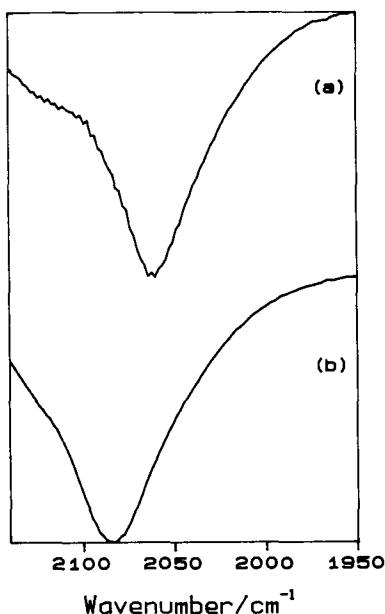


Fig. 20. IR spectrum of CO adsorbed on EUROPt3: (a) after reducing at 573 K; (b) after heating to 773 K.

alumina-supported catalyst has been achieved on the assumption that defect and terrace sites are involved [80].

A result recently obtained from an alumina-supported catalyst indicates the potential use of infrared spectroscopy in characterising the morphology of platinum catalysts [94]. The standard EUROPt3 catalyst has a very low metal loading (0.3% w/w) and a commensurately small particle size. The final stage in the preparation of this catalyst is a reduction in flowing hydrogen: the activity of the catalyst for neohexane conversion has been reported to change markedly when the temperature of this reduction is increased from 300 to 500°C [95]. Fig. 20a shows the infrared spectrum of CO adsorbed on a catalyst reduced at the lower temperature; a single band centred about 2061 cm^{-1} is observed. On heating to 500°C and re-cooling, an irreversible change occurs to give the spectrum in fig. 20b, where the band is some 23 cm^{-1} higher in wavenumber. The most obvious interpretation of this change is that initially the adsorption sites on the catalyst consist almost entirely of metal atoms of low coordination, which are converted to terrace sites on heating. The phenomenon cannot be simply explained by the sintering together of catalyst particles, since hydrogen chemisorption studies show that the particle size is not significantly changed. The most probable explanation is that initially the catalyst particles are approximately spherical (and, because of their small size, have almost all of their atoms at edge sites), but are converted to flat platelets at higher temperatures. This interpretation is supported by a recent EXAFS study on a similar catalyst [96].

Carbon monoxide adsorption has also been studied on platinum films evaporated onto the halides of alkali or alkaline earth metals; the resulting spectroscopic data are summarised in ref. [9]. The notable feature is the occurrence in most of these studies of bands in the $2030\text{--}2050\text{ cm}^{-1}$ range, below that observed on most supported catalysts. Although the possibility of contamination must be considered in some of these studies, especially those in which the evaporation was carried out in an atmosphere of carbon monoxide, it may also be

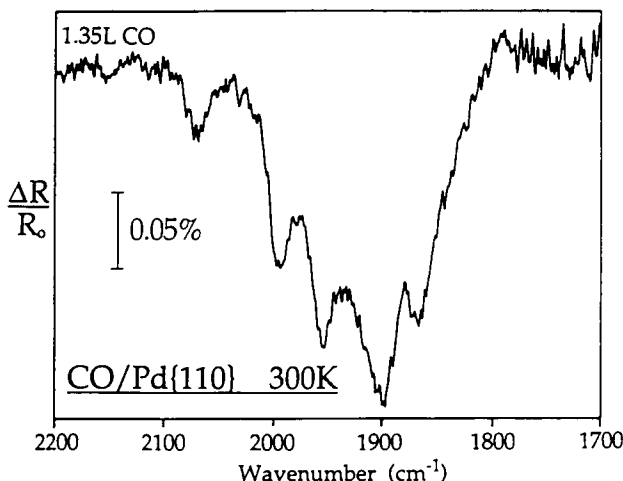


Fig. 21. IR spectrum of CO adsorbed on Pd(110) at 300 K and $\theta = 0.6$ [102].

the case that films offer sites of exceptionally low coordination, perhaps individual atoms protruding above the terraces.

3.3. CO on other metals

Extension of the arguments presented in section 2.1 would suggest that the lower frequency found for carbon monoxide at defect sites on platinum should be typical of the majority of transition metals, while the IB metals should show the same behaviour as copper. Unfortunately, the influence of defects has not been investigated systematically on any of these metals, so this possibility remains conjectural. There is, however, some evidence available for the probable adventitious influence of defects in various studies from nominally low-index surfaces.

The only other metal for which the number of different single-crystal faces investigated rivals the cases of copper and platinum is palladium, where the (100), (110), (111) and (210) surfaces have been studied [97–102]. Sadly, spectra from palladium exhibit two features which render interpretation and comparison very difficult. The first is that adsorption can give rise to linear, doubly- and triply-bridging species, often simultaneously. Secondly, these bands are subject to large chemical shifts which cause their frequencies to increase with coverage, augmenting the coupling shift: band positions are accordingly very strongly coverage-dependent. When these factors are combined with an adsorbate-induced surface reconstruction, which has been found to occur on Pd(110) [103], spectra of alarming complexity can result, as fig. 21 illustrates. However, at low coverages on this surface, the band due to doubly-bridging carbon monoxide displays a shoulder to low frequency which loses intensity at higher coverages, finally disappearing completely (fig. 22). This is reminiscent of the behaviour of defect sites on Pt(111), and may well be attributable to the same cause.

In passing, it is worth noting that the surface reconstruction produced by carbon monoxide adsorption on Pd(110) demonstrates a potential problem in the use of probe molecules that we have not previously identified – the probe molecule may change the very morphology that it is being used to monitor. Reconstruction is, of course, most commonly observed with atomic adsorbates, but the palladium case does establish rather conclusively that carbon monoxide

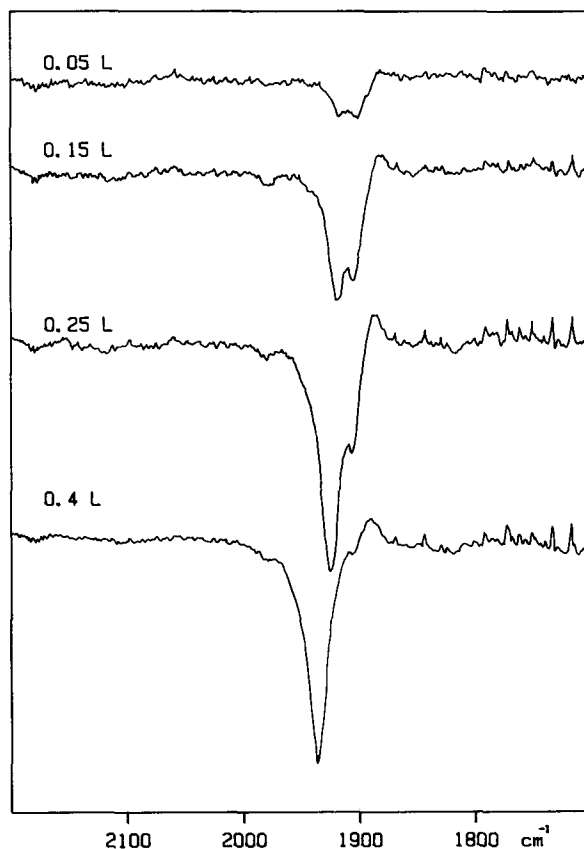


Fig. 22. Low-coverage IR spectra of CO adsorbed on Pd(110) at 140 K as a function of exposure. After Harrison [104].

can act in the same manner. For in-situ studies of catalytic reactions where carbon monoxide is a reactant or product, any morphological changes induced by the adsorbate may well be relevant to the reaction, but under other conditions they are likely to prove misleading.

We return now to the chemical shift observed for palladium. The sign of this demonstrates that the fall in the enthalpy of adsorption which takes place as the coverage increases is accompanied by a rise in the intrinsic vibrational frequency. Since defects are generally characterised by a stronger adsorption enthalpy than terrace sites, one might anticipate that other metals manifesting such positive chemical shifts for carbon monoxide would also yield a lower frequency for molecules adsorbed at defect sites. Ruthenium may be a case in point. Here, the vibrational frequency of adsorbed carbon monoxide shows a marked increase with coverage which almost certainly entails a positive chemical shift augmenting the effect of dipolar coupling. On Ru(001), Pfnür et al. observed a band that exhibited a strikingly rapid change of frequency at low coverages and which could under appropriate conditions be resolved into a doublet [105]. The high- and low-frequency components of this doublet were attributed to molecules at the centre and edge of islands; defects were considered as a possible cause, but eliminated because the low-frequency component disappeared at higher coverages. In view of what is now known about coupling interactions, however, the behaviour seems entirely consistent with the low-frequency band being due to molecules adsorbed at

defects which dominate the spectra at low coverages but lose intensity through coupling at higher ones.

Several infrared studies of carbon monoxide adsorption on various faces of nickel have been reported, but in no case does there appear to be any definite evidence for the involvement of defects. There is, however, some evidence that the correlation between adsorption enthalpy and frequency follows the same pattern as on platinum, in that the weakly bound forms of carbon monoxide generated by co-adsorption of sulphur [166] and hydrogen [107,108] both exhibit higher than normal frequencies for the stretch mode of the linearly adsorbed molecule.

On silver and gold, the frequency of adsorbed carbon monoxide falls with increasing coverage [43,109,110], implying a chemical shift which is negative and sufficiently large to more than offset the coupling shift. For this reason, as well as by analogy with copper, defect sites on these metals might be expected to give higher vibrational frequencies. Among the few studies on single crystals, there is an observation of a doublet band with the high-frequency component appearing at lower coverages than its counterpart [111], providing some support for this view.

There is an evident dearth of published investigations into the influence of defects on spectra from metals other than copper and platinum. Further studies should establish whether the simple model described in section 2.1 is valid generally or is an oversimplification. Much more importantly, they should also generate basic data of great help in interpreting spectra from catalysts.

4. Other probe molecules

Despite the almost universal use of carbon monoxide as a probe for infrared studies, the molecule does present some difficulties which the preceding section has highlighted. The strength of its dynamic dipole, which was, ironically, a principal reason for its original selection as a probe, leads to coupling effects so large that the spectrum of a mixture of species tends to become dominated by the species with the highest vibrational frequency. Mixed isotope experiments can circumvent this problem, but these are difficult to perform and interpret even when there are only two differently bound species present. When there are three or more such species, as in the case of a partially oxidised copper catalyst, or even a clean palladium single-crystal surface at an appropriate coverage [102], deconvolution of the various coupling interactions becomes a herculean task, as we shall discuss in section 5.1. There would accordingly be considerable advantage in using a probe which gave an infrared spectrum sensitive to surface structure, but which did not suffer from such dramatic coupling effects.

Two possible contenders were noted in section 2.1, nitrogen and nitric oxide. The dinitrogen molecule has a smaller dipole than carbon monoxide, and its vibrational frequency appears to be sensitive to its binding site. However, the strength of nitrogen's infrared absorption is still sufficient for strong intensity transfers to occur between molecules bound to terrace and defect sites, or between $^{14}\text{N}_2$ and $^{15}\text{N}_2$ in isotopic mixtures [24,112], and there are other practical difficulties. Because nitrogen is quite weakly adsorbed by metals, catalyst studies would frequently have to be carried out at low temperatures, which would rule out most in-situ applications. Moreover, the molecule is easily displaced by more reactive species, such as hydrogen and, inevitably, carbon monoxide.

Table 4

Wavenumbers for the N–O stretch in nitrosyl complexes (after Agrawal and Trenary [114])

Geometry	$\tilde{\nu}$ (cm ⁻¹)	
Terminal linear	1600–2000	
Terminal bent	1525–1700	
Two-fold bridge	1480–1545	
Three-fold bridge	1320–1545	
Hyponitrite ^{a)} (O–N–N–O)	1045–1285	} Doublet
	930–1240	

^{a)} Refs. [115–117].

Nitric oxide, however, appears to have more substantial advantages as a probe molecule for infrared studies.

4.1. Nitric oxide

The disadvantages which limit the applications of nitric oxide as a probe are the complexity of its spectra, as outlined in section 2.1, and its high reactivity, which leads to its oxidising many of the more reactive metals under relatively mild conditions. Its chief advantage over carbon monoxide is that the bands in the spectrum of the adsorbed molecule are frequently very well separated, so that intensity shifts due to coupling are smaller, despite the molecule's strong dynamic dipole.

The gas-phase ¹⁴N¹⁶O molecule has a value for $\tilde{\omega}_e$ of 1904.2 cm⁻¹, compared to 2376.4 cm⁻¹ for NO⁺, the large increase on ionisation reflecting the strongly anti-bonding nature of the outer electron [113]. In coordination compounds, a wide range of N–O stretching frequencies have been reported; the correlation between these and bonding geometry is indicated in table 4 and has served as a guide to the interpretation of spectra from surfaces. The trend is similar to that found with carbon monoxide, bridging ligands giving lower frequencies than on-top ones (whether linear or bent), but the shifts are generally greater. It has also been remarked [118] that bands from metals in the first transition row are significantly higher (by, typically, 50 cm⁻¹) than those from the second and third row. This trend, which is not observed with carbon monoxide, is attributed to the heavier metals achieving a more favourable energy match between their d-electrons and the π^* orbital of the ligand.

Vibrational spectroscopy has been used to investigate the adsorption of nitric oxide onto catalysts and extended surfaces far less often than in the case of carbon monoxide, but nonetheless the total number of such studies is considerable. Here, we shall concentrate on experiments involving platinum, the metal which has been most widely used in single-crystal studies, and one which presents fewer problems arising from dissociation of the nitric oxide.

Following adsorption on Pt(111) at low temperatures, two bands, with wavenumbers close to 1500 and 1700 cm⁻¹, are observed [119–121]. The low-frequency band, which is the first to appear, is usually attributed to a doubly-bridged species, and the high-frequency band, which dominates the spectrum at high coverages, to an on-top one. From mixed isotope spectra, Hayden [121] established that the high-frequency band exhibited coupling and chemical shifts of +33 and –13 cm⁻¹, respectively, while the corresponding values for the low-frequency band were <5 and +18 cm⁻¹. The negative chemical shift for the on-top species is surprising, since weaker bonding to the substrate is normally associated with a strengthening of the N–O bond. At higher temperatures, Dunn et al. [119] observed that the low-frequency

band was replaced by one near 1600 cm^{-1} , while on a $\{111\}$ -oriented foil [122], an additional band was found at 1335 cm^{-1} . On Pt(100) at 300 K, Gardner et al. observed a band at 1596 cm^{-1} at low coverage which moved to 1641 cm^{-1} at $\theta = 0.5$: correlation with LEED indicated an adsorption site between the on-top and symmetrical bridge positions. At lower temperatures, further adsorption produced a band at 1680 cm^{-1} . Adsorption on a hexagonally reconstructed Pt(100) surface at low temperatures also gave a band at 1680 cm^{-1} , before further adsorption lifted the reconstruction.

From alumina-supported catalysts at room temperature, Primet et al. [124,125] obtained spectra dominated by a band near 1800 cm^{-1} , with a much weaker feature near 1600 cm^{-1} . The main band was markedly asymmetric, with a shoulder to low wavenumber, and its position varied somewhat with mean particle size, being lower on larger particles. Brown and Gonzalez [126] reported a band from silica-supported platinum at 1760 cm^{-1} , as did Fang and White [127] for a catalyst supported on titania. In the latter case the main band was accompanied by a subsidiary one close to 1700 cm^{-1} . Spectra obtained by de Jong et al. [128] from silica-supported platinum gave major bands at 1780 and 1600 cm^{-1} , together with a much weaker one at 1935 cm^{-1} which was attributed to adsorption on partially oxidised sites. Morrow et al. [129] monitored the spectrum of nitric oxide on silica-supported platinum as a function of temperature. They observed three bands; one centred around 1785 cm^{-1} which was dominant near room temperature; one near 1620 cm^{-1} which dominated at higher temperatures and at low coverages, and a third band near 1690 cm^{-1} , which was favoured at low temperatures but was converted into the other two states on warming.

Recently, Agrawal and Trenary [114] have studied nitric oxide adsorption on two Pt(111) surfaces with different defect densities and also on a vicinal kink-stepped surface with terraces approximately 12 atoms wide. Correlations with spectra from adsorbed carbon monoxide were used to monitor the influence of defects, as was comparison with spectra from surfaces where defect sites had been specifically blocked with adsorbed oxygen. Room-temperature adsorption on a smooth Pt(111) surface gave two bands similar to those observed by Hayden (fig. 23), while the stepped surface gave markedly more complex spectra, with an additional band above 1800 cm^{-1} (which did not appear at low temperatures), and a doublet near 1600 cm^{-1} (fig. 24). The high- and low-frequency components of this doublet were attributed to molecules adsorbed at step and kink sites, respectively. Selective blocking of step sites at low temperature with atomic oxygen eliminated the band (fig. 25). On the basis of these and other experiments, the assignments given in table 5 were suggested.

The range of frequencies observed in the spectrum of adsorbed nitric oxide on platinum certainly suggests that it has the promise of becoming a useful species to probe substrate morphology. Because of the large wavenumber separation between the different bands, coupling effects are much less severe than for carbon monoxide. However, interpretation of spectra remains a daunting problem. The very disparate spectra obtained from Pt(111) and Pt(100) suggest substantially different bonding regimes on the two surfaces, and there is evidence from VEELS to indicate that Pt(110) may be different again [130]. If these differences can be fully interpreted, very precise morphological characterisation of catalysts might be possible, but for this to become practicable, it will first be necessary to obtain data from a much wider range of single-crystal surfaces. Changes with temperature also seem to be an important factor which needs further study.

4.2. Hydrocarbon and related species

Metal catalysts are, of course, widely used in reactions involving hydrocarbons. This factor, combined with the relatively low absorption intensities of hydrocarbons in the infrared (which

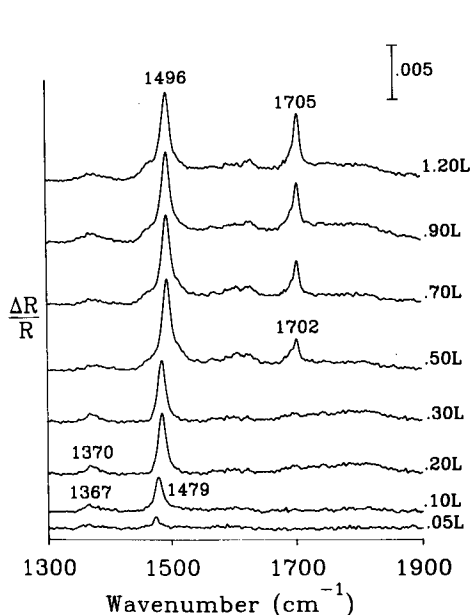


Fig. 23. IR spectra of NO adsorbed on Pt(111) at 300 K as a function of exposure [114].

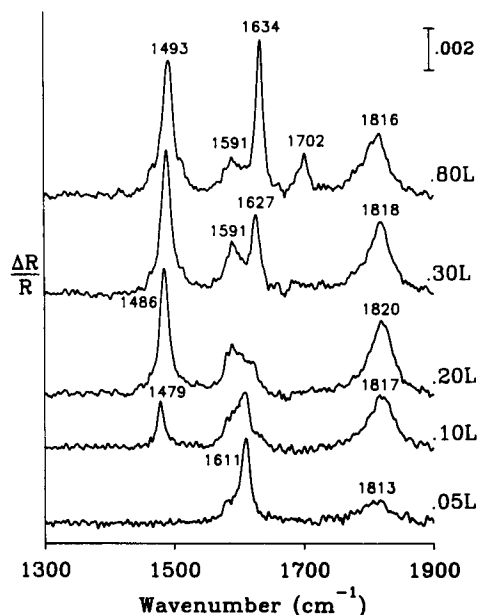


Fig. 24. IR spectra of NO adsorbed at 300 K on a stepped surface vicinal to Pt(111) [114].

minimises coupling effects), suggests that they would prove suitable as probes of catalyst morphology, particularly for in-situ studies, provided that the position of their absorption bands is sufficiently sensitive to changes in this morphology. As yet, there have been few attempts to exploit this possibility, but some promising results have been obtained.

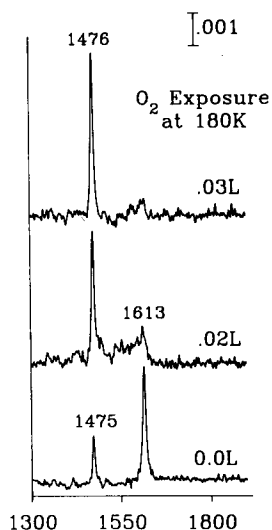


Fig. 25. Influence of pre-adsorbed oxygen on the spectrum of NO on a defective Pt(111) surface. NO exposure of 0.03 L at 180 K in each case [114].

Table 5

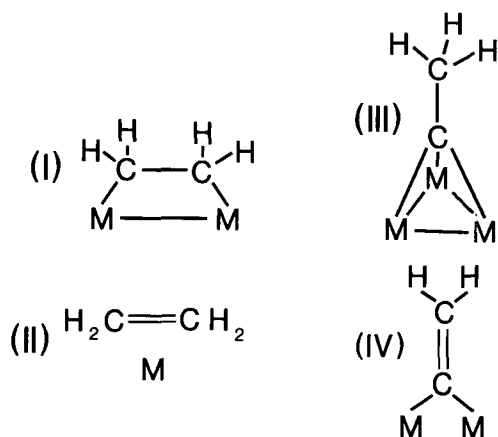
Assignment of N–O stretching bands on surfaces vicinal to Pt(111) as suggested by Agrawal and Trenary [114]

Geometry	$\tilde{\nu}$ (cm ⁻¹)
On-top linear on terraces	1700–1725
On-top linear at steps	1813–1837
On-top bent at steps	1605–1640
Two-fold bridge	1476–1509
Three-fold bridge	1365–1378

A comprehensive review by Sheppard discusses and classifies the types of infrared and energy loss spectra which have been reported for hydrocarbons adsorbed on single-crystal substrates [131]. Here we shall concentrate on ethylene, the hydrocarbon molecule which has been most thoroughly investigated. Non-dissociative adsorption (which generally occurs at low temperatures) can give rise to either a di- σ or a π species (fig. 26 I and II), or, in a few cases, to both species simultaneously. At higher temperatures a range of decomposition products have been obtained, of which ethylidyne and vinylidene (fig. 26 III and IV) are the best characterised. Other species, such as vinyl ($\text{CH}=\text{CH}_2$) and a variety of polymeric species, have also been observed or suggested, but none of these has yet found use in structural determinations.

The distinctive geometry involved in the bonding of ethylidyne to the surface suggests that this species should occur only on surfaces with local C_{3v} symmetry (i.e. with (111)-type terraces). This does appear to be the case. The occurrence of an ethylidyne moiety bonded to a square of metal atoms has been noted in cluster compounds [132], but this apparently has no analogue on (100) surfaces. The two C_2H_4 species and ethylidyne have also been clearly identified in spectra from supported catalysts; single-crystal data have been invoked to give detailed interpretations of spectra from supported palladium [133], platinum [134–136] and nickel [137]. A major finding from these correlated studies is the observation that in the presence of hydrogen ethylidyne hydrogenates more slowly than either C_2H_4 species and is hence presumably not an intermediate in the catalytic hydrogenation of ethylene.

Virtually all the single-crystal infrared studies carried out to date have employed low-index faces, so it is not yet clear whether the use of hydrocarbons as morphological probes extends

Fig. 26. Bonding of adsorbed ethylene (I) di- σ species, (II) π -bonded species, (III) ethylidyne, (IV) vinylidene.

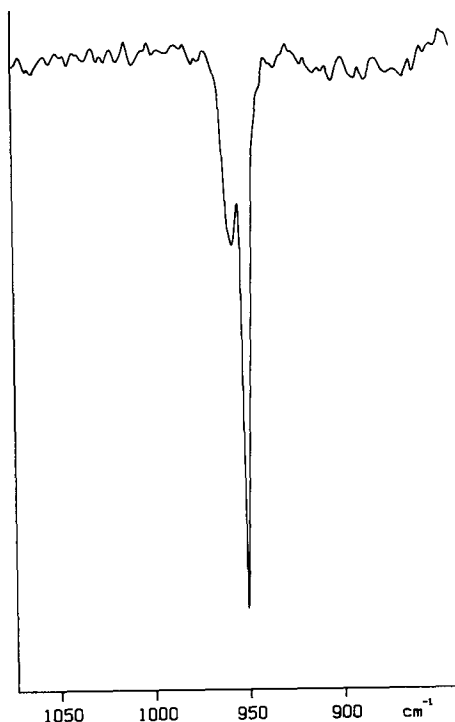


Fig. 27. ν_4 (out-of-plane wagging mode) band of C_2H_4 adsorbed on a surface vicinal to Ag(100). The two components are at 950 and 956 cm^{-1} . After Slater [138].

to the identification of defects. However, a very recent investigation of π -bonded ethylene on a silver crystal having a significant defect density shows a doublet band whose high-frequency component has been tentatively identified with molecules adsorbed at steps (fig. 27). Further studies on a wider range of substrates should help establish whether this is a general phenomenon. The situation is likely to prove more complicated than in the case of carbon monoxide, since reaction and partial dissociation may well occur at steps, leading to a chemical modification of the local environment which may itself produce frequency shifts. It is also possible that various substituted hydrocarbons, including the fluoro-, nitrile and isonitrile derivatives, may prove useful probes of substrate morphology [139], but as yet very little work has been carried out in this area.

5. Related systems in which coupling effects arise

There exist two situations, rather more complex than those considered so far, to which the same physical principles apply and in which relevant work has been carried out recently.

5.1. Three or more species co-existing on the surface

Our discussion of coupling effects has so far concentrated on the situation where only two species need to be considered. Circumstances may well arise, however, in which the adlayer

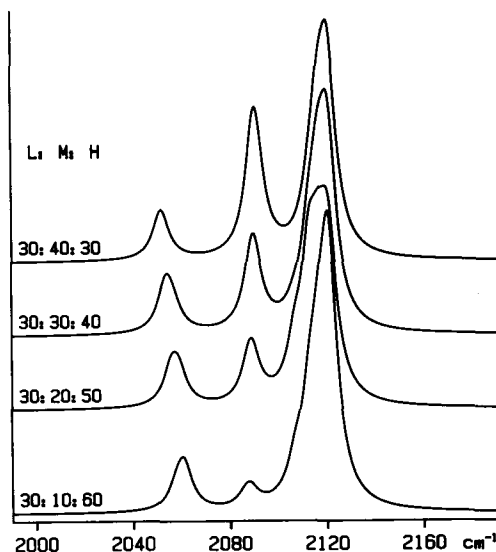


Fig. 28. Calculated spectra for islands containing the indicated percentages of low (L), medium (M) and high (H) frequency CO species.

contains three or more species whose vibrational frequencies are sufficiently close for significant coupling effects to arise between all of them. An example of this is the case of carbon monoxide on an oxidised copper surface, which was considered in section 3.1.4, and on which a mixed isotope investigation has been carried out [56]. Another example is the CO/Pd(110) system [100–103], where the extreme complexity of the infrared spectra demonstrates that even in the most controlled of situations – when the substrate is an atomically clean single-crystal surface – a multitude of species may arise simultaneously.

The case of three species interacting has been modelled numerically by Browne [140,141], who also considered the effects of finite island size in such systems. Fig. 28 shows spectra typical of many such simulations. The model system for this calculation consisted of an assemblage of small islands of adsorbate, each 50 Å in diameter and containing three different CO species with singleton wavenumbers at 25 cm⁻¹ intervals. The proportion of the lowest-frequency species has been held fixed, while the relative proportions of the two higher-frequency species are varied. Only the middle band in the spectrum shows apparently simple behaviour: as the proportion of the species from which it principally derives is increased, the band intensity increases at constant wavenumber. The lowest band, meanwhile, shows a small reduction in intensity and a marked downward shift in wavenumber. More complicated behaviour is shown by the highest-frequency band, which maintains an almost constant position while its intensity falls as the percentage of the relevant species is reduced from 60% to 30%. The detailed intensity changes are complex. The spectrum from a mixture containing 50% of the highest-frequency species actually has a lower *peak* intensity than either the 40% or 30% mixtures: the lower peak height, however, is compensated by a marked broadening of the band. This broadening is associated with edge effects. As was noted in the earlier discussion of the spectra in fig. 2, edge molecules experience a lower dipolar field than central molecules, which may give rise to a shoulder to low-frequency in spectra from a single species. When several species are present, these low-frequency modes may further couple with the vibrations of another, lower frequency, species, thereby greatly enhancing their

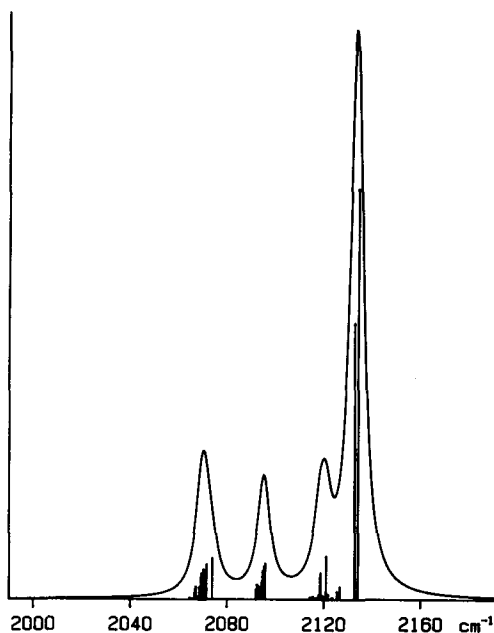


Fig. 29. Spurious band generated by coupling effects in an island containing three different CO species. Vertical bars indicate the position and relative absorption intensity of the individual vibrational modes.

intensity. Under extreme conditions, it is even possible for the low-frequency modes to detach themselves from the main band and give the apparent, but of course wholly spurious, impression that an additional species is present. This is illustrated in fig. 29, which shows a spectrum from a single three-species island, together with the individual vibrational modes that generate the spectrum.

The range of spectra produced by adlayers consisting of more than two species seems to be of such complexity that generalisations are difficult to draw. Simulations of $^{12}\text{CO}/^{13}\text{CO}$ spectra indicate that experimental mixed isotope studies are unlikely to prove of great help in interpreting spectra from these more complex systems: the additional bands introduced by the second isotope, together with the almost unavoidable overlap of bands from the different isotopes, serves only to complicate the matter further. The behaviour of such systems emphasises the need for a probe molecule exhibiting a smaller dynamic dipole than carbon monoxide.

5.2. Alloy surfaces

A bimetallic surface might be regarded as an extreme case of surface defects in which the chemical, as well as the structural, identity of the atoms varies. Alloy catalysts are of course of great significance, particularly in the petroleum industry, and most modern commercial catalysis by metals employs multi-component catalysts [142].

An early example of the application of dipolar coupling concepts to the study of bimetallic catalysts was the work of Ponec's group on platinum alloys [143,144]. In this investigation, it was found that, although alloying with either copper or lead caused a reduction in the observed frequency of carbon monoxide adsorbed on platinum, the explanation of this frequency reduction was different in the two cases. From analysis of experiments using

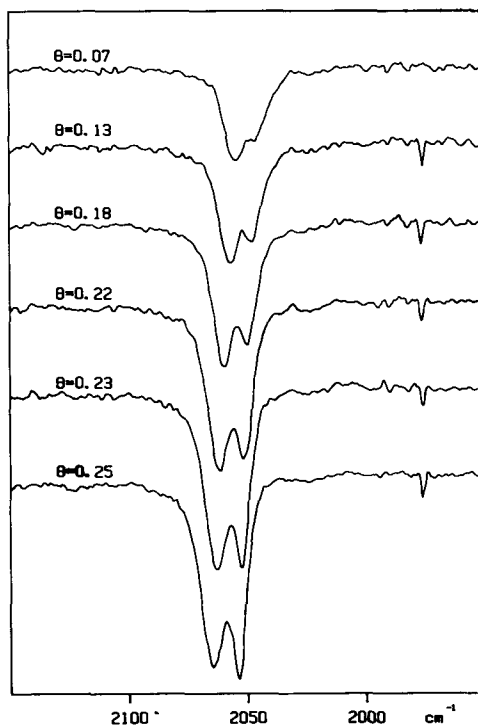


Fig. 30. RAIR spectra of CO adsorbed on a $\text{Pt}_{0.25}/\text{Rh}_{0.75}(111)$ surface at 300 K and the coverages indicated.

$^{12}\text{CO}/^{13}\text{CO}$ mixtures, it was concluded that in the case of the copper alloy the frequency reduction was entirely attributable to a decreased dipolar shift brought about by the dilution of surface platinum atoms by the copper. With lead, however, this essentially geometrical effect was insufficient to explain the observed frequency reduction, and an additional “electronic” effect had to be invoked. Although the influence of surface defects on the platinum (as discussed at length in section 3.2) will surely lead to some changes in the quantitative interpretation of the experimental results, these general conclusions are unlikely to be altered. More recently, dipolar coupling theory and mixed isotope experiments have been used to characterise ruthenium–copper catalysts [145].

Less work has been carried out on single crystal and other extended surfaces. However, a study of carbon monoxide adsorption on the $\text{Pt}_{0.25}/\text{Rh}_{0.75}(111)$ surface which is currently in progress by Chesters’ group gives some indication of potential applications in this area. Spectra obtained from this adsorption system at room temperature show a doublet structure, in which the higher-frequency component is attributed to molecules adsorbed on platinum atoms and the lower one to those on rhodium (fig. 30). Interactions between these species have been probed using $^{12}\text{CO}/^{13}\text{CO}$ mixtures together with computer modelling of the system.

6. Concluding remarks

The possibility of correlating results from single-crystal surfaces with those from less well-defined substrates is one of the great potential advantages of infrared spectroscopy.

During the past few years, several notable applications of this have appeared in the literature, and such applications will surely increase as instrumentation improves. (And, although this review has been restricted to metal surfaces, we note that with semiconductors too correlations can be drawn between single crystals and less perfect substrates, as the recent work of Jakob and Chabal demonstrates rather elegantly [147].) Two areas of technique development which are of particular importance here are the widespread adoption of Fourier transform spectrometers (in all the relevant spectroscopies – RAIRS, DRIFTS and transmission spectroscopy) and the development of UHV systems that also allow measurements to be made in situ at higher pressures.

In such comparisons, the effects of dipolar coupling interactions are of great importance but have not hitherto been properly appreciated. As we have noted elsewhere [148,149], coupling influences catalyst spectra in a variety of ways, but the most far-reaching of these is the transfer of intensity from low- to high-frequency bands in spectra from strongly absorbing species. While it has long been appreciated that carbon monoxide is such a species, it is only in the past few years that the importance of surface defects in influencing its spectrum has become evident. By producing wavenumber shifts of a few tens of cm^{-1} (in either direction, depending on the substrate), defects introduce the ideal conditions for distortion by coupling effects to occur.

While these distortions may occasionally prove advantageous in transferring intensity to a feature which might otherwise be undetectably weak, they are usually deleterious and, in particular, they make quantitative interpretation of the adsorbate spectrum very difficult. The use of isotopic mixtures permits some control over the coupling interactions, but interpretation of the resulting spectra is often extremely difficult even when only two types of binding site co-exist on the surface, and may well prove impossible for more complicated systems. In the long term the most promising method of resolving this difficulty appears to be by the use of a probe molecule with a smaller dynamic dipole (and hence weaker infrared absorption intensity). There is an element of irony in this situation, since the strong interaction of carbon monoxide with infrared radiation was a major factor in its original adoption as a universal probe molecule. However, the dramatic improvements in instrumentation which have occurred during the past few years mean that far more weakly adsorbing species can now be studied with comparative ease. (Particularly on high-area supported materials: sensitivity still poses something of a problem in RAIRS, although the situation is improving rapidly.)

Very little work in this area has been done to date, especially in single-crystal studies, where experiments on high-index surfaces should yield the most precisely controlled evaluation of the influence of defects. Some possible contenders for probe molecules were discussed in section 4. Nitric oxide may be suitable under conditions where it does not react, mainly because changes in its adsorption site generate such large wavenumber shifts that the disadvantage of its strong dynamic dipole is neutralised. There is also a glimmering of evidence that some hydrocarbon species may prove useful as morphological probes. However, more comprehensive and detailed studies will certainly be needed before carbon monoxide's unique importance as a probe molecule can become seriously threatened.

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