THE CHEMISORPTION OF CARBON MONOXIDE ON PALLADIUM SINGLE CRYSTAL SURFACES: IR SPECTROSCOPIC EVIDENCE FOR LOCALISED SITE ADSORPTION

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Combined IR reflection--absorption and LEED studies of the room temperature adsorption of carbon monoxide on the (100), (111) and (210) surfaces of palladium are reported. The C--O stretch frequency on the (100) surface varies from 1895 cm^{-1} at low coverages to 1949 cm^{-1} at $\theta = 0.5$. A further strong shift to higher frequency is observed during the compression stage for $\theta > 0.5$. On the (111) surface the C--O stretch frequency is found at 1823 cm^{-1} at very low coverages, rising to 1936 cm^{-1} at $\theta = 0.5$. In the compression stage above $\theta = 0.5$ a second peak is observed above 2000 cm^{-1}. On the much more open (210) surface, where surface atoms with the next nearest neighbour distance of 2.73 A do not exist, the behaviour of the IR band resembles surprisingly that of the (100) surface. The infrared reflection studies provide detailed information on the CO/Pd system which other surface techniques have not as yet revealed, namely, evidence for surface specificity and localised site adsorption at low CO coverage. The frequency shifts observed in the spectra are discussed in terms of the three important intermolecular interaction mechanisms, namely, dipole--dipole coupling, direct intermolecular repulsion and indirect effects via the metal atoms.

1. Introduction

Recent work on the pyrolysis of carbonyl cluster compounds [1--3] has demonstrated the similarity between the metal--ligand interaction in metal carbonyls and CO chemisorption on small metal clusters. Recent quantum chemical calculations [4--6] for CO chemisorbed on such clusters also verify a bonding picture based on metal carbonyl chemistry [7,8] and confirmed by UV photoelectron spectroscopy

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[9–12]. To what extent this picture can be extended to the chemisorption of CO on single crystal surfaces remains, however, a subject of some controversy. Unfortunately, most surface techniques, with the exception of LEED structure analysis [13], do not detect the surface specificity and sensitivity to localised site adsorption predicted by the models. Even photoelectron spectroscopy is of limited use in this respect: the UPS spectra for CO/Pd are practically identical for the three low-energy planes [14,15]. On the other hand, high resolution surface vibrational spectroscopy is sensitive to such parameters, as might be surmised from the early work of Eischens and Pliskin on supported metal catalysts [16]. Recent interest in the vibrations in adsorbed layers has been evoked by the application of energy loss spectroscopy to chemisorption on metals [17]. In the present investigation we have applied the infrared reflection–absorption method to the adsorption of CO on the (100), (111) and (210) surfaces of palladium. The intrinsically high resolution of the technique allows the movement and structure of the C–O stretch frequency as a function of coverage to be studied in detail [18]. However, it is not possible at present to observe the low frequency vibrations of chemisorbed CO and in this respect IR and electron loss clearly complement each other.

Previous IR reflection–absorption spectra from the roomtemperature chemisorption of CO on polycrystalline palladium [19] showed a single band at 1920 cm^{-1}, which shifted to higher frequencies with increasing coverage. On rough, unannealed films deposited at low temperature two bands were observed, one at 2112 cm^{-1} and the other at 1974 cm^{-1}. The high frequency band disappeared on warming, not to appear again on re-cooling, indicating that the surface sites giving rise to absorption above 2000 cm^{-1} were associated with high index planes, as well as with edge and kink sites. The continuous shift of the IR band during the transition into the compression region on the smooth surface led us to believe that localised site sensitivity was not particularly apparent in IR measurements of this nature. The interpretation of the spectra in terms of "linear" and "bridge-bonding" [16] was thus rejected. The present results on palladium single crystal surfaces show that this conclusion is not altogether correct and that the co-ordination number of the surface site does indeed play a role in determining band position. However, as has been argued earlier [20], a two-fold bridge-site would not necessarily imply the presence of two strong σ-bonds to each metal atom as in the ketonic analogue of organic chemistry.

2. Experimental

Details of the combined IR/LEED system and of the polarisation modulation technique used for recording IR reflection–absorption spectra have been given elsewhere [21]. In essence, polarization modulation consists in dividing the IR beam from the source into two components polarized perpendicular and parallel to the plane of incidence. The two beams are then recombined, such that radiation from

each component falls in alternate half-cycles on the surface. Due to the IR surface selection rule, absorption of radiation through a vibrational excitation in the adsorbate complex can only occur for the parallel component, thus giving rise to a "pseudo"-double beam technique. The three single crystal faces, (100), (111) and (210), used in the present study, were cut from a Marz grade palladium single crystal obtained from Materials Research Corporation. Before spark erosion cutting, the faces were oriented using a Laue back-scattering method. The resulting circular or elliptical discs (thickness 2 mm, diameter 8–10 mm) were then re-oriented on a polishing jig to within $\frac{1}{2}°$ of the desired orientation and subsequently polished with successively finer diamond pastes down to 0.25 μm. No chemical or electrochemical polishing techniques were employed. After repeated cycles of argon ion bombardment (500 eV, 1–5 μA at 600°C) and short anneals (800°C), the main impurities (S, P, and C, as detected by Auger spectroscopy) on the (1000 and (111) surfaces were removed. The procedure for the (210) surface was somewhat different: in order to minimise ion bombardment damage the surface was subjected to heating cycles at 400°C for one hour followed by bombardments (200 eV, 0.5 μA) for only a few minutes. The final annealing was carried out a 700°C. Because of the overlap of the carbon KLL peak with the palladium MNN peaks it was difficult to determine with Auger spectroscopy alone whether carbon had been completely eliminated. The reproducibility of the IR spectra and the LEED structures was considered an additional test for surface cleanliness. The presence of small amounts of carbon and sulphur generally lead to a broadening of the IR band with its maximum shifted to higher frequency. Co-adsorption effects of this nature will form the subject of a later investigation.

3. Results and discussion

3.1. General remarks

In sections 3.2–3.4 below we describe and discuss the IR observations from the three palladium surfaces. The corresponding LEED observations are referred to and depicted diagrammatically. Since the latter are fairly well documented in the literature [22–25], however, they will not be discussed in detail here. The infrared results are interpreted in terms of a simple model which is then discussed in more detail in section 3.5. The features of this model are:
(i) For a given metal at low coverage the position of the C–O stretch frequency depends on the number of metal atoms co-ordinated to the CO molecule and hence on the geometry of the localised adsorption site.
(ii) At high coverages intermolecular interactions (dipole–dipole, intermolecular repulsion and indirect effects via the metal electrons) determine almost completely the position of the C–O stretch.
(iii) At intermediate coverages it is not possible to separate the effects under (i) and (ii) because of their mutual interaction.

3.2. CO/palladium(100)

Fig. 1 shows the growth of the IR band attributed to the C–O stretch frequency as a function of increasing coverage. The band was observed initially at 1895 cm^{-1} (all wavenumber values are ± 2 cm^{-1} in this paper), and shifted continuously to higher frequencies. The half-coverage position was determined from the LEED pattern, which is indicative of the so-called c(4 × 2)R45° surface structure [22,23]. The LEED patterns for the ordering stage at $\theta = 0.4-0.5$, for the c(4 × 2)R45° structure and for the compression stage at $\theta > 0.5$ are depicted schematically in fig. 2. In matrix notation the c(4 × 2)R45° structure is described by the two domains
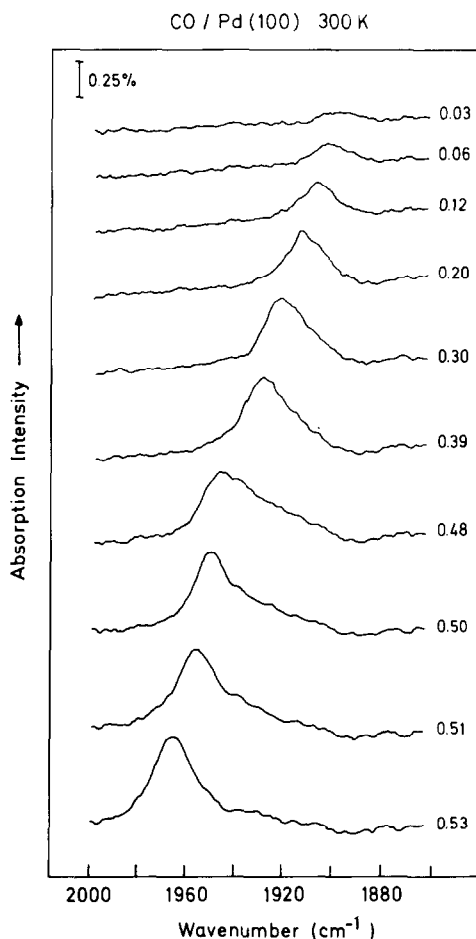
CO / Pd (100)   300 K

Fig. 1. IR absorption band for the C–O stretch frequency in the system CO/Pd(100) at 300 K as a function of increasing coverage.
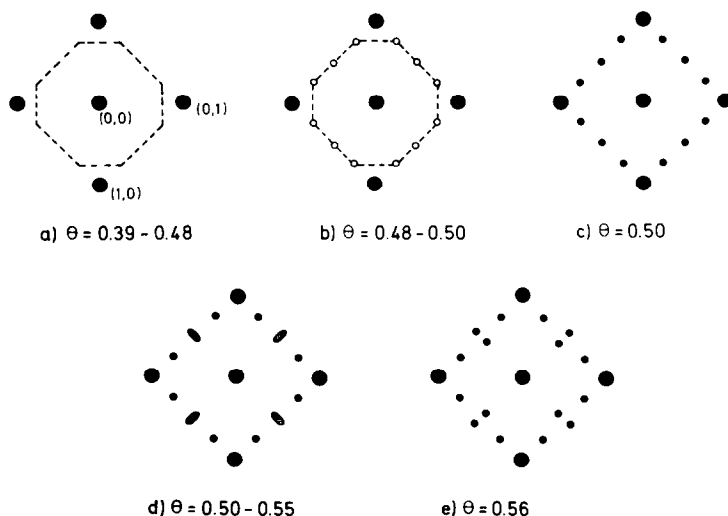
a) $\Theta = 0.39 - 0.48$ b) $\Theta = 0.48 - 0.50$ c) $\Theta = 0.50$

d) $\Theta = 0.50 - 0.55$ e) $\Theta = 0.56$

Fig. 2. LEED sequence as function of coverage for CO/Pd(100).

$\left(\begin{smallmatrix}1 & 1\\ -0.5 & 1.5\end{smallmatrix}\right)$ and $\left(\begin{smallmatrix}0.5 & 1.5\\ -1 & 1\end{smallmatrix}\right)$ of a coincident site lattice at $\theta = 0.5$ and corresponds to the LEED pattern of fig. 2c. (In the paper of Tracy and Palmberg [23] additional spots at the $(\pm\frac{1}{4}, \pm\frac{1}{4})$ positions are visible, which could indicate the two domains with transformation matrices $\left(\begin{smallmatrix}1 & 1\\ -2 & 2\end{smallmatrix}\right)$ and $\left(\begin{smallmatrix}2 & 2\\ -1 & 1\end{smallmatrix}\right)$. The latter would be described as $(\sqrt{2} \times 2\sqrt{2})R45°$ in conventional notation and would correspond to a coverage of only 0.25. However, the $(\pm\frac{1}{4}, \pm\frac{1}{4})$ features can also be considered as multiple diffraction overlayer spots of the $c(4 \times 2)R45°$ structure [26].) The important feature of this pattern is to be found in its unusual symmetry: it is possible without intensity analysis to predict the nature of the adsorption sites with some certainty [22], a situation rarely encountered in LEED. Assuming all CO molecules are adsorbed on equivalent sites (a very reasonable assumption in the light of the IR results reported here), then the observation of the two domains means that only the so-called bridge sites come into question. This is depicted in fig. 3a for one of the two domains. Fig. 3b shows the direction of compression at $\theta > 0.5$ for the same domain. The sequence of spectra in fig. 1 indicates a continuous shift of the IR band to ~1930 cm^{-1} at $\theta = 0.40$. (Coverage values under $\theta = 0.50$ were determined by assuming a linear relationship between integrated absorption intensity and number of molecules absorbed, and normalising to half-coverage using the LEED pattern. For this set of spectra the values are accurate to ±0.02. Above $\theta = 0.5$ coverage can be determined directly from the LEED pattern [23].) Between $\theta = 0.4$ and 0.5, which is characterised by the appearance of an octagonal ring in LEED (figs. 2a, b) and hence corresponds to the ordering of the adlayer, the intensity at 1930 cm^{-1} was reduced and another component of the band emerged at 1949 cm^{-1}. This peak, corresponding to the $c(4 \times 2)R45°$ structure, reached a maximum at $\theta = 0.50$

a) $\Theta = 0.5$ b) $\Theta > 0.5$

$$— \begin{pmatrix} 1 & 1 \\ -2 & 2 \end{pmatrix}$$

$$--- \begin{pmatrix} 1 & 1 \\ -0.5 & 1.5 \end{pmatrix}$$
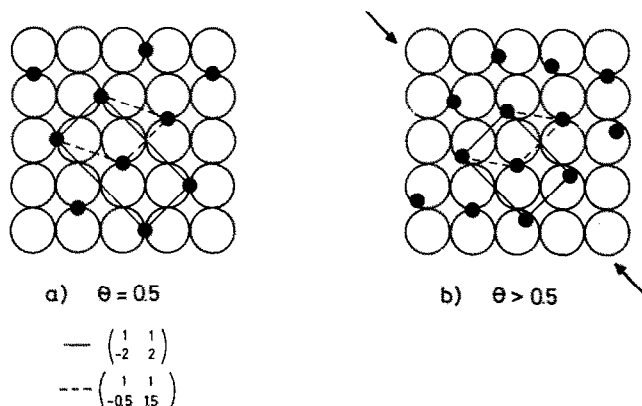
Fig. 3. (a) One of the two possible domains of the c(4 X 2)R45° structure showing the two unit cell descriptions. (b) The direction of compression of the c(4 X 2)R45° structure for the same domain. The filled circles represent CO molecules, but are not intended to convey their size relative to the metal atoms.

with fwhm = 14 cm^{-1}. The asymmetric form suggests, however, that the ordering was not complete at room temperature. The fact that the shift of the band is continuous, except for the small jump during the ordering, leads us to believe that bridge sites are also occupied in the range of disordered adsorption from zero coverage up to $\theta = 0.4$. The shift is caused by intermolecular interactions, mainly by indirect effects via the metal electrons. The compression of the ordered structure above $\theta = 0.5$ was accompanied by a broadening of the peak and a simultaneous shift to higher wavenumbers. At 300 K and an equilibrium CO pressure of 10^{-6} Torr, which corresponds to $\theta = 0.61$, the IR band was found at 1983 cm^{-1}. The shift in wavenumber of the band maximum as a function of θ is shown graphically in fig. 4 for the whole coverage range investigated. Of particular interest is the increased slope after $\theta = 0.5$, which is concomitant with the increased rate of fall in adsorption energy during compression (see below and ref. [23].) Both effects are due to the strong intermolecular repulsion discussed in section 3.5, which in this coverage region determines the position of the C—O stretch frequency.

At higher temperatures and CO equilibrium pressures between 10^{-6} and 10^{-8} Torr it was possible to vary the surface coverage between 0.40 and 0.55. Under these conditions we were able to study the ordering of the c(4 X 2)45° structure and the subsequent compression with more precise control of coverage. Fig. 5 depicts the transition from c(4 X 2)R45° to the compression in the coverage range 0.50—0.53. The doublet structure in the peak indicates the co-existence of domains of c(4 X 2)R45° and the compressed structure on the surface. This can also be seen in LEED: fig. 2d shows the smearing of the $(\pm\frac{1}{2}, \pm\frac{1}{2})$ features. If the compression stage was attained by directly exposing the clean surface to a CO pressure of $\sim 10^{-7}$ Torr with the crystal at 300 K, a second band at 2096 cm^{-1} was observed (fig. 6a).
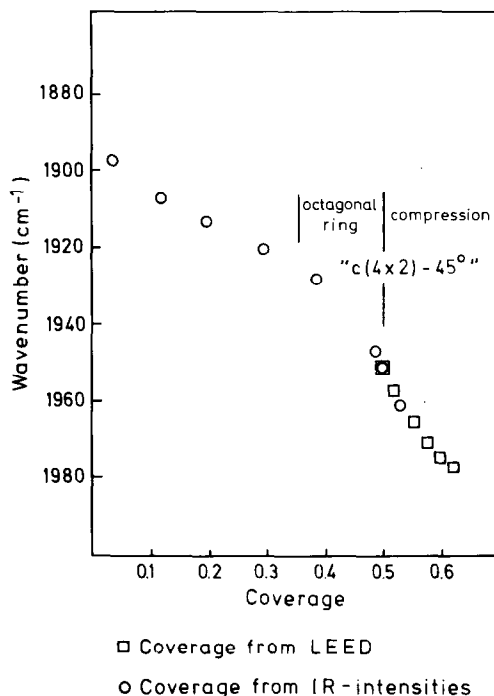
Fig. 4. The shift in IR frequency as a function of coverage for CO/Pd(100).

On heating to 400 K and then re-cooling in 1×10^{-7} Torr this peak then disappeared (fig. 6b) and the peak below 2000 cm^{-1} shifted slightly to higher wavenumbers. Pumping the CO away to $\sim 10^{-9}$ Torr also removed the second peak (fig. 6c). A quantitative investigation was not carried out because of the poor reproducibility of the intensity ratio between the two peaks (maximum 1 : 3). This could have been due to the difficulty in controlling accurately the rate at which the compression stage was reached. It seems likely that due to the "fast compression" and the reduced mobility at higher coverages some CO molecules are adsorbed initially in energetically unfavorable adsorption sites directly over Pd atoms ("linear bonding"). Sites of single co-ordination are considered to be responsible for the appearance of a high frequency band as in the case of Pt [27,28]. It is interesting to note that no change in the LEED pattern could be observed for the transition from figs. 6a to 6b.

   Pritchard [29] first reported the use of a coverage-dependent parameter — namely, the work function change — as a monitor for coverage in the determination of isosteric adsorption energies. The method was also used by Tracy and Palmberg [30] for the system CO/Pd(100). Here we report similar measurements using the IR band as coverage monitor, whereby it was also assumed that a linear relationship
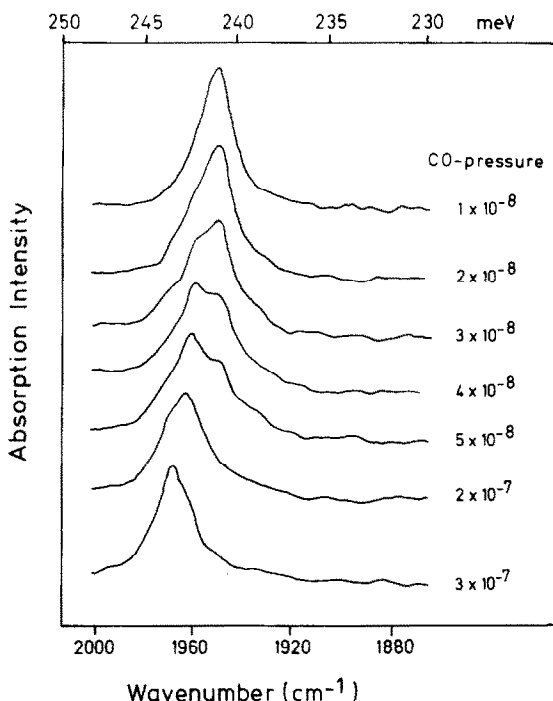
Fig. 5. The IR absorption band in the coverage range 0.50–0.53 at 330 K for CO/Pd(100).

between the measured parameter (in this case integrated absorption intensity) and number of adsorbed molecules existed. The measurements were performed by first plotting isotherms and then constructing isosteres. Direct plotting of isosteres was
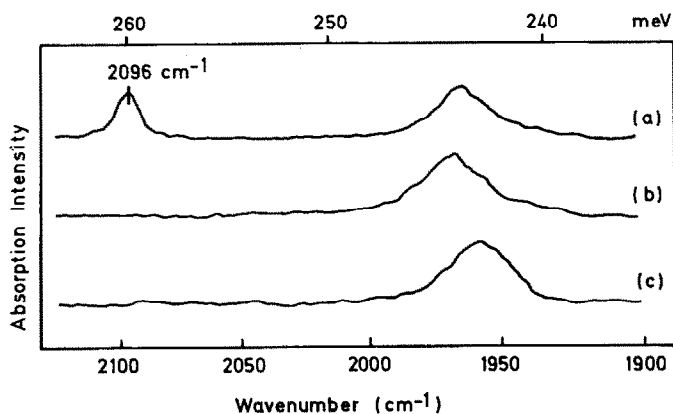

Fig. 6. "Fast compression" on Pd(100) at 300 K. (a) 1×10^{-7} Torr; (b) 1×10^{-7} Torr, 300 K after warming to 400 K in 1×10^{-7} Torr; (c) pumping down to $<1 \times 10^{-9}$ Torr.

not possible, because of the temperature-dependent reflection coefficients of the metal surface. The results are shown in fig. 7, where the curve obtained by Tracy and Plamberg is also indicated. We note the steady fall until $\theta = 0.4$ and the sharp decrease of ~30 kJ mol^{-1} occurring just before $\theta = 0.5$. The present results thus confirm the dramatic reduction in adsorption energy associated with the ordering process.

3.3. CO/palladium(111)

The system CO/Pd(111) is particularly interesting in that the (111) surfaces of several metals show identical LEED behaviour during CO adsorption [24,31–34]. Unlike Pd(100), the (111) surface exhibits a constant initial adsorption energy which corresponds to the initially stationary IR band shown in fig. 8. Coverages given for this set of spectra were obtained as for Pd(100) and normalised to $\theta = 0.33$ with LEED. Because of the rather broad IR band at this coverage and the extreme shifts observed in the sequence, coverage estimation is only accurate to ±0.03. The LEED investigations at 300 K showed the behaviour described by Ertl and Koch [24]. Before a coverage of 0.33, weak diffuse spots indicative of a ($\sqrt{3} \times \sqrt{3}$)R30° structure were observed. Between $\theta = 0.32$ and 0.35 these spots became sharp. After further CO exposure the additional spots again become diffuse and split, as shown in fig. 9. At low temperatures a continual splitting of the spots can be observed until a pattern is reached which corresponds to a c(4 $\times$ 2) structure on the surface at $\theta = 0.5$ [31]. Although it was possible at 300 K to reach $\theta = 0.5$ by reference to the appropriate isotherm [24,31], we were not able to observe a clear
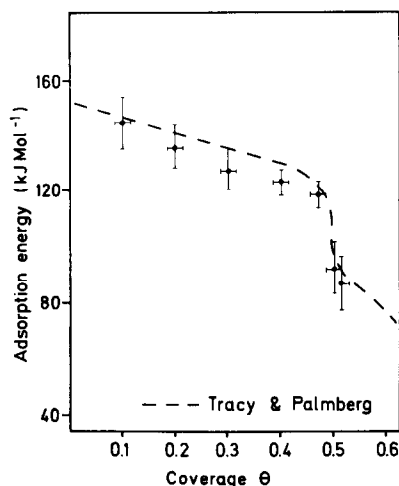

Fig. 7. Adsorption energy as a function of coverage for CO/Pd(100). The dashed curve corresponds to the result of Tracy and Palmberg [23,30].
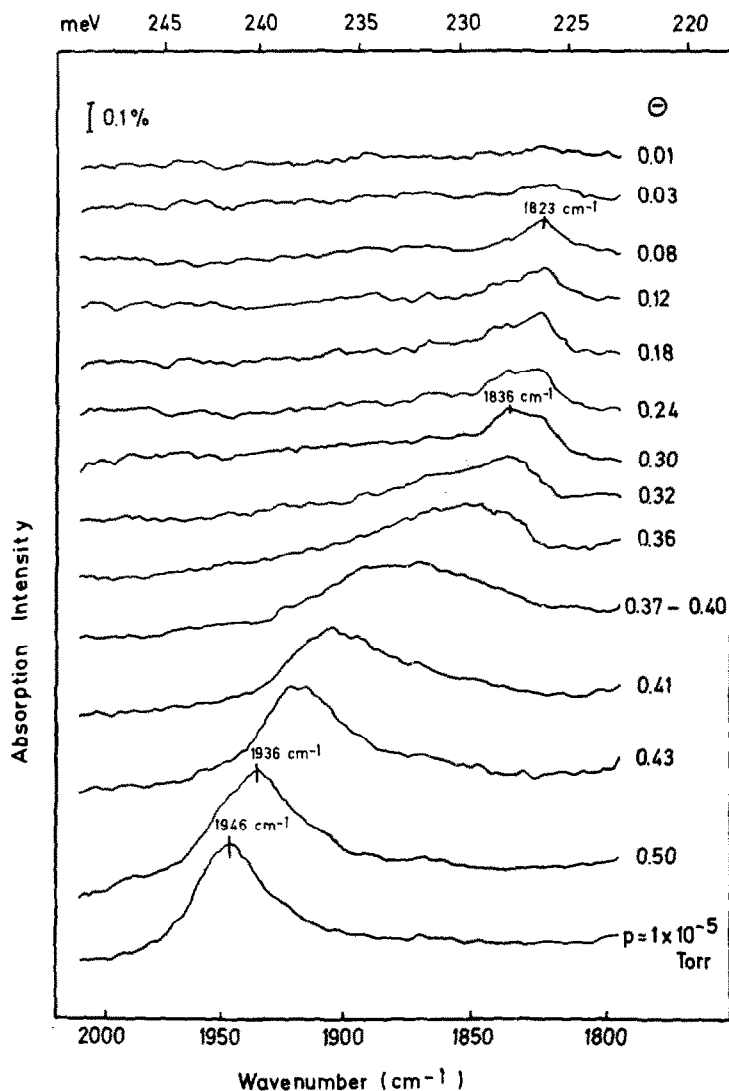
Fig. 8. IR absorption band for the C–O stretch frequency in the system CO/Pd(111) at 300 K as a function of increasing coverage.

c(4 X 2) pattern. It is assumed that the degree of ordering was too poor, or more likely that the c(4 X 2) domains were too small, leading to diffraction broadening. The extra features due to the c(4 X 2) structure are also depicted in fig. 9d. The corresponding surface model of fig. 10 shows both structures, with surface sites occupied as indicated by the IR data discussed below.
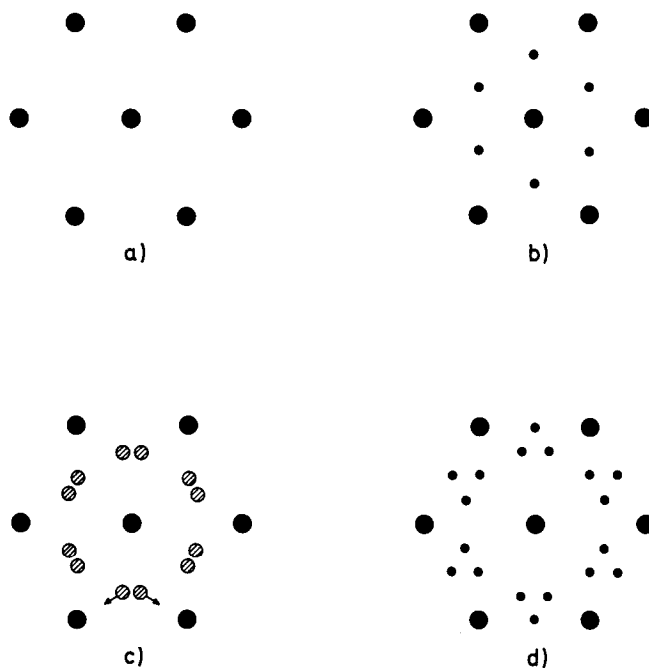
Fig. 9. (a–c) LEED sequence as function of coverage for CO/Pd(111). (d) The c(4 × 2) structure—possibly occurring multiple diffraction features are not shown.

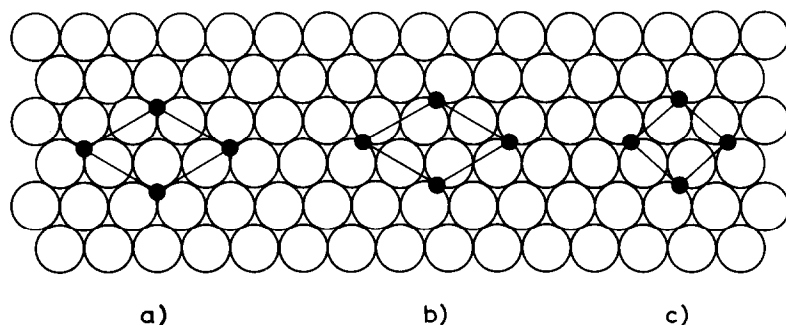Fig. 10. (a) ($\sqrt{3}$ × $\sqrt{3}$)R30° structure for CO/Pd(111) with sites of three-fold co-ordination. (b) One of the three possible domains of the ($\sqrt{3}$ × $\sqrt{3}$)R30° structure with sites of two-fold co-ordination ("bridges-sites"); the other two domains are formed by shifting the unit cell into the other two kinds of bridge site available (in a sense these domains are only anti-phase domains as opposed to the rotational domains of the c(4 × 2) structure). (c) One of the three possible domains of the c(4 × 2) structure with sites of two-fold co-ordination.

The C–O stretch frequency was found at 1823 cm^{-1}, 72 cm^{-1} lower than that on Pd(100), and remained stationary until $\theta = 0.18$. The appearance of a second peak at 1836 cm^{-1}, which gradually shifted the maximum of the band envelop over to higher frequencies, was accompanied by weak additional features indicative of the $\sqrt{3}$ structure. On further increase of coverage an extremely broad band was formed until about $\theta = 0.42$–0.43 when a narrower peak emerged. At $\theta = 0.50$ the band was at 1936 cm^{-1} with fwhm $\sim$30 cm^{-1}, the total shift being 113 cm^{-1}. This behaviour is seen more clearly in fig. 11, where the frequency shift as a function of coverage is depicted graphically. At coverages above 0.50 a further shift of the band to higher frequencies occurred. Simultaneously a second band grew at 2092 cm^{-1} as shown in fig. 12. Unlike the situation on Pd(100) the appearance of this high frequency band did not depend on the speed with which the compression stage was reached, nor was it irreversibly removed by warming at constant CO pressure. The bands were found, however, at almost identical frequencies; 2096 cm^{-1} was recorded on Pd(100).

From previous work on this system [24,25,31] we know that the adsorption energy remains constant at $\sim$140 kJ mol^{-1} until $\theta = 0.33$. At this point it decreases sharply by about 9 kJ mol^{-1} and then falls further. In a similar way the sticking
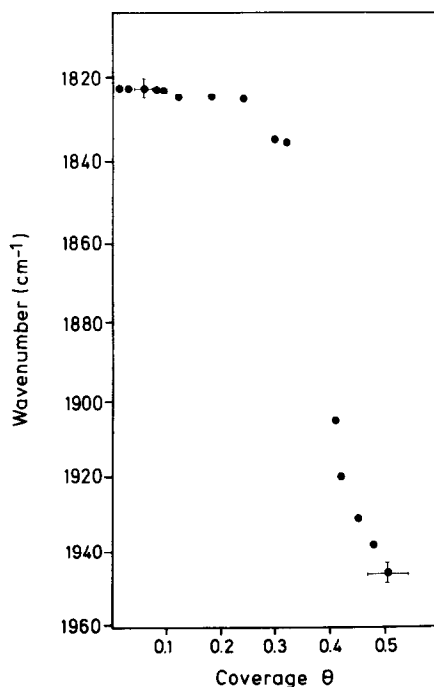
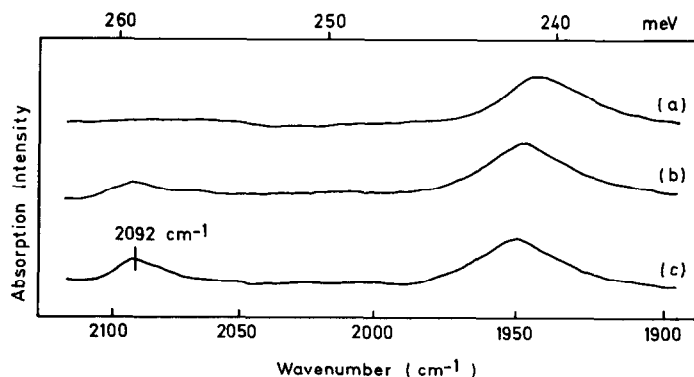Fig. 11. The shift in IR frequency as a function of coverage for CO/Pd(111).

Fig. 12. IR absorption bands at 300 K and $\theta > 0.5$ for CO/Pd(111). Equilibrium pressures (a) 1.5×10^{-8}, (b) 1×10^{-6} and (c) 1×10^{-5} Torr CO.

coefficient remains at unity until one-third coverage is reached. In conjunction with the new IR data presented here we can propose the following model for adsorption on the surface. At low coverages a disordered adsorption takes place. Because of the appearance of the IR band at 1823 cm^{-1} adsorption sites of three-fold co-ordination appear to be favoured. This assignment is based on an overview of the spectra from all three surfaces investigated and is justified in more detail in section 3.5. The growth of the IR band at constant frequency reinforces previous arguments based on adsorption energy and sticking coefficient that favour island formation and attractive forces between the admolecules. The shift in the main component of the band to 1836 cm^{-1} just under one-third coverage is connected with the ordering process on the surface. A similar effect was seen above just before the establishment of the c(4 $\times$ 2)R45° structure on the (100) surface. However, the broadness of the band in the range 0.32–0.37, where the $\sqrt{3}$ structure is sharp, suggests that a strict localisation on sites of three-fold co-ordination does not take place. Because of the high mobility of CO on the homogeneous (111) surface [35], it would appear that some molecules have already moved to sites of two-fold co-ordination ("bridge-sites") whilst remaining in a $\sqrt{3}$ configuration. A further small increase in coverage causes an enormous shift in the IR band (seen most dramatically in fig. 11), which suggests that the compression to c(4 $\times$ 2) is accompanied by a general movement of admolecules into bridge sites. However, a second mechanism begins to play a role at these coverages. Because of the higher density of metal atoms on the (111) compared to the (100) surface, the strong intermolecular repulsion effects referred to above are expected to become important at a lower relative coverage. Thus it is possible that after $\theta = 0.40$ the position of the IR band, and indeed the relationship of adlayer to substrate, are determined mainly by this effect and less by localised site adsorption. The high frequency band above half-coverage is clearly due to a "linear"-bonded species. It is, however, uncertain whether this band really comes

from the compressed c(4 × 2) structure. Until these experiments are repeated at low temperatures we would tend to the view that the 2092 cm^{-1} band is due to CO linearly adsorbed on Pd atoms left exposed by the poor ordering of the c(4 × 2) structure.

3.4. CO/palladium(210)

As the structure model of fig. 13 shows (the outermost layer of metal atoms is represented by full circles), the (210) surface has a very open structure. In contrast to the situation on the (111) and (100) surfaces, the minimum separation of 2.73 Å does not occur in the first layer. In the [001] direction the interatomic distance is 3.88 Å, and in the [1$\bar{2}$1] direction 4.75 Å. For this reason we find in the outermost layer none of the two-fold co-ordination sites which appear to play such an important role in the chemistry of the (100) and (111) surfaces. However, we might expect that atoms in the second and third layers may also be involved in direct bonding due to the open nature of the surface.

The LEED pattern from the clean surface is depicted schematically in fig. 14a: no evidence for facetting or reconstruction of the surface was found. At low CO exposures (<0.5 L) the symmetry of the diffraction pattern did not change, although relative intensity changes were noticed, an observation which Conrad et al. [25] have attributed to the initial formation of a (1 × 1) overlayer. At higher CO exposures (>0.5 L) weak streaks were observed, which indicated rows of molecules parallel to the [001] direction. The separation between the rows would be random in the [1$\bar{2}$0] direction, whereas that between the molecules in the rows would match the spacing of the substrate atoms. Further addition of CO to equilibrium partial pressures above 1 × 10^{-8} Torr caused a thickening of the streaks at
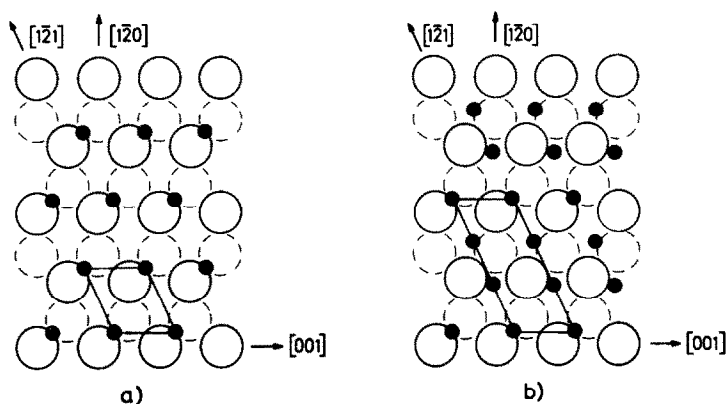

Fig. 13. (a) Surface model of the assumed (1 × 1) structure for CO/Pd(210). (b) Surface model of the (1 × 2) structure.
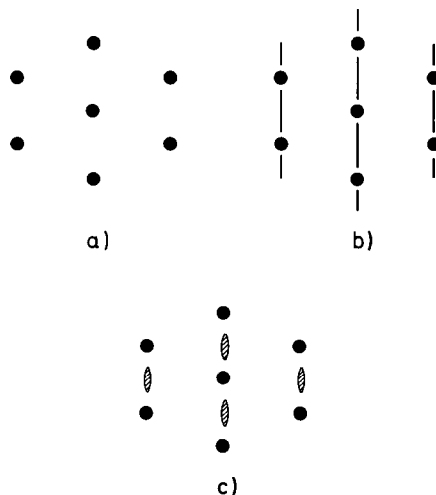
Fig. 14. (a–c) LEED sequence as a function of coverage for CO/Pd (210).

the half-order positions, indicating the presence of a co-incident site lattice [25]. In the corresponding IR sequence (fig. 15) the C–O stretch frequency was observed initially at 1878 cm^{-1}. Because of the poor ordering on the surface, coverage assingments based on a combination of LEED and IR integrated absorption intensities were not possible. For this reason exposure values in Langmuir are given for the sequence of spectra in fig. 15. As in the case of the (100) and (111) surfaces, the position of the band maximum shifted to higher frequencies as a function of coverage. Thus at an equilibrium CO pressure of 1×10^{-6} Torr the band was found at 1980 cm^{-1}, compared to 1983 cm^{-1} at the same pressure on the (100) surface. No peak was observed above 2000 cm^{-1}, not even at high coverages. The course of the shift as a function of relative coverage, based on IR integrated absorption intensity alone, is depicted in fig. 16. This curve illustrates the frequency jump that occurred between 0.30 and 0.40 L exposure immediately prior to the loss of periodicity in the [1$\bar{2}$0] direction.

   The interesting feature of this set of spectra is the strong resemblance to the (100) surface: the frequency at low coverages is only 20 cm^{-1} lower, the frequency at 1×10^{-6} Torr CO is virtually identical, and the course of the shift is not too dissimilar for the two faces. For the (100) surface we have already discussed the important role played by bridge sites, and the (210) sequence is at first sight somewhat surprising. Particularly on the (210) surface we might have expected some indication, perhaps already at low coverages, for linearly-bonded CO. In the absence of further evidence we therefore conclude tentatively that bridge sites involving surface atoms in both first and second layers are occupied. This is indicated schematically in the surface model of fig. 13a. It is thus possible that the CO molecular axis is no longer parallel to the surface normal. A component of the dipole moment
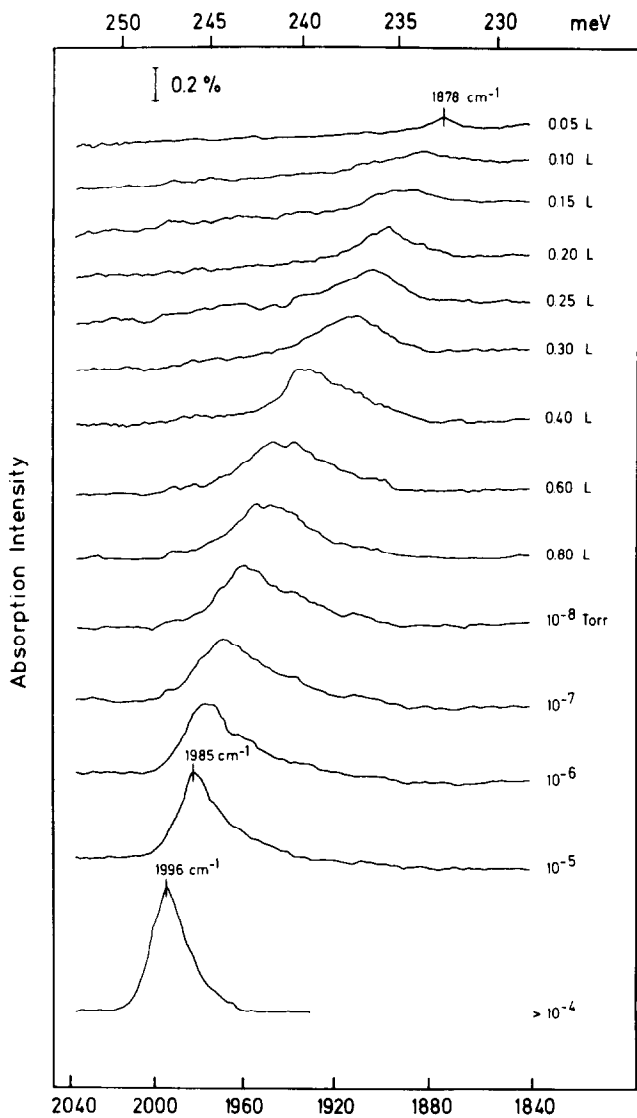
Fig. 15. IR absorption band for the C–O stretch frequency in the system CO/Pd(210) at 300 K as a function of increasing coverage.

would, however, still exist perpendicular to the surface in order to satisfy the IR surface selection rule [36]. If the (210) surface is considered as a stepped (100) surface (this is perhaps more clearly seen on the higher index planes of the progression (210), (310), (410), etc.), this proposal gains in plausibility. After the formation of
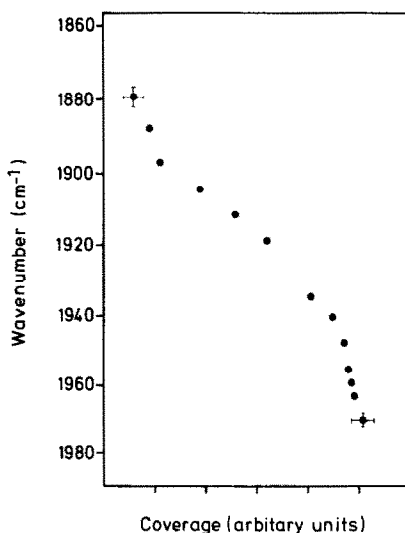
Fig. 16. The shift in IR frequency as a function of relative coverage for CO/Pd(210).

streaks in the diffraction pattern, which followed directly the frequency jump of the IR band, the adsorbed molecules begin to feel the effect of intermolecular repulsion. This is indicated by the increased rate of shift of the band to higher frequencies after exposures >0.5 L. A sharp decrease in adsorption energy also begins at approximately the same coverage [25]. At this point the influence of localised site adsorption becomes less important in a way similar to that discussed for the (100) and (111) surfaces above. The streak formation is indicative of a compression of the rows in the [1$\bar{2}$0] direction, resulting at higher coverages in a poorly defined (1 X 2) co-incident site lattice. A possible surface model of this structure is shown in fig. 13b and is essentially that proposed by Conrad et al. [25]. The maximum surface concentration implied by the model is 8.5×10^{14} molecules/cm^{-2} as opposed to a concentration of 5.3×10^{14} molecules/cm^{-2} in fig. 13a. Further evidence supporting a compression structure of this nature is found in a comparison with the Pd(100) surface. For an equivalent absolute surface concentration an almost identical C—O stretch frequency was observed in the two cases. The strict maintenance of substrate periodicity in the [001] direction suggests a compression behaviour similar to that on the (100) surface, where the intermolecular distance in one [100] direction remains constant but decreases continuously in the other. The question of the orientation of the CO molecules relative to the surface normal at these high coverages must remain open at this stage.

3.5. Localised site adsorption and intermolecular interactions

Eischens and Pliskin first drew attention to the possible relationship between the position of the C—O stretch frequency and the nature of the CO adsorption site

[16,37,38]. For the supported metals Ni, Pd and Pt bands above 2000 cm^{-1} were assigned to "linear" or "terminal" species and bands below 2000 cm^{-1} to "bridged" species by analogy with the IR spectra of metal carbonyl compounds. Fig. 17 shows the Eischens and Pliskin spectra for CO adsorbed on silica-supported palladium as a function of increasing coverage. The apparent multiplicity of bands was attributed to the heterogeneity of the surface; the bands could be removed by pumping in the reverse order of appareance. Later Blyholder [39,40] proposed a simple model for the chemisorption bond based on the σ and $d\pi-p\pi^*$ scheme accepted for the metal carbonyls [7,8]. The extent of $d\pi-p\pi^*$ bonding was considered to be the main factor controlling the position of the C–O stretch frequency. These ideas have been generally confirmed by recent quantum chemical calculations, in particular by Batra and Bagus for CO adsorbed on a small nickel cluster using the SCF-X$_\alpha$-SW method [6] as well as by other authors [4,5]. It should be noted, however, that the early qualitative models probably underestimated the importance in the overall bonding scheme of the σ-bond formed by the interaction of CO 5σ with the appropriate combination of metal s, p and d orbitals. Blyholder's more recent CNDO calculations for CO adsorbed as Ni clusters [5,41] provide, moreover, some theoretical substance to the Eischens and Pliskin concept of localised site adsorption: an increase in the number of substrate atoms co-ordinated to the CO molecule results in a reduction in the C–O stretch frequency. At higher co-ordination numbers the chemisorption bond is considered to contain a higher π-character due to increased back-donation of metal electrons, leading to the reduced C–O stretch frequency. It is important at this stage to recognise that the CO molecule can be adsorbed at sites of two-, three- and possibly four-fold symmetry without necessarily forming a strong σ-bond to each metal atom. Because large numbers of atoms probably participate in the chemisorption bond [35], even the concept of two-or
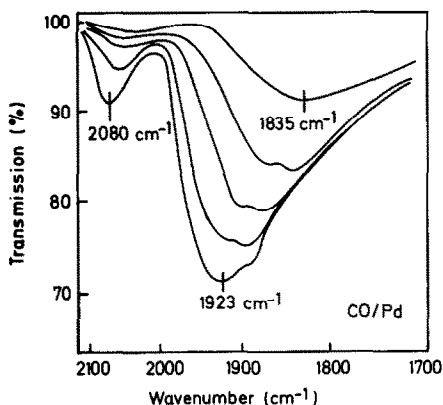

Fig. 17. The C–O stretch region for CO adsorption on silica-supported Pd as a function of increasing coverage (after Eischens and Pliskin [16]).

three-fold co-ordination must be treated with care. Thus the localised bonding concept presented in this paper is not identical with that of Eischens and Pliskin, or indeed with that of later authors [42], where two-fold sites are compared directly with bridging CO's in the metal carbonyls in a way suggestive of the ketonic analogue in organic chemistry. It would nonetheless still be possible to perform a normal co-ordinate analysis for a bridging CO, for example, using the C_{2v} point group and to derive force constants for each of the normal modes. The prerequisite for such a treatment is, of course, that all vibrations are active in the context of the IR surface selection rule, which is infact not the case.

For localised site adsorption of palladium surfaces it is now possible to assign frequency ranges to sites of a particular co-ordination. Here we consider only the "singleton" [43]; i.e. the absorption band due to isolated CO molecules at low coverages as opposed to the domain absorption band at high coverages.

(1) Single co-ordination (or linear bonding) is expected to produce a C—O stretch frequency in the range 2050—2120 cm^{-1}. On single crystal surfaces we have as yet observed linearly bonded species near 2080 cm^{-1} only at high coverages but, as stated above, these appear to result from poor ordering of the adlayer and are thus probably decoupled from the high coverage domains. On high area thin films the high frequecy band at 2112 cm^{-1} was found already at low coverages [19].

(2) Two-fold co-ordination sites would give rise to a band in the range 1880—2000 cm^{-1}. This assignment follows quite reasonably from the combined LEED/IR results on the Pd(100) surface. At a coverage of 0.5 we know that the CO molecules must be two-fold co-ordinated if they are to occupy equivalent adsorption sites. The IR results show that this is indeed the case. It is therefore assumed that in the ordering stage between θ = 0.4 and 0.5 and at lower coverages bridge sites are also occupied: no drastic shifts are observed other than the gradual shift associated with the interaction effects discussed below and the ordering effect just below θ = 0.5.

(3) Three-fold co-ordination sites are expected to produce a band in the region 1800—1880 cm^{-1}. The evidence for this comes mainly from the spectra themselves, namely, the enormous shifts encountered on Pd(111) between θ = 0.33 and 0.40 from below 1850 cm^{-1} into the region of two-fold co-ordination. Two other pieces of indirect evidence can also be cited. In the metal carbonyls three-fold co-ordinated CO has a stretch frequency at 1800 cm^{-1} or lower [3,44—46], although these parallels with inorganic chemistry should not be taken too far (vide supra): the molecule dien-W(CO)$_3$, for example, has a terminal CO stretch at 1718 cm^{-1} [47]. Secondly we note that electron loss measurements on the (111) faces of Ni [48] and Pt [27,49] also produce bands below 1880 cm^{-1}. IR and loss measurements on the (100) faces of Pd and Ni [48,50], respectively, where no sites of three-fold symmetry exist, show no such band. Generally speaking we would not expect the three spectral regions given above to apply exactly for other metals. The trend, however, is expected to be the same.

King and co-workers [43,51] have recently demonstrated the importance of *dipole—dipole coupling* in the IR reflection—absorption spectra of CO adsorbed on

Pt ribbons of primarily (111) orientation. This coupling mode leads to a continuous shift of the absorption band to higher frequencies as a function of increasing coverage [52] and to a domain absorption for a coupled system where the admolecules vibrate in phase. Thus even at $\theta \sim 0.5$ the C—O stretch absorption band remains relatively narrow. Except for low coverages on Pd(111), where island formation and a transition between localised sites appears to occur, the same situation pertains for Pd surfaces. However, these shifts are considerably greater than in the case of platinum. (Shigeishi and King [43] report a shift of approximately 40 cm^{-1} up to half-coverage similar to results on polycrystalline platinum from this laboratory [53]. Horn and Pritchard [28] on the other hand observe a discontinuous growth of the absorption band and a smaller shift for a bulk (111) crystal.) Tracy and Palmberg [23] have concluded that dipole—dipole interactions, at least as far as the heat of adsorption at high coverage is concerned, are not as important as direct and indirect interactions. At low coverages on palladium surfaces it would therefore appear that a combination of dipole—dipole coupling and indirect effects via the substrate are responsible for the coverage-dependent frequency behaviour. At higher coverages, and this seems to be for $\theta \geqslant 0.4$–0.5, a third effect begins to make itself felt, namely that of direct intermolecular repulsion. The latter affects the chemisorption bond so profoundly that the influence of localised site adsorption is virtually removed, the heat of adsorption falls rapidly and the C—O stretch band shifts at a much higher rate to higher frequencies. We address ourselves now to the problem of describing these two additional interaction mechanisms.

The *indirect interaction* between adsorbed CO molecules leading to frequency shifts was first discussed by Blyholder [39,40] in the context of his simplified MO model. The adsorption of further CO molecules on a metal surface leads qualitatively to a reduced back-donation into the CO 2π orbital. The result is a reduction in the adsorption energy and an increase in the CO stretch frequency. Indirect interaction via the metal electrons have been put on a somewhat sounder theoretical footing by Grimley and co-workers [54—56] who have shown that it can also be responsible for the appearance of energetically stable ordered adlayers over large areas of the metal surface. The energy of this interaction is expected to be an order of magnitude smaller than the binding energy between the adsorbed molecules and the surface. A further development of this work has been provided by Einstein and Schrieffer [57,58], who have calculated that the interaction can lead to repulsion between adsorbates adsorbed on nearest neighbour sites and to attraction on next-nearest neighbour sites on a (100) surface, even if the influence of d electrons is neglected. Strong attractive interactions of this nature could offer some explanation for the island formation of $(\sqrt{3} \times \sqrt{3})R30°$—CO structures on the (111) surfaces of many metals. The *intermolecular repulsion* is caused by the overlap of wave functions on adjacent molecules as they are packed in closer together at higher coverages. Due to the Coulomb repulsion between the electrons, the interaction between the partially occupied 2π orbitals results in their being raised in energy, which in turn reduces the occupation number. The direct consequence is a decrease in the

energy of the chemisorption bond, seen in the dramatic reduction in adsorption energy at high coverages and the corresponding strong shift in the C–O stretch frequency. We can now qualitatively explain the differences in the spectra for platinum and palladium. The small shifts encountered in the adsorption system CO/Pt(111) are probably due to the fact that the extent of the interaction between metal electrons and the 2π orbital of CO is less important than for palladium surfaces. This can be surmised from the high frequency of the C–O stretch and seems to imply, at least at low coverages, that singly co-ordinated sites are responsible for the adsorption band. The low occupation number of the 2π orbital means that the two effects just discussed do not play such an important role in the platinum system.

In concluding, it is worthwhile to compare briefly the spectra of figs. 1, 5, 6, 8, 12 and 15 with the Eischens and Pliskin spectra of fig. 17. We see that the latter results can easily be explained in terms of adsorption on a multiplicity of crystal planes and that even the shifts as a function of coverage are clearly discernible in the polycrystalline work. More interesting, perhaps, is a later paper of Baddour et al. [59] where the CO spectrum on silica-supported palladium was investigated at different intervals during catalyst "break-in". The reaction involved was CO oxidation. The dramatic differences in the spectra were interpreted as arising from a redistribution of crystal planes caused by the reaction energy of the oxidation process. This conclusion is also strongly supported by the present results.

Acknowledgements

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