JOURNAL OF CATALYSIS **44**, 328–331 (1976)

IR Reflection–Absorption Spectroscopy of CO Adsorbed on Platinum and Palladium

Since the pioneering work of Eischens and Pliskin on the ir spectrum of CO adsorbed on platinum and palladium catalyst samples (*1*), the problem of assignment has remained controversial. Eischens and Pliskin offered at the time a relatively simple explanation for band positions, which still has its adherents and is perhaps even reinforced by the current "surface molecule" approach to chemisorption. This assignment, based on the interpretation of metal carbonyl spectra, suggested that bands in the spectrum above 2000 cm^{-1} were due to CO "linearly bonded" through the carbon atom to an atom of the adsorbent. Bands below 2000 cm^{-1} were, on the other hand, assigned to "bridge bonded" CO positioned between two adsorbent atoms. Bridge-bonded CO was regarded as forming two σ-bonds to the surface, resulting in a stronger chemisorption bond and a much reduced C–O stretch frequency compared to linear CO. Several recent papers use this concept to interpret the ir spectra of CO on polycrystalline palladium (*2–4*). Blyholder (*5*) later proposed an alternative model whereby the position of the band in the spectrum is determined by the degree of $d\pi$–$p\pi^*$ bonding, which in turn depends on the nature of the surface site and the overlap conditions. In particular, strong π-bonding would result in a CO stretch frequency below 2000 cm^{-1}.

In the present Note we report infrared reflection–absorption spectra (*6*) from CO adsorbed on polycrystalline Pt and Pd films. From compact films of the two metals a single CO stretch frequency is observed above 2000 cm^{-1} in the case of platinum and below 2000 cm^{-1} in the case of palladium. The gross features of the Eischens and Pliskin spectra are thus reproduced in that these authors observed the strongest band at 2070 cm^{-1} for CO on silica-supported Pt and at 1930 cm^{-1} for CO on silica-supported Pd (see Figs. 7 and 10 of ref. *1*). The multiplicity of bands is, however, not reproduced.

The particular experimental method employed in this laboratory (polarization modulation) has been described elsewhere (*7*). The UHV-ir cell was basically that used in earlier thin film transmission work (*8*), but suitably modified for a single reflection from an optically polished glass flat. The base pressure in the cell, measured with a nude ionization gauge, was 5×10^{-10} Torr, but rose to 1×10^{-9} Torr during deposition of palladium and to 5×10^{-9} Torr during deposition of platinum. The spectra of Figs. 1 and 2a–f refer in each case to an adsorption sequence on one film. Scans were made at 1 cm^{-1} s^{-1}, and successive scans, if required, were added and stored in a Nicolet signal averager.

The room temperature adsorption sequence for a palladium film deposited at 420 K shows a single band below 2000 cm^{-1}, which shifts from ca. 1930 cm^{-1} to 1987 cm^{-1} with increasing coverage (Fig. 1a–d). The small residual signal from the annealed Pd films at room temperature allows the spectra to be presented without baseline subtraction. No bands were found above 2000 cm^{-1}. This is in contrast to films evaporated at low temperatures (*7*) where peaks both below and above 2000 cm^{-1} were observed, the latter disappearing on annealing. Assuming that the high deposition temperature produces reasonably compact films, which offer only low index faces, we can then make certain comparisons with the LEED and adsorption heat data for CO/Pd (*9*).

The isosteric energy of adsorption remains in general relatively high and constant ($\sim$140 kJ mol^{-1}) during the initial stages of adsorption. It then falls at higher coverages, accompanied by out-of-register LEED patterns, which indicate a continuous compression of the unit cell. It has hitherto been argued (*7*) that this reduction in the adsorption energy causes the band to shift to higher frequencies. However, recent work on the CO/Pt(111) system by King and Shigeishi (*10*) involving coverage measurements indicates that the shift involved there occurs largely before the onset of compression. These authors attribute shifts of this nature to dipole–dipole coupling effects. The peak in Fig. 1 does, however, become somewhat narrower after the formation of the compression structures on the surface, probably because surface heterogeneity no longer plays any role.

The corresponding room temperature adsorption sequence for a Pt film deposited at 420 K shows a single band *above* 2000 cm^{-1}, which shifts from ca. 2060 cm^{-1} to 2080 cm^{-1} with increasing coverage (Fig. 2a–f; here difference spectra were taken). The spectra are similar to those obtained by Shigeishi and King (*10*) on a Pt ribbon showing preferentially (111) orientation and by Horn and Pritchard (*11*) on a Pt(111) single crystal.

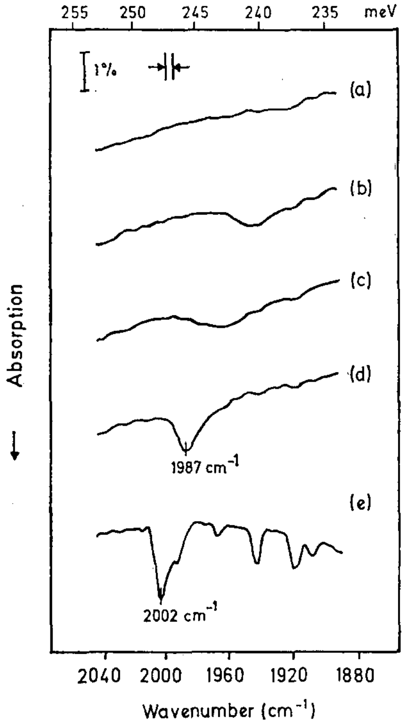

FIG. 1. IR reflection absorption spectra for CO chemisorbed on a palladium film deposited at 420 K. (a) Clean surface; (b) 3 L; (c) 10 L; (d) 1×10^{-6} Torr (all at 300 K); 1 L = 1 Langmuir = 1×10^{-6} Torr s; (e) cooling in 1×10^{-6} Torr to 190 K. The differences in reflectivity between the two components in the polarization modulation become more apparent on cooling, giving rise to the residual water vapor spectrum in Fig. 1e

With the platinum measurements we were able to operate at greater sensitivity, but even then were unable to detect anything much below an exposure of 3 L. The band would appear suddenly after an exposure of 2–3 L. It is thus possible that contamination effects played a role. Platinum films deposited at low temperatures revealed also one absorption band (above 2000 cm^{-1}). The sequence obtained was in fact very similar to that of Fig. 2a–f, except that the position of the band at 190 K and 1×10^{-6} Torr occurred at 2093 cm^{-1}. This spectrum is shown in Fig. 2g. Unfortunately the LEED patterns and adsorption energies for CO on the low index faces of platinum have not been so extensively investigated as those of palladium. Some very recent results for the Pt(111) face (*12*) indicate that the adsorption behavior resembles that on Pd(111): there is a similar initial heat of

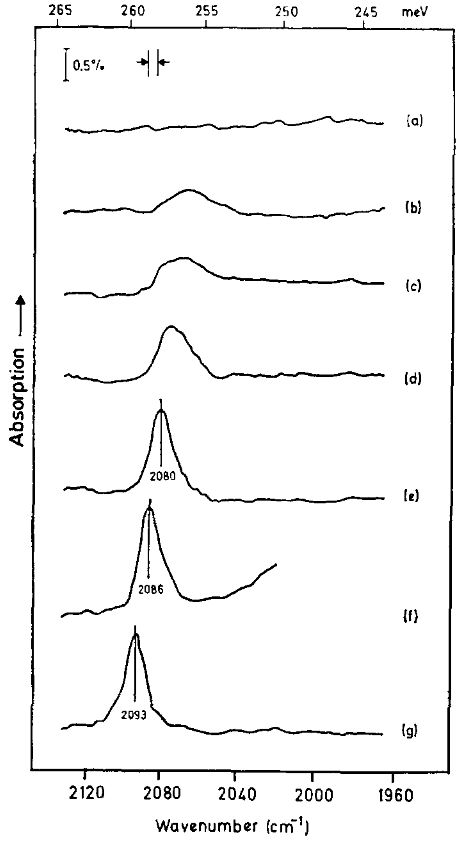

FIG. 2. (a)–(f) IR reflection–absorption spectra for the adsorption of CO on a platinum film deposited at 420 K. (a) Clean surface; (b) 3 L; (c) 15 L; (d) 30 L; (e) 1×10^{-6} Torr (all at 300 K); (f) cooling in 1×10^{-6} Torr CO to 190 K. The same temperature-dependent reflectivity effects show up in (f), giving rise to a sharply irregular difference spectrum. (g) Spectrum from a rough platinum film which had been deposited at low temperature *in vacuo;* 190 K and 1×10^{-6} Torr.

adsorption, which remains constant until the formation of a compression structure, whereby the unit cell becomes progressively smaller as the temperature is lowered or the pressure is increased. If these results are similar to those that would be obtained on other low-index faces (as yet CO adsorption on Pt(100) and Pt(110) has not been studied in those regimes of temperature and pressure that are likely to give rise to the compression structures), then the series of platinum spectra in Fig. 2a–f are to be interpreted in the same way as those for palladium. The albeit smaller shift to higher frequencies would be caused by dipole–dipole interactions (*10*). The sharpening of the peak is due to the decreasing influence of surface heterogeneity as the CO surface net goes out of registry with the adsorbent net; otherwise no pronounced change is observed at the onset of compression. The major difference between the two systems, however, remains the position of the absorption band. For compact films the CO/Pd band is found below, and the CO/Pt band is found above 2000 cm^{-1}. A careful search down to 1750 cm^{-1} revealed no other bands in the CO/Pt spectrum.

In explaining this important difference it does not seem appropriate to invoke solely linear bonding in the platinum system and solely bridge-bonding in the palladium system. The existence of compression structures on the low index planes of Pd and at least on the Pt(111) face is not compatible with the linear vs bridge-bonding viewpoint. Secondly, the apparent formation of these structures under similar conditions in the present experiments is not accompanied by significant changes in the spectra other than somewhat increased frequency shifts. It is more likely that the difference is due to the nature of the chemisorption bond formed with the surface in each case and that the symmetry of the adsorption sites on the low index faces before the onset of compression plays only a minor role. A further indication is provided by the work function change as a function of coverage for CO/Pt(111), which is initially negative before turning slightly positive (*12*). The work function, however, always increases for CO on the low index faces of Pd, the maximum change at high coverages being of the order of 1.2 eV (*9*). In terms of the Blyholder model (*5*) the Pt–CO chemisorption bond involves a smaller contribution from $d\pi$–$p\pi^*$ bonding, the latter still considered important in the bonding scheme despite the increased emphasis places on σ-bond formation in recent theoretical models for the CO/Ni system (*13*). The multiplicity of absorption bands, found particularly in palladium experiments involving very small particles (*1–4*), must be ascribed to the presence of a wide variety of surface sites offering varying degrees of π- and σ-bonding.

ACKNOWLEDGMENTS

The authors wish to thank G. Ertl, K. Horn, D. King, M. Neumann, and J. Pritchard for fruitful discussions. In particular they are indebted to Professor King for sending a manuscript of his paper prior to publication. Financial support for this work from the Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 128 is gratefully acknowledged.

REFERENCES

1. Eischens, R. P., and Pliskin, W. A., *Adv. Catal.* **10,** 1 (1958).

2. Soma-Noto, Y., and Sachtler, W. M. H., *J. Catal.* **32,** 315 (1974).

3. Palazov, A., Chang, C. C., and Kokes, R. J., *J. Catal.* **36,** 338 (1975).

4. Rice, R. W., and Haller, G. L., *J. Catal.* **40,** 249 (1975).

5. Blyholder, G., *J. Phys. Chem.* **68,** 2772 (1964).

6. See, for example, Greenler, R. G., *J. Chem. Phys.* **44,** 310 (1966), **50,** 1963 (1969); *Japan. J. Appl. Phys.* (*Suppl.*) **2,** Pt. 2, 265 (1974); Pritchard, J., *J. Vac. Sci. Tech.* **9,** 895 (1972); Pritchard, J., Catterick, T., and Gupta, R. K., *Surface Sci.,* **53,** 1 (1975).

7. Bradshaw, A. M., and Hoffmann, F., *Surface Sci.* **52,** 449 (1975).

8. Bradshaw, A. M., and Vierle, O., *Ber. Bunsenges. Phys. Chem.* **74,** 630 (1970).

9. Conrad, H., Ertl, G., Koch, J., and Latta, E. E., *Surface Sci.* **43,** 462 (1974).

10. Shigeishi, R. A., and King, D. A., *Surface Sci.,* in press.

11. Horn, K., and Pritchard, J., to be published.

12. Ertl, G., Neumann, M., and Streit, M., to be published.

13. See, for example, Batra, I. P., and Bagus, P. S., *Solid State Comm,* **16,** 1097 (1975); Cederbaum, L. S., Domcke, W., von Niessen, W., and Brenig, W., *Z. Physik* **B21,** 381 (1975).

F. M. Hoffmann
A. M. Bradshaw[1]

Institut für Physikalische Chemie und
Theoretische Chemie der Technischen
Universität München
8046 Garching, Germany (BRD)

Received February 23, 1976

---

[1] Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 1000 Berlin 33, Germany.