

Infrared Reflection Spectrum of CO on Pt Foil

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MUCH of the vast literature on infrared spectra of chemisorbed species deals predominantly with transmission techniques.¹ Relatively little work has been carried out using reflection methods; the small surfaces of samples and the relatively poor sensitivity of conventional dispersion spectrophotometers make such measurements difficult. We have now been able to record the infrared reflection spectrum of CO chemisorbed on Pt foil using a multiple-scan interference spectrometer.

The experimental arrangement used is shown schematically in Figure 1. Radiation from a

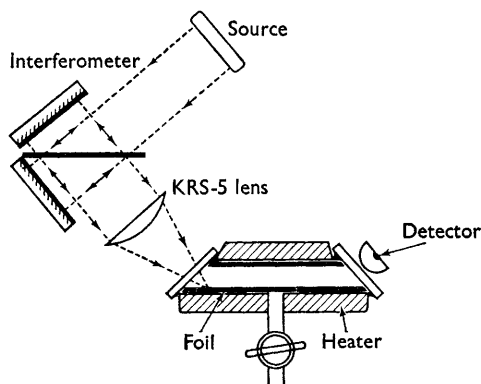


FIGURE 1. Experimental arrangement.

Globar source was passed through the optical system of a Block Engineering Co. Model 195TC interference spectrometer. A suitable collimating condenser was not available, so that an $F/2$ lens of KRS-5 was used to converge the beam. The sample, a smooth Pt foil of *ca.* 9 cm.² geometrical area rolled into a roughly cylindrical form, was contained in a small cell (~ 6 mm. i.d., 100 mm. long) fitted with KBr windows. The geometry suggests that about 5 reflections occurred. The arrangement shown has the advantage that radiation emitted by the sample and cell is not amplified and detected. Successive interferograms² obtained at a rate of 1 per sec. were initially recorded on magnetic tape and were then added coherently using a Block Engineering Co. Model 310 Coadder, a small time-averaging computer. Data reduction was carried out digitally with an IBM 301 computer, using a Block Engineering Co. paper tape punch as interface.²

Spectrum A of Figure 2 was recorded using 100 interferograms after the Pt sample had been

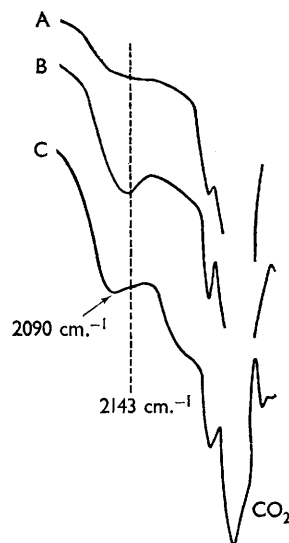


FIGURE 2. Infrared spectra: CO on Pt foil.

(Each spectrum resulted from the summation of 100 1-second interferograms. The range 2500—250 cm.⁻¹ was covered with a resolution of 15—18 cm.⁻¹.)

- A: background, after mild reduction and degassing.
- B: 1 hour after introduction of 30 torr CO.
- C: after removal of CO, at approx. 10^{-3} torr pressure.

subjected to mild degassing and reduction (degassed at 150° at 10^{-6} torr; heated in 30 torr of Pd-diffused H₂ for 1 hr. at same time; evacuated for 1 hr.; heated in 30 torr H₂ for 3 hr.; then degassed for 5 hr.). Only the 1800—2500 cm.⁻¹ region is shown in Figure 2 because no useful information was obtained in other regions. The dotted line indicates the position of the 2143 cm.⁻¹ CO band. The ordinates are arbitrary. Spectrum B was recorded 1 hr. after 30 torr CO had been introduced. The CO was then removed by pumping for 5 min., and spectrum C was recorded.

The "background" changed somewhat during the CO treatment and subsequent degassing, probably because of removal of an oxide layer by CO. The sample became more reflecting, indicating that the reduction with hydrogen had been

insufficient. The change in background precluded the computation of a ratio spectrum. However, comparison of the single-beam spectra A, B, and C shows that a band centring near 2143 cm^{-1} was formed when CO was introduced, and that a band near 2090 cm^{-1} remained when the CO was removed. The band remaining when the pressure had been reduced to 10^{-3} torr is close to the position expected for the band of chemisorbed CO and is ascribed to the Pt-C \equiv O surface complex,³ in direct analogy to the surface species observed on supported Pt by transmission methods.

Similar experiments were carried out with Pd and Rh, but these did not yield useful spectra. However, the results with Pt are interesting in

that they point to a potential approach to the infrared spectral study of small surfaces. As only a short time is required to record a spectrum, the interferometric techniques should be useful for kinetic studies, particularly with supported metals. With improvements in fore-optics and a sample arrangement permitting 20 or 30 reflections it should be possible to study reactions on surfaces where the effects of support are minimised, as with thick evaporated metal films, and where the surface geometry is well defined, as with single crystals.

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¹ See the extensive review, "Infrared Spectra of Adsorbed Species", L. H. Little, Academic Press, New York, 1966.

² M. J. D. Low, *J. Chem. Educ.*, 1966, **43**, 637.

³ Ref. 1, pp. 47 ff.