Reflection Spectroscopy of Chemisorbed Carbon Monoxide under Ultrahigh Vacuum Conditions

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INFRARED spectra of chemisorbed gases on metal surfaces have usually been measured by transmission methods which require the metals to be in very finely divided forms with poorly defined surface structures. Reflection techniques should permit the study of better defined bulk metal surfaces, including single crystals, and enable spectra to be related to other measurements giving structural information. In spite of this attraction reflection methods have been used very seldom.[1,2] They are inherently insensitive near normal incidence because there is almost a node in the electric field of the radiation at the surface. Recently Greenler[3] has predicted that the use of very large angles of incidence should lead to much stronger absorption. Moreover at large angles of incidence the amount of adsorbate in the light path is very significantly increased by the secant of the angle of incidence, and the radiation component polarised parallel to the plane of incidence is favourably oriented to interact with dipoles normal to the surface.

We report here the successful application of this approach to carbon monoxide adsorbed on thick polycrystalline copper films deposited under ultrahigh vacuum conditions. This system was chosen for two reasons. Firstly it is known that copper films deposited at room temperature are non-porous.[4] Consequently enhancement of the spectrum by transmission through porous metal surface layers may be neglected, although it probably occurred in some previous reflection work.[1] Secondly transmission measurements[5] with very thin copper films at low temperatures had previously indicated[6] a single band at 2100 cm.$^{-1}$ with a high extinction coefficient.

A Pyrex vacuum infrared cell with mica windows was used. It had a transmission of 55% at 2100 cm.$^{-1}$ and after bakeout at 200°, background pressures of 10^{-9} torr could be obtained regularly. The reflecting copper surfaces were prepared in the cell by evaporation on to microscope slides at room temperature. The slides were hinged and were brought together after film deposition to provide two parallel copper surfaces, 70 mm. long and $\frac{1}{2}$ mm. apart, which formed a light guide. Monochromatic radiation from the exit slit of a Grubb-Parsons M2 grating monochromator was focussed on to the entrance to the light guide, and the transmitted radiation was detected with a Golay cell. The detector signal was digitally recorded on punched tape and spectra were plotted by the graphical display facility of an ICT 1905E computer after using averaging and convolution methods to improve the signal-to-noise ratio.

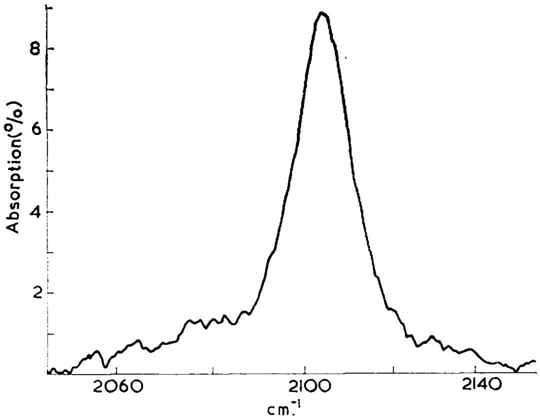

FIGURE. *Infrared spectrum of* CO *on copper films at* 1 *torr.*

The Figure shows the spectrum relative to that of the bare films after admitting CO at 1 torr. Surface potential measurements have shown that this pressure is necessary to give maximum coverage at room temperature. The single, relatively strong, absorption band at 2105 cm.$^{-1}$ was removed by evacuation and restored by reintroducing CO. The result is in good accord with the transmission results on thin films[6] and on silica-supported copper.[7]

The absorption intensity is complicated by the simultaneous occurrence of several reflections differing in multiplicity and angle of incidence. To a first approximation the amount of adsorbate is the same in rays which have suffered different numbers of reflections, because a larger number of reflections implies a smaller angle of incidence and a smaller secant. Taking the maximum coverage as one-quarter[4] and a factor of 50 for the secant effect we estimate an average extinction coefficient of about 2×10^{-18} molecule^{-1} cm.^{2}. This is of the same order of magnitude as that found in transmission experiments with CO on platinum[7] and copper,[6] but this average value may be of little real significance in view of the strong dependence on angle of incidence, predicted by Greenler, and on plane of polarization. However the unexpected intensity of the band, whether due to dipole orientation or the Greenler effect, indicates that infrared reflection spectroscopy with single-crystal surfaces is definitely practicable.

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