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A Practical Application of Infrared Reflection Spectroscopy to the Study of the Gas–Metal Interface*

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Description is given of a versatile cell for obtaining infrared spectra of a gas–metal interface by multiple specular reflection off the metal surface. The cell will fit into the optical assembly of a commercially available reflectance spectrometer and can be used under ultrahigh vacuum or high pressure flow conditions. The metal reflecting plates are clamped onto a central block containing an external well which can be accommodated with a cartridge heater or a suitable liquid coolant—thereby giving a total temperature range of ca. 80–800°K. Provisions are included for variations in the total number of reflections and for an angle of incidence fixed between 45 and 70°.

The experimental conditions necessary for obtaining spectra of surface species are outlined, and results are given for an application of the technique to carbon monoxide interaction with electropolished copper at 40–175°C.

INTRODUCTION

Infrared reflection spectroscopy has to date received only limited application in gas–metal adsorption studies (*1*, *2*) in spite of the fact that it permits the use of bulk nonsupported metal samples. Recently, several publications have appeared which deal with the theoretical feasibility of such investigations (*3–5*), but little emphasis has been placed on the development of practical experimental systems. Of the papers which do present reflectance spectra of gaseous species adsorbed on metallic surfaces (*3–10*), the infrared cells are generally inadequately described for reproduction, have poor vacuum properties, or require considerable modification of the optical assemblies in commercially available spectrophotometers.

The reflection technique is beset with the constant problem of conducting surface studies by infrared spectroscopy—that of incorporating a sufficient quantity of adsorbed material in the light beam to be detectable by a standard spectrometer. This difficulty is usually overcome by multiple reflection from highly polished surfaces. However, there are additional complications due to the changes in the electromagnetic radiation which occur upon reflection at an interface (*1–3*).

The state of polarization, the angle of incidence, and the total number of reflections are the most significant parameters of the system. Greenler (*4*) has considered the relationship of these parameters to each other and their effect on the expected intensity of the infrared spectral bands. His calculations reveal the optimum conditions to be, for parallel polarized radiation and a particular angle of incidence, the number of reflections which reduce the background energy to 37% of its initial value. Angles of 70–80° are generally preferred for metallic surfaces (*3–5*, *11*, *12*).

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Cell Design

Figure 1 illustrates the modified version of a pair of cells which were originally designed and constructed for the authors by the Wilks Scientific Corporation, South Norwalk, Conn. These cells can be used in the Wilks Model 8 internal reflection infrared spectrometer or in any Perkin-Elmer Infracord with the additional Model 8 optical assembly. The design is intended for use with ultrahigh vacuum conditions and sample temperatures up to 500°C. Dual gas leads permit the use of static or flow systems.

Vacuum Properties

The cell body, with removable top, can be entirely machined from block stainless steel so that the only possible places for vacuum leaks are around the gas leads, the join between the two flanges, and around the windows. The gas leads can be permanently affixed to the cell by welding or silver soldering, and should be connected to ultrahigh vacuum valves. An excellent seal can be obtained around the flange area by a knife-edge seal (*13*) using a soft metal gasket (Au, Ag, or OFHC Cu are preferable, but soft Al is adequate). The diagram depicts five equally spaced bolts for clamping the two flanges; however, an even number of bolts is more efficient, and at least six or eight should be used.

Irtran-2 has been chosen as the window material due to its ability to withstand high temperature and its chemical stability. One-in. circular disks, 2 mm thick, were attached to the window frames with Dow Corning Silastic RTV. Due to the elastic texture of the latter, the thermal expansion and brittle characteristics of the Irtran-2 presented no vacuum problems. This sealant is capable of withstanding temperatures of 250°C and appears to be adequately baked out over a long period of time to give vapor pressures which are at least lower than 10^{-6} Torr at sample temperatures of 250°C. However, for an ultra-

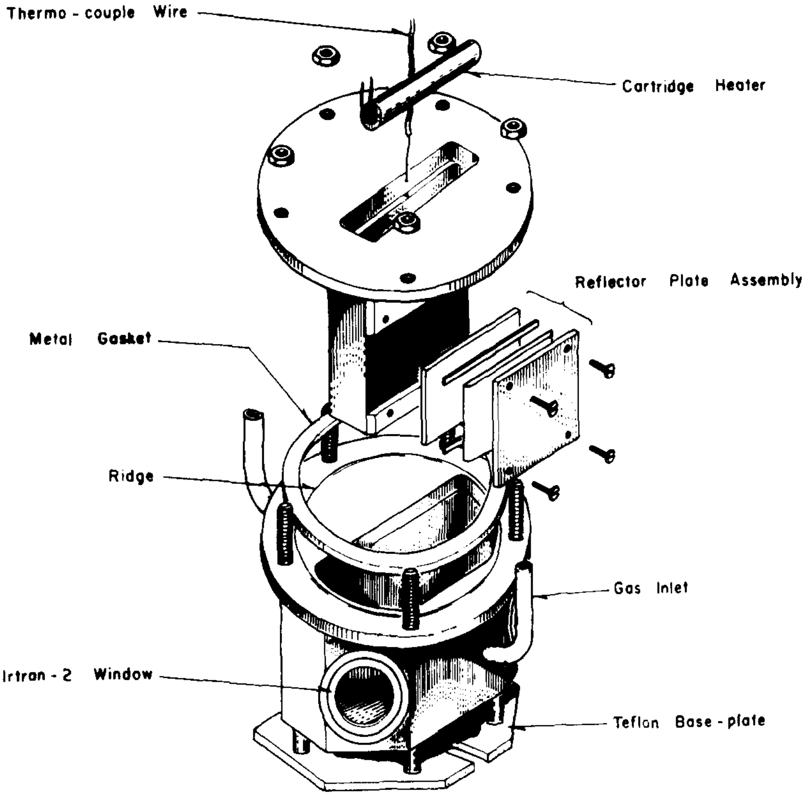

FIG. 1. Exploded view of multiple reflection infrared cell.

high vacuum system, Schkolnick's method (*14*) using Vacseal is recommended, with a cooling system added around the window frames. Infrared window-metal seals also seem to be a promising consideration (*15*).

Optical Assembly

The metal reflector plates have specific dimensions: the back plate is 55 × 19 × 2 mm, and the front, 50.8 × 19 × 2 mm. The plates are plane parallel to each other and separated by bar spacers (preferably of the same material as the plates) placed along the top and bottom edges of each. The light beam from the source is directed into the cell through one window, impinges upon the back plate, multiply reflects between the two plates, then reflects off the back plate through the second window and is focused into the spectrometer slit by a series of mirrors.

The angle at which the walls supporting the windows is placed, and the depth to which the back plate is inset into the block are dependent upon the angle of incidence required. The thickness of the spacers determines the approximate number of reflections expected for the particular angle of incidence used.

Reproducible positioning of the cells into the spectrometer is accomplished by alignment of the base plate on the floor of the instrument.

Heating Conditions

The well into which the cartridge heater is placed extends into the block above the plates. The sample plates are thus heated via the block and the pressure plate, and may suffer from a slight temperature gradient. An aluminum pressure plate has been used in the present work to improve thermal conductivity to the front plate. The thermocouple well sets into the back portion of the block down to the mid-center position of the reflector plates, and the temperature at this point can be controlled within ±1°C. The cell stands on legs attached to a Teflon base plate, thereby reducing heat transfer to the instrument. For operation at high temperatures, and for optimum temperature control, the cells can be surrounded by an insulating material; also the instrument can be placed on a jack and moved from the cells during bakeout. For temperatures less than ambient, the well can be filled with a suitable liquid coolant.

Experimental Methods

The initial experimentation was predominantly concerned with determining the feasibility of the cell design and experimental technique. The results presented here were obtained with cells constructed according to the design shown in Fig. 1; however, to reduce expense the bodies were constructed from sheet stainless steel and joined by silver soldering.

Optical Arrangement

The Wilks Model 8 optical assembly is supplied with 45° angle of incidence (*16*) and the cells as originally constructed were designed for this angle. However, tests made with thin films of barium stearate on silver mirrors indicated the necessity of using higher angles of incidence. The maximum angle which could be obtained within the space limitations of the instrument was 70°, and the spectra reproduced here were obtained by using a 70° angle of incidence and 0.5-mm spacers (ca. 37 reflections). These conditions conform closely to Greenler's optimum conditions (*4*).

Figure 2 indicates the changes made in the apparatus to accommodate this change of incidence angle. For the present studies, only one mirror in each beam has been altered in position to realign the light; however, repositioning all the mirrors relative to 70° incidence should greatly improve the focusing and enhance the spectra obtained (*4*).

Instrumentation

The Band intensities recorded for chemisorbed species in the order of 0.01 absorbance units and thus required the use of ordinate scale expansion. A Perkin-Elmer expansion attachment was used with a 10 mV chart readout recorder; maximum ex-

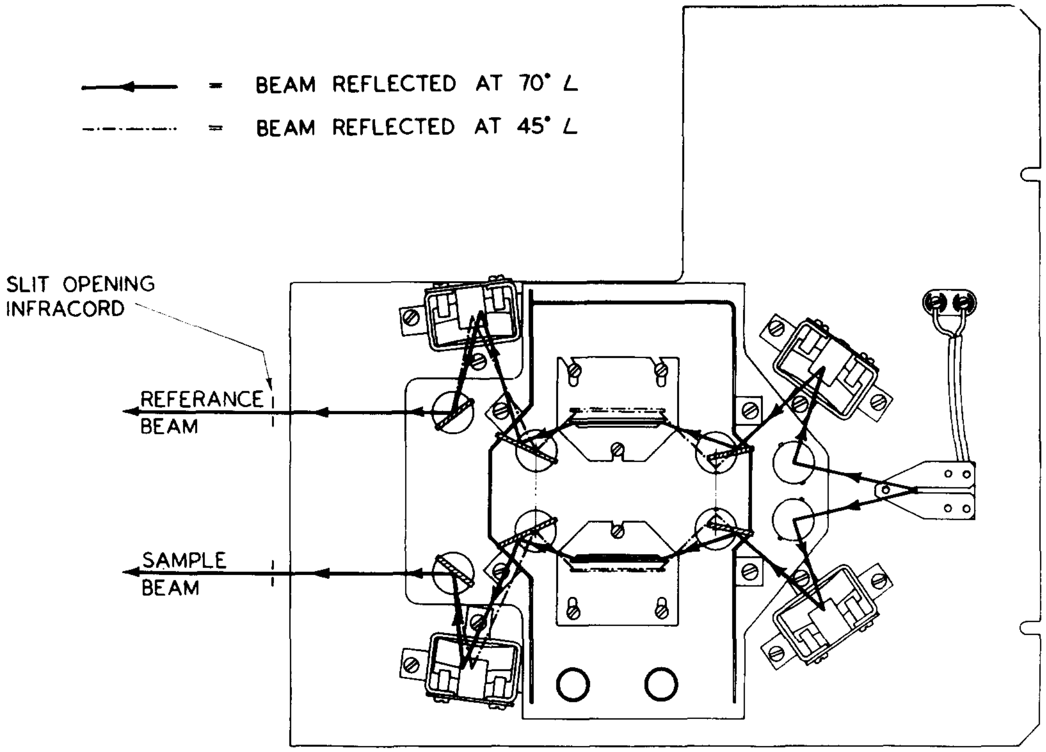

FIG. 2. Schematic of Wilks Model 8 optical assembly with the angle of incidence changed to 70°.

pansion reproduced 1% transmission differences on the infracord drum as a 2.5 mV signal on the recorder.

With highly polished surfaces and the instrument flushed with nitrogen to reduce atmospheric interference, the noise level could be kept below 5 scale divisions on the expansion recorder (100 scale divisions = 10 mV), and slit widths less than the maximum could be employed. Pen response was always set relative to the expanded scale.

The infrared radiation source was found to be more highly parallel polarized, and since in addition each beam penetrated the windows at a 25° angle of incidence with the cell design used, the light being admitted to the plates was predominantly parallel polarized. In addition, AgCl stacked plate polarizers were placed between the sampling cells and the instrument slits, in the "transmission" sampling area of the Wilks Model 8 (*16*). Unless otherwise stated, the spectra presented here were obtained with the polarizers oriented to transmit preferentially the parallel radiation component.

Metal Plates

Copper plates were machined to specification from 99.99% Cu sheet. The surface to be mirror polished was first roughly ground with Buehler Carbimet Silicon Carbide wet grinding paper, 400 Grit, and then polished electrolytically in 1:1 H_3PO_4:H_2O electrolyte (*17*). When the surface had obtained a sufficiently high luster, the plate was immediately removed from the acid solution, and quickly washed in a strong jet of warm distilled water before disconnecting the voltage source. Further washing was then carried out with distilled water and with ethanol.

Experimental Conditions for Gas–Metal Interaction

The cells were connected to a glass high vacuum system capable of evacuation to

10^{-6} Torr. Gas pressures were measured by McLeod gauges. Efforts were made to minimize the vapor pressures of mercury and stopcock grease exposed to the catalyst by means of a U-trap in each line maintained at —80°C.

Hydrogen used for reduction was purified by passage through a Deoxo unit and then a molecular sieve trap cooled by liquid nitrogen.

The carbon monoxide was reagent grade further purified by multiple distillation at liquid nitrogen temperatures.

Two series of experiments were carried out with carbon monoxide and copper. In Series E, the copper plates were reduced at 200°C in 1000 Torr of hydrogen flowing at a rate of 0.5 ml/sec. In Series F, the freshly polished surfaces were reduced in 1000 Torr of hydrogen at 200°C under static conditions.

The infrared spectra were recorded with the reference cell under vacuum (ca. 10^{-6} Torr) and, unless otherwise designated, with gas phase CO in the sample cell.

Results

Fluctuations in temperature and unequal temperatures in the two cells were found to cause significant changes in the spectral base line. These effects were presumed to be due to slight variations in the angle of incidence and the total intensity of light reflected, resulting from thermal expansion of the metallic assembly inside the cell. A reproducible base line could be maintained by controlling the temperature within ±1°C; however, it was necessary to refocus the light beams each time the reaction temperatures were changed.

The base line obtained was also a function of the polarization state of the reflected light. The ratio of the parallel component to that of the perpendicularly polarized component increased markedly as the frequency decreased, especially on the higher range of the instrument (4000–1250 cm^{-1}). The presence of a parallel polarizer in each beam was found to maintain a more uniform base line, and, in accordance with the observations of Francis and Ellison (*11*), to enhance the spectra of surface species which favorably absorb the parallel component.

Series E

The reflectance spectrum of the freshly prepared copper plates of Series E displayed two intense bands in the sample beam at 1610 and 1425 cm^{-1}, as well as smaller bands at 2350 cm^{-1}, and in the 3600–3800 region. These bands were found to exhibit interesting properties with regard

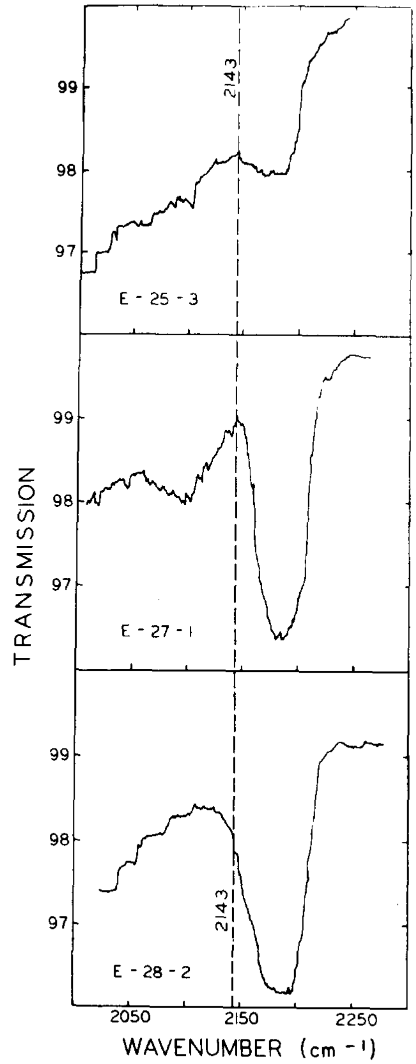

FIG. 3. Reflectance spectra of copper exposed to carbon monoxide at 175°C: (E-25-3) 10 Torr CO after 5 min (without polarizers); (E-27-1) 10 Torr CO after 10 hr; and (E-28-2) after evacuation at 175°C.

to the significance of the polarization state of the reflected light. The bands at 1610 and 1425 cm^{-1} were due only to parallel polarized radiation, whereas the vibrations giving bands at 3600–3800 cm^{-1} absorbed only perpendicular radiation. At least one of the bands in the 3600–3800 cm^{-1} region appeared to be due to atmospheric interference, as was that at 2350 cm^{-1}.

With these copper surfaces, reduced in flowing hydrogen, CO was admitted to the sample cell at 175 and at 115°C. At both temperatures an absorption band which coincided with the high frequency band of the gaseous carbon monoxide doublet slowly grew in intensity in the presence of CO, and remained on the surface after evacuation of the gas (Fig. 3). Figure 4 shows the effect of removing the species giving the 2180 cm^{-1} band by heating under vacuum. The material was rapidly removed when the temperature reached ca. 220°C. Spectra 4, 5, and 6 also exhibit the influence of temperature upon the base line—the light beam was refocused and the base line was raised between spectrum 5 and 6.

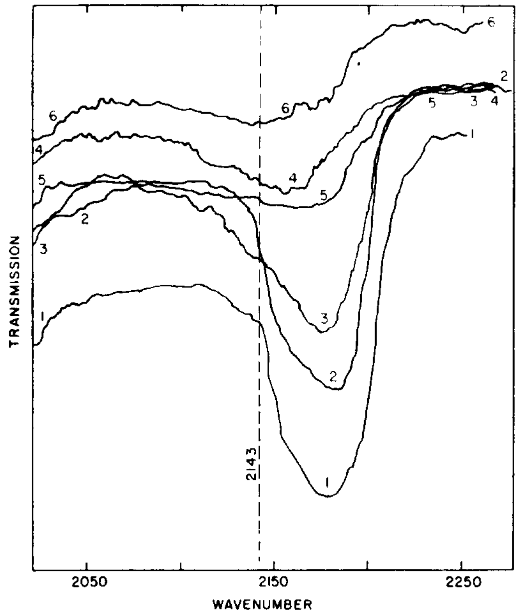

FIG. 4. Spectrum changes of the CO surface species while heating and evacuating (E-Series): (1) Hi Vac for 5 min, $T = 175°\mathrm{C}$; (2) Hi Vac for 1 hr, $T = 219°\mathrm{C}$; (3) Hi Vac for 1.25 hr, $T = 222°\mathrm{C}$; (4) Hi Vac for 1.5 hr, $T = 229°\mathrm{C}$; (5) Hi Vac for 2 hr, $T = 229°\mathrm{C}$; and (6) Hi Vac for 4 hr, $T = 233°\mathrm{C}$.

F Series

The interaction of carbon monoxide with copper reduced in static hydrogen was observed at 40, 80, 115, and 175°C. In this series, bands due to surface species were observed at ca. 2110, 2180, and 2300–2350 cm^{-1} with the gas present in the cell, but disappeared upon evacuation. The 2110 cm^{-1} band appeared after the plates had been exposed to CO for some time (Fig. 5)

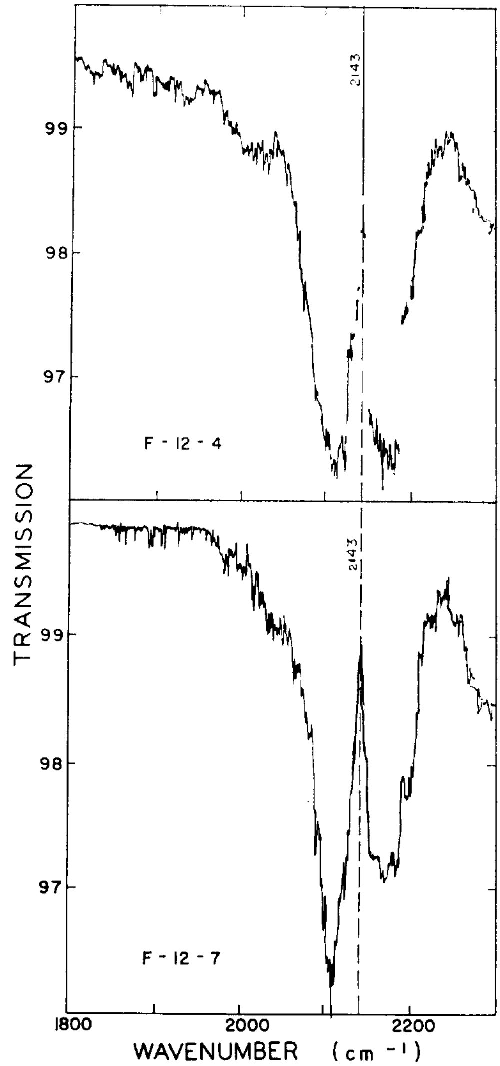

FIG. 5. Reflectance spectra of copper surfaces in 17.5 Torr CO at 40°C (F-Series): (F-12-4) after 20 min; and (F-12-7) after 8 hr.

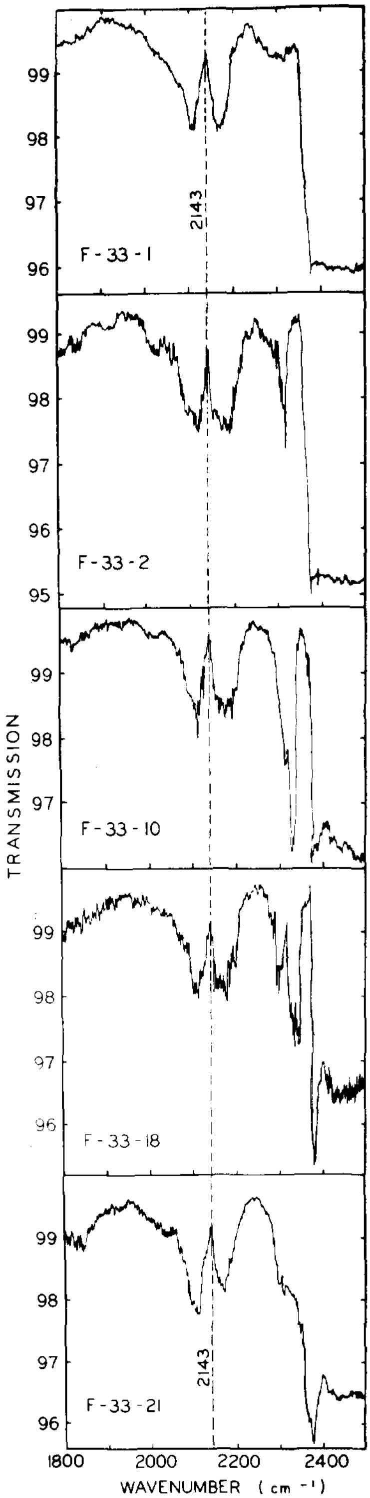

Fig. 6. Reflectance spectra of copper surfaces in 11.8 Torr CO at 115°C (F-Series): (F-33-1) after 5 min; (F-33-2) after 20 min; (F-33-10) after 18 hr; (F-33-18) after 20 hr; and (F-33-21) after 24 hr.

and seemed to reach an eventual state of equilibrium. The maximum intensity was not related to temperature although its rate of appearance increased with temperature. This band was usually preceded by an unstable band in the 2300–2350 cm^{-1} region. The latter was most prevalent at the higher temperatures and could be reduced in intensity by placing a liquid nitrogen cooled trap in the cell line. The 2180 cm^{-1} band was only obtained at the higher temperatures and after the copper had been subjected to long-term exposure to hydrogen.

Figure 6 shows some members of a sequence of spectra run over a period of 24 hr during which time the 2300–2350 cm^{-1} band periodically grew in intensity, shifted its maximum to higher frequencies, split into a doublet, then decreased in intensity. Eventually a significant band appeared for gaseous CO_2, and at the same time, the 2110 cm^{-1} band became more intense.

DISCUSSION

In comparing the results of previous investigations into phosphate ion contamination of electropolished copper surfaces (*18–20*), it appears that the rinsing treatment used after electropolishing in the present work would leave some phosphate on the surface, and that the plates of Series E may have been covered by as much as a monolayer of residue. The intense bands at 1610 and 1425 cm^{-1} which were removed by heating may thus have been due to water which was physically adsorbed or entrapped in this residue.

The band centered at 2180 cm^{-1} was the result of CO interacting with the material present after the residue had been exposed to hydrogen, and this interaction may have been one of chemisorption or chemical reaction. The 220°C temperature at which the absorption band rapidly disappeared corresponds with the decomposition temperature for basic copper carbonate; however, the position of the band in the infrared spectrum is more akin to that of a carbonyl stretching frequency rather than a carbonate. Also, since a value of 2173 cm^{-1} has been reported elsewhere for CO adsorbed on CuO (*7*), it would appear that the 2180 cm^{-1} band obtained here may have been due to CO adsorbed on a heterogeneous copper surface—i.e., in the presence of water, oxide, phosphate, carbonate, or other contaminants.

The F-Series spectra correspond more nearly with the results of others for CO chemisorbed on copper: Bradshaw *et al.* (*10*) obtained an infrared absorption band at 2105 cm^{-1} for evaporated copper films under ultrahigh vacuum conditions; Smith and Quets (*21*) reported values of 2110–2120 cm^{-1} for CO adsorbed on supported copper at 40–200°C. This band appears to be due to a weakly held chemisorbed species in equilibrium with the gas phase, and is probably due to CO on a metallic copper site.

Smith also obtained a band at 2350 cm^{-1} during the oxidation of CO on copper at room temperature (*22*). However, since the present spectra were recorded at elevated temperatures, this band cannot be due to physically adsorbed CO_2 as Smith proposes, but rather to a surface intermediate formed during the reaction of carbon monoxide with surface oxide. The linear $M{-}O{=}C{=}O$ surface species discussed by others (*23, 24*) seems a plausible explanation.

The spectral data which we have obtained for the carbon monoxide–copper system have been presented here mainly in the light of academic interest. Our work to date has been primarily concerned with developing the use of reflection spectroscopy in gas–solid surface chemistry in an effort to devise an experimental method which is more satisfactory to those who wish to operate with unsupported metals of high purity. The feasibility of the technique for infrared study of adsorbed material seems without question. However, it is necessary to carry out these studies with very clean surfaces in an ultrahigh vacuum system in order to be more knowledgeable of the true surface state under which the infrared spectra are obtained.

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