JOURNAL OF CATALYSIS 4, 163–171 (1965)

Adsorption of Carbon Monoxide on Copper

Infrared Absorption Spectra and Thermodesorption

A. W. SMITH* AND J. M. QUETS

From the Parma Research Laboratory, Union Carbide Corporation, Parma, Ohio

Received July 14, 1964; revised August 6, 1964

The chemisorption of carbon monoxide occurs in two states with about 10 kcal/mole and 20 kcal/mole heat of adsorption and with low activation energies for adsorption. The infrared absorption spectra and thermodesorption characteristics for both these states are complex. In addition, thermodesorption indicates the presence of a state with a higher activation energy for desorption than these. The infrared spectra of physically adsorbed carbon monoxide and carbon monoxide chemisorbed on silica are also given. The frequency of the carbon monoxide spectra is related to the type of bonding with the surface.

I. INTRODUCTION

This study of the adsorption of carbon monoxide on copper was undertaken as part of a program on the oxidation of carbon monoxide over copper catalysts. An apparatus was constructed to allow the measurement of infrared absorption spectra and thermodesorption from −196° to 500°C. The results of this infrared and thermodesorption study show that the two chemisorption states, already indicated by surface potential measurements (*1*) are both complex. An interpretation of the results is given based on the ability of carbon monoxide to act both as an electron donor and an acceptor in forming a chemical bond with the surface.

II. EXPERIMENTAL

The vacuum system used for these experiments is of the ultrahigh vacuum type. It was not baked out but background pressures of 1×10^{-8} Torr were obtained. An omegatron mass spectrometer on the system revealed that the background pressure consisted almost entirely of H_2O, CO_2, and CO.

Both the cell used for the thermodesorption measurements and that used for the infrared studies could be cooled to −196°C and maintained at any temperature between −196° and 500°C or heated at a constant rate of temperature rise. A cut-away drawing of the infrared sample holder is shown in Fig. 1.

This container consists of a sample space through which gas may flow by means of the tubes coming out of the top. The sample is held in a stainless steel clip between the two inner windows. The space between the windows not occupied by the sample is only a small fraction of a millimeter so that as little as possible of the gas spectra will be recorded. The windows are sealed onto the ends of tubes which can be removed to change samples or to change windows. A gold wire gasket is used to seal the flanges on which these tubes are welded. Stainless steel is used throughout and the welding is done by the "Heliarc" process.

Two kinds of windows are used. Sapphire windows sealed onto metal tubes were obtained from Advanced Vacuum Products, Inc. These windows can be heated to 500°C or cooled to −196°C with no difficulty. Calcium fluoride windows were also used to cover a longer wavelength region. These

---

* Present Address: Boeing Scientific Laboratories, P. O. Box 3981, Seattle 24, Washington.

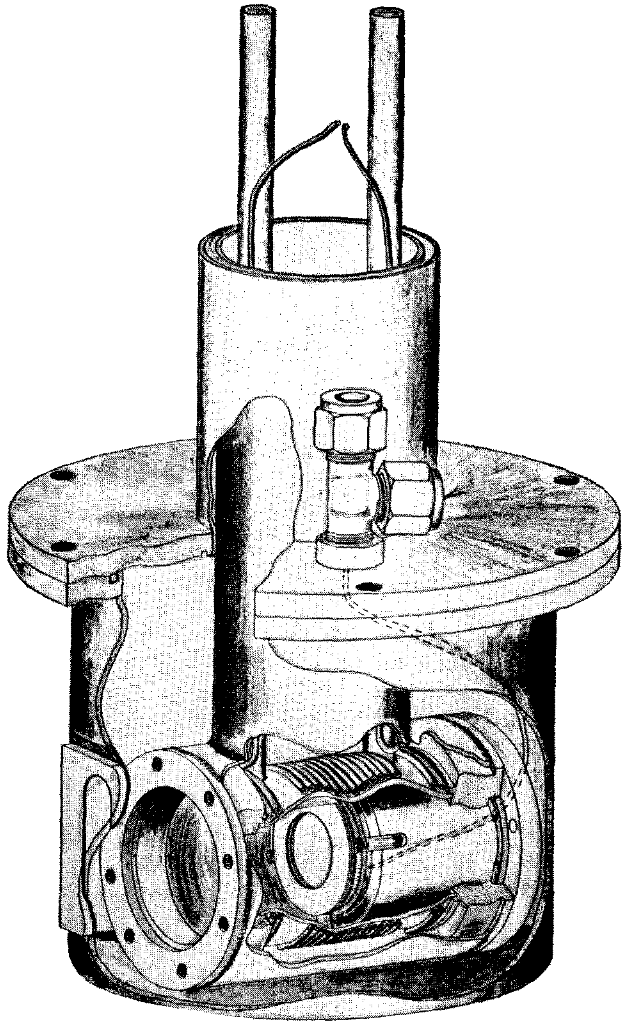

FIG. 1. Infrared cell.

were sealed with silver chloride onto platinum foil which had been silver soldered onto the ends of stainless steel tubes. Care must be taken that the silver chloride does not come into contact with the stainless steel and that the windows be cooled slowly and evenly after the silver chloride has been allowed to melt. The calcium fluoride windows have been cycled between —78° and 250°C with no difficulty. The first time they were cooled to —196°C, however, one of the windows cracked.

Surrounding the sample volume is a space which can be filled with liquid nitrogen, dry ice, or cooled with cool gas. Nichrome heating wire in this space is wrapped around the sample volume. By these means any temperature between —196° and 500°C can be maintained. Outside of this space is a vacuum which acts as an insulator and keeps the windows from fogging. This vacuum is continuously pumped. A rubber "O-ring" is used to seal the vacuum, and the outer calcium fluoride windows are held in place with rubber cement. The thermocouple wire is led into the vacuum to make contact with the inner windows which support the sample holder.

The infrared samples were disks 25 mm in diameter and about 0.5 mm thick. They were prepared in the following way. Copper nitrate solution was mixed with silica or alumina to give a thick paste. The paste was dried at 110°C to give a cake which was crushed and screened through a 150-mesh screen. A weighed amount of this material was transferred to a 1 inch diameter die and pressed at 500 psi for a few minutes. The pressure was then released and the pellet carefully removed from the die. Before the sample was placed in the infrared absorption apparatus, it was heated in hydrogen at 140°C for 24 hr. This was done in a grease-free Pyrex system. The particle size of the copper was determined by X-ray line broadening; the approximate values obtained are given in Table 1. This table also includes the percentage of copper in the sample and the weight thickness of the pellet.

TABLE 1
SAMPLE PROPERTIES

Sample	Support	Copper particle size (Å)	Pellet weight thickness (mg/cm²)
10% Copper on alumina	Alon-C (surface area 80 m²/g)	~800	60
10% Copper on silica	Cabosil (surface area 200 m²/g)	~100	30
20% Copper on silica	Cabosil (surface area 200 m²/g)	~200	30

A Perkin-Elmer Model 12-C single-beam infrared spectrometer was used with a calcium fluoride prism. This spectrometer was modified so that the beam was brought to an external focus after passing through the monochromator. The sample was placed at the focus. After passing through the sample, the beam was refocused on the infrared detector. There are two advantages to this arrangement. By placing a sample which scatters light at a focus, considerably less light is lost than when it is away from the focus. By using monochromatic light the heating of the sample by the beam is greatly decreased and lower temperatures can be obtained. The slits of the monochromator were programed to give nearly constant energy in the monochromatic beam at all frequencies. In all cases reported in this paper the width of the absorption band due to adsorbed species is much greater than the spectral band width of the monochromatic light.

For the thermodesorption studies reagent grade copper shot was packed into a 6-mm Pyrex U-tube. This was sealed onto the vacuum system and placed into a vacuum-jacketed furnace, which could be cooled with liquid nitrogen or cooled nitrogen gas. Any desired heating rate could be obtained by the use of a simple motor-driven temperature controller. Gases were let into the tube by an all-metal valve, while the other end was connected through a similar valve to the omegatron mass spectrometer.

The copper shot was oxidized and reduced several times to clean the surface. The thermodesorption characteristics become constant after several oxidation-reduction cycles. The completion of reduction was determined when no carbon dioxide was formed while passing carbon monoxide over the sample at 250°C.

Thermodesorption runs were carried out by letting gas into the sample at appropriate temperatures and pressures. Then the gas was pumped out and the sample heated at a constant rate while the gas desorbed was determined by the mass spectrometer.

Reagent grade gases were used throughout.

III. INFRARED ABSORPTION RESULTS

The adsorption of carbon monoxide on copper metal produces a number of adsorbed species which show infrared absorption bands. Some absorption spectra are seen in Fig. 2. In this experiment carbon monoxide was let into the sample chamber at liquid nitrogen temperature. After saturating the sample, the carbon monoxide was

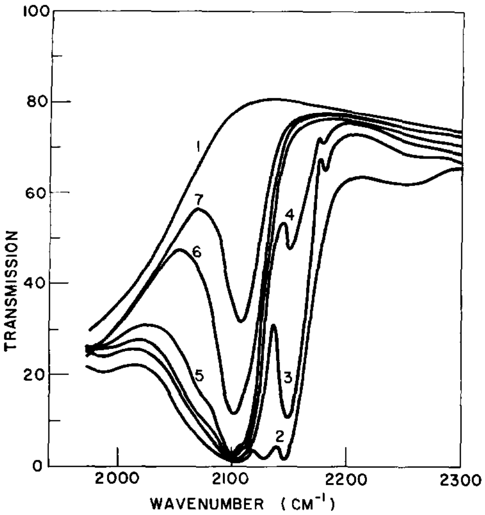

FIG. 2. Spectra of carbon monoxide adsorbed on copper (10% copper on Cabosil) at low temperature: 1. −188°C in vacuum; 2. −195°C in 200 Torr CO; 3. −188°C CO pumped off; 4. −150°C; 5. −70°C; 6. +5°C; 7. +40°C.

pumped out, and the chamber was heated at a rate of 0.03°C/sec.

In Fig. 2 there is indication of one or two absorption bands in the 2100 to 2120 cm^{-1} region which persist above room temperature. Other experiments have shown that the absorption band at about 2120 cm^{-1} persists after evacuation at room temperature for 15 days. In the presence of gaseous carbon monoxide, the band at 2100 cm^{-1} is still present at 200°C.

There is a broad band centered at 2070 cm^{-1} which is still present at −70°C but gone by +5°C.

Three weak bands occur together: a sharp band at 2180 cm^{-1} and two broad bands at 1990 cm^{-1} and 2250 cm^{-1}. These peaks have completely disappeared by the time −70°C is reached. It may be noticed that the transmission decreases at 1850 cm^{-1} as the temperature is increased. This is due to a general decrease of the transparency of the sample at these frequencies with increasing temperature and has nothing to do with the adsorbed gas.

None of these low temperature bands were noted by Kavtaradze and Sokolova (*2*). Since they did not use monochromatic light, their samples may have been considerably warmer than they thought.

The band at 2150 cm^{-1}, which is still in evidence at −150°C, and the band at about 2130 cm^{-1} which disappears as soon as the gas is pumped out, are not specific to copper, but occur on pure Cabosil. This is shown in Fig. 3. Also on Cabosil the sharp -OH band at 3750 cm^{-1} is converted to a broad band at 3620 cm^{-1} attributed to hydrogen-bonded -OH groups (*3*). This is shown in Fig. 4. The hydrogen-bonded band disappears on pumping out carbon monoxide and the sharp -OH band returns. This indicates that the physically adsorbed carbon monoxide which has the absorption band at 2130 cm^{-1} is responsible for the change in the -OH band.

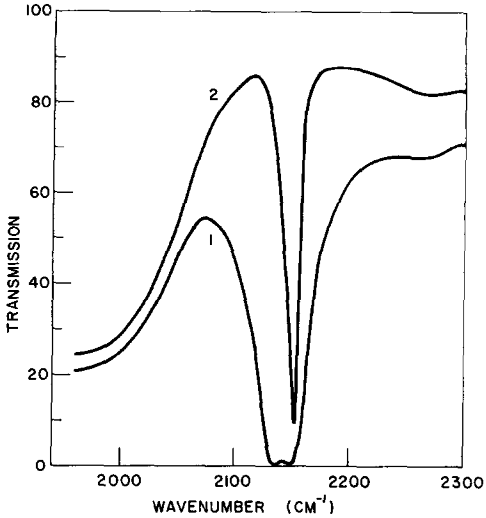

FIG. 3. Adsorption of carbon monoxide on silica (Cabosil): 1, in 100 Torr CO at −195°C; 2, 30 min after CO removed at −188°C.

Further resolution of the adsorption bands in the 2100 to 2120 cm^{-1} region is obtained by slowly introducing carbon monoxide and measuring the spectra as the surface coverage increases. This is shown in Fig. 5. The gas was introduced at a very low leak rate at −188°C. An adsorption band at 2125 cm^{-1} occurred first followed by the appearance of a band at 2100 cm^{-1}. Later the bands at 2070 cm^{-1} and 2150 cm^{-1}

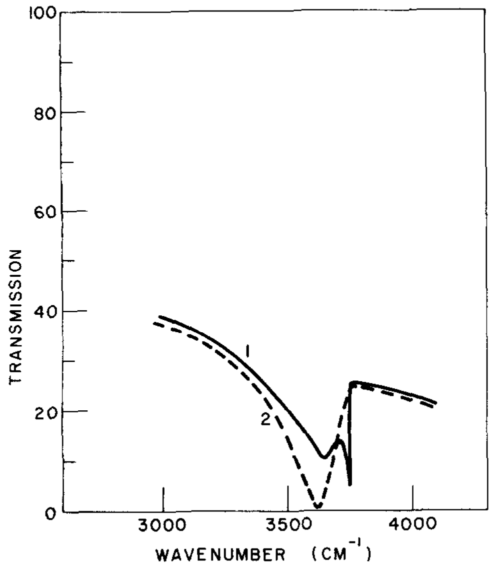

FIG. 4. Effect of carbon monoxide on —OH bands of silica (Cabosil): 1. —188°C in vacuum; 2. —195°C in CO.

begin to appear. At —188°C it is possible to partially resolve the bands at 2100 cm^{-1} and 2125 cm^{-1}. At 25°C the bands are too broad and only a frequency shift in the over-all band with coverage is observed. There is also an apparent shift in each of these two bands with coverage at —188°C, as is seen in Fig. 5. However, since the bands are not well resolved, it is difficult to determine the real magnitude of these shifts.

Spectra of carbon monoxide absorbed on copper supported on alumina were also obtained. Both Alon-C and "Linde 0.3 A," a gamma and an alpha alumina, were used as supports. In both cases, the band remaining after evacuation at room temperature was centered at 2110 cm^{-1} in contrast to the work already reported on silica where the same band occurred at 2120 to 2125 cm^{-1}. It is not apparent whether this difference is due to the chemical nature of the support or to the fact that 10% copper on the lower area aluminas forms larger particles than does 10% copper on the silica. On a sample of 20% copper on silica, where larger particles occur, this band occurred at 2117 cm^{-1}.

The effect of oxygen on the infrared spectrum of carbon monoxide on copper at room temperature has been discussed by Eischens and Pliskin (*4*). They showed that the addition of oxygen caused the band at 2100 cm^{-1} to "shift" to 2120 cm^{-1}. This effect has been confirmed here. However, the results

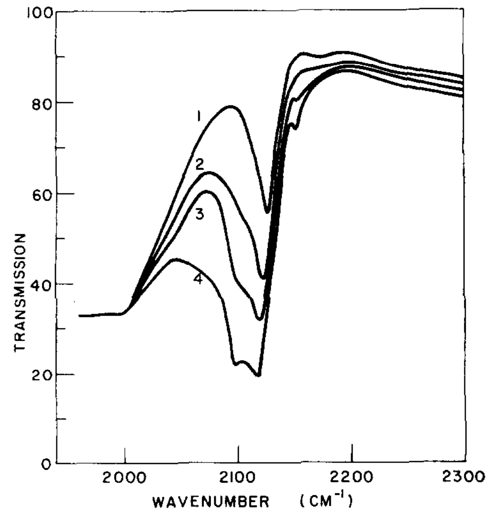

FIG. 5. Adsorption of carbon monoxide on copper (10% copper on Cabosil) at —188°C: 1-4. after successive time intervals with low rate of CO flowing into cell.

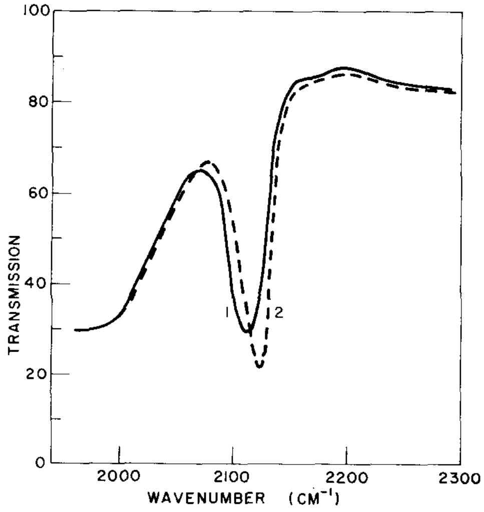

FIG. 6. Effect of hydrogen on carbon monoxide adsorption band (10% copper on Cabosil): 1. after addition and removal of CO at —20°C; 2. after H_2 added at —20°C.

shown in Fig. 5 indicate that there are two bands and suggest that the result of oxygen is to depress one and enhance the other. By pumping alone at room temperature, a "shift" is noticed—the band occurring in the 2120 cm^{-1} region at lowest coverage. It has also been discovered here that hydrogen can cause the same effect as oxygen. This is shown in Fig. 6. The band center moves from 2110 cm^{-1} to 2123 cm^{-1} in this experiment.

In addition to the bands already noted, a weak band at 1420 cm^{-1} has been observed. It has about the same band width as the 2100 cm^{-1} band at room temperature in the presence of CO. Its absorption is about 5% of the 2100 cm^{-1} band. Due to the high absorption of the silica and of the water vapor in the beam path, this band is somewhat uncertain.

IV. THERMODESORPTION RESULTS

Upon heating a surface at a constant rate of temperature rise, adsorbed gas is given off over a range of temperatures, giving a bell-shaped curve. This experiment has been dubbed thermodesorption in a theoretical analysis of the effect (*5*). If the entropy of the activated state is the same as that of the absorbed state, a width of the peak of about 20° at 300°K is obtained for heating rates used here (0.1°C/sec). All of the peaks reported here are much wider than this, indicating either an entropy factor much less than 1 or a spread in activation energies for desorption. It was felt that the latter assumption is more reasonable, especially since many of the peaks show structure. Assuming a normal entropy factor, a reasonable approximate formula relating the activation energy for desorption, E, to the temperature of the thermodesorption peak $T_{\max}$ is,

$$E = 0.07\ T_{\max}$$

where $T_{\max}$ is in °K and E is in kcal/mole. This equation has been used here in calculating activation energies for desorption.

Figure 7 shows the thermodesorption curves for carbon monoxide adsorbed under different conditions. Although the partial pressures obtained were not calibrated in absolute units (maximum pressures were less than 10^{-2} Torr), the three curves in Fig. 7 are all in the same units.

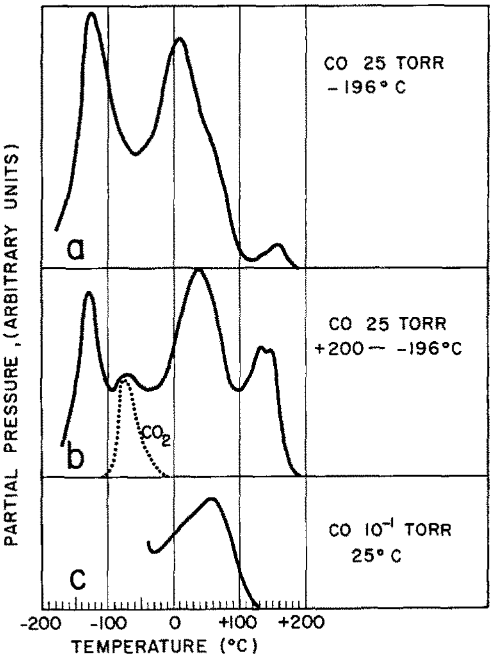

FIG. 7. Thermodesorption of carbon monoxide from reduced copper shot.

These results show two major peaks. The low temperature state desorbs at —130°C which gives an activation energy of about 10 kcal/mole. This peak is broad but shows no definite structure. The other major peak occurs at 10°C, giving an activation energy of about 20 kcal/mole. This peak has a shoulder at higher temperatures.

Adsorption of CO at —196°C is rapid, filling the states that cause both of these peaks. Thus, the activation energy for adsorption is small, and therefore, the activation energy for desorption nearly equals the heat of adsorption. Trapnell (*6*) obtained a heat of adsorption of 9.3 kcal/mole at —70°C, which agrees with the lower temperature thermodesorption peak. Beebe and Wildner (*7*) obtain activation energies, varying with coverage, from 20 to 14 kcal/mole at 0°C; Dell, Stone, and Tiley (*8*) obtained a value of about 17 kcal/mole at

20°C. These values correspond to the high temperature thermodesorption peak.

There is, in addition to these two major peaks, a double thermodesorption peak at about 150°C; this gives an activation energy of 30 kcal. This peak is enhanced by long exposure to high pressure and at high temperatures. This is seen in Fig. 7(b). The high temperature shoulder on the second major peak has grown also, shifting this peak to somewhat higher temperatures. Also, some CO_2 was desorbed during this run. This appears to be due to an impurity in the system (perhaps on the glass) which formed CO_2 which was then adsorbed on the copper. Or it might have been due to oxygen dissolved in the copper which was not completely removed by previous treatments.

Figure 7(c) shows that exposure at low pressures at room temperature does not fill the state which produces the high temperature thermodesorption peak. It fills mainly the state which was only a shoulder in Fig. 7(a). The high temperature state has not been observed in other studies and needs more work to substantiate and characterize it.

If carbon monoxide is let in at −196°C until only a small fraction of the surface is covered, then the thermodesorption curve is the same as that in Fig. 7(c), in that the desorption occurs only in the higher temperature part of the second peak.

V. Discussion

The filled molecular orbitals of carbon monoxide consist *(9)* of an unshared pair on the carbon atom, an unshared pair on the oxygen atom, a σ-bonding orbital, and two π-bonding orbitals. There are also, unfilled, a σ-antibonding orbital and two π-antibonding orbitals. The formation of metal carbonyls consists of donation of electrons from the unshared pair on the carbon atom to the metal plus back-bonding from filled *d* orbitals of the metal to the π-antibonding orbitals on the carbon atom. With electrons placed in the antibonding orbital, the carbon oxygen bond is weakened, and the infrared absorption band is shifted to lower frequencies. This happens both in the metal carbonyls and in adsorption of carbon monoxide on metals which form carbonyls. For the metals with filled *d* shells such as copper, silver, and gold the adsorption of carbon monoxide is much weaker and the shift in frequency is either small as in copper or actually positive as in silver or gold. The infrared bands of carbon monoxide absorbed on gold and silver occur at frequencies of 2174 cm^{-1} and 2182 cm^{-1}, respectively *(10)*, whereas, the fundamental frequency for gaseous carbon monoxide is 2143 cm^{-1} *(11)*.

However, the frequency corresponding to CO^+ is 2184 cm^{-1} *(11)*. It is apparent that the addition of electrons to the carbon monoxide molecule weakens the carbon–oxygen bond while removing electrons from it strengthens the bond. While there are objections *(12)* to treating the shifts in frequency of carbon monoxide on adsorption as due simply to the formation of ions, it is valid to consider this effect as partially responsible for the shifts.

The surface potential of copper or gold becomes more positive upon adsorption of carbon monoxide in contrast to the *d* metals, where it becomes more negative *(13)*. Exposure of copper at −183°C to carbon monoxide results in an increase in surface potential until about one-quarter of the surface is covered, whereupon the surface potential decreases until at a coverage of about one-half (the maximum uptake at low pressure) the surface potential is about one-half of the maximum value. Since the addition of carbon monoxide to copper at −188°C results in new infrared bands appearing as the coverage increases, the decrease in surface potential should be attributed to new species rather than an inductive effect lowering the dipole contribution of all adsorbed molecules. The bond between most chemisorbed molecules and metals is covalent but with an ionic contribution *(14)*. The dipole moment of carbon monoxide is small (0.118 Debye units) *(15)*, indicating that the surface potential due to carbon monoxide adsorption is due to charge transfer between the molecule and the metal.

TABLE 2
ADSORPTION STATES OF CARBON MONOXIDE ON COPPER

State	Infrared frequency (cm^{-1})	Desorption energy from infrared experiment (kcal/mole)	Thermodesorption energy (kcal/mole)	Heat of adsorption (kcal/mole)	Rate of adsorption	Surface potential	Coverage
0	a 2130	6	—	—	—	—	Pressure dependent
(on SiO_2)	b 2150	9	—	—	—	—	
I	a 1990						
	2180						
	2250	9	10	9.3[a]	Fast	−0.16[d]	~1/4[d]
	b 2070	14			at −196°C		
II	a 2100	21		20–14[b]			
			20		Fast	+0.32[d]	~1/4[d]
	b 2120	26		17[c]	at −196°C		
III	—	—	30	—	Slow	—	—

[a] Reference *6*.
[b] Reference *7*.
[c] Reference *8*.
[d] Reference *1*.

Table 2 is an attempt to correlate the results of various experiments. The infrared spectra tend to indicate more detail than is obtained by other measurements. The State III, which is only observed in thermodesorption measurements, may be due to diffusion into small pores of the copper. The surface is definitely roughened by the oxidation-reduction treatment. Both States I and II are complex. Even the thermodesorption results show that State II is made up of overlapping peaks. The infrared results indicate that there are several discrete states rather than a continuous variation in bonding with coverage.

An interesting correlation can be seen from a plot of the frequency shift between gaseous carbon monoxide and adsorbed carbon monoxide versus the heat of adsorption (assuming this equals the activation energy for desorption). This is shown in Fig. 8 and includes both adsorption on copper and silica. It is tempting to assume that the bands at 2120 and 2150 are due to positive ions; those at 2100 and 2130 are due to neutral atoms, and that at 2070 is due to a negative ion. However, the shift from a neutral to a positive ion is 41 cm^{-1} in the gas, whereas, the shift with the adsorbed carbon monoxide is 20 cm^{-1} on both copper and silica. These data should be valuable for a quantum mechanical treatment of carbon monoxide adsorption. The adsorption of carbon monoxide on copper is due to both a donation of electrons plus back bonding into a π orbital. Apparently the several states on copper vary principally in the amount of electron donation. The more firmly bound states are more positively charged and hence show less of a frequency

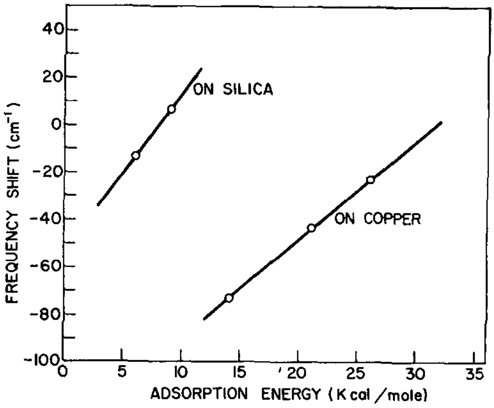

FIG. 8. Frequency shift versus adsorption energy.

shift in the carbon–oxygen bond. Possibly the electrons play the same role in adsorption on silica without the acceptance of electrons into the π orbitals.

The three weak bonds at 1990, 2180, and 2250 suggest some interaction between carbon monoxide molecules. For example, carbon suboxide, which has two C–O units bonded to one carbon atom, has three bands, at 1980, 2190, and 2290 (*16*).

REFERENCES

1. PRITCHARD, J., *Trans. Faraday Soc.* **59,** 437 (1963).

2. KAVTARADZE, N. N., AND SOKOLOVA, N. P., *Dokl. Akad. Nauk. SSSR* **146,** 1367 (1962).

3. MCDONALD, R. S., *J. Phys. Chem.* **62,** 1168 (1958).

4. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catalysis* **10,** 1 (1958).

5. SMITH, A. W., AND ARANOFF, S., *J. Phys. Chem.* **62,** 684 (1958).

6. TRAPNELL, B. M. W., *Proc. Roy. Soc. (London)* **A218,** 566 (1953).

7. BEEBE, R. A., AND WILDNER, E. L., *J. Am. Chem. Soc.* **56,** 642 (1964).

8. DELL, R. M., STONE, F. S., AND TILEY, P. F., *Trans. Faraday Soc.* **49,** 195 (1953).

9. ORGEL, L. E., "An Introduction to Transition Metal Chemistry Ligand Field Theory," p. 135. Methuen, London, 1960.

10. KAVTARADZE, N. N., AND SOKOLOVA, N. P., *Zh. Fiz. Khim.* **36,** 2804 (1962).

11. HERZBERG, G., "Spectra of Diatomic Molecules." D. Van Nostrand Co., Princeton, New Jersey, 1955.

12. LITTLE, L. H., AND AMBERG, C. H., *Can. J. Chem.* **40,** 1997 (1962).

13. SIDDIQI, M. M., AND TOMPKINS, F. C., *Proc. Roy. Soc. (London)* **A268,** 452 (1962).

14. GUNDRY, P. M., AND TOMPKINS, F. C., *Quart. Rev. (London)* **14,** 257 (1960).

15. MCCLELLAN, A. L., "Tables of Experimental Dipole Moments." W. H. Freeman, San Francisco, California, 1963.

16. HERZBERG, G., "Molecular Spectra and Molecular Structure." D. Van Nostrand, New York, 1945.