THE EFFECT OF SURFACE COVERAGE ON THE SPECTRA OF CHEMISORBED CO[1]

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An *in situ* cell was constructed and modifications made in a spectrometer so that the infrared spectra of chemisorbed molecules could be obtained over a wide range of sample temperatures and gas pressures. The effect of varying the surface coverage was studied for carbon monoxide chemisorbed on silica-supported Pd, Ni and Pt. The spectra of carbon monoxide on Ni and Pd showed an increase in the number of bands with increasing surface coverage indicating that these samples were heterogeneous. The changes in the spectra of $C^{12}O$ and $C^{13}O$ on Pt which are observed as the surface coverage is varied are attributed to interaction effects.

Introduction

Many fundamental catalyst studies have been concerned with determining the reason for the generally observed decrease in heat of chemisorption as surface coverage increases. Attempts have been made to explain this phenomenon on the basis of surface heterogeneity,[2] repulsive interactions between adsorbed atoms[3] and changes in work function of the adsorbent surface induced by the adsorbed gas.[4] Observation of the effect of surface coverage on the infrared spectra of chemisorbed carbon monoxide provides a new method of attack on this problem.

Some pertinent information can be obtained from the number of bands in the spectra at a single stage of surface coverage as shown in the original spectra of chemisorbed CO.[5] However, these single stage spectra do not reveal the relative strength of bonding for the chemisorbed CO contributing to each band or the effect of interaction on the band positions. To obtain this information the spectra of chemisorbed CO were studied as a function of surface coverage over silica-supported Pt, Pd and Ni. Isotope shift data were also obtained using chemisorbed $C^{13}O$.

In order to carry out this work efficiently it was necessary to design apparatus in which the infrared spectra could be obtained while the samples were subjected to a wide range of temperatures and pressures. Successful development of this *in situ* apparatus not only makes it possible to study the effect of surface coverage but also opens the way to infrared studies of chemisorbed molecules while reactions are in progress.

Experimental Method

In Situ **Cell.**—The main difficulty in the design of an *in situ* cell is imposed by the limitation that the beam path cannot be obstructed by glass or other materials which are not transparent to infrared radiation. Windows of CaF_2 or other salts which pass infrared radiation in the wave length regions of primary interest must be sealed to the body of the cell. Ideally, this seal should be able to withstand high temperatures so that the entire cell can be baked out to remove residual gases. However, the salt plates crack easily under stress and it is difficult to match the thermal expansion of the salt with that of any material which is suitable for the body of the cell. Because of these difficulties it was necessary to compromise on the design and construct a cell in which the salt-glass seal could be kept cool while the sample was heated.

The *in situ* cell is shown in Fig. 1. It has 50 mm. diameter CaF_2 windows, A, which are sealed to the cell body with glyptal resin. The sample, B, is supported inside a tungsten-wound quartz furnace, C, by a 25 mm. CaF_2 plate, D. A 35 mm. CaF_2 plate is used as a gas convection shield, E, to protect the top window from the hot gases rising from the furnace. The shield is not sealed to the cell so it can expand and contract freely with changes of temperature. The shield is not necessary at pressures lower than one cm. The sample temperature is measured by a Pt–Pt, Rh thermocouple, F, which has its junction, G, in a slot in the CaF_2 plate which supports the sample. The entire furnace can be lowered out of the cell for sample changing by opening the standard taper joint, H, which is sealed with Apiezon W wax, and disconnecting the clamps, L, which hold the heating wire leads, I. The cell is evacuated and gas admitted through J. It is held in place by clamps around J and K. The cell has been used at sample temperatures as high as 540° and it probably could go up to 800°. The CaF_2 windows are cooled with an air jet when the cell is used at high temperatures.

Modification of the Perkin–Elmer Spectrometer.—In the conventional Perkin–Elmer spectrometer the infrared beam travels horizontally when passing through the sample. The horizontal beam is a disadvantage when solid catalyst samples are used because the face of the salt plate holding the sample must be in a vertical position and it is difficult to keep the sample from falling off. Another disadvantage of the conventional spectrometer is that there is only a 4 in. space for the sample cell between the infrared source housing and the monochromator. This is not long enough to accommodate an *in situ* cell which requires that the salt windows be kept cool while the sample is heated.

To overcome these disadvantages a Perkin–Elmer spectrometer equivalent to Model 12C was modified by mounting an additional source unit containing globar, plane mirror and spherical mirror above the spectrometer. The beam travels downward vertically from the spherical mirror in the upper source unit and is focused on the sample at a point approximately midway between the upper and lower source units. A plane mirror making an angle of 45° with the horizontal bedplate of the spectrometer reflects the beam on to the spherical mirror in the lower source unit, after which the beam follows a normal path through the spectrometer. Changes in the optics associated with this modification make it possible to have a space of 10 in. for the *in situ* cell.

Preparation of Samples.—The preparation of samples used in this work was essentially the same as reported in the initial development of the technique for observing the infrared spectra of gases chemisorbed on metals.[5] The metals were dispersed by making pastes from solutions of metal salts and non-porous silica. The pastes were dried at room temperature and pressed manually into a thin layer on a 25 mm. CaF_2 plate. The sample thickness was of the order of 0.012 g./cm.^{2} and the concentration of metal after reduction was 7.4–9.1% by weight.

The CaF_2 plate holding the sample was inserted into the quartz furnace and the cell assembled as shown in Fig. 1. The sample was dried under vacuum at temperatures in the 100–200° range and then reduced in H_2 at 200–350°.

Figure 2 is an electron micrograph of a silica-supported

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[1] This paper was presented at the AAAS Conference on Catalysis and at the Ohio State University Symposium on Molecular Structure and Spectroscopy in June 1955.

[2] H. S. Taylor, THIS JOURNAL, **30**, 145 (1926).

[3] J. K. Roberts, *Proc. Roy. Soc.* (*London*), **A152**, 445 (1935).

[4] M. Boudart, *J. Am. Chem. Soc.*, **74**, 3556 (1952).

[5] R. P. Eischens, W. A. Pliskin and S. A. Francis, *J. Chem. Phys.*, **22**, 1786 (1954).

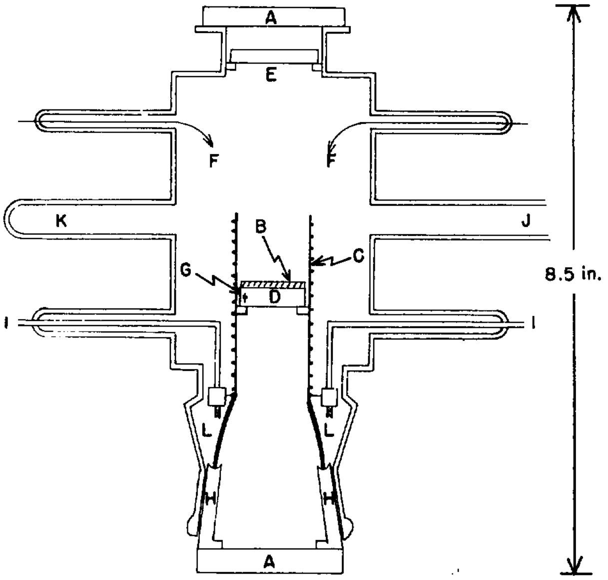

Fig. 1.—*In situ* cell for infrared study of chemisorbed gases.

platinum sample.[6] This shows the platinum particles as dark spots dispersed on the lighter silica. These particles are too small to allow conclusions as to their shape. Direct measurement from the electron micrograph shows that the diameters of these particles fall in the range 40–100 Å. with an average of about 70 Å. Determination of the crystallite size by X-ray line broadening gave values of 80 and 90 Å. in two different trials[7]. At room temperature this sample chemisorbed 16.4 cc. of CO per gram of Pt. This corresponds to one molecule of CO for every seven atoms of Pt in the sample. If it is assumed that this result means that one out of seven Pt atoms is on the surface of the particles the particle size can be calculated. The assigned size will depend on the shape assumed for the particle and the crystal face exposed. If the particle is assumed to be a cube with (100) faces exposed the edge is calculated as 85 Å. Assumption of an octahedron with (111) faces exposed leads to a value of 105 Å. tor the edges. The resolution of the electron microscope is not good enough to distinguish whether the Pt particles are spheres, cubes or octahedra. The agreement between the crystallite size determined by X-ray and the particle size determined by the electron micrograph and chemisorption measurements shows that the particles are single crystals. Single crystals of Pt would be either cubes or octahedra if they were large enough to be well formed. Since it is not known whether single crystals of this size would be well formed it is not possible to come to a firm conclusion regarding the shape of the particles. Extensive work has not been carried out to determine the nature of the Pd and Ni samples. It is assumed that they are similar to the Pt sample in that the metal is concentrated in small particles rather than being evenly distributed on the carrier surface.

The sample preparation is a critical step in obtaining spectra of chemisorbed CO. The basic problem is to obtain a sample which will transmit a usable amount of infrared radiation and which at the same time has sufficient area so that the absorption bands of the chemisorbed CO will be measurable. In the case of non-metallic adsorbents one can often work in a spectral region where the adsorbent is relatively transparent, so that satisfactory spectra can be obtained if the scattering losses are reduced by the use of small particles. However, metals absorb strongly in the infrared region, so there was considerable doubt when the work was started whether it was possible under any circumstances to obtain usable samples. This work has shown that satisfactory spectra can be obtained when metallic particles having dimensions of 100 Å. or less are dispersed in a medium consisting of non-porous spheres of silica having diameters in the 150–200 Å. range.

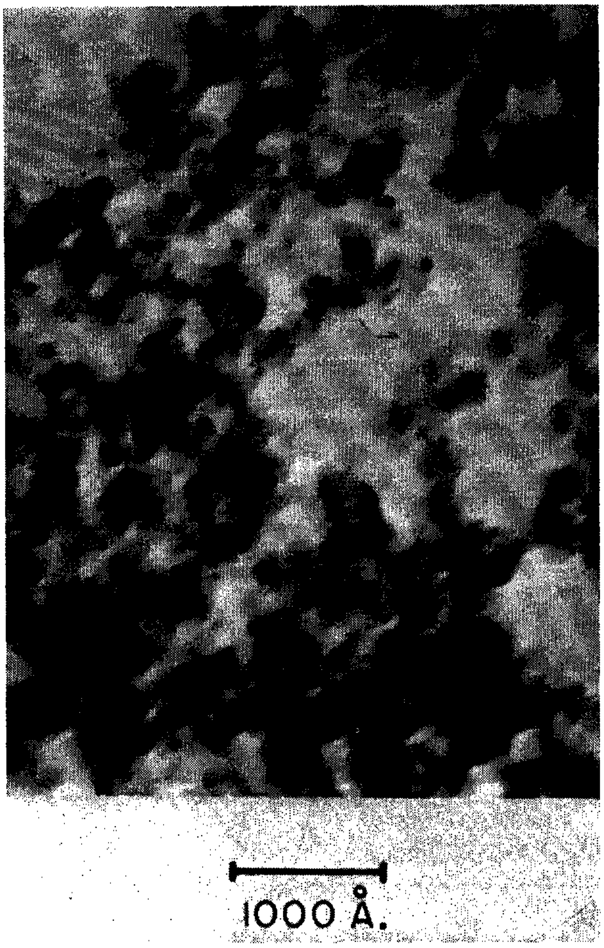

Fig. 2.—Electron micrograph of platinum (9.1 wt. %) on Cab-O-Sil.

Recording of Spectra.—Spectra were obtained in the 2.5–7.5 μ region using a CaF_2 prism. The sample cell was left in the beam at all times and backgrounds were determined on either the oxidized or reduced samples. In most cases conditions were sufficiently stable so that reproducible background spectra could be obtained over a period of several hours, and even days in many cases. For the best samples the transmission near 5 μ with no chemisorbed CO was about 6%, although many samples were studied for which the transmission at this position was as low as 2%. Because of the low transmission of the samples slit widths of about 0.2 mm. were required at 5 μ in order to obtain a signal-to-noise ratio of about 200. The corresponding spectral slit width is about 0.02 μ.

Results and Discussion

Spectra of CO on Pd.—The spectrum of CO on Pd has more than one band and makes possible a study of surface heterogeneity based on the effect of fractional surface coverage, θ, on the rate of growth of the bands. Under equilibrium conditions if all of the bands increase at the same relative rate as θ increases, it would be known that the position of the band was not a function of bonding strength and that the factors which produce a multiple band spectrum are not related to surface heterogeneity. A difference in the growth rate would indicate that the surface was heterogeneous and that the first bands to appear were associated with the most strongly bonded CO. A third possibility is that an increase in θ would produce new bands coupled with the disappearance of bands formed at

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[6] This electron micrograph was obtained by H. M. Allred of this Laboratory.

[7] The X-ray work was done by P. H. Lewis of this Laboratory.

low coverages. This would show that the structure of the chemisorbed CO was a function of θ.

Figure 3 shows the results of experiments designed to determine the effect of θ on the spectrum of CO chemisorbed on Pd at 25°. The general procedure was to add the CO in small batches and determine the spectrum after each addition. Direct determination of θ by addition of measured amounts of CO is not feasible because the dead space, including a volume in a liquid N_2 trap, is nearly 2,000 cc. (S.T.P.) and the sample chemisorbs less than 0.1 cc. Approximate values for the relative amounts of chemisorbed CO represented by each spectrum could be obtained by comparing the total integrated intensities of the bands for each spectrum. This method is not accurate because of interaction effects which influence the intensities of the bands. This factor will be discussed when the spectrum of CO on Pt is considered. Fortunately exact values of θ are not necessary to interpret the results when the spectra are of the type shown in Fig. 3.

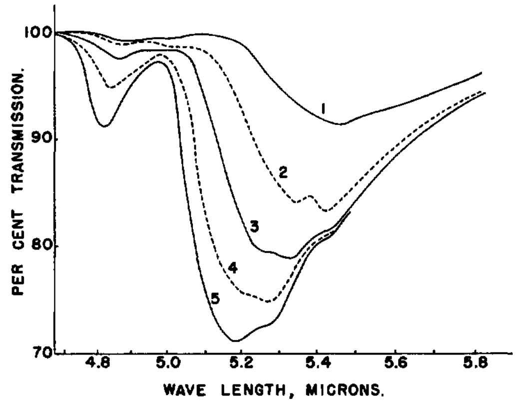

Fig. 3.—Spectra of CO chemisorbed on Pd as influenced by surface coverage with curves numbered according to increasing surface coverage.

Spectrum 1 shows that a band at 5.45 μ is the first to appear. In the second spectrum a band appears at 5.3 μ. New bands at 4.85 and 5.2 μ are evident in the third spectrum. These develop in the fourth and fifth spectra with the 4.85 μ band having proportionally more growth than the 5.2 μ band. Although there is some overlapping, it can be seen that the longer wave length bands are detectable first and in some cases may be complete before the shorter wave length bands are detectable. Evacuation removes the bands in the reverse order of their appearance.

The spectral evidence that the number of bands increases with surface coverage shows that the Pd surface is heterogeneous. This heterogeneity appears to be the type in which the surface is divided into a relatively few portions which differ from each other but which are relatively homogeneous within themselves. On this basis each band represents a homogeneous portion. It is plausible to identify these portions with the major crystal faces.

The spectra in Fig. 3 divide themselves into two parts with the region near 5 μ serving as the dividing line. In the spectra of metal carbonyls bands in the 4.8–5.0 μ region have been attributed to CO bonded through the carbon to single metal atoms. Data are available for carbonyls of nickel,[8] iron,[9,10] cobalt,[11] manganese[12] and rhenium.[12] On this basis it appears that the 4.8–5.0 μ bands in the chemisorption spectra are due to CO bonded to a single surface atom. This structure will be referred to as linear CO. In the case of iron nonacarbonyl,[9] iron tetracarbonyl[10] and dicobaltoctacarbonyl[11] bands are also found in the 5.4–5.5 μ region and are assigned to CO bridged between two metal atoms, so it is reasonable to attribute the 5.4–5.5 μ bands in the chemisorption spectra to bridged CO. There is no previous experience on which to interpret the bands in the 5.0–5.4 μ region but the pattern of change produced by increasing surface coverage suggests that these bands should be assigned to bridged CO rather than to CO bonded to a single metal atom.[5] This interpretation implies that only the band at 4.83 μ in Fig. 3 is due to linear CO. This CO may be adsorbed on the single sites left vacant by the random pairing of the atoms adsorbing bridged CO.

The CO contributing to the 4.83 μ band is weakly held. The spectra in Fig. 3 represent an increase in pressure from 10^{-4} to 0.1 mm. The 4.83 μ band becomes more intense if the pressure is increased further. It is removed immediately if the pressure is reduced to 10^{-4} mm. The spectrum of CO on Pt also has a band near 4.83 μ. The CO contributing to this band is strongly bonded. This shows that the band position for linear CO on different metals is not a measure of the chemisorption bond strength.

The spectra of CO chemisorbed on Pd as well as the spectra discussed later of CO on Ni show that the positions of the bands due to bridged CO are sensitive to bond strength. Spectra of linear CO on Pd, Ni and Pt show little or no sensitivity of band position to bond strength. Since the closest distances between the metal atoms is the same on all major crystal faces of Pd (f.c.c.), the strength of bonding could affect the angle between the two metal–carbon bonds of bridged CO through variation in the length of the metal–carbon bond. There is some previous indication that the band position of bridged CO is sensitive to this angle.[9]

Spectra of CO on Ni.—The effect of decreasing θ on the spectrum of CO on Ni is shown in Fig. 4. Spectrum 1 was obtained at room temperature at a pressure of 0.1 mm., spectrum 2 after pumping at 10^{-4} mm. for 12 minutes and 3 after 2 hours and 25 minutes. When the pump-off rate at 25° became inconveniently slow the temperature was increased to 100° for 4 and 150° for 5.

The 5.0 μ region serves as a dividing line between bands due to linear and bridged CO as was observed with CO on Pd. The longer wave length bridged CO is the most strongly held. Spectrum 5 shows evidence of two bands in the short wave length region (<5.0 μ). In spectrum 1 the band at 4.82 μ

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(8) B. L. Crawford, Jr., and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938).

(9) R. K. Sheline and K. S. Pitzer, *J. Am. Chem. Soc.*, **72**, 1107 (1950).

(10) R. K. Sheline, *ibid.*, **73**, 1615 (1951).

(11) J. W. Cable, R. S. Nyholm and R. K. Sheline, *ibid.*, **76**, 3373 (1954).

(12) E. O. Brumm, M. A. Lynch, Jr., and W. Sesny, *ibid.*, **76**, 3831 (1954).

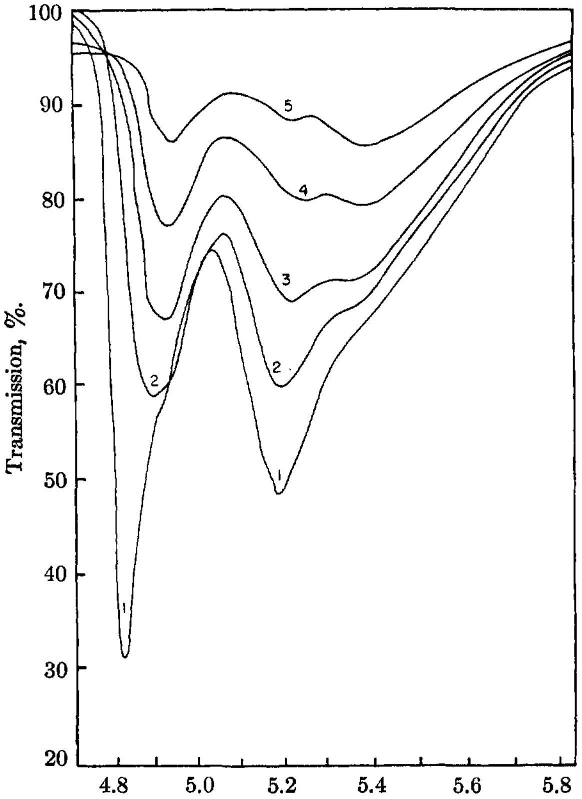

Fig. 4.—Effect of prolonged evacuation on spectra of CO chemisorbed on Ni with curves numbered according to decreasing surface coverage.

is the most intense while the 4.90 μ band is most intense at lower coverages. Addition of $Ni(CO)_4$ to the system produced a sharp band at 4.85_3 μ so neither of the two bands can be accounted for by assuming that nickel carbonyl was present on the surface. This point is substantiated by the fact that any nickel carbonyl which may have been formed would be expected to be frozen into the adjacent liquid nitrogen trap. The possibility that the 4.90 μ band results from a single CO on a Ni atom while the 4.82 band is due to more than one CO on a single atom was considered. Evidence for this would be provided if the 4.90 μ band increased with decreasing coverage. There is an indication that the 4.90 μ band is more intense in spectrum 2 than in spectrum 1. However, the bands are too close together to warrant a firm conclusion on this point so the possibility that the short wave length bands are sensitive to the strength of bonding cannot be ruled out in this case.

As the CO was removed by pumping at 100° a new band appeared at 4.56 μ. This band increased at 150° and disappeared at 300°. The significance of this band has not been established. High temperature work with CO on Ni is complicated by the fact that the Ni may be oxidized or carbided.

The evidence concerning surface heterogeneity indicated by the effect of θ on the spectrum of CO chemisorbed on Ni apparently is subject to the interpretation previously discussed for CO on Pd. It should be noted that the bands in Figs. 3 and 4 show a slight shift to shorter wave lengths as the amount of CO on the surface is increased. This shift is attributed to interaction effects which will be discussed in connection with the spectrum of CO on Pt.

Spectra of CO on Pt.—The method of studying surface heterogeneity which was used for Pd and Ni is not applicable to Pt because the spectrum of CO on Pt has only one intense band and this band is in the short wave length region. Since it cannot be assumed that the wave length positions of bands due to linear CO are sensitive to variations in bond strength, no conclusion regarding the heterogeneity of the Pt is warranted from the fact that the spectrum shows only a single sharp band. To circumvent this difficulty surface coverage experiments were conducted with a mixture of $C^{12}O$ and $C^{13}O$ on the theory that the isotope shift (the displacement of the band caused by substitution of C^{13} for C^{12}) would provide information pertinent to the surface heterogeneity problem.

Figure 5 shows the spectrum of a chemisorbed mixture of $C^{12}O$ and $C^{13}O$ (ratio 1.7:1) at 25° with a pressure of 2 mm. It is assumed that under these conditions the Pt surface is fully covered with chemisorbed carbon monoxide. This assumption will be discussed later. The band near 4.82 μ is due to linear $C^{12}O$ and the band at 4.97 μ is due to the corresponding structure for $C^{13}O$. There were no other bands although in some Pt samples a band near 5.4 μ, attributed to bridged CO, has been observed.[5]

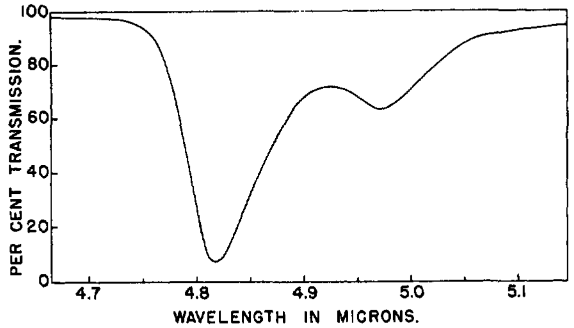

Fig. 5.—Spectrum of $C^{12}O$ and $C^{13}O$ chemisorbed on platinum.

It was expected that the isotope shift data would make possible the calculation of force constants for the metal–carbon and carbon–oxygen bonds. The force constant measures the resistance of the bond to change in length from its equilibrium value and an increase in the force constant is associated with an increase in bond strength. A theoretical treatment of the vibrations of the metal–C–O system was carried out. In this treatment it was assumed that the system was comparable to a linear XYZ type molecule,[13] but the mass of the metal was assumed to be infinitely large. Only the stretching vibrations were considered and interactions between the M–C and the C–O bonds were neglected. Theoretically the results of these calculations make it possible to relate the force constants to the ratio of the wave length positions of the chemisorbed $C^{13}O$ and $C^{12}O$. These relations for the case where the chemisorbed $C^{12}O$ band is near

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(13) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co. Inc., New York, N. Y., p. 173.

Table I

Effect of Pumping on the $C^{12}O$ and $C^{13}O$ Bands of Carbon Monoxide

Total time,[a] hr.	Band positions, μ		Isotope shift ratio	Absorbance[b]		Ratio of absorbances[c]	θ[d]
	$C^{12}O$	$C^{13}O$		$C^{12}O$	$C^{13}O$		
0	4.842[e]	5.023	1.037	1.334	0.164	8.1	1.00
0.07	4.855	5.019	1.034	1.112	.188	5.8	0.93
0.83	4.871	5.019	1.030	0.826	.203	4.1	.77
2.0	4.875	5.018	1.029	.748	.206	3.6	.72
5.5	4.880	5.019	1.029	.637	.200	3.2	.66
9.1	4.884	5.022	1.028	.559	.185	3.0	.58
12.7	4.887	5.023	1.028	.498	.173	2.9	.52
21.2	4.889	5.021	1.027	.392	.149	2.6	.40
26.5	4.893	5.022	1.026	.318	.128	2.5	.32
29.9	4.893	5.019	1.026	.290	.117	2.5	.30
36.5	4.897	5.019	1.025	.231	.101	2.3	.24
45.5	4.896	5.017	1.025	.177	.078	2.3	.18
51.9	4.895	5.022	1.026	.139	.062	2.2	.14

[a] Cumulative pump-off time at 200° and 10^{-4} mm. pressure. At zero time CO pressure was 2 mm. [b] Absorbance = log transmission of background/transmission of sample. [c] Actual ratio of $C^{12}O$ to $C^{13}O$ was 1.7/l. [d] Values of θ were determined from a separate experiment in which the CO was burned off with O_2. [e] The reason for the 0.02 μ difference in this value of the wave length for the $C^{12}O$ band at full coverage and those shown in Figs. 5 and 8 has not been established.

4.83 μ, as is true when Pt is the adsorbent, are shown in Fig. 6. Although calculated for the 4.83 μ band these curves may be used over the range in position of this band which is observed experimentally for Pt without markedly affecting the conclusions. On the basis of the curves in Fig. 6 it would be expected that the isotope shift ratio would increase with increasing strength of bonding between the carbon monoxide and the Pt.

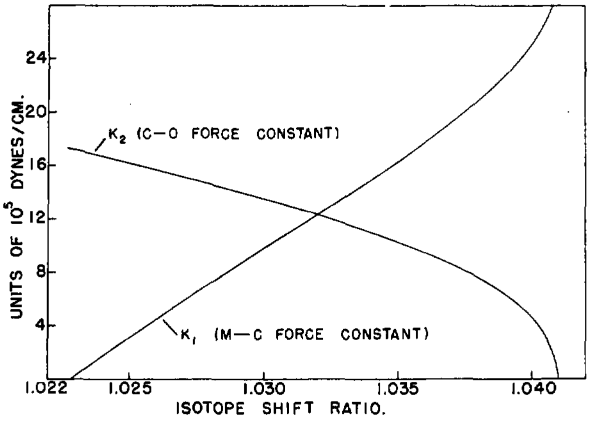

Fig. 6.—Calculated relations between force constants and isotope shift ratio for a 4.83 μ band of $C^{12}O$ chemisorbed on metals.

Table I gives the results of an experiment in which a chemisorbed mixture of $C^{12}O$ and $C^{13}O$ was pumped off at 200° over a period of two days. The following observations can be made from these data.

1. Initially the absorbance ratio for the $C^{12}O$ and $C^{13}O$ bands is much larger than the actual ratio of the numbers of $C^{12}O$ and $C^{13}O$ molecules. The ratio decreases with decreasing coverages to a value of 2.2 which is only slightly higher than the actual ratio of 1.7.
2. The absorbance of the $C^{12}O$ band decreases with time with the most rapid change occurring during the first five hours.
3. The absorbance of the $C^{13}O$ band increases during the first five hours and then decreases for the rest of the experiment.
4. The isotope shift ratio decreases rapidly during the first five hours and then decreases slowly. The isotope shift changes are due to an increase in the wave length of the $C^{12}O$ band—the $C^{13}O$ band position remains constant, within the limits of experimental accuracy, during the entire experiment. The isotope shift value for low surface coverage is about 1.026.

The artificially high initial ratio of the absorbance, the increase in the absorbance for the $C^{13}O$, and the decrease in the isotope shift ratio show that it is not possible to treat the Pt–C–O system as an ordinary molecule as was done in the calculations leading to Fig. 6. Evidently it is the inability to assess the influence of the adsorbed molecules on each other that invalidates this approach. Despite the fact that the data in Fig. 6 cannot be used directly they are of critical importance in showing that the changes in the spectra of CO on Pt produced by varying θ are due to interaction effects rather than to surface heterogeneity.

If it is assumed that the interaction effects are negligible at low values of θ, Fig. 6 can be used to determine the order of the Pt–C and the C–O bonds. An isotope shift ratio of 1.026 indicates force constants of 4.5 × 10^5 dynes/cm. for the Pt–C bond and 16 × 10^5 dynes/cm. for the C–O bond. These values correspond to a single bond between the platinum and carbon and a triple bond between the carbon and oxygen.

Figure 7 shows kinetic data for the removal of chemisorbed CO from Pt at 10^{-4} mm. and 200°. The absorbances (log scale) for the $C^{12}O$ and $C^{13}O$ bands are plotted as a function of the pump-off time. After five hours good straight lines are obtained. If it is assumed that over the linear portion the absorbance is directly proportional to the amount of chemisorbed CO, this part of the curve indicates that the removal of chemisorbed CO follows the simple first-order rate law.

The deviation from the straight line could be due solely to changes in absorbance per molecule or to this effect plus an initially high rate of pump-off. Therefore Fig. 7 by itself is not sufficient to determine the range of θ over which the simple first-order rate law is followed.

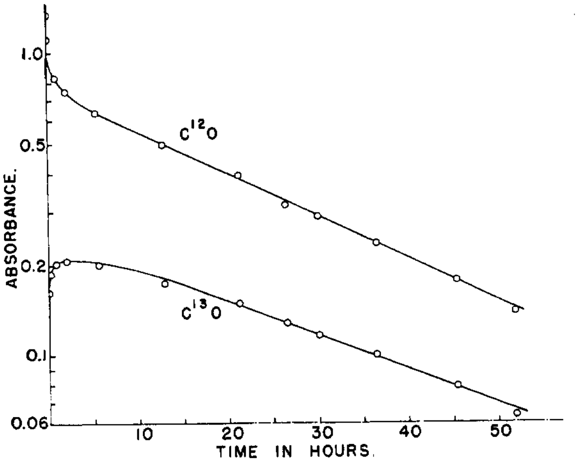

Fig. 7.—Effect of pumping time at 200° on the absorbance (log scale) of $C^{12}O$ and $C^{13}O$ chemisorbed on platinum.

In order to get values for the absorbance and wave length positions of the bands as a function of θ, experiments were conducted in which the chemisorbed CO was removed by oxidation rather than by pumping. This was done by starting at full coverage and adding small batches of O_2 to convert the chemisorbed CO to CO_2 which could be removed from the system by freezing into a liquid nitrogen trap. After a batch of O_2 was added the reaction was followed with a thermocouple gage until the pressure fell to the level observed before the addition. The spectra were recorded after the reaction was complete. At 200° it required less than a minute to consume batches of O_2 sufficient to oxidize 10% of a monolayer.

Determination of the position and intensity of the bands corresponding to full coverage was a critical factor in this experiment. At 25° the band was not sensitive to pressure in the range 2 to 10^{-4} mm. From this it was assumed that complete coverage was attained at this temperature. In order to reach the state of full coverage it was necessary to expose the sample to a pressure of 2 mm. of CO at 200° for $^1/_2$ hour in order to ensure removal of chemisorbed O_2. After this treatment the temperature was lowered to 25° and the gaseous CO pumped off at 10^{-4} mm. The apparatus was then closed off and the temperature brought back up to the oxidation temperature. The increase in temperature decreased the band intensity and increased the gas pressure. The first batch of O_2 was evidently consumed in oxidizing the gaseous CO since the pressure was decreased to the pump-off value and there was no change in the band. This shows that at least 10% of the chemisorbed monolayer was desorbed while increasing the temperature from 25 to 200°.

Figure 8 shows the results of oxidation experiments at 200° in which normal CO was removed. In the first run the absorbances are indicated by triangles and the wave lengths by squares. In the second run the absorbances are indicated by filled circles and the wave lengths by open circles. The differences between these two runs will be discussed later. The wave length for the $C^{12}O$ band is shown on the right ordinate and the absorbance on the left. The horizontal portions of the curves starting at $\theta = 1$ result from the fact that the part of the monolayer which has been desorbed in raising the temperature from 25 to 200° remains in the system. The curve is horizontal because the amount of chemisorbed CO does not change while the gaseous CO is being oxidized.

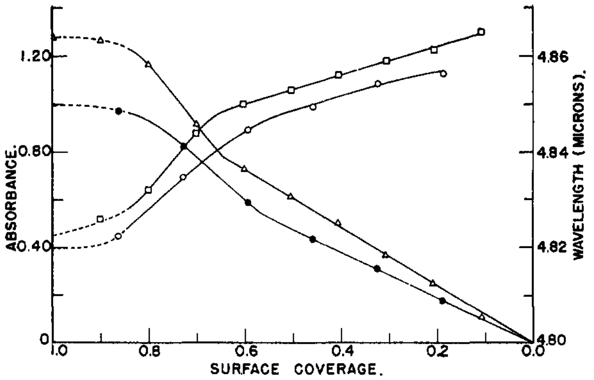

Fig. 8.—Effect of surface coverage on the absorbance and wave length of $C^{12}O$ chemisorbed on platinum.

After the gaseous CO is used up, further addition of O_2 decreases the amount of chemisorbed CO. The θ values were calculated from the amount of O_2 required to remove the chemisorbed CO. It was assumed that no oxygen was permanently chemisorbed until the CO was removed. This assumption was based on the consideration that oxygen and CO could not be chemisorbed at the same time in an equilibrium state while the CO_2 was being removed from the system. In following the reaction by observation of the band intensities it was found that the decrease in intensity coincided with the decrease in pressure as measured by the thermocouple gage. There was no evidence for changes in band intensity after reaching the minimum pressure. This shows that the oxygen is not rapidly chemisorbed followed by a slow reaction between chemisorbed oxygen and chemisorbed CO. Attempts were made to follow the band intensity as a function of time after addition of O_2. At 200° the reaction was complete in a few seconds and was too fast to be followed quantitatively. A qualitative conclusion from this aspect of the work was that the reaction is slightly slower in the ranges $\theta =$ 1.0–0.8 and 0.2–0 than it is in the middle range.

In Fig. 8 the absorbances and wave lengths are not a linear function of θ and the absorbance per molecule of adsorbed $C^{12}O$ is markedly increased above $\theta = 0.65$. This shows that at least part of the deviation from linearity in Fig. 7 is due to the increased absorbance per molecule of $C^{12}O$. When the absorbance values for a curve similar to Fig. 8, obtained by oxidation of the $C^{12}O$–$C^{13}O$ mixture, are applied to Fig. 7 it is concluded that the linear portion extends from a maximum of about $\theta =$ 0.66 down to $\theta = 0.1$ (measurements below $\theta = 0.1$ are not reliable because of the small intensity of the bands).

By combining the information obtained from Figs. 7 and 8 it has been established that at least part of the deviation from linearity in Fig. 7 is due to a variation in the absorbance values. Further consideration leads to the conclusion that this is not the only factor and that an initially high rate of pump-off is also important. This can be shown by plotting the logarithm of the θ values shown in Table I against the pump-off time. This curve is linear from the lowest coverages measured up to $\theta = 0.78$. The slope is much larger from $\theta = 0.78$ to $\theta = 1$. It is plausible to assume that the initial pump-off is high because the interaction effects are repulsive. Further study is required to determine the significance of the fact that the break in the absorbance *vs.* θ curve occurs near $\theta = 0.66$ while the break in the log θ *vs.* pump-off time occurs near $\theta = 0.78$.

Figure 8 presents data from two oxidation experiments which were run over the same sample. In order to explain the difference between these runs it is necessary to consider the sequence in which experiments were conducted on this sample. After the pump-off of the chemisorbed $C^{12}O$–$C^{13}O$ mixture at 200° (Fig. 7) the next experiment was an oxidation of the $C^{12}O$–$C^{13}O$ mixture at 200°. This was followed by the oxidation of normal CO at 200° which produced the curves indicated by the squares and triangles in Fig. 8. At this point an investigation of the effect of oxidation temperature was undertaken. Oxidation runs were carried out at 150, 175 and 250°. After the 250° run the sample which formerly chemisorbed 0.11 (S.T.P.) cc. of CO, as calculated from the amount of O_2 required to oxidize it, chemisorbed only 0.08 cc. The run indicated by the circles and filled circles in Fig. 8 was conducted after the 250° oxidation. Apparently oxidation at 250° produced a change in the Pt sample. It is unlikely that 250° would be high enough to affect the Pt and it is more reasonable to assume that the increased rate of oxidation caused localized overheating which was not indicated by the thermocouple.

The two runs in Fig. 8 follow the same general pattern. However, it appears that the break occurs at a lower value of θ (0.6 or 0.55) in the second run. If the decrease in the amount of chemisorbed CO from 0.11 cc. to 0.08 cc. was not accompanied by a decrease in Pt area so that the decrease of 0.03 cc. was due to leaving part of the surface uncovered, the break would shift to higher values of θ. This makes it appear that the decrease in the amount of chemisorbed CO is accompanied by a decrease in the Pt area, perhaps by redistribution of the exposed crystal faces.

The evidence presented here shows that the unusual spectral changes produced by changes in θ are due to interactions between chemisorbed molecules. These interactions produced changes in the wave length positions of the absorption bands and in the absorbance per molecule. These effects are most pronounced at values of $\theta > 0.66$. At coverages less than $\theta = 0.66$ interactions are also present but the effects are smaller in magnitude. Evidence for this is furnished by the changes in wave length position of the $C^{12}O$ band in Table I and in Fig. 8 and by changes in the $C^{12}O$–$C^{13}O$ absorbance ratio in Table I.

The fact that the interactions are most important at large values of θ indicates that they are not of the type which would result from changes in the work function of the surface.[4] It is believed that they are of a type which can be expressed by the introduction of an interaction term between adjacent CO molecules in the potential energy expression.[14] This results in the coupling of the motions of adjacent molecules. In the case of two $C^{12}O$ molecules the results would be two new vibrational modes with the molecules vibrating in-phase in the high frequency mode and out-of-phase in the low frequency mode. Only the high frequency mode would be capable of absorbing infrared radiation. In the case of one $C^{12}O$ and one $C^{13}O$ molecule the coupling is less effective since their zero-order frequencies are different. The new modes would be an in-phase mode involving predominantly $C^{12}O$ at the higher frequency and an out-of-phase mode involving predominantly $C^{13}O$ at a lower frequency. The in-phase mode will have the higher intensity. It is believed that this type of picture can explain the effects of surface coverage on the spectra of CO on Pt and that these effects predominate over any surface heterogeneity effects. This type of interaction is expected to be most important at large values of θ. Experiments are planned in which the ratio of $C^{12}O$ and $C^{13}O$ will be varied over a wide range in order to test this hypothesis more fully.

Conclusions

The work reported here was designed to determine the relative importance of surface heterogeneity, interaction between adjacent molecules, and changes in the work function of the surface by a study of the infrared spectra of chemisorbed CO as a function of surface coverage. As a corollary to the stated objective the utility of the infrared technique as a tool for the study of metal surfaces was being evaluated.

The increase in the number of bands in the spectra of CO on Pd and Ni with increasing surface coverage shows that these samples are heterogeneous. However, there is no evidence for the type of heterogeneity which would result from a continuous distribution of bonding energies over the surface sites. The heterogeneity indicated by the spectra of CO on these metals is that in which the surface is divided into two or three major components which must be considered individually in the distribution of sites. Each component is subject to interaction effects. This behavior is similar to that expected from the exposure of more than one crystal face.

There is no evidence of either type of heterogeneity for the Pt sample. The changes in the spectra of chemisorbed CO observed upon variation of the surface coverage are due solely to interaction effects. These interactions are between adjacent adsorbed molecules since the effects are largest at large values of θ. There is no evidence for interaction effects of the type associated with changes in the work function of the surface.

In evaluating the infrared technique as a tool for studying the nature of metal surfaces it is evident that it has produced evidence which is novel and

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[14] A similar explanation has been used by Decius for the effects of isotope substitution on the spectra of certain crystals: J. C. Decius, *J. Chem. Phys.*, **22**, 1941 (1954); **22**, 1946 (1954).

informative. In some respects the evidence is conclusive and in others conflicting. Despite the latter difficulty it is clear that this technique will prove to be extremely important in the study of adsorption and catalysis.

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THE RELATIONSHIP BETWEEN ADSORPTION KINETICS AND THE DEFECT SOLID STATE

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Whereas, the qualitative relationship between defect structure and catalysis is becoming more widely accepted, the fundamental problems which exist in establishing any exact correlation are not generally appreciated. An attempt is made to assess those relationships obtained at the surface of an oxide during adsorption and desorption of oxygen. Kinetics are developed and ambiguities discussed and assessed. The method of developing detailed kinetics from a study of variations in semi-conductivity is demonstrated.

Introduction

The early observations of the effect of the adsorption of gases on the semiconductivity of certain systems described by Dubar[1,2] have been extended to a systematic study of adsorption kinetics on various systems in the work of Gray and co-workers.[3–10] Other groups, particularly that of Anderson,[11–14] have studied similar effects, although not from the aspect of a kinetic study.

In developing the kinetic relationships certain fundamentals must be considered and it is at this stage that an initial difficulty of interpretation arises.

From the current theories relating to impurity semi-conduction it would appear that there should exist a relationship between the number of additional defects produced or destroyed in a semi-conducting medium during the adsorption of gas of suitable characteristics. From a statistical consideration it may be deduced that in a generalized form the number of free current carriers is related to the number of defects as

$$\frac{n(N - N_e + n)}{N_e - n} = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{-E/kT} \qquad (1)$$

after de Boer and van Geel[15] and Nijboer[16] where

n = no. of free electrons (carriers) excited into the conduction band at temp. T
N = no. of impurity levels in volume V
N_e = no. of electrons
E = the energy required to raise an electron from an impurity level to the conduction band
m, k and h have their usual significance

This is the generalized expression for a real crystal in which one may expect to find defects frozen into the lattice so that the number of defects exceeds the number of electrons. In the idealized case where $N = N_e$ then the expression reduces to

$$\frac{n}{\sqrt{N - n}} = (2)\ V^{1/2} \left\{\left(\frac{2\pi mkT}{h^2}\right)\right\}^{3/4} e^{-E/2kT} \qquad (2)$$

the factor (2) being introduced to cover the exigency of an impurity level containing paired electrons. Now if $n << N$ we have

$$\frac{n}{V} = (2)\ \sqrt{\frac{N}{V}} \left\{\frac{2\pi mkT}{h^2}\right\}^{3/4} e^{-E/2kT} \qquad (3)$$

which is the conventional Fowler–Wilson[17] expression.

If, however, the case of real crystals is considered and the same assumption is made that $n << N_e$ there are two limiting possibilities according as $n << N - N_e$ or $n >> N - N_e$. If $n << N - N_e$ we have approximately

$$n = \frac{N_e}{N - N_e} V \left\{\frac{2\pi mkT}{h^2}\right\}^{3/2} e^{-E/kT} \qquad (4)$$

while if $n >> N - N_e$

$$n = \sqrt{N_e V} \left\{\frac{2\pi mkT}{h^2}\right\}^{3/4} e^{-E/2kT} \qquad (5)$$

From this it might be deduced that at T_c for $n = n - N_e$ there would be expected to be a change in slope of the log σ against $1/T$ plot of two.

However, the complexity does not end here since there is the ambiguity as to the state of degeneracy. In the case of a large number of impurity centers (of the order 0.1%) it would be anticipated that ionization was considerable so that the assumption $n << N_e$ no longer holds. In this case a direct proportionality will exist at any given temperature be-

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