

J. H. DE BOER (The Hague, Netherlands). I quite agree with Dr. Czanderna when he says that silver oxide cannot be made from silver layers and oxygen by a thermal method. My own experience before World War II, if I remember well, is that a glow discharge in dilute oxygen oxidizes a silver layer to Ag_2O , while a treatment with ozone results in the formation of higher silver oxides, probably a mixture of Ag_3O and AgO .

R. A. VAN NORDSTRAND (Sinclair Research, Houston). On what grounds did you decide that the oxygen prefers to adsorb onto a tetrahedral site?

A. W. CZANDERNA. As far as I know this possibility has not been considered before for the adsorption of oxygen on silver and certainly is entitled to further justification. The preference for the adsorption of oxygen at the tetrahedral hole forming a quasi-surface compound " Ag_3O " was reached as follows: oxygen adsorption at these temperatures is dissociative and has a low activation energy which is typical of many metals. Yet, it is ap-

parent from the low temperature adsorption that the coverage of the surface with oxygen atoms is rate-limited. This is most probably because of a limited number of primary adsorption sites. It is not possible to account for the low coverage ($\theta = 0.45$) at low temperatures unless at least three silver atoms are bound to one oxygen atom. In fact, if all the silver atoms of the surface are assumed to be close-packed (ref. 20 of the paper), uniform coverage with atom ions at $\theta = 0.45$ (Fig. 10-12) would correspond to a true θ of 0.33 which would be the Ag_3O that has been proposed. While this quantitative agreement may be fortuitous, the assumptions made for the calculation do not appear to be wildly speculative because of the way the reproducible surface was prepared and the known repulsions of surface ions. Finally, oxygen atoms in Ag_2O occupy a position equivalent to the tetrahedral hole of three close-packed silver atoms, which means that this must be a preferred arrangement. The " Ag_3O " thus could also represent the simplest nucleus for the growth of Ag_2O on a silver surface when oxygen pressures are reached that make this thermodynamically feasible.

Molecular Orbital View of Chemisorbed Carbon Monoxide

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Carbon monoxide chemisorbed on metals is considered in the light of Hückel molecular orbitals for the metal-carbon-oxygen bonds. The Hückel molecular orbitals predict the existence of a partially filled π -molecular orbital which increases the metal-carbon bond strength but decreases the carbon-oxygen bond strength. In this model only effects in the π -bonding system are considered; *i.e.*, the σ -bonds are assumed constant. This model qualitatively explains: (1) the occurrence of several carbon-oxygen stretching frequencies in the infrared spectra of CO adsorbed on metals; (2) differences in spectra of CO adsorbed on evaporated and supported metals; (3) infrared band positions as a function of coverage; (4) the effect of adsorbing other gases in addition to previously chemisorbed CO; and (5) band shifts in going from adsorption on pure Ni to a Ni-Cu alloy.

Introduction

Recently, there has been accumulating a body of literature dealing with the infrared spectra of carbon monoxide adsorbed on metals. The carbon-oxygen stretching frequency for chemisorbed carbon monoxide has been observed from above 2100 cm^{-1} down to 1800 cm^{-1} . As a variety of adsorption parameters

are varied, the observed infrared bands shift their positions. For example, it has been observed that (1) the carbon-oxygen stretching frequency consistently shifts to higher wave numbers as the fractional surface coverage increases¹⁻⁴; (2) the relative intensities of bands for carbon monoxide on evaporated and supported films are different^{5,6}; (3) adsorption of

other gases after carbon monoxide shifts the observed band positions.¹ These and other phenomena have received scant explanation and certainly no over-all view of the nature of the metal-carbon-oxygen bonding system has been presented and used to attempt to explain or correlate these phenomena.

The principal structural conclusion drawn, first by Eischens and co-workers² and subsequently by other workers, from the observed spectra in the 5000 to 1400-cm.⁻¹ region was that bands above 2000 cm.⁻¹ represented a linear metal-carbon-oxygen system, while bands below about 1960 cm.⁻¹ were due to a bridge structure in which the carbon atom is bonded to two nickel atoms on the surface. These conclusions were based on a comparison to the spectra of a few carbonyls which give bands above 2000 cm.⁻¹ for linear metal-carbon-oxygen groups while Fe₂(CO)₉, which contains bridge carbonyl groups, gives a band⁷ at 1828 cm.⁻¹. However, Cotton and Kraihanzel^{8,9} have shown that in substituted carbonyls a linear metal-carbon oxygen system can have carbon-oxygen stretching frequencies down to 1800 cm.⁻¹. Thus the original correlation suggesting the bridge structure is not entirely valid. Recently, work in this laboratory has shown⁶ that for carbon monoxide chemisorbed on nickel the infrared spectrum over the entire range from 5000 to 300 cm.⁻¹ does not support the bridge structure. If it is assumed, as we do, that all of the carbon monoxide is adsorbed in the linear structure, the problem of explaining the various carbon-oxygen stretching frequencies for the one structure remains.

It is proposed that a simple molecular orbital view of the nature of the metal-carbon-oxygen bond will go a long way in at least qualitatively explaining and correlating the observed band positions and the few observations that have been made on intensities.

Theory

The general molecular orbital approach to bonding in carbonyls as given by Orgel,^{10,11} Ballhausen,¹² and Richardson¹³ is adopted and herein adapted to chemisorbed carbon monoxide. The bonding in an isolated carbon monoxide molecule is regarded¹⁴ as resulting from an sp₂-hybrid orbital of the carbon atom combining with the p_z-orbital of the oxygen to produce a σ -bond while the p_x- and p_y-orbitals of the carbon and oxygen atoms combine to produce two π -bonds. This leaves a lone pair of electrons on the oxygen 2s-orbital and a lone pair in a carbon sp₂-hybrid orbital, which can form a coordinate bond in a complex with a suitable acceptor orbital such as a d-orbital on a metal atom. This forms a σ -bond between the carbon atom and the metal atom. Since the formation of only

this σ -bond puts a large formal negative charge on the central metal atom it is usually stated that back donation from a metal d-orbital to the antibonding π^* -molecular orbital on the carbon monoxide ligand occurs to remove this excess negative charge and stabilize the bond. This statement about the π -bonding between the metal and the ligand seems a bit misleading in that at first glance it implies the placement of electrons in a high energy antibonding orbital. However, formation of simple Hückel molecular orbitals indicates that the molecular orbitals into which these electrons go are lower in energy than the metal d-orbitals.

The π -molecular orbitals are formed by combining a metal d-orbital labeled X_1 , carbon p-orbital labeled X_2 , and an oxygen p-orbital labeled X_3 . Following suggestions in Streitwieser¹⁵ based on the electronegativities of the atoms involved, the integrals are assigned values $H_{11} = \alpha - \beta$, $H_{22} = \alpha$, $H_{33} = \alpha + \beta$, $H_{12} = \beta$, $H_{23} = \beta$. Solution of the secular equation gives energies $E_1 = \alpha + 1.7\beta$, $E_2 = \alpha$, and $E_3 = \alpha - 1.7\beta$ corresponding to wave functions $\psi_1 = 0.21X_1 + 0.58X_2 + 0.79X_3$, $\psi_2 = 0.58X_1 + 0.58X_2 - 0.58X_3$, and $\psi_3 = 0.76X_1 - 0.56X_2 + 0.20X_3$. Since α and β are both negative numbers, $E_1 < E_2 < E_3$. The wave function for the lowest orbital places most of the charge on the carbon and oxygen atoms and adds to the bond strengths for both the carbon-oxygen and metal-carbon bonds. However, the second orbital, whose energy indicates that it is lower in energy than a metal d-orbital, is bonding for the metal-carbon bond but antibonding for the carbon-oxygen bond, since the wave function has a node between the carbon and oxy-

(1) R. P. Eischens and W. A. Pliskin, *Advan. Catalysis*, **10**, 1 (1958).

(2) R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.*, **60**, 194 (1956).

(3) C. E. O'Neill and D. J. C. Yates, *ibid.*, **65**, 901 (1961).

(4) C. W. Garland, *ibid.*, **63**, 1423 (1959).

(5) L. D. Neff, M.S. Thesis, University of Arkansas, 1962.

(6) G. Blyholder, Paper I-38, Proceedings of the Third International Congress on Catalysis, Amsterdam, 1964, North-Holland Publishing Co., Amsterdam.

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

(8) F. A. Cotton and C. S. Kraihanzel, *ibid.*, **84**, 4432 (1962).

(9) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(10) L. E. Orgel, "Transition Metal Chemistry," Methuen and Co. Ltd., London, 1950.

(11) L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(13) J. W. Richardson, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960.

(14) C. A. Coulson, "Valence," Oxford, New York, N. Y., 1952.

(15) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

gen atoms. A count of the electrons available indicates that this second π -molecular orbital would not be filled. In making this count, for example, for $\text{Cr}(\text{CO})_6$, it is assumed that each ligand forms a low energy σ -bonding orbital which is filled and a σ^* -antibonding orbital which is empty. To aid in counting, the electrons may be assumed distinguishable and the electrons originally in the carbon lone-pair orbital are placed in the σ -bond. The π -orbitals labeled ψ_1 , of which there are two for each ligand, one in the x -plane and one in the y -plane if the z -axis is the bonding axis, are all just filled by the electrons originally in the π -orbitals of the carbon monoxide ligands. This leaves the six electrons originally in the outer shell of the chromium atom to be spread out in the twelve ψ_2 -orbitals. Thus there is competition among the ligands for electrons to put in these orbitals.

While this picture is greatly oversimplified it should be qualitatively correct and will be shown to explain a number of observations. Here the picture has been presented in terms of molecular orbitals extending only over the metal and one ligand rather than over the entire molecule as should be done for a symmetric case like $\text{Cr}(\text{CO})_6$ because for the case of chemisorbed carbon monoxide, the octahedral symmetry is lost and only one carbon monoxide ligand will be dealt with. Further the σ - and π -bonds are assumed separable and all effects will be blamed entirely on the π -bonding. This means the problems to be treated will be limited to cases where one might reasonably expect the σ -bonding to remain approximately constant as an effect of a variable is observed.

One might wonder whether there is sufficient metal-carbon orbital overlap to produce orbitals like the Hückel orbitals calculated here. First, it is noted that even as the resonance integral H_{12} , which should be proportional to the overlap, is greatly decreased, the qualitative picture remains unchanged and the energy of ψ_2 remains below that of an electron in a metal d-orbital. A second and perhaps more convincing argument stems from a consideration of the observed carbon-oxygen stretching frequencies. If only a σ -bond is formed by the lone-pair electrons on the carbon atom, the carbon-oxygen stretching frequency for carbonyls would be expected to be very close to that of free carbon monoxide. In fact, this frequency is shifted to somewhat lower values. This is taken as an indication that π -bonding does occur with some charge occupying an orbital like ψ_2 which weakens the carbon-oxygen bond. Cotton and Kraihanzel^{8,9} have shown that as carbon monoxide in hexacarbonyls is replaced with ligands which do not π -bond, the availability of electrons to go into π -orbitals

of the remaining carbon monoxide ligands is increased with the result that the carbon-oxygen stretching frequencies are decreased. They observed frequencies down to 1800 cm^{-1} .

It might also be expected that as the electronic charge available to go into orbital ψ_2 is increased, the extinction coefficient for the carbon-oxygen stretching band would change. Jones¹⁶ has shown that as the extent of π -bonding increases, the extinction coefficient greatly increases for the carbon-nitrogen stretching band in a series of cyanide complexes which have bonding very similar to that in carbonyl compounds.

In applying the above considerations to chemisorption problems, a metal atom on the surface is regarded as the central atom in a complex with the surrounding metal atoms and the chemisorbed molecule as ligands. Here we do not have the high symmetry of the unsubstituted carbonyls. For the transition metals, the metal ligand atoms partially surrounding a particular surface metal atom will have available partially filled d-orbitals with appropriate symmetry to form π -bonds with the chosen surface atom and thereby compete with the adsorbed carbon monoxide for electrons from the adsorbent atom. The extent of the competition of the surrounding metal atoms for electrons which could go into a ψ_2 π -molecular orbital of the metal-carbon-oxygen system will determine the frequency and extinction coefficient for the carbon-oxygen stretching band of the adsorbed molecule. As an adsorbent atom occupies a position in different crystal faces or a position at an edge, corner, or dislocation, the number of surrounding metal atoms and hence the competition for electrons will vary.

Applications

1. *Bands for CO on Ni.* A Ni adsorbent atom in a 111 plane face or a 100 plane face has nine or eight surrounding Ni atoms, respectively. With this large number of ligands competing for electrons, the amount of electronic charge in the ψ_2 molecular orbitals of an adsorbed CO molecule would be expected to be small with the result that the C-O stretching frequency would be above 2000 cm^{-1} as in the unsubstituted carbonyls. However, for adsorbent atoms located at edges of planes, corners, and at dislocations, the number of surrounding nickel atoms can be around four, five, or six. On these sites the competition for electrons to go into the ψ_2 molecular orbitals of the metal-adsorbate system is materially reduced with the result that the C-O stretching band will occur at lower wave numbers. By analogy to the substituted carbonyls, the C-O

(16) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

stretching frequency for these sites would be expected to be below 2000 cm^{-1} and perhaps down to 1800 cm^{-1} . The spectra for CO on Ni usually show a band or bands around 2060 cm^{-1} and a broad band or bands around 1940 cm^{-1} . According to this molecular orbital view, the bands above 2000 cm^{-1} are regarded as due to CO adsorbed on regular crystal faces where the adsorbent Ni atoms have a high coordination number while the bands around 1900 cm^{-1} represent CO adsorbed on sites where the Ni atoms have a somewhat lower coordination number. The low coordination number sites would be expected to be somewhat more variable and poorly defined by virtue of the extra freedom granted by the low coordination number when compared to the high coordination number sites. For this reason, it is expected and found that the low frequency bands are somewhat broader and more variable than the high frequency bands. The occurrence of several different bands in both regions is a result of there being a number of different types of sites that can produce bands in both regions. Also, as expected, there is a continuous variation of sites so that the bands in the two regions which seem to represent the largest number of sites overlap each other. It should be noted that all of this is on the basis of only one adsorbate structure, *i.e.*, a linear metal-carbon-oxygen system.

A word of caution is due on the subject of trying to determine with any degree of accuracy the relative number of surface sites of different types by comparing the intensities of the different C-O bands. As already mentioned, the extinction coefficient is expected to increase as the electronic charge in the ψ_2 -orbital is increased. Since this effect is also used to explain the different frequencies, the extinction coefficient for the various bands is expected to increase as the frequency decreases. This has not been examined experimentally for chemisorbed CO, but if it occurs as predicted, the number of low coordination number sites could be considerably less than a casual glance at the spectra would suggest.

2. Supported and Evaporated Metals. The infrared spectra of CO adsorbed on silica-supported⁵ and evaporated⁶ Ni have been obtained in this laboratory. These spectra show the bands around 2060 cm^{-1} more intense than the band near 1900 cm^{-1} for the silica-supported samples while the reverse intensity pattern is observed for the evaporated samples. In producing the silica-supported Ni samples, the sample is heated for over 12 hr. at 400° in a stream of H_2 . This should produce sintered, well-defined crystallites which have a maximum of plane faces exposed and a minimum of edge atoms, dislocations, and amorphous material. This is supported by electron micro-

graph studies of deBoer and Coenen¹⁷ reported by Eischens. The adsorption sites on our silica-supported Ni should mostly be of the type to produce the high-frequency band. The evaporated metal is condensed in the vapor phase and the particles immediately quenched in oil. This would be expected to result in a more amorphous material with less well-crystallized particles. These particles should then have a larger proportion of sites which produce the low-frequency band. Thus this theory explains some of the differences we have observed in our samples.

A number of other reported spectra will now be commented on in the light of the arguments herein, but the conclusions are rather less clear. Eischens and workers^{2,18} have reported spectra for CO chemisorbed on silica-supported nickel in some of which the low-frequency band is the more intense while in others the high frequency band is more intense. Their published reduction procedures are a bit uninformative, but apparently a batch reduction procedure with temperatures from 200 to 350° was used for unspecified lengths of time. Apparently, their samples were treated at lower temperatures for shorter times than ours and so would have less crystal growth and sintering occurring. This would produce more sites that give the low-frequency bands. Thus we could explain the variability in observed bands on the basis of sintering and crystal growth rather than the usual arguments about completeness of reduction. Eischens¹⁹ and co-workers have also reported spectra for CO adsorbed on silica-supported Pt, evaporated Pt, and alumina-supported Pt with the high-frequency band at 2070 , 2050 , and 2050 cm^{-1} , respectively. If these data are to be explained on the basis of the degree of crystallinity of the Pt, it would be stated that the evaporated and alumina-supported samples are a little less crystalline so that the ligand Pt atoms are less effective in competing for electrons in these samples with the result that the C-O frequency is lower. Following this line, the alumina-supported Pt has a larger low-frequency band and a broader high-frequency band than the silica-supported Pt sample. A lower crystallinity for the alumina sample is also supported by the statement of Eischens² that the alumina-supported Pt is more difficult to reduce than the silica-supported Pt. The evaporated Pt sample showed no low-frequency band but the intensity of the high-frequency band was low, so it is difficult to tell if one should have been observed.

(17) J. H. deBoer and J. W. E. Coenen, as reported in ref. 1, p. 15.

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

(19) R. P. Eischens, Acceptance Address for American Chemical Society Award in Petroleum Chemistry, San Francisco, Calif., 1958.

The shift in frequency with changing support could also be interpreted in terms of electron-donating properties of the support. If it is assumed that alumina donates electrons, this would shift the bands for the alumina sample to lower frequencies than for the silica sample. At the present time, there are no data available to assess the extent of such an electronic effect.

Yang and Garland²⁰ have observed that for CO adsorbed on alumina-supported Rh, sintering decreases the intensity of a band at 1925 cm.⁻¹. They stated that this fact is not consistent with the assignment of the 1925-cm.⁻¹ band to a simple bridge structure. This fact is consistent with the interpretation that sintering increases the degree of crystallinity and thereby decreases the number of sites giving the low-frequency band.

In a similar manner, the data of O'Neill and Yates²¹ on the effect of using silica, alumina, or titania to support Ni for CO chemisorption studies can be discussed in terms of the degree of crystallinity of the supported Ni. They used a batch H₂ reduction treatment for only about 2 hr.

3. *Band Position as a Function of Coverage.* It has been observed that as the surface coverage increases, the frequencies of both the high- and low-frequency bands shift to higher values.¹⁻⁴ Two possible kinds of behavior can be predicted for the frequency as a function of coverage. One is that a particular band will simply shift its position to higher frequencies in a continuous manner as the coverage increases. The proposed model of the bonding explains this by noting that as the number of adsorbed molecules increases, the competition for the electrons of the surface atoms increases so that there is less charge available to put into each ψ_2 -orbital with the consequence that the C-O frequencies increase.

A second kind of behavior is predicted if the types of sites are distinct and the adsorbed CO is mobile enough to find the sites which give the highest heat of adsorption. The heat of adsorption would be expected to be greatest on the low coordination number metal atom sites which give the lower frequency bands. Eischens² has indeed observed that the chemisorbed CO which gives the bands below 2000 cm.⁻¹ is the most tightly held. After the lowest energy type of site is filled, the next lowest type which will give a band at a higher frequency will be filled. The result will be a band with its maximum at a high frequency and one or more shoulders on the low-frequency side.

Actually, both kinds of behavior are observed. On nickel the second kind of behavior is usually observed although the separation of bands and designation of shoulders is sometimes a matter of personal taste.

When chemisorbed CO is removed by pumping with or without heating, the bands are removed in just the reverse order in which they appear. This would seem to indicate that in the adsorption process the low energy sites are indeed occupied first.

4. *Effect of Other Gases on Adsorbed CO Bands.* The effect here is in terms of whether the added gas adsorbs with addition or removal of electrons from the metal substrate. If electrons are removed from the metal, the occupancy of the ψ_2 -orbitals is reduced with consequent raising of the C-O frequency. Addition of electrons gives the opposite effect. Eischens and co-workers have shown that the chemisorption of O₂, which is expected to dissociate and form oxide ions on the surface, thereby removing electrons, shifts the bands for CO chemisorbed on Fe and on Cu to higher frequencies. This is in accord with the model of bonding proposed. Eischens and co-workers^{1,19} have also shown that when H₂ is added to CO on Pt the C-O band is shifted to lower frequencies. From magnetic measurements²² and electrical resistance data,²³ it is generally believed that adsorbed hydrogen contributes electrons to the metal. The observed shift in the C-O band is in accord with hydrogen contributing electrons to the metal.

Yates and Garland²⁴ have observed the effect of adsorbing mercury vapor on the bands of CO chemisorbed on Ni. They observed that adsorption of Hg first caused the disappearance of the low-frequency band. Here this band has been ascribed to a site in which the Ni atom has a low coordination number. That means that this site is the most exposed and gives the highest energy of interaction so the Hg might well be expected to displace CO from these sites first. They further observed that the high-frequency band was shifted to a lower frequency, the bond strength of the Ni-C bond increased for the remaining CO after the Hg adsorption, and the extinction coefficient for the remaining CO was greatly increased. The authors were unable to explain these results. Since Hg has its outer d-orbitals completely filled, it would be expected to contribute electrons to the Ni substrate upon adsorption. This would put more electrons into ψ_2 -orbitals of the remaining CO groups with the observations just given following as a natural course.

5. *C¹²O and C¹³O Desorption.* Eischens, Francis,

(20) A. C. Yang and C. W. Garland, *J. Phys. Chem.*, **61**, 1504 (1957).

(21) C. E. O'Neill and D. J. C. Yates, *ibid.*, **65**, 901 (1961).

(22) P. W. Selwood, "Adsorption and Collective Paramagnetism," Academic Press, New York, N. Y., 1962.

(23) R. Suhrmann, *Z. Elektrochem.*, **60**, 804 (1956).

(24) J. T. Yates and C. W. Garland, *J. Phys. Chem.*, **65**, 617 (1961).

and Pliskin² observed that when a mixture of chemisorbed $C^{12}O$ and $C^{13}O$ is slowly desorbed by pumping and heating from a Pt surface, the intensity for the $C^{13}O$ band first increases and then decreases while the $C^{12}O$ band first decreases rapidly and then more slowly. They proposed to explain this result on the basis of dipole-dipole interaction of adjacent chemisorbed CO groups. An alternative explanation seems possible. On the basis of the model of bonding proposed here, the extinction coefficient for chemisorbed CO should increase as the coverage decreases. For slow desorption of $C^{12}O$ and $C^{13}O$ a kinetic isotope effect is expected with the lighter isotope coming off the surface faster. For the chemisorbed CO at almost complete coverage, the heat of adsorption is low and the isotope effect could be fairly large. If the rate at which $C^{13}O$ is being removed from the surface is less than the rate at which the extinction coefficient is being increased due mainly to $C^{12}O$ desorption, the intensity of the $C^{13}O$ band will initially increase. As CO is removed from the surface, the heat of adsorption for the CO increases so the activation energy for desorption increases, with the result that the difference in rate of desorption for $C^{12}O$ and $C^{13}O$ becomes less. As $C^{13}O$ is removed from the surface at more nearly the rate at which $C^{12}O$ desorbs, the intensity of the $C^{13}O$ band decreases even though the extinction coefficient may be increasing. The relative roles of dipole interaction and kinetic isotope effect in the observed phenomena do not seem to be readily determinable at present.

6. *Band Position on Alloys.* The only data giving the band position for CO on alloys that have been published are those of Eischens²⁵ for a 90% Ni-10% Cu alloy. Since Cu has its d-orbitals filled, it would be expected to donate electrons to the system which would put more charge in the ψ_2 -orbitals with a consequent lowering of the C-O stretching frequency. The data of Eischens show the CO bands on the alloy to be very similar to those on pure Ni except that the alloy bands are indeed shifted to lower frequencies by about 40 cm^{-1} .

In summary, the molecular orbital model of the metal-carbon-oxygen π -bonding system successfully qualitatively explains: (1) the occurrence of several carbon-oxygen stretching frequencies in the infrared spectra of CO adsorbed on metals; (2) differences in spectra of CO adsorbed on evaporated and supported metals; (3) infrared band positions as a function of coverage; (4) the effect of adsorbing other gases in addition to previously chemisorbed CO; and (5) band shifts in going from adsorption on pure Ni to a Ni-Cu alloy.

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Discussion

F. A. MATSON (University of Texas). The filling of the antibonding orbital should have a significant effect on the intensity of observed bands. Can such an effect be observed?

G. BLYHOLDER. I expect that such an effect could be observed, and, by analogy to the work of Jones (ref. 16 of the paper), it is expected to be a sizable effect.

E. HUTCHINSON (Stanford University, California). Would you expect that the effect of sintering on the geometry of a "central" atom is sufficiently pronounced to make it worthwhile to study the changes in the spectra of carbon monoxide adsorbed on evaporated or supported thin metal films as a function of time and temperature of sintering?

G. BLYHOLDER. Yes, and we expect to pursue this line of attack in the near future.

J. T. YATES, JR. (National Bureau of Standards, Washington, D. C.) (communicated). (1) Dr. Blyholder's view is that the spectrum of chemisorbed CO on Ni and other transition metals may be interpreted in terms of linear CO species adsorbed on metal atoms having various degrees of coordination with other metal atoms in the supported surface, the lower frequency bands being due to CO bonded to Ni atoms having less than the maximum number of neighbors. Although his theoretical deductions based on the spectra of substituted metal carbonyls may be qualitatively correct to some extent, he ignores a body of experimental data which supports the opposite point of view—namely, that both linear and bridged CO species are formed on crystalline Ni surfaces. Thus the work of Yates and Garland (*J. Phys. Chem.*, **65**, 617(1961)) established that both the low-frequency CO band centered at 1960 cm^{-1} and the band at 2035 cm^{-1} increased in relative intensity as the Ni crystallite average size was increased by increasing the percentage of Ni in the supported samples (as verified by X-ray line broadening studies). At the same time the relative intensity of the highest frequency band at 2080 cm^{-1} (which in my view is due to linear CO on dispersed Ni sites) decreased due to the decrease in the population of dispersed sites as the percentage of Ni was increased. Contrary to this, the Blyholder model would predict that the relative intensity of the 1960- cm^{-1} line would decrease as the number of fully coordinated Ni atoms in the surface was increased. Dr. Blyholder's argument is partially based on a comparison of spectra of CO on silica-supported Ni and Ni particles suspended in oil. Considerations of surface cleanliness in the case of the oil-suspended samples would seem to vitiate this comparison.

(2) It is suggested by Dr. Blyholder that a large kinetic isotope effect exists in the desorption of $C^{12}O^{16}$ and $C^{13}O^{16}$ and that this may explain the change in relative intensity of the two isotope bands during desorption from Pt as observed by Eischens. Calculations based on the classical mechanics of a linear three-body oscillator with end body of infinite mass (A. Adel, *Phys. Rev.*, **45**, 56(1934)) show that a change from $C^{12}O^{16}$ to $C^{13}O^{16}$ should result

(25) R. P. Eischens, *Z. Elektrochem.*, **60**, 782 (1956).