the scope of PhHgCCl₂Br reactions with olefins at room temperature has been studied with 14 examples, and PhHgCClBr₂ and PhHgCBr₃ also were found to transfer CClBr and CBr₂, respectively, at room temperature in good yield in 15–16-day reaction times.[109]

(107) D. Seyferth and C. K. Haas, *J. Organometal. Chem.*, **30**, C38 (1971).

(108) D. Seyferth, C. K. Haas, and S. P. Hopper, *ibid.*, **33**, C1 (1971).

(109) D. Seyferth and H. Shih, *Organometal. Chem. Syn.*, in press.

Infrared Spectra of Chemisorbed Molecules

ROBERT P. EISCHENS

Texaco Research Center, Beacon, New York   12508

Received January 13, 1971

If the surface chemistry of heterogeneous catalysis involves only factors which are found in conventional chemical systems, catalysis by metal surfaces may be viewed as another facet of metal–ligand coordination chemistry. Surface chemists would like to be able to utilize the vast amount of information which is available from studies of coordination chemistry. To do so would require knowledge of the nature of the functional groups in chemisorbed molecules, but this information has been difficult to obtain because the surface ligands comprise such a small fraction of the total sample. Techniques which provide infrared spectra of adsorbed molecules therefore constitute a major advance in studies of surface metal–ligand systems.

Some aspects of the infrared study of adsorbed molecules are as old as infrared spectroscopy. Spectra of adsorbed water were recognized in 1911 by Coblentz.[1] Subsequently, infrared spectroscopy was used quite extensively by mineralogists. Surface infrared spectra of many minerals were found to include bands attributable to adsorbed water and hydroxyl groups.[2] In retrospect, it is difficult to understand why the infrared work of mineralogists did not attract more attention among workers interested in the surface chemistry of catalysis. A probable contributory factor was the low level of interest in infrared spectroscopy in general because of the small number of instruments available. Commercial infrared apparatus was not common before 1945.

The first infrared study of chemisorbed molecules in our laboratory involved ammonia on silica–alumina cracking catalysts.[3] These catalysts are strong acids, and the question of interest was whether the acidity was protonic or of the Lewis type. It was expected that a protonic acid would chemisorb ammonia as NH_4^+, while the NH_3 configuration would be retained

for a Lewis acid. The spectra showed that Lewis acidity was predominant on a carefully dried sample; however, exposure of the Lewis sites to water produced protons. This approach to the study of surface acidity has been widely used. However, this subject is of rather specialized interest and will not be discussed in detail here.

In this Account I shall present examples of the use of infrared in surface chemistry which should be of interest to chemists who are not primarily concerned with catalysis. One example concerns the chemisorption of molecular nitrogen, the study of which has paralleled studies of molecular nitrogen as a ligand. A discussion of carbon monoxide on platinum will emphasize the variable of surface coverage. This variable has no exact counterpart in conventional coordination chemistry. The final example will illustrate how oxygen affects zinc oxide on which it is adsorbed.

Experimental Methods

The metal samples of greatest interest in catalysis are those in which small metal particles are dispersed on supports such as silica or alumina. Particle diameters are commonly in the range of 10–100 Å with 30 to 30,000 metal atoms in a particle. In the smaller particles almost all of the atoms are exposed surface atoms. About one-tenth of the atoms in a 100-Å particle are surface atoms. The supported-metal sample is most often prepared by impregnating the support with a salt of the metal and then reducing the salt with hydrogen at high temperatures. Samples prepared for infrared work usually have metal contents in the range of 2–9 wt % after reduction.

The spectra are obtained by transmission through the powder sample. Many designs of cells suitable for *in situ* infrared study have been used. Desirable design features are: sample temperature controllable over wide ranges both below and above room tempera-

Robert P. Eischens received his higher education at the University of Wisconsin (B.Sc.) and Northwestern (Ph.D.). He has been at Texaco Research Center since leaving Northwestern in 1949. His main research interest has been in studies of the fundamentals of catalysis with emphasis on chemisorption, isotope exchange, magnetic properties of catalysts, and ir spectra of adsorbed molecules. In 1968 and 1971, he was a member of the USA–Japan catalysis exchange program sponsored by the National Science Foundation.

(1) W. W. Coblentz, *J. Franklin Inst.*, **172**, 309 (1911).

(2) A. M. Buswell, V. Dietz, and W. H. Rodebush, *J. Chem. Phys.*, **5**, 501 (1931).

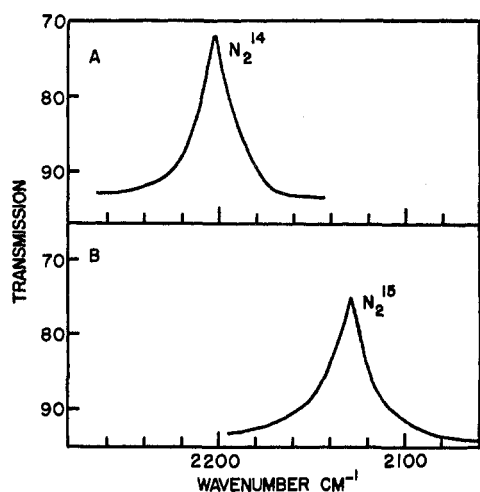(3) J. E. Mapes and R. P. Eischens, *J. Phys. Chem.*, **58**, 1059 (1954).

Figure 1.　Spectra of $^{14}N_2$ and $^{15}N_2$ chemisorbed on nickel.

ture, sample treatment and gas adsorption while sample is in the path of the infrared beam, short path length within the cell, independent measure of amount of adsorbate taken up, and cell windows which do not limit frequencies which can be scanned. Thus far, none of the cell designs has fulfilled all of these desired features. A description of the cell currently being used in our laboratory has been published.[4]

All of the results to be discussed were obtained by transmission through powder samples. Spectra of adsorbed molecules have also been obtained by transmission through evaporated metal films, by transmission through metal particles suspended in oil, and by reflection from mirror surfaces. There is general qualitative agreement among the spectral results obtained by the different methods.

Nitrogen on Nickel

An infrared band attributable to chemisorbed molecular nitrogen[5] was observed at about the time that inorganic chemists first isolated complexes having molecular nitrogen ligands.[6] In Figure 1, spectrum A shows the band due to nitrogen chemisorbed on nickel at room temperature, and spectrum B shows the band observed after chemisorbing the $^{15}N_2$ isotope. The frequency shift is consistent with the substitution of the larger mass of the $^{15}N_2$.

It was essential to show that the chemisorbed nitrogen retained its molecular form rather than being split into individually adsorbed atoms. Under the conditions of Figure 1, there is no isotope exchange between coadsorbed $^{14}N_2$ and $^{15}N_2$. This is an indication that the molecule does not adsorb as atoms. More definite proof of molecular adsorption was obtained by adsorbing a mixture of $^{14}N_2$, $^{15}N_2$, and $^{14}N^{15}N$. Three bands were observed. The appearance of the central band near 2160 cm^{-1}, due to chemisorbed $^{14}N^{15}N$,

showed that the nitrogen had not been split into atoms.

In chemisorption work, as well as in conventional inorganic chemistry, there is an interest in the specific structure and bonding involved in the coordination of nitrogen molecules. The two most easily visualized chemisorption possibilities are those in which nitrogen is in a linear form perpendicular to the surface, I, and the π-bonded case where the nitrogen is parallel to the surface, II.

$$Ni\!-\!N\!\equiv\!N \qquad\qquad \begin{array}{c} N\!\equiv\!N \\ \downarrow \\ Ni \end{array}$$
$$\quad\ \ \text{I} \qquad\qquad\qquad\qquad \text{II}$$

X-Ray studies have shown that nitrogen has the linear form in the complex nitrogenpentaammineruthenium(II) dichloride.[7] There is no comparable X-ray evidence for the chemisorption case; however, evidence for the linear form is seen in the high specific intensity of the infrared band. The intensity coefficient is about 18×10^{-17} cm/molecule (these units are obtained by integrating absorbance $vs.$ frequency bands and dividing the area by the number of adsorbed molecules in the sample volume transfixed by a beam area of 1 cm^2). This high specific intensity is comparable to values for the carbon–oxygen stretching bands of chemisorbed carbon monoxide and metal carbonyls. In these cases the specific intensities are about 50 times greater than for gaseous carbon monoxide.

Owing to the symmetry of molecular nitrogen, there is no change in dipole moment for the nitrogen–nitrogen stretching vibration. Consequently, for nitrogen gas there is no observable infrared band under ordinary conditions. The high intensity of the infrared band of chemisorbed nitrogen is taken as evidence for the linear structure, $Ni\!-\!N\!\equiv\!N$, because this structure involves the greatest decrease in the symmetry of the nitrogen–nitrogen bond.

The evidence provided by the infrared intensities is reasonably strong. However, more rigorous proof of the linear structure would include evidence for two $^{14}N^{15}N$ bands due to the structures $Ni\!-\!^{14}N\!\equiv\!^{15}N$ and $Ni\!-\!^{15}N\!\equiv\!^{14}N$. Because of the expected overlapping, the evidence for two bands would be observed as a broadening of the band of adsorbed $^{14}N\!-\!^{15}N$ compared to that of adsorbed $^{14}N_2$ or $^{15}N_2$. In the first studies of chemisorbed nitrogen, experimental evidence for the two $^{14}N\!-\!^{15}N$ species was sought but could not be detected. However, this negative result was not considered to be conclusive because the work had been done with a prism spectrophotometer of relatively poor resolving power.

The $^{14}N^{15}N$ experiment was repeated with a grating instrument.[8] This produced the spectrum shown in Figure 2. Experimental factors set 1 cm^{-1} as the lower limit of detectable differences in band half-widths (width measured at the level of one-half of the

(4) F. P. Mertens and R. P. Eischens, "The Structure and Chemistry of Solid Surfaces," G. A. Somorjai, Ed., Wiley, New York, N. Y., 1969.

(5) R. P. Eischens and J. Jacknow, Proceedings of the Third International Congress on Catalysis, North-Holland Publishing Co., Amsterdam, 1964, p 628.

(6) A. D. Allen and C. V. Senoff, Chem. Commun., 621 (1965).

(7) F. Bottomley and S. C. Nyburg, ibid., 897 (1966).

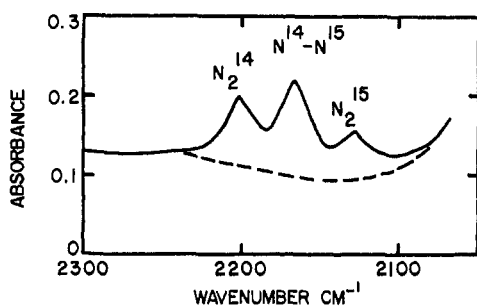(8) F. P. Mertens and R. P. Eischens, 152nd National Meeting of the American Chemical Society, New York, N. Y., 1966.

Figure 2. Spectrum of mixture of $^{14}N_2$, $^{15}N_2$, and $^{14}N^{15}N$ chemisorbed on nickel.

Figure 3. Spectrum of nitrogentris(triphenylphosphine)cobalt hydride containing $^{14}N_2$, $^{15}N_2$, and $^{14}N^{15}N$ (from ref 11).

maximum absorbance). The measured half-widths were 26 cm^{-1} for all three bands of Figure 2. The experiment represented by Figure 2 has been repeated a dozen times with similar negative results. Thus, the $^{14}N^{15}N$ experiment does not provide support for the linear form of chemisorbed nitrogen.

Although the $^{14}N^{15}N$ experiments do not confirm the linear structure, a question remains on the significance of the negative results. Calculated values[9] (based on assuming a linear triatomic XYZ molecule) of the differences in the nitrogen–nitrogen stretching frequency of Ni—$^{14}N\equiv^{15}N$, compared to Ni–$^{15}N\equiv^{14}N$, indicate an expected half-width broadening of 0.2 to 1.0 cm^{-1}. These calculations were made by computer using all reasonable values for the force constants which express the strength of the nickel–nitrogen (X–Y) and nitrogen–nitrogen (Y–Z) bonds. Since the experimental uncertainty of 1 cm^{-1} is large relative to the calculated half-width broadening, the failure to observe broadening is not necessarily in conflict with the intensity evidence for the linear structure.

Attributing failure to find broadening of the $^{14}N^{15}N$ band to limitations in experimental technique is not consistent with a recent publication by Chernikov, et al.[10] These workers claim observation of half-width broadening as large as 4–5 cm^{-1} in the $^{14}N^{15}N$ experiment with chemisorbed nitrogen. Unfortunately, the half-width data are given in tabular form and cannot be reconciled with their spectra from other $^{14}N^{15}N$ experiments which do not show evidence of broadening. It is also worth noting that the calculations, referred to above, indicate that an unreasonably strong nickel–nitrogen bond (about 30 kcal/mole) would be required to produce a broadening as large as 4–5 cm^{-1}.

Infrared studies of complexes of molecular nitrogen offer a better opportunity for observing $^{14}N^{15}N$ broadening than do studies of chemisorbed nitrogen. In the chemisorption experiments difficulties of getting transmission through the sample require that instruments be operated with relatively wide slits, and consequently optimum resolution is not attained. However, even under more promising spectral conditions, a
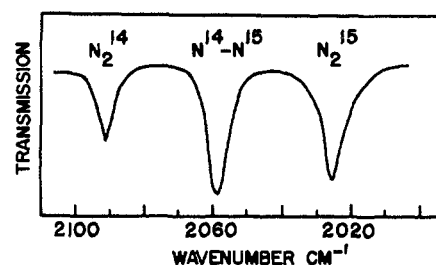
broadening of the $^{14}N^{15}N$ band was not detected for nitrogentris(triphenylphosphine)cobalt hydride by Yamamoto, et al.[11] This is shown in Figure 3.

Despite the Russian work referred to above, it is likely that the first acceptable evidence for $^{14}N^{15}N$ broadening will come from studies of nitrogen complexes. If the broadening is not observed with complexes in which X-ray data show the nitrogen to be linear, then a reappraisal of the validity of using a simple linear triatomic model in the frequency calculation will be necessary.

Ligand–Ligand Interactions

In metal–ligand systems it is commonly observed that the infrared bands of one ligand are shifted by the effect of other ligands. Numerous sophisticated studies have been devoted to understanding the specific mechanism of these ligand–ligand interactions. Similar effects are observed when two adsorbates are simultaneously chemisorbed on a metal particle. The best experimental examples involve chemisorbed carbon monoxide. The frequency of the carbon–oxygen stretching band may increase by as much as 150 cm^{-1} due to coadsorption of highly electronegative elements such as chlorine or oxygen. This is comparable to the carbon–oxygen frequencies observed in chlorocarbonyls.

There are also a few examples of coadsorbates causing a decrease in the carbon–oxygen frequency. However, these decreases are relatively small, 5–10 cm^{-1}. Coadsorbed hydrogen produces such a decrease. This may be attributed to an effect opposite to that of the electronegative elements, i.e., the hydrogen tends to transfer an electron to the metal and chemisorb as a proton. Thus, the direction of the shift of the carbon–oxygen frequency may be taken as an indicator of the direction of electron transfer which accompanies the chemisorption of the coadsorbate.

Carbon Monoxide on Platinum

Adsorbate–adsorbate interactions must also be considered when only a single species is adsorbed. With a single adsorbate the interactions may be studied as a function of surface coverage. One possible type of interaction would be analogous to that of the coadsorbate case discussed above. Since the metal par-

(9) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1945, eq II 198 and II 199, p 173.

(10) S. S. Chernikov, S. G. Kuz'min, and Yu G. Borod'ko, Russ. J. Phys. Chem., 42, 1071 (1968).

(11) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, J. Amer. Chem. Soc., 93, 371 (1971).

ticles have a large number of surface atoms, the ad-sorbate taken up at the early stages of surface coverage may affect the nature of the metal and thereby have an influence on the adsorbate taken up at later stages. For a specific example such as carbon monoxide on platinum, this type of interaction could be expected to produce a change in the carbon–oxygen stretching frequency. When the changes are small the effect would be experimentally observed as a shift in frequency as the surface coverage is increased.

Use of these frequency shifts to study adsorbate interactions is complicated by the possibility that the surface platinum atoms may not be equivalent with respect to their ability to form bonds with carbon monoxide. Any surface metal atom has neighboring metal atoms. These neighbor atoms may be on the surface or in the layer immediately below the surface. Due to differences in crystal habit, the metal–metal coordination would likely cause variation in the bonding affinity of surface sites. This variation could cause a shift in frequency with changes in surface coverage because carbon monoxide would tend to adsorb preferentially on the sites of strongest bonding.

The complications caused by the possibility of surface heterogeneity can be circumvented by the use of two isotopic species of a single compound. The isotopic species ^{13}CO was used by Hammaker et al.,[12] in a study of the interactions between carbon monoxide molecules chemisorbed on platinum. Carbon monoxide was considered as a simple dipole and the interactions were those expected between adjacent parallel dipoles. Although this type of interaction complicates interpretations of the spectra of adsorbed molecules, there would be a more serious problem if evidence for dipole–dipole interactions were not observed because this would require abandonment of the physical picture which visualizes the chemisorbed carbon monoxide as an array of molecules with the carbon–oxygen axis parallel to each other and perpendicular to the surface.

The dipole–dipole interaction concept for interpreting changes in the spectra of chemisorbed carbon monoxide as a function of surface coverage was adapted from the work of Decius,[13] who used this approach to explain anomalous intensity effects produced by isotopic substitution in carbonate and nitrate crystals. Dipole–dipole interaction is expected to produce both frequency shifts and changes in band intensities. Because frequency shifts might be caused by factors such as surface heterogeneity, the study of intensities produces the most definitive results.

Figure 4 shows a series of spectra observed as a mixture of ^{12}CO and ^{13}CO ions added in small doses to a platinum-on-silica sample. It is seen that there are two carbon–oxygen stretching bands attributable to the chemisorbed carbon monoxide. One band is near 2060 cm^{-1} and the other near 2000 cm^{-1}. The 2060-
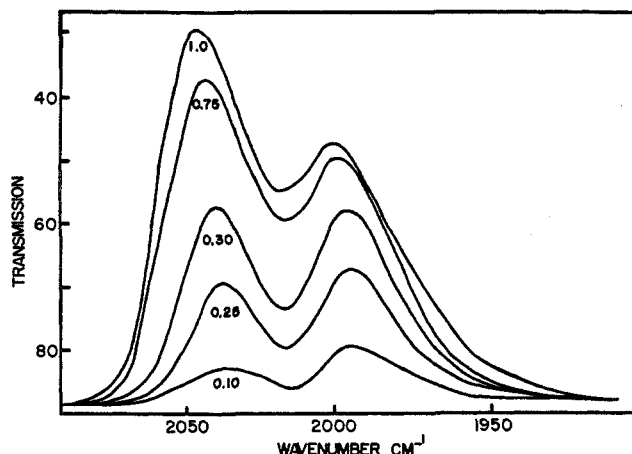

Figure 4. Spectra of a mixture of 36% ^{12}CO and 64% ^{13}CO chemisorbed on platinum at various fractional surface coverages.

cm^{-1} band is similar to that observed when pure ^{12}CO is chemisorbed. The 2000-cm^{-1} band is consistent with the ^{13}CO isotope. At first glance it would appear reasonable to refer to the band near 2060 cm^{-1} as the ^{12}CO band and the one near 2000 cm^{-1} as the ^{13}CO band. However, as discussed below, this nomenclature involves a misleading oversimplification, so they will be referred to as the high- and low-frequency bands.

The isotope mixture, used to obtain the data of Figure 4, contained 36% ^{12}CO and 64% ^{13}CO. It is apparent that band intensities observed at the lowest coverages are consistent with the 1:2 ^{12}CO:^{13}CO ratio. However, the relative intensity of the high-frequency band increases with increasing coverage. This intensity anomaly is attributed to dipole–dipole interactions.

Hammaker considered the chemisorbed carbon monoxide as a two-dimensional array on the platinum surface. For any single carbon monoxide molecule the interaction with other adsorbed molecules will be a function of the number of neighboring molecules and the distance to these neighbors. Simple crystal faces were used as a pattern to calculate the number of nearest neighbors, next-nearest neighbors, etc. at selected surface coverages. It is reasonable to assume that the chemisorbed molecules are uniformly distributed rather than being clumped together because the dipole–dipole interaction produces a small repulsive force. The dipole–dipole interactions were used to calculate the relative intensities of the high- and low-frequency bands at various stages of surface coverage. The calculated results reproduce the experimental results shown in Figure 4.

Although the two-dimensional array was used in the calculations, the mechanism of the dipole–dipole coupling effect can be most readily illustrated by reference to a single pair of chemisorbed carbon monoxide molecules. The carbon–oxygen stretching vibrations in the coupled pair must be either in phase or 180° out of phase. For the in-phase vibration, the two

(12) R. M. Hammaker, S. A. Francis, and R. P. Eischens, *Spectrochim. Acta*, 21, 1295 (1965).
(13) J. C. Decius, *J. Chem. Phys.*, 23, 1290 (1955).

oxygens are simultaneously approaching, or going away from, their respective carbons (III). In the out-of-phase mode one oxygen is going toward the carbon while the other is moving away (IV).

$$
\begin{array}{cccc}
\text{O} & \text{O} & \text{O} & \text{O} \\
\uparrow & \uparrow & \downarrow & \uparrow \\
\mid & \mid & \mid & \mid \\
\text{C} & \text{C} & \text{C} & \text{C} \\
& \text{III} & & \text{IV}
\end{array}
$$

Dipole–dipole coupling will occur whether there is one carbon monoxide species or a mixture of two isotopic species. When only one species is present, a single infrared band is produced. This is the band of the coupled in-phase vibration. The intensity of this band is twice that of a single carbon–oxygen stretching, i.e., the overall intensity is the same as would be obtained if the two molecules were not coupled. The out-of-phase vibration does not cause infrared absorption because within the pair the dipole moment change associated with the carbon–oxygen stretching is canceled.

With a mixed isotope pair, the in-phase mode again produces an infrared absorption which is almost equivalent to that of the two molecules vibrating independently. The out-of-phase mode may cause a small absorption because the cancelation is not complete due to the differences between the ^{12}C and ^{13}C. However, for practical purposes the situation with respect to infrared absorption intensities is the same for the mixed pair as for the single-species pair.

A critical portion of the explanation of the dipole–dipole coupling effect is not obvious but is indicated by the results of detailed calculations.[12] It is found that the frequency of the in-phase mode for the mixed isotope pairs will be in the same region as the frequency expected for pure ^{12}C species. The frequency expected for the out-of-phase band of the mixed pair would be similar to the frequency of the in-phase band for the pure ^{13}C species. Thus, the mixed-pair in-phase mode contributes to the absorption at the high-frequency position while the out-of-phase mode contributes little or no infrared absorption at the low-frequency position.

At high coverages, where coupling is important, the high-frequency band represents the sum of the absorptions of the in-phase modes for both $^{12}C–^{12}C$ and $^{12}C–^{13}C$ pairs while the low-frequency band represents the in-phase mode of $^{13}C–^{13}C$ pairs, with only an insignificant contribution from the $^{12}C–^{13}C$ out-of-phase mode. This unequal contribution of the coupled $^{12}C–^{13}C$ pair causes the intensity effects shown in Figure 4.

The dipole–dipole coupling interactions would be expected to create a similar effect in the case of nitrogen chemisorbed in the linear form. Van Hardeveld and Van Montfoort[14] applied the dipole coupling concept to chemisorbed nitrogen. Their treatment was similar to that outlined for carbon monoxide with the exception that the calculations were based on a linear array of
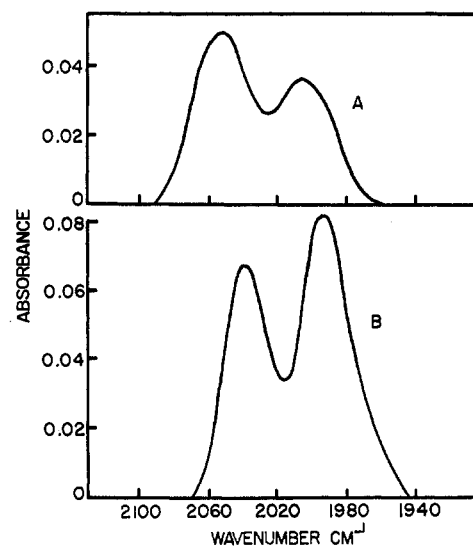
(14) R. Van Hardeveld and A. Van Montfoort, Surface Sci., 17, 1 (1969).

Figure 5. Spectra of a mixture of 36% ^{12}CO and 64% ^{13}CO chemisorbed on platinum; spectrum A, showing interaction effect due to stratification; spectrum B, after heating to give more uniform distribution.

nitrogen adsorption sites rather than a two-dimensional array. The nitrogen results showed good agreement between calculated and experimental results. However, there is an unexplained difficulty in that the nitrogen bands show a small shift toward lower frequency as the coverage increases. The detailed dipole–dipole calculations predict that increasing coverage will cause a small shift to higher frequency as is seen in Figure 4.

It is reasonable to ask whether the anomalous intensities of Figure 4 may not be attributed to a preferential adsorption of ^{12}CO. However, the effect is observed in situations where there is no significant quantity of residual gas after the admission of doses of the isotopic mixture. Thus, both components must be completely adsorbed.

The chemisorption and spectral observations of Figure 4 were carried out at 200°. The high temperature was used to ensure that the carbon monoxide would be uniformly distributed throughout the sample. In cases where the chemisorption bonding is strong, as for carbon monoxide on platinum (about 50 kcal/mole), a stratification problem is encountered at low temperature. Each sample disk contains the equivalent of several thousand layers of metal particles. The initial doses of adsorbate will concentrate on particles near the outer edges of the disk while the platinum particles further inside the disk remain bare. This stratification can produce misleading results in experiments designed to study interaction effects as a function of surface coverage.

Stratification is illustrated in Figure 5, where spectrum A was observed after adding an amount of 36% ^{12}CO–64% ^{13}CO mixture equivalent to a surface coverage of about 10%.[12] Comparison of the relative intensities of the high- and low-frequency bands with those of Figure 4 indicates a degree of interaction expected at high coverage. Spectrum B was observed
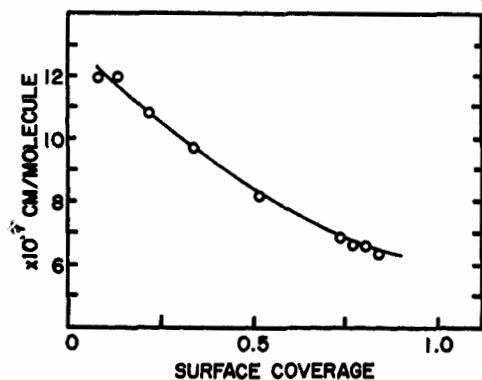
Figure 6.   Intensity per molecule as a function of surface coverage for carbon monoxide chemisorbed on platinum.

Figure 7.   Effect of adsorbing oxygen on a sample of zinc oxide which contains carbon and nitrogen as impurities.

after heating to 200° and cooling to room temperature. Now the relative band intensities are consistent with a low surface coverage. The change in relative band intensities in going from A to B shows that the heating has provided the mobility needed to redistribute the carbon monoxide and thereby decrease the interaction.

Specific Intensity of Chemisorbed Carbon Monoxide

Since the Figure 5 experiment was carried out in a closed system, the same amount of chemisorbed carbon monoxide is present for both spectra. However, the total integrated intensity of the bands in B is about 50% greater than in A. The dipole–dipole interaction involves a transfer of intensity from the low- to the high-frequency band. This concept does not predict a change in the total intensity. Thus, the intensity increase shows that dipole–dipole coupling is not the only factor involving band intensity and surface coverage.

An understanding of the specific intensities of chemisorbed molecules is important because it is necessary to the interpretation of experiments in which infrared is used to follow reactions on surfaces. The earliest studies indicated that the specific intensity of carbon monoxide on platinum was greater at high coverages.[15] This was determined by titrating the chemisorbed carbon monoxide with oxygen at 200° and converting it to CO_2. Hammaker and Lin, using volumetric adsorption measurements, also found that the specific intensity was greater at high coverage.[16] The opposite result was reported by Seanor and Amberg,[17] who determined surface coverage by gravimetric methods. Our data on this system[18] are displayed in Figure 6. These data were obtained at 200° using gravimetric apparatus described previously.[4] They show that the specific intensity is greater at low coverage, in agreement with the results of Seanor and Amberg.

Theoretical treatments of carbon–oxygen stretching intensities for metal carbonyls and chemisorbed carbon monoxides have been published.[19,20] Both are based
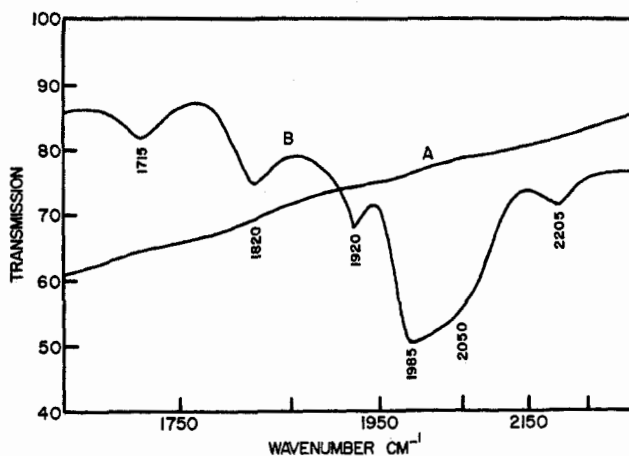
on the premise that a decrease in π bonding with increasing coverage would produce an increase in frequency and a decrease in specific intensities. These intensity predictions are consistent with the data shown in Figure 6, and the frequency predictions also agree with experimental observations.

A decrease in specific intensity with coverage is also observed with the nitrogen–nickel system.[5] However, in this case there may be a simple explanation since higher pressures, required to increase weak chemisorption of nitrogen, also cause some physical adsorption. The physically adsorbed nitrogen adds to the weight adsorbed but does not contribute to the infrared band. The reverse situation, where the specific intensity appears to be small at low coverage, is sometimes observed, as for carbon monoxide on nickel, because a portion of the carbon monoxide dissociates. In the above two cases the changes of intensity with coverage may be attributed to changes in the nature of the adsorption. Situations such as these may be misleading, but major interest lies in cases where such factors are not involved in the changes in specific intensity.

Oxygen on Impure Zinc Oxide

In the previous examples the similarity between chemisorption on metals and metal–ligand chemistry is easily seen. These are typical of numerous other examples of the application of infrared to surface chemistry in that, given a prior knowledge of the chemistry of the metal–ligand system, a reasonable prediction of the nature of the chemisorbed species can be made. This situation does not prevail for oxygen adsorption on impure zinc oxide.[21] In this case the results could not be predicted and perhaps not even explained.

This problem is illustrated in Figure 7 with a sample of zinc oxide containing carbon and nitrogen impurities (designated ZnO(C,N)). Spectrum A was observed with the sample under vacuum. Spectrum B was ob-

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

(16) K. C. Lin, Ph.D. Thesis, Kansas State University, 1968, University Microfilms, 69-4163.

(17) D. A. Seanor and C. H. Amberg, *J. Chem. Phys.*, **42**, 2967 (1965).

(18) F. P. Mertens and R. P. Eischens, unpublished results.

(19) T. L. Brown and D. J. Darensbourg, *Inorg. Chem.*, **6**, 1971 (1967).

(20) G. Blyholder, *J. Phys. Chem.*, **68**, 2772 (1964).

(21) D. M. Smith and R. P. Eischens, *J. Phys. Chem. Solids*, **28**, 2135 (1967).

served after exposure to oxygen. It is seen that exposure to oxygen produces a series of bands in the 1700–2100-cm^{-1} region. These bands are clearly related to the presence of impurities because similar bands are not produced when oxygen is added to pure zinc oxide.

The zinc oxide of Figure 7 was prepared by thermal decomposition of zinc oxalate under vacuum. Carbon impurity in the concentration range of 0.5% is common to these decompositions unless they are carried out in an oxidizing atmosphere. Nitrogen is not a common impurity. Its source was either the ammonium oxalate or zinc nitrate which were used to prepare the zinc oxalate.

The bands of spectrum B are similar to those of carbon–oxygen and nitrogen–oxygen stretching vibrations. This suggests that the oxygen may have reacted with impurity atoms on the zinc oxide surface. However, similar bands were observed when chlorine or $^{18}O_2$ were used instead of normal oxygen. The bands are not consistent with any species expected on the basis of chlorine reacting with surface impurities. The failure to observe an isotope shift with $^{18}O_2$ is another indication that the bands do not represent species formed by reaction between the impurities and the adsorbed gas.

An alternative hypothesis is that the observed bands are due to low-energy electronic transitions between impurity energy levels within the zinc oxide. Electronic transitions commonly involve higher energies and consequently are observed at frequencies considerably higher than those of the infrared region. However, low-energy transitions may be observed in solids. These commonly appear as absorption edges, but in a few cases they resemble conventional infrared bands.

To differentiate between bands of electronic transitions and the atom–atom vibrations common to infrared absorptions, a sample was prepared in which the carbon impurity was labeled with 55% ^{13}C. The concept underlying this experiment was that ^{13}C would shift infrared bands but would not affect the bands if they were due to electronic transitions. The labeled impurity sample was prepared by decomposing zinc oxalate labeled with ^{13}C.

Since Figure 7 involved a sample which contained both nitrogen and carbon impurities, a new sample was prepared in which carbon was the only impurity. This eliminated some of the bands observed after exposure to oxygen in Figure 7 and suggests that these eliminated bands are related to the nitrogen impurity. Recently Smith and VanDort confirmed this suggestion by preparing a zinc oxide sample in which nitrogen was the only impurity.[22] Upon exposure to oxygen they observed only the bands which were eliminated in going from ZnO(N,C) to ZnO(C).

In Figure 8, spectra A and B were observed after exposing ZnO(C) to oxygen and to chlorine. These show bands near 1990 and 1716 cm^{-1}. Spectrum C was ob-

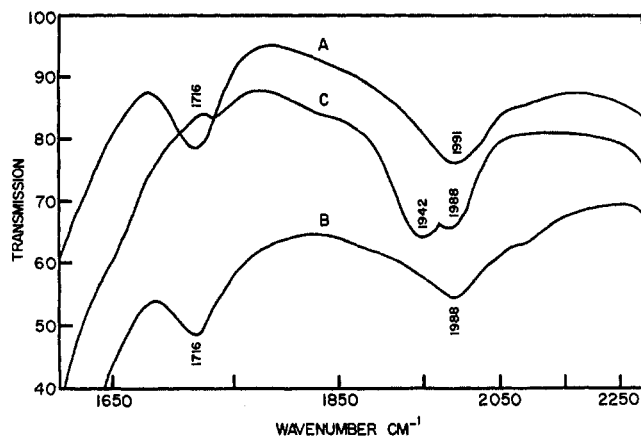(22) D. M. Smith and M. A. VanDort, unpublished results.

Figure 8. Spectra A and B, after adsorbing oxygen and chlorine on zinc oxide with carbon impurity; spectrum C, after adsorbing oxygen on zinc oxide with ^{13}C impurity.

served after adding oxygen to the ^{13}C-labeled sample. It is apparent that a new band has appeared near 1942 cm^{-1}. The shift from 1988 to 1942 cm^{-1} is that expected from the substitution of ^{13}C in a carbon–oxygen stretching vibration. This shows that the 1988-cm^{-1} band is a conventional infrared band and indicates that all of the other bands are also attributable to atom–atom vibrations.

Interpretation of the effects shown in Figures 7 and 8 must consider that the bands are due to carbon–oxygen and nitrogen–oxygen species which are not produced by reaction between the impurities and adsorbed oxygen. This indicates that the strong electron-withdrawing properties of oxygen and chlorine are responsible for significant changes within the bulk of the zinc oxide. The band at 1990 cm^{-1} is similar to that expected for the carbon–oxygen stretching in $Zn(CO)_n$. This suggests that a zinc carbonyl has been formed within the zinc oxide matrix. This would be a unique species since zinc is not known to form carbonyl-type compounds.

Suggestions for Further Reading

The examples of the use of infrared spectroscopy described here were selected to illustrate methods and concepts using problems of current interest. It was not feasible to illustrate the broad scope of the infrared methods which have produced hundreds of publications covering almost all adsorbate-adsorbent systems. A number of more comprehensive review articles have been written.[23–32]

(23) R. P. Eischens, Z. Elektrochem., 60, 782 (1956).
(24) R. P. Eischens and W. A. Pliskin, Advan. Catal., 10, 1 (1958).
(25) N. Sheppard, Proceedings of the Conference on Molecular Spectroscopy, Pergamon Press, London, 1960, p 277.
(26) A. V. Kieselev and V. I. Lygin, Russ. Chem. Rev., 31, 175 (1962).
(27) C. Amberg, "Applied Spectroscopy in Surface Research," Academic Press, New York, N. Y., 1966, Chapter 30.
(28) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966.
(29) V. Lorenselli, Chim. Anal., 48, 637 (1966).
(30) M. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, New York, N. Y., 1967.
(31) M. R. Basila, Appl. Spectrosc. Rev., 1, 289 (1968).
(32) D. J. C. Yates, Catal. Rev., 2, 113 (1968).