

# INFRARED SPECTRA OF ADSORBED GASES

By V. CRAWFORD†

(THE UNIVERSITY, MEDFORD, MASS., U.S.A.)

## 1. Introduction

THE infrared spectrometer has become firmly established as a useful and important tool for investigating the adsorption of gases on solids. Work published during the last ten years has described the results obtained in studies of both physical adsorption and chemisorption. It is the object of this Review to illustrate how spectroscopic methods may be used to contribute towards elucidating certain general problems of adsorption, and for this purpose examples will be chosen from some of the solid-gas systems which have been studied. The traditional distinction between physical adsorption and chemisorption will be observed although it is becoming increasingly evident that in certain instances there are no clear-cut criteria to enable such a distinction to be made with certainty.

## 2. Physical Adsorption

(A) **Spectroscopic Results to be expected from Perturbing Effects of Surface Forces on Adsorbed Molecules and vice versa.**—When a gas molecule approaches the surface of a solid, interaction between the molecule and the surface occurs, the interaction energy  $U(r)$  being a function of the distance  $r$  from the surface. Irrespective of its functional form,  $U(r)$  satisfies the following conditions:

$$U = 0 \quad \text{at } r = \infty$$

and  $U = \infty \quad \text{at } r = 0$

If the adsorption minimum in the potential curve,  $U(r)$  plotted against  $r$ , is located at values of  $r$  where there is practically no overlap between the wave functions of the adsorbed molecules and the lattice of the solid, then physical adsorption has occurred. In this case the perturbing effects of the surface might be manifested in the following ways.

(i) The surface forces distort one "side" of the adsorbed molecule more than the other, and this induced asymmetry might be expected to result in the occurrence of new bands in the spectrum of the adsorbate, *i.e.*, bands which for reasons of symmetry are forbidden in the spectrum of the isolated, unperturbed adsorbate molecules. Further, this effect should be particularly marked in the case of highly symmetrical molecules and, depending on the degree of distortion, the degeneracy of vibrations may either be reduced or completely destroyed.

(ii) It is well known that in passing from gaseous to condensed phases the frequencies of the corresponding bands are diminished. Since in physical

† Present address: Physical Chemistry Laboratories, Imperial College of Science and Technology, S. Kensington, London, S.W.7.

adsorption the perturbing effects of the surface forces on the adsorbate molecule are comparable to those of the surrounding molecules in the liquid state, the frequency shifts would be expected to be of a similar order of magnitude to that observed in passing from the gas phase to the liquid state. Indeed, the magnitude of the frequency shift might perhaps prove useful in distinguishing between physical adsorption and chemisorption in doubtful cases.

(iii) In carrying out a statistical thermodynamic study of the adsorbed phase, a model is chosen and various thermodynamic quantities of interest are computed for certain assumed degrees of freedom of the adsorbed molecule. Comparison of the computed with the experimental quantities then permits deductions to be made concerning the degrees of freedom lost by the adsorbate in passing from the gaseous to the adsorbed phase. It might be expected that study of band shapes and, in particular, high-resolution studies, would provide direct information about the degrees of freedom of molecules in the adsorbed state.

(iv) Condon<sup>1</sup> has studied the infrared spectrum induced by electrical fields and, as might have been expected, found the selection rules for the induced spectrum to be the same as those for Raman spectra. It was also shown that the intensity of bands induced by electrostatic forces should depend on the square of the field strength. Study of the infrared spectra of adsorbed molecules on ionic adsorbents should then permit determination of the field strength prevailing at the adsorption equilibrium distance.

(v) It has been suggested<sup>2</sup> that in a previous study of the adsorption of ammonia on barium fluoride, hydrogen bonding between adsorbate molecules on the surface was neglected. Since hydrogen bonding has been very successfully studied by infrared spectroscopy, it might be expected that the same technique would provide direct information on the occurrence of hydrogen bonding in the adsorbate on the surface.

(vi) Statistical and thermodynamic studies of the adsorbed phase almost invariably neglect the perturbation of the adsorbate on the adsorbent. Nevertheless, the presence of adsorbate molecules would be expected to perturb the adsorbent surface. This effect should be easily detectable spectroscopically if the surface possesses chemical functional groups which terminate the bulk structure of the solid, *e.g.*, OH on a silica surface. Thus when a molecule is adsorbed near the OH group, the motions of the atoms of the group are perturbed and consequently a shift in the group vibration frequency might be expected.

**(B) Experimental Requirements.**—Having indicated the type of information which might be obtained from a study of the infrared spectra of adsorbed molecules, we must consider whether such spectra are in fact physically realisable. The intention here is not to discuss details of the types of cell and methods of sample preparation that have been used, but

<sup>1</sup> E. U. Condon, *Phys. Rev.*, 1932, **41**, 759.

<sup>2</sup> R. M. Dell and R. A. Beebe, *J. Phys. Chem.*, 1955, **59**, 754.

rather to direct attention to the special combination of circumstances which make it possible to obtain well-defined spectra.

Since a layer of liquid 1—100  $\mu$  thick is sufficient to give measurable absorption bands, a monolayer 10 Å thick would require 1,000 traversals of infrared radiation to give measurable spectra. Owing to surface scattering, however, radiation is lost on each traversal. This loss due to scattering by individual particles can be greatly diminished by using particles of a size less than the wavelength of the incident radiation; but decreasing the particle size increases the specific surface of the adsorbent and so the means used to reduce scattering has the simultaneous beneficial effect of ensuring that a correspondingly greater amount of gas is adsorbed at a given pressure. It is this fortunate combination of factors which makes possible the spectroscopic study of adsorbed molecules.

In practice, however, it is found that a layer of powder has a marked residual scattering even though the particles of which it composed satisfy the size criterion for minimum scattering. This is undoubtedly due to the formation of agglomerates having an effective size greater than the wavelength of the incident radiation. On the other hand, adsorbents in the form of gels or porous glasses seem to scatter much less radiation than a powder of equivalent path length and specific surface. The reason for this, it has been suggested,<sup>3</sup> is that the individual surfaces are separated from each other more often than in the case of a layer of powder.

In addition to losses due to scattering, possible additional losses may occur because of absorption by the adsorbent. However, since many solids do not exhibit strong absorption in certain regions of the spectrum, this leaves certain frequency ranges available for study.

The major requirements then for obtaining well-defined spectra are these: (i) That there be a sufficiently high concentration of adsorbed gas in the path of the incident radiation; this can be secured by using an adsorbent of sufficiently high specific surface. (ii) Scattering by particles of the adsorbent should be eliminated or at least diminished as much as possible and this can be achieved by using particles of a size smaller than the wavelength of the incident radiation. (iii) The adsorbent should be transparent to infrared radiation.

The remainder of this section will now be devoted to experimental evidence illustrating and confirming the expectations enumerated in section 2(A).

**(C) Perturbation of the Surface by the Adsorbate.**—As indicated previously, perturbation of the surface by the adsorbate should be detected very easily if the surface possesses functional groups. Indeed, the very first infrared absorption study of a solid-gas system<sup>4</sup> was with one demonstrating just this effect.

<sup>3</sup> N. Sheppard, *Spectrochim. Acta*, 1959, **14**, 249.

<sup>4</sup> N. G. Yaroslavsky and A. N. Terenin, *Doklady Akad. Nauk S.S.S.R.*, 1949, **66**, 885.

In their pioneering studies on the infrared spectra of physically adsorbed molecules, Yaroslavsky and Terenin<sup>4</sup> used as adsorbent a porous glass-like silica. Since it was several mm. thick and absorbed the long-wavelength radiation their work was confined to the near-infrared region (5000—10,000  $\text{cm}^{-1}$ ). A band was found at 7325  $\text{cm}^{-1}$  and assigned to the first overtone of the fundamental frequency of the surface OH groups. The location of this band was subsequently confirmed by Yaroslavsky<sup>5</sup> and by Yaroslavsky and Karyakin.<sup>6</sup> On the adsorption of gases and vapours this band is broadened, reduced in intensity (sometimes disappearing), and displaced to lower frequencies.

The effect on the surface OH groups of gases which are physically adsorbed is demonstrated nicely by the work of Yaroslavsky and Karyakin<sup>6</sup> on the adsorption of nitrogen on porous glass. After degassing at 550°, the sharp peak at 7325  $\text{cm}^{-1}$  was obtained. The adsorbent at -180° was then exposed to 1 atm. pressure of nitrogen and the spectra were recorded at 1, 10, 20, and 120 min. respectively after the admission of the nitrogen. After 20 min. the 7325  $\text{cm}^{-1}$  band disappeared and was replaced by one at 7257  $\text{cm}^{-1}$ , the latter band appearing 1 min. after the admission of nitrogen. The 7325  $\text{cm}^{-1}$  band was undetectable after 20 min., but the 7257  $\text{cm}^{-1}$  band increased in intensity between 20 and 120 min. Since the original band at 7325 was obtained on raising the temperature to 20°, this suggests that the shift of the OH frequency is caused by physical adsorption of nitrogen. Similar results were obtained on adsorption of oxygen except that in this case the admission of oxygen at -180° resulted in (i) the instantaneous disappearance of the 7325  $\text{cm}^{-1}$  and appearance of the 7257  $\text{cm}^{-1}$  band and (ii) the finding that the 7325  $\text{cm}^{-1}$  band is only restored on heating to 200°.

Sidorov,<sup>7</sup> using transparent plates of glass, obtained the spectra not only of surface groups but also of several different types of molecule in the adsorbed phase. Carbonyl-containing adsorbates such as acetone and benzaldehyde cause the OH overtone band to be widened, increased in intensity, and displaced to lower frequency, the displacements being 370 and 290  $\text{cm}^{-1}$ , respectively, for acetone and benzaldehyde. Similar effects on the first overtone band of OH have been reported by Filimonov.<sup>8,9</sup> For example, exposure of silica gel to the vapour of chlorobenzene and nitromethane produced shifts of 140 and 160  $\text{cm}^{-1}$ , respectively.

Some very comprehensive studies of the silica surface have been carried out by McDonald.<sup>10</sup> The adsorbent used was Aerosil 2491 or Cabosil which is a pure fumed silica. Before degassing, the adsorbent showed a

<sup>5</sup> N. G. Yaroslavsky, *Zhur. fiz. Khim.*, 1950, **24**, 68.

<sup>6</sup> N. G. Yaroslavsky and A. V. Karyakin, *Doklady Akad. Nauk S.S.S.R.*, 1952, **85**, 1103.

<sup>7</sup> A. N. Sidorov, *Doklady Akad. Nauk S.S.S.R.*, 1954, **95**, 1235.

<sup>8</sup> V. N. Filimonov, *Optika i Spektroskopiya*, 1956, **1**, 450.

<sup>9</sup> V. N. Filimonov and A. N. Terenin, *Doklady Akad. Nauk S.S.S.R.*, 1956, **109**, 982.

<sup>10</sup> R. S. McDonald, *J. Amer. Chem. Soc.*, 1957, **79**, 850.

sharp band at 3749 and a broader one at 3400  $\text{cm}^{-1}$ . On out-gassing, the former increased and the latter decreased in intensity until after prolonged evacuation at 300–350° only the 3749  $\text{cm}^{-1}$  band remained. This was assigned as the 0–1 stretching frequency of OH groups oriented in such a way as to be incapable of interacting with their surroundings. The effect on this band of physically adsorbed rare-gas atoms and non-polar molecules was then investigated, and in every case the OH frequency diminished as shown in Table 1.

TABLE 1. *Perturbation of free OH frequency of Aerosil by various adsorbates.*

Adsorbate	Polarisability ( $\text{\AA}^3$ )	OH Frequency ( $\text{cm}^{-1}$ )	Frequency shift ( $\text{cm}^{-1}$ )
None	—	3749	—
Argon	1.65	3741	8
Krypton	2.54	3733	16
Xenon	4.13	3730	19
Nitrogen	1.76	3725	24
Oxygen	1.60	3737	12
Methane	2.60	3717	32

McDonald sought a correlation between the frequency shifts produced by the various adsorbates and their polarisabilities. In the case of the rare gases there appeared to be such a correlation, for argon, krypton, and xenon which have polarisabilities<sup>11</sup> of 1.65, 2.54, and 4.13  $\text{\AA}^3$  produced frequency shifts of 8, 16, and 19  $\text{cm}^{-1}$ , respectively. However, oxygen and nitrogen show no such correlation. These molecules have approximately the same polarisability<sup>11</sup> (1.60 and 1.76  $\text{\AA}^3$  respectively), yet produce frequency shifts of approximately 12 and 24  $\text{cm}^{-1}$  respectively. Frohnsdorff and Kington<sup>12</sup> have suggested that the reason for this is to be found in the difference in the quadrupole moments of these molecules ( $\text{O}_2 < 0.1 \text{\AA}^2$ ;<sup>13</sup>  $\text{N}_2 < 0.5 \text{\AA}^2$ <sup>14</sup>). Very approximate calculations based on various assumed positions and orientations of the quadrupole show that interaction between proton and quadrupole moment can satisfactorily account for the frequency difference provided the effective protonic charge is not less than  $\sim 0.2 \times 10^{-10}$  e.s.u. The suggestion that the quadrupole moment of nitrogen cannot be ignored is reinforced by a study of the intensities of the OH bands. Thus, McDonald's high-pressure measurements show that the free OH band disappears at higher relative pressures for oxygen than for nitrogen, indicating that the latter molecule perturbs the OH group more strongly than oxygen does. This is in accordance with the fact that

<sup>11</sup> Landolt-Börnstein, "Zahlenwerte und Funktionen", Vol. I, Part 3, 1951, p. 510.

<sup>12</sup> G. J. C. Frohnsdorff and G. L. Kington, *Trans. Faraday Soc.*, 1959, **55**, 1173.

<sup>13</sup> W. V. Smith and R. Howard, *Phys. Rev.*, 1950, **79**, 132.

<sup>14</sup> C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy", McGraw-Hill, New York, 1955, p. 365.

the quadrupole of nitrogen interacts with the field gradient of the OH group, giving a higher heat of adsorption.

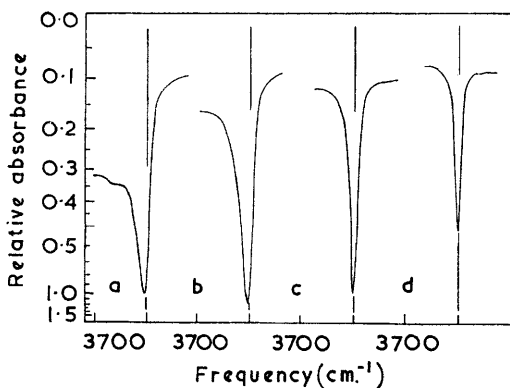


FIG. 1. Infrared absorption due to SiOH of Cabosil (12.5 mg./cm<sup>2</sup>, pressed at 12,000 lb./in.<sup>2</sup>). (a) Before degassing; peak at 3747 cm<sup>-1</sup>. (b) After degassing for 30 min. at 500° in vacuo; peak at 3748 cm<sup>-1</sup>. (c) After degassing for 15 min. at 940° in vacuo; peak at 3749 cm<sup>-1</sup>. (d) After degassing for 8.5 hr. at 940° in vacuo; peak at 3750 cm<sup>-1</sup>.

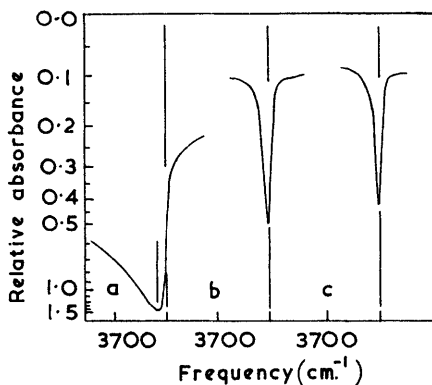


FIG. 2. Infrared absorption due to SiOH of Mallinckrodt Special Bulky Silicic Acid (12.5 mg./cm<sup>2</sup>, pressed at 12,000 lb./in.<sup>2</sup>). (a) Degassed for 30 min. at 500° in vacuo; peak at 3740 cm<sup>-1</sup>. (b) Degassed for 15 min. at 940° in vacuo; peak at 3748 cm<sup>-1</sup>. (c) Degassed for 8.5 hr. at 940° in vacuo; peak at 3748 cm<sup>-1</sup>. (Figs. 1 and 2 are reproduced, with permission, from R. S. McDonald, *J. Phys. Chem.*, 1958, **62**, 1168.)

More recently, McDonald<sup>15</sup> described an infrared study of silanol groups on the surface of two varieties of pure amorphous silica, Mallinckrodt Special Bulky Silicic Acid (MSBS), which is a pure precipitated silica, and Cabosil. The results indicate that OH on the surface of silica exists in different states. Thus the shift and narrowing of the residual SiOH band of MSBS is much more pronounced than for Cabosil as indicated in Figs. 1 and 2.

<sup>15</sup> R. S. McDonald, *J. Phys. Chem.*, 1958, **62**, 1168.

The breadth of the band after degassing at 500° (Fig. 2a) shows that silanol groups of MSBS interact with each other much more than those of Cabosil which has not been degassed at all. However, degassing at 940° in a vacuum for eight hours destroyed hydrogen bonding and left appreciable amounts of isolated silanol groups on the surface of both silicas. As a result of the degassing the absorption band of surface silanol groups was narrowed and displaced to higher frequency. This would indicate that the groups destroyed during outgassing had an environment markedly different from those which remained after outgassing.

Very recently, Folman and Yates<sup>16</sup> studied effects due to hydrogen bonding between physically adsorbed molecules and the OH groups present on the surface of porous silica glass.

In this case the surface OH groups show a very strong absorption even after evacuation for eleven hours at 450°. The band is not only much wider than the normal OH band but it is also highly asymmetric. This implies that the band is composite, consisting of a narrow band at approximately 3740 cm.<sup>-1</sup> due to isolated OH groups, and another broader band at a lower frequency. Since hydrogen bonding is known to produce broad bands, it can be inferred that the broadening in the observed band is probably due to OH groups hydrogen-bonded to adjacent groups.

On adsorption of sulphur dioxide, chloroform, acetone, and ammonia a new broad band appeared in each case and at a frequency lower than that attributed to OH on the free surface. The results obtained are shown in Table 2.

TABLE 2. *Shifts in OH frequencies produced by various adsorbates on the surface of porous silica glass.*

Adsorbate	Temp.	Average displacement (cm. <sup>-1</sup> )
SO <sub>2</sub>	24°	115
CH <sub>3</sub> Cl	24	110
(CH <sub>3</sub> ) <sub>2</sub> CO	25	330
	75	305
	135	270
NH <sub>3</sub>	25	820
	75	750
	100	710
	150	640

In each case the new band appearing at lower wave-number is attributed to perturbation of the surface OH groups by the adsorbate as a result of hydrogen-bond formation. At room temperature the magnitude of the perturbation of the surface OH groups increases in the order CH<sub>3</sub>Cl < SO<sub>2</sub> < (CH<sub>3</sub>)<sub>2</sub>CO < NH<sub>3</sub>, the last compound forming a particularly

<sup>16</sup> M. Folman and D. J. C. Yates, *Proc. Roy. Soc.*, 1958, *A*, 246, 32.

strong hydrogen bond. Later work<sup>17</sup> showed that within experimental error  $\Delta\nu$  is independent of coverage and that  $\nu_3$ , the half-width of the perturbed OH band, increases with increasing temperature.

In the case of acetone and ammonia, where measurements were made at several temperatures, the magnitude of the shift decreases with rise in temperature. This behaviour is similar to that displayed by solutions in which hydrogen bonding is present.

**(D) Perturbation of the Adsorbate by the Surface.**—The infrared absorption spectra of methane, ethylene, acetylene, and hydrogen adsorbed on porous glass were investigated by Sheppard and Yates.<sup>18</sup> In addition to obtaining the spectra, they simultaneously determined the coverage. This work provided the first definite infrared spectroscopic evidence which clearly showed the perturbing effect of surface forces on adsorbed molecules, and for this reason will be considered in some detail. Their results are shown in Table 3, which lists not only the frequencies for the adsorbed state but also those for the corresponding liquids and gases. It will be noted that: (i) Where data are available, the frequencies in the adsorbed phase are either lower than or equal to those of the corresponding liquids; thus the perturbing effects of the surface forces are greater than those of the surrounding molecules in the liquid. (ii) All the shifts in frequency are small and approximately 2% of the gaseous value, indicating that no change in chemical species could have occurred as a result of adsorption.

TABLE 3. Frequencies (in  $\text{cm}^{-1}$ ) of bands of adsorbed molecules.

Molecule	Gas	Liquid	Adsorbed	$\nu_{\text{gas}} - \nu_{\text{adsorbed}}$
CH <sub>4</sub>	$\nu_3$ 3018.8 <sup>a</sup>	3018	3006	12.8
	$\nu_1$ 2916.5 <sup>b</sup> (R)	—	2899	17.5
C <sub>2</sub> H <sub>4</sub>	$\nu_9$ 3105.5 <sup>c</sup>	3105	3100	5.5
	$\nu_{11}$ 2989.5 <sup>c</sup>	2980	2980	9.5
	$\nu_1$ 3019.3 <sup>c</sup> (R)	—	3010	9.3
C <sub>2</sub> H <sub>2</sub>	$\nu_3$ 3287 <sup>c</sup>	—	3240	47
H <sub>2</sub>	$\nu_1$ 4160.2 <sup>d</sup> (R)	—	4131	29.2

<sup>a</sup> D. R. J. Boyd, H. W. Thompson, and R. L. Williams, *Proc. Roy. Soc.*, 1952, *A*, 213, 42.

<sup>b</sup> B. P. Stoicheff, C. Cumming, C. E. St. John, and H. L. Welsh, *J. Chem. Phys.*, 1952, 20, 498.

<sup>c</sup> G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," New York, Van Nostrand, 1945.

<sup>d</sup> G. Herzberg, *Canad. J. Res.*, 1950, 28, *A*, 144.

As indicated previously, when a molecule is adsorbed it is necessarily distorted to some extent. If the adsorbate is a highly symmetric polyatomic molecule, this reduction in its symmetry on transference from the

<sup>17</sup> M. Folman and D. J. C. Yates, *J. Phys. Chem.*, 1959, 63, 183.

<sup>18</sup> N. Sheppard and D. J. C. Yates, *Proc. Roy. Soc.*, 1956, *A*, 238, 69.



gaseous to the adsorbed phase allows vibrations to appear in the spectra which previously were forbidden. Also, vibrations which are degenerate in the isolated gas molecule may have the degeneracy lifted or completely destroyed, depending on the extent to which the symmetry is reduced. Thus in the case of methane the totally symmetric vibration  $\nu_1$  which occurs at  $2916 \text{ cm.}^{-1}$  in the Raman spectrum is, as expected, unobserved in the infrared spectra of the gaseous and the liquid phases. In the adsorbed phase, however, a band occurs in the infrared spectrum at  $2899 \text{ cm.}^{-1}$  and is assigned to  $\nu_1$ .

The  $\nu_3$  band is a triply degenerate C-H stretch and if, on adsorption, the symmetry of the molecule were reduced from  $T_d$  (free gas) to  $C_{3v}$  in the adsorbed phase,  $\nu_3$  would be split into two components of symmetry species  $E$  (doubly degenerate) and  $A_1$  (non-degenerate) whose intensities would be approximately in the ratio 2:1. If, however, transference of methane from gas to adsorbed phase should reduce its symmetry from  $T_d$  to  $C_{2v}$ , the degeneracy of  $\nu_3$  would be completely destroyed, yielding three bands of approximately equal intensity. Sheppard and Yates in fact obtained a single, broad, but fairly symmetrical band.

(i) *Rotational degrees of freedom.* It is well known that the bands of a spherical-top molecule consist of  $P$ ,  $Q$ , and  $R$  branches, each branch consisting of lines which correspond to transitions between quantised rotational levels of the molecule. However, a sharp fine structure will be seen only as long as the molecules can absorb radiation without interruption. This can be accomplished, for instance, by increasing the pressure of the absorbing gas, in which case the individual lines become broadened. When this becomes sufficiently great, the individual rotational lines merge but the merging may have very little effect on the overall shape of the band. Sheppard and Yates then attempted to obtain some information about rotational degrees of freedom from the effects of rotational motions on the shape of the  $\nu_3$  band of adsorbed methane. Three possibilities, which in principle can be distinguished spectroscopically, are conceivable, namely: no free rotation in the adsorbed state; free rotation about one axis, probably perpendicular to the surface; and three degrees of rotational freedom.

No fine structure was observed in the spectrum of adsorbed methane at  $90^\circ\text{K}$ , whereas the spectrum of the gas phase exhibited clear fine structure. This, however, does not necessarily rule out the possibility of free rotation, as the individual rotational energy levels may have merged. Consequently, detailed calculations as follows were made of the shapes of the bands to be expected for methane adsorbed in the three ways suggested.

*Case I.* The molecule may be so strongly adsorbed that the rotational degrees of freedom present in the gas phase become torsional oscillations on adsorption. Since rotational fine structure is absent, most of the intensity occurs in a single peak and so the overall shape of the band should be well represented by a Lorentz-type curve, *viz.*,

$$\ln(I_0/I) = a/[(\nu - \nu_0)^2 + b^2]$$

where  $\nu_0$  is the centre of the band,  $2b$  is its half-width, and  $a/b^2 = \ln(I_0/I)_{\nu_0}$ .

*Case II.* Two degrees of rotational freedom are lost on adsorption, the remaining one being about an axis perpendicular to the plane of the surface. In this case the rotational energy levels are given by

$$E_r(K) = K^2 h^2 / 8\pi^2 I \quad \text{where } K = 0, 1, 2, \dots$$

the selection rules being  $\Delta K = \pm 1$  for perpendicular bands and  $\Delta K = 0$  for parallel bands. As usual, the relative intensities depend largely on the factor  $\exp[-E_r(K)/kT]$ , the statistical weights being 1 if  $K = 0$  and 2 if  $K > 0$ .

*Case III.* No rotational degrees of freedom are lost on adsorption. In this case the energy levels are given by the familiar expression

$$E_r(J) = J(J + 1) h^2 / 8\pi^2 I \quad \text{where } J = 0, 1, 2, \dots$$

the relative intensities of the rotational lines being roughly proportional to  $\exp[-E_r(J)/kT]$  times the mean value of the statistical weights for the upper and lower levels  $[(2J + 1)^2]$ .

The results of the calculation showed that Case III can very definitely be ruled out, for it allocates too much intensity to the *P* and *R* branches. So Cases I and II remain for consideration. Unfortunately, the experimental evidence available does not permit a clear-cut and decisive distinction to be made between these two alternatives.

(ii)  $\nu_1$  Band. Since the magnitude of the induced dipole moment is proportional to the polarisability for a fixed field strength, and since the polarisability ellipsoid of methane is a sphere, the induced dipole moment will be independent of the orientation of the molecule. Hence the band shape is independent of rotational motions and the spectrum should consist of a single peak corresponding to a *Q* branch. On the basis of the free rotational model, the width of the  $\nu_1$  band should be less than that of  $\nu_3$ , for the latter consists of *P*, *Q*, and *R* branches. Thus a simple comparison of the relative widths of the two bands might seem to favour the free-rotational model. On the other hand, the greater width of the  $\nu_3$  band could possibly also be due to an unresolved splitting of the three-fold degenerate vibration due to surface forces.

(iii) *Hydrogen.* The absorption band of adsorbed hydrogen was found to be symmetrical with a half-width of about  $21 \text{ cm.}^{-1}$ . Unfortunately, the shape of the band is not decisively helpful in distinguishing between models I (no free rotation on the surface) and II (free rotation about an axis perpendicular to the surface).

The Raman spectrum of hydrogen has been obtained several times<sup>19</sup> and consists of a very strong *Q* branch together with widely spaced but

<sup>19</sup> F. Rasetti, *Phys. Rev.*, 1929, 34, 367.

weaker rotational wings. These rotational branches do not appear in the infrared spectrum of adsorbed hydrogen, but it would be invalid to conclude from this that the hydrogen molecule in the adsorbed state has completely lost its rotational degrees of freedom. The absence of the rotational structure could be due to insufficient hydrogen on the surface of the adsorbent.

Crawford and Dagg<sup>20</sup> had obtained the spectrum of hydrogen at high pressure under the influence of electrostatic fields and confirmed Condon's prediction that the intensity of bands induced by electrostatic fields varies as the square of the field strength. Sheppard and Yates combined their intensity measurements with the data of Crawford and Dagg and computed the field strength to be about  $7 \times 10^6$  v/cm. at the equilibrium adsorption distance. This figure is of the right order of magnitude and clearly shows that the calculation of field strengths outside the adsorbent surface from intensity measurements is along the right lines.

### 3. Chemisorption

If the minimum in the plot of  $U(r)$  against distance occurs at sufficiently small values of  $r$  so that overlap of wave functions cannot be neglected, chemisorption has occurred. In this case the forces which hold the molecules to the surface are of an exchange nature and result in the formation of new bonds. Here several problems are of interest and it is worth inquiring what contributions might be expected from the application of infrared techniques. In the case of chemisorption these techniques were pioneered by Eischens and his colleagues.<sup>21,22</sup> The objective is to obtain a metal adsorbent which (i) will cause as little radiation as possible to be lost by scattering, and (ii) have a specific surface such as to ensure that sufficient gas is chemisorbed to give a well-defined spectrum. Since metals are very good absorbers of infrared radiation, this is an additional source of loss and might seem to make impossible the application of infrared techniques to a study of chemisorption on metals. The absorption coefficient, however, is dependent on the size of the metal particle, and so infrared study of chemisorption is rendered possible because of the happy circumstance that the means used to diminish scattering of radiation and increase the specific surface simultaneously make the adsorbent transparent to infrared radiation. Thus Eischens *et al.*<sup>21,22</sup> have shown that metal particles of size  $3 \times 10^{-2}\mu$  are opaque but that satisfactory spectra can be obtained provided the gas is chemisorbed on metal particles  $\leq 10^{-2}\mu$ . In practice the metal particles are dispersed in a non-porous silica support, the particles of which are in the range  $1.5-2.0 \times 10^{-2}\mu$ .

**(A) Surface Heterogeneity.**—Probably the most significant single property of adsorption is the energetics of the process. The differential heat of

<sup>20</sup> M. F. Crawford and I. R. Dagg, *Phys. Rev.*, 1953, **91**, 1569.

<sup>21</sup> R. P. Eischens, W. A. Pliskin, and S. A. Francis, *J. Chem. Phys.*, 1954, **22**, 1786.

<sup>22</sup> R. P. Eischens, W. A. Pliskin, and S. A. Francis, *J. Phys. Chem.*, 1956, **60**, 194.

chemisorption falls markedly with coverage, this variation of heat with coverage being quite complex in some cases. The fall in heat has been attributed to surface heterogeneity<sup>23</sup> and repulsive interactions between adsorbed species.<sup>24</sup> Since interactions are never large, it seems that in those cases where there is a marked fall in initial heat, this is to be attributed to the heterogeneity of the surface.

In particular, the chemisorption of carbon monoxide on metals has been abundantly studied, and by analogy with the structure of metallic carbonyls, carbon monoxide chemisorption might be expected to take place by a single-site mechanism. At the surfaces of nickel<sup>25</sup> and tungsten films<sup>26,27</sup> some evidence for this had been advanced but recently alternative possibilities have been suggested.<sup>28</sup> Thus, on molybdenum and rhodium films the chemisorption of carbon monoxide was found to be almost exactly equal to that of hydrogen, and on tantalum it was approximately equal to that of oxygen, suggesting that on these metals the carbon monoxide molecule covers two sites. On iron and tungsten the chemisorption was respectively 1.2 and 1.4 times that of hydrogen, thus implying mixed one- and two-site chemisorption. Observation of the infrared spectrum of chemisorbed carbon monoxide and variation in the spectrum with coverage might be expected to provide some information on the heterogeneity of metal surfaces towards carbon monoxide.

A good example of the study of surface heterogeneity by observing variations in the infrared spectra of a chemisorbed species with coverage is provided by the work of Eischens, Pliskin, and Francis,<sup>22</sup> on the spectra of carbon monoxide chemisorbed on silica-supported palladium. The results are shown in Fig. 3, spectra *A—E* being recorded at progressively higher coverages. In interpreting the spectra the following considerations are pertinent.

(a) With increasing coverage all bands might grow at the same relative rate. The implication of this would be that the position of the band was not a function of the bond strength and that the multiple band spectrum is not due to surface heterogeneity.

(b) The bands might grow at different rates and this would be good evidence that the surface was heterogeneous. In this case the bands appearing first would be associated with the most strongly bonded carbon monoxide.

(c) It is conceivable that as the coverage increases new bands might appear while simultaneously bands formed at low coverages might disappear. This would indicate that the structure of the chemisorbed carbon monoxide was a function of coverage.

<sup>23</sup> H. S. Taylor, *J. Phys. Chem.*, 1926, **30**, 145.

<sup>24</sup> J. K. Roberts, *Proc. Roy. Soc.*, 1935, **A**, **152**, 445.

<sup>25</sup> O. Beeck, A. E. Smith, and A. Wheeler, *Proc. Roy. Soc.*, 1940, **A**, **177**, 62.

<sup>26</sup> B. M. W. Trapnell, *Proc. Roy. Soc.*, 1951, **A**, **206**, 39.

<sup>27</sup> Sir Eric Rideal and B. M. W. Trapnell, *Proc. Roy. Soc.*, 1951, **A**, **205**, 409.

<sup>28</sup> M. A. H. Lanyan and B. M. W. Trapnell, *Proc. Roy. Soc.*, 1955, **A**, **227**, 387.

Referring again to Fig. 3 it will be noticed that as coverage increases new bands appear at 1835, 1887, 2062, and 1923  $\text{cm}^{-1}$ . The last two bands increase in intensity with increasing coverage, the 2062  $\text{cm}^{-1}$  band growing proportionately more than the 1923  $\text{cm}^{-1}$  band. On desorption the bands disappear in the reverse order of their appearance, indicating that the species responsible for the 2062  $\text{cm}^{-1}$  band is the least tightly bound.

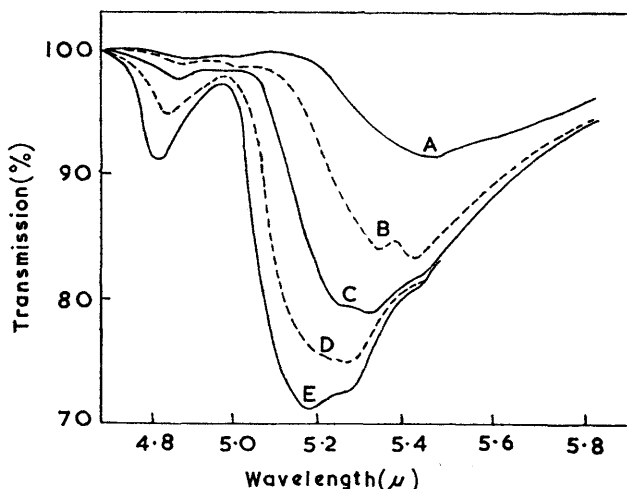


FIG. 3. Effect of increasing surface coverage on the spectrum of carbon monoxide chemisorbed on palladium. (Coverage increases from A to E.)

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

The bands formed are assigned by analogy with the spectra of metal carbonyls, and their spectra are of two types. Carbonyls of nickel,<sup>29</sup> iron,<sup>30,31</sup> cobalt,<sup>32</sup> manganese,<sup>33</sup> and rhenium,<sup>33</sup> in which the carbon monoxide is bound to the metal atom *via* the carbon, have bands in the 2083—2000  $\text{cm}^{-1}$  region. On the other hand, in the case of dicobalt octacarbonyl,<sup>32</sup> iron nonacarbonyl,<sup>30</sup> and iron tetracarbonyl<sup>31</sup> bands occur in the 1852—1818  $\text{cm}^{-1}$  region and these are attributed to carbon monoxide bridging two metal atoms. On this basis, then, the bands found for carbon monoxide chemisorbed on palladium indicate that the gas occurs on the surface bound in two ways: (i) linearly to a single metal atom as  $\text{Pd}-\text{C}\equiv\text{O}$  and (ii) bridged between two metal atoms, *i.e.*, the carbon is bonded to two metal atoms as in (A). The spectroscopic evidence then is that the surface

<sup>29</sup> B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, 1938, **6**, 525.

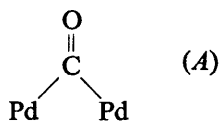
<sup>30</sup> R. K. Sheline and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1950, **72**, 1107.

<sup>31</sup> R. K. Sheline, *J. Amer. Chem. Soc.*, 1951, **73**, 1615.

<sup>32</sup> J. W. Cable, R. S. Nyholm, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1954, **76**, 3373.

<sup>33</sup> G. O. Brumm, M. A. Lynch, and W. Sesny, *J. Amer. Chem. Soc.*, 1954, **76**, 3831.

is heterogeneous and in particular indicates the presence of two types of site.



In the case of carbon monoxide on platinum, the spectrum shows only a single intense band which occurs in the short-wavelength region and is attributed to  $\text{Pt}-\text{C}\equiv\text{O}$ . With increasing coverage no additional bands appear but the one intense band does shift its position. Since in this case increasing coverage does not result in a multiplicity of bands, it is impossible to say whether the observed shift is due to heterogeneity or interaction between molecules.

As previously mentioned, linearly chemisorbed carbon monoxide on palladium produced a band at  $2070 \text{ cm.}^{-1}$  which was readily removed on desorption. In contrast, the linearly chemisorbed gas on platinum is strongly bonded and so the band position for linear carbon monoxide on different metals is no indication of the chemisorption bond strength.

Further spectroscopic evidence relating to the heterogeneity of the adsorbent surface is provided by the work of Yang and Garland<sup>34</sup> on the infrared spectra in the region  $1700-4000 \text{ cm.}^{-1}$  of carbon monoxide on rhodium surfaces. The metal in this instance was supported on a high-area alumina and spectra were taken of carbon monoxide chemisorbed on both sintered and unsintered surfaces. Not only were simpler spectra obtained in the case of the unsintered surface, but in addition the behaviour of the bands on desorption was different for the two types of surface. Here then is additional spectroscopic corroboration of a fact which has long been known, *viz.*, that the character of an adsorbent surface varies with the conditions under which it has been prepared. In this particular case the difference was shown to be due to the presence of adsorbed water on the surface of the unsintered sample.

Assignment of the spectra obtained and their variation with coverage would indicate that on the adsorbents used, there were present at least three types of site. The type of site and the band obtained from carbon monoxide chemisorbed on it are indicated in Table 4.

More recent spectroscopic evidence for the heterogeneity of an adsorbent surface is provided by the work of Terenin and Roev<sup>35</sup> on the spectra of nitric oxide adsorbed on transition metals and their oxides.

(i) *Metals.* Iron, chromium, and nickel were obtained in the disperse state by adsorbing the corresponding metal carbonyl on alumina gel and then decomposing it *in vacuo* at  $150^\circ$ . The spectra obtained for nitric oxide chemisorbed on the metals dispersed in alumina are summarised in Table 5.

<sup>34</sup> A. C. Yang and C. W. Garland, *J. Phys. Chem.*, 1957, **61**, 1504.

<sup>35</sup> A. Terenin and L. Roev, *Spectrochim. Acta*, 1959, 946.

In interpreting these results the following facts are pertinent. In the presence of an electron acceptor, nitric oxide is easily converted into the  $\text{NO}^+$  ion, in which case the vibration frequency of  $1876 \text{ cm.}^{-1}$  for the nitric oxide molecule in the gaseous state is displaced to  $2000\text{--}2400 \text{ cm.}^{-1}$ .<sup>36</sup>

TABLE 4. Location of bands (in  $\text{cm.}^{-1}$ ) in spectra of CO on rhodium.

Sample preparation	Coverage	$\begin{array}{c} \text{OC} \quad \text{CO} \\ \diagdown \quad / \\ \text{—Rh—} \end{array}$		$\begin{array}{c} \text{O} \\    \\ \text{C} \\   \\ \text{—Rh—} \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{C} \\ / \quad \backslash \\ \text{>Rh—Rh<} \end{array}$
2% Rh, unsintered	All	2027	2095	—	—
8% or 16% Rh, unsintered	Low	—	—	2040	—
	High	2027	2095	2055	1905
8% or 16% Rh, sintered	Low	—	—	2045	—
	High	2040	2108	2062	1925

TABLE 5. Frequencies (in  $\text{cm.}^{-1}$ ) of bands of NO adsorbed on Fe, Cr, Ni

Metal	Frequency	Desorption behaviour		
Iron	2008vs	Disappears on desorption at $20^\circ$		
	1805w } 1735w }		Disappear after 1 hour at $150^\circ$	
	1698w } 1660w } 1625w }	Disappear on desorption at $350^\circ$		
	Nickel		1850vs	
			1735w	
		1698w		
1660w				
1625w				
Chromium	2010	approx. the } Disappears after long desorption at room temperature		
	1905		} Disappear after heating	
	1830			
	1735			
	1698			
	1660			
	1625			

Alternatively, in the presence of an electron donor, nitric oxide is converted into the  $\text{NO}^-$  anion, which has a vibration frequency located at  $1000\text{--}1100 \text{ cm.}^{-1}$ .<sup>37</sup> In addition, with transition-metal atoms and ions

<sup>36</sup> W. R. Angus and A. H. Leckie, *Proc. Roy. Soc.*, 1935, *A*, **149**, 327.

<sup>37</sup> L. N. Short, *Rev. Pure Appl. Chem. (Australia)*, 1954, **4**, 41.

nitric oxide forms different types of covalent and co-ordinate bonds which are characterised by definite vibration frequencies.<sup>38</sup> For example, the characteristic frequency of N=O is known<sup>39</sup> to be located in the range 1700—1870  $\text{cm}^{-1}$ , and so the occurrence of a band in this region would be indicative of covalent bonding.

With this background, then, it is evident that the very strong band at 2008  $\text{cm}^{-1}$  in the case of iron indicates an ionised state of the chemisorbed molecule which might perhaps be attached to the surface as  $*\text{NO}^+$ , the asterisk representing a bond to the surface. Judged by the ready removal of this band on desorption, this kind of chemisorption is weak. Nevertheless, the nitric oxide molecule undergoes a pronounced change in its electronic structure which is reflected in the large shift of its vibration frequency on chemisorption.

In addition to this type of binding the bands at 1805 and 1735  $\text{cm}^{-1}$  are characteristic of a double bond between nitrogen and oxygen, and the nitric oxide molecule might perhaps be bound to the surface as  $*\text{N}=\text{O}$ .

The spectra in the case of chromium, like that of iron, indicate the occurrence of more than one type of binding.

(ii) *Oxides.* Here  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  were used as gels but NiO was prepared by the thermal decomposition of the nitrate. The spectrum of nitric oxide chemisorbed on  $\text{Fe}_2\text{O}_3$  gel is summarised in Table 6.

TABLE 6. *Frequencies (in  $\text{cm}^{-1}$ ) of bands of NO adsorbed on  $\text{Fe}_2\text{O}_3$  gel.*

Treatment	1927	1865	1806	1770	1738
On standing in contact with NO (12 hr.)		Increase in intensity			
Desorption at 20°		Dis-appears	Relative decrease in intensity	Dis-appears	Relative decrease in intensity
On admission of oxygen	Disappears and a broad intense band appears at 1620 $\text{cm}^{-1}$	Disappears			
Desorption on heating	Disappear at 150°				
	Bands at 1698, 1660, and 1625 $\text{cm}^{-1}$ disappear at 350°				

The bands here may be classified into two types according to their behaviour on desorption. Thus the group of bands above 1700  $\text{cm}^{-1}$  are removed at 150° whereas the group below 1700  $\text{cm}^{-1}$  disappear only at 350°. That this classification corresponds to two different types of adsorption centre is reinforced by the fact that oxygen acts only on the first

<sup>38</sup> W. Hieber and A. Jahn, *Z. Naturforsch.*, 1958, 13b, 195.

<sup>39</sup> W. G. Burns and H. J. Bernstein, *J. Chem. Phys.*, 1952, 20, 380.



group of bands. Tarte's results<sup>40</sup> indicate that the absorption bands of O—N=O are found in the range 1610—1690 cm.<sup>-1</sup> and so the bands 1700, 1665, and 1625 cm.<sup>-1</sup> are presumably to be ascribed to a covalent bonding of nitric oxide with oxygen atoms.

Nitric oxide on silica and alumina gives bands below 1700 cm.<sup>-1</sup>, but only in the case of the transition-metal oxides are bands found above 1700 cm.<sup>-1</sup>. Hence the bands above 1700 cm.<sup>-1</sup> are attributed to adsorption on metal cations of the oxides. In the case of transition-metal oxides, then, adsorption can occur on both cations and anions, and binding to the former may be either ionic or covalent.

It is noteworthy that in no case is there any spectroscopic evidence for the formation of NO<sup>-</sup>. In this respect the behaviour of nitric oxide is very similar to that of carbon monoxide which is always chemisorbed with electron transfer from the gas to the solid.

**(B) Mechanism of Chemisorption.**—During chemisorption the adsorbate undergoes chemical change which usually results in its dissociation into independent fragments. Consequently, any discussion of the mechanism of chemisorption should consider, not only the nature of the surface bonding, but also the nature of the new species formed during chemisorption: and it is with regard to the latter that infrared studies might prove most useful. For example, the chemisorption and hydrogenation of ethylene has proved particularly perplexing and any information derived from a spectroscopic study of the chemisorption would be pertinent in unravelling this particular heterogeneous reaction.<sup>41,42</sup>

*Chemisorption and hydrogenation of ethylene.* When ethylene is catalytically hydrogenated there also occurs an exchange reaction between a hydrogen atom of ethylene and gaseous hydrogen<sup>43</sup> which is readily demonstrated by the use of deuterium instead of light hydrogen. Farkas and Farkas<sup>44,45</sup> consider these two reactions as occurring independently of each other, and picture the hydrogenation as consisting of simultaneous addition of two atoms of the same hydrogen molecule adsorbed on the surface of the catalyst to a presumably physically adsorbed ethylene molecule:



On the other hand<sup>46</sup> they regard the catalytic exchange as involving a dissociative mechanism according to which the hydrocarbon is split on the surface of the catalyst into a hydrogen atom and a hydrocarbon radical

<sup>40</sup> P. Tarte, *J. Chem. Phys.*, 1952, **10**, 1570.

<sup>41</sup> D. D. Eley, *Quart. Rev.*, 1949, **3**, 209.

<sup>42</sup> J. K. Laidler, *Catalysis*, 1954, **1**, 168.

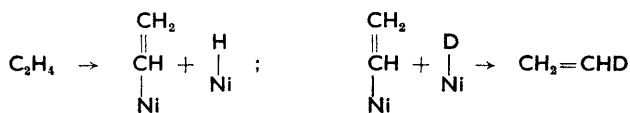
<sup>43</sup> A. Farkas, L. Farkas, and Sir Eric Rideal, *Proc. Roy. Soc.*, 1934, **A**, **146**, 630.

<sup>44</sup> A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1937, **33**, 827.

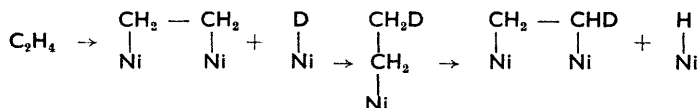
<sup>45</sup> A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 1939, **35**, 906, 941.

<sup>46</sup> A. Farkas and L. Farkas, *J. Amer. Chem. Soc.*, 1938, **60**, 22.

and subsequent reunion of the radical with a deuterium atom. The dissociative mechanism for exchange may be formulated as



In contrast to this view Horiuti and Polanyi<sup>47</sup> consider ethylene to be adsorbed "associatively", *i.e.*, by opening of the double bond. Addition of a hydrogen atom then leads to formation of the "half-hydrogenated state". This may either lose one hydrogen atom or take up a second, thus leading to either exchange or hydrogenation. According to this picture, exchange and hydrogenation are alternative processes of the same primary reaction, *viz.*, that resulting in the half-hydrogenated state. The views of Horiuti and Polanyi may be written:



Here the deuterium atom adds to give an ethylnickel radical which breaks up to form an adsorbed ethylene molecule and liberate a hydrogen atom.

Since these views were propounded much effort has been devoted to the hydrogenation and exchange reactions of ethylene with the object of discriminating between the dissociative and the associative mechanisms or some modification of them. Thus Twigg and Sir Eric Rideal<sup>48</sup> claimed that their results on ethylene hydrogenation and deuterium exchange at nickel surfaces could best be explained if the double bond opened on chemisorption, giving a complex bound by two-point attachment. Subsequent work<sup>49</sup> seemed to confirm this result.

During the course of time it has become clear that the reaction is far from simple, but the efforts of Beeck and his colleagues<sup>25,50,51</sup> have done much to elucidate the nature of the chemisorption of ethylene. By using nickel films it was shown that, if ethylene is carefully admitted so as never to build up an excess pressure, one ethylene molecule is adsorbed per four nickel sites. Admission of excess of ethylene leads to appearance of ethane in the gas phase. Since the hydrogen for this hydrogenation could only have come from the ethylene, the data were taken to mean that the primary adsorption is a dissociation of ethylene into acetylenic residues (occupying two sites) and two hydrogen atoms (each occupying one site). Excess of ethylene immediately removes pairs of \*H atoms, leaving pairs of empty

<sup>47</sup> I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.

<sup>48</sup> G. H. Twigg and Sir Eric Rideal, *Proc. Roy. Soc.*, 1939, *A*, **171**, 55.

<sup>49</sup> G. K. T. Conn and G. H. Twigg, *Proc. Roy. Soc.*, 1939, *A*, **171**, 70.

<sup>50</sup> O. Beeck, *Rev. Mod. Phys.*, 1945, **17**, 61.

<sup>51</sup> O. Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 118.

sites and the formation of ethane. The recent work of Jenkins and Sir Eric Rideal<sup>52</sup> has confirmed the results of Beeck *et al.* that most of the surface is covered with acetylenic and polymerised acetylenic radicals, *i.e.*, that ethylene undergoes dissociative adsorption.

At the present time there is no general agreement as to the mechanism of the hydrogenation or even of the way in which ethylene is chemisorbed. The reason for this is due partly to the complicated nature of the reaction and partly to the difficulty of devising a "one-result" experiment which will enable an unambiguous decision to be made in favour of one of the competing points of view. Consequently, the Reviewer looks forward to the contribution which infrared spectroscopy of the surface phase can make towards the solution of this stubborn problem.

The work of Eischens and Pliskin<sup>53,54</sup> shows that in the case of ethylene chemisorbed on Cabosil-supported nickel either dissociative or associative chemisorption may occur depending on the prevailing experimental conditions.

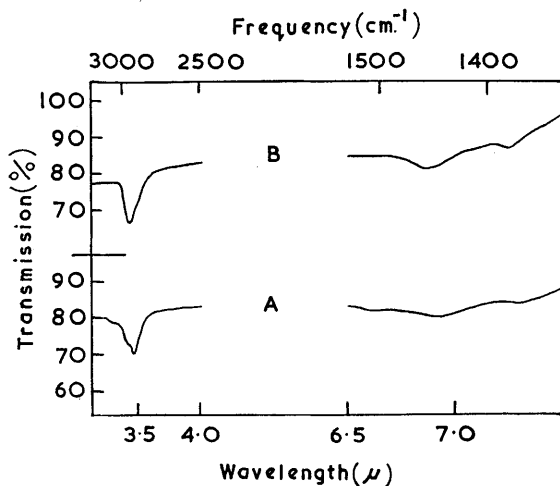


FIG. 4. Infrared spectra of (A) ethylene chemisorbed on hydrogen-covered nickel and (B) the same after treatment with hydrogen.

(Figs. 4, 5, and 6 are reproduced, by permission, from R. P. Eischens and W. A. Pliskin, *Adv. Catalysis*, 1958, 10, 1.

(a) The adsorbent was a Cabosil-supported nickel (9.2 weight %) which had been reduced at 350° and cooled, and the hydrogen had been pumped out for five minutes at room temperature. It is assumed that under these conditions the nickel remains covered with adsorbed hydrogen. The spectrum obtained when ethylene is chemisorbed on such a surface is shown in Fig. 4A. The C-H stretching bands occur in the region 2967—

<sup>52</sup> G. I. Jenkins and Sir Eric Rideal, *J.*, 1955, 2490.

<sup>53</sup> R. P. Eischens and W. A. Pliskin, *Adv. Catalysis*, 1958, 10, 1.

<sup>54</sup> R. P. Eischens and W. A. Pliskin, *J. Chem. Phys.*, 1956, 24, 482.

2857  $\text{cm}^{-1}$  in saturated hydrocarbons and above 3003  $\text{cm}^{-1}$  in olefins. Consequently, the bands in the 2890  $\text{cm}^{-1}$  region of spectrum A are assigned to C-H stretch vibrations for groups in which there are no double bonds on the carbon. The band at 1447  $\text{cm}^{-1}$  is assigned to C-H deformation which changes the H-C-H angle. Its occurrence shows that there are at least two hydrogen atoms on the carbon. Hence the combined presence of bands characteristic of C-H stretch and HCH deformation implies that in this case the chemisorption is associative.

When the chemisorbed ethylene  $\text{H}_2\overset{*}{\text{C}}-\overset{*}{\text{C}}\text{H}_2$  (asterisks representing a bond to the adsorbent) shown in spectrum A of Fig. 4 is treated with 2 mm. of hydrogen at 25°, spectrum B results. Treatment with hydrogen, therefore, produces a shift of the 2890  $\text{cm}^{-1}$  band, whereas the 1447  $\text{cm}^{-1}$  band is increased in intensity and displaced to 1458  $\text{cm}^{-1}$ . The most significant change, however, is in the appearance of the small but sharp band at 1379  $\text{cm}^{-1}$ . This is assigned to the symmetrical  $\text{CH}_3$  deformation, and the increase in 1447  $\text{cm}^{-1}$  intensity is explained as being due to a super-position of the  $\text{CH}_3$  asymmetrical deformation on the  $\text{CH}_2$  deformation. These effects imply the presence of the half-hydrogenated state,  $\cdot\text{CH}_2\cdot\text{CH}_3$ , *i.e.*, ethyl radicals. Thus the information contained in Fig. 4 provides spectroscopic evidence for the theory of Horiuti and Polanyi.<sup>47</sup>

(b) When ethylene is adsorbed on "bare" nickel obtained by evacuation of the hydrogen at 350° for  $\frac{1}{2}$  hour or on hydrogen-covered nickel at 150°, spectrum A of Fig. 5 is obtained. By comparing Figs. 4 and 5 it will be seen that the intensity of the C-H bands in A of Fig. 5 is small compared with those of the associatively chemisorbed ethylene shown in A of Fig. 4. When ethylene chemisorbed on bare nickel is treated with hydrogen at 35°, the band intensities increase as shown in Fig. 5B and this would seem to indicate that the species A is the spectrum of dissociatively chemisorbed ethylene.

Pickering and Eckstrom<sup>55</sup> recently obtained infrared spectra in reflection of ethylene adsorbed on rhodium and nickel films. The metals were evaporated on to the mirrors of a multiple reflection cell,<sup>56</sup> and scans taken before and after adsorption. It was found that when ethylene is added in excess to new rhodium mirrors it is adsorbed with dissociation to produce ethane.

The spectrum of acetylene chemisorbed at 35° on either a hydrogen-covered or a bare nickel surface is shown in Fig. 6. This spectrum is similar to that of Fig. 4B which was assigned to the half-hydrogenated ethylene. The same spectrum was also obtained when acetylene was chemisorbed on a deuterium-covered surface. It seems, then, as if chemisorption of acetylene could involve a self-hydrogenation process, and Pliskin and Eischens point out that the infrared evidence is consistent with the work

<sup>55</sup> H. L. Pickering and H. C. Eckstrom, *J. Phys. Chem.*, 1959, **63**, 512.

<sup>56</sup> J. U. White, *J. Opt. Soc. Amer.*, 1942, **32**, 285.

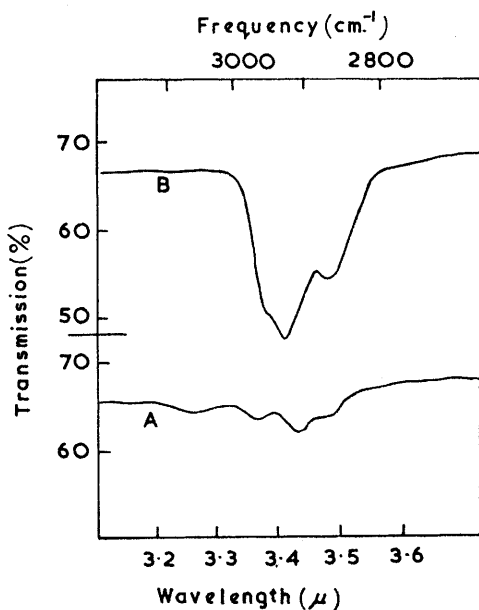


FIG. 5. Spectrum of (A) ethylene chemisorbed on bare nickel and (B) the same after treatment with hydrogen.

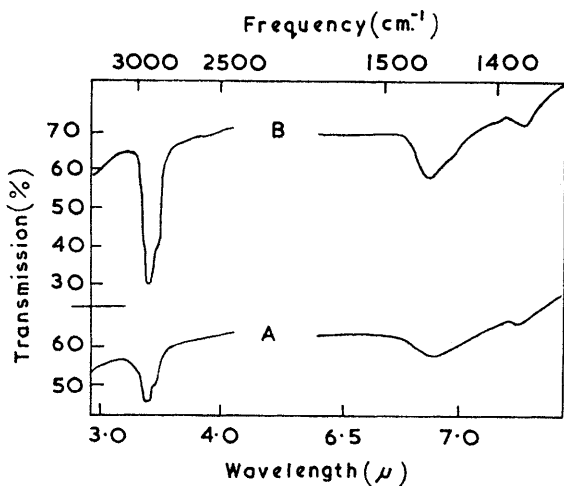


FIG. 6. Spectrum of (A) acetylene chemisorbed on nickel and (B) the same after treatment with hydrogen.

of Douglas and Rabinovitch.<sup>57</sup> These authors found that deuterioacetylene was self-hydrogenated on nickel supported on kieselguhr to a mixture of deuterated ethylenes, the greater proportion of which is  $C_2D_4$ . This seems to indicate that the effect is independent of any hydrogen which might have remained on the surface as a result of preparation of the catalyst. However, since residual surface hydrogen after reduction is always a problem, the present conclusion must be that evidence for self-hydrogenation is indicative rather than rigorously convincing.

**(C) Effect of the Support.**—Almost all the work to date has been on adsorbents which have been supported on silica or alumina. That the support is not inert has been known for some time. For example, Selwood<sup>58</sup> noticed that the concentration of electron holes in nickel oxide films can be increased if the films are supported on  $\gamma$ -alumina. Similarly, Hüttig<sup>59</sup> showed that zinc oxide and ferric oxide as single oxides are poor catalysts for some hydrogenation–dehydrogenations, yet when they are combined their catalytic activity is markedly increased.

Independent spectroscopic evidence of this activity of the support is provided by Terenin and Roev<sup>55</sup> for the case of oxide adsorbents. Thus nitric oxide adsorbed on nickel oxide gives a band at  $1805\text{ cm.}^{-1}$ , but when nitric oxide is chemisorbed on nickel oxide dispersed in alumina gel this band is shifted to  $1850\text{ cm.}^{-1}$ . More pronounced changes are found in the spectrum of nitric oxide chemisorbed on mixed  $Fe_2O_3$ – $Al_2O_3$  gel. In addition to the bands at 1927, 1938, and  $1806\text{ cm.}^{-1}$  found with ferric oxide gel alone, new bands appear at 1980 and  $2125\text{ cm.}^{-1}$ , indicating the presence of new adsorption centres. This is not very surprising for, since the oxide adsorbents and supports are semiconductors, the support can be expected to affect the nature and concentration of defects in the oxide adsorbent.

The “inert” support is also known to affect the catalytic activity of a metal adsorbent dispersed in it.<sup>60</sup> Confirmatory spectroscopic evidence for this is provided by Terenin and Roev<sup>55</sup> who deposited iron from iron pentacarbonyl on aluminium oxide and also on zinc oxide and nickel oxide. The nitric oxide band at  $2008\text{ cm.}^{-1}$  for the  $Fe_2O_3$ – $Al_2O_3$  system was found at  $1985\text{ cm.}^{-1}$  for the Fe–NiO system, indicating that there is indeed an interaction between the support and chemisorbed nitric oxide *via* the iron atom. When nitric oxide is adsorbed on iron dispersed on zinc oxide, instead of the one band there are now two, one being at 2040 and the other at  $1915\text{ cm.}^{-1}$ . It is evident that the zinc oxide is far from inert and the support can markedly influence the metal sites.

Eischens and Pliskin<sup>54</sup> show that, for chemisorption of carbon monoxide on supported metal adsorbents, changing the carrier can bring about

<sup>57</sup> J. E. Douglas and R. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1952, **74**, 2486.

<sup>58</sup> P. W. Selwood, *Bull. Soc. chim. France*, 1949, 489.

<sup>59</sup> G. F. Hüttig, *Discuss. Faraday Soc.*, 1950, **8**, 215.

<sup>60</sup> J. Sheridan, *J.*, 1945, 470.

very marked changes in the spectrum of chemisorbed carbon monoxide. The effects observed by them are shown in Fig. 7. Changing the carrier from silica to  $\gamma$ -alumina results in (i) a displacement to lower frequency of the band due to linear carbon monoxide and (ii) a large increase in the intensity of the band due to bridging carbon monoxide.

Fig. 8 shows that a similar result is obtained when hydrogen is added to carbon monoxide chemisorbed on platinum supported on silica.<sup>21</sup> In this

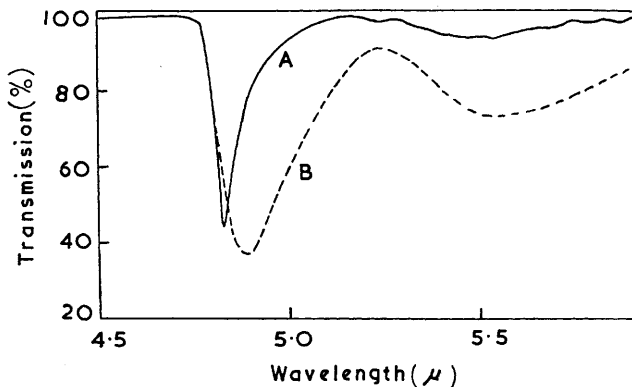


FIG. 7. Spectrum of carbon monoxide chemisorbed on (A) silica-supported and (B) alumina-supported platinum.

(Figs. 7 and 8 are reproduced, by permission, from R. P. Eischens and W. A. Pliskin, *Adv. Catalysis*, 1958, 10, 1.

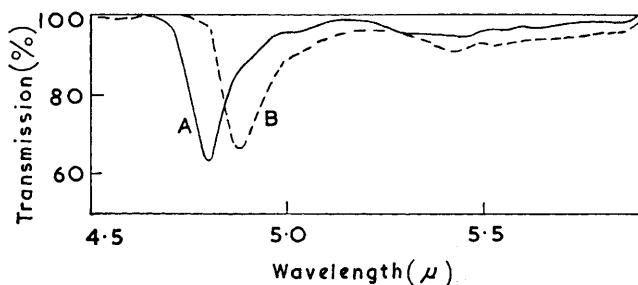


FIG. 8. Spectrum of (A) carbon monoxide chemisorbed on silica-supported platinum and (B) the same after treatment with hydrogen.

case, however, the effects are not nearly as marked as those demonstrated in Fig. 7. Since no bands are produced in the  $3700\text{ cm.}^{-1}$  region (OH) or near  $2800\text{ cm.}^{-1}$  (C-H region), this negative evidence might be taken as indicating that no significant amounts of  $\text{HO}\text{>C=Pt}$  or  $\text{H}\text{>C=Pt}$  are formed.

In addition, formation of these structures would diminish the intensity of the band in the  $2040\text{ cm.}^{-1}$  region due to linear carbon monoxide. This occurs to a slight extent but is accompanied by a simultaneous increase in

the band at approximately  $1840\text{ cm.}^{-1}$  due to bridging carbon monoxide. It seems, then, as if addition of hydrogen has not decreased the amount of carbon monoxide chemisorbed but has converted some linearly bonded carbon monoxide into the bridging form.

The material reviewed here indicates the potential value of studying the infrared spectra of adsorbed gases. So far, results have been obtained almost exclusively for gases either physically adsorbed on high-area silica or chemisorbed on silica-supported metals and metal oxides. Since spectroscopic evidence has been presented which indicates that the support is not inert, it becomes imperative to determine to what extent the observed effects can be attributed to interaction between the adsorbate and the adsorbent. This will have to be done before the spectroscopic results obtained for gases adsorbed on supported metals can usefully be compared with the results obtained on evaporated metal films.

Despite this it can safely be predicted that infrared spectroscopic studies will increase in the future and advances will probably come in the following three directions, *viz.*, (i) increasing the frequency range available for study, (ii) the obtaining of high-resolution spectra, and (iii) the obtaining of fairly reliable intensity measurements. Attainment of the last objective will not be easy but a start has been made in this direction.<sup>61</sup>

The writing of this Review was supported in part by the U.S. Air Force.

<sup>61</sup> L. H. Little, *J. Phys. Chem.*, 1959, **63**, 1616.