

# SOME STUDIES OF PHYSICAL AND CHEMICAL ADSORPTION BY MEANS OF INFRA-RED SPECTROSCOPY

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## INTRODUCTION

Infra-red spectroscopy is now recognized to be an experimental technique of great actual and potential importance in the investigation of molecular adsorption on surfaces. It has been the subject of a number of detailed recent reviews<sup>1-5</sup>, and for this reason no attempt will be made to give a comprehensive treatment of the subject in the present paper. Instead, the main types of application to problems of physical adsorption and chemisorption will be outlined against the background of an account of the development of this type of work in the Department of Colloid Science, and later the University Chemical Laboratories, of Cambridge University.

## INFRA-RED STUDIES OF PHYSICAL ADSORPTION

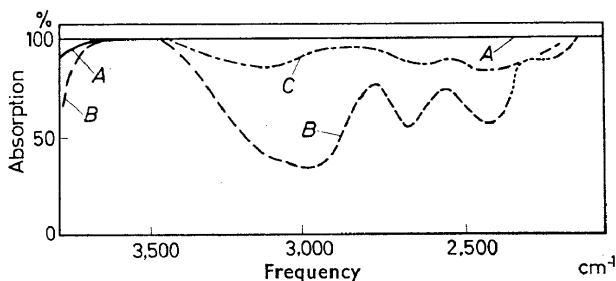
In Cambridge this type of work was commenced as a result of a conversation between myself and Dr D. J. C. Yates, another member of the Department of Colloid Science. Yates had observed some interesting and unexpected phenomena while measuring length changes produced in a tube of porous glass by the adsorption of various gases<sup>6</sup>, and he wished to know whether infra-red spectroscopy could throw any additional light on his results. I had previously discussed the possibility of obtaining infra-red spectra of adsorbed molecules with other colleagues, but it was then concluded that one or two more orders of magnitude in sensitivity were needed in order to get useful results using the standard spectroscopic techniques of those days. Indeed, at that time the only previous work in this field that I was aware of had been carried out by Pimentel, Garland and Jura<sup>7</sup>, and was concerned with the adsorption of deuterium oxide on silica-gel. In that case it had proved to be necessary to incorporate the pieces of silica-gel in paraffin wax after adsorption of the deuterium oxide in order to minimize scattering of radiation; from the adsorption point of view this was clearly not an ideal procedure.

Further discussion with Yates revealed, however, that the adsorbent he had been using (micro-porous Vycor silica glass) had the advantage over most common adsorbents of high specific area (*e.g.* powdered materials) that it scattered a surprisingly small amount of visible radiation, and presumably even less infra-red radiation. This meant that one might hope to traverse many interfaces with a beam of infra-red radiation without great loss of energy. We next calculated the effective path-length of methane through which infra-red radiation would pass assuming: (a) that the beam

traversed two walls of the cylindrical sample of porous glass (wall thickness, *ca.* 1 mm, and specific area *ca.* 150 m<sup>2</sup>/g); and (b) that each surface of the internal pores was covered with a monolayer of the adsorbed gas. The result of this calculation (one monolayer  $\equiv$  0.2 mm path-length) implied that very strong infra-red bands should in principle be obtainable, and so (after carefully checking the orders of magnitude involved!) we decided that the system was very advantageous for infra-red work for frequencies above about 2000 cm<sup>-1</sup>. Below this frequency, it was to be expected that a 2 mm thickness of silica would absorb all the infra-red radiation.

### Some spectroscopic evidence for the nature of surfaces and of adsorption processes

Our first preliminary experiment consisted of placing a tubular sample of the porous glass in the open infra-red beam so that an image of a Nernst filament coincided with its axis. This sample was found to absorb all infra-red radiation at frequencies lower than about 4000 cm<sup>-1</sup> (*Figure 1(A)*), and



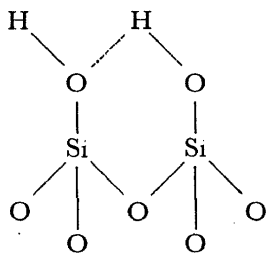
*Figure 1.* (A) The infra-red spectrum obtained by passing radiation through a tubular sample of porous glass before cleaning; (B) the infra-red spectrum of the same sample after removal of adsorbed water and hydrocarbons by heating and evacuation; (C) the absorption band observed with a surface coverage of 0.04 when ammonia is adsorbed on porous glass (after Yates, Sheppard and Angell<sup>1a</sup>)

we concluded that we had observed our first infra-red absorption band of an adsorbed species, water adsorbed from the atmosphere, as a complete black-out. As we had expected, this preliminary experiment made it clear that, in order to obtain useful results with other adsorbed molecules, it would be necessary to design and build a cell in which the porous glass sample could be freed from the water and hydrocarbon molecules (normally physically adsorbed on the surface) by heating *in vacuo* up to 300 or 400°. After some thought, such a cell was designed, and the clean glass sample was shown to have some of the expected transparency at frequencies above 2000 cm<sup>-1</sup>. However, only *some* of the expected transparency for a very strong black-out absorption band persisted between about 3850 and 3500 cm<sup>-1</sup>, as shown in *Figure 1(B)*. In view of the high-temperature treatment of the glass, it seemed most improbable that any physically adsorbed water could remain on the glass but, nevertheless, the position of the band strongly suggested the continued presence of hydroxyl groups. In fact, as we then concluded, we were observing absorption bands of hydroxyl groups attached to the

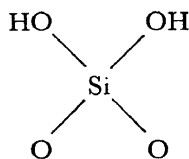
## ADSORPTION STUDIES BY INFRA-RED SPECTROSCOPY

surface by chemical bonds. The infra-red spectrum showed us at once, therefore, that it was misleading to consider the silica surface as solely that of an oxide, and more generally that the infra-red method was capable of providing direct (and unexpected) information about the nature of the surface itself.

We subsequently found (see below) that we were not the first to reach this conclusion about the silica surface by spectroscopic methods, but that Professor Terenin and colleagues in Leningrad<sup>8-11</sup> had been making analogous deductions about surface hydroxyl groups, and the manner in which they interact with adsorbed gas, since 1949 (*i.e.* starting 5 years previously), using the first overtone of the hydroxyl absorption bands as observed with plates of silica-gel and porous glass. To these workers appears to go the credit for making the first systematic studies of adsorption phenomena by infra-red spectroscopy, although work of a related nature on water adsorbed on montmorillonite and other mineral systems had previously been carried out by Coblenz<sup>12</sup>, and by Buswell, Krebs and Rodebush<sup>13</sup>. More recent infra-red work by McDonald<sup>14,15</sup>, Folman and Yates<sup>16</sup>, Kiselev<sup>17</sup>, and others has shown that differently prepared silica surfaces have different numbers of hydroxyl groups, and that these are differently distributed over the surface; they may occur in isolation on the surface, in adjacent pairs or groups (I)<sup>15,16</sup>, and possibly as pairs of hydroxyl groups



(I)

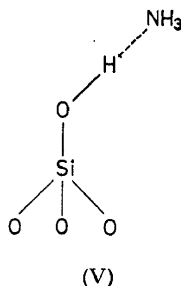


(II)

attached to the same silica atom (II)<sup>17</sup>. The importance of this type of direct information provided by infra-red spectroscopy about the chemical nature of surfaces is clear.

The second piece of work attempted in Cambridge was to obtain an infra-red spectrum from ammonia physically adsorbed on the cleaned glass<sup>18</sup>. We observed the broad and undistinguished absorption band centred near 2900  $\text{cm}^{-1}$  that is shown in *Figure 1(C)*. Yates rightly insisted that the spectroscopic measurements should be made in parallel with conventional adsorption measurements, so that the approximate coverage of the surface could be calculated. It was found that this broad band resulting from the adsorption of ammonia could be detected at a fractional coverage of 1/70th of a monolayer, and it was clear, therefore, that we had high spectral sensitivity. The position and width of this band suggested the presence of very strong hydrogen bonding and, taking into account the system being studied, it seemed more likely that this should arise from hydroxyl groups than from amino

groups. Therefore, we postulated that this band arose from surface hydroxyl groups perturbed by hydrogen bonding to the nitrogen atoms of the adsorbate as in (III) below:



an hypothesis that has been shown to be correct by additional work of Sidorov<sup>20</sup> and Folman and Yates<sup>16,19</sup>.

It was at this stage that we became aware of the then recently published paper by Sidorov<sup>20</sup> on the infra-red spectra in the 4000–2000  $\text{cm}^{-1}$  region of a range of molecules adsorbed on porous glass. Apart from the work of

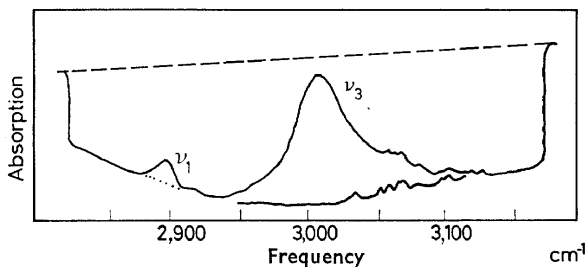


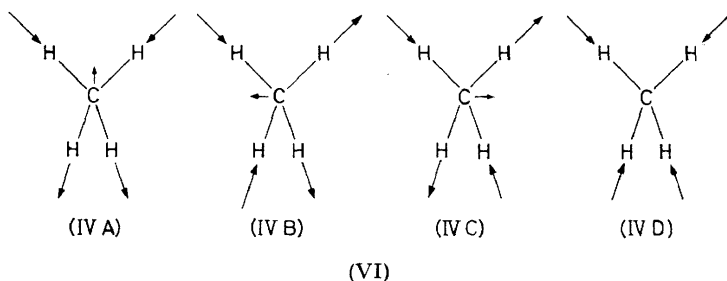
Figure 2. The  $\nu_3$  and  $\nu_1$  absorption bands of methane adsorbed on porous glass (after Sheppard and Yates<sup>21</sup>)

Pimentel *et al.*<sup>7</sup> on adsorbed deuterium oxide mentioned earlier, this appears to have been the first paper primarily concerned with the infra-red spectra of adsorbed molecules in the fundamental vibration frequency region. We also learnt from it of the earlier overtone work of Professor Terenin's group<sup>8–11</sup>.

Yates and I next studied the spectra in the C—H bond-stretching region of some small hydrocarbons physically adsorbed on the glass<sup>21</sup>. For this work, a cell had to be constructed which could be heated to 350° in order to remove physically adsorbed water, and cooled to near liquid-air temperature in order to give sufficient adsorption with volatile molecules. These requirements posed some difficult problems in experimental technique which were in due course successfully overcome by Yates. The first spectrum obtained was from adsorbed methane (see Figure 2), and this turned out to be particularly instructive<sup>21</sup>.

### Relaxation of infra-red selection rules caused by surface forces

In the gas phase, methane has a single infra-red active C—H bond-stretching vibration frequency,  $\nu_3$ . This is triply degenerate and has three mutually perpendicular component vibrations (IV A, B and C), each of which gives rise to a change in electrical dipole moment which is the requirement for the occurrence of an infra-red absorption band. A fourth C—H stretching vibration  $\nu_1$  (IV D) does not give rise to an oscillating dipole moment and, therefore, does not appear in the infra-red spectrum of gaseous methane at normal pressures, although its frequency is known from the



Raman spectrum. The spectrum of adsorbed methane showed a strong band at  $3006\text{ cm}^{-1}$  clearly to be attributed to the  $\nu_3$  vibration, but in addition a second weaker, but easily detected, band appeared at  $2899\text{ cm}^{-1}$ , *i.e.* only removed by  $18\text{ cm}^{-1}$  from the gas phase frequency of  $\nu_1$ , and, therefore, to be assigned to this vibration of the adsorbed molecule.

The operation of the selection rule which normally causes  $\nu_1$  to be infra-red-inactive depends on the molecule having strict tetrahedral symmetry. The effect of the one-sided surface forces must be to distort this symmetry, and this will cause the selection rule to become inoperative in whatever way the adsorbed molecule is oriented with respect to the surface. The new absorption band is, therefore, a direct consequence of the interaction between the adsorbed molecule and the surface. We also obtained evidence of a "forbidden" CH band in the spectrum of adsorbed ethylene, and an additional one has since been observed by Little<sup>22</sup>. Karagounis and Peter<sup>23</sup> have observed other examples of relaxation of selection rules caused by adsorption in the case of a number of larger molecules. At the other extreme the only vibration frequency of hydrogen, which is infra-red-forbidden, has been observed as a result of surface perturbations<sup>21</sup>. At Yates' suggestion, the intensity of this band was measured and used to calculate an approximate value of the electrical field at the glass surface<sup>21</sup>.

$\nu_3$  and  $\nu_1$  for the adsorbed methane molecules occur at frequencies only slightly lower (by  $13$  and  $18\text{ cm}^{-1}$  respectively) than the gas phase value, as is to be expected for physical adsorption; with this thickness of porous glass, it was possible to detect the stronger band when the surface coverage was as small as 1 per cent.

### Evidence for rotational motions of adsorbed molecules

Another point of considerable interest in the spectrum of adsorbed methane is the different half-widths ( $28$  and  $10\text{ cm}^{-1}$  respectively) for the

$\nu_3$  and  $\nu_1$  absorption bands (*Figure 2*); why do they differ so greatly? At an earlier stage, Yates had asked whether information about the rotational motions of adsorbed molecules was obtainable from infra-red spectra. I had replied that such information was hardly ever obtainable from molecules in condensed states where continued and rapid interruptions to rotational motions would normally lead to a blurring-out of rotational structure. In any case, the shape of the  $\nu_3$  infra-red band of adsorbed methane did not even approximate to a smoothed-out version of the gas-phase vibration-rotation contour, for, whereas the latter has a very prominent central  $Q$  branch with well separated  $P$  and  $R$  wings, the former rises fairly smoothly in intensity towards a broad central maximum.

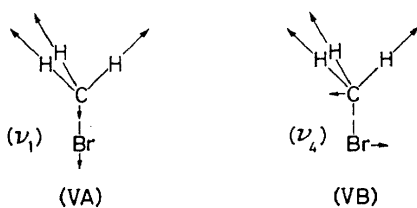
The  $P$  and  $R$  branches of the gas-phase  $\nu_3$  band are well spread out and separated from the central  $Q$  branch because of the operation of a statistical weight factor,  $(2J + 1)^2$  in addition to the Boltzmann factor  $\exp(-E_{\text{rot}}/kT)$  in determining the relative distribution of molecules among the rotational energy levels,  $E_{\text{rot}}$ . Here  $J$  is the rotational quantum number and  $kT$  has the usual significance<sup>21</sup>. This pattern of energy-level population is a consequence of free three-dimensional rotation, and it occurred to me that the Van der Waals' forces holding the molecule to the surface might have the effect of restricting rotation about axes parallel to the surface (these motions would require atoms to be pulled away from the surface) but still allow essentially free rotation about the third axis perpendicular to the surface. A result of such a fixed rotational axis would be that the relative intensities of lines in the  $P$  and  $R$  branches (arising from fluctuating dipole moment components parallel to the surface that are modulated, *i.e.* carried round, by rotation) would be determined only by the Boltzmann factor. The statistical weight would be 2 in each case, corresponding to clockwise or anti-clockwise rotation about the fixed axis. In this case, the combined  $P$  and  $R$  branches would give rise to a band of considerably reduced half-width in comparison with the case of three-dimensional rotation, and the intensity of the band should rise smoothly towards the centre. It proved to be easy to fit the observed width and shape of the  $\nu_3$  band in the adsorbed state on the basis of this model, after making due allowance for the superimposed  $Q$  branch caused by the dipole-moment component parallel to the rotation axis.

It is also easy to account for the narrower  $\nu_1$  band in the adsorbed state on the basis of this same hypothesis. In this case only a  $Q$  branch is to be expected, as the fluctuating dipole change which gives rise to infra-red activity this time finds its origin in a dipole moment induced in the methane molecule by the surface forces; this induced dipole moment is of necessity perpendicular to the surface and coincident in direction with the assumed single rotation axis. This same conclusion can be deduced in more orthodox terms by taking into account Condon's assertion<sup>24</sup> that the selection rules for an infra-red spectrum induced by an external electrical field will be the same as for the Raman spectrum.

An alternative qualitative explanation of the relative widths of the  $\nu_3$  and  $\nu_1$  bands of adsorbed methane could be based on the fact that the first of these is a triply-degenerate vibration and the second a singly-degenerate one. The same forces which result in adsorption might, in principle, have the effect of causing the component of the vibration  $\nu_3$  perpendicular to the surface to

differ somewhat in frequency from the two components parallel to the surface. If this splitting of frequencies is less than the half-width of the absorption bands of the individual components, the result might be a broad but somewhat asymmetrical band;  $\nu_1$  might well be narrower because it consists of a single component band. This alternative hypothesis did not seem to be as satisfactory as the previous one<sup>21</sup>, because it can only account qualitatively for the relative band-widths, and the observed  $\nu_3$  band showed only slight asymmetry; on the other hand, although the single-rotation-axis hypothesis accounted very satisfactorily in a quantitative fashion for the half-width of  $\nu_3$ , the agreement might have been a chance one. It seemed desirable, therefore, to attempt to distinguish between the alternative hypotheses by experimental means, and in particular by a study of the band-width of  $\nu_3$  as a function of temperature. For, if the width is caused by rotational motions, at lower temperatures this should become narrower by a readily calculable amount. An incipient splitting of a vibrational degeneracy would, on the other hand, be expected to become greater at low temperatures (resulting in a broadening of the band or a resolution into separate components), as the methane molecule is then held more closely to the surface. It was not easy to carry out this type of experiment on methane, because its adsorption is rather temperature-sensitive and, for adequate sensitivity, only a small temperature range would have been available near liquid nitrogen temperatures using the cell we had available. It was, therefore, planned to carry out an analogous experiment on the C—H stretching absorption bands of methyl bromide. This is appreciably physically adsorbed on porous glass at room temperature, and could, therefore, readily be studied down to liquid nitrogen temperatures; the measurements were carried out by Dr Mathieu<sup>25</sup>.

The  $\nu_1$  and  $\nu_4$  C—H stretching absorption bands of methyl bromide give rise to dipole changes parallel and perpendicular to the C—Br axis respectively (V A and B):



(VII)

The contours of the gas-phase bands reflect the fact that the dipole change of  $\nu_1$  is modulated only by rotation about the greater axes of inertia that are perpendicular to the C—Br axis, and that of  $\nu_4$  (much broader with readily resolved fine structure) is modulated also by rotation about the three-fold axis of low moment of inertia. If it is assumed (as previously for methane) that, in the adsorbed state, the molecule rotates only about the three-fold axis with the bromine atom held to the surface (spectroscopic evidence for

the orientation with respect to the surface is given below), then we should expect the  $\nu_4$  band to be much broader than  $\nu_1$  in the adsorbed state; this was found to be the case<sup>25</sup>. However, once again it might have been postulated that the greater width of  $\nu_4$  in comparison with  $\nu_1$  is to be accounted for by incipient splitting of the two-fold degeneracy of  $\nu_4$  resulting from surface forces acting on molecules lying flat on the surface.

Considering next the quantitative aspects of the problem, because rotations about the large inertial axis contribute only slightly to the gas-phase band-width of  $\nu_4$ , the rotation hypothesis suggests that  $\nu_4$  in the adsorbed state should have a band contour similar to a blurred-out version of the

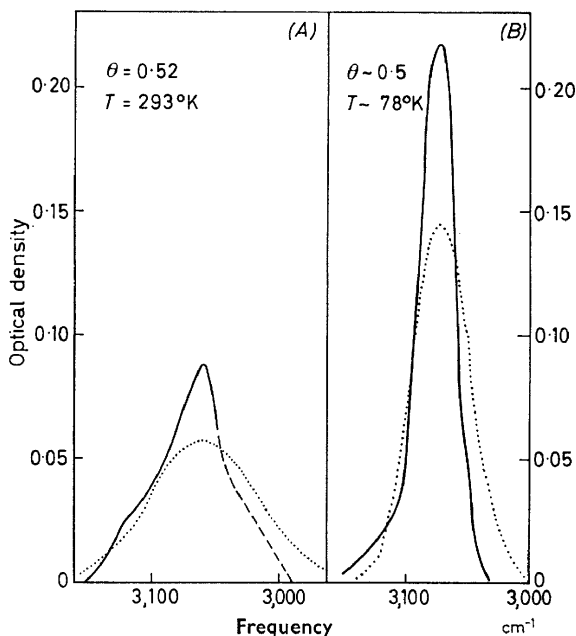


Figure 3. The  $\nu_4$  absorption band of adsorbed methyl bromide at a surface coverage,  $\theta$ , of about 0.5 on porous glass (A) at 293°K, and (B) at  $\sim 78^\circ\text{K}$ . The superimposed dotted curves represent the band contours calculated on the hypothesis that the methyl bromide molecule is in free rotation about the three-fold axis. (Reproduced by permission of *Z. Elektrochem.*, from Mathieu, Sheppard and Yates<sup>25</sup>.)

gas-phase contour, and this is so<sup>25</sup>. Figure 3(A) compares the observed  $\nu_4$  band at a surface coverage of about 0.5 at 293°K, with the calculated one based on the single-rotation-axis hypothesis; although the experimental curve shows somewhat greater intensity in the centre of the band, the agreement is fairly good. Figure 3(B) compares the observed and calculated band contours at the much lower temperature of about 78°K. In contradiction to the split-degeneracy hypothesis, the over-all band sharpens up markedly on cooling without splitting into components, and the quantitative sharpening is



in very good agreement with predictions based on the single-rotation-axis hypothesis. The latter is clearly to be preferred<sup>25</sup>.

In the case of adsorbed methyl bromide, the infra-red spectrum of the surface hydroxyl groups (see Mathieu, Sheppard and Yates<sup>25</sup>) shows clearly that the molecules are held to the surface by hydrogen-bonding between the hydroxyl groups and bromine atoms; this is consistent with a picture that presumes that there is rotation about the axis of the C—Br bond itself but not about axes perpendicular to this.

The idea (generated for us by these adsorption experiments) that band-width phenomena in condensed states might be not uncommonly caused by rotational motions when a molecule has one or more low moments of inertia, had been suggested earlier by Welsh and his colleagues<sup>26</sup> in connection with some Raman spectra of liquid methane. We have since found it a very profitable starting-point for interesting infra-red studies in solution<sup>27</sup>, where the available spectral regions are less limited than when spectra are observed against a strong silica background. W. J. Jones reported on a considerable number of examples of such band-width phenomena in an earlier paper to this Conference, and others have made similar studies<sup>28,29</sup>. This more extensive work has shown that although blurred-out rotational contours are to be found in solution in many cases, often the centres of the bands show enhanced relative intensity. Whatever the cause of this phenomenon, it accounts for the somewhat anomalous band contours  $\nu_4$  of adsorbed methyl bromide, and shows that our original discussion of the  $\nu_3$  band-contour of adsorbed methane in terms of a smoothed-out gas-phase contour was perhaps too naïve. Although there seems now to be no doubt that this wide band is to be interpreted in terms of rotational motions of the adsorbed molecules, it is, perhaps, unwise to rule out the possibility of some degree of three-dimensional rotation on the surface in this case. However, the band in the adsorbed state does not show such extensive rotational wings as the analogous one in carbon tetrachloride solution<sup>29</sup>, and rotation about a single axis still explains the observed band shape most readily.

## Conclusion

The few examples discussed above show that, in addition to giving measurements of the small changes in vibration frequencies suffered by molecules on physical adsorption, infra-red spectra can provide direct evidence for molecular distortions by surface forces through changes in the selection rules, and for the rotational motions on the surface by means of band-width phenomena. For all this information to be deducible from an infra-red spectrum it is necessary for the adsorbed molecule to be small and symmetrical and in this sense the examples chosen for discussion have been somewhat favourable cases; nevertheless, they do illustrate well the over-all scope of the method. For the future, it is to be hoped that long-wavelength infra-red spectroscopy will enable measurements to be made of the low-frequency vibrations of the adsorbed molecule as a whole against the surface, and so provide even more direct information about the strength and nature of surface forces in physical adsorption.

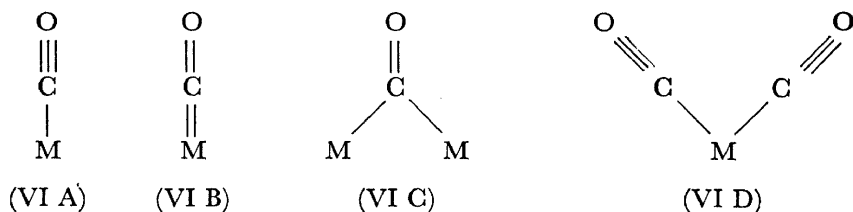
## SOME CHEMISORPTION STUDIES BY INFRA-RED SPECTROSCOPY

### Introduction

The applications of infra-red spectroscopy to chemisorption problems will be illustrated mainly with reference to some spectra of hydrocarbons adsorbed on silica-supported metals.

The study of chemisorption on transparent or partially-transparent adsorbents by infra-red methods does not necessarily lead to any greater experimental difficulties than are encountered in physical adsorption work. It is to be expected, moreover, that the changes in spectra on chemisorption will be more profound than for physical adsorption as new surface species are formed. The projected study of chemisorption on *metals*, however, raises the particular difficulty that a metal is normally opaque to infra-red radiation and so will reflect all the energy if the sample is in the form of a coherent mirror, or will tend to absorb a great deal of energy if the sample is in the form of a porous film or "metal black"<sup>2</sup>.

The first successful work in this field appears to have been carried out by Eischens, Francis and Pliskin<sup>30,31</sup> of the Texas Oil Company in the U.S.A. They found that they could obtain spectra from molecules chemisorbed on metals provided that the metal particles were sufficiently small ( $<100\text{\AA}$ , *i.e.* much smaller than the wavelength of radiation), and that they were separated from each other by a transparent support such as high-area powdered silica. The first successful work used carbon monoxide as the adsorbate and, for example, it was possible to show that some of the carbon monoxide was adsorbed "linearly" to a single metal atom (VI A or B) and some in a "bridged" form, being attached to a pair of metal atoms (VI C)<sup>30,31</sup>. Later



spectroscopic work has indicated that, on certain metals, a proportion of the carbon monoxide molecules may be adsorbed in pairs on the same metal atoms (VI D)<sup>32</sup>.

In Cambridge, when we first heard of this work, we were engaged in spectroscopic physical adsorption studies on porous Vycor glass. Because a porous glass sample of a given total area scatters much less energy than a powdered silica sample, we thought that better results might be obtained by repeating the type of experiment carried out by Eischens and his colleagues using porous glass as the silica support. In particular, we aimed to obtain the much weaker absorption bands of adsorbed hydrocarbons.

Dr Little succeeded in obtaining infra-red transmitting samples of metals dispersed on porous glass, and from these obtained good infra-red spectra from adsorbed hydrocarbons<sup>33</sup>. It turned out, however, that it was only

possible to incorporate a rather limited amount of metal in the silica glass without causing the sample to be shattered. This meant that our silica background spectrum was more pronounced than those obtained by Eischens and his colleagues, so that we were unable to obtain spectra in the useful region of C—H angle-bending vibrations near  $1400\text{ cm}^{-1}$ . However, good spectra were obtained in the C—H bond-stretching region near  $3000\text{ cm}^{-1}$  with a coherent tubular metal-on-glass sample that could be placed (in a suitable cell) vertically in the infra-red beam of a standard double-beam spectrometer<sup>33</sup>. Furthermore, the large over-all size of the adsorbent sample made it possible to make approximate quantitative measurement of the amount of adsorbed gas, and hence to study the absolute as well as the relative intensities of the infra-red absorption bands. The transmission of a suitable sample in the  $3000\text{ cm}^{-1}$  region was 10–15 per cent but, by operating the spectrometer with wider slits than normal and by using a fluorite prism, the spectra showed sufficient detail to enable useful deductions to be made about the structure of adsorbed species. The spectra were interpreted, insofar as this was possible, using correlation rules derived principally from the detailed analysis of hydrocarbon spectra. The C—H bonds of carbon atoms attached directly to the metal surface might be expected to have absorption bands differing somewhat in both frequencies and intensities from those of the analogous hydrocarbons. Although this does introduce some uncertainty in the interpretation procedure, the spectra of some metal-alkyl compounds that Dr Clark has measured suggest that the changes in spectrum caused by adjacent metal atoms is usually not great<sup>34</sup>; in any case, C—H bonds not directly attached to metals are expected to give normal absorption bands. Because the hydrocarbons studied by these techniques are only physically adsorbed to the silica support when this is used alone, it is naturally assumed that the hydrocarbon groups detected after removal of physically adsorbed material are chemisorbed to metal atoms<sup>33,35,1,3</sup>. It should not be forgotten, however, that, although the spectroscopic evidence often suffices to determine something of the nature of the surface hydrocarbon group, it does not so readily determine the type of atom to which it is attached. It is just possible that, in some of these cases, the metal may have acted as a catalyst for the reaction of a hydro-carbon with the silica surface, although the fact that different metals often give different spectra (see below) is a point in favour of the assumption that the chemisorption is to metal.

The work that we have done in this field has been of two main types. Dr Little studied the spectra obtained from the chemisorption of acetylene and ethylene on several different metals supported on porous glass<sup>33</sup>, while Dr Clark has studied those of a wider range of hydrocarbons adsorbed on similar samples of platinum<sup>34</sup>. When we were still at the stage of developing our experimental techniques Pliskin and Eischens<sup>35</sup> published some spectra of hydrocarbons chemisorbed on nickel; since then, the same authors<sup>1,3</sup> have described more detailed and extensive results using nickel which parallel in many ways our work on several other metals. As an example of this type of work, we shall discuss below some spectra obtained by Dr Clark<sup>34</sup> from propylene and methylacetylene chemisorbed on silica-supported platinum.

*Figures 4(A) and 4(B) show the infra-red spectra obtained from propylene*

( $\text{CH}_3\cdot\text{CH}:\text{CH}_2$ ) and methylacetylene ( $\text{CH}_3\cdot\text{C}:\text{CH}$ ) respectively in the  $3000\text{ cm}^{-1}$  region after leaving the platinum-Vycor glass sample in contact with the gaseous hydrocarbons overnight. The gas-phase and weakly

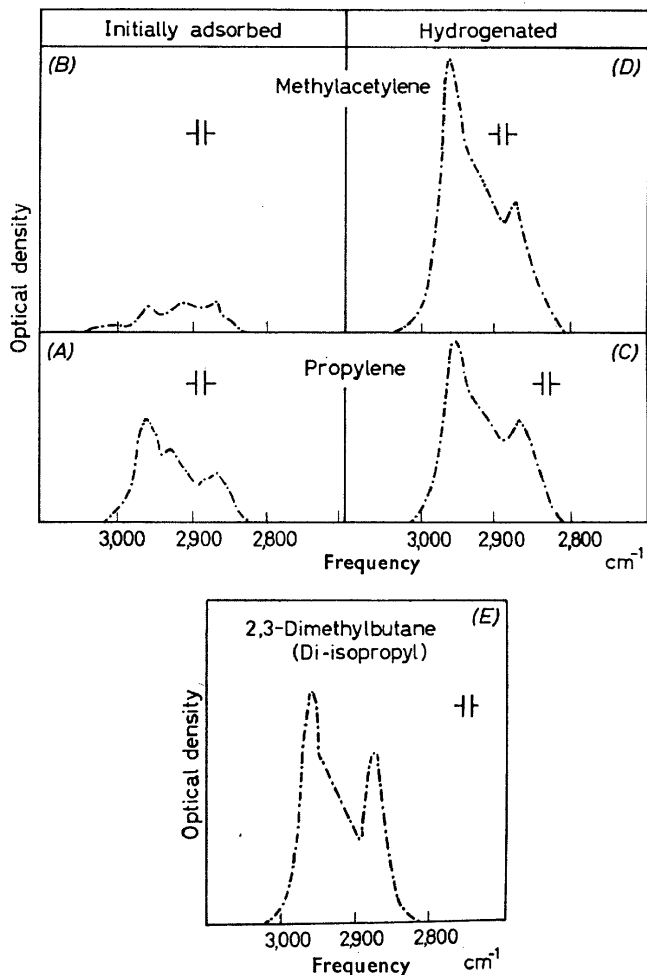
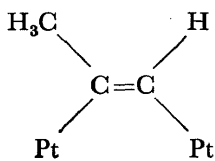


Figure 4. The absorption bands in the C—H bond-stretching region for (A) propylene initially adsorbed on a porous-glass supported platinum sample and (C) after hydrogenation of the chemisorbed species; (B) and (D) represent analogous spectra obtained from adsorbed methylacetylene; (E) is the spectrum of 2,3-dimethylbutane (di-isopropyl) in the same region (with narrower spectral slits)

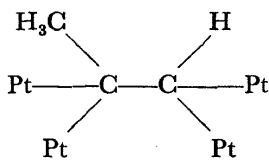
adsorbed hydrocarbons were removed by several hours pumping before the spectra were taken. In the case of propylene, at the end of the period of contact with the catalyst, the gas-phase was shown to be unchanged in composition by measurement of its infra-red spectrum. Figures 4(C) and 4(D) show the spectra obtained after hydrogen had been added to the system

containing the initially adsorbed hydrocarbon species, and then excess hydrogen removed by pumping. The hydrogenation procedure does not cause the initially adsorbed species to be desorbed into the vapour phase, but instead gives rise to a new surface species.

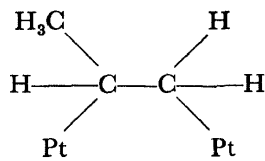
The spectrum of the initially adsorbed species obtained from propylene, *Figure 4(A)*, shows no bands of appreciable intensity above  $3000\text{ cm}^{-1}$ , and hence it is probable (but not absolutely certain, see data cited previously<sup>33</sup> on certain metal-vinyl compounds) that it has only saturated C—H bonds. In any case the prominent band at  $2980\text{ cm}^{-1}$  (with a companion near  $2850$



(VII A)



(VII B)



(VII C)

$\text{cm}^{-1}$ ) is almost certainly to be assigned to a  $\text{CH}_3\text{—C}$  group, and the considerable over-all intensity-increase in the spectrum on hydrogenation of the surface species suggests that more than one additional C—H bond has been formed. This implies that the initial species is more likely to have been formed by a dissociative mechanism leading to species of the general types (VII A) or (VII B) rather than by an associative mechanism leading to (VII C).

At this stage, the spectral data probably do not justify a more detailed discussion of the structure of the initially adsorbed species; but, in the spectrum of the hydrogenated species, the methyl band at  $2980\text{ cm}^{-1}$  is doubled in intensity, and the spectrum as a whole, *Figure 4(C)*, bears a very strong resemblance to that of an isopropyl group (compare the spectrum of 2,3-dimethylbutane, or di-isopropyl, in *Figure 4(E)*). The linear butenes, butene-1 and *cis*-butene-2, adsorbed on silica-supported platinum<sup>34</sup> give analogous spectra after hydrogenation which are equally readily to be interpreted as originating in *s*-butyl groups attached to the surface.

The spectrum of the initially adsorbed species from methyl acetylene, *Figure 4(B)*, is less strong (as would be expected from the presence of a smaller proportion of C—H bonds) and not very well-defined. However, the weak band at  $3015\text{ cm}^{-1}$  suggests the presence of some  $=\text{CH—}$  groups, and the lack of a strong band near  $2970\text{ cm}^{-1}$  (compare with the analogous one obtained from adsorbed propylene) suggests that the surface species contains less than one methyl group per  $\text{C}_3$ -unit. Possibly there are several different initially-adsorbed species contributing to the spectrum. On hydrogenation once again a methyl-rich species, almost certainly an isopropyl group, is obtained (*Figure 4(D)*).

Pliskin and Eischens<sup>35</sup> have previously published a spectrum of propylene on nickel which is considerably different from that of *Figure 4(A)*, and has its strongest peak at  $2880\text{ cm}^{-1}$ ; their spectra obtained from the butenes on

nickel<sup>1</sup> differ in an analogous way from our results on platinum. These authors appear to have published no spectra for hydrogenated surface species derived from propylene, but their results from chemisorbed and hydrogenated butenes on nickel show that the final product is an n-butyl group attached to the surface in marked and interesting contrast to the s-butyl groups found with platinum.

As always in adsorption work, due allowance must be made for slight differences in experimental technique used in the two sets of studies\*, and further work is needed to complete the picture. Nevertheless, it is surely clear from these examples that infra-red spectra are capable of providing considerable insight into the reactions between hydrocarbons and supported-metal catalysts, and the same type of information is undoubtedly obtainable from many other similar adsorption and catalyst systems using well-established spectroscopic techniques of the types described above.

Up to now, oxide-supported metal samples have been responsible for nearly all the fruitful infra-red studies of adsorption on metals, and such metal catalysts are of importance because of their wide industrial applications. However, from the more academic point of view, it would be a great simplification if spectroscopic work could be done on evaporated metal samples, where the supporting substrate may be expected to play a less significant part in the adsorption process and the vacuum conditions can be made more rigorous. Preliminary experiments have already been carried out using, on the one hand, multi-reflection techniques between mirror-like metal deposits<sup>36,37</sup> and, on the other hand, transmission measurements through the more porous type of evaporated metal film<sup>1,3,38</sup>. In several cases, the results have been promising, although much remains to be done before the experimental conditions required for this type of work can be considered to be well worked out. A considerable possibility for development lies in this direction.

As in other fields, infra-red spectroscopy has shown itself to be a physical method of great flexibility and, therefore, widespread application, in studying adsorption processes and systems. In the chemisorption field, it appears so far to be the only method capable of giving useful direct information about the structures of surface species involving adsorbate molecules which are both as simple as carbon monoxide, and as complex as some of the hydrocarbons discussed above.

## Summary

A survey is given of the scope of the infra-red spectroscopic method as applied to the study of physical adsorption and chemisorption systems.

It is shown that the spectra of high-area silica samples give information about the presence of hydroxyl groups in various types of location on the "oxide" surface.

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\* One point of difference concerns the Vycor porous-glass support used by us and the Cabosil powdered silica used by Eischens and his colleagues<sup>1</sup>; however, we have been able to reproduce their spectra from butenes on nickel using porous glass as the support<sup>1,34</sup>. Another difference concerns the preparation of the metal samples; Eischens and Pliskin<sup>1</sup> obtained well-defined spectra from butenes only on "hydrogen-covered" nickel prepared by cooling down the metal sample from 350° in an atmosphere of hydrogen, whereas our platinum sample had been evacuated after reduction at 380° and before cooling. However, with other olefins on platinum, we have obtained identical spectra whichever way the metal sample was prepared, and so neither experimental difference is necessarily of significance.

## ADSORPTION STUDIES BY INFRA-RED SPECTROSCOPY

The spectra obtained from ammonia, methane, methyl bromide and hydrogen physically adsorbed on porous silica-glass are discussed. Modification of surface hydroxyl absorption bands by ammonia and methyl bromide shows that some of these molecules are held to the surface by hydrogen bonds. The surface forces bring up otherwise "forbidden" absorption bands of symmetrical adsorbed molecules and the absorptions bands show small frequency changes compared with the gas phase. Band contours and widths give information about the freedom, or otherwise, of rotational motions on the surface for molecules which have one or more small moments of inertia.

In the field of chemisorption, the work on carbon monoxide chemisorbed on oxide-supported metals is briefly reviewed. A more detailed account is given of spectra obtained from the chemisorption of hydrocarbons on silica-supported metals with particular reference to the spectra obtained from propylene and methylacetylene adsorbed on this type of platinum catalyst. The spectra give considerable information about the nature of the initially-formed surface species and those formed by subsequent surface hydrogenation.

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