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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

INFRARED STUDIES OF ADSORPTION
ON SILICA AND PLATINUM

by

Ian A. Cody

A thesis submitted to the School of Graduate
Studies in partial fulfillment of the requirements
for the degree of Ph.D. in Chemistry

UNIVERSITY OF OTTAWA

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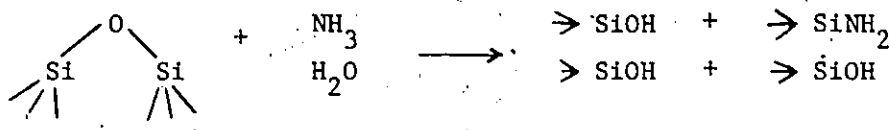
ABSTRACT

This thesis is concerned with the application of infrared spectroscopy to studies of (a), the nature and reactivity of silica surfaces which have been degassed at elevated temperatures (400 - 1200°C) under vacuum conditions and (b), with studies of reactions of catalytic interest on silica supported platinum (Pt/SiO₂). A summary of results is given below.

A. Silica

The isolated hydroxyl groups on silica give rise to a strong infrared absorption band centered at 3748 cm⁻¹ which is slightly asymmetric to the low wavenumber side and has a half width of about 8 - 10 cm⁻¹. A high resolution infrared spectroscopic examination of this band has failed to show that any resolvable fine structure can be detected when atmospheric compensation in the double beam spectrometer is perfect. This result contradicts some, but not all, earlier work where observed fine structure has been attributed to the presence of both geminal and isolated hydroxyl groups. It has been found that when the double beam compensation has been intentionally disturbed so as to give a net absorption of water vapour in the reference beam, the spectra reported by others, with apparently resolvable fine structure, can be reproduced. It is concluded that the spectra obtained by some other workers may be distorted for similar reasons and that there is no spectroscopic evidence which allows one to distinguish between geminal and isolated silanol groups if one or both are present.

When a silica surface is evacuated at a temperature beyond 400°C, a new reactive site, possibly a strained bridge, is formed as a result of the collapse of isolated hydroxyl groups. This site was active for the chemisorption of H₂O and NH₃ and the reaction stoichiometry was envisaged as follows:



The silanols generated in the above absorb at 3741 cm⁻¹ and are distinct from the aforementioned isolated hydroxyls. Isotopic substitution data has been used to prove that SiNH₂ groups were formed when NH₃ is the reactant. However, pyridine and trimethylamine adsorb without disrupting the bridge via simple coordination at a centre capable of acting as a Lewis acid. Additional evidence suggests that the site is not symmetric as drawn above and that one side of the bridge is more reactive than the other. A careful examination of the adsorption of NH₃ indicates that reaction also proceeds preferentially on one of the silicon atoms.

Another type of reaction between dehydroxylated silica and either NH₃ and H₂O has also been observed when higher pressures of these reactants are added and although the active sites themselves are not responsible for this secondary reaction, the regions of the surface in the neighbourhood of the sites are also likely to be strained to some degree and may facilitate such a reaction.

Other reactions on silica have been studied and used as a precursor to the Pt/SiO₂ studies. At high temperatures (>600°C), HCN and C₂N₂ have been found to react extensively with silica and three major bands between 2300 - 2000 cm⁻¹ are formed. Using isotopic frequency shift data

in conjunction with force constant calculations, the species were shown to be SiCN, SiNC and SiNCO.

B. Pt/SiO₂

The reactions of even simple molecules on supported metal surfaces are often not well characterised by their infrared spectra because of extensive energy losses due to scattering by the dispersed metal. However, in this work, good quality spectra have been obtained as a result of the development of refined procedures for catalyst preparation and definitive results have been obtained for the first time for the adsorption of ammonia and pyridine on Pt/SiO₂. Isotopic substitution techniques have shown that ammonia adsorbs as a single species Pt:NH₃. Controlled oxidation of this species gave a partially oxidised product, possibly Pt:NHO, whereas the adsorption of ammonia on an oxidised Pt surface produced different species which were thought to be PtONH₂ and PtO₂NH. However, pyridine does not attach to Pt by means of a simple coordinate bond and it is believed that a single species is adsorbed through a π electron interaction with the surface.

In general, complex spectra resulted from the adsorption of various amines and nitriles on Pt/SiO₂ and only tentative conclusions could be reached. A strong $\nu_{\text{C}\equiv\text{N}}$ band was always observed following the adsorption of HCN and CH₃NH₂ accompanied by several bands in the ν_{NH} and ν_{CH} regions. It was concluded that extensive dissociation must have occurred and that a complex variety of adsorbed species could have been generated from reactive CN radicals. However, in nitriles possessing a C-C bond such as CH₃CN, C₆H₅CN and CF₃CN, less complex spectra were observed and it appeared that C-C bond cleavage did not predominate,

thus preventing the formation of CN radicals. The main mode of adsorption of C_6H_5CN , CF_3CN and CH_3NC was via coordination, whereas CH_3CN dissociatively adsorbed.

CHAPTER 1

INTRODUCTION

In the past twenty years, the study of the chemistry of surfaces has undergone a revolution as a result of an entirely new approach to chemical structure determination.

The development of new and sophisticated physical methods in diffraction techniques, electrochemistry and spectroscopy has provided the means of obtaining a direct "view" of the behaviour of molecules, radicals and ions that are reacting at surface sites. Such information can be correlated with macroscopic properties of a system (such as heat of absorption) to give a much more complete picture of surface phenomena.

Great advances have been made in the resolving power of instruments and in LEED, field ionization, field emission, and electron microscopy, the surface under study can be scrutinized on an atomic scale. However, each of these methods requires ultra high vacuum conditions which precludes a simultaneous study of reactants and surface species. With some spectroscopic techniques though, in particular infrared spectroscopy, the solid phase, the interphase and the gas (or liquid) phase can be monitored together which is an invaluable advantage in any study of heterogeneous catalysis.

Physically adsorbed species (which cannot be studied by high vacuum methods) are generally easily identifiable in the infrared because of only small changes in frequency from their gas phase analogues, but chemisorbed species may exhibit complex spectra as a result of a strained configuration or dissociation of the adsorbing molecule and quite often there are no models for comparison.

In cases where the adsorbed species cannot be identified by a reference comparison then different adsorption conditions may be used to test some of the properties of the species. For instance, variations in pressure and temperature, the effect of co-adsorption of other molecules or adsorption of an isotope of the molecule may help to identify the species.

From adsorption studies much can also be learnt about the nature of the solid support. For example, hydrogen bonding of various molecules of the surface hydroxyl groups of silica causes shifts in position of the SiOH absorption band from which a value of the basicity of the groups may be ascertained. Chemisorption of molecules, on the other hand, may distinguish different types of surface hydroxyl groups on silica.

In general, a study of the intensity shape and frequency of the spectral bands of the solid and the adsorbate may reveal information about the nature of adsorption, the configuration of the adsorbed species and the type of site involved.

Some of the prerequisites of a successful surface study by infrared spectroscopy are that the solid be transparent over a wide range of the infrared spectrum, and that it has a high surface area

such that there are a sufficient number of sites for the adsorbed molecules to produce a measurable absorption spectrum. As well, a high surface area material will necessarily have small particle size (in this work from 20-50 Å) which will reduce scattering of the incident radiation.

A majority of infrared studies have been with oxides such as silica, alumina and silica-alumina, in fact, the first successful spectroscopic experiments of adsorbed molecules were carried out in Russia, using porous glass¹, and silica gel². Since then other oxides such as TiO, MgO, CaO, NiO and ZnO have been looked at, and, as well, the technique has been extended to studies of the metals themselves.

In order to obtain transmission spectra of adsorbates on metals, the sample must be either very thin or finely dispersed. The latter condition has been employed in this thesis. But finely divided metals tend to reform as aggregates and it is necessary to support them on a high surface area material which has greater stability, such as silica (SiO₂). Again compromises must be made to minimize scattering and absorption by the adsorbent, and in favourable cases the transmission of supported metal samples may approach the same level as with the support alone.

The extensive use of silica as a support for metals may be attributed to its relative inertness to chemical attack which allows a representative study of the material to be conducted without the interference of metal-silica interactions or support-adsorbate reaction. However, this does not mean that silica does not interact with adsorbates, in fact the popular use of silica in chromatography illustrates

that it is capable of physically adsorbing many molecules and in the presence of other materials, such as Al_2O_3 , may even be an effective catalyst (e.g. hydrocarbon cracking).

Therefore in any study of a supported metal-adsorbate systems it is important to have prior knowledge of the extent of the support-adsorbate interaction by first studying the infrared spectrum of this system alone.

Perhaps the most important use of silica as a support is that it is commercially available as a very high surface area material which subsequently allows that the metal can also be very finely dispersed, resulting in good quality spectra.

This thesis concerns both studies of silica and of silica supported metals, in particular, platinum, and though these studies are not unrelated, as alluded to above, an overall appreciation of the work done may be better achieved by discussing them initially, in separate parts. A separate introduction to metal studies is to be found in Chapter 7.

SILICA STUDIES

Studies concerning silica surfaces are very extensive, but several excellent reviews³⁻⁷ have been published which summarize the important aspects of the field. Most of these studies are concerned with the nature and concentration of surface functional groups which play a critical role in determining the extent and nature of adsorption.

Infrared Spectra

When finely divided silica is pressed in a die at about 70 kg cm^{-2} it becomes self supporting and can then be placed into a suitable infrared cell so its transmission spectra may be observed. Providing the optical thickness of the pressed disc is not too large (ca 40 mg cm^{-2}), then absorption features of the type shown in Figure 1-1a can be observed.

Figure 1-1a shows the principal bands obtained when an aerosil silica (see later) is placed in a vacuum infrared cell and evacuated to 300°C for 1 hour to remove moisture. The vibrational modes giving rise to this spectrum are:⁸

810 cm^{-1}	Si-O symmetric stretch
$1100\text{-}1200 \text{ cm}^{-1}$	Si-O antisymmetric stretch
1875 cm^{-1}	combination modes
2000 cm^{-1}	
1640 cm^{-1}	overtone
3748 cm^{-1}	Si-OH
3500 cm^{-1}	

The main interest in surface studies is with the region from $3800\text{-}3400 \text{ cm}^{-1}$ since it is here that hydroxyl group absorption occurs. Hydroxyl groups have been shown to exist because they readily interact by hydrogen bonding with adsorbed molecules, and quickly exchange with D_2O at a rate which is not consistent with slow bulk diffusion.⁹⁻¹³

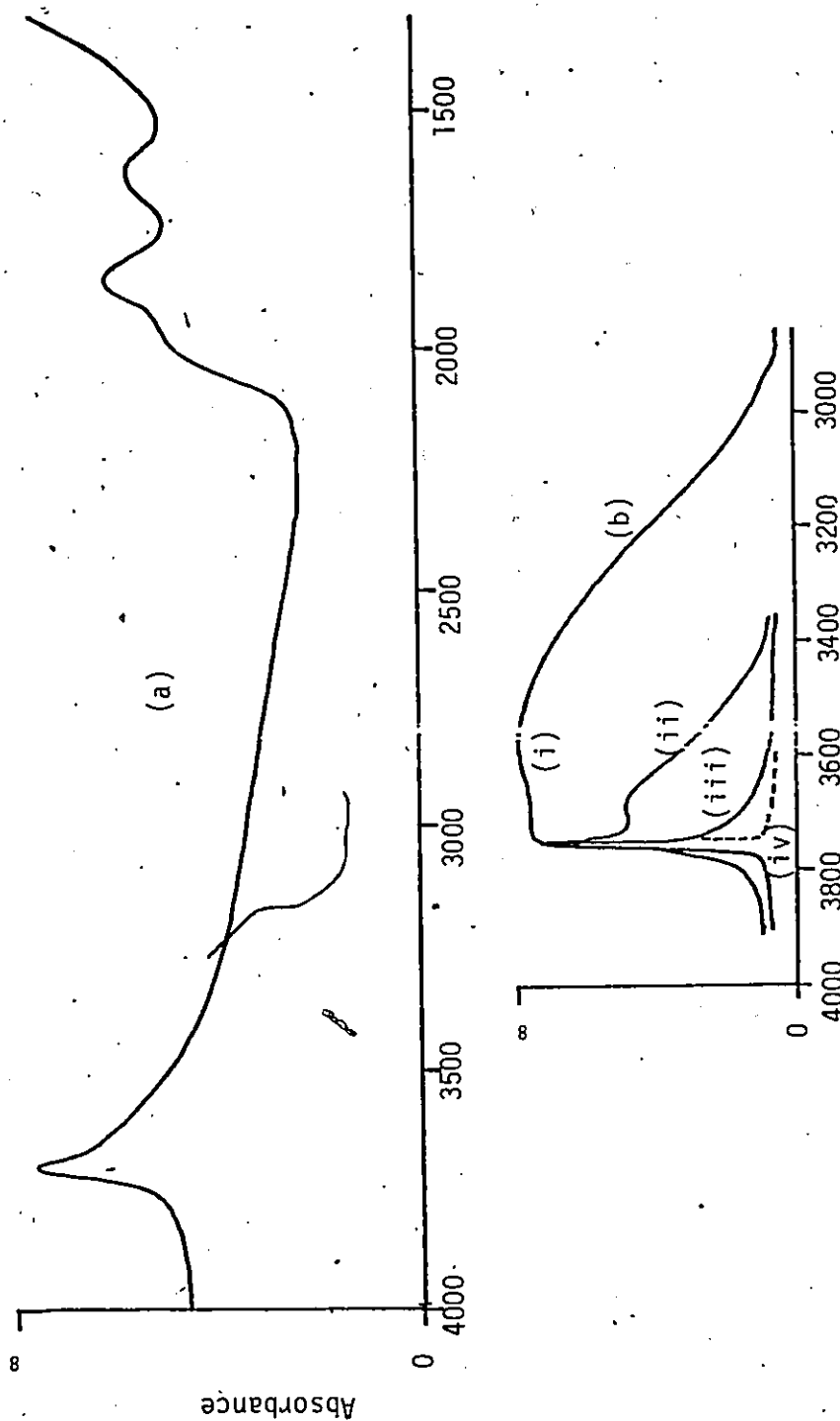


FIGURE 1-1

- (a) 200 mg of Cabosil HS5 silica pressed into a 2.5 cm diameter disc at 1000 psi (40 mg cm⁻²) and evacuated at 300°C for 1 hr. The sample is totally adsorbing below 1350 cm⁻¹.
- (b) 10 mg cm⁻² silica disc. SiOH profile at various stages of degassing; (i) before evacuation, (ii) 1 hr at 150°C, (iii) 5 hr at 500°C, (iv) 5 hr at 600°C (dotted curve).

In Figure 1-1b, this region of the spectrum is shown for various stages of degassing of the surface. Initially the spectrum contains a broad band centered around 3500 cm^{-1} and a single sharp band at 3748 cm^{-1} . As the degassing temperature is raised, the broad band is gradually removed and at 800°C only a narrow band at 3748 cm^{-1} remains. This latter band is attributed to a free hydroxyl group unperturbed by its neighbours.¹⁴ The absence of rotational fine structure implies that these hydroxyl groups are not freely rotating though, and some interactions, either with neighbouring groups or with lattice modes, prevents free rotation¹⁵ (though there may be restricted rotation). The assignment of the free hydroxyl species to the 3748 cm^{-1} band was made by comparing spectra to those of dilute solutions of alcohols in non-polar solvents where sharp narrow contours of unperturbed hydroxyl groups have been found.⁵

The broad absorption feature centered around 3500 cm^{-1} (Figure 1-1b(i)) which persists with degassing temperatures up to 400°C has been attributed to both molecular water and hydrogen bonded hydroxyl groups. Fripiat et al^{16,17} contended that molecular water was retained on silica gel up to 300°C , and Balkin et al⁷³ have reported that molecules of water remained on previously degassed aerosil silica samples (from 200 to 800°C) up to 200°C but were removed at 400°C . However, studies by Hockey²⁶ and Klier et al⁷⁸ indicate that physically adsorbed water may be removed at room temperature from aerosils and Hsils (wet precipitated silica). Young¹⁸ first characterized the interaction of water with aerosil silicas. He found that the major portion of the surface is hydrophobic, based on the considerably lower surface area

observed for water vapour absorption compared to a nitrogen determined surface area. The actual amount of water adsorbed could be directly related to the number of free hydroxyls present^{18,19,21,27,28,69-75}.

Recent spectroscopic studies of water adsorption by Galkin¹⁹ support Young's¹⁸ contention of the direct interaction between water and hydroxyl groups because the intensity of the 3748 cm^{-1} band was observed to diminish proportionately with the pressure of adsorbed water vapour, when the silica sample was placed in a monochromatic beam of radiation (preventing radiative heating of the surface). An alternate hypotheses for molecular adsorption of water at non-hydroxyl surface centres had been earlier proposed²⁰ because no observable loss in intensity of the 3748 cm^{-1} band occurred when water was adsorbed, however as shown by Galkin et al²¹, the temperature of the surface can be raised to as much as 80°C in the sampling area of certain types of spectrometer which makes it impossible to accurately assess the perturbation of hydroxyl groups at room temperature.

Hambleton et al^{22,23} discussed two possible assignments for the 3500 cm^{-1} band of silica. In order to avoid interference from atmospheric water, the spectra of a deuterated surface was analyzed, in particular a band at 2620 cm^{-1} (3550 cm^{-1} is the OH analogue). It has been observed that if molecular D_2O is dosed onto an evacuated surface at room temperature, two new bands appear at 2550 and 2690 cm^{-1} which are assignable to the O-D stretching frequency of adsorbed D_2O and to the perturbed surface deuteroyl groups respectively²⁴. Assuming these assignments are correct then the band at 2620 cm^{-1} might correspond to the OD stretching frequency of strongly hydrogen bonded

molecules of D_2O . If 2620 cm^{-1} was to be assigned to perturbed $SiOD$ groups, then the perturbing agent could not be D_2O because the 2550 and 2690 cm^{-1} bands can apparently be removed at higher temperatures of degassing than that at 2620 cm^{-1} and it seems unlikely that a system which produces stronger hydrogen bonds, i.e. that produces a shift of the surface OD groups to 2620 cm^{-1} , should be more easily evacuated than a system which shifts the normal OD frequency from 2760 cm^{-1} to only 2690 cm^{-1} . However, if the 2620 cm^{-1} band is due solely to bound molecular water then there should be a broad band corresponding to the perturbed OD groups lying at a frequency below 2620 cm^{-1} . Such a band is not observed. The only other possible assignment can be made by assuming that other sites are initially present on the surface corresponding to surface hydroxyl groups which are held in closely adjacent positions producing strong interaction and a consequent shift away from the frequency of non-bonded hydroxyl groups; the broadness of the band is a result of there being an array of these sites where the hydroxyl groups may be at varying distances from each other.

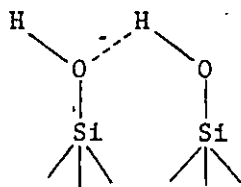


Diagram 1-1

Anderson and Wickersheim⁶⁹ have shown that by studying the combination and overtone regions of the hydroxyl absorption spectrum it can be definitely determined that the appearance of a band at 4420 cm^{-1} indicates the presence of a new hydroxyl species. This band has been interpreted as a combination of the stretching and bending

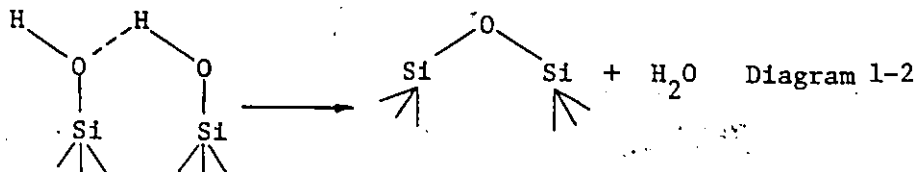
modes of the SiOH group which must have a fundamental stretching frequency of about 3500 cm^{-1} .

Other support for this hypothesis is the experimental result that no observable change in the 1640 cm^{-1} region occurs when a silica containing normal hydroxyl species (and the 3550 cm^{-1} band) is subjected to deuteration²². If the 3550 cm^{-1} band had been due to hydrogen-bonded water molecules, some change should have been observed in the intensity of 1640 cm^{-1} (SiOH for H_2O). Hambleton et al²² claim that once a powdered silica has been degassed at room temperature, virtually no change occurs in the intensity at 1640 cm^{-1} and that the amount of molecular water remaining on the surface is miniscule. When a powdered aerosil silica is pressed into a disc at relatively high pressures, up to 5 tons cm^{-2} , small amounts of water may be trapped²² and remain in the disc even up to 450°C ²², but at lower pressures (e.g. 70 kg cm^{-2}) most water is removed.

More important perhaps, is the observation of Galkin et al²⁵, which shows that the amount of water which remains on the surface is dependent on the original surface hydroxyl concentration. They found that more water was retained after pumping at 25°C for 8 hr on a silica surface which had been previously degassed at 400°C , than one which had been degassed at 200°C (higher hydroxyl concentration). Conversely more water was initially adsorbed on surfaces which had high initial hydroxyl concentrations. Water which is observed to emanate from a surface that has been degassed at higher temperatures, subsequent to the initial 75°C degassing step, arises from the collapse of the hydrogen-bonded hydroxyl groups^{18,26,27} shown in Diagram 1-2.

Providing the degassing temperature does not exceed 400°C, water can be reversibly adsorbed and desorbed¹⁸ which suggests that siloxane bridges formed on dehydroxylation can be reformed, i.e. dissociative chemisorption of water

i.e.



Once degassing temperatures exceed 400°C, cooling and rehydration does not regenerate all of these hydroxyl sites and the 3550 cm⁻¹ band does not regain it's original intensity, i.e. the surface becomes partially resistant to vapour phase hydrolysis^{5,26,29} (Figure 1-2a). Beyond 400°C, the number of hydroxyls reformed by hydrolysis is further diminished, until at 800°C, the surface becomes totally hydrophobic (see Figure 1-2ii). At this stage of degassing there are known to be about 1.4 ± 0.1 hydroxyls/100 Å².⁴¹ Further degassing up to 1100°C continues to remove hydroxyl groups, though the mechanism for removal has not been clearly resolved²⁶⁻²⁹. The number of hydroxyl groups remaining at this stage is very small³⁰.

Polymorphs of silica and model surfaces

The silicon atom has the same outer electronic structure as carbon but differs from that element in a number of ways, particularly in its inability to form multiple bonds. Only one oxide is stable at 25°C (SiO₂) although it can exist in a number of crystalline forms. In each of these forms there is a tetrahedral arrangement of four bonds

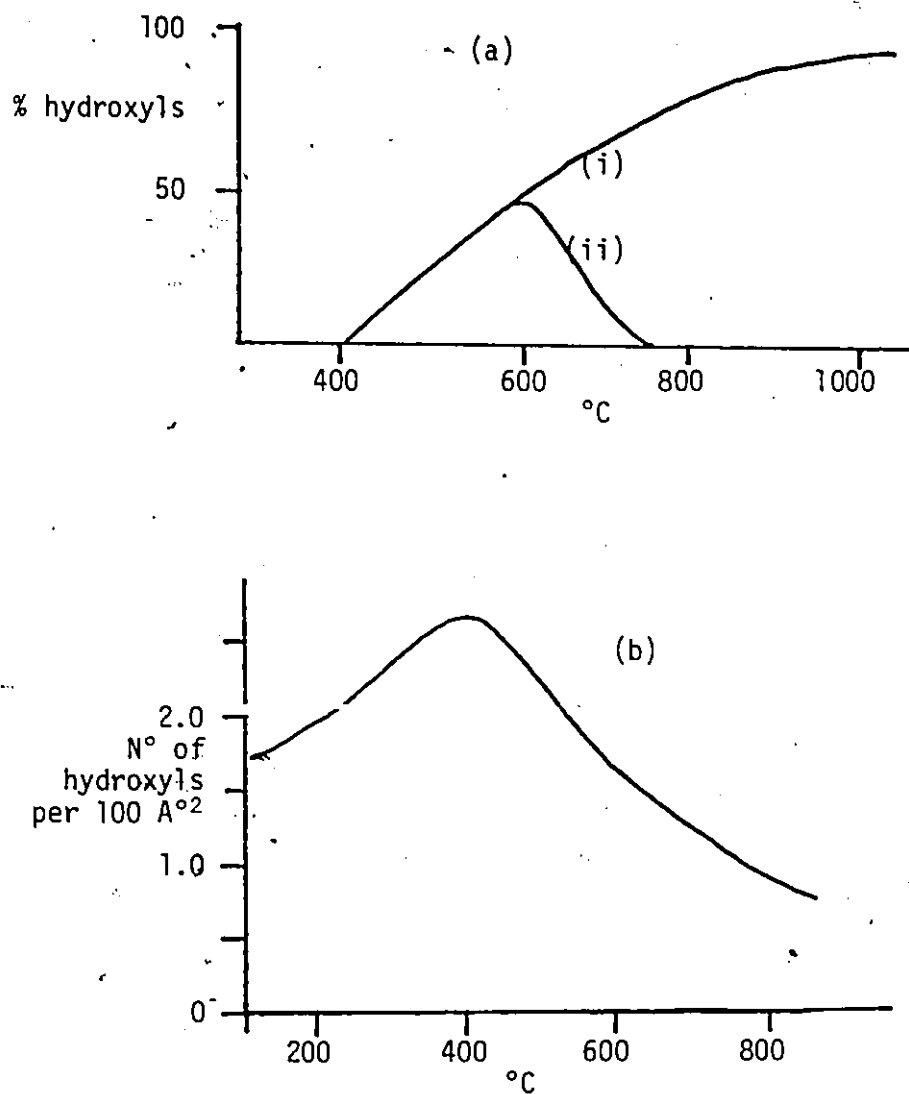
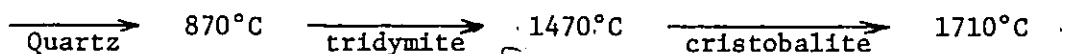


FIGURE 1-2

- (a) Percentage of original SiOH groups at various stages of degassing and facility for subsequent rehydration by water vapour, (saturation vapour pressure).
 (i) hydroxyls condensed; (ii) hydroxyls rehydrated.
 (From G.J. Young, J. Coll. Sci., 13, 67 (1958).)
- (b) Number of hydroxyls on silica surface at various degassing temperatures. (From G.A. Galkin et al., Russ. J. Chem., 43, (8) 1117 (1969).)

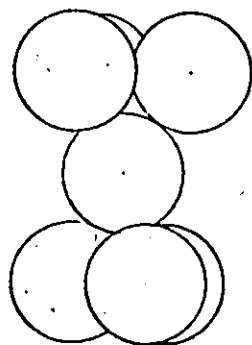
from each silicon atom extending into an infinite 3-dimensional network³¹. The fact that silicon does not form simple molecules like $O=Si=O$ at ordinary temperatures has been attributed to the fact that the silicon-oxygen bond has about 50% ionic character³², which does not allow for multiple bond (covalency) formation. Thus silicon may be regarded as being present as Si^{4+} ion and the oxygens as O^{2-} ions, in which, according to Bragg³³ the distance between oxygen atoms of any one structural group is always $2.6 - 2.8 \text{ \AA}$.

The three principal crystalline forms of silica, cristobalite, tridymite and quartz are built up in networks in which every oxygen atom is common to two tetrahedral SiO_4 groups. This process of oxygen sharing is just an extension of a silicate ion sheet with cross-linking to neighbouring sheets above and below the plane. In cristobalite and tridymite, only the manner in which the crosslinking is made differs; but in quartz the regular arrangements are distorted into a spiral of $O-Si-O-Si-O$ chains which lie on a trigonal screw axis³⁴ (Figure 1-3). The three polymorphs are not readily interconvertible, as is shown by the fact that all 3 forms are found as minerals and the stable temperature ranges of the silicas are well separated.

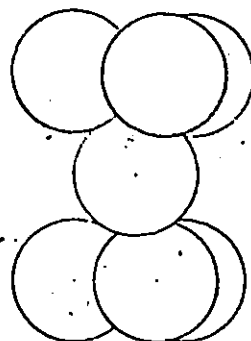


Furthermore, each of the 3 forms exists in a low and high temperature modification (α and β respectively) with the following transition points;

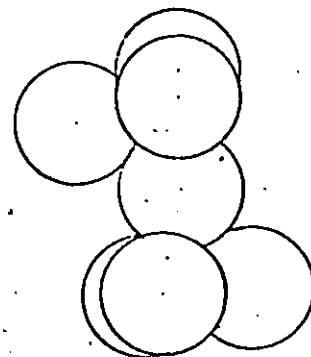
$\alpha - \beta$ quartz, 573°C ; $\alpha - \beta$ tridymite $120-160^{\circ}\text{C}$ and $\alpha - \beta$ cristobalite $200-275^{\circ}\text{C}$. The fact that, in the last two cases, the transitions can be studied at temperatures at which the particular polymorphic forms



Tridymite



Cristobalite



Quartz

FIGURE 1-3

are metastable, is an indication of the difficulty of interconverting the three forms of silica³¹.

The difference between tridymite and cristobalite is like that between wurtzite and zinc-blende, the two forms of ZnS, but the α and β forms of any one of the three SiO_2 varieties differ only in detail, there being slight rotations of the tetrahedra, without any alteration in the way in which the tetrahedra are linked. The change from quartz to tridymite is sluggish because it involves the breaking and rejoining of Si-O-Si bonds whereas the change from $\alpha \rightarrow \beta$ quartz occurs without bond breaking and is easily reversible.

The idealized structures of β tridymite and β cristobalite are given in Figure 1-4. In these representations the oxygen atoms are placed midway between, and on the straight line joining the pairs of silicon atoms. Such a structure, however, renders a smaller than usual Si-O value ($1.54 \text{ \AA}$). A somewhat deformed structure, where the O atoms do not lie exactly along a straight line joining the Si atoms, gives a more satisfactory Si-O distance³⁵ (see Table 1-1).

Amorphous Silicas

The silica which is used in the laboratory for infrared studies consists of two types: gels and aerosils. Although these silicas are ostensibly amorphous in appearance, a great deal of effort has been spent by some authors in trying to ascertain to what degree crystallinity exists and how closely these silicas can be related to the properties of the polymorphs described above²⁶,

Although only aerosil silica has been used in this laboratory it is important to recognize the differences between aerosils and gels

TABLE 1-1

Bond Distances and Angles in Crystalline Silicas

	Si-O distance O (Å)	Si-O-Si angle (degrees)
α quartz	1.61	142
α cristobalite	1.59	150

(from Reference 29)

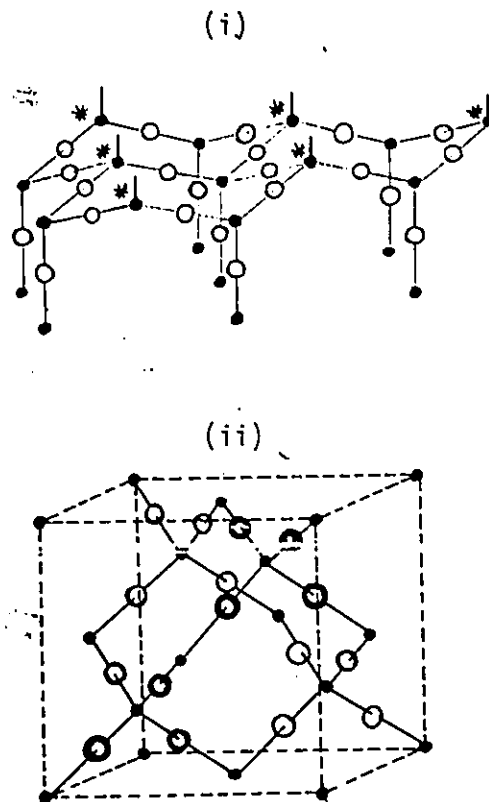


FIGURE 1-4

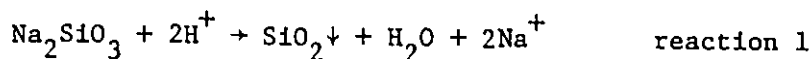
Models of the silica surface.

The solid black dots represent silicon atoms.

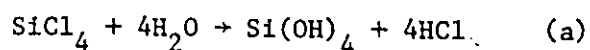
(i) The 0001 face of β tridymite. First layer silicon atoms are asterisked.

(ii) β cristobalite.

since a great deal of the foundation studies of silica surfaces have been performed on gels. The precipitation of an amorphous gel can be effected by acidifying an aqueous solution of sodium silicate, or by the hydrolysis of silicon tetrachloride.



or



Gels which are formed by wet hydrolysis or precipitation have comparable properties, in that the surface is totally hydroxylated in the freshly prepared state although the porosity of the sample depends on the rate of formation of the silica³⁶. The properties of gels have been found to be dependent on the number of different types of hydroxyl groups present and to the variation in pore size^{14,37,38}.

Aerosils however are somewhat different. They are prepared by the flame hydrolysis of silicon tetrachloride in a stream of hydrogen and air (at $\sim 1000^\circ\text{C}$), the ratios of each of the three components in the flame controlling the particle size and surface characteristics¹⁸. Aerosils are basically non micro-porous materials as is illustrated by the rapid equilibrium achieved with water vapour (compared with gels)¹⁸, and it is probable that the only pores and crevices which exist at room temperature are as a result of pressing the powder into a disc for infrared studies³⁹, and in samples pressed only to 70 kg cm^{-2} (as in this work) there is only a weak infrared band at 3650 cm^{-1} (see below) that is characteristic of the existence of internal pores (see Figures 1-1b).

In any case, thermal dehydroxylation above 500°C irreversibly removes the species responsible for the 3650 cm^{-1} band in gels (they cannot be regenerated by treatment even in liquid water). This according to Hockey²² corresponds to a process of "annealing" whereby relatively weak hydrogen bonds are replaced by the regular siloxane lattice.

The 3650 cm^{-1} band appearing in silica gel spectra is representative of hydroxyl groups which are perturbed as a result of interparticle contact. As the particles are brought into closer proximity (higher pressures of disc preparation) the intensity of the band increases²³. In this sense, the 3650 cm^{-1} hydroxyl species is unlike the 3748 and 3550 cm^{-1} species because it is reliant on bulk density and is observed to be unavailable for reactions with some molecules which readily attack the other surface hydroxyls^{22,23,39}.

The aerosil spectrum only has the 3650 cm^{-1} band if the powder is first treated in boiling water and then dried below 150°C³⁹. Under such treatment the specific surface area decreases while the size of the silica globules grows to such an extent that a large amount of water is retained inside them³⁹. In aerosils so treated and in all gels, the loss of water on ignition (to 400°C) does not solely represent the number of hydrogen bonded hydroxyl groups, but, as well, the amount of bulk water or bulk hydroxyl groups which are held internally and which will not react with common surface reactive molecules like D_2O . Hence a false estimate of the number of hydroxyl groups held at the surface is obtained if gravimetric determination of water is the only probe used. Davydov et al³⁹ showed that by

observing the amount of exchange of a known amount of D_2O , a measure of the surface hydroxyl content can be achieved.

Earlier work by Hockey³⁶ and DeBoer and Vleeskens⁴⁰ had indicated that silica gels approach a constant surface coverage of about 4.6 hydroxyl groups per $100 \text{ \AA}^2$ when the surface is rehydrated after degassing to 450°C . This is close to that of the 100 surface of β cristobalite and the 0001 face of β tridymite (see Figure 1-4). They both concluded that on freshly prepared silicas the surface must approximate either one of these crystalline forms because the lattice movement which gives rise to the loss of water by dehydroxylation must be small. In this model each surface silicon atom is attached to one hydroxyl group. Peri and Hensley⁴¹ however disputed the model given by DeBoer and Vleeskens⁴⁰ because it could not be reconciled with the observed stoichiometry of reactions with molecules like $AlCl_3$, BCl_3 and $SiCl_4$, (on an identically prepared surface to that of DeBoer and Vleeskens) since only one hydroxyl group should be expected to react with each halide molecule, yet often the reaction appeared so as to consume two hydroxyls simultaneously.

In a study of silica gels previously degassed at temperatures ranging from 100°C - 800°C , Peri⁴¹ measured the amount of HCl produced on the initial reaction of the particular chloride used and compared it to the amount of HCl produced by the subsequent hydrolysis of the chlorinated surface. From this data he estimated what he thought was the number of paired hydroxyls initially present on the surface of the gel.

For example, if an AlCl_3 molecule reacts with n surface hydroxyls then the ratio, R , for the amount of HCl produced before and after reaction, is:

$$R = \frac{\text{HCl on hydrolysis}}{\text{HCl on initial reaction}}$$

For AlCl_3 $R = \frac{3-n}{n}$

$$\therefore n = \frac{3}{R+1}$$

and percentage of paired hydroxyls is

$$\%_{\text{paired}} = \frac{200(n-1)}{n}$$

Using this calculation, a high incidence of paired hydroxyls was calculated for samples which were predried at low temperatures. Peri also used Monte Carlo statistical techniques to simulate the random dehydroxylation of a surface which was initially totally hydroxylated. The faces of two possible crystal models (Figure 1-4) were thought to resemble his silicas. The 0001 face of β tridymite if randomly dehydroxylated would, according to Peri, have only 1.5 hydroxyl groups per $100 \text{ \AA}^2$ after reaction of all possible neighbouring pairs, which is well below the average of 4.6 hydroxyls per $100 \text{ \AA}^2$ observed. On the other hand, the random dehydroxylation of the 100 face of β cristobalite, (which is initially totally hydroxylated, with each silicon atom having geminal hydroxyl groups attached), produced a surface of about 4.6 hydroxyls per $100 \text{ \AA}^2$ which exist as either vicinal or geminal pairs.

i.e.

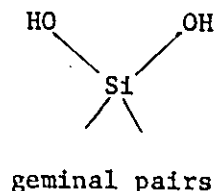
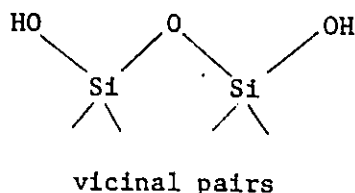


Diagram 1-3

Each hydroxyl would then be close enough to react in a 2:1 ratio with AlCl_3 , BCl_3 or SiCl_4 .

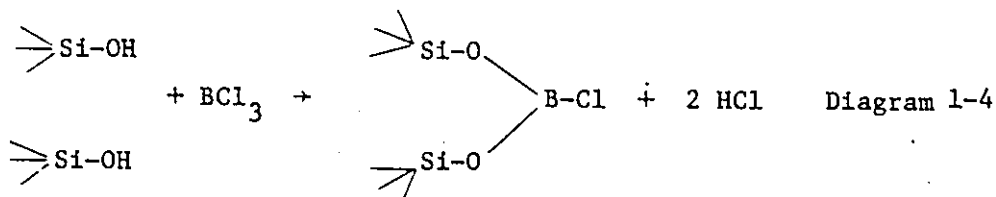
However, Hockey⁴² has recently discounted the theory of Peri⁴¹ and of previous workers⁴⁰, on the grounds that any attempts to find one crystal plane to represent a finely dispersed silica cannot be correct. It has been shown by electron microscopy and small angle X-ray diffraction⁴³, that silica gels exist as primary aggregates of 10 Å in "diameter" which can be clumped together into bulks of up to 100 Å "diameter".

Even if a powdered silica does exist, as, for example, β cristobalite, it should still expose different faces since, in a lower ordered crystalline structure of this type the anion-cation arrays are not the same at each face. One must assume that a number of crystal planes exist. Hockey⁴² further illustrated that Peri's⁴¹ assessment of paired hydroxyls based on the HCl hydrolysis ratio was also invalid because the HCl produced in the reaction of the chloride (e.g. BCl_3) with the surface hydroxyl groups may be less than the amount of HCl actually measured. This possibility may arise due to a further reaction of the adsorbed surface chloride species with water molecules, which can form from the collapse of internal hydroxyl groups, up to 600°C, thus producing more HCl.

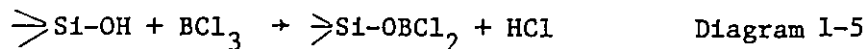
A much better method for the determination of the number of surface hydroxyl groups is by the chemical analysis of the solid phase after reaction of (e.g.) BCl_3 , for the chlorine content.

Using probe molecules BCl_3 , SiCl_4 and Me_2SiCl_4 , Hockey⁴² determined that on a fully hydroxylated surface of a silica gel, there are 4.6 hydroxyl groups per $100 \text{ \AA}^2$ of which 1.4 ± 0.1 groups exist as single non-bonded species, and the remaining 3.2 groups are paired hydroxyls. On the basis of the residual chlorine determination, no scheme could be adapted to compromise Peri's model of the surface where all the hydroxyls are paired.

Thus, in the following scheme



only one chlorine is expected for each hydroxyl pair. However the number of hydroxyls determined by assuming this scheme is higher than the number determined by an independent thermogravimetric study⁴⁴. Calculations which are consistent with the observed chlorine contents, can only be obtained if another reaction is included which produces two chlorines for each hydroxyl group.



As the pretreatment temperature is raised, the ratio of Cl:B increases, which is consistent with the increasing predominance of the latter reaction as paired hydroxyls become progressively removed. (Fripiat's⁴⁵ work with diborane supports this scheme).

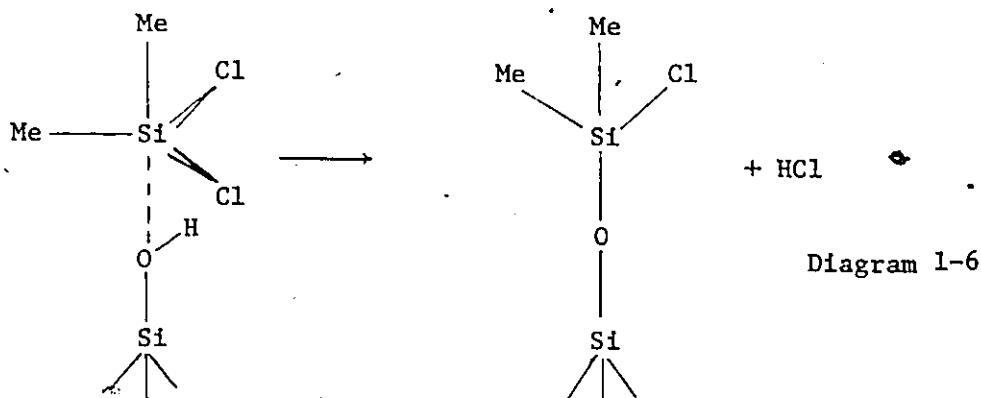
At a degassing temperature of 500°C, all paired hydroxyls are removed (Figure 1-1b) leaving 1.4 hydroxyl groups per 100 Å², which remains constant up to 600°C. Hockey has named these remaining isolated hydroxyls as "Type A" and those which are paired and can be more easily removed, as "Type B". The value of 1.4 single hydroxyl groups (A sites) obtained from 25°C up to 600°C⁴⁵⁻⁴⁸ indicates their temperature stability, whereas the progressive removal of B sites implies a sterically controlled dehydroxylation²². It should be noted however that when a range of silicas is used that have varying pore size and different surface areas, the situation on degassing is complex and there is no really clear cut differentiation between free and hydrogen bonded hydroxyl types³⁷. The fact that the infrared band for hydroxyl absorption extends continuously from 3748 cm⁻¹ to lower frequencies demonstrates this. The term 'A-type' hydroxyls, then, simply refers to the surface state existing when hydroxyls are sufficiently far away from each other so as not to hydrogen bond (about 3.2 Å or greater)^{39,49}.

Reactions with A-Type Hydroxyls

In the aforementioned reactions with BCl₃ it has been observed that there is a non specific attack of hydroxyl groups, both A and B type hydroxyls reacting equally.

Certain chlorinated silanes however have been shown by Hockey⁴⁶ to react specifically with only the A type hydroxyls. Di- and trimethyl substituted chlorosilanes react selectively and completely with the single surface hydroxyls, whereas the monomethyl and

tetrachlorosilanes also interact with the hydrogen bonded surface groups, although the reaction with these groups is slower. The selectivity of the bulkier di- and trimethyl chlorosilanes has been associated by Hockey⁴⁶ with the formation of a bimolecular transition state in which the methyl chlorosilane has the form of a trigonal bipyramid, as shown in Diagram 1-6.



Loss of HCl is easily facilitated since the bond angle of Si-O-H of the single surface hydroxyls is purported to be 113° (implying that these groups are bound largely covalently)⁴⁷. Elimination of HCl then yields a stable product and reversion to a tetrahedral configuration. Thus single hydroxyl groups which have their oxygen atoms pointing away from the surface, should react 1:1 with both di- and trimethyl chlorosilane, but hydrogen bonded hydroxyls should not be expected to react because the transition state in Diagram 1-6 is unlikely to be formed because of a sterically hindered approach to the oxygen atom of a bonded hydroxyl.

The non selectivity of BCl_3 has been similarly explained by Hockey⁴⁶. The molecule is initially planar but in its transition state would be tetrahedrally arranged so that the chlorine atoms are

held away from the surface and can react equally well with single or hydrogen bonded hydroxyls.

Hockey⁴⁶ concluded that for solids preheated at less than 500°C the reaction with di- and trimethyl chlorosilanes is 1:1 based on chlorine analysis of the solid phase. However, pretreatment above 500°C produced lower chlorine analyses, which were rationalized as being due to some 1:2 reaction of the chlorosilanes with OH groups.

Snyder and Ward³⁷ have also done an extensive study on the reaction of trimethyl chlorosilane (TMCS), but on a variety of porous silicas which were reacted in their freshly prepared (totally hydroxylated state). They observed, interestingly, that the reaction rate for TMCS was higher on a sample in which the relative number of free hydroxyls was lower, which is contrary to the hypothesis of Hockey⁴⁶ who proposed that TMCS could react only with free hydroxyls.

They proposed that some other "reactive hydroxyl" must be available to attack TMCS, and that these are strongly hydrogen bonded hydroxyls where the non-bonded proton (see Diagram 1-1 should have an acidity higher than that of free hydroxyls and therefore have a greater ability to interact with TMCS. The same effect was observed by Yates et al⁵⁰.

The relevancy of this work to that on dehydroxylated silicas containing only 'A type' hydroxyls, is not clear but it does illustrate a reaction feature which is not available from studies on 'A type' alone:

The thesis afforded by Snyder and Ward³⁷ is, nevertheless, at variance with Hockeys⁴⁶ interpretation of the reactions with the

chlorosilanes, and the concept of a "1:1" or "1:2" reaction with the "free hydroxyl groups" on silica should be regarded as dubious, especially as these ratios were determined in the presence of an infrared band at 3500 cm^{-1} , which conceivably implies the presence of some of Snyder and Wards reactive hydroxyls.

However, other work on "dried surfaces" (degassed up to 600°C or higher) also points to the existence of multiple reaction sites. Peri⁴⁷, for example, has found that when SiCl_4 was reacted with a silica predried at 800°C , over 40% of the SiCl_4 molecules apparently reacted simultaneously with two hydroxyl groups. This was believed to be due to the close proximity of two hydroxyl groups on a structured surface.

The hydroxyl groups remaining on silica beyond 600°C were considered by Peri to be immobile in the light of the extremely slow loss of these groups from the surface even at elevated temperatures whereas any migration of hydroxyl groups or protons would presumably cause rapid formation and elimination of water. Mobility of hydroxyl groups also seemed to Peri to be inconsistent with his observation of the SiCl_4 reaction behaviour in which the hydroxyls were paired in some cases and single in other cases. This being the case, then the original surface hydroxyl arrangement must be the important factor determining the way molecules react. Both types of pairs shown in Diagram 1-3 may not necessarily be hydrogen bonded. In the case of vicinal hydroxyls, removal of water would be difficult because this requires edge linking of the SiO_4 tetrahedra, and geminal hydroxyls are probably not bonded to their partners because a five or six

membered ring is normally needed for intramolecular hydrogen bonding⁴⁹ and again water loss is difficult since this would require that $=Si=O$ is formed³¹.

Other workers have also concluded that there are multiple adsorption sites on dried surfaces. Hair and Hertl⁵¹ postulated the existence of closely situated hydroxyl groups to explain the kinetics of hydroxyl loss during the reaction of chlorosilanes on silicas containing only a 3750 cm^{-1} infrared band. They fitted their rate data to integrated rate equations of various orders until a linear plot was obtained over most of the reaction. For silanes containing two or more chlorines (Me_2SiCl_2 , $MeSiCl_3$) the observed order of reaction was 1.4 which means that on 40% of the active surface, the chlorosilanes react bifunctionally. Contrary to Snyder and Ward's work³⁷, Hair and Hertl⁵¹ observed no change in reaction order when some interacting hydroxyls were present. In their estimation, the observed analytical and spectroscopic data (discussed in Chapter 3) pointed to the existence of geminal hydroxyl pairs (Diagram 1-3).

Evans and White⁵² support the notion of Hair and Hertl⁵¹ that adjacent hydroxyl groups are required to explain the observed uptake of di- and trichloromethylsilanes. Steric hindrance effects do not seem to be important because monochlorotrimethylsilane, which occupies the same area when physically adsorbed as the di- and tri-chlorosilanes, is observed to react 1:1 only with hydroxyl groups.

Work by Peglar et al⁵³ illustrates yet another phenomenon. Reactions with $AlCl_3$ on silicas carrying only 'A type' hydroxyls were studied gravimetrically, and weight increases were observed which were

too large for a simple reaction with a single hydroxyl species to be the sole mechanism. Thus the reaction shown in Diagram 1-7 does not alone suffice

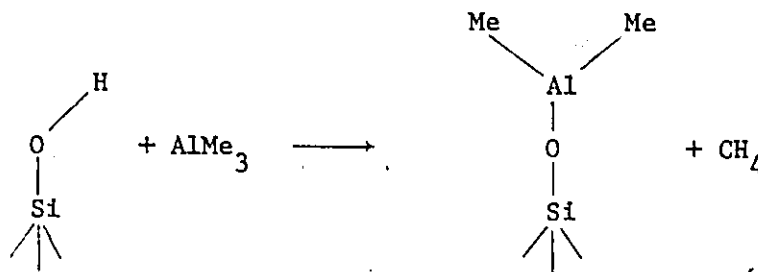


Diagram 1-7

The excess weight was not due to physically adsorbed AlMe_3 as shown by outgassing the surface at 120°C . Instead it was proposed that the reaction took place at a different type of site, a strained siloxane bridge, created by the dehydroxylation of nonlinear hydrogen bonded hydroxyls. Thus other reactions may proceed as shown in Diagrams 1-8 and 1-9.

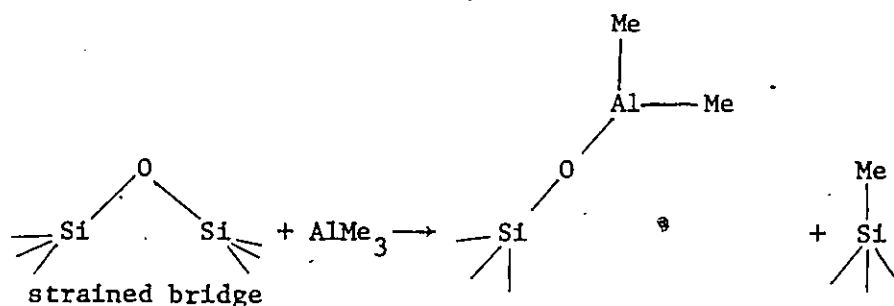


Diagram 1-8

and

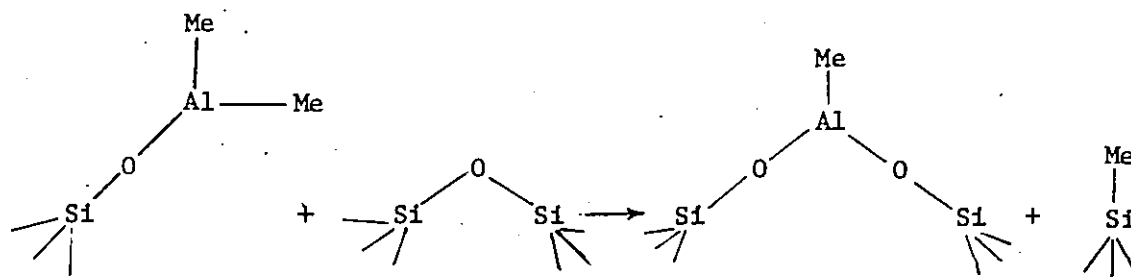
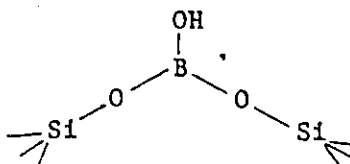


Diagram 1-9

The extent of the lack of agreement between different workers concerning reactions of electrophiles, like BCl_3 , is illustrated below. Bermudez's work with BCl_3 ⁵⁴ on silica which had been highly dehydroxylated (A type hydroxyls only) indicated the existence of >Si-OBCl_2 (I) species as well as $\text{>Si} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{BCl}$ (II) from geminal hydroxyls. He reasoned that this was so, because subsequent hydrolysis of the chemisorbed chlorides yielded absorption bands which are attributable to Boric acid, and that this could only have arisen from an hydrolysis product of species II, i.e. $\text{>Si} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{B-OH}$ (III).

Hockey⁴⁴, however, as previously stated, observed that the chlorine content upon initial chemisorption was consistent with species I only, when the surface is dehydroxylated, and furthermore, that the observed >B-OH ⁵⁵, intensity becomes progressively lower as the 'B type', hydrogen bonded hydroxyls are removed. Gravimetric work by Boehm et al⁵⁶ tends to support Hockey's⁴⁴ conclusions. Evidently the differences between the results of Bermudez⁵⁴ and Hockey⁴⁴ are in the sample preparation. Bermudez studied his reactions on surfaces which had been dehydroxylated to 700°C whereas Hockey's surface had been degassed to a maximum of 400°C only. Hockey's conclusions about the reactivity of BCl_3 with the hydroxyl groups are based on the observed drop in the intensity of the hydrolyzed product (species III) as the temperature for initial degassing was raised to 400°C. If the temperature range had been extended, a more exact comparison with Bermudez's work would have been possible; nevertheless an attempt to reconcile both pieces of work can be made. Firstly, it seems unreasonable that, beyond 400°C, geminal hydroxyls should suddenly appear to account for

the =BOH species observed by Bermudez. On the other hand, if a reaction was to occur whereby chemisorbed >Si-OBCl_2 species could interact with a strained siloxane bridge in a way similar to that proposed by Hockey, (Diagram 1-9), then a species

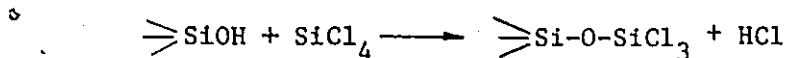


could explain the existence of a band due to =B-OH being present even though there are no remaining 'B type' hydroxyls. This scheme though is still not entirely satisfactory. The strained bridges proposed in Hockey's mechanism for AlCl_3 on silica, are formed from the collapse of B type hydroxyls, which are virtually all removed at 400°C .

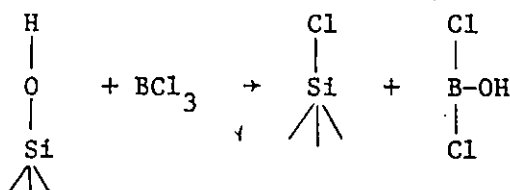
Hockey's⁴⁴ work shows that the intensity of the B-OH falls as the initial degassing temperature increases which implies that the bridges formed from 'B-sites' cannot be participating in the reaction with the >Si-BCl_2 species.

If there is a reactive bridge site present then it might be formed from the collapse of 'A type' hydroxyls. Such bridges would be expected to be highly strained (chemically active) because of the larger distances separating 'A type' hydroxyls compared with 'B type' hydroxyls. These highly strained siloxane sites have been observed before^{47,57} and were thought to be sites for chemisorption. Incorporating the existence of these sites, now enables a mechanism to be developed which satisfies the observations of both Hockey⁴⁴ and Bermudez⁵⁴. If the active sites begin to form beyond 400°C then one would expect to see the intensity of >B-OH begin to increase as Bermudez observed.

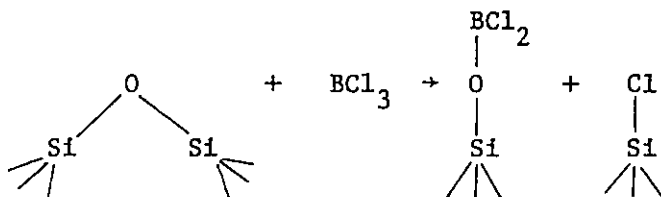
Hair and Hertl⁵⁸ have examined the reactions of other chlorine containing molecules such as PCl_3 , TiCl_3 , CCl_4 , SnCl_4 and GeCl_4 on silica surfaces which had been previously degassed to 800°C . They expected that a reaction analogous to that of chlorosilanes on silica might occur, viz.,



Although this type of reaction was observed for each of the above molecules it was also found that another reaction simultaneously occurred which resulted in the direct chlorination of the surface hydroxyl groups, evidenced by a higher Cl:metal ratio of adsorbates than the above reaction mechanism could give. A mechanism for direct chlorination was thought to be (for BCl_3),



No consideration was given to the possibility that active sites, which exist on 800°C degassed silicas, might be responsible in some part, for direct chlorination, i.e.



Preliminary studies by Morrow and Devi⁵⁹⁻⁶¹ illustrated that the chemical reactivity of these sites toward BF_3 superceded the

reaction with silanol groups. Though these sites had been postulated before, the first spectroscopic evidence has only recently been presented by Morrow and Devl⁵⁹ who observed the growth of 908 and 888 cm^{-1} bands corresponding to the decrease in intensity of the 3748 cm^{-1} SiOH band. Though 900 cm^{-1} is low for siloxane sites, it was thought that the special reactivity of the sites might be connected with a weaker than normal Si-O bond. But the existence of two bands is puzzling, because the site behaves chemically as if it were a simple Si-O-Si bridge (see Chapter 5).

The importance of these new active sites on dehydroxylated surfaces has not been much appreciated and a comprehensive study of their behaviour is the major theme of the silica work presented in Chapters 4 and 5.

From the previous literature it is apparent that a study of active sites on silica is intertwined with studies which have attempted to show the existence of geminal hydroxyl groups. The analytical and kinetic evidence provided by Hairs work⁵¹ with the chlorosilanes gives a convincing case for the existence of such species, but the spectroscopic proof that he and other workers⁶² provide is questionable. Hair claimed that the Si-OH band located at about 3750 cm^{-1} is resolvable into three component bands, 3751, 3747 and 3741 cm^{-1} which may be ascribed to the coupled mode of a geminal hydroxyl pair (3751, 3741 cm^{-1}) along with the single hydroxyl mode (3747 cm^{-1}). Furthermore, the integrated intensities of each of the components showed that the central band (3747 cm^{-1}) accounted for about 60% of the total band profile which fits the observed 1.4 order of

reaction obtained for the chlorosilane on this surface (i.e. 40% geminal pairs). Van Cauwelaert et al⁶² have observed a similar splitting of the Si-OH band, and though their interpretation of the assignment of bands differs slightly, they also conclude that the components observed are due to a geminal species co-existing with isolated hydroxyls. Geminal groups may be expected to produce absorption bands in this region since no hydrogen bonding is expected.

This work has been disputed by Hockey⁶³ and Morrow⁵⁹ and contradicted by earlier studies by Peri⁴⁷.

Peri⁴⁷ had noticed that reactions of SiCl_4 with silica followed by hydrolysis of the chemisorbed group (producing either $-\text{O}-\text{Si}(\text{OH})_3$ or $\begin{array}{c} -\text{O} \quad \text{OH} \\ \diagdown \quad / \\ \text{Si} \\ / \quad \diagdown \\ -\text{O} \quad \text{OH} \end{array}$) did not lead to the appearance of new bands in the hydroxyl region of the infrared spectrum, suggesting that geminal or even triplet hydroxyls are not readily distinguishable from the single species. Hockey⁶³ contended that the splitting was merely due to the fine structure of the gas phase spectra of residual water in the spectrometer. Morrow⁵⁹ could find no trace of shoulders in the band and no marked change in band shape was observed when the surface was treated with H_2O ¹⁸.

Van Cauwelaert⁶² however was adamant that the splitting was real. This prompted a careful study of the profile of the Si-OH band under various conditions to be done in this laboratory and findings support Hockey's work, namely that the band is structureless (see Chapter 3).

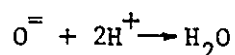
Thus, if geminal hydroxyls do exist, then they are not distinguishable by spectroscopic means.

Mobility of Surface Groups

When a silica surface is exposed to the high temperatures required to almost totally dehydroxylate a surface (1200°C) it is pertinent to consider whether any configurational change is taking place, corresponding to a shift from one isomorph to another, or in a more general sense, for an amorphous material, if the surface groups possess some degree of mobility.

Taylor originally defined dehydroxylation as being either an "homogeneous" process⁶⁴ whereby water is lost from all parts of the lattice or as "inhomogeneous"⁶⁵. In this latter process dehydroxylation was thought to proceed in three steps:

- 1) loss of oxide ions to expose donor regions and then



- 2) Cation (Si^{4+}) migration from donor to acceptor regions,
- and 3) Change in packing in the acceptor regions.

Although there does not seem to be clear evidence for either proton or oxide ion mobility from infrared surface studies⁴⁷, recent work by Rouxhet et al⁶⁶ using NMR techniques seems to indicate very extensive mobility at high temperatures.

Recent Studies of the Adsorption of Water

A. Hydroxylated silica

As has been mentioned previously, the adsorption and desorption of water is reversible on surfaces which have been degassed up to 400°C^{5,26,29}. Measurements of heats of adsorption on hydroxylated and partially dehydroxylated surfaces⁶⁷ indicates too, that water is

molecularly adsorbed to free hydroxyl groups and is dissociatively chemisorbed on dehydroxylated surfaces. That is, the 'bound' hydroxyls can be reversibly removed and reformed as long as the surface dehydroxylation has not diminished the hydroxyl population below a certain level. On totally hydroxylated surfaces, it has been proposed^{68,69,73} that water can be bound on adjacent hydroxyls as shown in Diagram 1-10.

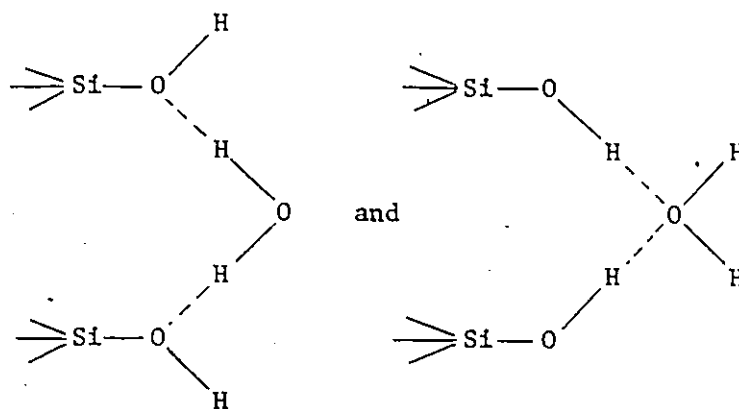


Diagram 1-10

When submonolayer amounts of water are added to totally hydroxylated surfaces, the heat of adsorption is observed to be high, ($17 \text{ kcal mole}^{-1}$)⁷³ perhaps because the water molecules are forced into making more than one hydrogen bond with the surface hydroxyls, the hydrogen bonds between the hydroxyl groups and water are in a strained orientation, and interaction energy is at a maximum.

However, according to Galkin et al⁷³ as more of the surface becomes covered, the number of bonds which can form becomes limited but those water molecules that do subsequently bond to hydroxyl groups are able to adopt a more favourable orientation with respect to the surface hydroxyl groups and the interaction energy drops.

(The heat of adsorption approaches the heat of condensation of water).

B. Dehydroxylated silica

Degassing the surface between 100°C and 400°C, actually increases the number of free hydroxyls¹⁹ as the absorption band due to perturbed hydroxyls and adsorbed water molecules disappears, corresponding to the liberation of free hydroxyls from interactions (Figure 1-2b). Once the surface has become degassed beyond about 400°C irreversible changes occur⁷⁰. Hydroxyl groups are removed which leave behind the new highly strained sites. The previously observed ability of the B type siloxane bridges (from the 'B hydroxyl' collapse) to rehydrate begins to diminish and at 850°C it does not occur at all (Figure 1-2a).

The coincidence of the appearance of new sites at 400°C, and the change in reactivity of 'B type' bridges at this temperature cannot be fortuitous. Evidently when the 'A type' hydroxyls are removed to form the active sites, the character of the whole surface undergoes change. Water adsorption is an effective monitor of this change. Kiselev et al^{19,21,71-73} have studied the behaviour of surfaces degassed to varying degrees and then interacted with various adsorbates, in particular water. They noticed that on surfaces degassed up to 600°C the adsorption of deuterated water diminished the free >Si-OD band intensity but on desorption at 25°C for 10 min (all physically bonded water removed), the >Si-OD band increased in intensity beyond its initial value. These two features indicate that the free hydroxyls are the major sites for physical adsorption of

water^{19,74} on relatively dehydroxylated surfaces, and that a site exists on which water can chemisorb to form new free hydroxyl species⁷⁴. When there is a low surface coverage of water on highly dehydroxylated sites (1100°C) very little change occurs in the free hydroxyl intensity which, according to Kiselev⁷⁵, means that single hydroxyls alone are not able to retain water molecules. Thus it was thought to be necessary for water molecules (or dimers) to form two hydrogen bonds with two hydroxyl groups (Diagram 1-10).

Only when the vapour pressure of water is high does the intensity of the 3748 cm^{-1} band begin to fall, suggesting that sufficient molecular association has taken place to enable bonding to occur simultaneously on two hydroxyl sites. This is confirmed by the presence of a band characteristic of liquid water ($3430\text{--}3450\text{ cm}^{-1}$).

Anderson and Wickersheim⁶⁹ observed that two bands appearing as the silica surface becomes progressively hydrated could both be attributed to water, a band at 3540 cm^{-1} corresponding to monomeric molecular water and another at 3400 cm^{-1} corresponding to water molecules forming a hydrogen bonded network on the surface. The co-existence of these bands seemed to indicate that the adsorption of water is not uniform. Further evidence for this non-uniformity was that free hydroxyl groups were observed to co-exist with the 3400 cm^{-1} band⁷³. Kiselev⁷⁵ has proposed that the new free hydroxyls formed as a result of dissociative chemisorption of water on the strained siloxane sites, are the centres for the adsorption of dimeric water which remain on the surface even up to degassing temperatures of 250°C. Two

absorption bands at ~ 3530 and $\sim 3700 \text{ cm}^{-1}$ which remain in the spectrum of a water treated sample degassed at 250°C were thought to be due to such a species which was bound to two surface silanols. Kiselev's proposal of dimeric water was based on the known spectra of matrix isolated dimeric water^{76,77} which has a high frequency OH band near 3700 cm^{-1} and a lower frequency band near 3550 cm^{-1} as well as the ν_1 and ν_3 modes of water

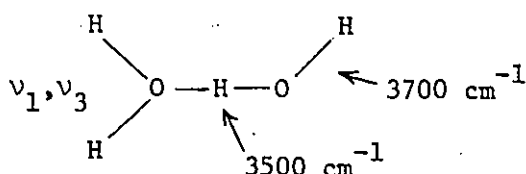


Diagram 1-10

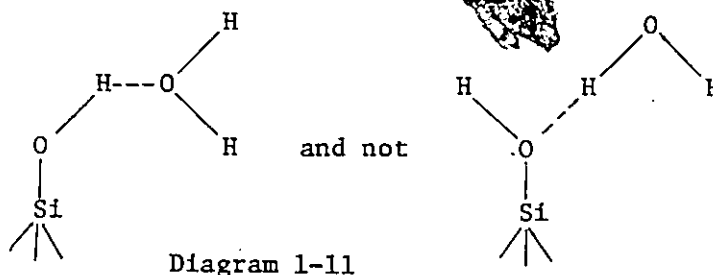
Kiselev et al⁷⁵ proposed that because the 3750 cm^{-1} free $\rightarrow\text{Si-OH}$ band was observed to be constant at low surface coverages of water on silica which had been pretreated above 900°C , then the free hydroxyls must be unable to retain water, and there must be a necessity for two hydrogen bonds between water molecules or their dimers and two surface silanols before adsorption of water can occur. These silanols were identified in the spectra as a low wavenumber shoulder on the 3750 cm^{-1} band. Larger quantities of water formed molecular associates.

Klier, Shen and Zettlemoyer⁷⁸ have monitored the spectra of the adsorption of water to partially hydrophobed silica in the near infrared region. The advantage of this approach is that there is no confusion as to which modes belong to adsorbed water and to silanols, owing to the fact that water has a strong combination band ($\nu_2 + \nu_3$)

at 5300 cm^{-1} which does not overlap any silica bands and is only observed when water is present. They noticed that the capacity for water adsorption diminished as the surface hydroxyl population dropped.

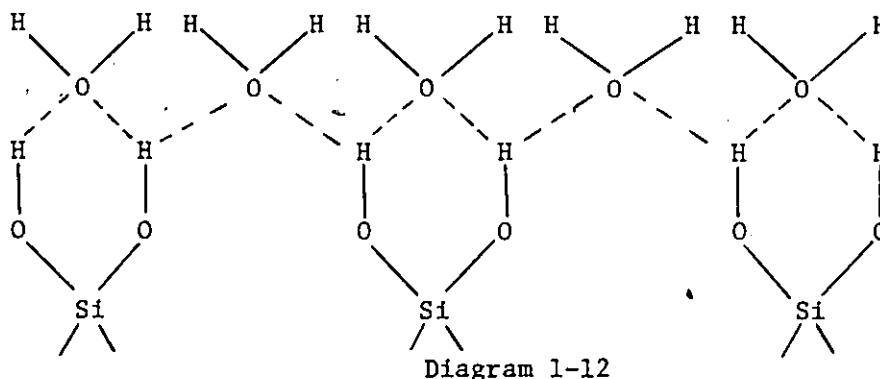
Also, no 5300 cm^{-1} band was noticeable after the silica sample had been outgassed at 170°C .

Changes in the Si-OH 2ν , (7310 cm^{-1}) and the H_2O ($\nu_2 + \nu_3$) band intensities with increased water adsorption demonstrated that the surface hydroxyls were the active centres for water adsorption. The 2ν band shifted downward by 100 cm^{-1} at the saturation vapour pressure of water, a value close to that observed for donor hydrogen bonds in water dimers⁷⁷, whereas $\nu_2 + \nu_3$ for water shifted by only 30 cm^{-1} . From this data Klier et al deduced that the silanols provided a donor band to adsorbing water molecules so that



is the likely configuration.

A structure involving geminal silanols and water,



was ruled out on the basis of the 1:1 relationship in the increase

in $\nu_2 + \nu_3$ of water with decrease in 2ν of SiOH, because this structure would require that water is initially bound to two surface hydroxyls, but with proceeding adsorption, one water molecule would become bound, an average to one hydroxyl by nonlinear hydrogen bonds. Hence geminal hydroxyls do not seem to be a part of the surface network.

On the basis of these observations it is also difficult to account for the formation of a dimeric water which is simultaneously attached to two surface hydroxyls (as proposed by Kiselev et al⁷⁵) if the only mode of attachment is where the surface hydroxyl is the donor end of the hydrogen bond.

In fact, Kiselev et al⁷⁹ have also studied the near infrared spectra of $\text{SiO}_2/\text{H}_2\text{O}$ systems for various silicas degassed at different temperatures and they too noted the linearity of the change in the $\nu_2 + \nu_3$ band of water and the 2ν band of SiOH but no interpretation was given to shifts in the band positions. They concluded that both free and bound hydroxyls were sites for water adsorption. The participation of bound hydroxyls was shown by the fact that the $\nu_2 + \nu_3$ band of water was greatly diminished if the surface had been previously degassed to 450°C , at which only hydrogen bonded hydroxyls should be removed. The free hydroxyls participate with and without the presence of bound hydroxyls.

However, on the basis of arguments given by Klier et al⁷⁸ in their rejection of a geminal hydroxyl surface arrangement, it seems unlikely that water is initially adsorbed on dehydroxylated silicas at two hydroxyl groups, even as monomeric water (Kiselevs proposal⁷⁵), since the quantitative relationship between the amount of adsorbed

water and the intensities of the $\nu_2 + \nu_3$ band of water and the 2ν band of silica indicate that, initially, water is bound to only one hydroxyl.

Further support for this idea comes from heats of adsorption studies on dehydroxylated silicas. Basset et al⁸⁰ report that a value of only 6 kcal mole⁻¹ is obtained for submonolayer coverage of water on these silicas, well below the value for the heat of condensation of water (9.8 kcal mole⁻¹).

Hence, extending the arguments of Galkin et al⁷³ pertaining to heats of adsorption of water on hydroxylated silica, to the case for dehydroxylated silica, a value less than the heat of condensation infers a single site adsorption, that is, interaction is at a minimum. It is important at this stage to clarify the situation for the adsorbed water interaction with free hydroxyls. That several workers in the past, e.g. Hockey⁴⁴, have observed no interaction of the free hydroxyls with multilayers of water even under reasonably hydroxylated conditions, is probably traceable to heating effect of the infrared beam on their sample²¹.

Chuiko et al⁸¹ had, like Hockey⁴⁴, observed no perturbation of the SiOH band with water or methanol, but they established that the amount of water adsorbed was related to the concentration of surface hydroxyls. In their opinion the silicon atoms of the surface silanols were the sites for adsorption.

Bascom and Timmons⁸² also noted that there was apparently no change in the intensity of the SiOH band for water adsorption on silica particles suspended in CCl₄, but they did consider, nevertheless,

that adsorbed water was held to the surface of silica by hydrogen bonding to the surface hydroxyls. They rationalized that any decrease in the SiOH intensity would be compensated for by the formation of free O-H bonds in adsorbed water.

However, there is no need to invoke these arguments, for as Kiselev⁷¹⁻⁷⁴, Anderson and Wickersheim⁶⁹ and Klier et al⁷⁸ have shown, the SiOH intensity is affected by water adsorption.

Kiselev⁷³ and Klier et al⁷⁸ have both emphasized that the interaction of water with surface hydroxyls is more easily facilitated if, subsequently, clusters can be formed, and that this requires that there is simultaneous adsorption of water at two hydroxyl sites.

On surfaces which contain both free and hydrogen bonded hydroxyls (i.e. on surfaces degassed below 400°C) associated water forms more readily than on surfaces containing only free hydroxyls (from references 73 and 75). This is illustrated by the fact that lower vapour pressures of water are required to totally remove the free hydroxyl species and to form associated water on hydroxylated silicas.

This may be because water can adsorb simultaneously at free hydroxyls and adjacent hydrogen bonded hydroxyls on fully hydroxylated surfaces where there is some optimum distance separating the hydroxyl groups for the preferred adsorption of water.

Thus, for a large population of free and non-linear hydrogen bonded hydroxyls adsorbing water molecules have a greater possibility of finding hydroxyls separated by this distance. As the bonded hydroxyls are removed by increased degassing temperatures,

higher vapour pressures are required because water adsorption at, say, 400°C is then pre-empted by the rehydroxylation of the surface. When the facility for chemisorptive rehydroxylation is removed (i.e., above 400°C), the adsorption of water then becomes solely dependent on the distance separating free hydroxyl groups and the vapour pressure required to just form molecular associations begins to fall until the optimum hydroxyl group separation is reached. This value appears to be about 0.9 hydroxyl groups per 100 Å² corresponding to a surface degassed at 800°C (from references 19 and 75).

None of the theories for water adsorption on silica proposed by any of the aforementioned authors place much emphasis on the type of surface that exists on highly dehydroxylated silicas, only noting that "some active site exists at which water seems to chemisorb".

In view of this lack of knowledge about what this site might be, theories of water absorption on these surfaces should be regarded with some reservation.

Summary

The diversity of experimental conditions that have been used to study the reactions of silica with the chlorosilanes, the methylchlorosilanes and of water prevents a singular interpretation of the nature of the surface and of reaction modes. Nonetheless, the following seems to have been established.

1. Geminal hydroxyl groups may exist on dehydroxylated silica, but there is no spectroscopic proof for this. Adjacent hydroxyls are required to explain

the kinetic and analytical observations made with chlorosilanes and methyl-chlorosilanes on dehydroxylated surfaces. However, more recent work with AlCl_3 indicates that strained bridge sites may also be involved.

2. Both bound and free hydroxyls interact with water but in the absence of bound hydroxyls, adsorption is favoured only at higher vapour pressures of water. Water appears to be bound at adjacent hydroxyl sites on fully hydroxylated surfaces but there is argument as to whether this is the mode of adsorption on a dehydroxylated silica. For example, Kiselev favours a multiple adsorption site, whereas Klier et al. consider that the water is bound at a single site as shown in Diagram 1-11.

3. Water is almost totally removed from silica by outgassing at room temperature.

4. A surface degassed below 400°C can be reversibly rehydroxylated with water vapour to form hydrogen bonded hydroxyls, (i.e., water is chemisorbed), whereas a surface which has been degassed at temperatures greater than 400°C cannot be totally rehydroxylated, and instead, new sites are formed which result in chemisorption of a different kind. It is this latter form of chemisorption that has been chosen for study in this thesis.

Several new features have been discovered and, in particular when water is adsorbed on surfaces with low hydroxyl concentrations, three new types of hydroxyl group have been proposed to exist (see Chapters 4 and 5).

Isotope Studies

The remaining sections of work on silica in this thesis, involve the determination of the nature and orientation of chemisorbed species from the adsorption of small molecules like NH_3 , HCN and cyanogen (C_2N_2).

It is quite noticeable in the surface chemistry literature that, in most instances, assignments of vibrational modes of adsorbed species are made solely on the basis of analogy with other compounds of known frequency or with the pre-adsorbed molecular species itself.

This can be quite a useful approach in general especially if the bands in the spectrum are few and well defined. However, in cases where many bands appear clustered together, or the position of absorption band varies widely, then assignments are not so readily made. For example, fundamental bands for nitrile absorption involving mainly the $\text{-C}\equiv\text{N}$ stretching mode are known to adsorb from 2350 cm^{-1} to 2000 cm^{-1} depending on the nature of the surface and upon the atoms adjoining the nitrile group. If there are multiple species co-existing on the surface then it becomes quite difficult to clearly assign bands observed unequivocally to a particular mode in a particular species, simply by a reference comparison. A relatively quick method exists to enable accurate assignments to be made.

This is the use of isotope substitution of the adsorbed species. When the mass of an atom of a molecule is altered by isotope replacement, the normal modes of vibration of the molecule will all be altered to some extent, and the extent of the change in the normal mode is directly measurable as the shift in frequency for that mode appearing in the infrared spectrum. The fact that there is a shift at all is proof that the isotopically replaced atom has been retained by the chemisorbed species upon adsorption. The magnitude of the shift cannot be immediately interpreted in the case of polyatomic adsorbed species and some calculation is required. (Actually partial

isotopic substitution generally does show how many atoms are present). However, the prime object of the calculation is to set up a suitable force field for the adsorbed species based on the observed normal vibrational frequencies. Then, if the calculated force field is a suitable description of the environment in which the species vibrates, isotope substitution in the molecule should only alter the kinetic energy of the adsorbed species and an expected frequency shift can be obtained and compared to the observed shift.

If there is no coincidence between the observed and calculated shift in frequencies then two considerations must be made. A change in the force field can be effected by changing force constant values given to the molecule. Providing this change of force constant values is judiciously made and the force constants are still physically realistic and capable of meaningful comparison with other similar molecules then the process of change is continued until a fit is obtained with the observed frequencies of the normal and isotopic molecules. In fact this process is not straightforward and will be discussed in more detail below.

If no fit can be achieved with the observed and calculated frequencies, except by using unrealistic force constants then a change must be made to the coordinates themselves, that is, a new configuration for the orientation of the species w.r.t. the surface should be considered (with corresponding new kinetic energy and potential energy terms) and the process of variation of the force field repeated to see if a fit can then be achieved.

This total procedure then enables the observed frequency

to be assigned to a normal mode of vibration of a particular species that has a particular surface orientation.

Evaluation of Force Constants from Vibrational Frequencies

Wilson's⁸³ 'GF' method has been employed to evaluate force constants in a program developed by Schachtschneider⁸⁴ where in general the G elements and the roots (λ) of the secular equation $|GF - \lambda E| = 0$ are known. Where necessary, the correction for anharmonicity in the deuterium stretches has been made for the observed frequency, (the correction factor is 1.011).

The use of isotopes to facilitate a calculation of the force field has the following purpose. Provided the number of force constants is not greater than the number of frequencies of the non-isotopically substituted species then a force field can be derived which can then be used to find the frequencies for the isotopically substituted molecule. If a match is obtained and the force constants are reasonable then one can be reasonably confident in assigning a certain structure to the species. Consider, for example, a system for which the secular matrix is described as

$$GF = \begin{vmatrix} g_{11} & g_{12} \\ g_{12} & g_{22} \end{vmatrix} \begin{vmatrix} f_1 & 0 \\ 0 & f_2 \end{vmatrix}$$

with roots λ_1 and λ_2 , then

$$\lambda_1 + \lambda_2 = g_{11}f_1 + g_{22}f_2 \quad (1)$$

and
$$\lambda_1\lambda_2 = (g_{11}g_{22} - g_{12}^2) f_1f_2 \quad (2)$$

Since the true roots and the G matrix entries are known then the corresponding force constant values can be found by solving equations (1) and (2). The required solutions are the values of f_1 and f_2 where the straight line (equation 1) cuts the rectangular hyperbola (equation 2). The values of the roots will determine whether the line cuts the hyperbola in two points, is tangential to it (one point) or does not cut it at all, when f_1 is plotted against f_2 . For a range of force constant values, for each pair of f_1 and f_2 , the corresponding roots λ_1 and λ_2 are evaluated, and a quantity

$$\chi^{i-1} = P_1(\lambda_1^i - \lambda_1^o)^2 + P_2(\lambda_2^i - \lambda_2^o)^2 \quad (3)$$

is evaluated, and is a measure of the lack of agreement between the calculated and true roots. The various values of χ for various values of f_1 and f_2 generate a surface in space f_1, f_2, χ in which the minimal values of χ^i represent satisfactory values of f_1 and f_2 . P_1 and P_2 are weighting factors.

In a refinement process, the object is to change the values of f_1 and f_2 for which the roots are in better agreement with the true roots. This is continued until χ^i is a minimum. It follows from equation (3) that

$$\chi^i = P_1(\lambda_1^i + \Delta\lambda_1^i - \lambda_1^o)^2 + P_2(\lambda_2^i + \Delta\lambda_2^i - \lambda_2^o)^2 \quad (4)$$

Now since $\Delta\lambda$ can be related to Δf , then χ can be expressed as a function of Δf . The best values are those which minimize χ and are found by solving two simultaneous equations in Δf_1^i and Δf_2^i by applying the condition $\partial\chi/\partial f_1^i = 0$ and $\partial\chi/\partial f_2^i = 0$.

Sometimes when full vibrational information is unavailable, isotopic frequencies can be used as initial data to develop the force field. For example, if an off diagonal term f_{12} had been introduced in the original matrix then a third equation from the isotopically substituted molecule would be required.

Symmetry

For the purposes of computer calculation, the derivation of symmetry coordinates is not warranted. However, in some instances there is an advantage of inserting such coordinates since the GF matrix will be in block form so that one can deal separately with those modes related by symmetry and avoid the need to supply the values of the roots of all modes.

CHAPTER 2

EXPERIMENTAL (GENERAL)

The Infrared Spectrometer

All infrared spectra have been obtained using a modified Perkin Elmer 13G Filter-Grating Spectrometer. For routine use, spectral slit-widths of 5-10 cm^{-1} have been used over a range extending from 3800 cm^{-1} to 600 cm^{-1} , although smaller spectral slit-widths have been used under specific circumstances which are dealt with individually.

The instrument has generally been used in a double beam mode although the single beam facility was occasionally employed.

One notable feature of the spectrometer is that the chopper is situated between the Nernst glower source and the sampling zone so that any possibility of inadvertently measuring emission spectra from a hot sample is eliminated. The spectrometer was flushed with a continuous flow of dry air from a Beckman Automatic Air drier.

General Equipment

Vacuum Line

A standard pyrex vacuum line was required in order to degass samples and for transfer of gases and vapours from container bulbs to a sample cell.

The principal features of the line include a mercury manometer (used to measure pressures of greater than 1 torr), a pirani vacuum gauge (to estimate pressures down to 10^{-4} torr), a mercury diffusion pump and a mechanical oil backing pump (pumping speed 25 litres min^{-1}). The main line was of wide bore (1" dia.) to make pumping more efficient. Two liquid nitrogen traps were placed between the main line and the pumps.

Generally a dynamic vacuum of about 10^{-4} torr was considered satisfactory for most experiments. The vacuum stopcocks and ground joints were lubricated with Apiezon 'N' grease.

Sample Cells

Two types of cell have been used and are represented in Figure 2-1. In both cells a ball joint system was used for connection to the vacuum line.

CELL A. A Room Temperature Cell

The cell shown in Figure 2-1a was designed in this laboratory especially for studies of the sample at room temperature. The body of the cell and the sample holder is quartz and the windows are either NaCl or CaF_2 (5.5 cm dia. and 5 mm thickness). NaCl windows were used when transparency below 1200 cm^{-1} was required. Glyptal was used to seal the windows to the quartz body.

The heating zone consists of a layer of asbestos matting over which is wound approximately three metres of Kanthal wire such that there are about four turns per centimetre. This in turn is

insulated by a thick coating of powdered asbestos. A small quartz tube may be inserted between the windings and the asbestos mat so that a thermocouple wire (chromel-alumel) can be inserted to determine the temperature at the surface of the cell. (The temperature at the sample surface is probably always less).

Temperatures up to 1200°C can be achieved, however, the lifetime of the heating wire is short under these conditions. Since high temperatures were often used the ground joint was lubricated with Apiezon H.

Though this cell is like many others that have been used in infrared studies, it has a unique feature that enables a more rapid replacement and setting of the sample. The sample holder consists of two concave annular discs, one on each arm of the forkpiece, which are held together by tension in the fork.

To place a sample (a 2.5 cm disc) inside the holder, the ends of the fork can be prised open with just light hand pressure, sufficient to allow a disc to slip in edge-ways. The other end of the forkpiece fits snugly into a matching sheath so that movement of the sample from the furnace to the windows is permitted but without twisting, so that the same orientation is always maintained with respect to the windows (and with respect to the infrared beam provided the cell position itself remains unchanged).

CELL B. A Variable Temperature Cell

The detailed features of this cell (Figure 2-1b) have been described elsewhere⁸⁵. Its importance in this work was to enable the

spectra of surfaces to be monitored at various measured temperatures, a function unavailable with the previously described cell. Due to the nearness of the heating block to the cell windows (CaF_2) the maximum temperature usable is about 400°C . The sample can also be cooled. To do this, the cell is first evacuated, then about 10 torr of either Ar or He is admitted. An external well is filled with a coolant liquid such as nitrogen, and subsequently, heat is removed from the sample by conduction. Temperatures of about -170°C may be achieved after about 10 minutes when the well is filled with nitrogen.

Materials

Silica

The silica used for both pure studies and for the supported metal work, was Cabosil H-S5 obtained from Cabot Inc. of Boston, U.S.A. It had a B.E.T. (N_2) surface area of $320 \text{ m}^2 \text{ g}^{-1}$.

Before use, the silica was preheated in air to 700°C in order to oxidize any organic contaminants. To render the powder suitable for spectroscopic examination it was pressed into a self-supporting disc. A 2.5 cm diameter die similar to that used in the preparation of KBr discs, with applied pressures of about 70 kg cm^{-2} maintained for just a few seconds served this purpose.

Under special circumstances when pressures higher than this were required for silica disc preparation, a hardened steel die was used of tempered F.N.S. steel (see Figure 2-2). A stainless steel sleeve fits over the projections and remains unstrained during pressing so that discs can be easily removed from the die even after pressing

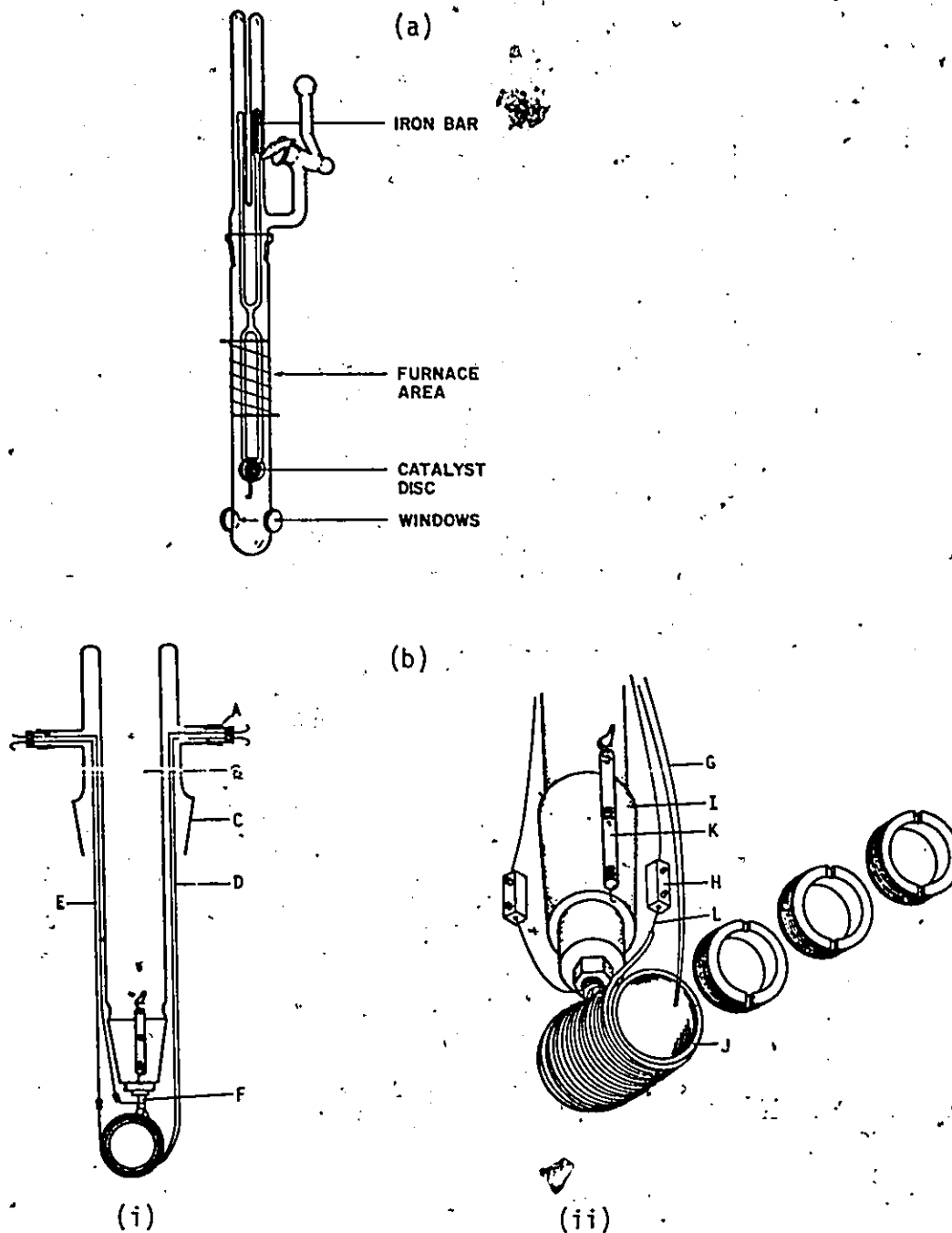


FIGURE 2-1

- (a) Infrared cell A. The lower section and the sample holder are made of quartz; the upper section, including stopcock, is constructed of pyrex. The distance from the windows to the heating area is 20 cm.
- (b) (i) and (ii). Infrared cell B: (reproduced from reference 84).
 (i) Schematic diagram of the sample cell. A, B10 cone and socket; B, coolant reservoir; C, B55 cone; D, thermocouple leads; E, copper leads to heating element; F, threaded copper rod.
 (ii) G, thermocouple leads; H, metal terminal connectors; I, copper socket; J, copper sample tube; K, stainless steel spring; L, Nichrome heating wire.

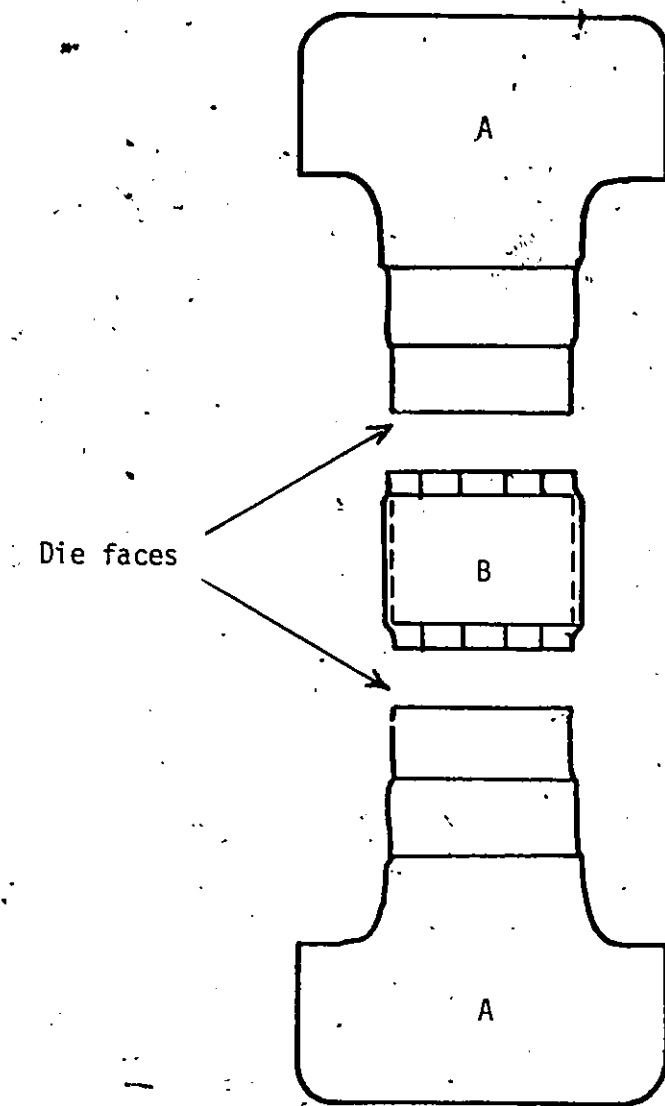


FIGURE 2-2

Hardened steel die for preparing discs at high pressure.

- A. End pieces with 2.5 cm diameter machined faces.
- B. Close fitting stainless steel collar.

to $11,000 \text{ kg cm}^{-2}$. In the conventional steel die this is not possible due to spreading of the metal.

With either die, and regardless of the pressure utilized, the removal of silica from the die faces after pressing was made easier by placing circular wafers of lens cleaning paper (2.5 cm diameter) between the powder and the polished faces to eliminate sticking.

In the preparation of very thin discs (3 mg cm^{-2}), a further precaution had to be observed to prevent the pressed disc from becoming distorted due to electrostatic charge differences between silica and the paper wafers; the wafers were impregnated with silica powder by pressing several times with larger amounts of silica (30 mg cm^{-2}) prior to their use in the preparation of thin discs.

In the general procedure, the disc was then placed in an infrared cell and evacuated to remove moisture and air from the cell. It is then ready for study by infrared spectroscopy.

Supported Metals

To make a disc of a metal supported on silica that is suitably transparent in the infrared from 4000 to 1200 cm^{-1} a strict procedure must be followed. Experience has shown that a lack of adherence to any one of the following steps tends to result in samples that cannot be successfully pressed or that are virtually opaque in the infrared region. The metal used exclusively in this work was platinum.

A one-gram sample of a salt of the metal (e.g. $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) was dissolved in about 70 ml of spectral quality acetone at room temperature, then two grams of silica powder were added slowly, with stirring, until a uniform slurry was obtained. The slurry was then left to dry at room temperature for one week, during which time, the conglomerates which formed were broken up lightly with a glass rod. After this period, the remaining lumps were pulverized in a mortar and pestle for at least thirty minutes. Pressure used was sufficient to form a fine powder but not so hard as to force the particles back together. At this stage the powder was observed to be dark coloured indicating the presence of metal oxides⁸⁶. (Platinum powders were generally light brown). The samples was then stored in a dessicator for a few days and reground for 10 minutes prior to use.

About 200 mg (40 mg cm^{-2}) of sample were used for disc preparation although with as little as 50 mg (10 mg cm^{-2}) it was possible to obtain a self-supporting disc. Again lens cleaning paper wafers were used to separate the powder from the die and prevent sticking. Pressures were always 70 kg cm^{-2} .

Reduction of the supported metal salt was carried out inside Cell A.

The sample was drawn up to the furnace zone in the fork holder and the cell, which was positioned horizontally on the vacuum line, was outgassed at 50°C for 6 hr.

Ultra pure hydrogen was obtained by passing commercial hydrogen (Union Carbide) through an electrically heated palladium thimble at 650°C (Mathey-Bishop HP-2 Hydrogen Purifier). Initially 400 torr of this hydrogen was admitted to the cell at room temperature and after five

minutes, degassed until the pressure was below 10^{-3} torr. (This may take fifteen minutes). Again 400 torr was admitted and the process repeated. (The main impurities evolved on outgassing at this step are HCl, formed during the reduction of the salt, H_2O from the sample exposure to the atmosphere and residual hydrocarbons, from reduction of acetone remaining in the powder. It seems to be important to be rid of most of these impurities before proceeding to higher temperatures.) The temperature of the sample was then slowly raised to $100^\circ C$ in increments of about $20^\circ C$. At each step, fresh hydrogen was admitted for twenty minutes and outgassed to a pressure of 10^{-3} torr.

Beyond $100^\circ C$, temperature increments of $50^\circ C$ were maintained, until $300^\circ C$, with fresh hydrogen being introduced at each temperature rise, and degassed to 10^{-3} torr just prior to the following temperature step. This series of steps took three hours. The temperature was only raised further when the residual pressure on the final outgassing at $300^\circ C$ had dropped below 5×10^{-4} torr.

The next temperature increase was to $400^\circ C$ where again fresh hydrogen (400 torr) was admitted several times over a period of about one hour. Finally the sample was degassed at $450^\circ C$ and cooled from this temperature in fresh hydrogen.

The best Pt/SiO_2 discs obtained using this procedure had the following specifications. If 100% T was set at 2100 cm^{-1} with the sample placed in the infrared beam, the transmission at 3800 cm^{-1} was 40%. If, however, 100% T was initially set at 2100 cm^{-1} without anything in the sample beam, then the sample placed in the beam, the transmission dropped to 40%. The same value was obtained for a silica sample of identical size.

This is far better transmission than reported elsewhere in the literature for samples of comparable size and percentage of metal (16% in the case of Pt), and is attributable to the use of a dry acetone slurry instead of commonly used water slurries, to the slow rate of drying of the slurry, and, to the care taken in the reduction procedure to remove impurities at low temperatures and to a slow temperature increase. Due to the absence of large amounts of moisture in the powder a much clearer region around 3600 cm^{-1} has been obtained enabling new species to be identified⁸⁷ which would not have been possible using powders derived from aqueous slurries.

Supported metals cannot be used indefinitely but their lifetime does depend on the type of adsorbate used. Regeneration of a surface can generally be achieved by outgassing the adsorbate used for ten minutes then treating the sample with 400 torr hydrogen for five minutes and outgassing for five minutes (both operations at room temperature). The sample is then treated in 400 torr H_2 at 400°C for one hour and cooled in fresh hydrogen. It should then be ready for re-use. A good test for surface quality is to observe the shape and intensity of a band appearing at 2100 cm^{-1} (due to Pt-H) when 400 torr of hydrogen is present in the cell at room temperature. A sharp profile of about 0.01 absorbance units is generally indicative of adequate surface activity. When this band becomes smaller, and/or broader, the catalytic activity of the surface is invariably found to be lower for other adsorbates, and a new pellet should be prepared.

Nitriles are notorious poisoners of catalysts and complete regeneration subsequent to surface nitrile formation is often impossible. However, with many other adsorbates such as NH_3 , H_2O and benzene several adsorption-desorption-regeneration cycles may be used without diminishing catalytic activity.

Chemicals

Commercially available gases and liquids which have been used for adsorption have been accepted as pure, though where impurities were suspected they were checked by using infrared or mass spectrometry (AEI MS 10 or MS 902 high resolution mass spectrometer). Any chemicals prepared in the laboratory were also checked by these methods. In some instances it was necessary to perform trap to trap distillations on the vacuum line to obtain purity. Before adsorbing any gas or vapour, a standard "freeze-pump-thaw" cycle was used to remove air.

HCN and HCl were prepared as dry gasses by simple displacement for the appropriate salt using H_2SO_4 addition in a nitrogen stream. (With HCN, it was found necessary to use 50% H_2SO_4 instead of concentrated, to avoid the formation of HCNO . The gases were dried over P_2O_5 in vacuum before storing in a bulb.

C_2N_2 and PH_3 were prepared by the methods given in Brauer^{88,89}, though with PH_3 the preparation was slightly modified by installing a second trap (CO_2) in order to trap subliming PH_4I .

CH_3NC was prepared as described by Casanova et al.⁹⁰, and NH_2NH_2 was obtained by distillation of $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$, in a nitrogen stream.

HCN, C_2N_2 and CH_3NC were always stored in the freezing

compartment of a refrigerator. NH_2NH_2 was stored in the dark.

In each of the following chapters, a small "experimental" section has been included to elucidate specific procedures.

CHAPTER 3

ISOLATED HYDROXYL GROUPS

The contention by Hair and Hertl⁵¹ and Van Cauwelaert, Jacobs and Uytterhoeven⁶² that the 3748 cm^{-1} absorption band has two distinct shoulders to high and low wavenumber, implying that the A type hydroxyls exist in a geminal form as well as isolated, has been investigated. According to Van Cauwelaert et al⁶² the shoulders were more pronounced at higher sample temperatures and that their exact position relative to the main band depended on the temperature. Using a curve analyzer, they "decomposed" the band contour into a three component curve which reflected the positions of these shoulders. Hair and Hertl have produced a spectrum which shows that at a sample temperature of 25°C , the same band consisted of three clearly resolved components, but this finding was later refuted by Hockey⁶³, Morrow and Devi⁵⁹ and contradicted by Peri and Hensley⁴¹. Hockey⁶³ claimed that the splitting observed was an artifact due to improper double-beam compensation in this region of strong infrared absorption by atmospheric water. Hockey's spectrum showed a relatively sharp band centred near 3748 cm^{-1} which was degraded into a tail on the low wavenumber side. When the spectrum was recorded in the presence of water vapour sharp 'spikes' appeared on the SiOH profile which were attributed to water absorption. This was confirmed by studying an Si-OD surface under the same conditions where no such 'spikes' were observed. In reply to Hockey's criticism of Hair

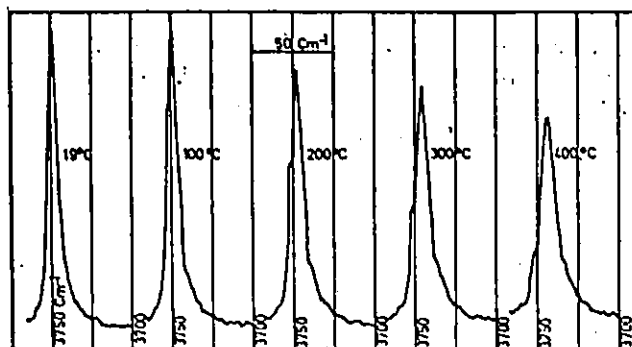


Figure 1. Photographs of the spectra of the A-type hydroxyls at different temperatures.

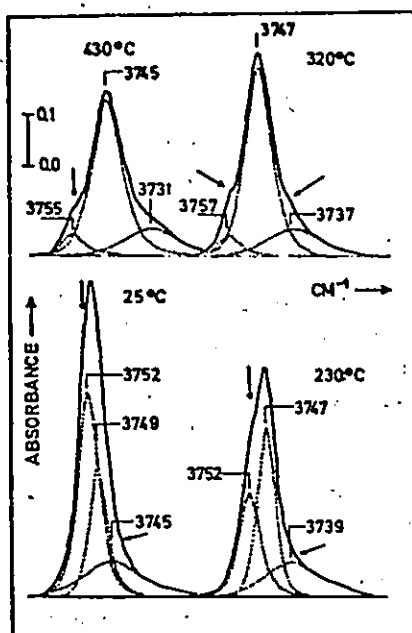


Figure 2 Resolved spectra of the A-type hydroxyls reproduced by the curve resolver. Solid lines are the experimental spectra obtained at 25, 230, 320, and 430°. The resolved components are the dashed lines.

FIGURE 3-1

Figures 1 and 2 from a paper by F.H. Van Cauwelaert et al.

J. Phys. Chem. 76, 1434 (1972)

indicating apparent shoulders in SiOH profile.

and Hertl's⁵⁸ work, Van Cauwelaert et al⁶² were convinced that their spectra were obtained under totally compensated conditions. Furthermore, they claimed that the appearance of distinct shoulders under these conditions could not be attributed to improper atmospheric absorption because such shoulders would not shift with changes in temperature in contrast to their observations. However, this would not necessarily be true if the shoulders were due to inverse absorption in an improperly compensated spectrometer and if the peak position of the SiOH band changed with temperature. They stated however that a perfectly straight base line was obtained in the 3750 cm^{-1} spectral region when the silica sample was removed from the sample beam of the double-beam spectrometer.

To illustrate the components of the SiOH band that Van Cauwelaert et al refer to, Figures 1 and 2 from their publication have been reproduced here and shown as Figure 3-1.

Definite shoulders appear, especially in the spectra of the sample at 430°C .

Incredibly, however, no such shoulders could be found in their spectra of the SiOD stretching band. According to Van Cauwelaert et al⁶², "the high frequency and middle frequency components lose their identity".

In the context of Van Cauwelaert et al's initial work on SiOH, the first part of this chapter details some interpretations and conclusions based on observations of the SiOH profile made in this laboratory, and the second part of the chapter deals with a

discussion of a more recent publication by Van Cauwelaert et al⁹¹, which divulges some of the experimental details that were lacking in their previous work.⁶² Subsequent attempts to duplicate their conditions and their results have been made.

Band Fitting

Various types of mathematical functions can be used to fit the absorption bands appearing in infrared spectra. The breadth of the bands in the vapour state at sub-atmospheric pressures is well known to be associated with Doppler broadening, whereas in condensed phases collision broadening is the major contributor to the band shape.

Mathematically Doppler broadening gives rise to a Gaussian band shape but collision broadening produces absorption band shapes that more closely fit a Cauchy function.⁹²

It has been observed that the absorption spectra of adsorbed state species have profiles that are neither pure Gaussian nor pure Cauchy but that they can be represented by some combination of the two.

Two such combinations are listed below:

Cauchy-Gauss Product

$$A(\nu)_P = x_1 [1 + x_3^2 (\nu - x_2)^2]^{-1} \cdot \exp[-x_4^2 (\nu - x_2)^2]$$

Cauchy-Gauss Sum

$$A(\nu)_S = x_1 [1 + x_3^2 (\nu - x_2)^2]^{-1} + x_5 \exp[-x_4^2 (\nu - x_2)^2]$$

The variables $x_1 \dots x_5$ are the band indices and $A(\nu)$ the intensity at a frequency ν . x_1 and x_5 are the maximal ordinates, x_2 is the abscissal location of the peak, and x_3 and x_4 characterize the half widths of the Cauchy and Gauss components.

Jones⁹³ has developed a program to fit a chosen number of symmetric component bands to an experimentally observed complex infrared band profile. All components are initially chosen to be either sum or product functions, and, by inspection of the experimental profile, the number of components is estimated and the position of each component maxima (x_2) is measured.

If the Cauchy-Gauss product function is used, then four estimated parameters are required, x_1 , x_2 , x_3 and x_4 .

At first, the experimental profile is fitted to a pure Cauchy function and a best fit is obtained for each variable, then these values are used as the initial values in a program which fits the curve to a chosen number of Cauchy-Gauss product components in which, initially, x_3 equals x_4 .

If the Cauchy-Gauss sum function is used, a fifth parameter (x_5) is required so that the individual heights of the Cauchy and Gauss components are expressed. Initially x_5 is always set to one tenth of x_1 since the expected ratio of the functions is 10:1 Cauchy: Gauss⁹³.

Numerical techniques have been developed for optimizing these indices using least squares methods.⁹³ When the program is executed, the optimal fit is indicated by key statistical parameters: DIS (discrepancy) is the root mean squared of the residual differences

between the calculated and the experimental spectrum in transmittance; WFM is the wavenumber of the maximum discrepancy; MAX is the maximum discrepancy at WFM. As well the program calculates the ratio of Cauchy to Gaussian functions used to obtain the optimal shape for each component (evaluated as the ratio of the half widths, $x_3/(x_3 + x_4)$). For the computed component bands to be meaningful the experimental profile must lie on a perfectly straight base line, although there is no necessity that the line be horizontal.

In Van Cauwelaert et al band fitting work⁶², no mention was made of the accuracy of their band fitting procedure, nor was a computed spectrum shown. As well they assumed a constant shape ratio for a Cauchy-Gaussian product function for all temperatures which is questionable.

The shape ratio was determined from a method used by Abramowitz and Baumann⁹⁴. Van Cauwelaert et al⁶² studied the profile of the hydroxyl stretching band in the oxides hydrogen zeolite Y, kaolinite and muscovite and found values of 65 ± 2.5 , 69 and 70% Cauchy character respectively. For the 3750 cm^{-1} band of silica, they found a value of 65% Cauchy-35% Gaussian based on the profile of the high frequency side of the band (the low frequency side is slightly asymmetric).

A Cauchy-Gauss product function was assumed into which values of x_1 and x_2 were substituted and a ratio of the values of the half band widths (x_3 and x_4) was found and used as a measure of the percentage Cauchy component.

When $\frac{x_3}{x_3+x_4}$ is 1.0 then the band is pure Cauchy but when 0.0, it is Gaussian. Values in between represent the fraction of either function.

Experimental

The silica samples were utilized in the form of discs of 5 mg cm^{-2} which were pressed at 70 kg cm^{-2} . They were heated for several hours at 750°C in cell A then cooled and transferred to cell B where they were again evacuated for 1 hr at 400°C. This procedure is similar to that used by Van Cauwelaert et al⁶². The purpose of degassing the sample at 750°C was to remove any B type hydroxyls and physically adsorbed water. About 10 torr of helium was added to the evacuated cell to ensure good thermal conductivity.

Spectra in the OH stretching region were recorded with a spectral slit width of 2.2 cm^{-1} at a scan speed of 4.9 $\text{cm}^{-1} \text{ min}^{-1}$, this value of the slit width being chosen because of optimum signal to noise ratio for digitization purposes. Band shapes did not alter with a narrower slit width, and identical, although "noisier" spectra were observed using a 1.4 cm^{-1} spectral slit width.

A spectral slit width of 1.0 cm^{-1} was achieved using another spectrometer (a Perkin-Elmer 180) and again the band shape was unaltered.

After dry air flushing, the total single beam absorption due to residual water is shown in Figure 3-2a, and a perfectly straight base line could be obtained in a double beam operation either with or without the sample cell in place, provided all sample areas were totally flushed with dry air.

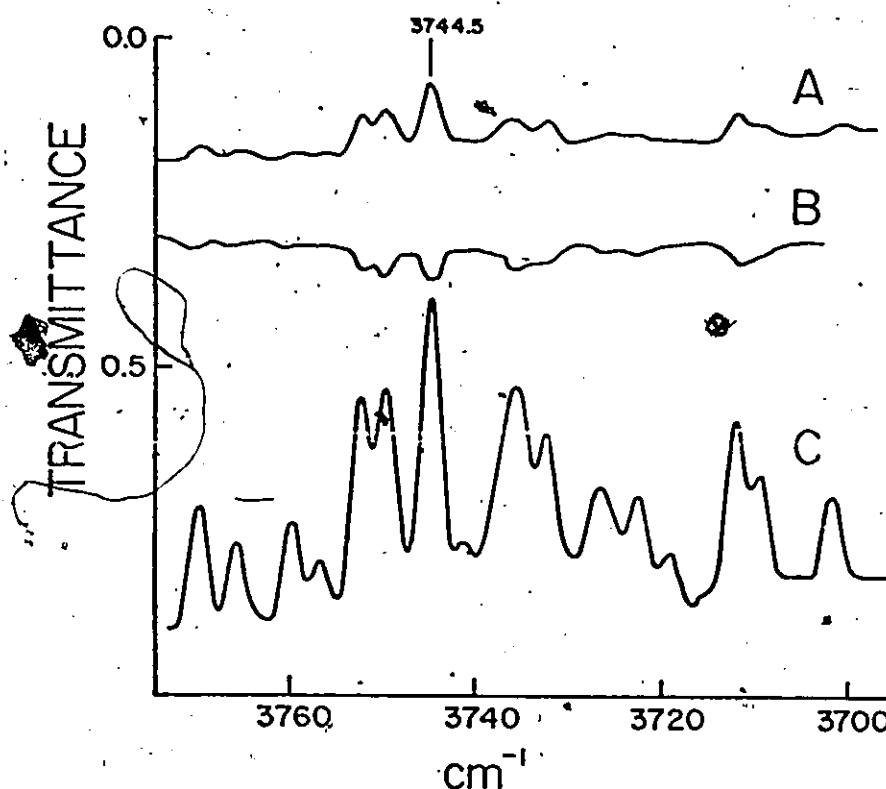


FIGURE 3-2

- A. Single beam spectrum of residual atmospheric water with complete flushing.
- B. Double beam spectrum of uncompensated cell.
- C. Single beam spectrum with sample chamber exposed to the atmosphere.

The transmittance scale applies to spectrum C; the other spectra are linearly displaced for purposes of presentation.

By "total flushing", it is meant that the gap between the source and beam convergence housings (i.e. the sampling area) was bridged with glass tubing; so that, apart from the space taken by the infrared cell in the sample beam, the path length of both sample and reference beams, from source to detector, was flushed with dry air. Spectra recorded under these conditions are referred to as "compensated".

An "uncompensated" spectrum refers to spectra recorded when the sampling area was totally open to the atmosphere and with a sample cell (path length 7 cm) in the sample beam only. The residual "uncompensated" spectrum is shown in Figure 3-2b and the total single-beam atmospheric spectrum under those conditions is shown in Figure 3-2c.

For computational purposes, the spectra were digitized at 0.2 cm^{-1} intervals between 3771.0 and 3684.2 cm^{-1} and band fitting computations were carried out on an IBM 360/65 computer using programs developed by Pitha and Jones⁹⁵ for fitting Cauchy-Gauss product or sum functions to the experimental spectral bands. Plots were recorded on a Milgo plotter.

Accuracies were expressed in terms of the parameters given before. All spectra were calibrated against atmospheric water bands and the experimental data reported are believed to be accurate to $\pm 0.2 \text{ cm}^{-1}$. SiOD surfaces were obtained by exchanging an SiOH surface several times in D_2O at room temperature before degassing to 400°C in cell B.

In an attempt to obtain discs prepared in the same way as revealed by Van Cauwelaert et al, in their second publication⁹¹ the

hardened die was used for pressing discs with loads up to 54,000 kg ($11,000 \text{ kg cm}^{-2}$). Loads higher than this could not be achieved without the die breaking. A hydraulic press capable of loads up to 270,000 kg was made available by the Aeronautics Division of the National Research Council of Canada.

Results

Experimental spectra of the SiOH band of silica at -145, 25, 200 and 400°C are shown in Figures 3-3a and 3-4a. The total band area and the wavenumber of the maximum absorption in each case is given in Table 3-1. These spectra are very different from those shown by Van Cauwelaert et al⁶² at the same temperature, (except for the spectrum at -145°C which is unique to this work), in that distinct shoulders on either side of the main absorption peak are absent.

Since the spectra observed by Van Cauwelaert et al⁶² had shoulders to high and low wavenumber of the main absorption band, a band analyzer was used to decompose this band into three components. They assumed that their Cauchy-Gauss product function had a 65% Cauchy character, in this fitting and although they did not say what their criterion of a "good fit" was, it is assumed here that a reasonable fit was achieved. However, there is no a priori reason to assume that the same shape ratio should be applied to all bands and at all temperatures over a 400°C range⁹². The parameters derived from a mathematical analysis of closely overlapping band systems depend very much on the type of function used and the number of components assumed. Therefore it is doubtful that their calculated band parameters are unique and

TABLE 3-1

Experimental Data for the Spectra shown in
Figures 3-3a and 3-4a

Temp °C	Wavenumber cm ⁻¹ (at maximum intensity)	Peak Intensity in absorbance	Band area
-145	3751.4	0.97	6.56
25	3748.2	0.76	6.11
200	3744.7	0.57	6.05
400	3740.6	0.41	5.63

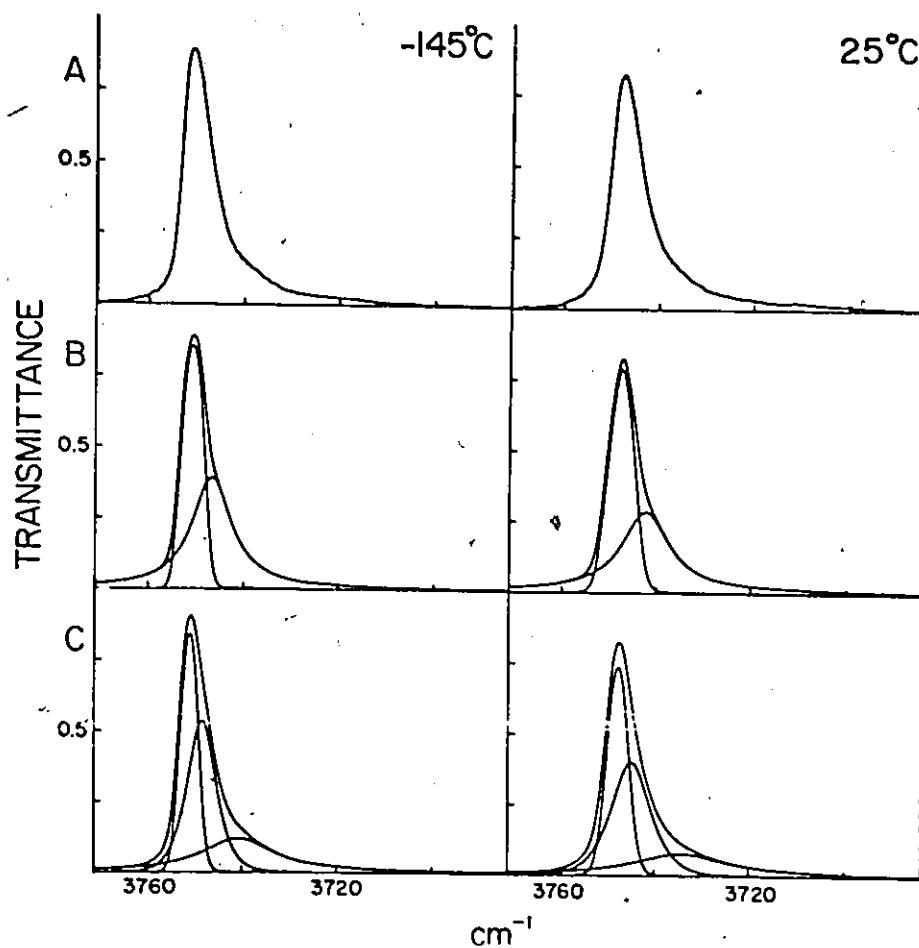


FIGURE 3-3

- A. Experimental spectra of SiOH band at -145°C and 25°C.
- B. Computed spectra using a 2-component sum function.
- C. Computed spectra using a 3-component product function.

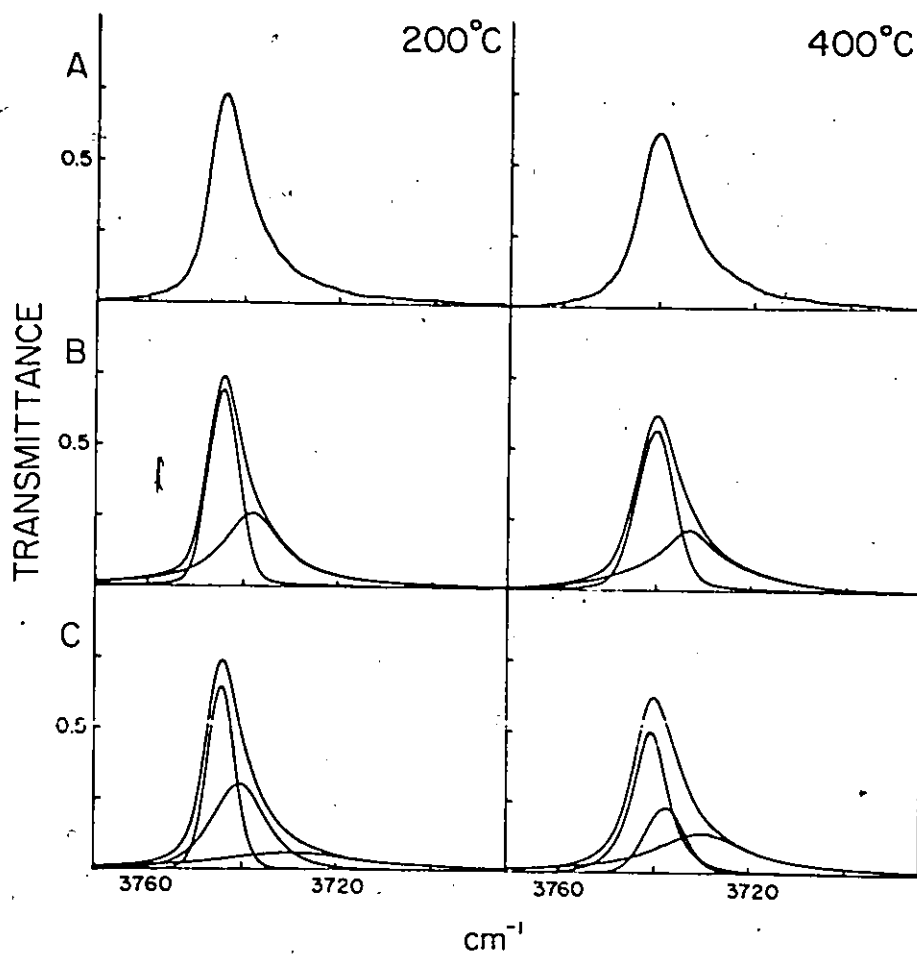


FIGURE 3-4

- A. Experimental spectra of SiOH band at 200°C and 400°C.
- B. Computed spectra using a 2-component sum function.
- C. Computed spectra using a 3-component product function.

certainly without stating some measure of error of their fit they are at best a rough guide.

To illustrate the above point a series of band fitting analyses of the SiOH profile have been carried out using a Cauchy-Gauss sum function and a Cauchy-Gauss product function^{95,96}.

Since there is a tail to low wavenumber of the main band it was attempted to fit the spectra to a two component curve, one strong band at the peak position and one weak band in the region of the tail, and, to a three component curve (one strong band with two weak bands in the tail). Figures 3-3b and 3-4b show the plotted results for the two band sum function and Figures 3-3c and 3-4c show the results for a three band product function. The data obtained from the use of these functions are collected in Table 3-2. In all cases, a good fit was considered to be when the discrepancy was 0.1 or less, this particular value being satisfactory for a very intense narrow band where errors are likely to be large where the band rises most steeply (hence DIS is greater in the low temperature spectra). The values of the parameters by which the accuracy of a particular fit was judged for the functions used in Figures 3-3 and 3-4, and for two other trial functions, are shown in Table 3-3. DIS is smaller for the three component curves and the fit could have been improved further by increasing the number of components. However this is meaningless where no distinct shoulders are present.

A satisfactory fit could also have been obtained by including a weak high wavenumber band, since any Cauchy or Gaussian function can be decomposed into as many components as desired. The

TABLE 3-2

Parameters for the Computed Spectra in
Figures 3-3 and 3-4

Function and (N) ^a	Temp °C	Wavenumber cm ⁻¹	Intensity absorbance	Half width cm ⁻¹	Shape ratio
S(2)	-145	3750.8	0.84	4.1	0.0
		3746.7	0.38	8.8	1.0
P(3)	-145	3751.2	0.80	3.2	0.54
		3748.5	0.33	6.1	0.70
		3740.8	0.05	17.7	0.99
S(2)	25	3748.0	0.68	4.7	0.11
		3742.7	0.14	11.4	0.88
P(3)	25	3748.2	0.58	4.1	0.55
		3745.4	0.22	8.7	0.70
		3735.1	0.03	23.9	0.99
S(2)	200	3744.5	0.51	5.9	0.29
		3738.5	0.13	13.8	1.0
P(3)	200	3744.7	0.45	5.5	0.64
		3741.0	0.15	12.1	0.69
		3730.8	0.02	33.9	0.99
S(2)	400	3740.7	0.36	7.8	0.38
		3733.6	0.10	15.7	0.52
P(3)	400	3741.2	0.30	7.2	0.79
		3738.1	0.11	9.3	0.41
		3730.7	0.06	22.6	0.99

^aS denotes the Cauchy-Gaussian sum function and P denotes the C-G product function. The number in parentheses is the number of components which were fitted. The shape ratio is the fraction of Cauchy character in a given band.

TABLE 3-3

Computed Parameters Which Reflect the
Accuracy of Some Trial Functions.

Function and (N) ^a	Temp °C	DIS ^b	WFM ^b	MAX ^b
S(2)	-145	0.014	3747.0	0.039
P(2)	-145	0.014	3752.2	0.033
S(3)	-145	0.009	3745.2	0.021
P(3)	-145	0.004	3752.2	0.013
S(2)	25	0.010	3749.2	0.038
P(2)	25	0.010	3746.8	0.031
S(3)	25	0.008	3749.4	0.021
P(3)	25	0.005	3746.8	0.014
S(2)	200	0.007	3749.0	0.016
P(2)	200	0.006	3766.4	0.014
S(3)	200	0.006	3751.6	0.016
P(3)	200	0.003	3749.8	0.008
S(2)	400	0.005	3742.4	0.016
P(2)	400	0.005	3742.6	0.015
S(3)	400	0.007	3765.4	0.015
P(3)	400	0.003	3751.4	0.008

^aSee footnote a, Table 3-2

^bSee Experimental Section for description of these terms

two band fit in itself is not significant because the tail to lower wavenumber is probably just a manifestation of intramolecular perturbations which are bound to be present in a sample of this type where the minute silica particles are in intimate and random contact with their neighbours.

This view has been discussed by Hambleton et al^{23,97}, and has been expressed by Van Cauwelaert et al⁶². Further, no significance is to be attached to the shape ratios listed in Table 3-2. The band fitting programs vary the shape ratio so as to obtain a best fit, and one may note that for the product function the shape ratios are near those used by Van Cauwelaert et al⁶², whereas, for the sum function, the main band was always given a high Gaussian character and the bands in the tail a Cauchy profile. The latter is not unexpected when an intense band is degraded to one side, as in this case, since, for equal height and area, a Gaussian function has a greater breadth near the peak⁹². Nor is a Gaussian profile unexpected for very narrow intense absorption bands, because the instrumental distortion factors essentially introduce a Gaussian perturbation on the true band shape⁹². Therefore as the half-band width approaches the spectral slit width (particularly true at low temperatures), then it is to be expected that the Gaussian contribution to an experimentally observed profile will increase.

The spectra for deuterated silica in the SiOD stretching region (2760 cm^{-1}) were the same as those reported by Van Cauwelaert et al⁶². These were fitted by the latter to a two band component curve. Spectra of the mixed isotopic species, obtained by partially

deuterating the sample again gave an excellent two or three band fit to the experimental data.

Discussion

As a result of these investigations on dehydroxylated silica discs which were pressed at only 70 kg cm^{-2} , that is, sufficient to render the disc self supporting, the following observations have been made with regard to the spectra of the isolated hydroxyl groups:

(1) the spectral bands attributable to isolated surface OH or OD groups are similar, (2) no distinct shoulders appear in the SiOH profile as the temperature is changed, (3) both the SiOH and SiOD band are slightly asymmetric to the low wavenumber side of the main band, and (4) both the SiOH and SiOD spectra can be fitted using band fitting techniques, to a two or a three component curve, as can the spectra of the mixed isotopic species. In conclusion, there is no spectroscopic evidence to suggest that the infrared spectrum of the SiOH groups is in any way different from that of SiOD groups (contrary to that purported by Van Cauwelaert et al⁶²).

Since no distinct shoulders appeared in the SiOH band of silica, it seemed that this was in contradiction with the work of Van Cauwelaert et al, though in their publication⁵⁸, it was not stated what pressures of preparation of the silica disc were used. On the assumption that they used reasonable pressures (sufficient to establish a self supporting disc), an attempt was made to duplicate their spectra by considering the possibility that because gaseous atmospheric water absorbs so strongly in this spectral region, then by intentionally

introducing a slight imbalance in the double beam compensation, it might be possible to produce SiOH spectra with shoulders, resembling their spectra.

The spectra shown in Figure 3-5 were recorded under conditions in which complete atmospheric compensation was not achieved. (see Experimental Section). These spectra clearly show shoulders on both sides of the main band and it can be seen by comparing the spectra in Figures 3-5 and 3-2, that the position of the bands of maximum intensity in the atmospheric water spectrum (or in the uncompensated double beam spectrum) coincide with the position of the main shoulders in the spectra shown in Figure 3-5. A dashed line has been drawn in Figure 3-5 to indicate the position of the strongest band at 3744.5 cm^{-1} .

In the experimental spectra shown in Figures 3-3a, 3-4a and 3-5, the peak position shifts to higher wavenumber, the peak intensity increases and the band width decreases as the temperature is lowered. Since the positions of the atmospheric water bands do not change with temperature, the shoulders in the uncompensated spectra apparently shift with temperature. The spectra in Figure 3-5 closely resemble those shown by Van Cauwelaert et al⁶² in their Figure 1, except that the 'dips', due to improper compensation, are quite large.

Van Cauwelaert et al⁶² also studied the effect of band shape of adsorbing benzene and triethylamine on silica. With benzene they reported that the overall band intensity decreased, but that the peak position did not change, whereas the peak position changed on adsorbing triethylamine and the relative intensity of the three components

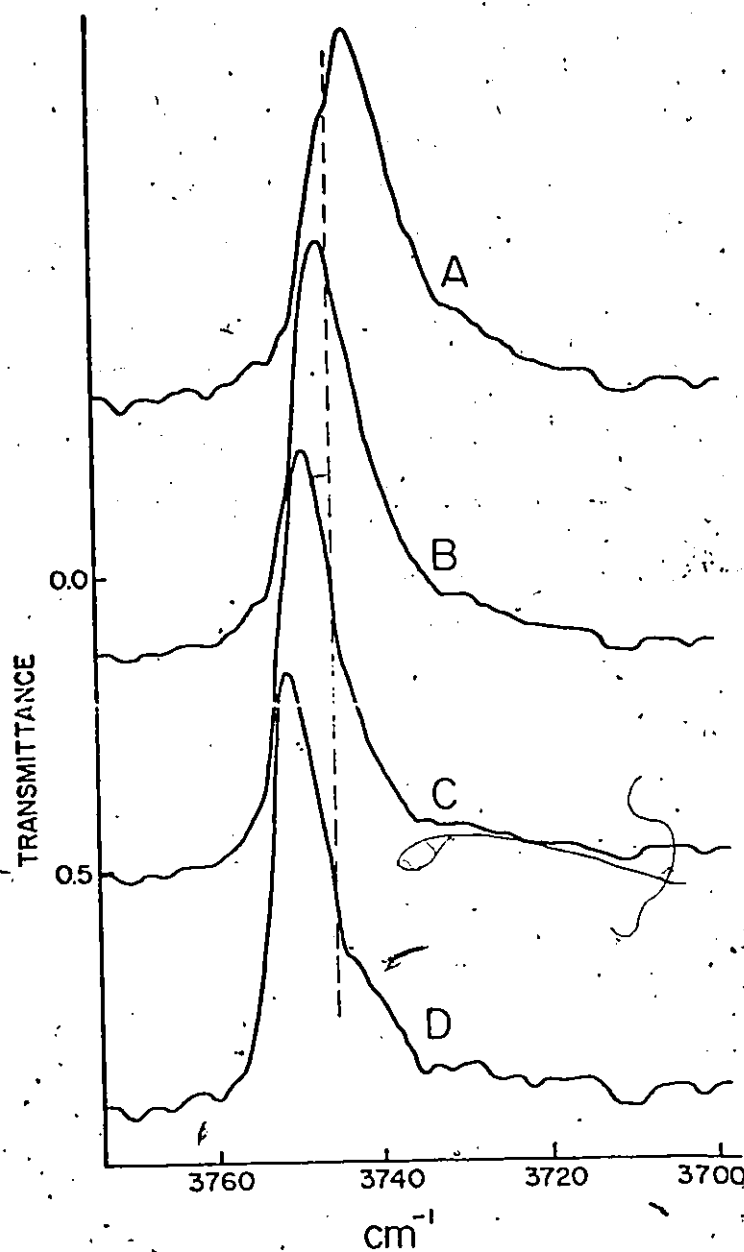


FIGURE 3-5

Experimental spectra of the SiOH band with an uncompensated cell.

A. 400°C; B. 200°C; C. 25°C; D. -145°C.

The scan speed was 20 $\text{cm}^{-1}/\text{min}$ and the peak positions are slightly shifted relative to the slower scans used for figures 3-3 and 3-4. The dashed line corresponds to the 3744.5 cm^{-1} band in Figure 3.2. The transmittance scale applies to spectrum D and other spectra have been linearly displaced for the purpose of presentation.

changed. These effects have been observed in this laboratory with an uncompensated spectrometer, the relative intensity of the shoulders varied again, because as the peak shifts, the 'dips' due to atmospheric water remain fixed as they do with temperature changes. With a perfectly compensated spectrometer, no shoulders were observed, although the strong central band decreased in intensity at a faster rate than did the tail to lower wavenumber. This is not unreasonable since a physically adsorbed species would be expected to interact with totally free hydroxyls as opposed to those that might be perturbed due to intramolecular interactions and hence adsorb at slightly lower wavenumber.

In a subsequent paper, Van Cauwelaert et al⁷¹ have revealed their experimental conditions. They prepared their samples using loads up to 5.15×10^5 kg for one minute. Under these conditions, the discs become glass-like in appearance. These pressures, they claim, are the cause of the formation of geminal hydroxyl groups. To substantiate this claim, a special die (mentioned in the General Experimental Section) was used in an attempt to reproduce the results of Van Cauwelaert et al, but even with this die, it was impossible to use loads greater than 5.2×10^4 kg. (It is difficult to see how they achieved loads of one magnitude greater with a die of the same diameter which was made from stainless steel only). Nevertheless, totally compensated spectra were obtained from the discs at pressures up to a maximum of $11,000 \text{ kg cm}^{-2}$ and again no shoulders were observed. Since it was not possible to duplicate Van Cauwelaert et al⁹¹ experimental details, then a further consideration of experimental

discrepancies is meaningless, nevertheless some of Van Cauwelaert's comments do warrant discussion. For example, their contention that Hair and Hertls⁵¹ observance of shoulders on the SiOH profile is also due to a pressure effect does not seem correct, since, in that instance, a pressure of only 20,000 lb in⁻² (1,400 kg cm⁻²) were used, a value well below those studied in this laboratory.

Furthermore, the fact that Van Cauwelaert et al^{62,91} were unable to observe any shoulders on the SiOD profile over a wide range of temperature and pressure is difficult to account for in a chemical argument. Even in the event that this is somehow possible, Van Cauwelaert et al cannot rightfully compare their spectroscopic observations to other experiments done on powdered silicas, since at these pressures, surface properties would be expected to be quite different. For example, a very large 3650 cm⁻¹ band is present when high pressures are used which means that interparticle distances are much smaller⁹⁷.

Hockeys⁶³ contention that the shoulders in Hair and Hertls⁵¹ SiOH profile is an artifact due to water absorption, is supported by this work. Van Cauwelaerts⁶² work, although not reproduced, must be viewed with doubt, and it can be certainly said that at 'reasonable' pressures there is no spectroscopic evidence for geminal hydroxyl groups.

Finally, there are two important points to be stressed concerning the general use of band fitting techniques. One is that care should be taken in applying such methods to deconvoluting overlapping band envelopes. It is important to stress ones criteria of

a "satisfactory fit", since an infinite number of such fits can be obtained if the permissible discrepancy (DIS) is large enough. This is particularly important when the bands are closely overlapping.

Secondly, when the spectral slit width approaches the half band width of any component, the instrumental distortion may determine the nature of the experimentally observed band profile, and analyses can be subject to error unless the instrument function is known accurately^{95,96}.

CHAPTER 4

THE SPECTROSCOPIC IDENTIFICATION OF
CHEMISORBED SPECIES ON SILICA

In Chapter 1 of this thesis some of the recent history of infrared studies of silica surfaces was summarized and it was evident that the emphasis of many of these studies had been to determine the properties of the surface at different concentrations of hydroxyl species.

The properties of fully hydroxylated silicas have been extensively studied and are generally understood, however, dehydroxylated silicas although widely used, are not yet well characterized mainly because it is not possible to transcribe their behaviour in terms of the properties of hydroxylated silicas. In fact a dehydroxylated silica behaves totally unlike an hydroxylated silica because it has a potentially active surface which can form strong chemical bonds with some adsorbates.

Several authors, (Peri⁴⁷, Kiselev^{19,75,98,99}, Borella¹⁰⁰, Hockey^{53,101}, Morrow^{60,61} and Little¹⁰²) have referred to the highly active nature of dehydroxylated silicas, and have noted the room temperature chemisorption of molecules such as H_2O ^{19,75}, NH_3 ^{97,102}, BF_3 , BCl_3 ^{60,61}, CH_3OH ^{98,99,100} and $AlCl_3$ ^{53,101}.

Some of the earliest work on dehydroxylated silicas was performed by Kiselev et al^{98,99} in a study of CH_3OH adsorption, where it was found that the degree of chemisorption increased as the hydroxyl

concentration diminished. More recently, Borella et al¹⁰⁰ ascribed the site for CH₃OH adsorption to a strained siloxane bridge. They envisaged that strain could develop as the surface hydroxyl population was diminished.

In the temperature range 0-400°C water is eliminated between neighbouring hydroxyls as in the final phase of the process of polycondensation of silicic acid and the bridges which result are non-reactive, but above this temperature the distances between SiOH groups becomes abnormally large and bridges which subsequently form are strained.

Borella et al¹⁰⁰ proposed that the following reaction occurred

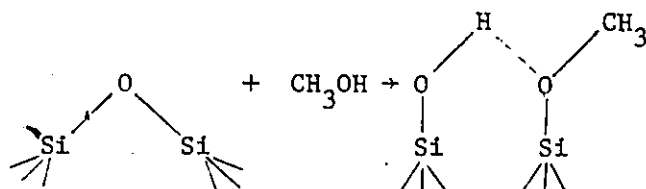
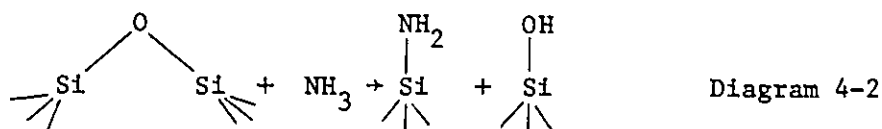


Diagram 4-1

They identified the infrared absorption bands in the C-H stretching range to be those of chemisorbed methanol, but the hydroxyl group supposedly produced was not distinguished from other hydroxyls which were present before the reaction commenced.

Kiselev et al¹⁹ in more recent work studied the water adsorption isotherm on highly dehydroxylated silicas and noted that the first additions of water vapour resulted in an increase in the integrated intensity of the 3748 cm⁻¹ silanol band, which they attributed to the reformation of hydroxyl groups by a chemisorptive process involving some reactive silxane sites.

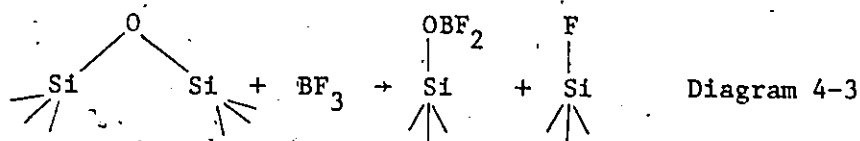
Peri⁴⁷ and Blomfield and Little¹⁰² showed that on dehydroxylated silicas, an SiNH_2 species apparently formed when NH_3 was adsorbed. Little and Blomfield¹⁰² cleared up a previous controversy⁴⁷ by showing that traces of chlorine were not necessary to facilitate chemisorption, but that the requirement was to have a dehydroxylated surface. They proposed that the reaction centre involved a strained site which reacted as shown below



Direct evidence for the existence of an active site was provided by Morrow and Devi⁶⁰ who showed that two infrared absorption bands at 908 and 888 cm^{-1} were formed as the intensity of the free silanol absorption band at 3748 cm^{-1} decreased at high degassing temperatures. This region of the spectrum is usually blanked out for transmission studies because of strong Si-O absorption bands but Morrow and Devi found that by using silica discs containing 10 mg cm^{-2} or less, a 'window' appeared between 950 and 850 cm^{-1} . Most workers use much larger discs ($\sim 40 \text{ mg cm}^{-2}$) because stronger spectral bands are produced in other regions but these samples have the disadvantage of not transmitting at all below 1350 cm^{-1} .

The relationship between the new bands and the active sites was proven⁶⁰ by adding small quantities of BF_3 to a silica which had been degassed to 1000°C; the 908 and 888 cm^{-1} bands were proportionally reduced for each dose added and new bands grew which were attributed to an SiOBF_2 species.

Unpublished work by Morrow (see reference 61) indicated that the adsorption of B_2H_6 to an active silica produced SiH species, and on this basis, Morrow and Devi⁶¹ ascribed the reaction of BF_3 to proceed analogously as follows



However, in each of the aforementioned studies there is no proof that the reaction to produce chemisorption does occur at a single bridge site. In fact, Morrow and Devi commented that the appearance of two bands (908 and 888 cm^{-1}) is inconsistent with a single bridge.

Work presented in this and the following chapter sets out to solve this problem.

It should be noted that the "active sites" referred to in this work are in no way analogous to the active silica surfaces discovered by Low¹⁰³⁻¹⁰⁵. Such surfaces were generated by a three step process, involving the reaction of 70 torr of CH_3OH with an Aerosil silica at $350^\circ C$ for 20 hrs (replacing nearly all surface hydroxyls with surface methoxyl groups), then degassing above $600^\circ C$ to remove the methoxyl groups. At this stage, silanol (3748 cm^{-1}) and silane (2300 cm^{-1}) bands appeared and there was some evidence for a surface acetylide. Degassing further, removed these groups and radical sites were formed which Low ascribed as



On this surface, H_2 , CO , NO and O_2 were found to be chemisorbed.

However, the surfaces discussed in this work do not have these properties. Morrow and Devi⁶¹, found that H_2 , and O_2 were not chemisorbed on a dehydroxylated silica, nor were there any free radical sites found (by a brief E.S.R. study).

Therefore, it is felt to be unwarranted to make further comparisons between the chemisorptive reactions observed by Low and those of this work.

In the present work, a study of the adsorption of H_2O , NH_3 , NH_2NH_2 , CH_3NH_2 , $(CH_3)_2NH$ and CH_3OH on highly dehydroxylated silica results in a reaction stoichiometry which is consistent with the active site being a single siloxane bridge.

These sites form when the degassing temperature under vacuum is greater than $400^\circ C$. In addition, a new type of $SiOH$ species has been identified for the adsorption of each of the aforementioned molecules.

A study of the adsorption of ammonia to active silica yielded spectra similar to those observed by Little and Blomfield¹⁰². Two absorption bands were observed in the N-H stretching region (near 3500 cm^{-1}) and another at 1550 cm^{-1} . On the basis of isotopic substitution experiments it has been shown in this thesis that the adsorbed species is indeed $SiNH_2$.

Prior to this study, assignments of these modes to $SiNH_2$, by other workers^{47,102}, must be considered to have been tentative since either $SiONH_2$ or $SiNH_3$ could have conceivably given rise to these spectral features. Finally, a method, first used by Peri⁴⁷, has been

used to generate very intense SiNH_2 bands without involving reactive sites. An additional band could be found in the window region which was attributed to an Si-N stretching mode of SiNH_2 .

In this chapter, only the cursory details of the adsorption phenomena on active silica have been given, and instead, emphasis has been placed on the identification of the surface species formed.

This information is a necessary prerequisite for a fuller study of the sites themselves, given in Chapter 5.

Experimental (for Chapters 4 and 5)

The silica samples used in this work contained either 4, 10 or 40 mg of silica per cm^2 of disc area and were pressed in the stainless steel die at 70 kg cm^{-2} for a few seconds. The 4 and 10 mg cm^{-2} discs were used when it was required that the disc be transmitting to radiation over the $950\text{--}850 \text{ cm}^{-1}$ region. The silica had been heated in air at 700°C prior to pressing (except where specified) in order to oxidize any hydrocarbon impurities.

The discs were mounted in cell A (see Chapter 2) where subsequent thermal treatments (up to 1200°C) and reactions were carried out.

Deuterated ammonia and methylamine and N-15 ammonia (95.4%) were obtained from Merck, Sharp and Dohme Ltd of Montreal, and partially deuterated ammonias were obtained by mixing NH_3 and ND_3 . Oxygen-18 water (98.5%) was obtained from the Oak Ridge National Laboratory and O-18 silica was prepared by heating silica in a water atmosphere at saturation vapour pressure for 3 hr at 450°C^{59} . (Several doses of water were used.)

Spectral slit widths of $2-5\text{ cm}^{-1}$ were used and all spectra were calibrated with reference to gas phase NH_3 ($3500-3300\text{ cm}^{-1}$), HBr ($2600-2400\text{ cm}^{-1}$) and H_2O ($3800-3700\text{ cm}^{-1}$ and $1600-1390\text{ cm}^{-1}$).

Where a "titration" of the active sites is referred to, it is meant that only very small doses of adsorbate were added. The measurement of a 'dose' was determined by expanding a given pressure of gas or vapour (NH_3 or H_2O) from a bulb, into a much larger volume comprising the whole vacuum line and cell. This gave a value for the ratio of the pressures before and after expansion. Then, knowing the volume of the cell, an initial pressure of gas in the bulb could be chosen so as to give $1\text{ }\mu\text{mole}$ of gas in the cell. The cell was left open to the vacuum line and bulb for 30 seconds to achieve an equilibrium pressure.

Complete saturation of the sites on a 10 mg cm^{-2} disc degassed to 1200°C required five such doses, that is, about $5\text{ }\mu\text{moles}$. However, in view of the large volumes involved, physical adsorption on the cell walls is also a factor and it is doubtful whether the amount added was the amount adsorbed. A more accurate assessment of the amount adsorbed may be achieved by using a vacuum microbalance in conjunction with simultaneous spectral measurements. (A system currently being devised in this laboratory). To obtain a fully deuterated and degassed silica, a repetitive cycle of adsorption then degassing had to be employed. An inactive silica was treated with several large doses (10 torr) of D_2O then degassed at 1000°C . Some SiOH which reappeared was again exchanged at room temperature with further doses of D_2O and the sample again degassed at high temperature. This cycle was repeated

several times until, after the degassing step, no SiOH was reformed and the only functional groups remaining were the isolated SiOD species (2763 cm^{-1}).

All adsorption reactions were performed at room temperature. Force constant calculations were carried out using the standard computer programs developed by Schachtschneider⁸⁴.

Results and Discussion

A. The Generation of the Active Sites

A 10 mg cm^{-2} untreated silica (i.e., without preheating in air at 700°C) was pressed at 70 kg cm^{-2} , then placed in cell A and subsequently degassed at various temperatures from 180°C to 1200°C . The disc was degassed for 1 hr at each temperature, cooled each time to room temperature and the spectral regions from $3800\text{--}3500\text{ cm}^{-1}$ and $950\text{--}850\text{ cm}^{-1}$ were monitored (Figure 4-1).

On an untreated silica, a large band always appeared on the low frequency side of the isolated silanol band, due to hydrogen bonded hydroxyls and bound water (Figures 4-1, A,B,C). As these species were desorbed, the transmission in the $950\text{--}850\text{ cm}^{-1}$ region was improved until a limiting temperature was reached somewhere between 460 and 675°C . At 675°C two bands were just detectable as weak superimposed peaks on a sharply sloping background (Figure 4-1D) but degassing at higher temperatures (900 and 1200°C) produced a marked increase in the intensity of these bands. On the other hand, the intensity of the 3748 cm^{-1} SiOH band was drastically reduced (Figure 4-1E,F).

If the above described degassing process was applied to a

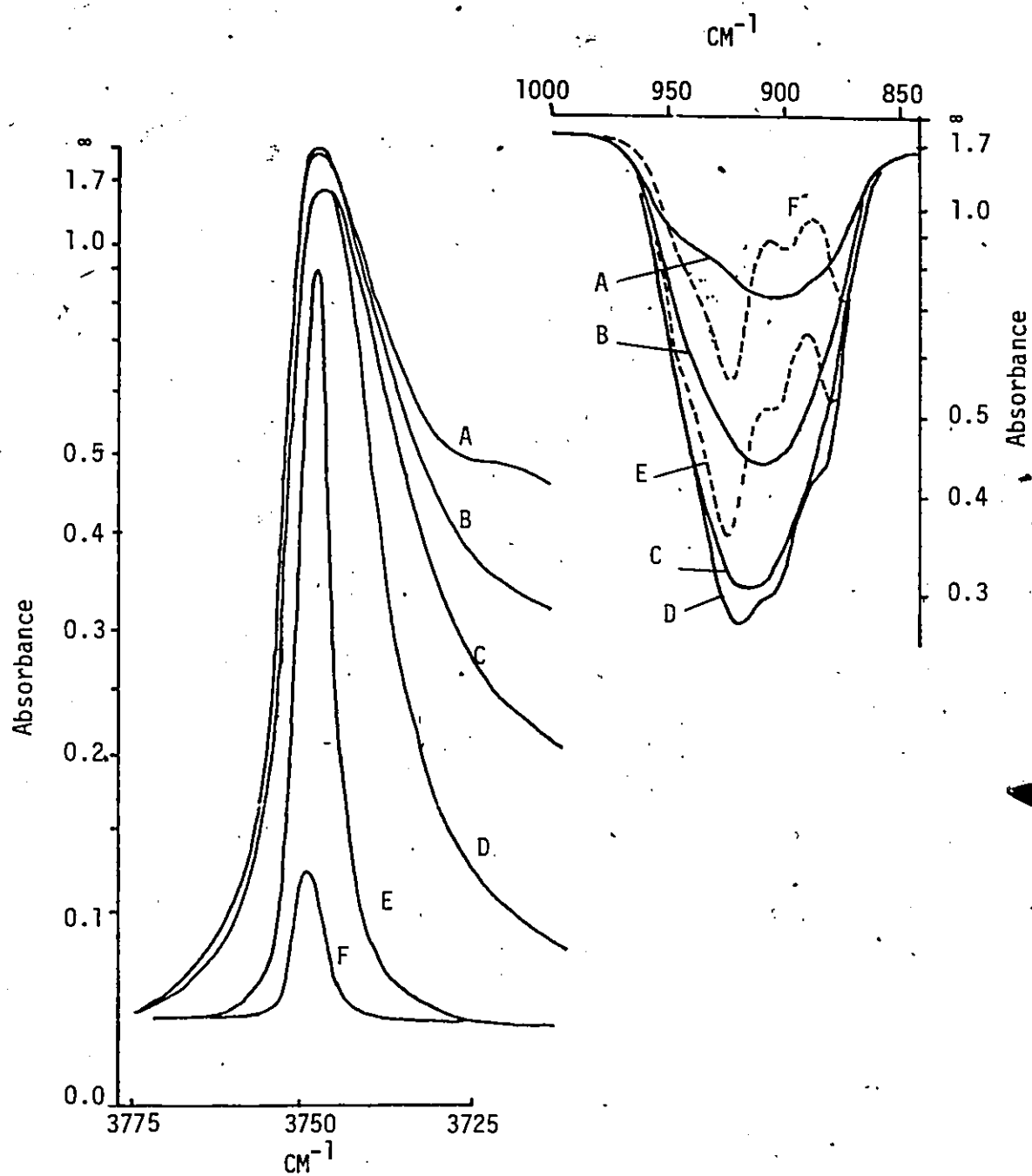


FIGURE 4-1

10 mg cm^{-2} silica degassed at various temperatures

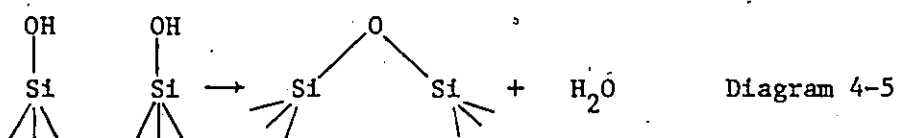
A. 180°C ; B. 300°C ; C. 460°C ; D. 675°C ; E. 900°C ;

F. 1200°C .

SiOH region was scanned at $20 \text{ cm}^{-1} \text{ min}^{-1}$.

pretreated silica, that is, one which had been heated in air for 12 hr at 700°C, the appearance of the 908-888 cm^{-1} bands began after evacuation at ~550°C. The pretreatment process effects the removal of most hydrogen bonded hydroxyls and it is evident from Figure 4-1 that active sites only begin to form after these groups are removed.

In most experiments conducted, the maximum temperature reached was about 1100°C at which point about 95% of the residual isolated normal SiOH groups were removed, corresponding to an absorbance of about 0.10 at 3748 cm^{-1} for a 10 mg cm^{-2} sample. The sites are generally assumed to be strained bridges, where adjacent silanols might interact as follows to eliminate water



Such a mechanism would account for the observation that the number of SiOH groups decreases as the temperature, and number of sites, increases.

B. Adsorption of NH_3 and H_2O

In agreement with previous work¹⁰², ammonia did not chemisorb on silica in the absence of a vacuum degassing treatment at high temperatures. However, the infrared spectrum shown in Figure 4-2B was obtained if 10 torr of NH_3 was reacted at 25°C with a 40 mg cm^{-2} silica sample which had been degassed at 1100°C prior to cooling. The reaction time was about five min and the excess gas phase was

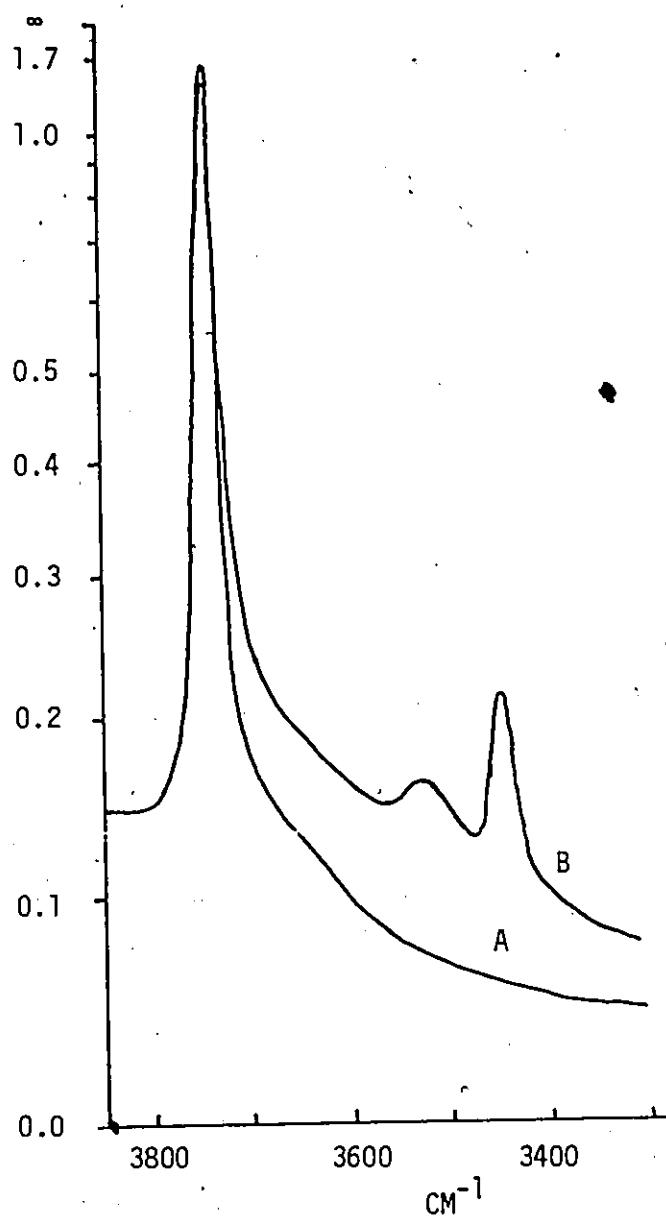


FIGURE 4-2

- A. 40 mg cm⁻² silica degassed at 1100°C; cooled to room temperature.
- B. Additions of 10 torr NH₃; left 5 min in cell, then degassed at room temperature.

evacuated until the pressure dropped to less than 10^{-4} torr. No further spectral changes resulted with further pumping at 25°C . The two new bands in the NH stretching region were observed at 3525 and 3447 cm^{-1} and were accompanied by an additional band at 1550 cm^{-1} (not shown). As well, a distinct shoulder appeared on the low wavenumber side of the sharp band in the background spectrum at 3748 cm^{-1} (due to residual isolated SiOH groups).

When ammonia was reacted with a similar sample which had been degassed at only 800°C prior to reaction, a weaker profile of the chemisorbed species was observed between $3600\text{--}3400\text{ cm}^{-1}$ and at 1550 cm^{-1} , and the 3748 cm^{-1} band was so intense that the shoulder was not observed. None of the above spectral features altered following prolonged evacuation at temperatures up to 300°C . Rather complex changes occurred when the sample was evacuated above this temperature and a discussion of this has been left for Chapter 5.

Following chemisorption of ND_3 on a 1100°C degassed deuterated silica (40 mg cm^{-2}) (normal $\text{SiOD} = 2763\text{ cm}^{-1}$) the only bands observed were at 2634 and 2528 cm^{-1} with relative intensities which were about the same as the $3525/3447\text{ cm}^{-1}$ pair, and a shoulder appeared at the low wavenumber side of the normal SiOD band. When an equimolar mixture of NH_3/ND_3 was similarly reacted, strong sharp bands appeared at 3491 , 2575 and 1390 cm^{-1} accompanied by the bands previously noted for NH_3 or ND_3 (see Figure 4-7B for a representative spectra of chemisorbed NH_3/ND_3).*

* Figure 4-7B actually shows chemisorbed NH_3/ND_3 formed by a method other than the reaction with the active sites, (described later). However, virtually identical spectra were obtained by either method.

The above mentioned spectra were all obtained from large sized discs which are opaque below 1350 cm^{-1} . By using smaller discs (10 mg cm^{-2}) it was possible to observe the window region between $950\text{--}850\text{ cm}^{-1}$ and hence monitor changes in the active site bands at $908/888\text{ cm}^{-1}$ in relation to increases in the intensities of bands due to the chemisorbed species. Furthermore, with thinner discs, the integrated intensity of the isolated hydroxyl band at 3748 cm^{-1} is smaller, and if the degassing temperature was high (1200°C) it was possible to reduce the intensity of this band to an extent which enabled the band which forms as the low wavenumber shoulder to the hydroxyl band, to be monitored clearly. This is illustrated in Figure 4-3.

The addition of 10 torr of NH_3 to a 10 mg cm^{-2} pellet degassed to 1200°C resulted in the instantaneous disappearance of the $908/888\text{ cm}^{-1}$ bands and the concomitant formation of bands due to chemisorbed ammonia. The low frequency shoulder on the hydroxyl band at 3748 cm^{-1} is now clearly distinguished as a band absorbing near 3741 cm^{-1} . Also, a broad shoulder appeared on the high frequency side of the window ($\sim 930\text{ cm}^{-1}$). By conducting several other experiments of this type it was ascertained that the intensity of the bands of the chemisorbed species was proportional to the original intensity of the bands at 908 and 888 cm^{-1} .

The analogous experiment with ND_3 (10 torr) adsorbed to a 10 mg cm^{-2} deuterated degassed silica resulted in the appearance of a shoulder band at 2758 cm^{-1} as well as the other bands previously observed in the spectrum of the 40 mg cm^{-2} sample. A low frequency shoulder was also observed at $\sim 880\text{ cm}^{-1}$, apparently the analogue of the $\sim 930\text{ cm}^{-1}$ band observed for NH_3 .

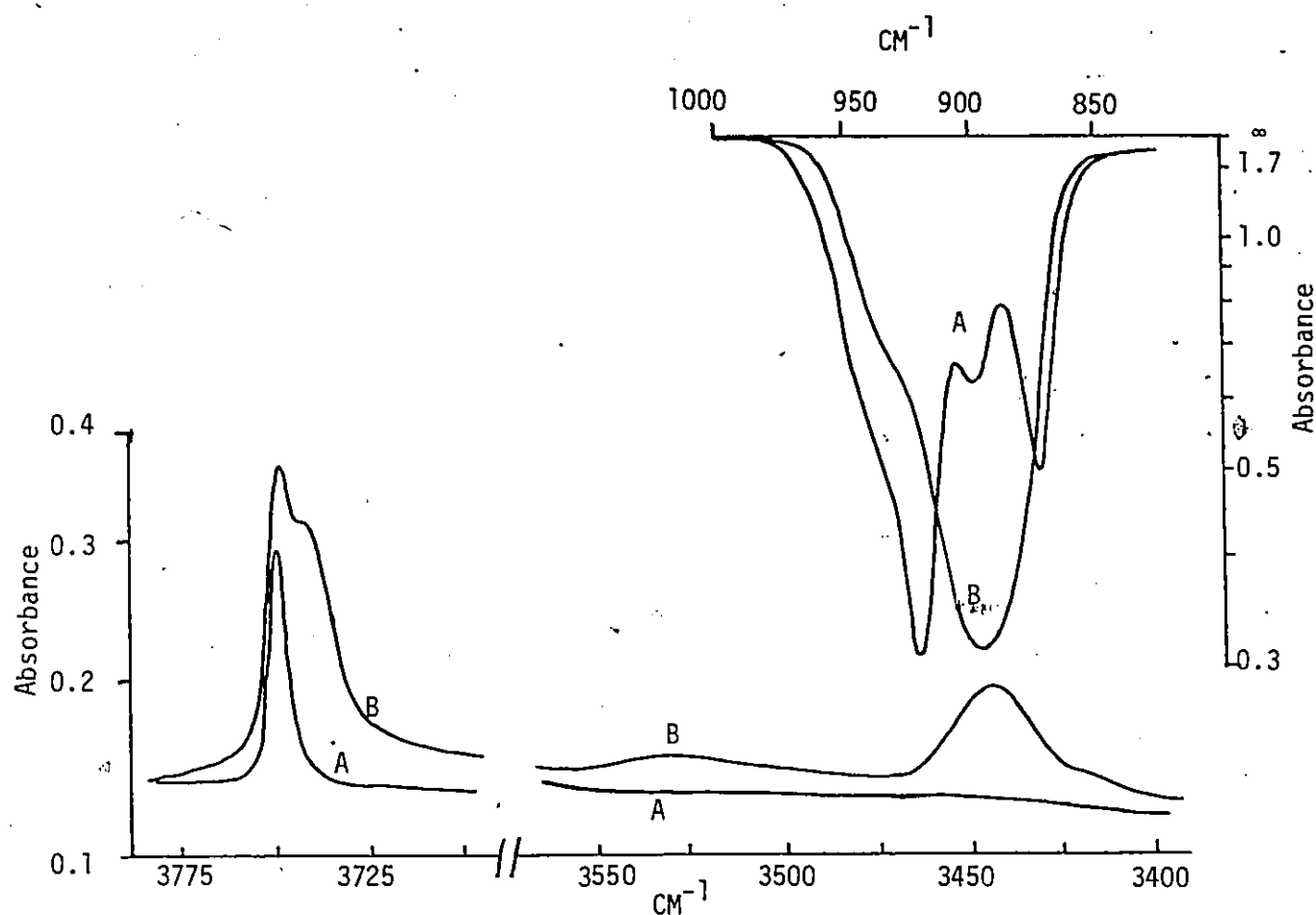


FIGURE 4-3

- A. 10 mg cm^{-2} silica degassed at 1200°C ; cooled to room temperature.
 - B. Addition of 10 torr of NH_3 ; left 5 min in cell, then pumped at room temperature for 5 min.
- SiOH and NH stretching regions were scanned at $40 \text{ cm}^{-1} \text{ min}^{-1}$.

A study of water adsorbed to a 10 mg cm^{-2} active silica revealed some similarities to the ammonia adsorption study but some differences were evident too.

When 10 torr of H_2O was adsorbed the $908/888 \text{ cm}^{-1}$ bands disappeared instantly, just as they did for NH_3 and the only new spectral feature was a band at 3741 cm^{-1} *. Further, the extent of disappearance of the $908/888 \text{ cm}^{-1}$ bands was in proportion to the growth of the 3741 cm^{-1} band as found by titrating an active surface with micromole doses of H_2O vapour. A series of spectra show this effect in Figure 4-4.

At the stage when the sites are consumed, (Figure 4-4E) the window region shows no trace of a shoulder. Therefore, the band which appeared at $\sim 930 \text{ cm}^{-1}$ for the adsorption of NH_3 may be related to the NH_3 chemisorbed species. This was confirmed by adsorbing NH_3 to various silicas having different concentrations of the sites; the integrated intensity of the $\sim 930 \text{ cm}^{-1}$ band appeared to be proportionate to the intensities of the 3525 , 3447 and 1550 cm^{-1} bands formed in each case.

Even on silicas with the highest numbers of active sites (i.e., those degassed at the highest temperatures) the $\sim 930 \text{ cm}^{-1}$ band only appeared as a shoulder, partially obscured by the high wavenumber edge of the "window". Likewise the $\sim 880 \text{ cm}^{-1}$ band for ND_3 was partially obscured by the low wavenumber edge of the "window".

* Actually a very weak band also appeared at 3720 cm^{-1} but represents an adsorbed species which is not formed by reaction with the active sites (see Chapter 5).

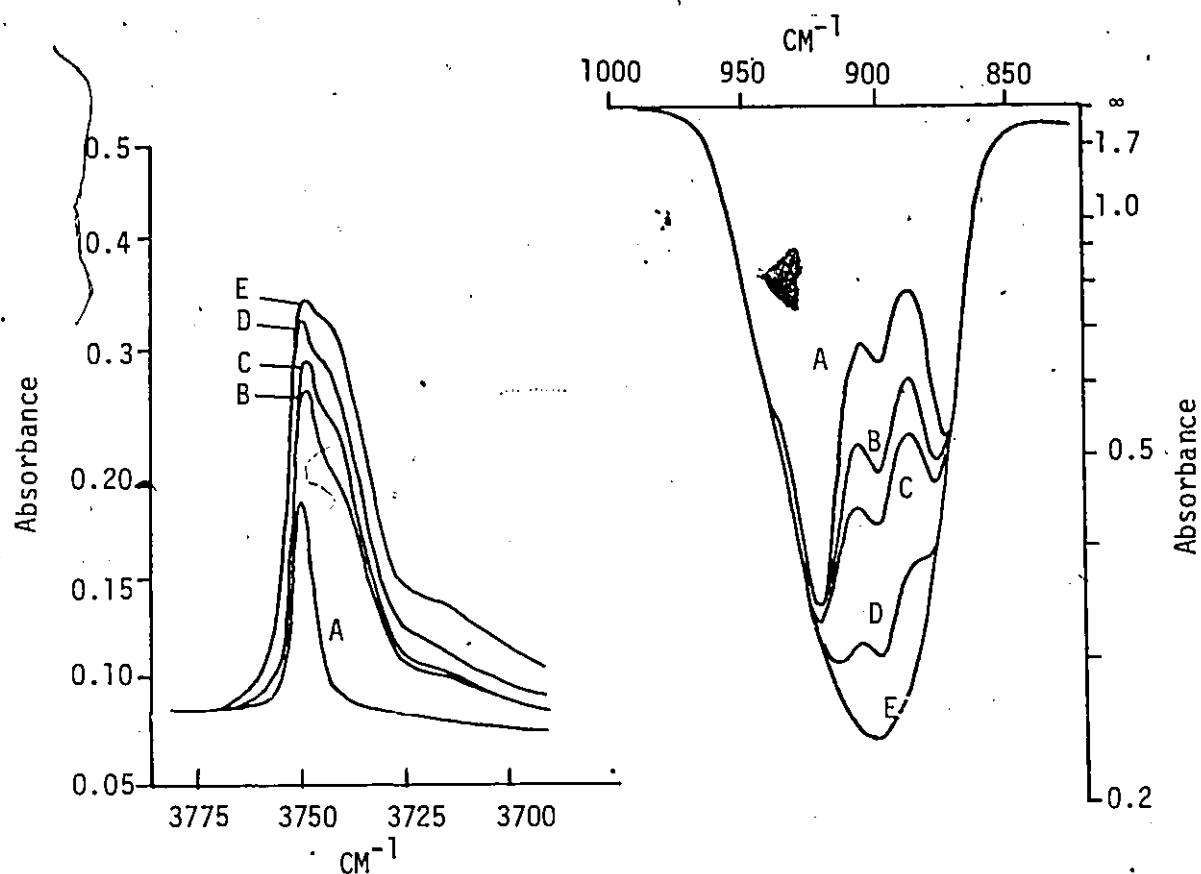


FIGURE 4-4

- A. 10 mg cm^{-2} silica degassed at 1200°C ; cooled to room temperature.
- B-D. Successive additions of H_2O ($< 1 \text{ torr}$).
- E. Additions of 5 torr of H_2O ; left 5 min in cell and pumped at room temperature for 5 min .

SiOH region was scanned at $40 \text{ cm}^{-1} \text{ min}$.

Another difference was observed between the adsorption of ammonia and that of water in that the spectral intensities of the 908/888 cm^{-1} bands were not diminished uniformly when small doses of ammonia were adsorbed, contrary to that shown for the water titration (Figure 4-4). The nature of this effect and the relevant spectra has been discussed in Chapter 5.

Basically, however, there was observed to be a one to one relationship between the disappearance of the 908/888 cm^{-1} bands and the growth of a band at 3741 cm^{-1} in the case of water and of bands at 3741, 3525, 3447, 1550 and $\sim 930 \text{ cm}^{-1}$ when NH_3 was the reactant.

In the above experiments with 10 mg cm^{-2} silicas, the 3741 cm^{-1} band was partially overlapped by the 3748 cm^{-1} silanol band. Even for very highly degassed silicas ($\sim 1200^\circ\text{C}$),* a small 3748 cm^{-1} band remained. However, if a deuterated degassed silica was prepared and subsequently small doses of NH_3 adsorbed it was found that only hydrogen containing chemisorbed species were formed and that no exchange took place, indicated by the fact that no 3748 cm^{-1} SiOH band was reformed. [Exchange only occurred after the active sites were consumed or if larger pressures of NH_3 (10 torr) were added to the cell.]

The spectra shown in Figure 4-5 was obtained after $\sim 5 \mu\text{mole}$ of NH_3 was reacted with a fully deuterated silica which had been previously degassed at 1000°C . A symmetrical band appeared in isolation at 3741 cm^{-1} with a half width of 12 cm^{-1} .

* At 1200°C the quartz cell begins to soften, making the total removal of 3748 cm^{-1} silanols virtually impossible with this apparatus.

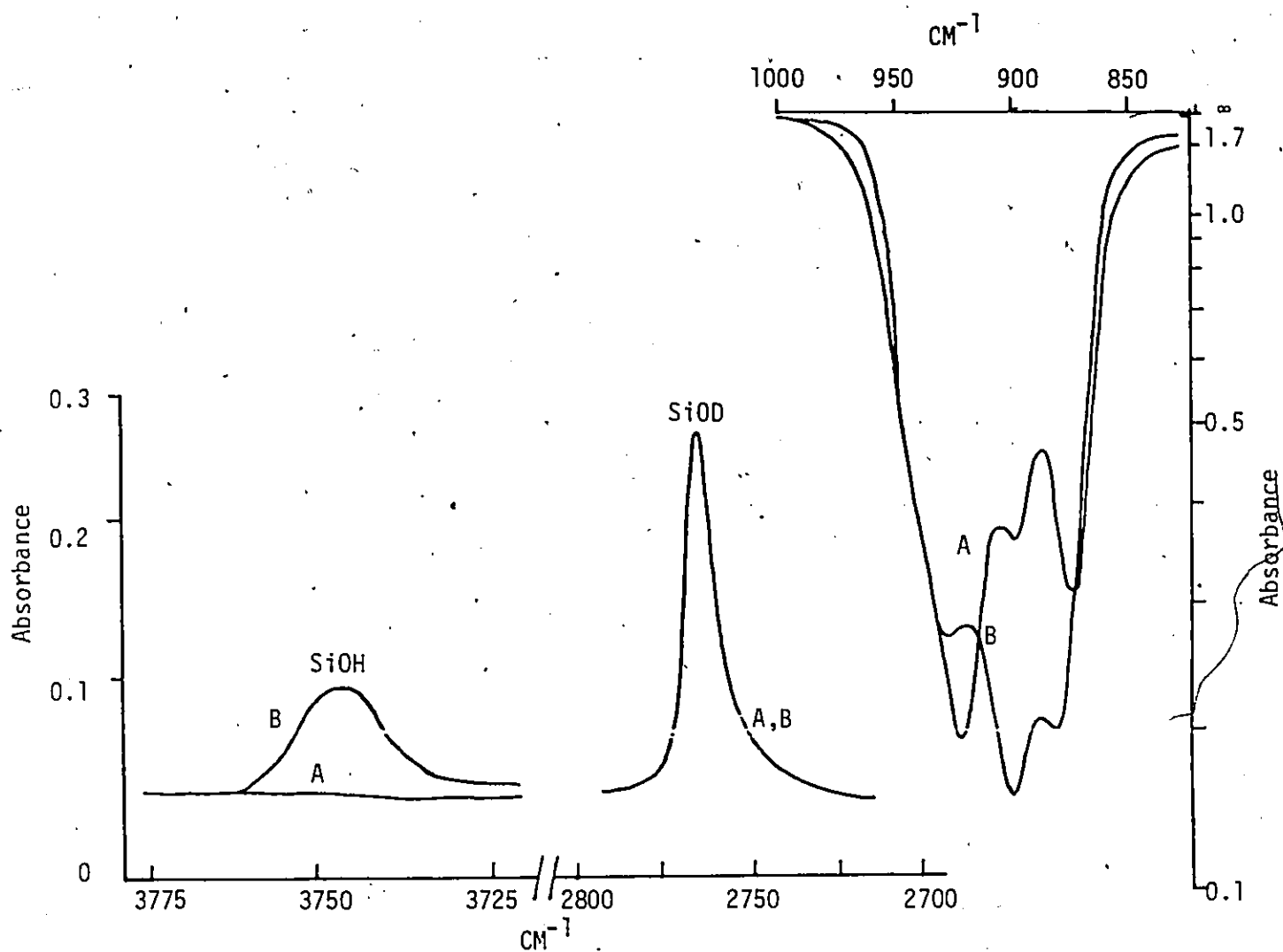


FIGURE 4-5

A. 10 mg cm^{-2} silica degassed at 1000°C ; cooled to room temperature.

B. Addition of $\sim 5 \text{ } \mu\text{mole}$ of NH_3 .

The SiOH and SiOD stretching regions were scanned at $20 \text{ cm}^{-1} \text{ min}^{-1}$.

When a degassed deuterated silica was reacted with micromole doses of H_2O vapour, again a 3741 cm^{-1} band appeared in isolation but in this case the band was somewhat flat-topped in appearance and had a half width of 19 cm^{-1} (Figure 4-6B). Again no exchange occurred.

For purposes of comparison, the spectra of H_2O added to a degassed normal (SiOH) silica is again displayed in Figure 4-6A. Graphical subtraction of the original SiOH band (3748 cm^{-1}) from the compounded profile of SiOH (3748 cm^{-1}) and SiOH (3741 cm^{-1}) (obtained in the titration of H_2O on a degassed normal surface), produced the same broad isolated band shown in Figure 4-6B. Also the spectrum of the band at 3741 cm^{-1} obtained in isolation in the NH_3 titration is again shown in Figure 4-6E to illustrate the clear difference in shape to that of the 3741 cm^{-1} band obtained with H_2O .

When small doses of water containing 98.7% Oxygen-18 were added to a deuterated degassed silica a broad band was observed, centered around 3735 cm^{-1} with a half-width of about 30 cm^{-1} (Figure 4-6C). This band had prominent shoulders to high and low wavenumber and could be "reconstructed" by summing two identical bands (such as are observed for H_2O^{16} , shown in Figure 4-6B), one centered around 3741 cm^{-1} and the other at 3730 cm^{-1} (Figure 4-6D). [The O-18 shift for the normal hydroxyl band at 3748 cm^{-1} is 11 cm^{-1}].

Mixed Isotope Adsorption Studies

When various mixtures of $\text{H}_2\text{O}/\text{D}_2\text{O}$ were added to a degassed normal silica (in ratios varying from 1:9 each way) both the 3741 and 2758 cm^{-1} bands appeared with intensities reflecting the initial H/D

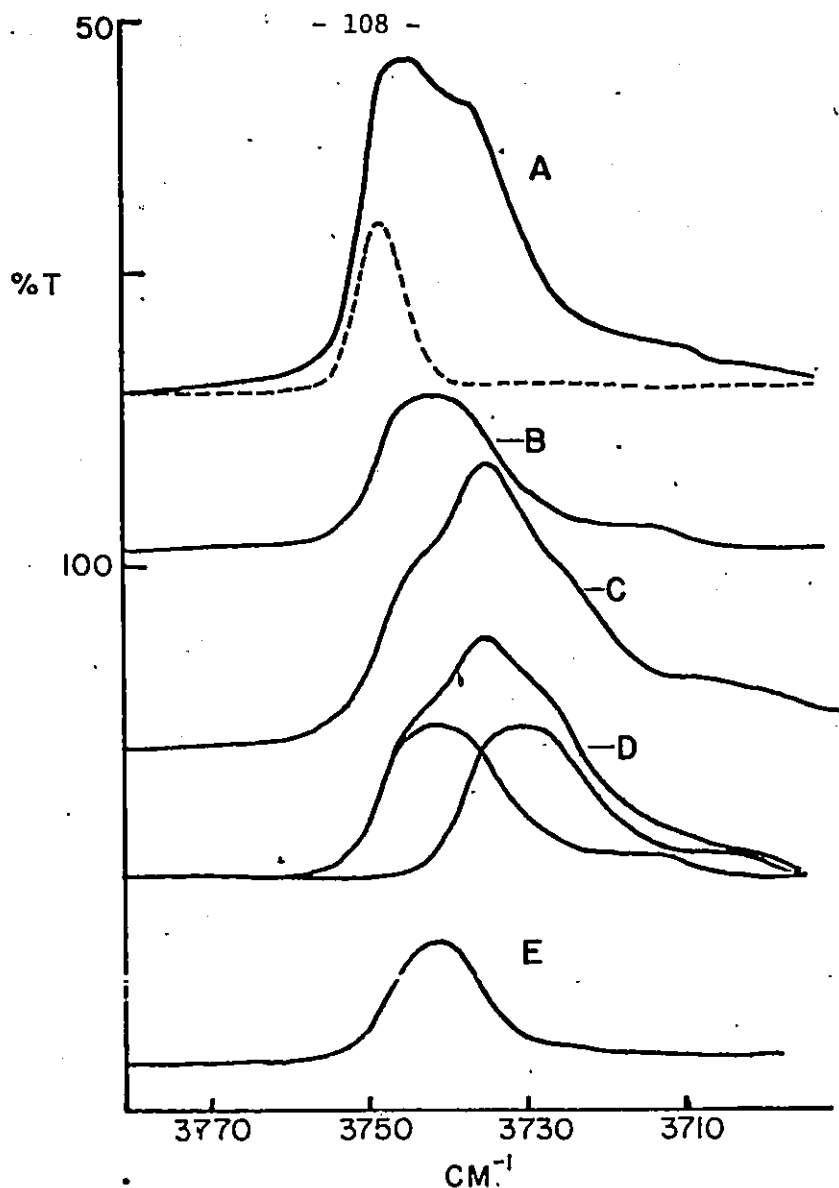


FIGURE 4-6

- A. Dashed line represents the residual 3748 cm^{-1} SiOH band on a silica which had been degassed at $\sim 1200^\circ\text{C}$. Solid spectrum obtained after admitting 10 torr H_2O at 20°C and evacuating excess.
- B. After adding $\sim 5\text{ }\mu\text{mole}$ of H_2O to a degassed deuterated silica.
- C. After adding H_2^{18}O to a degassed deuterated silica.
- D. Taking two spectra as in B, displacing one by 11 cm^{-1} to 3730 cm^{-1} and summing the two (see text).
- E. After adding $\sim 5\text{ }\mu\text{mole}$ of NH_3 to a degassed deuterated silica and evacuating the excess. The % T scale refers to A.

ratio. The half widths and band shapes were identical with that observed using pure H_2O or D_2O .

Another experiment was conducted whereby both pure ND_3 and an equimolar mixture of $\text{D}_2\text{O}/\text{H}_2\text{O}$ were adsorbed separately to the same silica disc. (The silica contained only 3748 cm^{-1} hydroxyl groups). The disc was degassed to 1200°C and the intensities of the 3748 , 908 and 888 cm^{-1} bands were noted. Small doses of $\text{D}_2\text{O}/\text{H}_2\text{O}$ were added just sufficient to remove the $908/888\text{ cm}^{-1}$ bands and a lone peak at 2758 cm^{-1} appeared. Its peak intensity was measured.

The chemisorbed species were then removed by degassing up to $\sim 800^\circ\text{C}$ and the original intensities of the 3748 , 908 and 888 cm^{-1} bands were regenerated, (see later for a discussion of this) then a sufficient dose of ND_3 was admitted to, again, just remove the spectral bands at 908 and 888 cm^{-1} . Again the peak intensity of the 2758 cm^{-1} SiOD band was measured, and was found to be exactly that of the previous value obtained for the $\text{D}_2\text{O}/\text{H}_2\text{O}$ titration.

Methanol Adsorption

When methanol was adsorbed to a degassed silica, the $908/888\text{ cm}^{-1}$ bands disappeared, an "ammonia type" SiOH band appeared at 3741 cm^{-1} ($\nu_{1/2} = 12\text{ cm}^{-1}$) and infrared bands characteristic of SiOCH_3 groups¹⁰⁷ were observed in the C-H stretching region.

Exchange

The 3741 cm^{-1} species obtained from the reaction of H_2O with the active sites could be rapidly exchanged to its deuterium analogue (absorbing at 2758 cm^{-1}) with 10 torr of either D_2O or ND_3 . Similarly,

the 3741 cm^{-1} band obtained after the adsorption of NH_3 also readily shifted to 2758 cm^{-1} , indicating exchange of the species. However, other bands appearing for chemisorbed ammonia were unaffected by the addition of 10 torr of either D_2O or ND_3 .

Conversely, if small amounts of HCl (1 torr) were reacted with a surface containing chemisorbed NH_3 , the two bands near 3500 cm^{-1} and the 1550 and 930 cm^{-1} bands all immediately disappeared, whereas the 3741 cm^{-1} band was unaffected, retaining the same position, intensity and half-band width.

Table 4-1 lists the half band widths of the 3741 cm^{-1} band and its deuterium analogue for the adsorption of different molecules.

C. Temperature Effects

As mentioned before, the lowest temperature at which the $908/888\text{ cm}^{-1}$ bands could be detected was $\sim 550^\circ\text{C}$; however, active sites appear to exist at lower temperatures than this because a band at 1550 cm^{-1} due to chemisorbed ammonia could be just observed when NH_3 was adsorbed on a 10 mg cm^{-2} silica which had been previously degassed at only 400°C^* . This band then, is a more sensitive indicator of the presence of active sites than the 908 and 888 cm^{-1} bands. The 1550 cm^{-1} band intensity increased if the initial degassing temperature was increased, and, also paralleled the increase in the $908/888\text{ cm}^{-1}$ bands when they were detectable.

It is concluded, therefore, that the new sites responsible

* For a 40 mg cm^{-2} silica, even greater sensitivity to the presence of active sites was achieved; the 1550 cm^{-1} band could be observed after degassing at 350°C .

TABLE 4-1
Half-widths of the 3741 and 2758 cm^{-1} Bands

Molecule Adsorbed	3741 cm^{-1}	2758 cm^{-1}
H_2O	19	-
D_2O		16
$\text{H}_2\text{O}/\text{D}_2\text{O}^{\text{a}}$	19	16
NH_3	12	
ND_3		11
CH_3OH	12	
$\text{NH}_3/\text{HCl}^{\text{b}}$	12	

^aRatios of $\text{H}_2\text{O}:\text{D}_2\text{O}$ varied from 1:9 to 9:1 made no difference to half-width values.

^bIndicates replacement of SiNH_2 species by SiCl (see Chapter 5).

for the $908/888\text{ cm}^{-1}$ bands, and which also react with H_2O , NH_3 and CH_3OH are formed in increasing numbers once the degassing temperature exceeds 400°C .

Once a sample has been degassed at a given temperature, the regeneration of the active sites responsible for the $908/888\text{ cm}^{-1}$ bands can be achieved at a much lower temperature. The absorption bands of chemisorbed water or ammonia were unaffected up to an evacuation temperature of 300°C but beyond this their intensities diminished and the $908/888\text{ cm}^{-1}$ bands began to reappear.

In the case of chemisorbed NH_3 , the two bands near 3500 cm^{-1} and the 1550 cm^{-1} disappeared at the same rate as the 3741 cm^{-1} bands. (At the same time the shape and frequency of the two bands near 3500 cm^{-1} became altered. This is discussed in detail in Chapter 5).

If a new sample was degassed at, say, 1100°C and was subsequently reacted with NH_3 or H_2O , then a secondary degassing temperature of only about 650°C was necessary in order to reproduce the initial intensity of the $908/888\text{ cm}^{-1}$ bands or to totally remove the bands of the chemisorbed species. The surface had the same properties as after the original degassing at 1100°C , because exactly the same infrared bands for either chemisorbed NH_3 or H_2O could be regenerated in a subsequent reaction. One possible explanation for the requirement of a lower temperature may be that bulk hydroxyls migrate to the surface and form new SiOH groups as others are removed (Hockey et al.⁴² has postulated such a mechanism for the hydrolysis of adsorbed chloro compounds during prolonged evacuation). If this were the case, then on a secondary degassing, such migration would essentially be non-

existent and stable sites could be generated at a lower temperature.

D. Identification of the Chemisorbed Species

When a small dose of water was adsorbed, only a band at 3741 cm^{-1} was formed. A single band absorbing at this high frequency is indicative of an hydroxyl group. This is confirmed by the apparent shift of 11 cm^{-1} for the O-18 analogue and by the fact that deuterium exchange only produces a band at 2758 cm^{-1} .

The 3741 and 2758 cm^{-1} bands are similarly positioned with respect to the isolated hydroxyl absorption bands at 3748 and 2763 cm^{-1} .

The question of the existence of surface geminal hydroxyl groups was discussed in Chapter 3 and is reconsidered here for highly degassed surfaces. The broadness of the 3741 cm^{-1} (see Figure 4-6B) when H_2O is the reactant may have been anticipated as being due to coupling between identical $\text{Si}(\text{OH})_2$ groups. If this were so then, as observed, the 3741 cm^{-1} band appearing in the case of NH_3 adsorption would have a smaller half-band width because $\text{Si}(\text{OH})(\text{NH}_2)^*$ would not be expected to couple appreciably. However, this idea can probably be rejected, since for water adsorption the band width remained constant for any H/D ratio (e.g., a 1:9 H_2O - D_2O mixture should give a spectrum in the ν_{OH} region which represents 95% SiOH-SiOD pairs and only 5% SiOH-SiOH pairs).

The possible reasons for the broadness and flat-topped appearance of the 3741 cm^{-1} band obtained with H_2O compared with that from NH_3 have been discussed in Chapter 5.

*The proof for the existence of SiNH_2 is discussed later.

If it is assumed for the moment that the sites correspond to a "reactive" symmetric siloxane bridge site, then the stoichiometry for the reaction could be presented as follows:

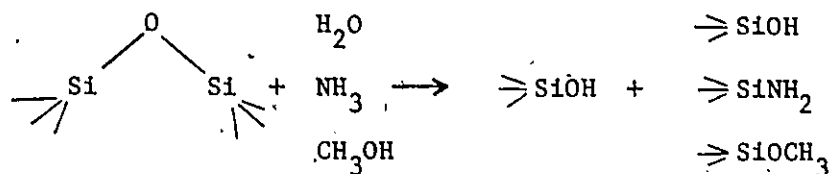


Diagram 4-6

which is to be contrasted to the reaction proposed for the reaction of BF_3 with the sites.⁶¹ (Diagram 4-3).

There has been no direct evidence provided thus far that the reactions proposed do occur at a single site and that there is a 1:1 correspondence between the number of SiOH groups formed and, for example, in the NH_3 adsorption case, the number of SiNH_2 groups formed.

However, the experiment which showed that the intensity of the 2758 cm^{-1} band was the same for the adsorption of either (1:1) $\text{D}_2\text{O}/\text{H}_2\text{O}$ or ND_3 , indicates that the number of hydroxyls formed in the NH_3 reaction is just half that of those formed in the H_2O . This implies that the formation of an hydroxyl group is accompanied by the production of one other SiNH_2 (for NH_3 adsorption) or SiOH (for H_2O).

E. The Structure of Chemisorbed Ammonia

The formation of surface SiNH_2 groups when ammonia has been reacted with highly dehydroxylated silica has been postulated by several workers who have used infrared spectroscopy as a means of detection.^{47,102} The assignment was based solely on the observation

of two bands near 3500 cm^{-1} which were assigned to the symmetric and antisymmetric NH stretching modes, and a band at 1550 cm^{-1} which was assigned to a deformation mode. As stated previously, this assignment must be considered tentative since SiONH_2 or co-ordinately bonded ammonia would give rise to identical spectral features. Low wave-number spectral data has been lacking in previous studies because silica was totally absorbing below about 1350 cm^{-1} . In earlier work^{47, 102}, ammonia was presumed to react, as shown in Diagram 4-2, with a reactive bridge site which was formed during the dehydroxylation process.

It has been found in this laboratory that the nature of the reaction of ammonia with active silica is complex. For the moment, however, these complexities will be ignored.

As described before, the adsorption of 10 torr of NH_3 to a 10 mg cm^{-2} active silica resulted in the appearance of an SiOH band at 3741 cm^{-1} and four other bands (3535 , 3447 , 1550 and 930 cm^{-1}). However, similar bands (with the same isotopic shifts, H/D, O-16/O-18 and N-14/N-15, to be discussed below) could be produced if 20 torr of NH_3 was allowed to react at 650°C for 2 hrs followed by removal of excess reactant. (Figure 4-7).

The silica (10 mg cm^{-2}) was degassed to 300°C only (to remove moisture) and hence contained no active sites. The reaction did not apparently proceed through an 'active site' type mechanism because no 3741 cm^{-1} SiOH was produced. Instead the increase in intensity of the N-H related bands, was accompanied by a decrease in the SiOH (3741 cm^{-1}) intensity.

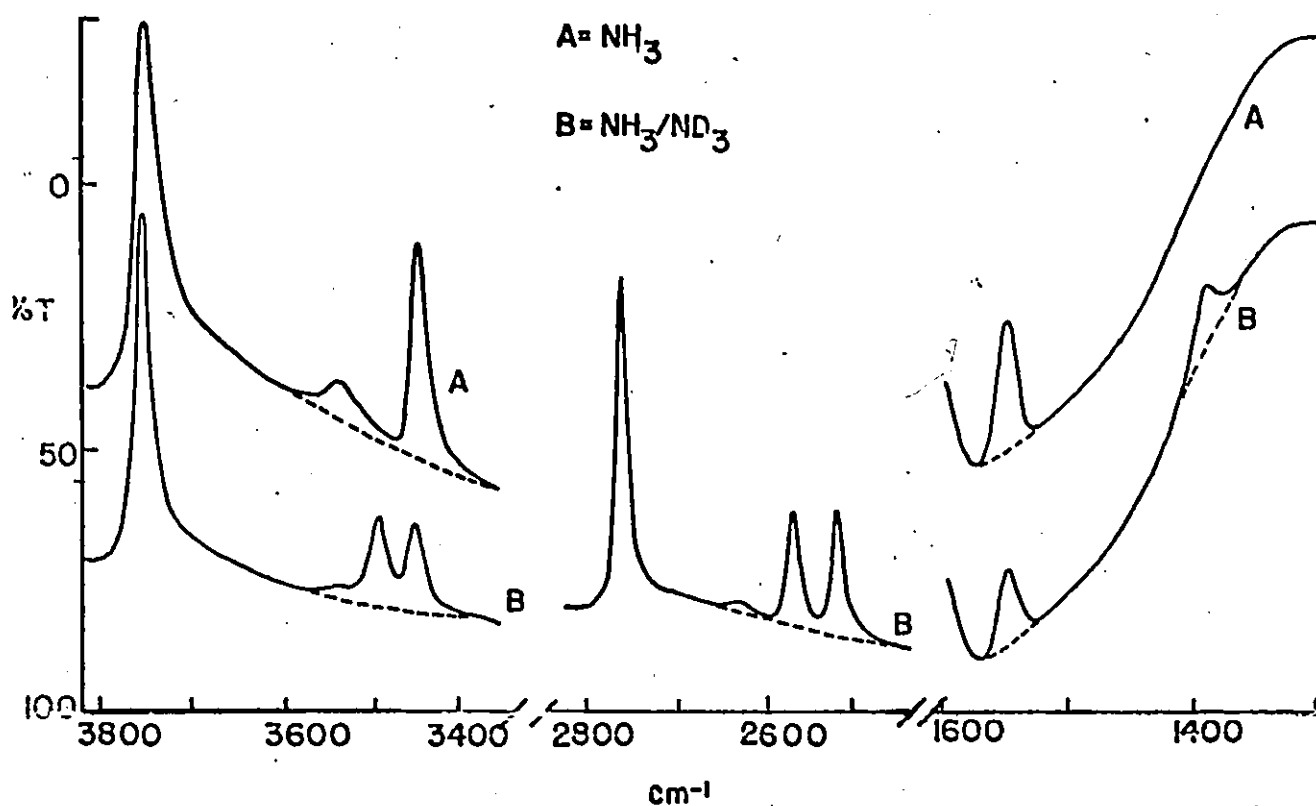


FIGURE 4-7

Infrared spectra of ammonia chemisorbed on a 40 mg cm^{-2} silica disc after reaction at 650°C .

- A. NH_3 ;
- B. 1 : 1 NH_3/ND_3 on a partially deuterated silica. Dotted lines refer to the silica background before reaction and strong bands at 3748 or 2763 cm^{-1} are due to residual SiOH or SiOD groups respectively. The % Transmission scale refers to B.

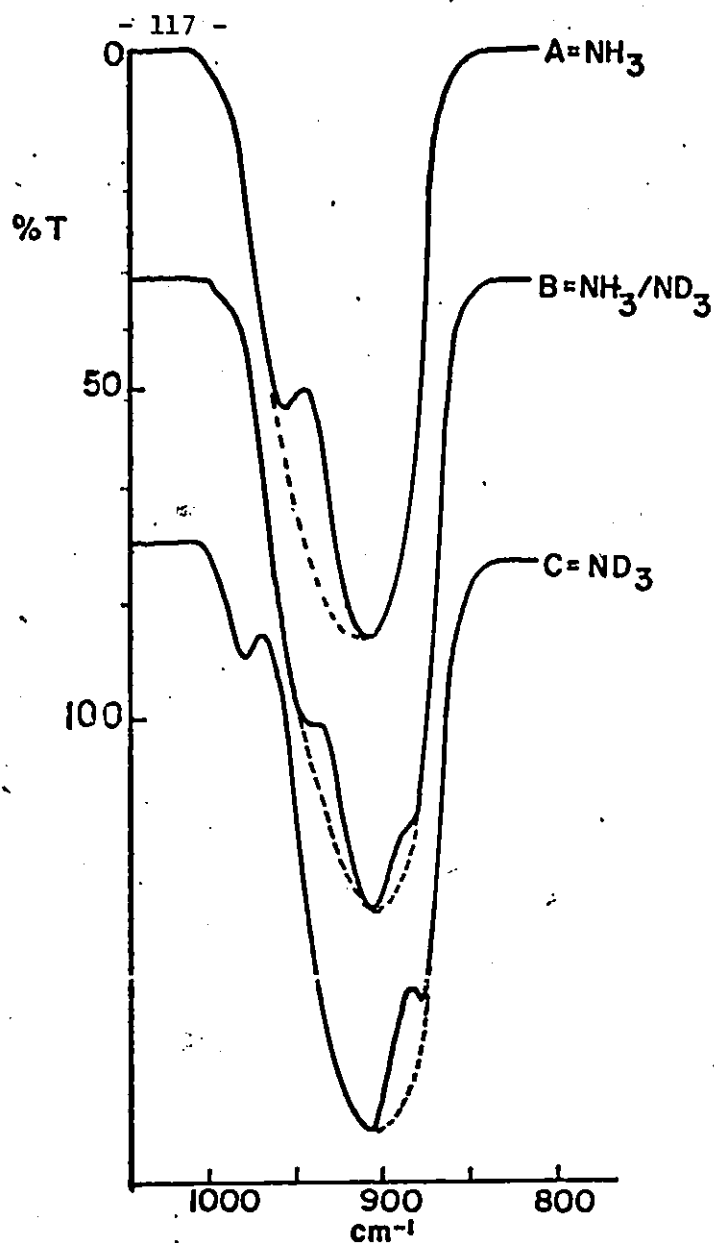


FIGURE 4-8

Infrared spectra of ammonia chemisorbed on a 4 mg cm^{-2} silica after reaction at 650°C . Dotted lines refer to the background before reaction. A, NH_3 ; B, a 1 : 1 NH_3/ND_3 mixture on a partially deuterated silica; C, ND_3 on a fully deuterated silica. The 967 cm^{-1} band is characteristic of the background spectrum of a fully deuterated silica, and corresponds to a band near 987 cm^{-1} in a non-deuterated silica (detectable only in $< 2 \text{ mg cm}^{-2}$ samples). The % T scale refers to A.

The infrared bands of the chemisorbed species were found to be at 3452, 3540 and 1550 cm^{-1} with a partly obscured band near 932 cm^{-1} (compared with 3525, 3447, 1550 and $\sim 930\text{ cm}^{-1}$ for NH_3 reacted with active sites).

The outstanding feature of the spectra of the adsorbed species obtained by this method was the high intensity obtainable for adsorption on even very thin discs. For example, with a 4 mg cm^{-2} silica, two "windows" of transparency occur between $1000\text{--}850\text{ cm}^{-1}$ and $750\text{--}600\text{ cm}^{-1}$ and following the reaction with NH_3 at 650°C a strong sharp band at 932 cm^{-1} was clearly observed whose intensity was proportional to the three higher wavenumber bands (Figure 4-8A).

The species responsible for these bands was extremely stable with respect to thermal degassing, virtually no changes in intensity were observed upon degassing at less than the reaction temperature of 650°C and temperatures as high as 1000°C were necessary to facilitate the disappearance of these bands. (compared with 650°C for NH_3 chemisorbed to the active sites).

The corresponding spectra following the reaction of a (1:1) $\text{NH}_3:\text{ND}_3$ mixture are shown in Figures 4-7B and 4-8B. The spectrum obtained when ND_3 was reacted with a 40 mg cm^{-2} silica (not illustrated) showed only the high and low frequency bands in the 2600 cm^{-1} region of Figure 4-7B, and no bands between $1600\text{--}1300\text{ cm}^{-1}$, but when reaction was carried out using a 4 mg cm^{-2} sample, an additional band at 882 cm^{-1} was observed (Figure 4-8C). [The additional feature at 967 cm^{-1} in the background spectrum of deuterated silica shown in Figure 4-8C results from a shift to low wavenumber of a corresponding band at

987 cm^{-1} in a non-deuterated silica and is not associated with the formation of chemisorbed species. The 987 cm^{-1} band can only be detected when less than 2 mg cm^{-2} silicas are used.]

All observed frequencies are listed in Table 4-2 along with the band positions following reaction with $^{15}\text{NH}_3$. No isotopic shifts were observed when NH_3 was reacted with an O-18 exchanged silica which contained 75% Si^{18}OH to 25% Si^{16}OH prior to reaction.

The reaction temperature of 650°C appeared to be an optimum value for maximum intensity for reaction times of 2 hr. Less intense spectra resulted if lower or higher temperatures were employed.

Analysis of Spectral Bands

The single chemisorbed species has four infrared absorption bands in the experimentally accessible regions between 4000-600 cm^{-1} . The 3540, 3452 and 1550 cm^{-1} bands shifted by small amounts on nitrogen-15 substitution, large amounts for deuterium substitution and not at all for Oxygen-18 substitution. Therefore, the 3540/3452 cm^{-1} pair can be assigned to vNH_x modes and the 1550 cm^{-1} to a NH_x deformation (δNH_x) mode.

The 932 cm^{-1} band likewise shifted for N-15 and D substitution but not for O-18 substitution, so it is unlikely that the surface species contains oxygen. The latter is important since an N-O stretching mode as for example in NH_2OH , might be expected to absorb near 932 cm^{-1} . Further, in view of there being only one new band as a result of partial deuteration (from the NH_3/ND_3 mixture) which lies almost midway between the two vNH_x (or vND_x) modes, shows that an

TABLE 4-2

Observed Wavenumbers¹ for Chemisorbed Ammonia

NH_3	NH_3/ND_3	ND_3	$^{15}\text{NH}_3$
3540 ^{*1}	3540		3527
	3494 [*]		
3452 [*]	3452		3447
	2634	2634 [*]	
	2578 [*]		
	2529	2529 [*]	
1550 [*]	1550		1547
	1390 [*]		
932 [*]	929		919
	882	882 [*]	

¹The band positions marked * were used in the force constant refinement calculation for SiNH_2 .

-NH₂ group is present. [Co-ordinated NH₃ would show three $\nu(\text{NH})$ modes on partial deuteration, one for NHD₂ and two for NH₂D].

The qualitative evidence clearly suggests that an SiNH₂ species has been formed, in which event, the 932 cm⁻¹ band could be assigned to a νSiN mode, or to a rocking mode of the SiNH₂ framework.

In order to investigate the nature of this mode, and to confirm the above assignments, a force constant calculation has been carried out using observable isotopic shift data.

Cain et al.¹⁰⁶ have studied the characteristic vibrations of an RNH₂ group which has C_s symmetry, by assuming that the R group can be considered a point of infinite mass. (10⁶ a.m.u. was used). The geometry, which is formally identical to SiNH₂ is illustrated below

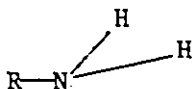


Diagram 4-7

The six internal co-ordinates are $r_1 = r_2 = r(\text{N-H})$,
 $d = r(\text{R-N})$, $\alpha = \angle\text{HNH}$ and $\beta_1 = \beta_2 = \angle\text{RNH}$.

The valence force field assumed is given in Table 4-3, and the symmetry co-ordinates in Table 4-4. Using Cain et al.¹⁰⁶ force constants (Table 4-4) and geometry (the R-N distance was assumed to be as in CH₃NH₂, 1.474 Å) it was possible to reproduce frequencies calculated by Cain et al and the calculation was then further extended to determine the frequencies of RNHD, RND₂ and R¹⁵NH₂ (Table 4-4).

The results clearly show that the so-called rocking modes, ν_4 and ν_6 underwent considerable isotopic shift with deuterium,

TABLE 4-3

Valence Force Field for RNH_2 and SiNH_2 ¹

	r_1	r_2	α	d	β_1	β_2
r_1	F_r	f_r	0	0	0	0
r_2		F_r	0	0	0	0
α			F_α	0	0	0
d				F_d	$f_{d\beta}$	$f_{d\beta}$
β_1					F_β	f_β
β_2						F_β

¹All force constants involving angle bending modes have been weighted by r or r^2 where r is the NH distance, in order to give units of mdyne/A.

TABLE 4-4
Symmetry Coordinates and Calculations for RNH_2^1

Species	Description	RNH_2^1	RNHD	RND_2	$\text{R}^{15}\text{NH}_2^3$
a' $S_1 = 1/\sqrt{2}(r_1+r_2)$	$\nu_s(\text{NH})\nu_1$	3370	3404	2560	6
$S_2 = \alpha$	$\delta(\text{NH}_2)\nu_2$	1634	1448	1207	4
$S_3 = d$	$\nu(\text{SiN})\nu_3$	780 ²	745	718	14
$S_4 = 1/\sqrt{2}(\beta_1+\beta_2)$	$\rho_s(\text{R-NH}_2)\nu_4$	687 ²	588	537	14
a'' $S_5 = 1/\sqrt{2}(r_1-r_2)$	$\nu_a(\text{NH})\nu_5$	3434	2517	2476	10
$S_6 = 1/\sqrt{2}(\beta_1-\beta_2)$	$\rho_a(\text{R-NH}_2)\nu_6$	967	853	712	3

¹Values calculated in ref. 106 were slightly different in some cases, probably due to differences in the number of significant figures in the G or F matrix. Force constants and geometry for RNH_2 were taken from ref. 106, the values of the former being $F_r = 6.40$, $F_\alpha = 0.65$, $F_d = 4.80$, $F_\beta = 0.47$, $f_r = 0.00$, $f_{d\beta}^r = 0.14$, $f_\beta^d = -0.03$ mdyne/A.

²The Potential Energy distribution indicates that these modes are mixed for this isotopic species.

³Calculated low wavenumber shift relative to $\text{RNH}_2(\text{N-14})$.

whereas, $\nu(\text{R-N})$ underwent a much smaller shift. [In this calculation and in that below, all calculated $\nu(\text{ND})$ modes were multiplied by a factor of 1.011 in order to account for anharmonicity¹⁰⁷.]

It is tempting to assign the 932 cm^{-1} band to $\nu(\text{SiN})$ of SiNH_2 on the basis of relatively small D shift (55 cm^{-1} for SiND_2) and from the N-15 shift. However, it is difficult to explain a priori, why the shift for SiNHD is so small or is non-existent (the 932 cm^{-1} band simply appeared broader when NH_3/ND_3 mixtures were reacted, with a slight shift to low wavenumber in the peak maximum).

Further, the $\nu(\text{SiN})$ frequency in a series of compounds with the general formula R_3SiNH is reported¹⁰⁸⁻¹¹⁰ to be in the range $820\text{--}822 \text{ cm}^{-1}$, the highest frequency being for $(\text{CH}_3)_3\text{SiNH}_2$ ¹⁰⁹.

Some assumptions concerning the geometry of a hypothetical SiNH_2 surface species are necessary in order to carry out a similar force constant calculation. Unfortunately, no structural data appears to be available for R_3SiNH_2 compounds, but for the $(\text{SiH}_3)_2\text{NH}$ ¹¹¹, $r(\text{Si-N})$ is $1.725 \text{ \AA}$ and $r(\text{NH}) = 0.995 \text{ \AA}$, whereas $4(\text{SiN})$ in $(\text{SiH}_3)_3\text{N}$ ¹¹² is $1.738 \text{ \AA}$.

It has been assumed, then, that reasonable bond lengths and angles for SiNH_2 are: $r(\text{Si-N}) = 1.74 \text{ \AA}$, $r(\text{NH}) = 1.00 \text{ \AA}$ and $\alpha = \beta = 110^\circ$.

A further assumption has to be made concerning ν_4 , the symmetric rocking mode (the antisymmetric rocking mode can then be calculated so as to fit the data) and since this is generally between $800\text{--}600 \text{ cm}^{-1}$ it has been used as a variable parameter varying from $850\text{--}600 \text{ cm}^{-1}$ in 50 cm^{-1} increments. The data for SiNH_2 , SiNHD and

TABLE 4-5
Calculated Wavenumbers for SiNH₂

ν_n	SiNH ₂	SiNH ₂ D	SiND ₂	Si ¹⁵ NH ₂ ¹
1	3451	3496	2529	6
2	1551	1388	1169	5
3	933	928	881	18
4	850	705	649	4
5	3536	2852	2639	11
6	1010	886	743	2
1	3450	3496	2529	5
2	1551	1388	1170	5
3	933	928	881	18
4	800	670	611	3
5	3536	2583	2640	11
6	1031	895	758	3
1	3450	3496	2529	5
2	1551	1388	1172	5
3	933	928	880	18
4	750	632	572	3
5	3536	2583	2640	11
6	1043	900	767	2
1	3450	3495	2529	5
2	1552	1387	1174	6
3	933	928	880	18
4	700	592	533	3
5	3536	2583	2640	11
6	1051	904	773	2
1	3450	3495	2529	5
2	1552	1387	1175	6
3	933	927	880	18
4	650	551	495	3
5	3536	2583	2640	11
6	1056	906	777	2
1	3450	3495	2529	5
2	1552	1387	1176	6
3	933	926	880	18
4	600	510	456	2
5	3536	2583	2640	11
6	1059	927	779	2

¹Low wavenumber shift relative to calculated SiNH₂ wavenumber.

²Force constants for ν_4 of SiNH₂ = 750 cm⁻¹ are: $F_r = 6.75$, $F_\alpha = 0.57$, $F_d = 4.89$, $F_\beta = 0.52$, $f_r = -0.01$, $f_{d\beta} = 0.06$, $f_\beta = 0.06$ mdyne/Å.

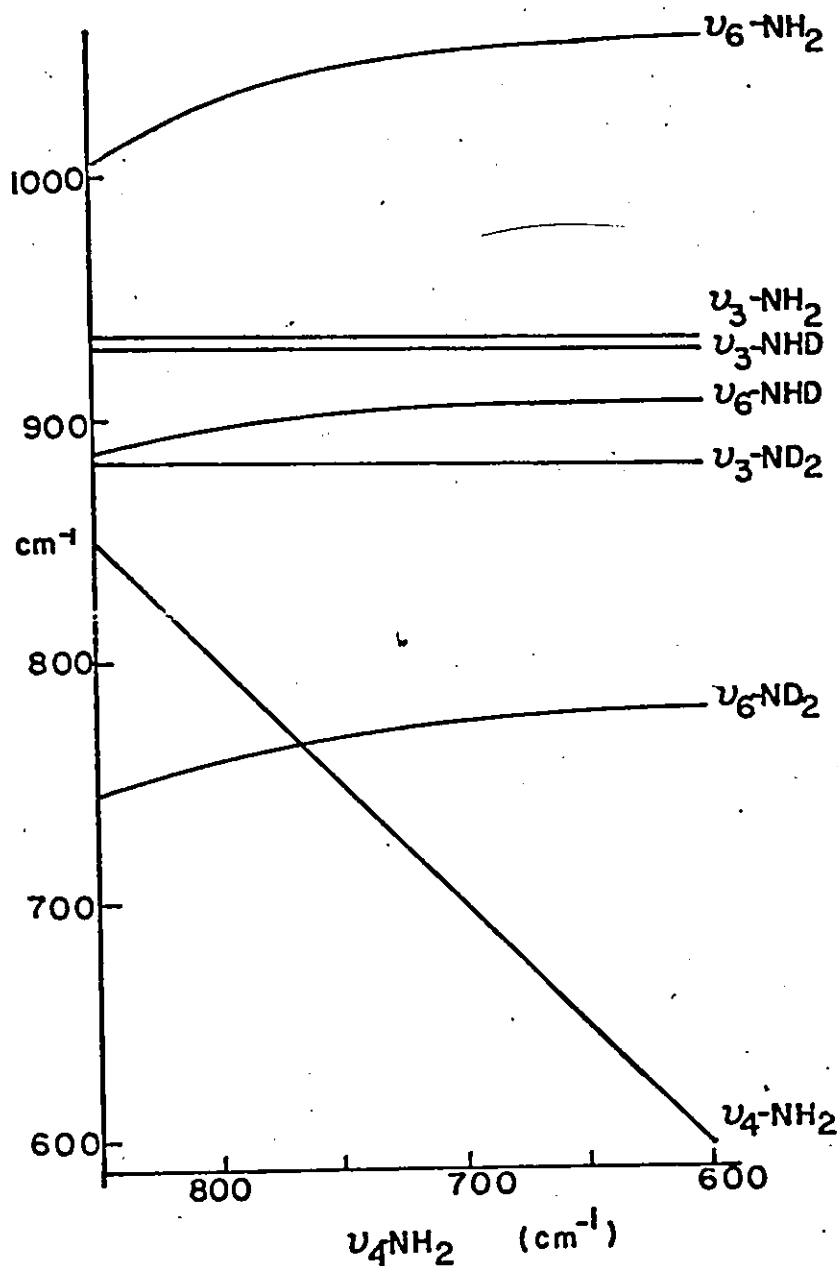


FIGURE 4-9

The plot of ν_6 and ν_3 of SiNH₂, SiNHD and SiND₂ against assumed values of ν_4 for SiNH₂. The vertical bars at the right refer to spectral bars where silica is totally absorbing when 4 mg cm⁻² samples are used.

SiND_2 , indicated with an asterisk in Table 4-2, was used as the "observed" wavenumbers in a force constant refinement calculation, the results of which are shown in Table 4-5. A mass of 28.0 a.m.u. for Si was assumed.

The calculated positions of the high wavenumber, NH stretching and bending modes agree well with the observed. A summary of the results for the three low wavenumber modes is shown in Figure 4-9, where several calculated frequencies have been plotted as a function of the variable parameter, ν_4 , for SiNH_2 .

The remarkable feature is the constant small shift predicted for ν_3 (SiN stretch) when going from SiNH_2 to SiNHD , a feature which conceivably explains the failure to detect a distinct band for this species since it is blended with the 932 cm^{-1} band of SiNH_2 . However, the peak maximum of the 932 cm^{-1} band was observed to shift to slightly lower wavenumber in the mixed isotope experiment. This, combined with the good agreement between the N-15 shift for ν_3 as opposed to that for ν_4 or ν_6 , lends confidence to the assignment of the 932 cm^{-1} species to the SiN stretching mode of a surface SiNH_2 species.

Although this model contains many assumptions, it is clear that the 932 cm^{-1} band cannot readily be assigned to rocking modes because a much larger H/D isotope shift would have been expected.

Also, the symmetric rocking mode in $(\text{Et}_3)\text{SiNH}_2$ is reported to absorb near 727 cm^{-1} which lies within the range anticipated above¹⁰⁹.

The range of frequencies "predicted" for ν_6 lies within one of the windows of transparency, but bearing in mind, (a), that the intensity of this band might be extremely low like that of the other

asymmetric mode (ν_5), (b) that there are already three bands in this spectral range when NH_3/ND_3 react and (c), that the background changes rapidly over a small frequency range (see Figure 4-8), the failure to detect this band is not necessarily surprising.

The calculated force constants for ν_4 of $\text{SiNH}_2 = 750 \text{ cm}^{-1}$ are given at the bottom of Table 4-5 and are similar to those reported for RNH_2 and methylamine¹⁰⁶. The values of the force constants for other choices of ν_4 differed only very slightly from those given in Table 4-5. Having proven that the surface species are SiNH_2 species, then, a probable mechanism for their formation is via a reaction with the isolated silanols which were observed to be diminished

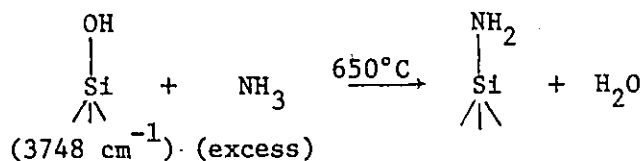


Diagram 4-8

Finally, with reference to NH_3 adsorbed to the active sites, an assignment can also be made to an SiNH_2 species on the basis of similar isotopic shifts.

F. Other Molecules

In order to determine whether a similar reaction would take place with other NH containing molecules, methylamines and hydrazine were reacted with a degassed silica.

In the case of methylamine, a single band at 3465 cm^{-1} was observed (degassing temperature 800°C prior to reaction) or at 2570 cm^{-1} for CD_3ND_2 in both cases accompanied by the new silanol band at 3741 cm^{-1} .

With both molecules a complex profile due to νCH or νCD modes was observed near 2900 and 2200 cm^{-1} , respectively. The reaction must therefore give $\text{SiNH}(\text{CH}_3)$ and SiOH .

The chemisorption of $(\text{CH}_3)_2\text{NH}$ gave no νNH bands but a 3741 cm^{-1} band appeared along with a complex νCH profile.

No dissociative chemisorption took place with $(\text{CH}_3)_3\text{N}$ but, a definite interaction with the surface occurred and is discussed fully in Chapter 5.

Hydrazine (NH_2NH_2) gave an overlapping three band profile in the νNH region, as well as a 3741 cm^{-1} SiOH band, indicating the reaction products were SiOH and SiNHNH_2 .

Many other molecules failed to react however, including H_2 , O_2 , CO , CO_2 , PH_3 , NO , HCN , HCl or C_2H_4 and CH_3CN .

Apart from H_2 , HCN and CH_3CN , the effect of elevated temperatures was not examined (H_2 did not react up to 600°C) so that large activation energies might also control the reaction. It is noted for example (as described in Chapter 6), that HCN reacts readily with silica at 800°C but not at all at room temperature. [Actually the reaction is complex, producing at least three products, but even at 800°C some sites remained and a large part of the HCN reaction appears to proceed by reaction with SiOH groups.]

Each of the molecules that do react however, are distinguished by the fact that they are reasonably strong Lewis bases (or Lewis acids in the case of BF_3 , BCl_3) which also have a hydrogen available for rupture. This premise is pursued in Chapter 5.

G. The Number of Sites

It would be desirable to measure the volume of H_2O or NH_3 which reacted with the new sites as a function of degassing temperature thereby facilitating a determination of the number of active sites.

However since (a), the quantities adsorbed are in the micro-mole range, (b), the cell has a large dead volume and (c) it is impossible to determine the extent of physical adsorption on the cell walls, such a measurement was not possible. However, if it is assumed that the relative band areas of the normal 3748 cm^{-1} band and the new 3741 cm^{-1} band reflect the relative proportions of the two types of SiOH , then when NH_3 is the reactant, the following ratio:

$$\frac{\text{Intensity of } 3748\text{ cm}^{-1} \text{ band after degassing at } 800^\circ\text{C}}{\text{Intensity of } 3741\text{ cm}^{-1} \text{ band after degassing at } 1100^\circ\text{C} \\ \text{and then reacting with } \text{NH}_3}$$

is approximately 10. That is the number of new $\text{SiOH } 3741\text{ cm}^{-1}$ species is approximately one-tenth of the number of normal $\text{SiOH } (3748\text{ cm}^{-1})$ species) on a fresh sample which had been degassed at 800°C . It is well known that a silica degassed to 800°C has about 1.4 ± 0.2 isolated hydroxyls per $100\text{ \AA}^2$, then the number of $\text{SiOH } (3741\text{ cm}^{-1})$ species formed at 1100°C (and therefore the number of active sites) is about 0.14 per $100\text{ \AA}^2$. This is a crude estimate, however, and will be better answered by simultaneous vacuum microbalance and infrared spectroscopic studies.

It was noted that the pretreatment procedure made no difference to the number of sites generated at a given temperature. [Three identical discs (10 mg cm^{-2}) were pretreated at different

temperatures in air (180, 460 and 700°C) then degassed to exactly the same temperature (650°C) and for each the number of sites produced, given by the 908/888 cm^{-1} intensities, was the same.]

Summary

It has been determined that Lewis bases such as NH_3 , CH_3NH_2 , CH_3OH and H_2O are capable of chemisorbing on active silica to form a new SiOH species. When NH_3 is adsorbed an SiNH_2 species is also formed. It seems probable that the reaction does take place at a siloxane bridge site because for every SiNH_2 formed it appears that one SiOH is also generated. However, the SiOH band obtained with H_2O is broader than that for NH_3 , suggesting some complexities may exist.

CHAPTER 5

THE NATURE OF HIGHLY DEGASSED SILICA

In the previous chapter it was shown that various molecules were capable of chemisorbing on dehydroxylated silica, and in the case of H_2O and NH_3 , chemisorbed species were identified which were consistent with a reaction at a bridge site of the type:

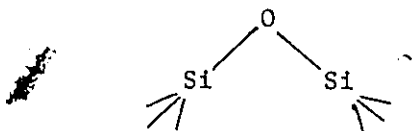


Diagram 5-1

where it was assumed that the bridge was symmetric.

The active sites were associated with two infrared bands at 908 and 888 cm^{-1} ⁶⁰. These bands were found to grow at the expense of the silanol band at 3748 cm^{-1} and were insensitive to D substitution but shifted upon O-18 exchange⁵⁹, suggesting that the sites did indeed contain only Si and O atoms. But certain evidence briefly discussed in Chapter 4, indicated that the sites are more complex than just a simple symmetric bridge. In the present work, a study of the adsorption of trimethylamine and pyridine supports this contention. Also in this chapter, a more detailed analysis has been made of the nature of the chemisorption of water and ammonia. It has been proposed that when water is adsorbed two distinct types of hydroxyl groups are formed from the active sites. Furthermore, other reactions have been shown to occur at secondary centres when higher pressures of NH_3 or H_2O are added. In the case of ammonia adsorption, some of the anomalies observed in the spectra of chemisorbed NH_3 by Little and Blomfield¹⁰²

have been reinvestigated in terms of the possibility of two types of SiNH_2 species being present, arising from two different mechanisms.

RESULTS AND DISCUSSION

A. The Evidence for a Complex Active Site

One of the reasons for doubting that a simple symmetric bridge site is responsible for chemisorption, is that it is difficult to account for two infrared bands at 908 and 888 cm^{-1} to be associated with an Si-O-Si mode unless the Si-O-Si angle is nearly 90° . In the more usual situation where the angle is $>120^\circ$, the symmetric and anti-symmetric stretching modes of Si-O-Si are widely separated (~ 800 and $\sim 1100\text{ cm}^{-1}$ respectively). In all of the chemisorption reactions discussed above, both the 908 and 888 cm^{-1} bands disappeared in unison*, giving the impression that a single site is present like that shown in Diagram 5-1, but a careful examination of the window region between 950 and 850 cm^{-1} , indicates that there is actually a third band present at $\sim 930\text{ cm}^{-1}$ which only appears when the sample is degassed up to 1200°C . It is probably present in the spectra of silica degassed at lower temperatures but is not as intense and becomes obscured by the totally absorbing region above 950 cm^{-1} (see Figure 5-1). This latter band is involved with the sites since it disappears from the spectrum when (e.g.) water is reacted with the surface. Therefore, it is difficult to assign the Si-O-Si modes to any of these bands. Other spectral features observed for the NH_3 and H_2O reactions with the

* In the case of the adsorption of NH_3 , this is not quite true, the ramifications of this are discussed later.

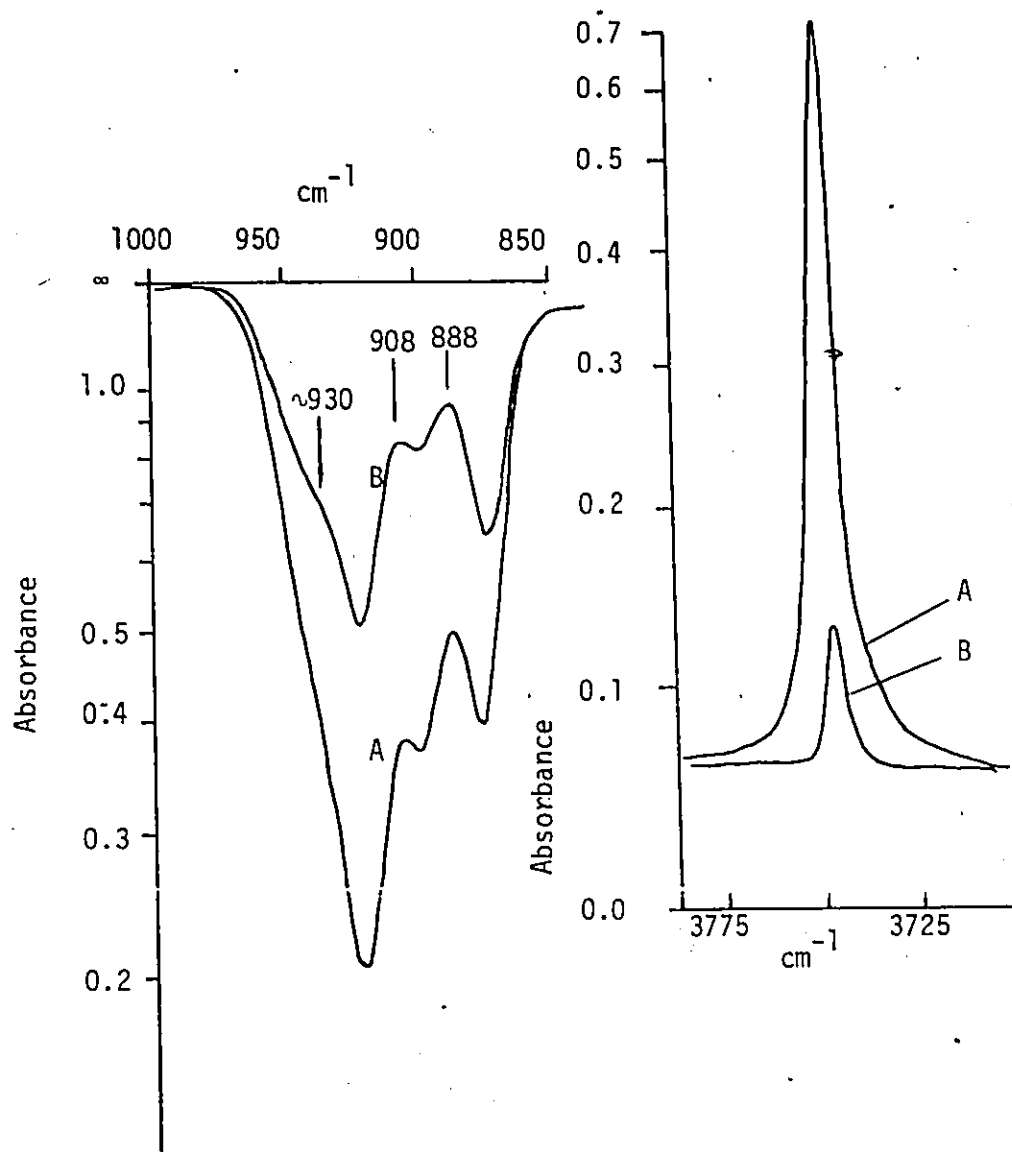


FIGURE 5-1

10 mg cm^{-2} silica degassed at

A 800°C; B 1200°C.

Spectra at room temperature

The SiOH region was scanned at 40 $\text{cm}^{-1} \text{ min}^{-1}$.

active sites, and briefly mentioned in Chapter 4, indicate that a simple symmetric siloxane bridge is not involved (see below).

The Broadness of the 3741 cm^{-1} Hydroxyl Band

As described in the previous chapter, when a degassed deuterated silica was reacted with micromole doses of H_2O vapour, a band at 3741 cm^{-1} appeared in isolation, with a half width of about 19 cm^{-1} , however, its shape differed from that which was produced in the case of NH_3 adsorption in that it was somewhat flat-topped and there was a weak residual tail at about 3720 cm^{-1} . When NH_3 and CH_3OH were added to an active silica the SiOH band also appeared at 3741 cm^{-1} but the half width was only 12 cm^{-1} and the band was much sharper ('Cauchy type' profile).

Also if, after the adsorption of NH_3 on the active sites, the resultant Si-NH_2 groups were exchanged to Cl groups with HCl (see later for a discussion of this mechanism) the SiOH band at 3741 cm^{-1} remained unchanged in intensity and half-width (see Table 4-1 of Chapter 4).

Since the half-width of the 3741 cm^{-1} hydroxyl band is unaltered, when different functional groups ($-\text{Cl}$, $-\text{NH}_2$ or $-\text{OCH}_3$) are adjacent to the hydroxyl group, (assuming that a bridge was reacted), then it does not seem feasible that hydrogen bonding should be responsible for the increased half-width of the 3741 cm^{-1} band when the hydroxyl is adjacent to another hydroxyl.

As mentioned in Chapter 4, a coupling of modes of a geminal species can also probably be discounted as a factor contributing to

the broadness of the band. Hence, it is possible that there may be two types of hydroxyl groups formed when water is reacted with the sites, which absorb at slightly different frequencies in the infrared (separated by 1-2 cm^{-1}) and each of which has a symmetric profile characteristic of the 3741 cm^{-1} band formed when (e.g.) NH_3 is the reactant. This further implies that the siloxane site at which chemisorption occurs is not a symmetric bridge, because the two silicon atoms forming such a bridge are apparently not in identical environments.

Ignoring for the moment the possibility that the active sites may not even be a bridge, the site may be schematically represented as

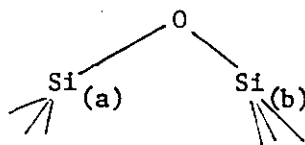


Diagram 5-2

If the postulate is correct, then, when NH_3 is adsorbed the nitrogen of the ammonia may be supposed to preferentially attack, for example, " $\text{Si}_{(a)}$ " and then, the SiOH which forms will always be on " $\text{Si}_{(b)}$ ", where the oxygen originates from the siloxane linkage.

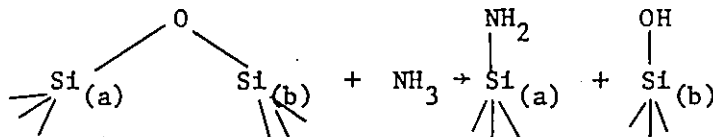


Diagram 5-3

When H_2O is adsorbed, again, attack may be at $\text{Si}_{(a)}$ and in this instance an $\text{Si}_{(a)}\text{-OH}$ should be formed from an oxygen of H_2O , as well as the $\text{Si}_{(b)}\text{-OH}$ originating from the bridge oxygen, and a broader infrared band profile might be expected as a result of the silicon atoms being in slightly different environments.

With O-18 water, the reaction should always give $\text{Si}_{(a)}^{18}\text{OH}$ and $\text{Si}_{(b)}^{16}\text{OH}$ with an $\sim 11\text{ cm}^{-1}$ separation of their infrared absorption bands. The asymmetry of the site might be proven by comparing the overlapping profiles obtained with the reaction of O-18 water on an O-16 silica to that of an O-16 water on an O-18 silica, however this is an impractical exercise since the O-18 exchange of siloxane oxygen is limited to about 60%⁵⁹.

Another approach though has provided evidence that an unsymmetrical bridge site may exist, that of the adsorption of pyridine and trimethylamine to the active sites and in the light of the findings from these studies a more detailed picture of the surface has been formulated. The adsorption of water and ammonia to active silica has been shown to be more complex than was supposed in Chapter 4.

B. The Adsorption of Pyridine and Trimethylamine

Unlike the reactions of water and ammonia, no dissociative chemisorption took place when 10 torr of pyridine was adsorbed to an active silica surface, but bands appeared in the $1650\text{--}1350\text{ cm}^{-1}$ range which were indicative of pyridine co-ordinately bound and of pyridine hydrogen bonded to SiOH groups.

Figure 5-2 shows the differences in the spectra of pyridine adsorbed on an inactive surface and an active surface. Bands at 1620, 1485 and 1451 are typical of co-ordinately bound pyridine whilst those at 1600, 1578, 1487 and 1442 cm^{-1} can be ascribed to an hydrogen bonded pyridine¹¹³. (A more detailed account of the spectra of co-ordinated pyridine is given in Chapter 9).

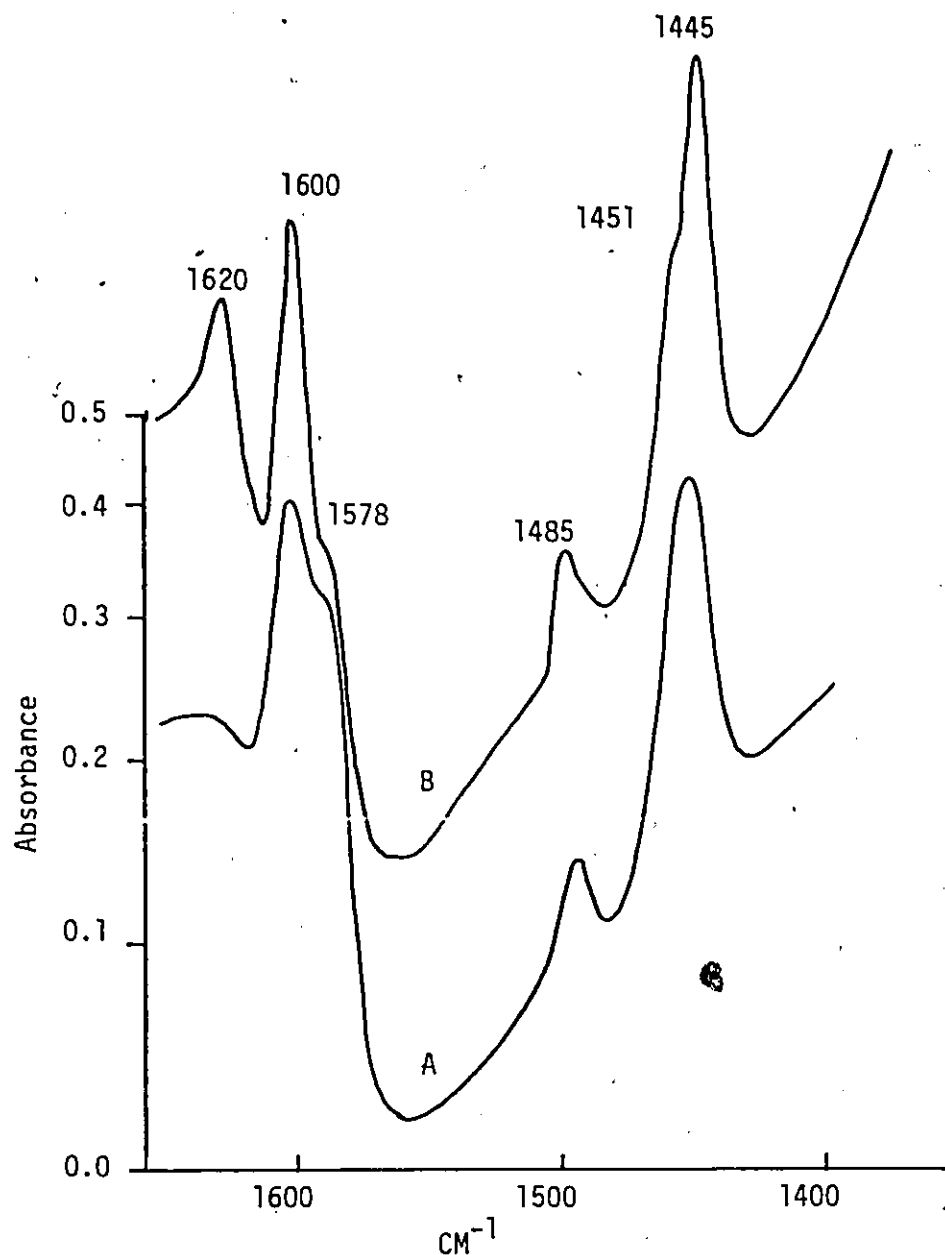


FIGURE 5-2

Addition of 10 torr of pyridine to a 40 mg cm^{-2} silica surface which had been degassed at A) 300°C (no active sites); B) 1000°C (active sites), then pumped at room temperature for 1 hr. Spectra B is displaced for purposes of presentation.

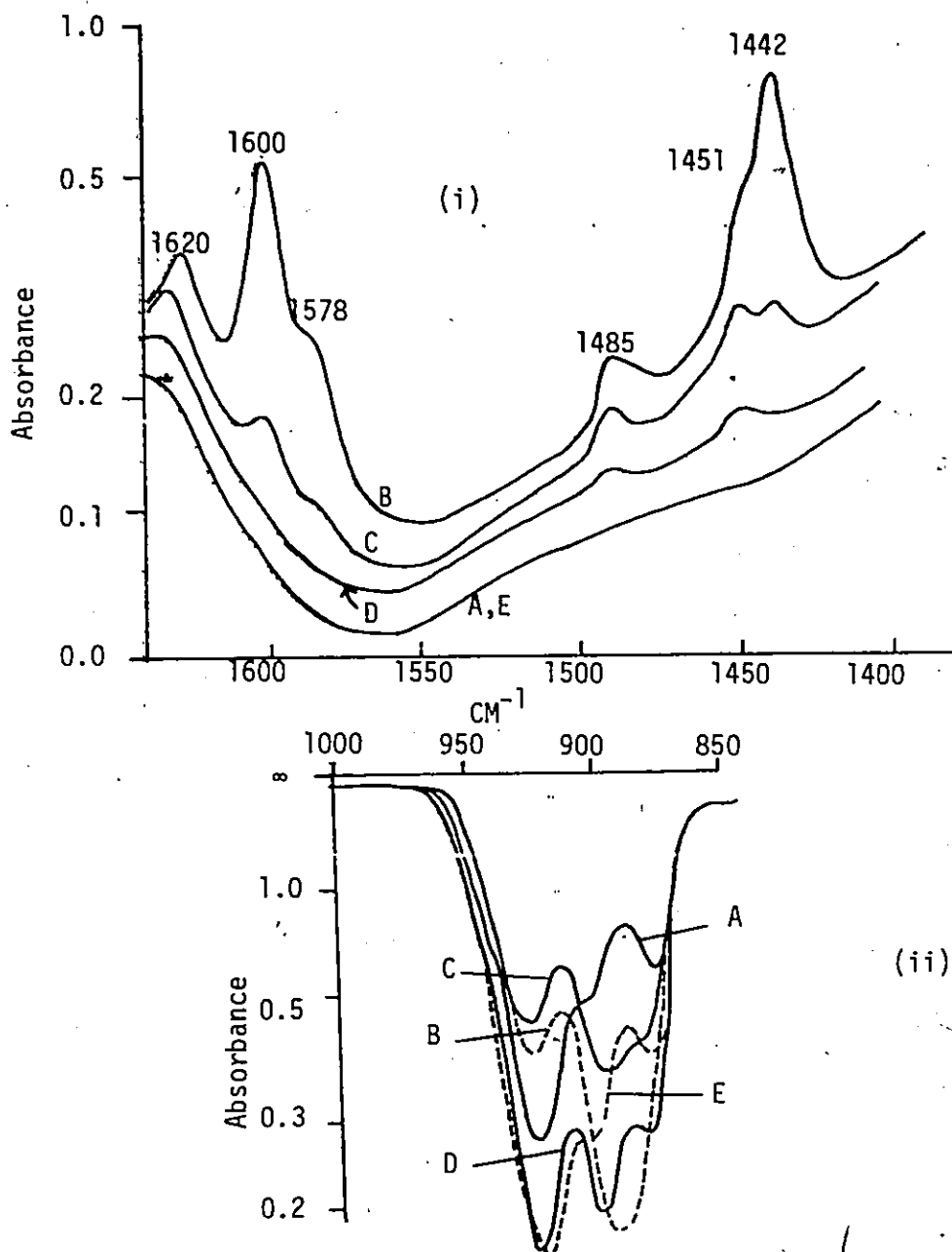


FIGURE 5-3

- A. 10 mg cm^{-2} silica degassed at 1000°C 12 hr and cooled to room temperature.
- B. Added 8 torr pyridine; spectrum after 5 min (same as spectrum after 12 hr.).
- C. Evacuated at room temperature 3 hr; D, 10 hr;
- E. Evacuated at 70°C 1 hr.

Spectra in the $1650\text{--}1350 \text{ cm}^{-1}$ region are displaced for the purpose of presentation. Absorbance scale refers to A.

An adsorption-desorption cycle for pyridine adsorbed to a 10 mg cm⁻² silica is shown over the spectral ranges 1650-1350 cm⁻¹ and 950-850 cm⁻¹ (Figure 5-3). Clearly the band at 888 cm⁻¹ is diminished relative to the 908 cm⁻¹ band, indicating, for the first time, that the species responsible for these two bands cannot be assigned to a single "active" site (Figure 5-3(ii)). The higher frequency band has shifted from 908 to 913 cm⁻¹ which is probably the natural position of this band in the absence of overlap of the 888 cm⁻¹ band. The intensity of the 913 cm⁻¹ band did not diminish even if the surface was left exposed to 8 torr of pyridine for 12 hr (at room temperature). Subsequent degassing at room temperature preferentially removed the hydrogen bonded species (compare the change in intensity ratio of the 1451:1442 cm⁻¹ bands in Figure 5-3(i)C and 5-3(i)D) although some of the co-ordinated species was removed too and the 888 cm⁻¹ band reappeared.

After degassing at 70°C for 1 hr, all bands due to both co-ordinated and hydrogen bonded pyridine disappeared and the original ratio of the 908:888 cm⁻¹ bands returned, although the intensity of each band was lower than in the original spectrum (compare Figures 5-3(ii)A and 5-3(ii)E. Although there was no evidence for any remaining chemisorbed species in other regions of the spectrum, the uniformly lower intensity of the 908 and 888 cm⁻¹ bands might be indicative that some sites have reacted by some chemisorptive process involving, perhaps, traces of impurities or cleavage of the pyridine molecule during desorption. For the moment it is proposed then, that pyridine is adsorbed in the following way:

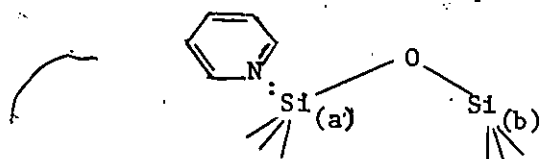


Diagram 5-4

Addition of D_2O to Silica Surface Containing Co-ordinated Pyridine

Figure 5-4 shows the effect of adding small amounts of D_2O to a silica containing virtually only co-ordinately bound pyridine. The reasons for adsorbing D_2O and not H_2O were two-fold. Firstly, H_2O absorbs in the $1600-1300\text{ cm}^{-1}$ region and could obscure the spectrum of adsorbed pyridine and also, any new hydroxyl species formed (OD) can be monitored without the presence of overlapping bands due to hydroxyls already on the surface.

Even the smallest addition of D_2O (<1 torr) caused a distinct change in the spectrum (Figure 5-4C); the bands due to co-ordinately bonded pyridine diminished as did the 908 cm^{-1} band and a small band appeared at 2758 cm^{-1} due to a new SiOD species (not shown) typical of that formed from active sites (see Chapter 4).

This is an important result because it shows that D_2O reacts by displacing pyridine, which is further evidence that the 908 and 888 cm^{-1} bands are part of the same site for chemisorption. (For example it might have been expected that with only small amounts of D_2O adsorbed, the " 908 cm^{-1} site" might have reacted with D_2O without displacement of pyridine at a hypothetical " 888 cm^{-1} site").

The SiOD band produced had a half-width of 16 cm^{-1} which is in accord with the existence of two types of hydroxyl overlapping, as discussed earlier.

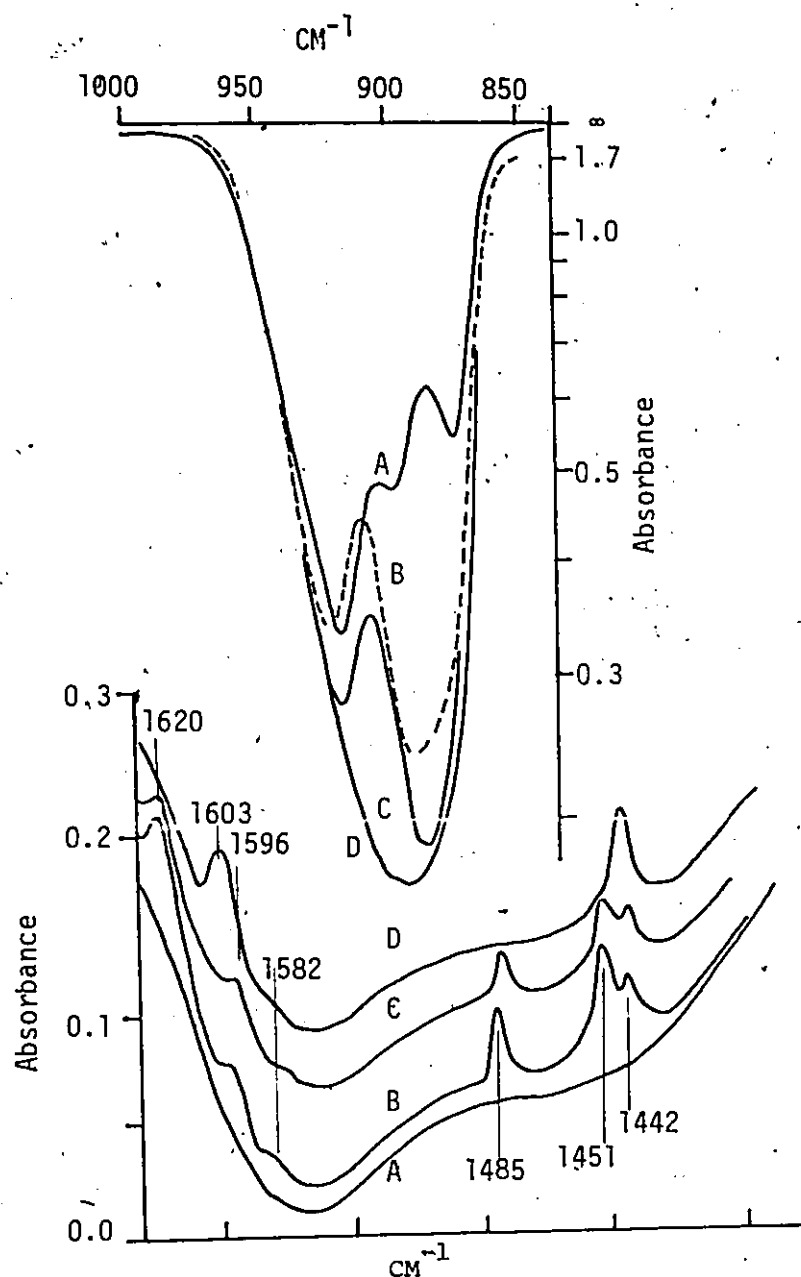


FIGURE 5-4

- A. 10 mg cm^{-2} silica degassed at 1000°C for 12 hr; cooled to room temperature.
- B. Added 2 torr pyridine for 1 min, then pumped 10 min at room temperature.
- C. Added < 1 torr D_2O .
- D. Added 2 torr D_2O for 30 sec. then pumped at room temperature for 10 min.

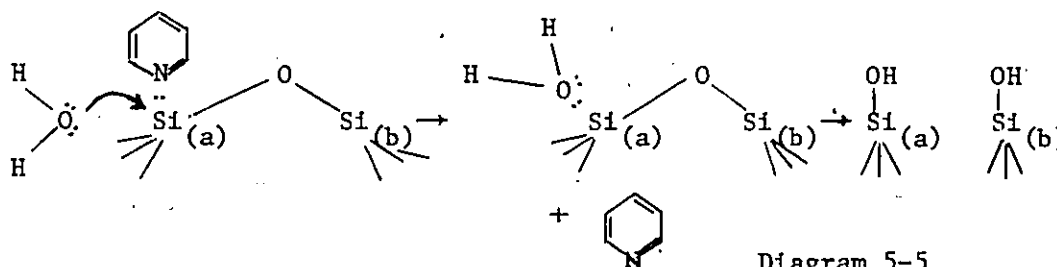
Spectra in the 1650-1350 cm^{-1} region are displaced for purposes of presentation. Absorbance scale refers to A.

When a higher pressure of D_2O was added (2 torr) for 30 seconds then pumped for 10 min, the 908 cm^{-1} band disappeared and bands grew at 1603 and 1445 cm^{-1} corresponding to pyridine hydrogen bonded to silanol groups. (The other bands normally seen for hydrogen bonded pyridine at 1487 and 1582 cm^{-1} were not distinguishable because of the weakness of the spectrum.)

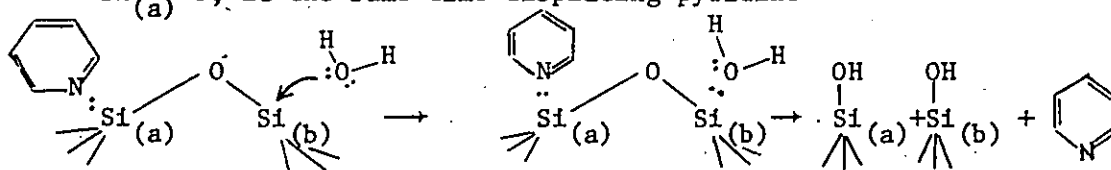
The appearance of an intensified spectrum (comparing Figures 5-4 C and D) for the hydrogen bonded species may be related to the effect of pumping, giving the pyridine molecules the required mobility to allow them to move from the vicinity of the reacted site to a silanol group to which they may subsequently hydrogen bond.

The displacement of pyridine by water may occur in two ways:

- 1) Water is initially adsorbed at the same site at which pyridine is adsorbed (e.g. $Si_{(a)}$) and the oxygen of water competes with the nitrogen of pyridine as a co-ordinative donor to the site ($Si_{(a)}$) then once adsorbed, each water molecule reacts dissociatively with $Si_{(b)}-O$ to form two hydroxyls



- 2) Water adsorbs co-ordinatively at $Si_{(b)}$ then reacts dissociatively with $Si_{(a)}-O$, at the same time displacing pyridine



Both these mechanisms assume a bridge site (an alternate site is discussed later) and there is no reason at this stage to favour one or the other.

Evidence for the existence of a co-ordination site on active silica is further supported by the results obtained from a reaction of trimethylamine (Me_3N) with active silica.

The addition of successive small amounts of Me_3N to an active surface (Figure 5-5), produced the same changes in the $950\text{--}850\text{ cm}^{-1}$ spectral region as did the adsorption of pyridine. However, unlike the pyridine case, the 908 and 888 cm^{-1} bands could not be regenerated until the surface had been degassed up to 200°C .

The addition of small doses (<1 torr) of either NH_3 or H_2O to preadsorbed Me_3N resulted in the displacement of the latter species (evidenced by a decrease in the intensity of the C-H stretching bands) and the 908 cm^{-1} band diminished concomitantly with the formation of bands due to either chemisorbed NH_3 or H_2O , which again shows, as in the case of pyridine adsorption, that dissociative chemisorption can only proceed if the site represented by the 888 cm^{-1} band is available.

The adsorption of the two aforementioned Lewis bases has shown that a Lewis acid site apparently exists on silica which has associated with it a characteristic absorption band at 888 cm^{-1} while the band at 908 cm^{-1} remains unaffected.

C. Re-examination of the Adsorption of Ammonia on Active Sites

The adsorption of NH_3 on a silica surface containing either co-ordinated pyridine or Me_3N , proceeded by a displacement of these

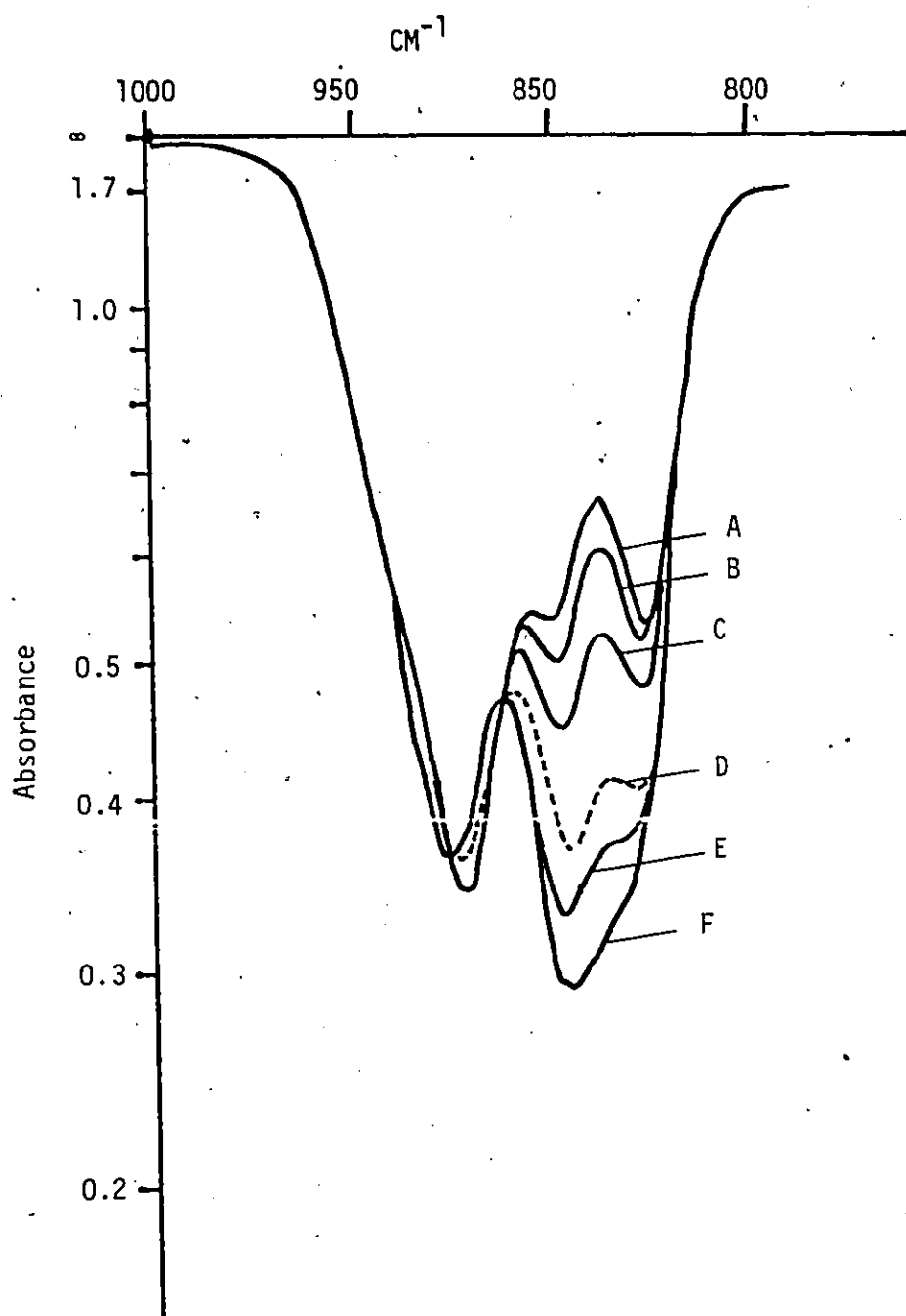


FIGURE 5-5

- A. 10 mg cm^{-2} silica, degassed at 1100°C 12 hr and cooled to room temperature.
- B-F. Successive additions of trimethylamine ($\sim 1 \text{ } \mu\text{mole}$ each).

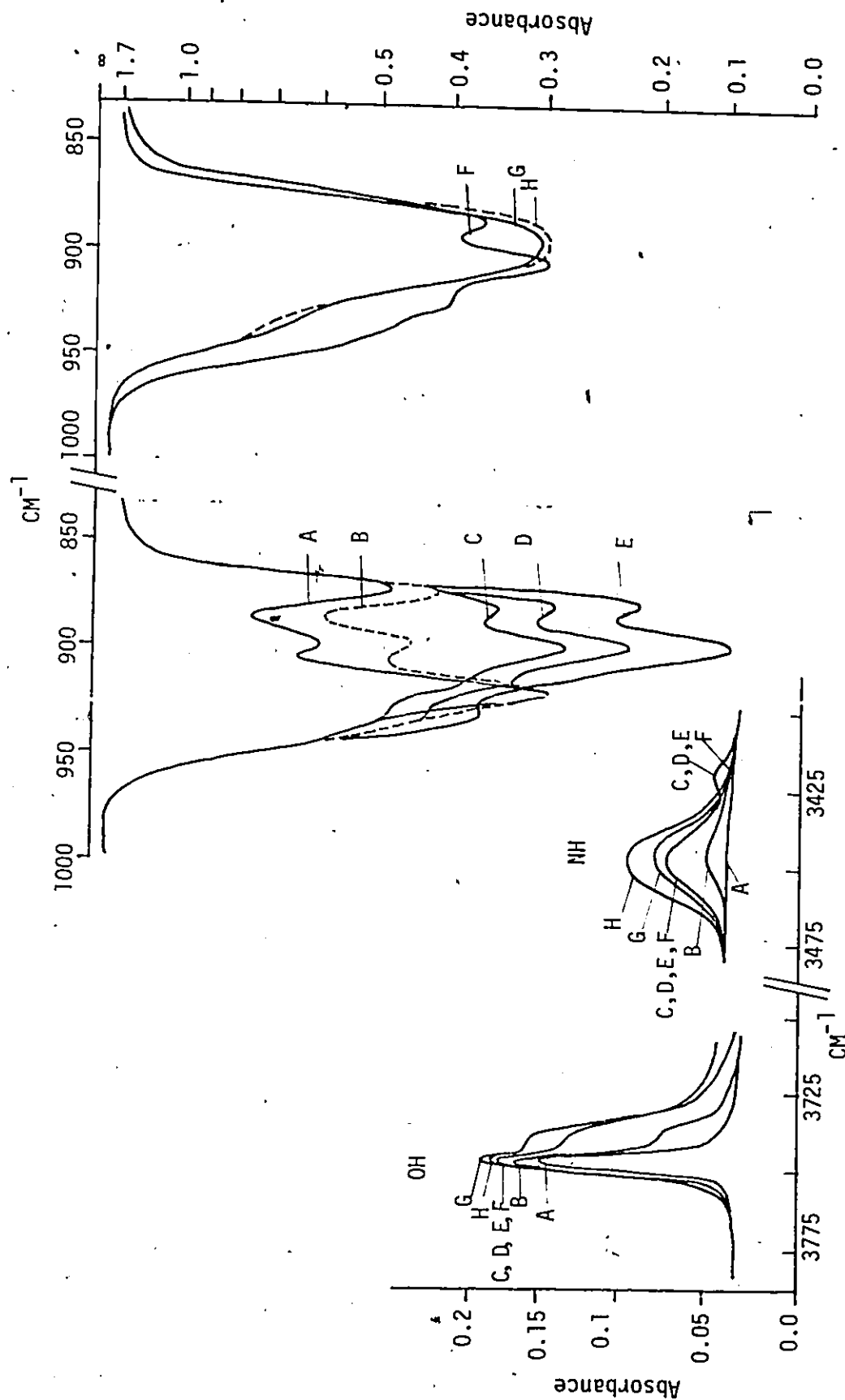


FIGURE 5-6

A. 10 mg cm^{-2} silica degassed at 1100°C 12 hr; cooled to room temperature.

B,C. Successive additions of $\sim 1 \mu\text{mole}$ of NH_3

D,E. Repeat scans (5 min per scan).

F. Pumped 5 min at room temperature.

H. Addition of 200 torr NH_3 ; left in cell for 1 min, then pumped for 5 min at room temperature.

The spectra of the window region have been separated into two parts for the purposes of presentation. The scan speed over the 3700-3400 cm^{-1} region was 40 $\text{cm}^{-1} \text{min}^{-1}$.

molecules, just as was observed for water adsorption to these surfaces, (shown in Diagram 5-6). However, contrary to the case with water there is evidence which favours one mechanism for displacement over the other when ammonia is adsorbed. A careful examination of the titration of NH_3 on active silica revealed that the mechanism given in Diagram 5-5 is the likely process.

It was found that, unlike water, the decrease of the 908 cm^{-1} band was not uniform with respect to the 888 cm^{-1} band when small increments of NH_3 were adsorbed, and a sequence, similar but not identical, to the adsorption of pyridine and Me_3N was observed. (If NH_3 is reacted with silica in large doses (exceeding 2 torr) the non uniform decrease in the 908 and 888 cm^{-1} bands is not apparent).

As Figure 5-6 shows, the first small increment of NH_3 (<1 torr) results in the formation of a 3741 cm^{-1} absorption band (SiOH), 3444 cm^{-1} (SiNH_2)*, and both the 908 and 888 cm^{-1} bands diminished in unison (Figure 5-6B). With the next increment, the intensity of the 888 cm^{-1} band decreased substantially, but the 908 cm^{-1} band appeared to shift to $\sim 928\text{ cm}^{-1}$ (c.f. 913 cm^{-1} for pyridine, Me_3N adsorption). Also a new band appeared at 3417 cm^{-1} (Figure 5-6C).

With time the 928 cm^{-1} band slowly changed into two bands at $\sim 930\text{ cm}^{-1}$ and $\sim 915\text{ cm}^{-1}$ (see Figure 5-6D,E) and the transmittance in the window region fell. The only vibration which is known to absorb near 930 cm^{-1} in the gas phase spectrum of NH_3 is the inversion mode, but in the condensed phase, or when NH_3 is physically or coor-

* Another broad weak band at 3520 cm^{-1} also appeared, but is not shown in Figure 5-6.

dinatively bonded this band should shift to 1100 cm^{-1} corresponding to the symmetric deformation mode. Therefore, the 928 cm^{-1} band is unlikely to represent a physically or co-ordinatively bound NH_3 but is probably the Si-N stretch of chemisorbed NH_3 . The initial sharpness of the band (Figure 5-6C) may be associated with the fact that the first small amounts of SiNH_2 are formed at sites of equivalent (low) activation energy but as other sites of higher energy are reacted the band becomes more diffuse corresponding to an array of site energies. The 915 cm^{-1} band may be associated with the original 908 cm^{-1} band and if this is so, then it is apparently of higher intensity than the 888 cm^{-1} band. More distinct spectra are obtainable by using ND_3 instead of NH_3 because there is no overlap of an Si-N stretching band.

The adsorption of ND_3 does clearly proceed by a preferential reaction of the " 888 cm^{-1} " site, as shown by the non uniform decrease of the 908 cm^{-1} band with respect to the 888 cm^{-1} band (Figure 5-7).

An "SiOH surface" was chosen for the adsorption of ND_3 because the 'window' region ($950\text{--}850\text{ cm}^{-1}$) of an 'SiOD silica' has a broad absorption band at 967 cm^{-1} (see Chapter 4, Figure 4-8) which could obscure spectral changes in the 908 cm^{-1} band.

No exchange of ND_3 was expected on an activated 'SiOH silica' provided only small doses were adsorbed, because chemisorption occurs preferentially. This was evidenced by the growth of only the SiOD band at 2758 cm^{-1} , formed by chemisorption but not of the 2763 cm^{-1} band (formed by exchange). Therefore, a band at 913 cm^{-1} , which remains after a small dose (<1 torr) of ND_3 had been adsorbed, (Figure 5-7C shows it clearly) cannot be confused with the Si-N

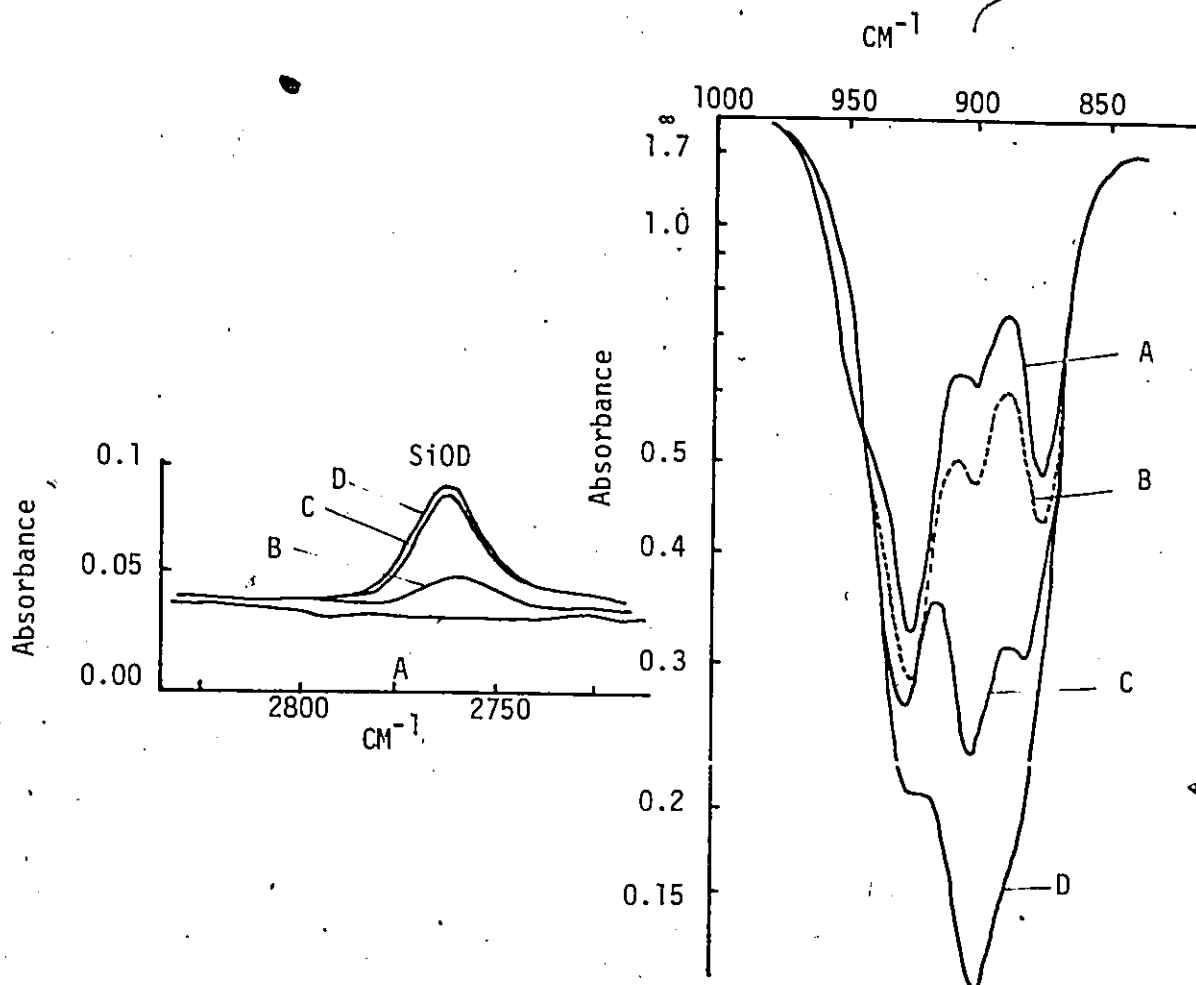


FIGURE 5-7

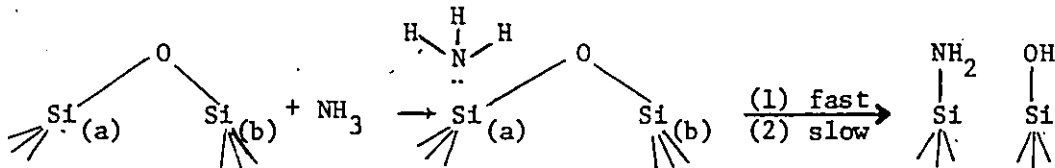
Addition of small increments of ND_3 to active silica.

- A. 10 mg cm^{-2} silica degassed at 1100°C 12 hr then cooled to room temperature.
- B,C. Successive doses of ND_3 (< 1 torr).
- D. Repeat spectrum after 1 hr.

stretch of an adsorbed SiNH_2 or SiNHD species, but must be one of the active site bands.

This is evidence that, during the titration of the active sites, ammonia is adsorbed at the same site as pyridine and Me_3N prior to being dissociatively chemisorbed, and therefore, since ammonia displaces pyridine and Me_3N from active silica, a mechanism similar to that given in Diagram 5-5 is favoured.

The first small increments of ammonia (NH_3 or ND_3) resulted in an equal decrease in the intensities of both the 908 and 888 cm^{-1} bands (shown in both Figures 5-6B and 5-7B) which infers that chemisorption is rapid, as the most reactive sites are reacted first, but then as more ammonia is admitted, the chemisorption step is slower and the lifetime of the co-ordinated species is increased and the band at 888 cm^{-1} then diminishes at a faster rate than the 908 cm^{-1} band.



(1) Initial titration; most active sites consumed

(2) Subsequent titration; less active sites consumed

Diagram 5-7

Hence the 888 cm^{-1} band is indicative of an adsorption process related to the " $\text{Si}_{(a)}$ " part of the bridge and the 908 cm^{-1} band, to " $\text{Si}_{(b)}$ ".

The rate of chemisorption became very slow near the end of the titration of the sites and the complete removal of the active site bands required the addition of up to 10 torr of NH_3 or of 1 torr followed by pumping.

If ammonia is co-ordinated as well as chemisorbed, then some evidence should be available in the spectrum of the N-H stretching region for such a species. In Figure 5-6C, the N-H stretching region is shown to have two bands, the symmetric stretching mode of SiNH_2 at 3444 cm^{-1} (the weak antisymmetric mode also appeared at $\sim 3525 \text{ cm}^{-1}$ but is not shown in the figure) and a smaller band at 3417 cm^{-1} . This latter band was not present when the first small dose of NH_3 was added (Figure 5-6B) and no co-ordination was indicated by the active site bands. Nor was it present after the sample had been pumped (Figure 5-6F).

Little and Blomfield¹⁰² observed a sharp band at 3420 cm^{-1} when 5 torr of NH_3 was adsorbed to a previously degassed (850°C) silica sample, which they attributed to NH_3 physically adsorbed to SiOH groups. They noted that the band was much sharper, and 20 cm^{-1} higher in frequency than a band appearing in the spectrum of a silica degassed to only 350°C . They attributed these changes to perturbations on the NH_3 modes by the new surface environment.

However, experiments in this laboratory seems to indicate that the 3417 cm^{-1} (or 3420 cm^{-1}) band is not due to physically adsorbed ammonia, but can be correlated with changes in the intensity of the 888 cm^{-1} band, and hence to a co-ordinated ammonia. For instance for small amounts of NH_3 adsorbed, the 3417 cm^{-1} band is present when the 888 cm^{-1} band intensity is diminished relative to the 908 cm^{-1} band (Figure 5-6C,D,E).

Figure 5-8 shows the spectra obtained for the adsorption of small doses of NH_3 and ND_3 on 40 mg cm^{-2} degassed silicas. The 3417

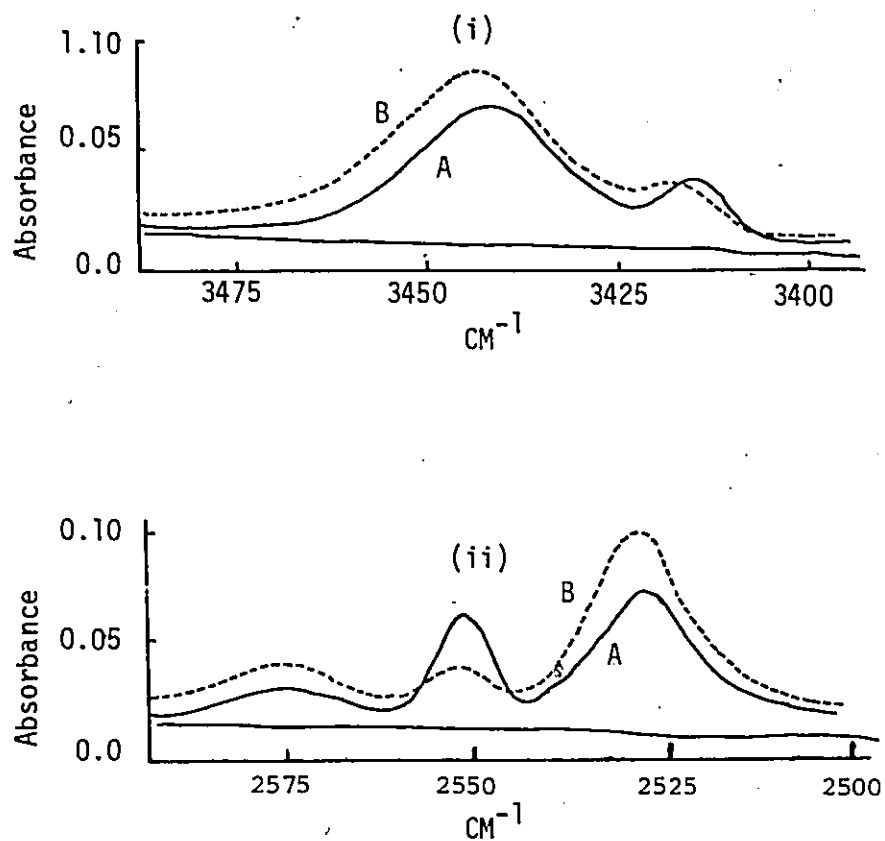


FIGURE 5-8

40 mg cm^{-2} silica degassed at 1100°C 12 hr, cooled to room temperature.

- (i) Addition of NH_3 to an SiOH surface.
- (ii) Addition of ND_3 to an SiOD surface.

A. Small dose of ammonia (< 1 torr).

B. Repeat spectrum after 3 hr.

Scan speed 20 $\text{cm}^{-1} \text{ min}^{-1}$.

cm^{-1} band decreased in intensity after the initial adsorption period but the 3444 cm^{-1} band grew (as did the 3525 cm^{-1} band, not shown). Though it is not possible to observe transmission in the spectral region from $950\text{--}850 \text{ cm}^{-1}$ with a 40 mg cm^{-2} disc, it may be inferred that the above changes in band intensity are related to continuing chemisorption of NH_3 from a co-ordinated SiNH_3 species.

If the 3417 cm^{-1} band represented a hydrogen bonded ammonia, as proposed by Little and Blomfield¹⁰², it is difficult to envisage why this bond should be formed preferentially initially and then break at a later stage, (manifested as a decrease in the 3417 cm^{-1} band intensity as in Figure 5-8(i)B), since no external treatments such as pumping or heating were applied.

The analogous band for ND_3 co-ordinated to silica (a fully deuterated silica in this case) appeared at 2552 cm^{-1} .

It should be noted that in Figure 5-8(ii), a band at 2578 cm^{-1} represents the N-D stretch of a small amount of SiNHD from which it might be inferred that the 2550 cm^{-1} band is a physically adsorbed NHD_2 species. However, if this were true it would be reasonable to expect to find another band due to physically adsorbed ND_3 in view of the high deuterium content of the surface and the adsorbate. But there is no evidence for any other band (it is not hidden under existing bands in the spectrum since pumping on the sample for 5 min made no difference to the shape and intensity of the 2578 and 2529 cm^{-1} bands). Therefore, the 2552 cm^{-1} band is very likely the fully deuterated analogue of the 3417 cm^{-1} band.

The antisymmetric stretching modes of gas phase ND_3 and NH_3

are at 2564 and 3444 cm^{-1} respectively, and therefore the 2552 and 3417 cm^{-1} bands of the co-ordinated species may plausibly be assigned to this mode.

Further evidence that the 3417 cm^{-1} mode is not due to a hydrogen bonded species is exemplified in Figure 5-9. Various pressures of NH_3 were adsorbed for 1 min then, instead of pumping, the excess gas phase NH_3 was condensed back into a trap kept at liquid nitrogen temperatures until the pressure approached $\sim 10^{-3}$ torr. The band at 3417 cm^{-1} diminished for higher initial pressures and the intensity of the symmetric stretching band of chemisorbed SiNH_2^* increased. If the 3417 cm^{-1} band was due to physically adsorbed ammonia then its intensity should either increase, or remain the same, but not decrease. The behaviour of this band can be rationalized if it is assumed that co-ordination is responsible, and that this process is favoured at moderate pressures (1-2 torr) but that at higher pressures more bridge sites are opened (chemisorption) and co-ordination is restricted to the sites that remain. Even at a pressure of 100 torr

a weak 3417 cm^{-1} band still exists which infers that electron deficient sites must still be present (Figure 5-9C). One explanation for this may be that strained bridges are also formed in pores, or subsurface layers, which only react when the pressure is high enough to allow the ammonia molecule to permeate to these zones, but then, if this were so, it is difficult to see how the absorption bands of SiNH_2 and SiOH could be virtually unchanged in frequency from those

* The band also shifted from 3444-3448 cm^{-1} as the admitted pressure of NH_3 was changed from <1 torr to 100 torr. This effect is referred to later.

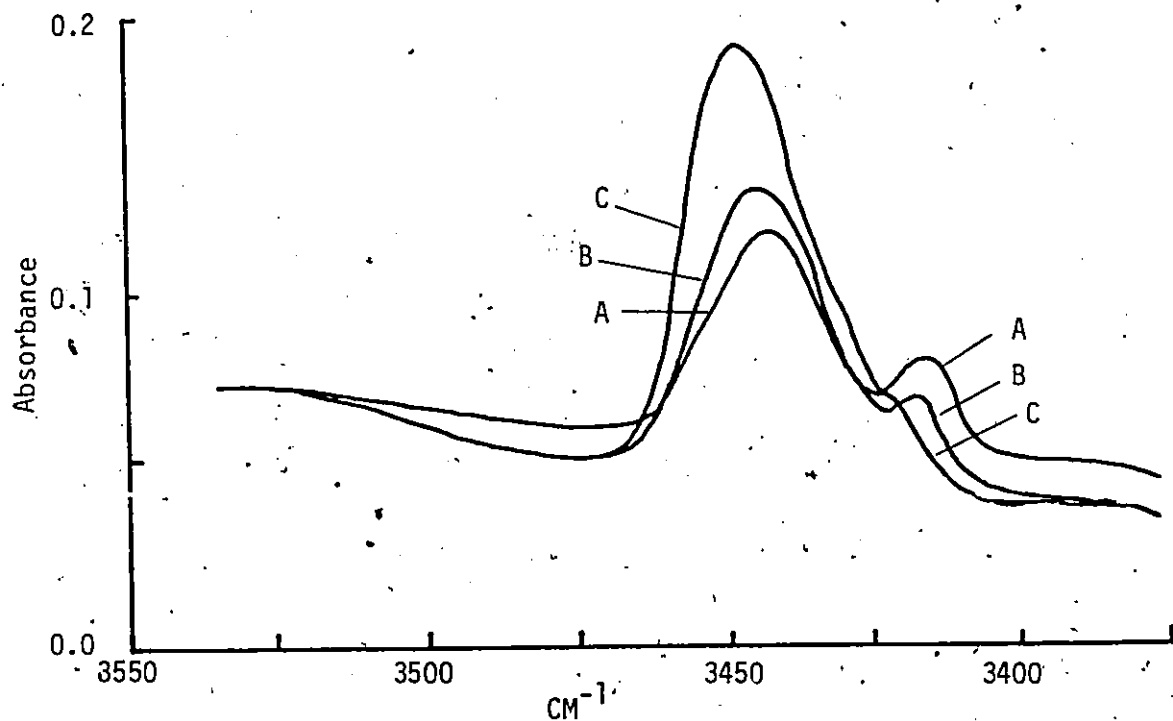


FIGURE 5-9

40 mg cm⁻² silica degassed at 1100°C 12 hr; cooled to room temperature.

Various pressures of NH₃ admitted for 1 min, then excess removed by condensation into a liquid N₂ trap until pressure ~10⁻³ torr.

A. ~1 torr.

B. 35 torr.

C. 100 torr.

Scan spread was 20 cm⁻¹ min⁻¹.

reacted at the first stages of the titration, unless it was somehow possible that each SiNH_2 and SiOH formed was able to emerge as a surface group.

Therefore a better explanation may be that there are active sites remaining which are under less strain, but which are capable of reaction as an 'active site' when the pressure of ammonia is higher.

The effects of higher pressure are also evident in Figure 5-6.

Addition of 10 torr of NH_3 has proportionately increased the intensities of both the SiOH 3741 cm^{-1} and SiNH_2 ($\sim 3447\text{ cm}^{-1}$) bands, implying that a continued reaction has occurred at bridge sites. However, the admission of a still higher pressure (200 torr) had a different effect. The SiOH (3741 cm^{-1}) band appeared not to grow but the SiNH_2 band intensity did increase and broadened considerably on the high wavenumber side. As well the band centre had moved to a higher frequency.

The change in shape and frequency of the SiNH_2 bands with increasing pressure of ammonia is better illustrated in the spectra of large discs (40 mg cm^{-2}). These effects are illustrated in Figure 5-10. For each addition of NH_3 , the gas phase was left in contact with the surface for 5 min, then evacuated for 1 hr at room temperature. With the first small addition of NH_3 (1 torr) to an active 40 mg cm^{-2} disc, the band centre of the symmetric stretch of SiNH_2 was at 3444 cm^{-1} and, like the 10 mg cm^{-2} series (Figure 5-6), the band had a marked asymmetry on the high wavenumber side (Figure 5-10B). Following the addition of 20 torr of NH_3 the band moved to 3446 cm^{-1} and the high wavenumber wing became noticeably broader (Figure 5-10C). At 200 torr, the band was centred at 3448 cm^{-1} (Figure 5-10D).



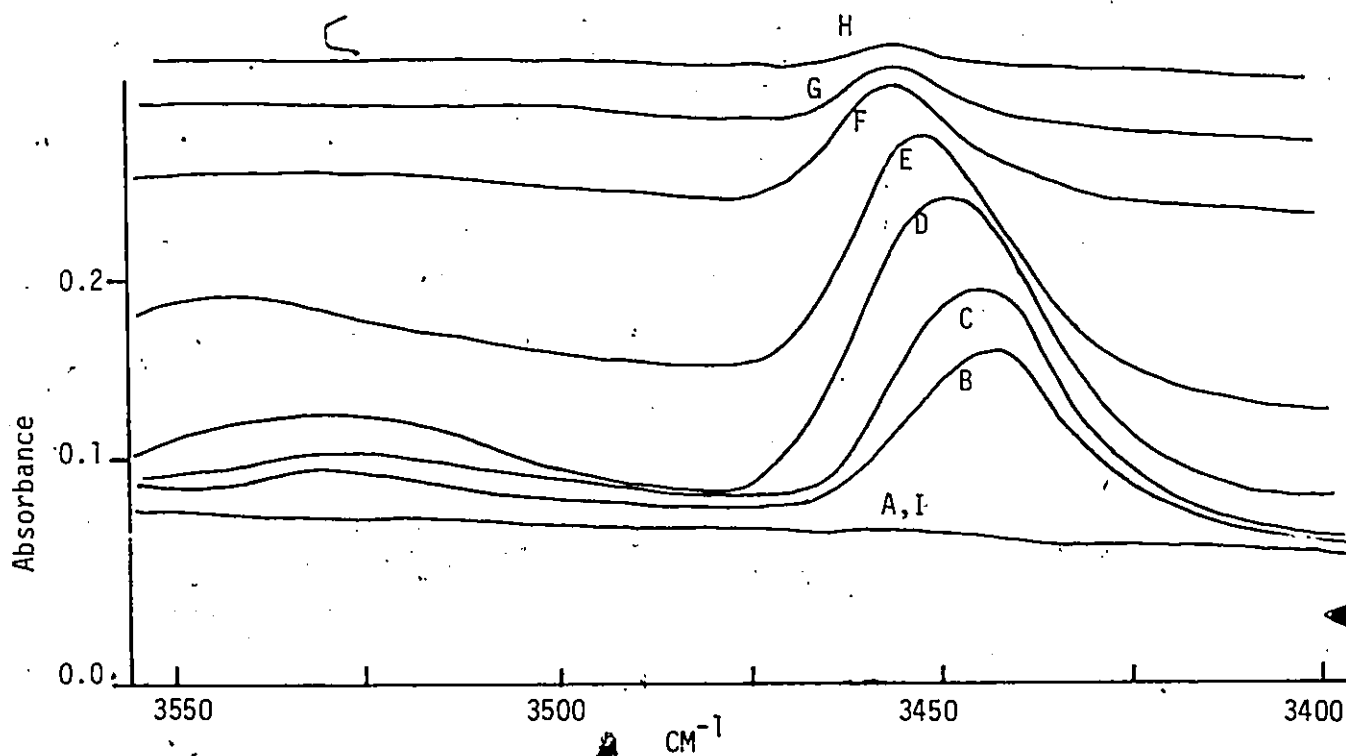


FIGURE 5-10

Desorption of chemisorbed ammonia; pressure maximum 200 torr.

A. 40 mg cm⁻² silica degassed at 1100°C, 12 hr; cooled to room temperature.

Admission of various pressures of NH₃ for 5 min, then pumped 1 hr. (at room temperature).

B. 2 torr; C. 20 torr, D. 200 torr.

Degassed at various temperatures for 1 hr.

E. 450°C. F. 650°C, G. 930°C, H, 1000°C, I, 1100°C.

Spectra E-H are displaced for the purposes of presentation.

Throughout this sequence of increased pressure, the anti-symmetric stretching band, initially at $\sim 3525 \text{ cm}^{-1}$ became considerably broadened and the peak maxima moved to $\sim 3530 \text{ cm}^{-1}$.

Subsequent degassing of the surface at temperatures up to 200°C had no effect on the frequency, shape or intensity of either band, but above this, the intensity of both bands diminished, and each was shifted to even higher frequencies.

At a degassing temperature of 450°C , the antisymmetric mode had moved to $\sim 3540 \text{ cm}^{-1}$ and the symmetric mode to 3450 cm^{-1} . After degassing at 650°C the frequencies were $\sim 3540 \text{ cm}^{-1}$ and 3452 cm^{-1} , the former, a weak broad band, but the latter was perfectly symmetric, and still a strong band (Figure 5-10F).

No further change in frequency was observed up to the disappearance of these bands at 1000°C (Figure 5-10G,H).

This sequence of adsorption and desorption seems to indicate that there are two distinct SiNH_2 species present, one with absorption maxima at 3444 cm^{-1} and 3525 cm^{-1} and another absorbing at 3452 and 3540 cm^{-1} .

For the moment it will be assumed that there are in fact two species formed, which, for clarity, are labelled as type 1 ($3444/3525 \text{ cm}^{-1}$) and type 2 ($3452/3540 \text{ cm}^{-1}$). Type 2 bands are identical with those reported in Chapter 4 which were observed for NH_3 reacted at 650°C .

No change was observed in the frequency of the δNH_2 mode at 1550 cm^{-1} during the aforementioned absorption-desorption cycle, thus this frequency is associated with both type 1 and type 2 SiNH_2 .

Similar pressure and degassing effects were noted for ND_3 absorbed to an active deuterated silica, and also for the adsorption of methylamine to active silica, though the effects were not so pronounced, (see Table 5-6).

Just as for NH_3 adsorption, the symmetric stretching band of SiND_2 and the lone N-H stretching band of CH_3NH_2 were initially asymmetric when small doses of these adsorbates were added, but became more symmetrical for higher pressure adsorbed. However, the shifts of the N-H or N-D bands to higher frequency were not so marked. When methylamine was degassed at 800°C , new bands appeared at 2218 and 2100 cm^{-1} due to SiCN and SiNC species (see Chapter 6).

Little and Blomfield¹⁰² had noted that degassing shifted the antisymmetric stretching mode of SiNH_2 from 3520 to 3540 cm^{-1} but had attributed this shift to the effect of the surface coverage of adsorbed species upon the interactions between neighbours. No shift was mentioned for the symmetric SiNH_2 band.

They assumed that as $-\text{NH}_2$ groups were progressively removed from the surface by degassing, closest neighbour interactions weakened, and the antisymmetric band shifted to higher frequencies.* But the change in position of this band must be related to the $3444\text{--}3452\text{ cm}^{-1}$ shift, and it is therefore difficult to account for the fact, that, during the first stages of the titration of the surface the first bands to appear were at 3444 cm^{-1} and 3520 cm^{-1} the lowest frequencies observed. In terms of Little and Blomfields theory¹⁰², these are the most perturbed. It could be argued that the species are clustered at

* Little and Blomfield only studied the shift of the band in the degassing step.

TABLE 5-1
Band Shifts in High Frequency Modes of
Chemisorbed Ammonias and Methylamine ^(a)

	Degassing Temperature	
	25°C	400°C
NH_3	3525	3540
	3447	3452
NH_3/ND^b	3492	3494
	2575	2578
ND_3	2628	2633
	2527	2530
CH_3NH_2	3465	3466
CD_3ND_2	2570	2570

^a200 torr was adsorbed for 5 min. A $\sim 1100^\circ\text{C}$ degassed 40 mg cm^{-2} silica was used in each case.

^bOnly the partial isotope bands shown.

low coverages, giving rise to higher perturbation, but it is unreasonable that these perturbations should diminish as the coverage increases (i.e. the band shifts to higher frequencies). Further, the presence of physically or co-ordinately bound NH_3 or H_2O had no effect on the shape or position of any of the SiNH_2 bands.

It was impossible to determine whether similar shifts occurred for the SiOH band (3741 cm^{-1}) when the pressures of adsorbed NH_3 were high.

Since the effects are only prominent on large discs (40 mg cm^{-2}) it is difficult to distinguish the new SiOH (3741 cm^{-1}) from the original SiOH at 3748 cm^{-1} because of the intensity of this latter band. Also, at high pressures, the hydroxyl band cannot be observed in isolation (i.e. as SiOH on a deuterated surface) because exchange with SiOD occurs.

Furthermore, it was difficult to ascertain whether any residual 3741 cm^{-1} SiOH was retained after degassing at 650°C , corresponding to the residual 3452/3540 SiNH_2 .

The Addition of HCl

The addition of ~ 1 torr of HCl at room temperature to a surface containing SiNH_2 and SiOH species generated from the reaction of 1 torr of NH_3 with the active sites had no effect on the SiOH species (3748 and 3741 cm^{-1}) but the SiNH_2 bands immediately disappeared and new strong bands grew at 3040 and 3145 cm^{-1} probably due to NH_4^+ species. However, if larger pressures of NH_3 were initially adsorbed on the

active surface (20 torr), the gas phase NH_3 removed, and then ~ 1 torr of HCl adsorbed, the complete removal of the SiNH_2 species could not be achieved. Just as in the degassing sequences, a residual band was left which was centered around 3452 cm^{-1} (Figure 5-11(i)). This band could not be removed unless higher pressures of HCl were adsorbed (~ 5 torr) [or if higher degassing temperatures were used].

The Origin of Type 2 SiNH_2

The effects of the pressure of admitted NH_3 are quite evident if one compares the spectra obtained from the adsorption of NH_3 on two separate 40 mg cm^{-2} active silicas, both degassed at 1100°C when the admitted pressures are 200 torr (Figure 5-10) and 20 torr of NH_3 (Figure 5-11(ii)).

In the case of the lower pressure adsorption (20 torr), the absorption maxima of the symmetric stretching band at 3444 cm^{-1} was about 0.10 absorbance but for 200 torr it is about 0.17 absorbance. Degassing both samples to 650°C for 1 hr removed all of the 3444 cm^{-1} component leaving only the 3452 cm^{-1} band. For the sample which had been submitted to only 20 torr of NH_3 , this band was small with an absorbance of about 0.02, (Figure 5-11(ii)I) whereas a much larger 3452 cm^{-1} band remained for the "200 torr treated silica", with an absorbance of about 0.06 (Figure 5-10F).

Hence, there appear to be two effects due to pressure. It is instrumental in forcing the reaction of more active sites to produce more "type 1" SiNH_2 (and 3741 cm^{-1} SiOH species), but as well it results in the formation of greater amounts of "type 2" SiNH_2 (3452 cm^{-1}).

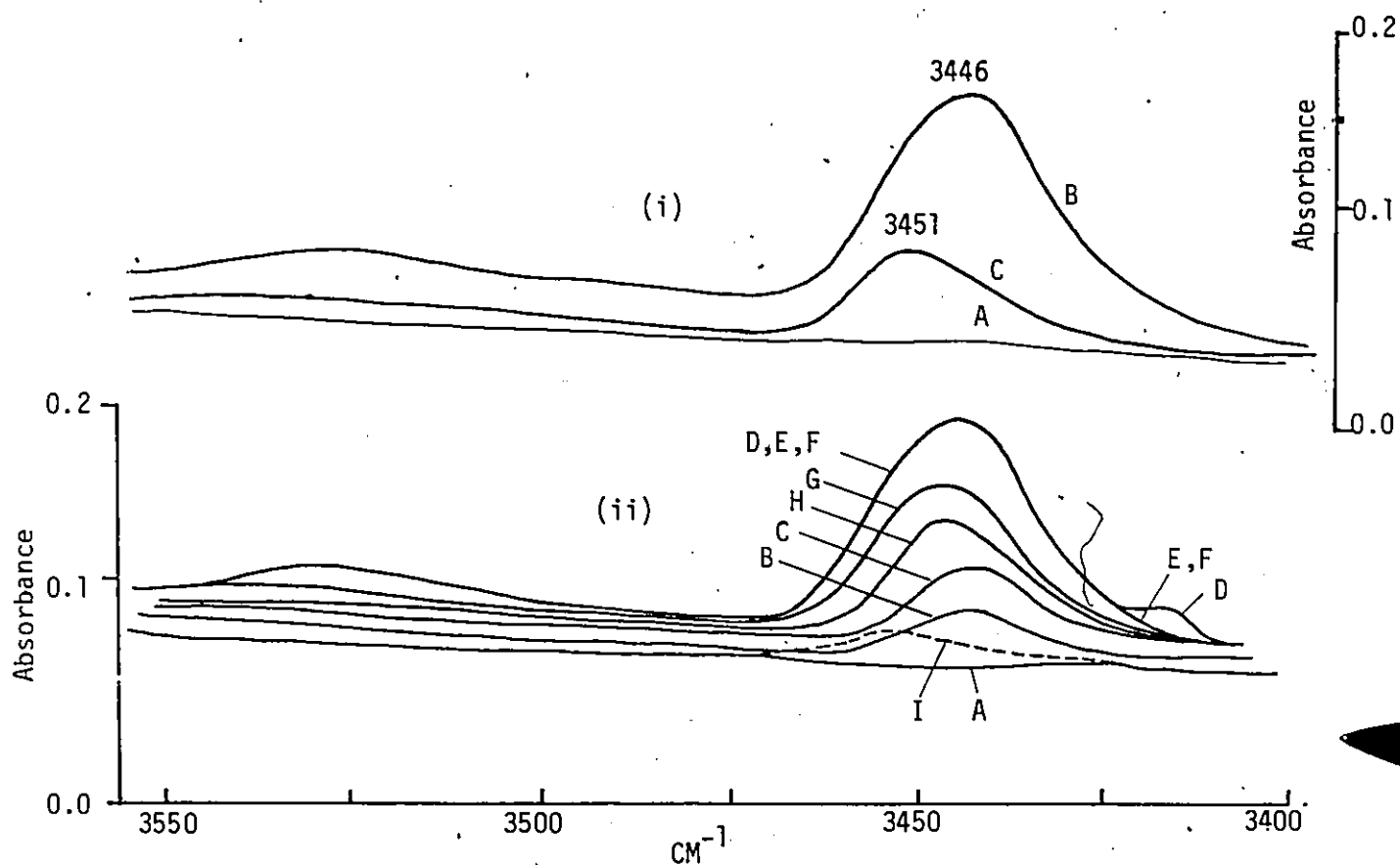


FIGURE 5-11

(i) Reaction of chemisorbed ammonia with HCl.

- A. 40 mg cm^{-2} silica degassed at 1100°C , 12 hr; cooled to room temperature.
- B. Addition of 20 torr of NH_3 . Left in cell for 5 min then pumped 5 min at room temperature.
- C. Addition of 1 torr. Left in cell for 15 min then pumped 5 min at room temperature.

(ii) Degassing chemisorbed ammonia; pressure maximum 20 torr.

- A. 40 mg cm^{-2} silica degassed at 1100°C ; cooled to room temperature.
- B. Addition of < 1 torr NH_3 , spectrum immediately; C, after 12 hr.
- D. Addition of 20 torr NH_3 for 1 min then pumped 5 min at room temperature.
- E-I. Degassed at various temperatures for 1 hr: E, 100°C ; F, 200°C ; G, 300°C ; H, 450°C ; I, 650°C .

Scan speed in (i) and (ii) was $20 \text{ cm}^{-1} \text{ min}^{-1}$.

In Figure 5-6 it is shown that beyond pressures of 10 torr of NH_3 , the 3741 cm^{-1} SiOH band did not increase in intensity whereas the SiNH_2 band did. It is also apparent that there was a slight decrease in intensity of the 3748 cm^{-1} band (comparing Figures 5-6G and H).

Apparently a reaction occurs to produce SiNH_2 species which does not involve reactive sites and which is favoured at higher pressures (>10 torr), or when all the sites have been reacted.

At lower pressures, when 1 torr of NH_3 is admitted to the cell (volume equal to ~ 300 cc) at room temperature, then for a silica disc of mass 200 mg, specific surface area $300 \text{ m}^2 \text{ g}^{-1}$ and containing ~ 0.15 sites/ $100 \text{ \AA}^2$ (see Chapter 4), then the number of molecules admitted to the cell is approximately equal to the number of sites. However, although 1 torr is nominally sufficient to consume all the sites it is unlikely that all molecules that enter the cell react with the sites due to the possibility of hydrogen bonding of NH_3 to the cell walls. Hence a 10-fold excess of NH_3 is conceivably necessary to react all sites (as observed).

If the sites are reacted in preference to some other mechanism which gives rise to type 2 SiNH_2 then this would explain why, at pressures of only 1 $\sim$ 10 torr of NH_3 , the $\sim 3447 \text{ cm}^{-1}$ band of SiNH_2 produced does not exhibit a broadness on the high wavenumber side (i.e., little type 2 SiNH_2 formed).

In order to determine how this proposed SiNH_2 might form, the SiOH profile was monitored carefully (Figure 5-12).

A small dose of NH_3 was added and the $3444/3525 \text{ cm}^{-1}$ and

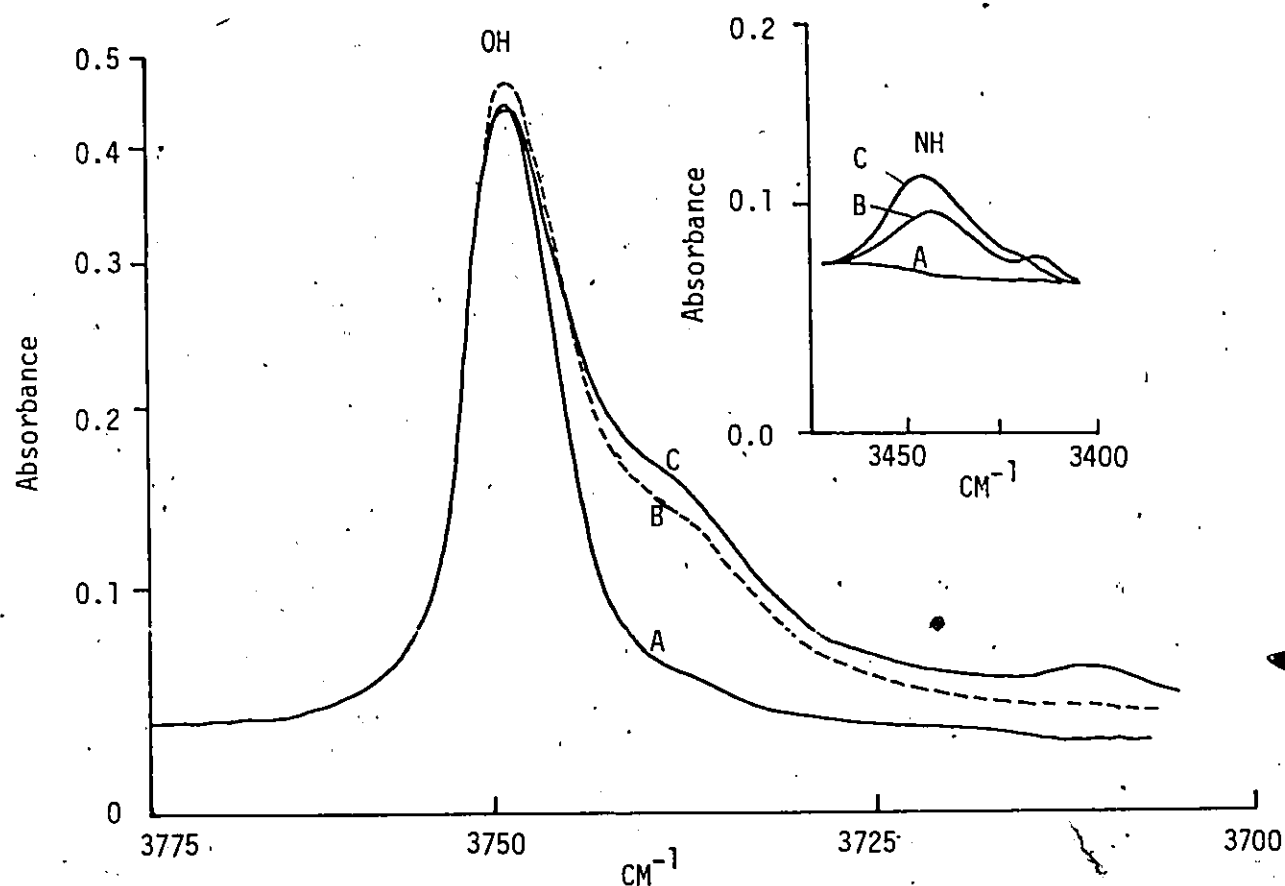


FIGURE 5-12

- A. 10 mg cm⁻² silica degassed at 1000°C 12 hr and cooled to room temperature.
- B. Admission of ~1 torr of NH₃.
- C. Admission of 120 torr NH₃ for 30 sec. then degassed at room temperature for 5 min.

Scan speed over OH region was 10 cm⁻¹ min⁻¹ and over NH region, 40 cm⁻¹ min⁻¹.

3741 cm^{-1} bands appeared. The peak maxima of the composite profile of 3741 and 3748 cm^{-1} band was centred at $\sim 3746 \text{ cm}^{-1}$ and was observed to have an intensity above that of the original 3748 cm^{-1} band (compare Figures 5-12A and B). Next, a large pressure (120 torr) of NH_3 was admitted for 30 seconds then desorbed for 5 min*. As expected the 3444 cm^{-1} band shifted to 3447 cm^{-1} and the intensity of the 3741 cm^{-1} further increased in intensity but the overall peak maxima at $\sim 3746 \text{ cm}^{-1}$ was observed to decrease slightly. This implies that the 3748 cm^{-1} component band has diminished.

It is recognized that this effect is small but was found to be a reproducible result.

One other spectral change occurred. A small band at 3720 cm^{-1} appeared (Figure 5-12C) following the addition of 120 torr of NH_3 . It is contended that the presence of this band is indicative of the presence of H_2O (see later). But the origin of this H_2O is unlikely to arise from moisture in the NH_3 sample because care was taken to predry the NH_3 over P_2O_5 several times before use.

It is believed that the above observations are consistent with the existence of a second kind of SiNH_2 which arises from the process depicted below

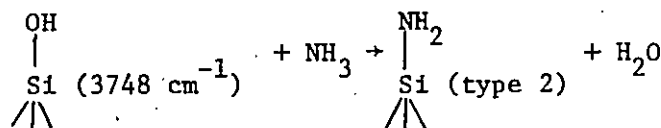


Diagram 5-8

Although it is well known that no reaction of free hydroxyls (3748 cm^{-1}) will occur with NH_3 , at room temperature, on an inactive

* There was no evidence for physically adsorbed NH_3 after pumping for 5 min.

silica (i.e., one degassed at temperatures lower than 400°C), there is reason to suspect that free hydroxyls are not in the same environment on a highly degassed surface.

For example, at the saturation vapour pressure of H_2^{18}O , exchange of the SiOH 3748 cm^{-1} hydroxyls to $\text{O-}^{18}\text{H}$ hydroxyls was observed to occur rapidly on a highly degassed surface at room temperature whereas to obtain a similar extent of exchange on an inactive silica, a temperature of 450°C is required. Since this mechanism must proceed by breakage of the Si-O bond, then it must be that on a highly degassed silica, the Si-O bond of the free hydroxyls is either weaker or the group is more accessible for attack by a bond breaking vehicle. For the same reasons, it is proposed, the formation of SiNH_2 from SiOH may also occur more easily.

The mechanism proposed in Diagram 5-8 is identical to that given for the formation of SiNH_2 species formed by reacting gas phase NH_3 over silica at 650°C (see Chapter 4). The 'properties' of type 2 SiNH_2 are similar to the "heat formed" SiNH_2 species. Both can only be totally desorbed at 1000°C (unlike type 1 which requires 650°C), both absorb at the same frequencies and both require higher pressures of HCl for exchange than does SiNH_2 type 1.

Assuming that the type 2 species is identical to the heat formed SiNH_2 , then the higher degassing temperatures cannot be related to surface-adsorbate bond strength, since the SiN stretching frequencies of type 1 and type 2 are about the same.

The type 2 SiNH_2 groups are apparently analogous to free hydroxyls and therefore neighbouring groups of other SiOH or SiNH_2

species are not likely to be in close proximity so their removal should require higher temperatures.

However, the experiment with HCl (refer Figure 5-11(1)) indicated that type 1 SiNH_2 groups were preferentially removed probably by exchange

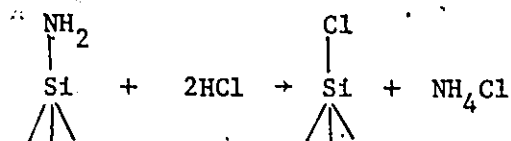


Diagram 5-9

In this reaction, proximity to neighbouring groups should not be a factor and it is possible that the type 1 SiNH_2 groups are more accessible to adsorbates.

It is concluded that there are two distinct types of SiNH_2 formed when NH_3 is adsorbed on active silica as opposed to an array of SiNH_2 species arising from differing neighbouring interactions or site energies, and the following is a summary of the properties of both types.

As coverage increases, the frequencies of the symmetric and antisymmetric stretching modes of SiNH_2 increase. Interactions between neighbouring SiNH_2 groups are probably not responsible for this effect since the frequency should decrease with increasing coverage. Both types of SiNH_2 have an Si-N stretch near 930 cm^{-1} , hence their Si-N bond strengths must be comparable, and therefore the different degassing temperatures that are required to remove these groups cannot be associated with a wide range of surface-adsorbate bond energies.

The SiNH_2 species which are formed by reaction at active sites are separated from SiOH groups by an amount which is determined

by the Si-Si distance in the original active siloxane bridge. At degassing temperatures above 300°C, the number of SiNH_2 groups diminished and the active site bands at 908/888 cm^{-1} are reformed until at 650°C their original intensity is restored. (Those formed at 650°C probably correspond to the most active bridges, that is, those in which the Si-Si distance is greatest). However, some SiNH_2 species remain (Figure 5-10F) even when all the original active bridges are reformed, and always absorb at 3452 cm^{-1} . Further increases in degassing temperature do not alter the frequency of this band. It seems to be more than coincidence that, at the temperature required to reform all original sites (650°C), the frequency of the symmetric stretching mode attains a constant value. It is proposed that those species remaining (3452 cm^{-1}) are formed by a process other than with the sites.

Two species seem to be distinguished by the reaction of HCl with SiNH_2 groups in that the addition of 1 torr of HCl to an SiNH_2 containing surface at room temperature, does not react with all SiNH_2 . Whilst the low wavenumber part of the band is removed rapidly, no further change occurs once the frequency of the band approaches 3452 cm^{-1} . Finally, the small, but reproducible changes in the SiOH profile indicate that at higher pressures of NH_3 , a new reaction occurs which involves the 3748 cm^{-1} hydroxyls and which appears to produce water. The reaction does not apparently involve active sites because the SiOH 3741 cm^{-1} band does not grow with the SiNH_2 band once pressures exceed 10 torr of NH_3 .

D. Water Adsorption

In Chapter 4 it was shown that as small increments of water vapour were admitted to an active silica surface, the 908 and 888 cm^{-1} bands were diminished uniformly as a broad band due to an SiOH band was formed at 3741 cm^{-1} .

In the light of the ammonia studies, water adsorption is proposed to occur as

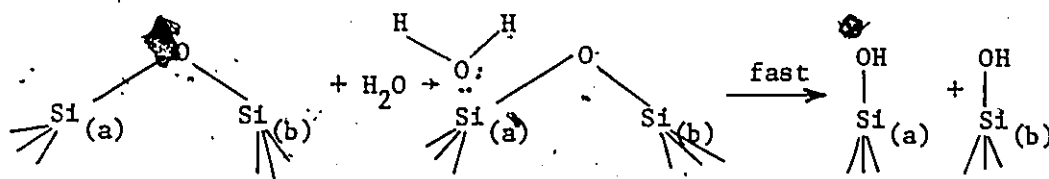


Diagram 5-10

The titration of water is again depicted in Figure 5-13. It is observed that toward the end of the titration cycle a weak broad band appears at 3720 cm^{-1} (Figures 5-13D and E). Degassing at 600°C completely removed this band (actually it could be removed at 250°C, see later), but the 3748 cm^{-1} band increased. In this particular sequence, 2 torr of H_2O was the maximum pressure adsorbed and it is probable that water desorbed from the cell walls could feasibly contribute to the reformation of the 3748 cm^{-1} , especially when the temperature for degassing is high. [When the degassing temperature is lower or is raised only slowly, it has been observed that the increase in the 3748 cm^{-1} band is not so marked.] The 3720 cm^{-1} band was much more prominent when larger amounts (10 torr) of water were added, and another broad band was also observed at 3520 cm^{-1} which appeared to grow in unison with 3720 cm^{-1} (see Figure 5-14). Degassing at 250°C

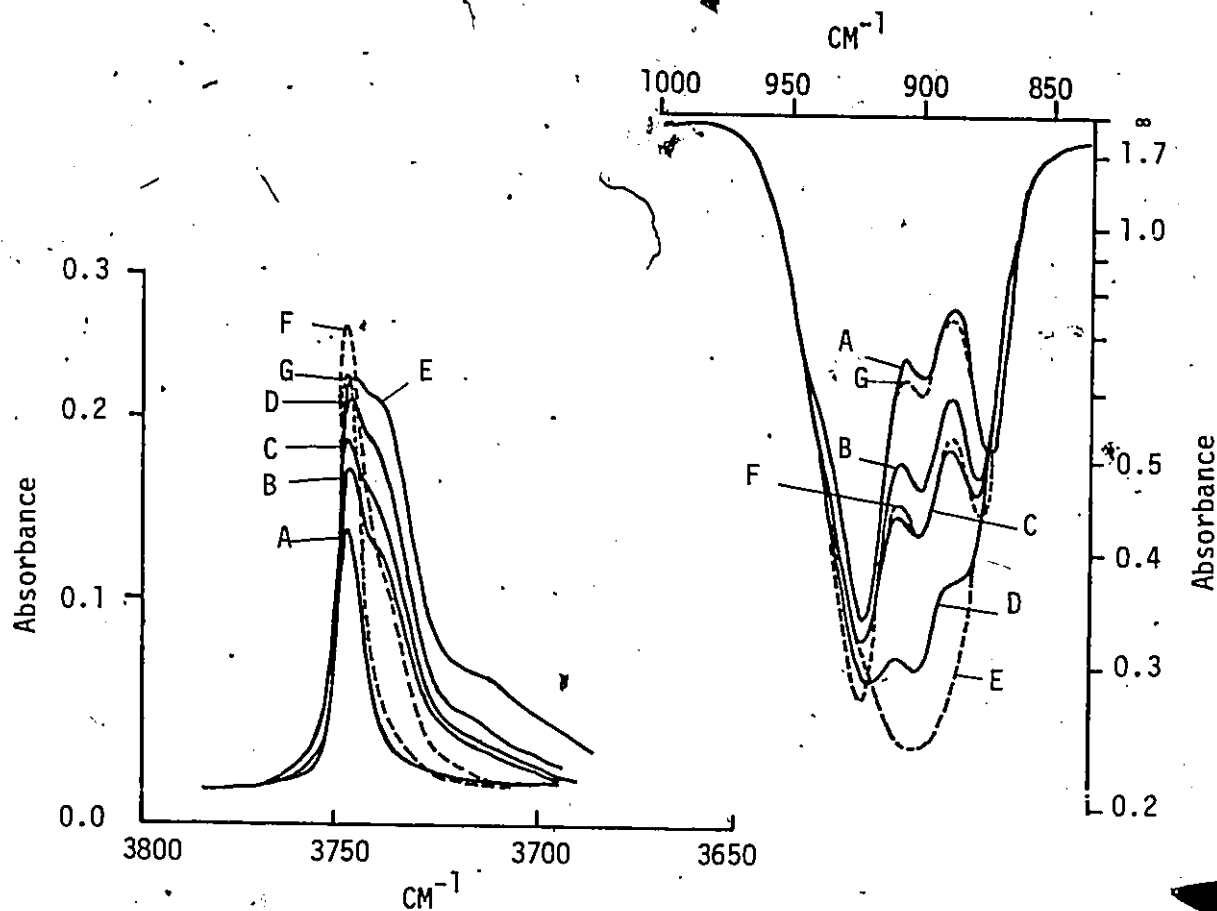


FIGURE 5-13

Adsorption-desorption cycle for NH_3

- A. 10 mg cm^{-2} silica degassed at 1100°C for 12 hr then cooled to room temperature.
 - B-D. Successive small doses of NH_3 (each dose $\sim 1 \mu\text{mole}$).
 - E. Addition of 2 torr of NH_3 for 1 min, then degassed at room temperature for 5 min.
 - F-G. Degassed at various temperatures for 1 hr; F, 600°C ; G, 800°C .
- Scan speed of $2800\text{-}3650 \text{ cm}^{-1}$ region was $40 \text{ cm}^{-1} \text{ min}^{-1}$.

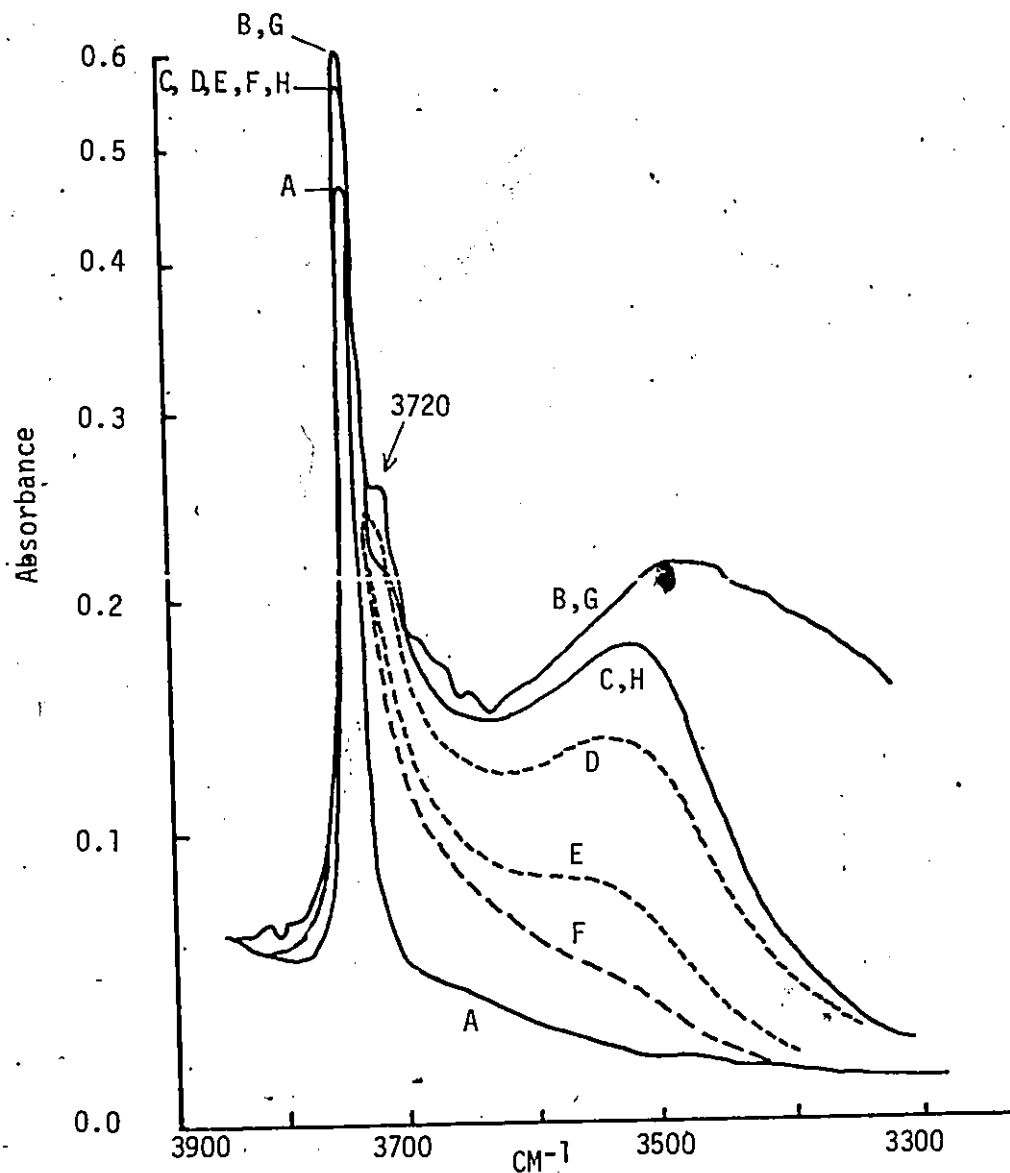


FIGURE 5-14

- A. 20 mg cm⁻² silica degassed at 1100°C for 12 hr, then cooled to room temperature.
- B. Addition of 10 torr of H₂O.
- C-E. Pumped at various temperatures for 1 hr; C, 150°C; D, 200°C; E, 250°C; F, 300°C.
- G. Readded 10 torr H₂O.
- H. Pumped at 150°C for 1 hr.

removed both these bands, but they could be immediately regenerated by again adding 10 torr of water. These new bands have been discussed by Kiselev et al.⁷⁵ (see Chapter 1), and briefly mentioned by Little and Blomfield¹⁰². Kiselev believed that molecularly bound water was responsible for the bands but Little and Blomfield, without proof, ascribed them to hydroxyl species.

Work in this laboratory has shown that the new species probably are hydroxyl groups which are indirectly related to the active sites in that they can only be formed when the surface has been degassed at temperatures sufficient to create sites ($>400^{\circ}\text{C}$) but are not actually formed from the sites. Although a small band at 3720 cm^{-1} appeared before the sites were consumed by H_2O , it continued to grow after the sites were reacted. Similarly, if the active sites were consumed by high pressures of NH_3 (200 torr), the excess gas phase removed and then water adsorbed, large bands at 3720 and 3520 cm^{-1} appeared.

The 3741 cm^{-1} hydroxyls do not appear to be the sites for the adsorption of the $3720/3520\text{ cm}^{-1}$ species. This was evidenced by the fact that no change occurred in the band shape or frequency of the 3721 cm^{-1} band when small amounts of water sufficient to form the 3720 cm^{-1} band, were adsorbed (larger amounts obscured the band).

Adsorption of O-18 Water

The addition of small amounts of H_2^{18}O to an active surface has been outlined in Chapter 4. However, the adsorption of higher pressures of H_2^{18}O to the active sites revealed other features. In

Figure 5-15 is shown the spectral changes which arise when a small amount (<1 torr) and then a large amount (2 torr) of H_2^{18}O is adsorbed to a degassed 10 mg cm^{-2} silica. Figure 5-15C shows that, as well as the composite SiOH profile centred at 3535 cm^{-1} resulting from the reaction of the active sites, two other broad overlapping features appear at ~ 3720 and $\sim 3710 \text{ cm}^{-1}$.

Kiselev⁷⁵ had proposed that when an excess of H_2O vapour was added to a dehydroxylated silica, it was adsorbed in the following way:

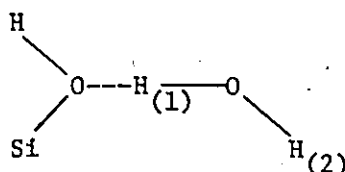


Diagram 5-11

In Kiselev's model, the stretching frequency of $\text{O-H}_{(1)}$ would be at 3520 cm^{-1} and of $\text{O-H}_{(2)}$ at 3720 cm^{-1} , similar to those found for the water dimer^{76,77}. But this model cannot be correct as the following arguments show.

The appearance of two bands in the H_2^{18}O titration, separated by close to 11 cm^{-1} (the expected shift for an O-16/O-18 exchanged hydroxyl) infers that the adsorbed water molecule results in the formation of two hydroxyl fragments, one O-16 and the other O-18. A band at 3520 cm^{-1} observed in the H_2^{16}O adsorption series (Figure 5-14) also appeared in the spectrum of the H_2^{18}O adsorption but no isotopic shift of this broad band could be detected.

A bridge-breaking reaction seems to have occurred, but the bridges cannot be the 'active site' bridges since the $3720, 3520 \text{ cm}^{-1}$ bands are also formed after these sites have reacted.

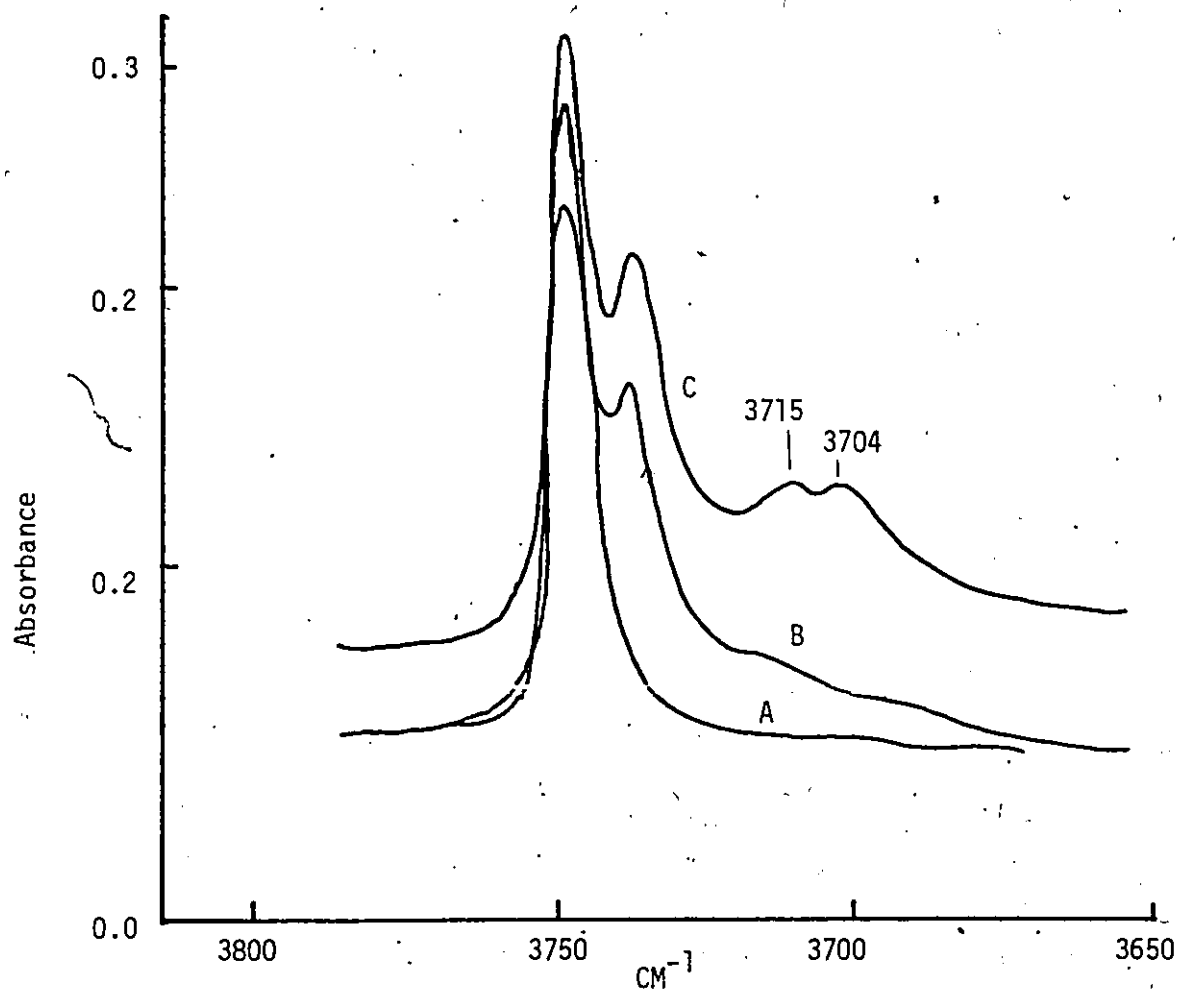


FIGURE 5-15

- A. 10 mg cm⁻² silica degassed at 1100°C for 12 hr, then cooled to room temperature.
- B. Admitted < 1 torr H₂¹⁸O.
- C. Admitted 2 torr H₂¹⁸O for 1 min, then pumped for 5 min at room temperature.

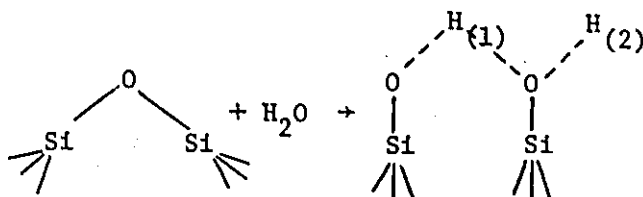


Diagram 5-12

Since the 3720 cm^{-1} band is related to the 3520 cm^{-1} band then a hydrogen bonded pair must exist, where the $\text{O-H}_{(1)}$ mode absorbs at 3520 cm^{-1} and $\text{O-H}_{(2)}$ at 3720 cm^{-1} . When the water adsorbed is H_2^{18}O , then there is a 50% chance of the O-^{18} being involved with $\text{O-H}_{(1)}$ (still 3520 cm^{-1}) and $\text{O-H}_{(2)}$ ($\sim 3710\text{ cm}^{-1}$).

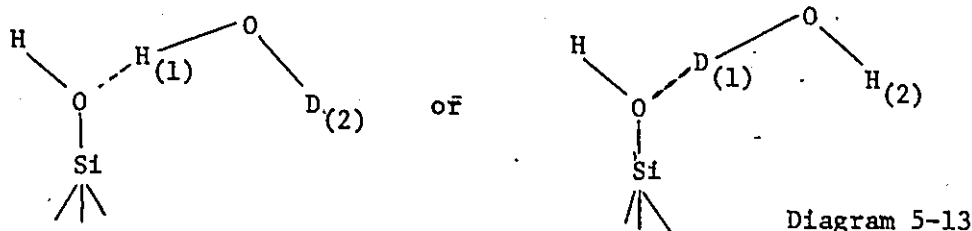
The intensities of the ~ 3720 and $\sim 3710\text{ cm}^{-1}$ bands are comparable (Figure 5-15) which may imply that no distinction is made between either silicon atom in the bridge by the attacking water molecule, and that this site, unlike the 'active sites', may be a symmetric bridge.

The possibility that a doublet at $3720/3710\text{ cm}^{-1}$ may be due to molecular water is considered. This can only arise if O-^{18} exchanges at the surface with O-^{16} of siloxane bridges or of surface hydroxyls. The SiOH band at 3748 cm^{-1} was unchanged for the addition of H_2^{18}O (2 torr), (Figure 5-15C), but the extent of exchange with siloxane bridge oxygens was not ascertained.

However, another isotope experiment also suggests that the 3720 cm^{-1} band is due to an hydroxyl and not bound water.

The adsorption of a 50:50 mixture of $\text{D}_2\text{O}/\text{H}_2\text{O}$ to an active silica showed that only the 3720 and 3520 cm^{-1} bands were formed in the O-H stretching region. (The deuterium analogues of these bands also formed.) If 3720 cm^{-1} was due to molecular water then a new band

would have been expected to absorb near 3670 cm^{-1} due to the stretch shown as $\text{O}-\text{H}_{(2)}$ (below) resulting from one of the two possible combinations with a mixed isotope.



No such band was found, so this scheme is probably incorrect.

In view of this result, it can be inferred that the 3710 cm^{-1} band appearing in Figure 5-15C is due to an $\text{O}-18$ hydroxyl species. These bridged hydroxyls were found to exchange rapidly in D_2O (at the same rate as the 3748 and 3741 cm^{-1} hydroxyls).

No other properties were investigated, but it is obvious that they must be very closely neighbouring hydroxyls since the temperature for condensation is 250°C (this would be unreasonably high for molecularly bound water). The temperature at which hydrogen bonded hydroxyls are removed from an inactive silica is 400°C .

E. The Nature of the Surface

The Origin of the $3720/3520\text{ cm}^{-1}$ Hydroxyls

When the silica surface is degassed at moderate temperatures ($25-400^\circ\text{C}$), the surface becomes dehydroxylated as hydrogen bonded hydroxyls are replaced by stable hydrophobic siloxane bridges (actually in the case of pretreated silicas, most hydrogen bonded hydroxyls have already been removed).

At a temperature corresponding to the onset of hydrophobicity

(400°C), the free hydroxyl concentration begins to diminish and new active sites are formed in their place.

The results of the adsorption studies of BF_3 and B_2H_6 ^{60,61} and H_2O and NH_3 (this work) seem to indicate that these active sites are unsymmetrical siloxane bridges. These sites do not have a uniform activity as the ammonia work showed, probably as a result of their formation from the collapse of an array of silanol groups of differing distances of separation, but they do seem to have a limiting strain energy in that the temperature required to regenerate sites after titration with ammonia is always about 650°C, and is independent of the original degassing temperature, whether it be 800 or 1200°C. As mentioned in Chapter 4, the higher temperatures initially required to form a given number of sites from an inactive silica, may be due to the migration of bound water to the surface which subsequently reacts to form more silanol groups. However, another phenomenon may also contribute. Once the active sites are formed, a new surface topography may exist. As chemisorption proceeds, the active sites are consumed, but basically the surface may remain in its new state, and subsequently much lower temperatures would be required to regenerate the sites because the chemisorbed species are likely to be in closer proximity to each other than the original hydroxyls.

In the vicinity of the strained sites there remain some free hydroxyls ($1.4 \pm 2/100 \text{ \AA}^2$ ^{O₂} after degassing at 800°C), and also the siloxane bridges resulting from the earlier collapse of the hydrogen bonded hydroxyls.

The bonds which form the active bridges are under strain,

some of which is likely to be imparted to neighbouring silicon and oxygen atoms. The proposed reaction of NH_3 with free hydroxyls (3748 cm^{-1}) at room temperature is probably a result of some strain in the silicon-oxygen bond of the silanol.

It is probable therefore, that siloxane bridges formed from the collapse of hydrogen bonded hydroxyls, and which are in the neighbourhood of active sites, are also strained to some extent, especially those which are close to the very active bridges.

Hence these bridges may have some tendency to re-open, and reform hydroxyls which absorb at 3720 and 3520 cm^{-1} .

The low temperatures required for the removal of these hydroxyls would suggest that the hydroxyls are closer together than the original hydrogen bonded hydroxyls of the inactive silica, and that the strain imparted to the bridge has had the effect of drawing the silicon atoms of the bridge closer together.

Hence, the appearance of a 3720 cm^{-1} band when excess water is added to a silica surface is an indicator of some surface strain.

Spectral Bands of the Active Sites

Assuming that NH_3 is co-ordinated, then chemisorbed (as discussed earlier) then the sites for adsorption must be distinct, as shown in Diagram 5-2, one site available for co-ordination and chemisorption and the other for chemisorption only.

The non-equivalence of the silicon atoms may be due to one of them lying in the second layer and therefore being less accessible for the initial co-ordination step.

An alternate scheme whereby the sites are proposed to be charged, does not seem tenable.

If for instance $\geq \text{Si}^+$, $\geq \text{Si-O}^-$ was responsible for the activity on silica, then it is difficult to explain how a singularly adsorbed NH_3 , Me_3N or pyridine could exist as co-ordinately bound species (a covalent bond should be formed).

Furthermore, it seems unlikely that H_2 or HCl would be unreactive on such a surface.

Morrow and Devi⁶¹ could not explain how two bands (at 908 and 888 cm^{-1}) could represent a strained bridge site. Actually there are at least three bands (another at $\sim 930 \text{ cm}^{-1}$), as shown in Figure 5-1. This latter band is associated with the co-ordination phenomenon because it disappears along with the 888 cm^{-1} band when pyridine is adsorbed, for example. These three bands cannot all be associated with the vibrational modes of the bridging oxygen. However, the Si-O modes of the oxygens connecting surface silicons with bulk silicons are likely to be different from the bulk Si-O-Si modes when the surface is strained.

Therefore the 930 and 888 cm^{-1} bands are proposed to be the Si-O modes related to " $\text{Si}_{(a)}$ " whilst the 908 cm^{-1} band is related to the Si-O mode of " $\text{Si}_{(b)}$ " where the oxygen atoms are in the second surface layer.

Reactivity of the 3741 cm^{-1} Hydroxyls

The hydroxyls formed from the active sites were found to be as accessible to D_2O and ND_3 as the free hydroxyls (3748 cm^{-1}).

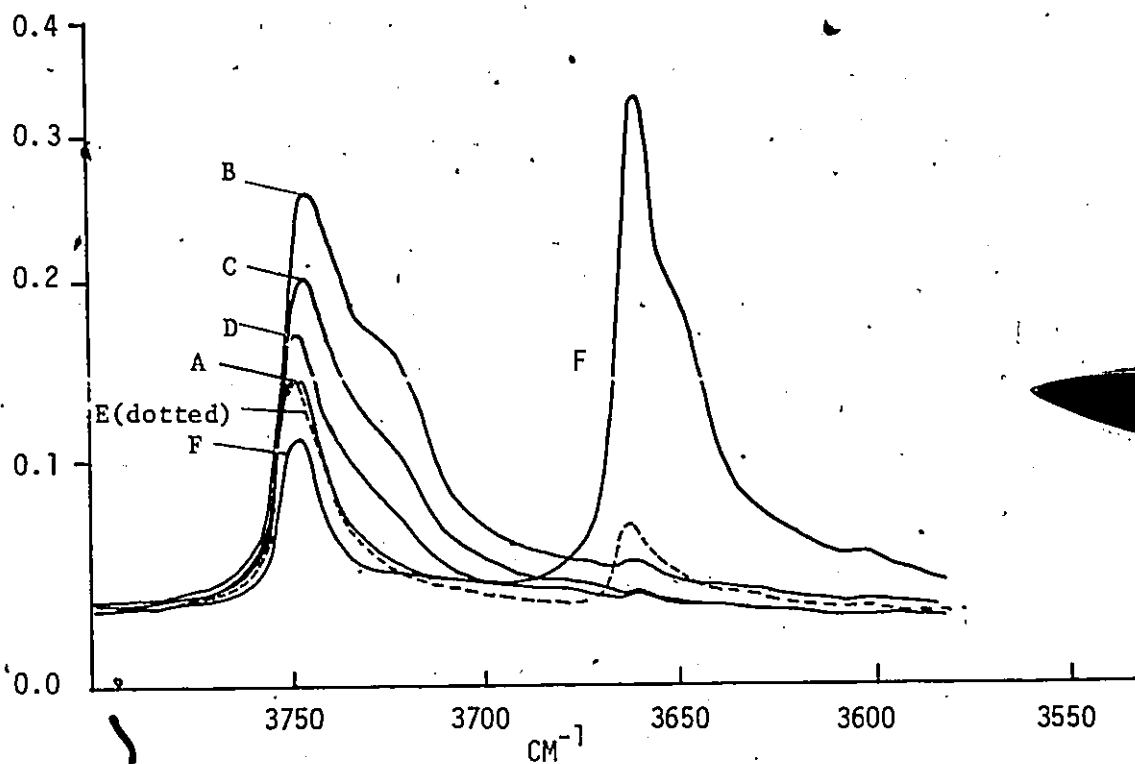


FIGURE 5-16
Reaction of 3741 cm^{-1} hydroxyls with BCl_3

- A: 10 mg cm^{-2} silica degassed at 1100°C for 12 hr, then cooled to room temperature.
- B. Addition of ~ 1 torr of H_2O (just sufficient to consume active sites).
- C. Addition of < 1 torr BCl_3 .
- D. Repeat spectrum after 30 min; E, after 3 hr.
- F. Evacuated cell for 12 hr at room temperature.

The two types of 3741 cm^{-1} species proposed to form when water is adsorbed could not be distinguished by rates of exchange.

The new hydroxyls, like the free silanols, did not react with HCl (as SiNH_2 did).

Differences between the new and free silanols are evident however. This was illustrated by the addition of BCl_3 to a surface containing both the 3748 cm^{-1} and 3741 cm^{-1} hydroxyls; the latter hydroxyls reacted preferentially. (see Figure 5-16).

Pumping for 16 hr, produced two BOH species near 3700 cm^{-1} ⁵⁴ formed in the same ratio as the $3748:3741\text{ cm}^{-1}$ SiOH band intensities (Figure 5-16F).

In a different experiment, the active sites were first reacted with NH_3 , the excess NH_3 removed, then HCl was added to exchange the $-\text{NH}_2$ groups. BCl_3 was added, and again, both the 3748 and 3741 cm^{-1} hydroxyls reacted, but this time, pumping did not produce BOH species.

From these experiments it might be tentatively concluded that $-\text{BOH}$ can only form on a dehydroxylated surface when there are hydroxyls formed at $\text{Si}_{(a)}$ and $\text{Si}_{(b)}$ (i.e. from reaction with H_2O). Apparently these hydroxyls are required for both types of $-\text{BOH}$ to form.

No further experiments were conducted with BCl_3 but it is certain that studies with this molecule and BF_3 will help to identify more of the properties of the 3741 cm^{-1} hydroxyl groups.

Summary

When silica surfaces are degassed at high temperatures, the surface becomes strained as active siloxane bridges are formed. The

strain extends to other parts of the surface, influencing the behaviour of the free silanols, and of neighbouring "inactive" bridges.

The adsorption of water or ammonia to such a surface results in interactions and reactions with each of the active sites, silanols and "inactive" bridges.

Subsequently, new hydroxyls form which absorb at 3741 cm^{-1} (two types in the case of water) and at 3720 and 3520 cm^{-1} , and the facility for exchange of the 3748 cm^{-1} hydroxyls is enhanced such that SiNH_2 or Si^{18}OH may be formed more readily than on an inactive surface.

CHAPTER 6

CYANIDES ON SILICA

There have been several infrared spectroscopic investigations of the reactions of hydrogen cyanide with oxide surfaces, and there is general agreement that polymers of HCN (mainly diamino maleonitrile) only form when active centres are present (e.g. B or Al atoms)¹¹⁴⁻¹¹⁷. Likewise, organic nitriles do not undergo any chemical interaction with pure silica, although strong physical adsorption can result from hydrogen bond interaction, between the nitrogen atom and the surface hydroxyl groups¹¹⁸⁻¹²¹.

Ruttenberg and Low¹²² have investigated the reactions of cyanogen with silica and although they found that the reaction was slight at 25°C, extensive reaction occurred at higher temperatures (up to 600°C). Their spectra indicated that several new surface species were formed which appeared to contain the $\text{-C}\equiv\text{N}$ group, as evidenced by the appearance of infrared absorptions between 2350 and 2000 cm^{-1} . In addition, gaseous HCN appeared to be produced as a result of interaction between C_2N_2 and surface silanol groups and polymeric HCN species were produced at the highest temperatures employed.

They assigned a pair of infrared bands at 2310 and 1465 cm^{-1} to a surface silylisocyanate (SiNCO) species, rather than to a silylcyanate (SiOCN) and the lower wavenumber bands (2218, 2098, 2080 cm^{-1}) were arbitrarily attributed to various unspecified cyanide species.

Eley et al.¹²³ have recently found that bands at 2308 cm^{-1} and 2110 cm^{-1} are produced when ethylisocyanate reacts with silica at high temperatures which they assigned to surface SiNCO and to the CN bands of diaminomaleonitrile respectively.

The above assignments were based on chemical rather than spectroscopic arguments, mainly by considering data from known cyano-silicon and isocyanatosilicon compounds. However, cyanides (-CN), isocyanides (-NC), cyanates (-OCN), isocyanates (-NCO), fulminates (-CNO), isofulminates (-ONC) and carbonyls (-CO), all have strong infrared absorption bands in the spectral region between 2350 and 2000 cm^{-1} , so the above assignments are to be considered tentative¹²⁴.

In this chapter, isotopic substitution data (carbon-13, nitrogen-15, oxygen-18, deuterium) along with force constant calculations have been used in order to more completely characterize the nature of the surface species which are produced when hydrogen cyanide, acetonitrile and cyanogen react with highly degassed silica surfaces. The present work also serves as a precursor to the interpretation of more complex systems involving similar reactions on silica supported metals (see Chapters 6 and 7).

Experimental

The silica samples contained $10\text{--}20\text{ mg cm}^{-2}$ and were pressed at about 70 kg cm^{-2} . In general, the silica had been heated at 700°C in air prior to pressing discs (in order to oxidize hydrocarbon impurities), although no differences were noted if this step was omitted.

The silica was heated in vacuum for two hours at 1000°C prior

to reaction. The discs were mounted in cell A where subsequent thermal treatments or reactions up to 1000°C could be carried out (specific details are given below).

All C_2N_2 and HCN isotopes were prepared from the appropriate KCN salt which had the following percentages of isotope atom:

Carbon-13 (60% and 95%); nitrogen-15 (95%); Oxygen-18 as O_2 (99.4%) and as H_2O (98.7% O-18) were obtained from Oak Ridge National Laboratory. The O-18 exchanged silicas were prepared by heating silica in H_2O^{18} vapour over a period of about 3 hours, during which several new additions of H_2O^{18} were made. A surface concentration of O-18 of about 60% was obtained. This value represents the ratio of $O^{18}-H$ to $O^{16}-H$ in the 3750-3730 cm^{-1} region. All spectra were recorded at spectral slit widths of about 5 cm^{-1} . Force constant calculations were carried out using the standard computer program of Schachtschneider⁸⁴.

Results

In agreement with other recent work¹¹⁴⁻¹¹⁷, no chemisorbed species or polymerization products were detected when 10 torr of HCN was left in contact with silica for times up to 24 hours and with sample temperatures ranging from 25°-500°C. However, if silica was heated at 800°C with 10 torr of HCN in the cell then the spectrum shown in Fig. 6-1a was observed after cooling to 25°C and evacuating until the pressure dropped to less than 10^{-4} torr. (It should be noted that the silica background absorption rises very steeply from 2150 to 2000 cm^{-1} , see Figure 1-1, of Chapter 1, but with a compensating silica disc in reference beam, this effect is cancelled. However, the

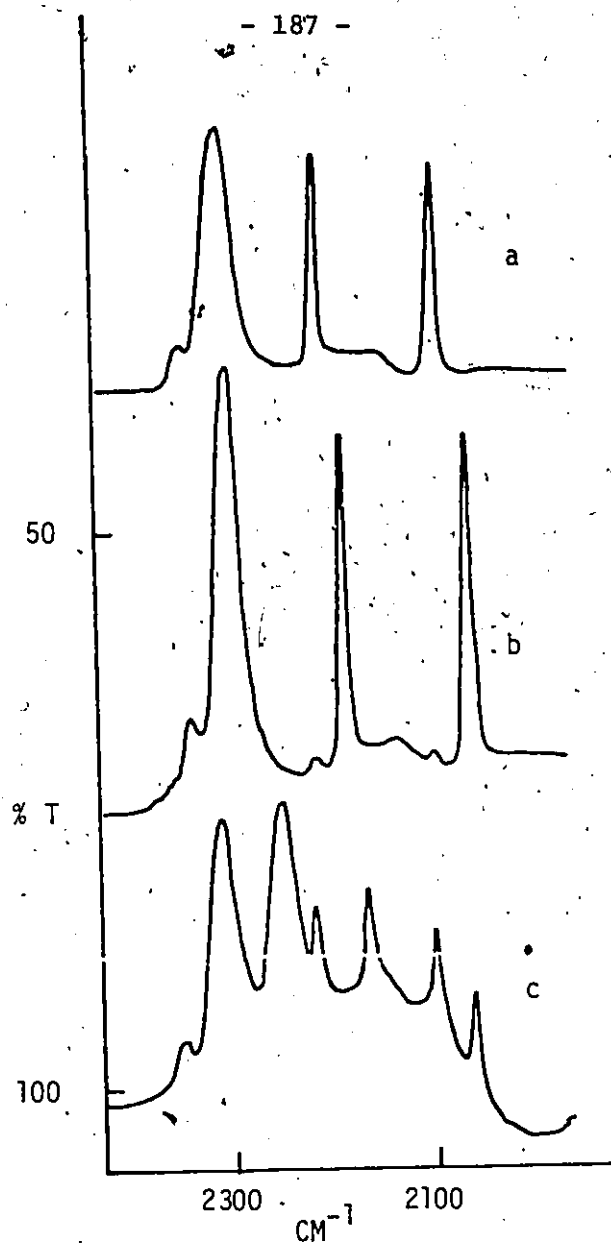


FIGURE 6-1

- a. Infrared spectrum after reaction of HCN with silica at 800°C.
- b. HC^{15}N (95% N-15) at 800°C.
- c. H^{13}CN (60% C-13) at 900°C. The % T scale refers to spectrum b.

remaining spectra in this chapter show this background rise, and Figure 6-4b is to be compared to Figure 6-1a).

Three sharp bands were observed at 2313, 2218 and 2100 cm^{-1} with weaker features near 2353 and 2150 cm^{-1} . The band profile did not change with prolonged evacuation and no additional spectral features were noted between 4000 and 1300 cm^{-1} . The corresponding spectra obtained after reacting nitrogen-15 and carbon-13 enriched HCN are shown in Figure 6-1b and 6-1c respectively, and the wave-numbers of all observed bands are listed in Table 6-1. No shifts in the band position resulted if deuterated hydrogen cyanide was used or if HCN was reacted with a deuterated silica. The ratio of the three strong bands varied as heating continued but the ratio of the intensity of the 2353/2313 cm^{-1} bands appeared to be constant.

No spectral changes resulted if 20 torr O_2 was added at 25°C but if the sample was subsequently heated at 200°C the 2100 and 2218 cm^{-1} bands decreased in intensity and that of the 2313 cm^{-1} increased. At the same time very weak bands at 1470 cm^{-1} and at 3070 cm^{-1} were just detectable and their intensities grew with the 2313 cm^{-1} band. All bands disappeared after heating at 500°C in O_2 .

The intensity of the three major bands increased more or less uniformly for reaction temperatures of greater than 800°C (though at lower temperatures some differentiation in the rate of growth of the bands was observed, see later) and the intensity of a weak feature near 2150 cm^{-1} grew dramatically. Spectra showing these effects after heating at 800°C and at 1000°C, are shown in Figures 6-2a and 6-2b respectively.

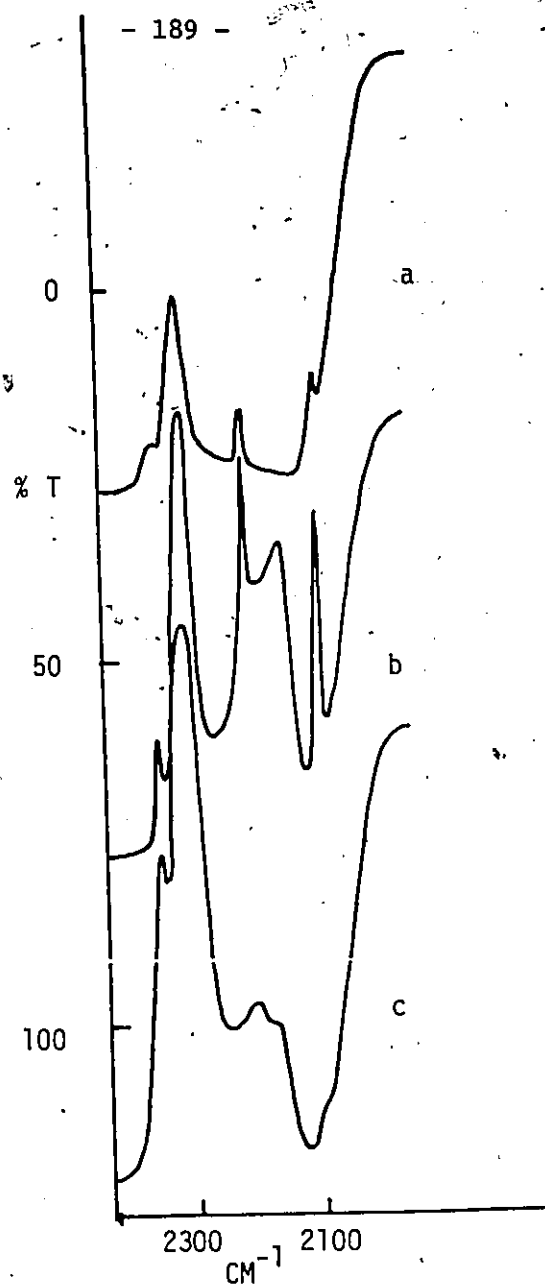


FIGURE 6-2

- a. Infrared spectrum after reacting HCN with silica at 800°C;
 - b. after reaction at 1000°C;
 - c. after heating sample b in O₂ at 400°C.
- The % T scale refers to spectrum b.

After heating in O_2 at $400^\circ C$, the 2313 cm^{-1} band again intensified whereas those to lower frequency disappeared or were diminished, leaving a broad doublet near $2150\text{--}2200\text{ cm}^{-1}$ (Figure 6-2c). The growth of the band near 2150 cm^{-1} was accompanied by the parallel growth of bands at 3450 and 3540 cm^{-1} , and several bands between $1370\text{--}1600\text{ cm}^{-1}$, the latter bands, at least, seeming to be related to polymeric species^{115,117,118}. Similar features near 2165 and 2185 cm^{-1} have been reported by Ruttenberg and Low¹¹⁸ when silica was heated with cyanogen at high temperatures which were likewise attributed to polymeric species. Part of the broad absorption near $2150\text{--}2200\text{ cm}^{-1}$ in Figure 6-1c is also due to polymer formation in this case.

The extremely weak 1470 cm^{-1} band was superimposed on the steeply rising background absorption due to silica and only appeared with appreciable intensity when the 2313 band was very intense (see Figure 6-4). The band at 3070 cm^{-1} likewise grew in intensity with the growth of the 2313 cm^{-1} band. The experimental isotopic shifts for the 1470 cm^{-1} band are given in Table 6-1.

In order to see if any of the three strong bands underwent a shift with oxygen-18, a silica containing about 60% O-18 was prepared. The ^{18}O distribution was measured with respect to the $O^{16}\text{--}H/O^{18}\text{--}H$ silanol band and does not necessarily reflect the degree of oxygen-18 exchange in the surface siloxane bridge sites. The 2218 and 2100 cm^{-1} bands showed no O-18 shift, whereas the 2313 cm^{-1} band maximum shifted to about 2305 cm^{-1} and had an irregular band shape as it was overlapped with the normal 2313 cm^{-1} band.

At the same time, the 1470 cm^{-1} band distinctly shifted to

TABLE 6-1

Observed Frequencies and Isotopic Shifts

Observed ν cm ⁻¹	C ¹³ shift ^a cm ⁻¹	N ¹⁵ shift cm ⁻¹	O ¹⁸ shift cm ⁻¹
3070	-	-	-
2353	60	10	-
2313	60	10	13 ^b
2218	51	30	0
2100	39	36	0
2078	58	20	0
1505	0	25	-
1470	0	30	34

^aAll shifts are to lower wavenumber relative to column 1. A dash (-) indicates that no measurement was made.

^bEstimated from Figure 6-3 (see text).

about 1436 cm^{-1} . In order to determine the O-18 shift of the 2313 cm^{-1} band more accurately, HCN was reacted with an O-16 silica at 800°C and a spectra was obtained like that in Figure 6-1a. An abscissal expanded spectrum from $2400\text{--}2200\text{ cm}^{-1}$ is shown in Figure 6-3a.

The sample was then heated at 300°C in O_2^{18} gas and the spectra shown in Figure 6-3b was obtained. The "spectrum" shown in Figure 6-3c results from the subtraction of that in Figure 6-3a from that in Figure 6-3b. The maximum intensity is at 2300 cm^{-1} which can be attributed to the corresponding O-18 containing species.

The same spectral features were produced when CH_3CN and CH_3NH_2 were used in place of HCN except that a spectrum of gaseous CH_4 was observed after reaction with CH_3CN .

As reported by Ruttenberg and Low¹²², the same bands were also produced when C_2N_2 was reacted with silica at temperatures in the range $25\text{--}500^\circ\text{C}$. The 2218 cm^{-1} band was initially observed at 2212 cm^{-1} and shifted to 2218 cm^{-1} as the reaction temperature was raised. The intensity of all bands increased with temperature and with reaction temperatures greater than 500°C an additional sharp band appeared at $2078\text{--}2075\text{ cm}^{-1}$ (Figure 6-4c). As the intensity of the $2353/2313\text{ cm}^{-1}$ bands increased, so did the intensity near 1470 cm^{-1} , and an additional shoulder appeared at 1505 cm^{-1} . The isotopic shifts of $2353/1505\text{ cm}^{-1}$ bands are given in Table 6-1, although no O-18 shifts could be measured, due to overlap by the stronger bands. No isotopic shifts were detected if C_2N_2 was reacted with a deuterated silica.

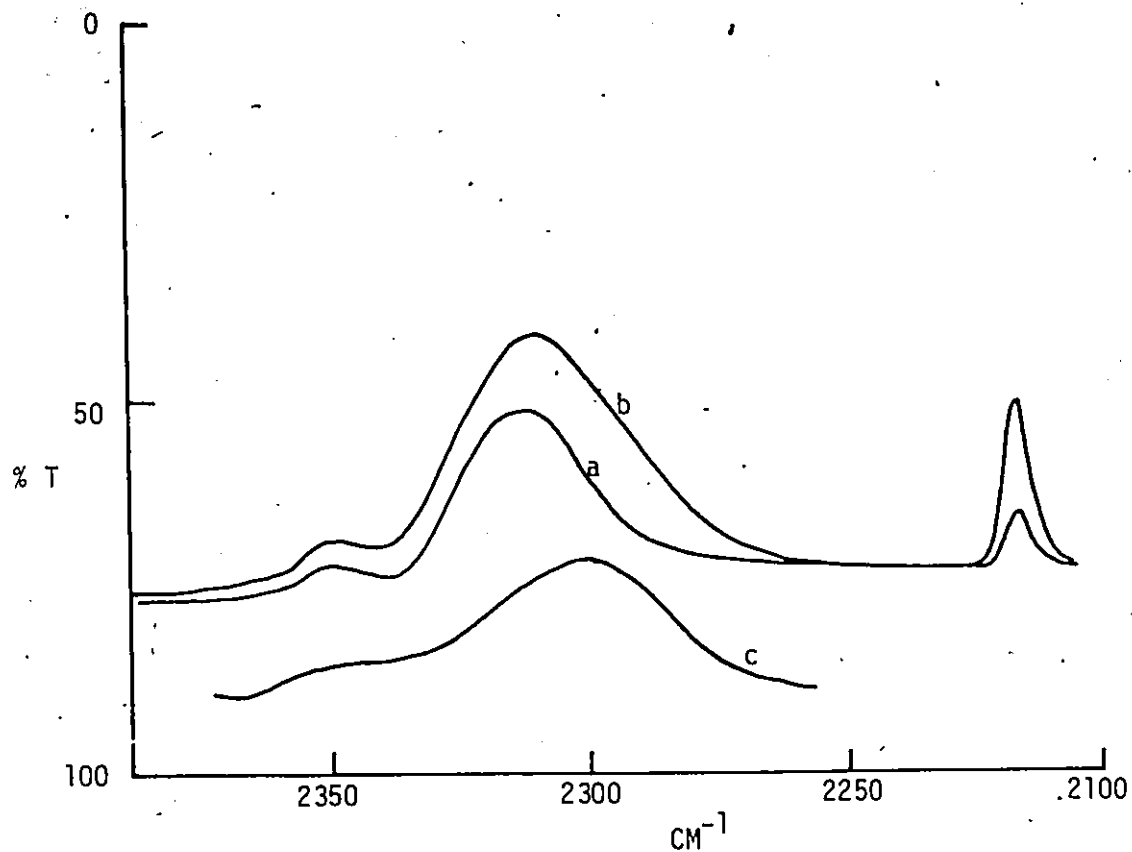


FIGURE 6-3

- a. Spectrum after reaction of HCN with silica at 800°C.
 - b. After reaction of 'a' with 99.5% oxygen-18 at 300°C.
 - c. Spectrum obtained after subtraction of 'b' from 'a' (see text).
- The % T scale refers to 'a' and 'b'.
The scan speed was 20 cm⁻¹ min⁻¹.

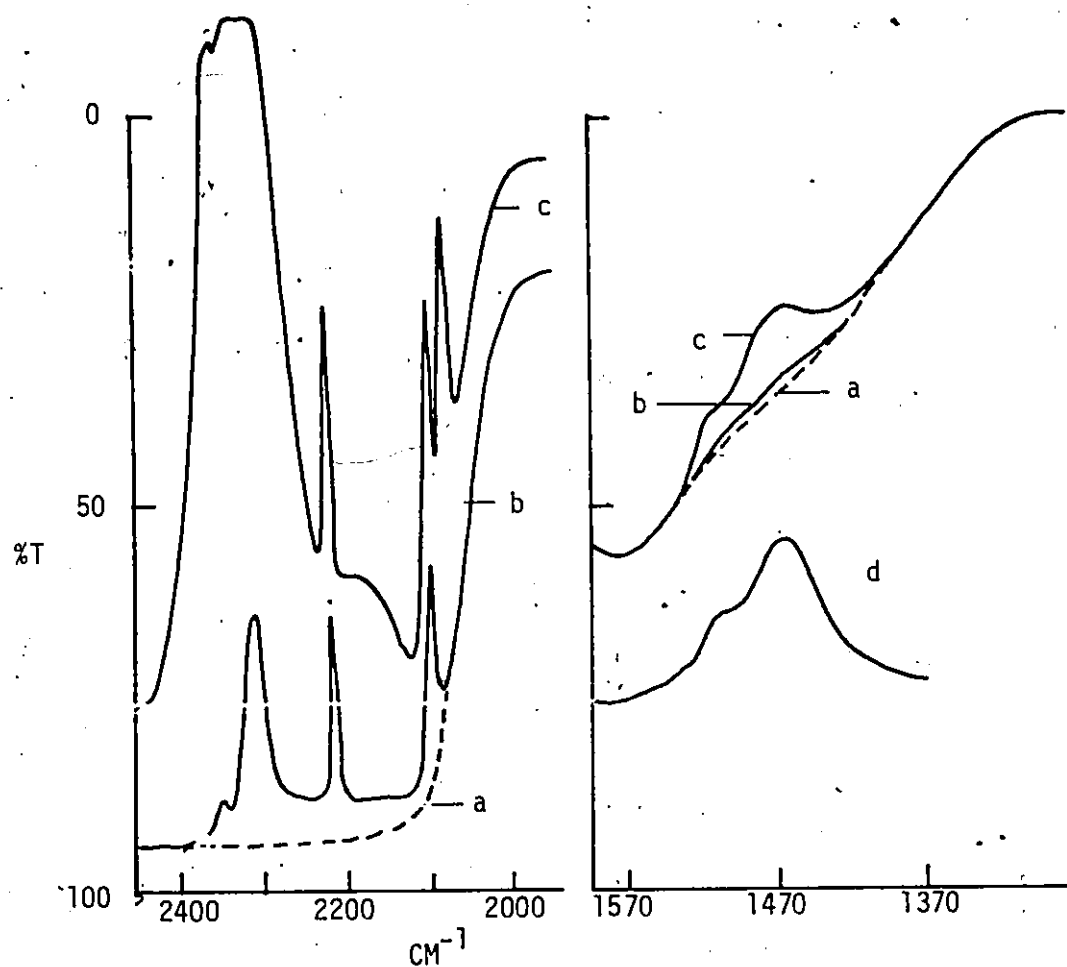


FIGURE 6-4

- a. Background spectrum without reference compensation;
- b. Spectrum after reaction of HCN with silica at 800°C;
- c. Spectrum after reaction of C_2N_2 with silica at 600°C;
- d. Spectrum 'c' recorded with a blank silica disc in the reference beam of the spectrometer.

The % T scale refers to a and b (and c on the left).

Discussion

Four new infrared bands are produced between $2400\text{--}2000\text{ cm}^{-1}$ when HCN, CH_3NH_2 , CH_3CN or C_2N_2 react with silica, and a fifth band (at 2078 cm^{-1}) is unique to the C_2N_2 reaction. Bands at 3070, 1505 and 1470 cm^{-1} grow in intensity at the same rate as the $2353/2313\text{ cm}^{-1}$ absorptions.

Ruttenberg and Low¹²² assigned the $2313/1470\text{ cm}^{-1}$ bands to a surface SiNCO species on the basis of comparison of these frequencies with known silylisocyanate species and ruled out the possibility that SiOCN was formed, although this species might seem more likely when C_2N_2 reacts with silanol groups. They arbitrarily attributed the lower wavenumber bands to "surface cyanides". Eley et al.¹²³ also found a band near 2308 cm^{-1} when ethylisocyanate reacted with silica at 573°K , which they attributed to the formation of a surface SiNCO species by analogy with the spectra of known silylisocyanates.

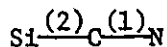
The assignments above must be considered tentative in view of the large number of carbon-nitrogen and carbon-oxygen-nitrogen species which could conceivably absorb in this spectral region.

From the isotopic shift data, it can be concluded that (a) none of the above species from HCN or C_2N_2 chemisorption contain hydrogen, (b) the species responsible for the 2100 and 2218 cm^{-1} bands contain carbon and nitrogen only, and (c) the species responsible for the $2313/1470$ bands contains carbon, nitrogen and oxygen. Further, no more than one new shifted band was observed from partial isotopic substitution, which suggests that one functional group is responsible for each set of bands and these contain only one C, N or O atom.

The 2218 and 2100 cm^{-1} bands are probably due to surface cyanides or isocyanides, which in turn are converted to the oxygen containing species responsible for the 2313 cm^{-1} band after heating in O_2 .

The expected C^{13} and N^{15} isotopic shifts for both bands assuming both structures as linear "molecules" have been calculated and the results are shown in Table 6-2.

The co-ordinates used for the calculation were as follows



and,

$$G = \begin{pmatrix} \mu_N + \mu_C & -\mu_C \\ -\mu_C & \mu_{\text{Si}} + \mu_N \end{pmatrix} \quad F = \begin{pmatrix} F_1 & F_{12} \\ F_{21} & F_2 \end{pmatrix}$$

A similar set of values were used for SiNC, except that the off diagonal element is $-\mu_N$. A mass of 28 or 100 was assumed for Si (since it is difficult to predict what value to use for a surface Si group). The calculation proceeds by finding the values of the force constants required to fit the observed frequencies. It was found that by allowing the values of each of the three force constants to vary resulted in only small values for F_{12} ($=F_{21}$). If F_{12} was fixed at zero and only F_1 and F_2 allowed to float, the predicted frequency shifts were still within ± 1 cm of the observed values. It was necessary to assume a value for the SiC and SiN stretching vibration (otherwise the number of force constants exceeds the number of frequencies). The values assumed were 608 cm^{-1} for $\nu(\text{SiC})$ based on this value for $\text{SiH}_3\text{CN}^{125}$, and 570 cm^{-1} for $\nu(\text{SiN})$, as this is a fairly

TABLE 6-2
Force Constant Calculations for SiCN and SiNC

Observed ν cm^{-1}	Species	ΔC^{13^a}	ΔC^{13}	diff	ΔN^{15}	ΔN^{15}	diff
		obs	calc		obs	calc	
2218	SiCN	51	51	0	30	30	0
	SiNC	51	43	8	30	37	7
2100	SiCN	39	48	9	36	28	8
	SiNC	39	39	0	36	36	0
2202	SiD ₃ CN ^b	51			32		
2198	Me ₃ SiCN ^c	51			31		
2095	Me ₃ SiNC ^c	40			35		

^a Δ is the frequency shift to lower wavenumber as compared with the value in column 1.

^bReference 125.

^cReference 126.

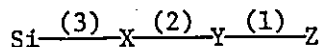
average value in several other SiNC containing compounds^{126,128-131}. The computed shifts were quite insensitive to the choice of parameter, identical $\nu(\text{CN})$ and $\nu(\text{NC})$ shifts being calculated if the $\nu(\text{SiC})$ and $\nu(\text{SiN})$ modes were as high as 900 cm^{-1} . The calculated values in Table 6-2 were for a mass 28 Si atom, using the above mentioned assumed SiC and SiN stretching modes. The data indicates that the 2218 cm^{-1} mode can be assigned to a surface SiCN whereas the 2100 cm^{-1} band can be assigned to a surface SiNC species. Both the band positions and the isotopic shifts are entirely consistent with these data for known silylcyanides and isocyanides¹²⁶. The calculations for SiCN and SiNC resulted in the following force constants: SiCN; $F_{\text{CN}} = 17.50$; $F_{\text{SiC}} = 3.14$ and $F_{12} = -0.19 \text{ m dyne \AA}^{-1}$ (for $\nu_{\text{SiC}} = 608 \text{ cm}^{-1}$). SiNC; $F_{\text{CN}} = 15.67$; $F_{\text{SiN}} = 2.77$; $F_{12} = -0.46$ (for $\nu_{\text{SiN}} = 570 \text{ cm}^{-1}$).

A similar calculation can, in principle, be carried out for various SiXYZ species, where X, Y and Z are any of C, N or O. However, it is necessary to make some assumption about the geometry. Possible surface species are SiOCN (cyanate), SiNCO (isocyanate), SiCNO (fulminate) and SiONC (isofulminate). Assuming that the XYZ portion is linear, then there should be one high frequency pseudoantisymmetric XYZ stretch ($2200 \pm 200 \text{ cm}^{-1}$) and one low frequency pseudosymmetric stretch ($1300 \pm 200 \text{ cm}^{-1}$), with the intensity of the latter being very low in view of the expected near zero dipole moment change in this vibrational mode. Further, the pseudosymmetric mode should show virtually no isotopic shift for substitution of the "middle" atom. Experimentally, the 1470 cm^{-1} band underwent no shift at all only for C-13 substitution, so the fulminate structures can be ruled out

from consideration (no silylfulminates or silylisofulminates are known).

The SiNC angle in silylisocyanates is linear or near linear¹³²⁻¹³⁴ and in view of the low frequency of this bending mode^{126,128-131}, it behaves as a pseudo linear molecule with respect to the SiNCO atoms¹³⁵⁻¹³⁶. Several force constant calculations have been carried out under this assumption. No silylcyanates are known, but this angle is expected to be linear or near linear and can be treated as such for the same reasons.

In a general valence force field treatment of the three stretching vibrational modes of a linear Si-X-Y-Z molecule there are six force constants (three diagonal, plus three off diagonal interaction constants). Designating the bonds as follows,



the principal (diagonal) force constants are F_1 , F_2 and F_3 , whereas the interaction constants, which are generally much smaller than the diagonal F 's, are f_{12} , f_{13} and f_{23} . The value of f_{13} is expected to be insignificant (and in what follows, has been set equal to zero) whereas, f_{12} is expected to be unusually large in view of the near equal masses of X-Y-Z in this linear structure; that is, there is generally strong coupling between $\nu(\text{YZ})$ and $\nu(\text{XY})$ modes, which has given rise to the terms "pseudosymmetric" and "pseudoantisymmetric" as used above. Because of the relatively large mass difference between Si and X ($X = \text{N}, \text{C}$ or O), the f_{23} term is also expected to be very small and also has been set equal to zero in the calculations.

The G and F matrices are.

$$G = \begin{bmatrix} \mu_Y + \mu_Z & -\mu_Y & 0 \\ -\mu_Y & \mu_X + \mu_Y & -\mu_X \\ 0 & -\mu_X & \mu_X + \mu_Z \end{bmatrix} \quad F = \begin{bmatrix} F_1 & f_{12} & 0 \\ f_{12} & F_2 & 0 \\ 0 & 0 & F_3 \end{bmatrix}$$

Because of the large expected values of f_{12} , the computation problem for a linear SiXYZ structure is much more awkward than for the SiXY structures discussed previously. Thus, two valence force constants could be assumed in SiXY case which are calculated from the values of $\nu(\text{SiX})$ and $\nu(\text{XY})$ for the "normal" molecule, and in turn, these force constants could be used to calculate the N^{15} and C^{13} shifts. The analogous procedure cannot be used for the SiXYZ (assuming three F's to be calculated from three stretching frequencies for the non-isotopic molecule) if f_{12} is large. In some cases, the calculated force constants may be unreasonably large or small, or may be imaginary. Even for the cyanate ion (OCN^-)¹³⁷ and the cyanate free radical¹³⁸, where the stretching frequencies are 2230/1260 cm^{-1} and 1922/1275 cm^{-1} respectively, the diagonal force constants are

imaginary without the inclusion of an appreciable interaction term.

For comparative purposes, the literature values^{137,138} for the cyanate ion are $F_{\text{CN}} = 15.47$, $F_{\text{CO}} = 11.46$ and $f_{\text{CN/CO}} = 1.15 \text{ mdyne } \text{\AA}^{-1}$, and for the NCO radical, $F_{\text{CN}} = 10.82$, $F_{\text{CO}} = 12.93$, $f_{\text{CN/CO}} = 2.56 \text{ mdyne } \text{\AA}^{-1}$.

Large interaction force constants have also been suggested for HCNO^{138} , $\text{Cl}_3\text{SiNCO}^{131}$ and $\text{H}_3\text{SiNCO}^{130}$. The computational problem is further complicated by the necessity of assuming a value for $\nu(\text{SiN})$

in SiNCO and $\nu(\text{SiO})$ in SiOCN. For silylisocyanates, 570 cm^{-1} was chosen as this is very close to the mean value reported for several known compounds^{126,128-131}, and is reported to be at 577 cm^{-1} in silylisocyanate¹⁹. Since no silylisocyanates are known, values ranging from 600 to 900 cm^{-1} were assumed, based on known ranges of the SiO stretching frequencies.

SiNCO Calculations

The results of some calculations for a linear SiNCO structure are shown in Table 6-3.

In the three force constant calculation (no interaction constants), the three frequencies of the normal molecule were used as input data for the refinement procedure, and the calculated F_g were then used to calculate the frequencies of the three isotopically substituted forms. [In all of this work, any mathematical solution for which a principal force constant was not in the range $2 < F < 25 \text{ mdyne } \text{\AA}^{-1}$ was rejected.] It can be seen that the calculated shifts, along with the values of the F_g are not reasonable. On the other hand, with the inclusion of the expected large interaction constant $f_{\text{CO/CN}}$, very good agreement between calculated and observed frequencies was achieved, and the values of the force constants are very close to those which have been quoted for other isocyanate systems. As additional data for the refinement procedure, the accurately known C^{13} and N^{15} shifts of the 2313 cm^{-1} band were employed. Further, the solution was mathematically well defined in that an identical result was produced regardless of the initial choice for F_{CN} and F_{CO} , all

TABLE 6-3

Force Constant Calculations for SiNCO

ν_1, ν_2, ν_3^a cm^{-1}	ΔC^{13^b} cm^{-1}	ΔN^{15} cm^{-1}	ΔO^{18} cm^{-1}	Force Constants ^c $\text{mdyne } \text{\AA}^{-1}$
2313	60	10	13	observed
1470	0	30	34	shifts
2313	58	1	46	19.94
1470	0	37	3	4.19
570				9.87
				0.0
2313	61	10	17	16.07
1470	0	30	33	13.80
570				3.77
				1.59

^aAssumed values only for ν_3 .

^bShift to lower wavenumber with respect to entry in column 1.

^cForce constants in order are F_{CO} , F_{CN} , F_{SiN} , $f_{\text{CO/CN}}$.

possible combinations of values between 10-18 mdyne $\text{\AA}^{-1}$ in units of one mdyne $\text{\AA}^{-1}$ having been tried.

SiOCN Calculations

A variety of calculations for a linear SiOCN structure are shown in Table 6-4. In the first four entries, three force constants were assumed, utilizing only the three stretching frequencies of the normal molecule, with the assumed values of ν_3 being 600, 700 and 800 cm^{-1} respectively, (the force constants become imaginary for ν_3 greater than 806 cm^{-1}). With the restriction that for any F, $2 < F < 25$ mdyne $\text{\AA}^{-1}$, two solutions were possible for $\nu_3 = 800 \text{ cm}^{-1}$. The agreement between the observed and calculated shifts is poor in all cases.

It is difficult to predict what value to assume for the ν_3 made in a linear SiOCN species, but values as high as 900 cm^{-1} might be possible on the basis of SiO stretching frequencies in known Si-O-R type compounds¹⁴⁰. The inclusion of a fourth force constant, $f_{\text{CO/CN}}$, is necessary for such a calculation, and this requires four frequencies. However, in order not to bias the calculation by including isotopic data, the value of F_{CO} was kept constant, and F_{CN} and F_{SiO} allowed to vary, using only the three frequencies of the normal molecule. The results for $\nu_3 = 600, 700, 800$ and 900 cm^{-1} are shown in entries 5-8 in Table 6-4. The initial guess value of F_{CO} could only be varied between 15-19 mdyne $\text{\AA}^{-1}$ in order to obtain an exact calculation of the frequencies of the normal molecule, and within this restriction, the calculated isotopic shifts for a given

TABLE 6-4

Force Constant Calculations for SiOCN

Calc No	ν_1, ν_2, ν_3^a cm ⁻¹	ΔC^{13b} cm ⁻¹	ΔN^{15} cm ⁻¹	ΔO^{18} cm ⁻¹	Force constants ^c mdyne Å ⁻¹
	2313	60	10	13	observed
	1470	0	30	34	shifts
1	2313	54	30	2	18.81
	1470	0	2	60	4.42
	600				10.98
					0.0
2	2313	58	24	6	17.26
	1470	0	6	60	7.64
	700				9.42
					0.0
3	2313	52	4	43	9.80
	1470	10	13	38	15.14
	800				10.94
					0.0
4	2313	40	2	62	7.07
	1470	20	8	24	15.50
	800				14.68
					0.0
5	2313	62	9	23	14.23
	1470	0	23	44	16.00
	600				4.07
					1.81
6	2313	60	7	29	13.00
	1470	2	21	44	16.00
	700				1.36
7	2313	54	4	42	10.50
	1470	8	16	38	16.00
	800				9.69
					0.67
8	2313	20	0	78	7.67
	1470	27	10	15	18.00
	900				15.75
					2.76
9	2313	61	10	18	14.94
	1470	0	22	47	15.14
	600				4.09
					1.71

^aAssumed values only for ν_3 .

^bShift to lower wavenumber with respect to entry in column 1.

^cForce constants, in order are: F_{CN} , F_{CO} , F_{SiO} , $f_{CN/CO}$

Note: In calculations 1-4 $f_{CN/CO}$ was fixed at 0. In calculations 5-8 F_{CO} was fixed at the value indicated. In calculation 9, four force constants were assumed to be variable and C^{13} and N^{15} data for ν_1 was utilized.

ν_3 value varied by about $\pm 2 \text{ cm}^{-1}$ at most. For $\nu_3 > 700 \text{ cm}^{-1}$, the calculated shifts differ greatly from the experimental shifts, and in any attempt to utilize C^{13} and N^{15} frequencies of the ν_1 mode in a full unrestricted refinement, the calculation did not converge.

However, the above mentioned calculated shifts were reasonably accurate for $\nu_3 = 600 \text{ cm}^{-1}$, and a full refinement utilizing these data was possible. This is shown in the last entry in Table 5-4 but even here, the agreement between the calculated ν_2 shifts for N-15 and O-18 substitution are poor, unlike the agreement for the SiNCO structure. An assumed value of 600 cm^{-1} for ν_3 seems unreasonably low, although no silylisocyanate are known to verify this.

It is concluded, nevertheless, that these calculations support the assignment of $2313/1470 \text{ cm}^{-1}$ bands to a linear surface silylisocyanate species, SiNCO.

Other Bands

The weak set of bands at 3070, 2353 and 1505 cm^{-1} appear to grow in intensity at the same rate as the $2313/1470 \text{ cm}^{-1}$ bands and Ruttenberg and Low¹²² (who only detected the 2353 and 3070 cm^{-1} bands, attributed these to unspecified overtones of SiNCO. However, considering the additional 1505 cm^{-1} band from the present work, and noting that the C-13 and N-15 isotopic shifts are nearly the same as for the $2313/1470 \text{ cm}^{-1}$ pair (no O-18 shifts could be measured because of band overlap problems), these bands might be assigned to an SiNCO species in a different environment.

However, it is difficult to account for the apparently

constant intensity ratio for the 2313/2353 cm^{-1} bands with such large variations in surface coverage. A $\text{Si}(\text{NCO})_2$ surface structure can probably be ruled out because of the absence of additional bands on partial isotopic substitution. Therefore, the overtone combination hypothesis seems most plausible. In support of this, the NCO bending mode is expected to lie in the range 600-800 cm^{-1} , and considering the difference $3070-2313 = 757 \text{ cm}^{-1}$, and allowing for slight anharmonicity, $2 \times 757 = 1514 \text{ cm}^{-1}$ (as opposed to 1505 cm^{-1}), the best assignment would be as follows: $3070 \text{ cm}^{-1} = \nu_1 + \nu_4$, $1505 = 2\nu_4$.

On the other hand, the SiNC bending mode (ν_5) is expected to be in the range 20-60 cm^{-1} as found in the known silylisocyanate compounds^{126,128-131}, and, with an assumed value of 40 cm^{-1} , the 2353 cm^{-1} band could be assigned to $\nu_1 + \nu_5$. The isotopic shifts of the 2353 cm^{-1} band would be expected (as found) to reflect those of the ν_1 band, and little C-13 isotopic shift is to be expected for ν_4 or $2\nu_4$. The origin of the relatively sharp band remains obscure because the observed isotopic shifts do not fit either the SiNC or SiCN structure (no shift was observed for O-18 substitution of the surface). Since it is only observed after reacting C_2N_2 at greater than 500°C prior to the start of extensive polymer formation, it is surmized that the band is indicative of some precursor to this process, possibly involving C-C≡N structures.

The mechanism for the formation of SiCN, SiNC and SiNCO is also unclear, since the relative proportions of each species are not known. However, the reaction of HCN does not appear to proceed via the active sites (Chapters 4 and 5). There is no diminution of bands

at $908/888\text{ cm}^{-1}$ at room temperature but on heating in HCN up to 800°C , a slight decrease in intensity is observed, which may be due to reaction of the sites with small amounts of H_2O produced in a reaction: $\text{SiOH} + \text{HCN} \rightarrow \text{SiCN} + \text{H}_2\text{O}$.

The presence of CH_4 when CH_3CN was reacted points to the following analogue with HCN; $\text{SiOH} + \text{HCN} \rightarrow \text{SiNCO} + \text{H}_2$.

CHAPTER 7

SUPPORTED METAL CATALYSTS

The following three chapters are each concerned with adsorption and catalysis on silica supported platinum.

In the studies of silica described in Chapters 4 and 5, the object was to establish the identity of an active site and the nature of the interaction between an adsorbate and the surface. However for silica supported metals, there is the additional possibility that a catalytic event can take place, and in this case, infrared spectroscopy may be used in an attempt to identify the chemisorbed species that act as the intermediate complexes in a reaction and which are perhaps responsible for the lowering of activation energy of a reaction¹⁴¹.

This can be achieved by either studying changes in the surface adsorbed species as reactants are converted to products in a dynamic flow system, or, as has been done in this work, the adsorbent may be studied in the absence of reactant and product gases under static conditions so that stricter controls can be employed. For example, the pressure of the adsorbing molecules can be finely altered and also one can choose to treat the surface with other molecules, once adsorption has occurred, so that changes in the spectral behaviour of the species may help in further characterization. Supported metal samples are not as well defined as the supports themselves because, for example, there may be a wide variation in particle

sizes of the metal resulting from non-uniform dispersion and there is the possibility that traces of the metallic salt may remain unreduced and act as alternate adsorption sites. The spectra of the adsorbed species may change as coverage increases because sites of lower reactivity may force different bonding characteristics. In catalysts of this type the number of active sites may be just a small fraction of the total number of surface atoms¹⁴², and it is often difficult to predict to what extent a catalytic event may proceed. So, in the absence of definitive information about the surface sites, some empirical approaches have been used, including trying to correlate bond lengths of metal-metal bonds to those within the absorbing molecule¹⁴³ (a reaction being favoured for equal bond lengths) or of matching the frequency of the adsorbate bond to be broken with that of the metal-adsorbate mode¹⁴⁴. Pauling¹⁴⁵ established an equation to estimate the "% d character" of metals, as a guide to catalytic behaviour, where the extent of "d character" is a measure of the d-orbital participation to hybrid bonding in the bulk of a metal, estimated from its known paramagnetic susceptibility. For example, the heats of adsorption of hydrogen and ethylene on various metals were found to decrease with increasing % d character ($\text{Cr} < \text{Fe} < \text{Ni} < \text{Rh}$)^{146,147}. On the other hand, the number of vacant d orbitals (d-holes) has been correlated in some instances with rates of hydrogenation (e.g. of styrene) and yet there is no clear relation between the number of d-holes and % d character. Both of these properties are defined from bulk properties whereas the hybridization of surface orbitals is likely to be different due to valency unsaturation and

more recently efforts have been made toward developing a quantum mechanical interpretation of the nature of metal surfaces to determine what orbitals are available¹⁴⁸.

The type of chemisorption to be expected also depends on the adsorbate itself, and to the degree of electron sharing or electron transfer. In terms of Paulings electronegativity (χ) the favoured type of bond passes from covalent to dative to ionic as $\Delta\chi$ becomes larger.

Compounds which commonly behave as poisons in catalytic processes are those with lone pairs of electrons and which have the option to bond datively. In the following chapters such types of molecules have been studied (NH_3 , pyridine, nitriles and amines) to determine how they adsorb to platinum (very little previous knowledge existed). Despite the fact that they can all be classed as 'potential poisons' it has been found that the manner of adsorption is different in each case, ranging from an apparent singly adsorbed species in the case of NH_3 and pyridine, and multiple species for the nitriles and amines (HCN , CH_3NH_2 , CH_3CN , benzonitrile, CF_3CN).

Platinum is an obvious metal to choose for these studies because of its predominant use as a commercial catalyst for hydrogenation and dehydrogenation reactions.

Properties of Supported Catalysts

So that the properties of metal catalysts can be monitored by the transmission of infrared radiation it is a necessary requirement that the sample should be finely dispersed so that scattering is minimized. But fine metal particles are not stable by themselves and

tend to sinter into larger crystallites, hence the need for a support. Again there are limits to the amount of metal which one can place on a support above which the transmission of radiation becomes unsuitably low due to crystallite size, but alternatively if the metal content is very low then it may be impossible to detect measurable spectral bands of the adsorbed species. In the present work however, a high load of Pt has been used (16%, compared to often used loads of 5-10%) but transmission losses have been minimized by virtue of the special technique for the catalyst preparation (see Chapter 2) and consequently excellent quality spectra were obtainable from $4000-1350\text{ cm}^{-1}$. This enabled, for example, a definitive study of traditionally weak absorption bands in the usually obscured region from $4000-3000\text{ cm}^{-1}$ (e.g. for NH_3 adsorption).

In supported samples the metal particle size is generally between 5 and $50\text{ \AA}$, which may render new properties of the metal that distinguish it from a bulk sample. For example, only weak broad lines are obtained in an X-ray diffraction pattern in contrast to the large sharp lines obtained for single crystals¹⁴⁹.

Also, a normally ferromagnetic metal such as Ni exhibits distinctly different magnetic properties in the dispersed state, in that magnetization becomes a function of field strength, which is not true of the bulk metal. A particle size effect has been postulated by Ross et al¹⁵⁰ in an X-ray photoelectron spectroscopy study of dispersed platinum (Pt/SiO_2) and Pt foil to account for a different chemical shift of the 4f electrons.

The influence of crystal size upon catalytic activity has

also been studied. For a totally dispersed sample (where the ratio of surface metal atoms to total metal atoms approaches unity), the number of different edges and faces exposed becomes maximized and a high degree of surface heterogeneity may be expected¹⁵¹. The samples used for this work probably have dispersion values lying between 0.4 and 0.7 corresponding to average crystallite sizes of about 50 and 20 Å, respectively. Calculations have been made^{152,153} to determine the percentage of metal atoms which maintain normal coordination for various crystal sizes; it was found that, below 50 Å there is a significant portion of atoms present which are abnormally coordinated (e.g. a 28 Å crystallite has 30% abnormal coordination). Such catalysts can be used to search for evidence for specific properties associated with edges and faces by varying the extent of dispersion.

As well as a primary alteration in surface geometry, due to small particle sizes, there is also the possibility that a finely dispersed metal might assume some of the lattice characteristics of the support and in these respects it might be expected that absorption studies of supported metals might not correlate with metal films or single crystals, however qualitative agreements do exist. According to Moss¹⁵⁴, one of the main reasons for any quantitative differences is the effect of catalyst poisoning due to residual atoms from the original metal salt (e.g. Cl). More drastic changes in catalyst activity occur just through usage. Most catalysts go through three levels of activity corresponding to an initial break in period, a steady state period and a deactivation period. Baddour¹⁵⁵ found significant differences in the spectrum of CO adsorbed to Pd during each of

these stages, which he attributed to a redistribution of the surface structure by diffusion of Pd atoms. A surface is not "broken-in" until it has been exposed to oxygen. It is Baddour's claim that in some cases a surface break-in may occur during a catalytic reaction, and since many adsorption studies are carried out in the absence of some reactants and products then this method may lead to a misinterpretation of (e.g.) steady state kinetics. To some extent, the effect of such surface changes have been taken into account in this thesis in that where irreversible surface poisoning occurred such that the surface could not be regenerated, then a fresh sample was used. This was mostly necessary to obtain reproducible spectra of the nitriles. Admittedly, the spectra may not be representative of the surface species occurring during a catalytic event where adsorption and desorption is continually taking place, but for the purposes of assignment of spectral bands to the adsorbed species it was felt to be warranted to keep the number of different species to a minimum.

As for studies with NH_3 and pyridine, no differences were discerned between adsorption on an 'unbroken' surface, a surface treated with oxygen then regenerated in hydrogen, or a surface which had been used up to twenty times.

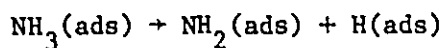
None of the following chapters are closely related mainly because the impetus for investigation was derived from a different source in each case, however, some aspects of each were found to be interrelated. Chapter 8 is concerned with the adsorption of NH_3 on Pt and its subsequent oxidation, Chapter 9 with pyridine on Pt and Chapter 10, with various nitriles and amines on Pt. A separate introduction to these problems is set out at the beginning of each chapter.

CHAPTER 8

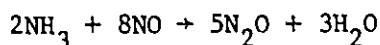
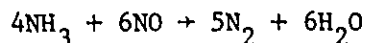
AMMONIA ON PLATINUM

Platinum is known as an efficient catalyst for the oxidation of NH_3 , and is used today (usually alloyed with rhodium) in the commercial production of nitric acid employing a method developed 70 years ago¹⁵⁶. Traditionally, chemists have studied such systems by monitoring the reactants and products in order to understand the gross functions of the catalysts without being concerned with specific surface-adsorbate interactions. But the latter is a necessary prerequisite toward more complete understanding of the complex reaction systems investigated. Today there is a renewed interest in this problem because of the recent impetus toward the development of catalysts for controlling automobile exhaust pollution. It has been discovered that ammonia is produced as an undesired side product of the reductive catalytic removal of nitrogen oxides (NO_x) by CO ¹⁵⁷ and conditions for its removal are being established¹⁵⁸. It is surprising therefore that there is still very little known about its mode of adsorption on noble metal catalysts although many mechanisms have been proposed to account for the observed gas phase products that appear under various oxidative conditions¹⁵⁹⁻¹⁶⁵. In the catalytic reaction between NO and NH_3 on a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, Otto et al¹⁵⁹ proposed that NH_3 was dissociatively chemisorbed and that the rupture of the N-H bond in the adsorbed species was the limiting step in the process because the reaction was observed to be zero order,

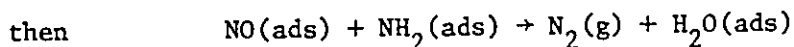
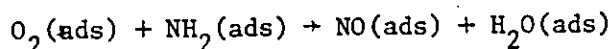
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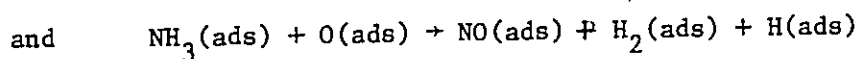
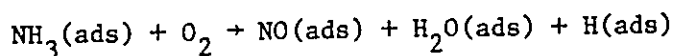
In the absence of oxygen, the following overall reactions were proposed to occur



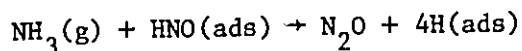
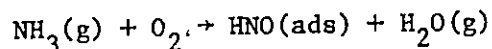
Ammonia oxidation exclusively with O_2 has been extensively studied and many mechanisms have been proposed¹⁶¹⁻¹⁶⁹. Bodenstein¹⁶¹ observed the formation of hydroxylamine and nitrous acid and thought that HNO was an adsorbed intermediate, but more recently, Nutt and Kapur¹⁶⁵ considered that the following steps occurred on a platinum catalyst



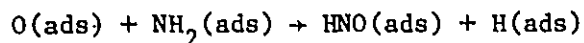
Fogel et al¹⁶⁶, on the other hand, contended that the reaction involved a co-ordinately bonded NH_3



At higher pressures of NH_3 and O_2 the production of N_2O has been observed^{167,168} and a nitroxyl radical was thought to be responsible



In the presence of oxygen, the reduction of NO by NH_3 is actually enhanced¹⁵⁸ and this has been interpreted by Markvart and Pour¹⁶⁹ as being due to an acceleration of the NH_3 dissociation step.



In none of the aforementioned studies has the identity of any of the adsorbed species been verified which is largely the reason for the array of mechanisms proposed.

This chapter attempts to show how NH_3 is initially adsorbed on platinum and how it subsequently behaves in the presence of pre-adsorbed and gaseous oxygen, by using the infrared spectroscopic technique. Some studies have been made by other workers in this direction and a summary of their results and interpretations follows.

Blyholder and Sheets¹⁷⁰ have studied the adsorption of ammonia on metallic films and concluded that it is co-ordinately adsorbed on Fe and V but tends to be dissociatively adsorbed on Ni and Pd. Co-adsorption of carbon monoxide on Ni and Pd surfaces helped to stabilize the formation of a co-ordinated undissociated ammonia and stronger infrared bands were observed for adsorbed NH_3 .

According to these authors, Ni and Pd cannot accommodate a charge transfer to form a covalent bond with ammonia unless there is also a drain of charge from the surface, in this case via back donation to the CO ligand (evidenced by a shift in ν_{CO} to lower wavenumber).

Prinet et al¹⁷¹ studied the adsorption of NH_3 on a $\text{Pt/Al}_2\text{O}_3$ which contained a submonolayer coverage of chemisorbed carbon monoxide,

and, like Blyholder and Sheets¹⁷⁰, they observed a decrease in ν_{CO} when NH_3 was adsorbed. No mention was made of an enhanced intensity for NH_3 bands, but it was concluded that ammonia was not dissociatively adsorbed to platinum.

The above views do not necessarily represent the general consensus of opinion regarding the mode of adsorption on Group VIII metals, in fact the literature indicates a wide disparity of observations and interpretations, some examples of other infrared studies into this problem illustrate this point.

Peri¹⁷² and Griffiths et al¹⁷³ have investigated the adsorption of ammonia on silica supported Ni and Pt respectively and concluded that it is co-ordinatively bound in each case. Pozdhyakov and Filiminov¹⁷⁴ agreed, but claimed that there was another dissociatively adsorbed form of ammonia also present on Ni and Pt, as well as on Fe, Pd and Ru.

In studies on Fe/SiO_2 , Nakata and Matsushita¹⁷⁵ have observed similar spectral features to those of Pozdhyakov and Filiminov¹⁷⁴, but instead attribute them to an amine ($-\text{NH}_2$) species, on the basis of isotopic substitution data.

Contour and Pannetier¹⁷⁶ have observed the deformation bands at 1615 and 1250 cm^{-1} for NH_3 adsorbed to $\text{Ir/Al}_2\text{O}_3$ surfaces and attributed these to a co-ordinated species though a band due to NH_4^+ was also identified at 1460 cm^{-1} .

In order to resolve the question of the mode of chemisorption of ammonia on platinum, and to distinguish between a co-ordinatively bound species and imine or amine fragments resulting from the

dissociative chemisorption, some isotopically substituted ammonias were reacted with Pt/SiO_2 catalysts and the adsorbed species were studied using infrared spectroscopy. It was concluded that ammonia is only co-ordinately bound to platinum.

Various oxygen treatments of ammonia over Pt/SiO_2 produced new infrared bands showing that a range of adsorbed intermediates exist on the surface prior to the formation of oxidation products.

Experimental

A 40 mg cm^{-2} Pt/SiO_2 sample was used, except where denoted, and contained 16% Pt by weight after reduction. Spectra were obtained with spectral slit widths $< 5 \text{ cm}^{-1}$ over the range $3800\text{--}800 \text{ cm}^{-1}$.

Bands appearing in the range $3400\text{--}3200 \text{ cm}^{-1}$ were calibrated against HCN vapour, and between $2550\text{--}2300 \text{ cm}^{-1}$, against HBr gas.

All spectra were measured at room temperature.

PtOH I. and PtOH II surfaces were prepared as described by Morrow and Ramamurthy¹⁷⁷, and PtO was obtained by degassing the Pt/SiO_2 sample at 300°C to remove all surface hydrogen, cooling to room temperature, adding 20 torr of O_2 for 10 min, followed by pumping at room temperature for 10 min.

A totally deuterated surface was prepared by introducing several doses of D_2 (30 torr) at 200°C .

Results and Discussion

A. Adsorption of NH_3

As previously reported by others¹⁷⁹⁻¹⁸¹, ammonia was found to be only hydrogen bonded on silica (provided there were no active

sites, see Chapter 4) with bands appearing near 3400, 3320 and 1625 cm^{-1} as well as a band envelope near 3000 cm^{-1} due to the hydroxyl stretch of SiOH perturbed by ammonia ($\text{SiOH} \cdots \text{NH}_3$). All bands could be removed by degassing the surface at room temperature for 1 min.

The above bands also appeared upon the admission of 10 torr of ammonia to a Pt/SiO_2 sample but were accompanied by a new band near 3260 cm^{-1} . Degassing this surface at room temperature did not remove all the bands and three new features were found at 3372, 3268 and 3155 cm^{-1} (see Figure 8-1B).

As well, a very weak band at 1600 cm^{-1} was observed when a compensating dehydrated silica pellet was placed in the reference beam. No other bands were observed*.

The intensity of each of these bands was found to be independent of the adsorption time (from 1 min to 5 hr) and even heating the surface in 10 torr ammonia at 300°C had no effect on the intensity. The same bands could also be produced when the admitted pressure of ammonia was 1 torr.

The peak height (and integrated band intensity) of the 3372 cm^{-1} band decreased rapidly as the degassing temperature was raised to 100°C. (Spectra were recorded when the surface had cooled to room temperature). Conversely the peak heights of the 3268 and 3155 cm^{-1}

* Sometimes bands were observed at 3444 and 1550 cm^{-1} , but these were attributed to a surface SiNH_2 species that can arise if the Pt/SiO_2 surface is degassed at temperatures beyond 400°C prior to adsorption. On occasions when it was necessary to raise the temperature beyond 400°C, it was found that the active sites formed on silica which give rise to this species (see Chapter 4) could be removed by treating the surface in 300 torr of H_2 at 350°C. No bands could be observed in the 980-800 cm^{-1} region when a 10 mg cm^{-2} Pt/SiO_2 sample was used (Platinum apparently catalyses the reaction of H_2 with the active sites, since on a pure silica surface, the sites are not consumed in H_2 , even up to 600°C).

bands were observed to increase slightly although the integrated peak intensity for each of these bands may not have changed, since in the case of the 3268 cm^{-1} band, the half intensity band width was larger prior to degassing at elevated temperatures (compare Figure 8-1B with Figure 8-1D).

Beyond this degassing temperature all three bands diminished relatively uniformly and at 300°C , no bands remained.

Adsorbed ammonia was not displaced by the addition of water vapour (saturation vapour pressure for 3 hrs).

The addition of 30 torr of CO to chemisorbed NH_3 apparently displaced the latter species because the absorption bands at 3372, 3268 and 3155 cm^{-1} all disappeared, and a band appeared at 2065 cm^{-1} which is the typical absorption frequency for chemisorbed CO at total surface coverage.

When NH_3 was adsorbed on a CO covered surface only one weak band was observable in the N-H stretching region at 3268 cm^{-1} . The addition of NH_3 to a partially CO covered surface resulted in a conventional spectrum of adsorbed ammonia though the bands were weaker. Apparently the enhancement of the NH band intensity observed by Blyholder and Sheets¹⁷⁰ for NH_3 adsorbed to partially CO covered Ni and Pd surfaces does not apply in this case.

Isotope Studies

If a deuterated Pt/SiO_2 surface was prepared, a similar series of spectra were obtained in the N-D stretching region when ND_3 was adsorbed; degassing at room temperature removed all physically

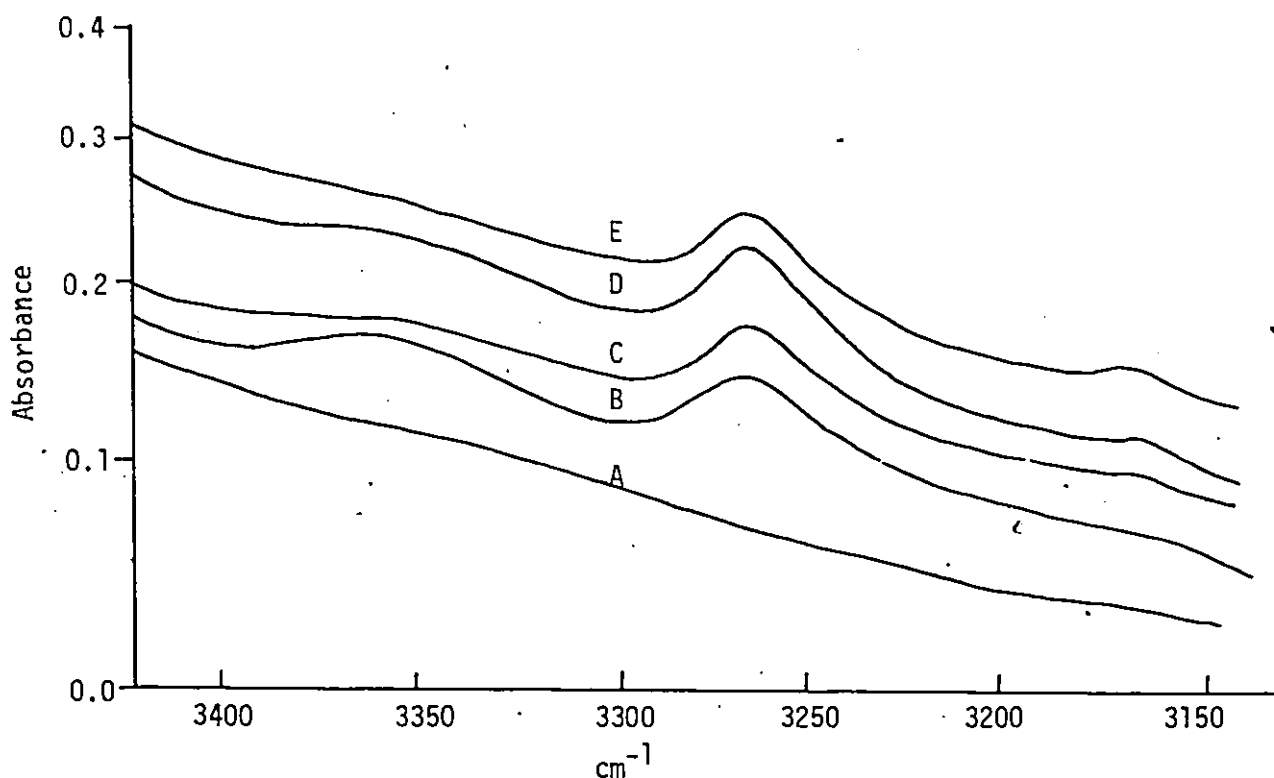


FIGURE 8-1

Desorption of Chemisorbed Ammonia

- A. $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.
 - B. Admitted 10 torr of NH_3 to cell for 5 min, then pumped for 5 min at room temperature.
 - C,D. Evacuated for 1 hr at various temperatures, C, 120°C ; D, 200°C .
 - E. Evacuated for 16 hr at 200°C .
- All spectra were recorded at room temperature.
 Scan speed was $20 \text{ cm}^{-1} \text{ min}^{-1}$.
 Spectra C, D and E were displaced for purposes of presentation.

adsorbed species, but bands remained at 2515, 2375 and 2315 cm^{-1} until the degassing temperature surpassed 200°C. Again, the high frequency band (at 2515 cm^{-1}) was preferentially removed up to 100°C. (The spectra obtained after degassing at this temperature is shown in Figure 8-2B). Subsequently, when a small amount of H_2 (of the order of 0.5 torr) was added to the deuterium substituted species a new band appeared at 2410 cm^{-1} (Figure 8-2C). Further increments produced another band at 2460 cm^{-1} (Figure 8-2D,E).

In order to obtain these spectra it was necessary to eliminate "negative absorption" due to atmosphere CO_2 by placing a matching blank cell in the reference beam of the spectrometer, in addition to the precautions usually taken to compensate for atmosphere bands. (This is described fully in Chapter 3).

The reverse experiment was also performed, that is, the addition of D_2 to a surface containing only chemisorbed N-H species, and again the 2550-2300 cm^{-1} region was monitored. In this case the first band to appear was 2460 cm^{-1} , with further additions producing 2410 cm^{-1} and then 2515, 2375 and 2315 cm^{-1} .

To complement these results, a 1:1 mixture of NH_3/ND_3 was adsorbed to a surface containing 50% SiOD and a spectrum very similar to Figure 8-2E was obtained.

Similar features were not observed in the 3400-3100 cm^{-1} region during the mixed isotope work because the broad closely overlapping bands which resulted were generally not resolvable. (Better separation is expected in the N-D region).

Finally, an experiment was performed with ND_3 on a 10 mg cm^{-2}

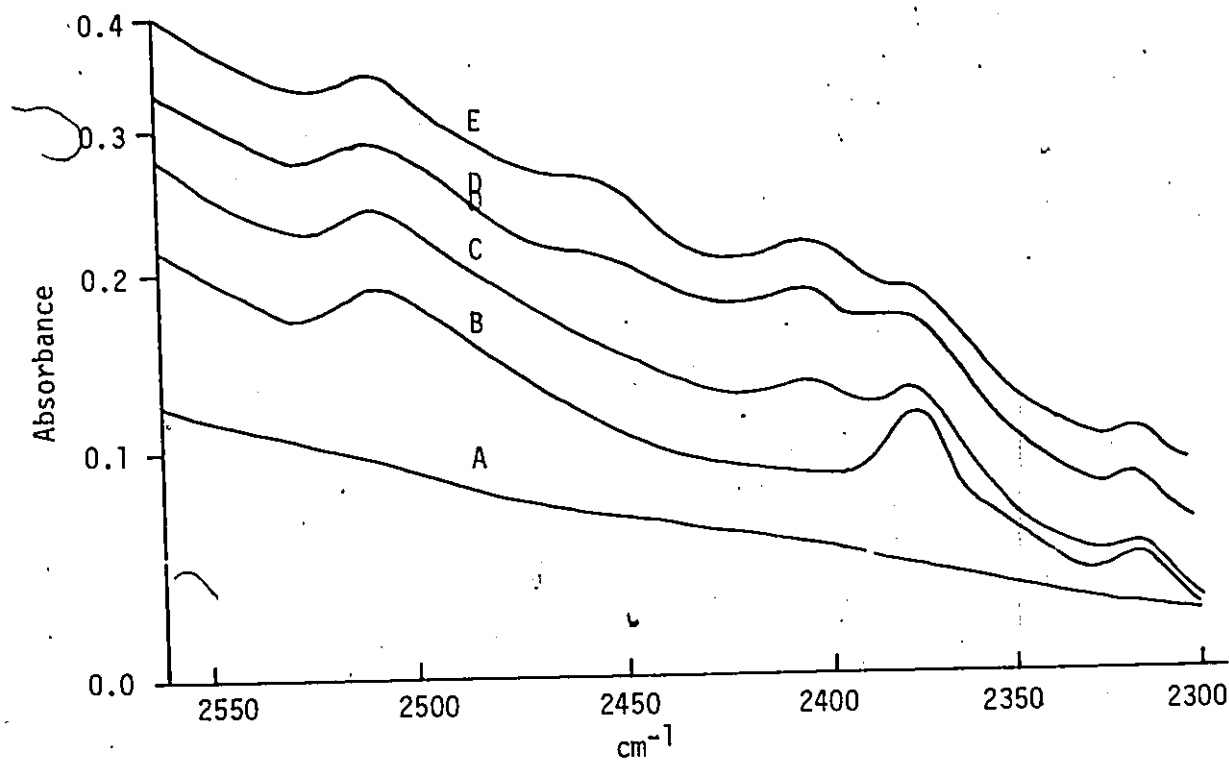


FIGURE 8-2

Production of mixed isotopes of chemisorbed ammonia

- A. $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$ (surface containing SiOD only).
- B. Admission of 10 torr of ND_3 ; left in cell for 5 min then pumped for 5 min at room temperature.
- C-E. Successive doses of H_2 (<1 torr); left in cell for 1 min then evacuated for 1 min.

Spectra C-E were displaced for purposes of presentation.

Pt/SiO₂ disc which contained only SiOD species. In this way it was possible to observe the 950-850 cm⁻¹ window region and a band at 833 cm⁻¹. No band was observed for NH₃ on a normal (SiOH) Pt/SiO₂ sample in this region.

Treatment in Hydrogen

When small amounts of hydrogen (<1 torr) were added to the surface containing the chemisorbed ammonia species, no change occurred in the intensity or frequency of the bands, but if the species were exposed to 60 torr of hydrogen, all three bands at 3372, 3268 and 3155 cm⁻¹ immediately diminished in intensity (Figure 8-3B).

Pozdhyakov and Filiminov¹⁷⁴ had observed that for NH₃ adsorbed on Pt, a band near 3280 cm⁻¹ diminished in 60 torr of hydrogen, but, that a band near 3380 cm⁻¹ had an enhanced intensity. In the present case both the 3372 and 3268 cm⁻¹ bands were observed to be shifted by about 10 cm⁻¹ to higher frequencies, (the 3155 cm⁻¹ band became too weak to measure its shift accurately) and a band appeared at 2120 cm⁻¹ due to Pt-H¹⁸².

Pumping out the hydrogen for one minute at room temperature produced the spectrum shown in Figure 8-3C. The intensity of all three bands was increased, though each band was slightly smaller than in the original spectrum (Figure 8-3A) probably as a result of some desorption of the species over the period of time that hydrogen was in the cell (15 min).

Another series of treatments with hydrogen and adsorbed ammonia is shown in Figure 8-3.

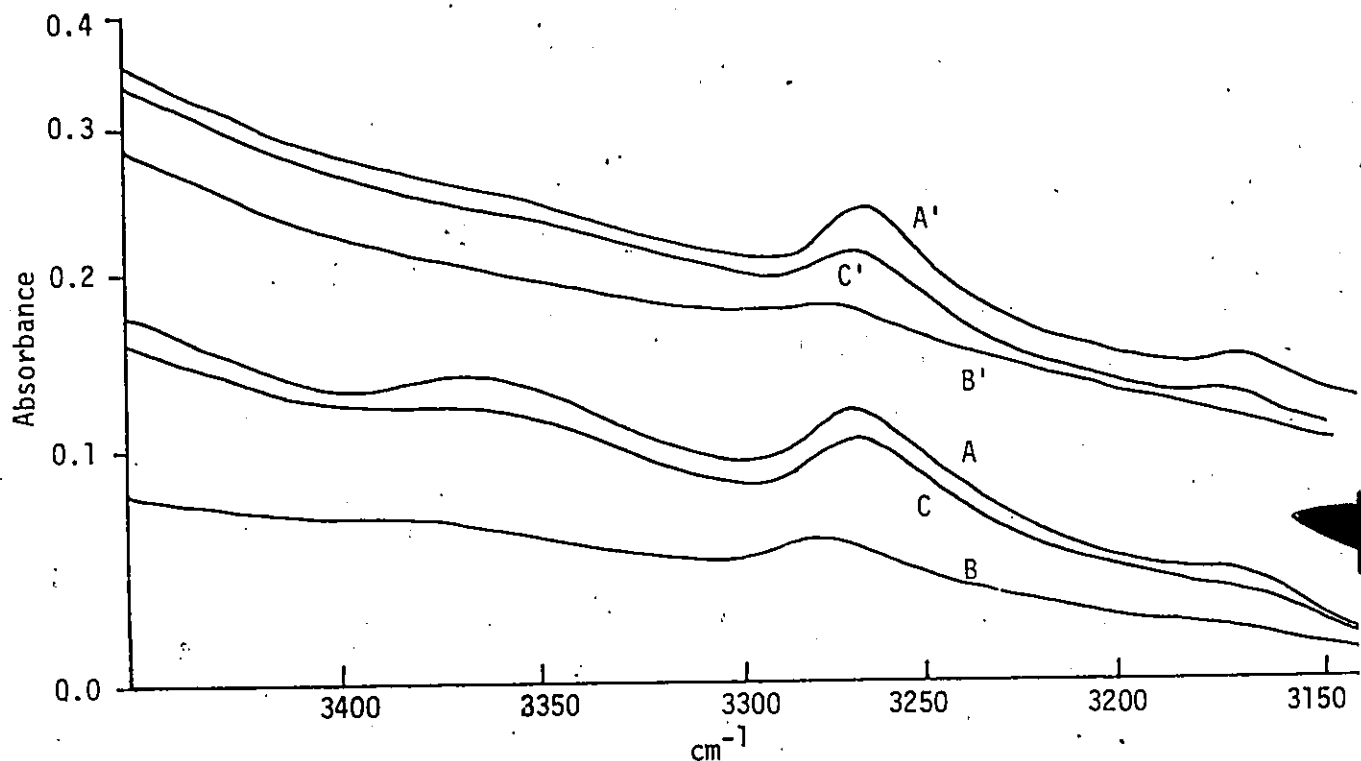


FIGURE 8-3

Treatment of chemisorbed ammonia with hydrogen using $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.

A. Admitted 10 torr NH_3 to Pt/SiO_2 for 5 min then pumped for 5 min at room temperature.

B. Admitted 60 torr of H_2 ; spectrum immediately.

C. Hydrogen removed after 15 min (pumping time 1 min)

A'. New Pt/SiO_2 sample. Admitted 10 torr of NH_3 for 5 min then pumped for 16 hr at 200°C .

B', C'. Same as B and C above.

The spectra of the primed series was displaced for purposes of presentation.

The scan speed was $20 \text{ cm}^{-1} \text{ min}^{-1}$.

Ammonia was adsorbed for 5 min, then degassed to 200°C for 16 hr, and, as shown in Figures 8-3A', B', C', there is virtually no absorption at 3372 cm^{-1} , only the 3268 and 3155 cm^{-1} bands are still prominent. The addition of hydrogen diminished the intensities of the two latter bands, but once the hydrogen was removed, the two bands increased in intensity although, as before, the intensities were not as great as in the original spectrum (compare Figure 8-3A' with 8-3C').

It was notable that the 3372 cm^{-1} band did not reappear.

Comparison with Previous Work

It is puzzling that only a weak band appeared at 1600 cm^{-1} for adsorbed NH_3 . Nakata and Matsuchita¹⁷⁵ observed a medium strength band in this region for NH_3 on Fe/SiO_2 . Pozdhyakov and Filiminov¹⁷⁴ reported a deformational vibration band at 1630 cm^{-1} which they attributed to ammonia co-ordinated to Pt/SiO_2 although no spectra were shown. On the other hand, Griffiths et al¹⁷³ made no mention of such a band.

In the present work, the partial deuteration experiment where the ND stretching bands were observed indicate that the chemisorbed species is Pt:NH_3 since the two new bands in this region at 2460 and 2410 cm^{-1} correspond to the N-D stretch in NH_2D and the symmetric stretch of NHD_2 respectively (the antisymmetric N-D stretch is expected to be virtually coincident with the frequency of the high wavenumber E mode of ND_3 and is therefore not distinguishable). An $-\text{NH}_2$ species would be expected to produce only one new band in the partial deuteration experiment, as was observed for isotopic work with the SiNH_2 species (Chapter 4).

Nakata and Matsuchita¹⁷⁵ found bands for ammonia adsorbed on Fe/SiO₂ at 3380, 3290, 1610 and 1550 cm⁻¹. They also conducted a partial deuteration experiment but instead monitored only the deformation region (because transmission from 4000-2000 cm⁻¹ was poor) which yielded a new band at 1400 cm⁻¹, and was attributed to a δ_{NHD} mode of Pt NHD. However the band at 1550 cm⁻¹ in the spectra of NH₃ on Fe/SiO₂ is due to SiNH₂ and this species is also known to have an infrared band around 1400 cm⁻¹ when partially deuterated (see Chapter 4). Hence the argument for an Fe NH₂ species is weakened because of interfering species adsorbing on the active support. That they made this error is surprising because they were aware of a band at 1550 cm⁻¹ due to SiNH₂.

In the present work, no bands could be found which could be attributed to a mixed isotope deformation mode when a NH₃/ND₃ mixture was adsorbed, but since only a very weak band was found for NH₃ on platinum, this is not surprising.

Pozdhyakov and Filiminov¹⁷⁴ noted similar changes to those shown in Figure 8-1 in the relative intensities of their higher wavenumber stretching band (3380 cm⁻¹) and their lower wavenumber band (3280 cm⁻¹) on degassing. They attributed this phenomena to the existence of two surface species, one involving a surface "N-H" species absorbing at 3280 cm⁻¹ and the other, a co-ordinatively bound Pt:NH₃, absorbing at 3380 and 3280 cm⁻¹. (They were also able to observe a band at 1200 cm⁻¹ on an MgO substrate characteristic of the symmetrical deformation mode of ammonia in co-ordination compounds¹²⁴.) However, in the present work it has been found that when the adsorbed species had been degassed to 200°C (Figure 8-1F), and small amounts of D₂ added (0.5 torr), a small band still appeared initially at 2460 cm⁻¹,

corresponding to the N-D stretch in NH_2D and then further addition of D_2 developed the other mixed isotope bands as listed in Table 8-1, although the band at 2515 cm^{-1} was weak. According to the postulates of Pozdhyakoy and Filiminov¹⁷⁴, degassing at 200°C is tantamount to removing all co-ordinatively bound ammonia from the surface since the intensity of the 3372 cm^{-1} band (corresponding to their 3380 cm^{-1} band) becomes very weak, but the above result shows that Pt:NH_3 is still present and there is no evidence for any other adsorbed species.

It cannot be argued that the addition of D_2 might be reforming a co-ordinated ammonia from a dissociated adsorbed species since experiments with small amounts of H_2 (<1 torr) added to adsorbed NH_3 did not change the intensity or frequency of the NH_3 absorption bands and neither were any new bands formed.

A small band at 3155 cm^{-1} , which has remained unnoticed by other workers, was observed to behave in an identical manner to that of the 3268 cm^{-1} band both on degassing and with treatment in hydrogen. This suggests that both bands are related to the same species, further discounting the concept of an 'N-H' species.

The band probably represents an overtone of the weak anti-symmetric 'deformation mode of Pt:NH_3 at 1600 cm^{-1} , enhanced in intensity by Fermi resonance interaction with the 3268 cm^{-1} band.

The band at 883 cm^{-1} for ND_3 adsorbed to a deuterated Pt/SiO_2 is probably related to the symmetric deformation mode of Pt:ND_3 . The analogous mode for Pt:NH_3 is expected to be between 1100 and 1300 cm^{-1} .

TABLE 8-1
Infrared Stretching Bands for Adsorbed
Ammonia on Platinum (cm^{-1})

NH_3	ND_3	NH_3/ND_3 (1:1)	$^{15}\text{NH}_3$
3372	2515	2515	3365
3268	2375	2375	3265
3155	2315	2315	3155

Intensity Effects

The fact that the 3372 cm^{-1} band diminishes on desorption up to 100°C and that the 3268 and 3155 cm^{-1} bands increase slightly, does not appear to be indicative of a separate species, since partial deuteration produces only bands which are consistent with a Pt:NH_3 species.

The unusual band intensity changes observed on degassing the surface species, or when hydrogen is added might be related to the fact that dipole interactions between neighbours alter with surface coverage.

The same anomalous intensity effects have been noted for the symmetric and antisymmetric stretches of SiNH_2 (see Chapter 4), and for surface methylene groups ($\text{M-CH}_2\text{-}$) on platinum and nickel¹⁹⁰. In all of these cases, including the present, the low wavenumber band corresponding to the symmetric stretching mode is much more intense than the high wavenumber band due to the antisymmetric stretch, contrary to the normal situation in the infrared spectra of free AH_2 or AH_3 type compounds.

Dipole imaging may explain these observations. The square root of the intensity of an absorption band (ν_1) is related to the change in dipole moment with respect to its normal co-ordinate Q_1 as follows

$$I^{1/2} \propto \left(\frac{\partial \mu}{\partial Q_1} \right) (=a_1)$$

where the change in dipole moment $\Delta\mu_1$ is given by

$$\Delta\mu_1 = a_1 Q_1$$

and Q_1 defines its direction.

The direction of change of the dipole moment for the anti-symmetric stretching mode is parallel to the surface. Therefore, the magnitude of $\Delta\mu_{\perp}$ of adsorbed NH_3 would be expected to be smaller than $\Delta\mu_{\perp}$ of an unperturbed or free molecule because of cancellation due to surface imaging. That is, $a_{\perp}$ will decrease relative to that of the free molecule. On the other hand, $\Delta\mu_{\perp}$ for the symmetric mode is perpendicular to the surface, and in this case will have an image in the same direction (see Figure 8-4). Hence the intensity would not be expected to be diminished relative to the free molecule. In such cases therefore, the intensity of an antisymmetric mode of an adsorbed NH_3 may be anomalously low, even to the point of being less intense than that of the symmetric mode.

A similar argument can be applied to explain the intensity variations in each mode as coverage decreases.

When the surface coverage is high, the adsorbed species are in close proximity and induced moments can be formed in neighbours. In this situation the reverse of surface imaging occurs; the $\Delta\mu_{\perp}$ of the symmetric mode induces a dipole in the opposite direction, whereas the direction of $\Delta\mu_{\perp}$ of the antisymmetric mode is in the same direction as it is for the induced dipole (Figure 8-4).

As the distance between neighbours increases, the spectral intensity of the symmetric mode (the 3268 cm^{-1} band) might be expected to be increased as the opposing induction decreases, whereas for the antisymmetric mode (the 3372 cm^{-1} band), the intensity should decrease. This is what is observed.

Once the surface had been degassed beyond 100°C , all three

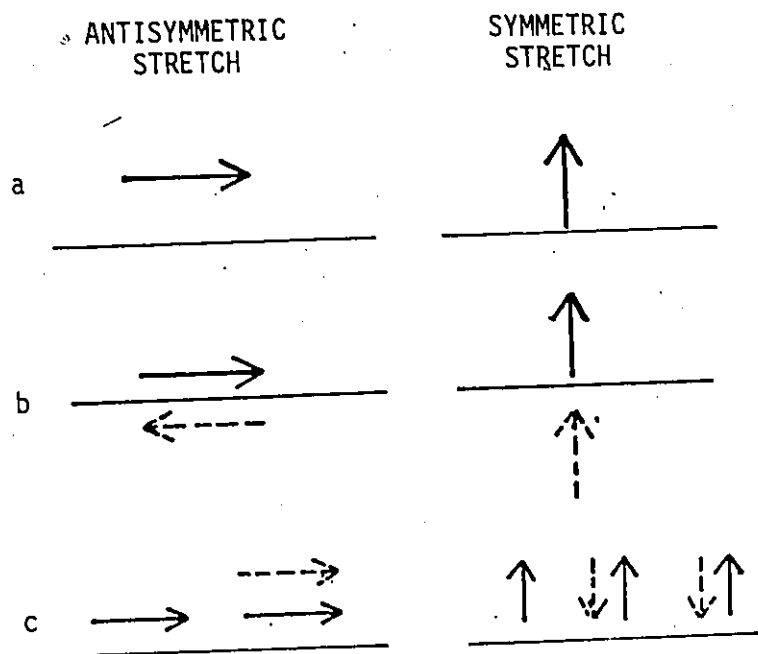


FIGURE 8-4

Chemisorbed ammonia (Pt:NH_3)

- Direction of dipole moment change with respect to surface.
- Surface imaging.
- Induction due to neighbour interaction.

bands decreased in intensity at a relatively uniform rate. Hence the surface population of adsorbed ammonias after degassing at 100°C probably represents the maximum coverage at which the distance between the adsorbed species is sufficient to make an induced dipole effect negligible. Any further drop in intensity with subsequent degassing may be then directly related to the population decrease of the adsorbed species.

C The addition of hydrogen lowered the intensity of all three bands. On this basis it is difficult to envisage how dipole effects due to hydrogen adsorption could equally effect the antisymmetric and symmetric modes of chemisorbed ammonia. Furthermore, adsorbed hydrogen is unlikely to have a strong dipole moment since the difference in electronegativity between H and Pt is small ($\text{Pt} = 2.2$; $\text{H} = 2.1$) and any inductive effect on neighbouring adsorbed NH_3 species should also be small.

It is also unlikely that intensity changes in the N-H stretching bands can be attributed to the instant dissociation of NH_3 by hydrogen (and then instant re-association when hydrogen is removed) because no new bands are formed during or after the admission of hydrogen, and further, the re-association of dissociated residues back into a co-ordinated NH_3 is unlikely to be instantaneous.

A possible explanation for the observed intensity changes may be drawn from the theory proposed by Blyholder and Sheets¹⁷⁰.

They observed that NH_3 adsorbed on Ni and Pd exhibited stronger absorption spectra when NH_3 and CO co-existed on these surfaces because CO behaved as a sink for the charge donated to the surface

by co-ordinately adsorbed NH_3 .

In the present work, the adsorption of NH_3 to platinum produced strong spectral bands without CO and the addition of small amounts of CO, sufficient to form only a submonolayer ($\theta \approx 0.1$)^{*}, produced no change in the NH_3 band intensities or frequencies. But, further additions of CO reduced the intensity of these bands and at a pressure of 1 torr of CO no bands for NH_3 remained.

However, on surfaces where CO was pre-adsorbed ($\theta \approx 0.1$) ν_{CO} shifted to lower frequencies ($2060 \rightarrow 2025 \text{ cm}^{-1}$) when NH_3 was subsequently adsorbed, which is indicative of the acceptance of charge by the CO ligand from the surface.

The frequencies of the valence vibrations $\nu(\text{A}_1)$ and $\nu(\text{E})$ of NH_3 are known to decrease with co-ordination to a metal due to a weakening of the N-H bond as a result of withdrawal of electrons from the nitrogen atom to form the metal-nitrogen bond. The intensities of the bands though, becomes greater as a result of an increase in dipole moment in the N-H bond and an intensification of $\Delta\mu_1$ ^{183,184}

In the case of H_2 adsorption, if H donates charge to the surface (Pt^--H^+), as was observed with studies of H and CO co-adsorption¹⁸², then the Pt-N bond would be weakened. As a result the dipole moment in adsorbed NH_3 would also be weakened as would the change in dipole moment of each mode and intensities of the valence vibrations $\nu(\text{A}_1)$ and $\nu(\text{E})$ would be lowered. Furthermore, a weakening in Pt-N bond strength would result in a stronger N-H bond and a shift to higher frequencies for all N-H modes.

* θ is the fractional surface coverage of adsorbate.

Since these effects were observed, then it is proposed that on a Pt-NH_3 surface, hydrogen can co-adsorb and is bonded as Pt^--H^+ . (By comparison, no changes were observed in the intensities of the N-H bands of >Si-NH_2 species on silica surfaces when hydrogen was added, but hydrogen is not adsorbed on silica).

A Cautionary Note

The use of silica supported metal catalysts has been widespread in recent years, mainly because silica has been regarded as inert and unlikely to affect the properties of the metal. However, if these catalysts are degassed at temperatures above 350°C , active sites are created on silica (see Chapter 4) at which chemisorption can readily occur. Under these circumstances the infrared spectra of an adsorbed species on a metal/SiO_2 catalyst may be confusing, especially if the properties of the adsorbing species on active silica have not been previously investigated.

Furthermore, the possibility that products formed from a surface interaction with silica may then react with the metal (and vice versa) and make interpretation of surface behaviour unnecessarily complex.

For example, the spectra shown by Pozdhyakov and Filiminov¹⁷⁴, Griffiths et al¹⁷³ and Nakata and Matsuchita¹⁷⁵ for ammonia adsorbed on silica supported metals, indicate that in each case their supported silica was active, because spectral features for SiNH_2 appear.

The observed differences in their spectra (intensity and frequency) and the different interpretations given by these authors

may be related to differences in surface properties resulting from the presence of these sites.

For this reason it is felt that it is wise to react the metal/SiO₂ surfaces in hydrogen after any high temperature pretreatments in order to ensure that such sites are removed*.

B. The Oxidation of Adsorbed Species on Platinum

To the authors knowledge, there has been just one infrared investigation of the reaction of adsorbed NH₃ with O₂, that of Griffiths et al¹⁷³. They observed the formation of an N₂O product, concomitant with the decrease of the absorption features due to Pt:NH₃, however this species was not chemisorbed and could be removed at 25°C. No intermediates were observed. One of the reasons for the absence of observed intermediates is that high pressures of oxygen are invariably used to force product formation. For example, Griffiths et al¹⁷³ used 10 torr of 12:1 O₂:NH₃ mixture at temperatures up to 150°C.

In the present work, only very small amounts of oxygen (0.5 torr) were added to the cell, sufficient to just partially oxidize the chemisorbed species, and new bands were observed which replaced the Pt:NH₃ features (Figure 8-5C). As well the D and N-15 isotopes of NH₃ and the O-18 isotope of O₂ were used to further elucidate the nature of the new bands. These bands are also shown in Figures 8-5 and in 8-6B.

*With reference to the study of the active sites on silica it would be interesting to study the effects of hydrogen on thin Pt/SiO₂ discs (10 mg cm⁻²) when sites are present. The formation of a new OH analogous to the 3741 cm⁻¹ (see Chapter 4) would be difficult to observe due to the broadness of the SiOH profile when metals are present.

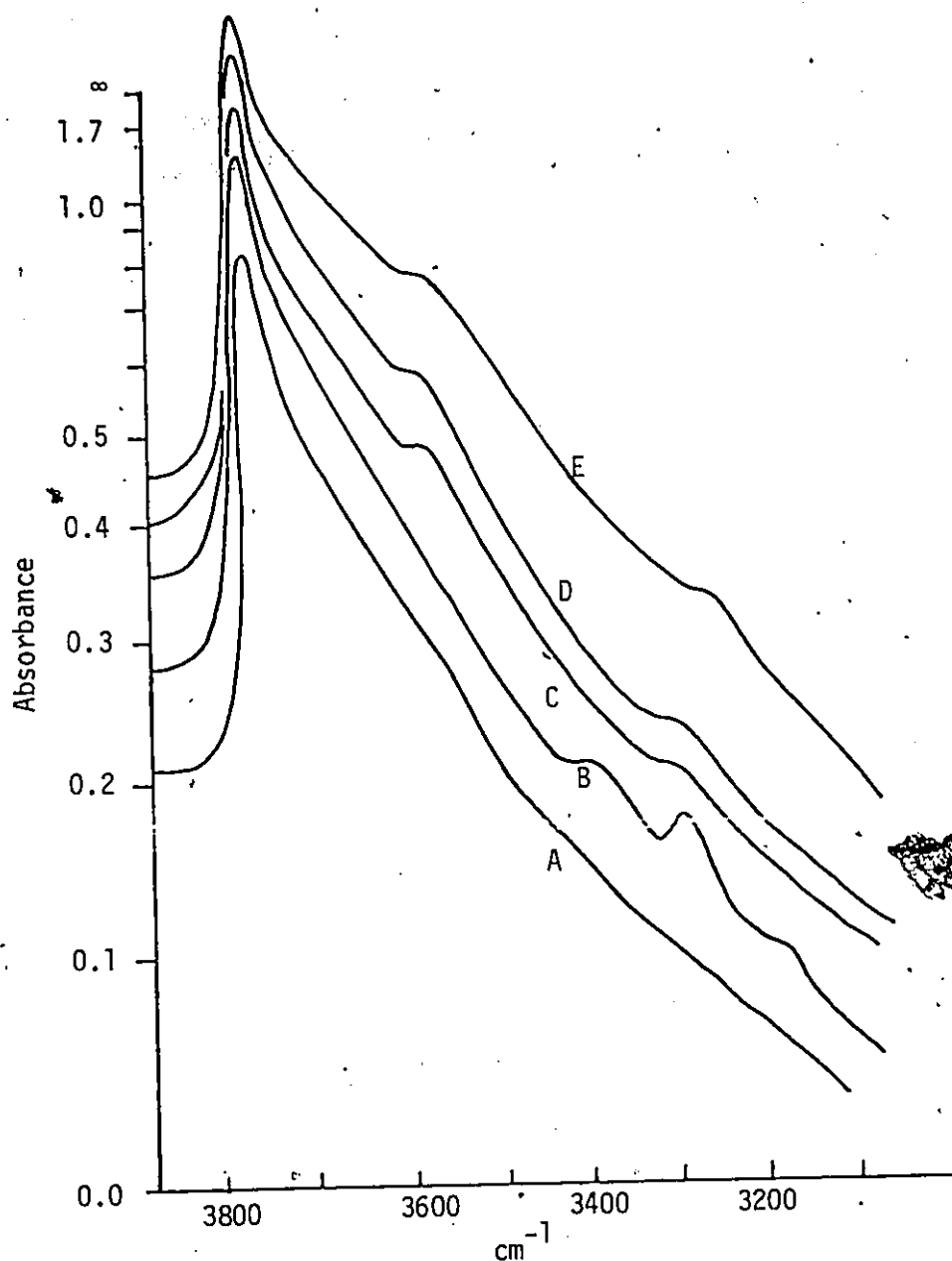


FIGURE 8-5

Treatment of chemisorbed ammonia with oxygen

A. Background spectrum of $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.

B. Admitted 10 torr of ammonia for 5 min, then pumped for 5 min at room temperature.

C, D and E. Addition of small dose of oxygen (~ 1 torr).

Spectra C refers to the addition of O-18 oxygen to an N-14 chemisorbed ammonia. D, O-16, N-14; E, O-16, N-15.

Spectra B-E were displaced for the purpose of presentation.

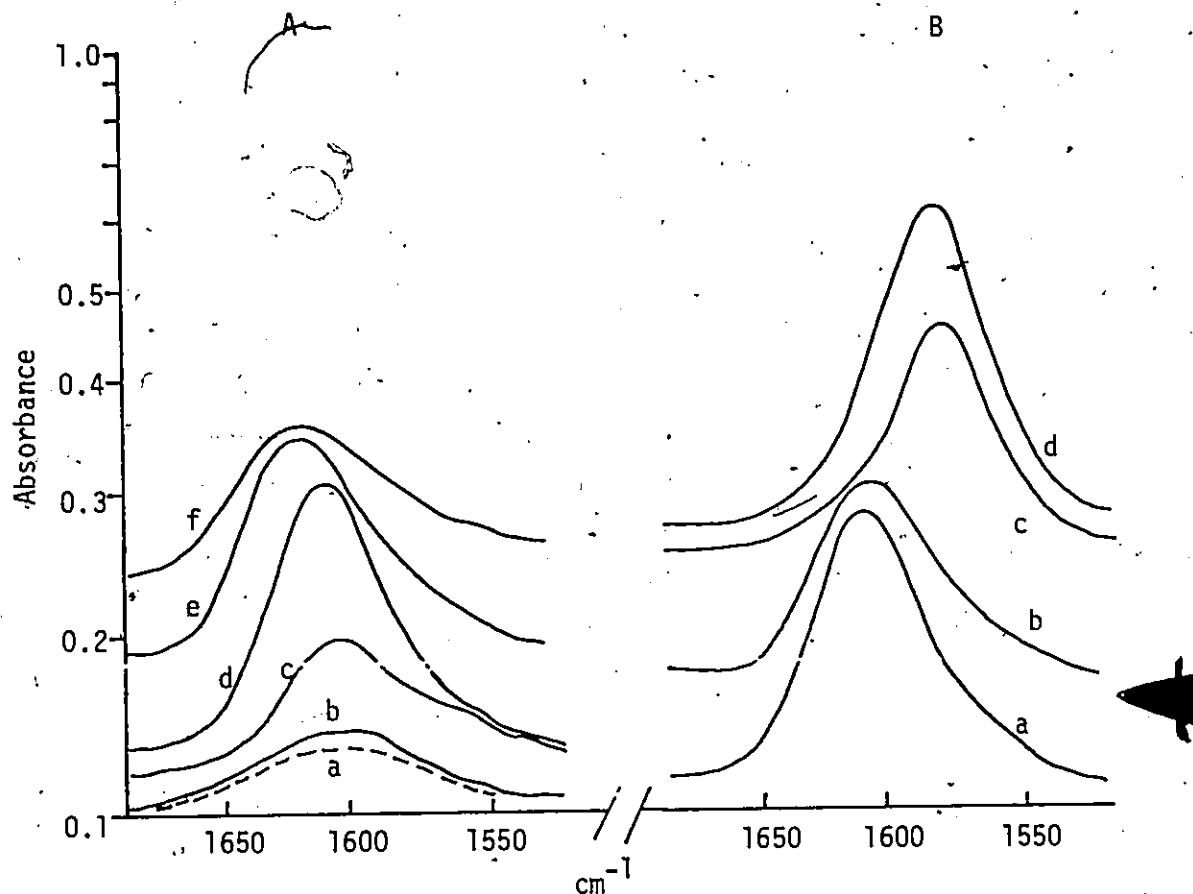


FIGURE 8-6 .

Treatment of chemisorbed ammonia with oxygen ($40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$).

A. a, Background; b, admitted 10 torr NH_3 5 min, then pumped for 5 min at room temperature. c-f, successive additions of oxygen. Each dose <1 torr.

B. Addition of oxygen (O-16 or O-18) to various isotopes of chemisorbed ammonia (N-14, N-15, H, D).

a, O-16, N-14, H; b, O-16, N-14, D; c, O-18, N-14, H;
d, O-16, N-15, H.

The same increment of oxygen was added in each case. In the spectra both A and B a silica pellet was placed in the reference beam to nullify a strong absorption band due to silica.

Care had to be taken so that the amount of oxygen added to the chemisorbed ammonia did not exceed a certain critical level, otherwise the band near 1600 cm^{-1} which appeared for each isotope, tended to shift to higher wavenumber. Figure 8-6A shows the sequence that the band profile follows.

The 1600 cm^{-1} related species is a transient intermediate; the addition of 0.1 torr of oxygen remove all bands from the spectrum but the subsequent addition of 10 torr of hydrogen reverted the species back to adsorbed NH_3 . It is apparent that the 1600 cm^{-1} band represents a partially oxidized intermediate between NH_3 and a free oxide of nitrogen, hence it is to be expected that beyond an optimum amount of added oxygen, the 1600 cm^{-1} band should begin to decrease in intensity corresponding to the fully oxidized product.

The accompanied shift to higher frequency may be ascribed to the formation of PtO (or PtOH I) once all of the 1600 cm^{-1} related intermediate has formed, which tends to draw charge from the surface.

An analogous case is the adsorption of oxygen (small amounts) to chemisorbed CO on platinum. The frequency of the $\text{vC}\equiv\text{O}$ band moved to higher values due to the withdrawal of charge from the surface by the oxygen in PtO^{189} . The surface is then limited in its capacity to donate charge back into the antibonding orbital of the ligand, resulting in a stronger $-\text{C}\equiv\text{O}$ bond.

The frequencies in row 1 of Table 8-2 are due to an hydroxyl species which forms when small amounts of oxygen are added to a platinum surface containing residual adsorbed hydrogen. If the Pt/SiO_2 surface was degassed at 400°C prior to the adsorption and oxidation of ammonia

TABLE 8-2
Infrared Bands for the Oxidation of
Adsorbed Ammonia on Platinum

	$^{14}\text{NH}_3^a$	$^{15}\text{NH}_3^a$	$^{14}\text{ND}_3^a$	$^{14}\text{NH}_3^b$
1	3549	3549	2620	3537
2	3265	3265	2397	3265
3	1605	1580(25) ^c	1605(0) ^c	1574(31) ^c

^awith O-16 O₂;

^bwith O-18 O₂

^cthe bracketted values indicate a shift from the normal isotope

(most surface hydrogen being removed) the hydroxyl band subsequently formed was much weaker. Further, the shift to 2620 cm^{-1} on deuteration is expected for a hydroxyl group that is bound to platinum^{177,178}.

The frequencies in row 3 show that an oxidized species is formed which is sensitive to N-15 and O-18 substitution. The species must contain N and O and its frequency is indicative of an N=O containing species.

Two mixed isotope experiments, one involving a 1:1 mixture of N-14 and N-15 NH_3 isotopes, the other using a 1:1 mixture of O-16 and O-18 oxygen, would serve to show whether more than one N or O atom is involved, but in the absence of this data it is reasonable to suppose that there is only one atom each of N and O, on the basis of the relatively large shifts observed for these isotopes.

No band shift is apparent for the deuterium substituted species although an adsorbed species of the type Pt:NHO may not be expected to exhibit large frequency shift for the deuterium analogue, and the above mentioned effect of excess oxygen to move the band to higher frequencies may mask a small shift due to an isotope effect.

There is some evidence that the band at 1605 cm^{-1} may be related to a hydrogen containing species because of the existence of a small band remaining in the N-H stretching region at 3265 cm^{-1} . It could be argued that this band may only represent residual chemisorbed un-oxidized ammonia species, however it persists throughout the addition of oxygen but disappears when excess oxygen is added, as does the 1605 cm^{-1} band. Also, the deuterium analogue produces a band at 2397 cm^{-1} and is clearly distinguished from the 2375 cm^{-1} of the chemisorbed ammonia species.

The addition of small amounts of hydrogen when the 1605 cm^{-1} band is present restores the original spectra of the chemisorbed NH_3 .

The intermediate formed seems to have some similarity to an intermediate formed in the case of nitric oxide chemisorption. Nitric oxide chemisorbed to Pt is known to absorb at 1800 cm^{-1} ¹⁵⁷ but unpublished works in this laboratory have indicated that the addition of hydrogen to chemisorbed Pt:NO also produces a band in the 1600 cm^{-1} region.¹⁸⁵

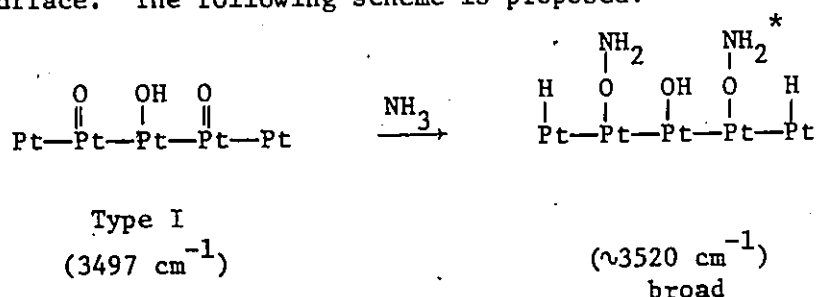
The oxidized species is therefore tentatively assigned to either at Pt:NO or a $\text{Pt:N} \begin{array}{l} \text{H} \\ \diagup \\ \text{=O} \end{array}$ species. If the former species is the correct assignment, then one must also assume that another species also exists which has an absorption band indicative of an N-H containing species.

In reactions occurring where NH_3 and O_2 are simultaneously passed over a catalyst, the possibility of oxygen being pre-adsorbed before reaction with ammonia, may lead to adsorbed intermediates other than that proposed above, in which ammonia was pre-adsorbed. Therefore, a study of the infrared spectra of ammonia adsorbed to various oxidized states of platinum was made.

Adsorption on PtO and PtOH (I and II)

Morrow and Ramamurthy^{177,178} have described how two types of PtOH can be formed on platinum. If these two species were formed separately, it was found that on PtOH II (platinum purported to be in a low oxidation state, $\nu_{\text{OH}} = 3544\text{ cm}^{-1}$) ammonia was adsorbed as it does on a normal surface with bands at 3372 , 3268 and 3155 cm^{-1} , but, on

PtOH I (platinum in a higher oxidation state, $\nu_{OH} = 3497 \text{ cm}^{-1}$) a new profile appeared with bands initially appearing at 3345, 3265 and 1490 cm^{-1} (Figure 8-7 shows the O-H and N-H stretching regions). This new profile was also obtained if NH_3 was adsorbed to a surface of PtO. Hence NH_3 may not be interacting with PtOH groups and therefore the observed decrease in intensity and shift to higher wavenumber of the PtOH band ($3493 \sim 3520 \text{ cm}^{-1}$), which occurs when NH_3 is adsorbed to a PtOH I surface is probably just a reflection of the change in oxidation state of the Pt surface when NH_3 is adsorbed; rendering a new environment for PtOH. This experiment indirectly confirms the theory proposed by Morrow and Ramamurthy¹⁷⁸, that the two 'types' of PtOH (I and II) are inherently the same but appear in different oxidation states of the surface. The following scheme is proposed:



The shift of the PtOH band is smaller than the PtOH I - PtOH II frequency separation¹⁷⁸ but this is probably due to the presence of an adjacent chemisorbed ammonia species. Also the region of PtOH absorption became indistinct (Figure 8-7D) and it was impossible to determine whether any PtOH I remained.

When the adsorbed species on PtOH I were degassed up to 100°C ,

*Evidence for PtONH_2 is presented later.

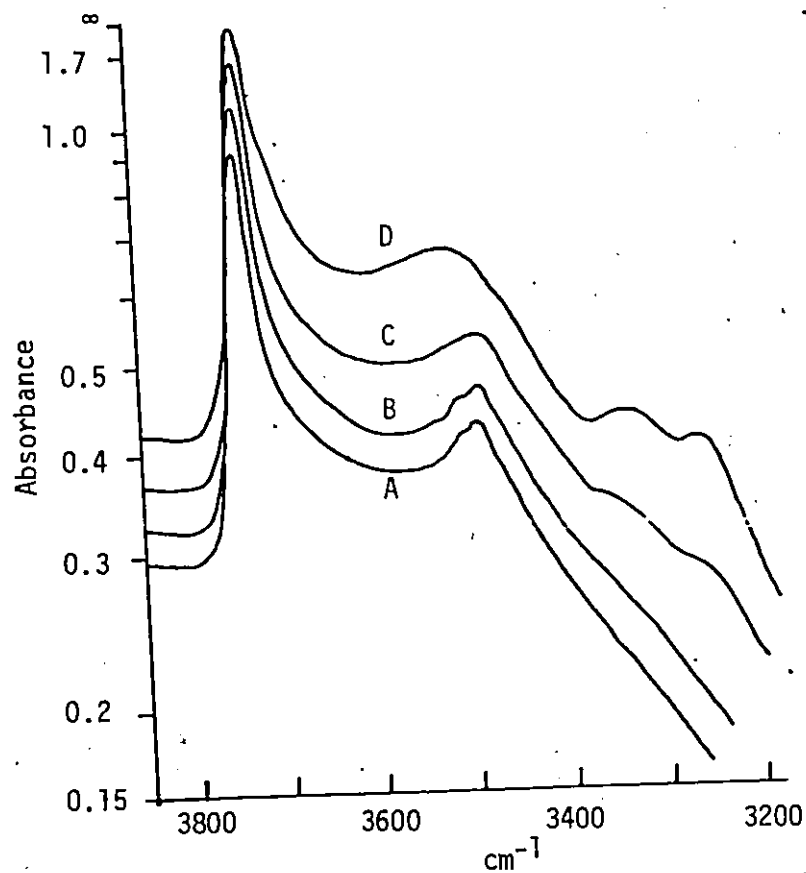


FIGURE 8-7

40 mg cm⁻² Pt/SiO₂.

- A. Spectrum of PtOH I (see text)
- B,C. Successive doses of NH₃ (<1 torr)
- D. Addition of 1 torr NH₃ for 1 min then pumped 1 hr at room temperature.

new bands grew together at 3308 and 1425 cm^{-1} as 3345 and 1490 cm^{-1} were removed. Further degassing to 200°C removed 3308 and 1425 cm^{-1} leaving bands which appear on a normal platinum surface (i.e., 3372, 3265 and 3155 cm^{-1}). Figure 8-8 shows the spectra from 3500-3100 cm^{-1} during these degassing steps.

Isotope substitution of NH_3 (N-15 and D) and of the surface (O-18) rendered extra data. Table 8-3 has the frequency values obtained for all isotopes used.

The 3308 and 1425 cm^{-1} bands disappeared when a small amount of hydrogen (1 torr) was added to the cell, and bands appeared at 3372 and 3268 cm^{-1} , characteristic of ammonia adsorbed on a normal platinum surface. The addition of oxygen (1 torr) also removed the 3308 cm^{-1} band but the only one new band appeared (at 1605 cm^{-1}), which was probably formed as a result of the oxidation of ammonia species formed on platinum and not platinum oxide. (There does not appear to be a uniform oxide surface as evidenced by the appearance of Pt:NH_3 bands at 3372 and 3268 cm^{-1} when the species adsorbed on the PtOH surface were degassed at 200°C.)

The adsorption of an NH_3/ND_3 mixture produced only one new band in the N-D stretching region at 2440 cm^{-1} .

A possible model for the initially adsorbed species is PtONH_2 . The shifts expected in the N-D stretch of this model, for N-15 and O-18 substitution are expected to be small for the symmetric mode and larger for the antisymmetric mode, which is what was observed. A single new band at 2440 cm^{-1} appearing on partial deuteration supports such a structure (analogous to the SiNHD spectra in Chapter 4) though

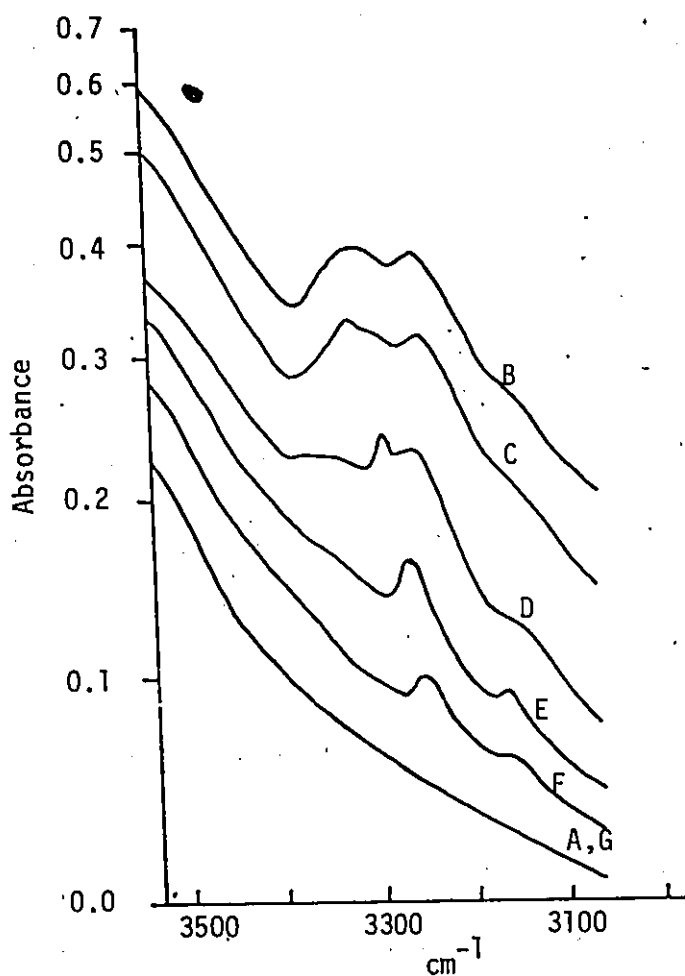


FIGURE 8-8

Desorption of chemisorbed ammonia from a PtOH I surface ($40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$).

- A. Background spectrum of PtOH I.
- B. Admitted 10. torr NH_3 for 5 min, then pumped 15 min at room temperature.
- C-G. Different stages of degassing, C, 16 hr at room temperature; D, 1 hr at 100°C ; E, 1 hr at 200°C ; F, 16 hr at 300°C ; G, 1 hr at 300°C .

Spectra B-F were displaced for purposes of presentation.

TABLE 8-3
Infrared Bands for Ammonia Adsorbed on
Oxidized Platinum (PtOH I)

	Band Positions (cm ⁻¹)					
	¹⁴ NH ₃ ^a	¹⁴ ND ₃ ^a	¹⁵ NH ₃ ^a	¹⁴ NH ₃ ^b	¹⁴ NH ₃ / ¹⁴ ND ₃ ^{a,c}	
Initial adsorption	3345	2487	3338	3338	-	2440
	3265	2375	3265	3263	-	2375
	1495	-	1495	1495		
New bands after de- gassing at 100°C	3308	2420	3305	3305	3305	2420
	1425	-	1425	1425	1425	

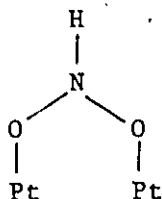
^a Adsorbed on O-16 PtOH I surface

^b Adsorbed on O-18 PtOH I surface

^c A 1:1 mixture. The N-H bands were closely overlapping in the spectrum of the initially adsorbed species.

the equivalent band expected for δ_{NHD} was not observed probably because it absorbs below the transmission cut-off at $\sim 1350 \text{ cm}^{-1}$. Also the apparent co-existence of a platinum-ammonia species with the species adsorbed on platinum oxide makes measurement of band positions for the latter species difficult.

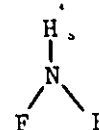
The species absorbing at 3308 and 1425 cm^{-1} seems to be bonded to PtO since no bands arise at these frequencies when a platinum-ammonia surface is degassed to 100°C . This species may be multiply bonded to the surface.



The partial deuteration experiment shows that this species contains just one hydrogen atom and only small shifts for N-15 and O-18, expected in a framework of this type, were observed in the high frequency mode. The 1425 cm^{-1} shifted into the total absorption region of silica in the fully deuterated case, indicating that it represents a mode involving hydrogen.

The shift with deuterium may appear to be inconsistent with the above structure, however there is evidence for large deuterium shifts in molecules of the same symmetry.

For instance ν_5 of is the antisymmetric δ_{NHF} mode and shifts from 1425 to 1042 cm^{-1} upon deuteration¹⁸⁶. In HBF_2 ¹⁸⁷ and NaHCO_2 ¹⁸⁸ the same mode is shifted from 1402 to 1195 cm^{-1} and 1380 to 1028 cm^{-1} , respectively.



Summary

On the basis of isotopic substitution studies, ammonia appears to be co-ordinatively bound to platinum without dissociation. Oxidation of this species produces a surface species which is altered by either hydrogen or oxygen treatment, and is assigned to either Pt:NO or Pt:NHO.

On a PtO (or PtOH I) surface there is some evidence for a PtONH_2 species which, on degassing, becomes $\text{Pt}_2\text{O}_2\text{NH}$.

CHAPTER 9

PYRIDINE ON PLATINUM

In recent years, pyridine has been used extensively as a probe molecule to ascertain the acidity of surfaces, as well as provide a measure of the distribution of acid sites present, and since it is both a Lewis and Brønsted base it has been used to characterize the type of acidity exhibited by oxide surfaces^{113,191-5}.

The most easily identifiable bands in the infrared spectrum of pyridine are those due to ring deformation modes. Parry¹¹³ has shown that when pyridine was adsorbed to either Lewis or Brønsted acid sites of an oxide surface, sharp bands were produced in the infrared region between 1650-1350 cm^{-1} , which depended on the nature of the solid oxide used. A prior analysis of chloroform solutions of each of pyridine, pyridine co-ordinatively bonded to BCl_3 and of pyridinium chloride, enabled Parry¹¹³ to qualitatively assign surface species to these forms.

Table 9-1 lists typical band positions of pyridine on acid solids. Barrow¹⁹⁶ has also observed differences in the spectra of co-ordinatively bonded pyridine and of the pyridinium ion.

On normal silica surfaces there are no acidic sites and pyridine is only weakly bound by hydrogen bonding (Figure 9-1B), however on a highly degassed silica (800°C), as mentioned in Chapter 4, pyridine exhibits bands which indicate that it is co-ordinatively bound to a Lewis acid site, and is related to the formation of active

TABLE 9-1

Infrared Bands of Pyridine on Acid Solids*

Hydrogen bonded (cm^{-1})	Bound as a Lewis base (cm^{-1})	Bound as a Brønsted-base (cm^{-1})
1440-1447 (vs)	1447-1460 (vs)	1485-1500 (vs)
1485-1490 (w)	1488-1503 (v)	1540 (s)
1580-1600 (s)	~1580 (v)	1620 (s)
	1600-1633 (s)	1640 (s)

*From reference 113.

vs = very strong; s = strong; v = variable; w = weak

sites on silica. Provided that pretreatment temperatures are kept below 400°C, and no active sites are formed, then for a silica supported metal, one should see bands which are only characteristic of the metal once hydrogen bonded species are removed (at 150°C).

To the authors knowledge the only interpretive study of pyridine adsorbed to a supported platinum was conducted by Primet et al¹⁹⁷ using a partially CO covered Pt/Al₂O₃ surface. The band for PtCO was observed to shift from 2065 to 1990 cm⁻¹ as pyridine was adsorbed and strong bands appeared in the 1650-1350 cm⁻¹ region at 1620, 1565, 1535, 1490, 1450, 1430 and 1405 cm⁻¹. In a separate study of pyridine adsorbed on Al₂O₃, bands were found at 1620, 1576, 1490 and 1450 cm⁻¹ which were attributed to pyridine co-ordinated to Al₂O₃. The bands at 1535 and 1430 cm⁻¹ in the Pt/Al₂O₃ spectra were assigned to a 2,2' dipyridyl species on the basis of a comparison with the spectral features of some metal complexes of this compound¹⁹⁸, a band at 1490 cm⁻¹ was ascribed to pyridine on Al₂O₃ and bands at 1620, 1565 and 1450 cm⁻¹ were assigned to either pyridine on Al₂O₃ or 2,2' dipyridyl on platinum. A 1405 cm⁻¹ band was unassigned. The choice of Al₂O₃ as a support has prevented Primet et al¹⁹⁷ from making definitive assignments, and interpretations other than those proposed by these authors are possible. For example, there is a possibility that pyridine could be co-ordinated to platinum, having bands at the same frequencies as those for pyridine on Al₂O₃. As well, bands at 1620, 1535 and 1490 cm⁻¹ might have equally been assigned to a pyridinium ion. These ambiguities could have been averted by using an inert support like silica.

The initial reason for studying the adsorption of pyridine

in this laboratory was to explore the possibility that a pyridinium ion might form as a result of reaction with surface adsorbed hydrogen. It was felt that if such a species could be observed then it would shed light on the much discussed problem of the nature of adsorbed hydrogen on platinum.

Hydrogen on Platinum

In recent years, much work has been published concerning the question of the nature of adsorbed hydrogen on platinum and although it is fairly well established that two types of Pt-H are identifiable by the technique of infrared spectroscopy, the manner in which these hydrogens are bound is still unresolved.

A weakly bonded Pt-H species is known to adsorb at 2120 cm^{-1} and a strongly bound species, with an absorption band near 2040 cm^{-1} has been postulated by Eischens and Plisken¹⁹⁹, Palazov et al²⁰⁰ and Dixon et al²⁰¹, although Primet et al²⁰² contend that the band is attributable to a CO impurity.

Both forms of adsorbed hydrogen are thought to be due to an atomic species since no band for PtHD has ever been found¹⁹⁹.

Mignolet²⁰³ has studied the adsorption of hydrogen on platinum by following the change of surface potential. A strongly bonded form produced a negative surface potential and a weakly bonded form gave rise to a positive surface potential. Although, at best, only two forms of hydrogen are identifiable by infrared spectroscopy for supported platinum catalysts, up to five different adsorbed hydrogens have been observed by the method of temperature programmed



desorption²⁰⁴, and by potentiodynamic studies of platinum single crystals²⁰⁵.

Eischens²⁰⁶ believed that hydrogen could be adsorbed to platinum as a proton because the addition of H_2 to a Pt/SiO_2 surface containing a partial monolayer of CO lowered the frequency of the CO stretching mode which he claimed was due to H atoms donating charge back to the metal.

Eley²⁰⁷, on the other hand, thought that hydrogen was found as a hydride because pretreatment of the surface with oxygen enhanced the intensity of the 2120 cm^{-1} band for weakly bonded hydrogen and that the hydrogen may be bound to patches of oxidized platinum. This idea was rejected by Eischens¹⁸⁹ because he observed that the intensity of a band for adsorbed CO was also enhanced by oxygen treatment but the position of the band indicated that CO was not bound to oxidized platinum.

It was felt that since pyridine is an excellent monitor of protonic hydrogen then it might elucidate the question of the polarity of adsorbed hydrogen.

Experimental

In each experiment for both silica and silica supported platinum, 40 mg cm^{-2} discs were used in cell A. Band positions from $1650\text{--}1350\text{ cm}^{-1}$ were calibrated against water vapour.

Results and Discussion

Studies of pyridine in this laboratory were initiated with an examination of the infrared absorption features obtained when

pyridine (10 torr) was adsorbed to a silica disc which had been previously degassed to 300°C (to remove moisture). Very strong bands appeared in the 1650-1350 cm^{-1} region, (Figure 9-1B, Table 9-2), comparable to Parry's¹¹³ observations for pyridine adsorbed on silica, and in the 4000-2000 cm^{-1} region, a broad absorption band appeared near 3000 cm^{-1} which was attributed to the hydroxyl stretch of the hydrogen bonded hydroxyl groups of silica. All of these bands disappeared when the surface was degassed at 150°C for 1 hr.

The addition of 10 torr of pyridine to a Pt/SiO_2 surface, followed by evacuation of the excess gas phase pyridine for 5 min revealed a spectrum containing some of the bands observed in the pyridine/ SiO_2 spectrum (Figure 9-1C) plus new bands at 1565, 1536, 1431 and 1410 cm^{-1} . Further pumping at room temperature for 30 min gradually lowered the intensities of the bands of the hydrogen bonded species, but the new bands were unaltered (Figure 9-1D). The hydrogen bonded species could be totally removed by pumping for prolonged periods (>24 hr) at room temperature, or by pumping at 150°C for 1 hr. In both cases, the new bands remained unaffected indicating that they could be attributed to a strongly adsorbed species. Some weak bands in the $\nu(\text{CH})$ region at 3072, 3040 and 3018 cm^{-1} were also observed after the hydrogen bonded species had been totally evacuated which are apparently related to those in the 1650-1350 cm^{-1} region. (No bands were observed in the $\nu(\text{CH})$ stretching region below 3000 cm^{-1} .) The new bands persisted until the degassing temperature was raised to 300°C.

If only small doses of pyridine were added (<1 torr instead of 10 torr) the initial spectrum was different in that the bands of

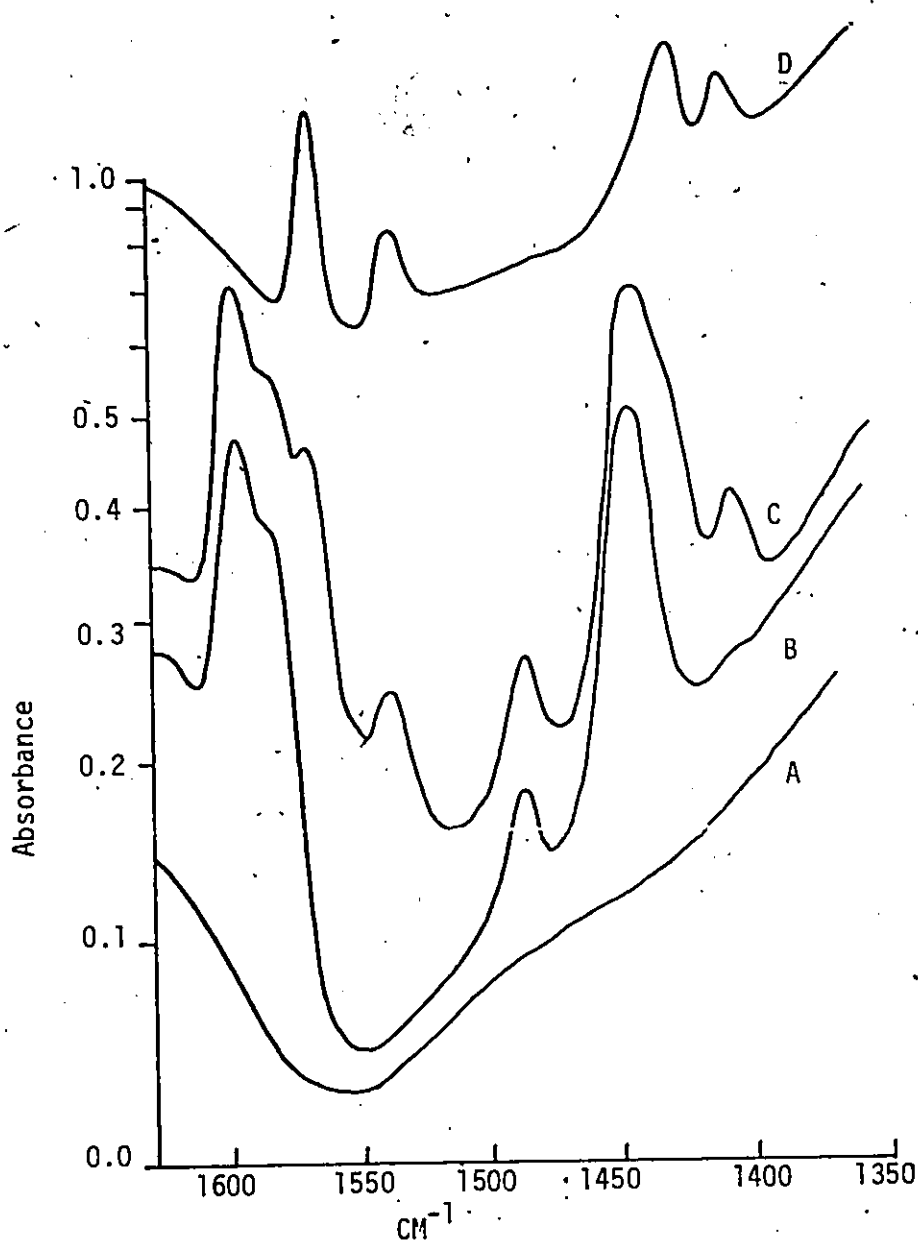


FIGURE 9-1
Pyridine adsorbed on silica, Pt/SiO₂

- A. Background spectra of Pt/SiO₂ (40 mg·cm⁻²). A similar background was observed for a 40 mg cm⁻² silica which had been degassed at 300°C for 1 hr.
 - B,C. Admitted 10 torr pyridine for 10 min then evacuated for 30 min at room temperature. B, on silica sample; C, on Pt/SiO₂
 - D. Pt/SiO₂ (c) evacuated at 150°C for 30 min.
- Spectra C and D were displaced for purposes of presentation.

TABLE 9-2

Infrared Bands of Pyridine and Pyridine-d₅
on Silica and Platinum, in the 1600-1350 cm⁻¹ Region

		Physically adsorbed species (cm ⁻¹)					Strongly bound species ^a (cm ⁻¹)			
Pyridine	SiO ₂	1596	1582	1485	1445					
	Pt/SiO ₂	1624	1595	1578	1487	1445	1567	1536	1431	1410
Pyridine-d ₅	SiO ₂ ^b	1565	1558	1547						
	Pt/SiO ₂ ^b	1565	1558	1547			1533	1506		

^a species which remain after degassing at 150°C are regarded as strongly bound.

^b surfaces deuterated prior to adsorption.

the hydrogen bonded pyridine were very weak whereas those of the strongly bound species were relatively strong with about one-third of the intensity of that shown in Figure 9-1. However, on repetitive scanning from $1650\text{--}1350\text{ cm}^{-1}$ (5 min per scan) the bands due to hydrogen bonded pyridine were observed to gradually diminish as the new bands intensified such that after 1 hr only the new bands were observed.

The bands representing the strongly bound species appear at about the same frequencies, and have the same relative intensities, as those observed by Primet et al¹⁹⁷ for pyridine adsorbed on $\text{Pt}/\text{Al}_2\text{O}_3$ though none of the new bands correspond to the ranges given for either Lewis or Brønsted adsorbed pyridine on acid solids, as given in Table 9-1. Also, a comparison of the observed frequencies in platinum-pyridine co-ordination complexes does not immediately identify the bands of the strongly bound species as those of a co-ordinated pyridine. Typically the main bands in the $1650\text{--}1350\text{ cm}^{-1}$ region in $[\text{Pt}(\text{Py})_4]\text{X}_2$ complexes²⁰⁸ (x=halide) are at 1610, 1485 and 1450 cm^{-1} . Nevertheless, it is obvious that species other than hydrogen bonded pyridine do exist on platinum. All the bands in the $1650\text{--}1350\text{ cm}^{-1}$ region observed for pyridine adsorption to SiO_2 and Pt/SiO_2 are listed in Table 9-2.

Hydrogenation of Adsorbed Pyridine

When 300 torr of hydrogen was added to a surface containing only the strongly bound pyridine species, small amounts of desorbed product were obtained, insufficient for gas phase infrared identification but sufficient for mass spectroscopic examination. Prominent peaks at $m/e = 85, 84$ and 57 indicated the presence of piperidine

($C_5H_{11}N$). The resultant adsorbed species had infrared bands at 2950, 2865, 1525 and 1460 cm^{-1} . These latter bands were also observed to appear when 10 torr of piperidine was adsorbed to a fresh Pt/SiO_2 surface, then degassed for 1 hr at room temperature. Further degassing at room temperature for 12 hr produced small bands at 1567, 1536, 1431 and 1410 cm^{-1} , indicating that pyridine, or a pyridine related molecule is a dehydrogenation product. The phenomenon of reversible hydrogenation and dehydrogenation is commonly observed for adsorbed saturated and unsaturated aliphatic and cyclic hydrocarbons¹⁹⁰ and is not unexpected for pyridine²⁰⁹.

If a surface containing only strongly bound pyridine was heated to 150°C in 300 torr of hydrogen, the subsequent products identified by mass spectrometry and infrared spectroscopy were exclusively ammonia and n-pentane. No infrared bands due to the surface species were observed after this operation.

Spectra of Adsorbed Pyridine- d_5

When pyridine- d_5 was adsorbed on a deuterated Pt/SiO_2 new bands appeared, some of which could be attributed to a physical adsorption on deuterated silica and others which persisted even after degassing at 150°C for 30 min (see Table 9-2). These latter bands were at 1533 and 1506 cm^{-1} and exhibited an identical profile to the 1567 and 1536 cm^{-1} pair of bands of strongly bound C_5H_5N . Absorptions corresponding to the $1431/1410\text{ cm}^{-1}$ bands of adsorbed C_5H_5N could not be observed, presumably because they had shifted into the total absorption region of silica ($< 1350\text{ cm}^{-1}$).

The observed deuterium shift from 1567 cm^{-1} to 1533 cm^{-1} is

consistent with the observed ν_{8b} mode of pyridine²¹⁰, though a similar shift on deuteration might be expected for the ν_{8b} mode of 2,2'-dipyridyl which also absorbs near 1567 cm^{-1} ^{198,211}. The 1536 cm^{-1} shift to 1506 cm^{-1} may possibly be assigned, on the basis of literature values^{212,213}, to an adsorbed 2,2'-dipyridyl since bands appear near these frequencies in the normal and deuterated molecules, but an assignment of the 1536 cm^{-1} band to a pyridinium ion species is unwarranted since a band which appears at 1532 cm^{-1} for the pyridinium ion is known to be shifted to 1307 cm^{-1} upon full deuteration,^{210,214} and no band was observed at 1490 cm^{-1} which is expected for a pyridinium species²¹⁰. Furthermore, when the surface was degassed at 400°C prior to the room temperature adsorption of $\text{C}_5\text{H}_5\text{N}$, ensuring that all physically and chemically adsorbed hydrogen was desorbed, the 1536 cm^{-1} band had the same intensity as it did on a hydrogen covered surface, making it unlikely that $\text{C}_5\text{H}_6\text{N}^+$ is formed under these circumstances. Nevertheless, it is possible that small amounts of hydrogen could result from the dissociative chemisorption of pyridine on platinum. Indeed if a dipyridyl is formed from pyridine, then hydrogen atoms might become available for adsorption to the surface or for further reaction with the adsorbed species.

When pyridine- d_5 was adsorbed on a hydrogen covered Pt/SiO_2 instantaneous exchange between the H of the SiOH groups and the D of deuterated pyridine was observed. This exchange could be taking place as either (a) direct exchange between the H of the SiOH groups and pyridine- d_5 or (b) as exchange between surface hydrogen on the metal and pyridine- d_5 with the resulting deuterium exchanging with SiOH

groups (catalyzed by platinum). When pyridine- d_5 was adsorbed on a surface that had been treated with carbon monoxide, or on one which had been degassed at 400°C for 50 hr (to remove surface hydrogen), very little deuteration of the SiOH groups took place. This means that (b), above, is the probable route for the exchange of ring hydrogens with SiOH hydrogens and also infers that pyridine may not be dissociatively chemisorbed (which would be required for the formation of a dipyridyl). On the other hand if the extent of exchange is limited, say to one H atom per pyridine molecule, then the number of deuterium atoms forming SiOD species may be very small because the number of adsorbed pyridine molecules is minor compared to the number of SiOH groups present. Thus exchange may be occurring but may not be manifested as a noticeable change in SiOH or SiOD intensity.

Oxygen Addition

An experiment with oxygen seems to indicate that two pyridine related species are present on platinum, which will be tentatively referred to below as species I and species II.

When 15 torr of oxygen was admitted to a surface containing only the strongly bound species, the 1567 and 1410 cm^{-1} bands (species I) were initially diminished in intensity with respect to the 1536 and 1431 cm^{-1} bands (species II). As well, all bands of the chemisorbed species (I and II) were shifted by about 5 cm^{-1} to higher wavenumber, and new bands appeared at 1610 and 1459 cm^{-1} (see Figure 9-2). When the oxygen was removed by degassing for 5 min, no immediate change occurred in the intensity of the species I and II spectral bands, or of the

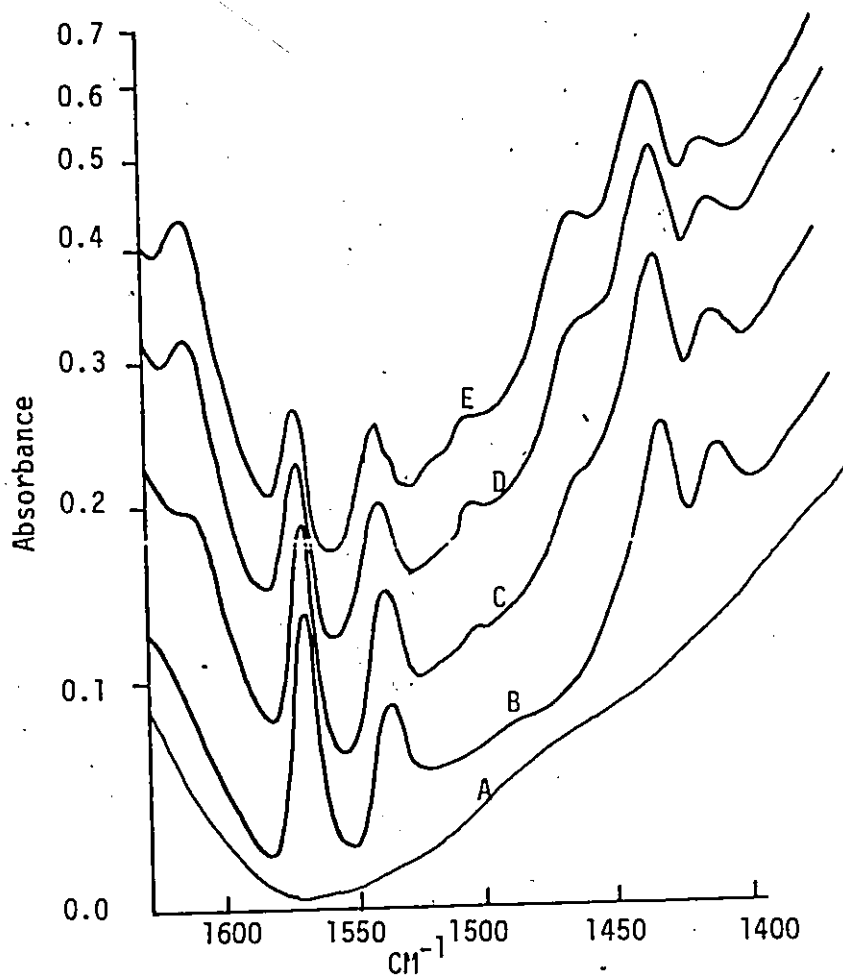


FIGURE 9-2

Treatment of chemisorbed pyridine in oxygen
using 40 mg cm⁻² Pt/SiO₂

- A. Background
- B. Admitted 10 torr of pyridine for 5 min, then degassed at 150°C for 1 hr.
- C. Added ~ 1 torr of oxygen; spectrum immediately.
- D. After 10 min.
- E. After 12 hr.

Spectra C, D and E were displaced for purposes of presentation.

1610 and 1459 cm^{-1} bands, but further pumping at room temperature (1 hr) caused the bands due to species I to be again enhanced. The 1610 and 1459 cm^{-1} bands could only be completely removed by degassing at 150°C. These latter bands may represent weakly bound species, but a comparison with the spectra of pyridine hydrogen bonded to silica (Figure 9-3B,C) shows that the band positions are not the same. However they are at the same frequency of the known bands of pyridine N-oxide which may indicate that this substance is physically adsorbed on the catalyst^{215,216}.

When the strongly bound species were exposed to 10 torr of oxygen for longer periods (24 hr) all the infrared bands disappeared. Short exposures of oxygen and subsequent degassing to 150°C always resulted in the appearance of a band to 2060 cm^{-1} probably due to a PtCO species arising from cracking and reaction with oxygen. A similar band appeared on non-oxygen treated surfaces only when degassing beyond 200°C. In this case, the band is probably due to a PtCN species. In the reverse experiment, the only bands which appeared when pyridine was adsorbed on a PtO/SiO₂ surface were those due to the species which is physically adsorbed on silica, that is, 1596, 1485 and 1445 cm^{-1} (Figure 9-3A).

If 10 torr of oxygen was admitted to a Pt/SiO₂ surface containing just the strongly bound species, the 1565 and 1410 cm^{-1} bands immediately diminished, as observed before, but then if the excess O₂ was removed by degassing at room temperature for 5 min, no further rapid changes in band intensity were observed. When the Pt/SiO₂ disc was left in a static vacuum for 12 hr, the ratio of species I and II band

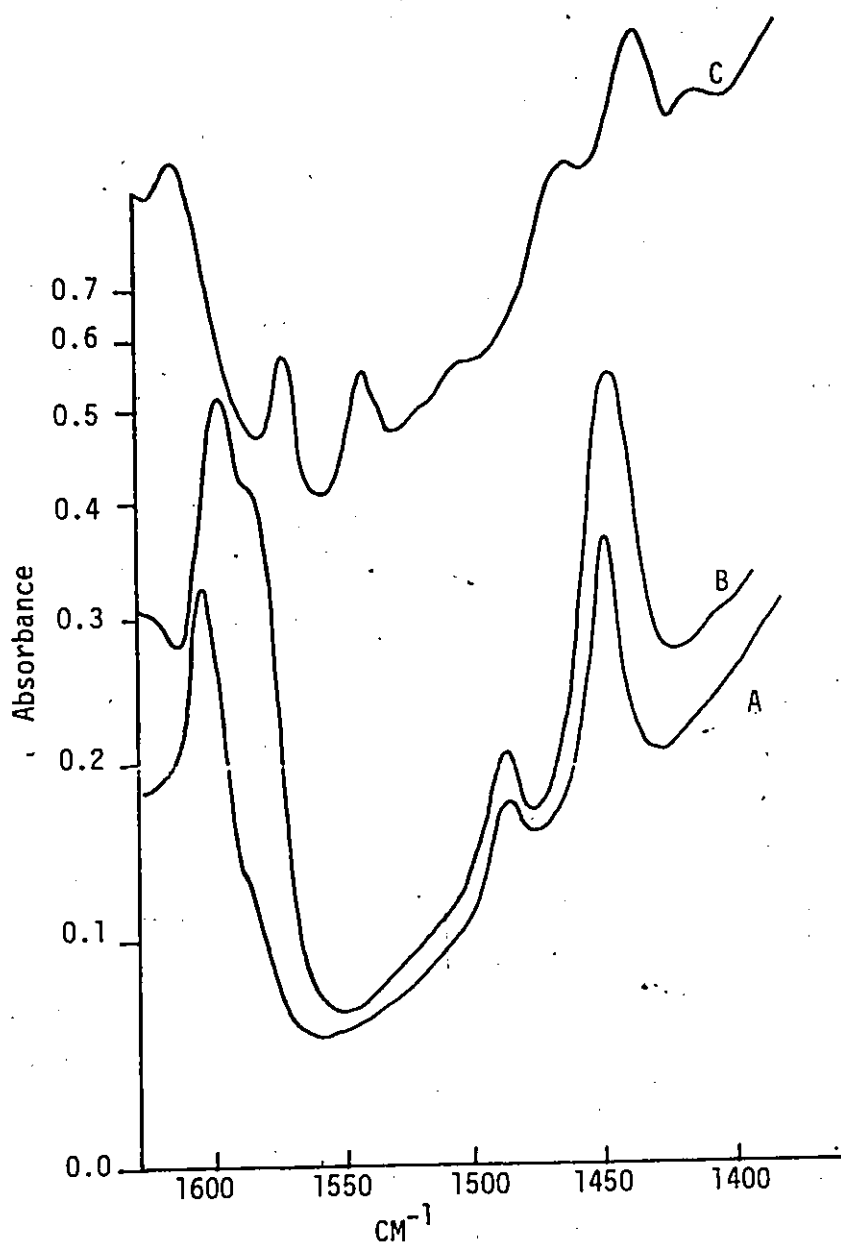


FIGURE 9-3

A comparison of band positions of pyridine adsorbed on PtO/SiO_2 and of pyridine chemisorbed on Pt/SiO_2 then treated in oxygen

- A. PtO/SiO_2 surface: 10 torr of pyridine admitted for 5 min, then degassed for 30 min at room temperature.
- B. SiO_2 surface: degassed at 300°C , cooled to room temperature then pyridine adsorbed as in A.
- C. Pt/SiO_2 surface: 10 torr of pyridine adsorbed for 5 min, then degassed at 150°C for 1 hr, cooled to room temperature then 1 torr O_2 added spectrum after 1 hr.

Spectra B and C were displaced for purposes of presentation.

intensities returned to approximately the same as it was prior to the oxygen addition, although the absolute values of the band intensities were lower.

This phenomenon suggests that there may be some preferred equilibrium concentration ratio of species I and II. However the results of the following experiments tends to refute this argument and to belie the existence of two species.

Temperature Effects

Pyridine was adsorbed to a Pt/SiO₂ disc in cell B and the spectra were studied over the temperature range -70 + +150°C. Though there was a narrowing of all bands, there was no evidence that one "species" was favoured over the other at any of these temperatures (i.e. the ratio of species I:II band intensities remained constant). Hence if there are two distinct species then it is improbable that they exist in equilibrium with each other. If this is so then the apparent 'equilibrium effect' with oxygen (before) may not be related to the existence of separate species after all, but is possibly a manifestation of unusual intensity effects upon selected modes of a single species (i.e. not all modes are expected to be affected equally when oxygen is added but in this instance the effect is such as to almost halve the intensity of the 1567 cm⁻¹ band but to leave the 1536 cm⁻¹ band virtually unchanged, see Figure 9-2).

In another experiment pyridine was adsorbed to a platinum surface which had been preheated to 150°C and the spectrum was exactly the same as for the room temperature adsorption experiment.

Adsorption of Pyridine on a PtCO/SiO₂ Surface

When a Pt/SiO₂ surface was left in contact with 30 torr of CO for 12 hr, then excess CO removed at room temperature, all sites were blocked for the subsequent chemisorption of pyridine on platinum, and the only bands initially present in the spectrum of the adsorbed species were those due to pyridine adsorbed on silica, and a band at 2060 cm⁻¹ due to PtCO.

If the reverse experiment was performed, whereby pyridine was adsorbed to Pt/SiO₂, degassed to 150°C and then CO admitted (8 torr) the intensity of each of the bands of chemisorbed pyridine was slowly diminished by about 50% over a 2.5 hr period and a band appeared at about 2020 cm⁻¹ (ν_{CO}).

There was no obvious trend for the preferential removal of species II compared to species I bands.

Addition of BF₃ to Adsorbed Pyridine

When BF₃ (1 torr) was added to a Pt/SiO₂ surface containing hydrogen bonded pyridine and the strongly bound species I and II, the bands due to hydrogen bonded pyridine immediately disappeared but those due to species I and II remained unaltered. New bands appeared which indicated that BF₃ had reacted with the silica support.

Apparently in both species I and II, the nitrogen lone pair is unavailable for attack by a Lewis acid.

Reaction with NH_3

Ammonia had no tendency to displace chemisorbed pyridine but conversely chemisorbed ammonia was rapidly displaced by pyridine. Since pyridine is known to have a greater nucleophilicity than ammonia²¹ toward platinum, this result is not unexpected.

Formation of Pyridinium Ion by HCl Addition

Pyridine was adsorbed to Pt/SiO_2 and the hydrogen bonded species pumped out. Subsequently 1 torr of dry HCl was admitted to the cell, which immediately altered the spectrum of the chemisorbed pyridine species, the bands at 1567, 1431 and 1410 cm^{-1} being reduced in intensity. A large new band appeared at 1487 cm^{-1} accompanied by the growth of a medium intensity band at 1536 cm^{-1} (Figure 9-4B). No further change occurred if HCl was left in the cell for 2 hr. Degassing at 75°C removed the new 1536 cm^{-1} and 1487 cm^{-1} bands and restored the intensities of the original bands. This indicates that the 1536 cm^{-1} band formed under these circumstances is not a chemisorbed species and is therefore not related to the band initially formed at that frequency, but is very likely due to a pyridinium ion which is known to have prominent bands at ~ 1530 and 1490 cm^{-1} ²¹⁰. The 2,2'-dipyridylium ion is known to have strong bands at 1600, 1500 and 1432 cm^{-1} ²¹² so its existence (and 2,2'-dipyridyl) can probably be discounted. It would seem from this experiment that the species adsorbed to platinum are pyridine molecules only.

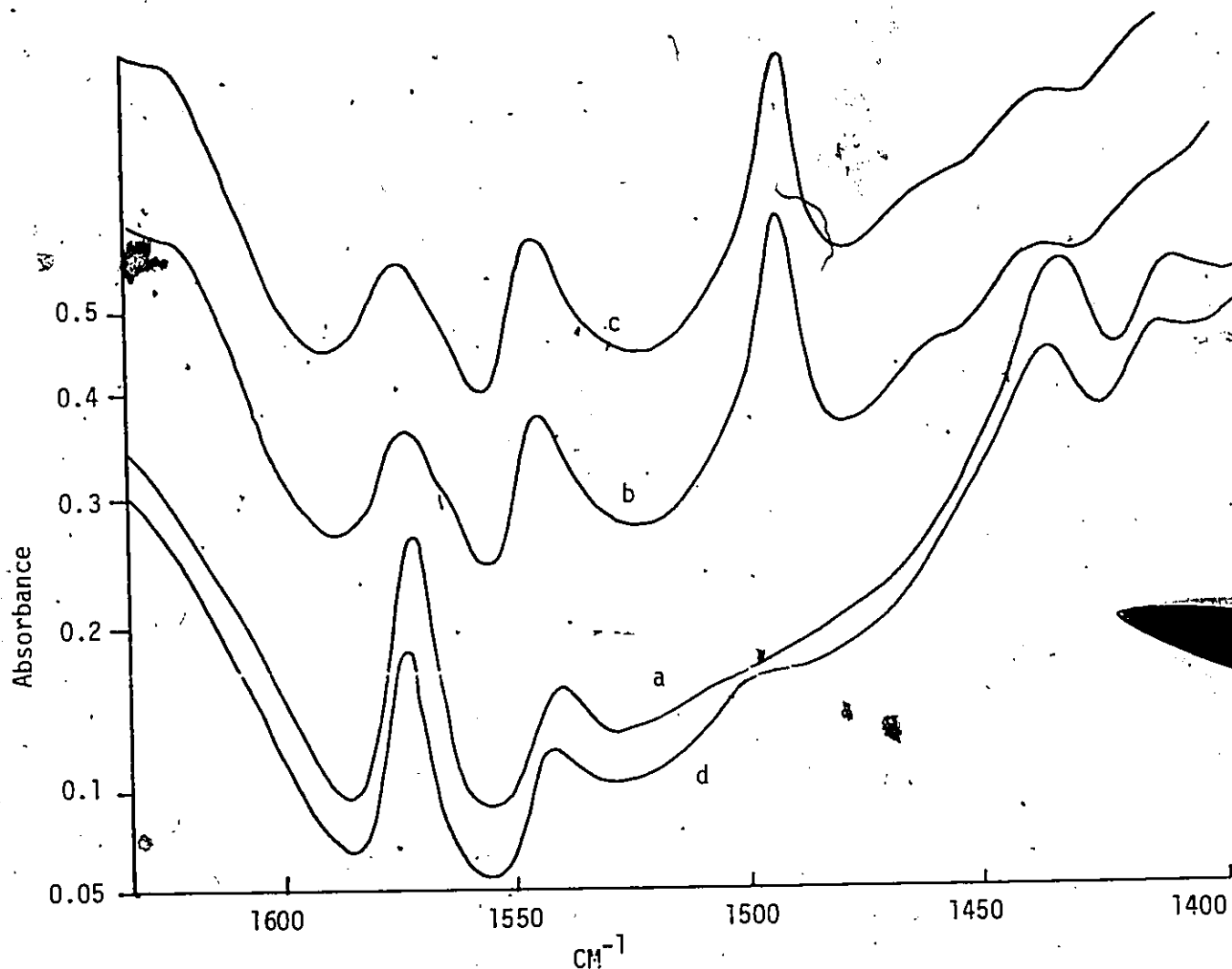


FIGURE 9-4 .

Treatment of chemisorbed pyridine with HCl
using $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$

- A. Admitted 10 torr pyridine for 5 min then pumped 150°C for 1 hr and cooled to room temperature.
 - B. Added ~ 1 torr HCl; spectrum immediately.
 - C. After 2 hr.
 - D. Pumped at 75°C for 12 hr and cooled to room temperature.
- Scan speed was $20 \text{ cm}^{-1} \text{ min}^{-1}$.

Conclusions

1. On the basis of the observed frequencies of the spectral bands of chemisorbed pyridine it would appear that a simple co-ordinated pyridine does not form on platinum. Metal complexes of co-ordinated pyridine have major bands near 1620, 1490 and 1450 cm^{-1} ²⁰⁸ and similar bands are formed for pyridine co-ordinated to silica (see Chapter 4) and to nickel²¹⁸, whereas in this work the bands are at much lower frequencies. However, the fact that BF_3 had no measurable effect on chemisorbed pyridine would appear to indicate that pyridine is either bound through the nitrogen atom, or that the reaction is sterically hindered.
2. The strongly bound species is not 2,2'-dipyridyl because of the absence of the expected two strong bands, one near 1620 cm^{-1} and the other in the range $1480\text{--}1450\text{ cm}^{-1}$. Therefore, the bands observed by Primet et al¹⁹⁷ at 1620 and 1450 cm^{-1} for pyridine on $\text{Pt}/\text{Al}_2\text{O}_3$ must be assigned to pyridine co-ordinated to Al_2O_3 . Indirect chemical evidence which suggests that the assignment to 2,2'-dipyridyl is incorrect is provided by the following observations; (a) the formation of pyridine N-oxide when O_2 is added; (b) the formation of piperidine when H_2 is added or of n-pentane and NH_3 when heated in H_2 at 150°C ; (c) the formation of pyridinium ion when HCl is added and not the 2,2'-dipyridylium ion. Further, there are no literature references to indicate that dipyridyls can be formed from pyridine over a platinum catalyst. In fact platinum is used for the dehydrogenation of piperidine to pyridine²¹⁹ and PtO is a recommended catalyst for the hydrogenation of 2,2'-dipyridyl to 2,2'-dipiperidyl²²⁰ which suggests that a conversion of pyridine to dipyridyl or vice-versa does not occur.

3. There is no evidence that a pyridinium ion is formed when pyridine is adsorbed on a hydrogen covered platinum surface.

The Identity of the Strongly Bound Species

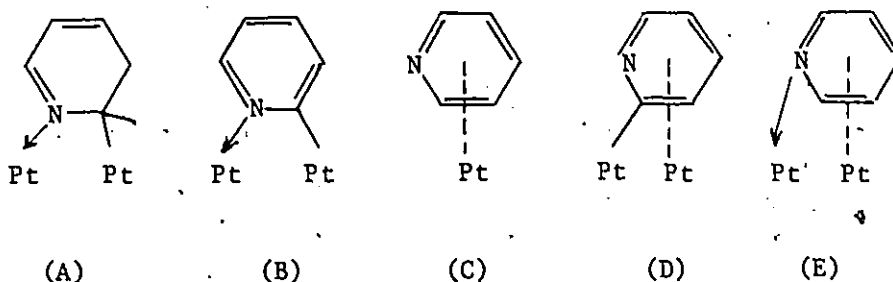
The alterations in relative band intensities when O_2 is added to strongly bound pyridine would seem to indicate that two distinct species are present, yet the weight of other evidence contradicts this as the following points show.

(i) Four bands appear in the $1650-1350\text{ cm}^{-1}$ region, the same number as appear in the spectra of liquid pyridine or of complexed pyridine²¹⁰ ($\nu_{8a,b}$ and $\nu_{19a,b}$), yet the oxygen experiment implies that there might be two pairs of bands belonging to two adsorbed species. On the other hand, it is difficult to account for the existence of only two bands for each species, when it is known that the adsorbate must be a pyridine like molecule since pyridinium ion, pyridine N-oxide or piperidine can be readily formed.

(ii) The ratio of the intensities of the so-called species I to II bands remained constant during the following: (a) as the temperature for degassing (accompanied by desorption) was raised from 150 to 300°C ; (b) when the temperature was varied from -70°C to $+150^\circ\text{C}$; (c) when CO was added, whereupon the adsorbed species was slowly desorbed; (d) when adsorption was carried out at 150°C instead of at 20°C ; (e) when small doses of pyridine were added so as to slowly build up the surface concentration to its maximum; (f) when the O_2 treated pyridine was degassed, the anomalous intensities slowly reverted to normal.

If two distinct species were present, one would have expected some clear indication of this in some of the above sequences.

The following can be considered as possible species which fit the spectroscopic observations.



The structures A and B are proposed to lie "edge-on" with respect to the surface whereas C, D and E are involved in π bonding and lie flat. Structures A, B and D have a conventional Pt-C σ bond at the '2'-position. The reasons for postulating binding at this position are two-fold. Firstly, it is known that pyridine is a poison of platinum surfaces, yet 2,6-dimethyl pyridine is much less so²⁰⁹, which implies that the "2"-position on pyridine has some special significance in connection with the mode of bonding. There are also closer spectral similarities with the known spectra of a "2-substituted" pyridine and that of the adsorbed species. For example, liquid 2-chloropyridine has bands at 1580, 1570, 1450 and 1420 cm^{-1} compared with 1580, 1570, 1480 and 1440 for liquid pyridine. Nonetheless, species A, above, can probably be discounted because there was no evidence for the existence of an aliphatic ν_{CH} stretching mode.

When CO was preadsorbed on a Pt/Al₂O₃ surface, Primet et al¹⁹⁷ observed a shift of the ν_{CO} band to lower wavenumber when benzene was subsequently adsorbed which they considered as strong evidence supporting the idea that benzene was π bonded to the surface and thus donating electrons. However, in the same paper they also reported a shift when pyridine was adsorbed which they attributed to electron donation from the nitrogen atom of pyridine or 2,2'-dipyridyl, not considering the possibility of π donation in this case. Each of the structures B to E provide charge to the platinum, either by donation from the nitrogen atom or from the ring. On the basis of the spectroscopic and chemical evidence so far discussed, it is not possible to choose between these. However, structures D and E would appear unreasonable on steric grounds since the conventional bond with the surface (the Pt-C σ bond in D or the Pt-N co-ordinate bond in E) would have to be at an appreciable angle with respect to the plane of the molecule. Therefore, structures B and C are the most likely ones and there is no reason to strongly favour one over the other on the basis of the present work. However, the fact that pyridine N oxide and pyridinium chloride were apparently so readily formed when O₂ or HCl were added, might favour structure C for which it could be assumed that the failure to co-ordinate with BF₃ is a steric reason if the π bonded pyridine is lying flat with the surface.

CHAPTER 10

NITRILES AND AMINES ON PLATINUM

This chapter is concerned with the adsorption of various carbon and nitrogen containing molecules on silica supported platinum surfaces.

There is surprisingly little published work which has been concerned with the adsorption of amines and nitriles on Group VIII metals. In view of the increased usage of metal catalysts for treatment of pollutants from industrial processes, such studies become important. Therefore, a study of the adsorption of nitriles and their amine analogues has been attempted in this laboratory in order to develop an understanding of the behaviour of C-N groups on a catalytic surface. It is known that Group VIII metals are active catalysts for the hydrogenation of nitriles²²¹ and therefore it was expected that similar surface intermediates might be formed from nitrile and amine adsorption.

The early infrared studies of adsorbed nitriles and amines on Group VIII metals generally lack detail. One of the reasons for this is undoubtedly due to the multitude of bands that are often obtained for even the simplest nitriles²²²⁻⁷. Also a species which may represent just a fraction of the adsorbates present may have a group which exhibits strong infrared bands (e.g. $\text{-C}\equiv\text{N}$) whereas other species which may be present in at least equal concentrations may

have no infrared bands at all (e.g. surface carbides or nitrides). Because of this, surface poisons may be present which cannot be detected by infrared spectroscopy and in order to acquire a reproducible set of adsorption data, a freshly prepared catalyst is often required for each experiment. The conditions for adsorption are also important, and any slight variations in pressure, temperature or adsorption time may alter the type and relative concentrations of the adsorbed species.

In order to understand the spectra of adsorbed C-N containing molecules, the bonding capabilities of cyanide ion to metals will be briefly discussed. The outer molecular orbitals of the CN^- ion may be represented in molecular orbital symbolism as $\text{KK}(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^0$. One of the consequences of efficient ligand-metal σ bonding is that the donor atom becomes more electropositive and therefore more receptive to back donation from the metal $d\pi$ electrons into the π_{2p}^* orbital. This relieves the metal of some negative charge which accumulates as a result of σ bonding²²⁸. Hence CN^- is capable of stabilizing metals in low oxidation states, but in this respect it is not as good as CO, RCN or RNC because it carries a negative charge and is therefore a poorer acceptor²²⁹. The strength of the $-\text{C}\equiv\text{N}$ bond then, is dependent upon the strength of the σ bond which is formed between metal and the ligand²³⁰. Jones²³¹ has formulated relationships to describe the force constants of metal cyanides, viz.

$$F_{\text{MC}} = a(S\sigma)_{\text{MC}} + b(S\pi)_{\text{MC}} \quad (1)$$

$$F_{\text{CN}} = c(S\sigma)_{\text{MC}} - d(S\pi)_{\text{MC}} \quad (2)$$

where F is the force constant, $(S\sigma)_{MC}$ and $(S\pi)_{MC}$ the strengths of the σ and π bonds in the metal-ligand bond, and a, b, c and d are arbitrary constants.

Thus when a bond is formed between a nitrile (RCN) and a metal, the $\nu_{C\equiv N}$ absorption mode would be expected to shift to higher frequencies if the bond were formed only with the unpaired electrons of the nitrogen atom as a result of the $C\equiv N$ force constant increasing, but the formation of an additional dative bond from the metal to the antibonding π_{2p}^* orbital of the nitrile tends to lower the $C\equiv N$ force constant and the frequency may be lowered²³².

For example, when nitriles are adsorbed to metal oxide adsorbents, they may form only a co-ordinate bond²³³⁻⁴ and the $C\equiv N$ frequency can be higher than the frequency of the free nitrile, but on metal surfaces there is the possibility of back donation and the frequency is generally lower^{222,229,234-6}. If the adsorbing nitrile is only physically bound, as it is on the hydroxyl groups of silica then the frequency is generally higher due to the formation of a weak hydrogen bond..

One of the earliest studies of the adsorption of C-N containing compounds was conducted by Kemball and Wolfe²³⁷ who found that the exchange of methylamine with deuterium was self poisoning and that this arose from the formation of strongly adsorbed residues. In subsequent studies of methylamine adsorbed on an evaporated platinum film, Kemball and Moss²³⁸ determined that fission of the C-N bond was the rate determining step for all products formed when H_2 was co-adsorbed. The main products were NH_3 and CH_4 but di- and trimethylamine

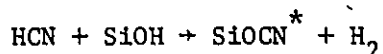
were also formed (identified by mass spectroscopy) which they attributed to the slower rate of hydrogenation of C fragments into CH_4 than of N residues into NH_3 .

To the authors knowledge there have been no infrared studies of the direct adsorption of methylamines (mono-, di-, or tri-) on platinum, but there have been some studies involving the adsorption of HCN on platinum whereby surface adsorbed amines have been proposed to exist. Dunken and Hobert²²⁵ investigated the adsorption of HCN on various silica supported metals (Rh, Pd, Ag) and like Kortum and Delfs²²⁷ they observed that there remained a chemisorbed species which had two broad bands near 3280 and 3340 cm^{-1} and a sharp band in the $\text{C}\equiv\text{N}$ stretching range (2160 cm^{-1} for Rh, 2080 and 2125 cm^{-1} for Pd and 2120 cm^{-1} for Ag). They only concluded that HCN had dissociated into H and CN groups*.

A more comprehensive study of HCN, BrCN and C_2N_2 adsorption on metals by Muller Litz and Hobert²²⁶ confirmed that an initial dissociation took place to produce adsorbed cyanides (MCN where M = Ni, Ir, Rh, Pd and Os and M was 25% by wt) but that, as well, a second slower process also occurred involving the production of polymers by a further dissociation of the initially adsorbed species. No attempt was made to identify these secondary products. They observed that HCN, BrCN and C_2N_2 produced similar spectral bands and they proposed

*It was also contended that a slow polymerization of HCN occurred on silica alone after an adsorption period of 3 days which was evidenced by a band at 1690 cm^{-1} that they attributed to a $-\text{C}=\text{N}$ species. As mentioned in Chapter 6, no reaction was observed with HCN on silica at ambient temperatures in this laboratory, even for adsorption periods of 3 days.

that this could only arise if each molecule had dissociated into a CN radical. The reaction of HCN at higher temperatures produced new CN bands at higher frequency and it was proposed that either a metal catalyzed reaction occurred with SiOH groups, or that this species was somehow formed on the metal itself.



Bands in the 2100-2170 cm^{-1} region were formed when oxygen was adsorbed to a nitrile covered surface, or alternatively if a nitrile was adsorbed to an oxygen covered surface. The lowest frequency CN related bands (2000 cm^{-1}) were thought to be due to MCN species adsorbed at defect zones in the metal where the electron density of the metal is higher. A table of frequencies from reference 226 is shown.

In a separate work, Anderson and Clark²⁴⁸ also found that there were two processes for the reaction of HCN and H_2 over evaporated metal films (Pt, Pd, W, Co, V and Cu). Products were formed over a 50-110°C temperature range and were deduced (by mass spectroscopy) to be; a) CH_2NH_2 by simple hydrogenation; b) C-N bond rupture to produce NH_3 and carbides (slowly forming CH_4); c) C-N bond formation producing $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, C_2 , C_3 hydrocarbons, $\text{C}_2\text{H}_5\text{NH}_2$ and CH_3CN . They found that HCN partially inhibited the H/D exchange process and concluded that a strongly bound species was formed as well as a weakly bound species. They proposed that initially HCN could adsorb as either:

* This species does not exist, as shown in Chapter 6, but SiNCO may be formed.

TABLE 10-1
Frequencies of Metal Cyanides

cm ⁻¹	Structure
2000-2100	M-C≡N (at defect sites)
2100-2170	M-C≡N
2170-2250	$\begin{array}{c} \text{C}\equiv\text{N} \\ \diagup \\ \text{M} \\ \diagdown \\ \text{O} \end{array} \quad \text{or} \quad \begin{array}{c} \text{M}-\text{C}\equiv\text{N} \\ \\ \text{M}-\text{O} \end{array}$
2250-2350	Si-OCN or M-OCN

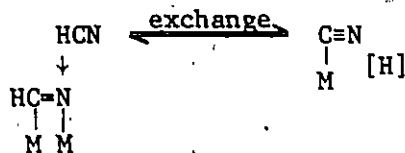


Diagram 10-1

Infrared spectral studies of higher molecular weight amines and nitriles however, indicate that the surface species which form are not so variegated as with HCN and CH_3NH_2 adsorption.

Oranskaya et al²²² adsorbed caprylonitrile ($\text{C}_7\text{H}_{15}\text{CN}$), butyronitrile ($\text{C}_3\text{H}_7\text{CN}$) and benzonitrile ($\text{C}_6\text{H}_5\text{CN}$) on Pt/SiO_2 and Pd/SiO_2 samples and found bands for each, in the region $2220\text{--}2190\text{ cm}^{-1}$ which they attributed to a co-ordinatively bonded molecular nitrile. They reasoned that the species was not a metal $\text{--C}\equiv\text{N}$ species because the frequency was slightly different for each adsorbate. However a band at 2160 cm^{-1} for butyronitrile was thought to be due to a surface cyanide. This band was distinguished in that it remained unchanged with the adsorption of CO whereas the $\nu_{\text{C}\equiv\text{N}}$ frequency of the co-ordinatively bonded species was shifted to higher wavenumber, corresponding to a decrease in the degree of dative back bonding from the metal to the nitrile, (as a similar dative bond forms in M--CO ²³⁹). Caprylonitrile and its hydrogenated analogue octylamine produced an identical series of stable surface compounds on Pt/SiO_2 which could be interconverted by pumping out the excess and then treating with hydrogen. They²²² proposed that the following series of compounds were formed.

$\text{CH}_3\text{CH}_2\text{NH}_2$, C_2N_2 , CH_3NC and CF_3CN in the hope that a clearer pattern of the adsorption characteristics of nitriles and amines might emerge. Each molecule was adsorbed on a silica supported Pt catalyst.

Experimental

All platinum samples were prepared as described in Chapter 2. The percentage of the metal was 16%. Except where specified, the surfaces used were degassed at 300°C prior to use to remove adsorbed H_2 . In some spectra shown, the absorption bands of the supporting silica were compensated for by placing a silica disc in the reference beam. Band frequencies in the $2200\text{--}2000\text{ cm}^{-1}$ region were calibrated with DCl .

Results and Discussion

- A) Adsorption of Methylamine (mono-, di- and tri-), HCN and C_2N_2 on Pt/SiO_2

Methylamine

An investigation of the adsorption of methylamine revealed that dehydrogenation occurred immediately because a band at 2070 cm^{-1} appeared, characteristic of a $-\text{C}\equiv\text{N}$ containing species. With 10 torr of CH_3NH_2 in the cell, the only other identifiable bands at 3387, 3323, ~ 2900 (broad), 1590, 1478 and 1437 cm^{-1} could all be assigned to CH_3NH_2 hydrogen bonded to silanol groups of the supporting silica.

Pumping for 5 min at room temperature removed virtually all physically adsorbed species, but a complex series of bands remained (see Table 10-2 and Figures 10-1(i) and 10-1(ii)) which are not

TABLE 10-2
Adsorption of Methylamine on Platinum

	$\nu(\text{NH})$ cm^{-1}	$\nu(\text{CH})$	$\nu(\text{CN})$	$2000-1300 \text{ cm}^{-1}$
a) 10 torr of CH_3NH_2 admitted	3387(s) 3323(s)	observed by hydrogen bonded SiOH band	2070(s)	1600(s) 1478(s) 1437(s)
b) Pumped 15 min at room temperature	3377(w) 3330(w) 3275(w) 3172(w) 3100(w)	2969(s) 2938(s) 2907(w)	2070(s)	$\sim$ 1520(w) 1505(w) 1470(m) 1433(m)
c) Pumped 15 hr at room temperature	3345(wsh) 3300(s) 3145(m) 3100(m)	2969(s) 2938(m) 2907(w)	2070(s) 2183(w)	1590(s) 1522(sb) 1470(w) 1433(w)
d) Pumped 100°C 2 hr	3300(s) 3180(m) 3110(m)	same	2070(s) 2183(m)	1590(vs) 1522(sb) 1470(m) 1433(w)
e) Added 150 torr H_2 for 10 min then pumped for 10 min	broad profile from $\sim 3350-3100 \text{ cm}^{-1}$; individual bands indistinct	same	2062(s)	1522(m) 1470(w) 1433(w)

w = weak; m = medium; s = strong; sh = shoulder; b = broad

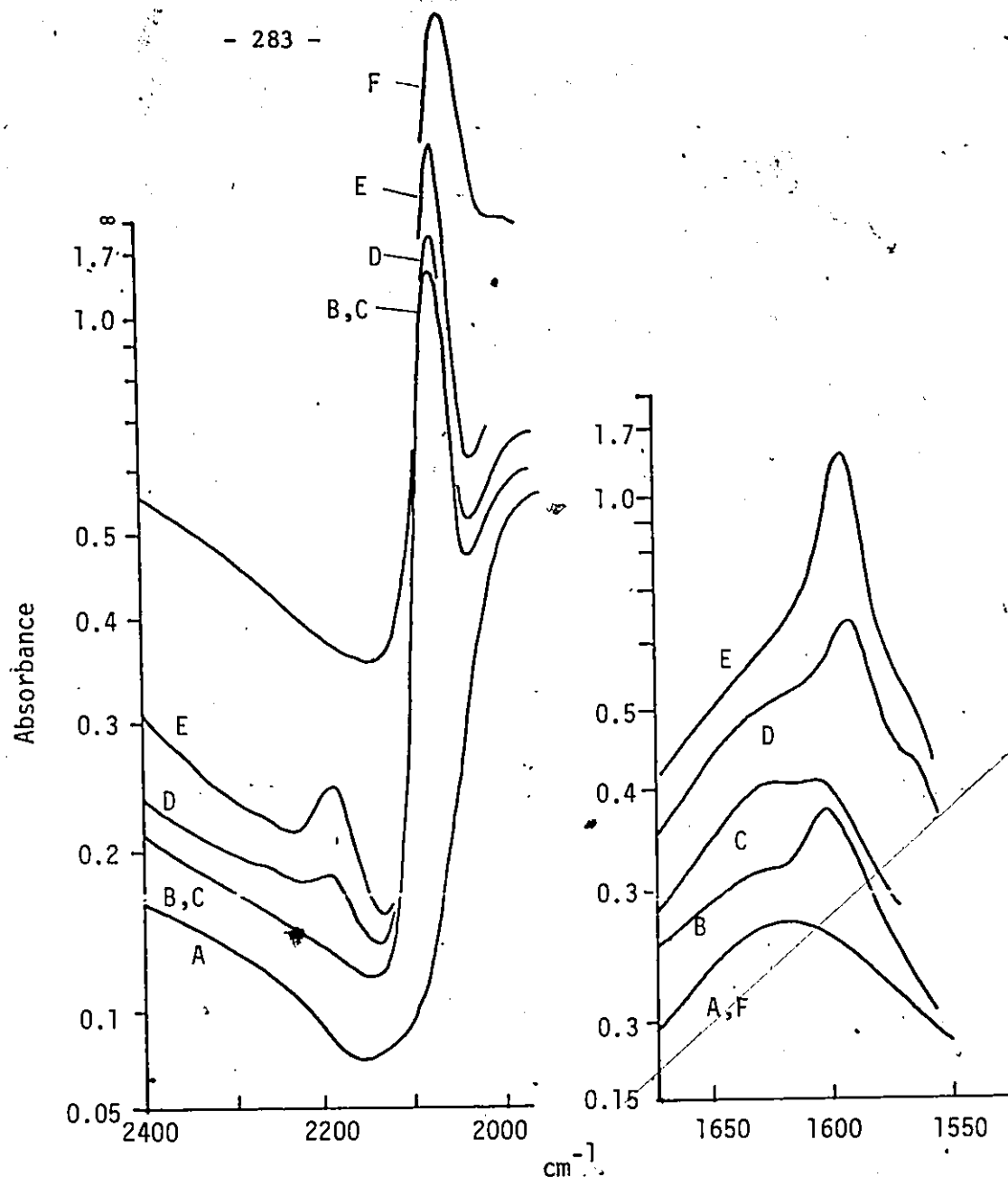


FIGURE 10-1(j)

Adsorption of methylamine

(see also Figure 10-1(ii))

A. Background spectra of $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.

B. Admitted 10 torr of CH_3NH_2 .

C, D. Degassed at room temperature; C, 5 min, D, 15 hr.

E. Degassed at 100°C for 2 hr then cooled to room temperature.

F. Admitted 150 torr of H_2 for 10 min then pumped for 10 min at room temperature.

Spectra B-E have been displaced for purposes of presentation (also F in the $2400\text{-}2000 \text{ cm}^{-1}$ region).

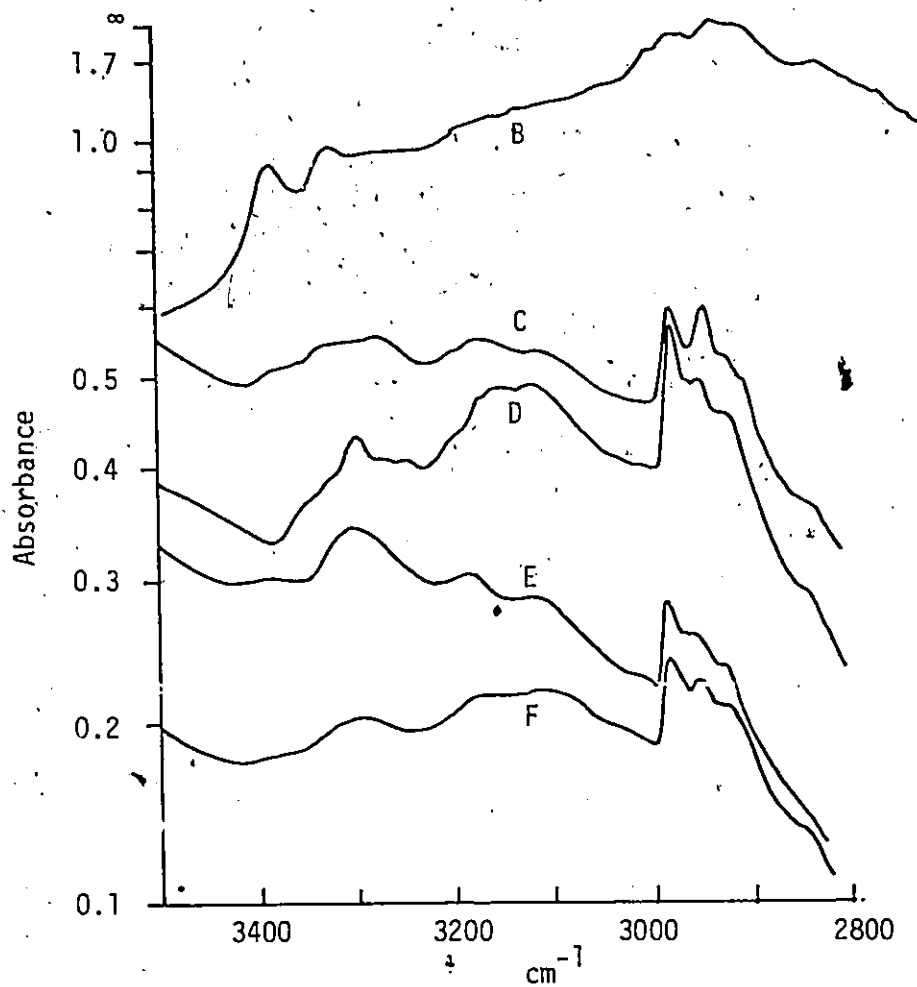


FIGURE 10-1(ii)

Adsorption of methylamine

(see also Figure 10-1(i) where sequences are described).

Background spectrum (A) is not shown.

associated with a simple chemisorbed CH_3NH_2 species. Pumping for prolonged periods (Figures 10-1(i)C,D and 10-1(ii)C,D) produced new complex features in the N-H stretching region as well as bands at 2183 cm^{-1} and 1590 cm^{-1} . These latter bands disappeared when H_2 was added (Figure 10-1(i)F) but reappeared upon prolonged pumping (not shown). When D_2 was admitted to the cell, again these bands disappeared but the 1590 cm^{-1} band did not reappear after prolonged degassing (16 hr at room temperature) which suggests that this band has its origin in a δ_{NH_2} mode rather than a $\nu_{\text{C=N}}$ mode. (Adsorption of CD_3ND_2 verified this point, no band was produced near 1600 cm^{-1} on degassing). The 2070 cm^{-1} band shifted to 2062 cm^{-1} in hydrogen and remained at this frequency when H_2 was removed. Experiments were also conducted with mixtures of H_2 and CH_3NH_2 to check whether the dehydrogenation of CH_3NH_2 could be suppressed by the presence of an excess of H_2 . It was observed that dehydrogenation was suppressed only with a forty-fold excess of H_2 , but a 2062 cm^{-1} band immediately formed when H_2 was removed.

It is very difficult to determine what species are present on the surface but from the multiplicity of bands appearing in the N-H stretching region it is clear that several species may exist. It is believed that no simple fragments exist on the surface and that even the band at 2070 cm^{-1} is not representative of M-CN because of the shift to 2062 cm^{-1} when H_2 was added. (This is discussed later in connection with HCN adsorption). The bands at ~ 3300 , 2183 and 1600 cm^{-1} appeared to grow together as the surface was degassed and may possibly be associated with a polymeric HCN product; however, the absorption

bands do not seem to coincide with the bands of diamino-maleonitrile which is a well known polymer product of HCN²⁴⁰.

The C-H region remained relatively unchanged throughout the degassing cycle except for a decrease in the intensity of a band at 2938 cm^{-1} , which may be related to $-\text{CH}_2-$ groups. The addition of hydrogen caused the band to increase which suggests that a surface skeletal C-H species may exist which can be reversibly hydrogenated to a $-\text{CH}_2-$ species.

Dimethylamine and Trimethylamine

The adsorption of dimethylamine produced only one band due to chemisorbed species in the $\nu(\text{NH})$ region, several in the $\nu(\text{C-H})$ region, and, after prolonged evacuation, two bands in the $\nu(\text{C}\equiv\text{N})$ region at 2153 and 1963 cm^{-1} (see Table 10-3). This suggests that dimethylamine also underwent dehydrogenation to give two distinct surface $\text{C}\equiv\text{N}$ containing species. The appearance of only one band in the $\nu(\text{N-H})$ region indicates that only a secondary amine is present. Bands at 1483 , 1440 and 1424 cm^{-1} are probably due to C-H bending modes.

The adsorption of trimethylamine produced one band in the $\nu(\text{NH})$ region (but only after prolonged pumping), several in the $\nu(\text{C-H})$ region and two bands were observed after short periods of adsorption in the $\nu(\text{C}\equiv\text{N})$ region. A strong band at 1561 cm^{-1} may be due to a

$>\text{C}=\text{N}$ stretching mode. Again, lower frequency bands at 1498 , 1456 and 1490 cm^{-1} are probably due to C-H bending modes. The production of unsaturated groups ($\text{C}=\text{N}$, $\text{C}\equiv\text{N}$) and an N-H band suggests that trimethylamine is dissociatively chemisorbed.

TABLE 10-3

Adsorption of Di- and Trimethylamine on Platinum

	VN _H Region		VCH Region		VCN Region		Bending Region	
	A	B	A	B	A	B	A	B
Adsorbed at 20°C for 15 m pumped for 10 m	3323(m)	-	2983(m)	2993(w)	2147(s)	2147(s)	1483(s)	1561(s)
	-	-	2948(s)	2975(s)	-	1975(m)	1440(sh)	1498(s)
	-	-	2912(s)	2912(sh)	-	-	1424(sh)	1456(sh)
	-	-	2873(m)	2873(m)	-	-	-	1409(s)
	-	-	2792(m)	2833(s)	-	-	-	-
Degassed for 18 h at 20°C	3307(w)	3355(wsh)	2975(wsh)	2993(sh)	2153(s)	2153(s)	1483(sh)	1561(s)
	-	-	2934(s)	2975(sh)	1963(m)	1965(m)	1424(sh)	1498(s)
	-	-	2909(sh)	2912(s)	-	-	-	1456(sh)
	-	-	2873(sh)	2852(m)	-	-	-	1409(s)
	-	-	2849(sh)	2758(w)	-	-	-	-
Added 200 torr of H ₂ at 20°C	3307(w)	3355(wsh)	2983(sh)	2975(sh)	2153(s)	2153(s)	1485(s)	1498(s)
	-	-	2909(bm)	2959(s)	2055(m)	2058(m)	-	1456(w)
	-	-	2836(sh)	2944(sh)	2000(w)	2000(m)	-	-
	-	-	2788(sh)	2890(m)	-	-	-	-
	-	-	-	2852(s)	-	-	-	-

A = (CH₃)₂NH
B = (CH₃)₃N

w = weak
m = medium
s = strong
sh = shoulder
b = broad

Table 10-3 lists the absorption bands observed at various stages of degassing and for the addition of H_2 to the adsorbed species for both di- and trimethylamine. Three bands appeared in the nitrile region when hydrogen added to either adsorbed di- or trimethylamine.

HCN

As mentioned in Chapter 6, no reaction took place when HCN was adsorbed on silica although there was a weak interaction with the $SiOH$ groups, producing bands at 3250 and 2100 cm^{-1} for physically adsorbed HCN, and a band at $\sim 3500\text{ cm}^{-1}$ due to hydrogen bonded silanols. However, an instantaneous reaction occurred when HCN was adsorbed on Pt/SiO_2 . Varied results were obtained depending on the conditions. Small amounts of HCN (1 torr) gave rise to prominent bands in the N-H stretching region and the $\nu_{C\equiv N}$ region which could be attributed to strongly bound species (Figure 10-2(i) and (ii)). A band at 2070 cm^{-1} was similar in shape and intensity to the band observed for the adsorption of CH_3NH_2 (see Figure 10-2(ii)B). The presence of N-H stretching bands indicates that HCN dissociates on platinum, however only a single weak C-H stretching band appeared at 2984 cm^{-1} (Figure 10-2(i)B) accompanied by a band at 1465 cm^{-1} . A band at 1610 cm^{-1} increased in intensity with progressive pumping at room temperature but immediately disappeared when H_2 was added. (Figure 10-2(ii)D). Pumping out H_2 for one hour at room temperature produced a new band at 1590 cm^{-1} (not shown) which could then be successively removed or reformed in the presence or absence of hydrogen (similar to a 1590 cm^{-1} band for CH_3NH_2). However, the band could not be regenerated after D_2

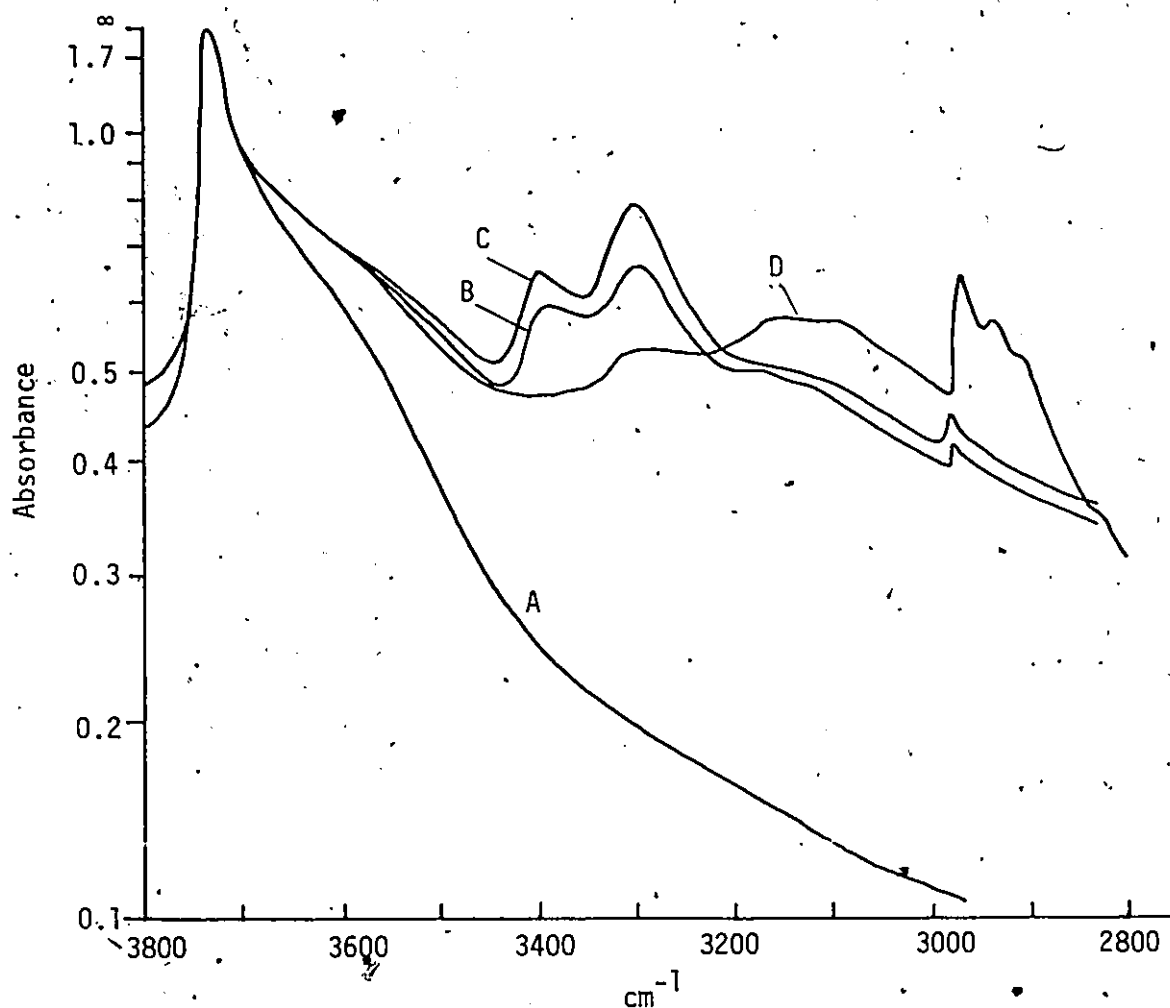


FIGURE 10-2(i)

Adsorption and hydrogenation of HCN

(see also Figure 10-2(ii)).

A. Background spectrum.

B. Admitted ~ 1 torr of HCN.

C. Evacuated for 1 hr at room temperature.

D. Admission of 300 torr of H_2 for 5 min, then evacuated for 15 min at room temperature.

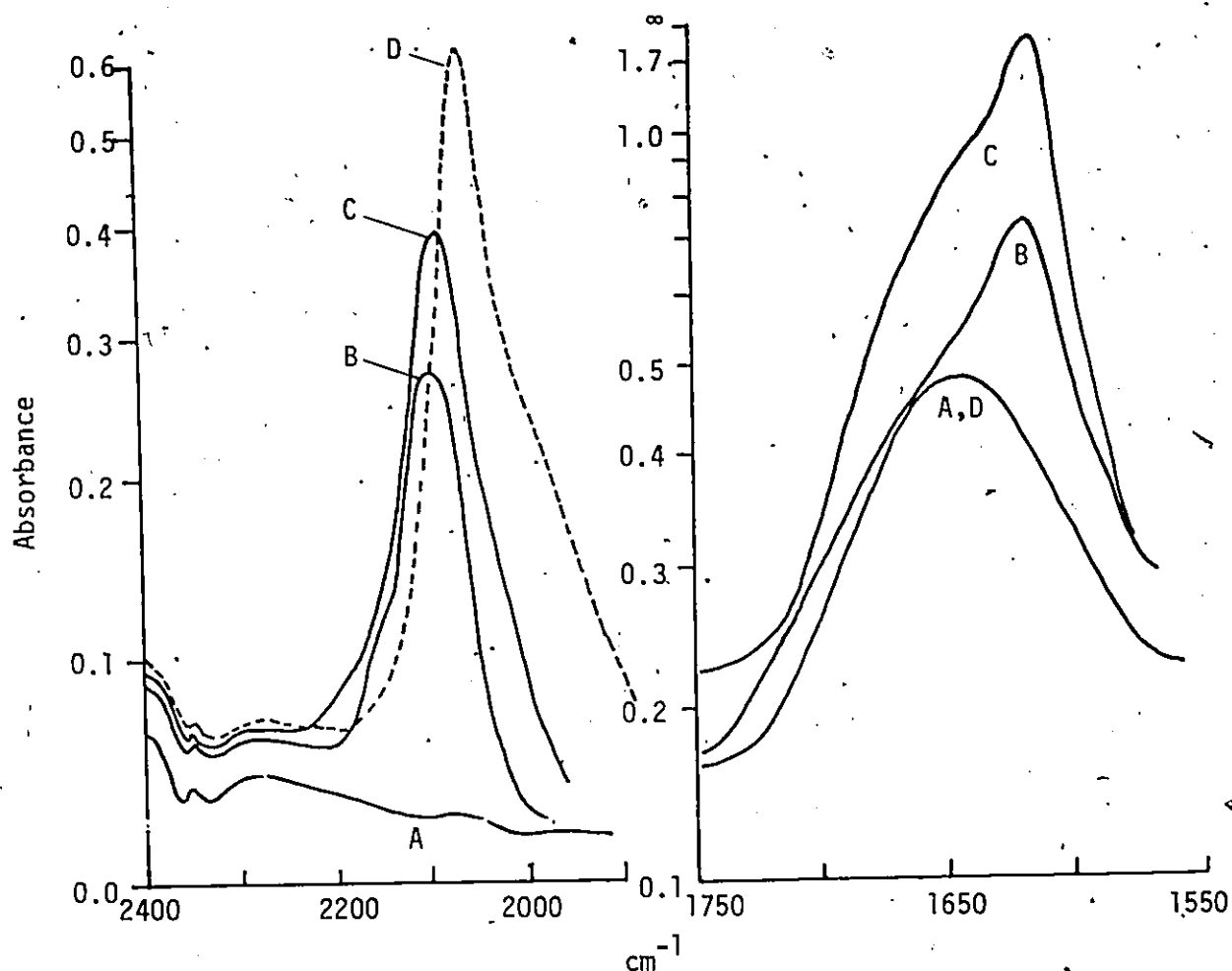


FIGURE 10-2(ii)

Adsorption and hydrogenation of HCN

(see also Figure 10-2(i) where sequences are described).

Negative absorption in the 2400-2000 cm^{-1} region is due to presence of CO_2 in the reference beam of the spectrometer.

Absorption due to SiO_2 has been cancelled out in the 2400 - 2000 region by placing a disc in the reference beam.

was added then pumped out which suggests that an -NH_2 species is responsible for this feature.

The addition of hydrogen produced new bands in the NH stretching region but the bands were indistinct due to a broad band near 3100 cm^{-1} resulting from the production of a physically adsorbed species which formed hydrogen bonds with silanol groups. Three prominent C-H bands grew at 2970 , 2936 and 2905 cm^{-1} and the 2070 cm^{-1} band shifted to 2060 cm^{-1} (Figure 10-2(i)D and (ii)D). At this stage, the spectrum closely resembled that obtained after CH_3NH_2 was adsorbed, treated in H_2 and pumped for 10 min (compare Figure 10-2(i)D with 10-1(ii)E). The band frequencies for HCN adsorption are shown in Table 10-4. Since no band was observed to form at 2183 cm^{-1} on pumping (as it did with CH_3NH_2) then a band at $\sim 1590\text{ cm}^{-1}$ common to HCN and CH_3NH_2 spectra is probably not associated with a species absorbing at 2183 cm^{-1} (despite the fact that these two bands grew together in the CH_3NH_2 series).

It is apparent that the species formed on initial adsorption and after H_2 is added are similar when either HCN or CH_3NH_2 react with Pt/SiO_2 . In fact if larger amounts of HCN were adsorbed (~ 10 torr), the spectrum obtained was almost identical to the initial adsorption spectrum for CH_3NH_2 , probably because more H atoms are available from the dissociation of HCN. It should be noted that the spectral bands listed for adsorbed CH_3NH_2 and HCN (in Tables 10-3 and 10-4) were obtained from the same Pt/SiO_2 sample. It was found that the spectra of the adsorbed species was very dependent upon the sample used. For some samples, the $\nu_{\text{C}\equiv\text{N}}$ band of adsorbed HCN was found to be as high as 2090 cm^{-1} , but the equivalent band for CH_3NH_2 was also found at this

TABLE 10-4

Adsorption of HCN (1 torr) to Pt/SiO₂. Frequencies (cm⁻¹)

Conditions	νN-H	νC-H	νC≡N	2000-1300 cm ⁻¹
Adsorbed 1 torr HCN	3413(m) 3308(m)	2981(w)	2070(s)	1810 ~1465 (broad)
Pumped 16 hr at room temperature	increased intensity	same	increased intensity	increased intensity same
Adsorbed 300 torr of H ₂ for 5 min	broad profile from ~3350 to ~3100 cm ⁻¹ individual bands indistinct	2970 2936 2905	2057(s) (increased intensity)	- ~1530(m) ~1470(w) 1430(w)
Pumped 15 min room temperature	(~same)	same	2057(s)	1590 same

frequency. Hence the values listed should not be regarded as the definitive frequencies.

When DCN was adsorbed on a silica disc containing only SiOH groups, instant exchange of the silanol groups occurred. Similarly on Pt/SiO₂ a rapid exchange took place, and a large band appeared at 2060 cm⁻¹. No band appeared near 1610 cm⁻¹ which confirms that the bands which appear at this frequency for HCN adsorption is probably related to an -NH₂ mode. The band at 2060 cm⁻¹ was broader than in the HCN case.

Muller-Litz and Hobert²²⁶ had assumed that a band formed near 2070 cm⁻¹ could be attributed to an M-CN species, however, there is reason to suspect that this is not so because of the band shift when H₂ is added and the different frequency for adsorbed DCN. It might be reasoned that such a shift could be related to the co-adsorption of H atoms at adjacent Pt sites. However, a series of isotope experiments tend to belie the existence of a simple M-CN species upon initial adsorption as discussed below.

Isotopically substituted hydrogen cyanides were adsorbed and the observed shifts did not fit a simple M-CN or M-NC model. (This is shown in Table 10-5). Care was taken to adsorb exactly the same amounts of each isotope. The same surface was used in each case and regenerated in O₂ at 200°C then H₂ at 400°C. Mixtures of C-12 and C-13 HCN were used so that the frequency shift could be directly measured, however with N-14/N-15 mixtures of HCN, the bands were too broad to be resolved and separate adsorptions had to be performed. This was repeated several times to ensure that the frequency shifts were not due to a change in sample condition.

A program was used to solve the quadratic equation for frequencies arising from a 2x2 matrix of potential and kinetic energy terms.

The calculation was performed with the M-CN model, for example, using the following information: 1) The three required force constants F_{MC} , F_{CN} and F_{RR} (the interaction force constant) and 2) the appropriate G matrix elements (similar to those used in Chapter 6 for the SiCN and SiNC problem). The three force constants were systematically varied within limits and frequencies for the normal molecule computed. If the computed frequency was within 1.0 cm^{-1} of the observed, then the calculation was extended to the other two isotopes, and the shifts computed. A range of frequencies was obtained, corresponding to the many combinations of the three force constants which produce reasonable solutions. The mass of the surface was given a value of 1000, and the limits to the force constants used were F_{RR} , $1.000 \rightarrow -1.000$; F_{CN} , $18.500 \rightarrow 15.000$; F_{MC} , $5.000-2.000$. A similar computation was set up for the M-NC model.

It can be seen from Table 10-4 that the models chosen do not fit the observed frequency shifts. The M-CN model may appear to produce shifts close to that of the observed values for the N-15 and C-13 shifts but these latter values both fall at the lower end of the allowed ranges which is not tenable. When one shift is at the low end of the range, the other should be at the upper limit.

The calculated values obtained for the shifts are compatible with those obtained in the SiCN, SiNC problem, though in this case the program calculated a range of acceptable values compared to

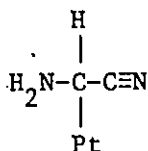
TABLE 10-5
Calculated and Observed Frequency Shifts
for Isotopes of Adsorbed HCN
(cm^{-1})

Isotope of HCN	Model ^a		Observed Frequency	Shift
	M-CN	M-NC		
C-12, N-14	-	-	2076.7	-
C-13, N-14	50.8-44.6	37.0-43.8	2033.7	43.0
C-12, N-15	26.5-31.5	38.4-32.6	2050.0	26.7

^aThe values listed are the ranges of frequency shifts possible for N-14 → N-15 and C-12 → C-13 isotopic substitutions.

Schachtschneider's program which evaluates single acceptable frequencies.

Hence, contrary to Muller-Litz and Hoberts²²⁶ proposition it appears that a simple M-CN product does not form. It had been assumed by these authors that the $\nu_{\text{C}\equiv\text{N}}$ band represented a separate and distinct species because no changes were observed in the band despite changes in other regions of the spectrum. However, in this work it has been found that the band does tend to increase in intensity along with other bands in the spectrum as the surface is degassed (see Figures 10-2(i) and (ii)). Since the band is affected by hydrogen addition it is tentatively proposed that the species may be of the type



producing bands at 3413, 3308 and 1610 cm^{-1} (NH_2); 2981 cm^{-1} (C-H) and 2070 cm^{-1} ($\text{C}\equiv\text{N}$). The addition of H_2 then produces an irreversible change; the $\nu_{(\text{C}\equiv\text{N})}$ band shifts to 2060 cm^{-1} and remains even when H_2 is removed. It is proposed that this may correspond to a cleavage of the above species, and that on successive pumping the following species are formed

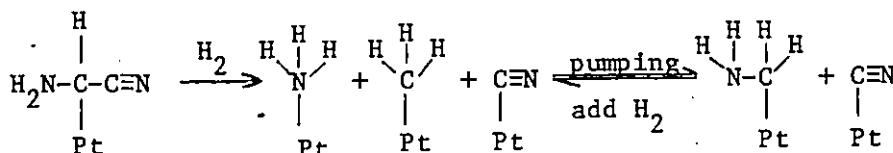


Diagram 10-3

The band at 1590 cm^{-1} which is formed when H_2 is removed may be due to the δNH_2 mode of a dissociatively adsorbed methylamine. This band was seen to form immediately when CH_3NH_2 was adsorbed then pumped out. No deformation mode of an adsorbed Pt:NH_3 could be identified but this is known to be of weak intensity (see Chapter 8). The appearance of a 2969 cm^{-1} band when H_2 is added is indicative of a methyl group. One inconsistency in this scheme is that the $-\text{CH}_2-$ stretch (at 2938 cm^{-1}) increases in intensity after H_2 is added, but this could be due to the hydrogenation of other carbide type residues. Also a broad band at $\sim 1465\text{ cm}^{-1}$ appearing upon initial adsorption remains unidentified.

No gas phase products could be observed following the addition of hydrogen to the adsorbed species.*

This scheme proposes that an M-CN species does form when H_2 is added. Unfortunately no isotopic shifts were measured for this band (at 2060 cm^{-1}) to support this contention. Other aspects of this work make it difficult to be assertive about the nature of the adsorbed species. For example, the $\nu(\text{C}\equiv\text{N})$ band was sometimes found to have a shoulder on the high wavenumber side (see Figure 10-2(ii)B) and when H_2 was added a broad feature was found on the low wavenumber side of the band (Figure 10-2(ii)D). It was probable that there is more than one $-\text{C}\equiv\text{N}$ containing species, but band broadening may also be due to a surface heterogeneity. This was illustrated by adsorbing HCN , removing the gas phase

*The gas phase was desorbed by pumping through a liquid nitrogen trap and then transferred to an infrared gas cell (10 cm length) for a study of the infrared spectra of the products. A vacuum stopcock outlet on this cell permitted the admission of any products into a mass spectrometer.

then heating the surface to 100°C. It was found that the half band width of the 2070 cm^{-1} band (measured at room temperature) was smaller after the surface had been heated.

Another band also formed near 2140 cm^{-1} after this heating process which was not identified.

Cyanogen (C_2N_2)

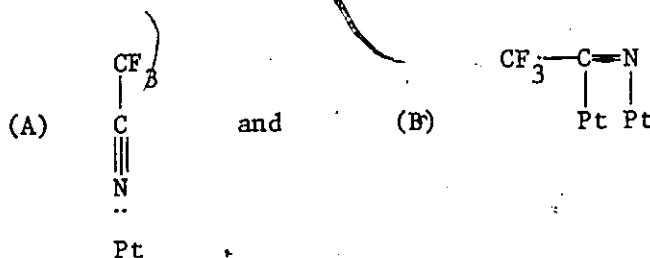
Four bands were observed in the $\nu(\text{C}\equiv\text{N})$ region ranging from 2230-2070 cm^{-1} when 3 torr of C_2N_2 was adsorbed on Pt/SiO_2 but no other bands appeared. Cyanogen is known to form radical cyanides when reacting with metals²⁴¹. The addition of 300 torr of H_2 produced an 'HCN-type' cyanide band located at 2060 cm^{-1} and complex bands subsequently appeared in the N-H and C-H stretching regions. No further experiments were attempted with cyanogen because of the complexity of the bands observed. In order to further resolve the adsorption characteristics of nitriles, several other molecules were chosen for study with which it was felt that the possibility of obtaining many surface species would be more restricted than in the case of HCN, CH_3NH_2 and C_2N_2 .

B) Trifluoroacetonitrile, Acetonitrile, Benzonitrile and their Amine Analogues

1) Trifluoroacetonitrile (CF_3CN)

Part of the reason for the complexity of adsorbed species obtained with HCN appears to be related to the dissociative chemisorption resulting in the production of H and CN radicals which further

react. This problem is averted with CF_3CN and a far simpler spectrum was observed following its adsorption on Pt/SiO_2 . On silica alone CF_3CN was only physically adsorbed and could be rapidly removed after pumping for 5 min at room temperature. Very little hydrogen bonding was observed and only a weak band was observed at 2270 cm^{-1} (the equivalent gas phase band appears at 2271 cm^{-1})²⁴²⁻³. When small amounts (1 torr) of CF_3CN were adsorbed to Pt/SiO_2 however, a strong band was observed at 2265 cm^{-1} with smaller bands at 1615, 1555 and 1455 cm^{-1} (Figure 10-3). Pumping at room temperature decreased the intensities of each of the bands in unison and no new bands appeared. The 2265 cm^{-1} band was still detectable after 24 hrs pumping at room temperature but was removed when the temperature was raised to 80°C and the cell degassed for 1 hr. It is apparent that CF_3CN is molecularly bound to Pt involving a weak dative bond resulting in a decrease in frequency of only 5 cm^{-1} *, but the band at 1615 cm^{-1} is suggestive of a $\text{C}=\text{N}$ species. The 1555 and 1455 cm^{-1} bands are probably representative of overtones and combinations of C-F modes. If the 1615 cm^{-1} band is not a deformational mode then one is tempted to assign two surface species to the spectral bands observed.



*The donating N lone pair is weakened by the strongly electron withdrawing CF_3 - group and only a weak co-ordinate bond is expected.

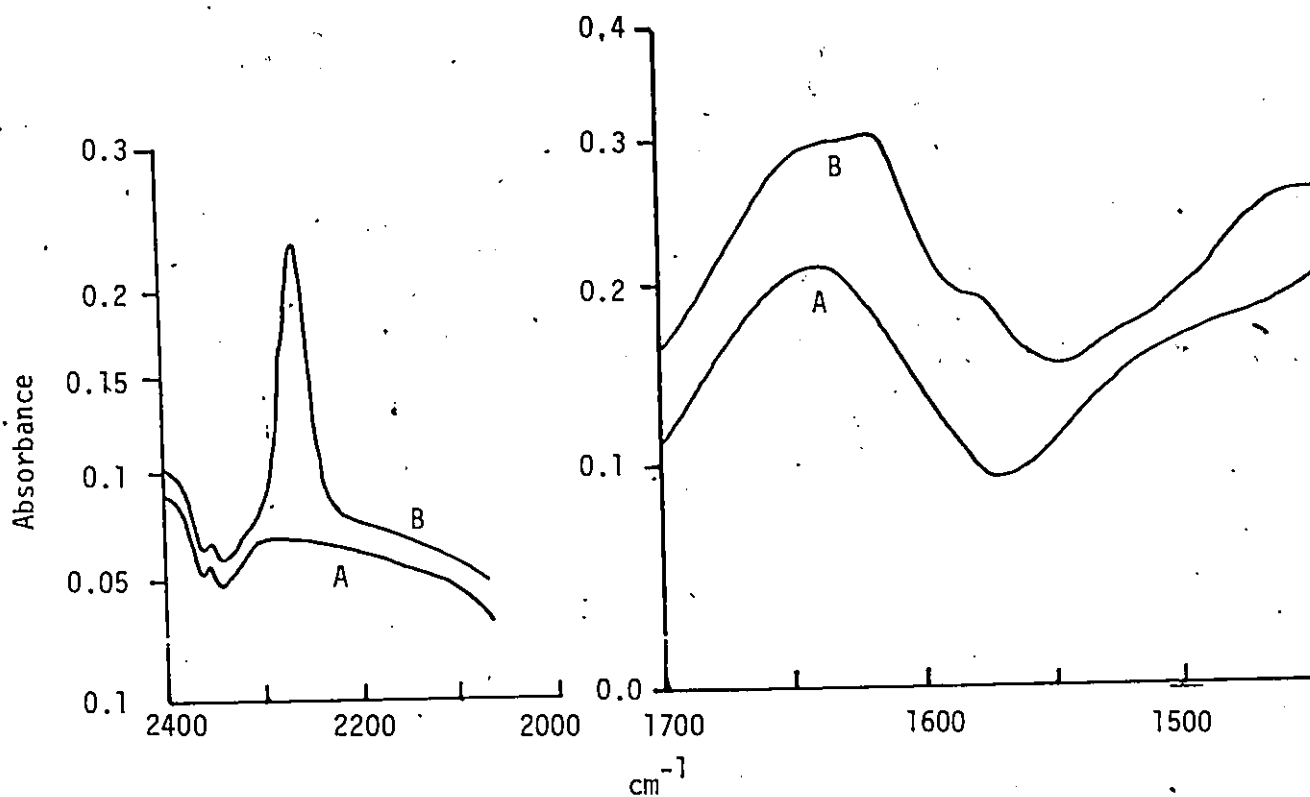


FIGURE 10-3

Adsorption of CF_3CN to a degassed Pt/SiO_2 (no surface hydrogen)

A. Background spectrum.

B. Admitted ~ 1 torr CF_3CN .

Negative absorption in 2400-2000 cm^{-1} region is due to presence of CO_2 in the reference beam of the spectrometer.

The existence of species (B) is supported by the results obtained when 1 torr CF_3CN was adsorbed to a Pt/SiO_2 surface containing pre-adsorbed hydrogen (i.e., the reduced surface was not degassed at 300°C prior to adsorption of CF_3CN). In this instance no $\nu(\text{C}\equiv\text{N})$ band appeared, but other bands were observed at 3393, 3320 and 3270 cm^{-1} (N-H species), 2915 cm^{-1} (C-H) and a broad band near 1520 cm^{-1} (see Figures 10-4(i) and (ii)). The absence of a band for $\nu(\text{C}\equiv\text{N})$ shows that CF_3CN does not co-ordinatively bond to hydrogen covered Pt. The readdition of CF_3CN (10 torr) did not alter the aforementioned bands but a band did appear at 2270 cm^{-1} which could be removed by pumping at room temperature for 5 min. Subsequently, the addition of H_2 (400 torr) immediately removed the band at 3320 cm^{-1} , but the 3393 and 3275 cm^{-1} bands remained and weak bands formed at 2960 and 1393 cm^{-1} (Figures 10-4(i)C.)

In a separate experiment a mixture of H_2 and CF_3CN (100 torr: 10 torr) was admitted to a Pt/SiO_2 surface and bands instantly formed at 3393, 3320, ~ 2900 (broad), 1690, 1665, 1608, 1493, 1446 and 1393 cm^{-1} (see Figures 10-5(i) and (ii)). After 12 hrs in H_2 , the 1690, 1665 and 1493 cm^{-1} bands disappeared indicating that they are due to a transient species but the 1608 cm^{-1} band was larger and a band appeared at 1755 cm^{-1} (Figure 10-5(ii)C,D). The gas phase was trapped and analyzed by infrared spectroscopy and mass spectrometry. The major product appeared to be $\text{CF}_3\text{CH}_2\text{NH}_2^*$ indicating that the nitrile bond had not cleaved, but trace amounts of other species were identified at low electron voltage on the AEI MS 10 mass spectrometer at m/e 17 and 30, which are probably due to NH_3 and C_2H_6 .

* This species is not formed in the absence of catalyst.

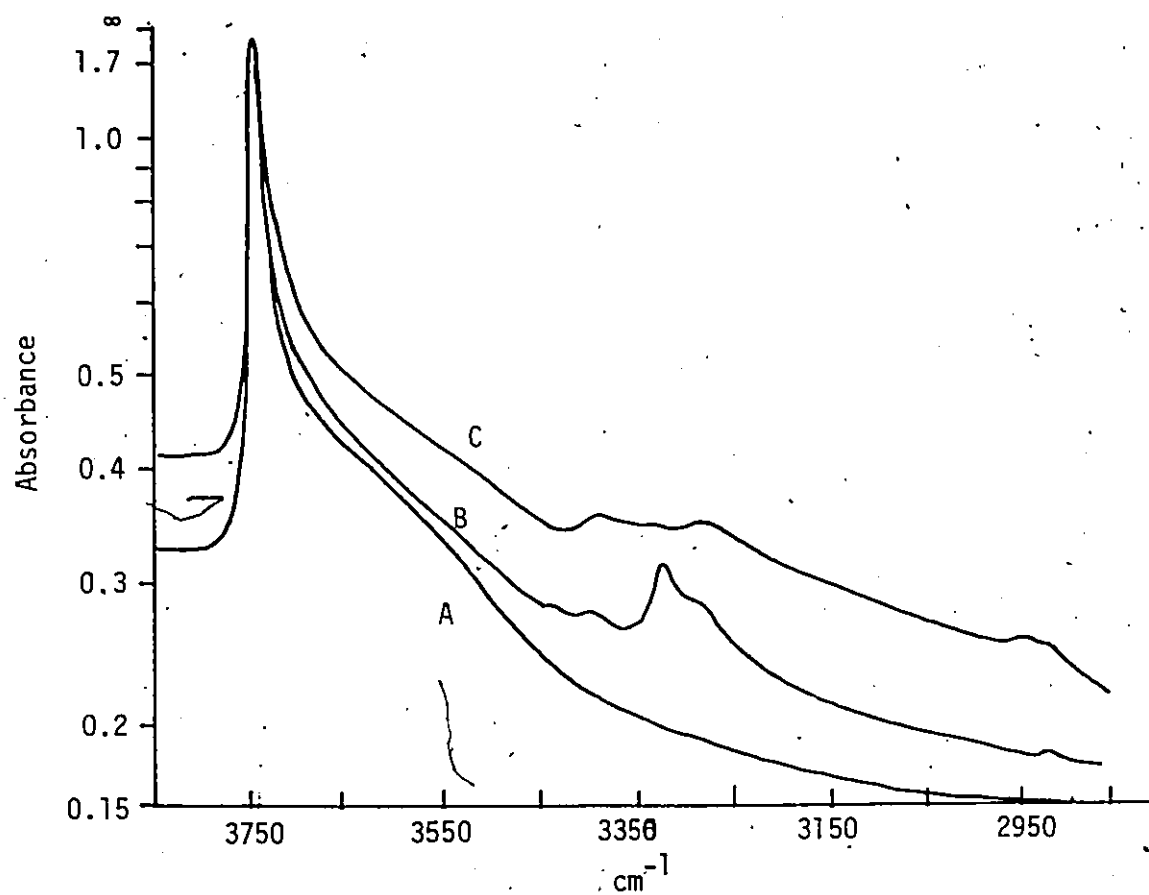


FIGURE 10-4(i)

Adsorption and hydrogenation of CF_3CN
(see also Figure 10-4(ii)).

- A. Background spectrum of $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$ (hydrogen covered surface).
- B. Admitted ~ 1 torr of CF_3CN .
- C. Admitted 300 torr of H_2 .

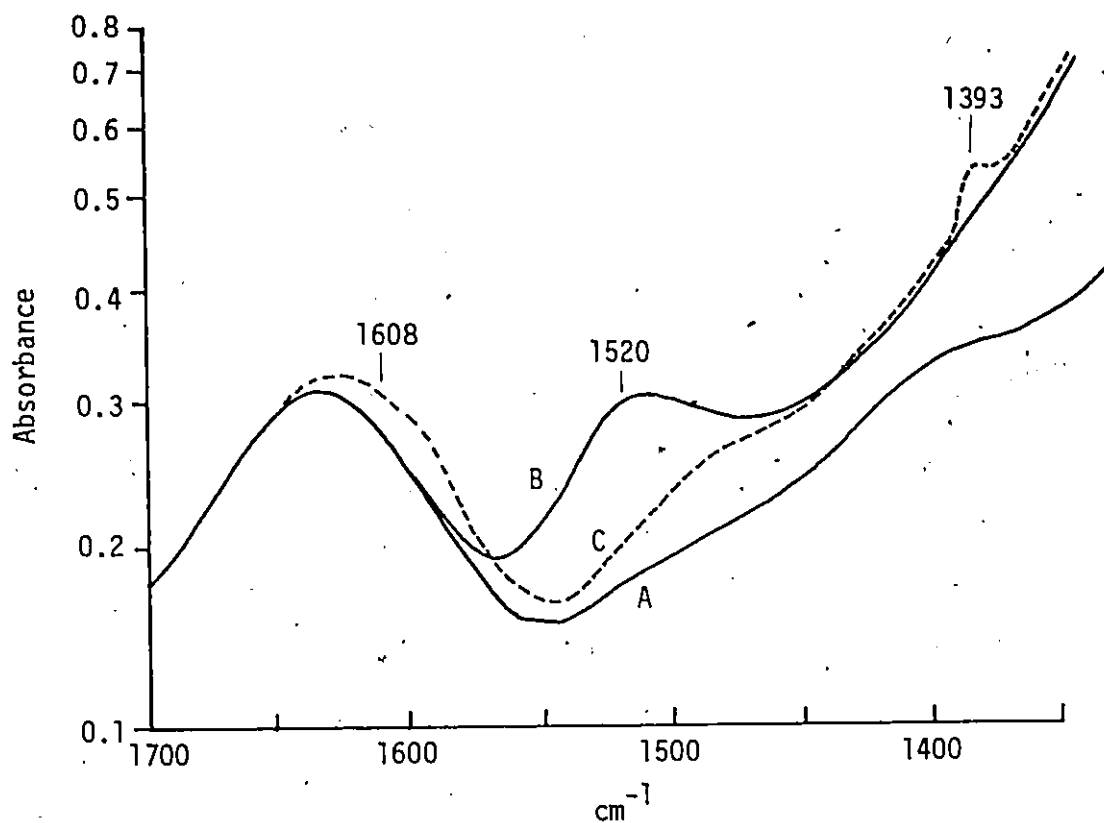


FIGURE 10-4(ii)

Adsorption and hydrogenation of CF_3CN .
(see also Figure 10-4(i) where sequences are described).
Scan speed for 1700-1350 cm^{-1} region was 20 $\text{cm}^{-1} \text{ min}^{-1}$.

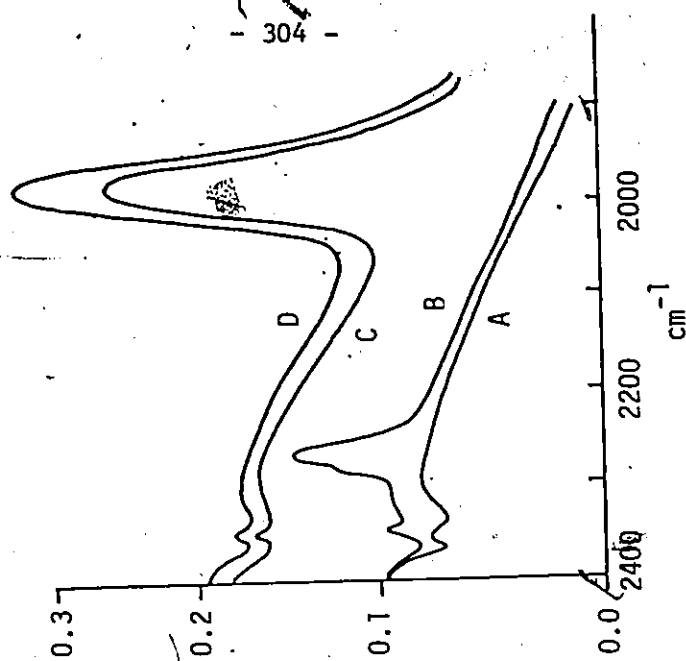
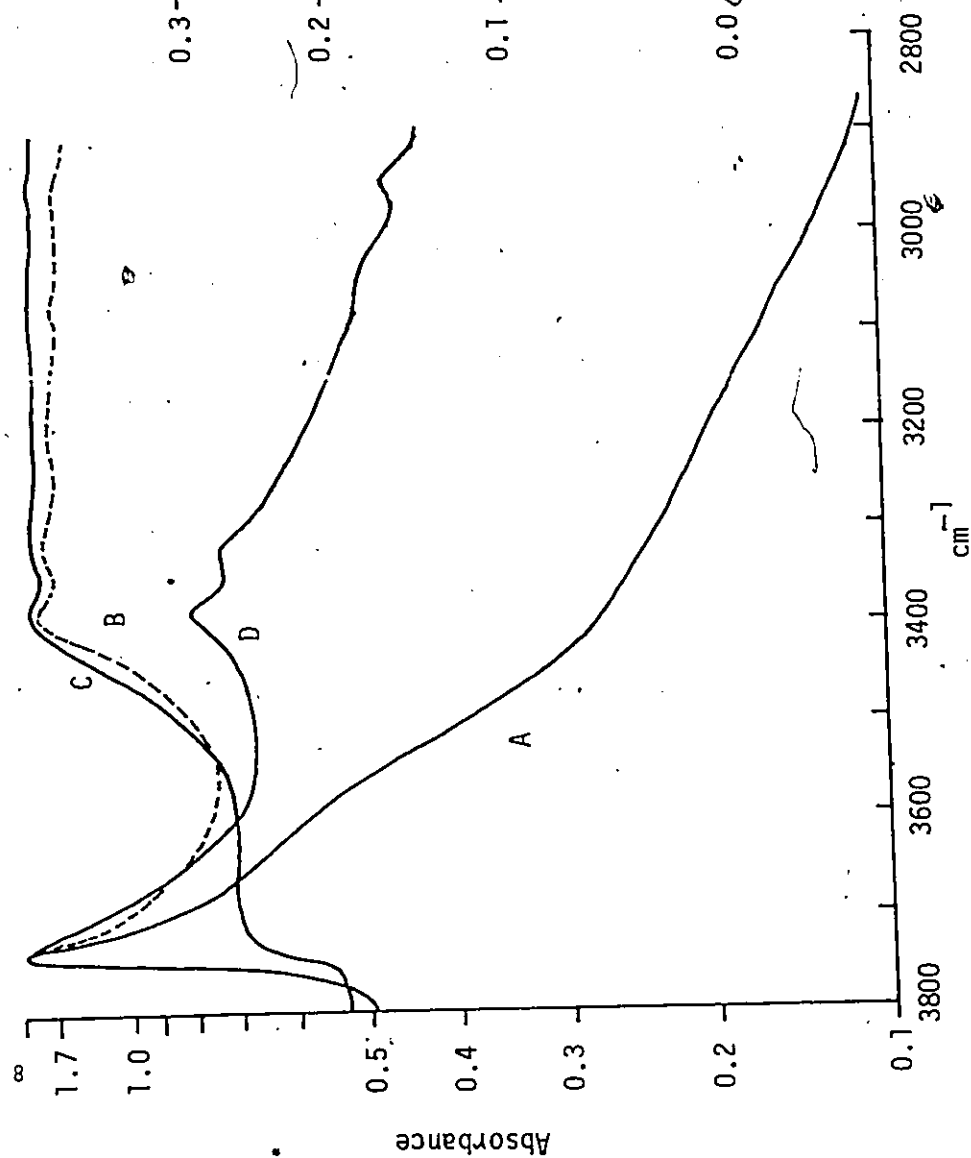


FIGURE 10-5(i)
Adsorption of a $\text{CF}_3\text{CN}/\text{H}_2$ mixture
(see also Figure 10-5(ii) where sequences are described).

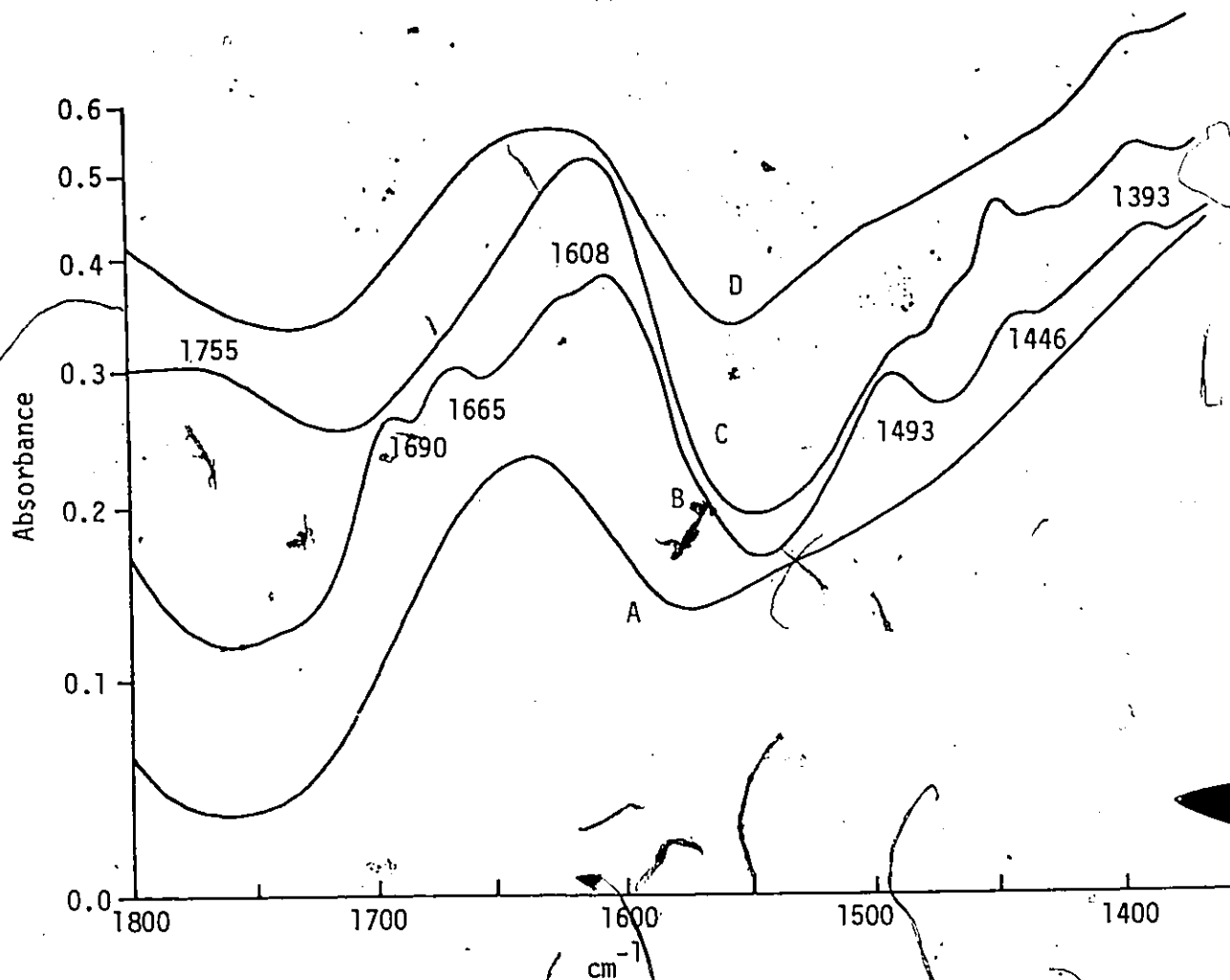


FIGURE 10-5(ii)

Adsorption of a $\text{CF}_3\text{CN}/\text{H}_2$ mixture.

(see also Figure 10-5(i)).

A. Background spectrum of $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.

B. Admission of 100 torr of a 10:1 mixture by volume of $\text{H}_2:\text{CF}_3\text{CN}$; spectrum immediately.

C. After 12 hr.

D. Evacuated for 5 min at room temperature, Negative absorption in the $2400\text{--}2000 \text{ cm}^{-1}$ region (see Figure 10-5(i)) is due to presence of CO_2 in reference beam.

Spectra B-D in $1800\text{--}1400$ and $2400\text{--}2000 \text{ cm}^{-1}$ regions were displaced for purposes of presentation.

The bands remaining after this desorption step were at 3393, 3320, ~3000, ~2960, 1985 (large) and 1393 cm^{-1} .

It is proposed therefore, that the addition of CF_3CN to a hydrogen covered Pt/SiO_2 surface results in the formation of a physically adsorbed product $\text{CF}_3\text{CH}_2\text{NH}_2$ (3393, 3320, 2960, 1608 and 1393 cm^{-1}) two surface species $\text{Pt}:\text{NH}_3$ (3270 cm^{-1}) and $\text{Pt} \text{ Pt} \begin{smallmatrix} \text{HC}=\text{CH} \\ | \quad | \\ \text{Pt} \quad \text{Pt} \end{smallmatrix}$ ($\nu_{\text{CH}} = 3000 \text{ cm}^{-1}$, $\nu_{(\text{C}=\text{C})} = 1755 \text{ cm}^{-1}$) and a partially dehydrogenated species which absorbs at 3370 cm^{-1} . (Note that the ratio of the intensity of the 3393:3320 cm^{-1} bands

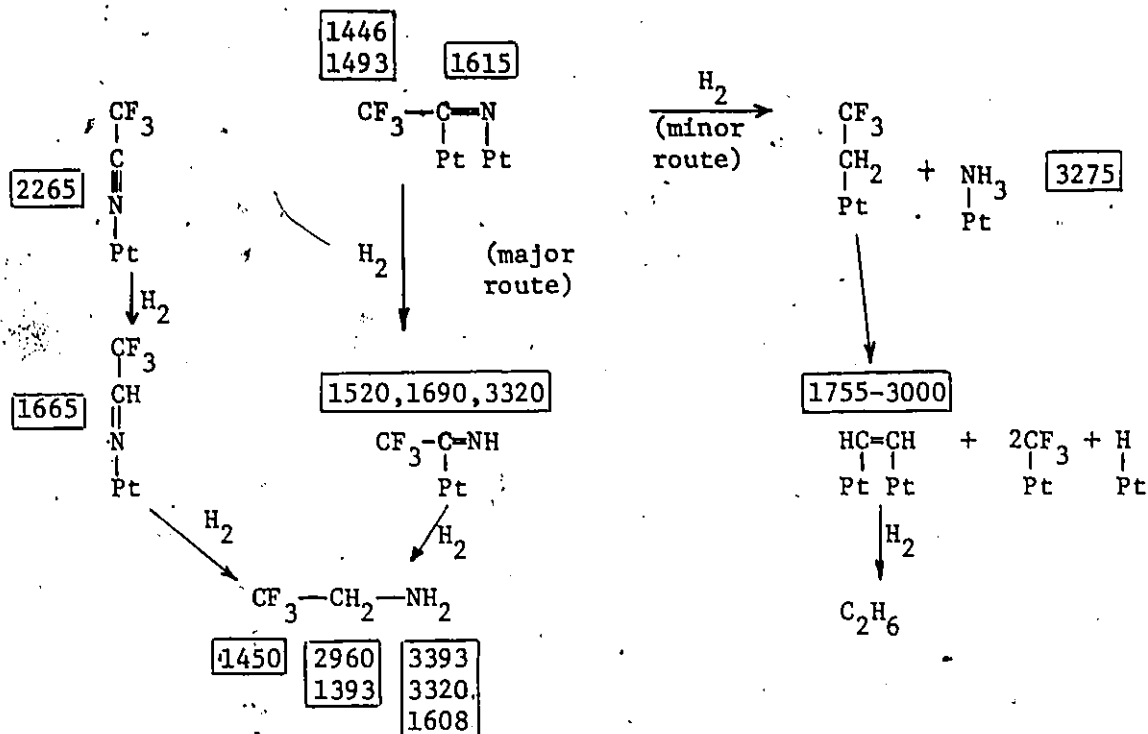
is too low to be due to a $\text{CF}_3\text{CH}_2\text{NH}_2$ species alone.) The structure may be $\text{CF}_3-\text{C}=\text{NH}$.

Pt The band at 1985 cm^{-1} is difficult to assign, being too low for a PtCN species (assigned to the 2060 cm^{-1} band for HCN adsorption). A PtNC species might be expected to absorb at a lower frequency than PtCN (on the basis of SiCN and SiNC frequencies, discussed in Chapter 6). The species is resistant to attack by hydrogen, which may be expected for a charge separated species (see section on CH_3NC adsorption).

Bands at 1690 and 1665 cm^{-1} are proposed to be due to $>\text{C}=\text{N}$ modes. Evidence for the existence of a physically adsorbed surface species $\text{CF}_3\text{CH}_2\text{NH}_2$ formed by hydrogenation of CF_3CN was provided by adsorbing $\text{CF}_3\text{CH}_2\text{NH}_2$. Bands were immediately formed at 3393, 3320, 2960, 1608 and 1393 cm^{-1} . No $-\text{C}\equiv\text{N}$ or $\text{C}=\text{C}$ modes were observed indicating that, once formed, $\text{CF}_3\text{CH}_2\text{NH}_2$ is resistant to dehydrogenation. The bands could be removed by pumping at room temperature for several hours.

Admittedly there is no direct proof for some of the species cited in the scheme and species such as CF_3-Pt and $\text{CF}_3\text{CH}_2-\text{Pt}$ are included so that the formation of other products (e.g. $\begin{smallmatrix} \text{H} & & \text{H}^3 \\ & \text{C}=\text{C} & \\ \text{Pt} & & \text{Pt} \end{smallmatrix}$) can be rationalized.

No CF_3H species was identified in the gas phase products by mass



Another minor process may be:

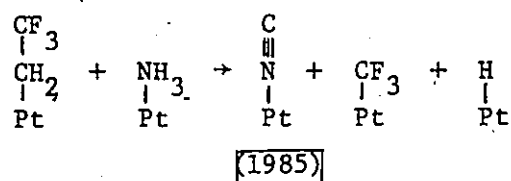


Diagram 10-4

The numbers in boxes are frequencies. They refer to the group frequencies associated with the species shown.

spectrometry which suggests that if the C-C bond is cleaved, that the CF_3 group is subsequently bound to the surface. There was no evidence of C-F cleavage. The adsorption scheme for CF_3CN is summarized in Diagram 10-4.

(ii) Acetonitrile (CH_3CN)

Acetonitrile is known to bond to solid oxide adsorbents such as silica, porous glass and silica alumina^{233,244} by interaction with the surface hydroxyl groups, and, in the case of silica alumina, by attachment to acidic sites²³³. Rapid desorption of CH_3CN from a silica surface can be achieved by pumping for a few minutes at room temperature because only weak hydrogen bonds are formed.

The main spectral features of the $\text{CH}_3\text{CN}/\text{SiO}_2$ system are bands at 3430 cm^{-1} (perturbed silanols), C-H band at 2950 cm^{-1} and a strong $\text{-C}\equiv\text{N}$ stretching band at 2268 cm^{-1} (the gas phase band is at 2267 cm^{-1}).

A band at 2292 cm^{-1} has been attributed by Low and Bartner²⁴⁴ to be a combination of the CH_3 symmetric deformation mode and the C-C stretching mode (1394 and 912 cm^{-1}). Conway et al²⁴⁵ have studied the adsorption of CH_3CN at Pt electrodes and determined that the following sequences occurred

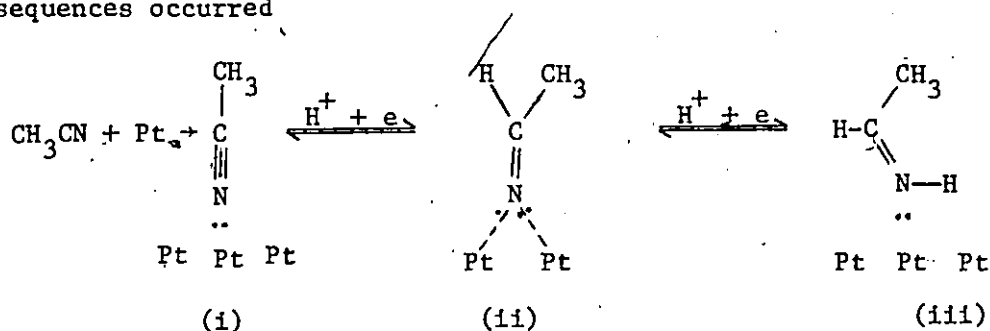


Diagram 10-5

It was considered that no dissociative adsorption via the methyl carbon took place and by analogy with H-blocking effects with benzonitrile and terphthalonitrile it was decided that in general nitriles do not associatively adsorb as $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{Pt} \quad \text{Pt} \end{array}$ at Pt electrodes.

However, to the authors' knowledge there have been no infrared studies of the adsorption of vapour phase CH_3CN on Pt. It has been found in this laboratory that the adsorbed species obtained on a Pt/SiO₂ catalyst are quite different from those formed on oxides such as silica, porous glass or silica alumina and although bands can be found which are attributable to $\text{CH}_3\text{CN}:\text{HOSi}$ species, other bands are formed which cannot be removed by pumping at room temperature, indicative of chemisorbed species (Figure 10-6). A dissociative chemisorption apparently occurs, involving the methyl group because the adsorption of CD_3CN to a degassed Pt/SiO₂ immediately results in the exchange of the surface silanols, a phenomenon which does not occur on silica alone. In other respects, acetonitrile behaved quite unlike CF_3CN . No bands were observed in the 2300-2100 cm^{-1} region due to CH_3CN co-ordinatively bonded to Pt, although bands for the nitrile stretch of CH_3CN in complexes such as $\text{PtCl}_2 \cdot 2(\text{CH}_3\text{CN})$ and $\text{PtBr}_2 \cdot 2(\text{CH}_3\text{CN})$ are known to be weak²³⁶. The expected frequency of a metal complexed CH_3CN is $\sim 2300 \text{ cm}^{-1}$ ²³⁵⁻⁶.

On a degassed Pt/SiO₂, the adsorption of CH_3CN produced two very weak bands in the NH stretching region near 3300 cm^{-1} but three fairly prominent bands appeared in the CH stretching region at 2880, 2932 and 2965 cm^{-1} , (Figure 10-6) (The NH bands are not shown.). Other bands were at 1507 and 1483 cm^{-1} . The profile in the C-H region is very much like that of adsorbed monoethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) (Figure 10-7(i) and (ii), which

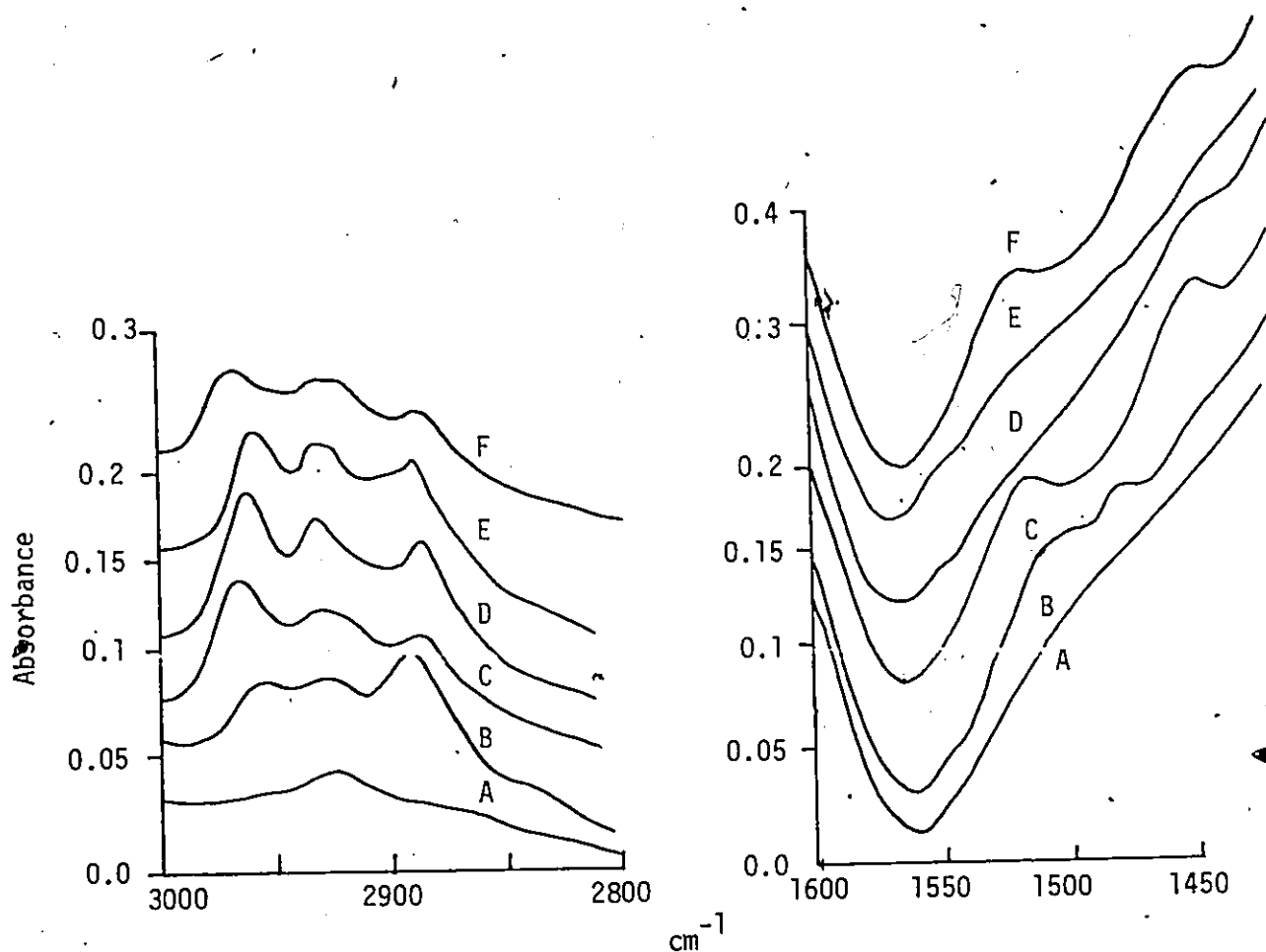


FIGURE 10-6

Adsorption and hydrogenation of CH_3CN .

A. Background spectrum of $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.

B. Admitted 20 torr CH_3CN for 5 min then pumped for 30 min at room temperature.

C. Admitted 100 torr of H_2 .

D, E. Evacuated at room temperature; D, 5 min; E, 16 hr.

F. Readmitted 100 torr of H_2 .

Spectra B-E were displaced for purposes of presentation.

probably means that CH_3CN is dissociatively adsorbed and is capable of self hydrogenation. As shown in Figure 10-6, the band at 2965 cm^{-1} is initially lower in intensity than the 2880 cm^{-1} band but the addition of hydrogen then pumping, produces an almost identical profile to that of adsorbed $\text{CH}_3\text{CH}_2\text{NH}_2$ in which the 2965 cm^{-1} band becomes larger than the 2880 cm^{-1} band. (compare Figures 10-7(i)B and 10-6D). At least two species must exist upon initial adsorption of CH_3CN in order that a 'methyl' absorption band at 2965 cm^{-1} can simultaneously appear with other C-H bands that are not related to the absorptions of a methyl group. A band at 2880 cm^{-1} is generally indicative of a bound $-\text{CH}_2-$ species. A bound Pt- CH_2 -species would be expected to have absorption bands near 2920 and 2880 cm^{-1} ¹⁹⁰ and perhaps the observed 2932 and 2880 cm^{-1} bands can be assigned to it. However the changes in the intensity ratios of these bands which occur upon hydrogenation implies that the 2932 cm^{-1} band is also associated with another species, possibly a $-\text{CH}$ -group. (This was found to be the case for C_2H_4 on Pt or Ni¹⁹⁰).

The 1507 and 1483 cm^{-1} bands are difficult to identify, being too high for known $-\text{CH}_2-$ deformations and too low for the symmetric $-\text{NH}_2$ deformation. On hydrogenation the 1483 cm^{-1} is shifted to 1455 cm^{-1} which is the range of $-\text{CH}_2-$ absorption, however, the 1507 cm^{-1} band shifted to 1520 cm^{-1} . A similar band was found in the spectrum of CF_3CN adsorbed to a hydrogen covered surface (Figure 10-4(ii)B).

The low intensity of the NH bands indicate that few NH containing species are formed, and since surface nitrogen is more readily hydrogenated than surface carbon²³⁷, then it is likely that a fully hydrogenated nitrogen containing product may be formed and desorbed.

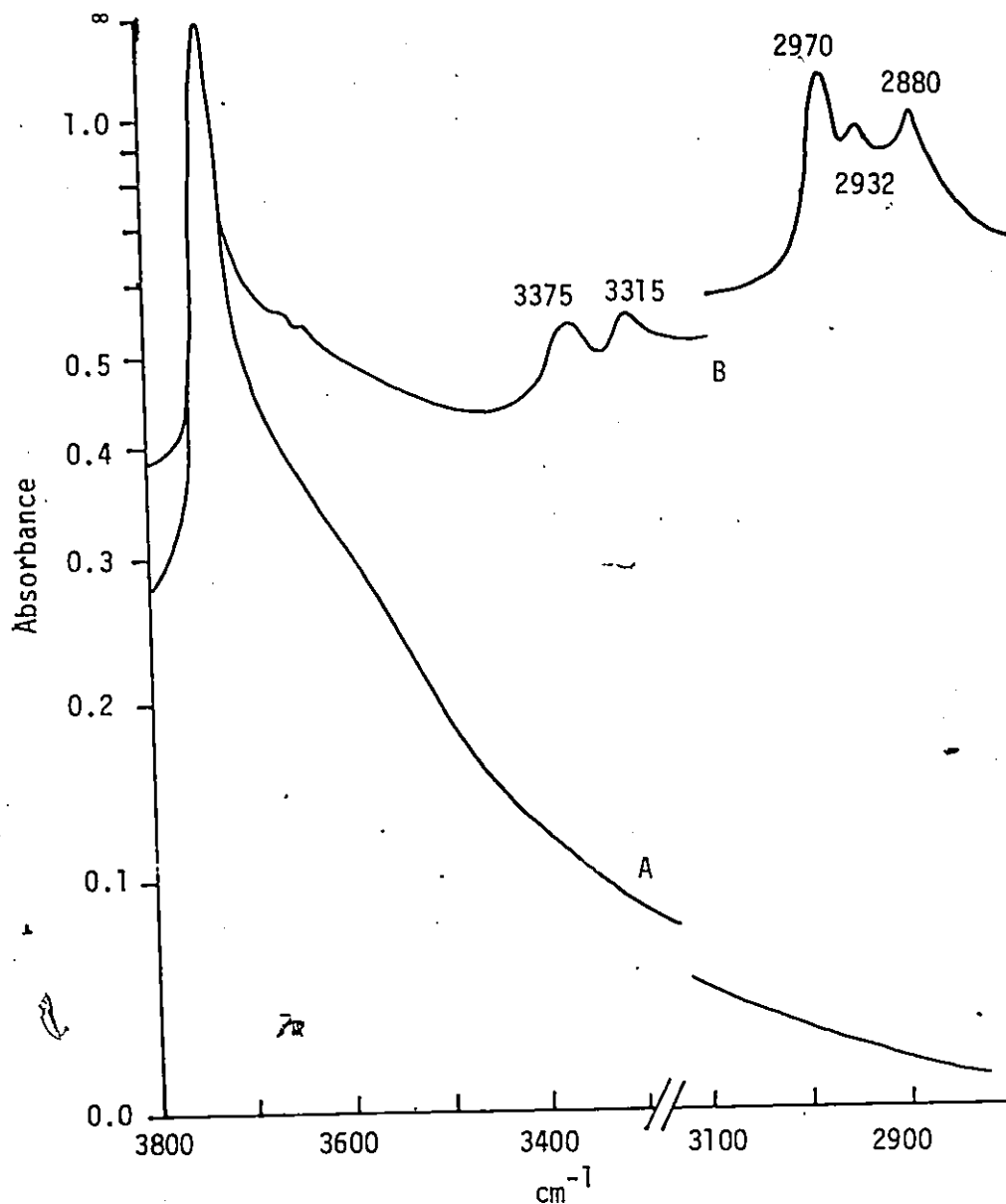


FIGURE 10-7(i)

Adsorption of monoethylamine.

(see also Figure 10-7(ii)).

A. Background spectrum of 40 mg cm⁻² Pt/SiO₂.

B. Admitted 10 torr monoethylamine for 5 min then evacuated for 10 min at room temperature

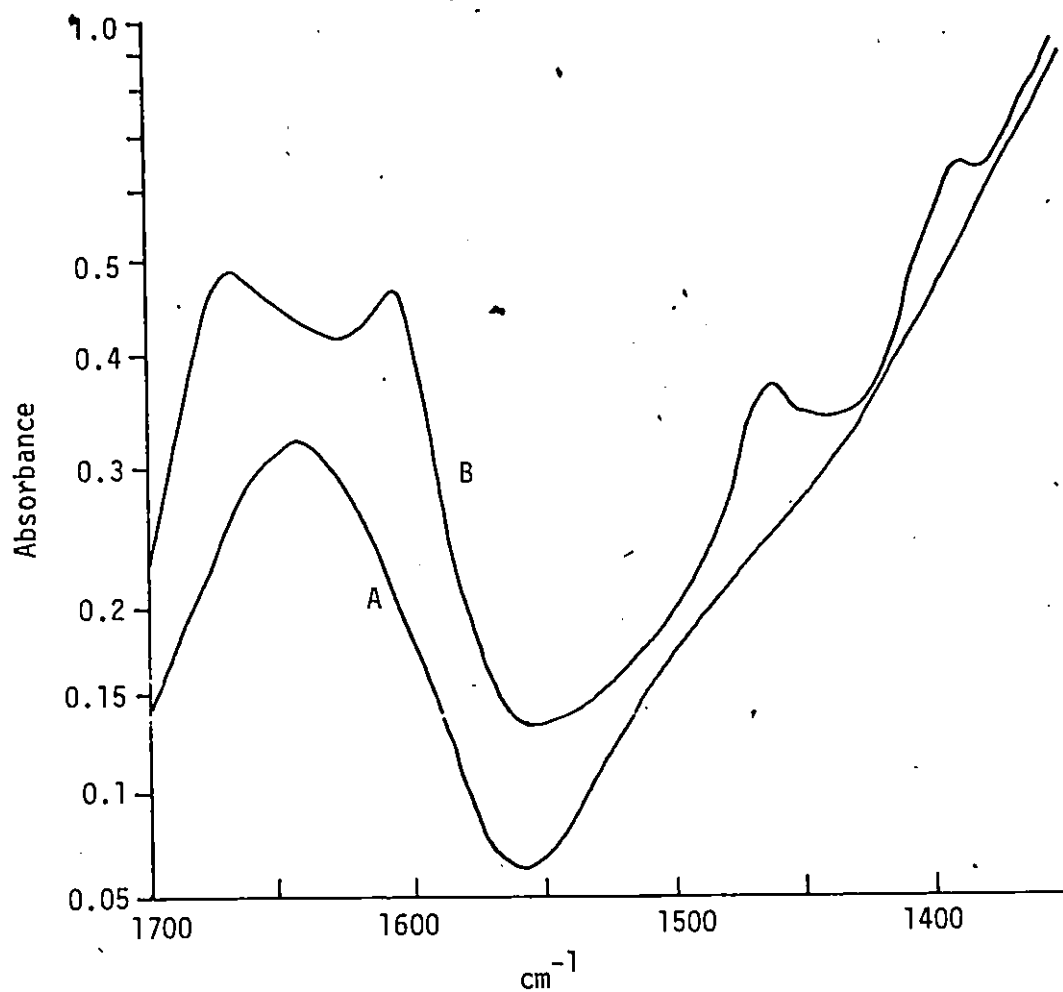


FIGURE 10-7(ii)

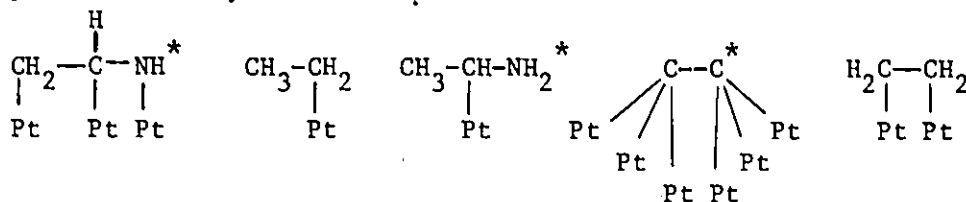
Adsorption of monoethylamine.

(see also Figure 10-7(i) where sequences are described).

Scan speed was $20 \text{ cm}^{-1} \text{ min}^{-1}$.

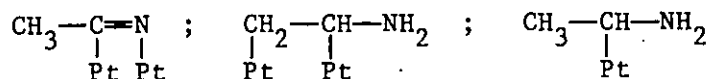
When mixtures of CH_3CN and H_2 were admitted to a Pt surface the resultant gaseous products were NH_3 and C_2H_6 indicating that C-N bond cleavage is favoured (contrary to CF_3CN hydrogenation).

The following surface species possibly exist though those marked with an asterisk are thought to be transitory species only or present in very small concentrations.



There is no evidence for C=C or C=N species in the spectrum. The band for the former is generally a weak feature and may not be observed, but a C=N band is expected to be intense, and its absence is construed as being due to lack of such a species.

Ethylamine, on the other hand, does seem to adsorb via a dehydrogenation of the -C-N grouping, indicated by a strong band at 1672 cm^{-1} , although strong bands at 3375 , 3315 and 1610 cm^{-1} indicate that a surface $-\text{NH}_2$ also exists (Figure 10-7(i) and (ii)). The only other features in the spectrum were bands at ~ 1460 and 1395 cm^{-1} indicative of $-\text{CH}_2$ and $-\text{CH}_3$ deformation modes. The absence of a band for an $>\text{N-H}$ species probably indicates that for the unsaturated species, the nitrogen atom is bound to the surface. The following species are thought to be present for adsorbed ethylamine.



The 1672 cm^{-1} band immediately disappeared when H_2 was added to the surface, confirming that it is due to an unsaturated group, probably $-\text{C}=\text{N}-$.

Even though CH_3CN would be expected to be more strongly co-ordinatively bound to Pt than CF_3CN , this mode of adsorption does not occur because the methyl group of CH_3CN apparently preferentially interacts with the surface (unlike that observed for adsorption on Pt electrodes)²⁴⁵ and ultimately results in the hydrogenation of the other atoms of the adsorbed species. As well the $\text{-C}\equiv\text{N}$ group is more susceptible to total hydrogenation in CH_3CN resulting in $\text{CH}_3\text{-CH}_3$ and NH_3 as the main products, which may be related to a preferred horizontal orientation of the molecule involving multiple points of surface binding.

In both CF_3CN and CH_3CN^* , no nitrile band forms near 2070 cm^{-1} such as was found with HCN , which is undoubtedly due to the maintenance of the C-C bond in both cases.

(iii) Methylisonitrile (CH_3NC)

One of the reasons for choosing to study this molecule was because of the potentially strong co-ordinating ability of the isonitrile group²²⁹. It was felt that only a simple adsorbed species might be formed, and that a frequency could be established for an adsorbed isonitrile.

The adsorption of CH_3NC on silica resulted in strong hydrogen bonding, probably of the type $\text{CH}_3\text{-}^+\text{N}\equiv\text{C}:\text{HOSi}$, with prominent bands at 2160 cm^{-1} (gas phase band at 2145 cm^{-1}) and 2960 cm^{-1} due to the $\text{C}\equiv\text{N}$ and C-H stretching modes respectively and a band at 3345 cm^{-1} due to perturbed hydroxyls. The species could be removed by pumping

* Occasionally a band formed at $\sim 1990\text{ cm}^{-1}$, especially if gas phase CH_3CN was left in contact with the surface for long periods (1 hr) and is perhaps assignable to a $\text{Pt-}^+\text{N}\equiv\text{C}$ species.

at room temperature. However, the adsorption of CH_3NC on Pt/SiO_2 produced a strongly bound species in addition to this hydrogen bonded species but the spectra was dependent upon the time of adsorption. For short periods of adsorption an apparently simple spectrum was obtained with bands at 2935, 2862, 2245 and 2172 cm^{-1} (Figure 10-8), but for longer periods these bands were all more intense and other bands appeared at 1450, 1430 and 1400 cm^{-1} , accompanied by variable broad bands in the $1600\text{--}1700\text{ cm}^{-1}$ and $3000\text{--}3400\text{ cm}^{-1}$ regions (not shown). The following discussion is concerned only with the spectra obtained after short period adsorptions because of difficulty in interpretation of the three lower wavenumber bands. It is apparent that further reaction occurs to form complex products.

Unlike chemisorbed CH_3CN , the $\text{C}\equiv\text{N}$ bond remained intact, as evidenced by bands at 2245 and 2172 cm^{-1} .

If mixtures of CH_3NC and H_2 were adsorbed, the same spectra were obtained as for CH_3NC adsorbed alone and an analysis of the gas phase, subsequent to adsorption, revealed only CH_3NC . Changes in the spectrum did occur if H_2 was left in contact with the chemisorbed species and in particular, two bands grew at 2060 and 2000 cm^{-1} as 2245 and 2172 cm^{-1} bands diminished. The 2245 cm^{-1} band is apparently not related to the species absorbing at 2172 cm^{-1} since the ratios of the intensities of these bands was altered when hydrogen was added. A new band also appeared at 1485 cm^{-1} and in the ν_{CH} stretching region the profile was similar to that obtained for CH_3CN adsorption.

The addition of D_2 instead of H_2 had a similar effect in producing new bands at 2060 and 2020 cm^{-1} but no exchange of 2935/2862 cm^{-1} bands occurred.

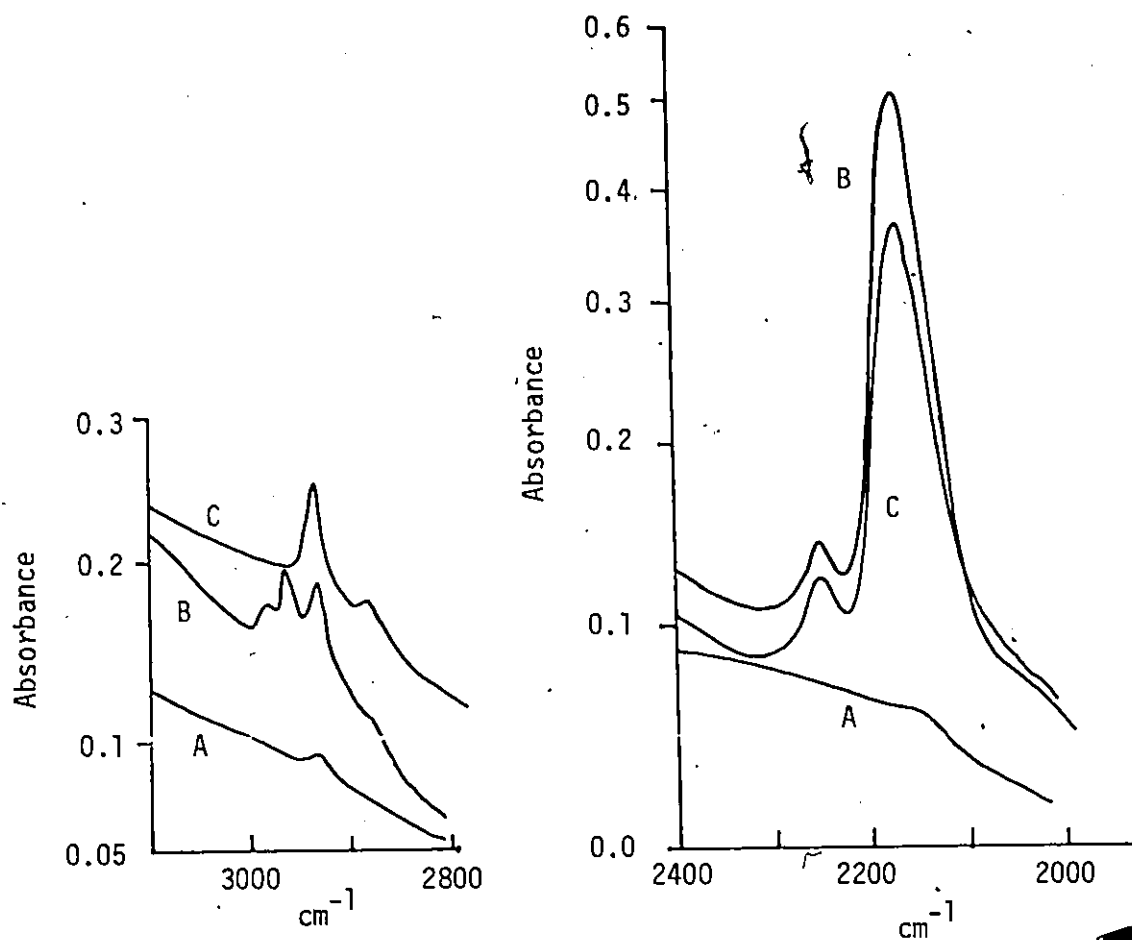


FIGURE 10-8

Adsorption of CH_3NC .

A. Background spectrum of $40 \text{ mg cm}^{-2} \text{ Pt/SiO}_2$.

B. Admitted 10 torr CH_3NC .

C. Evacuated for 15 min at room temperature.

Spectra B and C at left were displaced for purposes of presentation.

Even though only four bands appear in the spectrum of the initially adsorbed CH_3NC , the interpretation is deceptively complex. Assuming that the 2245 cm^{-1} band represents a separate species, then 2935 , 2862 and 2172 cm^{-1} might be supposed to represent a simple coordinatively bonded species (A) $\text{CH}_3-\text{N}^+\equiv\text{C} \rightarrow \text{Pt}^-$, but the ν_{CH} bands are at low frequencies for a CH_3^- mode. Alternatively a $-\text{CH}_2^-$ mode might be expected to absorb at these frequencies but the intensity ratio of the bands is unusual. For instance, if a species such as (B), $\text{Pt}-\text{CH}_2-\text{N}^+\equiv\text{C}^-$, were adsorbed, then a much stronger band would be expected near 2860 cm^{-1} . However, in view of the known versatility of RNC compounds to facilitate a bond with most metals²²⁹, it may be naive to assume that there is no interaction of the isonitrile group with the surface. A possible reason for the $\nu_{(\text{C}\equiv\text{N})}$ absorption mode being close to $\nu(\text{C}\equiv\text{N})$ of the gas phase band is that the effect of the strength of the Pt-C bond upon the frequency of $\nu_{(\text{C}\equiv\text{N})}$ may be offset by the back donation to the ligand (see equation 2, before). The identity of the 2245 cm^{-1} band is unknown.

The species resistance to hydrogenation may be related to the strong charge separation effect whereby the addition of one hydrogen atom to either the N or C atoms of the nitrile group would create a net charge. The slow formation of new bands in the $2100\text{--}2000 \text{ cm}^{-1}$ region may be related to a flipping of the nitrile group to form a cyanide which can be subsequently dissociated or hydrogenated, viz $\text{Pt}-\text{CH}_2-\text{C}\equiv\text{N}$. This would account for the formation of a CH_3-CN like C-H stretching region that appears after the surface species have spent long periods in hydrogen.

(iv) Benzonitrile (C_6H_5CN)

The spectral features observed for benzonitrile adsorbed on Pt/SiO_2 were similar to those reported by Oranskaya and Filiminov²²⁴, the key feature being a $\nu_{(C\equiv N)}$ absorption band at 2220 cm^{-1} which could not be removed by degassing at room temperature. The frequency $\nu_{(C\equiv N)}$ of a 1% CCl_4 solution of benzonitrile is at 2230 cm^{-1} whilst for benzonitrile adsorbed on silica the band is at 2238 cm^{-1} . The lowered $\nu_{C\equiv N}$ frequency of the species on Pt/SiO_2 suggests that benzonitrile forms a weak dative bond with platinum²²⁴. Other bands appear at 3070, 1600, 1495 and 1450 cm^{-1} which are probably all associated with aromatic ring vibrations (Figure 10-9(i) and (ii)). As observed by Oranskaya and Filiminov²²⁴, no dissociation of the aromatic C-H groups appeared to occur upon adsorption as evidenced by the lack of any bands due to a partially hydrogenated intermediate. This was confirmed in this laboratory by the observed lack of exchange between the adsorbed species and a Pt/SiO_2 surface containing exclusively SiOD groups (any H atoms formed by dissociation would have exchanged to produce SiOH groups).

Unlike Oranskaya and Filiminov's spectra, the intensity of the 2220 cm^{-1} nitrile band due to a co-ordinated species was very weak and disappeared on pumping at 100°C for 5 hr compared to 250°C ²²⁴. Also the hydrogenation of the surface species was observed with smaller pressures of H_2 than that used by Oranskaya and Filiminov²²⁴ and as a result, a step-wise hydrogenation was observed, with the nitrile group being preferentially reacted. (This was also observed by Volkova et al²⁴⁶ for hydrogenation of ethanol solutions of benzonitrile over a platinum powder). Figures 10-9(i) and (ii) show the hydrogenation

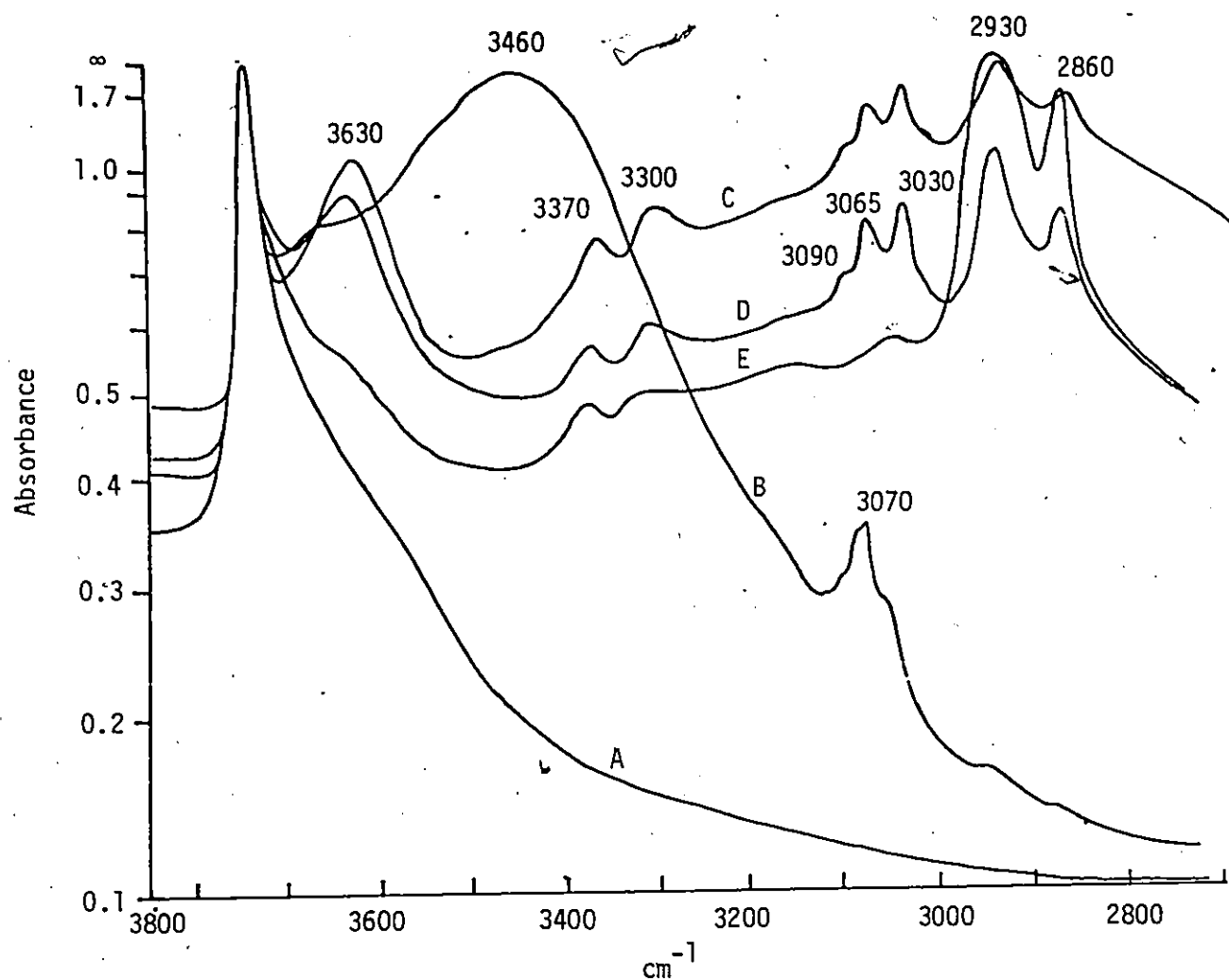


FIGURE 10-9(i)

Adsorption and hydrogenation of benzonitrile
(see also Figure 10-9(ii)).

- A. Background spectrum of 40 mg cm⁻² Pt/SiO₂.
- B. Admitted ~0.2 torr of benzonitrile.
- C. Admitted 10 torr of H₂.
- D. Evacuated for 16 hr at room temperature.
- E. Admitted 400 torr of H₂; spectrum after 12 hr.

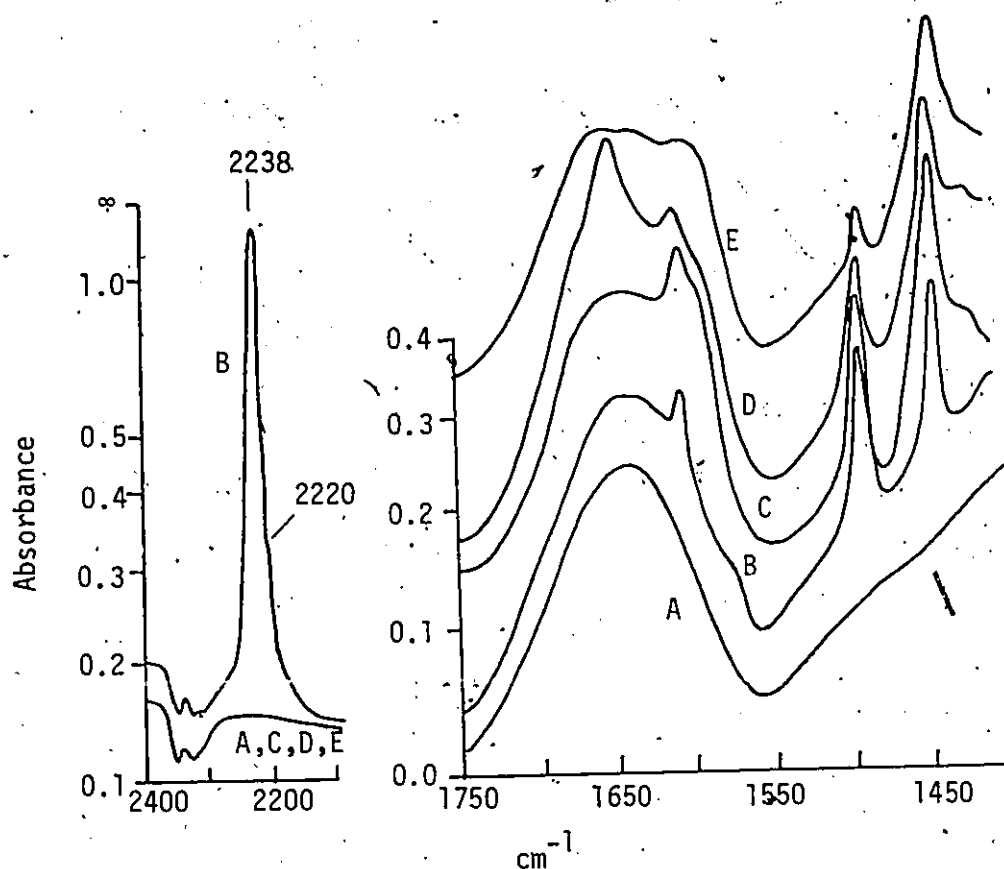


FIGURE 10-9(ii)

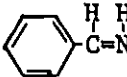
Adsorption and hydrogenation of benzonitrile.
 (see also Figure 10-9(i) where sequences are described).
 In the 1750-1400 cm^{-1} region, spectra B-E were displaced
 for the purpose of presentation.
 The negative absorption in the 2400-2000 cm^{-1} region
 reflects the presence of CO_2 in the spectrometer.

sequence. A broad band near 3460 cm^{-1} indicates hydrogen bonding of surface silanols by the nitrile group producing a band at 2238 cm^{-1} due to $\nu_{\text{C}\equiv\text{N}}$. The nitrile band indicative of co-ordinated benzonitrile is barely discernible at 2220 cm^{-1} . Following the addition of 10 torr of H_2 , both 2238 and 2220 cm^{-1} bands disappeared and the 3460 cm^{-1} band was replaced by two broad bands at 3630 and $\sim 2900\text{ cm}^{-1}$ (Figure 10-9(i)C and (ii)C) and new bands appeared at 3370 , 3500 and 1590 cm^{-1} (N-H), 3090 , 3065 and 3030 cm^{-1} (aromatic C-H), 2930 , 2860 and 1430 cm^{-1} ($-\text{CH}_2$).

These changes mean that both hydrogen bonded and co-ordinately bound benzonitrile are converted into partially and/or fully hydrogenated products. In both instances the nitrile group is completely hydrogenated. A hydrogen bonded hydroxyl at 3630 cm^{-1} ²⁴⁷ is indicative of an aromatic π electron interaction with the hydroxyl whilst the $\sim 2900\text{ cm}^{-1}$ feature can be assigned to the strong interaction between $-\text{NH}_2$ and SiOH . The 3090 , 3065 and 3030 cm^{-1} bands are characteristic of the ring C-H modes of adsorbed benzylamine, whereas 2930 , 2860 and 1430 cm^{-1} can be attributed to the CH_2 modes of a saturated cyclic structure. Pumping on the cell for 16 hrs removed some physically adsorbed species. The gas phase products arising from hydrogenation were analyzed by mass spectrometry, infrared spectroscopy and NMR and found to be mainly toluene and NH_3 , but no benzylamine was identified.* Neither of these products appear as adsorbed species.

(Toluene was adsorbed in a separate experiment and found to have bands at 3130 , 3120 and 3080 cm^{-1}). A band at 1650 cm^{-1} (Figure 10-9(ii)E)

*The adsorption of benzylamine on Pt/SiO_2 also resulted in the production of gas phase toluene.

is probably due to the C=N mode of a partially dehydrogenated benzyl-amine (, but unlike Oranskaya and Filiminov's²²⁴ spectra, no band was found at 3320 cm⁻¹ which they attributed to this species.

The readdition of 400 torr of hydrogen completed the hydrogenation of the aromatic ring and consequently bands at 3630, 3090, 3065 and 3030 cm⁻¹ disappeared as 2930 and 2860 cm⁻¹ bands increased in intensity. At this stage the cell was again degassed and the main products were methylcyclohexane and NH₃ (by mass spectrometry). The 1650 cm⁻¹ band disappeared corresponding to rehydrogenation of the side chain.

It is apparent that the hydrogenated species adsorbing on platinum are desorbed as further dissociated products, viz

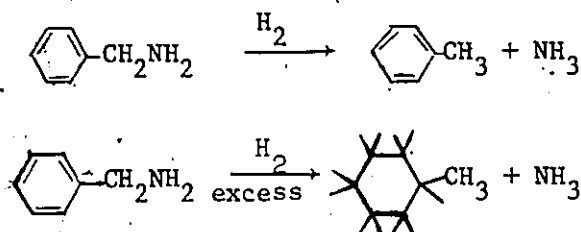
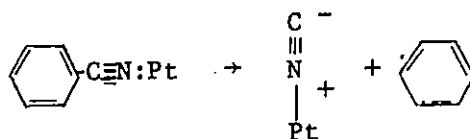


Diagram 10-6

One other feature of the adsorption of benzonitrile was that, occasionally a 1990 cm⁻¹ band appeared during the initial adsorption step, whose occurrence seemed to be related to the presence of pre-adsorbed hydrogen. It is possible that, to a small extent, a secondary reaction takes place involving cleavage of the C-C bond;



Summary

The adsorption of various nitriles and amines has produced different results in each case. For HCN, CH_3NH_2 and C_2N_2 , strongly adsorbed species were formed and a large band at 2070 cm^{-1} was always present. This band does not appear to be characteristic of a simple PtCN species.

Adsorbed di- and trimethylamine exhibited complex spectra and no attempt was made to characterize the species present, other than to recognize that dissociation and dehydrogenation had occurred. The adsorption behaviour of CH_3CN is quite different from that of HCN in that no strong $\nu_{(\text{C}\equiv\text{N})}$ features were observed and, upon the addition of H_2 , a surface adsorbed ethyl group was formed. As well, gas phase products were observed (ethane and NH_3) which reflect a cleavage of the C-N bond. Benzonitrile reacts somewhat similarly to CH_3CN because it produces gas phase hydrogenation products which also reflect C-N cleavage (toluene and NH_3), but whereas surface adsorbed benzylamine was definitely formed as a partially hydrogenated surface species, the equivalent amine (ethylamine) was not present in the CH_3CN hydrogenation experiment. Furthermore, benzonitrile is incapable of partial self hydrogenation, unlike CH_3CN . Oranskaya and Filiminov²²⁴ had observed that the alkyl cyanides, caprylonitrile and butyronitrile could co-ordinatively bond to Pt. However, in the present work, no band could be found to indicate that CH_3CN was also co-ordinatively bound.

The reaction of CH_3NC may result in the molecule being co-ordinatively bound, though other assignments are possible. The species is initially resistant to the addition of hydrogen but converts slowly into other products containing the nitrile group and to some " $\text{CH}_3\text{-CN-}$

like" hydrogenation products. The mode of adsorption of CF_3CN appeared to be through a co-ordinate bond and unlike CH_3CN no C-N cleavage occurred. It is believed that the lack of interaction of the CF_3 group with the surface, say, compared with the CH_3 group in CH_3CN , is responsible for this mode of adsorption, and for the subsequent formation of an undissociated hydrogenation product ($\text{CF}_3\text{CH}_2\text{NH}_2$).

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