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USE OF INFRA-RED SPECTROSCOPY TO INVESTIGATE ADSORPTION AND THE STRUCTURE OF SURFACE CHEMICAL COMPOUNDS

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I. INTRODUCTION

Up to the present time formal empirical or semi-empirical modes of description have been widely used in the field of adsorption, and little work has been done on elucidating the structure and condition of the adsorbing surface, ascertaining the mechanism of the adsorption process, and determining the thermodynamic properties of adsorption systems on this basis. Formally empirical modes of describing the results of adsorption measurements (for example, the "potential theory"[1,2] and the "non-uniform surface theory"[3], which are completely unconcerned either with the chemical nature of the surface and its physical structure or with the nature of adsorption interaction) are due to the qualitative character of the results which are usually obtained. Although the potential theory is of great value in classifying measurements of the adsorption of vapours by porous adsorbents and in predicting the temperature dependence of the adsorption of vapours by active carbons[2], it is unable to assist in clearing up fundamental questions of surface structure and the nature of the act of adsorption. The theory of adsorption on non-uniform surfaces[3] enables us to obtain formally energy distribution functions for adsorption sites from experimental adsorption isotherms, but these give no physical picture of the non-uniformity[4], and furthermore are based on the application of the Langmuir theory to individual sites on the surface, although the postulates of this theory are completely inapplicable to adsorption on non-uniform surfaces†.

Nevertheless, during the past fifteen years many accurate investigations have already been carried out, both on adsorption itself and on the differential heats of adsorption of adsorbates with different structure on adsorbents whose geometrical configuration and surface chemistry have been so fully characterised that the adsorption properties of the corresponding adsorbate–adsorbent systems can be expressed quantitatively in terms of numbers which describe the physicochemical characteristics of these systems quite reliably[7]. Such quantitative physicochemical characterisation of adsorption systems urgently requires corresponding changes in the theory of adsorption, in particular the formulation of a statistical thermodynamic theory of adsorption equilibria based on detailed information about the potential field of the surface and the motion of the molecules in adsorption complexes[7].

† The artificial assumption that individual portions of a mosaic surface are uniform[5,6] does not save the situation, since with the diminution in size of these portions which is necessary for the description of a non-uniform surface, their boundary regions begin to play a predominant part.

This task of theory in turn makes new demands on the experimental investigations. Among methods which enable us to obtain a comparatively detailed picture of the chemical structure of a surface and of the motion of the molecules in an adsorption complex, spectroscopic methods are extremely important. They have already given extremely valuable information on surface chemical compounds, which often determine the adsorption, chemisorption, and catalytic properties of a solid, and in the near future will probably also give direct information on the frequencies of vibration and rotation of molecules in adsorption complexes. Comparison of these frequencies obtained directly from spectra with frequencies calculated theoretically by means of potential-energy functions[8-11] is extremely important both for verifying the theory of adsorption forces and as a basis for complete statistical thermodynamic calculations of thermodynamic functions and adsorption equilibria solely from the geometrical, electrical, and magnetic properties (the geometrical and electronic structures) of the adsorbate and the adsorbent separately.

Apart from these tasks, which are important in developing a theory of adsorption, the spectroscopic method of investigating surface chemical compounds and adsorption complexes is also of great practical value. The preparation of effective fillers for media of different chemical types, particularly for polymers, the improvement of the properties of pigments, the improvement of adsorbents, supports for fixed liquid and solid phases, and capillaries for gas chromatography[12] and the production of specific adsorbents and catalysts by chemical modification of a solid surface make infra-red spectroscopy which is one of the main methods for analysing molecular structure, extremely useful for studying the properties of these systems. This method was first applied to the investigation of surface chemistry and adsorption in 1940[13], and was subsequently developed by Terenin and his coworkers[14-17]. An increasing amount of work is now being done in this field, even abroad, and the investigation of adsorbed molecules is regarded as an important new task of applied spectroscopy[18]. Several reviews[16,19-21] have been concerned mainly with catalysis, while others[14,15,17,22] have discussed the results of spectroscopic investigations of surface compounds and adsorption without relation to the problems and data of adsorption investigations. In conformity with the main lines of our work on the chemical modification of solid surfaces[12,29] and the theoretical calculation of the energy of adsorption[7,24-30] and of adsorption equilibria[9-11,30], this review will, therefore, survey research which makes it possible to apply infra-red spectroscopy to the solution of the fundamental problems of surface chemistry: the mechanism of adsorption interaction, the energy of adsorption forces, and the thermodynamics of adsorption.

II. TECHNIQUE FOR THE SPECTROSCOPIC INVESTIGATION OF SURFACES OF HIGHLY DISPERSE SUBSTANCES

Infra-red bands result from the absorption of energy in transitions between rotational and vibrational levels of molecules. The position of a band in the spectrum — corresponding to a wavelength λ (in μ) or a frequency $\nu = 1/\lambda$ (usually expressed in cm^{-1}) — is determined by the nature of the vibrations, and primarily by the energy of the bond and the mass of the vibrating atoms or groups. As a result of this, the vibrational bands of certain groups of atoms (for example OH, CH, NH, etc.) have similar frequencies in different molecules. Slight differences in the

position of the bands of these groups may be due to the effect of neighbouring groups in the molecule or to intermolecular interaction. Infra-red structural analysis is based on the identification of bands in the unknown spectrum by comparison with spectra of molecules having known structure. A quantitative measure of the number of particular groups in a molecule or of molecules per unit volume of a substance can be made from the intensity of the corresponding bands in the infra-red spectrum.

Infra-red spectroscopy can be used to solve a great variety of adsorption problems associated both with the weak interaction of physically adsorbed molecules with the adsorbent and also with the chemisorption of molecules leading to the formation of new surface compounds, *i.e.* to the chemical modification of a solid surface.

In the case of physical adsorption the spectroscopic method is used to investigate changes in the nature of bonds and the geometrical structure of adsorbed molecules and the state of surface groups on adsorption. Investigation of chemisorption and surface chemical compounds solves problems analogous to those involved in the structural analysis of organic compounds.

The absorption bands of adsorbed molecules are superimposed on a background of absorption by the adsorbent. Consequently the possibility of studying physical and chemical adsorption by this method is governed to a considerable extent by the success in overcoming the difficulties associated with interpretation of the spectrum and with preparation of the specimen for investigation, which should be transparent and yet contain several thousand surfaces of separation, covered with the compounds under investigation or with adsorbed molecules, in the path of the infra-red beam. At the present time, interpretation of the spectra of physically and chemically adsorbed molecules is based solely on empirical comparison with the spectra of compounds of known structure. However, the limitation on the sensitivity with which surface compounds and adsorbed molecules, and especially changes in their structure, can be detected is often very slight, and is due mainly to the intrinsic absorption of the adsorbent and the strong scattering of infra-red radiation by powders, the form in which adsorbents of practical interest with large surface areas, are generally used.

However, very important adsorbents of this type — active oxides, such as silica and aluminosilicates — have wide ranges of transparency, limited only by strong absorption bands due to skeletal (lattice) vibrations lying mainly in the region below 1000 cm^{-1}. Silicon dioxide, for example, possesses such absorption bands[31] in the neighbourhood of 1000–1200, 800, and 500 cm^{-1}.

Most of the infra-red radiation is lost by scattering. This is diminished by investigating adsorption processes on thin sheets of adsorbents like porous glass[32] or on specimens prepared from particles of adsorbent powder smaller than the wavelength of the radiation employed.

Such particles are selected either by sedimentation[33] or by precipitation in an electric field[34]. The scattering of infra-red radiation by powders is still further diminished by moistening them with liquid paraffin or by making them into thin disks by compressing the powdered adsorbent with KBr powder[35]. This latter method, however, makes further treatment of the adsorbent difficult, and in several cases leads to ion exchange between its surface compounds and the KBr[36]. From this point of view compressing the adsorbent alone into thin disks is more satisfactory[37].

Surface compounds and chemisorption on metals are usually investigated by depositing them on a support "Aerosil"‡[38-41] or aluminium oxide[42,43]. In this case, too, the scattering of the infra-red radiation can be diminished by pressing the carrier and the metal into disks[44,45]. This leads to some decrease in the metal surface available for chemisorption. In the preparation of disks from palladium on Aerosil, for example, an increase in pressure from 25 to 125 kg mm^{-2} decreases the metal surface available for chemisorption from 5.1 to 3.1 $m^2 g^{-1}$.[45]

In several cases chemisorption on oxides and metals is investigated by depositing them on surfaces which do not scatter infra-red radiation: porous glasses[46,47] or an aerogel[48]. It has proved possible to obtain spectra of surface compounds by passing the infra-red beam through metallic films[20,49] or by reflecting the beam from metallic mirrors[50,51].

All the researches on adsorption by Terenin and his coworkers[52-55] between 1948 and 1952 were carried out in the overtone region of the spectrum using a two-beam infra-red spectrometer of high dispersion having a glass optical system designed by Terenin and Yaroslavskii[56,57]. In this region it is possible to investigate the first overtones of the stretching vibrations of OH, NH, and CH groups in adsorbed molecules and surface compounds using high-sensitivity infra-red detectors and glass cells, which considerably facilitate the handling of the adsorbent specimen. In 1954 Sidorov[58] extended the investigations of adsorption processes into the fundamental region of the spectrum, where the absorption bands of almost all the fundamental frequencies of the vibrational spectrum are located. At the present time the first attempts are being made[59] to extend the investigations into the long-wavelength region of the spectrum (below 500 cm^{-1}), in which absorption bands of vibrations and rotations of chemisorbed and adsorbed molecules relative to the adsorbent surface may appear.

Most of the work now being carried out is in the fundamental region of the spectrum and uses double-beam infra-red spectrometers, which give every opportunity for obtaining differential spectra eliminating the absorption bands of the adsorbent skeleton. The spectra of surface compounds of adsorbed molecules are investigated with the specimen in a special vacuum cell. Existing designs of cells usually provide for the possibility of vacuum treatment at elevated temperatures and for obtaining the spectrum both of the specimen and of the bulk gas phase. Detachable cells of simplified design[60] enable the specimen to be treated by means of a separate vacuum apparatus. Most of the types of cells which have been described[39,61-64] are connected directly to a vacuum line and to a system for measuring out the material; they are intended to be fixed permanently in front of the spectrometer slit. Fig. 1 illustrates one of the best cells of this type[48], made of quartz with CaF_2 windows, which allows the spectrum to be obtained with the specimen placed in the infra-red beam, and the gas to be investigated and the specimen to be heat-treated up to 1000° when the latter is lifted by means of an electromagnet. Vacuum treatment of the specimen is considerably simplified by using cells made entirely of glass[65].

The cells are connected to a conventional vacuum system enabling the sample to be evacuated normally to 10^{-5}–10^{-6} mm Hg. The specificity of the conditions under which

‡ *I.e.* Cab-o-Sil, which is anhydrous, particulate, colloidal silica made by Cabot Corp. (Ed. of Translation).

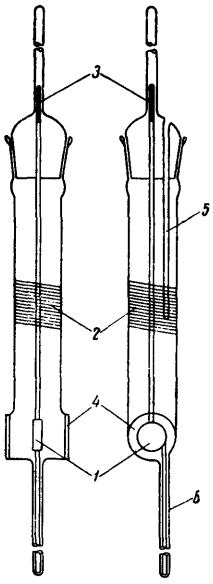


Fig.1. Quartz cell for the spectroscopic investigation of adsorption[48]:
1) specimen holder; 2) heater; 3) sealed-in iron rod for raising the specimen with an electromagnet; 4) windows; 5) well for thermocouple; 6) extension for fixing the holder in place.

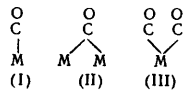
the spectra are obtained (the specimen being heated by the infra-red radiation) and of the conditions under which the powdered specimen has been prepared (by pressing), as well as the presence in the cell of windows made of hygroscopic materials (NaCl, LiF), make it difficult to investigate adsorption equilibria directly in the optical cell. The values of the degree of coverage of the surface with adsorbed molecules which are required are usually obtained from the vapour pressure on the basis of adsorption equilibrium measurements made in a special apparatus with an identical specimen of the adsorbent prepared under the same conditions.

III. SURFACE CHEMICAL COMPOUNDS AND CHEMISORPTION

1. Surface Compounds on Metals

The investigation of surface compounds on metals is of interest both for elucidating the mechanism of their catalytic action and for characterising their corrosion and getter properties. The most detailed research on metals using infra-red spectroscopy has been on the structure of the surface compounds of carbon monoxide, mainly in the USA by Eischens *et al.*[19,20,38,39,41] and by Garland[42,43]. Most of this work has been carried out on disperse metals distributed on the surface of carriers – Aerosils, porous glass, and aluminium oxide – by impregnating the carrier with a salt of the metal (for example, $RhCl_3.4H_2O$,[42] $Ni(NO_3)_2.6H_2O$[43]), decomposing the salt to the oxide, and then reducing the latter to the metal with hydrogen. Terenin[13] had previously suggested depositing the metal on a carrier by thermal decomposition of the metal carbonyls.

The structure of the surface compounds was determined from an investigation of the spectrum of the CO streching vibrations (in the 1800–2200 cm^{-1} range). Comparison of the position of the corresponding absorption band in the surface compounds and in carbonyls of known structure indicated[38,39,42] the existence of compounds of different structures on the surfaces of metals: linear, *i.e.* with a CO molecule linked with one metal atom (I); bridged, *i.e.* with a CO molecule linked to two metal atoms (II); and possibly two CO molecules linked with one metal atom (III);



From the intensities of the absorption bands it was concluded that with some metals (Cu,[20,38] Fe,[20] Pt,[38,39]) the linear configuration of the chemisorbed CO molecules predominates, while with other metals (Ni,[38,39] Pd,[38,39,66-68]) the bridge configuration is more important (Fig.2). In the case of chemisorption on Rh [42] (Fig.2) and Ni[16] all three types of compounds have been noted. As remarked elsewhere[39], with a linear configuration the position of the vibrational absorption band of CO is not very sensitive to the nature of the metal. The vibrational frequency of the bridge configuration is more sensitive to the type of metal, the effect of the carrier, and the type of surface treatment. Thus in the case of platinum deposited on Aerosil, the CO molecules exist predominantly in the linear form (the bridge forms amount to only 15%)[38,39] (Fig.3). When platinum is deposited on Al_2O_3, however, about half the total number of chemisorbed molecules are now in the bridge form[20] (Fig.3).

The effect of the carrier on the spectrum of carbon monoxide chemisorbed on nickel was also determined from

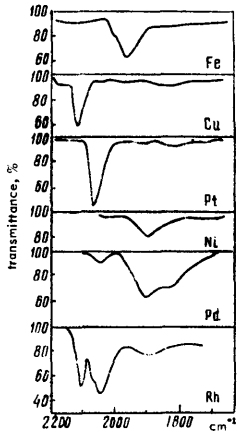


Fig.2. Spectra of carbon monoxide chemisorbed Fe,[20] Cu,[38] Pt,[38] Ni,[38] and Pd,[38] deposited on Aerosil, and on Rh [42] deposited on aluminium oxide.

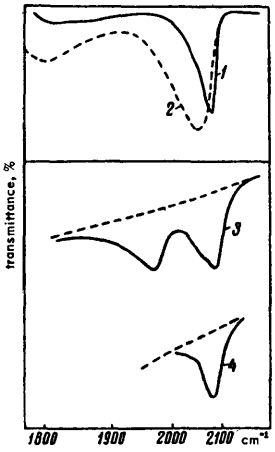


Fig. 3. Effect of carrier on spectrum of chemisorbed oxide[20]:
1) Pt deposited on silicon dioxide;
2) Pt deposited on aluminium oxide; and of surface treatment[43]: 3) freshly reduced Ni; 4) Ni poisoned with CS_2.

the relative intensities of the bands of the linear and the bridged CO structures when the nickel was deposited on aluminium oxide, titanium dioxide (anatase), and silica[65]. It was found that aluminium oxide and titanium dioxide have an appreciable influence on the strength of adsorption and the relative proportions of linear and bridged forms, while the effect of silica is slight.

The properties of the surface compounds of CO are affected also by the state of the metal on the carrier (aluminium oxide) surface. Yates and Garland[69] have shown that absorption bands of bridged and linear forms of surface compounds are observed on the surface of nickel in the crystalline phase (concentration of Ni by weight 25%). Only linear structures are formed on nickel which is highly dispersed (concentration 1.5%) on the carrier surface, and the strength of bonding of the surface compounds with the metal is decreased. Poisoning the metallic nickel surface with CS_2 vapour[43] causes blocking of the adsorption centres involved in the formation of the bridge type of surface compounds with CO (Fig. 3). The interaction of the CO surface compounds with O_2 and H_2 molecules is just as varied. The action of O_2 on CO chemisorbed on Fe [20] is accompanied by a considerable shift (0.4 μ) of the CO absorption band towards shorter wavelengths. With Cu [20] this displacement is less marked (0.04 μ). Treating the CO-metal surface compounds with hydrogen shifts the bands in the opposite direction. This phenomenon is especially marked when reactions are carried out in the surface layer at 200°.[66-68] When surface compounds of CO on Pd are treated with hydrogen (Fig. 4*a*)[67,68] a decrease in intensity of the absorption bands is observed for both linear (2085 cm^{-1}) and bridged (1960 cm^{-1}) structures, the latter band being clearly displaced towards lower frequencies. Treatment with oxygen (Fig. 4*b*) results in a greater decrease in intensity of the bands and their displacement in the opposite direction to 1995 and 2120 cm^{-1}. The observed difference in displacement of the absorption bands of the surface compounds of CO can be explained[20] by a change in the electronic state of the metal surface brought about by oxygen and hydrogen molecules chemisorbed in the course of the reaction.

Direct information on the structure of the surface compounds can be obtained from an investigation of their metal-carbon bonds. The absorption bands of chemical bonds of this type should lie at frequencies above 500 cm^{-1}. It is difficult to obtain a spectrum in this region mainly because of the strong infra-red absorption of the carrier (silica or alumina). Up to the present time it has only been possible to observe a band at 21 μ, which can be ascribed to a Pt–C chemical bond in the linear type of surface compound[20], with surface compounds of CO on highly disperse Pt pressed into KBr powder. In addition, with hydrogen and deuterium chemisorbed on platinum, absorption bands have been observed[70] at 4.74 and 4.87 μ, and also at 6.60 and 6.76 μ, which are ascribable to stretching vibrations of Pt–H and Pt–D bonds.

Among simple molecules of other types, the spectra of chemisorbed nitric oxide have been investigated in detail. The position of the absorption band of the NO molecule is an extremely sensitive criterion of its behaviour as an electron donor or an electron acceptor. This property of the molecule was used by Terenin and Roev to characterise the adsorption centres on the surfaces of the transition metals Fe, Ni, and Cr, their salts, and their oxides[71-74].

Investigation of the structure of surface compounds formed by the chemisorption of organic compounds on metals is of considerable interest. Compounds of ethylene and acetylene chemisorbed on a nickel surface have been studied in detail[20,40,41]. The spectrum of ethylene chemisorbed on a nickel surface covered with hydrogen shows absorption bands due to the stretching vibrations of the CH

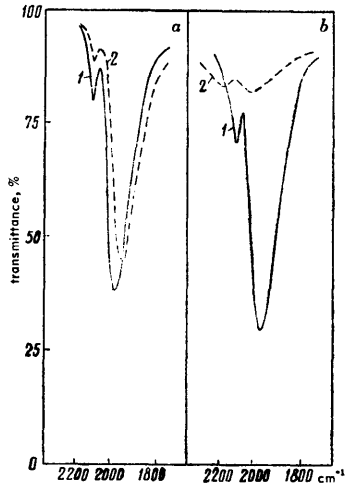


Fig. 4. Change in spectrum of carbon monoxide chemisorbed on Pd deposited on Aerosil, resulting from reaction with (*a*) hydrogen and (*b*) oxygen:
1) original spectrum; 2) after reaction[67].

bond of saturated hydrocarbons and a band due to the deformation vibrations of CH_2, the development of which indicates that a compound of type $\diagup CH_2 \cdot CH_2 \diagdown$ is formed on the surface. The intensity of the CH absorption bands is less in the spectrum of ethylene chemisorbed on a pure nickel surface (Fig.5). This evidently indicates the formation of a surface compound of type $\diagup CHCH \diagdown$ in this case. The increase in the CH absorption band intensity and the appearance of a band due to CH deformation vibrations in the CH_3 group when the surface compounds are treated with hydrogen (Fig.5) show that the surface compounds are hydrogenated to form ethyl radicals of the type $\diagup CH_2CH_3$ on the surface. The decrease in intensity of the CH absorption bands on evacuation may in turn indicate dehydrogenation of the surface radicals and their conversion into surface carbides.

The spectrum of the surface compounds in the chemisorption of acetylene on nickel is similar to that of surface ethyl radicals.

Analysis of the relative intensities of the 2950 and 2920 cm^{-1} bands, due to vibrations of the CH bond in CH_3 and in CH_2 groups, enables us to determine the relative proportions of these groups in surface radicals $[CH_2]_n.CH_3$. It was concluded on this basis[20] that the hydrogenation products of surface compounds of ethylene contain a large proportion of butyl radicals $CH_2CH_2CH_2CH_3$. The relative intensities of absorption bands due to stretching vibrations of the CH bonds at 2950, 2920, and 2870 cm^{-1}, the last of which is due to a group of type $-\overset{|}{C}H-$ or $-\overset{|}{C}H-\overset{|}{C}H_2$ in the surface compound, in turn indicate the number of carbon atoms in the surface compound which are directly linked to metal atoms. In this way it was deduced that butene molecules chemisorbed on nickel are joined to the nickel surface by all four carbon atoms[20].

Little *et al.*[47] estimated the intensities of the absorption bands of surface compounds of ethylene and acetylene chemisorbed on Pd, Cu, and Ni, and compared the results with those for the original compounds. The spectrum of C_2H_2 chemisorbed on Pd and Cu showed the presence of surface groups of olefinic type. In the chemisorption of C_2H_4 on Pd, absorption bands due to CH in saturated compounds were also observed. Treatment with hydrogen of surface compounds on these metals was also accompanied by an intensification of the absorption bands of saturated compounds and a decrease in the intensity of those of unsaturated compounds (Fig.5). The relative intensities of the absorption bands of CH_2 and CH_3 groups in the hydrogenated surface compounds indicate the existence on the surface of alkyl radicals of type $M.[CH_2]_n.CH_3$, and also that $n > 5$ for the hydrogenation of compounds of C_2H_2 on Pd and Cu, and that $n \simeq 3$ for C_2H_4 on Pd.

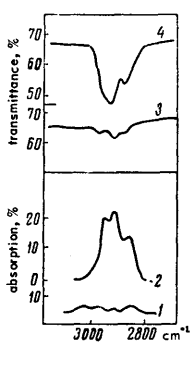


Fig.5. Spectrum of ethylene chemisorbed on Pd [47]: 1) before treatment with H_2; 2) after treatment with H_2; and on Ni [20]: 3) before treatment with H_2; 4) after treatment with H_2.

Such methods for investigating the structure of surface compounds can be considerably extended and used to study the surface compounds of hydrocarbons of the most varied structures. Furthermore, the possibilities of the method can be considerably increased by employing compounds obtained by replacing the hydrogen in the hydrocarbons by deuterium and by other atoms or groups.

The spectroscopic method has been employed also to investigate surface compounds of formic acid[44,75-77] and of stearic acid[51] on metals. The spectra observed in the chemisorption of the former acid agree satisfactorily with the hypothesis that the formate ion is produced on the metal surfaces.

2. Surface Compounds on Oxides

(*a*) Hydration and dehydration. All the various amorphous and crystalline forms of silica carry on their surface so-called "structural water" as a result of their production from aqueous solutions (silica gels), being leached with aqueous solutions (porous glasses), hydration of the surface formed at high temperatures (Aerosils, vitreous quartz), or being ground in water (crystalline silicas). From chemical and adsorption data, Kiselev[78] showed that this structural water consists of the hydroxyl groups of silicic acid chemically combined with the surface atoms of silicon. The absorption band due to the stretching vibrations of hydroxyl groups (7326 cm^{-1}) was detected in the overtone region of the spectrum in the very first spectroscopic investigations by Terenin and his coworkers on porous glass[52,54,55] and aerogel[53]. This band also appears clearly in the fundament range (3749 cm^{-1}) in the spectra of porous glass[58,60,79,80], silica gel[81-86], and Aerosil[37,87,88]. The observed bands are due to hydroxyl groups chemically combined with the surface atoms of silicon, since they remain in the spectra of specimens treated in a vacuum under conditions (heating to 150° and above) which remove the absorption band due to deformation vibrations of adsorbed water molecules[84,86], and where adsorption data[89-93] show that the adsorbed water is removed reversibly from the surface. The hydroxyl groups are located mainly on the surface of the different forms of silica, since the infra-red spectrum shows that they are perturbed by the adsorption of even feebly adsorbed substances, for example argon and nitrogen[94], and are readily substituted, being converted into OD by reaction with molecules of D_2O vapour[37,60,84-86,95,96]. The absorption band of the stretching vibrations of surface hydroxyl groups on strongly dehydrated forms of silica is very narrow, indicating the absence of interference between these groups. The half-width of the absorption band for porous glass treated in a vacuum at 550° is 50 cm^{-1} in the overtone range[54], and less than 15 cm^{-1} in the fundamental

range[94] (in the spectrum of Aerosil treated in a vacuum at 400°). This fact served as the basis for the view adopted in several papers[14,15,60,94] that the distribution of OH groups over a silica surface is completely "free".

Kiselev and Lygin[79,80] noted, however, that the narrow absorption band is observed only when the silica has been treated at high temperatures, with removal of most of the hydroxyl groups. But if adsorbed water has been removed from the surface of silica by vacuum treatment with moderate heating (up to 200°), the absorption band due to the stretching vibrations of the hydroxyl groups is considerably broadened and is unsymmetrical. This asymmetry in the spectrum of porous glass has been explained[60] by the presence of adsorbed H_2O molecules remaining on the surface after vacuum treatment at 470°, and the asymmetry in the spectrum of Aerosil powder by the Christiansen effect[94]. Neither of these causes can serve as an explanation, however, since under such conditions of treatment as heating in a vacuum to 470° all the adsorbed water is removed, while the Christiansen effect does not appear, since the same band contour is observed in the spectrum of silica powder moistened with liquid paraffin[37,80].

The observed form of the hydroxyl absorption band was explained by Kiselev and Lygin[79,85] who determined the spectra of silica gel and compared them with the hydroxyl concentrations on the surface obtained from the loss on heating of specimens[92] which had previously been subjected to a vacuum at different temperatures. Under conditions of complete hydration of the surface (treatment in a vacuum up to 200°) the mean distance between hydroxyl groups was found to be ~4 Å. Irregularity in the packing of the silicon–oxygen tetrahedra bearing hydroxyl groups, and in the orientation of their angles and edges, which is always present owing to the amorphous structure of silica gel produces a large number of hydroxyl group spacings of less than 3 Å on its surface, when treated under such conditions, so that hydrogen bonds can be formed between them. Hence the surface contains both "free" hydroxyl groups, separated from one another by more than 3 Å and not interacting with one another, and "combined" hydroxyl groups, which are close together (separated by < 3 Å) and are favourably oriented for the formation of hydrogen bonds between them.

In conformity with Terenin's first interpretation[15,52-55] the narrow bands were ascribed to such non-interacting "free" hydroxyl groups. The absorption in the longer-wavelength part of the band due to stretching vibrations of the surface hydroxyl groups, however, belongs to those groups on the same surface which are quite close together and are favourably oriented geometrically, interacting with one another by a weak hydrogen bond[79,80,85]. This view of the structure of the hydroxyl surface covering on silica is now adopted in many papers[37,97-100]. The idea of the existence of hydroxyl groups combined with one another on the surface of silica is used by Folman and Yates[97-99] to explain the variation in length of a rod of porous glass and in the spectrum of its hydroxyl groups when NH_3, $(CH_3)_2CO$, SO_2, and CH_3Cl are adsorbed on it.

The form of the absorption band due to the hydroxyl groups indicates that the relative proportions of free and interlinked groups are different on specimens of silica of different origin and subjected to different treatments (Fig. 6)[37]. Interlinked hydroxyl groups predominate on the surface of silica gels, the globules[23] in whose skeleton consist of arbitrarily packed silicon–oxygen tetrahedra resulting from polymerisation of the most hydrated form (monomeric molecules of orthosilicic acid); the absorption band due to the hydroxyl groups is, therefore, considerably broadened (Fig. 6*a*). Free hydroxyl groups predominate, however, on the surface of Aerosils, which have not undergone additional hydration (Fig. 6*b*), giving a narrow absorption band. These widely spaced free hydroxyl groups are very resistant to thermal dehydration. Even on treatment at high temperatures their absorption band only slowly decreases in intensity (Fig. 7)[37].

When hydrated silicas are dehydrated, the absorption band due to interlinked hydroxyl groups is the first to become weaker. When a not very strongly dehydrated silica surface is rehydrated, it is neighbouring hydroxyl groups, linked together by a hydrogen bond, which are restored first (Fig. 8)[84]. After partial thermal dehydration of the surface of silica gel at 400°, the hydroxyl covering can be completely reestablished by renewed hydration in water vapour[83,84]. When silica gel is treated above 400°, however, it is dehydrated irreversibly[83].

A hydroxyl covering exists on the surface of other oxides. Bands at 3698, 3737, and 3795 cm^{-1}, due to unlinked surface hydroxyl groups, remain in the spectrum of γ-aluminium oxide[48] after vacuum treatment, while the corresponding absorption bands in the spectrum of a deuterated specimen are at 2733, 2759, and 2803 cm^{-1}. With low treatment temperatures, each band is asymmetric towards low

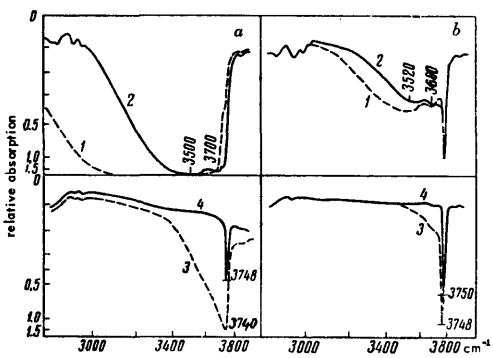


Fig. 6. Spectrum of hydroxyl groups of (*a*) silica gel and (*b*) Aerosil:
1) original specimen; 2) after vacuum treatment at 30° for 3 h; 3) at 500° for 30 min; 4) at 940° for 8 h.[37]

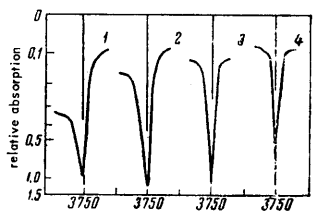


Fig. 7. Spectrum of Aerosil:
1) original; 2) after vacuum treatment at 500° for 30 min; 3) at 940° for 15 min; 4) at 940° for 8½ h.[37]

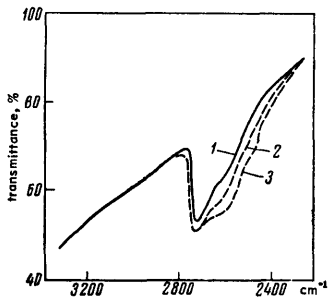


Fig. 8. Spectrum of deuterated silica gel: 1) vacuum treatment at 400°; 2) after contact with D_2O vapour for 30 sec and evacuating; 3) after contact with D_2O vapour for 2 h and evacuating[84].

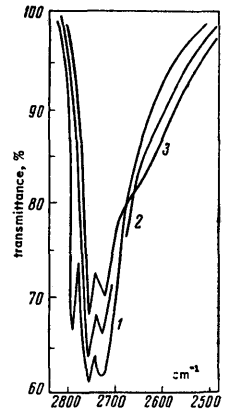


Fig. 10. Change in spectrum of surface OD groups on aluminium oxide during adsorption of acetylene[101]: 1) after treatment with deuterium at 600°; 2) on adsorption of acetylene at a pressure of 2 mm Hg; 3) at 5.9 mm Hg.

frequencies, owing to the superposition of absorption bands due to hydroxyl groups which are close together and interact with one another.

Each band can be ascribed to a set of hydroxyl groups possessing distinctive properties. The difference in properties between these groups is shown primarily by the order in which they are removed on dehydration, by their reactions with butene and NH_3, and by their ability to exchange with deuterium. With D_2, for example, the hydroxyl groups responsible for the absorption bands of highest and lowest frequency exchange first (Fig. 9), the intermediate band showing the slowest exchange.

A difference in properties between the various surface hydroxyl groups on aluminium oxide is observed also in the adsorption of acetylene and its derivatives[101] (Fig. 10). Thus when C_2H_2 is adsorbed on aluminium oxide covered with OD groups, the high-frequency OD band (2790 cm^{-1}) disappears first, whereas the other two OD absorption bands (2755 and 2735 cm^{-1}) merely decrease in intensity. Adsorption of C_2D_2 involves the disappearance of the high-frequency OH absorption band (3785 cm^{-1}) and the appearance of the high-frequency OD band (2785 cm^{-1}) indicating that only these groups take part in isotope exchange. The molecules of all adsorbates interact most strongly with hydroxyl groups corresponding to the high-frequency absorption band.

A difference in properties between surface hydroxyl groups appears also in the spectrum of the different modifications of titanium dioxide[102]. The spectrum of anatase heated at 150° in a vacuum shows absorption bands due to stretching vibrations of hydroxyl groups around 3675 cm^{-1} and in the range 3350–3100 cm^{-1} (Fig. 11). Vacuum treatment of a specimen at 350° leads to splitting of the band at 3675 cm^{-1}. Treatment of rutile under analogous conditions (evacuation at 350°) yields a spectrum with only one OH absorption band, at about 3680 cm^{-1}. The 3320 cm^{-1} band in the spectrum of rutile is due to surface NH groups formed in the preparation of the specimen. The hydrogen of the hydroxyl groups on titanium dioxide exchanges with deuterium at a greater rate than in the case of silica and aluminium oxide.

Several absorption bands due to surface hydroxyl groups are observed in the spectrum of an aluminosilicate catalyst[103].

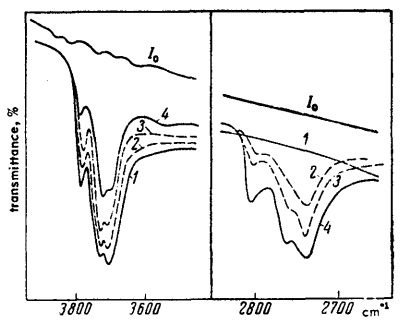


Fig. 9. Exchange between D_2 and H in OH groups of γ-aluminium oxide at 250°: 1) spectrum of original specimen; 2) after exchange for 15 min; 3) 45 min; 4) 18 h.[48]

(*b*) Surface esterification of oxides and hydroxides. Surface reactions yielding new compounds by the creation of a bond with the surface atoms of the adsorbent skeleton or by the replacement of existing surface groups provide wide possibilities of altering the properties of adsorbents. The hydrophilic properties of a hydrated silica surface can be replaced by hydrophobic properties by the formation of esters on the surface. The reaction of a silica gel surface with methanol was first observed by Kiselev and his coworkers[104] and then elsewhere[105-107]. Methylation on porous glass was investigated spectroscopically by Sidorov[58,60]. Adsorption of methanol on this material decreases the intensity of the absorption band of the surface hydroxyl groups (3750 cm^{-1}) and causes the

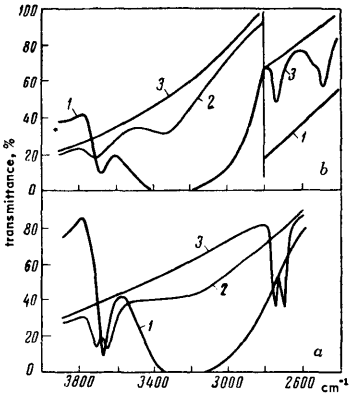


Fig. 11. Spectrum of (*a*) anatase evacuated at: 1) 150°; 2) 350°; 3) after exchange with deuterium at 350°; *b*) spectra of rutile obtained under the same conditions[102].

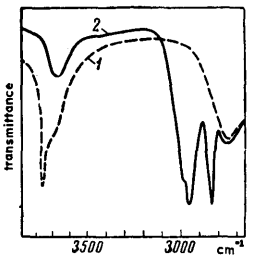


Fig. 12. Spectrum of porous glass after: 1) vacuum treatment at 430°–470°; 2) treatment three times in saturated methanol vapour at 430°–470° followed by evacuation at 430°–470°.[123]

appearance of bands due to C–H stretching vibrations in the methyl groups (2965 and 2862 cm^{-1}) (Fig. 12). Treatment of the surface with methanol at elevated temperatures (up to 470°) leads to an increase in the degree of methylation. However, it is not possible to replace all the surface hydroxyl by methoxy-groups§. The change in intensity of the hydroxyl absorption band indicates that 30% of them are methylated when Aerosil is heated in a current of methanol vapour[94]. The impossibility of complete replacement of surface OH by CH_3 groups is probably explained by steric hindrance[94]. Surface methyl groups are stable to heat treatment, and their absorption bands remain in the spectrum on heating to 400°.[60,94] The reverse reaction, the replacement of methyl by hydroxyl groups, is very slow[60].

Formation of new hydroxyl groups on the surface is also possible during methylation. Thus Stober[105] and Kiselev and Belyakova[107] found that the chemisorption of methanol increases with increasing dehydration of the surface. This indicates that methylation of the surface of silica gel can take place by rupture of Si–O–Si bonds with the formation of hydroxyl and methoxy-groups on the surface.

Esterification was also investigated spectroscopically with other oxides. For example, Babushkin and his coworkers[63,108,109] studied the reactions of methanol and ethanol with aluminium oxide. The spectrum of the chemisorbed alcohols contained bands due to the ether O—C link and to Al–O in surface compounds of the type >Al–O–CH_3.

Roev and Terenin[110] found a great variety of forms of surface compounds in an investigation over the range 800–1700 cm^{-1} of the spectra of methanol and ethanol chemisorbed on chromium oxide (Fig. 13). The bands at 942 and 859 cm^{-1} were interpreted as due to deformation vibrations of surface OH groups. The band at 1580 cm^{-1} in the case of the chemisorption of CH_3OH, and that at 1563 cm^{-1} with C_2H_5OH, as well as a series of bands within the range

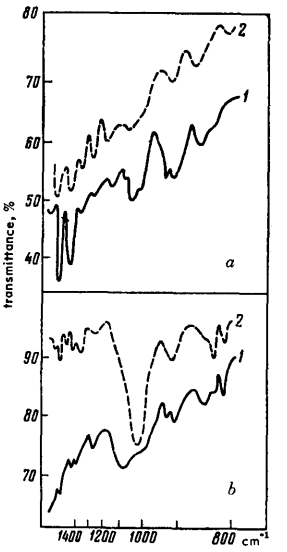


Fig. 13. Spectra of surface compounds obtained on treatment of chromium oxide with: *a*) ethanol; *b*) methanol: 1) treatment and desorption at 20°; 2) treatment at 150° and desorption at 200°.[110]

800–1000 cm^{-1}, were taken as indicating the presence of surface compounds containing a C=C bond. The absorption bands in the range 1000–1200 cm^{-1} were in turn assigned to surface compounds of the type Cr–O–C– in the case of the chemisorption of methanol, and to compounds of the type Cr–O–C–C– with ethanol.

§ In this and the following paragraph there seems some confusion as to whether CH_3 or CH_3O groups are present (Ed. of Translation).

(*c*) Trimethylsilylation of hydroxide surfaces. The most complete coverage of a silica surface by chemically grafted compounds was achieved in surface reactions with trimethylsilyl chloride. The extent of coverage of an Aerosil surface with trimethylsilyl groups was found[111] to be increased by preliminary hydration of the surface. In this case, however, hydroxyl groups still remained on the surface, and affected the adsorption properties, especially with respect to small molecules[7]. The accessibility of such remaining hydroxyl groups to absorbed water molecules was studied[112] from the infra-red spectra obtained by means of isotopic exchange of the OH groups of Aerosil with D_2O molecules. Exchange of surface OH groups by OD in an atmosphere of D_2O vapour is complete (Fig. 14*a*), apart from groups blocked at the point of contact by Aerosil particles. With a strongly modified Aerosil specimen (Fig. 14*b*), however, exchange is considerably less. This indicates that Aerosils which are strongly modified by trimethylsilyl groups, have a proportion of the hydroxyl groups remaining on the surface which are screened by the trimethylsilyl groups chemically grafted to the surface, and are therefore inaccessible to isotopic exchange with D_2O molecules.

Trimethylsilyl groups, located above the remaining surface hydroxyl groups, perturb the vibrational motion of the latter, so that the absorption maximum of the OD groups on a modified porous glass is shifted to 2740 cm^{-1} (Fig. 15)[113]. The spectrum shows that heating porous glass to 400° does not remove trimethylsilyl groups (2968 cm^{-1}) from the surface. It is only after the surface has been heated at 500° that OD groups alone remain, giving an absorption band at 2761 cm^{-1}, as in the spectrum of the original unmodified specimen.

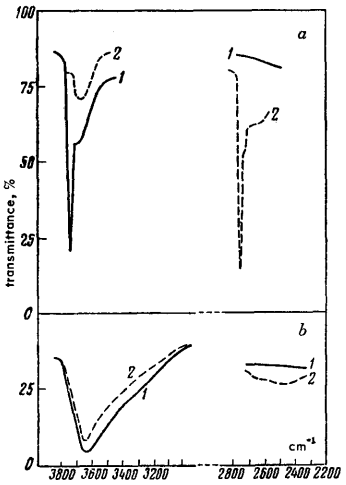


Fig. 14. Change in spectrum of surface OH groups of original Aerosil (*a*) and Aerosil modified with trimethylsilyl chloride (*b*), on treatment with D_2O:
1) original spectrum; 2) after reaction with D_2O.[112]

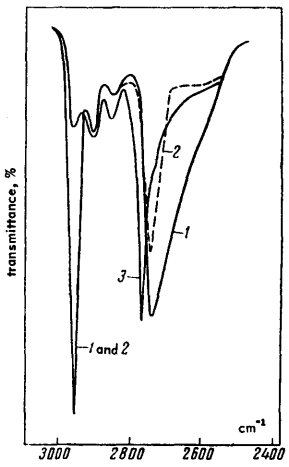


Fig. 15. Spectrum of porous glass modified with trimethylsilyl chloride after vacuum treatment at:
1) 200°; 2) 400°; 3) 500°.[113]

Infra-red spectroscopy has been used in conjunction with nuclear magnetic resonance to investigate surface compounds of formic acid on silica and alumina[114,115]. Organic radicals can be formed on oxide surfaces as a result of the chemisorption of a great variety of compounds. Little[46], for example, detected absorption bands of methyl and methylene groups in the spectra of ethylene chemisorbed on the oxides of Ni, Cu, and Pd. Infra-red spectra indicate that compounds similar to the carboxylate ion are formed when CO is adsorbed on the surface of zinc oxide[116].

3. Chemical Compounds on the Pore Surfaces of Zeolites

The surface chemistry of the channels in zeolites plays an extremely important part in the properties of the latter as adsorbents and molecular sieves. Work on the properties of zeolite surfaces is only now beginning to be developed, and only preliminary attempts have been made at applying infra-red spectroscopy to the investigation of surface chemical compounds on zeolites. Kington and Frohnsdorff[117,118] detected no absorption bands of OH groups in the spectrum of Linde zeolite type A heated at 400°. The spectrum of Linde zeolite type NaX and NH_4X was found[119] to contain a narrow band at 3500 cm^{-1}, which was assigned to surface OH groups of the zeolite. The mechanism of hydration of the zeolite surface was traced, a decrease in intensity of the absorption band of the NH group in the NH_4^+ ion being observed with the simultaneous appearance and increase in intensity of the OH band when a zeolite of type NH_4X was heated. The decrease in intensity of the OH band observed on heating above 400° was explained by the condensation of neighbouring groups with the elimination of H_2O.

Surface OH groups on zeolites are difficult to exchange for OD in saturated D_2O vapour. The absence of such exchange has been noted previously by Terenin in the case of the natural aluminosilicate bentonite[115].

4. Oxygen Compounds on the Surfaces of Carbon Adsorbents

It is difficult to obtain infra-red spectra of high quality for surface compounds on carbon adsorbents, including carbon blacks, owing to the great loss in infra-red radiation by scattering and to the continuous background absorption. Infra-red spectroscopy is therefore employed at the present time as an ancillary method for investigating surface chemical compounds only on a small number of carbon blacks which are most suitable for spectroscopic investigation, such as oxidised carbon black of the "Carbolac" type¶,[120] a highly disperse channel black of particle size 80–100 Å,[121] a channel black which has been specially oxidised with sodium hypochlorite solution, and a carbon black obtained by thermal decomposition of graphite oxide[122]. The spectra show the absorption bands of carbonyl groups and vibrations of the COH group, evidently forming part of phenolic, enolic, and lactone compounds, whose existence has been suggested on the basis of chemical investigations. The infra-red spectra also confirm that carbonyl and hydroxyl groups in these compounds which are close together are linked by hydrogen bonds. Far greater success in investigating the structure of surface chemical compounds on carbon adsorbents can evidently be achieved by employing electron paramagnetic resonance and spectroscopy in the far infra-red, where carbon adsorbents are more transparent.

IV. SIMULTANEOUS CHEMISORPTION AND PHYSICAL ADSORPTION

Interaction between molecules and an adsorbent surface can occur both by the strong interactions alone considered above, being in the limiting case chemical reactions with surface groups and atoms, and also as a result of weak forces, causing concentration of the molecules in the surface layer without any substantial change in their geometric structure or chemical properties. Depending on the chemical nature of the adsorbed molecules, the peculiarities of the electron density distribution in them, the nature and structure of the adsorbent surface, and the temperature, these processes can take place simultaneously and make different contributions to the total adsorption.

The chief spectroscopic manifestation of physical adsorption on surfaces covered with chemical groups is a decrease in intensity of the absorption band due to the surface groups, accompanied by the appearance of a new and usually broader band due to these groups displaced to longer wavelengths. The spectrum of the adsorbed molecules undergoes comparatively little change on adsorption. All changes in spectrum accompanying physical adsorption are completely reversible: vacuum treatment restores the original intensity of the adsorbent bands and removes those due to the adsorbed molecules.

Chemisorption may have spectroscopic features similar to those of physical adsorption. Thus the intensity of the absorption bands due to surface groups on the adsorbent may diminish during chemisorption owing to substitution of these by other groups. The absorption bands of many groups in chemisorbed molecules (for example, CH_2 and CH_3) may undergo little change on chemisorption. The distinguishing feature of chemisorption is the irreversibility of the spectroscopic changes in surface groups and chemisorbed molecules which accompany it. The type of changes undergone by a molecule on a surface can be most reliably established by studying its whole spectrum in order to determine whether its structure is preserved or destroyed and to determine the type of link between the molecule and a surface adsorbent atom. The results of chemical and adsorption measurements must also be taken into account.

In many cases, however, the whole spectrum cannot be studied owing to the overlapping of absorption bands due to the adsorbent skeleton and the adsorbed molecule, while investigations in the far infra-red, in which bands due to bonds between the molecule and the surface may appear, are only beginning. Owing to this difficulty, complete spectroscopic investigations of adsorption, in which proper account is not taken of chemical and adsorption data, may lead to contradictory conclusions as to the predominance of physical or of chemical adsorption and as to the part played by different adsorption "centres".

Nikitin *et al.*[60] observed no change in intensity of the absorption band due to free surface hydroxyl groups in an investigation of the adsorption of water on porous glass which had been heated in a vacuum at 470°. On desorption of water from the surface of the porous glass, however, the spectrum still contained absorption bands due to the stretching vibrations of OH groups, somewhat displaced relative to the absorption band of the "free" hydroxyl groups. These facts were interpreted as indicating that adsorption of water takes place not on the surface hydroxyl groups but on other sites on a porous glass surface. In later work with thin sheets of porous glass, Sidorov[123] noted a decrease in intensity of the absorption band of the "free" hydroxyl groups on a silica surface only at high relative pressures of water vapour. It was therefore concluded that hydroxyl groups provide adsorption centres only at high degrees of surface saturation of a porous glass surface. These conclusions did not agree with the adsorption data (see discussions elsewhere[124,125]).

Simultaneous processes of physical adsorption and other molecular changes appear in still more complicated form in the adsorption of ammonia on a partly dehydrated porous glass surface. The absorption band due to surface hydroxyl groups almost completely disappears on adsorption of ammonia, but vacuum treatment at 20° restores its original intensity[126]. The spectrum still contains the absorption bands due to stretching vibrations of NH groups at 3370 and 3280 cm^{-1} (Fig.16)[123]. A similar pattern of spectral change was observed by Sidorov[123] in the adsorption of phenol and chloroform on porous glass, and by Folman and Yates[97-99]

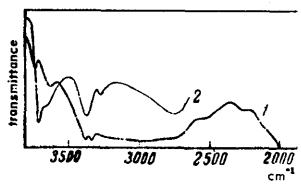


Fig.16. Spectrum of porous glass 0.5 mm thick: 1) in the presence of ammonia at 50 mm Hg; 2) after vacuum treatment for 15 min.[123]

¶ Series of channel carbon blacks made by Cabot Corp. (Ed. of Translation).

in the adsorption of methanol and ammonia. The preservation of absorption bands due to individual bonds in adsorbed molecules on evacuation of a specimen was explained, as in the case of water, by the adsorption of the molecules on "secondary" adsorption centres, the bonding energy of which was greater than the energy of a hydrogen bond.

Since the secondary centres are not directly represented in the spectra, great uncertainty in establishing their nature is noted in many papers[17,97,99,127]. This vagueness also arises because secondary centres are introduced in most cases to explain an adsorption process on dehydrated silicas; on the latter, however, physical adsorption can also be accompanied by *chemisorption*, the spectral manifestations of which are very similar to those used to justify the "secondary" centres of *physical* adsorption.

Ideas based on the existence of secondary centres of physical adsorption and their decisive role in the adsorption of water are incompatible with results in the overtone region of the spectrum previously obtained by Yaroslavskii[54]. The conclusions of Nikitin *et al.*[60] on the absence of interaction between adsorbed water molecules and surface hydroxyl groups are also inconsistent with results obtained by McDonald[37] in the fundamental region of the spectrum for the adsorption of water on Aerosil. In a recent paper Sidorov[100] remarks on the great part played by surface hydroxyl groups in the adsorption of water.

Finally, direct results on the adsorption of water and methanol[90-93,128] do not support the assumed existence of other surface centres, more active than hydroxyl groups, for their *physical* adsorption.

Direct measurements of the heats and entropies of adsorption of water vapour[93], ether[129], and t-butyl alcohol[130] on silica gels having hydrated and partly dehydrated surfaces showed that, firstly, these substances are reversibly adsorbed many times more strongly on a hydrated than on a dehydrated surface, and secondly that the decrease in heat of adsorption on dehydration of the surface is particularly large in the case of ether, the molecules of which can form hydrogen bonds only with surface hydroxyls, but not with one another, and do not react chemically with the dehydrated surface. A particularly important fact is that the decrease in heat of adsorption of ether due to dehydration just corresponds to the energy of two hydrogen bonds. Thirdly, the heats of adsorption of ether and t-butyl alcohol on hydrated silica gel exceed those of the hydrocarbons of corresponding structure – n-pentane and neopentane – also by the energy of two hydrogen bonds. Nevertheless, ether and n-pentane, and also isolated molecules of t-butyl alcohol and neopentane, have similar energies of adsorption on a non-polar adsorbent, graphite, where adsorption takes place essentially only under the influence of electrokinetic (dispersion) forces[7,131]. These new data leave no room for doubt that the most favourable sites for the reversible adsorption of oxygen-containing molecules, which can form hydrogen bonds with hydroxyl groups on the surface, are pairs of favourably arranged hydroxyl groups, and not dehydrated parts of a silica surface.

Nevertheless, the above facts indicate that the interpretation of the results of some spectroscopic investigations on complicated surfaces (on partly dehydrated silicas in the simplest case) is difficult and hence sometimes contradictory, while the mechanism of adsorption suggested on this basis does not explain all the phenomena, especially purely adsorption ones. Therefore further spectroscopic investigations are obviously necessary. With specimens of known surface structure and adsorption capacity, these would enable the effects of reversible physical adsorption to be separated from chemisorption (for example, hydration of the surface), and would allow us to establish the predominant role and detailed character of these processes when the chemical structure of the surface is varied in different ways.

V. PHYSICAL ADSORPTION

1. Mechanism of Physical Adsorption

(*a*) Change in spectrum of surface hydroxyl groups during adsorption. Direct and most reliable information on the mechanism of physical adsorption on hydroxylated surfaces is obtained by spectroscopic investigation of the interaction between the surface hydroxyl groups of silica and adsorbed molecules. The sensitivity of surface hydroxyl groups to adsorption interaction was first used by Terenin and Yaroslavskii in an investigation in the overtone range of the adsorption on porous glass of benzene, toluene, aniline, pyridine, phenol[14,52], water[54], nitrogen, and oxygen[55]. Kurbatov and Neuimin investigated in the overtone range the adsorption of chloroform, phenol, acetone, and water on aerogel[53]. Filimonov used the spectroscopic method to study the adsorption from the gaseous phase and from solution of a number of organic compounds on porous glass, on silica gel, and on an aluminosilicate catalyst[132,133]. Lyubimov and Egorov investigated the adsorption of water in the overtone range[134]. With saturated hydrocarbons and molecules having spherical symmetry like CCl_4, whose interaction with surface hydroxyl groups involves mainly dispersion forces, the absorption band due to these groups remains narrow and its displacement towards lower frequencies does not exceed 1%. The situation is similar in the adsorption of molecules possessing quadruple moments or small dipole moments. A typical case is the change in the absorption band of OH groups when N_2 molecules are adsorbed on porous glass at -180° (Fig. 17)[55]. The spectrograms show during adsorption a gradual disappearance

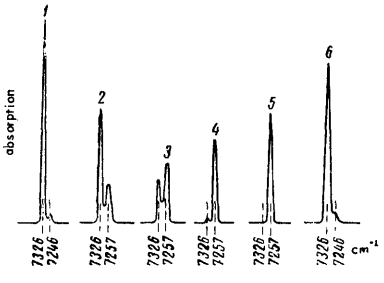


Fig. 17. Change in spectrum of surface hydroxyl groups of porous glass after adsorption of nitrogen at -180°:
1) original specimen; 2) after 1 min; 3) after 10 min; 4) after 20 min; 5) 2 h after admission of nitrogen; 6) heated with adsorbed nitrogen to +20°.[55]

of the absorption band at 7326 cm^{-1} due to free hydroxyl groups, and the appearance of a band at 7257 cm^{-1} due to hydroxyl groups perturbed by the adsorbed N_2 molecules. A typical feature of physical adsorption in this case is the restoration of the original band when the temperature of the specimen is raised to 20°, *i.e.* on desorption of the nitrogen.

The adsorption of molecules having large dipole moments, and especially of molecules able to form a hydrogen bond with surface hydroxyl groups, is accompanied by a large displacement (> 3%) and a broadening of the band due to the hydroxyl groups. With the adsorption of acetone, for example, the hydroxyl absorption band is displaced by 1000 cm^{-1} and is considerably broadened[132,133].

A typical effect of adsorption interaction involving formation of a hydrogen bond with surface hydroxyl groups is observed in the overtone range during the adsorption of water on porous glass[54]. The spectrum of the latter (Fig. 18) shows a decrease in intensity of the band at 7326 cm^{-1} due to surface OH groups and the appearance of an absorption band at 7140 cm^{-1} due to the adsorbed water molecules. At high vapour pressures absorption appears in the region of 6850 cm^{-1}, caused by molecules condensed in the capillaries and by surface hydroxyl groups which have formed hydrogen bonds with adsorbed water molecules.

The effect of dehydration of a silica surface on the adsorption of water is shown clearly on the spectrograms (Fig. 19) given by Kurbatov and Neuimin[53]. When water is adsorbed on a slightly dehydrated specimen of aerogel (curve *1*, Fig. 19) there is a considerable diminution in the absorption band of the surface hydroxyl groups accompanied by the appearance of bands due to adsorbed and capillary-condensed water (curve *2*). However, there is far less adsorption of water on a strongly dehydrated aerogel (curve *3*): the intensity of the absorption band due to the surface hydroxyl groups decreases only slightly and the bands due to adsorbed and capillary-condensed water appear only faintly in the spectrum (curve *4*). A satisfactory explanation of the observed variation in the spectrum of the surface hydroxyl groups can be given on the basis of ideas now current in adsorption research[93,124] on the mechanism of the adsorption of water on hydrated and dehydrated silicas. Adsorption data, which indicate a decrease in the amount of adsorption and in the heat of adsorption of water on dehydration of the surface, confirm that adsorption of a water molecule on two neighbouring surface hydroxyl groups, situated close together and favourably oriented, is energetically the most advantageous. In conformity with this,

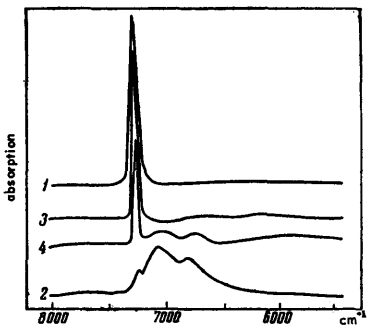


Fig. 19. Change in absorption spectrum of hydroxyl groups of porous glass on adsorption of water; 1) specimen subjected to vacuum treatment at 400°; 2) after capillary condensation of water; 3) vacuum treatment at 900°; 4) after capillary condensation of water[53].

the interaction of water molecules with hydroxyl groups should have a greater effect with a hydrated surface or with one that has been dehydrated at not too high a temperature, as is observed in Fig. 19.

The dominant role of neighbouring surface hydroxyl groups, close together and favourably oriented, in the adsorption of water on a hydrated surface is shown by Sidorov's results, in the fundamental range of the spectrum, on the adsorption mechanism on porous glasses of different degrees of hydration[100]. The spectrograms in Fig. 20[100] clearly show that, with increase in the temperature of vacuum treatment of the porous glass and removal of surface hydroxyl groups situated close together (narrowing of the 3749 cm^{-1} absorption band), the quantity of adsorbed water molecules also decreases. The governing role of surface hydroxyl groups in the adsorption of water molecules on silica was shown by Benesi and Jones[84], and by Kiselev and Lygin[86] in a spectroscopic investigation of the adsorption of water on silica gel having a fully hydrated surface. On adsorption of a monolayer of heavy water on silica gel containing surface OD groups[86], the intensity of the band due to the stretching vibrations of such groups

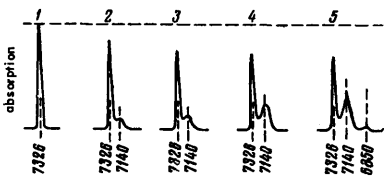


Fig. 18. Change in absorption spectrum of hydroxyl groups of porous glass on adsorption of water: 1) specimen treated in vacuum at 550°; 2) after adsorption of water at 4 mm Hg for 1½ days; 3) at 9 mm Hg for 4 h; 4) at 12 mm Hg for 1 h; 5) in saturated steam for 10 min[54].

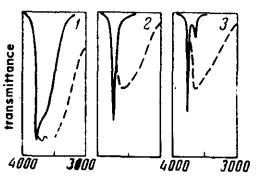


Fig. 20. Full lines: change in spectrum of hydroxyl groups of porous glass after being heated in a vacuum at different temperatures: 1) 300°; 2) 540°; 3) 650°. Broken lines: after remaining in water vapour at 16 mm Hg for 30 min[100].

(2760 cm^{-1}) is considerably diminished, and absorption bands appear due to stretching vibrations of adsorbed D_2O molecules (2680 cm^{-1}) and surface OD groups (2500 cm^{-1}) perturbed by the adsorbed water molecules (Fig. 21). However, the absorption band due to deformation vibrations of the OH groups of the adsorbed H_2O (1620 cm^{-1}) lies between the bands due to the deformation vibration of H_2O molecules in the vapour (1595 cm^{-1}) and in the liquid (1640 cm^{-1}). These facts suggest that the hydroxyl groups of completely hydrated silica gel are the main centres of reversible physical adsorption of water, which takes place by the formation of hydrogen bonds between surface hydroxyl groups and oxygen in the adsorbed water molecules.

The overtone OH band completely disappears on the adsorption of molecules having strong protophilic properties, such as aniline, pyridine[52], benzaldehyde, dioxan, etc.[14] To explain this effect by the formation of a strong hydrogen bond[15], as noted elsewhere[20], is inconsistent with our normal ideas, since formation of a hydrogen bond is always accompanied by a broadening and a displacement of the hydroxyl absorption band, not by its complete disappearance. It is quite possible, however, that overtone bands of perturbed hydroxyl groups are not observed owing to their considerable diffuseness, and perhaps also owing to the potential curve becoming more symmetrical on adsorption, making the OH bond vibration more harmonic, with an associated decrease in intensity of the overtone band of OH when perturbed by adsorption[17].

The possibilities of infra-red spectroscopy for studying the mechanism of adsorption are considerably increased by investigations in the fundamental region of the spectrum. McDonald[94], for example, was able to reveal extremely fine differences in the variation in the spectrum of the surface hydroxyl groups of Aerosil even with the weak van der Waals adsorption of different inert gases. The shift in the hydroxyl absorption band (3749 cm^{-1}) accompanying adsorption was found to be 8 cm^{-1} for argon, 16 for krypton, 12 for oxygen, 24 for nitrogen, and 34 for cyclohexane. The 3749 cm^{-1} band completely vanishes, a new band appearing at 3725 cm^{-1}, with the adsorption on the surface of considerably fewer N_2 molecules than are required for a complete monolayer (Fig. 22). This indicates the preferential adsorption of the first N_2 molecules on the hydroxyl groups of the silica. With the adsorption of argon and oxygen, the hydroxyl band disappears at higher vapour pressures than in the case of N_2, which, in conformity with the smaller shift in the hydroxyl band, indicates a weaker interaction, in comparison with N_2, between these molecules and hydroxyl groups. The stepwise change in position of the hydroxyl absorption band observed on the spectrograms is explained by a change in the mechanism of interaction of N_2 molecules with hydroxyl groups at these vapour pressures.

The polarisability of the adsorbed molecules cannot be the factor explaining the shift in the absorption band of the surface hydroxyl groups, since oxygen and nitrogen, for example, have almost identical polarisabilities, while the displacements are different, amounting to 12 and 24 cm^{-1}. Frohnsdorff and Kington[135] have shown that this latter difference can be explained by the proton–quadruple interaction between the surface hydroxyl groups and adsorbed molecules. These spectroscopic data are consistent with the observed[136] decrease in the adsorption of nitrogen at low degrees of surface coverage on dehydration of a silica surface.

Investigation in the fundamental range of the spectrum[58,123] also revealed a distinct variation in the displacement of the hydroxyl absorption band with the polarity of the adsorbed molecules and their ability to form a hydrogen bond. It has been shown with a large number of organic molecules[88] that the shift in the absorption band of the surface hydroxyl groups of Aerosil varies from 30 cm^{-1} (for the adsorption of cyclohexane) to 845 cm^{-1} (with pyridine).

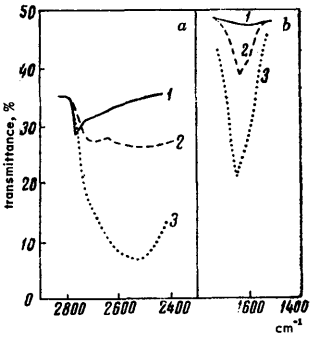


Fig. 21. Spectrum of (*a*) deuterated silica gel: 1) heated in vacuum at 200°; 2) after adsorption of a monolayer of D_2O; 3) under conditions of capillary condensation of D_2O, (*b*) original silica gel: 1) heated in a vacuum at 200°; 2) after adsorption of a monolayer of H_2O; 3) under conditions of capillary condensation of H_2O.[86]

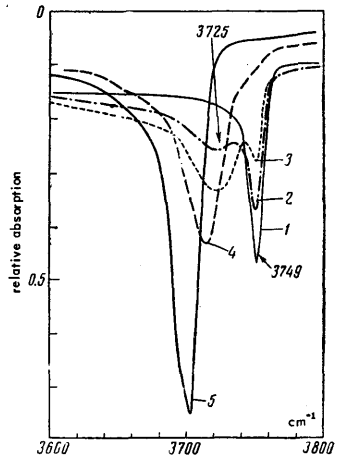


Fig. 22. Change in absorption spectrum of Aerosil on adsorption of N_2:
1) specimen heated in a vacuum at 300°–350°;
2) after adsorption of N_2 at -190° and 1.42 mm Hg;
3) 4.85 mm Hg; 4) 47.3 mm Hg; 5) under conditions of condensation of N_2 at -200°.[94]

Folman and Yates[97] found that the perturbation of the surface hydroxyl groups of porous glass by polar adsorbates increases in the order $CH_3Cl < SO_2 < (CH_3)_2CO < NH_3$; *i.e.* it increases with increasing ability to form a hydrogen bond.

(*b*) Change in spectrum of adsorbed molecules. The mechanism of adsorption interaction can be judged also from the changes in the spectrum of the adsorbed molecules themselves compared with their spectrum in the gaseous and liquid states. The absence from most papers of data on the surface coverage by adsorbed molecules introduces a certain vagueness into the characterisation of physically adsorbed molecules, since their interaction with one another at low degrees of surface saturation is closer to their interaction in the gas, while that at high surface saturations resembles more their interaction in the liquid. Nevertheless, it can be concluded that groups in molecules which do not make a fundamental contribution to the formation of an adsorption link are little perturbed by adsorption. Thus, for example, no displacement of the absorption maximum in bands due to the CH bond in a benzene ring and its aliphatic substituents can be established between the adsorbed and liquid states[123].

Nevertheless, a difference can be noted in the positions of the bands due to the CH bond and of the absorption bands due to stretching and deformation vibrations of the C–C bond in benzene molecules adsorbed at low surface saturations, the gas, and the liquid[137]. In particular, a band at 2223 cm^{-1}, a component of the CH deformation vibrations in the plane of the ring, appears in the spectrum of adsorbed benzene even at low degrees of coverage, although it is absent in the gas (Fig. 23).

The change in spectrum of an adsorbed molecule in turn allows us in several cases to ascertain the chemical group or bond in the molecule by which it is linked to the adsorption centre. Thus the increase in frequency of the absorption bands of the CH groups in benzaldehyde and acetone,

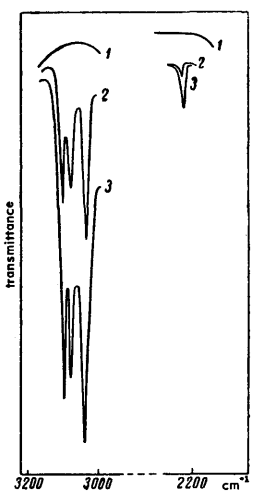


Fig. 23. Infra-red spectrum of: 1) Aerosil; and of benzene on Aerosil: 2) covered with 0.1 monolayer; 3) one monolayer[137].

and the decrease in frequency of the CO group, indicate that these molecules are joined to the surface hydroxyl groups of porous glass by the electronegative oxygen atoms of the carbonyl groups[123]. A change in the spectrum of a similar character is observed in the adsorption of aldehydes and ketones on Aerosil[88]. The formation of a hydrogen bond between surface hydroxyl groups of silica and aluminosilicates and amino nitrogen atoms in adsorbed molecules is indicated by the considerable displacement of the NH absorption band towards lower frequencies[123,132,138]. The change in the spectrum of an adsorbed molecule produced by a controlled variation of the geometrical and chemical structure of the adsorbent can in turn contribute to establishing the nature of the link between the adsorbed molecule and the surface of the adsorbent. The shift in the absorption band due to the OH stretching vibration in a water molecule adsorbed on halides formed by ions of different sizes and electronegativities indicates the formation of a preferential link between the hydrogen atom of the water molecule and the negative halide ion[139].

(*c*) Intensity of absorption bands of surface groups of absorbent and adsorbed molecules. Adsorption methods for obtaining isotherms and heats of adsorption usually give the aggregate effect of the interaction of a large group of molecules with many adsorption centres on the surface.. Apart from the simplest cases[7] this diminishes the possibility of separating the interaction of adsorbate molecules with different adsorption centres on the surface of the adsorbent and with one another. The great selectivity of infra-red spectroscopy eliminates these restrictions to a considerable extent, since in principle infra-red spectra enable us to characterise the state of every chemical group on the surface and every bond in the adsorbed molecule. Up to the present, however, investigations on these lines have not been widely developed owing to the difficulty of intensity measurement and to limitations in the sensitivity with which adsorbed molecules can be detected. In fact the accuracy of the intensity measurements, which is usually limited by distortions introduced by the finite width of the slit and the spectroscopic apparatus, is diminished in the case of adsorption investigations by the large background absorption and the scattering of infra-red radiation by adsorbents. These factors also lower the accuracy with which the concentration of adsorbed substances can be determined.

However, the employment of adsorbents of low scattering power, such as porous glasses and aerogels, and the pressing of powders into transparent disks, now enable measurements of the intensity of absorption bands due to adsorbed molecules to be made at comparatively low degrees of surface saturation. Absorption bands of CH groups in methane molecules adsorbed on porous glass, for example, can be observed at surface coverages below 0.004,[61] and below 0.1 with ethylene,[61,140] 0.01 with CO_2,[41] and 0.001 with butene[141]. At the same time, real values have been obtained for the extinction coefficients of physically adsorbed molecules per unit effective thickness of the layer and per unit volume of adsorbed substance[61] or per unit weight or volume of the adsorbent[46,47,141]. With the aim of employing infra-red spectroscopy to determine numbers of molecules adsorbed, Hoffman and Brindley[142] have investigated the dependence of the extinction coefficient of adsorbed molecules on the surface coverage of the adsorbate. In determining the intensity of absorption bands of adsorbed molecules and surface groups on the adsorbent, the possibility must be borne in mind of anomalous broadening of

the absorption bands[143], as well as the possibility of a change in intensity both as a result of perturbation of chemical bonds by adsorption forces and, perhaps, owing to the simultaneous occurrence of chemical reactions[144].

All these facts confirm that it is now already possible to utilise infra-red spectroscopy, within certain limits, for the quantitative analysis of physically adsorbed molecules at different surface saturations, with the aim of obtaining spectroscopic adsorption and desorption isotherms and comparing them with isotherms both of adsorption itself and of differential heats of adsorption and heat capacities of adsorption systems.

With physical adsorption due to stronger interactions, such as a hydrogen bond, and chemisorption, the task is considerably complicated. In this case the field of the adsorbent changes the bond polarity of the molecules, leading to a change in their absorption coefficient, which depends also on the surface saturation[98]. However, this fact can in turn be utilised to determine the redistribution of charge in the molecule[145,146] and to estimate the field over the adsorbent[61,140]. Investigation of the changes occurring during adsorption and desorption, in the absorption coefficient of the perturbed surface hydroxyl groups and of the groups in adsorbed molecules which interact with them at different degrees of surface coverage can give additional information on the mechanism of adsorption. Investigations of this type have been carried out only by Folman and Yates[98], who obtained curves for the variation of the optical density coefficient of surface OH groups perturbed by adsorbed molecules and for CH and NH groups during adsorption and desorption of CH_3Cl and NH_3 molecules on porous glass.

The combination of research on adsorption equilibria by ordinary adsorption methods with the utilisation of the spectroscopic possibilities noted here for determining adsorption equilibria and characterising the individual bonds in adsorbed molecules during adsorption and desorption will undoubtedly be further developed in the near future.

2. Energy of Adsorption

The most important characteristic of the energy of adsorption interactions is the heat of adsorption. No direct link has yet been found between the heat of adsorption and the spectroscopic observations on adsorption. However, the shifts in the absorption bands of the surface hydroxyl groups and the bonds of adsorbed molecules observed during adsorption are a consequence of the perturbation of surface groups by adsorbed molecules, and are governed by the energy of adsorption interaction.

A definite parallelism is evident between the displacements of the absorption band due to the surface hydroxyl groups of silica (Fig. 24) and the heats of adsorption of water vapour, benzene, and n-hexane[7,147]. These quantities are collated in the Table, the differential heat of adsorption at a moderate surface coverage being calculated both per mole of adsorbate (Q_a) and for the coverage of unit surface (Q_s). The agreement in the sequence of shifts in the absorption band of surface OD and OH groups and of heats of adsorption is shown especially clearly if we compare the displacements $\Delta\nu$ with the differential heats of adsorption calculated not per mole (Q_a) but per unit surface occupied by these molecules (Q_s).

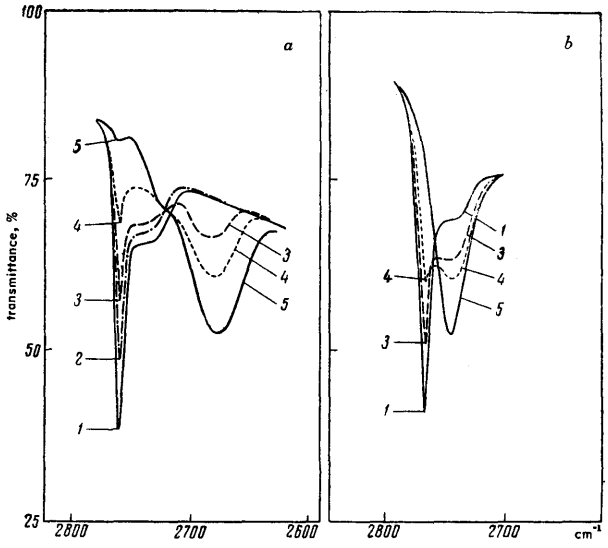


Fig. 24. Spectrum of Aerosil:
1) containing OD groups on the surface and vacuum treatment at 200° for 6 h; and also after adsorption of (*a*) benzene and (*b*) hexane to the extent of: 2) 0.1 monolayer; 3) 0.5 monolayer; 4) 1 monolayer; 5) with capillary condensation[147].

TABLE. Comparison of shifts in absorption band of surface OD and OH groups on silica with differential heats of adsorption per mole Q_a and per unit surface occupied by an adsorbate molecule Q_s with a coverage of half a monolayer.

Adsorbate	Differential heat of adsorption on hydrated silica surface[7,98]		Shift in absorption band of surface groups on adsorption $\Delta\nu$, cm^{-1}	
	Q_a, kcal mole^{-1}	Q_s, erg cm^{-2}	OD	OH
Water	12.5	800	260[112]	330[94]
Benzene	10.2	150	90[147]	110[94]
n-Hexane	8.5	100	26[147]	34[94]*

* Also on adsorption of cyclohexane.

The parallelism noted in the variation of heats of adsorption (which are a measure of the interaction of molecules with all force centres on the surface and in the bulk of the adsorbent) and of the shifts in the hydroxyl absorption bands (which measure the interaction of molecules with the hydroxyl groups alone) confirms that the energy of interaction with these groups makes a large contribution to that of adsorbed benzene and water molecules.

In the formation of relatively stable adsorption complexes (water, methanol, ether, and benzene on hydrated silica) direct spectroscopic determination of the energy of interaction is evidently possible by finding the equilibrium constants of these complexes at different temperatures, as is usually done in determining the bonding energy of complexes in solution[148]. In this connection it is necessary to

investigate both theoretically and experimentally (spectroscopically and calorimetrically) the energy of adsorption of complex molecules on surfaces bearing electric charges or dipoles, allowing for the distribution of electron density in the adsorbate molecules. Such a calculation has been made for the π bonds in the benzene molecule[26], and for the π and σ bonds by the molecular orbital method[28,29].

3. Thermodynamics of Adsorption

In connection with the general problem of the theoretical calculation of heats of adsorption and adsorption equilibria from the properties of the adsorbent and adsorbate alone[7,9-11,23], statistical methods for calculating total and free energy, the entropy of adsorption, and the heat capacity of the adsorbate are of great importance. Whereas with gaseous substances knowledge of the vibrational and rotational spectra of the molecules is sufficient for calculations of thermodynamic functions with an accuracy exceeding that of their direct measurement, the problem is considerably more complicated in the case of adsorbed substances. In the case of localised adsorption, we must have a model of the adsorption complex and know the vibrational and rotational frequencies of the molecule in the complex, as well as have information on the distribution of adsorbate molecules over the surface. In the case of non-localised adsorption, we must know the vibrational and rotational frequencies, and also have information on the migration of molecules along the surface. Up to the present time, entropy calculations (see review[149]) have been based merely on quite arbitrary assumptions as to the movement of molecules along the surface and the possible frequencies of vibration and rotation of an adsorbed molecule relative to the adsorbent surface. Only the first attempts have been made to estimate the frequencies of the vibrations[8-11] and restricted rotations[11] of adsorbed molecules from their theoretically calculated potential energy functions at the surface.

Apart from very rare exceptions, the problem of obtaining the data necessary for the calculation of the thermodynamic functions of adsorbed substances has not in general arisen in spectroscopic work on adsorbed molecules. Therefore only very incomplete data relating to an extremely restricted class of molecules and adsorbents can be obtained from these papers for a study of the thermodynamics of adsorption. Thus the previously considered spectroscopic criteria of the type and stability of the adsorption link can help to solve the question of the degree of localisation of adsorbed molecules. Slight perturbations of the surface hydroxyl groups correspond to weak physical and probably non-localised adsorption. Strong perturbations, corresponding to a stable hydrogen bond, or substitution of the surface hydroxyls by organic or organoelemental compounds indicate firm localisation of the molecules of these compounds on the adsorbent surface.

The slight change in the vibrational spectrum of adsorbate molecules in all cases of physical adsorption, noted earlier, allows us to neglect the change in thermodynamic quantities due to intramolecular motion[11]. In most cases, however, changes in the spectrum of the internal vibrations of adsorbed molecules yield valuable information on the structure of adsorption complexes. The most complete information on the structure of a complex can be obtained from a study of the full vibrational spectrum of molecules adsorbed on adsorbents having an ordered surface structure.

In this connection special interest attaches to the work of Karagounis and Peter on the vibrational spectra of aromatic compounds: 1,3,5-trichlorobenzene, biphenyl, naphthalene, etc., deposited on silver iodide and silica surfaces[145]; and aniline, phenol, *o*-, *m*-, and *p*-phenylenediamines, and *m*-xylene on KBr, AgI, NaCl, AgCl, and TlCl surfaces[146]. The decrease in intensity of the absorption bands due to vibrations perpendicular to the plane of the ring in a molecule having symmetrical substituents, for example, 1,3,5-trichlorobenzene, observed in these cases, indicates a planar arrangement of the molecule on the surface. Data on the intensification and the weakening of the bands due to vibrations in the plane of the ring, taking into account the structure of the molecule and the surface of the crystalline adsorbent, in turn allow us to orientate the adsorbed molecule relative to the force centres on the surface. Changes in intensity of the absorption bands in the vibrational spectra of adsorbed molecules also allow us to assess changes in orientation of the plane of the molecule relative to the force centres of the surface when unsymmetrical substituents are introduced into the benzene ring[146].

The alteration in the spectrum of acetylene and its derivatives on adsorption on aluminium oxide[101] suggests that the molecules of acetylene and methylacetylene are predominantly oriented towards the surface. Dimethylacetylene molecules are arranged parallel to the surface.

In setting up the partition functions, we must also take into account the change in the isomeric composition of adsorbed molecules. Thus Yoschino[150] showed from the intensities of the absorption bands that the relative proportions of the *cis* and *trans* forms of 1,2-dichloroethane and of the keto–enol isomers of acetylacetone are different in the adsorbed state from their proportions in the liquid state and in solution.

Spectroscopic data are of special importance in analysing the possible rotational motion of an adsorbed molecule relative to the adsorbent surface. Sheppard and Yates[61,140] studied the shapes of the absorption bands of methane and hydrogen adsorbed on porous glass with the aim of determining the rotational degrees of freedom of these molecules with respect to the surface. In the case of methane, the observed shape excludes the possibility of free rotation of the molecules about three mutually perpendicular axes. Whereas the shape of the ν_1 and ν_2 bands of adsorbed methane does not allow any conclusions to be reached concerning the restriction of the rotation of these molecules, the ν_3 band (triply degenerate asymmetric vibration of CH groups) is appreciably broader than the ν_1 band, and its shape is consistent with the hypothesis that methane molecules can rotate freely only about one axis. The shape of the ν_4 band (doubly degenerate CH stretching vibration) of CH_3Br molecules adsorbed on porous glass at room and low temperatures, and hence of the ν_3 band of the CH_4 molecule, has been shown[151] to be due solely to rotational motion of the molecules, and not to removal of degeneracy under the influence of the force field of the adsorbent. The change in the rotational structure of the absorption bands of CO_2 molecules on adsorption on Aerosil also provides evidence of the restriction of molecular rotation[41].

Considerably difficulties arise in the spectroscopic investigation of rotations of adsorbed molecules restricted by the existence on the adsorbent surface of potential barriers. Up to the present time it has proved possible to observe combined bands due to deformation vibrations and librations only in the case of water molecules adsorbed on a zeolite[117] and CsI[139] at high surface coverages. The

libration frequencies of the adsorbed water molecules in these cases are close to those of liquid water, and are evidently due to librations of water molecules associated together, not to their librations in the field of the absorbent.

Great uncertainty in calculations of the rotation component of the partition function arises also in determining the moments of inertia and the symmetry groups of adsorbed molecules. The appearance in the infra-red spectrum of absorption bands which are usually evident only in the Raman spectrum, observed in several cases [61,140,145,146], enables us to elucidate the change in symmetry resulting from the action of the force field of the adsorbent on the adsorbed molecule. Thus the appearance in the spectrum of methane adsorbed on porous glass of the 2899 cm^{-1} absorption band (Fig. 25), which is forbidden in the infra-red spectrum, indicates that the adsorbed molecule has symmetry C_{3v} or C_{2v} with respect to the surface, not T_d, which the methane molecule has in the gaseous state. The appearance in the spectrum of adsorbed ethylene of a band at 3010 cm^{-1}, which is absent from the infra-red spectrum, indicates a change in distribution of electron density in the molecule, as a result of which the symmetry of the molecule changes from V_h to C_{2v}, its principal plane being parallel to the surface of the adsorbent. Similarly, the appearance in the spectrum of hydrogen adsorbed on porous glass of the 4131 cm^{-1} band (Fig. 25), which does not occur in the infra-red spectrum, is evidence of a redistribution of charge in the molecule, resulting in a change in symmetry from $D_{\infty h}$ to C_{2v}.

A redistribution of electron density and a change in symmetry are indicated also by the appearance of the ν_5 band (3070 cm^{-1}) in the infra-red spectrum of ethylene adsorbed on porous glass [152], and of the ν_2 band (1950 cm^{-1}) in the spectrum of acetylene adsorbed on aluminium oxide [101]. These bands normally appear only in the Raman spectrum.

The vibration frequencies of adsorbed molecules relative to the surface lie in the inaccessible far infra-red region of the spectrum, and so far have not been investigated at all. Moreover, the vibrational bands of light molecules, linked to the surface by weak van der Waals forces, are evidently very diffuse, and can barely be observed. The vibrational and rotational bands of heavy molecules, or of molecules linked to the surface by stronger bonds, such as hydrogen bonds, however, should be more clearly developed. Investigation of such vibrations and rotations is of great interest for the solution of thermodynamic problems. At the present time only a few papers on the thermodynamics of adsorption can be cited in which spectroscopic data are utilised. Kington [117,118] studied the infra-red spectra of water adsorbed in the channels of crystals of Linde zeolite type A, and concluded that the water molecule is attached to the surface of the channels by the formation of hydrogen bonds between the hydrogen atoms of the water and the oxygen atoms of the zeolite framework. The molecules are not as strongly held as in liquid water. In Kington's opinion this explains the higher value which he obtained for the specific heat of adsorbed water compared with that of liquid water†.

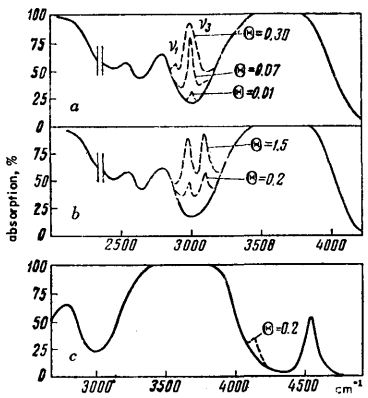


Fig. 25. Spectra of:
a) methane; *b*) ethylene; *c*) hydrogen, adsorbed on porous glass (broken curve: spectrum on adsorbed molecules; full curve: spectrum of porous glass; Θ: surface coverage) [61,140].

Kiselev and Lygin [155] attempted to use spectroscopic data to calculate the vibrational, rotational, and configurational entropies of water molecules adsorbed on hydrated silica surfaces. They considered two models, with a water molecule adsorbed on one and on two surface hydroxyl groups. Calculation of the vibrational entropy was based on the frequency of vibration along the hydrogen bond. The rotational entropy was calculated using models of a freely rotating molecule and a restricted rotor. The total calculated value was less than the experimental value, indicating the existence of other degrees of freedom of molecular motion which had not been taken into account, in particular, vibrations of the molecule parallel to the surface. The effect of non-uniformity of the surface on the configurational entropy must also be taken into account [156].

The change in spectrum of the surface hydroxyl groups of aerogel on adsorption of benzene and hexane [147] enabled a model of non-localised adsorption to be chosen for both cases. Calculated and experimental values of the decrease in entropy when half a monolayer is filled with benzene molecules are in satisfactory agreement if it is assumed that the adsorbed molecules possess mainly two-dimensional translational motion and free rotation in the plane of the ring. The entropy of adsorbed hexane considerably exceeds that of benzene, indicating the greater mobility of the adsorbed hexane molecules. This is consistent with spectroscopic and calorimetric data showing a stronger bond between benzene molecules and surface hydroxyls compared with hexane, and with theoretical estimates of the energy of this bond [26,28]. A complete analysis of the degrees of freedom of adsorbed hexane molecules cannot yet be carried out because of the absence of information on the restriction of internal rotations in the molecule on adsorption.

The examples which have been given provide evidence of the great possibilities of infra-red spectroscopy in the study of surface chemistry and molecular adsorption. However, these possibilities are often not fully utilised mainly owing to the absence of close links between spectroscopic and adsorption research. It is quite obvious that the problems which are now arising in the study of the properties of surface compounds and adsorption equilibria, as also the practical tasks of obtaining high-quality fillers or adsorbents

† High values for the specific heat of water, benzene, and hexane adsorbed on fine-pored silica gel having a hydrated surface have been obtained by Berezin *et al.* [153,154]

and supports for chromatography by the chemical synthesis of various compounds on their surface, can be solved only by combining spectroscopic and adsorption methods. It is also obvious that solution of these problems requires further improvement in the spectroscopic method, both by the development of new procedures for preparing specimens for investigation and by increasing the sensitivity and accuracy of determinations of the frequency, intensity, and shape of the absorption bands of adsorbate and adsorbent. It is also necessary to extend the investigations into the long-wavelength region of the spectrum, and to work systematically on the theoretical interpretation of the results of spectroscopic investigations of surface chemistry and adsorption. Combined use of the methods of infra-red spectroscopy and nuclear magnetic resonance will also provide great opportunities for studying the structure of surface chemical compounds and adsorption.

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