JOURNAL OF CATALYSIS 39, 173–180 (1975)

Infrared Spectra of Some Long-Chain Esters Adsorbed on Aerosil

J. ERKELENS AND TH. J. LIEFKENS

Unilever Research, Vlaardingen, The Netherlands

Received May 21, 1974; revised February 24, 1975

Infrared spectra of two long-chain esters, an aldehyde and two hydrocarbons adsorbed from a heptane solution on Aerosil were studied as a function of the surface concentration. Strong hydrogen bonding to surface hydroxyl groups was observed when methyl stearate was adsorbed on Aerosil dried at 120°C; in addition to this effect a weak interaction of the hydrocarbon chain could also be observed when the adsorption took place on Aerosil dried at 750°C. In the latter case a strong interaction between the double bond in adsorbed methyl oleate and the surface hydroxyl groups was also found to occur. The presence of two types of adsorption sites follows from a doubling of the carbonyl frequency. The bonding of tetradecanal was ascribed to an interaction of the carbonyl or the aldehydic-CH group.

INTRODUCTION

A number of publications have appeared which deal with infrared studies of the adsorption of molecules containing carbonyl groups on silica; especially acetone and acetaldehyde (*1–7*) have been studied. The spectra published show a strong band at about 3400 cm^{-1}, which is indicative of a hydrogen bonded interaction between the hydroxyl groups of the surface and the carbonyl oxygen atoms. Lorenzelli (*7*) reported a doubling in the carbonyl frequency of acetone adsorbed on Aerosil, which was attributed to a hydrogen bridge and a second unspecified type of interaction; this doubling was not observed by Young and Sheppard (*5*). Some studies were devoted to the role of hydroxyl groups as sites for the adsorbate molecules. Davydov *et al.* (*8*) concluded that the adsorption of trimethylmethanol on the silica surface occurs only by means of the surface hydroxyl groups.

However, the problem is more complicated if one believes with Peri and Hensley (*9*) that isolated geminal pairs as well as isolated single hydroxyl groups absorb at the same position in the infrared spectrum (freely vibrating hydroxyl groups). Hair and Hertl (*10*) studied silica surfaces, modified in different ways, which contained either freely vibrating hydroxyl groups or only hydrogen-bonded hydroxyl groups, or no hydroxyl groups at all. The authors observed that in the case of hexane each freely vibrating hydroxyl group acts as a specific adsorption site; with nonhydrocarbon compounds such as acetone, however, the geminal pairs act as single sites. Noller *et al.* (*11*) studied a series of electron pair donors with increasing pK_a values. In addition to the disappearance of the band of the freely vibrating surface hydroxyl groups at 3750 cm^{-1} (and the appearance of a broad band at lower wave numbers) a continuous absorption was observed with increasing pK_a values. This was explained by a detachment of the protons from the hydroxyl groups of the silica surface and formation of hydrogen bonds between adsorbed molecules.

The present paper describes an infrared

study of some long-chain esters, namely methyl stearate and oleate as well as an aldehyde (tetradecanal) and hydrocarbons (octadecane, 1-octadecene), adsorbed on pressed Aerosil disks from a heptane solution. This technique enabled us to obtain spectra as a function of the surface concentration by simply weighing the disk. Such a study has not been carried out previously, and only our preliminary results have been published (*12*).

METHODS

Aerosil (ex Degussa), a nonporous silica with a specific surface area of 170 m^2/g and a mean particle size of about 150 Å was used. The material can be pressed at 20 tons into thin disks (diameter 15 mm, weight about 25 mg), having a transmission of 20–40% at 1750 cm^{-1}. As a result of this compression the specific surface area decreased to 159 m^2/g; the pore volume was 0.386 ml/g; the mean pore radius, 49 Å; and the water content, 2.6% of the residue on ignition. The Aerosil disks were pretreated at 120°C for 5 hr and at 750°C for 22 hr in a dry stream of nitrogen (they will be called Aerosil 120 and Aerosil 750, respectively). The water content of an Aerosil 750 disk was 0.94% of the ignited residue and its BET surface area, 138 m^2/g.

Methyl oleate (purity 99.8%) was further purified by column chromatography over Al_2O_3 followed by vacuum distillation. Heptane (ex Hopkin and Williams) was treated with sulfur-free nickel catalyst, while passing through hydrogen. After settling of the catalyst the heptane was chromatographed over an Al_2O_3 column and subsequently distilled (boiling point 98.4°C). Other compounds were spectroscopically pure and used without further purification.

The spectra were recorded with a Grubb-Parsons GS 4 "double beam" spectrometer in the wavelength range 2.5–7.5 μm using an external recorder. A programmed slit was used. Above 7.5 μm the disk did not show any transmission. The scanning speed in the 2.5–3.5 μm range was 1 μm in 16 min and in the 5–7.5 μm range 1 μm in 4 min.

The experiments were carried out as follows. After the background spectrum of a disk had been recorded, the disk was transferred to a conical flask with ground stopper, containing a solution of the desired concentration of the adsorbate in 25 ml heptane. After shaking gently for 16 hr at room temperature, the disk was removed from the solution so that the heptane evaporated. Subsequently the disk was weighed and the spectrum was recorded again. Evaporation of the solution in the pores resulted in an excess adsorbed amount of roughly 0.1 mg, so that the resulting deviation from the equilibrium conditions may be neglected. After shaking a disk in pure heptane and subsequent evaporation to dryness, no weight increase of the disk was observed and neither was a change in the Aerosil spectrum established. It was checked from the spectrum and the weight of the disk after solvent extraction that no adsorbed material remained. Therefore, irreversible chemisorption of the various compounds with breaking of bonds may be excluded.

Thin layer chromatography was used to ascertain whether oleic acid, formed by hydrolysis of methyl oleate on silica, was present. To this end the methyl oleate was recovered from the disk by repeated extraction with optically pure light petroleum. The solution was carefully evaporated and about 150 μg of the residue was applied to a thin layer of silica gel (silica gel G, ex Merck). The eluent consisted of a mixture of 90% optically pure light petroleum, 10% diethyl ether and a few drops of acetic acid. After elution the plate was developed with a 10% solution of molybdophosphoric acid in absolute ethanol. No indication of free oleic acid was found. To investigate whether oxidation products

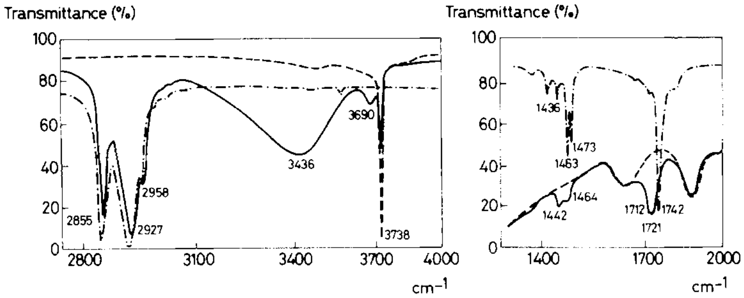

FIG. 1. Infrared spectrum of methyl stearate adsorbed on Aerosil 750: adsorbed ester (—), Aerosil disk (---) and solid film of ester (— ·).

were formed an eluent consisting of 50% optically pure light petroleum, 35% chloroform and 15% ethyl acetate was used. In this case the plate was developed with potassium iodide and starch. The absence of blue spots indicated that no oxidation products had been formed. The absence of oxidation was also confirmed by the fact that the spectrum of methyl oleate and methyl linoleate had not changed after the disks had been stored in air for 24 hr.

RESULTS

Figure 1 shows the decrease in intensity of the freely vibrating surface hydroxyl band at 3738 cm^{-1} and the formation of a broad intense band at about 3436 cm^{-1} for methyl stearate adsorbed on Aerosil 750. This indicates that these hydroxyl groups are involved in hydrogen bonding (*13–15*). A similar phenomenon was observed for other oxygen-containing molecules, e.g., methyl oleate, ethyl oleate and tetradecanal. Also in the case of the adsorption of methyl stearate on Aerosil 120 the 3738 cm^{-1} band disappeared; however, the formation of the broad 3436 cm^{-1} band could not be observed due to the presence of a broad band at the latter position, possibly due to water in the interior of the Aerosil (*16*) which was obviously not present with Aerosil 750. The ratio of the absorbances of the surface hydroxyl band at 3738 cm^{-1} measured before and after adsorption becomes zero near the end of the horizontal part of the isotherm (Fig. 2). This also indicates that in the concentration region studied the ester molecules are hydrogen bonded to freely vibrating hydroxyl groups. The same was observed for methyl oleate adsorbed on Aerosil 120 and 750 (Fig. 3). The three mentioned isotherms have a similar appearance; however, the one for methyl stearate adsorbed on Aerosil 750 differs strongly (Fig. 4).

For octadecane a band at 3690 cm^{-1} is

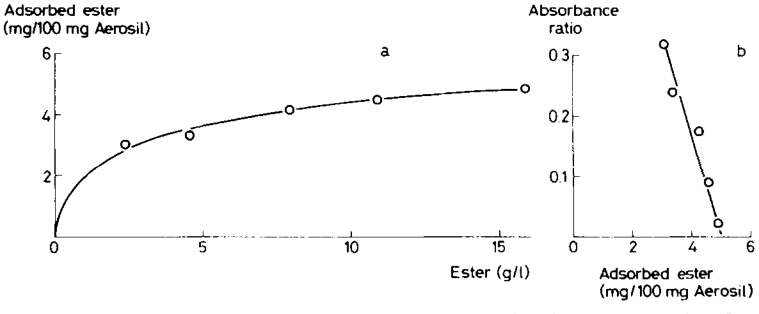

FIG. 2. Methyl stearate adsorbed on Aerosil 120; (a) isotherm, (b) absorbance ratio of surface hydroxyl band (3738 cm^{-1}).

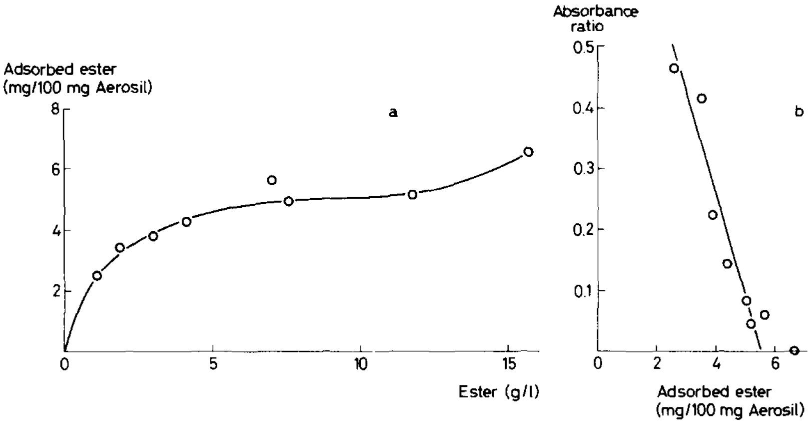

FIG. 3. Methyl oleate adsorbed on Aerosil 750; (a) isotherm, (b) absorbance ratio of surface hydroxyl band (3738 cm^{-1}).

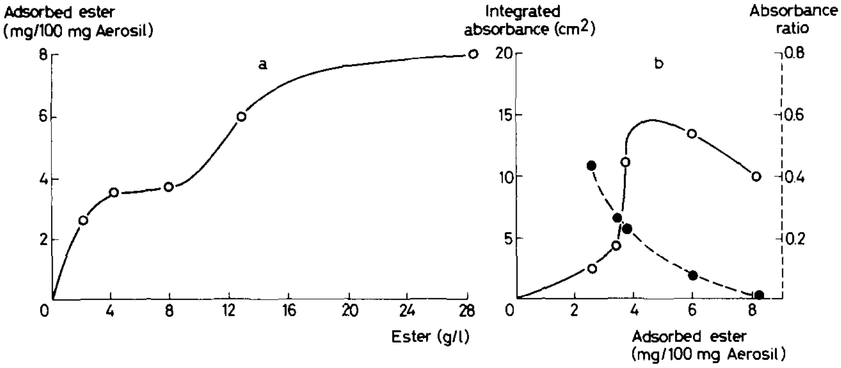

FIG. 4. Methyl stearate adsorbed on Aerosil 750; (a) isotherm, (b) absorbance ratio of surface hydroxyl band at 3738 cm^{-1} (●) and integrated absorbance of the band at 3690 cm^{-1} (○).

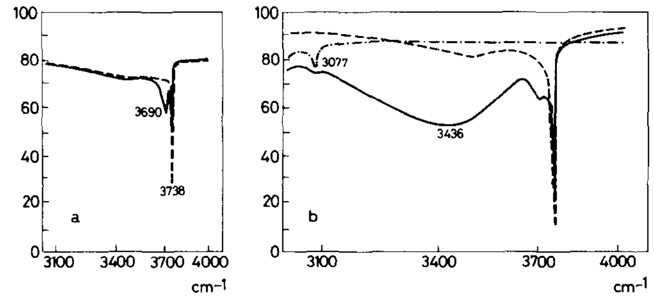

FIG. 5. Infrared spectrum of (a) octadecane and (b) 1-octadecene adsorbed on Aerosil 750; adsorbed hydrocarbon (—), Aerosil disk (---) and liquid film of alkene (—·).

TABLE I

Interpretation of Bands at 3436 and 3690 cm^{-1} in the Case of Adsorption on Aerosil 750[a]

Compound	3436		3690
	C=C	C=O	$-CH_2-$
Methyl oleate	+	+	±
Methyl stearate	−	+	+
Tetradecanal	−	+	+
Octadecane	−	−	+
1-Octadecene	+	−	+

[a] +, present; −, absent; ±, vague.

observed (Fig. 5a). With 1-octadecene in addition to the 3690 cm^{-1} band also a band at 3436 cm^{-1} is present (Fig. 5b), indicating a strong interaction of the double bond with the free surface hydroxyl groups in accordance with the decrease of the peak intensity of the $\nu{=}CH_2$ band at 3077 cm^{-1}. The band at 3436 cm^{-1} originates therefore from strong interactions of the surface hydroxyl groups with carbonyl groups as well as with double bonds (Table 1). This agrees with the fact that on adsorption of methyl oleate on Aerosil 750 the band at 3690 cm^{-1} is hardly observed, since the molecule can now be strongly bonded by means of the polar group as well as the double bond. In the latter case the weaker interaction of the surface hydroxyl groups with the saturated hydrocarbon chains of the adsorbed molecules plays a less important role.

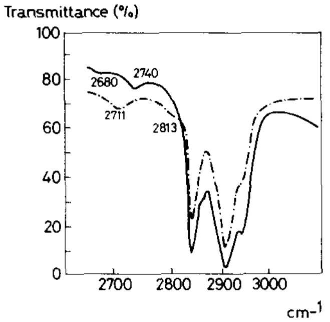

Fig. 6. Infrared spectrum of tetradecanal adsorbed on Aerosil 750; adsorbed aldehyde (—) and liquid film of aldehyde (—·).

In the spectrum of liquid tetradecanal a band occurs at about 2711 cm^{-1} and a somewhat weaker band at 2813 cm^{-1}, both due to the aldehydic-CH stretching frequency (*17*). When the compound is adsorbed on Aerosil 750, two bands appear at 2740 and 2680 cm^{-1}, the first one being the most intense (Fig. 6). The bands showed equal intensity when adsorbed on Aerosil 120.

DISCUSSION

In addition to the broad band at about 3436 cm^{-1} a very distinct band was observed at 3690 cm^{-1} in the spectrum of methyl stearate adsorbed on Aerosil 750 (Fig. 1). In Fig. 4b the integrated absorbance of the 3690 cm^{-1} band shows a maximum value at a surface concentration of about 4 mg/100 mg Aerosil, where the isotherm has a small but well-defined horizontal part. The band at 3738 cm^{-1} due to free surface hydroxyl groups was still present here. We suggest that the band at 3690 cm^{-1} can be assigned to a weak interaction of the saturated hydrocarbon chain with the freely vibrating surface hydroxyl groups. A similar band was also observed by Blomfield and Little (*18*), due to the interaction of adsorbed polymerized 1-butene with the surface hydroxyl groups of silica–alumina. The maximum mentioned above obviously appears because the surface hydroxyl groups originally engaged in the weak interaction with the hydrocarbon chain become hydrogen bonded to the carbonyl groups at higher surface concentration. Although one could argue that when Aerosil 120 was used, the 3690 cm^{-1} band would not be readily observable due to a possible overlap of the broad water band in the 3436 cm^{-1} region, it follows from the different character of the two isotherms (Figs. 2 and 4) that the weak interaction obviously does not take place when the surface is covered with water (Aerosil 120). The assignment of the 3690 cm^{-1} band is affirmed by the presence of this band in the case of adsorbed octadecane (Fig. 5), where obviously no other interaction can take place.

Geometric Considerations

The surface area per molecule of methyl oleate adsorbed on Aerosil 750 was roughly 120 Å^2, measured at the point where the band at 3738 cm^{-1} due to the free surface hydroxyl groups had disappeared. We assume that the entire silica surface area is accessible to methyl oleate molecules, since all surface hydroxyl groups become involved in the bonding. It can be expected that the space which an ester molecule occupies when it is adsorbed with the major axis perpendicular to the surface is about 25Å^2 (*19*). From this it would follow that in our case the molecule has a preferred orientation with the major axis parallel to the adsorbing surface. This, however, does not mean that the molecules necessarily are arranged along the surface when the solvent is present.

Unfortunately we do not know the number of freely vibrating hydroxyl groups present on our adsorbent. Hair and Hertl (*10*) who employed Cab-O-Sil with a surface area of 160 m^2/g which was heated at 800°C, i.e., conditions strongly resembling ours, quote a value of 1.70 hydroxyl groups/100 Å^2, which was composed of about 0.68 as single groups and 1.02 as geminal pairs. This would be in good agreement with the surface occupation of 0.8 methyl oleate molecules/100 Å^2 found by us, each methyl oleate molecule being bonded with the double bond and the carbonyl group to the surface hydroxyl groups. It may be expected that the amount of methyl stearate adsorbed on Aerosil 750 will exceed that of methyl oleate. This is due to the fact that in the former case only one freely vibrating surface hydroxyl group is engaged in the strong hydrogen bonding to the carbonyl group, while in the latter case the surface hydroxyl groups are bonded to the carbonyl group as well as to the double bond. This tendency is demonstrated by comparison of Figs. 3 and 4. It may be observed that at the point where, for methyl stearate, the freely vibrating surface hydroxyl groups have disappeared a number of hydroxyl groups engaged in a weak interaction would still be available to engage in strong hydrogen bonding (Fig. 4). Although the actual process of adsorption occurred at the solid–liquid interface, the results suggest that the adsorption of the esters is determined by the number of hydroxyl groups on the surface, rather than by competition between solvent and adsorbate.

Carbonyl Band

The spectra of methyl stearate and methyl oleate adsorbed on Aerosil 120 and 750 show a shift and doubling of the carbonyl band from 1742 to 1721 and 1712 cm^{-1} (Fig. 1). The position of the infrared absorption bands was independent of the amount adsorbed in the concentration range studied. It was, however, observed that with a high surface concentration of methyl oleate, exceeding 5 mg/100 mg Aerosil, an additional band appeared at 1742 cm^{-1}, which is almost at the same frequency as the carboxyl band in the pure compound. This indicates that a layer of nonhydrogen bonded adsorbed molecules was formed. In the relevant isotherm (Fig. 3a) a slight rise can indeed be observed. The doubling points to two types of hydrogen bonding of the carbonyl group of the ester molecule presumably involving single hydroxyl groups and geminal pairs (*9*). The doubling of the carbonyl frequency is obviously not due to the presence of the methoxy group. This follows from experiments with ethyl oleate and tetradecanal. Doubling was observed with both compounds when Aerosil 750 was used (although the effect was not very distinct with the former compound). It is feasible that removal of water creates the second type of adsorption site; in the case of ethyl oleate, however, also a steric hindrance due to the ethyl groups could prevent the interaction of the carbonyl group with one of the adsorption sites.

The question arises whether another explanation for the doubling would be possible, namely the formation of a Fermi doublet due to the shifted carbonyl vibration (due to adsorption) and the overtone of a deformation frequency. Such a doubling occurs in the spectrum of nonadsorbed propionaldehyde (*17*). It appears that methyl oleate, methyl stearate and ethyl oleate have only very weak bands near 870 cm^{-1}, which cannot be expected to participate in a Femi resonance. The observation that the doubling depends on the presence of water on the Aerosil surface suggests that this effect is preferentially explained by the presence of two types of sites on the surface.

CH_2- and CH_3-Band

The position of the bands due to the CH_2 and CH_3 stretching frequencies of the adsorbed molecules studied was on the average about 5 cm^{-1} higher than that of the liquid phase of the pure compound. The band at 2952 cm^{-1}, which occurs in the spectrum of the nonadsorbed methyl esters, will be assigned to the asymmetric stretching of the CH_3 group at the end of the chain as well as that in the methoxy group, since no distinction between the bands of these two groups was found in the spectrum of methyl butyrate used for calibration. The shift in the position of the CH_3-bands which occurs on adsorption obviously takes place for both types of CH_3 groups in the same way. The observed shift of the frequencies of the CH_2 and CH_3 vibrations indicates an interaction between the hydrocarbon chain of the adsorbed molecule and the Aerosil surface. The shift in the frequency of the methoxy group from 1437 (pure compound) to 1442 cm^{-1} on adsorption may be due to the effect caused by the binding of the carbonyl group, rather than by interaction of the methoxy group with the surface. The conclusions are in agreement with the well-known rule (*20*) that on condensation of a gaseous compound into its liquid, the stretching vibrations shift towards higher frequencies, whereas deformation frequencies show the opposite effect. Solid methyl stearate has two sharp infrared bands at 1463 and 1473 cm^{-1} due to CH_3 asymmetric bending and CH_2 scissoring vibrations, respectively, which are not present in the spectrum of the adsorbed molecules. This indicates that in the concentration region studied an ordering similar to that occurring in the solid phase does not take place in the adsorbed layer.

Aldehydic-CH Bands

Young and Sheppard (*6*) observed in their study of the adsorption of some small aldehydes that both components of the CH stretching doublet were equally shifted towards higher frequencies. This was explained by an interaction of the carbonyl group of the aldehyde with a surface hydroxyl group, causing a weakening of the CO double bond. An interaction of the aldehydic hydrogen atom with the surface oxygen atom on the other hand was expected to cause a lowering of the frequency of the CH-bands.

In our view, the bands observed by us for adsorbed tetradecanal (Fig. 6) near 2680 and 2740 cm^{-1} cannot be ascribed to a shift of the CH doublet, since the magnitude of the shift and the change in intensity would then be different for each of the components of the doublet. It is more probable that only shifts of the band at 2711 cm^{-1} (and not those of the weak 2813 cm^{-1} band) towards both directions were observed, indicating interaction of the carbonyl (2740 cm^{-1}) or the aldehydic-CH groups (2680 cm^{-1}) with the surface. In the case of adsorption on Aerosil 750 the fraction of the carbonyl group bonded to the surface must be greater than with Aerosil 120, which is in agreement with the appearance of the doubling of the carbonyl group in the former case. The observations can be explained by a change in the mode of bonding of the aldehyde molecule to the surface which occurs when water has been removed from the Aerosil surface.

CONCLUSIONS

The esters of long-chain fatty acids are adsorbed, after evaporation of heptane used as solvent, with the major axis parallel to the Aerosil surface, and hydrogen bonded by means of the carbonyl group to the surface hydroxyl groups. This follows from a comparison of the intensity data derived from the infrared spectrum with the adsorption isotherm.

Different types of adsorption isotherms for methyl stearate were found depending on the presence of water on the Aerosil surface.

A double bond in an unsaturated ester molecule is also bonded to surface hydroxyl groups. In the case of a saturated molecule a weak interaction of the hydrocarbon chain with the surface hydroxyl groups can be observed.

A doubling of the carbonyl band indicates two types of adsorption sites, presumably single surface hydroxyl groups and geminal pairs.

The adsorption of tetradecanal occurs by means of interactions of the carbonyl group or of the aldehydic-CH group with the Aerosil surface.

REFERENCES

1. Sidorov, A. N., *Dokl. Akad. Nauk SSSR* **95**, 1235 (1954).
2. Sidorov, A. N., *Zh. Fiz. Khim.* **30**, 995 (1956).
3. Folman, M., and Yates, D. J. C., *Proc. Roy. Soc., Ser. A* **246**, 32 (1958).
4. Folman, M., and Yates, D. J. C., *J. Phys. Chem.* **63**, 183 (1959).
5. Young, R. P., and Sheppard, N., *J. Catal.* **7**, 223 (1967).
6. Young, R. P., and Sheppard, N., *Trans. Faraday Soc.* **63**, 2291 (1967).
7. Lorenzelli, V., *Atti Accad. Naz. Lincei Cl. Sci. Fis., Mat. Natur. Rend.* **38**, 697 (1965).
8. Davydov, V. Y., Kiselev, A. V., and Lygin, V. I., *Russ. J. Phys. Chem.* **37**, 243 (1963).
9. Peri, J. B., and Hensley, A. L., *J. Phys. Chem.* **70**, 3168 (1966).
10. Hair, M. L., and Hertl, W., *J. Phys. Chem.* **73**, 4269 (1969).
11. Noller, H., Mayerböck, B., and Zundel, G., *Surface Sci.* **33**, 82 (1972).
12. Erkelens, J., and Liefkens, T. J., *J. Catal.* **5**, 542 (1966).
13. Coulson, C. A., *Research (London)* **10**, 149 (1957).
14. Cannon, C. G., *Spectrochim. Acta* **10**, 341 (1958).
15. Hadzi, D., "Hydrogen Bonding." Pergamon, London, 1959.
16. Erkelens, J., and Linsen, B. G., *J. Colloid Interface Sci.* **29**, 464 (1969).
17. Sbrana, G., and Schettino, V., *J. Mol. Spectrosc.* **33**, 100 (1970).
18. Blomfield, G. A., and Little, L. H., *J. Catal.* **14**, 213 (1969).
19. Wright, E. H. M., *J. Chem. Soc., London* 2267 (1964).
20. Mitra, S. S., *Solid State Phys.* **13**, 1 (1962).