

NEAR INFRARED CHARACTERIZATION OF WATER AND HYDROXYL GROUPS ON SILICA SURFACES

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Infrared absorption spectroscopy in the 1-3 micron region has been employed to investigate the behavior of surface hydroxyl groups and adsorbed water molecules during hydration and dehydration of silica gel. Interpretation of the infrared spectra has provided a general description of the adsorption process and a qualitative picture of the important hydrogen-containing species involved.

The presence of (1) non-hydrogen-bonded surface hydroxyl groups, (2) hydroxyl groups hydrogen-bonded to water molecules, (3) monomeric water hydrogen-bonded to surface hydroxyl groups, and (4) clusters of water molecules forming a hydrogen-bonded network has been inferred. The hydrogen bond between surface hydroxyls and water molecules is estimated to be of similar strength to hydrogen bonds in hydrargillite (γ Al(OH)₃). The bonding in the network water appears from the spectra to be similar to that in liquid water.

Use of infrared absorption spectroscopy to aid in the interpretation of data obtained by other experimental techniques is discussed.

1. Introduction

Contact electrification and surface electrical conductivity of silica are known to depend strongly on the detailed structure of the surface and on the presence of adsorbed water. As part of a broad investigation of electrical processes on oxide surfaces, absorption spectroscopy has been employed to monitor the behavior of surface structural OH groups and of adsorbed water molecules during hydration and dehydration of silica surfaces.

There is nothing novel about the use of infrared techniques for this purpose¹⁻⁶). However, in some studies of adsorption, detailed structural models of the surface have been employed to interpret the infrared spectra. It is our opinion that in certain instances this procedure has led to misinterpretation of the spectra. There has also been a tendency to utilize spectroscopic data to confirm conclusions based on highly detailed surface models. While the models and conclusions may be correct, it seems to us difficult to distinguish between certain of their details on the basis of infrared data alone. On the other hand, there appears to be unused information which can be derived from the spectra.

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Our approach has been to interpret the spectra as fully as possible and then to utilize the spectra to characterize the various hydrogen-containing species and their interactions with one another. The purpose of this paper is to describe the picture which emerges as a result of this approach.

2. Experimental

In this investigation grade 03 silica gel provided by the Davison Chemical Division of W. R. Grace and Company was used. Spectra were taken in the 1 to 3 micron range using a Cary Model 14RI spectrophotometer manufactured by Applied Physics Corporation⁷). The stretching fundamentals of OH and H₂O fall in the 2.5 to 3.0 micron range. Much of the previous work on silica and silica gel has emphasized this fundamental region. These absorptions are intense and their study requires the use of very thin samples or very dilute suspensions. Samples for spectra taken in this range were formed by pressing 270 mesh silica powder into discs with a density of about 15 mg/cm² as described by McDonald²).

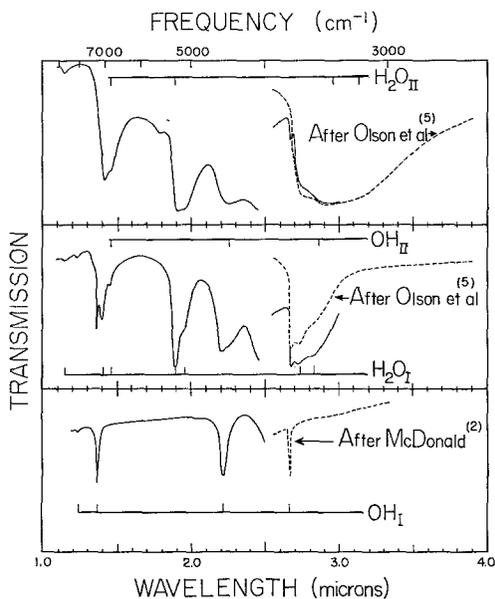


Fig. 1. The infrared spectrum of water and hydroxyl groups adsorbed on silica gel at various degrees of hydration. Spectra of other investigators in the 2.5 to 4 micron range are shown for comparison. Upper. In equilibrium with ambient air at room temperature (fully hydrated). Center. Spectra taken at 100° C in ambient air. Lower. Spectra taken in air at room temperature after dehydration at 750° C. (Spectrum after McDonald for a sample dehydrated at 940° C in vacuum.)

We have observed in addition the weaker absorptions corresponding to (1) the combined excitation of the OH stretching vibration and a bending mode associated with the Si-OH bond, (2) the combination of the bending and stretching frequencies of the water molecule, and (3) the first overtones of the OH and H₂O stretching vibrations. These combination and overtone bands fall near 2.3, 1.9, and 1.4 microns respectively (fig. 1). Samples for spectra taken between 1.0 and 2.5 microns were prepared by sanding large transparent silica gel particles into parallelepipeds roughly 1 × 3 × 10 mm. The surfaces were polished using either dry iron oxide or aluminum oxide powder.

The advantages of working in the combination and overtone range are several. It is possible, because of the weakness of the absorptions, to obtain

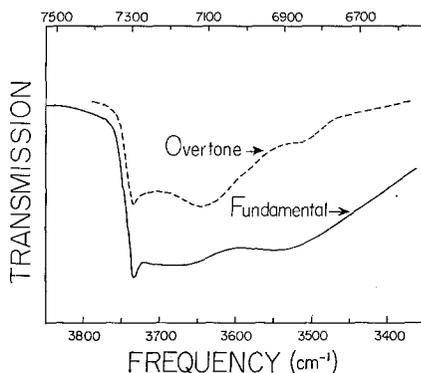


Fig. 2. Comparison of the overtone and fundamental spectra for samples at 100° C. The scales have been translated so that the OH_I peaks coincide.

spectra from samples on which correlated bulk measurements (e.g. surface conductivity and weight loss) can be made conveniently. The preparation and handling of optical samples are simplified as well. Furthermore, scattering by these samples is small compared to that of pressed disc samples used in the fundamental region. Most important, the absorptions of surface hydroxyl groups and adsorbed water molecules can be monitored separately in the combination regions whereas their fundamental and overtone spectra overlap badly. Simultaneous observation of combination and overtone absorptions during hydration and dehydration of thick samples assists in the interpretation of the overtone spectrum. Direct correlation (fig. 2) of overtone spectra obtained from thick samples and fundamental spectra obtained from pressed discs allows a more complete and positive interpretation of spectra in the 2.5 to 3.0 micron region.

3. Results and discussion

We have identified as spectroscopically distinct species at least two types of adsorbed water and two types of surface hydroxyl groups. The ab-

sorption bands corresponding to these species are indicated in fig. 1, and the "species" inferred from the infrared study are shown schematically in fig. 3.

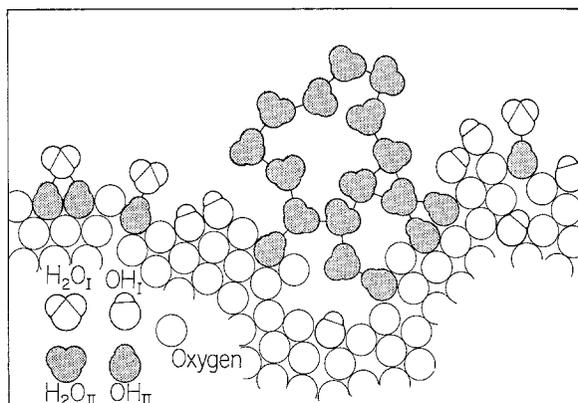


Fig. 3. Schematic picture of a partially hydrated silica surface.

The infrared observations which lead to this picture are as follows:

(1) Samples which have been fully dehydrated show only a sharp OH stretching fundamental at 2.67 microns (3740 cm^{-1}), the first overtone of this fundamental at 1.37 microns (7326 cm^{-1}) and a broader band at 2.20 microns (4550 cm^{-1}) which we assign as a combination of the OH stretching fundamental with an Si-OH bending mode having a frequency of about 800 cm^{-1} . (A similar combination is observed for OH in fused silica fig. 4.) The fundamental Si-OH bending mode has been observed directly in silica gel by Benesi and Jones ⁶) at 870 cm^{-1} . These bands are particularly sharp in samples which have been heated to temperatures above 500°C . The exceptionally high frequency of the stretching fundamental indicates that this OH group, which we label OH_I , does not participate in hydrogen bonding.

(2) In partially hydrated samples, the OH_I bands are less intense; in fully hydrated samples, they are missing altogether. The complete disappearance of this spectrum on hydration indicates that OH_I is a surface group which can interact with the adsorbing water molecules.

(3) On hydration, a second type of hydroxyl ion (OH_{II}) is observed. The presence of OH_{II} is most easily detected by the appearance of a new combination band at 2.26 microns (4420 cm^{-1}). Unfortunately, water absorptions obscure the OH_{II} stretching fundamental and overtone bands. However, we can infer the frequency of these bands from the observed shift in the combination band. This shift is composed of changes in each of the two combining frequencies. From the spectra of Benesi and Jones ⁶) we

conclude that the frequency of the Si-OH bending mode is about 70 cm^{-1} higher for OH_{II} than for OH_{I} . Our spectra show that the combination frequency of OH_{II} is about 130 cm^{-1} less than OH_{I} . Thus we infer that the fundamental stretching frequency of OH_{II} is roughly 200 cm^{-1} less than that of OH_{I} .

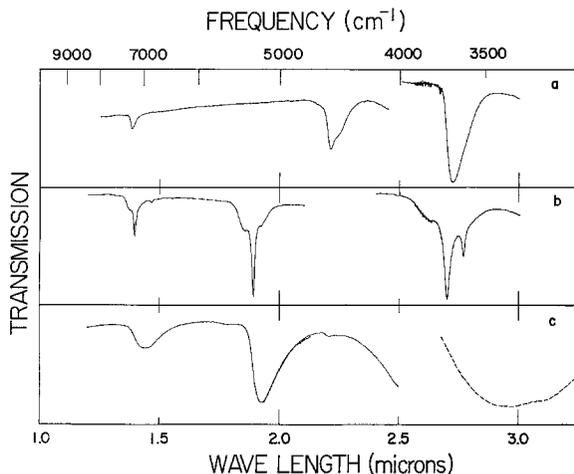


Fig. 4. a) The infrared spectra of OH in fused quartz (Optosil) (Sample thickness was $\frac{1}{16}$ inch for the 2.5–3 micron region and $\frac{11}{16}$ inch for the 1–2.5 micron region.) b) The infrared spectrum of CCl_4 saturated with water (Sample thickness was 1 cm for the 2.5–3 micron region and 10 cm for the 1–2.5 micron region.) c) The infrared spectrum of liquid water (Sample thickness was 10 microns in the 1–2.5 micron region. Spectra in the 2.5–4 micron region are after L. H. Jones, *J. Chem. Phys.* **22** (1954) 217.

(4) At low levels of hydration, two bands appear at 2.73 and 2.82 microns (3660 and 3540 cm^{-1}); two overtones of these bands appear at 1.41 and 1.46 microns (7090 and 6850 cm^{-1}), and an additional pair of bands appears near 1.9 microns (5290 and 5180 cm^{-1}). (fig. 1.) The parallel behavior of the intensities of these bands as the degree of hydration is varied and the similarity of relative intensities and splitting of each pair (fig. 2) argue that all these bands belong to the same molecular group. The occurrence of two OH stretching fundamentals split by roughly 100 cm^{-1} , the presence of a pair of weaker absorptions 1600 cm^{-1} higher in frequency than the fundamentals, the general profile of the absorption bands, and the growth of the bands with increasing water content (fig. 1) all argue that the molecular group is water. We label this type of water as H_2O_1 . The high frequency of the fundamentals and the overall sharpness of the spectrum indicate this is monomeric water i.e. individually adsorbed water molecules. (A similar spectrum is exhibited by trace amounts of water dissolved in CCl_4 , an inactive solvent (fig. 4).)

While we assign to $\text{H}_2\text{O}_\text{I}$ the bands at 2.82 and 1.46 microns, we recognize that OH_II may contribute in part to their intensity as implied by (3) above.

(5) The simultaneous appearance of the OH_II and the $\text{H}_2\text{O}_\text{I}$ spectra on hydration and the reciprocal relation of the OH_I and OH_II band intensities (see fig. 5) indicate that an OH_I group is converted into an OH_II group by interaction with an adsorbing water molecule. The 200 cm^{-1} shift of the OH_I fundamental on hydration suggests that this interaction is the formation of a hydrogen bond between the hydroxyl group and the oxygen of the water molecule. The formation of this bond is believed to be the primary adsorption mechanism.

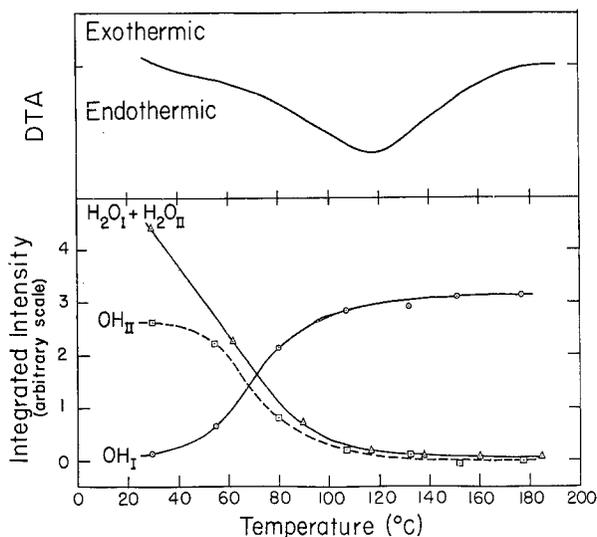


Fig. 5. Comparison of differential thermal analysis (DTA) of hydrated silica gel and the integrated intensity of the 1.9 ($\text{H}_2\text{O}_\text{I} + \text{H}_2\text{O}_\text{II}$), 2.20 (OH_I) and 2.26 (OH_II) micron bands. (Temperature was increased at about $4^\circ/\text{min}$.)

The strength of the hydrogen bond can be estimated from the OH stretching frequency by referring to empirical O-H length versus frequency curves⁸). Because these curves are based on the spectra of OH groups which are fully "immersed" in solid matrices, the frequencies of these groups are altered by solvent effects not fully experienced by surface hydroxyl groups. If we take the difference of 65 cm^{-1} between the OH_I frequency on the silica gel surface and internal OH in fused silica as an estimate of the necessary solvent effect correction, we conclude that the hydrogen bonds of which OH_II partakes are of about the same length (and strength) as those in hydrargillite ($\gamma\text{-Al}(\text{OH})_3$).

The energy of the bond between a surface hydroxyl group and a water

molecule can be estimated from the difference in the fundamental stretching frequencies between OH_I and OH_{II} using the relationship given by Lippincott and Schroeder⁸). The 200 cm^{-1} difference observed corresponds to an energy of roughly 2–3 kcal/mole. This is somewhat less than the bond energy of hydrogen bonds in liquid water or ice.

(6) On hydration, an additional broad, intense band with a minimum at 2.95 microns (3400 cm^{-1}) and a shoulder at 3.05 microns (3320 cm^{-1}) is observed. This band corresponds strongly in frequency and general appearance with the OH stretching bands of liquid water (fig. 4). We therefore assign this band to water molecules forming a hydrogen-bonded network on the surface. This network water we call H_2O_{II} . We do not observe the spectrum of H_2O_{II} explicitly in the combination and overtone region. By analogy with the spectrum of liquid water, we would expect these combination and overtone bands to fall on top of, and be masked by, the sharper bands of H_2O_I . Broadening of the 1.9 micron combination band during hydration is evidence for this.

(7) Appearance of the H_2O_{II} fundamental spectrum, and the broadening of the 1.9 micron combination band even at low water contents as well as the persistence of the H_2O_I spectrum to fairly high levels of hydration suggest a certain "patchiness" in the hydration process rather than the formation of complete molecular layers. Thus, even at low levels of hydration, further adsorption may take place on OH or H_2O groups with nearly equal probability.

We emphasize that the labeling scheme employed in the foregoing discussion is based on the infrared spectrum. We do not mean to imply that each spectroscopically distinguishable species corresponds to a unique surface configuration. Indeed, the asymmetric absorption on the long wave-length side of the OH_I bands, observed most clearly in the spectra of samples which have been dehydrated without being subjected to high temperatures, suggests that many local configurations are contained within what we classify broadly as OH_I . A more complete discussion of the shape of this band is given by Kiselev^{4b}). Several possible variations within species can be distinguished in fig. 3.

We now can use infrared spectroscopy in conjunction with other experiments to assist in their interpretation. An example of this approach is the combined differential thermal analysis-infrared study of hydrated silica gel. (fig. 5.) The differential thermal analysis curve exhibits a broad endothermic peak between room temperature and 180°C . Changes in the intensities of selected infrared absorption bands as the sample temperature is varied in the same way as during differential thermal analysis indicate that both H_2O_I and H_2O_{II} are driven off in this range.

Further infrared measurements are being made in conjunction with gravimetric experiments for determining the amounts of surface groups and adsorbed species present. When water is not present, the intensity of any of the hydroxyl absorption bands may be used to measure hydroxyl content. However, when adsorbed water is present, overlapping of the water and hydroxyl bands in the overtone and fundamental regions makes it necessary to use the combination bands. Similarly, the water combination is most convenient for monitoring adsorbed water. In both cases, however, the combinations are composed of more than one band. These must be separated graphically to obtain good intensity measurements. This is not straightforward for the H_2O combination because the shape of the overlapping bands is not known. For this reason it would be difficult to make measurements which could be used to decide, for example, whether water molecules adsorb on one or two OH groups.

In spite of difficulties encountered in the example discussed above, infrared measurements should be very useful in interpreting data from other experimental techniques. It is our hope that such methods will be useful not only in further studies of adsorption but also in studies of surface electrical conductivity and contact electrification as well.

Note added in proof. It has come to our attention that G. Wirzing (Naturwissenschaften **50** (1963) 466) has obtained spectra quite similar to ours and has recognized the significance of the 1.9 and 2.2 micron combination bands.

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References

- 1) R. P. Eischens and W. A. Pliskin, *Advances in Catalysis* **10** (Academic Press, New York and London, 1958) p. 1.
- 2) R. S. McDonald, *J. Phys. Chem.* **62** (1958) 1168.
- 3) G. J. Young, *J. Colloid Sci.* **13** (1958) 67.
- 4a) A. V. Kiselev, *10th Colston Symposium* (Butterworths, London, 1958) p. 210.
- 4b) A. V. Kiselev and V. I. Lygin, *Russian Chem. Rev.* **31** (1962) 175.

- 5) F. A. Olson, D. A. Reese and M. E. Wadsworth, Technical Report No. V. (Department of Metallurgy, University of Utah, July 1963).
- 6) H. A. Benesi and A. C. Jones, *J. Phys. Chem.* **63** (1959) 179.
- 7) Our instrument is the prototype for this series. The 14RI differs from the conventional Model 14 in several respects: Important for the present study is the use of Infrasil optics which permits continuous operation to 3 microns, and other changes which lead to increased energy and resolution (better than 1 cm^{-1}) throughout near infrared. Spectra can be taken while the sample is illuminated with dispersed or undispersed light.
- 8) E. Schwartzmann, *Z. Anorg. u. allgem. Chem.* **317** (1962) 176.