[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Study of the Interaction between Hydroxyl Groups of Aerosil Silica and Adsorbed Non-polar Molecules by Infrared Spectrometry[1]

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The sharp 3749 cm.$^{-1}$ absorption of a thoroughly degassed aerosil silica is the 0–1 transition of the stretching frequency of surface hydroxyl groups. "Bound" water is present mainly in the form of isolated surface hydroxyl groups. Adsorption on such a surface is dominated by hydrogen bonding. When molecules are adsorbed adjacent to hydroxyl groups, the intensity of the 3749 cm.$^{-1}$ band decreases and a new band appears at lower frequency. The residual intensity of the 3749 cm.$^{-1}$ band is a measure of the amount of free, surface hydroxyl groups remaining. The magnitude of the band shift is a measure of the strength of interaction between surface hydroxyl groups and adsorbed molecules. Very small shifts caused by adsorbed non-polar molecules such as nitrogen, oxygen, perfluoromethane, methane, cyclohexane and benzene, and rare gas atoms have been measured. Displacement of the hydroxyl frequency occurs in two distinct steps when argon, nitrogen and oxygen are adsorbed.

The functionality of surfaces and of adsorbed molecules is important in many surface phenomena such as nucleation, adhesion, lubrication and surface catalysis. In favorable cases, specific information concerning such functional groups can be obtained by infrared spectrometry to clarify thermodynamic information obtained by the usual techniques of surface chemistry. This application of infrared spectrometry has been delayed by the obstacle that present techniques require the equivalent of several thousand interfaces for infrared bands of surface groups, or of adsorbed molecules, to be measured. The loss of light at each interface must be less than one per cent. This is a difficult requirement to fulfill.

The first investigators in this field[2,3] minimized scattering losses by studying adsorption on a porous, glass-like silica similar to leached, but unfired, Vicor. More recently, spectroscopic studies of chemisorbed molecules have been carried out on silica–alumina cracking catalyst[4] and on particles of copper, nickel, palladium and platinum supported on silica.[5–7] Scattering was reduced by use of small particle-size adsorbents. Light losses were large, but significant details of the spectra were measured for samples transmitting 2 to 6% of the incident radiation. Attempts have been made to reduce scattering by supporting adsorbents in supposedly inert diluents such as alkali halide discs[8] and paraffin.[9] Scattering is intimately connected with surface properties. Whenever extraneous material is added to reduce scattering, it is questionable whether observed effects can be assigned with any degree of certainty to the interaction of adsorbent and adsorbate. It has been demonstrated that the alkali halides have a profound effect on the spectrum of chemisorbed ammonia.[10] Paraffin probably affects the spectra, also.

Russian workers[2,3,11–13] have demonstrated that the overtone and fundamental hydroxyl stretching bands of degassed porous glass are very sharp and that in the presence of polar and non-polar adsorbates, the band is broadened and shifted to lower frequency. The sharp 7326 cm.$^{-1}$ band of degassed porous glass has been assigned to the 0–2 transition of isolated surface hydroxyl groups.[3] The displacement of hydroxyl bands by adsorbed molecules is caused by hydrogen bonding. Non-polar molecules cause smaller displacements than polar molecules. Displacement of the 7326 cm.$^{-1}$ band by adsorbed nitrogen and oxygen has been reported.[12]

This paper describes measurements on the fundamental hydroxyl stretching band near three microns of a finely divided pure silica. Displacement of the band by interaction of surface hydroxyl groups with physically adsorbed non-polar molecules and rare gas atoms has been measured. The implications of the results in surface chemistry and in the study of hydrogen bonding are discussed.

Experimental

Materials.—The silica was Aerosil 2491, also known as Cabosil. It was used as received from the distributor.[14] It is a fluffy dry powder produced by burning silicon tetrachloride in an oxyhydrogen flame. The surface area was approximately 200 sq. meters per gram. BET isotherm measurements indicate a nitrogen monolayer at a relative pressure of about 0.1 at 77°K.

Argon, krypton and xenon were obtained from the General Electric Lamp Department in sealed bulbs equipped with breakoffs. Oxygen was prepared by heating C.P. reagent grade potassium permanganate. Matheson C.P. grade methane, Linde prepurified nitrogen and General Chemical Corp. perfluoromethane were used without further purification except that high boiling impurities were removed by condensation in a liquid nitrogen trap. C.P. reagent grade benzene and Eastman Kodak Co. ultraviolet solvent grade cyclohexane and methanol were used. These liquids were degassed by repeated cycles of freezing, evacuation and melting

Sample Preparation.—The silica powder was packed lightly into a 0.5 mm. thick, vacuum tight, silver chloride

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[1] Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 2, 1956.

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[14] Godfrey L. Cabot, Inc., Boston, Mass.

cell. The amount of silica in the beam was about 10 mg. per sq. cm. The cell was mounted in a conventional infrared cold cell similar to that described by Lord, *et al.*[15] The sample cell was connected to a gas handling system by a separate vacuum line. The silica was degassed, and gases were adsorbed and desorbed without removing the cell from the light path. The silver chloride cell was fused to the solid silver cell support for good heat transfer. Temperatures were measured with a thermocouple spot-welded to a thin piece of platinum which was, in turn, fused to the silver chloride cell window opposite from the silver support. The cell was placed in the undispersed radiation beam.

The silica was degassed by heating under high vacuum for several days at 300–350°. The cell was heated in place with a heating element from a pencil soldering iron in the liquid nitrogen well. The pressure over degassed silica was barely detectable with a thermister vacuum gage after 60 hours with the cell cut off from the pumps.

Spectrometer.—Spectra were measured with a Perkin-Elmer, Model 13U infrared spectrometer using a lithium fluoride prism with double pass optics and a standard thermocouple detector. The entire optical path was enclosed. Atmospheric absorption bands were completely eliminated by flushing the housing with air from which carbon dioxide and water vapor had been removed by cooling with liquid nitrogen. Radiation was scattered strongly by the silica; 10 to 30% of the incident radiation at 2.7 μ was transmitted. The slits were opened to 0.080 mm. to compensate for the loss of energy. The effective resolution at 3749 cm.$^{-1}$ was about 10 cm.$^{-1}$. The spectrometer was calibrated by means of water vapor lines.[16] The absolute frequency of the 3749 cm.$^{-1}$ line is estimated to be accurate to ±4 cm.$^{-1}$. All frequency shifts were measured relative to this line. For sharp lines, the frequency shifts are estimated to be accurate to ±4 cm.$^{-1}$.

Results

Degassing of Aerosil 2491 Silica.—The spectrum of silica before degassing (Fig. 1a) shows both a sharp band at 3749 cm.$^{-1}$ and a broader band at 3400 cm.$^{-1}$. The former increased in intensity and the latter decreased in intensity as the silica was degassed. Evacuation at room temperature eliminated most of the 3400 cm.$^{-1}$ band. Only the 3749 cm.$^{-1}$ band remained after degassing at 300–350° for several days. There was a pronounced tail on the low frequency side. This may be caused by the Christiansen filter effect.[17] The spectrum was not affected by prolonged degassing at 350–400°. The half-width of the 3749 cm.$^{-1}$ band at room temperature is about 15 cm.$^{-1}$. At −190°, the band center is at the same frequency, but the band is narrower and the peak intensity is higher. The spectral slit width was too great to measure the true band width at −190°. The band showed no signs of structure from −190 to +350°.

Shift of Hydroxyl Frequency by Adsorbed Vapors.—Table I lists the hydroxyl frequency shifts which have been observed at low surface coverage. Water, methanol, benzene and cyclohexane were adsorbed at 30°. Argon, krypton, xenon, nitrogen, oxygen, methane and perfluoromethane were adsorbed at −170°. Subsequent measurements for argon, nitrogen and oxygen adsorbed at −190° gave frequency shifts identical to those at −170°. The 3749 cm.$^{-1}$ band decreased in intensity, but remained at the same frequency, as gases were adsorbed.

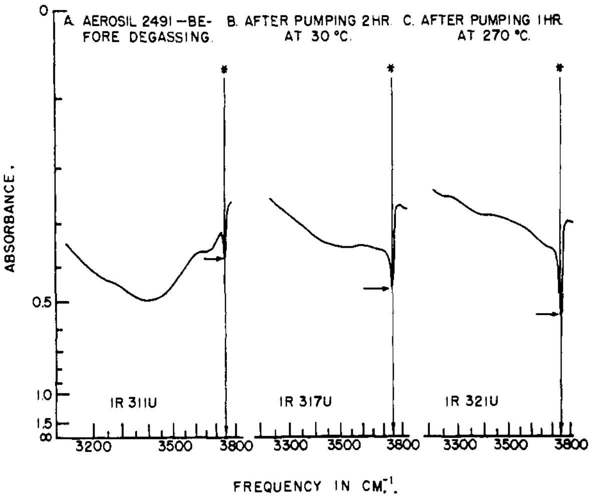

Fig. 1.—Spectra of Aerosil 2491 silica at various stages of degassing: A, before degassing; B, after degassing 2 hours at 30°; C, after degassing 1 hour at 270°. Horizontal arrows indicate peak intensity of 3749 cm.$^{-1}$ band.

A lowering of hydroxyl frequency has been observed for every gas which has been studied under conditions of temperature and pressure such that a reasonable fraction of the surface is known to have been covered with adsorbed molecules. No displacement of hydroxyl frequency has been observed for dry air at 30° and one atmosphere, or for helium at −190° and 200 mm. pressure, neither of which are adsorbed appreciably under these conditions. The peak intensity of the 3749 cm.$^{-1}$ band increased slightly when helium was introduced, probably because of a lowering of the temperature due to improved heat transfer between the silica and the cell walls.

TABLE I

PERTURBATION OF FREE HYDROXYL FREQUENCY OF AEROSIL SILICA BY VARIOUS ADSORBATES

Adsorbate	OH frequency (cm.$^{-1}$)	Frequency shift (cm.$^{-1}$)	Polarizability[18] (cm.^{3} × 10^{25})
None	3749	..	
Argon	3741	8	16.5
Krypton	3733	16	25.4
Xenon	3730	19	41.3
Nitrogen	3725	24	17.6
Oxygen	3737	12	16.0
Methane	3717	32	26.0
Perfluoromethane	3734	15	
Water	3690 (weak)	60	
	3415	330	
Methanol	3620 (weak)	130	
	3400	350	
Benzene	3640	110	
Cyclohexane	3715	34	

Adsorption and desorption equilibria were attained in a few minutes, as observed from the spectra. For each vapor, including water, the spectrum was identical with that of the degassed silica after evacuation for a few minutes at room temperature. Several spectra were obtained for each

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vapor under conditions such that part but not all of the hydroxyl groups were interacting with adsorbed molecules. This was judged by the intensity of the 3749 cm.$^{-1}$ band.

For xenon, nitrogen, methane, benzene, water and methanol, the displaced hydroxyl band was resolved from the 3749 cm.$^{-1}$ band. For adsorbed water and methanol, the spectrum was similar to Fig. 1a. For xenon, benzene and methane, the spectrum was similar to that for nitrogen, Fig. 2c. For cyclohexane, the displaced band was a distinct shoulder on the side of the 3749 cm.$^{-1}$ band. For argon, krypton, oxygen and perfluoromethane, the initial and displaced bands were not resolved from each other. The values for these gases are from spectra for which most of the intensity was considered to belong to the displaced band.

Measurements at High Relative Pressure.—Nitrogen, argon and oxygen have been studied over a larger range of pressures than other gases. Typical spectra are shown in Figs. 2 and 3. In each case, the band shifted in two distinct steps; first, by the amount given in Table I, and later, after vapor had been liquefied in the cell, by an additional amount which again depended on the adsorbate. There is no obvious relationship between the sizes of the two shifts for nitrogen, argon and oxygen. The integrated intensities of the displaced bands were greater than that of the initial 3749 cm.$^{-1}$ band. Relative integrated intensities and frequency shifts are given in Table II.

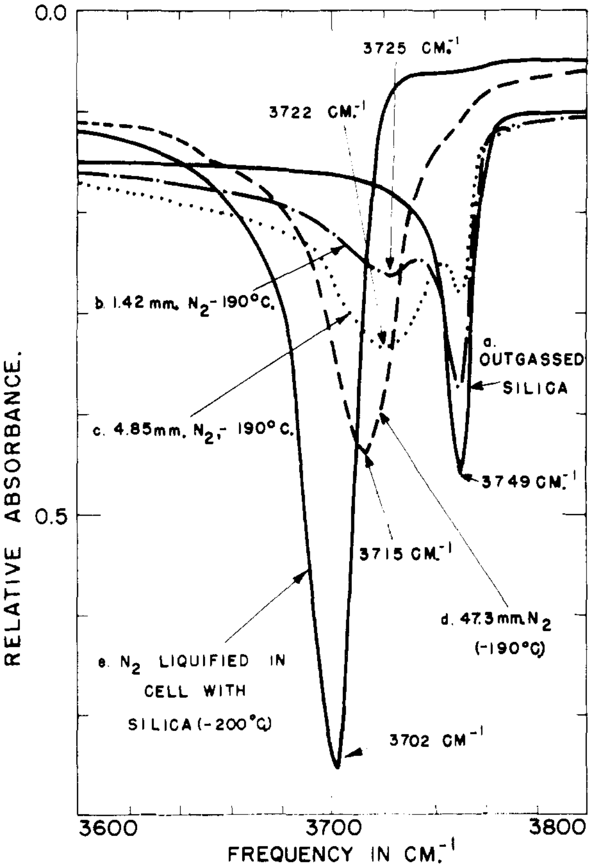

Fig. 2.—Spectrum of Aerosil 2491 silica in equilibrium with various pressures of nitrogen: a, degassed silica; b, 1.42 mm. at −190°; c, 4.85 mm. at −190°; d, 47.3 mm. at −190°; e, nitrogen condensed in cell with silica at −200°.

Table II

Frequency Shifts and Integrated Intensities of Hydroxyl Bands of Aerosil 2491 with Adsorbed Argon, Nitrogen and Oxygen

Adsorbate	Frequency shift (cm.$^{-1}$)	Half width (cm.$^{-1}$)	Integrated intensity
None	0	12	1.0 (arbitrary)
Argon (low relative pressure)	8	24	1.5
(vapor condensed in cell)	40	30	2.5
Oxygen (low relative pressure)	12	26	1.5
(vapor condensed in cell)	23	16	3.0
Nitrogen (low relative pressure)	24	34	2.0
(vapor condensed in cell)	43	23	3.5

For nitrogen, the intensity of the 3725 cm.$^{-1}$ band increased rapidly and the position of the peak remained nearly constant up to a pressure of about 5 mm. As the pressure was raised further, the peak shifted slowly to lower frequency. Between 5 and 50 mm. of nitrogen, the intensity of the displaced band increased slower than for pressures below 5 mm. For oxygen and argon, only one band appears up to relatively high pressure. At first, the peak intensity decreased as gas was adsorbed. The peak intensity passed through a minimum and began to increase as more gas was adsorbed. Meanwhile, the width of the band was increasing and the peak was shifting progressively to lower frequency. Eventually, the band became less sensitive to further increase in pressure. The spectra of Figs. 3b and 3e were measured at this point.

The temperature was lowered to condense the gases on the silica by pumping on the liquid nitrogen refrigerant. As each gas was being condensed, the transmission over the whole region under study, 3500 to 3800 cm.$^{-1}$, decreased abruptly to zero due to a large increase in scattering. As the cell filled with condensed gas, the transmission increased to a final value slightly higher than that of degassed silica.

Discussion

Assignment of Bands.—The sharp, 3749 cm.$^{-1}$ band is the 0–1 stretching frequency of hydroxyl groups oriented in such a way that they cannot interact with the surroundings, *i.e.*, projecting from the surface. This is consistent with the suggestion of Kurbatov and Newimin[3] that the sharp 7326 cm.$^{-1}$ band is the first overtone of isolated external hydroxyl groups. The assignment is supported by the following observations: (1) the frequency is higher than most vapor hydroxyl frequencies[19]; (2) the half width is less than 15 cm.$^{-1}$; (3) adsorbed molecules which have very weak external force fields cause the band to shift to lower frequency; and (4) the hydrogen exchanges very rapidly with D_2O vapor to form OD groups.

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(19) The hydroxyl stretching frequency for trimethylsilanol vapor is 3736 cm.$^{-1}$.

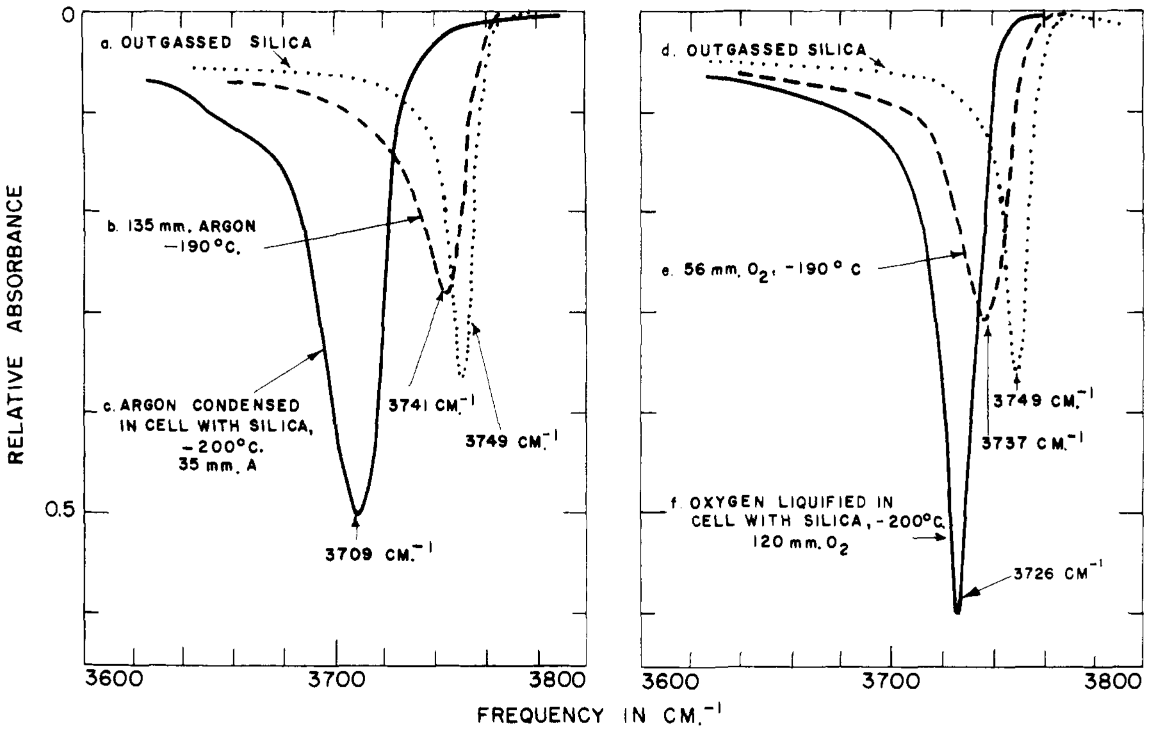

Fig. 3.—Spectrum of Aerosil 2491 in equilibrium with various partial pressures of argon and oxygen: a, degassed silica; b, 135 mm. argon at −190°; c, argon condensed in cell with silica, 35 mm. at −200°; d, degassed silica; e, 56 mm. oxygen at −190°; f, oxygen condensed in cell with silica at −200°.

The displaced band is the fundamental hydroxyl stretching frequency of hydroxyl groups which are interacting with nearby adsorbed molecules. For hydroxylic adsorbates, there is an additional contribution to the intensity of this band due to the hydrogen-bonded hydroxyl groups of the adsorbed molecules themselves.

Application to Surface Chemistry of Silica.—Frequency shifts, changes of intensity and appearance of forbidden bands indicate that the structure of adsorbed molecules and of functional groups of the surface have been altered by the forces of adsorption. When frequencies of adsorbed molecules are displaced from those of the stable condensed phase, the molecules must be on or very close to the solid surface. Similarly, when changes in infrared absorption frequencies of solid adsorbents are caused by adsorbed molecules, the functional groups of the solid must be in exposed positions.

As molecules are adsorbed adjacent to surface hydroxyl groups, the hydroxyl stretching frequency is lowered by hydrogen bonding. Hydroxyl groups which do not have molecules adsorbed adjacent to them retain the original frequency, 3749 cm.$^{-1}$. The intensity of this band is a measure of the number of hydroxyl groups which have not interacted with adsorbed gas molecules. The disappearance of this band indicates that all of the hydroxyl groups are interacting with at least one adsorbed molecule. If hydroxyl groups are uniformly distributed over the surface of the silica, disappearance of the 3749 cm.$^{-1}$ band is a possible criterion for completion of a monolayer. For nitrogen, the relative pressure is 0.1 for a BET monolayer at 77°K. This is several times higher pressure than that at which the 3749 cm.$^{-1}$ band disappears, indicating that nitrogen molecules are attracted preferentially to OH sites on the surface. Clearly, the surface is non-uniform. However, it is uncertain whether hydroxyl groups are spread uniformly over the surface with spaces between groups, or whether they are bunched together in patches. When argon and oxygen are adsorbed, the free hydroxyl band disappears at much higher relative pressures than for nitrogen. This indicates that the interaction of oxygen and argon with hydroxyl groups is much weaker than that of nitrogen, which is consistent with the smaller frequency shifts for oxygen and argon.

The intensity of the displaced band is an indication of the number of hydroxyl groups which are interacting with adsorbed molecules. However, the gradual shift of peak frequency and the continued increase in intensity after disappearance of the 3749 cm.$^{-1}$ band indicates that the displaced band cannot be used directly as a quantitative measure of the number of bonded hydroxyl groups.

The results for nitrogen indicate clearly that adsorption takes place in at least two stages. At first, molecules are adsorbed independently of each other. The fact that the bonded hydroxyl band remains at the same frequency up to a pressure of 5 mm. indicates that all bonded hydroxyl groups have the same surroundings. At this stage, each nitrogen molecule probably interacts with just one hydroxyl group. The fact that the peak shifts to lower frequency as more gas is adsorbed indicates that more nitrogen molecules are interacting with each hydroxyl group, or that the original adsorbed nitrogen molecules are being forced into more intimate contact with hydroxyl groups.

At this time, little reliance has been placed on small variations in intensity and no isotherms are included because of uncertainties in the temperature of the silica and because of the large loss of light by scattering. Silica is an excellent insulator; the amount of radiation falling on the sample from the source is sufficient to raise its temperature appreciably. There are small changes in background as vapor is liquefied in the cell. These changes may be indicative of variation in the number of absorbing hydroxyl groups. Further work is now underway to improve the temperature control and to increase the resolving power of the spectrometer. The sample will be placed in the monochromatic beam between the exit slit and the detector. Isotherms will be measured as the spectra are being determined. This seems preferable to relying on isotherm measurements on the same material obtained with other apparatus.

Application to Hydrogen Bonding.—The hydroxyl bands observed for silica are analogous to the free and bonded hydroxyl bands of solutions of alcohols and other hydroxylic materials in nonpolar solvents.[20] As for solutions, frequency shifts are probably a function of the energy of the bond between the hydroxyl group and the adsorbate.[21] The hydroxyl groups of silica offer advantages for the study of hydrogen bonding by infrared spectrometry. Because the hydroxyl groups are attached to a rigid network, their concentration and surroundings remain the same as the temperature is raised and lowered and as vapors are adsorbed. The sharpness of the 3749 cm.$^{-1}$ band indicates that initially the surface hydroxyl groups are relatively homogeneous. Very small shifts can be measured. Association of hydroxyl groups with each other can be neglected. There is no ambiguity about the position of the free hydroxyl band since it usually can be measured from the same spectrum as the displaced band. Interaction of hydroxyl groups with rare gas atoms and diatomic molecules can be studied. By controlling surface coverage, the system can be limited to single molecules or atoms interacting with single hydroxyl groups.

Shifts observed for oxygen, argon, nitrogen and other simple gases are of the size attributed to dielectric properties of solvents in the usual hydrogen bonding systems.[22] The polarizabilities of oxygen, argon and nitrogen are 16.0, 16.5 and 17.6 × 10^{-25} cm.^{3}, respectively. The corresponding frequency shifts are 12, 8 and 24 cm.$^{-1}$. It is apparent that the frequency shifts depend on an additional factor related to the chemical nature of the adsorbed molecules. The data for argon, krypton and xenon also seem to be dependent on a factor other than polarizability.

These results lead to the conclusion that frequency shifts in weak hydrogen bonds cannot be explained adequately in terms of macroscopic dielectric properties. The Kirkwood–Bauer–Magat theory[23] cited by Josien and Fuson[22] neglects important interactions on a molecular scale. For the usual hydrogen bonding systems in solution, complications due to varying orientations of interacting molecules are so great that detailed treatment is very difficult. The complexity is greatly reduced by symmetry in the system: surface group-adsorbed rare gas atom (or diatomic molecule). These simple cases seem to be more amenable to detailed theoretical treatment than systems involving hydrogen bonds in solution.

The increase in intensity as argon, nitrogen and oxygen are adsorbed is larger than might have been expected on the basis of intensities for solutions of alcohols in polar solvents.[24] Such increases of intensity imply changes in $\partial\mu/\partial r$ for the hydroxyl bond. However, Tsubomura[25] has pointed out that in view of the low energy of hydrogen bonds, the large changes in $\partial\mu/\partial r$ for the hydroxyl stretching band of phenol in solution can hardly be attributed to a change of electronic distribution in the hydroxyl group. It is all the more difficult to attribute changes of intensity reported above to changes in electronic configuration of the hydroxyl group. In the case of argon in particular, it seems necessary to account for the intensification of hydroxyl absorption by some other mechanism.

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