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ADVANCES IN THE USE OF INFRARED SPECTROSCOPY FOR THE CHARACTERISATION OF OH BONDS

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I. INTRODUCTION

The study of the structure of molecules and ions by infrared spectroscopy is based on the observed characteristic frequencies of vibration of such functional groups as OH, CH, NH, C=O, N=O, and many others. The existence of an absorption band in the frequency region typical of a given group conclusively demonstrates its presence in the compound under investigation.

The position of an absorption band within the characteristic frequency region depends on the interaction with neighbouring groups within the molecule and on intermolecular interaction; the shift of an absorption band within the characteristic region can thus be used to establish the position of the studied group relative to others and its reaction with neighbouring molecules.

This review is concerned with the spectroscopic characteristics of groups consisting of oxygen and hydrogen atoms, and only single groups of those atoms bound by a substantially covalent bond will be considered; groups containing hydrogen and oxygen bonded by purely ionic or hydrogen bonds will not be considered.

All the ions and molecules which we shall discuss below have at least one O–H bond. The hydrogen atom of this bond may be free or may participate in hydrogen bonding, so that all the systems which we shall consider can be represented by the formula $R_1-O-H\cdots R_2$, where R_1 is any atom or radical and R_2 is any proton-accepting molecule.

Modern methods have shown that hydrogen and oxygen atoms produce only the groups OH^-, OOH^-, $H\overset{O}{\diagdown\diagup}H$, HOOH, and the pyramidal $\begin{matrix}H\\H\end{matrix}\!\!\diagdown\!\overset{+}{O}\!-H$. For convenience we shall call these all oxygen–hydrogen or O_mH_n groups. When investigating the structure of new types of compound or evaluating their ability to form a hydrogen bond (alcohols, acids, carbohydrates, proteins) the nature of the O_mH_n groups present has always to be investigated.

Despite its importance this matter has not been sufficiently broadly discussed in Soviet or other literature. This review is the first to do so, and some of the conclusions may be controversial; it therefore includes, without exception, all the Soviet and available foreign literature from 1953 to May 1962 inclusive. The object of the review is to find methods for determining the form of O_mH_n groups and certain of their parameters by infrared spectroscopy, and to this end it compares the spectroscopic characteristics of compounds differing either in the form of their O_mH_n groups, the nature of neighbouring groups in the same molecule, or in intermolecular interaction.

There is no doubt of the advantage of infrared spectroscopy, since all physicochemical methods used for the analysis of such groups involve decomposition of the sample, and any O_mH_n groups present in the compound are converted into H_2O molecules and are only then recorded by some means. For example, the ignition of an organic compound containing hydrogen, whatever its nature, produces water; in some cases inorganic substances also give water molecules on ignition. In such cases the true nature of the oxygen and hydrogen in the initial compounds remains unknown. The formula for inorganic compounds is normally written as the oxides of the individual elements, with hydrogen as so many water molecules (nH_2O).

Since the bonding and mutual disposition of the oxygen and hydrogen atoms were unknown and could not be established from the water given off on decomposition of the sample, it is more correct under these conditions to use the above concept of oxygen–hydrogen groups (O_mH_n groups).

In reviewing the nature of the bond between hydrogen and oxygen atoms we meet with a number of obsolete concepts and terms, and we must therefore consider briefly the ideas which have existed up to the present, together with their foundations. A very large number of minerals and inorganic compounds give off water when heated, most frequently with a concomitant change in various physicochemical properties of the material; these changes, recorded by various methods, have served as a basis for the development of the concept of different "waters". Clearly the word "water" as used here has nothing in common with the concept of a water molecule, and it does not clarify the nature, bonding, or mutual disposition of the hydrogen and oxygen atoms; hence no method used for the investigation of "water" in inorganic compounds and which is associated with the removal of water can determine any of these parameters. Thus the concepts of constitutional, plus, zeolitic, cationic, etc., water which have arisen by the use of such methods must be considered as characterising the method of study rather than the form of the O_mH_n groups. We shall illustrate this with some concrete examples.

Chemical analysis of O_mH_n groups in inorganic compounds consists in the determination of the loss of water by the substance on heating. The use of this method led to the concepts of *minus "water"* (O_mH_n groups removed at temperatures up to 100°–110°) and *plus "water"* (O_mH_n groups removed above 100°–110°). The use of X-ray structural analysis for studying crystal hydrates led to the introduction of the concept of *structural "water"*, *i.e.* O_mH_n groups, the oxygen atoms of which occupy a definite position in each elementary cell of the crystal. The removal of these groups produces a change in the structure of the crystal.

Mineralogy uses its own system of classification of water in crystals. Structural "water" is divided into *cationic* and *anionic*. Cationic "water" comprises water which increases the basic properties of the cation in a salt formed fron a strong acid and a weak base; the oxygen atoms of this water form regular polyhedra around the cations. Anionic "water" comprises water which increases the acidic properties of the anion in a salt formed from a weak acid and a strong base; this water is normally directly attached to several cations.

In addition mineralogy uses the concept of *zeolitic* "water", which is intermediate between structural and adsorbed water. Zeolitic water is given off without destruction of the crystal lattice and without change in the anisotropy or transparency of the crystal. Moreover, as distinct from structural water, the removal of zeolitic water is accompanied by a decrease in specific gravity and refractive index (these parameters increase when crystal hydrates are dehydrated). On the other hand, zeolitic water differs from *adsorbed* water, which is removed without any change in the properties of the compound. Without considering

intermediate states, this concept of adsorbed water itself embraces two fundamentally different states; these are water *adsorbed in a mono-layer* and the *capillary-condensed* phase. *Interlayer* "water" found in layer minerals and allocated by mineralogists to a separate group, also has a number of specific properties. Interlayer water, like zeolitic, is removed over a wide range of temperatures without changing the crystal structure, but, like structural water and unlike zeolitic, with an increase in specific gravity and refractive index.

The spectroscopic study of compounds containing oxygen–hydrogen groups (usually the OH stretching frequencies are used) employs the terms *strongly bound* and *weakly bound* "water" or an OH group *disturbed by strong or weak hydrogen bonding*.

The most widely used terms are Pauling's *crystallisation* and *constitutional* "water". Crystallisation "water" is the water accompanying the compound when it is crystallised from an aqueous solution; constitutional "water" is water the loss of which changes the chemical nature of the substance. However, even these more valid concepts do not reflect the form of the O_mH_n groups, and even less do they reflect their geometrical and energetic parameters.

These examples show that each of the concepts named characterises either individual properties of the O_mH_n groups themselves (plus, minus, structural, strongly bound, capillary-condensed, water in a monolayer) or the influence of the O_mH_n groups on certain properties of the whole compound (constitutional, zeolitic, crystallisation), and none of these concepts discloses the basic characteristic of the O_mH_n groups, namely their type; hence they are purely arbitrary. This is because the methods of investigation have been indirect. Thus thermography, study of weight loss, change of refractive index, coefficient of refraction, solubility, and even X-ray structural analysis do not give direct information on the form of the O_mH_n groups. Data obtained by these methods are so indirect, and the definitions so imprecise, that they cannot be directly compared; thus it is impossible to establish any correlation between such apparently close concepts as zeolitic and crystallisation "water", or zeolitic and adsorbed "water", and so on.

These matters can only be clarified by using methods which can observe the oxygen–hydrogen groups directly. Such a method is infrared spectroscopy, which is also the simplest, most rapid, and requires small specimens.

II. SPECTROSCOPIC CHARACTERISTICS OF OH_n GROUPS

The object of this review is to analyse spectroscopic studies using infrared spectroscopy to investigate the form of O_mH_n groups†. We have collected more than 300 studies, relating to the spectra of 1500 compounds. In all these cases the nature of the OH_n groups was known beforehand, and the absorption bands ascribed to them have been reliably interpreted. Although the distribution of the compounds studied among the different classes is very uneven, a number of important and useful regularities can be observed.

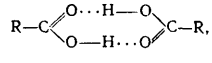
† Since of all possible O_mH_n groups having more than one oxygen atom only hydroperoxide groups are known, and as will be shown these are a special case of OH group, we shall in future refer only to OH_n groups.

The collected literature was analysed systematically so as to detect the spectroscopic properties of the OH_n groups in relation to their type or the nature of the atoms and bonds surrounding them. We first considered compounds containing the OH group, then systems having the $H\diagup O \diagdown H$ molecule, and finally compounds containing the ion OH_3^+.

Compounds containing the OH group formed the largest class, and it is therefore with these that it is easiest to follow the influence of the immediate and more distant environment on the vibrational properties of the OH group. Organic acids, alcohols, phenols, hydroxy-compounds, and oximes all contain the same C–O–H group, but in these various compounds the carbon atom of this group forms different bonds with different atoms. Comparison of the spectra of these compounds will enable the influence of the more distant environment to be observed. By comparing the spectra of various inorganic acids, organoelemental acids, hydroperoxides, surface OH groups, and hydroxides we can trace the influence of the atom directly bonded to the OH group on the vibrational properties of the latter. Finally, comparison of the spectra of acids, their acid salts, and organo-substituted acids will determine the influence of cations on the vibrational spectrum of the OH group.

1. Absorption Spectra of Hydroxyls (the O–H Group)

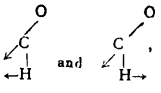
Organic acids are very convenient for study and were investigated long ago. The great expansion in polymer chemistry, biophysics, and medicine has increased interest in these compounds. Bellamy[1] has reviewed work on organic acids published up to 1953. The experimental data which had even then been accumulated enabled certain regularities to be established. Thus it was found that in the liquid and solid and sometimes even in the vapour phase acids exist as the dimers:



or higher polymers. The complexes are formed through strong hydrogen bonding, which leads to the reduction of the stretching frequencies of the OH group to 3000–2500 cm^{-1}. Most frequently these bands have a large half-width and lie in the region from 2750 to 2500 cm^{-1}. The integral and peak intensities differ substantially.

Most acids in the liquid state exhibit a band at about 935 cm^{-1}, which on deuteration is displaced to 675 cm^{-1}. In the crystals the intensity of this band falls and the half-width increases. Nearly all workers ascribe it to non-planar deformational vibrations of the C–O–H group.

Two strong bands in the range 1320–1210 cm^{-1} are related to combinations of the planar deformational vibration of the C–O–H group and stretching of the C–O group. The forms of these vibrations were later found:



and even to a first approximation cannot be considered as purely deformational vibrations of the COH group[2]. Others have also come to the same conclusion[3-12].

The deformational OH vibration becomes characteristic of the type of group only when the OH group is disturbed by hydrogen bonding or the hydrogen is replaced by deuterium[12,13]. The intermolecular vibrations of the associated molecules, or in other words the vibrations of the actual hydrogen bond[14,15] appear in the range 240–155 cm^{-1}.

Recent work confirms that the OH stretching frequencies normally lie in the region 3000–2500 cm^{-1}, but some studies on associated acids[14,16-18] have found absorption bands in the region 3300–3100 cm^{-1}.

Investigators as a rule do not indicate the degree of polymerisation of the substance studied, and the concentrations of solutions used cannot definitely establish this. The frequencies given in Table 1 under the heading "organic acids (free)" relate only to acids which were shown to be actually monomeric. All results obtained for dimeric and polymeric acids and for acids present in the crystalline state are given under the heading "organic acids disturbed by H bonding". This division is intended to demonstrate the great variation of the spectroscopic characteristics of OH groups with hydrogen bonding. Table 1 shows that there is practically no overlap between the regions of the stretching modes of OH groups disturbed and not disturbed by hydrogen bonding. An exception is given by Josien[23], who relates the bands at 3490–3420 cm^{-1} to the monomeric form of the acids because of their small half-width ($\Delta S_{\frac{1}{2}}$ = 50–100 cm^{-1}). As we shall see below, the band half-width is not a definite criterion of the formation of a hydrogen bond, although in most cases it increases the band width to several hundreds of reciprocal centimetres. This broadening with increasing polymerisation is seen particularly well with formic acid[16].

Alcohols. The spectroscopic characteristics of alcohols have also been reviewed previously[1]. The stretching frequency of the OH groups depends on the strength of the hydrogen bond. A weak bond reduces the frequency by 100–200 cm^{-1} and does not increase the band width ($\Delta S_{\frac{1}{2}}$ = = 50 cm^{-1}). With strong hydrogen bonding the frequency is reduced to 3400–3200 cm^{-1} and the half-width increases to 200 cm^{-1}. In the succeeding years a large number of alcohols of different types have been investigated. Comparison of these results shows that monomeric alcohols exhibit OH stretching frequencies of at least 3500 cm^{-1}, with a half-width of 20–70 cm^{-1}. A reliable assignment of the observed bands to dimers, trimers, and tetramers of the alcohols has only been made by Van Thiel and coworkers[52] and Cannon and Stace[53], so that, as with the acids, we have divided the alcohols only into free alcohols and those disturbed by hydrogen bonding (Table 1).

A typical spectrum of a highly dilute alcohol is that of t-butanol (Fig. 1)[55]. It contains a narrow band at about 3630 cm^{-1} due to undisturbed OH groups and two broad bands below 3500 cm^{-1} due to vibrations of the OH groups in associated molecules. Fishman and Drickamer[54] obtained the spectra of butanol at pressures from 1 to 12 000 atm; this experiment, in which any influence due to solvents was avoided, showed that a decrease in the distance between reacting molecules increases the probability of formation of complexes and very slightly affects the vibrations of free OH groups.

The frequency of planar and non-planar deformational vibrations of the OH group is very much less dependent on the degree of association of the molecules: thus the frequencies of the planar deformational vibrations are only increased by 120 cm^{-1} on passing from monomers to polymers (Table 1).

Phenols have been comparatively little studied, and their degree of association has not been determined. Gaseous phenols and their dilute solutions in inert solvents[126-128] exhibit bands of half-width $\Delta S_{\frac{1}{2}}$ = 15–60 cm^{-1} with a maximum at about 3730–3540 cm^{-1}. Phenols in the liquid

TABLE 1. Frequencies of the fundamental vibrations of hydroxyl-containing compounds in cm^{-1}*.

System	ν_{OH}	References	δ_{OH}	References	γ_{OH}	References
Organic acids	3590—3490	13,14,16,19—23	1284—1057	2,13,16,20,22,24	650—538	13,16,22
(free)	(2653—)	13,19,20	(973—865)	13,20,24	(546—421)	13
Organic acids	3300—2500	4,13,14,16—18,20, 21,25—38	1450—950	2,6,7,13,14,16, 18,20,29—33, 38—42	975—830	4,10,11,13,16—18, 27,28,30,31,36, 43—46
(disturbed by H bonding)	(—2260)	13,31	(1090—940)	13,31	(701—690)	13,31
Alcohols	3720—3500	9,14,23,33, 48—62	1330—1010	39,47—51,62—70	670—640	50,66,68
(free)	(2760—2655)	9,48—51,58	(950—770)	47—51,63—66	(490—475)	50,66,68
Alcohols	3530—2900	9,14,33,47—50, 52—57,60,71,72	1440—1140	9,14,18,33,50, 57,65—70,73,74	1090—858	57,74,75
(disturbed by H bonding)	(2577—2200)	47—50,72	(1100—875)	9,39,50,63,68,72		
Inorganic acids	3590—1900	25,33,76—91	1430—1000	76,79—93	1050—650	79—83
	(2655—2200)	83—86	(1086—860)	83—85,92		
Acid salts	3300—2200	77,82,86,88,89, 94—99	1400—1030	82,86,88,89,94—101	1020—400	82,89,95—100
Surface OH *groups* (free)	3770—3730	102—109	870—790	103—105,110		
Surface OH *groups* (disturbed by H bonding)	3660—3300	106—109,111,112	1150—935	110—112		
Metal hydroxides (alkali and alkaline earth)	3680—3530	113—120,129				
Metal hydroxides (other than alkali and alkaline earths)	3600—2800	81,120—124	1160—840	81,116,121—125		

* Frequencies in parentheses relate to the corresponding deuterated analogues.

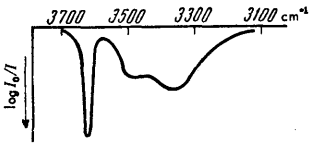


Fig. 1. Solution of t-butanol in CCl_4. C = = 0.2 M. [55]

state and their solutions in proton-accepting solvents, *i.e.* phenols with OH groups disturbed by hydrogen bonding, exhibit a wide band [3,128-131] in the region 3580–2250 cm^{-1}. The deformational vibrations of phenolic OH groups [3,5,14,129] lie in the region 1410–1170 cm^{-1}. In addition to these, salicylaldehyde has a band at 715 cm^{-1} which is also due to vibrations of the OH group. Deuterophenols have only been studied by two groups of workers [5,128]; the stretching and deformational modes lie in the ranges 2700–2480 and 980–925 cm^{-1} respectively.

Hydroxy-compounds. Of the compounds under consideration the hydroxy-compounds form the most complex and varied group, and the frequencies due to the OH groups of these compounds would be expected to appear over a wider range than in the case of other compounds, but the results of 22 studies which we have collected do not bear this out. All the compounds [132-140] exhibit OH stretching frequencies from 3620 to 2760 cm^{-1}, and deuterated hydroxy-compounds [138] from 2610 to 2200 cm^{-1}. The planar deformational vibrations of OH groups [8,134-147] and OD groups [138,142-145] have frequencies at 1475–915 and 1280–830 cm^{-1} respectively. Non-planar deformational vibrations appear [8,138-140,147] in the region 880–400 cm^{-1}.

Oximes have been the least fully investigated, and the existing information is not always fully accepted or sufficiently definite. A shift of the OH stretching frequency bands towards lower frequencies when hydrogen bonding occurs has been reliably established; thus it has been shown [148] that monomeric oximes and their deuterated analogues absorb at about 3650 and 2690 cm^{-1} respectively. Solutions in which the OH groups of oximes are somewhat disturbed by solvent molecules [149] have an absorption band at about 3500 cm^{-1}. Oxime polymers containing strong hydrogen bonds [148-150] have absorption bands right down to 2340 cm^{-1} and below [151]. The bands of planar deformational OH vibrations, in the presence or absence of hydrogen bonding, lie in the range [148,149,152,153] 1480–1200 cm^{-1}. We have quoted the overall range of frequencies, since although hydrogen bonding produces some increase in the frequency of deformational OH vibrations [148,152], the increase is less than the frequency changes occurring within the general class of oximes. The frequencies of the deformational vibrations thus cannot serve as a criterion of hydrogen bonding. Non-planar deformational OH vibrations have frequencies [148,150] from 930 to 420 cm^{-1}.

Dimethylglyoximes have been studied by two sets of investigators [150,151], who each recorded a large number of bands and suggested various interpretations. The bands at about 1800–1650 cm^{-1} are ascribed to stretching or deformational vibrations or to splitting of the levels in the two-humped potential valley.

Inorganic acids are a good class of compounds for investigating the influence of the radical R_1 in the compound R_1OH on the vibrations of the OH group. The published results on the absorption spectra of inorganic acids show convincingly that the stretching and deformational OH vibrations of all the compounds studied lie in the same regions of frequencies (Table 1). The vibrations of OH groups in organic-substituted acids also lie in the same regions [76,93].

Inorganic acids are not very volatile and form hydrogen bonds very readily, so that even their solutions in inert solvents cannot be considered *a priori* to contain monomeric forms, and hence all results obtained for the acids in the liquid or crystalline phase we have related to their polymeric forms, *i.e.* we have considered the acidic OH groups as being disturbed by hydrogen bonding. A characteristic of such compounds is the overlapping of the bands, which have half-widths of several hundreds of reciprocal centimetres. Aqueous solutions of inorganic acids cannot be compared with their solutions in other solvents, since the dissociation of strong acids in water produces the ion OH_3^+ (this matter will be considered in more detail below). Great care is needed therefore in the interpretation of the bands observed in the spectra of acids in the presence of water molecules.

Acid salts. The OH groups of acid salts exhibit frequencies in the same region as the corresponding acids (Table 1). The observed coincidence in the main frequencies of the OH vibrations would be expected, since the acidic OH groups in acids and acid salts are very similar in nature. The slight differences in the frequency ranges for the two types of compound must be related to their slightly different nature and to the fact that different materials were investigated. For the same reasons as in the case of the inorganic acids, all acid salts present in the solid and liquid phases are considered to be polymeric.

Some acid salts have two absorption bands in the OH stretching frequency region [100,154-156], the band with the lower frequency being in the region 2400–1900 cm^{-1}. This may be due either to different types of association of OH groups in the compound or to splitting of the energy levels because of the presence of two minima on the potential curve of the hydrogen bond.

The interpretation of the bands at about 1850–1580 cm^{-1} observed in certain acid phosphates, arsenates, and iodates [99,100,156-158] is even more indefinite. On the basis of their shift on deuteration these bands have been ascribed to vibrations of R–O–H groups, but the type of vibration has not been established, and the types of vibration suggested by different workers are very different [99,156,157]. They have been assigned to OH stretching vibrations, to OH deformational vibrations, and to vibrations of the H_2PO_4 group. In the first case the low frequency of the bands was ascribed either to very strong hydrogen bonding or to the appearance of a second minimum on the potential curve. The difficulty of interpretation is removed if it is assumed that in addition to acidic OH groups the compounds contain the OH_3^+ group, for which absorption in this region is characteristic (see below); the workers cited did not consider this possibility. The frequencies of these bands will not be taken into account in further discussions.

Hydroperoxides behave in the same way as the other types of compound considered above in respect of the spectroscopic characteristics of their OH groups.

Monomeric hydroperoxides have OH stretching vibration bands[159-162] at about 3580–3530 cm^{-1}. When hydrogen bonding occurs the frequency is reduced[161-172] to 3500–3000 cm^{-1}. As with the other compounds, monomeric hydroperoxides have narrower bands than their polymeric forms.

Deformational vibrations of the OH groups of polymeric hydroperoxides[163-168,170-172] lie in the region 1420–940 cm^{-1}, which also contains the frequencies 1320 and 1000–930 cm^{-1} found for hydroperoxide monomers[159,160]. Since there have only been two such studies, no definite conclusion can be drawn from these data. Bands due to non-planar deformational vibrations of the OH groups have been observed only for hydrogen peroxide[167] and isopropylbenzene hydroperoxide[166]; these bands lie in the region 880–700 cm^{-1}. Bands were also observed[167] at about 650–530 cm^{-1} and have been ascribed to intermolecular vibrations.

Organoelemental compounds. The OH groups of organoelemental compounds have stretching frequencies at from 3690 to 2300 cm^{-1}, depending on the degree of hydrogen bonding[56,156,173-179]. The formation of a hydrogen bond, as with other compounds, lowers the frequency of the vibrations and broadens the band to a width of several hundreds of reciprocal centimetres[56,156,175-177]. Bands due to planar deformational vibrations of the OH groups have been observed[156,177-181] at 1400–800 cm^{-1}. The frequency is increased slightly when hydrogen bonding occurs, but the increase is less than the frequency range in which the deformational vibrations of the various organoelemental compounds are observed. The bands due to non-planar deformational vibrations, observed in crystals of mono-, di-, and tri-methyl borates, lie[177] at about 650 cm^{-1}.

In addition to these bands some organic phosphorus compounds[156] have bands in the region 2350–1900 cm^{-1} and[156,173,174] at about 1700 cm^{-1}. As in the case of acid salts, these bands are shifted on deuteration, and can therefore be related to OH vibrations, but, again as with the acid salts, the type of vibration is unknown. These bands will not therefore be considered in future discussions.

Surface OH groups, because of their unusual situation, should not exhibit any particular spectroscopic characteristics, but Table 1 shows that this conclusion is incorrect. Free surface OH and OD groups[102-104] are characterised by narrow bands not more than 100 cm^{-1} in width[105,107]. The presence of even weak hydrogen bonding[111] broadens the band and shifts it from 3770 to 3300 cm^{-1}. The bands due to deformational vibrations of the free OH groups lie in the region 870–790 cm^{-1}; when disturbed by hydrogen bonding they are shifted to 1050 cm^{-1} (Table 1).

Hydroxides have been much studied, but the spectra obtained differ considerably (Table 1). They may be divided into two groups. The first group contains the alkali and alkaline earth metal hydroxides, which have very narrow bands (half-width 4–60 cm^{-1}) in the region 3680–3610 cm^{-1}. Their deuterated analogues[113-115] have bands in the range 2715–2630 cm^{-1}. When hydrogen bonding occurs, the bands due to OH stretching frequencies are shifted[115,116,129] to 3570–3530 cm^{-1}. No bands due to deformational vibrations were observed[116] in the spectra of these compounds in the usual region of 1800–400 cm^{-1}. The Raman spectra of these compounds[117] exhibit bands with frequencies of from 360 to 50 cm^{-1}, but these could not be interpreted.

The hydroxides of other metals have a quite different type of spectrum. The hydroxides of iron, aluminium, gallium, indium, zinc, etc., have broad diffuse bands in the region 3600–2800 cm^{-1}, due to OH stretching vibrations. The spectra also have bands due to deformational vibrations at about 1160–840 cm^{-1}. In addition to bands at 1060 and 841 cm^{-1}, technetium hydroxide[124] has a band at 1543 cm^{-1}.

The hydroxides of copper and vanadium apparently occupy a position intermediate between the above two types of compound; they exhibit stretching and deformational vibration bands at about 3570–3530 cm^{-1} and 790–470 cm^{-1} respectively[182].

2. Absorption Spectra of Water Molecules (the OH_2 Group)

So far we have considered compounds of the formula R_1OH, where R_1 is any radical or atom other than hydrogen. We shall now deal with the molecule H–O–H.

In the vapour state the various water molecules have the frequencies given in Table 2.

The investigation[188] of *water* in a nitrogen *matrix* at 20°K has enabled the spectroscopic characteristics of water molecules in various polymeric forms to be established; the frequencies and half-widths of the absorption bands are given in Table 2 and Fig. 2. Similar studies of water in a matrix of krypton, argon, or xenon[189,190] have shown the stretching frequency of water molecules to be in the range 3770–3660 cm^{-1} in each case. A distinct rotational structure has been observed in the region of deformational vibrations of H_2O, HDO, and D_2O molecules, the most intense bands[189] having the frequencies 1608–1602, 1413, and 1195 cm^{-1}. The spectra obtained for water in a nitrogen matrix are in complete agreement with Thiel's results[188] (Fig. 2). Investigation of water vapour in an atmosphere of nitrogen and carbon dioxide at 50 atm has shown that reaction between nitrogen and water molecules does not cause any substantial change in the spectrum of the latter, but carbon dioxide molecules, on the other hand, form hydrogen bonds with H_2O and D_2O molecules and so increase the frequency of their deformational vibrations[191] to 1610 and 1190 cm^{-1}.

The spectra of water dissolved in various solvents were investigated in another group of studies of

TABLE 2. Frequencies of the fundamental vibrations of water molecules.

	Composition	ν_3	ν_1	$\nu_2 = \delta_{OH}$	$\Delta S_{1/4\nu}$ and $\Delta S_{1/4\delta}$	$2\nu_2$	References
Vapour phase	H_2O	3755.8	3656.6	1594.6			183,184
	HDO	3707.5	2726.7	1402.2			183—186
	D_2O	2788.0	2671.5	1178.3			183—186
	$D_2^{18}O$	2764±5	2657±2	1169±2			187
In a nitrogen matrix at 20°K	monomer	3725	3627	1600	~20 ~8		188
	dimer	3691	3546	1620	~20 ~6		188
	trimer	3510	3355	1635	80 and 365		188
	polymer	3320	3240	1635	~30		188
Liquid phase	H_2O	3480±20	3425±10	1645±5		3290±20	
	D_2O	2580±20	2510±10	1215±5		2435±20	
	HDO	3420±10	2510±5	1460±5		2930±10	

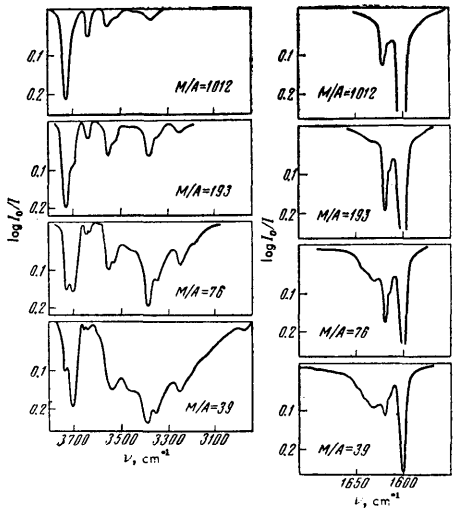


Fig. 2. Spectra of water in nitrogen matrices[188] at 20°K and molar ratios of from 1:1012 to 1:39.

OH_2 groups. Two bands were observed in the OH stretching frequency region, with half-widths less than 70 cm^{-1}; these frequencies, of 3705–3575 and 3650–3520 cm^{-1}, are very close to the frequencies for water vapour given in Table 2, so that as with the water vapour bands they are ascribed to antisymmetric and symmetric vibrations of the H_2O molecule respectively[129,192-195]. With D_2O molecules analogous bands of half-width 50 cm^{-1} have been observed[193,196] in the ranges 2766–2700 and 2655–2600 cm^{-1}.

A detailed study of water–pyridine binary mixtures and water–pyridine–carbon tetrachloride ternary mixtures has shown that when hydrogen bonding occurs the water spectrum loses the doublet character typical of solution in an inert solvent[194]. The bands due to OH stretching vibrations are shifted to 3500–3200 cm^{-1}, and the band due to deformational vibrations is shifted to 1665–1640 cm^{-1}. Similar results were obtained in another study[192].

Water in the liquid or crystalline phase consists wholly of H_2O molecules disturbed by hydrogen bonds. The spectroscopic data on water have been discussed in detail[194]. In the liquid phase, water of any isotopic composition exhibits broad absorption bands in the region of OH stretching vibrations. In the case of H_2O and D_2O molecules three maxima can be distinguished on the broad band, ascribed to symmetric and antisymmetric stretching vibrations and to the first overtone of the deformational vibration of the water molecule. There has as yet been no reliable allocation of the observed bands to ν_s and ν_{as} vibrations.

The suggested interpretation and the frequencies of the observed absorption bands are given in Table 2. Later studies have confirmed these results[197-201]. Slight variations in the frequencies obtained are due to the different experimental conditions and to insufficient experimental accuracy. A change of temperature of 20° is required to produce such a shift of frequency[200]. Since we are here concerned only with general characteristics, we shall not pursue this matter in any more detail.

In addition to the absorption bands mentioned, liquid water exhibits bands[201-203] at about 2100 and 710–645 cm^{-1}, due respectively to vibrations of the type $\delta_{OH} + \omega$ and ω. Recent work in the far infrared[204] has detected six bands in the region 230–140 cm^{-1} in the spectra of liquid light and heavy water. This is the first observation of the fundamental frequencies of the hydrogen bond in an absorption spectrum.

The first spectroscopic investigation of *ice*[205] detected absorption bands in the regions 3380–3140, 1650–1580, and 850–820 cm^{-1}. More recent studies[199,201,203,206,207] agree in general with these values. The spectrum of ice is little dependent on external conditions. Thus with reduction of the temperature from 0° to -170° the OH stretching frequency (ν_{OH}) is lowered by 60–40 cm^{-1} and the deformational (δ_{OH}) and intermolecular (ω) vibration frequencies are increased[207] by 25 and 15 cm^{-1} respectively. Similarly the external pressure has little effect on the spectrum of ice: increasing the pressure from 1 to 9000 atm only slightly increases the frequency due to OH stretching vibrations to 3600 cm^{-1} and slightly increases the intensity of the band due to deformational vibrations[208].

Depending on the temperature of freezing, water vapour produces either hexagonal or cubic ice[201,205]. Although both forms absorb in approximately the same region their spectra are quite different; thus cubic ice, obtained by condensation of the vapour at below -80°, has much narrower bands (Fig. 3).

The frequencies of intermolecular vibrations have been found from the Raman spectrum: they are[207] 310, 299, 230, and 212 cm^{-1}. Thus under different conditions the spectrum of ice may contain bands due to OH stretching vibrations of half-width from 50 to 300 cm^{-1} and with maxima over a wider range of frequencies (Table 3) than had previously been indicated[205].

The dependence of the spectrum of water on the nature of salts and acids dissolved in it has often been studied. Neither the concentration nor the nature of the ions produces any substantial change in the spectrum of the water[129,193,209-214]. The OH and OD stretching vibrations appear in the regions 3460–3260 and 2560–2470 cm^{-1} respectively. The deformational vibrations of H_2O and HDO molecules are found in the regions 1655–1620 and 1475–1450 cm^{-1}. Investigation of the fine effect due to influence of various ions on the spectrum of water has shown[129,211] that the position of the absorption bands of the water is more sensitive to the nature of the anion and less sensitive to the nature of the cation. Replacing

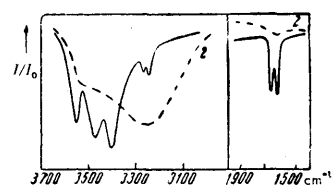


Fig. 3. Spectra of ice obtained by condensation of water vapour[201] at: 1) -80°; 2) -22°.

TABLE 3. Frequencies of the fundamental vibrations of water molecules.

System	ν_{OH}	References	δ_{OH}	References	γ_{OH}	References
In a crystalline phase	3600—3090	199,201,205, 207,208	1660—1580	199,201,205,207, 208	850—650	201,203,205, 208
Adsorbed on a surface	3580—3300	103,105,108, 215—217	1645—1620	102,103,105,108, 110,216—218		
In hydrated salts of oxygen-containing inorganic acids	3620—2700	33,77,80,82, 88,94,96,116, 123,129,195, 219—239	1670—1590	33,77,80,82,88, 94,96,116,123, 129,223—233, 240,241		
In hydrated halides	3600—2900	89,121,242—250	1670—1590	89,121,242—250		
In hydrated salts of organic acids	3530—3050	34,199,222, 251—253	1650—1614	34,199,222, 251—253		
In other crystal hydrates	3600—3120	254—263	1670—1600	255—254		

I^- ions by F^- ions reduces the OH and OD stretching frequencies by 160 and 90 cm^{-1} and increases the frequency of the HDO deformational vibrations by 50 cm^{-1}. The presence of Cl^- ions in solution does not produce any marked change in the spectrum of pure water. The presence in solution of various alkali and alkaline earth metal cations only produces a shift of 30 cm^{-1} in the band due to the OD stretching vibration.

In the adsorption of water molecules on an adsorbent the geometrical and force parameters of the water may be slightly altered, and its vibrational spectrum would then be expected to show a marked change. Most workers have studied the adsorption of water on silica gel; cellulose and Cellophane have also been studied as adsorbents[216,218]. Of course, as the coverage of the surface by the adsorbed material increases, interaction between individual adsorbed molecules will begin to show itself. The extreme cases of this coverage are a monolayer and capillary condensation. The frequency of the deformational vibration of water molecules adsorbed in a monolayer is 1620 cm^{-1}, and that of water molecules in a capillary condensed phase[102,103] is 1640 cm^{-1}. The bands due to OH and OD stretching vibrations in molecules adsorbed in a monolayer are narrower and have frequencies 150 cm^{-1} higher than in the corresponding bands for capillary condensed molecules. Other workers have given similar values for the frequencies. Table 3 gives the generalised data.

Crystal hydrates form the most fully investigated class of compound. Analysis of the collected results demonstrates convincingly that water molecules present in the most varied compounds all exhibit the same spectroscopic pattern. Crystal hydrates of salts of inorganic oxo-acids, halogen acids, and organic acids and hydrates of alkalis and other more complex compounds all have absorption bands due to water in the same frequency ranges (Table 3).

In all cases the OH stretching frequencies lie within the range 3620–2700 cm^{-1}. Only once[225] has a frequency outside this range been recorded (3690 cm^{-1}), but in another investigation[227] the same compound gave a different result (3570 cm^{-1}); we have therefore taken the value 3620 cm^{-1} for the upper limit of the OH stretching vibrations. The half-width of these bands varies from 70 to 400–500 cm^{-1}, but in such arbitrary fashion that it cannot be correlated with any parameters of the compounds. A good example is uranyl nitrate, for which the half-width of the bands due to the OH stretching vibrations is six times as great in the hexahydrate as in the dihydrate (Fig. 4).

The deformational vibrations of water molecules (δ_{OH}) in most crystal hydrates have a frequency of from 1670 to 1590 cm^{-1}; in very rare cases (5 out of 450 bromates, benzene sulphonates, and phosphates[77,249,264]) the frequency is increased to 1680 cm^{-1}. A δ_{OH} band below the normal lower frequency limit has been observed only in $CuCl_2.2H_2O$ and $MgCl_2.6H_2O$, which have a band at about 1560 and 1576 cm^{-1} respectively[244,247]. These deviations from the normal position of the δ_{OH} bands do not affect the discussion which follows, and are mentioned here only to demonstrate how few they are.

A different question arises in respect of other investigations[77,96] in which, in addition to bands at 1640–1620 cm^{-1}, bands were observed with frequencies at 1705–1680 cm^{-1}. As we shall see later, the question of the presence in crystal hydrates of water molecules having a deformational vibration frequency of above 1670 cm^{-1} is very important, and we shall therefore consider this matter in more detail. Three main facts must be borne in mind when evaluating the reliability of these reported results. Firstly, the spectra in which bands of frequency 1705–1680 cm^{-1} were found[96] have also been investigated by other workers, who give lower frequencies, namely[80] 1690 cm^{-1} instead of 1705 cm^{-1} and[77] 1670 cm^{-1} instead of 1680 cm^{-1}. We must therefore be very circumspect in considering the accuracy of the determination of these frequencies. Secondly, in all three investigations the observed bands were assigned to δ_{OH} vibrations on the tacit assumption that they could not be assigned to OH stretching vibrations or to vibrations of the phosphorus–oxygen anion, and in general this is not true. No use was made even of deuteration, which could have shown whether the hydrogen atom takes part in the vibration. Thirdly, even if it is considered that the band is due to vibrations in which the OH bond participates, and that the frequency of this band is in fact above 1670 cm^{-1}, we still do not have any foundation for making a definite interpretation. As will be shown below, the deformational vibrations of the hydroxonium ion are found in the region 1750–1670 cm^{-1}, and for some reason or other the presence of this ion was not considered. In view of the above, we shall not concern ourselves further with these bands.

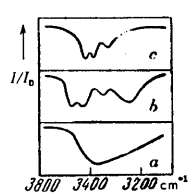


Fig. 4. Spectra of the stretching vibrations of the water of crystallisation of uranyl nitrate[207]: *a*) hexahydrate; *b*) trihydrate; *c*) dihydrate.

3. Absorption Spectra of Hydroxonium Ions (the OH_3^+ Group)

There have been seven investigations of the absorption spectrum of the *hydroxonium ion*. Infrared absorption and Raman methods, which give identical spectra for molecules of symmetry C_{3v}, give different results for the hydroxonium ion; there is no explanation of this in the literature. Since this review is concerned with the effects due to OH_n groups in the absorption spectrum, and the Raman spectrum of the hydroxonium ion is always less clear[265,266], we shall deal only with the frequencies obtained from the absorption spectra.

Studies of the hydroxonium ion in aqueous acid solutions at room temperature[210,267-269] and in crystal hydrates of acids and equimolar mixtures of water and acid[269-272] at -195° have given frequency values which are in good agreement; bands were always found in the ranges 3380–2650, 2150–2100, 1750–1670, and 1200–1130 cm^{-1}. The two high-frequency bands are always fairly weak and very broad; they were resolved only in two cases[270,271]. The band at about 1700 cm^{-1} is considerably narrower and stronger; it was always the most clearly developed in the absorption spectrum, and was therefore detected in all the investigations except one[272], in which it overlapped with two bands of higher frequency, forming a region of absorption at 2800–1650 cm^{-1}. The narrow band at about 1150 cm^{-1} ($\Delta S_{\frac{1}{2}}$ = 100 cm^{-1}) has a constant frequency but is of very low intensity.

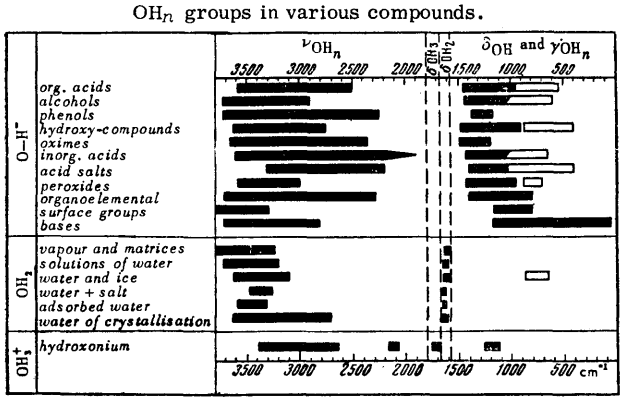
III. DEPENDENCE OF THE VIBRATIONAL SPECTRUM OF OH_n GROUPS ON THEIR STRUCTURE

We have been considering the spectroscopic characteristics of O–H⁻, O–O–H⁻, H–O–O–H, H–O–H, and



groups in 20 different classes of compounds and systems, and since we have included every published work at our disposal, any regularities we see must be considered to be of general application, and of use in molecular spectroscopic analysis. The collected data are shown visually in Table 4, in which the black strips represent the regions in which the fundamental planar vibrations of the OH_n groups appear, and the white strips the regions of non-planar vibrations of the OH group and H_2O molecules as a whole.

TABLE 4. Frequencies of the characteristic vibrations of OH_n groups in various compounds.



1. Determination of the Type of OH_n Group

The data lead to a result of great importance for spectroscopic studies, a result which enables definite establishment of the type of an OH_n group from its deformational vibrations. While the stretching frequencies of all OH_n groups appear in the same region, their deformational vibrations appear in completely different regions; they do not overlap under the influence of any intra- or inter-molecular interactions. Thus the frequencies of the deformational vibrations of water molecules and OH groups are always within the limits from 1680 to 1590 cm^{-1} and from 1500 to 600 cm^{-1} respectively. In all the systems studied, one of the frequencies of the deformational vibration of the OH_3^+ ion lies in the region from 1750 to 1670 cm^{-1}, which serves to distinguish it from the H_2O molecule and hydroxylic compounds‡.

This relationship is very useful analytically. In finding it we used all existing literature data, but these are purely experimental. For full confirmation of the relationship found experimentally we shall consider it in terms of the modern theory of molecular vibrations.

Let us consider to a first approximation the vibration of the angle R–O–H and follow the change of frequency of this vibration with change of its kinematic parameters. We shall consider the vibration to be characteristic in type and the angle to be constant and the same as in the free water molecule. In the water molecule the frequency of this vibration is 1595 cm^{-1}. If R is deuterium the frequency is lowered to 1402 cm^{-1}. In any real molecule the hydroxyl oxygen is attached to an even heavier atom R, and the R–O distance is usually greater than the value 0.96 Å characteristic of the O–H bond. Taking one of the lighter atoms, *e.g.* the boron atom, and taking the B–O distance as 1.2 Å,[273] these changes alone will reduce the frequency of the deformational vibration to 1180 cm^{-1}. Further increase in the mass of R will produce a further reduction in the frequency. Thus we see that changing only the kinematics of the R–O–H group must reduce the frequency of the deformational hydroxyl vibration by 300–400 cm^{-1} as compared with that of water. Clearly in the general case the effect will be more complex: there may be some increase in the bending force constant, and also participation of neighbouring bonds in the deformational OH vibration, and either may produce some increase in the frequency in comparison with the value of 1180 cm^{-1} which we have obtained. However, the factors which increase the frequency are slight, and it is therefore natural to expect the frequencies of the deformational vibrations of the OH groups to be always lower than those of the H–O–H molecules. Hydrogen bonding has very little effect on this frequency[101,274]. This is readily seen with Seignette salt (potassium sodium tartrate), in which four types of water molecule have been detected, distinguished by the strength of their interaction with neighbouring molecules, and having absorption bands in the range from 3537 to 3049 cm^{-1}; however, the frequency of the

‡ The band corresponding to the other deformational OH_3^+ vibration is of low intensity and its frequency coincides with that of OH vibrations; it cannot therefore serve as a basic analytical signpost.

deformational vibrations is 1650 cm^{-1} for molecules of all four types[252]. Thus we see that our relationship found experimentally is in full accord with theoretical views, which again confirms the correctness of our conclusion.

The difference between the frequencies of the deformational vibrations of the OH_3^+ and OH_2 groups is very much less. It has as yet no definite theoretical explanation, and so remains a purely experimental fact. However, it can be shown that within reasonable limits of the $H\overset{O}{\diagdown\diagup}H$ angle (115°–105°) and the O–H distance (1.09 to 0.96 Å) the diagonal term of the matrix of the kinematic coefficients of OH_3^+ ions derived by symmetry is always 6–18% greater than the corresponding coefficient for the water molecule; hence only the configuration of the OH_3^+ and OH_2 groups need be considered when explaining the observed difference in frequencies.

From all that has been said it follows that if, on the basis of any data, a band can be assigned to a deformational vibration of an OH_n group, then the frequency of the vibration will immediately indicate the type of group: OH_3^+, OH_2, or OH^-.

Having obtained a very simple and convenient analytical method for establishing the type of OH_n group, we must also consider the requirements of the method. We can readily establish, from the shift of the band on deuteration (the frequency decreases by a factor of 1.28–1.35), that it is caused by some vibration of one of the OH_n groups. The assignment of the band to a deformational vibration is only possible by analysing the whole spectrum, otherwise we cannot distinguish the bands due to deformational vibrations from the other bands, which we do not need, due to non-planar deformational vibrations of hydroxyls, vibrations of water molecules as a whole, and low-frequency deformational vibration of the OH_3^+ ion.

To establish the type of OH_n group, the band to be considered must have the highest frequency of all the bands in the range from 1800 to 400 cm^{-1} which is shifted on deuteration. It should also be remembered that all deformational vibration bands are of medium intensity and, in the case of OH^- and OH_2 groups, are as a rule weaker than stretching vibration bands. The band due to deformational vibration of the hydroxonium ion at about 1700 cm^{-1}, on the other hand, is usually stronger than both of its stretching vibration bands.

As stated earlier, neither hydrogen peroxide nor hydroperoxides exhibit any specific spectroscopic characteristics due to OH vibrations which distinguish them from other R–O–H compounds (Table 4).

Review of the spectroscopic characteristics of the various OH_n groups has shown that the type of group can only be established from the frequency of the deformational vibrations; no information of the type of OH_n group can be obtained from the OH stretching vibration spectrum. The tacit assumption of many investigators that hydroxy-groups have narrower OH stretching vibration bands than do water molecules is quite incorrect. As was shown in the appropriate subsections of Section II, when hydrogen bonding occurs alcohols, acids, phenols, oximes, etc., have absorption bands with half-widths of several hundred reciprocal centimetres (Fig. 1), while water molecules isolated in matrices or in low concentrations and in inert solvents have absorption bands narrower than 70 cm^{-1} (Fig. 2). It follows incontestably from these results that the half-width of a band due to an OH stretching vibration does not depend on the type of OH_n group and so cannot be used to establish the type. The half-width of such bands changes over very wide limits under the action of hydrogen bonding. This broadening has long interested investigators, but no regularity in it has yet been definitely established.

2. Hydrogen Bond Parameters from the OH Stretching Vibration Spectrum

The possibility of determining the type of OH_n group only from the frequency of its deformational vibration might create the impression that the study of stretching vibrations is worthless, but this is quite untrue, since it is just the OH stretching vibrations which are the most sensitive to intermolecular interaction.

Thus analysis of all the collected studies shows that the OH stretching frequencies appear in the range 3750–1900 cm^{-1}, and are independent of the type of OH_n group and of the type of compound in which it is present, but they are very sensitive to the condition of the OH_n groups: whether they are isolated, or disturbed by dispersion forces of molecules of inert solvent or by hydrogen bonding. The OH stretching frequencies for these cases fall within the ranges 3750–3600, 3600–3500, and 3500–1900 cm^{-1} respectively. Hence the OH stretching vibrations exhibit a characteristic frequency in relation to intramolecular influences, but the characterisation is lost if the group takes part in the formation of a hydrogen bond, however weak.

Since the type of OH stretching vibration remains characteristic in any system[275], the reduction in its frequency when hydrogen bonding occurs can only be due to a decrease in the force constant of the OH bond. Hence the study of OH stretching vibration spectra *cannot give information on the type of* OH_n *group, but can provide information on intermolecular interaction and the nature of the atom* R_2. Let us consider in more detail what parameters of the system can be found from the OH stretching vibration spectrum.

In any investigation the first thing noted is the number of bands. If we have a compound with only one OH group we should expect only one band in the OH stretching region, but, in fact, without considering fortuitous superimposition of frequencies, there are considerably more.

The number of bands observed in the OH stretching region is increased because of (*i*) the presence of various types of association[52,53,188,252], (*ii*) the appearance of overtones strengthened by Fermi resonance and of frequencies of type $\nu_{OH} \pm \omega$, where ω is the frequency of intermolecular vibrations[118,206,207,231,237,238,276,277], and (*iii*) splitting of a band because of tunnelling by the proton[37,38,131,154,155,234,277–284]. The interpretation of the spectrum in the region of OH stretching vibrations therefore presents immeasurably more difficulty than its interpretation in the region of OH deformational vibrations.

Such difficulties can usually be met by using a suitable method. The presence of various types of association can usually be established by investigating the variation of the intensities of the bands with temperature[55,284–286] or concentration[52,162,188]. The first overtone of the deformational vibration of the water molecule and the component frequencies of type $\nu_{OH} \pm \omega$ are easily distinguished by comparison with the spectra of the corresponding deuterated analogues. These bands are very often found in the spectra, and recent studies have shown that their number, frequencies, and intensities

depend markedly on the symmetry of the crystal rather than on its chemical composition[167,201,231,237] (Fig. 5).

To show proton tunnelling in the compound under investigation and to assign the observed doubling of the bands to this cause it is necessary to obtain the infrared and Raman spectra of the compound and its deuterated analogue[283]. The potential barrier between the two positions of the proton can then also be determined.

Thus in almost every case the combination of infrared spectroscopy with some other method can be used to interpret the bands due to OH stretching vibrations. If the type of OH_n group is already known, the number of different types of association present in the given system can be found from the number of bands due to purely stretching vibrations of the OH group.

When the corresponding OH stretching frequencies have been found for any OH_n group, the variation of the intensity of these bands with temperature can be used to evaulate the hydrogen bond energy. Measurements made on different compounds have shown this energy to vary from 0.9 to 9.0 kcal mole^{-1} [55,161,162,284,285,287-290]; it increases with the proton-donating strength of the compound. Thus in the series $Ca(OH)_2$, $Mg(OH)_2$, $Ni(OH)_2$, $Al(OH)_3$, $B(OH)_3$, AlOOH the energy increases from 2.35 to 6.85 kcal mole^{-1}.[287] If the hydrogen atom of the hydrogen bond is replaced by deuterium the energy of the bond is slightly less[291-293]; for ice at 0°K the difference is 0.3 ± 0.14 kcal mole^{-1}.[291]

Of no less interest are the second derivatives of the potential energy of the hydrogen bond with respect to the various vibrational coordinates, or in other words the force constants. These values are needed for calculations on the spectra of systems with hydrogen bonding; they can be calculated if the vibrational spectra of all the deuterated analogues of OH_n groups and their geometry are known. For organic acids[20,294], hydroperoxides[167], and water[250,295] they are respectively 0.42, 0.38, and 0.22×10^6 cm^{-2}. Comparison of the force constants with the energy values given above shows that with the hydrogen bond, as with other types of bond, the force constant varies in the same sense as the energy of the bond. The bending force constants of the hydrogen bond have been found to be: for formic acid dimers[20] 0.06, for ice[296] 0.05, and for halide hydrates[250] $(0.2-0.4) \times 10^6$ cm^{-2}. These values were obtained by assuming a linear hydrogen bond, but this is a very doubtful assumption for crystal hydrates, and a more correct value would be about 0.05×10^6 cm^{-2}. The non-diagonal force constants of the hydrogen bond are[20] less than 0.03×10^6 cm^{-2}.

In addition to the force parameters, the OH stretching frequency can provide a fairly accurate estimate of the distance between the oxygen atoms (R_{OO}) in the O–H · · · O system; this is possible because a large number of investigations have been made seeking the relationship between the shift of the OH stretching frequency from its position in the monomer and the length of the hydrogen bond (R_{OO})[25,78,91,151,287,297-301]. Most of the curves obtained coincide for the main part, but individual curves show slight variations (Fig. 6). There is no analogous relationship for OH deformational vibration bands, firstly because there is no single relationship[246] between the band shift δ_{OH} and the distance R_{OO}, and secondly because while such a relationship is observed for certain compounds, the change of frequency δ_{OH} is generally too slight. Simple relationships have been established between the shift of the OH stretching band and the ionisation constant, electronegativity of the proton acceptor, and the Hammett constant[50,61,127,290,302-305], but as a rule these only relate to a single class of compound, and therefore are not of great significance in the analytical application of infrared spectroscopy.

As has just been shown, the vibrational spectrum of OH_n groups can be used to find the energy of the hydrogen bond, its rigidity (force constant) and its length (R_{OO}); in each case we use only the frequencies and intensities of the corresponding absorption bands. In Section II it was stated several times that when hydrogen bonding occurs the OH stretching bands are considerably broadened; this has long been known, and for some reason is now considered to be necessarily so. The falseness of this assumption is shown by cases[112,201,306] where absorption bands shifted by 400–300 cm^{-1} have a half-width of less than 70 cm^{-1} (Figs. 3 and 7); the usual half-width of bands in this region is more than 200 cm^{-1}. A particularly good example is the case of ice[201], for which the spectrum obtained at -80° and a fixed water vapour pressure depends on the method of its production (Fig. 3): the different modifications of ice produced by the different conditions at the time of freezing have very different spectra. This result demonstrates clearly that under identical experimental conditions a given compound will exhibit different spectra even if only the mutual disposition of its molecules is changed. A slight rearrangement of the molecules changes the number of bands observed, their half-widths, and the positions of their maxima, which again demonstrates the complex nature of band half-widths, but brings us no nearer understanding them.

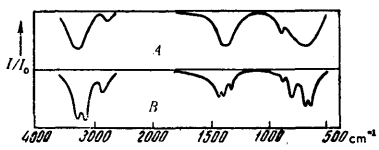


Fig. 5. Spectra of hydrogen peroxide[167] at 80°K: *A*) amorphous; *B*) crystalline.

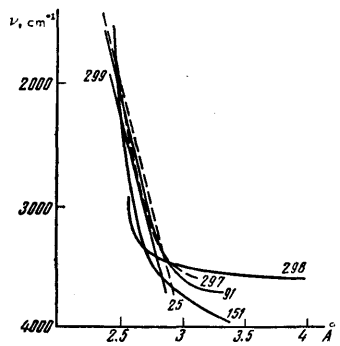


Fig. 6. Variation of the OH stretching frequency with the distance between the oxygen atoms, as obtained by different investigators: the numerals on the curves are the literature references.

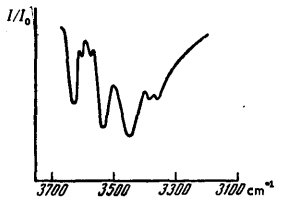
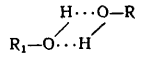


Fig. 7. Spectrum of aluminium hydroxide[112].

The spectroscopic study of compounds which form a hydrogen bond has established other relationships also. Thus it has been found that in most real systems the hydrogen bond is not linear; the O–H · · · O angle in these bonds[91,188,286,307-311], which are called conjugated, may reach 160°. Many investigators of the spectra of hydroxyl-containing compounds consider that two molecules of such a compound interact to form dimers with four-membered rings[52,55,162,188,286,289,296,312]:



Correct application of infrared spectroscopy is thus seen to provide considerable and varied information on the nature and interaction of the OH groups in the compound studied. The type of OH_n group can be found from the OH deformational frequency. The number of bands observed in the stretching frequency region can, in conjunction with information obtained by other methods, establish how many different OH^-, OH_2, and OH_3^+ groups are present in the given system. The OH stretching frequency can be used to find the length and energy of the hydrogen bond. All this information on the nature of the OH_n groups and their interaction is obtained from the number and frequencies of the observed absorption bands. Such important characteristics as the intensity and shape of the bands are not used at all, because no general relationship has yet been found between these properties and the intra- and inter-molecular parameters of the system under investigation. The finding of such a relationship will enable investigators to obtain new data on intermolecular effects.

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