Spectroscopic and Structural Aspects of Very Strong Hydrogen Bonds*

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Abstract

Features in vibrational spectra of systems with very short and strong hydrogen bonds are discussed with respect to possible types of the hydrogen bond potential. Particular attention is devoted to possibly symmetrical hydrogen bonds. Informations about some other physical properties and the structural characteristics are also considered.

Introduction

Most of the knowledge about hydrogen bonding stems from data gathered by various experimental methods on weak to medium strong bonds. Correlations between characteristic quantities such as X—H and X—H ... Y distances, infrared frequency shifts, enthalpies, NMR shifts, acidities, etc. have been established for such bonds and theoretical treatments usualy adopt corresponding parameters. In recent years data on strong bonds are becoming increasingly available showing that they are rather widespread in nature and, moreover, responsable for many important phenomena of the solid and liquid state, and possibly in biological systems. The strong hydrogen bonds present peculiar and challenging problems which often are not straight extrapolations of those appearing with weaker bonds. We shall be concerned in the following with some of those problems following the lead of infrared spectra.

Infrared spectroscopy has been in the past a source of most important informations on hydrogen bonding and still is the easiest method for their detection and characterisation. The most general manifestations of hydrogen bonding appearing in infrared spectra—band shifts and broadening, increase of absorption intensity—are well known. Very often, and particularly when the shift is of the order of 500 cm^{-1}, the X—H stretching band develops an irregular structure and more or less distinct submaxima. This is particularly well documented with dimeric and polymeric carboxylic acids[1]. The origin of the submaxima has been treated in terms of Fermi resonance of the ν X—H fundamental mode with combinations of internal modes[1] and good evidence for this has been recently presented[2]. More sophisticated approaches based on the interaction of ν X—H with the low frequency "intermolecular" mode of the hydrogen bond have also been advanced[3,4].

Very strong hydrogen bonds-spectral and other characteristics

With hydrogen bonds stronger than, for instance, those in carboxylic dimers the absorption pattern in the region above 1600 cm^{-1} is very peculiar. Instead of one, more or less structured, X—H stretching band there appear several, most often three bands (Fig. 1) which are connected with proton vibrations. This type of spectra has been designated (i) and the bands A, B, C[5] may be taken as characteristic of a class of very strong hydrogen bonds. As an excuse for this classification the fact may be taken that with type (i) spectra the usual correlations based on ν X—H shifts and other band characteristics loose their meaning since it simply cannot be decided which peak represents actually the stretching mode.

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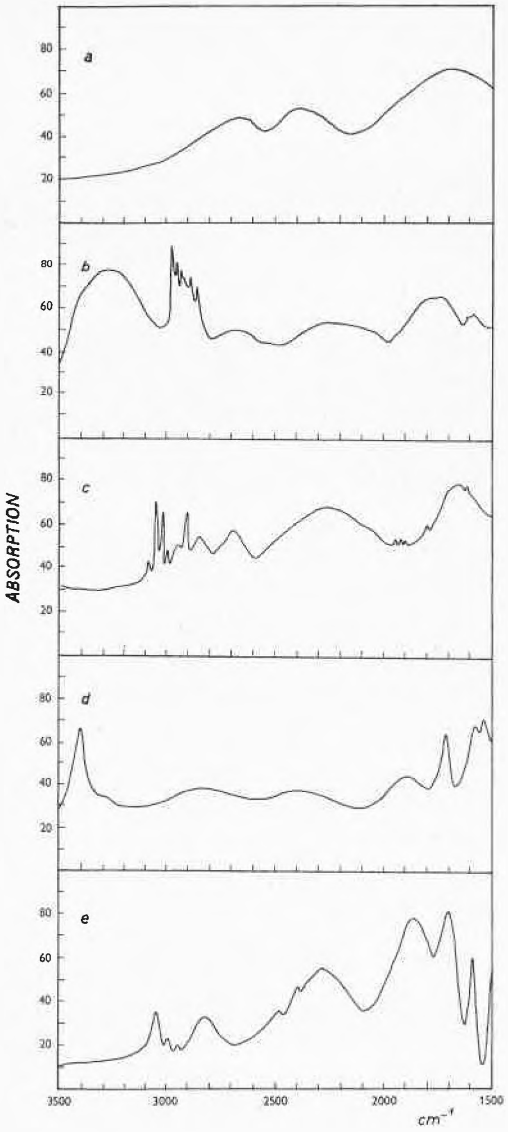

Fig. 1. Examples of (i) type spectra

a KH_2PO_4
b 2,3,4-trimethyl-pentane-2,4-phosphinic acid hydrate
c *p*-toluene seleninic acid
d acetylglycine
e adduct of trichloroacetic acid with dimethylsulphoxide

There are many one and two component, solid and liquid systems which exhibit this type of spectra. Examples (Table 1) of single component systems are inorganic and organic hydrogen phosphates and arsenates, arsinic, seleninic and phosphinic acids, and certain acid salts of carboxylic acids (type B[6]). The two component systems are in general adducts of acids with appropriate bases[7].

Table 1. Examples of hydrogen bonded crystals exhibiting type (i) infrared spectra

Compound	$R_{O\ldots O}$ (Å)	Frequencies of A, B, C bands (in cm^{-1})	Ref.
KH_2PO_4	2.48	2750, 2400, 1600	*a*
KH_2AsO_4	2.49	2700, 2350, 1680	*b*
$NaH_3(SeO_3)_2$	2.55	2750, 2350, 1600	*c*
KH-di-*p*-nitrobenzoate	2.48	2800, 2450, 1920	*d*
2,3,4-trimethyl-pentane-2,4-phosphinic acid hydrate	2.49	2600, 2120, 1630	*e*
Dibenzyl phosphate	2.49	2650, 2280, 1700	*f*
Phenylseleninic acid	2.52	2720, 2270, 1660	*g*
KH-phthalate	2.546	2900, 2450, 1900	*h*
Acetylglycine	2.558	2800, 2400, 1924	*i*
Dimethylarsinic acid	2.57	2700, 2350, 1740	*j*

a G. E. Bacon and R. S. Pease, *Proc. Roy. Soc. A 230* (1955) 359.
b D. H. Dickson and A. R. Ubbelohde, *Acta Crystallogr. 3* (1950) 6.
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j J. Trotter and T. Zobel, *J. Chem. Soc. 1965*, 4466.

Table 2. Equilibrium constants and enthalpies of association of chloroacetic acids with some oxo bases (in CCl_4, 25 °C)

Acid	Base*	K_{as} ($l \cdot mol^{-1}$)	ΔH ($kcal \cdot mol^{-1}$)
Monochloroacetic	DPSO	$1.55 \cdot 10^3$	6.5
	DMSO	$5.63 \cdot 10^3$	8.6
	TPPO	$7.16 \cdot 10^3$	10.2
	TOPO	$1.60 \cdot 10^5$	13.4
Dichloroacetic	DPSO	$2.37 \cdot 10^3$	6.9
	DMSO	$1.9 \cdot 10^4$	9.4
	TPPO	$4.36 \cdot 10^4$	12.2
	TOPO	$3.14 \cdot 10^5$	23.7
Trichloroacetic	DPSO	$4.77 \cdot 10^3$	7.4
	DMSO	$4.53 \cdot 10^4$	10.1
	TPPO	$7.00 \cdot 10^4$	13.9
	TOPO	$8.20 \cdot 10^5$	29.2

* DPSO = diphenylsulphoxide
DMSO = dimethylsulphoxide
TPPO = triphenylphosphine oxide
TOPO = trioctylphosphine oxide

Before analysing the features in type (i) spectra we shall briefly review the informations obtained by other methods. An illustration of the strength of these bonds is given by the equilibrium constants and enthalpies of formation for some acid-base systems in solution (Table 2). The data were obtained[8] by infrared spectrophotometry and the values of the thermodynamic quantities are much higher then the often quoted "average" hydrogen bond energies.

Crystal structure data are available for a score of substances exhibiting type (i) spectra. They show that $R_{O\ldots O}$ (the hydrogen bond lengths) are in the broad range of 2.57 Å to 2.45 Å (Table 1). Representatives of any type of association by hydrogen bonds are found in this small collection: open and ring dimers (acid salts of carboxylic acids and dimethylarsinic acid, respectively) chains and networks (phosphates), and even bonds between unlike molecules. Some are formally charged but others are neutral.

Semitheoretical potential functions[9, 10] for O—H ... O hydrogen bonds of 2.55 Å or less predict the existence of two rather closely spaced minima separated by a small barrier which allows the proton to tunnel between the minima nearer to one or the other oxygen (or other corresponding heavy atom). The minima may be equally deep or otherwise (Fig. 2) which depends on difference between the proton donating and accepting atoms or groups and their protonic energy levels. In general, it is expected that the structures of the type $(AHA)^-$ where AH is a Brönsted acid and A^- its conjugate base (mono or polyatomic) and similarly $(BHB)^+$ will have hydrogen bonds with equally deep minima which, however, may be distorted to unlike ones particularly in crystals under the influence of cooperative effects.

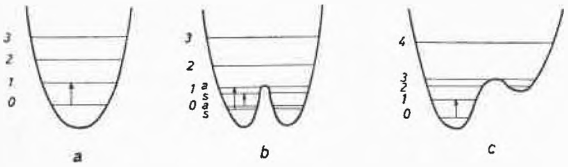

Fig. 2. Some schematic potentials with vibrational levels

a single minimum
b symmetric double minimum
c asymmetric double minimum

The X-ray diffraction studies and even those using neutron beams are not very helpful in providing detailed information about the type of potential and the proton motions. What can be learned from neutron diffraction measurements are the probable distances between the two minima after the corrections for thermal motions have been taken. However, even this is possible only to a lower limit of about 0.16 Å since at this limit the diffraction effects of a proton moving with a large amplitude in a flat central minimum are the same as for a proton tunneling between minima of this spacing[11]. Symmetrically divided proton densities i.e. half-density near to each oxygen may indicate either a statically disordered structure or tunneling. Such cases are e.g. ice[12] and boric acid[13]. However, the barrier is here too large to allow tunneling neither is there any other evidence for it except in connection with defects. If the distances between the heavy atoms around the bridging proton are unequivalent then it is clear that the proton has no equal probability of dwelling, i.e. the potential is asymmetric. For instance, the C—O bonds in one molecule of glycolic acid in rubidium hydrogen bisglycolate[14] are 1.212 and 1.308 Å, and in the other 1.241 and 1.264 Å, respectively. The proton is certainly fixed near the oxygen with the longest distance and the potential is considered to be asymmetric even without locating the proton. KH_2PO_4 (KDP) is a more difficult case. The neutron diffractions[15] show an elongated spot along the O ... O axis in which the protons may be placed about 0.30 Å apart. This is compatible either with a true or statistical equality of the potential minima as well as with a flat, central potential. KDP is representative of a large family of ferroelectrics and is undergoing the transition at 121 °K. This property prompted extensive investigations of which particularly those using nuclear magnetic resonance and relaxation methods have given more detailed information about proton dynamics. The proton motions are closely related to the mechanism of the spontaneous polarization and the changes near the transition are well reflected in the proton (and deuteron) correlation times. It is not possible to enter here the details, but for the present purpose it is enough to note that the potential is asymmetric so that the proton executes many oscilations in the deeper well before it jumps over to the other well. The mean time between the jumps in KD_2PO_4 is estimated to be 10^{-12} sec[16]. The jumps are assisted by energy from lattice vibrations and the jumps of a series of protons are correlated so that the potential wells exchange their depth. On the time scale of the diffraction experiment the minima are equalised and the diffraction picture shows an equal probability for the proton on both sides of the bond. In the ferroelectric phase the frequency of the vibrational mode assisting the protons goes to zero and the protons are practically frozen in on one side of the bonds. This is shown also in the diffraction picture[15]. KDP and RbDP have a third, high temperature phase[17], in which there is no appreciable proton jumping. For the following discussion of the infrared spectra it is important to note that the spectra of all three phases are essentially similar in the high frequency region i.e. each phase exhibits the A, B, C bands at about 2750, 2400 and 1600 cm^{-1}. There are, of course, important differences in the lower frequency regions. Informations about proton motions corresponding to those from the ferroelectrics are not available for other materials exhibiting type (i) spectra to which we are now coming back and will examine preferably in the two component systems.

The study of two component systems offers the advantage that with the choice of suitable acid-base pairs the strength of the hydrogen bonding can gradually be changed and thus its influence on spectral and other features may be systematically observed. Two such series were investigated; in one mono-, di-, and trichloro-

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acetic acids were the proton donors and as acceptors sulphoxides, phosphine oxides and similar oxo bases were used[7]. In the other series isothiocyanic acid was the donor and the bases were extended towards the weaker extreme[18]. The main results of these investigations combined with those on single component, solid systems will be here only summarised since the details are already published. The pattern of the A, B, C bands seems to be rather characteristic of the proton donor; the band frequency and the intensity are but little influenced by changes of phase or temperature. If the bond strength is increased the higher frequency band (A) will move to lower frequencies whereas those of bands B and C change very little. The intensity of A decreases whereas B, and particularly C, increases. This can be well observed with adducts of isothiocyanic acid which cover the range from the weakest bonds where the ν NH band has a simple contour to well developed (i) type spectra. This is due to the weak self association of HNCS which, in turn, is a strong donor of protons. The shift and intensity increase of the NH stretching band are linearly related[18]. This trend holds for the main peak up to the point where the extra bands B and C begin to appear, but also further on if the sum of the intensities of all three bands is considered. This point is of importance for the explanation of the origin of these bands.

Since the systems with (i) type spectra have $R_{O...O}$ distances for which potentials with comparably deep minima and low barriers are expected it was tempting to seek the explanation for the multiplicity of bands in terms of transitions between the split vibrational levels in such potentials[19]. This is shown schematically in Fig. 2. Moreover, it was possible to fit the observed frequencies of KDP to a reasonable potential[20]. However, it is this very example which casts the strongest doubts on this explanation because the bands A, B, C change very little throughout the crystalline phase changes where the potential must be changing considerably. At any rate, the instantaneous potential in KDP as seen by the proton is too asymmetric to give rise to such strong splitting as the A, B, C bands suggest. In the acid-base adducts the potential is estimated to change much more than the frequencies of the A, B, C bands reflect. The comparison of the frequencies predicted from model potentials with the observed bands is, however, not very reliable because of many factors which complicate the actual spectra, but nevertheless the trends in the A, B, C bands are too different from what one is expecting on hand of model potentials[21]. It is actually surprising that nothing like typical double minimum energy terms is in fact observed amongst the many examples. Probably in systems exhibiting type (i) spectra the difference between the two minima of potential energy exceeds the spacing between the ground and first excited level. The proton is thus located in the deeper well and this explains why the A, B, C bands are to some extend influenced by the structure of the proton donor. The location of the proton is shown also by other spectral features e.g. carbonyl frequencies.

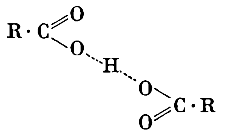
Since the explanation based on proton tunneling appears unlikely an alternative one was proposed[7]. The bands B and C are believed to be due to an intensity contributing interaction between the X—H fundamental, represented by band A, and overtones which are most likely those of X—H deformation vibrations. This is supported by the fact that the frequencies of the bands B and C roughly correspond to twice the δ X—H frequencies. It is also supported by the before mentioned intensity behaviour of all the three bands and by the fact that the bands appear in the RAMAN spectrum with a very similar pattern as in the infrared[22]. The necessary condition for the interaction between the fundamental and the overtones leading to the intensification of the latter is strong anharmonicity. This has now been proved beyond doubts[23, 8]. A quantitative background for this explanation is still lacking but, on the other hand, no strong objections against it exist amongst the known examples. An interesting explanation also involving overtones, has been proposed by CLAYDON and SHEPPARD[24]. They assume a single, broad ν OH absorption dissected by transmission regions in a pattern which foreshadows three separate bands. The generality of this hypothesis has been questioned[8].

Possibly symmetrical hydrogen bonds

From semi-theoretical model calculations as well as from non-empirical calculations of energy surfaces symmetrical hydrogen bonds should be formed when $R_{O...O}$ is shortened beyond 2.5 Å. By "symmetrical" are understood bonds with a single, central minimum of potential energy for the proton between two heavy atoms. The minimum may be more or less flat or may even have a small hump at the bottom and thus being more accurately considered a double minimum potential. However, if the top of the barrier is well below the lowest vibrational level the potential will be for all practical purposes indistinguishable from a flat bottomed one without barrier.

The best known representative of symmetrical hydrogen bonds is in the $(FHF)^-$ ion. The F ... F distance was determined by diffraction methods to be 2.264 Å (in $NaHF_2$[25]) and also an approximate central position of the proton was found but, as mentioned before, it is not possible to differentiate by these methods between the single minimum potential and one with closely spaced double minima. In principle it should be possible to deduce this from the vibrational energy levels which, however, requires a reliable assignment of the bands. For example, the infrared spectrum of KHF_2 shows fundamental bands at 1225 and 1450 cm^{-1}, and a probable overtone at 5099 cm^{-1}. A RAMAN active band is at 600 cm^{-1}. The first proposed assignment[26] of the two infrared bands was to the two allowed transitions between the split levels ($\nu_{0s} \rightarrow \nu_{1a}$ and $\nu_{0a} \rightarrow \nu_{1s}$), but this has been later changed in favour of the alternative assuming a single minimum. The 1450 cm^{-1} band would thus be the asymmetric stretching and that at 1225 cm^{-1} the deformation vibration[27]. Alternative assignments have also been discussed[28] showing the difficulties which arrise even in such a simple case. The solution to the problem of the potential function in the (FHF)$^-$ ion has been obtained by combining the isotope effect both in the vibrational spectra and on the F ... F distance[29]. In fact, model calculations in which both the proton and the heavy atom vibrations are taken in account show that with symmetrical potentials there should be no change in the distance between the heavy atoms on deuterium substitution whereas double minimum potentials should cause an elongation of the hydrogen bond[30].

Another interesting example of symmetrical hydrogen bonding is $HCrO_2$[31] which changes to a double minimum potential on replacing H by D. Potentially symmetrical hydrogen bonds are frequently encountered amongst the acid salts of carboxylic acids having the structure:



There are two main types of them. One, termed B by Speakman[6], contains pairs of molecules in which the C—O bond lengths are close to those found with neutral salts and undissociated acids, respectively. They typically exhibit infrared spectra of type (i)[5]. In the other type, A in Speakman's classification[6], the two molecules are equivalent and, most often, related by a centre of inversion or a two fold axis of rotation. The coincidence of the centre of the hydrogen bond with a crystallographic centre of symmetry is not a prerequisite for the equivalence of the molecules as shown, for instance, by the dileucine ion[32]. Neutron diffraction studies of a few acid salts have shown that the proton is indeed at or near the center of the hydrogen bond[33,34,35] but, again, they cannot exclude the possibility that the potential has two minima and a low barrier in between. Even before the results of neutron diffractions were known it was concluded from the infrared spectra that the symmetry followed from X-ray diffraction analyses was not merely statistical but that the hydrogen bond in type A acid salts must be very nearly symmetrical[36]. These spectra classified[5] as (ii) are in fact so characteristic that they were often used as a lead to later following diffraction studies. The most striking feature in these spectra is a very strong and broad absorption culminating somewhere between 600 and 1200 cm^{-1} which appears instead of the usual OH stretching band in the higher frequency region of the spectra (Fig. 3).

The spectroscopic approach to the problem of the symmetry of the hydrogen bond in type A acid salts is more difficult than in (FHF)$^-$ since the spectra are far more complex. The most important step is to locate the bands concerned with the vibrations of the O ... H ... O grupation, in particular the asymmetric stretching, and to study their behaviour on deuterium substitution and on cooling to low temperatures.

The assignment of the ν_{as} OHO vibration to the before mentioned strong absorption is considered to be now fairly certain. It is based on its dichroism in transmission and reflection (ATR) spectra of oriented samples, its absence from Raman spectra, and the mass effect[37]. Indeed, in some acid salts, e.g. those of trichloroacetic acids and in $NaH(CH_3COO)_2$, the ν_{as} OHO band moves to lower frequencies by a factor close to that in harmonic oscillators whereas in others e.g. potassium hydrogen anisate, it moves very little. There are also differences in trends on cooling. No appreciable shift of ν_{as} OHO in the acid acetates is observed when the samples are cooled to liquid nitrogen temperature, but in others this band moves to lower frequencies by as much as 30 p.c. From this it is quite evident that the potential is not the same in all type A acid salts. Concentrating on the mass effect some comparisons can be made with the results of calculations on model potentials. For the cases where the frequency ratio of the proton and deuterium stretching bands is close to 1.4 it is very likely that the potential is a single minimum one whereas for cases showing a ratio close to 1 an asymmetric double minimum one is more probable[21,30]. For any more definite and reliable statements about the shape of the potential function it would be necessary to observe several bands due to transitions between higher levels but the prospects of assigning these are not bright at all. However, there is some additional evidence in favour of the genuine symmetry of the hydrogen bond in certain acid salts or otherwise. A qualitative argument for the assymetry in those cases

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in which there is no or very little mass effect on the ν_{as} OHO frequency is offered by the crystallised adduct between pyridine-N-oxide and trichloroacetic acid[38]. The acid is connected to the base by an extremely short hydrogen bond of 2.41 Å which cannot possibly be symmetrical because of the structural differences of the two respective oxygens. The infrared spectrum is of type (i) and the ν_{as} OHO band does not move on deuterium substitution, but becomes weaker.

Evidence in favour of the symmetrical hydrogen bond in potassium hydrogen bistrifluoroacetate[39]—a representative of the acid salts of which the vibrational spectra are not contrary to such a bond—is derived from two other sources. One is the mass effect on the O ... O distance. Careful neutron diffraction analysis shows[40] that the distance is the same for hydrogen as for deuterium. This is a very strong argument. The other is less direct and is based on the deuterium quadrupole coupling constant (DQCC). This can be determined, *inter alia*, from measurements of the quadrupole perturbed deuteron magnetic resonance on single crystals and reflects the gradient of the electric field at the site of the deuteron. Thus DQCC is very sensitive to the charge distribution in the hydrogen bond which eventually determines the potential. The DQCC is correlated to the O ... O distance[41], and also to the OH stretching frequency[42], and assumes values between 315 (free OD in D_2O) and 56.0 kc/s. The latter value was obtained with potassium hydrogen maleate which contains most likely an intramolecular symmetric hydrogen bond[43]. A value even slighly smaller—55.6 kc/s—was obtained for the bistrifluoroacetate[44]. The DQCC calculated from charges obtained by the CNDO/II method under the assumption of a centrally placed proton are in good agreement with the observed values[45]. It should be emphasized that the DQCC for similarly short but asymmetric hydrogen bonds such as in the ferroelectric triglycine sulphate are considerably larger (79 kc/s[46]).

Besides the acid salts of carboxylic acids there are candidates for symmetrical hydrogen bonding to be found amongst other acid salts such as acid phenolates[47], oximates[48], and of inorganic acids. The dinitrate ion seems to be controversial. The infrared spectrum is of type (ii)[49], but X-ray structural data indicate a very large distance between the oxygens[50]. The halides besides fluorine and pseudohalides (NCS^-) are also prone to form dihalide ions in association with large cations (tetraalkyl ammonium, tetraphenyl arsonium and phosphonium, cesium), but the evidence of symmetry of hydrogen bonding in these salts comes only from vibrational spectra[51, 52], except for $CsCl \cdot \frac{1}{3}(H_3O^+HCl_2^-)$ for which only X-ray structural data are available[53]. A very short and potentially symmetrical hydrogen bond has been recently found in $KH_2PO_4 \cdot H_3PO_4$[54].

Contrasting the acid salts in formal charge of the hydrogen bonded ion are the half neutralized bases such as acetamide hemihydrochloride[55], picoline-N-oxide hemihydrobromide[56] and antipyrine hemiperchlorate[57] which have also extremely short hydrogen bonds and exhibit (ii) type infrared spectra. Particularly important amongst these positively charged complexes is the hydrated hydroxonium ion $H_5O_2^+$ which appears in dihydrates of hydrogen chloride[58], bromide[59] and of the perchloric acid[60]. By crystallographic criteria the hydrogen bond in these compounds might be symmetrical. The infrared spectrum of $H_5O_2^+$ in perchloric acid dihydrate has been treated in terms of such bonding although it is more similar to that of the H_3O^+ ion than to type (ii) spectra[61]. A representative of the intramolecular symmetrical hydrogen bond has already been mentioned—the acid ion of maleic acid. There is every reason to believe the genuine symmetry which seems to be undisturbed even if the whole molecule is made assymmetric by replacing one skeletal hydrogen by chlorine[62]. Interestingly enough, the spectrum cannot be classified under (ii) and the ν_a OHO stretching has not been located[63]. Another often quoted example of a short intramolecular bond is nickel dimethylglyoxime. The assignment of the ν_a OHO mode was controversed[64], but a recent reexamination of the infrared spectrum using a better instrument revealed that it is actually of type (ii) and that the ν_a OHO band moves on deuteration to lower frequencies[65] which puts this compound in line with others likely to contain symmetrical hydrogen bonds.

So far we have mentioned only two main types of infrared spectra of strongly hydrogen bonded compounds with a subdivision of type (ii) according to deuteration behaviour. This does not mean that there is a discontinuity in spectral features as the bonding increases in strength and that there ist a gap between type (i) and (ii) spectra. Indeed, there are examples in which there are still bands A and B indicated, but the band C has taken over most of the intensity and has spread out to lower frequencies assuming the appearance of the ν_a OHO band of type (ii) spectra, but is centered at higher frequencies. This occurs in some acid-base adducts[5] and also acid salts such as potassium hydrogen oxalate[66] and fumarate[67] (Fig. 3). From structure determination we know that the bond is not symmetric[68]. This is true also for the potassium hydrogen formate where the differences in the C—O bond lengths of both molecules are very small[69]. The spectrum[67] is in this case even closer to type (ii). The diffraction and the spectral data may be interpreted in terms of a strongly anharmonic and asymmetric potential rather than a double minimum one with a potential barrier. However, more experimental work is required before better founded conclusions can be offered.

The examples with extremely short or even symmetrical hydrogen bonds mentioned here are formally ions with either positive or negative overall charge. This might mislead to the conclusion that these charges are of major importance for the existence of such

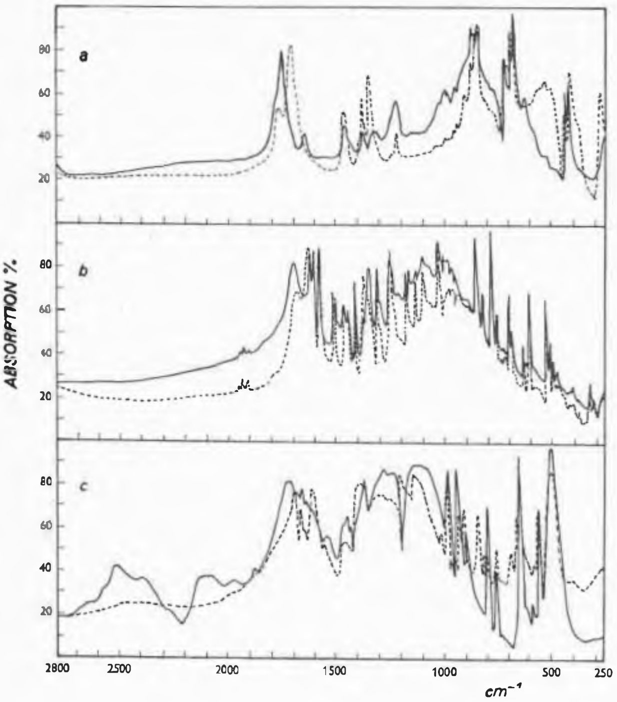

Fig. 3. Examples of (ii) and transition type spectra

a potassium hydrogen trichloroacetate
b potassium hydrogen dianisate
c sodium hydrogen fumarate
(—— normal; ... deuterated; all solids at −180°C)

bonds. One exemption, although not symmetrical, has been mentioned—the adduct of pyridine-N-oxide with trichloroacetic acid—and there are several more related ones at least from the spectroscopic point of view [7,18]. Di(*p*-chlor)diphenylhydrogenphosphate is also formally neutral but in the crystalline state the molecules are bonded to chains through extremely short bonds the centres of which coincide with a twofold axis [70]. The infrared spectrum [71] is also of type (ii) and thus the hydrogen bonding might indeed be symmetrical.

This brings us to the question about the factors favouring the formation of symmetrical hydrogen bonds or otherwise. In spite of the considerable number of examples no simple answer can be given. It is clear that a certain electronic and nuclear charge distribution is a prerequisite for the formation of very short hydrogen bonds. This is not only intuitively reached but can also be concluded from *ab initio quantum* mechanical calculations [72]. A very "soft" potential is likely to result which will easily be influenced by intermolecular factors—either squeezed to symmetrical or deformed to an asymmetrical one. This is shown by the fact that the acid salts of carboxylic acids of type A which can be melted or dissolved change radically their spectra from type (ii) to (i) [73] i.e. in the liquid state the hydrogen bond is not even approximately symmetrical. It is rather difficult to decide without further evidence whether the interactions in the crystal force the hydrogen bond into the symmetrical shape or whether the potential tends primarily to be symmetrical and exist as such in the crystal but is deformed in the liquid state. It would be necessary to have the hydrogen bonded entity in gaseous phase but this is not possible with the existing examples.

One further observation should be noted in connection with the structural influences on the type of potential. Apparently the O...O distance has but little influence on it. The (ii) and transition type spectra are found within a wide range of at least 0.1 Å ($R_{O \ldots O}$ between 2.45 and 2.57 Å) and the variety of nearly symmetrical potentials giving (ii) type spectra covers the range of 2.40 to 2.46 Å. This has been realised earlier [74] and is confirmed by new examples and more accurate length determinations.

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