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The manifestation of hydrogen bonding in the IR spectra of DL-threitol and erythritol (300–20 K)

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Abstract

The infrared (4000–400 cm^{-1}) and, in part, Raman spectra were recorded for the two isomeric polycrystalline sugar alcohols, DL-threitol and erythritol. Samples were pure substances and isotopically diluted OH/OD compounds. IR spectra were recorded in the 300–20 K range. Assignment of hydrogen bond structure sensitive out-of-plane bending vibrational modes for OH/OD-groups of different H-bond systems is based on isotope exchange and temperature variations. At least seven bands for threitol and two for erythritol correspond to differently H-bonded OH/OD-groups. Relative strengths and quantity of different H-bonds were evaluated. Unlike erythritol, threitol contains over 5% of weak H-bonds. The formation from the melt of a crystalline racemate as a molecular compound of D- and L-forms is suggested. Comparisons with previous neutron scattering results are discussed. In solution, all four OH-groups of both tetritols form H-bonds of equal strength in accord with the basicity of the solvent.

Keywords: Tetritols; IR spectroscopy; Hydrogen bonds

1. Introduction

A large number of investigations by X-ray and neutron scattering methods of the crystal structures of carbohydrates, including those of the sugar alcohols and tetritols, have been published [1]. The tetritol crystals, DL-threitol and erythritol (a *meso* compound), are formed from the isomeric molecules. For the former, DL-threitol, several structures were reported with three [2], nine [3] and four [4] molecules per unit cell. All H-bonds in both crystals are intermolecular. The first two of these studies claim the existence of three different H-bonded chains, whereas the last work [4] claims this number to be four. For erythritol, two types of H-bonds were found, with the shorter ones forming an infinite helical chain and the longer ones—a finite quadrilateral structure [5].

Both substances, being the simplest representatives of carbohydrates, are of interest for a correlation between the structural and spectral manifestations of H-bonding, especially as their IR spectra dominated by H-bond features (the skeletal bands are few in a number and not very strong). Nevertheless, in contrast with structural investigations, only few studies of carbohydrate IR spectroscopy have been reported to date, despite the advantages of the method, especially when combined with cooling [6–8]. For the tetritols, only the mull IR spectra in the Aldrich catalog [9] were avail-

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able prior to the previous work by several of the present authors [10]. The latter study could, indeed, relate the very different water sorption capabilities of the two tetritols to their IR spectroscopy.

In the present work, we report for the first time IR spectra, supplemented in part by Raman spectra of DL-threitol and erythritol, of the out-of-plane bending mode $\nu_4(\nu'_4)$ range of the OH(OD) groups down to 20 K, using isotopic dilution ($\leq 10\%$ of the doped isotope). These experimental methods eliminate the two major causes of H-bond band broadening. The low temperatures minimize thermal broadening and isotopic dilution eliminates vibrational coupling in the H-bonded chains and thus improving the resolution of H-bonds [11–13]. The various hydroxyl group bands resolved could then be related to the abundance and strengths of different H-bonds in both crystalline substances.

2. Experimental

Polycrystalline powders of pure D-, L- and DL-threitol-OH and erythritol were supplied by Aldrich. The OD(OH)-forms (90–95% isotopic purity) were recrystallized from ethanol-*d* or deuterium oxide [14], also supplied by Aldrich. The sample, a KBr pellet, or a fine powder or a crystal film (prepared from the melt at 90–120 °C) placed between KBr plates, was attached to the cold finger of an Air Products Displex CS-202 cryostat. The accuracy of the temperature measurements was ± 1.5 K. Binary solutions of the tetritols at concentrations of 0.08–0.16 mol dm^{-3} were prepared by weight in distilled and thoroughly dried (molecular sieves) Me_2SO-d_6 and pyridine (Py) (Aldrich). For spectral measurements, 0.1 mm CaF_2 cells were used. IR spectra were recorded on a Bruker 113v FTIR spectrometer. Raman spectra of the solid samples were measured on an RFS 100S spectrometer equipped with a Nd YAG laser (1064 nm). Spectral resolution was better than 2 cm^{-1} for all measurements.

Spectra were processed using the Bruker OPUS (v. 2.2) program; the accuracy of the band deconvolution is estimated as better than 5%. The effect of overlap (in pyridine solutions) with neighboring ν(CH) bands was taken into account. Relative probable errors in absorptivity and integrated intensity are estimated as less than 7%. Band positions are specified in cm^{-1} and the values in parenthesis refer to bandwidths.

The spectra of D-, L- and DL-forms of commercial threitol are identical and we refer to them without distinction. Neither could we observe distinctions between spectra of erythritol recrystallized from the melt and from solvents. For threitol, if not otherwise specified, we refer to spectra of samples recrystallized from the solvent. Temperature induced spectral changes for both tetritols were reversible and highly reproducible.

The spectral behavior of weak bands, sometimes observed at 798 and 1260 cm^{-1}, allowed their attribution of OH threitol with atmospheric moisture.

X-ray analyses of powder samples were carried out on a Philips model PW 1710 automatic powder diffractometer using a Cu anode.

3. Results and discussion

Solutions.—The spectra of both tetritols either in Me_2SO or in Py are identical. Fig. 1 reproduces the spectra of threitol with spectral parameters of the ν(OH) band summarized in Table 1. As expected, in Py, the more basic solvent, ν(OH) is lower and its width and integrated intensity are larger. The main band, next to the weaker ν(CH) band on it lower frequency side, is symmetric in both solvents

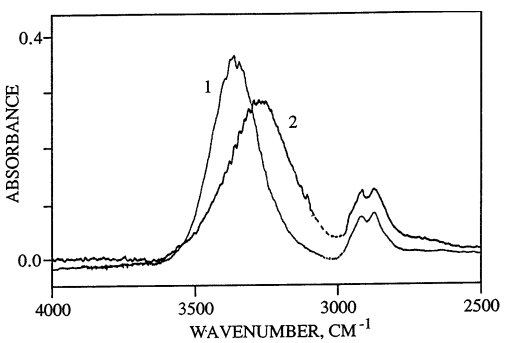

Fig. 1. IR spectra of DL-threitol in solutions: (1) Me_2SO-d_6; (2) pyridine. The spectra of erythritol are identical.

Table 1
Parameters for the ν(OH) band of erythritol, threitol and 1-butanol [15] in Me_2SO and pyridine (Py)[a]

Solvent	Me_2SO					Py				
Parameter	ν	γ	ε	A	$-\Delta H$	ν	γ	ε	A	$-\Delta H$
Erythritol	3366	190	109	5.60	20.7	3270	250	88	6.50	23.0
Threitol	3365	190	123	6.10	21.8	3270	240	88	6.60	23.1
1-Butanol	3377	156	137	5.80	21.2	3318	197	118	6.30	22.5

[a] ν and γ are the peak frequency and half-width in cm^{-1}, respectively; ε is the absorptivity in $dm^3\ mol^{-1}\ cm^{-1}$; A is the integrated intensity of the ν(OH) band (per OH-group), $(2.303/cl)\int \log(I_0/I)d\nu$ in 10^{-4} cm mmol; and $-\Delta H$ is the H-bond energy in kJ mol^{-1}.

with no indication of a multicomponent structure due to different H-bonds. The absorptivity and molar integral intensity per single OH-group were close to those for the single ν(OH) band of 1-butanol in solution [15]. Also, the H-bond energy estimated from both the ν(OH) band intensity enhancement (according to 'Iogansen's rule' [16]) and displacement are comparable to those of 1-butanol [15]. It may be concluded that, irrespective of the configuration of the isomer, all four hydroxyl groups of both tetritols form H-bonds of the same energy, in both solvents.

DL-*Threitol crystals*

Isotopically pure crystals. The threitol spectrum (Fig. 2(A)) at 300 K (Trace 1) shows several bands of medium or low intensity in the range below 1000 cm^{-1}. The three at 880 (35), 560 (10) and 477 (10) cm^{-1} are single and rather narrow while the 730 cm^{-1} feature is broad (>100 cm^{-1}) and poorly resolved. With decreasing temperature, all bands shift to higher frequencies. The band at 880 cm^{-1} blue shifts to 915 cm^{-1} at 20 K (Trace 5) and narrows down to 24 cm^{-1}. The bands 560 and 477 cm^{-1} shift only 3–4 cm^{-1} and their widths also change only insignificantly. The weak feature at 497 cm^{-1} emerges as a clear narrow band below 200 K (Trace 2) but does not significantly change upon further cooling. The wide feature at 730 cm^{-1}, unresolved at 300 K, develops into a set of seven narrow bands at 20 K (Trace 4) separated by 15–20 cm^{-1}.

Upon deuterium exchange (Fig. 2(B)), the three narrow bands at 760, 669 and 465 cm^{-1} are unaffected (best seen in Trace 4), with the first of them assignable to the out-of-plane CH vibration[1]. The bands discussed in the previous paragraph disappear, in support of their assignment to the ν_4 out of plane OH modes. Additionally, the OD-threitol crystal doped with OH-threitol spectrum (Fig. 2(B)) shows a peak at 909 cm^{-1}, of the ν_2 in-plane OD vibrations, as well as very weak ν_4 bands of the doped OH-groups (shaded in Fig. 2 and discussed below).

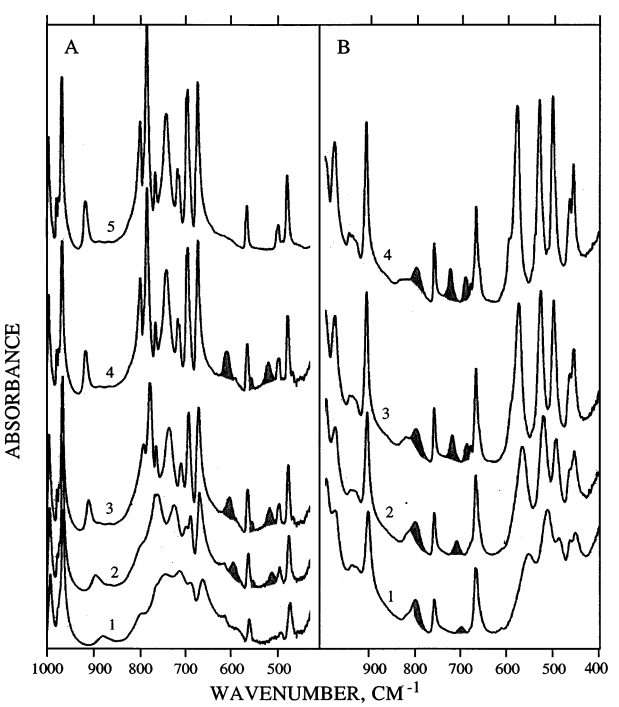

Fig. 2. The ν_4- and ν'_4-bands of isotopically pure and isotopically diluted samples recrystallized from the solvent at (1) 300, (2) 200, (3) 100, and (4) 20 K. Bands of doped isotope are shaded. (A) DL-Threitol-OH; (B) DL-threitol-OD. Trace A5 relates to commercial crystalline DL-threitol-OH at 20 K.

[1] This band is at 790 cm^{-1} in Me_2SO solution, and has analogs in spectra of pure secondary alcohols [9].

Table 2
Band positions (cm^{-1}) in the 1000–400 cm^{-1} range of OH/OD-threitol powder, estimated energies and relative abundance of different H-bonds[a]

OH-group	Threitol-OH + OD			Threitol-OD + OH			v_4 (average)	$-\Delta H$ (kJ mol^{-1})	Relative abundance (%)	
									Powder	Film
1	913.0						913.0	53.2	5.0	4.0
2	795.4	**608.3**			**799.3**		787.4	39.8	29	26
	779.5		*763.4*			*760.6*				
3	736.5						723.2	32.6	29	26
	710.0	**554.8**			**724.7**					
4	691.2			663.0 sh						
	669.0	**518.5**		670.0	**692.0**	*669.3*	680.1	28.4	29	26
				581.8	**681**?					
5	563.5			533.0			563.5	18.6	2.0	5.0
6	495.8			504.0			495.8	13.8	} 6.0	} 13.0
7	476.6		*465.8*	458.5?		*465.7*	476.6	12.5		

[a] Fonts: underlined, for H-bands of the matrix; **bold**, for the H-bands of doped molecules; and *italic* for skeletal bands

Further, one notes four well-separated narrow bands at 581.8 (14), 533.0 (10), 504.0 (9) and 458.5 (8) cm^{-1}. These correspond to the intensive and, at 20 K, well-structured OH-band at 730 cm^{-1} in OH-threitol. The OD-counterpart of the 913 cm^{-1} band is seen as a shoulder (≈ 663 cm^{-1}) on the skeletal band at 670 cm^{-1}. The OD counterparts of the OH-threitol bands at 560 and 477 cm^{-1} are outside the instrumental range. While the assignment of these bands to the v_4 vibrations is certain, the origin of the 458.5 cm^{-1} band in the OD spectrum is unclear, as it has no OH counterpart around 630 cm^{-1} in the OH-crystal.

Isotopically diluted crystals. A better understanding of structure of the wide v_4 OH/OD band (730 cm^{-1}/500 cm^{-1} at 300 K) is obtained from the spectrum of OD-groups diluted in OH-crystal and vice versa. The spectrum of doped OD crystals (Fig. 2(B)) in the 650–850 cm^{-1} region shows five peaks after cooling to 20 K. The 760 and 669 cm^{-1} peaks have been assigned to skeletal modes. The other peaks, shaded in the various traces of Fig. 2(B), show a gradual enhancement upon cooling. These bands represent uncoupled v_4(OH) bands in the mainly OD-threitol crystal. Analogously, the peaks shaded in the 500–620 cm^{-1} region in Fig. 2(A) represent the uncoupled v'_4(OD) modes in the mostly OH-threitol crystal. Peak positions of OH- and OD-threitol with doped OD or OH molecules, respectively, are summarized in Table 2. The positions of the uncoupled bands of OH-threitol as dopant appear at approximately the average positions of the coupled bands when this threitol is the main constituent of the crystal. This indicates that the splittings in the three pairs of peaks in the structured band of the pure OH-substance at (795.4 + 779.5), (736.5 + 710.0) and (691.2 + 669.0) cm^{-1} indeed originate from vibrational interactions of neighbors in H-bonded chains.

Turning to the v'_4 region in the mostly OD crystal (Fig. 2(B)), one notes a spectral structure which does not exhibit an analogous band pair structure. The relatively large wavenumber values of 30–50 cm^{-1} between the spectral peaks indicate the existence of different OD groups rather than a vibrational coupling analogous to that in the OH-crystal structure. This conclusion is further supported by the harmonic isotopic factor (1.36–1.37), relating these OD crystal bands to the isolated OH band positions (shaded peaks). In comparison, the isotopic ratio of decoupled OD-frequencies (mainly in OH-crystals) to the decoupled OH bands (mainly in OD-crystals) is significantly lower (1.30–1.33). This deviation of the v_4/v'_4 wavenumber ratios of the decoupled modes from the harmonic value also reflects the difference between OH- and OD-crystals—the diluted OH/OD band posi-

tions represent the H-bond arrangements in the host OD- and OH-crystals, respectively. Such differences may occur as a result of changes in the angles between neighboring H-bonds. A further indication of a difference between the OH- and OD-crystal structure has already been noted above by the existence at 458 cm^{-1} of an extra OD related peak in the OD crystal.

In Ref. [17] a unique structural change upon deuteration of trifluoroacetic acid tetrahydrate crystals was already pointed out. Isotopic effects on distances (0.06–0.08 Å) [18] and IR spectra [19,20] were also described for $H(D)CrO_2$, $H(D)CoO_2$ and $KH(D)C_2O_4$ crystals.

Temperature effects on the band parameters.—Usually, the temperature shift of the peak maximum upon cooling to lower (for ν_1) or to higher (for ν_4) frequencies is a definite characteristic of an H-band with wider bands being shifted more. The 'deformational' model of *T*-broadening [21] has successfully rationalized these experimental observations for H-bonded systems. Thus, lowering the temperature to 20 K effected a band narrowing by about a factor of 20 in the relevant *tert*-butanol bands [12] and in the present case 'isolated' threitol bands also demonstrate such a relation between bandwidth and blue shift of the peak position (Fig. 3). Thus, when band assignments are considered, the fact that a band is both narrow and exhibits a small *T*-shift should not exclude it from being assigned as an H-bond band. Moreover, when a wide band shifts, but from a certain temperature does not continue to reduce its width upon cooling, the existence of some residual disorder or a coupled H-bond system may reasonably be expected.

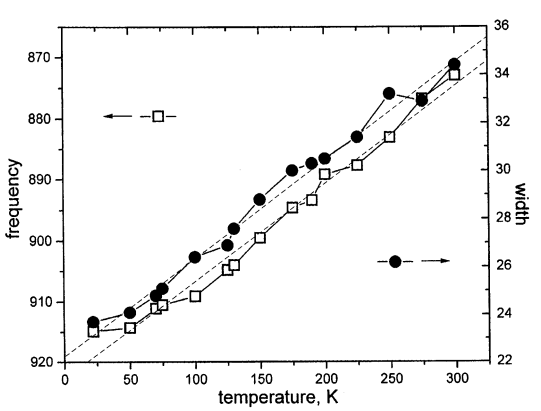

Fig. 3. Temperature dependence of the frequency and width of the 870 cm^{-1} band (room temperature value) of DL-threitol.

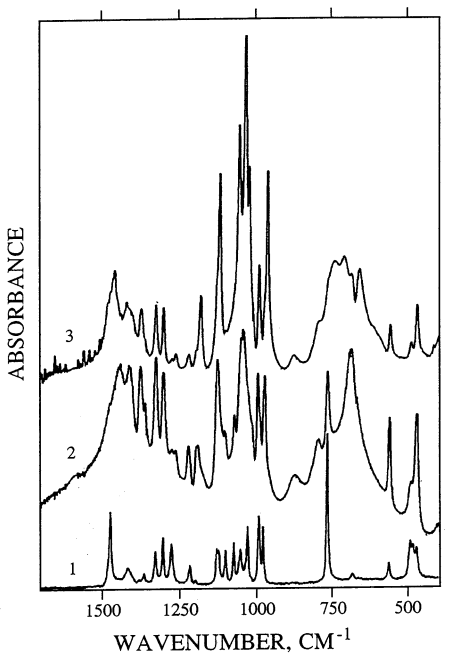

Fig. 4. Vibrational spectra of the different polycrystalline threitol samples (300 K). (1) Raman spectrum of commercial powder, (2) IR spectrum of film recrystallized from the melt, and (3) IR spectrum of commercial powder.

The absence of abrupt changes in the spectral properties of the band shown in Fig. 3 indicates an absence of phase transitions of threitol in the pertinent temperature range.

Some peculiarities of threitol crystallized from the melt.—It was found that the spectrum of the DL-threitol polycrystalline film produced from the melt is different in some details from that of the commercial crystals or samples recrystallized from a solvent. Fig. 4 reproduces the IR spectra at 300 K of DL-threitol samples produced with (Trace 2) and without (Trace 3) melting as well as the Raman spectra of the latter (Trace 1).

The IR spectra of polycrystalline films of DL-threitol and L-threitol prepared from the melt are identical and both (Fig. 4, Trace 2) are different from the spectra of the original commercial crystals (Fig. 4, Trace 3). Several of the 'fingerprint' bands in the powder spectrum (Trace 3), e.g., at 1470, 1420 and 1189 cm^{-1}, assigned to in-plane bending OH-vibrations (with assignment based on D-exchange)

change their structure or disappear in the spectrum of the film obtained from the melt (Trace 2). In the 'skeletal' mode region, the structure of the strongest band at 1040 cm^{-1}, the stretching $\nu(C-OH)$ vibration, is also different in the two IR spectra.

However, the most prominent differences between the spectra of both samples are in the range of the ν_4(OH) vibration at 730 cm^{-1}. In the spectrum of the polycrystalline film obtained from the melt (Trace 2), this band, assigned above to a superposition of ν_4-modes involving three chains of H-bonds, has half the width of its counterpart in the commercial sample (Trace 3). For this sample, recrystallized from melt, the skeletal band at 765 cm^{-1} (not affected by deuterium exchange, and assigned to the deformational –CH-mode) also appears with much (about three times) enhanced intensity.

As Fig. 4 shows, the low-frequency bands at 563 and 476 cm^{-1}, assigned to the ν_4 vibration of OH-groups forming weak H-bonds [10], change their relative intensity between both samples, but retain their width and position, when going from powder to film. Thus, different degrees of crystallinity cannot explain the rather drastic changes between the general spectral pictures obtained for the two crystalline forms in the 1600–600 cm^{-1} range. Moreover, X-ray powder diffraction (Fig. 5) also indicates a similar level of crystallinity for both samples.

No analogous differences between the two solid samples were found in the isolated ν_1 and ν_4 bands of isotopically diluted OH/OD-groups.

The identical spectra of the commercial pure D- and L-enantiomers and the racemate proves that racemic DL-threitol-OH crystallizes as a conglomerate of pure D- and L-enantiomers, in agreement with structural data [3]. The same conclusion follows from the spectra for 95% OH-threitol (doped with 5% OD groups) recrystallized from the solvent: this also exists as a conglomerate, in contrast to threitol-OD (see below). The observed differences in spectral features between the solid formed from the melt and the one crystallized from a solution may be attributed to changes in crystal structure or composition. Such change could well be a conversion of the racemic conglomerate of D- and L-threitol-OH on melting into a crystal of a binary molecular compound of the two enantiomers.

The X-ray powder pattern of the sample obtained from the melt is different from that of the commercial powder. The patterns are different in their relative peak heights and at least two peaks, hardly distinguishable in the solid, gain significant intensity in the solid from the melt (Fig. 5). This evidence of some structural change is also reflected in analogous changes in our IR results.

Such structural change is also manifested by the 765 cm^{-1} skeletal C–H band. It is very weak in the IR spectrum of the commercial powder and is the most prominent Raman band in this spectral region (Fig. 4). In the solid obtained from the melt it gains in IR intensity by a factor of three. This might be explained by the existence of a local center or element of symmetry in the former which is then absent in the latter solid, due to the presumed formation of the binary molecular compound following possible conformational changes [5,22].

In contrast to threitol-OH, this 765 cm^{-1} band is also prominent in the IR spectra of threitol-OD (Fig. 2(B)), as prepared by recrys-

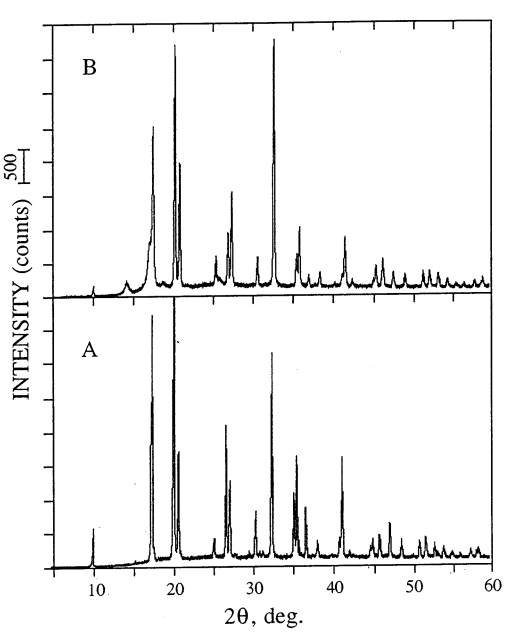

Fig. 5. X-ray powder pattern of DL-threitol solid samples. (A) commercial or recrystallized from a solvent, and (B) crystallized from the melt.

tallization from D_2O or OD-ethanol. The spectral changes for this band, between threitol-OD recrystallized from the solvent and in that obtained from the melt, were not observed for the threitol-OD solids. Possibly, threitol-OD, in contrast to its OH analog, undergoes this structural transformation at temperatures lower than the melting point. This further confirms the difference in structural properties between OH- and OD-crystals, pointed out above.

The decoupled ν_4 modes of the OH- and OD-threitols reflecting the structure of the H-bonds in the host crystal, do not change at all, indicating that the main H-bonded structure does not change significantly upon melting.

Erythritol.—The spectral region of this mode of erythritol (Fig. 6(A)) comprises one medium-intensity doublet band at 887 (12) cm^{-1}, 867 (12) cm^{-1} and a well-structured band near 730 (759.3, 740, 729, and 690) cm^{-1} (listed band positions are for 20 K). All bands shifted upon cooling and disappeared upon D-exchange. In erythritol-OD, the first doublet shifts isotopically to 611 cm^{-1} and coincides with a skeletal (unshifted isotopically) band, resulting in a higher intensity of the resulting composite band; the second band isotopically shifts to a structured at 556.6 and 538.7 cm^{-1}.

In the range of the OH-groups doped in the OD-crystal (Fig. 6(B)), the H-bands at 751.4 cm^{-1} corresponds to the structured bands of the pure substance at 730 cm^{-1}. The isotopically diluted OD-bands in OH-crystals are seen as a narrow peak at 548.0 with a shoulder at 540 cm^{-1}, a spectral region free of the other erythritol bands (Fig. 6(A), Trace 5). This frequency again coincides with the mean frequency of the double peaked OD-band of the pure substance and is assigned to OD-groups in H-bonded chains. The isotopic ratio is 1.37 with no significant indications of structure differences between the –OH and –OD solids. The D-counterpart of the second H-band (at 867 cm^{-1}) is not seen at this concentration of isotope.

For both OH- and OD-decoupled bands, a doublet structure is indicated. The latter is observed in a spectral range free of interference from OH-erythritol host solid bands, and its analysis is more reliable. The deconvoluted components at 539 (10.5) cm^{-1} and 548 (8.3) cm^{-1} have a 1:2 intensity ratio. The same intensity ratio is observed for the components of the decoupled ν_1 (not described here in detail), a mode based on the same H-bonds. For the latter, the low-frequency component shows the higher intensity, contrary to the present case. As H-bonding effects a red shift in the stretching mode along with a blue shift in the bending mode region, the observed split band structure corresponds to H-bonding of

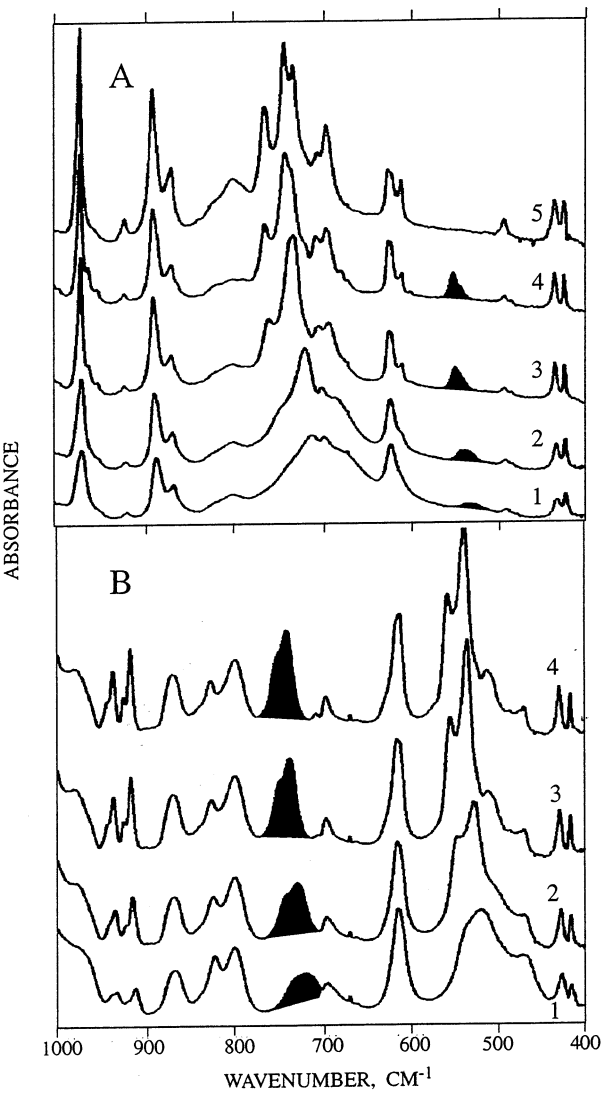

Fig. 6. The ν_4- and ν'_4-band of OH/OD erythritol. (A) ν_4/ν'_4 region of erythritol-OD in erythritol-OD crystals. Isotopically diluted bands are darkened. (B) ν_4/ν'_4 region of erythritol-OH in erythritol-OD crystals. Isotopically diluted bands are shaded. (1) 300, (2) 200, (3) 100, and (4) 20 K. Trace A5 is a pure commercial sample without doped isotope at 20 K.

different energies of 1.5 ± 0.5 kJ mol^{-1} [16]. A similar static irregularity of H-bonds in the chains was observed in ethanol crystals [13]. For the decoupled ν_4(OH)-band, the intensity ratio is reversed, possibly due to an accidental coincidence with a skeletal band. The alternative explanation of a change in the ratio of weaker and stronger bonds in H- and D-crystals is not reasonable.

Quantity and strength of H-bonds in tetritols.—While the frequency of ν_4-bands of alcohols may be significantly affected by environmental influences (the solvent, interaction with neighboring OH groups), their integrated intensities remain, essentially, unaffected [16]. Thus, when different OH-groups (and H-bonds) are present, the integrated intensity of these bands is a good measure for the relative abundance, as summarized in Table 2. The main conclusion is that, although not evident from X-ray studies, H-bonds other than those in the main chain may reach a relative abundance of 11–17%. It is also noted that after melting, the relative abundance of the weaker H-bonds (band positions < 600 cm^{-1}) is approximately doubled.

The ν_4(OH) wavenumbers can be related to H-bond energy (the enthalpy of H-bond formation in liquids) [16,20] by the following equation:

$$-\Delta H = 0.67 \times 10^{-4}\ \Delta\nu^2$$

where $\Delta\nu^2 \equiv (\nu_H)^2 - (\nu_0)^2$, the subscripts H and 0 pertaining to H-bonded and free molecules, respectively, and $-\Delta H$ and ν are in kJ mol^{-1} and cm^{-1}, respectively. The higher ν_4(OH) frequency is due to a higher potential barrier to changes of the X–OH angle, with an additional force constant expressing the H-bond attachment, schematically denoted by the X–OH···B. The relationship above, established for solutions, is valid for crystals [20], provided the H-bonds do not deviate from linearity. Structural data indicate that, for tetritols, the H-bonds angles are all over 155° [3]. For all four OH-groups of the tetritols the same $\nu_0 =$ 200 cm^{-1} was assumed, taken from the values for gas-phase monohydric alcohols [23]. The enthalpies are listed in Table 2. The accuracy is estimated to be ± 4 kJ mol^{-1} and, obviously, the relative changes are more reliable than the absolute values.

If the H-bonds in the crystal structure [3] are grouped according to H···A bond length, seven such groups may be distinguished in rough agreement with such band groupings in the IR spectra. However, it is impossible to directly correlate bond lengths and specific band positions. Bond energies are dependent upon both the bond lengths and geometrical factors. For erythritol, we suggest at least two types of H-bonds may be distinguished—one fairly strong (887 cm^{-1}) and a chained-system of lower ν_4 frequency (751 cm^{-1} at 20 K, when decoupled). At the lowest temperature (20 K), the chain reveals some residual irregularities. The corresponding estimated energies are 50 and 33.5 kJ mol^{-1}, respectively, and their relative abundance is about 1:4. In contrast to DL-threitol, no evidence for even weaker H-bonds was found, which was suggested as the explanation for the very different water-sorption capability of these crystals [10].

Neutron diffraction studies [5] first suggested the existence of two kinds of H-bonds. Of these, the shorter ones have a H···O bond length of 1.699(2) Å, a O – H···O bond angle of 173(2)°, and they also form infinite helical chains. The others, with H···O = 1.788(2) Å and a O–H···O bond angle of 164(2)°, form closed quadrilaterals. Our IR data for erythritol not only confirm the existence of two types of H-bonds, but also provide an estimate for their relative abundance. However, from our results that the ν_4 band with the lower frequency shows a splitting, it follows that it is the longer and weaker H-bonds that form the H-bonded chain. On the other hand, the shorter and stronger H-bond system appears as a non-structured band and so it may originate quadrilaterals which have an angle close to 90° between neighboring H-bonds.

Acknowledgements

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