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Infrared spectra and hydrogen bonding of pentitols and pyranosides at 20 to 300 K

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Abstract

Infrared spectra in the range 400–4000 cm^{-1} of three pentitols — ribitol, xylitol, D-arabinitol, and of three pyranosides — methyl α-D-manno-, methyl α-D-gluco- and methyl β-D-galactopyranoside, as polycrystalline solids of both the pure OH and > 90% isotopically substituted OD compounds, were recorded at 20–300 K. In the low temperature spectra of the OH substances, at least three isolated narrow bands in the stretching mode and about ten narrow bands in the out-of-plane-bending mode range (< 1000 cm^{-1}) are affected by cooling. Almost all have counterparts in the respective OD spectra with frequency ratios of 1.30–1.40. On this basis, they are assigned to OH groups bonded in H-bonds of different strengths (from 10 to 50 kJ mol^{-1}). The average number of the OH···O hydrogen bonds is found to be two to three times larger than indicated by the stretching mode only or by structural data. The newly measured peak frequencies of the very narrow decoupled stretching mode bands show a correlation between the red shift ($\Delta\nu$) and the H-bond length. As previously found for tetritols, the presence of weak H-bonds (bond energy < 14 kJ mol^{-1}) is related to the different water sorption capabilities of the pentitols. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Carbohydrates; Infrared spectra; Red shift; Hydrogen bonding energy

1. Introduction

A large number of investigations of crystal structures of carbohydrates by the X-ray diffraction and neutron scattering methods have been published, including the structures of sugar alcohols (alditols) and pyranosides [1]. In contrast with these structural investigations, only relatively few infrared spectroscopic studies of carbohydrates have been reported to date, despite the advantages of the method, especially when combined with cooling and isotopic exchange. The lowering of the temperature minimises thermal broadening and isotopic dilution eliminates vibrational coupling, which to a certain extent is always present and is manifested in spectra of the differently organised H-bonded chains. Thus, the resolution of infrared bands can be much improved in both the stretching and the out-of-plane-bending vibrational mode spectral ranges [2–4]. In some previous studies, cooling was indeed used, but not below 77 K [5,6]. The importance of the out-of-plane-bending range of the infrared spectrum for the study of carbohydrates at low temperatures was first shown by Katon et al. [7] 30 years ago, but so far only our own studies [8,9] made extensive use of it.

In the present work we report infrared spectra of the three isomeric pentitols and of three

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isomeric methyl pyranosides in the stretching mode range (ν_1 for the OH compounds and ν_1' for the OD compounds) and, for the first time, in the out-of-plane-bending mode range (ν_4 and ν_4') at temperatures down to 20 K. The chosen substances, being members of the large family of carbohydrates, involve sets of H-bonds of different geometry and energy. When measured in cold isotopically doped crystals, their spectra permit the assignment of a definite peak to a corresponding H-bond for analytical application in a wide sense of this term. These spectra also provide very accurate values of the spectral properties of the H-bonding, such as isotopic ratios and vibrational coupling, and their dependence on the geometry and energy of the H-bonds. The study of the pentitols is a continuation of our previous work with the tetritols [8,9] for the correlation of the infrared data with their structure — not done yet for the pentitols — and in connection with our interest in their different hygroscopic properties. Ribitol is four times less hygroscopic than the isomeric xylitol and arabinitol [10]. The crystal structures of ribitol and xylitol have been determined by means of X-ray diffraction [11,12], but only their infrared spectra at room temperature are available in the Aldrich catalogue [13]. Pyranosides were chosen because their infrared spectra in the OH stretching mode range were measured at relatively low temperatures (100 K) and correlations with O···O distances from neutron diffraction were attempted [5,6].

2. Experimental

Polycrystalline pure hydroxy compounds were obtained from Aldrich, Sigma or ICN Biomedicals. The deuteroxy forms (90–95% isotopic purity) were made by recrystallisations from ethanol-*d* or D_2O supplied by Aldrich. The sample for the infrared spectral measurements, a KBr pellet or a fine powder 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. The temperature-induced spectral changes for all substances were reversible and highly reproducible. Infrared spectra were recorded on a Bruker 113V FTIR spectrometer. The spectral resolution was better than 1 cm^{-1} for all measurements. The spectra were processed using the Bruker OPUS program (version 2.2). In the simplest cases the frequencies and bandwidth were determined after deconvolution with an estimated accuracy better than 2%. For a more valid comparison with other room temperature data, our 20 K band positions were corrected to 300 K by assuming a linear dependence of peak frequencies on temperature [6]. The corrections do not exceed 10% of the observed red shift values. Our samples were produced by recrystallisation from solution and spectra were not complicated by possible conformational polymorphic changes [14].

3. Results and discussion

The spectra of xylitol and methyl β-D-galactopyranoside, doped with 5–7% of the corresponding deuteroxy compound, are shown in Fig. 1 as typical examples of the change of the infrared carbohydrate spectrum associated with cooling from 300 to 20 K. Together with the narrowing and improvement of the resolution of the main bands of the OH(OD) matrix, new very narrow bands (with a width down to 3 cm^{-1}) grow in on cooling, especially in the low frequency range. Analogous changes appeared in the spectra of the other substances and are similar to published features resulting from cooling [5,9]. The spectra at 20 K of all polyols and pyranosides together with their OD counterpart in the 4000–2000 and 1000–400 cm^{-1} ranges are shown in Figs. 2–7. The spectra in the stretching mode range of pyranosides are similar to those reported in [5] at the relevant temperature, but demonstrate the better resolution achieved at the present lower temperatures and lower concentrations of the doping isotope. Peak frequencies, bandwidths (in parenthesis) and isotopic frequency ratios of the compounds studied are shown in Tables 1–8.

Stretching mode bands.—The spectra of the OH and OD crystals in the ν_1 and ν_1' ranges are similar in the number of strong narrow bands and their shapes (Figs. 2–7). The ν_1/ν'_1 ratios are 1.33–1.35 for both pentitols (Table 1) and methyl pyranosides (Table 2). This is true not only for the pure, but also for the isotopically diluted OH and OD groups. Some weak narrow bands of the latter are shown in Figs. 2–7. The spectra of the isotopically pure compounds have bands of a rather complicated structure, which reflects the presence of several types of single or chained H-bonds. The bands of doped OH and OD groups are considerably narrower, indicating the vibrational decoupling in H-bonded chains and spirals due to isotopic substitution.

In the simplest case, that of the xylitol spectrum, the OH region (3600–2900 cm^{-1}) comprises five bands for the isotopically pure hydroxy compound (Fig. 2(A)) and only four bands in the isotopically diluted spectrum (Fig. 2(A′)). The narrow ν_1 band at 3121 cm^{-1} of the doped OH group in the OD crystal is approximately at the mean value of the corresponding doublet for pure OH xylitol at 3142 and 3086 cm^{-1}. This suggests the presence of a H-bonded chain together with three other differently H-bonded OH groups. The same conclusion follows from the OD group bands (2200–2600 cm^{-1}) doped in an OH crystal of xylitol. The ν_1 bands of ribitol (Fig. 3) and arabinitol (Fig. 4) are more complicated and isotopic dilution is not very helpful, merely pointing to a complicated vibrational coupling in the pure OH crystals. Four to five different H-bonds may be expected from the existence of five hydroxyl groups per molecule, arranged in zigzag and spiral chains in the crystals, with a wide range of distances. The four or five components of the $\nu_1(\nu'_1)$ bands observed in the spectra of isotopically diluted OH and, especially, OD groups, are consistent with these expectations as well as with structural data [11,12].

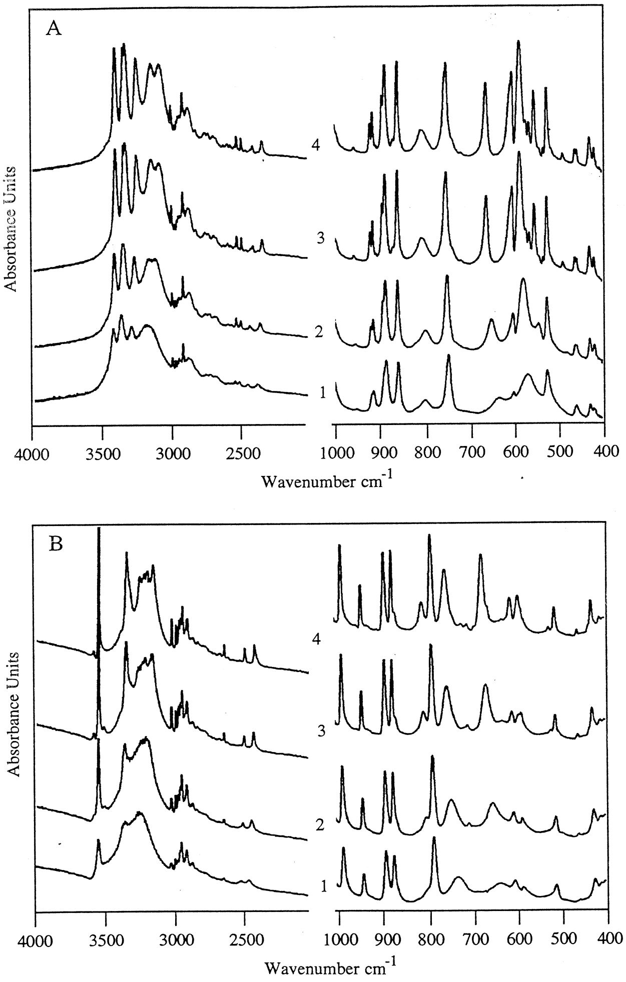

Fig. 1. Infrared spectra of xylitol (A) and methyl β-D-galactopyranoside (B), doped with 5% of OD groups, at various temperatures: 1–300 K, 2–200 K, 3–100 K, 4–20 K.

For the methyl pyranosides (Figs. 5–7), which contain four OH groups per molecule, four different H-bonds can be expected. The simplest spectra of the monoisotopic methyl α-D-manno- and methyl α-D-glucopyranoside (Figs. 5 and 6, respectively) are consistent with the observed structures [5,11]. The spectra of isotopically diluted OH(OD) groups of the methyl pyranosides confirm the existence of four differently H-bonded OH groups.

The ν_1 bands of the pure hydroxy-pentitols and hydroxy-pyranosides also show asymmetric background on both their low and high frequency sides, for which no reliable deconvolution is possible, but nevertheless indicate the presence of additional H-bonded OH groups. Even the isotopically diluted ν'_1 band of methyl β-D-galactopyranoside at 2396 cm^{-1} (Fig. 7(A)) is a composite band (Table 2) suggesting an OH···O interaction, additional to the four expected [2].

We conclude that in the OH(OD) stretching mode, the narrow and strong bands represent the number of ‘ordered’ OH···O contacts responsible for the periodic crystal structure. Additional H-bonds are responsible for the wide background, unresolvable in this spectral range, but show up as clear resolvable peaks in the ν_4 bending mode range.

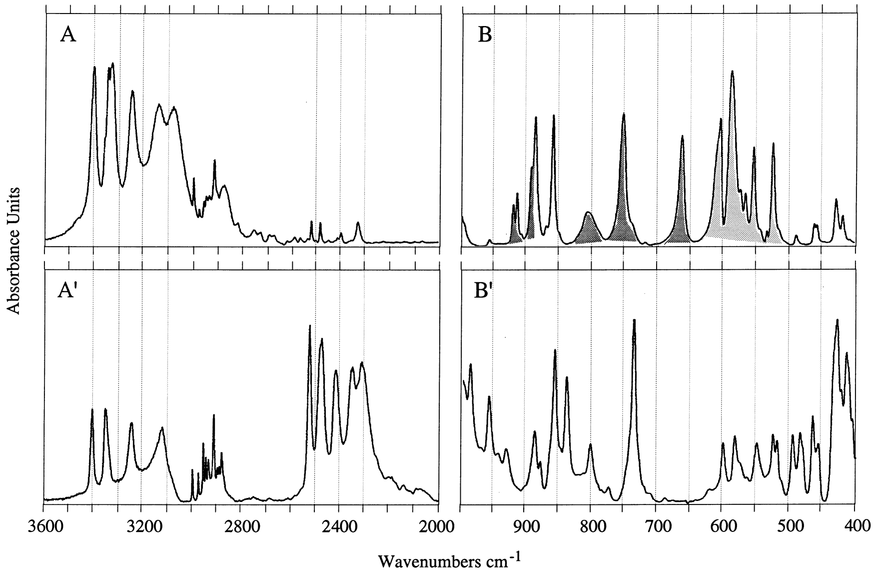

Fig. 2. Infrared spectra at 20 K of OH- and OD-polycrystalline xylitol in the $\nu_1(\nu'_1)$ (A and A′) and $\nu_4(\nu'_4)$ (B and B′) spectral ranges, doped with the opposite isotope. The ν_4 bands corresponding to ν_1 bands which disappear upon isotope exchange with deuterium are light-shaded and the extra ν_4 bands are dark-shaded.

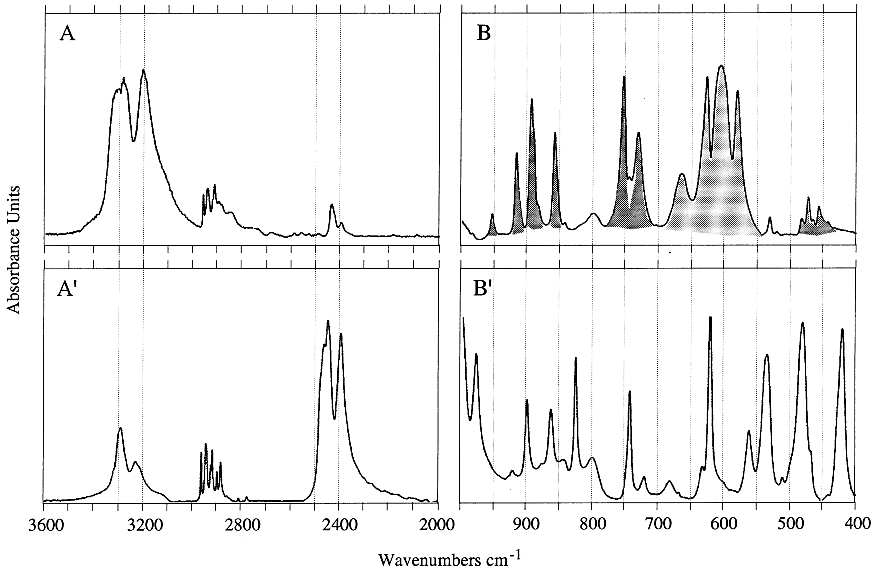

Fig. 3. Infrared spectra at 20 K of OH- and OD-polycrystalline ribitol in the $\nu_1(\nu'_1)$ (A and A′) and $\nu_4(\nu'_4)$ (B and B′) spectral ranges, doped with the opposite isotope. For the shading see the caption of Fig. 2.

Out-of-plane-bending mode bands.—The $\nu_4(\nu'_4)$ out-of-plane-bending vibrational mode below 1000 cm^{-1} comprise 10–15 narrow bands, which change drastically on isotopic exchange. The deuterium exchange reliably establishes the assignment of the narrow single bands to hydroxyl groups. Their frequencies at 20 K are given in Tables 3–8 together with their isotopic ratios, calculated relative abundance and energies (see below).

Some bands reveal a splitting of 25–30 cm^{-1}, for example, in the spectra of ribitol and methyl α-D-glucopyranoside (Figs. 3 and 6, respectively). In comparison, in linear hydrogen bond chains, as in methanol or hydrogen chloride crystals, the splitting reaches values of 80–100 cm^{-1} [15]. We therefore relate the smaller splitting in the present case to a coupling in non-linear chains of H-bonds. The xylitol and ribitol OH bands (Fig. 2(B), near 600 cm^{-1} and Fig. 3(B) near 620 cm^{-1}, respectively) are also perturbed by resonance interaction with an out-of-plane C–H skeletal band clearly seen in the corresponding OD spectra (Fig. 2(B′) and Fig. 3(B′), respectively).

While the ν_1/ν'_1 ratio of the stretching bands is close to the harmonic value (see Tables 1 and 2), the ratio of ν_4/ν'_4 varies within somewhat wider limits of 1.2–1.4. However, the xylitol ν_4 bands of the OH crystal at 920 and 860 cm^{-1} (Fig. 2(B)) disappear upon deuterium exchange (Fig. 2(B′)), without showing the expected ν'_4 OD analogues in the corresponding spectral range 600–700 cm^{-1}. Similarly, in the ribitol spectrum, the band at 890 cm^{-1} (Fig. 3(B, B′)) also has no clear counterpart around 600 cm^{-1}. The implication is that some H-bonds have an anomalous isotopic behaviour of their infrared bands with their isotopic frequency ratio deviating strongly from the harmonic value.

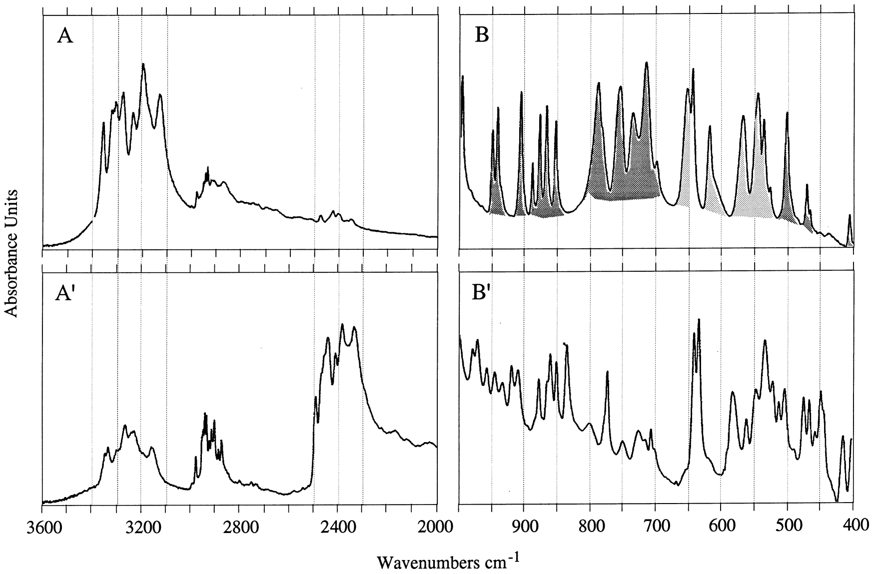

Fig. 4. Infrared spectra at 20 K of OH- and OD-polycrystalline arabinitol in the $\nu_1(\nu'_1)$ (A and A′) and $\nu_4(\nu'_4)$ (B and B′) spectral ranges, doped with the opposite isotope. For the shading see the caption of Fig. 2.

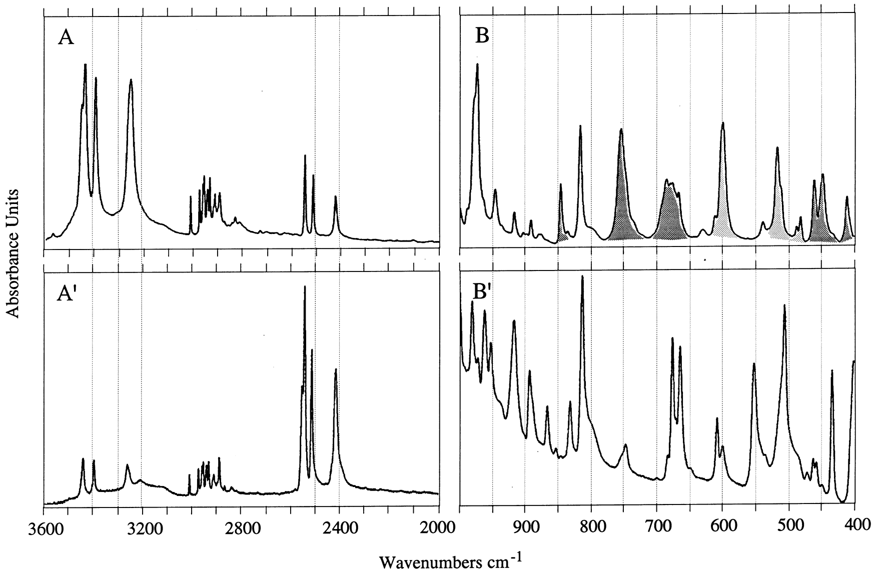

Fig. 5. Infrared spectra at 20 K of OH- and OD-polycrystalline methyl α-D-mannopyranoside in the $\nu_1(\nu'_1)$ (A and A′) and $\nu_4(\nu'_4)$ (B and B′) spectral ranges, doped with the opposite isotope. For the shading see the caption of Fig. 2.

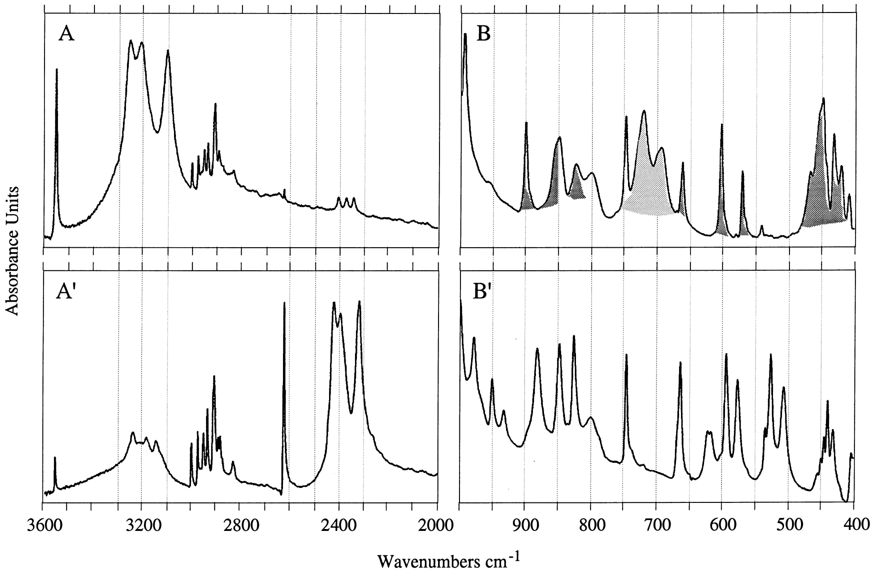

Fig. 6. Infrared spectra at 20 K of OH- and OD- polycrystalline methyl α-D-glucopyranoside in the $\nu_1(\nu'_1)$ (A and A′) and $\nu_4(\nu'_4)$ (B and B′) spectral ranges, doped with the opposite isotope. For the shading see the caption of Fig. 2.

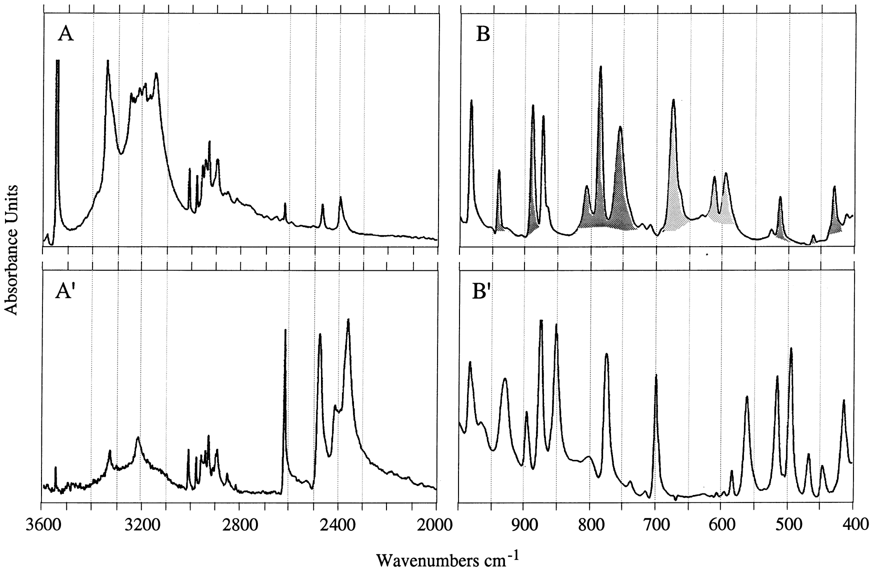

Fig. 7. Infrared spectra at 20 K of OH- and OD-polycrystalline methyl β-D-galactopyranoside in the $\nu_1(\nu'_1)$ (A and A′) and $\nu_4(\nu'_4)$ (B and B′) spectral ranges, doped with the opposite isotope. For the shading see the caption of Fig. 2.

In all spectra, the number of the bands in the ν_4 bending mode range sensitive to deuterium exchange is at least twice that in the ν_1 stretching mode region. In a previous publication [16] it was shown that for H-bonds that are close to linear, the red shift, due to H-bonding the O–H stretching mode, $\Delta\nu_1$ and the increase of corresponding the out-of-plane-bending mode frequency $\Delta\nu_4$, may be empirically correlated by:

$$\Delta\nu_4^2/\mathrm{cm}^{-2} = 2.5\ (\Delta\nu_1/\mathrm{cm}^{-1})^{1/2} - 18 \qquad (1)$$

Here $\Delta\nu_4^2 \equiv (\nu_4^{\mathrm{H}})^2 - (\nu_4^0)^2$ and $\Delta\nu_1 = \nu_1^{\mathrm{H}} - \nu_1^0$, the superscripts H and 0 pertaining to H-bonded and free molecules, respectively. The frequencies ν_1^0 and ν_4^0 were taken as those for isolated 1-butanol molecules in tetrachloromethane solution (3640 and 240 cm^{-1}) [17], respectively. It is thus possible to correlate between the ν_4 bands and their counterparts in the ν_1 region, and thus to attribute them to the same H-bonded OH group. In the present case, the largest deviations from this correlation (< 60 cm^{-1}) were found for methyl gluco- and galactopyranosides. For all others, three to four ν_4 bands observed it within ± 20 cm^{-1}. In Tables 3–7, the observed ν_4 bands that follow the correlation are numbered with a bold font and the corresponding peaks are light shaded in the spectra reproduced in Figs. 2–7. We note that each spectrum comprises additional bands, and in some cases their number is as many as twice that of the ν_1

Table 1
Peak frequencies and band widths in parentheses (cm^{-1}) at 20 K of stretching OH (ν) and OD (ν') bands in pure and isotopically diluted pentitol crystals, their isotopic ratios (ν/ν') [a]

Substance	Pure substances			Isotopically diluted		
	ν	ν'	ν/ν'	ν	ν'	ν/ν'
Ribitol	3316.8 sh	2464.3 sh	1.346	*3288 (33)*	2441 (25)	1.3480
	3287.8	2449.2	1.342	*3229 (39)*	2427 (24)	1.3304
	3208.7	2396.6	1.340	*3191 (88)*	2402.2	1.3426
				3110 (95)		
D-Arabinitol	3357.6	2492.8	1.347	3332.5	2474.2	1.3470
	3315.5			3298	*2443*	1.3500
	3278.2	2445.5	1.340	3263.2	2424.0	1.3462
	3239.3	2414.4	1.342	3226.8	2403.4	1.3430
	3198.9	2386.6	1.340	*3209* ($\nu' \times 1.34$)	*2395*	
	3131.9	2339.2	1.340	3158.1	2351.3	1.3430
Xylitol	3404.0 (21.0)	2525.7 (16.0)	1.348	3403.7 (16.7)	2519.1(6.5)	1.3512
	3346.4sh	2476.7 (27.0)	1.348	3351.5 (20.0)	2483.0 (6.7)	1.3498
	3331.1 (35)					
	3250.1 (28.5)	2419.7 (27.0)	1.343	3243.8 (23.0)	2399.0 (11.5)	1.3521
	3142.0 (120)	2351.9 (90)	1.336	3120.7 (45)	2330.8 (18.0)	1.3387
	3081.6	2313.7	1.332			

[a] In italic — from deconvolution.

Table 2
Peak frequencies (cm^{-1}) of stretching OH (ν) and OD (ν') bands of OH and OD groups in pure and isotopically diluted pyranoside crystals and their isotopic ratios (ν/ν') [a]

Substance	Pure substances			Isotopically diluted		
	ν	ν'	ν/ν'	ν	ν'	ν/ν'
Methyl α-D-glucopyranoside	3553.5 (10.3)	2627.0 (7.0)	1.353	3552.9	2626.3(3.1)	1.3528
	3254.7; 3209.3	2426.6; 2399.4	1.339	3236.4	*2404.8 (16.1)*	1.3458
	(100)	(62.0)		3183.0	*2373.1 (18.0)*	1.3413
	3103.7 (38.0)	2322.9(24.0)	1.336	3145.5	*2343.1 (14.6)*	1.3424
Methyl α-D-mannopyranoside	*3451.2 sh(15.8)*	2555.4sh	1.349	not observed		
	3436.2 (16.3)	2545.6 (7.0)	1.350	3439.1 (13.0)	2546.5 (6.1)	1.3505
	3393.6 (13.1)	2516.9 (8.0)	1.348	3395.2 (10.0)	2513.3 (6.1)	1.3509
	3252.8 (29.2)	2419.1 (16.0)	1.344	3260.7 (18.4)	2422.6 (12.1)	1.3460
Methyl β-D-galactopyranoside	3585.2 vw					
	3549.0 (8.0)	2621.9 (5.5)	1.354	3548.5	2621.8 (2.9)	1.3535
	3345.1 (27.0)	2481.2 (21.0)	1.348	3328.4	2469.1	1.3480
					2469.4 (8.9)	
					2464.7 (14.5)	
	3214.5 (sh);	2416.3 (sh)	1.330	3215.3	*2396.4*	1.3417
	3149.2	2367.0	1.330		*2397.1 (9.9)*	
					2389.6 (16.2)	
					2374.8 (26.3)	

[a] In italic — from deconvolution, band widths (cm^{-1}) in parentheses (exceedingly large widths are omitted).

Table 3
Peak frequencies (cm^{-1}) of the bands in the range below 1000 cm^{-1}, their isotopic ratios at 17 K, estimated H-bond energies (kJ mol^{-1}) and their relative abundance (%) for D-arabinitol crystal powder [a]

No. of OH group	OH crystal	OD crystal	ν_4/ν'_4	$-\Delta H$	Relative abundance
1	889.3 (3.3)	725.3	1.2261	50	1.0
2	878.7 (3.5)	706.9	1.2430	49	2.0
3	868.4 (4.3)	645.6n	1.3451	48	2.5
4	854.4 (4.0)	634.5	1.3466	46	2.1
5	791.5 (29.7)	584.7	1.3537	39	13.0
6	789.6 (10.7) sh	579.8	1.3618	39	4.0
7	756.0 (12.8)	561.5	1.3464	36	9.3
8	736.1 (13.1)	547.6	1.3442	34	6.2
9	716.4 (14.3)	533.7	1.3423	32	11.0
10	698.7 (38.1)	521.7	1.3393	30	9.4
11	653.3 (13.8)	474.8	1.3759	26	9.4
	645.0				
12	619.2 (6.1)	449.0	1.3791	23	2.3
13	610.4 (25.3)			22	6.0
14	569.2 (12.9); 561.5 [b]			19	7.0; 13.4 [b]
15	547.2 (9.7)			17	6.4
16	536.4(7.7)			17	3.0
	502.0; 501.0 [c]				
17	502.5 (5.9)			14	3.6
18	471.0 (3.6)			12	0.7
19	405.7 (3.4)			8	0.6

[a] In italic: skeletal bands, in parenthesis: the band width in cm^{-1}.

[b] Possibly a band due to an isotopically diluted group.

[c] Skeletal band also observed in Raman spectrum.

correlated bands. They are observed at both higher and lower frequencies than the latter, are narrow and show neither a splitting nor an asymmetry and all disappear upon deuterium exchange and therefore must be assigned to OH group ν_4 vibrations.

As for the tetritols [9], the ν_4 band positions and integrated intensities can be used for the estimation of the strengths and relative abundances of the H-bonds, respectively (in contrast with the stretching bands, their integrated intensities do not depend on frequency). The frequencies of the out-of-plane-bending vibration (ν_4) are related to the H-bond energy (i.e., the enthalpy of H-bond formation in liquids) by the relation [16,18a]:

$$-\Delta H\ (\mathrm{kJ\ mol^{-1}}) = 0.67 \times 10^{-4}\Delta\nu^2 \tag{2}$$

Here again, $\Delta\nu^2 \equiv (\nu_4^{\mathrm{H}})^2 - (\nu_4^0)^2$. The bending modes blue shift as a result of H-bonding, due to an additive contribution to bending force constant of the OH···O angle, proportional to the H-bonding energy. This relationship is also valid for evaluation of the H-bond energy in crystals [16]. Since no H-bond with angle < 150° is found for pyranosides [1], we assumed this relation to hold for all systems studied. The accuracy of this estimation is ± 4 kJ mol^{-1} and the relative changes are more reliable than the absolute values. Tables 2–7 list the calculated energies of the different H-bonds in the crystal along with their relative abundance (the estimated accuracy of the latter is 0.5%).

We conclude that clear peaks in the ν_1 region do not represent the full number of all the H-bonds. Taking into account the ν_4 region, the number of H-bonds estimated would increase. This increase will be by more than a factor three in arabinitol; in xylitol, the increase is by about a factor of two and by over 50% in ribitol. In methyl pyranosides, the increase is by a factor of three in the galactopyranoside derivative, a factor of four in the mannopyranoside and a factor of 2.5 in the glucopyranoside isomers.

Weak H-bonds and the hygroscopicity of polyols.—On the basis of the correlation above (Eq. (1)), we observe that all substances contain both strong (up to 55 kJ mol^{-1}) and as much weaker (less than 14 kJ mol^{-1}) H-bonds, with a very wide quantitative distribution (Tables 3–8). The finding of weak H-bonds in three of the pentitols confirms our conclusion [8] that the difference in water sorption ability of polyols is directly related to

Table 4
Peak frequencies (cm^{-1}) of the bands in the range below 1000 cm^{-1}, their isotopic ratios at 17 K, estimated H-bond energies (kJ mol^{-1}) and their relative abundance (%) for xylitol crystal powder [a]

No. of OH group	OH crystal	OD crystal	ν_4/ν'_4	$-\Delta H$	Relative abundance
1	920.3 (3.3)	[b]	[b]	54	1.2
2	914 (3.0)	[b]	[b]	53	1.6
3	893.7 (2.6)	[b]	[b]	51	1.0
4	887.2 (8.7)		[b]	50	8.5
	887.3; 888.0 [c]				
	858.2; 858.0 [c]				
5	860.0 (5.3)	[b]	[b]	47	5.2
6	805.4 (32.6)	[b]	[b]	40	14.2
7	753.6 (11.9)	551.1	1.3674	35	12.0
8	663.8 (10.9)	496.7; 485.5	1.3358; 1.3666	27	11.0
	602.3				
9	610.2 (8.1);	428.8	1.4019	22	6.5
	588.2 (11.7)			20	16.6
10	575.5 (15.3)			19	6.5
11	566.3 (3.2)			19	1.2
12	553.8 (7.6)			18	6.3
13	526.1 (2.9)			16	1.6
14	523.5 (5.2)			16	2.3
16	459.8 (9.8)			11	2.1
17	429.0 (4.4)			10	1.6
18	418.5 (3.2)			9	0.84

[a] In italic: skeletal bands, in parenthesis: the band width in cm^{-1}.
[b] OD counterpart unobserved.
[c] Skeletal band also observed in Raman spectrum.

Table 5
Peak frequencies (cm^{-1}) of the bands in the range below 1000 cm^{-1}, their isotopic ratios at 17 K, estimated H-bond energies (kJ mol^{-1}) and their relative abundance (%) for ribitol crystal powder [a]

No. of OH group	OH crystal	OD crystal	ν_4/ν'_4	$-\Delta H$	Relative abundance
1	917.0 (5.2)	682.5	1.3436	54	3.7
2	894.8 (4.4)	[b]	[b]	51	4.8
3	890.4 (4.7)	[b]	[b]	50	2.4
4	858.4 (4.6)	634.0	1.3539	47	4.5
5	753.9 (11.0)	562.3	1.3407	35	10.2
	742.8				
6	732.1 (14.4)	534.7	1.3692	33	9.6
7	667.5 (23.5)	486.4	1.3723	27	11.0
8	627.7; 604.9	480.7	1.2919	23	43.4
	621.0				
9	581.5 (10.2)	421.1	1.3809	20	7.8
10	473.0 (4.6)	[b]	[b]	12	1.6
11	457.8 (3.1)	[b]	[b]	11	0.9

[a] In italic: skeletal bands, in parenthesis: the band width in cm^{-1}.
[b] OD counterpart unobserved.

Table 6
Peak frequencies (cm^{-1}) of the bands in the range below 1000 cm^{-1}, their isotopic ratios at 17 K, estimated H-bond energies (kJ mol^{-1}) and their relative abundance (%) for methyl β-D-galactopyranoside crystal powder [a]

No. of OH group	OH crystal	OD crystal	ν_4/ν'_4	$-\Delta H$	Relative abundance
1	940.6 (2.2)	699.5	1.3447	56	3.3
2	889.5 (3.9)	683.0	1.3023	50	8.6
	873.2				
3	807.0 (11.0)	583.1	1.3840	41	8.3
4	786.7 (6.4)	561.3	1.4016	39	14.8
5	755.7 (16.2)	515.8	1.4651	36	26.7
6	675.9 (9.9)	495.3	1.3646	28	20.4
7	612.1 (5.5)	467.0	1.3107	22	4.0
8	594.4 (12.6)	446.1	1.3324	21	10.0
9	511.9 (3.3)			15	2.0
10	430.3 (4.5)			10	4.0

[a] In italic: skeletal bands, in parenthesis: the band width in cm^{-1}.

Table 7
Peak frequencies (cm^{-1}) of the bands in the range below 1000 cm^{-1}, their isotopic ratios at 17 K, estimated H-bond energies (kJ mol^{-1}) and their relative abundance (%) for methyl α-D-mannopyranoside crystal powder [a]

No. of OH group	OH crystal	OD crystal	ν_4/ν'_4	$-\Delta H$	Relative abundance
1	846.8; (3.5)	608.6	1.3914	45	4.8
	817.1				
2	755.2 (10.7)	552.8	1.3661	35	26.7
3	689.2 (16.0)	506.6	1.3561	29	15.0
	672.8 (14.0)	496 sh	1.3564	28	13.5
4	600.3 (8.5)	434.6	1.3826	21	22.3
	517.5				
5	488.7 (3.8)			13	0.5
6	482.2 (1.8)			13	0.8
7	461.7 (3.7)			11	5.0
8	448.3 (6.9)			11	10.4
9	412.3 (2.2)			8	2.1

[a] In italic: skeletal bands, in parenthesis: the band width in cm^{-1}.

the different amount of weaker H-bonds. Thus the 4–5% of such H-bonds in arabinitol and xylitol explains their four time larger hygroscopicity as compared with ribitol [10], which contains only 2.5% of such weak H-bonds. Table 9 shows the good correlation between the fraction of weak (< 14 kJ mol^{-1}) H-bonds in the polyols studied and their water sorption abilities. The yet unknown hygroscopic properties of the methyl pyranosides may be predicted accordingly.

Correlation of the red shift with H-bond length.—As was mentioned above, the narrow ν_1 bands can be related to the ordered periodical structure of crystal. The magnitude of their red shift from that of the 'free' molecule, may be correlated with the H-bond lengths. The decoupled ν_1 frequencies of isotopically diluted OH/OD groups are the most suitable for such correlation. Table 10 lists the red shifts relative to the free OH peak frequency of 1-butanol in a dilute CCl_4 solution together with the known neutron diffraction values [11,19,20] of H···O bond lengths. Fig. 8 shows the smooth non-linear correlation between these two parameters

$$\Delta\nu/\text{cm}^{-1} = 0.025\ (r_{\text{H}\cdots\text{O}}/\text{nm})^{-5.6} \qquad (3)$$

or a linear correlation on a logarithmic scale:

$$\log(\Delta\nu/\text{cm}^{-1}) = (-1.6 \pm 0.2) - (5.6 \pm 0.3)\log(r_{\text{H}\cdots\text{O}}/\text{nm})$$

with a correlation coefficient of $R = 0.970$.

Table 8
Peak frequencies (cm^{-1}) of the bands in the range below 1000 cm^{-1}, their isotopic ratios at 17 K, estimated H-bond energies (kJ mol^{-1}) and their relative abundance (%) for methyl α-D-glucopyranoside crystal powder [a]

No. of OH group	OH crystal	OD crystal	ν_4/ν'_4	$-\Delta H$	Relative abundance
1	901.8 (4.1)	664.2	1.3565	52	5.2
2	856.5 (15.4)	622.0	1.3746	46	12.5
	850.5				
3	826.3 (14.4)	600 sh	1.3772	43	6.6
	748.8				
4	731.4 (12.0)	[c]	[c]	33	4.5
	722.7 (14.4)	526.8	1.3724	32	16.7
5	699.0 (24.0)	507.2	1.3722	30	15.0
	692.7 (10.3)			29	2.4
	662.0				
	603.2				
6	571.0 (2.8)	420.0 sh	1.3595	19	2.5
7	469.5 (16.2)			12	8.8
8	454.8 (11.2), 421.0 (10) 440.3 [b]			10	22.7
9	408.5 (6.2)			8	2.9

[a] In italic: skeletal bands, in parenthesis: the band width in cm^{-1}.

[b] Possibly a band due to an isotopically diluted group.

[c] OD counterpart unobserved.

The Figure also includes data for β-L-arabinose [6], β-D-fructopyranose [5], L-sorbose and D-arabinose [21]. The latter follow the same correlation, but with higher deviations.

The current decoupled and hence more accurate peak frequencies yielded different results from those in Ref. [5], where an almost linear dependence of peak positions on the O···O distances was found. The present correlation of the red shift with H-bond length, $r_{H\cdots O}$, is more attractive since it relates to a larger body of data [16,18a,b] on diverse H-bonded A – H groups in condensed phases. Correlation (3) is seen to hold for H-bonds with O–H···O angles > 150°.

Isotopic frequency ratios of decoupled stretching bands.—In contrast to solution spectra, the narrow decoupled ν_1 bands in crystals allow the extraction of even very small changes in isotopic ratios. Red shifts in the range 100–500 cm^{-1}, corresponding to weak and medium H-bonds, may be correlated with the deviation of the ν_1/ν'_1 ratio from the harmonic value (Fig. 9).

An analogous dependency was found for hydrates [22]. The deviation of the ν_1/ν'_1 ratio from the harmonic values starts at a rather small strength of the H-bond, < 10 kJ mol^{-1}.

4. Conclusions

This study, together with our yet unpublished results for tetritols, demonstrates the more limited usefulness of spectral data in the OH stretching mode range as compared with the ν_4 bending modes, for the study of the H-bonding structure. Although the number of prominent strong bands in this range corresponds approximately to the number of H-bonding contacts indicated by structural methods, they reflect only from 25 to 60% of the total amount of hydroxyl groups present in the crystal. The well resolved bands in the stretching vibration range represent the main H-bonding network of H-bonds of medium

Table 9
N (abundance, %) of H-bonds with energy ($-\Delta H$) < 14.0 kJ mol^{-1} in polyol crystals and their water sorption capability, n_{Ws}, number of moles of water sorbed per mole of polyol [10]

Substance	−ΔH (kJ mol^{-1})	*N*	n_{Ws}
Threitol [8]	13.8–12.0	6.0	4.34
D-Arabinitol	14.3–8.4	4.9	3.21
Xylitol	11.5–9.0	4.5	3.03
Ribitol	12.3–11.3	2.5	0.76
Erythritol [8]		0	0.03

Table 10
Red shift $\Delta\nu_1$ (cm^{-1}, relative to ν_1 band of 1-butanol in CCl$_4$, 3640 cm^{-1}) and corresponding H···O distances (nm); shifts in parenthesis are values adjusted to 300 K [a1]

Substance	$\Delta\nu_1$	$r_{\mathrm{H\cdots O}}$	Substance	$\Delta\nu_1$	$r_{\mathrm{H\cdots O}}$
Methyl α-D-mannopyranoside	192 (177)	0.2052	xylitol	236 (216)	0.194
	201 (186)	0.1988		289 (264)	0.188
	245 (216)	0.1917		396 (348)	0.181
	379 (345)	0.1810		519 (457)	0.176
Methyl α-D-glucopyranoside	87 (97)	0.2328	arabinitol	308	0.186
	404 (364)	0.1772		342 (307)	0.182
	457 (417)	0.1770		377 (337)	0.177
	495 (455)	0.1738		431 (401)	0.175
				482 (432)	0.175
Methyl β-D-galactopyranoside	92	0.2746	ribitol	482	0.175
	312	0.2240		352 (322)	0.186
	428 (423)	0.1860		411 (381)	0.184
	438 (398)	0.1773		449 (409)	0.181
	458 (418)	0.1739		530 (490)	0.175

[a] Note: $r_{\mathrm{H\cdots O}}$ distances in pentitols-[11], in methyl α-D-mannopyranoside and methyl α-D-glucopyranoside-[19], in methyl β-D-galactopyranoside-[20].

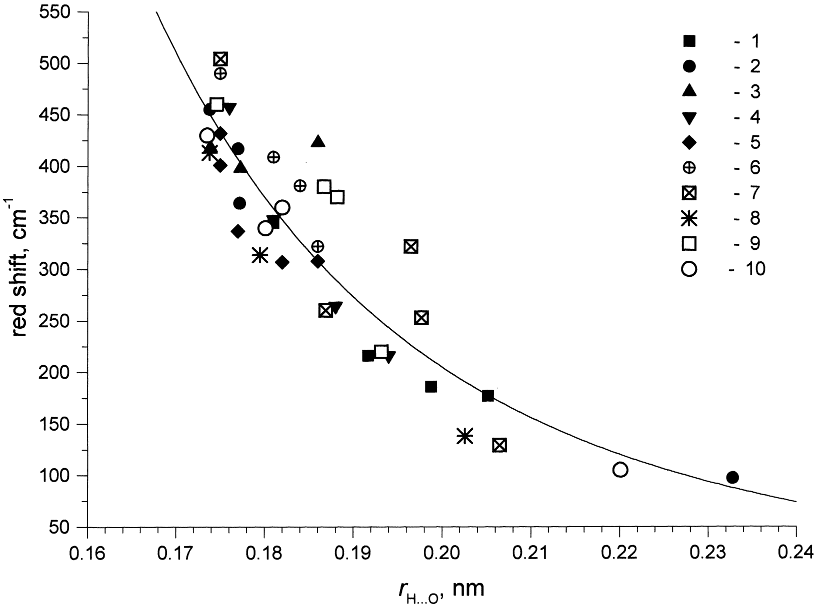

Fig. 8. Correlation of the red shift (in cm^{-1}) and the interatomic distance $r_{\mathrm{H\cdots O}}$ (in nm) in carbohydrates (1): 1- methyl α-D-mannopyranoside, 2- methyl α-D-glucopyranoside, 3- methyl β-D-galactopyranoside, 4- xylitol, 5- D-arabinitol, 6- ribitol, 7- D-fructopyranose [5], 8- β-L-arabinose [6], 9- L-sorbose [21], 10- D-arabinose [21].

strength (20–30 kJ mol^{-1}), responsible for the periodical crystal structure seen by X-ray diffraction and neutron scattering. It is this order that makes these bands narrow and, hence, prominent. Other ν_1 bands, corresponding to non-ordered hydroxyl groups, cannot be resolved reliably, as their intensities and widths depend on the frequency resulting bands that are either narrow but too weak (for weak H-bonds) or intense but too broad (for strong H-bonds).

In contrast all OH groups are clearly ob-

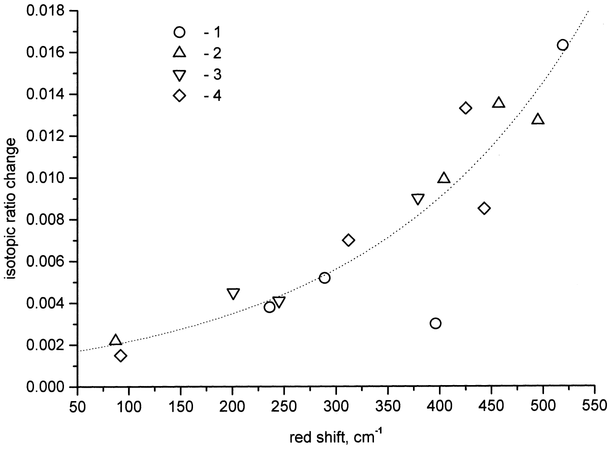

Fig. 9. Change of isotopic ratio of ν_1 vibrations of various OH groups relative to that of the free molecules in CCl_4 solution $[(\nu_1/\nu'_1)_{CCl_4} - (\nu_1/\nu'_1)_{cryst}]$ plotted against the red shift (in cm^{-1}) in crystals: 1- xylitol, 2- methyl α-D-glucopyranoside, 3- methyl α-D-mannopyranoside, 4- methyl β-D-galactopyranoside.

served in the out-of-plane-bending mode range. These ν_4 bands are rather narrow and well resolved in cold isotopically doped crystals. Their peak positions depend mainly on the H-bond strengths (for alignments that are close to linear) and their intensity is frequency independent. The number of weakly bonded OH groups may be related to the different water sorption capabilities of isomeric polyol crystals, a property that cannot be explained by the structural data alone.

The larger (by almost a factor of four) number of H-bond contacts found by infrared spectroscopy as compared with structural methods may be due to the sensitivity of the former to short range interaction as compared with the long range periodic order seen by the latter.

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