# INFRARED AND RAMAN SPECTRA OF ORTHORHOMBIC, MONOCLINIC AND CUBIC METABORIC ACID AND THEIR RELATION TO THE "STRENGTH" OF THE HYDROGEN BOND PRESENT

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### ABSTRACT

Infrared and Raman spectra of the three forms of metaboric acid (orthorhombic, monoclinic and cubic) are presented and discussed. The behaviour of the asymmetric stretching vibration  $v_{OH}$  and of the in-plane and out-of-plane deformations  $\delta_{OH}$  and  $\gamma_{OH}$  shows that hydrogen bonds of different "strengths" are present in the three forms of metaboric acid, in accordance with X-ray diffraction measurements. This phenomenon is explained in a qualitative way by a valence bond treatment of the structural centres present in the three forms of metaboric acid. The remaining vibrational modes are related to the analogous modes present in borates and polyborates of known structure.

### INTRODUCTION

In our previous Raman and infrared studies we have investigated problems concerned with both asymmetric and symmetric strong hydrogen bonds in solids and in solutions [1-10]. Some compounds contain both types of strong H-bonds in their structures; the Wegscheider salt  $3NaHCO_3 \cdot Na_2CO_3$  [3] is a typical example. Moreover, compounds having the same formula but different structures and consequently containing H-bonds of different strengths are known. The subject of the present work, metaboric acid (HBO<sub>2</sub>), is an example of such a compound. In fact HBO<sub>2</sub> can be prepared in three crystalline forms, namely orthorhombic (HBO<sub>2</sub>-III), monoclinic (HBO<sub>2</sub>-II), and cubic (HBO<sub>2</sub>-I), the structures of which are well defined in the literature [11-13]; however, very little is known about the Raman and infrared spectra of the three forms [14-20].

In this paper we give the results of a vibrational spectroscopic investigation on the three crystalline forms and the relation of the spectra to the strength of the H-bonds present in the three structures.

## EXPERIMENTAL

The three forms of metaboric acid can be prepared by using different pressure and temperature conditions [21].

Orthorhombic metaboric acid (HBO<sub>2</sub>-III) was prepared by dehydrating recrystallized orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) at 120°C for 48 h.

Monoclinic metaboric acid (HBO<sub>2</sub>-II) was obtained by dehydrating recrystallized orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) at 140°C for 78 h, using a partially open tube to prevent evaporation of water.

Cubic metaboric acid (HBO<sub>2</sub>-I) was firstly obtained by melting HBO<sub>2</sub>-II in a sealed tube at ~200°C. A few brilliant crystallites of HBO<sub>2</sub>-I appeared in the melt and grew very slowly; five months were required for complete crystallization. The crystals were washed with water and then with methanol. Secondly, HBO<sub>2</sub>-I was prepared according to a shorter method [22], which however requires a little HBO<sub>2</sub>-I to be initially available.

Raman spectra were obtained using a Jasco R300 spectrometer with a Lexel Ar<sup>+</sup> 4880-Å laser source. Infrared specta of Nujol and hexachlorobutadiene mulls were recorded with a Perkin-Elmer 225 spectrometer.

### DISCUSSION

The infrared and Raman spectra of orthorhombic metaboric acid  $(HBO_2-III)$  have been investigated by several workers [14-19]. In particular, Parsons [15] has published an analysis of its infrared and part of its Raman spectrum, including a vibrational assignment. A more complete Raman spectrum of this form was recently reported by Maya [19] in a paper on the Raman spectroscopic identification of polymeric ions in solution. In the same paper Maya also reported the Raman spectrum of monoclinic metaboric acid  $(HBO_2-II)$ . The latter spectrum seems to be the only one in the literature for this crystalline form, and we could find no report of its infrared spectrum.

As for the third crystalline form, i.e. cubic metaboric acid (HBO<sub>2</sub>-I), a partial infrared spectrum between 4000 and 1300 cm<sup>-1</sup> has been presented and discussed by Parsons et al. [20], but we could find no report of its Raman spectrum.

In this work we present the infrared and Raman spectra of the three crystalline forms, and in particular we discuss the asymmetric stretching vibration  $\nu_{OH}$  which indicates the strength of the H-bond [23].

The infrared spectra in the region  $4000-200 \text{ cm}^{-1}$  for orthorhombic, monoclinic and cubic metaboric acids are shown in Fig. 1(a), (b) and (c), respectively. The Raman spectra for the three forms are given in Fig. 2(a), (b) and (c) (for the region  $0-4000 \text{ cm}^{-1}$ ), and in Fig. 3(a), (b) and (c) (for the region  $0-1000 \text{ cm}^{-1}$ ), respectively. The frequencies of the infrared and Raman bands for each compound are listed in Tables 1, 2 and 3, respectively.

The infrared spectrum of orthorhombic metaboric acid (HBO<sub>2</sub>-III) shows a complex band centred at ~3280 cm<sup>-1</sup>, attributable to the  $v_{OH}$  stretching



Fig. 1 Infrared spectra of (a) HBO<sub>2</sub>-III, (b) HBO<sub>2</sub>-II, and (c) HBO<sub>2</sub>-I.



Fig. 2. Raman spectra of (a) HBO<sub>2</sub>-III, (b) HBO<sub>2</sub>-II, and (c) HBO<sub>2</sub>-I.

vibration, with maxima at 3375, 3280 and 3200 cm<sup>-1</sup> (Fig. 1a); comparable features are also present in the Raman spectrum at 3365, 3295 and 3195 cm<sup>-1</sup> (Fig. 2a).

In the infrared spectrum of monoclinic metaboric acid (HBO<sub>2</sub>-II) we observe a similar complex band shifted towards lower wavenumbers and centred at  $\sim 3070 \text{ cm}^{-1}$ , with maxima at 3190, 2925 and 2720 cm<sup>-1</sup> (Fig. 1b), while the Raman spectrum shows weak bands at 3130, 2930 and 2725 cm<sup>-1</sup> (Fig. 2b).



1000 800 600 400 200 0 cm<sup>-1</sup>

Fig. 3. Raman spectra of (a)  $HBO_2$ -III, (b)  $HBO_2$ -II, and (c)  $HBO_2$ -I in the region 0–1000 cm<sup>-1</sup>.

Finally, the infrared spectrum of cubic metaboric acid (HBO<sub>2</sub>-I) shows a very broad absorption band centred between 1500 and 1000 cm<sup>-1</sup>, with weaker and larger superimposed bands at ~2450, ~1900 and ~1700 cm<sup>-1</sup> (Fig. 1c); again, these features are also present in the Raman spectrum at ~2380, ~1980, ~1700 cm<sup>-1</sup> (Fig. 2c).

From the literature [24] we obtain a relationship between the frequency  $\nu_{OH}$  and the O···O interatomic distance. According to this relationship, we expect an average O···O distance of 2.74 Å for HBO<sub>2</sub>-III (average  $\nu_{OH} \sim 3280 \text{ cm}^{-1}$ ), and of 2.66 Å for HBO<sub>2</sub>-II (average  $\nu_{OH} \sim 3070 \text{ cm}^{-1}$ ), which is in good agreement in both cases with the X-ray structural data [11, 12].

The overall appearance of the HBO<sub>2</sub>-I spectra suggests the presence of stronger H-bonds. It is known, particularly from the infrared rather than the much less utilized Raman spectra, that the frequency of the asymmetric  $\nu_{OH}$  stretching mode shifts towards lower wavenumbers as the strength of the H-bond increases. Weaker submaxima are also noted in the spectrum. At the same time the barrier in the double-minimum potential function decreases. When the H-bonds are strong enough and are characterized by a double-minimum potential function with a low barrier, a trio of bands, referred to as A, B and C, appears. These bands are affected by deuteration and are therefore connected with proton motion. This type of absorption pattern is

IR Ram 3375 vs 3365 3280 vs 3295 3200 vs 3195		rarsons [15		Assignment	This wo	rk	Parsons		Assignment
3375 vs 3365 3280 vs 3295 3200 vs 3195	an	IR	Raman		IR	Raman	IR	Raman	
3280 vs 3295 3200 vs 3195	× c	3356 s )			975 sh	A A A A A A A A A A A A A A A A A A A			
3200 vs 3195	ó W	3257 s		HOU	960 m		956 w		
	Ś W	3195 s <sup>1</sup>			944 s		939 m		Vring
2650 vw		2646 vw			920 sh				<b>G</b> 1774
2460 vw		2475 vw			833 s, b		833 s, b		λОН
2410 vw		2415 vw				810 s	·	819a <sub>s</sub>	δring
		2342 vw			741 vs, t	•	745 s, b		) ring
2290 vw		2294 vw			665 vw,	sh	I		
2240 vw		2227 vw			650 m		650 w		мв—он
2190 vw		2188 vw			630 sh	638 vw			2
2150 vw		2151 wv			595 m	599 vs	595 w	598ª s	Ring "breathing"
					( )				vibration
MA 0602		WV 8802			580 sh				
2040 vw		2041 vw			550 vw,	sh	548 vw		
1945 vw		1942 vw					504 vw		
1905 vw		1905 vw			475 s	478 m	478 w, sh		T ning-OH
1759 vw		1754 vw			462 sh	469 m	462 m		ò ring
1475 sh		1473 m		7 (BO) ring	457 s				91117
1400 s 1460	۸۸ (	1397 vs.vb		P R-OH acumm	415 s	419 m			
1386 s				At the tar from here an		404 m			
1360 s		1360 vs)		Print of the second sec		370 vw, b			
1342 s 1343	MN .	1342 vs)		Sim		193 sh			
1280 m, b		1289 w				160 sh			
1241 m		1239 s		<sup>p</sup> B-OH, symni.		143 sh			
1198 s		1196 m		HOg		119 s			
1150 s		1147 s	-	у он		87 s			
		1132 m							
1100 s 1100	vw, b	1099 m		Юg					

Infrared and Raman spectra (cm<sup>-1</sup>) of  $HBO_{2}$ -III

**TABLE 1** 

## TABLE 2

Infrared and Raman spectra ( $cm^{-1}$ ) of HBO<sub>2</sub>-II, *p*-veatchite and caesium triborate

HBO <sub>2</sub> -II (monoclinic r 3- and 4- coor boron [12]	netaboric acid) rdinate	(Sr, Ca) [B <sub>3</sub> O <sub>4</sub> (OH) <sub>2</sub> ] <sub>2</sub> (p-veatchite) 3- and 4- coordinate boron [39]	CsB <sub>3</sub> O <sub>5</sub> (caesium triborate) 3- and 4- coordinate boron [40]
IR	Raman	IR [37] <sup>a</sup>	IR [38]
3190 vs			
_	3130 m		
2925 s	2930 w, b		
2720 sh	2725 vw		
2560 sh		1 4 4 4	
1650 w, sh		1660	
1485 sn			1455 m h
	1420	1451	1455 m, b
1400 vs b	1400 vw	1200 ~	
1400 VS, D	1341 vw	1330 \$	1350 m. b
1335 vs	1330 vw	<sup>ν</sup> <sup>B</sup> (3) <sup>-O-B</sup> (3) <sup>U</sup>	,,,
1318 sh		f i i i i i i i i i i i i i i i i i i i	1320 s, b
1290 sh		1286 s	,
	1264 vw	2	
			1250 vs, b
	1227 vw		
1205 s			
	1173 vw		
1124 vs	1135 vw		
		1105 m	
	1080 vw, b	1081 m	1080 s, b
1048 w		VB (D) - D-B( ()	
1010 s		1000 s $\begin{cases} B(3) = 0^{-1}B(4) \\ y = 0 \end{cases}$	1012 m, sh
980 w	980 vw	-BO	
960 m		966	967 s, b
		946 s )	
918 w	918 vw		907 s, vb
877 s			
		860	·
		836 m	847 s, b
803 m	<b>5</b> .0 <i>-</i>		797 s, b
	785 vs	880	
750		778 m	777 m, sn
758 m	765 sh		759 s
730 ch			149 S
790 511	710	710 m	709 a b
690 m	680 ch	710 m 680	102 s, b
653 m	655 m	665	659 m b
500 m	000 m	640	002
		635 s	

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HBO <sub>2</sub> -II (monoclinic 3- and 4- coo boron [12]	metaboric acid) ordinate	(Sr, Ca) [B <sub>3</sub> O <sub>4</sub> (OH) <sub>2</sub> ] <sub>2</sub> ( <i>p</i> -veatchite) 3- and 4- coordinate boron [39]	CsB <sub>3</sub> O <sub>5</sub> (caesium triborate) 3- and 4- coordinate boron [40]
IR	Raman	IR [37] <sup>a</sup>	IR [38]
620 vw	628 m		
		608 s	
		570	563 w
			547 w
533 w	536 s	530	530 s
518 m	522 s	515	510 s
502 w	455	495	
481 m	477 s	485	474 m, sn
	100	465	409 S
443 m	432 m		
413 m	207		
301 VW	397 W		
957	379 m		
337 m	246 -h		
340 m	340 SH		
	000 W 207 ch		
	202 m		
	235 m 277 m		
265 vw	211 111		
250 m			
200	226 w		
	198 s		
	185 sh		
	178 s		
	147 s		
	131 s		
	119 s		
	108 s		
	94 s		
	77 s		

 TABLE 2 (continued)

<sup>a</sup>In the literature only the intensities of strong and medium absorption bands are reported. As the infrared spectrum of aksaite, which contains the same structural moiety in the form of an isolated ring, shows weak and flat bands between 700 and 400 cm<sup>-1</sup>, it is reasonable to assign the absorption bands, which are also present in the same range in the spectrum of *p*-veatchite, to vibrational modes involving chains of boron—oxygen polyions. <sup>b</sup>The number in parentheses is the coordination number of the boron.

observed, for example, for metal dihydrogenphosphates and arsenates [25], organophosphoric and phosphinic acids [26], seleninic acids [27], and complexes of carboxylic acids with oxo-bases [28], and various explanations for this phenomenon have been advanced [29-31]. As the strength of the H-bond increases still further, the intensity of the trio of bands decreases and gradually they become indistinct and are replaced by a very broad

# TABLE 3

Infrared and Raman spectra (cm<sup>-1</sup>) of  $HBO_2$ -I, lead tetraborate and teepleite

IR       Raman       IR [38]       IR [43]       Raman [43] <sup>a</sup> $\sim 2450 \text{ m}, \text{ b}$ $\sim 2380 \text{ m}, \text{ b}$ $3565 \text{ s}$ $3535 \text{ s}$ $3535 \text{ s}$ $3536 \text{ s}$ $"OH$ $\sim 2450 \text{ m}, \text{ b}$ $\sim 2380 \text{ m}, \text{ b}$ $2299 \text{ m}$ $2101 \text{ w}$ $2299 \text{ m}$ $1783 \text{ m}$ $\sim 1700 \text{ m}, \text{ b}$ $1664 \text{ w}$ $1597 \text{ m}$ $1783 \text{ m}$ $\sim 1700 \text{ m}, \text{ b}$ $1664 \text{ w}$ $1597 \text{ m}$ $1200 \text{ ww}$ $\delta_{OH}$ $\sim 1700 \text{ m}, \text{ b}$ $\sim 1200 \text{ m}, \text{ b}$ $1166 \text{ s}$ $1171 \text{ w}$ $1200 \text{ ww}$ $\delta_{OH}$ $1183 \text{ vs, b}$ $1025 \text{ w}$ $1078 \text{ s, b}$ $1060 \text{ m}$ $1160 \text{ ww}$ $\delta_{OH}$ $993 \text{ vs, b}$ $970 \text{ w}$ $940 \text{ s, b}$ $932 \text{ vs}$ $950 \text{ m}$ $\mu_{BO}$ $895 \text{ m, b}$ $820 \text{ s}$ $804 \text{ s}$ $748 \text{ s}$ $\nu_{BO}$ $825 \text{ vs, b}$ $804 \text{ s}$ $748 \text{ s}$ $\nu_{BO}$ $\mu_{BO}$	HBO <sub>2</sub> -I (cubic metaboric acid) 4-coordinate boron [13]		PbO·2B <sub>2</sub> O <sub>3</sub> (lead tetraborate) 4-coordinate boron [44]	Na <sub>2</sub> B(OH) <sub>4</sub> (teepleite) 4-coordinal	Cl se boron [45]
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	IR	Raman	- IR [38]	IR [43]	Raman [43] <sup>a</sup>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				3565 s	3557 s
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				3535 s	3536 s / <sup>•OH</sup>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	~2450 m, b	~2380 m, b			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				2326 m	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				2299 m	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				2101 w	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	~1900 m, b	~1980 m, b		2049 w	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				1855 m	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-			1783 m	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	~1700 m, b	~1700 m, b			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				1664 w	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				1597 m	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1463 vs, b				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				$\sim 1449 \text{ sh}$	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				~1377 sh	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				1297 m	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	- 4 6 6 1	1240 w	1230 s, b		1200
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1183 vs, b				τ vw δου
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1000		1166 s	1171 w	1160
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1088 vs, b	1083 w	1078 s, b	1060 m	)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1025 w	1017 s, b		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	993 vs, b				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	·-	970 w			)
$\begin{array}{c} 932 \text{ vs} & 7 \text{ v}_{BO} \\ 895 \text{ m, b} & & & & & & & & & & & & & & & & & & $	945 vs, b		940 s, b		950 m {
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				932 vs	ν <sub>BO</sub>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		907 w			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	895 m, b				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			880 s, b		_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				860 w	}
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	825 vs, b	820 s			825 w μ <sub>BO</sub>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			804 s		•
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		780 s			
$742 \text{ s}$ $748 \text{ s}$ $\nu_{BO}$ $680 \text{ sh}$ $645 \text{ sh}$ $651 \text{ s}$ $626 \text{ s}$ $613 \text{ s}, \text{ sh}$ $618 \text{ s}$ $608 \text{ s}$ $614 \text{ s}$ $\gamma_{OH}$ $593 \text{ vs}$ $545 \text{ sh}$ $540 \text{ s}$ $529 \text{ w}$ $\delta_{BO}$ $520 \text{ sh}$ $511 \text{ s}$ $502 \text{ s}$ $500 \text{ m}$ $\delta_{BO}$		759 s	757 s, b		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	742 s				748s ⊮BO
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-		702 s		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	680 sh				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		645 sh	651 s		
613 s, sh618 s $608 s$ $614 s$ $\gamma_{OH}$ 593 vs545 sh540 s520 sh511 s529 w500 sh502 s500 m			626 s		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	613 s, sh	618 s	608 s	614 s	γон
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	593 vs				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F 9 9 1	545 sh	540 s		)
500  sh $502  s$ $500  m$	520 sh	511 s	500	529 w	δво
		500 sh	5U2 S		500 m J

TABLE 3	(continued	I)
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HBO <sub>2</sub> -I (cubic metaboric acid) 4-coordinate boron [13]		PbO-2B <sub>2</sub> O <sub>3</sub> (lead tetraborate) 4-coordinate boron [44]	Na,B(OH) (teepleite) 4-coordina	Na₂B(OH)₄Cl (teepleite) 4-coordinate boron [45]		
IR	Raman	IR [38]	IR [43]	Raman [	43] <sup>a</sup>	
472 s	478 vw		· · · ·			
122 m h	404 VW	420 m		430 w	8	
400 m, D	434 VW 410 sh	430 m 419 w		400 W	0 BO	
	385 vs	712 W				
361 s	367  m. sh					
	,	342 w				
317 s	321 m					
	305 m					
292 w						
270 s	271 m					
228 s	231 vs					
	164 sh					
	150 s					
	115 sh					
	104 m					

<sup>a</sup>A more recent vibrational study [46] on a single crystal of teepleite confirmed the assignment given above.

absorption band (termed D), which is usually centred below 1600 cm<sup>-1</sup>. This transition has been observed e.g. for acid oxalates of the alkali metals [32]

The infrared spectrum of HBO<sub>2</sub>-I shows both the broad band centred between 1500 and 1000 cm<sup>-1</sup> (band D) and the three components at higher wavenumbers (bands A, B and C) and is therefore an intermediate case. Thus we conclude that HBO<sub>2</sub>-I contains strong asymmetric H-bonds and that the spectral behaviour suggests an O…O interatomic distance in agreement with the experimental value of 2.49 Å [13]. Similar spectral behaviour has been recently observed by Hadži [33] for the case of sodium hydrogenformate.

Raman and infrared spectra indicate that the H-bonds present in the three forms of  $HBO_2$  have different strengths. In order to explain this phenomenon in a qualitative way we must both consider the structures known from X-ray measurements and also take into account general considerations about the strength of the H-bond as discussed in an earlier paper [2]. In the latter paper we noted that the strength of an H-bond depends on both the acidic character of the proton donor and the basic character of the proton acceptor. If we consider the three main structures representing an H-bond, according to the valence bond treatment,

 $\begin{array}{rcl} O_{I} & \rightarrow & O_{I} & H^{+} O_{II} & \leftrightarrow & O_{I} & H^{-} O_{II}^{*} \\ (\text{covalent}) & (\text{ionic}) & (\text{charge-transfer}) \end{array}$ 

a strong H-bond is possible when contributions of both the covalent and the



Fig. 4. Structure of a layer of HBO<sub>2</sub>-III [11].

charge-transfer structures become the same (strong symmetric H-bond) or comparable (strong asymmetric H-bond). This is possible only if the interacting groups have sufficiently strong acidic and basic character\*.

By extending these considerations to the case of  $HBO_2$ , we observe that in the structure of  $HBO_2$ -III (Fig. 4) the H-bonds occur between neutral, twocoordinate oxygen atoms which are linked with neutral, three-coordinate boron atoms. However, a few H-bonds in the structure of  $HBO_2$ -II (Fig. 5) (namely those having the shortest O…O interatomic distances and consequently the strongest bonds), and all the H-bonds present in the structure of  $HBO_2$ -I (Fig. 6) involve a three-coordinate oxygen atom with a formal positive charge linked to a four-coordinate boron atom with a formal negative charge. In these cases the three structures given above for the H-bond become

 $\begin{array}{rcl} O_{I}^{+-}H & O_{II} & \leftrightarrow & O_{I} & H^{+} & O_{II} & \leftrightarrow & O_{I} & H^{--}O_{II}^{+} \\ (\text{covalent}) & (\text{ionic}) & (\text{charge-transfer}) \end{array}$ 

and the increasingly acidic character of the  $O^+$ —H bond can explain the strengthening of some of the H-bonds in HBO<sub>2</sub>-II and of all the H-bonds in HBO<sub>2</sub>-I reasonably well.

Moreover, it is interesting to note that the cubic form  $HBO_2$ -I has a higher density and refractive index than the other forms, and also that it is very

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<sup>\*</sup>The formation of a strong H-bond is expected for  $\Delta p k_a \simeq 2$ .



Fig. 5. Part of the structure of HBO<sub>2</sub>-II projected on the (201) plane [12].



Fig. 6. A portion of the three-dimensional tetrahedral network of HBO<sub>2</sub>-I [13].

hard and has relatively small thermal vibrations [13]. All these different properties depend on the crystalline structure, which is directly related to the strength of the H-bond.

The presence of H-bonds of different strengths in the three forms can be further investigated by examining the remaining bands ( $\delta_{OH}$ ,  $\gamma_{OH}$ ,  $\nu_{OH}$ ...O) due to the H-bond. The in-plane deformation mode  $\delta_{OH}$  is generally difficult to assign because in polyatomic molecules it is usually coupled to other vibrational modes. However, the out-of-plane deformation  $\gamma_{OH}$  is generally a highly localized vibration [23, 24]. It has been shown experimentally that both the  $\delta_{OH}$  and the  $\gamma_{OH}$  vibrations give rise to strong bands in the infrared, which shift to higher wavenumbers as the strength of the H-bond increases. The  $\nu_{O-H=0}$  stretching vibration occurs at low frequencies, generally <300  $cm^{-1}$ , and is difficult to localize since it is often coupled to external vibrations or lattice modes. This vibration also shifts to higher wavenumbers as the strength of the H-bond increases. For example, in crystalline acetic acid (intermediate H-bond) it is observed at 198 cm<sup>-1</sup> [34], while in sodium hydrogendiacetate (strong symmetric H-bond) it is observed at 320 cm<sup>-1</sup> [35].

As regards the infrared and Raman spectra of the three forms of metaboric acid, we agree with Parsons' [15] assignment of the  $\delta_{OH}$  and  $\gamma_{OH}$  vibrations in the range 1220—1000 cm<sup>-1</sup> and at 833 cm<sup>-1</sup>, respectively, for HBO<sub>2</sub>-III. This assignment is confirmed by our infrared and Raman measurements (Table 1), and is also in agreement with an average O…O distance of 2.75 Å obtained by X-ray measurements [11]. The location of the  $\nu_{O-H}$ ...o stretching vibration is less evident. Nevertheless, we note that the Raman spectrum of HBO<sub>2</sub>-III shows two strong bands at ~100 cm<sup>-1</sup> (Table 1), i.e. in a region where this vibration might be expected on the basis of the R(O…O) value [24].

For the other forms of HBO<sub>2</sub> the  $\delta_{OH}$ ,  $\gamma_{OH}$  and  $\nu_{OH\dots O}$  vibrations are much more difficult to localize, since several attempts to prepare DBO<sub>2</sub>-I and DBO<sub>2</sub>-II were unsuccessful.

In the case of HBO<sub>2</sub>-I, [R(O···O) = 2.487 Å], we expect the  $\delta_{OH}$  band to lie between 1440 (the value for KHPh (2.54 Å) [36]) and 1542 cm<sup>-1</sup> (the value for NaH(CH<sub>3</sub>COO)<sub>2</sub> (2.44 Å) [35]); and by analogy we expect the  $\gamma_{OH}$  band to lie between 1090 and 1285 cm<sup>-1</sup>, using  $\gamma_{OH}$  band frequencies from the same two compounds. Therefore we may reasonably assign the band at 1463 cm<sup>-1</sup> to the  $\delta_{OH}$  vibration, while the infrared spectrum shows two strong bands at 1088 and 1183 cm<sup>-1</sup> for the  $\gamma_{OH}$  mode. At liquid-nitrogen temperature these bands do not show an appreciable shift; the spectrum shows a general narrowing of the band at 825 cm<sup>-1</sup>. The  $\nu_{O-H}$ ...O mode is expected to occur at about 250 cm<sup>-1</sup> [24]. In this region intense bands are observed in both the Raman and the infrared spectra (Table 3).

In the case of HBO<sub>2</sub>-II it is impossible to assign the vibrational modes  $\delta_{OH}$ ,  $\gamma_{OH}$  and  $\nu_{O-H\cdots O}$  both because of the lack of the corresponding deuterated compound, and also because the  $\delta_{OH}$  and  $\gamma_{OH}$  modes occur in the region of the stretching vibration of BO bonds characterized by both three- and fourcoordinate boron atoms (Table 2).

Finally, Tables 2 and 3 show the infrared and Raman spectra (where available) of some borates having structures similar to  $HBO_2$ -II and  $HBO_2$ -I, respectively.

Table 2 also shows the infrared spectrum of *p*-veatchite  $(Sr, Ca)[B_3O_4(OH)_2]_2$ [37] and caesium triborate CsB<sub>3</sub>O<sub>5</sub> [38]. These compounds have structures similar to that of HBO<sub>2</sub>-II, and, in particular, they contain both trigonallyand tetrahedrally-coordinated boron atoms [39, 40]. Their spectra are in good agreement with that of HBO<sub>2</sub>-II. As usual, the stretching modes involving trigonal boron occur above 1100 cm<sup>-1</sup>, while those involving tetrahedral boron occur below 1100 cm<sup>-1</sup> [38, 41]. The Raman spectrum of CsB<sub>3</sub>O<sub>5</sub> is only reported in the literature as a sketch [42]. This spectrum shows an intense band at about 770 cm<sup>-1</sup>, a band which is also present in our Raman spectrum of  $HBO_2$ -II. The infrared and Raman spectra of  $HBO_2$ -II are in agreement with the structure obtained by X-ray studies [12] (Fig. 5) and show the presence of both trigonally and tetrahedrally-coordinated boron atoms.

Table 3 also shows the spectra of lead tetraborate  $PbO\cdot 2B_2O_3$  [38] and teepleite Na<sub>2</sub>B(OH)<sub>4</sub>Cl [43]. These compounds contain tetrahedrally-coordinated boron atoms [44, 45]. The spectra of HBO<sub>2</sub>-I show intense bands in those regions where, in the spectra of PbO·2B<sub>2</sub>O<sub>3</sub> and teepleite, the vibrations of BO bonds (tetrahedrally-coordinated boron atoms) occur. This spectroscopic behaviour confirms the structure proposed for HBO<sub>2</sub>-I by X-ray measurements and shown in Fig. 6 [13].

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#### REFERENCES

- 1 A. Bertoluzza, C. Fagnano, M. A. Morelli and R. Tosi, Rend. Accad. Naz. Lincei, 58 (1975) 919.
- 2 A. Bertoluzza, C. Fagnano, M. A. Morelli and R. Tosi, Rend. Accad. Naz. Lincei, 60 (1976) 462.
- 3 A. Bertoluzza, M. A. Battaglia, P. Monti and M. A. Morelli, Int. Conf. Raman Spectrosc., 6th, Bangalore, India, 4–9 September, 1978.
- 4 A. Bertoluzza, G. B. Bonino and C. Fagnano, Rend. Accad. Naz. Lincei, 50 (1971) 140
- 5 A. Bertoluzza, M. A. Morelli and C. Fagnano, Rend. Accad. Naz. Lincei, 56 (1974) 1.
- 6 A. Bertoluzza and G. B. Bonino, Rend. Accad. Naz. Lincei, 48 (1970) 427.
- 7 A. Bertoluzza, G. B. Bonino and M. A. Morelli, Rend. Accad. Naz. Lincei, 49 (1970) 100.
- 8 A. Bertoluzza and G. B. Bonino, Rend. Accad. Naz. Lincei, 56 (1974) 931.
- 9 A. Marinangeli, M. A. Morelli, R. Simoni and A. Bertoluzza, Can. J. Spectrosc., 23 (1978) 173.
- 10 A. Bertoluzza, M. A. Morelli, C. Fagnano and R. Tosi, Rend. Accad. Naz. Lincei, 61 (1976) 465.
- 11 C. R. Peters and M. E. Milberg, Acta Crystallogr., 17 (1964) 229.
- 12 W. H. Zachariasen, Acta Crystallogr., 16 (1963) 385.
- 13 W. H. Zachariasen, Acta Crystallogr., 16 (1963) 380.
- 14 J. Goubeau and D. Hummel, Z. Phys. Chem., N. F., 20 (1959) 15.
- 15 J. L. Parsons, J. Chem. Phys., 33 (1960) 1860.
- 16 G. Nagarajan, Bull. Soc. Chim. Belg., 71 (1962) 431.
- 17 I. C. Hisatsune and N. H. Suarez, Inorg. Chem., 3 (1964) 168.
- 18 J. Krogh-Moe, Phys. Chem. Glasses, 6 (1965) 46.
- 19 L. Maya, Inorg. Chem., 15 (1976) 2179.
- 20 J. L. Parsons, A. H. Silver and M. E. Milberg, J. Chem. Phys., 34 (1961) 2192.
- 21 F. C. Kracek, G. W. Morey and H. E. Merwin, Am. J. Sci., 35 (1938) 143.
- 22 M. V. Kilday and E. J. Prosen, J. Am. Chem. Soc., 82 (1960) 5508.
- 23 D. Hadži and S. Bratos, The Hydrogen Bond, Vol. II, North-Holland, Amsterdam, 1976, p. 563.
- 24 A. Novak, Struct. Bonding (Berlin), 18 (1974) 177.
- 25 R. Blinc and D. Hadži, J. Mol. Phys., 1 (1958) 391.
- 26 S. Detoni and D. Hadži, Spectrochim. Acta, 20 (1964) 949.

- 27 S. Detoni and D. Hadži, J. Chim. Phys., 53 (1956) 760.
- 28 D. Hadži and N. Kobilarov. J. Chem. Soc. A. (1966) 439.
- 29 D. Hadži, Pure Appl. Chem., 11 (1965) 435.
- 30 S. E. Odinkov and A. V. Iogansen, Spectrochim. Acta, Part A, 28 (1972) 2343.
- 31 M. F. Claydon and N. Sheppard, Chem. Commun., (1969) 1431.
- 32 A. Novak, J. Chim. Phys., 72 (1975) 981.
- 33 D. Hadži, private communication.
- 34 G. L. Carlson, R. E. Witkowski and W. G. Fateley, Spectrochim. Acta, 22 (1966) 1117.
- 35 A. Novak, J. Chim. Phys., 69 (1972) 1615.
- 36 B. Orel and D. Hadži, Spectrochim. Acta, Part A, 31 (1975) 169.
- 37 E. V. Vlasova and M. G. Valyashko, Russ. J. Inorg. Chem., 11 (1966) 822.
- 38 C. E. Weir and R. A. Schroeder, J. Res. Natl. Bur. Stand., Ser. A. 68 (1964) 465.
- 39 I. M. Rumanova and O. Gaudymov, Kristallografiya, 16 (1971) 99.
- 40 J. Krogh-Moe, Acta Crystallogr., 13 (1960) 889; Acta Crystallogr., Sect. B, 30 (1974) 1178.
- 41 C. E. Weir and E. R. Lippincott, J. Res. Natl. Bur. Stand., Sect. A, 65 (1961) 173.
- 42 J. P. Bronswijk and E. Strijks, J. Non-Cryst. Solids, 24 (1977) 145.
- 43 W. E. Klee, Z. Anorg. Allg. Chem., 343 (1966) 58.
- 44 A. Perloff and S. Block, Acta Crystallogr., 20 (1966) 274.
- 45 M. Fornaseri, Period. Mineral., 18 (1949) 103.
- 46 V. Devarajan, E. Gräfe and E. Funck, Spectrochim. Acta, Part A, 30 (1974) 1235.
- 47 L. A. Kristiansen and J. Krogh-Moe, Phys. Chem. Glasses, 9 (1968) 96.
- 48 A. Bertoluzza, B. Righetti and S. Schiavina, Rend. Accad. Naz. Lincei, 53 (1972) 421.
- 49 A. Bertoluzza, C. Fagnano and P. Monti, Rend. Accad. Naz. Lincei, 55 (1973) 506.
- 50 J. P. Bronswijk, in G. H. Frischat (Ed.), Int. Conf. Physics Non-Cryst. Solids, 4th, 1976, Trans, Tech. Publ.: Aedermannsdorf, Switzerland.