Raman and FTIR spectra of $[Cu(H_2O)_6](BrO_3)_2$ and $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$

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Abstract

Raman and FTIR spectra of $[Cu(H_2O)_6](BrO_3)_2$ and $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ are recorded and analyzed. The observed bands are assigned on the basis of BrO_3^- and H_2O vibrations. Additional bands obtained in the region of v_3 and v_1 modes in $[Cu(H_2O)_6](BrO_3)_2$ are due to the lifting of degeneracy of v_3 modes, since the BrO_3^- ion occupies a site of lower symmetry. The appearance v_1 mode of BrO_3^- anion at a lower wavenumber (771 cm^{-1}) is attributed to the attachment of hydrogen to the BrO_3^- anion. The presence of three inequivalent bromate groups in the $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ structure is confirmed. The lifting of degeneracy of v_4 mode indicates that the symmetry of BrO_3^- anion is lowered in the above crystal from C_{3v} to C_1. The appearance of additional bands in the stretching and bonding mode regions of water indicates the presence of hydrogen bonds of different strengths in both the crystals. Temperature dependent Raman spectra of single crystal $[Cu(H_2O)_6](BrO_3)_2$ are recorded in the range 77–523 K for various temperatures. A small structural rearrangement takes place in BrO_3^- ion in the crystal at 391 K. Hydrogen bounds in the crystal are rearranging themselves leading to the loss of one water molecule at 485 K. This is preceded by the reorientation of BrO_3^- ions causing a phase transition at 447 K. Changes in intensities and wavenumbers of the bands and the narrowing down of the bands at 77 K are attributed to the settling down of protons into ordered positions in the crystal. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Raman spectra; IR spectra; Phase transitions

1. Introduction

Vibrational spectra of hydrated metal halates have been investigated by several workers [1–4]. $[Cu(H_2O)_6](BrO_3)_2$ is a member of the group, but it stands apart as it is the sixth example of Cu static structure inconsistent with the Jahn-Teller theorem [5]. It crystallizes in the cubic system. $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ is a heavily hydrated bromate, which crystallizes in the triclinic system [6]. Raman and infrared spectra of both these crystals are recorded and analysed. Temperature dependent Raman spectra of the single crystal $[Cu(H_2O)_6](BrO_3)_2$ are also recorded to understand the role of hydrogen bonding in the phase transition.

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2. Experimental

[Cu(H$_2$O)$_6$](BrO$_3$)$_2$ abbreviated as CuBH and [Al(H$_2$O)$_6$](BrO$_3$)$_3$·3H$_2$O abbreviated as AlBH were prepared from the respective aqueous solutions [5,6]. Partially deuterated analogues of CuBH abbreviated as CuBD and of AlBH termed as AlBD were prepared by repeated evaporation of deuterated solutions. A Spex Ramalog 1401 double monochromator equipped with a Spectra Physics model 165 Argon ion laser (514.5 nm) was employed to obtain Stokes Raman lines with a resolution better than 3 cm^{-1}. Raman spectra of a single crystal of CuBH were recorded at room temperature and at different temperatures from 77 to 473 K. A variable temperature cell fitted with a thermocouple Pt-100 was used and the temperature of the crystal was determined at each stage. AlBH is highly hygroscopic and, therefore, it was taken as powder in a sealed capillary tube. Raman spectrum of AlBD was also recorded. The FTIR spectra of the samples were recorded using a Bruker-IFS-66v spectrometer by polyethylene pellet method in the 50–400 cm^{-1} region and as KBr pellet method in the 400–4000 cm^{-1} region. Thermal analysis of CuBH was carried out from 50 to 550 °C in air atmosphere using Seiko Instruments.

3. Factor group analysis

The CuBH crystallizes in the cubic system with a space group $Pa\bar{3}(T_h^6)$ and the unit cell contains four formula units [5]. In the crystal BrO$_3^-$ ions occupy C$_3$ sites, the Cu atoms occupy the C$_{3i}$ sites and the water molecules occupy the general sites C$_1$. The number of optical modes at Brillouin zone at $k = 0$ were obtained by the correlation method developed by Fateley et al. [7]. They are distributed as:

$$\Gamma_{321} = 19A_g + 19E_g + 33F_g + 20A_u + 20E_u + 35F_u$$

AlBH crystallizes in the triclinic system with space group $P\bar{1}(C_i)$ having two formula units per unit cell [6]. All the atoms of the crystal are assigned to general positions. The optical modes in the crystal are:

$$\Gamma_{237} = 120A_g + 117A_u$$

4. Results and discussion

4.1. [Cu(H$_2$O)$_6$](BrO$_3$)$_2$

4.1.1. BrO$_3^-$ vibrations

The BrO$_3^-$ anion with C$_{3v}$ symmetry has four fundamental vibrations, symmetric stretching v_1, 805 (A_1); asymmetric stretching v_3, 805 (E); symmetric bending v_2, 418 (A_1); and asymmetric bending v_4, 358 (E) cm^{-1} [8]. For XY$_3$ pyramidal (C$_{3v}$) molecules $\Gamma = 2A_1 + 2E$, and all the modes are active both in the Raman and IR spectra [9].

Four bands at 819, 800, 789 and 771 cm^{-1} are obtained in Raman spectra in the Br–O stretching region (Fig. 1). Of these 819 and 789 cm^{-1} bands are highly intense, while the other two appear as shoulders. The intense bands vary in intensity with change of polarization. In the IR spectrum, an intense band is obtained in this region with two peaks at 820 and 792 cm^{-1}. Since both the v_1 and v_3 modes are Raman and IR active, it is difficult to assign the v_1 and v_3 modes separately. In the deuterated compound a broad band with a peak at 791 cm^{-1} is observed in the IR (Fig. 3b). Following the assignment done in Tb(BrO$_3$)$_3$·9H$_2$O [10] the band near 789 cm^{-1} is assigned to the v_1 mode. Attachment of hydrogen to the BrO$_3^-$ makes this mode to appear at a lower wavenumber (771 cm^{-1}).

In the symmetric bending mode region (v_2) a weak band appears at 429 cm^{-1} in the Raman spectra (Table 1.) In the IR a moderately intense band is present at 439 cm^{-1}. The doubly degenerate v_4 mode appears with its degeneracy lifted (371 and 384 cm^{-1}) in the Raman spectra. The 371 cm^{-1} band has larger intensity than the 384 cm^{-1} band. In the IR spectrum also two bands are observed at 360 and 393 cm^{-1} (Fig. 2a). In CuBD these two bands appear as a single broad band at 349 cm^{-1} (Fig. 2b).

The typical Cu^{II} sixfold-coordinated complex is a distorted octahedral array displaying (2 + 2 + 2) coordination about the copper ion [5]. Of

these one pair has larger Cu–ligand distance, in agreement with the static Jahn-Teller effect. However, in CuBU, copper ion is at a site having symmetry C_{3i}. Hence, the corresponding polyhedron has a single Cu–O(2) distance of 2.079 Å leading to dynamic Jahn-Teller effect. Therefore, bromate ion has a rigid body behaviour with a Br–O distance of 1.663 Å in the crystal [5]. Additional bands obtained in the region of v_3 and v_1 modes are due to the lifting of degeneracy of the v_3 mode, since the BrO_3^- ion occupies a site of lower symmetry. Therefore, the absence of multiple bands in the IR and Raman spectra confirms the X-ray data of the existence of one Br–O distance of 1.663 Å [5]. As observed in $Cd(BrO_3)_2 \cdot 2H_2O$, a mixing of the v_1 and v_3 modes can occur in the title compound and this explains the large intensity of the v_3 mode in the Raman spectra [3]. On deuteration, the lifting of degeneracy is reduced causing the appearance of only one band each in the region of v_3 and v_4 modes.

4.1.2. $[Cu (H_2O)_6]^{2+}$ vibrations

The $[Cu(H_2O)_6]^{2+}$ anion forms an octahedra with O_h symmetry. Brown et al. have calculated the vibrational modes of $M(H_2O)_6$ octahedra using normal coordinate analysis [11]. The fundamental modes of $Cu(H_2O)_6$ in Tutton salts are at v_1 (396 cm^{-1}), v_2 (299 cm^{-1}), v_3 (414 cm^{-1}), v_4 (264 cm^{-1}), v_5 (179 cm^{-1}) and v_6 (119 cm^{-1}). In CuBH, v_1 and v_3 modes of $[Cu (H_2O)_6]^{2+}$ anion fall in the bending mode region of BrO_3^- anion. The remaining modes v_2, v_4, v_5 and v_6 are in the lattice mode region. So an unambiguous assignment of internal modes of $[Cu(H_2O)_6]^{2+}$ is difficult. The Raman active v_5 mode is observed as a weak broad band at 179 cm^{-1} in the Raman spectra. In the IR spectrum a weak shoulder at 174 cm^{-1} is observed in this region. The strong broad band observed in the IR at 221 cm^{-1} is probably the IR active v_4 mode since this band is absent in the Raman spectra. The moderately intense peak at 122 cm^{-1} in Raman and a shoulder near 120 cm^{-1} in the IR are due to Raman
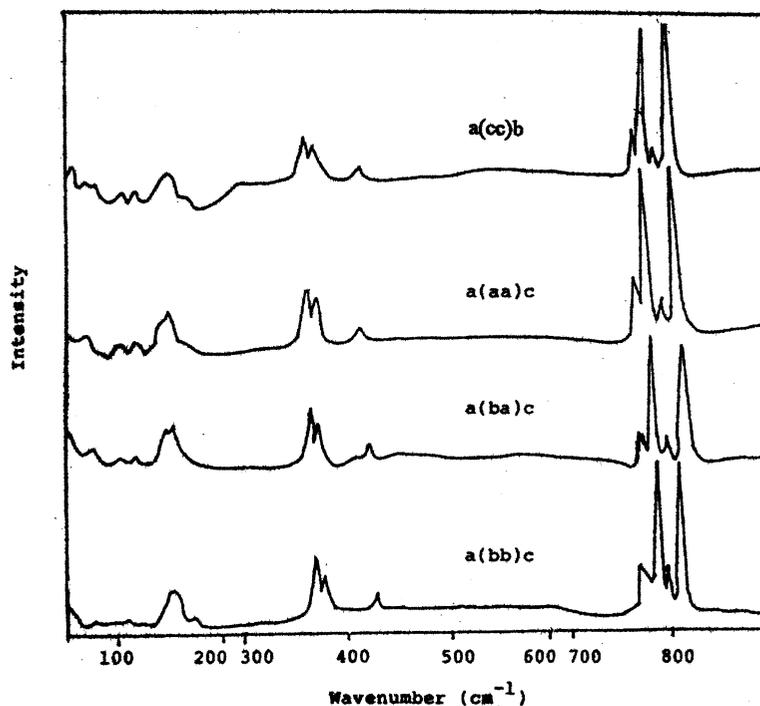

Fig. 1. Raman Spectra of $[Cu(H_2O)_6](BrO_3)_2$ in the region 50–900 cm^{-1} for a(bb)c, a(ba)c, a(aa)c and a(cc)b orientations.

Table 1
Spectral data (cm^{-1}) of [Cu(H$_2$O)$_6$](BrO$_3$)$_2$

Raman				FTIR		Assignments
a(bb)c	a(ba)c	a(aa)c	a(cc)b	CUBH	CUBD	
1	2	3	4	5	6	
56 vs	56 vw	56 vw	55 vw			Lattice modes
					61 w	
65 vw	65 vw	62 vw	65 vw	64 w		
78 m	78m	78w				
				89 s		
					94w	
110 vw	108 vw	109 vw	109 vw	110 s		v_6^c & BrO$_3^-$ libr.
122 m	120 w	121 vw	125 w	120 sh		
					134 w	
149 w	150 sh	150 sh				
			155 wbr	155 m		
	158 ms	158 ms			159 m	BrO$_3^-$ rot.
				174 sh		
179 w	175 w	178 sh				v_5^c
					195 w	
				221 mbr	231 m	v_4^c
					255 m	
					349 sbr	
				360 s		
371 ms	372 ms	374 m	371 m			v_4 BrO$_3^-$ & v_1^c
			393 m	393 s		
384 m	387 m	389 m				
429 w					422 vs	v_2 BrO$_3^-$ + v_3^c
				439 s		
					492 vw	
					575 w	lib. H$_2$O
771 sh	774 sh	775 sh	773 sh			v_1–v_3 BrO$_3^-$
789 vs	785 s	785 vs	785 vs	792 vs	791 vsbr	
800 sh	800 wsh	800 sh	802 vw	820 vs		
819 vs	821 vs	820 vs	823 vvs			
					938 w	Combinations
					1047 w	
				1128 vw		
					1261 vw	
					1368 w	
				1384 w	1384 w	
					1407 w	δ HOD & Combinations
				1520 sh	1520 sh	
				1595 m		v_2H$_2$O
				1624 sh	1608 m	
				2068 w		
					2521 vw	v OD
					2538 vw	
				2849 vw	2850 vw	
				2918 w	2922 vw	
				3149 sh		
					3401 sh	v_1–v_3 H$_2$O
				3455 ms	3428 ms	
				3516 ms	3519 m	
					3566 w	
				3666 w		
		v^c–v Cu(H$_2$O)$_6$				

and IR inactive ν_6 mode. These assignments agree with those reported by Rajagopal et al. [12].

4.1.3. H_2O vibrations

The vibrational frequencies of a free water molecule (C_{2v}) are at 3652 cm^{-1}, ν_1, 1595 cm^{-1}, ν_2 and 3756 cm^{-1}, ν_3 [13]. In the IR spectrum of CuBH, a highly intense broad band is observed with peaks at 3516 and 3455 and a shoulder at 3149 cm^{-1}. In CuBD, the intensity of this broad band is reduced by about 44% and peaks are obtained at 3566, 3519, 3428 and 3401 cm^{-1} (Fig. 3b). New, but weak bands appear at 2538 and
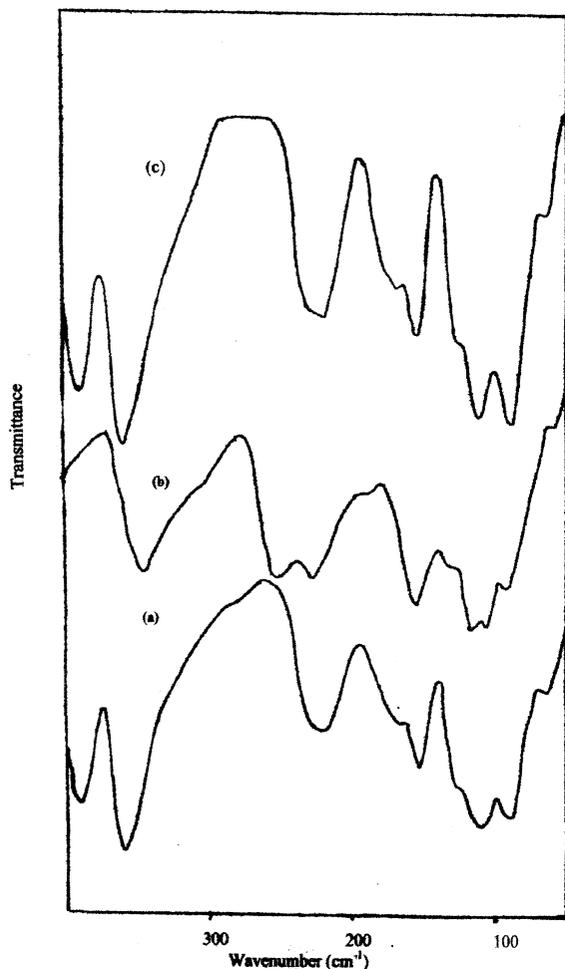

Fig. 2. FTIR Spectra of (a) $[Cu(H_2O)_6](BrO_3)_2$, (b) Partially deuterated $[Cu(H_2O)_6](BrO_3)_2$ and (c) $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ in the region 50–400 cm^{-1}.
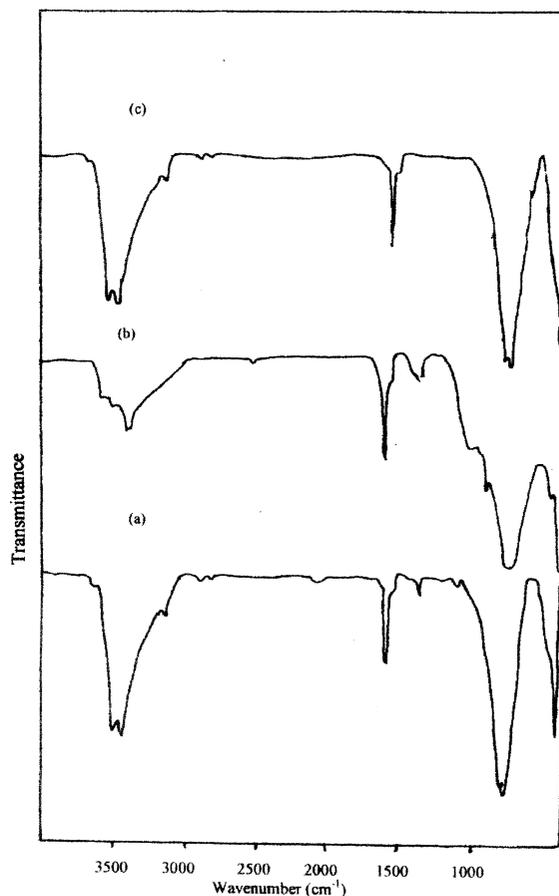

Fig. 3. FTIR Spectra of (a) $[Cu(H_2O)_6](BrO_3)_2$, (b) Partially deuterated $[Cu(H_2O)_6](BrO_3)_2$ (c) and $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ in the region 400–4000 cm^{-1}.

2521 cm^{-1} corresponding to OD stretching vibrations. In the bending mode region, a moderately intense band is observed at 1595 cm^{-1} with a shoulder at 1624 cm^{-1} (Fig. 3a). On deuteration, the intensity of this band is only slightly reduced (6%) and the shoulder disappears. New bands at 1407 and 1368 cm^{-1} also appear and they are assigned to δ HOD modes [3].

The appearance of additional bands in the stretching and bending mode regions of water indicates the presence of hydrogen bonds of different strengths in the crystal. The OH stretching modes appear at lower frequencies than in a free water molecule and this points to hydrogen bounds of moderate to weak strengths in agree-

ment with the O...O distances reported [5]. The $Cu-O_w$ coordination causes a down shifting of the water bending vibrations, while hydrogen bonding leads to an up shifting of these modes [14]. Therefore, the wavenumber of water bending modes is not much altered.

4.1.4. Lattice modes

Bands below 200 cm^{-1} are mainly due to the translational and rotational modes of BrO$^-$ ions and Cu atoms. A fairly intense broad band is observed around 158 cm^{-1} in Raman spectra. This is assigned to the BrO_3^- rotational mode [15] as they are more intense than translatory modes in Raman spectra.

4.2. $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$

4.2.1. BrO_3^- vibrations

The stretching and bending vibrations of bromate ion are assigned in comparison with the bands in CuBH. In the v_1 mode region, Raman spectrum gives an intense broad band at 792 cm^{-1} with shoulders at 771 and 808 cm^{-1} (Fig. 4a and Table 2). A moderately intense band observed at 838 cm^{-1} is assigned to the v_3 mode. In the IR, an intense broad band with peaks at 783 and 820 cm^{-1} is obtained, the former corresponding to the v_1
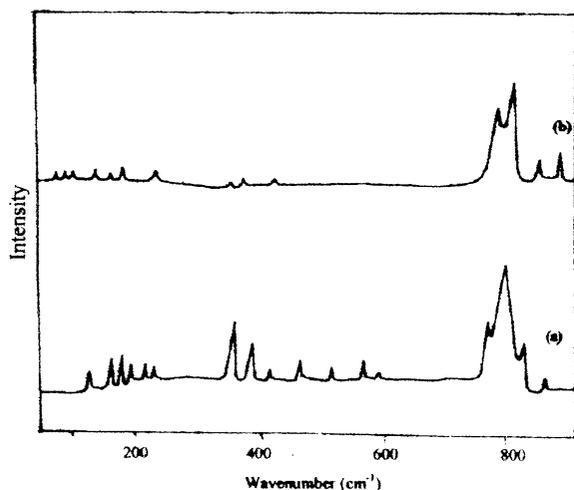

Fig. 4. Raman Spectra of (a) $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ (b) Partially deuterated $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ in the region 50–900 cm^{-1}.

mode and the latter to the v_3 mode. The v_2 mode gives two weak bands at 439 and 462 cm^{-1} in Raman spectrum and an intense band at 436 cm^{-1} with a shoulder at 454 cm^{-1} in the IR. The asymmetric bending mode v_4 appears with degeneracy lifted in both the IR and Raman spectra. On deuteration, the number of bands in the Raman spectrum is found to be reduced in the v_1 and v_2 mode regions (Fig. 4b). The bands are also shifted slightly to high wavenumber values. A good IR spectrum of the deuterated compound could not be obtained due to the highly hygroscopic property of the aluminium compound.

Three inequivalent bromate groups with Br–O distances ranging from 1.623(5) to 1.669 (4) Å are present in the crystal [6]. The presence of three bands in the v_1 mode region in the Raman spectrum is in agreement with the above structural information. The lifting of degeneracy of v_4 mode indicates that the symmetry of BrO$_3^-$ anion is lowered from C_{3v} to C_1. This also confirms the structural data that O–Br–O angles vary from 102.3(2) to 105.8(2)° [6].

4.2.2. $Al(H_2O)_6^{3+}$ vibrations

$Al(H_2O)_6^{3+}$ cation has an O_h symmetry, and the vibrational modes are $v_1(A_{1g})$, v_2 (E_g), v_3 (F_{1u}), v_4 (F_{1u}), v_5 (F_{2g}) and v_6 (F_{2u}). Of these v_1, v_2 and v_5 modes are Raman active, v_3 and v_4 modes are IR active and v_6 is inactive in both Raman and IR. In solutions, the v_1, v_2 and v_5 modes are reported to be at 525 447 and 340 cm^{-1}, respectively, [16,17]. Two weak bands at 555 and 508 cm^{-1} are observed in the Raman spectrum in the above region [18]. In $CsAl(SO_4)_2 \cdot 12H_2O$ [17], the v_2 $(AlO)_6$ is assigned around 473 cm^{-1} and the v_5 (AlO_6) around 349 cm^{-1}. They fall in the region of the bending modes of the BrO$_3^-$ ions and, therefore, an unambiguous assignment of bands is not possible.

4.2.3. H_2O vibrations

In the stretching modes region of H_2O an intense broad band extending from 3560 to 3350 cm^{-1} is obtained in the IR spectrum (Fig. 3c). Two intense peaks at 3516 and 3455 cm^{-1} and a shoulder at 3150 cm^{-1} are also obtained. In the bending mode region, a moderately lntense band is observed at

Table 2
Spectral data (cm^{-1}) and band assignments of $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O/D_2O$

$[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$		$[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O/D_2O$	Assignments
Raman	FTIR	Raman	
	63 vvw	65 vw	
	87 w	71 vw	Lattice modes
		79 w	
129 vvw	110 w	121 w	libr. BrO_3^-
	154 w		rot. $Al(H_2O)_6$
178 vw	169 w	160 w	
184 w			
194 w			
229 w	221 w	208 w	
232 w		225 w	
		345 w	
369 m	360 m	360 w	ν_4 BrO_3^- & ν_5 $Al(H_2O)_6^{3+}$
395 br	389 m	370 m	
439 w	436 ms	415 w	ν_2 BrO_3^- & ν_2 $Al(H_2O)_6^{3+}$
462 vw	454 sh		
508 w			ν_1 $Al(H_2O)_6^{3+}$
555 vw			
590 w	576 vw		
601 vw	593 vw		
771 sh	783 s	765 sh	ν_1 BrO_3^-
792 sbr		795 s	
808 sh			
838 m	820 s		ν_3 BrO_3^-
		861 m	
		875 w	
	1550 sh		ν_2 H_2O
	1595 s		
	1610 sh		
	2850 vw		
	2919 vw		
	3150 sh		$\nu_1-\nu_3 H_2O$
	3455 vs		
	3516 vs		
	3625 sh		

1595 cm^{-1} with shoulders at 1610 and 1550 cm^{-1}. The appearance of OH stretching modes at lower wavenumber than those of free state values [10] and of bending modes at higher wavenumbers indicate the presence of hydrogen bonds in the crystal. Due to hydrogen bonds, OH bending modes are usually shifted upwards. But correlation of Al atoms to the water O atoms causes a downward shift. Therefore, the intense OH bending modes appear without any shift in wavenumber values [13,14].

Nine inequivalent water molecule O atoms are present in the structure. Of these, six are coordinated to Al, two are corrdinated to two H atoms each and one is coordinated to a single H atom. Moreover, HOH angle varies from 94 to 117° [6]. The appearance of additional bands in the OH bending and stretching regions confirms the existence of hydrogen bounds of different strengths in the crystal in agreement with the X-ray study [6].

4.3. Temperature dependent Raman spectra of $[Cu(H_2O)_6](BrO_3)_2$

4.3.1. High temperature spectra

Raman spectra of CuBH are recorded in the region 50–1000 cm^{-1} at 299, 323, 343, 363, 383, 403, 423 and 473 K and the assignments of bands are as given in Table 3. At 323 K, the intensity of most of the bands is marginally (10–20%) increased. In the lattice mode region, the weak

Table 3
Raman spectral data and band assignments of $[Cu(H_2O)_6](BrO_3)_2$ at different temperatures

299 K	323 K	343 K	363 K	383 K	403 K	423 K	473 K	77 K	Assignments
69 vw			54 vvw	54 vw		61 vw	59 wbr	61 vw	Lattice modes
78 w	74 wbr	78 w	75 wbr	75 wbr	76 w	71 m	73 w	68 vw	
			105 w		102 w	91 vvw		85 vvw	
109 vw	109 vw	109 w	110 w	109 vvw		109 w		101 vvw	
124 w	124 w	124 w	123 w	123 vvw	126 w	123 w	116 wbr	118 vvw	v_6^c & BrO_3^- libr.
149 w	146 sh	147 sh	150 sh	151 sbr	150 s	150 s	147 m	145 m	rot. BrO_3^-
158 m	157 m	158 m	158 m					159 m	
178 vw	178 vw	175 wbr	176 wbr					172 w	v_5^c
371 ms	371 ms	371 ms	371 ms	371 ms	371 m	372 m	350 w	378 m	v_4 BrO_3^- & v_1^c
384 m	385 m	384 m	383 msh	383 msh	385 sh	388 sh		390 w	
					399 m	399 m	400 w		
429 w	429 w	429 w	429 w	429 w	429 w	429 w		416 w	v_2 BrO_3^- & v_3^c
					440 vw	441 w	440 w		
771 vw	771 m	770 m	773 msh	771 sh			778 m	775 ms	v_1–v_3 BrO_3^-
789 s	786 s	786 vs	784 vvs	784 vs	785 w	784 w		790 s	
				798 m	798 s	789 sh			
800 m	799 m	800 m	796 m	801 m	800 s	800 vs	801 ms	805 m	
					812 sh				
819 vvs	819 vvs	820 s	818 s	819 s	815 s	818 m	835 m	826 s	

Vvw, very very weak; vw, very weak; w, weak; m, medium; wbr, weak and broad; sh, shoulder; sbr, strong and broad; vs, very strong; s, strong; vvs, very very strong; ms, moderately strong; msbr, mdoderately strong and broad; tr, Translational vsbr, very strong and broad.; rot., rotational; libr., librational.
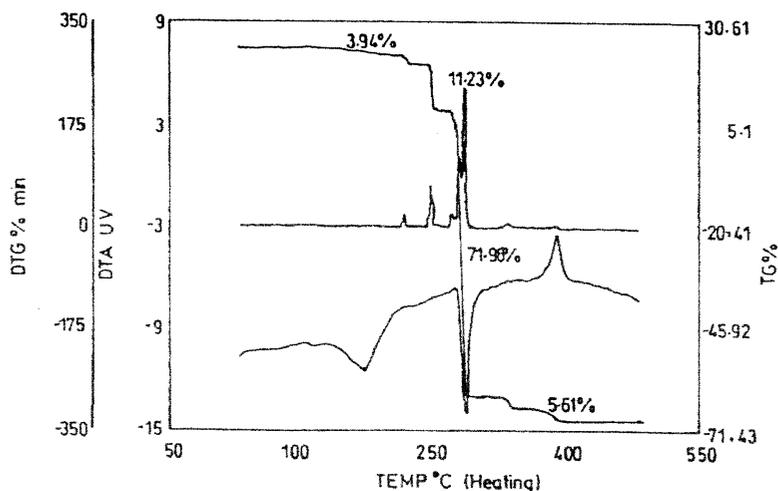

Fig. 5. TG,DTA,DTG curve of $[Cu(H_2O)_6](BrO_3)_2$.

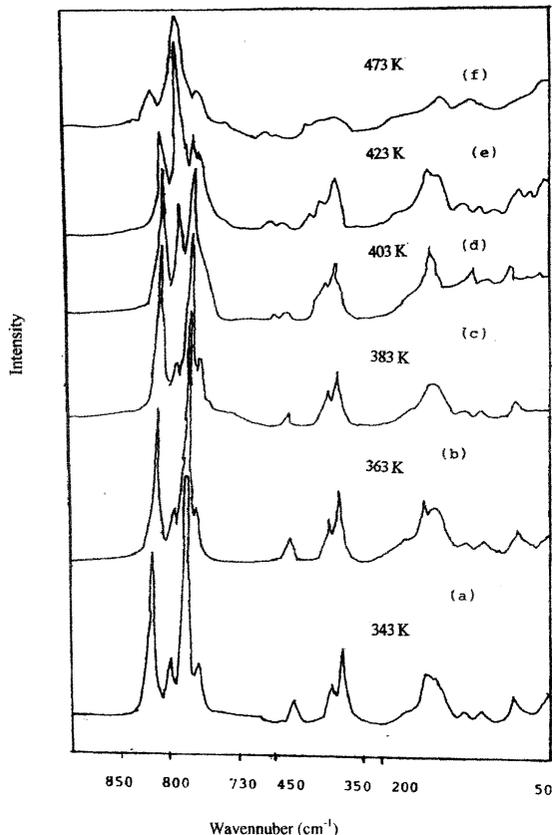Fig. 6. Raman Spectra of $[Cu(H_2O)_6](BrO_3)_2$ in the temperature range 343–473 K in the 50–900 cm^{-1} region.

bands at 69–78 cm^{-1} merge together to become a broad band (323 K). When the temperature is raised to 343 K, intensity of most of the bands again increases with the v_1 mode (789 cm^{-1}) of BrO_3^- exhibiting the maximum enhancement (120%) (Fig. 7a). At the same time, the intensity of the v_3 mode (819 cm^{-1}) decreases by about 28% (Fig. 7c). At 363 K a new weak band appears at 105 cm^{-1}. At 383 K the band at 800 cm^{-1} shows 96% intensity enhancement (Fig. 7b). The broad band from 360 to 392 cm^{-1} at 383 K corresponding to v_4 (BrO_3^-) vibrations further broadens to 355–404 cm^{-1} region at 403K (Fig. 6d) and another peak appears in it at 399 cm^{-1}. The band corresponding to the bending mode v_2 also increases in width. The intensity of 800 cm^{-1} band increases equal to those of 789 and 819 cm^{-1} bands. The broad band at 158 cm^{-1} becomes sharp as it approaches 403 K and it again

becomes broad at 423 K (Fig. 6e). The peak of this band is shifted to lower wavenumbers. At 423 K, the intensity of 800 cm^{-1} band is enhanced to about 600% of the intensity at room temperature (299 K). The 800 cm^{-1} band becomes the most intense band in the spectrum at 423 K. At 473 K most of the bands including 800 cm^{-1} band exhibit a reduction in intensity and they become broader (Fig. 6f). Most of the peaks are found to be shifted slightly to higher wavenumber than those at room temperature (Table 3).

Devanathan et al. have observed the frequency changes in the stretching region of BrO_3^- anion with temperature as completely reversible in $Cd(BrO_3)_2 \cdot 2H_2O$. Usually in hydrated bromates, spectral changes are accompanied by the loss of water molecule from the crystal with temperature. A structural change can take place either due to a change in temperature or due to a change in chemical composition [4,19,20].

DTA curve of CuBH exhibits a weak endotherm peak around 391 K (Fig. 5). No such change is observed in TG and DTG curves at this temperature and, therefore, no loss of water molecules takes place at 391 K. Changes in intensities of Raman bands between 383 and 403 K and the weak endotherm peak around 391 K indicate a small structural rearrangement taking place in BrO_3^- ion in the crystal.

T.G. Curve indicates 3.94 wt.% loss, in the crystal at 485 K. DTG also confirms this observation (Fig. 5) and is due to the loss of one water molecule from the crystal. In DTA, an intense peak is obtained at 447 K indicating a phase transition in the crystal. The large enhancement in intensity of the 800 cm^{-1} band at 423 K and the subsequent decrease in intensity of all BrO_3^- modes along with the shift in wavenumber values confirm the structural phase transition in the crystal. Hydrogen bonds in the crystal re rearranging themselves at these temperatures leading to the loss of one water molecule at 485 K. This is preceded by the reorientation of BrO_3^- ions that can cause this transition at 447 K [1].

4.3.2. Low temperature spectra

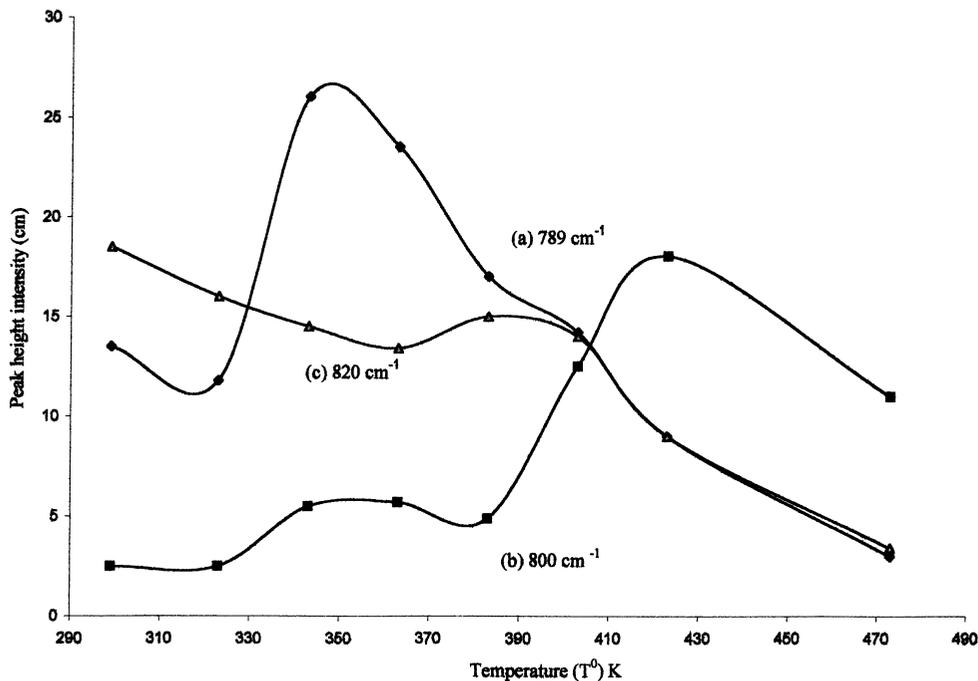Bands in the Raman spectra recorded at 77 K become narrow with slight modifications in inten-

Fig. 7. Raman Spectral intensity change with temperature in $[Cu(H_2O)_6](BrO_3)_2$ at (a) 789, (b) 800 and (c) 820 cm^{-1}.

sity and nature of bands. The band at 158 cm^{-1} is found to be resolved into two bands at 77 K. The intensity of 384 cm^{-1} band is enhanced and its intensity becomes equal to that of 371 cm^{-1}, both of them being v_4 (BrO_3^-) vibration. The v_3 mode of BrO_3^- ion at 820 cm^{-1} is shifted to 831 cm^{-1} and its intensity is slightly reduced. A few other bands are also shifted to higher wavenumber values. These changes in intensities and bands and the narrowing down of the bands are attributed to the settling down of protons into ordered positions in the crystal [21].

5. Conclusions

Additional bands obtained in the region of v_3 and v_1 modes in $[Cu(H_2O)_6](BrO_3)_2$ are due to the lifting of degeneracy of v_3 modes, since the BrO_3^- ion occupies a site of lower symmetry. Attachment of hydrogen to the BrO_3^- makes v_1 mode to appear at a lower wavenumber (771 cm^{-1}) also. The presence of three bands in the v_1 mode region in the Raman

spectrum of $[Al(H_2O)_6](BrO_3)_3 \cdot 3H_2O$ is in agreement with three inequivalent bromate groups in the crystal. The lifting of degeneracy of v_4 mode indicates that the symmetry of BrO_3^- anion is lowered from C_{3v} to C_1. The appearance of additional bands in the stretching and bending mode regions of water indicates the presence of hydrogen bonds of different strengths in both the crystals. A small structural rearrangement takes place in BrO_3^- ion in the crystal at 391 K. Hydrogen bonds in the crystal are rearranging themselves leading to the loss of one water molecule at 485 K. This is preceded by the reorientation of BrO_3^- ions causing a phase transition at 447 K. Changes in intensities and wavenumbers of the bands and the narrowing down of the bands at 77 K are attributed to the settling down of protons into ordered positions in the crystal.

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