Phase transition in betaine potassium bromide dihydrate studied by Raman scattering

Phase transition in betaine potassium bromide dihydrate studied by Raman scattering

Yu I Yuzyuk†§, A Almeida†, M R Chaves†, Filipa Pinto† and A Klöpperpieper‡

† Departamento de Física, IMAT (núcleo IFIMUP), CFUP,
Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal
‡ Fachbereich Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

Abstract. Polarized Raman spectra of betaine potassium bromide dihydrate were studied in the broad spectral range 5–3600 cm^{-1} and in the wide temperature interval 30–292 K, with special emphasis on the structural phase transition at 160 K, recently discovered. It is shown that this phase transition is related to the freezing of the successive reorientations of the water molecules. Peculiar features and the temperature evolution of hydrogen bonding in this compound are discussed.

1. Introduction

Betaine compounds exhibit a rich variety of crystal structures and interesting physical properties [1]. Recently, a new family of hydrates whose general formula is $[(CH_3)_3N^+CH_2COO^-]_n \cdot AB \cdot 2H_2O$ ($n = 1, 2$; A = K, Rb; B = Br, I) was produced. As is well known, the internal and the external vibrations of water molecules are more or less affected by the structural environment in the unit cell. Consequently, Raman scattering becomes a particularly adequate technique in the study of solid hydrates [2].

Betaine potassium iodide dihydrate ($n = 2$, A = K, B = I), BKI for short, is triclinic with the space group $P\bar{1}$ at room temperature [3]. Two water molecules in BKI are coordinated to K$^+$ ions and exhibit large angle reorientations without any signature of H-bonding at ambient temperature. A first order phase transition (PT) at $\sim$100 K was disclosed in BKI by dielectric studies [4]. The analysis of Raman spectra has identified this PT as of order–disorder type, closely associated with the freezing of the successive reorientations of water molecules [5].

Betaine potassium bromide dihydrate ($n = 1$, A = K, B = Br), hereafter denoted by BKBr, crystallizes into an orthorhombic structure (space group $Pbcm$) with four formula units in the unit cell. A recent x-ray study provided evidence for the existence of two types of water molecule in this compound [6]. BKBr represents a new type of crystal structure in the betaine family, since the coordination of the water molecules and consequently the system of hydrogen bonds in this crystal is completely different from that observed in other betaine dihydrates such as BKI and BCCD ($(CH_3)_3NCH_2COO \cdot CaCl_2 \cdot 2H_2O$). In fact the hydrogen atoms of the two water molecules in BKBr are engaged in various kinds of asymmetric hydrogen bond: O–H$\cdots$Br and O–H$\cdots$O. However, the identity of the water molecules is more or less

§ On leave from the Faculty of Physics, Rostov State University, Rostov-on-Don, Russia.

preserved as shown by the analysis of the Raman spectra. Although BKBr undergoes a PT at ~160 K also related to the water molecule reorientations [7], the Raman study presented in this work has revealed unique features and an interesting transformation of hydrogen bonds at the structural PT in this crystal.

2. Experimental details

Polarized Raman spectra have been measured on samples in the form of carefully oriented and optically polished rectangular parallelepipeds $5 \times 4 \times 3$ mm^3 with the axes a, b, c parallel to [100], [010] and [001], respectively. The crystallographic axes were determined with an accuracy of $\pm 1°$ by x-ray diffraction.

Raman spectra were excited using the polarized light of an Ar$^+$ laser Coherent Innova 90 ($\lambda = 514.5$ nm) in a right-scattering geometry. The scattered light was analysed using a Jobin Yvon T64000 spectrometer equipped with a CCD and a photon counting detector. The spectral slit width was about 1.5 cm^{-1}.

The samples were placed in a closed-cycle helium cryostat with a temperature stability of about ± 0.2 K. The actual sample temperatures were estimated to differ by less than 1 K from the temperature measured with a silicon diode attached to the sample holder. The temperature homogeneity in the sample was achieved with a copper mask set-up.

3. Results and discussion

3.1. Raman spectra at room temperature

According to x-ray data [6] the K$^+$ ions occupy a special fourfold position with the site symmetry C$_2$. The Br$^-$ ions, the betaines and the four water molecules occupy fourfold sites of C$_s$ (σ^{xy}) symmetry. The remaining four water molecules exhibit large-angle reorientations with respect to the mirror plane and are distributed among eightfold general positions with the probability $\frac{1}{2}$ [6]. Consequently, there are two types of water molecule in BKBr. Schematic projections of the crystal structure (betaines are not shown) onto the ab and bc planes at room temperature are presented in figure 1. One type of water molecule, labelled as H$_2$O(I), is coordinated to the potassium ion while the other one, labelled as H$_2$O(II), is not. In BKBr the water molecules have the following bond state: each hydrogen atom of the H$_2$O(I) molecule is involved in a hydrogen bond, one with another water molecule of the H$_2$O(II) type and the other with the Br$^-$ ion. The H$_2$O(II) molecule also forms hydrogen bonds with the same Br$^-$ ion and on the other hand with the oxygen atom (O2) of a carboxyl group of the betaine. The latter bond is strong enough to localize the corresponding proton in the mirror plane while the other proton together with the oxygen atom (O4) of the H$_2$O(II) molecule exhibit thermally activated flipping motion over the potential barrier between two equivalent positions (see figure 1(b)). Between two successive flips, the H$_2$O(II) molecules librate with large amplitudes. Due to the reorientational motion of the O4 atom, the H$_2$O(I) molecule, coupled via hydrogen bond O3–H33$\cdots$O4 with a disordered H$_2$O(II) molecule, exhibits apparently large angle librations about the Br$\cdots$H34–O3 bond lying in the ab plane. These large angle librations are expected to be correlated with the flipping motion of the H$_2$O(II) molecule preventing the breaking of the corresponding hydrogen bond between the two water molecules.

Provided that the lifetime in each of the O4 positions is sufficiently long (compared to the time-scale of the light scattering process), such dynamic disorder leads to a change in the Raman selection rules. Since the four H$_2$O(II) molecules are disordered among the eight sites of general symmetry, the number of degrees of freedom, considered in the factor-group
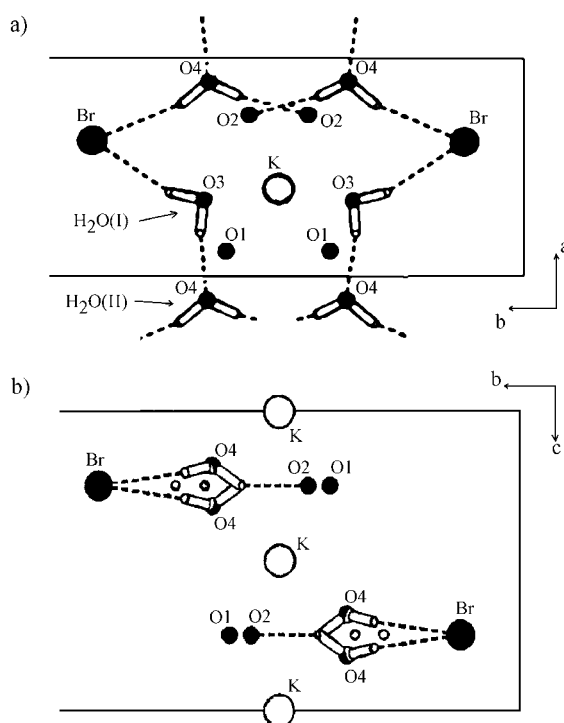
Figure 1. The topology of the hydrogen bonded network in BKBr at room temperature based on the x-ray diffraction data [6]. One half of the unit cell is displayed in two projections. O1 and O2 oxygens belong to the carboxyl group of the betaine molecules, which are not shown. O3 and O4 oxygens belong to the $H_2O(I)$ and $H_2O(II)$ molecules, respectively. Only $H_2O(II)$ molecules are displayed in (b).

analysis, has to be doubled. Consequently, the number of allowed vibrations of the $H_2O(II)$ molecules is twice that for the $H_2O(I)$ ones. The results of the factor group analysis for Raman active external vibrations of BKBr, where lattice vibrations of the heavy ions and the water molecules were considered separately, are the following:

K^+, Br^- and betaines: $\Gamma_{ext} = 6A_g + 7B_{1g} + 6B_{2g} + 5B_{3g}$

$H_2O(I)$: $\Gamma_{transl} = 2A_g + 2B_{1g} + B_{2g} + B_{3g}$

$$\Gamma_{libr} = \frac{A_g + B_{1g}}{rock} + \frac{2B_{2g} + 2B_{3g}}{wag; twist}$$

$H_2O(II)$: $\Gamma_{transl} = 3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}$

$$\Gamma_{libr} = \frac{3A_g + 3B_{1g} + 3B_{2g} + 3B_{3g}}{rock; wag; twist}.$$
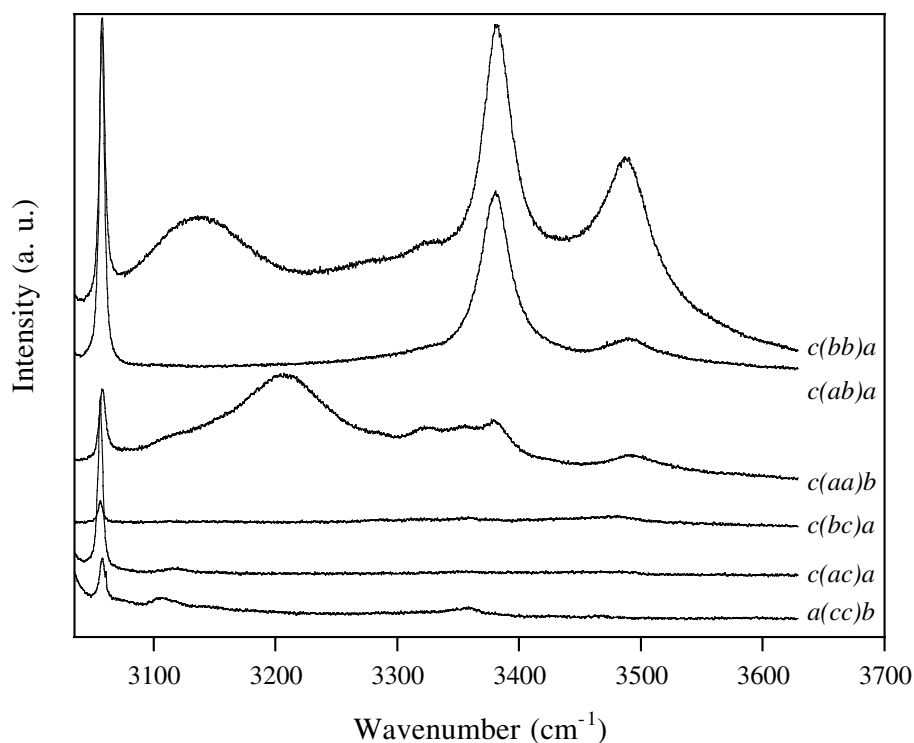
The room temperature Raman spectra of BKBr for six scattering geometries are shown in figures 2–4. As is known [2], the librations of the water molecules in solid hydrates are normally observed in the relatively broad spectral range from 350 to 900 cm^{-1}, and the translations in between 100 and 350 cm^{-1}. The flipping motions of the $H_2O(II)$ molecules, which are coupled via hydrogen bonds with the $H_2O(I)$ and the betaines, may yield a diffuse lineshape of the corresponding internal and external bands. It is clear that external vibrations of the disordered $H_2O(II)$ molecules must be strongly damped (or even overdamped) at the ambient temperature,
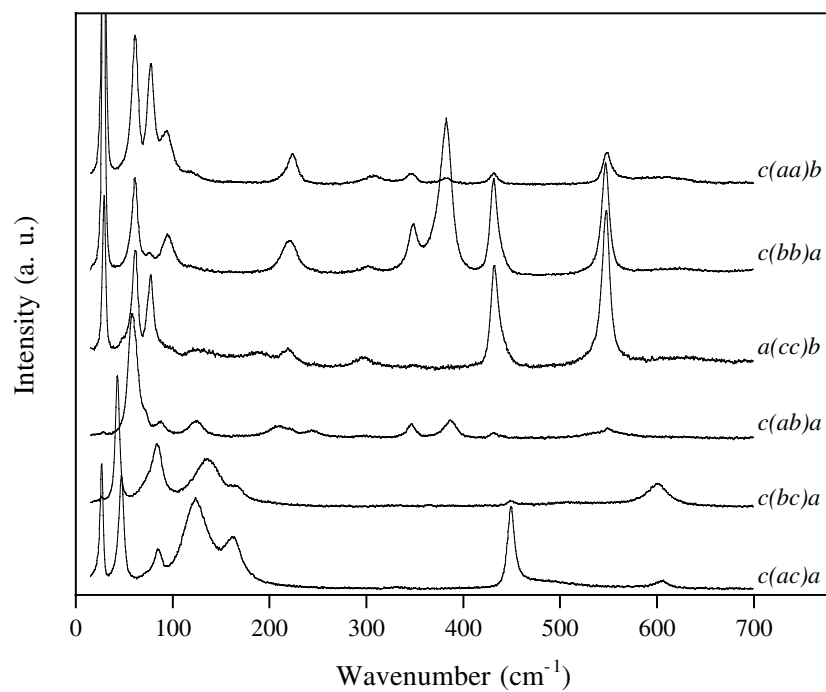
Figure 2. Low-frequency Raman spectra of BKBr at room temperature for six scattering geometries.
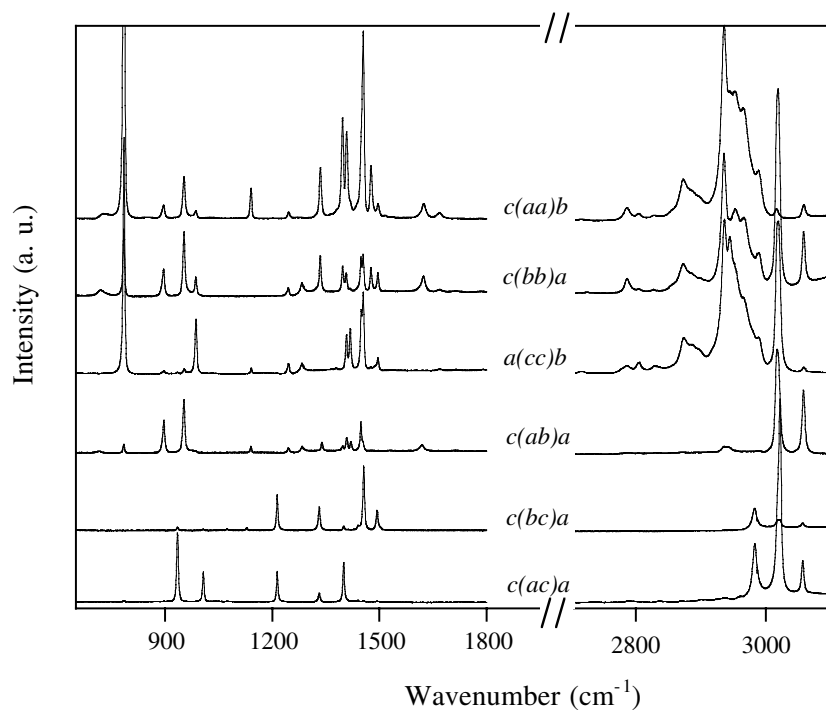
Figure 3. Overall Raman spectra of BKBr at room temperature in the region of the internal vibrations for six scattering geometries.

Figure 4. Raman spectra of BKBr at room temperature in the region of the stretching vibrations of the water molecules for six scattering geometries.

and therefore they could not be detected. In the Raman spectra of BKBr, presented in figure 2, most of the lines expected for heavy entities can be seen in the corresponding geometries. There are essentially broad bands probably associated with intramolecular translations admixed with librations which are visible in the frequency range 100–250 cm^{-1}. A weak and broad bands associated with the water librations were observed at $\sim$490 cm^{-1} in *ac* geometry (B$_{2g}$ modes) and at $\sim$610 cm^{-1} in all diagonal spectra (A$_g$ modes). Thus, in BKBr the frequencies of the water librations fulfil the usual sequence $\nu_{rock} > \nu_{wag}$, ν_{twist} [8]. The water molecules in BKBr are slightly distorted since they are asymmetrically bound to the oxygens and to the Br$^-$ ions (see figure 1). In this case a mixing between the out-of-plane librational modes (wag and twist) is expected [2] which hinders their precise assignment for the moment.

The betaines have rather rich vibrational spectra. The factor-group analysis predicts 102 Raman active internal modes for the betaines: 29A$_g$ + 29B$_{1g}$ + 22B$_{2g}$ + 22B$_{3g}$. Most of them have been observed in the spectral range 300–1800 cm^{-1} and only C–H stretching modes are well localized in between 2700 and 3050 cm^{-1} (see figures 2 and 3). The detailed assignment of the internal modes of the betaines is not the purpose of this paper and will be reported elsewhere [9].

The factor group analysis for the internal vibrations of the water molecules yields:

H$_2$O(I): $\Gamma(\nu_1^w) = \Gamma(\nu_2^w) = \Gamma(\nu_3^w) = $ A$_g$ + B$_{1g}$ + B$_{2u}$ + B$_{3u}$

H$_2$O(II): $\Gamma(\nu_1^w) = \Gamma(\nu_2^w) = \Gamma(\nu_3^w) = $ A$_g$ + B$_{1g}$ + B$_{2g}$ + B$_{3g}$ + A$_u$ + B$_{1u}$ + B$_{2u}$ + B$_{3u}$.

Accordingly 4A$_g$, 4B$_{1g}$, 2B$_{2g}$ and 2B$_{3g}$ bands in the region of stretching vibrations of the water molecules are expected. In fact the factor group analysis gives only the number of

Table 1. Hydrogen bonds and corresponding Raman bands in BKBr at room temperature.

	H-bond	Donor–acceptor distance (pm) [6]	Wavenumber (cm^{-1})	Raman intensity
$H_2O(I)$	O3–H33$\cdots$O4	265.5	3205	*aa*
	O3–H34$\cdots$Br	323.0	3487	*bb $\gg$ ab > aa*
$H_2O(II)$	O4-H44$\cdots$Br	339.6	3382	*bb > ab $\gg$ aa*
	O4–H43$\cdots$O2	271.5	3136	*bb > aa*
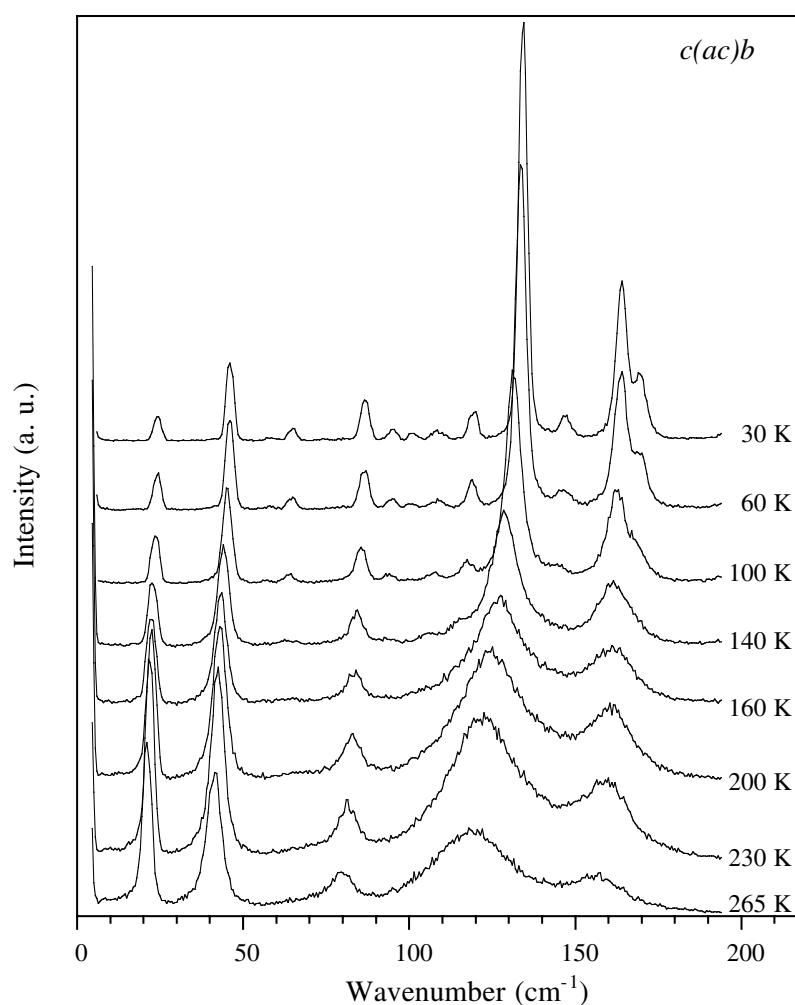
Figure 5. Temperature evolution of Raman spectra of BKBr in the region of external modes.

modes allowed by symmetry, but it does not provide any information concerning their relative intensity and their wavenumbers. Raman spectra in the region of stretching vibrations reflect the complicated set of water molecules in the unit cell and deserve a detailed discussion. As follows from the factor-group analysis Raman peaks in *ac* (B_{2g}) and *bc* (B_{3g}) geometries may appear only due to disorder of the $H_2O(II)$ molecules. In fact some hints of these peaks can be seen in figure 4 in the *ac* and *bc* geometries. The bending ν_2^w (free molecule value 1595 cm^{-1})
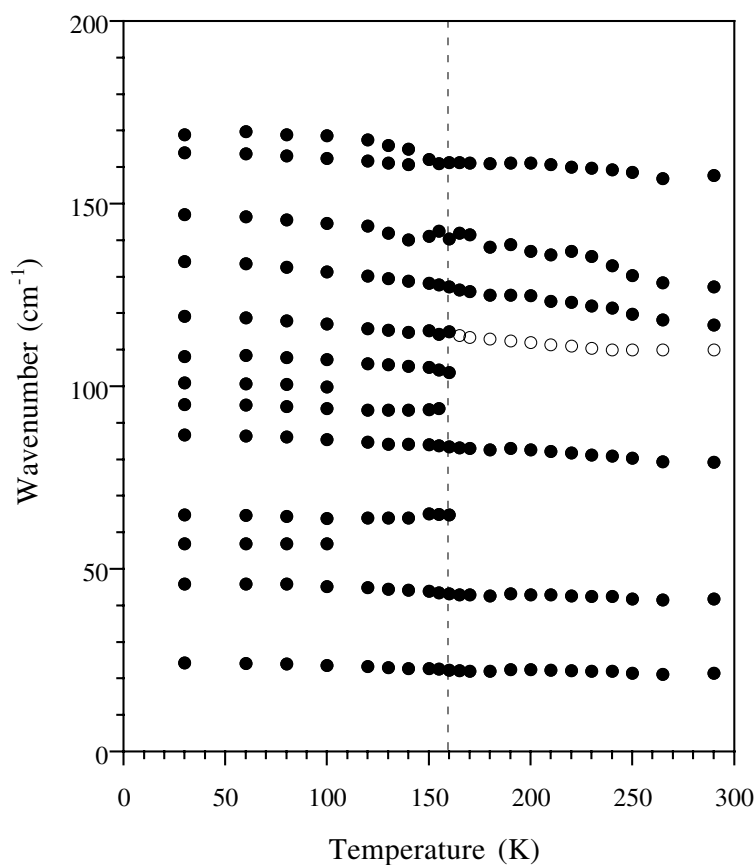
Figure 6. Temperature dependence of the frequencies of the fitted Raman peaks shown in figure 5. The vertical dashed line marks the phase transition temperature.

was found in the range 1620–1660 cm^{-1}, where the ν(C=O) vibration of the betaine is also observed (see figure 3). A weak band disclosed in *aa* geometry at 3320 cm^{-1} can be attributed to the $2\nu_2^w$ overtone. As can be seen in figure 4, there are four strongly polarized bands localised in the spectral range 3100–3600 cm^{-1} as expected. However, their positions strongly deviate from the free molecule values ($\nu_1^w = 3657$ and $\nu_3^w = 3756$ cm^{-1}). It is obvious that internal vibrations of the water molecules are strongly affected by the structural environment in the unit cell, and in particular, a downward shift of the stretching frequencies and an upward shift of the bending one is direct evidence of hydrogen bonding in the crystal.

As it is known, the intensities of the stretching O–H bands show a directional behaviour in the Raman scattering spectra. The highest intensities are observed when the electric vectors of both incident and scattered light are oriented parallel to the O–H direction. The Raman spectrum in *cc* geometry is very weak due to the preferential orientation of H-bonds along *a* and *b* axes. In BKBr the water molecules are involved in hydrogen bonds of different lengths with the nearest oxygens and the Br$^-$ ions. Due to this strong asymmetry, the O–H stretching vibrations are localized. In this case an assignment of the bands to the ν_1^w and ν_3^w fundamental modes of the free molecule actually has no meaning. Consequently it is necessary to consider two almost independent O–H stretching vibrations for each water molecule. The hydrogen
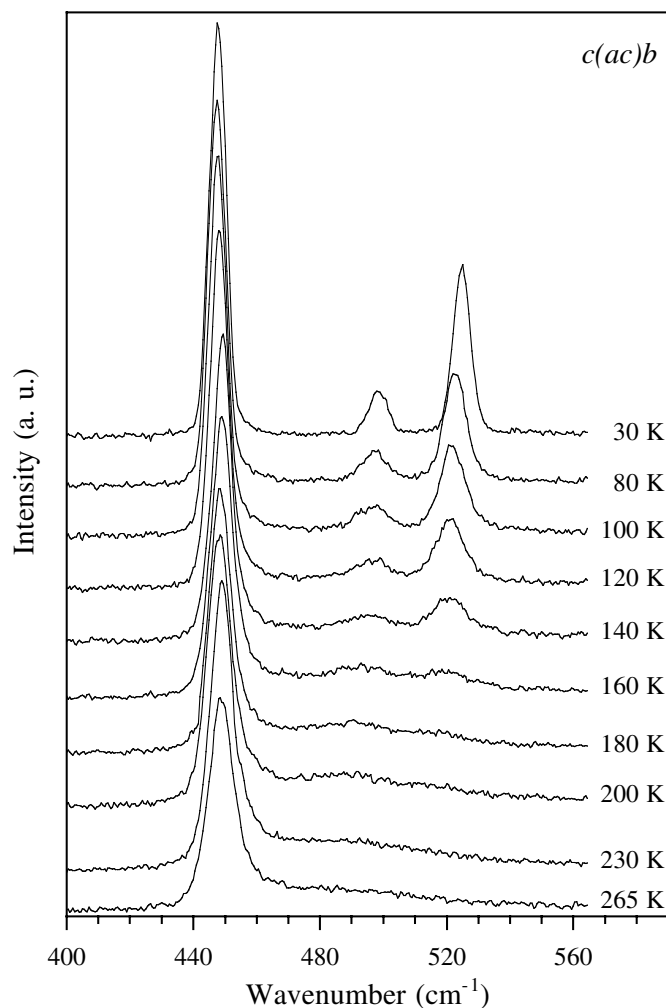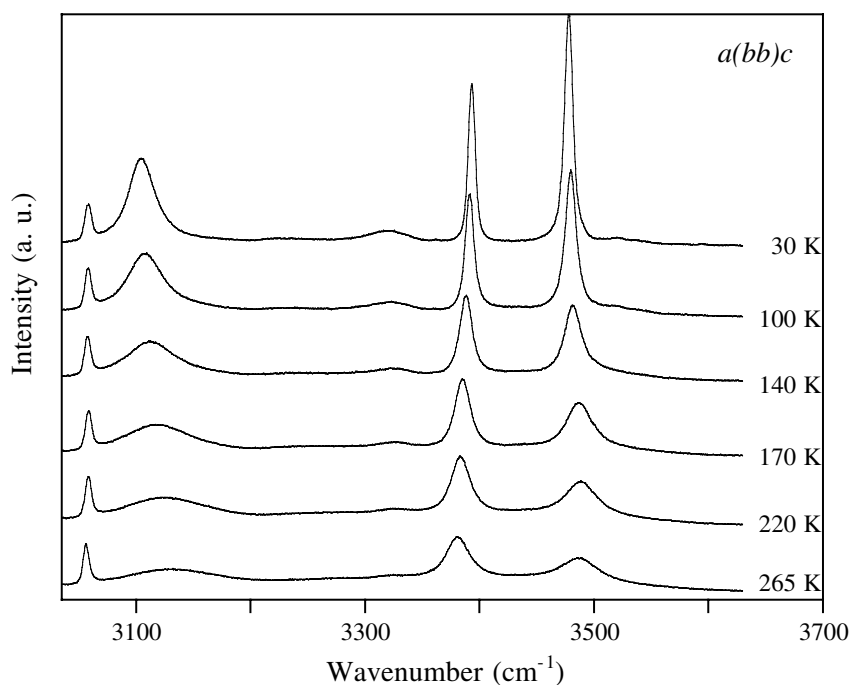
Figure 7. Temperature evolution of Raman spectra of BKBr in the region of the water librations.

bond between the $H_2O(II)$ molecule and the betaine (O4–H43 $\cdots$ O2) is the strongest one. The corresponding band is centred at about $3136\,\text{cm}^{-1}$ with the maximum intensity in *bb* geometry. Two nearest water molecules $H_2O(I)$ and $H_2O(II)$ are bound via H-bond O3–H33 $\cdots$ O4 along the *a* axis of the unit cell. Due to the reorientational motion of the $H_2O(II)$ molecule this H-bond is symmetrically bifurcated and gives rise to a broad band with a maximum in *aa* geometry located at about $3205\,\text{cm}^{-1}$. The two remaining bands at 3382 and at $3487\,\text{cm}^{-1}$ were assigned to the stretching vibrations of the weaker O–H $\cdots$ Br bonds. These bonds are oriented mostly in the *ab* plane of the unit cell (see figure 1). A tentative assignment is given in table 1.

3.2. Temperature evolution

Raman spectra of BKBr exhibit substantial temperature behaviour in certain regions where external and internal vibrations of the water molecules are expected. Internal modes of the

Figure 8. Temperature evolution of Raman spectra of BKBr in the region of the stretching vibrations.

betaines were also studied; however, they did not show any peculiarities related to the phase transition and therefore will be not discussed here.

As can be seen from figure 5 the low-frequency lines (below 100 cm^{-1}) exhibit a weak hardening and a natural narrowing on cooling. In contrast, the very broad bands localized above 100 cm^{-1}, and apparently associated with the water translations, show a significant temperature evolution indicating a considerable decrease in the anharmonicity of the water vibrations. The low-frequency (below 200 cm^{-1}) Raman spectrum in the $c(ac)b$ orientation was well fitted by a sum of six damped harmonic oscillators at room temperature, while the spectrum at 30 K was decomposed into a minimal set of 13 peaks. The fitting procedure was applied for each spectrum recorded in the temperature interval 30–292 K. The results are shown in figure 6. New Raman lines appear just below 160 K as a result of the changes of the selection rules in the low-temperature phase. Note that one more peak at about 110 cm^{-1} can be included in the fitting procedure above the PT temperature up to 295 K. This additional peak, shown by open symbols in figure 6, is strongly overlapped with the broad band centred at 118 cm^{-1} and slightly improves the fit quality.

The out-of-plane librations of water molecules form a broad band at ∼490 cm^{-1} in ac geometry at room temperature. As can be seen in figure 7 one more component at ∼520 cm^{-1} becomes visible below 230 K. This component apparently belongs to the disordered $H_2O(II)$ and is highly damped at the ambient temperature. On cooling both bands exhibit remarkable narrowing below the PT temperature.

The temperature evolution of Raman spectra of BKBr in the region of stretching vibrations of the hydrogen bonds in $a(bb)c$ geometry is shown in figure 8. The PT is clearly seen from the temperature dependence of the frequencies and halfwidths presented in figures 9 and 10,
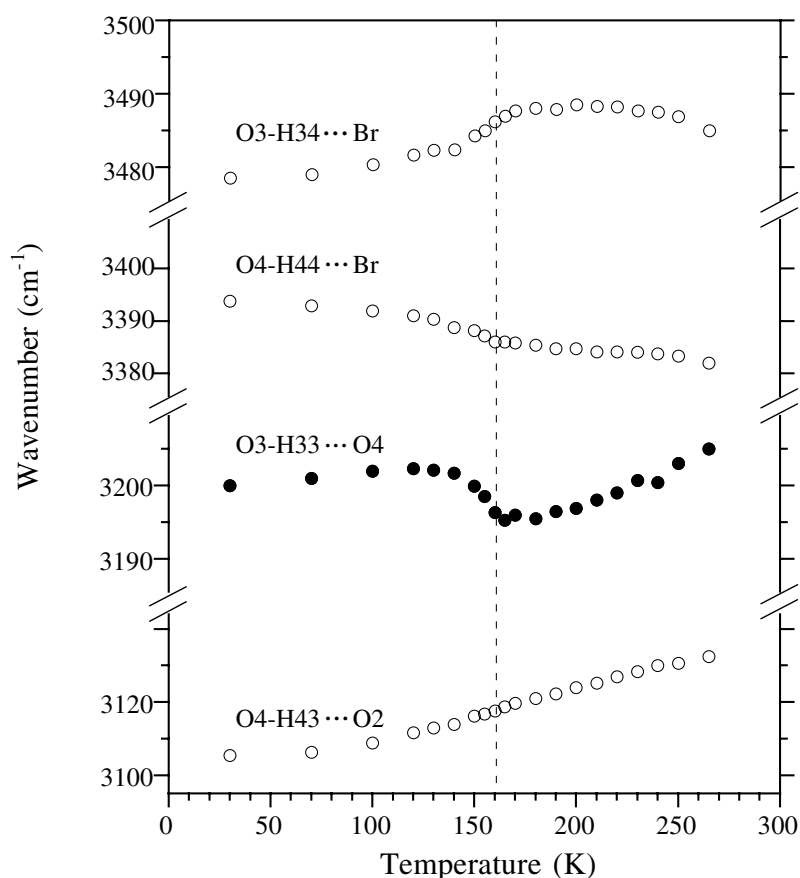
Figure 9. Temperature dependence of the frequencies of the stretching bands in BKBr observed in $a(bb)c$ geometry (open symbols) and $c(aa)b$ geometry (full symbols). A tentative assignment is given in table 1. The vertical dashed line marks the phase transition temperature.

respectively. A considerable downward shift of the peak frequency from 3135 to 3104 cm^{-1} is direct evidence that the corresponding O4–H43 $\cdots$ O2 hydrogen bond is strengthened on decreasing the temperature. The other H-bond of this H$_2$O(II) molecule with Br$^-$ ions becomes in turn weaker. Thus, in spite of the strong H-bonding, the water molecules exhibit nevertheless a 'rigid-body displacement' which bears witness to the water molecule behaviour as a structural entity. It is interesting to outline that hydrogen bonds of the H$_2$O(I) molecule also exhibit a temperature evolution below 160 K but in the opposite sense, i.e. the O3–H34 $\cdots$ Br bond strengthens with decreasing temperature while the other one (O3–H33 $\cdots$ O4) becomes weaker.

The halfwidths of the water vibration bands exhibit a significant temperature evolution, while the low-frequency mode at 25 cm^{-1}, attributed to the translation of the heavy entity, and the internal bending mode of the betaines (447 cm^{-1}), presented for comparison in figure 10, do not show any essential broadening. For all the bands, identified as water vibrations, the corresponding linewidth decreases rapidly with decreasing temperature due to the freezing of the large-amplitude reorientational motion. The decrease of the halfwidth from high temperature through T_c to low temperature seems to be continuous, which would imply a second order nature of the PT.
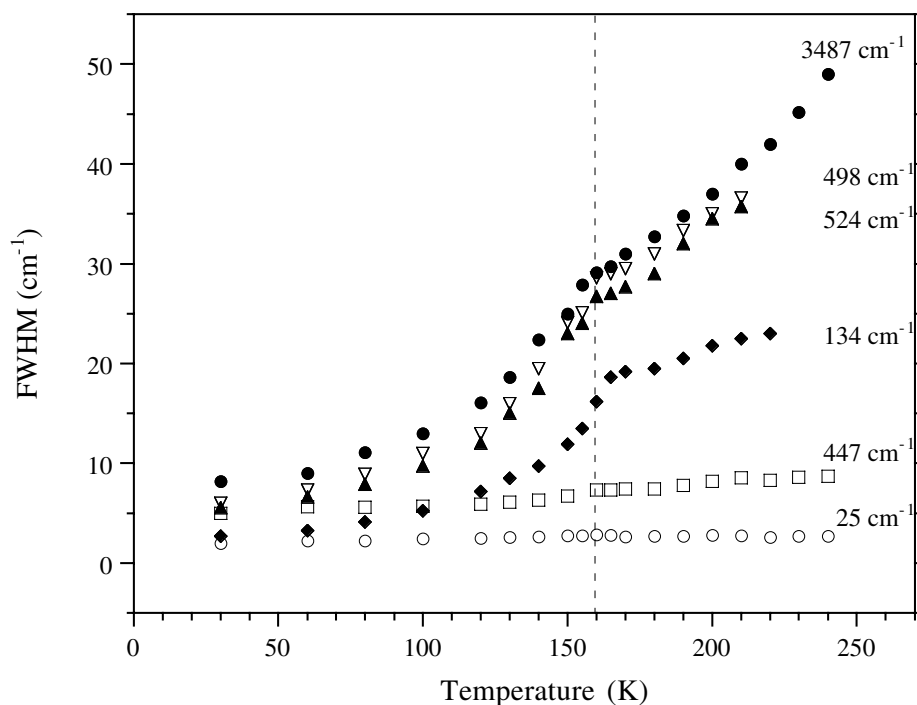
Figure 10. Temperature dependence of the halfwidths of selected Raman peaks in BKBr. The vertical dashed line marks the phase transition temperature.

Above T_c both librations are very weak and broad; moreover, the 524 cm^{-1} line is no longer visible above 240 K. A large broadening of the water molecule vibrations (498, 524 and 3487 cm^{-1} in figure 10) is an evidence of the substantial increasing in the amplitude of the reorientations near the room temperature. Dielectric losses observed in BKBr in this temperature range [7] may be caused by the thermally activated proton conductivity along the *a* axis. Apparently large-amplitude reorientations or even rotations of the water molecules form (perfectly oriented along the *a* axis) a dynamical network of hydrogen bonds, which can lead to the onset of proton conductivity.

4. Conclusions

In the family of betaine compounds BKBr represents a unique system of hydrogen bonds where two types of water molecule are engaged in strongly asymmetric hydrogen bonding. Detailed assignments of the polarized Raman spectra observed in the spectral range 3100–3600 cm^{-1} were proposed by assuming the localization of the O–H stretching vibrations. However, as follows from the general analysis of the Raman spectra, the identity of the water molecules is more or less preserved in the whole temperature range studied. The temperature dependence of the Raman spectra of BKBr has been studied with the aim of determining the mechanisms underlying the structural PT at 160 K. No soft mode was detected. The parameter most sensitive to the temperature changes is the halfwidth of the bands associated with the water vibrations. Their temperature dependence is related to the order–disorder mechanism of the PT at 160 K. The decrease of the halfwidth from the higher temperatures through T_c to the lower temperatures seems to be continuous, which would imply a second order nature of the

PT. Our results clearly show that the freezing of the water molecules reorientations is the most important mechanism that triggers the structural PT and leads to significant hydrogen bonding alterations. The orientation of the ordered water molecules in the low-symmetry phase seems to be the result of a compromise between a tendency to optimize both the $H \cdots O$ and $H \cdots Br$ attractive interactions in the unit cell.

Acknowledgments

References

[1] Schaack G 1990 *Ferroelectrics* **104** 147
[2] Lutz H D 1988 *Struct. Bonding* **69** 99
[3] Andrade L C R, Costa M M R, Paixão J A, Moreira J A, Almeida A, Chaves M R and Klöpperpieper A 1999 *Z. Kristallogr. NCS* **214** 83
[4] Almeida A, Chaves M R, Moreira J A, Pinto F and Klöpperpieper A 1998 *J. Phys.: Condens. Matter* **10** L773
[5] Yuzyuk Yu I, Almeida A, Pinto F, Chaves M R, Moreira J A and Klöpperpieper A 2000 *J. Phys.: Condens. Matter* **12** 1497
[6] Andrade L C R, Costa M M R, Paixão J A, Pinto F, Almeida A, Chaves M R and Klöpperpieper A 2000 at press
[7] Almeida A, Pinto F, Chaves M R and Klöpperpieper A 2001 to be published
[8] Falk M and Knop O 1973 *Water: a Comprehensive Treatise* vol 1, ed F Franks (New York: Plenum) ch 2
[9] Pinto F 2000 *PhD Thesis* University of Porto