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Raman spectra and phase transition in betaine potassium iodide dihydrate

Yu I Yuzyuk^{†§}, A Almeida[†], Filipa Pinto[†], M R Chaves[†],
J Agostinho Moreira[†] 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

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Abstract. Polarized Raman spectra of betaine potassium iodide dihydrate ($[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-]_2\text{KI} \cdot 2\text{H}_2\text{O}$) have been studied in the temperature range 40–290 K. The behaviour of betaine external modes and of water internal vibrations provides evidence for a first order phase transition of order–disorder type at 100 K. This phase transition is related to the freezing of the successive reorientations of water molecules. The temperature dependence of the halfwidth of the water stretching band centred at 3489 cm^{-1} (40 K) obeys an Arrhenius-type law corresponding to different activation energies below and above the critical temperature. The comparison of Raman and dielectric data allows us to identify two types of reorientation of water molecules.

1. Introduction

Betaine potassium iodide dihydrate ($[(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-]_2\text{KI} \cdot 2\text{H}_2\text{O}$), hereafter denoted as BKI) exhibits the lowest symmetry among the family of betaine compounds and it is triclinic with space group C_1^1 ($P\bar{1}$) [1] at room temperature. Recently, a first order phase transition (PT) very close to 100 K was evidenced and two relaxational modes with different behaviour in the high and low temperature phases were found from dielectric measurements [2]. A spontaneous polarization is not observed in the low temperature phase and the nature and the mechanisms underlying the PT are unknown as well as the symmetry of the low temperature phase so far.

The present contribution reports on a detailed Raman study of BKI in the temperature range 40–290 K. It is shown that PT in this new compound is of order–disorder type closely associated with the reorientations of water molecules.

2. Experimental details

Polarized Raman spectra have been measured on samples in the form of carefully oriented and optically polished rectangular parallelepipeds $5 \times 3 \times 2\text{ mm}^3$ with the axes X perpendicular to the (110) planes, Y parallel to $[\bar{1}10]$ and Z parallel to [001]. The crystallographic axes were determined with an accuracy of $\pm 1^\circ$ by x-ray diffraction.

Raman spectra were excited using the polarized light of an Ar^+ laser Coherent INOVA 90 ($\lambda = 514.5\text{ nm}$) in a right-angle scattering geometry. The scattered light was analysed using a

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

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 temperature stability of about $\pm 0.2 \text{ K}$. The temperature was measured with a gold–iron–chromel thermocouple attached to the sample holder. The actual sample temperatures were estimated to differ by less than 1 K from the temperature readings. Temperature homogeneity in the sample was achieved with a copper mask set-up.

3. Experimental results and discussion

3.1. Raman spectra at room temperature

According to x-ray data [1] the primitive unit cell contains one formula unit. Both I and K ions occupy special positions of C_1 symmetry, while all atoms of betaine ions and water molecules are in C_1 positions. The vibrational spectra of the crystal lattice is described in terms of 135 IR or Raman active optical and three acoustical phonon modes:

$$\begin{aligned} \Gamma_{\text{cryst}} &= (66A_g + 69A_u)_{\text{opt}} + (3A_u)_{\text{ac}} & \Gamma_{\text{tr}}(\text{K}) &= \Gamma_{\text{tr}}(\text{I}) = 3A_u \\ \Gamma_{\text{ext}}(2\text{H}_2\text{O}) &= \Gamma_{\text{ext}}(2\text{betaine}) = (3A_g + 3A_u)_{\text{tr}} + (3A_g + 3A_u)_{\text{lib}} \\ \Gamma_{\text{int}}(2\text{H}_2\text{O}) &= 3A_g + 3A_u & \Gamma_{\text{int}}(2\text{betaine}) &= 51A_g + 51A_u \end{aligned}$$

where subscript *ext* denotes external translational (*tr*) and librational (*lib*) vibrations, and *int* denotes internal ones.

As the crystal has a triclinic symmetry, all scattering geometries represent only phonons of A_g symmetry and contain equivalent information. Nevertheless all of them have been examined to obtain complete information, since some lines exhibit very different intensities for distinct scattering geometries. The low frequency Raman spectra of BKI for six different scattering geometries are shown in figure 1.

As follows from factor group analysis, both I and K ions have no Raman active modes and, thus, the low frequency Raman spectra (below 200 cm^{-1}) of BKI may include external vibrations of betaine and water. However external modes of water molecules are expected at higher frequencies. In fact, the librations of water molecules in solid hydrates are normally observed in the relatively broad spectral range from 350 to 900 cm^{-1} , and translations in between 100 and 350 cm^{-1} [3]. But librations usually give rise to rather weak and broad bands at ambient temperature and we have found no reliable evidence of these modes in Raman spectra of BKI at room temperature. Room temperature spectra are in good agreement with this assumption and, in fact, six Raman peaks were observed below 200 cm^{-1} corresponding to betaine external vibrations. Weak bands at 213 , 230 and 240 cm^{-1} observed in $Z(YY)X$ and $Z(XX)Y$ geometries (inset of figure 1) may be attributed to water translations. In spite of the triclinic symmetry of the crystal, these bands are observed in $Z(YY)X$ and $Z(XX)Y$ geometries and the proposed assignment is in agreement with structural features concerning the orientation of the water molecules in BKI. Namely, as shown in figure 1 of [1], water molecules form zig-zag chains of $(\text{H}_2\text{O}-\text{K}^+-\text{OH}_2) \cdots (\text{H}_2\text{O}-\text{K}^+-\text{OH}_2)$ units in the plane nearly perpendicular to the c axis of the unit cell. In this case, the water translations are represented as K^+-OH_2 and $\text{H}_2\text{O}-\text{OH}_2$ stretching and bending modes in the ab plane, while translations of water along the c axis are constrained by betaine. From the value of translational frequencies one can conclude that K^+-OH_2 interaction is weak since K^+ is not highly charged and the corresponding bond length is $\sim 0.331 \text{ nm}$. As known [3], in the case of strong interaction the corresponding translations are normally observed above 400 cm^{-1} .

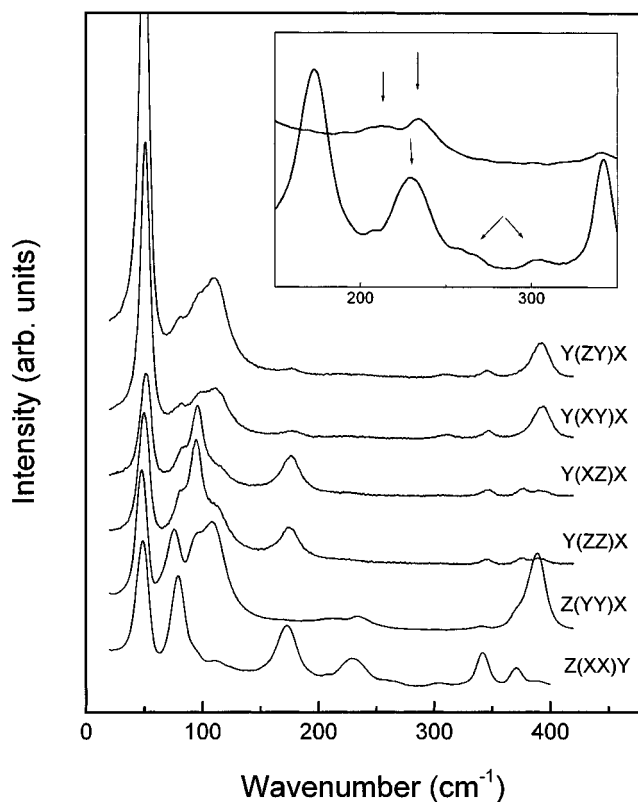


Figure 1. Low frequency Raman spectra of BKI at room temperature for six scattering geometries. The inset shows weak lines in $Z(Y Y)X$ (the upper spectrum) and $Z(X X)Y$ (the lower one) orientations.

Extremely weak features centred at 269 and 306 cm^{-1} can be considered as water librations, but a definite assignment of these bands is not yet given. Apparently, these bands can also arise from CH_3 torsion mode of betaine. Narrow lines at 342 and 372 cm^{-1} , also presented in figure 1, unambiguously belong to NC_4 bending vibrations of betaine.

Internal modes of betaine were found at their typical position and detailed assignments will be reported elsewhere. In contrast, as will be demonstrated below, stretching vibrations ν_1^w and ν_3^w of water molecules have not been observed near 3600 cm^{-1} in the room temperature spectra.

3.2. Temperature evolution

The occurrence of a PT is obvious from the temperature evolution of the external modes presented in figure 2, since an abrupt splitting was observed for temperatures below 100 K . The low frequency (below 200 cm^{-1}) Raman spectrum in the $Y(ZZ)X$ orientation was well fitted by a sum of six damped harmonic oscillators at room temperature, while the spectrum at 40 K was decomposed into a minimal set of 21 peaks. The fitting procedure was applied for each spectrum recorded in the temperature interval $40\text{--}290\text{ K}$. The results are shown in figure 3. Note that two peaks at 105 and 117 cm^{-1} were also added to the fitting procedure even above the PT temperature (at 105 and 110 K) to avoid deterioration of the fit quality.

This activation of the hard modes is direct evidence of the pretransitional short range ordering occurring in small regions of the sample above the PT temperature. The vicinity of the PT has been demonstrated [2] as a region of high critical fluctuations and therefore clusters of the low symmetry phase may start to appear above 100 K, while the macroscopic symmetry C_i^1 is preserved.

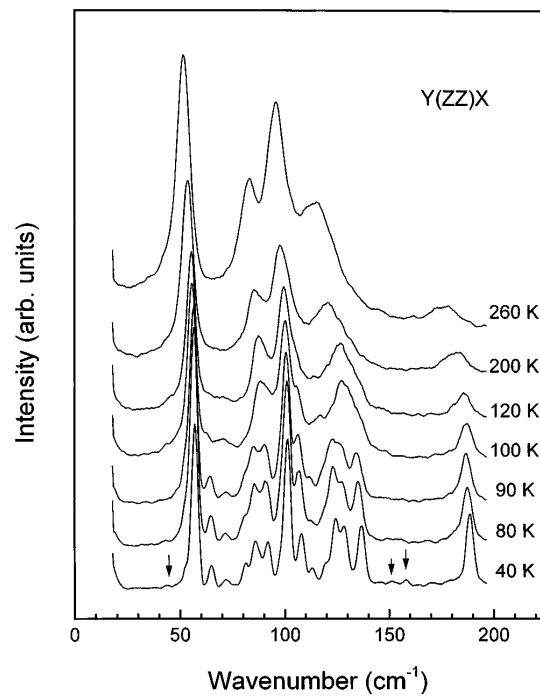
Numerous Raman lines observed in the low temperature phase can appear as a result of further lowering of the crystal symmetry from C_i^1 to C_1^1 . At this transition both I and K ions lose their special positions, all modes acquire A symmetry and become Raman active. If the translational symmetry is preserved and unit cell contains only one formula unit, 18 A modes below 200 cm^{-1} are expected. Spontaneous polarization was not found in the low temperature phase [2], and so an antiferrodistortive PT seems to be also probable. In this case the change in translational symmetry leads to the Brillouin zone folding and new lines are expected to appear [4–6]. No splitting has been found in the region of internal modes of betaine, and this fact apparently points to rather flat $\omega(k)$ dispersion curves of the corresponding phonon branches. In contrast, external modes usually exhibit considerable dispersion and form well separated components due to zone folding. Such a situation seems to occur in betaine calcium chloride dihydrate [5] and apparently takes place in BKI below 100 K. The low frequency shoulder at 53 cm^{-1} of the line at 56 cm^{-1} (value at 40 K) may be attributed to an activated zone boundary component. A weak line at 43 cm^{-1} indicated by an arrow in figure 2 may originate from a transverse acoustic (TA) branch. Usually TA branches have a lowest frequency at the edge of the Brillouin zone and therefore folded TA modes appear as hard modes between Rayleigh line and first optical mode of the parent phase. The longitudinal branch apparently has twice the frequency of the transverse one and presumably gives rise to one of the lines appearing between 60 and 80 cm^{-1} .

We must focus interest on the behaviour of the well separated line at 175 cm^{-1} (room temperature value) displayed in figure 2(a) and tentatively assigned to a betaine libration mode. As can be seen in figure 2(a), this line exhibits a gradual hardening and narrowing on cooling. As follows from the plot presented in figure 4, the temperature dependence of the halfwidth of that line exhibits a change of slope very near 100 K. These facts allow us to assume that betaine exhibits a freezing behaviour, i.e. a transition to smaller amplitude librations below the PT temperature.

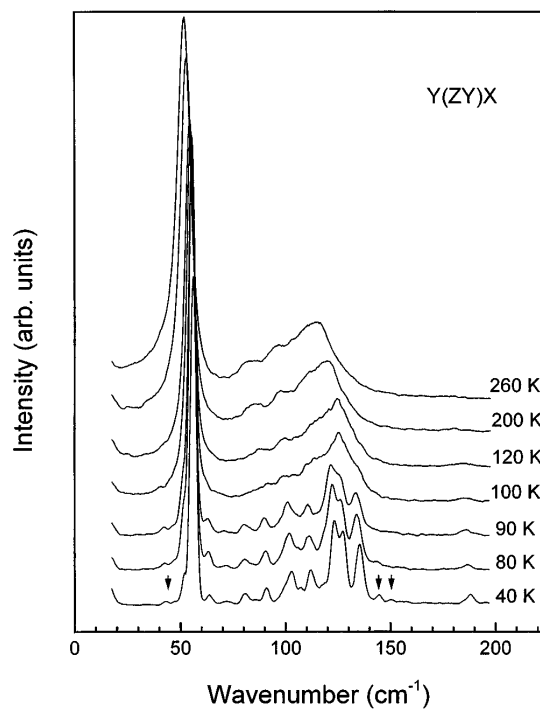
Internal vibrations of betaine were also examined, but they do not show any significant transformations on cooling down to 40 K.

As mentioned above, we failed to detect the stretching vibrations (ν_1^w and ν_3^w) of water molecules in the room temperature spectra, but it is noticeable that water vibrations start to appear on cooling, as can be seen from the temperature dependence of high frequency Raman spectra ($3200\text{--}3600\text{ cm}^{-1}$) presented in figure 5. One can assume that water molecules are rather weakly bound in the crystal lattice in the high temperature phase, that is they are only associated to monovalent K^+ ions and dynamically disordered. In the high temperature range water molecules reorient themselves rapidly and therefore the linewidths of their bands become larger. As a result, water librations and stretching modes are highly overdamped at ambient temperature. This assumption is in agreement with the recently reported x-ray data on BKI [1] at room temperature, where isotropic thermal factors of oxygen and hydrogen atoms of water molecules were found to have twice as large values with respect to other atoms in the unit cell.

On cooling below 150 K a broad band with a maximum at about 3500 cm^{-1} emerges from the background and can be assigned to symmetric stretching vibration (ν_1^w) of water molecules, which exhibit gradual freezing. As shown in figure 6, a considerable narrowing of this band and downward shift of the maximum occur at the PT. This is direct evidence of an abrupt and considerable slowing down of the motion of water molecules at the PT near 100 K.



(a)



(b)

Figure 2. Temperature evolution of Raman spectra of BKI in the region of external modes in Y(ZZ)X (a) and Y(ZY)X (b) scattering geometries. The arrows mark the weak lines.

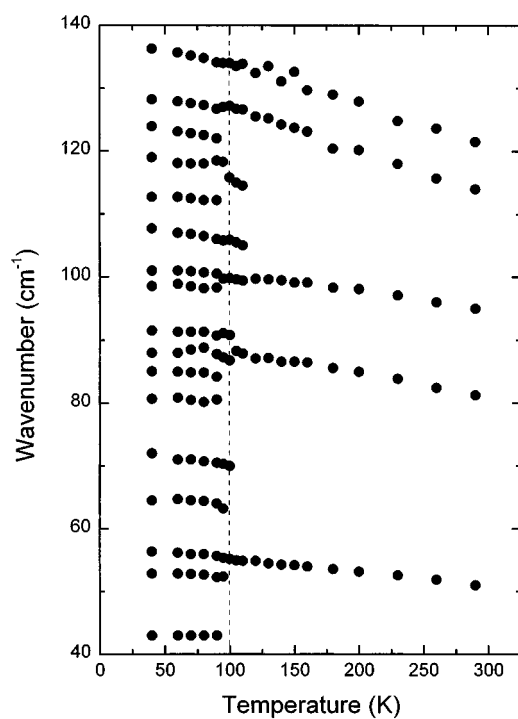


Figure 3. Temperature dependences of the frequencies of the decomposed Raman peaks shown in figure 2(a). The error bar is the same size as the symbols. The vertical dashed line marks the phase transition temperature.

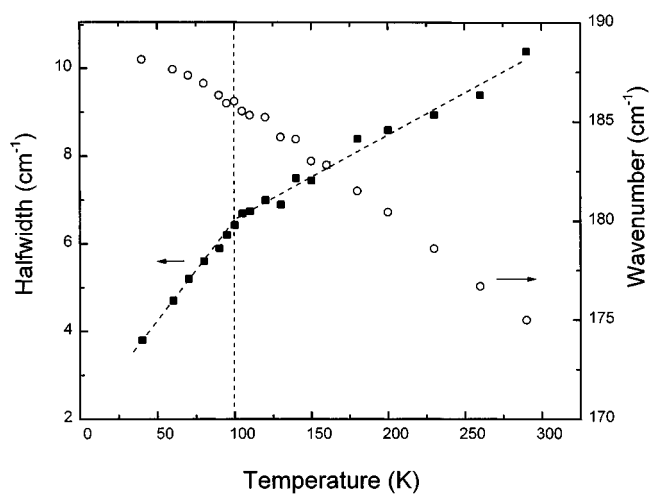


Figure 4. Temperature dependences of the halfwidth (full symbols) and the frequency (open symbols) of the line at 175 cm^{-1} (room temperature value) shown in figure 2(a). The vertical dashed line marks the phase transition temperature.

The observed downward shift of the peak maximum on cooling is consistent with the fact that the H bond is strengthened at lower temperatures [7, 8].

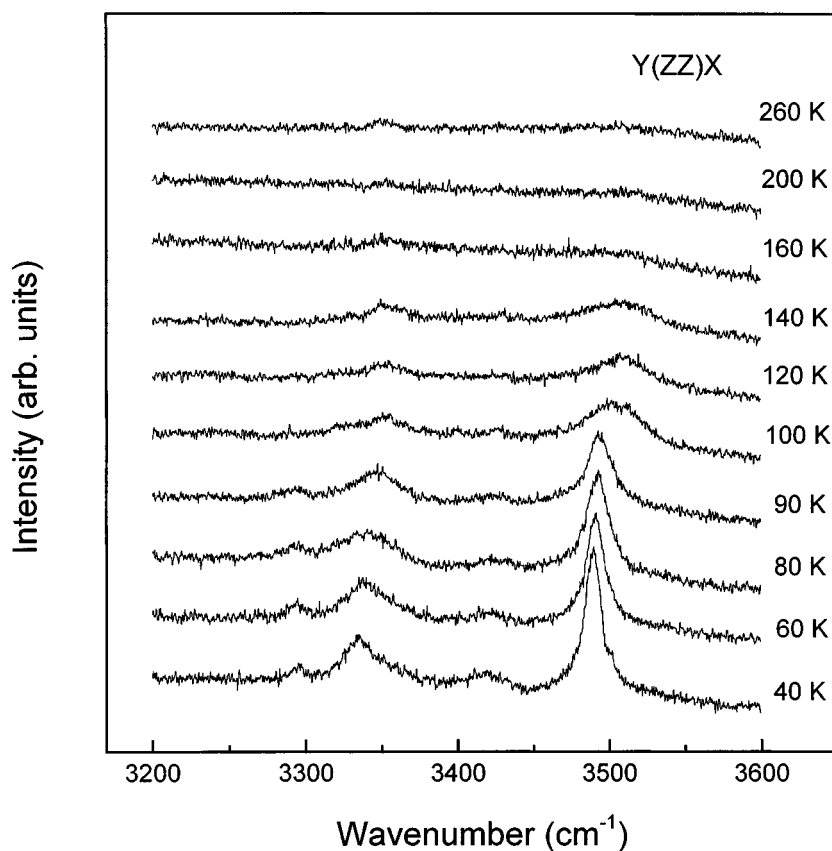


Figure 5. Temperature evolution of Raman spectra of BKI in the region of O–H stretching vibrations.

Furthermore, as we can see in figure 5 an additional broad band at 3330 cm^{-1} also emerges, giving evidence of permanent H-bond formation between water molecules and the carboxylic O(2) atom of betaine ions (O(3)–H31–O(2) in figure 1 in [1]). As proposed above from the temperature dependence of the halfwidth reported in figure 4, betaine exhibits freezing at the PT, in fact, due to H-bond formation. Note that the asymmetric stretching mode ν_3^w was not observed even at 40 K. This fact allows one to conclude that the low intensity of the ν_3^w mode is a result of nonsymmetrical interaction of water with surrounding ions, since only one proton is involved in the H bond with the O(2) oxygen atom of betaine, which plays the role of a proton acceptor.

To estimate the activation energy of reorientational motion of the water molecules the temperature dependence of the halfwidth ($\Delta\nu$) of the ν_1^w mode has been fitted by an Arrhenius equation: $\Delta\nu = B + A \exp(-E/kT)$. The Arrhenius plot of $\ln \Delta\nu$ versus $1000/T$ is given in the inset in figure 6 where we can see very clear two regimes, one below and another above the PT. Because of the rather high experimental error above 100 K we cannot estimate the activation energy with acceptable accuracy. Below 100 K the least squares fit yields the activation energy $\sim 2.5\text{ kJ mol}^{-1}$ with accuracy better than 10%. This value lies below the lowest limit of the range from 5 to 20 kJ mol^{-1} reported as a typical range of activation energy of reorientational motion in hydrates [3].

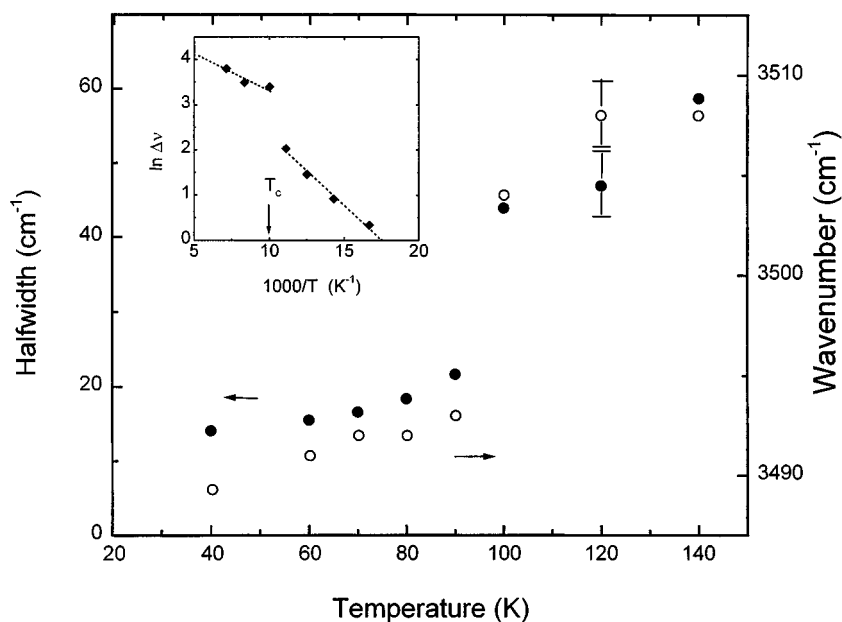


Figure 6. Temperature dependences of the halfwidth (full symbols) and the frequency (open symbols) of the ν_1^w band shown in figure 5. The typical error bar above 100 K is indicated, whereas below 100 K the error bar is the same size as the symbols. The inset shows an Arrhenius plot of $\ln \Delta\nu$ versus $1000/T$.

As shown in figure 6 the halfwidth of the ν_1^w band increases abruptly from 21 to 44 cm^{-1} at 100 K. The excess spectral halfwidth of the ν_1^w band acquired above 100 K may be considered as caused by the reorientational motion of water molecules. As shown by Bartoli and Litovitz [9] the orientational broadening of Raman lines allows us to estimate the corresponding reorientational time. The reorientational motion which affects the Raman lineshape was found to be rather fast ($\tau \sim 5 \times 10^{-12}$ s) with respect to the relaxation time observed in dielectric measurements [2]. One can conclude that Raman and dielectric measurements provide different aspects of reorientational motion in a crystal. We argue that above 100 K water molecules are involved in both slow and fast reorientations in different directions near the average sites. Fast reorientations increase Raman linewidth and prevent H-bond formation. The others are too slow to influence the Raman linewidth and correspond to simultaneous reorientations of the two water molecules in the unit cell related by the centre of symmetry. The study of dielectric susceptibility in the frequency range 100 kHz–13 MHz allowed us to calculate the activation energy of the slow reorientations. Its value is ~ 10 kJ mol^{-1} , and the corresponding correlation time is $\sim 10^{-9}$ s [2]. At 100 K, both reorientational processes, as evidenced by dielectric study [2] and the present Raman measurements, exhibit a slowing down and an order–disorder PT occurs.

At the ordering a considerable decreasing in the halfwidth of librations is expected, as their localization gives rise to well defined lines. As can be seen in figure 7, several new lines appear at low temperature in the region 450–600 cm^{-1} typical of water librations. This fact is again a strong indication that water molecules exhibit freezing in the low temperature phase and play an important role in the PT mechanism.

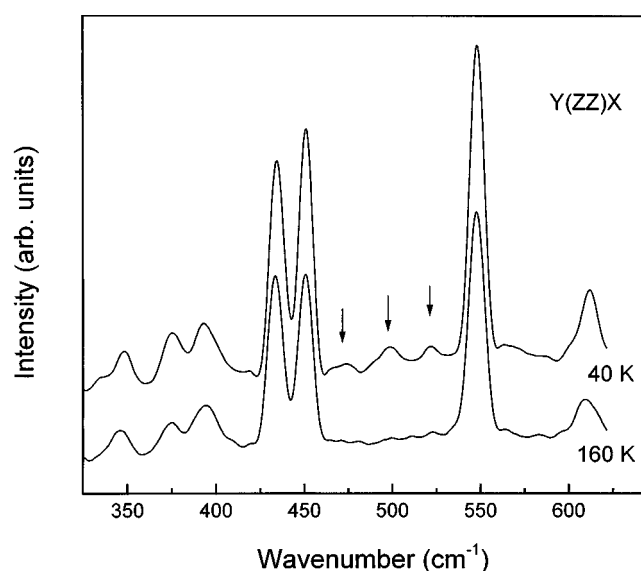


Figure 7. Raman spectra of BKI in the region of water librations. The arrows mark new lines observed below 100 K and attributed to water librations.

4. Conclusions

Raman spectra of BKI have been studied in several scattering geometries with special emphasis on the phase transition recently discovered at 100 K. Low frequency Raman spectra have been found to be in good agreement with factor-group analysis. All external vibrations of betaine and most of the water translations are observed at room temperature.

Our results clearly show that reorientations of water molecules represent the most important mechanism that triggers the PT in BKI at 100 K. Both Raman and dielectric [2] studies provide evidence of reorientational motions which occur on two different time scales. They exhibit considerable slowing down at the PT. The onset of ν_1^w band formation has been demonstrated below 150 K. This band grows gradually on further cooling and exhibits abrupt narrowing below 100 K. It is important to outline that gradual evolution of the ν_1^w band between 150 and 100 K lies in the region of critical fluctuations [2] and develops simultaneously with the softening of the low frequency relaxational mode observed in dielectric measurements.

The temperature dependence of Raman spectra provides evidence for a PT of order-disorder type. An abrupt splitting in the low frequency Raman spectra and the stepwise behaviour of the parameters of the ν_1^w band allow us to assume the first order character of this PT.

Acknowledgments

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