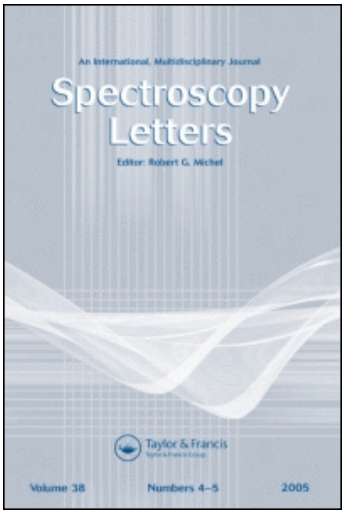

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Fourier Transform Vibrational Spectra of Magnesium Hydrogenphosphate Trihydrate H. The 2000-370 cm^{-1} Region

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FOURIER TRANSFORM VIBRATIONAL SPECTRA OF MAGNESIUM HYDROGENPHOSPHATE TRIHYDRATE

II. THE 2000–370 cm-1 REGION*

Key words: Magnesium hydrogenphosphate, newberyite, Fourier transform infrared spectra, Fourier transform Raman spectra.

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ABSTRACT

The Fourier transform infrared and Raman spectra of newberyite, $MgHPO_4 \cdot 3H_2O$, were studied in the 2000–370 cm-*1* region. Also investigated were the spectra of a series of partially deuterated analogues. By comparing the spectra recorded at room temperature and those obtained at the boiling temperature of liquid nitrogen and by studying the spectra of the series of partially deuterated newberyite an assignment was proposed for the observed bands. The spectra are fully in line with the crystallographic data and prove that the title compound is a true crystalline hydrate and does not contain H_3O^+ ions in its structure.

* Dedicated to our dear colleague and friend Prof. Heinz Dieter Lutz from the University of Siegen (Germany) on the occasion of his 65th birthday.

INTRODUCTION

Various structural characteristics of the title compound, $MgHPO_4 \cdot 3H_2O$ (usually referred to as newberyite+) as well as the conditions of its growth have been rather extensively studied [1–6]. Its crystal structure was determined, using X-ray diffraction, by Sutor [2] and refined by Abbona *et al.* [7]. It was found that newberyite crystallizes in the orthorhombic space group $Pbca - D_{2h}^{15}$ with $Z = 8$. Of the polyatomic entities in the structure, all hydrogenphosphate ions are structurally identical, whereas the water molecules are of three crystallographically non-equivalent types. The hydrogenphosphate ions form hydrogen bonds of considerable strength (the O · · · O distances are reported to be 261.5 pm) [7], whereas the H-bonds formed by the water molecules are considerably weaker (the $O_w \cdot \cdot \cdot O$ contacts range from 269.0 to 311.8 pm). One of these latter hydrogen bonds is reported to be bifurcated.

The conventional infrared and Raman spectra of protiated newberyite have been studied by Pechkovskii *et al.* [8], Mioč, Petranovic' and Minic' [9] and by Mioc and Minic' [10]. In addition to that, the infrared spectrum of the deuterated compound has been examined by Pechkovskii *et al.* [8]. On the basis of their infrared results, Pechkovskii *et al.* [8] and Mioč and Minic' [10] speculated that some of the bands may be indicative of the presence of H_3O^+ ions, despite the existence of direct structural data [2,7] which give no indication in that direction.

To the best of our knowledge, no Raman spectrum of deuterated newberyite has been reported, nor have the spectra of partially deuterated analogues been examined except in our very brief account [11] and the much more detailed study [12] which however, deals only with the O–H and O–D stretching regions in the Fourier transform infrared and Raman spectra of newberyite and a series of its deuterated analogues. The present paper, on the other hand, is devoted to the analysis of the 2000–370 cm^{-1} region where the water

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+ The mineralogical name is regularly used also for synthetic $MgHPO_4 \cdot 3H_2O$. This practice will be followed in this paper as well.

bending and librational modes as well as the stretching and bending vibrations of the hydrogenphosphate anions are expected to appear.

EXPERIMENTAL

The spectra were recorded from synthetic $MgHPO_4 \cdot 3H_2O$ (Carlo Erba) recrystallized from glacial acetic acid. The deuterated analogues were prepared by recrystallizing the protiated compound from partially deuterated acetic acid (made by dissolving acetic anhydride in H_2O/D_2O mixtures with an appropriate deuterium content).

The Perkin Elmer System 2000 FT-IR and a Perkin Elmer NIR FT Raman 1700 x instruments were used to record the Fourier transform infrared and Raman spectra respectively. The Nd : YAG laser emitting at 1064 nm was the excitation source for the Raman instrument. The low-temperature infrared spectra were obtained using a P/N 21525 variable-temperature cell (Graseby Specac) with KBr windows. The experimental details are given in Ref. 12. The GRAMS/386 package [13] was used to manipulate the spectra.

RESULTS AND DISCUSSION

The infrared spectra in the 2000 to 370 cm^{-1} region recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) are given in Fig. 1, whereas the RT Raman spectrum is shown in Fig. 2. Our Raman spectrum is very similar to that reported by Pechkovskii *et al.* [8] whereas the corresponding spectrum in Ref. 10 is of much lower quality. Our infrared spectra, on the other hand, are superior to those given in Refs. 8–10.

The bands appearing in the studied region are due either to vibrations which are predominantly localized in the HPO_4^{2-} anions or to the bending and librational modes of the water molecules**. Whereas the latter should be deuteration-sensitive with

**In the same region the appearance of band(s) related to the O-H(D) stretching of the hydrogenphosphate anions are also anticipated. This problem will be discussed later.

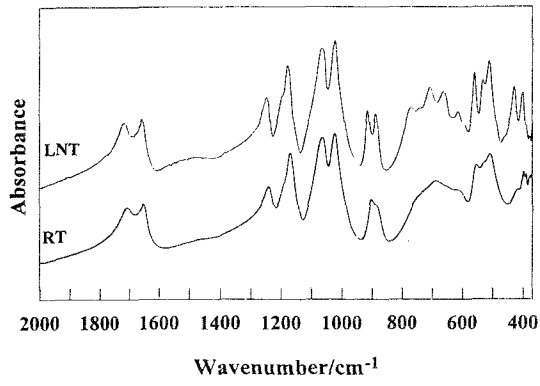

Fig. 1. Fourier transform infrared spectra of magnesium hydrogenphosphate trihydrate in the 2000–370 cm^{-1} region recorded at room temperature (RT) and the boiling temperature of liquid nitrogen (LNT)

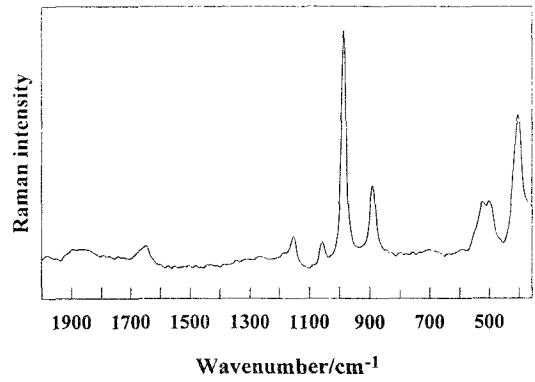

Fig. 2. Room-temperature Fourier transform Raman spectrum of magnesium hydrogenphosphate trihydrate in the 2000–370 cm^{-1} region

considerable isotopic ratios (> 1.3), the hydrogenphosphate vibrations should give rise to bands of which some should also be sensitive to deuterium-for-protium substitution [the in-plane and out-of-plane P–O–H or P–O–D bending modes and, to a lesser degree, the P–O(H) stretch] whilst the rest should be only negligibly sensitive to deuteration. Thus the behavior upon deuteration may serve as a reliable tool in distinguishing the bands due to vibrations mainly localized in the OPO_3 fragment of the HPO_4^{2-} anion from those which are due to modes in which the motion of the hydrogens is considerable or even predominant.

The vibrations of the hydrogenphosphate ions

As mentioned above, hydrogenphosphate anions of only one type are present in the structure. In the approximation of the site group (its symmetry is only C_1) eleven non-degenerate modes of the HPO_4^{2-} ions are expected, in addition to the O–H stretching vibration which was discussed earlier [12]. According to the selection rules of the factor group, each of the eleven vibrations should give rise to three components which are both infrared and Raman active and a fourth component only Raman active++. The discussion would be simplified if the P–O–H fragment is treated as if it were linear (which would be patently erroneous) and the three remaining P–O fragments were considered to be equivalent (which is approximately true [7]). Within such an approximation, the notation of the C_{3v} group could be applied. Thus, the four stretching vibrations could be divided into two modes of A_1 symmetry [one of them should be the deuteration-sensitive P–O(H) stretch] and one doubly degenerate mode of E symmetry. In addition, an A_1 and an E mode would be derived from the formerly triply degenerate (ν_4 for a PO_4^{3-} ion with T_d symmetry) bending mode and the doubly degenerate (under the T_d symmetry) ν_2 bending vibration should remain doubly degenerate.

The approximate frequencies at which these bands should appear could be estimated on the basis of previous studies of various hydrogenphosphate compounds (newberyite

++ The same is, of course, true for the components of the water bands.

included). The δ(P–O–H) vibration should be found in the 1300–1200 cm^{-1} region, the γ(P–O–H) between 900 and 750 cm^{-1}, the P–O stretches between 1150 and 900 cm^{-1} and the phosphate bending vibrations (originating from the triply degenerate F_2 and the doubly degenerate E modes of the idealized PO_4^{3-} ions) below 650 cm^{-1}.

In the infrared spectra of both protiated and deuterated newberyite the bands at 1180, 1067 and 1023 cm^{-1} have practically (but not quite) the same frequency+++ (*cf.* Fig. 3).

This clearly shows that they originate from vibrations of fragments in which the hydrons do not move appreciably and it is customary to attribute such bands to P–O stretchings localized predominantly in the PO_3 part of the hydrogenphosphate ions.

In the Raman spectra of the protiated compound (Fig. 4) the corresponding bands are found at 1150, 1057 and 985 cm^{-1}. On increasing the deuterium content in the sample the 1150 cm^{-1} band is gradually shifted towards higher frequencies (to 1166 cm^{-1} in the sample deuterated to the highest degree) whereas the 985 cm^{-1} band is shifted higher to 990 cm^{-1}. Such shifts could be explained if a somewhat mixed character of the predominantly P–O stretching modes is presumed or, alternatively speaking, if vibrational coupling with the δ(P–O–H) and/or δ(P–O–D) vibrations are assumed to be taking place. The corresponding shifts of the infrared bands are considerably lesser.

It may be noted that Pechkovskii *et al.* [8] report LNT infrared frequencies of 1195, 1175, 1065 and 1021 cm^{-1} and RT Raman frequencies of 1153, 1128 and 1055 cm^{-1}, whereas the RT infrared frequencies given by Mioč and Minic' [10] are 1170, 1065 and 1025 cm^{-1} and their Raman frequencies are 1165 and 1055 cm^{-1}.

The fourth of the P–O stretching modes, predominantly P–O(H) stretching in character, gives rise (Fig. 3 and Fig. 4) to bands at 914 cm^{-1} (infrared) and ≈ 890 cm^{-1} (Raman). It should be noted that the above-mentioned Raman band appears to be single, whereas the infrared frequency corresponds to the higher-frequency component of the 914/887 cm^{-1}

+++Unless specified otherwise, all listed frequencies are from the LNT spectra.

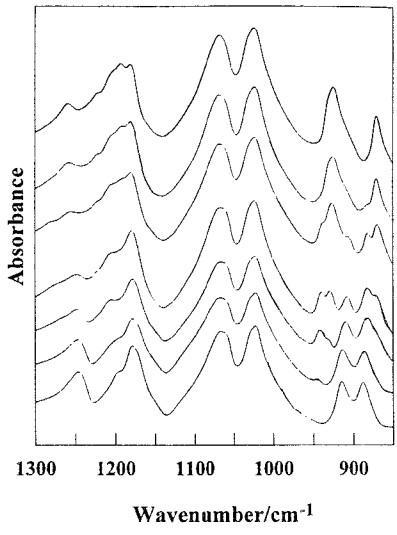

Fig. 3. LNT Fourier transform infrared spectra of a series of partially deuterated analogues of magnesium hydrogenphosphate trihydrate in the 1300–850 cm^{-1} region (the deuterium content increases from bottom to top and corresponds to 0 %, 5 %, 25 %, 50 %, 75 %, 90 % and 95 % deuterium respectively)

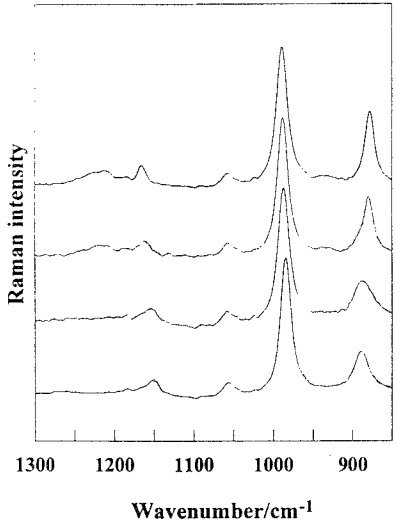

Fig. 4. RT Fourier transform Raman spectra of a series of partially deuterated analogues of magnesium hydrogenphosphate trihydrate in the 1300–850 cm^{-1} region (the deuterium content increases from bottom to top and corresponds to 0 %, 25 %, 75 % and 95 % deuterium respectively)

doublet***. The shift from 914 cm^{-1} in the infrared spectrum of the protiated compound to 870 cm^{-1} in that of its practically completely deuterated analogue (Fig. 3) shows that the band in question is due to a mode which is mainly P–O(H) stretching in character. The 914 cm^{-1} frequency is, it should be noted, higher than the corresponding one in $MnHPO_4 \cdot 3H_2O$ [15] which, in turn, is higher than that in the spectrum of $CaHPO_4 \cdot 2H_2O$ [14].

As in brushite, $CaHPO_4 \cdot 2H_2O$ [14] and $MnHPO_4 \cdot 3H_2O$ [15] the band appearing, in the infrared spectrum of the protiated $MgHPO_4 \cdot 3H_2O$, above 1200 cm^{-1} (its exact frequency here is 1247 cm^{-1}) was attributed to the δ(P–O–H) mode of the HPO_4^{2-} ions, the assignment being supported by the spectra of a series of partially deuterated analogues recorded at low temperature (Fig. 3). As seen, namely in the spectrum of the compound deuterated to the highest degree, a band attributable to the δ(P–O–D) mode appears at 924 cm^{-1} and the isotopic ratio of ≈ 1.35 is in the expected range. It should, however, be pointed out that in the spectrum of the sample deuterated to approximately 25 % the corresponding (of course, much weaker) band has a frequency of ≈ 930 cm^{-1}. On increasing the deuterium content, the band not only becomes stronger but is shifted towards lower frequencies to reach, in the spectrum of the compound with the highest deuterium content, the frequency of 924 cm^{-1}. Were it not for the spectra of brushite and $MnHPO_4 \cdot 3H_2O$ where an analogous behavior was observed [14, 15], the dependence of the δ(P–O–D) frequency on the deuterium content in the sample would be quite unusual. The order of the δ(P–O–H) frequencies is, again, $MgHPO_4 \cdot 3H_2O$ > $MnHPO_4 \cdot 3H_2O$ > $CaHPO_4 \cdot 2H_2O$. The assignment of the δ(P–O–H) mode in the spectrum of protiated $MgHPO_4 \cdot 3H_2O$ is in agreement with that of Pechkovskii *et al.* [8] and Mioč and Minic' [10]. It may be mentioned that on increasing the deuterium content in the sample a weak band at around 940 cm^{-1} at first appears, gradually gains in intensity and than becomes weaker to practically disappearing in the spectrum of the sample with the highest deuterium content. Such a behavior characterizes it as being due to a second-order mode of the HOD molecules.

***The lower-frequency component of this doublet is assigned to the γ(P–O–H) vibration (see below).

To the out-of-plane P–O–H bending vibration, we assigned the low-frequency component of the 914/887 cm^{-1} doublet in the infrared spectrum of the protiated compound. Again, the assignment is supported by the spectra of the series of partially deuterated analogues (Fig. 3 and Fig. 5). As seen, on going from the spectrum of the protiated towards that of the practically fully deuterated compound, the band at 887 cm^{-1} gradually disappears, whereas simultaneously the band at 665 cm^{-1} continuously gains in intensity. The isotopic ratio ($\approx$ 1.33) is similar to that encountered in the analogous cases of brushite [14] and of $MnHPO_4 \cdot 3H_2O$ [15] and shows that the 887 cm^{-1} band should be attributed to a mode in which the contribution from the motions of the hydrogen atoms is essential. Since in the structure of the title compound the water molecules do not participate in the formation of *strong* hydrogen bonds, it is difficult to believe that this band, at relatively high frequency, is a result of an H_2O libration*+ and the only remaining possibility is to attribute it to the γ(P–O–H) mode. Pechkovskii *et al.* [8] also assigned one of the bands in the corresponding region to the γ(P–O–H) mode, whereas Mioč and Minic' [10] report a lower, although not precise frequency (850–600 cm^{-1}). As in the previously discussed cases of the δ(P–O–H) and ν(P–OH) modes, the order of the γ(P–O–H) frequencies is $MgHPO_4 \cdot 3H_2O > MnHPO_4 \cdot 3H_2O > CaHPO_4 \cdot 2H_2O$.

If the above assignments are correct, then what remains to be done is the assignment of the mainly O–P–O bending vibrations (originating from the ν_4 and ν_2 PO_4 modes) which should appear below 650 cm^{-1} together with the water librations. In the corresponding region of the infrared spectra of the protiated compound, in addition to the broad and structured feature found between 800 and 580 cm^{-1} (see below) bands exist at 560, 532 and 511 cm^{-1}. The two latter bands could easily be taken as components of the ν_4 phosphate mode but the spectra of the partially deuterated analogues (Fig. 5) show that such is not the case with the 560 cm^{-1} band. As seen in the spectrum of the almost completely deuterated sample, peaks indeed exist around 532 and 513 cm^{-1}, but not around 560 cm^{-1} where an absorption *minimum* is found instead. Of little help are the

*+ Pechkovskii *et al.* [8] treat the whole region between 900 and 350 cm^{-1} as that in which the rocking H_2O/D_2O librations appear.

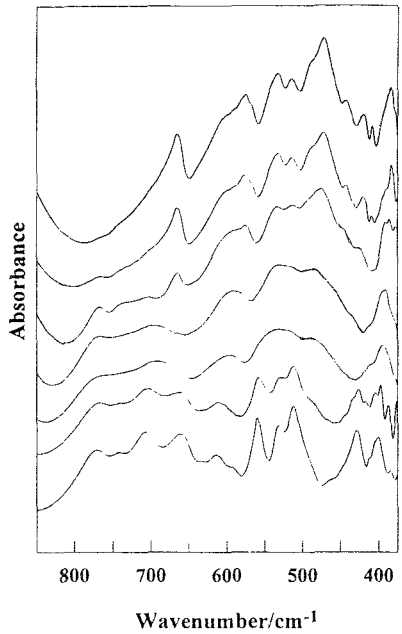

Fig. 5. LNT Fourier transform infrared spectra of a series of partially deuterated analogues of magnesium hydrogenphosphate trihydrate in the 850 –370 cm^{-1} region (the deuterium content increases from bottom to top and corresponds to 0 %, 5 %, 25 %, 50 %, 75 %, 90 % and 95 % deuterium respectively)

spectra of the samples with intermediate deuterium content since the whole region is obscured by bands due to librations of H_2O, HDO and D_2O molecules discussed below. In the corresponding region of the Raman spectra (Fig. 6), the maximum at 498 cm^{-1} gradually disappears on deuteration whereas the band at 521 cm^{-1} seems to persist irrespective on the deuterium content.

Because of similar reasons, the location of the components of the ν_2 phosphate vibration in the infrared spectra is difficult although bands do exist in the region below 450 cm^{-1} where their appearance is expected. On the other hand, a very strong Raman band exists at 401 cm^{-1} (Fig. 2), its infrared counterpart probably being the band with a frequency of 402 cm^{-1} (Fig. 8).

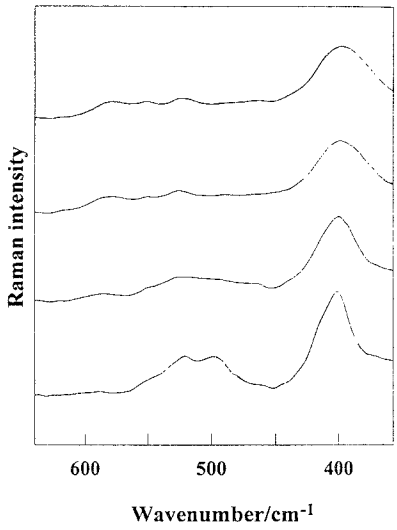

Fig. 6 RT Fourier transform Raman spectra of a series of partially deuterated analogues of magnesium hydrogenphosphate trihydrate in the 850 –370 cm^{-1} region (the deuterium content increases from bottom to top and corresponds to 0 %, 25 %, 75 % and 95 % deuterium respectively)

The bending vibrations and librations of the water molecules

The existence of three crystallographically non-equivalent water molecules (all lying at general positions) should result with three water bending bands and nine librational ones, even if only the site-group selection rules are taken into account. Each of these could be further split as a result of interactions between identical oscillators (correlation-field splitting).

In the infrared spectra of $MgHPO_4 \cdot 3H_2O$ recorded both at room and liquid-nitrogen temperatures only two clear maxima are seen – at 1717 and 1657 cm^{-1} in the LNT spectrum (Fig. 1) whereas in the Raman spectrum (Fig. 2) only one, quite asymmetric band (around 1650 cm^{-1}) is observed. This, of course, is unexpected in view of the existence of three crystallographically different water molecules even without taking into

account the possibility that the band *C* of the *A,B,C* trio could appear in the same general region [16]. This latter band, however, is expected to be broad and not very intense so that there is little doubt that the two relatively sharp maxima at 1717 and 1657 cm^{-1} are due to water bending vibrations. On the other hand, it may be suspected (mainly on the basis of the results for $CaHPO_4 \cdot 2H_2O$ and $MnHPO_4 \cdot 3H_2O$ [14, 15]) that the water molecules of one of the existing types give rise to multiple δ(HOH) bands with the intensity of the individual components of the series being much smaller than that of the 1717 and 1657 cm^{-1} bands. The pronounced asymmetry of the high-frequency side of the 1717 cm^{-1} band as well as the existence of a broad maximum around 1485 cm^{-1} are in line with such an interpretation. An alternative explanation would be that an accidental degeneracy of two of the expected three δ(HOH) vibrations (with a possible contribution to the whole complex feature from the C band of the A,B,C trio) is present.

The situation in the water bending region of the spectra of partially deuterated analogues is complicated. Namely, since three types of asymmetrically bound water molecules exist in the structure, six bands due to the bending vibrations of the HOD or DOH molecules are expected in the spectra of the slightly and almost completely deuterated analogues respectively. In any case, the presence of bands attributable to HOD bendings (see below) rules out the possibility of presence of H_3O^+ ions in the structure as speculated Pechkovskii *et al.* [8] or Mioč and Minic' [10] since no bands due to the H_2DO^+ and HD_2O^+ bending modes appear (Fig. 7).

In the region of water librations a broad and obviously complex feature is found between 800 and 580 cm^{-1} in the RT infrared spectrum of $MgHPO_4 \cdot 3H_2O$ (Fig. 8) whereas in the Raman spectrum the corresponding bands are expectedly, quite weak (Fig. 2). On the other hand, in the LNT infrared spectrum the centroid of the feature is found at higher frequencies than in the RT one, at least five defined maxima (with frequencies of 771, 743, 708, 662 and 614 cm^{-1}) being easily discernible on it (Fig. 8). Both the position of these bands (no hydrogenphosphate vibration is expected in this region) and their temperature dependence qualifies the discussed bands as being due to H_2O librations. Because of its pronounced temperature dependence, the LNT band at 428 cm^{-1} most probably originates

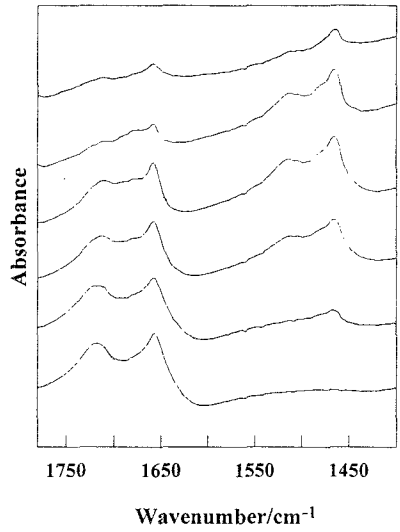

Fig. 7. LNT Fourier transform infrared spectra of a series of partially deuterated analogues of magnesium hydrogenphosphate trihydrate in the 1780 –1400 cm^{-1} region (the deuterium content increases from bottom to top and corresponds to 0 %, 5 %, 25 %, 50 %, 75 % and 95 % deuterium respectively)

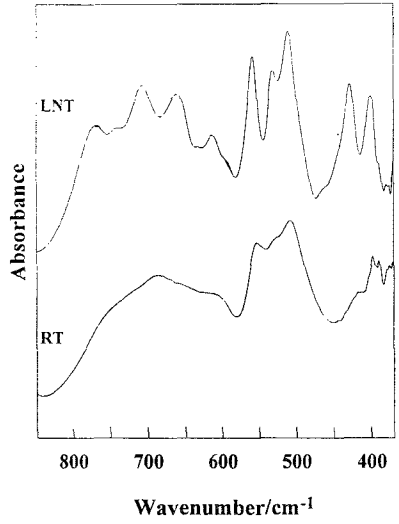

Fig. 8. Fourier transform infrared spectra in the 850–370 region of $MgHPO_4 \cdot 3H_2O$ at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT)

from one of the water librational motions as well. As discussed earlier, the 560 cm^{-1} infrared and the 498 cm^{-1} Raman one must have the same origin. The number of water librational bands is not surprising bearing in mind the existence of three types of water molecules, all of them being positioned on sites with C_1 symmetry which makes it possible for all librations to become infrared active and, quite probably, mixed in character. Thus, even in the site-group approximation, nine librational bands are likely to appear.

For a band to be assigned to water librations, it has to be deuteration sensitive, the D_2O librations being expected below 600 cm^{-1} (the frequencies of the HDO librations are dependent on their exact form). Indeed, in the infrared spectrum of the deuterated analogues (Fig. 5) changes in the above-mentioned regions are present, several bands which can be assigned to D_2O librations are seen in the spectrum of the sample deuterated to the highest degree and, moreover, the analogues of some of the H_2O librations certainly fall outside the studied region.

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