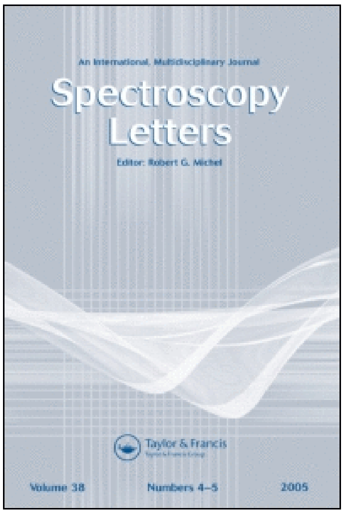

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Fourier Transform Vibrational Spectra of Magnesium Hydrogenphosphate Trihydrate. I. The O-H Stretching Region

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FOURIER TRANSFORM VIBRATIONAL SPECTRA OF MAGNESIUM HYDROGENPHOSPHATE TRIHYDRATE. I. THE O–H STRETCHING REGION*

Key words: Magnesium hydrogenphosphate trihydrate, newberyite, Fourier transform infrared spectra, Fourier transform Raman spectra, O–H stretching

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ABSTRACT

The Fourier transform (FT) infrared and Raman spectra of newberyite, $MgHPO_4 \cdot 3H_2O$ are studied in the region where the stretching vibrations of the water molecules (protiated and deuterated) and the O–H/O–D stretches of the hydrogenphosphate anions are expected to appear. The O–H stretching vibrations give rise to a complex feature known as the *A,B,C* trio. Since neither of the maxima found below 3000 cm^{-1} represents a true band arising from a given fundamental, it is pointless to correlate their frequencies with the observed O · · · O distances. In the water stretching region, the two bands with highest frequencies undoubtedly correspond to the antisymmetric and symmetric stretch of one type of the water molecules. The stretching vibrations of one of the remaining two types of H_2O molecules are clearly uncoupled and the O–H oscillator involved in the weaker hydrogen bond is responsible for a band at 3376 cm^{-1} whereas the rest of the water stretchings are apparently overlapped yielding the complex band below 3320 cm^{-1}. Thus the situation is again complicated and the

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

correlations between the frequencies and the $O_w \cdots O$ distances are inappropriate. The two bands at highest frequencies (3522 and 3483 cm^{-1} at RT) exhibit a positive temperature coefficient.

INTRODUCTION

The title compound, $MgHPO_4 \cdot 3H_2O$ appears as a natural mineral newberyite* (often associated with the guano deposits) and was found to be a constituent of urinary calculi, both in humans and in animals. This latter fact has provoked a considerable interest and various structural characteristics of this compound, its relation to struvite (magnesium ammonium phosphate hexahydrate) and the conditions of its growth have been studied [1–6].

The crystal structure of $MgHPO_4 \cdot 3H_2O$ was first determined (from a natural mineral) by Sutor [2] and later refined, again by X-ray diffraction, by Abbona *et al.* [7]. Whereas Sutor did not attempt to determine the positions of the hydrogen atoms, this was done by Abbona *et al.* [7]. Newberyite crystallizes in the orthorhombic space group *Pbca* with eight formula units in the crystallographic unit cell. The structure comprises one type of magnesium atoms and of hydrogenphosphate ions and three non-equivalent types of water molecules. As expected for a hydrogenphosphate, the hydrogen bond formed by the acidic hydrogen is quite strong (the $O_w \cdots O$ distance is reported [7] to be 261.5 pm). One of the six hydrogen bonds formed by the water molecules is also relatively short (269.0 pm), whereas the remaining $O_w \cdots O$ contacts range from 274.7 to 311.8 pm (one of the hydrogen bonds is reported to be bifurcated). Despite the existence of a network of hydrogen bonds, its electric conductivity was shown to be low [8].

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* This name newberyite is often used not only for the mineral itself but also for its synthetic analogue. This practice will be followed in this paper too.

The vibrational (conventional infrared and Raman) spectra of newberyite have also been studied. Thus, Pechkovskii *et al.* [9] studied the infrared spectra of the protiated and highly deuterated forms of newberyite and of its manganese analogue at room and liquid-nitrogen temperature and reported the room-temperature Raman spectrum (from, approximately, 1300 cm^{-1} down to 200 cm^{-1}) of the protiated form. The RT infrared spectra of $MgHPO_4 \cdot 3H_2O$ and its purported partially deuterated analogue were examined by Mioč, Petranović and Minić [10] and the vibrational (infrared and Raman) spectra of the protiated compound only* by Mioč and Minić [8]. The Raman spectrum reported by these authors is a conventional one, its quality is not very high and only the region below 3000 cm^{-1} is both shown and tabulated. It thus seems that the high-frequency region (to which the present paper is devoted) in the Raman spectrum of newberyite has not been dealt with so far.

Some time ago we have reported [11] a very brief account of our Fourier transform vibrational studies of newberyite and a series of its deuterated analogues. A more complete discussion of the spectra in the O–H (and O–D) stretching region will be given in the present paper whereas the remaining portions of the spectra will be discussed in due time [12]. The decision to divide the discussion into two parts was primarily based on the need to straighten up, as much as possible, the problems related to the attribution of the bands in this region and to the correlation of the observed frequencies with the hydrogen bonds present in the structure. This especially because we feel that in the previous work [8–10] not all bands in this region have been interpreted properly.

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* What is claimed, in Ref. 10, to be the partially deuterated form of $MgHPO_4 \cdot 3H_2O$ exhibits a spectrum which bears no resemblance to either their spectrum of the protiated compound or to our spectra of the partially deuterated newberyite. Thus, it is probably no coincidence that this spectrum has not been reported in the later study [8] by essentially the same authors.

EXPERIMENTAL

Magnesium hydrogenphosphate trihydrate was a commercial sample (Carlo Erba) recrystallized from glacial acetic acid. The deuterated analogues with a varying deuterium content were prepared by recrystallizing the protiated compound from partially deuterated acetic acid (prepared by dissolving acetic anhydride in H_2O/D_2O mixtures of appropriate composition).

The infrared spectra were recorded using the infrared interferometer Perkin-Elmer System 2000 FT-IR in the frequency range 4000 – 400 cm^{-1} with a resolution of 1 to 4 cm^{-1} (32 scans were ordinarily accumulated). The Fourier transform Raman spectra were recorded on a Perkin Elmer NIR FT Raman 1700 x instrument equipped with a Nd : YAG laser emitting at 1064 nm. Two hundred FT Raman spectra (at a resolution of 4 cm^{-1}) were accumulated.

The spectra were recorded, from both mulls and pressed KBr disks, starting at room temperature (RT) and going down to the boiling temperature of liquid nitrogen (LNT). The variable-temperature cell P/N 21525 (Graseby Specac) with KBr windows was used for the low-temperature measurements. The acquisition of the spectra was done by using the GRAMS ANALYST 2000 package [13] whereas for manipulations on the recorded spectra the GRAMS/386 [14] package was employed.

RESULTS AND DISCUSSION

The infrared spectra in the 3800 to 1800 cm^{-1} region of $MgHPO_4 \cdot 3H_2O$ recorded at RT and LNT are shown in Fig. 1a, the corresponding spectra of the practically completely deuterated analogue in Fig. 1b, whereas the high-frequency parts of the RT Raman spectra of protiated and highly deuterated (> 95 %) newberyite are given in Figs. 2a and 2b. These latter spectra are less reliable because

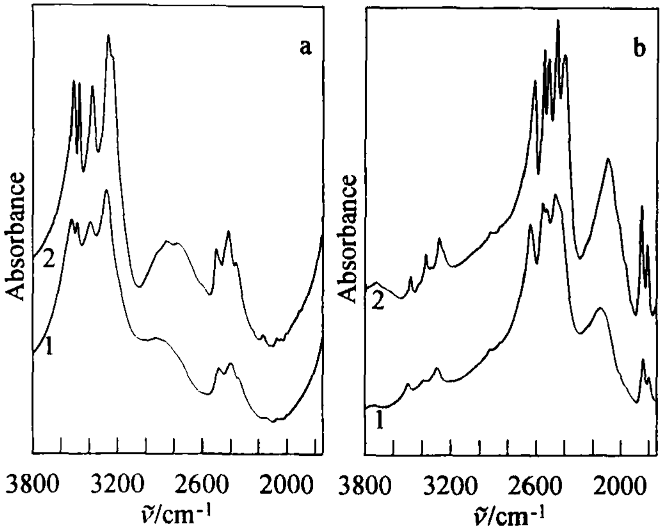

Fig. 1. The 3800–1800 cm^{-1} regions in the RT (1) and LNT (2) Fourier transform infrared spectra of $MgHPO_4 \cdot 3H_2O$ (a) and of $MgDPO_4 \cdot 3D_2O$ (b)

of the inherent low intensity of the bands arising from vibrations in which the motion of hydrons is predominant (of somewhat better quality is the spectrum of the deuterate).

The bands appearing in the above-mentioned region are, beyond doubt, due either to the fundamental stretching vibrations of the water molecules or to either the O–H or the O–D stretchings of the hydron-containing part of the hydrogenphosphate ions. To be precise, they may be only *related* to such modes.

As mentioned above, hydrogenphosphate anions of only one type are present in the structure so that, in the approximation of the site group, only one O–H stretching band due to the vibrations localized in the HPO_4^{2-} ions is expected. Since eight such ions exist in the unit cell, factor-group splitting of this mode (and of all other) should be present. On the other hand, the existence of three crystallo-

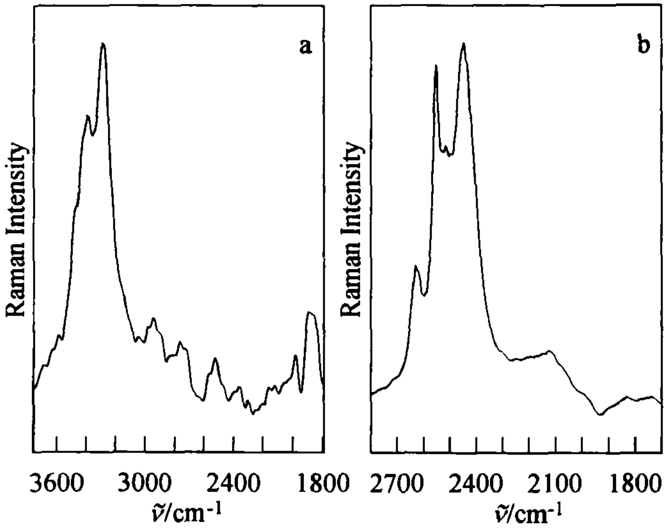

Fig. 2. The high-frequency regions in the Fourier transform Raman spectra of $MgHPO_4 \cdot 3H_2O$ (a) and of $MgDPO_4 \cdot 3D_2O$ (b)

graphically non-equivalent water molecules (all lying at general positions) is predicted to give rise, again in the site-group approximation, to six water stretching bands.

The true situation in the P–O–H stretching region may not be as simple as outlined above since it is well known that the O–H stretch of hydrogenphosphate and related anions often give rise to a complex feature known as the *A,B,C* trio. Although various explanations [15–19] for the origin of the trio have been advanced, the simplest yet most appealing one is that originally due to Hadži [15] and later refined by Claydon and Shepard [16] and Odinokov and Iogansen [18]. According to these authors, the two high-frequency components of the trio (*A* and *B*) are due to an Evans-type interaction between the fundamental O–H vibration and the overtone of the in-plane O–H bending, whereas the transmission window between the bands *B* and *C* is similarly explained assuming an interaction between the fundamental O–H vibration and the overtone of the out-of-plane O–H bending mode. It should perhaps be mentioned that we have observed a similar pattern in the spectra of several crystalline hydrates in the structure of which relatively strong hydrogen bonds are present [20,21].

The OH Stretching Vibrations of the Hydrogenphosphate Ions

As seen in Fig. 1, in the infrared spectra of newberyite the broad and complex bands (true or apparent) at around 2800 cm^{-1} and around 2400 cm^{-1} are reminiscent of the *A* and *B* components of the *A,B,C* trio (the *C* component is expected at lower frequencies). Since in the Raman spectrum a band with a frequency of 1270 cm^{-1} is reported [9], it seems that the transmission window between the *A* and *B* components of the trio could indeed be produced by interaction of the fundamental hydrogenphosphate O–H stretch with an 'overtone' of the in-plane POH bending. It should be pointed out that under the selection rules of the factor group of $MgHPO_4 \cdot 3H_2O$ no true overtone of a factor-group component of any vibration can be infrared active so that when speaking of 'overtones', suitable *combinations* of a *gerade* and an *ungerade* factor-group component* are actually meant. The clearly visible structure of the *B* band as well as that of band *A* is probably a results of additional vibrational coupling with some other second-order transitions.

In the Raman spectrum of the protiated form (Fig. 2a) the situation is less clear than in the corresponding spectrum of the highly deuterated analogue (Fig. 2b) where a maximum is visible at around 2130 cm^{-1} and a complex band centered around 1800 cm^{-1} is also seen. These two bands are clearly the analogues of the bands *A* and *B* of the trio.

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* Except for the combinations $B_{1g} \otimes B_{1u} = A_u$, $B_{2g} \otimes B_{2u} = A_u$ and $B_{3g} \otimes B_{3u} = A_u$ since the modes belonging to the A_u symmetry species are both infrared and Raman inactive. The direct products of A_u with B_{1g}, B_{2g} and B_{3g} yield representations for infrared active species.

All in all, we are convinced that the features below 3000 cm^{-1} are not *true* bands and therefore their frequencies should not be correlated with the individual O · · · O contacts as has been done by Mioč and Minić [8].

The OH Stretching Vibrations of the Water Molecules

The appearance of the spectrum above 3000 cm^{-1} is simpler than expected (even without taking into consideration the possibility of correlation-field splitting). In fact, the number of infrared and Raman bands is less than the expected six (Figs. 1 and 2). Only *five* bands are seen in the O–H stretching region of the infrared spectra of protiated newberyite and in the O–D stretching region of the spectrum of the highly deuterated analogue (the splitting of the bands and their relative intensities are somewhat different in the two spectra). The situation is similar in the Raman spectra but the overlap of the bands (especially in the case of the protiated form) is more extensive than in the infrared spectra.

It should be noted that the observed by us picture in the infrared spectra is similar to that found by other authors [8–10] but our spectra are of better quality and the Fourier transform method makes it possible to utilize various techniques for spectral manipulation. Furthermore we have studied a series of partially deuterated compounds (something that has not been done before) and, to best of our knowledge, report for the first time the Raman spectra in the O–H/O–D stretching region (as has already been mentioned).

According to the results of Abbona *et al.* [9] the water molecule W(9) has potential proton acceptors at furthest distances from its oxygen* (one of the hydro-

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* In fact, in the original paper, W denotes just the *oxygen atom* of a given water molecule. In order to simplify our notation, W (with a number in parentheses) will stand for the given water *molecule*. When only the oxygen atom is meant, it will be denoted by O (with the corresponding number in parentheses).

gen bonds could be bifurcated). Furthermore, the proton acceptors for the corresponding hydrogen bonds are *neutral* water molecules and not hydrogenphosphate oxygen which, understandably, carry a larger partial negative charge. Thus it seems quite reasonable to assign the two highest-frequency infrared bands (3522 and 3483 cm^{-1} at RT and 3510 and 3470 cm^{-1} at LNT) to the antisymmetric and symmetric stretching vibrations of the water molecules of this type (rather than attempt to correlate them with either of the reported $O_w \cdots O$ contacts as has been done, for example, by Mioč and Minić [8]). The larger separation of the corresponding bands in the spectrum of the highly deuterated analogue (Fig. 1b) is in line with such an interpretation (it is well known that the antisymmetric and the symmetric stretch of the water molecules are sensitive to deuteration to a different degree).

The present interpretation is easy to check additionally by studying the appearance of the corresponding bands in the spectra of the series of partially deuterated compounds. If, namely, the explanation is correct then approximately midway between the two components of the doublet at highest frequencies (in both the O–H and the O–D stretching region) a new band or a closely spaced doublet should appear as a result of the uncoupled stretches (O–H or O–D respectively) of the two forms of half-deuterated W(9) molecules – one formed when the deuterium-for-proton exchange takes part in the weaker hydrogen bond and the other when the protons involved in the stronger hydrogen bond are exchanged with deuterons. If this is so, the ‘central’ band(s) would at first increase and then diminish in intensity with the augmentation of the deuterium content in the sample. The experimentally found situation is exactly as predicted and bands with the predicted intensity behaviour are seen at 3488 and 3479 cm^{-1} in the O–H and at 2573 and 2567 cm^{-1} in the O–D stretching region (Fig. 3).

It is interesting that the frequencies of the corresponding bands in the spectra recorded at LNT are *lower* than those in the RT spectra (Fig. 4). In other words,

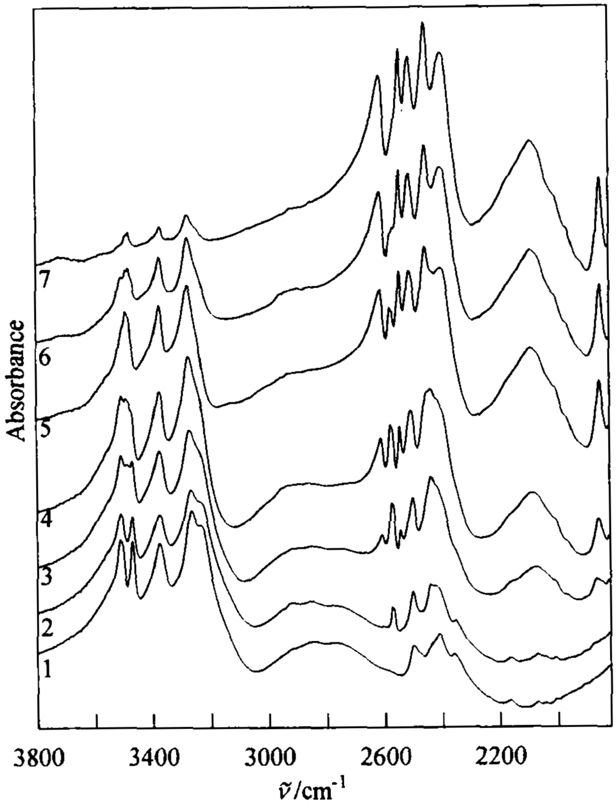

Fig. 3. The 3800–1800 cm^{-1} region in the LNT FT IR spectra of $MgHPO_4 \cdot 3H_2O$ (1) and a series of its partially deuterated analogues (the deuterium content increases on going from 2 to 7)

these bands are characterized by a *positive* temperature coefficient ($d\tilde{\nu}/dT > 0$), a behaviour which is expected [22] for linear or slightly bent hydrogen bonds (but *not* for bifurcated ones). Such is *not* the case with one of the hydrogen bonds formed by W(9) which was found [7] to be bifurcated. However, Lutz *et al.* [23] report a positive temperature coefficient even for the case of bifurcated hydrogen bonds and our present finding is in agreement with these authors.

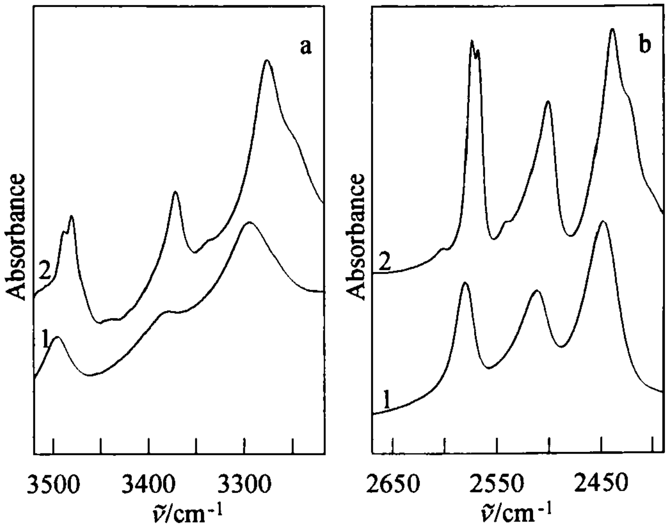

Fig. 4. The O–H stretching region in the FT IR spectra of highly deutrerated (> 95 %) $MgHPO_4 \cdot 3H_2O$ (a) and the O–D stretching region in the (2) spectra of slightly deutrerated (< 5 %) $MgHPO_4 \cdot 3H_2O$ (b) recorded at RT (1) and LNT (2) respectively

The exact assignment of the remaining bands is more complicated. The water molecule W(8) forms two quite different in length hydrogen bonds, the $O_w \cdots O$ contacts being of length 269.0 and 281.9 pm [7]. The difference in *strength* is probably even greater since the shorter contact is with a phosphate oxygen atom which accepts only one proton whereas the longer contact is with oxygen atom O(5) that serves as an acceptor of two hydrons. As we have shown [24], under such conditions the latter of the hydrogen bonds would be weaker than expected on the basis of the $O_w \cdots O$ distances alone. It would then follow that the two stretches of water W(8) would be uncoupled to a high degree and that the positions of the two stretching bands would depend only slightly on the deuterium content in the sample. This is true for the infrared band at 3376 cm^{-1} (Fig. 3) and we therefore assign it to a mode which is essentially O(8)–H(3) · · · O(5) stretch. The remaining stretching vibration of W(8) should then contribute to the complex band found below 3320 cm^{-1}.

It is not entirely clear whether the two stretching vibrations of W(7) would also appear below 3320 cm^{-1} as could be conjured on the basis of the appreciable intensity of the feature in question. Although the reported $O_w \cdots O$ distances for this type of water molecules are not greatly different (274.7 and 284.5 pm) and one is tempted to believe that the two stretching vibrations of these water molecules are better described as antisymmetric and symmetric H_2O modes rather than as uncoupled ones, it should not be forgotten that the longer contact is with an oxygen atom which serves as a proton acceptor of *two* hydrons. However, the sensitivity of the band maxima on the deuterium content in the sample is better explained if the presence of practically uncoupled water stretchings in this region is assumed.

The interpretation of the infrared spectra of crystalline hydrates is usually simplified if the spectra of isotopically diluted HOD molecules are studied. In samples with a low deuterium content, suitable for that purpose is the ν(OD) and in those with a high deuterium content – the ν(OH) region (the latter region is simpler to analyze since no interfering bands are expected there). As in the spectrum of the protiated form, there is little doubt that the two bands at highest frequencies (3488 and 3479 cm^{-1} or 2573 cm^{-1} and 2567 cm^{-1} for the O–H and O–D regions respectively) are due to the stretching vibrations involving the hydrons which form the two weakest hydrogen bonds although it is somewhat strange to find appreciable differences in the intensities of the two overlapped bands in the two regions (cf. Fig. 3 and Fig. 4). The situation is, however, far from being unique [25–27] and the differences in the intensities have been attributed to the differences in the form of the normal coordinates of the asymmetrically bonded water molecules when they are in one of the two possible orientations (H–O–D ·

$\cdots$O and D–O–H$\cdots$O respectively). In the course of our work on crystalline hydrates we have also found [28,29] examples of quite different in intensity ν(O–D) bands of isotopically isolated HOD molecules in crystals where only two types of hydrogen bonds are present in the structure and proposed, as one of the possible explanations, a non-statistical substitution of protons with deuterons. The recent work by Petruševski and Pejov [30] shows that such a situation is thermodynamically feasible.

The bands at 3371 or 2499 cm^{-1} in the O–H and O–D stretching region respectively (Figs. 3 and Fig. 4) most probably originate from the O(8)–H(3) or O(8)–D(3) stretchings but one of the stretching vibrations of W(7) might also be located there.

To summarize, we were unable to unequivocally locate the stretching vibrations of the W(7) type water molecules but the above analysis seems to convincingly show that it is not advisable to correlate the observed frequencies and the oxygen-to-oxygen distances without taking into account all the pertinent structural details.

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