

Infrared and Raman spectra of magnesium ammonium phosphate hexahydrate (struvite) and its isomorphous analogues. III. Spectra of protiated and partially deuterated magnesium ammonium phosphate hexahydrate

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Received 21 April 2005; accepted 10 May 2005

Available online 20 July 2005

Dedicated to our friend and colleague Prof. Galina A. Puchkovska on the occasion of her 70th birthday

Abstract

Magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (synthetic struvite) is a well-known biomineral, its major biological importance being related to its presence in human urinary sediments and vesical and renal calculi. The Fourier transform infrared and Raman spectra of magnesium ammonium phosphate hexahydrate were recorded and analyzed from room temperature (RT) down to the boiling temperature of liquid nitrogen (LNT). Also recorded and analyzed were the spectra of its partially deuterated analogues. The recorded spectra were compared with the corresponding ones of the previously studied potassium analogue. On the basis of such a comparison it was concluded that the main contribution to the intensity of the broad and structured feature in the O–H/N–H stretching region comes from the bands originating from the H–O–H stretches. The location of at least some of the stretching vibrations of the ammonium ions (albeit one of its deuterated forms) is possible in the spectrum of the sample containing $\approx 2\%$ deuterium. The bands at 2326 and 2277 cm^{-1} (and probably, at least partially, that at 2393 cm^{-1}) can be assigned with certainty to N–D stretching vibrations of isotopically isolated NH_3D^+ ions. The LNT Raman bands at 1702 and 1685 cm^{-1} are attributed to the $\nu_2\text{ NH}_4^+$ mode and those at 1477 and 1442 cm^{-1} are observed are attributed to the ν_4 mode. The relatively high frequencies (1302 and 1295 cm^{-1}) of some of the bands due to the ND bending vibrations of isotopically isolated NH_3D^+ ions are in line with the existence of quite strong hydrogen bonds formed by ammonium ions. The librations of the deuterated forms of water molecules may be coupled with the components of the phosphate ν_4 vibration.

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Keywords: Struvite; Magnesium ammonium phosphate hexahydrate; Biominerals; Infrared spectra; Raman spectra; Hydrogen-bond effects

1. Introduction

Continuing our work on the vibrational spectra of the members of the struvite¹ family [1,2], we now report

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¹ Struvite is actually the name of the mineral with composition corresponding to the formula $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ but (as in other similar cases) is often used to denote the synthetic substance with the above composition.

the results of the analysis of the vibrational (FT IR and FT Raman) spectra of struvite itself and a series of its deuterated analogues. Our interest in the spectra of the compounds of this family is twofold. On the one hand, both the spectra [2] and the results of the diffraction studies [3,4] show that hydrogen bonds of considerable strength are present in the structures of struvite (MNP), its potassium analogue, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (MKP) and of arsenstruvite, $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ (MNA) which is an interesting phenomenon by itself and, moreover, may qualify these three isomorphous compounds as potential protonic conductors [2]. On the other hand, struvite is a biomineral present in urolithes and other calculi [5,6], a fact related to

our extensive studies of various concrements and their constituents [7–24].

The members of the struvite family crystallize in the orthorhombic space group $Pmn2_1$ (C_{2v}^7) with $Z=2$ [3,4,25,26]. In the crystal structure of struvite all ions and two (out of four) types of water molecules occupy sites with C_s symmetry, while the other two types of H_2O molecules are on general positions² [3,4]. The water molecules are donors in six quite short hydrogen bonds that are among the shortest ever found in crystalline hydrates [27] with $O_w \cdots O$ distances ranging from 263 to 269.5 pm while the seventh contact (with another water molecule) is considerably longer (314.1 pm). Each ammonium ion forms one rather strong hydrogen bond (the $N \cdots O$ distance is 280 pm), the rest being weak (one may be trifurcated).

The infrared spectra of magnesium ammonium phosphate hexahydrate and its potassium analogue recorded at room temperature were studied some 30 years ago [28] and the RT Raman spectrum of struvite was also published [6]. In Ref. [28] an approximate description of the observed bands is given but some of the assignments are questionable and are not supported by direct experimental observations. Recently, we presented the results of the analysis of the vibrational spectra of the potassium analogue of struvite and of an extensive series of deuterated analogues [1] while in Ref. [2] the emphasis was placed on the analysis of the O–H(D)/N–H(D) stretching region of the vibrational spectra of protiated and partially deuterated $MgKPO_4 \cdot 6H_2O$ (MKP), $MgNH_4PO_4 \cdot 6H_2O$ (MNP) and $MgNH_4AsO_4 \cdot 6H_2O$ (MNA). In view of what has been said, the present paper will deal mainly with the comparison of the spectra of MKP and MNP.

2. Experimental

The crystalline struvite was synthesized according to the methods described by Abona et al. [29]. Employing the same general procedure, but using as solvents H_2O – D_2O mixtures with appropriate composition, a series of partially deuterated analogues was prepared, the highest content of deuterium being achieved when pure D_2O was used.

The Fourier transform infrared spectra were recorded (from both mulls and pressed KBr disks) on a Perkin–Elmer System 2000 infrared interferometer at room and liquid-nitrogen temperature (RT and LNT, respectively). The variable-temperature cell P/N 21525 (Graseby Specac) equipped with KBr windows was used for the low-temperature measurements. In order to obtain a good signal-to-noise ratio, 64 scans were collected and averaged at LNT while 32 scans appeared to be sufficient

at RT. The working resolution of the instrument was 4 cm^{-1} . For acquisition of spectra GRAMS ANALYST 2000 [30] was used. The FT Raman spectra were recorded (with a resolution of 2 cm^{-1}) on a Bruker RFS 100/s FT Raman instrument equipped with Nd:YAG laser emitting at 1064 nm. To achieve a good signal-to-noise ratio, 500 scans were accumulated and averaged. All Raman spectra were recorded under identical experimental conditions. The GRAMS/32 [31] package was used to manipulate the spectra.

3. Results and discussion

The Fourier transform infrared and Raman spectra of synthetic struvite at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) are presented in Figs. 1 and 2. The RT spectra are essentially identical with those reported in Refs. [6] and [28] and the LNT spectra are those given in Ref. [2]. Furthermore, as seen from Fig. 3, the infrared spectra of MNP are quite similar to those of MKP [1] (a fact already discussed in [2]), despite the fact that bands originating from the internal vibrations (and, possibly, also the external ones) of the ammonium ion are expected in the spectra of struvite.

3.1. Group theoretical arguments

As already mentioned, four types of water molecules are present in the structure of struvite while all ammonium ions are crystallographically identical [3,4]. As a consequence, $4 \times 3 = 12H_2O$ internal modes and $4NH_4^+$ internal modes should give rise to vibrational bands if ‘free’ H_2O and NH_4^+ entities are taken into account. Of the H_2O vibrations, eight are stretchings and four are bendings (two stretching and one bending mode for each non-equivalent water molecule), whereas the four normal vibrations of the ammonium ions are divided into two stretchings (ν_1 and ν_3) and two bending

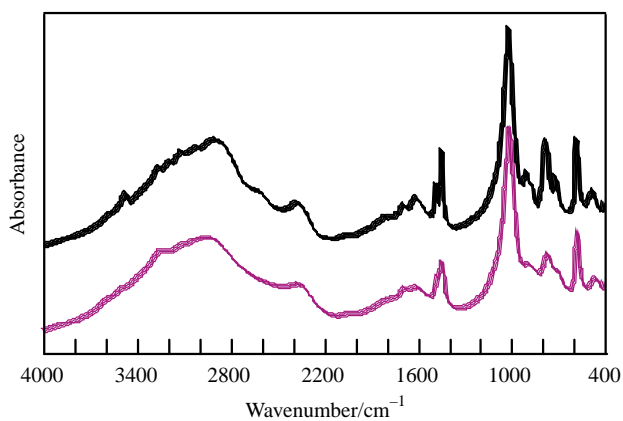


Fig. 1. Infrared spectra of $MgNH_4PO_4 \cdot 6H_2O$ recorded at RT (lower curve) and at LNT (upper curve).

² The interested reader should consult the projection of part of the structure given in Ref. [1].

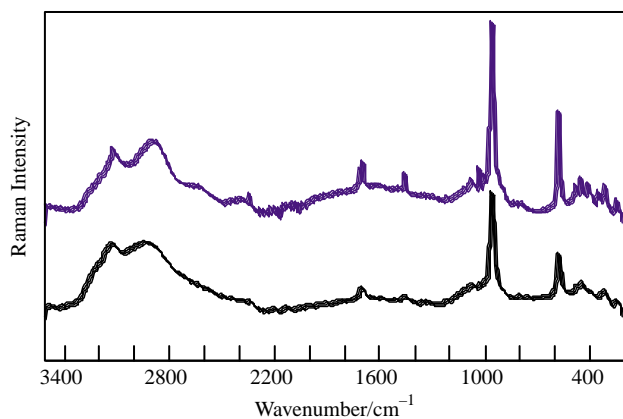


Fig. 2. Fourier transform Raman spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and at LNT (upper curve).

ones (ν_2 and ν_4). The ν_1 ammonium mode (of symmetry A_1) is non-degenerate, the ν_2 vibration (of the E symmetry type) is doubly degenerate and the ν_3 and ν_4 modes (both belong to the symmetry species F_2) are triply degenerate. As far as the group theoretical arguments are concerned, the situation with the vibrations of the ‘free’ PO_4^{3-} is exactly as that with the vibrations of the ammonium ions.

Since, obviously, we are dealing with entities that are constituents of a crystalline solid, the influence of both the static field (related to the symmetry of the sites on which a given entity is situated) and the correlation field (originating from interactions of identical oscillators) must be taken into account. Complete sets of correlation diagrams for changes on going from the molecular to the local group and, then, to the factor group of the space group are given in Ref. [1]. It should be noted that, as far as the group theoretical arguments are concerned, the situation with the ammonium ions is exactly the same as that of the PO_4^{3-} ions treated in Ref. [1]. The interested reader is referred to the above-mentioned correlation diagrams.

In the approximation of the molecular group, all internal H_2O modes are both infrared and Raman active, whereas of

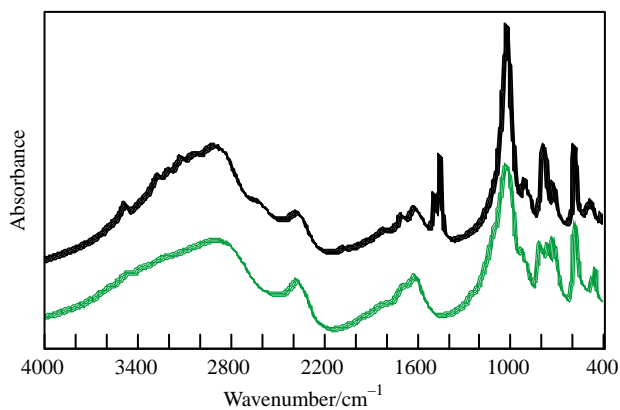


Fig. 3. Infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (lower curve) and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (upper curve) recorded at LNT.

the four normal NH_4^+ modes infrared active are only the two triply degenerate vibrations (the antisymmetric stretch and the antisymmetric bend). All four normal modes are Raman active. As mentioned, the four normal PO_4^{3-} modes are, from the symmetry point of view, analogous to those of the ammonium ions.

Under the influence of the local field, the degeneracies of the ammonium vibrations are removed and six modes of the A' type and three of the A'' type result. The symmetry of the H_2O modes in the site-group approximation depends on the location of the hydrons with respect to the crystallographic symmetry planes. Of the four types of H_2O molecules only those denoted $\text{O}_w(2)$ have two crystallographically equivalent hydrons each [4]. These molecules have a C_s local symmetry and their normal modes are of the A' type. The normal modes of the rest of the water molecules (those situated at general positions) in the site-group approximation are two of the A' type (the in-phase stretching and the bending mode) and one of the A'' type (the out-of-phase stretching vibration). The presence of the correlation field should cause a splitting of each site-group vibration of the molecules with the symmetry plane bisecting the H–O–H angle into components of A_1 and B_2 symmetry, whereas the A' modes of the H_2O molecules on general positions are also split into components of A_1 and B_2 symmetry and the A'' modes give rise to components of A_2 and B_1 symmetry (those of the A_2 type are infrared inactive). The site-group of the phosphate ions is identical with that of the NH_4^+ ions, their number in the unit cell is also identical to that of the ammonium ions and so everything said above for the NH_4^+ vibrations applies equally well to the phosphate modes.

As is well known, however, the group theory cannot predict how effective the correlation field would be and, consequently, how large the site-group splitting is expected to be and whether it should be observable at all. Yet, it is reasonable to expect that the correlation field would be stronger for the $\text{O}_w(3)$ and $\text{O}_w(4)$ types of water molecules since, they can be treated as mechanically coupled oscillators because pairs of such molecules are coordinated to the same Mg^{2+} ion. In view of the fact that the stretching vibrations will likely give rise to broad bands and, in addition to that, the number of the expected factor-group components is considerable, it is not very likely that separate bands originating from individual components would be seen in the infrared and Raman spectra. The spectral picture would be further complicated by the appearance of NH_4^+ bands in the same general region as the H_2O stretching vibrations.

In the case of the phosphate ions another effect must be taken into account. Namely, as the results of the crystal structure determinations show, the geometry of the PO_4^{3-} ions is such that, even in the crystal, the symmetry of the ions is close to the ideal T_d one as is clearly seen from the small values of the Baur's deformation indices [32] given in Table 1. This would then mean that it is not likely to observe the phosphate symmetric stretching band

Table 1
Deformation indices of the PO_4^{3-} ion in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$

Deformation index	$D(\text{P-O})$	$D(\text{O-P-O})$	$D(\text{O-O})$
Value	0.0017	0.0044	0.0021

and the components of the symmetric bending mode ν_2 with appreciable intensity and furthermore that the splitting of the two triply degenerate vibrations should not be very pronounced. Since, the values of all three deformation indices of the PO_4^{3-} ions in MNP are smaller than those in MKP, all mentioned effects would be more pronounced in the present case than in the previously [1] treated one.

3.2. Internal vibrations of the water molecules and ammonium ions

3.2.1. Stretching vibrations of the water molecules and ammonium ions

The O–H/N–H stretching region as well as the corresponding O–D/N–D one in the spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and the other two members of the struvite family (MKP and MNA) are discussed in detail in Ref. [2] so that only the most important points are briefly reviewed here.

As shown in Ref. [2] and is visible in Figs. 4 and 5 of the present paper, in the spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ a broad, asymmetric and somewhat structured band is present between 3800 and 2200 cm^{-1} in the infrared and from 3400 to 2200 cm^{-1} in the Raman spectra. The intensity and the shape of this band is obviously a result of at least two important factors. On the one hand, the breadth, the intensity and the frequency of the centroid of these bands are in line with the strength of the hydrogen bonds in the structure (especially those formed by the water molecules). On the other hand, the number of factor-group modes that give rise to bands in this region is considerable so that an extensive overlap is taking place. Since, the vibrations are probably anharmonic,

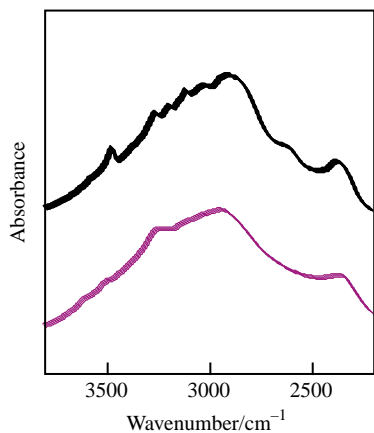


Fig. 4. Infrared spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and LNT (upper curve) in the region of the OH and OD stretching vibrations.

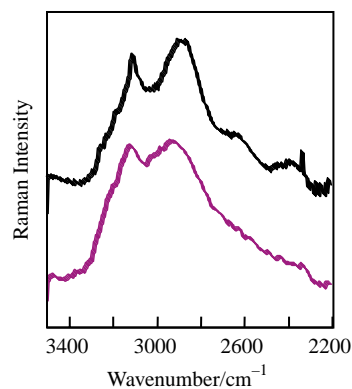


Fig. 5. Raman spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT and at LNT in the region of the OH and OD stretching vibrations.

second-order transitions are likely to be present in the same region, interacting with the fundamental H_2O and NH_4^+ stretching modes. As discussed in Ref. [2], in addition to the broad and strong band centered around 3000 cm^{-1} , a peak of non-negligible intensity reminiscent of the B band of the ABC trio [33] is present around 2400 cm^{-1} .

The fact that the infrared spectral picture is not very different in the case of the ammonium compound as compared with the spectrum of $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ (Fig. 6) is, as discussed [2], a clear indication that the main contribution to the intensity of the features in the O–H/N–H and O–D/N–D stretching regions comes from water modes whilst the N–H(D) stretches contribute to a lesser degree. This is logical if one takes into account the fact that the hydrogen bonds formed by the water molecules are stronger than those in which the ammonium ions take part and that, on the other hand, the strength of the X–H...Y hydrogen bonds and the intensity of the X–H stretching bands are proportional.

In order to simplify the spectral picture, the infrared spectrum of the analogue with ($\approx 2\%$) deuterium content was studied. Since, the situation is still complicated by the existence in the region, where the $\nu(\text{O-D})/\nu(\text{N-D})$ bands are expected,

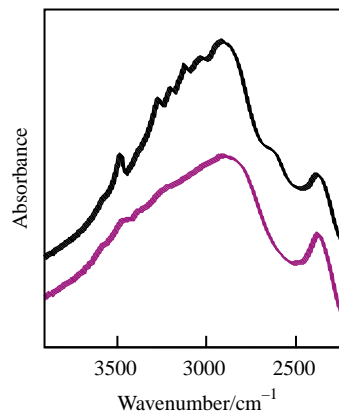


Fig. 6. Infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (lower curve) and $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (upper curve) recorded at LNT in the region of the OH stretching vibrations.

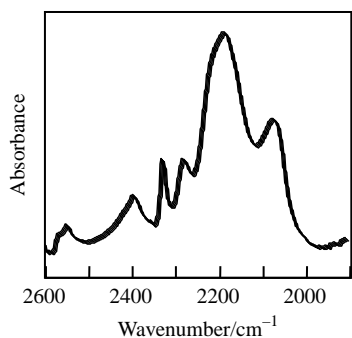


Fig. 7. Deconvoluted difference infrared spectrum recorded at LNT in the region of the stretching OD and ND vibrations, obtained by subtracting the spectrum of the protiated compound $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ from the spectrum of the analogue with low deuterium content ($\approx 2\%$ D).

of bands with a non-negligible intensity in the spectra of the protiated compound itself, a difference spectrum was obtained by subtracting the properly normalized spectrum of the protiated $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ from that of its slightly deuterated analogue. The result is shown in Fig. 7. In this spectrum, at least eight bands can be seen at frequencies of 2567, 2546, 2393, 2326, 2277, 2210, 2183 and 2070 cm^{-1} and they should be assigned to O–D stretches of isolated HOD molecules and/or to N–D vibrations of isotopically isolated NH_3D^+ ions. To vibrations of the latter type the bands at 2326 and 2277 cm^{-1} (and probably, at least partially, that at 2393 cm^{-1}) can be assigned with certainty since there are no such bands in the difference infrared spectrum of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ [1,2].

3.2.2. Bending vibrations of the water molecules and ammonium ions

The analysis of the vibrational spectra of the struvite in the region of the HOH bending vibrations is even more complicated than in the case of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ because, understandably, bands due to bending vibrations of the ammonium ions also appear in the discussed spectral region.

In the LNT Raman spectrum of struvite two bands at 1702 and 1685 cm^{-1} and another pair at 1477 and 1442 cm^{-1} are observed (Fig. 8), which are absent in the spectrum of the potassium analogue [1]. Hence, the former two are attributed to the ν_2 mode (doubly degenerate for T_d symmetry) and the latter two to the ν_4 mode (triply degenerate for T_d symmetry) of the ammonium ions. As expected, the bands at 1700 and 1686 cm^{-1} are barely seen in the LNT infrared spectrum of struvite (Fig. 8), whereas those originating from the components of the $\nu_4(\text{NH}_4)$ mode (this mode is infrared active even in the approximation of the molecular point group) show prominently in the infrared spectrum. In the LNT spectrum the frequencies of these bands are 1477 and 1441 cm^{-1} . The main contribution to the complex feature around 1600 cm^{-1} (similar to that found in the spectrum of MKP [1]) certainly comes from the $\delta(\text{HOH})$ vibrations or, perhaps, from modes having a considerable $\delta(\text{HOH})$ character.

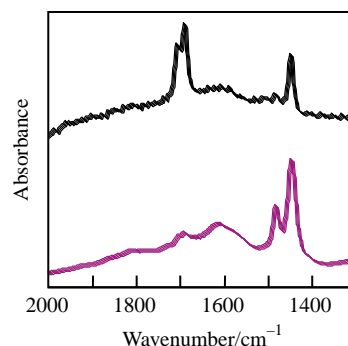


Fig. 8. Infrared (lower curve) and Raman (upper curve) spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the bending vibrations of the water molecules and ammonium ions.

In the region of the $\nu_4(\text{NH}_4)$ modes, more than two strong bands are found in the RT infrared spectrum, whereas in the LNT spectrum only two bands can be seen at 1477 and 1441 cm^{-1} (Fig. 9). In the room-temperature difference IR spectrum of the analogue with a small deuterium content ($\approx 2\%$ D), in the region of the ND bending vibrations of isotopically isolated NH_3D^+ ions, three bands (one at around 1290 cm^{-1} and two at $\approx 1250\text{ cm}^{-1}$) are observed, whereas at least five bands (at 1302 , 1295 , 1265 , 1250 and 1243 cm^{-1} ; the last one is only a shoulder) can be seen in the corresponding LNT spectrum (Fig. 10). All this implies the existence of some kind of disorder of the ammonium ions. It is worth mentioning that the frequencies at 1302 and 1295 cm^{-1} are rather high for this kind of vibrations [34] but, then, this is in line with the existence of one quite strong hydrogen bond formed by individual ammonium ions [3,4]. Similar frequencies for this kind of vibrations were found in the difference FTIR spectrum of slightly deuterated dittmarite ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) as well [23].

3.3. External vibrations of water molecules and ammonium ions

The incorporation of entities such as H_2O molecules or NH_4^+ ions in the crystal lattice leads to the appearance of

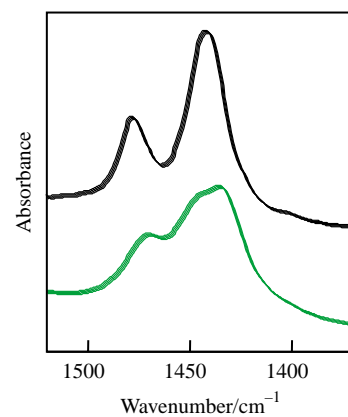


Fig. 9. Infrared spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and LNT (upper curve) in the region of the $\nu_4(\text{NH}_4)$ modes.

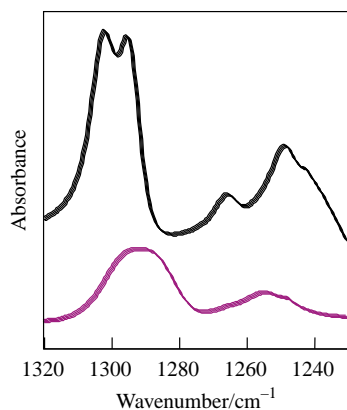


Fig. 10. Deconvoluted difference IR spectrum of the slightly deuterated ($\approx 2\%$ D) $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and LNT (upper curve) in the region of the ND bending vibrations of isotopically isolated NH_3D^+ ions.

external vibrational modes (hindered rotations and translations). In the approximation of the molecular point group the representation of the hindered H_2O rotations can be written as $A_2(\text{R}) \oplus B_1(\text{IR, R}) \oplus B_2(\text{IR, R})$ and that of the hindered rotations of the NH_4^+ ions as F_1 (both infrared and Raman inactive). Clearly, the symmetry lowering on going from the molecular point groups to the site groups should make all hindered rotations (librations) both infrared and Raman active but as long as these modes do not mix, the H_2O twisting libration and the NH_4^+ librations would not give rise to bands of appreciable intensity. On the other hand, the hindered translations of both the H_2O molecules and the ammonium ions should have relatively low frequencies and are likely to lose their ‘pure’ character and should be better described as lattice vibrations. These modes will not be further discussed.

In principle, it is relatively easy to locate the bands which are due to librations of the water molecules in the structure of a given crystalline hydrate, since the corresponding vibrations are temperature-sensitive, shifting towards higher frequencies on lowering the temperature and simultaneously gaining, at least apparently, in intensity. As long as the vibrations are relatively pure, the NH_4^+ librational bands (if present at all) should be of low intensity and the phosphate vibrations should not be temperature-sensitive.

As in the case with $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ [1] however, the expectations are borne out only partly. As Fig. 11 shows, most bands in the region below 1100 cm^{-1} have higher frequencies at LNT than at RT. This is true even for the very strong and broad band with an RT frequency of 1006 cm^{-1} which must originate from the components of the $\nu_3(\text{PO}_4)$ vibration at LNT is found at 1011 cm^{-1} . The shift may be small but is nevertheless real. A reasonable explanation may be that the temperature sensitivity is due to a water librational band overlapping the phosphate band and contributing to the shape, intensity and frequency of the broad feature. An analogous explanation has been given for the similar effect in the spectrum of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ [1].

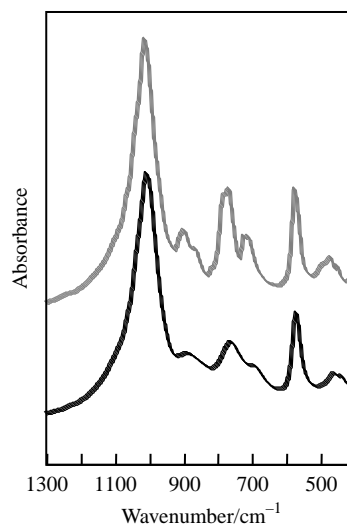


Fig. 11. Infrared spectra of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) at LNT (upper curve) in the region of the HOH and PO_4 external vibrations.

The bands appearing in the $950\text{--}600 \text{ cm}^{-1}$ region of the LNT infrared spectrum of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ are clearly very much temperature-sensitive. Such are the low intensity LNT bands at 897 and 862 cm^{-1} , the medium intensity ones at 783 , 766 cm^{-1} and the somewhat weaker bands at 722 and 710 cm^{-1} . Their apparent intensity (judged from the absorbance values at the maxima) appreciably increases on going from RT to LNT (Fig. 11), their apparent number also increased and the frequencies of the maxima were systematically higher. All these bands should be considered to arise from H_2O librations, since no phosphate vibration is expected to appear in the corresponding region and, as pointed out above, the ammonium librations should not give rise to bands of appreciable intensity. The analysis of the infrared spectra of the partially deuterated analogues (Fig. 12) confirms such an assignment. As is clearly seen, the intensity of the 897 , 862 , 783 , 766 , 722 and 710 cm^{-1} bands systematically decreases on increasing the deuterium content. Simultaneously, new bands appear which, in the spectrum of the analogue with highest obtained deuterium content, have frequencies 710 , 668 , 629 , 585 and 522 cm^{-1} , values which would be expected if these new bands are indeed due to D_2O librations. Without an a priori knowledge of the true form of the HOD librations, it is difficult to locate with certainty the bands originating from the modes of this type. Their frequencies must be between those of the H_2O and the D_2O librations but how close to the former or to the latter ones, would be determined by the nature of these vibrations for each of the four types of water molecules.

No bands with significant intensity attributable to water librations could be detected between 900 and 600 cm^{-1} in the Raman spectra of the partially deuterated analogues (Fig. 13).

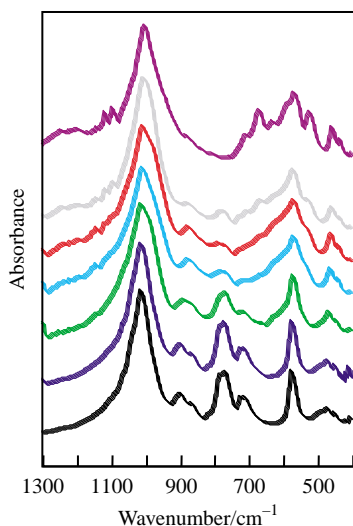


Fig. 12. Infrared spectra of partially deuterated analogues of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum).

3.4. Vibrations of the PO_4^{3-} ions

The situation with the vibrations of the phosphate ions in struvite is practically identical with that in the isomorphous $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ [1]. As in MKP, by far the strongest band in the Raman spectrum is that originating from the components of the symmetric stretching vibration ν_1 (its frequency is 943 cm^{-1}) whereas its infrared counterpart is perhaps the shoulder observed around 940 cm^{-1} in the infrared spectra of the partially deuterated analogues with a high deuterium content (Fig. 12). Such a spectral picture (very strong Raman band and exceptionally weak infrared one) is consistent with the very small values of the Baur's deformation indices, i.e. with a high effective symmetry, close to T_d . Again in line with such a geometry is the appearance, in the FTIR spectra, of a very strong and broad infrared band due to the components of the $\nu_3(\text{PO}_4)$ mode (triply degenerate for the 'free' PO_4^{3-} ions) and only weak bands (their frequencies are around 1070 , 1065 , 1020 , 990 and 915 cm^{-1}) assignable to this type of vibrations in the Raman spectrum (Fig. 13). As mentioned above, the infrared band is, at least apparently, somewhat temperature-sensitive, its frequency being 1006 cm^{-1} at RT and 1011 cm^{-1} at LNT (Fig. 11). The fact that in the spectrum of the analogue with highest deuterium content the corresponding band is found at 1001 cm^{-1} is an indication that one or more H_2O librational bands may be hidden under the strong phosphate stretching band. Another possibility is that coupling of the $\nu_3(\text{PO}_4)$ and $\delta(\text{DOD})$ modes takes place.

It should perhaps be mentioned that at low temperatures, shoulders are present on both sides of the intense $\nu_3(\text{PO}_4)$ band and, as mentioned, several low intensity bands are found in the Raman spectrum. Thus, although the effective symmetry is high, the lowered crystallographic symmetry of the phosphate

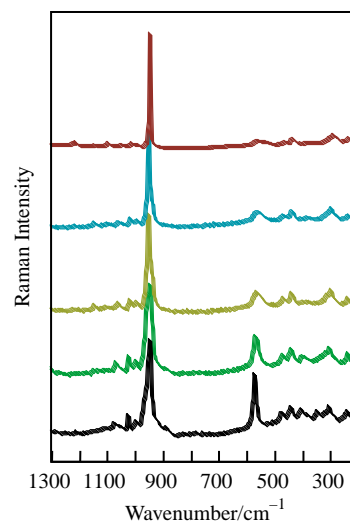


Fig. 13. Raman spectra of partially deuterated analogues of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum).

ions and/or the correlation field might have some effect and only because of the inherent breadth of the infrared $\nu_3(\text{PO}_4)$ bands this effect is not clearly visible in the FT IR spectra.

The picture in the region of the bending PO_4^{3-} vibrations in the spectrum of struvite is again quite similar to that in the spectrum of its potassium analogue. If only the spectrum of the protiated compound is taken into account, there would be no doubt that the asymmetric band at 571 cm^{-1} in the RT infrared spectrum and at 574 cm^{-1} at LNT (Fig. 11) should be attributed to the components of the $\nu_4(\text{PO}_4)$ mode. In the infrared spectra of the partially deuterated analogues (Fig. 12) the picture is complicated by the appearance, in the same region, of bands due to librations of the deuterated water molecules (HDO and/or D_2O) which may even be coupled with the components of the phosphate ν_4 mode. The situation in this region in the Raman spectrum (Fig. 13) is similar to that found in $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, which has already been thoroughly discussed [1].

In the region of the $\nu_2(\text{PO}_4)$ modes, two temperature sensitive bands (at 469 and 449 cm^{-1}) appear in the FT IR spectrum of (Fig. 11). It is evident from the spectra of the partially deuterated analogues (Fig. 12) that, on increasing the deuterium content, these bands change their shape and intensity and, at least seemingly, shift to lower frequencies (their frequencies in the spectrum of the compound with the highest deuterium content are 456 and 432 cm^{-1}). Therefore, these bands (at least one of them) can be attributed to the components of the $\nu_2(\text{PO}_4)$ mode or to Mg–O stretching vibrations³. In the Raman spectra, bands with similar intensity and shape as those found in the infrared spectra are observed in the region between 470

³ Bands with similar shape and intensity which appear at 448 and 428 cm^{-1} in the spectrum of dittmarite $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ have been attributed to the $\nu_2(\text{PO}_4)$ modes [23].

and 430 cm^{-1} (Fig. 13) as well. They are almost insensitive to deuteration, which implies that they can be attributed to $\nu_2(\text{PO}_4)$ and/or $\nu(\text{Mg}-\text{O})$ modes.

Acknowledgements

The investigation has been supported by funds from the Project MAK-002-97 by the German Federal Ministry of Education and Research, Federal Republic of Germany, by the Ministry of Education and Science, Republic of Macedonia and the Macedonian Academy of Sciences and Arts. The financial support from these sources is gratefully acknowledged. The helpful discussions with Professor V.M. Petruševski are sincerely appreciated.

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