



Very low H–O–H bending frequencies. IV. Fourier transform infrared spectra of synthetic dittmarite

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Abstract

The Fourier transform infrared spectra of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (the synthetic analogue of the mineral dittmarite) and of a series of its partially deuterated analogues have been studied as a part of our continuous work on compounds exhibiting very low water bending frequencies. Although, the presence of ammonium bands makes the assignments in this case more difficult than for the potassium analogues, the isomorphism between the compounds of the $\text{MNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ type ($\text{M} = \text{Mg}, \text{Co}, \text{Ni}, \text{Mn}$ and one of the polymorphs of $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$) and those which contain potassium instead of ammonium as well as the careful analysis of the spectra warrant the conclusion that in the presently studied compound the water bending mode appears at a frequency which is far more than 100 cm^{-1} lower than in the gaseous water. The spectra clearly show that the ammonium ions in the structure are involved in quite strong hydrogen bonds, a characteristic which is a precondition for a material to behave as a protonic conductor. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Magnesium ammonium phosphate monohydrate; Dittmarite; FT IR spectra; Very low water bending frequencies

1. Introduction

Dittmarite ($\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$) is a biomineral found (rather infrequently) in urinary calculi [1]. Its synthetic analogue is used in the production of fertilizers, fireproof materials, for extraction of divalent cations from sea-water [2] etc.

The complete structure of this compound has not been determined but Durif and Averbuch–Pouchot [3] have stated that the compounds of the MNH_4

$\text{PO}_4\cdot\text{H}_2\text{O}$ type ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}, \text{Cd}$ and Mg) are isomorphous with the analogous compounds containing potassium instead of ammonium ions. The determination of the structures of $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [4,5], $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (phase A) [6] and $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ [7] showed that this statement is essentially correct. All the above-mentioned compounds crystallize in the orthorhombic space group $Pmn2_1$ with two formula units in the unit cell.¹ Under the selection rules of the site group (C_s) all vibrations of the polyatomic groups (water molecules and ammonium and phosphate ions) become non-degenerate and

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¹ For $\text{CdNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ the structure of another form (phase B) has been determined [8] and refined [9].

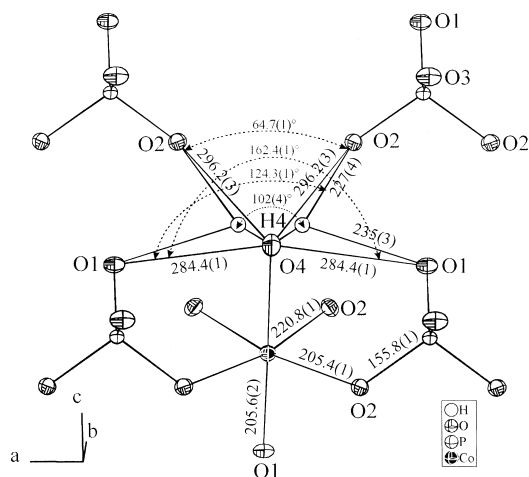


Fig. 1. Structure of $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (according to Ref. [5]).

infrared active and, under the factor-group (C_{2v}) selection rules split into two components. The factor-group modes for the water molecules transform as $2A_1 \oplus A_2 \oplus B_1 \oplus 2B_2$ and those of the ammonium and potassium ions are given by the representation $6A_1 \oplus 3A_2 \oplus 3B_1 \oplus 6B_2$, the A_2 modes being infrared inactive (see Ref. [15]). The twisting and rocking water librational modes are transformed, under the site-group selection rules into modes with A'' symmetry and give, each, one infrared active factor-group component of B_1 symmetry and one infrared inactive A_2 component. The wagging vibration gives two infrared active factor-group components (of A_1 and B_2 symmetry).

Particularly important for our present purposes is the recent re-determination of the structure of $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [5] which, in accordance with the plate-like habitus of the crystals, was described as being of the layered type with ammonium ions connecting the layers formed by Co octahedra and phosphate tetrahedra. It should be pointed out that in this structure all the essential features of the structure of $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ [7] are clearly mirrored. Of these, particular attention deserves the existence of water molecules (denoted² O4 in Ref. [5]) surrounded by six nearest neighbors—four phosphate oxygen atoms of

two crystallographically different types (labeled O1 and O2), one divalent and one monovalent ion (Fig. 1). The $\text{O}_w \cdots \text{O1}$ contacts are shorter than those of the $\text{O}_w \cdots \text{O2}$ type but (as in the structure of $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ [7]), they cannot correspond to normal hydrogen bonds since the two O1 atoms are located in the same general direction (of course, not in the same plane) as the two cations.³ On the other hand, the $\text{O2} \cdots \text{O4} \cdots \text{O2}$ angles are quite small (only 64.7° in $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ and 64.3° in $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ [7]) and, thus, the hydrogen bonds are again extremely unlikely to be formed with these two oxygen atoms only. Ultimately, it is practically certain that the hydrogen bonds are symmetrically bifurcated (the possibility is explicitly mentioned in both Refs. [5,7]) and such an arrangement seems to be important in explaining the origin of the very low H–O–H bending frequencies (see later). What differs in the two structures is, of course, the existence of a polyatomic univalent cation (NH_4^+) instead of the monoatomic potassium cation. According to Ref. [5], the ammonium ions in the structure of $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ are hydrogen bonded to four phosphate oxygen atoms of the O3 type, the $\text{N} \cdots \text{O}$ distances ranging from 278.5 to 296.5 pm. The shortest of these $\text{N} \cdots \text{O}$ contacts corresponds to rather strong hydrogen bonds which, considering the difference in the van der Waals radii of nitrogen and oxygen (≈ 154 pm for N and ≈ 140 pm for O) would be equivalent to $\text{O} \cdots \text{H} \cdots \text{O}$ bonds of 269 pm in length. Two further oxygen atoms are located at distances up to 320.4 pm from the nitrogen atoms of the ammonium ions.

The infrared spectra of compounds of the $\text{MNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ type ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}, \text{Cd}$ and Mg)⁴ have been studied by Fraissard and Étienne [10], Šoptrajanov [11] and Djordjević [12]. Despite the fact that these contributions are quite old, the existence of very low HOH bending frequencies has been indicated [11,12].

The problem of the very low H–O–H bending frequencies was revived recently. A thorough spectral study of $\text{NiKPO}_4\cdot\text{H}_2\text{O}$ (as mentioned, isomorphous with dittmarite) and its deuterated analogues has been published [13] with an overview of the whole problem

² The labeling scheme is different from that in Ref. [7]. The O4 oxygens in Ref. [5] correspond to O_w in Ref. [7], while O3 is used as a label in Ref. [7] for oxygen atoms which are equivalent to those denoted O2 in Ref. [5].

³ This despite the fact that these contacts are shorter than those with the O4 oxygen atoms.

⁴ The Raman spectrum of dittmarite has also been published [1].

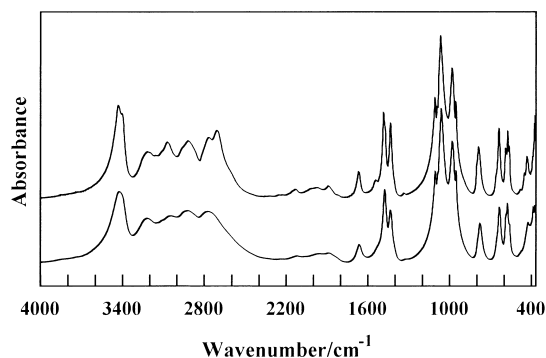


Fig. 2. Fourier transform infrared spectra of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ recorded at RT (lower curve) and at the LNT (upper curve).

and an extensive list of references (both old and more recent). As discussed in more detail in Ref. [13] and in the subsequent papers of the series devoted to the problem of very low HOH infrared bending frequencies [14,15], $\delta(\text{HOH})$ frequencies considerably lower than 1600 cm^{-1} are observed in the spectra of the compounds of the $\text{MKPO}_4\cdot\text{H}_2\text{O}$ family. Although various explanations (both intuitive and quantum mechanical) have been offered, it seems that the arrangement of the potential proton acceptors around the water molecules such as that found in the case of the $\text{MKPO}_4\cdot\text{H}_2\text{O}$ compounds and their ammonium analogues is one of the prerequisites for the appearance of very low water bending mode frequencies. That this is not the sufficient condition is demonstrated by the appearance of the spectra of a number of compounds of the $\text{MSO}_3\cdot\text{H}_2\text{O}$ [16] where the environment of the water molecules [16–18] is very similar to that found in the case of the $\text{MKPO}_4\cdot\text{H}_2\text{O}$ and $\text{MNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ compounds. In fact, in the H–O–H bending region of the spectra of the $\text{MSO}_3\cdot\text{H}_2\text{O}$ compounds ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$) [16] a clearly developed low frequency band exists only in the case of the nickel compound (its frequency is 1441 cm^{-1} ; additional bands are seen at higher frequencies). It should be noted that the hydrogen bonding in the nickel compound seems to be stronger than that in the case of the isotopic $\text{CoSO}_3\cdot\text{H}_2\text{O}$ and $\text{ZnSO}_3\cdot\text{H}_2\text{O}$.

In any case, the rather exceptional finding that the water bending in crystals may occur way below the gas-phase value makes the $\text{MKPO}_4\cdot\text{H}_2\text{O}$ compounds and their analogues very interesting for detailed experimental and theoretical studies. Thus, continuing

our work on the very low HOH bending frequencies, it was only natural to start reexamining the spectra of the compounds of the $\text{MNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ series.

As a first step in this direction we present here the results obtained in the course of our study of the Fourier transform infrared spectra of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (the synthetic analogue of the mineral dittmarite) and a series of its deuterated analogues recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT).

2. Experimental

The investigated compound was synthesized according to the method described by Kiehl and Hardt [19]. Partially deuterated analogues were obtained using the same general procedure, but using H_2O – D_2O mixtures with appropriate composition as solvents.

The Fourier transform infrared spectra were recorded on Perkin–Elmer System 2000 infrared interferometer. The spectra were recorded, from both mulls and pressed KBr disks, at room and liquid-nitrogen temperature (RT and LNT, respectively). The variable-temperature cell P/N 21525 (Graseby Specac) 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 (32 scans appeared to be enough at RT). The working resolution of the instrument was 4 cm^{-1} . For acquisition of spectra and manipulations on them the GRAMS ANALYST 2000 [20] and GRAMS 32 [21] packages were used.

3. Results and discussion

The Fourier transform infrared spectra of synthetic dittmarite at RT and the LNT are presented in Fig. 2. The room-temperature spectrum closely resembles those published in Refs. [1,10]. In order to make the discussion more systematic, the deuteration-sensitive bands will be treated separately from those that are due to phosphate modes.

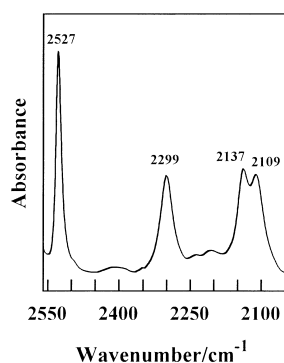


Fig. 3. Difference FTIR spectrum of slightly deuterated $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ in the O–D/N–D stretching region (the spectrum is obtained by subtracting the LNT spectrum of the protiated species from the corresponding spectrum of the sample deuterated to $w_D \approx 3\%$).

3.1. Deuteration-sensitive bands

Sensitive to deuterium-for-protium substitution would, of course, be bands which originate from or are related to vibrations of the water molecules and ammonium ions and their fully or partly deuterated analogues.

In the O–H and N–H stretching region of the infrared spectra of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ recorded at RT and LNT (Fig. 2) a complex band with several maxima is observed from 3600 to 2400 cm^{-1} . At RT the band at the highest frequency is single but asymmetric, whereas at LNT it is clearly split into two components (with frequencies 3428 and 3401 cm^{-1}). Four broad bands are seen below 3300 cm^{-1} at RT (some of them exhibit shoulders), whereas at LNT several new shoulders or weak bands appear. Since the factor-group splitting is expected to result with two infrared active components from the H–O–H symmetric stretch ν_1 , one such component from the antisymmetric water stretching mode ν_3 and seven factor-group components from the two NH_4^+ stretches (one non-degenerate and one triply degenerate under the T_d symmetry),⁵ the number of observed bands and shoulders does not exceed the expectations even if the possibility of librational

⁵ One factor-group component of the water ν_3 mode and one of the ammonium ν_3 mode are infrared inactive under the selection rules of the factor group C_{2v} .

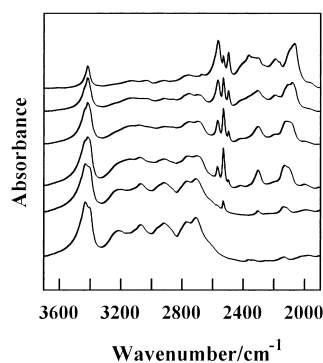


Fig. 4. FTIR spectra of protiated (bottom curve) and partially deuterated analogues of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ recorded at the LNT in the region of the stretching vibrations of water molecules and ammonium ions and of their partially deuterated analogues (the deuterium content increases from bottom to top).

interactions with second-order transitions is neglected.

Both Fraissard and Étienne [10] and Šoptrajanov [11] assigned the bands between 3250 and 2400 cm^{-1} in the spectrum of the protiated species to the NH_4^+ stretching vibrations and those at higher frequencies to the water H–O–H stretches. As discussed later, our present result fully support such an assignment.

In the difference spectrum⁶ of the slightly deuterated analogue (Fig. 3), at least four bands (with frequencies of 2527, 2299, 2137 and 2109 cm^{-1} at LNT) appear in the region where the bands due to uncoupled O–D and N–D stretching vibrations of HOD molecules and NH_3D^+ ions are expected. There is little doubt that the 2527 cm^{-1} band is due to the uncoupled O–D stretch of the isotopically isolated HOD molecules, whereas the remaining ones would then arise from N–D stretches of isotopically isolated NH_3D^+ ions. That the above-mentioned assignment of the 2527 cm^{-1} band is correct and that, consequently, the bands at 3428 and 3401 cm^{-1} in the LNT spectrum of the protiated compound are due to the ν_3 and ν_1 vibrations of *symmetrically bonded* water molecules with C_s symmetry is supported by the analysis of the spectra of the whole series of partially deuterated analogues of synthetic dittmarite (Fig. 4). As seen, namely, the increase of the deuterium content

⁶ In order to eliminate the bands due to vibrations of the protiated species, the properly normalized spectrum of the protiated compound was subtracted from that of the analogue deuterated to some 3%.

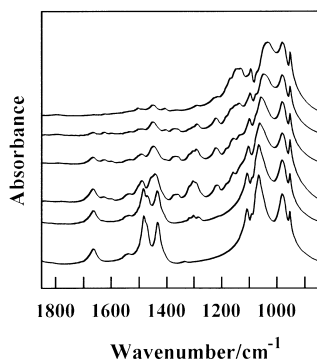


Fig. 5. FTIR spectra of protiated (bottom curve) and partially deuterated analogues of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ recorded, at LNT, in the $1850\text{--}850\text{ cm}^{-1}$ region (the deuterium content increases from bottom to top).

in the samples leads to appearance of a band at 2527 cm^{-1} (that mentioned earlier) which at first gains in intensity and then weakens to be replaced by two bands (at 2561 and 2494 cm^{-1}). These latter bands are, obviously, due to the two D_2O stretches, whereas the *single* 2527 cm^{-1} band must originate from the $\nu(\text{O}\text{--}\text{D})$ mode of HOD molecules with equal $\text{A}\cdots\text{H}\text{--}\text{O}_w\text{--}\text{H}\cdots\text{A}$ hydrogen bonds. The situation is very similar to that encountered in the spectra of partly deuterated analogues of $\text{NiKPO}_4\cdot\text{H}_2\text{O}$ [13].

Since the 2527 cm^{-1} band in the difference

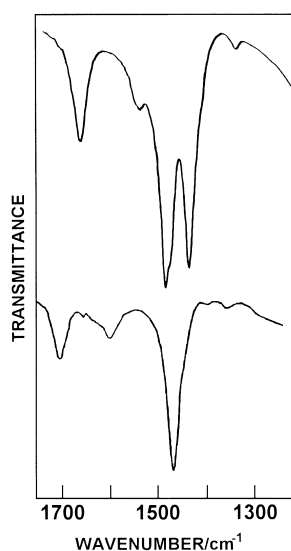


Fig. 6. Comparison of the LNT spectra of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (upper curve) and $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ (lower curve) in the $1750\text{--}1200\text{ cm}^{-1}$ region.

spectrum is, beyond doubt, due to the $\text{O}\text{--}\text{D}$ stretching mode of the HOD molecules, the remaining ones in the $\text{O}\text{--}\text{D}/\text{N}\text{--}\text{D}$ stretching region must arise from $\text{N}\text{--}\text{D}$ stretches of isotopically isolated NH_3D^+ ions. This would then imply that the ammonium anions form hydrogen bonds, which are, effectively, of three different strengths, the highest of the bands (at 2299 cm^{-1}) corresponding to the weakest of the H-bonds—that analogous to the bond which, in the structure of $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [5], is characterized by an $\text{N}\cdots\text{O}$ distance of 296.5 pm . It should at this point be mentioned that the frequencies of the bands at 2137 and 2109 cm^{-1} are, according to literature data [22], among the lowest ones assigned to $\text{N}\text{--}\text{D}$ stretching vibrations of isotopically isolated NH_3D^+ ions. This suggests that the ammonium ions in the structure of dittmarite are involved in quite strong hydrogen bonds (in agreement with the experimentally determined $\text{N}\cdots\text{O}$ distances for the isomorphous $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ [5]) and, consequently, dittmarite fulfills the prerequisite for any material to behave as a protonic conductor.

Deuteration-sensitive must, of course, be also the bands which are due to $\delta(\text{HOH})$ mode ν_2 and to the two NH_4^+ bending modes— ν_2 and ν_4 . All these bands are expected in the $1700\text{--}1400\text{ cm}^{-1}$ region: the symmetric ammonium bending mode ν_2 above 1600 cm^{-1} , the antisymmetric NH_4^+ bending ν_4 around 1400 cm^{-1} and the water bending vibration ν_2 also in the same general region. Of the two ammonium modes, ν_4 is expected to give rise to a strong band, probably split. As seen (Fig. 5) several bands, all of them deuteration-sensitive, are indeed present in this region.

Were it not for the fact that the presently investigated compound is believed to be isomorphous with $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ and thus the spectral features (other than those arising from ammonium ion vibrations) should be similar, it would be difficult to locate the $\delta(\text{HOH})$ band there. However, the comparison of the spectrum of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ with that of its potassium counterpart (Fig. 6) clearly shows that Fraissard and Étienne [10] missed a number of important spectral characteristics and made assignment which, from today's point of view are not acceptable.

Thus, these authors attributed only the band around 1650 cm^{-1} to the $\text{H}\text{--}\text{O}\text{--}\text{H}$ bending mode and

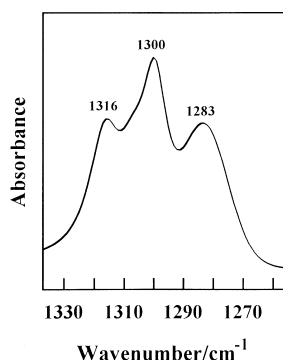


Fig. 7. Difference FTIR spectrum of slightly deuterated $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ in the $1335\text{--}1260\text{ cm}^{-1}$ region (the spectrum is obtained by subtracting the LNT spectrum of the protiated species from the corresponding spectrum of the sample deuterated to $w_D \approx 3\%$).

explained the strong bands in the $1500\text{--}1400\text{ cm}^{-1}$ region as due to NH_4^+ vibrations. In doing so, they failed to notice the rather peculiar changes in the $\text{H}_2\text{O}/\text{NH}_4^+$ bending region which are clearly visible in their table I which contains a schematic representation of the spectra of the whole series of $\text{MNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ compounds (a case of point is the difference between the features in the spectra of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ and $\text{MnNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$). Worse yet, in their table I where, for comparison purposes, the spectrum of $\text{MnKPO}_4\cdot\text{H}_2\text{O}$ is schematically given, Fraissard and Étienne [10] chose to report only the band appearing above 1650 cm^{-1} and to ignore the approximately equally strong band below 1450 cm^{-1} present in the spectrum of this compound [15]. Such an omission (whether done on purpose or inadvertently) is easy to explain—at that time there was no ready explanation for the existence of a band appearing considerably below 1600 cm^{-1} in a spectrum where the H_2O molecules are the only possible polyatomic species which could have vibrations with a frequency in the corresponding region. Consequently, the existence of bands with such low frequencies in the water bending region could be interpreted only as an experimental artifact.⁷

The history aside, as seen in Figs. 5 and 6, at least four bands are found in the infrared spectrum of protiated $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (the LNT frequencies are 1663 , 1536 , 1482 and 1432 cm^{-1}) and a shoulder

around 1472 cm^{-1} is also present. H bending frequencies. In the difference spectra of the slightly deuterated analogue⁸ (Fig. 7) three prominent bands (at 1316 , 1300 and 1283 cm^{-1}) appear in the region where the N–D bending vibrations of isotopically isolated NH_3D^+ ions are expected but where, by analogy with the compounds of the $\text{MKPO}_4\cdot\text{H}_2\text{O}$ type the $\delta(\text{HOD})$ would also appear. In fact, the frequency of the highest of these bands is almost equal to that found in the spectrum of slightly deuterated $\text{NiKPO}_4\cdot\text{H}_2\text{O}$ [13]. This should be no big surprise since the spectra of protiated $\text{NiKPO}_4\cdot\text{H}_2\text{O}$ and $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ are quite similar and this is also true for the spectra of $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ and $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ so that the $\delta(\text{HOD})$ bands in the spectra of all these compounds should appear at similar frequencies. Unfortunately, it is difficult to follow the changes caused by the increase of deuterium content in the samples since the features due to various partly deuterated ammonium species complicate the picture. It should, perhaps, be added that Fermi resonance between the $\nu_4(\text{NH}_4^+)$ and $\nu_2(\text{H}_2\text{O})$ modes can not be excluded since the latter vibration and two of the components of $\nu_4(\text{NH}_4^+)$ are, under the site-group approximation, of the same symmetry. Such an interaction would then be responsible for the frequency difference between the $\delta(\text{HOH})$ band in the spectrum of $\text{MgKPO}_4\cdot\text{H}_2\text{O}$ and the bands present in the spectrum of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ (see Fig. 6).

If, as seems most likely, the 1316 cm^{-1} band in the difference spectrum, of the slightly deuterated compound is attributed to the $\delta(\text{HOD})$ mode, the remaining two bands would originate from the N–D bendings of the NH_3D^+ cations. Their frequency is very high for this kind of vibrations [22] which, in accordance with the picture in the N–D stretching region, again suggests the presence of quite strong hydrogen bonds formed by ammonium ions.

Another (albeit indirect) proof that the H–O–H bending band in synthetic dittmarite has a low frequency is provided by the above-mentioned peculiar behavior of the bands in this region upon the change of the M^{II} cation in the series of $\text{MNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ compounds [10]. The shift of the bands on going from the nickel to the manganese

⁷ However, a report on the spectra of compounds of the $\text{M}^{\text{II}}\text{SO}_4\cdot\text{H}_2\text{O}$ type in which $\delta(\text{HOH})$ bands with quite low frequencies has been published some time earlier [23].

⁸ It contains $\approx 3\%$ D.

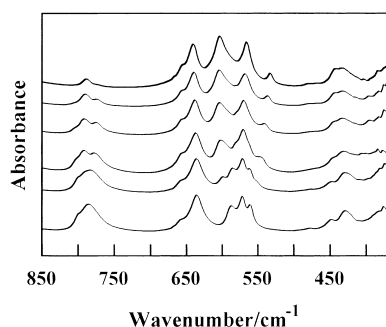


Fig. 8. FTIR spectra of protiated (bottom curve) and partially deuterated analogues of $\text{MgNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ recorded at LNT in the $850\text{--}370\text{ cm}^{-1}$ region (the deuterium content increases from bottom to top).

compound, namely, closely resembles the situation in the series of $\text{MKPO}_4\cdot\text{H}_2\text{O}$ compounds [12,14].

The group-theoretical arguments (see earlier) show that of the three H_2O librational modes, the twisting and rocking vibrations could give rise to only one band each, whereas the appearance of two bands in the infrared spectrum is expected for the wagging mode. However, the location of only one of these is a straightforward task. This is the band whose frequency at RT is 775 cm^{-1} and is shifted (Fig. 2) to 785 cm^{-1} in the LNT spectrum—a behavior characteristic for water librations. The asymmetric shape of this band (it has a shoulder at 798 cm^{-1} at LNT) may be an indication that it originates from the two closely spaced factor-group components of the wagging mode.⁹ The inspection of the spectra of a series of partially deuterated analogues (Fig. 8) shows that the increase of the deuterium content in the samples leads to the disappearance of this bands with simultaneous appearance of a new one around 603 cm^{-1} .

Another of the librational bands is apparently hidden among the phosphate bands appearing around 600 cm^{-1} . It is, namely, obvious that the increased deuterium content in the partially deuterated samples (Fig. 8) leads to the appearance of a new band around 440 cm^{-1} and changes are present also in the intermediate region.

The third of the water librations (the twisting mode, inactive under the molecular group selection

rules) quite probably gives rise to a very weak band and is thus impossible to find.

3.2. Phosphate vibrations

The low local symmetry (C_s) of the phosphate ions in dittmarite removes the degeneracies of the phosphate modes¹⁰ ν_2 , ν_3 and ν_4 and, in addition, all their components become infrared active as does the symmetric stretching mode ν_1 . In the present case, because of the isomorphism between the presently studied compound and $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$, it may be safely assumed that the phosphate ions in synthetic dittmarite are considerably distorted¹¹ and, consequently, the splitting of the $\nu_3(\text{PO}_4)$ mode should also be substantial.

The expectations are fully born out and the complex of strong bands below 1150 cm^{-1} (the LNT frequencies of the main maxima¹² are 1105 , 1063 and 978 cm^{-1} ; see Figs. 2 and 5) may be safely attributed to the components of the $\nu_3(\text{PO}_4)$ modes. On the other hand, the much weaker and sharper band at 951 cm^{-1} clearly originates from the in-phase P–O stretch ν_1 . The band originating from the phosphate ν_1 mode is easier to locate in the published Raman spectrum of this compound recorded at RT [1] in which by far the strongest band (that at 951 cm^{-1}) is undoubtedly due to the $\nu_1(\text{PO}_4)$ vibration¹³ whereas the incomparably weaker complex feature at higher frequencies (the value of 1057 cm^{-1} is given for the strongest of these weak peaks) is, by all means, the analogue of the infrared bands at approximately the same frequency which were attributed (see earlier) to the components of the $\nu_3(\text{PO}_4)$ mode. The almost exact coincidence of the infrared and the Raman frequency is worth mentioning.

¹⁰ Strictly speaking, it is not correct to use the labels applicable for ideally tetrahedral PO_4^{3-} ions (especially in cases when the geometric distortion of the phosphate ions is appreciable) but their utilization makes the discussion easier and more understandable.

¹¹ The distortion indices [24] for $\text{CoNH}_4\text{PO}_4\cdot\text{H}_2\text{O}$ are $D(\text{PO}) = 0.0416$ and $D(\text{OPO}) = 0.0180$, the former being ≈ 7 times larger and the latter approximately twice as high as the corresponding mean value for orthophosphates given in [24].

¹² The weak band at 1089 cm^{-1} may also originate from some of the factor-group components of the phosphate antisymmetric stretching or, alternatively, may be due to a second-order transition.

¹³ The frequency given in Ref. [12] is 948 cm^{-1} .

⁹ No band is seen at intermediate frequencies as would be expected if the band is due to the rocking libration.

In principle, the phosphate bands should not change on deuteration either their shape or the frequency. As seen in Fig. 5, this is only partly so: whereas the low-frequency part of the feature is unaffected by deuteration, its higher-frequency part gradually changes its appearance. This can easily be explained if the very low frequency of the water bending vibration is taken into account. Since, namely, the unperturbed $\delta(\text{HOH})$ frequency is for more than 100 cm^{-1} lower than the gas-phase value, the $\delta(\text{DOD})$ vibration would have a frequency similar to that of the highest components of the $\nu_3(\text{PO}_4)$ mode and the ND_4^+ bendings would also fall in the same region.

In the $670\text{--}510 \text{ cm}^{-1}$ region, the band at 635 cm^{-1} with a shoulder at 656 cm^{-1} can positively be attributed to components of the $\nu_4(\text{PO}_4)$ bending vibration since in the spectra of the deuterated compounds (Fig. 8) these bands practically do not change either their shape or intensity. On the other hand, changes on deuteration are clearly seen in the appearance of the complex feature below 600 cm^{-1} (some of these have been discussed above) despite the fact that some of the bands in this region must originate from components of the $\nu_4(\text{PO}_4)$ mode, either pure or coupled. The existence of water librational bands has already been discussed, whereas the presence of $\nu(\text{Mg}\text{--}\text{O})$ bands in this region can be ruled out because the $\text{Mg}\text{--}\text{O}$ bond is not strong enough to give rise to hindered translations with such a high frequency.

The bands at 448 and 428 cm^{-1} (443 and 433 cm^{-1} in the spectrum of the almost completely deuterated compound where they may appear to be intensified by the appearance of D_2O librations) are, somewhat tentatively, attributed to the components of the ν_2 phosphate mode.

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