

Infrared and Raman Spectra of Magnesium Ammonium Phosphate Hexahydrate (*Struvite*) and its Isomorphous Analogues. VIII. Spectra of Protiated and Partially Deuterated Magnesium Rubidium Phosphate Hexahydrate and Magnesium Thallium Phosphate Hexahydrate

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Dedicated to Professor Dušan Hadži on the occasion of his 90th birthday

Abstract

The infrared and Raman spectra of magnesium rubidium phosphate hexahydrate $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and magnesium thallium phosphate hexahydrate, $\text{MgTlPO}_4 \cdot 6\text{H}_2\text{O}$ were recorded at room temperature (RT) and the boiling temperature of liquid nitrogen (LNT). To facilitate their analysis, also recorded were the spectra of partially deuterated analogues with varying content of deuterium. The effects of deuteration and those of lowering the temperature were the basis of the conclusions drawn regarding the origin of the observed bands which were assigned to vibrations which are predominantly localized in the water molecules (four crystallographically different types of such molecules exist in the structures) and those with PO_4^{3-} character. It was concluded that in some cases coupling of phosphate and water vibrations is likely to take place. The appearance of the infrared spectra in the O–H stretching regions of the infrared spectra is explained as being the result of an extensive overlap of bands due to components of the fundamental stretching modes of the H_2O units with a possible participation of bands due to second-order transitions. A broad band reminiscent of the B band of the well-known ABC trio characteristic of spectra of substances containing strong hydrogen bonds in their structure was found around 2400 cm^{-1} in the infrared spectra of the two studied compounds.

Keywords: Magnesium rubidium phosphate hexahydrate; magnesium thallium phosphate hexahydrate; infrared spectra; Raman spectra; hydrogen-bond effects

1. Introduction

This study is another contribution to our systematic investigation of the vibrational spectra of struvite-type compounds with the general formula $\text{M}^{\text{I}}\text{M}^{\text{II}}\text{AO}_4 \cdot 6\text{H}_2\text{O}$ ($\text{M}^{\text{I}} = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}, \text{Tl}$; $\text{M}^{\text{II}} = \text{Mg}, \text{Ni}$; $\text{A} = \text{P}, \text{As}$) has been a subject of our interest for quite a long time, especially in the last decade.^{1–9} Our attention to this series of com-

pounds was arisen by noticing¹ the unusually broad, structured and intense feature in the X–H ($\text{X} = \text{O}$ or N) stretching region of the infrared spectrum of synthetic struvite, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. At that time, however, we did not have the possibility to either study the effect on the infrared spectra of lowering the temperature or the examine Raman spectra. We, of course, knew that the existence of six water molecules per formula unit could give rise to a multiplicity of bands, that the quite strong hydrogen bonds formed by

the water molecules could be responsible for the breadth of the bands and that the existence of four exchangeable protons on each ammonium ion in the formula unit could be the additional cause for the observed spectral picture. In order to eliminate at least one of the factors, the spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ were subjected to investigation.² It turned out that the appearance of the spectra of this compound in the X–H stretching region were not drastically different from that in the spectra of struvite itself. To further test the conclusion that the feature in question is related predominantly to vibrations (fundamental and/or second-order) of the water molecules, several additional compounds in which M^{I} ions are monoatomic and, hence, do not contain protons were studied. The two title compounds of the present communication are a part of the set of such species.

For the present study, the compounds $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTIPO}_4 \cdot 6\text{H}_2\text{O}$ and their deuterated analogues were prepared and their infrared and Raman spectra at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) were recorded.

The crystal structures of the two title compounds have been determined by X-ray diffraction.¹⁰ They both crystallize in the orthorhombic system (space group $Pmn2_1$), with $Z = 2$. In the unit cell, the M^{I} , M^{II} , PO_4^{3-} ions and two of the four crystallographically different water molecules lie on positions with C_s symmetry, while water molecules of the other two types occupy general positions. The water molecules in the structure are coordinated to the divalent cations forming, around each such cation, a slightly distorted octahedron. With the exception of the water molecule denoted as W_1 in the structure,¹⁰ the H_2O molecules are connected by hydrogen bonds to oxygen atoms from the PO_4^{3-} ions. The W_1 molecule forms one hydrogen bond with the W_2 water molecule as a proton acceptor. This is the only weak hydrogen bond in the structure of this compound, since the rest of such bonds can be characterized as being strong or very strong.

The infrared spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTIPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at room temperature have been studied by Banks et al.¹¹ To the best of our knowledge, the infrared and Raman spectra of these compounds and their deuterated analogues recorded at LNT have not been reported yet.

2. Experimental

The title compounds were synthesized according to the methods described by Banks et al.¹¹ The partially deuterated analogues were prepared analogously but using H_2O – D_2O mixtures of appropriate compositions as solvents. The highest content of deuterium in the samples was achieved using pure D_2O .

All infrared spectra were obtained using the Perkin-Elmer System 2000 infrared interferometer in the 4000–400 cm^{-1} region with a resolution of 2 cm^{-1} . They were re-

corded from both pressed KBr disks and Nujol mulls at RT and LNT, 32 spectra being accumulated and averaged. A low-temperature cell Graseby Specac P/N 21525 with KBr windows was used for obtaining LNT spectra. Far infrared spectra were recorded on a Bruker 113v interferometer in Nujol between polyethylene pellets. The FT Raman spectra were recorded (with a resolution of 2 cm^{-1}) on a Bruker RFS 100Ds FT Raman equipped with an Nd:YAG laser emitting at 1064 nm. To achieve good signal-to-noise ratio, 500 scans were accumulated and averaged. For spectra acquisition and management, the GRAMS ANALYST 2000¹² and GRAMS 32¹³ packages were used.

3. Results and Discussion

The Fourier transform infrared spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTIPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) are presented in Figs. 1 and 2, whereas the corresponding Fourier transform Raman spectra recorded at LNT are given in Fig. 3. As can be seen, the spectra of the two studied compounds are very similar, as expected for isostructural analogues.

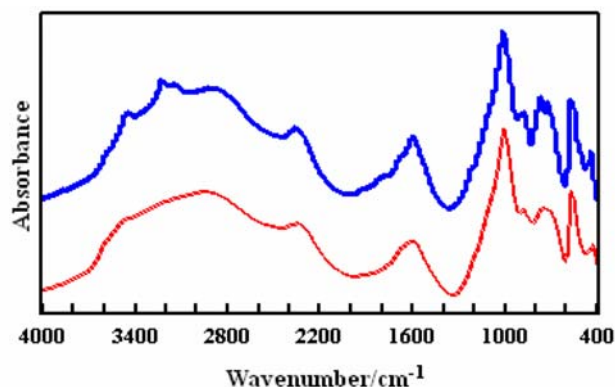


Fig. 1. Fourier transform infrared spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and at LNT (upper curve).

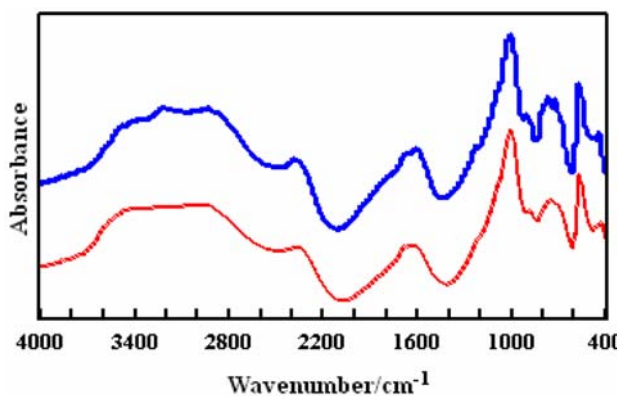


Fig. 2. Fourier transform infrared spectra of $\text{MgTIPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and at LNT (upper curve).

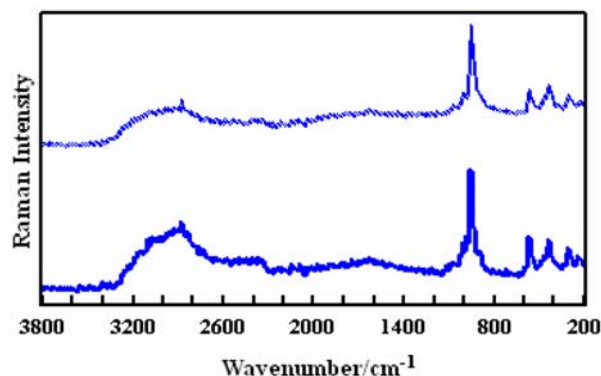


Fig. 3. Fourier transform Raman spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ (lower curve) and $\text{MgTiPO}_4 \cdot 6\text{H}_2\text{O}$ (upper curve) recorded at LNT.

3. 1. Internal Vibrations of the Water Molecules

The group-theory considerations, similar to those for the other studied orthorhombic struvite compounds,^{2–8} suggest that, due to the existence of a static field, three infrared and three Raman active internal vibrations of each type of water molecule are expected. Taking into account the presence of four types of water molecules and, in addition to that, the effect of the correlation field, the number of expected bands is significantly increased. A stronger correlation field is expected to affect the vibrations of the two types of water molecules occupying general positions, which can be regarded as mechanically coupled oscillators. Clearly, the appearance of separate bands should not be expected and extensive overlap must be present especially in the O–H stretching region where the natural width of the bands is likely to be considerable.

The expectations are fully born out in the O–H stretching regions in the spectra recorded at RT and LNT where a broad and asymmetric band with several shoul-

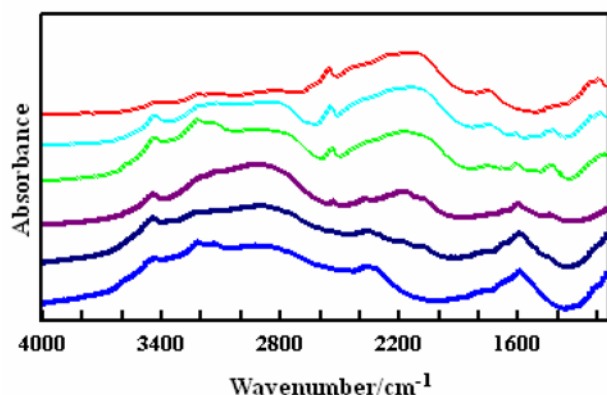


Fig. 4. Fourier transform infrared spectra of partially deuterated analogues of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and DOD stretching and bending vibrations (the content of deuterium increases from bottom to top spectrum; the deuterium content being 0, 5, 25, 50, 75 and 95 % respectively).

ders is observed between 3800 and 2200 cm^{-1} in the IR and from 3400 to 2200 cm^{-1} in the Raman spectra (Figs. 1–3). The feature is sensitive to deuteration (Fig. 4 and Fig. 5). In addition, a broad band with considerable intensity, reminiscent of the B band of the well-known ABC trio characteristic of spectra of substances containing strong hydrogen bonds in their structure and extensively discussed by Hadži¹⁴ was found around 2400 cm^{-1} in the infrared spectra of the two studied compounds.

A broad feature with substructure is observed between 2100 to 1350 cm^{-1} , in the region where bands from bending vibrations of water molecules are expected to appear. The general shape of the feature observed at RT is preserved in the LNT IR spectra (Figs. 1 and 2). Thus, in the LNT spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTiPO}_4 \cdot 6\text{H}_2\text{O}$,

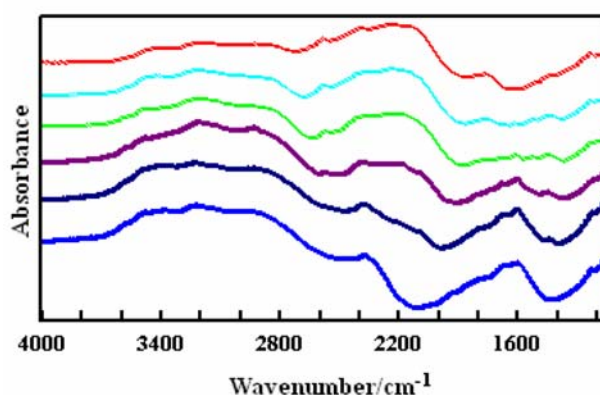


Fig. 5. Fourier transform infrared spectra of partially deuterated analogues of $\text{MgTiPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and DOD stretching and bending vibrations (the content of deuterium increases from bottom to top spectrum; the deuterium content being 0, 5, 25, 50, 75 and 95 % respectively).

in addition to the peaks at around 1680 and 1600 cm^{-1} , submaxima with lower intensity can be noticed at around 1950, 1800 and 1500 cm^{-1} . The spectral pattern in this region is very similar to that found in the spectra of the other studied orthorhombic struvite-type compounds.^{2, 4, 5, 8, 9, 11} The bands in this region are temperature sensitive i.e. the frequencies of some bands decrease and of other increase upon lowering the temperature. On deuteration these features are to lower frequencies, the spectral picture being complicated by the appearance in the above region of bands with O–D stretching character (Figs. 4 and 5).

The broadness of the feature and the number and the significant differences in the frequencies of submaxima can not be explained simply by the existence of four crystallographically different water molecules in the structure. It is not an easy task to specify the mechanism responsible for the appearance of multiple vibration bands but it is hard to believe that they should be attributed solely to fundamental bending HOH vibrations^{15–19} since the possibility that the substructure can be related to second-order transitions, interactions of the Fermi-resonance type (cou-

pling of overtones of lower frequency modes with fundamental vibrations) or other coupling effects should not be *a priori* discarded.

3. 2. External Vibrations of the Water Molecules

The comparison of the RT and LNT infrared spectra (Figs. 6 and 7) reveals the temperature dependence of all bands below 1000 cm^{-1} and their shift to lower frequencies in the LNT spectrum.

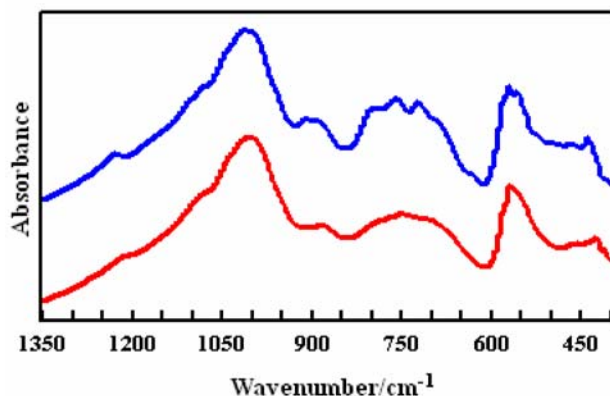


Fig. 6. Fourier transform infrared spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) at LNT (upper curve) in the region of the HOH and PO_4 external vibrations.

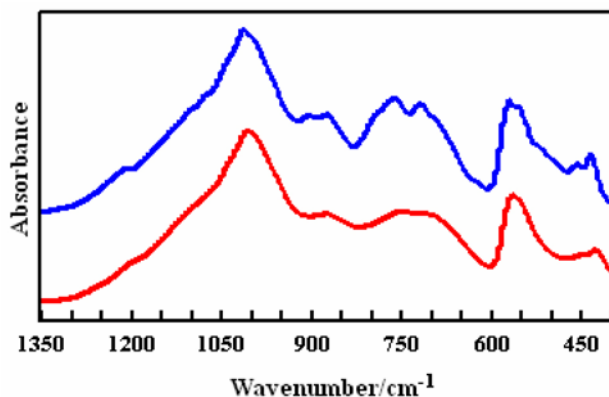


Fig. 7. Fourier transform infrared spectra of $\text{MgTlPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) at LNT (upper curve) in the region of the HOH and PO_4 external vibrations.

In the spectral analysis elaborated below, the band(s) around 575 cm^{-1} , in the LNT spectra of struvite-type compounds are related to the $\nu_4(\text{PO}_4)$ modes, and the lower intensity bands around 460 and 435 cm^{-1} to the $\nu_2(\text{PO}_4)$ and/or possibly to $\nu(\text{M}-\text{O})$ vibrations. This leaves the remaining bands appearing in the $920\text{--}610\text{ cm}^{-1}$ region to be attributed to external vibrations of the water molecules.

A thorough analysis of the RT and LNT spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and its partially deuterated analogues

(Figs. 6 and 8) suggests that the bands at 908 , 886 , 800 , 760 , 723 and 690 cm^{-1} , and possibly the band at around 525 cm^{-1} , can be assigned to water librational modes. In the spectra of the thallium analogue (Figs. 7 and 9) the corresponding bands appear at 905 , 872 , 793 , 763 , 720 and 690 cm^{-1} , and perhaps at around 520 cm^{-1} as well. The rationale behind such an assignment is as follows:

- the temperature sensitivity of the bands (Figs. 6 and 7);
- the systematic decrease in their intensity with increasing the deuterium content in the spectra of deuterated analogues (Figs. 8 and 9);
- the simultaneous appearance of new bands, which, in the spectrum of the rubidium analogue with highest deuterium content are observed at 675 , 650 , 602 , 540 , 515 and 500 cm^{-1} , and in the corresponding spectrum of the thallium analogue at 668 , 655 , 602 , 536 , 515 and 500 cm^{-1} , values that would be expected if these new bands are indeed due to D_2O librations.

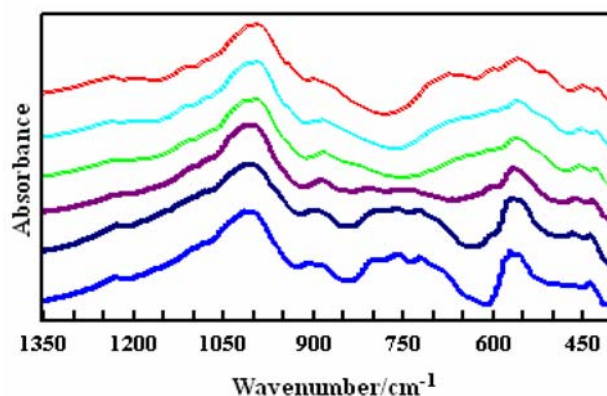


Fig. 8. Fourier transform infrared spectra of partially deuterated analogues of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum, the deuterium content being 0, 5, 25, 50, 75 and 95% respectively).

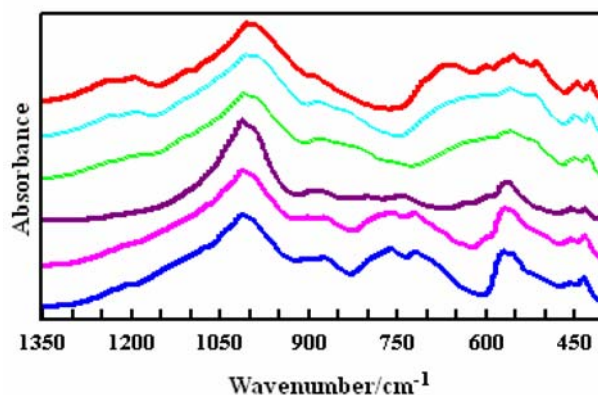


Fig. 9. Fourier transform infrared spectra of partially deuterated analogues of $\text{MgTlPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum, the deuterium content being 0, 5, 25, 50, 75 and 95% respectively).

Expectedly, in the Raman spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{MgTlPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT, bands with significant intensity attributable to librations of water molecules were not observed in the region between 900 and 600 cm^{-1} (Fig. 10).

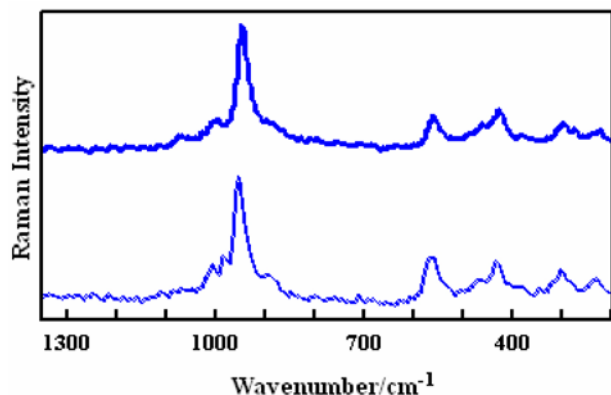


Fig. 10. Fourier transform Raman spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ (lower curve) and $\text{MgTlPO}_4 \cdot 6\text{H}_2\text{O}$ (upper curve) recorded at LNT in the region of the HOH and PO_4 external vibrations.

3. 3. Vibrations of the Phosphate Ions

Free phosphate ions have the structure of regular tetrahedra with T_d symmetry. They possess four normal vibration modes: ν_1 , ν_2 , ν_3 and ν_4 (ν_1 and ν_3 are stretching, whereas ν_2 and ν_4 are bending modes). All four modes are Raman active, and only ν_3 (antisymmetric stretching vibration) and ν_4 (antisymmetric bending vibration) are infrared active.

The group-theory considerations, similar to those for other studied orthorhombic struvite compounds,^{2–8} suggest that, taking into account the transformation of the symmetry types from T_d to C_s , up to nine bands would be expected in the infrared spectra as a result of internal vibrations of the PO_4^{3-} ion (three components of ν_3 and ν_4 each, two of ν_2 and one of ν_1), and at most three bands would appear in the Raman spectra (one component of the ν_2 mode and one for ν_3 and ν_4 each). Moreover, due to the influence of the correlation field, a total of 18 Raman active and 15 infrared active bands would be expected.

In the LNT infrared spectra of the studied compounds, one very strong band appears around $1015\text{--}1030\text{ cm}^{-1}$, in the region where components of the ν_3 modes are expected to appear. The band is not very sensitive to temperature changes and exchange of hydrogen with deuterium (Figs. 6–9) and shoulders can be noticed on both sides of it. While it is certain that the main part of its intensity is due to the components of the ν_3 mode of the PO_4^{3-} ions, the simultaneous presence of second-order transitions as well can not be ruled out.

In the region from around 1080 to 970 cm^{-1} in the Raman spectra of both compounds, there are several

low-intensity bands attributable to the ν_3 mode of the PO_4^{3-} ions (Figs. 10–12).

Taking into consideration the low value of the deformation indices calculated for $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ⁸ and most probably not very different in the case of the presently studied compounds, it would be difficult to detect with certainty the band due to the ν_1 mode in the infrared spectra of the protiated compound. This task is even more difficult because of the bands from librations of water molecules appearing in the same region. However, in the infrared spectra of the analogues with high deuterium content, the additional shoulders appearing at around 940 cm^{-1} (Figs. 8 and 9) could originate from the $\nu_1(\text{PO}_4)$ mode although it is also possible that it is due to some second-order transitions involving D_2O librations. In favour of the first assumption is the fact that in the Raman spectra of the rubidium analogue recorded at LNT (Figs. 10 and 11), a strong band appears at 953 cm^{-1} , the corresponding band in the Raman spectrum of the thallium analogue being found at 945 cm^{-1} (Figs. 10 and 12).

These bands can be with certainty assigned as due primarily to the $\nu_1(\text{PO}_4)$ mode. However, on going from the spectra of the protiated compounds to the analogues with the highest deuterium content, the half-width of these bands in the Raman spectra significantly decreases (Figs. 11 and 12) implying that the bands are not due to pure ν_1 modes but probably originate from $\nu_1(\text{PO}_4)$ vibrations coupled with some water libration. In accordance with such an assumption, the corresponding bands in the spectra of the analogues with the highest deuterium content appear at slightly lower frequencies (at 941 cm^{-1}).

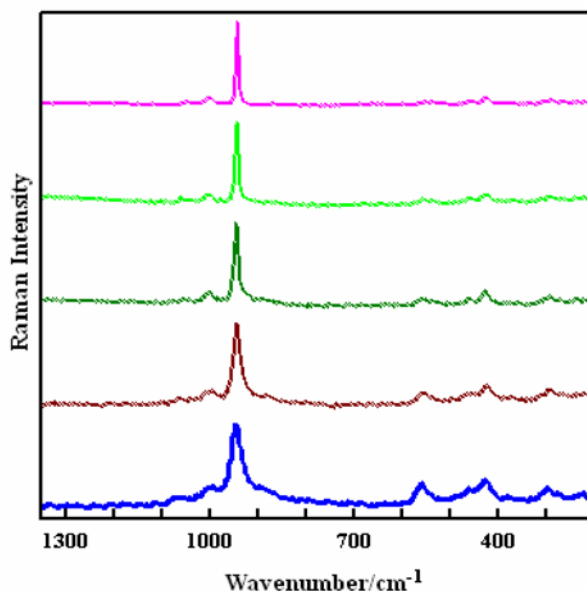


Fig. 11. Fourier transform Raman spectra of partially deuterated analogues of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum, the deuterium content being 0, 25, 50, 75 and 95% respectively).

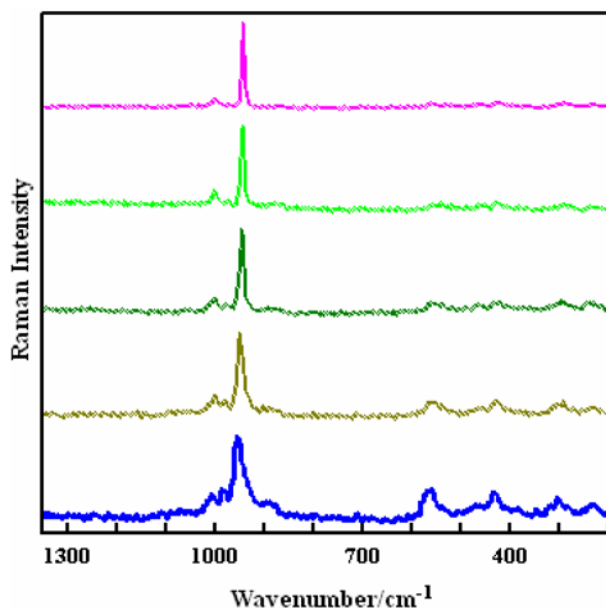


Fig. 12. Fourier transform Raman spectra of partially deuterated analogues of $\text{MgTiPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum, the deuterium content being 0, 25, 50, 75 and 95% respectively).

In the LNT infrared spectra of the studied compounds, the asymmetric bands at around 575 cm^{-1} (Figs. 9 and 10) can be attributed to the $\nu_4(\text{PO}_4)$ mode, the corresponding bands in the Raman spectra being found at about 560 cm^{-1} (Figs. 11 and 12). In the vibrational spectra of the partially deuterated compounds (Figs. 8, 9, 11 and 12), similarly as for the corresponding spectra of the other studied orthorhombic struvite-type compounds,^{2, 4, 5, 8, 9, 11} it can be noticed that with increasing deuterium content, these bands are shifted to lower frequencies and disappear. In the Raman spectra of the compounds with highest deuterium content, bands with very low intensity are observed below 560 cm^{-1} . As in the vibrational spectra of the other orthorhombic struvite-type compounds, the shifting and disappearing of the bands from the $\nu_4(\text{PO}_4)$ mode in the Raman spectra of the partially deuterated analogues can be explained as result of coupling of this vibration with some other mode, most probably HDO and/or D_2O librations (their bands in the Raman spectra are generally with low intensity). This elaboration is supported with the analysis of the Raman spectra of arsenostruvite ($\text{Mg-NH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$) and its partially deuterated analogues in the region of the $\nu_4(\text{AsO}_4)$ mode.⁶ Namely, in this region no bands from D_2O librations are observed and the band from $\nu_4(\text{AsO}_4^{3-})$ mode does not disappear on increasing the deuterium content in the sample.

In the infrared and Raman spectra of the studied compounds recorded at LNT in the region of the $\nu_2(\text{PO}_4)$ vibrations, low intensity and temperature-sensitive bands are observed at around 465 and 435 cm^{-1} (Figs. 6 and 7).

In the spectra of the partially deuterated analogues (Figs. 8, 9, 11 and 12), when increasing the deuterium content, these bands change their shape and intensity and shift slightly to lower frequencies. These bands can be attributed to $\nu_2(\text{PO}_4)$ modes and/or stretching Mg-O vibrations. If they (or at least one of them) are due to $\nu_2(\text{PO}_4)$ modes, then their temperature dependence can be explained by the possibility of coupling with other modes.

In the far-infrared (FIR) and in the Raman spectra region between 400 and 200 cm^{-1} , several bands are observed (Figs. 10–14). These bands very slightly shift to lower frequencies in the spectra of the deuterated analogues implying that their origin is related to the $\nu(\text{Mg-Ow})$ modes.

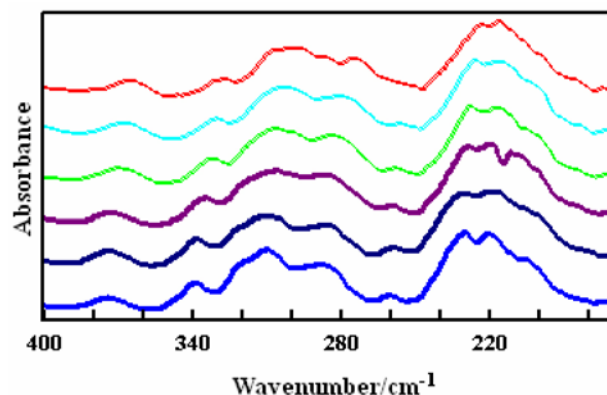


Fig. 13. Far-infrared spectra of $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT (the content of deuterium increases from bottom to top, the deuterium content being 0, 5, 25, 50, 75 and 95% respectively).

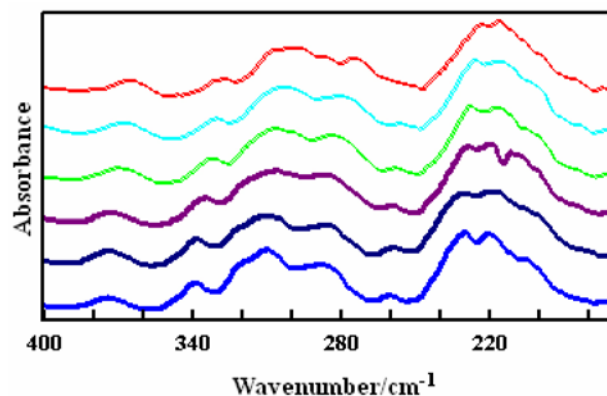


Fig. 14. Far-infrared spectra of $\text{MgTiPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT (the content of deuterium increases from bottom to top, the deuterium content being 0, 5, 25, 50, 75 and 95% respectively).

4. Conclusions

The thorough analysis of the Fourier transform infrared and Raman spectra recorded at room temperature and the boiling temperature of liquid nitrogen showed that in the O–H stretching region the broad and intense feature sensitive to deuteration must be a result of a number of

overlapping bands due to the stretching vibrations of the four different types of water molecules and its overall appearance is in agreement with the considerable strength of almost all hydrogen bonds formed by the H_2O molecules. In line with the presence of strong H-bonds is the presence of a rather strong broad band around 2400 cm^{-1} which is similar in position and shape with those found in the case of compounds with $\text{X}-\text{OH} \cdots \text{Y}$ systems with similar $\text{X} \cdots \text{Y}$ distances.

In the general region where the H–O–H bending bands are expected to appear, a broad feature is observed which can not be explained solely by the existence of four types of water molecules and its shape and broadness is likely to be due to interactions of the fundamental modes with some second-order transitions.

The location of the symmetric stretching band of the phosphate ions is, as expected, by far easier in the Raman than in the infrared spectra. It was concluded that in some cases coupling of phosphate and water vibrations is likely to take place.

5. Acknowledgements

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Povzetek

Posneti so bili infrardeči in Ramanski spektri heksahidratov magnezij-rubidijevega fosfata, $\text{MgRbPO}_4 \cdot 6\text{H}_2\text{O}$, in magnezij-talijevega fosfata, $\text{MgTiPO}_4 \cdot 6\text{H}_2\text{O}$, pri sobni temperaturi in pri temperaturi tekočega dušika. V pomoč pri njihovi analizi so bili posneti tudi njihovi delno devterirani analogi z različnimi koncentracijami devterija. Na osnovi efektov devteracije in hlajenja je bila ugotovljena narava trakov, ki so bili assignirani kot pretežno lokalizirana nihanja molekule vode (v strukturi so štirje kristalografsko različni tipi teh molekul) in nihanja PO_4^{3-} skupine. Ugotovljeno je bilo, da so nekatera nihanja fosfatnih skupin in vode najverjetneje sklopljena. Oblika infrardečega spektra v območju valenčnega nihanja O–H je pojasnjena kot rezultat močnega prekrivanja trakov komponent osnovnih valenčnih nihanj H_2O z nihanji prehodov drugega reda. Široki B trak značilnih spektrov substanc tipa ABC, ki imajo v strukturi močno vodikovo vez, se v analiziranih snoveh pojavlja okoli 2400 cm^{-1} .