



Infrared and Raman spectra of magnesium ammonium phosphate hexahydrate (*struvite*) and its isomorphous analogues.

I. Spectra of protiated and partially deuterated magnesium potassium phosphate hexahydrate

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Abstract

The Fourier transform infrared and Raman spectra of magnesium potassium phosphate hexahydrate and a series of its deuterated analogues were recorded and analyzed. By comparing the spectra recorded at room temperature with those obtained at the boiling temperature of liquid nitrogen and by studying the spectra of the series of partially deuterated $\text{MgKPO}_4 \cdot \text{H}_2\text{O}$ an assignment was proposed for the observed bands. The unusual behavior for bands originating from the ν_4 modes of PO_4^{3-} ions in the Raman spectra of partially deuterated analogues of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ was explained by coupling and mixing of the $\nu_4(\text{PO}_4)$ mode and D_2O librations.

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1. Introduction

Magnesium ammonium phosphate hexahydrate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (often referred to by its mineralogical name *struvite*) is a well-known biomineral, its major biological importance being related to its presence in human urinary sediments and vesical and renal calculi [1]. Magnesium potassium phosphate hexahydrate, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ and magnesium ammonium arsenate hexahydrate, $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ are isomorphous with *struvite* [2,3].

According to the literature data [2–5], all investigated compounds crystallize in the orthorhombic space group $Pmn2_1(C_{2v}^7)$ with $Z = 2$. It was found that all ions and two of the four crystallographically different H_2O molecules of crystallization occupy special positions with C_s symmetry, while the H_2O molecules of the other two types are at general positions (Fig. 1).

The H_2O molecules are coordinated to the divalent cation, building a distorted octahedron around it (Fig. 1) and act as donors in hydrogen bonds which are among the shortest ones ever found in crystalline hydrates [6]. In the crystal structure of all mentioned compounds [2–5], namely, the H_2O molecules are donors in six hydrogen bonds with $\text{O}_w \cdots \text{O}$ distances ranging from 263.0 to 269.5 pm in $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, from 262.3 to 270.1 pm in $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (the acceptors, in both cases, are phosphate oxygens) and from 261.9 to 269.8 pm in $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ (the acceptors are, understandably, the arsenate oxygens). The seventh contact, with a water molecule, corresponds to a relatively weak hydrogen bond (the $\text{O}_w \cdots \text{O}_w$ distance is 314.1 pm in *struvite* [5], 314.2 pm [2] in the potassium analogue and 314.9 pm in $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ [3].

The infrared spectra of magnesium ammonium phosphate hexahydrate and its potassium analogue recorded at room temperature (RT) have already been studied [7]. The RT Raman spectrum of *struvite* has also been published [8].

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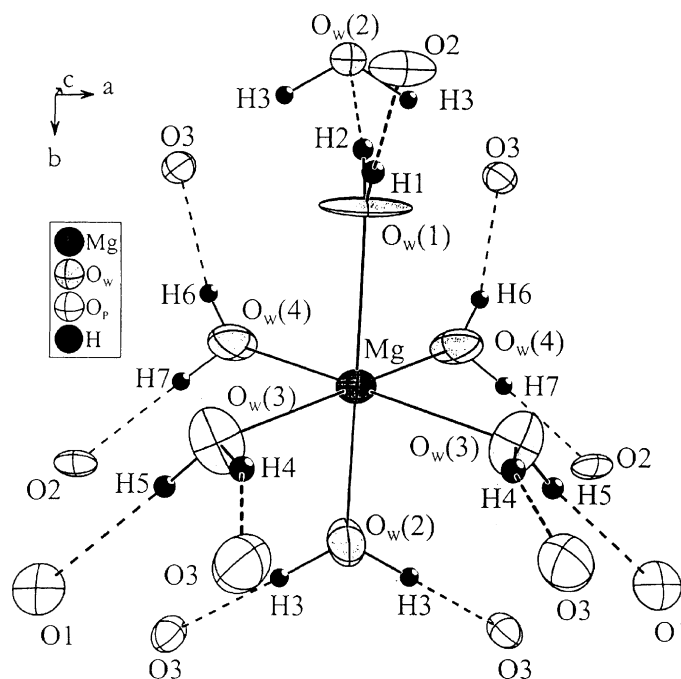


Fig. 1. Part of the crystal structure of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (dashed lines: hydrogen bonds).

To the best of our knowledge, vibrational spectra of arsenstruvite and its deuterated analogues have not been reported yet.

The vibrational spectra of the whole series of deuterated analogues of neither of the three compounds have been studied. This may be one of the reasons for some not completely resolved questions, which we have found interesting for investigation and tried to explain.

Since, of the three above-mentioned compounds, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ does not contain an ammonium ion in the formula unit, its spectra are, expectedly, the simplest ones. This is why we decided to analyze, in this paper, the Fourier transform infrared (FTIR) and Raman spectra of the protiated $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ and a series of its deuterated analogues. As will be discussed in some detail later on, it was found that especially interesting and useful for clarifying some problems are the difference spectra of the analogue with a low ($\approx 3\text{--}5\%$ D) deuterium content.

2. Experimental

The title compound was synthesized according to the method described by Mathew and Schroeder [2]. Partially deuterated analogues were obtained employing the same general procedure, but using as solvents $\text{H}_2\text{O}\text{--}\text{D}_2\text{O}$ mixtures with appropriate compositions. The highest content of deuterium in the samples was achieved using pure D_2O .

The infrared spectra were recorded on a 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} . Far infrared spectra were recorded on a Bruker 113v interferometer in Nujol between polyethylene pellets. For acquisition of spectra and manipulations on them the GRAMS ANALYST 2000 [9] and GRAMS 32 [10] packages were used. The FT Raman spectra were recorded (with a resolution of 2 cm^{-1}) on a Bruker RFS 100s 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. All Raman spectra were recorded under identical experimental conditions.

3. Results and discussion

The FTIR and Raman spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ at RT and the boiling temperature of LNT are presented at Figs. 2 and 3, respectively. The RT spectra closely resemble those published in Refs. [7,8]. In order to make the discussion more systematic, the deuteration-sensitive bands will be treated separately from those due to phosphate modes.

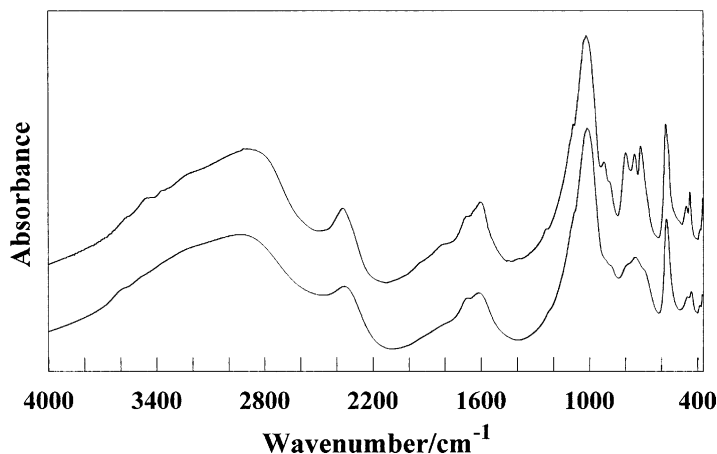


Fig. 2. Infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and at LNT (upper curve).

A quite complicated spectral pattern is expected in the infrared spectra owing (among others) to the presence of several types of H_2O molecules in the structure, the crystallization in a non-centrosymmetric space group (C_{2v}^7), the possibility for correlation-field splitting of the modes, etc.

3.1. Internal vibrations of the H_2O molecules

As already mentioned (and shown in Fig. 1), four types of H_2O molecules are found in the structure of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ [2]. The group theory approach shows that because of the static field, three infrared and three Raman active bands are expected from each type of H_2O molecules. In addition, the presence of the correlation field can cause a considerable increase in the number of bands (see Table 1). It is reasonable to expect that the correlation field is stronger for the two types of H_2O molecules occupying general positions since they can be treated as mechanically coupled oscillators because a pair of each $\text{O}_w(3)$ and $\text{O}_w(4)$ molecules are coordinated to the Mg atom.

3.1.1. Stretching vibrations of the H_2O molecules

The RT and LNT spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ reveal, in the OH stretching region, the existence of a broad, asymmetric and complex feature between 3800 and 2200 cm^{-1} in the infrared and from 3400 to 2200 cm^{-1} in the Raman spectra (Figs. 2 and 3). The low frequency of its centroid being in line with the structural data [2] which is in line with the existence of quite strong hydrogen bonds in the structure (as mentioned, they are among the strongest found in crystalline hydrates). The intensity and the shape of the feature are obviously a result of overlapping of numerous bands which either originate from fundamental stretching modes of the H_2O molecules (it should not be forgotten that four types of H_2O molecules exist in the structure) or are related to them through interactions with second-order transitions of appropriate frequency and symmetry.

The feature is deuteration sensitive (Fig. 4) and is shifted towards low frequencies without changing its shape appreciably.

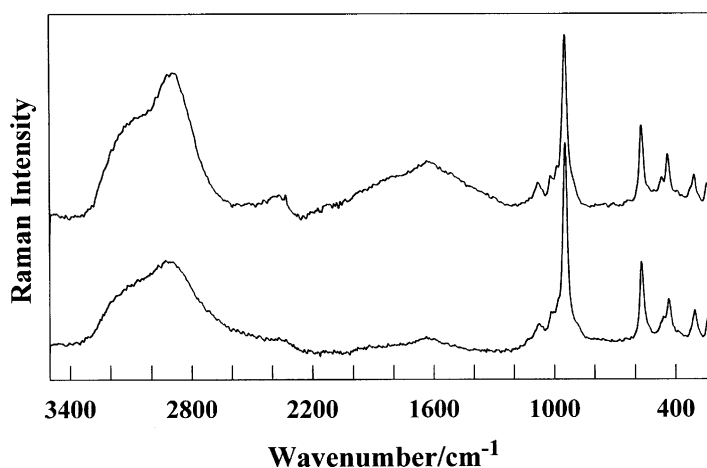


Fig. 3. Fourier transform Raman spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and at LNT (upper curve).

Table 1

The unit-cell group analysis for the three internal water modes and the water librations modes (a, b, c) and phosphate anion vibrations (d)

(a) Water molecule internal vibrations			
Mode	Molecular point group	Site group	Factor group
	C_{2v}	C_1	C_{2v}
ν_1, ν_2	A_1	$A(3)$	$A_1(3)$
			$A_2(3)$
ν_3	B_2		$B_1(3)$
			$B_2(3)$
Water molecule librations			
	C_{2v}	C_1	C_{2v}
τ	A_1	$A(3)$	$A_1(3)$
ω	B_1		$A_2(3)$
ρ	B_2		$B_1(3)$
			$B_2(3)$
(b) Water molecule internal vibrations (zy plane preserved)			
Mode	Molecular point group	Site group	Factor group
	C_{2v}	C_s	C_{2v}
ν_1, ν_2	A_1	$A'(3)$	$A_1(3)$
			A_2
ν_3	B_2	A''	B_1
			$B_2(3)$
Water molecule librations			
	C_{2v}	C_s	C_{2v}
τ	A_1	$A'(1)$	$A_1(1)$
ω	B_1		$A_2(2)$
ρ	B_2	$A''(2)$	$B_1(2)$
			$B_2(1)$

Table 1 (Continued)

(c) Water molecule internal vibrations (xz plane preserved)			
Mode	Molecular point group	Site group	Factor group
	C_{2v}	C_s	C_{2v}
ν_1, ν_2	A_1	A' (2)	$A_1(2)$
ν_3	B_2	A'' (1)	$A_2(1)$
			$B_1(1)$
			$B_2(2)$
Water molecule librations			
	C_{2v}	C_s	C_{2v}
τ	A_2	A' (1)	$A_1(1)$
ω	B_1	A'' (2)	$A_2(2)$
ρ	B_2		$B_1(2)$
			$B_2(1)$
(d) Phosphate anion vibrations			
Mode	Molecular point group	Site group	Factor group
	T_d	C_s	C_{2v}
ν_1	A_1	A' (6)	$A_1(6)$
ν_2	E		$A_2(3)$
ν_3	F_2	A'' (3)	$B_1(3)$
ν_4	F_2		$B_2(6)$

In principle, the spectral picture could become simpler if the spectra of the analogue with a small ($\approx 3\text{--}5\%$) deuterium content are studied. In such a case, namely, each distinct uncoupled O–D oscillator in the isotopically isolated HOD molecules should give a separate band indicative of the strength of hydrogen bond in which the given D atom is involved. In the present case, however, the situation is complicated by the existence, in the region where the $\nu(\text{O–D})$ bands are expected, of bands with a non-negligible intensity in the spectra of the protiated compound. In order to circumvent this obstacle, a difference spectrum was obtained by subtracting the properly normalized spectrum of the protiated $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ from that of its slightly deuterated analogue. The result is shown in Fig. 5.

As can be seen from the deconvoluted difference IR spectrum, four distinct bands appear in the O–D stretching region (their frequencies are $\approx 2540, 2420, 2200$ and 2090 cm^{-1}) whereas seven bands would be expected taking into account the number of non-equivalent deuterons in the structure.

Of the above-mentioned bands, that at the highest frequency can be attributed to the O–D stretching vibrations of the isotopically isolated $\text{H}(1)\text{--O}(w1)\text{--D}(2)\cdots\text{O}(w2)$ groupings where the $\text{O}(w1)\cdots\text{O}(w2)$ distance is reported [2] to be 314.2 pm and, in addition, the hydrogen bond deviates considerably from linearity. All this, of course, indicates that the interaction can just barely be considered as a hydrogen bond.

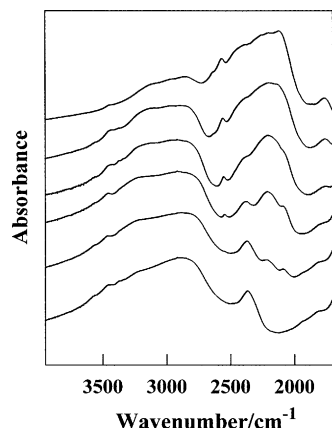


Fig. 4. Infrared spectra of partially deuterated analogues of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the OH and OD stretching vibrations (the content of deuterium increases from bottom to top spectrum).

The next band (at $\approx 2420 \text{ cm}^{-1}$) should, most probably, be attributed to the O–D stretching of the H(4)–O(w3)–D(5)···O(1) grouping where the O(w3)···O(1) distance is 270.1 pm and the O–H···O angles is given [2] as 160° .

The fact that the bands at lower frequencies are both broader and more intense is in line with the fact that the remaining hydrogen bonds are characterized by rather similar O···O distances (ranging from 262.3 to 264.9 pm) and O–H···O angles in the range from 159 to 172° . The bands in the $2300\text{--}2000 \text{ cm}^{-1}$ region are rather asymmetric and it is obvious that they are composed of several components.

In any case, the appearance of bands around 2090 cm^{-1} confirms the existence of quite strong hydrogen bonds in the studied compound. The Raman spectra (Fig. 3) are less informative but are in a general agreement with the appearance of the infrared ones.

3.1.2. Bending vibrations of the H_2O molecules

In the RT and LNT infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, one broad, temperature-sensitive feature extending from around 2100 to 1350 cm^{-1} is found (Fig. 6). Of the

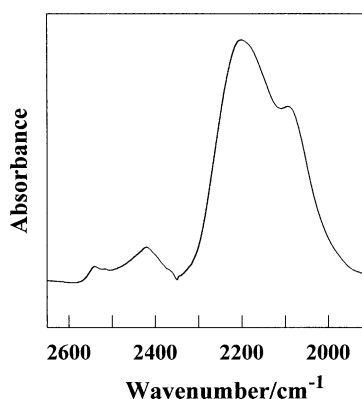


Fig. 5. Deconvoluted difference infrared spectrum recorded at LNT in the region of the $\nu(\text{OD})$ vibrations, obtained by subtracting the spectrum of the protiated compound $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ from the spectrum of the analogue with low deuterium content ($\approx 5\%$ D).

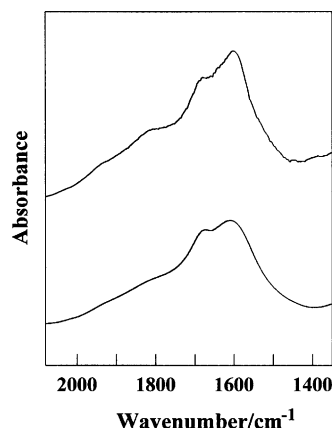


Fig. 6. Infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) and at LNT (upper curve) in the region of the HOH bending vibrations.

submaxima present on it, the two strongest ones have frequencies 1682 and 1600 cm^{-1} and, since they are affected by deuteration (Fig. 7), they can rather safely be assigned to $\delta(\text{HOH})$ vibrations or, in any case, to modes having a considerable $\delta(\text{HOH})$ character. The fact that the 1682 and 1600 cm^{-1} bands are broad and asymmetric can be attributed to the existence of four crystallographically different types of H_2O molecules in the structure of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ although it is not easy to pair each of the submaxima with a given type of H_2O molecule.

In fact, the situation is even more complicated by the existence of submaxima at the high-frequency side (the more prominent ones are found, at LNT, around 1935 and 1815 cm^{-1}) and also at the lower-frequency side (at 1530 and 1400 cm^{-1}). Multiple bands in the general HOH bending region (but extending over an even wider frequency region) have been reported several times

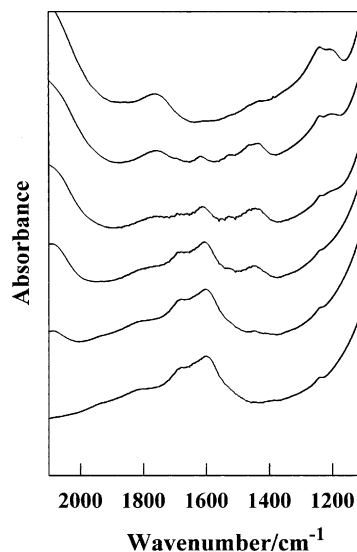


Fig. 7. Infrared spectra of partially deuterated analogues of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and DOD bending vibrations (the content of deuterium increases from bottom to top spectrum).

[11–15], different explanations for their origin (e.g. appearance of second-order transitions perhaps combined with Fermi-resonance type interactions with the fundamental $\delta(\text{HOH})$ vibrations; coupling of the water bending modes with low-frequency modes of the lattice via a mechanism of the Bertie–Falk type; the influence of chain and layer structure) being variously given in particular cases. In principle, all of the proposed explanations are physically reasonable and none of them (or their combination) can be automatically ruled out. However, if the appearance of the multiple bands in the $\delta(\text{HOH})$ region has a common origin (irrespective, of the particular structural characteristics of a given type of compounds), the definitive all-embracing explanation is still not within reach. On the other hand, it is clear that the prerequisite for any of the mechanisms to be operative, the H–O–H bending vibrations must be remarkably anharmonic—a property which is certainly compatible with the formation of strong hydrogen bonds by the H_2O molecules.

In the H–O–H bending region of the Raman spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Fig. 3), only a very broad and almost featureless band exists with a maximum around 1620 cm^{-1} .

3.2. External vibrations of H_2O molecules

It is generally relatively easy to locate the infrared bands which are due to librations of the H_2O molecules in the structure of a crystalline hydrate. As is well known, namely, apart from shifts on deuteration, the H_2O librational bands are temperature-sensitive, exhibiting a negative temperature coefficient (i.e. shifting towards higher frequencies on lowering the temperature) and gaining, at least apparently, in intensity when the temperature is lowered.

However, the comparison of the RT and LNT infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Fig. 8) indicates a temperature sensitivity of practically *all* bands with frequencies lower than 1100 cm^{-1} . Several bands, namely, become significantly more intense at LNT and practically all bands in

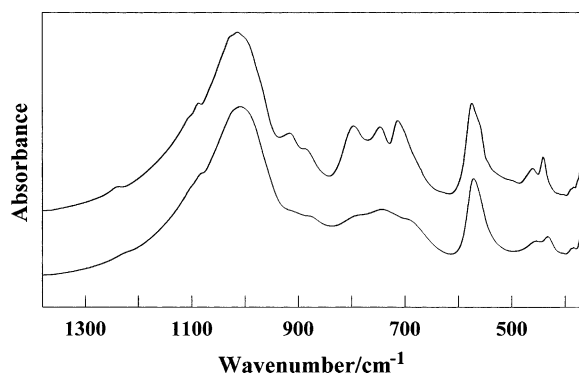


Fig. 8. Infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at RT (lower curve) at LNT (upper curve) in the region of the HOH and PO_4 external vibrations.

the above-mentioned region have higher frequencies at LNT than at RT.

The basic problem does not concern the *number* of such bands since even in absence of correlation splitting, twelve bands are expected in the infrared and Raman spectra, while the interactions of identical oscillators would increase the number of expected librational bands to 26 in the infrared and to 36 in the Raman spectrum of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$. What actually complicates the situation is the fact that bands originating from vibrations of PO_4^{3-} ions are expected in the same region and they should not be temperature-sensitive. Thus, although it is beyond doubt that the very strong band at 1008 (at RT) and 1014 cm^{-1} (at LNT) is due essentially to the $\nu_3(\text{PO}_4)$ vibrations, its temperature sensitivity may be an indication that water librational bands also contribute to the shape and intensity of this feature.

Since no fundamental phosphate vibration is expected in the $950\text{--}600 \text{ cm}^{-1}$ region, the low intensity bands at 916 and 884 cm^{-1} and the medium intensity ones at 796 , 746 and 714 cm^{-1} in the LNT spectrum of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ must be considered as due to water librations. The analysis of the infrared spectra of the partially deuterated analogues (Fig. 9) confirms such an assignment. As is clearly seen in Fig. 9, the intensity of the 916 , 884 , 796 , 746 and 714 cm^{-1} bands systematically decreases on increasing the deuterium content. Simultaneously, new bands appear and in the spectrum of the analogue with the highest deuterium content the frequencies of these new bands are 680 , 650 , 599 , 538 and 513 cm^{-1} . Thus it is

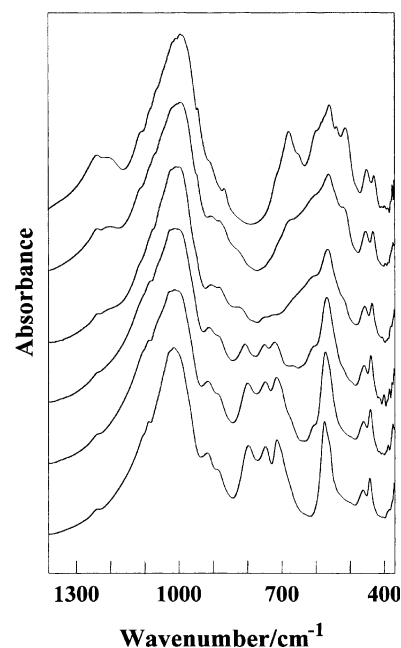


Fig. 9. Infrared spectra of partially deuterated analogues of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum).

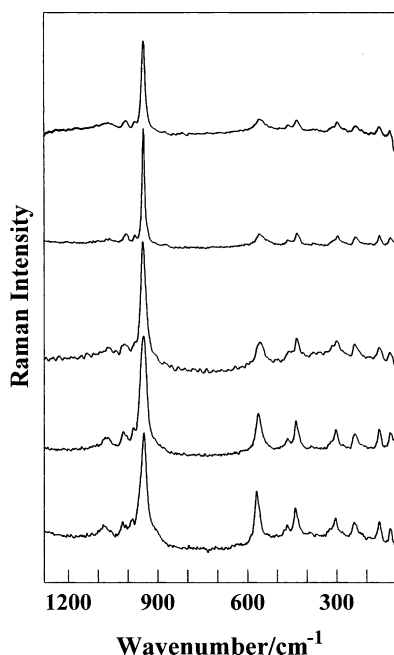


Fig. 10. Fourier transform Raman spectra of partially deuterated analogues of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ recorded at LNT in the region of the HOH and PO_4 external vibrations (the content of deuterium increases from bottom to top spectrum).

rather safe to attribute the enumerated bands to D_2O librations. At frequencies between those of the bands attributed to H_2O and to D_2O librations, bands which originate from HOD librations are expected but are difficult to locate with certainty.

In the region between 900 and 600 cm^{-1} in the Raman spectra of the partially deuterated analogues, no bands with significant intensity attributable to water librations could be detected (Fig. 10).

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

The free phosphate ions are regular tetrahedrons with T_d symmetry. These groups have four normal modes of vibration denoted ν_1 , ν_2 , ν_3 and ν_4 of which ν_1 and ν_3 are stretching and ν_2 and ν_4 are bending vibrations. All four modes are Raman active, whereas only ν_3 (the antisymmetric stretching vibration) and ν_4 (the antisymmetric bending vibration) are infrared active. The ν_3 and ν_4 modes are triply degenerate, ν_2 is doubly degenerate and ν_1 is non-degenerate.

The incorporation of the PO_4^{3-} ions in a crystal usually decreases their symmetry. How large, effectively, this deviation from ideal symmetry is, can be judged by the value of the Baur's indices [16], the smaller the values of these indices, the closer the phosphate ion is to a regular tetrahedron. So, the low values of the deformation indices of the PO_4^{3-} ions in $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Table 2) suggest high

Table 2

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

Deformation indices $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$	$D(\text{P}-\text{O})$	$D(\text{O}-\text{P}-\text{O})$	$D(\text{O}-\text{O})$
	0.0039	0.0054	0.0023

effective symmetry of these ions although their site symmetry is reduced to C_s .

Strictly speaking, under the selection rules of the C_s site group (see Table 1), the non-degenerate and infrared inactive ν_1 vibration is transformed to an infrared active A' mode, the doubly degenerate infrared inactive ν_2 vibration is changed into two infrared active components with A' and A'' symmetry, while two components of each of the triply degenerate ν_3 and ν_4 vibrations are transformed into type A' modes and one into type A'' (all three are infrared active). Thus, in the site-group approximation, nine bands should be expected in the infrared spectra as a result of the internal vibrations of PO_4^{3-} ions (three from each of ν_3 and ν_4 modes, two from ν_2 and one from ν_1). The correlation field may cause additional splitting of each vibration into two components. The A' type vibrations result in A_1 and B_2 type modes, and the A'' vibrations in A_2 and B_1 type modes. Consequently, 18 bands are expected to appear in the Raman spectrum, and 15 bands in the infrared spectrum (A_2 type modes are infrared inactive).

As is well known, however, the group theory can not predict how large the site-group splitting and how effective the correlation field would be. In fact, the small values of all Baur's indices lead to the conclusion that the site-group splitting of the bands should not be pronounced and that the infrared intensity of the ν_1 and ν_2 phosphate bands should not be high¹.

The expectations are borne out. In the region of $\nu_3(\text{PO}_4)$ modes in the FTIR spectra of the studied compounds, one very strong band appears above 1000 cm^{-1} which, as mentioned above, is somewhat temperature-sensitive and whose frequency is 1008 cm^{-1} at RT and 1014 cm^{-1} at LNT (Fig. 8). This band is shifted to lower frequencies in the spectra of the deuterated analogues and in the spectrum of the analogue with highest deuterium content appears at 994 cm^{-1} (Fig. 9). This shift of about 20 cm^{-1} can be assumed to result from coupling of the $\nu_3(\text{PO}_4)$ and $\delta(\text{DOD})$ modes.

In fact, in the low-temperature spectra shoulders are noticeable on both sides of this intense band, a fact which shows that the lowered symmetry of the phosphate ions and/or the correlation field might have some effect. The splitting of the ν_3 mode is more clearly seen in the Raman spectra where, in the region between 1080 and 970 cm^{-1} , several bands with low intensity are found

¹ As mentioned earlier the latter two modes are infrared inactive for the 'free' PO_4^{3-} ions.

(their frequencies are around 1075, 1015, 1005 and 985 cm^{-1}). Thus, the conclusion must be that the site-group splitting is operative but the inherent breadth of the infrared ν_3 bands prevents its effect to become clearly visible in the FTIR spectra.

The strongest band in the Raman spectrum (with a frequency of 946 cm^{-1}) is undoubtedly due to the ν_1 phosphate vibration, while the absence of a clear infrared counterpart is in line with the expectations based on the small values of the deformation indices. The only reasonable candidate for assignment to this mode is the shoulder observed around 945 cm^{-1} in the infrared spectra of the partially deuterated analogues with a high deuterium content (Fig. 9).

The asymmetric band at 570 cm^{-1} in the RT infrared spectrum and at 574 cm^{-1} at LNT (Fig. 8) can be attributed to the $\nu_4(\text{PO}_4)$ mode. In the spectra of the partially deuterated analogues (Fig. 9), on increasing the deuterium content in the sample, the band is gradually shifted to lower frequencies and in the spectrum of the sample analogue with the highest deuterium content the corresponding band appears at 561 cm^{-1} . The shift, however, may be only apparent since in the same region bands due to D_2O and/or HOD librations have appeared. The above statement should not be taken as a firm rejection of the notion that the phosphate ν_4 mode in the deuterated samples may not be pure, but coupled with librations of the deuterated H_2O molecules. In the far infrared spectra of the almost completely deuterated compound (Fig. 11), bands due to D_2O librations, corresponding to the intensive one found at around 575 cm^{-1} in the spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ cannot be observed. Accordingly, the strong band at 574 cm^{-1} in the infrared spectra of protiated analogue cannot be assigned to H_2O librations. The asymmetric band can also hardly be attributed to $\nu(\text{Mg}-\text{O})$ modes having in mind that the $\text{Mg}-\text{O}$ bonding is not strong enough to cause so high frequency of the hindered rotation.

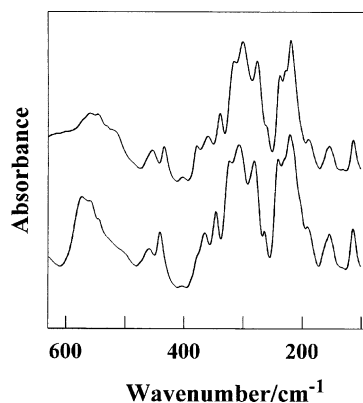


Fig. 11. Far-infrared spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (lower curve) and its almost completely deuterated analogue (upper curve) recorded at LNT.

In the LNT Raman spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, as in the infrared spectra, one relatively strong and asymmetric band appears at 569 cm^{-1} . It is evident from the spectra of the partially deuterated analogues (see Fig. 10) that on increasing the deuterium content in the sample, this band is shifted to lower frequencies and at the same time considerably decreases in intensity. At least two bands with low intensity are observed below 560 cm^{-1} in the Raman spectra of the compounds with the highest content of deuterium. Such a behavior is characteristic for bands due to librations, but not for those originating from the ν_4 modes of PO_4^{3-} ions if the latter are more or less pure. Accordingly, one intensive band due to D_2O libration should appear at around 420 cm^{-1} in the Raman spectrum of the compound with highest content of deuterium. Such a band is not observed in the spectra. As mentioned previously, the corresponding bands in the infrared spectra cannot be attributed to H_2O librations.

In this case, it seems reasonable to explain the situation by coupling and mixing of the $\nu_4(\text{PO}_4)$ mode and D_2O librations, which is additionally supported by broadening of the respective band in the spectra of the partially deuterated analogues with increasing the deuterium content. This explanation is supported by the fact that in the Raman spectra of the isomorphous $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$ and its partially deuterated analogues, in the region of the $\nu_4(\text{AsO}_4)$ mode, there are no bands from D_2O librations (or, at least, no oscillators 'suitable' for coupling appear in that region) and the band due to the $\nu_4(\text{AsO}_4)$ mode does not disappear with increasing the deuterium content [17]. But if so, it remains to elucidate why, opposite to the expectations two bands with very low intensity and lower frequency appear in the spectra of the almost completely deuterated analogue compared to the ones in the spectrum of the protiated compound. Namely [18], when two vibrational energy levels are accidentally degenerated due to the vibrational coupling (resonance interaction) between them, it is expected that due to mutual repelling of those levels two new quantum states are formed, each with a particular contribution from the unperturbed levels. As a result of this coupling, the new (perturbed) levels are expected to be shifted in both directions (to opposite higher and lower energies) with respect to the unperturbed ones. The magnitude of this shift will, however, depend on the magnitude of the interaction force constant in the vibrational potential which is responsible for the vibrational coupling. Also, particular intensity redistribution is expected to appear between the interacting modes.

In any case, such a considerable decrease in the intensity of a band/bands in the Raman spectra of deuterated analogues, which is not a result of an isotopic substitution in an oscillator giving rise to that band, is a phenomenon we have not observed in our experience and in literature data, either. The above explanation is an

attempt to elucidate this interesting event and remains open for discussion.

In the region of the $\nu_2(\text{PO}_4)$ modes, two temperature sensitive bands (at 461 and 441 cm^{-1}) appear in the FTIR spectrum of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Fig. 8). It is evident from the spectra of the partially deuterated analogues (Fig. 9) 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 content of deuterium are 450 and 429 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 stretching $\text{Mg}-\text{O}$ vibrations². In the Raman spectra, bands with similar intensity and shape as those found in the infrared spectra are observed in the region between 470 and 430 cm^{-1} (Fig. 10) 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.

Several bands are observed in the region between 400 and 250 cm^{-1} in the Raman and far-IR spectra of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (Figs. 10 and 11). In the spectra of the deuterated analogues, these bands are slightly shifted to lower frequencies, which suggests their assignment as due to vibrations related to stretching $\text{Mg}-\text{O}$ modes.

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References

- [1] F. Abbona, R. Boistelle, *J. Cryst. Growth* 46 (1979) 339.
- [2] M. Mathew, L.W. Schroeder, *Acta Crystallogr.* B35 (1979) 11.
- [3] G. Ferraris, M. Franchini-Angela, *Acta Crystallogr.* B29 (1973) 859.
- [4] A. Whitaker, J.W. Jeffery, *Acta Crystallogr.* B26 (1970) 1429.
- [5] G. Ferraris, H. Fuess, W. Joswig, *Acta Crystallogr.* B42 (1986) 253.
- [6] G. Chiari, G. Ferraris, *Acta Crystallogr.* B38 (1982) 2331.
- [7] E. Banks, R. Chianelli, R. Korenstein, *Inorg. Chem.* 14 (1975) 1634.
- [8] N.Q. Dao, M. Daudon (Eds.), *Infrared and Raman Spectra of Calculi*, Elsevier, Paris, 1997.
- [9] GRAMS ANALYST™ for PE-2000 FT-IR, Version 3.01B Level II, Galactic Industries, 1994.
- [10] GRAMS/32 Spectral Notebase, Version 4.10, Galactic Industries Corporation, 1996.
- [11] J.E. Bertie, M. Falk, *Can. J. Chem.* 51 (1973) 1713.
- [12] B. Šoptrajanov, V.M. Petruševski, *J. Mol. Struct.* 293 (1993) 101.
- [13] B. Šoptrajanov, V.M. Petruševski, *J. Mol. Struct.* 408/409 (1997) 283.
- [14] B. Šoptrajanov, V. Stefov, M. Žugić, V.M. Petruševski, *J. Mol. Struct.* 482–483 (1999) 109.
- [15] P. Piszczek, A. Grodzicki, O. Fauriskov Nielsen, B. Engelen, *J. Mol. Struct.* 604 (2002) 19.
- [16] W.H. Baur, *Acta Crystallogr.* B30 (1974) 1195.
- [17] V. Stefov, B. Šoptrajanov, M. Najdoski, B. Engelen, H.D. Lutz, in preparation.
- [18] S. Califano, *Vibrational States*, Wiley, New York, 1976.
- [19] B. Šoptrajanov, V. Stefov, I. Kuzmanovski, G. Jovanovski, H.D. Lutz, B. Engelen, *J. Mol. Struct.* 613 (2002) 7.

² 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 [19].