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

V. Stefov,*, B. Šoptrajanov, F. Spirovski, I. Kuzmanovski, H.D. Lutz, B. Engelen

*aInstitut za hemija, PMF, Univerzitet 'Sv. Kiril i Metodij', P.O. Box 162, 1001 Skopje, Macedonia
bMakedonska akademija na naukite i umetnostite, Skopje, Macedonia
cAnorganische Chemie, Universität Siegen, D-57068 Siegen, Germany

Received 24 July 2003; accepted 18 August 2003

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 MgKPO₄·H₂O an assignment was proposed for the observed bands. The unusual behavior for bands originating from the ν₄ modes of PO₄³⁻ ions in the Raman spectra of partially deuterated analogues of MgKPO₄·6H₂O was explained by coupling and mixing of the ν₄(PO₄) mode and D₂O librations.

© 2003 Elsevier B.V. All rights reserved.

Keywords: FTIR spectra; FT Raman spectra; Magnesium potassium phosphate hexahydrate

1. Introduction

Magnesium ammonium phosphate hexahydrate, MgNH₄PO₄·6H₂O (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, MgKPO₄·6H₂O and magnesium ammonium arsenate hexahydrate, MgNH₄AsO₄·6H₂O are isomorphous with struvite [2,3].

According to the literature data [2–5], all investigated compounds crystallize in the orthorhombic space group Pmn2₁ (C2ᵥ) with Z = 2. It was found that all ions and two of the four crystallographically different H₂O molecules of crystallization occupy special positions with Cs symmetry, while the H₂O molecules of the other two types are at general positions (Fig. 1).

* Corresponding author. Tel.: + 389-2-3117-055; fax: + 389-2-3226-865.
E-mail address: viktorst@iunona.pmf.ukim.edu.mk (V. Stefov).

The H₂O 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 H₂O molecules are donors in six hydrogen bonds with O₆···O distances ranging from 263.0 to 269.5 pm in MgNH₄PO₄·6H₂O, from 262.3 to 270.1 pm in MgKPO₄·6H₂O (the acceptors, in both cases, are phosphate oxygens) and from 261.9 to 269.8 pm in MgNH₄AsO₄·6H₂O (the acceptors are, understandably, the arsenate oxygens). The seventh contact, with a water molecule, corresponds to a relatively weak hydrogen bond (the O₆···O distance is 314.1 pm in struvite [5], 314.2 pm [2] in the potassium analogue and 314.9 pm in MgNH₄AsO₄·6H₂O [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].
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, MgKPO$_4$·6H$_2$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 MgKPO$_4$·6H$_2$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 ($<3–5\%$ 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 H$_2$O–D$_2$O mixtures with appropriate compositions. The highest content of deuterium in the samples was achieved using pure D$_2$O.

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 Brucker 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 MgKPO$_4$·6H$_2$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.
A quite complicated spectral pattern is expected in the infrared spectra owing (among others) to the presence of several types of H$_2$O molecules in the structure, the crystallization in a non-centrosymmetric space group ($C_{2h}$), the possibility for correlation-field splitting of the modes, etc.

3.1. Internal vibrations of the H$_2$O molecules

As already mentioned (and shown in Fig. 1), four types of H$_2$O molecules are found in the structure of MgKPO$_4$·6H$_2$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$_2$O 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$_2$O molecules occupying general positions since they can be treated as mechanically coupled oscillators because a pair of each O$_w$(3) and O$_w$(4) molecules are coordinated to the Mg atom.

3.1.1. Stretching vibrations of the H$_2$O molecules

The RT and LNT spectra of MgKPO$_4$·6H$_2$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$_2$O molecules (it should not be forgotten that four types of H$_2$O 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.
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

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular point group</th>
<th>Site group</th>
<th>Factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1, v_2$</td>
<td>$A_1$</td>
<td>$A(3)$</td>
<td>$A_1(3)$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$B_2$</td>
<td>$A(3)$</td>
<td>$A_2(3)$</td>
</tr>
</tbody>
</table>

Water molecule librations

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular point group</th>
<th>Site group</th>
<th>Factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1, v_2$</td>
<td>$A_1$</td>
<td>$A'(3)$</td>
<td>$A_1(3)$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$B_2$</td>
<td>$A''$</td>
<td>$B_2(3)$</td>
</tr>
</tbody>
</table>

(b) Water molecule internal vibrations (zy plane preserved)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular point group</th>
<th>Site group</th>
<th>Factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1, v_2$</td>
<td>$A_1$</td>
<td>$A'(3)$</td>
<td>$A_1(3)$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$B_2$</td>
<td>$A''$</td>
<td>$B_2(3)$</td>
</tr>
</tbody>
</table>

Water molecule librations

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular point group</th>
<th>Site group</th>
<th>Factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1, v_2$</td>
<td>$A_1$</td>
<td>$A'(1)$</td>
<td>$A_1(1)$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$B_2$</td>
<td>$A''(2)$</td>
<td>$B_2(1)$</td>
</tr>
</tbody>
</table>
In principle, the spectral picture could become simpler if the spectra of the analogue with a small (< 3–5%) 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 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 MgKPO₄·6H₂O 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 ~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 H(1)–O(w1)–D(2)⋯O(w2) groupings where the O(w1)⋯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.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular point group</th>
<th>Site group</th>
<th>Factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁, v₂</td>
<td>A₁</td>
<td>A’(2)</td>
<td>A₁(2)</td>
</tr>
<tr>
<td>v₃</td>
<td>B₂</td>
<td>A”(1)</td>
<td>B₂(2)</td>
</tr>
</tbody>
</table>

**Table 1 (Continued)**

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular point group</th>
<th>Site group</th>
<th>Factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁</td>
<td>A₁</td>
<td>A’(6)</td>
<td>A₃(6)</td>
</tr>
<tr>
<td>v₂</td>
<td>E</td>
<td>A’(6)</td>
<td>A₃(3)</td>
</tr>
<tr>
<td>v₃</td>
<td>F₂</td>
<td>A”(3)</td>
<td>B₃(3)</td>
</tr>
<tr>
<td>v₄</td>
<td>F₂</td>
<td></td>
<td>B₂(6)</td>
</tr>
</tbody>
</table>
The next band (at \( \approx 2420 \text{ cm}^{-1} \)) should, most probably, be attributed to the O–D stretching of the H(4)–O(\text{w3})–D(5)···O(1) grouping where the O(\text{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 2300–2000 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\(_2\)O molecules

In the RT and LNT infrared spectra of MgKPO\(_4\)·6H\(_2\)O, one broad, temperature-sensitive feature extending from around 2100 to 1350 cm\(^{-1}\) is found (Fig. 6). Of the 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\(_2\)O molecules in the structure of MgKPO\(_4\)·6H\(_2\)O although it is not easy to pair each of the submaxima with a given type of H\(_2\)O 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...
different explanations for their origin (e.g., appearance of second-order transitions perhaps combined with Fermi-resonance type interactions with the fundamental δ(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 δ(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 H2O molecules.

In the H–O–H bending region of the Raman spectra of MgKPO4·6H2O (Fig. 3), only a very broad and almost featureless band exists with a maximum around 1620 cm⁻¹.

3.2. External vibrations of H2O molecules

It is generally relatively easy to locate the infrared bands which are due to librations of the H2O molecules in the structure of a crystalline hydrate. As is well known, namely, apart from shifts on deuteration, the H2O 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 MgKPO4·6H2O (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 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 MgKPO4·6H2O. What actually complicates the situation is the fact that bands originating from vibrations of PO4³⁻ 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 ν3(PO4) 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 950–600 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 MgKPO4·6H2O 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
rather safe to attribute the enumerated bands to D$_2$O librations. At frequencies between those of the bands attributed to H$_2$O and to D$_2$O 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 $v_1$, $v_2$, $v_3$ and $v_4$ of which $v_1$ and $v_3$ are stretching and $v_2$ and $v_4$ are bending vibrations. All four modes are Raman active, whereas only $v_3$ (the antisymmetric stretching vibration) and $v_4$ (the antisymmetric bending vibration) are infrared active. The $v_3$ and $v_4$ modes are triply degenerate, $v_2$ is doubly degenerate and $v_1$ 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 MgKPO$_4$·6H$_2$O (Table 2) suggest high

| Deformation indices of the PO$_4^{3-}$ ion in MgKPO$_4$·6H$_2$O |
|-----------------|-----------------|-----------------|
| MgKPO$_4$·6H$_2$O | D(P–O) | D(O–P–O) | D(O–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 $v_1$ vibration is transformed to an infrared active $A'$ mode, the doubly degenerate infrared inactive $v_2$ vibration is changed into two infrared active components with $A'$ and $A''$ symmetry, while two components of each of the triply degenerate $v_3$ and $v_4$ 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 $v_3$ and $v_4$ modes, two from $v_2$ and one from $v_1$). 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 $v_1$ and $v_2$ phosphate bands should not be high$^1$.

The expectations are borne out. In the region of $v_2$(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. 9). 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 $v_3$(PO$_4$) and $\delta$(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 $v_2$ 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 \(\nu_3\) 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 \(\nu_1\) 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 \(\nu_1(\text{PO}_4)\) 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\(_2\)O and/or HOD librations have appeared. The above statement should not be taken as a firm rejection of the notion that the phosphate \(\nu_2\) mode in the deuterated samples may not be pure, but coupled with librations of the deuterated H\(_2\)O molecules. In the far infrared spectra of the almost completely deuterated compound (Fig. 11), bands due to D\(_2\)O librations, corresponding to the intensive one found at around 575 cm\(^{-1}\) in the spectra of MgKPO\(_4\)·6H\(_2\)O cannot be observed. Accordingly, the strong band at 574 cm\(^{-1}\) in the infrared spectra of protiated analogue cannot be assigned to H\(_2\)O librations. The asymmetric band can also hardly be attributed to \(\nu(\text{Mg}–\text{O})\) modes having in mind that the Mg–O bonding is not strong enough to cause so high frequency of the hindered rotation.

In the LNT Raman spectra of MgKPO\(_4\)·6H\(_2\)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 \(\nu_2\) modes of PO\(_4^{3-}\) ions if the latter are more or less pure. Accordingly, one intensive band due to D\(_2\)O 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\(_2\)O librations.

In this case, it seems reasonable to explain the situation by coupling and mixing of the \(\nu_2(\text{PO}_4)\) mode and D\(_2\)O 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 MgNH\(_4\)AsO\(_4\)·6-H\(_2\)O and its partially deuterated analogues, in the region of the \(\nu_2(\text{AsO}_4)\) mode, there are no bands from D\(_2\)O librations (or, at least, no oscillators ‘suitable’ for coupling appear in that region) and the band due to the \(\nu_2(\text{AsO}_4)\) 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

![Graph](image-url)
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 MgKPO$_4$·6H$_2$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 Mg–O vibrations.$^2$

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 $\sigma(\text{Mg–O})$ modes.

Several bands are observed in the region between 400 and 250 cm$^{-1}$ in the Raman and far-IR spectra of MgKPO$_4$·6H$_2$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 Mg–O modes.

Acknowledgements

The investigation has been supported by funds from the Project MAK-002-97 by the German Federal Ministry of Education and Research, Federal Republic of Germany and by the Ministry of Education and Science, Republic of Macedonia. The financial support is sincerely appreciated by the authors. The authors are very grateful to Professor V.M. Petruševski, Ass. Professor Lj. Pejov and Dr M. Zugik for the helpful discussions.

References


$^2$ Bands with similar shape and intensity which appear at 448 and 428 cm$^{-1}$ in the spectrum of dittmarite MgNH$_4$PO$_4$·H$_2$O have been attributed to the $\nu_2(\text{PO}_4)$ modes [19].