INFRARED AND RAMAN SPECTRA OF MAGNESIUM AMMONIUM PHOSPHATE HEXAHYDRATE (STRUVITE) AND ITS ISOMORPHOUS ANALOGUES.

V. VIBRATIONAL SPECTRA OF MAGNESIUM RUBIDIUM ARSENATE HEXAHYDRATE AND MAGNESIUM THALLIUM ARSENATE HEXAHYDRATE

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Polycrystalline samples of struvite-type MgRbAsO$_4$·6H$_2$O and MgTlAsO$_4$·6H$_2$O in both protiated and deuterated forms have been prepared for the first time by a precipitation method. Detailed analysis of their infrared (IR) and Raman (R) spectra recorded at room temperature (RT) and liquid nitrogen temperature (LNT) has been carried out and assignment of the vibrational bands has been proposed. The observed spectral pictures confirm the isostructurality of the two arsenate salts in agreement with the structural data. Similarly to other struvite-type and structure-related arsenate salts, the $v_1$(AsO$_4$) modes appear at higher frequencies than the $v_3$(AsO$_4$) vibrations. Low intensity and temperature sensitive bands that could be assigned as due to stretching Mg–O vibrations and $v_4$(AsO$_4$) modes are observed below 500 cm$^{-1}$ in the LNT IR spectra of the studied compounds, at 472 cm$^{-1}$ and 445 cm$^{-1}$ for the rubidium analogue and at 470 cm$^{-1}$ and 440 cm$^{-1}$ for the thallium analogue. In the far-infrared and Raman spectra many bands are observed between 400 cm$^{-1}$ and 200 cm$^{-1}$, most of which are sensitive to deuteration, suggesting that they are not pure but coupled and can be related to $v$(Mg–Ow) modes. On the other hand, a band around 405 cm$^{-1}$ in the spectra of the protiated compounds most probably is due to $v_2$(AsO$_4$) mode because of its frequency position, intensity and slight sensitivity to deuteration.

Keywords: magnesium rubidium arsenate hexahydrate; magnesium thallium arsenate hexahydrate; infrared spectra; Raman spectra
na повисоки фrekvenции од $v_3(\text{AsO}_4)$. Лентите со послаб интензитет кои се температурно осветливени, а во инфрацрвениот спектр снимени на ниски температури се забележени под 500 cm$^{-1}$, може да се припишат на валентни Mg$^2+$–O вибрации и на модови на $v_2(\text{AsO}_4)$, на 472 cm$^{-1}$ и 445 cm$^{-1}$ за рубидиумовият аналог и на 470 cm$^{-1}$ и 440 cm$^{-1}$ за таллиумовото аналого. Во спектрите снимени во далечната инфрацрвена област и во раманските спектри се забележуваат многу ленти помеѓу 400 cm$^{-1}$ и 200 cm$^{-1}$, од кои повеќето се чувствитиви на деутерирање, што сугерира дека тие не се чисти, туку спрегнати и можат да бидат поврзани со модовите на $v(\text{Mg}–\text{Ow})$. Од друга страна, поради нејзината фrekvenција, интензитет и мала чувствителност на деутерирање, лентата на околу 405 cm$^{-1}$ во спектрот на протонираниот соединенија најверојатно се должи на модовите на $v_2(\text{AsO}_4)$.

Ключни зборови: магнезиум рубидиум арсенат хексахидрат; магнезиум талнум арсенат хексахидрат; инфрацрвени спектри; рамански спектри

1. INTRODUCTION

Magnesium ammonium phosphate hexahydrate, MgNH$_4$PO$_4$•6H$_2$O (often referred to by its mineralogical name struvite) is a well-known biomineral. Its major biological importance is related to its presence in human urinary sediments and vesical and renal calculi [1, 2]. Besides this, struvite presents a problem in sewage and wastewater treatment. Recovery of phosphorus from waste streams as struvite and recycling these nutrients into agriculture as a fertilizer appears to be a promising potential application [3–6]. More recently, Zhou et al. demonstrated that struvite-type/struvite-related phosphates are promising materials for nonlinear optical (NLO) applications [7]. For instance MgCsPO$_4$•6H$_2$O exhibited the strongest second harmonic generation (SHG) response among the reported UV NLO phosphates related to the presence of isolated and aligned PO$_4$ groups in the structure of the hexahydrate salt [7].

With this contribution we continue the study of the vibrational spectra of arsenate crystal hydrates with the general formula $M'MgAsO_4$·$6H_2O$ ($M' = \text{NH}_4$, K, Rb, Tl) having struvite-type or closely related structures which have been a subject of our research in the last fifteen years [8–13]. Here, we have focused on rubidium and thallium representatives, MgRbAsO$_4$·$6H_2$O and MgTlAsO$_4$·$6H_2$O that are very little known. To the best of our knowledge, besides the determination of their crystal structure [14] no other data about the title compounds were reported so far. The aim of the present paper is to report and interpret the infrared and Raman spectra of MgRbAsO$_4$·$6H_2$O and MgTlAsO$_4$·$6H_2$O and to give insights on the spectra-structure correlations.

The crystal structures of the title compounds have been determined from single crystal X-ray diffraction at room temperature [14]. They belong to the struvite-type family and crystallize in the orthorhombic system, space group $Pmn2_1$, with $Z =$ 2. The crystal lattice of both isomorphous compounds is built up from slightly distorted [Mg(OH)$_2$]$\text{AsO}_4$ octahedra, AsO$_4$ tetrahedra and [M$^2+$O$_{10}$] polyhedra (M$^+$, Mg$^{2+}$ and As$^{5+}$ lie on sites with $C_1$ symmetry) which are connected by an extensive network of hydrogen bonds. In the unit cell there are four crystallographically different water molecules of crystallization, two of which have $C_1$ symmetry, while the other two have $C_1$ symmetry. This results in the formation of seven different hydrogen bonds, six of them between the water molecules and the O atoms of the orthoarsenate groups, while the seventh one is between two water molecules, OW1 and OW2 following the notation given in ref. [14]. The former type of hydrogen bonds can be described as medium to strong ranging from 260.8 to 267.5 pm and 261.7 to 268.1 pm in the Rb and Tl compound, respectively. The latter type is the weakest hydrogen bond present in the crystal lattices with a distance of 313.9 pm in the rubidium compound, accordingly 308.2 pm in the thallium one. It should be mentioned that the hydrogen bond distances in the titled arsenates are very similar to these in MgKAsO$_4$·$6H_2$O determined at room temperature [9, 15]. Herein, we report the preparation of polycrystalline powders of MgRbAsO$_4$·$6H_2$O and MgTlAsO$_4$·$6H_2$O, their deuterated analogues and the subsequent spectroscopic analyses.

2. EXPERIMENTAL

In the literature there are no reports on the synthesis of polycrystalline powders of MgRbAsO$_4$·$6H_2$O and MgTlAsO$_4$·$6H_2$O. In this regard, we have designed a precipitation procedure which is similar for the two arsenate salts. The first stage includes mixing of a solution of rubidium chloride or thallium nitrate (10 cm$^3$ with $c = 0.1$ mol/dm$^3$) with a solution of rubidium chloride or thallium nitrate (in both cases 10 cm$^3$ with $c = 0.2$ mol/dm$^3$). Then,
with continuous stirring, solutions of magnesium sulfate (10 cm³ with \( c = 0.25 \text{ mol/dm}³ \)) and sodium hydroxide (10 cm³ with \( c = 0.1 \text{ mol/dm}³ \)) were successively added. The synthesis was carried out at room temperature. It is interesting to note that in the case of MgRbAsO₄·6H₂O synthesis, the precipitation process started with the addition of MgSO₄ solution, while for the MgTlAsO₄·6H₂O synthesis, the precipitation occurred only after the addition of NaOH solution. The beakers containing the respective precipitate and mother liquor were sealed with parafilm and were left in a refrigerator at 5 °C. After 5 days of aging the precipitates they were filtered and washed carefully with a small volume of water and a mixture of water/ethanol/acetone (a volume ratio of 1:3:1). The synthesized compounds were dried on the Büchner funnel in an air flow and then at room temperature for 2 hours.

The deuterated analogues were prepared in an analogous procedure as the protiated compounds using H₂O-D₂O mixtures of appropriate composition instead of H₂O.

The infrared spectra of the protiated and deuterated forms of the studied compounds were obtained using the Perkin-Elmer System 2000 infrared interferometer in the 4000–200 cm⁻¹ region with a resolution of 2 cm⁻¹. Both pressed KBr disks and Nujol mulls at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) were used with 32 spectra being accumulated and averaged. Significant changes were not observed in the spectra recorded in the two matrices: KBr and Nujol mull. LNT spectra were recorded using a low-temperature cell Graseby Specac P/N 21525 with KBr windows. Far infrared spectra were obtained using Nujol and polyethylene pellets.

Raman spectra were recorded at room temperature using a micro-Raman spectrometer LabRam 300 (Horiba Jobin-Yvon). This instrument was equipped with two lasers: He–Ne laser operating at 633 nm (6 mW power on sample) and a double frequency Nd:YAG laser at 532 nm (5 mW power on sample). A microscope Olympus MPlanN with magnification of 50 and 100 was also used. The spectra were recorded with a resolution of 2 cm⁻¹ and acquisition times between 10 and 40 s, with 15–30 scans. The GRAMS ANALYST 2000 software package was used for spectra acquisition [16] and GRAMS 32 [17] for spectra management.

X-ray diffractograms of the powder samples of the investigated compounds were recorded and analyzed to confirm the identity of the synthesized products. A Rigaku Ultima IV powder X-ray diffractometer (CuKα radiation) was used for the X-ray powder diffraction (XRPD) measurements. Each sample was manually dispersed over a silicon sample plate and the data were collected at room temperature on a D/tex detector in the 2θ range from 5 to 80° (scan rate 2°/min). CuKα radiation was obtained from a generator set at 40 kV and a current of 40 mA. The XRPD patterns (Fig. 1) are typical for the orthorhombic struvite-type arsenate compounds [9]. In addition, the experimental XRPD pattern of MgRbAsO₄·6H₂O matches all peaks in the reference pattern (PDF-044-0453).

![Fig. 1. Scattered intensities as a function of the diffraction angle in MgRbAsO₄·6H₂O (lower curve) and MgTlAsO₄·6H₂O (upper curve). (offset spectra are presented). Intensities in the above figure are in arbitrary units (Intensity / a. u.)](image)

3. RESULTS AND DISCUSSION

The infrared spectra of MgRbAsO₄·6H₂O and MgTlAsO₄·6H₂O recorded at RT and at boiling liquid nitrogen temperature (LNT) are given in Figures 2 and 3, and their Raman spectra recorded at RT are presented in Figure 4. The assignment of the IR and Raman bands to specific vibrational modes in the spectra of the two salts is given in Tables 1 and 2. As one would expect, the vibrational spectra of the studied two compounds recorded at RT and LNT are very similar due to their isotypism. In addition, they are very similar to the vibrational spectra of MgKAsO₄·6H₂O previously reported by our research group [9]. It should be mentioned here that MgKAsO₄·6H₂O undergoes a reversible phase transition at 263 K with a transformation from orthorhombic (Pmn₂₁) to monoclinic (P112₁) crystal system [15]. However, our spectroscopic data [9] revealed that this polymorphous transition does not significantly affect the appearance of the LNT IR spectra of the potassium analogue, which are still very much alike the ones obtained for MgRbAsO₄·6H₂O and MgTlAsO₄·6H₂O. The identical conclusion has been deduced for the spectra of the other related com-
pounds with formula $M^I M^{II} XO_4 \cdot 6H_2O$ ($M^I = NH_4, K, Rb, Cs, Tl; M^{II} = Mg, Co, Ni; X= P, As$) no matter if they crystallize in the orthorhombic, hexagonal, cubic or monoclinic system and/or correspondingly they have four, two or one crystallographically different water molecules of crystallization in their structure [8, 9, 13, 18-25]. The only difference that is evident in these spectra is in the region of the HOH librations and is dependent on the number of the crystallographically different water molecules of crystallization that exist in the structure and the type of the anion (phosphate or arsenate).

Fig. 2. Infrared spectra of MgRbAsO$_4 \cdot 6H_2O$ recorded at LNT (lower curve) and at RT (upper curve) (offset spectra are presented).

Fig. 3. Infrared spectra of MgTlAsO$_4 \cdot 6H_2O$ recorded at LNT (lower curve) and at RT (upper curve) (offset spectra are presented).

Fig. 4. Raman spectra of MgRbAsO$_4 \cdot 6H_2O$ (lower curve) and MgTlAsO$_4 \cdot 6H_2O$ (upper curve) recorded at RT (offset spectra are presented).
Table 1

Assignments of the vibrational bands in the IR and Raman spectra of MgRbAsO$_4$·6H$_2$O with their estimated intensities $^a$)

| 0 % D | about 95 % D | Assignments |
|-------|-------------|-------------|
| IR spectra | Raman spectra | IR spectra | Raman spectra |
| RT | LNT | RT | RT | LNT | RT |
| 3800–2100 vs, br | 3800–2000 vs, br | 3500–2200 w, br | Related to $\nu$(HOH) |
| 2700–1550 vs, br | 2700–1550 vs, br | 2600–2000 w, br | Related to $\nu$(DOD) |
| 2000–1350 m, br | 2000–1350 m, br | 1900–1350 vw, br | Related to $\delta$(HOH) |
| 1350–1000 m, br | 1350–1000 m, br | Around 1200 vw | Related to $\delta$(DOD) |
| 930 s | | 816 vs | 824 vs | $\nu$(AsO$_4$) |
| 900 s | 905 s | | L(H$_2$O) |
| 828 s | 830 s | | L(H$_2$O) |
| 735 w | 740 m | | L(H$_2$O) |
| 704 w | 710 m | | L(H$_2$O) |
| 810 vs | 810 vs | 815 s | 820 s | $\nu$(AsO$_4$) |
| 680 s | | 645 m | $\nu$(D$_2$O) |
| 590 m | | 570 m | $\nu$(D$_2$O) |
| 548 m | | 519 m | $\nu$(D$_2$O) |
| 470 vw | 472 w | 460 vw | 465 w | related to $\nu$(Mg–O) and/or $\nu$(AsO$_4$) |
| 442 vw | 445 w | 436 w | 436 vw | 435 w |
| 405 m | 413 w | 401 m | 403 vw | $\nu$(AsO$_4$) |
| 362 vw | 370 vw | 355 vw | 370 vw | $\nu$(Mg–O) |
| 303 m | 298 vw | 293 m | 288 vw | $\nu$(Mg–O) |
| 230 m | 234 vw | 225 m | 223 vw | $\nu$(Mg–O) |
| 210 m | | 205 m | $\nu$(Mg–O) |

$^a$) Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad, $\nu$: stretching, $\delta$: bending, L: libration
Table 2
Assignments of the vibrational bands in the IR and Raman spectra of MgTlAsO$_4$·6H$_2$O with their estimated intensities $^a$

| 0 % D | About 95 % D | Raman spectra | Assignments |
|-------|--------------|---------------|-------------|
|       |              | IR spectra    |             |
|       |              | LNT           | RT          |
| 3800–2100 | 3800–2000   | 3500–2200     | Related to ν(HOH) |
| vs, br  | vs, br       | w, br         |             |
|        |              |               | Related to ν(DOD) |
| 2700–1550 | 2700–1550    | 2600–2000     | Related to δ(HOH) |
| vs, br  | vs, br       | w, br         |             |
| 2000–1350 | 2000–1350   | 1900–1350     | Related to ν(HOH) |
| m, br   | m, br        | vw, br        |             |
|        |              |               | Related to ν(DOD) |
|        |              | 1350–1000     | Related to δ(HOH) |
| m, br   | m, br        | m, br         |             |
|         |              | 814 vs        | Related to ν(AsO$_4$) |
|         |              | 795 vs        | Related to ν(AsO$_4$) |
| 795 vs  | 795 vs       | 805 s         | Related to ν(AsO$_4$) |
|         |              | 675 s         | Related to ν(Mg–O) and/or ν(AsO$_4$) |
|         |              | 645 m         | Related to ν(Mg–O) and/or ν(AsO$_4$) |
|         |              | 580 m         | Related to ν(Mg–O) and/or ν(AsO$_4$) |
|         |              | 555 m         | Related to ν(Mg–O) and/or ν(AsO$_4$) |
|         |              | 510 m         | Related to ν(Mg–O) and/or ν(AsO$_4$) |
| 470 vw  | 470 w        | 460 vw        | Related to ν(AsO$_4$) |
| 440 vw  | 440 w        | 430 w         | Related to ν(AsO$_4$) |
| 405 m  | 413 w        | 402 m         | Related to ν(AsO$_4$) |
| 383 m  | 380 vw       | 375 m         | Related to ν(AsO$_4$) |
| 304 m  | 335 vw       | 293 m         | Related to ν(AsO$_4$) |
| 285 w  | 296 vw       | 273 w         | Related to ν(AsO$_4$) |
| 223 m  | 248 vw       | 219 m         | Related to ν(AsO$_4$) |

$^a$ Estimated intensities: s: strong, m: medium, w: weak, v: very, sh: shoulder, br: broad, ν: stretching, δ: bending, L: libration

3.1. Internal vibrations of water molecules

The available data is in agreement with the existence of four types of crystallographically different water molecules of crystallization in the crystal structures of the studied compounds [14].

The group theory considerations, previously reported for the orthorhombic struvite-type compounds [8, 9, 18–22, 24], imply that due to the existence of a static field three IR and three Raman active bands are expected from each type of water molecule. Furthermore, taking into account the correlation field, the number of the bands could be significantly increased.

A closer look in the stretching HOH region in the RT and LNT spectra of the titled compounds (Figs. 2–4) and the spectra of the compounds with formula M$^+$/M$^{ll}$/XO$_4$·6H$_2$O (M$^+$ = NH$_4$, K, Rb, Cs, TI; M$^{ll}$ = Mg, Co, Ni; X = P, As), no matter the crystal system [8, 9, 13, 18–25], in the region between 3800 cm$^{-1}$ and 2200 cm$^{-1}$ in the IR spectra and between 3500 cm$^{-1}$ and 2200 cm$^{-1}$ in the Raman spectra, one wide and asymmetric band with many shoulders is observed that is more intensive in the IR spectra and is sensitive to deuteration (Figs. 2–4). This is clearly a result of overlapping of several bands resulting in such a wide and asymmetric band. All of these bands are due to stretching vibrations of water molecules and/or are related to them. The position and the width of this asymmetric band infer that medium to strong hydrogen bonds exist in...
the structure of the studied compounds which is consistent with the structural data. On the other hand, the sharp band with lower intensity at higher frequency (in general higher than 3450 cm\(^{-1}\)), suggests the existence of weaker hydrogen bonds in the systems, which is again in accordance with the structural data. Deuteration also affects these bands shifting them to lower frequencies (Fig. 5).

3.2. External vibrations of the water molecules

Comparison of the RT and LNT infrared spectra (Figs. 2 and 3) implies temperature sensitivity of all bands below 1000 cm\(^{-1}\). After a systematic analysis of the RT and LNT spectra of the protiated and partially deuterated forms of MgRbAsO\(_4\)·6H\(_2\)O (Figs. 2 and 6), as well as H\(_2\)O/D\(_2\)O isotopic shifts of the bands, we assigned the bands at around 930 cm\(^{-1}\), 900 cm\(^{-1}\), and some of the bands around 830 cm\(^{-1}\), 740 cm\(^{-1}\) and 710 cm\(^{-1}\) to the librational modes (Table 1). In the spectra of the thallium analogue (Figs. 3 and 7), the corresponding bands are assigned at around 930 cm\(^{-1}\), 900 cm\(^{-1}\), and some of the bands around 830 cm\(^{-1}\), 740 and 700 cm\(^{-1}\) (Table 2). Namely, all these bands in the spectra of both compounds are quite temperature sensitive (Figs. 2 and 3) and their intensities systematically decrease in the spectra of the deuterated analogues, when increasing the deuterium content (Figs. 6 and 7). Simultaneously, new bands appear which, in the spectrum of the rubidium analogue with highest deuterium content, have wavenumbers of 680 cm\(^{-1}\), 645 cm\(^{-1}\), around 590 cm\(^{-1}\) and 570 cm\(^{-1}\), 548 cm\(^{-1}\) and 519 cm\(^{-1}\), and in the spectrum of the thallium analogue the corresponding wavenumbers are 675 cm\(^{-1}\), 645 cm\(^{-1}\), around 580 cm\(^{-1}\), 555 cm\(^{-1}\) and 510 cm\(^{-1}\), values that are expected if these new bands are indeed due to D\(_2\)O librations.
Furthermore, the high frequencies of some H₂O librational bands arise from the considerable strength of the hydrogen bonds formed by the water molecules [26], which is in accordance with the structural data showing existence of water molecules involved in formation of strong hydrogen bonds [14].

In the Raman spectra of MgRbPO₄·6H₂O and MgTiPO₄·6H₂O recorded at RT, no bands with significant intensity are observed in the region from around 900 cm⁻¹ to 500 cm⁻¹ that could be attributed to librations of the water molecules (Fig. 4).

3.3. Vibrations of the arsenate ions

Free phosphate ions have tetrahedral symmetry i.e. T₄ symmetry. Four normal vibrational modes ν₁, ν₂, ν₃ and ν₄, exist for this type of groups, vibrations assigned as ν₁ and ν₃ being stretching, and ν₂ and ν₄ bending vibrations. All four modes are Raman active, and ν₃ (antisymmetric stretching vibration) and ν₄ (antisymmetric bending vibration) being IR active.

The group-theory considerations predict that the transformation of the symmetry type from T₄ to C₃ gives rise to nine bands in both infrared and Raman spectra corresponding to internal vibrations of the AsO₄³⁻ ion (three components of ν₁ and ν₄ each, two of ν₂ and one of ν₃). Moreover, due to the influence of the correlation field, a total of 15 infrared active and 18 Raman active bands would be expected.

In the region of the ν₁ modes in the LNT IR spectra of the studied compounds, one very intensive and asymmetric band with several shoulders (more prominent in the spectrum of the rubidum analogue) is observed at around 800 cm⁻¹ that is very sensitive to temperature and deuterium exchange (Figs. 2, 3, 6 and 7). It was previously discussed that some of these shoulders are due to HOH librations. In the IR spectrum of the analogue with the highest deuterium content this band is less asymmetric with a center at around 820 cm⁻¹ for the rubidium compound (Fig. 6) and 805 cm⁻¹ for the thallium analogue (Fig. 7). These bands can be with great certainty assigned to the ν₁(AsO₄) modes, whereas the less intensive bands to the ν₁(AsO₄) vibrations. In this region in the Raman spectra compounds one very intensive band appears at 816 cm⁻¹ and 814 cm⁻¹ for rubidium and thallium analogue, respectively, that is attributed to the ν₁(AsO₄) vibrations. In the spectra of the compounds with the highest deuterium content these bands become narrower and shift to higher wavenumbers, 824 cm⁻¹ and 821 cm⁻¹, respectively. This finding suggests that the ν₁ mode is not pure but probably coupled with a libration mode. In line with this hypothesis, as previously mentioned, the bands from the ν₁(AsO₄) appear at higher frequencies in the spectra of the analogues with higher deuterium content compared to ones for the protiated analogues.

It should be also noted that in both studied compounds, the ν₁(AsO₄) modes appear at higher frequencies than the ν₁(AsO₄) vibrations. The same spectral feature has been established in the vibrational spectra of orthorhombic MgNH₄AsO₄·6H₂O and MgKAsO₄·6H₂O [8, 9] and the cubic form of MgCsAsO₄·6H₂O [13], whereas for Mg₂KH(AsO₄)·15H₂O it was found that both ν₁(AsO₄) and ν₃(AsO₄) modes have practically the same wavenumbers at around 830 cm⁻¹ [11]. This finding is consistent with spectroscopic studies on different arsenate compounds (natural and synthetic) [27–31]. This spectroscopic behavior of ν₁ and ν₃ modes of AsO₄³⁻ is opposite to the commonly observed for other XO₄ tetrahedral groups where the ν₁ wavenumbers are lower than the ν₃ wave-numbers.
In the region below 500 cm\(^{-1}\) in the LNT IR spectra of the studied compounds, low intensity bands that are temperature sensitive are observed at 472 cm\(^{-1}\) and 445 cm\(^{-1}\) for the rubidium analogue and at 470 cm\(^{-1}\) and 440 cm\(^{-1}\) for the thallium analogue (Figs. 6 and 7). In the spectra of the partially deuterated analogues (Figs. 6 and 7) these bands are slightly shifted to lower frequencies with increasing the deuterium content. These bands could be assigned as due to stretching Mg–O vibrations and \(\nu_4(\text{AsO}_4)\) modes. In the far-infrared (Fig. 8) and Raman spectra (Fig. 9) of both studied compounds many bands are observed in the region between 400 cm\(^{-1}\) and 200 cm\(^{-1}\) most of which being sensitive to deuterium exchange, suggesting that they are not pure but coupled and can be related to \(\nu(Mg–Ow)\) modes. On the other hand, the band around 405 cm\(^{-1}\) in the spectra of the protiated compounds most probably originates from the \(\nu_2(\text{AsO}_4)\) modes because of its frequency position, intensity and slight sensitivity to deuteration.

4. CONCLUSION

There is a wealth of literature data regarding the analyses of the vibrational spectra of various phosphates, but much less data for the analogous arsenate compounds. The results from this study are a contribution to the understanding of the vibrational spectra of arsenate crystal hydrates with the general formula M\(^{I}\)MgAsO\(_4\)·6H\(_2\)O (M\(^{I}\) = NH\(_4\), K, Rb, Tl) having struvite-type or closely related structures. Here, the focus was on the very little known rubidium and thallium representatives, MgRbAsO\(_4\)·6H\(_2\)O and MgTlAsO\(_4\)·6H\(_2\)O. It has to be pointed out that in their vibrational spectra the \(\nu_1(\text{AsO}_4)\) modes appear at higher frequencies than the \(\nu_3(\text{AsO}_4)\) modes as in the other previously studied arsenate crystal hydrates. It has also been shown that \(\nu_1(\text{AsO}_4)\) and \(\nu_3(\text{AsO}_4)\) vibrations are not pure but there is probably coupling between them and/or with some water librational modes. The librational modes appear at quite high frequencies showing existence of strong hydrogen bonds involving water molecules in agreement with the structural data.

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