

Fourier transform infrared and Raman spectra of manganese hydrogenphosphate trihydrate

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Abstract

The FTIR spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ and a series of deuterated analogues and the Raman spectrum of the protiated compound were recorded and analyzed. The O–H stretchings of the HPO_4^{2-} ions give rise to a complex feature (the A,B,C trio) of which only the two former components are clearly visible, the third component (C) possibly contributing to the breadth of the bands in the H–O–H bending region and/or the appearance of multiple bands in this region. The P–O–H in-plane bending can be identified with certainty, whereas the assignment of the P–O–H out-of-plane bending is somewhat tentative. The spectrum of water in the stretching region is simpler than expected. Only two bands of considerable intensity are observed in the $\delta(\text{HOH})$ region, although three different types of water molecules are present in the structure. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Continuing our recent studies on the vibrational spectra of hydrogenphosphates [1–3] we now summarize the results of our investigation of the Fourier transform (FT) infrared spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ and of its partially deuterated analogues recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) as well as of its FT Raman spectrum recorded at room temperature. The infrared spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$, its magnesium analogue and their completely deuterated compounds recorded at room and low temperature, as well as the room temperature Raman spectra

of the protiated compounds were previously studied by Pechkovskii et al. [4]. Previously we published a brief account of our study on the vibrational spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ [1] and, recently, a more detailed analysis of the O–H stretching region in the FT infrared and Raman spectra of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and its partially deuterated analogues¹ [2]. As it is well-known, the study of the partially deuterated analogues, especially those containing isotopically isolated HOD molecules (in such a case, the correlation-field effects are eliminated) is particularly valuable when the spectrum of water is the point of interest. If the half-deuterated water molecules are surrounded practically exclusively by their H_2O counterparts, i.e. if only slightly deuterated samples

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¹The report on the results of the analysis of the spectrum of newberite in the region below 2000 cm^{-1} is in preparation [3].

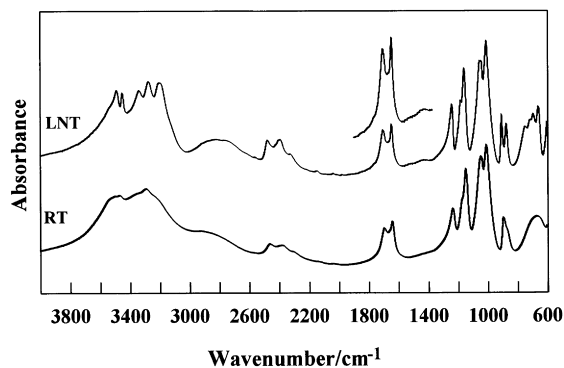


Fig. 1. FTIR spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT).

are studied, suitable for studying is the O–D stretching region. On the contrary, if the isotopic isolation is accomplished by D_2O molecules, the O–H stretching region is to be studied. In the former case, the picture is even clearer if the method of differential spectroscopy is used and the spectrum of the protiated compound is subtracted from that of the analogue with small deuterium content².

The determination, by X-ray diffraction, of the crystal structure of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ [5] confirmed the hypothesis [6] that it is isomorphous with $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (newberyite). Both compounds crystallize in the orthorhombic system (space group $Pbca$) with eight formula units per unit cell. One type of hydrogenphosphate ions involved in the formation of quite strong hydrogen bonds (the O···O distance in the case of the manganese compound, calculated on the basis of the data of Cudennec et al. [5], is 261.7 pm) and three crystallographically non-equivalent types of water molecules forming H-bonds of various strength (one of them is bifurcated) exist in their structure [5,7]. In the structure of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ the $\text{O}_w \cdots \text{O}$ distances are 276.4 and 285.3 pm, 277.5 and 270.8 pm and, finally, 296.2 and 297.9/319.2 pm for the three types of hydrate water molecules respectively. All polyatomic units occupy sites with C_1 symmetry.

² The analogous procedure is impossible to apply to the O–H stretching region since it is virtually impossible to prepare samples with *all* protons being replaced by deuterons.

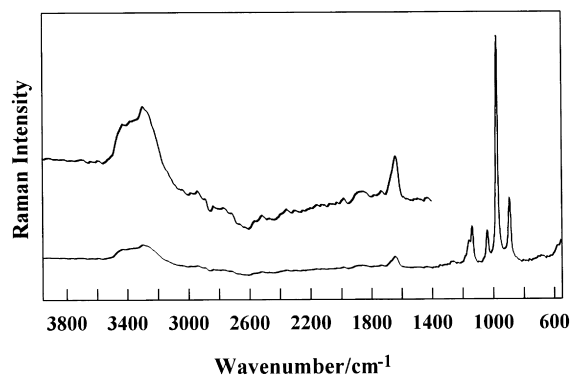


Fig. 2. FT Raman spectrum of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ recorded at room temperature.

2. Experimental

The investigated compound was synthesized according to the method described by Cudennec et al. [5]. The deuterated compounds were prepared analogously, using $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures with an appropriate deuterium content.

The infrared spectra were recorded (from pressed KBr discs) on the infrared interferometer Perkin Elmer System 2000 FT-IR in the 4000 to 600 cm^{-1} frequency region, usually with a resolution of 4 cm^{-1} . The low temperature cell P/N 21525 (Graseby Specac) with NaCl windows was used for recording the infrared spectra at the boiling temperature of liquid nitrogen. The FT Raman spectra were recorded (with a resolution of 4 cm^{-1}) on a Perkin Elmer NIR FT-Raman 1700x instrument equipped with a Nd:YAG laser emitting at 1064 nm.

3. Results and discussion

The FT infrared spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ recorded at RT and LNT and its FT Raman spectrum (RT) are shown in Figs. 1 and 2, respectively.

As expected for a rather strongly H-bonded hydrogenphosphate, the anion O–H stretchings give rise to a complex infrared feature (A,B,C trio [8]) of which two components (centered around 2800 and 2400 cm^{-1}) are clearly visible (Fig. 1). The spectral picture is very similar to that observed in the spectra of the isomorphous magnesium analogue [2].

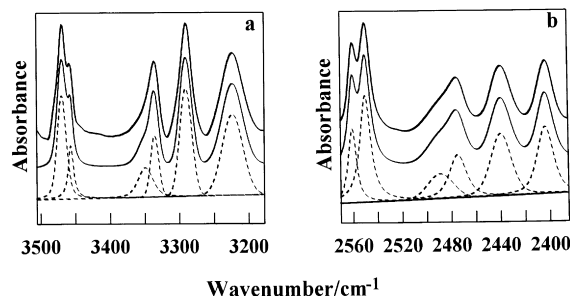


Fig. 3. The results of the curve-fitting procedure in the $\nu(\text{O-H})$ and $\nu(\text{O-D})$ regions in the spectra of samples containing isotopically isolated HOD molecules (**a** and **b** respectively).

In the water stretching region of the LNT infrared spectrum, *five* bands are observed, rather than at least *six* as expected having in mind the crystallographic data [5]. As second-order transitions may appear, besides the fundamental vibrations, in the same region and correlation-field splitting may also be present, the spectra look simpler than expected. The appearance of the feature in the analogous region of the RT Raman spectrum (Fig. 2) is similar to that in the RT infrared spectrum.

As can be seen (Fig. 3(a) and (b)) in the spectra of samples containing isotopically isolated HDO molecules, the picture is very similar in both the O–H and the O–D stretching regions but, again, only five maxima are observed. However, a curve-fitting procedure with *six* model functions of the Gauss–Lorentz type yielded a satisfactory reconstruction of the corresponding spectral regions. The frequencies of the component bands in the O–H stretching region were 3469, 3456, 3348, 3335, 3290 and 3223 cm^{-1} , and

those in the $\nu(\text{O-D})$ region were 2560, 2549, 2489, 2474, 2438 and 2403 cm^{-1} . The bands at the two highest frequencies are undoubtedly caused by the vibrations of the water molecules which form the weakest hydrogen bonds. Somewhat surprising (but, in a way, similar to the case of the magnesium analogue [2]), the intensities of the two highest frequency bands in the O–H and O–D stretching region are reversed (Fig. 3), implying a non-statistical deuterium-for-proton substitution with a preference for the oxygens involved in the formation of somewhat stronger hydrogen bonds. An altered intensity order of the corresponding bands in the O–H and O–D stretching region was found in the case of partially deuterated newberyite [2] but, judging from the intensities of the bands, in this case the oxygens involved in the formation of somewhat weaker hydrogen bonds seem to be “preferred” by deuterons.

In the water bending region of the IR spectra of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ recorded at room and at low temperature (Fig. 1), two bands (better separated in the LNT spectrum where their frequencies are 1700 and 1643 cm^{-1}) are observed with several additional maxima in the 1600–1400 cm^{-1} region (only one clearly visible band, at around 1640 cm^{-1} , is found in this region of the RT Raman spectrum). As *three* types of water molecules exist in the structure [5], at least three bands are expected in this region both in the IR and in the Raman spectrum and, in addition, the band C of the A,B,C trio is also expected in this region. A curve-fitting procedure using four components (Fig. 4), carried out for the 1740–1600 cm^{-1} region, could reconstruct the spectrum of the compound with the highest deuterium content (in such a case, the HOH molecules are isotopically

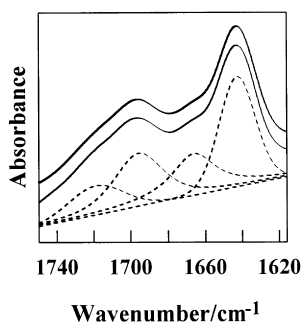


Fig. 4. The results of the curve-fitting procedure in the $\delta(\text{H-O-H})$ region in the spectrum of a sample containing isotopically isolated HOH molecules.

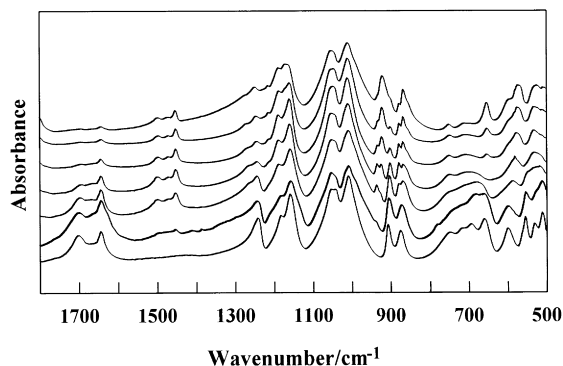


Fig. 5. The LNT infrared spectra of a series of partially deuterated analogues of $\text{MnHPO}_4 \cdot 3\text{H}_2\text{O}$ (the deuterium content, on going from bottom to top is 0%, 5%, 25%, 50%, 75%, 90% and 95%).

isolated with HOD and DOD molecules so that complications arising from correlation-field effects can be avoided). The broad peaks on the low-frequency side of the 1643 cm^{-1} peak (Fig. 1) were not taken into account. All together, the situation in the water bending region is, in some way, similar to that encountered in the case of brushite [9], $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ where *one* clear peak and several broad maxima on both sides of it are observed, although *two* types of water molecules are present in the structure. The somewhat tentative explanation of this finding is that one half of the water molecules give rise to *multiple* bands related to the H–O–H bending [9].

The appearance, in the spectra of partially deuterated analogues with varying deuterium content (Fig. 5), of HOD bending bands below 1550 cm^{-1} eliminates the possibility of H_3O^+ ions being present in the structure of this compound as suggested by Pechkovskii et al. [4] and, in the case of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, by Mioč and Minić [10]. Namely, if such ions do exist, bands from H_2DO^+ and HD_2O^+ should also appear in the spectra, which is obviously not the case.

The band at 1240 cm^{-1} in the infrared spectrum of the protiated compound is clearly a result of the HPO_4^{2-} $\delta(\text{P–O–H})$ vibration(s)³. The correctness of this assignment is confirmed by the spectra of the

³ Alternatively, this mode can be described as the in-plane bending of the hydrogen bond in the crystal. Similarly, the band denoted, in the text later, as out-of-plane P–O–H bending could be treated as the out-of-plane bending of the hydrogen bond.

partially deuterated analogues with different deuterium content recorded at LNT (Fig. 5). Namely, on going from the spectrum of the protiated compound to that of the analogue with the highest deuterium content, the band in question becomes continuously weaker, whereas at 924 cm^{-1} a new band appears which continuously gains in intensity and, surprisingly, shifts slightly to lower frequencies (in the spectrum of the compound with the highest deuterium content its counterpart is at 920 cm^{-1}). It should be noted that in the same region of the spectra of the partly deuterated analogues, a new band appears at around 940 cm^{-1} which, on increasing the deuterium content, at first gains in intensity and then disappears, a behaviour characteristic for HDO modes [11]. As the frequency is too high for a fundamental libration, the band must be caused by a second-order transition involving some HDO libration. When comparing the spectra given in Fig. 5 it should be borne in mind that in the case of samples with relatively high deuterium content bands due to D–O–D bending appear in the region around 1200 cm^{-1} .

In the infrared spectra of the protiated compound and its deuterated analogues the bands at 1182, 1158, 1058, 1052 and 1007 cm^{-1} have practically the same frequencies (Fig. 5), an indication that they are caused by P–O stretching vibrations localized mainly in the PO_3 part of the hydrogenphosphate ion. In the Raman spectrum (Fig. 2) of the protiated compound the P–O stretching bands are found at 1154, 1135, 1035 and 971 cm^{-1} , the frequency differences showing that the correlation field is rather strong. The P–O(H) stretch (to which we attribute the band at 905 cm^{-1}) behaves rather strangely on going from the spectrum of the protiated to the spectrum of the almost completely deuterated compound. Namely, the band at 905 cm^{-1} not only continually loses intensity and finally disappears, but the band remaining in the vicinity of 905 cm^{-1} shifts slightly towards lower frequencies. It should be pointed out that a similar situation was encountered in the case of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [9]. It is more difficult to follow the behaviour of the P–O(D) counterpart whose frequency in the spectrum of the practically completely deuterated sample is 866 cm^{-1} . In the room-temperature Raman spectrum of the protiated compound (Fig. 2) the P–O(H) stretching band is found at 889 cm^{-1} .

Again as in $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [9], to the $\gamma(\text{P}-\text{O}-\text{H})$ vibration we attribute the temperature and deuteration sensitive band at 873 cm^{-1} , the $\gamma(\text{P}-\text{O}-\text{D})$ band being found at 651 cm^{-1} (the isotopic ratio is 1.34).

In the region between 800 and 630 cm^{-1} in the IR spectra there is a complex feature, better resolved at LNT (Fig. 1). In the spectra of the partially deuterated analogues (Fig. 5) it gradually disappears on increasing the deuterium content which clearly shows that these bands are caused by librations of water molecules. As expected, in the Raman spectrum (Fig. 2) the intensity of the corresponding bands is very low.

Taken all together, we believe that the present assignment is a reliable one as it is based on a detailed analysis of the spectra of the protiated compound and its partially deuterated analogues recorded at different temperatures (from ambient down to LNT) with only the assignment of the $\gamma(\text{P}-\text{O}-\text{H})$ mode being somewhat tentative.

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