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Intercalation of Water into Anhydrous Vanadyl Phosphate Studied by the Infrared and Raman Spectroscopies

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The course of intercalation of water into α_I-VOPO$_4$ and its monohydrate has been studied by infrared and Raman spectroscopy. The mechanism of hydration has been proposed on the base of these measurements. No formation of vanadyl phosphate monohydrate was observed during hydration of the anhydrous form under ambient conditions. The vanadyl stretching band appears to be especially sensitive to atoms coordinated to the vanadium within an octahedral arrangement in the host lattice structure. During the intercalation its position at 1035 cm^{-1} in the anhydrous form changes to 995 cm^{-1}, typical for mono- and dihydrates. The additional peak at 1017 cm^{-1} occurring in the initial stages of intercalation has been explained by the random stacking of intercalated and nonintercalated layers in the sample. ©1999 Academic Press

INTRODUCTION

Compounds based on vanadyl phosphate are of great interest because of their oxidation catalytic properties. The structure of vanadyl phosphate dihydrate $VOPO_4 \cdot 2H_2O$ has been determined by Tietze using X-ray diffraction (XRD) (1) as tetragonal, space group *P*4/*nmm*, $a = 6.202$ Å and $c = 7.410$ Å. Tachez *et al.* (2) used neutron powder diffraction for deuterated compounds regarding the positions of hydrogen atoms and determined the space group *P*4/*n*, $a = 6.215$ Å and $c = 7.403$ Å. The layers are built up of PO$_4$ tetrahedra linked to distorted VO$_6$ octahedra by sharing the four equatorial oxygen atoms. The coordination number of VO$_6$ octahedron is completed by axial oxygen; one of them is a vanadyl oxygen, and the second one belongs to the interlayer water molecule coordinated to vanadium. The second water molecule is bonded by the weak H-bridges between layers. An anomalous thermal behavior of the vanadyl phosphate dihydrate has been found in the temperature range of 3–42°C, where the *c*-parameter decreases with increasing temperature, whereas the *a*-parameter remains constant (3). This behavior is explained by changes in hydrogen bonds.

Anhydrous vanadyl phosphate, VOPO$_4$, exists in several structural modifications: the layered α_I-and the slightly different α_{II}-modifications (4, 5), the three-dimensional structure of orthorhombic β-VOPO$_4$ (6), modifications γ-and δ-VOPO$_4$ (7, 8) with structures related to $(V^{IV}O)_2P_2O_7$ (9, 10), and recently described ε-VOPO$_4$ (11) related to β-modification. The most important of them is α_I-VOPO$_4$ ($a = 6.20$ Å, $c = 4.18$ Å), which is formed by dehydration of $VOPO_4 \cdot 2H_2O$. This modification has the layered structure and is most convenient for intercalation reactions. During dehydration the structure of the VOPO$_4$ layers remains unchanged; the coordination polyhedron of the vanadium atom is completed by oxygen from the adjacent layer. This vanadyl oxygen, because of its strong bonding to vanadium, is a relatively poor ligand for the vanadium in the adjacent layer and could be replaced by other molecules that are stronger ligands. Consequently α_I-VOPO$_4$ is a good host structure for the intercalation of convenient organic molecules. Intercalation compounds of vanadyl phosphate with aliphatic and aromatic amines (12–14), heterocycles (15), alcohols and diols (16), carboxylic acids (17), and their amides (18) have been studied. From this point of view, vanadyl phosphate dihydrate can be regarded as an intercalate of α_I-VOPO$_4$ with water. Vanadyl phosphate dihydrate also reacts with cations in the presence of a reducing agent changing the oxidation state of V(V) to V(IV) simultaneously (19–21).

The course of dehydration of $VOPO_4 \cdot 2H_2O$ has been studied by measuring the change of the thickness of the crystal across the layers during the heating (thermomechanical analysis, TMA), DTA and thermoelectric power (22), and XRD measurements (3). The interlayer water is released in two steps during the heating of $VOPO_4 \cdot 2H_2O$. The first molecule of water is liberated at 44°C producing

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the monohydrate with $c = 6.3$ Å. The second dehydration step occurs at 80°C. The time course of intercalation of water into α_I-$VOPO_4$ has been followed by TMA and XRD (23). Both methods did not show formation of monohydrate. During intercalation, the broadening and the shift of positions of the (00*l*) diffraction lines were observed (3). These phenomena were explained by formation of a Hendricks–Teller disordered layered structure which is composed of the α_I-$VOPO_4$ and $VOPO_4 \cdot 2H_2O$ layers.

Owing to the instability of the anhydrous $VOPO_4$ when exposed to air, the water molecules intercalate at room temperature by simply containing the compounds under ambient conditions. The course of intercalation of water molecules into anhydrous vanadyl phosphate and vanadyl phosphate monohydrate has been studied by infrared (IR) and Raman spectroscopy. The mechanism of the intercalation reaction of water molecules with deuterates $VOPO_4 \cdot 1D_2O$ and $VOPO_4 \cdot 2D_2O$ was compared with the direct hydration process of anhydrous $VOPO_4$. The aim of this work was to contribute to the elucidation of the mechanism of the intercalation of water in α_I-$VOPO_4$.

EXPERIMENTAL SECTION

Materials and Methods

Vanadyl phosphate dihydrate $VOPO_4 \cdot 2H_2O$ was prepared by the long-term boiling of V_2O_5 in aqueous phosphoric acids (24). Anhydrous compounds $VOPO_4$ were obtained by the dehydration of the corresponding hydrate at a temperature of about 300°C in vacuum for 4 h.

$VOPO_4 \cdot 2D_2O$ was prepared by the intercalation of D_2O vapor into anhydrous $VOPO_4$. Anhydrous vanadyl phosphate was kept over D_2O at laboratory temperature for two days. Vanadyl phosphate monohydrate was obtained by heating $VOPO_4 \cdot 2H_2O$ at 52°C for 2 h in vacuum. $VOPO_4 \cdot D_2O$ was prepared in a way similar from $VOPO_4 \cdot 2D_2O$ at room temperature. All pure phases (α_I-$VOPO_4$, $VOPO_4 \cdot H_2O$, $VOPO_4 \cdot 2D_2O$, $VOPO_4 \cdot D_2O$) were controlled by XRD using an HZG-4 diffractometer (Fraiberger Präzisionsmechanik, Germany). After the preparation, all the products were kept in closed evacuated ampules. Their structure was checked by XRD.

FTIR Spectroscopy

Infrared measurements were carried out using a Nicolet Impact 400 Fourier transform infrared (FTIR) spectrophotometer in a H_2O-purged environment. An ambient-temperature deuterated triglicine sulphate (DTGS) detector was used for the wavelength range from 400 to 4000 cm^{-1}. A Happ–Genzel apodization function was used in all regions and the spectral resolution was 2 cm^{-1}. Approximately 300 scans were coadded to achieve the signal-to-noise ratio shown.

The baseline horizontal attenuated total reflection (ATR) accessory with ZnSe crystal ($n = 2{,}4$ at 1000 cm^{-1}) was used for measurements of infrared spectra of the samples. The horizontal sample surface permits convenient acquisition of IR spectra with minimal sample preparation. The samples are not destroyed by milling and pressing as is the case of KBr pellets. The reactions with KBr and water, which occur usually in pellets, are eliminated. In our experiments the effective pathlength was approximately a few μm (angle of incident, 60°: number of reflections, 7). The ATR correction was made to eliminate the dependence of the effective pathlength on the wavelength. After some trials it was found that the best results were obtained if a sample is for a definite time exposed to the external conditions without removing the sample from the crystal between the subsequent spectral measurements. A special through sampling plate was used to minimize adsorption of water at the measured surface of the sample. The measurements of the vibration spectra of each compound were repeated five times using five different samples of the same material. No changes of the studied spectral features were observed between the results.

FT-NIR Raman Spectroscopy

FT Raman spectra were collected using a Fourier transform near-infrared (FT-NIR) spectrometer Equinox 55/s (Bruker) equipped with FT Raman module FRA 106/S (Bruker). The samples were irradiated by a focused laser beam with a laser power 100 mW of Nd-YAG laser (1064 nm, Coherent). The scattered light was collected in backscattering geometry. A quartz beamsplitter and Ge detector (liquid N_2 cooled) were used to obtain interferograms and 128 interferograms were co-added and then processed by the Fourier transformation with Blackman–Harris 4-term apodization a zerofilling factor 8 to obtain final FT Raman spectra in the range 4000 - (−1000) cm^{-1} with 4 cm^{-1} resolution.

The FT Raman spectra of pure well-defined species ($VOPO_4$, $VOPO_4 \cdot 1H_2O$, $VOPO_4 \cdot 2H_2O$, $VOPO_4 \cdot 1D_2O$ and $VOPO_4 \cdot 2D_2O$), were obtained in a sealed glass ampule. The glass ampule was placed in a sample holder and aligned by the motorized *x*-*y*-*z* sample stage to achieve the optimal optical condition of irradiation of the sample and of the collection of the scattered light. The FT Raman spectra collected during the intercalation of water were obtained from the samples placed in the aluminum cup. The aluminum cup was optically prealigned using sulfur as a sample, and then the sulfur was replaced by the particular sample studied.

RESULTS

Course of Intercalation of Water Molecules into $VOPO_4$ and $VOPO_4 \cdot 1H_2O$

The spectrum of the anhydrous vanadyl phosphate α_I-$VOPO_4$ (0 min.) and its progressive intercalates with

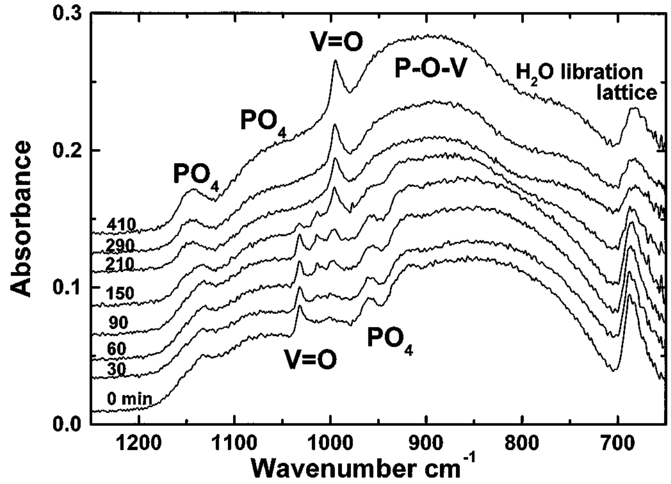


FIG. 1. The ATR infrared spectrum of anhydrous $VOPO_4$ and spectra upon a progressive hydration by water molecules under ambient conditions.

atmospheric water is given in Fig. 1. The last spectrum (410 min.) coincides with the spectrum of vanadyl phosphate dihydrate $VOPO_4.2H_2O$, which was prepared by the direct procedure described in Experimental section. The product is yellow with a slight green tint, indicating that the vanadium has not been significantly reduced (15, 21). The spectra of progressive intercalates of vanadyl phosphate monohydrate $VOPO_4.1H_2O$ are given in Fig. 2. The bands of vibrations of PO_4 tetrahedral, of the vanadyl group $V=O$, of the P–O–V group, and of the water molecules can be identified in the all spectra. The assignments of the vibration bands observed in the spectra of the anhydrous $VOPO_4$, monohydrate $VOPO_4 \cdot 1H_2O$, and dihydrate $VOPO_4 \cdot 2H_2O$ are presented in Table 1. The last three columns contain the assignments of the spectral bands of vanadyl phosphate dihydrate proposed by other authors (20, 21, 25) (the published data were mostly measured in KBr pellets). The stretching vibrations of OH groups of water molecules are given only in Table 1, as this part of the ATR spectra is too noisy for presentation. As the published interpretation of the bands is not unique, we have performed measurements of the vibration spectra of the mono- and dideuterate $VOPO_4 \cdot 1D_2O$ and $VOPO_4 \cdot 2D_2O$ and of the Raman spectra of all compounds. This allowed us a more precise interpretation of the obtained spectra (26).

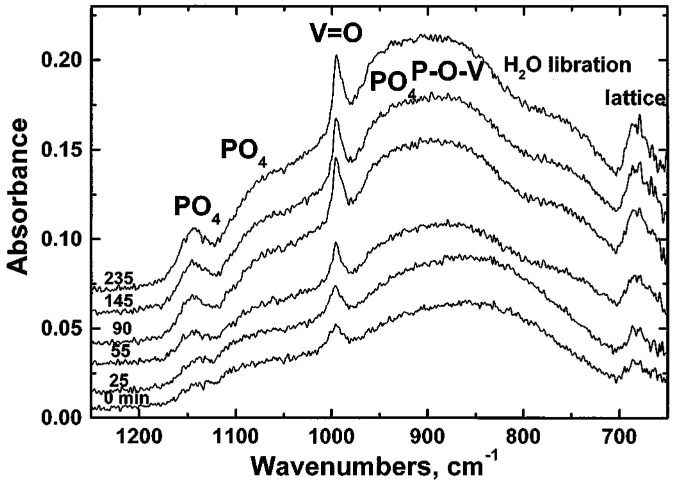


FIG. 2. The ATR infrared spectrum of $VOPO_4 \cdot 1H_2O$ and spectra upon a progressive hydration by water molecules under ambient conditions.

The Raman spectra of anhydrous vanadyl phosphate α_I-$VOPO_4$ and of its monohydrate (which is identical with the Raman spectrum of dihydrate) are given in Fig. 3. Unfortunately, it was not possible to measure the kinetics of the hydration process by Raman spectroscopy, because the partial escape of water molecules due to the laser beam occurred during the measurements. The spectra corresponding to the different stages of the sample hydration between the anhydrous form and the dihydrate form (spectra 1, 2, 3 in Fig. 3) were obtained by the regulation of the incident beam power and of the number of scans used. The antisymmetric $\nu_3(PO_4)$ vibration is not observed in the Raman spectra. In addition, the bands of symmetric bending vibrations $\nu_4(PO_4)$ at 579 and 541 cm^{-1} and bands of antisymmetric bending vibrations $\nu_2(PO_4)$ at 460 and 433 cm^{-1} are observed in the Raman spectra of samples. The bands at about 300 cm^{-1} belong, probably, to deformation δ (O–V–O) vibrations (25). Water libration modes observed at about 800 cm^{-1} in the infrared spectrum are inactive in the Raman spectra.

The analysis of the infrared spectra (Figs. 1, 2) and the Raman spectra (Fig. 3) give the following results:

- During the intercalation of water molecules the position of the band of vanadyl stretching vibration $V=O$ at 1035 cm^{-1} in the anhydrous form moves to 995 cm^{-1}, typical for mono- and dihydrate. The same shift was observed in the Raman spectra. A peak at 1017 cm^{-1} is observed in the first stages of intercalation.
- The band of symmetric stretching vibration $\nu_1(PO_4)$ is especially active in the Raman spectra and it is split into two maximums. These maximums change their profile during hydration. The analogous change is observed for the symmetric bending vibrations $\nu_4(PO_4)$ and antisymmetric bending vibrations $\nu_2(PO_4)$ and for δ (O–V–O) vibrations.
- The bands of the degenerate antisymmetric stretching vibration $\nu_3(PO_4)$ are active only in the infrared spectra (26) and the position of the bands is only slightly shifted under hydration.
- The broadened band in the infrared spectrum at about 920 cm^{-1} containing the mixture of overlapping bands

TABLE 1
The Assignments of the Observed Vibration Bands of $VOPO_4$, $VOPO_4 \cdot 1H_2O$, and $VOPO_4 \cdot 2H_2O$

Vibration	$VOPO_4$ anhydrous	$VOPO_4 \cdot 1H_2O$	$VOPO_4 \cdot 2H_2O$	$VOPO_4 \cdot 2H_2O$ (20)	$VOPO_4 \cdot 2H_2O$ (21)	$VOPO_4 \cdot 2H_2O$ (25)
$\nu_3(PO_4)$ antisymnetric stretch	1133 cm^{-1} 1075 cm^{-1} broad	1133 cm^{-1} 1075 cm^{-1} very broad	1130 cm^{-1} 1075 cm^{-1}	1182 1086 $\nu_3(PO_4)$		1072 F 1022 cp $\nu_{as}(P–O)$ 1160 cp
$\nu_1(PO_4)$ symmetric stretch	959 cm^{-1} 917 cm^{-1} 830 cm^{-1} very broad δ (P–O–V)	960 cm^{-1} 920 cm^{-1} 830 cm^{-1} very broad δ (P–O–V)	947 cm^{-1} 880 cm^{-1} broad δ (P–O–V)	ρ (H_2O) 950 cm^{-1} $\nu_4(PO_4)$ δ (P–V–O) 906 cm^{-1} $\nu_4(PO_4)$ or ρ r(H_2O)	940 cm^{-1}	900 cp ν(P–O) 940 TF ν (V=OH) 980 cm^{-1} ν(V=O)
Lattice	688 cm^{-1}	688 cm^{-1}	675 cm^{-1}	680	680 cm^{-1} δ (O–V–O)	860 cp 672 f δ (V–OH) or δ (P–OH)
V = O stretching	995 cm^{-1} 1031 cm^{-1}	995 cm^{-1}	995 cm^{-1}	1033 cm^{-1} 995 cm^{-1}	1030 cm^{-1}	
ρ (H_2O)				570 cm^{-1} $\rho w H_2O$		560 cp δ_{as} (O–P–O) 420 cp 395 F δ_s (O–P–O) 320 F δ_{as} (O–V–O)
ν_2 (H_2O)		1601 cm^{-1}	1607 cm^{-1}	1608 cm^{-1}	1620 cm^{-1}	1590 cm^{-1} 1620 cm^{-1}f δ (HOH)
				3136 cm^{-1} $\nu_1(H_2O{=}V)$	3150 cm^{-1} broad	
ν_1 (H_2O)	3592 cm^{-1} sharp	3294 cm^{-1} broad	3294 cm^{-1} broad 3100 cm^{-1} broad	3374 cm^{-1} ν_1 (H_2O)	3600 cm^{-1} sharp ν_1 ($H_2O{=}V$)	3180 cm^{-1} cp 3350 cm^{-1} cp 3520 cm^{-1} cp ν (OH)
ν_3 (H_2O)		3592 cm^{-1} sharp	3544 cm^{-1} sharp	3568 cm^{-1} $\nu_3(H_2O)$		3540 cm^{-1} ν(OH)
Libration H_2O			700–800 cm^{-1}			

Note. The last three columns contain the assignments proposed by other authors (20, 21, 25).

$\nu_1(PO_4)$, δ (P–O–V), and δ (H_2O) changes its profile during hydration. The analogous change is observed for the bands of δ (V–O–V) vibrations in the Raman spectra.

- We did not observe the spectrum corresponding to the vanadyl phosphate monohydrate during the intercalation of anhydrous vanadyl phosphate.

Replacement of D_2O Molecules in $VOPO_4 \cdot 1D_2O$ and $VOPO_4 \cdot 2D_2O$ by Water Molecules

The replacement of D_2O molecules by the molecules of atmospheric water appears in the monodeuterate $VOPO_4 \cdot 1D_2O$ and dideuterate $VOPO_4 \cdot 2D_2O$ when exposed to air. The changes of infrared spectra during this process are shown in Fig. 4. The infrared spectrum of monodeuterate $VOPO_4 \cdot 1D_2O$ (0 min.) is compared with its spectrum after 400 min. hydration when no more spectral changes are registered. Analogously, the infrared spectrum of dideuterate of $VOPO_4 \cdot 2D_2O$ (0 min.) is compared with its spectrum after 480 min. of progressive intercalation by water molecules. The Raman spectra of mono- and dideuterate of the vanadyl phosphate and its hydrates by atmospheric water are given in Fig. 5. Spectra (1) and (2) in Fig. 5 correspond to different stages of monodeuterate dried by the laser beam.

The analysis of the progressive hydration process of mono- and dideuterates gives the following results:

- Position of the band of vanadyl stretching vibration V=O remains constant when the D_2O molecules are replaced by the H_2O molecules.

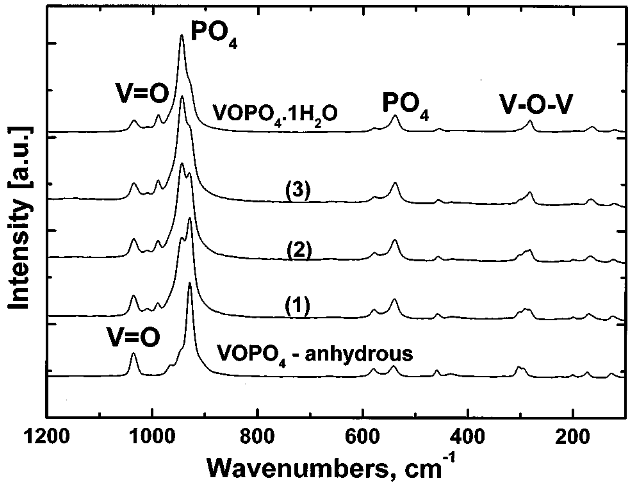


FIG. 3. The Raman spectra of $VOPO_4$, $VOPO_4 \cdot 1H_2O$ ($VOPO_4 \cdot 2H_2O$), and intermediate states of hydration.

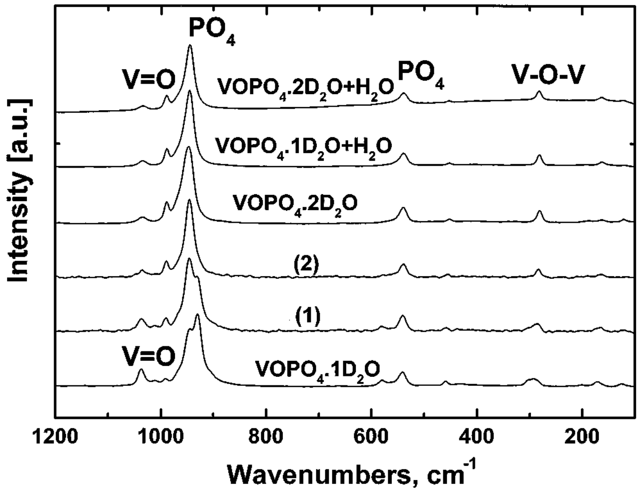


FIG. 5. The Raman spectra of $VOPO_4 \cdot 1D_2O$, $VOPO_4 \cdot 2D_2O$, and spectra upon a hydration by atmospheric water molecules.

- The shape and position of the $\nu_1(PO_4)$ and $\nu_3(PO_4)$ stretching vibrations of the pure monodeuterate slightly differ from that of the dideuterate. Some differences are observed also in the region of the δ (P–O–V) vibrations.
- In the course of hydration, the bands corresponding to the D_2O stretching vibrations in both deuterates vanish and bands of water libration and stretching modes gradually appear. These bands appear already in early stages of hydration.
- The equilibrium spectra obtained for both hydrated deuterates differs not only one from the other but also from the spectra of the corresponding hydrates. The difference is especially remarkable in the region of the δ (P–O–V) vibrations at 750–850 cm^{-1}.

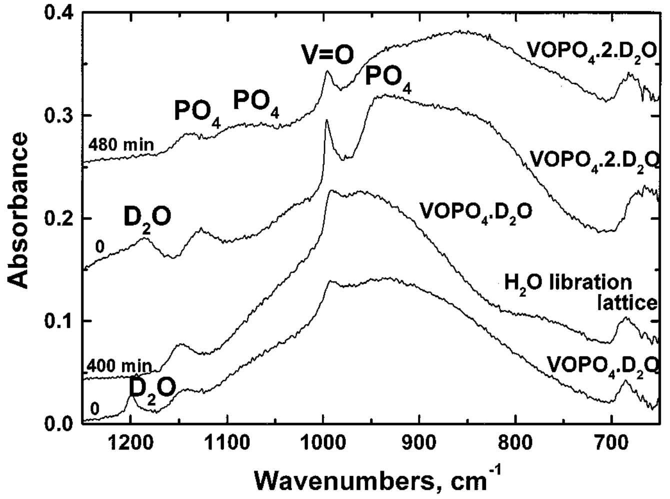


FIG. 4. The ATR infrared spectrum of $VOPO_4 \cdot 2D_2O$, $VOPO_4 \cdot 1D_2O$, and spectra upon a progressive hydration by atmospheric water molecules.

DISCUSSION

The arrangement of water molecules in the vanadyl phosphate dihydrate $VOPO_4 \cdot 2H_2O$ according to the structure data (27) is illustrated in Fig. 6. The first water molecule (W_1) is directly bonded to a vanadium atom completing its octahedron in an opposite position to the V = O short

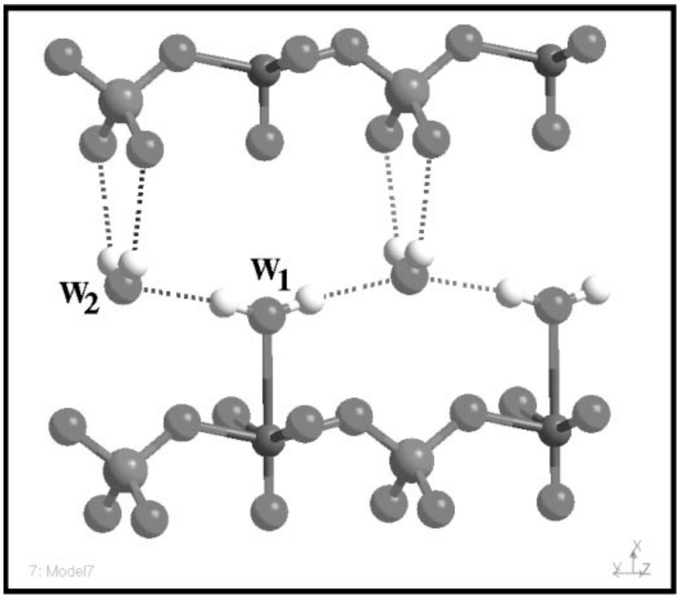
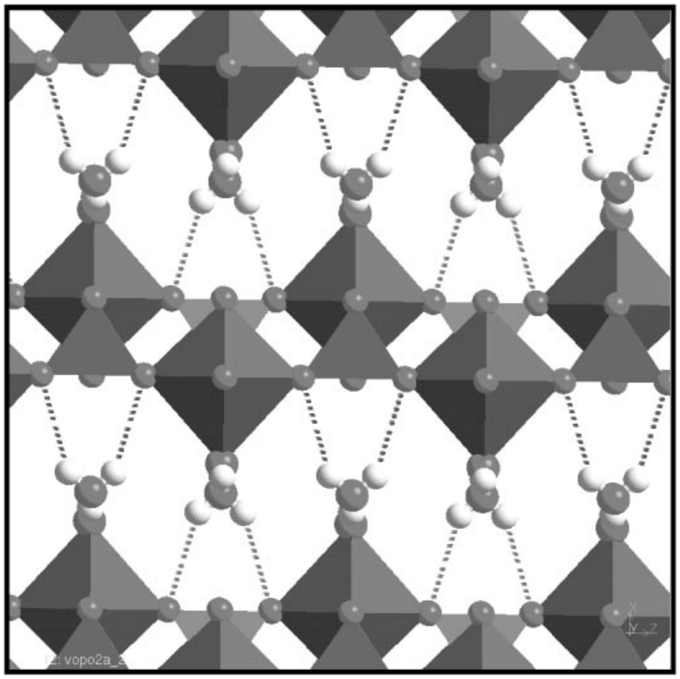
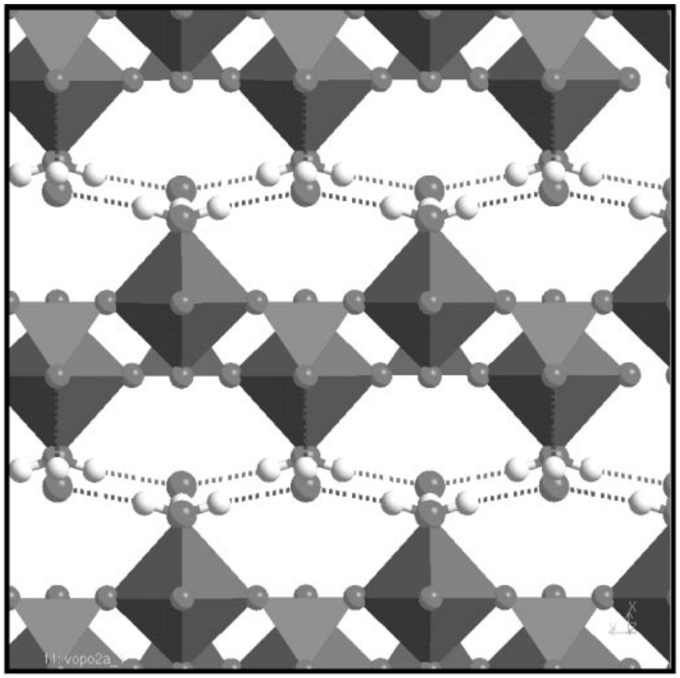


FIG. 6. Positions of water molecules adjacent to $VOPO_4$ layers in $VOPO_4 \cdot 2H_2O$.



(a)

FIG. 7a. The layered structure of $VOPO_4 \cdot 2H_2O$ showing the hydrogen bonding system between the second more loosely bonded water molecule and oxygen atoms of the PO_4 tetrahedron.



(b)

FIG. 7b. The layered structure of $VOPO_4 \cdot 2H_2O$ showing the hydrogen bonding system between two different types of water molecules.

bond. The network of hydrogen bonds is marked with dotted lines. One can see the regular system of hydrogen bonds W_2–O between the second more loosely bonded water molecule (W_2) and oxygen atoms (O) of the PO_4 tetrahedron (Fig. 7a) and the second hydrogen bond system W_2–W_1 between two distinct water molecules (Fig. 7b). The W_2–W_1 hydrogen bonds are weaker than the W_2–O bonds as it has been found in (3). Vanadyl phosphates with lower water content were prepared by dehydration of the $VOPO_4 \cdot 2H_2O$ at elevated temperatures in a vacuum. In this process the water molecules leave the host structure with the largest interlayer distance ($c = 7.403$ Å). At the first stage of dehydration, the second water molecule (W_2) escapes first and the monohydrate with interlayer distance $c = 6.3$ Å is created (22). It has been detected by XRD. Later, the water molecule W_1 escapes and the anhydrous vanadyl phosphate is created ($c = 4.2$ Å) (3).

The monohydrate infrared spectrum differs from the dihydrate one (see Fig. 2). The stretching vanadyl band is especially sensitive to the local coordination of a vanadium atom (18) and the shift of this band when we are going from anhydrous to hydrated form is explained by this fact. In the monohydrate and in the dihydrate the vanadyl band V$=$O remains in both the spectra at the same position (995 cm^{-1}), indicating coordination of the first W_1 molecule in vanadyl octahedron. The antisymmetric vibration band $\nu_3(PO_4)$ and the δ (P–V–O) vibration band with the maximum at about 830 cm^{-1} are slightly shifted to higher wavenumbers from the monohydrate to the dihydrate. These shifts indicate that the system of hydrogen bonding of W_2 to the oxygen of PO_4 tetrahedral affects its stretching and bending modes. The water libration modes at about 800 cm^{-1} are missing in the spectrum of vanadyl phosphate monohydrate, which supports the supposition that these libration modes belong to the second water (W_2) molecules. The Raman spectra of the mono- and dihydrate are nearly the same as the $\nu_3(PO_4)$, δ (P–O–V) and the water vibrations are not Raman active.

The spectrum of anhydrous vanadyl phosphate differs from the spectra of hydrates much more (see Fig. 1). The absence of water in the structure leads at first to a shift of the vanadyl band V$=$O to a higher wavenumber, 1031 cm^{-1}. In this compound $(VOPO_4)_n$ sheets are linked together by the coordination of oxygen atoms of the vanadyl group V$=$O in the vanadyl octahedron of the neighboring sheet. The presence of the symmetric stretching vibration band $\nu_1(PO_4)$ in the infrared spectrum is probably connected with the internal stress in the anhydrous sample leading to the deformation of the phosphorous tetrahedron. This band is very intensive in the Raman spectrum and the ratio of its two maximums is different in anhydrous and hydrated forms; in the course of the hydration process the two maximums overflow (see Fig. 3).

The changes of the infrared spectra during the intercalation of water into anhydrous vanadyl phosphate α_I-$VOPO_4$ are rather dramatic (Fig. 1). In the initial stages of the intercalation the existence of both positions of the vanadyl stretching band is observed: at the 1035 cm^{-1} corresponding to the anhydrous form and at 995 cm^{-1} indicating the coordination of the first molecule of water (W_1) to vanadium atom. Another peak is observed at 1017 cm^{-1}, belonging most probably to the vanadyl stretching band and indicating some other possibility of bonding of the first water molecule in the anhydrous starting material. We suppose that this peak corresponds to the vibration of the vanadyl group which connects the empty interlayer species with species filled with water molecules in adjacent layers. In the spectrum at 150 min. (Fig. 1) all three vanadyl peaks are observed at the same time when the water libration modes at about 800 cm^{-1} appear. As these libration modes are not present in the spectrum of vanadyl phosphate monohydrate, they must correspond to the second W_2 molecule bonded by weak H-bridges between layers. The spectrum of the pure monohydrate has never been observed. In agreement with the authors of Ref. (23) we assume that the layers of $VOPO_4 \cdot 2H_2O$ appear among the layers of α_I-$VOPO_4$ and $VOPO_4.1H_2O$ randomly in the crystal during the intercalation of water (the so-called Hendricks–Teller disordered layer lattice) (28). The intercalation of the water molecules W_2 follows the anchoring of the water molecules W_1 immediately and anhydrous, mono-, and dihydrate forms are observed simultaneously in the infrared spectrum. In the course of the intercalation the two higher maximums of vanadyl stretching vibrations disappear and the shape of the spectrum approaches the spectrum of vanadyl phosphate dihydrate. During the hydration process the band of the antisymmetric $\nu_3(PO_4)$ vibration shifts to the higher wavenumber together with the observation of the water libration modes which demonstrates the influence of the system of hydrogen bonding of second W_2 water molecules to PO_4 oxygens on PO_4 stretching and bending modes. The existence of the three different positions of the vanadyl stretching bands in the Raman spectra confirm the simultaneous presence of anhydrous and hydrate forms in all phases of the intercalation.

The study of the replacement of D_2O molecules by atmospheric water using vibration spectroscopy strongly supports the interpretation of water libration modes at about 800 cm^{-1} in the infrared spectrum of the vanadyl phosphate dihydrate as they are missing in the deuterates (see Fig. 4). The position and shape of D_2O bending vibration bands are slightly different in the spectrum of monodeuterate and dideuterate. The sharp maximum at about 1200 cm^{-1} is observed in monodeuterate and a broad maximum at about 1180 cm^{-1} with a shoulder at 1200 cm^{-1} is observed in dideuterate. It is connected with the existence of two differently bonded D_2O molecules. Bands of the stretching vibration of D_2O in the dideuterate have the same shape as that of H_2O in dihydrate (see Table 1). In agreement with the authors of Ref. (21) the sharp bands near 3600 and 1620 cm^{-1} in the spectrum of $VOPO_4 \cdot 2H_2O$ are due to the water molecules W_1 which are strongly bonded to vanadium atoms. The additional lattice water molecule (W_2) is indicated by the broadband near 3300 and 1620 cm^{-1} in the spectrum of the dihydrate. In the bending vibration at 1620 cm^{-1}, sharp and broad bands are superimposed. In the spectrum of $VOPO_4 \cdot 2D_2O$ these bands are only shifted to the lower wavenumbers: a broadband at about 2450 cm^{-1}, a sharp maximum at about 2650 cm^{-1}, and a shoulder at 2300 cm^{-1} (this part of the spectrum is not shown in Fig. 4). Positions of the D_2O bands in vanadyl phosphate deuterates indicate that D_2O molecules in $VOPO_4 \cdot 2D_2O$ are bonded in the same way as the H_2O molecules in $VOPO_4 \cdot 2H_2O$.

CONCLUSIONS

A progressive intercalation of atmospheric water molecules into anhydrous vanadyl phosphate α-$VOPO_4$ and monohydrate $VOPO_4 \cdot 1H_2O$ has been studied by ATR FTIR spectroscopy. In contrast to the deintercalation, the intercalation of water is not a two-step process. The spectrum of the pure monohydrate was not observed. Molecules of water probably fill the interlayer space randomly, creating a Hendrick–Teller disordered layer lattice which is composed from α_I-$VOPO_4$, $VOPO_4 \cdot 1H_2O$, and $VOPO_4 \cdot 2H_2O$ layers. The Raman spectra support the interpretation of vibration modes of a PO_4^{3-} ion in the IR spectra and the simultaneous existence of anhydrous and hydrated domains in the first stages of intercalation. Study of the replacement of D_2O by H_2O in $VOPO_4 \cdot 1D_2O$ and $VOPO_4 \cdot 2D_2O$ confirmed the interpretation of H_2O libration modes in the IR spectra of hydrates.

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