Polarized Raman and infrared vibrational analysis of (VO)$_2$P$_2$O$_7$ single crystals

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Received 20 October 2000

Abstract

Single crystals of the low dimensional spin system compound (VO)$_2$P$_2$O$_7$ were studied by polarized Raman spectroscopy and FT-IR spectroscopy in the spectral range 100–1400 cm$^{-1}$. Characteristic groups of modes were compared with literature data of structurally related compounds. Though some differences to vibrational spectra of the referred compounds were detected, we achieved a satisfactory assignment of most of the high-energy modes to vibrations of the P$_2$O$_5$ polyhedra and the VO$_5$ pyramids. In particular, we report the observation of an unusual softening of the prominent V=O vibration which we explain by the interlayer interaction of neighboring V and O atoms—an effect, which has been observed in NaV$_2$O$_5$, as well. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 63.20. − e; 63.20.Ry; 63.22. + m

Keywords: Raman spectroscopy; Infrared spectroscopy; Single crystals; (VO)$_2$P$_2$O$_7$

1. Introduction

Vanadyl pyrophosphate ((VO)$_2$P$_2$O$_7$) as a low dimensional spin system is subject to current interest because of the magnetic properties of its V$^{4+}$ sublattice. Initially it has been proposed to possess model character for a two-legged Heisenberg spin ladder by, among others, Johnston et al. [1] and was investigated theoretically by Barnes and Riera [2]. Subsequent investigations revealed that the magnetic properties are dominated by alternating antiferromagnetic spin-$\frac{1}{2}$ chains along the crystallographic $b$ direction [3,4].$^1$ Meanwhile, most observation support the model of two independent alternating antiferromagnetic spin-chains, which gives a plausible explanation for the second excitation first observed in inelastic neutron scattering experiments [3]. In Ref. [5] we report on the observation of the second spin-gap by Raman scattering and thus could resolve a discrepancy.

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$^1$Throughout this paper we denote the crystal axes in accordance with Ref. [8], i.e. the longest edge of the crystallographic unit cell is the $b$ axis.
A coupling of the spin system to the lattice vibrations was reported in Ref. [6] for three phonons in the low-energy region. Grove et al. observed an anharmonicity in the temperature dependence of the phonon frequency, which they attributed to the interaction of phonons with the spin system for phonon energies below the maximum of the magnon dispersion at \( \sim 15.5 \text{ meV} \) (125 cm\(^{-1}\)). The details of the spin-phonon coupling in (VO\(_2\))P\(_2\)O\(_7\) are, however, not yet cleared up. A full analysis of all phonons in the large unit cell, to our knowledge, has not been performed before.

Recently, single crystals of macroscopic size have become available [7], and we report polarized and depolarized Raman spectra as well as infrared phonon spectra from all three crystal surfaces. Based on a full group-theoretical analysis and on a comparison to known compounds with similar bonds we are able to assign the modes in the high-energy region (\( > 550 \text{ cm}^{-1}\)) of the compound. The structure of (VO\(_2\))P\(_2\)O\(_7\) was first published by Gorbunova and Linde et al. [8]. The crystallographic unit cell comprises 8 formula units of (VO\(_2\))P\(_2\)O\(_7\). The compound consists of chains of VO\(_5\) polyhedra, which are linked along the \( b \)-axis through the terminal bonds of P\(_2\)O\(_4\)\(^{2-}\) double-polyhedra (Fig. 1). The P\(_2\)O\(_4\)\(^{2-}\) connect these chains in [100] direction via their P-O-P bridging bonds to a three dimensional structure.

### 2. Experimental procedure

The (VO\(_2\))P\(_2\)O\(_7\) sample, a single crystal with a size of approximately 1 mm\(^3\), was prepared as described by Prokofiev et al. [7]. Polarized Raman spectra were recorded with a DILOR XY 800 triple spectrometer in combination with a liquid nitrogen cooled CCD. The spectral resolution was 1.3 cm\(^{-1}\), as excitation we used the 5683 Å line of an Kr\(^{+}\) laser. The sample was mounted in a liquid helium bath cryostate and measurements were performed at 5 K and at room temperature. The room temperature IR-reflectivity spectra were recorded with a BRUKER IFS 66v fourier spectrometer, with the spectral resolution set to 2 cm\(^{-1}\). The IR spectra were Kramers–Kronig transformed and the phonon frequencies determined from the maxima in the imaginary part of the transform.

### 3. Factor group analysis

The crystal structure of (VO\(_2\))P\(_2\)O\(_7\) has been examined experimentally in several studies, and the general conclusion is that it belongs to the orthorhombic system Pca\(_2\)\(_1\), with eight formula units per crystallographic unit cell [8,9]. A detailed refinement of X-ray data by Nguyen et al suggests a monoclinic P2\(_1\) structure [10]. However, the differences between the structures are very small and presumably related to the crystal production process. An X-ray study on our samples which followed up the Raman measurements confirmed the orthorhombic Pca\(_2\)\(_1\) symmetry and thus justified the choice of...
Table 1
Summary of the factor group analysis of \((\text{VO})_2\text{P}_2\text{O}_7\). R, T, r and i.r. denotes rotations, translations, Raman active modes and IR active modes, respectively.

<table>
<thead>
<tr>
<th>Factor group species (C_{2v})</th>
<th>8 (\text{P}_2\text{O}_7) ((C_1) sites)</th>
<th>16 (\text{VO}) ((C_1) sites)</th>
<th>Optical modes</th>
<th>Acoustic modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Internal modes</td>
<td>External modes</td>
<td>Internal modes</td>
<td>External modes</td>
</tr>
<tr>
<td>(A_1 (r, \text{i.r.}))</td>
<td>42</td>
<td>6T, 6R</td>
<td>4</td>
<td>12T, 8R</td>
</tr>
<tr>
<td>(A_2 (r))</td>
<td>42</td>
<td>6T, 6R</td>
<td>4</td>
<td>12T, 8R</td>
</tr>
<tr>
<td>(B_1 (r, \text{i.r.}))</td>
<td>42</td>
<td>6T, 6R</td>
<td>4</td>
<td>12T, 8R</td>
</tr>
<tr>
<td>(B_2 (r, \text{i.r.}))</td>
<td>42</td>
<td>6T, 6R</td>
<td>4</td>
<td>12T, 8R</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>24T, 24R</td>
<td>48T, 32R</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 2
Correlation scheme for the internal modes of \(\text{P}_2\text{O}_5^-\) in \((\text{VO})_2\text{P}_2\text{O}_7\).

<table>
<thead>
<tr>
<th>Free ion symmetry (C_{2v})</th>
<th>Site symmetry (C_1)</th>
<th>Factor group symmetry (C_{2v})</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 (A_1)</td>
<td></td>
<td>21 (A_1 (r, \text{i.r.}))</td>
</tr>
<tr>
<td>4 (A_2)</td>
<td></td>
<td>21 (A_2 (r))</td>
</tr>
<tr>
<td>4 (B_1)</td>
<td></td>
<td>21 (B_1 (r, \text{i.r.}))</td>
</tr>
<tr>
<td>6 (B_2)</td>
<td></td>
<td>21 (B_2 (r, \text{i.r.}))</td>
</tr>
</tbody>
</table>

This symmetry for our factor group analysis. To obtain an overview over the phonon spectra we assumed the pyrophosphate polyhedra to possess \(C_{2v}\) point symmetry as a close approximation to the true structure. In the refinement of Ref. [10] this polyhedra has \(C_1\) point symmetry and would give us almost no information from the correlation scheme.

The factor group analysis was performed using the tables provided by Rousseau et al. [11] and is summarized in Table 1. The correlation scheme for the internal modes of the \(\text{P}_2\text{O}_7\) groups is given in Table 2. Without the external modes \((\text{VO})_2\text{P}_2\text{O}_7\) will possess 46 \(A_1\) + 46 \(A_2\) + 46 \(B_1\) + 46 \(B_2\) Raman-active vibrations with selection rules \(xx, yy, zz(A_1)\) and \(xy(A_2), xz(B_1), yz(B_2)\) and 46 \(A_1\) + 46 \(B_1\) + 46 \(B_2\) infrared-active vibrations with polarizations \(z, x, y\), respectively. Most of the observed Raman lines were found to coincide with IR lines, confirming the assignment of the structure to the noncentrosymmetric 29th space group.

4. Results and discussion

We base the assignment of the observed spectral features to vibrations of the \(\text{P}_2\text{O}_7\) and VO polyhedra on a comparison with structurally related materials. The phonon spectra of the pyrophosphate (diphosphate, \(\text{P}_2\text{O}_7\)) group was studied intensively in solution [12,13], in melted [14,15] and in crystalline compounds [16–21]. All authors accordingly found that the pyrophosphate vibrations are distributed with decreasing frequency in the order \(v_{\text{as}}\text{PO}_3 > v_s\text{PO}_3 > v_s\text{POP} > \delta\text{OPO} > \delta\text{POP}\), which was established by Bues et al. [14]. \(v_{\text{as}}\) and \(v_s\) refer to asymmetric and symmetric stretching vibrations of the terminal (\(\text{PO}_3\)) or bridge (\(\text{POP}\)) bonds, respectively; \(\delta\) refers to the corresponding-bond bending vibrations, which are naturally lower in frequency. The frequencies for each of these types of vibrations in different compounds are always within the same frequency range, so that an unambiguous assignment of the high-energy modes of \((\text{VO})_2\text{P}_2\text{O}_7\) is possible.

In comparison to the pyrophosphate group with 21 vibrational modes of the free molecule (symmetry \(C_{2v}\)) the diatomic vanadyl group exhibits only one stretching vibration, which in the crystal splits into four modes for all possible symmetries (see Table 1). Its frequency was found to depend on...
bond length as well as on crystalline surrounding. The vanadium atoms are situated in a pyramidal environment of oxygen atoms (Fig. 1). Its base is formed by the terminal oxygen atoms of the \( \text{P}_2\text{O}_7 \) groups and with the oxygen atom \( \text{O1} \) of the vanadyl group on top of the pyramid. The apical oxygen \( \text{O1} \) is bonded to the vanadium ion with a relatively short bond length of 1.57 \( \text{Å} \), whereas the base corner oxygens have distances to the vanadium atom of about 2\( \text{Å} \). The short bond is typical of the \( \text{V}=\text{O} \) vanadyl group which involves both \( \pi \) and \( \sigma \) bonding. This distorted pyramidal or octahedral environment, if we consider the apical oxygens \( (\text{O1}) \) of neighboring layers, too, with one short \( \text{V}=\text{O} \) bond is characteristic for other vanadium phosphor oxides and vanadates like \( \text{NaV}_2\text{O}_5 \). We will compare studies on those materials with our results and discuss differences in structure and frequency.

The Raman spectra of \( (\text{VO})_2\text{P}_2\text{O}_7 \), Fig. 2 displays an overview, revealed many lines which are concentrated in three energy regions. The most prominent peaks appear at \( 920 \text{ cm}^{-1} \) (see inset of Fig. 2). These peaks become weak \( (< 5\% ) \) in the depolarized geometries \( (xy, zx, yz) \), and we therefore assign them to \( \text{A}_1 \) symmetry. A second group of peaks is found in the high-energy region from \( 1050 \) to \( 1250 \text{ cm}^{-1} \), 3 of which are seen in \( \text{A}_1 \) scattering geometry and 13 in \( \text{A}_2, \text{B}_1 \) and \( \text{B}_2 \) geometries (Fig. 3). Below \( 500 \text{ cm}^{-1} \) we found a multitude

![Fig. 2. Raman spectra of (VO)\(_2\)P\(_2\)O\(_7\) at 5 K in A\(_1\) symmetry. Shown in the inset is an expanded view and a four line least squares fit to the largest peaks around 915 cm\(^{-1}\).](image)

![Fig. 3. High-energy part of the Raman spectra of (VO)\(_2\)P\(_2\)O\(_7\) at 5 K. These modes are due to the PO\(_3\) stretching vibrations in the P\(_2\)O\(_7\) polyhedra.](image)

![Fig. 4. Low-energy part of the Raman spectra of (VO)\(_2\)P\(_2\)O\(_7\) at 5 K.](image)
of lines in all scattering geometries (Fig. 4). The observed modes above 700 cm\(^{-1}\) are summarized in Table 3. Besides these main features weak structures were found at 800 and 1000 cm\(^{-1}\). We will first discuss the main Raman peaks at 920 cm\(^{-1}\) and then continue in descending order of frequency, beginning with the modes at 1200 cm\(^{-1}\).

The polarized IR reflection spectra showed a similar subdivision as observed in the Raman spectra (Fig. 5). The most intense peaks are in the region between 900 and 1300 cm\(^{-1}\), and several less intense peaks are observed below 650 cm\(^{-1}\). Differences were found in the position of the main peaks in \(x\), \(y\) and \(z\) polarizations, respectively. We performed a Kramers–Kronig transformation on these spectra to obtain the frequencies of the underlying phonon modes from the calculated absorbance and summarized the ones above 700 cm\(^{-1}\) in Table 3, as

<table>
<thead>
<tr>
<th>IR-reflectance</th>
<th>Raman shift</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x)</td>
<td>(y)</td>
<td>(z)</td>
</tr>
<tr>
<td>743w</td>
<td>750w</td>
<td>750vw</td>
</tr>
<tr>
<td>913vs</td>
<td>913vs</td>
<td>913vs</td>
</tr>
<tr>
<td>917vs</td>
<td>917vs</td>
<td>917vs</td>
</tr>
<tr>
<td>919w</td>
<td>919vs</td>
<td>919vs</td>
</tr>
<tr>
<td>926s</td>
<td>929vs</td>
<td>929vs</td>
</tr>
<tr>
<td>937vs</td>
<td>939w</td>
<td>939w</td>
</tr>
<tr>
<td>1062vs</td>
<td>1083w</td>
<td>1083w</td>
</tr>
<tr>
<td>1113m</td>
<td>1120m</td>
<td>1125s</td>
</tr>
<tr>
<td>1131vs</td>
<td>1137w</td>
<td>1137s</td>
</tr>
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<td>1147s</td>
<td>1146vs</td>
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<td>1172w</td>
<td>1170w</td>
<td>1170m</td>
</tr>
<tr>
<td>1188s</td>
<td>1196s</td>
<td>1196s</td>
</tr>
<tr>
<td>1200s</td>
<td>1200s</td>
<td></td>
</tr>
<tr>
<td>1219vs</td>
<td>1219vs</td>
<td>1214s</td>
</tr>
<tr>
<td>1242vs</td>
<td>1242vs</td>
<td></td>
</tr>
<tr>
<td>1262vs</td>
<td>1262vs</td>
<td></td>
</tr>
</tbody>
</table>

Intensity: vs very strong, s strong, m medium, w weak, vw very weak
peaks are most intense in can be seen in the expanded view in Fig. 2. All spectra of (VO)$_2$O$_7$ already published unpolarized IR data on (unpolarized) transmission spectrum of obtained a spectrum which is comparable to an well. Summing up these calculated absorbances we obtained a spectrum which is comparable to an (unpolarized) transmission spectrum of (VO)$_2$P$_2$O$_7$ and found good correspondence to already published unpolarized IR data on (VO)$_2$P$_2$O$_7$ and related compounds [21,22]. Comparing our measurements at 5 K and room temperature we found no evidence for a structural phase transformation. The phonon anomaly of the modes near 123 cm$^{-1}$ was confirmed although it was not quite as strong as in Ref. [6]. With the exception of the modes around 915 cm$^{-1}$ which will be discussed below, all other vibrational modes generally harden by less than 1% when lowering the temperature from 293 to 5 K.

4.1. VO vibrations

The strong Raman peak around 915 cm$^{-1}$ consists of four lines at 913, 917, 919 and 929 cm$^{-1}$, as can be seen in the expanded view in Fig. 2. All peaks are most intense in $xx$ polarization and less but equally intense in $yy$ and $zz$ polarizations (Fig. 3). The number of lines and the polarization fit well with the assignment of this mode to the stretching vibrations of the vanadyl groups, which are oriented along the $a$ crystal axis (Fig. 1). The splitting into four modes arises from the four slightly different crystal sites of the VO$_5$ pyramids in the large crystallographic unit cell. In crystalline V$_2$O$_5$ and alkali vanadates like LiV$_2$O$_5$ and NaV$_2$O$_5$ the related vibrations were found to exhibit frequencies at 994, 984 and 969 cm$^{-1}$, respectively [23–25]. Although the VO$_5$ pyramids are stacked in a similar way in the vanadates and in (VO)$_2$P$_2$O$_7$, the interlayer distance between the vanadium atom and the apical oxygen atom from neighboring layers (V–O1') is smaller in (VO)$_2$P$_2$O$_7$. This distance was found to influence strongly the vanadyl vibrational frequency, which was demonstrated by Loa et al. by Raman scattering under pressure on NaV$_2$O$_5$ [26,27]. They found that the frequency of the V=O bond weakens from 969 to $\sim$ 919 cm$^{-1}$ when applying a pressure of 15 GPa, in connection with a contraction of the $c$-axis and the decrease in the V–O1' interlayer distance from 3 to 2.3 Å. The increasing influence of the interlayer V–O1' bond effectively weakens the intralayer V=O1 bond which leads to the observed softening. In (VO)$_2$P$_2$O$_7$ at atmospheric pressure the distance is approximately 2.3 Å and the Raman frequencies match those in NaV$_2$O$_5$ under high pressure, thus confirming our assignment to the V = O stretching vibrations.

This picture is further supported by the observation of an up to now unreported anharmonicity of these modes as a function of temperature. Fig. 6 shows the relative frequency shift of two of the four modes between room temperature and 5 K. The two other ones which are not depicted show similar behavior. The modes exhibit a softening of 0.5% (about 5 cm$^{-1}$) upon cooling. Both the application of hydrostatic pressure on the crystal, as shown with NaV$_2$O$_5$, and the lowering of the temperature result in a contraction of the crystallographic unit cell. Hence through the decreasing layer distance the interlayer V–O1' bond influences increasingly the intralayer V=O1 bond, which in effect lowers the V=O1 mode frequency. (The observed frequency shift of about 5 cm$^{-1}$ corresponds to a specific shift of 0.017 cm$^{-1}$/K.) If we suppose this mechanism to work comparably in NaV$_2$O$_5$ and (VO)$_2$P$_2$O$_7$, a simple linear estimate would give a contraction of the crystallographic $a$-axis of 0.08 Å from room temperature to 5 K and thus give a linear thermal expansion coefficient of Fig. 5. Room temperature polarized far-infrared reflectivity spectra of (VO)$_2$P$_2$O$_7$ single crystals for the $E||a$, $E||b$ and $E||c$ polarizations. The symmetric P–O–P bond stretching vibration appears in $y$ and $z$ polarization and is marked by an asterisk.
activity should occur in the corresponding polarization, which can be seen in Fig. 5, upper panel. Therefore we assigned the strong band at 926 cm$^{-1}$ in the IR(x) spectra to the infrared active counterpart of the V = O vibration.

4.2. $P_2O_7$ vibrations

The asymmetric PO$_3$ terminal stretching vibrations ($v_{as}$PO$_3$) of the P$_2$O$_7$ group in different compounds are usually observed in the high-energy region from roughly 1050 to 1250 cm$^{-1}$. From the correlation of the free-ion symmetry to the factor group symmetry 32 asymmetric PO$_3$ stretching modes are expected in the Raman spectra, 8 in each of the symmetries $A_1$, $A_2$, $B_1$ and $B_2$, respectively, 24 of them being IR active as well. We observed 4 strong or medium intense modes in $A_1$, 3 in $A_2$ and 5 in $B_2$ symmetry, respectively. In the $y(\ast\ast)y$ scattering geometry we observed only 2 weak modes in $A_2$ symmetry, which may be due to the generally weaker scattering efficiency on this surface.

The IR spectra revealed 12 medium or intense peaks between 1100 and 1300 cm$^{-1}$. With the exception of the modes with the highest energy ($\geq 1219$ cm$^{-1}$), the majority of the observed vibrational frequencies are close to those of the Raman lines which supports the premise of the crystal structure not being centrosymmetrical. The number of observed Raman and IR modes is smaller than predicted by group theory. For obvious physical reasons (see for example Ref. [19]) it has been established that those vibrational modes of

$\alpha_0 \approx 3 \times 10^{-5}$ K$^{-1}$. This value, which has the same size as for other layered compounds,$^2$ could be proven by temperature dependent X-ray scattering, which we have planned for the future. Similar compounds were studied in Refs. [28–30]. Mahadevan et al. [21] examined Rb$_3$(VO)$_3$ (P$_2$O$_7$)$_2$ and CsVOP$_2$O$_7$. They observed the V=O stretching vibration at 978 cm$^{-1}$ in the Cs compound and at 913 cm$^{-1}$ in the Rb compound and related it to the different bond lengths of the apical oxygen of 1.592 and 1.606 Å, respectively. These numbers confirm both the plain dependence of the vibrational frequency on the V = O bond length and the influence of the crystal environment.

As the VO dipoles are almost entirely oriented along the $a$-axis of the (VO)$_2$P$_2$O$_7$ crystal, IR

$^2$For example the interlayer thermal expansion coefficient in graphite $\alpha_0 \approx 3 \times 10^{-5}$ K$^{-1}$ [32].
The factor group are strong in the Raman spectra, which are derived from totally symmetric vibrational modes of the free-ion and, vice versa, those are strong in the IR spectra, which are derived from antisymmetric free-ion vibrations. If we consider the correlation of the terminal stretching modes of the \( \text{P}_2\text{O}_7 \) polyhedra to the factor group symmetry, we find in \( A_1 \) symmetry (with the symmetry of the free-ion mode given in parentheses) \( 2v_s(A_1) \) and \( 2v_{as}(A_1) \) modes and the same numbers for the other symmetries allowed in the factor group. Whereas this argument holds reasonably for the region of the \( v_{as}PO_3 \) vibrations, where 3 stronger peaks could be observed in most scattering geometries, it fails for the region of the \( v_sPO_3 \) modes, where only weak peaks with less than \( \frac{1}{4} \) of the intensity of the \( v_{as}PO_3 \) vibrations could be observed. This is one of the remarkable differences of the spectra of \( (\text{VO})_2\text{P}_2\text{O}_7 \) in comparison to other compounds containing \( \text{P}_2\text{O}_7 \) groups. In the alkaline earth compounds \( \alpha\text{-Ca}_3\text{P}_2\text{O}_7, \alpha\text{-Sr}_2\text{P}_2\text{O}_7 \) and \( \alpha\text{-Ba}_2\text{P}_2\text{O}_7 \) the \( v_sPO_3 \) vibrations appear as dominant between 1050 and 1100 cm\(^{-1} \) [17], whereas the \( v_{as}PO_3 \) have lower intensities in the spectra. A similar picture is given by the Raman spectra of \( \text{Rb}_2(\text{VO})_3(\text{P}_2\text{O}_7)_2 \) [21] or \( \text{Fe}_2\text{P}_2\text{O}_7 \) [30].

Our observations concerning the intensities of the terminal stretching vibrations are supported by the unpolarized spectra of \( (\text{VO})_2\text{P}_2\text{O}_7 \) reported in Ref. [22], which—much less resolved—show a similar distribution of spectral features as our measurements.

In the IR spectra strong modes appear between 900 and 1000 cm\(^{-1} \) in \( x \) and \( z \) polarization, which we assign to the \( v_sPO_3 \) vibrations. Whereas this assignment is satisfactory for the \( z \) polarization, it is not free of ambiguity in the \( x \) polarization. Here we had expected the \( V=O \) vibrations assigned to the 926 cm\(^{-1} \) mode before as well as the asymmetric \( v_{as}POP \) bridge stretching vibration. In \( y \) polarization we observed only weak reflection structures in the spectral region under discussion. A possible explanation could be the strong anisotropy of the crystal structure along the \( b(y) \) and \( c(z) \) axis. The first is the direction of the alternating \( V^4+ \) chains and the anisotropy could result in different dipole moments for the \( v_{as}PO_3 \) vibrations along the \( b \) and \( c \) axis.

The \( vPOP \)-bridge bending vibrations are to a certain extent characteristic for the \( \text{P}_2\text{O}_7 \) polyhedra, since in the free-ion symmetry \( C_{2v} \), there is only one symmetric \( vPOP \) vibration (\( A_1 \)) and one asymmetric \( v_{as}POP \) vibration (\( B_2 \)). Factor-group splitting leads to 2 symmetric or asymmetric bridge stretching vibrations in all representations of the group \( C_{2v} \). On the above stated grounds that crystalline modes derived from symmetric or antisymmetric molecular vibrations are strong in the Raman or IR spectra, respectively, the symmetric vibration is usually (i.e. in a variety of compounds) found to appear strongly in the Raman spectra around 750 cm\(^{-1} \) [17–20], whereas the IR activity depends on the amount of the \( POPO \) angle and disappears with vanishing dipole moment when the bridge is stretched linearly. The frequency of the \( v_{as}POP \) vibration is expected to be about 200 cm\(^{-1} \) higher than the symmetric one.

We observed the symmetric POP stretching vibration in the IR spectra in \( y \) and \( z \) polarization at 750 and 743 cm\(^{-1} \), respectively (Fig. 5). A closer examination of the polarization of the free-ion vibration as well as the orientation of the pyrophosphate groups on the two inequivalent sites within the crystal unit cell reveals that the set of \( \text{P}_2\text{O}_7 \) polyhedra with \( POPO \) angles of 161° is oriented to interact predominantly with radiation polarized in \( z \) direction whereas the set of \( \text{P}_2\text{O}_7 \) polyhedra with angles of 144° interacts predominantly with \( y \) polarized light. The conclusion would be that the different \( POPO \) angles result in different bond stretching vibrational frequencies, with the smaller bonding angles resulting in the higher frequency. This question has been addressed by Sarre et al. [31] by comparing different hydrogenopyrophosphates. They found no correlation of bond angles to \( v_{as}POP \) from one compound to another, but this does not necessarily hold for different bond angles within one compound. For the same reasons which have been mentioned in the discussion of the \( vPOPO \) vibrations the \( vPOP \) vibration, as derived from a totally symmetric free-ion mode, is expected to appear in the Raman spectra with fairly large intensity. Surprisingly this was not found to be the case and the mode appears only very weakly in the Raman spectra at 750 cm\(^{-1} \). We assigned the asymmetric \( v_{as}POP \) stretching vibration to...
a strong peak in the IR spectra at 937 cm$^{-1}$. If this mode has the same frequency in the Raman spectra, it may be hidden by the very strong vanadyl vibrations around 920 cm$^{-1}$.

In the spectral region below 600 cm$^{-1}$ the PO$_3$ terminal bending vibrations are expected. Since about two thirds of all internal modes of the P$_2$O$_7$ group appear in this region, an unambiguous assignment of vibrational modes to spectral features was not possible. In the study of Sarr et al. [31] a linear relation between the bridge angle and the frequency of the bridge bending vibration $\delta$POP was established. Applying this relation to the vanadyl anion of (VO)$_2$P$_2$O$_7$ and considering bridge angles of 144 and 161$^\circ$, we expect Raman and IR lines around 300 and 245 cm$^{-1}$, respectively. A specific assignment was not carried out although some candidates for this mode are present in both the Raman and the IR spectra. Below roughly 220 cm$^{-1}$ external modes of the pyrophosphate and vanadyl units are observed. The low frequency modes at 70, 118 and 123 cm$^{-1}$, which have been reported to interact with the spin system [6], presumably originate from rigid vibrations of the VO$_5$ or P$_2$O$_7$ polyhedra.$^3$

5. Summary and conclusions

Single crystals of (VO)$_2$P$_2$O$_7$ were examined by polarized Raman and infrared spectroscopy. We observed more than 80 phonon modes of which we assigned the high frequency ones (around 915 cm$^{-1}$) to the V=O stretching vibrations and, by comparison with other compounds, the highest frequency ones to vibrations of the P$_2$O$_7$ polyhedra. The assignment to V=O out-of-plane stretching vibrations is strongly supported by the observation of an unusual peak shift as a function of temperature of these modes. It is explained by the interaction of the V atom with oxygen atoms of neighboring layers from the similarity with the pressure effect observed in $\alpha$-NaV$_2$O$_5$. By analogy with the data of Loa et al. [26] on pressure dependent Raman scattering on $\alpha$-NaV$_2$O$_5$, we roughly estimate a thermal expansion coefficient of (VO)$_2$P$_2$O$_7$ along the crystallographic $\alpha$-axis to $\alpha_T \approx 3 \times 10^{-5}$ K$^{-1}$, a rather large value but typical for layered compounds. In contrast to these modes most of the other modes reveal a normal behavior as a function of temperature, i.e. they exhibit a slight mode hardening with decreasing temperature.

The low frequency modes are more or less evenly distributed between $\approx 100$ and $\approx 600$ cm$^{-1}$, originating from bond bending modes and external modes of the VO$_5$ and P$_2$O$_7$ polyhedra. To most of the observed Raman modes we found infrared counterparts, which is in accordance with the assignment of the noncentrosymmetric Pca$_2$$_1$ space group to the crystal structure. Some vibrational modes, which are usually strong in related compounds, were found to be weak in (VO)$_2$P$_2$O$_7$.

Acknowledgements

Fruitful discussions with Z.V. Popović are gratefully acknowledged. This work was supported by Deutsche Forschungsgemeinschaft, through SPP 1073.

References


$^3$The anharmonic mode at 123 cm$^{-1}$ we find in (xx) and (zz) scattering geometry different from Ref. [6] where it was reported to occur in all parallel polarizations.