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1 **Raman spectroscopic study of the uranyl minerals vanmeersscheite**

2 **$\text{U}(\text{OH})_4[(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_2]\cdot 4\text{H}_2\text{O}$ and arsenouranylite**

3 **$\text{Ca}(\text{UO}_2)[(\text{UO}_2)_3(\text{AsO}_4)_2(\text{OH})_2]\cdot (\text{OH})_2\cdot 6\text{H}_2\text{O}$**

4
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14
15 **Abstract**

16 Raman and infrared spectra of secondary uranyl phosphate vanmeersscheite and
17 Raman spectrum of secondary uranyl arsenate arsenouranylite were recorded and
18 interpreted and the spectra related to the structure of the minerals. Observed bands
19 were attributed to the stretching and bending vibrations of uranyl, phosphate and/or
20 arsenate units and OH (H₂O and OH⁻) units. Phosphuranylite sheet topology is
21 characteristic for both minerals. U-O bond lengths in uranyl were calculated from the
22 spectra and compared with those inferred for vanmeersscheite from the X-ray single
23 crystal structure analysis. O-H...O hydrogen bonds in both minerals were also
24 inferred using the Libowitzky empirical relation.

25
26 *Keywords:* uranyl minerals, vanmeersscheite, phosphate, Raman spectroscopy,
27 arsenouranylite, arsenate, Raman spectroscopy, U-O (uranyl) bond
28 lengths, , O-H...O bond lengths

30 **Introduction**

31

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32 Vanmeersscheite, $U(OH)_4[(UO_2)_3(PO_4)_2(OH)_2] \cdot 4H_2O$, is a rare orthorhombic
33 secondary uranium mineral in the uraniferous zone of an altered granite pegmatite
34 from Kobokobo, Lusungu River district, Kivu Province, Congo Zaire, RDC. It was
35 found in association with metavanneersscheite and studtite [1, 2]. Walenta described
36 vanmeersscheite from Menzenschwand, Black Forest, Germany [3, 4] and its arsenic
37 analogue arsenovanmeersscheite, $U(OH)_4[(UO_2)_3(OH)_2(AsO_4)_2] \cdot 4H_2O$, from the
38 same locality [3]. Arsenuranylite, $Ca(UO_2)[(UO_2)_3(AsO_4)_2(OH)_2] \cdot (OH)_2 \cdot 6H_2O$, is
39 also a rare orthorhombic secondary uranyl mineral from the oxidized zone of a
40 uranium deposit containing arsenic-bearing sulfides in Cherkasar uranium deposit, 30
41 km northwest of Pap, Chatkal Range, Uzbekistan where it was found in association
42 with schoepite, paraschoepite (?), metazeunerite, nováčekite and uranospinite.
43 Arsenuranylite was also found at Menzenschwand, Black Forest, Germany [2, 5].
44
45

46 Both minerals studied, vanmeersscheite and arsenuranylite, are topologically
47 related because they possess the same phosphuranylite-type anion sheet topology. The
48 phosphuranylite-type sheet is second most commonly observed sheet among the
49 uranyl orthophosphates and uranyl orthoarsenates that have layered structures. This
50 phosphuranylite-type sheet consists of dimers of edge-sharing uranyl pentagonal
51 dipyramidal coordination polyhedra that share edges with uranyl hexagonal
52 dipyramidal coordination polyhedra to form chains. Phosphate, $(PO_4)^{3-}$,
53 (vanmeersscheite) and arsenate, $(AsO_4)^{3-}$, (arsenuranylite) tetrahedra share edges with
54 the hexagonal dipyramids of a given chain and vertices with an adjacent chain to form
55 sheet of the general composition $[(UO_2)_3(XO_4)_2(O,OH)_2]$, where $X = P, As$. The
56 interlayer is occupied by cations, such as Ca^{2+} , and in both minerals also by U^{6+} very
57 probably as $(UO_2)^{2+}$, along with $(OH)^-$ and/or water molecules [6].
58

59 According to Burns [7], the interlayer of the structures of minerals of the
60 phosphuranylite group is complex, and some contain more than one type cation and
61 water molecules. The structure of vanmeersscheite is unusual because it contains
62 uranyl ions in all three common coordinations – tetragonal, pentagonal and hexagonal
63 dipyramids. Tetragonal dipyramids are located between the sheets with the uranyl
64 ions extending roughly parallel to the sheets. Uranyl tetragonal dipyramids in the
65 vanmeersscheite interlayer share vertices with only two phosphate tetrahedra, one

66 from each adjacent sheet. Linkage of uranyl phosphate sheets through interlayer
67 uranyl polyhedra results in open three-dimensional structure [7]. It may be assumed
68 similar structural arrangement also in arsenuranylite because of similar chemical
69 formula and $\text{UO}_2:\text{XO}_4$ molar ratio. Differences are in contents of Ca^{2+} , H_2O and OH^- .
70 The arsenuranylite formula is close to the phosphuranylite formula. The difference is
71 only in the water, and hydroxyl content and in that arsenuranylite contains As^{5+}
72 instead of P^{5+} [2]. The presence of oxonium in the crystal structure of phosphuranylite
73 was not proved [[8]; [Frost et al., in press].

74

75 The structure of vanmeersscheite contains UO_2O_4 , UO_2O_5 and UO_2O_6
76 polyhedra. There are two symmetrically distinct UO_2O_4 polyhedra that occur between
77 the sheets, and each provides intersheet bonding by sharing an anion with a single
78 $(\text{PO}_4)^{3-}$ tetrahedron of each sheet. Additional intersheet/linkage is provided by
79 hydrogen bonds [7, 9-11]. Similar phosphuranylite-type anion sheet topology was
80 observed e.g. in phosphuranylite, arsenuranylite, dumontite, dewindtite, phurcalite,
81 phuralumite, bergenite, upalite and mundite [1, 6, 7, 10]. In comparison with
82 phosphuranylite, vanmeerschsscheite and arseuranylite structures with those of other
83 mineral mentioned is that these three minerals contain U^{6+} in the interlayers.

84

85 Space group of vanmeersscheite is $\text{P}2_1\text{mn} = \text{C}^7_{2v}$ and $Z = 4$, while the space
86 group of arsenuranylite is $\text{Bmmb} = \text{D}^{17}_{2h}$ and $Z = 6$ [Anthony et al. 2003].
87 Vanmeersscheite contains four symmetrically distinct U^{6+} in its crystal structure,
88 three in the $[(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_2]$ sheets and one in the interlayer [1]. In the sheets,
89 there are all distorted asymmetric uranyls ,O-U-O, with U-O bond lengths ranging
90 from 1.76 to 1.97 Å in the sheets (pentagonal and hexagonal dipyramids), and
91 approximately 2.00 Å in the interlayer (tetragonal dipyramids) [1]. These lengths
92 differs from those inferred by Burns [7, 9, 10] for uranyl natural and synthetic
93 compounds (~ 1.8 Å). It may be therefore assumed that the crystal structure of
94 vanmeersscheite should be refined. Details of crystal structure of arsenuranylite are
95 not known, however, it may be assumed that this structure may be similar to that of
96 vanmeersscheite.

97

98 Raman spectroscopy has proven very useful for the study of minerals [12-14].
99 Indeed Raman spectroscopy has proven most useful for the study of diagenetically

100 related minerals as often occurs with carbonate minerals [15-19]. Some previous
101 studies have been undertaken by the authors using Raman spectroscopy to study
102 complex secondary minerals formed by crystallisation from concentrated sulphate
103 solutions [20]. Very few spectroscopic studies of nickel silicates have been
104 forthcoming and what studies that are available are not new. Few Raman studies of
105 any note are available [21, 22]. The aim of this paper is to study Raman and infrared
106 spectra of vanmeersscheite and Raman spectrum of arsenuranylite. The paper is a part
107 of research on vibrational spectroscopy of secondary minerals inclusive those
108 containing uranyl ion.

109

110 **Experimental**

111 **Minerals**

112

113 The vanmeersscheite mineral was obtained from the Mineralogical Research
114 Company and originated from Kobokobo, Congo. This sample is a 'type' mineral.
115 The chemical composition of this mineral has been published [23] (page 617). The
116 mineral corresponds to the formula above $U(OH)_4[(UO_2)_3(PO_4)_2(OH)_2].4H_2O$. The
117 arsenouranylite originated from the Cherkasar deposit, Uzbekistan and corresponds to
118 the formula $Ca(UO_2)[(UO_2)_3(AsO_4)_2(OH)_2].(OH)_2.6H_2O$ [reference [23] page 37].

119 **Raman spectroscopy**

120

121 The crystals of vanmeersscheite and arsenuranylite were placed and oriented
122 on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives
123 and part of a Renishaw 1000 Raman microscope system, which also includes a
124 monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra
125 were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between
126 100 and 4000 cm^{-1} . Repeated acquisition using the highest magnification was
127 accumulated to improve the signal to noise ratio. Spectra were calibrated using the
128 520.5 cm^{-1} line of a silicon wafer. Details of the technique have been published by the
129 authors [12, 15-19, 24-31].

130 **Mid-IR spectroscopy**

131 Infrared spectra of vanmeersscheite or arsenuranylite were obtained using a
132 Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond
133 ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of
134 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s . Spectra
135 were co-added to improve the signal to noise ratio.

136 Spectral manipulation such as baseline adjustment, smoothing and normalisation
137 was performed using the Spectracalc software package GRAMS (Galactic Industries
138 Corporation, NH, USA). Band component analysis was undertaken using the Jandel
139 ‘Peakfit’ software package which enabled the type of fitting function to be selected
140 and allowed specific parameters to be fixed or varied accordingly. Band fitting was
141 done using a Lorentz-Gauss cross-product function with the minimum number of
142 component bands used for the fitting process. The Lorentz-Gauss ratio was
143 maintained at values greater than 0.7 and fitting was undertaken until reproducible
144 results were obtained with squared correlations of r^2 greater than 0.995.

145

146 **Results and discussion**

147

148 In the crystal structure of vanmeersscheite and very probably also of
149 arsenuranylite, there are four symmetrically distinct U^{6+} , three in the uranyl anion
150 layers and one in the interlayer, and two symmetrically distinct P^{5+} in vanmeersscheite
151 and probably also two symmetrically distinct As^{2+} in arsenuranylite [1]. $\text{D}_{\infty\text{h}}$
152 symmetry is characteristic for free unbonded $(\text{UO}_2)^{2+}$ unit, while T_d symmetry for free
153 and unbonded $(\text{PO}_4)^{3-}$ and $(\text{AsO}_4)^{3-}$ units. However, any symmetry lowering of the
154 units in the crystal structure may be connected with splitting of doubly or triply
155 degenerate vibrations and their Raman and infrared activation [8, 15-17, 25, 26, 28,
156 30, 32]. Tetragonal dipyramidal UO_2O_4 (in the interlayer), pentagonal dipyramidal
157 UO_2O_5 and hexagonal dipyramidal UO_2O_6 (in the layers) uranyl coordination
158 polyhedra were observed in the crystal structure of vanmeersscheite [1] and may be
159 probably expected also in the crystal structure of arsenuranylite.

160

161 *Vanmeersscheite*

162

163 The Raman spectra of vanmeersscheite may be conveniently divided into
164 sections depending upon the type of vibration being determined. The Raman spectrum
165 of Vanmeersscheite in the 800 to 1300 cm^{-1} region is shown in Figure 1. This region
166 contains the bands attributable to the $(\text{PO}_4)^{3-}$ and $(\text{UO}_2)^{2+}$ stretching vibrations.
167 Figure 2 reports the spectra in the 100 to 800 cm^{-1} region; this region contains the
168 bands attributable to the $(\text{PO}_4)^{3-}$ and $(\text{UO}_2)^{2+}$ bending vibrations. The Raman
169 spectrum of the hydroxyl stretching region of vanmeersscheite is displayed in Figure
170 3. Raman spectra may be complimented by the infrared spectra even though bands in
171 the infrared spectrum may be broader. Figure 4 displays the infrared spectrum of
172 vanmeersscheite in the 550 to 1250 cm^{-1} region and Figure 5 the infrared spectrum in
173 the OH stretching region.

174

175 Raman band at 938 cm^{-1} and infrared band at 884 cm^{-1} are assigned to the ν_3
176 $(\text{UO}_2)^{2+}$ antisymmetric stretching vibrations. Raman band at 860 cm^{-1} and infrared
177 band at 795 cm^{-1} are attributed to the ν_1 $(\text{UO}_2)^{2+}$ symmetric stretching vibrations. U-O
178 bond lengths in uranyls calculated with the Bartlett and Cooney empirical relations
179 [33] are ($\text{\AA}/\text{cm}^{-1}$) 1.756/938, 1.753/860, 1.796/884 and 1.816/795. Average U-O bond
180 length, inferred from the X-ray single crystal structure analysis is 1.88 \AA [1].
181 Calculated U-O bond lengths are close to ~ 1.8 \AA , inferred by Burns [7, 9, 34] for
182 uranyl natural and synthetic compounds. These values differ from those observed by
183 Piret and Deliens [1]. As mentioned above, and based upon the results of the Raman
184 spectra reported in this paper, the crystal structure of vanmeersscheite should be
185 therefore be revised and refined.

186

187 Raman bands at 1208, 1153, 1131, 1121, 1110, 1102, 1086 and 1017 cm^{-1} , and
188 infrared bands at 1183, 1091 and 1029 cm^{-1} are connected with the split triply
189 degenerate $(\text{PO}_4)^{3-}$ antisymmetric stretching vibrations, however, some of these bands
190 may be related to the δ U-OH bending vibrations. Raman bands at 1013 and 1008 cm^{-1}
191 and infrared bands at 1003 and 966 cm^{-1} are assigned to the ν_1 $(\text{PO}_4)^{3-}$ symmetric
192 stretching vibrations. To the split triply degenerate ν_4 (δ) $(\text{PO}_4)^{3-}$ bending vibrations
193 are attributed Raman bands at 650, 624, 571 and 566 cm^{-1} and infrared bands at 673,

194 627 and 578 cm^{-1} , while Raman bands at 453, 442 and 418 cm^{-1} may be attributed to
195 the split doubly degenerate $\nu_2(\delta)$ (PO_4)³⁻ bending vibrations. Raman bands at 363 and
196 323 cm^{-1} may be connected with ν (U-O_{ligand}) vibrations, and those at 290 and 250 cm^{-1}
197 to the split doubly degenerate $\nu_2(\delta)$ (UO_2)²⁺ bending vibrations, and bands at 223-
198 226 cm^{-1} to the lattice vibrations.

199

200 The ν OH stretching vibrations of molecular water and hydroxyls are related
201 to Raman band at 3390 cm^{-1} and infrared bands at 3358, 3284, 3255 and 2913 cm^{-1} .
202 O-H...O hydrogen bond lengths inferred from the Libowitzky relation [35] are 2.79 Å
203 (Raman) and 2.78, 2.75, 2.73 and 2.64 Å (infrared). Molecular water may be also
204 characterized by the δ H₂O bending vibration at 1580 cm^{-1} (Raman) and 1612 cm^{-1}
205 (infrared). The infrared band at 1441 cm^{-1} is associated with the
206 δ U-OH bending vibration.

207

208 *Arsenuranylite*

209

210 The Raman spectrum of arsenuranylite in the 100 to 1100 cm^{-1} region is
211 displayed in Figure 6. The OH stretching region of arsenuranylite is reported in
212 Figure 7. Raman bands at 926 and 883 cm^{-1} are assigned to the ν_3 (UO_2)²⁺
213 antisymmetric stretching vibrations and bands at 795 and 787 cm^{-1} to the ν_1 (UO_2)²⁺
214 symmetric stretching vibrations and the ν_1 (AsO_4)³⁻ symmetric stretching vibrations.
215 Bartlett and Cooney [36] empirical relations enable to calculate the U-O bond lengths
216 in uranyls, which are ($\text{Å}/\text{cm}^{-1}$) 1.766/926, 1.797/883, 1.816/795, 1.824/787. As in the
217 case of vanmeersscheite, calculated U-O bond lengths in uranyls are close to ~ 1.78 Å,
218 inferred by Burns [7, 10, 37, 38] for natural and synthetic uranyl compounds.

219

220 The triply degenerate (AsO_4)³⁻ antisymmetric stretching vibration was not
221 observed in the Raman spectrum of arsenuranylite. As mentioned above, bands at 795
222 and 787 cm^{-1} may be related to the ν_1 (AsO_4)³⁻ symmetric stretching vibrations and
223 the ν_1 (UO_2)²⁺ symmetric stretching vibrations. The split triply degenerate $\nu_4(\delta)$
224 (AsO_4)³⁻ bending vibration and the split doubly degenerate $\nu_2(\delta)$ (AsO_4)³⁻ bending
225 vibration are observed at 494, 466 and 422 cm^{-1} and 388 and 344 cm^{-1} , respectively.

226 Bands at 298 and 259 cm^{-1} are assigned to the ν_2 (δ) $(\text{UO}_2)^{2+}$ bending vibrations and
227 those at 213, 170 and 150 cm^{-1} to lattice vibrations.

228

229 The presence of water molecules and hydroxyls in the crystal structure of
230 arsenuranylite is connected with the bands at 3507, 3480, 2966, 2926, 2872 and 2846
231 cm^{-1} corresponding to the U-O...O hydrogen bond lengths 2.91, 2.88, 2.65, 2.64, 2.63
232 and 2.625 Å inferred from the Libowitzky empirical relation [35]. A band at 1733 may
233 be related to the δ H_2O bending vibration or to a combined band, and those at 1452
234 and 1305 to the δ U-OH bending vibrations. Libration modes of water molecules are
235 observed at 561 and 558 cm^{-1} .

236 **Conclusions**

237

- 238 (a) Raman and infrared spectra of vanmeersscheite and Raman spectrum of
239 arsenuranylite, both minerals possessing the phosphuranylite uranyl anion sheet
240 topology, were studied and interpreted.
- 241 (b) $D_{\infty h}(\text{UO}_2)^{2+}$ and $T_d[(\text{PO}_4)^{3-}, (\text{AsO}_4)^{3-}]$ symmetry structural lowering is
242 connected with splitting of degenerate vibrations and Raman and/or infrared
243 activation of Raman or infrared forbidden vibrations. Symmetrically distinct
244 uranyl units were observed in both mineral structures the concept of which is in
245 agreement with the available vanmeersscheite crystal structure inferred from X-
246 ray single crystal structure analysis by Piret and Deliens [Piret, Deliens 1982].
- 247 (c) U-O bond lengths in uranyls calculated from the ν_1 and ν_3 $(\text{UO}_2)^{2+}$ wavenumbers
248 with Bartlett empirical relation [Bartlett, Cooney 1989]. These values are close to
249 those inferred for natural and synthetic uranyl compounds by Burns [Burns 1999,
250 2005; Burns et al. 1996, 1997].
- 251 (d) O-H...O hydrogen bond lengths in the crystal structures of vanmeersscheite and
252 arsenuranylite were correlated on the basis of Libowitzky relation. A set of
253 hydrogen bonds is observed in the crystal structures of both studied minerals.

254

255 **Acknowledgments**

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259 **References**

260

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319

320

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325

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327

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329

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332 Figure 5 Infrared spectrum of vanmeersscheite in the 550 to 1250 cm^{-1} region

333

334 Figure 6 Raman spectrum of arsenuranylite in the 800 to 1300 cm^{-1} region

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336 Figure 7 Raman spectrum of arsenuranylite in the 100 to 700 cm^{-1} region

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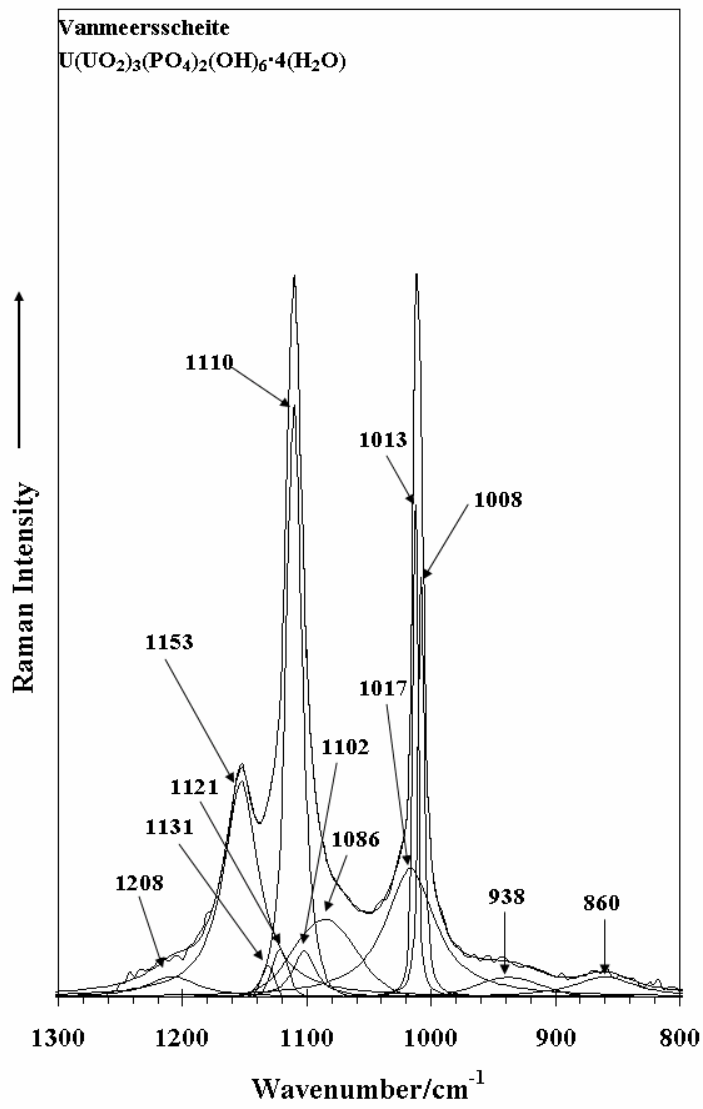
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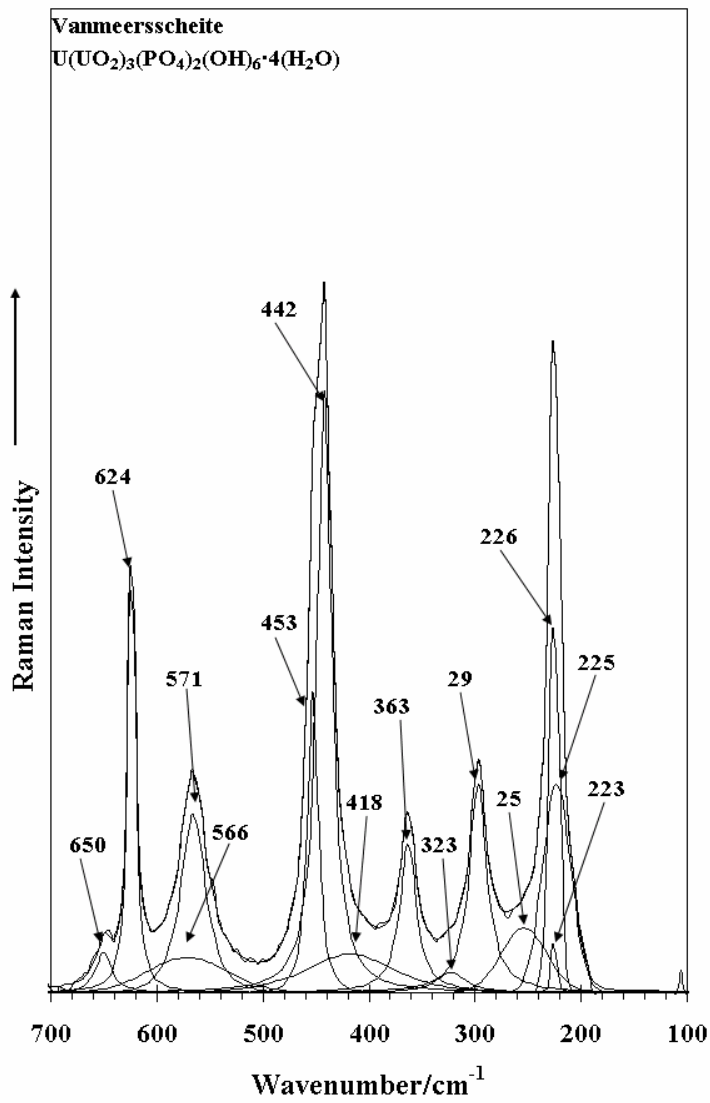


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354 **Figure 1**

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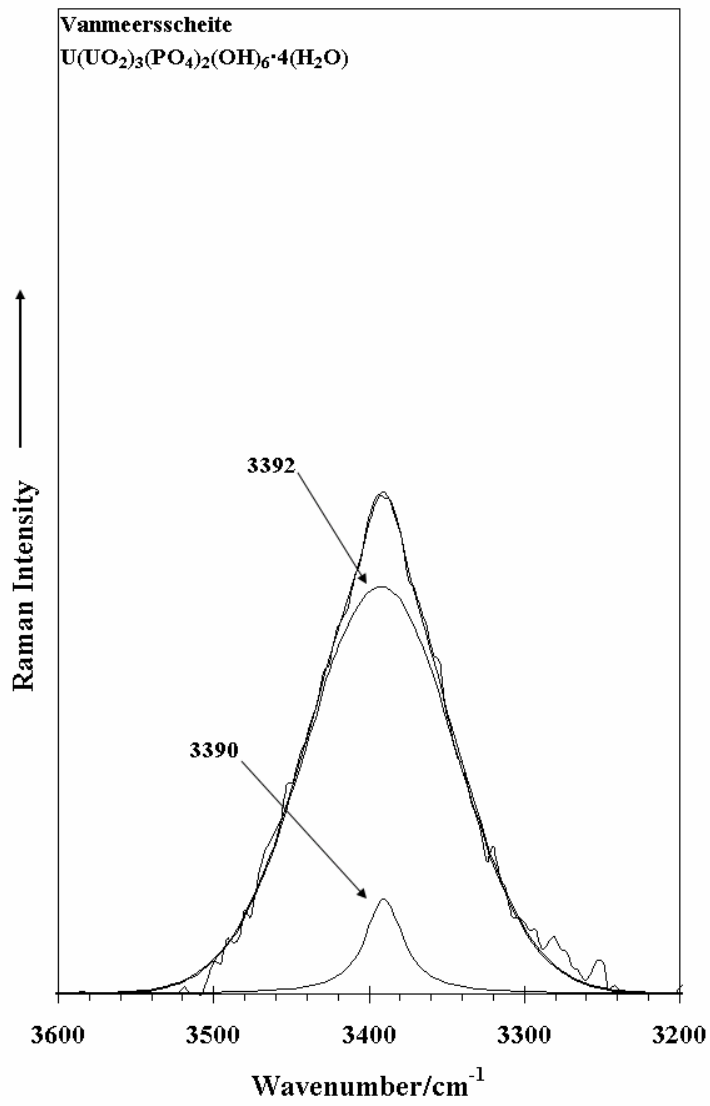


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358 **Figure 2**

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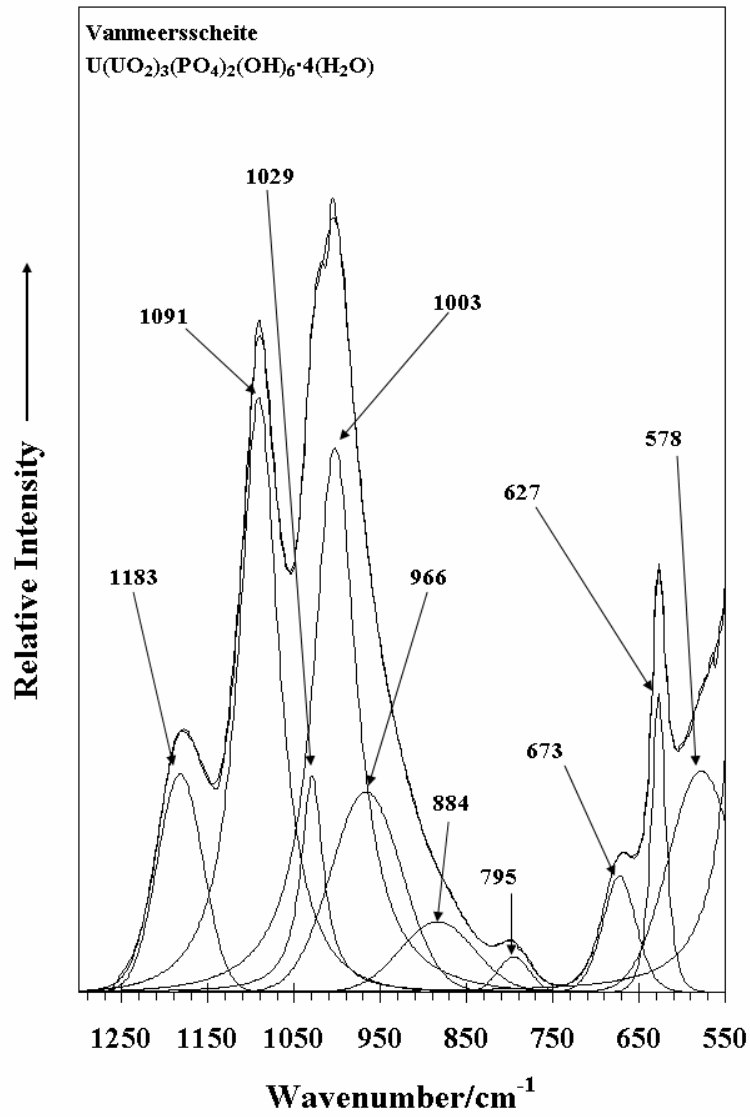


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362 **Figure 3**

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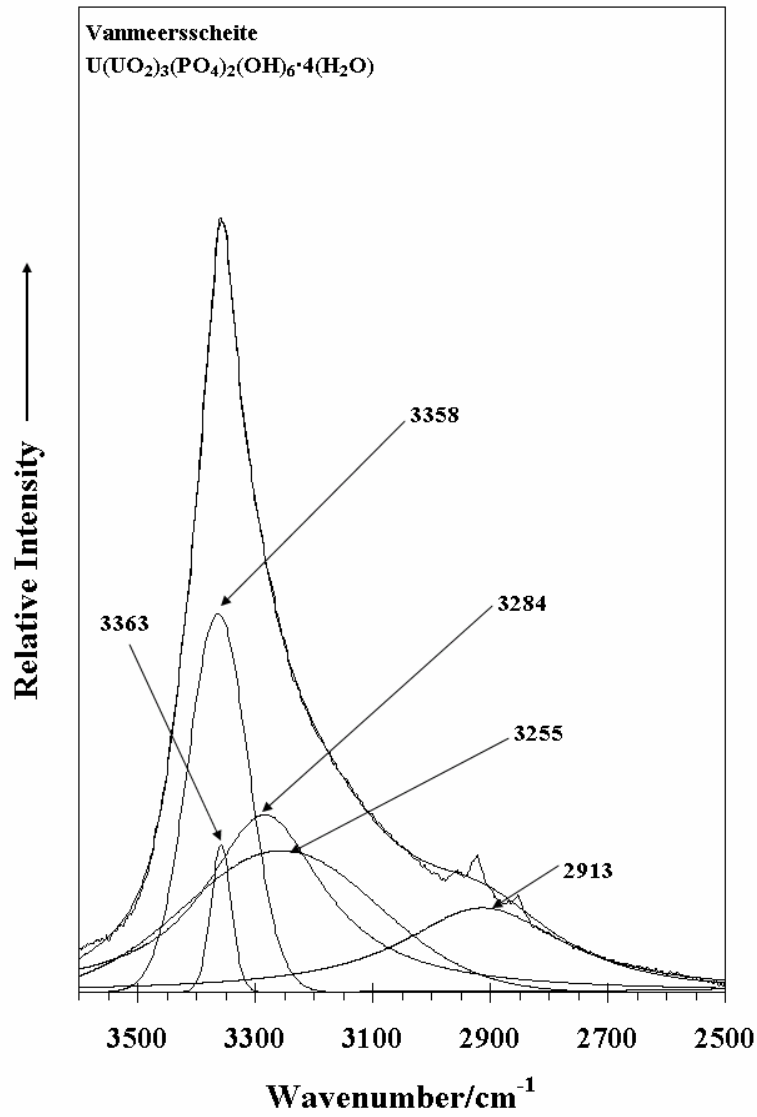
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366 **Figure 4**

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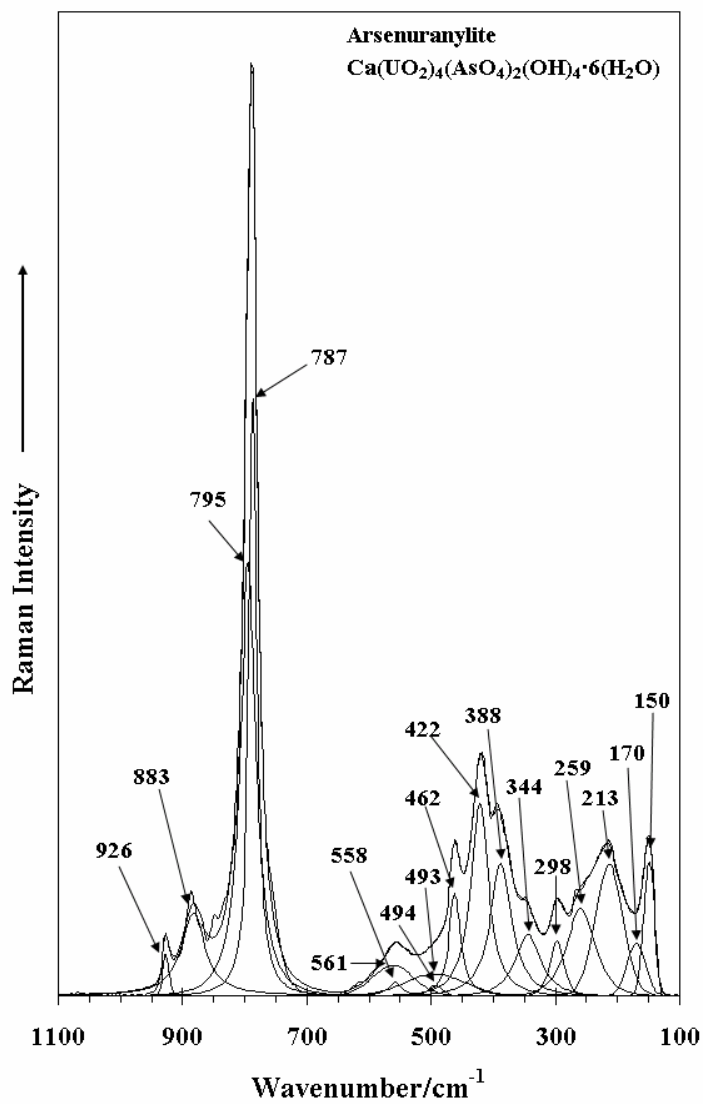


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371 **Figure 5**

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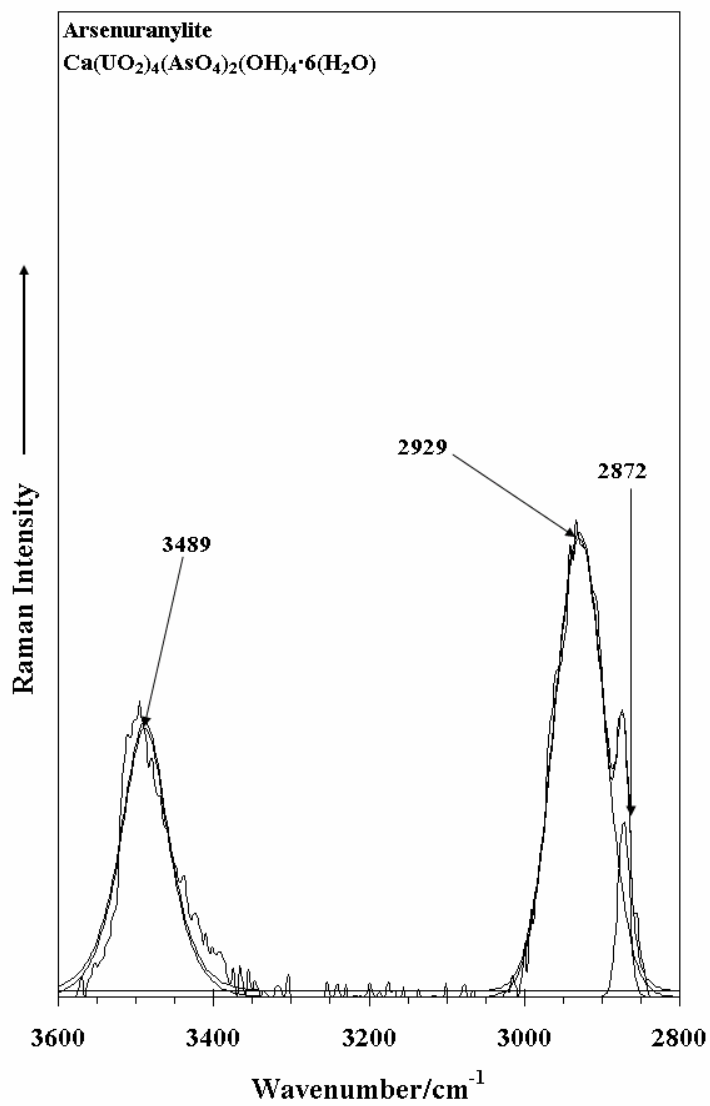


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375 **Figure 6**

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379 **Figure 7**

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