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Vibrational spectroscopy of selected natural uranyl vanadates

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Abstract

Raman spectroscopy has been used to study a selection of uranyl vanadate minerals including carnotite, curienite, francevillite, tyuyamunite and metatyuyamunite. The minerals are characterised by an intense band in the 800 to 824 cm^{-1} region, assigned to the ν_1 symmetric stretching vibrations of the $(UO_2)^{2+}$ units. A second intense band is observed in the 965 to 985 cm^{-1} range and is attributed to the ν_1 (VO_3) symmetric stretching vibrations in the (V_2O_8) units. This band is split with a second component observed at around 963 cm^{-1}. A band of very low intensity is observed around 948 cm^{-1} and is assigned to the ν_3 antisymmetric stretching vibrations of the (VO_3) units. Bands in the range 608-655 cm^{-1} may be attributed to molecular water librational modes or the stretching modes $\nu(V_2O_2)$ units. Bands in the range 573-583 cm^{-1} may be connected with the ν $(U\text{-}O_{equatorial})$ vibrations or ν (V_2O_2) units. Bands located in the range 467-539 cm^{-1} may be also attributed to the ν $(U\text{-}O_{equatorial})$ units vibrations. The bending modes of the (VO_3) units are observed in the 463 to 480 cm^{-1} range – there may be some coincidence with ν $(U\text{-}O_{equatorial})$. The bending modes of the (V_2O_2) in the (V_2O_8) units are located in a series of bands around 407, 365 and 347 cm^{-1} (ν_2). Two intense bands are observed in the 304 to 312 cm^{-1} range and 241 to 264 cm^{-1} range and are assigned to the doubly degenerate ν_2 modes of the $(UO_2)^{2+}$ units. The study of the vibrational spectroscopy of uranyl vanadates is complicated by the overlap of bands from the (VO_3) and $(UO_2)^{2+}$ units. Raman spectroscopy has proven most useful in assigning bands to these two units since Raman bands are sharp and well separated as compared with infrared bands. The uranyl vanadate minerals are often found as crystals on a host matrix and Raman spectroscopy enables their in-situ characterisation without sample preparation.

Keywords: carnotite, curienite, francevillite, tyuyamunite, vanadates, Raman spectroscopy, infrared spectroscopy

Introduction

A number of uranyl vanadates have been discovered [1-4]. These include carnotite $(K_2(UO_2)(V_2O_8).3H_2O)$ [5], tyuyamunite $(Ca(UO_2)(V_2O_8).9H_2O)$ [6], metatyuyamunite $(Ca(UO_2)(V_2O_8).3H_2O)$ [2], strelkinite $(Na_2(UO_2)(V_2O_8).6H_2O)$, curienite $(Pb_2(UO_2)(V_2O_8).5H_2O)$ [7], francevillite $(Ba,Pb(UO_2)(V_2O_8).5H_2O)$ [3, 8-10] and vanuralite $(Al(OH)(UO_2)_2(V_2O_8).3H_2O)$. The presence of vanadium in minerals presents the most complicated of systems especially as it

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• Author for correspondence (r.frost@qut.edu.au) relates to mineral species and their crystallisation from solution. This complication is exacerbated by the range of oxidation states in the natural environment, including the supergene zone. These include V(III), V(IV), V(V). Polymerisation of V(V) as $(VO_4)^{3-}$, in more concentrated solutions, gives rise to three types of complex anions. If the pH is between 9 and 13, pyrovanadates [$(V_2O_7)^{4-}$, $(HV_2O_7)^{3-}$,$(H_2V_2O_7)^{2-}$] are formed, in the pH range 5 to 9 metavanadates [$(V_3O_9)^{3-}$, $(V_4O_{12})^{4-}$, $(H_2V_3O_{10})^{3-}$, $(HV_3O_{10})^{4-}$,$(V_5O_{15})^{5-}$,] are predominantly formed, and as solutions become more acidic decavanadates [$(V_{10}O_{28})^{6-}$] are formed. The uranyl vanadates are part of a mineral classification described as the uranyl micas and may be compared with minerals such as autunite and torbernite and related minerals. However, their uranyl anion sheet topology is differing [11]. These minerals may contain divalent cations represented by Ca^{2+} (tyuyamunite and meta tyuyamunite), Pb^{2+} (curienite), Mn^{2+} (fritzscheite), Ba^{2+} (francevillite) and Cu^{2+} (sengerite); the minerals may also contain the monovalent cations and are represented by K^+ (carnotite), Na^+ (strelkinite), Cs^+ (margaritasite) and also a mineral with trivalent cations Al^{3+} (vanuralite) . The X-ray crystallographic studies of curienite and francevillite have been undertaken. [7, 9] However the observed U-O bond lengths are far too short making the results not correct. The best data available for the X-ray crystallography of francevillite comes from Mereiter. [10] There is an obvious lack of knowledge of the single crystal X-ray studies of these minerals.

All the uranyl vanadate minerals exhibit a layer structure with [$((UO_2)_2V_2O_8)_n)^{2n-}$] units with the cation in the interlayer [12]. The vanadium atoms are coordinated by five oxygen atoms in the form of square pyramids. Two polyhedra share a common edge forming $(V_2O_8)^{6-}$ groups [11, 12]. Considerable discrepancies exist to the attribution of bands for the uranyl vanadates [12]. Such discrepancy arises because of the overlap of the bands assigned to the $(UO_2)^{2+}$ or (VO_x) units. As well uncertainty is influenced by the type of vanadium unit present in the structure. Wilkins writes "the presence of condensed vanadate ions is also consistent with the presence of strong vanadate infrared absorptions well outsides the range expected for isolated $(VO_4)^{3-}$ tetrahedra" [13]. The work of Appleman and Evans showed that $(V_2O_8)^{6-}$ units are present in the crystal structure of uranyl vanadates [14]. Botto et al. used the following building blocks to assign spectra (V_2O_2) double bridges, terminal (VO_3) groups, $(UO_2)^{2+}$ units and secondary U-O bonds [15]. The free vanadate ion $(VO_4)^{3-}$ has tetrahedral T_d symmetry. Ross reports the free aqueous vanadate ion as having a ν_1 (A_1) mode at 874 cm^{-1}, the ν_2 mode of E symmetry at 345 cm^{-1}, the ν_3 mode of F_2 symmetry at 855 cm^{-1} and the ν_4 mode also of F_2 symmetry at 345 cm^{-1}. For perfect T_d symmetry the first two modes are Raman active/infrared inactive and the last two modes both Raman and infrared active. According to Botto, bands in the 870 to 894 cm^{-1} range may be assigned to the ν_3 antisymmetric stretching modes of VO_3 units [15]. Čejka attributed bands in these positions to the ν_3 antisymmetric stretching vibrations of $(UO_2)^{2+}$ units [12]. Some authors assigned this latter vibration to bands around 980 cm^{-1}. Chernorukov et al. ascribed the band at 880 cm^{-1} to ν_3 of the $(UO_2)^{2+}$ units and the band at 740 cm^{-1} to ν_1 of the $(UO_2)^{2+}$ units for synthetic uranyl vanadates [16]. The attributing of the band at 740 cm^{-1} to the ν_1 $(UO_2)^{2+}$ vibration is erroneous. Chernorukov et al. applied this assignment also in some other papers concerning IR spectra of synthetic uranyl vanadates [12, 17, 18]. However, in the paper in which are discussed calculated wavenumbers of (VO_5) and (UO_7) units in the IR and Raman spectra of synthetic uranyl vanadates [19] and compared with the spectra of M^+ and M^{2+} synthetic uranyl vanadates, Chernorukov et al. attribute wavenumbers of bands located ad 885±10 and 810±10 cm^{-1} to the ν_3 antisymmetric and ν_1 symmetric $(UO_2)^{2+}$ stretching vibrations [$\nu_3(A_2'')$ $(UO_7) = \nu_3$ $(UO_2)^{2+}$ and $\nu_2(A_1')$ $(UO_7) = \nu_1$ $(UO_2)^{2+}$; $UO_7 = UO_2O_5$] , respectively and assume that bands observed in 750-735 cm^{-1} in the spectra of uranyl vanadates are connected only with vibrations of V-O bonds inVO_5 polyhedra (C_{4v} symmetry) [ν_4 (B_1) (Raman active), ν_2 (A_1), ν_7 (E) – both IR and Raman active] [19]. Recently Frost and co-workers have applied Raman microscopy to the study of quite complex mineral systems [20-26].As part of our ongoing research into secondary mineral formation using Raman microscopy complimented with infrared spectroscopy, we report the Raman spectra of the uranyl vanadate minerals.

Experimental

Minerals

The minerals were obtained from a number of sources including Museum Victoria. The following Table shows the minerals studied in this work.

Mineral	Formula	Mineral Identification	Place of origin
Curienite	$Pb_2(UO_2)(V_2O_8).5H_2O$	Minresco	Mounana Mine, Haut Ogoue, Gabon
Carnotite	$K_2(UO_2)(V_2O_8).3H_2O$	M17518	Nucla, Colarado, USA
Carnotite	$K_2(UO_2)(V_2O_8).3H_2O$	M9281	Radium Hill, Olary, South Australia
Carnotite	$K_2(UO_2)(V_2O_8).3H_2O$	M22553	Paradox valley, Colarado, USA
Francevillite	$Ba,Pb(UO_2)(V_2O_8).5H_2O$	M43680	Mounana V-U Mine, Haut Ogove, Gabon
Francevillite	$Ba,Pb(UO_2)(V_2O_8).5H_2O$	M36658	Mounana, Gabon
Francevillite	$Ba,Pb(UO_2)(V_2O_8).5H_2O$	Minresco	Mounana Mine, Haut Ogoue, Gabon
Tyuyamunite	$Ca(UO_2)(V_2O_8).9H_2O$	M36658	Near Grants, Valencia Co., New Mexico, USA
Tyuyamunite	$Ca(UO_2)(V_2O_8).9H_2O$	M33787	Chinle Formation, Steen Mine, Monticello, Utah, USA
Tyuyamunite	$Ca(UO_2)(V_2O_8).9H_2O$	M27401	Chihuahua, Mexico
Meta-tyuyamunite	$Ca(UO_2)(V_2O_8).3H_2O$	Minresco	Monument #2 Mine Monument Valley, Apache County Arizona, USA

Raman microprobe spectroscopy

The crystals of the uranyl vanadate minerals were placed and orientated on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. In order to ensure that the correct spectra are obtained, the incident excitation radiation was scrambled. Previous studies by the authors provide more details of the experimental technique. Spectra at controlled temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published by the authors [21, 24, 27-30]. Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

Infrared absorption spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s.

Results and discussion

The Raman spectra of selected minerals belonging to the uranyl vanadate group are shown in Figures 1 and 2. The results of the band component analyses are reported in Table 1. The Table also includes some published data on the infrared spectrum of carnotite. The problem of studying the spectroscopy of uranyl vanadates is that the ν_1 of the $(UO_2)^{2+}$ units overlaps with the ν_1 of the $(VO_4)^{3-}$ units. Farmer based upon the spectra of Moenke suggested that the ν_1 of the $(VO_4)^{3-}$ units was found at 900 cm^{-1} and that ν_3 of $(VO_4)^{3-}$ units was at 860 cm^{-1}. The ν_2 bending mode of the $(VO_4)^{3-}$ units was not observed in the infrared spectrum but the ν_4 band was observed at 480 cm^{-1}. There was some debate about the attribution of the bands with the band at 900 cm^{-1} being also assigned to the ν_2 of the $(UO_2)^{2+}$ units. However such an attribution is clearly incorrect with the ν_2 (δ) $(UO_2)^{2+}$ bending modes being found at 285 and 250 cm^{-1} [12]. It may well be that the attribution by Farmer is some sort of misprint. All the uranyl vanadate minerals exhibit a layer structure with $[((UO_2)(V_2O_8))_n]^{2n-}$ units. According to Burns , the vanadium atoms are coordinated by five oxygen atoms in the form of a square pyramid with two polyhedra sharing a common edge forming $(V_2O_8)^{6-}$ units[11]. Botto et al. suggested that as well as the $(V_2O_8)^{6-}$ units and its fragments – (V_2O_2) bridges and terminal (VO_3) units occur in the layers [15, 31].

The question arises as to what is the vibrating unit concerning the vanadate ions. There are a number of possibilities for $(V_2O_8)^{6-}$ or $(VO_4)^{3-}$. It is probable that fragments of these units are the source of the Raman spectra. Further it is likely because of the polymeric nature of the vanadate units that other vibrating species such as (VO), (V_2O_2), (VO_3) and others will be observed, further complicating the assignment of bands. Saadi divided the vibrations of the (V_2O_8) units in two categories: (VO_3) (V-O bonds with apical oxygens and those corresponding to the shortest V-O bonds), and the system (V_2O_2) formed of two V-O-V bridges in which V-O bonds are longer [32]. ν_1 (VO_3) is IR active and the most intensive bands in the spectra are attributed to this vibration (965-986 and 974-987 cm^{-1}, respectively). Wavenumbers of these vibrations are higher than those corresponding to $(VO_4)^{3-}$ (780-830 cm^{-1}) and $(V_2O_7)^{4-}$ (880-850 cm^{-1}). ν_3 (VO_3) is also IR active. Its intensity is lower than that of ν_1 (VO_3) and is located for the both groups in the range 841-859 cm^{-1}. As far as two bridges V-O-V of (V_2O_2) in (V_2O_8) concerns, symmetric and antisymmetric vibrations are IR active. The antisymmetric vibrations may be found in the range 627-648 cm^{-1} and 620-635 cm^{-1}, respectively. Saadi suggested wavenumbers of the symmetric vibrations lie lower than 600 cm^{-1}.

Figure 1 shows a number of highly polarised bands in the 960 to 985 cm^{-1} range. These bands are assigned to the symmetric stretching modes of the $(VO_4)^{3-}$ units. In previously published works bands in these positions to the antisymmetric modes of ν_3 of $(UO_2)^{2+}$ units. This assignment appears incorrect. Low intensity and broad bands are observed in the spectra in the 858 to 865 cm^{-1} range. These bands are attributed to the antisymmetric ν_3 vibrations of the (VO_3) and/or $(UO_2)^{2+}$ units. Bands in the infrared spectrum between 880 and 905 cm^{-1} are assigned to the antisymmetric modes ν_3 of the $(UO_2)^{2-}$ units. The bands are of very low intensity in the Raman spectra. Such an assignment is in agreement with the assignment of bands in the infrared spectrum of synthetic uranyl vanadates by Chernorukov et al. [11, 18]. In the Raman spectra of the uranyl vanadates an intense band is observed in the 738 to 768 cm^{-1} range. The band may be resolved into two bands with the most intense band being observed at around 743 cm^{-1}. Chernorukov et al.[19] observed also bands near 740 cm^{-1}. In some papers, however, Chernorukov et al. [17, 19] erroneously assigned bands in the infrared spectrum of synthetic uranyl vanadates at 740 cm^{-1} to ν_1 of the $(UO_2)^{2+}$ units. Later, the same author [19] unambiguously attributed these bands to the ν_2 and/or ν_3 (VO_5) units.

In order to assist with the assignment of bands, the appropriate methodology is to undertake empirical calculations using the position of the bands in the Raman or infrared spectra to predict the U-O bond lengths and then to compare these bond lengths with the available X-ray diffraction data. [12] Such empirical relations have been devised. Empirical relations expressing that wavenumber of the symmetric stretching vibration $\nu_1 = f(\nu_3)$ cm^{-1} , i.e. $\nu_1 = 0.94\ \nu_3$ cm^{-1} and $\nu_1 = 0.89\ \nu_3 + 21$ cm^{-1} have been proposed. With these two relations, it is possible to can calculate approximate wavenumbers of the symmetric or antisymmetric stretching vibration $(UO_2)^{2+}$. The average bond lengths according to Burns are ~1.8 Å. [11] This means that bands in the 856 – 866 cm^{-1} region observed in the Raman spectra of curienite, francevillite and metatyuyamunite may be attributed to the ν_3 $(UO_2)^{2+}$ at 862 cm^{-1} provides a corresponding bond length $R_{U-O} = 1.791_5$ Å . The corresponding bond length from X-ray diffraction is 1.788(7) Å.

Chernorukov et al. calculated wavenumbers of antisymmetric and symmetric stretching vibrations and bending vibrations of UO_2^{2+} in the complex $[(UO_2)O_5]^{8-}$ and obtained these values: 885 ± 10 (IR), 810 ± 10 cm^{-1} (RA), and concluded that the bending vibration δ UO_2^{2+} is located lower than 400 cm^{-1} as mentioned above [19]. These calculated values agree with our observed data. If one uses these values for calculation of U-O bond lengths in uranyl [11, 33], one obtains 1.775(9) and 1.800(6) Å, respectively. Uranyl U-O bond lengths in synthetic uranyl vanadates containing Cs^+ and K^+ and natural francevillite are [1.785 and 1.781], [1.803 and 1.797], and [(1.791 and 1.801) and (1.789 and 1.813)] cm^{-1}, respectively. These values are comparable with those calculated by empirical relations using correct wavenumbers for the uranyl antisymmetric and symmetric stretching vibrations.

There have been many papers written on the infrared spectra of uranyl vanadates. Yet very few papers describe the bending modes. Whilst there is the potential overlap of the stretching modes of the uranyl and vanadate units, such is not the case for the bending modes which should be well separated. Čejka reports the doubly degenerate bending modes of the $(UO_2)^{2+}$ units for the autunite minerals at 298 and 254 cm^{-1} (page 551) [12]. Recently Frost et al. reported the Raman spectra of some selected vanadate minerals [27, 34]. The bending modes of the VO_4 units were described in the wavenumber range 340 to 460 cm^{-1}. The most intense band in the Raman spectrum of descloizite was observed at 339 cm^{-1} with a corresponding weak band in the infrared spectrum at 336 cm^{-1}. The bands were attributed to the ν_2 bending mode. In the low wavenumber region of the uranyl vanadates (Figure 2), a number of significant bands are observed. The most intense bands of the uranyl vanadates are observed around 370 cm^{-1} and are assigned to the δ bending modes of (V_2O_2) units [22]. Bands are observed over the 345 to 410 cm^{-1} region. Bands are observed in the Raman spectra of the uranyl vanadates in the range from 463 to 474 cm^{-1} and are assigned to the δ (VO_3) bending modes. Intense bands are observed in the 304 to 312 cm^{-1} region and in the 236 to 264 cm^{-1} range. These bands are assigned to the ν_2 bending modes of the $(UO_2)^{2+}$ units. Bands in the 150 to 230 cm^{-1} region are ascribed to lattice modes.

The attribution of the bending modes of the (VO_3) units appears partly to be in agreement with the published infrared data from Botto et al. [15, 31]. These researchers assigned bands in the infrared spectra in the 612 to 670 cm^{-1} region to water librational modes. In the Raman spectra of the uranyl vanadates, bands are observed in the 608 to 651 cm^{-1} range and may also be attributed to water librational modes. Such bands are expected to be intense in the infrared spectra but weak in the Raman spectra as may be observed in Figure 1. Botto et al. described bands in the 447 to 583 cm^{-1} range to equatorial U-O stretching vibrations [15] . In this work, we have assigned bands in the 464 to 479 cm^{-1} region to the ν_5 (VO_5) bending modes [19]. There may be some coincidence or overlapping of bands. Botto et al. also based their spectroscopic analysis on VO_3 units. Botto et al. described bands in the 350 cm^{-1} region to the bending modes of V_2O_2 units. These bands may be attributed to the δ (VO_3) and or δ (V_2O_2) units. Saadi studied IR spectra of M^+ uranyl vanadates (Na tetrahydrate, anhydrous K, Rb, Cs, NH_4, Ag, Tl) and M^{2+} uranyl vanadates tetrahydrates (Cu, Zn, Cd, Sr, Pb) in the range 600-1100 cm^{-1}. ν_3 UO_2^{2+} was observed in the range 876-893.4 cm^{-1} and 880-891 cm^{-1}, respectively; ν_1 UO_2^{2+} was not attributed in this thesis, however, it may be found in the range 789-814 cm^{-1} and 793-812 cm^{-1}, respectively. [32]

Carnotite (and curienite)

The number of studies of the vibrational spectroscopy of uranyl vanadates is small [19]. Previous studies have shown that the dominant peak in the Raman spectrum of uranyl vanadates was a peak near 738 cm^{-1} which was wrongly assigned to the symmetric stretching mode of the uranyl ion [35, 36] [37]. In this work we find the most intense peak at 738 cm^{-1} for the sample from paradox valley, Colarado and at 746 cm^{-1} for the sample from Nucla, Colorado. A carnotite mineral sample from Radium Hill, Olary, South Australia also gave a strong band at 745 cm^{-1}. A second band may be resolved in the spectrum of the Nucla sample at 753 cm^{-1}. These bands are assigned to the ν_2 and/or ν_7 vibrations of (VO_5) units [19]. A second intense band is observed at around 975 cm^{-1}. The band is assigned to the symmetric stretching mode of the vanadate units. The assignment of the band in this position is in good agreement with the assignment of Chernorukov et al. [19] In the infrared spectrum of synthetic carnotite Baran and Botto assigned the infrared band at 740 cm^{-1} to the ν_3 antisymmetric stretching mode and the band in the Raman spectrum at 737 cm^{-1} to the ν_1 symmetric stretching mode of the $(UO_2)^{2+}$ units [5]. Our spectroscopic analysis does not agree with these assignments.

In the infrared spectrum of carnotite a band is observed at 465 cm^{-1} and is assigned to the bending mode of the (VO_3) [ν_5 (VO_5)] units [19]. Raman bands are observed at 470 cm^{-1} and are assigned to this vibration. A second band is observed at 464 cm^{-1} for the carnotite from Paradox valley, Colorado and is also assigned to this vibration. The band is observed at 465 cm^{-1} for curienite. These bands, however, may be also assigned to the ν(U-$O_{equatorial}$) vibrations [36]. A set of bands is observed at around 404-410, 368-374, and 347 to 362 cm^{-1}. These bands are assigned to the bending modes of the (VO_3) units. Raman bands are observed at 304 and 241 cm^{-1} for carnotite and are assigned to the ν_2 bending modes of the $(UO_2)^{2+}$ units. The bands are observed at 312, 288 and 264 cm^{-1} for curienite.

Francevillite

The crystal structure of francevillite has been determined [9]. Francevillite contains Ba and consequently the UO bond distances are shorter than for many uranyl vanadates [10]. As a consequence it is expected that the $(UO_2)^{2+}$ symmetric stretching vibrations will occur at a higher wavenumber. Čejka suggests that the ν_3 vibration of the $(UO_2)^{2+}$ units of francevillite should occur at approximately 880 cm^{-1} and that the ν_1 modes should be at around 800 or 824 cm^{-1} (page 560) [12]. In this work we find the most intense band in the Raman spectrum of francevillite to be at 747 cm^{-1}. The same value is obtained for all three francevillites studied in this work. The band shifts to 750 cm^{-1} at liquid nitrogen temperature. According to Chernorukov et al. [19], this band may be attributed to the ν_2 or ν_7 (VO_5) unit vibrations. Two bands are observed at 976-980 and 964-966 cm^{-1} and are attributed to the ν_1 symmetric stretching modes of the (VO_3) units. The observation of two bands suggests the non-equivalence of the VO bonds. A moderately intense Raman band is observed at 828 cm^{-1} for francevillite. This band is assigned to the ν_1 symmetric stretching vibrations of the $(UO_2)^{2+}$ units. A second band is observed at around 866 cm^{-1} and is assigned to the ν_3 (VO_3) or ν_3 $(UO_2)^{2+}$ vibrations. The vibrational spectroscopy of the bending region of francevillite has not been reported. Raman bands are observed in the 463 to 485 cm^{-1} and are attributed to the δ (VO_3) bending modes. A second set of bands is found around 405, 370 and 342 cm^{-1} and are attributed to the δ bending modes of the (VO_3) or $(V_2O_2)^{\text{units}}$.

Tyuyamunite and metatyuyamunite

Botto et al. reported the infrared spectrum of synthetic and natural metatyuyamunite [15]. The ν_3 bands of the $(UO_2)^{2+}$ units were given as 803 and 814 cm^{-1} for synthetic metatyuyamunite and 808 cm^{-1} for natural metatyuyamunite. The ν_1 bands of the $(UO_2)^{2+}$ units was given as 748 cm^{-1} in the infrared and 747 cm^{-1} in the Raman spectrum. According to Čejka [12] such a band assignment is open to question. The assignments were based upon a comparison of uranyl vanadates and uranates. Such a comparison is invalid as the structures and uranyl anion sheet topologies of the two sets of uranyl phases are different. For the three tyuyamunites studied the most intense band is observed at around 743-748 cm^{-1}. The position of the band for metatyuyamunite is slightly less and is observed at 742 cm^{-1}. As all uranyl vanadates concerns, Chernorukov et al. [19] assign these strong bands to the ν_2 and/or ν_7 (VO_5) unit vibration. Raman bands are observed in the range 827 to 832 cm^{-1} and are ascribed to the ν_1 symmetric stretching modes of the $(UO_2)^{2+}$ units. Two bands assigned to this vibrational mode are observed for metatyuyamunite at 824 and 793 cm^{-1}. These bands are assigned to the ν_1 symmetric stretching modes of the $(UO_2)^{2+}$ units. The profile of the 950 to 1000 cm^{-1} region is complex for the tyuyamunite minerals. An intense band is observed at around 970 to 979 cm^{-1} and is assigned to the ν_1 symmetric stretching mode of the (VO_3) units. The band is observed at 963 cm^{-1} for metatyuyamunite. No antisymmetric stretching bands were observed for either the $(UO_2)^{2+}$ or (VO_3) units for tyuyamunite. A band is observed at 865 cm^{-1} for metatyuyamunite which is attributed to the antisymmetric stretching vibration of the $(VO_3)^{\text{or}}$ more probably $(UO_2)^{2+}$ units.

U-O bond lengths in uranyl were calculated for the uranyl vanadates studied with the empirical relation by Bartlett and Cooney[38], in which wavenumbers of the ν_1 $(UO_2)^{2+}$ symmetric stretching vibrations are used. The values obtained for carnotite [(1.784_7 and 1.784_7); 1.785_7 Å], curienite [1.785_7 Å], francevillite [1.784_7; (1.784_7 and 1.824); 1.781_8 Å], tyuyamunite [1.783_8; 1.782_8; 1.778_9 Å] and metatyuyamunite [1.786_7; 1.818 Å] are in agreement with the bond lengths from single crystal structure analysis [19]. In the case of some spectra of carnotite and francevillite, two bands attributed to the ν_1 $(UO_2)^{2+}$ were observed. This indicates that two structurally distinct uranyls may be present in the crystal structure. They also agree with the U-O bond lengths in uranyl calculated with various empirical relations expressing $R_{U-O} = f [\nu_3 (UO_2)^{2+}]$ Å [12, 33] from the IR spectra of uranyl vanadate minerals. These values vary approximately in the range 1.770-1.798 Å [12].

Conclusions

The vibrational spectroscopy of the uranyl vanadate minerals including carnotite, curienite, francevillite, tyuyamunite and meta tyuyamunite have been characterised using Raman spectroscopy. The advantages of Raman spectroscopy are highlighted with the application to the study of these minerals. The minerals are rapidly analysed in-situ with minimal sample treatment other than orientation of the host matrix under the microscope. Bands in the Raman spectrum are well separated and don't suffer from the complexity of the overlap of broad bands as occurs with infrared spectroscopy. This separation of the bands enables the attribution of the bands in the Raman spectra. These assignments using Raman spectroscopy goes a long way to overcoming the confusion in the literature on the assignations of the Raman bands based upon infrared spectroscopy.

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Table 1 Results of the Raman spectroscopic analysis of selected uranyl vanadates.

Carnotite			Curienite	Francevillite			Tyuyamunite			Meta tyuyamunite	Suggested assignments
M17518	M22553				M33948	M43680	M27401	M33787	M36658		
Raman 298 K	Raman 298 K	IR published [39]	Raman	Raman 298 K	Raman 298 K	Raman 298 K	Raman 298 K	Raman 298 K	Raman 298 K	Raman 298 K	
				1162 1145							PO_4 impurity
				1070							
975	985 973		976 959	976 964	980 966	977 965	975	979 967	970	963	ν_1 (VO_3) symmetric stretching vibrations in the (V_2O_8)
948	950	900		948	948						
		860	860	858	866	861				865	ν_3 of $(UO_2)^{2+}$
837 826	825		825	828	826 787	829	827	828	832	824 793	ν_1 of $(UO_2)^{2+}$
746	753 738		741	747	747	747	747	768 743	748	742	ν_2 and/or ν_3 (VO_5)
644 608	641		655	645	645	609	644 608	644	646	651	Water librational modes or the stretching modes $\nu(V_2O_2)$ units
582	583		569		582		582	580	575	573	Equatorial U-O vibrations [15]
525	539		534	524	527	526	525	538	537	529	

	508							522			
470	480 464	480	465	467 463	471	485 470	470	479	499 474	469	ν (U-$O_{equatorial}$) units
404 368 347	408 374 360		410 374 362	391 369 353	406 370 342	405 370	404 369 345	406 363	408 365	410 371	bending modes of the (V_2O_2) in the (V_2O_8) units
304 241	315 272 253		312 288 264	305 261	304 256 241	304 240	304 239	310 246	304	308 255	ν_2 of $(UO_2)^{2+}$
227	223		234	233	227			229	236	230	M-O stretching mode Lattice modes
186 160	195		193	203 152	188	186 163	186 155	185 174	176		Lattice modes

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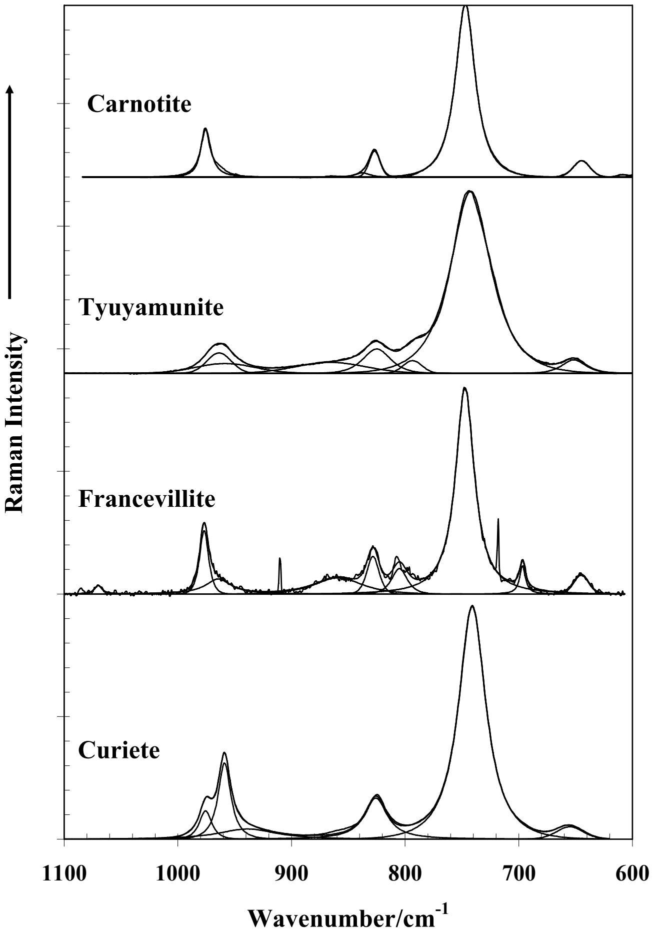
Carnotite
Tyuyamunite
Francevillite
Curiete
Raman Intensity
1100
1000
900
800
700
600
Wavenumber/cm-1

Figure 1

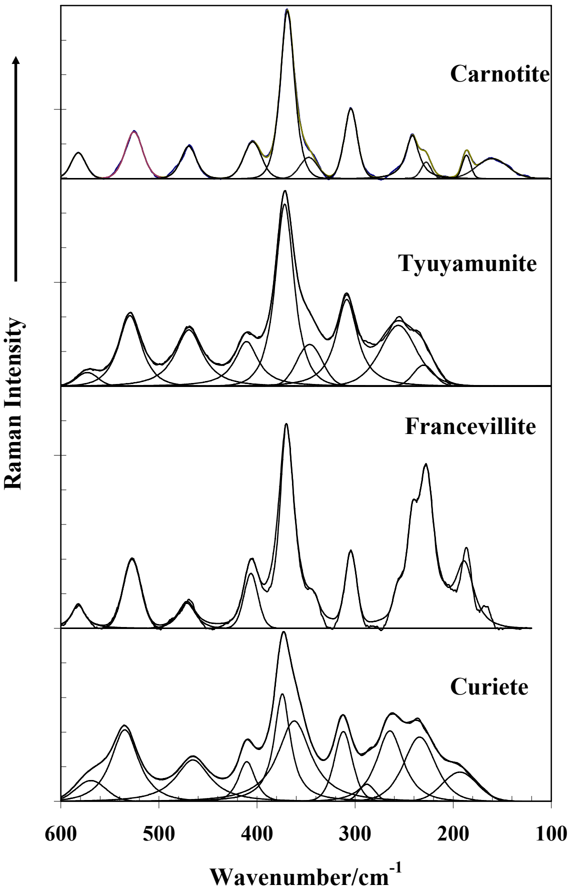
Carnotite
Tyuyamunite
Francevillite
Curiete
Raman Intensity
600
500
400
300
200
100
Wavenumber/cm^{-1}

Figure 2