

Molecular Structure of the uranyl mineral andersonite – A Raman spectroscopic study

Ray L. Frost*, Onuma Carmody, Kristy L. Erickson, Matt L. Weier and Jiří Čejka[†]

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[†] National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

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Abstract

The molecular structure of the mineral andersonite, a uranyl tricarbonates, has been studied by Raman microscopy at 298 and 77 K and ATR infrared spectroscopy. Raman bands are observed at 3558, 3510 and 3415 cm^{-1} and infrared bands at 3559, 3502, 3388, 3270 and 3120 cm^{-1} enabling estimates of the hydrogen bond distances of 2.98, 2.91, 2.80, 2.77, 2.70₇ and 2.70₁ Å to be estimated. The wide range of values shows the water molecules are not equivalent in the structure of andersonite. Two well resolved Raman bands at 1092 and 1080 cm^{-1} assigned to the ν_1 symmetric stretching modes of the $(\text{CO}_3)^{2-}$ units prove the existence of two non-equivalent carbonate units. A single peak at 832 cm^{-1} resolvable into two bands at 833 and 831 cm^{-1} is attributed to the overlap of the symmetric stretching modes of the $(\text{UO}_2)^{2+}$ units and the ν_2 bending modes of the $(\text{CO}_3)^{2-}$ units. The ν_4 in-plane bending region is characterised by three Raman bands at 745, 726 and 698 cm^{-1} confirming the loss of symmetry of the carbonate anion and the non-equivalence of the carbonate units. Raman spectroscopy at 298 and 77 K assists in the assignation of bands to the structure of andersonite.

Keywords: andersonite, liebigite, uranyl carbonate, dehydroxylation, dehydration, infrared and Raman spectroscopy

1. Introduction

Uranyl carbonate solid state and solution chemistry plays one of the most important roles in the actinide chemistry, mineralogy, geochemistry and “environmental chemistry” with regard to uranium(VI) migration in natural waters and to spent nuclear fuel problems. Actinide carbonate complexes inclusive those of

* Author to whom correspondence should be addressed (r.frost@qut.edu.au)

uranium are to be reflected in migration from a nuclear waste repository or in accidental site contamination. To gain an understanding of the geochemical behavior of such materials, a fundamental knowledge of actinide carbonate chemistry and mineralogy seems to be needed [1]. The study of the uranyl carbonates has been undertaken for an extended period of time [2, 3]. There are a significant number of compounds containing the uranyl ion [4]. Included in these are many uranyl carbonates [5-7]. These uranyl carbonates may be divided into those based upon tricarbonates, tetracarboxates (e. g. fontanite), dicarbonates (e. g. zellerite), hydroxocarbonates (e. g. rabbittite), those with single carbonate in the formula such as rutherfordine (UO_2CO_3) [8-10], blatonite ($\text{UO}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) [11] and joliotite $\text{UO}_2\text{CO}_3 \cdot \sim 2\text{H}_2\text{O}$ [12], and uranyl carbonates containing also other anions, e.g. sulfate, fluoride and silicate anions, such as schröckingerite, albrechtschraufite and lepersonnite [13]. Sharpite is a hydrated calcium uranyl hydroxocarbonate [$\text{Ca}(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_4 \cdot 6\text{H}_2\text{O}$] [14, 15]. Many of these minerals have been synthesised [16, 17]. The uranyl tr carbonate solids are, without questions, the most thoroughly studied actinyl(VI) carbonate solids [1, 18-20]. Among the tricarbonates minerals is the mineral andersonite [$\text{Na}_2\text{Ca}(\text{UO}_2)_6(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$] [21-23] where x is variable but may be a number between 5 and 6.

Crystal structures of most of synthetic and natural uranyl tricarbonates have been determined. All uranyl tr carbonate complexes display a hexagonal dipyrmidal coordination geometry where three bidentate carbonate ligands lie in a hexagonal plane, and the trans oxo ligands occupy coordination site above and below the plane. This means that uranyl oxygens are located in the apexes of the uranyl coordination polyhedra, i.e. hexagonal dipyrmid, while six carbonate ligands are bidentately bonded in the uranyl equatorial plane. According to Burns [24-26], these structures are based upon finite clusters of polyhedra of higher bond valence. The cluster $(\text{UO}_2)(\text{CO}_3)_3$ is composed of a $\text{U}\Phi_6$ ($\Phi = \text{O}^{2-}$) hexagonal dipyrmid that shares three equatorial edges with CO_3 triangles. In addition to the $(\text{UO}_2)(\text{CO}_3)_3$ cluster, the structure of andersonite contains two symmetrically distinct $\text{Na}\Phi_6$ octahedra, one $\text{Ca}\Phi_7$ polyhedron, and one H_2O hydrogen bonded into the structure. The $\text{Na}\Phi_6$ octahedra and $\text{Ca}\Phi_7$ polyhedra link to each other, as well as to the $(\text{UO}_2)(\text{CO}_3)_3$ cluster, forming a complex heteropolyhedral framework structure. The structure of andersonite contains a channel along [001] that contains disordered H_2O groups [21, 25-27]. Many of these minerals may be readily synthesised and their chemistry studied by the normal analytical techniques [18, 19].

Coda et al. found that the structure was trigonal with space group R_{3m} . The number of formula units per unit cell was found to be 18 [28]. Coda et al. proposed a structure in which the U is in a hexagonal dipyrmid structure with two apical oxygens closer to one U than the second at 1.81 and 1.78 Å. In the structure six equatorial oxygens belong to the three bidentate carbonate anions [28]. One of the difficulties in studying the infrared (and Raman) spectra of uranyl carbonates is the potential overlap of bands associated with $(\text{UO}_2)^{2+}$ and the $(\text{CO}_3)^{2-}$ units. The region for the symmetric stretching vibration of the $(\text{CO}_3)^{2-}$ units is a spectral window free from bands ascribed to the $(\text{UO}_2)^{2+}$ units. One potential overlap is between the antisymmetric stretching vibrations of the $(\text{CO}_3)^{2-}$ units and the δ bending water modes. Another major difficulty is the possible overlap of the symmetric stretching modes of the $(\text{UO}_2)^{2+}$ units and the bending modes of the $(\text{CO}_3)^{2-}$ units. There is

another consideration caused by the presence or absence of water in the structure. The presence of water may cause significant shifts in the bands associated with both $(\text{UO}_2)^{2+}$ units and $(\text{CO}_3)^{2-}$ units.

In this work we attribute bands at various wavenumbers to vibrational modes of andersonite using Raman spectroscopy at both 298 and 77 K complimented with infrared spectroscopy.

2. Experimental

2.1 Minerals

Two samples of andersonite were obtained from Museum Victoria. The first sample was type mineral m33701 and originated from Grants, New Mexico, USA and the second sample m27399 originated from Moab, Utah, USA. The minerals were analysed by X-ray diffraction for phase purity and by electron probe for chemical composition.

2.2 Raman microprobe spectroscopy

The crystals of andersonite 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 liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Details of the technique have been published by the authors [29-32].

2.3 Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the $4000\text{--}525 \text{ cm}^{-1}$ 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 .

Spectral manipulation such as baseline adjustment, smoothing and normalisation was performed using the GRAMS® software package (Galactic Industries Corporation, Salem, NH, USA).

3. Results and discussion

The number of observed bands assigned to the carbonate vibrations in the infrared and Raman spectra of andersonite samples studied indicates the symmetry decrease of carbonate ions from D_{3h} to C_{2v} or lower. This causes activation of all vibrations, the ν_1 symmetric stretching, the ν_2 symmetric bending, the ν_3 antisymmetric stretching, and the ν_4 antisymmetric bending vibrations in IR and Raman spectra, and splitting of the doubly degenerate ν_2 and the triply degenerate ν_3 and ν_4 vibrations [15].

The Raman spectra at 298 and 77 K together with the infrared spectra of the two andersonite type minerals in the 950 to 1200 cm^{-1} range are shown in Figure 1. The results of the analyses of the spectra are reported in Table 1. In andersonite there are two structurally distinct $(\text{CO}_3)^{2-}$ units [28] and as a consequence two symmetric stretching modes are predicted. Figure 1 clearly shows two well resolved bands at 1092 and 1080 cm^{-1} for andersonite m33701. The relative intensity of the bands is 2.42/1. The bands shift to 1097 and 1082 cm^{-1} in the 77 K spectrum with a relative intensity of 2.02/1. There is a significant shift in relative intensity of these two bands upon cooling to liquid nitrogen temperature. This suggests that andersonite undergoes structural change upon cooling to liquid nitrogen temperature. The Raman spectrum of andersonite m27399 shows identical spectra. Two bands are observed at 1091 and 1079 cm^{-1} with an intensity ratio of 1.95/1 which shift to 1098 and 1079 cm^{-1} upon cooling to liquid nitrogen temperature with an intensity ratio of 1.4/1. The change in the intensity ratio is 0.4 for the first andersonite sample and 0.55 for the second sample. The infrared spectra of sample m33701 show two bands at 1092 and 1080 cm^{-1} with an intensity ratio of 1/3. These bands are attributed to the symmetric stretching modes of the $(\text{CO}_3)^{2-}$ units. These bands overlap with a multitude of bands which may be attributed at least in part to water librational modes. Infrared bands are resolved at 1067, 1032, 998 and 975 cm^{-1} . Two infrared bands are observed in the spectrum of sample m27399 at 1092 and 1084 cm^{-1} but are of low intensity. Čejka reported two bands for the infrared spectra of andersonite at 1092 and 1080 cm^{-1} with the first band a shoulder on the second [33].

The $(\text{CO}_3)^{2-}$ antisymmetric stretching bands are shown in Figure 2. The figure also includes the bands due to the δ HOH bending vibrations. What is clearly evident is that the Raman spectra do not show any bands in the δ HOH spectral region. This is due to the very low scattering cross section for water. Two bands are observed in the Raman spectrum of sample m33701 at 1406 and 1370 cm^{-1} with an intensity ratio of 0.117 which shift to 1097 and 1082 cm^{-1} in the 77 K spectrum with an intensity ratio of 0.178. In the infrared spectrum two bands are observed at 1375 and 1347 cm^{-1} which are assigned to the ν_3 antisymmetric stretching vibrations. Bands are also observed at 1578, 1558 and 1523 cm^{-1} which may also be ascribed to the antisymmetric stretching vibrations. Čejka reported ν_3 vibrational modes at 1570, 1522 and 1378 cm^{-1} [33]. Other low intensity infrared bands are observed at 1691, 1665, 1636 and 1596 cm^{-1} and may be attributed to δ HOH bending vibrations. The observation of four bands at different wavenumbers is interpreted in terms of the strength of hydrogen bonding of water. The band at 1596 cm^{-1} is at a position equivalent to water vapour and represents very weak hydrogen bonding. The bands at 1691 and 1665 cm^{-1} represent strong hydrogen bonding. Bands for δ HOH bending modes were also reported in the spectra of synthetic andersonites at 1660 cm^{-1} and also a around 1690 cm^{-1} (not marked) by Čejka [33].

The spectra in the 800 to 940 cm^{-1} region are shown in Figure 3. This is one of the regions where there is potential overlap between the symmetric stretching modes of the $(\text{UO}_2)^{2+}$ units and the ν_2 bending modes of the $(\text{CO}_3)^{2-}$ units. In the Raman spectrum of andersonite sample m33701 a band is observed at 832 cm^{-1} which may be resolved into two components at 833 and 831 cm^{-1} . The band shifts to 835 cm^{-1} in the 77 K spectrum where two bands at 835 and 833 cm^{-1} may be resolved. The intensity ratio changes from 0.542/1 in the 298 K spectrum to 1.78/1. There is a significant shift in the ratio of the intensity of the bands upon cooling to liquid nitrogen temperature. For the sample andersonite m27399 two bands are observed at 833 and 830 cm^{-1} which shifts to 835 and 832 cm^{-1} in the 77 K spectrum. In the infrared spectrum low intensity bands are observed at 848 and 833 cm^{-1} . Čejka reported two infrared bands at 848 and 851 cm^{-1} [33]. The problem of band overlap between the symmetric stretching modes of the $(\text{UO}_2)^{2+}$ units and the ν_2 bending modes of the $(\text{CO}_3)^{2-}$ units is exacerbated by the non-equivalence of the $(\text{CO}_3)^{2-}$ units in the structure of andersonite. A number of bands are observed in the infrared spectrum at 914, 911, 901, 898 and 887 cm^{-1} . These bands are not observed in the Raman spectra and may probably be assigned to water librational modes.

However, two bands or a band and a shoulder near 900 cm^{-1} and 913 cm^{-1} observed in the IR spectra of natural and synthetic andersonite ([34-36] were assigned to the $\nu_3 \text{UO}_2^{2+}$. The doubling of the number of absorption bands of this vibration was observed also in the case of natural metatorbernite [37] and its synthetic analogue [38]. The increase of the number of absorption bands related to the $\nu_3 \text{UO}_2^{2+}$ (890 cm^{-1} , shoulders at 902 and 932 cm^{-1}) was observed in the IR spectrum of liebigite [5]. The O-U-O angles in the equatorial plane of the hexagonal dipyramid, the uranium coordination polyhedron in andersonite, vary in the range 53.2-69.6°. Electrostatic field of such distorted polyhedrons strongly influences the structure as well as the symmetry of the uranyl group which may cause formation of geometrically different uranyl groups. Thus the increase of the number of uranyl vibrations in the IR spectrum of andersonite can be inferred. The character of a very weak broad absorption band assigned to the $\nu_1 \text{UO}_2^{2+}$ shows the possibility of overlapping of several absorption bands which supports this conclusion [15]. The U-O bond lengths in uranyl in andersonite are 1.81(2) and 1.78(2) Å according to Coda et al. [20] Using an unpublished empirical relation for uranyl carbonates [$R = 1.0882 + 65.3555 (\nu_3 \text{UO}_2^{2+})^{-2/3}$ Å, $r = 0.856$, Čejka – unpublished results] calculated U-O bond lengths for 914 and 901 cm^{-1} are 1.7821 and 1.7888 Å respectively. These values are in agreement with those published by Coda et al. [28]. It is not known whether the bands at 833 and 831 cm^{-1} are due to the ν_1 symmetric stretching mode of the $(\text{UO}_2)^{2+}$ units or the out of plane ν_2 bending modes of the $(\text{CO}_3)^{2-}$ units. It is probable that both bands overlap or occur at the same wavenumber. A band in the 800 to 830 cm^{-1} has been previously observed in the Raman spectra and has been attributed to the ν_1 band of the $(\text{UO}_2)^{2+}$ units [17]. Such an assignment is open to question because of the obvious overlap of the two vibrations. However, it may be assumed that the bands at 833 and 831 cm^{-1} may be attributed to the $\nu_1 \text{UO}_2^{2+}$. Calculated range ($\nu_1 = 0.94 \nu_3$ and $\nu_1 = 0.89 \nu_3 + 21 \text{ cm}^{-1}$ (for details see Čejka [25]) corresponds to 859-834 (for 914) cm^{-1} and 845-823 (for 901 cm^{-1}). An empirical relation [$R = 0.575 + 106.5 (\nu_3 \text{UO}_2^{2+})^{-2/3}$ Å, [39] enables to calculate the U-O bond lengths in uranyl which are 1.778 Å (for 833 cm^{-1}) and 1.780 Å (for 831 cm^{-1}). These values are also in agreement with the data by Coda et al. (1981). Neither Coda et al. [28] nor Mereiter (1986)

[27]inferred from the X-ray single crystal structure analysis the presence of two structurally distinct uranyls in the structure of andersonite. On the contrary, Raman and infrared spectra of andersonite prove the presence of two structurally non-equivalent uranyls. An alternative explanation rests with the factor group analysis of the unit cell in which factor group splitting may result in the observation of the two bands at 833 and 831 cm^{-1} .

The Raman and infrared spectra of the two andersonite samples in the 650 to 800 cm^{-1} region are shown in Figure 4. This spectral region represents the ν_4 in-plane bending region of the $(\text{CO}_3)^{2-}$ units. Two bands are observed in the 298 K Raman spectrum at 742 and 696 cm^{-1} . The first band is resolved into two components in the 77 K spectrum at 745 and 726 cm^{-1} . This splitting is probably due to the removal of the degeneracy. For the andersonite sample m27399, the Raman spectrum at 298 K shows three bands at 744, 732 and 697 cm^{-1} with better band separation in the 77 K spectrum with bands observed at 749, 732 and 701 cm^{-1} . Increased complexity is observed in the infrared spectrum of andersonite m33701. Four bands are observed at 797, 726, 716, 702 and 695 cm^{-1} . The observation of five bands is ascribed to the loss of degeneracy and the non-equivalence of the carbonate units. For the second andersonite sample, four bands are observed at 798, 778, 724 and 697 cm^{-1} . Čejka reported two bands at 727 and 700 cm^{-1} [21].

The Raman spectra of the low wavenumber region are shown in Figure 5. This spectral region shows the ν_2 $(\text{UO}_2)^{2+}$ bending modes. In the 298 K spectrum of andersonite m33701 bands are observed at 299, 284, 242, 224, 182 and 164 cm^{-1} . Čejka reported bands in the infrared spectrum at 286, 268 and 255 cm^{-1} [21]. The most intense band is observed at 224 cm^{-1} . In the Raman spectrum of andersonite sample m33791 at 77 K, bands are observed at 307, 289, 277, 268, 230, 220, 189 and 169 cm^{-1} . The Raman spectrum of andersonite sample m27399 is different from the first sample. Raman bands are observed at 298, 285, 251, 224, 214, 182 and 164 cm^{-1} . The spectra in this region are more complex than would be expected. It would appear that at the molecular level the two andersonite minerals are different. This was in part observed in the ν_4 spectral region. The results of the Raman spectra lead to the conclusions that not only are the UO bond lengths different but that some of the $(\text{UO}_2)^{2+}$ units are not equivalent. Čejka suggested a possible coincidence of ν_2 δ $(\text{UO}_2)^{2+}$ and UO ligand vibrations [33]. Differences between the two studied samples of andersonite may be caused by their different conditions of formation in nature which may especially influence the arrangement of a hydrogen bonding network in originating mineral species.

The Raman and infrared spectra of the ν OH stretching region of the two andersonite minerals are shown in Figure 6. In the Raman spectrum of m33701 three bands are observed at 3558, 3510 and 3415 cm^{-1} . Upon cooling to liquid nitrogen temperature, better band separation is obtained and five bands may be resolved at 3559, 3502, 3388, 3270 and 3120 cm^{-1} . The infrared spectrum of sample m33701 shows a similar pattern with bands observed at 3545, 3512, 3406, 3369, 3211 and 3194 cm^{-1} . Čejka reported peak maxima at 3563, 3430 and 3220 cm^{-1} [33]. In the Raman spectrum of sample m27399 bands are found at 3558, 3526 and 3409 cm^{-1} in the 298 K spectrum and at 3560, 3548, 3411, 3368 and 3115 cm^{-1} in the 77 K spectrum. The set of infrared bands with different wavenumbers provides a basis for

the description of hydrogen bonding in andersonite. By using an empirical expression based upon the work of Libowitzky, estimated hydrogen bond distances may be calculated from the infrared water stretching bands [40]. The bands observed at 3545, 3512, 3406, 3369, 3211 and 3194 cm^{-1} give hydrogen bond distances of 2.98, 2.91, 2.80, 2.77, 2.70₇ and 2.70₁ Å. Such measurements are difficult to obtain by X-ray diffraction and neutron activation studies of minerals are very few. These values show there is a wide distribution of hydrogen bond distances as might be expected for the structure of andersonite. Hydrogen bond distances of >2.80 Å may be considered as weak hydrogen bonds whereas at least comparatively the hydrogen bond distances of <2.70 Å may be considered as strong hydrogen bonds.

4. Conclusions

This work serves to show the application of Raman spectroscopy for the in-situ analysis of a uranyl tricarbonates mineral known as andersonite. The use of the microscope and associated Raman spectrometer allows single crystals are selected for the analysis. It should be noted there is almost no sample preparation apart from the alignment of the crystals in the incident beam. Raman spectroscopy may be used with a thermal stage allowing spectra to be obtained at any temperature. The collection of Raman data at liquid nitrogen temperature enables significantly improved band separation. Raman spectroscopy has by its very nature normally narrow bands as compared with infrared spectroscopy, and by obtaining data at 77 K, improved signal to noise is achieved.

The mineral andersonite is an interesting mineral because of its structure with 18 formula units per unit cell and with non-equivalent carbonate and non-equivalent UO bonds. Infrared and Raman spectroscopy confirm the non-equivalence of both units by the observation of additional bands for the $(\text{CO}_3)^{2-}$ units. Two symmetric stretching modes of the $(\text{CO}_3)^{2-}$ units are observed confirming the presence of non-equivalent carbonates. This non-equivalence is translated into the antisymmetric stretching region where multiple ν_3 stretching vibrations are observed. One of the difficulties in studying uranyl carbonates is the potential coincidence of the symmetric stretching modes of the uranyl group and the out-of-plane bending modes of the carbonate units.

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Table 1 Results of the Raman and infrared spectra of andersonite

m33701			m27399		
Raman 298K	Raman 77K	IR	Raman 298K	Raman 77K	IR
Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)	Band Centre (cm ⁻¹) / Intensity (%)
3558 / 1.68 3510 / 3.14 3415 / 21.19	3559 / 0.80 3502 / 6.03 3388 / 17.23 3270 / 2.16 3120 / 1.48	3608 / 1.09 3545 / 1.20 3512 / 3.23 3406 / 5.76 3369 / 21.94 3360 / 0.83 3211 / 11.96 3194 / 3.27	3558 / 1.10 3526 / 3.72 3409 / 25.72	3560 / 1.54 3548 / 0.99 3411 / 6.66 3368 / 3.35 3115 / 2.50	3607 / 1.71 3545 / 0.84 3516 / 6.40 3409 / 9.07 3406 / 1.65 3307 / 7.46 3193 / 1.47 3115 / 5.53 2920 / 1.16
		1691 / 0.45 1665 / 1.15 1636 / 1.37 1596 / 2.49 1578 / 1.34 1558 / 7.33 1541 / 2.67 1523 / 2.43 1517 / 3.52 1517 / 2.28			1658 / 2.60 1600 / 0.79 1577 / 4.81 1557 / 7.00 1523 / 2.42 1511 / 3.34
1406 / 0.37 1370 / 3.16	1409 / 0.42 1373 / 2.36	1426 / 1.55 1375 / 8.44 1347 / 4.29 1321 / 3.09	1406 / 0.36 1370 / 2.03		1430 / 4.43 1377 / 7.55 1350 / 3.73 1321 / 2.53
1092 / 6.83 1080 / 2.82 928 / 0.43	1097 / 5.74 1082 / 2.84	1138 / 0.19 1110 / 0.19 1092 / 0.12 1080 / 0.35 1067 / 0.10 1032 / 1.08 998 / 0.33 975 / 0.11	1091 / 6.37 1079 / 3.27	1098 / 5.46 1082 / 3.90	1166 / 0.48 1118 / 0.89 1092 / 0.04 1084 / 1.73 1079 / 0.14 1062 / 1.71 1020 / 3.09 985 / 1.35
		914 / 0.27 911 / 0.35 901 / 0.71 898 / 1.24 887 / 0.04 887 / 1.01			914 / 0.16 912 / 0.53 901 / 0.71 898 / 1.24 886 / 1.10 874 / 0.11
833 / 15.12 831 / 27.86 742 / 3.73 696 / 0.96	835 / 23.53 833 / 13.23 745 / 2.67 726 / 0.35 698 / 0.47	848 / 0.41 833 / 0.02 797 / 0.44 726 / 0.40 716 / 0.27 702 / 0.19 695 / 0.36 687 / 0.12	833 / 16.32 830 / 26.37 744 / 1.69 732 / 2.27 697 / 0.75	835 / 23.65 832 / 11.42 749 / 1.54 732 / 2.64 701 / 0.63	851 / 0.16 846 / 0.21 798 / 0.36 778 / 0.38 724 / 0.54 697 / 0.59

	575 / 1.00 497 / 0.39 473 / 0.62		568 / 1.56 467 / 0.96 351 / 0.78	648 / 1.07 578 / 2.28 364 / 0.81	
299 / 1.77 284 / 1.94 272 / 0.32	320 / 0.30 307 / 1.70 289 / 3.41 277 / 0.13 268 / 0.49		298 / 0.43 285 / 1.01	311 / 3.47 292 / 4.58 279 / 1.24 262 / 11.05	
242 / 0.39 224 / 6.74 182 / 0.65 164 / 0.90	230 / 5.89 230 / 2.84 220 / 1.16 189 / 1.40 169 / 1.06 148 / 0.32		251 / 0.32 224 / 2.58 214 / 0.90 182 / 0.35 164 / 0.82 138 / 0.33	247 / 1.35 231 / 7.67 214 / 2.20	

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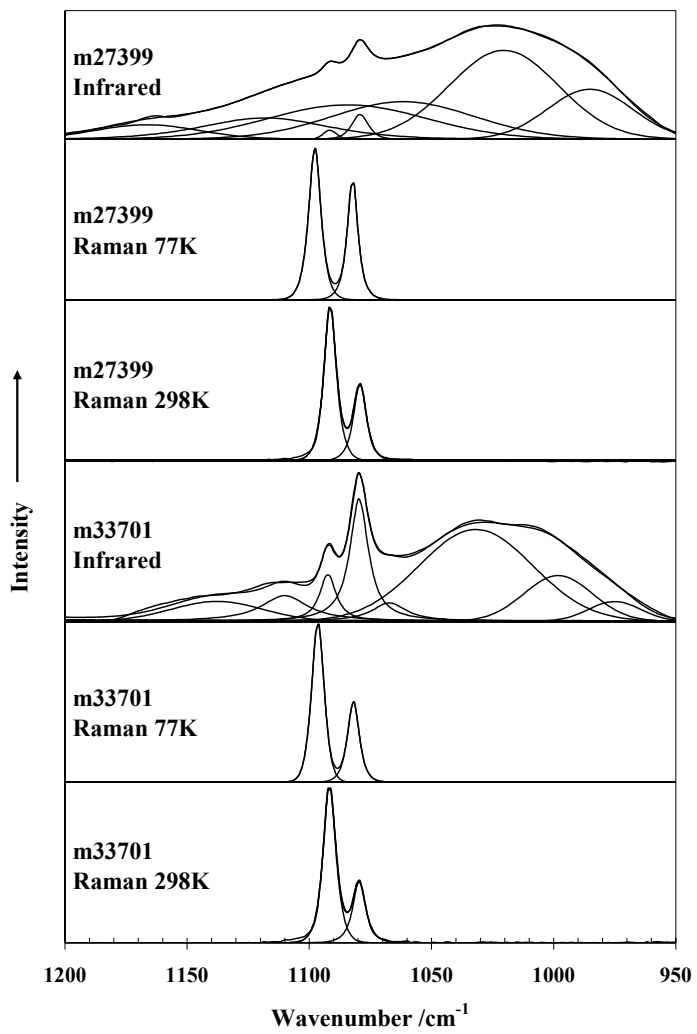


Figure 1

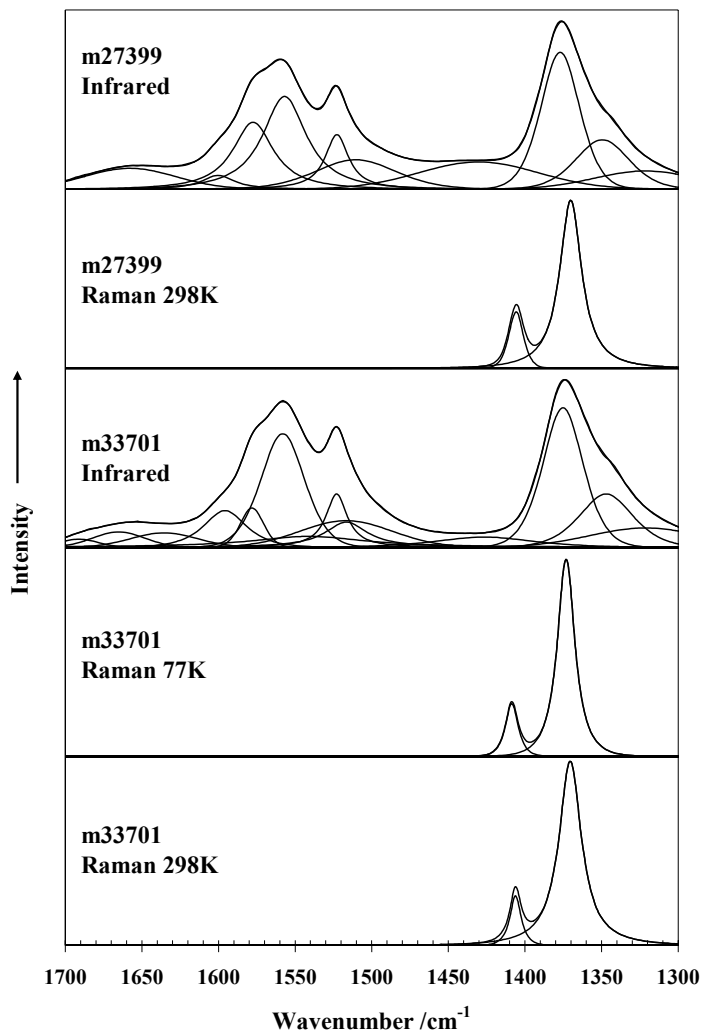


Figure 2

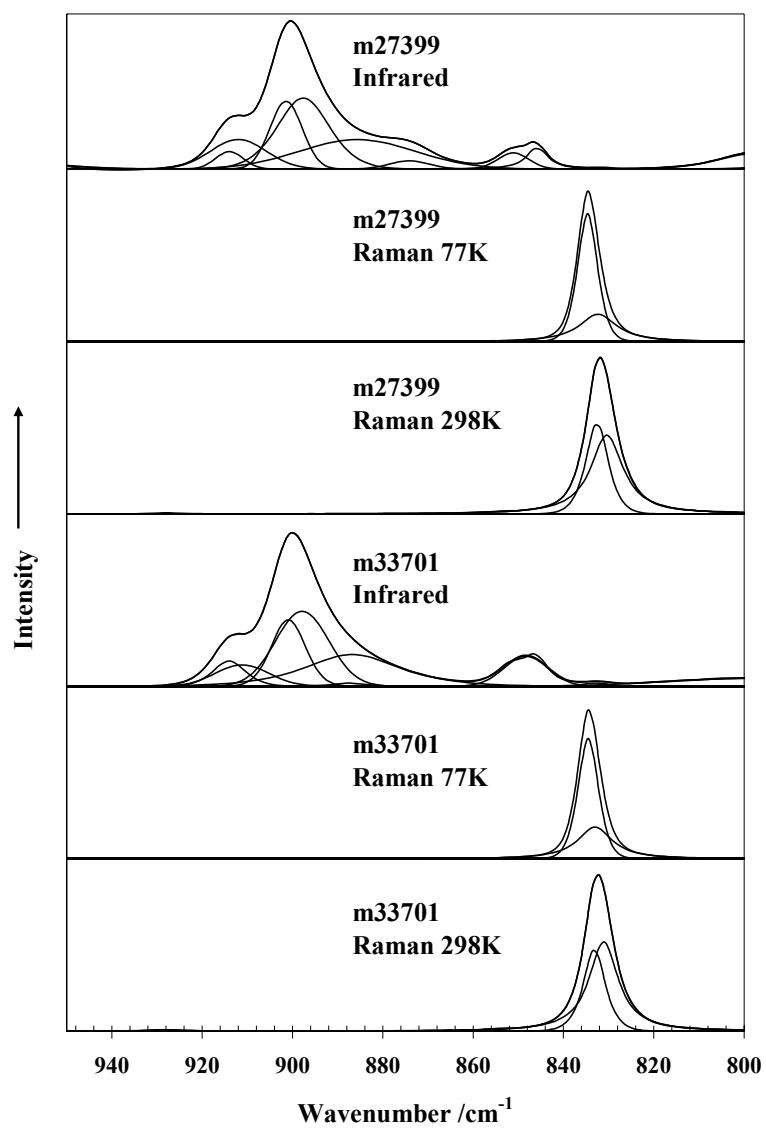


Figure 3

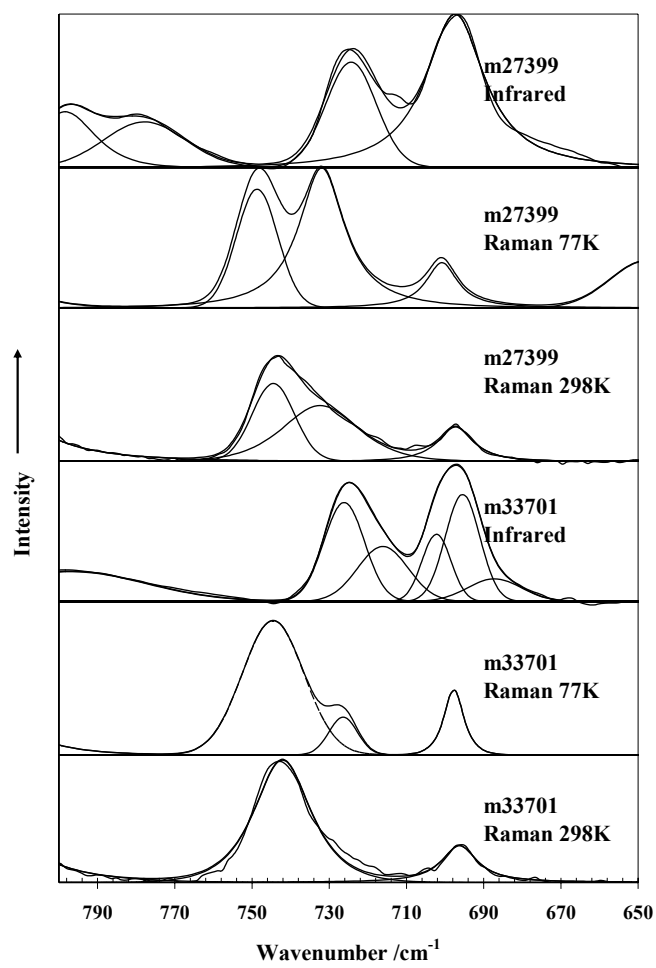


Figure 4

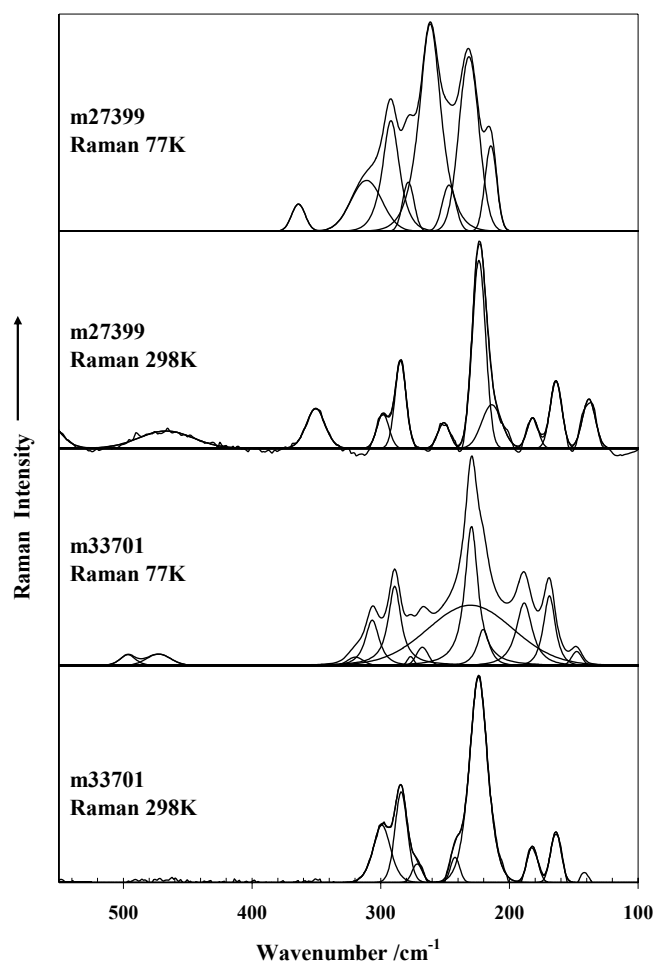


Figure 5

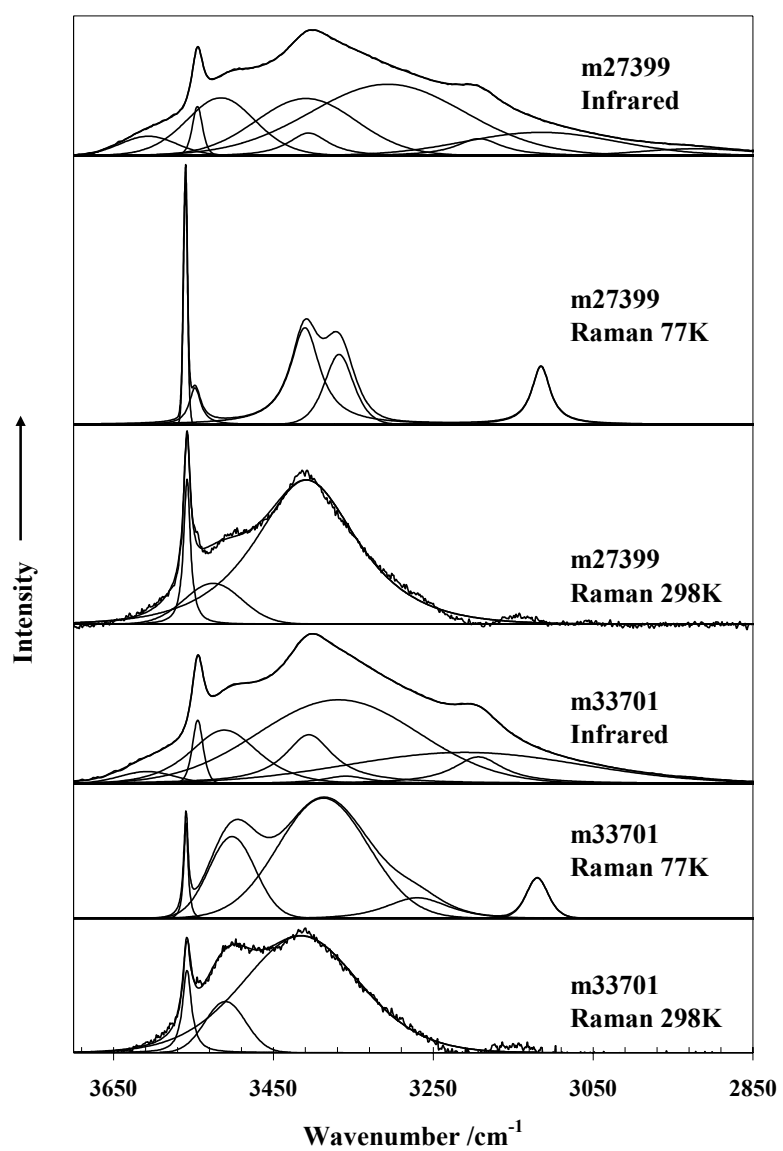


Figure 6

