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Raman and infrared spectroscopy of the manganese arsenate mineral allactite

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Abstract

The mineral allactite $[\text{Mn}_7(\text{AsO}_4)_2(\text{OH})_8]$ is a basic manganese arsenate which is highly pleochroic. The use of the 633 nm excitation line enables quality spectra of to be obtained irrespective of the crystal orientation. The mineral is characterised by a set of sharp bands in the 770 to 885 cm^{-1} region. Intense and sharp Raman bands are observed at 883, 858, 834, 827, 808 and 779 cm^{-1} . Collecting the spectral data at 77 K enabled better band separation with narrower bandwidths. The observation of multiple AsO_4 stretching bands indicates the non equivalence of the arsenate anions in the allactite structure. In comparison the infrared spectrum shows a broad spectral profile with a series of difficult to define overlapping bands. The low wavenumber region sets of bands which are assigned to the ν_2 modes (361 and 359 cm^{-1}), the ν_4 modes (471, 452 and 422 cm^{-1}), AsO stretching vibrations at 331 and 324 cm^{-1} , and bands at 289 and 271 cm^{-1} which may be ascribed to MnO stretching modes. The observation of multiple bands shows the loss of symmetry of the AsO_4 units and the non equivalence of these units in the allactite structure. The study shows that highly pleochroic minerals can be studied by Raman spectroscopy.

Key Words- allactite, arsenate, flinkite, retzian(La,Ce,Nd), Raman spectroscopy

INTRODUCTION

The locality of Langban, Sweden is renown for the number and variety of the minerals found in this area [1, 2]. Among the many minerals is a basic manganese arsenate known as allactite. The mineral was also known as [elfstorpite](#). [However this name was recently discredited \(2004\)](#). Allactite $[\text{Mn}_7(\text{AsO}_4)_2(\text{OH})_8]$ is a basic arsenate of manganese which is found in the Moss and Bratffors Mines Nordmark and Langban Varmland and also at the Franklin and Stirling Hill Mines, Ogdensburg, Sussex County, New Jersey, USA [3]. The mineral is a rare secondary mineral which is noted for its very strong pleochroism [4]. The mineral is a blood red in the X direction, pale yellowish in the Y direction and a green colour in the Z-direction. The mineral thus takes on different appearances depending on the orientation and varies from brownish-red through to colourless or white. The mineral is monoclinic with point group $2/m$. The cell parameters are $a=11.0$, $b=12.1$, and $c=5.5$ [4, 5].

The Raman spectra of the tetrahedral anions in aqueous systems are well known. The symmetric stretching vibration of the arsenate anion (ν_1) is observed at 810 cm^{-1} and coincides with the position of the asymmetric stretching mode (ν_3). The

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symmetric bending mode (ν_2) is observed at 342 cm^{-1} and the out-of-plane bending modes (ν_4) is observed at 398 cm^{-1} . Of all the tetrahedral oxyanions spectra, the positions of the arsenate vibrations occur at lower wavenumbers than any of the other naturally occurring mineral oxyanions spectra. Farmer lists a number of spectra of arsenates including the basic copper arsenates olivenite and euchroite [6]. The effect of the arsenate ion in a crystal will be to remove the degeneracy and allow splitting of the bands according to factor group analysis. The ν_1 and ν_3 bands of olivenite and euchroite were observed at $860, 828, 790\text{ cm}^{-1}$ and 830 and 770 cm^{-1} respectively. The bending modes were found at 493 and 452 cm^{-1} for olivenite and at 475 and 410 cm^{-1} for euchroite. No ν_2 bands were shown. This is no doubt related to the fact the bands are found below 400 cm^{-1} , which makes the measurement by infrared spectroscopy difficult.

Raman spectroscopy has proven extremely useful for the study of arsenate minerals [7-15]. Many of the arsenate vibrations occur at positions below the lower detection limit of the infrared spectrometer, thus making Raman spectroscopy advantageous for the study of arsenate minerals.

As part of a comprehensive study of the molecular structure of minerals containing oxyanions such as arsenate using Raman and infrared spectroscopy, we report the Raman properties of the above named basic manganese arsenate.

EXPERIMENTAL

The mineral samples

The allactite mineral sample was obtained from The Australian Museum. The mineral (Mineral Reference d26827 from The Australian Museum) originated from Nordmarken, Sweden. EDX measurements gave a chemical analysis of As_2O_5 as 31.0 % and MnO as 58.2% with some MgO and CaO present as impurities. No sulphate or phosphate was found in the analyses.

Raman microprobe spectroscopy

Crystals of the allactite mineral was orientated on a polished metal surface on the stage of an Olympus BHSM microscope equipped with 10x and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Details have been published. [16-18] Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

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 to 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 .

Spectroscopic manipulations such as baseline adjustment and normalization

were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and specific parameters to be fixed or varied accordingly. [16-18] Band fitting was done using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared regression coefficient of R^2 greater than 0.995.

RESULTS and DISCUSSION

Many arsenate minerals are difficult to measure using infrared spectroscopy as the bands are below the detection limits of the instrument. Such a difficulty is even more pronounced when measuring using an ATR technique. Raman spectroscopy does measure easily below 500 cm^{-1} and can approach the Rayleigh line depending on the quality of the filter system. The Raman spectra at 298 and 77 K together with the DRIFT spectra are shown in Figures 1 to 3. Fig. 1 shows the spectra in the 200 to 600 cm^{-1} region. Fig. 2 displays the Raman spectra in the 250 to 500 cm^{-1} region. Fig. 3 reports the spectra both Raman and infrared in the 3000 to 3800 cm^{-1} region. The results of the analyses of the Raman at 298 and 77 K are reported in Table 1.

The free arsenate ion has tetrahedral symmetry and thus should have four bands of which two are infrared active with theoretical values of ν_3 (F_2) 887 cm^{-1} and ν_4 (F_2) 463 cm^{-1} . The Raman active modes are observed at 837 (A_1) and 349 (E) cm^{-1} . Upon coordination of the arsenate ion to the copper atom, then the symmetry of the arsenate ion reduces to C_{3v} and may further reduce to C_{2v} . The implication is that all bands will be both infrared and Raman active. The 298 K Raman spectra show an intense band at 827.3 cm^{-1} which shows a slight shift to 827.5 cm^{-1} in the 77 K spectra. A shoulder on the higher wavenumber side of the 298 K band occurs at 834.1 cm^{-1} . This band is resolved into a band at 843.9 cm^{-1} in the 77 K spectrum. The 827.0 cm^{-1} band is sharp with a bandwidth of 9.3 cm^{-1} in the 298 K spectrum and 8.0 in the 77 K spectrum. One possible assignment is that this band together with the 827.3 cm^{-1} band are attributable to the ν_1 (AsO_4) symmetric stretching mode. The infrared spectra show a complex spectral profile with a number of broad overlapping bands making up the experimental spectrum. No bands are found around these positions in the infrared spectrum.

The Raman spectra at 298 K show two bands on the high wavenumber side at 858.5 and 883.0 cm^{-1} which are observed at 860.7 and 886.2 cm^{-1} in the 77 K spectra. These two bands may be attributed to the (B_{2u}) vibrational mode. Two bands are also found on the low wavenumber side of this complex pattern at 808.4 and 779.0 cm^{-1} in the 298 K spectrum and at 807.0 and 777.5 cm^{-1} in the 77 K spectrum. These bands may also be described by the (B_{2u}) mode. Two strong infrared bands are found at 937.3 and 997.7 cm^{-1} which may correspond to the Raman bands.

The low wavenumber region of allactite is complex and it is difficult to separate the Raman bands according to their symmetry. The spectrum of the low wavenumber region of olivenite may be divided into three separate regions: (a) 400 to 480 cm^{-1} (b) 340 to 370 cm^{-1} and (c) 250 to 300 cm^{-1} . It is proposed that these three regions define the (a) ν_4 modes (b) ν_2 modes and (c) AsO stretching and bending and

lattice modes. The ν_2 bending vibration should be intense and is observed as a broad band at 359.6 cm^{-1} in the 298 K spectrum and as two bands at 361.1 and 359.2 cm^{-1} in the 77 K spectrum. The observation of this mode below 400 cm^{-1} has been predicted for arsenates but not reported. The ν_4 modes are observed as multiple bands at 471.0 , 452.0 , and 422.0 cm^{-1} in the 298 K spectrum. The bands are significantly better band separated in the 77 K spectrum. The Raman spectra of allactite show intense but broad bands at 330.6 , 298.3 and 271.0 cm^{-1} . The first band resolves into two bands at 331.2 and 324.6 cm^{-1} in the 77 K spectrum. It is possible that these bands are due to AsO stretching vibrations. The bands observed at 289 and 271.0 cm^{-1} in the 298 K spectrum and at 271 and 285 cm^{-1} in the 77 K spectrum may be attributed to MnO stretching vibrations.

The Raman spectra of the hydroxyl stretching region shows two distinct bands at 3561.1 and 3488.8 cm^{-1} in the 298 K spectrum and 3566.9 and 3496.1 cm^{-1} in the 77 K spectrum. The first band is very narrow with a band width of 6.5 cm^{-1} (298 K) and 5.0 cm^{-1} (77K). The second band has a width of 21.6 cm^{-1} reducing to 16.8 cm^{-1} at 77 K. The infrared spectra show a much broader spectral profile. Bands are observed at 3674.3 and 3650.2 cm^{-1} . Bands in these positions are not observed in the Raman spectra. It is considered these bands are due to adsorbed water. Two less intense bands are observed at 3567.5 and 3438 cm^{-1} . These bands are in similar positions to the Raman bands and are assigned to the PH stretching vibrations of the hydroxyl units in the allactite structure. Two lower intensity Raman bands are observed in the 298 K spectrum at 3445.5 and 3292.1 cm^{-1} . In the 77 K spectrum a band is found at 3284.7 cm^{-1} with other very low intensity bands at 3512.0 and 3443.5 cm^{-1} . In the infrared spectrum low intensity bands are observed at 3490 , 3442 and 3288 cm^{-1} which appear to correspond to the Raman bands. The reason why there are multiple bands in this spectral region is attributed to the non-equivalence of the OH units in the allactite structure. Not all the OH units are in the same positions in the structure.

CONCLUSIONS

The secondary arsenate minerals are not easily measured by infrared spectroscopy. The bands fall below 400 cm^{-1} and are broad consisting of a many banded overlapping spectral profile. Such difficulties are avoided by collecting the Raman spectra where excellent band separation is obtained. This band separation is enhanced by obtaining spectra at 77 K. Further Raman spectroscopy is a better technique for studying minerals as the spatial resolution is around 1 micrometre. The use of the 633 nm laser was suitable for measuring the highly coloured and highly pleochroic mineral allactite.

Acknowledgments

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REFERENCES

- [1]. G. Aminoff, Geol. Foren. Forh. 40 (1918) 535.
- [2]. G. Aminoff, Geol. For. Forh. 43 (1921) 24.
- [3]. G. Flink, Z. Krist. Festband P. v. Groth 58 (1923) 356.
- [4]. E. Welin, Arkiv foer Mineralogi och Geologi 4 (1968) 499.
- [5]. P. B. Moore, Amer. Miner. 53 (1968) 733.
- [6]. V. C. Farmer, *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, 1974.
- [7]. R. L. Frost, W. N. Martens and P. A. Williams, J. Raman Spectrosc. 33 (2002) 475.
- [8]. R. L. Frost, W. Martens, P. A. Williams and J. T. Kloprogge, J. Raman Spectrosc. 34 (2003) 751.
- [9]. R. L. Frost and M. Weier, Neues Jahr. Miner., Monatshefte (2004) 575.
- [10]. R. L. Frost and M. Weier, Neues Jahr. Miner., Monatshefte (2004) 317.
- [11]. J. T. Kloprogge and R. L. Frost, App. Spec. 54 (2000) 517.
- [12]. W. N. Martens, R. L. Frost, J. T. Kloprogge and P. A. Williams, Amer. Miner. 88 (2003) 501.
- [13]. W. Martens, R. L. Frost and P. A. Williams, J. Raman Spectrosc. 34 (2003) 104.
- [14]. W. Martens, R. L. Frost and J. T. Kloprogge, J. Raman Spectrosc. 34 (2003) 90.
- [15]. W. N. Martens, J. T. Kloprogge, R. L. Frost and L. Rintoul, J. Raman Spectrosc. 35 (2004) 208.
- [16]. R. L. Frost, P. A. Williams, J. T. Kloprogge and P. Leverett, J. Raman Spectrosc. 32 (2001) 906.
- [17]. R. L. Frost, P. M. Fredericks, J. T. Kloprogge and G. A. Hope, J. Raman Spectrosc. 32 (2001) 657.
- [18]. R. L. Frost, P. A. Williams, W. Martens, J. T. Kloprogge and P. Leverett, J. Raman Spectrosc. 33 (2002) 260.

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Figure 2 Raman spectra at 298 and 77 K of allactite in the 250 to 500 cm^{-1} region.

Figure 3 Raman spectra at 298 and 77 K and infrared spectrum of allactite in the 3000 to 3800 cm^{-1} region.

298K Raman				77K Raman				ATR-IR			
Center cm ⁻¹	FWHM cm ⁻¹	Area %	Assignment	Center cm ⁻¹	FWHM cm ⁻¹	Area %	Assignment	Center cm ⁻¹	FWHM cm ⁻¹	Area %	Assignment
								3674.3	27.1	0.9	
								3650.2	44.5	1.5	
								3576.5	109.2	2.5	
								3558.0	12.9	0.1	
3561.1	6.5	4.8		3566.9	5.0	5.1					
3523.0	53.8	1.2									
3488.8	21.6	10.0		3496.1	16.8	11.2					
3445.5	21.2	1.3						3438.0	320.7	5.3	
3395.2	131.5	0.9									
3292.1	27.2	1.8		3284.7	20.2	1.2					
								1415.6	152.8	9.7	
								1274.1	246.6	2.7	
								1080.6	28.6	1.5	
								1050.7	45.1	4.2	
1010.6	14.4	0.1						1022.1	21.7	0.7	
								997.7	51.4	17.1	
908.5	32.2	0.7						959.9	27.8	2.3	
883.0	14.7	4.2		886.2	7.5	1.8		937.3	58.5	22.7	
				860.7	8.1	10.8		873.9	13.8	0.3	
858.5	10.0	8.2		847.4	2.0	0.1		866.2	77.1	6.3	
				843.9	27.5	22.8					
834.1	17.2	16.6		834.3	9.0	4.7					
827.3	9.3	25.6		827.5	8.2	24.2					
				807.0	8.7	4.5					
808.4	12.3	3.2						810.4	37.6	2.2	
779.0	10.8	3.3		777.5	9.5	2.8					
742.6	22.3	0.5						755.2	70.2	2.5	
								713.3	13.8	0.4	
633.1	22.4	0.2						628.1	82.2	11.9	
								547.7	55.6	5.0	
470.2	9.7	0.3		471.0	8.5	0.3					
451.7	33.4	1.6		453.2	9.5	2.2					
422.3	18.7	1.5		423.6	6.9	0.8					
393.3	27.7	1.8		396.0	6.6	0.2					
376.7	16.9	0.6		378.8	6.8	0.3					
359.6	15.9	2.7		361.1	8.9	2.5					
350.1	12.0	0.7		352.9	8.3	1.1					
330.6	16.2	0.8		331.2	9.1	0.6					
322.7	15.3	1.1		324.6	5.5	0.3					
298.3	20.5	2.1		299.0	12.4	0.9					
				295.1	4.1	0.1					
287.5	13.2	0.6		285.0	6.6	0.3					
271.0	18.7	0.7		274.4	9.1	0.7					
				262.4	7.6	0.1					
240.9	85.0	2.3		244.3	4.3	0.0					
				237.7	4.4	0.0					
				212.9	11.6	0.1					
197.3	19.5	0.5		198.5	11.6	0.3					
158.2	4.1	0.1									

Table 1 Results of the Raman and infrared spectral analysis of allactite

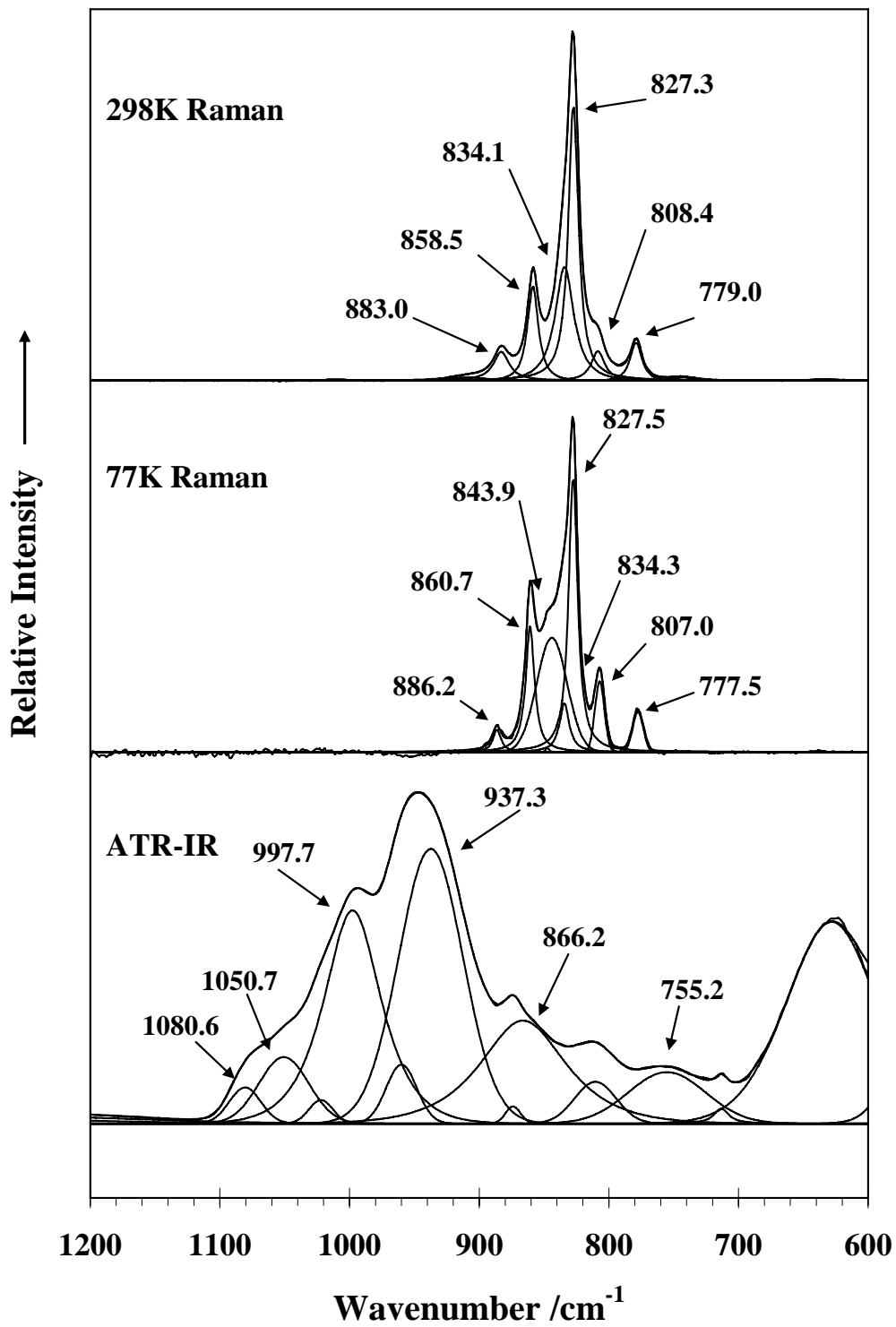


Figure 1

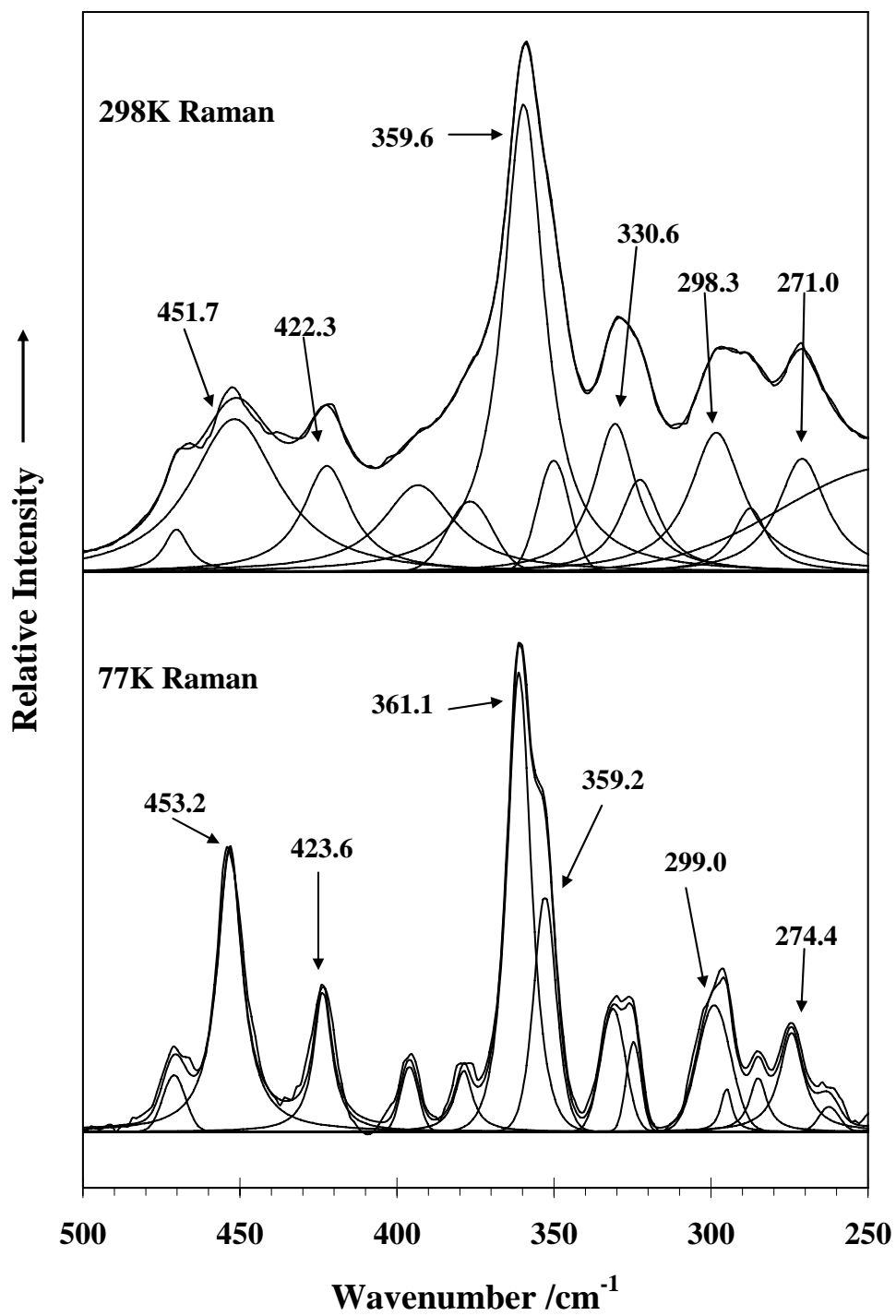


Figure 2

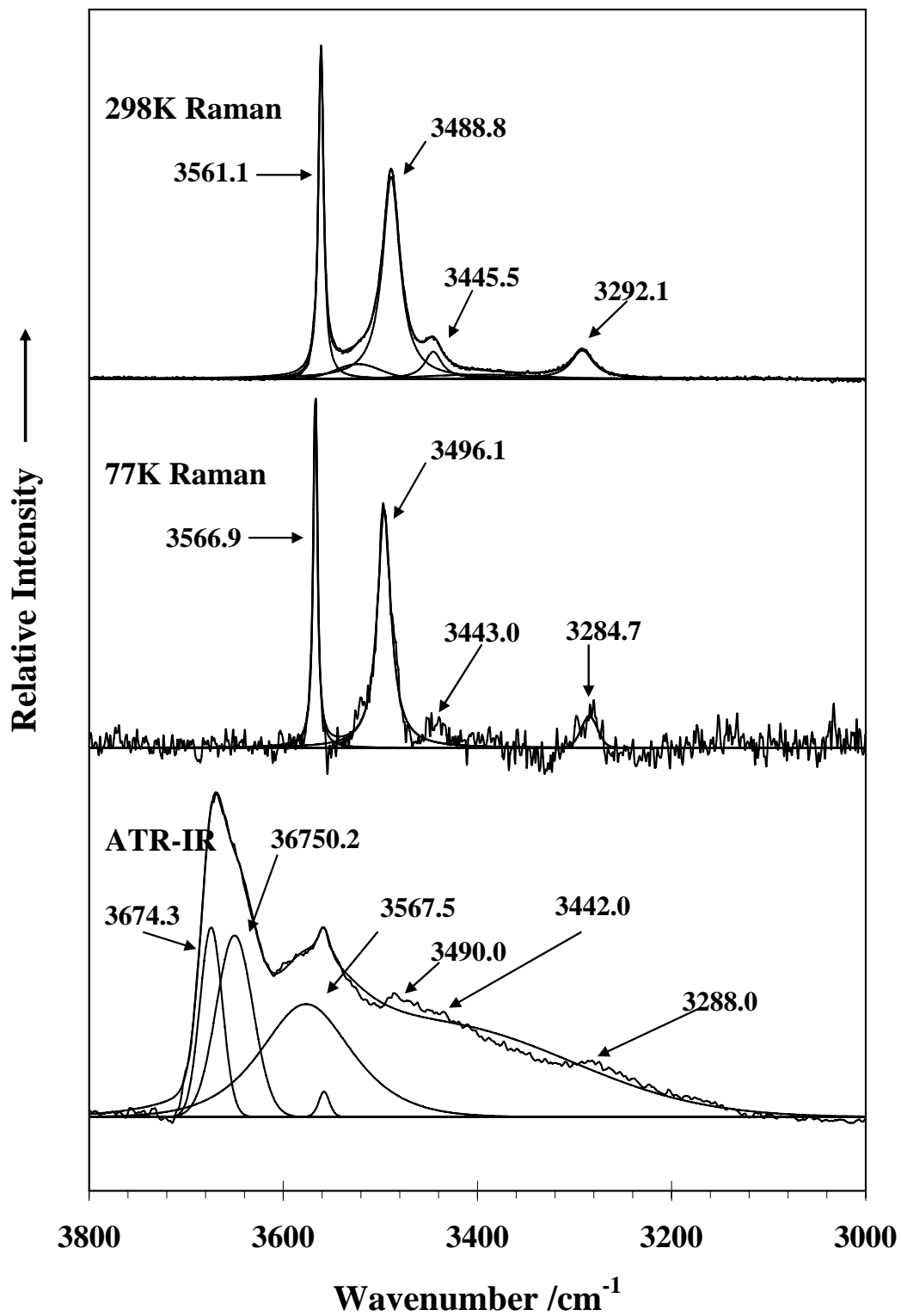


Figure 3