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A Raman spectroscopic study of the uranyl selenite mineral haynesite

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Abstract

The mineral haynesite, a uranyl selenite, has been characterised by Raman spectroscopy at 298 and 77 K. Two bands at 811.5 and 800.2 cm^{-1} are assigned to the symmetric stretching modes of the $(UO_2)^{2+}$ and $(SeO_3)^{2-}$ units respectively. These values give calculated U-O bond lengths of 1.799 and/or 1.801 Å. The broad band at 861.8 cm^{-1} is assigned to the ν_3 antisymmetric stretching mode of the $(UO_2)^{2+}$ (calculated U-O bond length 1.813 Å). Additional bands are observed in the 77 K spectrum. In the spectroscopy of selenite compounds the position of the antisymmetric stretching vibration occurs at lower wavenumbers than the symmetric stretching mode and thus the band at 746.6 cm^{-1} is attributed to the ν_3 antisymmetric stretching vibration of the $(SeO_3)^{2-}$ units. The ν_4 and the ν_2 vibrational modes of the $(SeO_3)^{2-}$ units are observed at 418.5 cm^{-1} and 472.1 cm^{-1}. Bands observed at 278.3, 257.3 and 218.8 cm^{-1} are assigned to OUO bending vibrations.

Key words: selenite, Raman spectroscopy, U-O bond length, uranyl.

Introduction

Haynesite is the uranyl hydroxy selenite of formula $(UO_2)_3(OH)_2(SeO_3)_2.5H_2O$ and is orthorhombic [1]. The mineral is one of a number of known uranyl selenite minerals which includes derriksite $[Cu_4UO_2(SeO_3)_2(OH)_5.H_2O]$ [2,3], marthozite $[Cu(UO_2)_3(SeO_3)_3(OH)_2.7H_2O]$ [4,5], piretite $[Ca(UO_2)_3(SeO_3)_2(OH)_4.4H_2O]$ [6-8], guilleminite $[Ba(UO_2)_3(SeO_3)_2(OH)_4.3H_2O]$ [9-11], demesmaekerite $[Pb_2Cu_5(UO_2)_2(SeO_3)_5(OH)_5.2H_2O]$ [3,7,12] and larisaite $[Na(H_3O)(UO_2)_3(SeO_3)_2O_2.4H_2O]$ [13]. These minerals are naturally occuring and it is possible to synthesise uranyl selenites with different cations such as strontium [11].

The spectroscopy of selenites is interesting in that like many mineral arsenates, the symmetric stretching mode is observed at higher wavenumbers than the antisymmetric stretching modes [14]. The values for ν_1 for sodium, calcium and copper selenites occurs at 788, 784 and 774 cm^{-1} (see Table 6.34 of Reference 12). In contrast the values for the ν_3 antisymmetric stretching modes occur at 740, 713 and 714 cm^{-1}. The value for ν_2 bands occurs between 449 and 461 cm^{-1} and ν_4 between 387 and 427 cm^{-1} [14]. Bäumer et al [1999] proved that in the case of infrared spectra of M^{2+} selenites monohydrates the stretching vibrations of selenite units are located in the regions $760 \leq \nu_1\ SeO_3 \leq 855\ cm^{-1}$ and $680 \leq \nu_3\ SeO_3 \leq 775\ cm^{-1}$ [15]. Khandelwal and Verma [1976] and Verma [1999] attributed the Raman (infrared) bands in the

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spectra of UO_2SeO_3 at 381 and 389 (390) cm^{-1} to the ν_4 $(SeO_3)^{2-}$, at 497 (500) cm^{-1} to the ν_2 $(SeO_3)^{2-}$, 724 and 731 (700) cm^{-1} to the ν_3 $(SeO_3)^{2-}$, 829 (820-840) cm^{-1} to the ν_1 $(SeO_3)^{2-}$, and bands at 878 (875 sh) and 884 (920-940) cm^{-1} to the ν_1 and ν_3 $(UO_2)^{2+}$, respectively [16,17]. The same authors assigned observed Raman and infrared bands for e.g. $(NH_4)_2(UO_2)_2(SeO_3)_3.6H_2O$ at 384, 390 (395), 475 (498), 731 and 829 (700 and 830), and 800 (808) cm^{-1} to the ν_4, ν_2, ν_3 and ν_1, respectively, and those at 879 and 883 (872), and (900) cm^{-1} to the ν_1 and ν_3 $(UO_2)^{2+}$, respectively. Similar spectra were observed and interpreted for $K_2(UO_2)_2(SeO_3)_3.2H_2O$, $(NH_4)_2(UO_2)(SeO_3)_2$, and $K_2(UO_2)(SeO_3)_2.3H_2O$.

Čejka reported the infrared spectrum of haynesite [18] both by DRIFT and KBr absorption [19]. Significant differences in the two spectra were obtained. The DRIFT spectrum showed much greater complexity. Čejka reported the $(UO_2)^{2+}$ symmetric stretching mode as two bands at 850 and 820 cm^{-1}. The $(UO_2)^{2+}$ antisymmetric stretching mode was registered as two bands at 905 and 862 cm^{-1}. Čejka reported the selenite ν_1 mode of haynesite at ~820 cm^{-1} and the ν_3 mode at 738 and 800 cm^{-1}. In the light of the values for the divalent cationic selenites above the value of ν_1 at ~820 cm^{-1} appears high, however this corresponds with the Bäumer´s conclusions. Čejka also suggested that the ν_2 band was at 471 cm^{-1}. This value is high compared with the values of the ν_2 bending modes above, however, it is in agreement with the Khandelwal´s assignment [16]. The value of ν_4 was not reported [19] but is available from the paper by Khandelwal [16]. There is the possibility of overlap between the symmetric stretching bands of $(SeO_3)^{2-}$ and $(UO_2)^{2+}$. Čejka suggested that the bands in the infrared spectrum at 820, 471, 738 were attributable to the ν_1, ν_2 and ν_3 bands of $(SeO_3)^{2-}$. However the potential overlap of bands makes assignment difficult. Čejka also points out that the mineral haynesite may contain not only OH- units but also H_3O^+ units which will complicate the spectra of haynesite. It is noted from the Table 6.34 of Reference 12 that the band positions for hydrated selenites are at higher positions than for the anhydrous compounds. Deliens and Piret assume that the chemical formula of haynesite was $(H_3O)_2(UO_2)_3(OH)_4(SeO_3)_2.H_2O$ [1]. This possibility of water molecules in the formula cannot be excluded. Chukanov et al. conclude from the X-ray crystal structure analysis and infrared spectra of larisaite that $(H_3O)^+$ ions are present in its crystal structure and assume from the infrared spectra of haynesite [13] the presence of these ions also in the crystal structure of haynesite, and that the total amount of the $(H_3O)^+$ions lowers in the order haynesite $\rightarrow$ larisaite $\rightarrow$ piretite.

Raman spectroscopy has proven most useful for the characterisation of secondary uranly contianing minerals [20-25]. In order to identify and characterise the vibrational spectrum of haynesite this research reports the Raman spectrum of haynesite at 298 and 77 K and relates the spectra to the structure of the mineral.

Experimental

Minerals

Two haynesite samples (Museum Victoria Registered numbers M25802 and M30643) were obtained from Museum Victoria. The haynesites originated from the Repete Mine, Blanding, San Juan Co., Utah, USA. The samples were analysed by X-ray diffraction and EDX measurements. No mineral impurities were detected.

Raman microprobe spectroscopy

The crystals of haynesite 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 [22,23,26,27].

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation 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 allows specific parameters to be fixed or varied accordingly. 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 correlations of r^2 greater than 0.995. Further details on the manipulation of the data has been published (JRS in Press).

Results and discussion

The free linear uranyl group, $(UO_2)^{2+}$, symmetry $D_{\infty h}$, has four normal vibrations but three fundamental bands only: ν_1 (approximately 900-700 cm^{-1}) – the symmetric stretching fundamental, only Raman active; ν_2 (δ) (approximately 260-180 cm^{-1}) - the doubly degenerate bending fundamental, only IR-active; ν_3 (approximately 1000-850 cm^{-1}) – the antisymmetric stretching fundamental, only IR active. Distortion of the uranyl group or change in the local symmetry can result in the removal of the degeneracy and Raman activation of the ν_2 mode and IR activation of the ν_1 mode. The chemistry of the selenite ion and selenite containing compounds will resemble the chemistry of the sulphite ion and its compounds [28]. The symmetry of the selenite ion should be similar to that of sulphite which has a tetrahedral symmetry with one vacant orbital thus making C_{3v} symmetry [28]. The selenite ion thus has four fundamentals: ν_1 (approximately 790-806 cm^{-1} or 760-855 cm^{-1}) – the symmetric stretching vibration; ν_2 (aproximately 430-461 cm^{-1}) – the bending vibration; ν_3 (approximately 714-769 cm^{-1} or 680-775 cm^{-1}) – the degenerate stretching vibration; ν_4 (approximately 387-418 cm^{-1}) – the doubly degenerate in-plane bending vibration. All vibrations are Raman and infrared active.

The Raman spectra of haynesite at 298 and 77 K are displayed in Figure 1. Two distinct bands of almost equal intensity are observed at 808 and 800 cm^{-1}

(according to the Bartlett-Cooney relation (1989), the calculated U-O bond lengths are 1.799 Å (811.5 cm^{-1}) and 1.811 Å (800.2 cm^{-1}) [29]. Two low intensity bands are found at 861.8 and 743 cm^{-1}. The band at 861.8 cm^{-1} (1.813 Å) is assigned to the ν_3 antisymmetric stretching mode of the $(UO_2)^{2+}$. The band is broad with a band width of 24.7 cm^{-1}. No band as reported from the infrared spectra of Čejka at 905 cm^{-1} (1.781 Å) was observed. However, such infrared bands near 900 cm^{-1} were observed in some synthetic ammonium (900 cm^{-1}, 1.785 Å), potassium (892 cm^{-1}, 1.790 Å; or 880 cm^{-1}, 1.799 Å) and strontium uranyl selenites (909 cm^{-1}, 1.778 Å, X-ray an average 1.821 Å) [11 16]. The molar ratio Sr:U:Se = 1:3:2 in the formula of the strontium uranyl selenite hydrate, prepared by Almond and Albrecht-Schmitt [11], $Sr[(UO_2)_3(SeO_3)_2O_2].4H_2O$, is similar to the M^{2+}(or M^{+}_2):U:Se molar ratio observed for guilleminite [10],marthozite [30], larisaite [13] and may be also to piretite [6] and haynesite [1]. All these uranyl selenites may have similar uranyl anion sheet topology, which is based on the phosphuranylite topology [31-33]. The band is observed at 866.5 cm^{-1} (1.810 Å) in the 77 K spectrum with a band width of 16.6 cm^{-1}. The band shows strong asymmetry and a second band may be resolved at 856.4 cm^{-1} (1.818 Å) with a bandwidth of 32.0 cm^{-1}. The two bands at 811.5 (1.799 Å) and 800.2 cm^{-1} (1.811 Å) are well separated and must belong to the symmetric stretching modes of the $(UO_2)^{2+}$ and $(SeO_3)^{2-}$ units. These bands are very sharp with band widths of 14.8 and 13.5 cm^{-1}. In the 77 K spectrum the band at 811.5 cm^{-1} in the 298 K spectrum may be resolved into two components at 812.1 (1.798 Å) and 804.1 (1.807 Å) cm^{-1} with band widths of 12.6 and 8.4 cm^{-1}. The band at 800.2 cm^{-1} in the 298 K spectrum shifts to 798.3 (1.812 Å) cm^{-1} with a band width of 12.0 cm^{-1}. All calculated U-O bond lengths in uranyls agree with those inferred for uranyl synthetic and natural compounds by Burns [31-33] and also with uranyl selenite minerals with similar uranyl anion sheet phosphuranylite-type topology, as guilleminite and marthozite. Bands close to 850-860 cm^{-1} may be also attributed to the ν_1 $(UO_2)^{2+}$ (866.5 cm^{-1}, 1.747 Å; 856.4 cm^{-1}, 1.756 Å). The calculated U-O bond lengths in uranyl, however, are too short.

Khandelwal and Verma and Verma [16,17] assume that a strong Raman but weak infrared band around 800 cm^{-1} in the spectra of the uranyl selenite complexes they studied should be due to the ν_1 $(SeO_3)^{2-}$ and the bands in the Raman spectra at 731 and in the range 814-829 cm^{-1} to the split ν_3 $(SeO_3)^{2-}$, corresponding to the bands around 700-730 cm^{-1} and 816-838 cm^{-1} in the infrared spectra. In the infrared spectra, they observed an intense band at 900 cm^{1} attributed to the ν_3 $(UO_2)^{2+}$. This vibration is Raman forbidden and therefore does not appear in the Raman spectra. The authors assigned a strong Raman band doublet at around 860-878 and 868-884 cm^{-1} to the ν_1 $(UO_2)^{2+}$ with the conclusion that this would normally be infrared forbidden, but appears in the infrared spectra of the synthetic uranyl selenites studied as a weak shoulder around 860-880 cm^{-1}. They did nod observed any band assignable to the ν_3 $(UO_2)^{2+}$ in the Raman spectra of the compounds studied. Some empirical relations may be used for the calculation of the ν_1 $(UO_2)^{2+}$ wavenumber from the ν_3 $(UO_2)^{2+}$ wavenumber (e. g. $\nu_1 = 0.939\nu_3$ cm^{-1}; $\nu_1 = 0.89\nu_3 + 21$ cm^{-1}; $\nu_1 = 0.795\nu_3 + 107$ cm^{-1}. For the ν_3 = 900 cm^{-1} ν_1 = 845 or 822 or 822 cm^{-1}, and for the ν_3 = 880 cm^{-1} ν_1 = 826 or 804 or 807 cm^{-1}) [29]. This clearly shows that the attribution of the Raman bands and infrared shoulders in the range 860-883 cm^{-1} published by Khandelwal and Verme [16] is not correct. On the contrary, some of the bands or shoulders in the range 800-835 cm^{-1} originally assigned to the ν_1 or ν_3 $(SeO_3)^{2-}$ should be attributed to the ν_1 $(UO_2)^{2+}$.

Which band is assigned to which unit is open to question. However the lower wavenumber band more closely fits the band position of the $(SeO_3)^{2-}$ units and the higher wavenumber band the symmetric stretching mode of the $(UO_2)^{2+}$ units. The higher wavenumber band splits into two components in the 77 K spectrum. This splitting could be accounted for by the non-equivalence of the two UO bonds in the $(UO_2)^{2+}$ units.Thus the band at 811.5 cm^{-1} in the 298 K spectrum and the two bands in the 77 K spectrum at 812.1 and 804.1 cm^{-1} are attributed to the ν_1 symmetric stretching mode of the $(UO_2)^{2+}$ units and the band at 800.2 cm^{-1} in the 298 K spectrum and 798.3 cm^{-1} in the 77 K spectrum is assigned to the symmetric stretching mode of the $(SeO_3)^{2-}$ units. The band at 743 cm^{-1} is in the same position as for the divalent selenetites and is assigned to the ν_3 antisymmetric stretching vibration of the $(SeO_3)^{2-}$ units. The band position is in good agreement with that reported by Čejka from the infrared spectrum of haynesite at 738 cm^{-1} [19]. In the infrared spectrum of the mineral piretite a band was observed at 732 cm^{-1} and was assigned to the ν_3 antisymmetric stretching modes of the $(SeO_3)^{2-}$ units [6].

The low wavenumber region of the spectrum of haynesite is reported in Figure 2. An intense band is observed at 418.5 cm^{-1} with a band width of 20.3 cm^{-1} and is assigned to the ν_4 mode of the $(SeO_3)^{2-}$ units. The band is observed at 426.2 cm^{-1} in the 77 K spectrum with a band width of 19.0 cm^{-1}. This band shows some asymmetry at 77 K and a low intensity band at 412.5 cm^{-1} (FWHH=13.7 cm^{-1}) is found. The ν_4 mode for hydrated magnesium selenite is observed at 412 cm^{-1} and for hydrated calcium selenite at 418 cm^{-1} [14]. For these hydrated divalent selenites an additional band was observed at 375 cm^{-1} which was also ascribed to the ν_4 mode. Thus the band observed in the Raman spectrum of haynesite at 367.4 cm^{-1} (298 K) and at 366.7 cm^{-1} (77 K) is also attributed to the ν_4 bending mode. The bands at 472.1 (298 K) and 477.8 (77 K) cm^{-1} are assigned to the ν_2 vibrational mode. This band is observed at 449 cm^{-1} for Na_2SeO_3, 461 cm^{-1} for $CuSeO_3$, 457 cm^{-1} for $PbSeO_3$ [14]. It is noted that the the band at 418.5 cm^{-1} is strongly asymmetric on the higher wavenumber side and a band at 437.0 cm^{-1} may be resolved. In the 77 K spectrum this band shows better band separation and the band is observed at 441.6 cm^{-1}. A low intensity band is observed at 582.0 cm^{-1} and one possible assignment of this band is to an hydroxyl deformation mode. The band is broad with a band width of 35.9 cm^{-1}. The band is observed at 584.9 cm^{-1} in the 77 K spectrum. Čejka reported an infrared band at 523 cm^{-1} and suggested the band could be due to $U\text{-}O_{lig}$ vibrations.

A low wavenumber band is observed at 341.6 cm^{-1}. One possible assignment is that this band is due to a U-O vibration. The spectra in the 100 to 300 cm^{-1} region are shown in Figure 3. This region is the region where OUO bending modes may be observed. The spectra are complex. Two bands are observed at 278.3 and 257.3 cm^{-1} with an additional band at 218.8 cm^{-1} in the 298 K spectrum. In the 77 K spectrum An additional band is observed at 289.2 cm^{-1} as well as the bands at 274.4, 257.3 and 225.4 cm^{-1}. These bands are attributed to the O-U-O bending vibrations. Both these bands show complexity with more than one component observed in these positions. Bands observed at wavenumbers less than 300 cm^{-1} are connected with the split ν_2 (δ) $(UO_2)^{2+}$ bending, ν ($U\text{-}O_{ligand}$), δ ($U\text{-}O_{ligand}$), and lattice vibrations. In addition two bands are observed at 156.6 and 142.0 cm^{-1} in the 298 K spectrum. These bands are simply described as lattice modes.

The Raman spectra of haynesite in the 3200 to 3800 cm^{-1} at 298 and 77 K are shown in Figure 4. The spectra suffer from a lack of signal to noise. Perhaps this is not unexpected since the scattering cross section for water and/or OH units is small. Raman spectroscopy is an inherently poor technique for measuring these units. Nevertheless a band is found at 3476.1 cm^{-1} in the 298 K spectrum which shifts to 3477.3 cm^{-1} in the 77 K spectrum. In addition bands at 3593.7 and 3387.3 cm^{-1} may be observed. Čejka reported infrared bands at 3433 and 3250 cm^{-1} [19]. Čejka also observed bands at 2970, 2925 and 2850 cm^{-1} [19]. No bands were observed in these positions in the Raman spectra. One possibility is that these bands may be due to organic impurities.

However, it should be mentioned that also Vochten et al. [6] observed a band at 2927 cm^{-1} and assigned it to the ν OH (H_2O). Bäumer et al. [15] attributed bands in the region $2900 \leq \nu\ OH \leq 3350\ cm^{-1}$ to the ν OH, e. g. in the case of $BeSeO_3.H_2O$. The observed Raman spectra of haynesite prove that some hydrogen bonds are formed in the crystal structure of haynesite which may influence its structure stability. According to Libowitzky, the O-H…O bond lengths may be approximately ~2.88 (3476.1 cm^{-1}/298 K), ~3.3 (3593.7/77 K), ~2.88 (3477.3/77 K), and ~2.79 (3387.3/77 K) Å. It is not possible to infer the presence of $(H_3O)^+$ ions in the crystal structure of haynesite from its Raman spectra as assumed by Deliens and Piret [1],discussed also by Čejka et al. [19] and proposed by Chukanov et al. [13] from the comparison of the infrared spectra of haynesite and larisaite.

Conclusions

Raman spectroscopy at 298 and 77 K has been used to characterise the uranyl selenite known as haynesite. In contrast to the infrared spectrum as published by Čejka [19], the Raman spectra shows clearly resolved bands with good band separation enabling better identification and assignment of the bands. Bands are identified in terms of the structure and symmetry of the $(UO_2)^{2+}$ and $(SeO_3)^{2-}$ units. U-O bond lengths in uranyl and hydrogen O-H…O bond lengths are inferred from the Raman spectra.

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Figure 1 Raman spectra at 298 and 77 K of haynesite in the 600 to 1000 cm^{-1} region.

Figure 2 Raman spectra at 298 and 77 K of haynesite in the 300 to 600 cm^{-1} region.

Figure 3 Raman spectra at 298 and 77 K of haynesite in the 100 to 300 cm^{-1} region.

Figure 4 Raman spectra at 298 and 77 K of haynesite in the 3200 to 3800 cm^{-1} region.

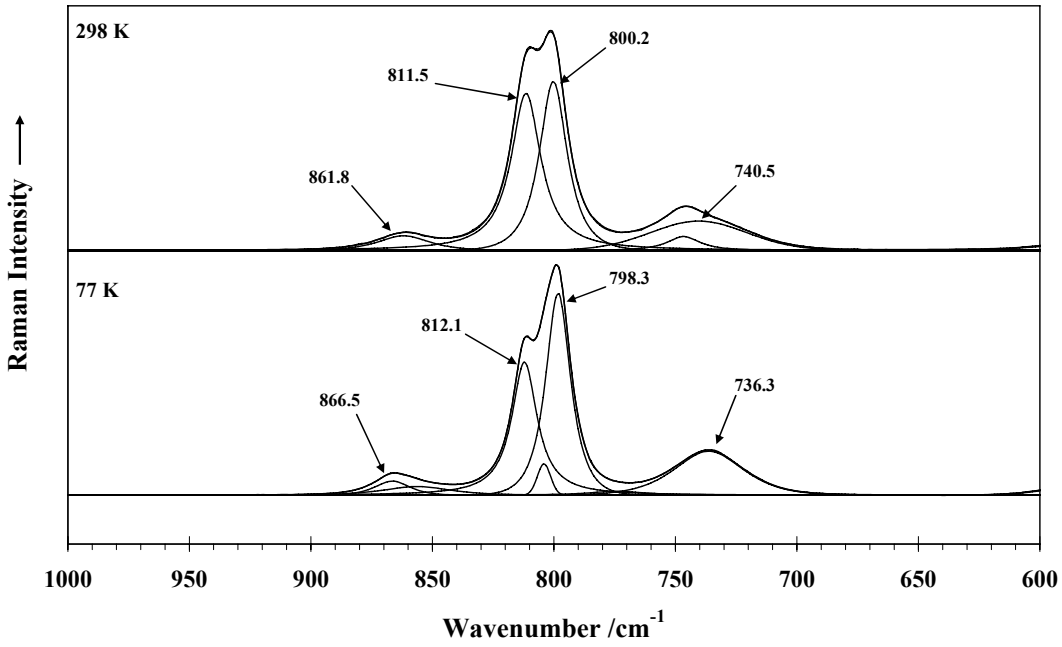
298 K
800.2
811.5
861.8
740.5
77 K
798.3
812.1
736.3
866.5
Raman Intensity
1000
950
900
850
800
750
700
650
600
Wavenumber /cm-1

Figure 1

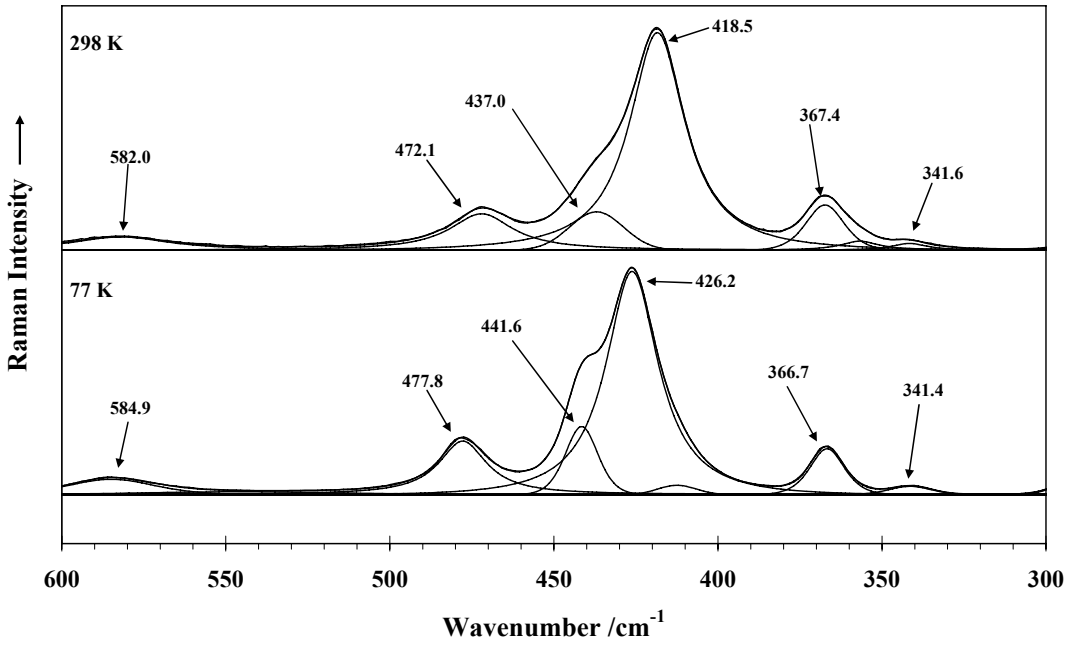
298 K
418.5
437.0
367.4
582.0
472.1
341.6
77 K
426.2
441.6
366.7
477.8
341.4
584.9
Raman Intensity
600
550
500
450
400
350
300
Wavenumber /cm-1

Figure 2

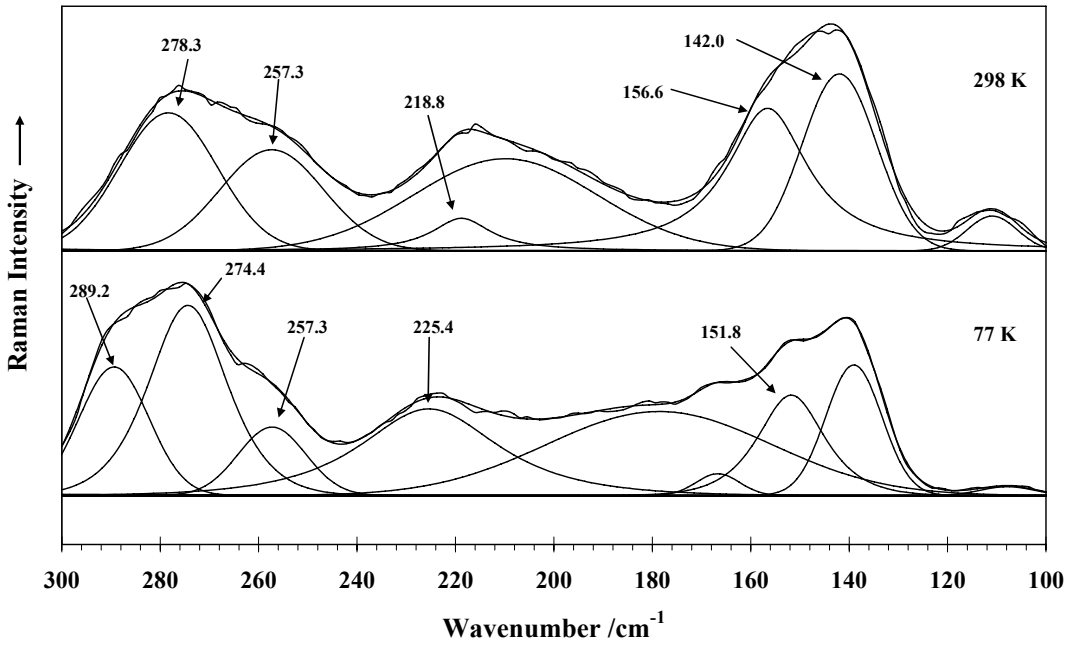
278.3
257.3
218.8
156.6
142.0
298 K
289.2
274.4
257.3
225.4
151.8
77 K
Raman Intensity
300
280
260
240
220
200
180
160
140
120
100
Wavenumber /cm-1

Figure 3

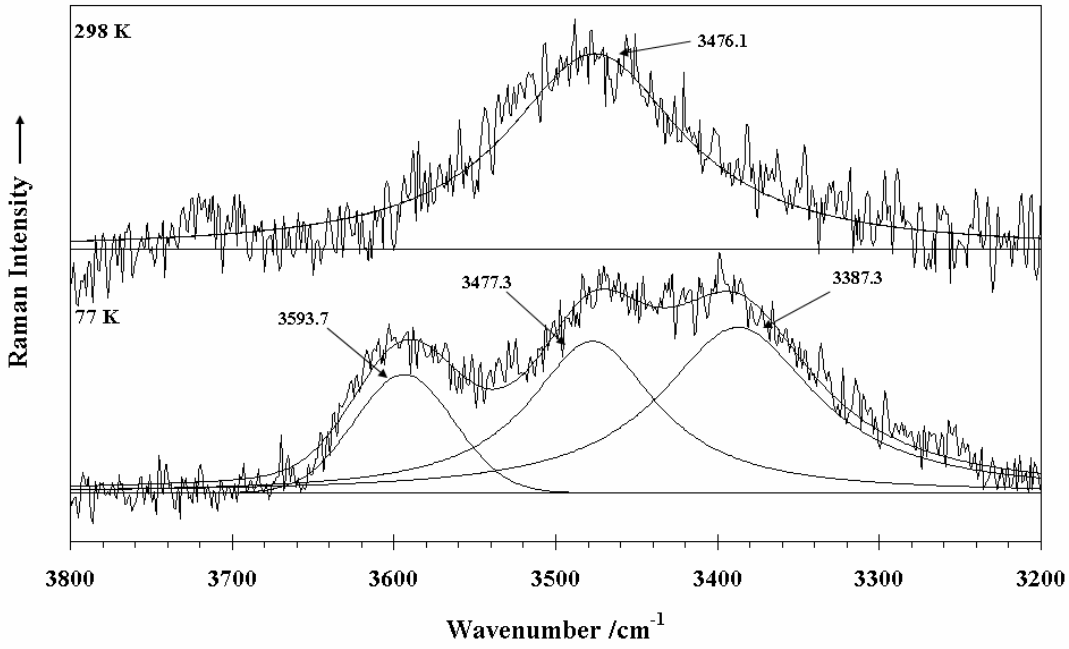
298 K
3476.1
77 K
3593.7
3477.3
3387.3
Raman Intensity
3800
3700
3600
3500
3400
3300
3200
Wavenumber /cm-1

Figure 4