

VIBRATIONAL SPECTROSCOPIC STUDY OF SYNGENITE FORMED DURING THE TREATMENT OF LIQUID MANURE WITH SULPHURIC ACID.

J. Theo Kloprogge*¹, Roelof D. Schuiling², Zhe Ding¹, Leisel Hickey¹, David Wharton¹ and Ray L. Frost¹

¹ Centre for Instrumental and Developmental Chemistry, Queensland University of Technology, 2 George Street, G.P.O. Box 2434, Brisbane, Qld 4001, Australia

² Department of Geochemistry, Institute of Earth Sciences, Utrecht University, P.O. Box 80021, 3508 TA Utrecht, The Netherlands

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Abstract

Syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$), formed during treatment of manure with sulphuric acid, was studied by infrared, near-infrared and Raman spectroscopy. C_s site symmetry was determined for the 2 sulphate groups in syngenite ($P2_1/m$), so all bands are both infrared and Raman active. The split ν_1 (2 Raman + 2 infrared bands) was observed at 981 and 1000 cm^{-1} . The split ν_2 (4 Raman + 4 infrared bands) was observed in the Raman spectrum at 424, 441, 471 and 491 cm^{-1} . In the infrared spectrum only 1 band was observed at 439 cm^{-1} . From the split ν_3 (6 Raman + 6 infrared) bands 3 298 K Raman bands were observed at 1117, 1138 and 1166 cm^{-1} . Cooling to 77 K resulted in 4 bands at 1119, 1136, 1144 and 1167 cm^{-1} . In the infrared spectrum 5 bands were observed at 1110, 1125, 1136, 1148 and 1193 cm^{-1} . From the split ν_4 (6 infrared + 6 Raman bands) 4 bands were observed in the infrared spectrum at 604, 617, 644 and 657 cm^{-1} . The 298 K Raman spectrum showed 1 band at 641 cm^{-1} , while at 77 K 4 bands were observed at 607, 621, 634 and 643 cm^{-1} . Crystal water is observed in the infrared spectrum by the OH-libration mode at 754 cm^{-1} , OH-bending mode at 1631 cm^{-1} , OH-stretching modes at 3248 (symmetric) and 3377 cm^{-1} (antisymmetric) plus a combination band at 3510 cm^{-1} of the H-bonded OH-mode plus the OH-stretching mode. The near-infrared spectrum gave information about the crystal water resulting in overtone and combination bands of OH-libration, OH-bending and OH-stretching modes.

Keywords: infrared spectroscopy, manure, near-infrared spectroscopy, Raman spectroscopy, sulphate, syngenite

*Corresponding author: phone +61 7 3864 2184 or 2407, fax +61 7 3864 1804, E-mail: t.kloprogge@qut.edu.au

Introduction

Syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) forms a relatively rare sulphate double salt in (metamorphic) evaporite deposits in addition to the normal salt minerals such as gypsum, anhydrite and halite [1,2]. Zepharovic [3] recognised syngenite as a naturally occurring mineral for the first time in the Zechstein salt deposits of the Kalusz Mine, Galicia in 1872. Syngenite has also been described in volcanic rocks as fine coatings and as fillings of basaltic lavas, e.g. from the Vesuvius, Italy [4,5]. In addition Cavarretti et al. [6] described syngenite from the Cesano geothermal field north of Rome, Italy. Siegel et al. [7] and Lindholm et al. [8] described syngenite underlain by calcite and gypsum as thin crusts on the exposed surface of a lava flow from a local vent 5 miles NE of Mount Dromedary and 1 mile S of the terminus of the Walcott Glacier, Antarctica. The syngenite was thought to be a diagenetic product formed at the expense of gypsum by reaction with aerosols in the atmosphere rich in sulphate. Syngenite has also been found as a guano mineral in guano deposits formed in caves due to bats [9]. Here the syngenite is associated with aphtitalite, monetite, whitlockite, gypsum and organic material.

Although syngenite was discovered in 1872, it was synthesised already about twenty years earlier, in 1850 by J.A. Philips as a by-product during the process of vinegar fermentation [10]. Since then, it has been found as a mineral in salt stains on bricks together with gypsum [11,12]. It was also identified by one of the authors of this paper (RDS) as salt stains on the Institute of Earth Sciences, Utrecht University, The Netherlands. Sulphate minerals such as gypsum, bassanite, anhydrite and syngenite are also observed in cement [13]. Salem [14] observed the formation of syngenite together with arcanite and gypsum during gaseous corrosion using water vapour and SO_2 gas of $K_2O-CaO-SiO_2$ glasses.

Dankiewicz and Wieczorek-Ciurowa [15] studied the thermal behaviour of syngenite because it was formed as an intermediate product in one of the methods developed for the production of mineral fertilisers from naturally occurring polyhalite $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$. The syngenite described in this paper is a product also formed during the production of fertiliser. However, here liquid pig and calf manure is used as the starting material which is mixed with sulphuric acid to fix the ammonium present in the manure.

In a number of recent publications Kloprogge and co-workers have reported on the infrared, near-infrared and Raman spectroscopy of basic aluminium sulfate [16-20], gypsum [21], celestine [22] and minerals of the group of the so-called alums and pseudo-alums [23,24]. This paper forms a continuation of the study of inorganic sulphate compounds and naturally occurring sulphate minerals in our laboratory. In this paper for the first time, in addition to the infrared spectrum, the Near-infrared and Raman spectra of syngenite will be reported and a detailed band assignment will be given.

Sample origin

The sample of syngenite was produced as a several mm thick scale in a manure treatment plant at Eibergen, the Netherlands. This plant, owned by AMV (which stands for Agricultural Minerals Treatment) treats annually approximately 135,000 tons of liquid pig and calf manure. In order to prevent smell problems, the fresh manure was mixed with sulphuric acid. This strongly reduced the ammonia emission, but adding additional sulphate ions to the system increased the problem of syngenite formation. After filtration to remove coarse solids, HNO_3 is used to break down H_2S before aeration. After aeration and cleaning the exhaust air, sulphuric acid is mixed with the liquid fraction to fix ammonium, and the acidified mixture is degassed to prevent excessive foam formation. In the next step the liquid is transferred to a large vacuum vessel. There it flows over a system of pipes, through which boiling water is passed. Thanks to the vacuum, the manure boils already at 60°C . The heat of condensation is recovered and used to heat the water. In this concentration step of the manure, the solubility product of syngenite is exceeded, resulting in scaling. The syngenite scales strongly reduced heat transfer. This technical problem has been solved by partially substituting (waste) nitric acid for sulphuric acid to break down H_2S and prevent smell problems, and by more frequent washing. The presence of mainly syngenite plus a minor amount of another related mineral, ammonium nitrate, was confirmed by X-ray diffraction (XRD).

Analytical techniques

X-ray powder diffraction

The sample was characterised by X-ray powder diffraction (XRD). The XRD analyses were carried out on a Philips wide-angle PW 1050/25 vertical goniometer applying $\text{CoK}\alpha$ radiation. The samples were measured at 50 % RH in stepscan mode with steps of $0.02^\circ 2\theta$ and a scan speed of 1.00° per minute from 2 to $75^\circ 2\theta$.

Infrared and Near-infrared spectroscopy

The samples were finely ground for one minute, combined with oven dried spectroscopic grade KBr (containing approximately 1 wt% sample) and pressed into a disc under vacuum. The spectrum of the sample was recorded in triplicate by accumulating 512 scans at 4 cm^{-1} resolution between 400 cm^{-1} and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform infrared spectrometer equipped with a LITA detector.

The NIR absorption spectroscopy analyses were performed on a Perkin Elmer System 2000 NIR-FT Raman spectrometer equipped with a Spectron Laser Systems SL301 Nd:YAG laser operating a wavelength of 1064 nm. For the samples 32 scans were accumulated at a spectral resolution of 16 cm^{-1} using a mirror velocity of $0.2\text{ cm}^{-1}/\text{s}$ to get an acceptable signal/noise ratio.

Raman microscopy at 298 and 77K

The sample was placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) and collected at a resolution of 2 cm^{-1} and a precision of $\pm 1\text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Repeated acquisition on the syngenite crystal using the highest

magnification (50x) were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Spectra at low temperatures were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England). Samples were placed on a circular glass disc, which fitted over the silver plate of the thermal stage. For spectra at 77 K, nitrogen gas from liquid nitrogen passed through a small hole in this plate immediately below the centre of the glass disc. Because of the increased optical path, spectra at 77K are noisier and require longer accumulation times. Spectra were obtained using 20-second scans for up to 30 minutes using the special short 50X (UWLD) objective. A lower Raman signal was obtained using this objective owing to the low numerical aperture of this long working distance objective. This, combined with the aberration of the stage window, results in a decreased signal compared with that run without the thermal stage.

Spectral manipulations

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectralcalc 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 Lorentz-Gauss 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.

Results and discussion

The first unit cell parameters and space group of syngenite were determined by Laskiewicz [25] and Kurylenko [26] describing it as a monoclinic mineral with space group $P2_1/m$ but with significantly different unit cell parameters. Aruja's data [11] on natural and synthetic syngenite were rather close to the original data presented by Laskiewicz [25]. The first report on the crystal structure was however based on the space group $P2_1$ on the basis of the positive piezoelectric effect [27]. The space group of $P2_1/m$ was confirmed by the calculations of Corazza and Sabelli [28] and by Nizamutdinov et al [29] who used NMR to show that the crystal water molecules take up a position of symmetry C_s confirming that the crystal structure must have a plane of symmetry.

The structure of syngenite can be roughly divided in two parts associated with the potassium and the calcium atoms in the unit cell (Fig. 1). The K atoms are surrounded by eight oxygen atoms at the seven corners of a very irregular cube lacking one corner plus one oxygen atom on the centre of one face. The potassium polyhedra, repeated by mirror planes build up a straight chain in the c direction. These chains are then linked together to form a wavy sheet in the c direction parallel to (100). The Ca atoms are surrounded by nine oxygen atoms. Three of these oxygen atoms lie on the mirror plane, while the other six are symmetrically placed on both sides of the same mirror plane. The Ca polyhedra form a zigzag chain along the c direction, while each Ca polyhedron shares three corners on one side and two corners on the other side with the K polyhedra thereby forming the bridge between the potassium containing sheets. The Ca chains form wavy planes roughly in the bc plane.

The sulphur atoms are present in two special positions with a relatively regular tetrahedral coordination. Table 1 gives the relevant parameters of both the sulphate groups in terms of bond lengths and angles. The S_1 tetrahedron shares two oxygen atoms with a Ca polyhedron on one side and two other oxygen atoms with a Ca polyhedron on the other side. The complex of S_1 tetrahedra, with the Ca chains, make up a sheet parallel to (100). In addition, the S_1 tetrahedra make additional bridges among the potassium sheets. All of the S_2 tetrahedra share one edge with each of its surrounding K polyhedra and one edge with a Ca polyhedron to form further bonds between the K sheets and the Ca chain [28]. One oxygen atom does not take part in the formation of the two sulphate tetrahedra because it belongs to the crystal water molecule. The water molecule takes part in the polyhedron around the Ca atom but its interaction with the Ca is weak. The protons form a strong hydrogen bond to one of the oxygen atoms surrounding S_2 linked to the Ca atom [30].

The Infrared and Raman spectra will be mainly governed by the sulphate and water modes. Theoretically, when the sulphate retains its full symmetry (T_d) four modes of vibration will be observed: $\nu_1(A_1)$ at 983 cm^{-1} , $\nu_2(E)$ at 450 cm^{-1} , ν_3 at 1105 cm^{-1} and $\nu_4(F_2)$ at 611 cm^{-1} . The A_1 (symmetric stretching) and E (bending) modes are Raman active only, while the F_2 stretching and bending modes are both Raman and infrared active. Ross [31] reported a site symmetry of C_s or C_1 for the sulphate in syngenite. This will lead to either $6 A' + 3 A''$ or $9 A$ ergo nine Raman and nine infrared active modes for each sulphate group [32]. The crystal structure data as shown in Table 1 reveal that only two S-O bonds are identical in each sulphate group leading to a point group of C_s . In addition, it is shown that the two sulphate groups, although having the same point group, are not identical as the bond lengths and angles are different and the oxygen atoms are bonded to different cations. Therefore two times nine active bands are expected in both the Raman and infrared spectra. Based on the C_s point group 18 possible modes for the Raman spectrum of syngenite can be identified based on $\Gamma = 2 \times (6 A_g + 3 B_g) = 12 A_g + 6 B_g$ [33]. However, based on the work by Moenke [34,35] Ross [31] reported an incorrect number of ten infrared vibrations. The crystal water molecule will be present in the form of OH-stretching, -bending and translation modes around roughly $3000\text{-}4000$, 1600 and 750 cm^{-1} . The relevant data of the factor group analysis are represented in Table 2.

Figure 2 shows the Raman and infrared spectrum in the region between 400 and 1300 cm^{-1} . The weak bands in the Raman spectrum at 298 K are clearly enhanced in the spectrum at 77 K due to increased signal-to-noise ratio combined with thermally induced minor shifts and decreased bandwidths. Table 3 gives a full overview of all observed bands in comparison to in the literature reported spectra of syngenite and related minerals such as gypsum, arcanite, görgeyite, etc. The syngenite spectrum is governed by two strong bands at 981 and 1004 cm^{-1} that can be ascribed to the ν_1 modes of the two sulphate groups. The weak bands at higher frequencies at 1118 , 1137 , 1142 and 1166 cm^{-1} can be ascribed to the splitting of the ν_3 mode of both sulfate groups. The sulphate ν_4 mode can only be observed as a single broad unresolved band at 641 cm^{-1} , which splits into four bands upon cooling to 77 K at 607 , 621 , 634 and 643 cm^{-1} . Finally the sulphate ν_2 mode is present at room temperature as four bands at 424 , 441 , 471 and 491 cm^{-1} . Upon cooling to 77 K the lowest frequency band disappears due to a shift towards the second band and now only one broader band is observed at 441 cm^{-1} , due to overlap together with two bands at 472 and 492 cm^{-1} . The spectra reported by Orekhov [33] are almost identical to our Raman spectra. These spectra reveal the same split in four bands as observed in our Raman spectra with bands at 429 , 440 , 472 and 493 cm^{-1} . Our results mean that from

the expected 18 bands based on a site symmetry of C_s only 14 bands can actually be observed in the Raman spectrum and that not all the expected splittings are fully displayed. No bands associated with the OH-modes of the crystal water are observed in the Raman spectrum.

The associated infrared spectrum is more complex as it shows not only the spectrum of syngenite but also of some associated ammonium nitrate, which can be expected when manure rich in NH_4^+ is treated with HNO_3 (see description in sample origin). Characteristic of the ammonium nitrate in the low frequency region are the ν_2 and ν_4 ammonium modes at 1677 and 1398 cm^{-1} together with the nitrate ν_3 mode at 1438 cm^{-1} (Fig. 3). The crystal water of the syngenite is easily observed as an OH-bending mode at 1631 cm^{-1} and an associated libration mode at 754 cm^{-1} . This band has been wrongly ascribed by Ross [31] to the water bending mode at 750 cm^{-1} together with the correctly assigned bending mode at 1685 cm^{-1} .

In contrast to the bands reported by Ross [31] and by Gadsden [36] the ν_1 modes of the two sulphate groups, strongly present in the Raman spectrum, are observed as very weak bands at 980 and 999 cm^{-1} , while the ν_3 modes at 1100 cm^{-1} , which were very weak in the Raman spectrum, are present as very strong bands in the infrared spectrum (Fig. 4). Band component analysis indicates the presence of five bands; a broader band at 1095 cm^{-1} which represents the nitrate ν_1 mode of the ammonium nitrate together with five bands at 1110, 1125, 1136, 1148 and 1193 cm^{-1} due to the split of the ν_3 modes of the two sulphate groups under the site symmetry of C_s . These values agree well with those at 1110, 1126, 1140 and 1194 cm^{-1} reported by Ross [31]. Cavaretta et al. [6] however reported only a weak shoulder at 990 cm^{-1} for the ν_1 mode and three bands at 1110, 1135 and 1185 cm^{-1} for the ν_3 mode.

The sulphate ν_2 mode is only visible as a very weak band at 438 cm^{-1} (Fig. 5), while others reported a split in two bands at 442 and 470 cm^{-1} [31], 437 and 470 cm^{-1} [36] and 440 and 472 cm^{-1} [33]. Only the spectrum shown by Cavaretta et al. [6] shows a single band at 435 cm^{-1} similar to the band observed in this study. It is interesting that in the corresponding Raman spectrum, discussed above, a split in four bands was observed. The region characteristic for the split ν_4 mode around 600 cm^{-1} reveals four relatively sharp bands at 657, 644, 617 and 604 cm^{-1} plus a much broader band at 596 cm^{-1} (Fig. 5). This broader band, which was also reported by several others [6,33], is unexpected based on the theoretical predictions and can not be assigned at this stage. These bands are much stronger in the infrared spectra than in the corresponding Raman spectra at 298 and 77 K. As for the ν_1 mode, again disagreement exists between various publications on the number of bands observed for the ν_4 mode. Ross [31] reported four bands at 661, 647, 630 and 611 cm^{-1} , Gadsden [36] listed three bands at 661, 647 and 611-603 cm^{-1} , while Cavaretta et al. [6] showed a doublet at 650 and 610 cm^{-1} accompanied by a much stronger band at 595 cm^{-1} .

The high-frequency region between 3000 and 4000 cm^{-1} is characteristic for the OH-stretching modes of the crystal water in the syngenite (Fig. 6). The Raman spectrum at 298 K shows a broad band at 3301 cm^{-1} with a clear shoulder at 3378 cm^{-1} . Upon cooling to 77 K these bands become clearly separated due to a decrease in the bandwidths and a small shift to 3296 and 3384 cm^{-1} , respectively. The crystal water molecule is connected via its oxygen O_2 to two neighbouring K atoms and further away via a weak interaction with the Ca atom. The two protons located at different positions in the crystal structure form two strong hydrogen bonds to the oxygen O_5 of the S_2 sulphate group resulting in two different OH-stretching bands.

The corresponding infrared spectrum shows a much more complex pattern. This is partly due to the fact that it shows the presence of the ammonium nitrate by the ammonium ν_1 and ν_3 modes at 3078 and 3310 cm^{-1} , respectively, in addition to the syngenite bands. Similar to the Raman spectra two OH-stretching bands are observed at 3248 and 3377 cm^{-1} together with a not previously observed band at 3510 cm^{-1} . Cavaretta et al. [6] also reported three bands at 3300, 3390 and 3600 cm^{-1} . The first two bands they ascribed to the stretching vibrations of molecular water. Comparison between the Raman and infrared spectra shows that the first band is strong in the Raman and relatively weak in the infrared spectrum while for the second band the situation is the opposite (Fig. 7). This indicates that the 3248 cm^{-1} band represents the symmetric mode and the 3377 cm^{-1} band the antisymmetric mode of the crystal water. The origin of the last band at 3510 cm^{-1} in our work and 3600 cm^{-1} in the work by Cavaretta et al. [6] possibly represents a combination band of the OH-stretching mode plus a hydrogen bond stretching mode normally observed at 200 cm^{-1} .

The near-infrared (NIR) spectral region has been defined to extend from roughly 700 to 3500 nm (14285 to 2860 cm^{-1}). The only vibrations in the NIR region between 4000 and 8000 cm^{-1} are those associated with hydrogen atoms associated with hydroxyl groups in the case of syngenite and with ammonium groups in the case of the ammonium nitrate. Rossman [37] reported for minerals average band positions for OH-groups and H₂O in the NIR region around 4200 cm^{-1} as being due to M-OH motions, 5200 cm^{-1} as the H₂O combination mode (bend + stretch) and around 7100 cm^{-1} as the first OH stretch overtone. This means that NIR spectroscopy is a very suitable technique to study syngenite in addition to infrared and Raman spectroscopy.

Figure 8 shows the band component analysis of the NIR spectrum in the region between 4000 and 7000 cm^{-1} . The results of the band component analysis and the possible assignments are summarised in Table 4. The first two bands at the low frequency side of the spectrum at 3959 and 4132 cm^{-1} are assigned to the combination bands of the OH-libration vibration and the symmetric and antisymmetric OH-stretching vibrations, respectively. The three strong bands at 4643, 4837 and 5025 cm^{-1} are the combination bands of the OH-bending vibration and the OH-symmetric stretching vibration, the OH-antisymmetric vibration and the H-bonded OH combination band, respectively. At this point the origin of the bands at 4300, 5173, and 5634 cm^{-1} remains unclear. The last three broad bands at 6010, 6389 and 6696 cm^{-1} can without doubt be attributed to the overtone of the OH-symmetric stretch, the combination of the OH-symmetric and antisymmetric stretching vibrations and the overtone of the OH-antisymmetric stretching vibration.

Conclusions

The treatment of manure with sulphuric acid has led to the crystallisation of syngenite crystals with a size of 1-2 mm, which are very suitable for spectroscopic analysis. Detailed understanding of the crystal structure based on X-ray diffraction in combination with infrared and Raman spectroscopy has shown that the site group symmetry of the sulphate groups S₁ and S₂ in the crystal structure must be without doubt C_s and not C₁ as indicated in some publications as an alternative site symmetry. Significant is also the observation of both the symmetric and antisymmetric OH-stretching modes plus the combination band of the OH-stretching mode with the hydrogen bonded OH resulting in a band at 3510 cm^{-1} , which has only been published once before. Most of the theoretically predicted bands have been observed in both the Raman and infrared spectra, although some bands appear to be too low in intensity to

be observed. In the infrared spectrum 13 of the predicted 18 bands were observed while in the Raman spectrum 10 at 298 K and 13 at 77 K of the predicted 18 bands were observed. Further, this paper has presented for the first time the near-infrared spectrum of syngenite showing the overtone and combination modes of the crystal water molecule present in the syngenite crystal structure.

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Table 1. Interatomic distances and bond angles in the sulphate groups with their standard deviations [28].

Bond	Length (Å)	σ (Å)
S ₁ -O ₁	1.464	0.006
S ₁ -O ₆	1.474	0.006
S ₁ -O ₇ (2x)	1.478	0.004
S ₂ -O ₃	1.462	0.006
S ₂ -O ₄	1.464	0.006
S ₂ -O ₅ (2x)	1.478	0.005
Atoms	Angle (°)	σ (°)
O ₁ -S ₁ -O ₆	107.9	0.3
O ₁ -S ₁ -O ₇	111.7	0.2
O ₇ -S ₁ -O ₆	109.4	0.2
O ₇ -S ₁ -O _{7'}	106.7	0.4
O ₃ -S ₂ -O ₄	109.2	0.4
O ₅ -S ₂ -O ₃	109.8	0.2
O ₅ -S ₂ -O ₄	110.8	0.2
O ₅ -S ₂ -O _{5'}	106.5	0.6
Anion	Balancing cations	
O ₁	S ₁ , 2 K, Ca	
O ₃	S ₂ , 4 K	
O ₄	S ₂ , 4 K	
O ₅	S ₂ , K, Ca, H	
O ₆	S ₁ , 2 K, Ca	
O ₇	S ₁ , 2 Ca	

Table 2 Factor group analysis of sulphate in syngenite.

Syngenite monoclinic $P2_1/m C_{2h}^2$				
C_s	I	σ_h		
A'	1	1	$T_x, T_y; R_z$	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
A''	1	-1	$T_z; R_x, R_y$	α_{yz}, α_{zx}

		$\nu_1(A_1)$		$\nu_2(E)$				$\nu_3(F_2)$				$\nu_4(F_2)$							
	T_d	983 cm^{-1}		450 cm^{-1}				1105 cm^{-1}				611 cm^{-1}							
	C_s	A'		A'		A''		A'		A'		A''		A'		A'		A''	
IR	C_{2h}^2	B_u	B_u	B_u	B_u	A_u	A_u	B_u	B_u	B_u	B_u	A_u	A_u	B_u	B_u	B_u	B_u	A_u	A_u
Raman	C_{2h}^2	A_g	A_g	A_g	A_g	B_g	B_g	A_g	A_g	A_g	A_g	B_g	B_g	A_g	A_g	A_g	A_g	B_g	B_g

Table 3. Infrared and Raman band positions of syngenite ($K_2Ca(SO_4)_2 \cdot H_2O$) compared to in the literature reported spectra of syngenite and related minerals such as gypsum ($CaSO_4 \cdot 2H_2O$), arcanite (K_2SO_4), görgeyite ($K_2Ca_5(SO_4)_6 \cdot H_2O$) and polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$).

This study Syngenite			[33]	[38]		[31]	[36]	[6]		[36]			Assignment Syngenite
IR	Raman 298 K	Raman 77 K	Raman 298 K	Raman 298 K	IR	IR	IR	Syngenite IR	Görgeyite IR	Polyhalite IR	Gypsum IR	Arcanite IR	
	424		429	429		442	437	435	435	445			$\nu_2(E)A_u + A_g SO_4$
439	441	441	440	441	442				455	455-50			$\nu_2(E) B_g SO_4$
	471	472	472	473		470	470		485	485-80	470-60		$\nu_2(E) B_g SO_4$
	491	492	493	494						510			$\nu_2(E) A_g SO_4$
									530	540			
596			603					595	590				?
604		607	608	609	605					612-04	605-595		$\nu_4(F_2) B_u + B_g SO_4$
617		621	622	622	612	611	611-03			625		620	$\nu_4(F_2) B_u + A_g SO_4$
		634	632	635	645	630		640	620				$\nu_4(F_2) B_g SO_4$
644	641	643	644	644	648	647	647	650	645				$\nu_4(F_2) A_u + A_g SO_4$
657			661	664		661	661			660-53	673		$\nu_4(F_2) A_u + A_g SO_4$
754						750	750	745		755	720	728	OH-lib
980	981	982	981	983	980			990	990	1000-992		990-80	$\nu_1(A_1) B_u + A_g SO_4$
999	1004	1007	1004	1005	1002		1002?			1018	1018		$\nu_1(A_1) B_u + A_g SO_4$
1110			1081	1084	1108	1110	1110-05	1110	1050	1105	1093	1115-00	$\nu_3(F_2) B_u SO_4$
1125	1117	1119	1117	1119	1125	1126	1136-25	1135			1124		$\nu_3(F_2) B_u + B_g SO_4$
1136	1138	1136	1139		1140	1140	1140				1150-42	1150-30	$\nu_3(F_2) B_u + A_g SO_4$
1148		1144		1143									$\nu_3(F_2) B_u SO_4$
	1166	1167	1165	1168						1160-44			$\nu_3(F_2) A_u + B_g SO_4$
1193				1198	1192	1194	1195-89	1185	1200	1180		1195-85	$\nu_3(F_2) A_u SO_4$
										1215-04		1310	
1631						1685	1685	1610	1600	1670	1630		OH-bend
3248								3300	3200	3290			Sym. OH-stretch
3377						3320	3320	3390	3490	3335			Antisymm. OH-stretch
										3440	3430		
											3560		
3510								3600					Comb H-bond + OH-stretch

Table 4. Near-infrared band positions for syngenite.

Observed band position (cm ⁻¹)	Relative intensity	Sum of mid-IR band position (cm ⁻¹)	assignment
3951	3.1	4002	Comb. OH-lib + OH-sym. stretch
4132	1.9	4131	Comb. OH-lib + OH-antisym. stretch
4643	31.4	4879	Comb. OH-bend + OH-sym. stretch
4300			?
4837	9.2	5008	Comb. OH-bend + OH-antisym. stretch
5025	16.4	5141	Comb. OH-bend + H-bond OH
5173	10.3		?
5634			?
6010	12.0	6494	Overtone OH-sym. stretch
6389	3.4	6625	Comb. OH-sym. + OH-antisym. stretch
6696	8.8	6754	Overtone OH-antisym. stretch

Figure captions

- Fig. 1 Projection of the syngenite crystal structure along the b-axis
- Fig. 2 Infrared and Raman spectra (298 and 77 K) of syngenite in the region between 400 and 1300 cm^{-1} .
- Fig. 3 Band component analysis of the infrared spectrum in the region between 1350 and 1750 cm^{-1} showing the ammonium nitrate vibrations.
- Fig. 4 Band component analysis of the infrared spectrum in the region between 950 and 1350 cm^{-1} showing the split ν_3 and weak ν_1 sulphate modes of syngenite plus the ν_1 nitrate mode of the ammonium nitrate.
- Fig. 5 Band component analysis of the Raman spectrum in the region between 400 and 850 cm^{-1} showing the single ν_2 and split ν_4 sulphate modes plus the water libration mode of syngenite.
- Fig. 6 Infrared and Raman spectra (298 and 77 K) of syngenite in the region between 2950 and 3700 cm^{-1} .
- Fig. 7 Band component analysis of the infrared and Raman OH-stretching region between 3000 and 3600 cm^{-1} showing the symmetric and antisymmetric OH-stretching modes of the crystal water of syngenite plus the infrared active ν_1 and ν_3 ammonium modes of the ammonium nitrate.
- Fig. 8 Band component analysis of the near-infrared spectrum of syngenite in the region between (a) 3800 and 5500 cm^{-1} and (b) 5500 and 7000 cm^{-1} .

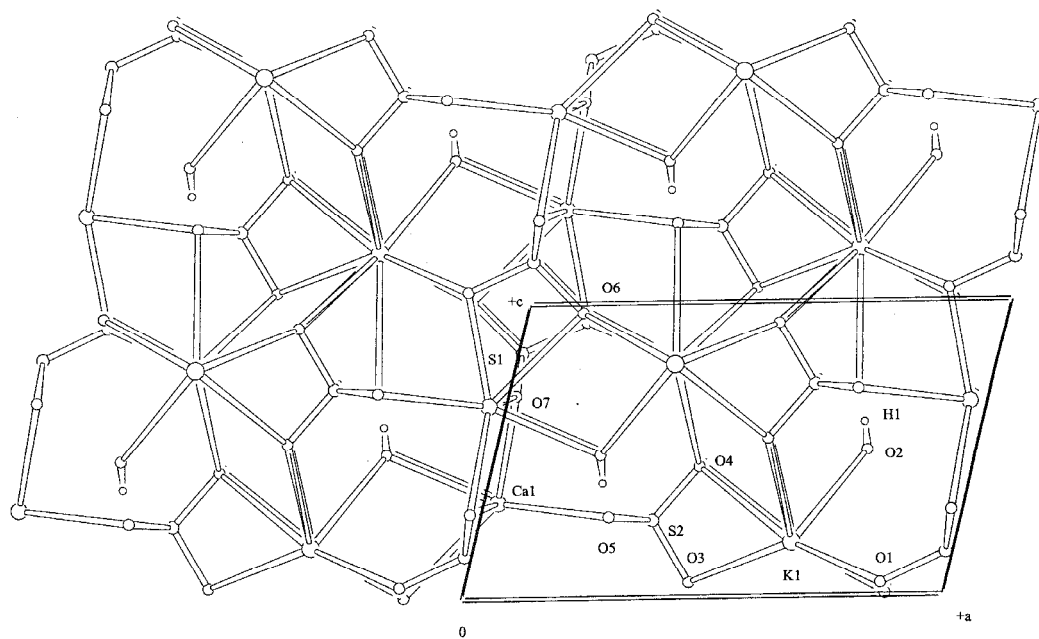


Fig. 1

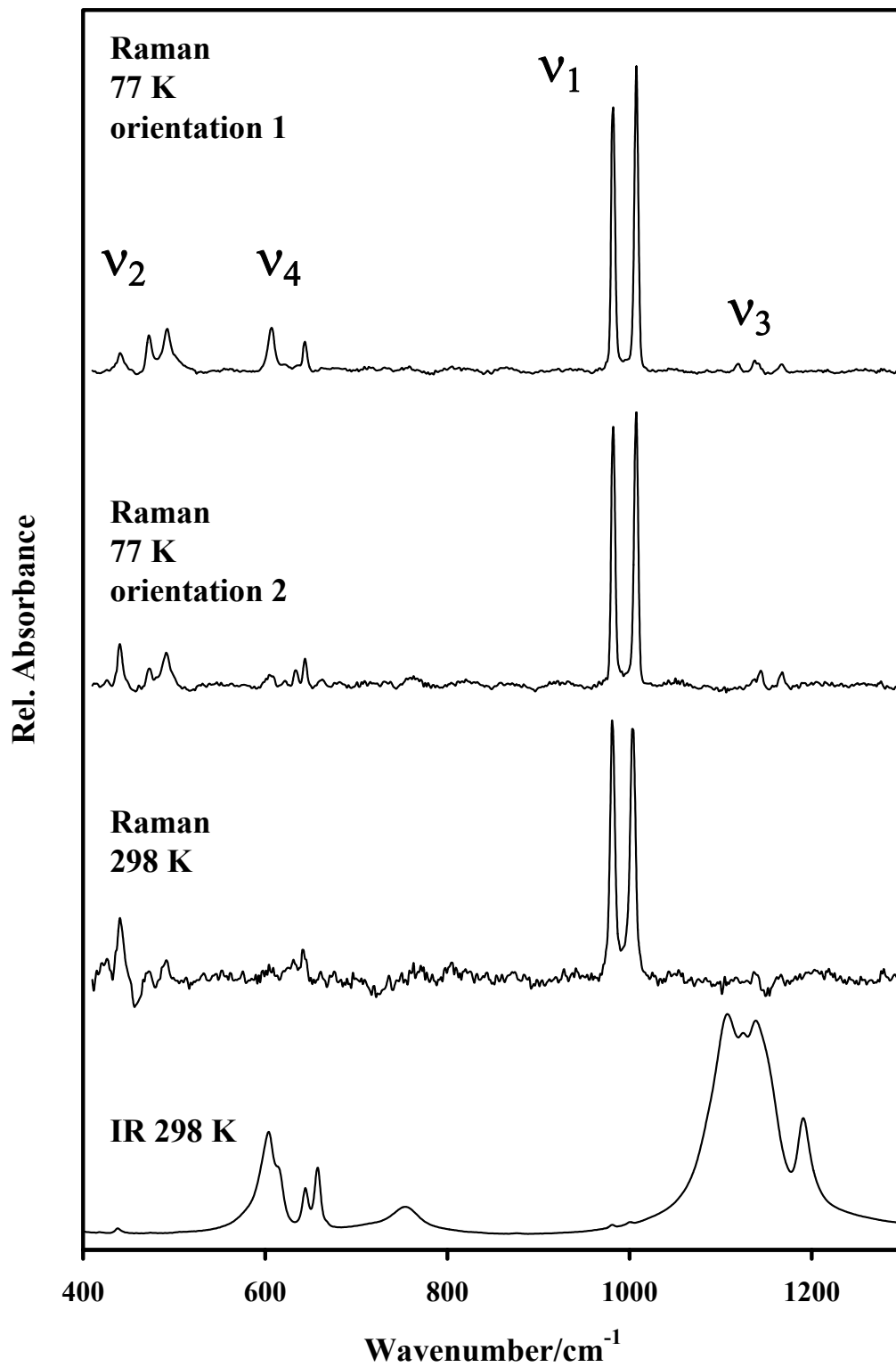


Fig. 2

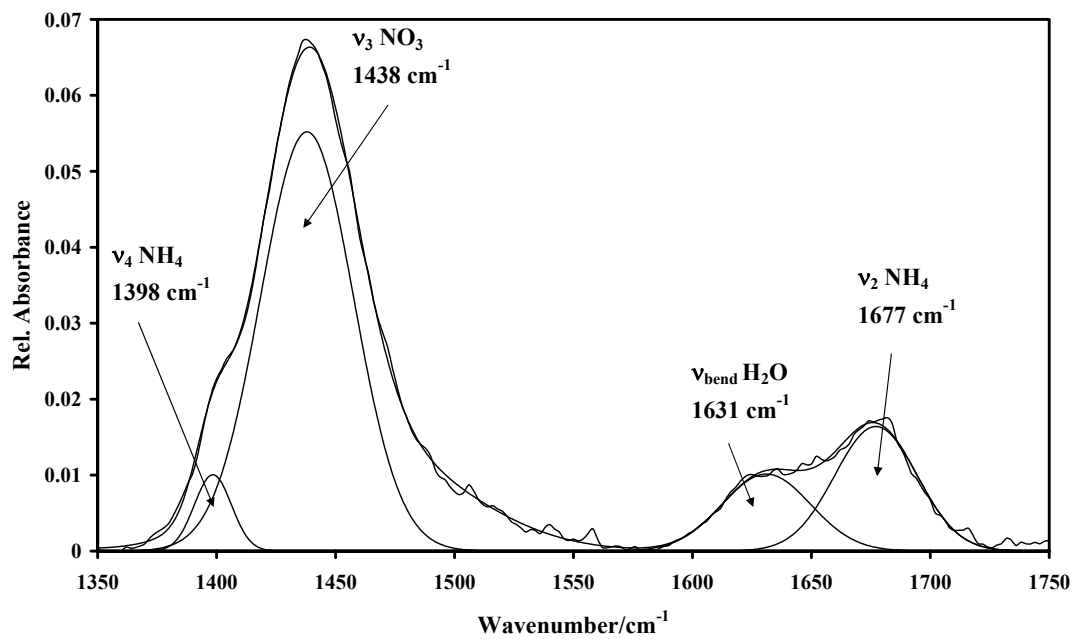


Fig. 3

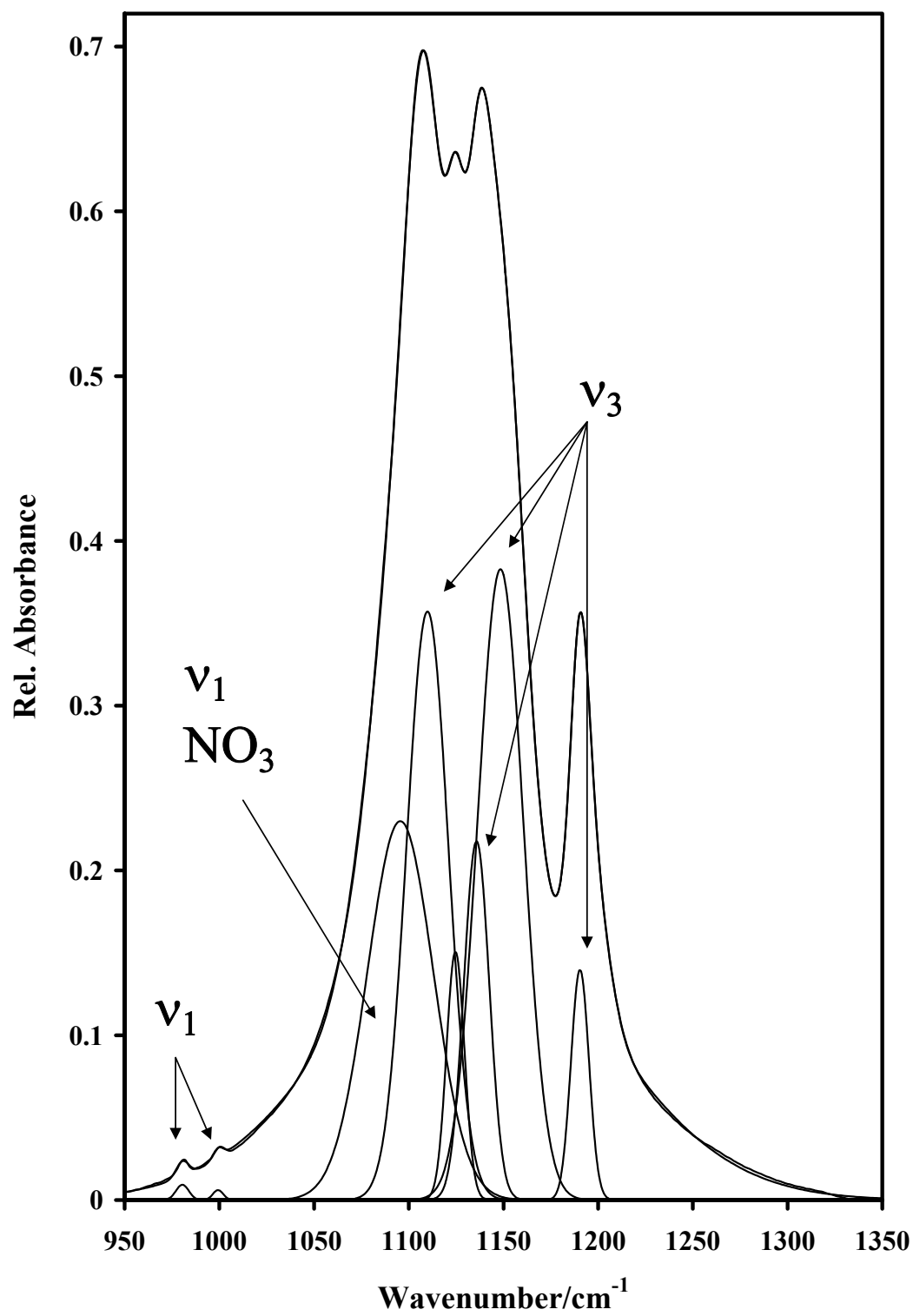


Fig. 4

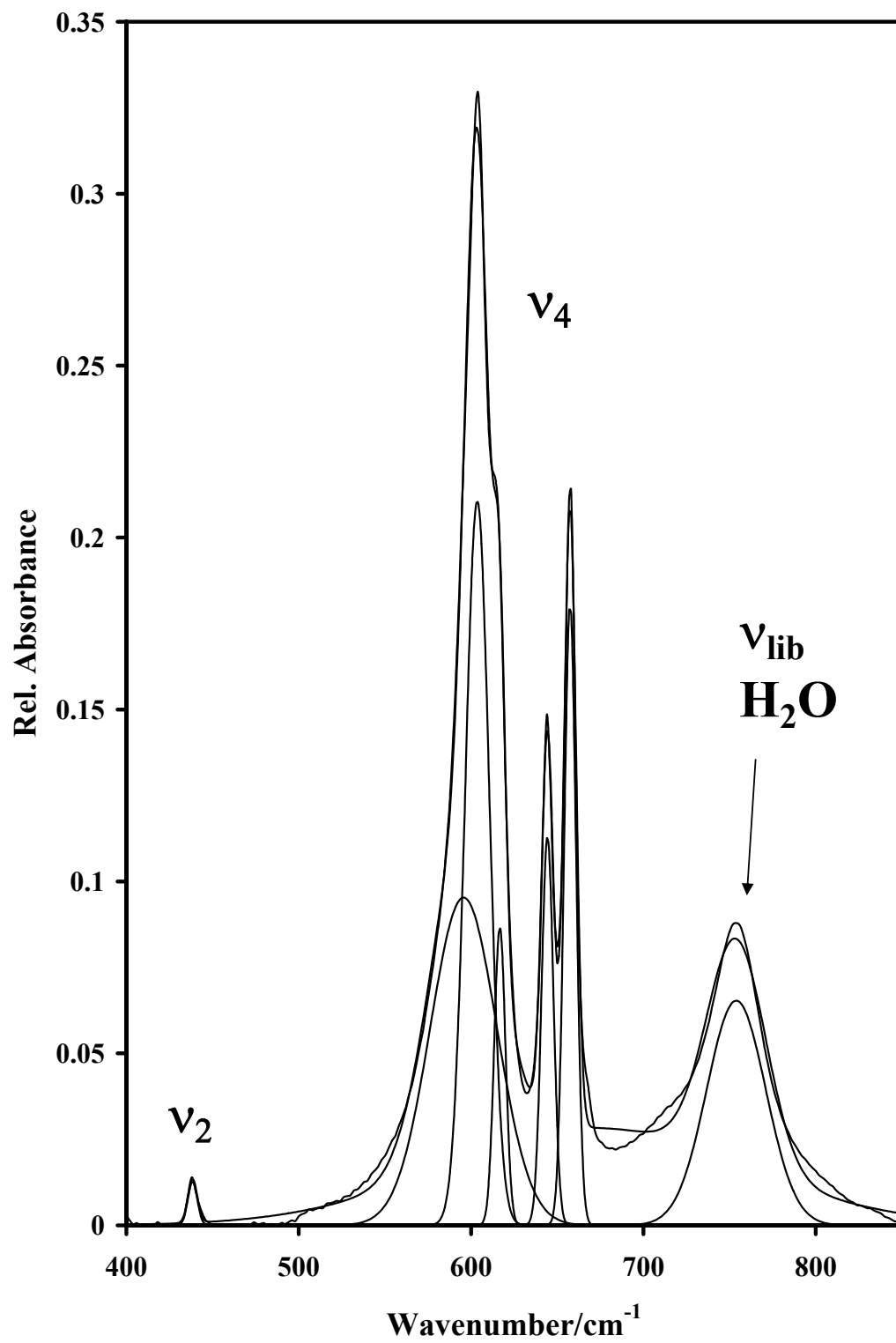


Fig. 5

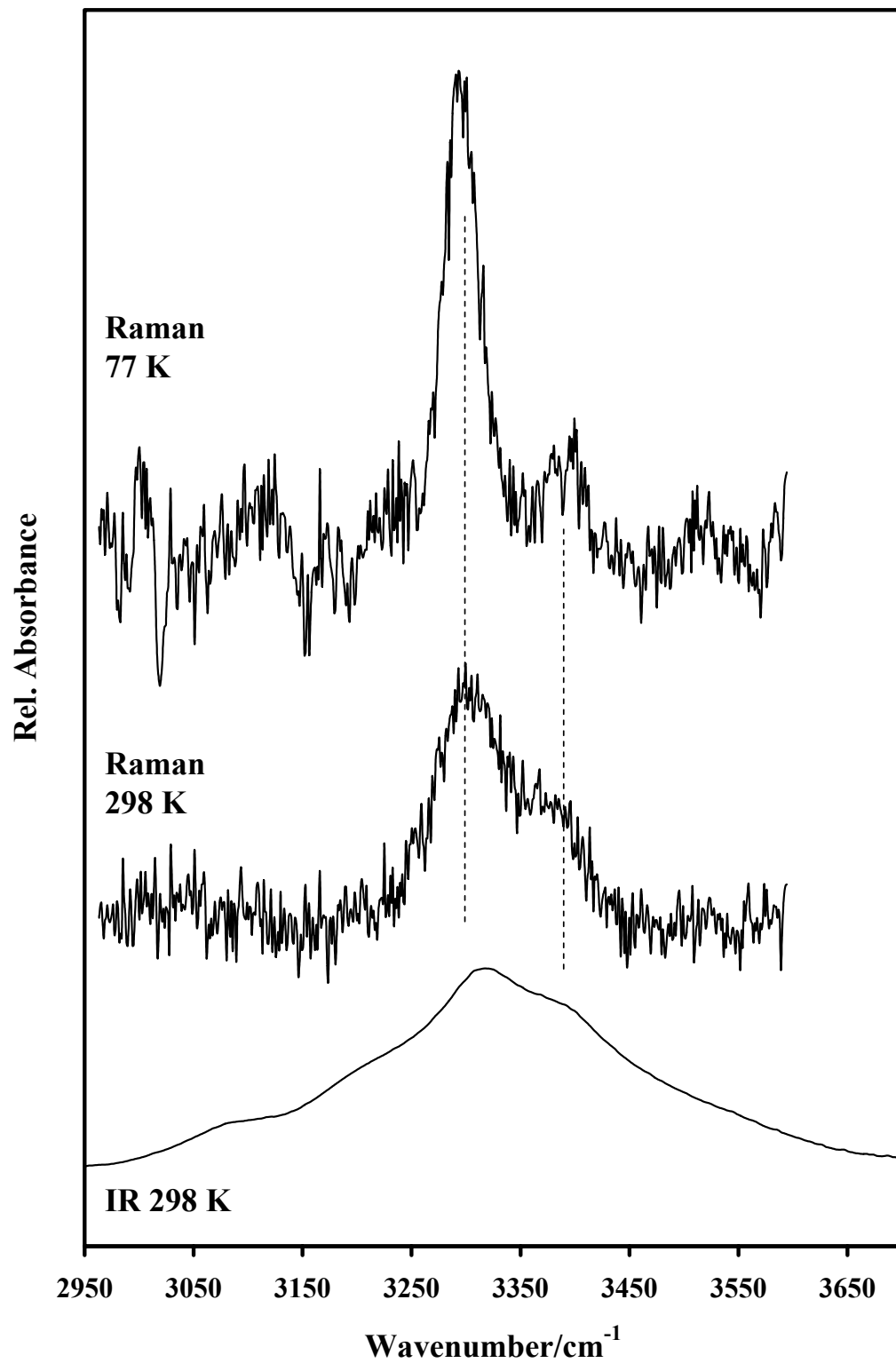


Fig. 6

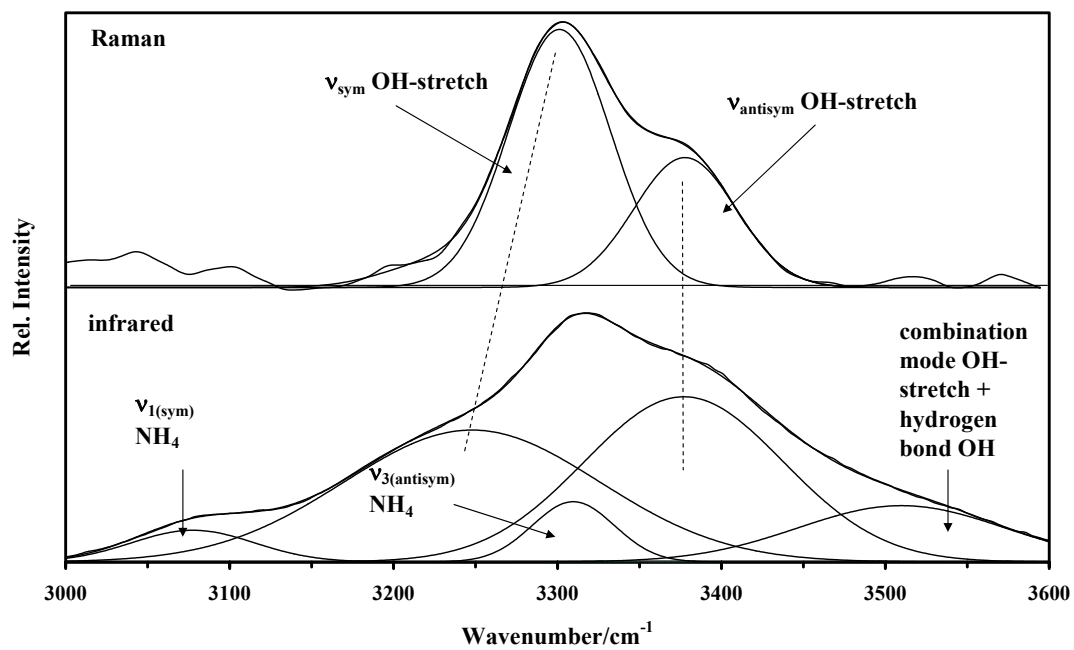


Fig. 7

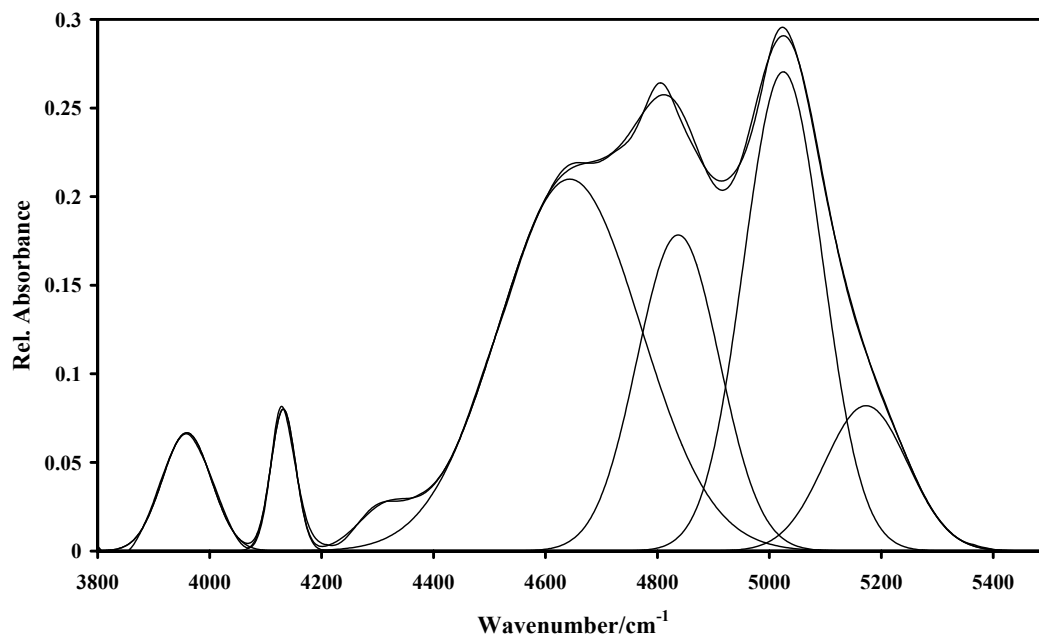


Fig. 8a

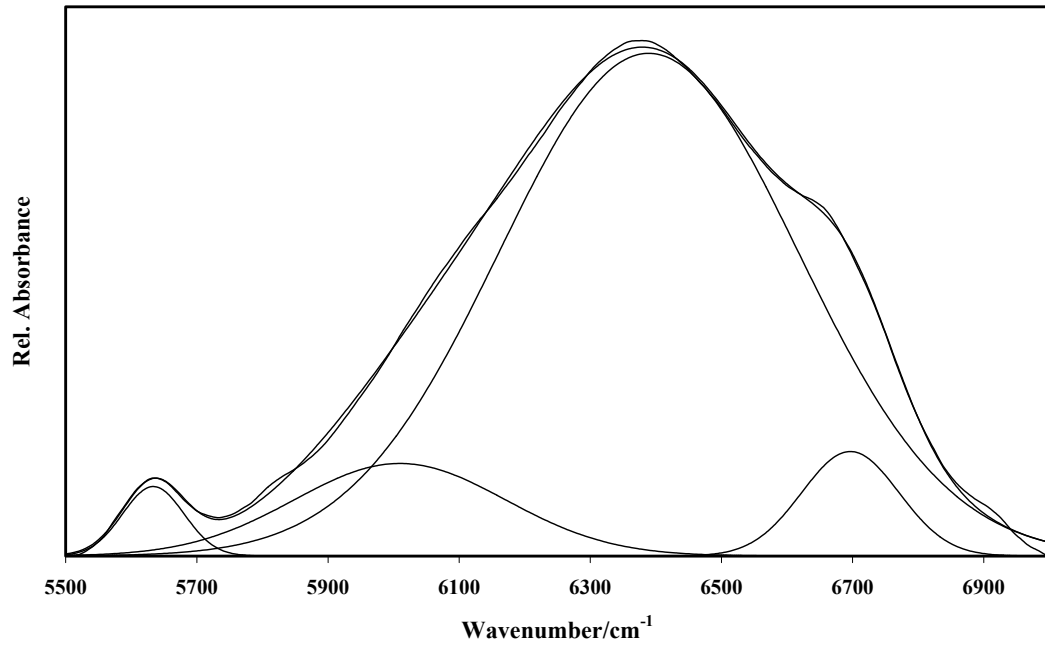


Fig. 8b