

# Polarised Raman spectroscopy using the inVia™ Raman microscope



The Renishaw inVia confocal Raman microscope

## Introduction

The full characterisation of materials through Raman spectroscopy often involves not only the measurement of the vibrational modes (or phonons), but also their relative intensities as a function of polarisation, so that the material symmetry can be determined. Material symmetry can be connected to a wide range of properties including molecular symmetry, the relative positions of atoms in the molecule, crystal symmetry and the relative position/orientation of packed molecules in a solid.

The intensities and position of bands in a Raman spectrum often depends on the relative orientation of the materials symmetry axes to both the polarisation direction of the exciting laser light and polarisation direction of the collected scattered Raman light. Measuring the Raman spectrum for the different incident and scattered light polarisation directions allows the intensity to be compared to various selection rules. If the symmetry of the vibration is determined, the material symmetry and its Raman tensor can be comprehensively characterised. The application of polarised Raman spectroscopy measurements often includes: identifying crystal structure of solids; investigating orientation of materials; isomer identification; analysis of the structure of molecules in liquid form and characterising directional strain/stress in materials.

Understanding the basics of the theory behind polarised Raman scattering—namely the Raman scattering selection rules and how to perform these measurements on an inVia Raman microscope allows the Raman microscope to become a powerful tool for characterising the materials at hand. A review of the details for two case studies will illustrate the application of polarised Raman spectroscopy and its power in materials characterisation.

## Molecular vibrational symmetry in liquids and depolarisation ratios

For solutions (randomly oriented molecules),  $\text{CCl}_4$  is well suited and often used to introduce the polarized Raman spectroscopy concept. Through group theory  $\text{CCl}_4$  is described by the  $T_d$  point group. There is only one totally symmetric stretching vibration for  $\text{CCl}_4$ ,  $A_1$ , and the remaining vibrations for  $\text{CCl}_4$  are asymmetric and transform as E and T symmetry. From the theory of the Raman effect [1] it is well determined that the depolarisation ratio,  $\rho = I_{\perp}/I_{\parallel}$  where  $I_{\perp}$  and  $I_{\parallel}$  are the Raman intensities measured with a polarisation perpendicular and parallel to the excitation polarisation respectively, follows the relation of  $0 \leq \rho < \frac{3}{4}$  for totally symmetric vibrations and  $\rho = \frac{3}{4}$  for non-symmetric vibrations. The  $\text{CCl}_4$  Raman spectrum for parallel and perpendicular is shown in Figure 1. The  $\rho$  for the  $459 \text{ cm}^{-1}$  band tends toward 0 and must be the  $A_1$  totally symmetric vibration, while the two remaining strong vibrations at  $283 \text{ cm}^{-1}$  and  $315 \text{ cm}^{-1}$  have a  $\rho$  of  $\frac{3}{4}$ , and must be the non-totally symmetric vibrations that transform as E and T symmetries. A detailed discussion of the polarised Raman spectroscopy of molecules can be found in [1].

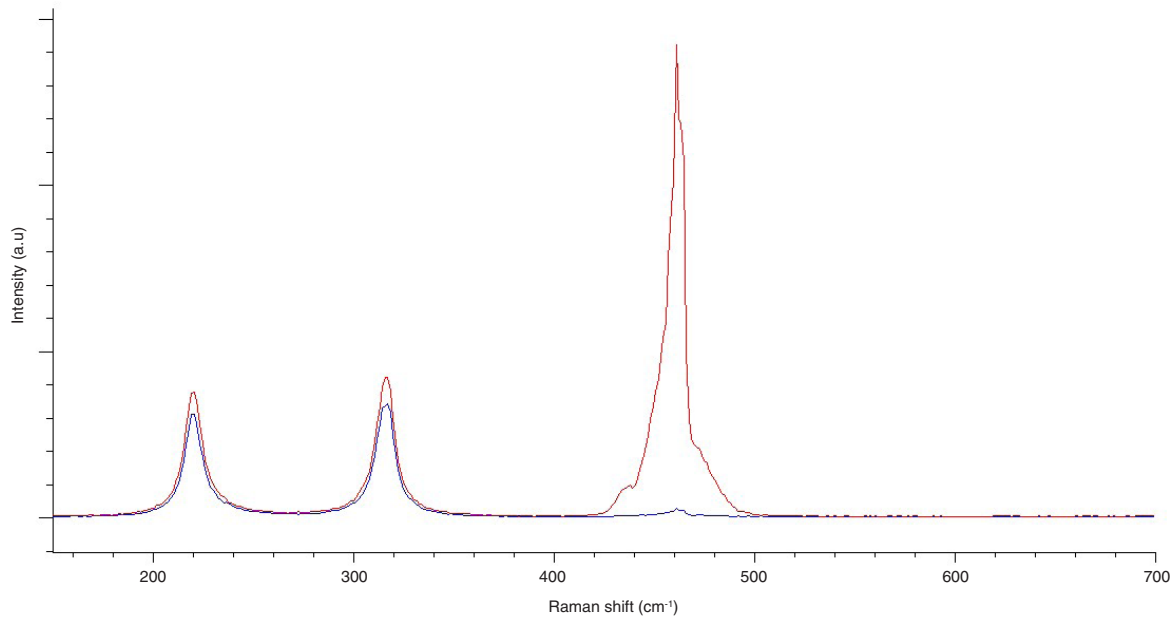


Figure 1. Raman spectra of  $\text{CCl}_4$  collected in parallel (red) and perpendicular (blue) polarisation configurations. Here it can be seen that the depolarisation ratio,  $\rho = I_{\perp}/I_{\parallel}$  for the  $459 \text{ cm}^{-1}$  band is  $\sim 0.01$  and for the  $220 \text{ cm}^{-1}$  and  $315 \text{ cm}^{-1}$  bands is  $\sim 0.75$ .

## Raman scattering selection rules in crystals

To make best use of the polarized Raman capabilities of a Raman microscope it is important to understand the common nomenclature used in the Raman community for describing the incident laser and Raman scattered polarisation directions.

Porto notation [2] is a concise way of describing the polarisation configuration of Raman measurements. It is used to denote the propagation direction and polarisation of incident and scattered photons relative to an axis of the medium. Porto notation has the following form:

$$k_i(\hat{e}_i, \hat{e}_s)k_s$$

where  $k_i$  and  $k_s$  are the wavevector directions of the incident and observed scattered photons respectively, and  $\hat{e}_i$  and  $\hat{e}_s$  are the polarisation directions of their respective electric fields.

It is standard for Raman polarisation measurements to use a perpendicular coordinate system X, Y and Z. For cubic, tetragonal, and orthorhombic crystals, the X, Y and Z-axes are by convention aligned with the a, b and c-axes of the crystal respectively.

In the case of unpolarised light the polarisation direction is denoted by -. For example,  $Z(-,-)\bar{Z}$  is shorthand for incident light propagating along the Z-axis (crystal c-axis) and the observed scattered light propagating in the opposite direction (i.e. backscattered), with both the incoming and outgoing light unpolarised.  $Z(X, Y)\bar{Z}$  denotes backscattering of light, but this time with the incident beam polarised in the X-direction and the scattered beam analysed in the Y-direction.

More traditionally, if the direction of the incident and observed scattered light polarisation are perpendicular, the setup is described as being cross polarised e.g.  $Z(X, Y)\bar{Z}$ . Parallel polarisation describes the direction of the polarisation for the incident and observed scattered light as the same e.g.  $Z(X, X)\bar{Z}$ .

The relative amplitude of Raman scattering for a given Raman mode is governed by its Raman tensor. The form of the Raman tensor is a matrix that describes how light with a particular direction and polarisation interacts with the molecules to produce Raman intensity in a scattering direction and polarisation. The elements of R are determined by vibration mode symmetry. The Raman tensor must have a non-zero component for a mode to be Raman active. Raman tensors can be derived from group theory [3] and the Raman tensors for all crystal groups were determined and described by Loudon [4]. It is useful to write the intensity of the Raman scattered light from a mode in terms of the Raman tensor, R:

$$I \propto |\hat{e}_i \cdot R \cdot \hat{e}_s|^2$$

For crystalline materials, an excellent and simplistic sample to consider is diamond. Diamond has a face centred cubic structure and belongs to the  $Fd\bar{3}m$  space group, it has 3 triply degenerate  $T_{2g}$  vibrations. The Raman tensors for these vibrations in the  $\langle 100 \rangle$  coordinate system are:

$$R_1 = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} R_2 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{bmatrix} R_3 = \begin{bmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{bmatrix}$$

For the Raman active phonons (vibrations), Equation (2) predicts the intensity for each of the laser polarisations and scattered polarisation directions. The  $R_1$  mode is Raman active, and is observed in the  $Z(Y, X)\bar{Z}$  scattering configuration:

$$I_{R1} \sim |\hat{e}_i \cdot R_{R1} \cdot \hat{e}_s|^2 = \left| \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \right|^2 = \left| \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ d \\ 0 \end{bmatrix} \right|^2 = d^2$$

Similar analysis for the  $R_2$  and  $R_3$  modes in the  $Z(Y, X)\bar{Z}$  scattering configuration reveals they are not going to be observed in this measurement configuration i.e.  $I_{R2} = 0$ ,  $I_{R3} = 0$

#### Polarisation options on the inVia Raman microscope

inVia can be configured for a comprehensive range of polarisation measurements collected in the backscatter geometry. This means in the  $X(, )\bar{X}$ ,  $Y(, )\bar{Y}$ ,  $Z(, )\bar{Z}$  all polarisation options are available. Here the polarisation options for  $Z(, )\bar{Z}$  will be discussed. (The instrument configuration for the other laser/ scattering directions are the same with the exception that the samples crystal axes are aligned differently).

Polarisation optics are available in both manual and motorised forms.

When the system is in its default configuration without wave plates / analyser inserted, the lasers are polarised in X.

- Standard optics Z(X, -) $\bar{Z}$
- Changing the detection of the scattered light
  - Polariser from analyser kit inserted Z(X, X) $\bar{Z}$
  - Polariser and  $\frac{1}{2}$  wave plate from analyser kit inserted Z(X, Y) $\bar{Z}$
- Changing the polarisation of the laser light
  - $\frac{1}{2}$  waveplate is inserted between laser and sample Z(Y, -) $\bar{Z}$
  - $\frac{1}{4}$  waveplate is inserted between laser and sample Z(-, -) $\bar{Z}$
  - Variable  $\frac{1}{2}$  waveplate is inserted between laser and sample at angle  $\theta$  Z( $\theta$ , -) $\bar{Z}$

It is possible to combine the polarisation of the observed scattered light and laser to get the following options  $Z(Y, X)\bar{Z}$ ,  $Z(Y, Y)\bar{Z}$ ,  $Z(\theta, X)\bar{Z}$ ,  $Z(\theta, Y)\bar{Z}$ , etc.

Here we demonstrate measurements on two different materials to illustrate the benefits of polarised Raman measurements on inVia.

## Investigating the Raman modes of GaN

Gallium nitride (GaN) is a semiconductor used in blue LEDs and high speed transistors. It is an up and coming material and a significant effort has been made to understand its physics and growth to the level to which devices can be made. The 2015 Nobel Prize was awarded for developments in GaN material. GaN comes in two forms; cubic and hexagonal. Hexagonal GaN is the most important as this is used to make devices. Raman is an important tool for characterising GaN and is used to investigate crystal structure, defect doping and uniformity [5].

Hexagonal GaN belongs to the  $P6_3mc$  space group and has nine optical modes at its Brillouin zone centre. The  $2B_1$  modes are neither Raman nor IR active and thus are called silent modes. The remaining  $A_1$ ,  $E_1$ , and  $2E_2$  modes are Raman active. The  $E_1$  and  $2E_2$  normal modes are each doubly degenerate, each normal mode consisting of two modes propagating perpendicular to the  $c$ -axis as well as to each other. Hence, each of these normal modes is described by two Raman tensors, one propagating in  $x$  and one in  $y$ . To distinguish between the  $2E_2$  modes, they are labelled  $E_2^{low}$ ,  $E_2^{high}$  representing the lower and higher frequency  $E_2$  mode, respectively. The  $A_1$  and  $E_1$  modes are polar modes and the macroscopic electric field associated with these modes causes them to split into longitudinal optical (LO) and transverse optical (TO) components. A letter in parenthesis is typically used to show the direction of the dipole associated with the phonon. The wave vector for the  $A_1$  mode is oriented along the  $c$ -axis.

The Raman tensors for GaN are as follows:

$$R_{A_1(z)} = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix}, R_{E_1(x)} = \begin{bmatrix} 0 & 0 & c \\ 0 & 0 & 0 \\ c & 0 & 0 \end{bmatrix}, R_{E_1(y)} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{bmatrix}, R_{E_2} = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, R_{E_2} = \begin{bmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are non-zero tensor components.

Renishaw's inVia Raman microscope has backscattered collection optics and can probe any combinations of parallel and perpendicular polarisations. For this work an inVia Raman microscope equipped with a 532 nm laser excitation source was used to examine a  $1 \mu\text{m}$  GaN layer grown on a sapphire wafer. The polarisation of the incident and scattered light was varied using motorised polarisation optics. Figure 2 shows the Raman spectra collected from a variety of different polarisation. There is strong agreement with the Raman selection rules for GaN as expected. Table 1 summarises the results. The variation in stress and strain causes a minute splitting in the degeneracy of the  $E_2$  mode [6] and thanks to the excellent spectral resolution of the inVia Raman microscope it is possible to resolve this shift illustrated in Figure 3.

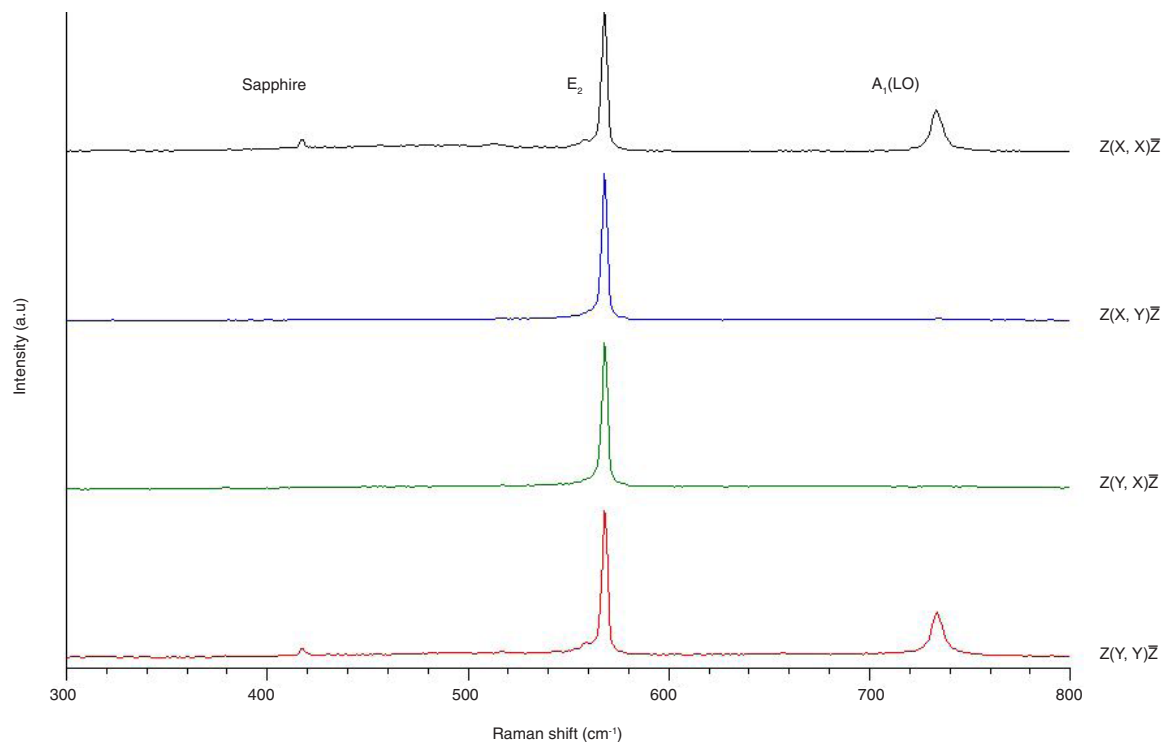


Figure 2. Raman spectra of GaN on sapphire collected with different experimental setups. Porto notation for each setup is given on the right.

Experimental setup	Visible modes
Z(X, X) $\bar{Z}$	A <sub>1</sub> (LO), E <sub>2</sub>
Z(X, Y) $\bar{Z}$	E <sub>2</sub>
Z(Y, X) $\bar{Z}$	E <sub>2</sub>
Z(Y, Y) $\bar{Z}$	A <sub>1</sub> (LO), E <sub>2</sub>

Table 1 – allowed modes of GaN

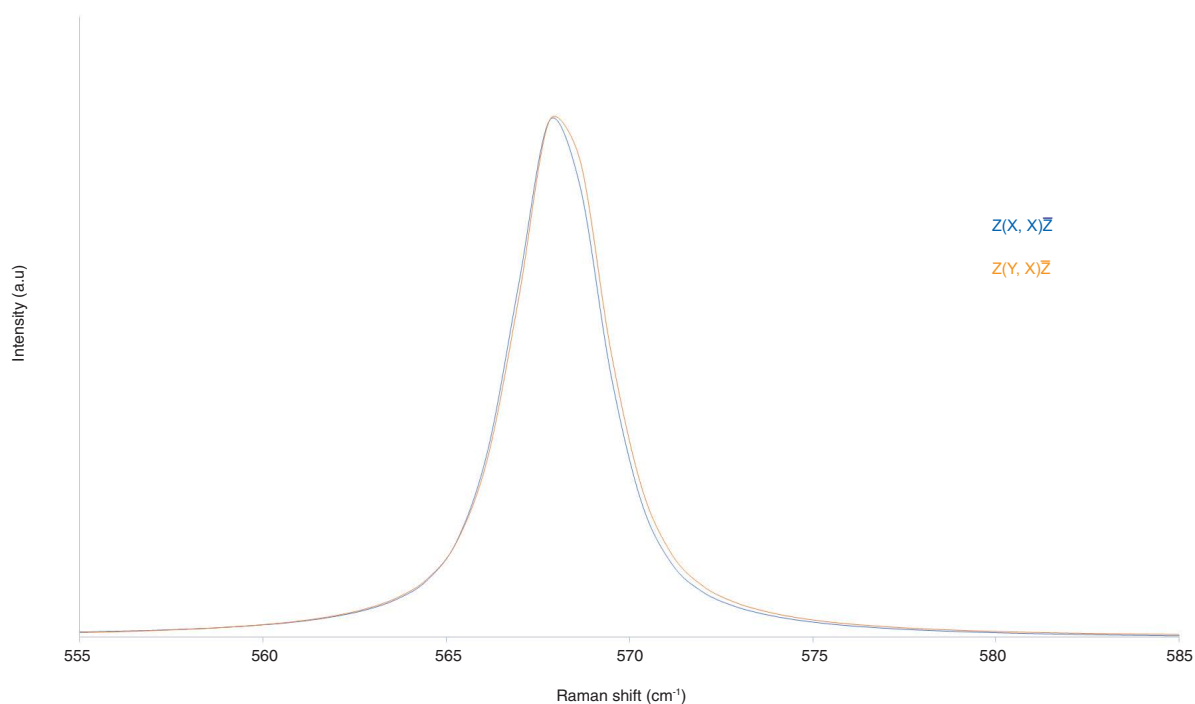


Figure 3. Raman spectra of GaN on sapphire collected with Z(X, X) $\bar{Z}$  and Z(Y, X) $\bar{Z}$ . This illustrates the ability of the inVia system to resolve the extremely small splitting of the degeneracy of the E<sub>2</sub> mode as a result of strain in the material. Here the change in peak centres is ~0.064 cm<sup>-1</sup>.

### Identifying the orientation of ReS<sub>2</sub> flakes

ReS<sub>2</sub> is one of the burgeoning 2D materials from the transition metal dichalcogenide (TMD) group. It is a semiconductor with a band gap of ~1.5 eV. A single monolayer of ReS<sub>2</sub> consists of one lattice of rhenium atoms sandwiched between two lattices of sulfur atoms. Atomically thin samples of ReS<sub>2</sub> can be made by mechanical exfoliation or grown using CVD. ReS<sub>2</sub> has a distorted 1T crystal structure due to a Peierls distortion, which results in it having a low symmetry structure and a large number of Raman modes (illustrated in Figure 4). These modes have a variety of Raman selection rules which can be probed using polarised measurement. To do this the incident laser polarisation was rotated through 360 degrees in 20-degree increments. This is easy to achieve on inVia, as there is an option for motorised polarisation optics, allowing such measurements to be carried out using the software with no manual intervention. Results showing the polarisation dependence of the Raman selection rules for selected modes of ReS<sub>2</sub> are shown in Figure 5. Here it can be seen that the modes all have 2-fold symmetry, but are offset from one another. Knowledge of the polarisation dependence of Raman modes is useful as it can be used to determine the crystal orientation of samples, for ReS<sub>2</sub> the b-axis lies parallel to the polarisation axis of the 211 cm<sup>-1</sup> Raman mode.

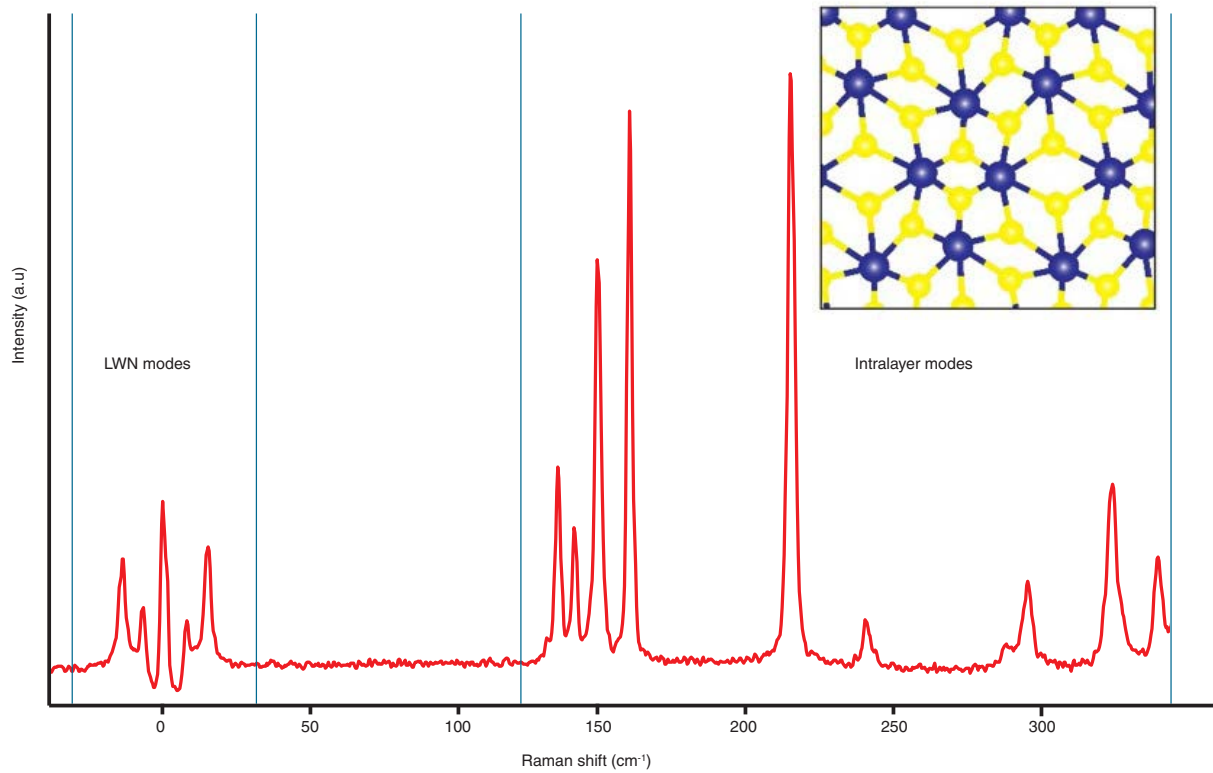


Figure 4. Raman spectra of a 4-layer  $\text{ReS}_2$  flake. The inset shows the crystal structure of  $\text{ReS}_2$ .

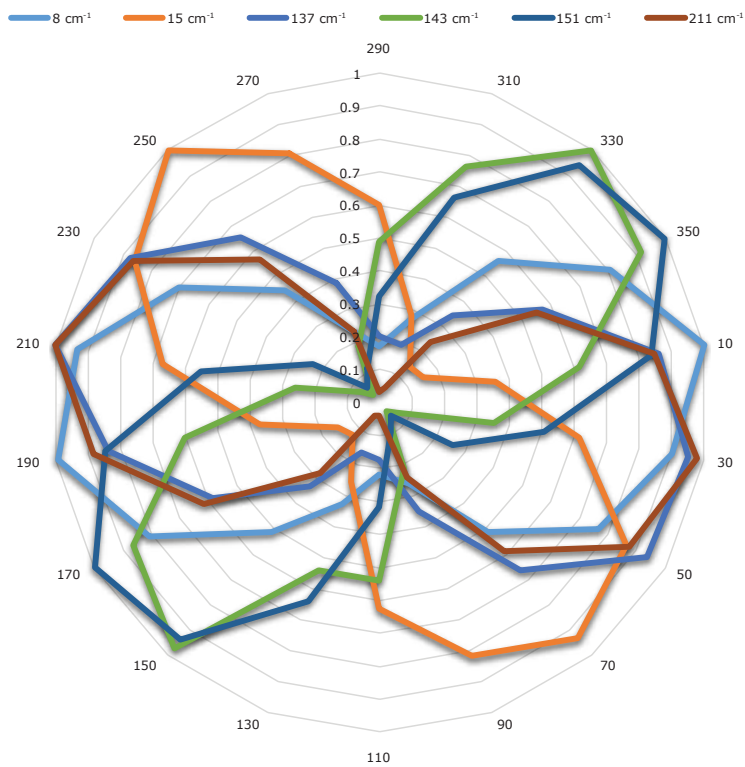


Figure 5. Radial plots of the normalised intensity of  $\text{ReS}_2$  Raman modes as a result of changing incident laser polarisation. This plot illustrates the polarisation dependence of the Raman selection rules for each mode.

ReS<sub>2</sub> has lower symmetry than other TMDs, it has an inversion centre and does not exhibit any rotational symmetry. Applying a 180-degree rotation about the in-plane axis i.e. turning the flake upside down, reverses the sign of the two non-equivalent in-plane crystallographic axes. This is a very important property as it means that ReS<sub>2</sub> can occur in two different configurations, coined upside-up and upside-down which are energetically similar but symmetrical non-equivalent. This anisotropy will affect device structures and also may generate sub domains when growing ReS<sub>2</sub> using CVD, so it is vital that it can be detected. It has been found that polarised Raman spectroscopy is the perfect tool for doing just this [7]. Figure 6 illustrates polarised Raman measurements taken from flakes in both configurations, these plots cannot be mapped to each other using rotations (physically corresponding to rotating the flake or the polarisation) and as such are unique indicators of the configuration of a given flake.

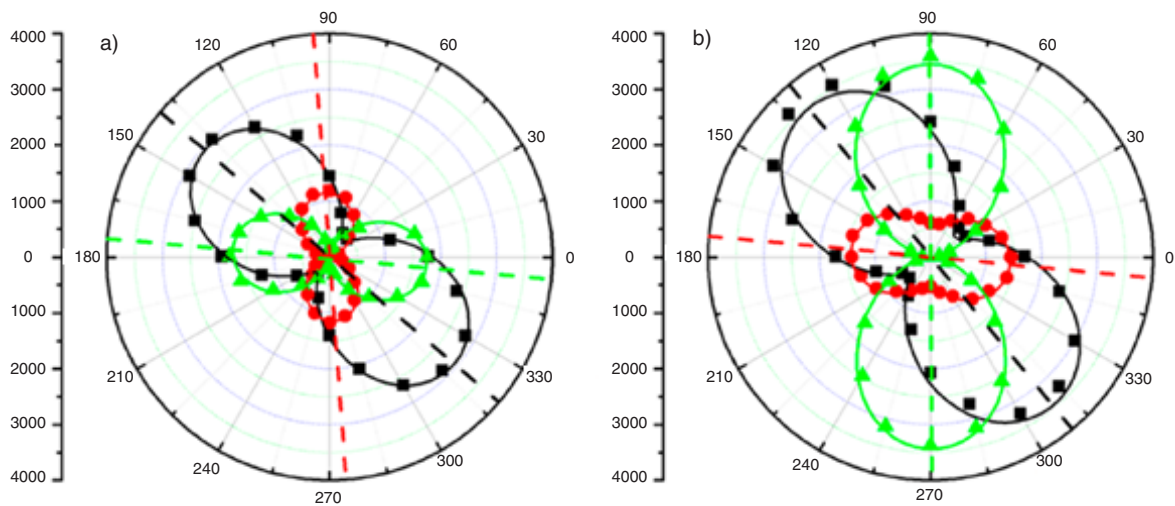


Figure 6. Radial plots of the intensity of ReS<sub>2</sub> Raman modes at 150, 160, and 211 cm<sup>-1</sup> (black squares, red circles, and green triangles, respectively) as a result of changing incident laser polarisation. a) was acquired from a flake in the upside-up configuration, b) was acquired from a flake in the upside-down configuration. Image taken from reference 7.

Here we use these results to investigate the orientation and top surface of a mechanically exfoliated flake consisting of 4 layers. Results are shown in Figure 7, here 7a) matches Figure 6b) indicating the flake is in the upside-down configuration. Measurements of the 211 cm<sup>-1</sup> mode indicate the direction of the b-axis which is confirmed by the optical image of the flake (Figure 7b).

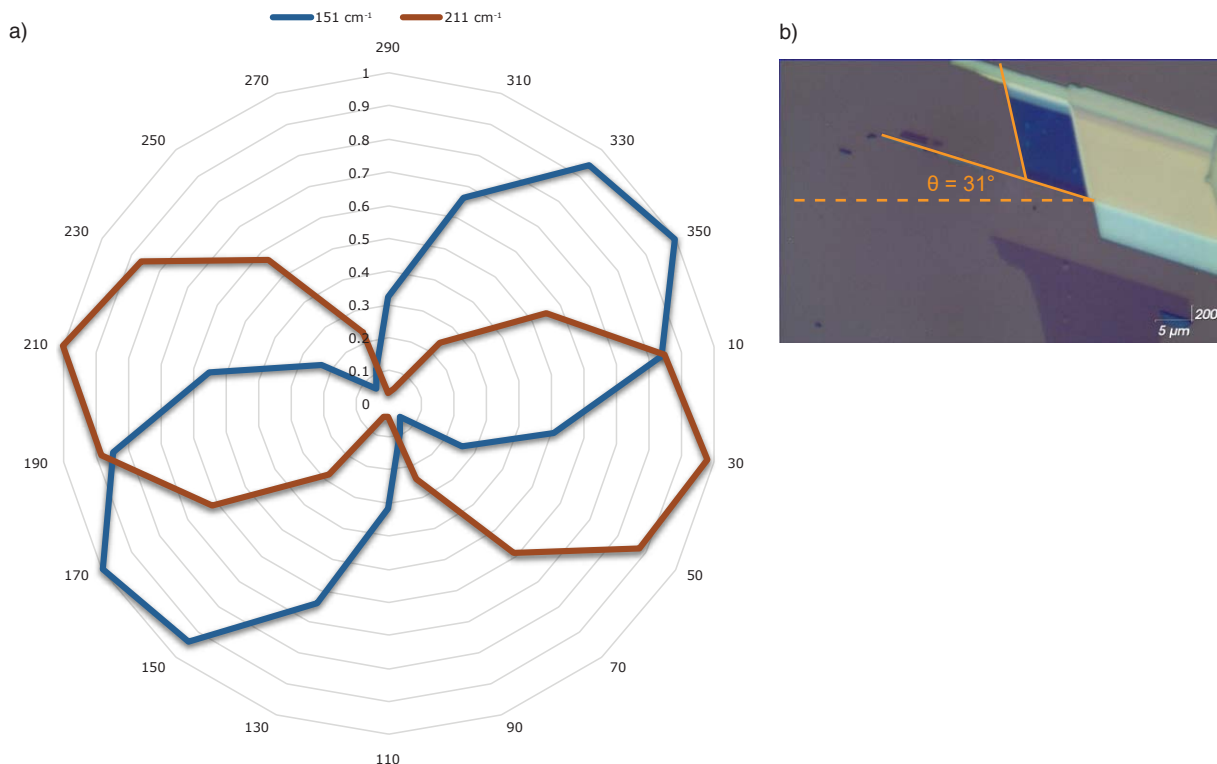


Figure 7a) Change in intensity of ReS<sub>2</sub> Raman modes with variation of incoming laser polarisation. b) optical image of measured flake. The angle of the b-axis is 31 degrees in good agreement with the polarisation data from the 211 cm<sup>-1</sup> Raman band.

## Conclusion

In this note, the fundamental theory of polarised Raman spectroscopy has been discussed. This technique has been demonstrated on gallium nitride thin films to determine the orientation of the crystallographic axis of the films, and allowed variations in directional strain to be probed. Analysis of the 2D material rhenium disulfide enables the Raman selection rules to be examined for a large number of Raman modes. Due to the unusual symmetry of rhenium disulfide it was also possible to use polarised Raman measurements to determine whether the sample was upside-down or upside-up on the substrate. These measurements highlight just a few ways in which polarised Raman measurements can be used to better characterise samples. This technique is applicable to a wide range of application areas including biology, polymer science, pharmaceutical, material science and nanotechnology.

In addition, it has been demonstrated that the inVia confocal Raman microscope is an ideal tool for polarisation studies thanks to:

- The comprehensive polarisation options available, allowing both manual and automated polarisation experiments to be conducted in a range of geometries
- Its high sensitivity allowing weak and partially extinguished modes to be measured
- The low depolarisation ratios that can be achieved

## Acknowledgements

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## References

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