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TM001 - Introduction to Raman spectroscopy   WiRE™ 5

What is Raman scattering?

Raman scattering is named after the Indian scientist C.V. Raman who discovered the effect in 1928. If light of a single colour (wavelength) is shone on a material, most scatters off with no change in the colour of the light (Rayleigh scattered light). However a tiny fraction of the light (normally about 1 part in 10 million) is scattered with a slightly different colour (Raman scattered). This light changes colour because it exchanges energy with vibrations in the material. This makes Raman scattering an excellent tool for probing vibrations in materials.

The aim of Raman spectroscopy is to analyse the Raman scattered light and infer from it as much as possible about the chemistry and structure of the material.

More on Raman scattering

Scattering occurs when an electromagnetic wave encounters a molecule, or passes through a lattice. When light encounters a molecule, the vast majority of photons (>99.999%) are elastically scattered; this Rayleigh scattering has the same wavelength as the incident light. However, a small proportion (<0.001%) will undergo inelastic (or Raman) scattering where the scattered light undergoes a shift in energy; this shift is characteristic of the species present in the sample. This process is shown in in Figure 1.

Before Raman scattering   After Raman scattering
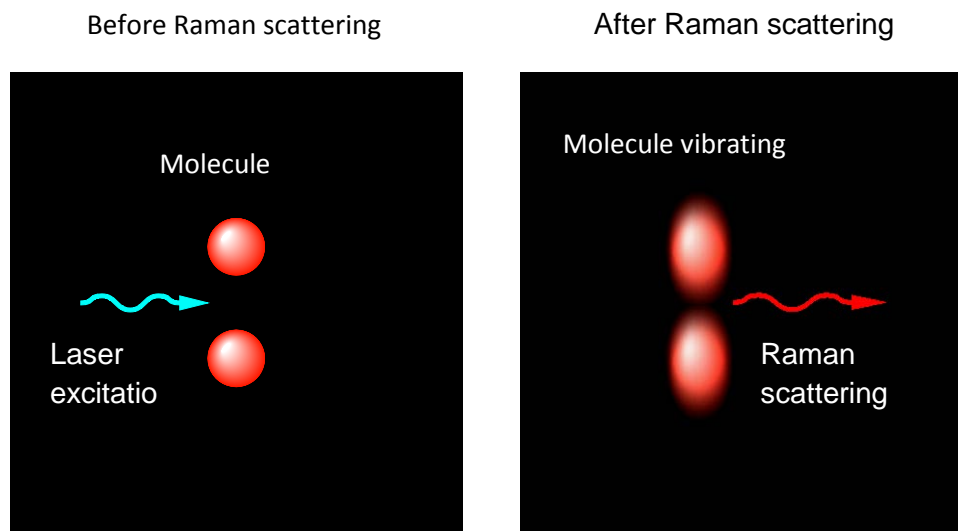

Fig. 1. Schematic diagram of the Raman effect

Figure 2 illustrates the transitions accompanying Rayleigh and Raman scattering. The electric field of the incident light distorts the molecule's electron cloud, causing it to undergo electronic transitions to a higher energy 'virtual state'; not a true quantum mechanical state of the molecule. Raman scattering results in the release of a scattered photon with different energy to the incident photon; the difference in energy is equal to the vibrational transition, ΔE. The relative intensity of stoeks ans anti-Stokes lines at room temperature is shown in Figure 3.

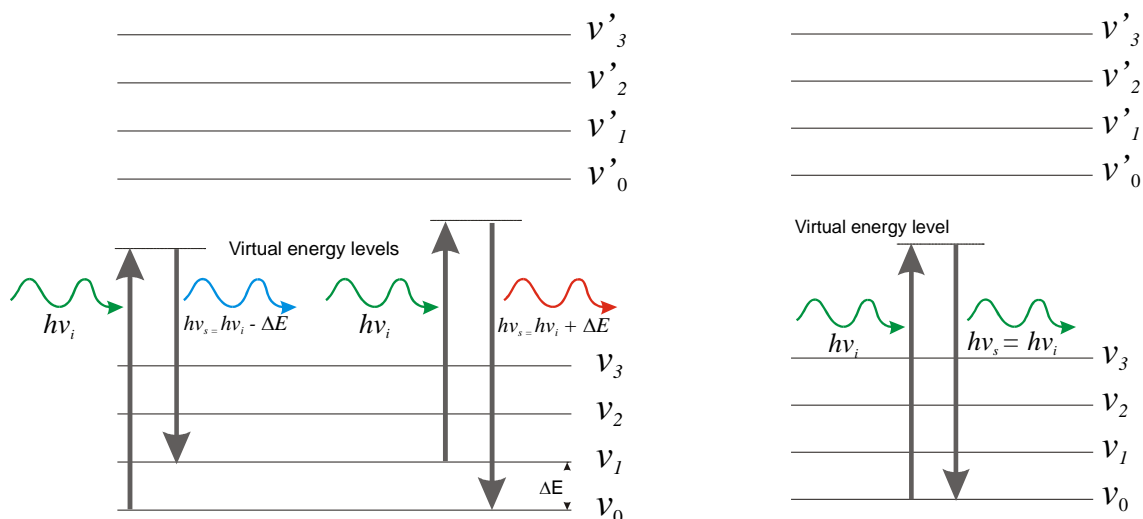**RENISHAW**
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Fig. 2. The electronic transitions accompanying Raman scattering (left), Rayleigh scattering (right)
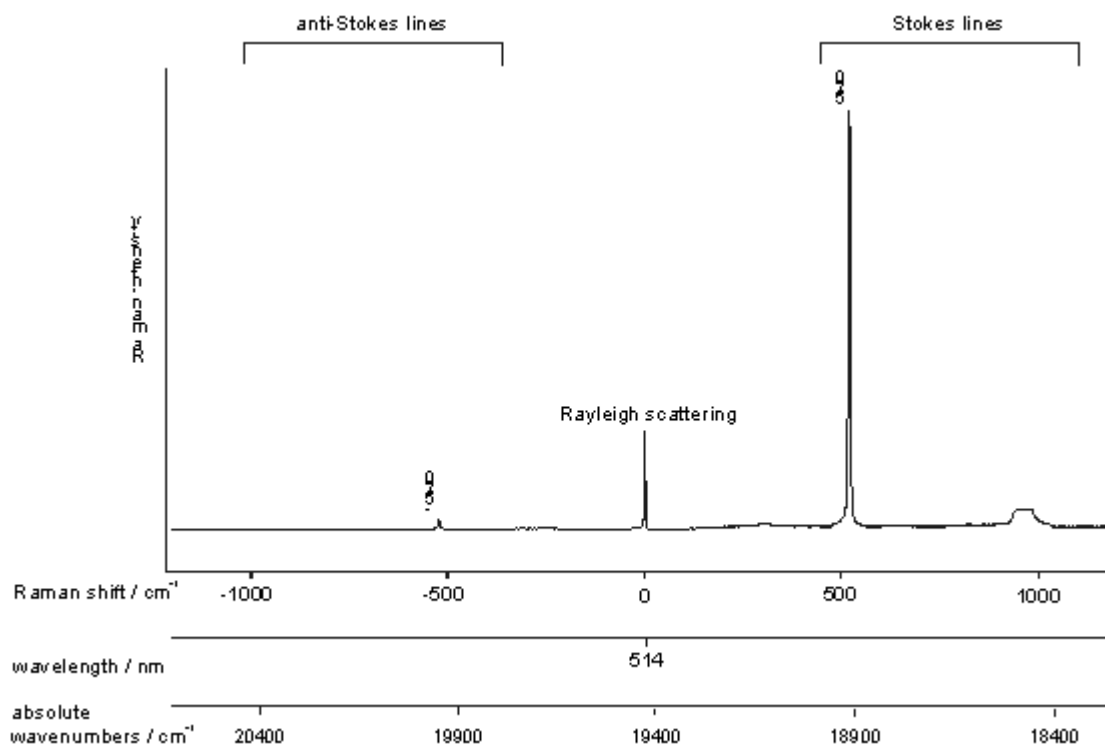

Fig. 3. Raman spectrum of silicon (514 nm excitation) showing the Rayleigh scattering at the laser wavelength and the Stokes and anti-Stokes line of the Raman scattering

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What does a Raman spectrum look like?

Figure 4 shows the Raman spectra of two carbon based species, diamond and polystyrene. In Raman spectroscopy we are interested in how much the scattered light differs from the incident light, so the spectrum is normally plotted against the difference between the two - the Raman shift.

Diamond has one main Raman band only because the tetrahedral lattice is symmetrical and all the carbon atoms and connecting bonds are equivalent.

Polystyrene has different functional groups consisting of differing atoms and bond strengths. Each Raman band represents either a discrete function group (e.g. C-H from benzyl group at ~3200 cm^{-1}) or a combining of small groups into a larger group (e.g. C_6H_5R breathing mode from benzyl group at ~1000 cm^{-1}).
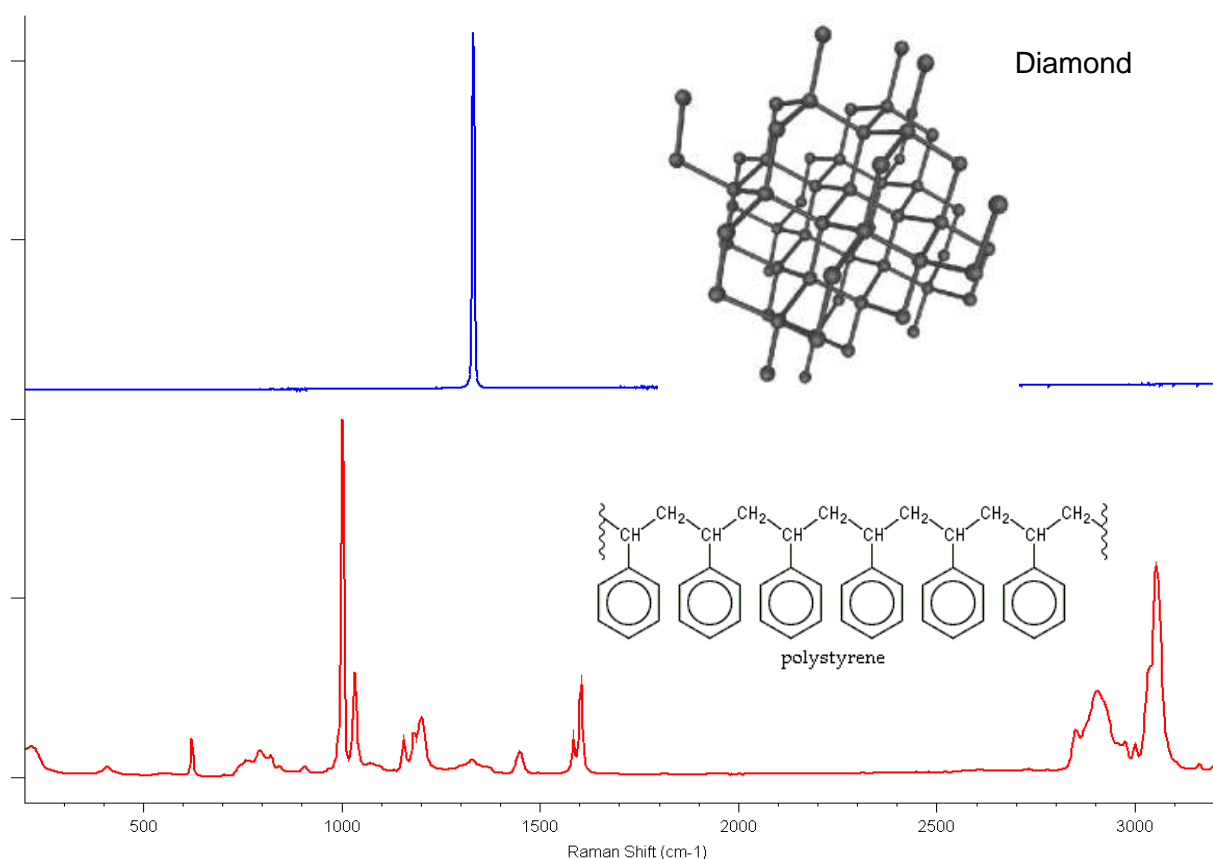
Fig. 4. Raman spectra of diamond and polystyrene

The bottom axis of the graph represents the energy of the Raman shift (measured in cm^{-1}) and may be plotted right-to-left or *vice versa*. A value of 0 cm^{-1} would indicate that no energy has been exchanged with the sample and the incident light is scattered with no change in wavenumber. Carbon-hydrogen bonds give rise to Raman bands around 3000 cm^{-1}, due to the small mass of hydrogen and resulting high frequency vibrations. Peaks at lower wavenumber relate to lower energy vibrations such as those of bonds to carbon or oxygen.

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What information can you get from Raman spectroscopy?

Raman bands can be analysed to obtain chemical and structural information for the material identification, investigation of material properties and spatial analysis. The table below illustrates the variety of results that can be obtained from point and mapping measurements.
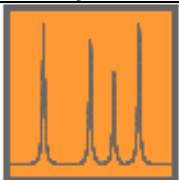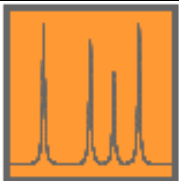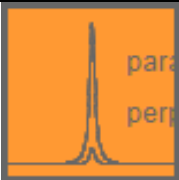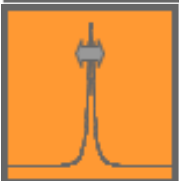
	Band parameter		**Information**
Univariate		Characteristic Raman frequencies	Identification (material composition)
		Compare characteristic Raman frequencies	Differentiation
		Intensity variation with changing polarisation	Crystallographic orientation
		Variation in absolute / relative intensity	Absolute / relative concentration
		Variation in Raman band width	Crystallinity; Temperature
		Variation in Raman band position	Stress state
Multiple spectra	Any of the above parameters applied to multiple spectra: • Univariate – based on raw data or curve fitting. • Multivariate – algorithm based *e.g.* DCLS, PCA, MCR-ALS or EmptyModelling™.		Any of the above information in conjunction with different dimensions such as time, temperature, distance, area, and volume, *e.g.* • Thickness (Intensity with depth – 1D) • Domain size and distribution (Intensity with area – 2D / 3D)

Table 1. Information obtainable from analysis of different Raman band parameters.

Raman spectroscopy obtains such information by probing the vibrational states of materials. Renishaw's inVia can also be used for photoluminescence (PL) measurements, which is a competing effect to Raman. PL is typically much stronger in intensity and is a function of the electronic states of the material. The PL effect can sometimes provide an unwanted broad background that can mask the Raman bands. However, PL measurements can also provide useful complementary information on material properties such as conjugation, structural vacancy, and atomic substitutions.

What does a micro-Raman instrument usually consist of?

It usually consists of:

- A monochromatic light source (normally a laser)
- A means of shining the light on the sample and collecting the scattered light (often this is a microscope)
- A means of filtering out all the light except for the tiny fraction that has been Raman scattered (often holographic 'notch' or dielectric 'edge' filters)
- A device (such as a diffraction grating) for splitting the Raman scattered light into component wavelengths, i.e. a spectrum.
- A light-sensitive device for detecting this light (normally a CCD camera)
- A computer to control the instrument and the motors and analyse and store the data

Figure 5 shows the layout of Renishaw's inVia Reflex Raman microscope, with all the key components highlighted.

Fig. 5. Renishaw's inVia Reflex Raman microscope

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