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M1 - Introduction to Raman spectroscopy   WiRE™ 2

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) exchanges energy with vibrations in the material and is scattered with a slightly different colour (Raman scattered) because of its changed energy.

The general 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.
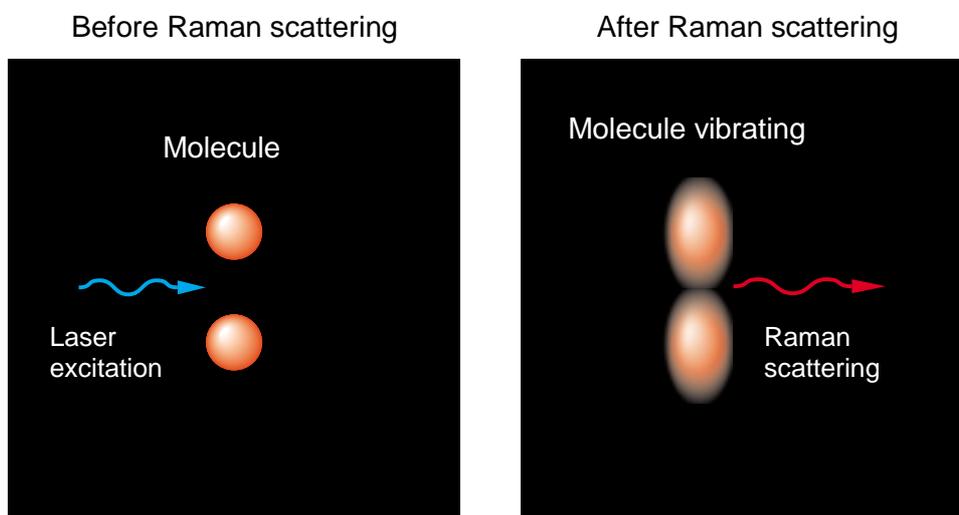

Fig. 1. Schematic diagram of the Raman effect

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. These processes are detailed diagrammatically in Figure 1.1.

The Raman effect is complementary to infrared spectroscopy. Molecular vibrations are sampled in both techniques, however different fundamental selection rules regarding the activity of specific vibrations results in the spectra of each giving different information. More specifically infrared spectroscopy requires a dipole moment change through the vibration, whilst Raman requires a change in polarisability. That is, the distortion of the molecule's electron cloud during the vibration must cause the molecule to interact differently with the electric field of the incoming photon.. The consequences of these rules can be considered by comparing the activity of C=C and C=O bonds as an example. In IR spectroscopy the CO vibration will appear stronger, as there is a large dipole moment change during the vibration. C=C will not be seen in the IR spectrum, as there is no dipole moment . Raman spectroscopy will exhibit a much stronger vibrational mode for CC as the change

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in polarisability of this group is greater than that of CO. Raman allows additional spectral information to be acquired, significantly aiding chemical analysis and identification.

Figure 1.2 below 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 being equal to the vibrational transition, ΔE.
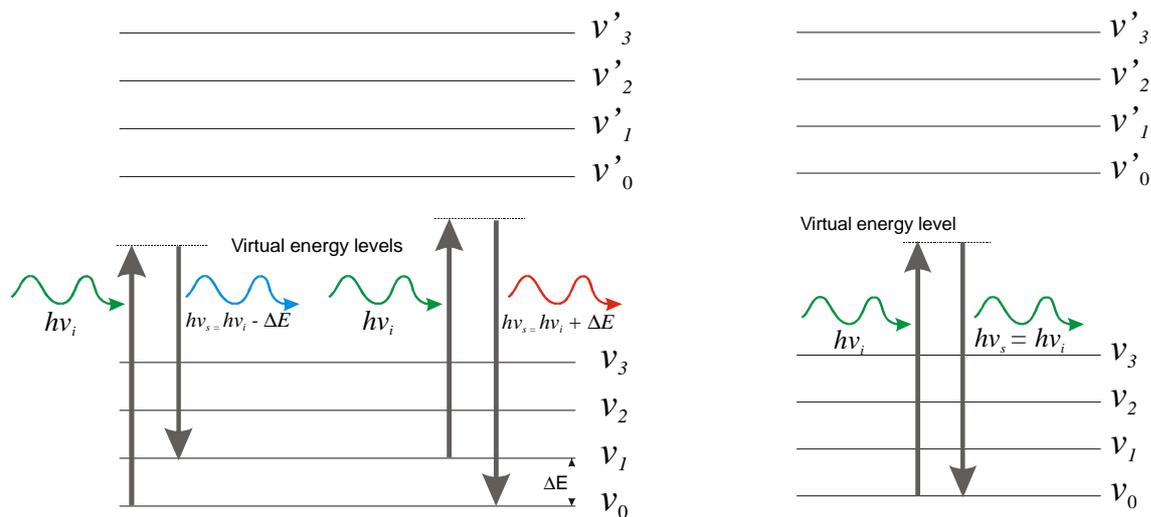
Fig. 2. The electronic transitions accompanying Raman scattering (left), Rayleigh scattering (right)
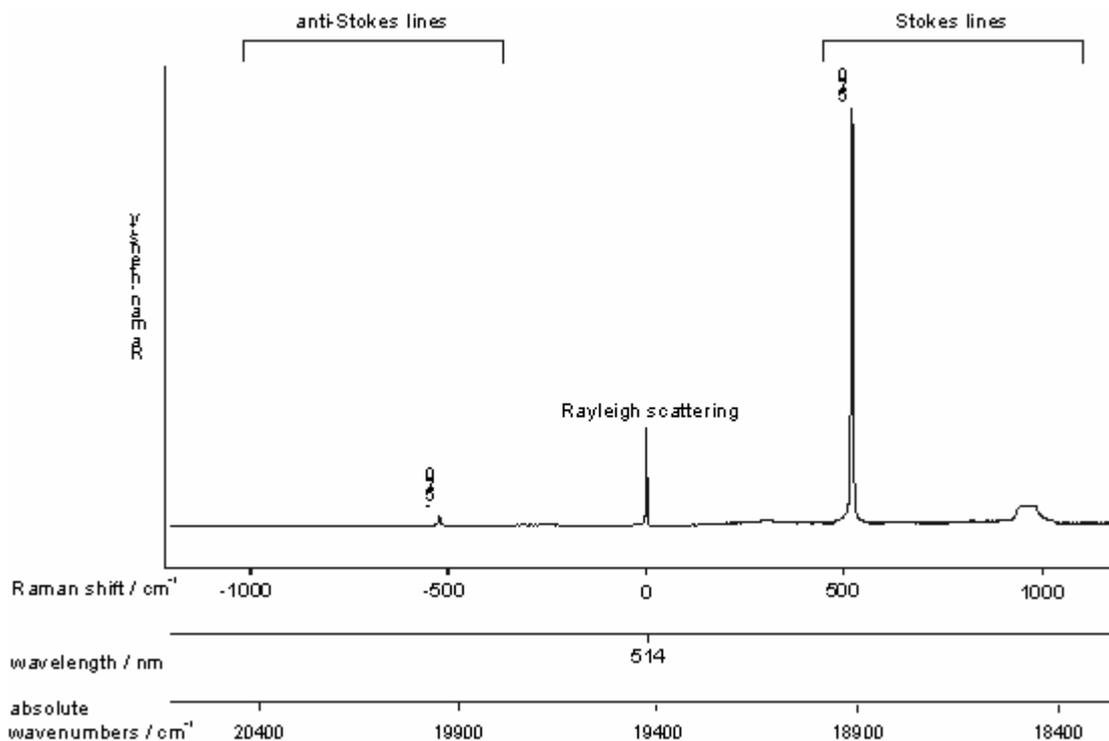
Fig.3. Raman spectrum of silicon (514 nm excitation) showing the Rayleigh scattering at the laser wavelength and the Stokes and anti-Stokes line of the Raman scattering

2

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What does a Raman spectrum look like?

Figure 1.4 shows the Raman spectra of two drugs, amphetamine and methamphetamine. 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.
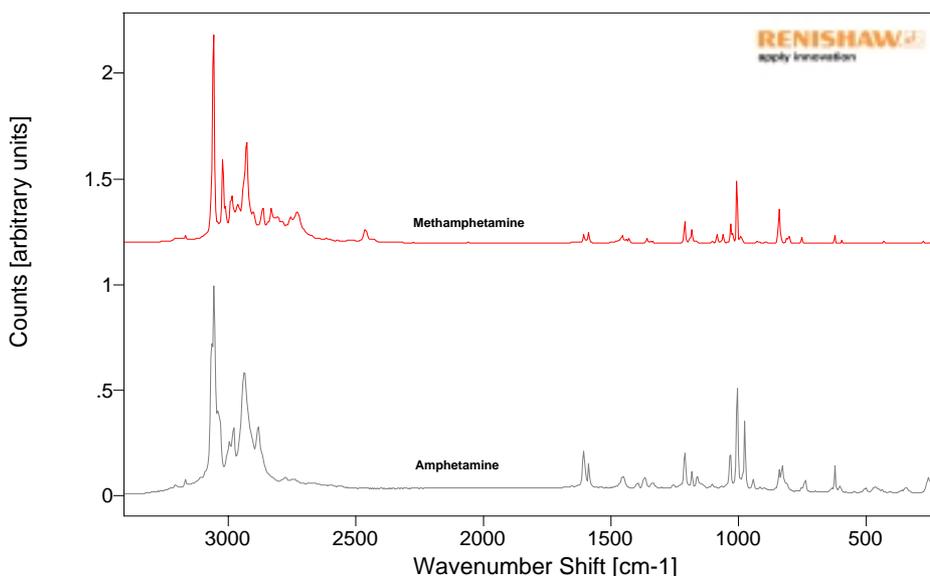

Fig. 4. Raman spectra of amphetamine and methamphetamine

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.

Amphetamine and methamphetamine are very similar molecules, and because of this their Raman spectra are similar. However, if you carefully compare the two spectra you will see differences.

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

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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

Who uses Raman spectroscopy?
The advent of high power, stable lasers saw a renaissance of Raman spectroscopy in the 1970's These days it is hard to think of an area where the technique is **not** used. Its ability rapidly and non-destructively to analyse materials has seen its success in areas such as semi-conductor research, thin film technology, polymer studies, biomedical applications, pharmaceutical chemistry and process lines.