Understanding Raman Spectroscopy
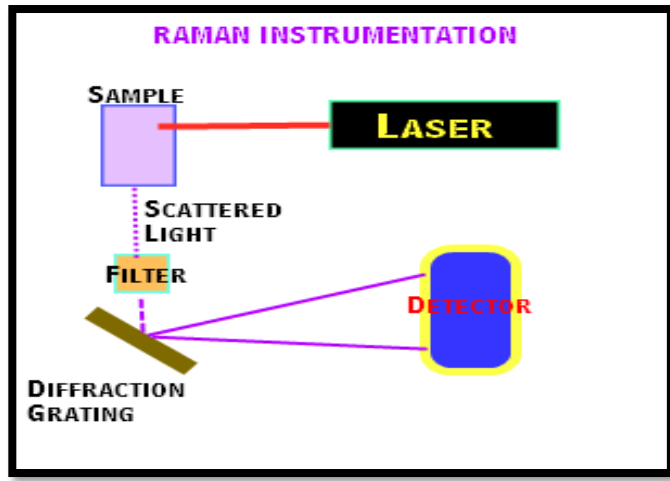## Principles and Theory

Basic Raman Instrumentation

Figure 1

Raman Theory

Raman scattering is a spectroscopic technique that is complementary to infrared absorption spectroscopy. The technique involves shining a monochromatic light source (i.e. laser) on a sample and detecting the scattered light. Above is a simple schematic of a Raman spectrometer (Figure1).

The majority of the scattered light will pass through the sample without interaction. The result is the detector will receive energy that is of the same frequency as the excitation source; this is known as Rayleigh or elastic scattering. A very small amount of the scattered light (~ 1 in 10^7) is shifted in energy from the laser frequency. This shift is known as a Raman or Stokes shift. At room temperature, the anti-Stokes-shifted Raman energy is weaker than the Stokes-shifted energy-thus they are usually ignored and removed by filters. This due to interactions between the incident electromagnetic waves and the vibrational energy levels of the molecules in the sample. In other words, the interaction can be viewed as a perturbation of the molecule's electric field. Viewed at the molecular energy level (Figure 2), the Rayleigh scattering (no interaction) and the Stokes shift (interaction) are energy difference between the incident and scattered photons is represented by the arrows of different lengths.
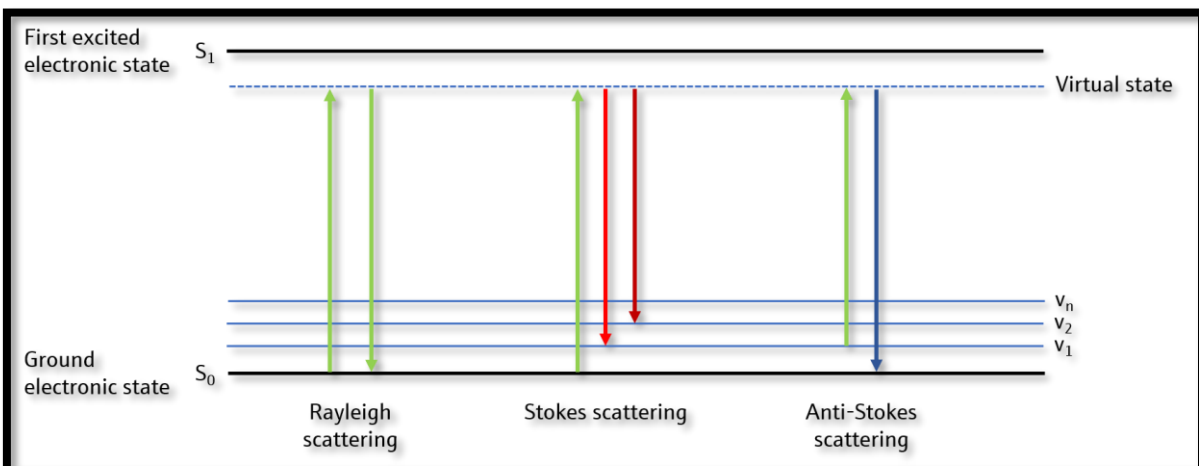

Figure 2

Vibrational Raman spectroscopy is not limited to intramolecular vibrations. Crystal lattice vibrations and other motions of extended solids are Raman-active. Their spectra are important in such fields as geochemistry and mineralogy. For Raman selection rules it can simply explained by electromagnetic field interactions within the molecule's bonds. The dipole moment, P. induced in a molecule by an external electric field, E, is proportional to the field as shown in Equation 1.

$$P=\alpha E$$

Equation 1

The proportionality constant α is the polarizability of the molecule. The polarizability measures the ease with which the electron cloud around a molecule can be distorted. The induced dipole emits or scatters light at the optical frequency of the incident light wave. The change in the polarizability within the bond gives rise to Raman scattering. Scattering intensity is proportional to the square of the induced dipole moment.

If a vibration does not greatly change the polarizability, then the polarizability derivative will be near zero, and the intensity of the Raman band will be low. The vibrations of a highly polar moiety, such as the O-H bond, are usually weak. An external electric field cannot induce a large change in the dipole moment and stretching or bending the bond does not change, giving weak or not Raman signal. Typical strong Raman scatterers are moieties with distributed electron clouds, such as carbon-carbon double bonds. The pi-electron cloud of the double bond is easily distorted in an external electric field. Bending or stretching the bond changes the distribution of electron density substantially and causes a large change in induced dipole moment.
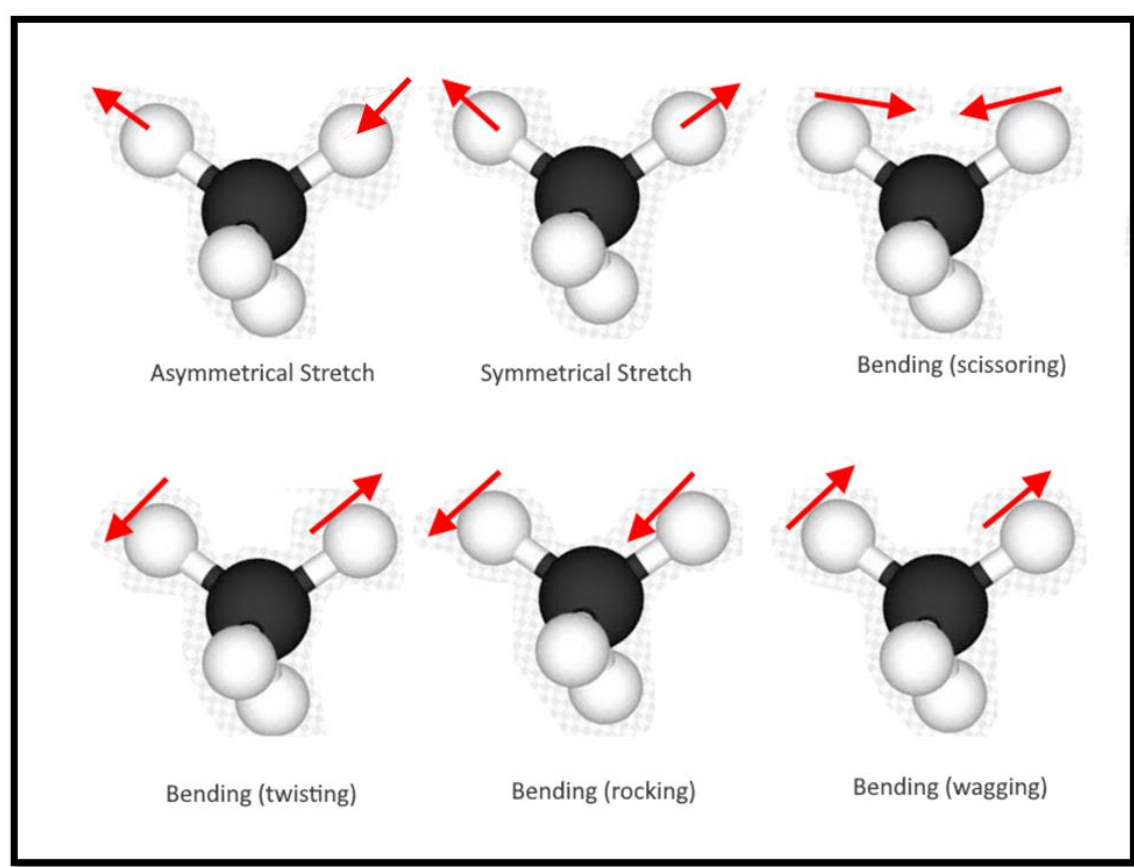

Figure 3

For polarizable molecules, the incident photon energy can excite vibrational modes of the molecules, yielding scattered photons which are diminished in energy by the amount of the vibrational transition energies giving rise to the peaks in a Raman spectrum. The number of peaks is related to the number of degrees of freedom a molecule contains (Figure 3).

To be Raman active a molecule must have a change in its polarizability. Polarizability is a difficult concept to visualize. The easiest way to describe it is as the relative tendency of the electron cloud to be distorted from its normal shape.
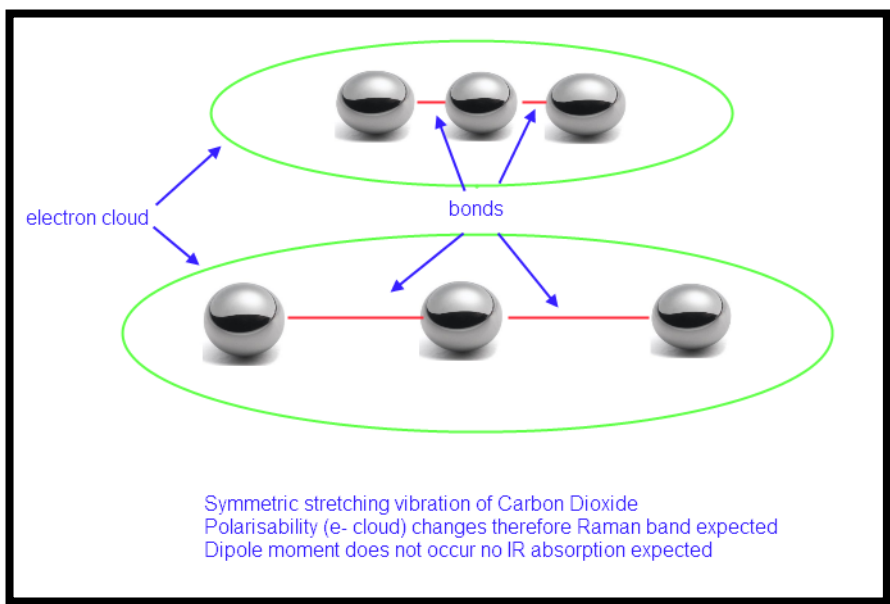
Visual Explanation:

electron cloud
bonds

Symmetric stretching vibration of Carbon Dioxide
Polarisability (e- cloud) changes therefore Raman band expected
Dipole moment does not occur no IR absorption expected

Figure 4

electron cloud
bonds

Asymmetric stretching vibration of Carbon Dioxide
Polarisability (e-cloud) does not change during vibration no Raman
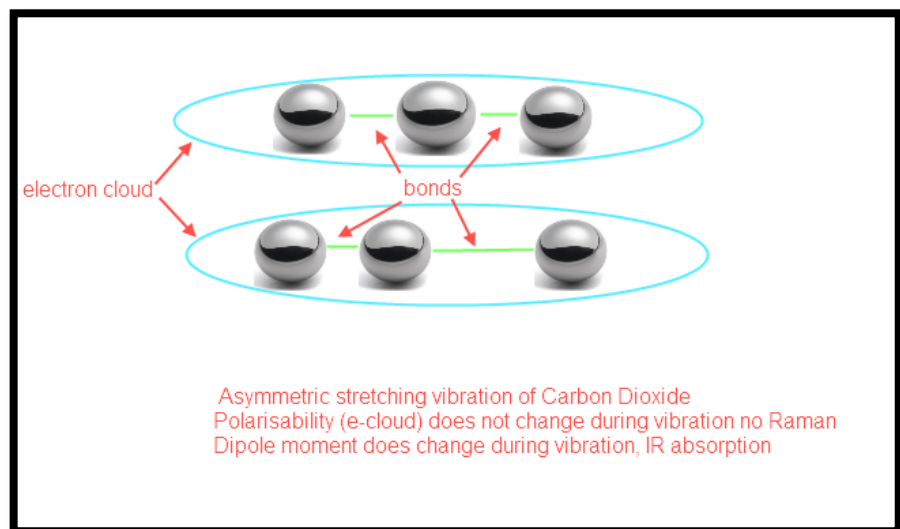Dipole moment does change during vibration, IR absorption

Figure 5

A Raman spectrum (Figure 6) is defined by plotting the intensity of this "shifted" light versus frequency results in a Raman spectrum of the sample. Generally, Raman spectra are plotted with respect to the laser frequency such that the Rayleigh band lies at 0 cm^{-1}. On this scale, the band positions will lie at frequencies that correspond to the energy levels of different functional group vibrations. The Raman spectrum can thus be interpreted similar to the infrared absorption spectrum.
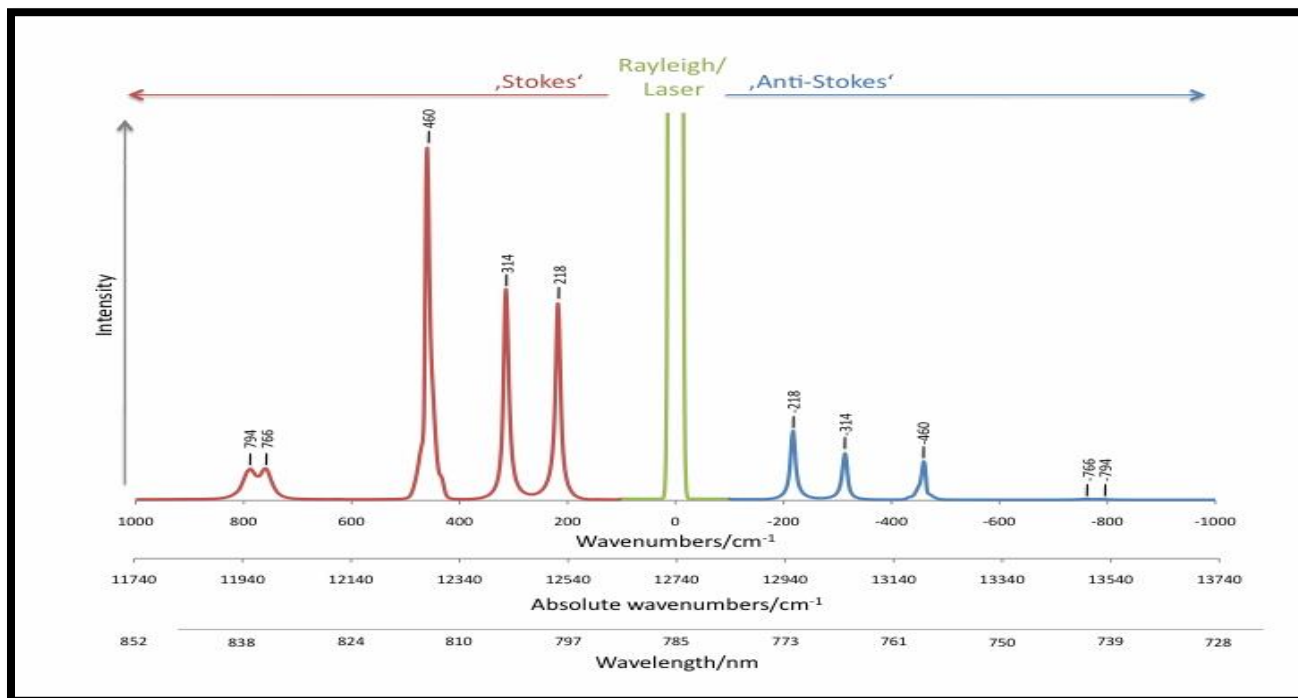
Figure 6

Advantages of Raman spectroscopy

1. Sample Preparation; Little to no sample preparation is required is most cases. The sample can be placed into the holder position and a spectrum can be retrieved.
2. Water as a solvent; Water is a weak scatterer; thus, it can be used as a solvent for a 'difficult sample' - no special accessories are required for measuring in a aqueous solutions.
3. No need for nitrogen purging of the optical bench; Water and carbon dioxide vapors are very weak scattering species.
4. Cheap and sample holders; Inexpensive glass sample holders are ideal in most cases.
5. Cleaner Spectra; Raman spectra are "cleaner" than mid-IR spectra - Raman bands are narrower, and overtone and combination bands are generally weak.
6. Wide range of molecules to investigate; The standard spectral range reaches well below 400 cm^{-1}, making the technique ideal for both organic and inorganic species.
7. Investigate weak IR bands; Raman spectroscopy can be used to measure bands of symmetric linkages which are weak in an infrared spectrum such as C=C, C-S and S-S.

Disadvantages of Raman Spectroscopy

1. Due to the low Raman intensities the detector sensitivity is paramount
2. Instrumentation is more expensive than typical mid-range IR
3. Laser can destroy sections of the sample if the power setting is too high
4. Fluorescence caused by the laser is a major concern with some samples

Abbreviated Raman Bond Correlation Chart

Wavenumber Range (cm–1)	Group	Intensity
100–210	Lattice vibrations	Strong
150–430	Xmetal-O	Strong
250–400	C-C aliphatic chain	Strong
425–550	S-S	Strong
460–550	Si-O-Si	Strong
490–660	C-I	Strong
505–700	C-Br	Strong
550–790	C-Cl	Strong
580–680	C=S	Strong
630–1250	C-C aliphatic chains	Moderate
670–780	C-S	Strong
720–800	C-F	Strong
990–1100	Aromatic rings	Strong
1020–1225	C=S	Strong
1050–1210	Sulfonamide	Moderate
1315–1435	Carboxylate salt	Moderate
1320–1350	Nitro	Very strong
1365–1450	Aromatic azo	Very strong
1450–1505	Aromatic ring	Moderate
1550–1610	Aromatic/hetero ring	Strong
1550–1700	Amide	Strong
1600–1710	Ketone	Moderate
1610–1740	Carboxylic acid	Moderate
1625–1680	C=C	Very strong
1630–1665	C=N	Very strong
1690–1720	Urethane	Moderate
1710–1725	Aldehyde	Moderate
1710–1745	Ester	Moderate
1730–1750	Aliphatic ester	Moderate
1735–1790	Lactone	Moderate
1740–1830	Anhydride	Moderate
1745–1780	Acid chloride	Moderate
2020–2100	Isothiocyanate	Moderate
2070–2250	Alkyne	Strong
2220–2260	Nitrile	Moderate
2530–2610	Thiol	Strong
2770–2830	CH2	Strong
2810–2960	C-CH3	Strong
2870–3100	Aromatic C-H	Strong
2900–2940	CH2	Strong
2980–3020	CH=CH	Strong
3010–3080	=CH2	Strong
3150–3480	Amide	Moderate
3150–3480	Amine	Moderate

Contact the TRACES Manager for further details.