Raman Spectroscopy

Rotational and vibrational frequencies of a molecule can be conveniently studied by Raman spectroscopy. Raman effect was predicted by Smekel in 1923 and discovered by C.V.Raman in 1928. Raman effect may be defined as a phenomenon due to which the scattering of light has a slightly different frequency from that of incident light due to the change in the atomic oscillations within the molecule. Raman spectroscopic measurements are usually carried out in the visible region of electromagnetic radiation. In this technique sample preparation requires careful filtration to remove all traces of suspended matter.

Theory of Raman spectroscopy (Raman effect):

When a beam of monochromatic radiation passes through a transparent medium, the photons of energy $h\upsilon$ collide with the molecules of the medium. Most of the collisions are elastic and the scattered radiations have the same energy as the incident photons are called Raleigh scattering. This can be explained when a ball bearing striking a rigid table, the ball bearing bounces off the table without any loss of energy. However a small fraction of collisions it may happen that energy is exchanged between the photons and molecules during the collision. Such collisions are called inelastic. If the collisions are inelastic then the deflected photons have either higher or lower energy than the incident photons are called Raman scattering. In Raman scattering case, the energy is either given or taken away from the molecule as a result of these collisions. The fundamental equation for the energy conservation is,

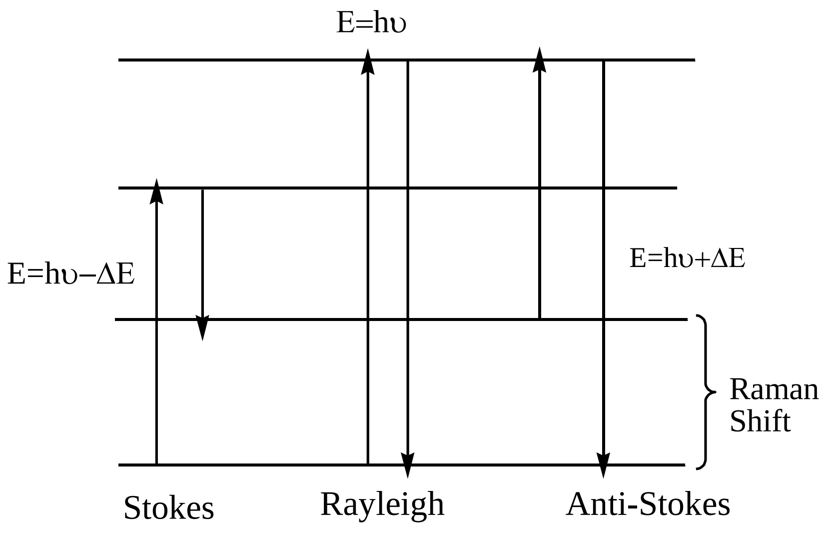
$$E-E' = \upsilon - \upsilon'/h$$

Where υ and υ' are the frequencies of the incident photon and the scattered radiation respectively. E represents the energy before the collision and E' represents the energy after collision. The above eq. can also be written as,

$$\Delta E/h = \upsilon - \upsilon'$$

When a photon is absorbed by a molecule in the ground vibrational state, the absorbed photon raises the energy of the molecule to a higher vibrational energy level. Since the excited energy level is unstable for the molecule, there is two processes can occur. Either the excited molecule may return to its ground state and emits the radiation with the same energy and frequency as the exciting radiation. This is called Rayleigh scattering, Or some of the excited molecules may return not to a ground state but to different excited vibrational state and emits radiation which are lower in the frequency than the incident radiation. These are called Stokes lines. It can be explained when a ball bearing striking a drum, if the surface of the drum is stationary when the ball bearing hits, it will start oscillating at its own frequency and the ball bearing will be reflected with less energy. The amount of energy lost by the bearing equals to the energy taken up by the oscillation of the drum.

In some other cases, if the molecule already in the first excited state, the photon absorbed by such a molecule raises to some high unstable energy state. This molecule then returns to the ground vibrational state and emits a radiation which is higher in frequency than the incident radiation. These are called Anti-Stokes lines. It can be explained, if the drum is already oscillating when the ball bearing hits the drum, the drum will give energy to the ball bearing and the ball bearing will bounce back with increased energy. The probability of a molecule to be in the first excited state is always lower as compared to be in the ground state. Thus the intensity of the Stokes lines is always greater than the Anti-Stokes lines.



Raman Spectra and Infra Red Spectra-Similarities and differences

Similarities:

1. Both these methods are used for determining the internal vibrations of molecules.
2. Both these methods applicable to the analysis of covalently bonded molecules rather than to ionic compounds.
3. Both the methods depend on the vibrations of a molecule.

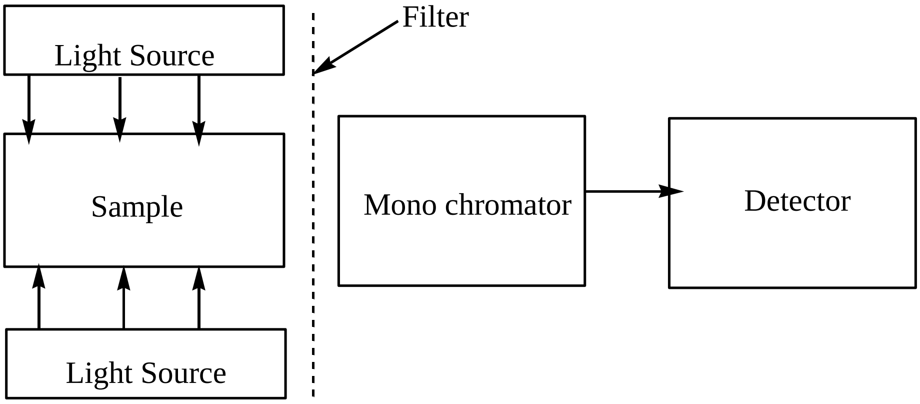
Differences:

S.No.	Raman Spectra	Infrared Spectra
1	It is due to the scattering of light by the vibrating molecules.	It is due to the absorption of light by vibrating molecules.
2	Polarizability of the molecule will decide whether the Raman spectra will be obtained or not.	The presence of a permanent dipole moment in a molecule will decide the IR spectra.
3	Optical systems are made of glass or quartz.	Optical systems are made up of crystals such as NaBr, CaF_2…
4	In Raman spectroscopy vibrational frequencies of large molecules can be measured.	In IR spectroscopy vibartional frequencies of very large molecules can’t be measured.

5	Concentrated solutions must be used to increase the intensity of weaker lines.	Generally dilute solutions are preferred.
6	Water can be used as solvent.	Water can’t be used as solvent.
7	Homonuclear diatomic molecules are often found to be active.	These are not found to be active.
8	Sometimes photochemical reactions take place in the regions of Raman lines and create problems.	Photochemical reactions do not take place.
9	Substances under investigations must be pure and colourless.	This condition is not severe.
10	This method is very accurate, but is not very sensitive.	This method is accurate and sensitive.

Instrumentation of Raman spectroscopy:

In Raman spectrometer the sample is irradiated with monochromatic light and the scattered light is observed at right angles to the incident radiation. Raman spectrometer consists of a light source, sample holder, a monochromator and detector. It can be shown as follows….



1. Source of Light:

Since the intensities of scattered radiation are very weak i.e. about 0.01% of the incident radiation, an extremely intense source of radiation is needed. Usually Mercury lamps are surrounded to the sample tube. The blue line at $4358A^0$ in the mercury arc spectrum is most useful for the scattering experiment. Now a days lasers are used as source of radiation due to their high intensity. One of the advantages of laser source is, no filtering of radiation is necessary because from these sources the energy output is in the form of monochromatic narrow parallel beam. The resolution is better than that of mercury excited line because the liquid of the laser line is smaller. Ar-Kr mixed gas laser are preferentially used with argon line at $4880A^0$ and krypton lines at 5682 and $6471A^0$.

2. Sample holder:

For the study of Raman effect the type of sample holder to be used depends upon the intensity of source, the nature and availability of the sample. The sample usually liquid is taken in a sample tube with an optical window at the end. Water is used as solvent for Raman spectra of inorganic materials. Since both the incident and scattered radiation are at ultra-violet or visible frequencies, the sample cells made up of glass or quartz can be used. When laser beam is used as source, it is simply focused into a capillary tube containing the liquid or powdered solid sample.

3. Filter:

Liquid filters are placed between the source and the sample tube. Different filters are used for different excitation radiation. For example, for $4538A^0$ excitation a saturated solution of $NaNO_2$ is used to remove the ultraviolet lines. The functions of filters are,

1. To isolate a single exciting line.
2. To remove high energy radiation, that may cause fluorescence.

3. Monochromators:

In most Raman spectrometers diffraction grating is used as dispersing element due to their high dispersive power. The gratings made of glass, quartz or plastic are used.

4. Detectors:

In Raman spectrometers two types of detectors are used.

They are 1.Photographic emulsions
2. Photoelectric transducers.

Photographic Detectors:

One of the simple detectors is photographic plate. The scattered light from the glass window of the sample tube is passed through a prism or grating and then focused on a photographic plate. Photographic materials consist of light-sensitive emulsions coated on a glass plate or plastic film. The emulsion contains light sensitive crystals of silver halide suspended in gelatin. On exposure the silver halide crystals that receive radiation form a latent image. On chemical treatment the exposed silver halide crystals converts into a black deposit of silver at the site of latent image. After development the emulsion is fixed in a solution that dissolves the unexposed silver halides. Finally the photographic material is thoroughly washed to remove the chemicals used in the development and fixing.

Devices known as microdensitometers are used to obtain the optical density required for quantitative analysis. In quantitative analysis the ratio of powers of the analyte line to the internal standard line is plotted against the concentration.

Photoelectric Detectors:

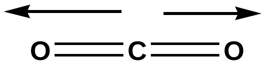
The Photomultiplier tube and Photodiode are exclusively used recently in Raman spectroscopy. PMT is a combination of photoemissive cathode and an internal electron multiplying chain of dynodes. The scattered radiation is transmitted through the PMT envelope and falls on the Photocathode. A photoelectron released by photo cathode and is attracted to the first dynode, which is coated with photoemissive material like BeO, GaP or Cs and gains energy and by its impact, releases several secondary electrons. These are attracted to the next dynode and release several more electrons each. This process continues until the last dynode (Anode) receives avalanche (multiple) of electrons. The multiplied photo current is measured directly between the last dynode and anode. The response time is about 0.5nsec with GaP dynode surface. A potential difference of 75-100V maintains between adjacent dynodes.

Applications of Raman spectroscopy:

a. Applications in Inorganic chemistry:

i. Structure of CO_2: the mutual exclusion rule states that if a molecule has a centre of symmetry then any vibration that is inactive in IR will be active in the Raman and vice versa. For a symmetrical linear molecule, such as CO_2, three fundamental vibrations are expected. Out of these two are IR active and one is Raman active.

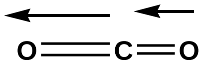
The modes of vibrations expected in CO_2 molecule are Symmetric stretching, asymmetric stretching and bending vibrations.



Symmetric stretching

Raman active

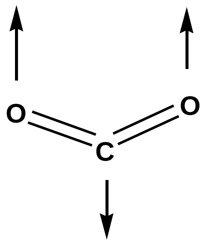
1389cm^{-1}



Asymmetric stretching

IR active

2350cm^{-1}



Bending

IR active

667cm^{-1}

The observation of two bands at 667cm^{-1} and 2350cm^{-1} in the infrared and one band at 1389cm^{-1} in the Raman spectrum confirms the symmetrical linear structure for CO_2.

Structure of N_2O:

If N_2O is also symmetrically linear it should show Raman spectrum similar to CO_2, but if it is unsymmetrical then symmetric stretching would become active both in IR and Raman. The spectrum of N_2O shows three bands at 2225, 1285, 589cm^{-1} in the IR and one in the Raman spectrum confirms the unsymmetrical structure for N_2O.

N_2O : 1. Symmetric stretching: 2225cm^{-1} : IR active
2. Asymmetric stretching: 1285cm^{-1} :IR & Raman active.
3. Bending : 589cm^{-1} : IR active.

Structure of CO:

It gives Raman line at 2155cm-1 which is similar to -C≡N of 2200cm-1. This shows like cyanides, carbon monoxide is having -C≡O. This is in agreement with the suggestion $\overset{\longleftarrow}{\text{that}}$ CO in C=O and the $\overset{\longrightarrow}{\text{isocyanide}}$ group is N=C.

Structure of H_2O:

The triatomic molecules having a linear bent structure should exhibit three Raman lines. In the Raman spectrum of water two frequencies have been recorded at 1665 and 3600cm^{-1}. In addition certain other bands also been observed which may be recognized to polymerized molecules such as $(H_2O)_2$ and $(H_2O)_3$.