Raman Spectroscopy

Raman spectroscopy is a useful method for studying the rotational and vibrational frequencies of molecules. The Raman effect was first predicted by Smekel in 1923 and later discovered by C.V. Raman in 1928. This effect is characterized by the scattering of light with a slightly different frequency from that of the incident light, resulting from changes in atomic oscillations within the molecule.

Typically, Raman spectroscopic measurements are conducted in the visible region of the electromagnetic spectrum. When using this technique, careful sample preparation is essential, often involving thorough filtration to eliminate all traces of suspended matter.

Theory of Raman spectroscopy (Raman effect):

When a beam of monochromatic radiation passes through a transparent medium, the photons with energy hν interact with the molecules of the medium. Most of these interactions are elastic, meaning that the scattered photons have the same energy as the incident photons, and this phenomenon is known as Rayleigh scattering. This can be explained by envisioning a scenario where a ball bearing strikes a rigid table, and the ball bearing bounces off the table without any loss of energy, similar to Rayleigh scattering.

However, in a small fraction of collisions, it is possible that energy is exchanged between the photons and molecules during the interaction. These collisions are termed inelastic. In the case of inelastic collisions, the scattered photons can have either higher or lower energy than the incident photons, and this is referred to as Raman scattering. In Raman scattering, energy is either transferred to or from the molecule as a result of these collisions.

The fundamental equation for energy conservation in the context of Raman scattering is not provided in your text. If you have a specific equation or aspect of Raman scattering you would like to know more about, please feel free to ask, and I'll be happy to provide further information.,

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

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,

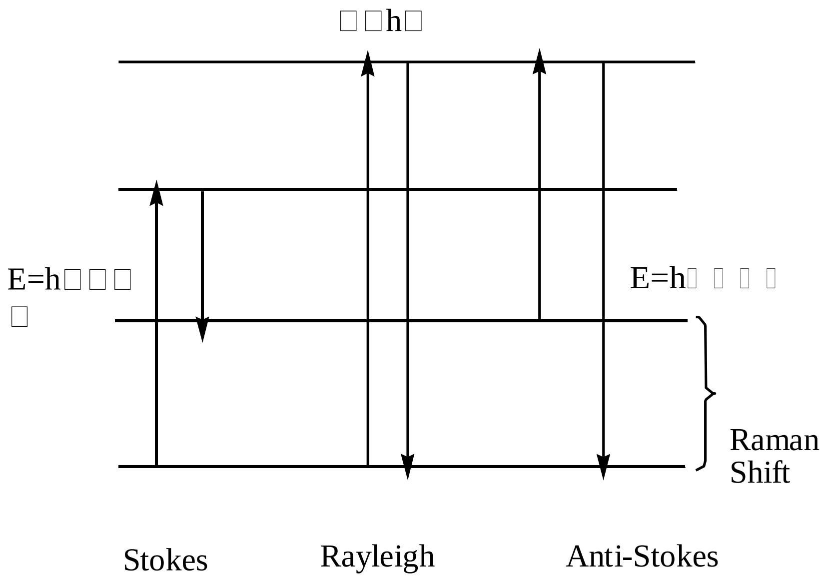
$$\Delta E/h = \upsilon-\upsilon'$$

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 cases, when a molecule is already in its first excited state, the absorption of a photon by that molecule can elevate it to a higher, unstable energy state. Subsequently, the molecule returns to its ground vibrational state and emits radiation that has a higher frequency than the incident radiation. These lines in the Raman spectrum are referred to as Anti-Stokes lines.

This phenomenon can be likened to a drum that is already vibrating when a ball bearing strikes it. In this scenario, the drum imparts energy to the ball bearing, causing it to bounce back with increased energy.

It's important to note that the probability of a molecule being in its first excited state is typically lower compared to it being in the ground state. Consequently, the intensity of the Stokes lines (associated with lower energy) is generally greater than that of the Anti-Stokes lines (associated with higher energy)in Raman spectroscopy.

Raman Spectroscopy



Raman Spectra and Infra Red Spectra-Similarities and differences

Similarities:

1. Both these methods are used for determining the internal vibrationsof 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.

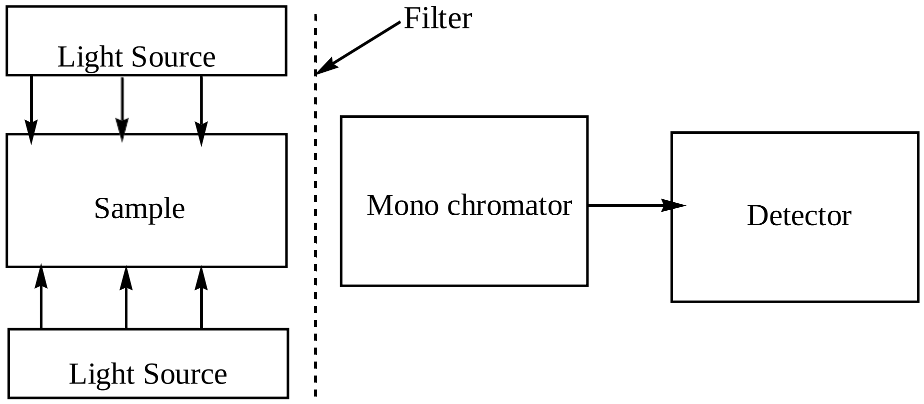
Differences:

S.No.	Raman Spectra	Infrared Spectra
1	Raman spectra result from the scattering of light by vibrating molecules.	IR spectra arise from the absorption of light by vibrating molecules.
2	The Raman spectra's obtainability hinges on the molecule's polarizability	The presence of a permanent dipole moment in a molecule determines the IR spectra.
3	Raman spectra optical systems are typically constructed using glass or quartz.	IR Optical systems are made up of crystals Ex. NaBr, CaF2…
4	These systems allow for the measurement of vibrational frequencies in large molecules..	In Raman spectra, it may not be possible to measure the vibrational frequencies of very large molecules.

5	In Raman spectra, concentrated solutions are often employed to enhance the intensity of weaker lines.	Generally dilute solutions are preferred in IR
6	Water can be used as solvent for spectra	Water can't be used as solvent.
7	Homo-nuclear diatomic molecules are frequently active in Raman spectra	These are not found to be active in IR
8	Photochemical reactions often occur in the regions of Raman lines, posing challenges	Photochemical reactions do nottake place.
9	Substances under investigation must be pure and colorless in Raman spectroscopy	This condition is not severe in IR
10	The Raman method is highly accurate but not very sensitive.	IR method is accurate and sensitive.

Instrumentation of Raman spectroscopy:

In a Raman spectrometer, a monochromatic light source irradiates the sample, and the scattered light is observed at right angles to the incident radiation. The components of a Raman spectrometer typically include a light source, a sample holder, a monochromator, and a 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 mixedgas laser are preferentially used with argon line at 4880A^0 and krypton lines at 5682 and 6471A^0.

2. Sample holder:

The choice of sample holder for studying the Raman effect is contingent upon several factors, including the intensity of the light source and the characteristics and accessibility of the sample. Typically, a liquid sample is placed within a sample tube that has an optical window at one end. In cases involving inorganic materials, water is frequently employed as a solvent for acquiring Raman spectra. Given that both the incident and scattered radiation fall within the ultraviolet or visible frequency range, sample cells crafted from glass or quartz are suitable. When a laser beam serves as the light source, it is simply focused into a capillary tube that contains either 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 NaNO2 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 straightforward detection methods involves the use of a photographic plate. In this setup, the scattered light emerging from the glass window of the sample tube undergoes a process wherein it's directed through a prism or grating and subsequently focused onto a photographic plate. These photographic materials typically consist of light-sensitive emulsions coated either on a glass plate or a plastic film. Within the emulsion, light-sensitive silver halide crystals are suspended in gelatin. During exposure, the silver halide crystals that receive radiation create a latent image. Through chemical treatment, these exposed silver halide crystals transform into a black deposit of silver at the exact location of the latent image. Following this, the emulsion goes through a fixing process in a solution that dissolves the unexposed silver halides. Finally, the photographic material undergoes thorough washing to eliminate the chemicals used during 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 againstthe concentration.

Photoelectric Detectors:

In recent times, Raman spectroscopy has primarily employed Photomultiplier Tubes (PMTs) and Photodiodes. A PMT is a specialized device that combines a photoemissive cathode with an internal electron multiplication chain of dynodes. Here's how it operates:

Scattered radiation is directed through the PMT's envelope and reaches the Photocathode. Upon reaching the Photocathode, a photoelectron is emitted and attracted to the first dynode, which is coated with a photoemissive material like BeO, GaP, or Cs. At this point, the photoelectron gains energy and, upon impact, releases multiple secondary electrons. These secondary electrons are then attracted to the next dynode and each release several more electrons through the same process. This cascade of electron multiplication continues until it reaches the final dynode, also known as the Anode, where an avalanche of electrons is collected.

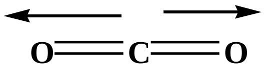
The amplified photo current is directly measured between the last dynode and the anode. The PMT boasts a rapid response time of approximately 0.5 nanoseconds when equipped with a GaP-coated dynode surface. To maintain this electron multiplication chain, a potential difference of 75-100 volts is maintained between adjacent dynodes.

Applications of Raman spectroscopy:

a. Applications in Inorganic chemistry:

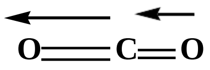
i. Structure of CO2: the mutual exclusion rule states that if a molecule has a centre of symmetry then any vibration that is inactive in IR will be active in the Raman and vice versa. For a symmetrical linear molecule, such as CO2, three fundamental vibrations are expected. Out of these two are IR active and one is Raman active.

The modes of vibrations expected in CO2 molecule are Symmetric stretching, asymmetric stretching and bending vibrations.


Symmetric stretching

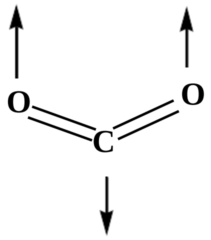
Raman active

1389cm^{-1}
1


Asymmetric stretching

IR active

2350cm^{-}


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 that CO in C=O and ← the 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 $(H_2O)_3$.