

# RAMAN SPECTROSCOPY

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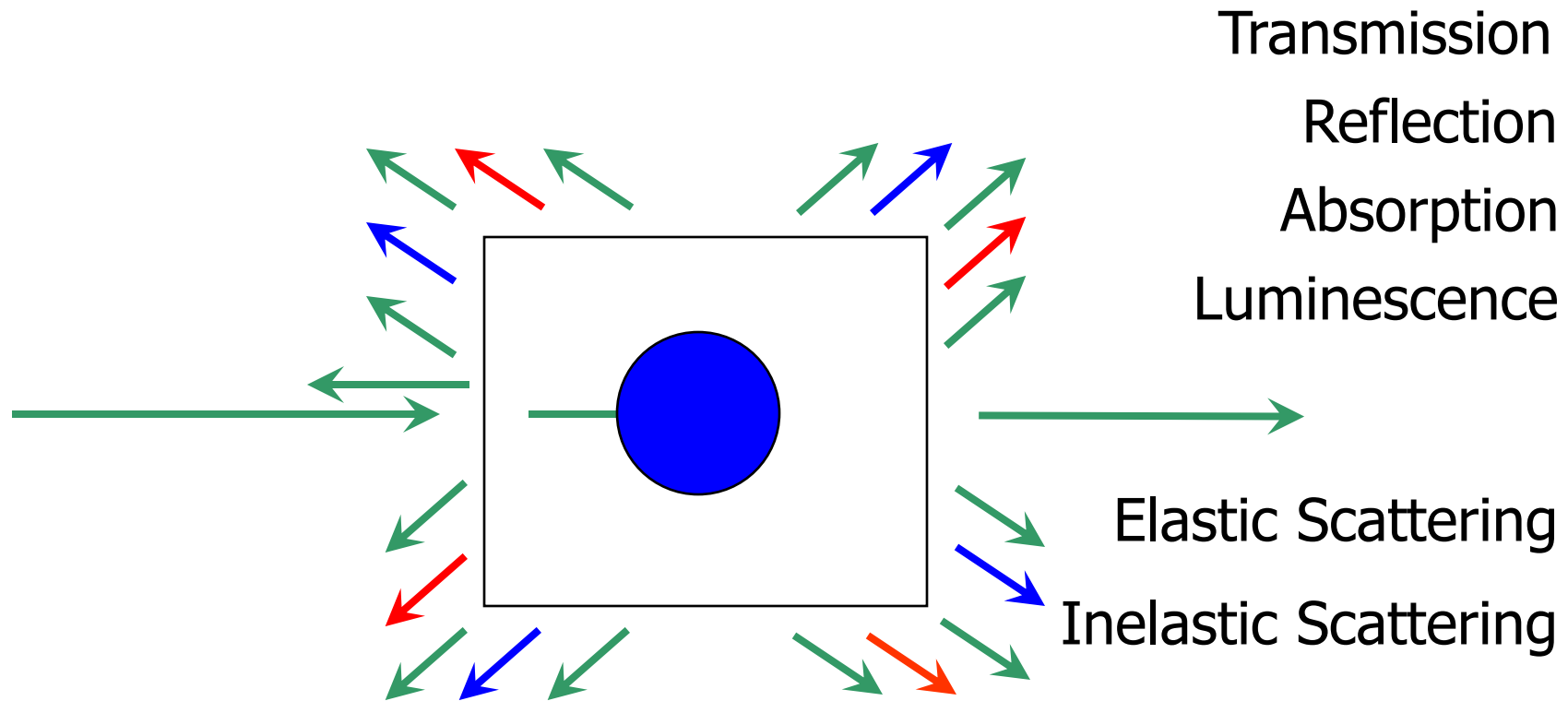


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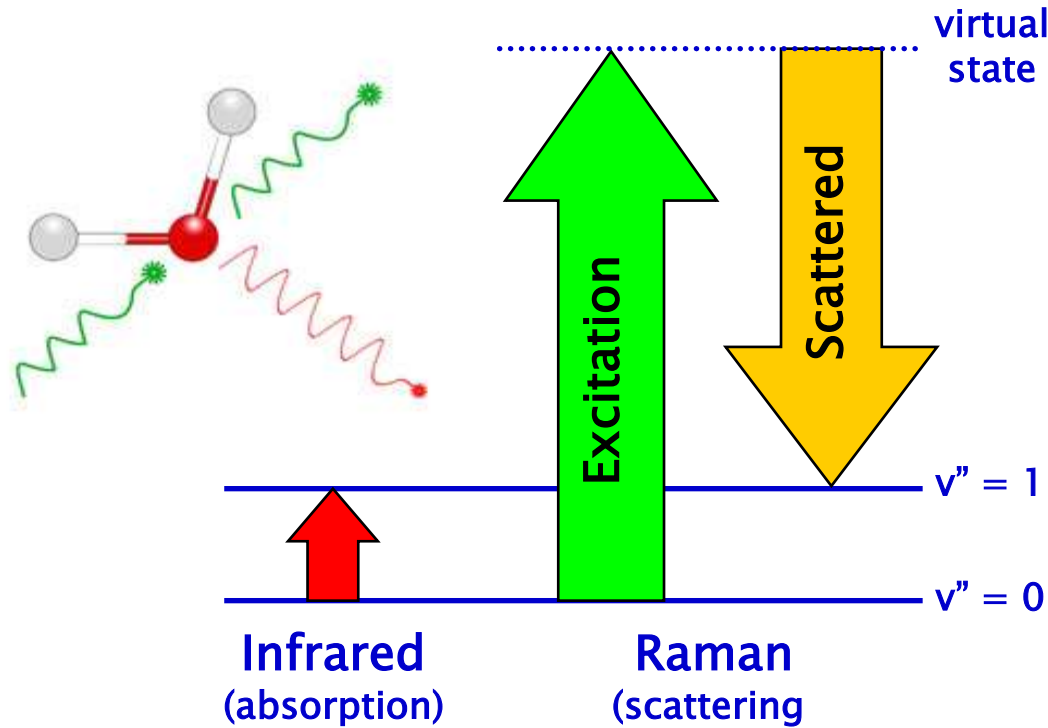


# What happens when light falls on a material?

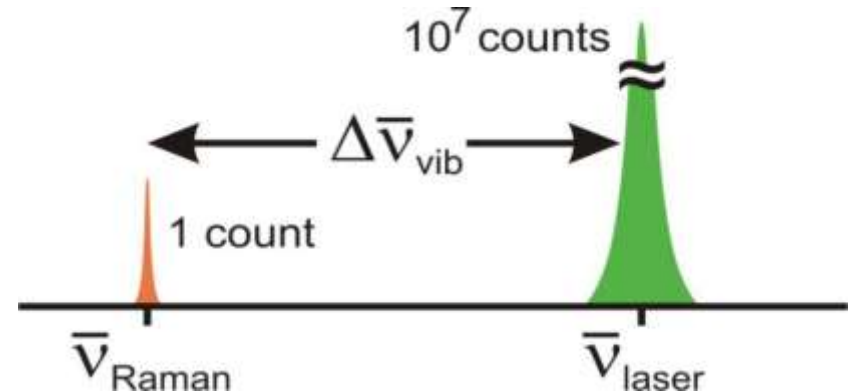


# Raman Spectroscopy

1 in  $10^7$  photons is scattered inelastically



Rotational Raman  
Vibrational Raman  
Electronic Raman



# Concept of normal modes in a molecule

- There are  $3N$  possible movements in a molecule made of  $N$  atoms, each of which moving in one of three directions,  $x$ ,  $y$  and  $z$ .
  - There are three translational movements: all atoms in the molecule moving in  $x$ ,  $y$  or  $z$  direction at the same time.
  - There are three rotational movements around  $x$ ,  $y$  or  $z$ -axis
    - Linear molecules are exceptions because two axes that are perpendicular to the molecular axis are identical.
  - The rest of movements are vibrational movements
    - For linear molecules,  $3N - 5$  movements
    - For non-linear molecules,  $3N - 6$  movements
  - All vibrational movements of the sample can be described as linear combinations of vibrational normal modes.

# INTRODUCTION

- **Raman spectroscopy** is the measurement of the wavelength and intensity of inelastically scattered light from molecules. The **Raman** scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations.
- Raman spectroscopy is used to determine the molecular motions, especially the vibrational one.

# PRINCIPLE

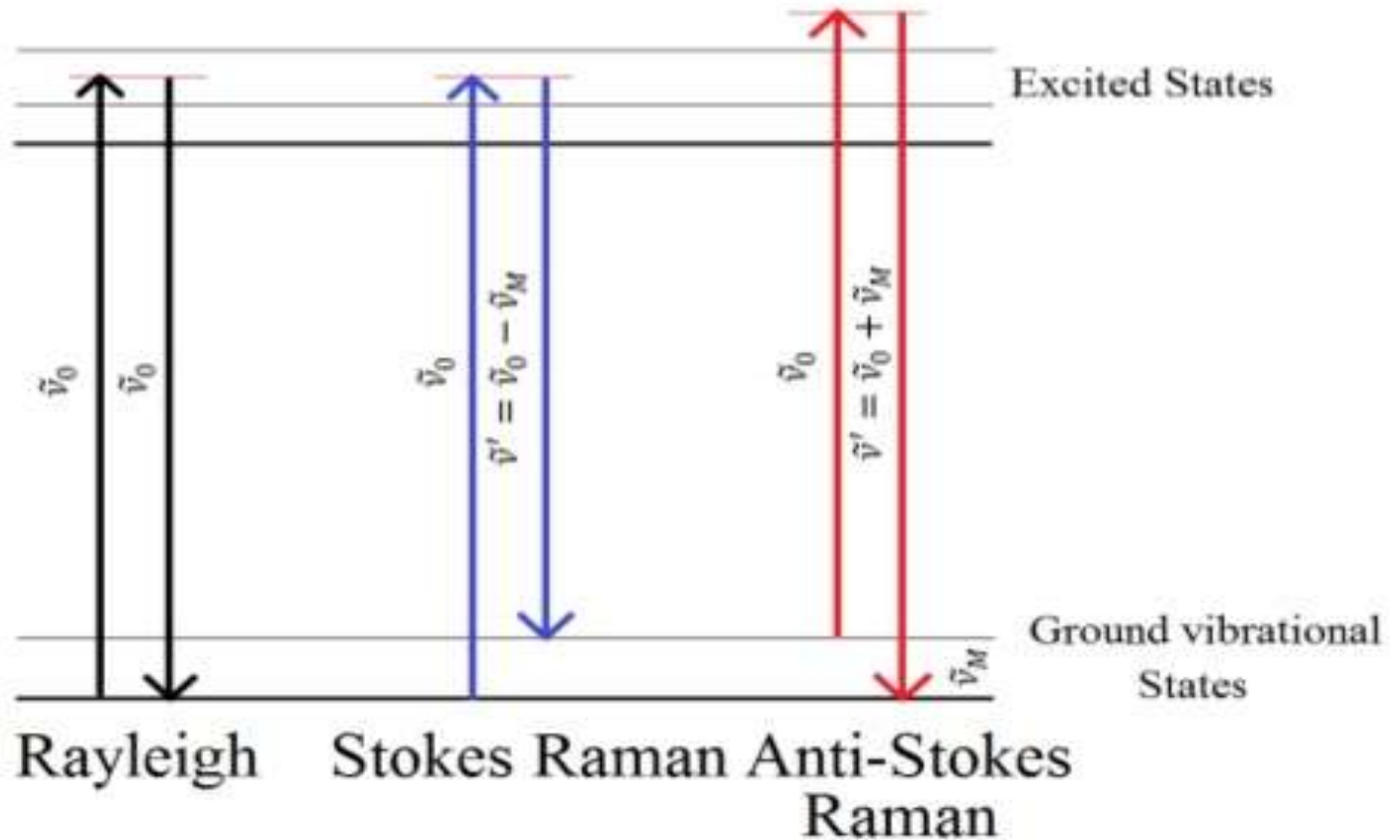
- When monochromatic radiation is incident upon a sample then this light will interact with the sample in some fashion. It may be reflected, absorbed or scattered in some manner. It is the scattering of the radiation that occurs which gives information about molecular structure
- Raman is based on scattering. The sample is irradiated with a coherent source, typically a laser. Most of the radiation is elastically scattered (called the Rayleigh scatter).
- A small portion is inelastically scattered (Raman scatter, composed of Stokes and anti-Stokes portions). This latter portion is what we are particularly interested in because it contains the information in which we are interested.



# Time lap

- 1923 – Inelastic light scattering is predicted by A. Smekel
- 1928 – Landsberg and Mandelstam see unexpected frequency shifts in scattering from quartz
- 1928 – C.V. Raman and K.S. Krishnan see “feeble fluorescence” from neat solvents
- 1930 – C.V. Raman wins Nobel Prize in Physics
- 1961 – Invention of laser makes Raman experiments reasonable
- 1977 – Surface-enhanced Raman scattering (SERS) is discovered
- 1997 – Single molecule SERS is possible

Frequency :-



This difference is called **Raman frequency** or **Raman shift**.

# Theory of raman spectra

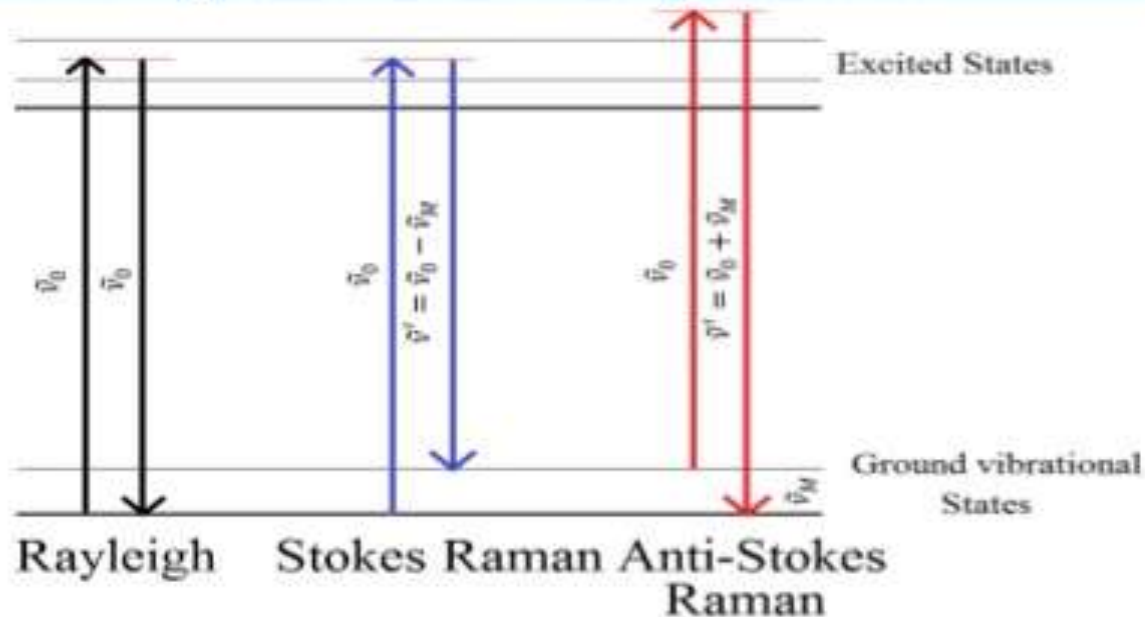
Two cases may arise depending upon whether a collision between a photon and molecules in its ground state is elastic or inelastic in nature.

**Case 1- if the collision is elastic** – this leads to the appearance of unmodified lines (or unmodified frequency of light) in the scattered beam and this explains **rayleigh scattering**.

**Case 2- if the collision is inelastic** – there will be exchange or transfer of energy between the scattering molecules and the incident photon.

The frequency of scattered light and the incident photon which is either higher or lower than that of the incident photon is **called raman frequency**.

Total energy before collision  total energy after collision



# Condition for raman spectroscopy

Vibrational modes that are more polarizable are more Raman-active

Examples:

- $\text{N}_2$  (dinitrogen) symmetric stretch
  - \_ cause no change in dipole (**IR-inactive**)
  - cause a change in the polarizability of the bond – as the bond gets longer it is more easily deformed (Raman -active)
  
- $\text{CO}_2$  asymmetric stretch
  - \_ cause a change in dipole (**IR-active**)
  - \_ Polarizability change of one C=O bond lengthening is cancelled by the shortening of the other – no net polarizability (Raman-inactive)
  - \_ Some modes may be both IR and Raman-active, others may be one or the other!

# Condition for raman spectroscopy

- ❖ Raman spectra occurs as a result of **oscillation of a dipole moment**, induced in a molecules by the oscillating electric field of an incident wave.
- ❖ As the induced **dipole moment is directly proportional to the polarisability of the molecules**, the molecules must possess anisotropic polarisability which should change during molecular rotation or vibration for vibrational or rotational-vibrational raman spectra.
- ❖ Anisotropic **polarisability depends upon the orientation of the molecules**.
- ❖ In the presence of an **electric field**, the electron cloud of an atom or **molecules is distorted or polarised**.

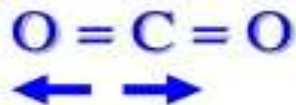
# Mutual Exclusion Principle

For molecules with a center of symmetry, no IR active transitions are Raman active and vice versa

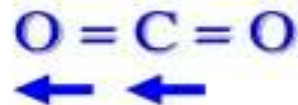
⇒ *Symmetric molecules*

IR-active vibrations are not Raman-active.

Raman-active vibrations are not IR-active.



Raman active  
IR inactive



Raman inactive  
IR active

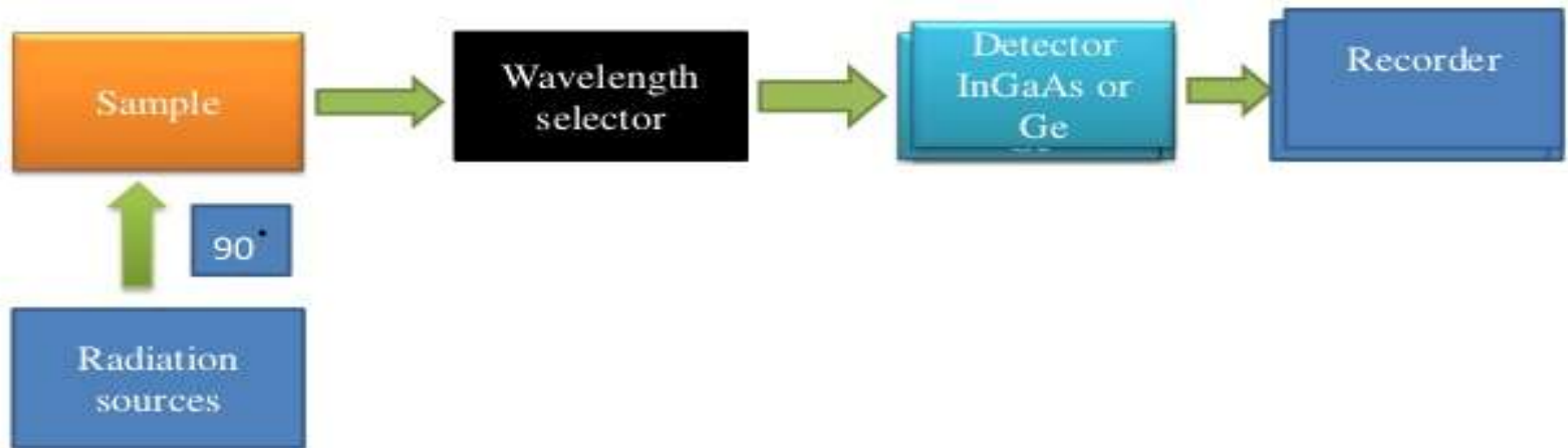
# **Raman Instrumentation**

# **There are following component involves.**

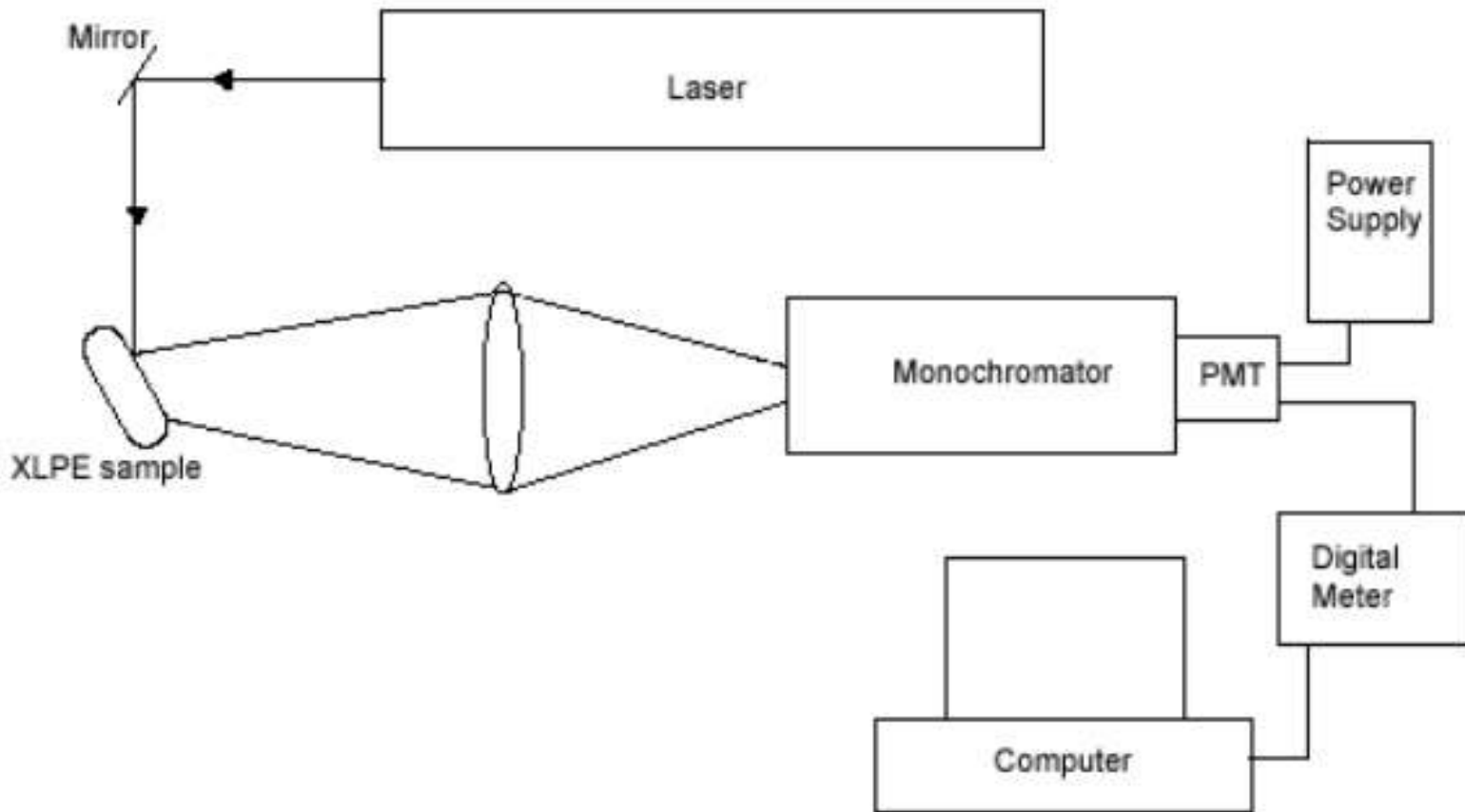
1. Laser or source of light
2. Filter
3. Sample holder
4. detector



# The block design dispersive Raman scattering system:



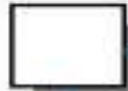
Block diagram



**Flow diagram dispersive Raman scattering system:**

# INSTRUMENTATION

Sample cell



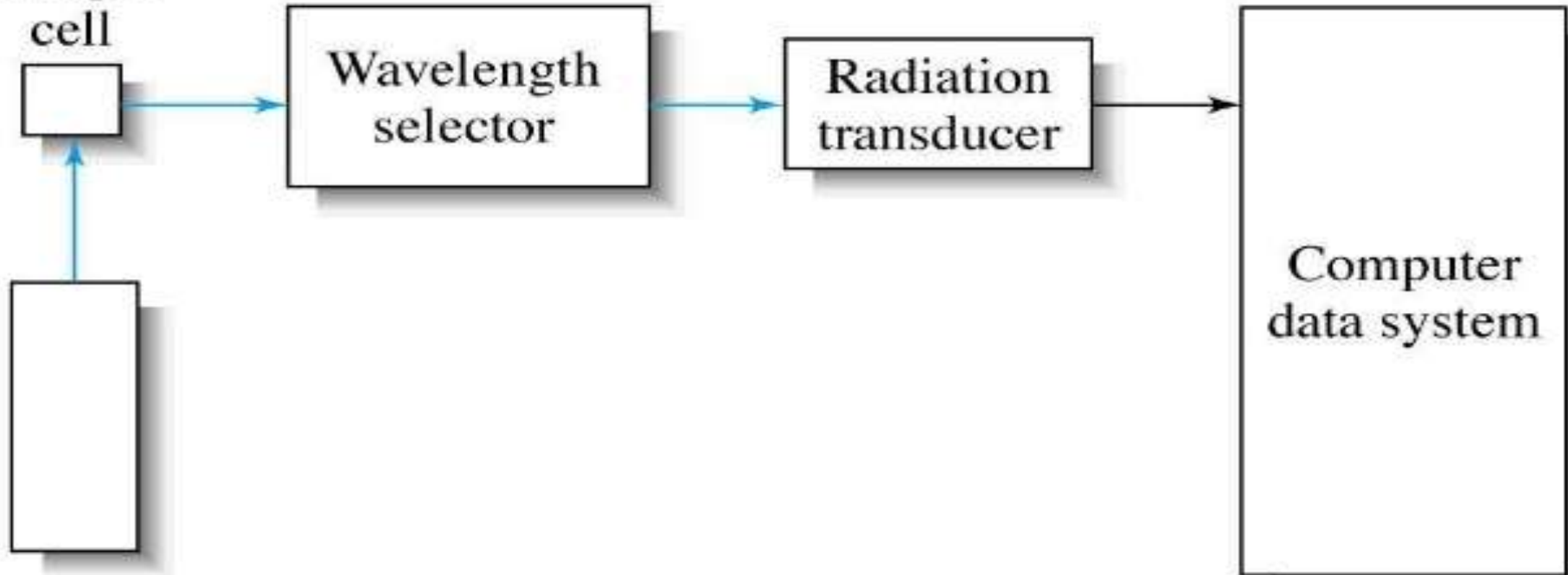
Wavelength selector

Radiation transducer

Computer data system



Laser source



# INSTRUMENTATION

- Instrumentation for modern Raman spectroscopy consists of three components:
  - laser source
  - sample illumination system
  - suitable spectrometer.

## 1) Source:

- The sources used in modern Raman spectrometry are nearly always lasers because their high intensity is necessary to produce Raman scattering of sufficient intensity to be measured with a reasonable signal-to-noise ratio.
- Because the intensity of Raman scattering varies as the fourth power of the frequency, argon and krypton ion sources that emit in the blue and green region of the spectrum have an advantage over the other sources.

## Some Common Laser Sources for Raman Spectroscopy

<b>Laser Type</b>	<b>Wavelength, nm</b>
Argon ion	488.0 or 514.5
Krypton ion	530.9 or 647.1
Helium-neon	632.8
Diode	785 or 830
Nd-YAG	1064

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Source used now a days are laser because high intensity is necessary to produce Raman scattering

## 2. Sample Illumination System

- ❑ **Liquid Samples:** A major advantage of sample handling in Raman spectroscopy compared with infrared arises because water is a weak Raman scatterer but a strong absorber of infrared radiation. Thus, aqueous solutions can be studied by Raman spectroscopy but not by infrared.
- This advantage is particularly important for biological and inorganic systems and in studies dealing with water pollution problems.
- ❑ **Solid Samples:** Raman spectra of solid samples are often acquired by filling a small cavity with the sample after it has been ground to a fine powder. Polymers can usually be examined directly with no sample pretreatment.
- ❑ **Gas samples:** Gases are normally contained in glass tubes, 1-2 cm in diameter and about 1mm thick. Gases can also be sealed in small capillary tubes

# 3. Raman Spectrometers

- Raman spectrometers were similar in design and used the same type of components as the classical ultraviolet/visible dispersing instruments.
- Most employed double grating systems to minimize the spurious radiation reaching the transducer. Photomultipliers served as transducers.
- Now Raman spectrometers being marketed are either Fourier transform instruments equipped with cooled germanium transducers or multichannel instruments based upon charge-coupled devices.

## 4.detector

- Researchers traditionally used single points detectors such as **photocounting, photomultiplier(PMT)**, not because of the weakness of a typical raman signal, longer exposure times were often required to obtains raman spectrum of a decent quality.
- Now days multichannel detectors like **photodiode arrays(PDA), charged couple devices(CCD)**
- Sensitivity & performance of modern CCD detectors are high.



# Differences between IR and Raman methods

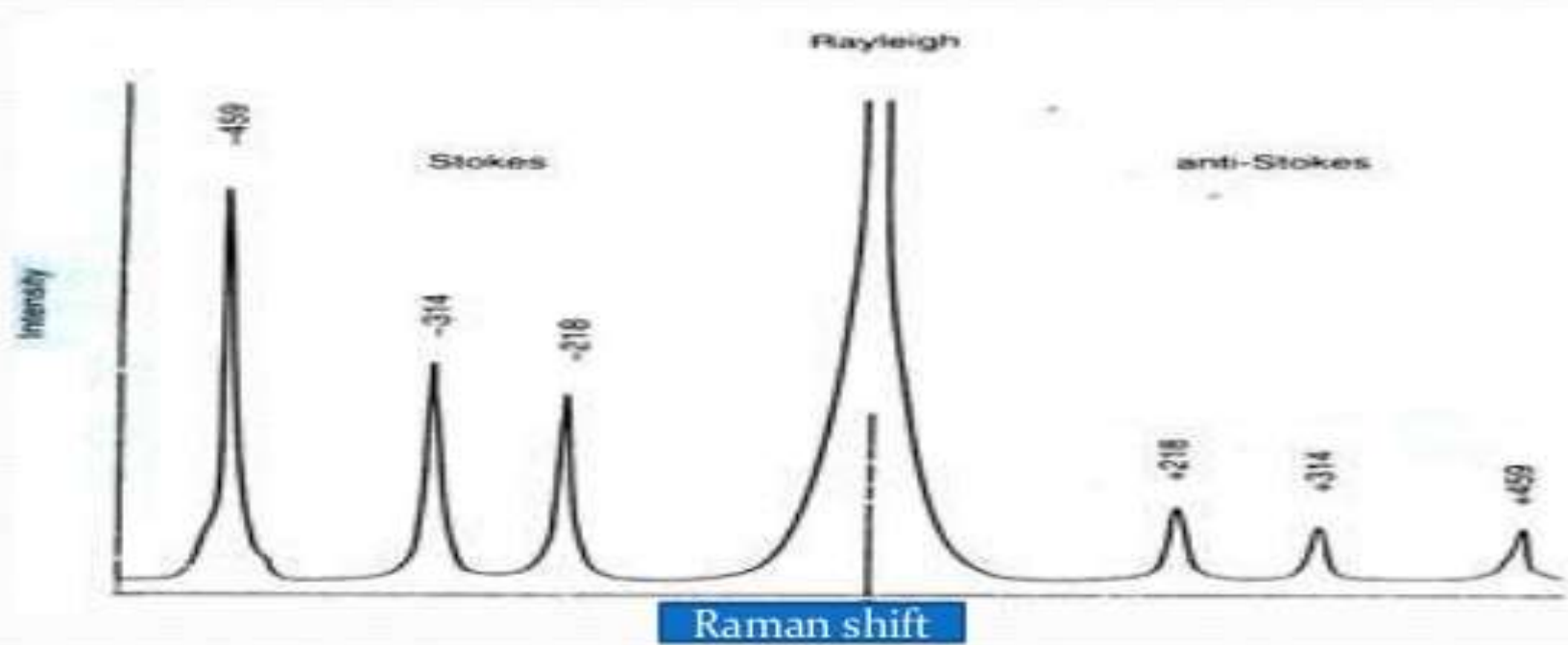
S.No	Raman	IR
01	It is due to the scattering of light by the vibrating molecules.	It is the result of absorption of light by vibrating molecules.
02	The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment.
03	The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment due to that vibration.
04	Water can be used as a solvent.	Water cannot be used due to its intense absorption of IR.
05	Sample preparation is not very elaborate, it can be in any state.	Sample preparation is elaborate Gaseous samples can rarely be used.
06	Gives an indication of covalent character in the molecule.	Gives an indication of ionic character in the molecule.
07	Cost of instrumentation is very high	Comparatively inexpensive.

# DIFFERENCE

RAMAN	INFRA RED
<ul style="list-style-type: none"><li>•It is due to the scattering of light by the vibrating molecules.</li><li>•The vibration is Raman active if it causes a change in polarisability.</li><li>•The molecule need not possess a permanent dipole moment.</li><li>•Water can be used as a solvent.</li><li>•Sample preparation is not very elaborate, it can be in any state.</li><li>•Gives an indication of covalent character in the molecule.</li><li>•Cost of instrumentation is very high</li></ul>	<ul style="list-style-type: none"><li>•It is the result of absorption of light by vibrating molecules.</li><li>•Vibration is IR active if there is change in dipole moment.</li><li>•The vibration concerned should have a change in dipole moment due to that vibration.</li><li>•Water cannot be used due to its intense absorption of IR.</li><li>•Sample preparation is elaborate Gaseous samples can rarely be used.</li><li>•Gives an indication of ionic character in the molecule.</li><li>•Comparatively inexpensive.</li></ul>

# Raman spectrum

- Typical Raman spectrum
- Plot of signal intensity vs Raman shift
- (Raman shift, in  $\text{cm}^{-1}$  = energy of photon in - energy of photon out)



# APPLICATION

## Raman Spectra of Inorganic Species

- The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed.
- In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700  $\text{cm}^{-1}$ , a region of the infrared that is experimentally difficult to study.
- These vibrations are frequently Raman active, however, and peaks with  $\Delta\nu$  values in this range are readily observed.
- Raman studies are potentially useful sources of information concerning the composition, structure, and stability of coordination compounds.

# APPLICATION

(cont.)

- **Raman Spectra of Organic Species**

Raman spectra are similar to infrared spectra in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds.

Raman spectra yield more information about certain types of organic compounds than do their infrared counterparts.

- **Quantitative applications**

Raman spectra tend to be less cluttered with peaks than infrared spectra. As a consequence, peak overlap in mixtures is less likely, and quantitative measurements are simpler. In addition, Raman sampling devices are not subject to attack by moisture, and small amounts of water in a sample do not interfere.

- **Biological Applications of Raman Spectroscopy**

Raman spectroscopy has been applied widely for the study of biological systems.

The advantages of his technique include the small sample requirement, the minimal sensitivity toward interference by water, the spectral detail, and the conformational and environmental sensitivity.

**Thank you for your attention!**

