



Raman Spectrum & Spectroscopy

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Chandrashekhar Venkata Raman

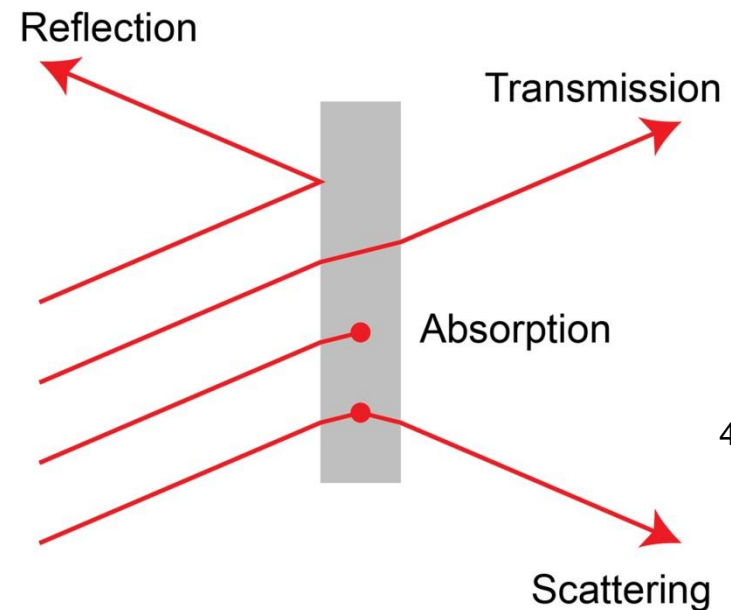
- November 7, 1888 - November 21, 1970 in Southern India.
- 1907 – was posted in Calcutta as Assistant Accountant General.
- 30 papers were published.
- Research – acoustics and optics
- Pioneered Indian science – founded Indian Academy of Sciences, founded Indian Journal of Physics (editor)
- Won the Nobel prize in 1930 for Physics.
- Discovered the “Raman effect”.



C.V. Raman (Purohit)

Origin of Raman scattering:-

- When a monochromatic radiation of frequency ν is passed through a non absorbing medium, it is found that most of it is transmitted without any change, and some of it is scattered. If the scattered energy is analyzed by means of a spectrometer, the bulk of the energy is found at the frequency of the incident beam ν_0 but a small portion of the scattered energy will be found at frequencies $\nu = \nu_0 - \nu_m$. The scattering of radiation with change of frequency is called Raman scattering.

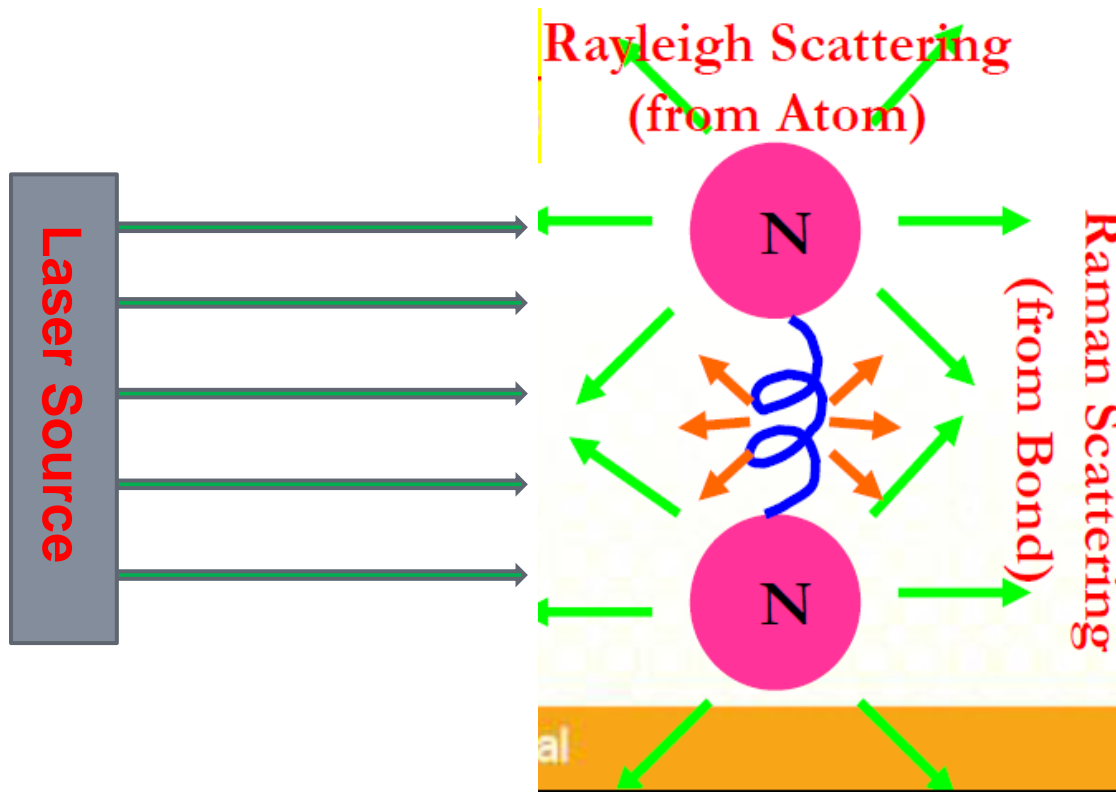


[The different fundamental light processes during material interaction](#)

- When light is scattered from a molecule most photons are elastically scattered (Rayleigh). The scattered photons have the same energy (frequency/wavelength) as the incident photons.
- However, a small fraction of light (approximately 1 in 10^7 photons) is scattered at optical frequencies usually lower than, the frequency of the incident photons. The process leading to this inelastic scattering is termed the Raman effect. Raman scattering can occur with a change in *vibrational*, rotational or electronic energy of a molecule. Physicists/Chemists are concerned primarily with the vibrational Raman effect. The term Raman effect usually means vibrational Raman effect only.
- The difference in energy between the incident photon and the Raman scattered photon is equal to the energy of a vibration of the scattering molecule. A plot of intensity of scattered light versus energy difference is a **Raman spectrum**.

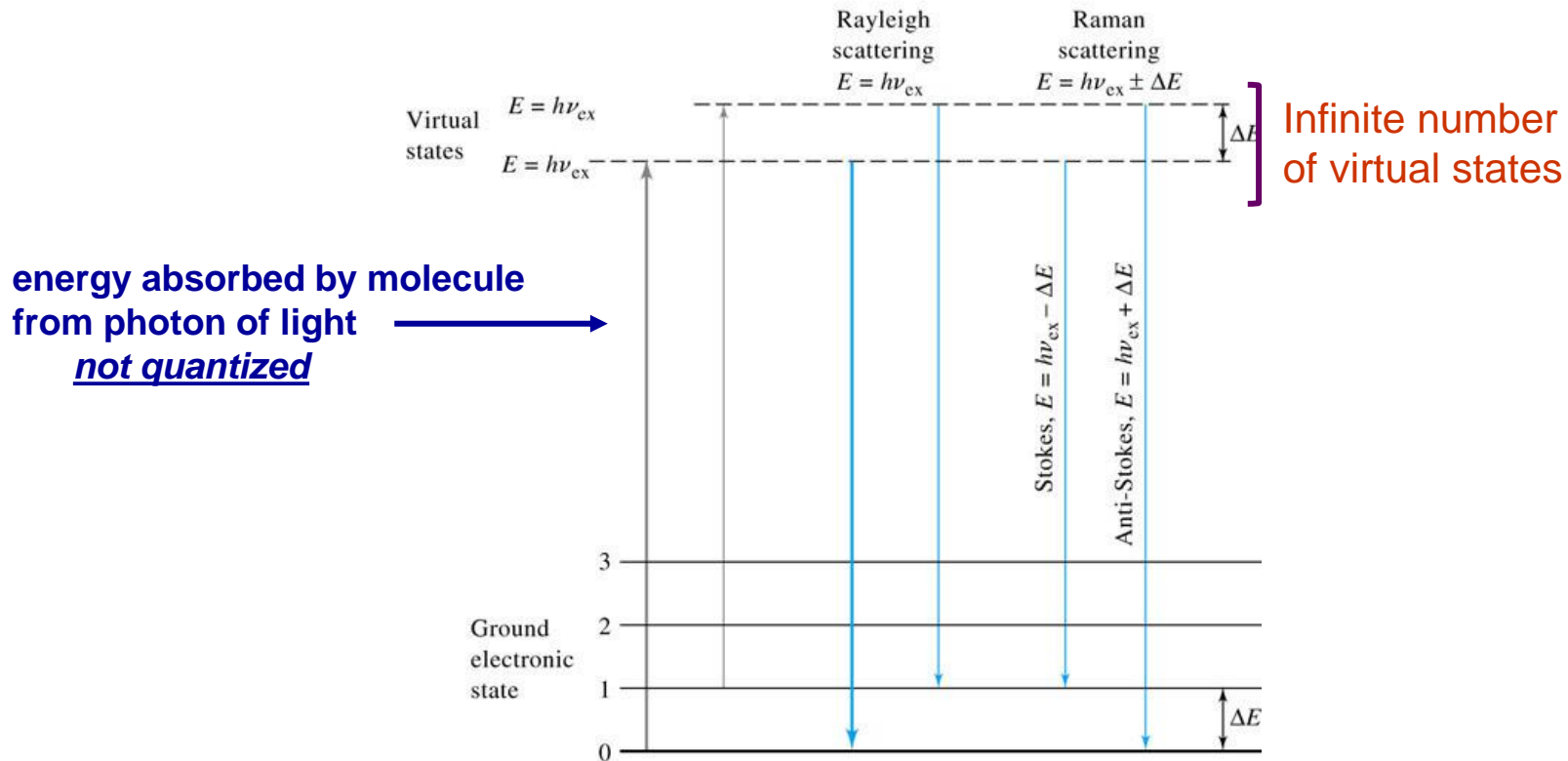
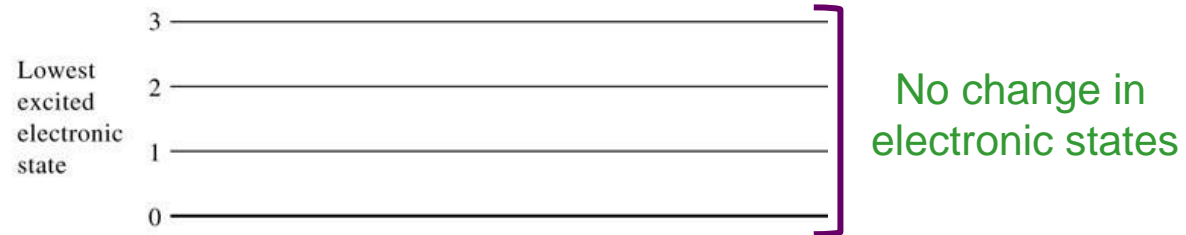
$$\Delta \nu (\text{cm}^{-1}) = \frac{1}{\lambda_{\text{Incident}} (\text{cm})} - \frac{1}{\lambda_{\text{Scattered}} (\text{cm})}$$

Basic Principles of Raman Spectroscopy:

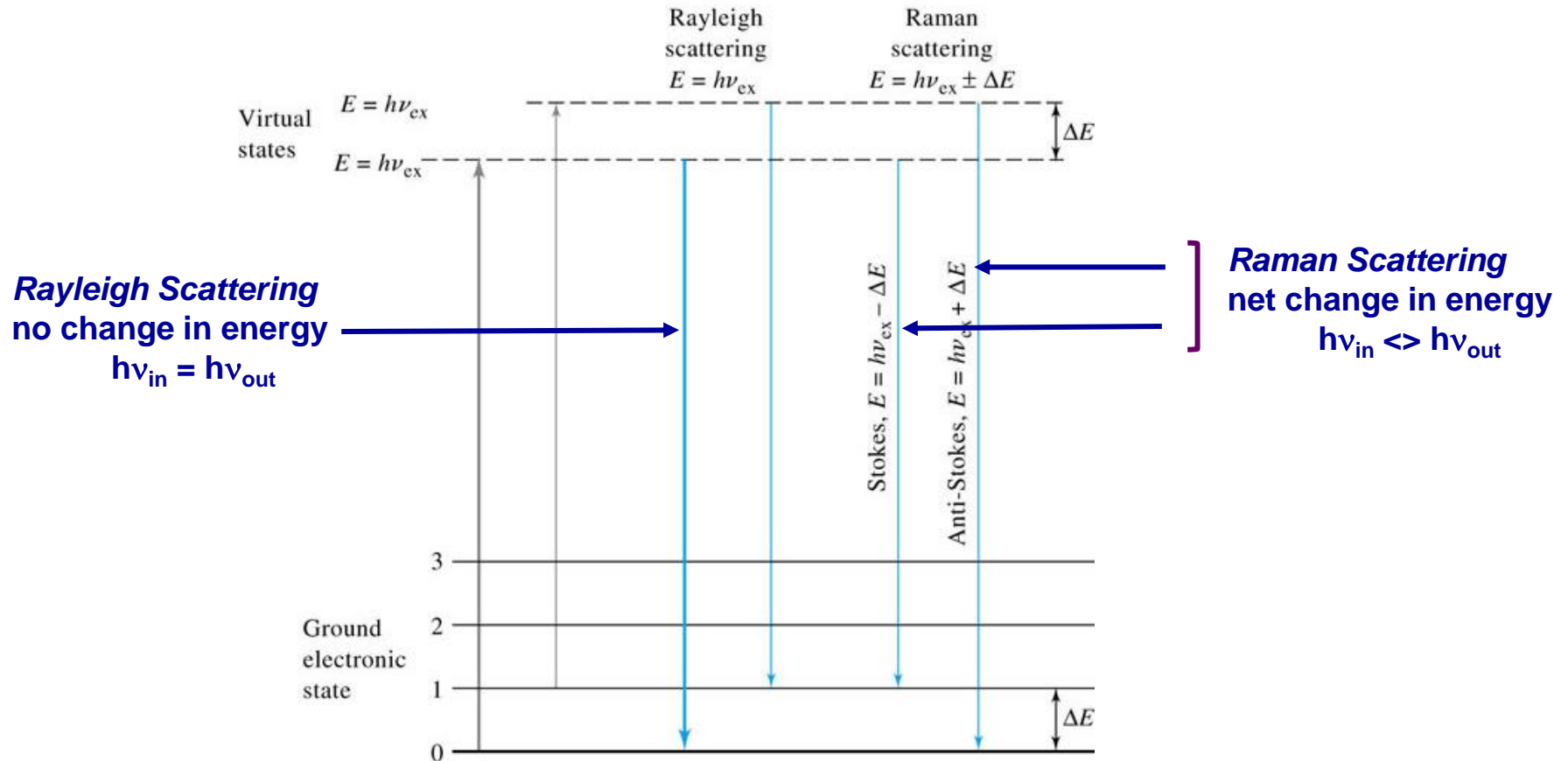


- Rayleigh scattering:
 - occurs when incident EM radiation induces an oscillating dipole in a molecule, which is re-radiated at the same frequency
- Raman scattering:
 - occurs when monochromatic light is scattered by a molecule, and the scattered light has been weakly modulated by the characteristic frequencies of the molecule

- light is scattered by the sample at various angles by momentary absorption to virtual state and reemission

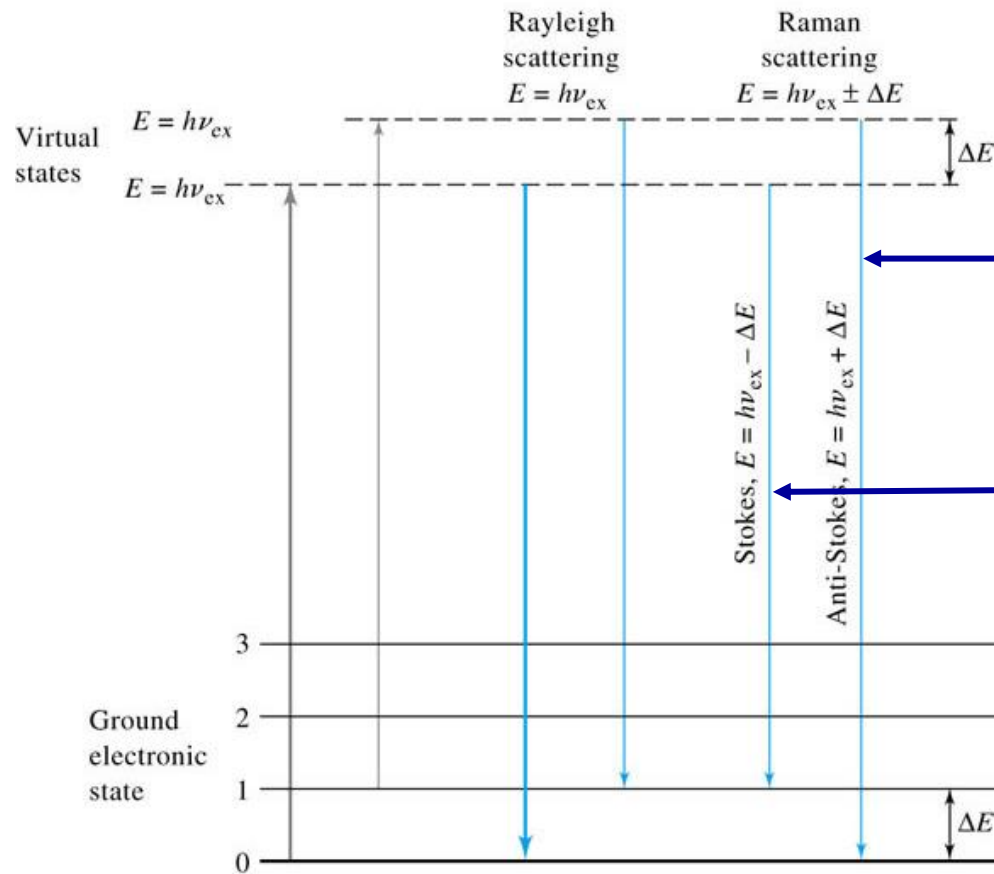


- some scattered emissions occur at the same energy while others return in a different state



Elastic: collision between photon and molecule results in no change in energy

Inelastic: collision between photon and molecule results in a net change in energy



Two Types of Raman Scattering

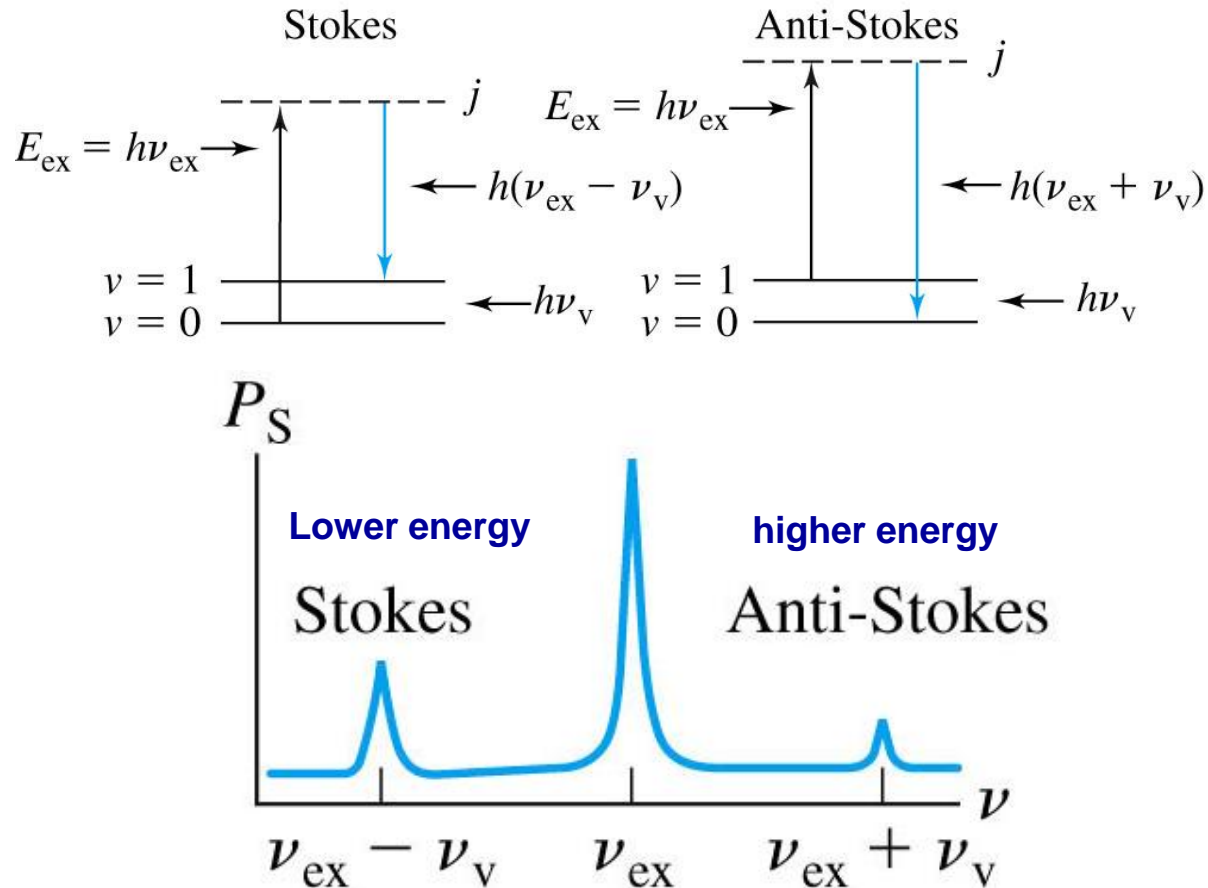
Anti-Stokes: $E = h\nu + \Delta E$

Stokes: $E = h\nu - \Delta E$

$\pm\Delta E$ – the energy of the first vibration level of the ground state – IR vibration absorbance

\therefore Raman frequency shift and IR absorption peak frequency are identical

- Resulting Raman Spectrum



Probability of Emission \propto Observed Intensity

Raleigh scattering \gg Stokes \gg anti-Stokes

difference in population of energy levels of vibrational transitions

Intensity of Raman lines are 0.001% intensity of the source

- ✓ The heavy arrow on the far left depicts the energy change in the molecule when it interacts with a photon. The increase in energy is equal to the energy of the photon $h\nu$.
- ✓ The second and narrower arrow shows the type of change that would occur if the molecule is in the first vibrational level of the electronic ground state.
- ✓ The middle set of arrows depicts the changes that produce Rayleigh scattering. The energy changes that produce Stokes and anti-Stokes emission are depicted on the right. The two differ from the Rayleigh radiation by frequencies corresponding to $\pm\Delta E$, the energy of the first vibrational level of the ground state. If the bond were infrared active, the energy of its absorption would also be ΔE . Thus, the Raman frequency shift and the infrared absorption peak frequency are identical.
- ✓ The relative populations of the two upper energy states are such that Stokes emission is much favored over anti-Stokes. Rayleigh scattering has a considerably higher probability of occurring than Raman because the most probable event is the energy transfer to molecules in the ground state and reemission by the return of these molecules to the ground state.
- ✓ The ratio of anti-Stokes to Stokes intensities will increase with temperature because a larger fraction of the molecules will be in the first vibrationally excited state under these circumstances.

Raman Scattering Process:-

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- ✓ The Raman effect arises when a photon is incident on a molecule and interacts with the **electric dipole (polarizability)** of the molecule.
- ✓ It is a form of electronic (more accurately, vibronic) spectroscopy, although the spectrum contains vibrational frequencies.
- ✓ In **classical** terms, the interaction can be viewed as a **perturbation** of the molecule electric field.
- ✓ In **quantum** mechanics the scattering is described as an excitation to a **virtual state** lower in energy than a real electronic transition with nearly coincident de-excitation and a **change in vibrational** energy.
- ✓ The **scattering event** occurs in 10^{-14} **seconds or less**. Thus, the virtual state description of scattering works.

Absorption (Excitation): 10^{-15} s

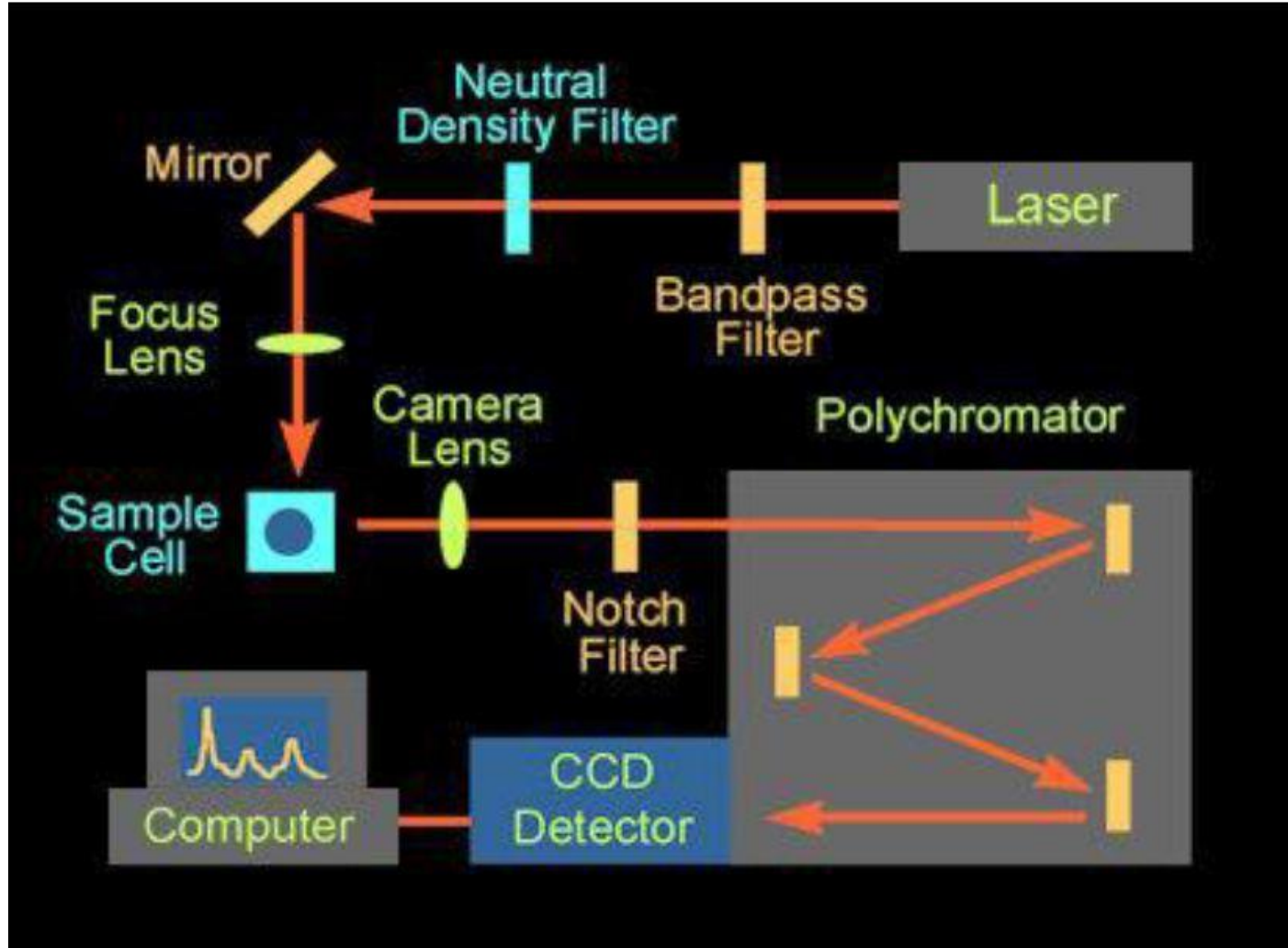
Internal Conversion and Vibrational Relaxation: $10^{-14} - 10^{-11}$ s

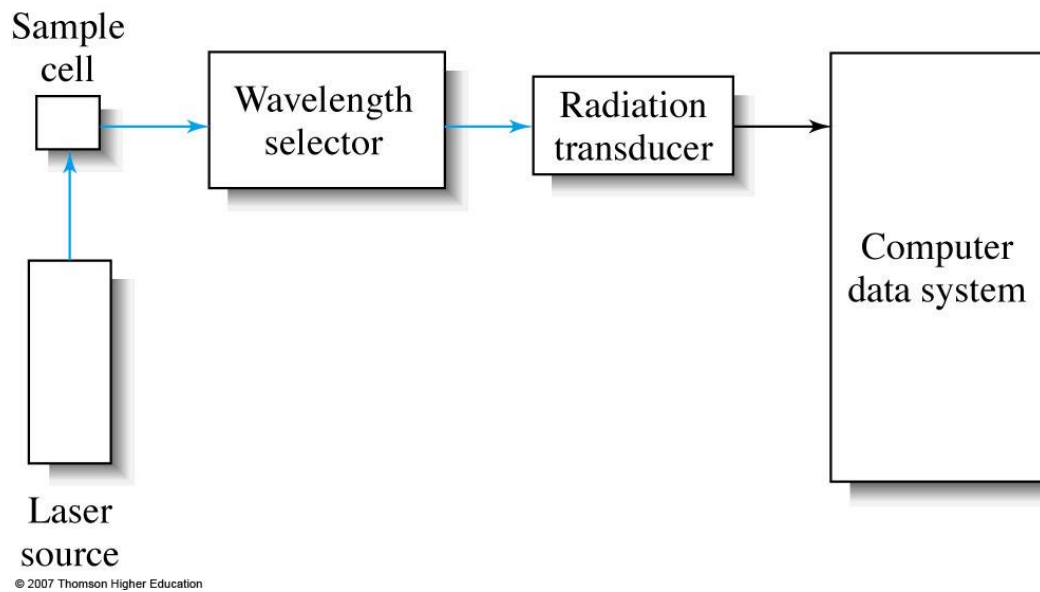
Fluorescence: $10^{-9} - 10^{-7}$ s; **Phosphorescence:** $10^{-3} - 10^2$ s

Raman Spectroscopy:-

Experimental setup:-

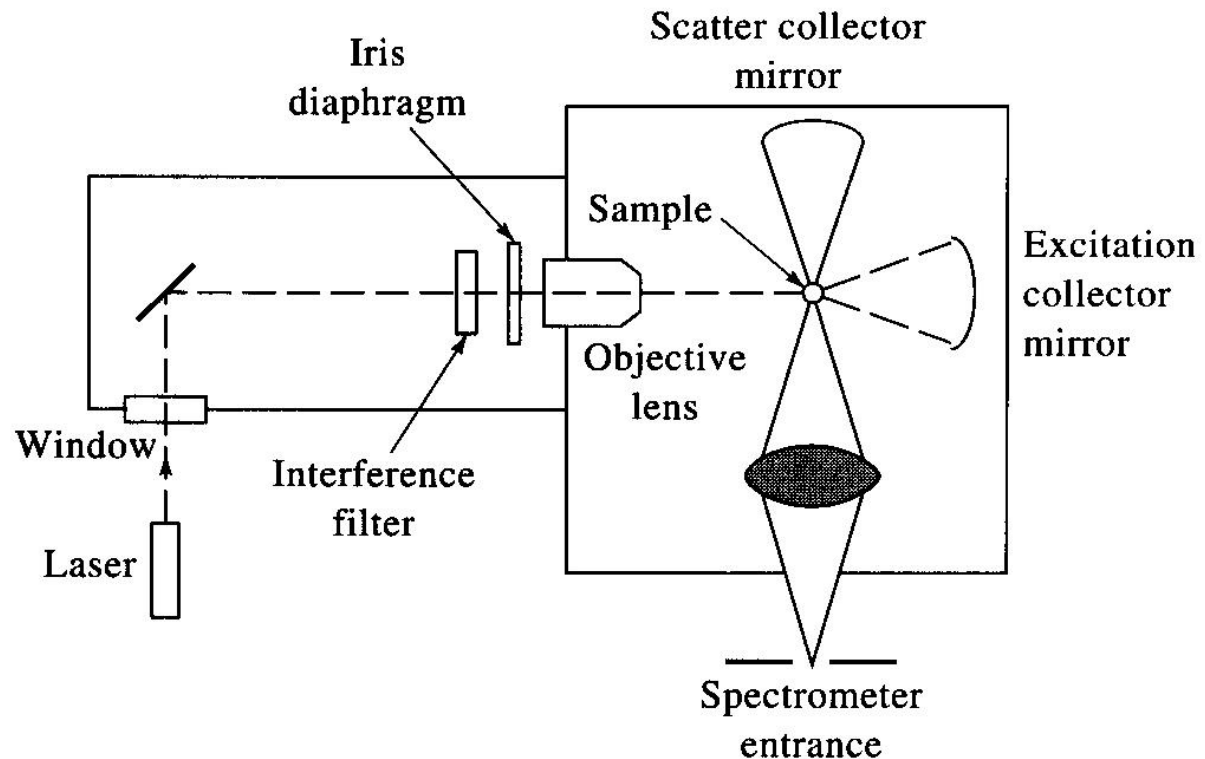
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A Raman system typically consists of four major components:

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrometer).
4. Detector (Photodiode array, CCD or PMT).



Types Of Raman Spectroscopy:-

- Resonance Raman spectroscopy (RRS)
- Surface-enhanced Raman spectroscopy (SERS)
- Micro-Raman spectroscopy
- Nonlinear Raman spectroscopic techniques

Raman spectroscopy used:-

✓ **In general it is suitable for analysis of:**

- Solids, powders, liquids, gels, slurries and gases
- Inorganic, organic and biological materials
- Pure chemicals, mixtures and solutions

In general it is not suitable for analysis of:

- Metals and their alloys

✓ **Typical examples of where Raman is used today include:**

- Art and archaeology – characterisation of pigments, ceramics and gemstones
- Carbon materials – structure and purity of nanotubes, defect/disorder characterisation
- Chemistry – structure, purity, and reaction monitoring
- Geology – mineral identification and distribution, fluid inclusions and phase transitions
- Life sciences – single cells and tissue, drug interactions, disease diagnosis
- Pharmaceuticals – content uniformity and component distribution
- Semiconductors – purity, alloy composition, intrinsic stress/strain

ADVANTAGE & DISADVANTAGE:-

a) Qualitative Information

- i. characteristic regions for different groups as in IR
- ii. Raman correlation charts available
- iii. Good for aqueous based samples
- iv. Useful for a variety of samples, organic, inorganic & biological

b) Quantitative Information – *not routinely used*

- i. fewer technical problems than IR, fewer peaks
- ii. Interference from fluorescence
- iii. Higher cost
- iii. Signal weak – require modified Raman methods
 - 1) Resonance Raman spectroscopy allows detection of 10^{-3} -> 10^{-7} M by using lasers light with wavelength approaching *electronic* absorption
 - 2) Surface enhanced Raman spectroscopy places samples on metal or rough surfaces that increase Raman scattering

THANK YOU