Raman Spectroscopy

Sir Chandrasekhara Venkata Raman
7 November 1888 – 21 November 1970
Indian physicist
Work: in the field of light scattering

Main Discovery (Observation)
when light traverses a transparent material, some of the deflected light changes wavelength and amplitude (a very rare phenomenon one in 10 million).
This phenomenon was a new type of scattering of light.
subsequently termed as the Raman effect (Raman scattering)
Raman won the 1930 Nobel Prize in Physics and
was the first Asian person to receive a Nobel Prize in any branch of science.
He topped the bachelor's degree examination at the University of Madras with honours in physics from Presidency College at age 16.
In 1954, the Government of India honoured him with the first
Bharat Ratna the most prestigious award

National Science Day February 28 in honour of Raman Effect

Raman spectroscopy

- a spectroscopic technique typically used to determine vibrational modes of molecules,
- rotational and other low-frequency modes of systems may also be observed.
- Raman spectroscopy is used to identify molecular structure.
- Raman spectroscopy relies upon inelastic scattering of photons, known as Raman scattering.
- A source of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range is used, although X-rays can also be used.

Selection Rule

In contrast to IR spectroscopy, where there is a requirement for a change in dipole moment for vibrational excitation to take place, Raman scattering requires a change in polarizability.

A Raman transition from one state to another is allowed only if the molecular polarizability of those states is different.

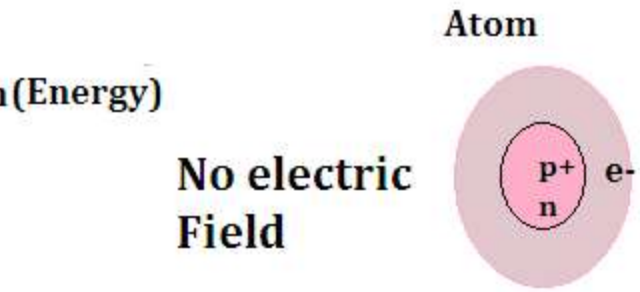
Induced dipole moment $\propto$ Field Strength (Energy)

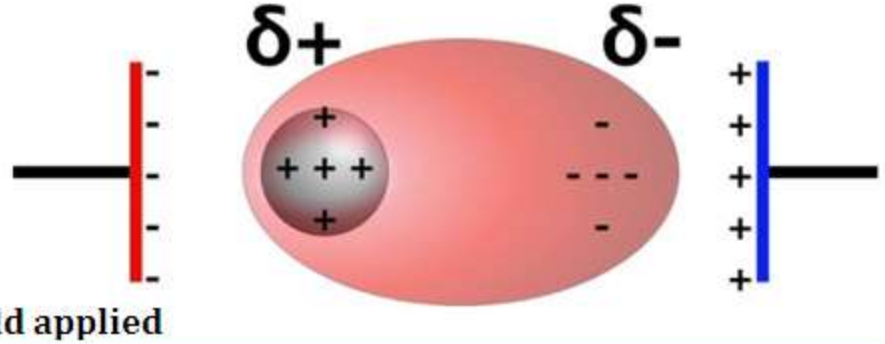
$$\therefore \mu_i = \alpha E$$

Induced dipole Energy

Where,
α is polariseability of the molecule.

Polariseability of the molecule is defined as ***induced dipole moment per unit strength of the field***



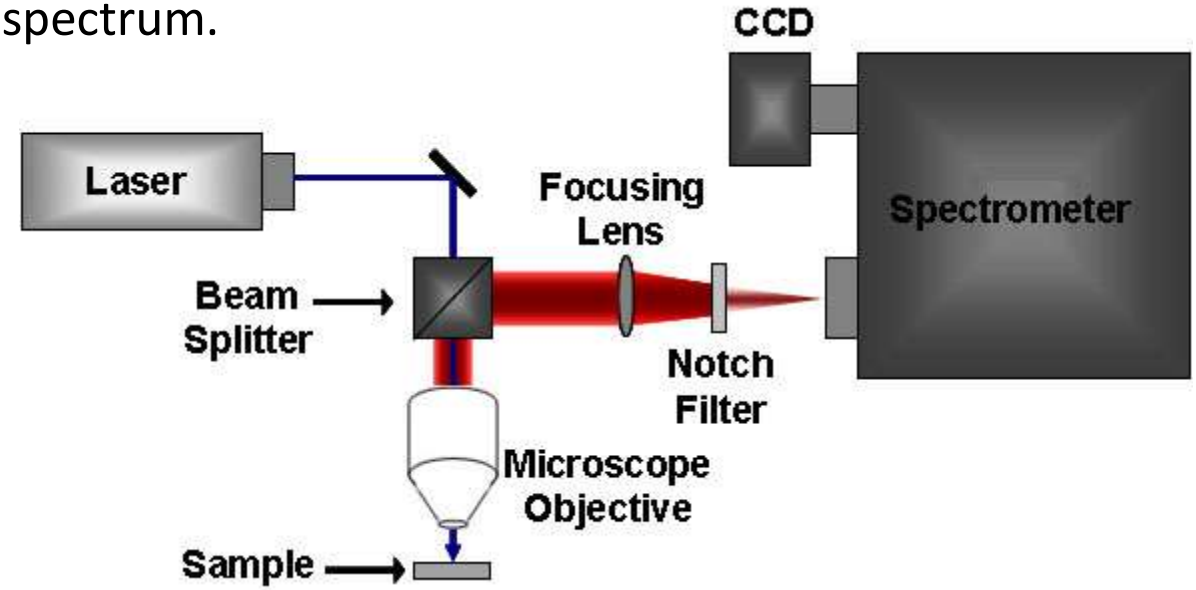


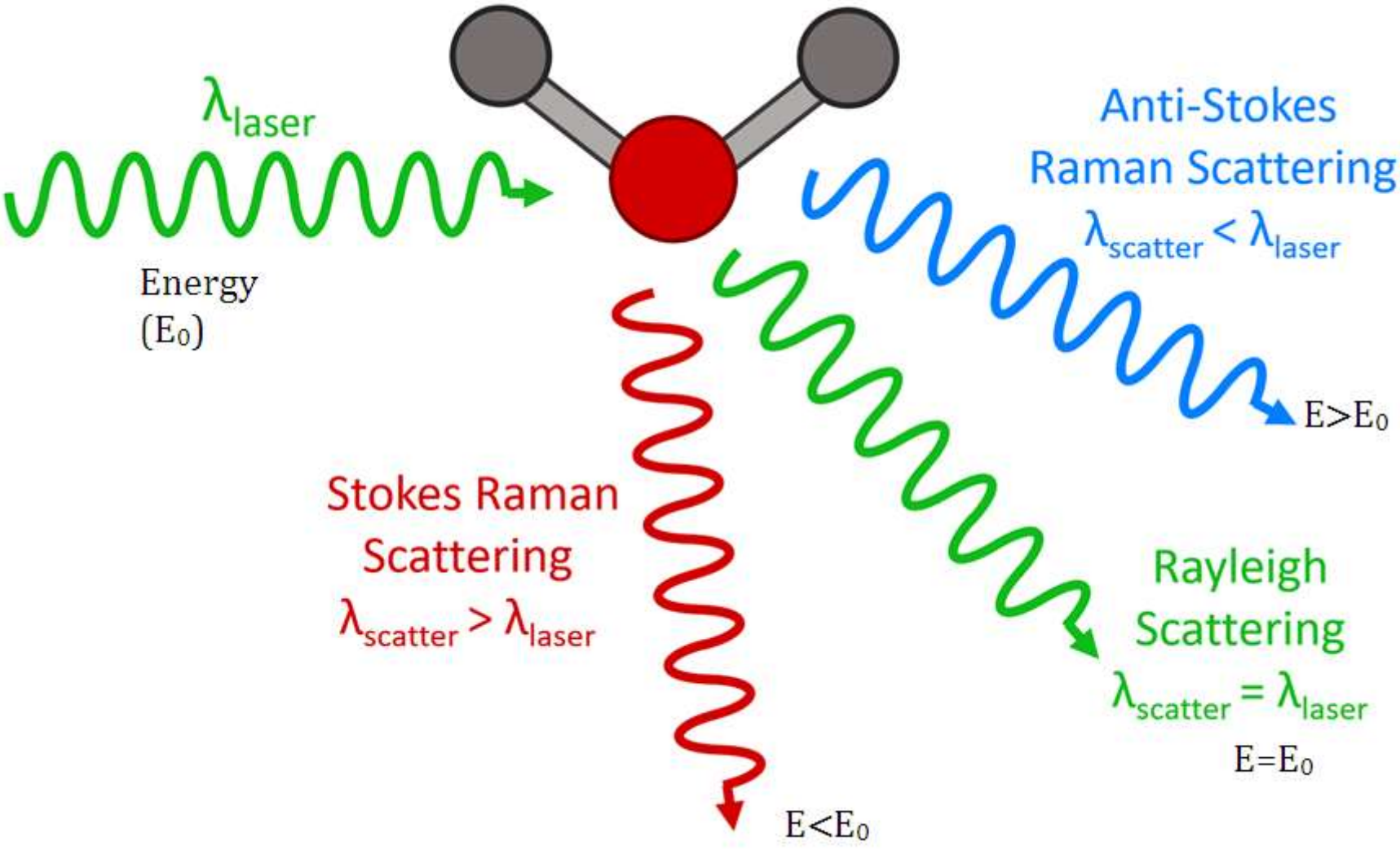
Polarizability is a measure of how easily an electron cloud is distorted by an electric field. Typically the electron cloud will belong to an atom or molecule or ion.

Instrumentation

A modern, compact Raman spectrometer consists of several basic components,

1. including a laser that serves as the excitation source to induce the Raman scattering.
2. A solid state lasers are used in modern Raman instruments with wavelengths of 532 nm, 785 nm, 830 nm and 1064 nm.
3. The laser energy is transmitted to and collected from the sample by fiber optics cables (Beam Filter).
4. A notch or edge filter is used to eliminate Rayleigh and anti-Stokes scattering and the remaining Stokes scattered light is passed on to a dispersion element, typically a holographic grating.
5. A (Coupled Charged Device) CCD detector captures the light, resulting in the Raman spectrum.



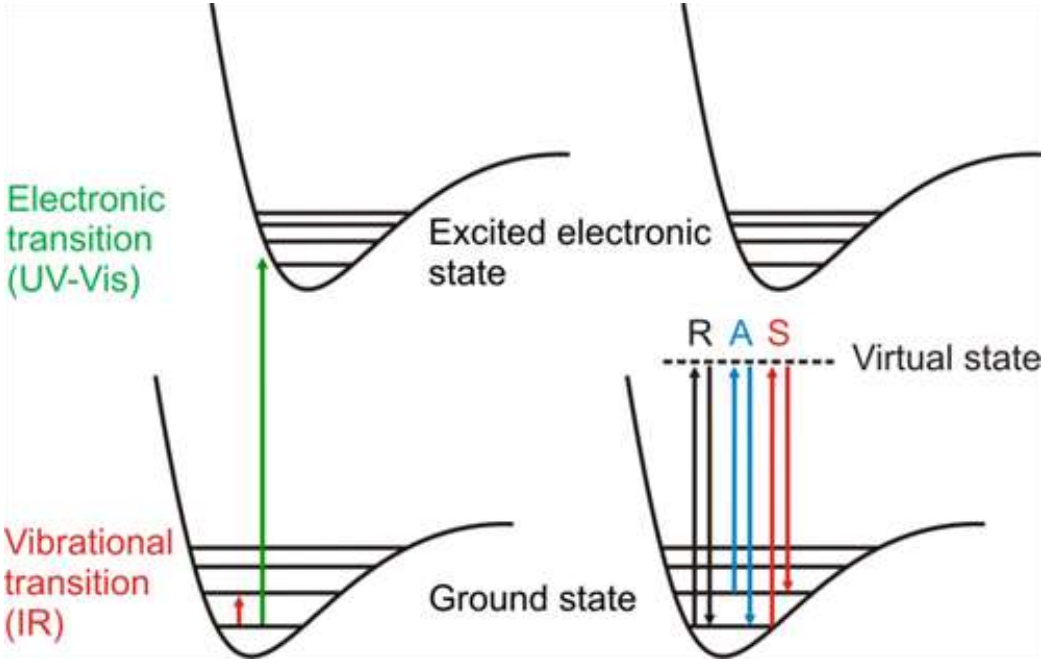

λ_{laser}
Energy
(E_0)
Anti-Stokes
Raman Scattering
$\lambda_{scatter} < \lambda_{laser}$
$E > E_0$
Stokes Raman
Scattering
$\lambda_{scatter} > \lambda_{laser}$
$E < E_0$
Rayleigh
Scattering
$\lambda_{scatter} = \lambda_{laser}$
$E = E_0$

What is Raman Scattering?

When light is scattered by molecule, the oscillating electromagnetic field of a photon induces a polarisation of the molecular electron cloud which leaves the molecule in a higher energy state with the energy of the photon transferred to the molecule.

This can be considered as the formation of a very short-lived complex between the photon and molecule which is commonly called the **virtual state** of the molecule.

The virtual state is not stable and the photon is re-emitted almost immediately, as scattered light.



Three types of scattering processes that can occur when light interacts with a molecule.

1. Rayleigh Scattering: Elastic in nature i. e. no change in energy
2. Raman Scattering: Inelastic in nature i. e. Change in energy

   These scattering are of two types

a. Stokes Lines: $\lambda_{Scattering} > \lambda_{Rayleigh} (\Delta E_{Scattering} < \Delta E_{Rayleigh})$
b. Antistokes Lines $\lambda_{Scattering} < \lambda_{Rayleigh} (\Delta E_{Scattering} > \Delta E_{Rayleigh})$

   $E = hc/\lambda \Rightarrow E \propto 1/\lambda$

Rayleigh Scattering (Elastic Scattering)

In most of the scattering events, the energy of the molecule is unchanged after its interaction with the photon; and the energy, and therefore the wavelength, of the scattered photon is equal to that of the incident photon.

This is called **Elastic** i. e. energy of scattering particle is conserved or Rayleigh scattering.

Raman Scattering (Inelastic Scattering)

In a much rarer event (approximately 1 in 10 million photons)Raman scattering occurs.

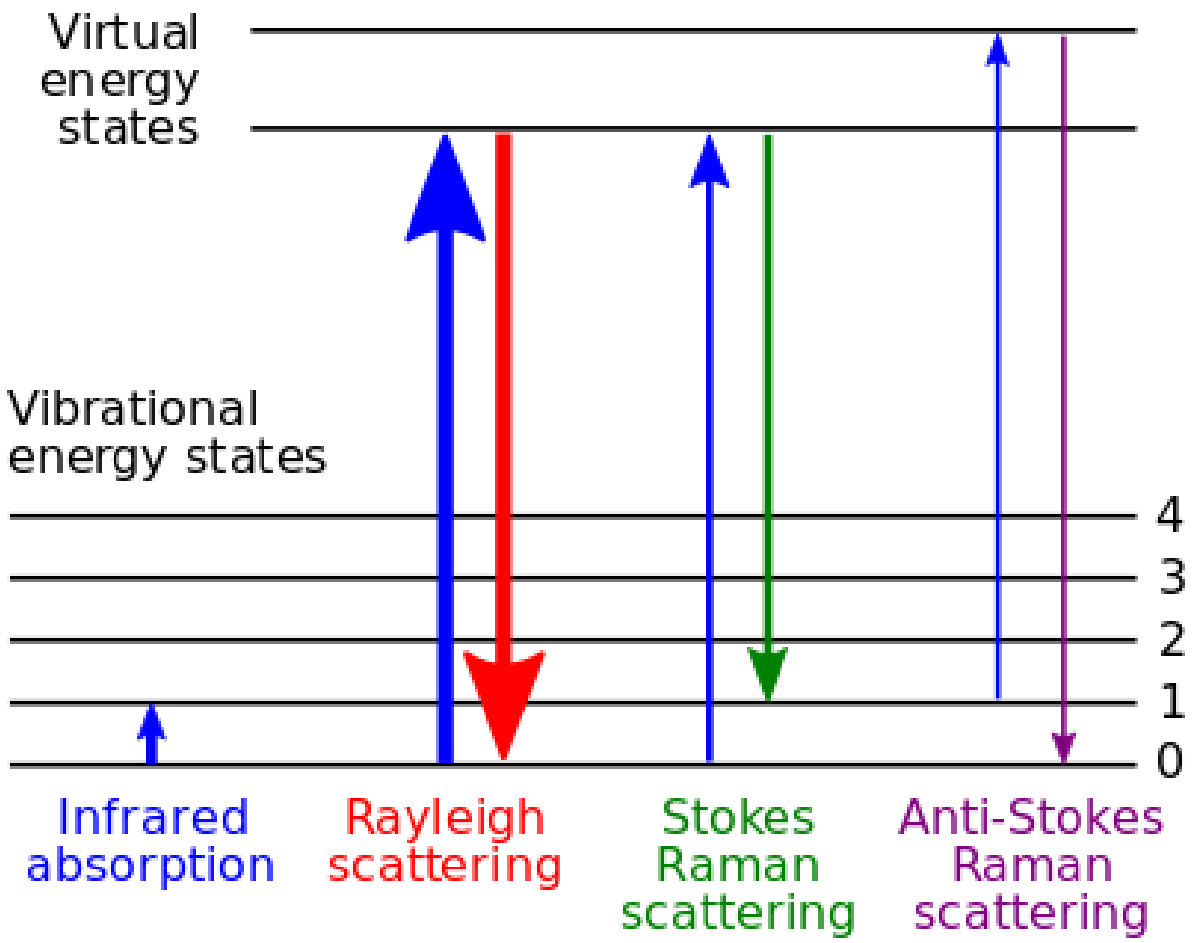
which is an **Inelastic scattering** process with a transfer of energy between the molecule and scattered photon.

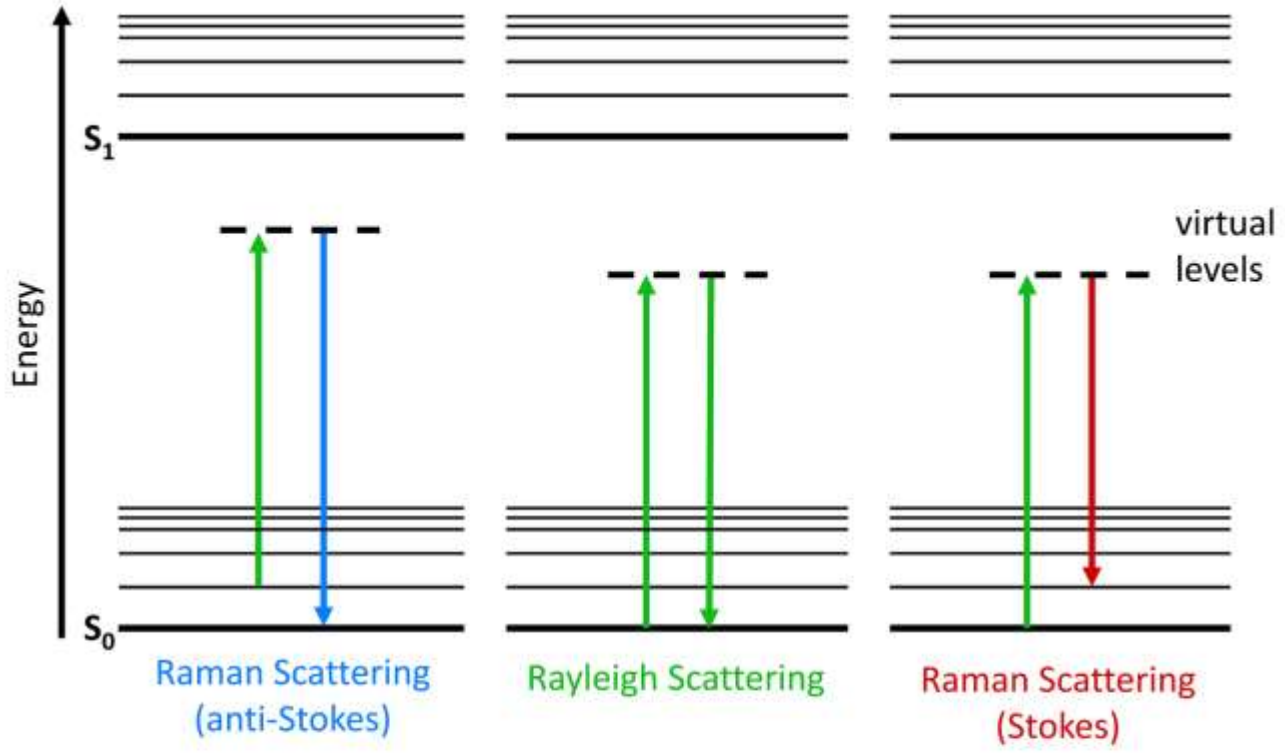
Stokes Scattering

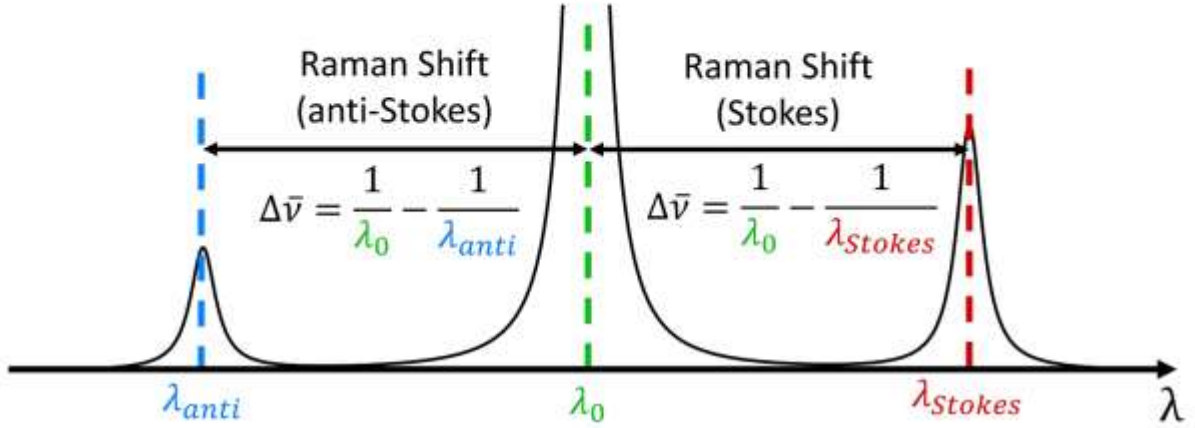
If the molecule gains energy from the photon during the scattering (excited to a higher vibrational level) then the scattered photon loses energy and its wavelength increases which is called Stokes Raman scattering (after G. G. Stokes).

Anti-Stokes Scattering

Inversely, if the molecule loses energy by relaxing to a lower vibrational level the scattered photon gains the corresponding energy and its wavelength decreases; which is called Anti-Stokes Raman scattering.


Virtual
energy
states
Vibrational
energy states
4
3
2
1
0
Infrared
absorption
Rayleigh
scattering
Stokes
Raman
scattering
Anti-Stokes
Raman
scattering


Energy
S_1
S_0
virtual levels
Raman Scattering (anti-Stokes)
Rayleigh Scattering
Raman Scattering (Stokes)


Raman Shift (anti-Stokes)
$\Delta\bar{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_{anti}}$
Raman Shift (Stokes)
$\Delta\bar{\nu} = \frac{1}{\lambda_0} - \frac{1}{\lambda_{Stokes}}$
λ_{anti}
λ_0
λ_{Stokes}
λ

S. No.	Raman Spectroscopy	IR Spectroscopy
1	Raman spectra result from **scattering of light** by vibrating molecules	IR spectra result from **light absorption** by vibrating molecules
2	Raman activity results from change of **polarizability** of a molecule	IR activity results from changing **dipole moment**
3	In Raman, a monochromatic light beam of high intensity **laser** can be used in **UV, visible or IR regions.**	In IR spectroscopy the range is **limited to IR frequencies**
4	In Raman, scattered light is observed at **right angles** to the direction of the incident beam	in IR, the absorption signal is measured in the **same direction** as the incident beam.
5	The sample can be measured **directly** in glass a container	IR technique requires solid **sample preparation** using KBr or CSi powder
6	Due to very high intensity of radiation, very **small portion** of sample is needed.	Comparatively **more sample** is required.
7	**Higher cost** of the Raman spectrometer.	**Comparatively lower cost**

Thank you

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