Raman Spectroscopy

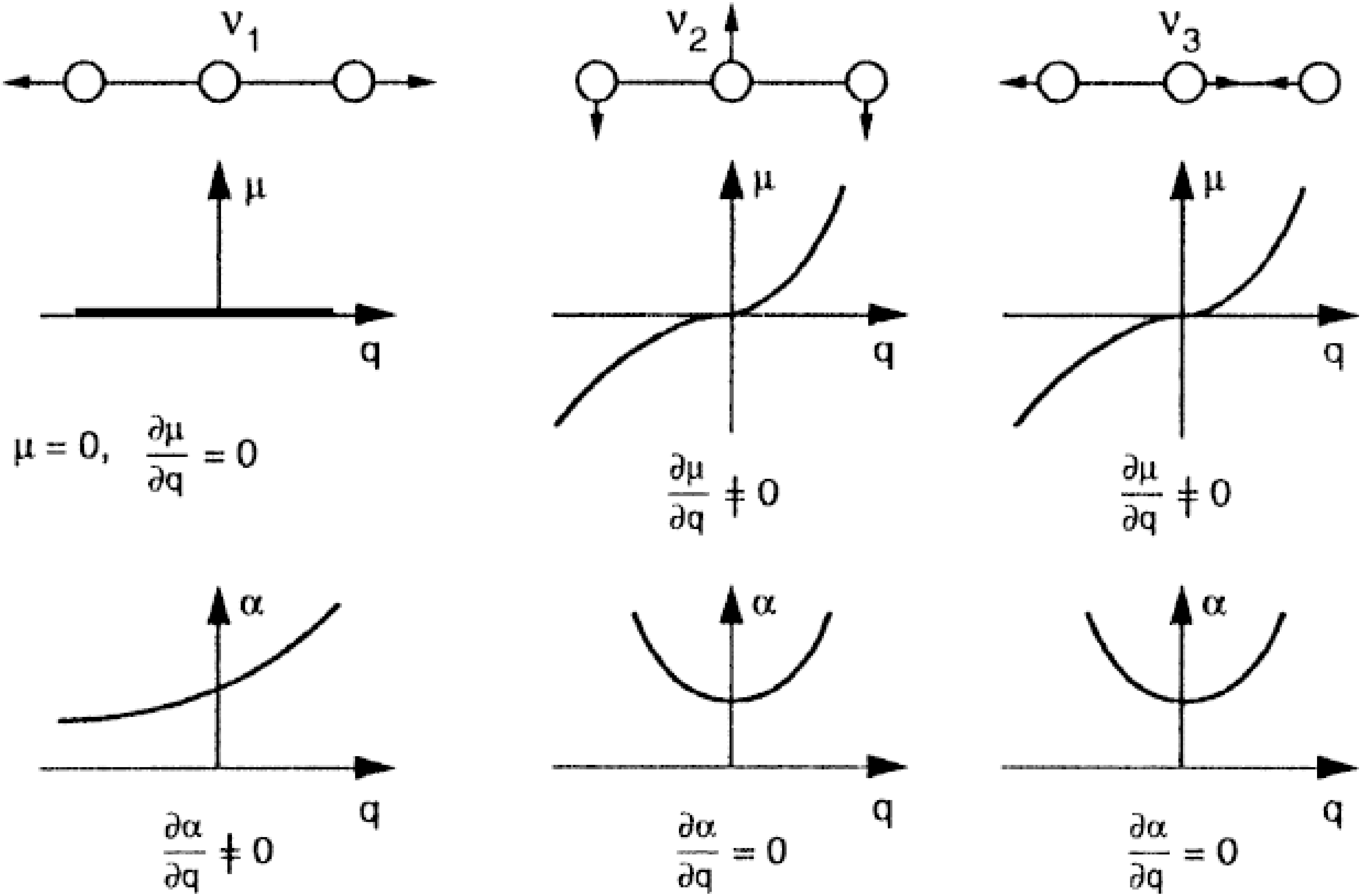
When a substances (in any state) is irradiated with a monochromatic light of definite frequency(v),the light scattered at right angle to the incident light contains lines of **1.** Incident frequency and **2.**Also of lower frequency

Sometimes lines of higher frequency are also obtained that of the incident beam will be scattered. It is called **Raman scattering.**

The line with lower frequency are called **Stoke's lines**.

Also, the line with higher frequency are called **Antistoke's lines**.

The line with the same frequency as that of the incident light is called **Rayleigh line**.


ν_1
ν_2
ν_3
μ
q
$\mu = 0, \quad \frac{\partial\mu}{\partial q} = 0$
$\frac{\partial\mu}{\partial q} \neq 0$
$\frac{\partial\mu}{\partial q} \neq 0$
α
$\frac{\partial\alpha}{\partial q} \neq 0$
$\frac{\partial\alpha}{\partial q} = 0$
$\frac{\partial\alpha}{\partial q} = 0$

Classical Picture of Raman

Induced Polarization

Polarizability

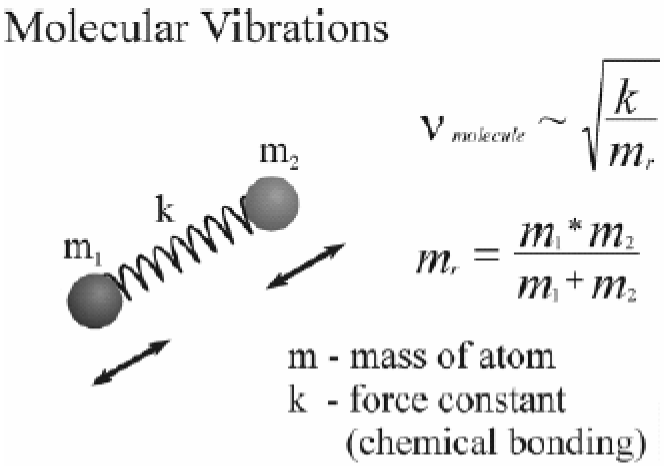
$$E(x,t) = E_0 \cos(\omega t - kx)$$

$$\mu = \alpha \cdot E$$

$$\mu = \alpha \cdot E_0 \cdot \cos(\omega_L t)$$

$\alpha = \alpha(Q)$, Q is the vibrational coordinate,

$$\alpha = \alpha_0 + \left[\frac{\partial \alpha}{\partial Q}\right] \cdot Q + \cdots , \qquad Q = Q_0 \cdot \cos(\omega_M t)$$



Molecular Vibrations

$$\nu_{molecule} \sim \sqrt{\frac{k}{m_r}}$$

$$m_r = \frac{m_1 * m_2}{m_1 + m_2}$$

m - mass of atom
k - force constant
(chemical bonding)

$$\mu = \alpha \cdot E_0 \cdot \cos(\omega_L t) + \left[\frac{\partial \alpha}{\partial Q}\right] \cdot Q_0 \cdot E_0 \cdot \cos(\omega_M t) \cdot \cos(\omega_L t)$$

$$\mu = \alpha \cdot E_0 \cdot \cos(\omega_L t) + \left[\frac{\partial \alpha}{\partial Q}\right] \cdot Q_0 \cdot E_0 \{\underline{\cos[(\omega_L - \omega_M)t)]} + \underline{\cos[(\omega_L + \omega_M)t]}\}$$

Stokes Raman

Anti-Stokes Raman

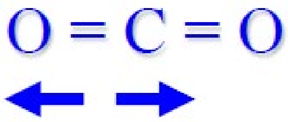
Raman Spectroscopy

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

⇒*Symmetric molecules*

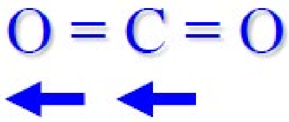
IR-active vibrations are not Raman-active.

Raman-active vibrations are not IR-active.



$O = C = O$

Raman active
IR inactive

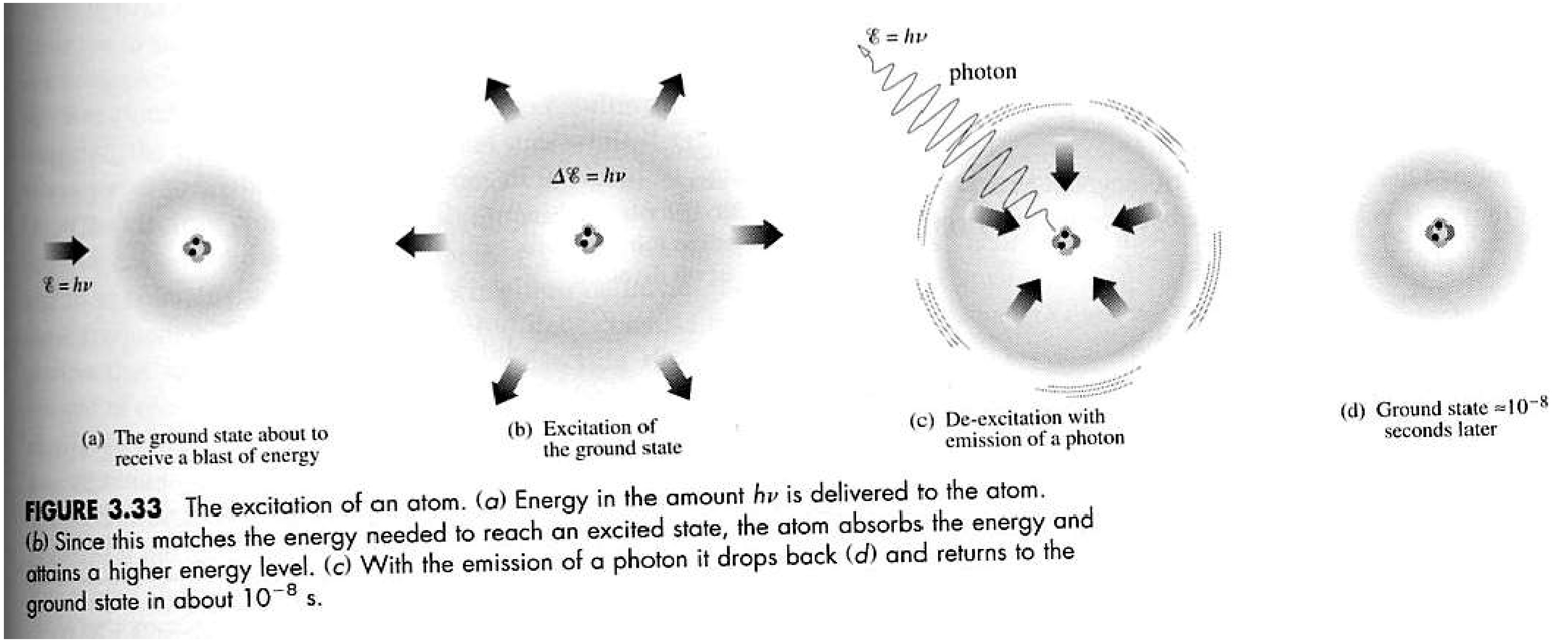


$O = C = O$

Raman inactive
IR active

Raman Spectroscopy

Rayleigh Scattering:- Occurs when incident EM radiation induces an oscillating dipole in a molecules, which is re-radiated at the same frequency.



(a) The ground state about to receive a blast of energy

(b) Excitation of the ground state

(c) De-excitation with emission of a photon

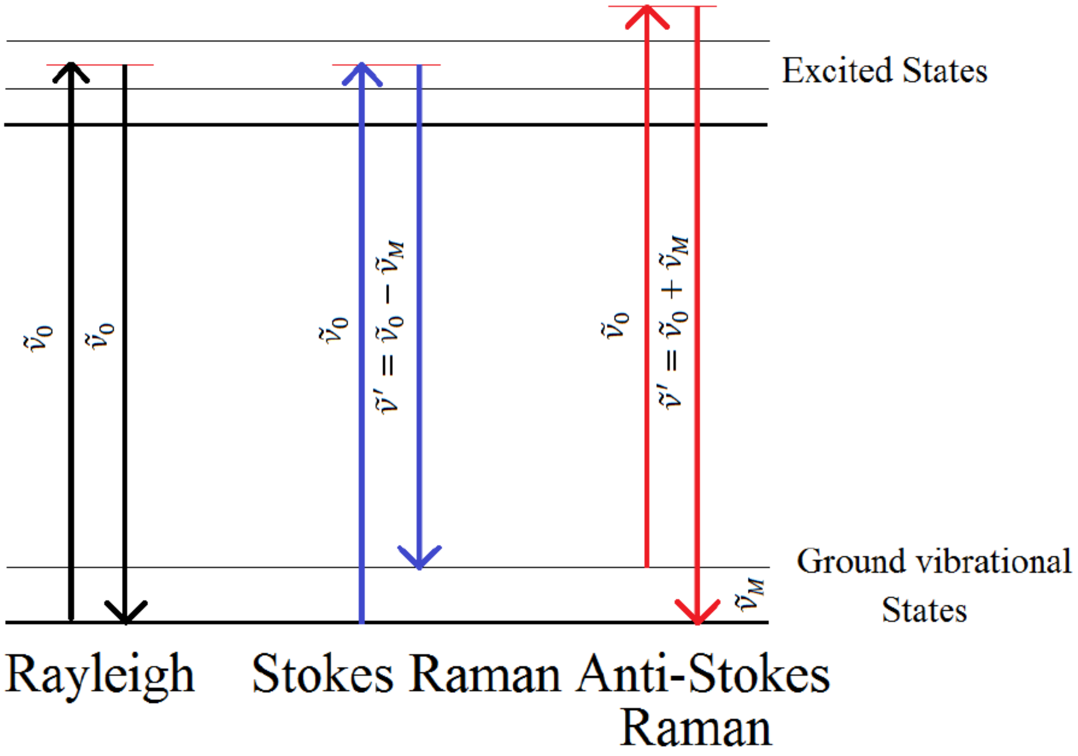
(d) Ground state $\approx 10^{-8}$ seconds later

FIGURE 3.33 The excitation of an atom. (*a*) Energy in the amount $h\nu$ is delivered to the atom. (*b*) Since this matches the energy needed to reach an excited state, the atom absorbs the energy and attains a higher energy level. (*c*) With the emission of a photon it drops back (*d*) and returns to the ground state in about 10^{-8} s.

- Elastic (λ does not change)
- Random direction of emission
- Little energy loss

$$(E_{sc})_\theta = \frac{8\pi^4(\alpha')^2(1+\cos^2\theta)E_0}{\lambda^4 d^2}$$

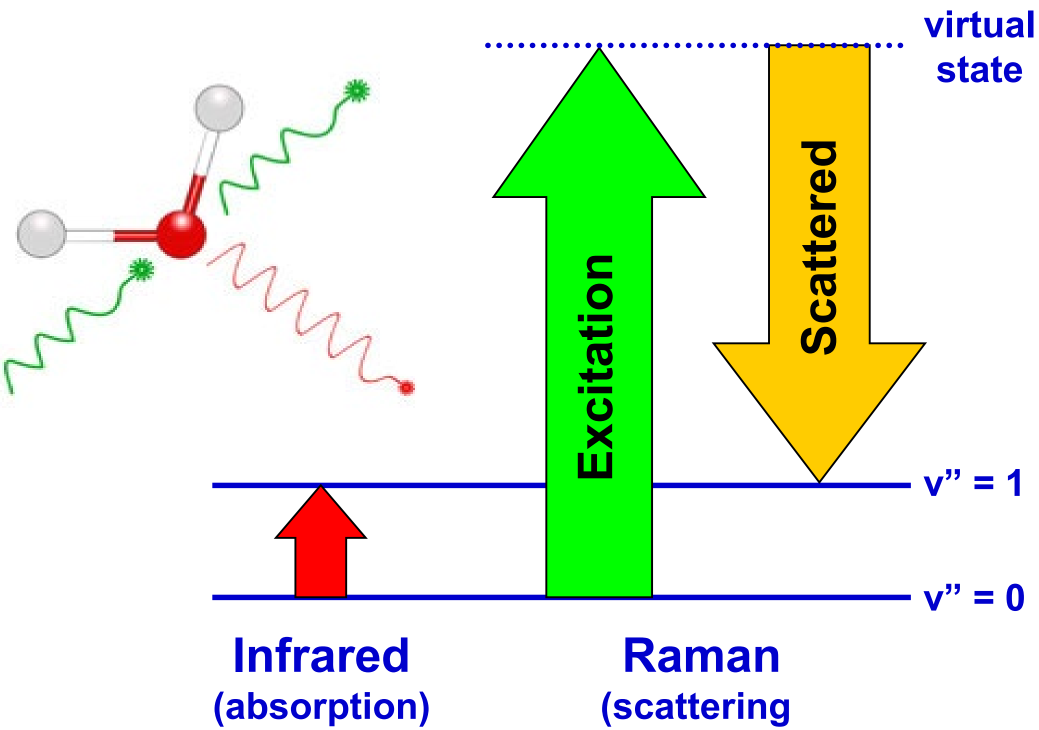
Raman Spectroscopy



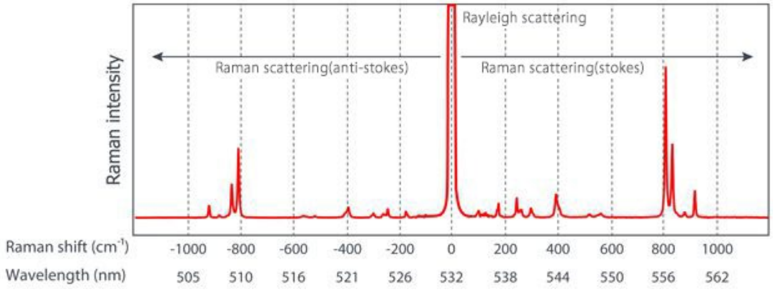
This difference is called **Raman frequency** or **Raman shift.**

Raman Spectroscopy

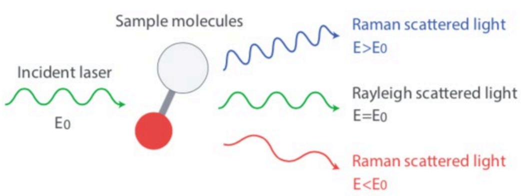
1 in 10^7 photons is scattered inelastically

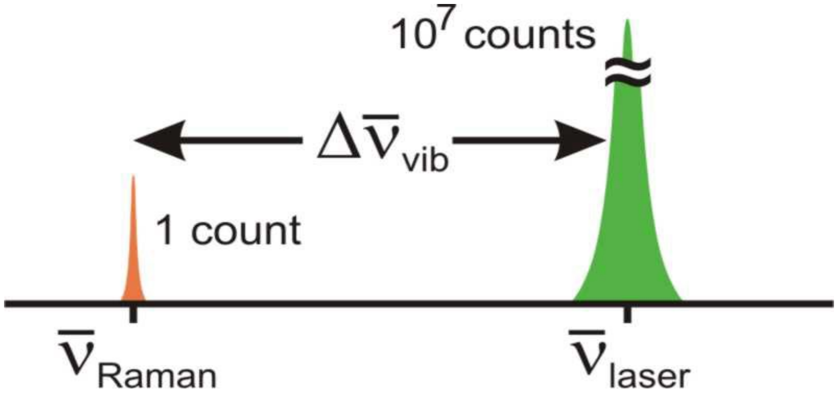


Rotational Raman
Vibrational Raman
Electronic Raman



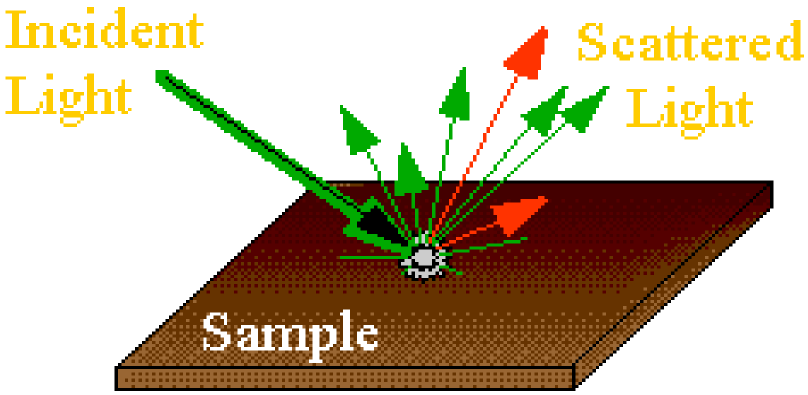
Scattering of light by molecules





Raman Scattering

Selection rule: Δv = ±1
Overtones: Δv = ±2, ±3, …



$$\mu_z(t) = \alpha_{zz}^{equil}\vec{E}_{\max}\cos 2\pi\nu_0 t +$$

$$\boxed{\frac{1}{2}\frac{d\alpha_{zz}}{dr}\Delta r_{\max}}\vec{E}_{\max}\cos 2\pi(\nu_0+\nu_{vib})t +$$

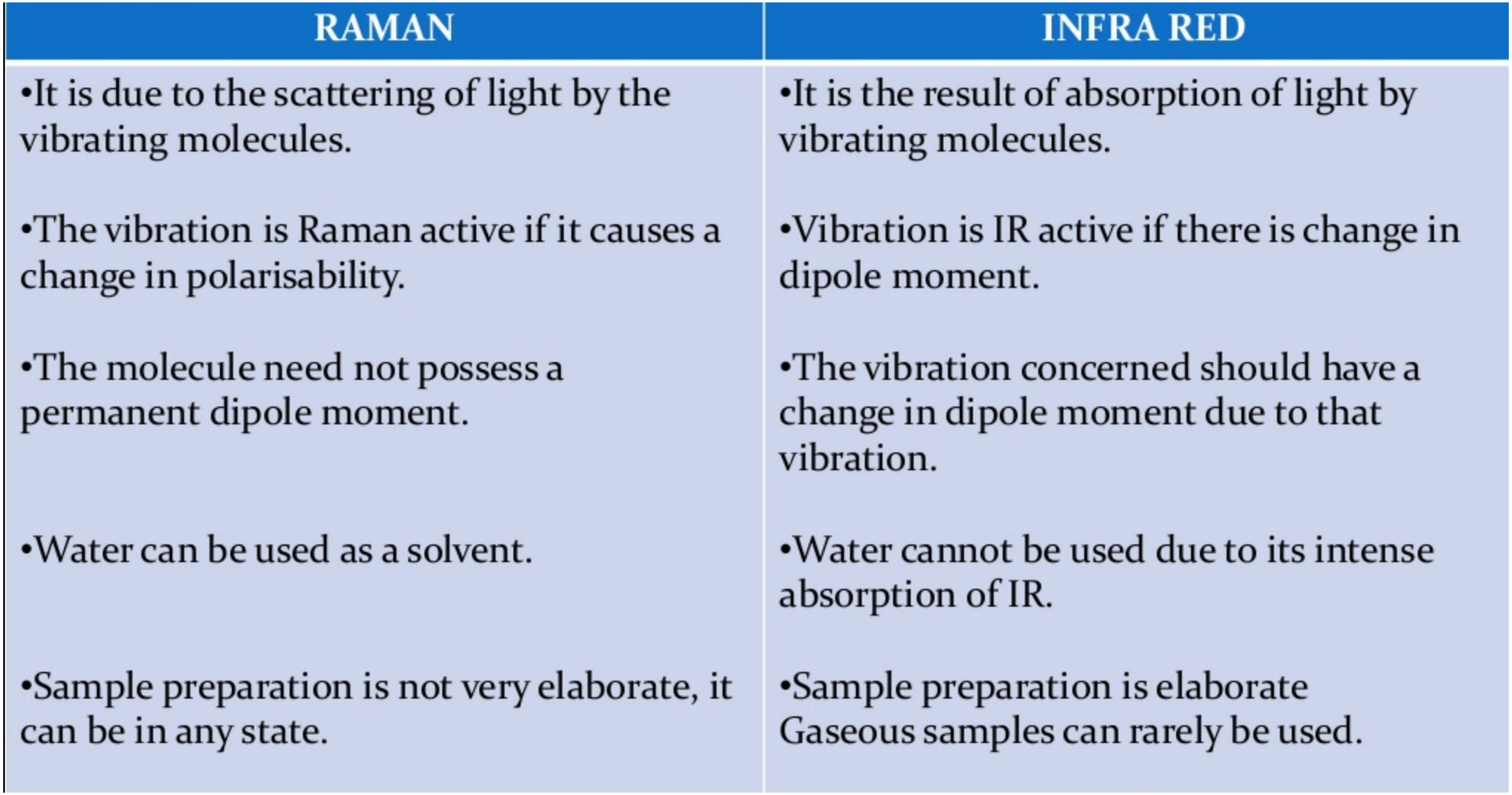
$$\boxed{\frac{1}{2}\frac{d\alpha_{zz}}{dr}\Delta r_{\max}}\vec{E}_{\max}\cos 2\pi(\nu_0-\nu_{vib})t$$

Must also have a change in polarizability

Classical Description does not suggest any difference between Stokes and Anti-Stokes intensities

$$\frac{N_1}{N_0} = e^{-\frac{h\nu_{vib}}{kT}}$$

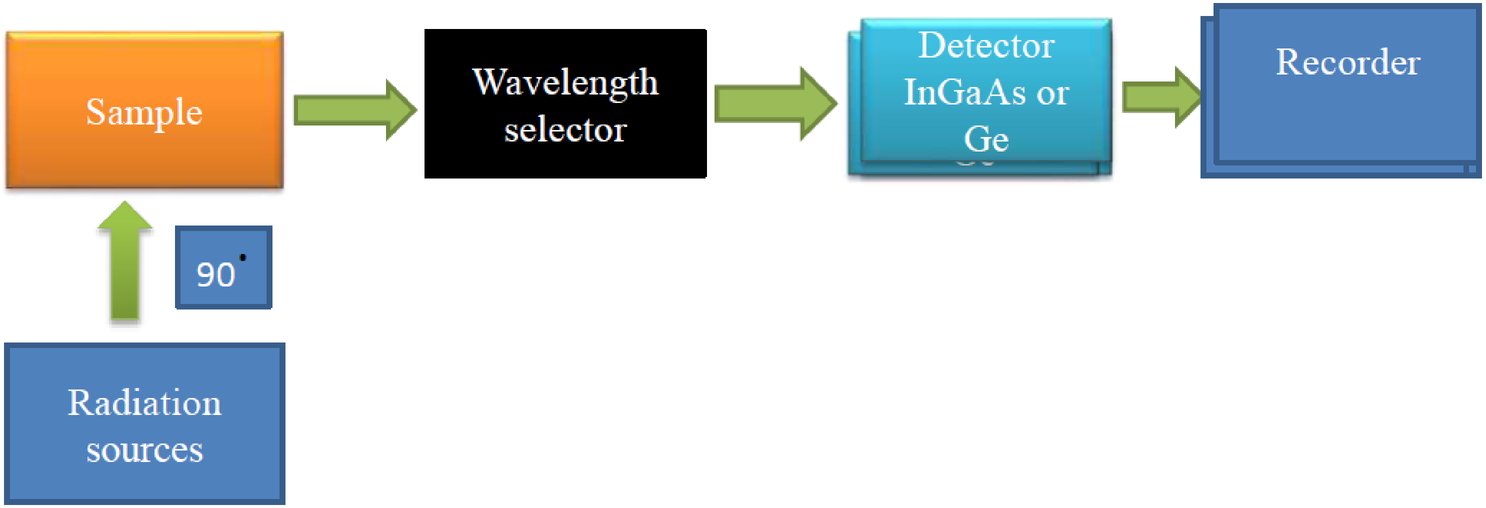
Raman vs infrared



RAMAN	INFRA RED
•It is due to the scattering of light by the vibrating molecules.	•It is the result of absorption of light by vibrating molecules.
•The vibration is Raman active if it causes a change in polarisability.	•Vibration is IR active if there is change in dipole moment.
•The molecule need not possess a permanent dipole moment.	•The vibration concerned should have a change in dipole moment due to that vibration.
•Water can be used as a solvent.	•Water cannot be used due to its intense absorption of IR.
•Sample preparation is not very elaborate, it can be in any state.	•Sample preparation is elaborate Gaseous samples can rarely be used.

Raman Spectroscopy

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



Sample

Wavelength selector

Detector InGaAs or Ge

Recorder

90°

Radiation sources

Raman Spectroscopy - lasers

- Lasers are generally the only source strong enough to scatter lots of light and lead to detectable raman scattering.
- Lasers operate using the principle of stimulated emission.
- Electronic population inversion is required to achieve gain via stimulated emission (before the fluorescence lifetime is reached)
- Population inversion is achieved by "pumping" using lots of photons in a variety of laser gain media

S.No.	Laser	wavelength
01	Nd:YAG	1064nm
02	He:Ne	633nm
03	Argon ion	488nm
04	GaAlAs diode	785nm
05	Co_2	10600nm
06	Ti-Sapphire	800nm

Raman Spectroscopy - lasers

A :- He:Ne laser

- Filled with 7:1 He & Ne gas optimum output of 6328 Å
- High voltage excitation is preferred

B :- Nd:YAG System

- A typical laser system –the neodymium-doped yttrium aluminum garnet or Nd+3
- YAG is a cubic crystalline material
- Crystal field splitting causes electronic energy level splitting
- Nd:YAG laser are optically pumped using a flash tube or laser diodes.
- These are the one of the most common type of laser.
- It emits 1064 nm wavelength

Raman Spectroscopy - filters

- It is therefore essential to have monochromatic radiations.
- For getting monochromatic radiations filters are used.
- They may be made of nickel oxide glass or quartz glass.
- Sometimes a suitable colored solution such as an aqueous solution of ferricyanide or iodine in CCl_2 may be used as a monochromator.

Raman Spectroscopy – sample holder

- For the study of raman effect the type of sample holder to be used depends upon the intensity of sources ,the nature and availability of the sample.

- The study of raman spectra of gases requires samples holders which are generally bigger in size than those for liquids.

- Solids are dissolved before subjecting to raman spectrograph.
- Any solvents which is suitable for the ultraviolet spectra can be used for the study of raman spectra.

- **Water** is regarded as **good solvents** for the study of inorganic compounds in raman spectroscopy.

Raman Spectroscopy – detectors

- 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.

Raman Spectroscopy – advantages

- Water can be used as solvent.
- Very suitable for biological samples in native state (because water can be used as solvent).
- Although Raman spectra result from molecular vibrations at IR
- frequencies, spectrum is obtained using visible light or NIR
- radiation.
- =>Glass and quartz lenses, cells, and optical fibers can be used.
- Standard detectors can be used.
- Few intense overtones and combination bands => few spectral overlaps.
- Totally symmetric vibrations are observable.
- Raman intensities a to concentration and laser power.

IR vs Raman Spectroscopy

- Simpler and cheaper instrumentation.
- Less instrument dependent than Raman spectra because IR spectra are based on measurement of intensity ratio.
- Lower detection limit than (normal) Raman.
- Background fluorescence can overwhelm Raman.
- More suitable for vibrations of bonds with very low polarizability (e.g. C–F).