# SPECTROSCOPY

- interaction of EMR with matter.

- EMR → dual characters

    → electric and magnetic fields are perpendicular
    → travel with velocity of light.

## Molecular Spectra:

- from HOMO to LUMO.

- Band spectra due to → rotational

                 → vibrational

$$\Delta E = E_2 - E_1$$

$$\Delta E = h\gamma$$

- Absorption spectra → from lower energy to higher energy.

- Emission spectra → from higher energy to lower energy.
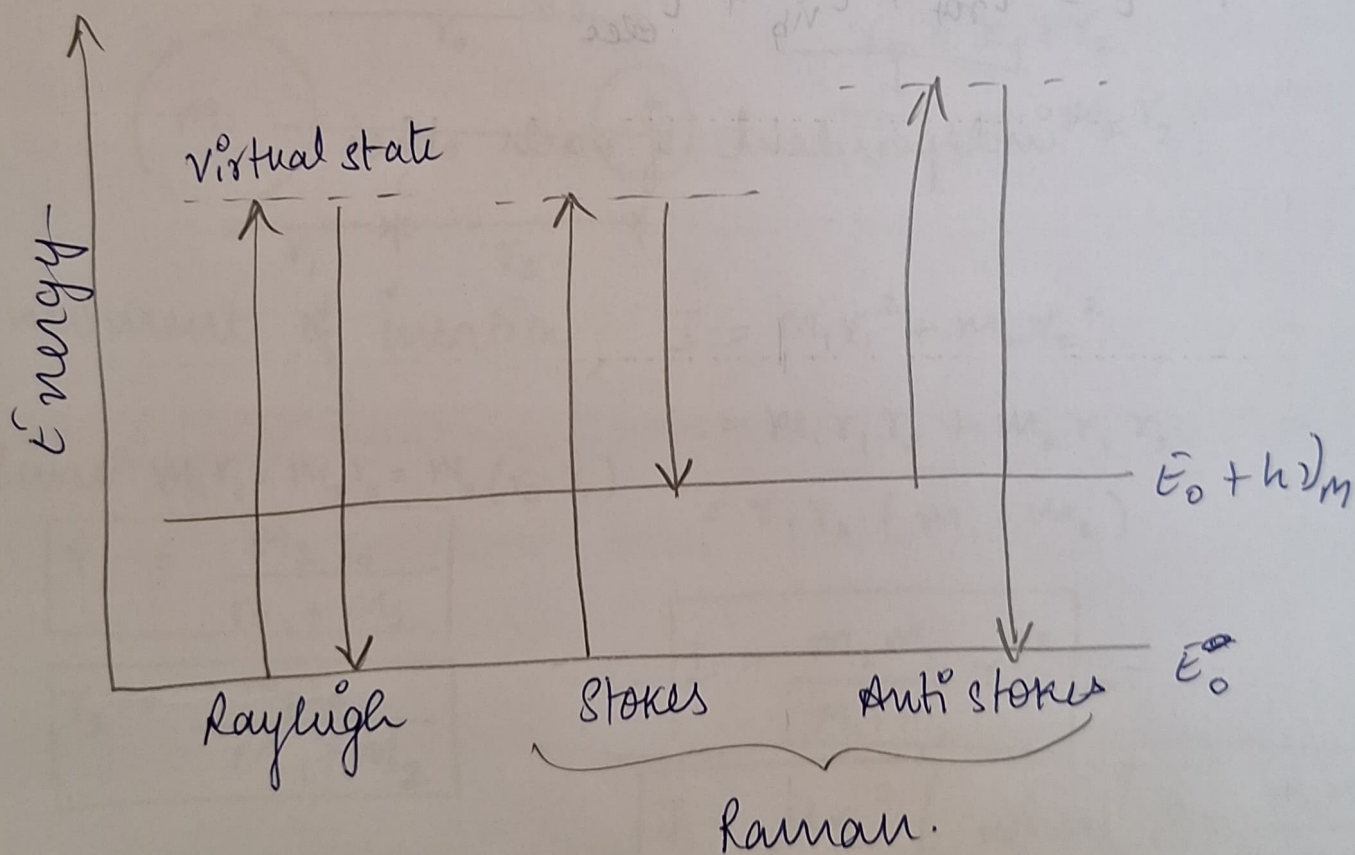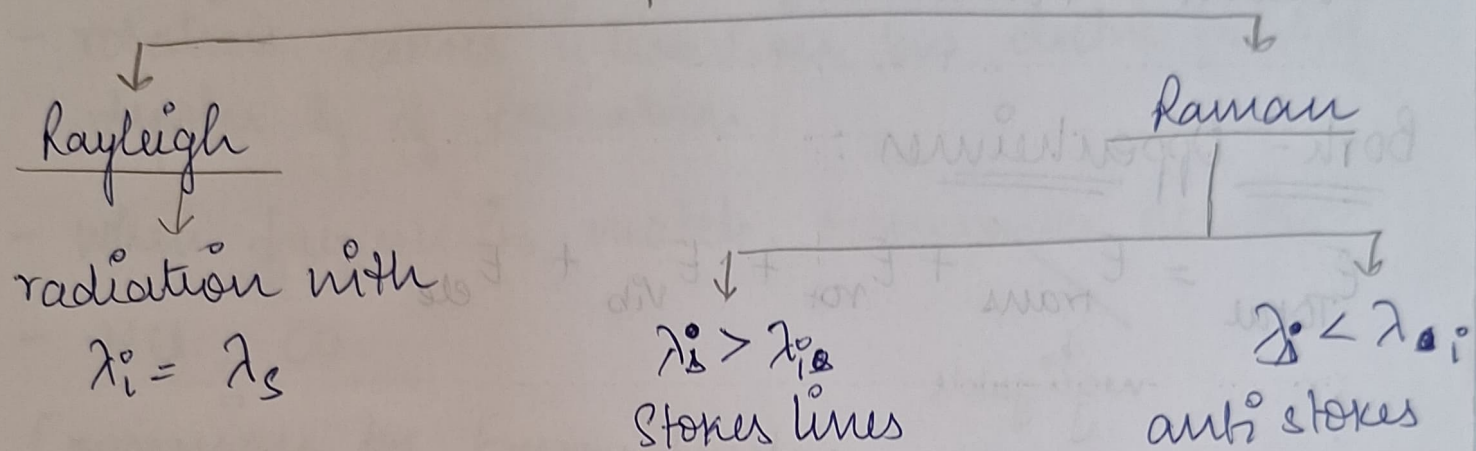
$$\bar{\gamma} = \frac{1}{\lambda} \qquad E = hc\bar{\gamma}$$
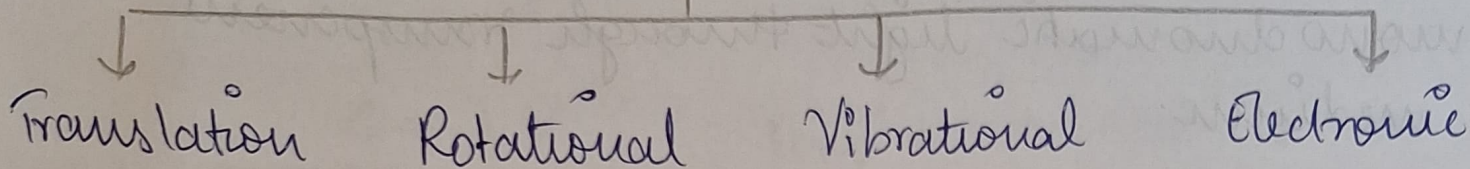
$$c = \lambda v \qquad 1\,cm^{-1} = 1.99 \times 10^{-23}\,J$$

| REGION | CHARACTERISTICS |
|---|---|
| Radiofrequency | - $10\,cm \rightarrow 1\,cm$<br>- Nuclear & electronic spin reversal. |
| Microwave | - $1\,cm \rightarrow 100\,\mu m$<br>- rotational spectroscopy. |
| IR region | $100\,\mu m - 1\,\mu m$<br>Vibrational spectroscopy |
| Visible & UV | $1\,\mu m$ to $10\,nm$<br>Electronic states, change in distribution of valence $e^-$ |
| X rays | $10\,nm - 100\,pm$<br>Change in electronic dist. of inner $e^-$ |
| $\gamma$ rays | $100\,pm - 1\,pm$<br>rearrangement of nuclear particles. |

# Raman Spectroscopy :

- monochromatic light through transparent medium.

Rayleigh ———————————————→ Raman

**Rayleigh**

radiation with
$$\lambda_i = \lambda_s$$

$\lambda_s^o > \lambda_{i_o}^o$
Stokes lines

$\lambda_s^o < \lambda_{o_i}^o$
anti stokes

Energy →

virtual state

Rayleigh          Stokes          Anti stokes

$E_o + h\nu_m$

$E_o^o$

⎵————— Raman —————⎵

# Types of Energy

```
                    |
    ↓           ↓           ↓              ↓
Translation  Rotational   Vibrational    Electronic
```

## Born - Oppenheimer :

$$E_{Total} = \cancel{E_{trans}} + E_{rot} + E_{vib} + E_{ele}$$

↓
negligable

$$\therefore E = E_{rot} + E_{vib} + E_{elec}$$

↓
independent of each other

# ROTATIONAL SPECTROSCOPY:

- microwave region.

- has to possess permanent dipole moment

- rotation causes interaction b/w electric field of dipoles & of radiation.

- when frequencies match, resonance occurs.

- HCl., CO.

## Expression for Energy levels:
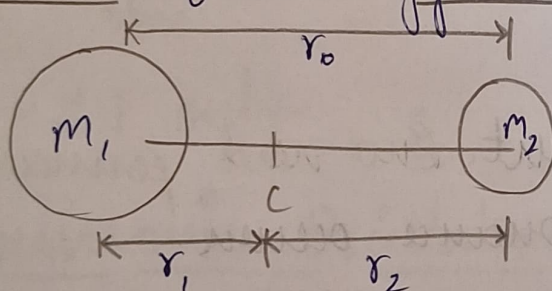


$$r_0 = r_1 + r_2$$

$$m_1 r_1 = m_2 r_2$$

moment of inertia, $I = m_1 r_1^2 + m_2 r_2^2$

$$= m_1 r_1 r_2 + m_2 r_1 r_2$$

Since $m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$

$$= r_1 r_2 (m_1 + m_2)$$

$$\boxed{r_1 = \frac{m_2 r_0}{m_1 + m_2}}$$

$$\boxed{r_2 = \frac{m_1 r_0}{m_1 + m_2}}$$

$$\therefore \boxed{I = \frac{m_1 m_2}{m_1 + m_2} r_0^2}$$

$$\boxed{I = \mu r_0^2} \quad \text{where} \quad \boxed{\mu = \frac{m_1 m_2}{m_1 + m_2}}$$

- rotational energy,

$$E_r = \frac{1}{2} I \omega^2$$

$$E_r = \frac{L^2}{2I} \qquad \therefore L = I \omega \qquad \text{where} \quad L = \frac{\sqrt{J(J+1)}}{2\pi}$$

$$\therefore E_J = \frac{h}{8\pi^2 I c} J(J+1)$$

$$\boxed{\varepsilon_J = BJ(J+1)} \quad \text{where } B = \frac{h}{8\pi^2 I c}$$

$$\boxed{\Delta J = \pm 1 \text{ only}}$$

- First line at $2B$ and distance between any two lines is also $2B$.

## VIBRATIONAL SPECTROSCOPY:

- IR radiation
- change in dipole moment (no need permanent)
- frequency matches → resonance occurs.

$CO_2$ → no permanent dipole

→ symmetric / asymmetric / bending stretch

<u>IR active</u>

## Simple Harmonic Oscillator:

- every type of bond has unique vibrational frequency
- not static but vibrating.

oscillation frequency,

$$\upsilon_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\bar{\upsilon}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \rightarrow \text{ in terms of wave no.}$$

$$E_\upsilon = \left(\upsilon + \frac{1}{2}\right) h \upsilon_{osc} \qquad k \rightarrow \text{ bond strength}$$

- energy levels are equally spaced, dist. b/w
  2 is $\upsilon_{osc}$
- $\Delta \upsilon = \pm 1$ only, $\varepsilon_0 \rightarrow$ zero point energy.

### Anharmonic Oscillator :

$$PE = D_{eq}\left[1 - e^{a(r_0 - r)}\right]^2$$

where $D_{eq} \rightarrow$ depth of curve

$r_0 \rightarrow$ bond length

$$\varepsilon_\upsilon = \frac{E_\upsilon}{hc}$$

$$= \left(\upsilon + \frac{1}{2}\right) \bar{\upsilon}_e - \left(\upsilon + \frac{1}{2}\right)^2 \bar{\upsilon}_e \, x_e$$

where $x_e \rightarrow$ anharmonicity const.

$\bar{\upsilon}_e \rightarrow$ oscillation frequency

$\upsilon \rightarrow$ vibrational quantum no.

- Space b/w levels decreases as vibrational quantum no. increases

$$\Delta V = \pm \text{anything}$$

- Change in dipole moment.

$$V_0 \rightarrow V_1 \text{ fundamental}$$
$$V_0 \rightarrow V_2 \text{ first overtone}$$
$$V_0 \rightarrow V_3 \text{ second overtone}$$

- Hot bands → at higher temperatures, additional lines in the spectrum from higher energy levels.

# ELECTRONIC SPECTROSCOPY :

- HOMO to LUMO.
- UV visible region
- $\sigma$ to $\sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
- can occur with any molecule
- vibrational changes → coarse structure
  rotational changes → fine structure.
- Homonuclear molecules info can be obtained
  ⇒ significance of electronic spectroscopy

# Vibrational Coarse Structure:

- ground state → $\varepsilon''$ $v''$
- excited state → $\varepsilon'$ $v'$

| (0,0) | 1,0 | 2,0 | 3,0 | 4,0 |
|---|---|---|---|---|
| | | | | |

$cm^{-1} \longrightarrow$
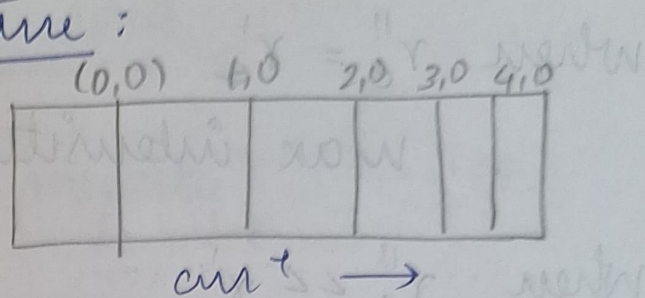
- start from $v''=0$, spectrum called PROGRESSION
- at higher levels, lines converge, anharmonicity

# Intensity of Lines:

- no selection rule
- excited state, more internuclear distance cause antibonding.
- start from centre cause centre max probability

# FRANK CONDON PRINCIPLE:

[ An electronic transition takes place so rapidly that the vibrating molecule doesn't change its intermolecular distance during transition appreciably.

- always verticle transitions.
- when $r_e'' < r_e'$

    max intensity at v,o line

- when $r_e'' = r_e'$

      max intensity at 0,0 line

- when $r_e'' \ll r_e'$

      • continuum since transition results in molecule breaking dissociation energy