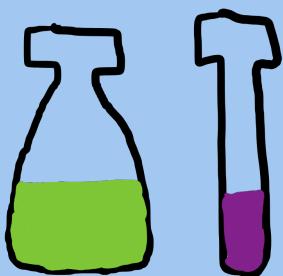


Chemistry



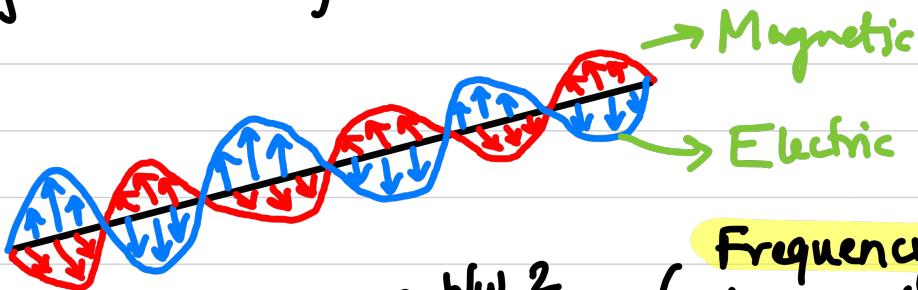
Molecular Spectroscopy

U-1 Molecular Spectroscopy

→ Branch which deals with electromagnetic radiation with matter

→ Important features of electromagnetic radiation

- i) Dual character → particle & wave
- ii) Waves are associated w electric & magnetic fields oscillating \perp^{m} to each other



Wavelength → distance b/w 2 successive crests & troughs
 $\lambda ; \text{m, nm, } \text{\AA}$

Frequency
↳ No of cycles completed in certain amount of time $\nu ; \text{Hz, s}^{-1}$

Wave No. → No of complete waves of cycles in unit distance
 $\bar{\nu} ; \text{cm}^{-1}$

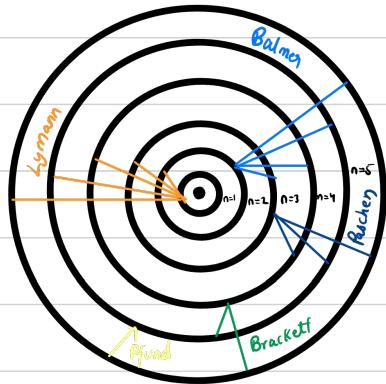
$$\bar{\nu} = \frac{1}{\lambda} \quad *$$

Energy → $E = h\nu$
 $h = 6.625 \times 10^{-34} \text{ Js}$

$$c = \lambda\nu \quad *$$

Atomic Spectra

- Arises due to electronic transitions from 1 atomic orbital to another
- Gives rise to line spectra



Molecular Spectra

- Arises due to transitions from HOMO to LUMO
- Gives rise to band spectra due to rotational & vibrational transition along w/ electronic

Quantisation of Energy

→ or quantise

- Energy levels in atoms/molecules are discrete
- Energy can be absorbed only in packets
 - called quanta
- Freq. of light absorbed during transition of 2 energy levels depends on difference in energy b/w 2 energy levels

$$\Delta E = E_2 - E_1 \quad = h\nu$$

Absorption spectrum

- Observed when atom/ molecule absorbs energy & moves from lower to higher energy level



Emission Spectrum

- Arises when molecule comes from higher to lower energy level



Spectroscopic Units

$$E = h\nu$$

expressed in joules

$$\bar{\nu} = \frac{1}{\lambda}$$

$$\& c = \lambda\nu$$

$$E = hc\bar{\nu}$$

$$\text{So, } c = \frac{\nu}{\bar{\nu}} \Rightarrow \nu = c\bar{\nu}$$

$$E = hc\bar{\nu} \Rightarrow$$

$$\boxed{\bar{\nu} = \frac{E}{hc}}$$

* Spectroscopic unit of Energy is cm^{-1}

↳ Energy is expressed in wav

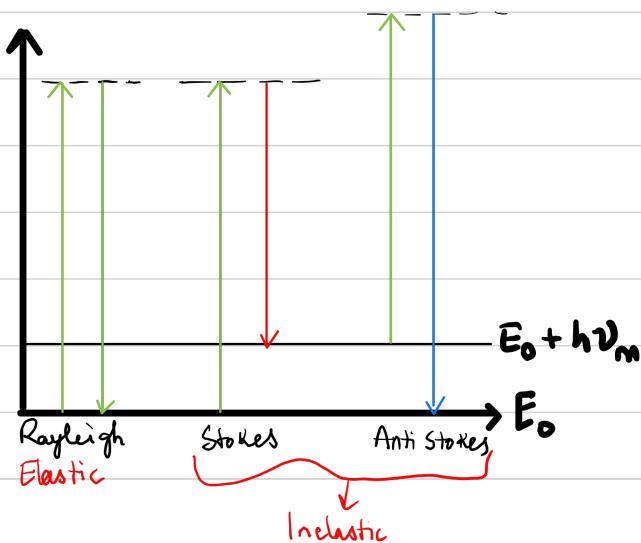
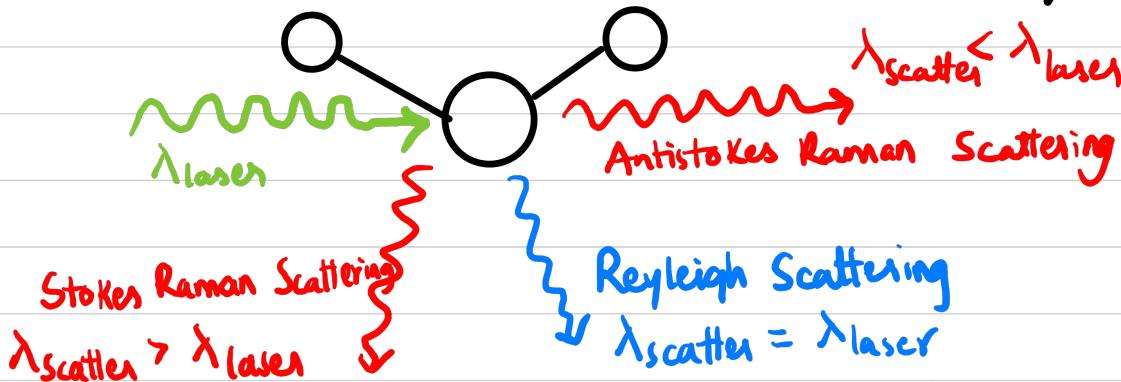
$$1 \text{ cm}^{-1} = 1.99 \times 10^{-23} \text{ J}$$

Different Region of Electromagnetic Spectrum

Region	Wavelength	Other Info
Radiofrequency	10m - 1cm	NMR, ESR Nuclear & e^- spin reversal
Microwave	1cm - 100mm	Rotational spectroscopy Rotational levels
Infrared	100μm - 1μm	Vibrational spectroscopy Vibrational levels
Visible & UV	1μm - 10nm	UV - Visible spectroscopy Electronic States Change in electronic distribution of valence electrons
X-ray region	10nm - 100pm	X-ray spectroscopy Change in electronic distribution of inner electrons
γ -ray region	100pm - 1pm	γ -ray spectroscopy Rearrangement of nuclear particles

Raman Spectroscopy

→ When monochromatic radiation passes through transparent medium, based on scattered radiation's wavelength there are 3 types



Different type of energies possessed by molecule

↓ ↓ ↓ ↓

Translational Rotational Vibrational Electronic

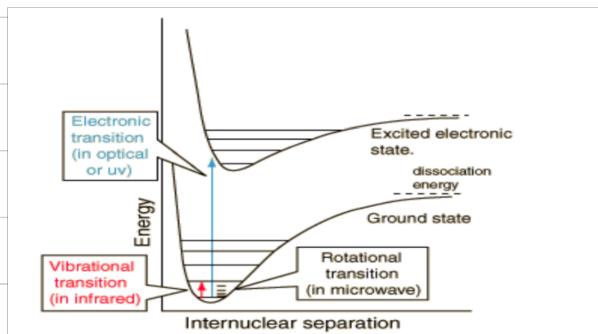
Total Energy = $E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$
↳ but usually negligible
so!!

Born - Oppenheimer Approximation

$$T.E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$$

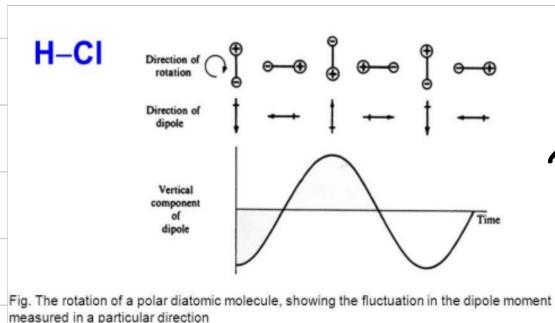
↳ all 3 are independent of each other

$$E_{\text{rot}} \ll E_{\text{vib}} \ll E_{\text{elec}}$$



Rotational Spectroscopy

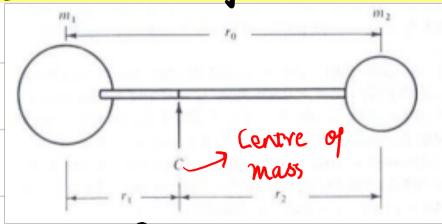
- It absorbs in **microwave region**
- It must possess permanent dipole moment
- Rotations of molecule w PDM will cause change in electric dipoles which interact with electric component of Electromagnetic Radiation



H₂ & CO → show Rotational spectra
H₂, Cl₂, CO₂ → Don't

When frequencies match, resonance occurs & molecule absorbs energy & goes to higher rotaional levels & rotational spectrum is recorded

Derivation for Rotational energy levels



$$\bullet \quad r_0 = r_1 + r_2$$

→ By balancing moments,

$$m_1 r_1 = m_2 r_2$$

and,

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 \\ &= \frac{m_2 r_2 r_1^2}{r_1} + \frac{m_1 r_1 r_2^2}{r_2} \\ &= r_1 r_2 (m_1 + m_2) \end{aligned}$$

$$\text{and, } m_1 r_1 = m_2 r_2 = m_2 (r_0 - r_1)$$

$$(m_1 + m_2) r_1 = m_2 r_0$$

$$\text{and, } m_2 r_2 = m_1 (r_0 - r_2)$$

$$(m_1 + m_2) r_2 = m_1 r_0$$

$$I = \frac{m_2 r_0}{m_1 + m_2} \times \frac{m_1 r_0}{m_1 + m_2} \times \cancel{m_1 + m_2}$$

$$= \frac{m_1 m_2 r_0^2}{m_1 + m_2} = \cancel{M} r_0^2$$

\cancel{M}
Reduced Mass

→ Rotational energy, $E_r = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} \quad (L = I \omega)$

and by Schrodinger's eq,

$$L = \frac{\sqrt{J(J+1)}}{2\pi} \cdot h$$

Rotational Quantum No

$J = 0, 1, 2, 3, \dots$

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

Joules

$$E_J = \frac{h}{8\pi^2 I c} \cdot J(J+1) \text{ cm}^{-1}$$

★

$$\text{Now, } B = \frac{\hbar}{8\pi^2 I c} \text{ cm}^{-1}$$

J

0

1

2

3

$$\epsilon_J = BJ(J+1)$$

$$B$$

$$2B$$

$$6B$$

$$12B$$

$$6 \quad \dots \quad 42B$$

$$5 \quad \dots \quad 30B$$

$$4 \quad \dots \quad 20B$$

$$3 \quad \dots \quad 12B$$

$$2 \quad \dots \quad 6B$$

$$1 \quad \dots \quad 2B$$

$$0 \quad \dots \quad 0$$

→ Gross Selection Rules

1) Molecule should possess P.D.M

2) $\Delta J = \pm 1$

$$\gamma_0 = \sqrt{\frac{I}{M}}$$

$$= \sqrt{\frac{\frac{n}{8\pi^2 \epsilon c} \cdot J(J+1)}{\mu}}$$

$$\rightarrow \Delta \epsilon_{J \rightarrow J+1} = \bar{\nu} = 2B J(J+1) \text{ cm}^{-1}$$

J

0

1

2

3

$$\Delta \epsilon_{J \rightarrow J+1}$$

$$2B \text{ cm}^{-1}$$

$$4B \text{ cm}^{-1}$$

$$6B \text{ cm}^{-1}$$

$$8B \text{ cm}^{-1}$$

$$\dots$$

$$5 \quad \dots \quad 30B$$

$$4 \quad \dots \quad 20B$$

$$3 \quad \dots \quad 12B$$

$$2 \quad \dots \quad 6B$$

$$1 \quad \dots \quad 2B$$

$$0 \quad \dots \quad 0$$

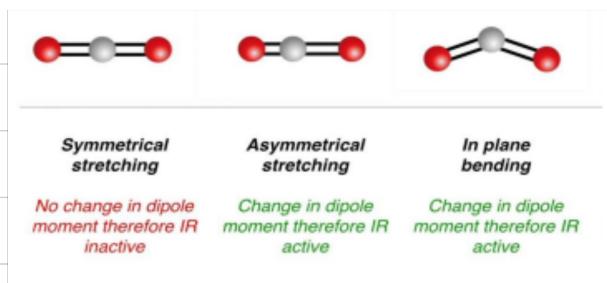
$$4B \quad 8B \quad 12B \quad \text{cm}^{-1}$$

Note: Made with Goodnotes

Some of the higher levels are populated at room temp

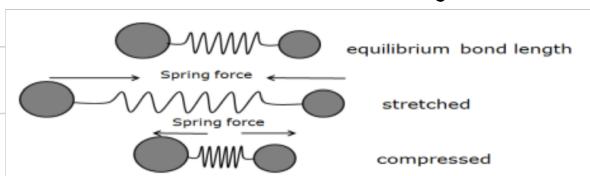
Vibrational Spectroscopy

- It absorbs IR radiation
 - Vibration must be associated with **change in dipole moment**.
 - Vibration can result in change in electric dipoles which interact with **electrical component** of EMR
 - When frequencies match, **Resonance** occurs & molecule absorbs energy & goes to higher vibrational levels and exhibits **vibrational spectrum**
 - HCl, CO, H₂O → Show vibrational spectra
H₂, U₂ → Don't
- except : CO₂ ⇒ No PDM but is IR active
cuz :



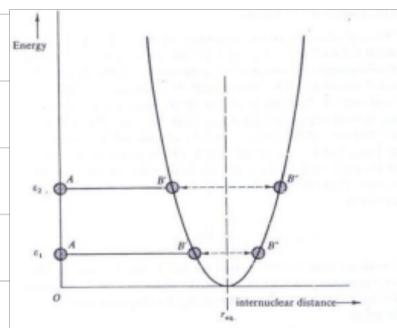
Vibrational Spectroscopy of diatomic molecule (Simple Harmonic Oscillator)

- Every bond in a molecule has unique natural vibrational frequency
- So, IR spectrum for every molecule is different and is like **fingertips of humans**
- Bonds are vibrating, not static



→ Obeys Hooke's Law

→ $E = \frac{1}{2} K (r - r_{eq})^2$ → gives parabolic curve



$$\rightarrow \nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz}$$

$$\bar{\nu}_{osc} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

$$\rightarrow E_v = \left(v + \frac{1}{2}\right) h\nu_{osc} \text{ Joules}$$

$$E_v = \left(v + \frac{1}{2}\right) \bar{\nu}_{osc} \text{ cm}^{-1}$$

v	E_v
0	$\bar{\nu}_{osc}/2 \text{ cm}^{-1}$
1	$3\bar{\nu}_{osc}/2 \text{ cm}^{-1}$
2	$5\bar{\nu}_{osc}/2 \text{ cm}^{-1}$

Vibrational Spectroscopy - Anharmonic Oscillator

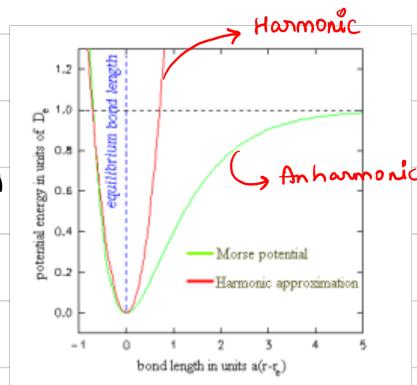
→ In Reality, Potential is anharmonic cuz when a bond is stretched beyond a point, it breaks & molecule dissociates.

→ By Schrodinger eq,

$$\epsilon_v = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e \chi_e \text{ cm}^{-1}$$

antiharmonicity constant

vibrational quantum number $\Rightarrow 0, 1, 2, 3 \dots$



Gross Selection Rules

→ Change in dipole moment should be there

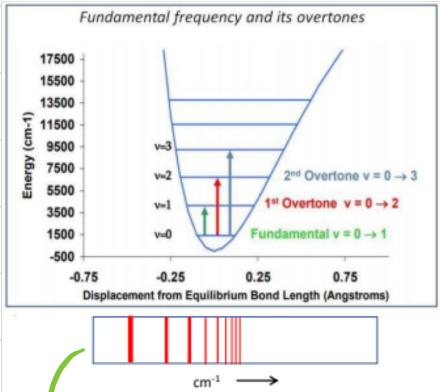
→ $\Delta v = \pm 1, \pm 2, \pm 3 \dots$

→ Most transitions start from $v=0$ (most populated)

$v=0 \rightarrow v=1 \rightarrow$ Fundamental frequency $\rightarrow \Delta E = \bar{\nu}_e (1 - 2\chi_e) \text{ cm}^{-1}$

$v=0 \rightarrow v=2 \rightarrow$ First overtone $\rightarrow \Delta E = 2\bar{\nu}_e (1 - 3\chi_e) \text{ cm}^{-1}$

$v=0 \rightarrow v=3 \rightarrow$ Second overtone $\rightarrow \Delta E = 3\bar{\nu}_e (1 - 4\chi_e) \text{ cm}^{-1}$



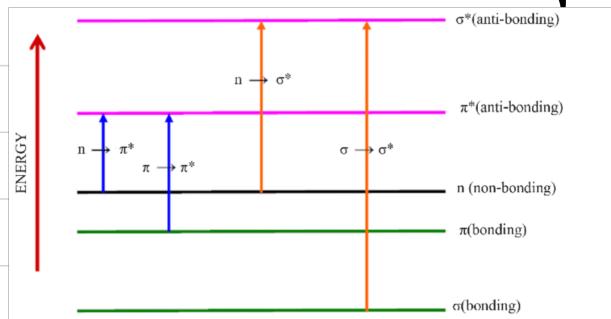
For higher values of v , spacing b/w lines in spectrum decreases

Note: At higher temp, additional values are visible in spectrum as higher vibrational levels also get populated, & lines originating from higher vibrational levels are called **hot bands**

$$\Delta E_{2 \leftarrow 1} = \bar{\nu}_e (1 - 4n_e) \text{ cm}^{-1}$$

Electronic Spectroscopy

→ Electronic transitions occur from **HOMO** to **LUMO**



→ Transitions in UV - Visible region

→ All molecules can undergo electronic transitions

Here, only transition occurs for

- i) $\sigma \rightarrow \sigma^*$
- ii) $\pi \rightarrow \pi^*$
- iii) $n \rightarrow \pi^*$

Born - Oppenheimer Approximation

$$E = E_r + E_v + E_e$$

↑ Total Energy ↑ Vibrational Energy
 ↓ Rotational Energy ↓ Electronic Energy

$$\text{and, } \Delta E_{\text{Total}} = \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E_{\text{elec}}$$

$$\Delta E_{\text{Total}} = \Delta E_{\text{rot}} + \Delta E_{\text{vib}} + \Delta E_{\text{elec}}$$

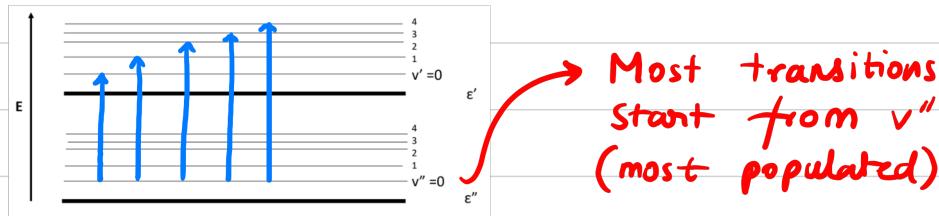
$$\Delta E_{\text{rot}} \times 10^6 \simeq \Delta E_{\text{vib}} \times 10^3 \simeq \Delta E_{\text{elec}}$$

→ Electronic Transitions are accompanied by vibrational & rotational changes
 ↳ coarse structure ↳ fine structure

→ It is used for finding more info about homonuclear species like H_2, N_2 which are inactive in IR & Microwave region

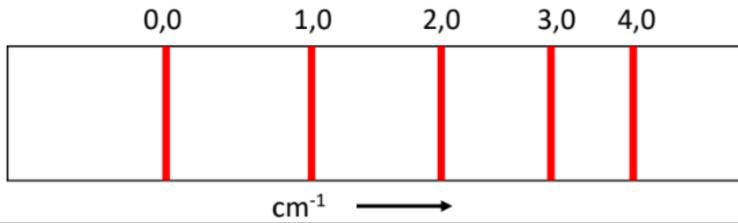
Vibrational Coarse Structure

- Ground state energy levels denoted by $\epsilon'' \& v''$
- Excited state energy levels denoted by $\epsilon' \& v'$
- No selection rules



- Resulting spectrum is called **progression** and lines are denoted by (v', v'')

Spectrum showing Progression

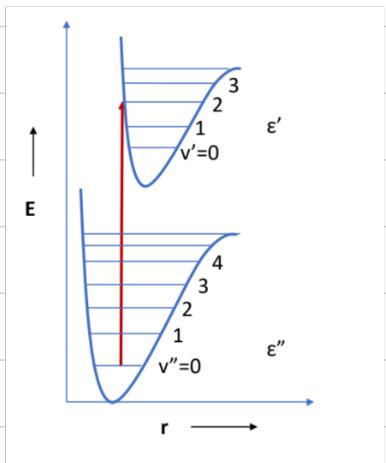


Franck - Condon Principle

→ All lines in spectra are not of same intensity though no selection rule exist

An electronic transition takes place so rapidly that a vibrating molecule doesn't change its **internuclear distance appreciably** during transition

Which means all are vertical transitions



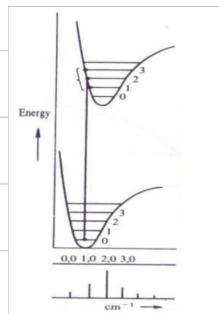
3 possibilities of vibrational-electronic transitions

r_e'' : internuclear distance of ground state
 r_e' : excited "

i) $r_e'' < r_e'$

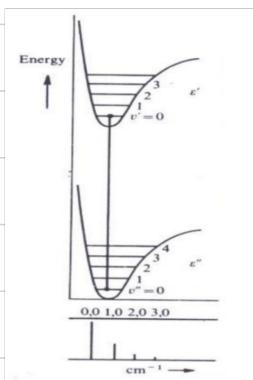
→ Maximum Intensity
for $(v', 0)$ line

vibrational level in
excited state to
which electronic transition
takes place



ii) $r_e'' = r_e'$

→ Max Intensity
for $(0,0)$ line



iii) $r_e'' > r_e'$

→ Spectrum shows
continuum

