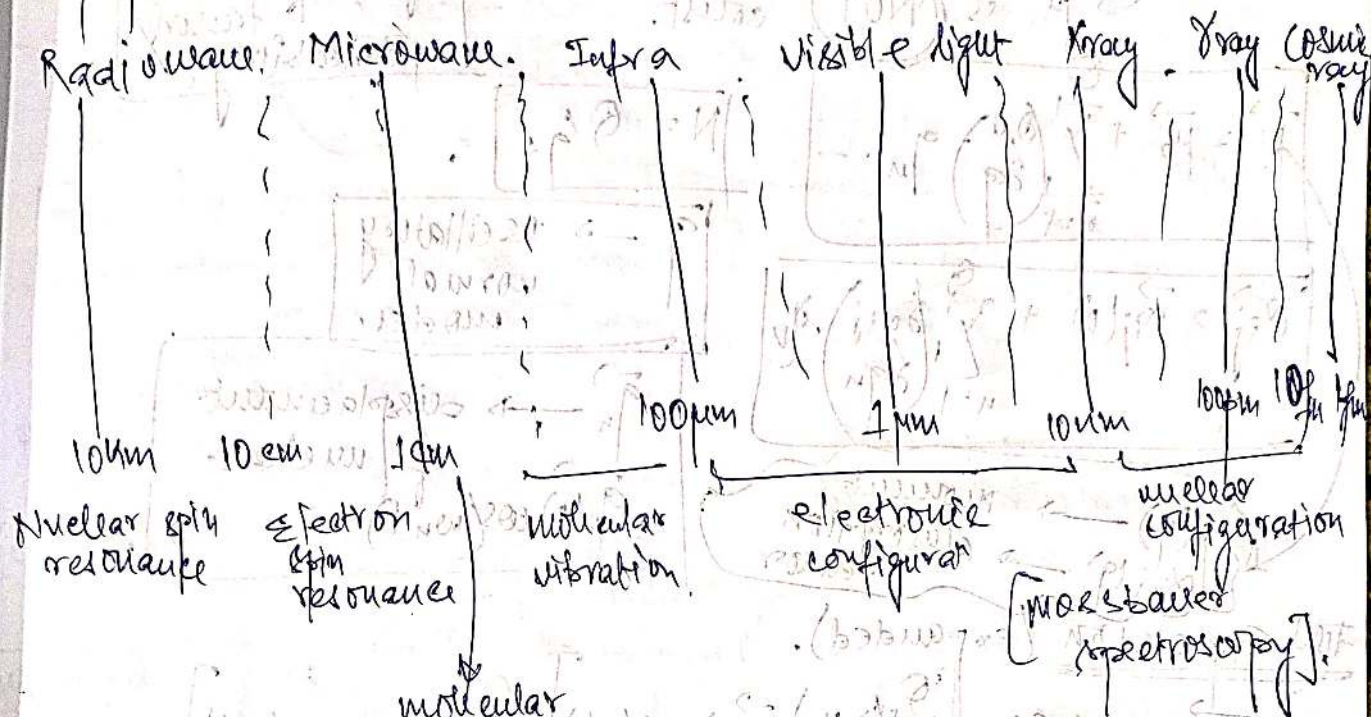


8	3	25.
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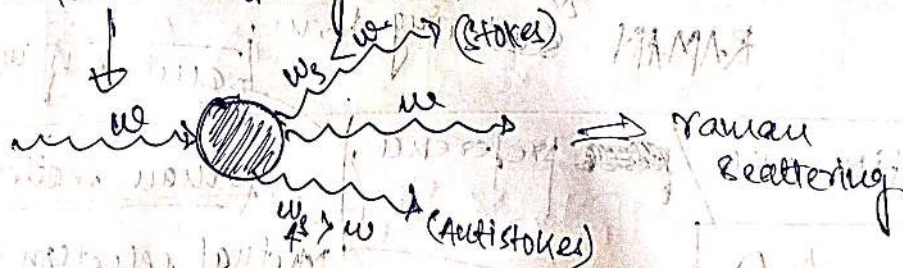


Type/Scale	Energy	Wavelength	Frequency
electronic	~ eV	~ 1 $\mu\text{m}$	$(3-15) \times 10^{14} \text{ Hz}$
vibrational	~ eV	~ 10 $\mu\text{m}$	$(3-30) \times 10^{13} \text{ Hz}$
rotation	~ eV	~ 100 $\mu\text{m}$	$(3-20) \times 10^{12} \text{ Hz}$

Raman scattering.

① Elastic scattering  $\rightarrow$  Rayleigh scattering

② Elastic scattering



## Classical theory of RAMAN scattering.

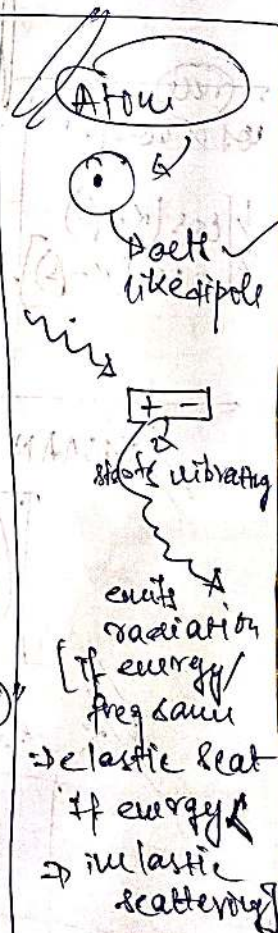
Net dipole moment:  $\vec{p} = \vec{\mu} + \alpha \vec{E}$

Diagram illustrating the components of the net dipole moment:

- $\vec{\mu}$ : permanent dipole
- $\alpha \vec{E}$ : induced dipole
- $\vec{E}$ : electric field
- $\vec{p}$ : primary dipole (nuclear)

"off resonance with electronic transition": Assumption [NOT considered in classical theory].

$\vec{E} \Rightarrow$  incident ray of light.  
 "induced dipole"  $\rightarrow E_0 \cos(\omega t)$





$$\vec{P}(t) = \vec{P} + \alpha_{ij} \vec{E}(t)$$

$\vec{P}$  is **NOT** const.

polarization  
 $\alpha_{ij} \Rightarrow$  polarizing tensor  
 polarizability.

$$\vec{P} = \vec{P}_0 + \sum_{n \neq 0} \left( \frac{\partial \alpha_{ij}}{\partial q_n} \right) q_n \sim$$

$$N = \frac{1}{2} N_A$$

$q \rightarrow$  oscillatory normal modes.

$$\alpha_{ij} = \alpha_{ij}(0) + \sum_{n=1} \left( \frac{\partial \alpha_{ij}}{\partial q_n} \right) q_n$$

$q_n \rightarrow$  displacement of nucleus  
 $= q_n(0) \cos(\omega_n t)$

$\mu(q) \rightarrow$  moment  
 $\alpha_{ij}(q) \rightarrow$  absorption tensor

Full Expression (expanded).

$$\vec{P}(t) = \mu(0) + \left[ \sum_{n=1} \left( \frac{\partial \mu}{\partial q_n} \right) q_n(0) \cos(\omega_n t) \right] + \left[ \alpha_{ij}(0) E \cos(\omega t) \right] +$$

permanent dipole

infrared scattering

Rayleigh scattering

$$\frac{1}{2} \sum_{n=1} \left( \frac{\partial \alpha_{ij}}{\partial q_n} \right) \left\{ \cos(\omega + \omega_n) + \cos(\omega - \omega_n) \right\}$$

rule  
 $\cos \alpha \cos \beta$

$$\frac{1}{2} [\cos(\alpha + \beta) + \cos(\alpha - \beta)]$$

Anti-Stokes

Stokes.

RAMAN scattering term.

RAMAN selection rule

preference

center of mass.

$$\left( \frac{\partial \alpha_{ij}}{\partial q} \right) \neq 0$$

IR selection rule

$$\left( \frac{\partial \mu}{\partial q} \right) \neq 0$$

Raman scattering.  
 mutual selection rule  
 with inversion symmetry.

If  $q$  mode is Active.  $R \neq IR$  Active

without inversion symmetry.

If  $q$  mode is Active. Raman = IR active.



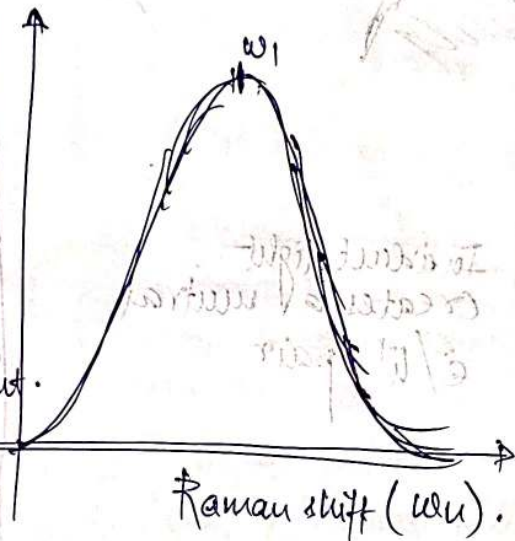
point groups for crystals:

we'll be given character table or plots for  $\chi_{ij} / \chi_{ij}$

(Fact) for  $H_2O$  wtu is Raman active It is also IR active.

$\omega_n = \omega_0 - \omega_s$   
 incident radiation freq  
 Raman shift.  
 [char. of system]

Scattered freq  
 $(\omega_s)$   
 variation of incident.



[RAMAN spectrum].

- \* stretching mode.
- \* bending mode.
- \* BREATHING mode.

we'll use ANIMATION for Benzene [different molecules] use treat as molecule. NOT as a lattice still ok.

classical theory for solid.

$$\vec{P} = \epsilon_0 \chi_{ij} \vec{E}$$

$$\chi_{ij} = \epsilon_0 \alpha_{ij}$$

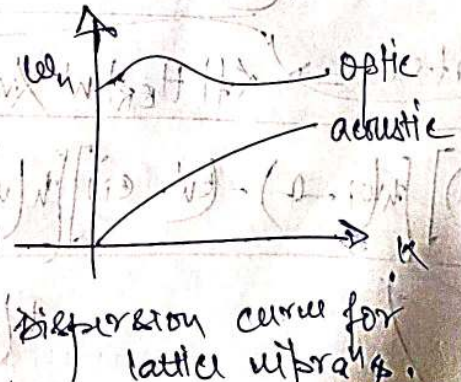
susceptibility  
 polarizability.

QUANTUM THEORY of RAMAN SCATTERING.

To work with vibrations, we consider phonons.

phonon  $\rightarrow$  quanta of lattice vibrations.

diatomic unit cell  
 (nearest neighbour interaction).  
 based on connectivity graph.



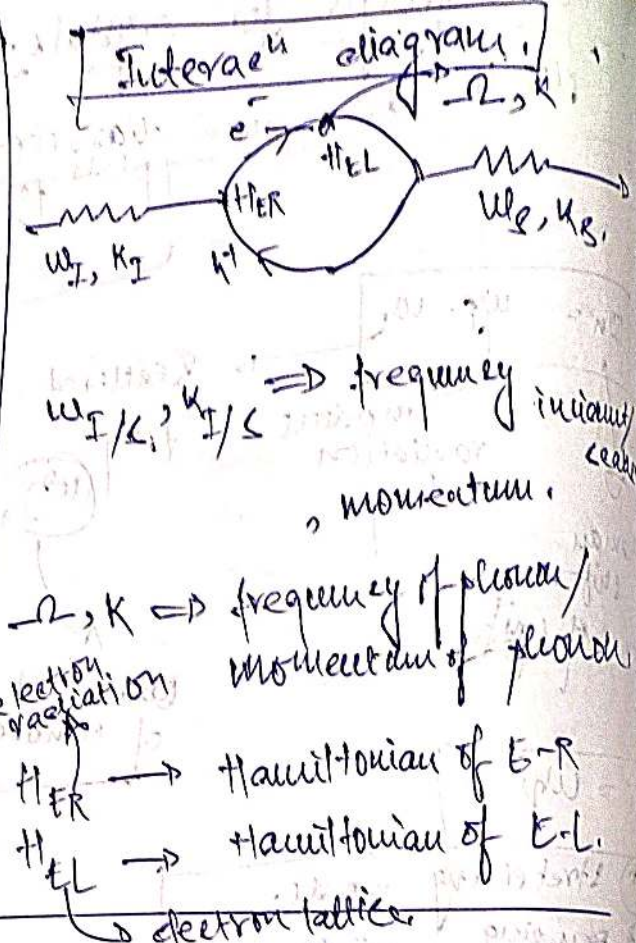
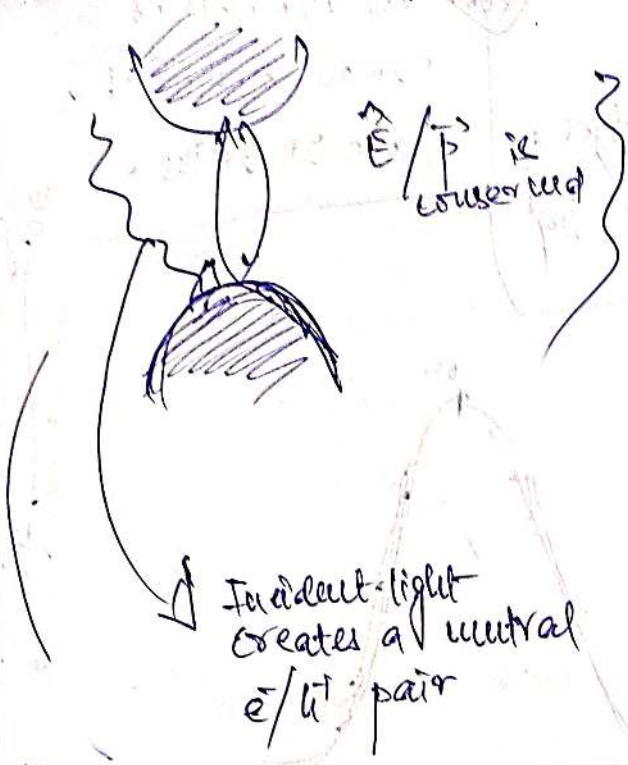
dispersion curve for lattice vibrations.

Fermi rule.



Fermi Golden Rule describes transition probability from one quantum states to another (usually continuous) under weak perturbation.





FERMI GOLDEN RULE

① 1st vortex:  $\frac{\langle n | H_{ER} | i \rangle}{\hbar\omega_i - (E_n - E_i)} \Rightarrow \Gamma \Rightarrow$  transition probability

after 2nd vortex:  $F = \frac{\langle n' | H_{EL} | n \rangle \langle n | H_{ER} | i \rangle}{[\hbar\omega_i - (E_n - E_i) - \hbar\Omega - (E_{n'} - E_n)] [\hbar\omega_i - (E_n - E_i)]}$

$\Rightarrow \frac{\langle n' | H_{EL} | n \rangle \langle n | H_{ER} | i \rangle}{[\hbar\omega_i - (E_n - E_i)] [\hbar(\omega_i - \Omega) - (E_{n'} - E_i)]}$

after 3rd vortex  $\Rightarrow \frac{\langle f | H_{ER} | n' \rangle \langle n' | H_{EL} | n \rangle \langle n | H_{ER} | i \rangle}{[\hbar\omega_i - (E_n - E_i)] [\hbar(\omega_i - \Omega) - (E_{n'} - E_i)] [\hbar(\omega_f - \Omega) - (E_f - E_i) - (E_{n'} - E_n)]}$

$\hbar(\omega_f - \Omega) - (E_f - E_i) - (E_{n'} - E_n) \Rightarrow \hbar(\omega_i - \Omega) - \hbar\omega_n$

$\Rightarrow \frac{\langle f | H_{ER} | n' \rangle \langle n' | H_{EL} | n \rangle \langle n | H_{ER} | i \rangle}{[\hbar\omega_i - (E_n - E_i)] [\hbar(\omega_i - \Omega) - (E_{n'} - E_i)] [\hbar(\omega_i - \Omega) - (E_f - E_i)]}$



→ conservation of energy:

$$\hbar \omega_i = \hbar \omega_f + \hbar \Omega$$

→ conservation of momentum

$$\hbar k_i = \hbar k_f + \hbar K$$

$K$ : Brillouin zone,

$K \sim 10^8$  (atom),

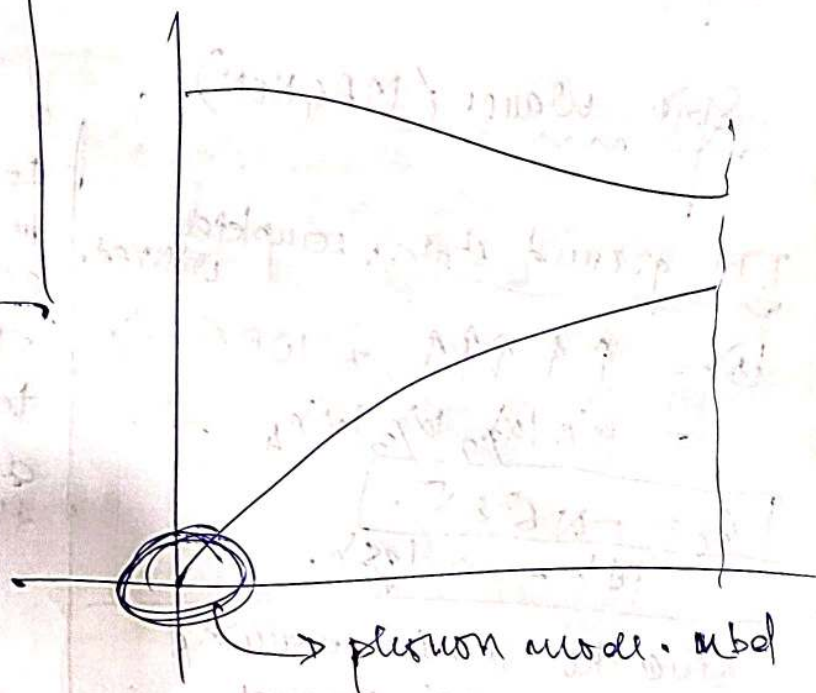
$K_i \sim 10^5$  (light),

$K_s \sim 10^5$  (light)

$\therefore K$  has to be limiting and very small.

$\therefore$  vibrational modes are VERY SMALL to match order  $10^8 \rightarrow 10^5$ .

Semi classical.



⊗ For Raman, hence we see mostly optical mode.

⊗ For LARGE molecules, we see acoustic mode.

TUESDAY

Mostly we deal with lattice vibra<sup>n</sup>

Applications:

- (1) Graphene spectrum [Raman spectroscopy]
- (2) G peak, D peak, D' peak, 2D peak.
- (3) Scattering probability of these "peaks".

- (1) Strain in the lattice.
- (2) Binding the molecules.
- (3) ~~Electronic~~ Raman scattering: info of electronic state.
- (4) Spin-phonon coupling.