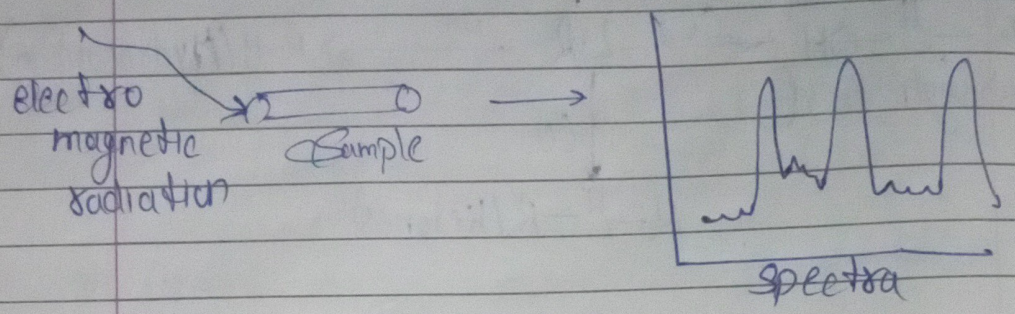
UNIT-2

SPECTROSCOPY



It is a branch of science which deal with determination of structure of compound through the interaction of electro magnetic radiation with matter.

Electromagnetic radiation

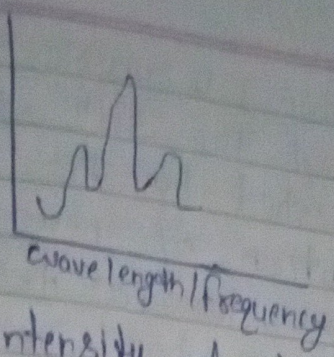
It has dual character Particle/waves. Wave consist of oscillating electric & Magnetic field ⊥ to each other.

Electromagnetic Spectrum : It is an arrangement of electromagnetic radiation in order of increasing wavelength or decreasing frequency

Cosmic Rays / Gamma rays / X-rays / U.V / Visible / I.R / Microwave / Radiowave
0.001 Å 3×10^{13} Å

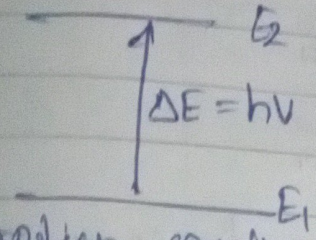
Spectra

Absorbed radiations / Transmitted radiation

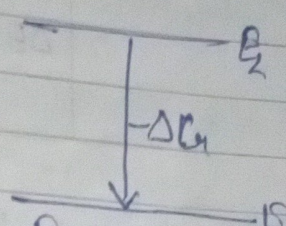


Clock off intensity of absorbed transmitted radiation v/s frequence or wavelength.

Origin of spectra :



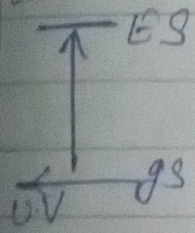
Absorption spectra (UV, IR)

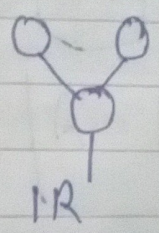


Emission spectra

Electromagnetic Radiations bring about change in

- electronic state
- Vibrational state
- Rotational state





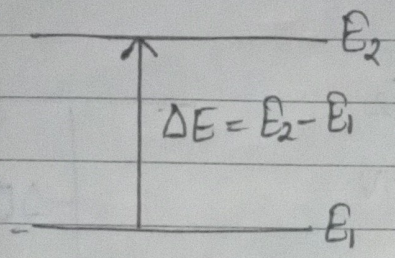
Microwave

U.V- visible Spectroscopy / ultra violet visible / Electronic spectroscopy

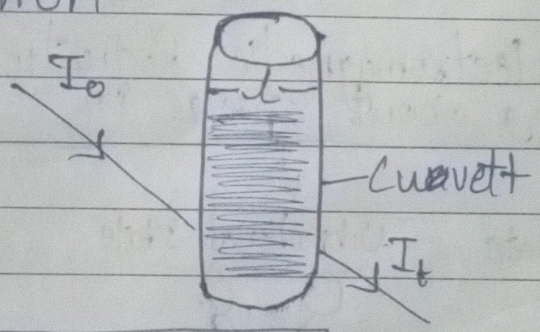
Range UV → 100nm to 400nm

visible 400nm to 800nm

Principle :- When U.V visible radiation is pass through the soln of organic compound it gets absorbed by the compound.
This absorbtion of energy in UV visible region occurs due to transition b/w electronic energy level with in the molecule. Therefore also known as electronic spectroscopic



Principle of UV spectrosopy is based on Lambert Beer's law which is law of obserbtion



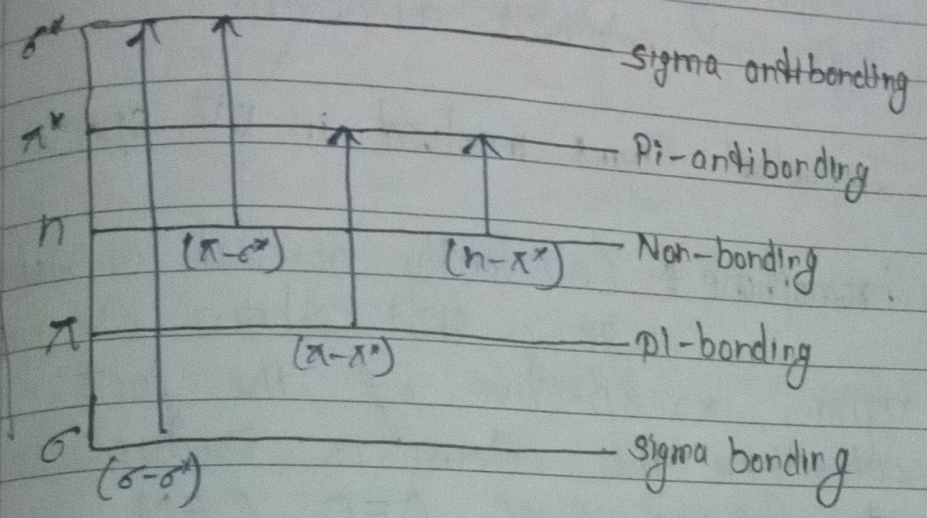
$$\log \frac{I_0}{I_t} = \varepsilon C l = A$$

where, I_0 = Intensity of incident light
I_t = " " transmitted light
C = conc. of soln in moles
ε = Molar Absorptivity cofficient
A = Absorbance.

Electronic transitions

Q1. Explain different type of electronic transition ~~envelp~~ envolved in UV visible spectroscopy.

Q2. Give possible electronic transition in $CH_3-CH_2-CH_3$, $CH_3CH=CH_2$, $CH_3CH=O$



(i). $(\sigma-\sigma^*)$ ÷ It's of highest energy and found in saturated hydrocarbon (alkanes CH_4)

(ii) $(n-\sigma^*)$ ÷ Saturated hydrocarbon with hetroatom (O, N, S, X)

Ex = alkyl halide (CH_3Cl)

(iii) $(\pi-\pi^*)$ ÷ ~~Unsaturat~~ Unsaturated hydrocarbon

For ex ÷ alkene & alkyne $CH_2=CH_2$, $CH\equiv CH$

(iv) $(n-\pi^*)$ ÷ Unsaturated hydrocarbon with hetroatom

Ex ÷ $H_2C=O$, $C\equiv N$

Note :- (i) Usually compound having conjugation are UV active

(ii) $\Delta E = \frac{hc}{\lambda}$

(iii) Longer is conjugated system lesser is ΔE and higher is λ_{max}

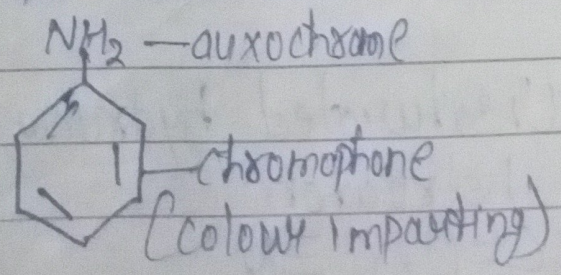
(iv) Length of conjugative system is very high in coloured compound.

Important Terms involved in UV spectroscopy

Chromophone :- Covalently bonded unsaturated group that show UV-visible region, irrespective of the fact whether the colour is produce or not. for ex :- C=C, C=O, C≡N

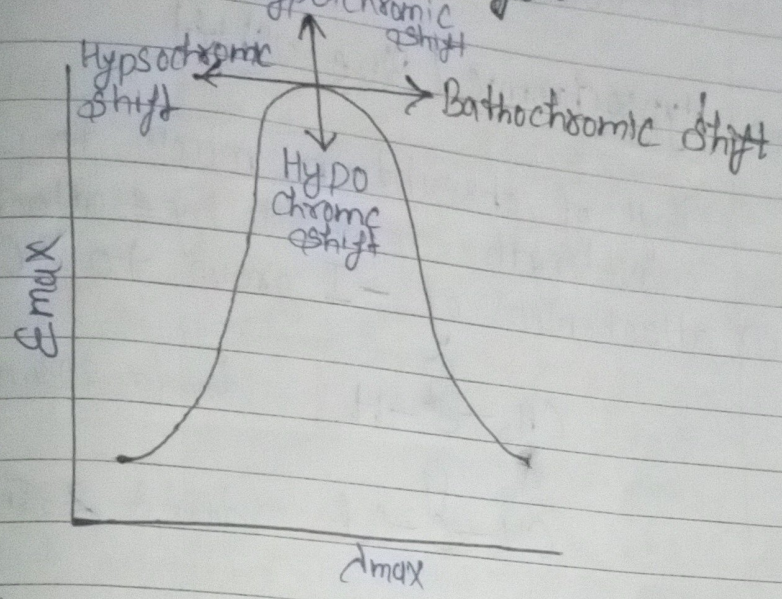
Auxochrome :- Any group whose presence brings about a ship of absorbtion band towards the longer wavelength is called Auxochrome. It is due to is ability to extend conjugation. for ex :- NH_2, OR etc

Thus chromophone is colour imparting where as auxochrome is colour enhancing



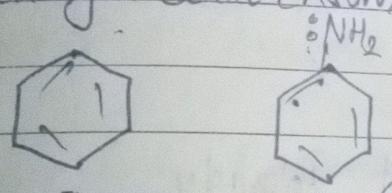
Absorption & Intensity Shift

Q. Write a short note on UV shift?



Imp. Bathochromic shift :- Shift of absorption maxm towards longer wavelength by :-

(i) Attaching an auxochrome



λmax = 254nm λmax = 280nm

(ii) By increase in conjugation

- $C_6H_5CH=CH-C_6H_5$ = λmax 313nm

$C_6H_5CH=CH-CH=CH-CH=CH-C_6H_5$ λmax = 377nm

(iii) By change of solvent Polarity :- λmax increases with decreases in polarity.

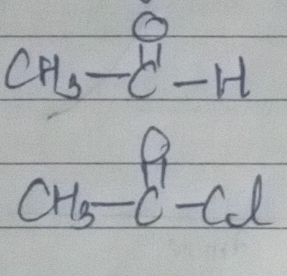
Acetone + water → λ_{max} = 264nm

Acetone + hexane → λ_{max} = 279nm

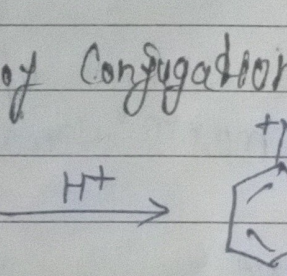
Imp **Hypsochromic / Blue shift**

Shift of absorbtion max^m to shorter wavelength achieved by : ~~attachment~~

(i) attachement of −I group to >C=O

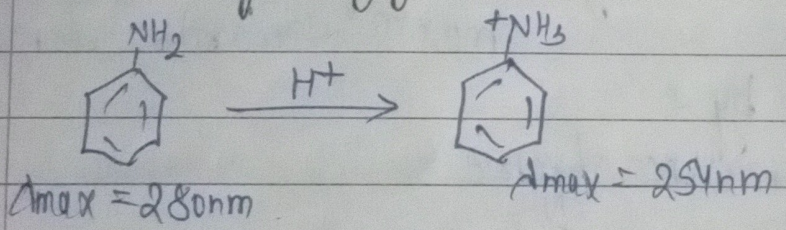


λ_{max} = 293nm



λ_{max} = 235nm

(ii) Removal of Conjugation



(iii) By change in solvent Polarity

λ_{max} decrease with increase in polarity

- **Hyperchromic Shift** Effect which leads to increase in molar absorptivity (intensity of absorption)

Ex: Auxochrome

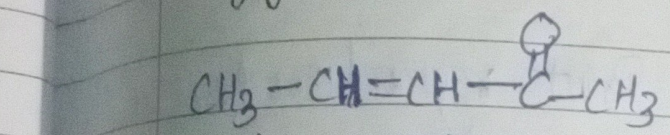
Hypochromic shift : Effect which leads to decrease in molar absorptivity. For exp Group which distort geometry.

Application of UV visible spectroscopy

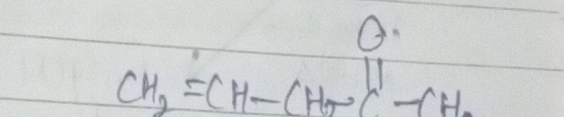
(i) determination of chromophric functional group.

λ_{max} above 200nm show pressence of group such as : carboxylic, carbonyl, nitro etc.

(ii) Distinction b/w isomeric conjugated & non-conjugated compound.



λ_{max} = 227 nm



λ_{max} = 200nm

(iii) Quantitative Analysis : Conc. of unknown soln can be calculated by Lambert Beer's law :

$$\boxed{C = \frac{A}{\varepsilon l}} \text{ g/l}$$

(iv) Distinction b/w Cis & Trans : Trans absorb at longer wave-length than corresponding cis due to steric hinderance

Increase in Stability → Decrease in Energy → Absorption at longer λ

Note: Solvent effect: Most suitable solvent for UV spectroscopy is one which doesn't absorb in region under investigation for ex: Ethanol, Methanol, & Cyclohexane

Vibrational / IR SPECTROSCOPY

- Far
- Middle
- Near

This technique help in identification of compound that is functional group analysis.

IR spectra into two parts
- → Functional group region (4000 to 1300 cm^{-1})
- → Finger Print region (1300 to 625 cm^{-1})

Principle of IR spectroscopy

Q Explain different types of Molecular vibration taking place IR.

Q Discuss various molecular vibration found in AX_2 molecules.

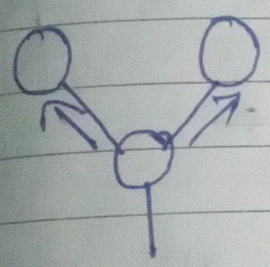
Absorbtion in IR region occurs due to excitation molecules from lower to higher vibrational state. In IR spectroscopy absorbed energy rings about pre-dominant changes in vibrational energy. Due to absorbtion of IR

radiation the molecule get exited from lower to next higher vibrational level, due to this increased amplitude & oscillating dipole sets in the molecule. Thus absorption of IR radiation by a molecules causes change in it's electric dipole moment.. Interaction of this electric vector of IR radiation leads to absorption of energy.

Imp IR radiation causes stretching and bending of Bond.

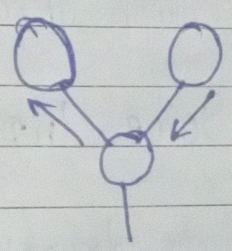
Stretching Vibration :- Atoms remain in a same bond axis there is change in bond length

(a)



symmetric stretching (movement of atom w.r.t central atoms is in same dirn)

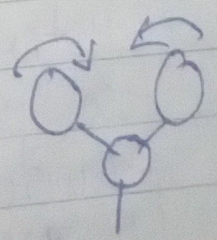
(b)



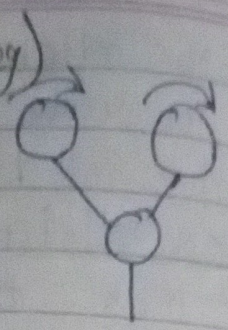
asymmetric stretching (one atom approaches central atom where as other move away)

(2) Bending Vibration :- Change in bond angle w.r.t original bond axis.

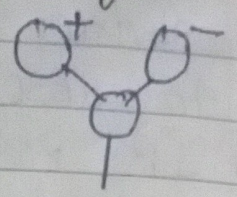
(a) Scissoring Vibrations (in plane bending) Two atoms approach each other.



(b) Rocking vibrations (in plane bending)
Movement of atom takes place in same dirn

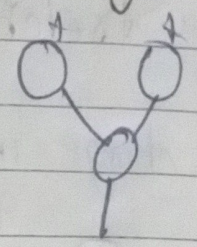


(c) Twisting vibrations (out of plane bending)
One atom move up and other move down w.r.t common atom



(d) Wagging vibrations (out of plane bending)

Two atoms simultaneously move up & down plane w.r.t common atom.



Some Important points :-

* Such transition which are a complete by change in dipole moment of a molecule are IR active

* Homonuclear diatomic (H_2, O_2, N_2) molecule are inactive because of zero dipole moment for all bond length

* Heteronuclear diatomic molecule (CO, CN) so variation in dipole moment due to fluctuation in Bond length therefore IR active.

* Polyatomic molecules develop flucuating dipole because of certain mode of vibration therefore IR active (H_2O, N_2O)

~~No of fundamental vibration~~

Number of fundamental vibrations

For linear molecules = 3n-5

For non-linear " = 3n-6

n → no. of atoms

Give no. of fundamental vibration in

(i) H_2 molecules = 1

(ii) H_2O molecules = 3

Principle of IR spectroscopy is based on hookes law

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}}$$

K → force constant

μ → reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

* Greater the masses of attached atom lower the IR frequency at which the bond absorbs

IR spectra include following region :-

① Functional Group region

(i) 3600 – 3200 cm^{-1} → OH, NH_2
(ii) 3200 – 3000 cm^{-1} → C–H
(iii) 2300 – 2100 cm^{-1} → –C≡C–, C≡N
(iv) 1900 – 1700 cm^{-1} → >C=O of aldehyde, Ketones, Acids

② Finger Print region

Its region below 1500 cm^{-1} and is characteristic of a molecules as a whole. Every compound has unique absorbtion pattern in this region. Just as every person has unique finger print. It is not possible for any two different compound to have exactly same IR spectra. Superimposibility of IR spectra of two compound is taken as evidance for identity of two compound.

Application :- ① Functional group determination
② Detection of hydrogen bonding.

ν_{O-H} (Vibrational frequency of O-H bond) of intermolecular H-Bonding depends on dilution

ν_{O-H} of intra molecular H-Bonding doesn't depend on dilution.

2) Identity of two compounds by superimposibility of IR spectra

3) Purity of compound - impure compound cause extra band and reduce sharpness.

4) Progress of reaction

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{NaBH_4} R-\overset{OH}{\overset{|}{C}H}-R$$

ν_{C-O} $\qquad$ ν_{O-H}

Difference b/w IR & UV

IR spectra	U.V spectra
1) Cause bending & stretching vibrations	Electronic transition takes place.
2) Spectra expressed in frequency (wave no unit)	Generally expressed in terms of wavelength (nm units)
3) Mainly for functional group determination	Specially for confirming presence of conjugated system (carbonyl group)
4) Possible to differentiate b/w inter & intra molecular H-bonding	Not possible.

(Gaseous state for identification)

Microwave / Rotational Spectroscopy

Principal: Spectra arises from transition b/w rotational energy level of gaseous molecule on the absorbtion of radiation of microwave region. (1 to 100 cm^{-1})

This spectroscopy deals with pure rotational motion of molecule

- Thus spectra shown by molecule which posses permanent dipole moment

The molecules are grouped as microwave active

Microwave active: Having permanent dipole moment Ex: HCl, HF, CO, CN

Microwave inactive: No permanent dipole moment Ex: H_2, N_2, O_2

When a molecule having dipole moment rotate, it generate and electric field which interact with electric ~~field~~ component of microwave radiation. During the interaction there would be-

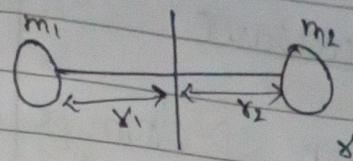
(i) Transfer of energy from incident radiation to molecule in this absorbtion microwave spectrum will be formed

(ii) Transfer of energy from molecule to incident radiation, in this case emission microwave spectrum is formed

A rotating molecule whose nuclei are seprated by definite mean distance make fitted by rigid rotator with free axis of rotation.

$$\text{Rotational const } (B) = \frac{h}{8\pi^2 I_c}$$

$I_c \rightarrow$ moment of Inertia (around center)



rigid rotator

Selection Rule :- Only those transition is permitted in which their is an increase and decrease by unity in rotational quantum ~~num~~ number.

$$\boxed{\Delta J = +1}$$

$J_0 \rightarrow J_1 \rightarrow J_2 \rightarrow J_3$ (allowed transition)

$J_1 \rightarrow J_3 \rightarrow J_5$ (for bidden ")

Application of Microwave

→ Structural determination of Ozone, OCS (carbonyl Sulphide) xenon oxyfluoride

→ Abundance of isotopes

→ Moment of inertia can be calculated by rotational frequency.

Limitations :- → Substance to be study must be in gaseous state.

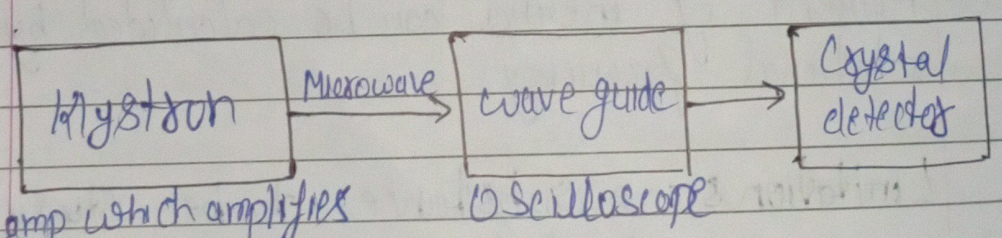
→ It is fundamentally not suitable for ~~categories~~ categorizing new compound.

→ Microwave spectrum is a property of molecule as a hole & it is not possible to relate certain part of spectrum to certain part of molecule.

Difference b/w Microwave & IR

Microwave	IR
1- Absorption spectrum is characteristics of absorbing molecule as a whole.	Characteristics of functional group
2 Resolution lines are more	less
3 Substance must be in gaseous state	IR or solid liquid
4 Spectra obtained is absorption + emission	Nearly always absorption.

Block Diagram



Lamp which amplifies microwave.

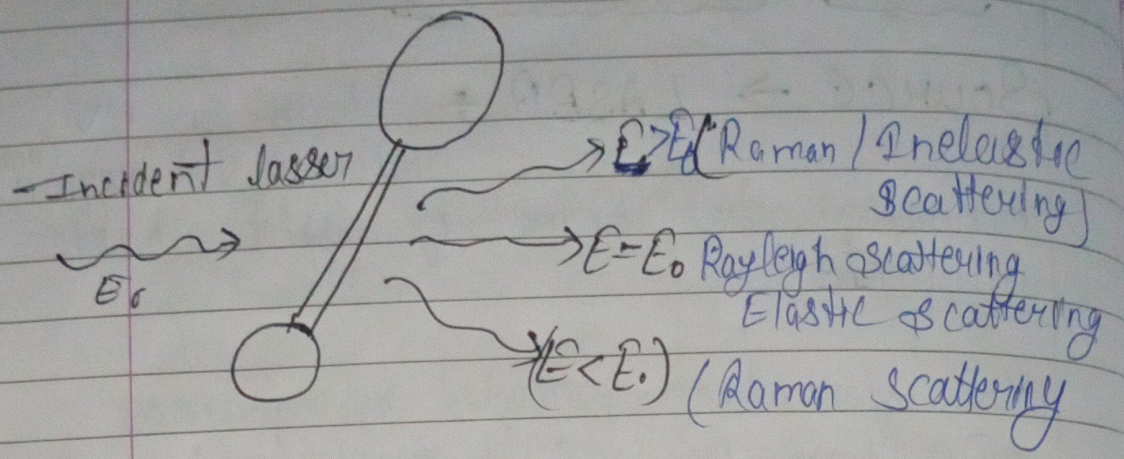
RAMAN SPECTROSCOPY

Source → LASER : It is in UV, visible & IR (near) region, monochromatic beam of light basic principle

The information provided by Raman spectroscopy result from light scattering process (Quantum theory). When light interact in a molecule in a gases, liquid & solid

(i) Majority of photons are scattered as same energy as incident of photons Describe as elastic elastic scattering Raleigh scattering

(ii) Small number of photon will be scattered as Different frequency than the incident photon. The process is known as inelastic scattering / Raman scattering



Raman Effect / Raman Scattering

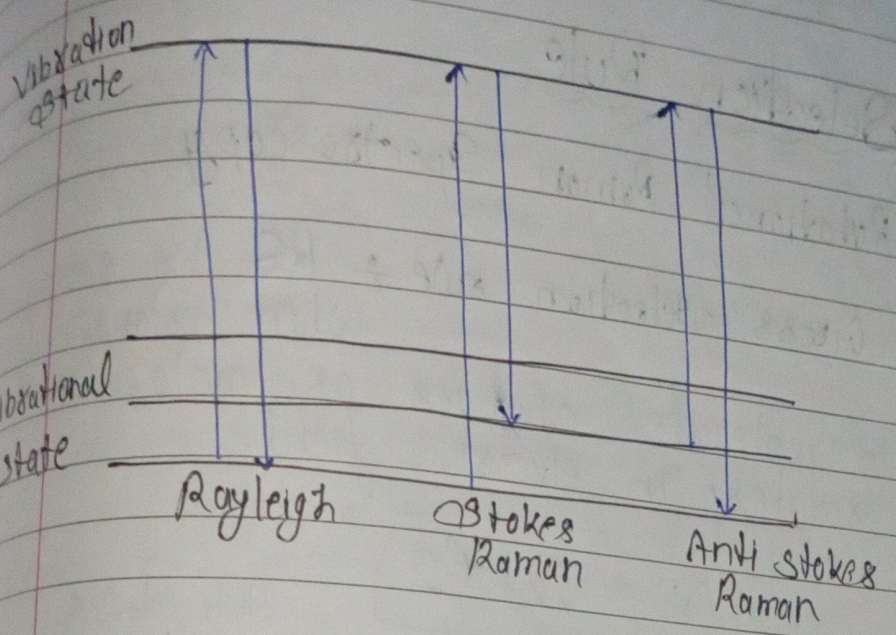
Two kind of Raman scattering can be observed

i) Incident Photon loose energy too molecule causing it do go too and existed vibration state scattered photon will have less energy compared to incident photon (Stokes lines / Stokes Raman)

ii) Instant photon gain energy from molecule as molecule loses energy from higher to lower vibrational stress. The scattered photon will have more energy compared to incident photon (Anti Stokes line)

iii) At room temper most molecule are in vibrational brown state so their is heighter probability of Stokes

Raman and thus Raman spectroscopy is offered as stokes Raman



Raman Shift Change in photon energy occurs because molecule may vibrate during the time electron oscillate in resonance with applied field. A vibrational mode that changes molecular polarazibiligy reserve result in change of incident photon energy. The difference in

energy b/w incident photon and inelastic scattered photon is called Raman shift.

Selection Rule

① Rotational Raman Spectroscopy

(i) Gross selection rule :- RS is observed when polarazibility of molecule changes as molecule rotates in electric field.

$$\boxed{\Delta J = 0, \pm 2}$$

→ Stokes

Anti Stokes

Rayleigh

② Vibrational Raman

Polarazibility of molecule changes as it vibrate

(ii) Specific Selection rule $\boxed{\Delta v = \pm 1}$

* Some Important point related to Raman

1. Raman is similar to IR as they have region useful for functional group & finger print region.

2 IR & Raman are complementry
for ex: studies on bond angle, bond length & other structural confirmation required Raman data in addition to IR.

3 With increase in temper there is decrease in seperation on indivisual Raman line from parent line.

4 Raman scattering is possible for molecule even when vibrational quantum number is zero.

5 Covalent diatomic molecule show intense Raman line.

6 Electrovalent diatomic molecule → No Raman line

7 Raman active molecule are linear molecule (H_2, O_2, CO_2, HCl)
Symmetric molecules → CH_3Cl, CH_3F
Asymmetric " → $CH_2=CHCl$ (Vinyl chloride)

Application

1- Can be used for characterising chemical composition structure of solid, liquid, gas, power, gel. & slurry

2 Homonuclear diatomic molecules can be analysis as well as tri atomic molecules can be study and structural nature (linear, symmetric, Angular) can be known.

3 Gives idea about binding forces of atom in a lattice & strength & nature of forces in crystal.

4 Help in study of phenomeon of electrolytic desociation & degree of hydrolysis

5 ~~Hence~~ Help to differentiate b/w open & closed chain compound.

6 No. of molecules of water of crystallization can be determinent.

7 Complex compound can also be study.

Difference —

Raman Spectroscopy	IR Spectroscopy
Due to scattering of light by vibrating molecule	Result of absorbtion of radiation by vibrating molecule.
Vibration is Raman active if it causes change in polarizability.	Vibration is IR active if there exist change in dipole moment
Water can be used as solvent	Water cann't be used as solvent.
Consentrative soln are preffered	Generally dilute soln are preffered.
Sample container is made up of glass/pots	In IR made of NaCl, KCl, KBr etc.
Homo nuclear diatomic molecule are Raman active	Inactive
Cost of Raman is very high	Comparatively inexpensive.