

Unit- SPECTROSCOPY

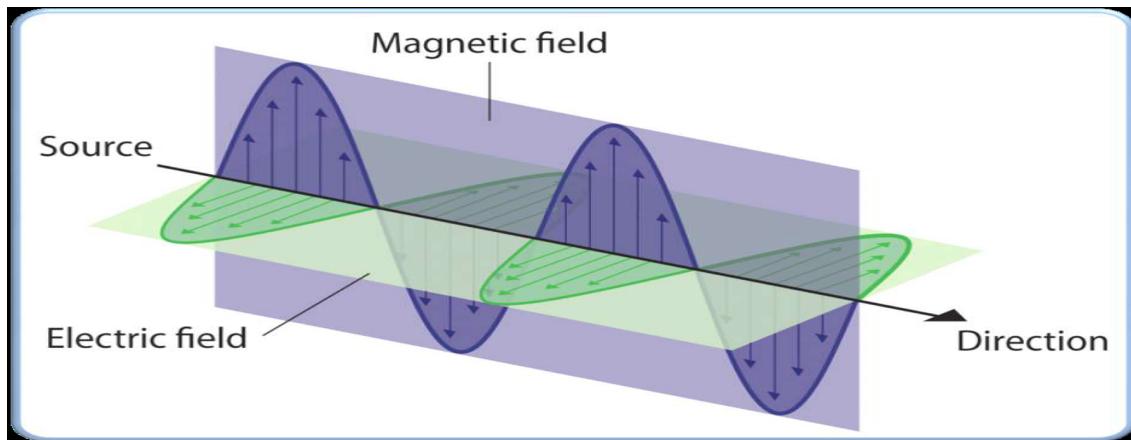
Spectroscopy

- It is the branch of science that deals with the study of interaction of electromagnetic radiation with matter.

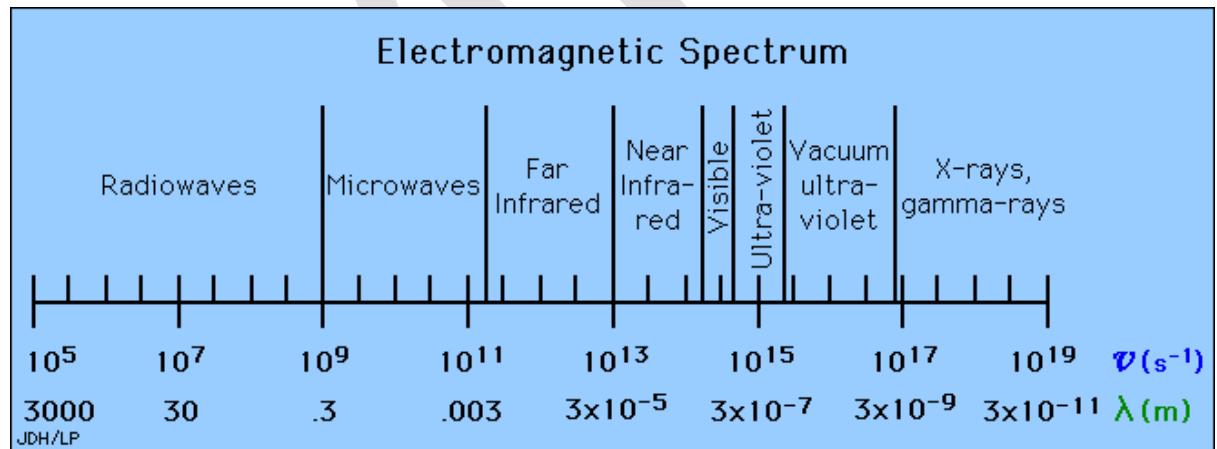
Electromagnetic Radiation

- Electromagnetic radiation consist of discrete packet of energy called as photons.
- A photon consists of an oscillating electric field (E) & an oscillating magnetic field (M) which is perpendicular to each other.

Energy of photon: $E = h\nu = h c / \lambda$; where h = plank's constant and ν = frequency.



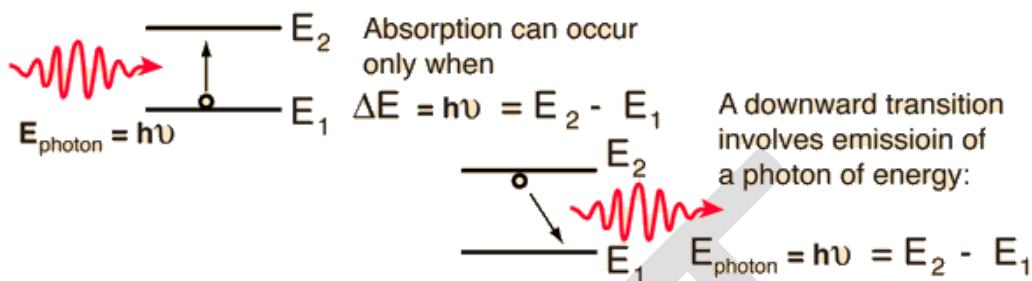
Based on the energy, electromagnetic radiation has been divided into different regions. for example, The region of electromagnetic spectrum that human beings can see is called visible region or visible spectrum.



Molecular Property

1. Electronic Energy Levels:

- At room temperature the molecules are in the lowest energy levels E_0 .
- When the molecules absorb UV-visible light from EMR, one of the outermost bond / lone pair electron is promoted to higher energy state such as $E_1, E_2, \dots E_n$, etc is called as electronic transition:



$$\Delta E = h\nu = E_n - E_0 \text{ where } (n = 1, 2, 3, \dots \text{ etc.})$$

$\Delta E = 100-10000 \text{ kJ/mole.}$

2. Vibrational Energy Levels:

- The spacing between energy levels are relatively small i.e. **1 to 100 kJ/mole.**
e.g.
- When IR radiation is absorbed, molecules are excited from one vibrational level to another or it vibrates with higher amplitude.
- The spacing between energy levels are even smaller than vibrational energy levels. i.e $\Delta E_{\text{vibrational}} < \Delta E_{\text{electronic}}$

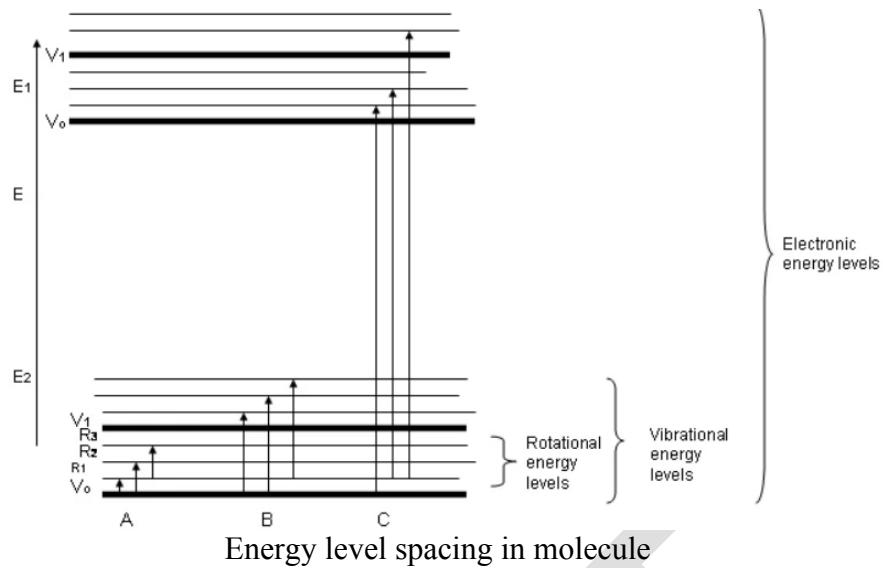
3. Rotational Energy Levels:

- Energy level spacing **0.01-1 kJ/mole.**
- The spacing between energy levels are even smaller than vibrational energy levels. i.e $\Delta E_{\text{rotational}} < \Delta E_{\text{vibrational}}$
- When IR radiation is absorbed, molecules are excited from one rotational level to another or it vibrates with higher amplitude

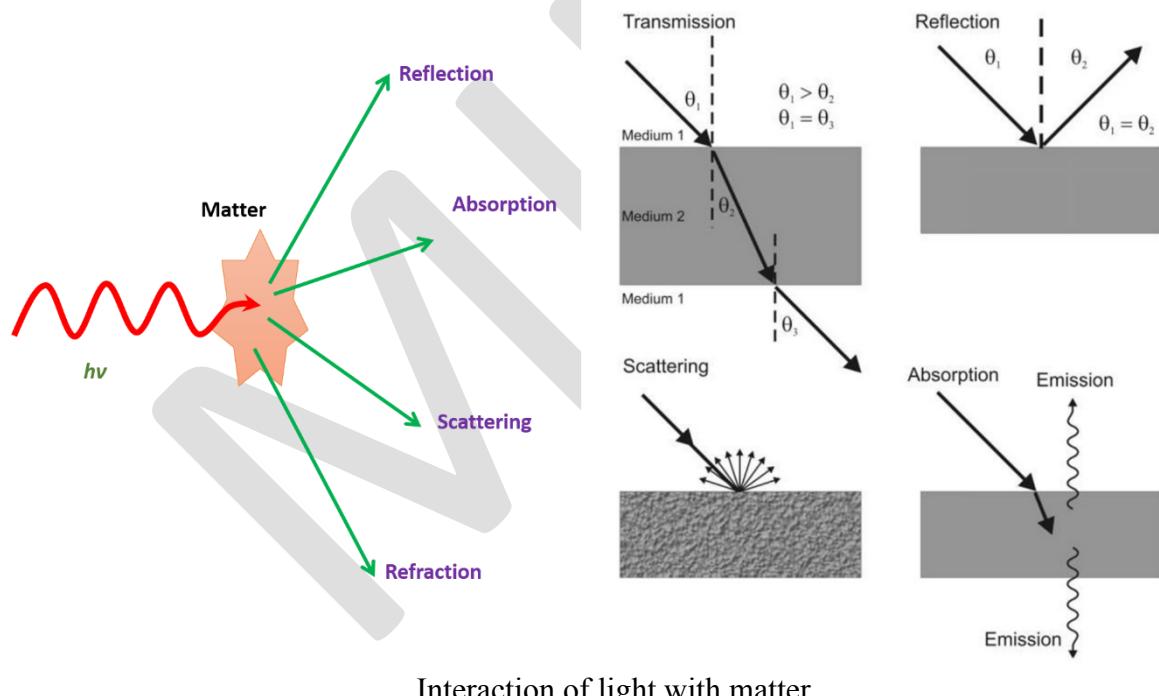
$$\text{Hence, } \Delta E_{\text{rotational}} < \Delta E_{\text{vibrational}} < \Delta E_{\text{electronic}}$$

Thus, total energy of the molecule can be represented as follows

$$\Delta E = \Delta E_{\text{rotational}} + \Delta E_{\text{vibrational}} + \Delta E_{\text{electronic}}$$



Type of processes during interaction of matter with EM radiation: As shown below, various processes occurs during interaction of matter with radiation



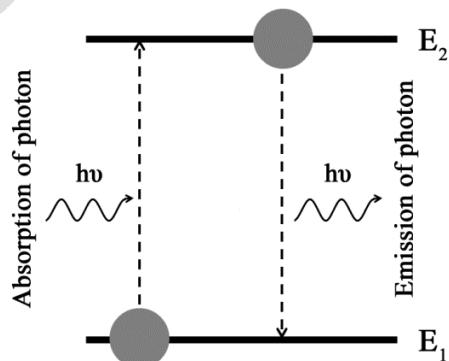
Relation of Electromagnetic spectrum and the atomic/molecular processes:

Molecules undergo processes like rotation, vibration, electronic transitions, and nuclear transitions. The energies underlying these processes correspond to different regions in the electromagnetic spectrum:

Electromagnetic	Effect on molecule	Technique	Information obtained
-----------------	--------------------	-----------	----------------------

radiation		used	
Radio frequency waves	Nuclear and electron spin transition	Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR)	<ul style="list-style-type: none"> ➤ Molecular structure ➤ Purity of the sample, ➤ Chemical environment
Microwaves	Molecular rotational transition	Rotational spectroscopy	<ul style="list-style-type: none"> ➤ Force constant, ➤ Bond length ➤ Bond angle ➤ Isotope composition
Infrared radiation	Vibrational transition	IR spectroscopy	<ul style="list-style-type: none"> ➤ Functional group, ➤ force constant, bond length ➤ bond angle, ➤ Isotope composition ➤ Quantitative analysis
Raman Spectroscopy	Vibrational transition	IR and microwave spectroscopy	<ul style="list-style-type: none"> ➤ Chemical structure, ➤ Phase and polymorphy, ➤ crystallinity ➤ Molecular interactions
UV-Visible Radiation	Electronic transition	UV-Visible spectroscopy	<ul style="list-style-type: none"> ➤ Qualitative and quantitative information of matter
Mass Spectroscopy	Ionisation process	Mass spectrometer	<ul style="list-style-type: none"> ➤ Physical, Chemical and structural properties ➤ Isotope composition

- A molecule can possess energies in different forms such as vibrational energy, rotational energy, electronic energy, etc.
- A molecule can jump from one energy level to another by absorbing or emitting a photon of energy that separate the two energy levels (as shown in figure).



Type of spectroscopy used for study of molecule

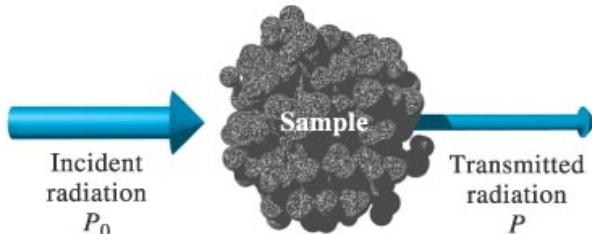
Spectroscopic technique	Process involved	EM Range	Information gained about molecule
UV-Visible spectroscopy	Absorption	10 nm – 1000 nm	Electronic transition
Infrared Spectroscopy	Absorption	0.01cm – 1000 nm	Vibrational energy level spacing
Microwave Spectroscopy	Absorption	1 cm – 0.01 cm	Rotational energy level spacing
Raman spectroscopy	Scattering	532 and 633 nm	Rotational and vibration energy level spacing

Apart from above spectroscopic technique, combination of above mentioned technique can also be used for the study of molecule. Such as Vibronic spectroscopy, Rotational-Vibrational spectroscopy

INTERACTION OF EMR WITH MATTER:

The interaction of electromagnetic radiation with matter causes the atoms and molecules to absorb energy and go to a higher energy state. Since this state is unstable, they need to emit radiations to return to their normal states. This gives rise to emission and absorption spectra.

Absorption Spectroscopy measures the amount of light absorbed by a sample by this process.

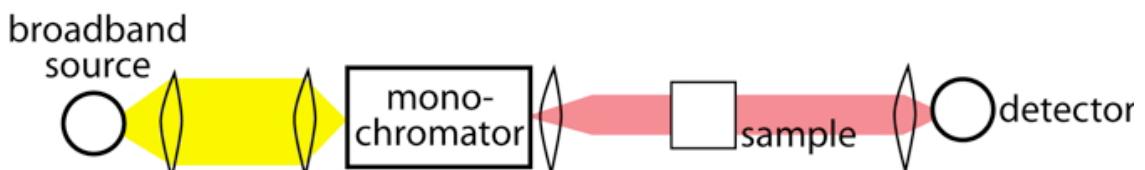


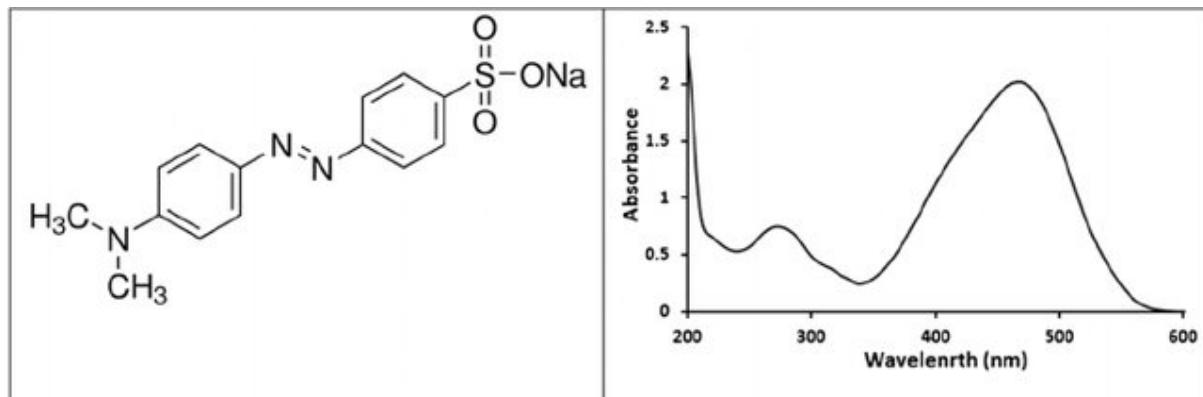
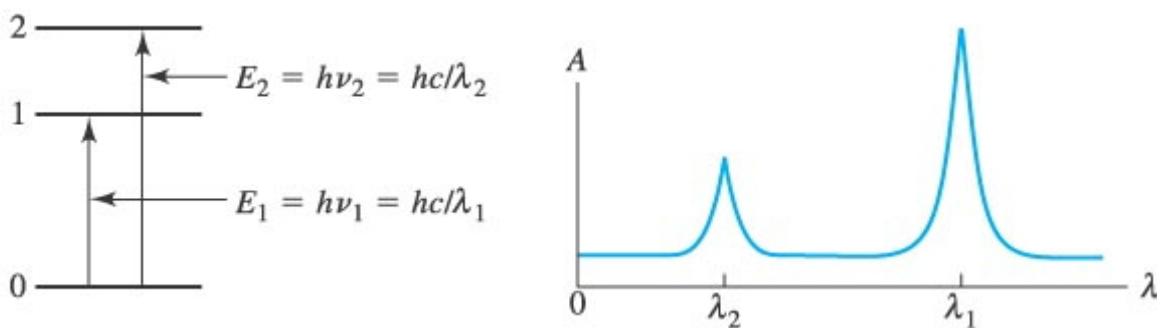
For atoms: **Atomic Absorption Spectroscopy**

For molecules: **Molecular Absorption Spectroscopy**

The Absorption Spectrum plots the amount of light absorbed by a sample as a function of photon wavelength.

Absorption Spectrometer

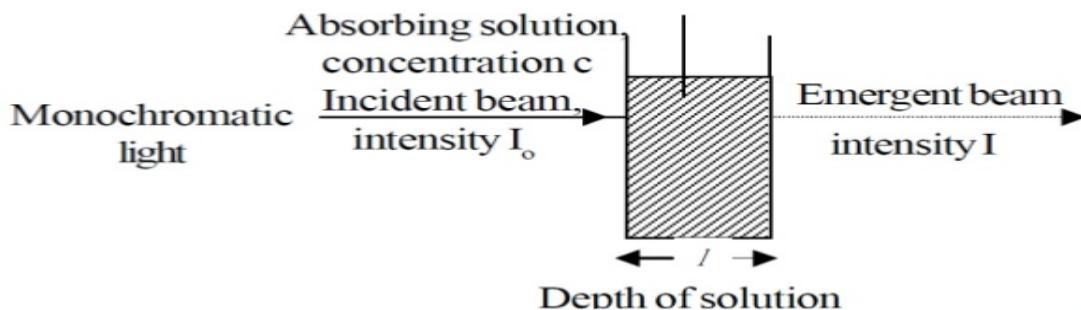




Typical Absorption spectra of Methylene Orange

ABSORPTION LAWS

Beer-Lambert's Law: When a monochromatic radiation is passed through a solution, the decrease in the intensity of radiation passing through sample solution is directly proportional to the intensity of the incident light.



The intensity of the emitted light decreases exponentially as the thickness and concentration of the absorbing medium increases.

$$\log \frac{I_0}{I} = \epsilon cl$$

where, I_0 = intensity of incident light

I = intensity of transmitted light

ϵ = molar absorptivity coefficient in $\text{cm}^2\text{mol}^{-1}$

c = concentration in mol L^{-1}

l = path length of absorbing solution in cm^{-1}

$$A = \text{Absorbance} = \log(I_0/I) = \epsilon cl$$

Thus, the above equation shows linear relationship between absorbance and the concentration of the absorbing molecule (or chromophore).

Transmittance is another way of describing the absorption of light. Transmittance (T) is simply the ratio of the intensity of the radiation transmitted through the sample to that of the incident radiation:

$$\%T = I/I_0 \times 100$$

Also, $A = \log(1/T)$
where, T = Transmittance

Deviations from Beer-Lambert law:

- i. **High sample concentration:** The Beer-Lambert law generally holds good only for dilute solutions. At higher concentrations, the molecules come in close proximity thereby influencing their electronic properties.
- ii. **Chemical reactions:** If a molecule undergoes a chemical reaction and the spectroscopic properties of the reacted and unreacted molecules differ, which result in the combined absorbance from reacted and unreacted molecules. Thus the deviation from Beer-Lambert law is observed.
- iii. **Instrumental factors:** As ϵ is a function of wavelength, Beer-Lambert law holds good only for monochromatic light. Use of polychromatic radiation will result in deviation of Beer-Lambert's law.

Q1. A compound having concentration 10^{-3} g/l resulted absorbance value 0.20 at λ_{max} 510 nm using 1 cm cell. Calculate its absorptivity and molar absorptivity values. Molecular weight of compound is 400.

Ans: Concentration of compound,; $l = 1 \text{ cm}$; $A = 0.20$

Molecular weight of compound = 400
Molar concentration,

Q2: Calculate absorbance if percentage transmittance of a solution is 80.

Ans:

Q3: When UV light is passed through a solution, the radiant power is reduced to 50%. Calculate absorbance.

Ans: Let initial radiant power = P_0
Radiant power leaving the solution = P

Q4: The molar absorption coefficient of tyrosine in water is $1280 \text{ M}^{-1}\text{cm}^{-1}$ at 280 nm. Calculate the concentration of a tyrosine solution in water if the absorbance of the solution is 0.34 in a 1 cm path length cell.

Ans: Given:

$$\lambda = 280 \text{ nm}$$

$$l = 1 \text{ cm}$$

$$A = 0.34$$

From Beer-Lambert Law:

Q5: Calculate the concentration of a tryptophan solution that gives an absorbance of 0.25 at 280 nm in a 1 mm path length cell (Given $\epsilon = 5690 \text{ M}^{-1}\text{cm}^{-1}$).

Ans: The concentration of the given sample can be estimated using Beer-Lambert law:

ULTRA VIOLET-VISIBLE SPECTROSCOPY

- When a sample absorbs UV light, VALENCE ELECTRONS are promoted to higher energy levels in accordance with the frequency of absorbed light.
- The UV spectrum of a compound gives information about its electronic structure. In other words, a sample with pi electrons, with pi bonds, with lone pairs, with conjugation, will show characteristic absorption of UV light.

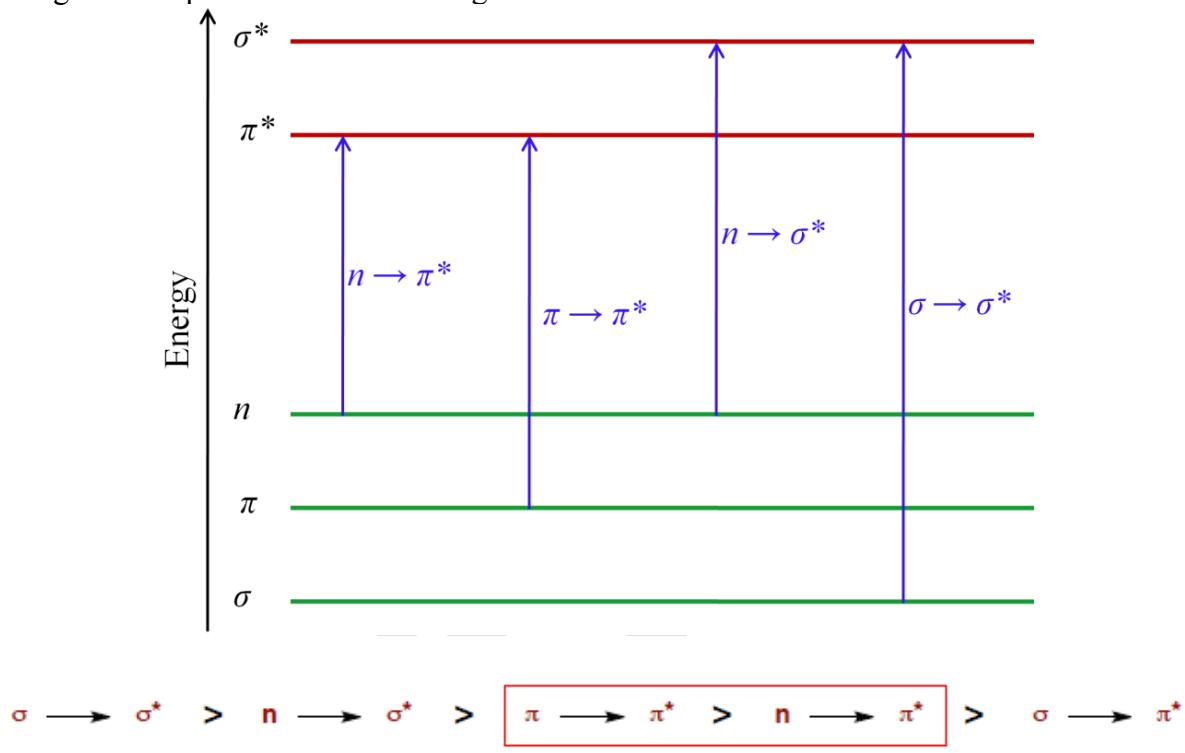
Type of electron in molecule	Orbital involved	Type of molecule	Orbital Diagram
σ bonded - electron	σ -orbital	Compound which only have σ -bond	<p style="text-align: center;">σ bonds</p>
π bonded - electron	π -orbital	Compound which have multiple bond	<p style="text-align: center;">π_p</p>
Nonbonding -electron	Nonbonding orbital	Compound which have lone pair of electron	

- UV region is divided into
- Near UV (wavelength region nearer to the visible region, $\lambda \sim 250 \text{ nm} - 400 \text{ nm}$)
- Far UV region (wavelength region farther to the visible region, $\lambda \sim 190 \text{ nm} - 250 \text{ nm}$)
- Vacuum UV region ($\lambda < 190 \text{ nm}$).

- Ordinary UV-Visible measurements are carried out from about 200nm to 800 nm. Below 200nm, the measurements are done under vacuum to avoid absorbance signals from air components like CO₂. Therefore, region below 200 nm is called vacuum UV.

Electronic Transitions:

The absorption of UV and visible light is through the transition of an electron in the molecule from lower to a higher energy molecular orbital. The various electronic transitions observed in organic compound are shown in Figure below:



The possible electronic transitions are:

$\sigma \rightarrow \sigma^*$ transition:

- $\sigma \rightarrow \sigma^*$ transition is a high energy process
- lies in the vacuum UV region.
- electron from σ orbital is excited to corresponding anti-bonding orbital σ^* .
- Alkanes, wherein only $\sigma \rightarrow \sigma^*$ transition is possible show absorption bands ~ 150 nm wavelength.

e.g. Methane (CH₄) has C-H bond only and can undergo $\sigma \rightarrow \sigma^*$ transition and shows absorbance maxima at 125 nm.

$\pi \rightarrow \pi^*$ transition:

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π^* .
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo $\pi \rightarrow \pi^*$ transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.

- In an aliphatic ketone, for example, the absorption band around 185 nm arises due to the $\pi \rightarrow \pi^*$ transition in the carbonyl group.

n → σ* transition:

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of $n \rightarrow \sigma^*$ transition.
- These transitions usually require less energy than $\sigma \rightarrow \sigma^*$ transitions.
- The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in UV region is small (150-250 nm).

n → π* transition:

- An electron from non-bonding orbital is promoted to anti-bonding π^* orbital.
- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.
- $n \rightarrow \pi^*$ transitions require minimum energy and show absorption at longer wavelength around 300 nm.

σ → π* transition & **π → σ*** transition

- These electronic transitions are forbidden transitions & are only theoretically possible.

Thus, $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.

When a molecule is subjected to UV range, a spectrum is obtained in spectrophotometer. The spectrum consists of **bands** which are the plots between absorbed light and wavelength. Through the study of these bands we can elucidate the molecular structure.

TERMS USED IN UV / VISIBLE SPECTROSCOPY

CHROMOPHORE: The part of a molecule responsible for imparting colour, are called as chromophores.

OR

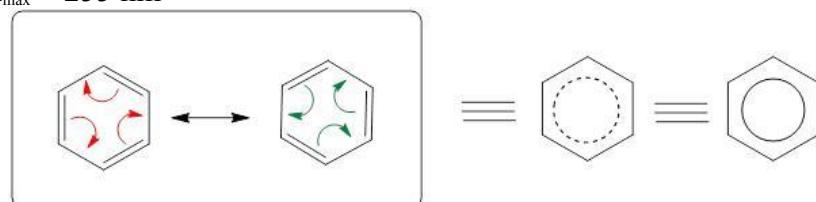
The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$ transitions. e.g. NO₂, N=O, C=O, C=N, C≡N, C=C, C=S, etc.

AUXOCHROME

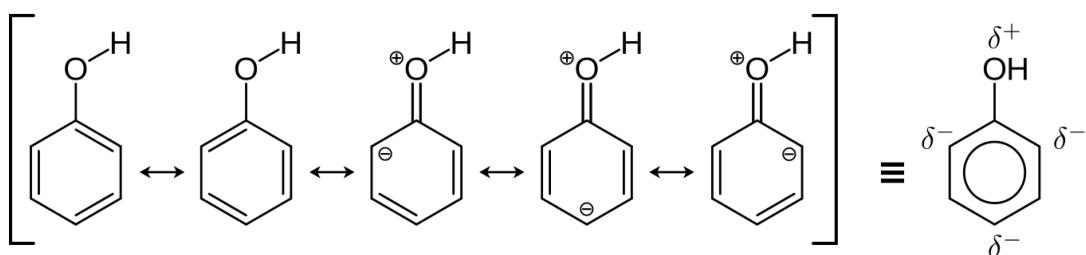
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of absorption.

OR

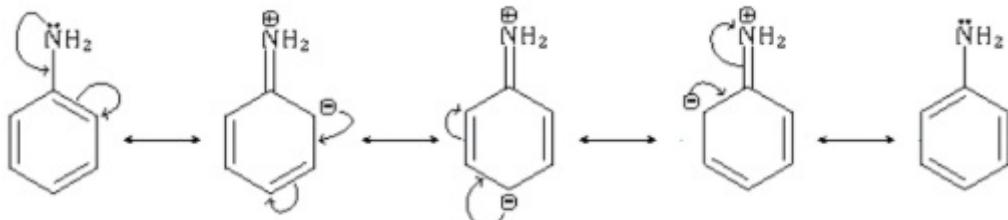
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.
e.g. Benzene $\lambda_{\max} = 255$ nm



Phenol $\lambda_{\max} = 270$ nm



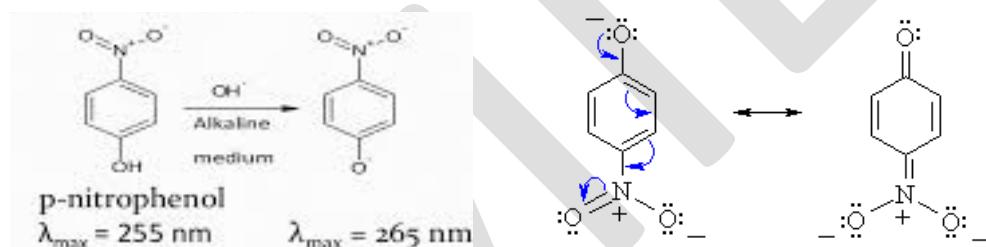
Aniline $\lambda_{\max} = 280 \text{ nm}$



ABSORPTION AND INTENSITY SHIFTS:

1. Bathochromic Shift (Red Shift)

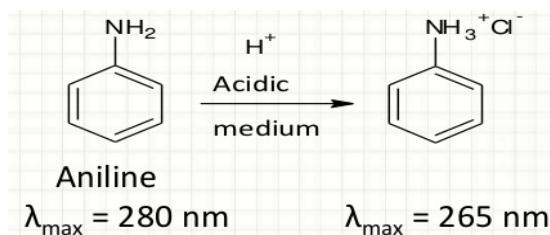
- When absorption maxima (λ_{\max}) of a compound shifts to longer wavelength, it is known as Bathochromic shift or red shift.
- The effect is due to presence of an Auxochrome or by the change of solvent. e.g. An Auxochrome group like $-\text{OH}$, $-\text{OCH}_3$, causes absorption of compound at longer wavelength.
- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



2. Hypsochromic Shift (Blue Shift)

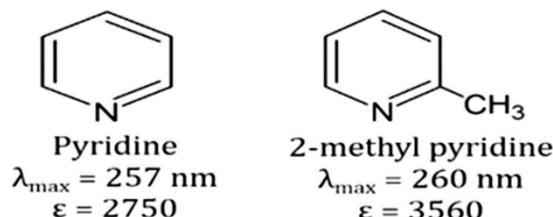
When absorption maxima (λ_{\max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.

- The effect is due to presence of a group causes removal of conjugation or by the change of solvent.
- Aniline shows blue shift in acidic medium, it loses conjugation.



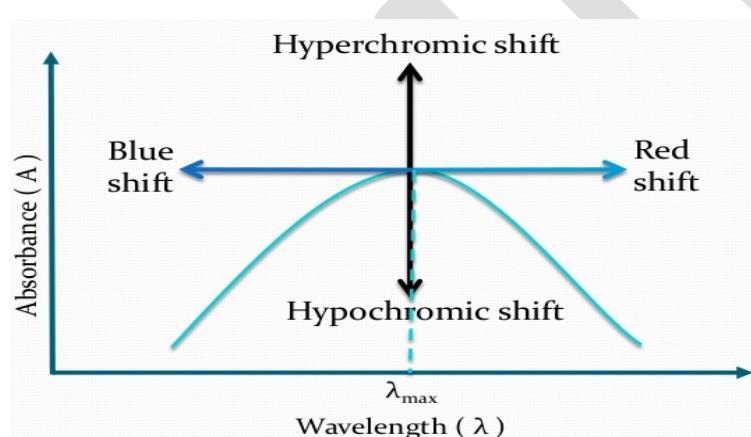
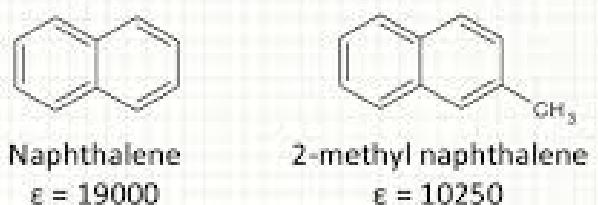
3. Hyperchromic Effect: When absorption intensity (ϵ) of a compound is increased, it is known as hyperchromic shift. If Auxochrome introduces to the compound, the intensity of absorption increases

Increase in absorbance can be due to the induction effect of CH_3 group present in 2-methyl pyridine which result in the increase in the electron density as a consequence transition probability increases.

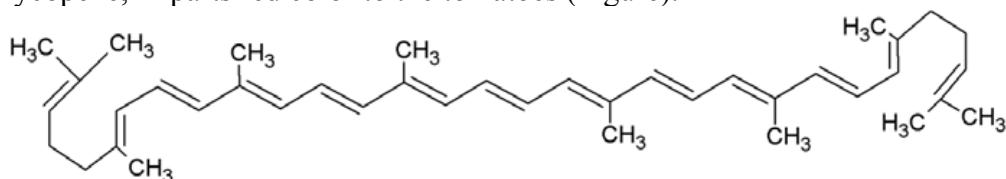


4. Hypochromic Effect:

When absorption intensity (ϵ) of a compound is decreased, it is known as hypochromic shift. The decrease in the value of absorbance is due to hypochromic effect of methyl group which distorts the chromophore by forcing the rings out of coplanarity resulting in the loss of conjugation.



➤ The molecules that absorb in far UV, near UV, and visible regions of the electromagnetic spectrum invariably have unsaturated bonds. A highly unsaturated alkene, lycopene, imparts red color to the tomatoes (Figure).



As can be seen from its structure, lycopene is a highly conjugated alkene. As compared to the simple non-conjugated alkenes that typically absorb in vacuum UV region, absorption spectrum of lycopene is hugely shifted towards higher wavelengths (or lower energy).

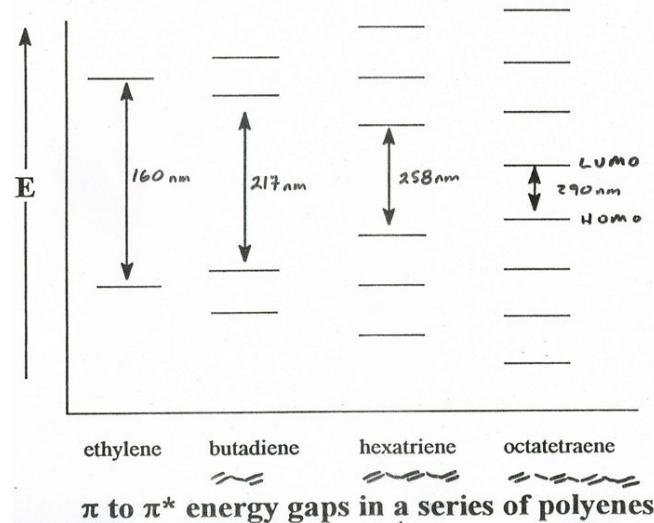
➤ **Factors causing shifts in UV-VIS spectroscopy:**

1. Conjugation:

Conjugation brings about a bathochromic shift in the absorption bands.

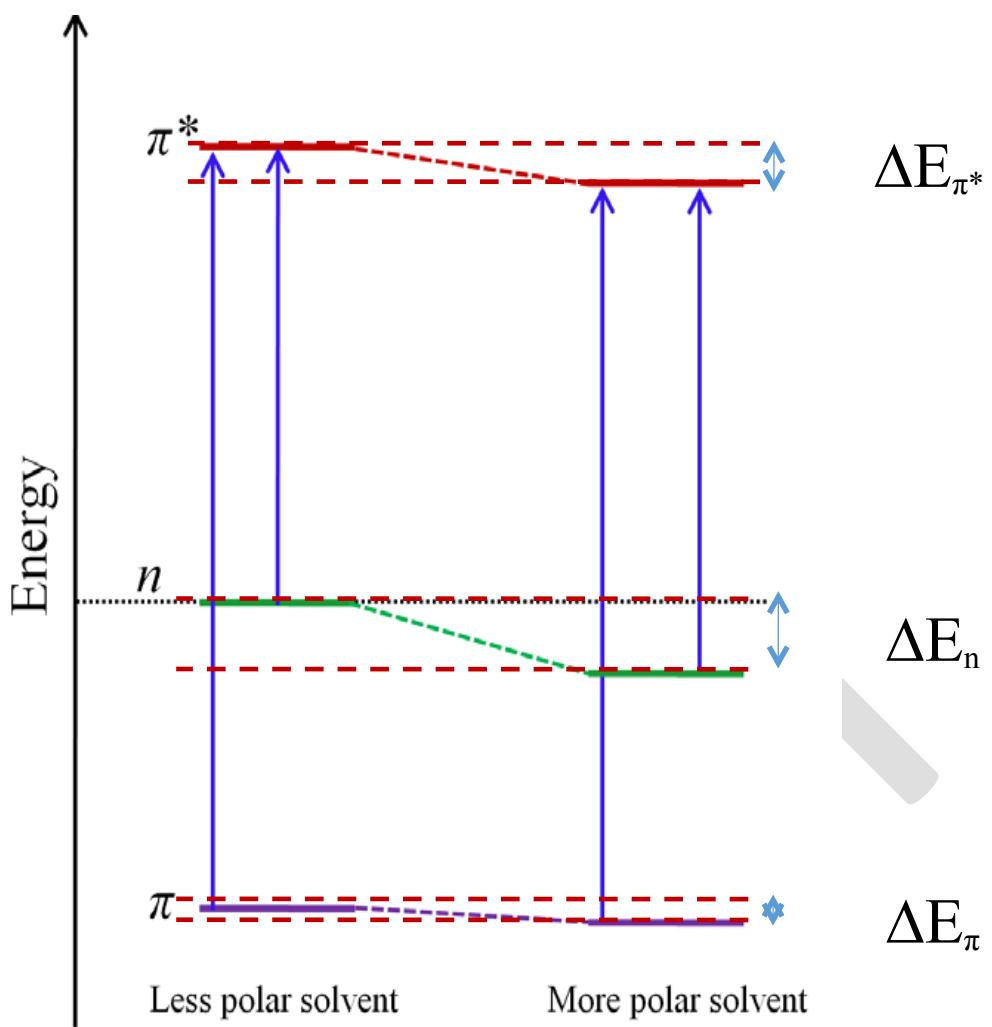
The higher the extent of conjugation, the more is the bathochromic shift.

Increase in Conjugation decreases the energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Therefore, the electronic transition becomes possible even at lower energy (higher wavelength).



2. Auxochrome:

- Auxochromes are the chemical groups that result in a bathochromic shift when attached to a chromophore.
- They exhibit bathochromism by extending conjugation through resonance.
- **Solvents:** The solvents used in any spectroscopic method should ideally be transparent (non-absorbing) to the electromagnetic radiation being used.
 - Polarity of solvents is an important factor in causing shifts in the absorption spectra.
 - The two electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respond differently to the changes in polarity.
 - Polar solvents stabilize all the three molecular orbitals (n , π , and π^*), albeit to different extents (Figure).
 - The non-bonding orbitals are stabilized most.
 - π^* more polar than π in polar molecules. hence, π^* better stabilized than π in polar solvent
 - $\pi \rightarrow \pi^*$ transition undergoes bathochromic shift with increasing polarity of solvent
 - Hydrogen bonding stabilizes n more than π^* in polar solvents
 - $n \rightarrow \pi^*$ undergoes hypsochromic shift
 - peak absorbance is reduced due to stabilization of nonbonding electrons



Nonbonding orbital stabilizes more than antibonding π orbital and bonding π orbital as shown in the above figure. Following is the *order of decrease in energy of respective molecular orbital*

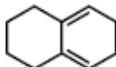
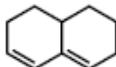
$$\Delta E_\pi < \Delta E_{\pi^*} < \Delta E_n$$

APPLICATIONS OF UV / VISIBLE SPECTROSCOPY

- Qualitative & Quantitative Analysis: It is used for characterizing aromatic compound and conjugated olefins specially which absorbs radiation in UV region.
- It can be used to find out molar concentration of the solute under study.
- Detection of impurities: It is one of the important method to detect impurities in organic solvents.
- Study of Chemical kinetics
- Structure elucidation of organic compounds
- Quantitative analysis of pharmaceutical substances
- Determination of molecular weight using Beer's law.

WOODWARD FIESER RULES

Woodward Fieser Rules for Dienes

		
s-trans	homoannular (cisoid)	heteroannular (transoid)
base values:	217 nm	253 nm
		214 nm

Increments:

For each additional conjugated double bond + 30 nm

For each exocyclic double bond + 5 nm

For each alkyl group + 5 nm

For each of the following groups:

- OR + 6 nm

- O(C=O)R + 0 nm

- Cl + 5 nm

- Br + 5 nm

- SR + 30 nm

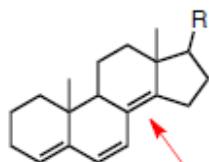
- NR₂ + 60 nm

- Ph + 60 nm

not affected by solvent

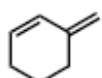
Where both types of cyclic dienes are present, the base with the longer λ_{max} is used.

CAUTION!



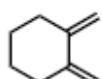
This compound had **three** exocyclic double bonds; the indicated bond is exocyclic to **two** rings.

$\lambda_{\text{max}} \text{ calc} = 284$



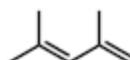
this is **not** a heteroannular diene; must use base value for acyclic diene.

$\lambda_{\text{max}} \text{ calc} = 232$

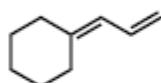


this is **not** a homoannular diene; must use base value for acyclic diene

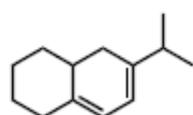
$\lambda_{\text{max}} \text{ calc} = 237$

examples

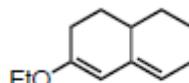
acyclic diene	217 nm
3 alkyl subst	15 nm
calculated value	232 nm
observed	234 nm



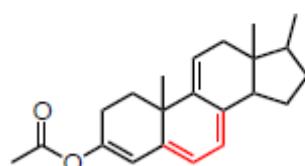
acyclic diene	217 nm
2 alkyl subst	10 nm
1 exocyclic db	5 nm
calculated value	232 nm
observed	236 nm



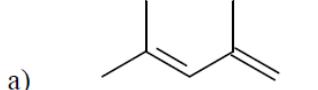
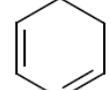
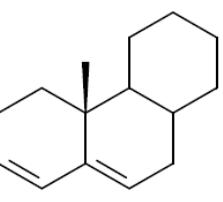
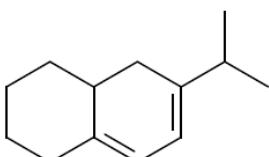
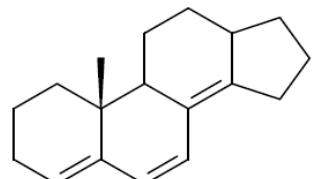
cisoid diene	253 nm
4 alkyl subst	20 nm
1 exocyclic db	5 nm
calculated value	278 nm
observed	275 nm

examples

transoid diene	214 nm
3 alkyl subst	15 nm
1 OR subst	6 nm
1 exocyclic db	5 nm
calculated value	240 nm
observed	241 nm



cisoid diene	253 nm
2 conj db	60 nm
5 alkyl subst	25 nm
1 acyl subst	0 nm
3 exocyclic db	15 nm
calculated value	353 nm
observed	355 nm

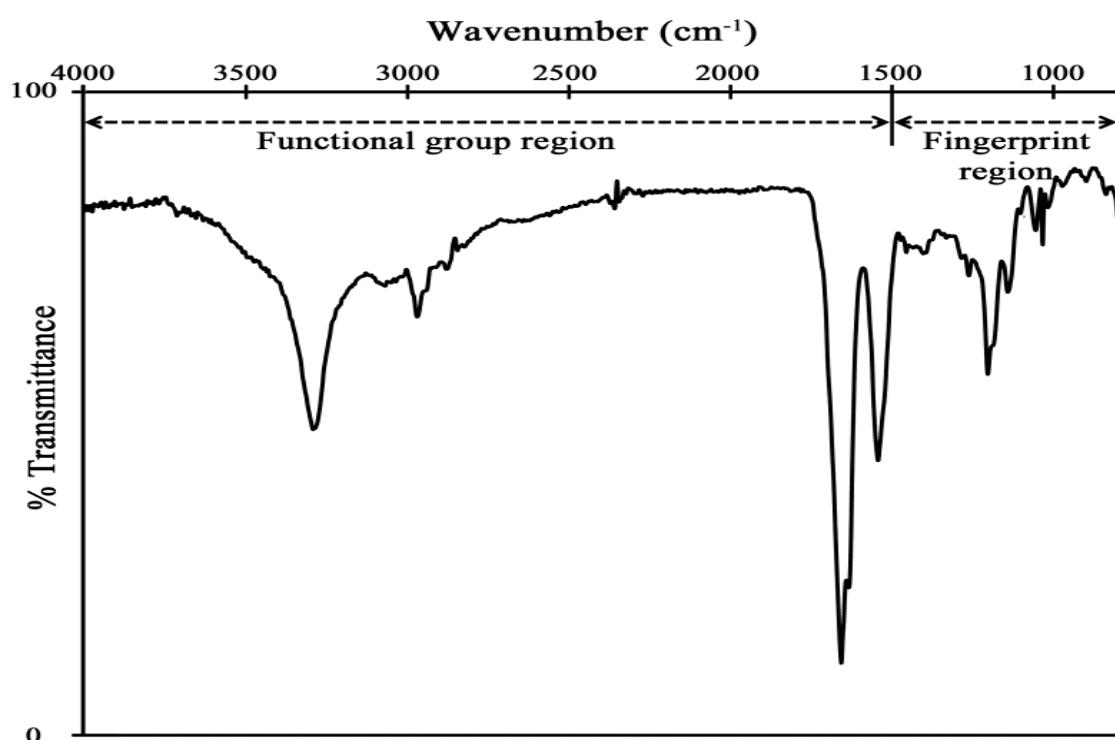
 a) Base value: 217 nm alkyl groups: 3x5 15 nm calculated: 232 nm observed: 234 nm	 b) Base value: 253 nm alkyl groups: 2x5 10 nm calculated: 263 nm observed: 256 nm	 c) Base value: 214 nm alkyl groups: 3x5 15 nm Exocyclic double bond: 5 nm calculated: 234 nm observed: 235 nm
 d) Base value: 253 nm alkyl groups or ring residues: 4x5 20 nm Exocyclic double bond: 5 nm calculated: 278 nm observed: 275 nm	 e) Base value: 214 nm alkyl groups or ring residues: 5x5 25 nm Exocyclic double bond: 3x5 15 nm extra conjugation: 1x30 30 nm calculated: 284 nm observed: 283 nm	

INFRA RED SPECTROSCOPY

Infrared Spectroscopy is the analysis of molecule interacting with infrared radiation. This can be analysed in three ways by measuring absorption, emission and reflection. When infrared radiation was absorbed by molecule, transition of electron from vibrational ground state to vibrational excited state occurs. Hence, It is also called as **vibrational spectroscopy.**

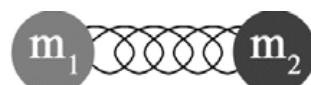
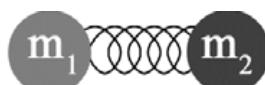
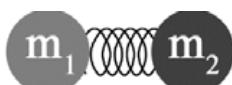
Range of the IR spectrum

- ❖ Peaks that are found in the region 4000 cm^{-1} to 1400 cm^{-1} indicates the presence of **functional group** in the molecule. This region is called as functional group region. These peaks can be used to identify and determine the functional groups of an unknown compound.
- ❖ Peaks that are found in the region 1400 cm^{-1} to 667 cm^{-1} are unique to each molecule, and acts like a fingerprint, and thus this region is known as **fingerprint region** and is used to compare the spectra of one compound to another.
- ❖ Thus IR spectra is the finger print of a molecule.



Hooke's law and frequency of vibration (IR Spectroscopy Principle)

The bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms.



If the masses of the atoms are m_1 and m_2 , the frequency of stretching vibration of the diatomic molecule can be given by the Hooke's law:

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (1.1)$$

where, v is the frequency of vibration, k is the spring constant, and μ is the reduced mass in Kg.

Where m_1 and m_2 is the mass of individual atom taken in Kg

in gram and in gram

N_A is the Avogadro number which is 6.023×10^{23} and M_1 and M_2 are the atomic mass

Dividing equation 1.1 by λ gives:

$$\frac{v}{\lambda} = \frac{1}{2\pi\lambda} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (1.2)$$

$$\frac{1}{\lambda} = \frac{1}{2\pi(\lambda v)} \sqrt{\frac{k}{\mu}}$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

The spring constant, k is the measure of the bond strength. **The stronger the bond, the higher the k , and consequently the higher is the frequency of vibration.**

	K (dyne/cm)	Bond length (Å)	Frequency (cm ⁻¹)
HCl	527667	1.274	2990
HBr	386800	1.41	2650
HI	290000	1.61	2310
CO	1860000	1.13	2170
NO	1550000	1.15	1904

These characteristic vibration frequency is called Natural frequency of vibration.

➤ When infrared radiation interact with molecule, then it causes the vibration between the atoms of the molecules

➤ Vibration between atoms of molecule occur when,

Applied infrared frequency = Natural frequency of vibration

Then, Absorption of IR radiation takes place and a peak is observed.

- Different functional groups absorb characteristic frequencies of IR radiation. Hence gives the characteristic peak value.

Therefore, **IR spectrum of a chemical substance is a finger print of a molecule for its identification.**

Criteria for a compound to absorb IR radiation

The two essential criteria's for a molecule to be IR active are:

1. Correct wavelength of radiation
2. Change in dipole moment

1. Correct wavelength of radiation:

A molecule to absorb IR radiation, the natural frequency of vibrations of some part of a molecule is the same as the frequency of incident radiation.

2. Change in dipole moment:

A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment.

- All the homonuclear diatomic molecules such as H₂, N₂, O₂, etc are IR inactive.
- All Heteronuclear diatomic are always IR active due to present of permanent dipole. This is because atom in diatomic molecule have electronegative differences. E.g. Vibration of carbon monoxide (C=O).

MOLECULAR VIBRATIONS:

There are 2 types of vibrations:

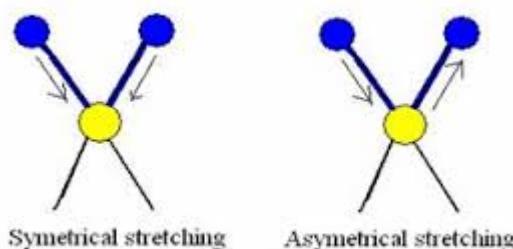
- Stretching vibrations
- Bending vibrations

1. Stretching vibrations:

- Vibration or oscillation along the line of bond.
- There occurs a change in bond length.
- Occurs at higher energy: 4000-1250 cm⁻¹.
- It is of 2 types:
 - a) Symmetrical stretching
 - b) Asymmetrical stretching

a) **Symmetrical stretching:** 2 bonds increase or decrease in length simultaneously.

b) **Asymmetrical stretching:** in this, one bond length is increased and other is decreased.



2. Bending vibrations

- Vibration or oscillation are not along the line of bond
- These are also called as deformations
- In this, bond angle is altered
- Occurs at low energy: $1400\text{-}666\text{ cm}^{-1}$
- These are of 2 types:
 - a) In plane bending: scissoring, rocking
 - b) Out plane bending: wagging, twisting

a) In plane bending

- **Scissoring:** This is an in plane bending in which 2 atoms approach each other and bond angles decreases.
- **Rocking:** Movement of atoms take place in the same direction.

b) Out plane bending

- **Wagging:** 2 atoms move to one side of the plane. They move up and down the plane.
- **Twisting:** One atom moves above the plane and another atom moves below the plane.

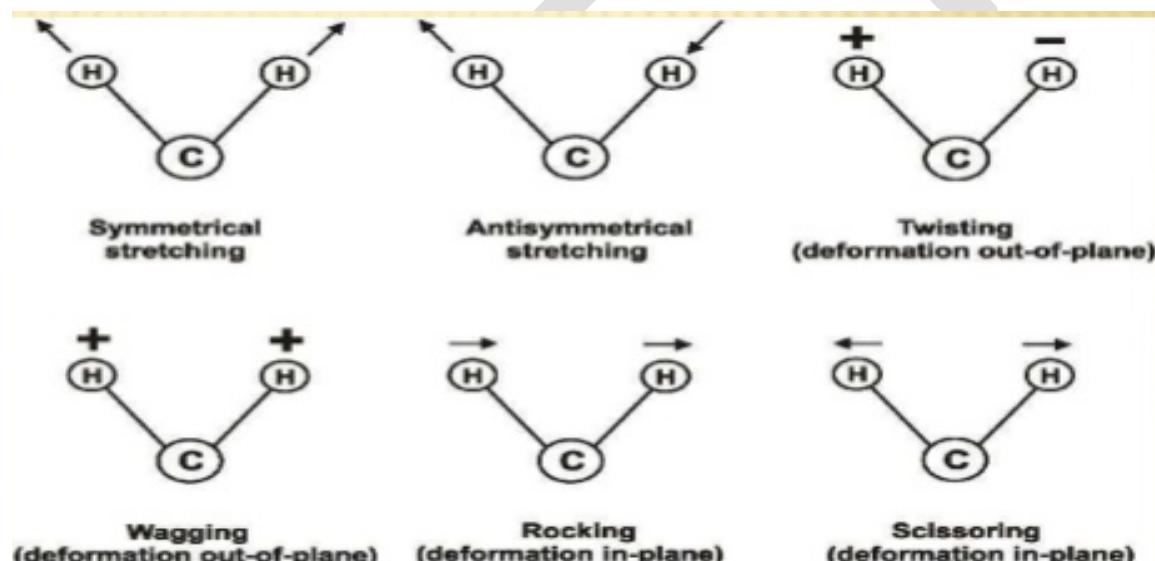


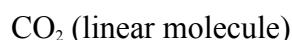
Diagram showing different molecular vibrations in IR spectroscopy

Number of fundamental vibrations:

For a linear molecule = $3n - 5$, where n is the number of atoms.

For a non-linear molecule = $3n - 6$

Example



$$n = 3, \text{ no of fundamental vibrations} = 3n - 5 = (3 \times 3) - 5 = 4$$



$$n = 3, \text{ no of fundamental vibrations} = 3n - 6 = (3 \times 3) - 6 = 3$$

CH_4 (nonlinear molecule)

$$n = 5, \text{ no of fundamental vibrations} = 3n - 6 = (3 \times 5) - 6 = 9$$

Vibrational modes of CO_2

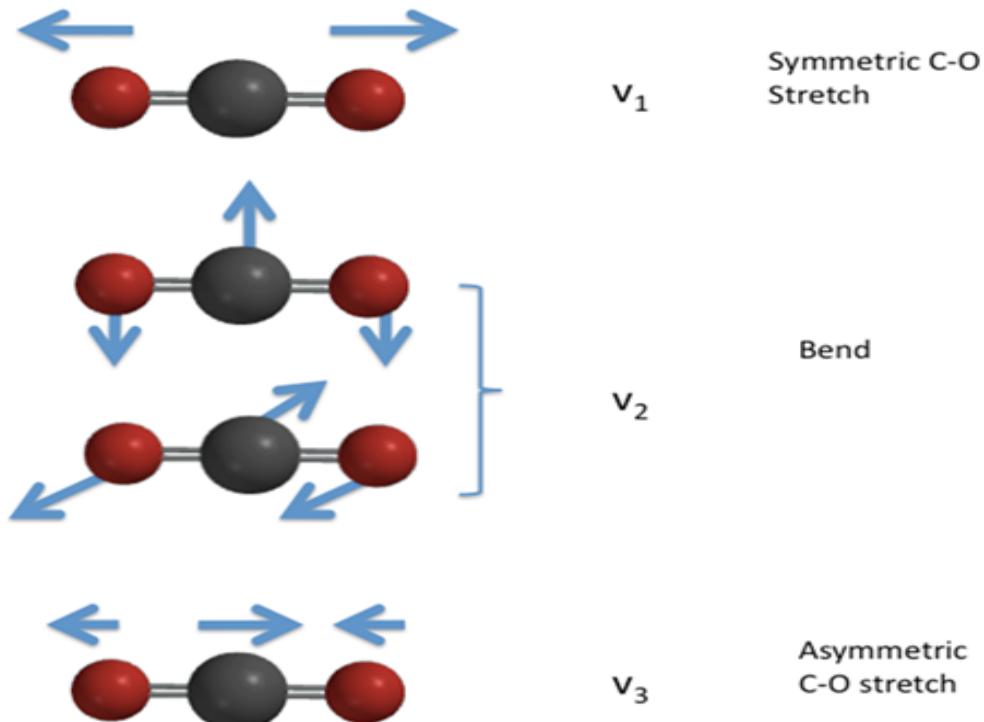


Fig. Vibrational mode of CO_2

- The symmetric stretch does not result in a change of the initially zero dipole moment, so it is IR-inactive.
- The asymmetric stretch does result in a change in dipole moment so it is IR active.
- The bend also results in a change in dipole moment so it too is IR-active.

To sum up, carbon dioxide has 3 IR-active vibrational modes.

Interpretation of an IR spectra

FUNCTIONAL GROUP REGION (4000-1500 cm^{-1}):

1. The most common application of IR spectroscopy is perhaps to identify the functional groups.
2. This is possible because different functional groups vibrate at different frequencies allowing their identification.

3. Region from $4000\text{-}1500\text{ cm}^{-1}$ in an IR spectrum is useful for identification of functional groups,

The wavenumbers for some of the stretching mode vibration in molecule in Table:

Bond	Molecule	Wavenumber (cm^{-1})
C–O	Alcohols, ethers, esters, carboxylic acids, etc.	1300 – 1000
C=O	Aldehydes, ketones, esters, carboxylic acids	1750 – 1680
C=O	Amides	1680 – 1630
N–H (Stretching)	Amines and amides	3500 – 3100
–N–H (Bending)	Amines and amides	1640 – 1550
O–H	Alcohols	3650 – 3200
C–N	Amines	1350 – 1000
S–H	Mercaptans	2550

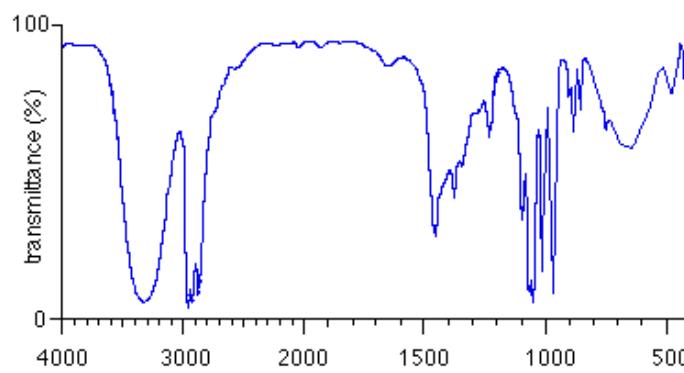
FINGER PRINT REGION ($1500\text{-}600\text{ cm}^{-1}$):

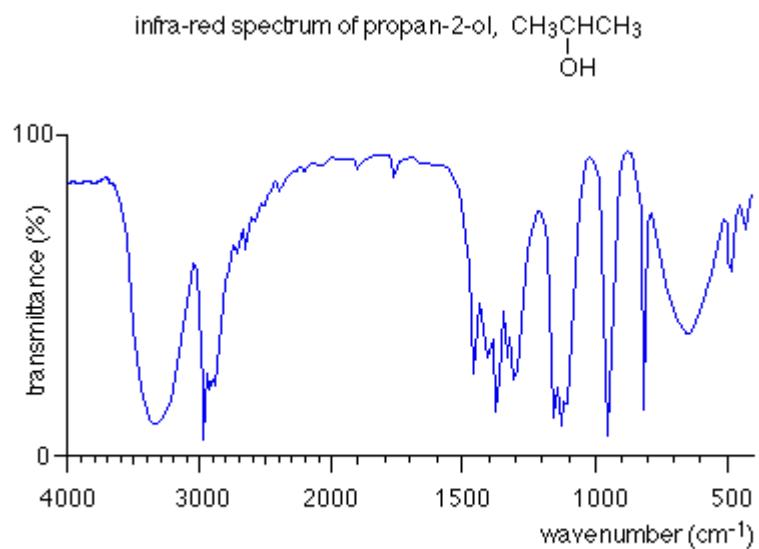
- The region below 1500 cm^{-1} ($1500\text{-}667\text{ cm}^{-1}$) is known as finger print region.
- It contains number of vibrations caused by bending and stretching vibrations.
- This region shows a number of vibrations which makes it complex.
- However each organic group has its own unique absorption pattern in this region.
- The molecules containing same functional groups show similar absorption above 1500 cm^{-1} , but if the molecules are different, then the spectra differ in finger print region. On the other hand if along with high frequency region (above 1500 cm^{-1}), the finger print region also matches, the two molecules are of same compound.
- This region thus provides confirmation of identity of molecules.
- **No two compounds except enantiomers can have similar IR spectra.**

Example: Consider the example of propane-1-ol and propane-2-ol.

Compare the IR spectra of propan-1-ol and propan-2-ol.

infra-red spectrum of propan-1-ol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$





Both spectra are quite similar in the functional group region, but their absorption patterns in the fingerprint region are completely different.

Factor effecting vibrational frequency:

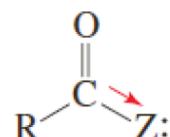
1. **Bond order:** Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency

Absorption frequency increases with increasing bond order (and bond strength)

Bond	Frequency (cm^{-1})	Bond	Frequency	Bond	Frequency
C-C	< 900	C-O	970 - 1250	C-N	1250-1020
C=C	1680 - 1620	C=O	1630-1780	C=N	1690-1640
C≡C	2260 - 2100	C≡O	2100	C≡N	2260-2220

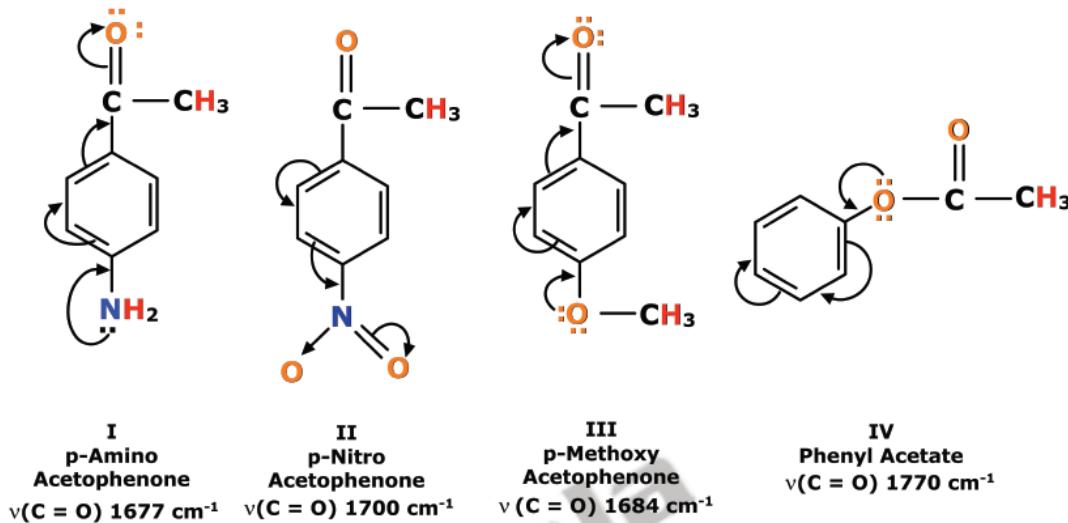
2. **Electronic Effects: Resonance and Inductive:**

(a) Inductive Effect



	Attachments	Inductive effect	Bond length	Force constant	Frequency
Electron Deficient	Alkyl group	+i	Increases	Decreases	Decreases
Electron Rich	Cl, Br, I, OH	-i	Decreases	Increases	Increases

(b) Resonance Effect: As the molecule have π -electron leading to conjugation results in the delocalization of electron over 3-4 atoms or even more. This weakens the multiple bond (such as C=O). This can result in the decrease in vibrational frequency.

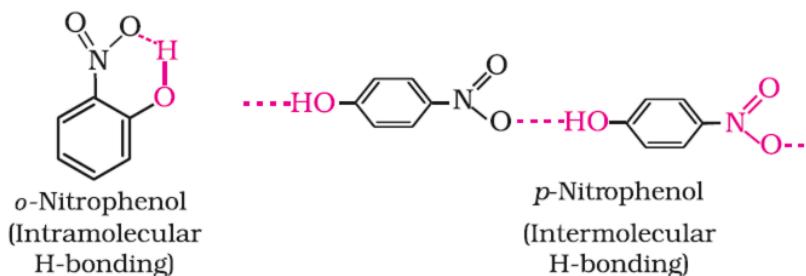


3. Hydrogen Bonding:

- The presence of hydrogen bonding changes the position and shape of an infrared absorption band.
- Stronger the hydrogen bonding, greater is the absorption shift from the normal values which result in red shift in IR spectra.



- The two types of hydrogen bonding (intramolecular and intermolecular) can be differentiated by the use of infrared spectroscopy.



Application of IR

- **Qualitative Analysis:** Main application of IR spectroscopy is compound identification and molecular structure.
- Determination of Purity of a sample.
- Studying progress of the reaction
- Identification of functional group
- Distinguish between inter and intra molecular H bonding: IR spectra of the compound at different concentration are recorded with increase in concentration, the absorption band due to inter molecular H-bonding increases while that due to intra molecular H-bonding remains unchanged.
- Structural information: IR spectra provides valuable information regarding molecular symmetry, dipole moments, bond strength, characteristic absorption etc.
- Analysis of petroleum hydrocarbons oils and greases content.

Q1: If the stretching frequency of a hydrogen molecule is 1.2×10^{14} vibrations/sec. Calculate the wavenumber where hydrogen molecule absorption band will be observed in an IR spectrum.

Solution: The frequency of hydrogen stretching can be represented in terms of wavenumbers as follows: $\bar{\nu} = 1/\lambda = \nu/c \text{ cm}^{-1}$

Hydrogen, however, is a homodiatomeric molecule; the stretching vibration does not cause any change in the dipole moment. Therefore, hydrogen will not show absorption in the IR of 4000 cm^{-1} and consequently will not appear in an IR spectrum.

Q2: Calculate the frequency (in Hz and cm^{-1}) of O-H band, if the force constant and reduced mass of the atom pair are and , respectively.

Solution: and

Q3. ${}^1\text{H}{}^{35}\text{Cl}$ has force constant value of . Calculate the fundamental frequency in wavenumber.

Solution: ,

Q.4: the value of force constant is same for $^{16}\text{O}-^1\text{H}$ and $^{16}\text{O}-^1\text{D}$. If the fundamental vibrational frequency of $^{16}\text{O}-^1\text{H}$ is 3600 cm^{-1} . Calculate the fundamental vibrational frequency of $^{16}\text{O}-^1\text{D}$.

Solution: and

Now,

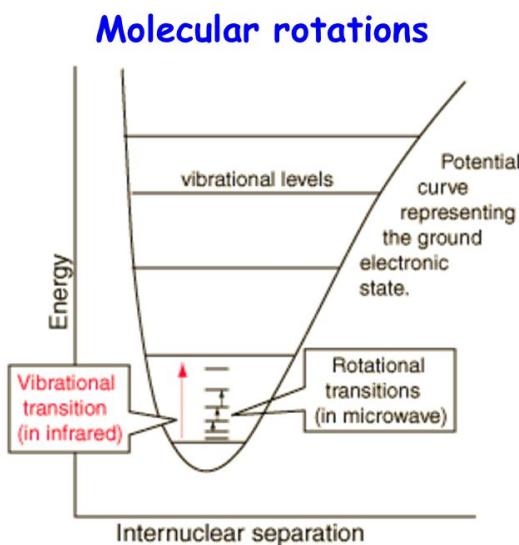
Q5: Calculate the force constant of the CO molecule, if its fundamental vibrational frequency is 2140 cm^{-1} . (At. Mass of and)

Solution:

And
Thus

Rotational Spectroscopy/Microwave Spectroscopy

Radiation used in rotational spectroscopy is $3 \times 10^{10} \text{ Hz}$ to $3 \times 10^{14} \text{ Hz}$ which comes in microwave region of electromagnetic radiation. Hence **Rotational spectroscopy** is also known as **microwave spectroscopy**.



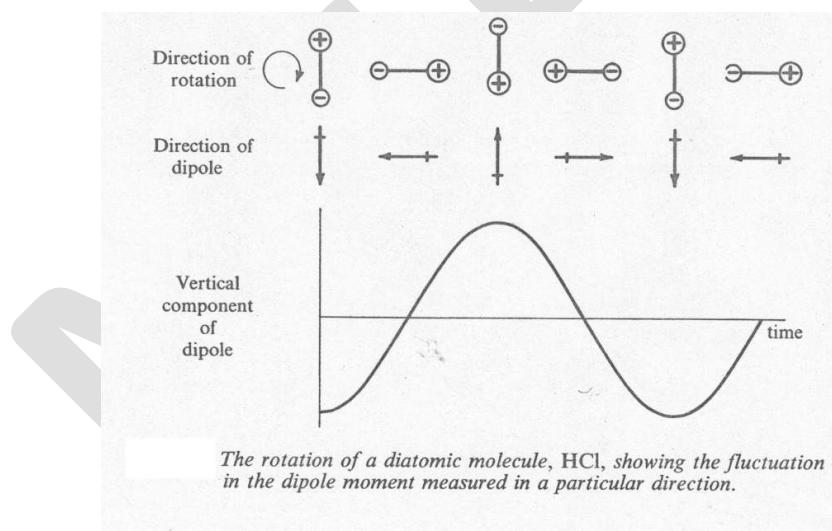
Rotational spectroscopy is the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. Rotational spectroscopy deals with pure rotational motion of molecule and the rotational degree of freedom is only possible in gas phase where distance between molecules is large enough to consider them as isolated molecule. Therefore microwave studies are done only in gaseous state.

- Rotational spectroscopy is sometimes referred to as *pure* rotational spectroscopy to distinguish it from rotational-vibrational spectroscopy where changes in rotational energy occur together with changes in vibrational energy.
- **Rotational spectroscopy** uses microwave radiation to measure the energies of rotational transitions for molecules in the gas phase. Thus rotational spectroscopy is also known as **Microwave spectroscopy**

Principle: When a molecule having permanent dipole moment rotates, it generates an electric field which interact with the electric component of the microwave radiation falling on it. During interaction, energy can be absorbed or emitted and thus gives rise to spectrum.

- If the molecule absorb the energy from incident microwave radiations, it jumps from lower rotational energy level to higher rotational energy level and it exhibits **Absorption Microwave Spectrum**.
- If molecule emits the energy (Energy is transferred from molecule to the emitted microwave radiation), it moves from high rotational energy level to lower rotational energy level and it exhibits **Emission Microwave Spectrum**.

Mechanism: When the frequency of the oscillation of rotating polar molecule becomes exactly equal to the frequency of electric field of incident microwave radiation, then the phenomenon of resonance occurs and at this stage the absorption of radiations (transfer of energy) takes place.

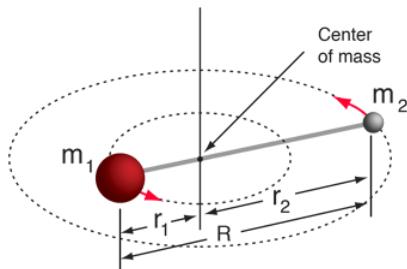


Condition for Microwave absorption:

- Only those molecules which have permanent dipole moment can interact with electric field component of microwave radiation, and are called microwave active molecules.
- Rotational spectroscopy is only practical in the gas phase where the rotational motion is quantized.

Interpretation of pure rotational spectra:

Let us consider a rigid rotating diatomic molecule (Rigid rotor) i.e. Molecules in which bonds don't distort under the stress of rotation.



Let m_1 and r_1 be the mass of atom and distance from centre of gravity for atom 1. Similarly, m_2 and r_2 be the mass of atom and distance from centre of gravity for atom 2.

At centre of gravity , $m_1r_1 = m_2r_2$

Since , $I = mr^2$

where I = Moment of Inertia (which is a measure of an object's resistance to changes in its rotation rate)

m = mass of molecule/ atom, r = distance

In case of diatomic molecule the above expression becomes

$$\begin{aligned} I &= m_1r_1^2 + m_2r_2^2 \\ &= (m_1r_1)r_1 + (m_2r_2)r_2 \\ &= m_2r_2r_1 + m_1r_1r_2 \quad (m_1r_1 = m_2r_2) \end{aligned}$$

$$I = r_1r_2(m_2 + m_1) \quad (1)$$

$$\begin{aligned} m_1r_1 &= m_2r_2 \\ m_1r_1 &= m_2(r_0 - r_1) \quad (r_2 = r_0 - r_1) \\ m_1r_1 &= m_2r_0 - m_2r_1 \\ m_1r_1 + m_2r_1 &= m_2r_0 \\ r_1(m_1 + m_2) &= m_2r_0 \end{aligned}$$

$$r_1 = m_2r_0/(m_1 + m_2) \quad (2)$$

Similarly

$$r_2 = m_1r_0/(m_1 + m_2) \quad (3)$$

Putting the values of (2) and (3) in (1), we get

$$I = \{m_1m_2/(m_1 + m_2)\} \times r_0^2$$

$$I = \mu r_0^2$$

and

Where μ is in Kg as we have calculated in vibrational spectroscopy.

Energy levels of rigid diatomic molecular rotation

We know that energy of rotating molecules is given by

$$E_J = (h^2/8\pi^2I) \cdot J(J+1)$$

To convert energy from Joule to cm^{-1} , divide the above equation with hc .

$$E_J / hc = h^2/8\pi^2I \cdot hc \cdot J(J+1)$$

$$E_J/hc = h/8\pi^2I \cdot c \cdot J(J+1)$$

$$\text{Or, } E_J = B \cdot J(J+1)$$

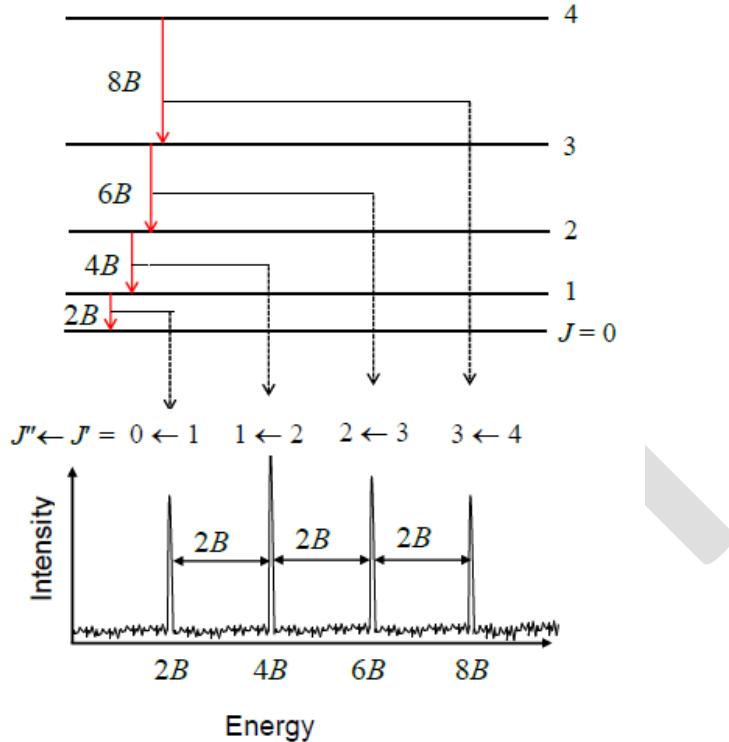
Where, $B = h / 8\pi^2I \cdot c$ (known as **rotational constant**)

In equation, $E_J = BJ(J+1)$, B is constant

So, value of E_J depends on J

$$\begin{aligned}
 \text{If } J = 0; \quad E_J = 0 \\
 J = 1; \quad E_J = 2B \\
 J = 2; \quad E_J = 6B \\
 J = 3; \quad E_J = 12B
 \end{aligned}$$

So, we can say that rotational motion is a quantized motion having fixed energy values for each rotational level.



Energy gap between two energy levels

$$\begin{aligned}
 \Delta E_J &= E_{J+1} - E_J = B(J+1)(J+1+1) - BJ(J+1) \\
 &= B(J+1)(J+2) - BJ(J+1) = B(J^2 + 2J + J + 2) - BJ(J+1) = B(2J+2) \\
 \Delta E_J &= 2B[J+1]
 \end{aligned}$$

When $J=0$

$$\Delta E_J = 2B$$

$J=1$

$$\Delta E_J = 4B$$

$J=3$

$$\Delta E_J = 6B$$

$J=4$

$$\Delta E_J = 8B$$

So transitions are equispaced with spacing $2B$ i.e. the distance between two lines (equally spaced) in pure rotational spectra of any molecule will be $2B$.

Determination of bond length of diatomic molecules (rotor)

$$I = \mu r^2$$

$$r =$$

$$\text{Since } I =$$

$$\mathbf{r} =$$

Selection rule for rotational spectra

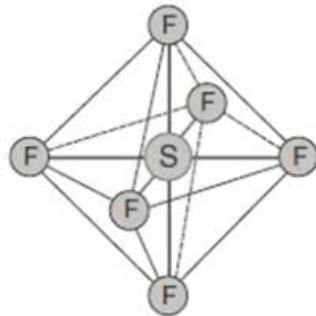
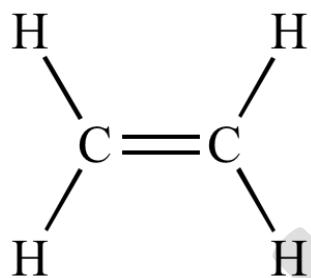
1. In case of rotational spectra, only those transitions are allowed in which there is an increase or decrease by unity in the rotational quantum number i.e.

$$\Delta J = \pm 1$$

2. Molecule should possess permanent Dipole moment.

Microwave inactive molecules

1. No dipole moment
2. Homonuclear diatomic molecules like O₂, N₂
3. Symmetrical linear molecules such as CO₂
4. Any molecule with a centre of inversion is microwave inactive such as C₂H₄ and SF₆.



Applications of rotational spectroscopy

1. Determination of bond length of a polar molecule
2. Determination of symmetry in a molecule
3. Determination of dipole moments of gaseous molecules

Q1: From the rotational microwave spectrum of ¹H³⁵Cl, we find that B = 10.59342 cm⁻¹. Given that the masses of ¹H and ³⁵Cl are 1.0078250 and 34.9688527 amu, respectively, determine the bond length of the ¹H³⁵Cl molecule.

Solution :

in gram where

=Avogadro number

Thus reduced mass in gram,

Now ,

Now Given $B = 10.93429 \text{ cm}^{-1} = 1093.429 \text{ m}^{-1}$

Kg m^2

Q2. The first rotational line in the rotational spectrum of CO is observed at 3.84235 cm^{-1} . Calculate the rotational constant (B) and bond length of CO. The relative atomic weight C = 12.00 and O = 15.9994, the absolute mass of H = $1.67343 \times 10^{-27} \text{ kg}$.

Solution: amu

=Avogadro number

Thus

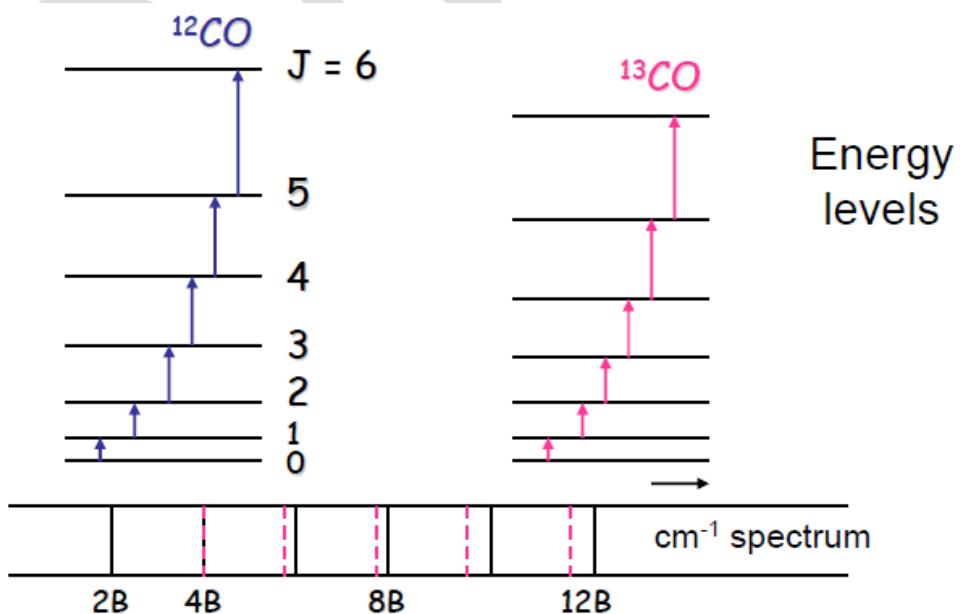
Now Given $2B = 3.84235 \text{ cm}^{-1}$,

thus $B = 1.92117 \text{ cm}^{-1} = 192.117 \text{ m}^{-1}$

Kg m^2

Effect of isotopic substitution

On changing from $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{16}\text{O}$, atomic mass increases, B decreases ($\propto 1/I$), so energy of levels becomes lower.



RAMAN SPECTROSCOPY

Raman spectroscopy was discovered by C. V. Raman in 1928. It determines vibrational and rotational level spacing from the energy (wavenumber) shifts of scattered light. Similar to IR spectroscopy, Raman spectroscopy also provide information about the vibrational motion in molecule.

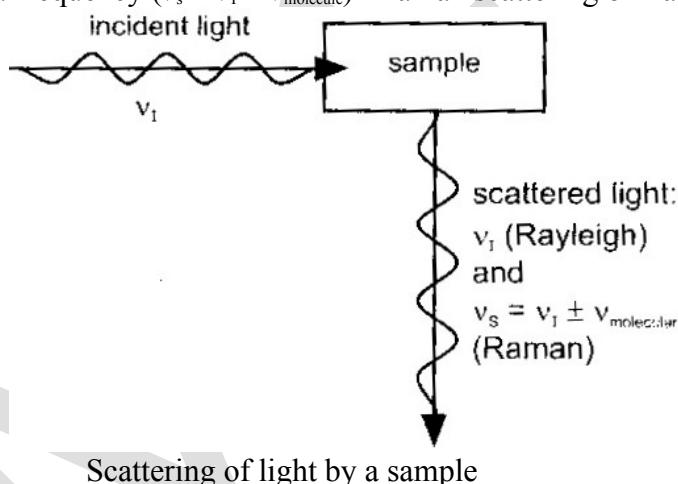
THEORY OF RAMAN SPECTROSCOPY

Raman spectra are acquired by irradiating a sample with a powerful laser source of visible or near-infrared monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle between 0 to 180 Degree (most often 90 degree) depending on sample. At the very most, the intensities of Raman lines are 0.001 % of the intensity of the source; as a consequence, their detection and measurement are somewhat more difficult than are infrared spectra.

Rayleigh Scattering and Raman Scattering

The frequency of the scattered light can be:

- at the original frequency (ν_i) "Rayleigh scattering" *very strong*.
- at some shifted frequency ($\nu_s = \nu_i \pm \nu_{\text{molecule}}$) "Raman scattering or Raman



Scattering of light by a sample

Excitation of Raman Spectra

Raman shift can correspond either to rotational, vibrational or electronic frequencies.

$$\Delta\nu = |\nu_i - \nu_s|$$

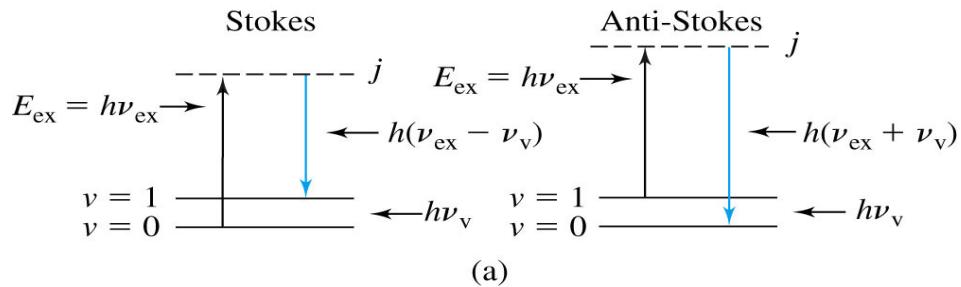
Radiation scattering to the lower frequency side (to the red side) of the Rayleigh line is called *Stokes* scattering.

Radiation scattering to the higher frequency side (to the blue side) of the Rayleigh line is called *anti-Stokes*

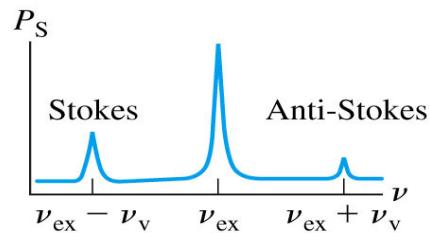
A Raman spectrum can be obtained by irradiating a sample of carbon tetrachloride (Fig 18-2) with an intense beam of an argon ion laser having a wavelength of 488.0 nm (20492 cm^{-1}). The emitted radiation is of three types:

1. Stokes scattering
2. Anti-stokes scattering

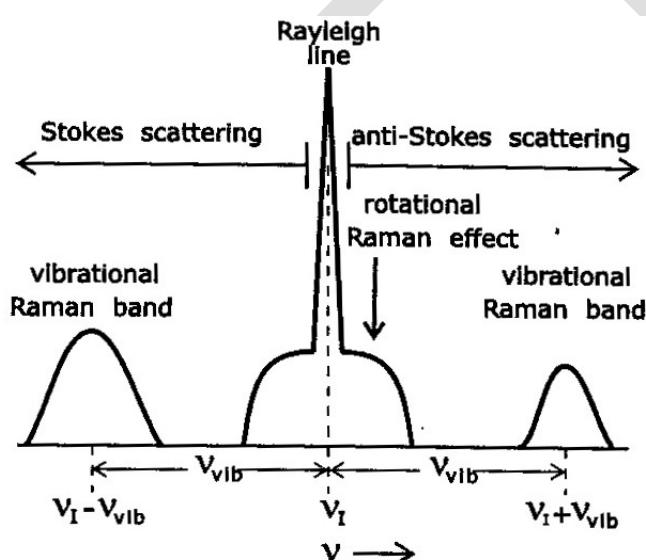
3. Rayleigh scattering



(a)



(b)



Schematic diagram of Raman spectrum showing vibrational and rotational Raman effects

Criteria for a compound to be Raman active

- A molecular vibration is Raman active when there is change of polarizability during vibration of molecule upon absorption of radiation.
- In contrary to IR, All the homonuclear diatomic molecules such as H₂, N₂, O₂, etc are Raman active because they can exhibit change in polarizability.
- Similar to IR, all Heteronuclear diatomic are always Raman active.

Nature of Polarizability

Polarizability is the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field or presence of a nearby ion or dipole.

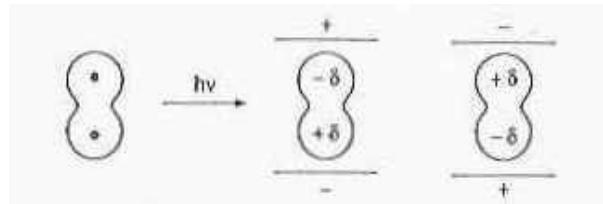


Figure 1-14 Polarization of a diatomic molecule in an electric field.

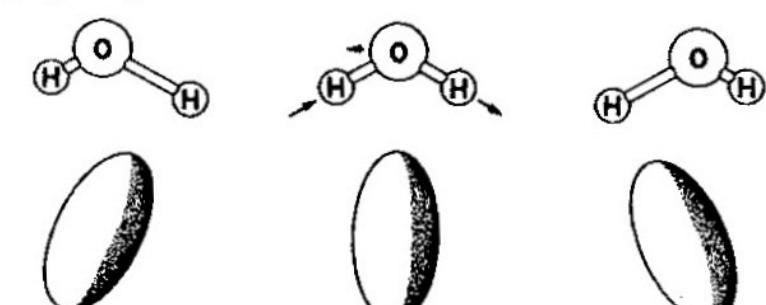
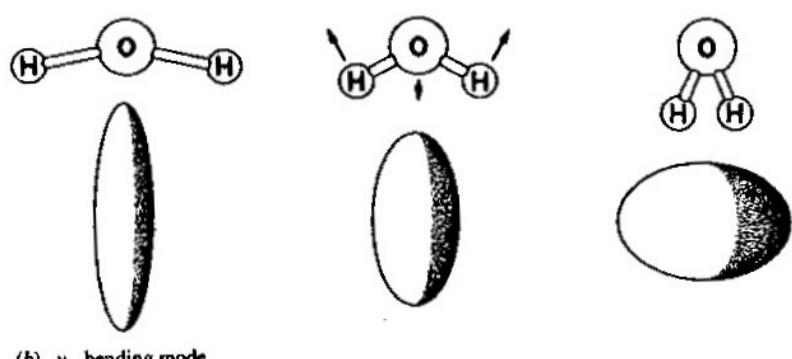
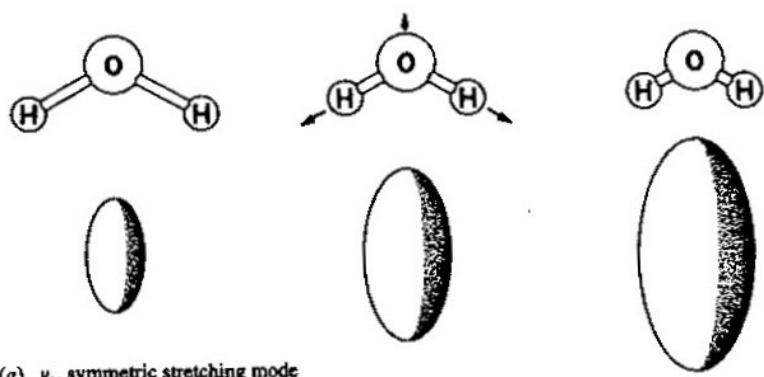
Polarisation of diatomic molecule in an electric field

Raman Activity of Molecular Vibrations

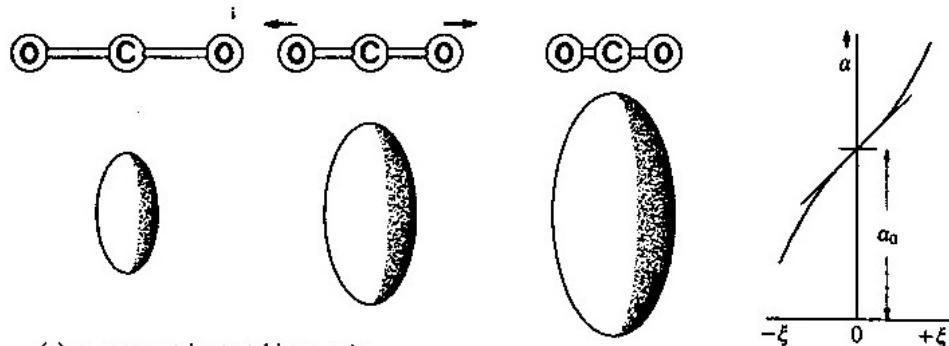
- In order to be Raman active, a molecular rotation or vibration must cause some change in a component of the molecular polarizability. The change can either be in the magnitude or the direction of the polarizability ellipsoid.
- Polarizability ellipsoid is a three-dimensional body generated by plotting $1/\sqrt{\alpha}$ from the centre of gravity in all directions.

Note: *This rule must be contrasted with that for IR activity that requires change in the net dipole moment of the molecule*

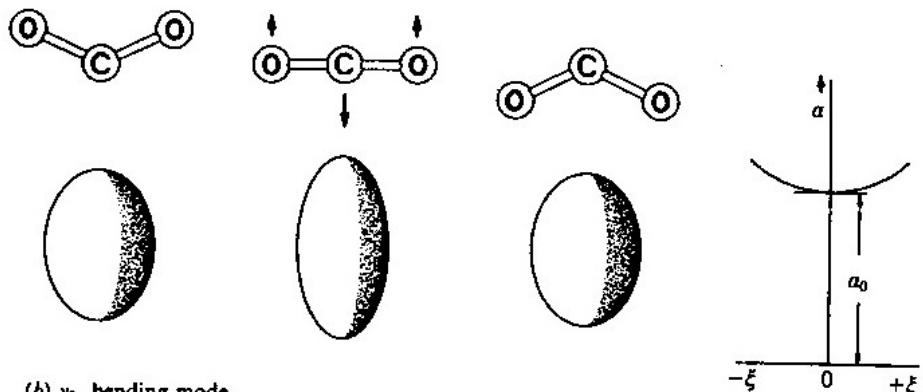
Raman Activity of H₂O Vibrations



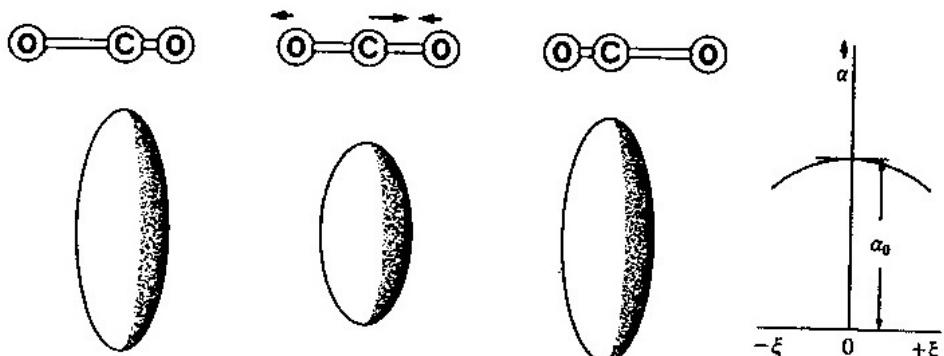
Raman Activity of CO₂ Vibrations



(a) ν_1 , symmetric stretching mode



(b) ν_2 , bending mode



(c) ν_3 , asymmetric stretching mode

Rule of Mutual Exclusion

If a molecule has a center of symmetry, then Raman active vibrations are infrared inactive, and vice versa. If there is no center of symmetry, then some (but not necessarily all) may be both Raman and infrared active.

Mode of vibration of CO_2	Raman	Infra-red
ν_1 : symmetric stretch	Active	Inactive
ν_2 : bending	Inactive	Active
ν_3 : asymmetric stretch	Inactive	Active

Comparison between FT and dispersive Raman FT-Raman

Fluorescence-free Raman spectra by 1064nm excitation

Simple measurement of bulk samples due to advantage of sample compartment

Dispersive Raman

Better spatial resolution for microscopy applications (down to 1 μm)

Higher sensitivity and shorter measurement times for non fluorescing samples

Selection of different excitation lines (488-785nm).

APPLICATIONS OF RAMAN SPECTROSCOPY

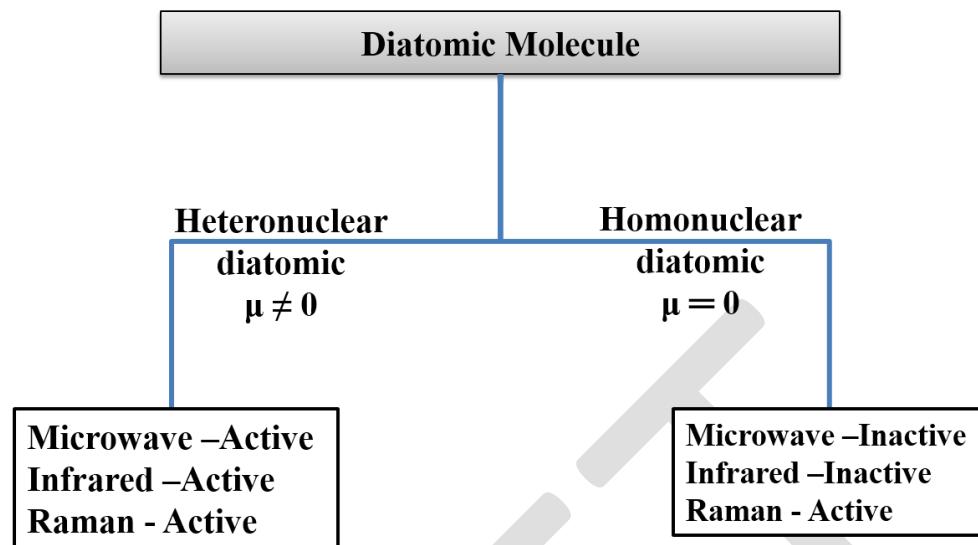
1. **Qualitative tool for identifying molecules** from their vibrations.
2. **Quantitative Raman measurements:** Raman spectroscopy is not sensitive since Raman scattering is weak. But resonance Raman spectra offer higher sensitivity, e.g. fabric dyes studied at 30-50 ppb.
3. **Raman Spectra of Inorganic Species** The Raman technique is often superior to infrared for spectroscopy investigating inorganic systems because aqueous solutions can be employed. *In addition, the vibrational energies of metal-ligand bonds are generally in the range of 100 to 700 cm⁻¹, a region of the infrared that is experimentally difficult to study.* These vibrations are frequently Raman active.
4. **Raman Spectra of Organic Species** Raman spectra are similar to infrared spectra in that they have regions that are useful for functional group detection and fingerprint regions that permit the identification of specific compounds.
5. **Biological Applications of Raman Spectroscopy** Raman spectroscopy has been applied widely for the study of biological systems. The advantages of his technique include the small sample requirement, the minimal sensitivity toward interference by water, and the conformational and environmental sensitivity.
6. **Analysis of food and nanomaterials using Raman spectroscopy**

Raman vs IR spectroscopy

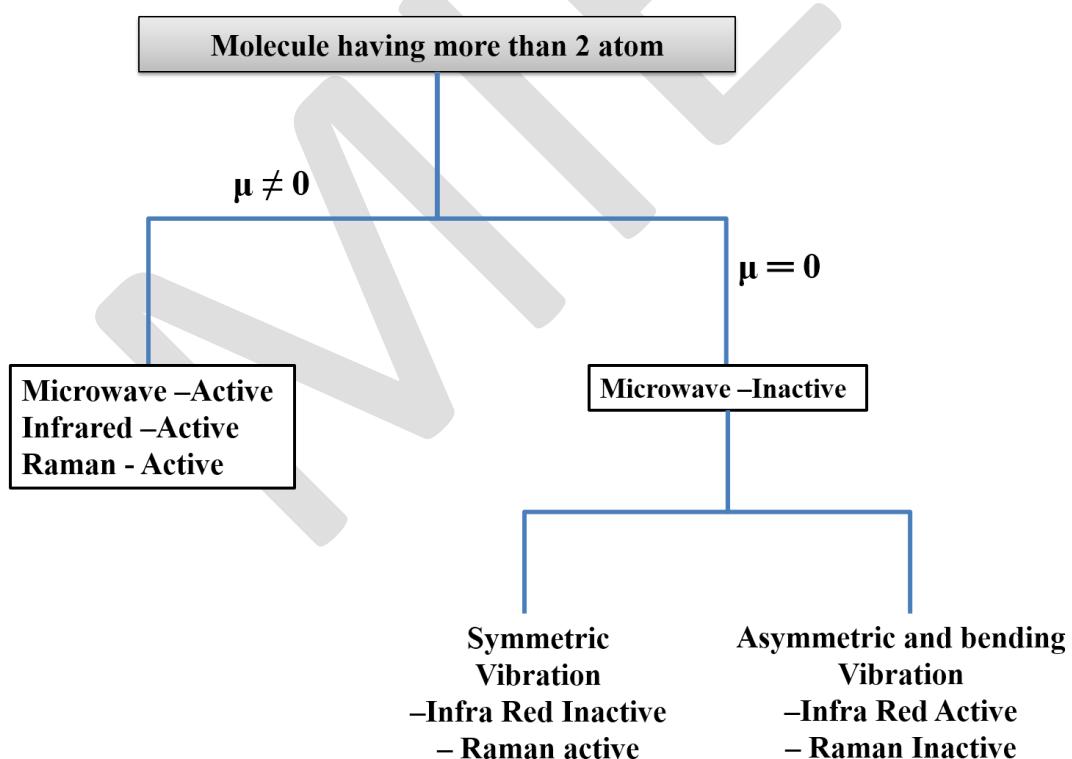
Raman spectroscopy	IR spectroscopy
It is due to the scattering of light by the vibrating molecules	It is the result of absorption of light by vibrating molecules.
The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment
The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment owing to that vibration.
Water can be used as a solvent	Water cannot be used owing 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.
Gives an indication of covalent character in the molecule	Gives an indication of ionic character in the molecule.
Cost of instrumentation could be very high.	Comparatively inexpensive.

How to identify whether molecule is Microwave, infrared or Raman active

For Diatomic molecule



For molecule having more than two atom

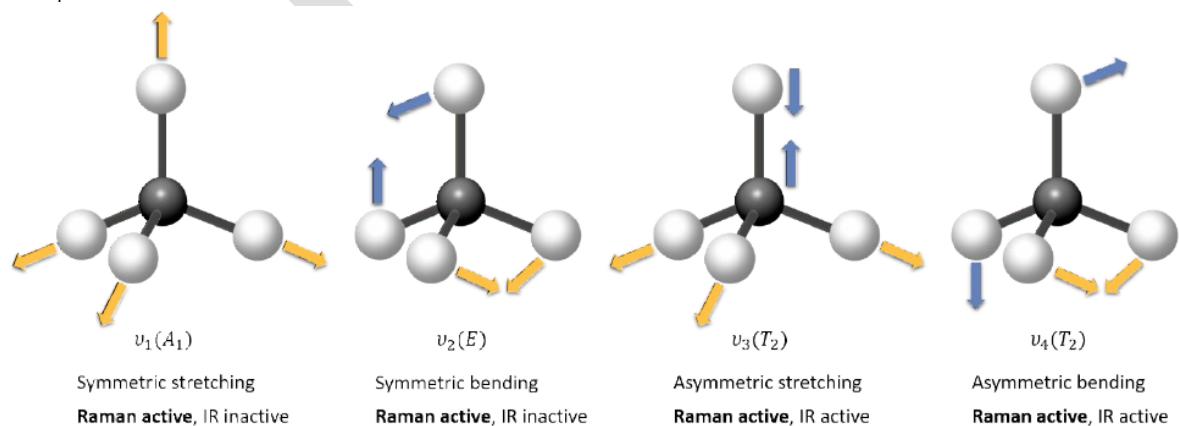


Some problem on IR, Raman and Microwave spectroscopy

Q.1. Among H₂, F₂, HBr, CO, CO₂, D₂O, CCl₄, NH₃, CHCl₃, CH₃Cl, CO, NO, OCS, SF₆, CH₄ molecule identifies which will be IR, microwave and Raman active. Also give reason.

Molecule	Microwave	IR Active	Raman Active	Reason
H ₂ , F ₂	Inactive	Inactive	Active	$\mu = 0$, linear molecule
CO ₂ , SF ₆	Inactive	Symmetric mode - Inactive Bending and asymmetric stretch - Active	Symmetric mode - Inactive Bending and asymmetric stretch - Active	$\mu = 0$, Inversion symmetry
CH ₃ Cl, CHCl ₃	Active	Active	Active	$\mu \neq 0$,
D ₂ O, NH ₃	Active	Active	Active	$\mu \neq 0$, bend molecule
OCS, NO, CO, HBr,	Active	Active	Active	$\mu \neq 0$, linear molecule
CH ₄ , CCl ₄	Inactive	Symmetric mode - Inactive Symmetric bending - Inactive Asymmetric stretching - Active Asymmetric bending- Active	All mode Active	$\mu = 0$, No inversion symmetry

CH₄ Molecule



Q.2. Compare the possible electronic transition in H₂ and HBr molecule and CO molecule.

Solution:

1. H₂: This molecule have only σ orbital, thus only $\sigma \rightarrow \sigma^*$ transition are possible
2. HBr: This molecule have σ orbital and nonbonding orbital, thus $\sigma \rightarrow \sigma^*$ transition and $n \rightarrow \sigma^*$ transition are possible
3. CO: This molecule consists of σ orbital, π orbital and nonbonding orbital.
Thus following electronic transition is possible in given molecule.
 - a. $\sigma \rightarrow \sigma^*$ transition
 - b. $\pi \rightarrow \pi^*$ transition
 - c. $n \rightarrow \sigma^*$ transition
 - d. $n \rightarrow \pi^*$ transition

Q.3. Predict the possible electronic transition is possible for CH₃COOCH₃.

Solution:

CH₃COOCH₃ : this molecule have σ bond and π bond along with lone pair on oxygen molecule. Thus this molecule consists of σ orbital, π orbital and nonbonding orbital.
Thus following electronic transition is possible in given molecule.

1. $\sigma \rightarrow \sigma^*$ transition
2. $\pi \rightarrow \pi^*$ transition
3. $n \rightarrow \sigma^*$ transition
4. $n \rightarrow \pi^*$ transition