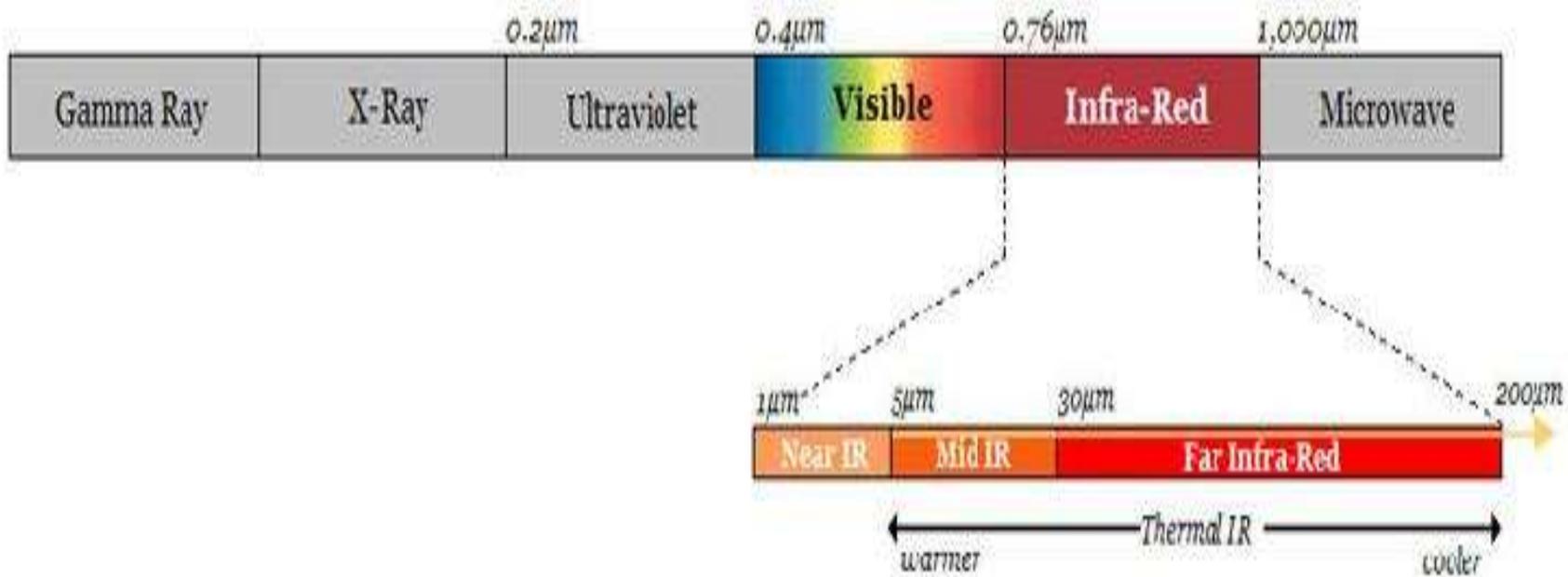
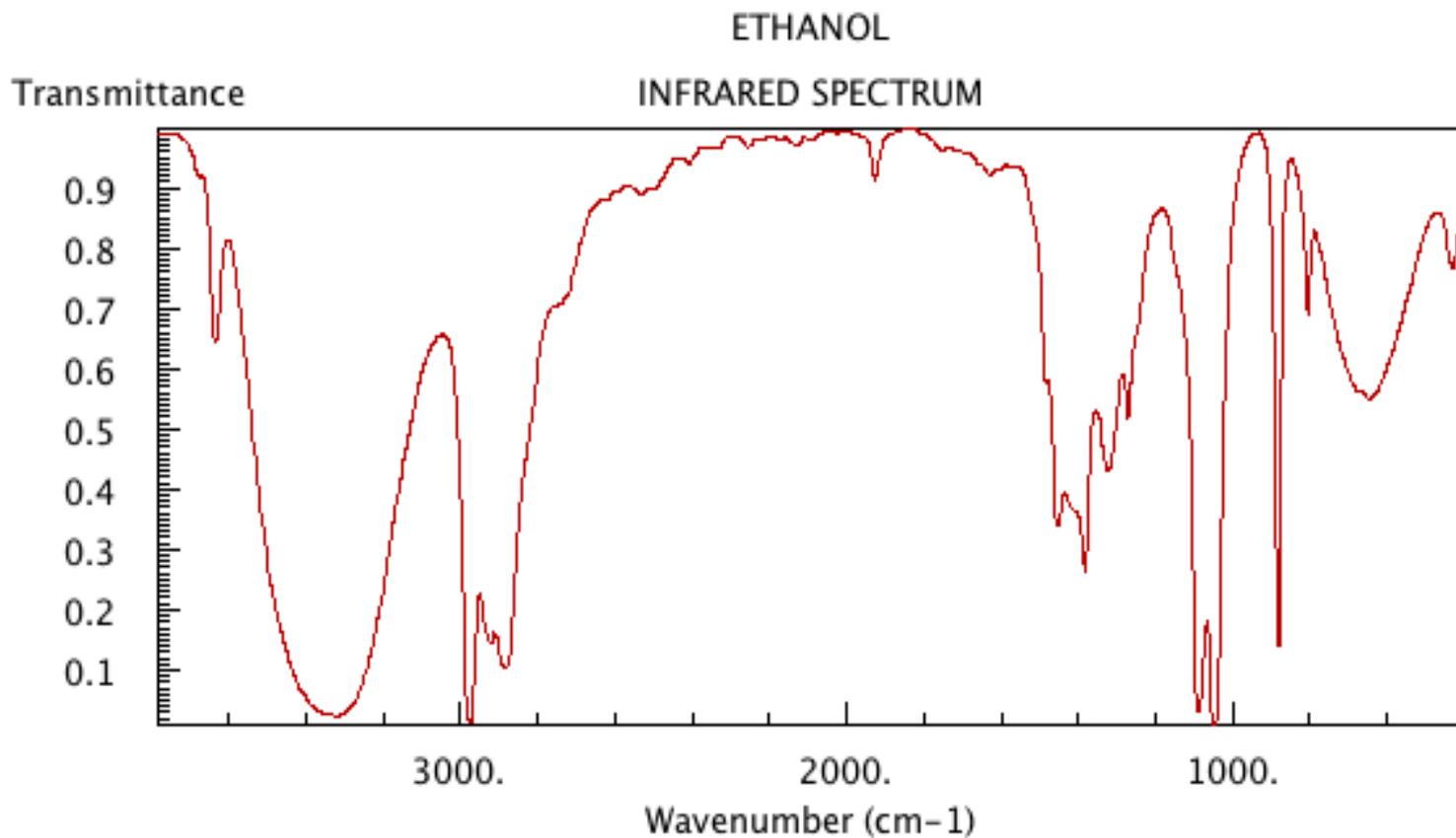




INFRARED SPECTROSCOPY

- IR spectroscopy is the study of interaction between infrared radiations and matter.
- Infrared radiations refers broadly to that part of electromagnetic spectrum between visible and microwave region.





IR spectrum of ethanol

PRINCIPLE

- The principle of IR spectroscopy is related to the vibrational and rotational energy of a molecule.
- When the frequency of the IR radiation is equal to the natural frequency of vibration, the molecule absorb IR radiation.
- Absorption of IR radiation causes an excitation of molecule from a lower to the higher vibrational level.
- Each vibrational level is associated with a number of closely placed rotational level.
- Therefore the IR spectroscopy is also called as “vibrational-rotational spectroscopy”

- 
- All the bonds in a molecule are not capable of absorbing IR energy but those bonds which are accompanied by a change in dipole moment will absorb in the IR region and such transitions are called IR active transitions.
 - The transitions which are not accompanied by a change in dipole moment of the molecule are not directly observed and are considered as IR inactive.

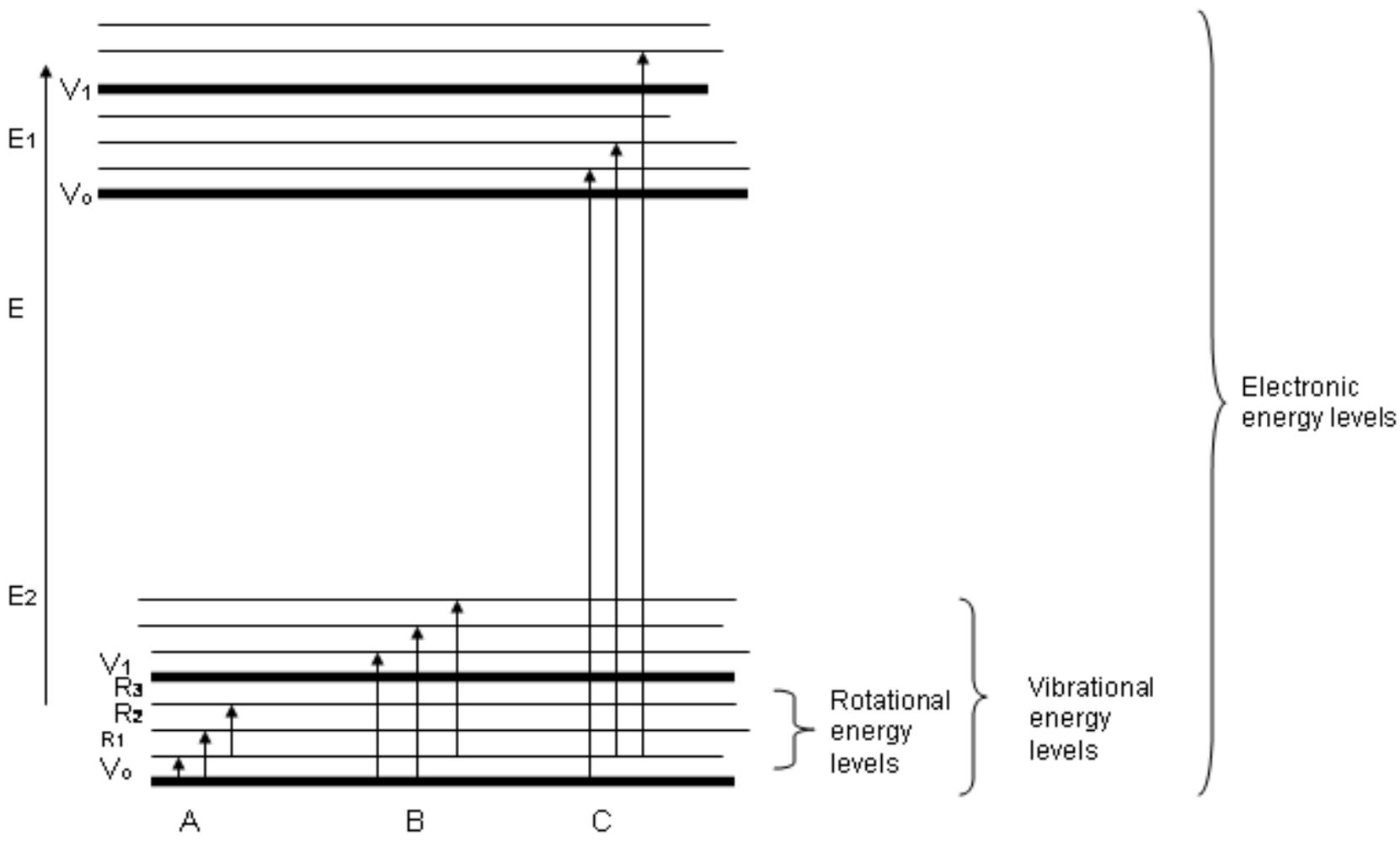
- 
- In IR spectroscopy the changes in the vibrational energy depends upon
 - i. Mass of the atoms present in a molecule
 - ii. Strength of the bonds
 - iii. Arrangement of atoms within the molecule
 - No two compounds except the enantiomers can have the similar IR spectra.

THEORY

- When a molecule absorb radiation with a frequency less than 100 cm^{-1} ,molecular rotation takes place and if a molecule absorb more energetic radiation in the region of 10^4 to 10^2 cm^{-1} , molecular vibration takes place.
- A single vibrational energy change is accompanied by a large number of rotational energy changes and thus the vibrational spectra appear as vibrational rotational bands.

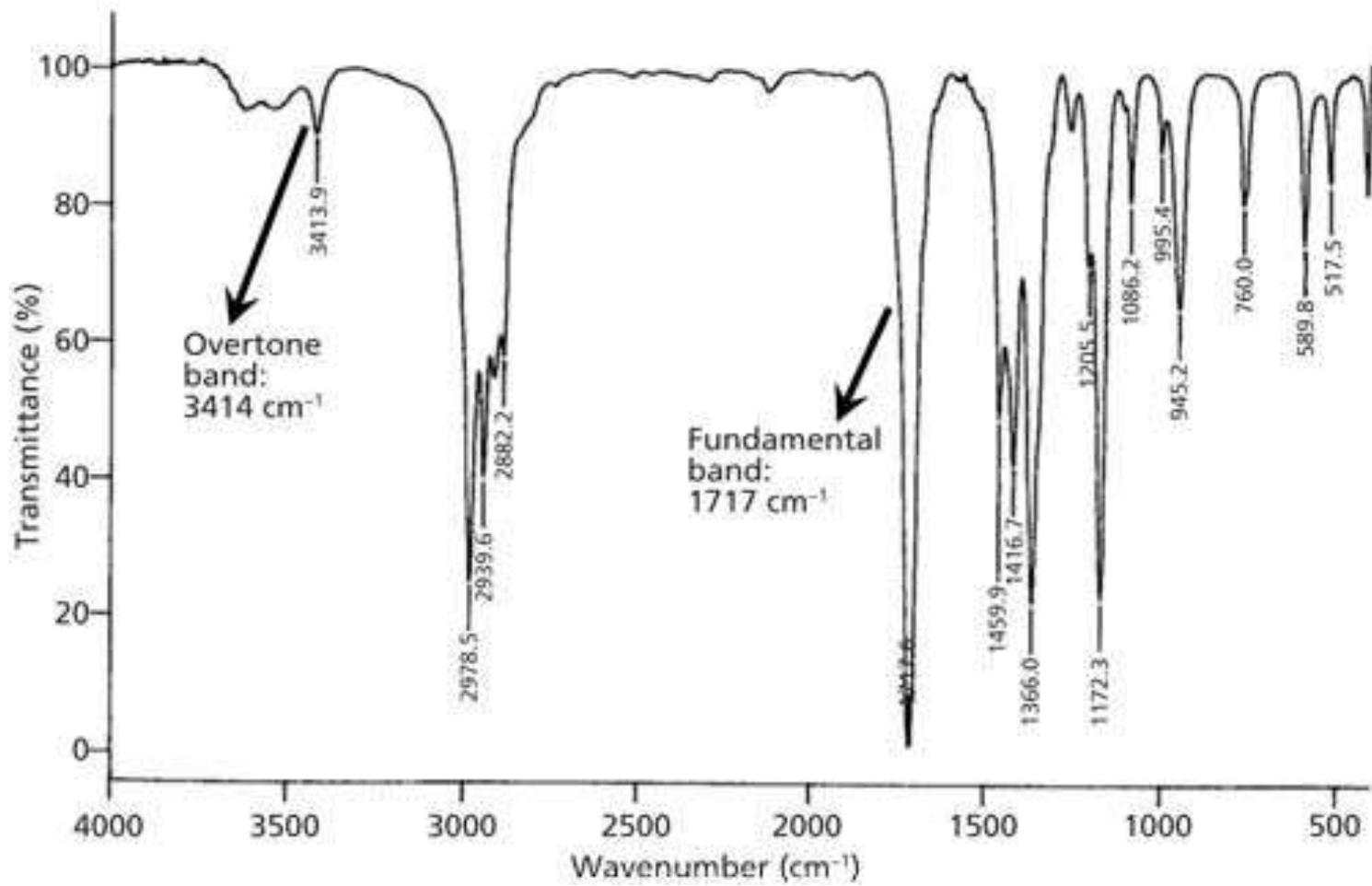
FATE OF ABSORBED RADIATION

- There are 3 main process by which a molecule can absorb radiation, each of these route involve an increase of energy which is proportional to the light absorbed.
 - i. First route occurs when absorption of radiation leads to a higher rotational energy level in a rotational transition.
 - ii. Second occurs when absorption of radiation leads to a higher vibrational energy level in a vibrational transition.
 - iii. Third occurs when absorption of radiation leads to a higher electronic energy level in its electronic transitions.



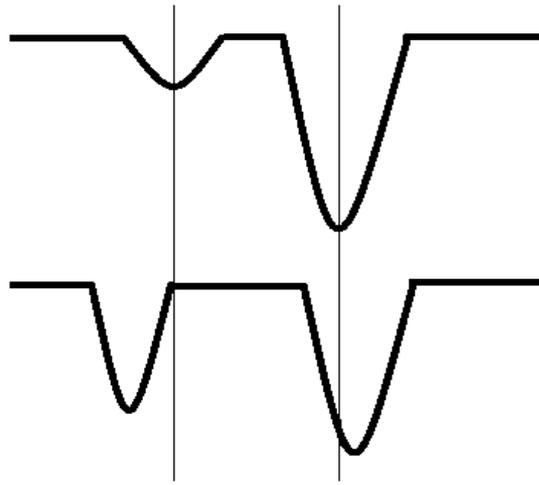
Energy level diagram

- Two criteria must be satisfied by a molecule for the absorption of IR radiation:
 - i. The molecule should possess vibrational and rotational frequency.
 - ii. The molecule must give rise to asymmetrical charge distribution.
- Three main type of absorption bands occur in IR spectra:
 - i. Fundamental
 - ii. Overtone
 - iii. combinational



FERMI RESONANCE

- Interactions which occur between fundamental and overtone or combinational bands are known as Fermi resonance.
- This phenomenon can be observed whenever two fundamental or a fundamental and overtone bands have nearly the same energy.
- Here molecule transfer its energy from fundamental to overtone and back again and so that the each level become partially fundamental or partially overtone in character.
- As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands.

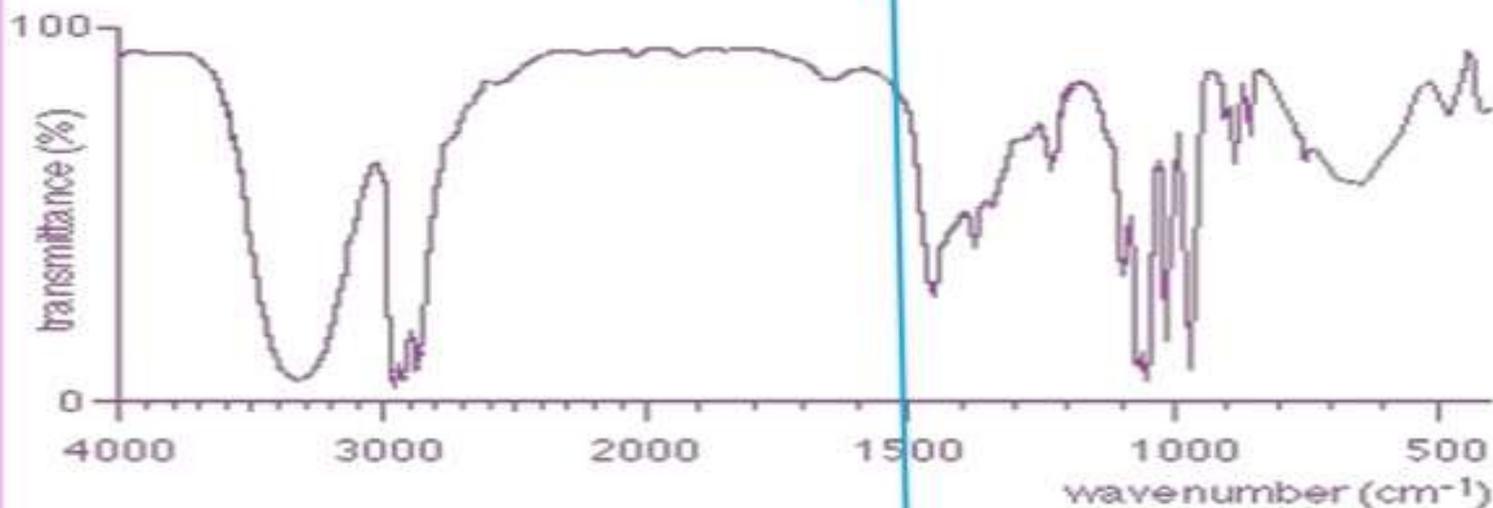


- E.g.: CO₂
 - It normally shows fundamental band at 1337 cm⁻¹ and overtone at 1334.6 cm⁻¹ .
 - But due to the effect of Fermi resonance the first band shift towards higher frequency and give rise to two bands at 1285.5 cm⁻¹ and 1388.3 cm⁻¹ .

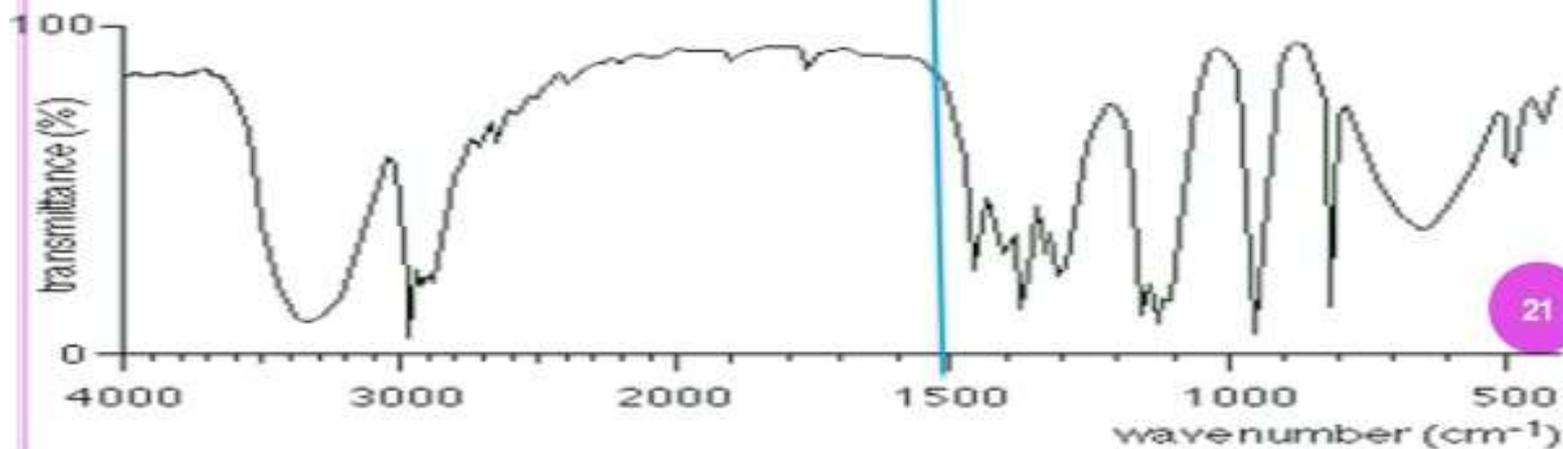
FINGERPRINT REGION

- In IR, the region below 1500 cm^{-1} is rich in many absorption bands and the region is known as fingerprint region.
- Here the number of bending vibrations are usually more than the number of stretching vibrations.
- In this region, small difference in the structure and constitution of a molecule results significant changes in the absorption bands.
- Many compounds show unique absorption bands in this region and which is very useful for the identification of the compound.

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



infra-red spectrum of propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$



- Fingerprint region can be sub-divided into three:

i. 1500-1350 cm^{-1}

- Here doublet near 1380 cm^{-1} and 1365 cm^{-1} shows the presence of tertiary butyl group in the compound.

ii. 1350-1000 cm^{-1}

- All classes of compounds having groups like alcohols, esters, lactones, acid anhydrides show characteristic absorptions (s) due to C – O stretching.

iii. Below 1000 cm^{-1}

- Distinguishes between cis and trans alkenes and mono and disubstitutions at ortho, meta, para

VIBRATIONS

- Two types of vibrations are;

1. Stretching

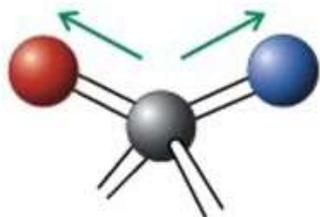
- i. Symmetric
- ii. Asymmetric

2. Bending

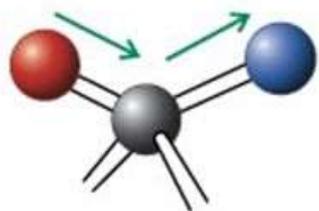
- i. Scissoring
- ii. Rocking
- iii. Wagging
- iv. Twisting

Many possible absorptions per molecule exist: stretching, bending,...

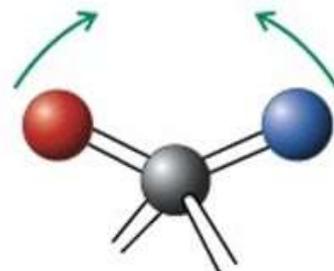
Vibrational modes leading to IR absorptions:



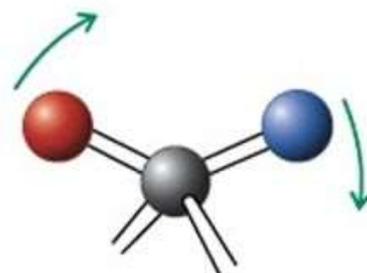
Symmetric stretching vibration (both outside atoms move away from or toward the center)



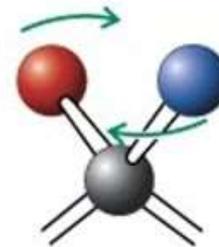
Asymmetric stretching vibration (as one atom moves toward the center, the other moves away)



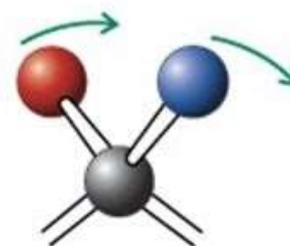
Symmetric bending vibration in a plane (scissoring)



Asymmetric bending vibration in a plane (rocking)



Symmetric bending vibration out of a plane (twisting)



Asymmetric bending vibration out of a plane (wagging)

FACTORS INFLUENCING ABSORPTION

1. Symmetry

- Symmetric compounds do not possess dipole moment and are IR inactive.
- E.g. symmetric acetylene



2. Coupling

- There are so many factors which cause coupled vibration in IR and it will influence the intensity and shape of the absorption bands.
- E.g. normally the band due to $\text{C}=\text{C}$ bond is around at 1650 cm^{-1} but due to mechanical coupling of two C C systems in allene give two bands at 1960 and 1970 cm^{-1}

3. Fermi resonance

- Fermi resonance results in an unexpected shift in energy and intensity of the bands.
- E.g. the overtone of C-H deformation mode at 1400 cm^{-1} is always in Fermi resonance with the stretch of the same bond at 2800 cm^{-1} .

4. Hydrogen bonding

- It can change the shape and position of IR bands.
- Stronger the H-bonding greater the absorption shift.

Intermolecular- broad bands

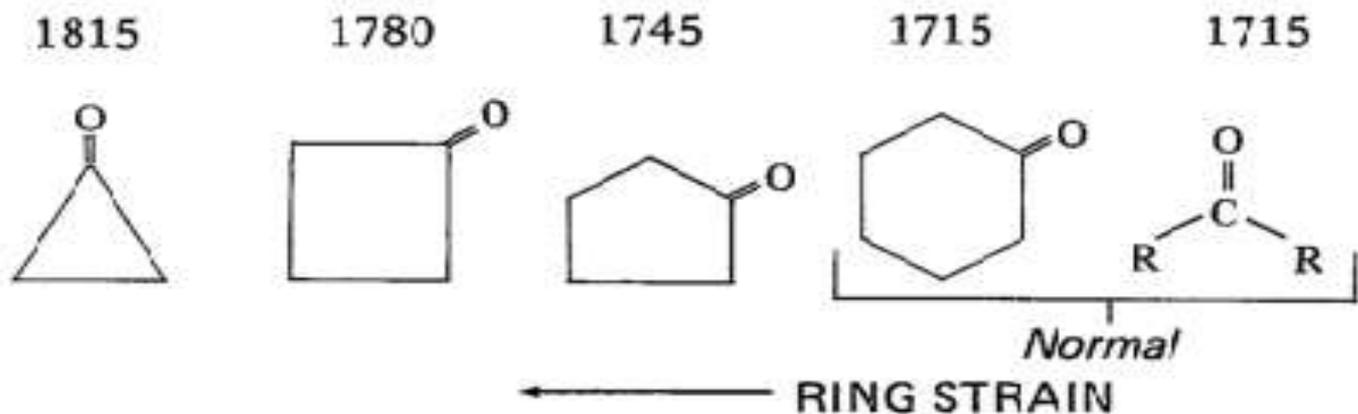
Intra-molecular-sharp bands

5. Electronic effect

- Electronic effects such as inductive, mesomeric and field effect may cause shift in absorption bands due to the change in absorption frequency.
- E.g. inductive – acetone(1715 cm^{-1}) and chloroacetone(1725 cm^{-1})
mesomeric-acetophenone(1693 cm^{-1}) and P-aminoacetophenone(1677 cm^{-1})

6. Bond angles

- Difference in bond angles can also leads to the changes is absorption bands.
- E.g.



SAMPLING

- Samples of the same substance shows shift in absorption bands as we pass from solid to gases and hence the samples of different phases have to be treated differently in IR spectroscopy.
- **Sampling of solids**
 - Solids run in solution
 - Mull technique
 - Pressed pellet technique
 - Solids films

1. Solid run in solution

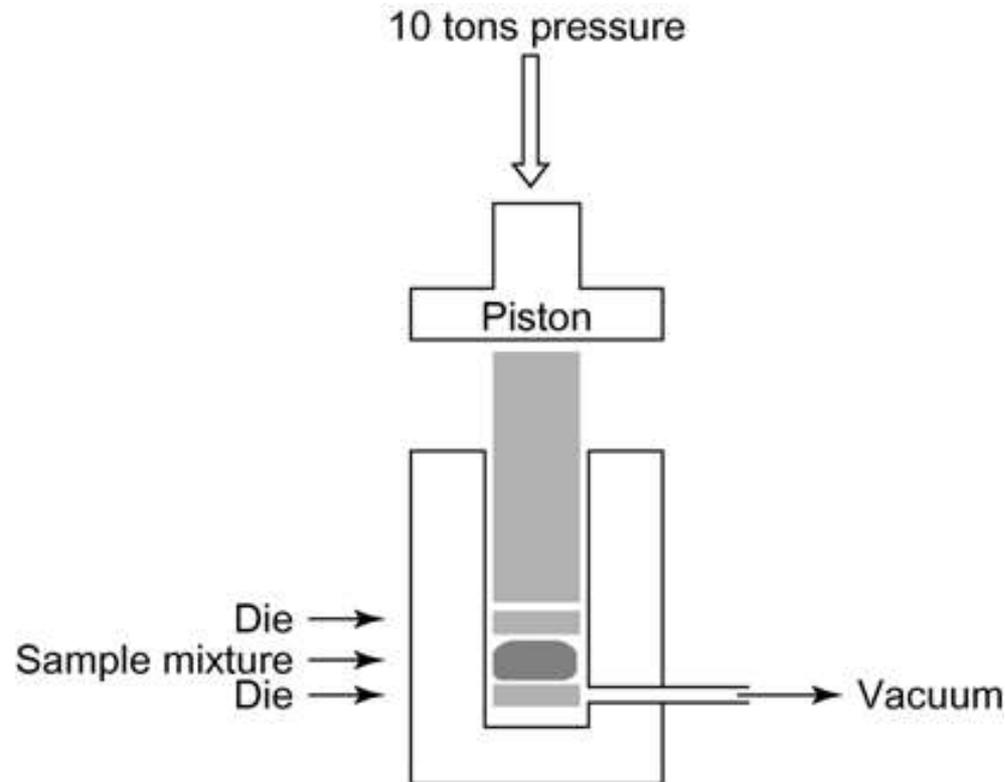
- Dissolve solid sample in non-aqueous solvent (which should be IR inactive) and place a drop of this solution in alkali metal disc and allow to evaporate, leaving a thin film which is then mounted on a spectrometer.
- E.g. of solvents – acetone, cyclohexane, chloroform, carbon tetrachloride etc.

2. Mull technique

- Finely powdered sample + mulling agent (Nujol) and make a thick paste (mull). Transfer the mull to the mull plates and the plates are squeezed together to adjust the thickness it is then mounted in spectrometer.

3. Pressed pellet technique

- Finely powdered sample is mixed with about 100 times its weight of KBr in a vibrating ball mill and the mixture is then pressed under very high pressure in an evacuable die to form a small pellet(1-2mm thick and 1cm in diameter).



- Advantages:-

- Eliminates bands which appear due to mulling agent.
- Pellets can be stored for longer period of time.
- Concentration of sample can be adjusted.

- Disadvantages:-

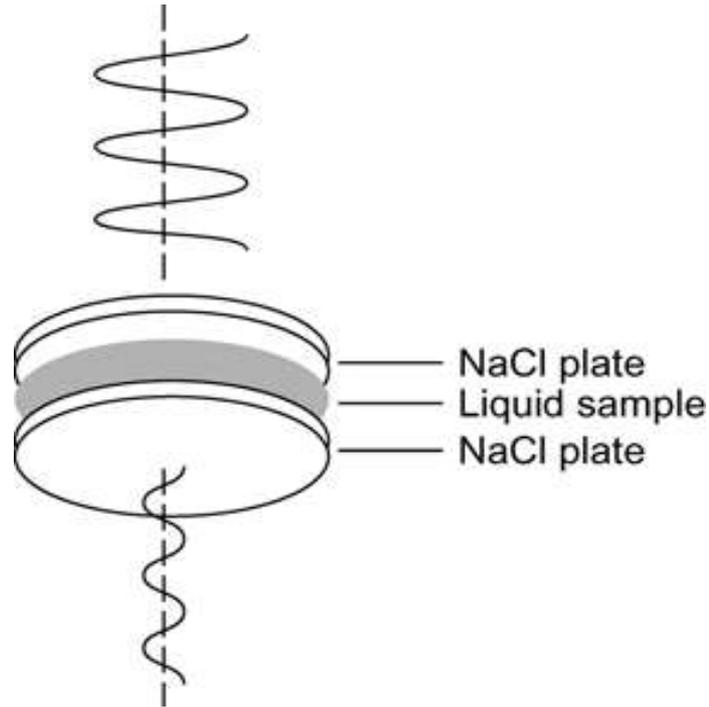
- Not suitable for polymers which are difficult to bind with KBr.
- High pressure may change the crystallinity of the sample.

4. Solid films.

- Here amorphous solid is dissolved in volatile solvents and this solution is poured on a rock salt plate (NaCl or KBr), then the solvent is evaporated by gentle heating.

• Sampling of liquids

- Liquid sample can be sandwiched between two alkali halide plates (NaCl , KBr , CaF₂).
- The sample cell thickness is 0.01-0.05mm.



• **Sampling of gases**

- Here gases sample is introduced into a glass cell made up of NaCl.
- Very few organic compounds can be examined as gases.
- E.g.: 1,4-dioxane.

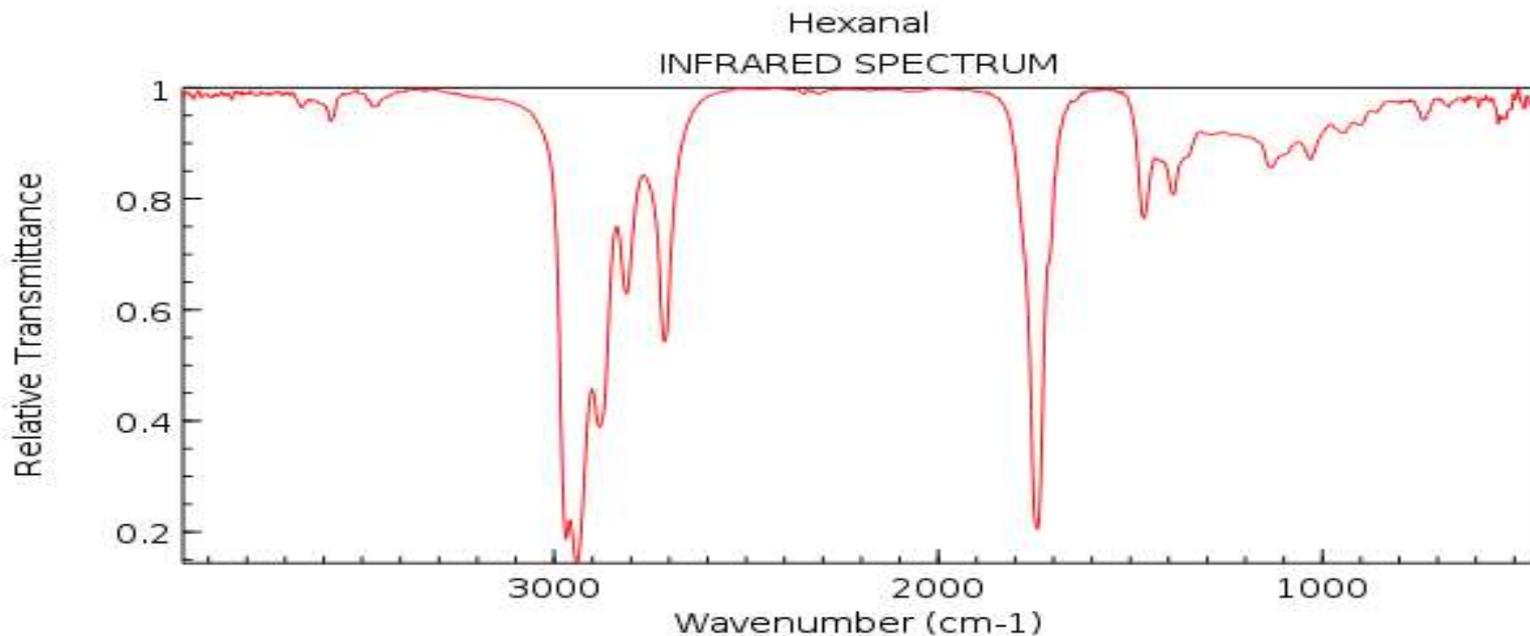
• **Sampling of solutions**

- Here 1-5% of solution is placed in a solution cell made up of metal halides and a second cell containing the pure solvent act as a reference.
- Important solvents used are:-chloroform , CCl_4 , Carbon disulphide etc.

APPLICATIONS OF IR SPECTROSCOPY

1. Identification of an organic compound

- The identity of an organic compound can be established from its fingerprint region by comparing the sample spectrum with the known spectrum of the compound.
- E.g. spectrum of n-hexanal



2. Qualitative determination of functional groups

- The presence or absence of absorption bands help in predicting the presence of certain functional group in the compound.

Type of bond	Wavenumber (cm ⁻¹)	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

3. Distinction between 2 types of H-bonding

- If a compound having intra-molecular H-bonding it will show broad bands in IR spectrum and if a compound having intermolecular H-bonding then it will show sharp well defined bands.
- E.g. o-nitrophenol shows broad bands due to intra-molecular H-bond whereas p-nitrophenol shows sharp bands due to intermolecular H-bonding.

4. Quantitative analysis

- It can be done by measuring the intensity of the absorption bands.
- E.g. xylene exists as mixture of 3 compounds which shows absorption bands at

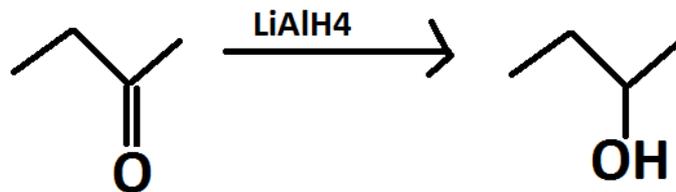
ortho-740cm⁻¹

meta-880cm⁻¹

para-830cm⁻¹

5. Study of chemical reactions

- It is useful for studying the chemical reactions.
- E.g.: reduction of butan-2-one to form butan-2-ol

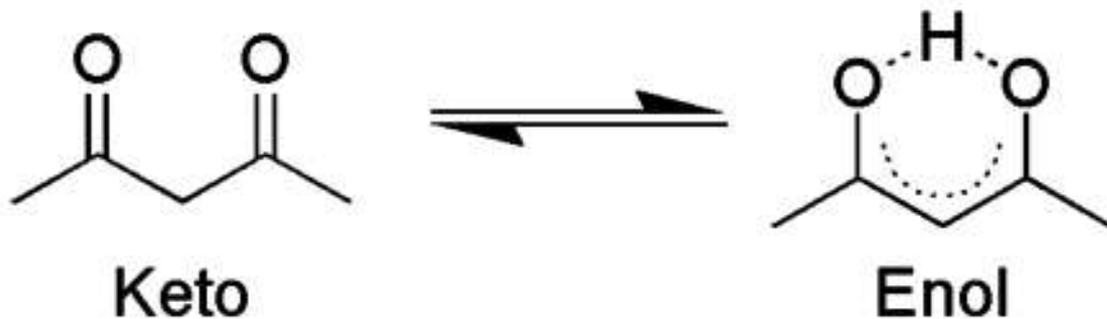


Butan-2-one
(1710 cm⁻¹)

Butan-2-ol
(3300 cm⁻¹)

6. Study of keto-enol tautomerism

- Diketones and ketoesters exhibit keto-enol tautomerism and this can be studied using IR spectrum of the compound.
- E.g.: Ethyl acetoacetic ester.



C=O – 1733 cm^{-1}
- 1710 cm^{-1}

O---H – 3300 cm^{-1}
C=O – 1645 cm^{-1}



THANK YOU