IR SPECTROSCOPY

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- IR spectroscopy is the study of interaction between infrared radiations and matter at certain condition to give spectrum. i.e.

- Matter + IR (EMR) $\xrightarrow{\text{Condition}}$ IR Spectrum

Here matter, EMR & Condition are very important which gives idea about different types of spectrum.

Matter

In atomic spectroscopy matter is an atom while in molecular spectroscopy matter should be molecule which interact with EMR to get spectra.

A molecule must produce

i. Electronic /Nuclear motion and it changes 4 types of energy

a. Electronic energy

b. Vibrational energy

c. Rotational energy

d. Translational energy

However Translational energy is dissipated as heat & is not involved in molecular spectra. So (d) is not subject of discussion.
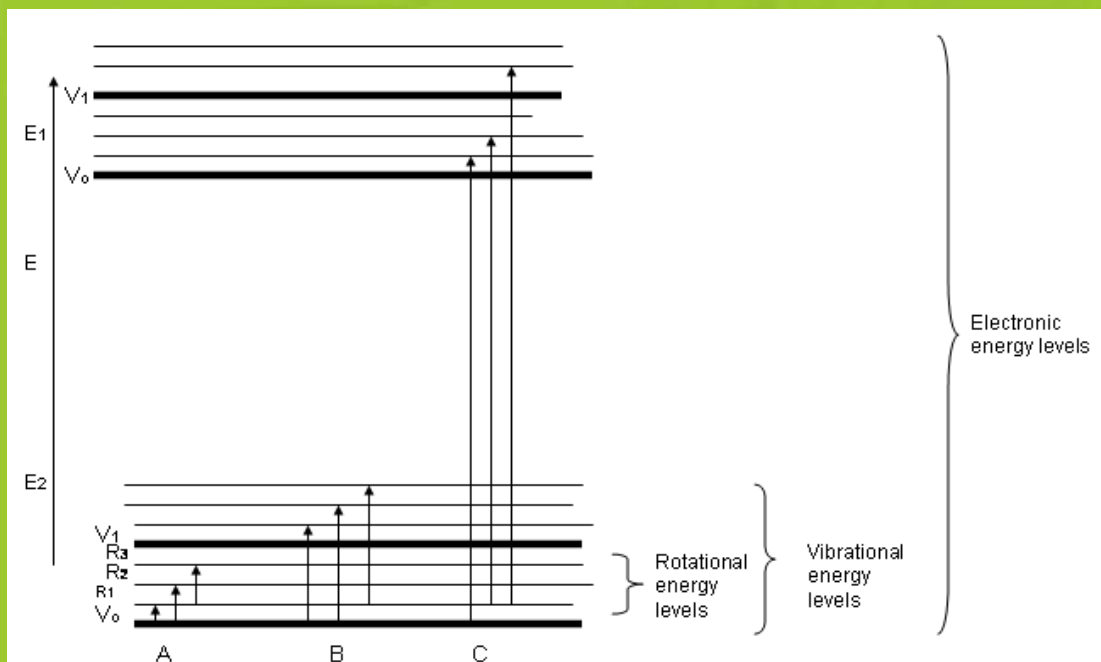
i.e.

Total energy 'E' is

$E = E_{ele} + E_{nucl}$

or, $E = E_{ele} + E_{vib} + E_{rot}$

But $E_{rot} < E_{vib} < E_{ele}$

10^{-23} 10^{-21} 10^{-19}

How does Transition Occur
From Boltzmann's distribution law
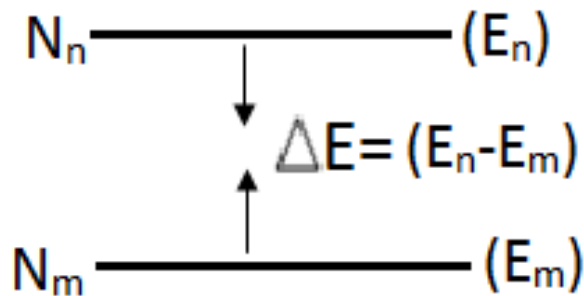
$$\frac{N_n}{N_m} = e^{-\triangle E/RT}$$

Where
Nn = No. of molecules in state n
Nm = No. of molecules in state m
R = gas constant
T = Temperature

When energy level of EMR is equal to $\triangle$E then transition occurs from state m to n & we get transition peak

$$N_n \underline{\hspace{4cm}} (E_n)$$
$$\triangle E = (E_n - E_m)$$
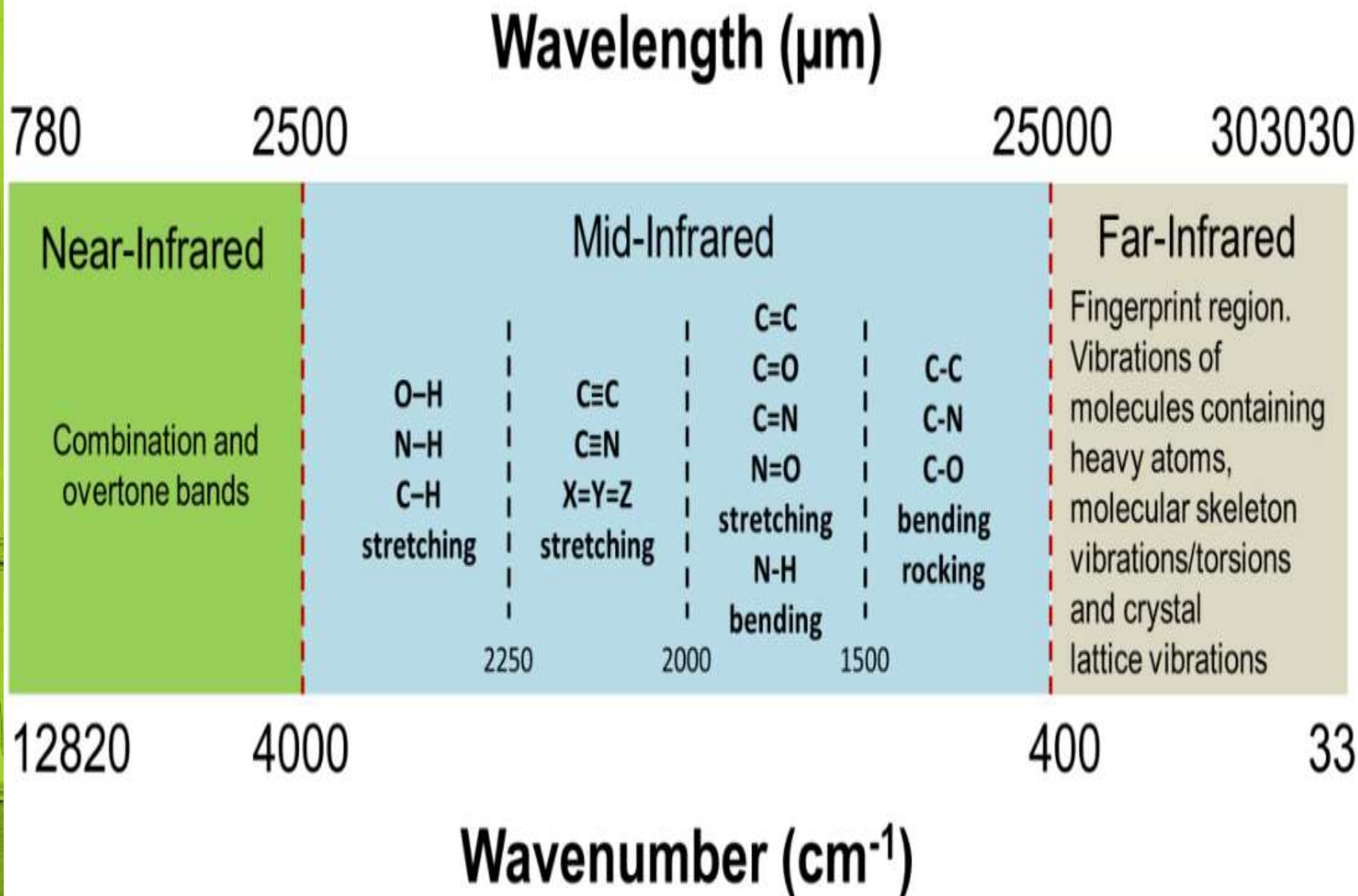$$N_m \underline{\hspace{4cm}} (E_m)$$

Where
Nn = No. of molecules in state n
Nm = No. of molecules in state m
En = energy level of molecule n
Em = energy level of molecule m

Type of Energy Transfer	Region of the Electromagnetic Spectrum	Spectroscopic Technique
Absorption	γ-ray	Mossbauer
	X-ray	X-ray absorption
	UV-Vis	UV-Vis
		Atomic absorption
	Infrared	Infrared (IR)
		Raman
	Microwave	Microwave
		Electron spin resonance (EPR)
	Radio waves	Nuclear magnetic resonance (NMR)
Emission (thermal excitation)	UV-Vis	Atomic emission
Photoluminescence	X-ray	X-ray fluorescence
	UV-Vis	Fluorescence
		Phosphorescence
		Atomic fluorescence

E

IR Region

Wavelength (μm)

| 780 | 2500 | | | | | 25000 | 303030 |

Near-Infrared	Mid-Infrared					Far-Infrared
Combination and overtone bands	O–H N–H C–H stretching	C≡C C≡N X=Y=Z stretching	C=C C=O C=N N=O stretching N-H bending	C-C C-N C-O bending rocking		Fingerprint region. Vibrations of molecules containing heavy atoms, molecular skeleton vibrations/torsions and crystal lattice vibrations
		2250	2000	1500		

| 12820 | 4000 | | | | | 400 | 33 |

Wavenumber (cm⁻¹)

Condition

- 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 i.e. polar.
- Three main type of absorption bands occur in IR spectra:
    i. Fundamental
    ii. Overtone
    iii. combinational

Basic of IR Spectroscopy

A molecule having mass m_1 & m_2 associated with bond (force) expressed as force constant k. Bond strength of a molecule has been calculated by Hooke's law as

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

Where:

μ = reduced mass = $\frac{m_1 m_2}{m_1 + m_2}$

In terms of the wavenumber ($\bar{v}$)

$$\bar{v} = \frac{v}{c} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

Where:
c = speed of light = 3×10^{10} cm/sec

So bond strength depends upon force constant k & reduce mass of a molecule which gives wave number of IR radiation absorbed.

6. Calculation of Molecular Vibrations

The stretching frequency $\bar{\nu}$ (cm^{-1}) of C-H can be calculated as follows:

$k = 5\times10^5$ dyne/cm
$m_1 = C = 12/6.02\times10^{23} = 1.99\times10^{-23}$ g
$m_2 = H = 1/6.02\times10^{23} = 0.167\times10^{-23}$ g
$c = 3\times10^{10}$ cm/sec

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{\nu} = \frac{1}{2 \times 3.14 \times 3\times10^{10}}\sqrt{\frac{5\times10^5(1.99\times10^{-23} + 0.167\times10^{-23})}{1.99\times10^{-23} \times 0.167\times10^{-23}}}$$

$$\bar{\nu} = 3023 \; cm^{-1}$$

The observed values for C–H bonds are in the region 3320-2700 cm^{-1}, which differ from the calculated values as the calculation does not take into account the environment of the C–H group within the molecule.

Force constants (k):

Single bond $= 5\times10^5$ dyne/cm

Double bond $= 10\times10^5$ dyne/cm

Triple bond $= 15\times10^5$ dyne/cm

1) Increase in bond strength from single to double to triple bond (Figure 7).

C–N bond

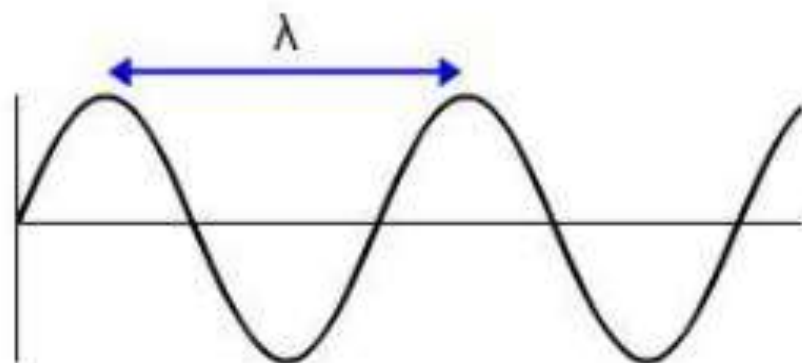$k = 5 \times 10^5$ dyne/cm

$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23}$ g

$m_2 = N = 14/6.02 \times 10^{23} = 2.33 \times 10^{-23}$ g

$c = 3 \times 10^{10}$ cm/sec

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{v} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{5 \times 10^5 (1.99 \times 10^{-23} + 2.33 \times 10^{-23})}{1.99 \times 10^{-23} \times 2.33 \times 10^{-23}}}$$

$$\bar{v} = 1145 \ cm^{-1}$$

C=N bond

$k = 10 \times 10^5$ dyne/cm

$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23}$ g

$m_2 = N = 14/6.02 \times 10^{23} = 2.33 \times 10^{-23}$ g

$c = 3 \times 10^{10}$ cm/sec

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{v} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{10 \times 10^5 (1.99 \times 10^{-23} + 2.33 \times 10^{-23})}{1.99 \times 10^{-23} \times 2.33 \times 10^{-23}}}$$

$$\bar{v} = 1619 \ cm^{-1}$$

C≡N bond

$k = 15 \times 10^5$ dyne/cm

$m_1 = C = 12/6.02 \times 10^{23} = 1.99 \times 10^{-23}$ g

$m_2 = N = 14/6.02 \times 10^{23} = 2.33 \times 10^{-23}$ g

$c = 3 \times 10^{10}$ cm/sec

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{v} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{15 \times 10^5 (1.99 \times 10^{-23} + 2.33 \times 10^{-23})}{1.99 \times 10^{-23} \times 2.33 \times 10^{-23}}}$$

$$\bar{v} = 1983 \ cm^{-1}$$
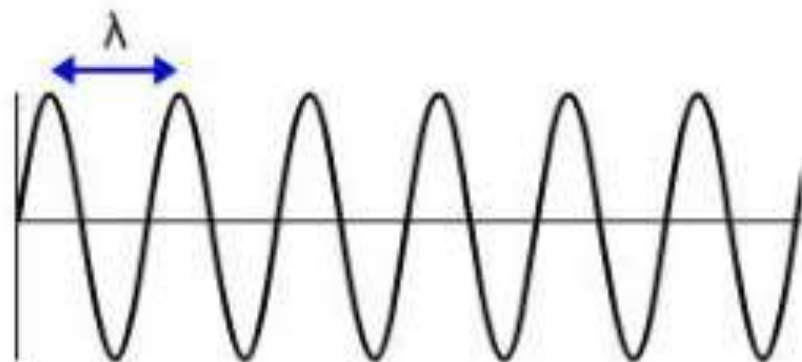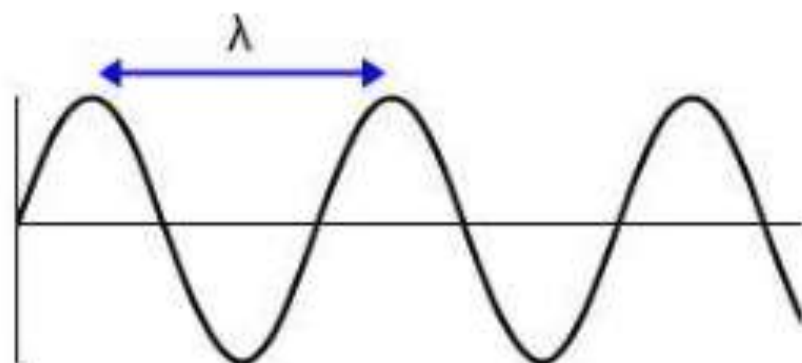
Figure 7: Comparison of wavelength, stretching frequency, and wavenumber of bonds with different strengths (i.e. single, double, and triple bonds).

2) Decrease in reduced mass (μ)

C–S bond

k = 5x10^5 dyne/cm

m_1 = C = 12/6.02x10^{23} = 1.99x10^{-23} g

m_2 = S = 32/6.02x10^{23} = 5.32x10^{-23} g

c = 3x10^{10} cm/sec

$$\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{\upsilon} = \frac{1}{2 \; x \; 3.14 \; x \; 3x10^{10}}\sqrt{\frac{5x10^5(1.99x10^{-23} + 5.32x10^{-23})}{1.99x10^{-23} \; x \; 5.32x10^{-23}}}$$

$$\bar{\upsilon} = 985 \; cm^{-1}$$

C–H bond

k = 5x10^5 dyne/cm

m_1 = C = 12/6.02x10^{23} = 1.99x10^{-23} g

m_2 = H = 1/6.02x10^{23} = 0.167x10^{-23} g

c = 3x10^{10} cm/sec

$$\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{\upsilon} = \frac{1}{2 \; x \; 3.14 \; x \; 3x10^{10}}\sqrt{\frac{5x10^5(1.99x10^{-23} + 0.167x10^{-23})}{1.99x10^{-23} \; x \; 0.167x10^{-23}}}$$

$$\bar{\upsilon} = 3023 \; cm^{-1}$$

Comparison of wavelength, stretching frequency, and wavenumber of bonds with different reduced masses (μ).

Wavenumber (cm⁻¹)
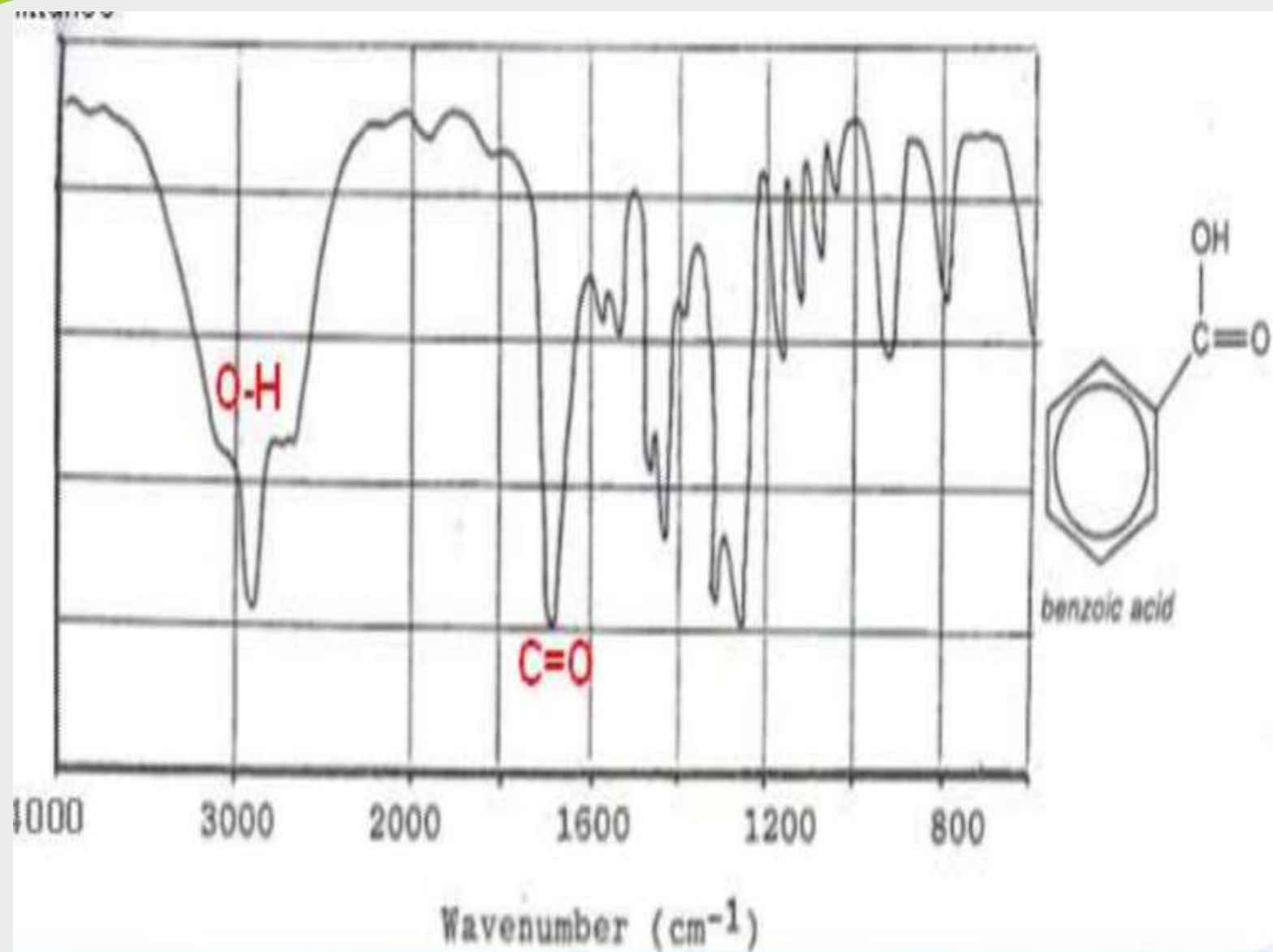
Requirements of IR radiation Absorption

2. $\underline{\text{Electric Dipole:}}$

$$\overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}\text{- - - - -}\overset{\delta+}{H}\text{—}\overset{\delta-}{Cl}$$
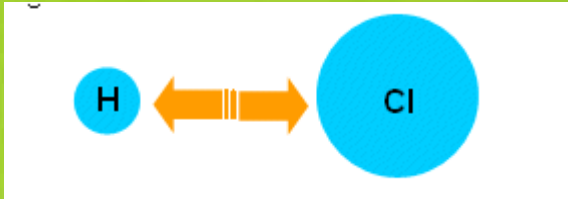
- Only polar molecule absorbed IR radiation & change in dipole moment so polar molecule is IR active molecule.

- In case of O_2, N_2, Cl_2 **NO NET change in dipole moment** occurs thus they cannot absorb IR radiations & do not show IR spectra

Two types changes occur in molecule :
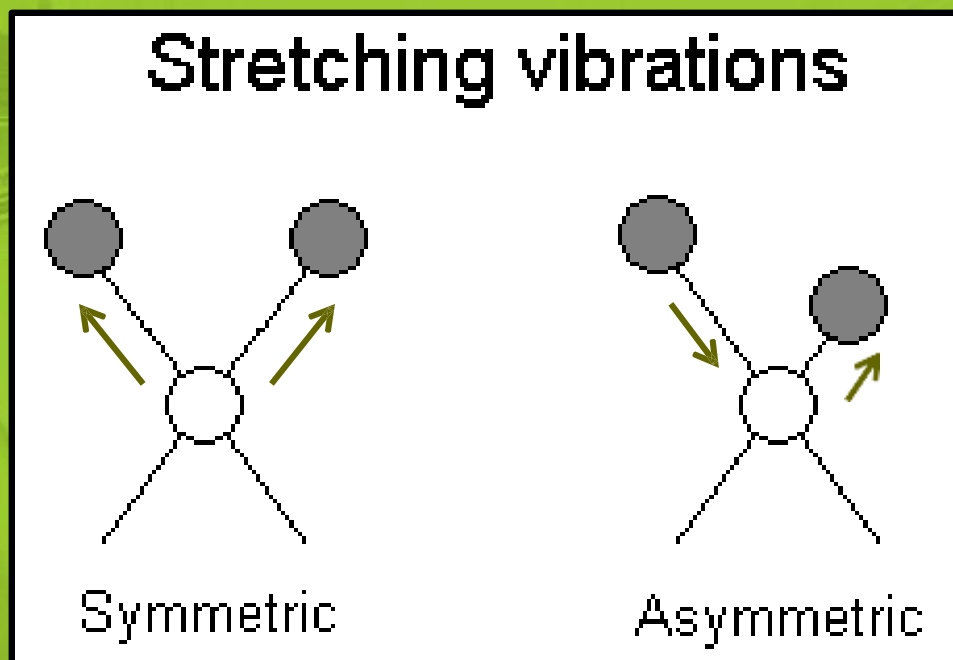
- **Molecular rotations:**

  Rotational transitions are of little use to the spectroscopist.

- **Molecular vibrations**

  The positions of atoms in a molecules are not fixed; they are subject to a number of different vibrations

TYPES OF MOELCULAR VIBRATIONS

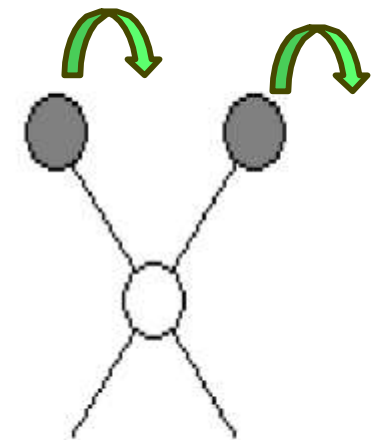**Stretching:** Change in inter-atomic distance along bond axis

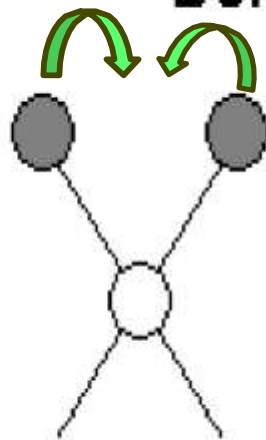# TYPES OF MOLECULAR VIBRATIONS

Bending: Change in angle between two bonds. There are four types of bend:
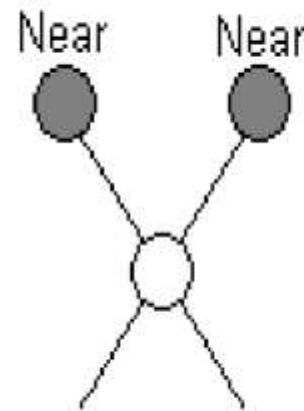
- Rocking
- Scissoring
- Wagging
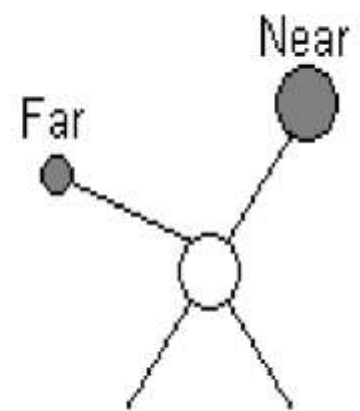- Twisting

Bending vibrations

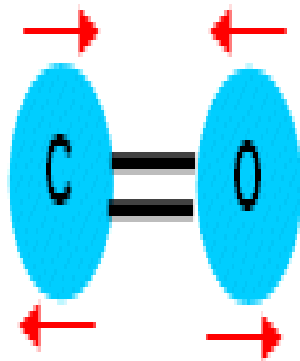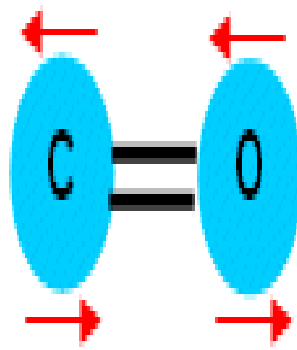In-plane rocking   In-plane scissoring   Out-of-plane wagging   Out-of-plane twisting
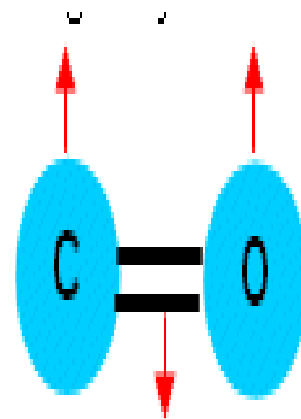
o Carbon dioxide can vibrate in the following ways:

Symmetric Stretch   Asymmetric Stretch   Bending

Below is the infrared spectrum of ethanol with some identified fingerprints:

C-H stretching
3001-2850 cm⁻¹

C—O stretching
1200-1000 cm⁻¹

O-H stretching
3700-3000 cm⁻¹

C-O-H bending
1500-1200 cm⁻¹
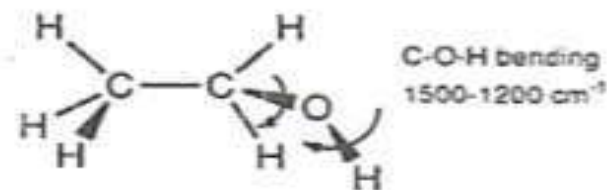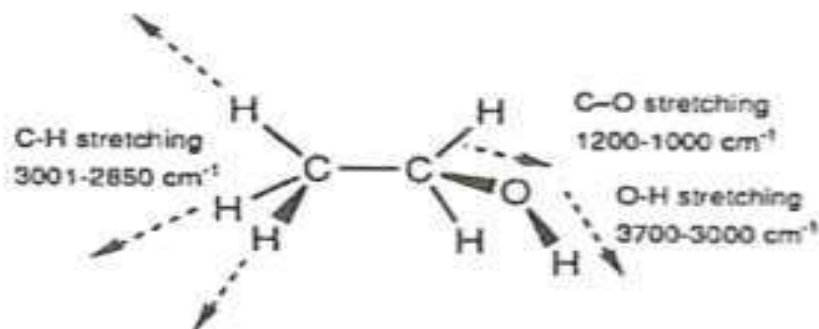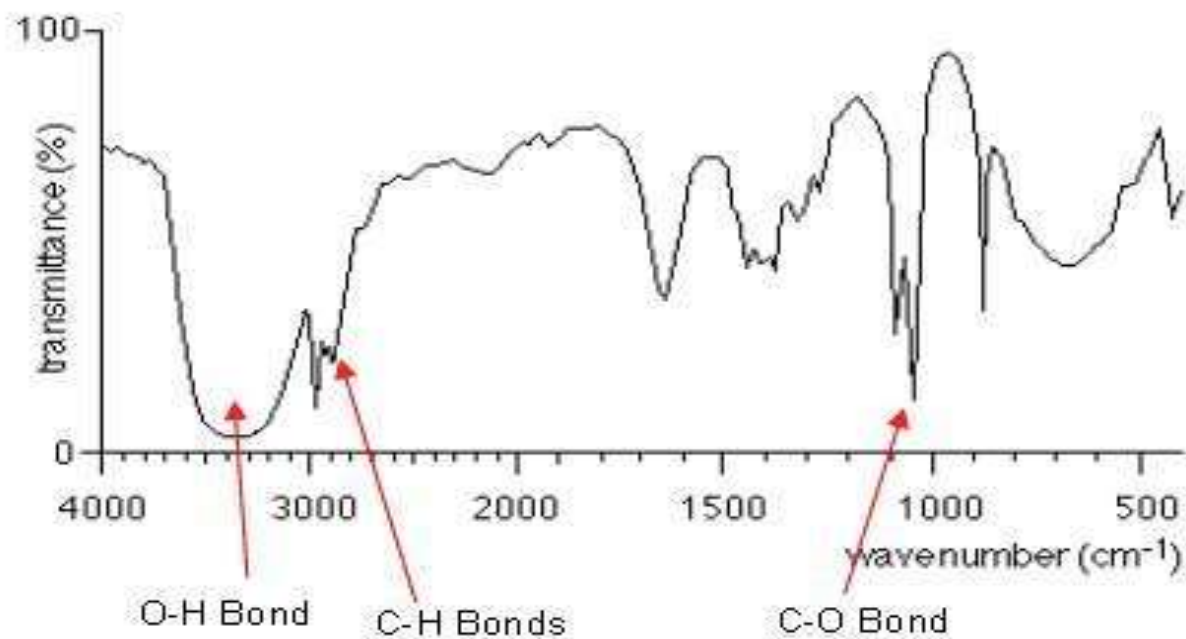
Vibrational frequency

- A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. **The frequency of the periodic motion is known as a vibrational frequency**

Factors affecting Vibrational frequency

- Vibrational coupling
- H-Bonding
- Electronic effect
- Field effect
- Nature of solvent

(Will discuss later)

Vibration modes

1. Normal mode of an <u>oscillating system</u> is a pattern of motion in which all parts of the system move <u>sinusoidally</u> with the same frequency

1. Combination Bands are observed when more than two or more fundamental vibrations are excited simultaneously. These combination modes arise from the anharmonicities of the oscillators which leads to an interaction of the vibrational states in polyatomic molecules.

Vibration modes

3. Overtones (multiples of given frequency) results from excitation from ground state to higher energy states.

Overtones occur when a vibrational mode is excited from v=0 to v=2, which is called the first overtone, or v=0 to v=3, the second overtone.
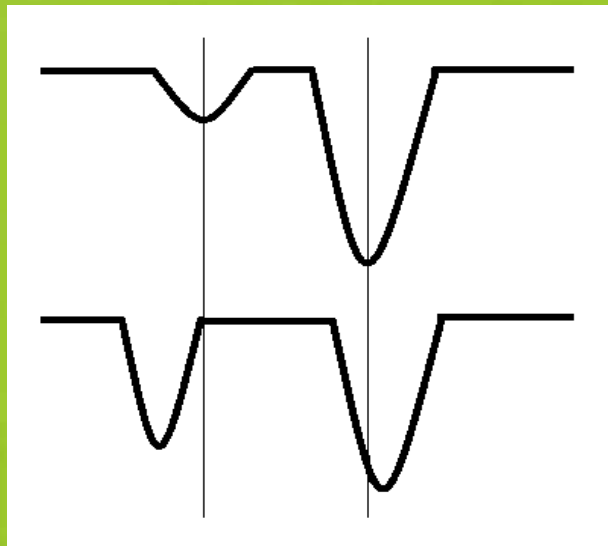
0 --> 1 (fundamental)

0 --> 2 (first overtone)

0 --> 3 (second overtone)

0 --> 4 (third overtone)

0 --> 5 (fourth overtone)

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.: CO_2
 ◦ 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, $CH_3CH_2CH_2OH$
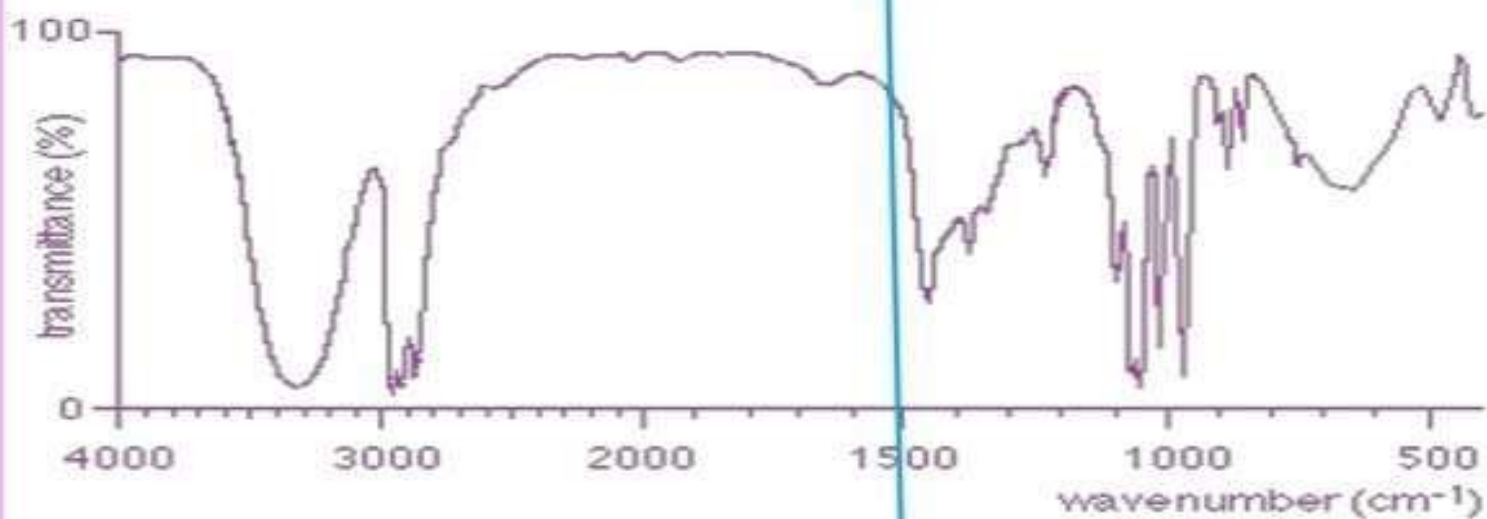
infra-red spectrum of propan-2-ol, CH_3CHCH_3
OH
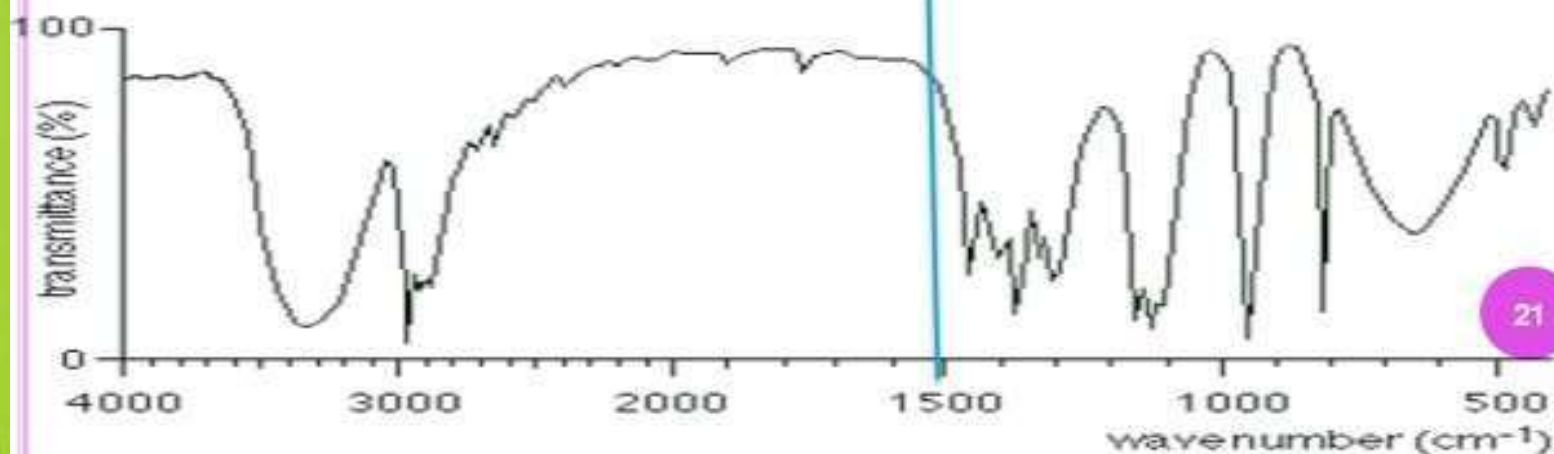
- Fingerprint region can be sub-divided into three:
  i. 1500-1350 cm^{-1}
     - Here doublet near 1380 cm^{-1} and 1365 cm^{-1} shows the presence of tertiary butyl group in the compound.
  ii. 1350-1000 cm^{-1}
     All classes of compounds having groups like
     - alcohols, esters , lactones, acid anhydrates 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

Conventional IR Spectroscopy

Fourier transform IR Spectroscopy

Dispersive or non dispersive instruments like monochromator and prisms

Frequency domain spectra

Interferometers are used

Time domain spectra

High signal to noise ratio.

APPLICATIONS OF IR SPECTROSCOPY

•Infrared spectroscopy is widely used in industry as well as in research.

Some of the major applications of IR spectroscopy are as follows:

1. Identification of functional group and structure elucidation

➢Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is 4000-1500 cm$^-$ while that of finger print region is 1500-400 cm^{-1}.

➢ In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined.

➢Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as finger print region of the molecule. It can be determined by characteristic peaks.

infra-red spectrum of propan-2-ol, CH_3CHCH_3 / OH
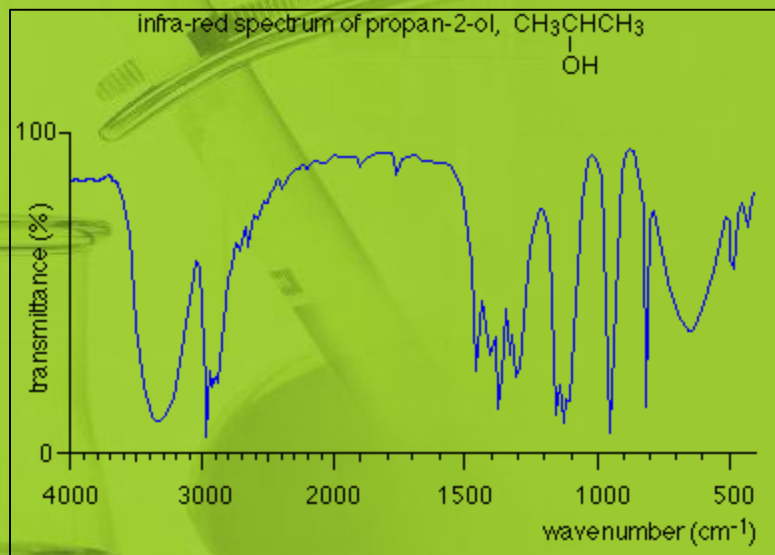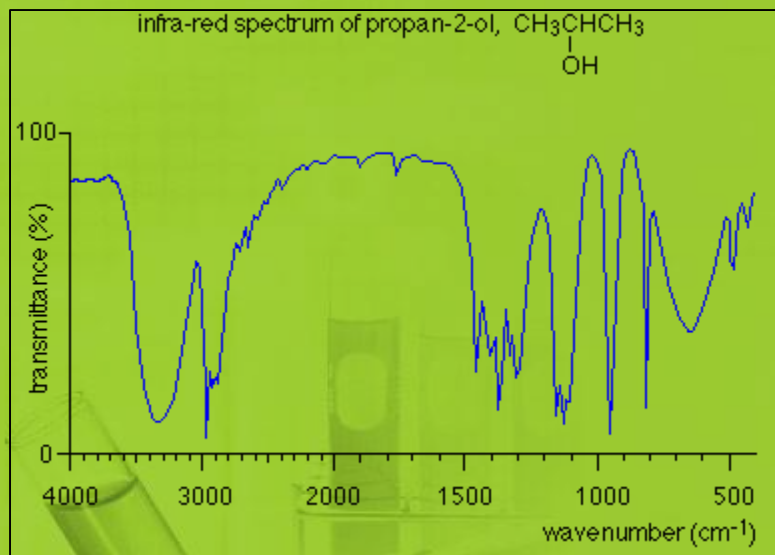
Using the fingerprint region

• Compare the infra-red spectra of propan-1-ol and propan-2-ol.

• Both compounds contain exactly the same bonds.

• Both compounds have very similar troughs in the area around 3000 cm^{-1} - but compare them in the fingerprint region between 1500 and 500 cm^{-1}.

• The pattern in the fingerprint region is completely different and could therefore be used to identify the compound.
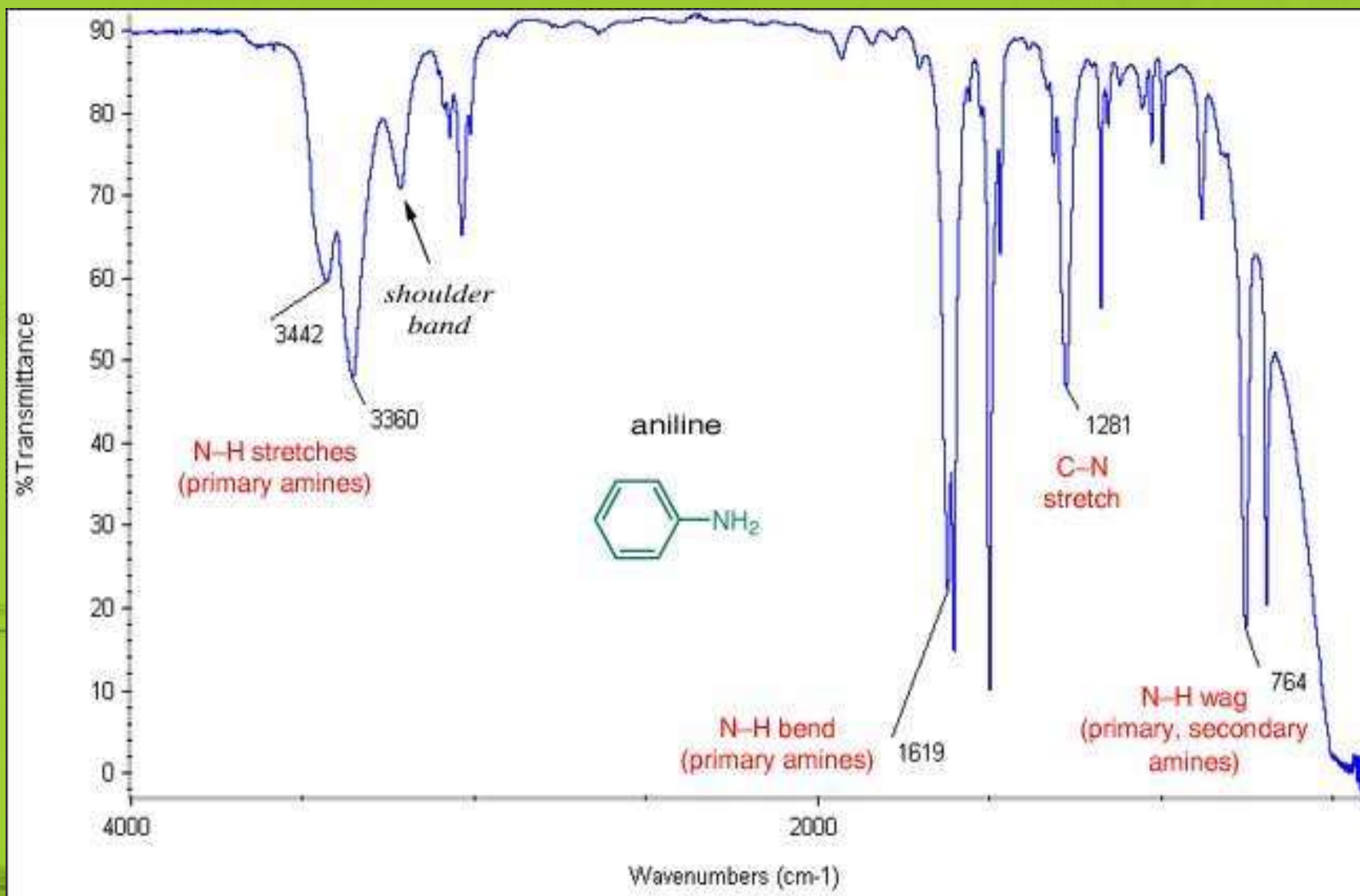
Table of IR Absorptions

| Sr. No.	Functional Group	Characteristic Absorption(s) (cm^{-1})
1	Alkyl C-H Stretch	2950 - 2850 (m or s)
2	Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
3	Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
4	Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
5	Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
6	Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
7	Amine N-H Stretch	3500 - 3300 (m)
8	Nitrile C≡N Stretch	2260 - 2220 (m)
9	Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
10	Amide N-H Stretch	3700 - 3500 (m)

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Ketones
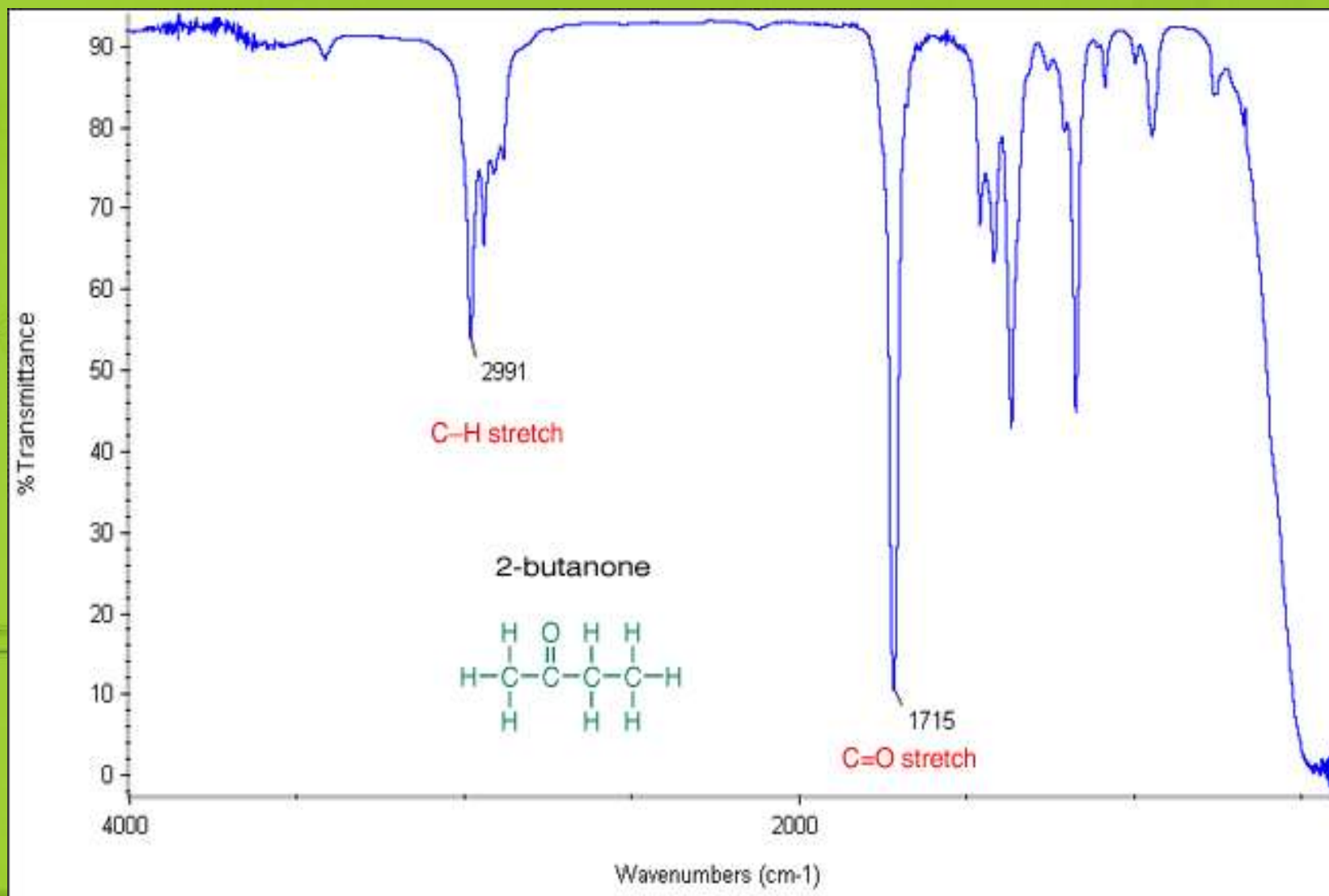
Amines

Alcohols
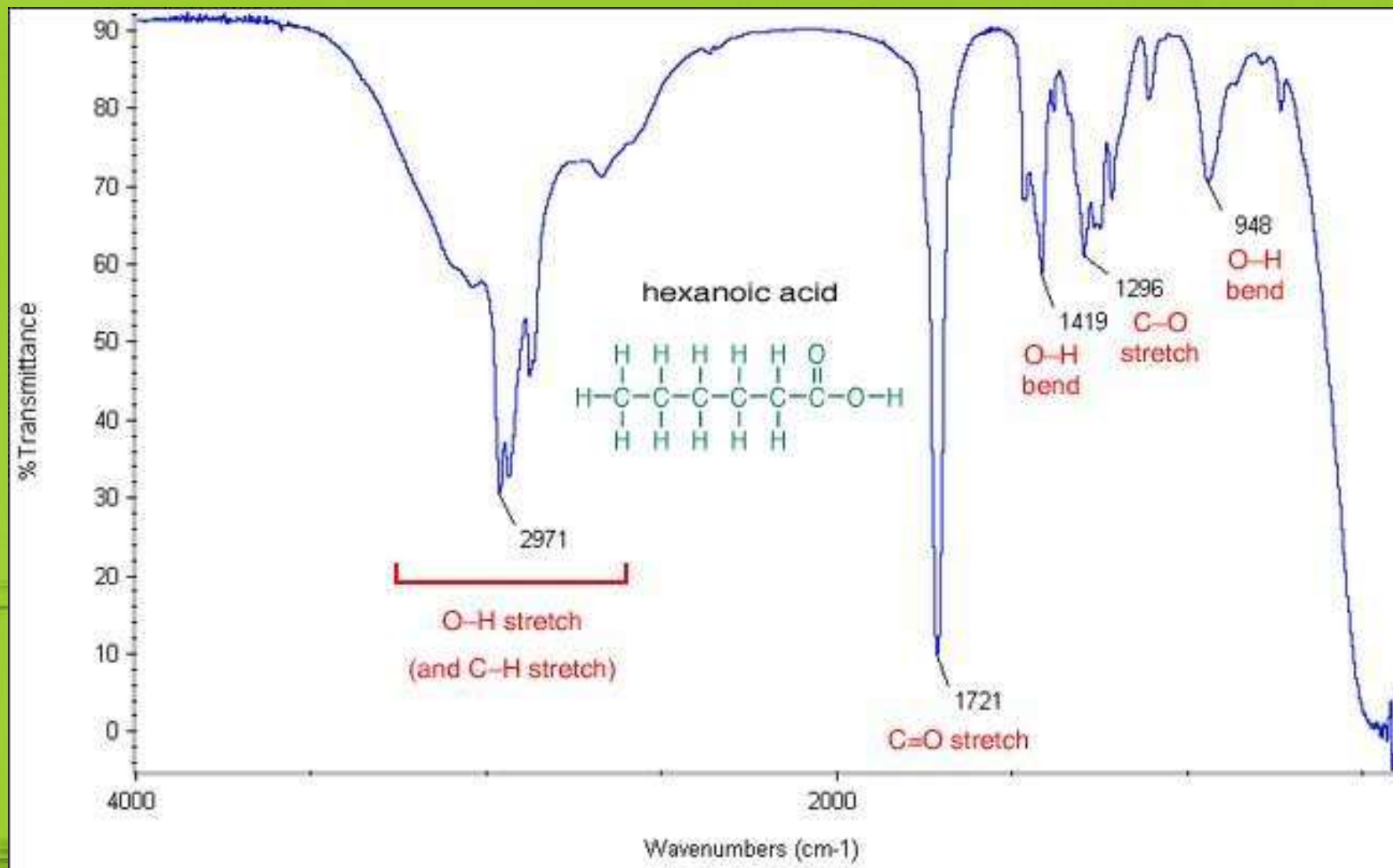
APPLICATIONS OF IR SPECTROSCOPY

2. Identification of substances

IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not. This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two <u>compounds</u> will produce identical spectra is almost zero. So if two compounds have identical IR spectra then both of them must be samples of the same substances.

APPLICATIONS OF IR SPECTROSCOPY

3. Studying the progress of the reaction

Progress of chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is observed.

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APPLICATIONS OF IR SPECTROSCOPY

4. Detection of impurities

IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound.

APPLICATIONS OF IR SPECTROSCOPY

5. Quantitative analysis

The quantity of the substance can be determined either in pure form or as a mixture of <u>two or more</u> compounds. In this, characteristic peak corresponding to the drug substance is chosen and log I0/It of peaks for standard and test sample is compared. This is called base line technique to determine the quantity of the substance.