BansilalRamnathAgarwal Charitable Trust's

VISHWAKARMA INSTITUTE OF INFORMATION TECHNOLOGY

Department of Engineering & Applied Sciences

F.Y.B.Tech

Course Material (A brief reference version for students)

Course: Material Science

Unit 4: Material Characterisation Techniques (AY 2022-23)

Unit 4 - Material characterization Techniques

Objective: To provide the students with basic knowledge of materials, to enable them to use structure-property relationship in appropriate engineering applications

Contents:
X-ray diffraction technique

Spectroscopic Techniques - Fundamentals of spectroscopy,

a) **Ultraviolet (UV)-Visible spectroscopy**- Principle of UV-Visible spectroscopy, Beer- Lambert's law, Types of electronic transitions, Terms related to UV – Visible spectroscopy, Instrumentation of UV – Visible spectroscopy, Applications of UV- Visible spectroscopy
b) **Infrared(IR) spectroscopy** –Principle of IR spectra, requirements of IR absorption, Calculation of vibrational frequency, Modes of vibration, Factors influencing IR spectra, Instrumentation of IR spectroscopy, Applications of IR spectroscopy

Study of morphology: Optical and Electron microscopy

4.1 X-ray Diffraction (XRD) Techniques:

Introduction:

Materials are the backbone of Mechanical, Civil as well as Electronics Engineering. Material characterization is essential to ensure quality of standard materials in engineering practice and also for discovering new materials for development of novel technologies. This unit tries to explore few basic microscopic techniques like X-ray.

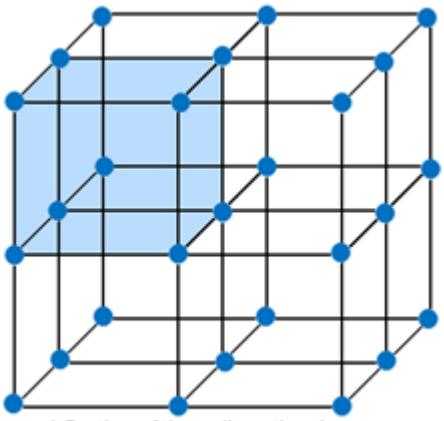
4.1.1 Crystalline solids:

Most of us are familiar with large chunks table salt (NaCl) or sugar, which have definite shape with sharp faces. This is attributed to crystalline nature.

A crystal is a three dimensional periodic array of atoms in a solid. A crystal is thus arrangement of a basis on a periodic lattice.

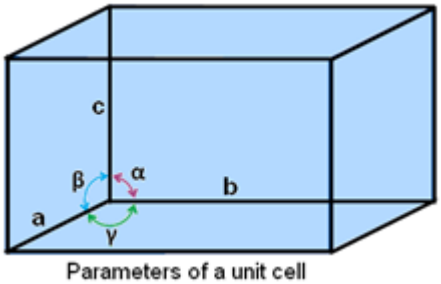
Crystal lattice and unit cell:

The crystal lattice is the ***symmetrical three-dimensional structural arrangements of atoms, ions or molecules (constituent particle) inside a crystalline solid as points.*** It can be defined as the geometrical arrangement of the atoms, ions or molecules of the crystalline solid as points in space.



A Portion of three dimentional cubic lattice and its unit cell

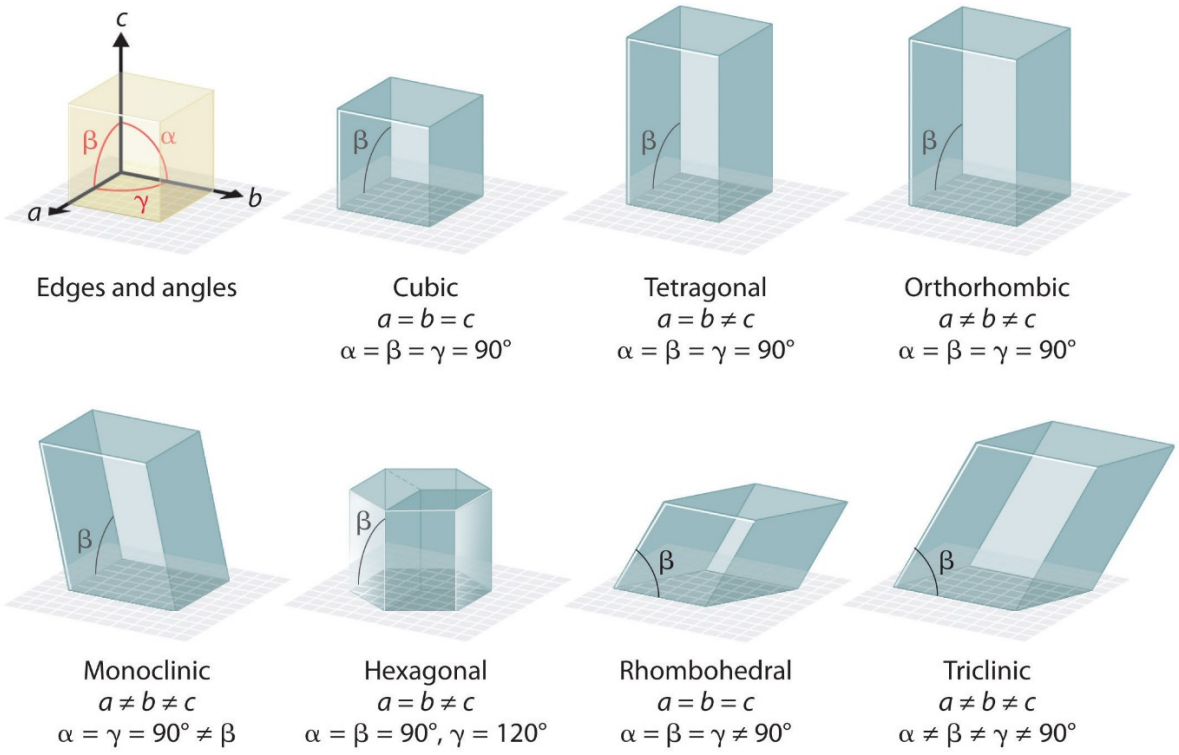
Unit Cell: The smallest portion of a crystal lattice is called Unit Cell. By repeating in different directions unit cell generates the entire lattice.



Parameters of a unit cell

Parameters of a unit cell:

- A unit cell is characterized by six parameters. These parameters are three edges (a, b and c) and angles between them (α, β and γ).
- Dimensions along the edges of a unit cell is represented by a, b and c.
- Edges of unit cell may or may not be mutually perpendicular.
- The angle between b and c is represented by α, between a and c by β and between a and b by γ.
- There are 7 types of unit cells, defined by edge lengths (a,b,c) respectively along the x,y,z axis and angles α, β, and γ



4.1.2 Seven Crystal systems:

In three dimensions (3D), there are 7 crystal systems as shown in Fig. 3.2. They are

1) Cubic
2) Tetragonal
3) Orthorhombic
4) Rhombohedral
5) Hexagonal
6) Monoclinic
7) Triclinic

Fig.shows the unit cells of these seven systems. A unit cell is defined as the smallest unit which can fill up the complete crystal by translation. a, b and c are called the lattice parameters and represent

the length of the unit cell along the three crystallographic axes of the unit cell and α, β and γ are the angles between the unit cell axes.It should be noted that the crystallographic axes need not be identical to x-y-z axes.

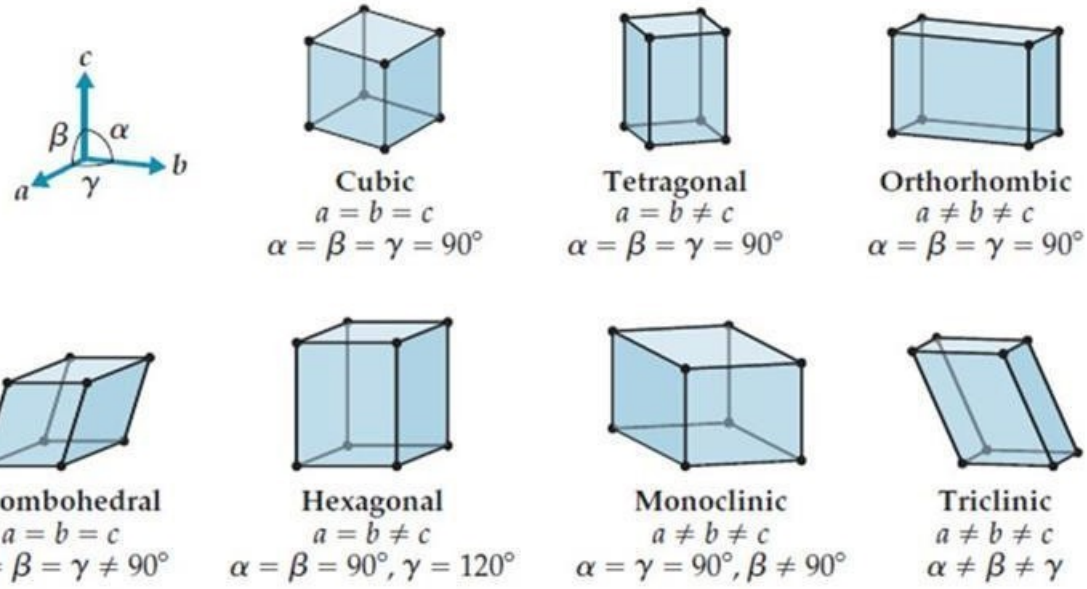


Fig. 3.2 Seven 3-D crystal systems

Bravais Lattices

There are only 14 possible crystal lattices, which are called Bravais Lattices.

4.1.3 Miller Indices:

While studying crystallography, understanding crystal planes are of high importance. Miller Indices are the mathematical representation of the crystal planes. The concept of Miller Indices was introduced in the early 1839s by the British mineralogist and physicist William Hallowes Miller.

The orientation and direction of a surface or a crystal plane may be defined by considering how the crystal plane intersects the main crystallographic axes of the solid.

Crystallographic Planes:

We know that crystal lattices are the infinite array of points arranged periodically in space. These points can be joined together by drawing a straight line and by extending these lines in the three-dimension we notice that they appear to be a set of crystal planes or Crystallographic Planes. The crystal lattices are constructed by the set of parallel lines known as the Crystallographic Planes.

The lattice points have different mechanical, electrical, or optical properties in different directions, this will make the study of crystal structure difficult. To overcome this difficulty, we will choose a set of crystal planes such that the properties of the crystal lattice remain unchanged in the direction of the crystal plane. In order to choose specific crystal planes, a famous mineralogist William Hallowes Miller introduced a method known as the Miller Indices. Basically, Miller Indices are the mathematical representation of the

set of parallel Crystallographic Planes.

Miller Indices Definition:

After joining the crystal lattice points by straight lines, those straight lines were assumed to be the set of parallel crystal planes extending them in three-dimensional geometry. The problem that arose was the explanation of the orientation and direction of these planes. Miller evolved a method to designate the orientation and direction of the set of parallel planes with respect to the coordinate system by numbers h, k, and l (integers) known as the Miller Indices. The planes represented by the hkl Miller Indices are also known as the hkl planes.

Therefore, the Miller Indices definition can be stated as the mathematical representation of the crystallographic planes in three dimensions.

Construction of Miller Planes:

Let us understand the steps involved in the construction of Miller Planes one by one. To construct the Miller Indices and the Miller Plane we follow the following method:

Step 1:

Consider a point or an atom as the origin, construct a three-coordinate axis and find the intercepts of the planes along the coordinate axis.

Step 2:

Measure the distance or the length of the intercepts from the origin in multiples of the lattice constant.

Step 3:

Consider the reciprocal of the intercepts. Reduce the reciprocals of the intercepts into the smallest set of integers in the same ratio by multiplying with their LCM.

Step 4:

Enclose the smallest set of integers in parentheses and hence we found the Miller indices that explain the crystal plane mathematically.

Rules for Miller Indices

- Determine the intercepts (a,b,c) of the planes along the crystallographic axes, in terms of unit cell dimensions.
- Consider the reciprocal of the intercepts measured.
- Clear the fractions, and reduce them to the lowest terms in the same ratio by considering the LCM.
- If a hkl plane has a negative intercept, the negative number is denoted by a bar ($\bar{}$) above the number.
- Never alter or change the negative numbers. For example, do not divide -3,-3, -3 by -1 to get 3,3,3.
- If the crystal plane is parallel to an axis, its intercept is zero and they will meet each other at infinity.
- The three indices are enclosed in parenthesis, hkl and known as the hkl indices. A family of planes is represented by hkl and this is the Miller index notation.

General Principles of Miller Indices:

- If a Miller index is zero, then it indicates that the given plane is parallel to that axis.
- The smaller a Miller index is, it will be more nearly parallel to the plane of the axis.
- The larger a Miller index, it will be more nearly perpendicular to the plane of that axis.
- Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane.
- When the integers used in the Miller indices contain more than one digit, the indices must be separated by commas to avoid confusions. E.g. (3,10,13)
- By changing the signs of the indices 3 planes, we obtain a plane located at the same distance on the other side of the origin.

Determine the Miller Indices of Simple Cubic Unit Cell Plane 1,∞,∞

- **Ans:**
- Given that we have a plane 1,∞, ∞
- our aim is to determine the Miller indices for the given set of the plane. We know that we have a set of rules for determining the miller indices and they are as follows:
  Step 1:
- Consider the given plane 1,∞, ∞
  Step 2:
- Take reciprocals of the intercepts,
  1/1, 1/∞,1/∞
  Step 3:
- Take LCM of these fractions to reduce them into the smallest set of integers.
- 1,0,0
- Therefore, the miller indices for the given plane is 1,0,0.

Fig. shows some typical (hkl) planes. The procedure for obtaining (hkl) values is tabulated in Table

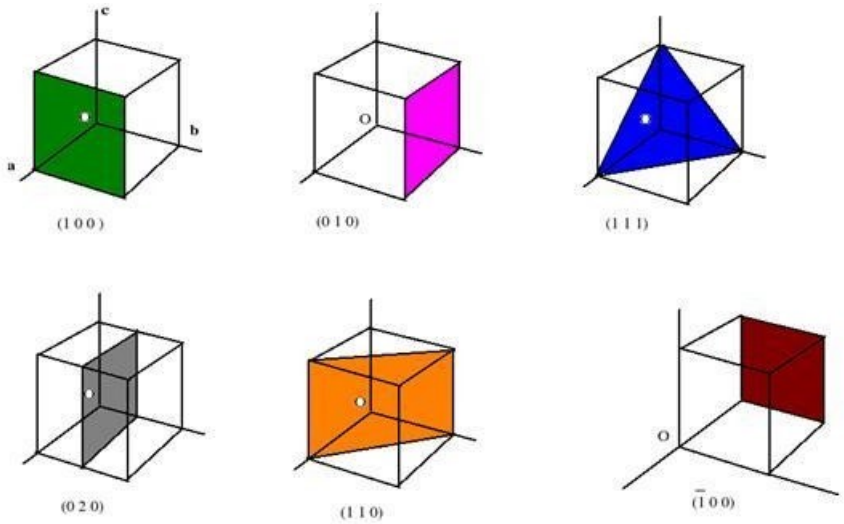


Fig. Representation of crystallographic planes with Miller indices mentioned at the bottom

Examples:

Table : Procedure for finding Miller indices

Sr. No.	Intercepts a b c	Reciprocals a b c	Reduction	Miller Indices
1	1 ∞∞	1/1 1/∞1/∞	1 0 0	(1 0 0)
2	∞ 1 ∞	1/∞1/1 1/∞	0 1 0	(0 1 0)
3	1 1 1	1/1 1/1 1/1	1 1 1	(1 1 1)
4	∞½ ∞	1/∞2/1 1/∞	0 2 0	(0 2 0)
5	1 1 ∞	1/1 1/1 1/∞	1 1 0	(1 1 0)
6	-1 ∞∞	-1/1 1/∞1/∞	-1 0 0	(-1 0 0)

Example: Let the intercepts are x = 2a, y = 3/2b, z = c.

Example: Let the intercepts are x = 2a, y = 3/2b, z – c. We first form the set (x/a,y/b ,z/c) =(2, 3/2,1) Then invert it (1/2 , 2/3,1) and finally multiply by a common (factor) denominator. Which is 6, to obtain the miller indices (3 4 6).

Important Features of Miller Indices:

Some important features of Miller indices have been mentioned below as:

1. A plane that is parallel to in the least one of the coordinate axes comes with an intercept of infinity (∞) and consequently, the Miller index for the said axis becomes zero.
2. All of the similarly spaced parallel planes having a specific alignment come with the same index number (h k I).
3. Miller indices don't only give the definition of the specific plane but a combination of many parallel planes.
4. Only the ratio of indices is considered important over everything else. The planes do not matter.
5. A plane fleeting over the origin is defined in comparison to a parallel plane that has nonzero intercepts.
6. Altogether the parallel equally far planes consist of the same Miller indices. Therefore, the Miller indices are used in relation to a set of parallel planes.
7. A plane that is parallel to anyone out of the many coordinate axes comes with an intercept of infinity.
8. If the Miller indices relating to two planes comes with the same ratio, for example, 844 and 422 or 211, then the planes can be proved as parallel to each other.

9. If h k I am the Miller indices relating to a plane, then the plane will divide or cut the axes into a/h, b/k, and c/l equivalent sections individually.

10. If the integers that are being used in the Miller indices comprise more than one single digit, the indices must be parted by commas for precision, for example (3, 11, 12).

11. In a family the crystal directions are not necessary to be parallel to each other. Likewise, not all members in a family of planes are supposed to be parallel to each other.

12. By altering the signs of entirely each one of the indices of a crystal direction, we find the antiparallel or conflicting direction. By altering the signs of each and every one of the indices of a plane, we get a plane that is situated at a similar distance on the other side of its origin.

4.1.4 Material characterization by X-ray diffraction:

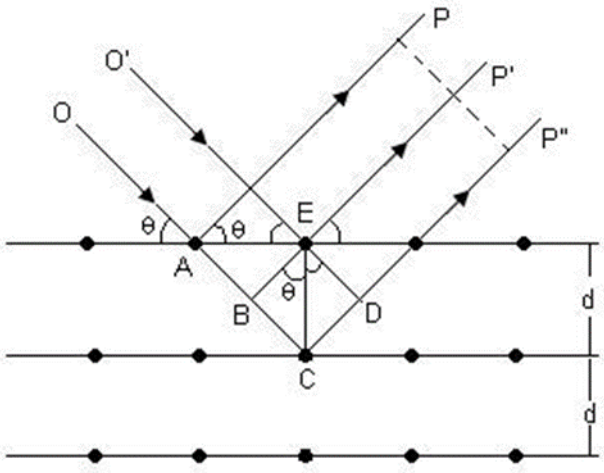
Why XRD?:

- Measure the average spacings between layers or rows of atoms
- Determine the orientation of a single crystal or grain
- Find the crystal structure of an unknown material
- Measure the size, shape and internal stress of small crystalline regions

X-ray diffraction and Bragg's law:

The inter-atomic spacing in crystals is of the order of 1Å. Because of the short wavelength (comparable to the inter-planer distance), X-rays are scattered by adjacent atoms in crystals which can interfere and give rise to diffraction effects. When X-rays enter into a crystal, each atom acts as a diffraction centre and crystal as a whole acts like a three dimensional diffraction grating. The diffraction pattern so produced can tell us much about the internal arrangement of atoms in crystal.

Let us consider a crystal made up of equidistant parallel planes of atoms with the inter-planer spacing dhkl. Further, consider a monochromatic x-ray beam of wavelength λ having a common wave front, falls at an angle θ on the planes as shown in Figure. Each atom scatter the x-rays more or less uniformly in all directions, but because of the periodic arrangement of atoms, the scattered radiation from all atoms in a set of planes is in phase where they interfere constructively. In all other directions, there is destructive interference.



Let us consider a crystal made up of equidistant parallel planes of atoms with the inter-planer spacing d_{hkl}. Further, consider a monochromatic x-ray beam of wavelength λhaving a common wave front, falls at anangle θ on the planes as shown in Figure. Each atom scatter the x-rays more or less uniformly in all directions, but because of the periodic arrangement of atoms, the scattered radiation from all atoms in a set of planes is in phase where they interfere constructively. In all other directions, thereis destructive interference.

Consider two of the incoming x-ray OA and O′E inclined at an angle θ with the topmost plane of the crystal and are scattered in the directions AP and EP′, also at an angle θ with that plane. Since the path length of the rays OAP and O′EP' are the same, they arrive at P and P′ respectively in phasewith each other and again form a common wavefront. This is the condition for scattering in phase by single plane of the crystal.

Now, let us consider X-ray scattering from two adjacent planes $(hkl)_1$ and $(hkl)_2$ as shown in Figure. If EB and ED are perpendicular to the incident and scattered wavefront respectively, the total path O′CP′is longer than the path OEP′ by an amount BC+CD

$$BC = CD \tag{1}$$

Now, from the right angle triangle EBC and EDC, we have

$$BC = d\sin\theta = CD$$

So, Path difference=BC+CD = $2d \sin\theta$

(2)If two consecutive planes scattered in phase with each other then we know that the path difference must be equal to an integral multiple of wavelength, i.e. Path difference= $n\lambda$, where n = 0, 1, 2 ... gives the orderof reflection. Thus the condition for constructive interference (in-phase scattering) by a set of equidistant parallel planes in a crystal is given by

$2d \sin\theta = n\lambda$

This is the well known Bragg's law, which was first derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. Thus diffraction (constructive) occurs for certain discrete values of θ for which the Bragg's condition is fulfilled.

As $(\sin\theta)_{max} = 1$, we get, $\frac{n\lambda}{2d} \leq 1$

That is, λ must not be greater than twice the interplaner spacing, otherwise no diffraction will occur.

Exercise: Determine the angle through which an X-ray of wavelength 0.440Å be reflected from the cube face of a rocksalt crystal (d = 2.814Å) for first, second and third order reflection.

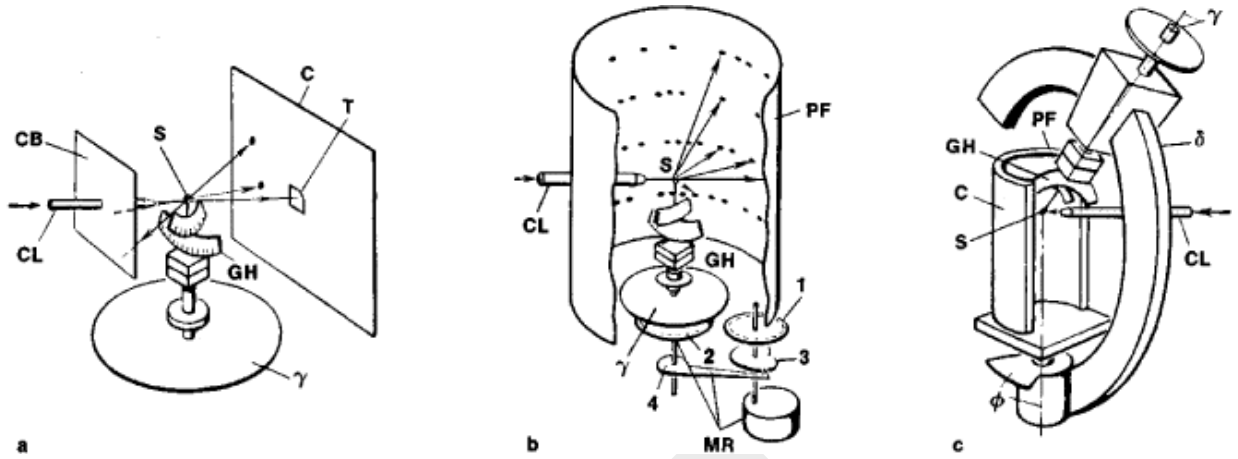
Exercise: Determine the wavelength of the diffraction beam, when a beam of X-ray having wavelengths in the range 0.2Å to 1Å incident at an angle of 9° with the cube face of a rocksalt crystal (d = 2.814Å)

4.1.5 Experimental X-ray diffraction Methods:

To satisfy Bragg's law, it is necessary to vary either the angle of inclination of the specimen to the beam or the wavelength of the radiation. The three standard methods of X-ray crystallography are

a) **Laue Method**: A stationary single crystal is irradiated by a range of X-ray wavelengths.
b) **Rotating crystal Method**: A single crystal specimen is rotated in a beam of monochromatic X-rays.
c) **Powder Method**: A polycrystalline powder specimen is kept stationary in a beam of monochromatic radiation.

Of these techniques, Laue method is used only for known crystal orientation measurement.



The powder method assumes that all orientations are present in the sample, so that regardless of the angle of incidence, there will be a grain in the proper orientation for each reflection (diffraction). The patterns are very useful for identification of unknowns. There are compiled indexes of powder diffraction data for minerals, as well as inorganic compounds and organic compounds.

If the Miller indices of the diffraction peaks are known, it is possible to determine the unit cell parameters of the material from the peak positions. Cell parameters can then be used to determine composition if the cell variation with composition is known.

Bragg's law is the essential condition which must be satisfied to get x-ray diffraction.where, θ is called the grazing angle, angle between incident x-ray and sample surface.

n is the order of diffraction (integral number)

λis the wavelength of incident x-ray

d is the interplanar distance i.e. distance between two consecutive parallel planes with Miller indices (h, k, l), e.g. $d^2=\frac{a^2}{h^2+k^2+l^2}$ for cubic crystal.

a is the lattice parameter

h, k, l are the Miller indices

For typical value of d = 1.5 Å, n=1 and sin θ_{max} = 1, we get upper limit of wavelength for first order.

$$n\lambda=2d \sin\theta$$

$$=2 \times 1.5 \times 1 = 1 \times\lambda\Rightarrow\lambda = 3A°$$

If λ is greater than 3Å, the value of sin θ becomes greater than 1 which is not possible.Therefore there will be no reflection if λ is greater than 3Å.

Usually, the 2nd and higher order diffraction patterns are weak and hence neglected.

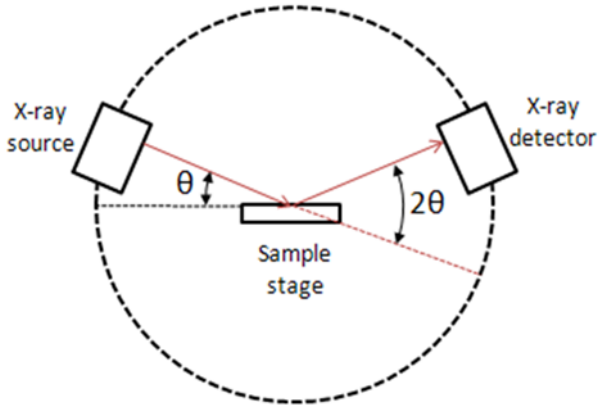
4.1.6 X-Ray Diffractometer:

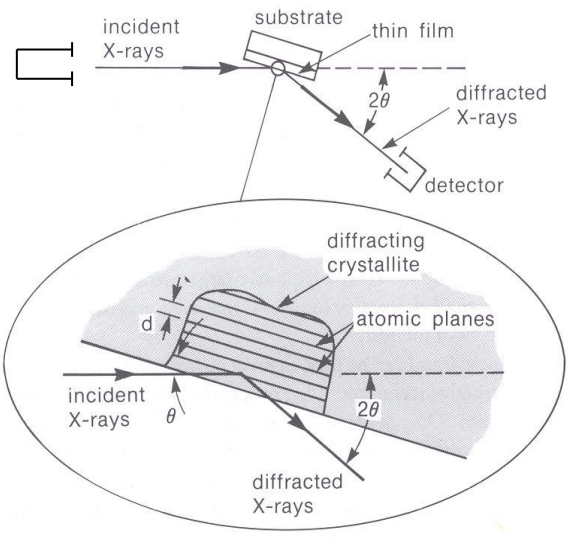
Instrumentation:

Essential parts of diffractometer:

1) Source of X-ray: X-ray tube
2) Optics required to get collimated incident and diffracted X-ray
3) The goniometer, the platform that holds the sample, optics, detector, and/or X-raytube
4) Sample and sample holder
5) Monochromator
6) Detector to detect diffracted X-rays from the sample

A powder X-ray diffractometer consists of an X-ray source (usually an X-ray tube), a sample stage, a detector and a way to vary angle θ. The X-ray is focused on the sample at some angle θ, while the detector opposite the source reads the intensity of the X-ray it receives at 2θ away from the source path. X-ray is incident on the sample and gets scattered from crystallographic planes. Thesescattered (diffracted) rays are detected by detector. Detector records the diffraction angle and peak intensity of diffracted beams. Usually X-ray tube is kept stationary, sample and detector is rotated. Here, the incident angle i.e. angle between incident ray and sample is θ and diffracted angle i.e. angle between incident beam and detector angle is 2θ (Fig.).

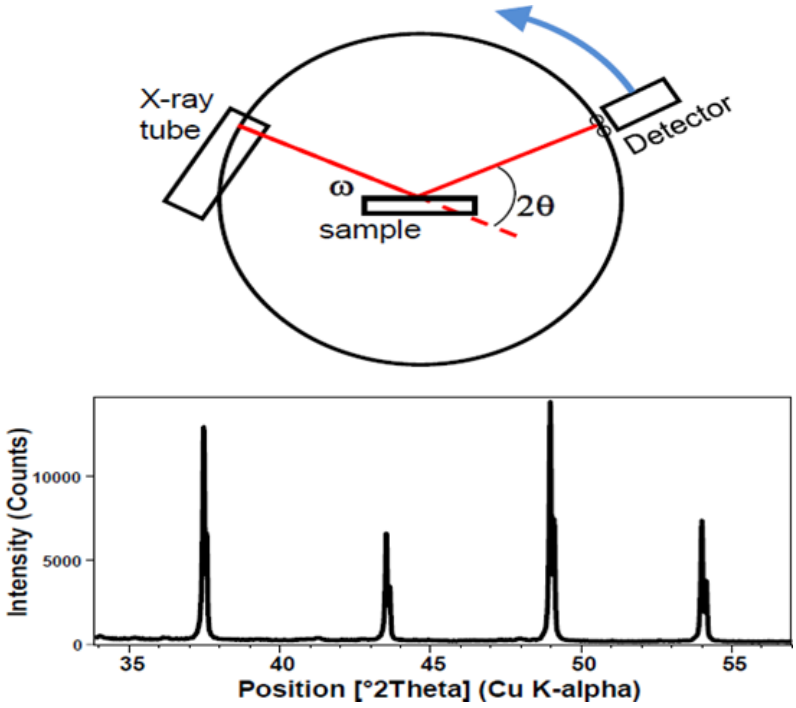




The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

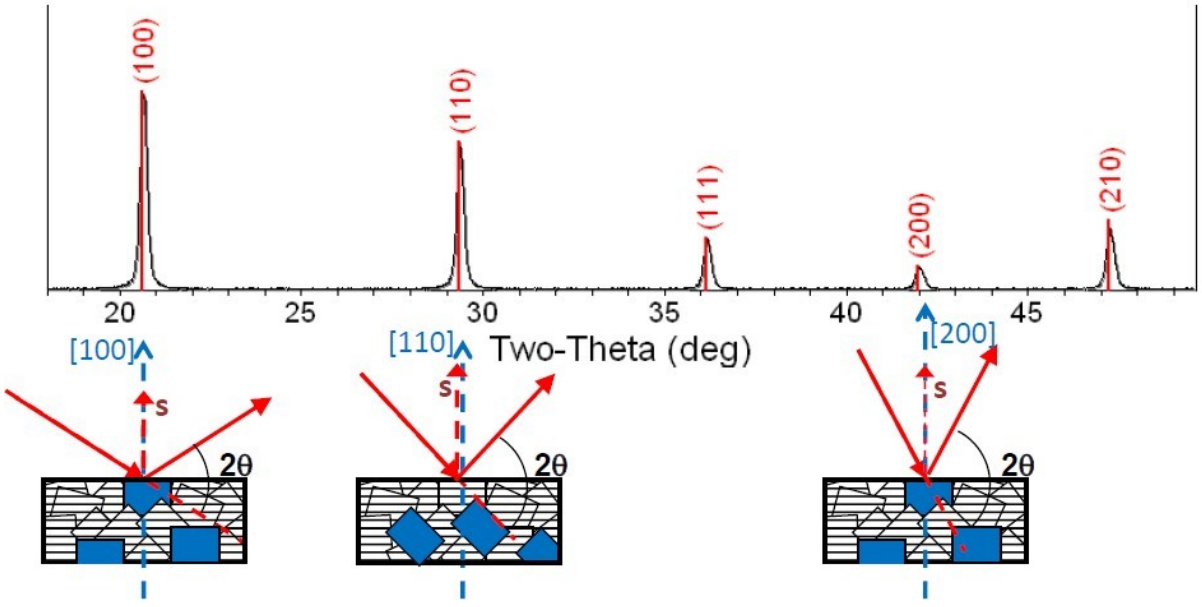
An X-ray diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample.

- The detector moves in a circle around the sample
- The detector position is recorded as the angle 2theta (2θ)
- The detector records the number of X-rays observed at each angle 2θ
- The X-ray intensity is usually recorded as "counts" or as "counts per second"
- To keep the X-ray beam properly focused, the incident angle omega or theta changes in conjunction with 2θ.This can be accomplished by rotating the sample or by rotating the X-ray tube.



The x-ray diffractometer continuously records data during the process when both the source and detector rotate. Peak intensity occurs when the d-spacings in the lattice planes of the mineral sample are appropriate to the value of the diffract x-rays. Results are presented as peak positions and x-ray counts in a table. The Bragg equation calculates the d-spacing of each peak. Once you know all the d-spacings in the sample, you can compare these to the d-spacings of known materials for identification purposes typically commercially available databases. Known d-spacings for reference are available from several sources, including the International Centre for Diffraction Data (ICDD).

A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.



- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

Since most materials have unique diffraction patterns, compounds can be identified by using a database of diffraction patterns. The purity of a sample can also be determined from its diffraction pattern, as well as the composition of any impurities present. A diffraction pattern can also be used to determine and refine the lattice parameters of a crystal structure. A theoretical structure can also be refined using a method known as **Rietveld refinement**.

4.1.7 Analysis of XRD:

XRD is a fundamental tool to understand

1) crystallinity: if the material is crystalline or amorphous
2) phase purity: if only one type of material (e.g. NaCl) is present
3) phase analysis: if there are more than one phase (e.g. KCl in NaCl) then what is their relative concentrations
4) structure and lattice parameters of the phases present in the specimen
5) Strains present in the specimen
6) Crystallite size, especially in nano materials

1)Qualitative analysis:

i) Crystalline versus amorphous:

A crystalline sample gives rise to an XRD pattern with several peaks due to Bragg diffraction from the periodically placed planes (Fig.)

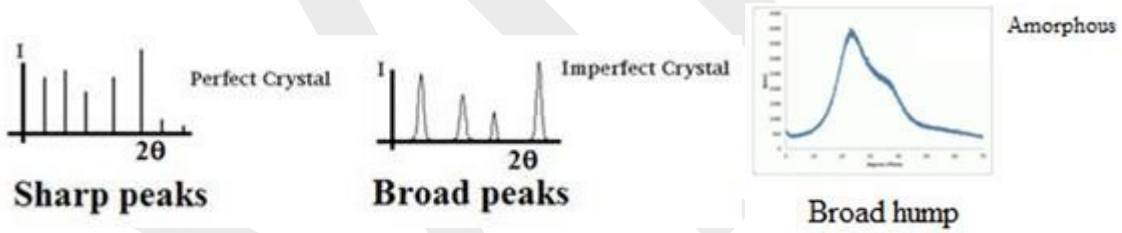
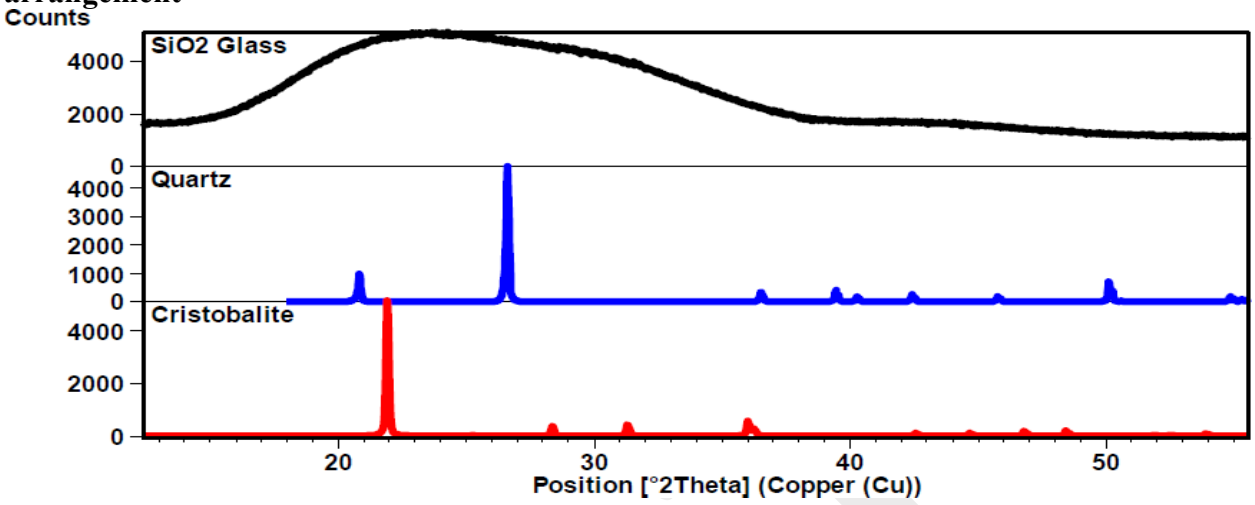


Fig: XRD pattern of perfect crystal, imperfect crystal and liquid/gas and amorphous materials

- The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal
- Amorphous materials like glass do not have a periodic array with long-range order, so they do not produce a diffraction pattern. Their X-ray scattering pattern features broad, poorly defined amorphous 'humps'.

X-rays scatter from atoms in a material and therefore contain information about the atomic arrangement



The three X-ray scattering patterns above were produced by three chemically identical forms of SiO_2

- Crystalline materials like quartz and Cristobalite produce X-ray diffraction patterns
  - Quartz(*Trigonal/Hexagonal*) and Cristobalite (*Tetragonal)* have two different crystal structures
  - The Si and O atoms are arranged differently, but both have long-range atomic order
  - The difference in their crystal structure is reflected in their different diffraction patterns
- The amorphous glass does not have long-range atomic order and therefore produces only broad scattering features

ii)Phase identification

Each "phase" produces a unique diffraction pattern. The diffraction pattern of each phase is unique like our fingerprints. In analysing the diffraction pattern we usually match experimental data, the position (2θ) and relative peak intensity (I) of diffracted peaks with standard reference data in the database for already known materials (e.g. NaCl). This is computerised. Modern computer programs (e.g. Fullprofsuite for **Reitveld analysis**) can be used for phase identification i.e. to find out phases present in the sample by comparing experimental diffraction data with single-phase X-ray powder diffraction patterns compiled in a database. For this purpose, the International Centre of Diffraction Data has collected known powder patterns found in the Powder Diffraction File (PDF) to help identify various substances.

So to identify the phase, basic requirement is to have actual experimental diffraction data, standard reference data and software used for search/match. The match can reveal information about the sample including d-spacing, present elements and crystalline phases.

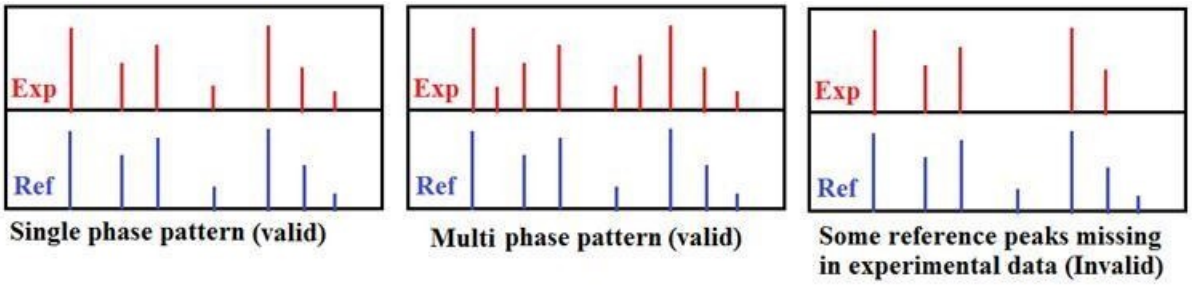
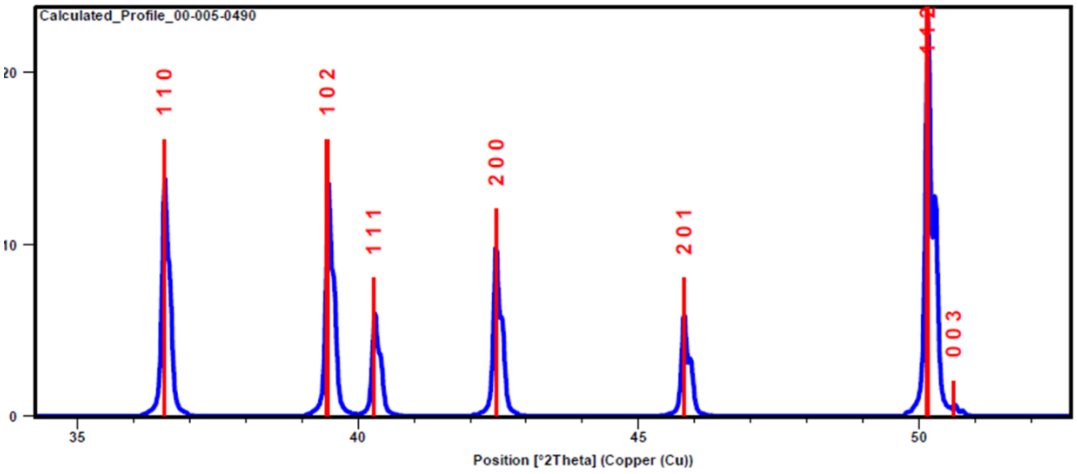


Fig: Valid or invalid pattern matching

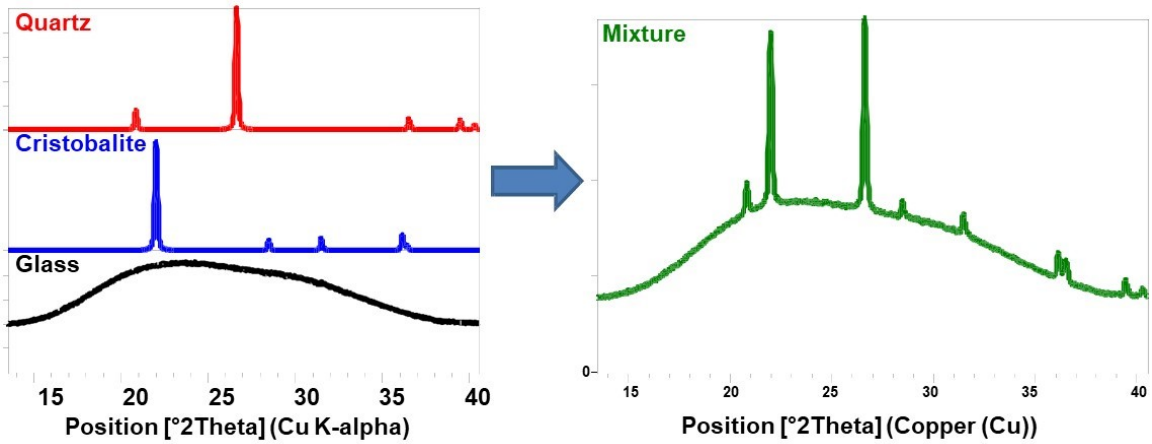
Diffraction pattern calculations treat a crystal as a collection of planes of atoms. Each diffraction peak is attributed to the scattering from a specific set of parallel planes of atoms.

•Miller indices (hkl) are used to identify the different planes of atoms

•Observed diffraction peaks can be related to planes of atoms to assist in analyzing the atomic structure and microstructure of a sample



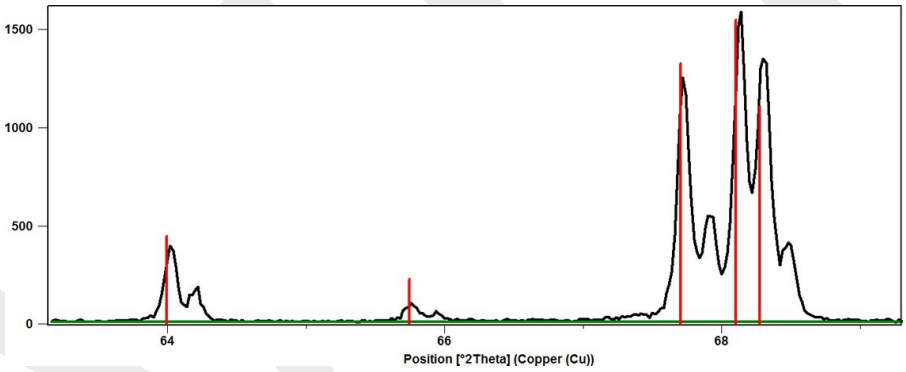
The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.



- From the XRD pattern you can determine:
  - What crystalline phases are in a mixture
  - How much of each crystalline phase is in the mixture (quantitative phase analysis, QPA)
  - If any amorphous material is present in the mixture

iii) Number of phases present:

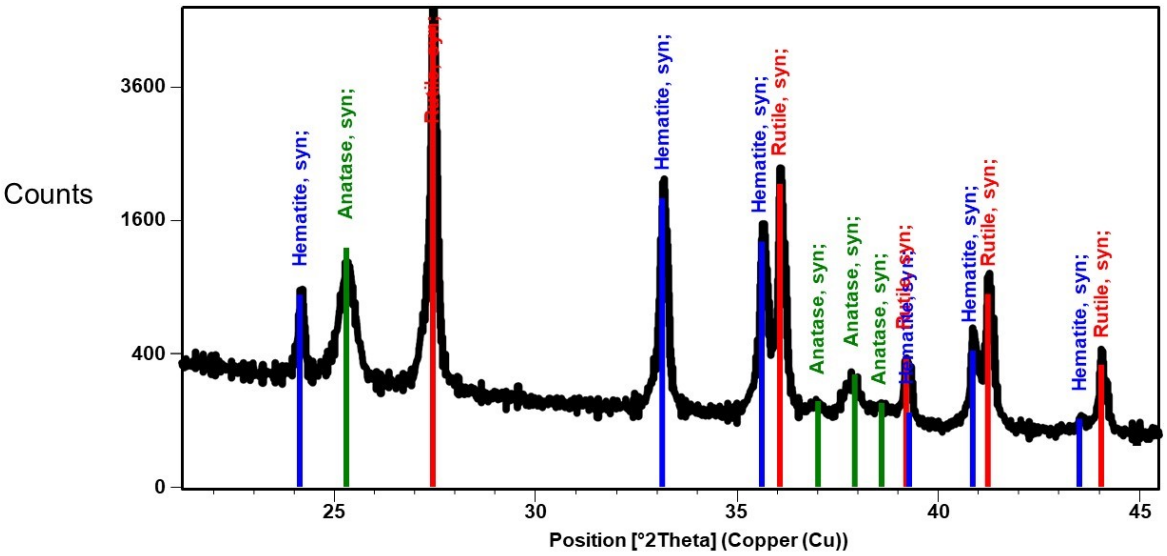
Experimental XRD data are compared to reference patterns to determine what phases are present



- The reference patterns are represented by sticks
- The position and intensity of the reference sticks should match the data

(A small amount of mismatch in peak position and intensity is acceptable experimental error)

The X-ray diffraction pattern is a sum of the diffraction patterns produced by each phase in a mixture.



Each different phase produces a different combination of peaks

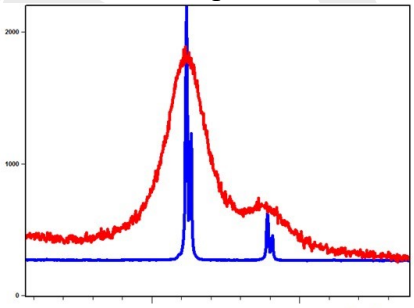
iii) Crystal size:

A decrease in the crystallite size causes an increase in the width of the diffraction.

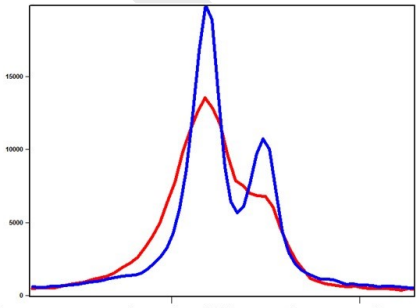
Diffraction peak broadening may contain information about the sample microstructure.

- Peak broadening may indicate:
  - Smaller crystallite size in nanocrystalline materials
  - More stacking faults, microstrain, and other defects in the crystal structure
  - An inhomogeneous composition in a solid solution or alloy

However, different instrument configurations can change the peak width, too. When evaluating peak broadening, the instrument profile must be considered.



These patterns show the difference between bulk ceria (blue) and nanocrystalline ceria (red)



These patterns show the difference between the exact same sample run on two different instruments.

2) Quantitative analysis:

i) Determination of the lattice parameters:

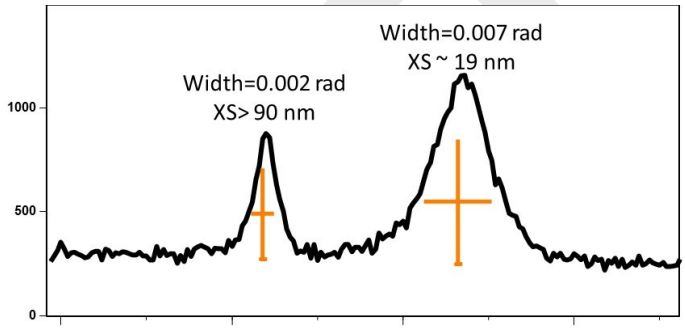
- Convert the observed peak positions, °2theta, into d_{hkl} values using Bragg's Law:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta}$$

- Determine the Miller indices (hkl) of the diffraction peaks from the published reference pattern

ii) Crystal size measurement:

A decrease in the crystallite size causes an increase in the width of the diffraction.
Diffraction peak broadening may contain information about the sample microstructure.



$$\text{Size} = \frac{Kh}{\text{Width} * \cos \theta}$$

The line broadening can be a measure of the average size of the crystallites by using the Scherrer formula

$$D_v = \frac{\lambda}{\beta cos\theta}$$

Where, D_v is the average particle size, λ is wave length of the radiation and β is the FWHM(full width at half maximum) of the reflection peak that has the same maximum intensity in the diffraction pattern (integral breadth of the peak located at angle θ). K is the Scherrer constant. The Scherrer constant (K) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9 (0.9 is taken for spherical particles and the value changes with morphology) . The size obtained from the Scherrer formula yields the apparent or average crystallite-size for a material.

4.1.9Advantages and limitations of XRD:

The main advantages of x-ray diffraction are:

- It is a rapid and powerful technique for identifying unknown minerals and materials
- It only requires preparation of a minimal sample for analysis
- Interpreting the resulting data is relatively straightforward
- XRD measurement instruments are widely available

XRD does, however, have certain limitations:

- To best identify an unknown powder material, the sample should be homogeneous.
- Typically XRD analysis requires access to standard reference data .
- Preparation of samples often requires grinding them down to a powder
- If the crystal sample is non-isometric, then the indexing of patterns can be complex when determining unit cells

4.2 Spectroscopy:

Spectroscopy is the branch of science that deals with the study of interaction of electromagnetic radiation with matter. Spectroscopy is one of the powerful tools available for the study of atomic and molecular structure and is used in analysis of wide range of samples

4.2.1 Fundamentals of spectroscopy:

Spectroscopy

It deals with interaction of electromagnetic radiation with matter.
Due to these interactions, energy is absorbed or emitted by the matter. Measurement of radiation frequency is done experimentally to give change in energy involved.
Spectroscopy means measurement of spectrum of a sample containing atoms or molecules.
Spectrum is a graph of intensity of absorbed or emitted radiation by sample verses frequency (ν) or wavelength (λ).
The study of spectroscopy can be carried out under the following heads:

1. Atomic spectroscopy: This spectroscopy is concerned with the interaction of electromagnetic radiation with atoms which are most commonly in their lowest energy state called ground state
2. Molecular spectroscopy: This spectroscopy deals with the interaction of electromagnetic radiation with molecules. This results in transitions between rotational and vibrational energy levels in addition to electronic transitions

The most important atomic and molecular transitions related to the successive regions are

X- ray	K and L shell electrons

Far ultra violet	Middle shell electrons
Near untraviolet	Valency electrons
Visble	
Near and mid infra red	Molecular vibrations
Far infra red	Molecular rotations and low lying vibrations
Microwave	Molecular rotations

Defn.*: Spectroscopy is the analysis of the electromagnetic radiation absorbed or emitted by atoms or molecules.*

4.2.2 Types of spectroscopy

a) **Absorption spectroscopy**: results when molecule undergoes change in energy from lower energy to higher energy with the absorption of photon of energy hν, if hν is equal to energy difference ΔE.

In absorption spectroscopy, a beam of polychromatic light falls on a sample. Part of light is absorbed by the sample and remaining part is transmitted. The intensity of transmitted light coming from sample is measured at different wavelengths by suitable photo detector. This information is presented as a graph of intensity of absorbed radiation. Spectrum of sample consist of number of absorption bands with different intensity.

b) **Emission spectroscopy:** results when molecule falls from higher energy to lower energy with emission of photon of energy hν.

In this technique, sample is subjected to intense source of energy like electrical arc. As a result, sample is vaporized and electrons in the sample are excited to higher energy state. When these electrons come back to ground state energy level, they emit radiation. These radiations are analysed by spectrophotometer to generate spectrum that gives information about atoms present in the sample.

4.2.3 Electromagnetic radiations and electromagnetic spectra:

1) **Electromagnetic radiations:** it is a form of energy that is transmitted through space with high velocity. Each electromagnetic radiation is characterized by wavelength (λ), wave number (cm^{-1}) and frequency (ν). The energy associated with electromagnetic radiation is given by $E=hc/\lambda$ or $E= h\nu$..

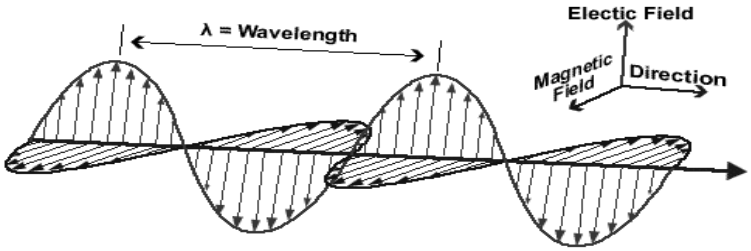
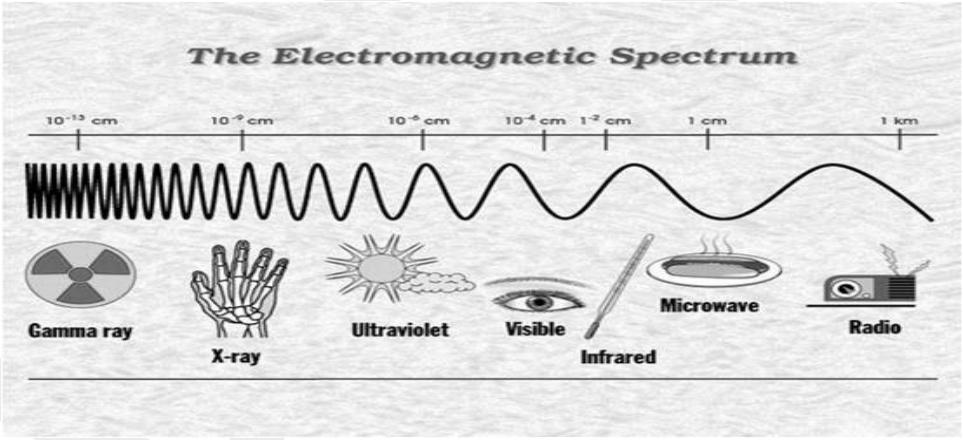


Fig: Electromagnetic radiation

2) **Electromagnetic spectra**: The entire range of electromagnetic radiations starting from gamma rays, X rays to microwaves and radio waves are covered in electromagnetic spectra. It shows the range of electromagnetic radiations with different wavelengths hence associated with different energies. As wavelength goes on increasing, energy associated goes on decreasing.



4.2.4 Molecular spectroscopy:

1) Molecular spectroscopy: It deals with the interaction of electromagnetic radiation with molecules. These interactions result in rotational, vibrational and electronic transitions of energy levels. Total internal energy of molecule is given by

$$E_{int} = E_{elec} + E_{vib} + E_{rot}$$

i) **Rotational energy** -This type of energy is associated with overall rotation of the molecule with the atoms considered as fixed point masses.

ii) **Vibrational energy** – This type of energy is associated with the oscillation of atoms of molecule which are considered as point masses about equilibrium position. When molecule absorbs energy, the increase in vibration motion of molecule is usually accompanied by increased rotation of the same molecule. This combination provides the basis for IR absorption spectroscopy.

iii) **Electronic energy** - This type of energy is associated with the motion of electrons considering nuclei of atoms of a molecule as fixed point, to move from the ground state to excited state.

iv) **Relation between these energies can be shown as:**

$$E_{electronic} > E_{vibrational} > E_{rotational}$$

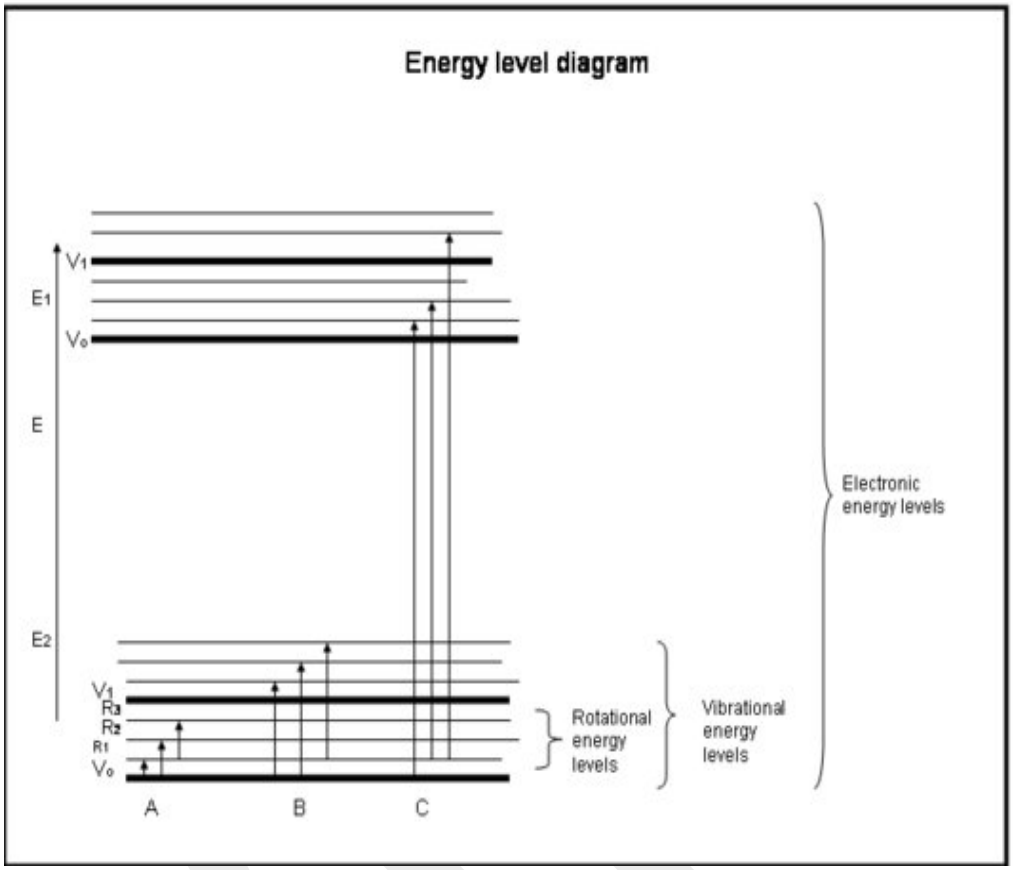
2) Molecular absorption of electromagnetic radiation: When molecules absorb electromagnetic radiation, it gets excited from ground state energy level to excited state. When it returns to ground state, it gives bands that are characteristic of that molecule, known as molecular spectra.

Total energy states of molecule include electronic, vibrational and rotational levels. All energy components are quantized.

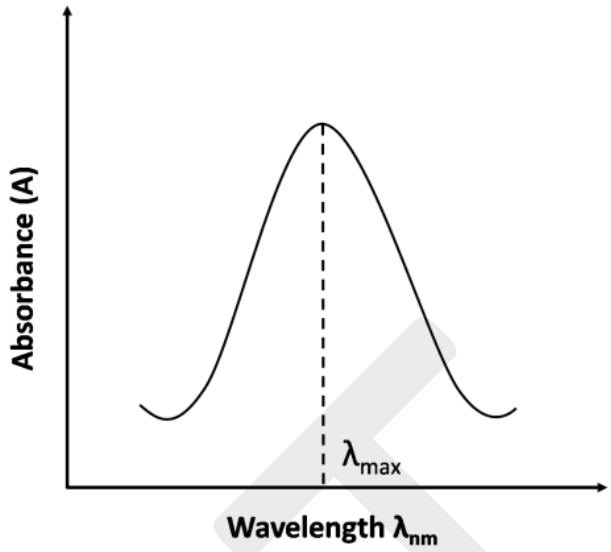
Rotational energy levels of a molecule are very closely spaced. Little energy is required for rotational energy transitions which occur in microwave region. Rotational absorption spectra is in the form of single lines.

Vibrational energy levels are placed further apart. Vibrational energy transitions require more energetic photons than rotational transitions. These transitions occur in infrared region. **Vibrational transitions are accompanied by rotational transitions**. Thus, a typical vibratonal absorption spectra consist of complex bands instead of single lines.

When molecules absorb photons in UV Visible regions, electronic transitions take place from ground state to excited state. **Electronic transitions are accompanied by vibrational and rotational transitions**. These transitions result into molecular spectrum involving band of wavelength rather than a single line, therefore, broad absorption spectra is observed. The value at which maximum absorption takes place is called λ_{max} value.



UV – Visible absorption spectra



4.2.5 UV – Visible spectroscopy:

UV- Visible absorption spectroscopy is powerful tool for structural determination and quantitative analysis.

Principle of UV- Visible spectroscopy:

i)UV and visible radiations are more energetic radiations. Absorption of these radiations by any substance brings about electronic excitations. These excitations are accompanied by vibrational and rotational changes that result in spectrum. As a result, bands in UV –visible spectrum are relatively broad. Electronic excitation responsible for absorption in UV – Visible region can be mostly $\pi \longrightarrow \pi^*, \eta \longrightarrow \sigma^*, \eta \longrightarrow \pi^*$ transitions.

ii) Quantitative analysis using UV – Visible spectrophotometer can be done according to Beer's law. According to Beer's law, the absorbance of monochromatic light from UV – Visible region by substance is directly proportional to concentration of substance in solution, for constant path length.

Laws of absorbance of radiation:

i) **Lamberts law**: *When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to path length.* Let intensity of incident radiation = I

Rate of decease in intensity of incident radiation with thickness dx of the medium will be $\frac{-dI}{dx}$

$\frac{-dI}{dx} \propto I$ $\quad\quad$ $\therefore KI = \frac{-dI}{dx}$ (K is proportionality constant)

$\therefore \frac{dI}{I} = -K.dx$

On integrating equation between the limits $I = I_o$ at $x = 0$ and $I = I_t$ at $x = x$ (length of solution)

$\therefore \int_{I_0}^{I_t} \frac{dI}{I} = \int_0^x -K.dx$

$\ln \frac{I_t}{I_0} = -Kx$ $\quad\quad$ $I_t = I_0 . e^{-Kx}$

ii) **Beers law:** *When a beam of monochromatic light is passed through a transparent solution, decrease in intensity of incident radiation is directly proportional to concentration.*

Let intensity of incident radiation = I

Rate of decease in intensity of incident radiation with concentration dC of the medium will be $\frac{-dI}{dC}$

$\frac{-dI}{dC} \propto I$ $\quad\quad$ $\therefore KI = \frac{-dI}{dC}$ (K is proportionality constant)

$\therefore \frac{dI}{I} = -K.dC$

On integrating equation between the limits $I = I_o$ at $C = 0$ and $I = I_t$ at $C = C$

$\therefore \int_{I_0}^{I_t} \frac{dI}{I} = \int_0^C -K.dC$

$\ln \frac{I_t}{I_0} = -KC$ $\quad\quad$ $I_t = I_0 . e^{-KC}$

iii) **Combined law (Beer – Lambert's law):**

$\ln \frac{I_t}{I_0} = -K.x.C$

$2.303 \log \frac{I_t}{I_0} = -K.x.C$

$$\log \frac{I_t}{I_0} = -\frac{K}{2.303}.x.C$$

$$\log \frac{I_0}{I_t} = \frac{K}{2.303}.x.C$$

$$\frac{K}{2.303} = \epsilon$$

ϵ = absorption coefficient $A = \log \frac{I_0}{I_t}$ = absorbance

$$\boxed{A = \epsilon.C.x}$$

$T = \log \frac{I_t}{I_0}$ = transmittance $A = -\log T$

Electronic transitions:

When energy is absorbed by a molecule in UV Visible region, it brings changes in electronic energy of molecule because of transition of valence electrons.
3 types of electrons are involved in organic molecule:

i) **σ electrons**: electrons forming single bonds are called σ electrons. These are involved in forming bonds in saturated hydrocarbon such as C-H bonds
ii) **π electrons**: electrons involved in forming double bonds are called as π electrons. These are involved in forming bonds in unsaturated hydrocarbon.
iii) **η electrons**: these are non bonded or lone pair of electrons and are not involved in bonding between atoms in molecules

When energy is absorbed in UV Visible region, **possible electronic transitions** are:

σ ⟶ σ*,σ ⟶ π*,π ⟶ σ*,π ⟶ π*,η ⟶ σ*,η ⟶ π*

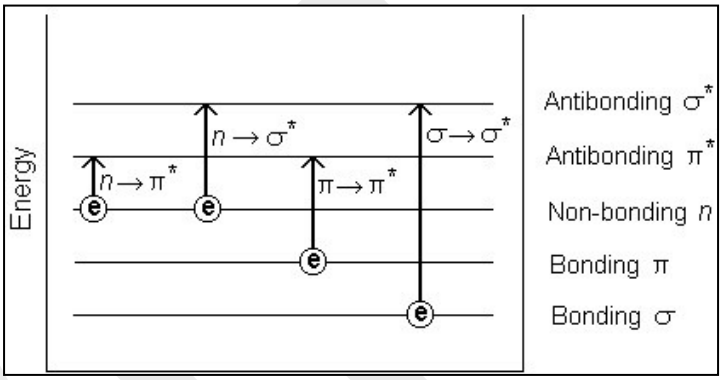
Out of these, σ⟶ π*,π ⟶ σ*are considered as **forbidden** transitions.

i) $\boldsymbol{\sigma \rightarrow \sigma^*}$ **:**These transitions are observed in saturated hydrocarbons. Energy required for these transitions is very large. Absorption band occur in the far UV region (126-135nm).For e.g. methane has λ_{max} at 121.9nm, ethane at 135 nm.

ii) **π ⟶ π*:** These transitions are involved in transition of electrons from bonding π to antibonding π* orbital. These transitions occur in molecules having π electron system such as alkenes and alkynes. For e.g. ethylene shows intense band at 174nm and weak band at200nm due to π to π* transition. λ_{max} value increases with increase in conjugation.

iii)**η ⟶ σ*:** Saturated hydrocarbons with lone pair of electrons/non bonding electrons undergoes these transitions. The energy required is less than that of σ to σ* transitions. Corresponding absorption bands appear near UV region (180-200nm) For e.g. aliphatic alcohols, alkyl halides show such transitions.

iv) **η ⟶ π*:** These type of transitions are shown by unsaturated molecules which contain atoms such as oxygen, sulphur, nitrogen. Absorption band of aldehydes and ketones usually occur in the range of 270-300nm.



Terms related to UV Visible spectroscopy:

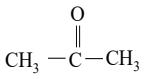
i) **Chromophore**: *is a functional group containing multiple bonds capable of absorbing radiation in UV-visible region. e.g. C=O, C=C, N=O, C=N etc.*
While interpreting UV –visible spectroscopy, following points are to be considered.

a) Non conjugated alkenes show an intense absorption below 200 nm therefore inaccessible to UV spectrophotometer.

e.g. λ_{max} for ethylene (CH_2=CH_2) is 171 nm.

b) Non –conjugated carbonyl group give a weak absorption in the region 200- 300nm.

e.g. Actone has λ_{max} = 279 nm



Acetone

c) When double bonds are conjugated in a compound, λ_{max} is shifted to longer wavelength.

e.g. 1,5 – Hexadiene : λ_{max} = 178 nm (non conjugated system)

2,4 – Hexadiene : λ_{max} = 227 nm (conjugated system)

Absorptions of Organic Molecules
Alkanes:
• Saturated molecules that lack lone pairs
• Only transitions possible are $\boldsymbol{\sigma \rightarrow \sigma^*}$
• high energy; absorb UV radiation at very short wavelengths
• not accessible using UV spectroscopy

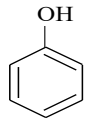
Alcohols, Ethers, Amines, & Sulfur Compounds:
• Saturated molecules with lone pairs of electrons
• Important transitions are $\boldsymbol{\eta \longrightarrow \sigma^*}$
• high energy, most often at wavelengths shorter than 200 nm
• alcohols and amines: 175 – 200 nm
• thiols and sulfides: 200 – 220 nm

Alkenes & Alkynes:
• Important transitions are $\boldsymbol{\pi \longrightarrow \pi^*}$
• high energy, but impacted by substitution
• simple alkenes: 175 nm
• simple alkynes: 170 nm
Carbonyls:
• Important transitions are $\boldsymbol{\pi \longrightarrow \pi^*}$ (188 nm)
• $\boldsymbol{\eta \longrightarrow \pi^*}$: also possible (280 – 290 nm)
• sensitive to substitution

ii) **Auxochrome**: *is a saturated functional group which does not absorb radiation in UV range but when attached to chromophore changes both wavelength & intensity of absorption.*
e.g. –OH, -NH_2,- Cl.
It causes shift in absorption to longer wavelength. It is a group, which extends the conjugation of chromophore by sharing of non bonding electrons.

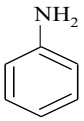
Benzene

$\lambda_{max} = 255$ nm



Phenol

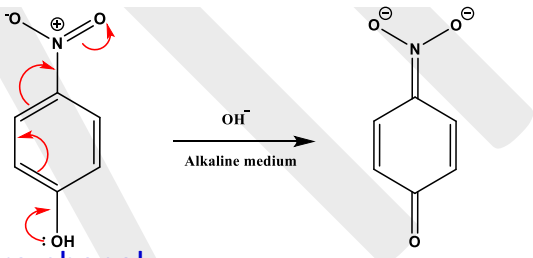
$\lambda_{max} = 270$ nm



Aniline

$\lambda_{max} = 280$ nm

iii) **Bathochromic shift/Red shift:** *The shift of absorption maxima (λ_{max}) to a longer wavelength due to substitution or solvent effect is known as bathochromic shift or red shift.*

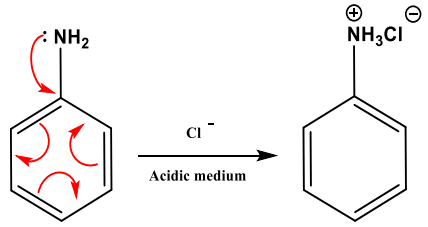


P-nitro phenol

$\lambda_{max} = 255$ nm

$\lambda_{max} = 265$ nm

iv) Hypsochromic shift/Blue shift: *The shift of absorption maxima (λ_{max}) to a shorter wavelength due to substitution or solvent effect is known as hypsochromic shift or blue shift.*



Aniline

λ_{max} = 280 nm λ_{max} = 265 nm

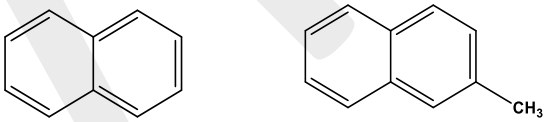
v) Hyperchromic shift: *An increase in intensity of absorption maxima is called hyperchromic shift. It is observed due to introduction of auxochrome.*

Pyridine 2-methyl pyridine

λ_{max} = 257 nm λ_{max} = 260 nm

∈ = 2750 ∈ = 3560

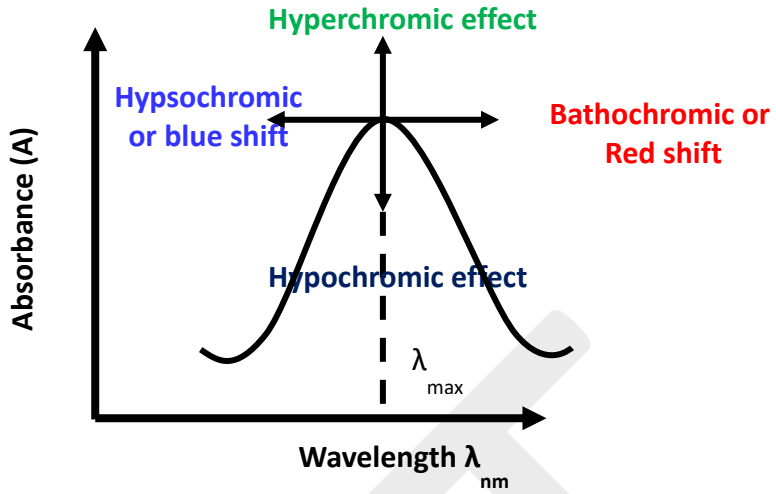
vi) Hypochromic shift: *Decrease in intensity of absorption maxima is called hypochromic shift. It occur due to introduction of groups that distorts the original geometry of the molecule*



Naphthalene 2-methyl naphthalene

∈ = 19000 ∈ = 10250

These shifts and effects on the absorption can be shown as



Instrumentation of UV Visible Spectroscopy

Various components of UV Visible spectroscopy and their **functions** are as follows

i) **Radiation source**: It gives a source of continuous electromagnetic radiation in the required region. Tungsten filament lamp is most commonly used for visible radiations (Wavelength range 400 to 750nm).Hydrogen discharge lamps are used for UV radiations (Wavelength range200 to 400nm)

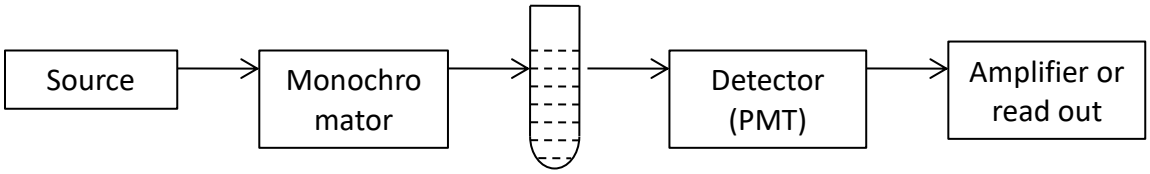
ii) **Monochromators**: Radiation source provide polychromatic light which is passed through monochromator. Monochromators disperse radiation according to wavelength. Dispersing element may be prism or grating. Position of dispersing element is adjusted to vary wavelength passing through exit slit. Thus it helps to give monochromatic light.

iii) **Sample holder:** Sample holders are used to hold sample solution and reference solution. They are constructed of the material which does not absorb radiation in the UV Visible region. Optically matched fused glass cells are used for visible spectroscopy whereas **Corex glass or quartz cells** are used for UV spectroscopy. (Glass absorbs radiations of wavelength less than 350 nm hence not used for UV spectroscopy but can be used for visible spectroscopy)

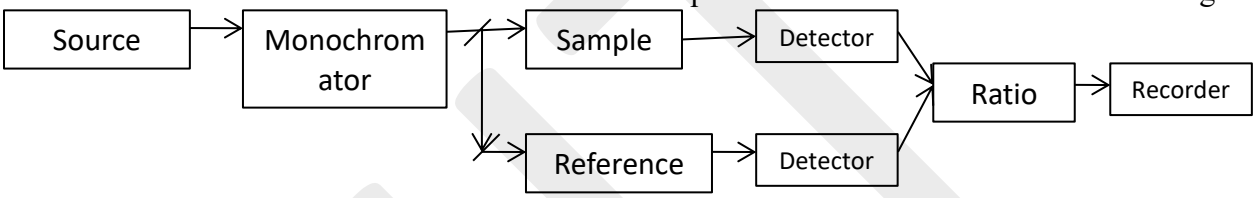
iv) **Detectors**: A detector is a transducer that converts electromagnetic radiation into an electron flow and consequently into current or voltage in readout circuit. Phototubes, photomultiplier tubes, photovoltaic cells etc. are used for the purpose.

v) **Amplifiers and readout**: signal received from the detector is amplified and read on recorder.

Single beam spectrophotometer: In this, a sample is examined to determine the amount of radiation absorbed at a given wavelength. The results are compared with a reference obtained in a separate measurement.



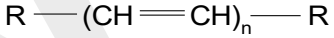
Double beam spectrophotometer: In double beam instrument, a monochromatic beam of radiation is split into two components of equal radiant power. One beam is passed through sample and other through reference solution. The two beams, one from sample and other from reference are focused on detector. The output is connected to amplifier and is transmitted further to a recorder. Absorbance or transmittance of the sample is recorded as a function of wavelength.



Applications of UV Visible spectroscopy:

i) **Detection of functional group**: The technique is applied to detect presence or absence of chromophore, the absence of absorption band at particular wavelength may be regarded as an evidence for the absence of functional group. If spectrum is transparent above 200 nm it shows absence of conjugation ,carbonyl group, benzene or other aromatic compound, Bromo or Iodo group

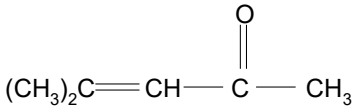
ii) **Extent of conjugation:** Can be employed for polyenes i.e.



Increase in conjugation shifts absorption to longer wavelength.

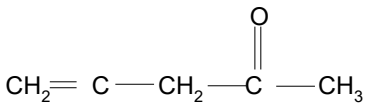
iii) **Distinguish between conjugated and non-conjugated double bonds**: The technique helps in distinguishing a conjugated compound from a non conjugated compound.

1) Conjugated system (peak appear at longer wavelength)



4,4 dimethyl pent-3-en-2-one

2) Non conjugated system (peak appear at shorter wavelength)



4-methyl pent-4-en-2-one

iv) **Identification of an unknown compound**: It is useful in identifying chemical substances by comparing spectra of unknown samples with that of standard substance

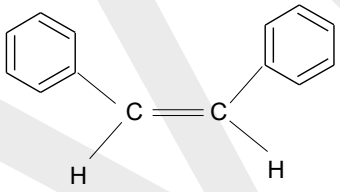
v) **Examination of polynuclear hydrocarbons**: Benzene and other polynuclear hydrocarbons have characteristic spectra of their own which can be compared with spectra of known polynuclear compounds.

vi) **Quantitative estimation of solute in solution**: It is useful in determining very low concentration of solutions which cannot be determined by volumetric or gravimetric method

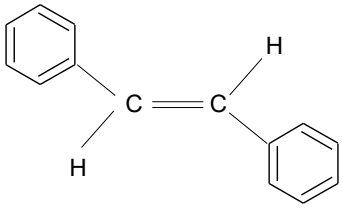
vii) **Detection of impurities**: It is used in detection of impurities. Impurities may give different peak position other than standard

viii) **Study of kinetics of reaction**: It is useful in studying kinetics of the reactions by following change in concentration of reactants and product with time during reaction

ix) **Determination of configuration of molecules**: The technique is useful in distinguishing two geometrical isomers. This distinction is possible when one of the isomers is forced to be non coplanar by steric hindrance. For e.g. cis – Stilbene has λ_{max}= 274 nm whereas trans-Stilbene has λ_{max}= 294 nm



cis stilbene



trans stilbene

4.2.6 Infrared spectroscopy:

Introduction:

UV and Visible spectrum provides information about the structure of molecules that contain double bond or triple bond or two or more conjugated double bonds. IR spectrum provides information about functional groups of molecule and also useful for identification of molecule. IR spectrum is obtained by exposing molecules of compound to electromagnetic radiation of IR region.

Principle of IR spectra:

A molecule is not rigid. Atoms and molecule continuously rotate, vibrate and move from one point to other. The atoms in the molecule vibrate in many different ways and each vibration requires different energy i.e. molecule has number of vibrational energy levels each of which is quantized. If molecule absorbs IR radiation, it gets excited to higher vibrational energy level. The type of IR wavelength absorbed by the molecule depends on the type of atoms and chemical bonds in the molecule, In IR spectrum, position of peak is specified in terms of frequency (ν) or wavelength(λ) or wave number ($\bar{\nu}$) of IR radiation absorbed.

Parts of IR spectrum:

The electromagnetic radiations having wavelength range 0.78 to 200 μ or wave number range 12800 to 50 cm^{-1} are called infrared radiations.
The infrared region is further divided into three regions:

Near Infrared region	**Infrared region**		Far Infrared region
	Functional group region	Finger Print region	
12800 to 4000 cm^{-1}	4000 to 667 cm^{-1}		667 to 50 cm^{-1}

IR spectroscopy is not only useful in elucidation of structure of organic compounds but also useful in quantitative determinations.
The technique is based upon a simple fact that a chemical substance shows selective absorption in the infrared region. After absorption of IR radiations, the molecules of chemical substance vibrate at many rates of vibration, giving rise to close packed absorption bands, called IR absorption spectra. Various bands will be present in IR spectrum which will correspond to the characteristic functional groups and bonds present in chemical substance.

The region between 4000 - 1250 cm^{-1} is called as ***functional group region*** whereas from 1250-909 $cm^{-1}$is called as ***fingerprint region***. Absorption bands in this region are very complex and characteristic for a particular organic molecule.909 to 667 cm^{-1} is characteristic region for aromatic compound.

Band positions in infrared spectrum may be expressed conveniently by wave number $\bar{\nu}$, whose unit is cm^{-1}. The relation between wave number $\bar{\nu}$, wavelength λ and frequency ν is as follows

$$\nu = \frac{c}{\lambda}$$

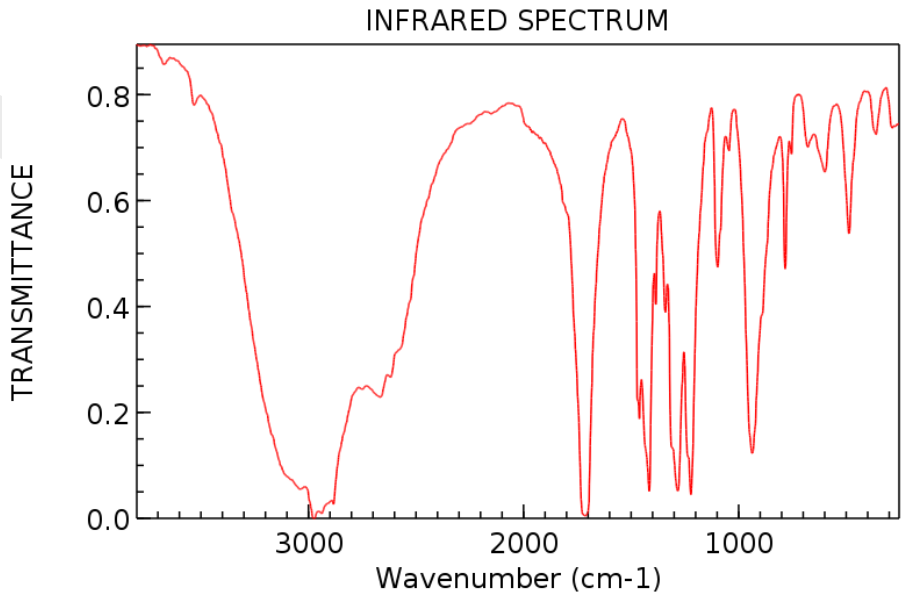
$$\text{or} \quad \bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

where 'c' is velocity of light.

Infrared spectra:

Spectra is generally a graphical representation of % Transmittance on Y- axis and wavenumber or wavelength on X- axis.

Band intensities are expressed in % Transmittance.



Requirements of IR absorption/conditions for absorption of IR radiation:

For a molecule to absorb IR radiations, it has to fulfill following requirements-

1) **Correct wavelength of radiation**: A molecule absorbs radiation only when the natural frequency of vibration of some part of a molecule (i.e. atom or group of atoms present in molecule) is the same as the frequency of incident radiation.
When frequency of vibration of a bond and frequency of IR radiation used for excitation match perfectly then only IR energy is absorbed.
For e.g. natural frequency of vibration of HCl molecule is about 8.7×10^{13} sec^{-1} (2890 cm^{-1})
When IR radiation is permitted to pass through a sample of HCl and the transmitted radiation is analysed by the IR spectrophotometer, it is observed that part of radiation which has a frequency of 8.7×10^{13} sec^{-1} (2890 cm^{-1}) has been absorbed by HCl molecule whereas the remaining frequencies of the radiations are transmitted. Thus, the frequency 8.7×10^{13} sec^{-1} is characteristic of HCl molecule.
After absorbing the correct wavelength of radiation, the molecule vibrates at an increased amplitude. This occurs at the expense of the energy of IR radiation which has been absorbed.

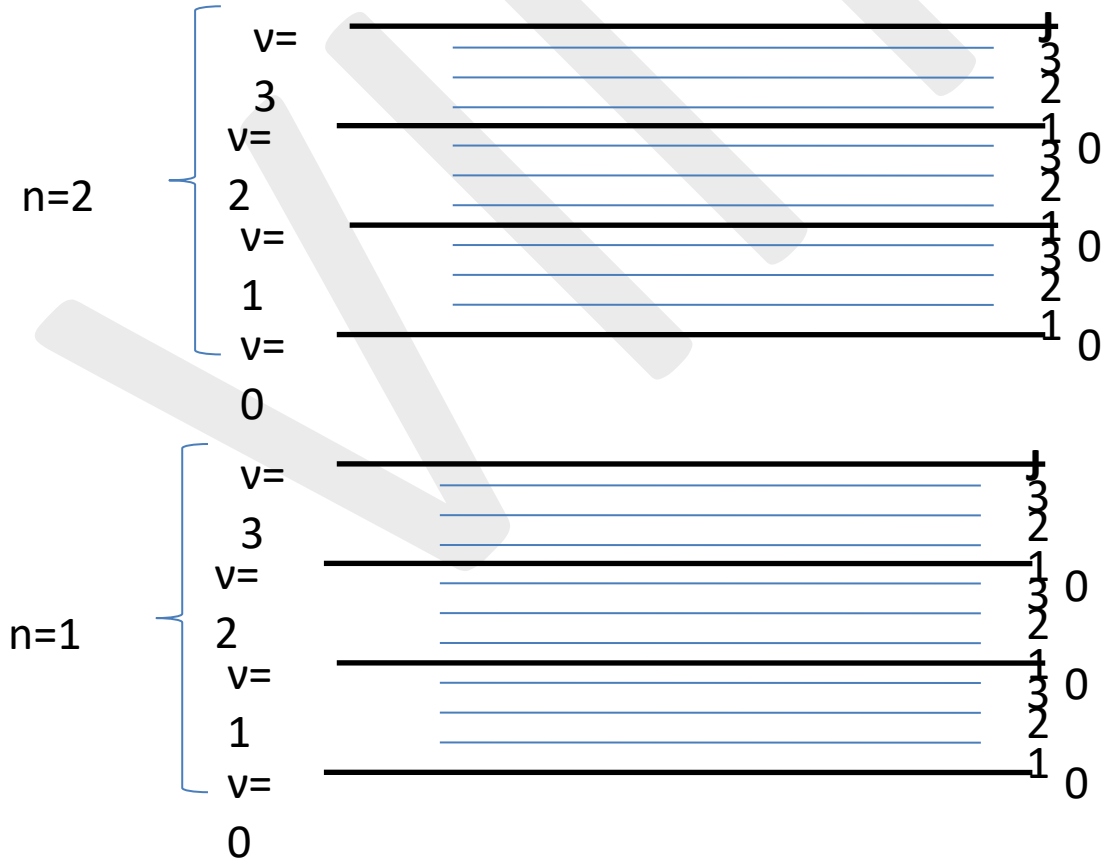
2) **Electric Dipole:** This is another condition for a molecule to absorb IR radiation. A molecule can only absorb IR radiation when its absorption causes a change in its electric dipole (dipole moment).
Only those vibrations which result in change in dipole moment, absorb IR radiation. Such vibrations are said to be IR active.
A molecule is said to have electric dipole when there is a slight positive and a slight negative electric charge on its component atoms. When the molecule having electric dipole is kept in the electric field (molecule kept in the beam of IR radiation), the field will exert forces on the electric charges in the molecules. Opposite charges will experience forces in opposite directions. This tends to decrease separation. As the electric field of the IR radiation is changing its polarity periodically, it means that the spacing between charged atoms (electric dipoles) of the molecule also changes periodically.

When these charged atoms vibrate, they absorb IR radiation from the radiation source. If the rate of vibration at charged atoms in a molecule is fast, the absorption of radiation is intense, thus, IR spectrum will have intense absorption bands. On the other hand, when the rate of vibration of charged atoms in a molecule is slow, there will be weak bands of IR spectra.
Symmetrical diatomic molecules like O_2, N_2 do not possess electrical dipole. They can not be excited by infra red radiation and thus do not give rise to IR spectra. Such molecules are IR inactive.

Further, no change in dipole moment is produced by the carbon- carbon double bond stretching of the symmetrical molecule like ethylene. Since there is no change in dipole moment, the bond does not absorb infrared radiation. On the other hand, substitution of a bromine for a hydrogen atom to form bromoethylene destroys the symmetry around the double bond. The stretching of double bond now generates a significant changes in dipole moment and strong absorbance in infrared is observed.

Origin of Infrared spectra:

Consider diatomic molecule AB. Such molecule consists of two nuclei corresponding to atoms A and B and their corresponding electrons. These electrons contained in atoms can exist in number of energy levels. When excited, i.e. when energy is absorbed, the transition of electrons occurs from low energy level to higher energy level. On returning to low energy level, it emits spectral lines of frequency determined by the difference in two energy levels



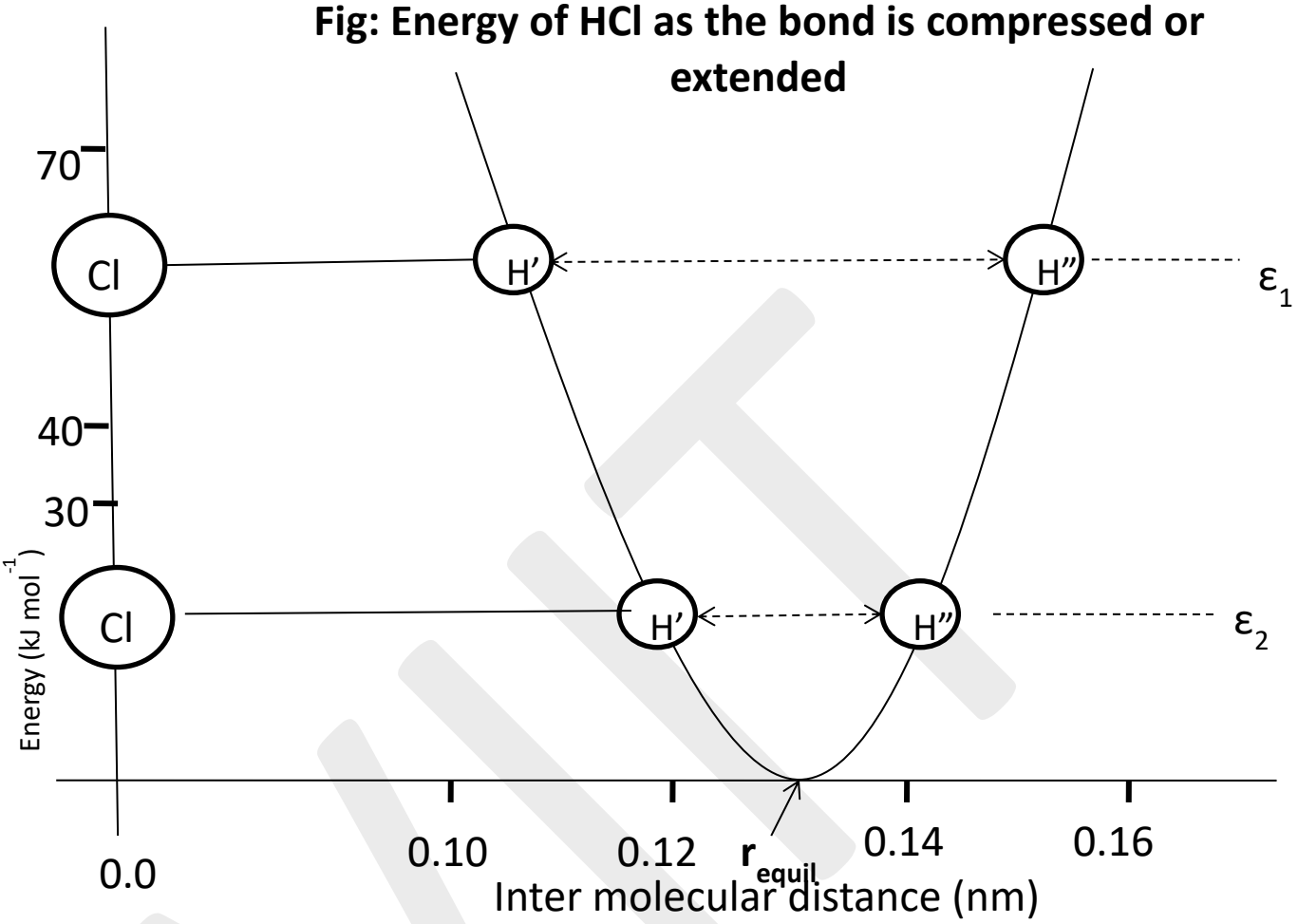
Energy required for exciting emission will be least for rotation and higher for vibrational and still greater for electronic transitions. Thus, if the excitation energy is kept so small as to produce only transition from one rotational quantum level to another within vibrational level, the emission spectra observed would correspond to changes in rotational quantum numbers. Such type of spectra is called ***rotational spectrum***. Since energy involved is small, these spectra are found in the ***far infra red.***

If the energy required for excitation is still higher and sufficiently large to cause transition from one vibrational quantum to another within given electronic level, emissions are observed corresponding to the change in vibrational quantum numbers. Change in vibrational level involves change in rotational levels, resulting in spectrum known as ***vibrational rotational spectrum.*** Since energies involved are still higher such type of spectra are found in the ***near infrared region.***

Vibration of diatomic molecule:

Consider a diatomic molecule. On one hand there is a repulsion between the positively charged nuclei of both atoms and between their negative electron clouds whereas on the other hand there is attraction between the nucleus of one atom and electrons of other. The two atoms settle at a mean inter nuclear distance such that these forces are just balanced and the total energy of whole system is minimum. Squeezing the atoms more closely together will cause the repulsive forces to rise rapidly, while pulling them apart is resisted by the attractive force. Any attempt to distort bond length requires input of energy. At the minimum energy, the inter nuclear distance is referred as equilibrium distance r_{equil} or more simply as bond length.

Fig: Energy of HCl as the bond is compressed or extended



The compression and extension of bond may be linked to the behavior of spring, and we may extend the analogy by assuming that the bond, like a spring, obeys Hooke's law.

$$f = -k(r - r_{equil})$$

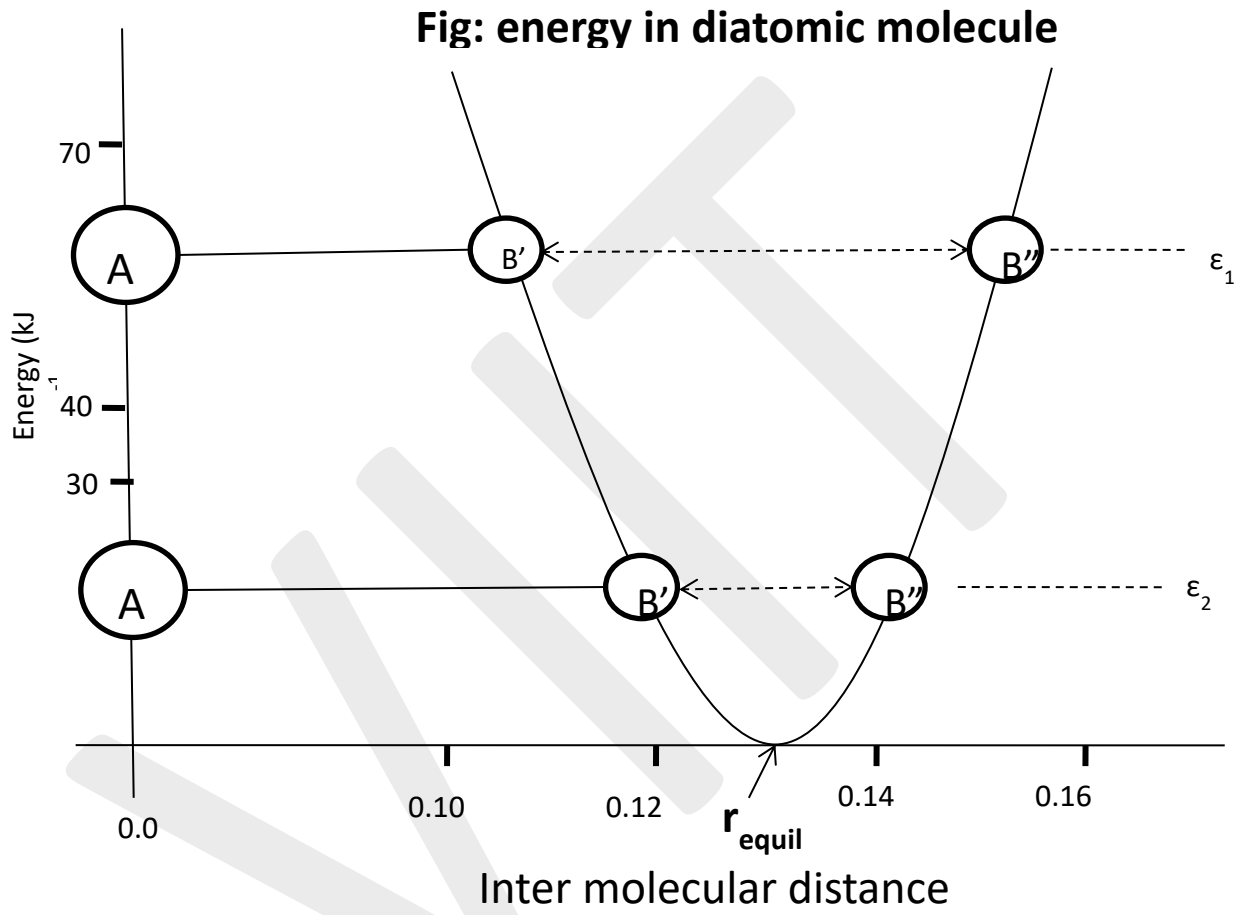
Where 'f' is the restoring force, 'k' is force constant, and 'r' is inter nuclear distance.

In this case the energy curve is parabolic and the value of energy is given by (by applying Hooke's law)

$$E = \frac{1}{2}k(r - r_{equil})^2$$

The model of a vibrating diatomic molecule is considered as so called simple harmonic oscillator model.

Calculation of vibrational frequency:



Whenever molecule is vibrating, it will experience path along B'---r_{equil}----B" i.e. compression ------equilibrium -------extension. As the energy is increased the higher oscillation occurs. Number of oscillations will remain same per unit time i.e. vibrational frequency remain constant but the oscillations will be vigorous.

Consider ω_{osc}= vibrational frequency or oscillation frequency. Classically it is shown by

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{in Hz}$$

k= frequency constant

μ= reduced mass

$\mu = \frac{m_1\ m_2}{m_1+m_2}$ where m_1 and m_2 are masses of atoms

To convert oscillation frequencies into wave number, divide by 'C' where 'C' is velocity of light ($\bar{\nu} = \frac{\nu}{c}$)

$\bar{\omega}_{osc} = \frac{\omega_{osc}}{C} = \frac{1}{2\pi C}\sqrt{\frac{k}{\mu}}$ in cm^{-1}

(a) Frequency of vibration is directly proportional to force constant (k) i.e. bond energy. Thus stronger bonds will have higher frequency of vibration.

(b) Frequency of vibration is inversely proportional to reduced masses of atoms.

Relation between force constant, frequency and bond length: As the bond order increases, the force constant increases hence frequency increases while bond length decreases. Thus, frequency of C-C single bond is less than that of double bond which in turn is less than triple bond.

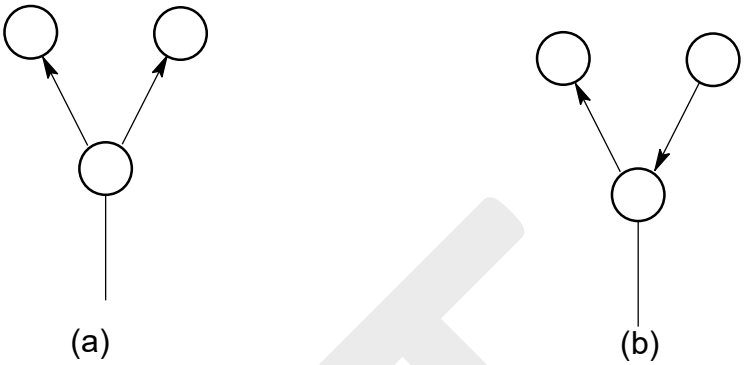
Modes of vibration:

Since IR spectrum is concerned with the vibrational modes, it will be pertinent to know how many modes of vibrations are possible in molecules. For nonlinear molecule containing 'N' atoms, there are '3N' degrees of freedom, of which, 3 are rotational, 3 are translational and remaining (3N-6) are vibrational. These vibrations involve transition of molecule from lower energy level (V_0) to higher vibrational level (V_1) . These (V_0 to V_1) are called as fundamental modes of vibration .For linear molecules fundamental modes of vibrations will be (3N-5).

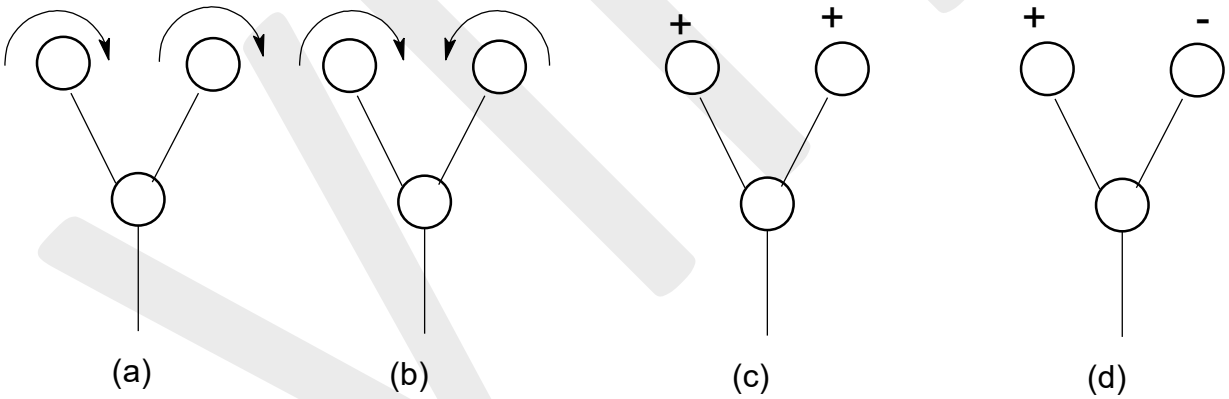
Molecule	N	Geometry of the molecule	Fundamental modes of vibration
NO	2	Linear	1
CO_2	3	Linear	4
H_2O	3	Non- linear	3
NH_3	4	Non- linear	6
CH_4	5	Non- linear	9
C_6H_6	12	Non- linear	30

There are 2 kinds of fundamental vibrations (i) stretching vibrations (ii) Bending vibrations

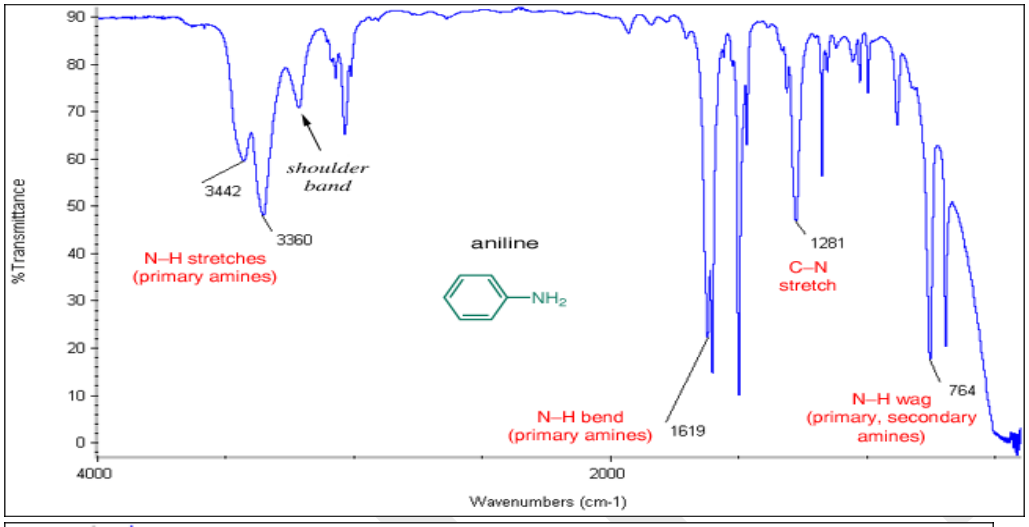
(i) **Stretching vibrations**: The distance between the two atoms (i.e. bind length) increases or decreases but atoms remain in the same plane. These modes of vibrations are further divided into (a) Symmetrical stretching vibrations and (b) Assymetrical stretching vibrations

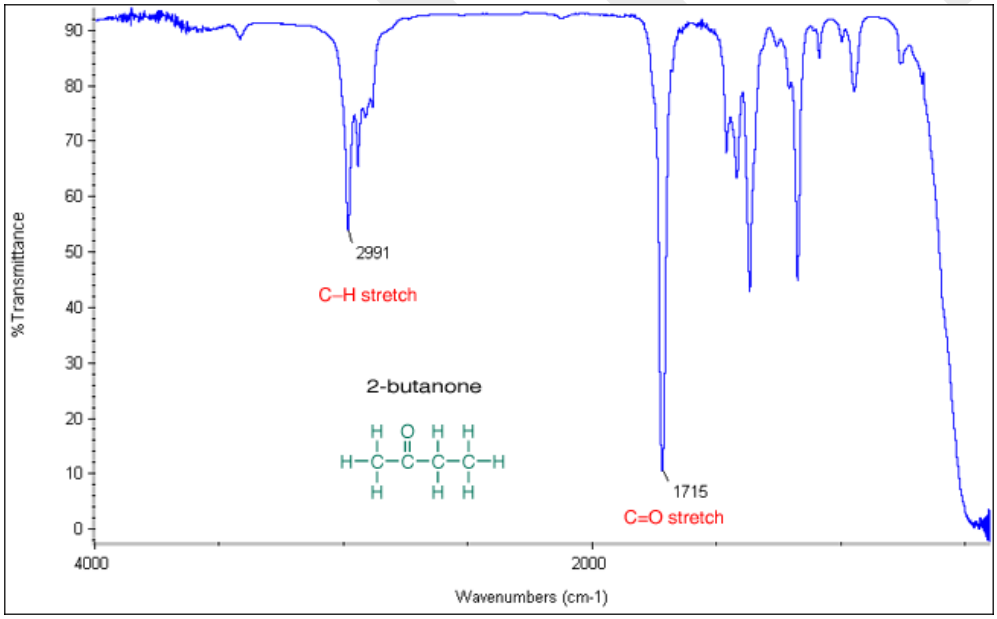


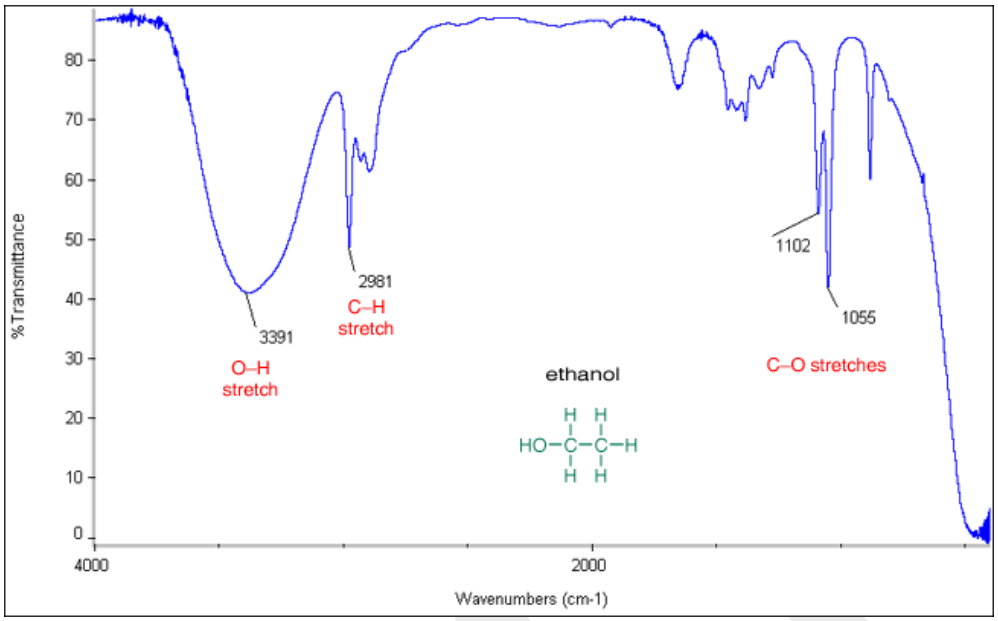
(ii)**Bending vibrations**: The position of the atoms changes relatively to the original bond axis. These modes are further divided into 4 types, (a) Rocking (b) Scissoring (C) Wagging and (d) Twisting. Scissoring and Rocking are in- plane whereas Wagging and Twisting are out-of -plane



Representative IR spectra:







Factors influencing IR absorption:

It has been found that the calculated value of frequency of absorption for a particular bond is never exactly equal to its experimental value. This is due to the fact that vibrations of each group is influenced by the structure of the molecules in the immediate neighborhood of the bond. The value of absorption frequency is shifted since the force constant of a bond changes with its electronic structure. Frequency shifts also takes place on working with same substance in different states (solid, liquid, vapour state)

Following are some factors responsible for shifting the vibrational frequencies:

i) **Fermi Resonance and Dipole moment**: In IR spectrum, absorption bands are spread over a wide range of frequencies. It may happen that the energy of an overtone level coincides with fundamental mode of different vibration. A type of resonance occurs as in case of coupled pendulums. This type of resonance is called "Fermi Resonance" in which a molecule transfers its energy from fundamental to overtone and back again.
For a particular vibration to result in IR absorption energy, the vibration must cause a change in dipole moment. In a symmetrical molecule due to its symmetry, the vibration does not cause any appreciable change in dipole moment and the IR band is said to be inactive. For e.g. CO_2 is linear and 4 fundamental modes of vibrations are expected for it.

Out of these, symmetrical stretching vibrations are IR inactive since it produces no change in dipole moment of the molecule.

ii) **Inductive effect**: The introduction of electron donating groups such as alkyl group cause (+I) effect which results in the lengthening or weakening of bond and hence force constant is lowered and wave number of absorption decreases.(+I) effect deceases double bond character of carbonyl group. As single bond character increases, frequency deceases.

Consider the frequencies of absorption of the following compounds

Acetaldehyde CH_3-CHO 1745 cm^{-1}

Acetone CH_3COCH_3 1715 cm^{-1}

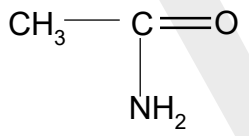
Aldehydes absorption is at higher frequency than ketone. In ketones, there are 2 'R' groups showing +I effect whereas in aldehyde, there is only one 'R' group. Carbonyl group in aldehyde has more double bond character so frequency is higher.

Electron withdrawing atom or group causes (-I) effect. e.g. Cl. This results in increase in bond order, force constant and hence frequency of absorption.

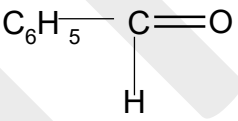
Acetone CH_3COCH_3 1715 cm^{-1}

Chloroacetone CH_3COCH_2Cl 1725 cm^{-1}

iii) **Resonance (Mesomorphic effect)**: Mesomorphic effect causes lengthing or weakening of a bond which lowers the frequency of absorption



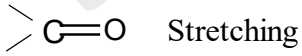
Acetamide



Benzaldehyde

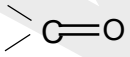
Stretching

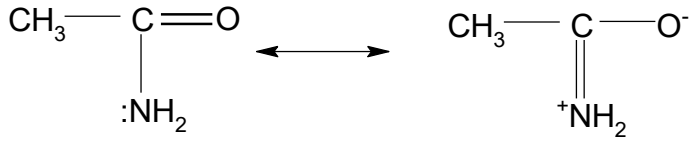
1660 cm^{-1}



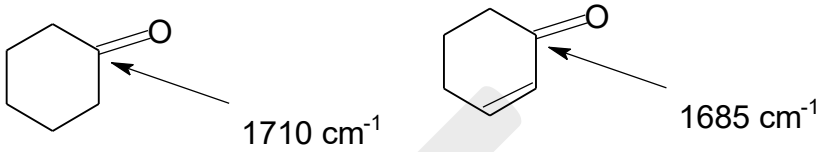
Stretching

1745 cm^{-1}

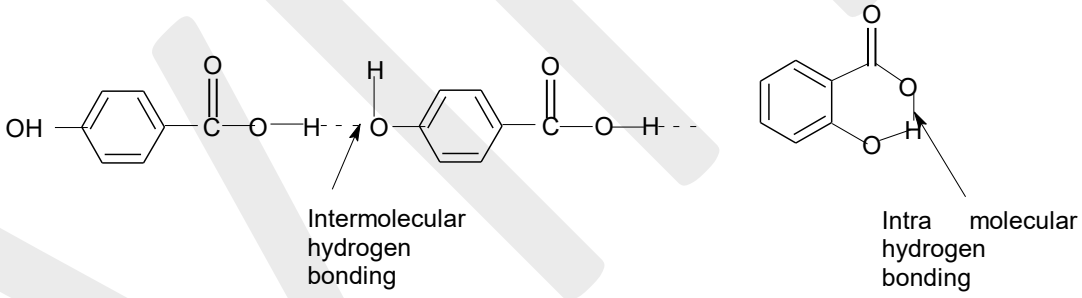
Here band due to  stretching in acetamide appears at lower frequency due to participation of lone pair of electrons of 'N' in resonance



When the carbonyl group is conjugated to a carbon- carbon double bond, there is electron donating resonance effect, which decreases the double bond character of carbonyl group, this decreases the stretching frequency of carbonyl group.
Electron donating (+R) group decreases stretching frequency and electron withdrawing (-R) group increases stretching frequency of carbonyl group.



Hydrogen bonding: Carboxylic acids, alcohols, phenols, amines, amides show strong hydrogen bonding effect. Hydrogen bonding increases the O-H bond length so bond strength decreases. Thus, hydrogen bonding lowers the frequency. Stronger the hydrogen bonding, greater is the absorption shift towards lower frequency.
Generally, intermolecular hydrogen bonds give rise to broad bands whereas band arising from intra-molecular hydrogen bonds are sharp and well defined.
e.g.Aliphatic –OH free 3650 cm^{-1}
Aliphatic –OH hydrogen bonded 3350 cm^{-1}

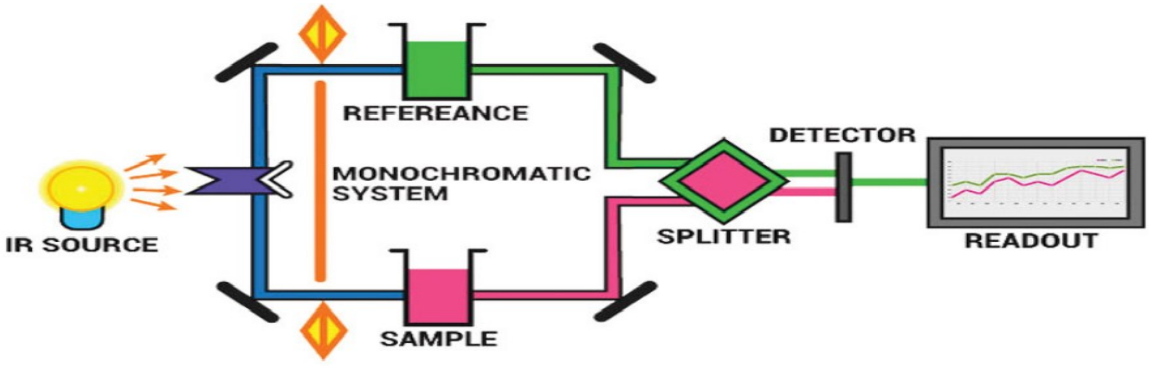


Effect of dilution:
Intermolecular H- bonds depends upon concentrations. On dilution, the intensities of intermolecular H-bonds decrease due to intervening solvent molecules and finally disappear. Intramolecular hydrogen bonds are independent of concentration. Thus, to distinguish intermolecular and intramolecular H-bonding, the spectra of are scanned at two different concentrations.

3.5.10 Instrumentation of IR Spectroscopy

The instrumentation of infrared spectroscopy is illustrated below. First, a beam of IR light from the source is split into two and passed through the reference and the sample respectively. Now, both of these beams are reflected to pass through a splitter and then

through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.



The main parts of IR spectrometer are as follows:

i) Radiation source
ii) Sample cells and sampling of substances
iii) Monochromators
iv) Detectors
v) Recorder

i) IR radiation sources

IR instruments require a source of radiant energy which emit IR radiation which must be steady, intense enough for detection and extend over the desired wavelength.
Various sources of IR radiations are as follows.
Nernst glower
Incandescent lamp
Mercury arc
Tungsten lamp
Glober source
Nichrome wire

ii) Sample cells and sampling of substances

IR spectroscopy has been used for the characterization of solid, liquid or gas samples.
a) Solid – Various techniques are used for preparing solid samples such as pressed pellet technique, solid run in solution, solid films, mull technique etc.

b) Liquid – Samples can be held using a liquid sample cell made of alkali halides. Aqueous solvents cannot be used as they will dissolve alkali halides. Only organic solvents like chloroform can be used.

c) Gas– Sampling of gas is similar to the sampling of liquids.

iii) Monochromators

Various types of monochromators are prism, gratings and filters.

Prisms are made of Potassium bromide, Sodium chloride or Caesium iodide.

Filters are made up of Lithium Fluoride and Diffraction gratings are made up of alkali halides.

iv) Detectors

Detectors are used to measure the intensity of unabsorbed infrared radiation.

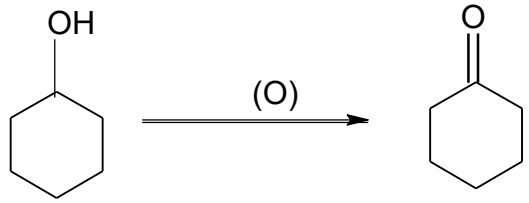
Detectors like thermocouples, Bolometers, thermisters, Golay cell, and pyro-electric detectors are used.

v) Recorders

Recorders are used to record the IR spectrum.

3.5.11 Applications of IR spectroscopy:

1) **Determination of Structure and functional groups:**
   (a) Identification of functional group: In IR spectroscopy, almost all functional group absorb characteristically within definite range. e.g strong absorption band between 1600 to 1900cm^{-1} indicates the presence of carbonyl group. Further study of spectra reveals whether it is aldehyde, ketone, ester, amide etc.
   (b) Comparison with fingerprint region: The region below 1500 cm^{-1} is rich in many absorptions which are caused by stretching and bending vibrations. Some molecules containing same functional group show similar absorption above 1500 cm^{-1} but their spectra differ in fingerprint region. The identity of an unkown compound can also be revealed by comparing its IR spectra with a set of spectra of unkown compounds under identical conditions.
2) **Study of course of reaction (Kinetics of a chemical reaction)**: A comparison between IR spectra of reactants and products can help to determine the course of a reaction



Cyclohexanol Cyclohexanone

IR spectrum of cyclohexanol shows a strong band at about 3550 cm^{-1} which is characteristic of alcoholic –OH group. For its product cyclohexanone, this band disappears and a new band appears at 1710 cm^{-1} which is characteristic of keto group (carbonyl functional group)

3) **Hydrogen bonding**: IR spectroscopy gives information regarding the hydrogen bonding. Bands due to hydrogen bonding appears at lower frequency

e.g.Aliphatic –OH free 3650 cm^{-1}

Aliphatic –OH hydrogen bonded 3350 cm^{-1}

4) **Distinction between intermolecular and intra molecular hydrogen bonding**

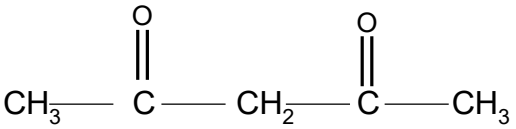
IR spectroscopy can also distinguish between intermolecular and intra molecular hydrogen bonding as in case of phenols, alcohols, salicylic acid etc.

This is done by taking series of IR spectra of a compound at different dilutions. As dilution increases the absorption band due to inter molecular hydrogen bonding disappears while that of intra molecular hydrogen bonding remain unchanged

5) **Detection of impurities**: IR spectra of impure sample will show extra absorption bands. By comparing with IR spectra of pure compound, presence of impurity can be detected. e.g. presence of cyclohexanone in cyclohexanol can be detected by presence of carbonyl absorption band.

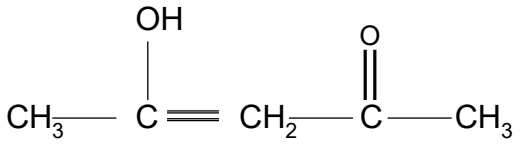
6) **Study of isomerism**:

Keto enol tautomerism can be studied by IR spectra. IR spectra shows characteristic absorption of carbonyl group along with a broad –O-H and C=C stretching frequencies for enol form



Acetyl acetone

Keto form

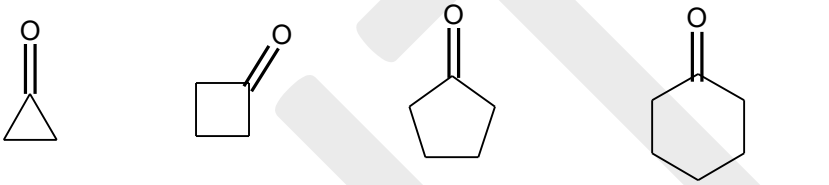


Acetyl acetone

Enol form

Geometrical isomers: Geometry and symmetry of molecule influences frequency and intensity of vibration

7) **Determination of size of ring ketones**: Ring strains in cyclic ketones shifts the carbonyl group stretching frequency to higher wavelength value. Angle strain in rings causes carbonyl group to have more electron density and stiffer bonds. This enables us to differentiate the ring ketones



1818 cm^{-1}	1775 cm^{-1}	1740 cm^{-1}	1710 cm^{-1}
cyclopropanone	cyclobutanone	cyclopentanone	cyclohexanone

Miscellaneous applications:

1) Identifying atmospheric pollution: quality and quantity of pollutants can be identified by IR spectroscopy. Water pollutants can be identified
2) Measurement of ethanol in breath can be detected easily by IR spectroscopy by device called as intoximeter
3) Measurements of paints and varnishes: Paints and varnishes are measured by reflectance method, where sample is irradiated by IR and reflected light is introduced into IR instrument. This technique is used to identify the paint on appliances or automobiles without destroying the surface. It can also be used in identifying and examining old paintings and artifacts. From this information, fake 'masterpieces' can be identified
4) In industry, IR is used to determine impurity in raw material to ensure good product

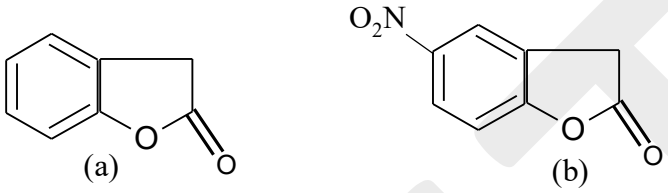
3.5.12 Important Infrared Absorption Frequencies

Sr.No.	Frequency Region cm^{-1}	Type of vibration	Functional group
1	3640-3610	O-H stretch, free hydroxyl	Alcohols, phenols
2	3500-3200	O-H stretch, H-bonded	Alcohols, phenols
3	3400-3250	N-H stretch	Primary, secondary amines, amides
4	3300-2500	O-H stretch	Carboxylic acids
5	3330-3270	-C $\equiv$ C-H,C-H stretch	Alkynes (terminal)
6	3100-3000	C-H stretch	Aromatics
7	3100-3000	=C-H stretch	Alkenes
8	3000-2850	C-H stretch	Alkanes
9	2830-2695	H-C=O, C-H stretch	Aldehydes
10	2260-2210	C $\equiv$ N stretch	Cyanides/nitriles
11	2260-2100	-C $\equiv$ C- stretch	Alkynes
12	1760-1665	C=O stretch	Carbonyls (general)
13	1760-1690	C=O stretch	Carboxylic acid
14	1750-1735	C=O stretch	Esters, saturated aliphatic
15	1740-1720	C=O stretch	Aldehydes, saturated, aliphatic
16	1730-1715	C=O stretch	α,β-unsaturated esters
17	1715	C=O stretch	Ketones, saturated aliphatic
18	1710-1665	C=O stretch	α,β-unsaturated aldehydes, ketones
19	1680-1640	-C=C- stretch	Alkenes
20	1650-1580	N-H bend	Primary amines
21	1600-1585	C-C stretch (in ring)	aromatic
22	1550-1475	N-O asymmetric stretch	Nitro compounds
23	1500-1400	C-C stretch (in ring)	Aromatic
24	1470-1450	C-H bend	Alkanes
25	1370-1350	C-H rock	Alkanes
26	1360-1290	N-O symmetric stretch	Nitro compound
27	1335-1250	C-N stretch	Aromatic amines
28	1320-1000	C-O stretch	Alcohols, carboxylic acids, esters,ethers
29	1300-1150	C-H wag(-CH_2X)	Alkyl halides
30	1250-1020	C-N stretch	Aliphatic amines
31	1000-650	=C-H bend	Alkenes
32	950-910	O-H bend	Carboxylic acids
33	910-665	N-H wag	Primary, secondary amines

34	900-675	C-H (out of plane)	Aromatic
35	850-550	C-Cl stretch	Alkyl halides
36	725-720	C-H rock	Alkanes
37	700-610	-C ≡ C-H:C-H bend	Alkynes
38	690-515	C-Br stretch	Alkyl halides

Illustrative examples:

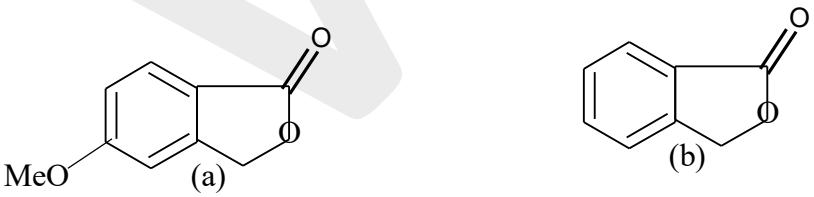
1) Which of the following will absorb at higher frequency? Justify.



(b) will absorb at higher frequency than (a)

In case of (b) electron withdrawing nitro group is present at para position with respect to ring oxygen atom. The electron pair on this ring oxygen atom is pulled towards the nitro group. The polarization of carbonyl group is thus inhibited. Therefore C=O has more double bond character. The bond length is consequently decreased in turn bond strength is increased increasing force constant, obviously raising absorption frequency. In case of (a), the ring oxygen is attached to phenyl ring. The phenyl ring has electron withdrawing effect to limited extent.

2) Which of the following will absorb at higher frequency? Justify.



(b) will absorb at higher frequency than (a)

In case of (a), the C=O group is in conjugation with aromatic ring having electron donating methoxy group at para position. The carbonyl group is easily polarized increasing C-O bond

length, consequently bond strength is decreased .Hence force constant is decreased. Hence drop in absorption frequency.

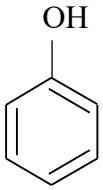
3) How will you distinguish by using IR spectra

(a) CH_3CH_2OH (b) CH_3CH_2CHO

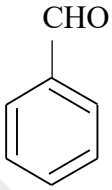
(a) Shows stretching frequency at 3640-3610 cm^{-1} due to O-H stretching

(b) Shows stretching frequency due to aldehyde in the region 1740 -1720 cm^{-1}. The presence of aldehyde is confirmed by occurance of additional two bands at 2830 and 2695 cm^{-1} due to C-H stretching

4) How will you distinguish by using IR spectra



(a)



(b)

(a) Shows stretching frequency of O-H at 3500-3200 cm^{-1}

(b) Shows carbonyl stretching frequency at 1710-1665 cm^{-1}, additionally at 2830-2695 cm^{-1} for C-H stretch of aldehyde

5) Calculate approximate frequency of the C-H stretching from the following data k=500Nm^{-1}, Mass of carbon atom= $20x10^{-24}$, Mass of hydrogen atom=$1.6x10^{-24}$

According to Hook's law,

ω_{osc}= vibrational frequency or oscillation frequency.

$$\omega_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{in Hz}$$

k= frequency constant

μ= reduced mass

$\mu = \frac{m_1\ m_2}{m_1+m_2}$ where m_1 and m_2 are masses of atoms

k= frequency constant= 500Nm^{-1}=$5x10^5 g/s^2$ (1N= 10^3 g/s^2)

$$\omega_{osc} = \frac{1}{2 \times 3.14}\sqrt{\frac{(5 \times 10^5)(20 + 1.6)10^{-24}}{(20 \times 10^{-24})(1.6 \times 10^{-24})}}$$

$$\omega_{osc} = 9.3 \times 10^{13} \text{ Hz}$$

6) Calculate possible number of fundamental vibrations in CO_2, CH_4, NO, C_2H_6

Since CO_2 and NO are linear, fundamental modes of vibration = 3N-5

fundamental modes of vibration of CO_2= 3x3-5=4

fundamental modes of vibration of NO= 3x2-5=1

CH_4, and C_2H_6 are non linear , fundamental modes of vibrations = 3N-6
fundamental modes of vibrations of CH_4 = 3x5-6 = 9
fundamental modes of vibrations of C_2H_6 = 3x8-6=18

4.3 Study of morphology: Optical and Electron microscopy

Optical microscopy:

The **optical microscope**, also referred to as a **light microscope**, is a type of microscope that commonly uses visible light and a system of lenses to generate magnified images of small objects.

Basic optical microscopes can be very simple, although many complex designs aim to improve resolution and sample contrast.

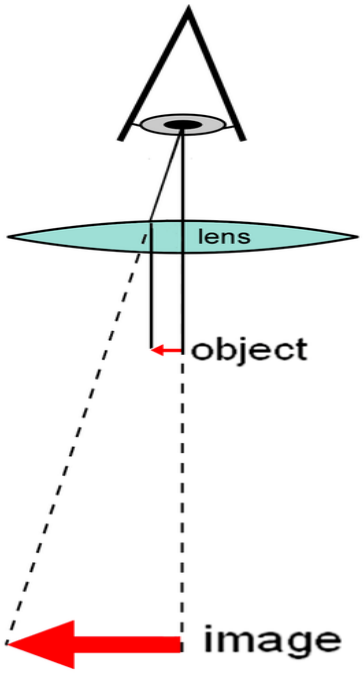
Types:

There are two basic types of optical microscopes: **simple microscopes and compound microscopes.** A simple microscope uses the optical power of single lens or group of lenses for magnification. A compound microscope uses a system of lenses (one set enlarging the image produced by another) to achieve much higher magnification of an object.

The vast majority of modern research microscopes are compound microscopes while some cheaper commercial digital microscopes are simple single lens microscopes.

Simple microscope:

A simple magnifier or microscope is a converging lens of small focal length. A simple microscope uses a lens or set of lenses to enlarge an object through angular magnification alone, giving the viewer an erect enlarged virtual image. The use of a single convex lens or groups of lenses are found in simple magnification devices such as the magnifying glass, loupes, and eyepieces for telescopes and microscopes.



Magnification (m) of microscope, for the image formed at near point 'D', with the focal length '*f*'' is given by the formula

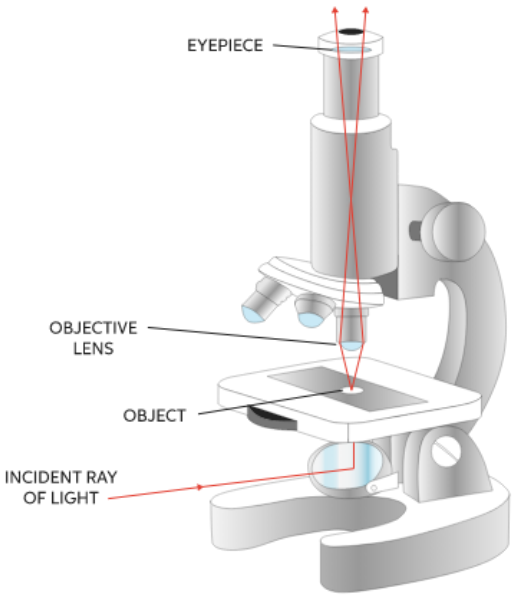
$$m = \left(1 + \frac{D}{f}\right)$$

Since D is about 25 cm, to have a magnification of six, one needs a convex lens of focal length, $f = 5$ cm

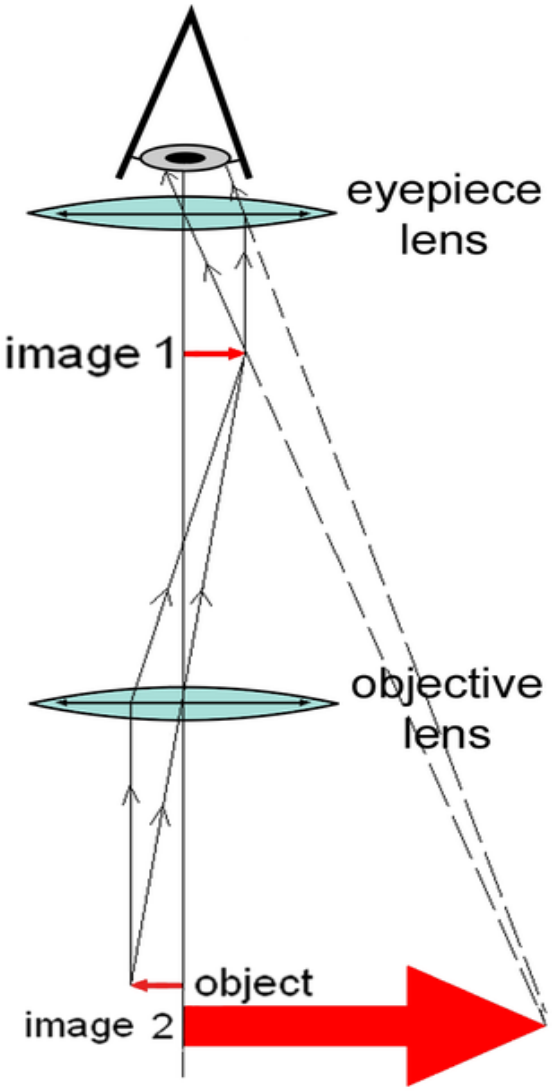
A simple microscope has a limited maximum magnification (≤ 9) for realistic focal lengths. For much larger magnifications, one uses two lenses, one compounding the effect of the other. This is known as a compound microscope

Compound microscope:

A compound microscope has two converging lenses called the objective and eyepiece. The image by the objective lens works as the object for the eyepiece lens. The objective lens is placed near the object or specimen to be seen. The eyepiece lens is placed near the eye of an observer.



A compound microscope uses a lens close to the object being viewed to collect light (called the objective lens) which focuses a real image of the object inside the microscope (image 1). That image is then magnified by a second lens or group of lenses (called the eyepiece) that gives the viewer an enlarged inverted virtual image of the object (image 2). The use of a compound objective/eyepiece combination allows for much higher magnification. Common compound microscopes often feature exchangeable objective lenses, allowing the user to quickly adjust the magnification.



Working:

A compound microscope works on the principle that the objective lens produces a real, magnified and, inverted image of the specimen. The final image that can be seen from the eyepiece lens is virtual,

magnified, and inverted. The working of the compound microscope uses the phenomenon of reflection of light.

• The small object or specimen is placed on the glass slide.

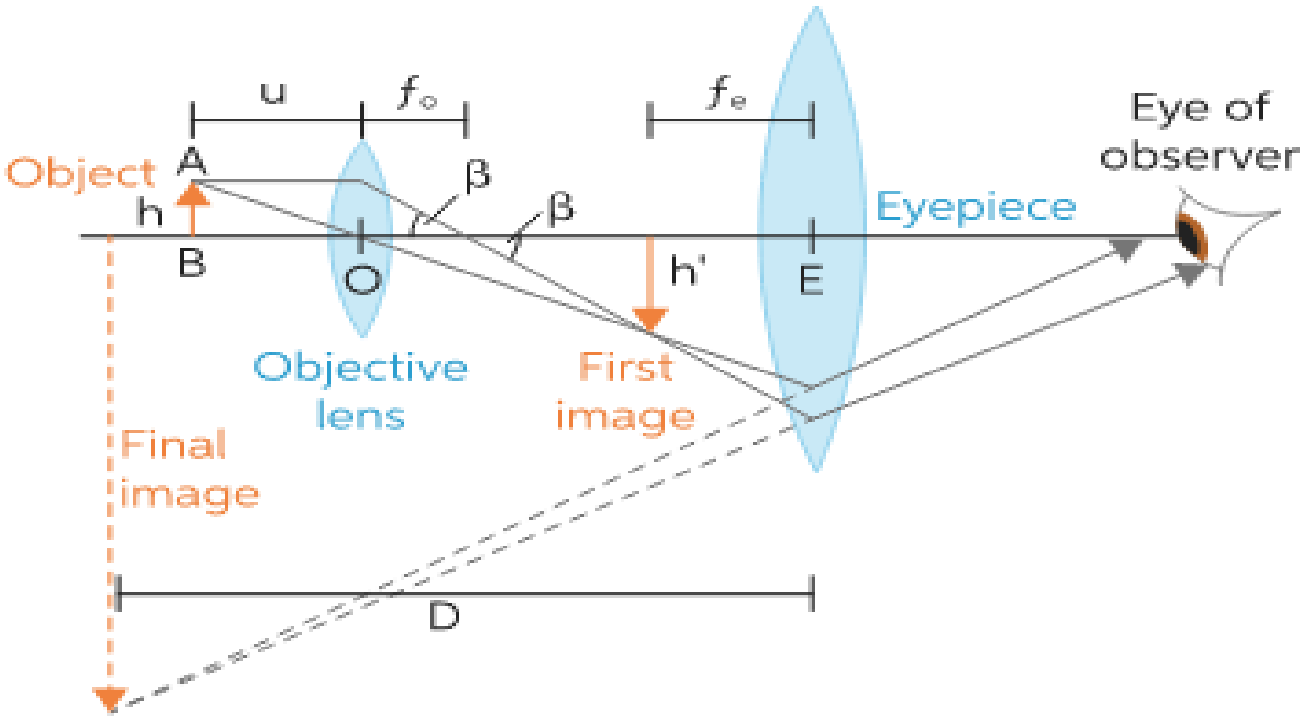
• The incident ray of light is reflected from the mirror illuminator on to the object placed on the slide.

• The objective lens produces a real, magnified, and inverted image of the object.

• The image produced works as the object for the second lens, the eyepiece. This results in a further magnification of the real and inverted image. A virtual, magnified and, inverted image of the specimen is observed.

Angular Magnification of Compound Microscope

The ratio of the angle subtended by the final image to the angle subtended by the object at the near point is referred to as the angular magnification of the compound microscope due to the eyepiece lens.



The ratio of the size or the height of the first image to the size of the object is referred to as the linear magnification of the compound microscope due to the objective lens. If the objective lens produces a real and magnified image of size h' when the size of the object is h, then the linear magnification of the compound microscope is represented as,

$$m_L = \frac{h'}{h}$$

The real, magnified, and inverted image of the first image of the object is produced by the objective lens near the focal point of the eyepiece lens. If the distance between the second focal point of the objective lens and the first focal point of the eyepiece lens is represented by 'L' and 'f_o' represents focal length of the objective lens, then the linear magnification,

$$m_L = \frac{L}{f_o}$$

If 'D' represents the near point i.e. the distance between the object and the observer and 'f_e' represents focal length of the eyepiece lens, then the angular magnification of the compound microscope,

$$m_A = \left(1 + \frac{D}{f_e}\right)$$

The product of the linear magnification due to the objective lens and the angular magnification due to the eyepiece lens represents the total magnification of the compound microscope. Hence, the total magnification is represented as,

$$m = m_L \times m_A$$

$$m = \frac{L}{f_o} \times \left(1 + \frac{D}{f_e}\right)$$

When the final image is formed at infinity, the angular magnification due to the eyepiece is given by

$$m_A = \left(\frac{D}{f_e}\right)$$

Thus, the total magnification, when the image is formed at infinity, is

$$m = \left(\frac{L}{f_o}\right) \times \left(\frac{D}{f_e}\right)$$

Clearly, to achieve a large magnification of a small object (hence the name microscope), the objective and eyepiece should have small focal lengths. In practice, it is difficult to make the focal length much smaller than 1 cm. Also large lenses are required to make L large.
For example, with an objective with fo = 1.0 cm, and an eyepiece with focal length fe = 2.0 cm, and a tube length of 20 cm, the magnification is

$$m = \left(\frac{L}{f_o}\right) \times \left(\frac{D}{f_e}\right)$$

$$m = \left(\frac{20}{1}\right) \times \left(\frac{25}{2}\right)$$

$$m = 250$$

Applications of Compound Microscope
A Compound microscope has its applications in various fields:

1) A phase-contrast compound microscope is used in the study of the structures of blood cells or bacteria. A phase-contrast objective lens and a phase illuminator are used in this type of microscope to view the required magnified image of the specimen.

2)Metallurgical compound microscopes are used in chemical industries to view magnified images of the samples consisting of different types of metals. These are used to find any cracks or imperfections in precious stones or metals.

3) A polarizing compound microscope is used in geology in the study of minerals. This type of compound microscope uses an analyzer and a polarizer to determine the difference in the colors in the optical path of the object to be studied under the microscope. It is also used in the chemical industry to study the structure of chemicals and compounds.

Limitations of optical microscope:

The primary limitations of optical microscopes, including resolution, magnification and surface view

1) **Resolution limit of optical microscopes**: When an optical microscope with transmitted light is used at very high magnifications, the image of point objects may be distorted. They may be seen as fuzzy discs that are surrounded by diffraction rings, known as Airy discs. These diffraction rings limit the ability of the optical microscope to resolve fine details of the sample. The resolving power of an optical microscope is a measure of the ability of the microscope to distinguish between two adjacent structural details, without the interference of Airy discs.

.2) **Low magnification**: The maximum magnification that can be achieved by an optical microscope typically ranges from 500x to 1500x. While this level of magnification has many purposes and can be useful for a number of practical applications, it is considerably lower than the magnification that can be achieved with electron microscopy. In contrast, an electron microscope may be able to provide magnifications greater than 160,000x.

3**) Poor surface view**: Similar to the magnification limitation of optical microscopy, the surface view of the sample with an optical microscope is sufficient for many purposes, but can be a limiting factor.

Electron microscopy:

In contrast to the optical microscope, the electron microscope uses electron beams as the source of illumination, and it has higher resolution and can be used to observe smaller structures than can be visualized using an optical microscope.

Depending on the mechanism by which the electron beam is detected, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to take images of a surface and section, respectively.

1) Scanning Electron Microscopy(SEM):

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

Electron microscopes use electrons for imaging in a similar way that light microscopes use visible light. Unlike transmission electron microscopes (TEMs), which detect electrons that pass through a very thin specimen, SEMs use the electrons that are reflected or knocked off the near-surface region of a sample to create an image. Since the wavelength of electrons is much smaller than that of light, the resolution of SEMs is superior to that of a light microscope.

How a Scanning Electron Microscope Works

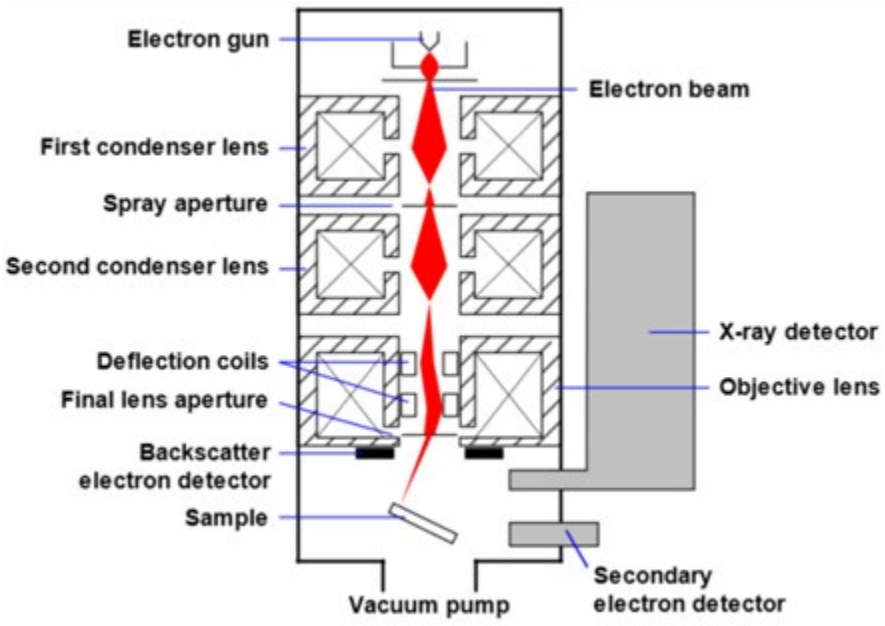
A **scanning electron microscope** (**SEM**) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector (Everhart–Thornley detector)

Specimens are observed in high vacuum in a conventional SEM, or in low vacuum or wet conditions in a variable pressure or environmental SEM, and at a wide range of cryogenic or elevated temperatures with specialized instruments

The main SEM components include:

- Source of electrons
- Column down which electrons travel with electromagnetic lenses
- Electron detector
- Sample chamber
- Computer and display to view the images

Electrons are produced at the top of the column, accelerated down, and passed through a combination of lenses and apertures to produce a focused beam of electrons which then strikes the surface of the sample. The sample itself is mounted on a stage in the chamber area and (unless the microscope is designed to operate at low vacuums) both the column and the chamber are evacuated by a combination of pumps. The level of the vacuum will depend on the design of the microscope.



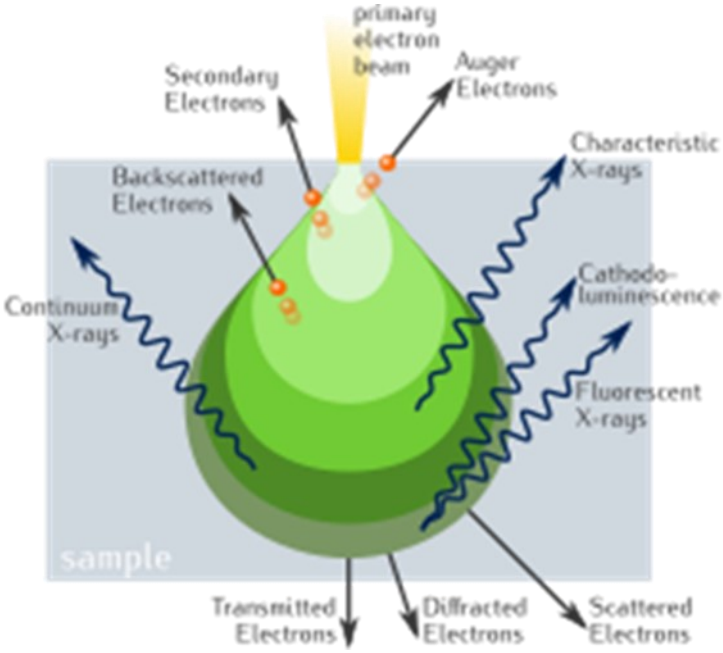
Schematic of a scanning electron microscope.

The position of the electron beam on the sample is controlled by scan coils situated above the objective lens. These coils allow the beam to be scanned over the surface of the sample. This beam rastering or scanning enables information about a defined area on the sample to be collected. As a result of the electron-sample interaction, a number of signals are produced. These signals are then detected by appropriate detectors.

Fundamental Principles of Scanning Electron Microscopy (SEM):

- The scanning electron microscope (SEM) produces images by scanning the sample with a high-energy beam of electrons.
- As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X-rays.
- These signals are collected by one or more detectors to form images which are then displayed on the computer screen.
- When the electron beam hits the surface of the sample, it penetrates the sample to a depth of a few microns, depending on the accelerating voltage and the density of the sample. Many signals like secondary electrons and X-rays are produced as a result of this interaction inside the sample.

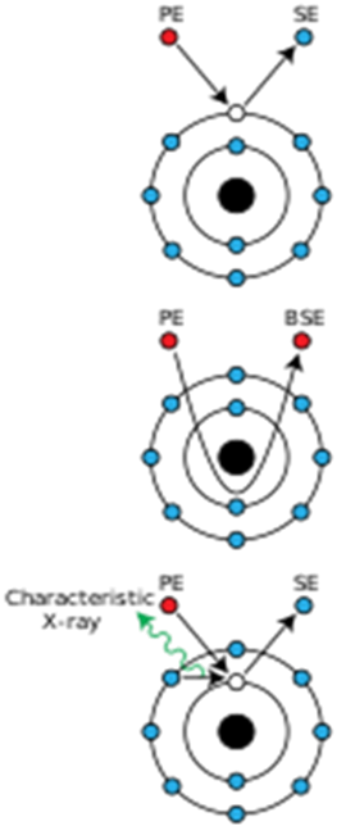
• Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample.
• These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD) that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis), visible light (cathodoluminescence—CL), and heat.



Electron–matter interaction volume and types of signal generated

• Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample.
• As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element).
• Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam.

• SEM analysis is considered to be “non-destructive”; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.



Advantages of SEM:

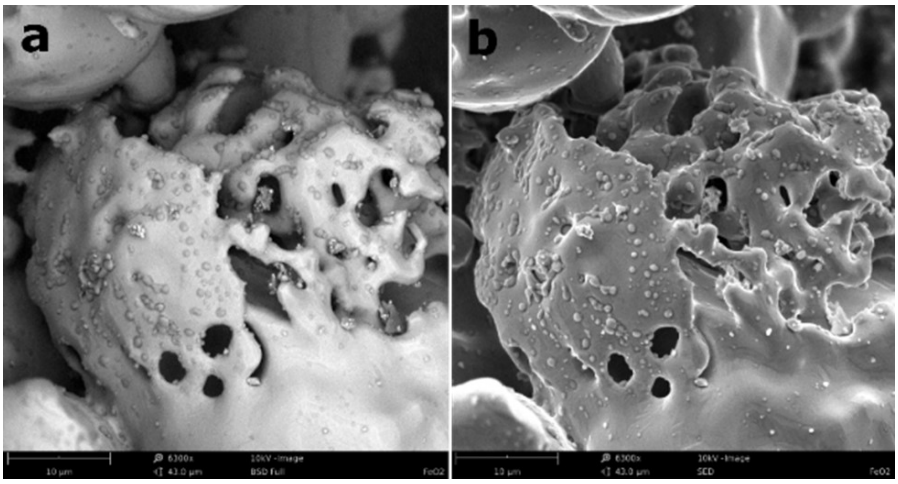
1)Scanning electron microscopy has a broad range of research and practical applications.

2)It provides detailed, topographical images, providing versatile data.

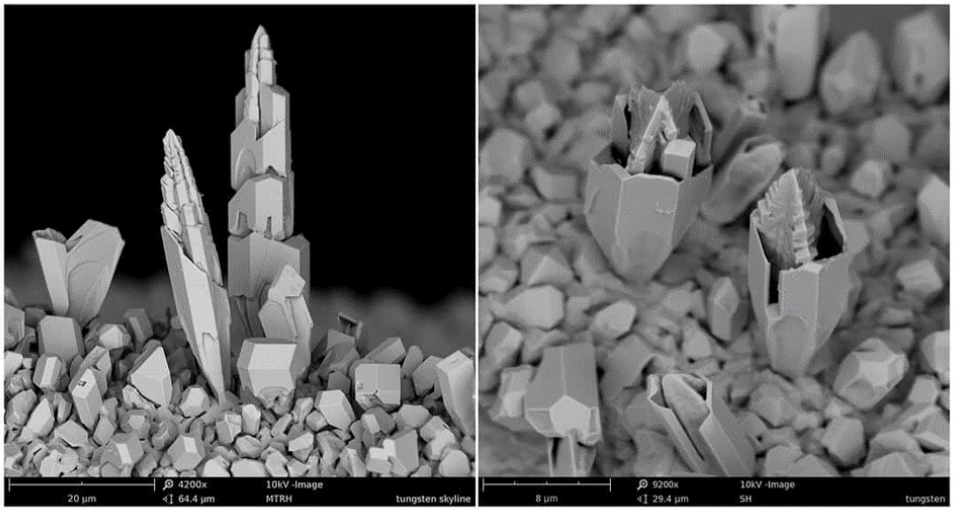
3) Given proper training, SEM equipment is straightforward to operate, and specialist but user-friendly software supports it. Modern SEM data comes in digital form.

4)It is a rapid process, and instruments can complete analysis in under five minutes.

5) There is a degree of sample preparation necessary, but usually this is minimal.



BSE (left) and SE (right) images of FeO2 particles



Backscattered electron image of Tungsten particles

Applications of SEM:

SEMs can be used in a variety of industrial, commercial, and research applications.

1) MATERIALS SCIENCE

SEMs are used in materials science for research, quality control and failure analysis.

In modern materials science, investigations into nanotubes and nanofibers, high temperature superconductors, mesoporous architectures and alloy strength, all rely heavily on the use of SEMs for research and investigation.

In material science industry, from aerospace and chemistry to electronics and energy usage, have only been made possible with the help of SEMs.

2) NANOWIRES FOR GAS SENSING

Researchers are exploring new ways nanowires can be used as gas sensors by improving existing fabrication methods and developing new ones. Electron microscopy is vitally important in helping characterise nanowires and understanding their gas sensing behaviour.

3) SEMICONDUCTOR INSPECTION

Reliable performance of semiconductors requires accurate topographical information. The high resolution three dimensional images produced by SEMs offers a speedy, accurate measurement of the composition of the semiconductor.

In fact, in all semiconducting wafer manufacturing processes, SEMs are one of three essential quality control tools used. In the case of repetitive daily quality control tests.

4) MICROCHIP ASSEMBLY

Microchip production is increasingly relying on SEMs to help gain insight into the effectiveness of new production and fabrication methods. With smaller and smaller scales and materials, as well as the potential of complex self assembling polymers, the high resolution, three-dimensional capacity of SEMs is invaluable to microchip design and production.

As the Internet of Things (IoT) becomes more prevalent in the day to day lives of consumers and manufacturers, SEMs will continue to play an important role in the design of low cost, low power chipsets for non-traditional computers and networked devices.

5) FORENSIC INVESTIGATIONS

Criminal and other forensic investigations utilise SEMs to uncover evidence and gain further forensic insight. Uses include:

- analysis of gunshot residue
- jewellery examination
- bullet marking comparison
- handwriting and print analysis
- examination of banknote authenticity.
- paint particle and fibre analysis
- filament bulb analysis in traffic incidents

Since SEMs offer the ability to examine a wide range of materials at high and low magnification without sacrificing depth of focus, their use in forensic sciences makes it possible to draw conclusions, identify material origins and contribute to a body of evidence in criminal and legal matters.

The desktop Phenom GSR instrument is specifically designed for automated gun shot residue analysis.

6) BIOLOGICAL SCIENCES

In biological sciences, SEMs can be used on anything from insects and animal tissue to bacteria and viruses. Uses include:

- measuring the effect of climate change of species.
- identifying new bacteria and virulent strains
- vaccination testing
- uncovering new species
- work within the field of genetics

7) SOIL AND ROCK SAMPLING

Geological sampling using a scanning electron microscope can determine weathering processes and morphology of the samples. Backscattered electron imaging can be used to identify compositional differences, while composition of elements can be provided by microanalysis. Valid uses include:

- identification of tools and early human artefacts
- soil quality measurement for farming and agriculture
- dating historic ruins
- forensic evidence is soil quality, toxins etc.

8) MEDICAL SCIENCE

Broadly speaking, SEMs are used in medical science to compare blood and tissue samples in determining the cause of illness and measuring the effects of treatments on patients (while contributing to the design of new treatments). Common uses include:

- identifying diseases and viruses
- testing new vaccinations and medicines
- comparing tissue samples between patients in a control and test group
- testing samples over the lifespan of a patient

2) Transmission electron microscopy (TEM):

Transmission electron microscopy (**TEM**) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image. The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid. An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a scintillator attached to a charge-coupled device.

Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes, owing to the smaller de Broglie wavelength of electrons. This enables the instrument to capture fine detail—even as small as a single column of atoms, which is thousands of times smaller than a resolvable object seen in a light microscope. Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences.

Why transmission electron microscopy is used?

This technology can tell us about the structure, crystallization, morphology and stress of a substance whereas scanning electron microscopy can only provide information about the morphology of a specimen. However, TEM requires very thin specimens that are semi-transparent to electrons, which can mean sample preparation takes longer.

Working:

Parts of TEM:

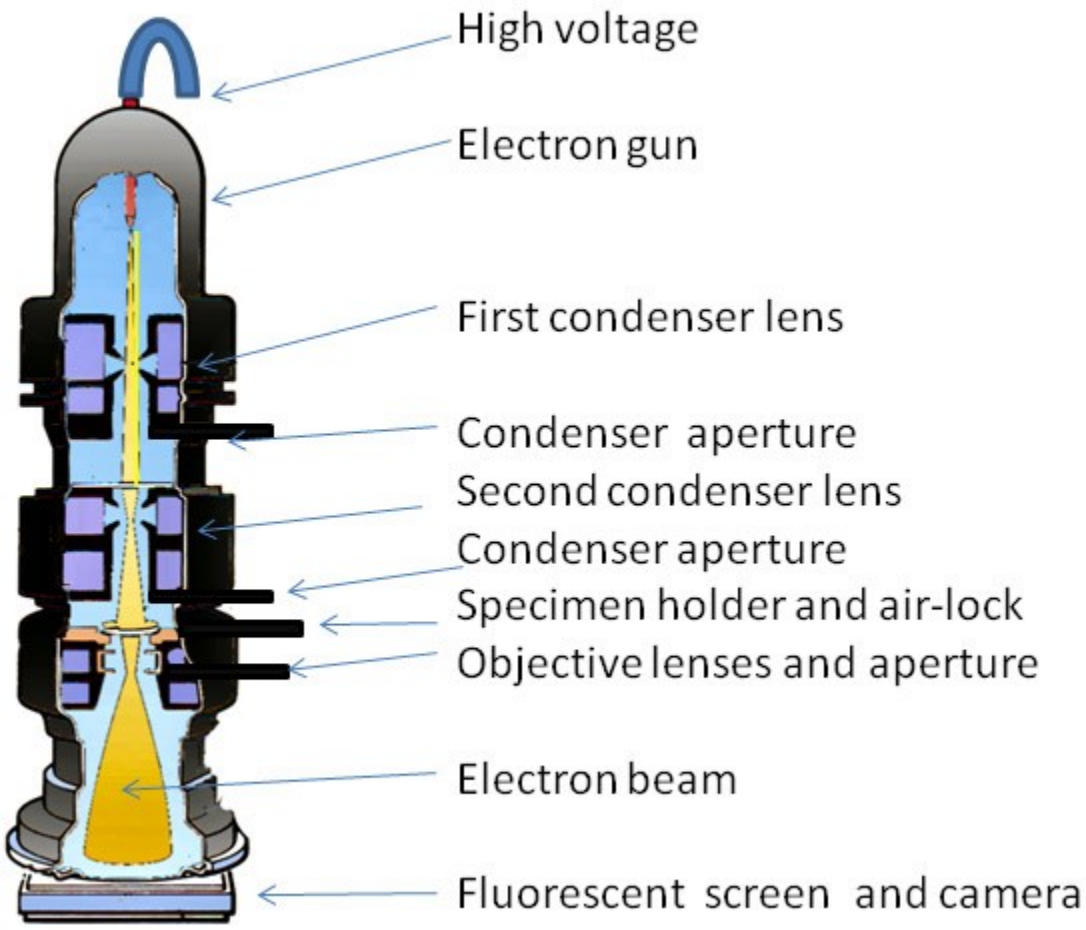
Their working mechanism is enabled by the high-resolution power they produce which allows it to be used in a wide variety of fields. It has three working parts which include:

1. Electron gun
2. Image producing system
3. Image recording system

The working mechanism is a sequential process of the parts of the TEM:

- A heated tungsten filament in the electron gun produces electrons that get focus on the specimen by the condenser lenses.
- Magnetic lenses are used to focus the beam of electrons of the specimen by the assistance offered by the column tube of the condenser lens into the vacuum creating a clear image (the vacuum allows electrons to produce a clear image without collision with any air molecules which may deflect them.)
- On reaching the specimen, the specimen scatters the electrons focusing them on the magnetic lenses forming a large clear image, and if it passes through a fluorescent screen it forms a polychromatic image.

- The denser the specimen, the more the electrons are scattered forming a darker image because fewer electron reaches the screen for visualization while thinner, more transparent specimens appear brighter.



Applications of TEM:

A Transmission Electron Microscope is ideal for a number of different fields such as:

- life sciences
- nanotechnology
- medical
- biological and material research

- forensic analysis
- gemology and metallurgy
- industry and education
    - TEMs provide topographical, morphological, compositional and crystalline information.
    - The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture.
    - This information is useful in the study of crystals and metals, but also has industrial applications.
    - TEMs can be used in semiconductor analysis and production and the manufacturing of computer and silicon chips.
    - Technology companies use TEMs to identify flaws, fractures and damages to micro-sized objects; this data can help fix problems and/or help to make a more durable, efficient product.

Advantages of TEM:

- TEMs offer the most powerful magnification, potentially over one million times or more
- TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields
- TEMs provide information on element and compound structure
- Images are high-quality and detailed
- TEMs are able to yield information of surface features, shape, size and structure
- They are easy to operate with proper training

Disadvantages of TEM:

- TEMs are large and very expensive
- Laborious sample preparation
- Operation and analysis requires special training
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber
- TEMs require special housing and maintenance
- Images are black and white
- Electron microscopes are sensitive to vibration and electromagnetic fields and must be housed in an area that isolates them from possible exposure.

- A Transmission Electron Microscope requires constant upkeep including maintaining voltage, currents to the electromagnetic coils and cooling water.

Comparison of SEM and TEM:

	Scanning Electron Microscopes (SEM)	**Transmission Electron Microscopes (TEM)**
Electron stream	Fine, focused beam	Broad beam
Image taken	Topographical/surface	Internal structure
Resolution	Lower resolution	Higher resolution
Magnification	Up to 2,000,000 times	Up to 50,000,000 times
Image dimension	3-D	2-D
Sample thickness	Thin and thick samples okay	Ultrathin samples only
Penetrates sample	No	Yes
Sample restriction	Less restrictive	More restrictive
Sample preparation	Less preparation required	More preparation required
Cost	Less expensive	More expensive
Speed	Faster	Slower
Operation	Easy to use	More complicated; requires training