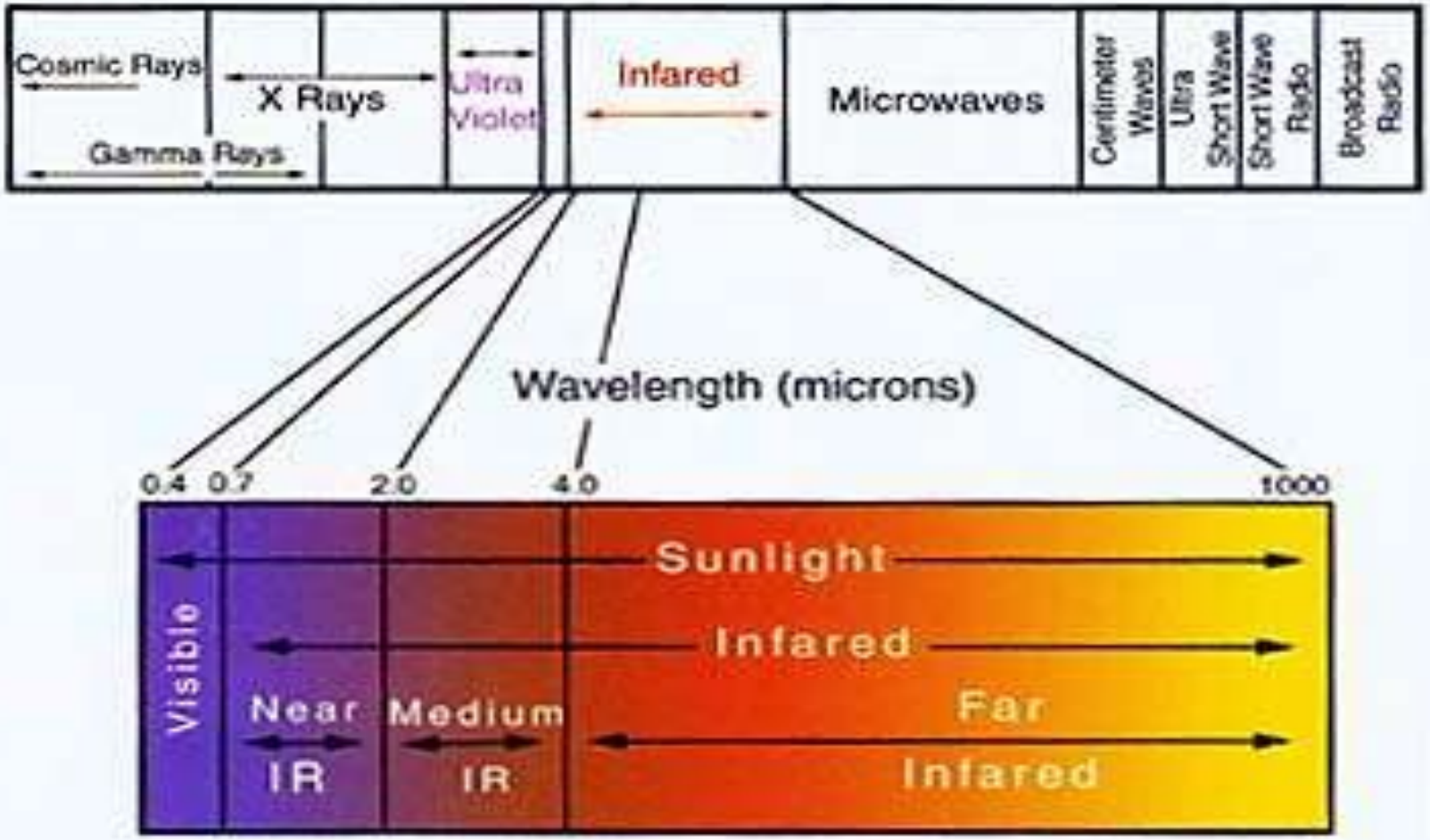
IR SPECTROSCOPY

Electromagnetic Spectrum

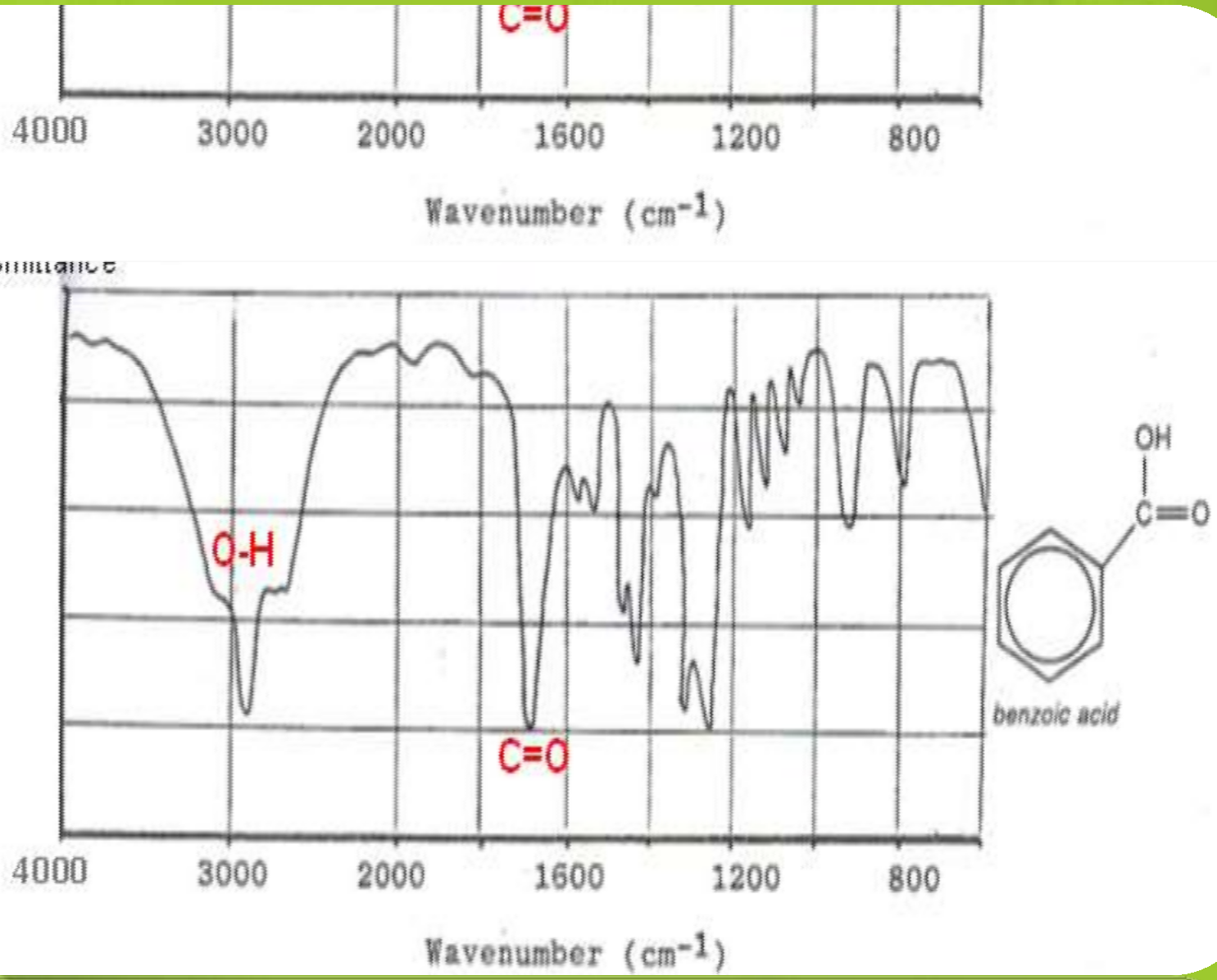


IR Region

Region of IR	Wave length (μm)	Wave number (cm^{-1})
Near IR (Overtone region)	0.8-2.5	12,500-4000
Mid IR (Vibration- rotation region)	2.5-50	4000-200
Far IR (Rotation region)	50-1000	200-10
Most used	2.5-25	4000-400

Principle of IR Spectroscopy

- When IR light is passed through a sample of organic compound some of the frequencies are absorbed while others are transmitted.
- Plot of Absorbance or Transmittance Vs Wave no. gives an IR spectrum
- But conventionally **Wave No. Vs % Transmittance** is plotted (because the numbers are more manageable)


C=O
4000
3000
2000
1600
1200
800
Wavenumber (cm-1)
O-H
C=O
OH
C=O
benzoic acid

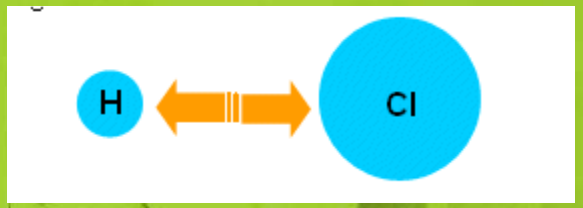
Requirements of IR radiation Absorption

1. Correct wavelength of radiation

If a molecule absorbs radiation only when natural frequency of vibration of some part of molecule is same as frequency of incident radiation.

Requirements of IR radiation Absorption

2. Electric Dipole:



- If a frequency of vibration of HCl molecule exactly matches with that coming from the source **NET TRANSFER of energy takes place** → change in amplitude of molecular vibration → absorption of radiation
- In case of O_2, N_2,Cl_2 **NO NET change in dipole moment** occurs thus they cannot absorb IR radiations & do not show IR spectra

Two types changes occur in molecule :

- **Molecular rotations:**

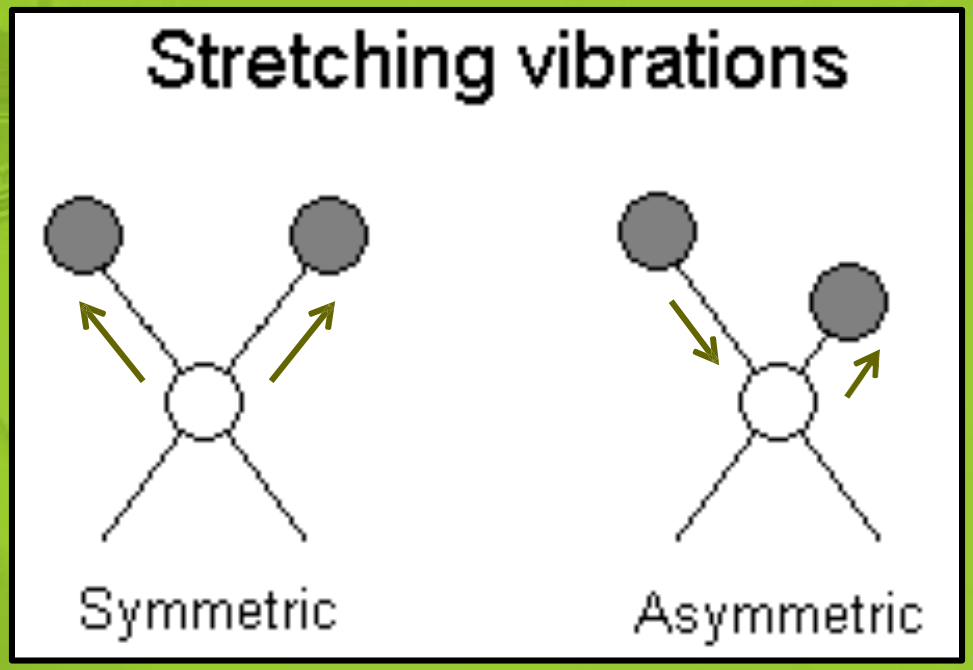
  Rotational transitions are of little use to the spectroscopist.

- **Molecular vibrations**

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

TYPES OF MOELCULAR VIBRATIONS

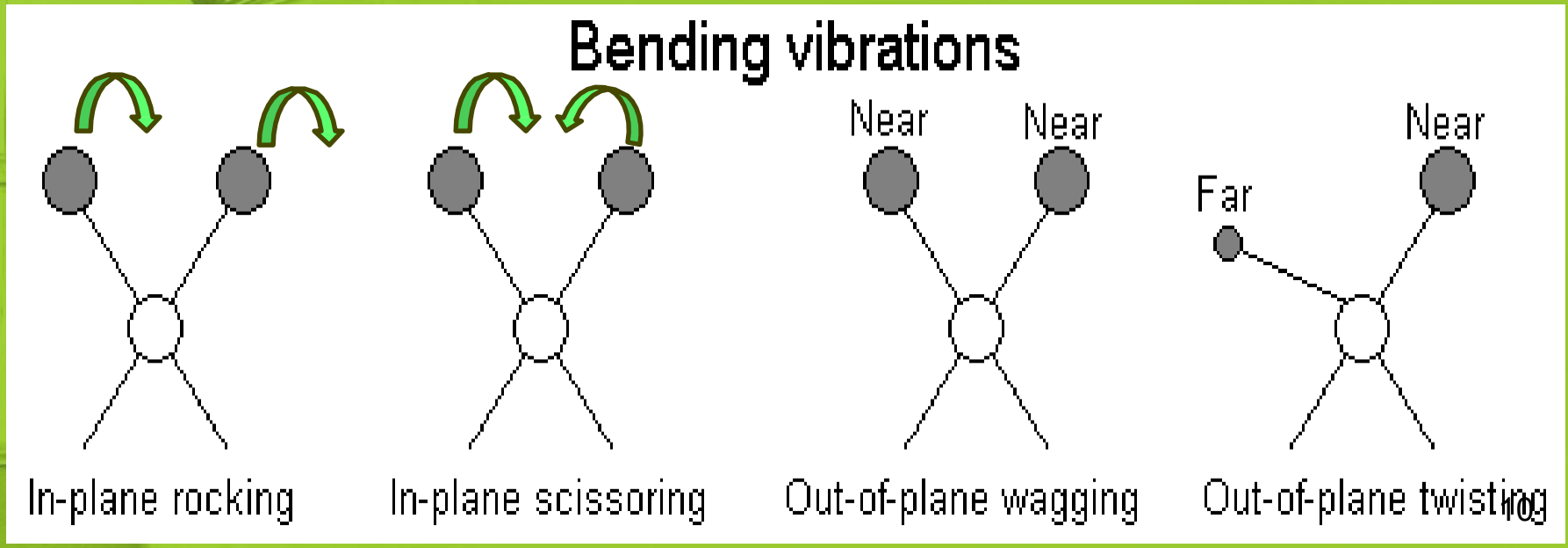
Stretching: Change in inter-atomic distance along bond axis



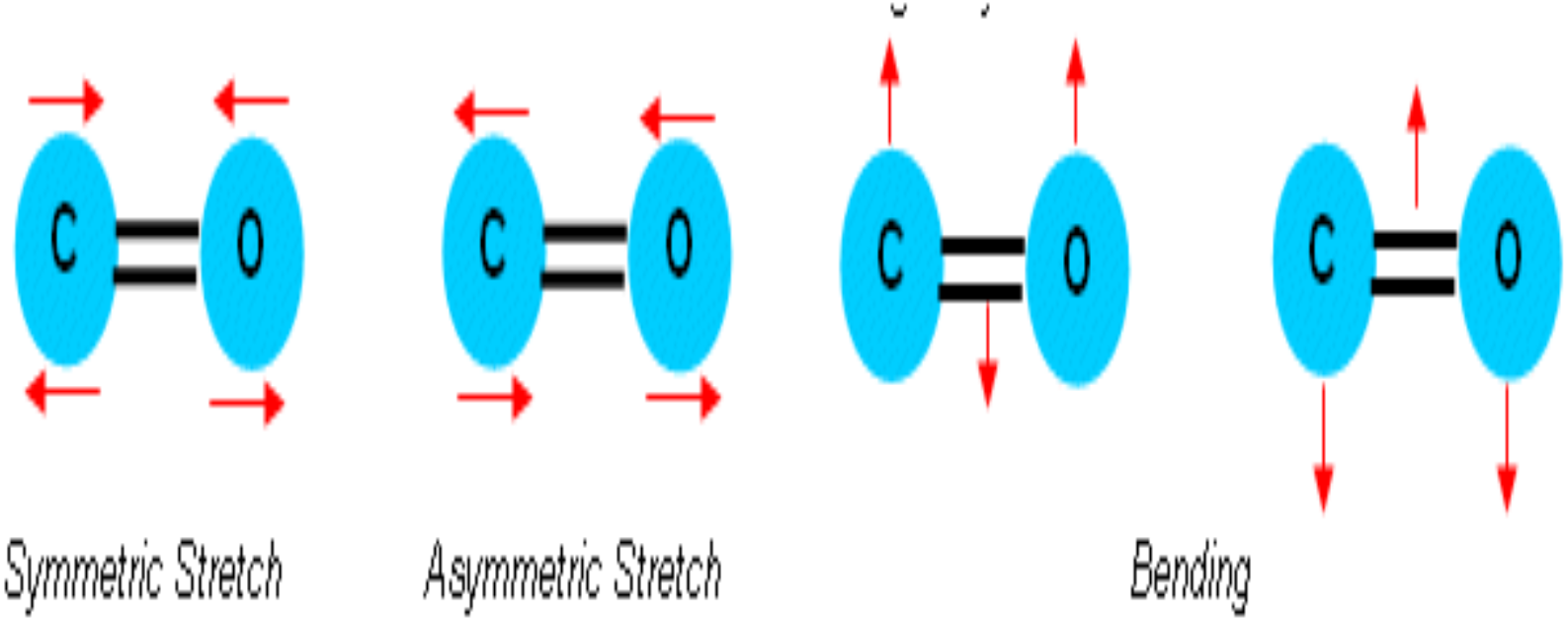
TYPES OF MOLECULAR VIBRATIONS

Bending: Change in angle between two bonds. There are four types of bend:

- Rocking
- Scissoring
- Wagging
- Twisting

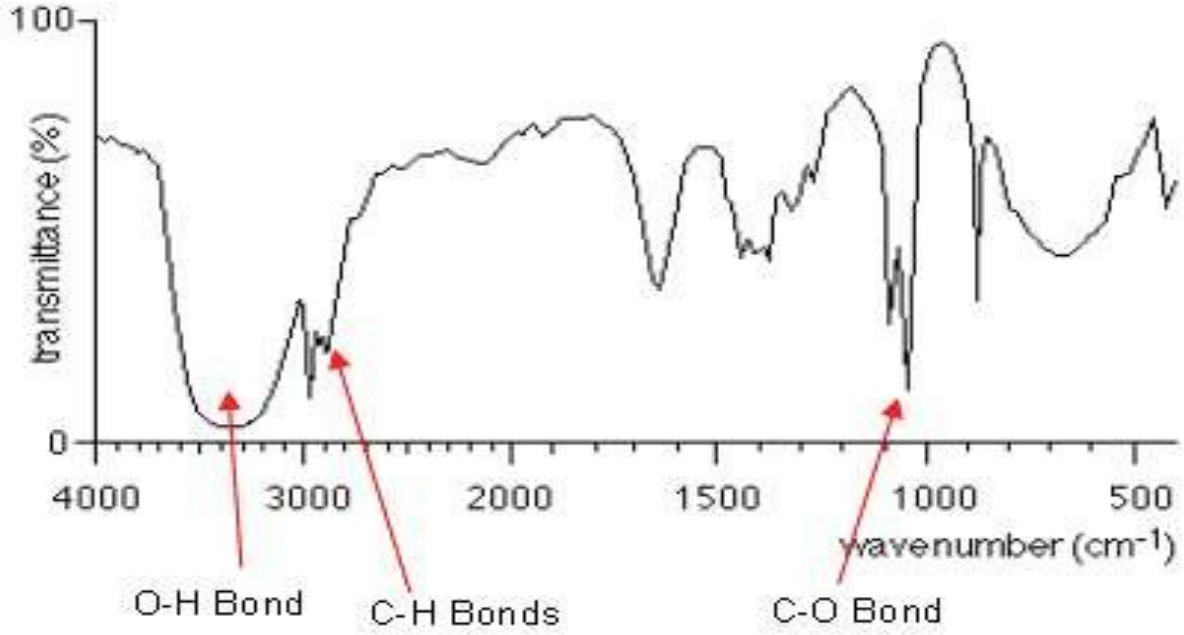


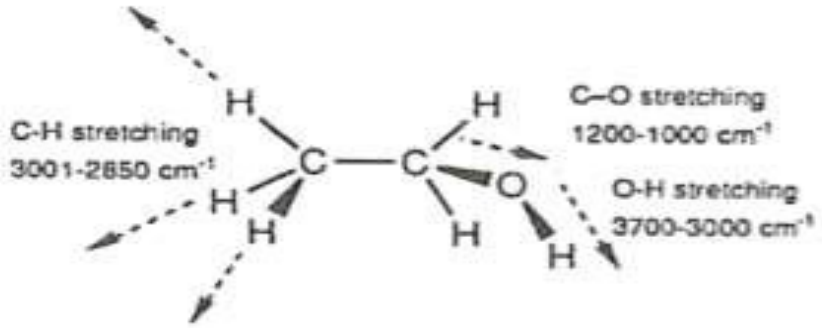
- Carbon dioxide can vibrate in the following ways:

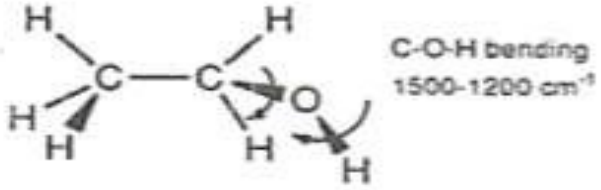


Symmetric Stretch *Asymmetric Stretch* *Bending*

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







Vibrational frequency

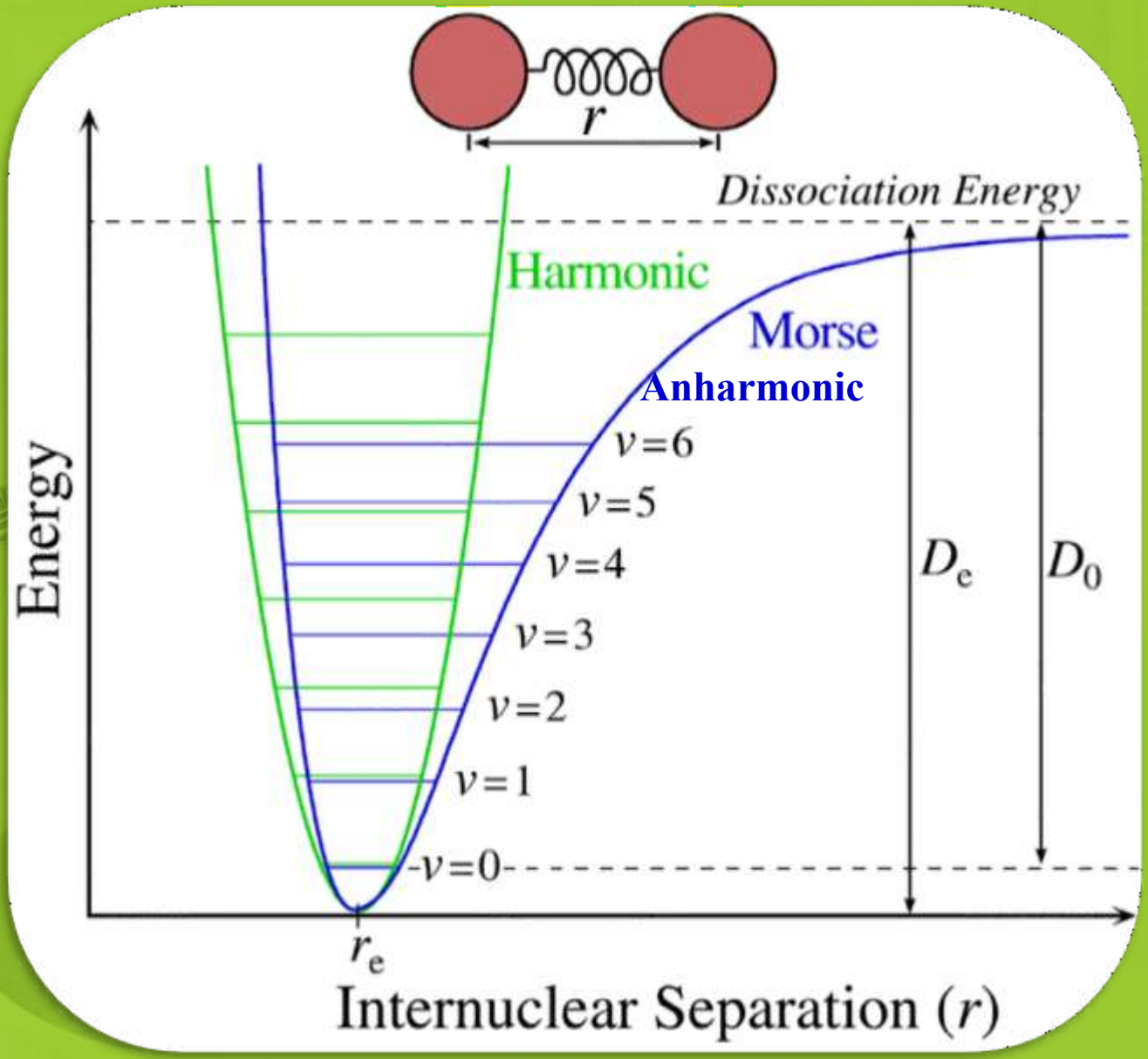
- A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. **The frequency of the periodic motion is known as a vibrational frequency**

Factors affecting Vibrational frequency

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

(Will discuss later)

Potential energy diagrams of oscillators



- **Simple harmonic motion** is a type of periodic motion where the restoring force is directly proportional to the displacement.

- **Anharmonicity** is the deviation of a system from being a harmonic oscillator. An oscillator that is not oscillating in simple harmonic motion

Vibration modes

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

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

Vibration modes

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

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

   0 --> 1 (fundamental)

   0 --> 2 (first overtone)

   0 --> 3 (second overtone)

   0 --> 4 (third overtone)

   0 --> 5 (fourth overtone)

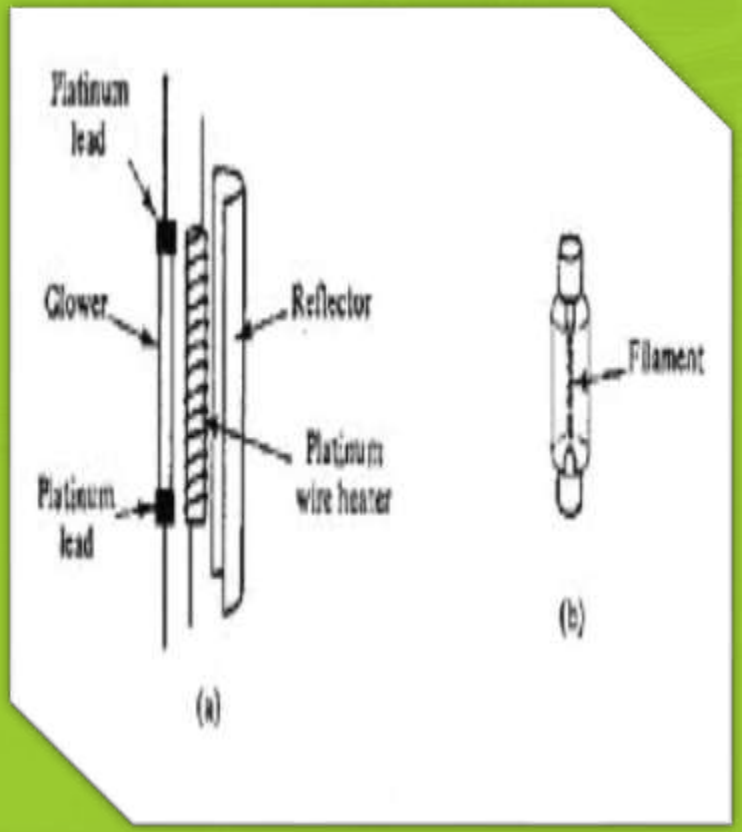
Instrumentation

- IR radiation source
- Wavelength selector (Monochromator)
- Sample Holder or cell
- Detector
- Recorder

Sources: Inert solids heated electrically to temp of 1500-2000K

1. Nernst Glower:

- Consists of **cylinder** of **rare earth oxides** formed into a cylinder of diameter 1-2mm length approx. 20mm.
- **Platinum discs** are attached at the ends of cylinder to permit electrical connection.
- They are heated to a temp of **1200-2200K** where IR radiations are emitted.



Nernst Glower:

- Rare earth metals have **large –ve temperature coefficient** of electrical resistance. (A **negative temperature coefficient** (NTC) occurs when a physical property (such as thermal conductivity or electrical resistivity) of a material lowers with increasing temperature, typically in a defined temperature range.)
- Temp is inversely related to resistance
- At low temp, they provide high resistance to flow current and as cylinder gets heated resistance gets reduced allowing conduction of current.
- If large amount of current flows through cylinder it can destroy the source.
- To avoid this source circuit should be designed to limit the current.

2. The Globar source

- Similar to nernst glower it is also made up of cylinder
- Material used is **silicon carbide**
- Length of cylinder is 50mm & diameter is 5mm
- It has **positive temperature coefficient** of electrical resistance
- At low temp, they provide low resistance to flow current and as cylinder gets heated resistance increases allowing conduction of current.
- To avoid excessive heating water cooling is necessary
- At high temp source emits IR radiations.

3. Incandescent wire source (nichrome wire)

- Cylinder in the above sources is tightly wound by spiral wire of nichrome / rhodium
- It is electrically heated at 1100 k

4. Mercury arc:

- Quartz jacketed tube Hg vapors
- Electricity passed through Hg vapour provides radiations

4. Tungsten filament : used in Near IR

5. CO_2 laser source:

- Detection of pollutants in air.

Wavelength Selectors

Output from a wavelength selector is a band of wavelengths.

- ❑ Filters
- ❑ Monochromators
  - Entrance slit
  - Collimating lens or mirror
  - Dispersion element (prism or grating)
  - Focusing lens or mirror
  - Exit slit

Difference between Monochromator & Filter

	Monochromator	*Filter*
Means of selection	Diffraction	Absorption
Wavelength width	Narrow	Wide
Cost	Expensive	Cheap
Portability	None	Very
Capable of recording spectra	Yes	No
Suitable for quantitative analysis	Yes	Yes

❑ Filters

- Filters are very simple: they are sheets of plastic or glass that simply absorb wavelengths other than those required for the analysis.
- Generally, the range of wavelengths allowed by a filter is relatively wide

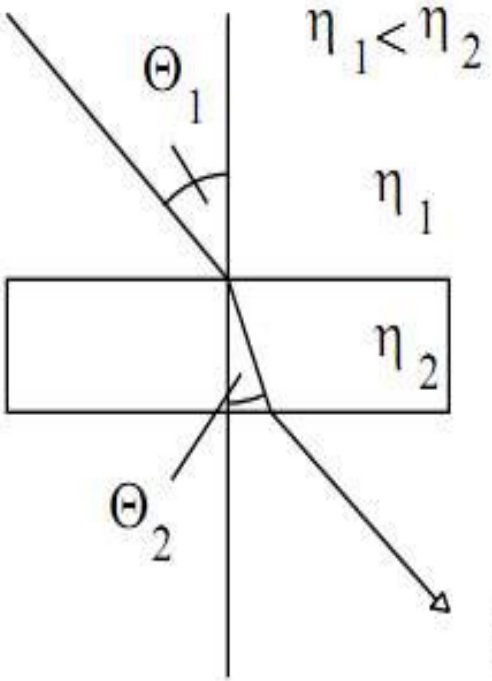
❑ Monochromators

- are far more complicated, and comprise a series of optics inside a lightproof box, which has entry and exit slits which allows the radiation of all wavelengths in and a narrow range of wavelengths out.

Prism

- The white light pass through a piece of glass and be divided into a rainbow spectrum.
- The problems with a prism include relatively poor throughput (the total amount of light passes through is significantly less than the amount that went in) and the difficulty in finding materials that diffract different wavelength ranges.

Prism: (many older instruments)

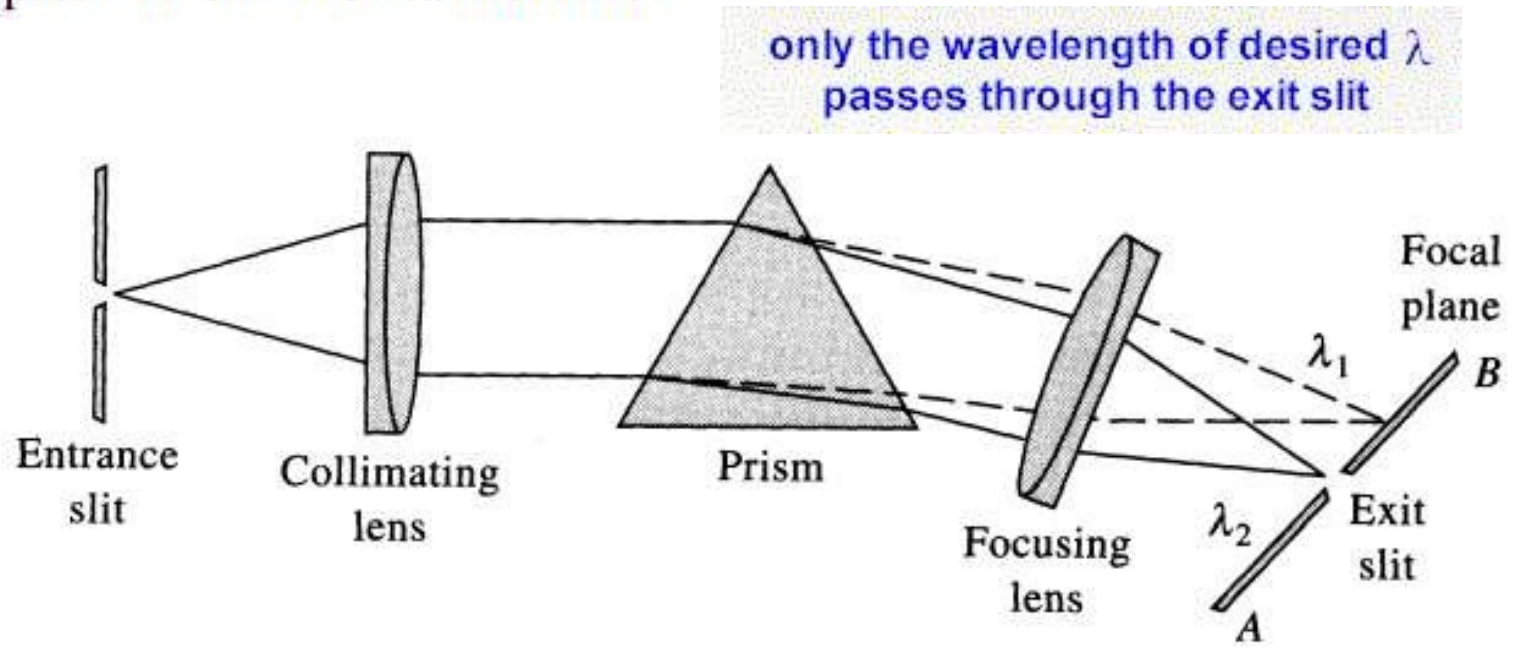


$$\frac{\sin\Theta_2}{\sin\Theta_1} = \frac{\eta_1}{\eta_2} = \frac{v_2}{v_1} = \frac{\upsilon_2 \cdot \lambda_2}{\upsilon_1 \cdot \lambda_1}$$

Snell's Law

Short wavelengths refracted more!

Typical Prism Monochromator

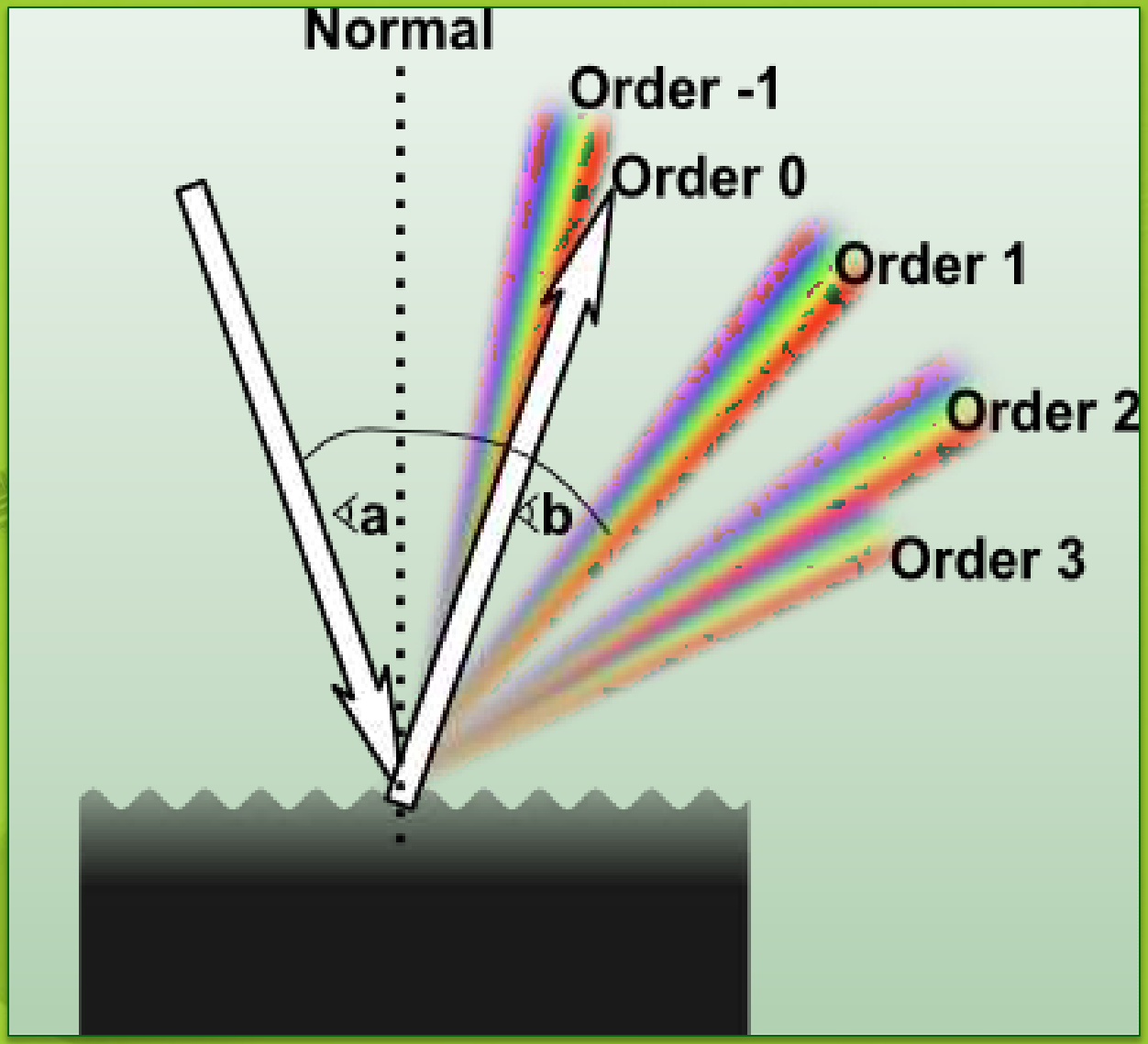


- **Entrance slit** allows source radiation to illuminate the first lens which collimates the light spreading it across the face of the prism.
- Prism disperses radiation into component wavelengths and the second lens focuses the spectrum at the focal plane.
- An exit slit selects the band of radiation to reach the detector.

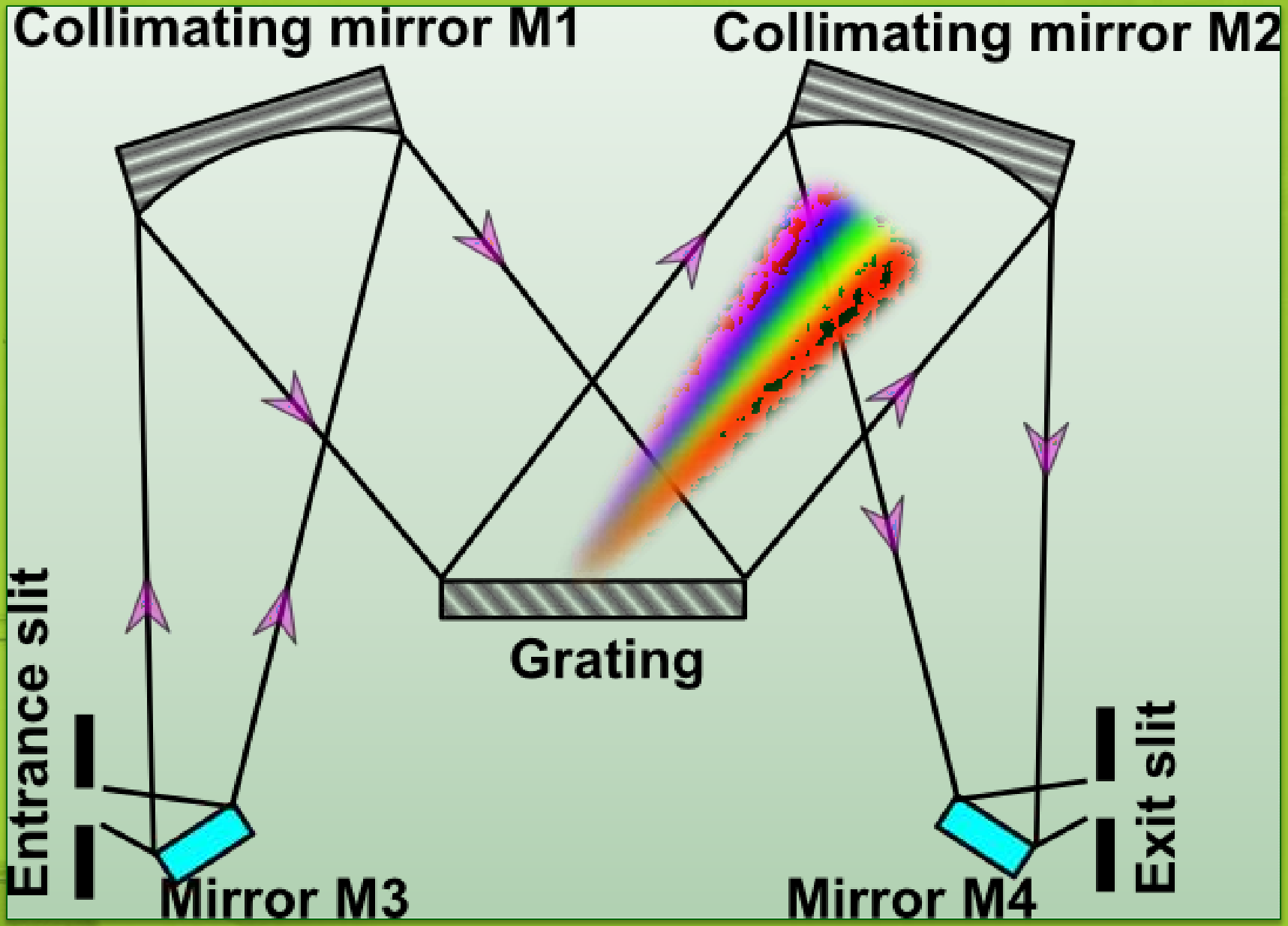
Gratings

- It is a device which consists of a series of parallel & closely spaced grooves rules on glass or any reflecting surface
- Gratings are of two types
  - ✓ Transmission Gratings
  - ✓ Reflection Gratings
- UV gratings have 2000-6000 grooves per mm
- IR gratings have 10-100 grooves per mm
- Materials used for construction are Quartz, NaCl,KBr..

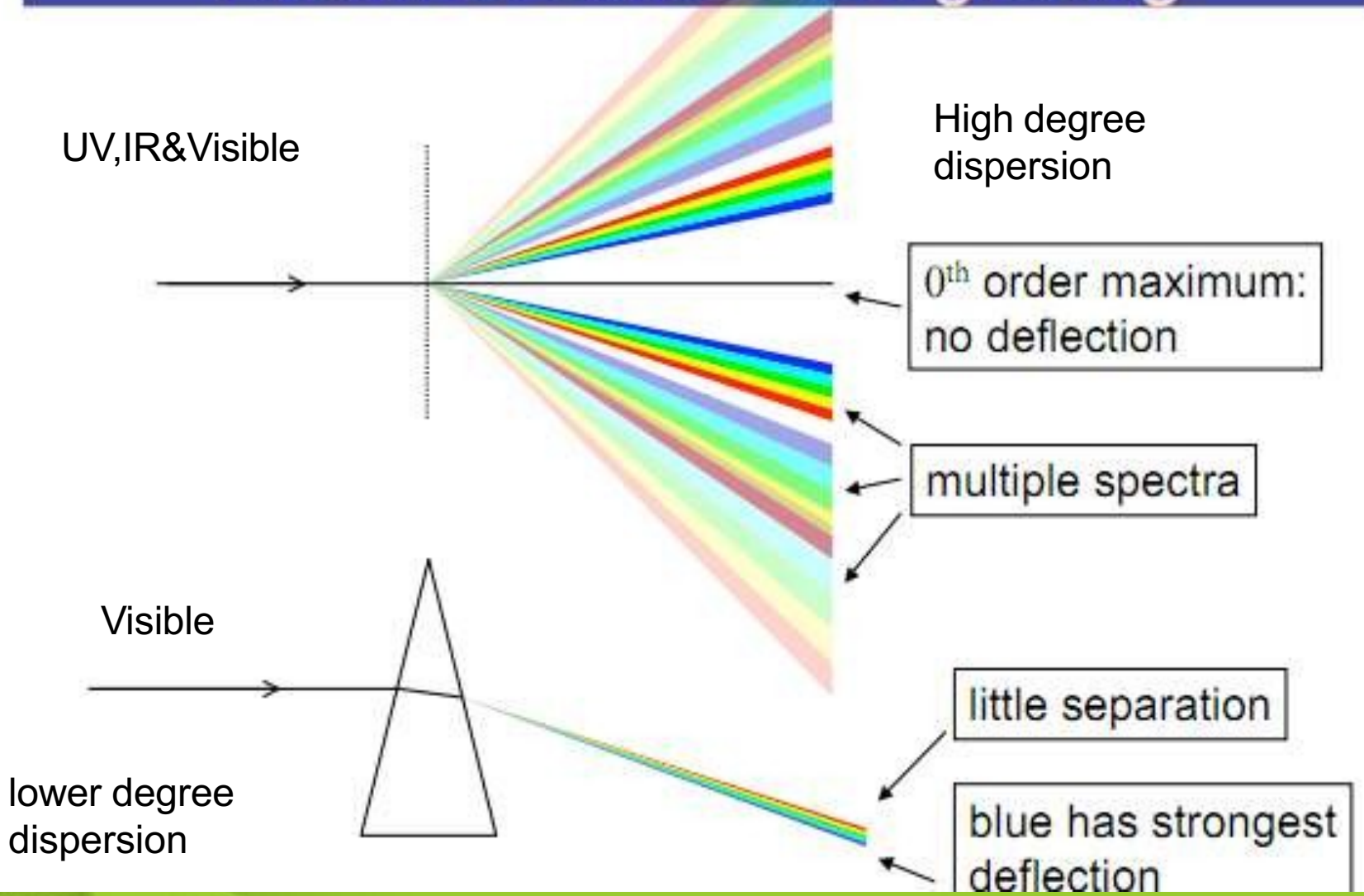
Diffraction Gratings



Monochromator



Prism vs diffraction grating



Handling of samples in IR

- Sampling techniques in IR depend on whether the sample is a

  ✓ Gas - Gas cell

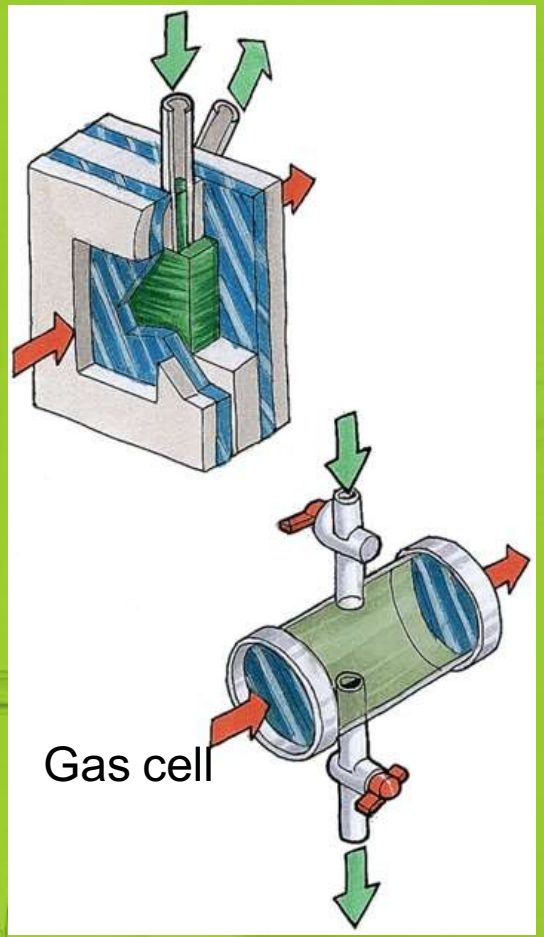
  ✓ Liquid - Thin film

  ✓ Solid - KBr disks

  - Mulls

  - Deposited films

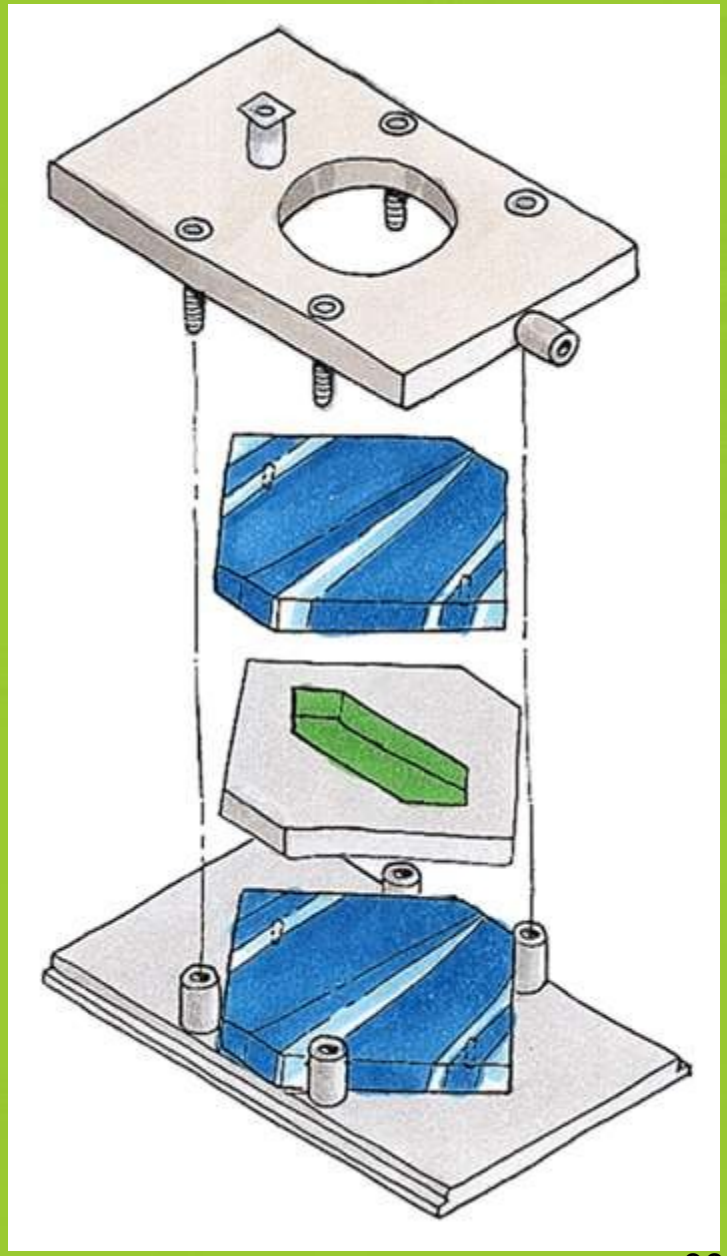
Gases



- Infrared transparent windows allow the cell to be mounted directly
- Internal mirrors are used which permit the beam to be reflected several times through the sample to increase the sensitivity
- In vapor phase rotational changes in molecule occur freely & these low frequency processes can modulate the higher energy vibrational ba3n5ds

Liquids

- It consists of a sampling liquid as a thin films squeezed between two infrared transparent windows like NaCl flats
- The salt plates or rock salt flats must be optically polished & cleaned immediately after use.
- Toluene, chloroform etc are used to clean them.
- They should be dry & handled only by their edges



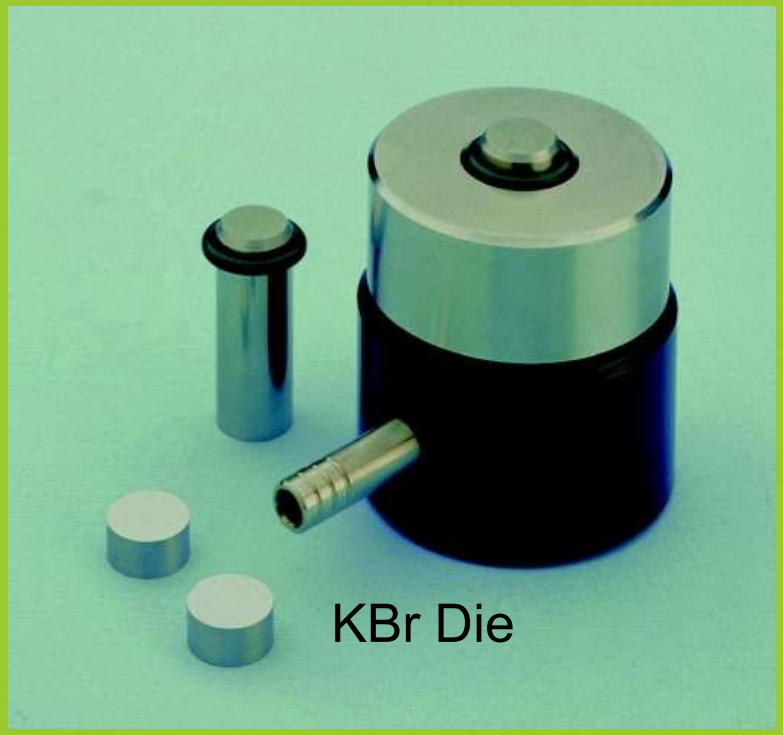
Liquids

- The thickness of the film can be adjusted by varying pressure used to squeeze the flats together(0.01-0.1 mm)
- It consists of two windows of pressed salt sealed and separated by thin gaskets of Teflon, copper or lead that have been wetted with mercury. The windows are usually made of **sodium chloride, potassium chloride or cesium bromide**.
- There are two cells first cell containing sample & second one containing pure solvent placed in reference beam
- By the reference beam solvent absorptions are cancelled out & spectrum recorded is that of solute alone.

Solids
a) KBr Disks

- It is prepared by grinding the sample with KBr & compressing the whole into a transparent water or disk.
- KBr must be dry, & hence grinding is carried out under infrared lamp to avoid condensation of atmospheric moisture which gives rise to broad absorptions
- Grinding is done in a agate mortar pestle / commercial ball mills
- Poorly ground mixtures lead to disks that scatter light than they transmit
- Particle size of 2μm must be achieved to avoid scattering

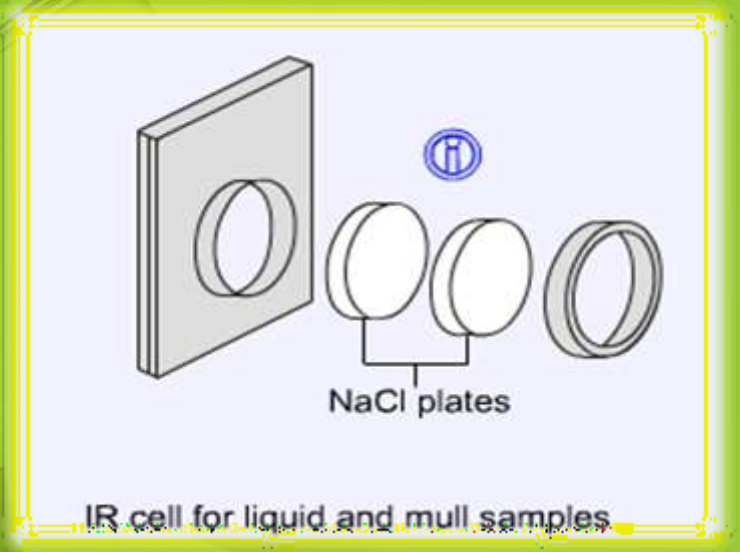
Hydraulic press



- Compression of a cohesive disks require high pressure.
- Special die are used from which air can be evacuated by hydraulic compression (10 tonnes load)
- Disks thus formed are easy to handle

Solids
b) Mulls

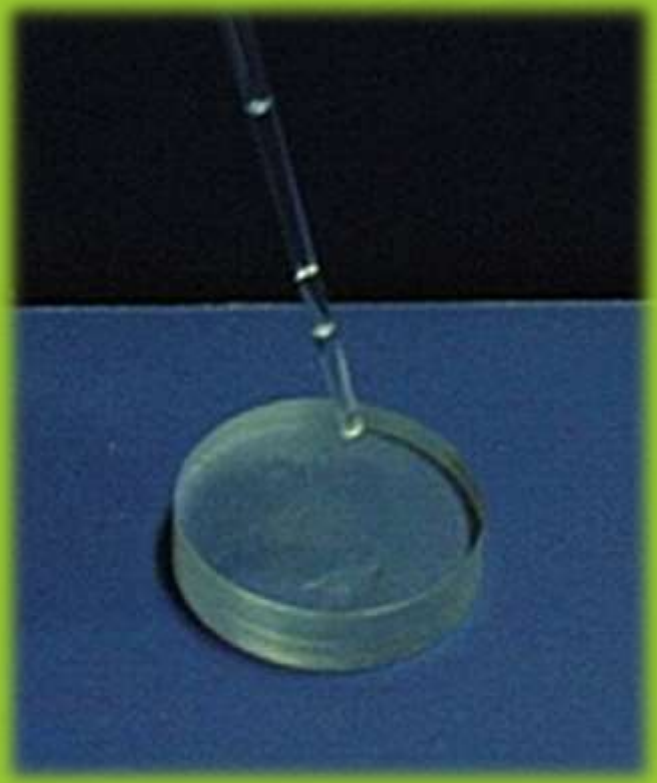
- Pastes prepared by grinding the sample with a drop of oil the mull is the squeezed between transparent windows as for liquid samples
- Mulling agent should ideally be infrared transparent, but this is never true
- Liquid paraffin (Nujol) is used to prepare Nujol mulls which is transparent over a wide range in IR spectrum.



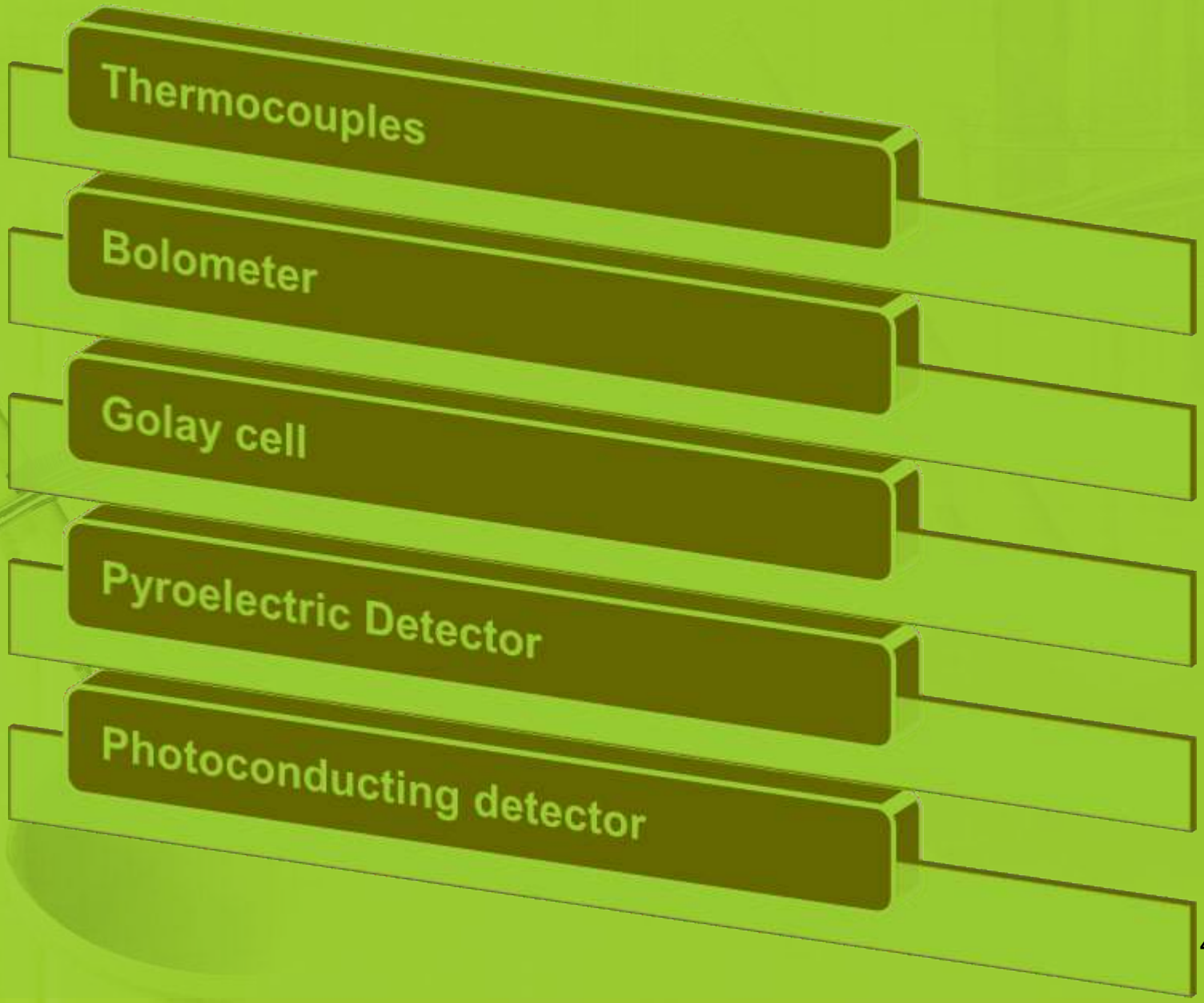
IR cell for liquid and mull samples

Solids
c) Solid Films

- Solid films can be deposited onto NaCl plates by allowing a solutions in a volatile solvent to evaporate drop by drop on the surface of the flat.
- Polymers & various waxy or fatty materials often give excellent spectra in this way.

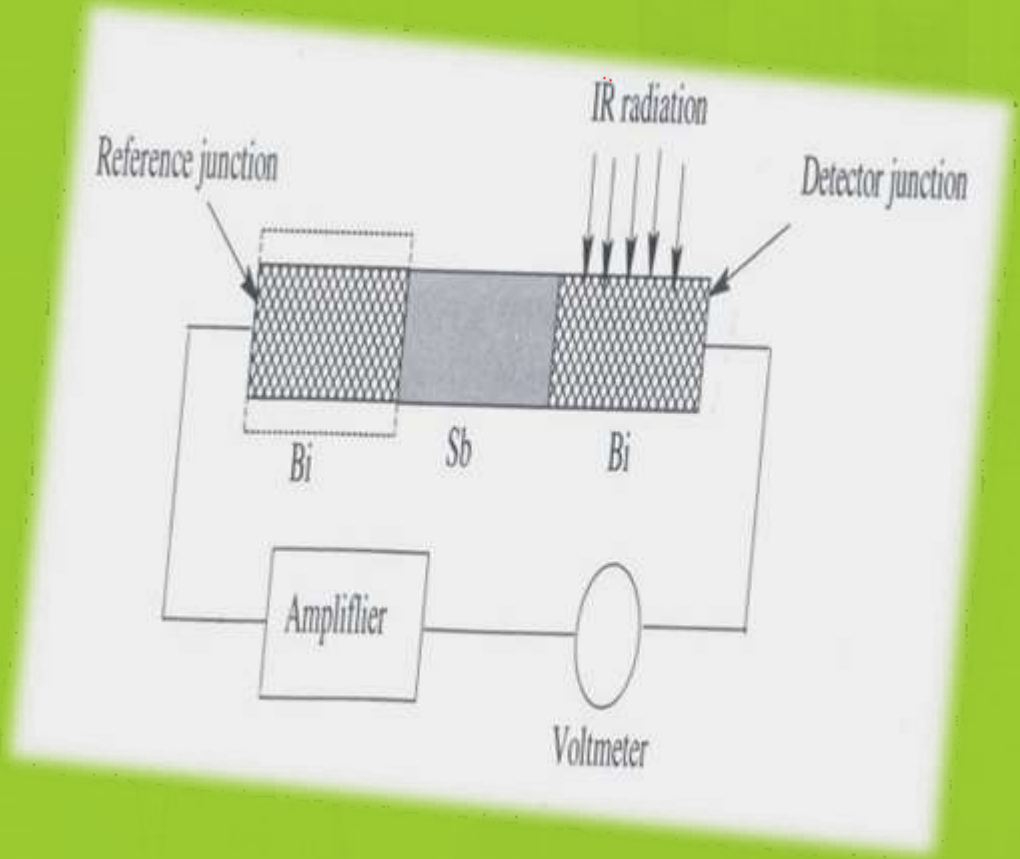


IR Detectors



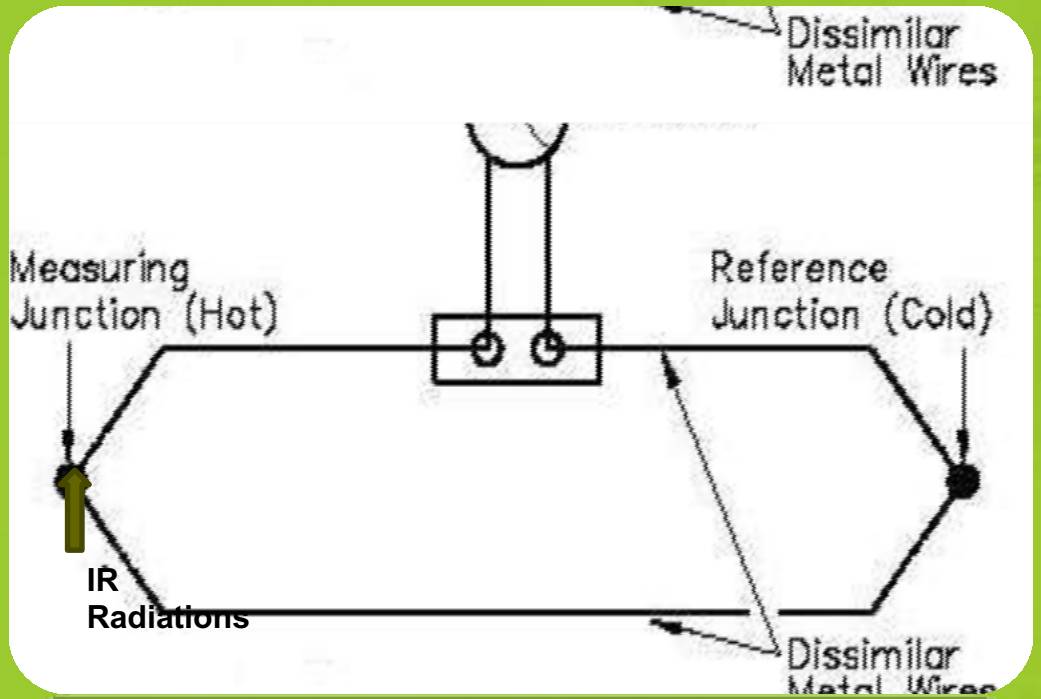
Thermocouple

- It consists of a pair of junction formed when 2 ends of metal such as Bismuth & antimony are fused to either ends of dissimilar metal wires.
- Heating capacity of absorbing element is small as to detect the change in temperature.
- Potential varies in the 2 junctions with the difference in temperature.



Thermocouple

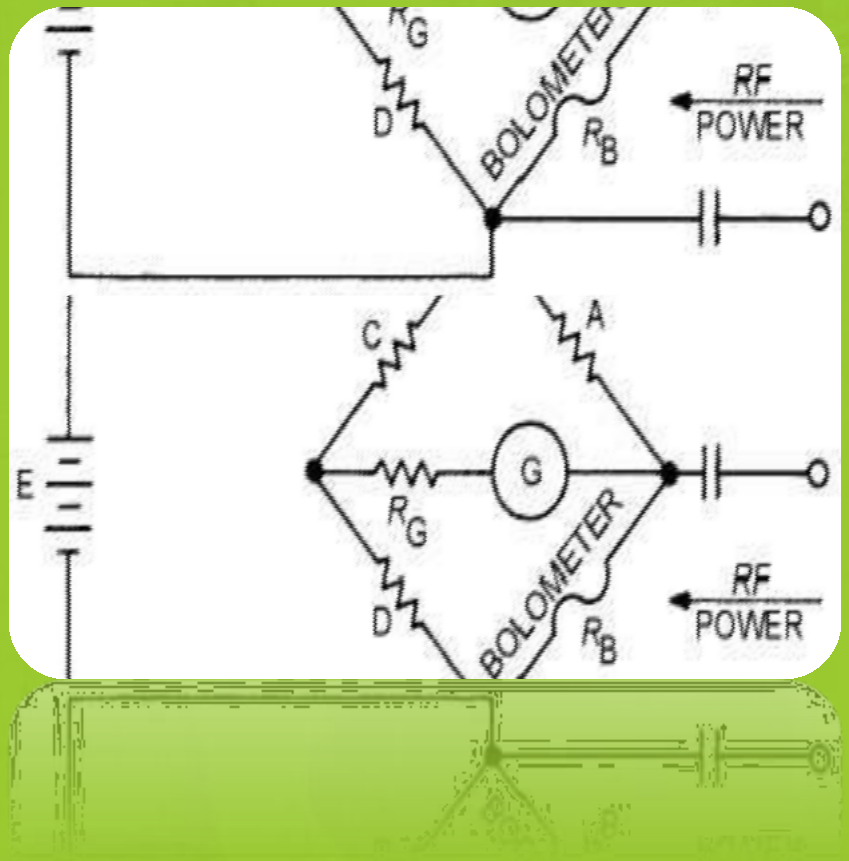
- One junction is Cold junction which is reference junction kept at constant temperature not exposed to IR radiations
- The other junction is Hot junction exposed to IR radiations which increases temperature of junction.
- Temperature difference due to falling IR radiations generates the potential difference which amounts to Ir radaitions.



- Hot junction is generally blackened to improve its heat absorbing capacity.

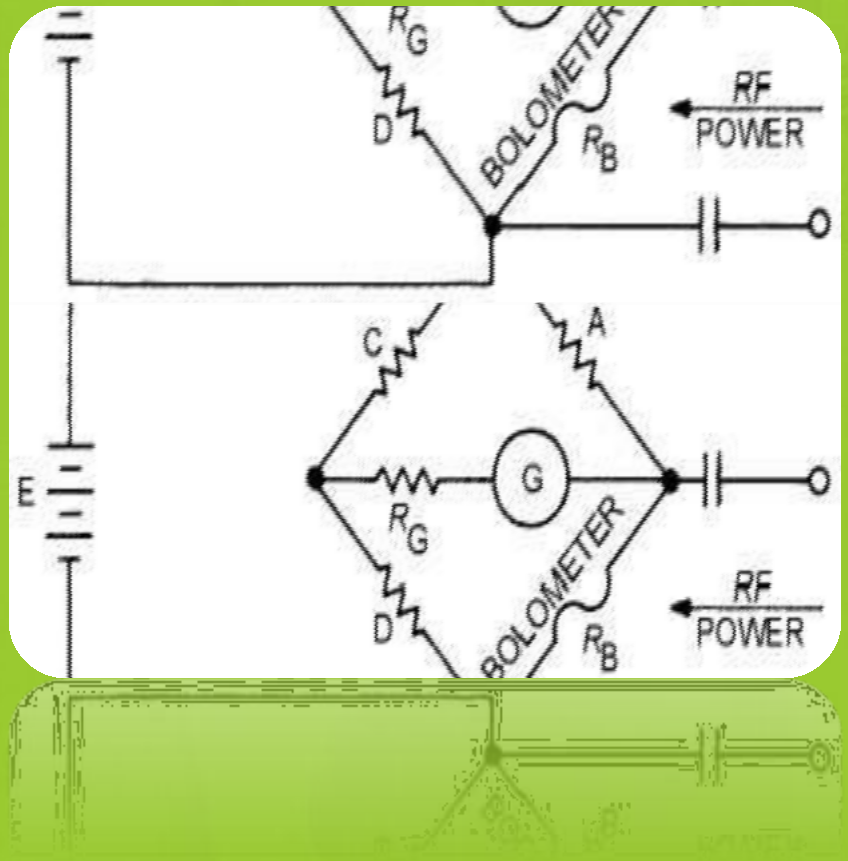
Bolometer

- It is a type of resistance thermometer constructed from strips of metals such as platinum or nickel or from semiconductors.
- They show a relatively large change in resistance as a function of temperature.
- It forms one of the arm of wheatstones bridge a similar strip is used as balancing arm which is not exposed to the falling IR radiations.



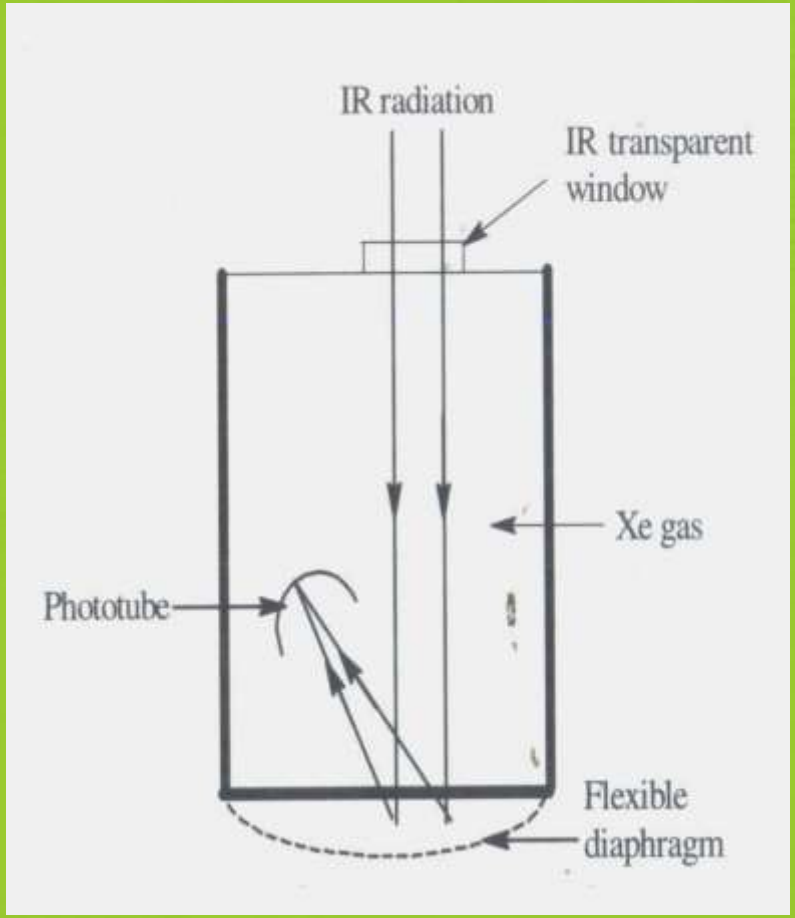
Bolometer

- If IR radiations fall the bridge becomes unbalanced due to change in the resistance occurred due to change in temperature
- This causes current to flow which is measure of intensity of IR radiations.



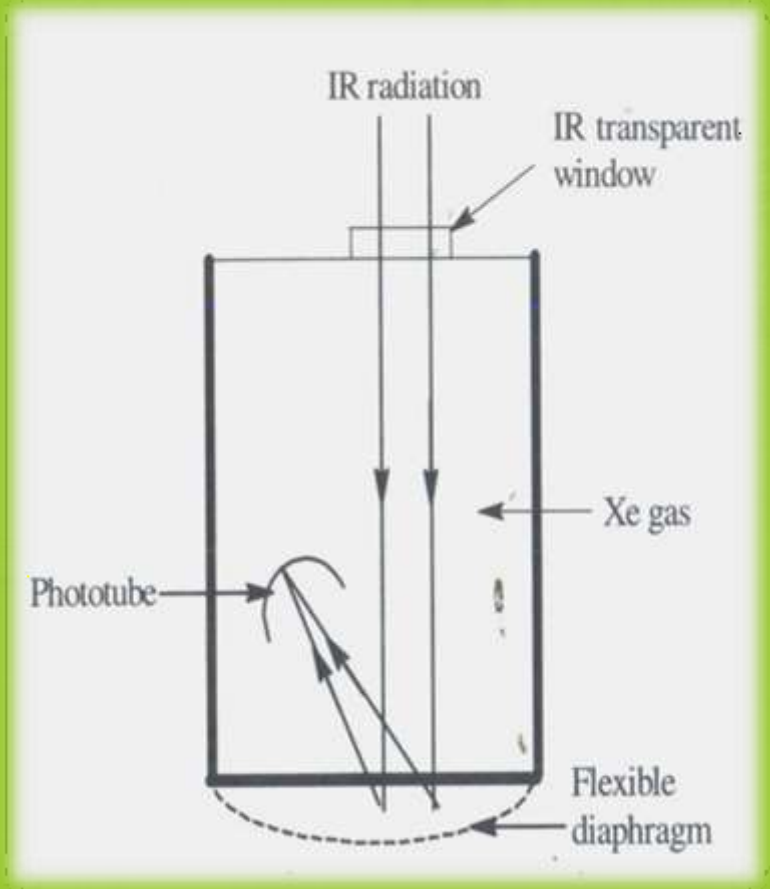
Golay cells

- They are sensitive gas thermometers
- Xenon gas is contained in a small cylindrical chamber which contains a blackened membrane on one side while other side has a flexible diaphragm; silvered outside.
- A beam of light is reflected from the silvered surface to cathode at a vacuum phototube.



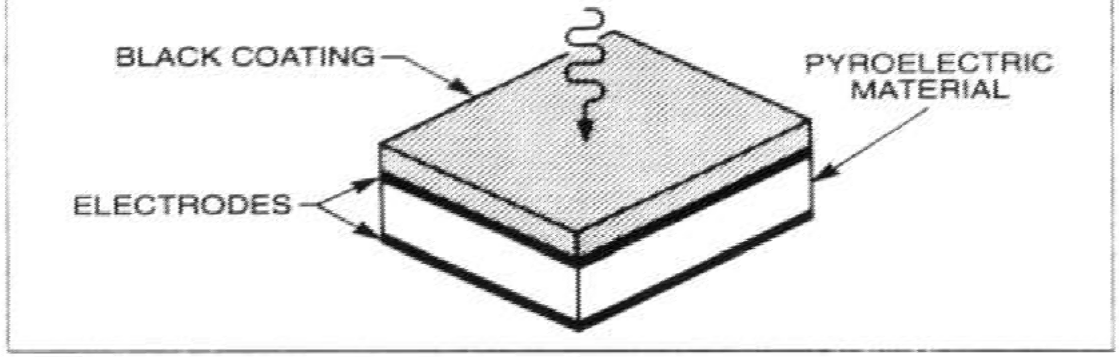
Golay cells

- When IR radiations fall on the blackened membrane it is heated which in turn heats xenon gas by conduction, resulting in increase in pressure causes distortion of silvered diaphragm
- As a result the fraction of reflected light which strikes the active surface of phototube is changed leading to change in photocurrent this is related to the falling IR radiations.



Pyroelectric Detectors

- They are constructed from single crystalline water of pyroelectric material which are dielectric materials which have special thermal & electrical properties.
- Eg deuterated triglycine sulphate
- When an electric field is applied across any dielectric material electrical polarization takes place.
- The magnitude of polarization is a function of dielectric constant of that material
- This pyroelectric crystal is sandwiched between 2 electrodes which are IR transparent.



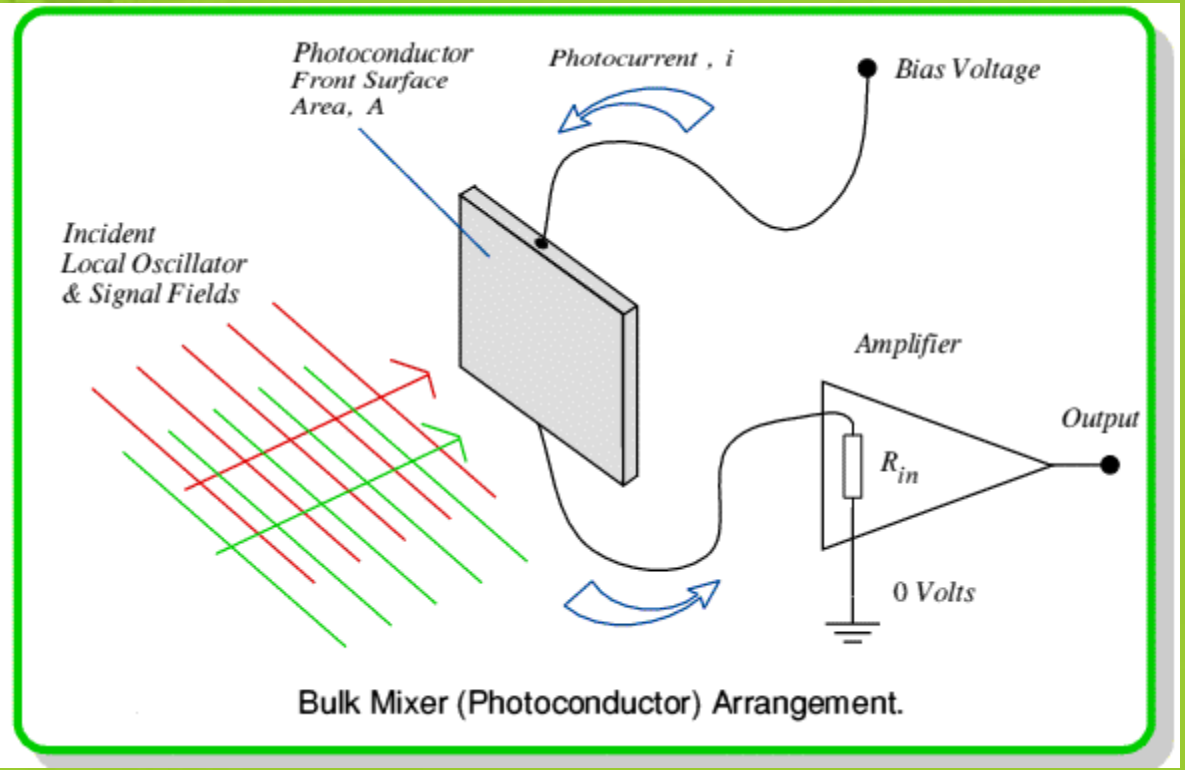
Schematic of a pyroelectric detector.

Pyroelectric Detectors

- The pyroelectric crystal acts as a temperature dependent capacitor
- When IR radiations fall there is a change in temperature, which alters the charge distribution across the crystal which can be detected as a current in an external circuit connecting to two sided of capacitor.
- Magnitude of current is directly proportional to surface area of crystal and rate of change of polarization with temperature.

Photo Conducting Detector

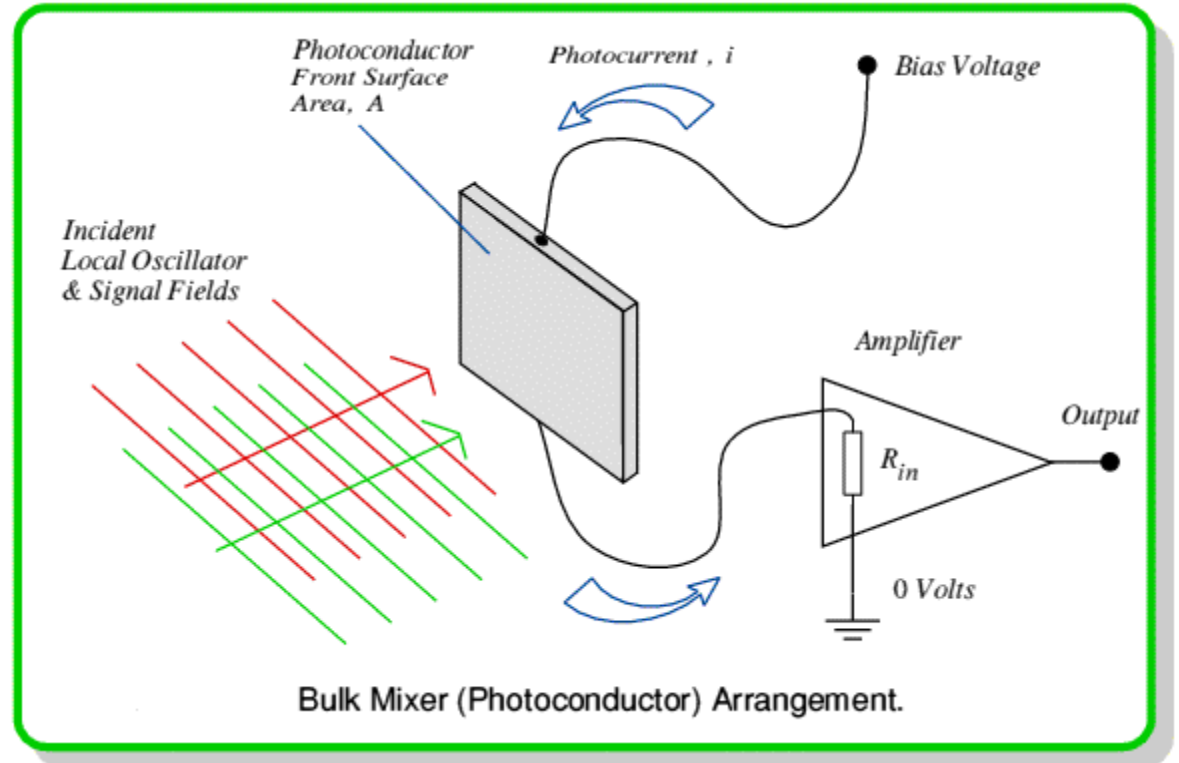
- They consists of a thin film of semiconductor material such as lead sulphide, mercury cadmium telluride or Indium antimonide deposited on Non conducting glass surface & sealed into an evacuated envelope to protect semiconductor from atmosphere



Bulk Mixer (Photoconductor) Arrangement.

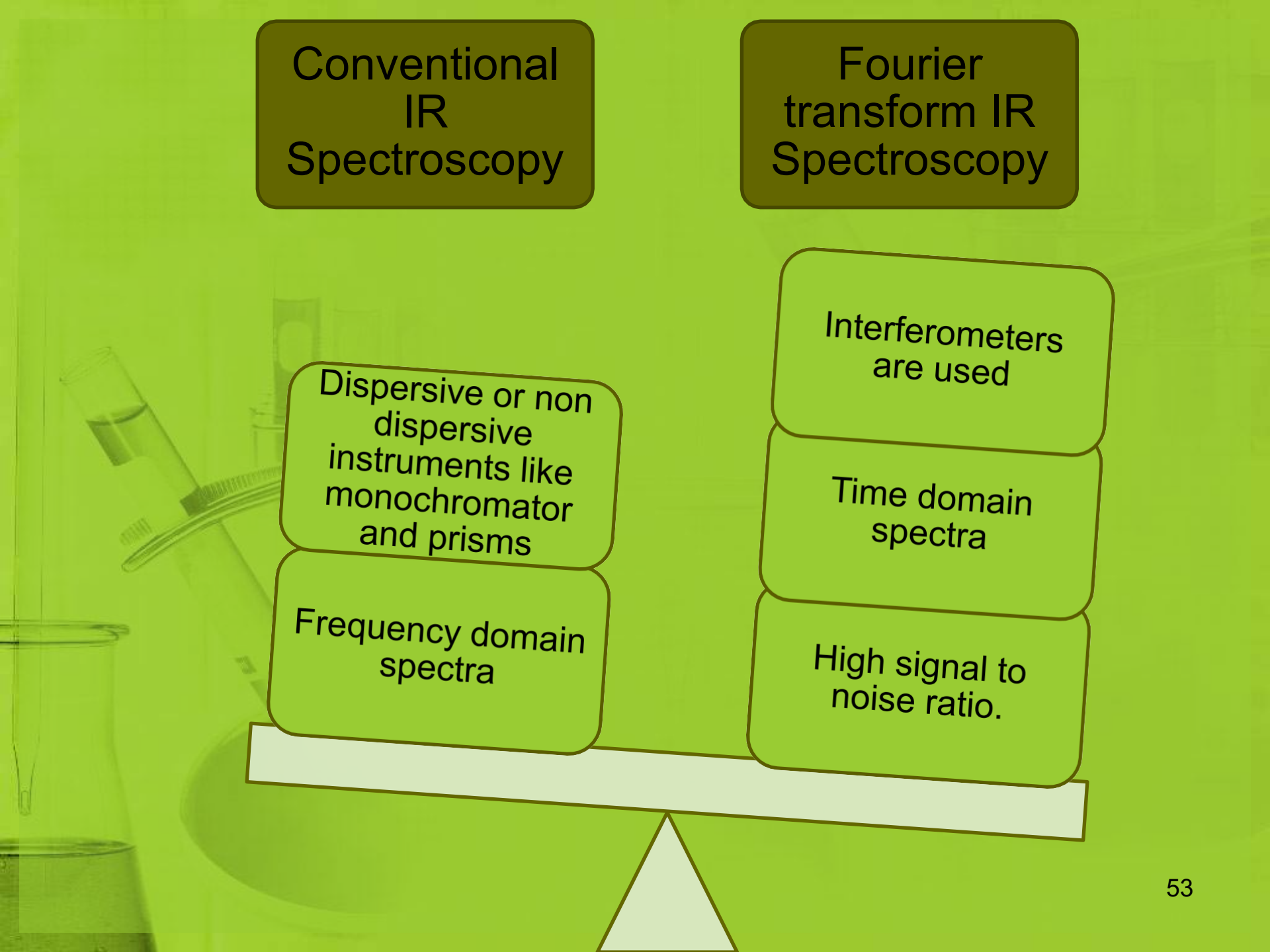
Photo Conducting Detector

- Absorption of radiation by these materials promote non-conducting valence electrons to a higher energy conducting state thus decreasing electrical resistance of semiconductor.

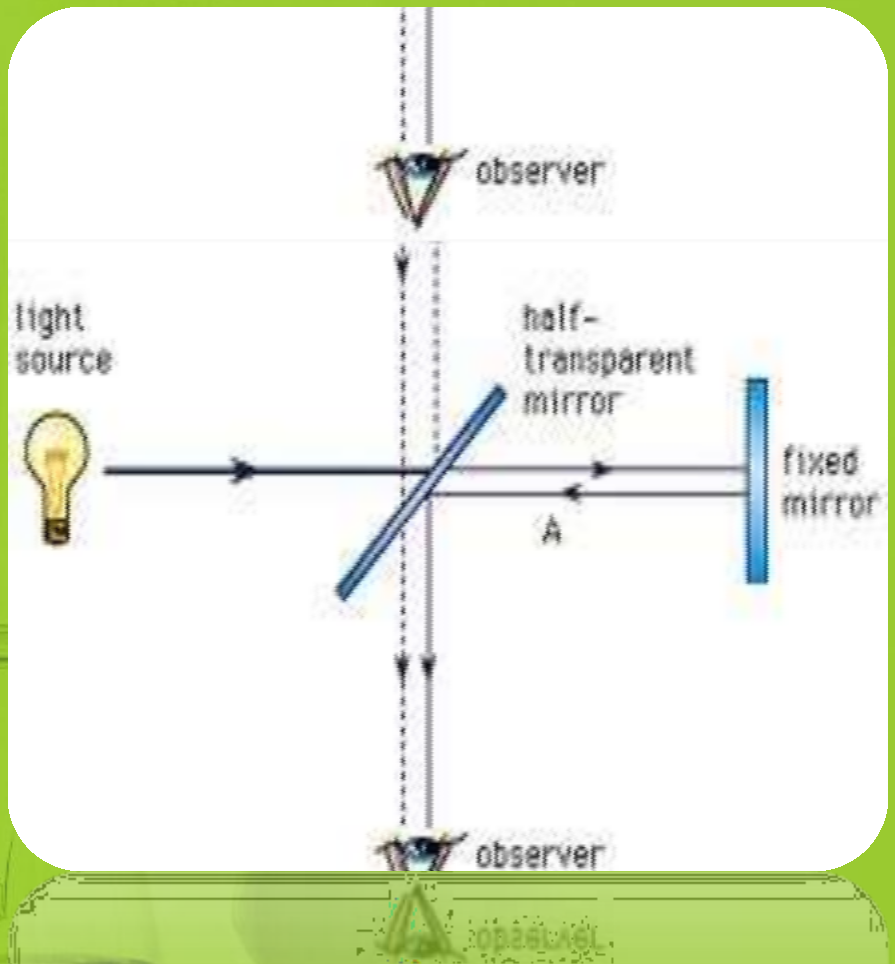


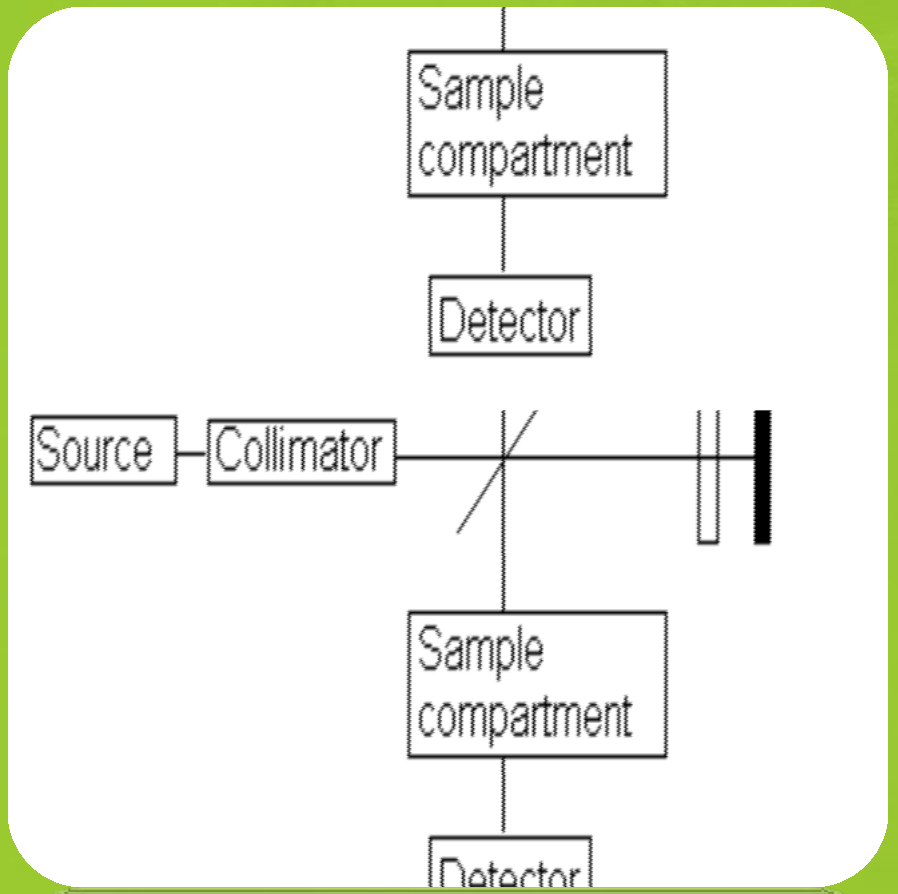
Bulk Mixer (Photoconductor) Arrangement.

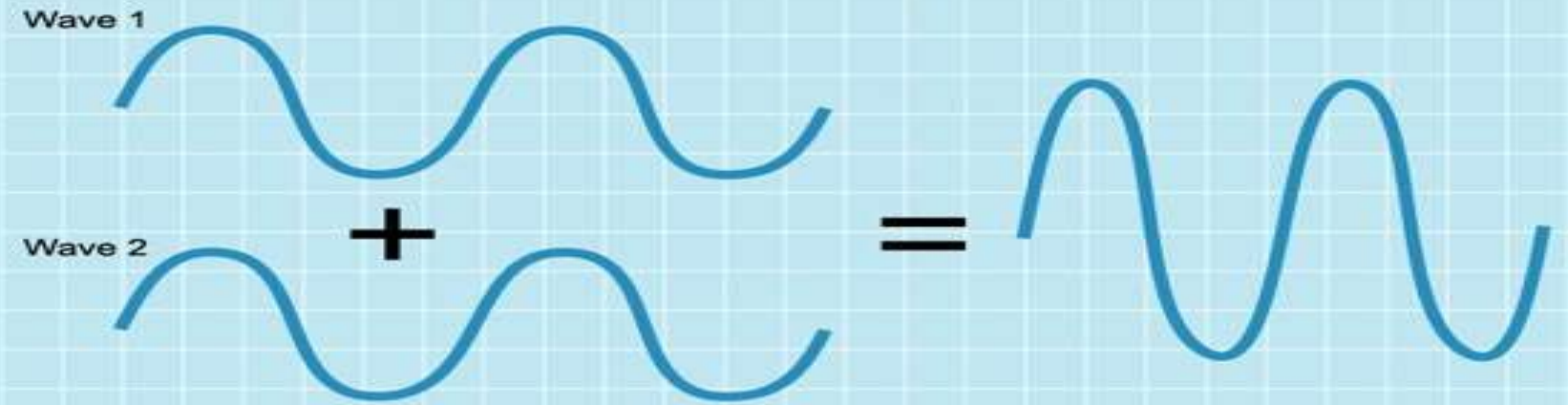
Conventional IR Spectroscopy	Fourier transform IR Spectroscopy
Dispersive or non dispersive instruments like monochromator and prisms	Interferometers are used
Frequency domain spectra	Time domain spectra
	High signal to noise ratio.



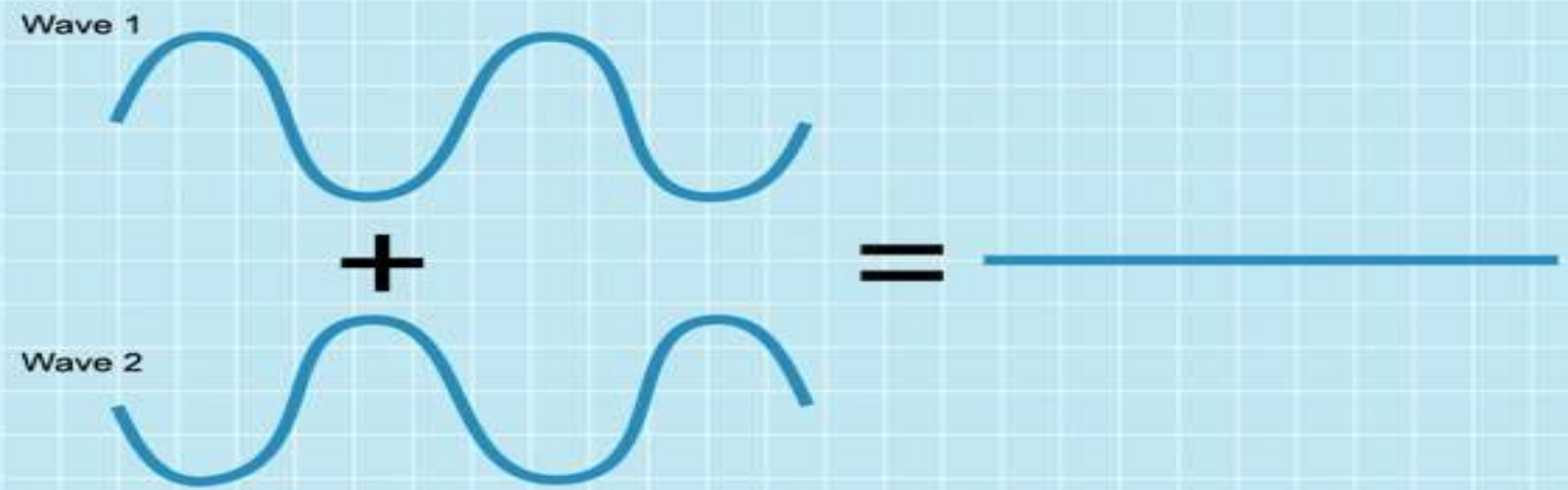
FTIR : Michealson interferometer







Constructive interference

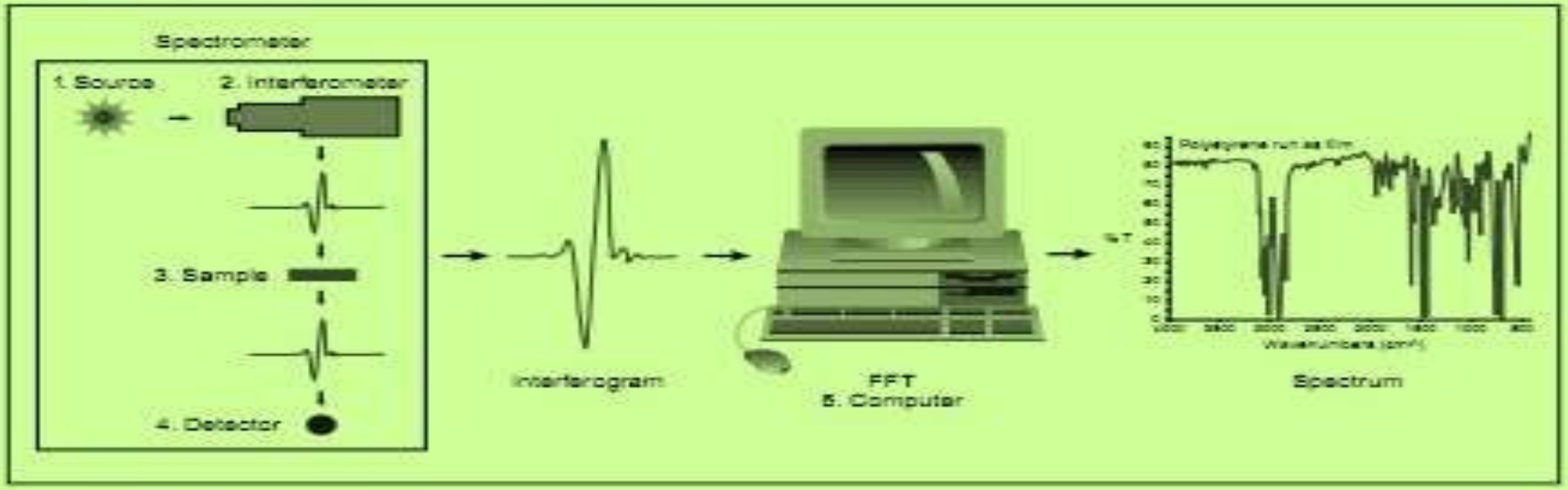


Destructive interference

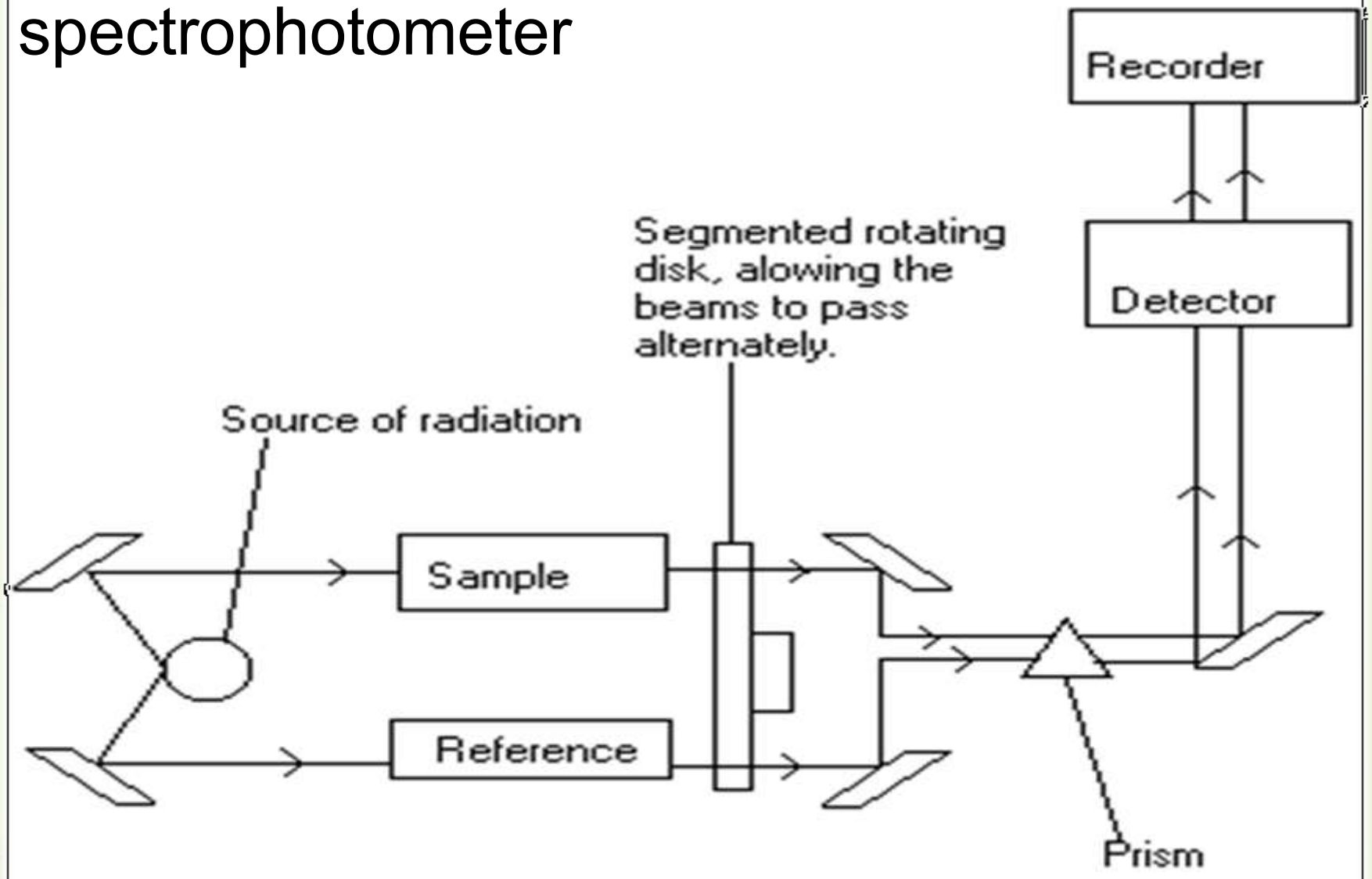
The Sample Analysis Process

The normal instrumental process is as follows:

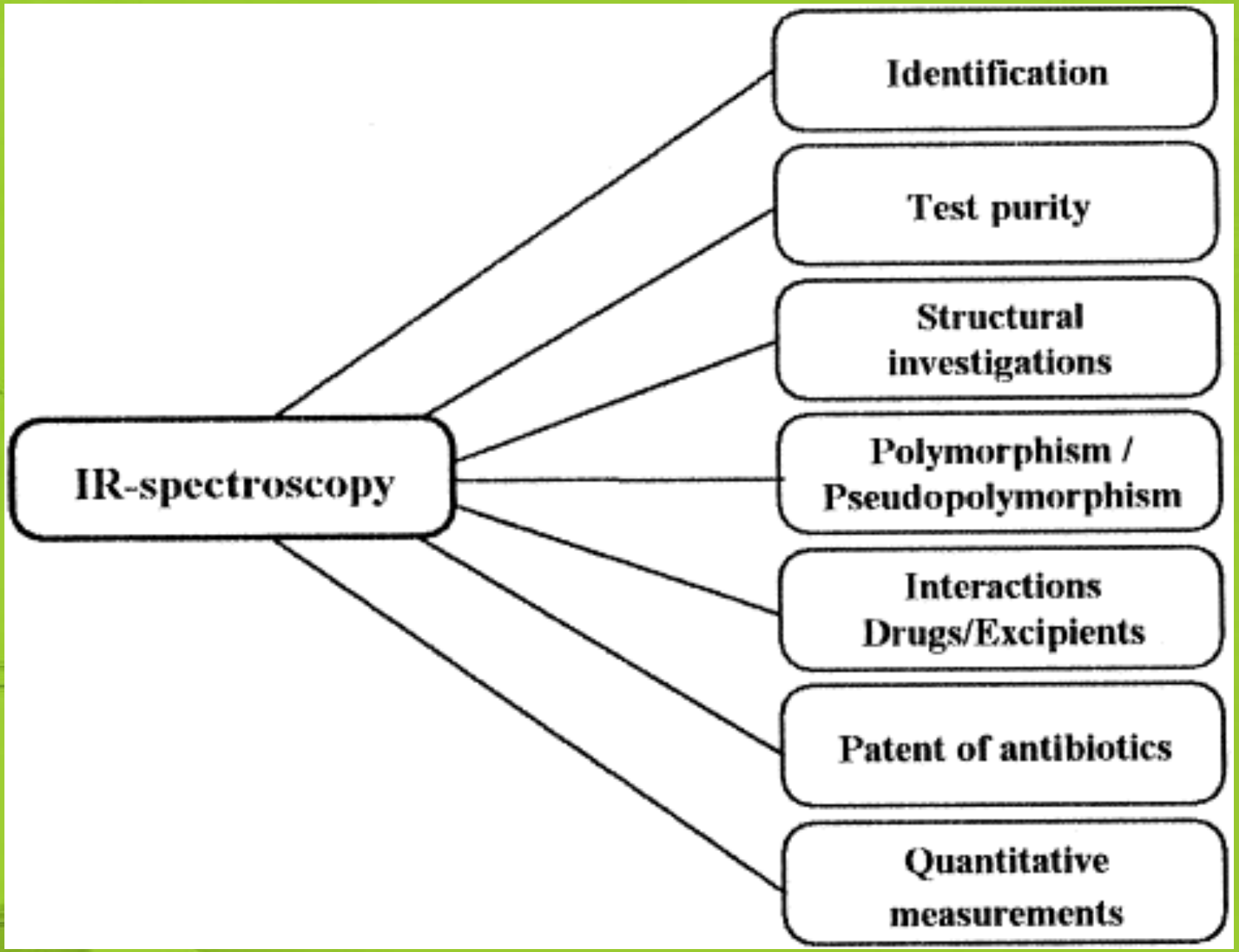
1. **The Source:** Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).
2. **The Interferometer:** The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exits the interferometer.
3. **The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.
4. **The Detector:** The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.
5. **The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.



Double beam infrared spectrophotometer



Infrared spectrophotometer


IR-spectroscopy
Identification
Test purity
Structural investigations
Polymorphism / Pseudopolymorphism
Interactions Drugs/Excipients
Patent of antibiotics
Quantitative measurements

APPLICATIONS OF IR SPECTROSCOPY

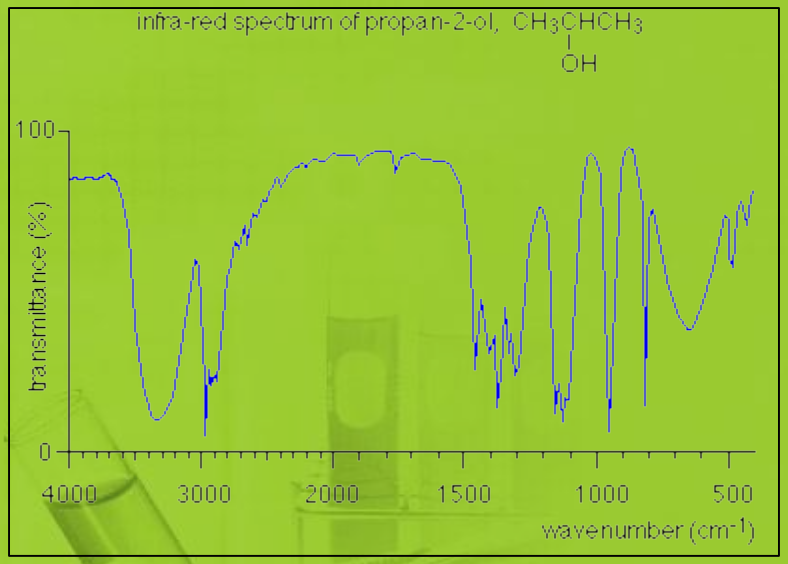
•Infrared spectroscopy is widely used in industry as well as in research.
Some of the major applications of IR spectroscopy are as follows:

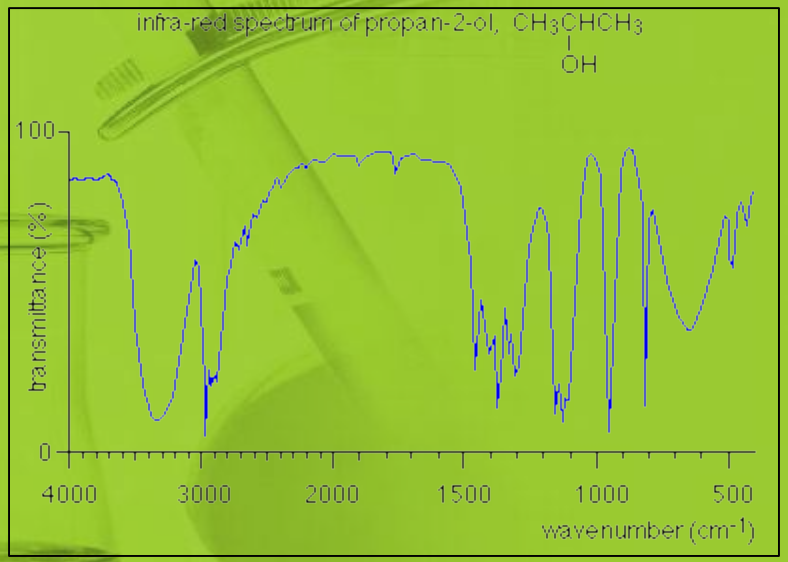
1. Identification of functional group and structure elucidation

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

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

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





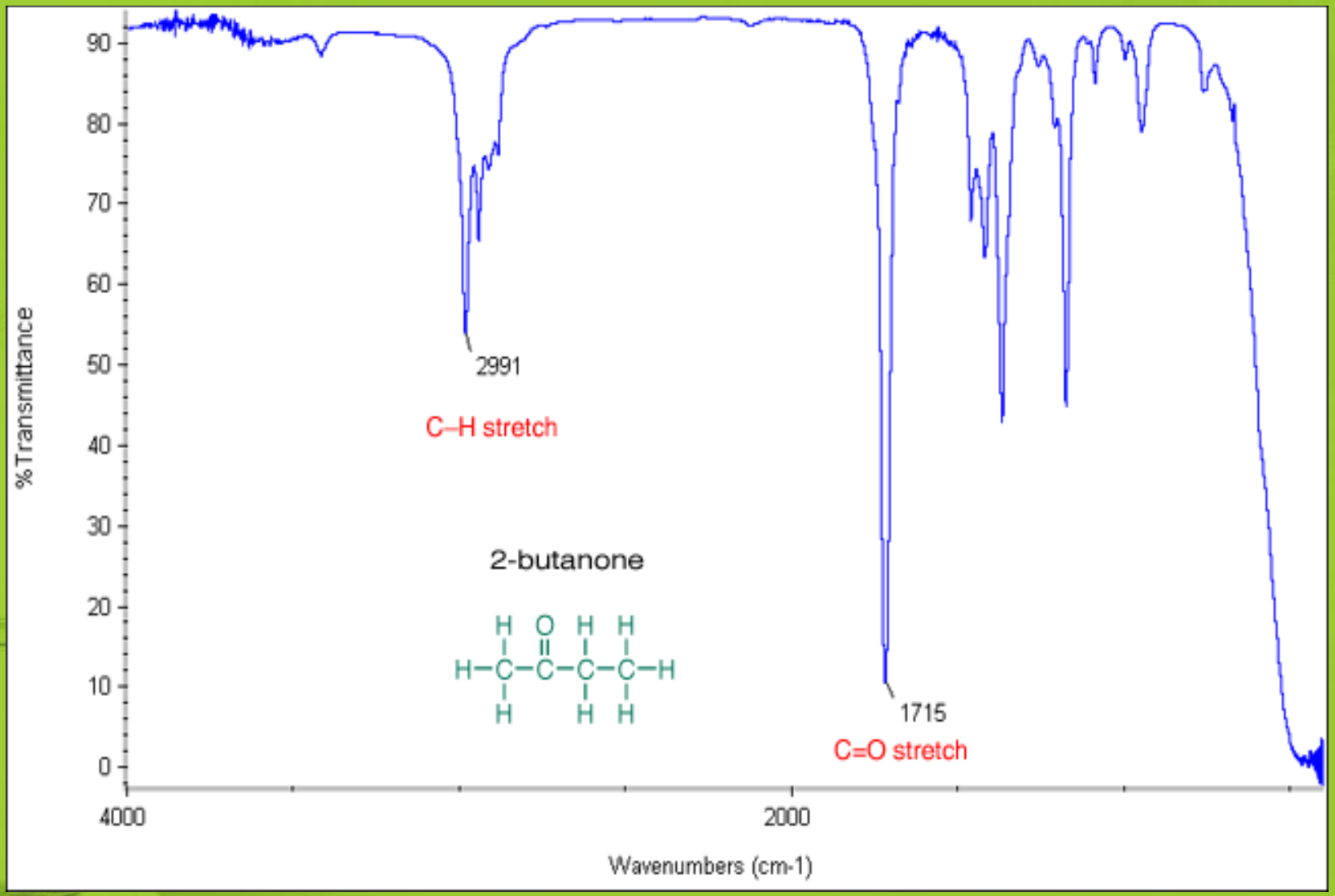
Using the fingerprint region

- Compare the infra-red spectra of propan-1-ol and propan-2-ol.
- Both compounds contain exactly the same bonds.
- Both compounds have very similar troughs in the area around 3000 cm^{-1} - but compare them in the fingerprint region between 1500 and 500 cm^{-1}.
- The pattern in the fingerprint region is completely different and could therefore be used to identify the compound.

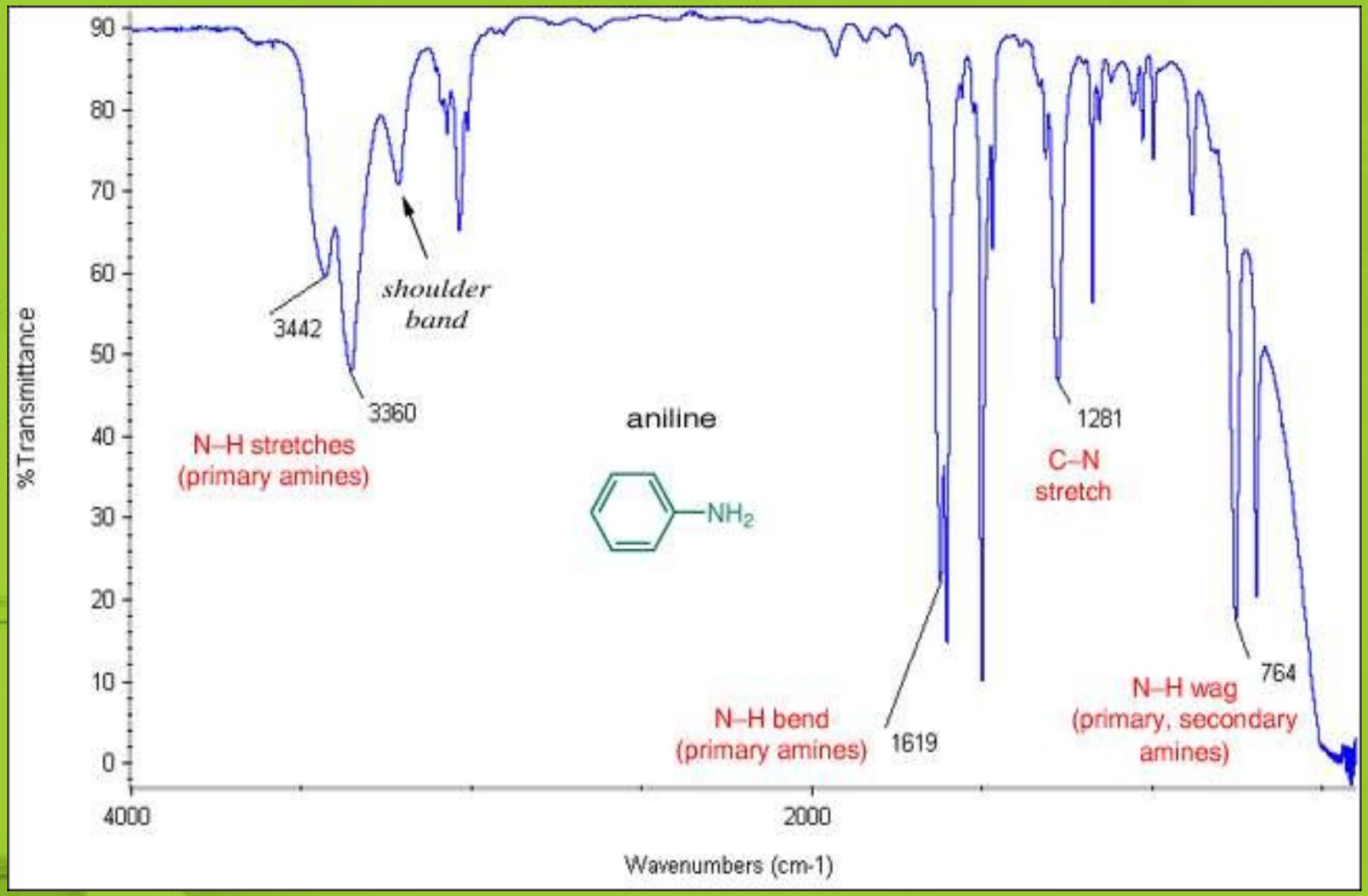
Table of IR Absorptions

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

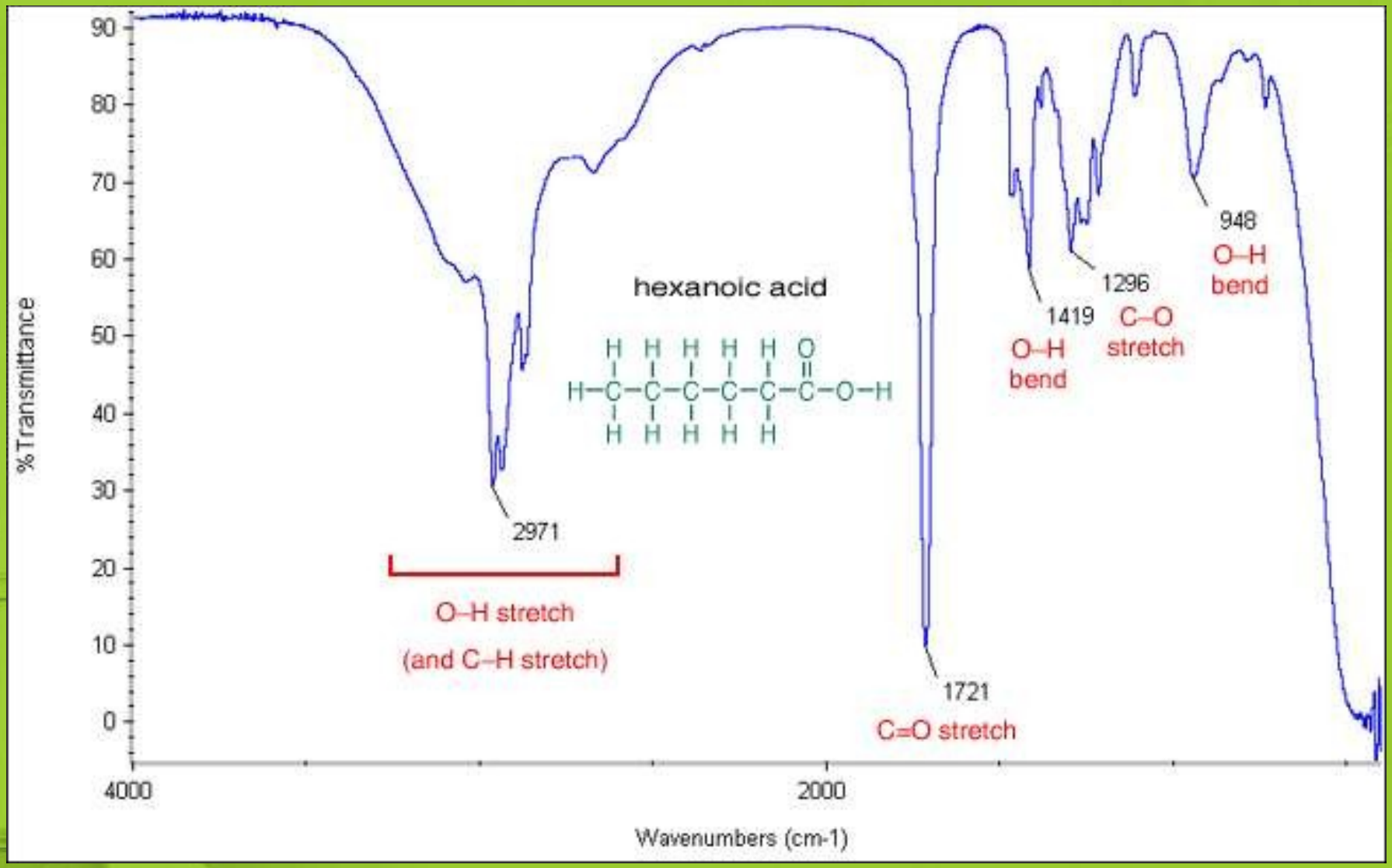
Ketones


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
2991
C–H stretch
1715
C=O stretch
2-butanone

Amines


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
3442
3360
shoulder band
N–H stretches (primary amines)
aniline
NH2
1619
N–H bend (primary amines)
1281
C–N stretch
764
N–H wag (primary, secondary amines)

Alcohols


% Transmittance
90
80
70
60
50
40
30
20
10
0
4000
2000
Wavenumbers (cm-1)
hexanoic acid
2971
O–H stretch
(and C–H stretch)
1721
C=O stretch
1419
O–H
bend
1296
C–O
stretch
948
O–H
bend

APPLICATIONS OF IR SPECTROSCOPY

2. Identification of substances

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

APPLICATIONS OF IR SPECTROSCOPY

3. Studying the progress of the reaction

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

APPLICATIONS OF IR SPECTROSCOPY

4. Detection of impurities

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

APPLICATIONS OF IR SPECTROSCOPY

5. Quantitative analysis

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

Disadvantages of IR in Quantitative analysis

- Non adherence of beers law
- Complexity of spectra


THANK YOU!