# 3. INFRARED SPECTROSCOPY

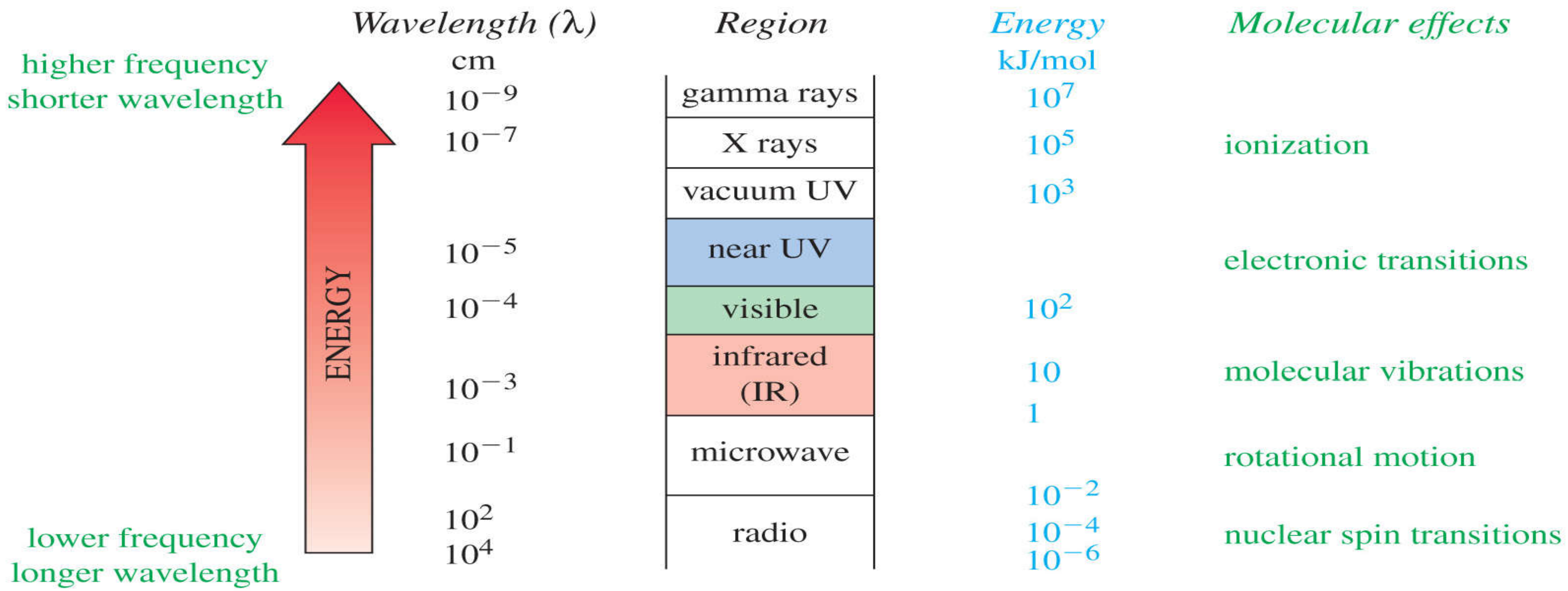
After completing this course, students will be able to explain

- Principles of IR spectrophotometry
- the instrumentation of IR spectrophotometry
- Interpretation of IR spectra
- their use in pharmaceutical analysis

## Infrared Spectrophotometry

- Concerned with the study of absorption of infrared radiation, which causes vibrational transition in the molecule
- Hence, IR spectroscopy also known as Vibrational spectroscopy
- IR radiation does not have enough energy to induce electronic transitions as seen with UV
- Provides mostly information about the presence or absence of certain functional groups
- The IR spectrum is commonly known as the finger print of compounds
- The spectrum bands in the IR spectrum represent the functional groups and bonds present in the cpds

# The Electromagnetic Spectrum



## Introduction….

- The IR region of the electromagnetic spectrum is divided into three regions
  - Near infrared region: 0.8-2.5 µm (12,500–4,000 $cm^{-1}$ )
  - Middle infrared region: 2.5-50 µm (4,000-200 $cm^{-1}$ )
  - Far infrared region: 50-1000 µm (200-10 $cm^{-1}$)

## Principle of IR spectroscopy

- When IR radiations between 4000-400 $cm^{-1}$ are passed through a sample, some of the radiations are absorbed by the sample and are converted into energy of molecular vibrations
- The other radiations which do not interact with the sample are transmitted through the sample without being absorbed
- Different functional groups absorb characteristic frequencies of IR radiation, gives the characteristic peak value
- The plot of % transmittance against wave number is called the infrared spectrum of the sample

## Molecular vibrations

There are 2 types of vibrations for molecules

1. Stretching vibrations
2. Bending vibrations

- Stretching frequencies are higher than corresponding bending frequencies

## 1. Stretching vibrations:

- The distance between two atoms increases or decreases, but atoms remain in the same bond axis (need high energy)
- Occurs at higher energy: 4000-1250 $cm^{-1}$

2 types:

a) Symmetrical stretching

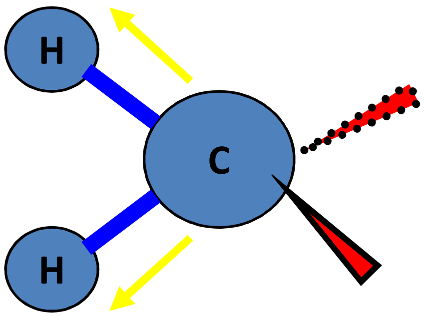
b) Asymmetrical stretching

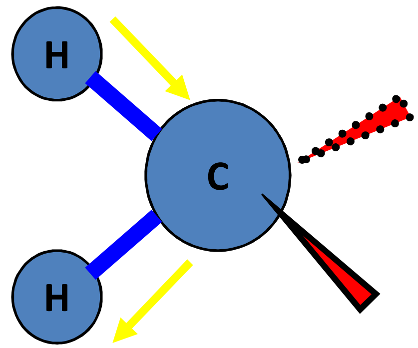
a) Symmetrical stretching:

- two bonds increase or decrease in length simultaneously

b) Asymmetrical stretching

- one bond length is increased and other is decreased




2. Bending vibrations

- The position of atoms changes relative to the original bond axis

  (Effect on angle and requires low energy)

- bond angle is altered

- Occurs at low energy: 1400-666 $cm^{-1}$

Examples: In plane bending: scissoring, rocking

## In plane bending

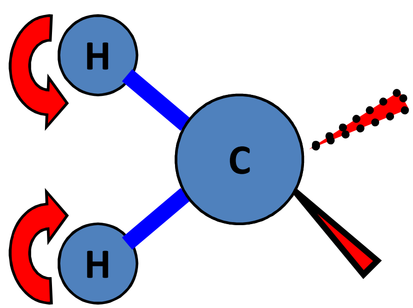
i. Scissoring:

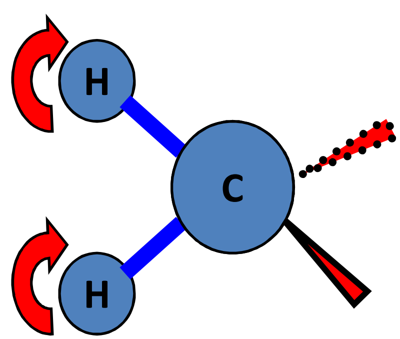
– 2 atoms approach each other

– Bond angles are decrease

ii. Rocking:

– Movement of atoms take place in the same direction



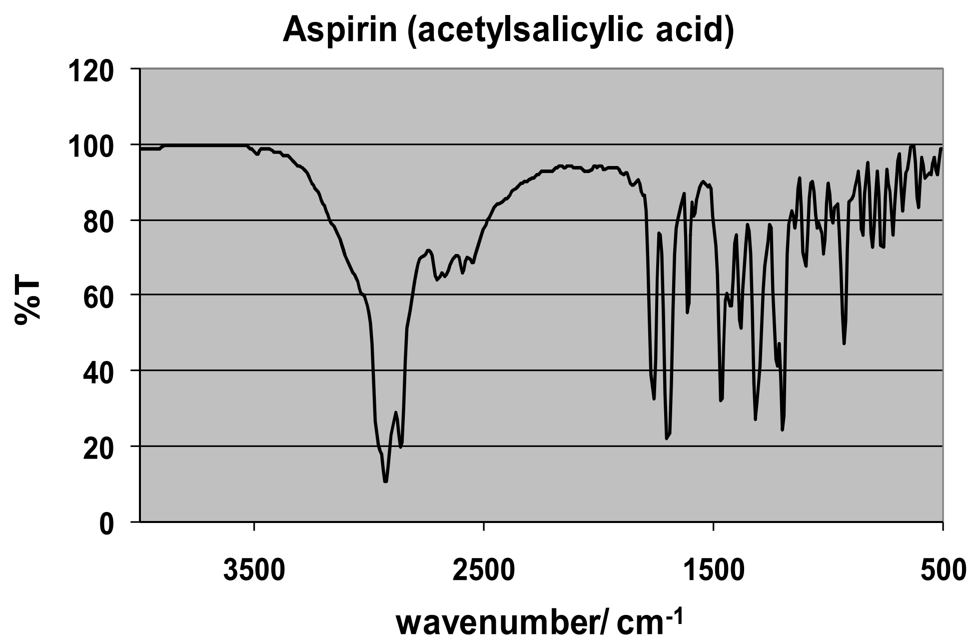
- The stretching energy of a bond **is greater than** its bending energy.
- Therefore stretching absorption of a bond appear at **higher frequency** than the bending absorption of the same bond.

| | |
|---|---|
| **Mostly stretching vibrations**<br><br>**(Functional gp. Region)** | **Mostly bending vibrations**<br><br>**(Fingerprint region)** |

4000 1400 650 **$cm^{-1}$**

## Spectrum presentation

- Infrared spectra are displayed as %T (percent transmittance) versus wave number (4000- 400 cm-1)
- Compared with UV/visible the spectrum is inverted
- The spectrum is rich in peaks



## Region of IR spectrum

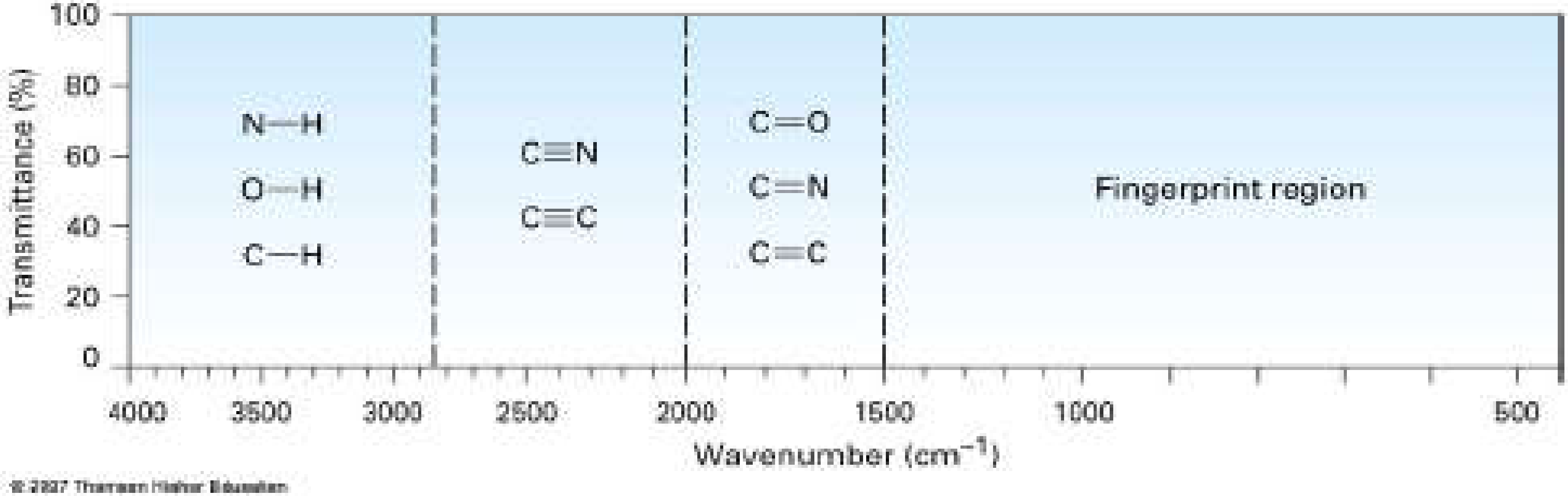
- A molecule absorbs IR radiations of various wave lengths upon the nature of groups or bonds present in it and gives characteristic absorption bands
- The presence of characteristic absorption band indicates the presence of a particular functional group
- There are two general regions in the infrared spectrum

1. group frequency region/ functional group region

- The stretching and bending vibrational bands associated with specific structural or functional groups are observed frequently

## 2. Finger print region

- vibrational frequencies are affected by the entire molecule
- absorption in fingerprint region is characteristic of the molecule as a whole
- unique for any given organic compound
- This region finds widespread use for identification purpose by comparison with library spectra
- the fingerprint region of an unknown compound can be compared with the fingerprint region of a known sample, and if they match exactly, the unknown and known are identical




Most functional groups absorb at about the same energy and intensity, independent of the molecule they are in

- A sharp band around 2200-2400 cm-1 would indicate the possible presence of a C-N or C-C triple bond

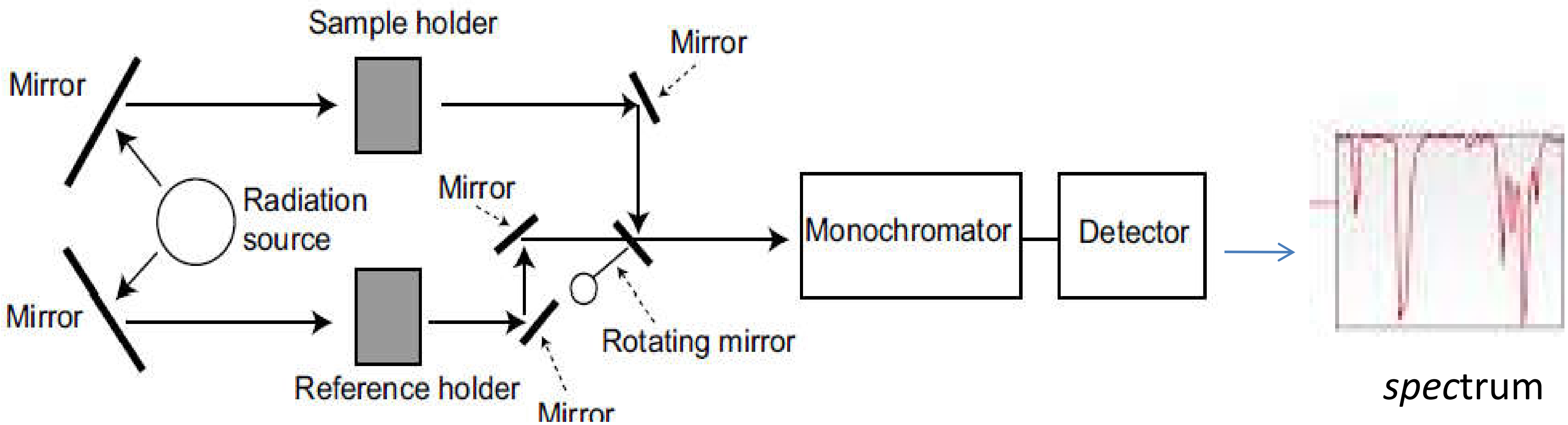
# Instrumentation

Two types of IR spectrometers are commonly used

## 1) dispersive type

- IR is separated into individual frequencies by dispersion (grating or monochromator
- The radiation source emits continuous IR radiation that is split into two equivalent beams that pass through the sample and the reference holder
- The beam then passes into the monochromator, which disperses each into a continuous IR spectrum
- Record a spectrum in frequency domain

# Instrumentation



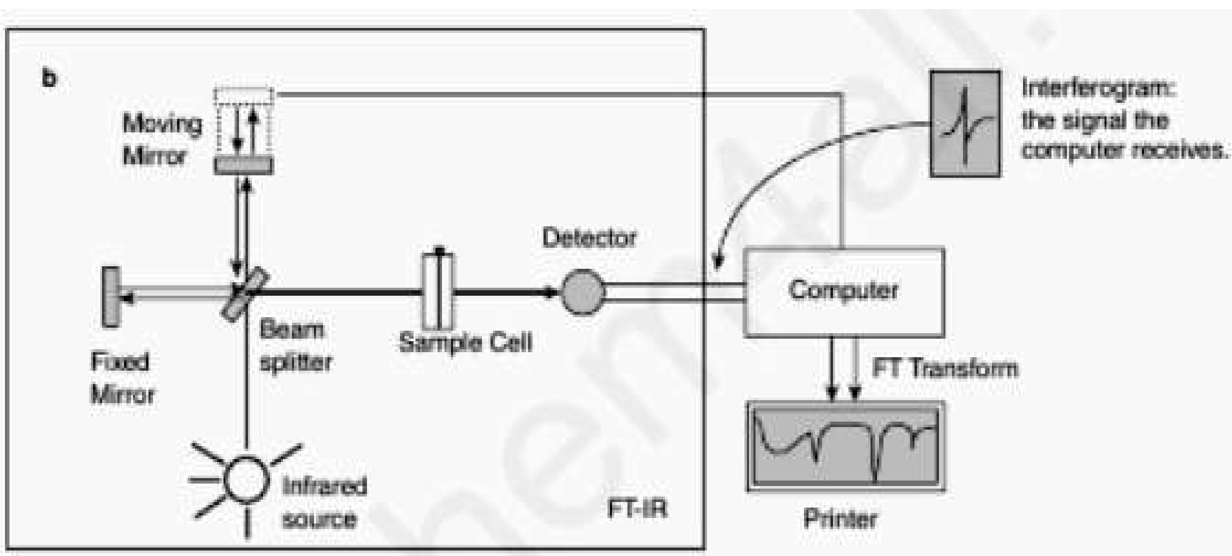
## 2. Fourier transform (FTIR)

- monochromator is replaced by an interferometer
- the light source is focused using an interferometer
  - allows the desired wavelengths and block the undesired wavelengths
- In a Fourier transform IR instrument, the principles are the same except that the monochromator is replaced by an interferometer.
- An interferometer uses a moving mirror to displace part of the radiation produced by a source, thus producing an interferogram, which can be transformed using an equation called the ‘Fourier transform’ in order to extract the spectrum from a series of overlapping frequencies.
- A mathematical equation called Fourier transform can separate individual frequencies from the Interferogram, producing spectrum identical to that obtained with dispersive instruments

$$\text{Time} \xrightarrow{\text{FT}} \text{Frequency}$$

2. FTIR………

- In recent years, Fourier transform instruments have become very common
- a full spectral scan can be acquired in about 1 s, compared with the 2–3 min required for a dispersive instrument
- Both of the instruments nearly identical spectra for a given compound in the range of 4000- 400 cm-1
- FTIR spectrometers provide the IR spectrum rapidly

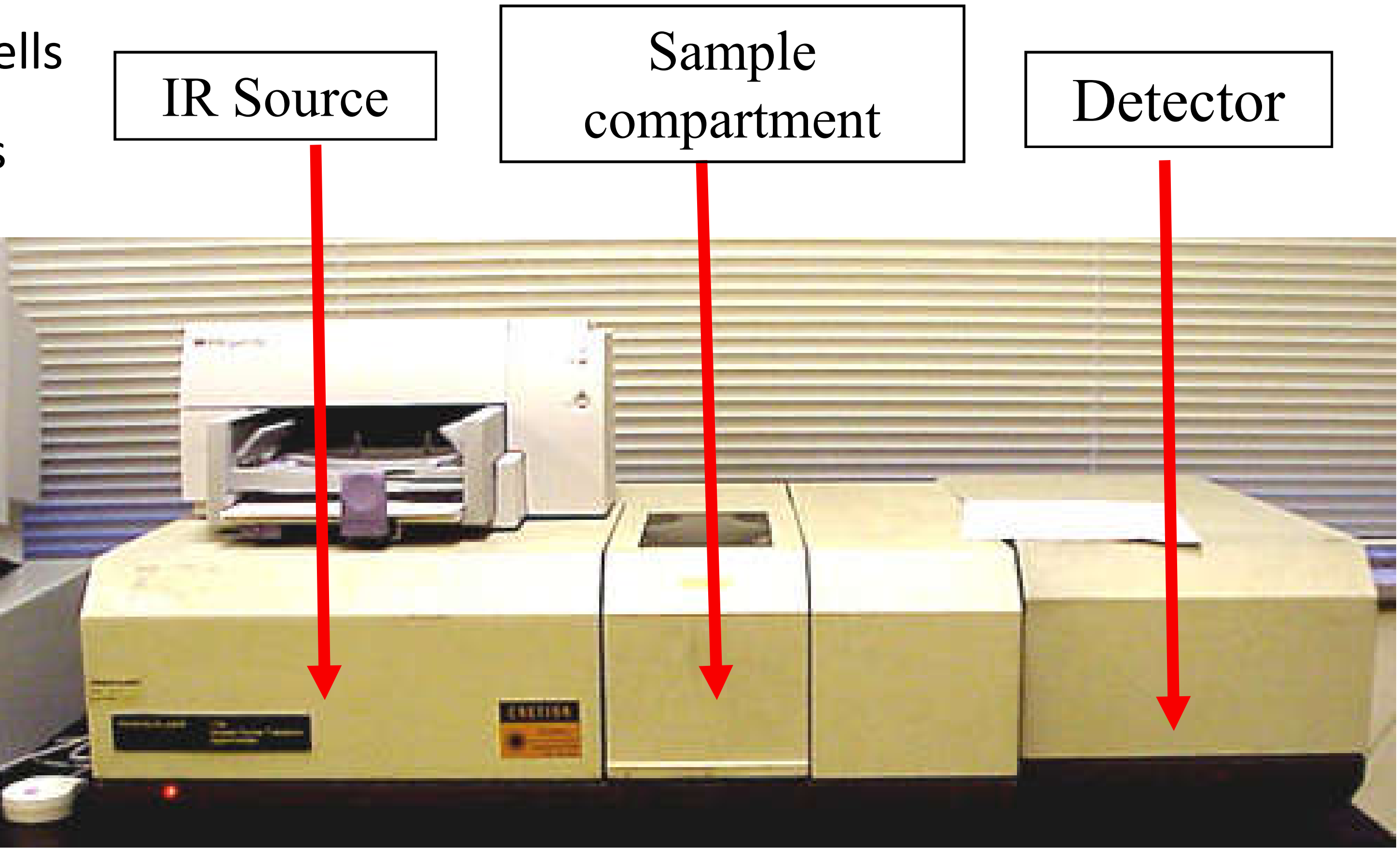


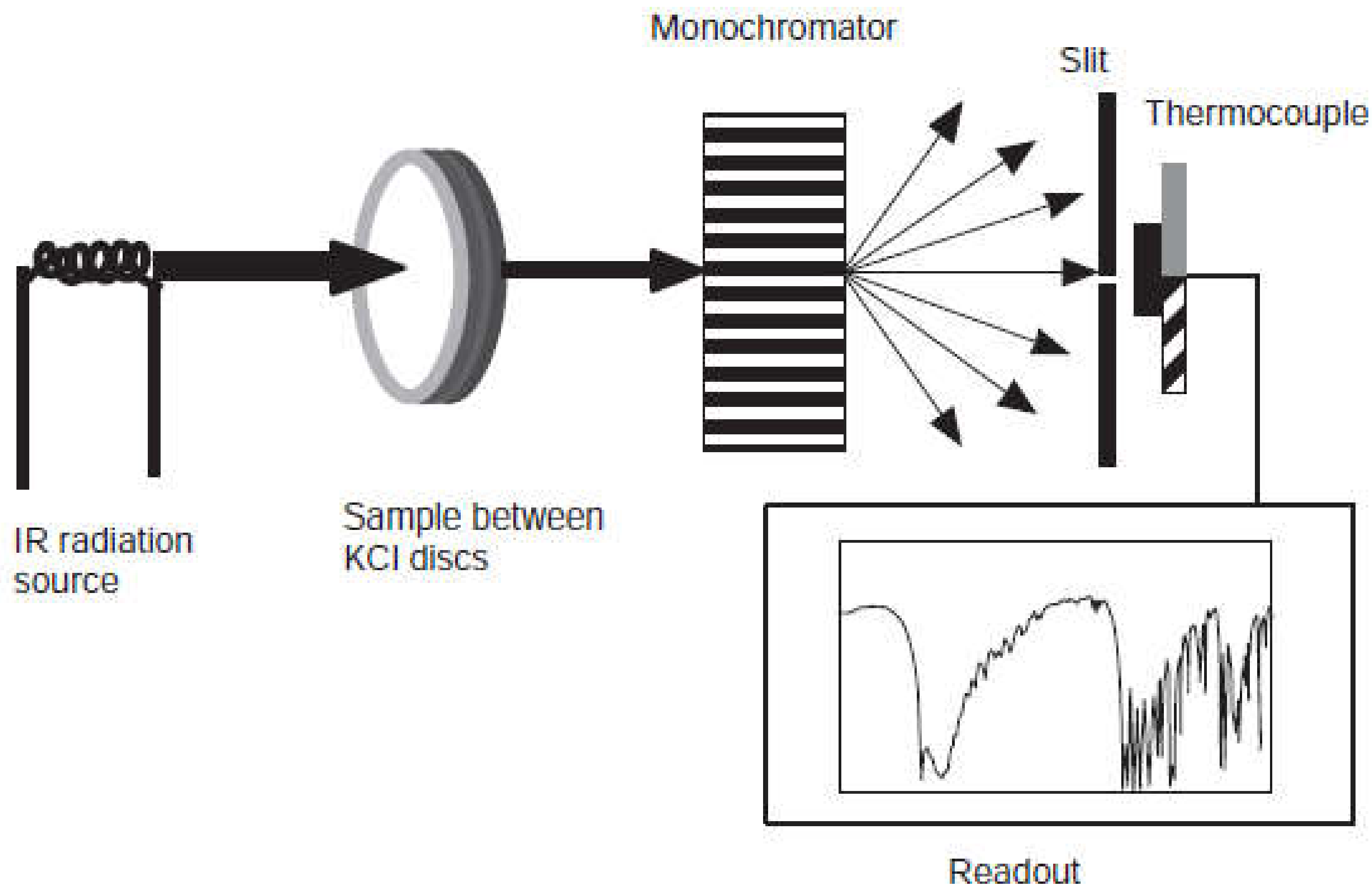

FT–IR instruments

## Instrumentation

The components of IR spectrometer are

- Radiation source
- Monochromators
- Sample cells
- Detectors






The essential components for a dispersive IR instrument

## 1. Radiation source

- heated solids are used
- The common temperature required to emit the IR radiation is 1,500–2,000 K
- Most commonly used radiation sources are:
  - Nernst glower:
    - Composed of metal oxides, e.g. zirconium, yttrium and thorium oxides, and is heated to produce IR radiation
  - Globar source:
    - Silicon carbide is generally used as a globar source

## 2. SAMPLE CELL

- Made up of alkali halides like NaCl or KBr

## 3. Monochromators

- convert polychromatic light into monochromatic light
- the light passed through the sample is dispersed so that an individual wave number can be monitored by the detector across the range of the spectrum
- The most commonly used monochromators are

  a) metal halide prisms (KBr, LiF, CeBr)

  b) NaCl prisms

  c) gratings

## 4. Detectors

- The principle relies upon the thermal effect of IR radiation
- Thermal detectors are commonly used in IR spectrometry
  - Sensors that measure radiation by means of the change of temperature of an absorbing material
- The commonly employed thermal detectors are
  - Thermocouples
  - Bolometer
  - Golay detector
  - Pyroelectric detector

## PREPARATION OF SAMPLES FOR INFRARED SPECTROSCOPY

- To determine the infrared spectrum of a compound, one must place the compound in a sample holder, or cell. In infrared spectroscopy, this immediately poses a problem.
- Glass and plastics absorb strongly throughout the infrared region of the spectrum. Cells must be constructed of ionic substances typically **sodium chloride or potassium bromide**.
- Potassium bromide plates are more expensive than sodium chloride plates but have the advantage of usefulness in the range of 4000 to 400 $cm^{-1}$.
- Sodium chloride plates are used widely because of their relatively low cost. The practical range for their use in spectroscopy extends from 4000 to 650 $cm^{-1}$.
- Sodium chloride begins to absorb at 650 $cm^{-1}$, and any bands with frequencies less than this value will not be observed. Since few important bands appear below 650 $cm^{-1}$, sodium chloride plates are in most common use for routine infrared spectroscopy.

## Samples

- Infrared spectra may be obtained for liquid, solid and gases samples
- Spectra of solids are obtained as alkali halide discs (KBr ), mulls and films

### Alkali halide discs

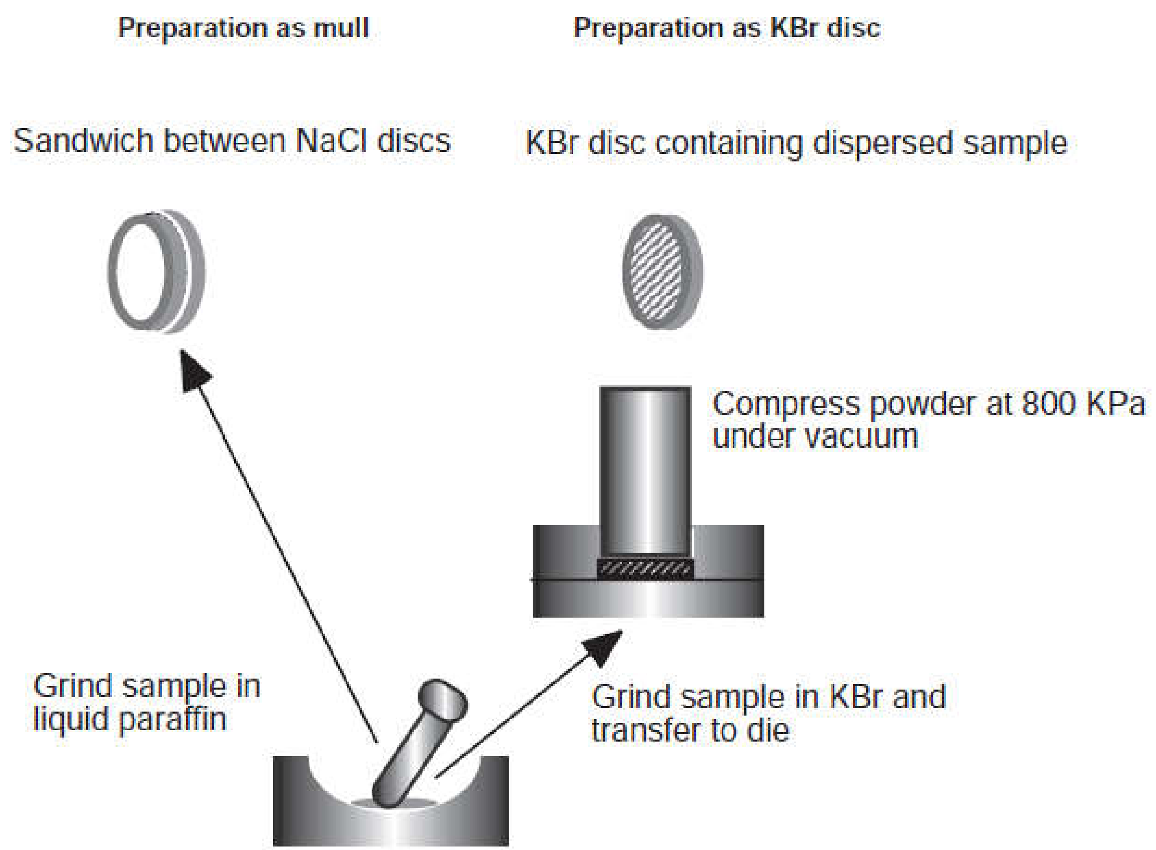
1. A milligram of the fine ground sample is mixed with about 100 mg of dry alkali halide(KBr) powder in a mortar
   - commonly used is potassium bromide (KBr), which is completely transparent in the mid-IR region
2. The mixture compressed in a die under high pressure to form transparent KBr disc

   Under pressure, the KBr melts and seals the compound into a matrix.

   a KBr transparent disc that can be inserted into an IR a sample holder is formed

- the weight of the sample is about 1% of the weight of KBr used

**Fig. 5.6**
Preparation of samples as discs and mulls.



IR transparent Salt Plates

## Mulls

- The sample is mixed with mineral oil to form a smooth paste
- The most commonly used mulling agent is Nujol (liquid paraffin)
- The paste is placed between salt plates made up of NaCl or KBr

## films

- The sample is dissolved in a solvent, most commonly carbon tetrachloride($CCl_4$) and it is evaporated on the surface of a NaCl and KBr cells

## Liquid samples

- A drop of a liquid organic compound is placed between a pair of sodium chloride or potassium bromide plates
- When the plates are squeezed gently, a thin liquid film forms between the two plates
- The sample is run as a film sandwiched between two NaCl or potassium chloride (KCl) plates
- A spectrum is referred to as neat spectrum since no solvent is used
- Compounds  analyzed must be free of water

## Gas samples

- A gas sample cell consists of a cylinder of glass or sometimes a metal
- The cell is closed at both ends with an appropriate window materials (NaCl/KBr) and equipped with valves for introduction of the sample
- pathlength must be correspondingly greater, usually 10 cm or longer
- The cells can be filled by flushing or from a gas line

# INFORMATION OBTAINED FROM IR SPECTRA

- IR is most useful in providing information about the presence or absence of specific **functional groups.**

- IR can provide a **molecular fingerprint that can be used when** comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.

- IR **does not provide detailed information or proof of molecular** formula or structure. It provides information on molecular fragments, specifically functional groups.

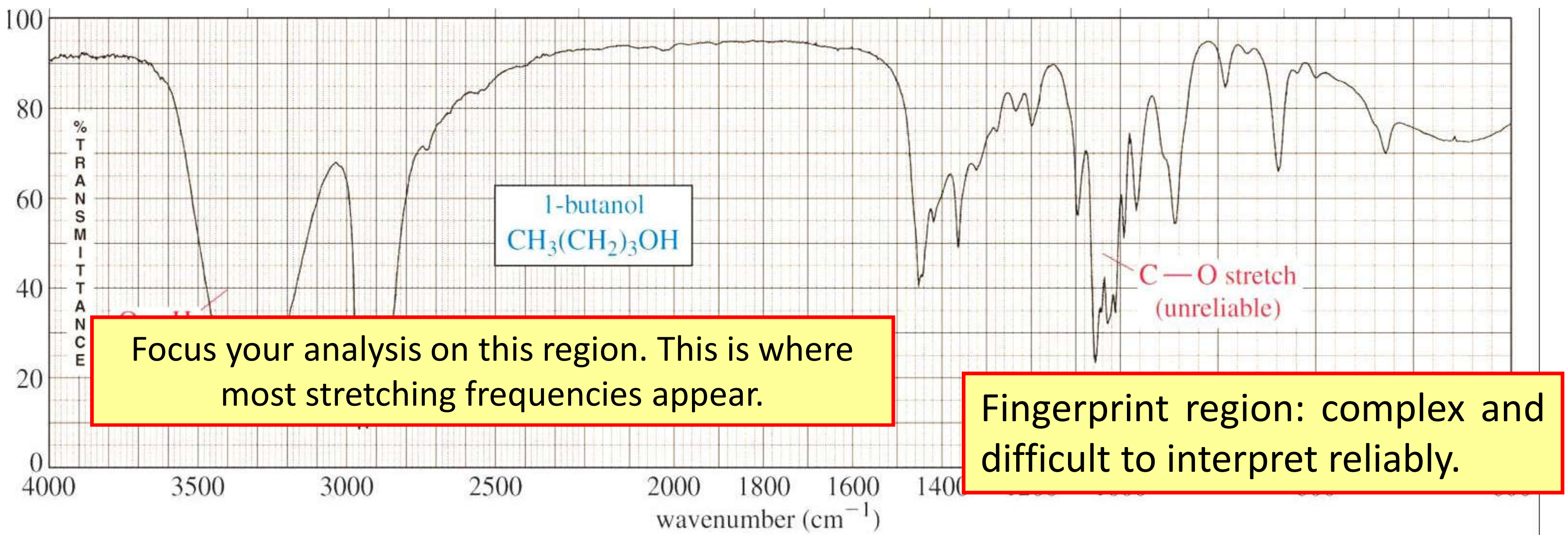
- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.

## Interpretation of the IR spectra

- organic molecules contain many atoms. As a result, there are many stretching and bending modes
- IR spectra have many absorption bands
- Interpretation of the IR spectra is mainly based on the frequencies at which a band occurs within a molecular structure
- The region 4,000–1,500 $cm^{-1}$ easier is to interpret than 1,500–650 $cm^{-1}$
- The most readily assigned absorptions are usually at > 1500 cm-1
- The bands < 1500 cm-1 are in the fingerprint region of the spectrum where the absorption is very complex and it is difficult to be confident in the assignment of absorptions to particular functional groups

## The Fingerprint Region

- is normally a complex area showing many bands, frequently overlapping each other
- This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum
- As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 $cm^{-1}$



- We divide the IR spectrum into five zones, based upon the energy of photons absorbed common functional groups.
- The zones and functional groups are summarized below:

a) Zone 1 (3700–3200 cm-1): alcohol O–H, amine N–H

b) Zone 2 (3200–2700 cm-1): alkyl C–H, aryl C–H, aldehyde C–H, carboxylic acid O–H

c) Zone 3 (2300–2000 cm-1): alkyne

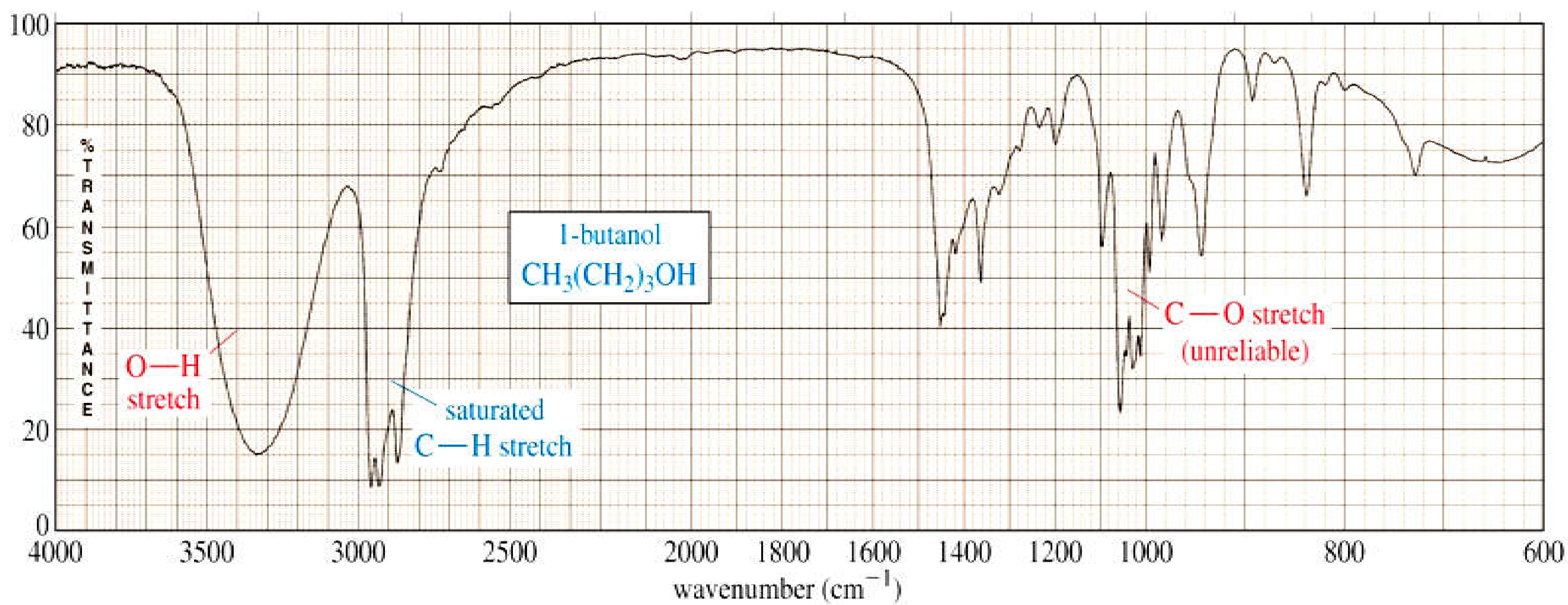
d) Zone 4 (1850–1650 cm-1): carbonyl functional groups

e) Zone 5 (1680–1450 cm-1): alkene, benzene ring

- Alcohol, Amine:
  - the O–H and N–H stretches are usually broadened due to hydrogen bonding
- Carboxylic acid:
  - must have two bands: broad O–H stretch in zone 2 and C=O stretch in Zone 4
- Aldehyde:
  - must have two sets of bands: 2900 and 2700 $cm^{-1}$ in zone 2 ( alkyl C–H stretches), and C=O stretch in zone 4
- Carbonyl: often the most intense peak in the entire spectrum
- Benzene ring: must have bands at about 1600 $cm^{-1}$

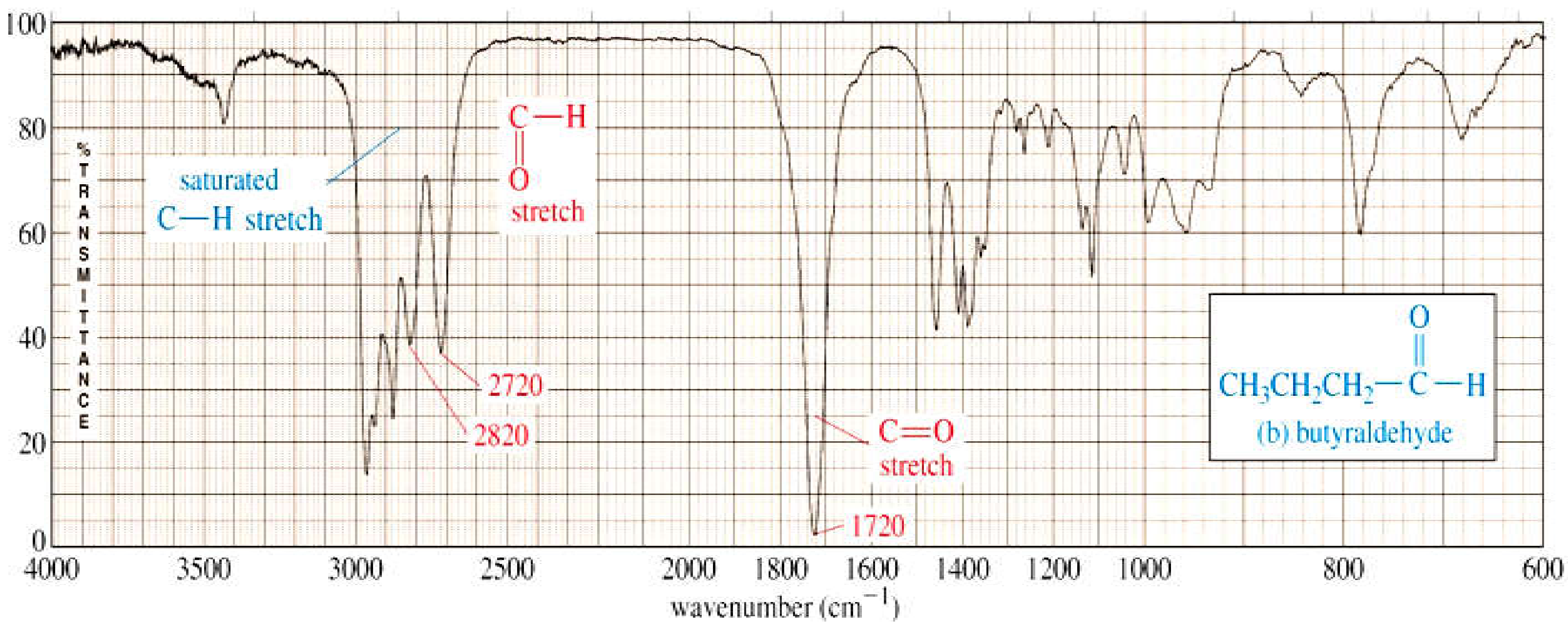
# IR spectrum of an Alcohol

- The most prominent band in alcohols is due to the O-H bond,
- it appears as a strong, broad band in the range of about 3000 - 3700 $cm^{-1}$



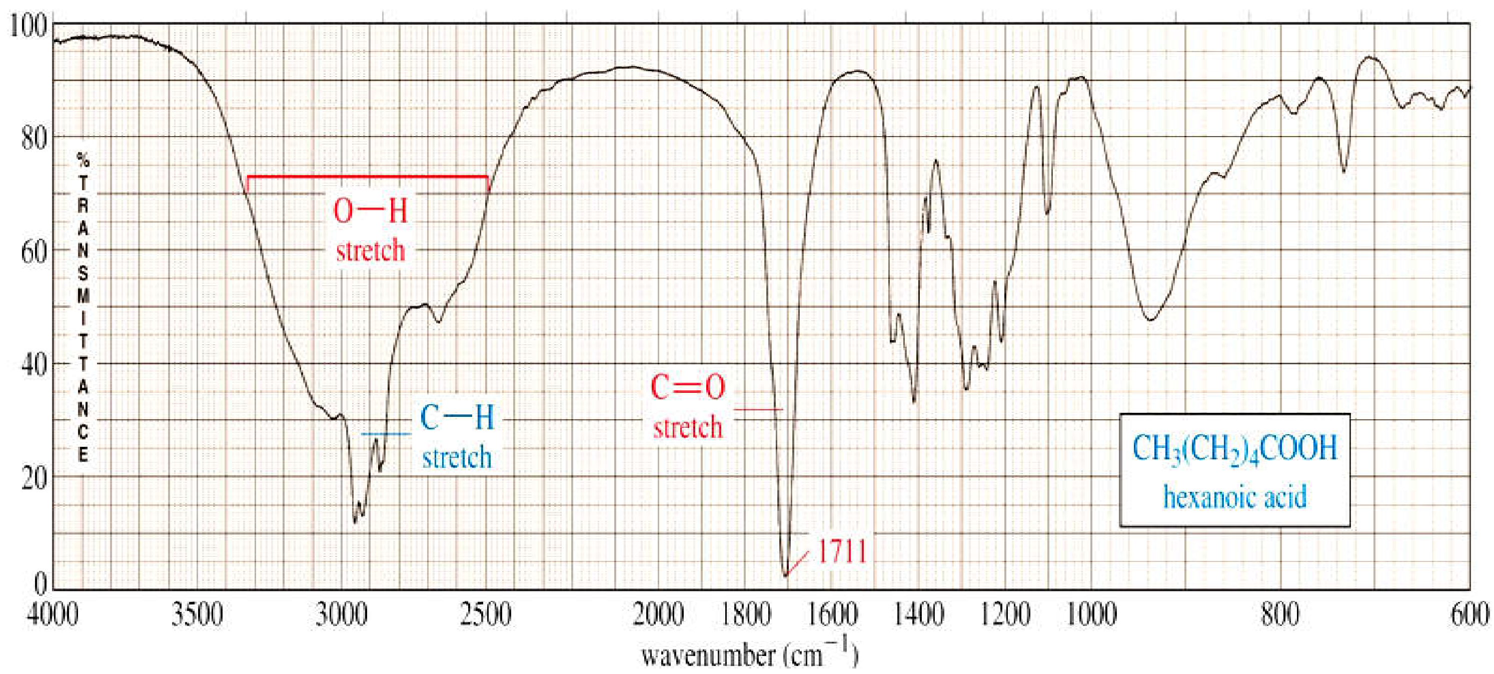
# IR spectrum of Aldehydes

- Carbonyl compounds contain the C=O functional group
- Aldehydes show a strong, prominent, sharp band around 1710 - 1720 $cm^{-1}$ (right in the middle of the spectrum) due to C=O bond
- they also show a pair of medium bands about 2700 and 2800 $cm^{-1}$ due to C-H



# IR spectrum of a carboxylic acid

- A carboxylic acid has both the O-H bond and the C=O bond
- carboxylic acids show a very strong and broad band between 2800 and 3500 $cm^{-1}$ for the O-H stretch
- they also show the strong absorption band in the middle of the spectrum around 1710 $cm^{-1}$ corresponding to the C=O stretch



# IR spectra of amines

- The most characteristic band in amines is due to the **N-H bond stretch** in the range of about 3200 - 3600 $cm^{-1}$
- it appears as a weak to medium, somewhat broad band (not as broad as the O-H band of alcohols)
- Primary amines have two bands in the N-H region
- Secondary amines have only one band
- Finally, tertiary amines have no N-H bonds

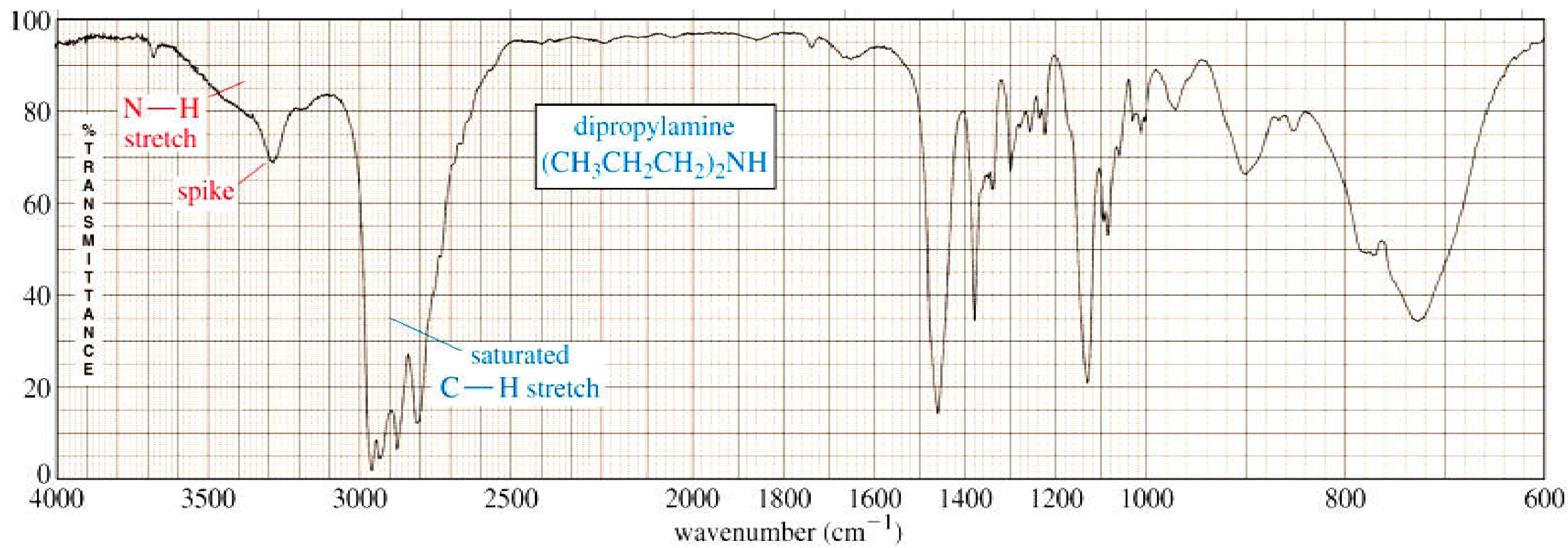


**TABLE 17-2 Abbreviated Table of Group Frequencies for Organic Groups**

| Bond | Type of Compound | Frequency Range, $cm^{-1}$ | Intensity |
|---|---|---|---|
| C—H | Alkanes | 2850–2970 | Strong |
| | | 1340–1470 | Strong |
| C—H | Alkenes ( >C=C<H ) | 3010–3095 | Medium |
| | | 675–995 | Strong |
| C—H | Alkynes (—C≡C—H) | 3300 | Strong |
| C—H | Aromatic rings | 3010–3100 | Medium |
| | | 690–900 | Strong |
| O—H | Monomeric alcohols, phenols | 3590–3650 | Variable |
| | Hydrogen-bonded alcohols, phenols | 3200–3600 | Variable, sometimes broad |
| | Monomeric carboxylic acids | 3500–3650 | Medium |
| | Hydrogen-bonded carboxylic acids | 2500–2700 | Broad |
| N—H | Amines, amides | 3300–3500 | Medium |
| C=C | Alkenes | 1610–1680 | Variable |
| C=C | Aromatic rings | 1500–1600 | Variable |
| C≡C | Alkynes | 2100–2260 | Variable |
| C—N | Amines, amides | 1180–1360 | Strong |
| C≡N | Nitriles | 2210–2280 | Strong |
| C—O | Alcohols, ethers, carboxylic acids, esters | 1050–1300 | Strong |
| C=O | Aldehydes, ketones, carboxylic acids, esters | 1690–1760 | Strong |
| $NO_2$ | Nitro compounds | 1500–1570 | Strong |
| | | 1300–1370 | Strong |

## APPLICATIONS OF IR SPECTROSCOPY

- Used in the identification of functional groups in the organic compounds
  - Example: –NH, –OH, –CO, etc., functional groups analysis
- Used in the detection of impurities
- IR spectra mainly used in structure elucidation to determine the functional groups
- Qualitative "fingerprint" check for identification of drugs
- Quality control of pharmaceutical formulations