IR Spectroscopy: Fundamentals and Applications
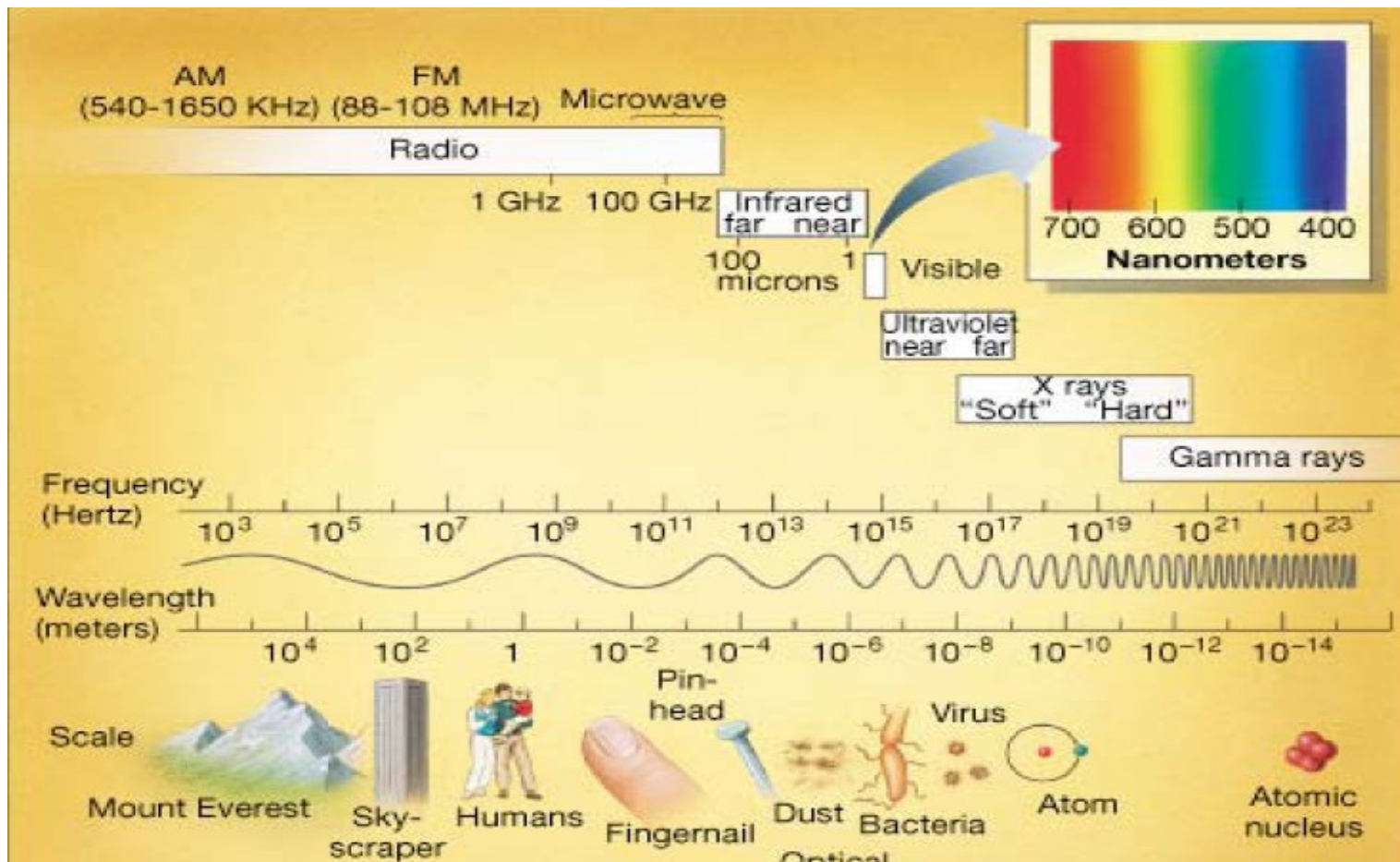
Presented By:

Dr. Joohee Pradhan

INFRARED SPECTROSCOPY: Outline of Presentation

- Introduction
- Units & measurement
- Range of IR radiation
- Principle
- Theory- Molecular vibrations
- Vibrational Frequency- Hook's Law
- Number of Fundamental vibrations
- Factors affecting vibrational Frequency
- Instrumentation
- Sampling Techniques
- IR Spectrum-Examples
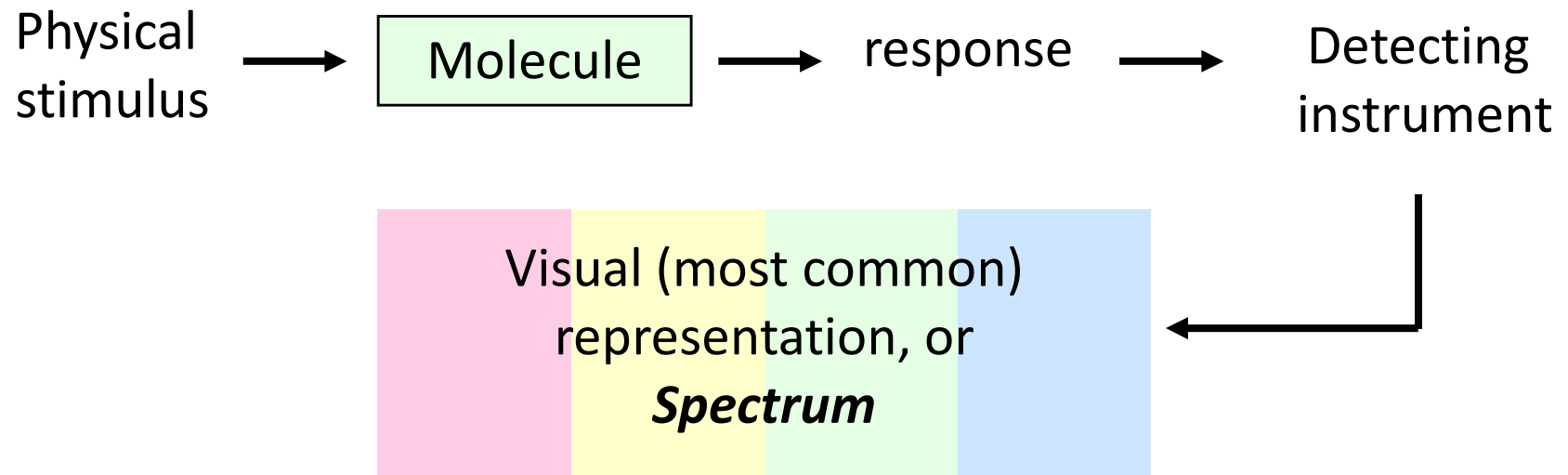- Advantages & disadvantages
- Applications

Wide Range of Types of Electromagnetic Radiation in nature.
1. Only a small fraction (350-780 nM is visible light).
2. The complete variety of electromagnetic radiation is used throughout spectroscopy.
3. Different energies allow monitoring of different types of interactions with matter.
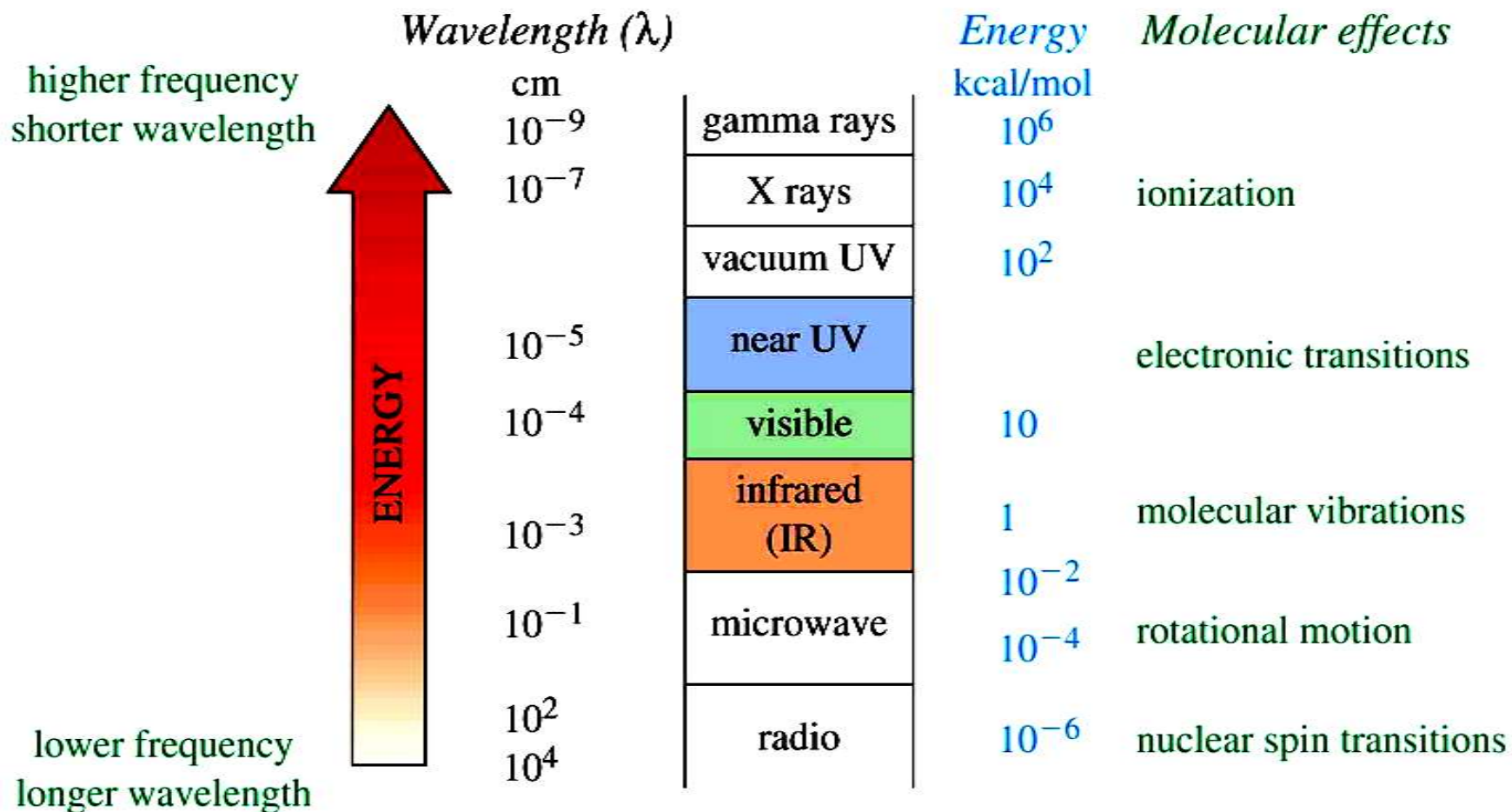
$$E = h\nu = hc/\lambda$$

SPECTROSCOPY - Study of spectral information

Physical stimulus → Molecule → response → Detecting instrument

Visual (most common) representation, or *Spectrum*

Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum.

EFFECT OF ELECTROMAGNETIC RADIATION
ON MOLECULES

Wavelength (λ)		Energy	Molecular effects
higher frequency shorter wavelength	cm	kcal/mol	
	10^{-9} gamma rays	10^6	
	10^{-7} X rays	10^4	ionization
	vacuum UV	10^2	
	10^{-5} near UV		electronic transitions
	10^{-4} visible	10	
	infrared (IR) 10^{-3}	1	molecular vibrations
		10^{-2}	
	10^{-1} microwave	10^{-4}	rotational motion
lower frequency longer wavelength	10^2 10^4 radio	10^{-6}	nuclear spin transitions

ENERGY

The unit used on an IR spectrum is
Wavenumbers $\bar{\nu}$

$$\bar{\nu} = \text{wavenumbers (cm}^{-1}) = \frac{1}{\lambda}$$
wavelength (cm)

$$\nu = \text{frequency} = \bar{\nu} \, c$$

C = speed of light
$= 3 \times 10^{10}$ cm/sec

or

$$\nu = \left(\frac{1}{\lambda}\right) c = \frac{c}{\lambda}$$
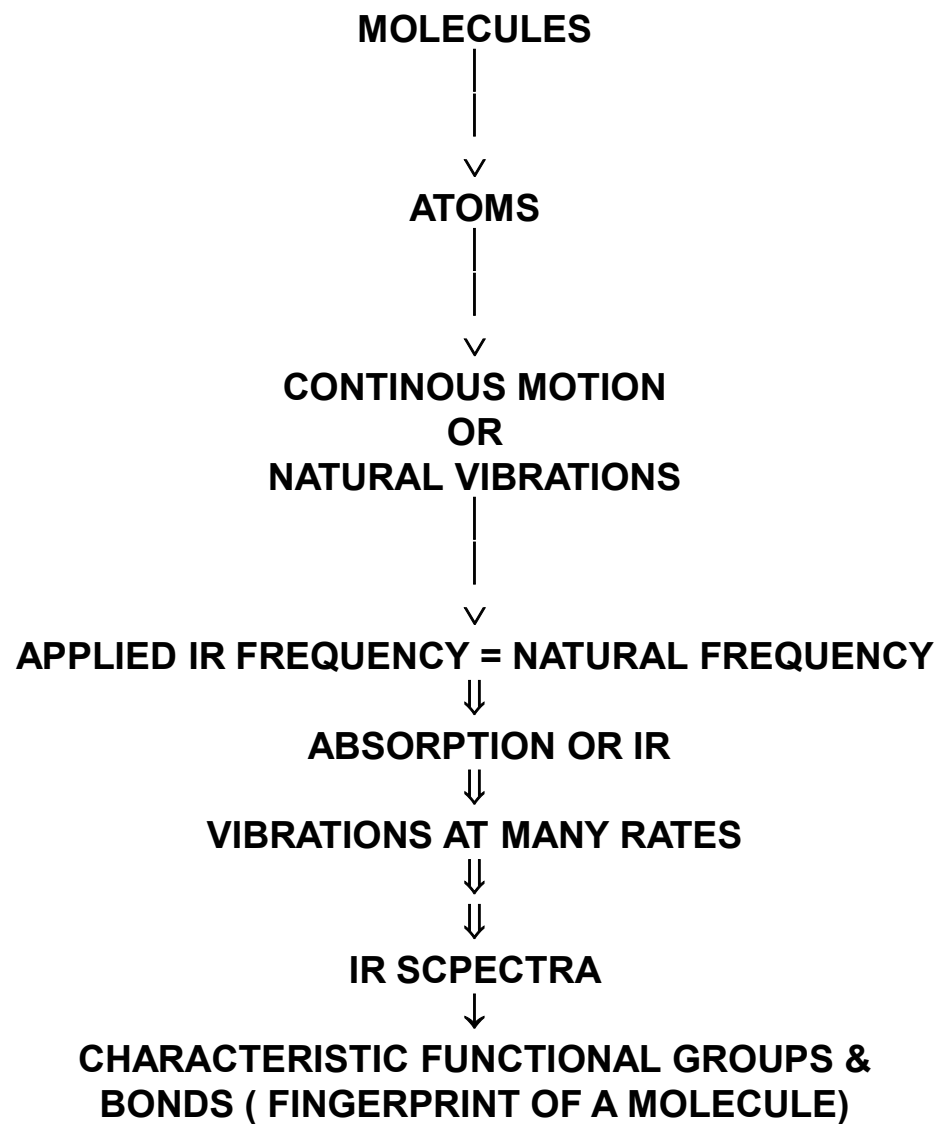
$$\frac{\text{cm/sec}}{\text{cm}} = \frac{1}{\text{sec}}$$

wavenumbers are directly proportional to frequency

Range of IR

- **Near IR:** 0.8 to 2.5μm (12000cm^{-1} – 4000cm^{-1})
- Analyzing mixtures of aromatic amines
- Determination of protein, fat, moisture, oil content.

- **Middle IR:** 2.5 to 15μm (4000cm^{-1} – 667cm^{-1})
- Also known as vibration- rotation region.
- This region is divided into:
1. *Group frequency region*: **4000cm^{-1} – 1500cm^{-1}**
2. *Fingerprint region*: **1500cm^{-1} – 667cm^{-1}**

- **Far IR:** 15 to 1000μm (667cm^{-1} – 10cm^{-1})
- Study of inorganic or organometallic compounds
- Sensitive to changes in overall structure of the molecule

MOLECULES

|

v

ATOMS

|

v

CONTINOUS MOTION
OR
NATURAL VIBRATIONS

|

v

APPLIED IR FREQUENCY = NATURAL FREQUENCY

⇓

ABSORPTION OR IR

⇓

VIBRATIONS AT MANY RATES

⇓
⇓

IR SCPECTRA

↓

CHARACTERISTIC FUNCTIONAL GROUPS &
BONDS (FINGERPRINT OF A MOLECULE)

Principle – IR Spectroscopy

Infrared radiation is largely thermal energy.
It induces stronger **molecular vibrations** in covalent bonds, which can be
viewed as springs holding together two masses, or atoms.

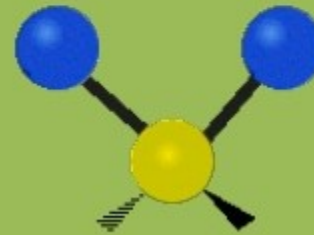**Specific** bonds respond to (absorb) **specific** frequencies

equilibrium
bond length

stretched

compressed
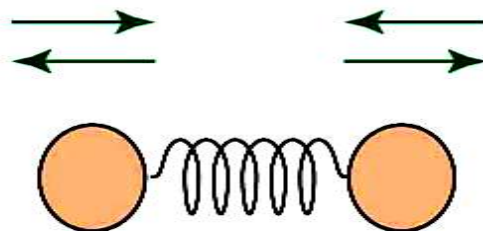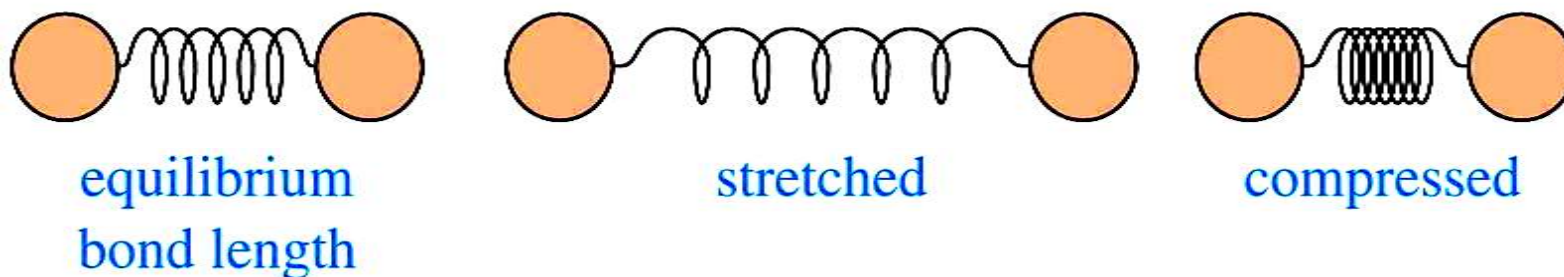
• Types of Molecular Vibrations

• **Stretching Vibrations**: in which bond length changes that require more energy.
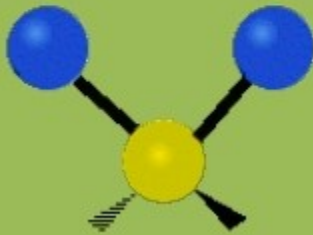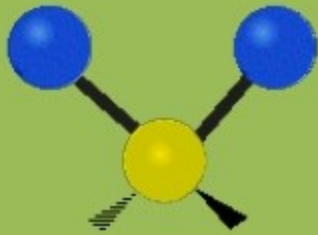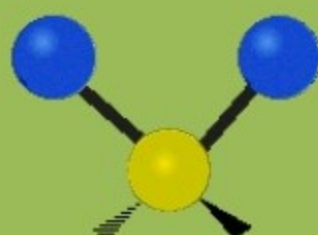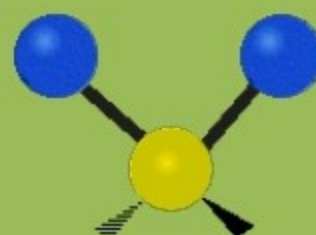
Symmetrical stretching

Asymmetrical stretching

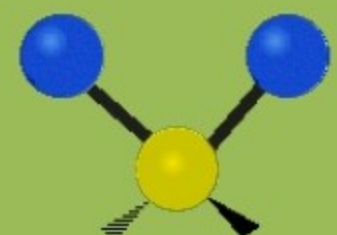• **Bending Vibrations**: in which bond angle changes that require less energy.

Rocking

Twisting

Scissoring

Wagging

Number of Vibrational Modes:

➤ Decided by no. of Vibrational degrees of Freedom (DOF)

➤ Every atom in a molecule has 3 DOF in three Cartesian coordinates which defines its position in space.

➤ 3n= Vibrational DOF + Translational DOF +Rotational DOF
       (where n=No. of atoms)

We have to calculate Vibrational DOF

- for linear molecules, number of types of vibrations:

  3n= Vibrational DOF + Translational DOF (3) +Rotational DOF (2)

  Vibrational DOF= 3n-3-2 =3n-5
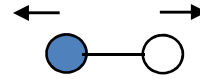
- for non-linear molecules, number of types of vibrations: 3n= Vibrational DOF + Translational DOF (3) +Rotational DOF (3)
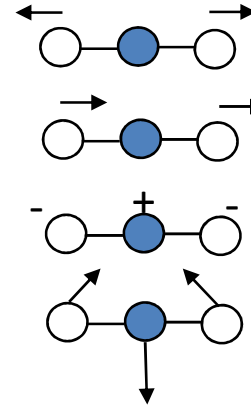
  Vibrational DOF= 3n-3-3 =3n-6

Examples:

1) HCl: 3(2)-5 = 1 mode

2) CO_2: 3(3)-5 = 4 modes

moving in-out of plane

3) C_6H_6: 3n-6=3(12)-6=30

- why so many peaks in IR spectra?
    - Overtones (2x, 2y), Combination (x+y. x+2y, 2x+y) and Difference bands (x-y. 2x-y, 2y-x etc.): 10-100 times less intense than fundamental
- observed vibration can be less then predicted because
    - symmetry (no change in dipole)
    - energies of vibration are identical
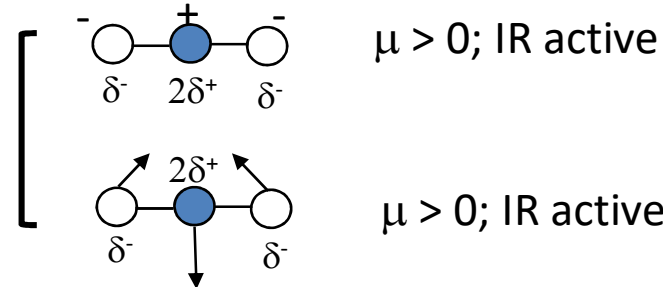   - absorption intensity too low
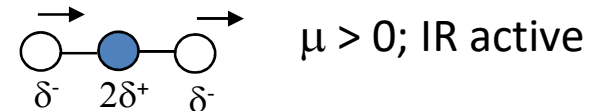   - frequency beyond range of instrument
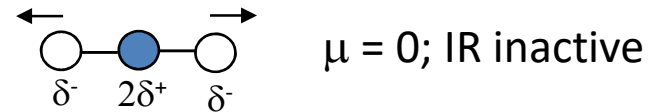
IR Active Vibrations:

- In order for molecule to absorb IR radiation:
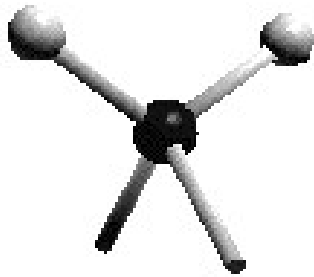 - vibration at same frequency as in light
  - but also, must have a change in its *net dipole moment* as a result of the vibration
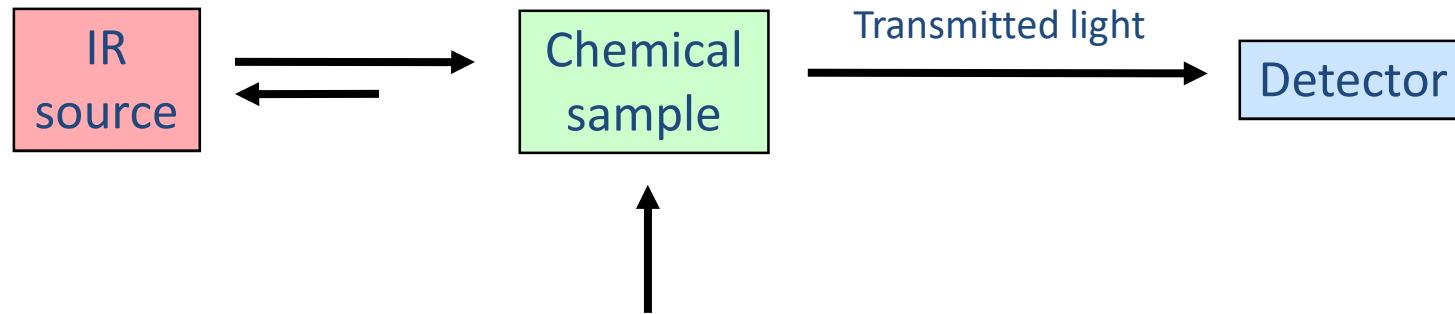
Examples:

1) CO_2: 3(3)-5 = 4 modes

degenerate –identical energy single IR peak

$\mu = 0$; IR inactive

$\mu > 0$; IR active

$\mu > 0$; IR active

$\mu > 0$; IR active

TRANSMISSION vs. ABSORPTION

When a chemical sample is exposed to the action of **IR LIGHT**, it can **absorb** some frequencies and **transmit** the rest. Some of the light can also be reflected back to the source.

```
┌──────────┐                    ┌──────────┐    Transmitted light    ┌──────────┐
│   IR     │   ──────────→      │ Chemical │    ──────────────→      │ Detector │
│ source   │   ←──────────      │  sample  │                         │          │
└──────────┘                    └──────────┘                         └──────────┘
                                      ↑
```

From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the *x*-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the *y*-axis in percentage units.
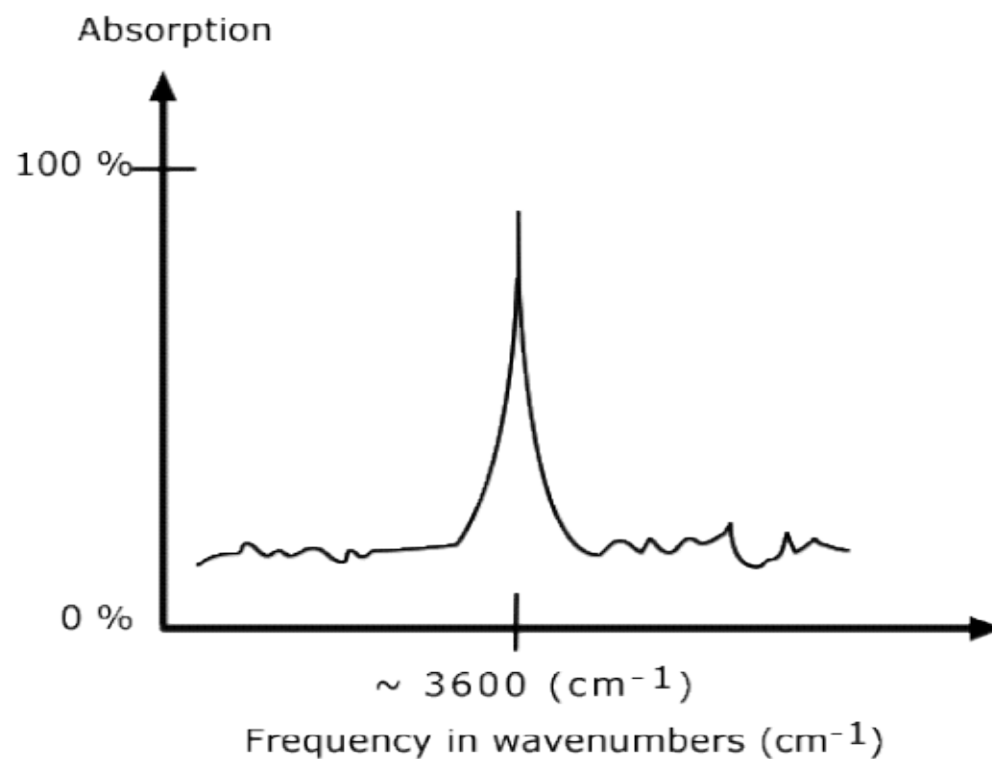
The graph above shows a spectrum in **absorption** mode.

AN IR SPECTRUM IN TRANSMISSION MODE
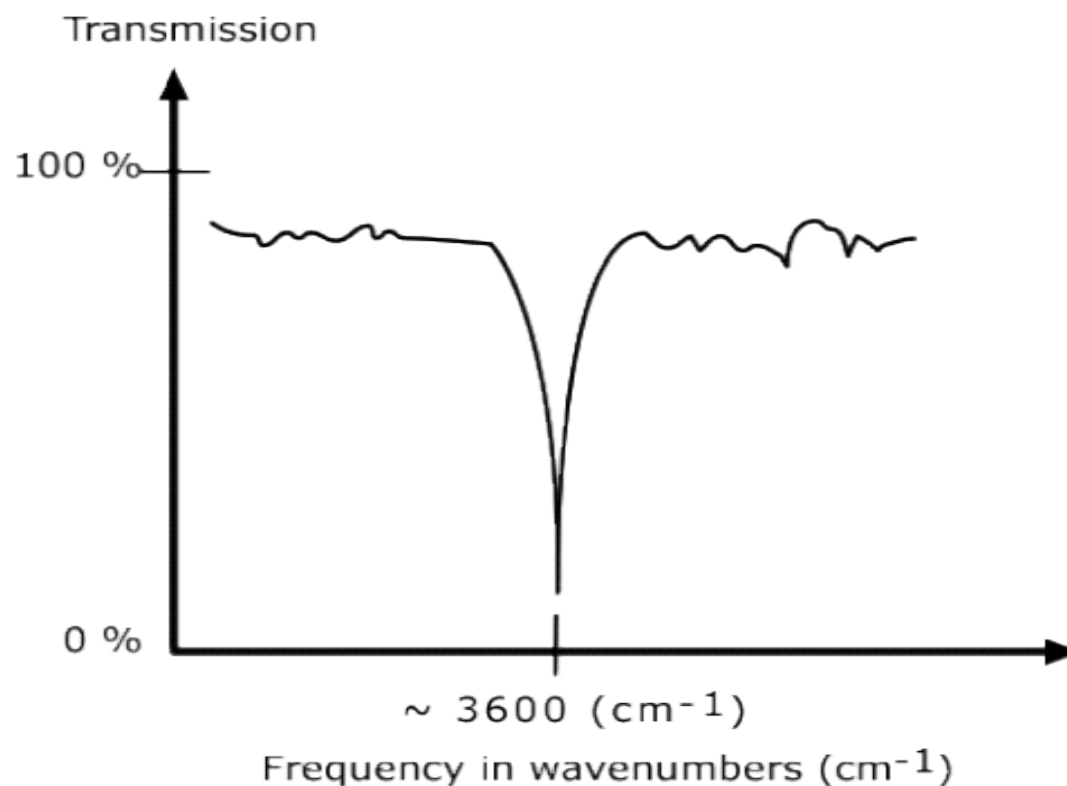
The graph above shows a spectrum in **transmission** mode.
This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

CLASSIFICATION OF IR BANDS

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis.
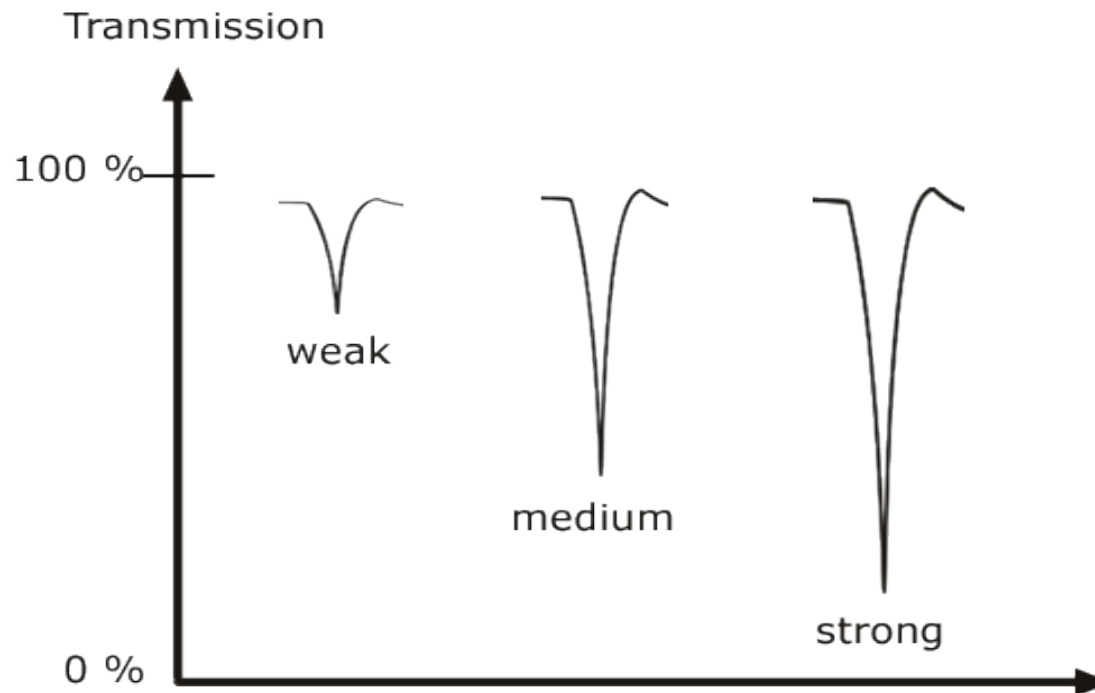
INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active**.

The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.

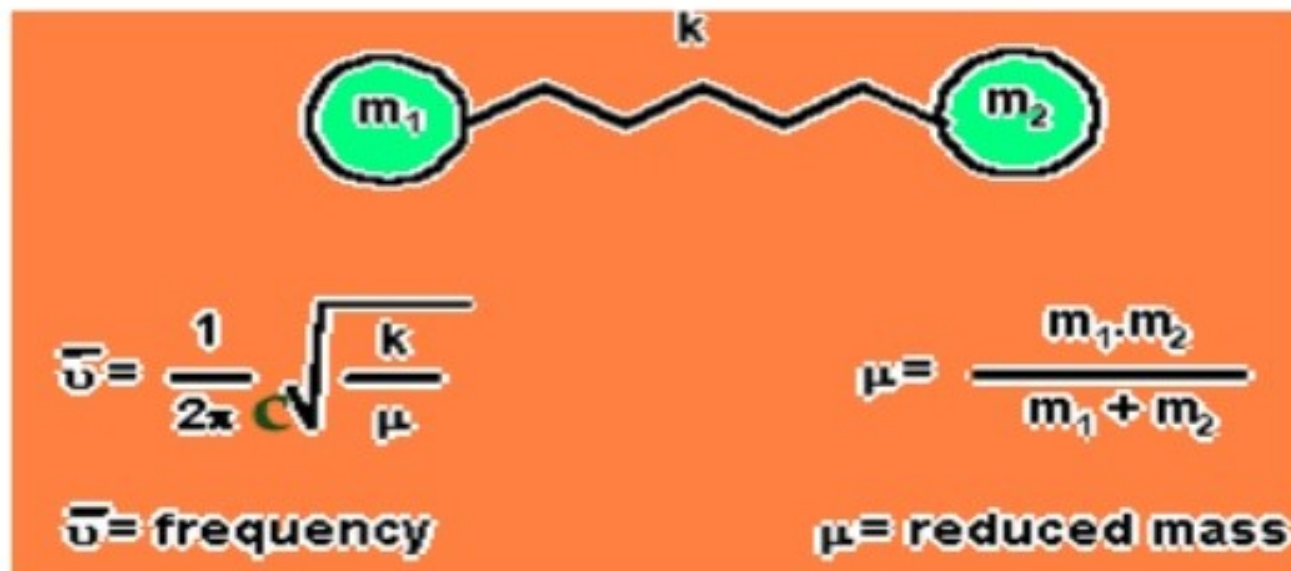STRONG   MEDIUM   WEAK   NOT OBSERVABLE
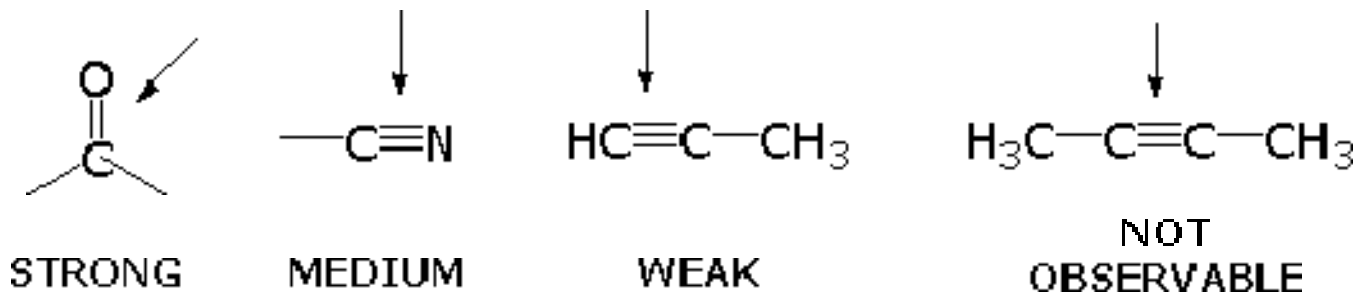
INFRARED BAND SHAPES

Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.
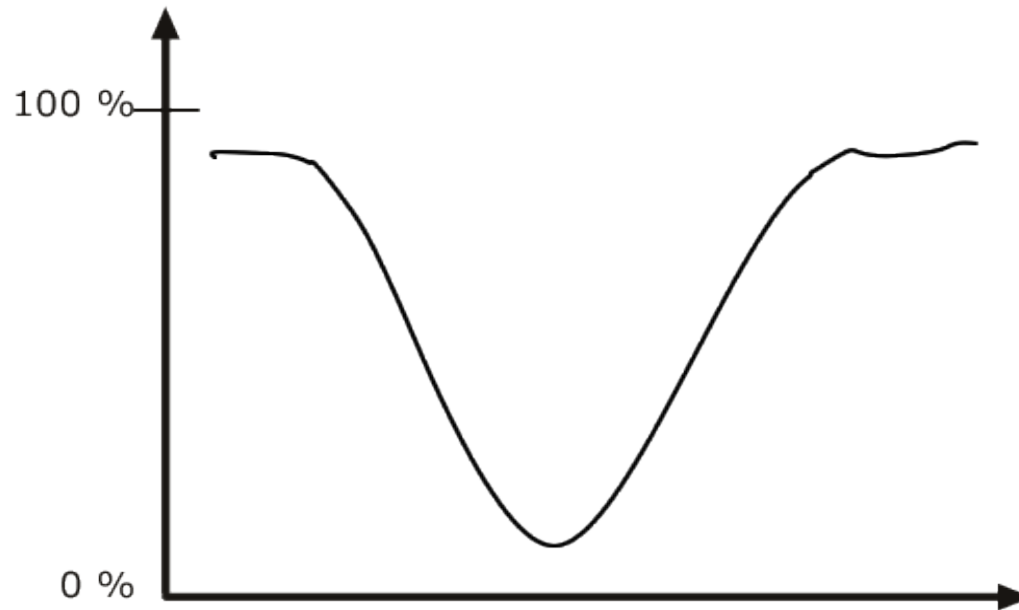
Vibrational Frequency

- The value of stretching vibrational frequency of bond can be calculated by using Hooke's law.

- Hooke's law states that the vibrational frequency of a bond is directly proportional to the bond strength and inversely proportional to the masses at the ends of the bond.

$$\bar{\upsilon} = \frac{1}{2\pi\, c}\sqrt{\frac{k}{\mu}} \qquad\qquad \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

$\bar{\upsilon}$ = frequency $\qquad\qquad\qquad\qquad$ μ = reduced mass

Vibrational frequency or wave number depend upon following:

1. BOND STRENGTH

The frequency of vibration will be directly proportional to strength of bond (K).

E.g.- Stretching vibration of triple bond will appear at high frequency than that of either a double or single bond

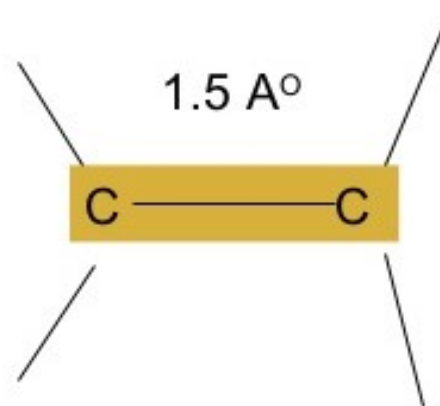| C≡C	C=C	C-C
Frequency= 2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

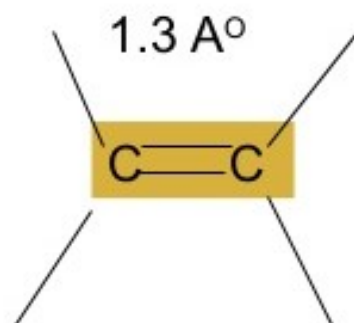## 2. MASS : Vibrational frequency is inversely proportional to the masses at the ends of the bond.

C-H	C-C	C-O	C-Cl	C-Br	C-I
3000	1200	1100	750	600	500 Cm^{-1}

3. Hybridization:

- Hybridization affects the bond strength or force constant(K).
- Bonds are stronger in order :

$$SP \quad > \quad SP^2 \quad > \quad sp^3$$

$$3300 \text{ CM}^{-1} \qquad 3100 \text{ CM}^{-1} \qquad 2900 \text{ CM}^{-1}$$

1.20 A°   1.3 A°   1.5 A°

H — C≡C — H   C = C   C — C
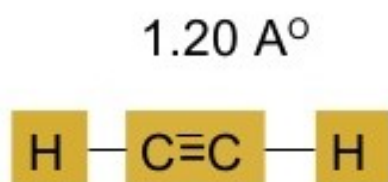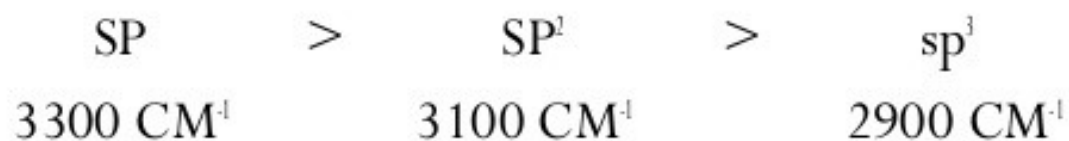
Factor affecting vibrational frequency

1. Coupling interaction.

2. Fermi resonance.

3. Hydrogen bonding.

4. Electronic displacement effects.

1. Coupling interaction

- It is expected that there is a stretching absorption frequency for an isolated C-H bond. But in case of Methylene(-CH2-) group, two absorption occurs which corresponds to symmetric & asymmetric vibrations.

- Asymmetric vibration always takes place at high wave number compared with symmetric vibration.

- These are knows as coupled vibrations because vibration occurs at different frequencies than that required for an isolated C-H stretching.

Symmetric
(a)

Asymmetric
(b)

Fig. 3.25 : Stretching vibrations in methylene group.
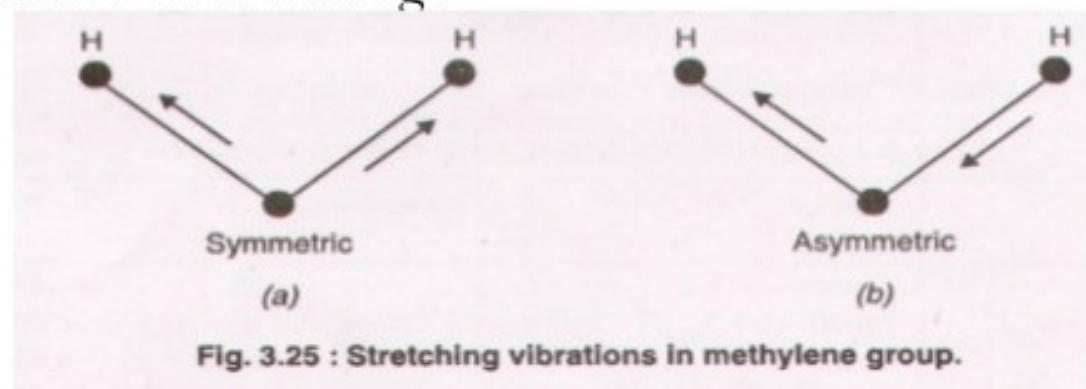
2. Fermi resonance

- It occurs when a fundamental vibration couples with an overtone or combination band.

- When an overtone or a combination of band has the same frequency to a fundamental, two bands appear close together.
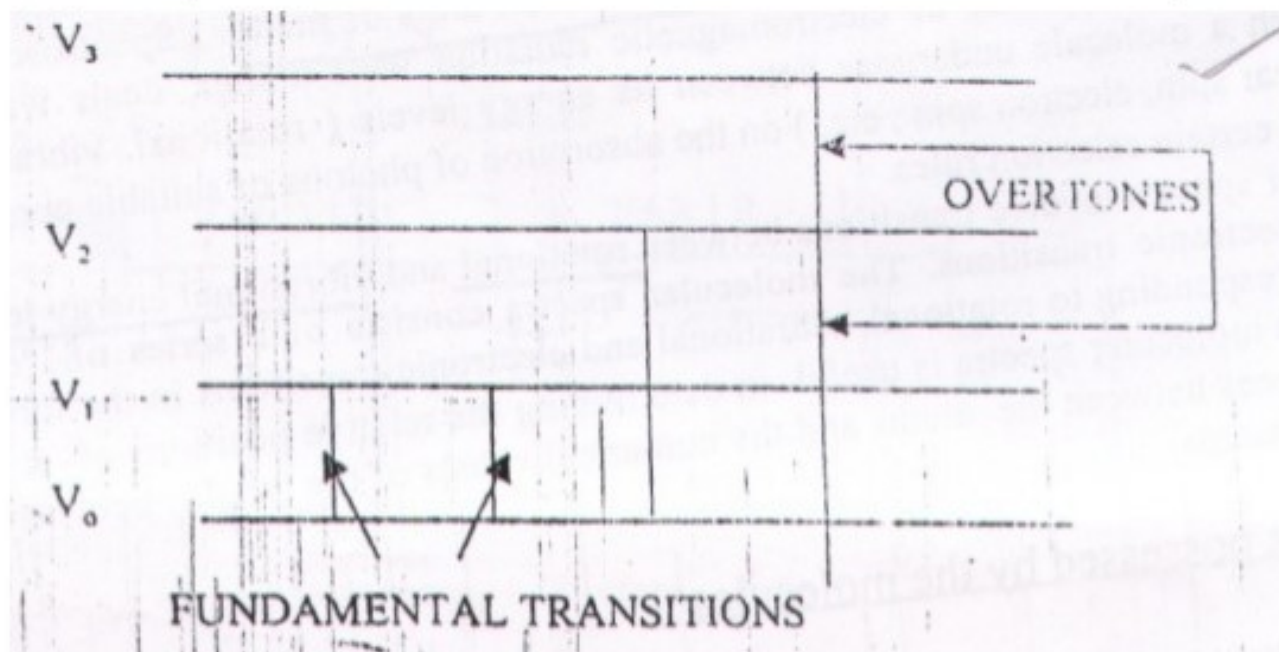
- The effect is greatest when the frequencies match, and the two bands are referred to as a *Fermi doublet*.

- When two bonds share a common atom as in the case of a linear tri-atomic molecule CO_2, consisting of two CO bonds (O=C=O), two fundamental stretching vibrations: symmetric and asymmetric takes place.

- As the symmetric stretching vibration produces no change in the dipole movement of the molecules, it is inactive in the IR spectra.

- In the asymmetric vibration, one oxygen approach the carbon atom as other may be away. Asymmetric stretching vibration appears in the IR region 2330 cm-1

3. Hydrogen bonding

➢Hydrogen bonding gives rise to downward frequency shifts.

➢Stronger the bonding, greater the absorption shift towards lower wave number from normal value.

➢Generally, intermolecular hydrogen bonds are sharp and well

  defined.

➢ Intermolecular hydrogen bonds are concentration dependent. On dilution, intensities of such bands decreases and finally disappears.

Inter-molecular Hydrogen bonding

example, absorption occurs at 3300 cm^{-1}.
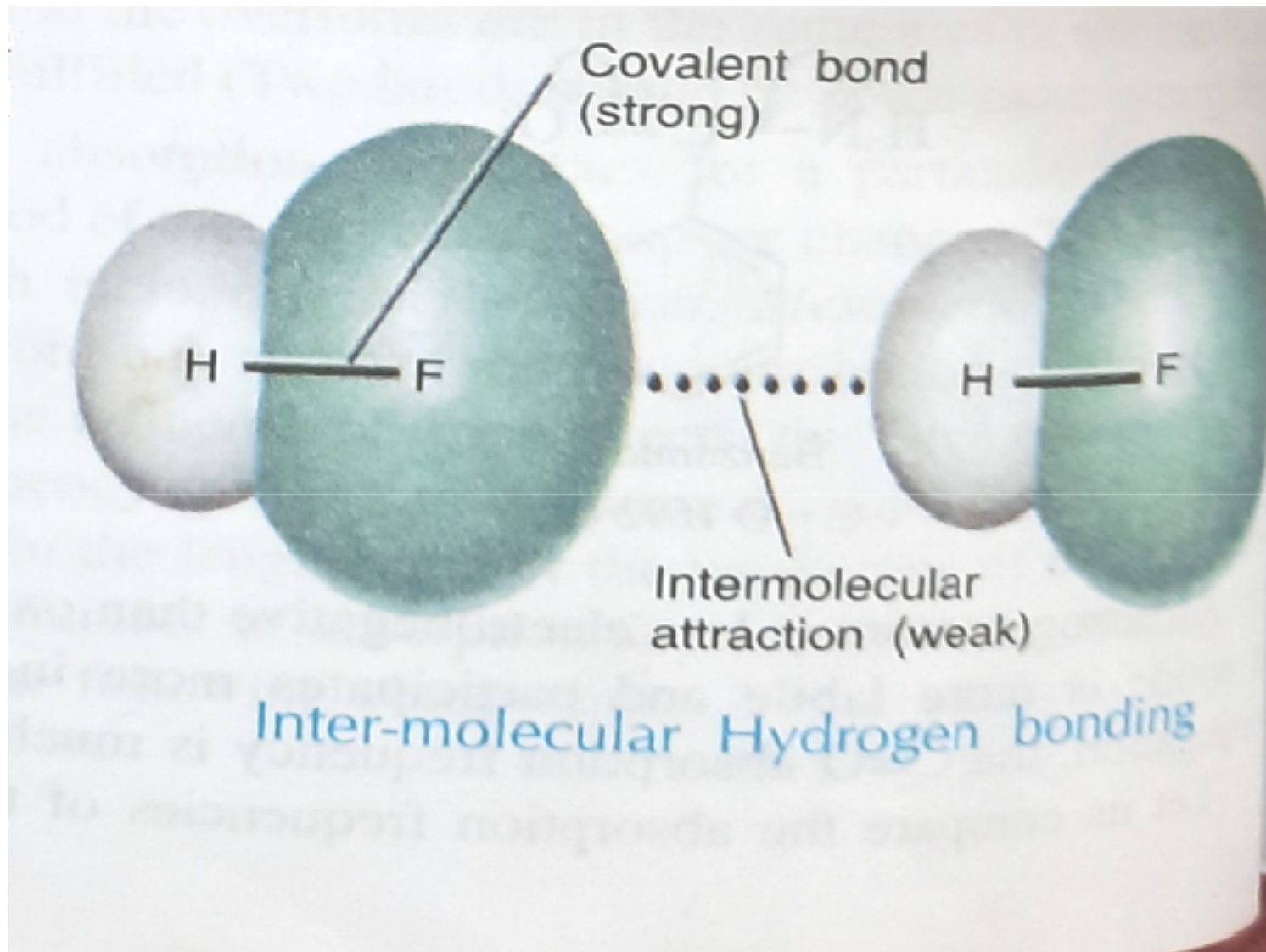
spectra, absorption occurs at 3300 cm^{-1}.

In aliphatic alcohols, a sharp band* appears at 3650 cm^{-1} in dilute solutions due to free O—H group while a broad band is noticed at 3350 cm^{-1} due to hydrogen bonded O—H group. Alcohols are strongly hydrogen bonded in condensed phases. These are usually associated as dimers and polymers which result in the broadening of bands at lower absorption frequencies. In vapour state or in inert solvents, molecules exist in free state and absorbs strongly at 3650 cm^{-1}.

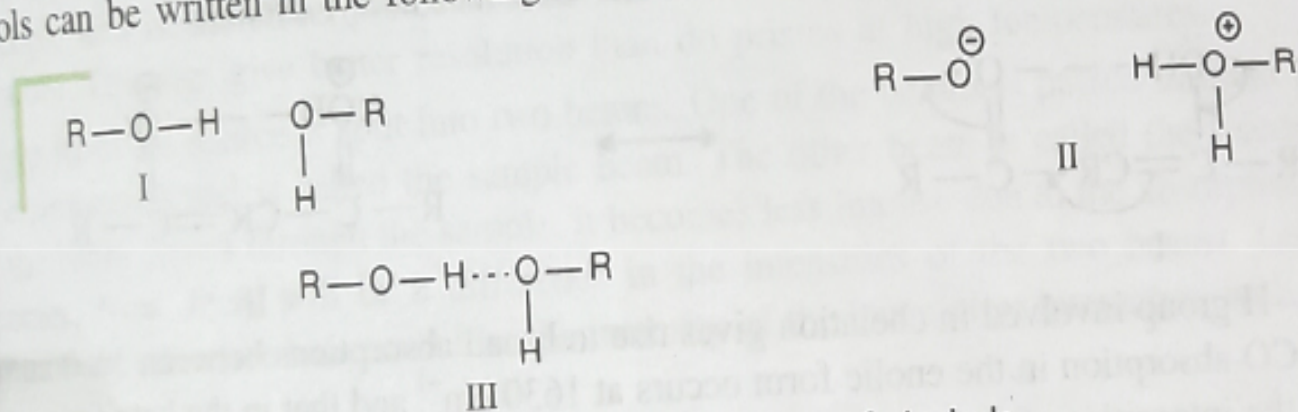Alcohols can be written in the following resonating structures.

Fig. 3.9. Resonating structures of alcohols.

Structure III is the hybrid of structures I and II. This results in the lengthening of the original O—H group. The electrostatic force of attraction with which hydrogen atom of one molecule is attracted by the oxygen atom of another molecule makes it easier to pull hydrogen away from the oxygen atom. Thus, small energy will be required to stretch such a bond (O—H) and hence absorption occurs at a lower wave number.

dilute solutions of di- and polyhydroxy

Intramolecular hydrogen bonding can be observed in dilute solutions of di- and polyhydroxy compounds in carbon tetrachloride where no intermolecular hydrogen bonds are formed. Under these conditions, it was observed that a number of cyclic and acyclic diols have two bands and others have a single band in the O—H stretching mode region.

The spectrum of glycol in dilute carbon tetrachloride shows two vO—H bands at 3644 cm^{-1} and 3612 cm^{-1}. The band at 3644 cm^{-1} is due to free O—H and that at 3612 cm^{-1} is due to O—H···O bonding. As the absorption shift (32 cm^{-1}) is small, the type must be intramolecular hydrogen bonding. Out of the two possible conformations of ethylene glycols, only staggered syn conformation can form an intramolecular hydrogen bond. The occurrence of a strong band arising from the intramolecular
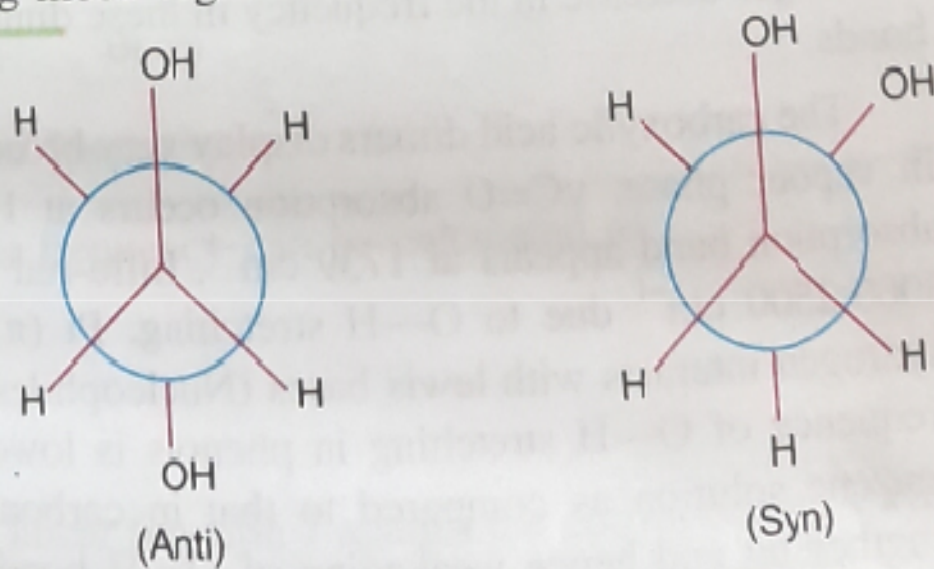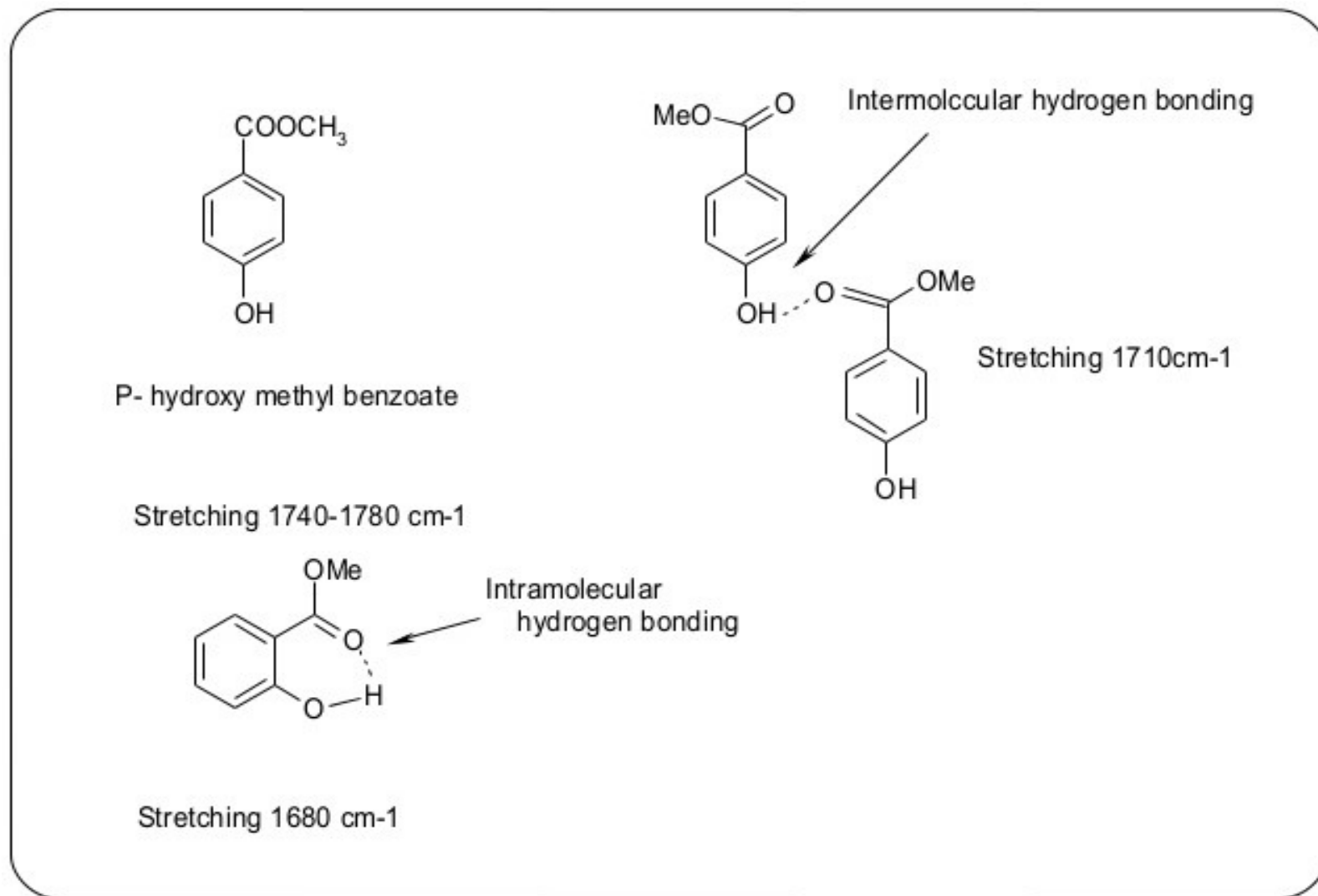

Fig. 3.10. Anti and Syn conformations of Ethylene glycol.

*The band due to free O—H group is usually less intense while that due to bonded O—H group is broad and sharp.

v Str. Free O-H > v Str. Intermol. H bonded O-H > v Str. Intramol. H bonded O-H

4. Electronic Displacement Effect

- The frequency shifts from normal position of absorption occur because of electronic effects which include: Inductive effect, mesomeric effect, configuration effect or field effect.

- Under the influence of these effects, the force constant (K) or the bond strength changes and its absorption frequency shifts from the normal value.

• Inductive effects are divided into two parts:

+ve inductive effect	-ve inductive effect

Eletron deficient

e.g Alkyl group

Bond length ↑

K ↓

Frequency ↓

Electron rich

e.g CL, BR, I, OH

Bond length ↓

K ↑

Frequency ↑

(i) Formaldehyde (HCHO)   1750 cm^{-1}
(ii) Acetaldehyde (CH$_3$CHO)   1745 cm^{-1}
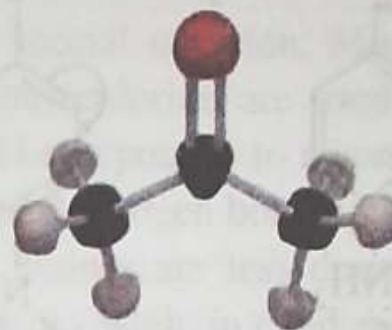(iii) Acetone (CH$_3$COCH$_3$)   1715 cm^{-1}

Formaladehyde   Acetaldehyde   Acetone

Note. Aldehydes absorb at higher wave number than ketones.

The introduction of an electronegative atom or group causes–I effect which results in the bond order to increase. Thus, the force constant increases and hence the wave number of absorption rises. Now, let us consider the wave numbers of absorptions in the following compounds:

(i) Acetone (CH$_3$COCH$_3$)   1715 cm^{-1}
(ii) Chloroacetone (CH$_3$COCH$_2$Cl)   1725 cm^{-1}
(iii) Dichloroacetone (CH$_3$COCHCl$_2$)   1740 cm^{-1}
(iv) Tetrachloroacetone (Cl$_2$CH—CO—CHCl$_2$) 1750, 1778 cm^{-1}

In most of the cases, mesomeric effect works alongwith inductive effect and cannot be ignored. Conjugation lowers the absorption frequency of C=O stretching whether the conjugation is due to α, β-unsaturation or due to an aromatic ring. In some cases, inductive effect dominates over mesomeric effect while reverse holds for other cases. *Mesomeric effect* causes lengthening or the weakening of a bond leading in the lowering of absorption frequency. Consider the following compounds:

In these two cases, –I effect is dominated by mesomeric effect and thus, the absorption frequency falls.
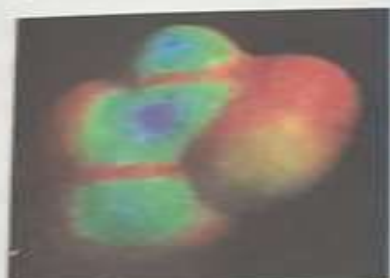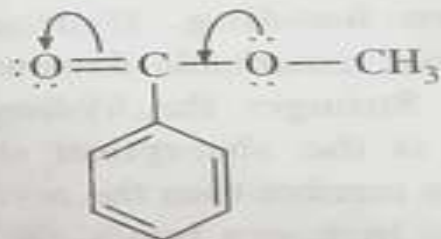
Methyl Vinyl Ketone
$v\,C=O\;1706\;cm^{-1}$
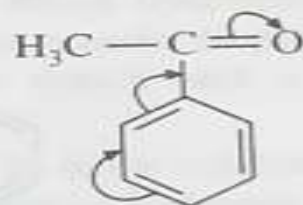
Acetophenone
$v\,C=O\;1693\;cm^{-1}$

In some cases, where the lone pair of electrons present on an atom is in conjugation with the double bond of a group, say carbonyl group, the mobility of the lone pair of electrons matters. Let us compare the absorption frequencies of $v\,(C=O)$ stretching in amides and esters.
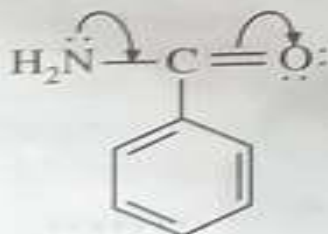
Benzamide
$v\,C=O\;1693\;cm^{-1}$
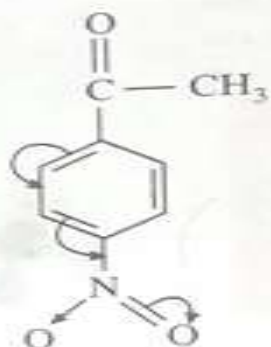
Methyl benzoate
$v\,C=O\;1730\;cm^{-1}$

As nitrogen atom is less electronegative than oxygen atom, the electron pair on nitrogen atom in amide is more labile and participates more in conjugation. Due to this greater degree o conjugation, the C=O absorption frequency is much less in amides as compared to that in esters.
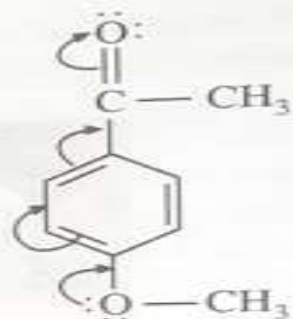
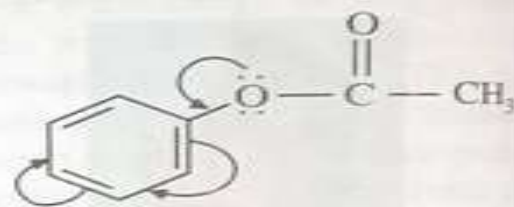Let us compare the absorption frequencies of the following compounds:
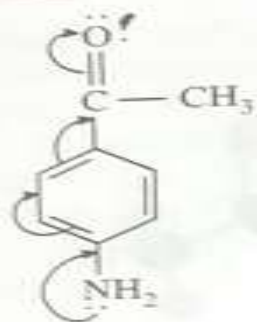
| I	II	III	IV
p-Amino Acetophenone	p-Nitro Acetophenone	p-Methoxy Acetophenone	Phenyl Acetate
v C=O 1677 cm⁻¹	v C=O 1700 cm⁻¹	v C=O 1684 cm⁻¹	v C=O 1770 cm⁻¹

Due to the low electronegativity of nitrogen atom, the lone pair of electrons participates mor in conjugation in compound I as compared to that in compound III. Thus, in compound I, v (C=O absorption occurs at lower wave number compared to that in compound III. In compounds II an IV, inductive effect dominates over mesomeric effect and hence absorption takes place a comparatively higher frequencies.

It is important to note that only inductive effect is considered when the compound i meta substituted.

In para substitution, both inductive and mesomeric effects become important and the dominatio of one over the other will decide the wave number of absorption. In ortho substitution, inductiv effect, mesomeric effect alongwith steric effect are considered. In ortho substituted compounds, th lone pairs of electrons on two atoms influence each other through space interactions and chang the vibrational frequencies of both the groups. This effect is called **Field effect**. Consider orth haloacetophenone.
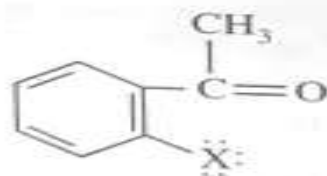
The non-bonding electrons present on oxygen atom and halogen atom cause electrostat repulsions. This causes a change in the state of hybridisation of C=O group and also makes it g go out of the plane of the double bond. Thus, the conjugation is diminished and absorption occu at a higher wave number. Thus, for such ortho substituted compounds, cis absorbs (field effect) a a higher frequency as compared to the trans isomer.

3. Hydrogen bonding

- Mesomeric effect works along with inductive effect. In some cases, inductive effect dominates mesomeric effect and vice versa.

- Configuration decreases the wavenumber of absorption. Oxygen atom of esters is more electronegative than nitrogen atom of amide. Hence, one pair of electron pair of nitrogen atom of amides participate more in conjugation thereby decreasing the absorption frequency of C=O group of amide.

Compound	Wave Number (cm-1)
Benzamide	1663
Phenylacetate	1730

Instrumentation

Basic Design and Mode of operation

- normal IR instrument similar to UV-vis
- main differences are light source ,detector and material of construction
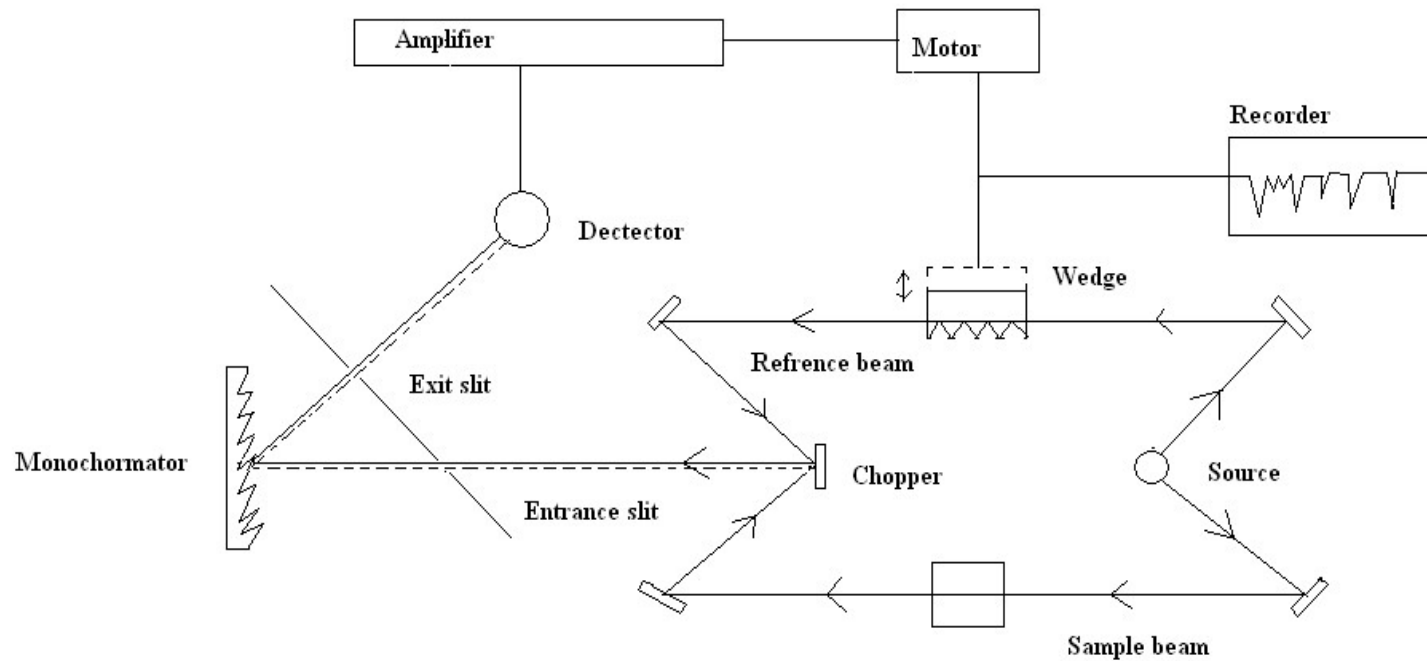
IR Radiation sources

➢ Tungsten filament lamp →

➢ Nernst glower:
a. Zirconium, Yttrium,Thorium
b. Heated to 1000 to 1800°c
c. Radiation – 7100cm^{-1} (1.4μm)

➢ Globar source:
a. Silicon carbide
b. Heated to 1300 to 1700°c
c. Radiation – 5200cm^{-1} (1.9μm)

➢ Mercury arc
a. Heated quartz – shorter wavelength
b. Mercury plasma – longer wavelength

➢ Nichrome wire or coil
a. Heated by passage of current to 1100°c

Monochormators
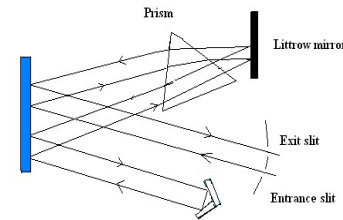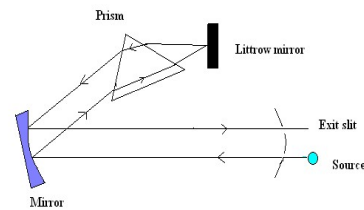
-        can't use glass prism, since absorbs IR
-        reflective grating is common

➢ **Prisms**

Two types:

1.Single pass   2.Double pass

Prism
Littrow mirror
Exit slit
Source
Mirror

Prism
Littrow mirror
Exit slit
Entrance slit

➢ **Gratings**

Grating Normal
Facet Normal
Incident Light
γ
α
Diffracted Light
β
d
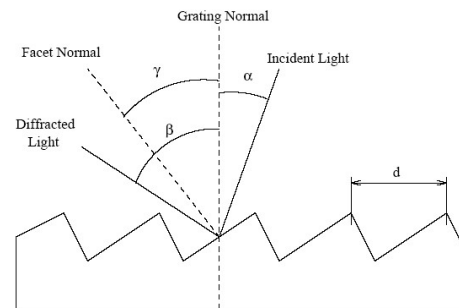
Sample cells & Sampling techniques

❖ Gases

- Gas cell – 10cms
- Multi pass gas cells

❖ Liquids

▪ Thin film squeezed between 2 IR transparent windows.
▪ $\cong$ 0.1 - 0.3mm thickness
▪ Below 250cm^{-1} – CsI flats, sample with water CaF$_2$ flats

❖ Solids

Four techniques:
1. KBr discs/ pellets/ pressed pellet technique
2. Mulls
3. Deposited films
4. Solutions

1.   KBr discs:
- 0.1 – 2.0% by wt.
- Particle size - $< 2\mu m$.
- Hydraulic pressure – 10 tons load.
- Discs: 13mm- diameter, 0.3mm- thickness.

2. Mulls:
- Grinding sample with a drop of oil.
- Nujol (liquid paraffin)
- Complement: Hexacholorobutadiene & chlorofluorocarbon.

3. Deposited films:
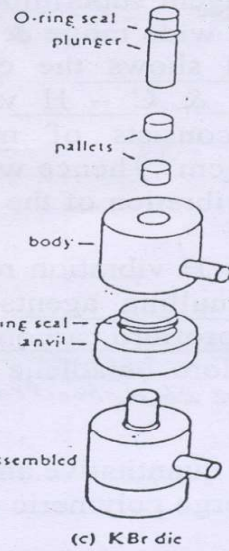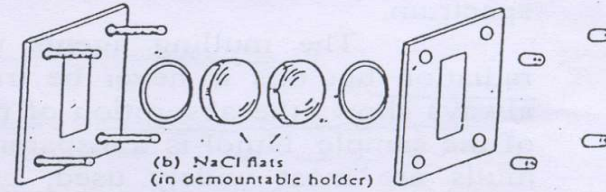- Solution in a volatile solvent on a NaCl flat.

4. Solutions:
- Solvent – CCl_4, CS_2, $CHCl_3$
- Complementary pair - CCl_4 & CS_2

• Gas cell
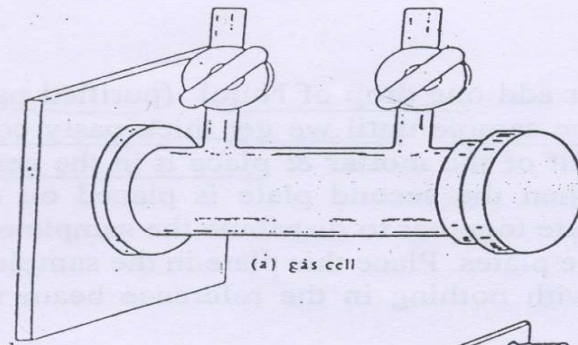
• NaCl flats

• KBr die

• Solution cell

• Variable path length cell

(a) gas cell

O-ring seal
plunger

pellets

body

O-ring seal
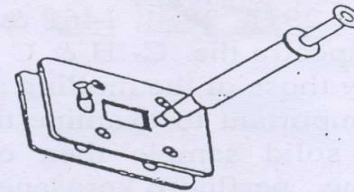anvil

assembled

(b) NaCl flats
(in demountable holder)

(c) KBr die

(d) solution cell
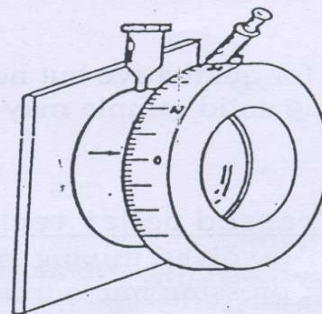
(e) variable path-
length cell

Detectors

two main types in common IR instruments

a)   <u>Thermal Detectors</u>

1.) Thermocouple

- two pieces of dissimilar metals fused together at the ends

- when heated, metals heat at different rates

- potential difference is created between two metals that varies with their <u>difference</u> in temperature

- usually made with blackened surface (to improve heat absorption)

- placed in evacuated tube with window transparent to IR (not glass or quartz)

- IR "hits" and heats one of the two wires.

- can use several thermocouples to increase sensitivity.
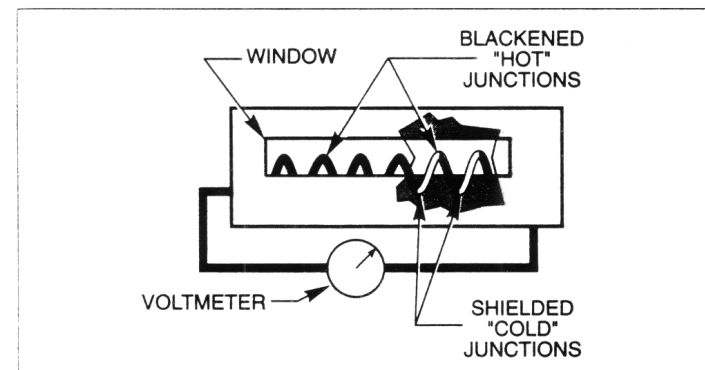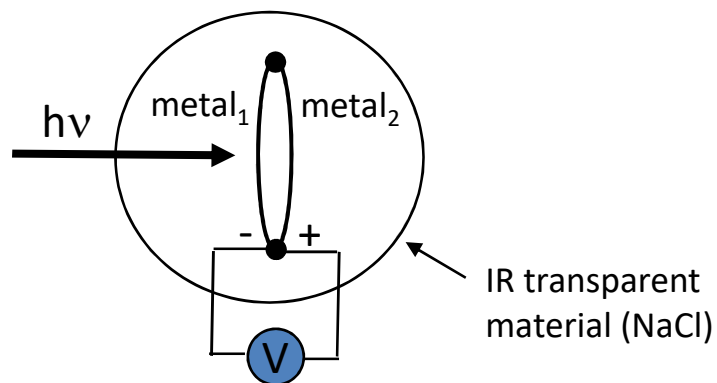
Fig. 5 Schematic drawing of a thermopile detector.

2.) Bolometer

- strips of metal (Pt, Ni) or semiconductor that has a large change in resistance to current with temperature.
- as light is absorbed by blackened surface, resistance increases and current decreases
- very sensitive
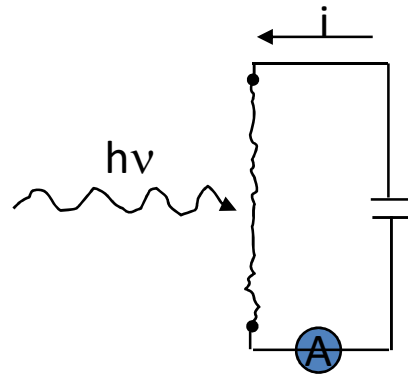
b) Photoconducting Detectors

- thin film of semiconductor (ex. PbS) on a nonconducting glass surface and sealed in a vacuum.
- absorption of light by semiconductor moves from non-conducting to conducting state
- decrease in resistance → increase in current
- range: 10,000 -333 cm^{-1} at room temperature
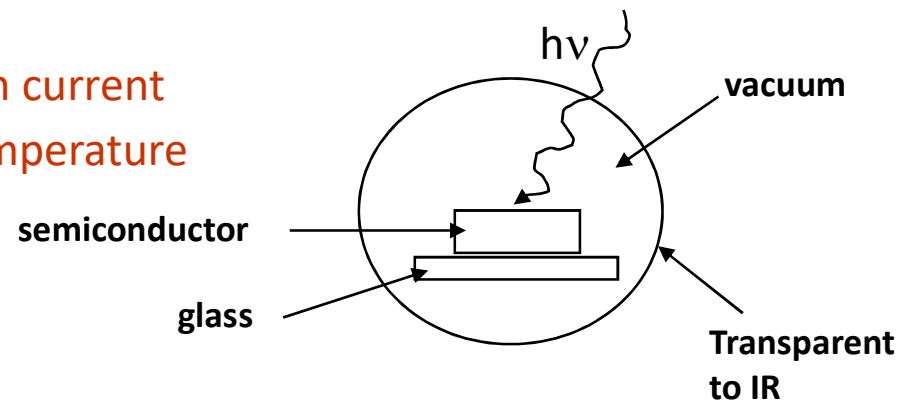
c) <u>Pyroelectric Detectors</u>

- pyroelectric (ceramic, lithium tantalate) material get polarized (separation   of (+) and (-) charges) in presence of electric field.

- temperature dependent polarization

- measure degree of polarization related to temperature of crystal

- fast response, good for FTIR
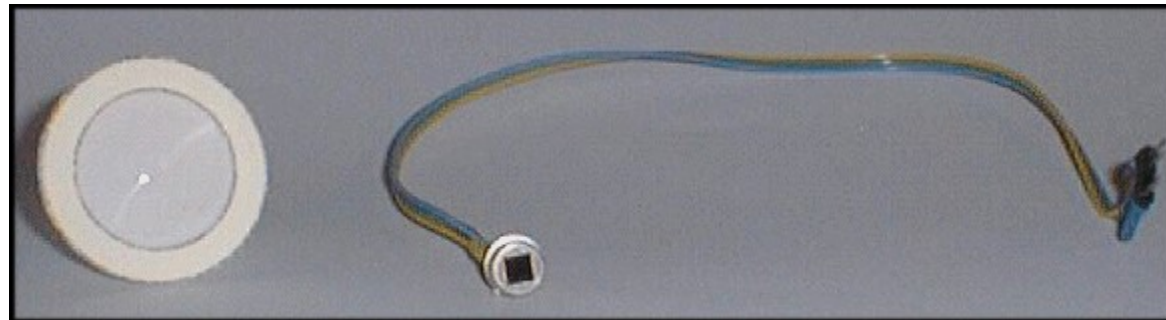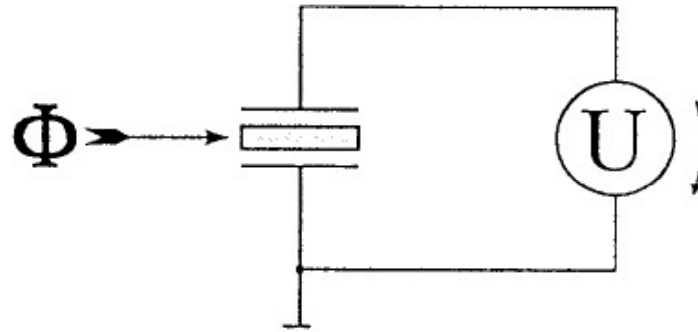
Fourier Transfer IR (FTIR) – *alternative to Normal IR*

- Based on Michelson Interferometer
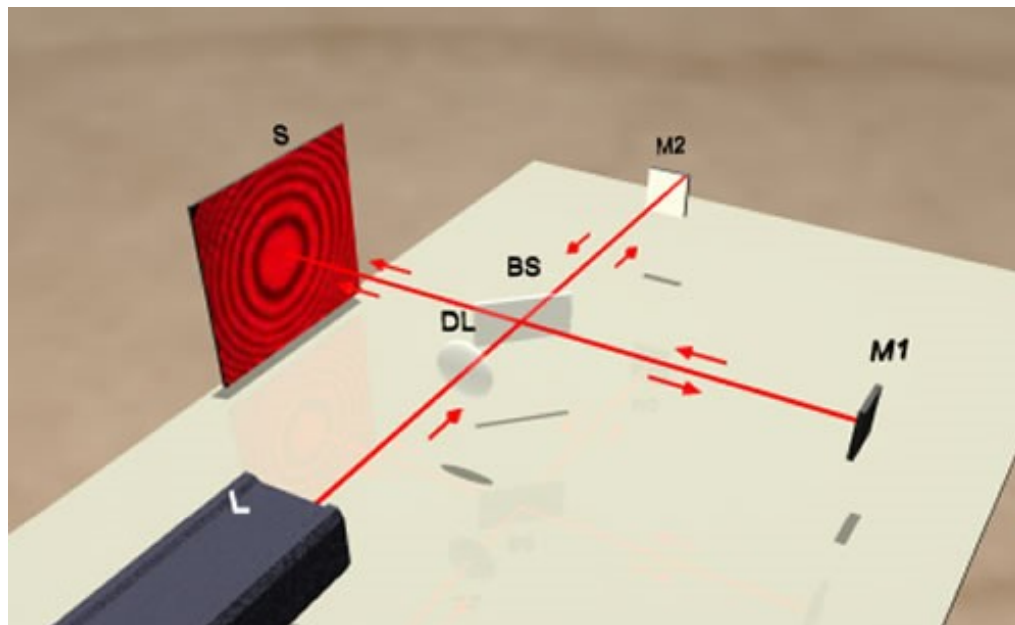
Principal:

1) light from source is split by central mirror into 2 beams of equal intensity

2) beams go to two other mirrors, reflected by central mirror, recombine and pass through sample to detector

3) two side mirrors. One fixed and other movable

a) move second mirror, light in two-paths travel different distances before recombined

b) constructive & destructive interference

c) as mirror is moved, get a change in signal

Advantages of FT IR Spectrophotometer

FT-IR spectrometers have numerous performance advantages over traditional dispersive infrared instrumentation. Virtually all infrared spectrometer manufacturers are now using FT designs instead of dispersive. The benefits of upgrading to an FT-IR from an existing dispersive infrared instrument will be immediately evident in spectral quality, data collection speed, reproducibility of data, and ease of maintenance and use.

IR Spectrophotometer: Advantages

1. All kinds of material can be analyzed.
2. Provides lot of information.
3. Fast and easy.
4. Very small amount of sample is required.
5. Less expensive.

Disadvantages

1. IR spectra cannot be obtained for Mono atomic substances e.g.: helium, argon.
2. IR spectra cannot be obtained for Homonuclear diatomic molecules like O_2, N_2.
3. Works best for pure substances but not for complex mixtures.

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.

IR Absorption Regions

In general, the IR spectrum can be split into four regions for
interpretation:

- $4000 - 2500$ cm^{-1}: Absorption of single bonds formed by hydrogen
                            and other elements e.g. O–H, N–H, C–H

- $2500 - 2000$ cm^{-1}: Absorption of triple bonds e.g. C≡C, C≡N

- $2000 - 1500$ cm^{-1}: Absorption of double bonds e.g. C=C, C=O

- $1500 - 400$ cm^{-1}:   This region often consists of many different,
                            complicated bands, called the fingerprint region.
                            It is rarely used for identification of particular
                            functional groups

Summary of IR Absorptions
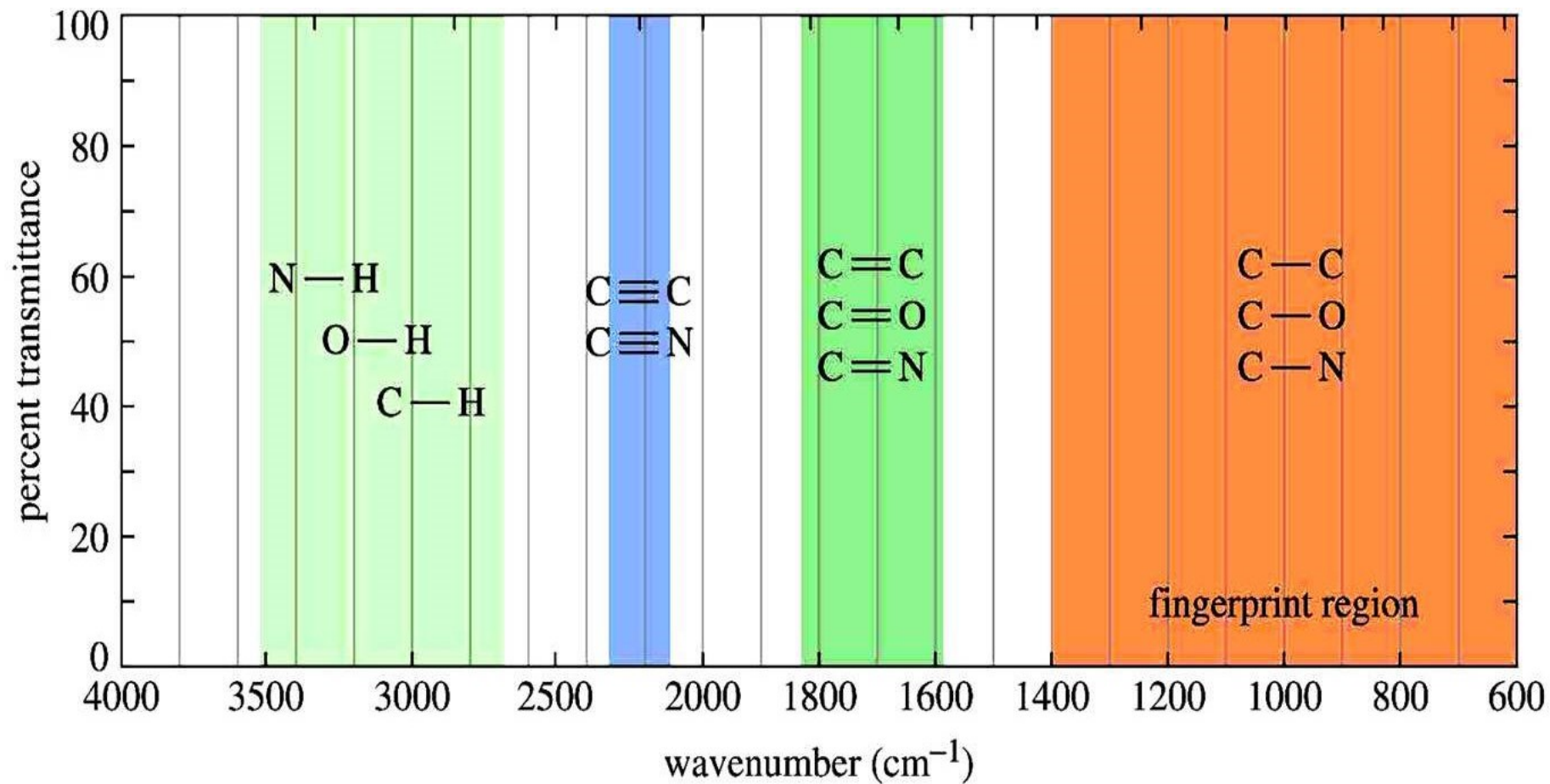
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 5th ed. Pearson Education Inc., 2003

Typical IR Absorption Regions

WAVELENGTH (μm)

| 2.5 | 4 | 5 | 5.5 | 6.1 | 6.5 | 15.4 |

O-H C-H	C≡N	Very	C=O	C=N	C-Cl
N-H	C≡C	few		C=C	C-O
	X=C=Y	bands			C-N
					C-C
	(C,O,N,S)			N=O N=O*

4000   2500   2000   1800 1650 1550   650

FREQUENCY (cm⁻¹)

55
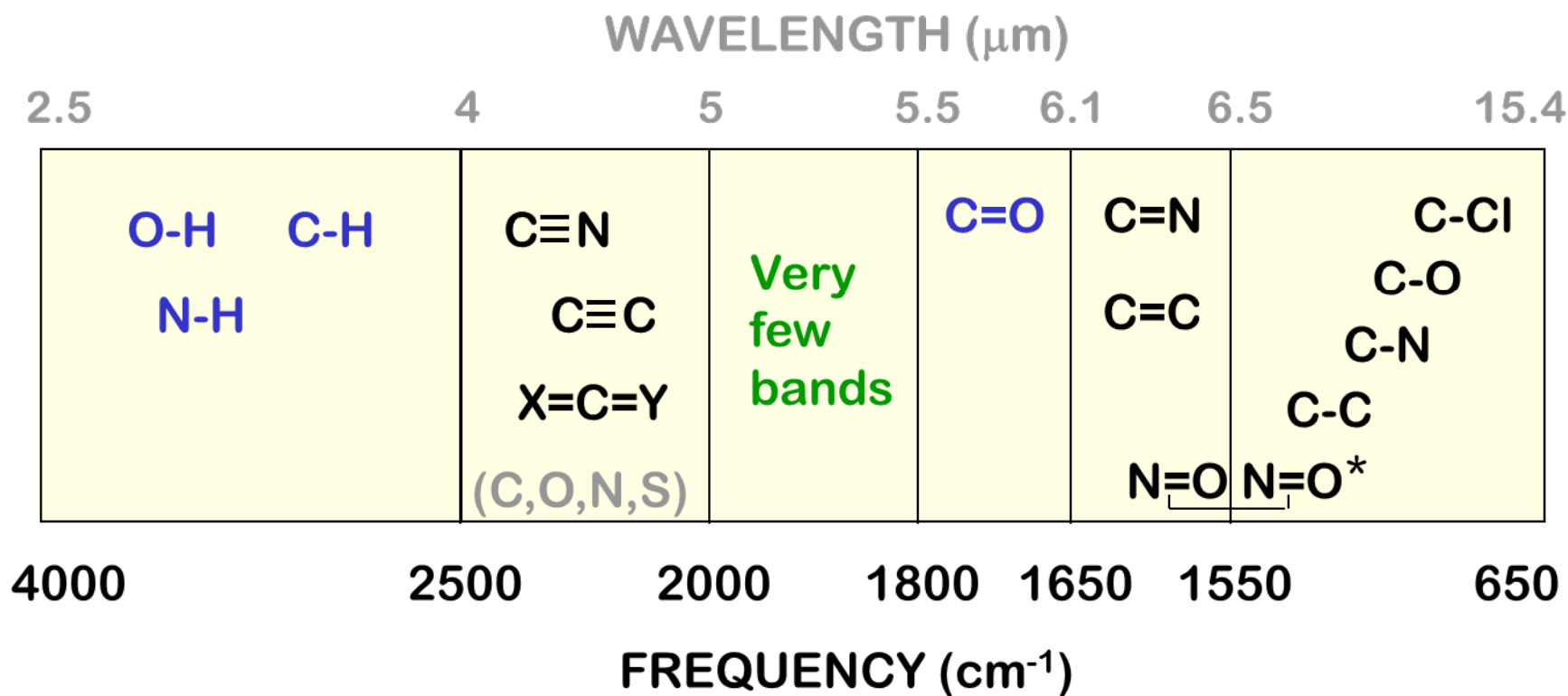
Examples: IR Spectrum of Alcohols
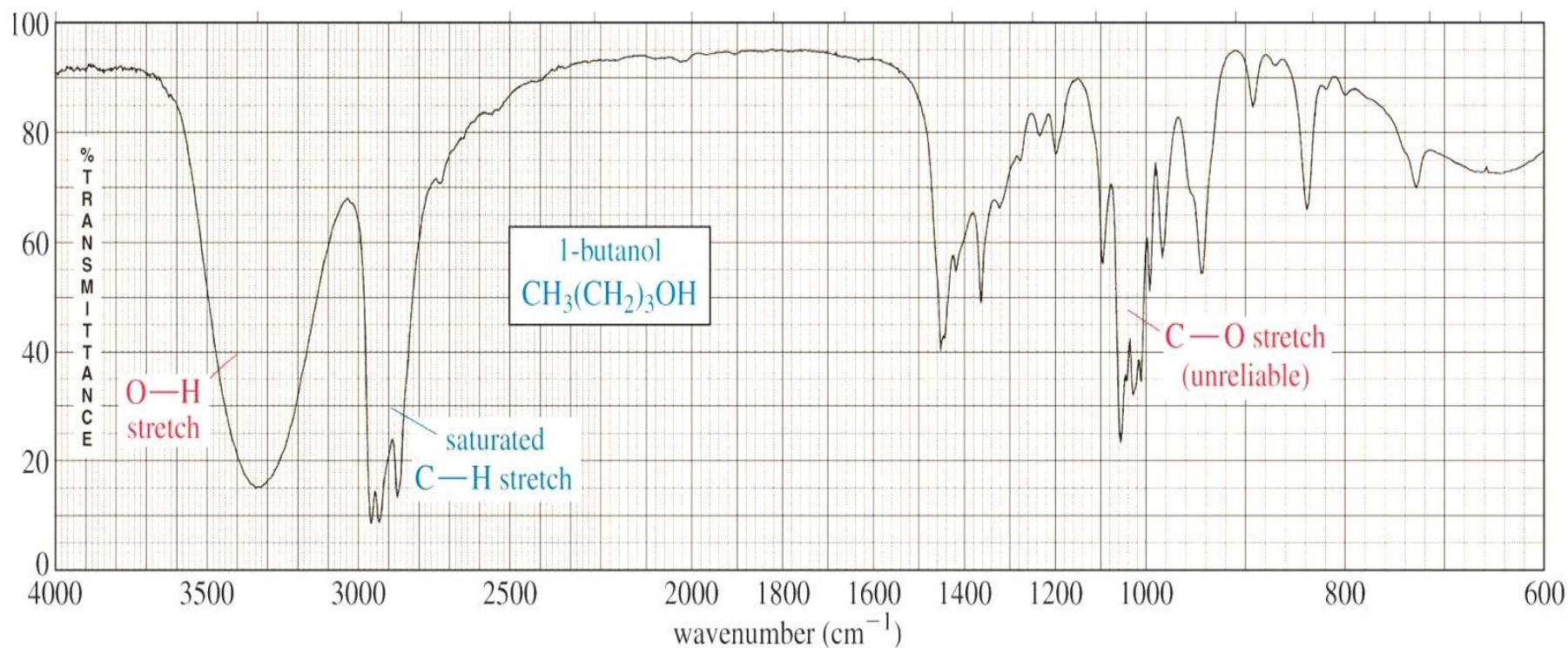
Focus your analysis on this region. This is where most stretching frequencies appear.

Fingerprint region: complex and difficult to interpret reliably.
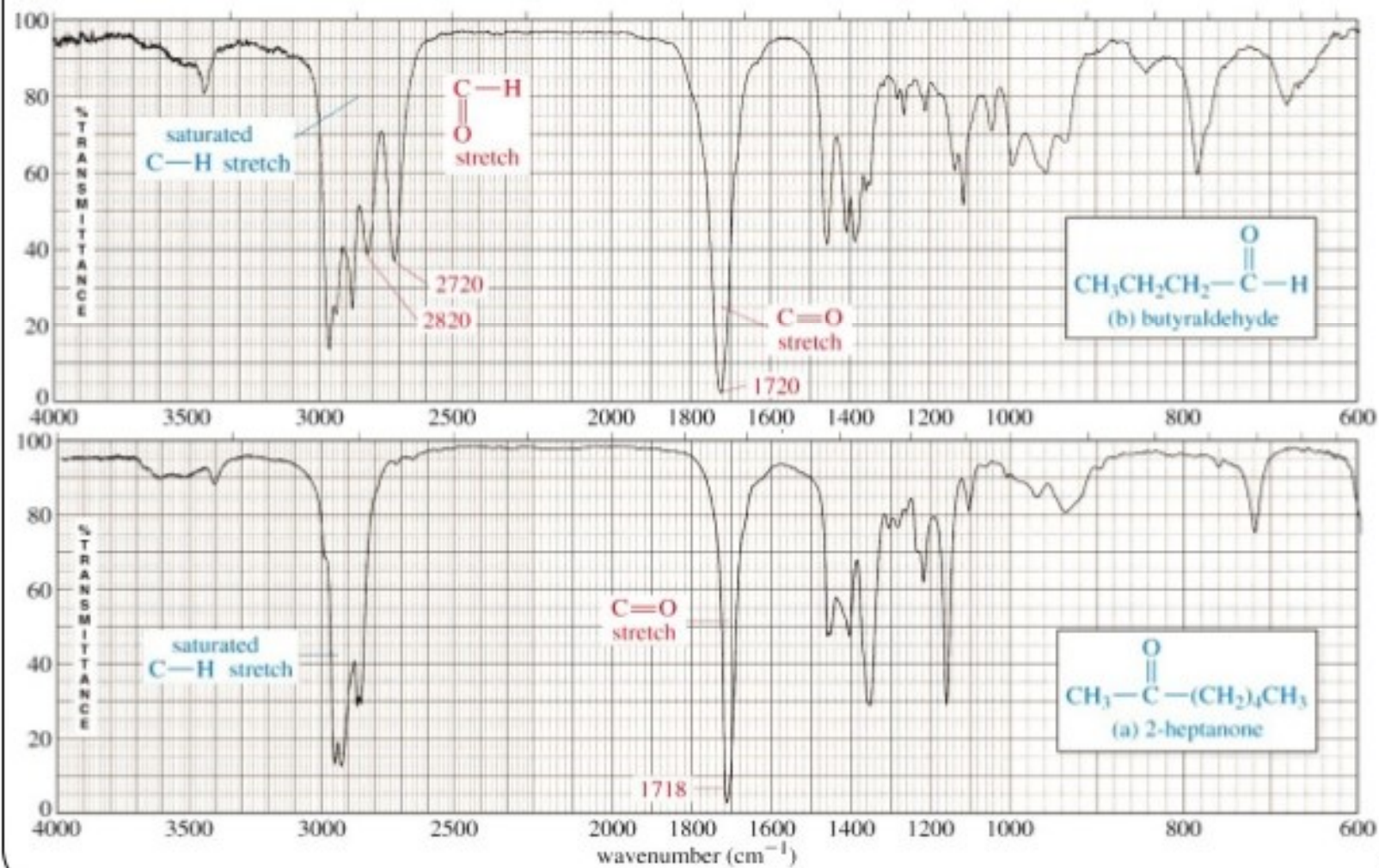
Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

Functional Group	Characteristic Absorption(s) (cm^{-1})
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C≡C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (m,m)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C≡N Stretch	2260 - 2220 (m)
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)
Amide N-H Stretch	3700 - 3500 (m)

IR SPECTRUM OF ALDEHYDES AND KETONES

(b) butyraldehyde:
$$CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

- saturated C—H stretch
- C—H / C=O stretch
- 2720
- 2820
- C=O stretch
- 1720

(a) 2-heptanone:
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4CH_3$$

- saturated C—H stretch
- C=O stretch
- 1718

wavenumber (cm^{-1})

IR SPECTRUM OF A CARBOXYLIC ACID

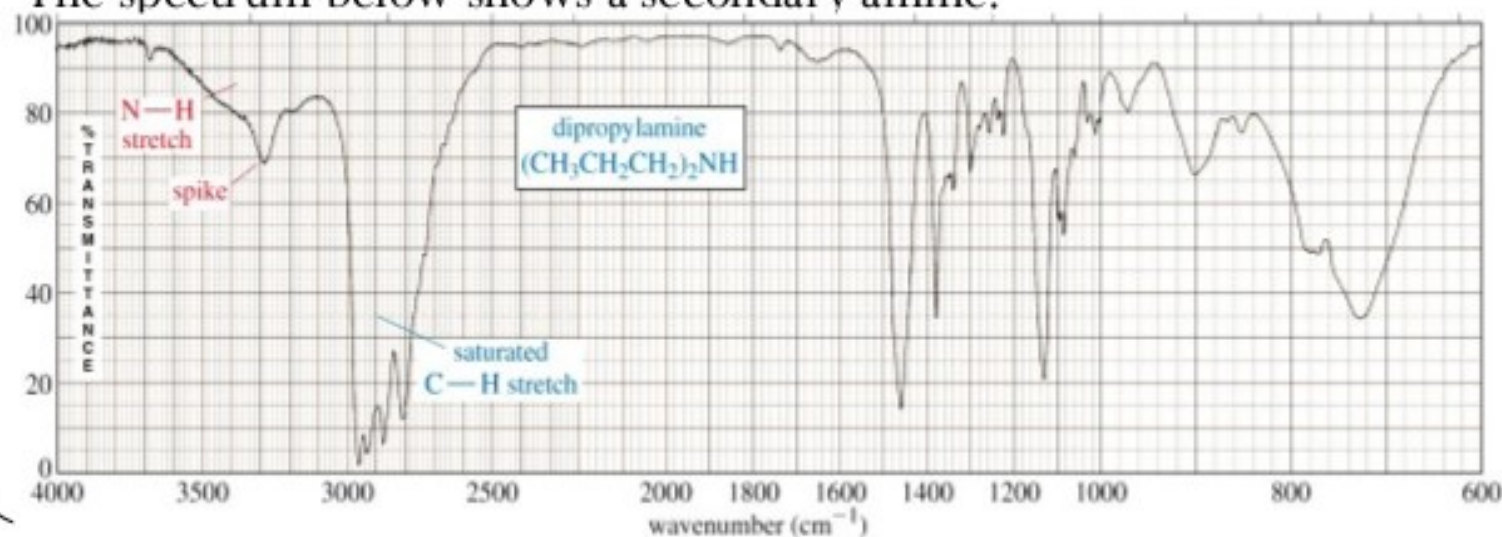A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm⁻¹** for the O-H stretch and also show the stake-shaped band in the middle of the spectrum around **1710 cm⁻¹** corresponding to the C=O stretch.
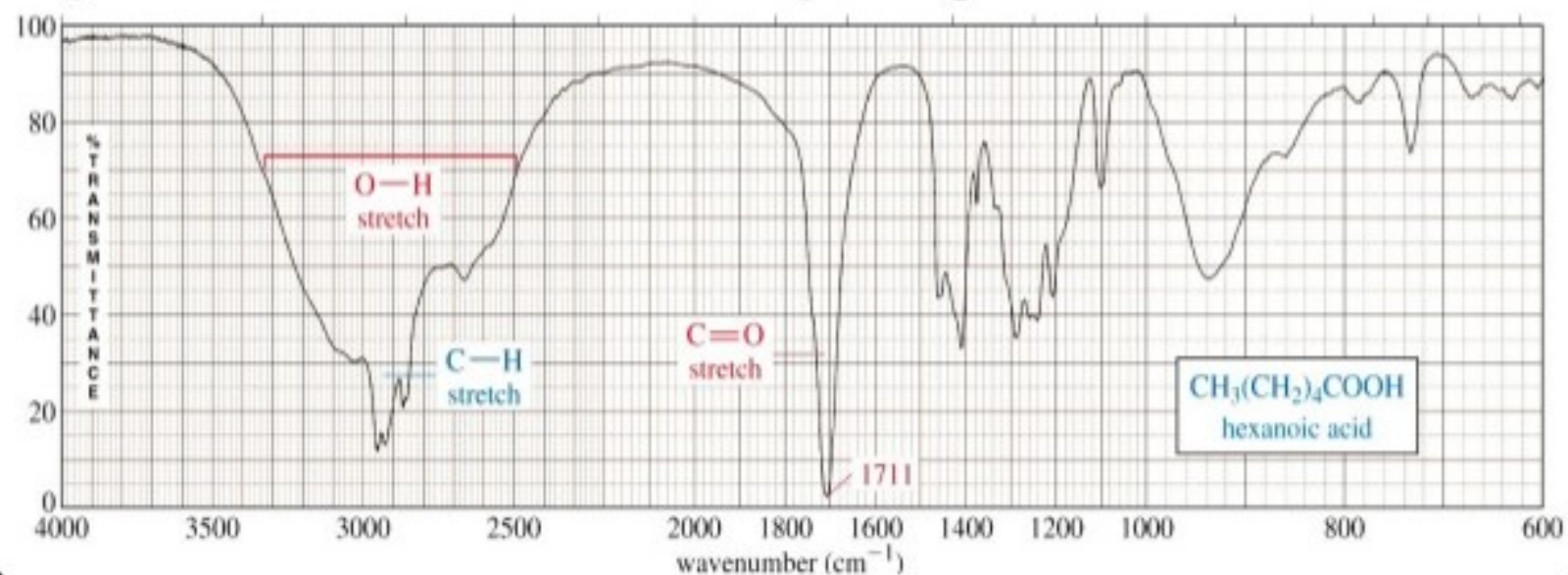
IR SPECTRA OF AMINES

➤The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band. This band is positioned in the range of about **3200 - 3600 cm⁻¹**.

➤Primary amines have two N-H bonds, therefore they typically show two spikes. Secondary amines have only one N-H bond. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether.

The spectrum below shows a secondary amine.

IR SPECTRUM OF AMIDES

The amide functional group combines the features of amines and ketones because it has both the **N–H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm⁻¹** for the N-H stretch. At the same time they also show the stake-shaped band around **1710 cm⁻¹** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.
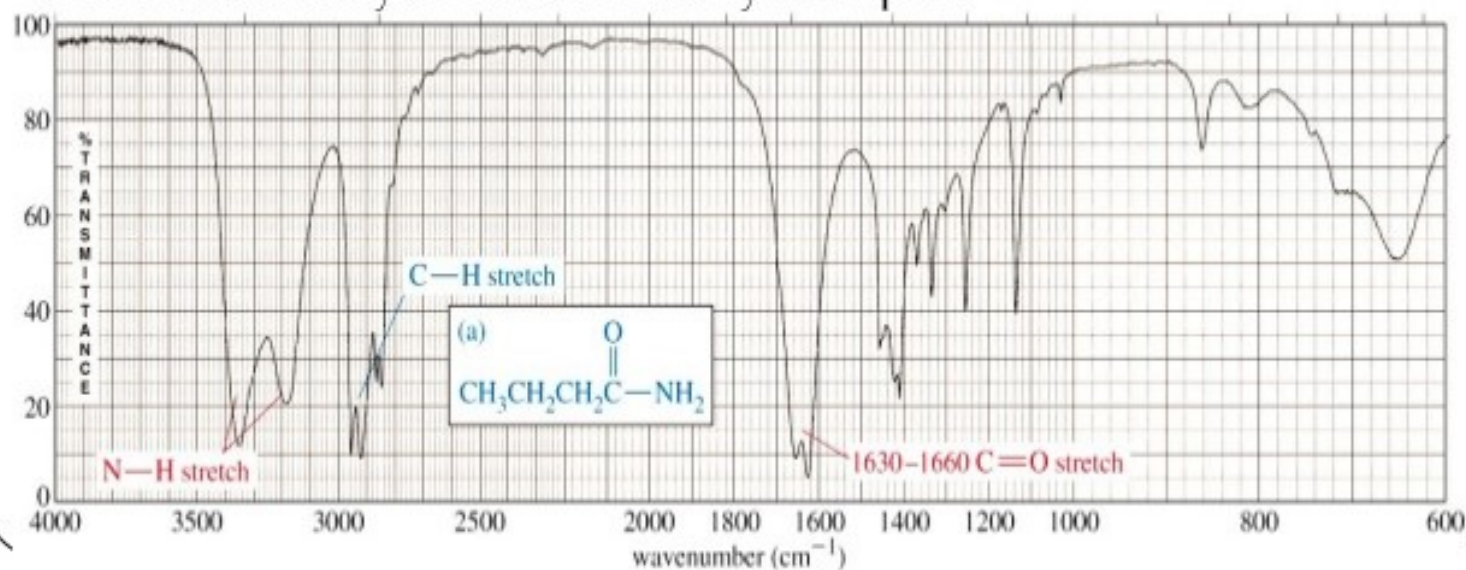
APPLICATIONS OF IR SPECTROSCOPY
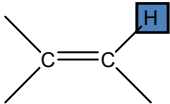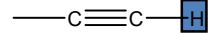
- Identification of functional groups & structure elucidation of organic compounds.

- Quantitative analysis of a number of organic compounds.

- Study of covalent bonds in molecules.

- Studying the progress of reactions.

- Detection of impurities in a compound.

- Ratio of cis-trans isomers in a mixture of compounds.

- Shape of symmetry of an inorganic molecule.

- Study the presence of water in a sample.

- Measurement of paints and varnishes.

Applications of IR

1.) Qualitative Analysis (Compound Identification)
   - main application
   - Use of IR, with NMR and MS, in late 1950's revolutionized organic
      chemistry
➤ decreased the time to confirm compound identification 10- 1000 fold
➤ examine what functional groups are present by looking at group
      frequency region- 3600 cm^{-1} to 1200 cm^{-1}

Abbreviated Table of Group Frequencies for Organic Groups

| Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C-H	Alkanes	2850-2970	Strong
C-H	Alkenes	3010-3095 675-995	Medium strong
C-H	Alkynes	3300	Strong
C-H	Aromatic rings	3010-3100 690-900	Medium strong
0-H	Monomeric alcohols, phenols Hydrogen-bonded alchohols, phenols Monomeric carboxylic acids Hydrogen-bonded carboxylic acids	3590-3650 3200-3600 3500-3650 2500-2700	Variable Variable, sometimes broad Medium 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 1300-1370	Strong

Fingerprint Region (1200-700 cm^{-1})

- region of most single bond signals

- many have similar frequencies, so affect each other & give pattern characteristics of   overall skeletal structure of a compound

- exact interpretation of this region of spectra seldom possible because of complexity

- complexity → uniqueness
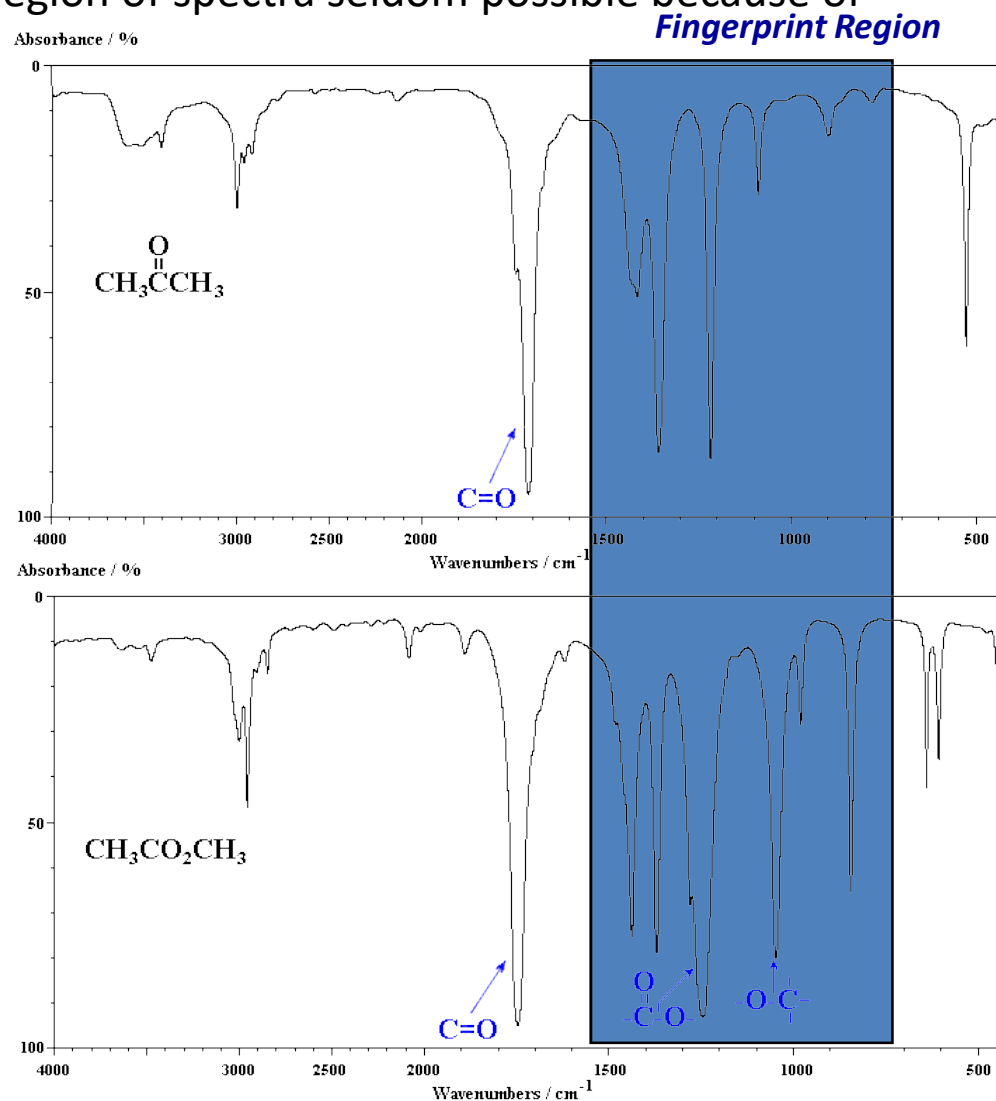
Computer Searches

- many modern instruments have reference IR spectra on file (~100,000 compounds)
- matches based on location of strongest band, then 2nd strongest band, etc overall skeletal structure of a compound
- exact interpretation of this region of spectra seldom possible because of
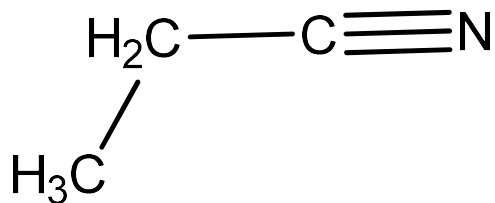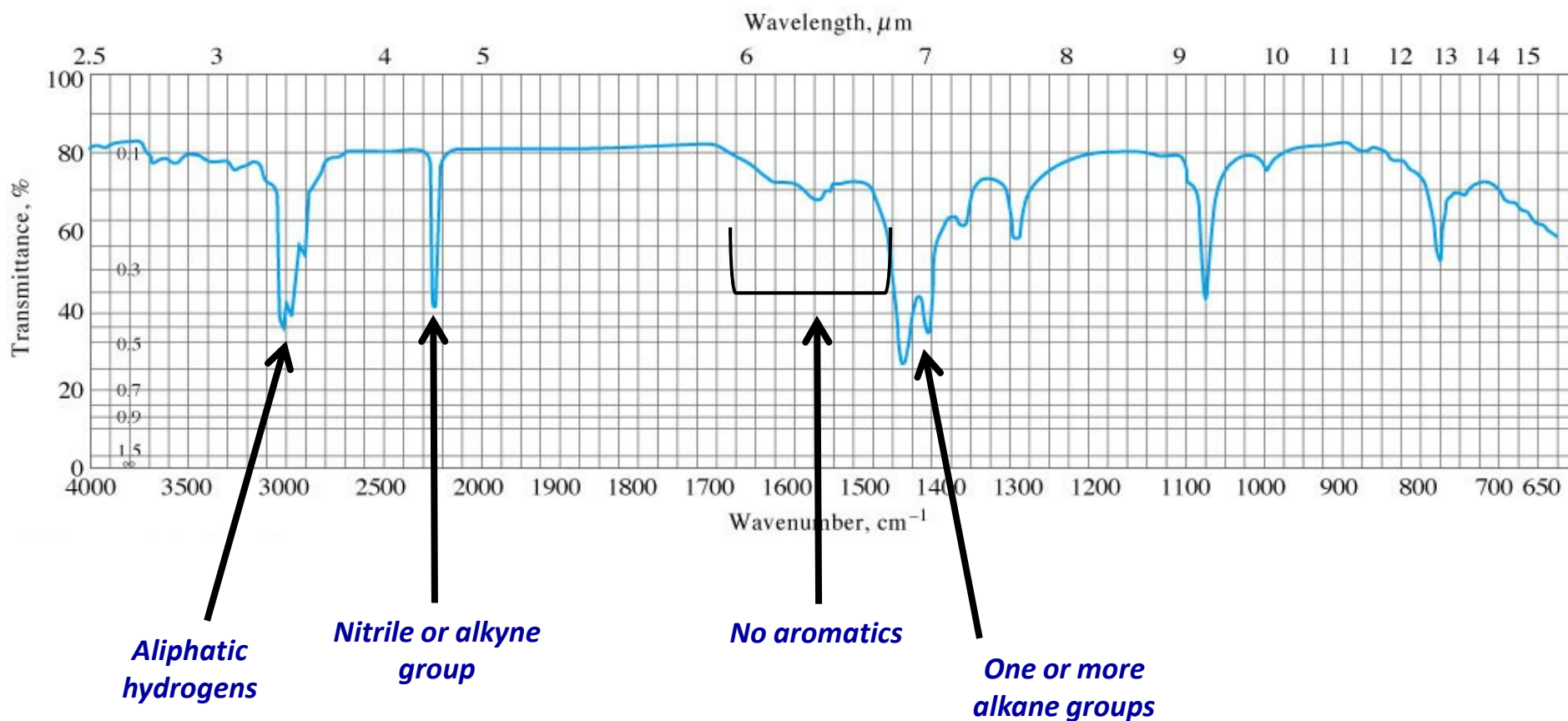

Bio-Rad SearchIT database of ~200,000 IR spectra
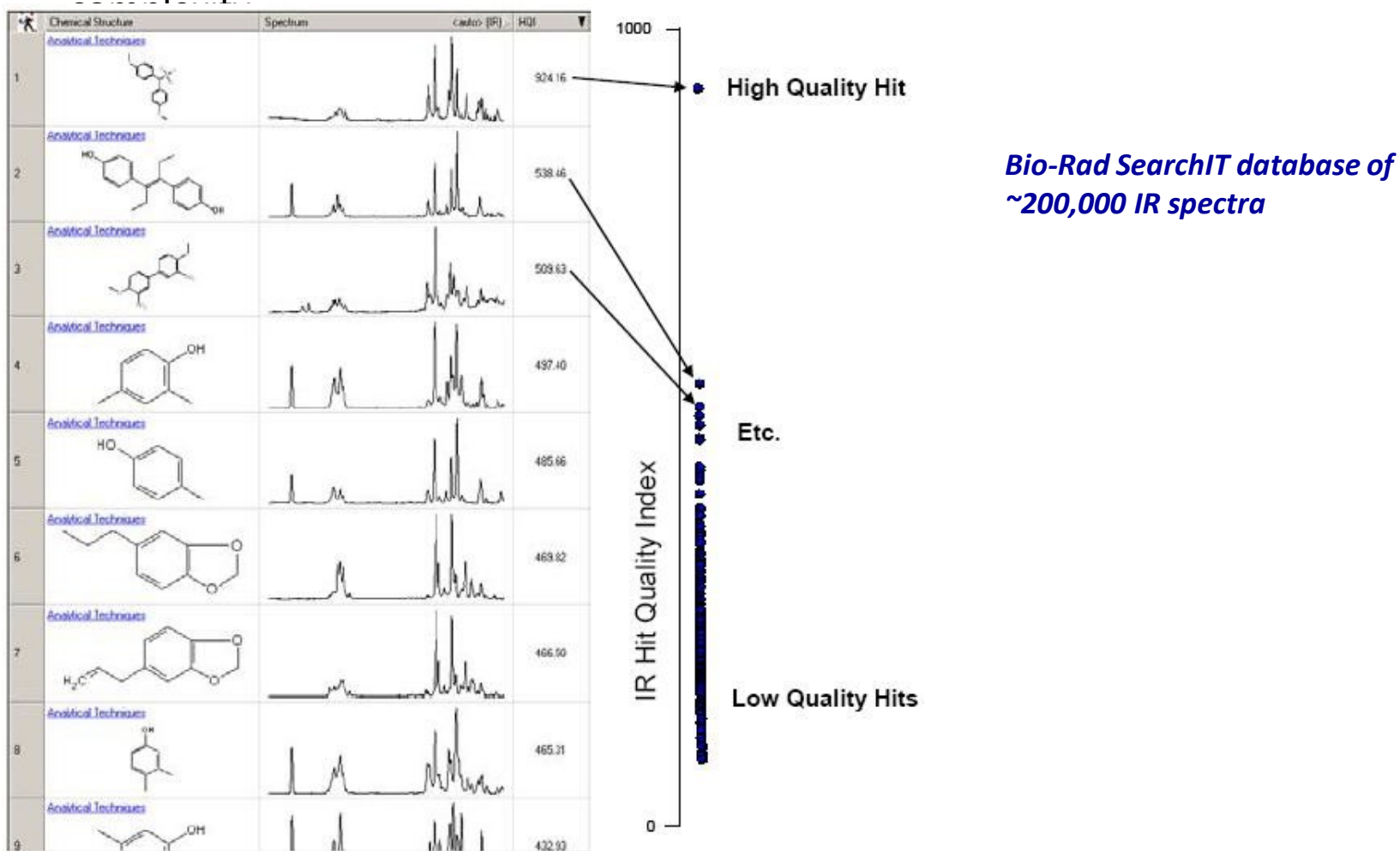
2.) Quantitative Analysis

- not as good as UV/Vis in terms of accuracy and precision

▶ more complex spectra

▶ narrower bands (Beer's Law deviation)

▶ limitations of IR instruments (lower light throughput, weaker detectors)

▶ high background IR

▶ difficult to match reference and sample cells

▶ changes in ε ($A = \varepsilon bc$) common

- potential advantage is good selectivity, since so many compounds have different IR spectra

▶ one common application is determination of air contaminants.

Contaminants	Concn, ppm	Found, ppm	Relative error, %
Carbon Monoxide	50	49.1	1.8
Methylethyl ketone	100	98.3	1.7
Methyl alcohol	100	99.0	1.0
Ethylene oxide	50	49.9	0.2
chloroform	100	99.5	0.5

Example : The spectrum is for a substance with an empirical formula of C_3H_5N. What is the compound?

Wavelength, μm

Aliphatic hydrogens

Nitrile or alkyne group

No aromatics

One or more alkane groups

$H_2C — C \equiv N$

H_3C

LIMITATIONS OF IR SPECTROSCOPY

- Cannot determine the molecular weight of the compound.

- Does not give information about the relative position of different functional groups in a molecule.

- From the single IR spectrum of an unknown substance, it is not possible to know whether it is pure compound or a mixture of compound.

- Sample cells are made of halaogen salts which are susceptible to moisture.

- Gas samples cannot be analyzed as they lack sensitivity.

THANK YOU