

# Spectroscopy

# SPECTROSCOPY

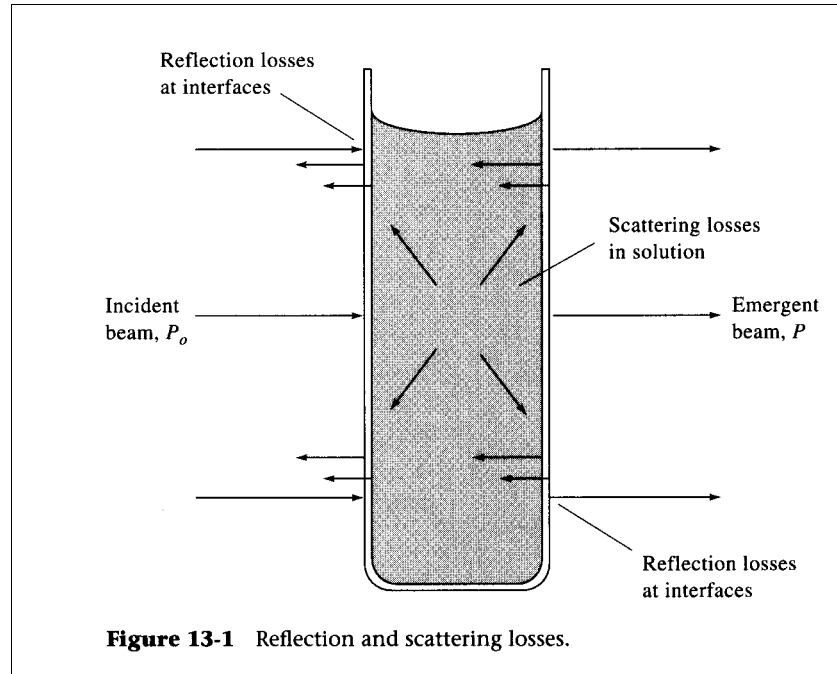
It is a branch of science which deals with interaction of electromagnetic radiations with matter.

Applications: It provides us a scope to know more about the structure of molecules or atoms.

It is a tool in chemical analysis of a wide range of samples.

This interaction of electromagnetic radiations with matter induces a variety of transitions in them.

# REFLECTION AND SCATTERING LOSSES



- 1) In atom electrons get excited from lower to higher energy state and emit absorbed energy when come back to lower electronic level.
- 2) The energy absorbed or emit is quantized and having fixed wavelength.
- 3) A plot of intensity of wavelength of radiations emitted or absorbed against corresponding wavelength or frequency is called spectrum.
- 4) The atomic spectra are simpler because they have electronic transitions only.
- 5) Molecular spectra are complicated because they involve electronic , vibrational , rotational and transitional transitions depending upon the nature of radiations absorbed.

# MOLECULAR ENERGIES

1. Translational Energy
2. Rotational Energy
3. Vibrational Energy
4. Electronic Energy

# TRANSITIONAL ENERGY

Kinetic energy possessed by a molecule due to its motion in space is Transitional Energy.

Average Transitional Energy is  $=\frac{3}{2}kT$

Where  $k$  = Boltzmann constant

# ROTATIONAL ENERGY

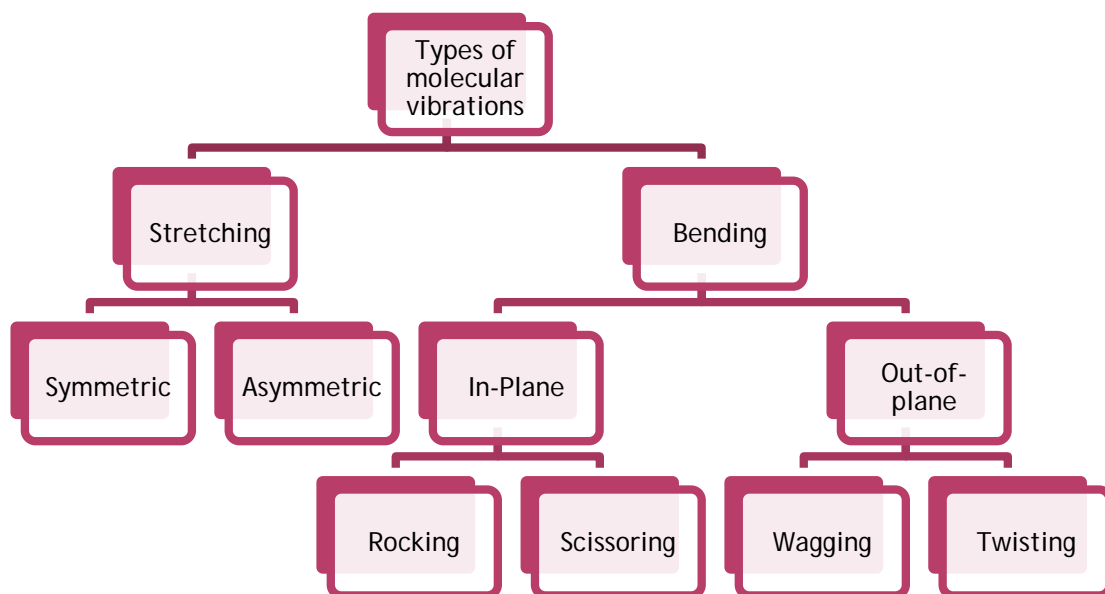
The energy involved in rotation of molecule or its part ,about the centre of gravity is Rotational Energy.Its value for

Linear molecule=Two Rotational degrees of freedom.

Non linear molecule=Three Rotational degrees of freedom.

**Vibrational Energy** :The energy involved in causing the vibrations in molecule is Vibrational Energy.

MODES OF MOLECULAR VIBRATIONS( $AX_2$  )





A linear molecule with  $n$  atoms having  $(3n-5)$  vibrational degrees of freedom.

A non linear molecule with  $n$  atoms having  $(3n-6)$  vibrational degrees of freedom.

Calculate vibrational degrees of freedom for the following molecules.

$\text{CH}_4, \text{NH}_3, \text{CO}_2, \text{H}_2\text{O}, \text{C}_2\text{H}_2, \text{etc}$

# Electronic Energy

The energy involved in excitation of electron to higher energy level or due to change in distribution of electron by cleavage of bond is electronic Energy.

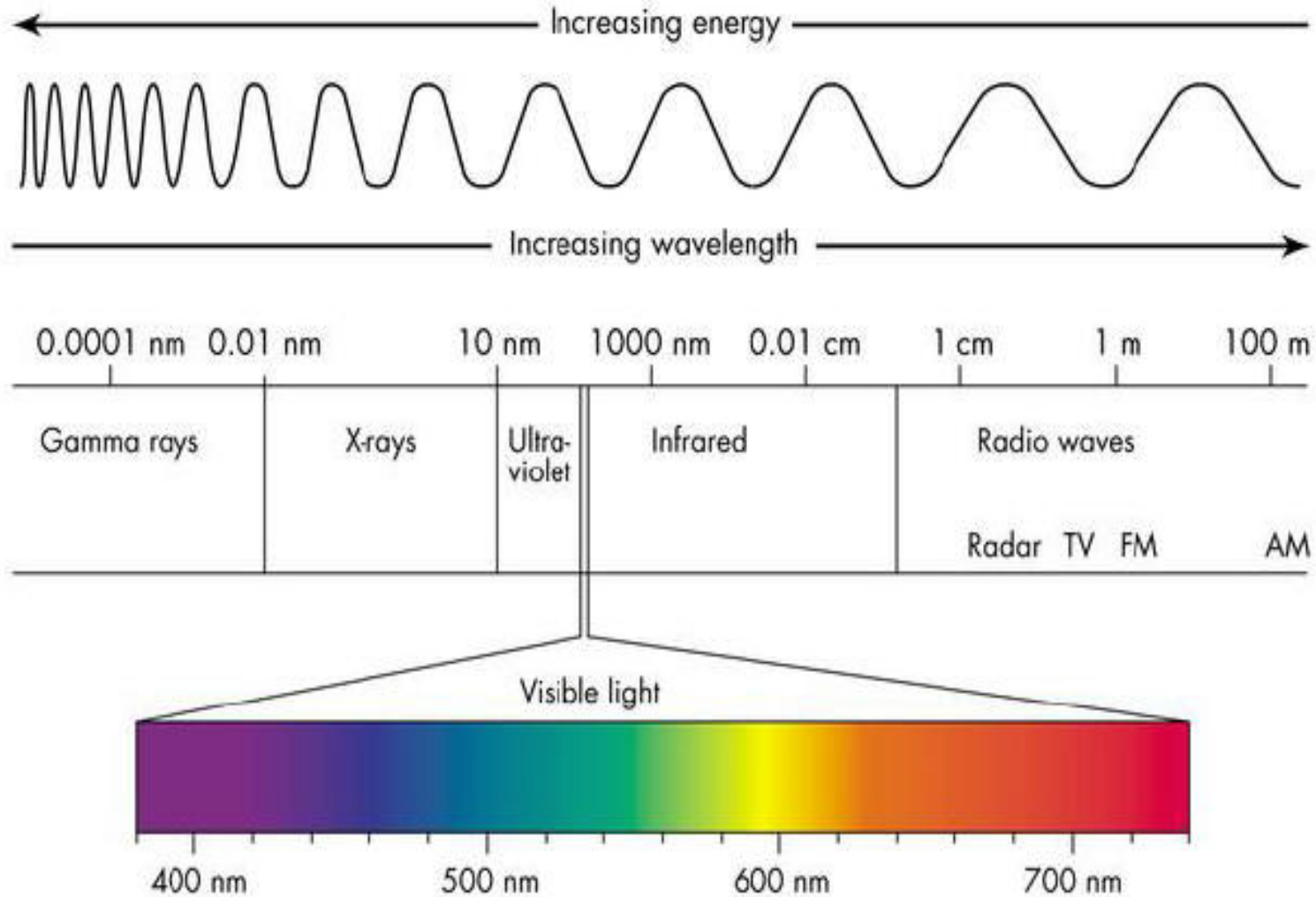
At room temperature translational energies are closely spaced and continuous.

$$E(\text{total})=E(e)+E(v)+E(r)$$

The relative magnitude of these energies are as follows-

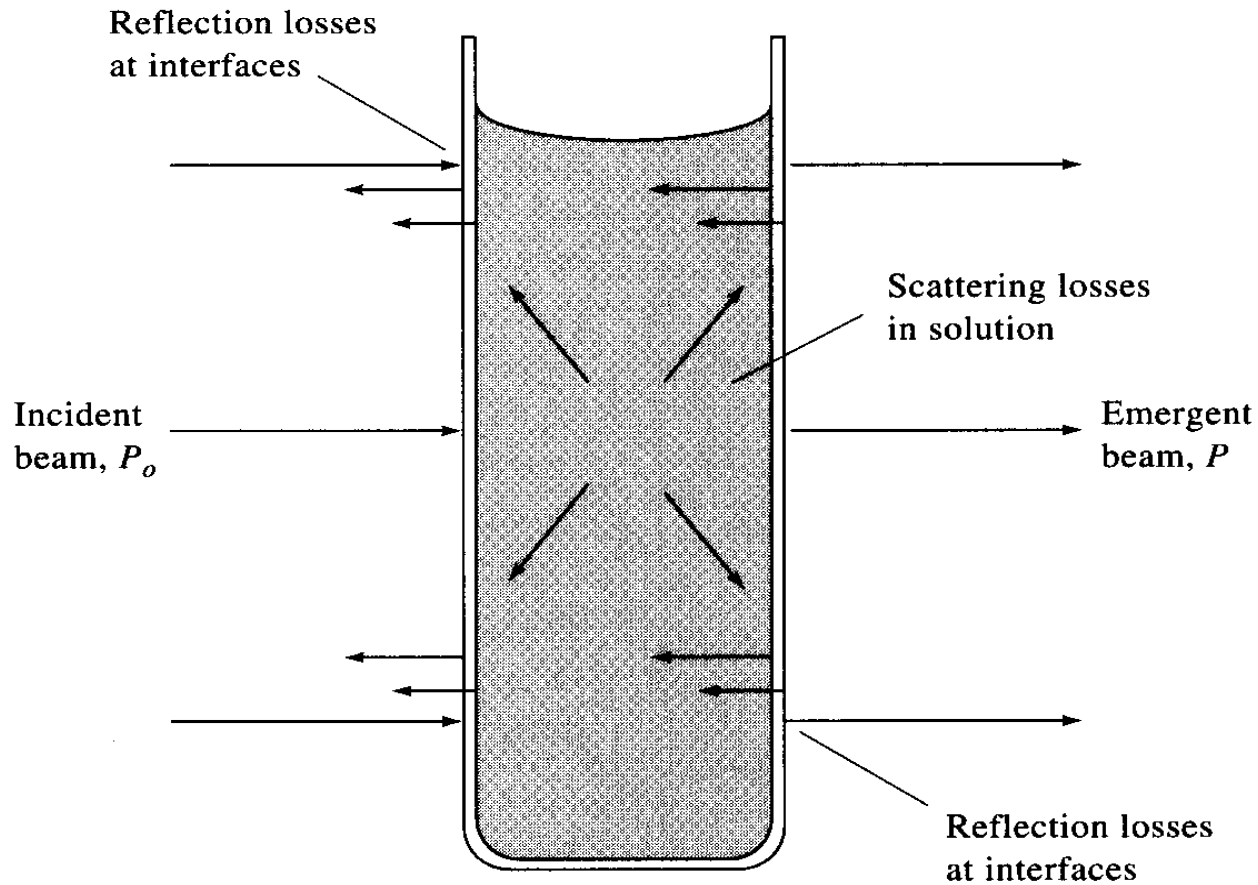
- a) The energy difference between two electronic level is much larger as compared to vibrational level belongs to same electronic level.
- b) The two rotational levels are still closer and have less energy difference.

# SPECTRA OF LIGHT



# IR Spectroscopy

# REFLECTION AND SCATTERING LOSSES



**Figure 13-1** Reflection and scattering losses.

# LAMBERT BEER'S LAW

- ◉ When the beam of monochromatic radiations is passed through a homogeneous absorbing solution , the rate of decrease of intensity ,with thickness of absorbing medium is proportional to the intensity of incident radiation as well as to the concentration of the solution.
- ◉  $-dI/dx=K.C.I$  where,
- ◉  $K$ =Molar Absorption Coefficient
- ◉  $C$ =Concentration of the Solution &
- ◉  $I$ =Intensity of light

# INFRA RED SPECTROSCOPY

- Definition-Vibrational spectroscopy involve the transition between vibrational energy level of the molecule on absorption of radiation falling in the spectral range of (500-4000  $\text{cm}^{-1}$ )
- A single vibrational energy change is accompanied by a large no of rotational energy changes, thus Principle-Vibrational spectra appears as Vibrational rotational bands.

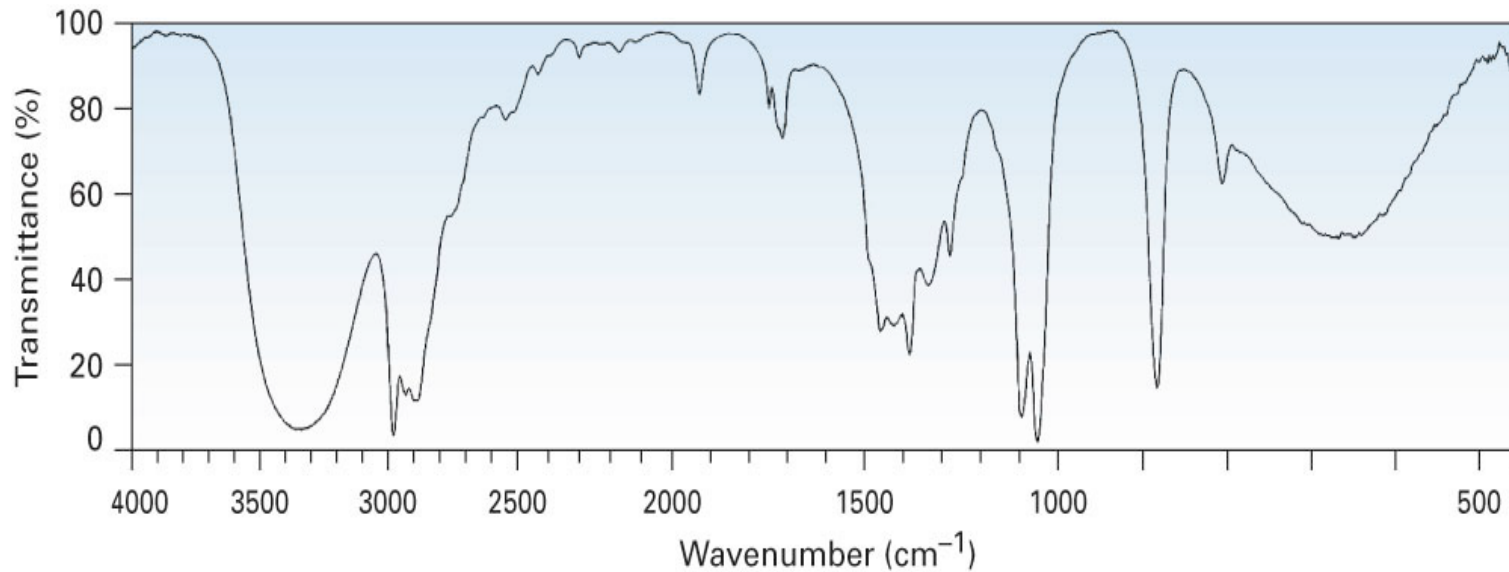
# ENERGY CHANGE

- ⦿ 1-100 KJ/mole
- ⦿ Each line of vibrational structure is associated with rotational fine structure that is why it is also called rotational- vibrational spectroscopy.



# IR SPECTRA

Normally it is a plot of Percentage transmittance against wave no.



# PRINCIPLE

- The atoms which constitute a covalent molecules are not stationary. They are continuously vibrating and rotating in a no. of ways.
- The absorption in IR region is due to change in dipole moment or rotational -vibrational level. When radiations with frequency range less than  $100\text{cm}^{-1}$  are absorbed, molecular rotations takes place in the substance and hence discrete lines are formed in the spectrum as the absorption is quantized.

- ⦿ During the vibration of the molecule, if there occur a change in dipole moment it'll lead to generation of oscillating electrical field. Now if the frequency of this field is equal to the frequency of fluctuating electrical field of radiation, there occur a phenomenon of resonance & hence energy can be transferred from the radiation to the molecule or vice versa. This'll lead to the **basis of IR Spectroscopy.**

# TYPE OF MOLECULAR VIBRATIONS( $AX_2$ )

## Types of molecular vibrations

Stretching

Symmetric

Asymmetric

Bending

In-Plane

Out-of-plane

Rocking

Scissoring

Wagging

Twisting

- In IR Spectroscopy absorb energy, bring predominant change in vibrational energy, which depend upon
  - Mass of atoms present in molecule
  - Strength of the bond
  - Arrangement of atoms within the molecule

# IMPORTANT

- ◉ No two compounds have similar IR spectra except enantiomers (mirror image molecules)
- ◉ Only those molecules which exhibit change in dipole moment during the vibrations can exhibit IR spectra.
- ◉ Homonuclear diatomic molecule ( $H_2$ ,  $N_2$ ,  $O_2$ ,  $Cl_2$ ,) do not show change in the dipole moment during vibrations, so they do not exhibit IR spectra.

# IR ACTIVE MOLECULES

- ◉ **IR Active molecules** are those molecules which do have permanent dipole moment hence exhibit a change in dipole moment during the vibration.
- ◉ There're some molecules which do not have dipole moment but some of there vibrational modes are accompanied by change in dipole moment, hence lead to the generation of IR Spectra.
- ◉ Example- Anti-symmetric stretching & bending modes of vibration of  $\text{CO}_2$  molecule result in variation of dipole moment. Thus  $\text{CO}_2$  molecule becomes IR active although it lacks permanent dipole moment.

# VIBRATIONAL FREQUENCIES

- ◉ A simple harmonic oscillator can be considered as a model for a vibrating diatomic molecule. So fundamental vibrational frequency ( $\nu_0$ ) of such a molecule behave like a simple harmonic oscillator and is given by its equation.
- ◉ Here  $k$ =Force Constant of the bond & related to its strength

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

- ◉  $K$ =force constant of the bond & related to its strength
- ◉  $\mu = (m_1 m_2) / (m_1 + m_2)$  is called reduced mass
- ◉  $m_1$  &  $m_2$ =masses of two atoms



# VIBRATIONAL FREQUENCY DEPEND ON

Bond strength and Reduced mass

In case of the polyatomic molecules No. of vibrational modes are

For linear molecules- $(3n-5)$

For nonlinear molecules- $(3n-6)$

# GROUP FREQUENCY


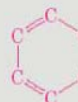

- Absorption stretching or bending vibrations are characteristics of particular functional group in many molecules. Such frequencies are known as **Group frequency**
- Eg-absorption of  $C_6H_5COCH_3$  is
- at  $3050\text{cm}^{-1}$  C-H(aromatic)
- $1700\text{cm}^{-1}$  CO
- So IR spectra permits recognition of the type of functional group in organic molecules.
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# REGION OF IR SPECTRA

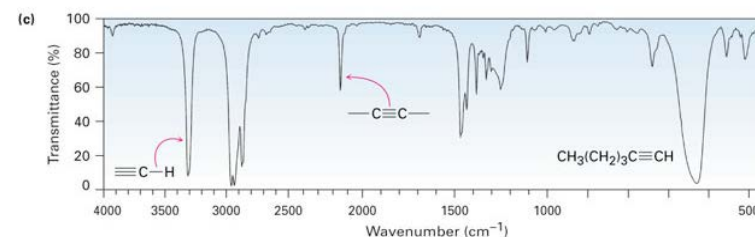
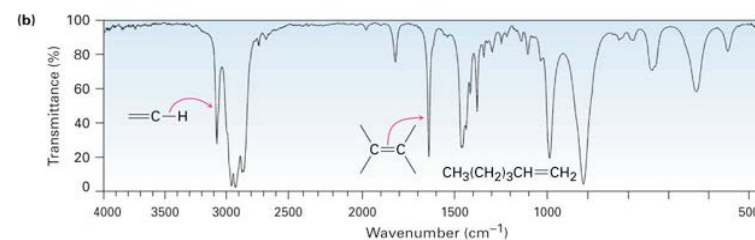
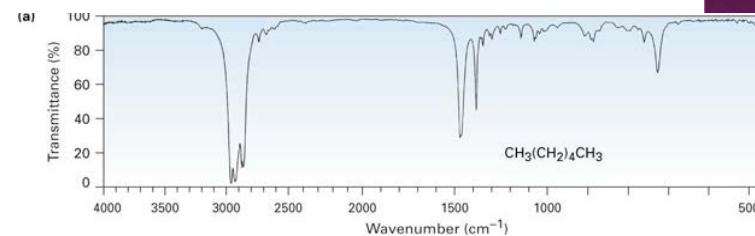
- ◉ IR spectra are commonly divided into 3 regions:
  1. Functional group region: It's a high frequency region between  $4000-1300\text{ cm}^{-1}$ . This is because of the characteristic stretching frequency for important functional groups such as C=O, OH & NH.
  2. Fingerprint Region: It's a middle frequency region ( $1300-900\text{ cm}^{-1}$ ). In this region complex absorption occurs due to combinations of interacting vibrational modes, providing the unique fingerprint for every molecule.
  3. Low frequency region ( $900-650\text{ cm}^{-1}$ ): It provides general classification of molecules from the pattern of absorption such as substitution pattern on benzene ring. The absence of absorption in this region can provide a good evidence for the absence of aromatic compound.

# CHARACTERISTIC ABSORPTIONS

**TABLE 12.1** Characteristic IR Absorptions of Some Functional Groups

Functional group class	Band position (cm <sup>-1</sup> )	Intensity of absorption
Alkanes, alkyl groups C-H	2850-2960	Medium to strong
Alkenes =C-H C=C	3020-3100 1640-1680	Medium Medium
Alkynes ≡C-H -C≡C-	3300 2100-2260	Strong Medium
Alkyl halides C-Cl C-Br C-I	600-800 500-600 500	Strong Strong Strong
Alcohols O-H C-O	3400-3650 1050-1150	Strong, broad Strong
Aromatics 	3030	Weak
	1660-2000	Weak
	1450-1600	Medium
Amines N-H C-N	3300-3500 1030-1230	Medium Medium
Carbonyl compounds <sup>a</sup> C=O	1670-1780	Strong
Carboxylic acids O-H	2500-3100	Strong, very broad
Nitriles C≡N	2210-2260	Medium
Nitro compounds NO <sub>2</sub>	1540	Strong

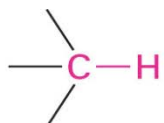
<sup>a</sup>Carboxylic acids, esters, aldehydes, and ketones.



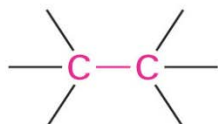
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# INFRARED SPECTRA OF SOME COMMON FUNCTIONAL GROUPS

**Alkanes**



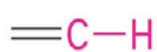
2850–2960  $\text{cm}^{-1}$



800–1300  $\text{cm}^{-1}$

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**Alkenes**



3020–3100  $\text{cm}^{-1}$



1640–1680  $\text{cm}^{-1}$



910 and 990  $\text{cm}^{-1}$



890  $\text{cm}^{-1}$

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**Alkynes**



2100–2260  $\text{cm}^{-1}$



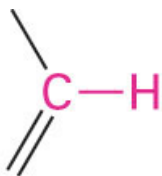
3300  $\text{cm}^{-1}$

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# IR: AROMATIC COMPOUNDS

- Weak C-H stretch at  $3030\text{ cm}^{-1}$
- Weak absorptions  $1660 - 2000\text{ cm}^{-1}$  range
- Medium-intensity absorptions  $1450$  to  $1600\text{ cm}^{-1}$
- See spectrum of phenylacetylene, Figure 12.15

**Aromatic compounds**



$3030\text{ cm}^{-1}$  (weak)



$1660-2000\text{ cm}^{-1}$  (weak)

$1450-1600\text{ cm}^{-1}$  (medium)

# IR: ALCOHOLS AND AMINES

O-H 3400 to 3650  $\text{cm}^{-1}$  Usually broad and intense  
N-H 3300 to 3500  $\text{cm}^{-1}$  Sharper and less intense than an O-H

**Alcohols**      —O—H      3400–3650  $\text{cm}^{-1}$  (broad, intense)

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**Amines**      —N—H      3300–3500  $\text{cm}^{-1}$  (sharp, medium intensity)  
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# APPLICATIONS OF IR SPECTROSCOPY

1. To ascertain hydrogen bonding in the molecule. -Inter and intra molecular hydrogen bonding can be identified taking series of IR Spectra of the compound at infinite dilution.

On increasing the dilution ,absorption band due to intermolecular H-bonding will be diminishes while intra molecular H-bonding remains unchanged.

Contd....



# APPLICATIONS OF IR SPECTROSCOPY

2. It provides valuable information about symm. dipole moment and bond length.
  3. It distinguishes positional isomers.
  4. It is used for rapid quantitative analysis of mixture of compound in pollution detection and milk analysis.
  5. Determination of force constants from vibrational spectrum.
- Contd ...

# APPLICATIONS OF IR SPECTROSCOPY

6. In establishing the identity of compounds. eg benzaldehyde and phenylmethyletones both shows absorption peaks at  $1700\text{cm}^{-1}$  indicating keto group in both compounds.
  7. In determination of impurity in sample.- impure sample shows some extra peaks so by comparing with pure compound impurities can be detected.
- Contd-

# APPLICATIONS OF IR SPECTROSCOPY

8. Identification of functional group in organic molecules'
9. Elucidation of structure.