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.

$$\frac{-dI}{dx} \alpha C.I.$$

$$\frac{-dI}{dx} = KC.I.$$

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 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.

I.R. Region

- 4000-667Cm^{-1} Ordinary IR Region
- 1250- 4000Cm^{-1} near IR Region
- 667-500Cm^{-1} Far IR Region

Energy change

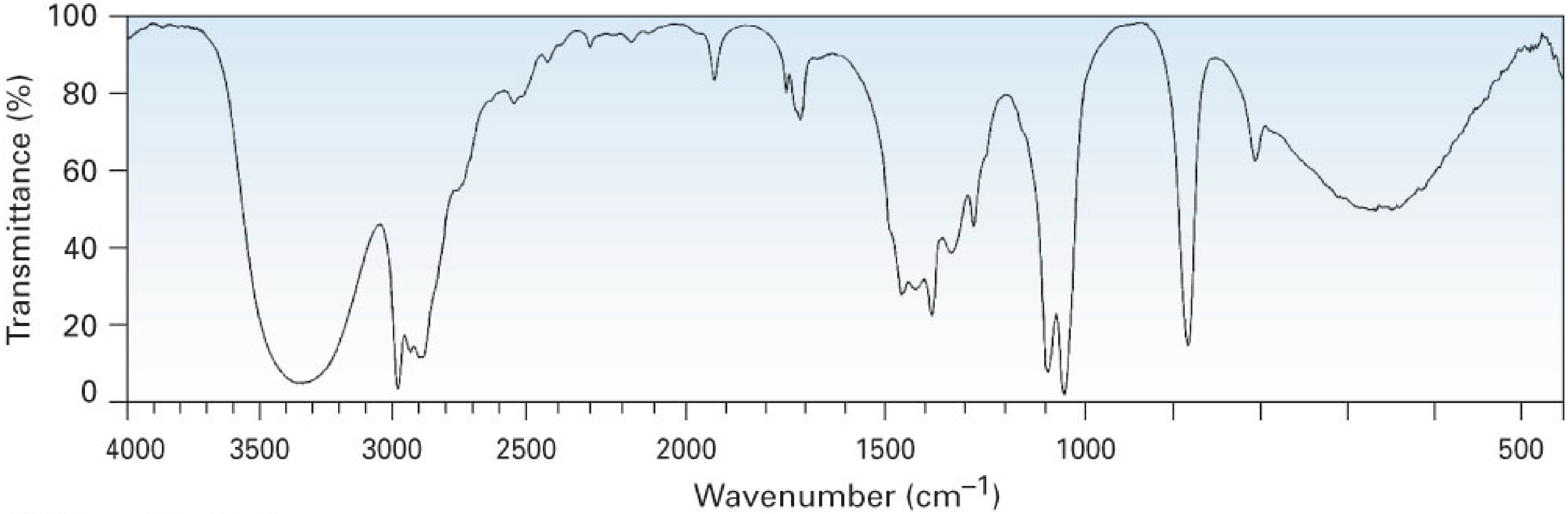
- 1-100 KJ/mole
- Each line of vibrational structure is associated with rotational fine structure that is why it is also called rotational- vibrational spectroscopy.

I R Spectra

- Absorption of I R radiation is expressed
- In lemda
- In wave no.

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

IR spectra



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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.

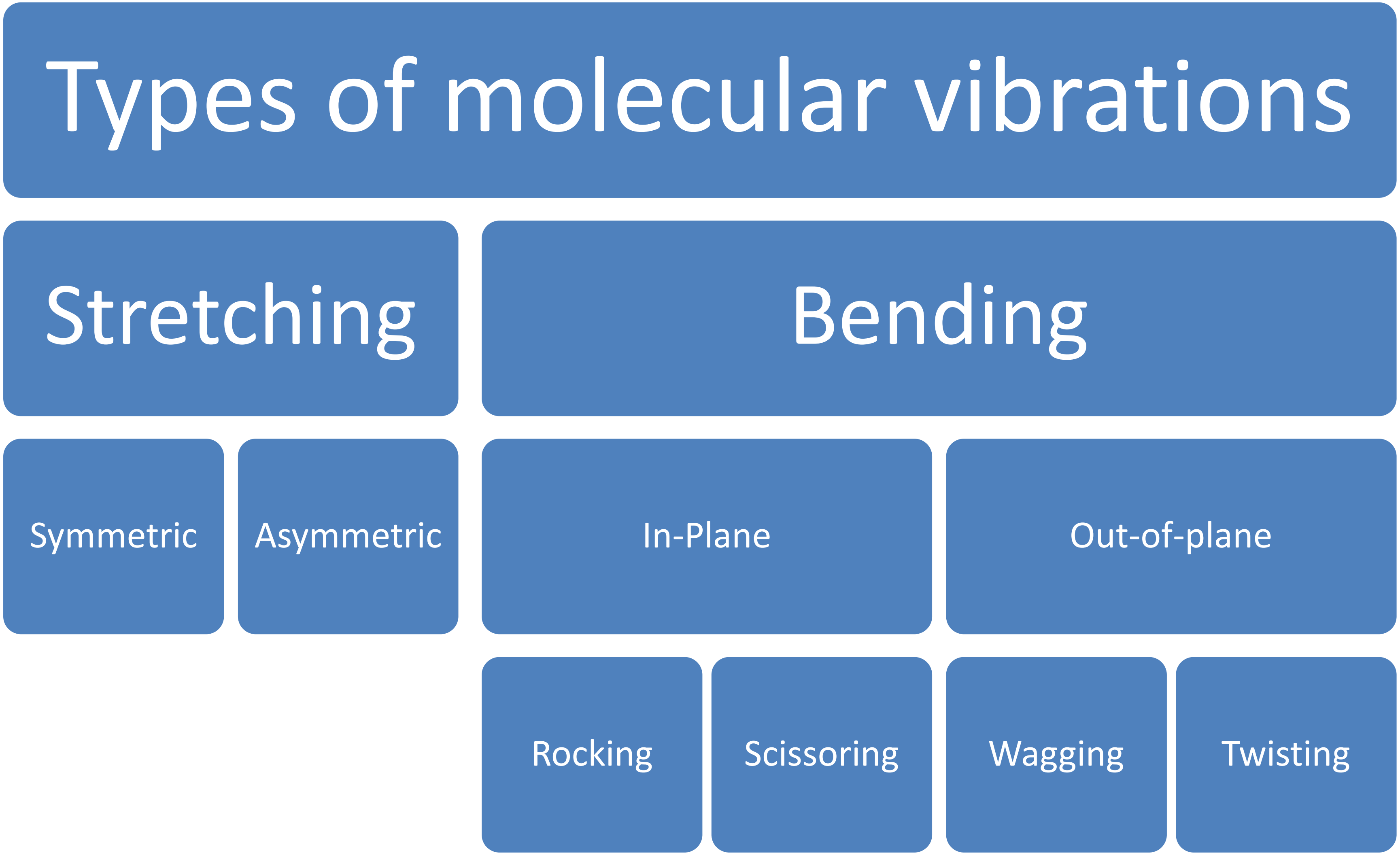
Contd-

- .When radiations with energy more than 10^2 - 10^4 cm^{-1} are passed through the sample of the substance,molecular vibrations and ratations changed and such absorptions are a quantised.
- Clearly a single vibrational energy change is accompanied by large no of rotational energy changes,so vibrational spectra appears as vibrational rotational spectra.
-

Contd-

- 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

Bending

Symmetric

Asymmetric

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,)donot 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 $C0_2$ molecule result in variation of dipole moment.Thus $C0_2$ 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 (V_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 stength

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

- K=force constant of the bond & related to its strength
- μ= (m1m2)/(m1+m2) is called reduced mass
- m1 & m2=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 characterstics of purticular functional group in many molecules Such frequencies are known as **Group frequency**
- Eg-absorption of $C_6H_5COCH_3$ is
- at 3050Cm-1 C-H(aromatic)
- 1700Cm-1 CO
- So IR spectra permits recognition of the type of functional group in organic molecules.
-

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 cm^{-1}.This is because of the characteristic stretching frequency for important functional groups such as C=0,OH & NH.
2. Fingerprint Region: It's a middle frequency region(1300-900 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 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

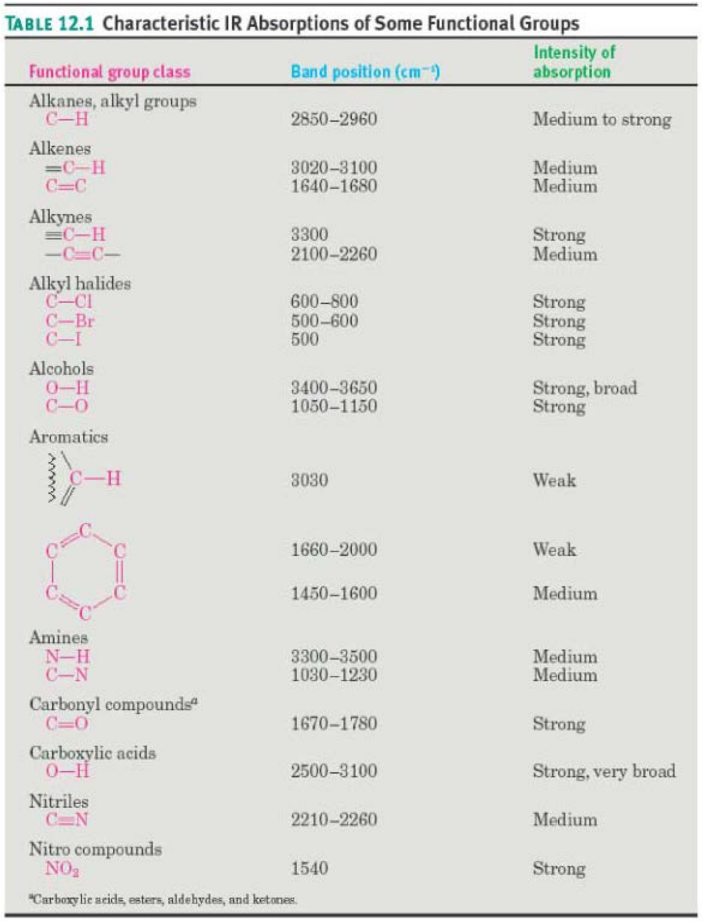


TABLE 12.1 Characteristic IR Absorptions of Some Functional Groups

Functional group class	Band position (cm^{-1})	Intensity of absorption
Alkanes, alkyl groups		
C—H	2850–2960	Medium to strong
Alkenes		
=C—H	3020–3100	Medium
C=C	1640–1680	Medium
Alkynes		
≡C—H	3300	Strong
—C≡C—	2100–2260	Medium
Alkyl halides		
C—Cl	600–800	Strong
C—Br	500–600	Strong
C—I	500	Strong
Alcohols		
O—H	3400–3650	Strong, broad
C—O	1050–1150	Strong
Aromatics		
C—H	3030	Weak
	1660–2000	Weak
	1450–1600	Medium
Amines		
N—H	3300–3500	Medium
C—N	1030–1230	Medium
Carbonyl compounds[a]		
C=O	1670–1780	Strong
Carboxylic acids		
O—H	2500–3100	Strong, very broad
Nitriles		
C≡N	2210–2260	Medium
Nitro compounds		
NO_2	1540	Strong

[a] Carboxylic acids, esters, aldehydes, and ketones.

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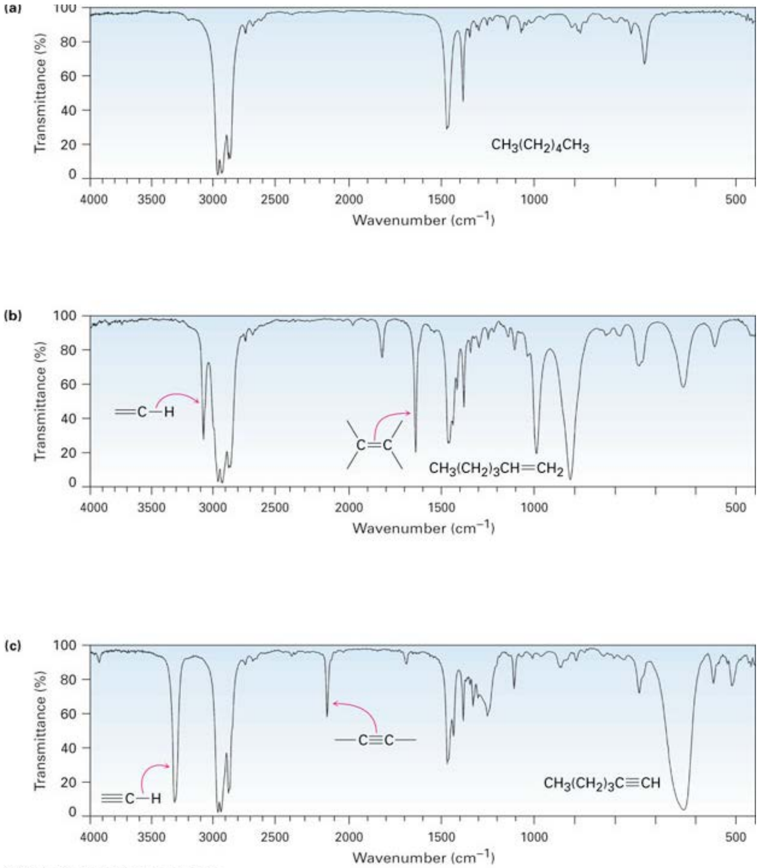

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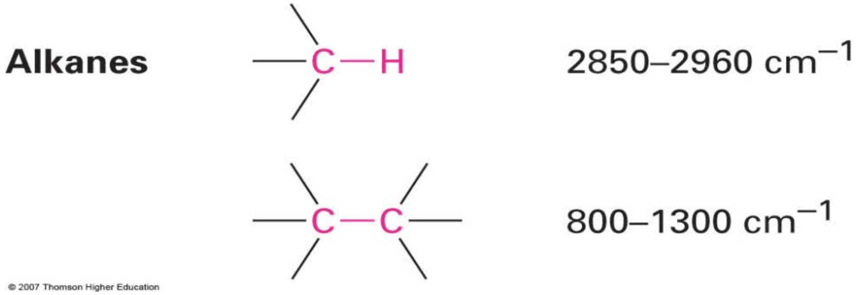
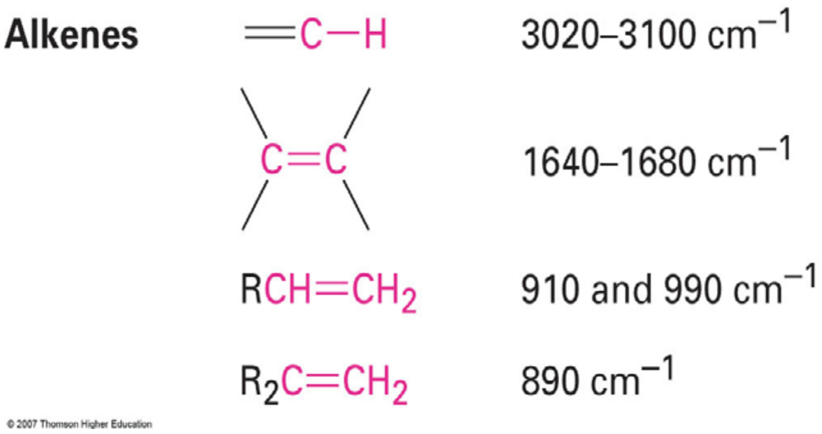
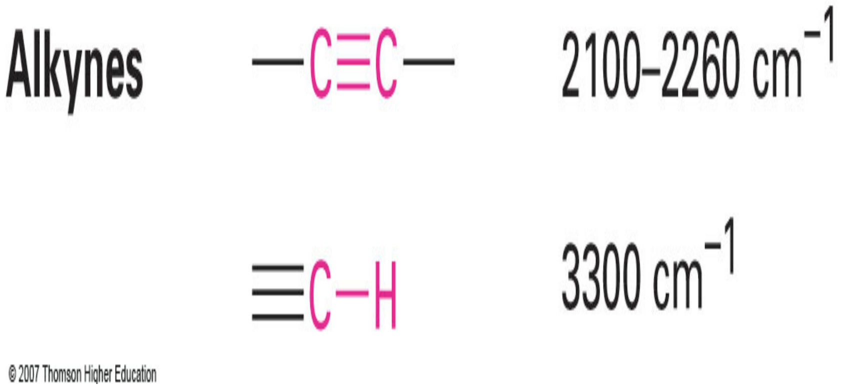
Infrared Spectra of Some Common Functional Groups



Alkanes	$-\mathrm{C}-\mathrm{H}$	2850–2960 cm^{-1}
	$-\mathrm{C}-\mathrm{C}-$	800–1300 cm^{-1}



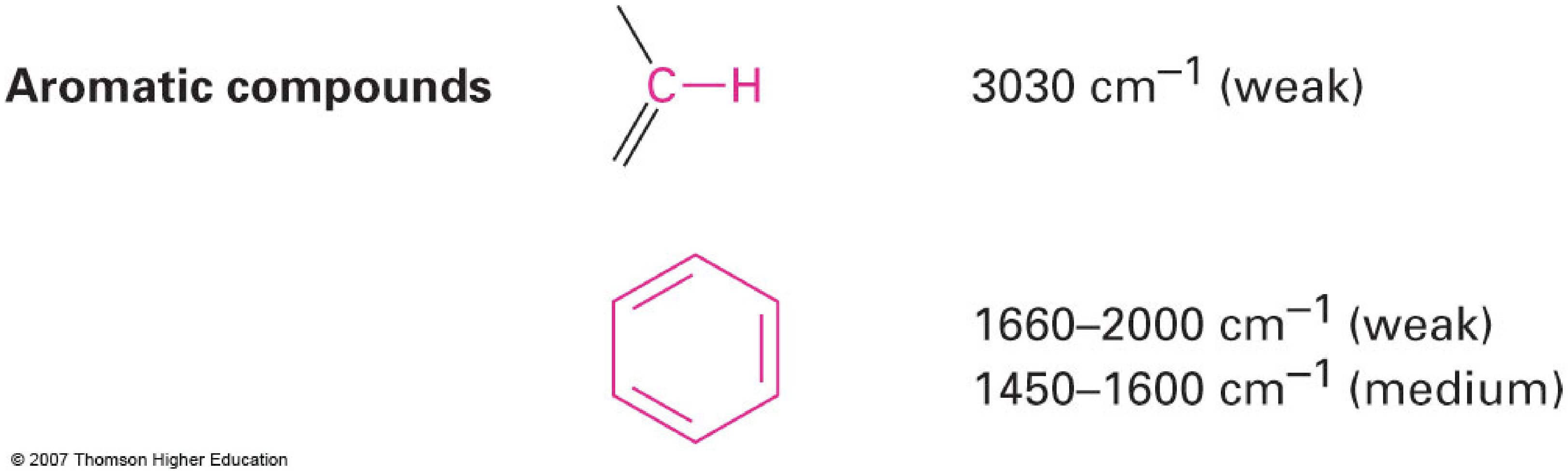
Alkenes	$=\mathrm{C}-\mathrm{H}$	3020–3100 cm^{-1}
	$\mathrm{C}=\mathrm{C}$	1640–1680 cm^{-1}
	$\mathrm{RCH}=\mathrm{CH_2}$	910 and 990 cm^{-1}
	$\mathrm{R_2C}=\mathrm{CH_2}$	890 cm^{-1}



Alkynes	$-\mathrm{C}\equiv\mathrm{C}-$	2100–2260 cm^{-1}
	$\equiv\mathrm{C}-\mathrm{H}$	3300 cm^{-1}

IR: Aromatic Compounds

- • Weak C–H stretch at 3030 cm−1
- • Weak absorptions 1660 - 2000 cm−1 range
- • Medium-intensity absorptions 1450 to 1600 cm−1
- • See spectrum of phenylacetylene, Figure 12.15



Aromatic compounds	C—H	3030 cm^{-1} (weak)
		1660–2000 cm^{-1} (weak) 1450–1600 cm^{-1} (medium)

IR: Alcohols and Amines

O–H 3400 to 3650 cm−1   Usually broad and intense

N–H 3300 to 3500 cm−1 Sharper and less intense than an O–H

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

Amines	—N—H	3300–3500 cm^{-1} (sharp, medium intensity)

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 provide valuable informations 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 benzeldehyde and phenylmethylketones both shows absorption peaks at 1700cm-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.