INFRARED SPECTROSCOPY

Theory and Application

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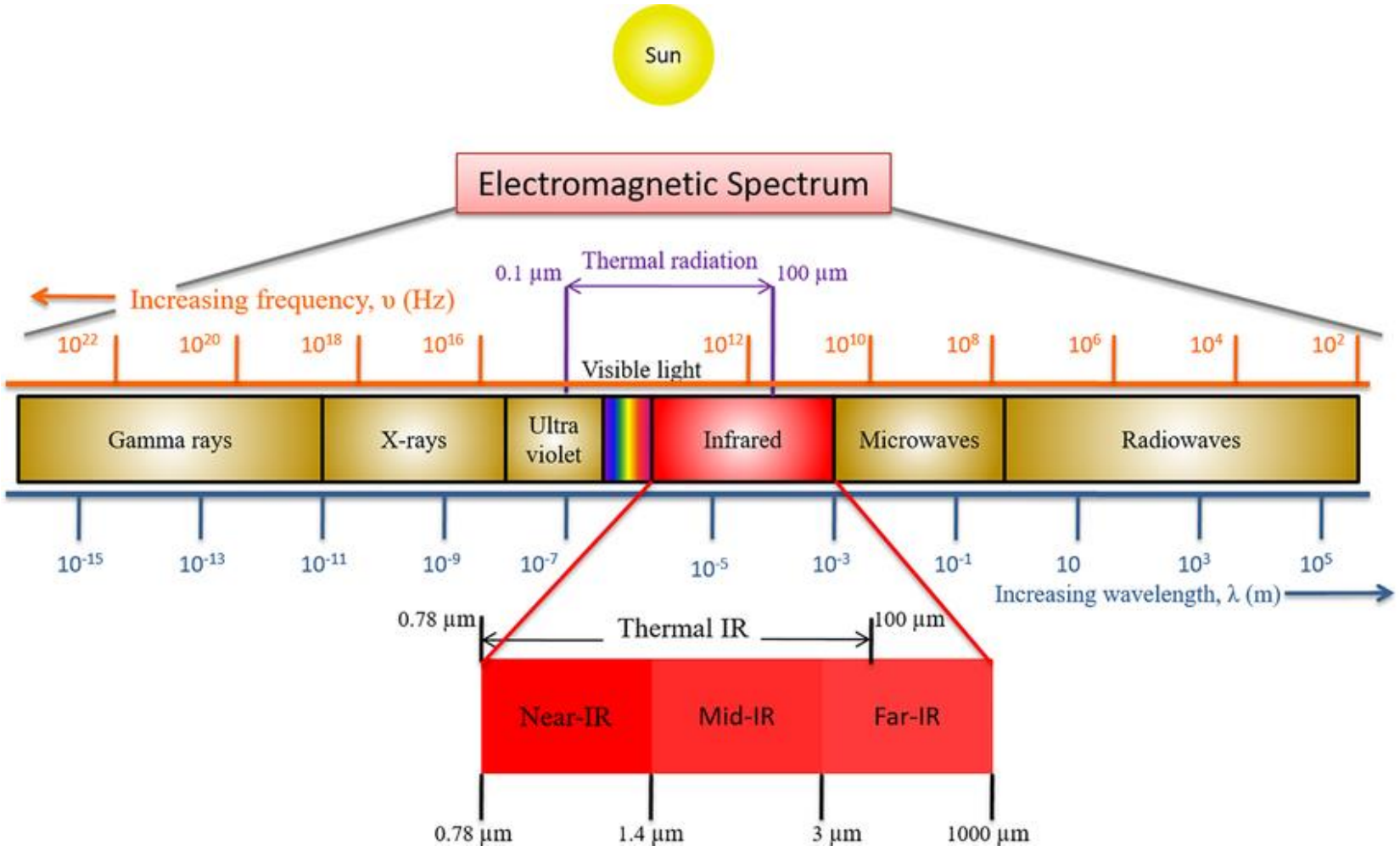
Introduction

- Infrared Spectroscopy deals with the study of absorption of infrared radiation by molecules results in vibrational transitions.
- IR Spectra provides a wealth of information regarding structure of organic molecules
- Infrared radiation refers broadly to that part of electromagnetic spectrum between visible and microave region.


Sun
Electromagnetic Spectrum
Increasing frequency, υ (Hz)
0.1 µm
Thermal radiation
100 µm
10^{22} 10^{20} 10^{18} 10^{16} 10^{12} 10^{10} 10^{8} 10^{6} 10^{4} 10^{2}
Visible light
Gamma rays
X-rays
Ultra violet
Infrared
Microwaves
Radiowaves
10^{-15} 10^{-13} 10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10 10^{3} 10^{5}
Increasing wavelength, λ (m)
0.78 µm
Thermal IR
100 µm
Near-IR
Mid-IR
Far-IR
0.78 µm
1.4 µm
3 µm
1000 µm

The unit used on an IR spectrum is

Wavenumbers $\bar{\nu}$

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

wavelength (cm)

ν = frequency = $\bar{\nu}\, c$

C = speed of light
= 3×10^{10} cm/sec

or

$$\nu = \left(\frac{1}{\lambda}\right) c = \frac{c}{\lambda}$$

$$\frac{cm/sec}{cm} = \frac{1}{sec}$$

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.

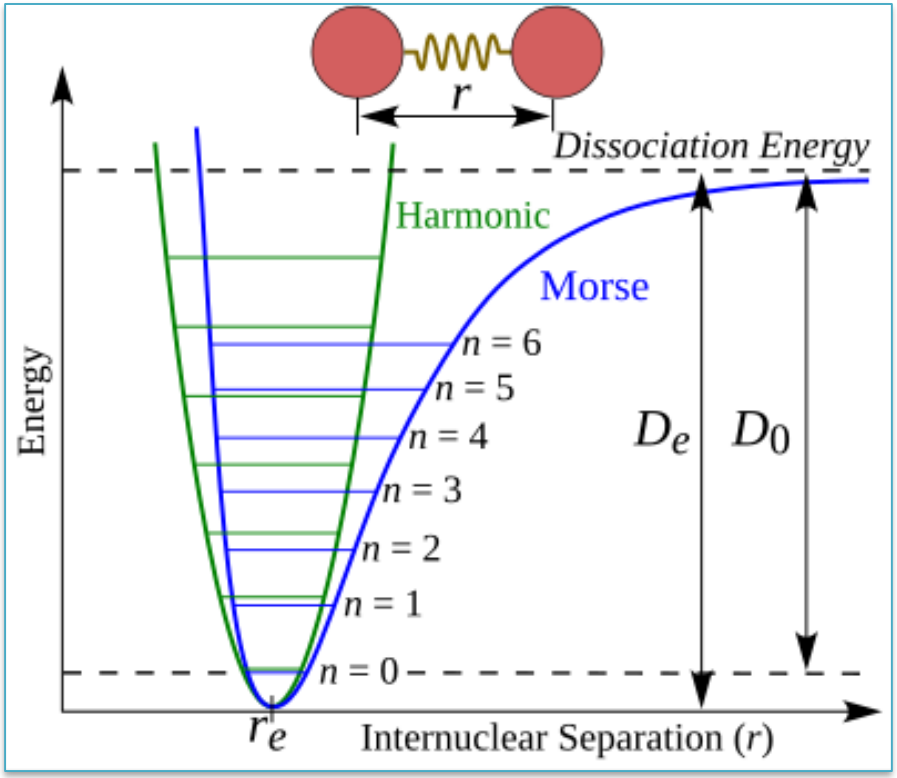
- This region is divided into:

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

Mores Potential Energy Diagram



Absorption in IR region causes transition between Vibrational levels due to vibration of atoms in a particular covalent bond. These transitions are quantized. In this process those frequencies of IR radiations match with natural frequency of covalent bonds in a molecule, are absorbed and corresponding peaks are observed.

At lowest temp. molecules are in their lowest vibrational energy levels, the potential energy diagram approximates that of harmonic oscillator. But at higher temp. the deviations do occur. Transitions from G. S. to the 1st excited state absorb light strongly and give rise to intense band called the **Fundamental bands.**

Change in vib energy= $E_{vib(v=1)} - E_{vib(v=0)}$ where $E_{vib} = (v+1/2)hv$

$= hv$

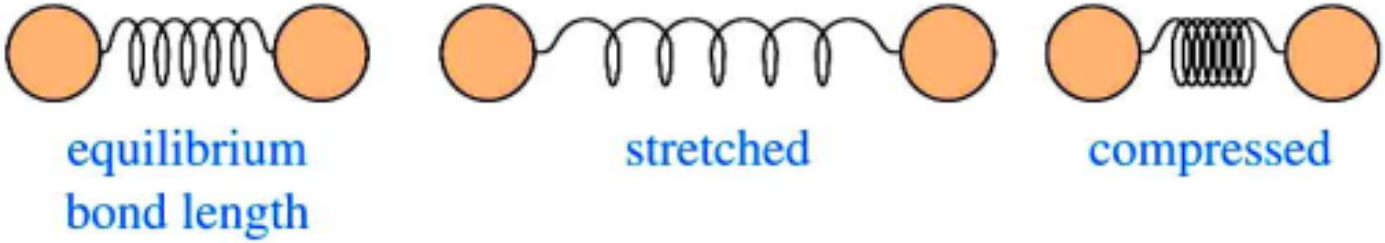
There may be some transitions from ground state to higher energy states, known as **Overtones.** Weak overtone bands are observed at 2v, 3v…with reduced intensity.

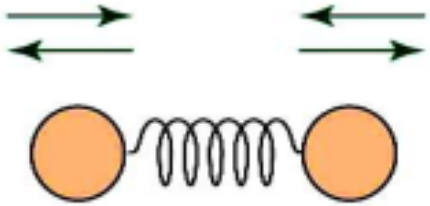
Two vibrational frequencies ν_1 and ν_2 may couple, giving rise to a vibration of new frequency, known as **Combination bands.**

Difference bands results from difference between two interacting bands $\nu_1 - \nu_2$

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.

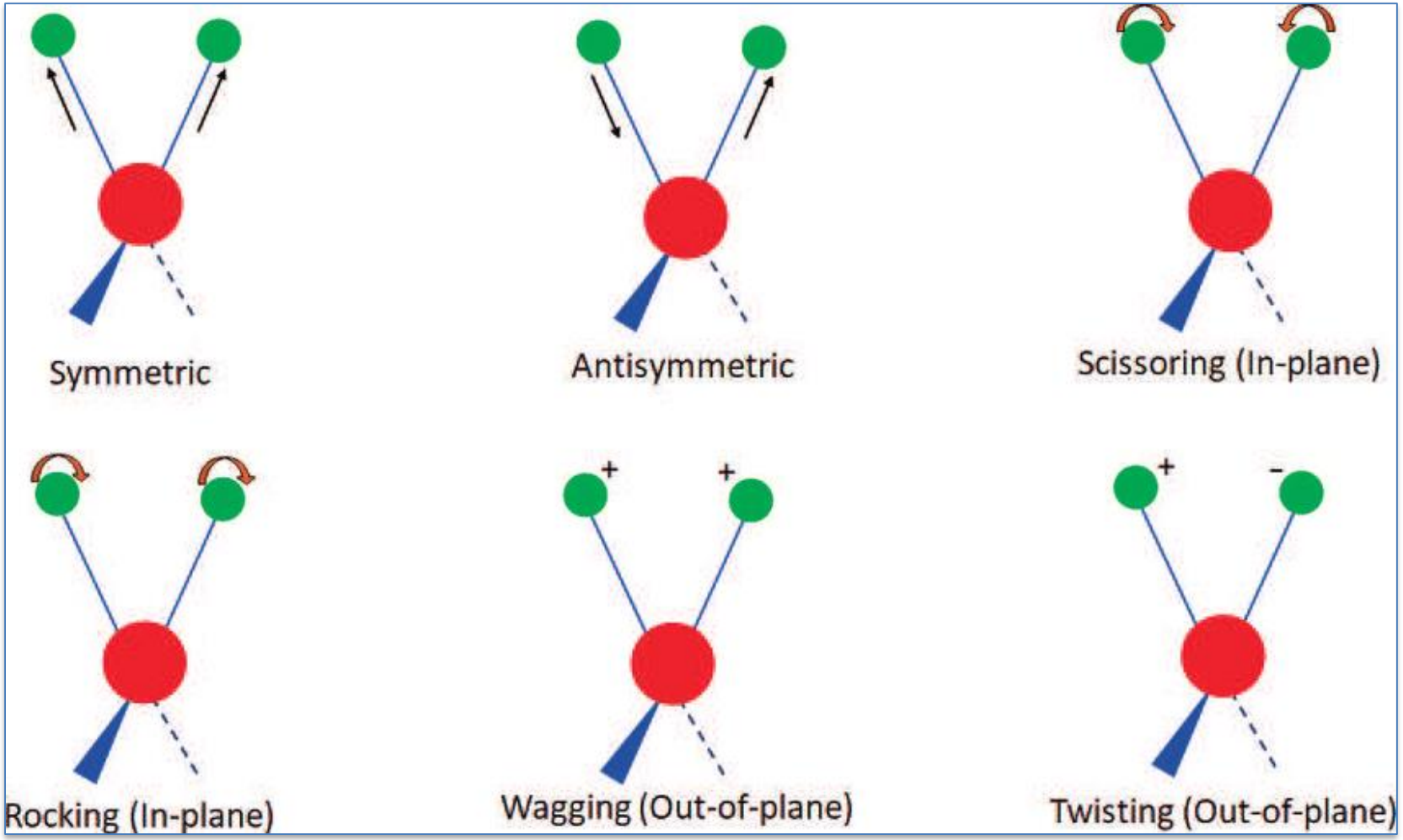
Specific bonds respond to (absorb) **specific** frequencies





Types of Molecular vibrations

Stretching Vibrations: Bond length changes which requires more energy.
Bending Vibrations: Bond angle changes that requires less energy.



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)

- for linear molecules, number of types of vibrations:

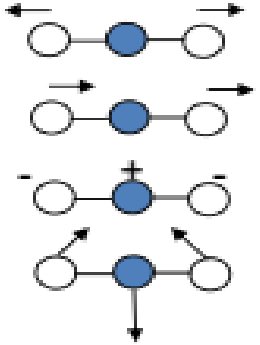
3n= Vibrational DOF + Translational DOF (3) +Rotational DOF (2)
Vibrational DOF= 3n-3-2 =3n-5

- 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 vibration:

In order for a molecule to absorb IR radiation

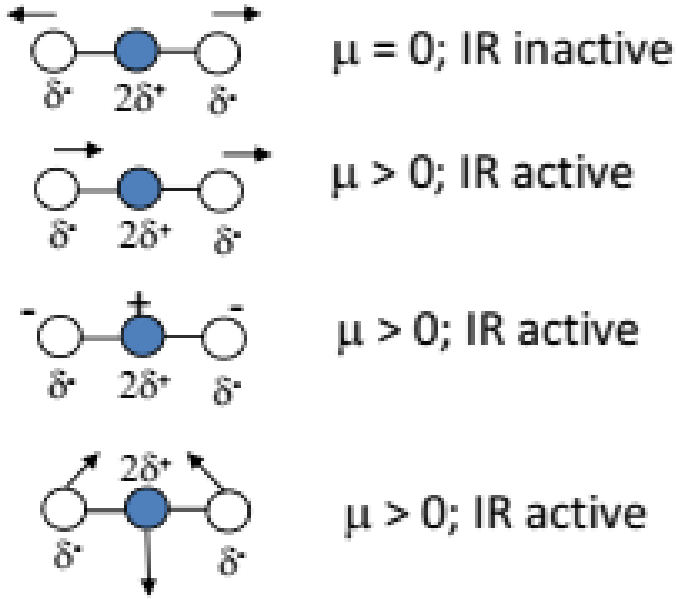
i) Vibrational frequency of a bond should match with IR frequency

ii) There must be a change in the dipole moment as a result of vibration.

Example:

CO_2 : 3n-5 = 3x3-5= 4 modes

Among them 3 modes are IR active.



Vibrational frequency

The value Vibrational frequency can be estimated from Hook′s law. Hook′s law states that the vibrational frequency of a bond is directly proportional to the bond strength and inversely proportional to the reduced mass. So vibrational frequency increases with increase in bond strength and decrease in reduced mass of constituting atoms.

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

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

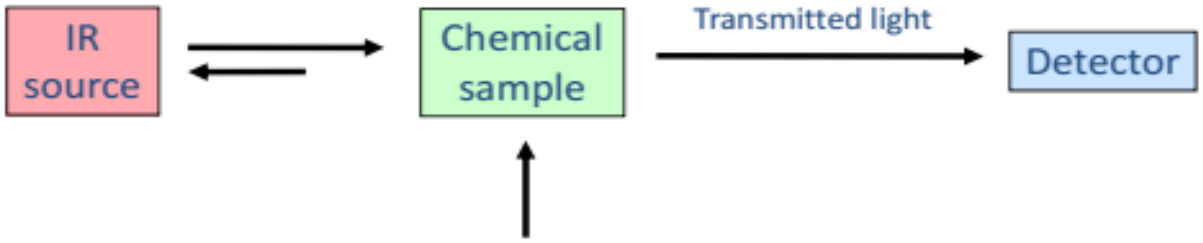
K for triple bond = 15x 10^5 dyne/cm

K for double bond = 10x 10^5 dyne/cm

K for single bond = 5x 10^5 dyne/cm

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.

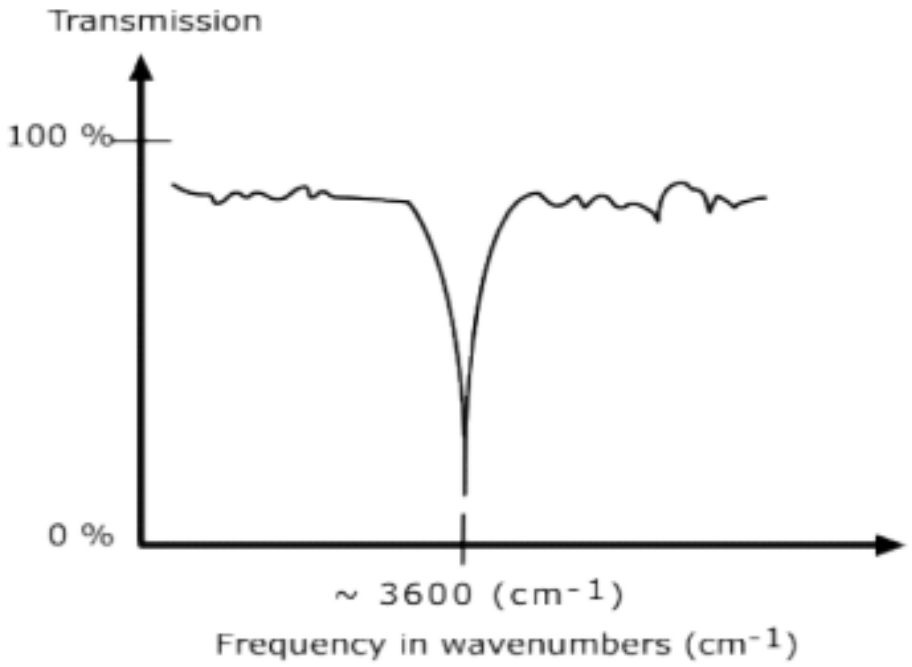


From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

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

Light Source for IR: Nernst Glober, a molded rod containing zirconium oxide, yttrium oxide, and erbium oxide that is heated to around 1500°C by electrical means. Metal halide prism is used as cell container.

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.

Uses of IR spectroscopy

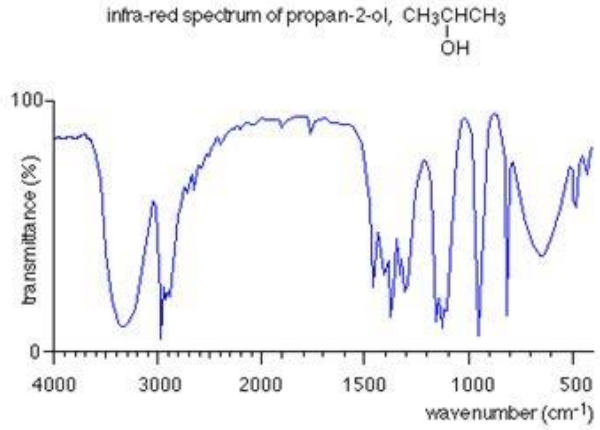
• A Particular functional group in different compounds will absorb at particular frequency. Eg >C=O functional group present in different compound absorb at 1715 cm^{-1}

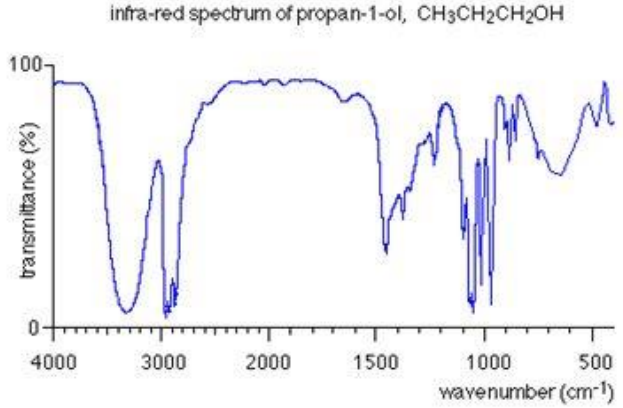
•The progress of a chemical reaction can be monitored by examining spectra of aliquot withdrawn. $RCH(OH)CH_3$ $RCOCH_3$
The peak for –OH stretching near 3570 cm^{-1} is expected to disappear with appearance of a peak for carbonyl at 1715 cm^{-1}

•This spectroscopy is applied to establish the identity of two samples.
The region **1430-910 cm^{-1}** contains number of absorptions particularly caused by bending vibrations as well as caused by C-C, C-O, and C-N stretching vibrations and known as **Finger Print Region. This region is uniquely characteristics of each molecule and seems to serve as finger print of a molecule.**

Fingerprint region

The **fingerprint region** is found on the right hand side of an infrared spectrum from about 1500-500 cm^{-1}. It can be used to compare two similar compounds.



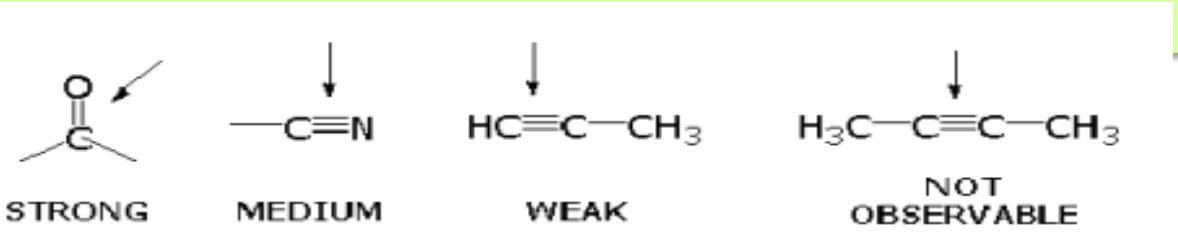


INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active**.
Molecules with centre of symmetry are IR inacive. Eg C=C symmetrical stretching frequencies of ethylene and trans 1,2-dichloro ethylene are IR inactive.
Carbon monoxide (CO), Iodine monochloride (Icl) absorb IR light.
But Hydrogen (H_2), nitrogen (N_2), chlorine (Cl_2) symmetrical diatomic molecules are IR inactive.

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 (C-H) and symmetric bonds produce weak or non observable bands.



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}

Characteristics Absorptions in Different Type of Compounds.

1. Hydrocarbon

- **Alkane:** C-C stretching vibration : 1330-800 cm-1 (very weak band due to small change in dipole moment).

  $>C(CH_3)_2$: Coupled vibrations of two frequencies. One is for symmetric and other for antisymmetric stretching vibrations.

- C-H Stretching vibration for alkane: 2960-2850 cm^{-1}

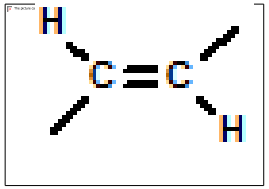
  for alkene >C=C-H : 3030-3010 cm^{-1}

  for alkyne : 3300 cm^{-1}

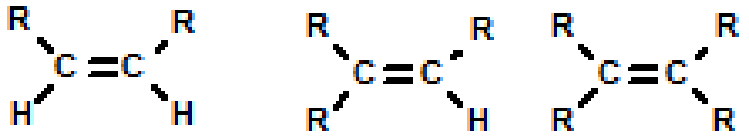
  So stretching vibration for C-H bond is dependent on the nature of hybridization of the carbon attached to H. Higher the s character higher will be the strength of bond so stretching frequency increases in the order sp3<sp2<sp.

- C-H bending Vibration for alkane: 1485-1340 cm^{-1}

Alkene : Infrared spectra of alkenes give important information about substitution pattern, as observer in C-H stretching vibration.
Most intense band for C=C stretching appears in the region 1670-1640 cm^{-1}

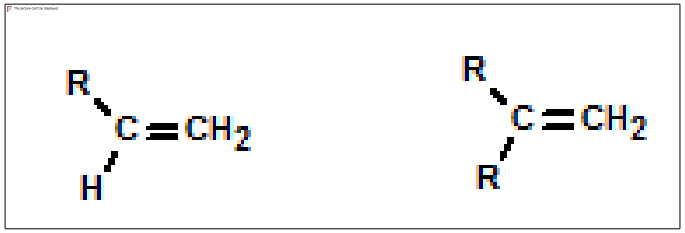


For trans alkene C=C stretching band is absent as no change in dipole moment occurs.

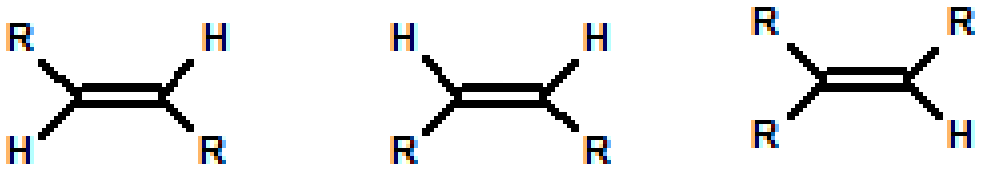


In these alkenes also, the C=C stretching is often weak or absent. This absorption, if present, occurs in the region 1675 -1650 cm^{-1}. The reason being that there is no change in the dipole moment. Also, *the more the substitution at the double, the lesser the intensity and greater the frequency of absorption*.

The =C-H bending absorptions of alkenes appear as strong bands at lower frequencies and indicates the substitution pattern at the double bond.



910, 990 cm^{-1} 890 cm^{-1}



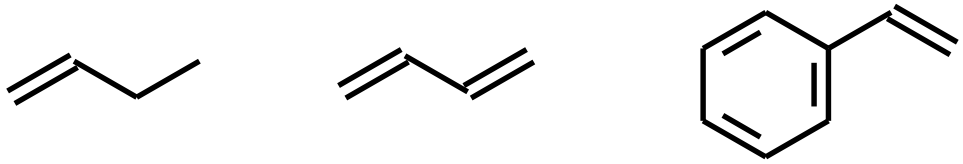
Trans (960,980cm^{-1}) cis (675-730cm^{-1}) 800-847 cm^{-1}

Alkyne: Absorptions resulting from stretching vibrations of acetylenic compounds occur in the region 2275-2085 cm-1

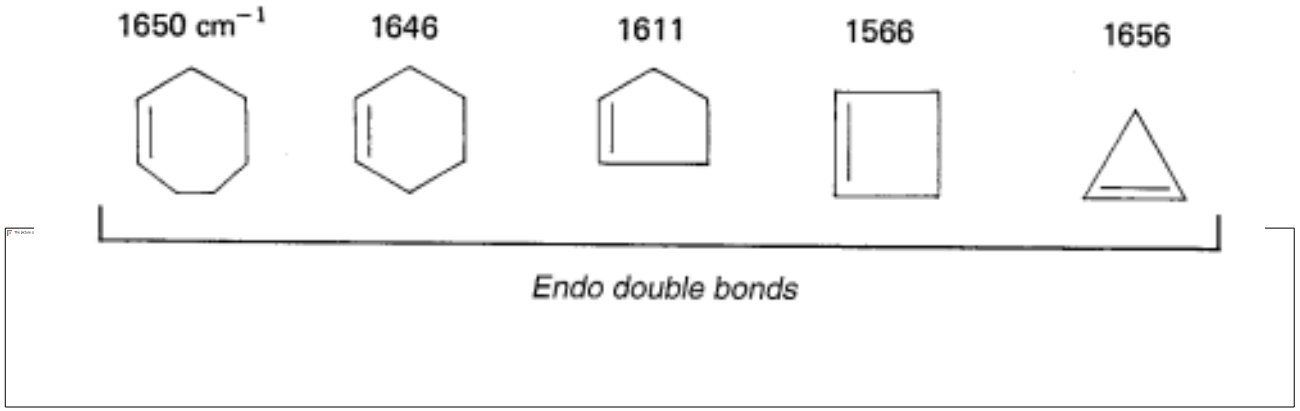
2140-2100 cm-1 2260-2190 cm-1

Weak absorption bands are observed as dipole moment change is low due to only inear expansion and contraction.

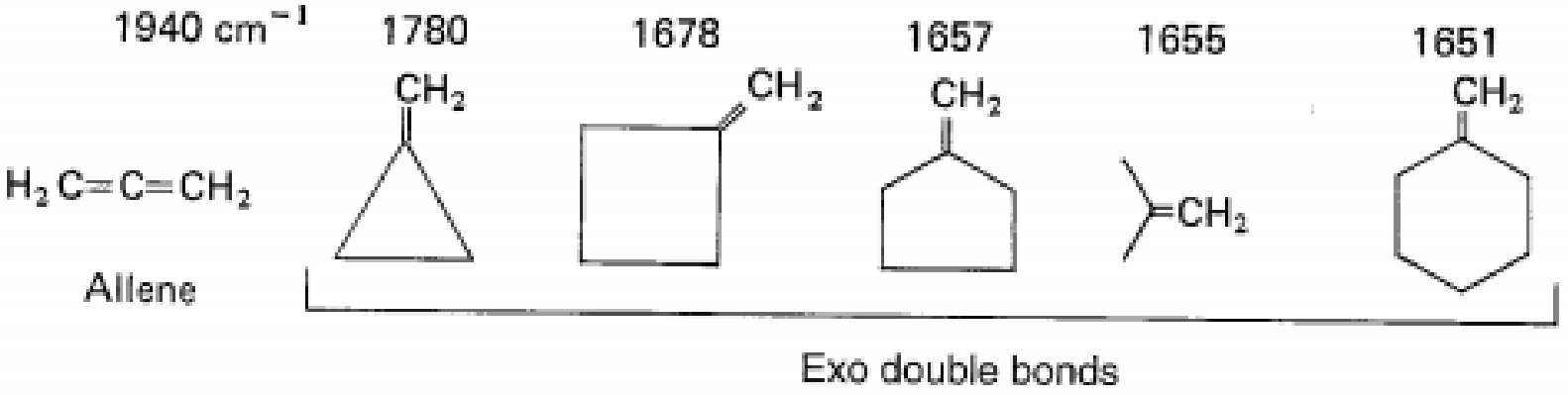
Conjugated double bond: Conjugation lowers the absorption frequency C=C bond. Double bonds acquire more single bond character through resonance and force constants decrease.



1650 cm^{-1} 1630 cm^{-1} 1630 cm^{-1}



Ring size effects with external double bonds



With decrease in ring size , the external angles become >C-C=CH2 become greater, sigma bonds of C=C double bonds get more s character with removal of p-character leading to strengthening and stiffening of double bonds. The foece constant k is increased and absorption frequency increases.

Mononuclear Aromatic Hydrocarbon

Aromatic =C-H stretching band occurs in the range 3100-3000 cm^{-1}.
Four absorption bands which are particularly diagnostic of aromatic character occur at ~ 1600,1580, 1500 and 1450 cm^{-1} caused by C=C skeletal in plane stretching vibrations.

The most informative bands of aromatic compounds occur in the range between 900-675 cm^{-1} which result from out of plane bending mode of the ring –C-H bonds.
For in plane bending vibration occurs in the region 1300-1000 cm^{-1}
Characteristic pattern of C-H out of plane bending bands are observed for substituted benzene.

i) Monosubstituted benzene: Two strong absorption bands at 750 and 700 cm-1
ii) 1,2-disubstituted benzene: strong absorptions in the range 770-735 cm-1
iii) 1,3-disubstituted benzene: 800-750 cm-1
iv) 1,4-disubstituted benzene: 840-810 cm-1.

Overtone or combination bands of weak intensity appear in between 2000-1870 cm-1

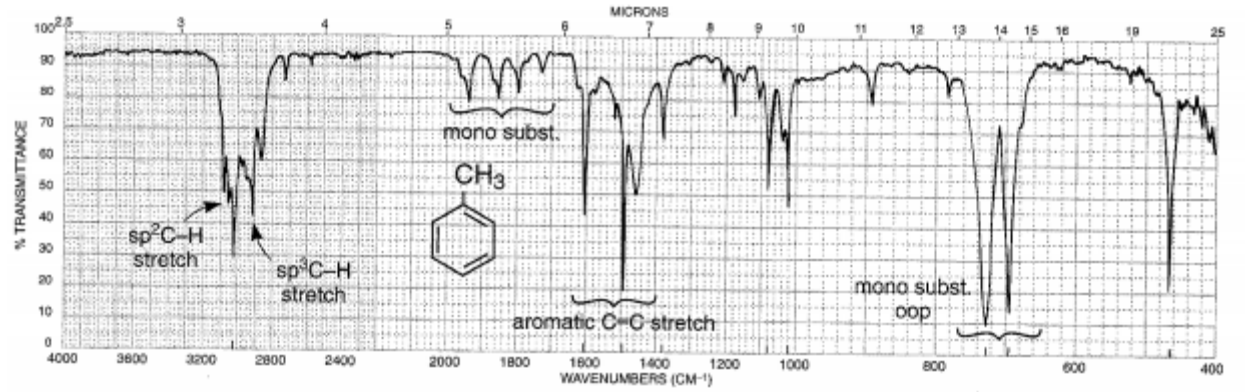


FIGURE 2.23 The infrared spectrum of toluene (neat liquid, KBr plates).

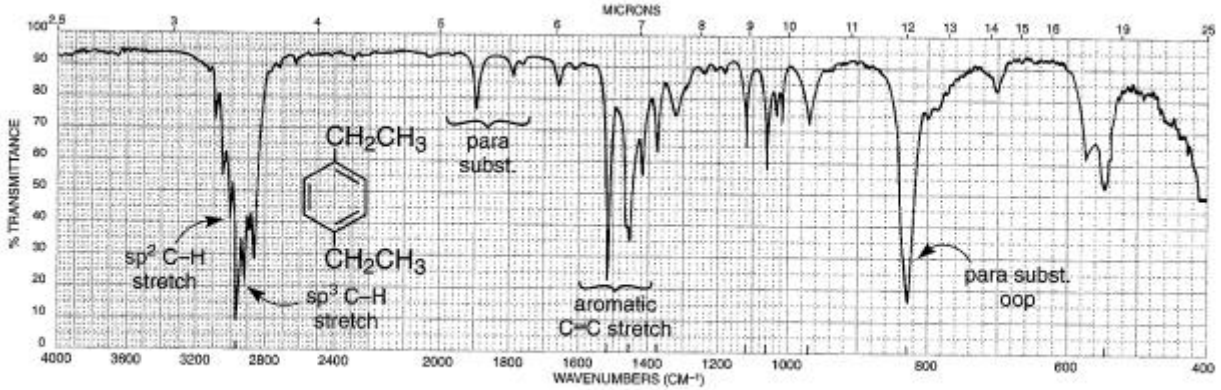
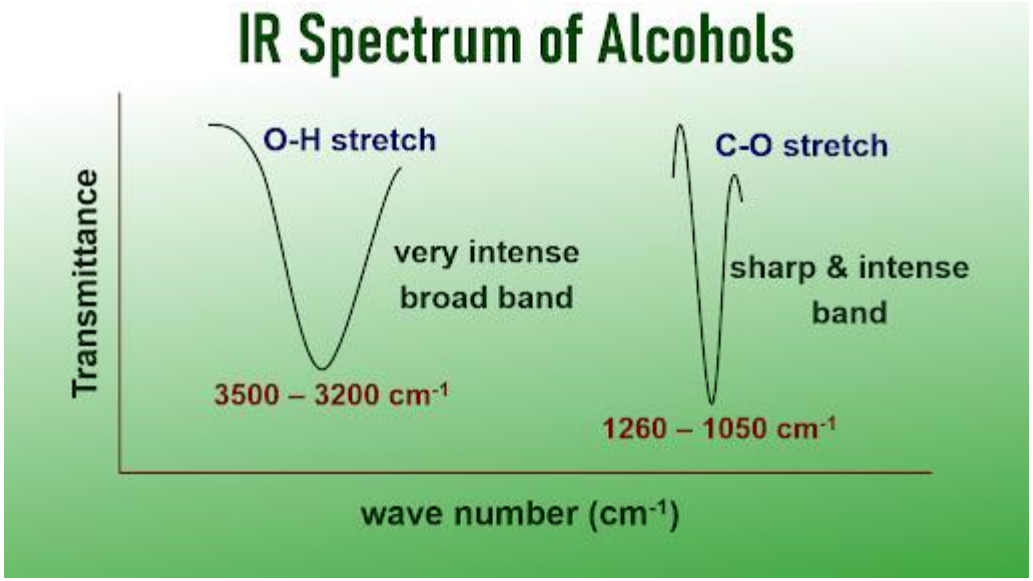
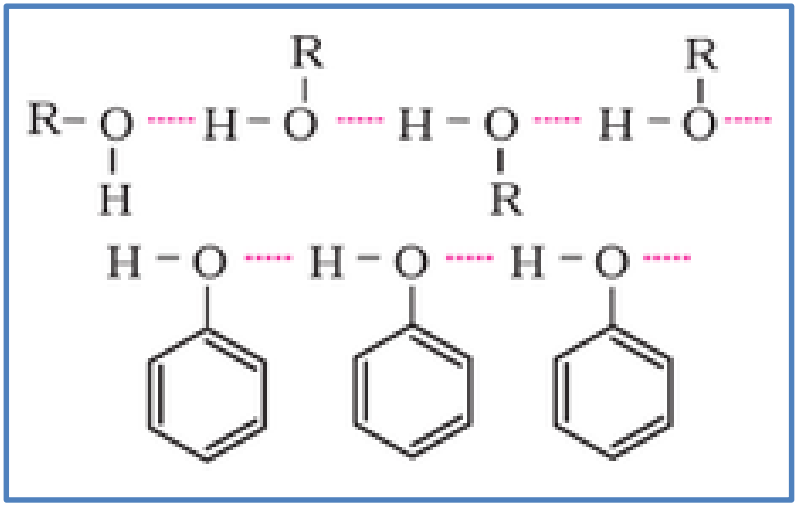


FIGURE 2.26 The infrared spectrum of *para*-diethylbenzene (neat liquid, KBr plates).



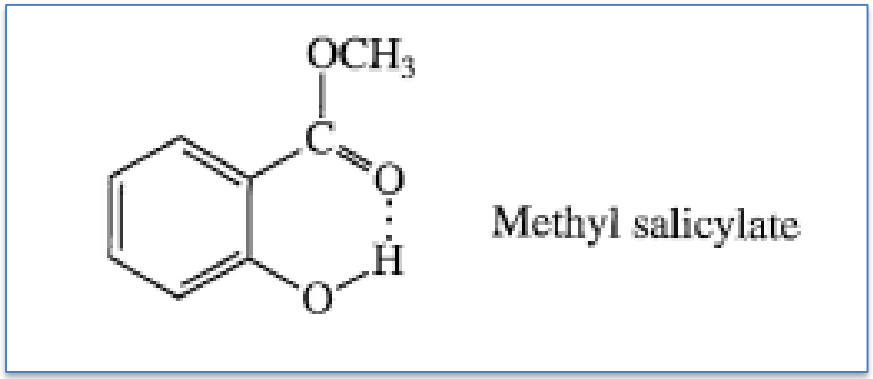


Alcohols and phenols remain associated through H-bonding and exist in dynamic polymeric association. O-H bonds become lengthened and weakened and stretching frequency is lowered.

On dilution, a sharp free O-H stretching frequency will appear at 3600 cm-1.

In benzene stretching frequency is lowered by 40-100 cm-1

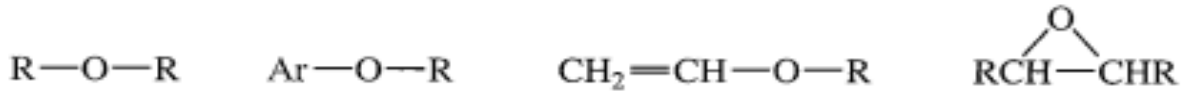
Effect of H-bonding in IR spectra of phenolic -OH



Methyl salicylate

Intra molecular H-bonding between carbonyl group and phenolic OH shifts the broad –OH band to a lower frequency, centered at 3200 cm-1

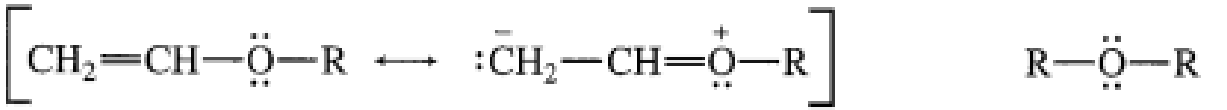
Ethers



Dialkyl ethers | Aryl ethers | Vinyl ethers | Epoxides

Dialkyl Ethers: Two absorption bands are observed. One is strong at 1120 cm^{-1} due to asymmetric stretching and another is weak due to symmetric stretching at 850 cm^{-1}

Aryl alkyl ether: Strong band (asymmetric stretching) at 1250 cm^{-1} and 850 cm^{-1}
Vinyl alkyl ether: Strong band at 1220 cm^{-1} and weak band at 850 cm^{-1}



Resonance
1220 cm^{-1}

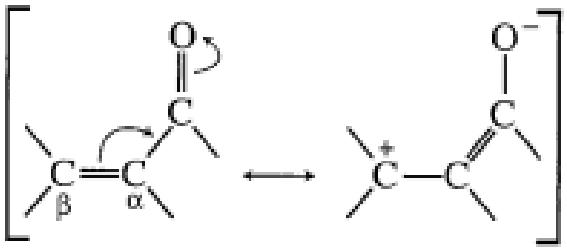
No resonance
1120 cm^{-1}

Carbonyl Compounds

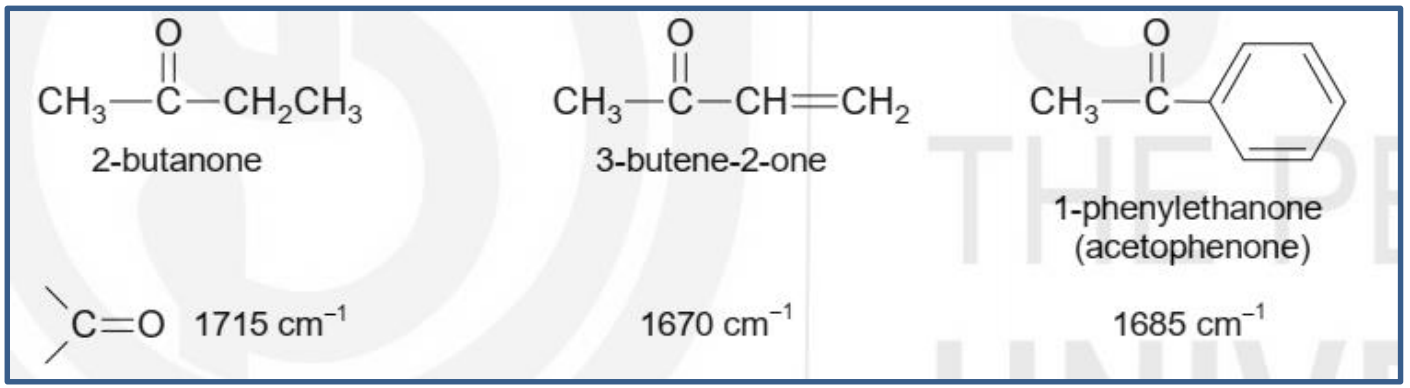
Carbonyl >C=O group of ketones absorb in the region 1754-1667 cm^{-1}.

The position of absorption frequency is sensitive to

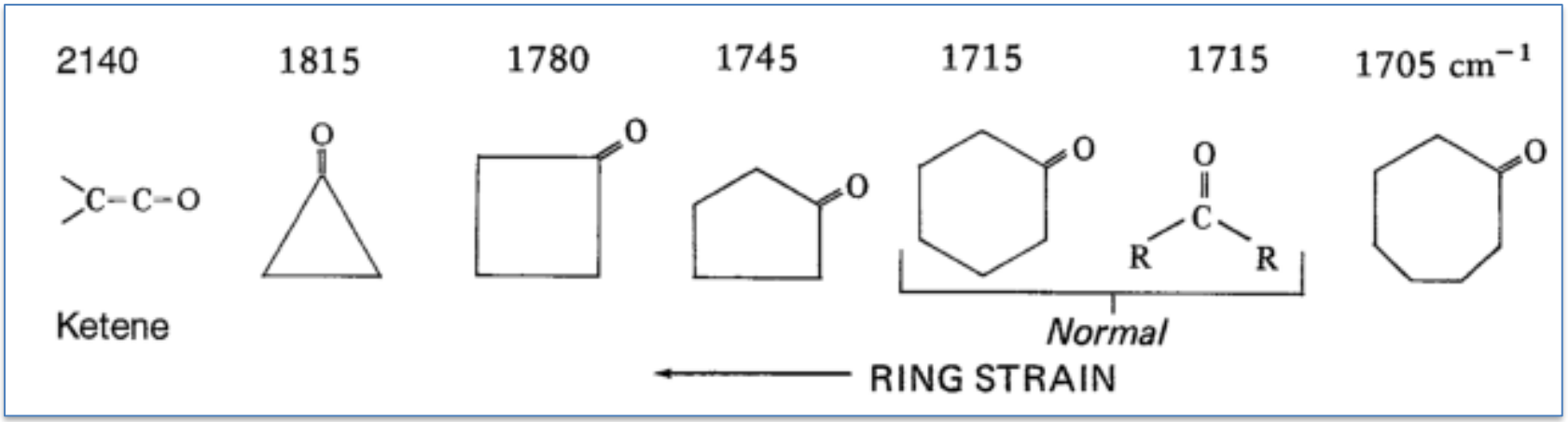
i) Degree of conjugation



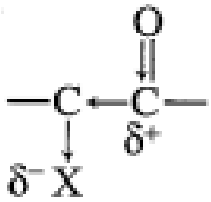
Conjugation of carbonyl group with C=C or an aryl group lowers the stretching frequency by 30-40 cm^{-1}



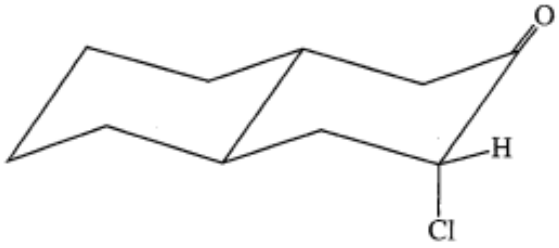
ii) Ring size for cyclic ketones



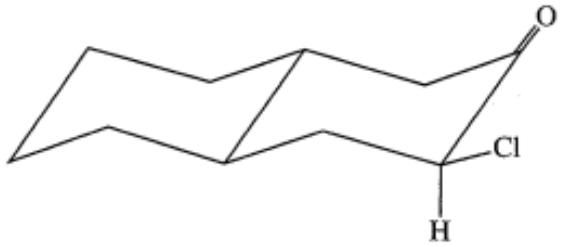
iii) Effect of α-substituent



>C=O stretching frequency is increased. Electron withdrawing effect of halogen removes electron density from O to C of carbonyl ,thereby strengthen the >C=O bond.

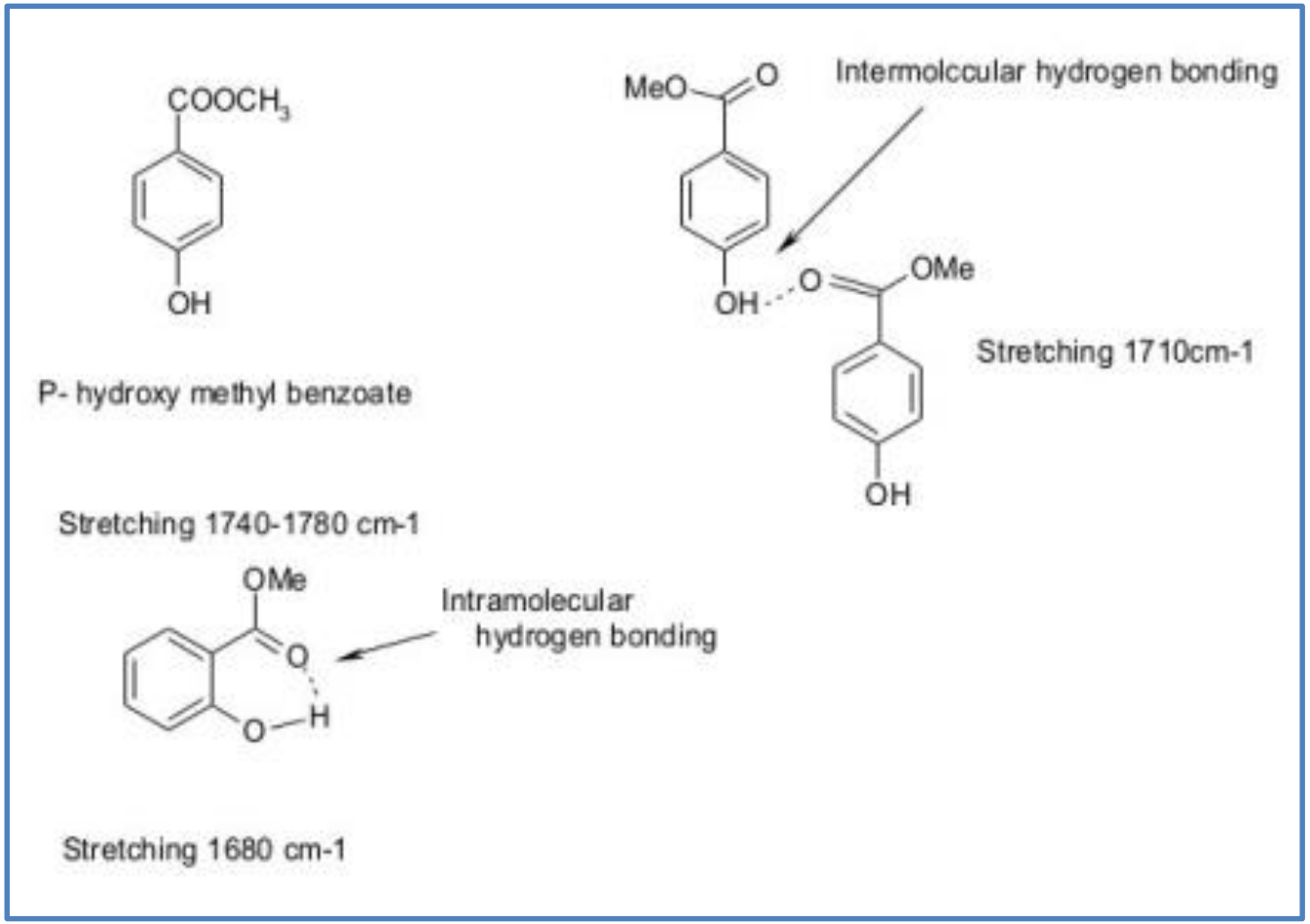


Axial chlorine
~1725 cm^{-1}

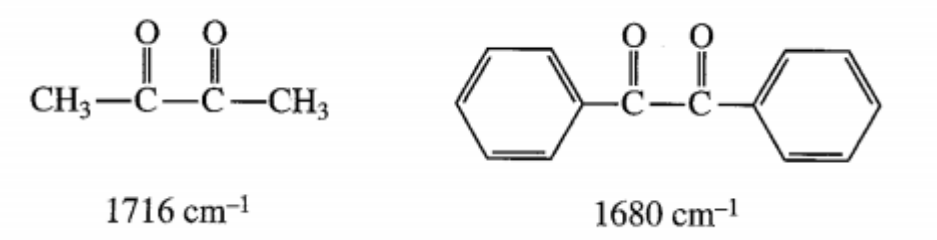


Equatorial chlorine
~1750 cm^{-1}

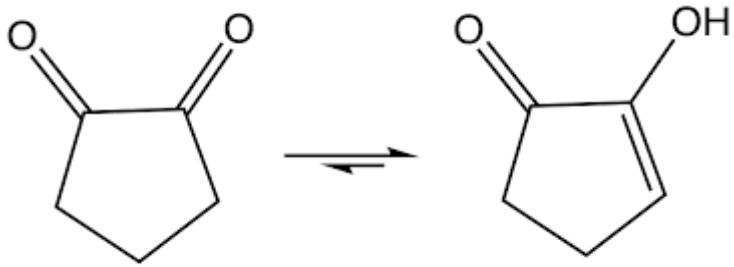
iv) Effect of H-bonding



IR Spectra of α and β-diketone



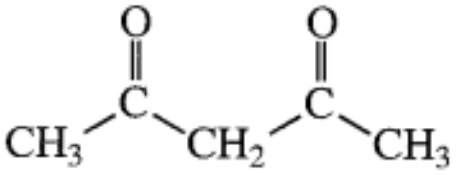
They remain in transoid conformation and does not form any enol form.

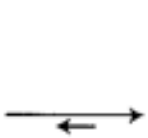


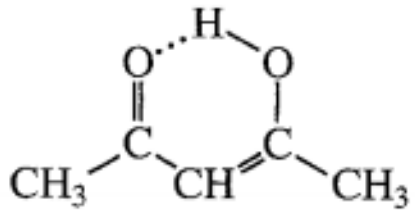
Rigid cis form gets stabilised by enolisation followed by intramolecular H-bonding. ν_{CO} : 1690 cm^{-1}

ν_{OH} : 3300 cm^{-1}

$\nu_{C=c}$: 1640 cm^{-1}





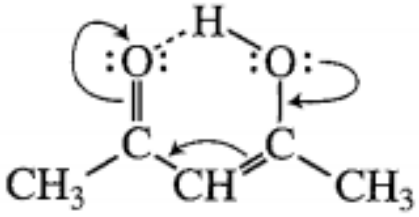


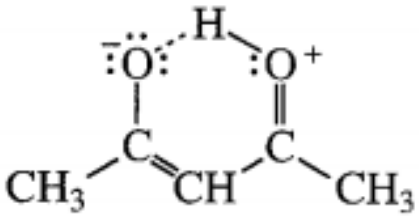
Keto tautomer

C═O doublet
1723 cm^{-1} (symmetric stretch)
1706 cm^{-1} (asymmetric stretch)

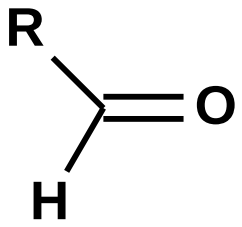
Enol tautomer

C═O (hydrogen-bonded), 1622 cm^{-1}
O—H (hydrogen-bonded), 3200–2400 cm^{-1}



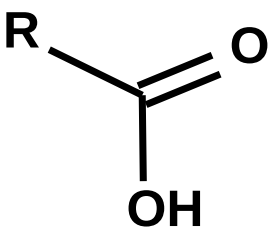


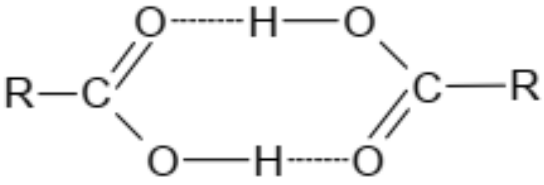
IR Spectra of Aldehydes



>C=O stretching frequency is observed in 1740-1720 cm-1 (strong).
Two weak bands owing to C-H stretching vibrations are observed at 2820 cm-1 and 2720 cm^{-1}.
α, β-unsaturated aldehydes : >C=O stretching frequency is observed in the range 1710-1690 cm^{-1}.

IR Spectra of Carboxylic Acid





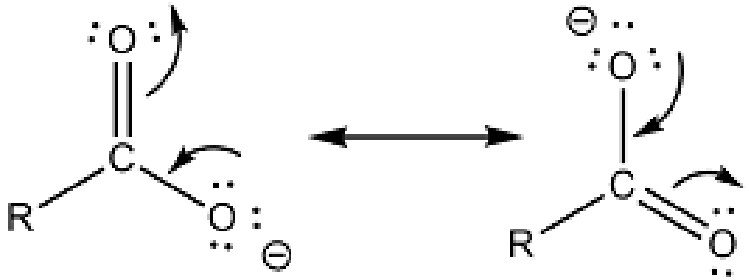
Dimer of carboxylic acid showing hydrogen bonding

>C=O stretching absorption occurs in the range 1730-1700 cm^{-1}. For solid and or concentrated solution the broad absorption band is due to dimeric form.
On extensive dilution with an inert solvent absorption ν_{CO} is at 1761 cm^{-1} for monomer and absorption ν_{CO} is at 1718 cm^{-1} for dimer.

Benzoic acid ν_{CO} : 1701 cm^{-1}
Salicylic acid: ν_{CO} : 1665 cm^{-1}
p-hydroxy benzoic acid ν_{CO} : 1680 cm^{-1}

For dimer ν_{OH} : 2700-2500 cm^{-1}
For dilute solution free OH absorption : 3570 cm^{-1}

Carboxylate ion

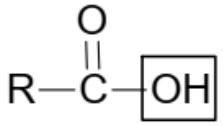


Do not show absorption in the region 1724-1667 cm^{-1}. Two absorptions due to symmetric and asymmetric >C-O stretching vibrations near 1580 cm^{-1} and 1359 cm^{-1}.

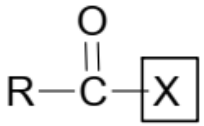
Ester and Lactone

More electronegative Oxygen is included in place of $–CH_2$ in ketone. So absorption occurs at 30 cm^{-1} higher wave number than ketone.

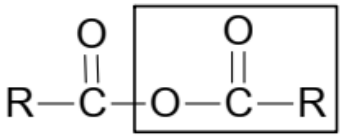
Effect of Substitution on Carbonyl Stretching Frequency



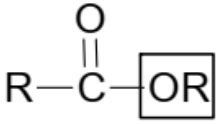
A carboxylic acid



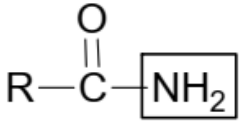
A carboxylic acid halide
X = Halogen



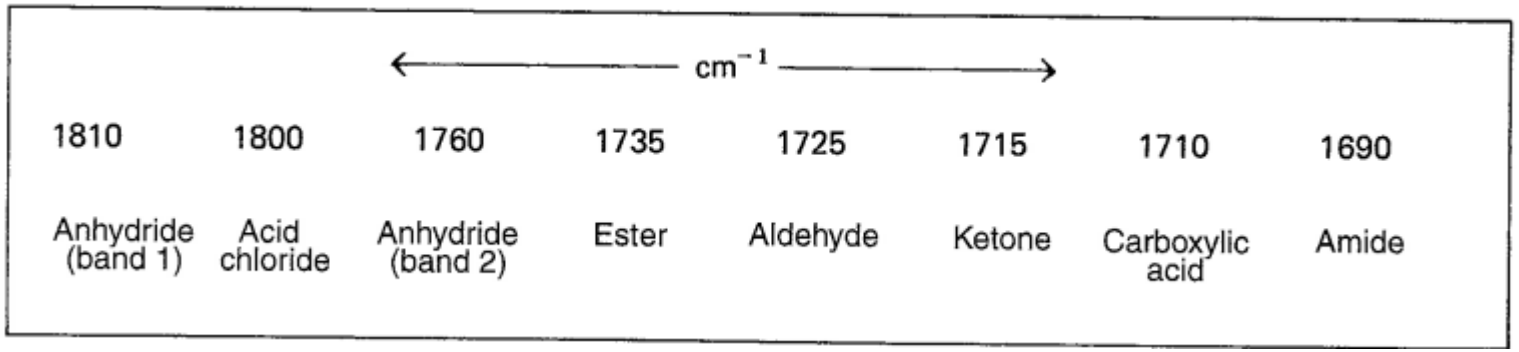
A carboxylic acid anhyldride



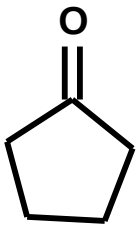
An ester

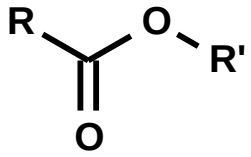


An amide

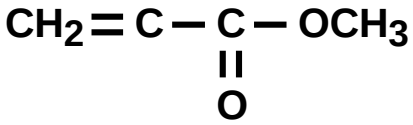


Carboxylic acid: ν_{CO} : 1761 cm^{-1} ; Ester: ν_{CO} : 1745 cm^{-1} ;
Acid halide: : ν_{CO} : 1815-1790 cm^{-1} ; Acid anhydride: : ν_{CO} : 1760-1740 cm^{-1} and 1850-1800 cm^{-1}
Amide : 1680-1630 cm^{-1}

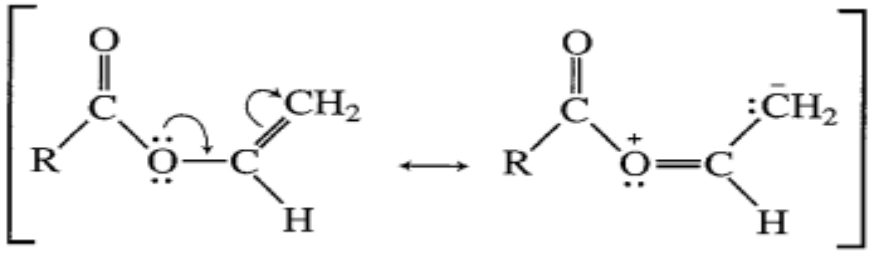




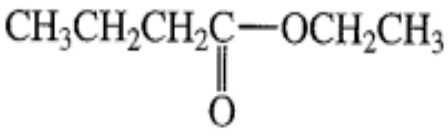
>C=O stretching frequency for above two compounds appear at 1745 cm-1. But for ester an additional strong and broad stretching frequency is observed in the range 1300-1000cm-1 due to –C-O stretching vibration.



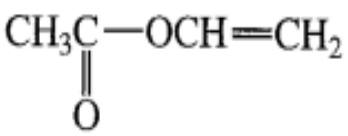
Methyl methacrylate: ν_{CO}: 1725 cm^{-1}



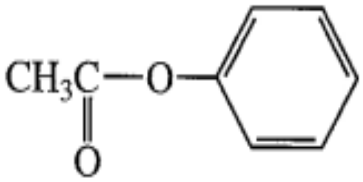
Conjugation occurs in reverse direction, so that >C=O bond gets strengthened. ν_{CO} appears at 1762 cm-1.



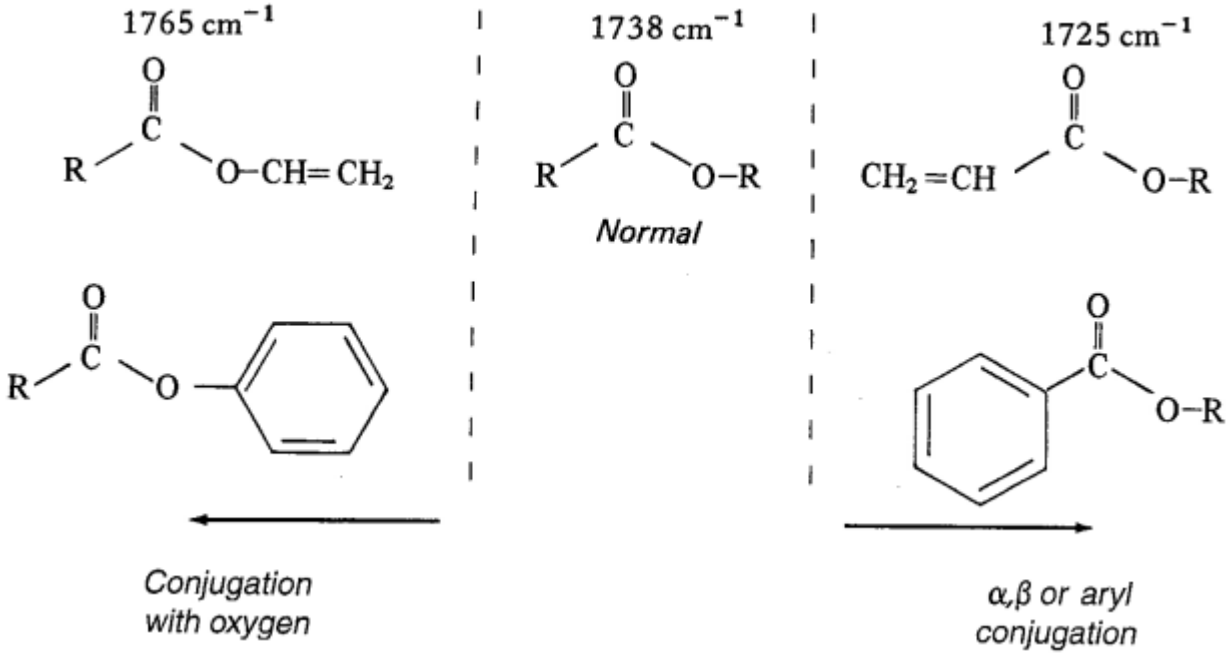
Ethyl butyrate
1738 cm^{-1}



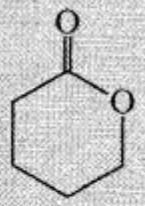
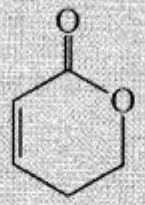
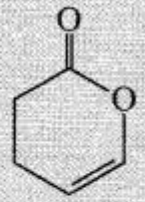
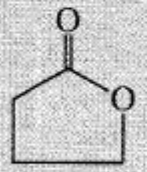
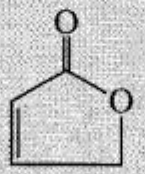
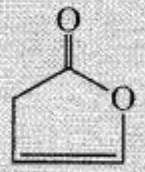
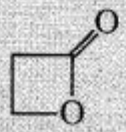
Vinyl acetate
1762 cm^{-1}



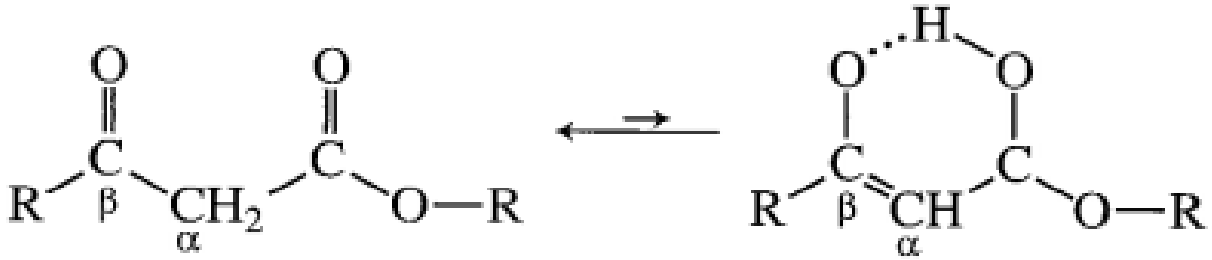
Phenyl acetate
1765 cm^{-1}



EFFECTS OF RING SIZE, α,β UNSATURATION, AND CONJUGATION WITH OXYGEN ON THE C=O VIBRATIONS IN LACTONES

Ring-Size Effects (cm^{-1})	α,β Conjugation (cm^{-1})	Conjugation with Oxygen (cm^{-1})
 1735	 1725	 1760
 1770	 1750	 1800
 1820		

B-Keto ester and Anhydrides

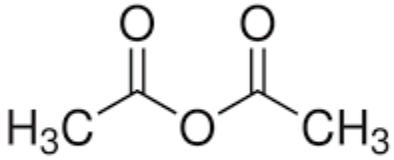


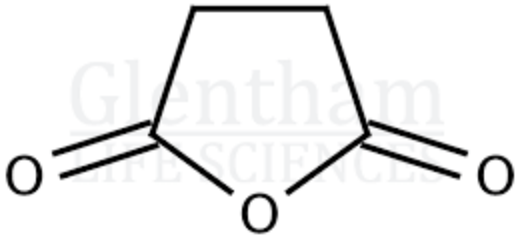
Keto tautomer

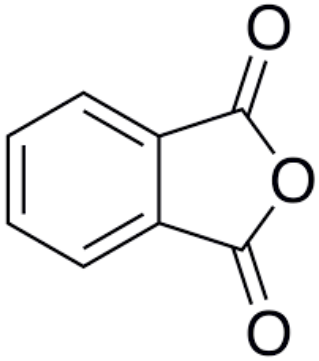
Enol tautomer

Absorption due to both keto and ester groups are observed at 1724 cm-1 and 1750 cm-1.

A weak band at 1650 cm-1 , which is due to >C=O H-bonded to enolic OH group.

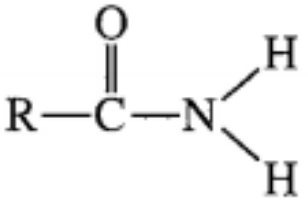




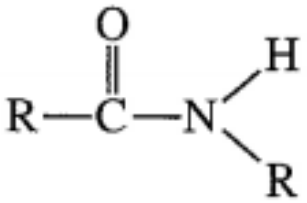


Asymmetric	1820 cm-1	1865 cm-1	1850 cm-1
Symmetric	1760 cm-1	1780 cm-1	1790 cm-1

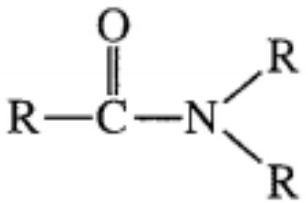
Cyclic and acyclic amides (lactams)



Primary amide

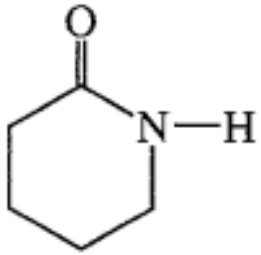


Secondary amide

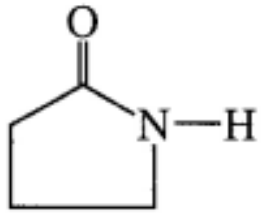


Tertiary amide

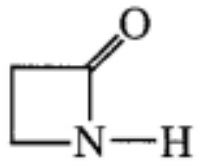
>CO stretching vibration appears in the range 1680-1640 cm-1. Two peaks for N-H stretching frequencies at 3500 cm-1 and 3400cm-1 for primary amide.



~1660 cm^{-1}



~1705 cm^{-1}



~1745 cm^{-1}