B. Sc. III Year (Sem-VI)

Chapter-2

Infra Red Spectroscopy

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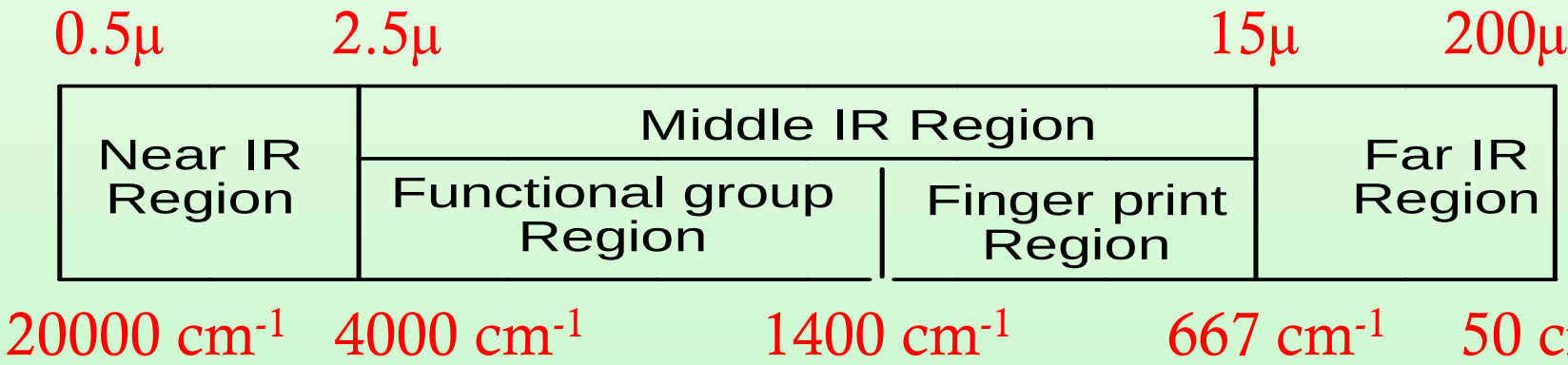
Introduction

- IR spectroscopy is used for detection of functional group in known and unknown compounds.
- In IR spectroscopy absorption of radiation takes place by sample, hence it is the kind of absorption spectroscopy.
- The Infra Red region of electromagnetic radiation is extended from 0.5μ to 200μ or 20000 cm^{-1} to 50 cm^{-1}.
- IR region is divided in three sub regions as follows.
- a) Near IR region : 0.5μ to 2.5μ (20000cm^{-1} to 4000cm^{-1})
- b) Middle IR region : 2.5μ to 15μ (4000cm^{-1} to 667cm^{-1})
- c) Far IR region : 15μ to 200μ (667cm^{-1} to 50cm^{-1})

- **IR Region :**

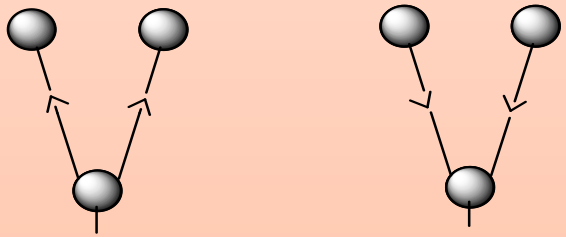


- The most important region for organic chemist is middle IR region or vibrational IR region i.e. 4000cm^{-1} to 667cm^{-1}

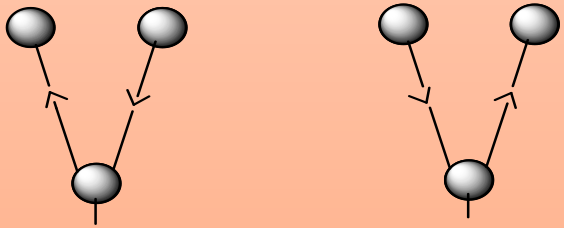
- When the IR radiation is passed through sample in this region, compound undergo molecular vibration.

Types of Vibrations

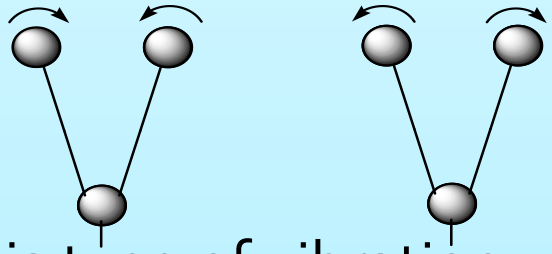
- There are main two types of vibrations :
- **a) Stretching Vibrations :**
- In this type of vibration, the distance between two atoms gets increased or decreased from central atom without affecting bond axis. Such type of vibration is called as stretching vibrations.
- Stretching vibrations are of two types :
- **i) Symmetric Stretching :**
- In this stretching vibration, movement of atoms with respect to central atom in the same direction.



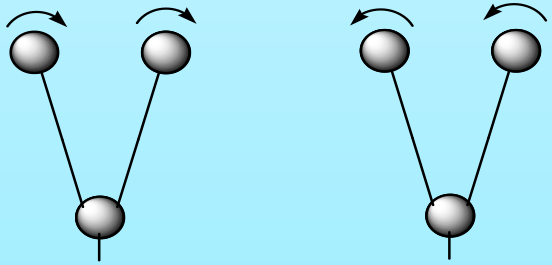
- **ii) Asymmetric Stretching :**
- In this stretching vibration, one of the atom approaches to central atom while other away from it.



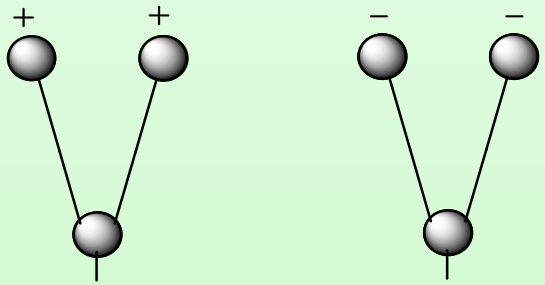
- **b) Bending Vibrations :**
  In this type of vibration, change in the position of atoms with respect to the original bond axis. Such type of vibration is called as bending vibrations.
- There are four types of bending vibrations :
- **i) Scissoring :** In this type of vibration, two atoms approaches to each other with change in their bond angle.



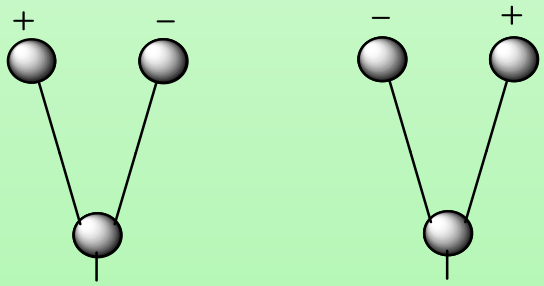
- **ii) Rocking :** In this type of vibration, movement of two atoms in the same direction.



- **iii) Wagging :** In this type of vibration, two atoms move up and down with respect to plane of the central atom.



- **iv) Twisting :** In this type of vibration, one of the atom move up to the plane and other moves down to the plane with respect to central atom.



Functional group Region

- The region between 4000 cm^{-1} to 1400 cm^{-1} is called as functional group region. Most common functional groups shows absorption band in this region due to stretching vibrations.
- The characteristics IR group frequencies of various functional groups are discussed as follows :

S.No.	Examples	Functional group	IR region
1	Alkanes	C-H	3000-2800 cm^{-1}
2	Alkenes	=C-H	3100-3000 cm^{-1}
		C=C	1670-1560 cm^{-1}
3	Alkynes	≡C-H	3300-3100 cm^{-1}
		C≡C	2200-2100 cm^{-1}
4	Alcohols, phenols	-OH	3600-3200 cm^{-1}

5	Carboxylic acids	-COOH	3600-2500 cm^{-1}
6	Aldehydes	C-H of –CHO	2900-2700 cm^{-1}
7	Ketones,amide, ester, aldehyde	>C=O	1850-1650 cm^{-1}
8	Aromatic compounds	C=C =C-H	1600-1400 cm^{-1} 3100-3000 cm^{-1}
9	Nitro compound	$-NO_2$	1500-1200 cm^{-1}
10	Amines	N-H	3600-3200 cm^{-1}
11	Cyanides	C≡N	2280-2250 cm^{-1}

Finger Print Region

- The region between 1400 cm^{-1} to 667 cm^{-1} is known as Finger print region. In this region absorption band caused due to stretching and bending vibrations.
- Finger print region is divided into following three regions :
- **a) Region between 1400 cm^{-1} to 1300 cm^{-1} :**
- Appearance of doublet near 1380 cm^{-1} shows presence of tertiary butyl group. Out of two strong bands of $-NO_2$ group, one appear in finger print region at 1350 cm^{-1}.

- **b) Region between 1300 cm^{-1} to 1000 cm^{-1} :**
- Alcohols, esters lactones and acid anhydride shows characteristics absorption in this region.
- In alcohol C-O stretching of primary alcohol appears at 1050 cm^{-1}, C-O stretching of secondary alcohol appears at 1100 cm^{-1} and C-O stretching of tertiary alcohol appears at 1150 cm^{-1}.
- In phenol C-O stretching appears at 1200 cm^{-1} and in ether C-O stretching appears at 1070 cm^{-1}
- **c) Region between 1000 cm^{-1} to 667 cm^{-1} :**
- In monosubstituted benzene absorption band at 710-690 cm^{-1},
- ortho disubstituted benzene appears at 770-735 cm^{-1},
- m-disubstituted benzene appears at 810-770 cm^{-1}
- p-disubstituted benzene appears at 850-810 cm^{-1}.

How will you distinguish between primary, secondary and tertiary alcohol by IR spectroscopy

- In primary alcohol, C-O stretching of appears at 1050 cm^{-1}, e.g. In 1-propanol C-O absorption band appears at 1050 cm^{-1}
- In secondary alcohol, C-O stretching of appears at 1100 cm^{-1}, e.g. In 2-propanol C-O absorption band appears at 1100 cm^{-1}
- In tertiary alcohol, C-O stretching of appears at 1150 cm^{-1}, e.g. In 2-methyl-2-propanol C-O absorption band appears at 1150 cm^{-1}
- Due to different IR values for C-O stretching of primary, secondary and tertiary alcohol, we can differentiate primary secondary and tertiary alcohol by using IR spectroscopy .

Interpretation of IR spectra of following Organic compounds :

- 1] Ethane : CH_3-CH_3

  2950 cm^{-1} due to C-H stretching

- 2] Ethene : CH_2=CH_2

  3080 cm^{-1} due to =C-H stretching

  1650 cm^{-1} due to C=C stretching

- 3] Ethyne : CH≡CH

  3280 cm^{-1} due to ≡C-H stretching

  2150 cm^{-1} due to C≡C stretching

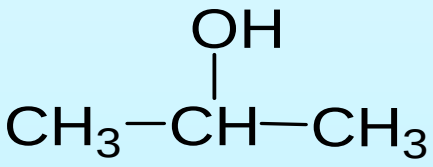
- 4] 1-propanol : CH_3-CH_2-CH_2-OH

  2981 cm^{-1}

  3391 cm^{-1}

  1050 cm^{-1}

- 5] 2-propanol :

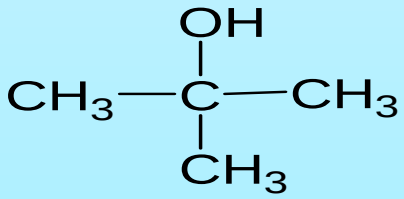


  2980 cm^{-1}

  3370 cm^{-1}

  1100 cm^{-1}

- 6] 2-methyl-2-propanol (t-butyl alcohol) :



  2990 cm^{-1}

  3325 cm^{-1}

  1150 cm^{-1}

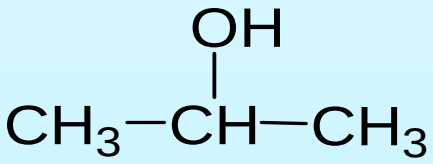
- 4] 1-propanol : CH_3-CH_2-CH_2-OH

  2981 cm^{-1} due to C-H stretching

  3391 cm^{-1} broad strong band due to O-H stretching

  1050 cm^{-1} due to C-O stretching

- 5] 2-propanol :

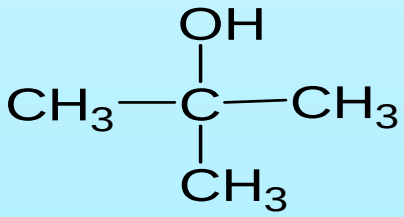


  2980 cm^{-1} due to C-H stretching

  3370 cm^{-1} broad strong band due to O-H stretching

  1100 cm^{-1} due to C-O stretching

- 6] 2-methyl-2-propanol (t-butyl alcohol) :

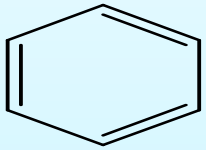


  2990 cm^{-1} due to C-H stretching

  3325 cm^{-1} broad strong band due to O-H stretching

  1150 cm^{-1} due to C-O stretching

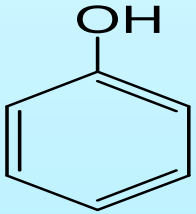
- 7] Benzene :



3050 cm^{-1}

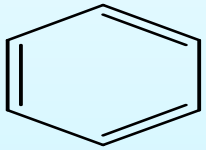
1600, 1590, 1550 cm^{-1}

- 8] Phenol :



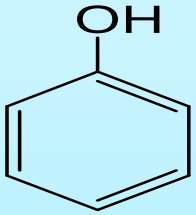
- 3065 cm^{-1}
- 3315 cm^{-1}
- 1200 cm^{-1}
- 1620, 1590, 1495 cm^{-1}

- 7] Benzene :



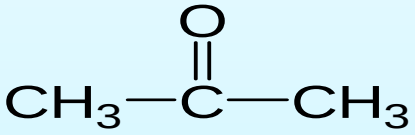
3050 cm^{-1} due to Ar-H stretching
1600, 1590, 1550 cm^{-1} due to C=C stretching

- 8] Phenol :



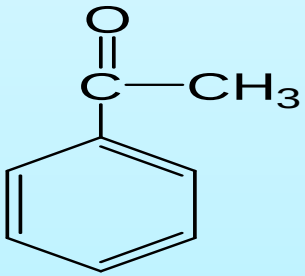
- 3065 cm^{-1} due to Ar-H stretching
- 3315 cm^{-1} broad strong band due to O-H stretching
- 1200 cm^{-1} due to C-O stretching
- 1620, 1590, 1495 cm^{-1} due to C=C stretching

- 9] Acetone :



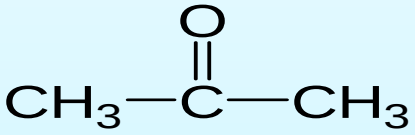
- 1720 cm^{-1}
- 2965 cm^{-1}

- 10] Acetophenone :



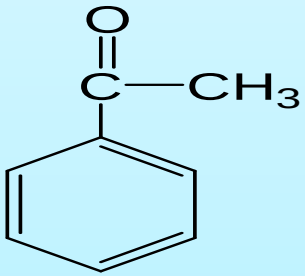
- 3080 cm^{-1}
- 2975 cm^{-1}
- 1710 cm^{-1}
- 1620, 1575, 1500 cm^{-1}

- 9] Acetone :



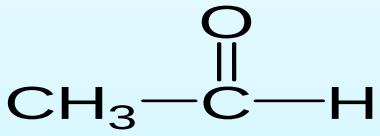
- 1720 cm^{-1} due to C=O stretching
- 2965 cm^{-1} due to C-H stretching

- 10] Acetophenone :



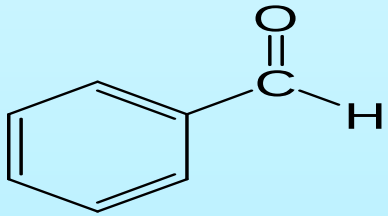
- 3080 cm^{-1} due to Ar-H stretching
- 2975 cm^{-1} due to C-H stretching
- 1710 cm^{-1} due to C=O stretching
- 1620, 1575, 1500 cm^{-1} due to C=C stretching

- 11] Acetaldehyde :



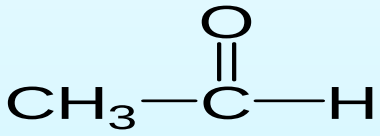
- 1745 cm^{-1}
- 2965 cm^{-1}
- 2700, 2850 cm^{-1}

- 12] Benzaldehyde :



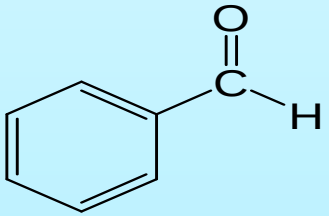
- 3071 cm^{-1}
- 1725 cm^{-1}
- 2730 cm^{-1}
- 1620, 1575, 1500 cm^{-1}

- 11] Acetaldehyde :



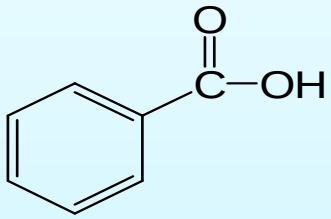
- 1745 cm^{-1} due to C=O stretching
- 2965 cm^{-1} due to C-H stretching
- 2700, 2850 cm^{-1} due to C-H stretching of –CHO

- 12] Benzaldehyde :



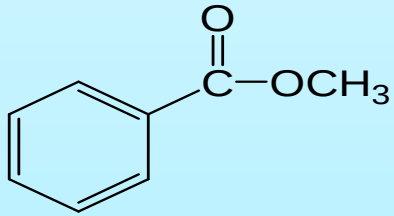
- 3071 cm^{-1} due to Ar-H stretching
- 1725 cm^{-1} due to C=O stretching
- 2730 cm^{-1} due to C-H stretching of –CHO
- 1620, 1575, 1500 cm^{-1} due to C=C stretching

- 13] Benzoic acid :



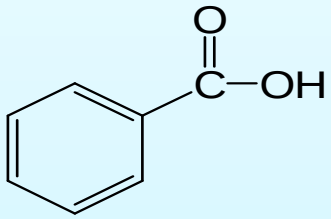
- 3071 cm^{-1}
- 3350 cm^{-1}
- 1730 cm^{-1}
- 1645, 1595, 1485 cm^{-1}

- 14] Methyl benzoate :



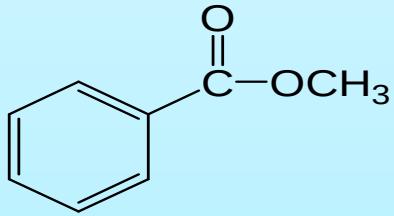
- 3075 cm^{-1}
- 1230 cm^{-1}
- 1745 cm^{-1}
- 1630, 1590, 1485 cm^{-1}
- 2910 cm^{-1}

- 13] Benzoic acid :



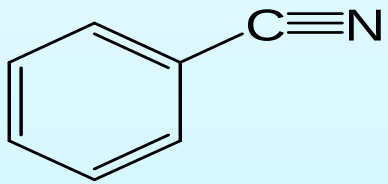
- 3071 cm^{-1} due to Ar-H stretching
- 3350 cm^{-1} due to O-H stretching
- 1730 cm^{-1} due to C=O stretching
- 1645, 1595, 1485 cm^{-1} due to C=C stretching

- 14] Methyl benzoate :



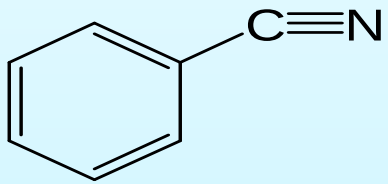
- 3075 cm^{-1} due to Ar-H stretching
- 1230 cm^{-1} due to C-O stretching of ester
- 1745 cm^{-1} due to C=O stretching of ester
- 1630, 1590, 1485 cm^{-1} due to C=C stretching
- 2910 cm^{-1} due to C-H stretching

- 15] Phenyl cyanide:



- 3075 cm^{-1}
- 2210 cm^{-1}
- 1630, 1590, 1485 cm^{-1}

- 15] Phenyl cyanide:



- 3075 cm^{-1} due to Ar-H stretching
- 2210 cm^{-1} due to C≡N stretching
- 1630, 1590, 1485 cm^{-1} due to C=C stretching

Hooks Law :

- Hooks law is applicable to determine the vibrational frequency of absorption band. The stretching vibrational frequency of a bond can be calculated by applying Hooks law.
- " If bond strength increases and the reduced mass decreases the value of the vibrational frequency increases." Mathematically Hooks law can be represented as ...

Vibrational frequency (v) $= \frac{1}{2\pi c}\left[\frac{k}{\frac{m1.m2}{m1+m2}}\right]^{1/2} = \frac{1}{2\pi c}\sqrt{\frac{k}{u}}$

- Where, μ (Reduced mass) = $\frac{m1.m2}{m1+m2}$

c = Velocity of radiation

k = Force constant

Thank You ……