

**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH**  
**UNIVERSITY GRANTS COMMISSION**

CHEMICAL SCIENCES

CODE:O1

**3.13. Structure determination of organic compounds**

**3.13.1. UV-Vis**

- **Beer-Lambert Law**

The Beer–Lambert law, also known as Beer's law, the Lambert–Beer law, or the Beer–Lambert–Bouguer law which deals with a linear relationship between the absorbance and the concentration, molar absorption coefficient and optical coefficient of a solution and is represented as  $A = \epsilon cl$ ,

where  $A$  is absorbance,  $\epsilon$  is molar absorption coefficient,  $c$  is molar concentration and  $l$  is optical coefficient.

The molar absorption coefficient is highly dependent on a sample and is a measure of how strong the sample absorb at a particular wavelength of light. The concentration is simply the moles  $L^{-1}$  (M) of the sample dissolved in the solution, and the length is the length of the cuvette used for the absorbance measurement and is typically 1 cm.

- **Transmittance and absorbance:**

The transmittance,  $T$ , of a solution is defined as the ratio of the transmitted intensity ( $I$ ), over the incident intensity ( $I_0$ ) which is expressed as  $T = I/I_0$ .

Absorbance is a logarithm of incident intensity and transmitted intensity, so  
 $A = \log_{10} I_0/I$  or  $A = -\log_{10} I/I_0$  or  $A = -\log_{10} T$ .

- **Chromophore:** The functional groups ( $C=C$ ,  $-N=N-$  etc) which absorb at wave length longer than 180 nm are called chromophores.
- Other chromophores include nitro, carbonyl, nitroso, thiocarbonyl, suphoxide group and aromatic rings.
- In an extensively conjugated system, the absorption band is shifted towards longer wave length and therefore the transition shifts to the visible region. e.g.  $Ph-(CH=CH)_n-Ph$  the  $\pi-\pi^*$  transition lies in the UV region where  $n = 1, 2$ ; as  $n$  increases, delocalization of  $\pi$ -electrons over the entire skeletal frame-work occurs and hence, the electronic transition shifts to the visible region.

- **Auxochrome:** Auxochrome refers to an atom or group of atom which does not show absorption band on its own, however, when it is in conjugation with a chromophore, it causes a bathochromic shift. For example, C=C group is a chromophore in ethylene, when one of the H-atom is replaced by a halogen atom, it causes bathochromic shift and hyperchromic effect is produced. This is due to fact that the lone pair of electron on the halogen atom is participated with the alkene group. So, the halogen atom will be called Auxochrome.
- **Bathochromic shift:** If the  $\lambda_{\max}$  is shifted to longer wave length, then it is called bathochromic shift or red shift.
- **Hypsochromic shift:** If the  $\lambda_{\max}$  is shifted to shorter wave length, then it is called hypsochromic shift or blue shift.
- **Hyperchromic shift:** If the intensity of an absorption band increases with reference to its molar extinction coefficient  $\epsilon_{\max}$ .
- **Hypochromic shift:** If the intensity of an absorption band decreases with reference to its molar extinction coefficient  $\epsilon_{\max}$ .
- **Woodward-Fieser Rules for calculating Absorption Maximum:** Woodward formulated an empirical rule for calculating the  $\lambda_{\max}$  in case of dienes. These rules have been modified further by Fieser in 1948.

The various rules for calculating the absorption maximum in case of dienes and trienes are summarized in the tabular form.

Transition involved $\pi-\pi^*$	
Parent value for butadiene system or a cyclic conjugated diene	217 m $\mu$
Acyclic triene	245 m $\mu$
Homonuclear conjugated diene	253 m $\mu$
Heteronuclear conjugated diene	215 m $\mu$
Increment for each substituent	
Alkyl substituent or ring residue	5 m $\mu$
Exocyclic double bond	5 m $\mu$
Double bond extending conjugation	30 m $\mu$
Auxochrome	
-OR	6 m $\mu$
-SR	30 m $\mu$
-Cl, -Br	5 m $\mu$
-NR <sub>2</sub>	60 m $\mu$
-OCOCH <sub>3</sub>	0 m $\mu$

- Chromophore Increment in Carbonyl Compounds:**

**Chromophore Increment in nm (or mμ) for the position with respect to the carbonyl group**

	$\alpha$	$\beta$	$\gamma$	$\delta$
-OH	+ 35	+ 30	-	+ 50
-OAc	+ 6	+ 6	+ 6	+ 6
-Cl	+ 15	+ 12	-	-
-Br	+ 25	+ 35	-	-
-OR	+ 35	+ 30	+ 17	+ 31
-SR	-	+ 85	-	-
-NR <sub>2</sub>	-	+ 95	-	-

- Auxochrome acting as a substituent:**

Auxochrome	Increment in nm position of the substituent		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Alkyl	+ 3	+ 3	+ 10
OH, OR	+ 7	+ 7	+ 25
Cl	0	0	+ 10
Br	+ 2	+ 2	+ 15
NH <sub>2</sub>	+ 13	+ 13	+ 58
NHAc	+ 20	+ 20	+ 45
NR <sub>2</sub>	+ 20	+ 20	+ 85
O <sup>-</sup>	+ 11	+ 20	+ 75





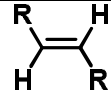




- **Fluorescence and Phosphorescence**

When a molecule absorbs light of shorter wave length and emits light of comparatively longer wave length, then that phenomenon is called fluorescence.

On the other hand when a substance emits light of longer wave length even when the irradiating light is removed, is known as phosphorescence.

### 3.13.2. IR

- **Typical Vibrational Wave Number for different Functional group**

Group	Mode	Range (cm <sup>-1</sup> )	Intensity
	C-H (s)	3000-2850	
-CH <sub>3</sub>			
			
		2900-2880	
-CH <sub>3</sub>	C-H (b)	1470-1430	
-CH <sub>3</sub>	CH <sub>3</sub> (sb)	1390-1370	
	CH <sub>2</sub> (r)	700-750	
-C≡C-H	CH (s)	3300	
	CH (s)	980-960	
	C=C (s)	1680-1620	
-O-H	O-H (b)	1410-1220	
-O-H	O-H (s)	3650-3590	
	C-OH (s)	1150-1050	
	N-H (ss/as)	3500-3300	
=N-H			
	C=O (s)	1780-1680	
Hydrogen bonds	O-H (s)	3570-3200	

- **Relation between IR stretching frequency and bond order:**

The shorter the bond length, the stronger will be the bond and hence IR stretching frequency of the bond will be higher.

for example, the IR stretching frequency of P-O bond varies in the order  $\text{Me}_3\text{PO} < \text{Cl}_3\text{PO} < \text{F}_3\text{PO}$ ;

In all the molecules the P=O bond polarizes as  $\text{P}^+-\text{O}^-$  due to electronegativity difference between P (2.19) and O (3.44) atom. If we consider,  $\text{Cl}_3\text{PO}$  and  $\text{F}_3\text{PO}$ , then it can be seen that the P atom gets more positive character in  $\text{F}_3\text{PO}$  than in  $\text{Cl}_3\text{PO}$ , because of more electron withdrawing effect of F (3.98) than Cl (3.16). Therefore, to balance the charge on P atom, the lone pair of electron on the halogen atoms (F or Cl) participates in conjugation with P atom and hence the P=O bond gets triple bond character to some extent, hence the bond order of P=O bond becomes higher. Therefore, the bond order of P=O bond becomes greater in  $\text{F}_3\text{PO}$  than in  $\text{Cl}_3\text{PO}$ . On the other hand, the Me-group is electron releasing group, so it does not create any excess positive charge on P atom.

As we know, with the increasing of bond order, bond length decreases and hence IR stretching frequency increases. Therefore, the stretching frequency of the molecules vary in the order  $\text{Me}_3\text{PO} < \text{Cl}_3\text{PO} < \text{F}_3\text{PO}$ .

### 3.13.3. NMR ( $^1\text{H}$ & $^{13}\text{C}$ ) Spectroscopy

All the atomic nuclei possess nuclear spin,  $I$ , which can be integral (1,2,3, etc) or half integral ( $1/2$ ,  $3/2$ ,  $5/2$ ,  $7/2$  etc). Each of the proton and the neutron has spin  $1/2$ . It is very difficult to predict the spin of a nucleus. However, there are some rule which can help in predicting the nuclear spin.

- If the mass number  $A$  is odd, then nuclear spin  $I$  is half integral. Thus, in case of  $^1\text{H}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $I = 1/2$  and in case of  $^{11}\text{B}$ ,  $I = 3/2$ .
- If the mass number  $A$  and atomic number  $Z$  both are even, then spin is zero. Thus in case of  $^4\text{He}_2$ ,  $^{12}\text{O}_6$ ,  $^{16}\text{O}_8$ ,  $I = 0$ .
- If the mass number  $A$  is even but the atomic number  $Z$  is odd, then the spin is integral. Thus in case of  $^2\text{H}_1$ ,  $^{14}\text{N}_7$ ,  $I = 1$  while that for  $^{10}\text{B}_5$ ,  $I = 3$ .
- **Chemical shift:** The difference between the magnitude of the magnetic field at which molecular nuclei and free nuclei resonate is called chemical shift.

The measurement of chemical shift is not possible using free nucleus, rather chemists use those compounds which shows a sharp singlet. The most frequently used reference compound is tetramethylsilane (TMS). The chemical shift is defined in parts per million (ppm).

- **Reason for using TMS as reference compound:**

- (i) It has twelve equivalent protons as its structure is  $\text{Si}(\text{CH}_3)_4$ . Since, all the protons are in the same environment, TMS gives a single intense peak in its NMR spectrum.
  - (ii) It is low boiling ( $27^\circ\text{C}$ ) substance and therefore can easily be recovered once the spectrum is recorded.
  - (iii) It is chemically inert.
  - (iv) The methyl groups in TMS are highly shielded by the external magnetic field. Further, TMS shows NMR at very high magnetic field strength compared to other protons.
- Two scales ( $\delta$  and  $\tau$ ) are used for recording NMR spectrum and the two scales are related as

$$\delta + \tau = 10 \text{ or } \tau = 10 - \delta.$$

- On the  $\delta$  scale,  $\delta$  is set equal to zero at the reference peak of TMS.
- On the  $\tau$  scale,  $\tau$  is set equal to 10 at the reference peak of TMS.
- **Shielding and Deshielding of protons:**

If an electron releasing substituent is directly or indirectly attached with the bare proton, then the electron density around the bare proton increases and hence that proton will be shielded and so absorbs at higher magnetic field, as a result that proton will resonate at higher magnetic field and show lower  $\delta$ -value. This phenomenon is called shielding effect.

On the other hand, if an electron withdrawing substituent is directly or indirectly attached with the bare proton, then the electron density around the bare proton decreases and hence that proton will be deshielded and so absorbs at lower magnetic field, as a result that proton will resonate at lower magnetic field and show higher  $\delta$ -value. This phenomenon is called deshielding effect.

- **Nuclear Spin-Spin Interaction:**

The magnitude of the splitting between the lines of a given multiplet is given by the spin-spin coupling constant  $J$  which is measured in Hz units.

- **Some rules for calculating the number of expected lines in the NMR spectra:**

- (i) The protons of the same group do not interfere among themselves, for instance, the three protons of methyl group do not interact with one-another.
- (ii) The multiplicity of a group of equivalent protons is determined by the neighboring protons, for example if  $n$  equivalent protons couple with a proton which is attached with the adjacent carbon, then the number of peaks or signals will be  $n+1$ .

- **Pascal's Triangle for calculating Intensities of NMR signals**

Number of protons, n	Number of NMR lines	Relative intensities
0	1	1
1	2	1 1
2	3	1 2 1
3	4	1 3 3 1
4	5	1 4 6 4 1
5	6	1 5 10 10 5 1
6	7	1 6 15 20 15 6 1

- **The proton NMR spectrum of a molecule gives us the following information**

- The number peaks helps to know how many kinds of protons are present in a molecule.
- The intensities of the peaks tells about the number of protons of each kind are present in a molecule.
- The position of the peaks represent the electronic environment of each kind of proton.
- The splitting of peak into several peaks indicates the environment of a proton with respect to each other in a molecule.

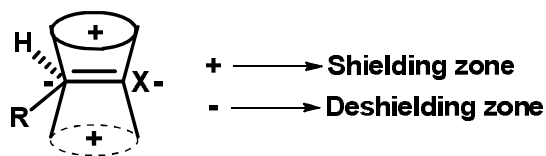
- **Reason for different chemical shift of different types of protons and their applications:**

The shielding that a proton experiences is a combination of at least three types of electronic circulation which causes a change in the effective magnetic field ( $H_{\text{eff}}$ ) which is different from the applied magnetic field ( $H_0$ ). These are (a) local diamagnetic effect, (b) diamagnetic and paramagnetic anisotropic effect and (c) interatomic ring current as in aromatic compounds.

- Local diamagnetic effect:** It is produced by the circulation of pair of electrons with which the proton is attached with other nucleous. This is dependent on the inductive effect of the atoms or group of atoms with which the proton is linked.



- (b) **Diamagnetic and paramagnetic anisotropic effect:** When a molecule of the type  $\text{HC}=\text{X}$  where,  $\text{X} = \text{CH}_2, \text{O}, \text{N}, \text{S}$ , etc, is placed in an external magnetic field  $[\text{H}_0]$ , there will be circulation of the p-electrons of the  $\text{C}=\text{X}$  system which would produce an induced diamagnetic field  $[\text{H}_{\text{eff}} = \text{H}_0 - \sigma\text{H}_0]$ , in between C & X and a resultant paramagnetic field  $[\text{H}_{\text{eff}} = \text{H}_0 + \sigma\text{H}_0]$ , on either side of C & X. The induced diamagnetic field is maximum at the centre of  $\text{C}=\text{X}$  while the resultant paramagnetic field is highest in the region of olefinic proton (in case of olefins) and aldehydic protons (in case of aldehydes). So, there will be a shielding zone (+) in between C & X and a deshielding zone (-) on either side of C & X as shown below.

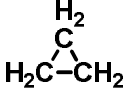
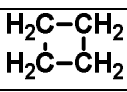
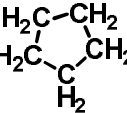
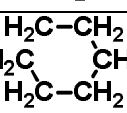
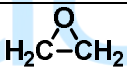

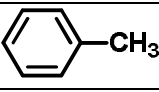
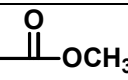


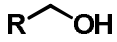
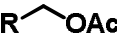
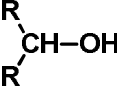
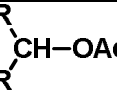
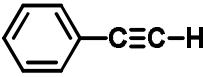
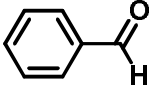
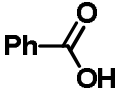
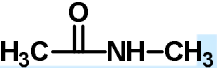
- Distinction between 1°, 2°, and 3° alcohols from their  $^1\text{H}$  NMR spectra in a particular solvent:** If the spectrum of the alcohol is recorded in solvents like  $\text{d}_6\text{-DMSO}$  which is able to form strong intermolecular hydrogen bonding with the  $-\text{OH}$  group, chemical exchange is retarded and the expected multiplicity is observed. This in  $\text{d}_6\text{-DMSO}$ , the  $1^\circ\text{-OH}$  proton appears as a triplet,  $2^\circ\text{-OH}$  appears as a doublet and  $3^\circ\text{-OH}$  proton gives a singlet.

Text with Technology



- Some important chemical shift values:

Compound	Structure	Chemical shift value ( $\delta$ ) in ppm	
Acyclic hydrocarbon	$\text{H}_3\text{C}-$	0.9	
	$- \text{CH}_2$	1.25	
	$- \text{CH}$	1.5	
Cyclic hydrocarbon		0.3-0.5	
		1.97	
		1.51	
		1.43	
	Cyclooctane or Cycloheptane	1.53	
Epoxide		2.30 (methylene protons)	
Epoxide opened diol		3.60 (methylene protons)	
Methyl protons attached with CO	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{R}$ (R = H, alkyl, OH, OR, NH <sub>2</sub> )	1.97-2.2	
Methyl protons attached with C=C	$\text{H}_3\text{C}-\text{C}=\text{C}$	1.6-1.8	
Methyl group attached to any aromatic ring		2.34	
Methyl group attached to O and N	$-\text{OCH}_3$	3.50 (aliphatic)	3.70-4.0 (aromatic)
	$-\text{NCH}_3$	2.2 (aliphatic)	3.0 (aromatic)
		3.65-3.75	

<b>-CH<sub>2</sub> and -CH attached to -OH and -OAc</b>		3.60
		4.10
		3.90
		5.0
<b>Acetylenic proton</b>		2.5-3.0
<b>Aldehydic proton</b>		9.86
<b>Carboxylic acid</b>		11.95
<b>Amines</b>	0.3-2.2 (aliphatic)	2.6-4.7 (aromatic)
<b>Amides</b>		8.15

#### • Coupling Constant (*J*):

In cases where the chemical shifts between two groups of nuclei involving in electron coupled spin-spin interactions are large compared with the multiplet species, the separation of the adjacent components in a multiplet will be equal to each other and also to the separation of the components in the multiplet arising from the second group involved in mutual splitting. This separation which is a direct measure of the effectiveness of the spin-spin interaction is known as coupling constant (*J*).

*J* is independent of the strength of the magnetic field. Its magnitude depends on

1. Gyromagnetic ratio ( $\gamma$ ) of the nuclei ( $\gamma$  of <sup>13</sup>C is 1/4<sup>th</sup> that of <sup>1</sup>H).

$$J_{1H-1H} = 0.5-17.5 \text{ Hz}$$

$$J_{13C-1H} = 120 \text{ Hz (sp}^3\text{-C)}$$

$$J_{13C-1H} = 160 \text{ Hz (sp}^2\text{-C)}$$

$$J_{13C-1H} = 250 \text{ Hz (sp-C)}$$

2. Structural and stereochemical relationship of the interacting nuclei:

**Structure:** J of aromatic protons

$$J_{ortho} = 8-10 \text{ Hz}$$

$$J_{meta} = 2-3 \text{ Hz}$$

$$J_{para} = 0-0.5 \text{ Hz}$$

**Stereochemistry:** J of two vicinal *cis*-olefinic protons is 10-12 Hz.

J of two vicinal *trans*-olefinic protons is 16-17.5 Hz.

In rigid cyclohexane system;

J of two vicinal trans diaxial protons  $J_{a,a} = 8-10 \text{ Hz}$  and  $J_{a,e}$  or  $J_{e,e} = 2-3.5 \text{ Hz}$ .

- **$^{13}\text{C}$  NMR Spectroscopy:**

In  $^{13}\text{C}$  NMR spectrum analysis we need to record at least two types of spectra

- (i) **Wide bond decoupling or proton noise decoupling or commonly known as NDC spectrum:** This spectrum records only the number of non equivalent C-atoms as singlet by continuous irradiation of all the protons in the molecule, e.g. the NDC spectrum of  $\text{CH}_3\text{CH}_2\text{CH}_3$  gives two singlets, one at  $\delta_{\text{C}} 15.6$  (two equivalent C atoms) and the other at  $\delta_{\text{C}} 16.1$  for the methylene C-atom.

This spectrum however does not provide any information about the degree of protonation of the C-atoms. This information for the degree of protonation of the C-atoms in the molecule may be obtained by any one of the following three types of C-spectrum.

- (a) **Single Frequency off Resonance Decoupled (SFORD) spectrum:** In this technique all parts of the protons attached to a particular C-atoms are irradiated so that the individual non equivalent protonated 'C'-signals are now split due to spin-spin interaction with an attached proton, the multiplicity is dependent on the number of attached H atoms, the non protonated C appears as a singlet.

The SFORD spectrum is quite satisfactory when the C-chemical shifts are widely different, however, when the  $\delta_C$  values of the C-atoms are very close to each other, in that cases the components of the multiplicity of one C-atom overlaps with those of another C-atoms are in very close chemical shifts making it extremely difficult to ascertain the degree of protonation of the carbon atoms. For this reason, now a days the degree of protonation of the C-atom is determined by either DEPT (Distortionless Enhancement Polarization Transfer) spectrum or APT (Attached Proton Test) spectrum.

- (b) DEPT spectrum: Due to transfer of polarization from H to C, the carbon signals undergo phase transfer with the  $\text{CH}_3$  and CH carbon appearing on the +ve side and the  $\text{CH}_2$  carbon on the -ve side, the quaternary carbon signals thought out of base *ie.* the signals are not observed.
- (c) In APT spectrum the  $\text{CH}_3$  and CH carbons appear on the +ve side of the spectrum and the  $\text{CH}_2$  & quaternary non-protonated C-signals appear on the -ve side of the spectrum.

Thus, from a combination of the NDC spectrum and either SFORD or DEPT or APT spectrum it is possible to ascertain .....

- (1) The number of non equivalent C-atoms and (2) the degree of protonation of each C-atoms in an organic compound.
- Two dimensional NMR (2D NMR): This may be of two types. Correalation between two different nuclei of the same type ( $^1\text{H}^1\text{-}^1\text{H}^1$ ) is called homonuclear correlation or HOMCOR or simply correlation spectroscopy or COSY.
- When correlation takes place between two different types of nuclei ( $^1\text{H}\text{-}^{13}\text{C}$ ) is called heteronuclear correlation or HETCOR. HETCOR are of two types.....
  - (a) direct  $^1\text{H}\text{-}^{13}\text{C}$  coupling (1-bond  $^1\text{H}\text{-}^{13}\text{C}$  correlation), which is called HMQC (Heteronuclear Multiple Quantum Coherance); (b) long range  $^1\text{H}\text{-}^{13}\text{C}$  coupling [generally 3 bond correlations are strong, sometimes 2-bond correlation also observed. This is called HMBC (Heteronuclear Multiple Bond Coherance).

### 3.13.4. Mass Spectrometry

Mass spectrometry is the most convenient method for determining the molecular mass of the compound and its elemental composition.

The molecular ion is known as parent ion which is commonly designated as  $M^+$ . It is positively charged molecule with an unpaired electron.

- Some important features of the parent ion peak are.....
- 1. In case of aromatic compound the molecular ion peak is comparatively much intense due to the presence of  $\pi$ -electrons.
- 2. Conjugated olefins shows more intense molecular ion peak compared to the corresponding non-conjugated olefins with the same number of unsaturation.
- 3. Unsaturated compounds give more intense peak compared to saturated molecules.
- 4. The relative abundance of saturated hydrocarbon is more than the corresponding branched chain compound having the same number of carbon atoms.
- 5. The substituent groups like  $-OH$ ,  $-OR$ ,  $-NH_2$  etc lowering ionization potential increases the relative abundance in case of aromatic compounds.
- 6. If the molecular ion peak in the mass spectrum is absent, then the compound under examination will be highly branched or tertiary alcohol. In case of primary and secondary alcohol, the intensity of molecular ion peak becomes very small.
- 7. In case of halo (Cl or Br) compounds, isotope peaks are also observed along with molecular ion peak. In case of chloro compounds  $M^+$  and  $(M^+ + 2)$  peaks are found with the intensity ratio 1:3. Whereas in case of bromo compounds,  $M^+$  and  $(M^+ + 2)$  peaks are found with the intensity ratio 1:1.
- **McLafferty rearrangement:**
- This reaction deals with the migration of  $\gamma$ -hydrogen atom followed by cleavage of a  $\beta$ -bond.
- The rearrangement also deals with the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc.
- A six membered transition state is formed during the course of the rearrangement.

