Dr Amanpreert Kaur Sodhi

Chapter 3 SPECTROSCOPY AND ITS APPLICATIONS

SAQ – Short Answer Type Questions

Q. 1. What is Frank Condon Principle ? *(Dec. 2007)*

Ans. The transition between two electronic states take place according to this principle. The vibrational structure of the electronic transition can be studied with the help of this principle.

This principle states that because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond.

If we consider absorption of a quantum by a atomic molecule in the ground state then transition must occur along a vertical line according to definition of Franck Condon principle. Because this principle says that internuclear distance does not change with the electronic transition. Hence the most probable transition according to Franck Condon principle is from V_0 of E_0 to V_2 of E_1 *i.e.* $V_0 \rightarrow V_2$. The probability for other transitions are low.

Q. 2. What are different components of spectrophotometer ?

Ans. Spectrophotometer is actually the instrument which records the absorbed wavelength by the sample and display the facts in the form of a spectra. For different types of spectroscopies, of course construction of the spectrophotometer is different. But all the absorption spectrophotometer mainly consists of :

(A) A Radiation source

(B) A Sample cell

(C) A dispersing element

(D) A Recorder

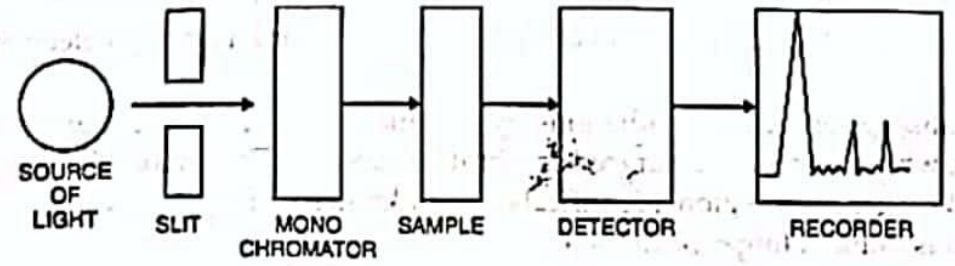
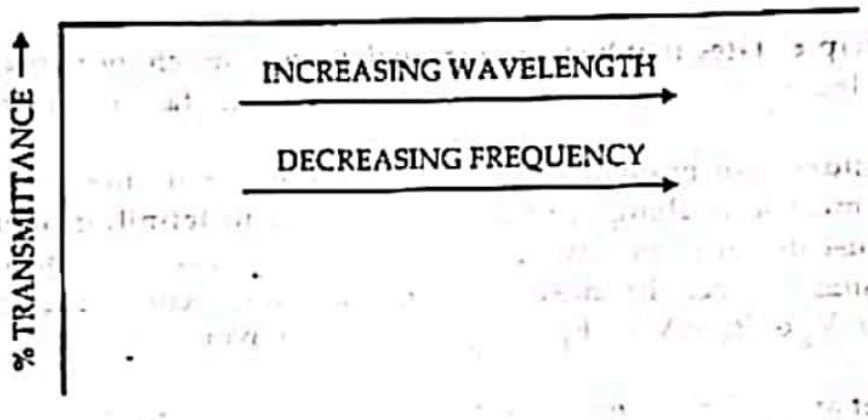


Fig. Important Components of U.V.—Visible Spectrophotometer (Single beam spectrophotometer)

Q. 3. What do you understand by IR spectra ?

(Dec. 2007, May 2007, Dec. 2006)

Ans. The IR spectra is obtained as a result of irradiation of the molecule by infrared radiations. When a molecule absorbs infrared radiations the energy is not so high to jump to higher energy levels. This only causes the vibration of atoms of molecules. The organic compounds starts vibrating at high speed about the covalent bonds. This vibration is due to vibration of atoms about covalent bonds by which the atoms are attached to each other. The different compounds absorbs the infrared radiations in different regions of the spectrum. This gives rise to infrared absorption bands at a specific wavelength or frequency. The bonds are specified by wave number $\frac{1}{\lambda}$ in the spectrum. The vibrational or infrared spectrum of an organic compound gives the % transmittance and wavelength or frequency at which band is formed.



Vibrational spectroscopy is mainly concerned with the study of those molecules which shows the change in dipole moment during vibration. The molecules having zero dipole moment or have a permanent value of dipole moment cannot be studied by vibrational spectroscopy. The homonuclear diatomic molecule like H_2, N_2, O_2 etc. do not show vibrational spectra where as the heteronuclear diatomic molecule (HCl, Co etc.) show vibrational spectra because their dipole moment changes with change in bond length due to vibration between atoms attached by covalent bonds. The change in dipole moment generates the oscillating electric field. The IR spectra is generated due to resonance which arises when frequency of the oscillating electric field is similar to the frequency of electric field oscillating in the plane perpendicular to the plane of propagation of electromagnetic radiations.

The absorption of infra radiations by organic molecules results various types of vibrations, which leads to the infrared or vibrations spectra. The region 1300–900 cm^{-1}, of IR is called Finger Print region. Identification of unknown compound with that of known compound is done in finger print region.

antibonding molecular orbital (π^*). So π e will occupy π bonding molecular orbital *i.e.* ground state. On absorption of energy the π e will get excited to higher energy orbital *i.e.* π^* or π antibonding molecular orbital $(\pi \rightarrow \pi^*)$.

If the molecule has *n* electrons also the possible transitions for *n* electrons, which will occupy *n* molecular orbital (*i.e.* nonbonding molecular orbital) in the ground state may be *n* to σ^* and for *n* to π^*. $(n \rightarrow \sigma^*)$ and $(n \rightarrow \pi^*)$ or $n \rightarrow \sigma^*$.

Transitions from bonding and π to antibonding π^* and σ^* respectively, *i.e.* $\sigma \rightarrow \pi^*$ and π to σ^* can also take place. But according to selection rule, these transistion are forbidden and are of very weak in intensity.

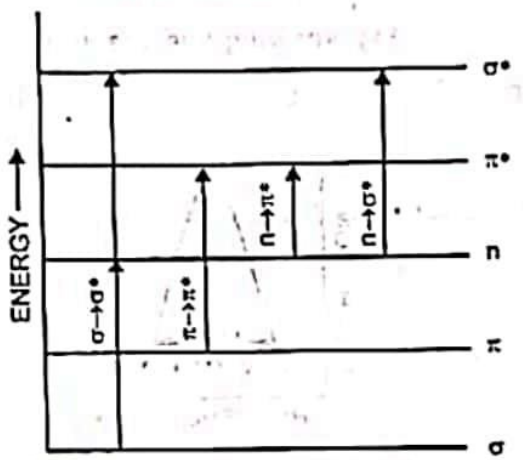


Fig. Different Electronic Transitions

The different transitions obey the following trend of energy requirement.

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

When an electromagnetic radiation in U.V. region (200-400 nm) or visible region (400-800 nm) pass through the sample compound having multiple bond in its structure, a part of the incident light is absorbed. This absorption imparts energy which leads to different transitions of valence electrons in the sample molecule. Since sigma electrons are tightly held and higher amount of energy is required to excite σ electrons, so it is outside the range of usual spectrophotometers.

Q. 6. What are Chromophores ? *(May 2010, 2009)*

Ans. Chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or visible region.

The absorption occurs irrespective of the fact whether colour is produced or not.

There are two types of chromophore :

(*i*) In which π electrons are present and hence $\pi \rightarrow \pi^*$ transitions are shown e.g. ethylene, acetylene, Benzene etc.

(*ii*) Those which have both n and π electrons so that these show $n \rightarrow \pi^*$ transitions in addition to $\pi \rightarrow \pi^*$ transitions.

Examples are carbonyls (>C=O), nitriles ($R-C \equiv N$), Nitrocompounds ($R-NO_2$) etc.

Q. 7. What is an auxochrome ? ***(May 2010)***

Ans. An auxochrome is a colour enhancing group. It does not itself act as a chromophore, but when it is bonded to a chromophore, it increases the absorption value in terms of l and intensity. Because a new chromophore is formed due to this combination. Examples of auxochrome are $-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{S}H$ etc. All the auxochromes have n electrons.

Q. 8. What is Bathochromic shift ?

Ans. It is the effect by virtue of which the absorption maximum is shifted towards longer wavelength due to presence of an auxochrome or by change of solvent. This shift is called Red Shift.

Factors Causing Bathochronic Effect

(*i*) Presence of auxochrome.

(*ii*) Nature of solvent.

(*iii*) Extention in conjugation.

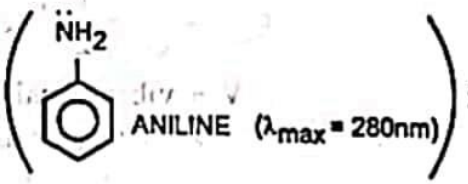
Q. 9. What is Hypsochromic shift ?

Ans. It is the effect by virtue of which the absorption maxima is shifted towards the shorter wavelength. This is called **Blue shift.** Removal of conjugation or changes in polarity of the solvent, are the two factors responsible for blue shift :—

1. Removal of Conjugation : Butadiene shows absorption maxima at 270 nm but ethene shows at 180-190 nm. This blue shift in ethene is because of removal of conjugation.

$CH_2 = CH_2$ Ethene

$CH_2 = CH - CH = CH_2$ Butadiene

2. Polarity of Solvent : If aniline 

ANILINE (λ_{max} = 280nm) is taken in acidic solvent, the lone pair of electron present on N will not show conjugation with p-bond system of benzene ring. Hence a blue shift is caused which will lead the absorption to lower wavelength. (Blue Shift)

Q. 10. What do you understand by intensity shift ?

Ans. Hyperchromic Effect or Shift : It is the effect by virtue of which intensity of the absorption maximum increases. Introduction of an auxochrome increases the value of the intensity of the wavelength absorbed.

Hypochromic Effect or Shift : It is the effect by virtue of which the intensity of the absorption maxima decreases. This effect or shift is called Hypochromic effect or shift. The introduction of the group which distort the geometry of the molecule course hypochromic effect. For example ε_{max}/intensity for biphenyl and 2-methyl biphenyl is 19000 and 10250 respectively. The substitution of methyl group in biphenyl cause hypochromic shift due to distortion caused by it.

Q. 11. What are isobestic points ?

Ans. The spectrum of new compound can be compared with spectrum of the known compounds. This is called finger printing.

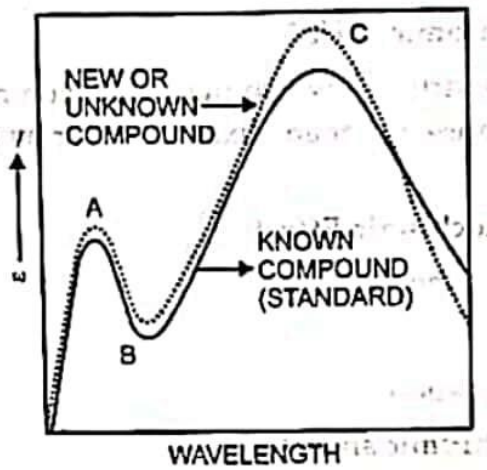


Fig. Showing Isobestic Points

The points A, B and C marked in the figure above where the λ_{max} value is same for the two compounds are called **Isobestic Points.**

Q. 12. What is Zero point energy for Simple Harmonic Oscillator ?

Ans. For a simple harmonic oscillator, the vibrational energy is represented as E_{vib} and

$$E_{vib} = \left(V + \frac{1}{2}\right) h\nu_{vib}$$

V = vibrational quantum number
(It gives us idea about the position of the molecule in vibrational level. where value of V can be V = 0, 1, 2, ...)

ν_{vib} = vibrational frequency

h = Planck's constant

$$\bar{\nu} = \frac{c}{\lambda} = c\,\bar{\nu}_{vib}$$

$$E_{vib} = \left(V + \frac{1}{2}\right) hc\bar{\nu}_{vib}$$

If the molecule is present in the ground state *i.e.* $V = 0$; $E_{vib} = \frac{1}{2} hc\bar{\nu}_{vib}$ *i.e.* in ground state, molecule is not inactive, it is vibrating. This energy is called **Zero Point Energy.**

Q. 13. Why are electronic absorption bands generally broad as compared to infra red ?

Ans. Every electronic transition is accompanied by vibrational and rotational change which contributes to the broadening of band whereas IR band is due to only rotational transition.

Q. 14. Selection rules for IR. *(May 2009)*

Ans. For simple harmonic oscillator $\Delta V = \pm 1$ and for a harmonic oscillator $\Delta V = +1, \pm 2, \pm 3, \ldots$.

Q. 15. Give the range of IR, UV and Visible regions of electromagnetic spectrum.

Ans.

ν (Hz) ⟶		
3×10^{12}	3×10^{14}	3×10^{16}
IR	Vis.	U.V.
100 μm	1000 nm	10 nm
←λ		

Q. 16. Give high resolution NMR of ethanol.

Ans. In pure ethanol:

$$\overset{(a)}{CH_3}\overset{(b)}{CH_2}\overset{(c)}{OH}$$

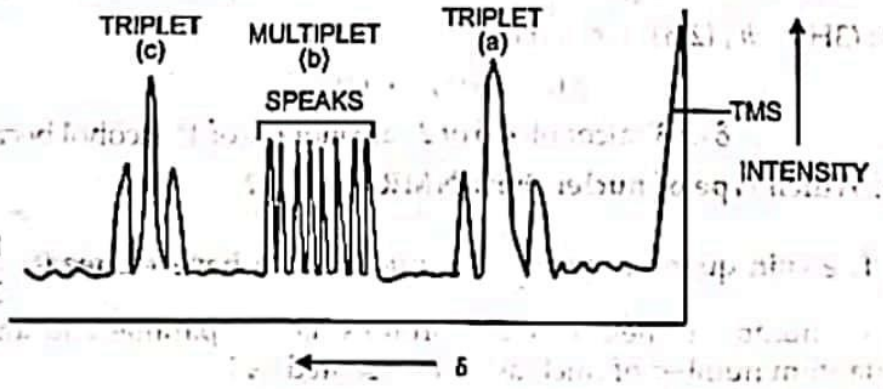


Fig. Showing NMR spectrum of $\overset{(a)}{CH_3}\overset{(b)}{CH_2}\overset{(c)}{OH}$ (Ethanol)

Q. 17. What is coupling constant ? *(Dec. 2008, May 2007, Dec. 2006)*

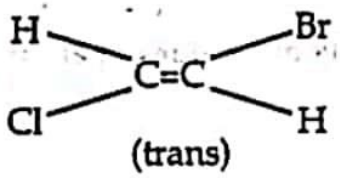
Ans. The distance between the centre of two adjacent peaks in a multiplet is constant and is known as coupling constant (J). It is measured in **Hz or Cps.**

If we take the spectrum of a sample at two different radiofrequencies then the value of chemical shift changes but the value of J does not change.

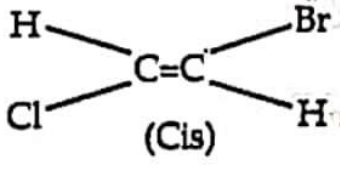
By comparing the value of J between peaks, one can assure that whether the given signal is a doublet or two singlets. Similarly by running the sample at two different radiofrequencies, and then comparing the value of J for both the spectras, it can be concluded that what is the nature of given signal. In other words, it can be said that if J changes, the signal is not a multiplet, but of J does not change signal is multiplet.

In case of geometrical isomers :

$$J_{trans} > J_{cis}$$



(trans) J = 13-18 cps



(Cis) J = 7-12 cps

Fig. Showing different J values for cis and trans isomers.

Q. 18. How many kinds of signals are obtained in NMR spectrum of CH_3CH_2OH and how will you distinguish primary, secondary and tertiary alcohols on basis of PMR. *(May 2007, Dec. 2006)*

Ans. Three kinds of signals are obtained in NMR spectrum of $\overset{a}{C}H_3\overset{b}{C}H_2O\overset{c}{H}$.

For *a* ; (3H) ; *b* ; (2H) ; *c* ; (1H)

$$\delta(c) > \delta(b) > \delta(a)$$

δ of 3° alcohol < δ of 2° alcohol < δ of 1° alcohol because of +I effect.

Q. 19. Which type of nuclei show NMR spectra ?

Ans. The spin quantum number of nucleus can have values 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2 etc. depending on number of neutrons and protons having parallel and antiparallel spins. The spin quantum number of nucleus is represented as I.

Number of protons	Number of neutrons	I
Even	Even	0
Odd	Odd	integer (1, 2, 3...)
Even	Odd	half integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$)
Odd	Even	half integer ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \cdots$)

Spinning of various particles in the nucleus leads to net spinning of the nucleus about an axis. Now the nucleus is a charged particle. When this charged particle spins about its axis (when $I \neq 0$ *i.e.* $I > 0$), it acts as a small magnet (nuclear magnet) and hence must have some magnetic moment.

Q. 20. How many NMR signals are observed in the spectrum of :

(*i*) CH_3COOCH_3 **(*ii*)** $CH_3—CH_2$–C$_6$H$_4$–$CH_2—CH_3$.

(*iii*) CH_3OCH_3 **(*iv*)** $CH_3CH_2CH_3$.

Ans. (*i*) Two signals

$$\overset{(a)}{CH_3}-\overset{O}{\overset{\|}{C}}-O-\overset{(b)}{CH_3}$$

(*ii*) Three signals

$$\overset{(a)}{CH_3}-\overset{(b)}{CH_2}-C_6H_4-\overset{(b)}{CH_2}-\overset{(a)}{CH_3}$$

(c) (c) above the ring; (c) (c) below the ring

(*iii*) One signal

$$\overset{(a)}{CH_3}O\overset{(a)}{CH_3}$$

(*iv*) Two signals

$$\overset{(a)}{CH_3}\overset{(b)}{CH_2}\overset{(a)}{CH_3}$$

Q. 21. What is precessional frequency ?

Ans. To understand precessional motion of nucleus let's take the example of a top. Spinning top shows the precessional motion. If we see the spinning top carefully it can observed that top show spinning around its axis and simultaneous rotating around the vertical axis. This vertical axis is actually of earth's gravitational field. This motion is called processional motion and the top is said to be precessing around the vertical axis of earth's gravitational field. This resulted because of interaction between spin and earth's

gravity acting vertically downwards. It is called gyroscopic motion. Now let's consider a magnetic nucleus ($I > 0$) *e.g.* proton, spinning in an externally applied magnetic field. It can be observed that proton precesses about the axis of external magnetic field in the same manner in which a spinning top precess under the influence of gravity.

It is known that

$w = \gamma H_0$

w = angular precessional frequency

H_0 = applied field in gauss

γ = gyroscopic ratio $= \frac{2\pi\mu}{h\,I}$

μ = magnetic moment of spin

I = spin of quantum number of spinning magnet

h = planck constant

As $w = 2\pi\nu$

So, $\gamma H_0 = 2\pi\nu$

ν = precessional frequency which may be defined as number of revolutions per second made by magnetic moment vector of the nucleus around the external field H_0.

Or It may be defined as equal to the frequency of electromagnetic radiation in megacycles/sec. necessary to induce a transition in nucleus from one spin state to another.

Q. 22. What do you understand by chemical shift ? *(Dec. 2009)*

Ans. The difference in the absorption position w.r.t. TMS signal is called chemical shift.

Chemical shift (δ) can be represented as :

$$\delta = \frac{\Delta\nu \text{ in Hz or Cps}}{\text{Operating frequency in Mega cycles/MHz}}$$

Units of δ are ppm.

where $\Delta\nu$ = difference in frequency in Cps between the absorption frequency of sample and TMS (the reference compound)

For TMS, $\delta = 0$ ppm

Chemical shift can be represented as τ (tau). It is related to δ.

$$\tau = 10 - \delta$$

Q. 23. What is the effect of presence of halogen on chemical shift of proton. Why ?.

Ans. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If deshielding is more for proton then its d value will be more.

e.g. $\overset{(b)}{CH_3}\overset{(a)}{CH_2}F$, two signals are expected for this sample molecule. One for (*a*) 2H and one for (*b*) 3H protons. As (*a*) type of protons are more near to —F, an electronegative atom having —I effect. So it will withdraw the *e* density around (*a*) type of protons towards itself. Hence (*a*) will undergo deshielding more as compare to (*b*) type of protons. The later is more distant from —F.

Q. 24. How will you verfiy that a particular signal in NMR spectrum arises from —OH, —NH, —SH groups ? ***(Dec. 2007, May 2007, Dec. 2006)***

Ans. δ of H of —OH > δ of H of — NH > δ of —SH because of the effect of electronegativity as the trend of electronegativity is O > N > S.

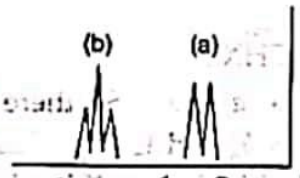
Q. 25. Indicate diagramatically the spritting of signals in NMR spectra of

(*i*) $CH_2Br - CHBr_2$ ***(Dec. 2009, 2008)***

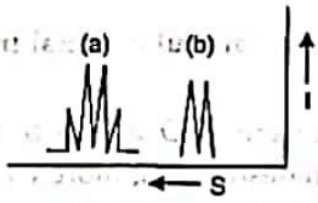
(*ii*) $CH_3 - CHBr_2$

(*iii*) $CH_3 - CH_2Br$

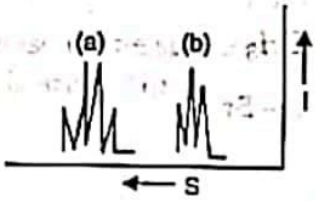
Ans. (*i*) $\overset{(a)}{CH_2Br}—\overset{(b)}{CHBr_2}$



(*ii*) $\overset{(b)}{CH_3}—\overset{(a)}{CHBr_2}$



(*iii*) $\overset{(b)}{CH_3}—\overset{(a)}{CH_2}—Br$



Q. 26. Why TMS is taken as standard for measuring chemical shift ?

(May 2010, Dec. 2008, 2007)

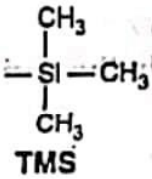
Ans. TMS is Tetramethyl silane, is taken as standard for measuring chemical shift because :

(*i*) it is chemically inert

(*ii*) It is highly volatile

(*iii*) It has max. no. of equivalent protons

(*iv*) Silicon being electropositive in nature, results in shielding (Max.)



TMS

Q. 27. What is the effect of presence of a halogen on the chemical shift of alkene ?

Ans. Shielding and deshielding effects of halogens in case of an alkene :

e.g. $\overset{a}{H_2}C=\overset{a}{CH_2}$. In this case one type of four protons are present. So all the four protons will show one signal.

In presence of halogen, $\overset{(b)}{H_2}C=\overset{(a)}{CH}X$;

There are two types of protons *i.e.* *a* and *b*. So there will be two signals in NMR spectrum of haloalkene. Such that $\delta_a > \delta_b$ and $I_b > I_a$. This is so because of presence of halogen near proton of a type cause deshielding as X is a halogen and is electronegative in nature. So it tries to attract the e^- density around proton towards itself causing deshielding of the proton. Deshielding leads to downfield shift *i.e.* high value of δ. This attributes to $\delta(a) > \delta(b)$. As the no. of protons responsible for (*b*) signal is greater than (*a*) so $I_{(b)} > I_{(a)}$.

Q. 28. How will you verify that a particular signal in NMR spectrum arises from —OH, —NH or —SH groups ?

Ans. The electronegativity pattern is O > N > S. So proton attached to more electronegative atom will suffer from deshielding more which will result into downfield shift so higher value of chemical shift. Hence δ for H of –OH group > δ for H of —NH group > δ for H of — SH group.

Q. 29. The ^{1}HNMR spectrum of C_4H_9Br consists of a single line. What could be its structure ? ***(May 2011)***

Ans. Its structure may be $CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br$.

Because all the (9H) nine protons are equivalent.

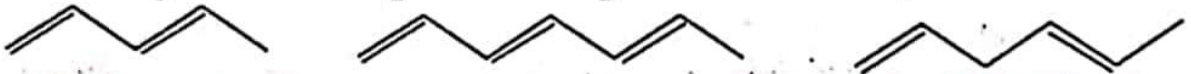
Q. 30. Match each absorption band with the following groups :

Functional goup	$>C=O$	$-\overset{|}{N}-H$	$-O-H$	$-C\equiv C-$
$\bar{v}$ cm^{-1}	3400	2050	1700	3350

Ans. *(May 2011)*

$>C=O$	1700
$-\overset{|}{N}-H$	3350
$-O-H$	3400
$-C\equiv C-$	2050

Q. 31. Arrange the following in increasing order of UV absorption maxima.



(Dec. 2011)

Ans.

Q. 32. Cause of chemical shift in NMR. *(Dec. 2009)*

Ans. Cause of chemical shift in NMR :

Chemical shift is caused by shielding and deshielding of protons. When the protons in a molecule are shielded, net magnetic field experienced by protons is less than applied magnetic field (H_0). So more magnetic field is required to being these proton in resonance with radio frequency. This shift in the magnetic field to higher side is called upfield shift. Likewise presence of electronegative gp/atom in the molecule decreases the e density around the protons of the molecule. So protons get deshielded *i.e.* magnetic field experienced by protons is more than H_0. So less magnetic field is required to bring these protons in resonance with radio frequency. This shift in the magnetic field towards lower side is called down field shift.

Q. 33. What is the difference between allowed and forbidden transition ? *(May 2012)*

Ans. Forbidden transitions are the transitions which are not allowed according to selection rule but still takes place *e.g.* $\pi \rightarrow \sigma^*, \sigma \rightarrow \pi^*$. The signal for the forbidden transitions are very weak and not intense in the spectrum whereas for an allowed transitions, *e.g.* $\pi \rightarrow \pi^*, n \rightarrow \pi^*$ etc. The signals are sharp and intense in the UV – vis spectrum.

Q. 34. What is the range of peak identification region in IR spectrum ? *(May 2012)*

Ans. The peak identification region in IR wavelength range is $0.8\mu - 200\mu$. It is further divided into three regions :

Near IR region = 0.8 – 2.5μ

IR region = 2.5 – 15μ

Far IR region = 15 – 200μ.

Q. 35. Sharp peaks are seldom observed in UV spectrum. Explain. *(May 2012)*

Ans. Because in UV – vis range, the electronic transitions take place *i.e.* every electronic change is accompanied by vibrational and rotational change as well. This is so because in a molecule every electronic band consists of vibrational levels and each vibrational level consists of rotational levels.

Q. 36. Give the possible electronic excitations for : *(May 2012)*

(*i*) $CH_2CH{=}CH_2$ (*ii*) CH_3CHO

Ans. (*i*) $CH_2{-}CH{=}CH_2$

(*a*) $\sigma \rightarrow \sigma^*$

(*b*) $\pi \rightarrow \pi^*$

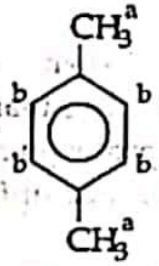
(*ii*) $CH_3{-}\overset{\overset{O}{\|}}{C}{-}H$

(*a*) $\sigma \rightarrow \sigma^*$ (*c*) $n \rightarrow \sigma^*$

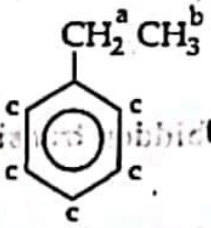
(*b*) $\pi \rightarrow \pi^*$ (*d*) $n \rightarrow \sigma^*$

Q. 37. How ^1H NMR can be used to distinguish *p*-$CH_3C_6H_4CH_3$ from $C_2H_5C_6H_5$? *(May 2012)*

Ans.



Two signals will be observed. There are two sets of protons.



In case of three signals will be observed.

There are three different sets of protons :

a(2H)

b(3H)

c(5H)

Hence *p* – $CH_3C_6H_4CH_3$ can be distinguished from $C_2H_5C_6H_5$.

Q. 38.Hydrogen chloride can undergo stretching vibration only, while carbon dioxide can undergo stretching and bending vibrations. Explain. ***(Dec. 2011)***

Ans. HCl can undergo stretching vibration only because it is a diatomic molecule whereas CO_2 is a polyatomic molecule so it will undergo both stretching and bending vibrations.

Q. 39. Discuss the principle of UV/Visible spectroscopy. ***(Dec. 2011)***

Ans. Principle of UV/visible spectroscopy : when an electromagnetic radiation in UV-region (100-400 nm) or visible region (400-750 nm) is made to pass through a compound having multiple bonds in its structure, it is observed that a part of incident radiation is absorbed. This results into transition of valence electrons. As σ electrons are held tightly and very high energy is required for the excitation of σ electrons, so it is outside the range of usual spectrophotometer.

LAQ Long Answer Type Questions

Q. 1. Explain a UV-vis double beam spectrophotometer.

Ans.

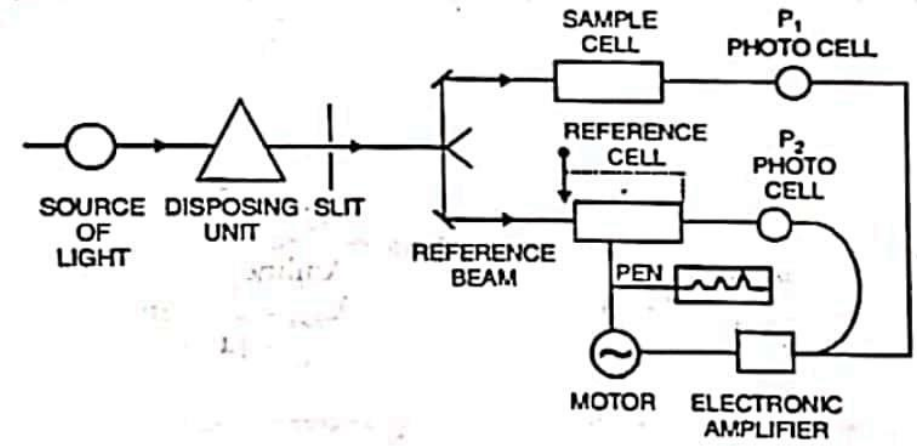


Fig. Double Beam Spectrophotometer

The incident radiation is dispersed with help of rotating prism. Different wavelengths of the light are separated by prism and then selected by slits such that rotation of prism cause series of continuously increasing wavelengths to pass through the slits. The selected beam is monochromatic which is divided into two beams of equal intensity.

One beam of monochromatic light is passed through sample cell having sample dissolved in a suitable solvent and other beam is passed through the reference cell having only solvent (same as in which sample is dissolved). Each absorbance/transmittance measurement on the sample is accompanied by a simultaneous measurement on the pure solvent. The intensity of the respective tamsmitted beams are then compared over the

whole wavelength range of instrument. (The spectrophotometer electronically substracts the absorption of solvent in reference beam from the absortion of the sample). Hence the effects due to absorption of light by the solvent are minimised. In this way, the absorbance or transmittance characteristic of the compound alone can be measured. The signal for the intensity of absorbance versus corresponding wavelength is automatically recorded on the graph. The spectrum is usually plotted as A (absorbance) against l (wavelength). When light actually passes through sample, it absorbs light and intensity of light is lowered. The photocells P_1 and P_2 will receive a weak beam from sample cell and an intense beam from reference cell respectively. This results into generation of alternating current which flows from photoelectric cells to amplifier. The amplifier is connected to a servomotor which in turn is connected to Pen-recorder. Thus it records the absorption bands automatically.

Q. 2. Explain absorption and Intensity shifts. ***(May 2007, Dec. 2006)***

Ans. Absorption and Intensity Shifts :

(*a*) Bathochromic Effect/Red Shift : It is the effect by virtue of which the absorption maximum is shifted towards longer wavelength due to presence of an auxochrome or by change of solvent. This shift is called Red Shift.

Factors Causing Bathochronic Effect

(*i*) Presence of auxochrome

Benzene shows λ_{max} at 255 nm whereas aniline shows absorption at 280 nm.

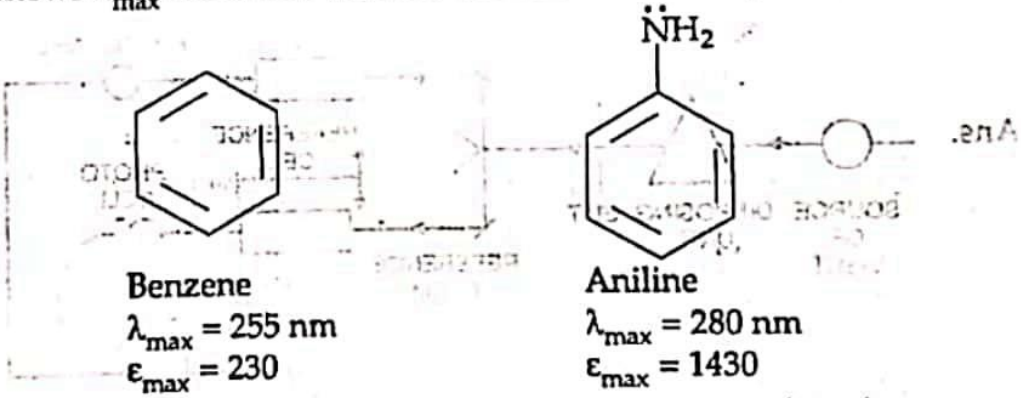


Fig. showing effect of auxochrome (—$\ddot{N}H_2$) on chromophore 

Benzene is a chromophore whereas —$\ddot{N}H_2$ group is an auxochrome, which when gets attached to benzene, it forms aniline *i.e.* a new chromophore where *n* electrons on N of —$\ddot{N}H_2$ group will enter into conjugation with the chromotophore and hence extends the conjugation with π electrons of benzene. This results into increase in absorption maxima (λ_{max}). This is so because extended conjugation reduces energy difference between the ground state and the excited states. This results into shift of absorption to longer wavelength with simultaneous increase in intensity of the absorption band.

Effect of Addition of Auxochrome to Chromophore can be summarized as :

Chromophore (with πe) (or with n and πe) λ_{max} of chromophore + Auxochrome (having n electrons) ⟶ New Chromophore

(ii) Nature of solvent

$\pi \rightarrow \pi^*$ transitions

If we consider the π electrons of the carbonyl group, the ground state is less polar and excited state is more polar. So, more dipole-dipole interactions of the sample with solvent will take place in the excited state and hence it will lead to decrease in energy of the excited state *i.e.* π^*.

So less energy is required for the $\pi \rightarrow \pi^*$ transitions and hence higher λ value is absorbed.

If the polarity of the solvent is increased, it will lead to decrease in energy of π^* molecular orbital and hence will raise the λ_{max} value.

Conclusion. With the increase in polarity of the solvent, the $\pi \rightarrow \pi^*$ of the carbonyl group will show higher value of λ_{max} and $n \rightarrow \pi^*$ transition will show absorption at lower value of λ_{max}.

(iii) Extention in conjugation

In an alkene the most probable transition occurs from $\pi \rightarrow \pi^*$ at 170-190 nm.

In the case of conjugated diene there are two π bonds as shown.

$CH_2 = CH_2$	$CH_2 = CH—CH = CH_2$
Ethene	Butadiene
(an alkene)	(conjugated diene)

In case of butadiene as there are two π bonds, the π orbitals of separate alkene groups combine to form new orbitals *i.e.* two molecular orbitals π_1 and π_2 (where $\pi_1 = \pi + \pi$ and $\pi_2 = \pi - \pi$) and two antibonding molecular orbitals π_3^* and π_4^* (where $\pi_3^* = \pi^* + \pi^*$ and $\pi_4^* = \pi^* - \pi^*$). Thus, the energy difference between HOMO and LUMO decreases. How ?

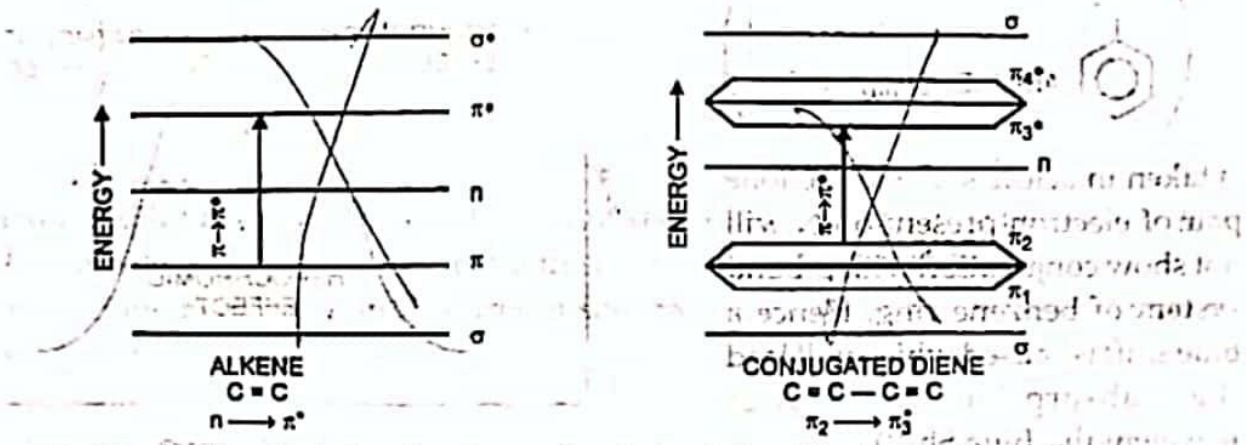


Fig. showing the effect of conjugation on the electronic transition in conjugated diene

As butadiene has four π electrons, these four π electrons will occupy the ground state *i.e.* π_1 and π_2. On absorption of energy the excitation of π electrons will take place from HOMO to LUMO. HOMO is π_2 as Energy of π_2 is more that of π_1. LUMO is π_3^* because out of two unoccupied molecular orbitals π_3^* is of lower energy hence it will be lowest unoccupied molecular orbital. Hence HOMO to LUMO transition results into $\pi_2 \rightarrow \pi_3^*$ transition.

Thus, energy difference between HOMO and LUMO ($\pi_2 \rightarrow \pi_3^*$) decreases as compare to that in case of alkene, where energy difference between π and π^* is more. Because HOMO and LUMO for ethene are π and π^* respectively. As it is clear from the figure that ΔE for HOMO to LUMO transition for ethene is more than for butadiene.

i.e. why absorption bond for butadiene appears at 217 nm while for ethene at 170-190 nm.

As the extent of conjugation increases, the energy difference between HOMO and LUMO decreases and absorption wavelength increases. So it can be interpreted that the wavelength of absorption increases with increase in conjugation.

(*b*) Hypsochromic Effect or Shift/Blue Shift

It is the effect by virtue of which the absorption maxima is shifted towards the shorter wavelength. This is called **Blue shift.** Removal of conjugation or changes in polarity of the solvent, are the two factors responsible for blue shift :

1. Removal of Conjugation

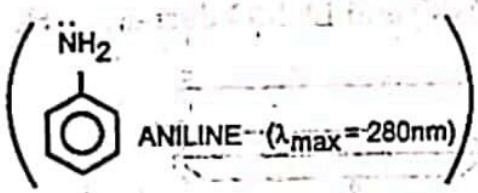
Butadiene shows absorption maxima at 270 nm but ethene shows at 180-190 nm. This blue shift in ethene is because of removal of conjugation.

$CH_2 = CH_2$ $\qquad\qquad$ $CH_2 = CH - CH = CH_2$

Ethene $\qquad\qquad$ Butadiene

2. Polarity of Solvent

If aniline



is taken in acidic solvent, the lone pair of electron present on N will not show conjugation with p-bond system of benzene ring. Hence a blue shift is caused which will lead the absorption to lower wavelength. (Blue Shift)

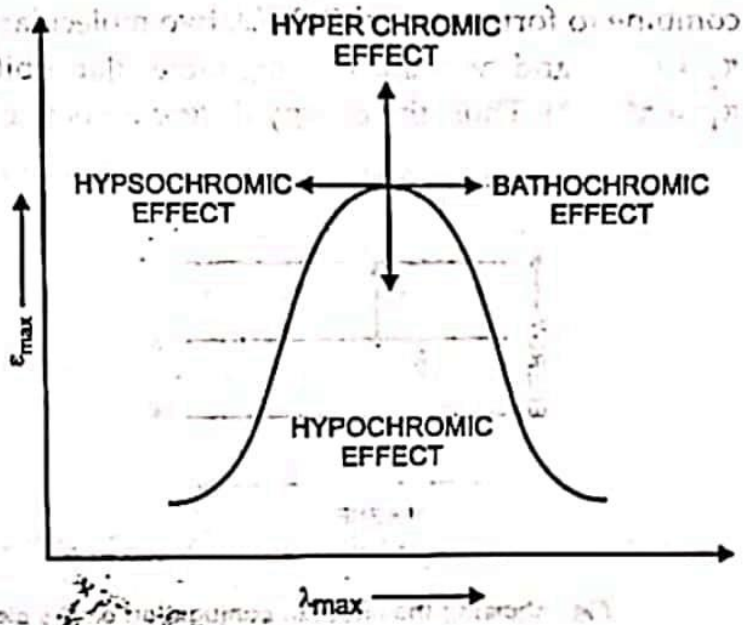


Fig. Showing Absorption and Intensity Shifts

The *n* electrons on N in aniline, if taken in acidic solvent will form a bond with H^+ from solvent and will form $C_6H_5\overset{\oplus}{N}H_3$ and hence no longer available for extension of conjugation.

3. Hyperchromic Effect or Shift : It is the effect by virtue of which intensity of the absorption maximum increases. Introduction of an auxochrome increases the value of the intensity of the wavelength absorbed.

4. Hypochromic Effect or Shift : It is the effect by virtue of which the intensity of the absorption maxima decreases. This effect or shift is called Hypochromic effect or shift. The introduction of the group which distort the geometry of the molecule course hypochromic effect. For example ε_{max}/intensity for biphenyl and 2-methyl biphenyl is 19000 and 10250 respectively. The substitution of methyl group in biphenyl cause hypochromic shift due to distortion caused by it.

Q. 3. On the basis of IR spectroscopy, how can you distinguish among 1-hexyne, 1-hexene and hexane.

Ans. The vibrational frequency is given by :

$$\nu = \frac{1}{2}\sqrt{\frac{K}{\mu}}$$

K = Force constant

μ = reduced mass

Value of force constant increases with the strength of bond *i.e.* Single, double and triple bond. Stronger the bond, more is the value of force constant.

From the formula

$$\nu \propto \sqrt{K}$$

Therefore the vibrational frequency will be maximum for triple bond and minimum for single bond.

Hence the order of vibrational frequency will be :

$$\nu_{hexyne} > \nu_{hexene} > \nu_{hexane}$$

Q. 4. Explain intensities and line widths in the spectra. ***(May 2010)***

Ans. Widths and Intensities of the Spectral Lines : In the spectras, the spectral lines or different signals are not sharp but these have some finite width. In any molecular spectroscopy, the two important features of spectral lines are : (*i*) How sharp/broad are the lines *i.e.* line width. (*ii*) How strong is the line *i.e.* intensity of line.

$$\mu = \frac{(1.673\times10^{-27}\ \text{Kg})\times(5.895\times10^{-26}\ \text{Kg})}{1.673\times10^{-27}\ \text{Kg} + 5.895\times10^{-26}\ \text{Kg}}$$

$$= 1.627\times10^{-27}\ \text{Kg}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad \therefore 4\nu^2\pi^2\times\mu = K$$

$$= 4\times(8.667\times10^{13}\ \text{sec}^{-1})^2\times3.14\times1.627\times10^{-27}\ \text{kg}$$

$$= 483.1\ \text{Kg sec}^{-2}$$

$$= 483.1\ \text{N/m}$$

Q. 6. How can one establish whether a carbonyl group is part of aldehyde, ester or ketone, by using IR spectroscopy.

Ans. $CH_3-\overset{\overset{O}{\|}}{C}-H$ (Aldehyde) $\quad CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$ (Ester) $\quad CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (Ketone)

In aldehyde one methyl group atttached to carbonyl group has +I effect, whereas +I effect is more in ketone than aldehyde as in ketone two methyl groups are attached to carbonyl group. Due to electron releasing inductive effect of methyl group, the value of K decreases hence $\bar{\nu}$ at which carbonyl group will show absorption will be less in ketone as compare to aldehyde.

But in case of ester, $-OCH_3$ (–I effect) group is attached to carbonyl group on one side and $-CH_3$ (+I effect) group is attached on the other side. Hence the value of $\bar{\nu}$ at which carbonyl group will show absorption will be least.

$$\bar{\nu}_{ester} > \bar{\nu}_{aldehyde} > \bar{\nu}_{ketone}$$

Q. 7. Explain different electronic transitions possible in sample molecules.

(May 2010, Dec. 2008, May 2008)

Ans. 1. $\sigma \rightarrow \sigma^*$

It is a high energy process, since σ bonds are very strong. The organic compound in which all the valence shell electrons are σ electrons do not show absorption in the normal U.V. region *i.e.* 180-400 nm *e.g.* of $\sigma \rightarrow \sigma^*$ is methane *i.e.* a saturated hydrocarbon.

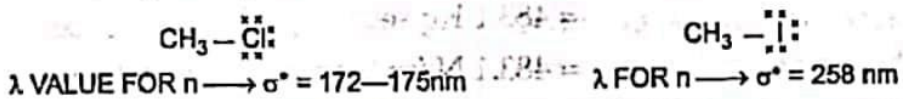
This transition require high energy *i.e.* short wavelength. The usual spectroscopic technique cannot be used below 200 nm since oxygen present in air begins to absorb strongly in this region. To study such a transition the entire path length must be evacuated. The region below 200 nm is called vacuum U.V. region. This region is less informative.

2. $n \rightarrow \sigma^*$

This type of transition takes place in saturated hydrocarbons having one hetero atom with lone pair of electrons *e.g.* halides, alcohols, ethers, amines etc.

$n \rightarrow \sigma^*$ transitions require less energy than $\sigma \rightarrow \sigma^*$ transitions but majority of compounds in this class show no absorption in the near U.V. region.

Effect of the size of Halogen Atom : In saturated alkyl halides **energy requirement for $n \rightarrow \sigma^*$ transition decrease with increase in size of the halogen atom** because it leads to decrease in electronegativity.



Due to more electronegativity of Cl than I *n* electrons of Cl are difficult and excite hence more energy or shorter wavelength is required.

Similarly amines absorb at higher wavelength as compare to alcohol.

Effect of H bonding : Alcohols and amines can show H-bonding with the solvent molecules. This takes place due to presence of lone pair of electrons on heteroatoms. As *n* electrons of the sample molecule are involved in hydrogen bonding, more energy is required for their transistion to higher energy molecular orbital. Hence **H-bonding shifts the ultra-violet absorptions to shorter wavelength.**

3. $\pi \rightarrow \pi^*$ transistions

Unsaturated molecules show this type of transition. For example alkene, alkyne, carbonyl compounds, aromatics etc. This transition requires still less energy as compared to $n \rightarrow \sigma^*$ transition and hence absorption of longer wavelength takes place. Absorption occur within the range of ultraviolet spectrophotometer.

4. $n \rightarrow \pi^*$ transitions

An electron of unshared electron pair on the hetero atom get excited to π^* orbital. This type of transition require least amount of energy and hence absorption of highest value of λ takes place. Examples of the molecules showing $n \rightarrow \pi^*$ transitions are carbonyls *i.e.* Aldehydes, Ketones, Carboxylic acids, Esters etc.

Saturated aldehydes show both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions at around 290 nm and 180 nm respectively. Absorption occuring at smaller wavelength is usually intense. Extinction coefficient of $n \rightarrow \pi^*$ is quite low as compare to $\pi \rightarrow \pi^*$. In addition to these two, $n \rightarrow \sigma^*$ transition also takes place in case of carbonyl compounds.

It can be summed up as that in carbonyl compounds two types of transition [(*i*) and (*ii*)] take place.

(*i*) High Energy Transitions, which include $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions. The signal for both the transitions are intense.

(*ii*) **Low Energy Transitions.** $n \rightarrow \pi^*$ transition requires less energy and signal is a weak bond.

Q. 8. (*a*) How size of halogen atom and H-bonding effects $n \rightarrow \sigma^*$ transitions.

(*b*) Benzene shows absorption at 255 nm while aniline shows absorption at 280 nm. Why ?

Ans. (*a*) n–σ^* transition : This type of transition takes place in saturated hydrocarbons having one hetero atom with lone pair of electrons *e.g.* halides, alcohols, ethers, amines etc.

$n \rightarrow \sigma^*$ transitions require less energy than $\sigma \rightarrow \sigma^*$ transitions but majority of compounds in this class show no absorption in the near U.V. region.

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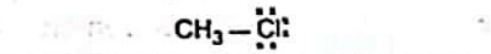
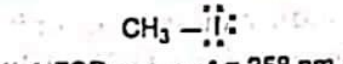




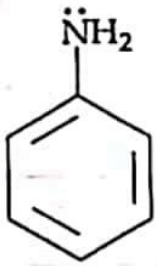
Due to more electronegativity of Cl than I n electrons of Cl are difficult and excite hence more energy or shorter wavelength is required.

Similarly amines absorb at higher wavelength as compare to alcohol.

Effect of H bonding : Alcohols and amines can show H-bonding with the solvent molecules. This takes place due to presence of lone pair of electrons on heteroatoms. As n electrons of the sample molecule are involved in hydrogen bonding, more energy is required for their transistion to higher energy molecular orbital. Hence **H-bonding shifts the ultra-violet absorptions to shorter wavelength.**

(*b*) benzene shows λ_{max} at 255 nm whereas aniline shows absorption at 280 nm.

Benzene
$\lambda_{max} = 255$ nm
$\varepsilon_{max} = 230$



Aniline
$\lambda_{max} = 280$ nm
$\varepsilon_{max} = 1430$

Fig. showing effect of auxochrome (—$\ddot{N}H_2$) on chromophore

Benzene is a chromophore whereas —$\ddot{N}H_2$ group is an auxochrome, which when gets attached to benzene, it forms aniline *i.e.* a new chromophore where *n* electrons on N of —$\ddot{N}H_2$ group will enter into conjugation with the chromotophore and hence extends the conjugation with π electrons of benzene. This results into increase in absorption maxima (λ_{max}). This is so because extended conjugation reduces energy difference between the ground state and the excited states. This results into shift of absorption to longer wavelength with simultaneous increase in intensity of the absorption band.

Q. 9. Butadiene (CH_2= CH—CH = CH_2) shows absorption at higher wavelength than ethene (CH_2=CH_2). Why ?

Ans. Normally the absorption of U.V. visible light results in excitation from ground state to higher energy state. The higher energy states are called high energy molecular orbital or antibonding molecular orbital. The highly probable transition on the absorption of quantized energy is from HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital).

In an alkene the most probable transition occurs from $\pi \rightarrow \pi^*$ at 170-190 nm.

In the case of conjugated diene there are two π bonds as shown.

$CH_2 = CH_2$	$CH_2 = CH—CH = CH_2$
Ethene	Butadiene
(an alkene)	(conjugated diene)

In case of butadiene as there are two π bonds, the π orbitals of separate alkene groups combine to form new orbitals *i.e.* two molecular orbitals π_1 and π_2 (where $\pi_1 = \pi + \pi$ and $\pi_2 = \pi - \pi$) and two antibonding molecular orbitals π_3^* and π_4^* (where $\pi_3^* = \pi^* + \pi^*$ and $\pi_4^* = \pi^* - \pi^*$). Thus, the energy difference between HOMO and LUMO decreases. How ?

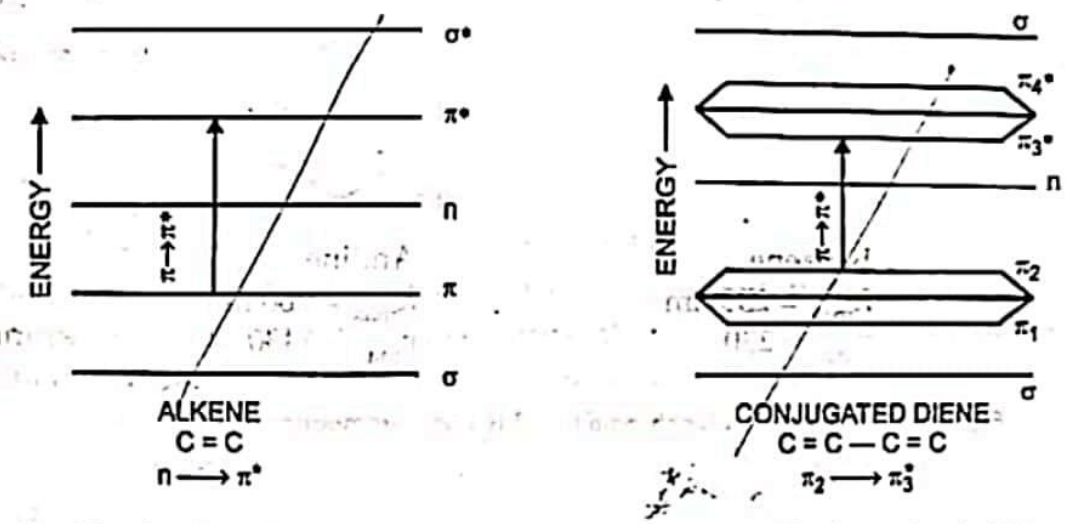


Fig. Showing the effect of conjugation on the electronic transition in conjugated diene

As butadiene has four π electrons, these four π electrons will occupy the ground state *i.e.* π_1 and π_2. On absorption of energy the excitation of π electrons will take place from HOMO to LUMO. HOMO is π_2 as Energy of π_2 is more that of π_1. LUMO is π_3^* because out of two unoccupied molecular orbitals π_3^* is of lower energy hence it will be lowest unoccupied molecular orbital. Hence HOMO to LUMO transition results into $\pi_2 \rightarrow \pi_3^*$ transition.

Thus, energy difference between HOMO and LUMO ($\pi_2 \rightarrow \pi_3^*$) decreases as compare to that in case of alkene, where energy difference between π and π* is more. Because HOMO and LUMO for ethene are π and π* respectively. As it is clear from the figure that ΔE for HOMO to LUMO transition for ethene is more than for butadiene.

i.e. why absorption bond for butadiene appears at 217 nm while for ethene at 170-190 nm.

As the extent of conjugation increases, the energy difference between HOMO and LUMO decreases and absorption wavelength increases. So it can be interpreted that the wavelength of absorption increases with increase in conjugation.

Q. 10. How Polarity of solvent effects different electronic transitions ?

Ans. Let us consider few transitions of the carbonyl group and see the effect of changing the polarity of the solvent on the absorption maxima (λ_{max}) value.

(*i*) $n \rightarrow \pi^*$ transitions

In the carbonyl compounds, if we consider *n* electrons, the ground state is more polar as compare to excited state. The hydrogen bonding with the solvent molecules takes place to less extent with the carbonyl group in the excited state and more in the ground state. Hence if polarity of the solvent is increased, the H-bonding shown by carbonyl in ground state increases. So more energy is required for $n \rightarrow \pi^*$ transition and hence the absorption moves to shorter wavelength *i.e.* blue shift or Hypsochromic effect (as explained in the next topic).

For example λ_{max} of acetone is 279 nm in hexane but 264 nm in water.

(*ii*) $\pi \rightarrow \pi^*$ transitions

If we consider the π electrons of the carbonyl group, the ground state is less polar and excited state is more polar. So, more dipole-dipole interactions of the sample with solvent will take place in the excited state and hence it will lead to decrease in energy of the excited state *i.e.* π*.

So less energy is required for the $\pi \rightarrow \pi^*$ transitions and hence higher λ value is absorbed.

If the polarity of the solvent is increased, it will lead to decrease in energy of π*

molecular orbital and hence will raise the λ_{max} value.

Conclusion. With the increase in polarity of the solvent, the $\pi \rightarrow \pi^*$ of the carbonyl group will show higher value of λ_{max} and $n \rightarrow \pi^*$ transition will show absorption at lower value of λ_{max}.

Q. 11. Explain the applications of UV-Visible spectroscopy in explaining.

(a) Extent of Conjugation ***(Dec. 2008)***

(b) Keto-enol Tautomerism

(c) Isobestic points.

Ans. (a) Extent of Conjugation : λ_{max} value increases with increase of conjugation. It is found that the absorption occurs at 420 nm if eight double bonds are present in a conjugated system. Such as alkene will appear coloured to human eye.

The following isomers can be easily distinguish :

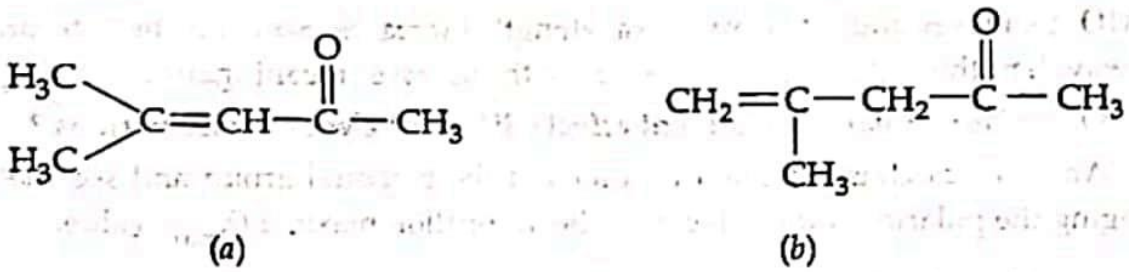


Fig. Showing conjugated (a) and non-conjugated (b) dienes.

$n \rightarrow \pi^*$ transitions for (a) will appear at longer wavelength as compared to $n \rightarrow \pi^*$ transitions for (b) because of conjugation present in (a).

A bathochromic and hyperchromic shift can be seen while comparing the spectrum of conjugated trienes and conjugated dienes.

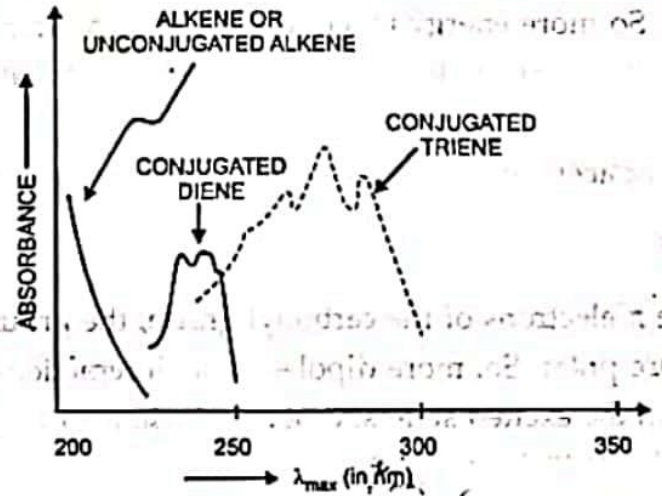


Fig. Absorption in conjugated and unconjugated systems

(b) Keto-enol Tautomerism : If a molecule exist in two tautomeric forms, preference of one over the other can be detected by U.V. spectroscopy.

2-Hydroxy pyridine $\rightleftharpoons$ 2-pyridone

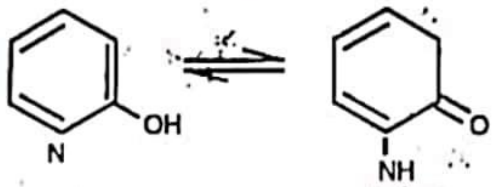


Fig. Showing tautomers

The spectra of these two compounds were found to favour 2-pyridone which is α,β-unsaturated ketone and equilibrium is shifted to right.

(c) Isobestic points : UV-Vis spectroscopy is very useful technique in establishing the identity of the new and unknown compounds. The spectrum of new compound can be compared with spectrum of the known compounds. This is called **finger printing.**

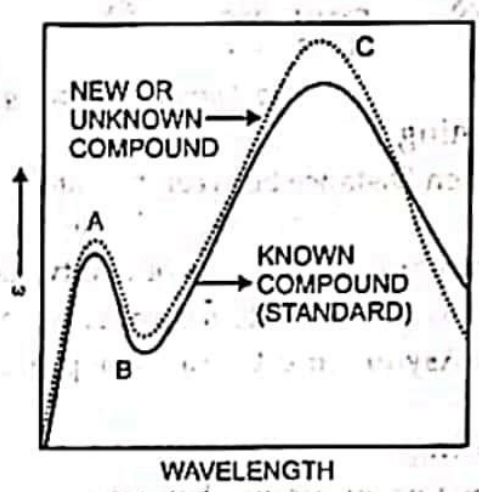


Fig. Showing Isobestic Points

The points A, B and C marked in the figure above where the λ_{max} value is same for the two compounds are called **Isobestic Points.**

Q. 12. Explain Basic Principle of IR spectroscopy. ***(May 2012, 2009)***

Ans. Absorption in IR region is because of change in vibrational and rotational levels because a single change in vibrational energy is accompanied by large no. of rotational energy changes. So, absorption of IR radiation brings predominant changes in the vibrational energy. Atoms in the molecule are not held rigidly. It can be visualized as balls tied with springs where balls are atoms and springs are bonds. To explain vibrations in molecules let us take example of AX_2 types of groups. When IR light passes through the sample, molecule shows two types of vibrations :

I. Stretching
II. Bending

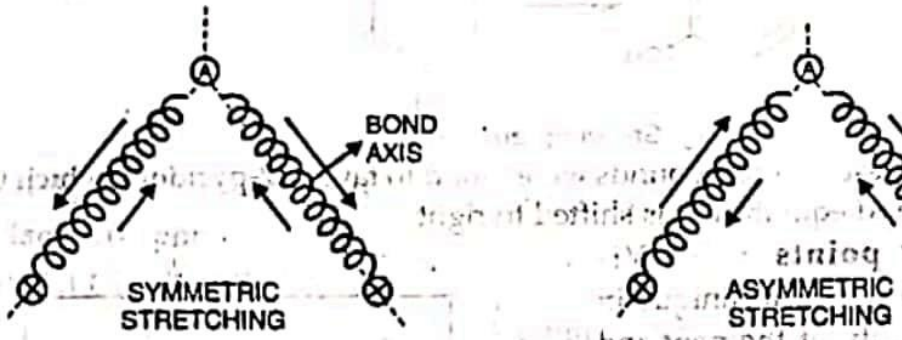


Fig. Showing Stretching vibrations in polyatonic molecule

I. Stretching

When Distance between two atoms is increasing or decreasing but atoms remain in same bond axis *i.e.* no change in the bond angle.

Stretching vibration is of two types :

(*a*) Symmetric. Movement of atoms w.r.t. particular atom is in the same direction.

(*b*) Asymmetric. One atom approaches the central atom while the other departs from it.

II. Bending

Position of atoms changes w.r.t. original bond axis *i.e.* bond angle changes but internuclear distance does not change. There are four types of bending vibrations.

(*a*) Scissoring. When two atoms approach each other.

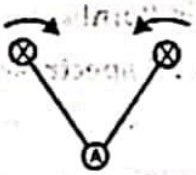


Fig. Showing Scissoring

(*b*) Rocking. When the atoms is in the same direction.

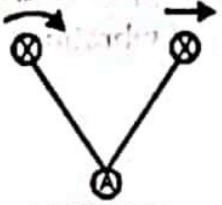


Fig. Rocking

(c) **Wagging.** When two atoms move above or below the plane w.r.t. central atom.

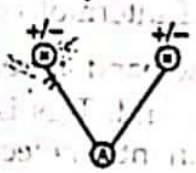


Fig. Wagging

(d) **Twisting.** One of the atom move up and other moves below the plane w.r.t. central atom.

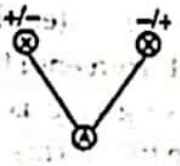


Fig. Twisting

[positive sign (+) represents motion from the page towards the reader and negative sign (–) represents motion away from the reader]

Examples of AX_2 groups are —CH_2, —NO_2, —NH_2 etc.

These vibrations are called **Fundamental vibrations.** Sometimes **overtones** also appears in addition fundamental transitions or fundamental vibrations. **Beats** are also observed sometimes which arise due to combination or difference frequencies. These are explained later in the chapter. For a particular bond, stretching vibration appears at higher frequency as compared to bending vibration hence, in the IR spectrum absorption band appearing for stretching vibration is at higher frequency as compare to band appearing for bending vibration.

Q. 13. Explain application of IR spectroscopy in :

(i) Inter and Intra molecular H-bonding.

(ii) Keto-enol Tautomerism.

(iii) Detection of Conjugation. ***(Dec. 2010)***

Ans. (i) Inter and Intra molecular H-bonding. Infrared technique is used to distinguish between two types of H-bonds *i.e.* intermolecular and intra molecular H-bond. H-bond result into (*i*) shift of $\bar{v}$ for the O—H bond, towards lower value. (*ii*) Intermolecular H-Bond results into formation of a broad band at lower $\bar{v}$ value and intramolecular H-Bond results into a sharp band at lower $\bar{v}$ value than the $\bar{v}$ value at which non-hydrogen bonded O—H group (free - OH group) will show its signal.

Dilution reduces the intermolecular H-bond but has no effect on intramolecular H-bond, so if the sample is analysed after the dilution and if it shows diminishing of the

band (that was at lower $\bar{v}$ value and was expected due to H-bonding), it results that band at lower $\bar{v}$ value was because of intermolecular H—bond. But if after dilution, sample does not show any effect on the band appearing at low $\bar{v}$ value, it results that band is because of intra molecular H-bond. This is so because dilution reduces inter-molecular H-bond but it has no effect on intramolecular H-bond.

(ii) Keto-enol Tautomerism : Keto-enol tautomers can be distinguished from each other by other by using IR- Spectroscopy *e.g.*

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH_2$$

(keto) (*a*) (enol) (*b*)

(*a*) form is keto form, it is different from enol form (*b*) by the fact that >C = O group is present but in case of enol, >C = O group is absent by instead, –OH group and >C = C< groups are present. Hence the two forms can be distinguished from each other.

(iii) Detection of Conjugation. It is a very useful technique in detection of conjugation. For example molecular formular of a sample molecule is C_5H_8O. Its structural formulae can be :

$$H_3C-\overset{\overset{O}{\|}}{C}-CH=CH-CH_3 \quad \text{Or} \quad CH_3-\overset{\overset{O}{\|}}{C}-CH_2=CH-CH_2$$

(*a*) (*b*)

But if the structural formulae is (*a*), there will be effect of conjugation as :-

$$CH_3-\overset{\overset{O}{\|}}{C}-CH=CH-CH_3 \longleftrightarrow CH_3-\overset{\overset{O^-}{|}}{C}=CH-\overset{\oplus}{C}H-CH_3$$

Conjugation will result into decrease in value of K *i.e.* bond constant/force constant between C and O. It will result into decrease in value of $\bar{v}$ for C = O is less than expected it means the sample molecule C_5H_8O has structural formula (*a*), Otherwise (*b*).

Q. 14. Using IR spectroscopy, how will you determine whether the oxygen in an organic compound is present as a carbonyl or hydroxyl group.

(May 2007, Dec. 2006)

Ans. $\underset{\text{Carbonyl}}{C=O}$ $\underset{\text{Hydroxyl}}{-OH}$

The value of K for carbonyl > for –OH. Hence $\bar{v}$ for $>C=O$ is more than –OH

Q. 15. Describe briefly the theory of NMR. What information can be obtained from NMR absorption peaks ?

Ans. If a proton is placed in a magnetic field then it starts precessing (at a certain frequency) [Frequencies of nuclei at the fields normally applied, lie in radio frequency

region of the electromagnetic spectrum. So, NMR is a radio frequency technique *e.g.* at 12T, protons show frequency about 500 MHz (radio frequency)]

It is capable of taking up one of the two orientation w.r.t. axis of external magnetic field

(*i*) alignment with the field and (*ii*) alignment against the field.

(*i*) means magnetic field of proton aligns with applied magnetic.

(*iv*) means magnetic field of proton aligns against the applied magnetic field.

The first state is of lower energy and second state is of higher energy.

If the proton is in lower state, it can pass to the higher state by absorbing energy, from the source of **radiowaves** ($3 \times 10^6 - 3 \times 10^{10}$ Hz).

From the higher energy state, the proton can come down to lower energy state by releasing energy. The transition from one energy state to other is called **flipping of proton.**

This transition (from lower energy state to higher energy state) can be brought about by the absorption of a quantum of electromagnetic radiation in the radiowave region with energy $h\nu$.

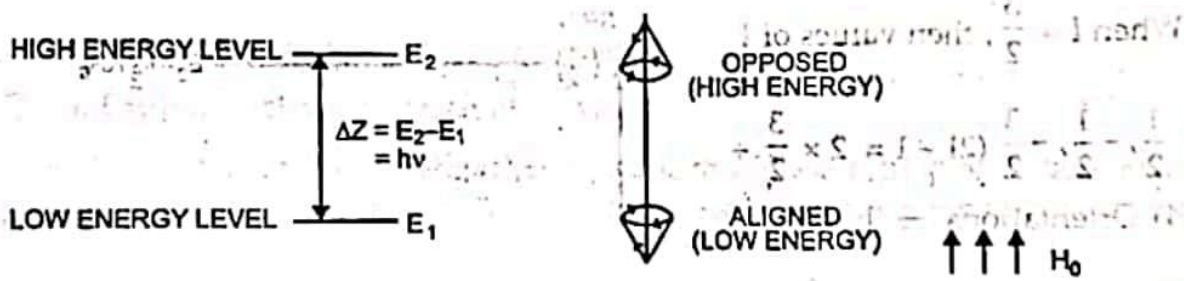


Fig. Energy level of proton

The energy (ΔE) required for the flipping of proton depends on strength of external field. Stronger the field greater the tendency of proton to remain aligned with it and higher will be frequency or energy of radiation required to flip the proton to higher energy. (The precessional frequency of the proton is directly proportional to strength of external magnetic field)

Nuclear spin is the characteristic of nucleus and is represented by spin quantum no. of the nucleus *i.e.* I. For a given magnetic nucleus, there are (2I + 1) orientations possible in the presence of externally applied magnetic field, which are represented by I′.

As nucleus behave as a magnet its magnetic moment μ can be represented as

$$\mu = g_n \mu_n I'$$

or $$\mu = KI'$$

where $$K = g_n \mu_n$$

as g_n = Lande splitting factor and

μ_n = nuclear magnetic factor

I′ can have (2I + 1), orientations or values because for a given value of I, I′ can have values from I to –I *i.e.* total 2I + 1 values. This means that keeping H_0 constant a nucleus with a spin (I) has 2I + 1 energy levels in presence of external magnetic field.

In the absence of the external magnetic field, all these orientations have same energy. But when a magnetic field of strength H is applied, each orientation corresponds to different value of Energy E.

$$E = -\mu H$$

where μ is magnetic moment of the nucleus

$$E = -g_n \mu_n I' H$$

$$E = -KI'H$$

When I = 0, I′ = 0, hence E = 0 and 2I + 1 = 1

This means that nuclei with 0 spin, show no splitting in magnetic field, means only one energy level. Hence no flipping of spin is possible.

When $I = \frac{3}{2}$, then values of I′ $= \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ (2I + 1 = $2 \times \frac{3}{2}$ + 1 = 4) Orientations ⇒ hence for energy levels of energies $-\frac{3}{2}KH$, $-\frac{1}{2}KH$, $\frac{1}{2}KH$, $\frac{3}{2}KH$.

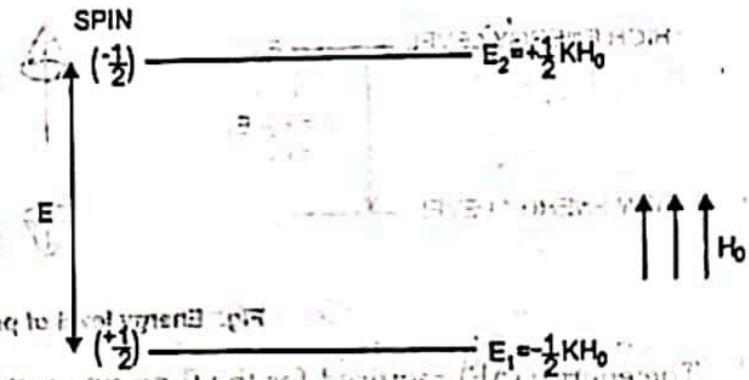


Fig. Showing lower and higher energy levels of the proton along with corresponding Spin of nucleus and energy of the states in presence of external magnetic field H_0

For the proton $I = \frac{1}{2}$ so different possible orientations for I are 2I + 1 *i.e.* $2 \times \frac{1}{2} + 1 = 2$, these are $I' = +\frac{1}{2}$ and $I' = -\frac{1}{2}$.

Energy for state $I' = +\frac{1}{2}$, E_1

$$= -\frac{1}{2} KH_0$$

and Energy for state, $I' = -\frac{1}{2}$,

$$E_2 = \frac{1}{2}KH_0$$

$$\Delta E = E_2 - E_1$$

i.e.
$$= \frac{1}{2}KH_0 - \left(-\frac{1}{2}KH_0\right)$$

$$\Delta E = \pm KH_0$$

Now we know that $\Delta E = h\nu$

$$h\nu = \pm KH_0$$

$$\nu = \frac{\pm KH_0}{h}$$

$$= \pm \frac{KH_0}{h} \; ; \text{K is constant} = g_n\mu_n$$

Here ν is precessional frequency of nucleus.

Q. 16. Explain instrumentation of NMR.

Ans. A sample under investigation is taken in a glass tube placed between two magnets. A radio frequency radiation (60 MHz) is made to fall on the sample. It can be done by feeding energy into coil wound around the sample. The spectrophotometer can work in either two ways.

(*i*) Keeping magnetic field constant and radiofrequency may be varied gradually.

(*ii*) Keeping radiofrequency constant and varying the magnetic field.

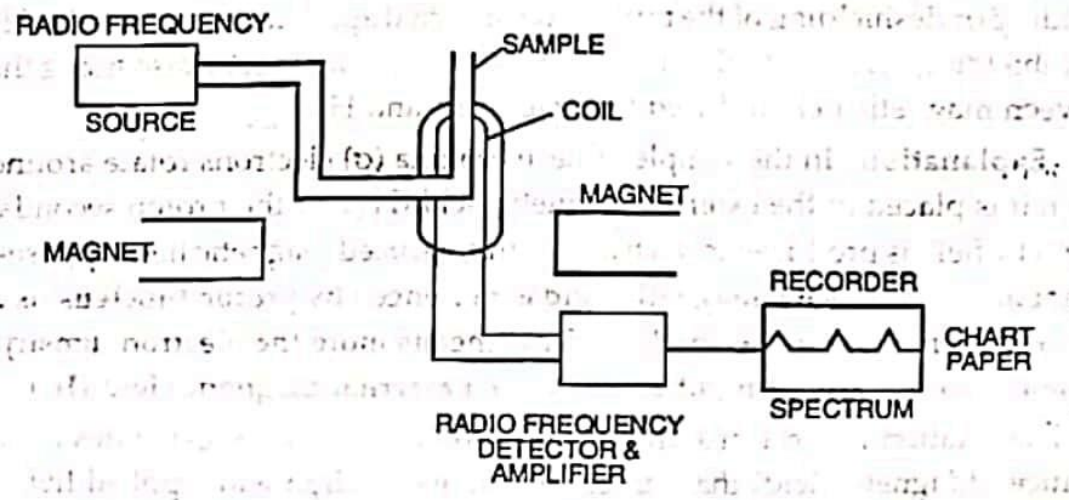


Fig. Nuclear Magnetic Resonance Spectrophotometer

For practical purposes, radiofrequency source is held steady at a said frequency (60 MHz) and field strength is varied (Two energy levels appear for the proton when it is placed in external magnetic field H_0).

As the field strength increases, the precessional frequency of each set of protons increases. Now the precessing proton will absorb energy from the radiofrequency source only if the precessing frequency is same as frequency of radiofrequency beam *i.e.* when **quantum energy hν of electromagnetic radiation is equal to the energy difference between two energy states at the field strength H_0** when this occurs nucleus and radiofrequency beam are said to be in resonance. Hence the technique is known as nuclear magnetic resonance. (In simple words, condition of strong effective coupling when the frequencies of two oscillators are identical is called **Resonance**).

Absorption of energy results into signal. Such spectrum is called **nuclear magnetic resonance spectrum.**

A precessional frequency of the other sets of protons is different from the frequency of the radiofrequency source. Magnetic field is increased further and at resonance other sets of protons also show signal at different values of H_0. Hence signals for other set of protons are also obtained on the spectrum.

Q. 17. Explain : (*i*) Shielding and deshielding of protons ***(May 2008)***

(*ii*) Chemical shift. ***(Dec. 2007, May 2007, Dec. 2006)***

Ans. (*i*) Shielding and deshielding of protons : When the sample molecule is placed in magnetic field, there is interaction between the magnetic nuclei and external magnetic field (H_0). But the (σ) electrons present in the sample molecule are also having value of magnetic moment *i.e.* electrons have spin and charge so these also behave as tiny magnets. So on applying magnetic field to the sample, there will be interaction between magnetic field of (σ) electrons and external magnetic field (H_0) also. These interactions results into shielding or deshielding of the nuclei from external applied magnetic field (H_0). Shielding or deshielding results into chemical shift. In this topic we will be discussing the interaction between magnetic field induced by σ electrons and H_0.

Explanation : In the sample molecule sigma (σ) electrons rotate around the nuclei. When it is placed in the external magnetic field (H_0). At the proton secondary/induced magnetic field is produced in such a way, this induced magnetic field opposes the applied magnetic field. Thus **net magnetic field experienced by proton (nucleus) is diminished.** Hence proton is said to be **shielded. That means more the electron density around the nucleus, more is shielding of nucleus from external magnetic field (H_0).**

The rotation of electrons around the neighboring nuclei generates a magnetic field (Induced Magnetic field) that can either oppose or align with applied field at proton. If the induced magnetic field opposes the applied field, then proton is said to be **shielded. If the induced magnetic field aligns with applied magnetic field, then net magnetic**

The MRI technique is used widely to detect physiological abnormalities and to observe metabolic processes. With functional MRI, blood flow in different regions of the brain can be detected and related to the mental activities of the patient.

X-rays are known to be dangerous on account of the ionization caused. The harm of MRI is that it cause extraction of loose fillings from teeth. Otherwise there is not any other convincing evidence of its harmfulness.

Q. 21. Explain application of NMR in H-bonding.

Ans. Proton showing hydrogen bonding absorbs at a low field *i.e.* more/high value of chemical shift as compare to a proton which is not showing hydrogen bonding. The reason for this is that if a proton shows hydrogen bonding, it is attached to highly electronegative atom. It results into depletion of electron density around the proton, which leads to deshielding and **hence high value of chemical shift.**

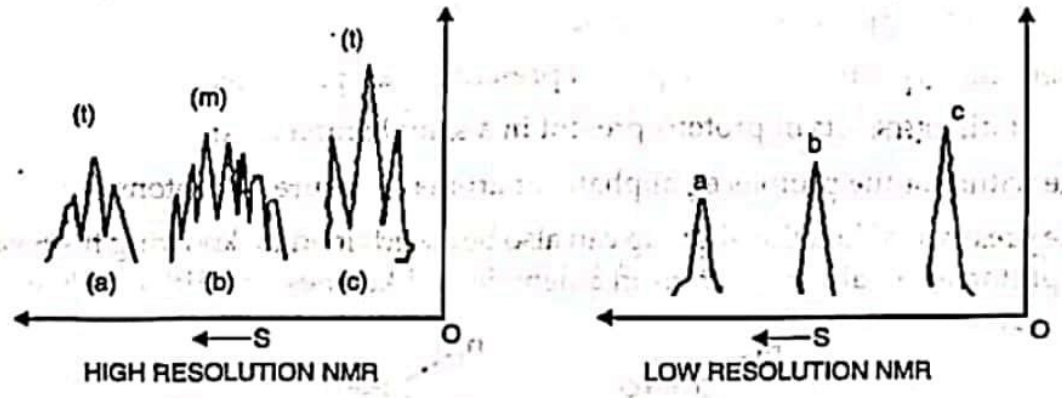
Intermolecular and intramolecular hydrogen bonding can be easily distinguished by changing the concentration of the sample. If the hydrogen bonding is intermolecular, then dilution of the sample results into decrease in the extent of hydrogen bonding. Hence the signal in NMR of proton shifts upfield whereas dilution has no effect on intramolecular hydrogen bonding.

Temperature has effect on the hydrogen bonding. With the increase in temperature, the extent of hydrogen bonding falls. Thus, signals in NMR appears at smaller δ value for H nuclei showing hydrogen bonding, at high temperatures.

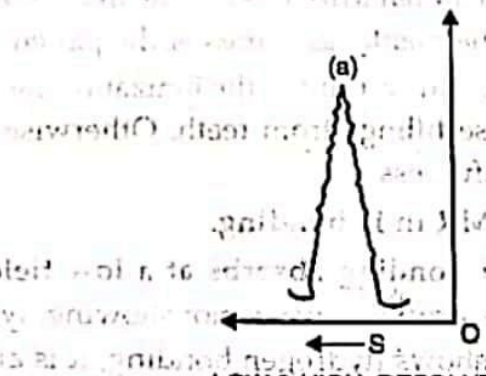
Q. 22. Draw low and high resolution NMR of :

(*i*) $CH_3CH_2\ CHCl_3$ **(*ii*)** $CH_3CCl_2CH_3$ **(*iii*)** $CH_2(CH_2Cl)_2$

Ans. (*i*) $CH_3CH_2\ CHCl_3$

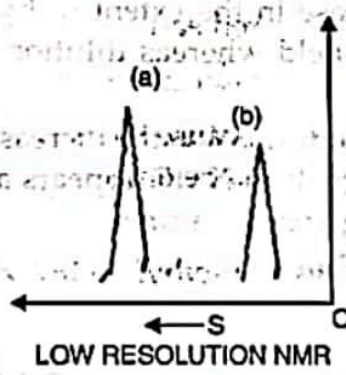


(*ii*) $CH_3CCl_2CH_3$

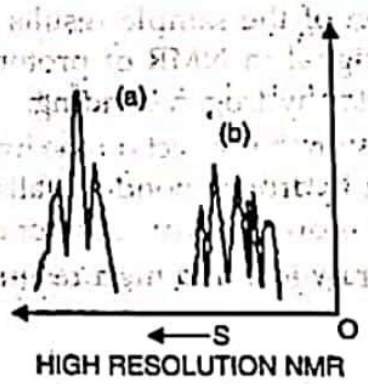


LOW & HIGH RESOLUTION NMR

(*iii*) $CH_2(CH_2Cl)_2$



LOW RESOLUTION NMR



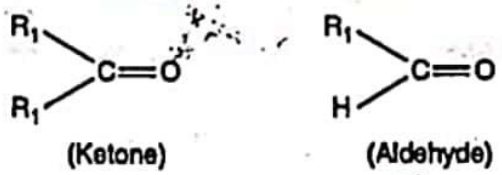
HIGH RESOLUTION NMR

Q. 23. (*a*) Give brief account on significance of the chemical shift in NMR.

(*b*) Why TMS is taken as a standard for measuring chemical shift ? Can we take tetra ethyl silane as a standard ?

Ans. (*a*) Significance of chemical shift : Chemical shift gives us brief inset of the structural aspect of sample molecules such as :

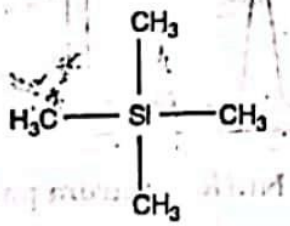
1. Chemical environment of the proton present in sample molecular.
2. No. of different sets of protons present in a sample molecular.
3. The nature of the protons eg aliphatic or aromatic nature of protons.
4. The presence of functional group can also be ascertained by knowing the S value of proton eg S value of protons in aldehyde and ketones are different like :



(Ketone) (Aldehyde)

S value of protons of alkyl group (R_1) is different from S value of proton and aldehyle.

(*b*) TMS is tatramethyl silane.



It is used as standard for the following reasons :

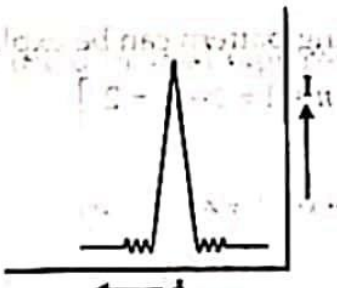
1. All the twelve protons are equivalent.
2. Due to low value of electronegativity of si, the shielding effect is maximum. So maximum value of magnetic field is required to bring the absorption of energy of motion ofthis So S = 0.
3. TMS is miscible with all organic solvents.
4. It is highly volatile. So the sample is recovered easily.
5. It does not take part in any intermolecular association with sample.

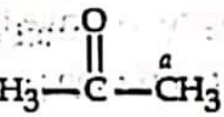
No we can't use tetraethyl silane as standard, because it has two sets of protons and hence two signals with different splitting pattern will be obtained, so it won't be easy to measure S for the sample.

Q. 24. Explain the NMR spectrum of acetone, methyl alohol and benzene.

(May 2008)

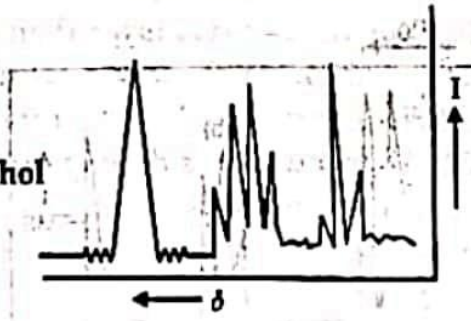
Ans. (*i*) **Acetone**

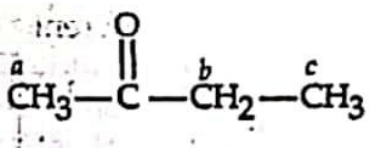




No. of Protons	Signal
a (6H)	= singlet

(*ii*) **Methyl alcohol**

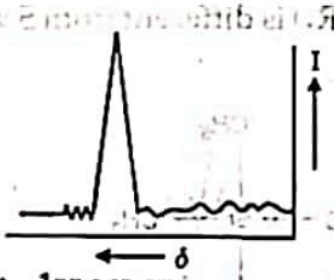




No. of Protons	Signal
a (3H)	singlet
b (2H)	quarlet
c (3H)	triplet

$\delta(a) > \delta(b) > \delta(c)$

(iii) Benzene



No. of Protons Signal
a (6H) = 1 singlet

Q. 25. Draw and explain ^1H NMR spectrum pattern for $Cl_2CH–CHCl-CHCl_2$. *(Dec. 2011)*

Ans. $Cl_2-\overset{a}{C}H-\overset{b}{C}HCl-\overset{a}{C}HCl_2$

There are two sets of protons

a (2H)

b (1H)

So there will be two signals and intensity for signal (*a*) will be more than (*b*)

i.e. $I_{(a)} > I_{(b)}$ ...(1)

The electronegative effect on (*a*) set of protons will be more than on (b) so for this reason deshielding effect will be experienced by (*a*) set of protons more than on (b). Deshielding effect results into down field shift so less value of external magnetic field is required by the (*a*). Set of protons to show flipping hence high value of chemical shift will be shown

i.e. $\delta_a > \delta_b$ ...(2)

According to $n+1$ rule the splitting pattern can be explanined as :

For (*a*) set of proton : $n+1=1+1=2$

So a doublet appears for (*a*) and

For (*b*) set of protons $= n+1=2+1=3$ ...(3)

So a triplet appears for (*b*)

On combining results as shown in (1), (2) and (3)