

Chapter - 7

Spectroscopy

INTRODUCTION

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. All different forms of electromagnetic radiations travel at the same velocity but characteristically differ each other in terms of frequencies and wave length. (Table 1)

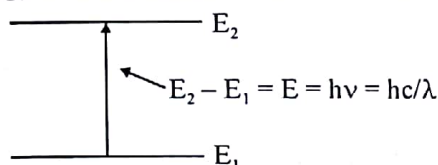
Table 1: The Electromagnetic Spectrum

Radiation type	Wavelength λ , (Å)	Frequency $\nu = c/\lambda$ (Hz)	Application
Radio	10^{14}	3×10^4	
Nuclear magnetic Resonance	10^{12}	3×10^6	Spin orientation
Television	10^{10}	3×10^8	
Radar	10^8	3×10^{10}	
Microwave	10^7	3×10^{11}	Rotational
Far infrared	10^6	3×10^{12}	Vibrational
Near infrared	10^4	3×10^{14}	
Visible	$8 \times 10^3 - 4 \times 10^3$	$3.7 \times 10^{14} - 7.5 \times 10^{14}$	
Ultraviolet	3×10^3	1×10^{15}	Electronic
X-rays	1	3×10^{18}	
Gamma rays	10^{-2}	3×10^{20}	Nuclear transition
Cosmic rays	10^{-4}	3×10^{22}	

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important.

Absorption of Different Electromagnetic Radiations by Organic Molecules

In absorption, through the mechanism of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy (E_1) to state of higher energy (E_2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.



Energy transition for any electromagnetic radiation

Since $E = h\nu = hc/\lambda$, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiation to ultraviolet regions to infrared region and then radio frequencies, as we move gradually to the lower frequency region.

Ultraviolet-Visible Spectroscopy: (λ 200 - 800 nm) studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from π or non-bonding orbitals. It commonly provides the knowledge about π -electron systems, conjugated unsaturations, aromatic compounds & conjugated non-bonding electron system etc.

Infrared Spectroscopy: ($\bar{\nu}$ 400 - 4000 cm^{-1}) studies the changes in the vibrational and rotational movements of the molecule. It is commonly used to show the presence or absence of functional group which have the specific vibration frequencies viz C = O, NH_2 , OH, CH, C - O etc.

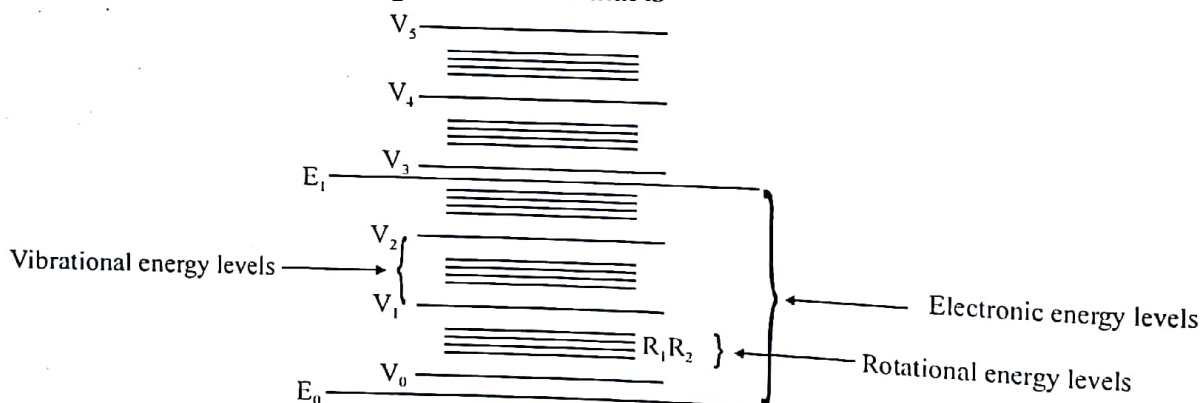
Nuclear Magnetic Resonance: (radio frequency ν 60 - 600 MHz) provides the information about changes in magnetic properties of certain atomic nuclei. ^1H and ^{13}C are the most commonly studied nuclei for their different environments and provide different signals for magnetically non-equivalent nuclei of the same atom present in the same molecule.

ULTRAVIOLET-VISIBLE SPECTROSCOPY

1. Introduction

Ultraviolet-visible spectroscopy (electronic spectroscopy) involves the spectroscopy of photons (spectrophotometry) which uses light in the visible, and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. The absorption of radiation in the UV-Visible radiation by a molecule leads to the transitions amongst different electronic levels of the molecule. The absorption of radiation in the UV-Visible region of the spectrum is dependent on the electronic structure of the absorbing species like, atoms, molecules, ions or complexes. It forms the basis of analysis of different substances such as inorganic, organic and biochemical. UV-Visible spectroscopy is of most use for identifying conjugated systems which tend to have strong absorptions.

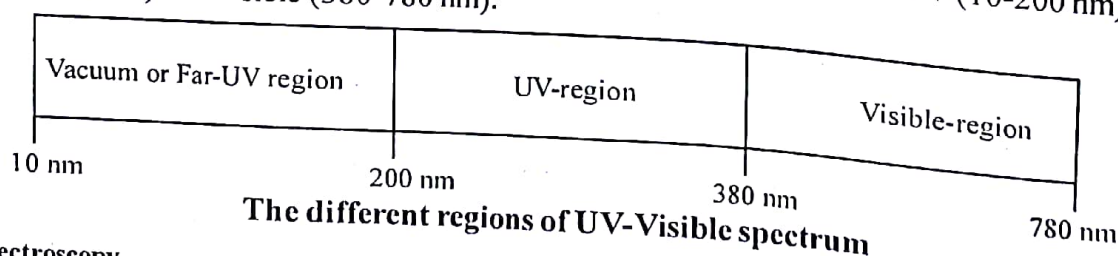
Electronic spectra arise from transitions between electronic energy levels accompanied by changes in both vibrational and rotational states. At room temperature, the majority of the molecules are in the lowest vibrational state of the lowest electronic energy level, (the ground state). When continuous radiation is passed through a transparent material, a portion of the radiation may be absorbed. As a result of absorption molecules or atoms pass from a state of low energy (ground state) to high energy (excited state). The electromagnetic radiation that is



absorbed this energy exactly equal to the energy difference between the excited and ground state. Due to the absorption of electromagnetic radiation in ultraviolet-visible region, the transitions take place between different electronic energy levels. As a rule energetically favoured electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and the resulting species is called an excited state.

2. Different regions of Ultraviolet-Visible Spectroscopy

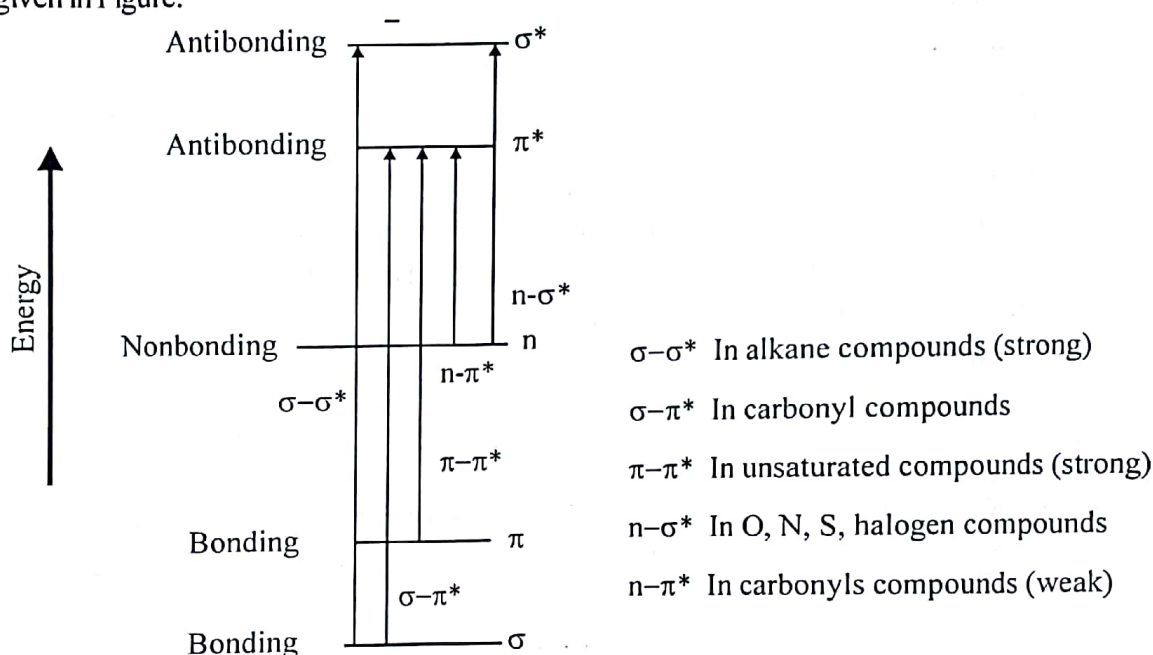
The UV-Visible portion is divided into three regions; the vacuum or Far-UV (10-200 nm), Near-UV (200-380 nm) and Visible (380-780 nm).



The near ultraviolet region (200-400 nm) out to 200 nm extends this energy range to 143 kcal/mole and the visible region (400-800 nm) of the spectrum comprises photons of energies 36 to 72 kcal/mole. The above energies are sufficient to promote or excite a molecular electron to a higher energy orbital.

3. Different electronic transitions in Ultraviolet-Visible spectroscopy

The electrons of all the compounds other than alkanes, may undergo several possible transitions of different energies. When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. For most of the molecules the lowest lying molecular orbitals are the σ bonds. The π -orbitals lie at somewhat higher energy levels, and the nonbonding orbitals, that holds the unshared pair of electrons lie even at high energies. The unoccupied, or antibonding orbitals (σ^* , π^*), are of highest energy. The most possible electronic transitions of σ , π and n electrons are given in Figure.



Different electronic transition in UV-Visible spectroscopy.

$\sigma-\sigma^*$ transitions

An electron in a bonding orbital (σ) is excited to the corresponding antibonding orbital (σ^*). The energy required is large, as the σ bonds are very strong. For example, methane (which has only C-H bonds, and can only undergo $\sigma-\sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima due to $s-s^*$ transitions are not seen in typical UV-visible spectra (200-700 nm), but occurs below 200 nm. The study of such transitions is done in vacuum ultraviolet region since below 200 nm the oxygen present in air begins to absorb.

$n-\sigma^*$ transitions

Saturated compounds containing one hetero atom with unshared pairs (i.e., non-bonding electrons) are capable of $n-\sigma^*$ transitions, such as alcohols, ethers, amines and sulfur compounds. These transitions usually need less energy than $\sigma-\sigma^*$ transitions. They can be initiated by light whose wavelength is in the range 150-250 nm. For example, in saturated alkyl halides, the energy required for this transition decreases with an increase in the size of the halogen atom (or a decrease in the electro negativity of the atom). Due to the greater electronegativity of the chlorine atom (than

iodine) the non bonding (n) electrons on chlorine are comparatively difficult to excite, as these electrons are tightly bounded to the nucleus. Since this transition is more probable in methyl iodide so its molar excitation coefficient is also higher than methyl chloride.

Also, these transitions are sensitive to hydrogen bonding. For example, alcohols form hydrogen bonds with the solvent molecules which occurs due to the presence of non bonding electrons on the hetero atoms and thus ν - s^* transitions requires greater energy.

π - π^* transitions

These transitions require an unsaturated group in the molecule to provide the π electrons for examples alkenes, alkynes, aromatics, carbonyl compounds etc. These transitions usually need less energy than n - σ^* transitions. In the case of alkenes, there are several transitions possible, but the π - π^* are of lowest energy and are observed nearly 175-190 nm. The saturated carbonyl compounds shows the π - π^* transitions (\sim 150 nm) in addition to n - π^* .

n - π^* transitions

Compounds containing one hetero atom with non-bonding electrons (n) are capable of n - π^* transitions. These transitions require the least amount of energy than all other transitions and therefore absorption bands are generally observed at longer wavelengths. Carbonyls-unsaturated systems incorporating nitrogen or oxygen atoms can undergo n - π^* transitions (\sim 285 nm). Despite of the fact this transition is forbidden by the selection rules ($\epsilon = 15$), it is the most often observed and studied transition for carbonyls. This transition is also sensitive to constituents on the carbonyl.

4. Selection rule and Beer-Lambert law:

The following selection rules are:

1. Electronic transitions are allowed if the orientation of the electron spin does not change during the transition.
2. If the symmetry of the final and initial functions are different; these are called the spin and symmetry selection rules, respectively. However the forbidden transition can still occur, but will give rise to weak absorptions.

According to the Beer-Lambert law, the absorbance A , of the solution is directly proportional to the path length (l = the length of the cell containing the solution, in cm) and the concentration of the absorbing species (c , in moles per litre), according to equation:

$$A = \log(I_0/I) = \epsilon \cdot c \cdot l$$

Where, A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, ϵ is a constant known as the molar absorptivity or molar extinction coefficient, and is a characteristic of the molecule. The molar absorptivity is expressed in $100 \text{ cm}^2 \text{ mol}^{-1}$. It is a measure of the intensity of the absorption and usually ranges from 0 - 10^6 (unit of $100 \text{ cm}^2 \text{ mol}^{-1}$). The greater the probability of the absorption and its associated electronic transitions, the greater the ϵ value for that transition.

5. Solvents used in the UV-Visible spectrophotometry

A good solvent should not absorb ultraviolet radiation in the same region as the substance whose spectrum is to be determined. Also, solvent has large effect of on the fine structure of an absorption band. For example, the non polar solvent does not H-bond with solute, and the spectrum of the solute closely approximates the spectrum that would be produced in the gaseous state, where fine structures

can often be observed. In polar solvents, the hydrogen bonding forms a solute-solvent complex, and the fine structure may disappear.

The solvents also have the ability to influence the wavelength of ultraviolet light that will be observed. For example polar solvents shifts transitions of the $n-\pi^*$ type to shorter wavelength. A list of common solvents is given in Table. Amongst the solvent given in table, water, ethanol and hexane are commonly used because they remain transparent in the ultraviolet region of the spectrum where interesting absorption peaks from the sample molecules are likely to occur.

Table: Wavelength (λ_{\max}) values of some common solvents used in UV-Visible spectrophotometry

S.No.	Solvents	λ_{\max} values
1.	Acetonitrile	190
2.	Chloroform	240
3.	Cyclohexane	195
4.	1,4-Dioxane	215
5.	95% Ethanol	205
6.	n-hexane	201
7.	Methanol	205
8.	Isooctane	195
9.	Water	190

Some useful terms in Ultraviolet-Visible spectroscopy

Chromophores

The coloured substances owe their colour due to the presence of one or more unsaturated groups responsible for electronic absorption. These groups are called chromophore (color loving), e.g.: $C=C$, $C \equiv C$, $C=N$, $C=O$, $N=N$, NO_2 etc are the common examples of the compounds containing chromophoric groups.

Table: Absorptions of simple chromophores in the UV-Visible spectrophotometry.

Chromophoric Group	Examples	Transitions	λ_{\max} (nm)	ϵ_{\max}
ROH	Methyl alcohol	$n-\sigma^*$	180	200
ROR	Di-ethylether	$n-\sigma^*$	188	1995
$R_2C=CR_2$	Ethylene	$\pi-\pi^*$	171	15,000
$RC \equiv CR$	Acetylene	$\pi-\pi^*$	170	10,000
R-X, X=Cl	Methyl chloride	$n-\sigma^*$	173	200
X = Br	n-Propyl bromide	$n-\sigma^*$	208	300
X = I,	Methyl iodide	$n-\sigma^*$	259	400
RCHO	Acetaldehyde	$n-\pi^*$	290	15
		$\pi-\pi^*$	180	10,000
R_2CO	Acetone	$n-\pi^*$	280	15
		$\pi-\pi^*$	180	900

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RCOOH	Acetic acid	$n-\pi^*$	205	41
RCOOR	Ethyl acetate	$n-\pi^*$	205	69
RCONH ₂	Acetamide	$n-\pi^*$	210	—
RNO ₂	Nitrobenzene	$n-\pi^*$	275	17
		$\pi-\pi^*$	200	5,000
R-NH ₂	Trimethylamine	$n-\sigma^*$	190	3950
R-C \equiv N	Acetonitrile	$n-\pi^*$	160	—
R-N=N-R	Azomethane	$n-\pi^*$	340	4.5

When sample molecules are exposed to UV-light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. The nuclei that the electrons hold together in bonds play an important role in determining which wavelengths of radiation are absorbed. The nuclei determine the strength with which the electrons are bound and thus influence the energy spacing between ground and excited states. Hence the characteristic energy of a transition and the wavelength of the radiations are absorbed are properties of a group of atoms rather than of electrons themselves. Since similar functional groups will have electrons capable of discrete classes of transitions, the characteristic energy of these energies is more representative of the functional group than the electrons themselves. Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions.

6. Effect of Substitution on the chromophore

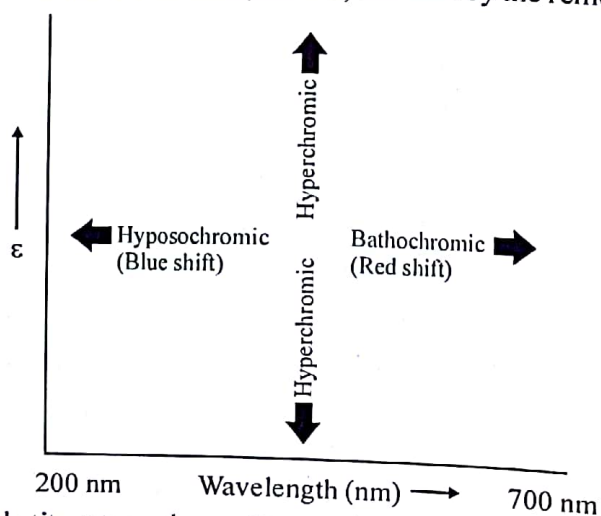
Substituents may have the following effects on a chromophore:

Bathochromic shift (red shift)

The shift of an absorption maximum towards longer wavelength (lower energy) is commonly known as bathochromic shift or red shift. It may be produced by a change of medium (solvent) or by the presence of an auxochrome.

Hypsochromic shift (blue shift):

The shift towards shorter wavelength (higher energy) is known as hypsochromic shift or blue shift. This may be caused by the change of medium (solvent) and also by the removal of conjugation.



Effect of substituents on the position and intensity of an absorption band.

Hypochromic shift:

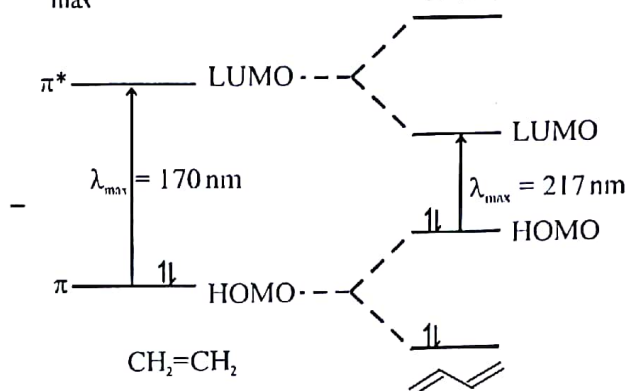
An increase in intensity leads to the hyperchromic shift. For example, the intensities of primary and secondary bands of phenol are increased in phenolate.

Hypochromic shift:

A decrease in intensity leads to the hypochromic shift. For example, the intensities of primary and secondary bands of benzoic acids are decreased in benzoate.

7. Effect of conjugation on the chromophore

Increasing conjugation λ_{\max} increases because the energy gap in between HOMO and LUMO decrease



According to quantum mechanics, conjugated olifines assumed as a 1-D box

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$$

$$\Delta E = \frac{h^2}{8mL^2} [n_{\text{LUMO}}^2 - n_{\text{HOMO}}^2]$$

$$\Delta E \propto \frac{1}{L^2}$$

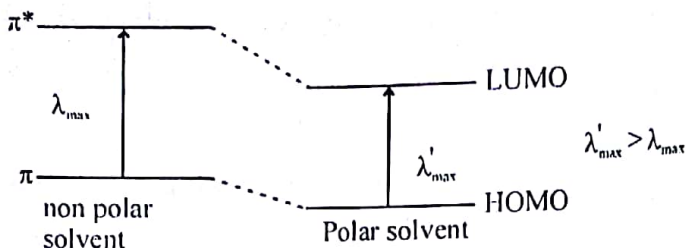
Conjugation causes bathochromic shifts in the absorption maxima of chromophores, this can be explained on the basis of the relative energy levels of the π -orbitals. When two double bonds are conjugated, the four p-atomic orbital combine to generate four π -molecular orbitals (two are bonding and two are antibonding). The energetically most favourable π - π^* excitation occurs from the highest energy bonding p-orbital (HOMO) to the lowest energy antibonding p-orbital (LUMO). Increased conjugation brings the HOMO and LUMO orbitals closer together. The energy (ΔE) required to effect the electron promotion is therefore less and the wavelength that provides this energy is increased correspondingly (remember $\lambda = hc/\Delta E$). Thus, the more highly conjugated the system, the smaller the HOMO-LUMO gap, E , and therefore the lower the frequency and longer the wavelength. The colours we see in inks, dyes, flowers etc. are typically due to highly conjugated organic molecules.

8. Effect of solvent on the chromophore

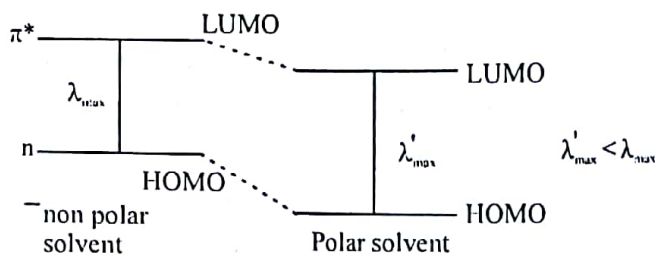
The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. The Franck Condon principle states that electronic transitions involve the movement of electrons, including those of the solvents, but not the movement of atoms. Increasing polarity of solvent λ_{\max} increased for π - π^* transition (allowed transition) and λ_{\max} decreased for n - π^* transition.

Order of interaction of orbital with polarity of solvent = nonbonding > Antibonding > Bonding

Increasing in polarity λ_{\max} increased because due to polarity π^* -antibonding orbital are more stabilized than π -bonding molecular orbital, due to this the energy gap between HOMO and LUMO decrease

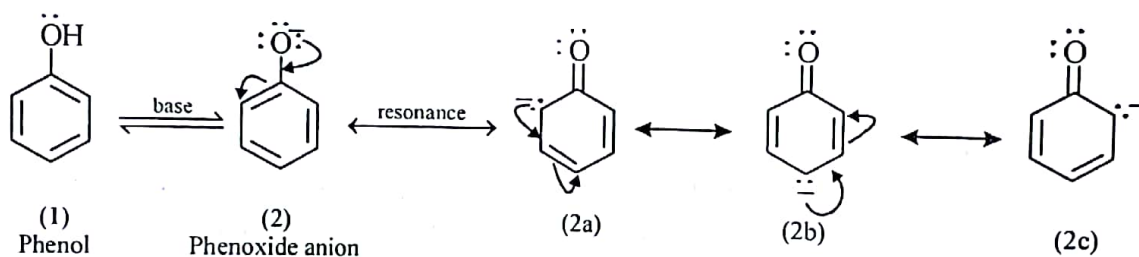
hence λ_{\max} increase

Increasing the polarity λ_{\max} decrease in $n \rightarrow \pi^*$ transition because of nonbonding orbital are more stabilized than the π^* -orbital and due to this the energy gap in between HOMO and LUMO increase

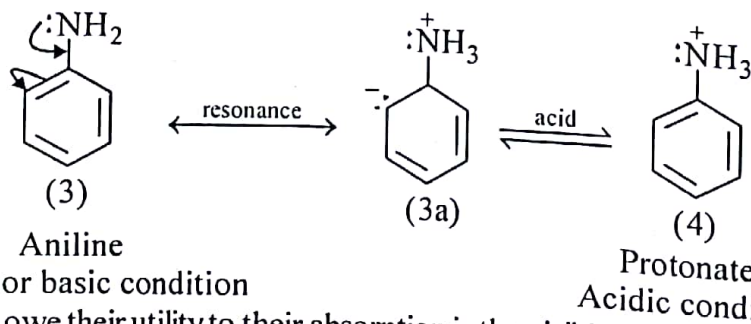


9. Effect of pH on the chromophore

The UV-Visible spectra of some of the compounds, especially certain substituted aromatic compounds, show the dramatic changes with a change in the pH of the solvent. Phenols and substituted phenols are acidic and display striking changes to their absorptions upon the addition to base. The removal of the acidic proton increases the conjugation of the lone pairs on the oxygen with the p-system of the aromatic ring, leading to a decrease in the energy difference between the HOMO and LUMO orbitals, resulting in red shift along with an increased intensity of the absorption.

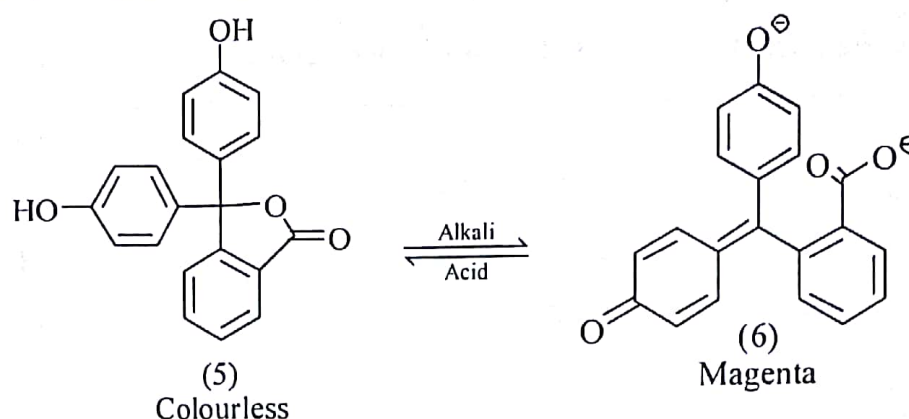


When aromatic amine is treated with acid, a blue shift is observed with a decrease in intensity which is due to the loss of the overlap between the amine lone pair and the aromatic π -system. For example, the conjugation of the lone pair of electrons on the nitrogen atom of aniline (3) with the π -bond system of the benzene is removed on protonation (4). Aniline absorbs at 230 nm, but in acidic condition the main peak is almost identical with that of benzene which absorbs at 203 nm.



Many pH indicators owe their utility to their absorption in the visible region of the UV-Visible spectrum. Changes to the pH lead to changes in the indicator chromophore, and result in reliable colour changes at predictable pH values. One such example is that of the phenolphthalein (5), which is a phenol and can be deprotonated at elevated pH to give the anions (6), extending the chromophore and leading to

a substantial bathochromic shift. Thus the anion of phenolphthalein is deep magenta in colour, while un-ionised form phenolphthalein is colourless.



The pKa of the acid-base equilibrium is 9.4, at acidic and neutral pH there is insufficient anion to detect the colour by eye, and it appears colourless. As the pH approaches the pKa, the concentration of anion increases and at pH 8.2, the colour becomes visible to the eye. As the pH 8.2 is close to neutrality, phenolphthalein is widely used to show the end point in weak acid-strong base titrations.

10. Isosbestic point:

If the two substances, each of which obeys Beers law, are in equilibrium, the spectra of all the equilibrium mixtures at a total concentration intersect at a fixed wavelength. This point, is termed as isoesbestic point, is the wavelength at which absorbance's of the two species are equal. The presence of the two species in equilibrium can be identified by the appearance of an isoesbestic point in the UV spectrum.

11. Woodward-Fieser rules

Woodward-Fieser Rules for calculating the λ_{\max} values in dienes

The conjugated diene exhibits an intense band in the region from 217 to 245 nm, owing to the $\pi-\pi^*$ transition. The position of this band appears to be quite insensitive to the nature of the solvent. Many simple conjugated dienes exist in a planar conformation. Generally, alkyl substituents produce bathochromic shifts and hyperchromic effects. However, with certain patterns of alkyl substitution, the wavelength increases but the intensity decreases. The 1, 3-dialkylbutadienes possess too much crowding between alkyl groups to permit them to exist in the s-trans conformation. They convert, by rotation around the single bond, s-cis conformation which absorbs at longer wavelengths but lower intensity than the corresponding trans conformation. But in cyclic dienes, where the central bond is apart of the ring system, the diene chromophore is held rigidly in either the s-trans (transoid) or the s-cis (cisoid) orientation. The incremental contribution of substituents is added to this base value from the Table.

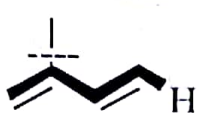

Table: Empirical rules for calculating λ_{\max} values in case of different dienes.

Diene with appropriate parent value	Add an increment for any extra conjugated π -bonds in specific dienes		Add increments to any substituents in specific dienes	
(a) Acyclic and heteroannular (double bond in two adjacent ring) diene = 217 nm	C=C	+30	R(CH ₃)	+5
	C=C-C=C	+40	Cl	+5
	Exocyclic	+5	OH, OR	+5
	C=C		OCOR	0
(b) Homoannular diene (double bonds within one ring) = 253 nm			O ⁻	-
			SR	+30
			NR ₂	+60

Ayclic Dienes

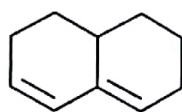
The base value for the acyclic dienes is 217 nm.

Illustration: Calculate the λ_{\max} of different acyclic dienes:

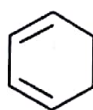
1.		Acyclic butadiene	= 217 nm
		One alkyl substituent	= + 5 nm
		Calculated value	= 222 nm
		Experimental value	= 220 nm
2.		Acyclic butadiene	= 217 nm
		2 alkyl substituent (2×5)	= + 5 nm
		1-Exocyclic C=C	= + 10 nm
		Calculated value	= 232 nm
		Experimental value	= 237 nm

Cyclic Dienes:

There are two types of cyclic dienes, with two different base values. These are heteroannular diene and homoannular diene. The base value for the heteroannular diene (12) is 217 nm whereas for homoannular diene (13) is 253 nm.

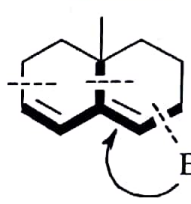
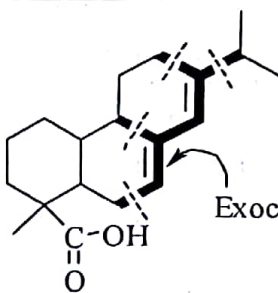


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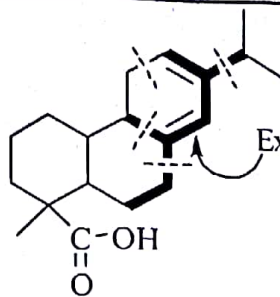


(13)

Illustration: Calculate the λ_{\max} of different cyclic dienes:

1.		Heteroannular diene	= 214 nm
		3-alkyl substituents (3×5)	= + 15 nm
		1-Exo C=C	= + 5 nm
		Calculated value	= 234 nm
		Experimental value	= 235 nm
2.		Heteroannular diene	= 214 nm
		4-alkyl substituents (4×5)	= + 20 nm
		1-Exo C=C	= + 5 nm
		Calculated value	= 239 nm
		Experimental value	= 240 nm

3.



Homoannular diene	= 253 nm
4-alkyl subs (4 × 5)	= + 20 nm
	= + 5 nm
Calculated value	<u>= 278 nm</u>
Experimental value	= 275 nm

Woodward-Fieser Rules for calculating the λ_{\max} values in unsaturated carbonyl compounds (Enones)

The carbonyl compounds have two main UV-transitions (i) π - π^* (ii) n - π^* . The conjugation of the double bond with a carbonyl group leads to intense absorption corresponding to π - π^* transition of the carbonyl group. The absorption in simple enones normally occurs in the region between 220 and 250 nm. The n - π^* transition is less intense and occurs in between 310-330 nm.

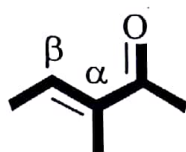
Table: Empirical rules for calculating λ_{\max} values in case of different enones.

Enones β α O -C=C-C-X	Enones with appropriate parent value	Add an increment for any extra conjugated π -bonds in specific Enones		Add increments to any substituents in specific Enones				
				α	β	γ	δ	
If, X=H	207 nm	C=C	+30	R				
X=C (part of five-membered ring)	202 nm	C=C-C=C	+40	(CH ₃)	10	12	18	18
		Exocyclic	+5	Cl	15	12	-	-
		C=C	OH	35	30	-	-	
			OR	6	6	-	-	
X=C (Acyclic Or part of six-membered ring)	215 nm	C=C		OCOR	-	75	-	-
				O ⁻	-	85	-	-
				SR	-	95	-	-
				NR ₂				

The structural modifications of the chromophore have pronounced effects on the π - π^* transitions, but no effect on the n - π^* transitions. The incremental contribution of substituents is added to this base value from the Table.

Illustration: Calculate the λ_{\max} of different enones:

1.



Acyclic enone	= 215 nm
α -alkyl subs	= +10 nm
β -alkyl subs.	= +12 nm
Calculated value	<u>= 237 nm</u>
Experimental value	= 240 nm

2.		Cyclic six membered enone	= 215 nm
		Extending conjugation	= +30 nm
		Homoannular diene	= +39 nm
		δ-ring residue	= +18 nm
		Calculated value	= 302 nm
		Experimental value	= 300 nm
3.		Cyclic five membered enone	= 202 nm
		OH α-substituent	= +35 nm
		β-ring residue	= +18 nm
		Calculated value	= 249 nm
		Experimental value	= 249 nm
4.		Cyclic six membered enone	= 215 nm
		Extending conjugation	= +30 nm
		γ-ring residue	= +18 nm
		d-ring residue	= +18 nm
		Exo-cyclic double bond	= +5 nm
		Calculated value	= 286 nm
		Experimental value	= 288 nm
5.		Cyclic six membered enone	= 215 nm
		Extending conjugation	= +30 nm
		γ-ring residue	= +18 nm
		2-δ-ring residue	= +36 nm
		Exo-cyclic double bond	= +5 nm
		Calculated value	= 338 nm
		Experimental value	= 339 nm

Woodward-Fieser Rules for calculating the λ_{\max} values in aromatic carbonyl compounds

Woodward and Fieser rules can be used to calculate the λ_{\max} value for the $\pi-\pi^*$ transition. Depending on the nature of the aromatic carbonyl compounds different base values exist. The following different base values are taken for aromatic carbonyl compounds.

- (i) For aromatic aldehydes base value is 250 nm.
- (ii) For aromatic ketones base value is 246 nm.
- (iii) For aromatic carboxylic acid or esters base values are 230 nm.

The incremental contribution of substituents is added to this base value from the Table.

Table: Empirical rules for calculating λ_{\max} values in case of different aromatic carbonyls.

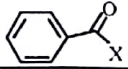
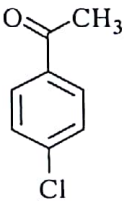
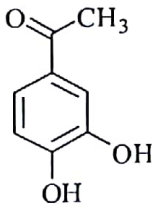
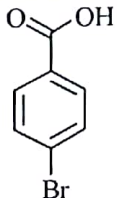
Aromatic carbonyls 	Aromatic carbonyls with appropriate parent value	Add increments to any substituents in specific Enones			
			o	m	p
If, X=H	250 nm	CH ₃	3	3	7
X=C	246 nm	Cl	0	0	10
X=OH, OR	230 nm	OH, OR	7	7	25
		OCOR	-	-	-
		O ⁻	15	15	80
		SR	-	-	-
-	-	NR ₂	20	20	85

Illustration: Calculate the λ_{\max} of different aromatic carbonyls:

1.		Aromatic carbonyl compound	= 246 nm
		-Cl substitution at para position	= +10 nm
		Calculated value	= 256 nm
		Experimental value	= 254 nm
2.		Aromatic carbonyl compound	= 246 nm
		OH substitution at meta position	= +7 nm
		OH substitution at para position	= 25 nm
		Calculated value	= 278 nm
		Experimental value	= 281 nm
3.		Aromatic carbonyl compound	= 230 nm
		-Br substitution at para position	= +15 nm
		Calculated value	= 245 nm
		Experimental value	= 245 nm

12. Application of Ultraviolet Spectroscopy

Detection of functional groups:

This technique can be used to identify the presence of a chromophore. The absence of a band at a particular wavelength may be regarded as an evidence for the absence of a particular group in the compound. If the spectrum of the compound is transparent above 200 nm, it shows the absence of:

- Conjugation
- A carbonyl group
- Benzene or aromatic compounds
- Bromo or iodo atoms

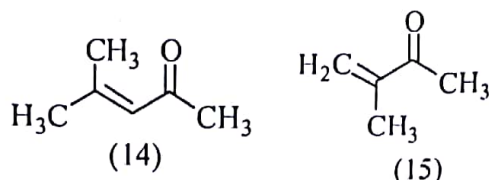
As isolated double bond or some other atoms or groups may be present. It means that no definite conclusion can be drawn if the molecule absorbs at a wavelength lower than 200 nm.

Extent of conjugation

The extent of conjugation can be estimated by using ultraviolet spectroscopy. Addition in unsaturation with the increase in the number of double bond shifts the absorption to longer wavelength.

Distinction between conjugated and non-conjugated compounds:

It also distinguishes between conjugated and non-conjugated compounds. The following isomers can be readily distinguished since one is conjugated and the other is not. The forbidden band for the carbonyl group in the compound (14) will appear at longer wavelength than that of the compound (15).



Identification of an unknown compounds:

An unknown compounds can be identified by comparing its spectrum with the known spectra. If the two spectra coincide, the two compounds must be identical. If the two spectra do not coincide, then the expected structure is different from the known compound.

Quantitative analysis:

UV-Visible spectroscopy can be used to determine the concentration of a particular compounds in a solution. Since it is based on the Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length it is necessary to know how quickly the absorbance changes with concentration.

$$A = \log(I_0/I) = \epsilon \cdot c \cdot l$$

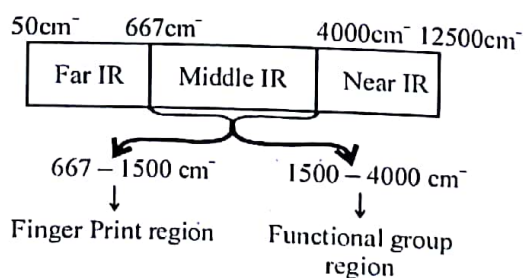
For example estimation of anthracene and naphthalene can be carried out using UV-Visible spectroscopy. In ethanol anthracene absorbs at 375 nm ($\log \epsilon = 3.87$), naphthalene absorption does not interfere in this region. A standard solution of anthracene-naphthalene mixture can be prepared and the measurement of anthracene can be done at 375 nm. From Beer Lambert law the concentration of pure anthracene can be calculated and hence, the proportion of anthracene in the mixture.

Examination of polynuclear hydrocarbons:

Benzene and polynuclear hydrocarbons have characteristic spectra in the ultra violet and visible region. Thus the identification of the polynuclear hydrocarbons can be made by comparison with the spectra of known polynuclear compounds. The presence of substituents on the ring generally shifts the absorption maximum to longer wavelength. For example, the naphthalene shows absorption at 210 and 272 nm, the added conjugation in anthracene and tetracene causes bathochromic shifts of these absorption bands.

IR SPECTROSCOPY

Important Points



Condition For IR Active: Molecule which changes their dipole moment during vibration can give IR spectra

$$\frac{\partial \mu}{\partial t} \neq 0$$

Note: Except HOMO diatomic molecule all molecule can give IR spectra.

Molecule which contain permanent dipole moment their all fundamental vib modes are IR active.

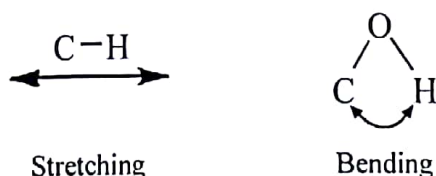
Molecule which have permanent dipole moment is zero except HOMO diatomic some mode's are IR active and some modes are inactive.

- I.R. spectrum arises due to excitation of vibrational and rotational energy levels of the molecule or individual functional groups. It is also called Vibrational spectroscopy. The I.R. region of the electromagnetic spectrum may be divided into three main sections :
 - Near infrared (overtone-region) $0.8 - 2.5 \mu\text{m}$ ($12500 - 4000 \text{ cm}^{-1}$)
 - Middle infrared (vibration-rotation region) $2.5 - 50 \mu\text{m}$ ($4000 - 200 \text{ cm}^{-1}$)
 - Far infrared (rotation region) $50 - 1000 \mu\text{m}$ ($200 - 10 \text{ cm}^{-1}$)
- The I.R. spectrum in the frequency range 4000 cm^{-1} to 666 cm^{-1} is important for organic chemistry. In the I.R. spectroscopy the absorbed energy brings about predominant changes in the vibrational energy which depends upon:
 - Masses of the atoms present in a molecule.
 - Strength of the bonds and
 - The arrangement of atoms within the molecule.
- It has been found that no two compounds except the enantiomers can have similar infrared spectra. The value of the stretching vibrational frequency of a bond can be calculated by the application of Hooke's law which may be represented as :

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

THE MODES OF STRETCHING AND BENDING

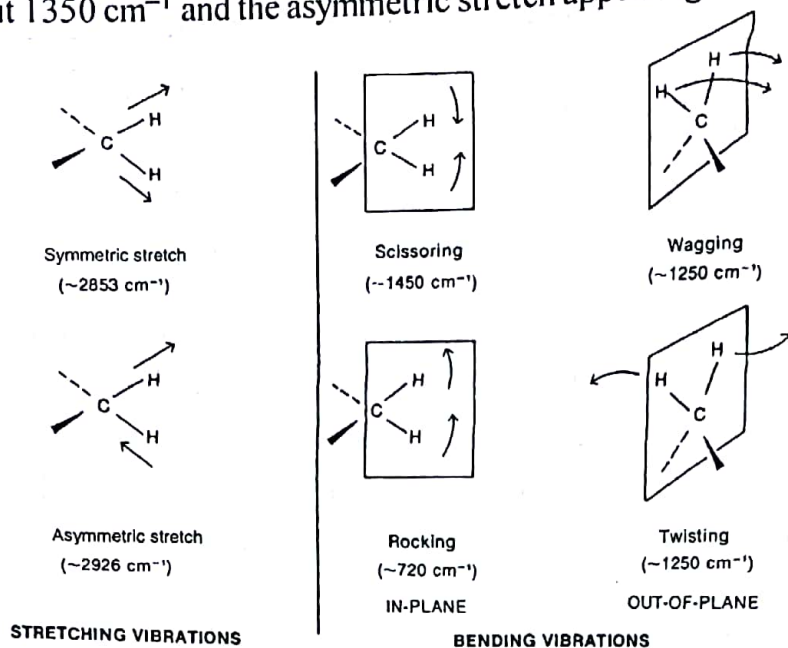
The simplest types, or modes, of vibrational motion in a molecule that are infrared active—that is, which give rise to absorptions—are the stretching and bending modes.



However, other, more complex types of stretching and bending are also active. The following illustrations of the normal modes of vibration for a methylene group introduce several terms. In general, asymmetric stretching vibrations occur at higher frequencies than symmetric stretching vibrations; also, stretching vibrations occur at higher frequencies than bending vibrations. The terms scissoring, rocking, wagging, and twisting are commonly used in the literature to describe the origins of infrared bands.

In any group of three or more atoms, at least two of which are identical, there are two modes of stretching: symmetric and asymmetric. Examples of such groupings are $-\text{CH}_3$, $-\text{CH}_2-$ (see page 17), $-\text{NO}_2$, $-\text{NH}_2$, and anhydrides. The methyl group gives rise to a symmetric stretching vibration at about 2872 cm^{-1} and an asymmetric stretch at about 2962 cm^{-1} . The anhydride functional group gives two

absorptions in the C=O region because of the asymmetric and symmetric modes of stretch. A similar phenomenon occurs in the amino group, where a primary amine (NH_2) usually has two absorptions in the N-H stretch region while a secondary amine (R_2NH) has only one absorption peak. Amides exhibit similar bands. There are two strong N=O stretch peaks for a nitro group, with the symmetric stretch appearing at about 1350 cm^{-1} and the asymmetric stretch appearing at about 1550 cm^{-1} .



	Symmetric Stretch	Asymmetric Stretch
Methyl	 $\sim 2872\text{ cm}^{-1}$	 $\sim 2962\text{ cm}^{-1}$
Anhydride	 $\sim 1760\text{ cm}^{-1}$	 $\sim 1800\text{ cm}^{-1}$
Amino	 $\sim 3300\text{ cm}^{-1}$	 $\sim 3400\text{ cm}^{-1}$
Nitro	 $\sim 1350\text{ cm}^{-1}$	 $\sim 1550\text{ cm}^{-1}$

The vibrations we have been discussing are called fundamental absorptions. They arise from excitation from the ground state to the lowest-energy excited state. Usually the spectrum is complicated because of the presence of weak overtone, combination, and difference bands. Overtones result from excitation from the ground state to higher energy states, which correspond to integral multiples of the frequency of the fundamental (ν). For example, you might observe weak overtone bands at 2ν , 3ν , Any kind of physical vibration generates overtones. If you pluck a string on a cello, the string vibrates with a fundamental frequency. However, less intense vibrations are also set up at several overtone frequencies. An absorption

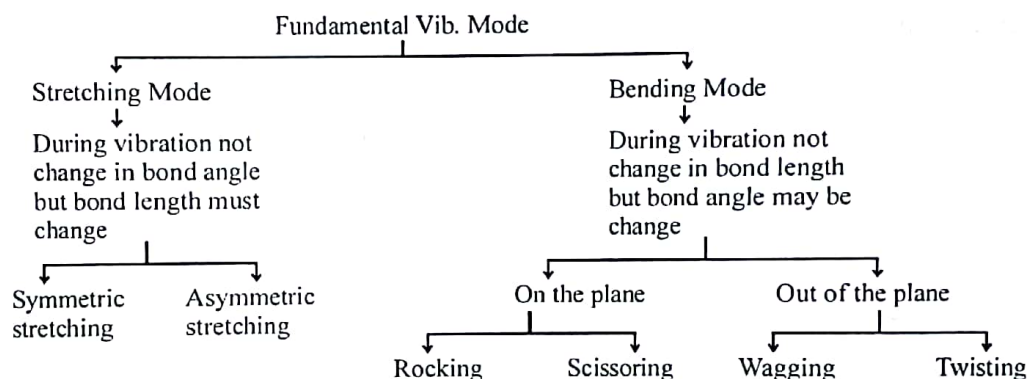
in the infrared at 500 cm^{-1} may well have an accompanying peak of lower intensity at 1000 cm^{-1} and overtone.

When two vibrational frequencies ($\bar{\nu}_1$ and $\bar{\nu}_2$) in a molecule couple to give rise to a vibration of a new frequency within the molecule, and when such a vibration is infrared active, it is called a combination band. This band is the sum of the two interacting bands ($\bar{\nu}_{\text{comb}} = \bar{\nu}_1 + \bar{\nu}_2$). Not all possible combinations occur. The rules that govern which combinations are allowed are beyond the scope of our discussion here.

Difference bands are similar to combination bands. The observed frequency in this case results from the difference between the two interacting bands ($\bar{\nu}_{\text{diff}} = \bar{\nu}_1 - \bar{\nu}_2$).

One can calculate overtone, combination, and difference bands by directly manipulating frequencies in wavenumbers via multiplication, addition, and subtraction, respectively. When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called Fermi resonance. Again, only certain combinations are allowed. Fermi resonance is often observed in carbonyl compounds.

Although rotational frequencies of the whole molecule are not infrared active, they often couple with the stretching and bending vibrations in the molecule to give additional fine structure to these absorptions, thus further complicating the spectrum. One of the reasons a band is broad rather than sharp in the infrared spectrum is rotational coupling, which may lead to a considerable amount of unresolved fine structure.



Number of Fundamental Vibration Mode's

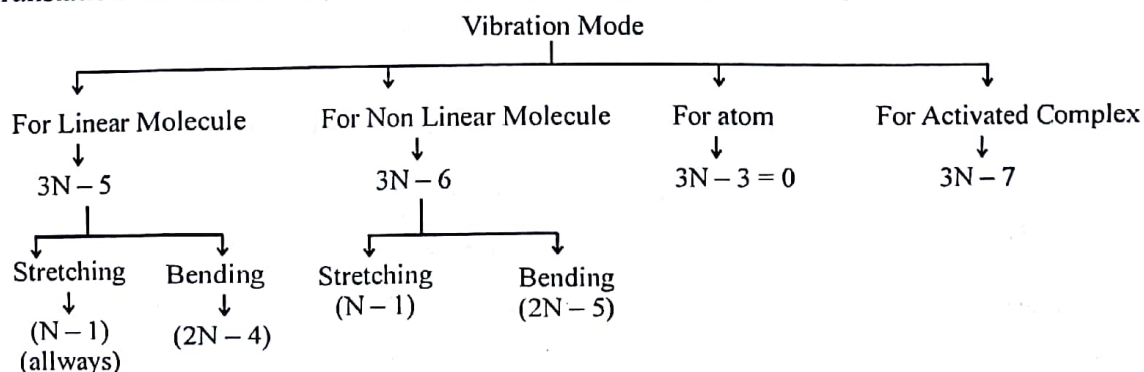
Number of vibration modes = $3N - (\text{Rotation Mode} + \text{Translation Mode})$

N = Number of atom in the molecule

For linear molecule rotational mode = 2

For nonlinear molecule rotational mode = 3

Translation mode for atom, molecule (linear or non linear) = 3 always

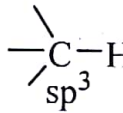



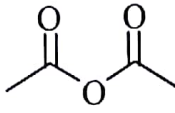
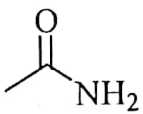
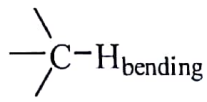
Q. Calculate the number of fundamental vibrational mode stretching or bending mode for the following molecule

Molecule	Shape	Vibrational Mode	Stretching (N-1)	Bending
H ₂ O	Nonlinear	3×3-6=3	2	1
NH ₃	Nonlinear	3×4-6=6	3	3
SO ₃	Nonlinear	3×4-6=6	3	3
C ₂ H ₂	Linear	3×4-5=7	3	4
C ₂ H ₄	Nonlinear	3×6-6=12	5	7
SF ₆	Nonlinear	3×7-6=15	6	9
XeF ₄	Nonlinear	3×5-6=9	4	5
Benzene	Nonlinear	3×12-6=30	11	19

In cyclic compound like benzene, cyclohexane have a specific vibrational mode known as breathing vibrational mode.

Important Group Frequencies

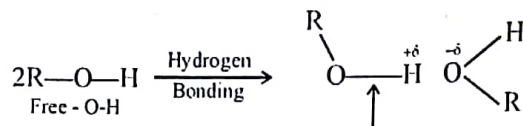
Fundamental Peak	Due to
3300 – 3650 cm ⁻¹	due to O–H stretching frequency
3200 – 3400 cm ⁻¹	N–H frequency in 1° – amine → two peak 2° – amine → one peak 3° – amine → no peak
≈ 3300 cm ⁻¹	due to ≡ C – H _{stretching} (1-Alkyne)
2900 – 3050 cm ⁻¹	C = C _{sp²} – H _{stretching} (In alkene, cyclo alkene aromatic compound)
2800 – 2950 cm ⁻¹	 (In Alkane, cyclo alkane (–CH ₃ , –CH ₂ –, )
2720 cm ⁻¹ – 2820 cm ⁻¹	Character stic peak of aldehyde C–H _{stretching} (due to fermi resonance)
2500 – 3000 cm ⁻¹ Broad peak	Character stic of –COOH group due to O–H _{stretching}
2200 – 2400 cm ⁻¹	C ≡ C _{stretching} , C ≡ N _{stretching}
2050 – 2200 cm ⁻¹	C = C = O _{str.} , C = C = C _{str.} , O = C = O, C = C = NH _{str.}

1750 – 1980 cm^{-1}	$\text{M} \rightarrow \text{CO}_{\text{str.}}$
1790 – 1800	Acid Halide $\text{—}\overset{\parallel}{\text{C}}\text{—Cl}$
1810 – 1870	$\text{—}\overset{\parallel}{\text{C}}\text{—F}$
1750 – 1780 cm^{-1} , 1800 – 1830 cm^{-1}	 Anhydride
1740 – 1760 cm^{-1}	$\text{—}\overset{\parallel}{\text{C}}\text{—OR}$ Ester
1730 – 1750 cm^{-1}	$\text{—}\overset{\parallel}{\text{C}}\text{—H}$ Aldehyde
1720 – 1740 cm^{-1}	$\text{—}\overset{\parallel}{\text{C}}\text{—OH}$ Carboxylic acid
1700 – 1720 cm^{-1}	$\text{R—}\overset{\parallel}{\text{C}}\text{—R}$ Ketone
1690 – 1700 cm^{-1}	 (Amide)
1650 cm^{-1}	$\text{C}=\text{C}_{\text{stretching}}$ (Alkene)
1490, 1555, 1605, 1655 cm^{-1}	Aromatic $\text{C}\equiv\text{C}_{\text{stretching}}$
1530, 1360 cm^{-1}	Characteristic of $\text{—}\overset{\text{O}}{\parallel}{\text{N}}\text{—O}$ group
1450 – 1485 cm^{-1}	 $\text{—}\overset{\diagup}{\text{C}}\text{—H}_{\text{bending}}$
1450	$\text{C—C}_{\text{stretching}}$
1050 – 1300	C—X (X = O, N, F)
900 – 960	$\text{C—H}_{\text{bending}}$ in trans Alkene
690 – 730	$\text{C—H}_{\text{bending}}$ in cis Alkene
800 – 850 cm^{-1}	Pera substituted
750 – 800 cm^{-1} , 680 – 715 cm^{-1}	Meta-substituted
690 – 750 cm^{-1}	Ortho substituted
300 – 480 cm^{-1}	$\text{M—Ligand}_{\text{stretching}}$

Hydrogen Bonding

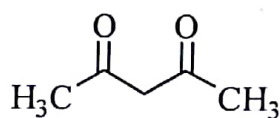
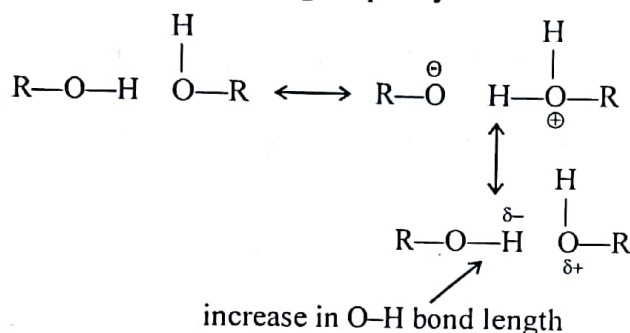
Stronger the hydrogen bonding, greater is the absorption shift towards lower wavenumber than the normal value. Generally, bands due to intramolecular hydrogen bonds are sharp whereas intermolecular hydrogen bonds give rise to broad bands and these depend on concentration.

Due to hydrogen bonding the original O-H bond is lengthened (weakened) due to electrostatic attraction between the hydrogen atoms of the molecule and oxygen atoms of the other, and thus the force constant of the O-H bond is reduced resulting in a decrease in its stretching frequency.

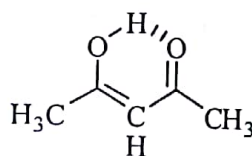


- (i) increase in bond length
- (ii) decrease in force
- (iii) decrease in $\bar{\nu}$

Further, the hydrogen bond can be regarded as a resonance hybrid of the following resonating structures, so that hydrogen bonding involves a lengthening of the original O-H bond. This bond is consequently weakened. So the stretching frequency is lowered.



Keto



Enol

$$\bar{\nu}_{\text{C}=\text{C}_{\text{str}}} \quad \text{—}$$

$$1650 \text{ cm}^{-1}$$

$$\bar{\nu}_{\text{C}=\text{O}} \quad 1720$$

$$1645$$

$$\bar{\nu}_{\text{O}-\text{H}_{\text{str}}} \quad \text{—}$$

$$3350 \text{ cm}^{-1}$$

Distinction between Inter-and Intramolecular Hydrogen Bondings

A compound with intramolecular hydrogen bonding shows almost the same O-H stretching in the concentrated solution as in the very dilute solution, this means O-H stretching value does not change with dilution in the cases of intramolecular hydrogen bonding while the same changes with dilution in the case of intermolecular hydrogen bonding. Thus dilution can be used to distinguish between inter and intramolecular hydrogen bonds.

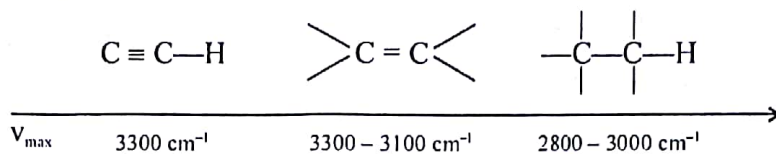
Electronegativity

As the electronegativity of a bonded atom increases, the shortening of bond length occurs and the large force constant leads to increased vibrational frequency. For example, the decreasing order of

electronegativity of carbon in alkane, alkene and alkyne is:

alkyne > alkene > alkane

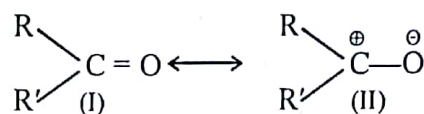
The C–H stretching frequencies of these compounds are also in the same order :



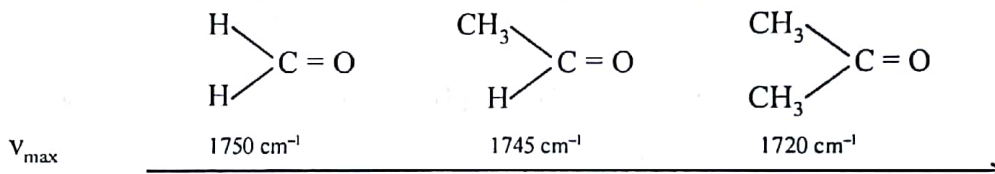
- Electronegativity of carbon of the C–H bonds in increasing order.
- Force constant is in decreasing order.
- ν_{\max} is also in decreasing order.

Inductive Effect

A carbonyl compound may be considered as a resonance hybrid of the following structures



The stretching frequency of a carbonyl group decreases with increasing number of alkyl groups attached to carbonyl carbon. This is due to +I effect of alkyl groups which favours the structure (II) and lengthens (weakens) the carbon-oxygen double bond, and hence its force constant is decreased resulting in the lowering of the C = O stretching frequency.



- carbon-oxygen bond length in increasing order (structure II)
- force constant in decreasing order
- ν_{\max} is decreasing order

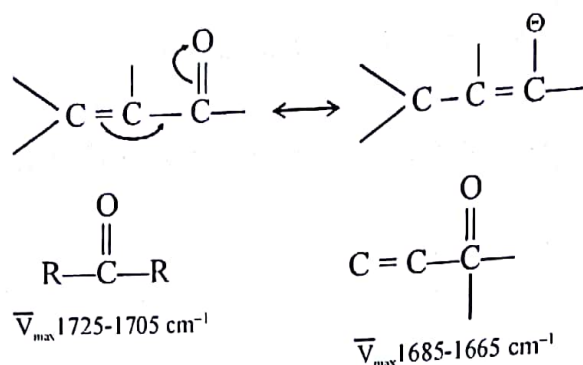
Similarly, when a group with –I effect is attached to a C = O groups, it favours the structure (I) and its stretching frequency is increased due to decrease in bond length or increase in the force constant of the carbon-oxygen double bond. For example, CH_3COCH_3 , CH_3COCF_3 and CF_3COCF_3 show $\nu_{\text{C}=\text{O}}$ bands at 1720, 1769 and 1810 cm^{-1} , respectively

Resonance Effects

Due to $p-\pi$ and $\pi-\pi$ conjugation single bonds get partial double bond character and double bonds get partial single bond character. When a single bond acquires a partial double bond character through resonance, the vibrational frequency of the bond is expected to be greater than the normal value because of the shortening of bond length. On the other hand, when a double bond possesses a partial single bond character, the vibrational frequency is expected to be lower than the normal value because of the weakening of the bond strength through resonance.

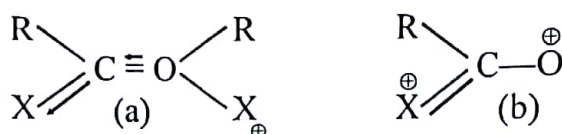
(i) C = O Stretching frequency of saturated and α , β -unsaturated compounds.

In an α , β -unsaturated carbonyl compound $\pi-\pi$ conjugation takes place. Due to this conjugation C = O group has a partial single bond character. Thus the C = O bond becomes longer than that in a saturated carbonyl compound; as a result the C = O bond strength decreases and its vibrational frequency becomes less than that of the C = O groups in the saturated carbonyl compound.



(ii) C = O stretching frequency of acid derivations

The absorption frequency of saturated aliphatic keto group of a neat sample is 1715 cm^{-1} . Replacement of an alkyl group of a saturated aliphatic ketone by a heteroatom (X) shifts the carbonyl absorption. The direction of the shift depends on whether the inductive effect (a) or resonance effect (b) predominates.



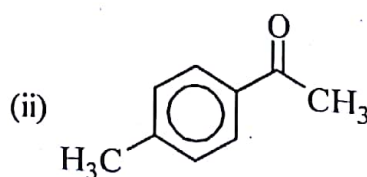
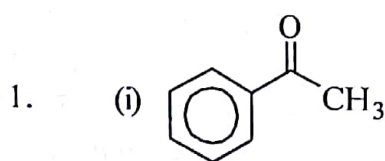
The inductive effect reduces the length of C = O bond and thus increases its force constant and the frequency of the absorption. The resonance effect increases the C = O bond length and reduces its force constant and the frequency of absorption.

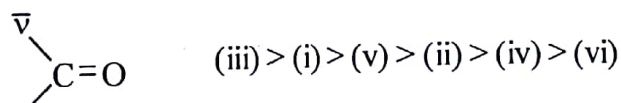
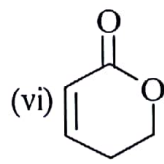
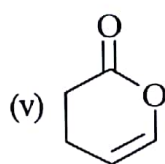
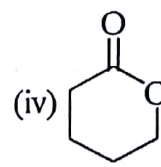
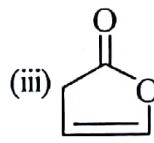
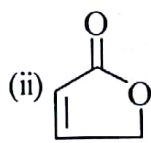
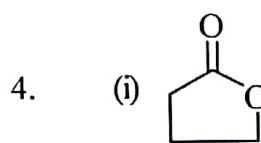
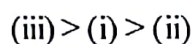
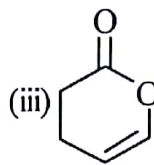
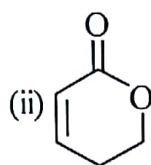
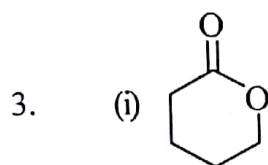
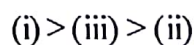
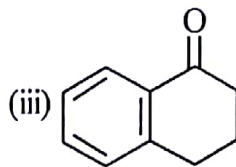
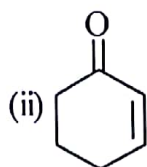
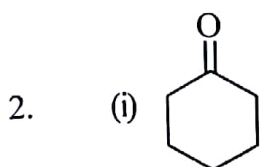
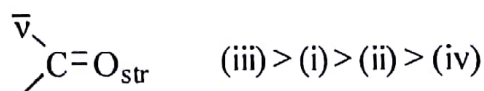
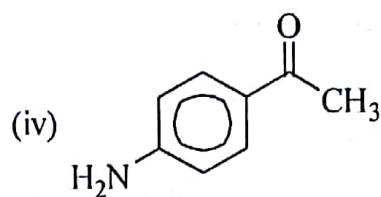
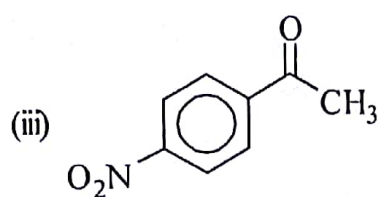
Table 1. The carbonyl absorption of $\text{R}-\overset{\text{X}}{\text{C}}=\text{O}$ compounds

X	$\nu_{\text{max}} \text{ C}=\text{O}$	
Cl	$1815 - 1785 \text{ cm}^{-1}$	
Br	1812 cm^{-1}	Inductive effect predominates
OH	1760 cm^{-1}	
OR	$1750 - 1735 \text{ cm}^{-1}$	
NH ₂	$1695 - 1650 \text{ cm}^{-1}$	Resonance effect predominates
SR	$1620 - 1690 \text{ cm}^{-1}$	

An NH₂ group has -I effect as well as +R effect but the latter predominates. Due to the +R effect, the C = O group in an amide gets a partial single bond character and possesses lower vibrational frequency ($\bar{\nu}_{\text{max}} \text{ C}=\text{O}$, 1650 cm^{-1}) than in the corresponding ester (C = O, $1750-1735 \text{ cm}^{-1}$).

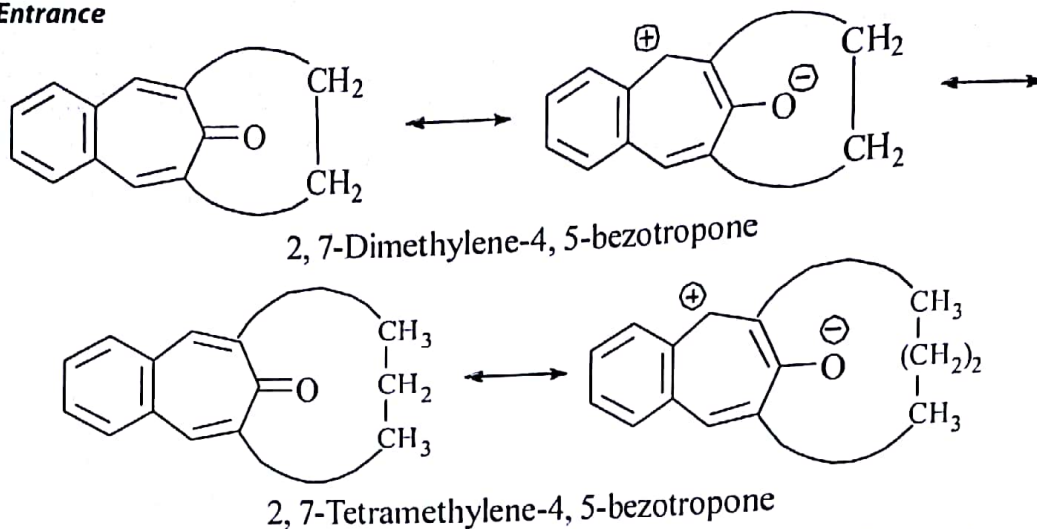
In the case of an ester the -I effect of the alkoxy group predominates over its +R effect.

Illustration:



Steric effects

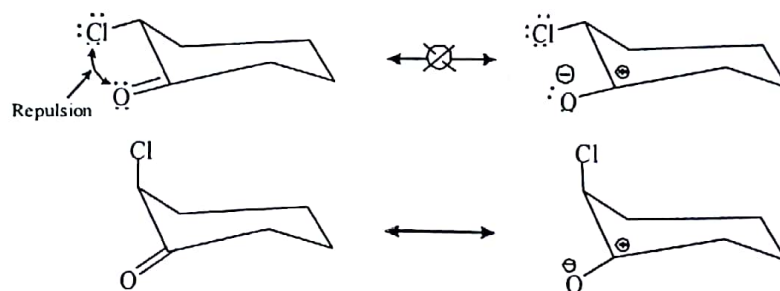
Steric effects such as steric inhibition of resonance, transannular effect, etc. influence stretching frequencies of bonds. For example, the $\nu_{\text{O-H}}$ stretching frequency of phenol is 3330 cm^{-1} . This frequency is due to the intermolecular hydrogen bonding. In contrast to phenol 2, 6-di-tert-butyl phenol, in which steric hindrance prevents intermolecular hydrogen bonding absorption band is obtained at 3600 cm^{-1} . Similarly the C=O stretching frequency of 2, 7-dimethylene-4, 5-benzotroponone is 1596 cm^{-1} where as tetramethylene-4, 5-benzotroponone has a C=O stretching ($\nu_{\text{C=O}}$) at 1724 cm^{-1} .



In the latter compound, the C=O group is formed out of the plane of the molecule and being non-planar, steric inhibition of resonance occurs and the compound shows normal value for $\nu_{C=O}$. Whereas in the former case C-O double bond lengthens owing to conjugation of the C=O π bond with the rest of the molecule and as a consequence $\nu_{C=O}$ comes down.

Field effects

Electrostatic or steric through space interaction between two groups within a molecule is called field effect. This field effect often influences the vibrational frequencies of both the groups. It has been observed that the $\nu_{C=O}$ is higher when the Cl atom of α -chlorocyclohexanone occupies the equatorial position when it is in the axial position. In the equatorial position, the electron cloud of the Cl atom and that of the oxygen atom experience electrostatic repulsion as a result of which carbon-oxygen bond does not acquire a partial single bond character, if it does so, it will have to face a greater repulsion.

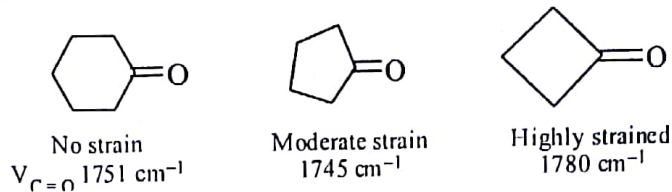


X	Y	$\bar{\nu}_{C=O}$
H	H	1720
H	Br	1724
Br	H	1734
Br	Br	1740

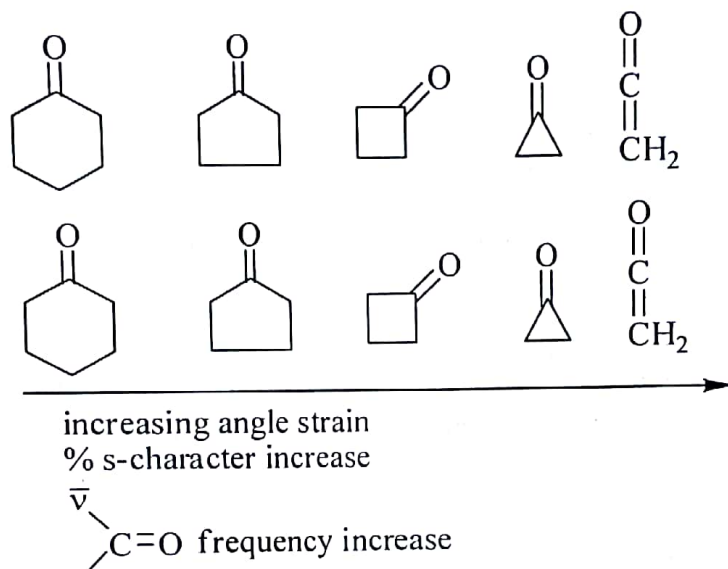
Ring size

Carbonyl stretching frequency in cyclic ketones having ring strain is shifted to higher value. The C-CO-C bond angle in strained rings is reduced below the normal value of 120° (acyclic and six

membered cyclic ketones have the normal C-CO-C angle of 120° . This leads to an increase in s-character in the sp^2 orbital of carbon involved in the C=O bond. Hence, the C=O bond is shortened (strengthened) resulting in an increase in the ($\nu_{C=O}$) frequency.



$$\nu_{C=O} \propto \frac{1}{\text{Bond angle}} \propto \text{ring strain}$$



Due to ring strain, bond strength of external double bond length increase.

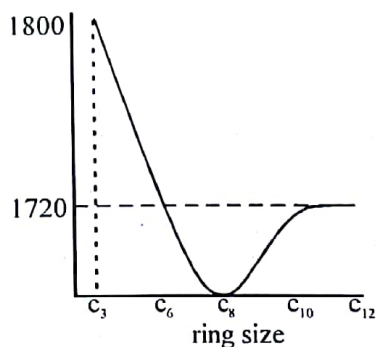
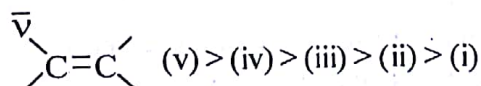
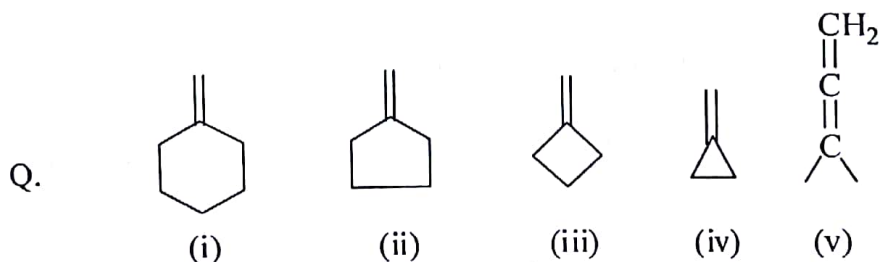
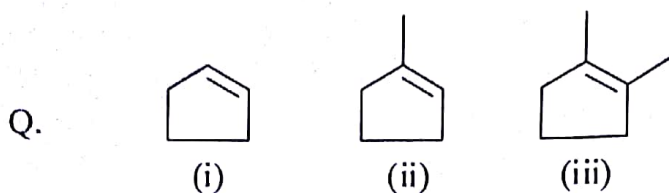
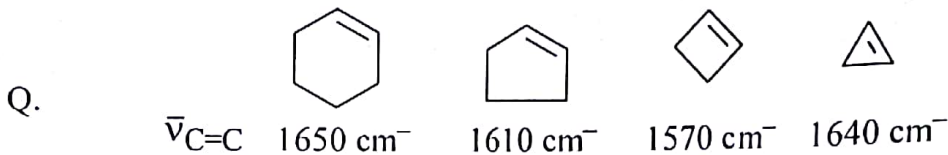


Illustration:

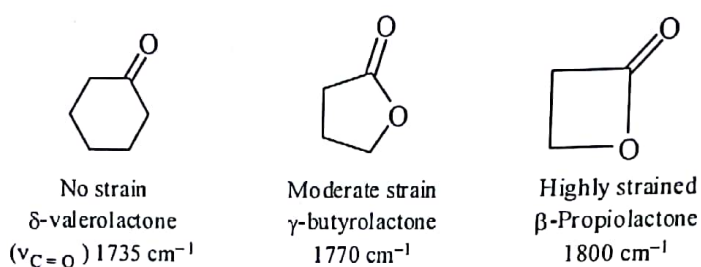




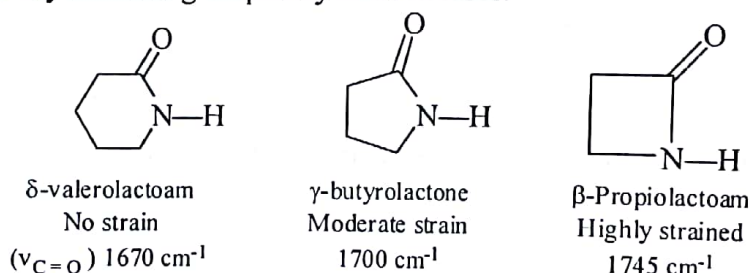
$$\bar{\nu}_{C=C} \text{ (iii)} > \text{(ii)} > \text{(i)}$$



Similar to the ketones, as ring strain in lactones increases, the carbonyl stretching frequency also increases.

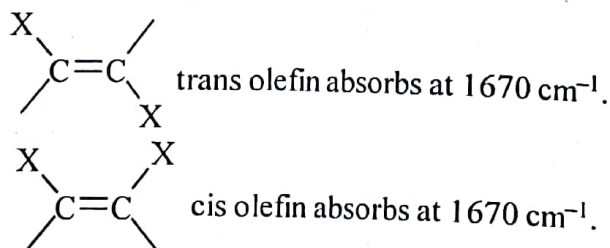


The C = O frequency in lactams too depends on the ring size. Similar to that ketones and lactones as the ring strain in lactams increases, the s-character of sp^2 carbon of C = O also increases and thus the carbonyl stretching frequency also increases.



Alkenes

C = C stretching vibrations are moderate to weak absorptions at 1680 – 1620 cm^{-1} . Vinyl group absorbs near 1640 cm^{-1} – C = C – R.



Internal double bonds are less intense in IR than terminal bonds. Olefinic bond stretching vibration in conjugated dienes without a centre of symmetry produce two C = C stretching bands. 1, 3-pentadiene shows absorption at 1650 cm^{-1} and 1600 cm^{-1} . Symmetrical 1, 3-enhanced olefinic absorption near 1625 cm^{-1} . Absorption frequency of > C = C is reduced by 30 cm^{-1} when conjugated > C = O. Olefinic C – H stretching vibrations above 3000 cm^{-1} result from aromatic, acetylenic, or olefinic C – H stretching. The most characteristics of olefinic are out of plane C – H bending vibrations at 1000 cm^{-1} –

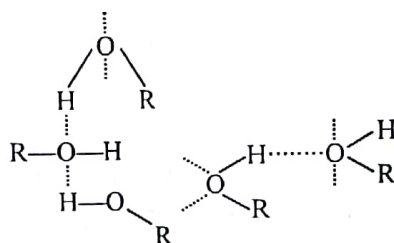
650 cm^{-1} . they are very strong bands.

Acetylenes have two stretching vibrations $\text{C} \equiv \text{C}$ stretching band occurs at 2260 cm^{-1} . In monosubstituted acetylene $\text{R} - \text{C} \equiv \text{CH}$, the $\text{C} \equiv \text{C}$ stretching occurs at $2140 - 2100\text{ cm}^{-1}$. $\text{C} - \text{H}$ stretching of $\text{R} - \text{C} \equiv \text{C} - \text{H}$ occurs at $3333 - 3267\text{ cm}^{-1}$. This is a strong band narrower than hydrogen bonded OH and NH bands, which occur in the same region.

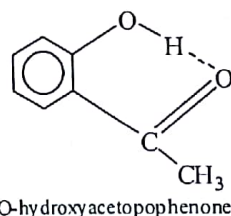
$\text{C} - \text{H}$ bending vibrations of acetylenes occurs at $700 - 610\text{ cm}^{-1}$ (strong band).

Aromatic hydrocarbons: The most prominent and most informative bands in the spectra of aromatic compounds occur in the low frequency range between $900 - 675\text{ cm}^{-1}$. Aromatic $\text{C} - \text{C}$ stretching bands occur between 3100 and 3000 cm^{-1} .

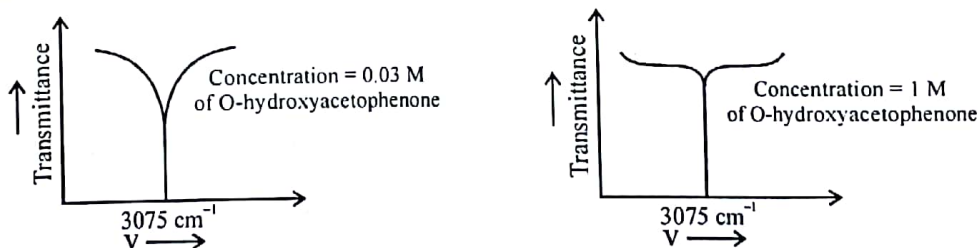
Alcohols and Phenols : $\text{O} - \text{H}$ stretching and $\text{C} - \text{O}$ stretching are characteristics of alcohols and phenols. If OH is "free" (non-hydrogen bonded) then strong absorption occur at $3650 - 3580\text{ cm}^{-1}$. Such sharp absorptions occur only in very dilute solutions of alcohols in non-polar solvents. Intermolecular hydrogen bonding increases as the concentration of the solution increases and the $\text{O} - \text{H}$ stretching frequency is shifted to lower values.



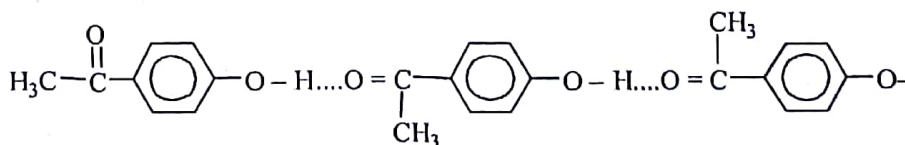
Strong intramolecular hydrogen bonding occurs in ortho-hydroxyacetophenone and here again the $\text{O} - \text{H}$ stretching frequency is less than in free phenol.



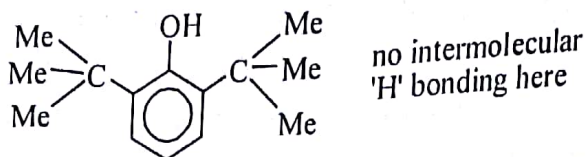
OH stretching absorption occurs at 3077 cm^{-1} . This absorption is broad, shallow and independent of concentration.



$\text{HO} - \text{C}_6\text{H}_4 - \text{COCH}_3$ shows free hydroxyl peak at 3600 cm^{-1} in dilute CCl_4 solution and broad strong peak at 3100 cm^{-1} in the neat sample (no solvent). This is due to intermolecular 'H' bonding in the pure sample.



In 2,6-ditertiaryphenol, steric hindrance prevents H-bonding.



Non-bonded -OH stretching is observed in this compound. C-O stretching vibrations in alcohols/phenols produce a strong band in the $1260 - 1000 \text{ cm}^{-1}$.

Ethers

The characteristics of ethers in the IR is the C-O-C stretching vibrations—it is 1150 to 1085 cm^{-1} for aliphatic ethers (e.g. COC). C-O-C asymmetric stretching occurs at 1275 to 1200 cm^{-1} along with 1075 to 1020 cm^{-1} and C=C stretching here is at higher intensity than in olefins. This C=C stretching usually occurs as a doublet at 1620 cm^{-1} and 1640 cm^{-1} .

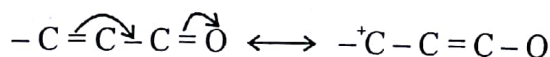
Carbonyl compounds

The absorption band for the carbonyl group (C=O) is very strong and sharp, hence easy to recognise. A strong absorption in the region 1660 to 1850 cm^{-1} generally points to the carbonyl group is a ubiquitous (i.e. widespread) structural feature in organic compounds. (Though C=C occurs in the above frequency range, the intensity will be only moderate). The carbonyl group forms part of various functional groups such as aldehydes, ketones, acid chlorides, esters, acid amides and acid anhydrides. Frequency of absorption of a neat sample of a saturated ketone (aliphatic) viz. 1715 cm^{-1} is taken as normal.

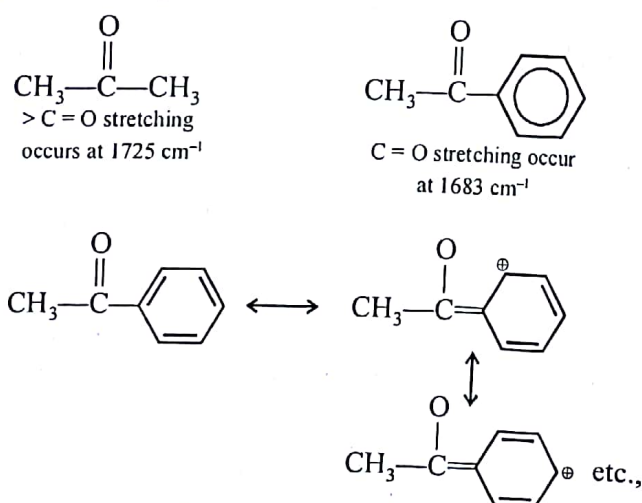
(aliphatic ketones: 1725 to 1700 cm^{-1} ;

alkaryl: 1700 to 1680 cm^{-1} ; diaryl: 1670 to 1660 cm^{-1})

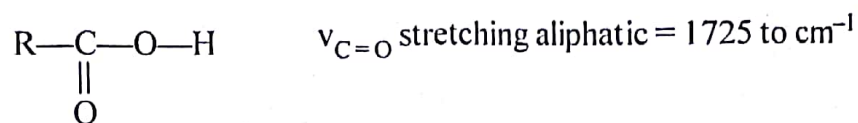
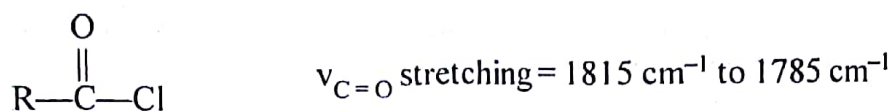
conjugation of C=O with C=C resulting resonance



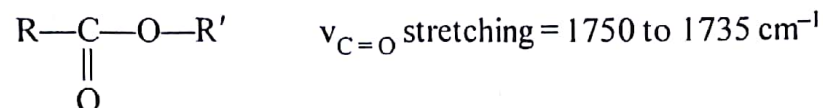
It reduces double bond character between C and O of carbonyl group. Hence absorption occurs at lower frequency (wave number).



More canonical structures are possible with single bond between "C" and "O" of carbonyl group. Absorption of >C=C< in conjugation with carbonyl occurs at lower frequency than that of isolated >C=C< .

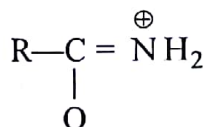


aromatic = 1700 to 1680 cm^{-1} (monomeric form)



Here OH, OR and Cl groups are electron attracting. Inductive effect enhances = O (double bond character).

In $\text{R}-\text{C}-\text{NH}_2$ there is resonance and the canonical form is

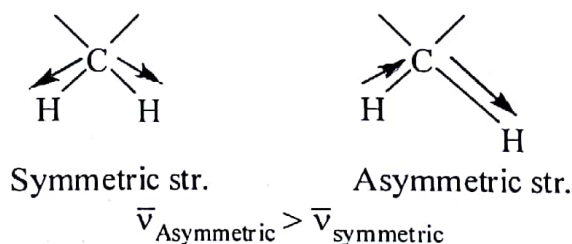


Hence C = O stretching of RCONH_2 is 1695 – 1650 cm^{-1} .

β -diketone shows broad band at 1640 – 1540 cm^{-1} . The displaced absorption results from intramolecular H-bonding.

Coupled Vibration

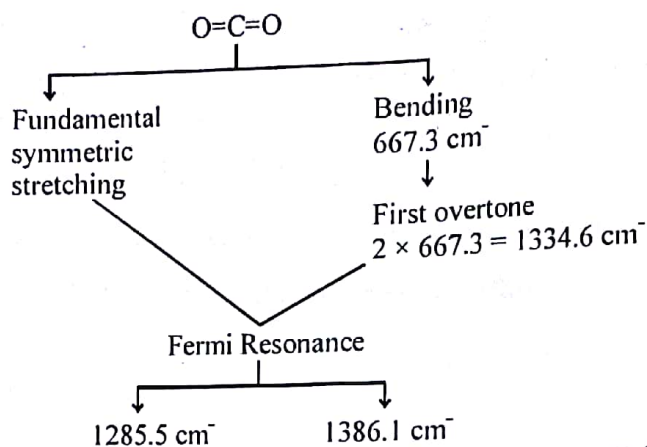
An isolated C–H bond exhibit one stretching frequency but in case of methylene group ($-\text{CH}_2-$) or methyl group ($-\text{CH}_3$) two absorption frequency occur. Which correspond to symmetric stretching and asymmetric stretching



Fermi Resonance

The energy resonance between fundamental band and adjacent overtone, due to this both band shifted from their original position in which one goes to higher frequency and another goes to lower frequency and become almost same intensity this phenomena is known as Fermi resonance.

Fermi resonance was first observed was Enrico Fermi in CO_2 molecule



The intensity of both peak after Fermi Resonance is allmost same (1 : 0.9) because after Fermi Resonance fundamental peak become partial over tone and over tone peak have partial fundamental charactor.

Example: In aldehyde C–H stretching, two peak occur at 2720 cm^{-1} due to Fermi Resonance.

Illustration: An organic compound with molecular formula C_3H_7NO shows absorption data in the region 3415 (m) , 3236 (m) , $3030 - 2899 \text{ (m)}$, 1668 (s) , 1635 (s) and $1460 \text{ cm}^{-1} \text{ (s)}$. Give the probable structure of the compound.

Solution: $CH_3CH_2CONH_2$

Illustration: An organic compound A with molecular formula, C_3H_9N shows the following peaks in the infrared spectrum;

(i) $3012 \text{ cm}^{-1} \text{ (m)}$, (ii) $3425 \text{ cm}^{-1} \text{ (s)}$, (iii) $3236 \text{ cm}^{-1} \text{ (m)}$, (iv) $1615 \text{ cm}^{-1} \text{ (m)}$.

When the compound A is treated with nitrous acid, we obtain a compound B which shows a strong peak at 3430 cm^{-1} . Identify A and B.

Solution: (i) Two bands at 3425 cm^{-1} and 3236 cm^{-1} are due to asymmetrical and symmetrical N–H stretching. Clearly, the compound contains – NH_2 group. (ii) The bands at 3012 cm^{-1} is due to C–H str while the band at 1615 cm^{-1} is due to N–H bending. The probable compound is $CH_3CH_2CH_2NH_2$. When it is treated with nitrous acid, – NH_2 is converted into OH group which shows a strong peak at 3430 cm^{-1} .

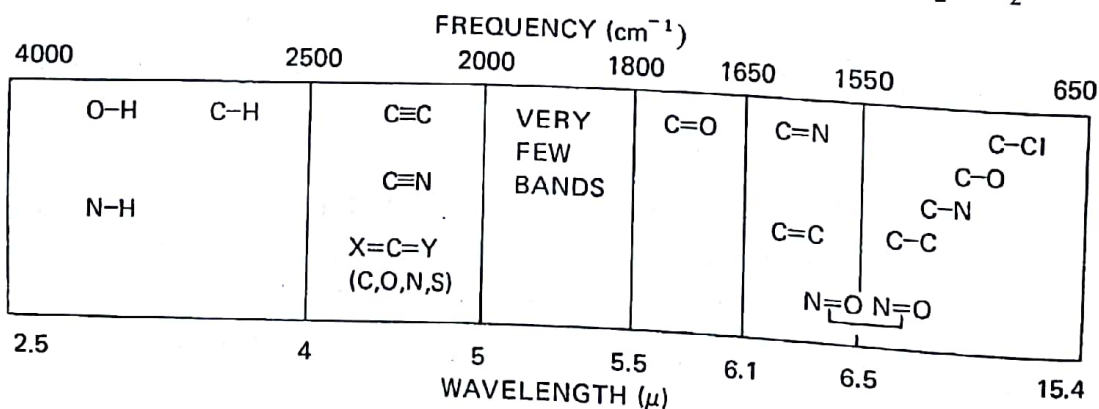
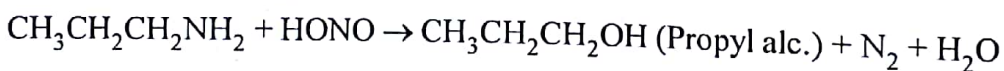


FIGURE The approximate regions where various common types of bonds absorb (stretching vibrations only; bending, twisting, and other types of bond vibrations have been omitted for clarity).

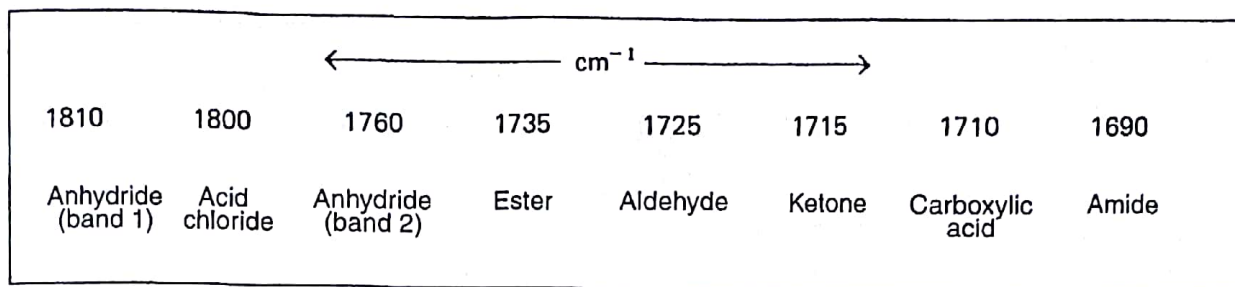


FIGURE Normal base values for the C=O stretching vibrations for carbonyl groups.

NMR SPECTROSCOPY

Introduction

The nuclei of many elemental isotopes have a characteristic spin (I). Some nuclei have integral spins (e.g. $I = 1, 2, 3 \dots$), some have fractional spins (e.g. $I = 1/2, 3/2, 5/2 \dots$), and a few have no spin, $I = 0$ (e.g. ^{12}C , ^{32}S , ^{16}O , ^{32}S , etc). Nuclei with even atomic numbers and even mass numbers are invisible in NMR. Isotopes of particular interest and use to organic chemists are ^1H , ^{13}C , ^{19}F and ^{31}P , all of which have a $g = 1/2$.

- Essentials of an NMR spectrometer are a powerful magnet a radio-frequency generator, and a radio frequency detector.
- The sample is dissolved in a solvent, most commonly CDCl_3 or D_2O and placed in a sample tube which is then suspended in the magnetic field and set spinning.
- Deuterated solvents are used to eliminate ^1H signals from the solvent.

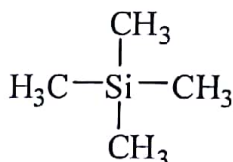
Chemical Shift:

Table of characteristic proton NMR chemical shifts

Type of proton	Type of compound	Chemical shift range, ppm
RCH_3	1° aliphatic	0.9
R_2CH_2	2° aliphatic	1.3
R_3CH	3° aliphatic	1.5
$\text{C}=\text{C}-\text{H}$	vinyllic	4.6–5.9
$\text{C}=\text{C}-\text{H}$	vinyllic, conjugated	5.5–7.5
$\text{C}\equiv\text{C}-\text{H}$	acetylenic	2–3
$\text{Ar}-\text{H}$	aromatic	6–8.5
$\text{Ar}-\text{C}-\text{H}$	benzylic	2.2–3
$\text{C}=\text{C}-\text{CH}_3$	allylic	1.7
$\text{HC}-\text{F}$	fluorides	4–4.5
$\text{HC}-\text{Cl}$	chlorides	3–4
$\text{HC}-\text{Br}$	bromides	2.5–4
$\text{HC}-\text{I}$	iodides	2–4
$\text{HC}-\text{OH}$	alcohols	3.4–4
$\text{HC}-\text{OR}$	ethers	3.3–4

RCOO-CH	esters	3.7-4.1
HC-COOR	esters	2-2.2
HC-COOH	acids	2-2.6
HC-C=O	carbonyl compounds	2-2.7
RCHO	aldehydic	9-10
ROH	hydroxylic	2-4
ArOH	phenolic	4-12
C=C-OH	enolic	15-17
RCOOH	carboxylic	10-13.2
HC-NHR	amine	1.5-2.0
RNH ₂	amino	1-5
RNHC(=O)R'	amides	5-8.5

- If we were dealing with nuclei isolated from other atoms and electrons, any combination of applied field and radiation that produces a signal for one nucleus would produce a signal for all identical nuclei.
- Hydrogen or carbon nuclei in organic molecules are not isolated from other atoms, they are surrounded by electrons which are caused to circulate by the presence of the applied field.
- The circulation of electrons around a nucleus in an applied field is called diamagnetic current and the nuclear shielding resulting from it is called diamagnetic shielding.
- The difference in resonance frequencies among the various hydrogen or carbon nuclei within a molecule due to shielding or deshielding is generally very small.
- It is customary to measure the resonance frequency (signal) of a reference compound.
- The reference compound now universally accepted is tetramethylsilane (TMS).



Chemical shift (δ): The shift of an NMR signal from the signal of TMS. Normally given in parts per million (PPM).

$$\delta = \frac{\text{Shift in frequency from TMS(Hz)}}{\text{Frequency of spectrometer (Hz)}}$$

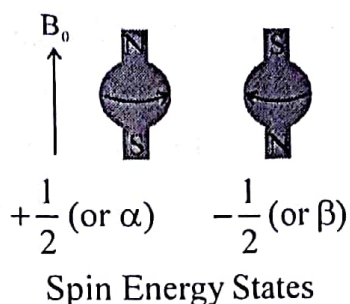
NMR phenomenon

1. A spinning charge generates a magnetic field. The resulting spin-magnet has a magnetic moment (μ) proportional to the spin (I).

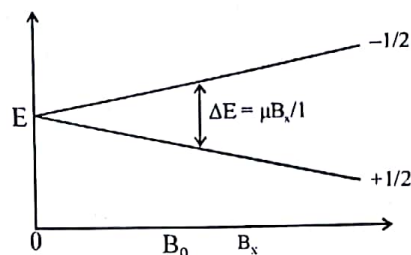


2. In the presence of an external magnetic field (B_0), two spin states are, $+1/2$ and $-1/2$. The magnetic moment of the lower energy $+1/2$ state is aligned with the external field, but that of the higher energy, $-1/2$

2 spin state is opposed to the external field. The arrow representing the external field points North.



3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The following diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases.



For NMR purpose, this small energy difference (ΔE) is usually given as a frequency in units of MHz (10^6 Hz), ranging from 20 to 900 MHz, depending on the magnetic field strength and the specific nucleus being studied.

Chemical Shift

- The electron(s) surrounding the proton in covalent compounds and ions are responsible for different NMR spectrum for different compounds. Since electrons are charged particles, they move in response to the external magnetic field (B_0) so as to generate a secondary field that opposes the much stronger applied field. This secondary field **shields** the nucleus from the applied so B_0 must be increased in order to achieve resonance (absorption of RF energy).
- The frequency of an NMR transition depends on the local magnetic field experienced by the nucleus and is expressed in terms of the **chemical shift**, δ , the difference between the resonance frequency of nuclei in the sample and that of a reference compounds :

$$\delta = \frac{\nu - \nu^0}{\nu^0} \times 10^6$$

A common standard for ^1H , ^{13}C or ^{29}Si spectra is Tetramethylsilane $\text{Si}(\text{CH}_3)_4$, abbreviated as TMS. When $\delta < 0$ the nucleus is said to be **shielded** relative to the standard; $\delta > 0$ corresponds to a nucleus that is **deshielded** with respect to the reference.

The H chemical shift in CH_4 is only 0.1 because the H nuclei are in an environment similar to that in Tetramethylsilane, but the H chemical shift is $\delta = 3.1$ for H in GeH_4 . Chemical shift are different for the same element in inequivalent positions within a molecule.

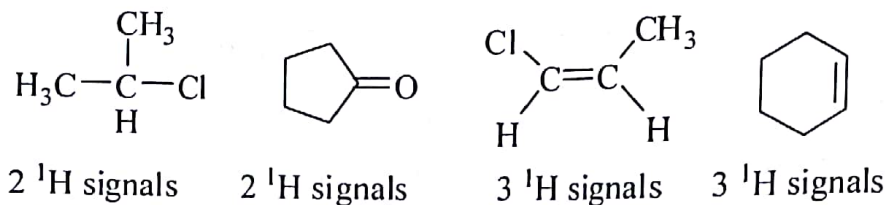
Chemical Equivalence

- All the protons found in chemically identical environments within a molecule are chemical equivalent and they often exhibit the same chemical shift. Thus all protons in trimethylsilane (TMS), benzene, cyclopentane or acetone have same δ value.
- Protons that are chemically equivalent are also magnetically equivalent, however in cases. Protons

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that are chemically equivalent are not magnetically equivalent.

- Equivalent atoms have the same chemical environment and may be related by symmetry.
- Molecules with one set of equivalent atoms give one NMR signal.
- Two or more sets of equivalent atoms give a different NMR signal for each set.



Chemical shift depends on:

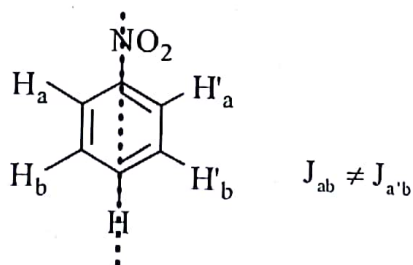
- Electron density → Induced magnetic field → shielding and deshielding
- Electron density depends on electronegativity of near by atoms hybridization of nearby atoms magnetic induction within an adjacent π bond.

Note:

- The number of signals shows how many different kinds of protons are present.
- The location of the signals shows how shielded or deshielded the proton is.
- The intensity of the signal shows the number of protons of that type.
- Signal splitting shows the number of proton on adjacent atoms.

Magnetic equivalence: Magnetically equivalent nuclei are isochronous have identical chemical shift and have equal coupling (J) to every other nuclei in the molecule.

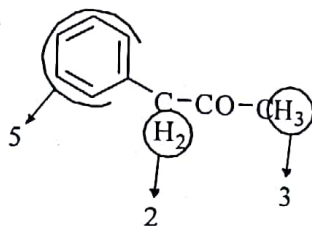
Similarly, if two nuclei are magnetically equivalent, they give a single signal and do not split one another.



Chemically identical nuclei (H_a and H'_a) is different to H_b .

Integrals and Integration

- In the NMR spectrum, the area under each peak is proportional to the number of hydrogen generating that peak. Hence in phenyl acetone. The area ratio of the three peaks is 5 : 2 : 3, the same as the ratio of the number of the three types of hydrogen.



Local Diamagnetic Shielding

(A) Electronegativity effects (Electronegativity = E.N.)

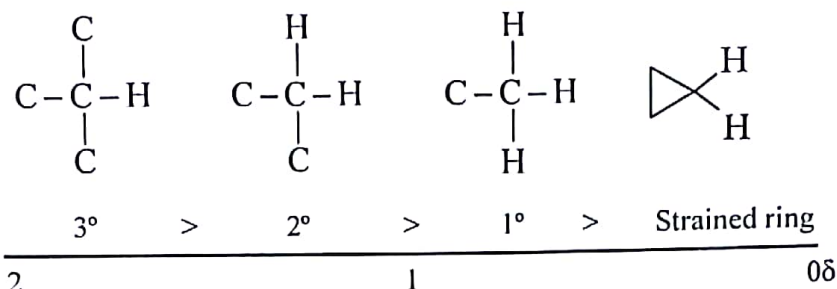
E.N. \uparrow , $\delta \uparrow$ (Electronegativity of attached element increase, chemical shift increase)

Electronegative substituents attached to a carbon atom, because of their electron withdrawing effects, reduce the valence electron density around the proton attached to that carbon.

These electron shield the proton from applied magnetic field. This effect is called Local Diamagnetic Shielding.

(B) Hybridization effect

sp^3 Hydrogen



sp^2 hydrogen

in an sp^2 - 1s C-H bond, the carbon atom has more s character (33% s) which effectively renders it "more electronegative" than on sp^3 carbon. (25% s). This result in less shielding for the H molecules than in an sp^3 - 1s bond. Thus

δ for vinyl hydrogen \rightarrow 5 - 6 ppm

δ for aromatic hydrogen \rightarrow 7 - 8 ppm (high δ value due to anomalously large chemical shift due to anisotropy)

δ for aldehyde proton \rightarrow 9 - 10 ppm (high δ value due to anomalously large chemical shift due to anisotropy)

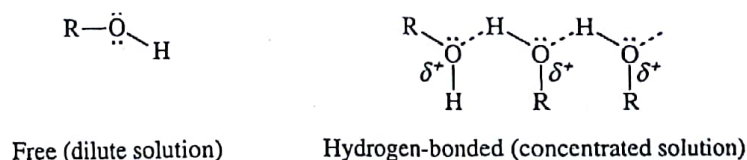
sp hydrogen

Acetylenic protons have greater δ value than sp^2 carbon protons.

(C) Influence of Hydrogen Bonding

Proton that can exhibit hydrogen bonding exhibit extremely variable absorption positions over a wide range. The more hydrogen bonding that take place, the more deshielded a proton becomes. The amount of H-bonding is often a function of concentration of temperature.

At high dilution (no H-bonding), hydroxyl proton absorb near 0.5-10 ppm. In concentrated solution, their absorption is closer to 4-5 ppm.



MAGNETIC ANISOTROPY

When it is placed in a magnetic field, the π electrons in the aromatic ring system are induced to circulate around the ring. This circulation is called a ring current. The moving electrons generate in a loop of wire

through which a current is induced to flow. The magnetic field covers a spatial volume large enough that it influences the shielding of the benzene hydrogens. The benzene hydrogens are said to be deshielded by the diamagnetic anisotropy of the ring. All groups in a molecule that have π electrons generate secondary anisotropic fields. In acetylene, the magnetic field generated by induced circulation of the π electrons has a geometry such that the acetylenic hydrogens are shielded. Hence, acetylenic hydrogens have resonance at higher field than expected.

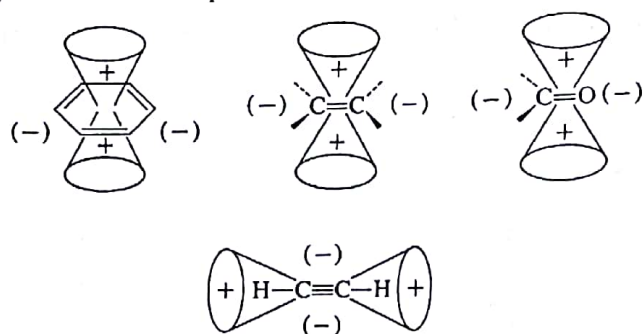


Fig. Anisotropy caused by the presence of π electrons in some common multiple bond systems.

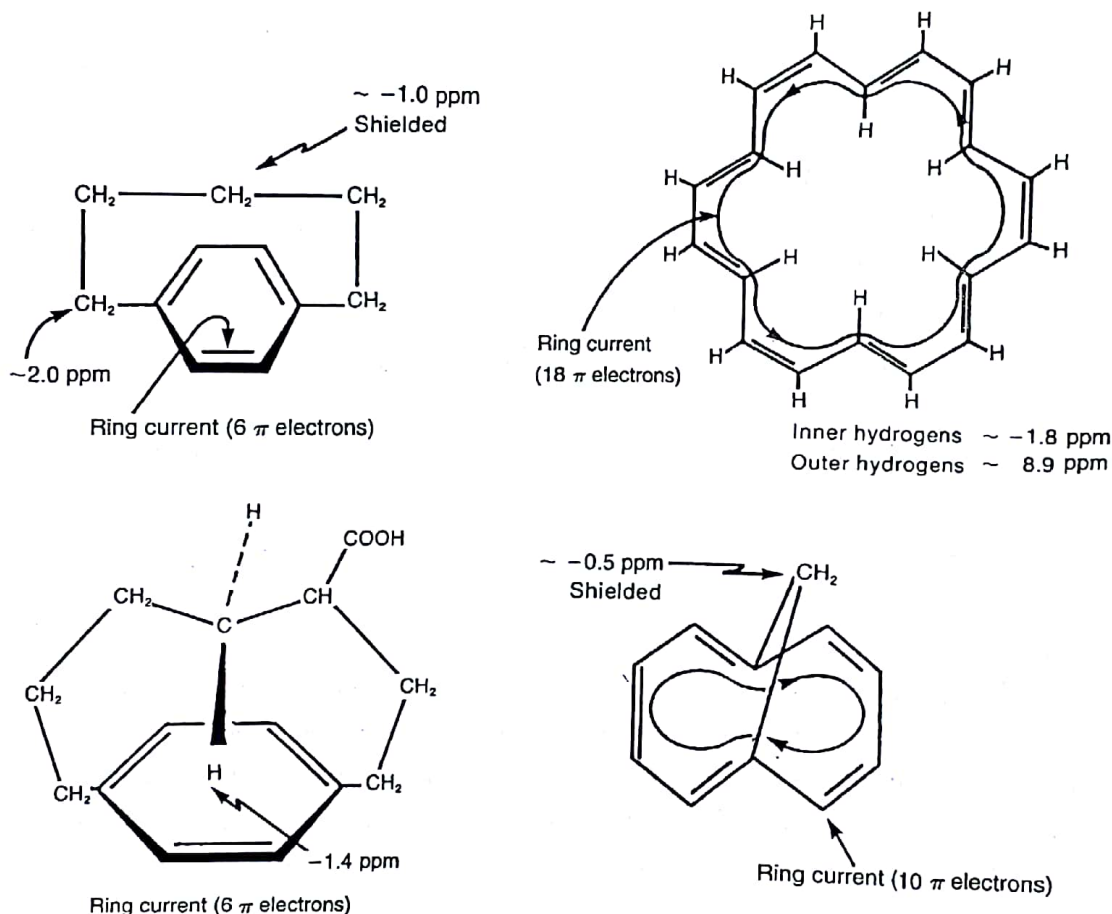
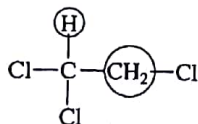


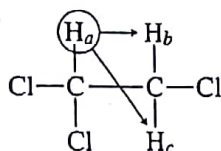
Fig. The effects of anisotropy in some actual molecules.

SPIN-SPIN SPLITTING RULE

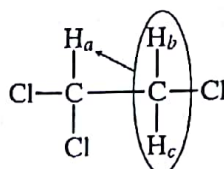
In 1,1,2-trichloroethane there are two chemically distinct types of hydrogens:



On the basis of the information one would predict two resonance peaks in the NMR spectrum of 1,1,2-trichloroethane, with an area ratio (integral ratio) of 2:1. In reality, the high resolution NMR spectrum of this compound has five peaks: a group of three peaks (called a triplet) at 5.77 ppm and a group of two peaks (called a doublet) at 3.95 ppm. The methine (CH) resonance (5.77 ppm) is said to be split into a triplet, and the methylene resonance (3.95 ppm) is split into a doublet. The area under the three triplet peaks is 1, relative to an area of 2 under the two doublet peaks. This phenomenon, called spin-spin splitting, can be explained empirically by the so-called $n + 1$ Rule. Each type of proton "senses" the number of equivalent protons (n) on the carbon atom(s) next to the one to which it is bonded, and its resonance peak is split into $(n + 1)$ components.

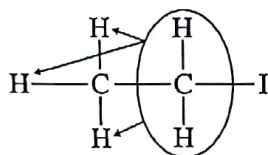


Two neighbors give a triplet
($n + 1 = 3$) (area = 1)

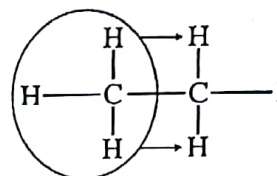


Equivalent protons
behave as a group

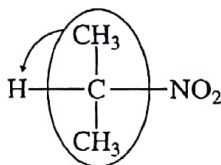
One neighbor gives a doublet
($n + 1 = 2$) (area = 2)



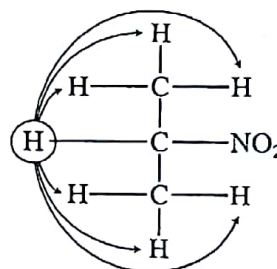
Three equivalent neighbors give a quartet
($n + 1 = 4$) (area = 2)



Two equivalent neighbors give a triplet
($n + 1 = 3$) (area = 3)



One neighbor gives a doublet
($n + 1 = 2$) (area = 6)



Six equivalent neighbors give a septet
($n + 1 = 7$) (area = 1)

THE ORIGIN OF SPIN-SPIN SPLITTING

Spin-spin splitting arises because hydrogens on adjacent carbon atoms can "sense" one another. The hydrogen on carbon A can sense the spin direction of the hydrogen on carbon B. Proton A is said to be coupled to proton B. Its magnetic environment is affected by whether proton B has a $+\frac{1}{2}$ or a $-\frac{1}{2}$ spin state. Thus, proton A absorbs at a slightly different chemical shift value in type X molecules than in type Y molecules. In fact, in X-type molecules, proton A is slightly deshielded because the field of proton B is aligned with the applied field, and its magnetic moment adds to the applied field. In Y-type molecules, proton A is slightly shielded with respect to what its chemical shift would be in the absence of coupling. In this latter case, the field of proton B diminishes the effect of the applied field on proton A.

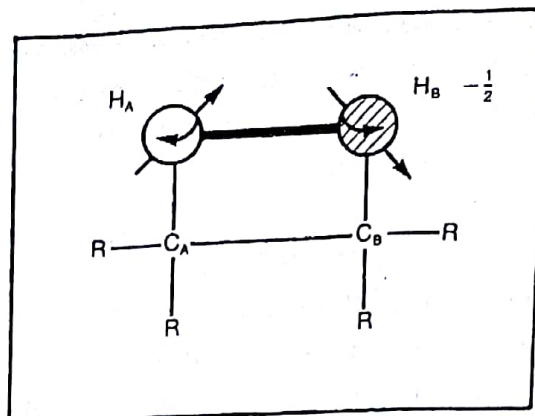
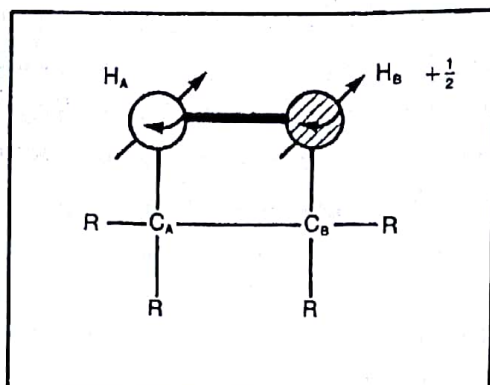
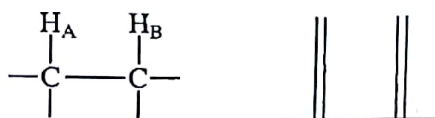


Fig. Two different molecules in a solution with differign spin relationships between protons H_A and H_B .

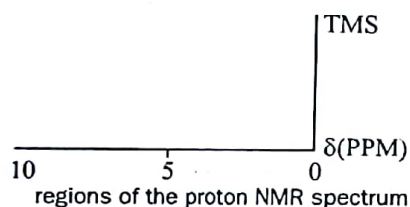
Since in a given solution there are approximately equal numbers of X- and Y-type molecules at any given time, two absorptions of nearly equal intensity are observed for proton A. The resonance of proton A is said to have been split by proton B, and the general phenomenon is called spin-spin splitting. Of course, proton A also "splits" proton B since proton A can adopt two spin states as well. The final spectrum for this situation consists of two doublets:



REGIONS OF THE PROTON NMR SPECTRUM

$$\text{Chemical Shift } (\delta) = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\text{Operating frequency}} \times 10^6 \text{ PPM}$$

$$\tau + \delta = 10$$



Me ₄ Si				
10.5	8.5	6.5	4.5	3.0
protons on unsaturated carbons next to oxygen: aldehydes	protons on unsaturated carbons: benzene, aromatic hydrocarbons	protons on unsaturated carbons: alkenes	saturated CH ₃ CH ₂ CH next to oxygen	saturated CH ₃ CH ₂ CH not next to oxygen
δ (p.p.m.) 0.0				

PROTONS ON SATURATED CARBON ATOMS

Chemical shift:	Atom	Electronegativity	Compound	¹ H NMR shift, p.p.m.
	Li	1.0	CH ₃ -Li	-1.94
	Si	1.9	CH ₃ -SiMe ₃	0.0
	N	3.0	CH ₃ -NH ₂	2.41
	O	3.4	CH ₃ -OH	3.50
	F	4.0	CH ₃ -F	4.27

	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃
¹ H NMR shift, p.p.m.	3.06	5.30	7.27

Approximate chemical shifts for methyl groups

No electron-withdrawing functional groups	Less electron-withdrawing functional groups X	More electron-withdrawing functional groups X
Me at about 1 p.p.m.	MeX at about 2 p.p.m. (i.e. add 1 p.p.m.)	MeX at about 3 p.p.m. (i.e. add 2 p.p.m.)
aromatic rings, alkenes, alkynes	carbonyl groups: acids (CO ₂ H), esters (CO ₂ R), ketones (COR), nitriles (CN) amines (NHR) sulfides (SR)	oxygen-based groups: ethers (OR), esters (OCOR) amides (NHCOR) sulfones (SO ₂ R)

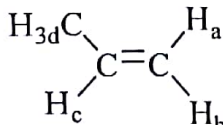
Chemical shifts of protons in CH, CH₂, and CH₃ groups with no nearby electron-withdrawing groups

CH group		CH₂ group		CH₃ group
	0.4 p.p.m. downfield ←		←	
1.7 p.p.m.		1.3 p.p.m.		0.9 p.p.m.

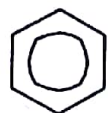
Number of NMR Signal

Number of NMR signal tell us about how many different kind of proton are present in the molecule.

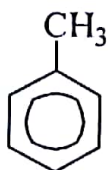
- Chemically equivalent proton gives 1-NMR signal
- Chemically non equivalent proton gives different NMR signal

Compound	Number of NMR signal
CH ₄	1 NMR signal
CH ₃ -CH ₃	1
CH ₂ =CH ₂	1
CH ₃ -CH ₂ -Cl	2
	4

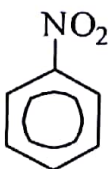
IIT-JAM/M.Sc. Entrance



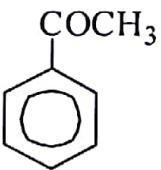
1



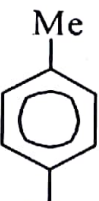
4



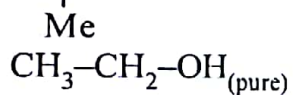
3



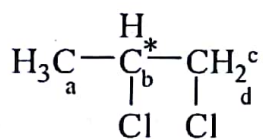
4



2



3

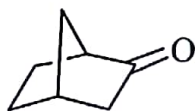


4

Here c & d are diastereotopic proton



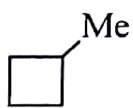
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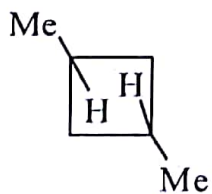
10



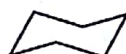
4



6

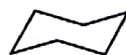


3



2

(-89°C)



1 (Room temperature)

Splating of the Signal

Splating of the signal tell us about heigh bouring environment of the proton that is they give the information of number of neighbouring proton in the molecule.

* Due to spin-spin interaction with neighbouring proton NMr signal splated according to $(2NI + 1)$ rules

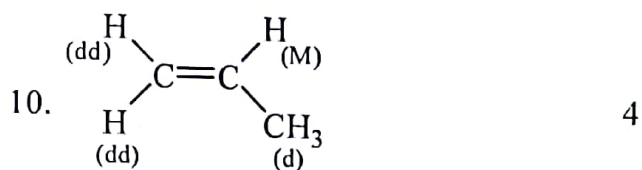
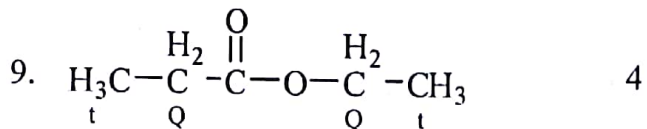
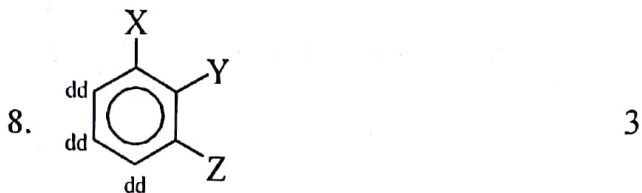
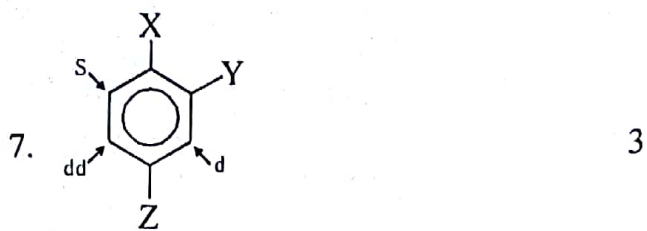
N = number of neighbouring proton

I = nuclear spin quantum number of neighbouring proton.

Example:

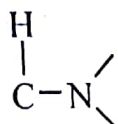
Compound	Signal
1. $\text{H}_3\text{C}-\underset{\downarrow}{\text{C}}(\text{H})_2-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\downarrow}{\text{C}}\text{H}_3$ (t) (Q) (S)	3
2. $\underset{t}{\text{CH}_3}-\underset{q}{\text{CH}_2}-\underset{s}{\text{NH}_2}$	2
3. $\text{H}_3\underset{(s)}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{(s)}{\text{NH}_2}$	2
4.	5
5. $\text{H}_3\underset{t}{\text{C}}-\underset{dQ}{\text{C}}(\text{H})_2-\overset{\text{O}}{\parallel}{\text{C}}-\underset{t}{\text{H}}$	3
6.	5

s = singlet
 d = doublet
 t = triplet
 Q = Quartet
 M = Multiplat



Spleating / Coupling with hetro nucleia

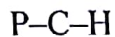




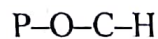
No splitting



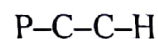
Splitting



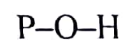
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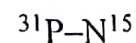
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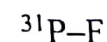
Splitting



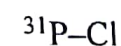
No splitting



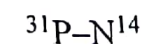
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Splitting



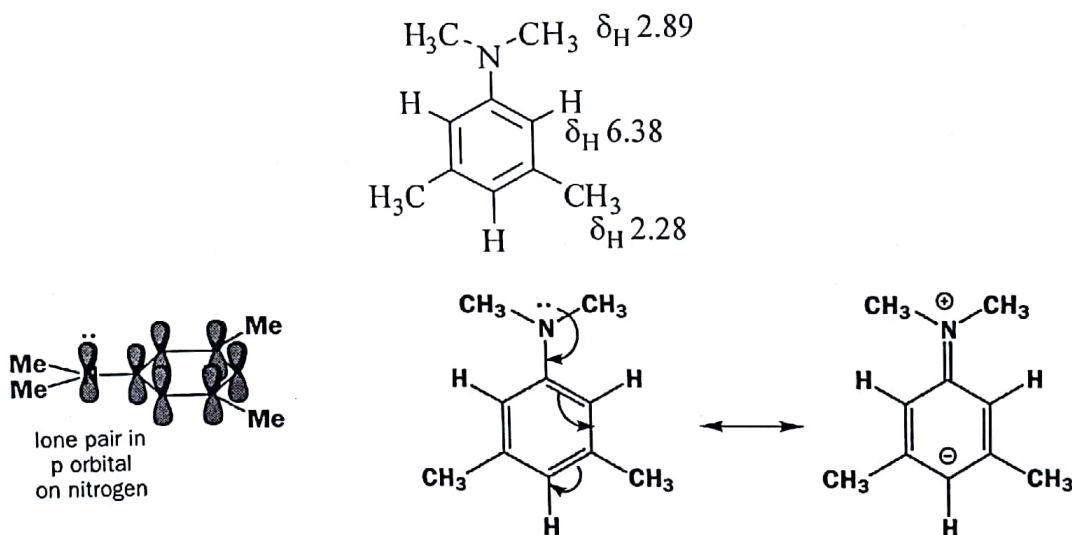
No splitting



No splitting

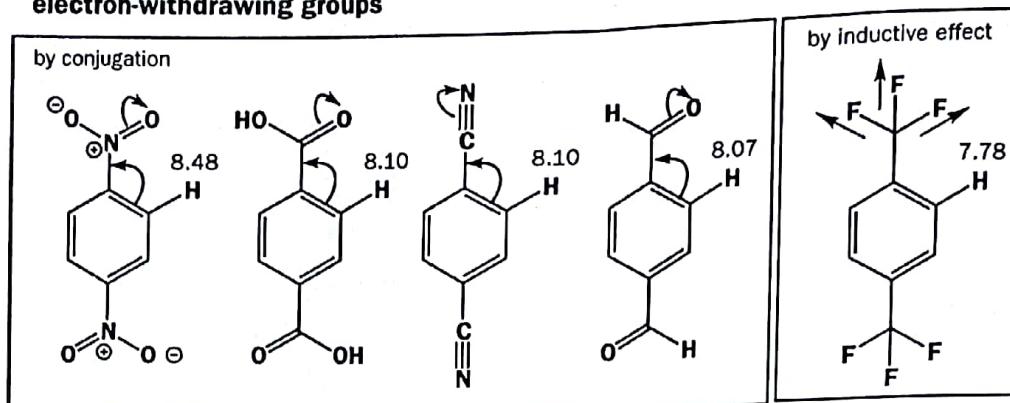
Uneven electron distribution in aromatic rings

The ^1H NMR spectrum of this simple aromatic amine has three peaks in the ratio 1:2:2, which must correspond to 3H:6H:6H. The 6.38 ppm signal clearly belongs to the protons round the benzene ring, but why are they at 6.38 and not at around 7.2 ppm? The solution to both these puzzles is the distribution of electrons in the aromatic ring. Nitrogen feeds electrons into the π system, making it electron rich: the ring protons are more shielded and the nitrogen atom becomes positively charged and its methyl groups more deshielded. The peak at 2.89 ppm must belong to the NMe_2 group.



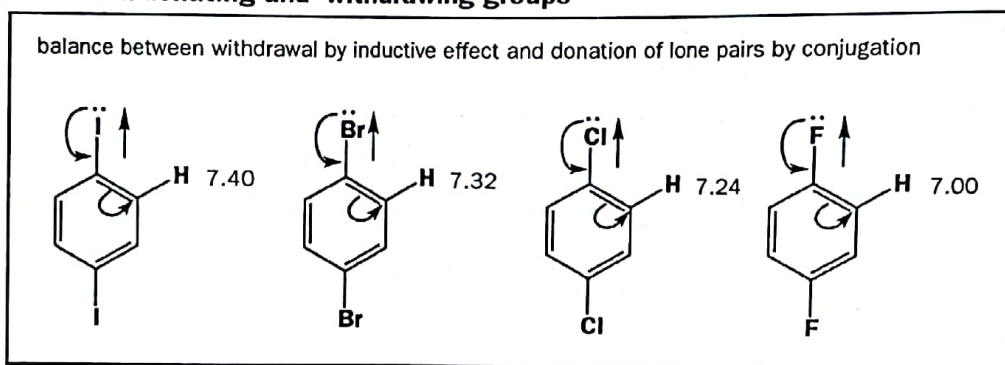
How electron donation and withdrawn change chemical shifts

electron-withdrawing groups



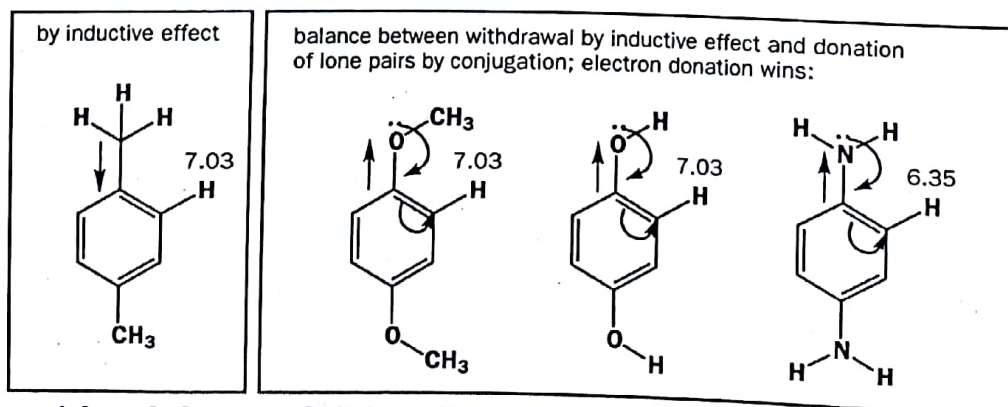
The largest shifts come from groups that withdraw electrons by conjugation. Nitro is the most powerful. Then come the carbonyl and nitrile group followed by groups showing simple inductive withdrawal. CF_3 is an important example of this kind of group—three fluorine atoms combine to exert a powerful effect. In the middle of our sequence, around the position of benzene itself at 7.27 ppm, come the halogens, whose inductive electron withdrawal and lone pair donation are nearly balanced.

electron-donating and -withdrawing groups



Alkyl groups are weak inductive donors, but the groups which give the most shielding—perhaps surprisingly—are those containing the electronegative atoms O and N. Despite being inductively electron withdrawing (the C-O and C-N σ bonds are polarized with $\delta^+ \text{C}$), on balance conjugation of their lone pairs with the ring makes them net electron donors. They increase the shielding at the ring hydrogens. Amino groups are the best. Note that one nitrogen-based functional group (NO_2) is the best electron withdrawer while another (NH_2) is the best electron donor.

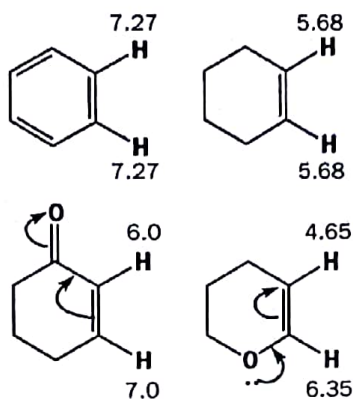
electron-donating groups



Electron rich and electron-deficient alkenes

A conjugating and electron-withdrawing group such as a ketone removes electrons from the double

bond as expected. The nearer the C=O group is only slightly downfield from cyclohexene but the more distant one is over 1 ppm downfield.



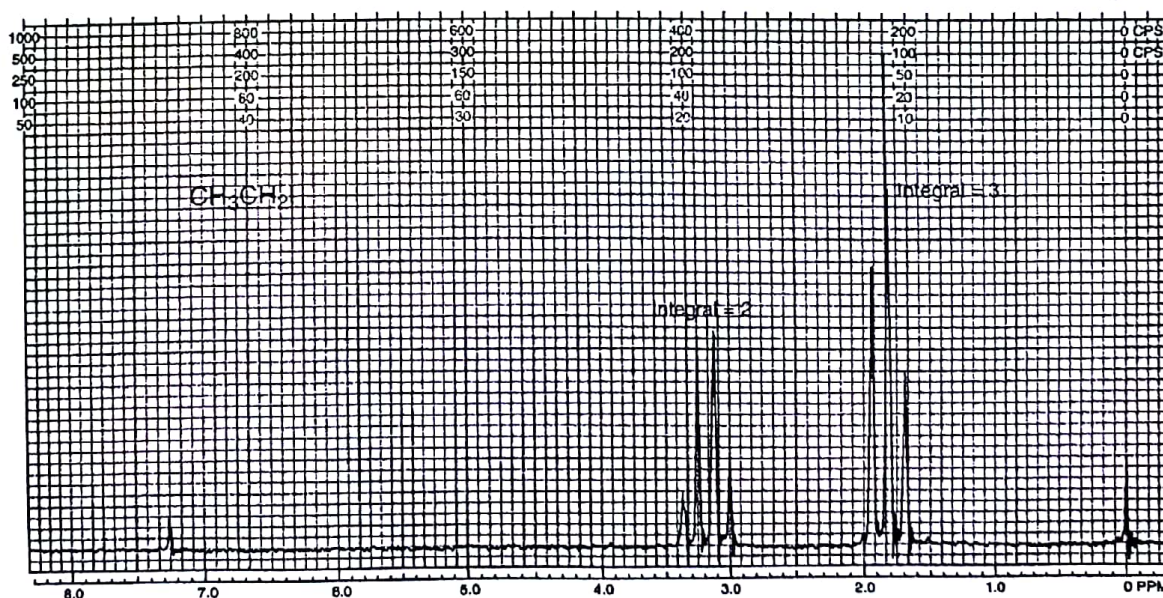
Oxygen a conjugating electron donor is even more dramatic. It shifts the proton next to it downfield by the inductive effect but pushes the more distant proton upfield a whole 1 ppm by donating electrons.

THE COUPLING CONSTANT

The distance between the peaks in a simple multiplet is called the coupling constant J . The coupling constant is a measure to how strongly a nucleus is affected by the spin states of its neighbour. The spacing between the multiplet peaks is measured on the same scale as the chemical shift, and the coupling constant is always expressed in Hertz (Hz). In ethyl iodide, for instance, the coupling constant J is 7.5 Hz. The spectrum in Figure was determined at 60 MHz; thus, each ppm of chemical shift (δ unit) represents 60 Hz. Inasmuch as there are 12 grid lines per ppm, each grid line represents $(60 \text{ Hz})/12 = 5 \text{ Hz}$. Notice the top of the spectrum. It is calibrated in cycles per second (cps), which are the same as Hertz, and since there are 20 chart divisions per 100 cps, one division equals $(100 \text{ cps})/20 = 5 \text{ cps} = 5 \text{ Hz}$. Now examine the multiplets. The spacing between the component peaks is approximately 1.5 chart divisions, so

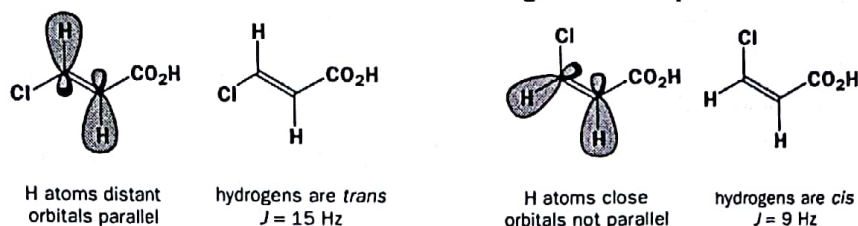
$$J = 1.5 \text{ div} \times \frac{5 \text{ Hz}}{1 \text{ div}} = 7.5 \text{ Hz}$$

That is, the coupling constant between the methyl and methylene protons is 7.5 Hz. When the protons interact, the magnitude (in ethyl iodide) is always of this same value, 7.5 Hz. The amount of coupling is constant, and hence J can be called a coupling constant.



Coupling is a through bond effect

Coupling is in fact a 'through bond effect' because of the way coupling constants vary with the shape of the molecule. The most important case occurs when the protons are at either end of a double bond. If the two hydrogens are *cis*, the coupling constant J is typically about 10 Hz, but if they are *trans*, J is much larger, usually 15-18 Hz. These two chloro acids are good examples.



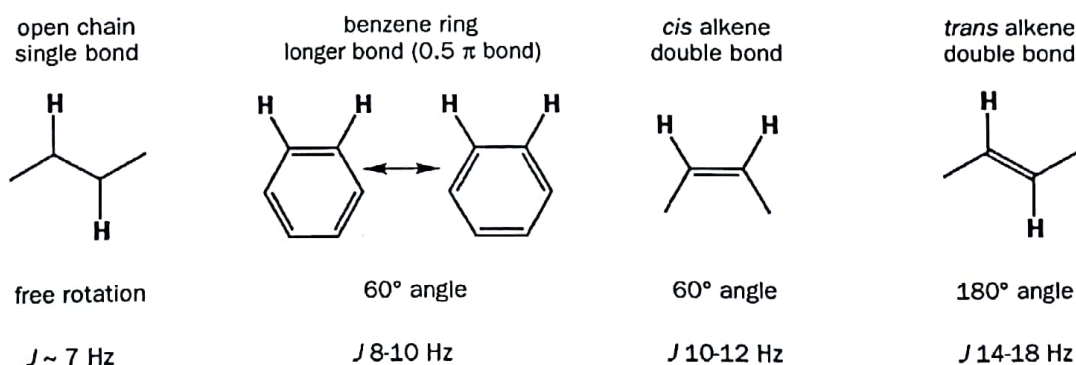
Coupling constants depend on three factors

Factors affecting coupling constants

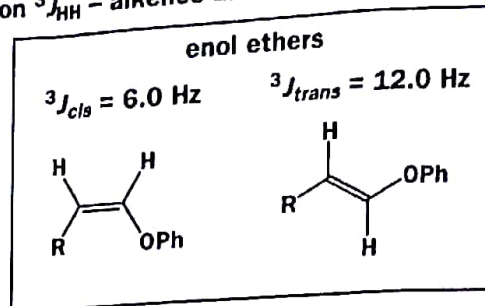
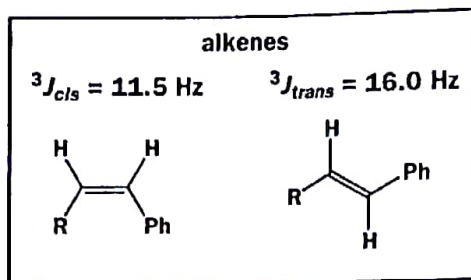
- Through bond distance between the protons.
- Angle between the two C-H bonds.
- Electronegative substituents.

The coupling constants we have seen so far have all been between hydrogen atoms on neighbouring carbon atoms—in other words, the coupling is through three bonds (H-C-C-H) and is designated $^3J_{\text{HH}}$. These coupling constants $^3J_{\text{HH}}$ are usually about 7 Hz in an open-chain, freely rotating system such as we have in heptanone. Coupling ($^3J_{\text{HH}}$) across double bonds are usually larger than 7 Hz (11 Hz in cyclohexenone). $^3J_{\text{HH}}$ couplings are called vicinal couplings because the protons concerned are on neighbouring carbon atoms. But across a double bond there is no rotation and the angle between the two C-H bonds is fixed: they are always in the same plane. In the plane of the alkene, the C-H bonds are either at 60° (*cis*) or 180° (*trans*) to each other. Coupling constants in benzene rings are slightly less than those across *cis* alkenes because the bond is longer (bond order 1.5 rather than 2).

$^3J_{\text{HH}}$ coupling constants

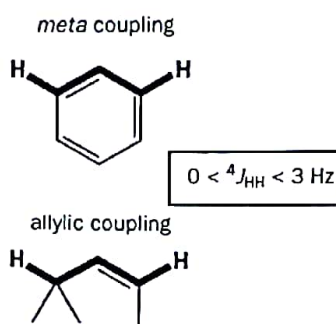


The effect of the third factor, electronegativity, is easily seen in the comparison between ordinary alkenes and alkenes with alkoxy substituents, known as enol ethers. One pair has a phenyl group at one end of the alkene and the other has an OPh group. For either pair, the *trans* coupling is larger than the *cis*, as you would now expect. But if you compare the two pairs, the enol ethers have much smaller coupling constants. The *trans* coupling for the enol ethers is only just larger than the *cis* coupling for the alkenes. The electronegative oxygen atom is withdrawing electrons from the C-H bond in the enol ethers and weakening communication through the bonds.

effect of electronegative substituents on $^3J_{\text{HH}}$ - alkenes and enol ethers

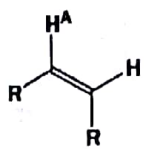
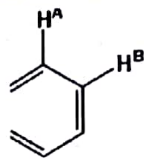
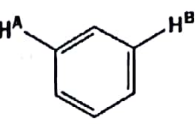
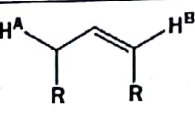
Long-range coupling

Four bond coupling $^4J_{\text{HH}}$ is usually zero. However, it is seen in some special cases, the most important being meta coupling in aromatic rings and allylic coupling in alkenes. In both, the orbitals between the two hydrogen atoms can line up in a zig-zag fashion to maximize interaction. This arrangement looks rather like a letter 'W' and this sort of coupling is called W-coupling. Even with this advantage, values of $^4J_{\text{HH}}$ are usually small, about 1-3 Hz.

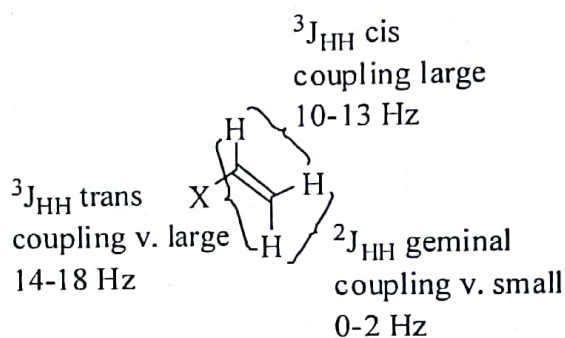


Typical Coupling Constant

Geminal $^2J_{\text{HH}}$		
saturated		10-16 Hz
unsaturated		0-3 Hz
Vicinal $^3J_{\text{HH}}$		
saturated		6-8 Hz
unsaturated <i>trans</i>		14-16 Hz

unsaturated <i>cis</i>		8–11 Hz
unsaturated aromatic		6–9 Hz
Long-range ${}^4J_{HH}$		
<i>meta</i>		1–3 Hz
allylic		1–2 Hz

Coupling constants in a vinyl group



PASCAL'S TRIANGLE

Intensity ratios of multiplets derived from the $n + 1$ Rule follow the entries in the mathematical mnemonic device called Pascal's triangle. Each entry in the triangle is the sum of the two entries above it and to its immediate left and right.

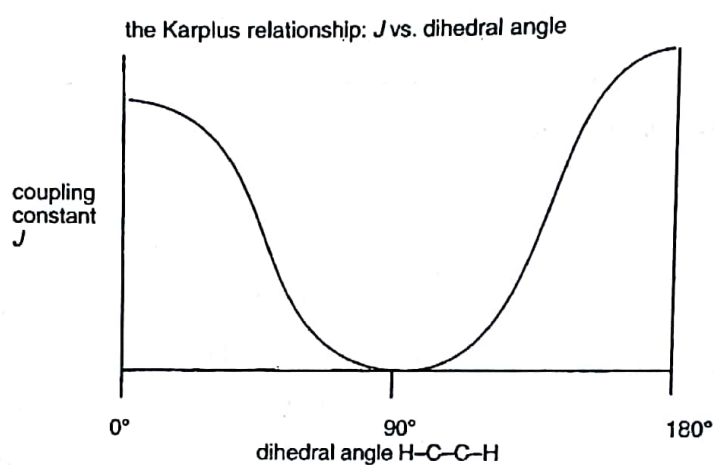
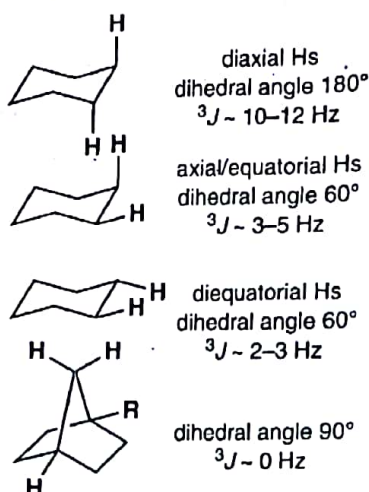
Singlet	1
Doublet	1 1
Triplet	1 2 1
Quartet	1 3 3 1
Quintet	1 4 6 4 1
Sextet	1 5 10 10 5 1
Septet	1 6 15 20 15 6 1

Pascal's Triangle

Using NMR to study conformation: the Karplus relationship

The coupling constants in a cyclohexane tell us that coupling is greatest when the C–H bonds involved are most parallel—in other words when their dihedral angle is close to 180° or 0° . C–H bonds in simple cyclohexanes can have dihedral angles of only 60° or 180° , but by examining coupling constant in a

range of other compounds, it is possible to draw up a description of the way coupling varies with dihedral angle. The complete correlation was worked out by Karplus in the 1960s and is called the Karplus relationship. It is easiest to understand as a graph of J against dihedral angle.



Examine the graph above carefully and note these principal features:

- Coupling is largest at 180° when the orbitals of the two C–H bonds are perfectly parallel (the in a trans alkene or the trans-diaxial C–H bonds of a cyclohexane).
- Coupling is nearly as large at 0° when the orbitals are in the same plane but not parallel (the situation in a cis alkene).
- Coupling is zero when the dihedral angle is 90° - orthogonal orbitals do not interact.
- The curve is flattened around 0° , 90° and 180° - J varies little in these regions from compound to compound.
- The curve slopes steeply at about 60° and 120° - J varies a lot in this region with small changes of angle and from compound to compound.
- Numerical values of J vary with substitution, ring size, etc., but the Karplus relationship still works - It gives good relative values.

EXERCISE - I

Single Correct Type

Infrared Spectroscopy

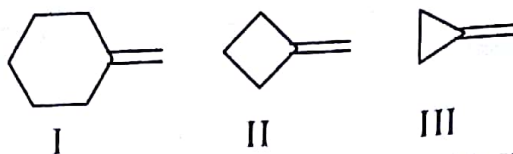
- Hooke's law relates the restoring force, f to the displacement q as
 (a) $f = -Kq$ (b) $f = Kq$ (c) $f = Kq^2$ (d) $f = -Kq^2$
- The intensity of an absorption band is always proportional to the
 (a) Atomic population
 (b) Molecular population of the initial state
 (c) Molecular population of the final state
 (d) Temperature
- The vibrational stretching frequency of diatomic molecule depends on
 (a) Force constant (b) Masses of two atoms
 (c) Both a and b (d) None
- Force constant is expressed in
 (a) Dynes cm^{-1} (b) dyne \AA^{-1} (c) Nm^{-1} (d) All
- For HCl, $\mu = 1.63 \times 10^{-27}$ kg, the observed frequency $\bar{\nu} = 2890 \text{ cm}^{-1}$ or $\nu = 8.67 \times 10^{13}$ Hz. The force constant K is
 (a) $4.83 \text{ m dyn \AA}^{-1}$ (b) $8.43 \text{ dynes cm}^{-1}$
 (c) $483 \mu\text{m}^{-1}$ (d) Both a and c
- q for NO, CO, HCl is 0.048 \AA , 0.05 \AA , 0.10 \AA . Thus q is
 (a) Larger when the force constant is smaller
 (b) Smaller when the force constant is smaller
 (c) Larger when the force constant is larger
 (d) None
- Since the nuclei in a polyatomic molecule do not always vibrate in a simple harmonic manner, there arises
 (a) Harmonicity (b) Anharmonicity in molecular vibrations
 (c) Fundamental frequencies (d) All
- The frequency of vibration of H_2 is 4159 cm^{-1} and dissociation energy is 4.5 eV . Assuming that it vibrates as a SHO, its vibrational quantum number corresponding to dissociation energy, D is
 (a) 8 (b) 10 (c) 7 (d) 6
- The vibrations, without a centre of symmetry are, active in
 (a) Infrared but inactive in Raman (b) Raman but inactive in IR
 (c) Raman and IR (d) None

IIT-JAM / M.Sc. Entrance

10. The frequency of vibration of a bond is a function of
(a) Force constant of the bond (b) Masses of the atoms involved in bonding
(c) Both a and b (d) Bond order
11. The order of decreasing vibrational frequency for C – Cl, C – Br, C – C, C – O and C – H is
(a) C – H, C – C, C – O, C – Cl, C – Br
(b) C – Cl, C – Br, C – C, C – H, C – O
(c) C – O, C – H, C – Br, C – Cl, C – C
(d) C – Br, C – Cl, C – C, C – O, C – H
12. The increasing order of stretching frequencies for $C \equiv C$, $C = C$ and $C - C$ is
(a) $C - C > C = C > C \equiv C$ (b) $C \equiv C > C = C > C - C$
(c) $C - C > C = C < C \equiv C$ (d) $C = C < C - C > C \equiv C$
13. Ethanol and glycol in CCl_4 exhibit broad O – H str. near 3350 cm^{-1} in IR spectra. On dilution with CCl_4 , the spectrum of glycol does not change but that of ethanol exhibits a sharp band at 3600 cm^{-1} in addition to band at 3350 cm^{-1} because
(a) Intermolecular H-bonding is concentration dependent
(b) Intramolecular H-bonding is not affected on dilution
(c) Both a and b
(d) None
14. In the IR spectrum of acetyl chloride, a weak band near 1750 cm^{-1} results from
(a) inductive effect
(b) Fermi resonance between $C = O$ band and first overtone
(c) conjugation effect
(d) All
15. Compound, C_5H_{10} shows absorption at 1380 cm^{-1} . It is
(a) Pentene (b) Cyclopentane (c) Pentyne (d) All
16. Ketenes absorb in IR at a very high frequency (2150 cm^{-1}) because
(a) The inner C is sp -hybridised
(b) The more s character in a bond, the stronger it is
(c) Inner C is sp^2 hybridised (d) Both a and b
17. Ring strain in lactone (cyclic ester) or a lactam (cyclic amide)
(a) Increases carbonyl stretching frequency
(b) Decreases carbonyl stretching frequency
(c) Increases $C = C$ frequency (d) Decreases $C = C$ frequency
18. In α -haloketones
(a) Two $C = O$ stretching bands are observed
(b) One band has normal frequency

- (c) Other band is at higher frequency due to eclipsed interaction between halogen atom and C = O group
- (d) All statements are correct
19. A compound C_8H_6 decolorises Br_2 in CCl_4 and gives a white precipitate with Tollen's reagent. It has sharp band at 3300 cm^{-1} and weak bands at $3085, 2110\text{ cm}^{-1}$. It is
- (a) Phenyl acetylene (b) Phenyl propylene
(c) Phenyl ethylene (d) Octene
20. A compound of molecular formula C_8H_8O has a strong infrared absorption band near 1690 cm^{-1} . The most likely structure for the compound is
- (a) $C_6H_5CH_2CHO$ (b) $C_6H_5\text{CH}=\text{CH}_2$
(c) $HO-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2$ (d) $C_6H_5COCH_3$
21. The wave number of IR absorption is the reduced mass.
- (a) directly proportional to (b) inversely proportional to
(c) independent of (d) directly proportional to square of
22. The number of vibrational degrees of freedom in $C_6H_5CH_3$ will be
- (a) 39 (b) 15 (c) 18 (d) 40
23. Which of the following molecules will not show infrared spectrum?
- (a) H_2 (b) HCl (c) CH_4 (d) H_2O
24. The phosphorescence spectrum of the excited species is due to
- (a) Singlet to triplet transitions (b) Triplet to singlet transitions
(c) Vibration modes (d) Electron spin transitions
25. Among the isomers of C_4H_6 given below, the compound which exhibits absorption band at 3300 cm^{-1} and 2220 cm^{-1} in the IR spectrum, is
- (a) 1,3-butadiene (b) 1-butyne (c) 2-butyne (d) cyclobutene
26. Monomeric saturated aliphatic carboxylic acids show carbonyl stretching frequency near 1760 cm^{-1} while saturated aliphatic ketones near 1720 cm^{-1} because
- (a) Mesomeric (M) effect is dominant in acids over the inductive (I) effect
(b) I effect is dominant in carboxylic acids over the mesomeric effect
(c) I effect in ketones is dominant over the M effect.
(d) M effect in ketones is dominant
27. The exceptionally low carbonyl stretching frequency (1650 cm^{-1}) in 2, 4, 6-cycloheptatrienone is due to
- (a) Conjugation effect (b) Steric effect
(c) Field effect (d) Electronic effect

28. The correct order of IR stretching frequency of the C=C in the following olefins is

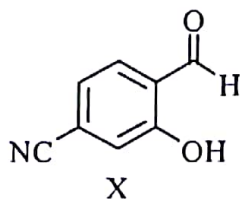


- (a) I > II > III (b) II > III > I (c) III > II > I (d) III > I > II

29. The bond that gives the most intense band in the infrared spectrum for its stretching vibration is

- (a) C-H (b) N-H (c) O-H (d) S-H

30. The IR stretching frequencies (cm^{-1}) for the compound X are as follows:
3300-3500 (s, br); 3000 (m); 2225 (s); 1680 (s).



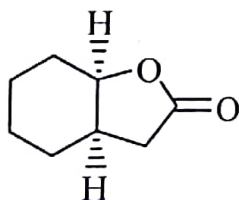
The correct assignment of the absorption bands is

- (a) $\bar{\nu}_{(\text{OH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CH})} = 3000$; $\bar{\nu}_{(\text{CN})} = 2225$; $\bar{\nu}_{(\text{CO})} = 1680$
 (b) $\bar{\nu}_{(\text{OH})} = 3000$; $\bar{\nu}_{(\text{CH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CN})} = 2225$; $\bar{\nu}_{(\text{CO})} = 1680$
 (c) $\bar{\nu}_{(\text{OH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CH})} = 3000$; $\bar{\nu}_{(\text{CN})} = 1680$; $\bar{\nu}_{(\text{CO})} = 2225$
 (d) $\bar{\nu}_{(\text{OH})} = 3000$; $\bar{\nu}_{(\text{CH})} = 3300 - 3500$; $\bar{\nu}_{(\text{CN})} = 1680$; $\bar{\nu}_{(\text{CO})} = 2225$

31. In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at

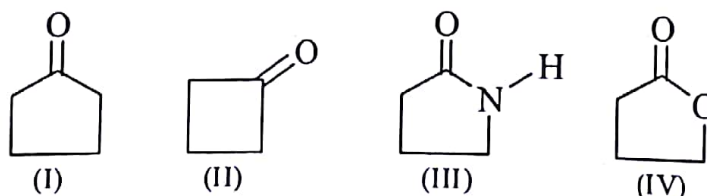
- (a) 1670 cm^{-1} (b) 1700 cm^{-1} (c) 1730 cm^{-1} (d) 1760 cm^{-1}

32. In the IR spectrum, carbonyl absorption band for the following compound appear at



- (a) 1810 cm^{-1} (b) 1770 cm^{-1} (c) 1730 cm^{-1} (d) 1690 cm^{-1}

33. Arrange in the decreasing order of carbonyl frequency



- (a) IV > I > II > III (b) I > IV > III > II (c) IV > II > I > III (d) II > IV > I > III

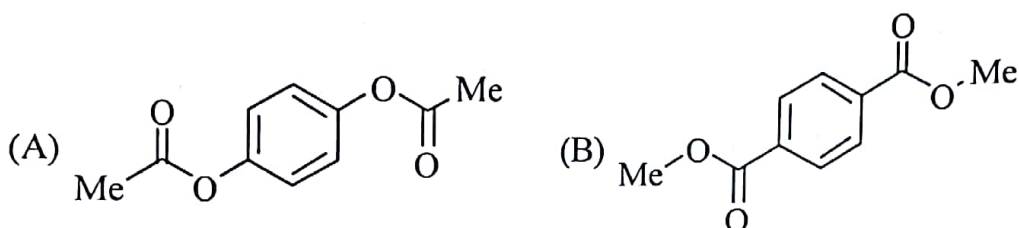
NMR Spectroscopy

34. The ^1H NMR spectrum of $\text{CH}_3\text{OCHClCH}_2\text{Cl}$ will exhibit

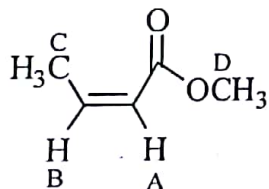
- (a) A three proton doublet. One proton singlet and a two proton doublet
 (b) A three proton singlet. One proton singlet and a two proton doublet
 (c) A three proton singlet. One proton triplet and a two proton doublet

- (d) A three proton triplet. One proton triplet and a two proton triplet
35. An organic compound with molecular formula $C_3H_6Cl_2$ exhibits only one signal in the 1H NMR spectrum. The compound is
 (a) 2, 2-dichloropropane (b) 1, 2-dichloropropane
 (c) 1, 3-dichloropropane (d) 1, 1-dichloropropane
36. 1H -NMR spectrum of compound with molecular formula $C_4H_9NO_2$ shows δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d, 3H), 1.20 (t, 3H) ppm. The structure of the compound that is consistent with the above data is
 (a) $CH_3NHCOOCH_2CH_3$ (b) $CH_3CH_2NHCOOCH_3$
 (c) $CH_3OCH_2CONHCH_3$ (d) $CH_3CH_2OCH_2CONH_2$
37. Which of the following has three types of hydrogens in the following compounds
 (a) $Br - CH = CH_2$ (b) $CH_3 - CH_2 - CH_3$
 (c) $C_6H_5CH_3$ (d) $CH_3 - CH_2 - CH(CH_3) - NO_2$
38. Only one signal is present in the PMR spectra of
 (a) C_3H_4 , C_3H_6 (b) C_4H_6 , C_5H_{12} (c) C_8H_{18} , C_2H_6O (d) All
39. How many Hertz does 1 ppm correspond to for an PMR spectrometer operating at a radio frequency of 60 MHz and 100 MHz?
 (a) 6 Hz, 10 Hz (b) 60 Hz, 100 Hz (c) 100 Hz, 60 Hz (d) None
40. Compound $C_4H_{10}O$ gave PMR spectrum consisting of two groups of lines (multiplets) with relative intensities in the ratio 3 : 2. Other compound of the same formula exhibited two lines with relative area of 9 : 1. Compounds are
 (a) Diethyl ether (b) t-Butyl alcohol (c) Both a and b (d) None
41. Distance between the centres of the peaks of doublet is called
 (a) Coupling constant (b) Spin constant
 (c) Spin-spin coupling (d) None
42. The PMR spectra of H_2 , CH_4 , C_2H_6 and C_6H_6 exhibit
 (a) Singlet (b) Doublet (c) Triplet (d) Quintet
43. A proton H_b is coupled to four equivalent protons H_a . The multiplicity and the relative intensity of lines in the signal H_b is
 (a) Doublet, 1 : 4 (b) Triplet 1 : 4 : 6
 (c) Quintet, 1 : 4 : 6 : 4 : 1 (d) Quartet 1 : 4 : 6 : 4
44. The peaks expected in low-resolution NMR spectrum of vinyl chloride and ethyl cyclopropane are
 (a) 3, 5 (b) 5, 3 (c) 6, 3 (d) 3, 6
45. The NMR frequency in MHz of bare H^1 in a magnetic field of intensity 1.4092 tesla is (given $g_N = 5.585$, $\mu_N = 5.05 \times 10^{-27} JT^{-1}$)
 (a) 60 MHz (b) 120 MHz (c) 100 MHz (d) 15 MHz
46. At room temperature, the number of singlet resonances observed in the 1H NMR spectrum of $Me_3CC(O)NMe_2$ (N, N-dimethyl pivalamide) is
 (a) 3 (b) 4 (c) 5 (d) 2

47. Which of the following compounds is expected to show a sharp singlet for one of its proton at $\delta \geq 8$ ppm in ^1H NMR spectrum, given that this signal remains unaffected on shaking the solution thoroughly with D_2O ?
- (a) $\text{CH}_3\text{CO}_2\text{H}$ (b) $\text{CH}_3\text{CONHC}_6\text{H}_5$
 (c) $n\text{-C}_6\text{H}_{13}\text{C} \equiv \text{CH}$ (d) $n\text{-C}_6\text{H}_{13}\text{CHO}$
48. ^1H NMR spectrum of [18]-annulene shows
- (a) only one peak at δ 7.2 (18H) (b) only one peak at δ 5.0 (18 H)
 (c) two peaks at δ 9.0 (12 H) and δ - 3.0 (6H)
 (d) two peaks at δ 9.0 (6 H) and δ - 3.0 (12 H)
49. Compounds A and B exhibit, two singlets, each in their ^1H NMR spectra. The expected chemical shifts are

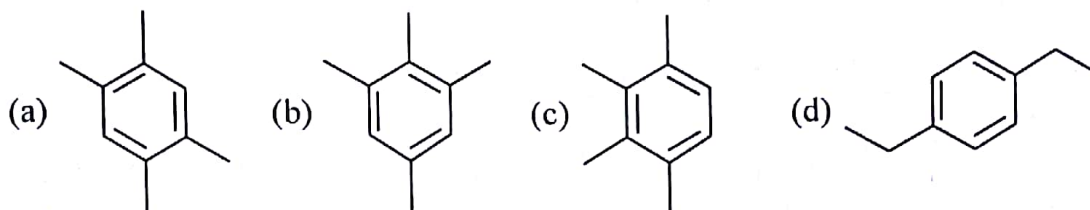


- (a) 6.9 and 2.1 for A; 7.7 and 3.9 for B (b) 7.7 and 3.9 for A; 6.9 and 2.1 for B
 (c) 6.9 and 3.9 for A; 7.7 and 2.1 for B (d) 7.7 and 2.1 for A; 6.9 and 3.9 for B
50. An organic compound (MF; $\text{C}_8\text{H}_{10}\text{O}$) exhibited the following ^1H NMR special data: δ 2.5 (3H, s), 3.8 (3H, s), 6.8 (2H, d, J 8 Hz), 7.2 (2H, d, J 8 Hz) ppm. The compound, among the choices, is
- (a) 4-ethylphenol (b) 2-ethylphenol (c) 4-methylanisole (d) 4-methylbenzyl alcohol
51. Appropriate ^1H NMR chemical shifts (δ) for the protons A-D for the following compounds are



- (a) A-6.8; B-5.7; C-3.9; D-2.1 ppm (b) A-6.8; B-5.7; C-2.1; D-3.9 ppm
 (c) A-5.7; B-6.8; C-3.9; D-2.1 ppm (d) A-5.7; B-6.8; C-2.1; D-3.9 ppm
52. In 400 MHz ^1H NMR spectrum of organic compound exhibited a doublet the two times of the doublet are at δ 2.35 and 2.38 ppm. The coupling constant (J) value is
- (a) 3 Hz (b) 6 Hz (c) 9 Hz (d) 12 Hz
53. In NMR spectroscopy, the product of Nuclear 'g' factor (g_N), the nuclear magneton (β_N) and the magnetic field strength (B_0) gives the
- (a) energy of transition from α to β state
 (b) chemical shift
 (c) spin-spin coupling constant (d) magnetogyric ratio

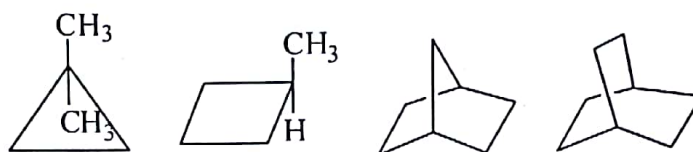
54. An organic compound having the molecular formulae $C_{10}H_{14}$ exhibited two singlets in the 1H NMR spectrum and three signals in the ^{13}C NMR spectrum the compound is



55. The 1H NMR spectrum of a dilute solution of a mixture of acetone and dichloromethane in $CDCl_3$ exhibits two singlets of 1 : 1 intensity. Molar ratio of acetone to dichloromethane in the solution is

(a) 3 : 1 (b) 1 : 3 (c) 1 : 1 (d) 1 : 1

56. No. of signals in 1H NMR in the given molecules are



(a) 3, 4, 4, 3 respectively (b) 2, 6, 4, 2 respectively
(c) 2, 4, 6, 2 respectively (d) 2, 4, 2, 6 respectively

57. What will be the change in value of γ (gyromagnetic ratio) if we double the applied magnetic field

(a) It will remain same (b) It will get doubled
(c) It will become half (d) It will become four times

58. Chemical shift value of proton attached to hetero atom depends upon

(A) Concentration (B) Temperature
(C) Solvent (D) External applied magnetic field

Which statement are correct

(a) Both (A) and (B) (b) (A), (B) and (C)
(c) (A), (B), (C) and (D) (d) (A), (C) and (D) only

59. A PMR spectrometer operates at 300 MHz. Find the value of magnetic field.

Given: $g_N = 5.585$ and $\beta_N = 5.05 \times 10^{-27} \text{ JT}^{-1}$.

(a) 7.05 T (b) 6.38 T (c) 7.58 T (d) 5.93 T

60. H^1 , C^{13} , F^{19} , P^{31} have nuclear spin equal to

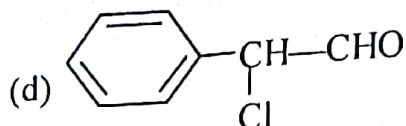
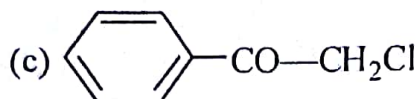
(a) 1/2 (b) 1 (c) 0 (d) 3/2

61. In p-xylene, the ratio of methyl protons to ring protons is 6 : 4 while for mesitylene, it is

(a) 6 : 4 (b) 3 : 2 (c) 9 : 3 (d) 6 : 3

62. A compound of molecular formula C_8H_7ClO shows a prominent band in its IR spectrum at 1690 cm^{-1} . 1H NMR spectrum revealed only two major types of protons in the ratio of 5 : 2. Which one of the following structures best fits the above data?





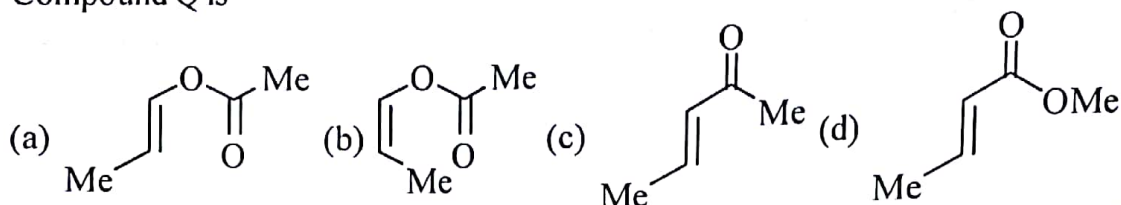
63. An organic compound Q exhibited the following spectral data.

IR: 1760 cm^{-1}

$^1\text{H NMR}$: $\delta(\text{ppm})$: 7.2 (1H, d, $J = 16.0\text{ Hz}$), 5.1 (1H, m), 2.1 (3H, s), 1.8 (3H, d, $J = 7.0\text{ Hz}$)

$^{13}\text{C NMR}$: $\delta(\text{ppm})$: 170 (carbonyl carbon).

Compound Q is

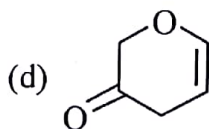
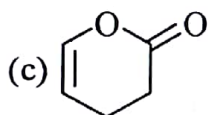
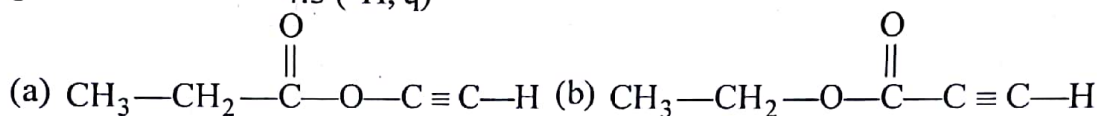


64. The NMR spectrum of a compound with molecular formulae $\text{C}_5\text{H}_6\text{O}_2$ is shown below. IR spectrum shows medium intensity band at 3270 and 2180 cm^{-1} . Draw structure of compound.

δ 1.3 (^3H , t)

δ 2.8 (^1H , s)

δ 4.3 (^2H , q)



Ultraviolet Spectroscopy

65. Compare solvent shift on the $n \rightarrow \pi^*$ transition of acetone

(a) $\text{H}_2\text{O} = \text{CH}_3\text{OH} = \text{C}_2\text{H}_5\text{OH} = \text{CHCl}_3 = \text{C}_6\text{H}_{14}$

(b) $\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{CHCl}_3 > \text{C}_6\text{H}_{14}$

(c) $\text{H}_2\text{O} < \text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH} < \text{CHCl}_3 < \text{C}_6\text{H}_{14}$

(d) $\text{H}_2\text{O} > \text{CH}_3\text{OH} < \text{C}_2\text{H}_5\text{OH} < \text{CHCl}_3 < \text{C}_6\text{H}_{14}$

66. The ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm and a secondary band at 271 nm .

(i) If a solution of benzonitrile in water, with a concentration of 1×10^{-4} molar, is examined at a wavelength of 224 nm , the absorbance is determined to be 1.30. The cell length is 1 cm.

What is the molar absorptivity of this absorption band?

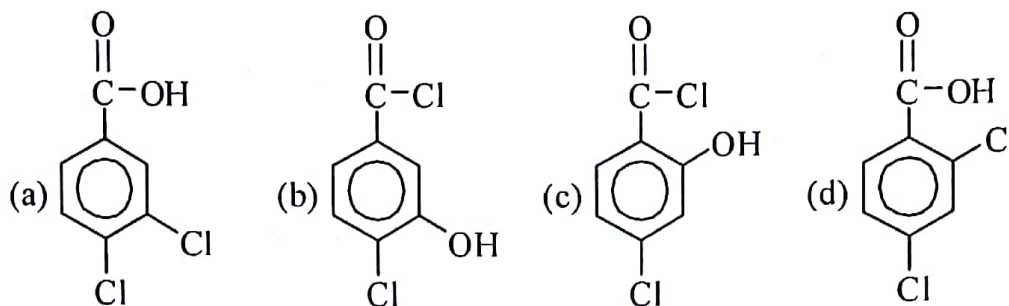
(a) 2.3×10^4 (b) 3.3×10^4 (c) 1.3×10^4 (d) 4.3×10^4

(ii) If the same solution is examined at 271 nm , what will be the absorbance reading ($\epsilon = 1000$)? What will be the intensity ratio, I_0/I ? Respectively

(a) 0.1, 1.26 (b) 0.2, 2.26 (c) 0.3, 3.26 (d) 0.4, 4.26

67. The structural formula that are consistent with the following observations.

An acid, $C_7H_4O_2Cl_2$, shows a UV maximum at 242 nm.



68. Match the following

Column I

- (1) Cyclopentene
- (2) Dimethyl ether
- (3) Methyl vinyl ether
- (4) Triethylamine
- (5) Cyclohexane
- (6) Acetaldehyde

Column II

- (P) $n \rightarrow \sigma^*$
- (Q) $\sigma \rightarrow \sigma^*$
- (R) $n \rightarrow \pi^*$
- (S) $\pi \rightarrow \pi^*$
- (T) $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$

(a) 1-P, 2-S, 3-T, 4-S, 5-Q, 6-T

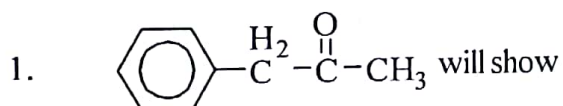
(b) 1-S, 2-P, 3-T, 4-P, 5-Q, 6-T

(c) 1-S, 2-P, 3-Q, 4-T, 5-Q, 6-P

(d) 1-T, 2-P, 3-S, 4-P, 5-Q, 6-T

EXERCISE - II

One or More Than One Correct Type

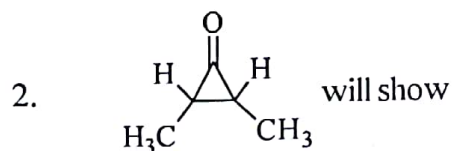


(a) tautomerism

(b) 3 signals

(c) IR frequency around 1715 cm^{-1}

(d) Nucleophilic substitution reaction

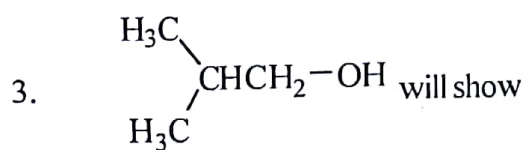


(a) quartet

(b) 1 doublet

(c) triplet

(d) 2 doublets



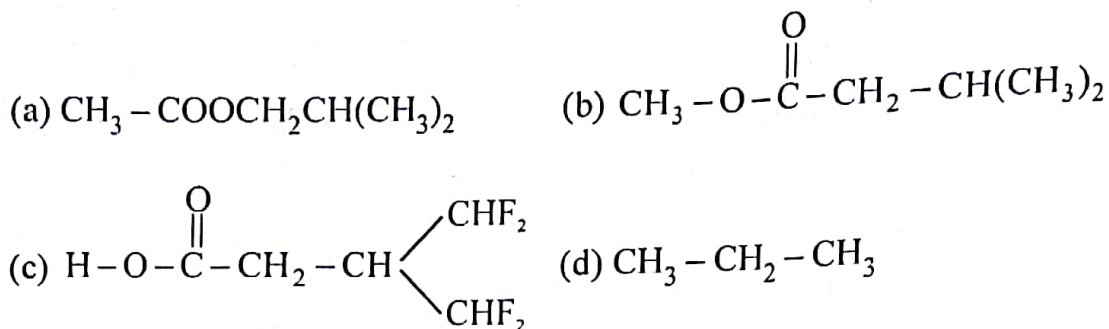
(a) triplet

(b) septet

(c) doublet

(d) singlet

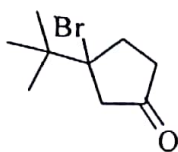
4. Two doublets are shown by



EXERCISE - III

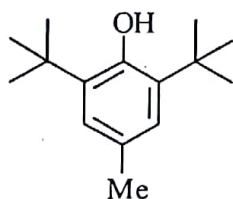
Numerical Answer Type

1. Total number of ^1H NMR signals in the given compounds is



2. Total number of ^1H NMR peaks in the given compound $\text{Cl}_2\text{HC} - \text{CH}(\text{OCH}_2\text{CH}_3)_2$ is _____.

3. Total number of ^1H NMR peaks in the given compound is:



4. Total number of deshielded electrons in the [18] annulene is _____.

5. $\delta_{\text{H}}(\text{OH})$ value (in ppm) for different compounds A, B and C is 2.0, 5.0 and 11.0. The most acidic compound among A, B and C is that which has δ value is _____.

6. Total number of ^1H NMR signals in the diammonium EDTA is _____.

7. Total number of ^1H Signals in the zwitterion form of glycine is _____.

8. The compound shows a proton-NMR peak at 240 Hz down field from the TMS peak in a spectrometer operating at 60 MHz. What are the value of the chemical shift δ in the ppm relative to TMS?

9. A proton has resonance 90 Hz downfield from TMS when the field strength is 1.41 Tesla (14,100 Gauss) and the oscillator frequency is 60 MHz.

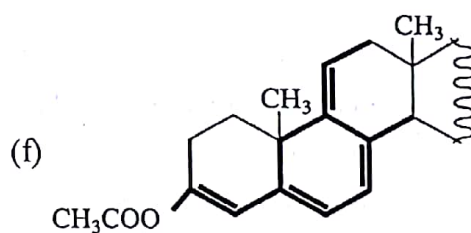
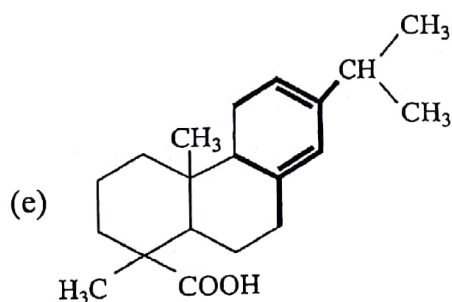
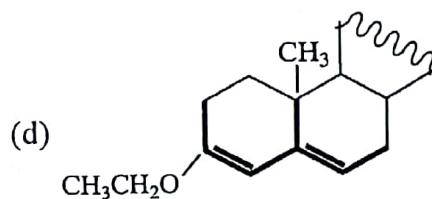
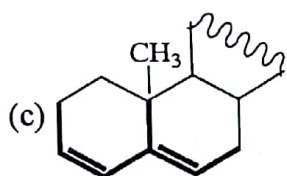
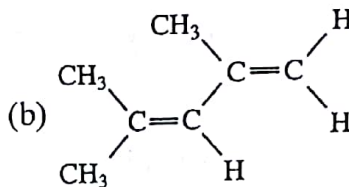
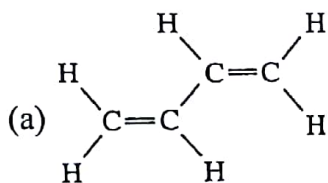
(a) What will be its shift in Hertz if the field strength is increased to 2.82 Tesla and the oscillator frequency to 120 MHz?

(b) What will be its chemical shift in parts per million (δ)?

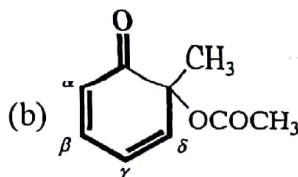
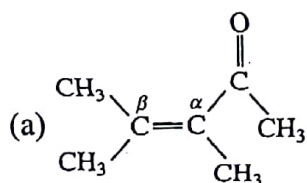
10. The following compound, with the formula $C_4H_8O_2$, is an ester. Give its structure and assign the chemical shift values.

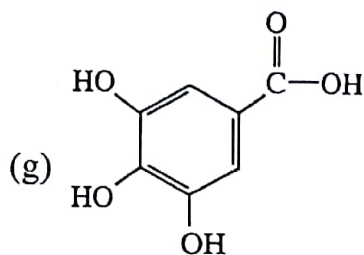
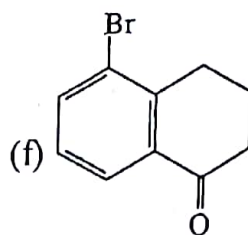
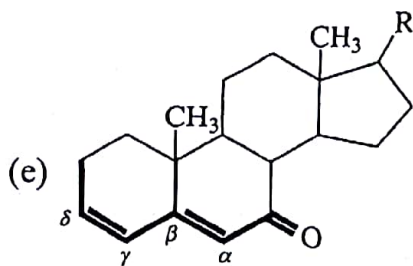
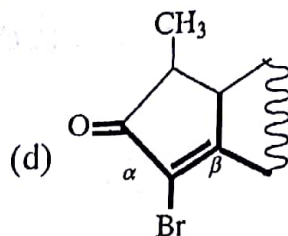
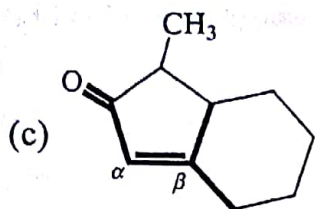


11. Calculate λ_{max} for the following



12. Calculate λ_{max} for the following

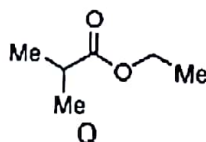
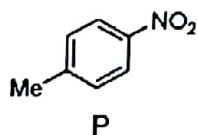




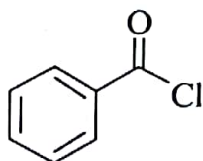
EXERCISE - IV

Previous Year Question

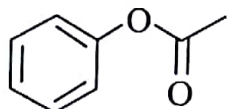
- The number of normal modes of vibration in naphthalene is
(a) 55 (b) 54 (c) 48 (d) 49
- IR active molecule(s) is/are
(a) CO₂ (b) CS₂ (c) OCS (d) NO₂
- The number of proton NMR signals for the compounds P and Q, respectively, is



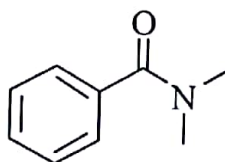
- (a) 3 and 4 (b) 3 and 5 (c) 4 and 3 (d) 5 and 4
- At an operating frequency of 350 MHz, the shift (in Hz) of resonance from TMS (tetramethylsilane) of a proton with chemical shift of 2 ppm is _____
 - The CORRECT order of carbonyl stretching frequencies for the following compounds is



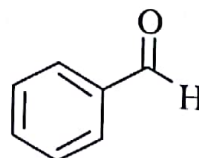
I



II



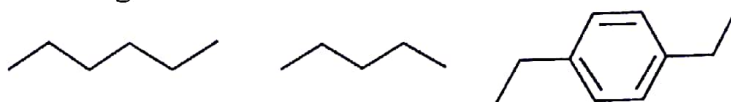
III



IV

- (a) II < I < III < IV (b) I < III < II < IV
(c) IV < II < III < I (d) III < IV < II < I

6. Among the following hydrocarbon(s), how many of them would give rise to three groups of proton NMR peaks with 2:2:3 integration ratio?



7. The nuclear spin quantum number (I) of a nucleus is $\frac{3}{2}$. When placed in an external magnetic field, the number of possible spin energy states it can occupy is _____.

ANSWER KEY**EXERCISE - I**

- | | | | | | | |
|-------|-------|------------------|-------|-------|-------|-------|
| 1. a | 2. b | 3. c | 4. d | 5. d | 6. a | 7. b |
| 8. a | 9. c | 10. c | 11. a | 12. b | 13. c | 14. b |
| 15. d | 16. d | 17. a | 18. d | 19. a | 20. d | 21. b |
| 22. a | 23. a | 24. b | 25. b | 26. b | 27. a | 28. c |
| 29. c | 30. a | 31. d | 32. b | 33. d | 34. c | 35. a |
| 36. a | 37. a | 38. d | 39. b | 40. c | 41. a | 42. a |
| 43. c | 44. a | 45. a | 46. a | 47. d | 48. c | 49. a |
| 50. c | 51. c | 52. d | 53. a | 54. a | 55. b | 56. b |
| 57. a | 58. b | 59. a | 60. a | 61. c | 62. c | 63. a |
| 64. b | 65. c | 66. (i) c (ii) a | 67. c | 68. b | | |

EXERCISE - II

- | | | | |
|----------|--------|--------|----------|
| 1. a,b,c | 2. a,b | 3. c,d | 4. a,b,c |
|----------|--------|--------|----------|

EXERCISE - III

- | | | | | | | |
|------|--|---------------|--------------|-------|------|------|
| 1. 4 | 2. 11 | 3. 4 | 4. 12 | 5. 11 | 6. 3 | 7. 2 |
| 8. 4 | | 9. (a) 180 Hz | (b) 1.50 ppm | | | |
| 10. | Ethyl acetate (ethyl ethanoate) | | | | | |
| 11. | (a) 214 nm (b) 229 nm (c) 234 nm (d) 240 nm (e) 278 nm (f) 353 nm | | | | | |
| 12. | (a) 249 nm (b) 302 nm (c) 231 nm (d) 256 nm (e) 280 nm (f) 251 nm (g) 269 nm | | | | | |

EXERCISE - IV

- | | | | | | | |
|------|----------|------|--------|------|------|------|
| 1. c | 2. a,b,c | 3. a | 4. 700 | 5. d | 6. 2 | 7. 4 |
|------|----------|------|--------|------|------|------|