

UNIT-1 : UV Spectroscopy

Notes by Mr. V. M. DESAI

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Lecture Plan:

Lect. No.	Contents of Syllabus	Date
	Unit-1) Introduction to Spectroscopy (3Lectures)	
1	<ul style="list-style-type: none">➤ Introduction : Frequency, Amplitude, Energy, Wavelength, Wave number & their relation (For MCQ)➤ Numerical problems on Frequency, Energy, Wavelength and Wave number	
2	<ul style="list-style-type: none">➤ Regions of Electromagnetic radiation (Electromagnetic Spectrum)➤ Interaction of radiation with matter- Absorption, Emission, Fluorescence and scattering	
3	<ul style="list-style-type: none">➤ Types of spectroscopic methods (For MCQ)➤ Advantages of spectroscopic methods	
	Unit-2) UV Spectroscopy (5Lectures)	
4	<ul style="list-style-type: none">➤ Introduction<ul style="list-style-type: none">i) Beer-Lamert's Lawii) Chromophore & Auxochrome IMP	
5	<ul style="list-style-type: none">➤ Types of electronic transition IMP<ul style="list-style-type: none">i) Bathochromic Effect Or Red Shiftii) Hypsochromic Effect Or Blue Shiftiii) Hyperchromic Effect &iv) Hypochromic Effect	
6	<ul style="list-style-type: none">➤ Effect of conjugation on position of UV band	
7	<ul style="list-style-type: none">➤ Applications of UV spectroscopy: MIMP<ul style="list-style-type: none">i) Extent of Conjugationii) Distinguish between conjugated & non-conjugate dieneiii) Detection of Geometrical (cis-trans) isomersiv) Detection of Chromophorev) Detection of Impuritiesvi) Strength of Hydrogen bond	
8	Calculation of by Woodward and Fisher rules for -	
9	<ul style="list-style-type: none">i) Dienesii) Enones	

The Roots of Education are **Bitter, But the Fruit is Sweet.**

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Previous Year asked University Questions:

UV Spectroscopy: (Theory questions)

Q. 1) Define the terms Chromophore and Auxochrome with suitable examples. Dec.16, April16

Q. 2) State and explain Beer-Lamberts law. April16

Or State and derive equation for Beer-Lamberts law

Q.3) Explain types of electronic transitions produced by absorbing UV-visible radiation.

Q.4) Explain the following terms used in UV-spectroscopy: IMP

a) Chromophore and b) Auxochrome

c) Bathochromic (Red) shift d) Hypsochromic (Blue) shift

Or Explain Chromophore and Auxochrome with suitable examples. April2016

Q. 5) Explain how UV spectroscopy is used to determine –

i) Extent of conjugation Oct.2015 Dec.16 MIMP April 2016

ii) Study of Geometrical isomers Or MIMP April 2016

Distinguish between Cis and Trans isomer Oct.2015 Dec.16

iii) Detection of Impurities

iv) Strength of Hydrogen Bond

v) Detection of Chromophore

IR Spectroscopy: (Theory questions)

Q.1) Explain the **fundamental modes of vibrations** involved in IR spectroscopy. Oct.2015 Dec.16 April 2017

Q.2) Calculate fundamental modes of vibrations of following molecules;

a) Benzene b) Methane c) Water d) Ammonia e) Ethene

Q. 3) State **Hook's law**. Give its mathematical expression. April-2016/17

Q. 4) Explain how does the **resonance effect** causes change in IR absorption frequency of $>C=O$ (carbonyl) group. Oct.2015

Q. 5) Explain how **hydrogen bonding** affects IR absorption in carboxylic acids. Dec.2016

Q. 6) What is **selection rule**? Explain IR active and inactive transitions with suitable examples April2016 IMP April 2017

“Only I Can Change My Life. No One Can Do It for Me.”

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NMR Spectroscopy

Q. Define chemical shift. Explain how inductive effect changes chemical shift value. April 16, Oct.15

Q. What are magnetic and non-magnetic nuclei? Explain it with suitable example April2016, Oct.15 April-17

Or Explain magnetic and non-magnetic nuclei with suitable example.

Q. Which compound is used as a reference in PMR spectroscopy? Why? April2017 Dec.16

Or What is TMS? Why it used as a reference in PMR spectroscopy? Oct.15

Q. Write note on spin-spin coupling Dec.2016

Q. What is shielding and deshielding of the protons? Explain with suitable examples. Dec.16

Mass Spectroscopy

Q.1) Draw neat schematic diagram of mass spectrometer and name the components. April.2016

O Draw neat and labeled schematic diagram of mass spectrometer Oct.15

Q. 2) Explain McLafferty rearrangement in carbonyl compounds with suitable example. April16/17 Oct.15

Q. 3) How can you determine molecular weight by mass spectroscopy? April 2017

Or Give application of mass spectroscopy to determine the molecular weight of the compound. Dec.16

Multiple Choice Questions (MCQ):

Introduction to Spectroscopy:

Q. 1) The energy of electromagnetic radiation is directly proportional to _____Dec.2016 a) ν b) $\bar{\nu}$ c) λ **d) both a & b**

Q. 2) The advantages of spectroscopic analysis include _____
a) rapid b) non destructive Oct 2015 Dec.2016
c) small sample requirement **d) All of these** Apr-16/17 oct.15

Q. 3) The electromagnetic radiations having **longest wavelength** are _____ rays Apr-16/17
a) visible rays b) infrared rays **c) radio waves** d) gamma

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Q. 4) The highest energetic electromagnetic radiations are_____ April2016
a) visible rays b) infrared rays c) radio waves **d) gamma rays**

Q.5) The lowest energetic electromagnetic radiations are_____ April2016
a) visible rays b) infrared rays **c) radio waves** d) gamma rays

Q. 6) The energy(E) carried by photon is equal to_____ Oct.2015
a) $h\nu$ b) hc/λ c) h **d) both a & b**

UV Spectroscopy:

Q.1) _____type of electronic transitions requires **least energy**. April2017
a) $\sigma \rightarrow \sigma^*$ b) $\pi \rightarrow \pi^*$ c) $n \rightarrow \sigma^*$ **d) $n \rightarrow \pi^*$**

Q. 2) The **highest energy** electronic transition is_____ Oct.2015 Dec.16
a) $\sigma \rightarrow \sigma^*$ b) $\pi \rightarrow \pi^*$ c) $n \rightarrow \sigma^*$ d) $n \rightarrow \pi^*$

Q. 3) The electronic transition for **longer wavelength** is_____ April2017
a) $\sigma \rightarrow \sigma^*$ b) $\pi \rightarrow \pi^*$ c) $n \rightarrow \sigma^*$ **d) $n \rightarrow \pi^*$**

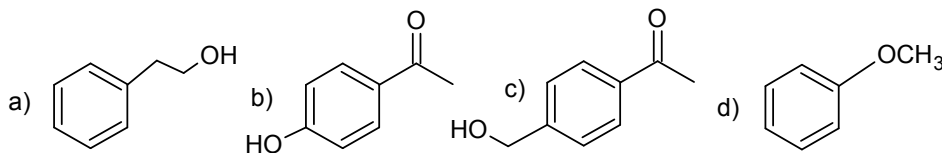
Hint: Energy order is $\sigma \rightarrow \sigma > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$ **Least Energetic**
Wavelength order is $\sigma \rightarrow \sigma < n \rightarrow \sigma^* < \pi \rightarrow \pi^* < n \rightarrow \pi^*$ **Longer wavelength**

Q. 4) The shift of absorption band **to shorter wavelength** is called _____shift. April 16
a) Bathochromic b) hyperchromic **c) hypsochromic** d) hypochromic
a) Red shift **b) Blue shift** c) Yellow shift d) None of these

Q.5) The shift of absorption band to **longer wavelength** is called _____shift. Dec.2016
a) Bathochromic b) hyperchromic c) hypsochromic d) hypochromic

Q. In Bathochromic or red shift _____ April 2017
a) λ_{\max} increases b) λ_{\max} decreases c) ϵ_{\max} increases d) ϵ_{\max} decreases

Q. 6) The compound shows **Bathochromic or red shift on the addition of a dilute alkali is _____ SET**



Ans. (b) Hint: Phenolic compd. on addition of alkali forms phenoxide ion and hence it shows red shift

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Q. 7) Compared to ketones, **conjugated enones** show_____ NET Exam

- a) same ϵ_{\max} & λ_{\max} b) lower ϵ_{\max} & higher λ_{\max}
c) higher ϵ_{\max} & lower λ_{\max} d) higher ϵ_{\max} & λ_{\max}

Hint: Trans absorbs at higher λ in UV spectrum as compared to cis

Q.8) A typical example of Chromophore is _____ Oct.2015

- a) $-\text{NH}_2$ b) $-\text{OH}$ c) $-\text{Cl}$ **d) $-\text{NO}_2$** Oct.2015
a) $-\text{NH}_2$ b) $-\text{OH}$ c) $-\text{Cl}$ **d) $>\text{C}=\text{O}$**

Q.9) An example of Auxochrome is _____

- a) $>\text{C}=\text{C}<$ b) $>\text{C}=\text{O}$ c) NO_2 **d) $-\text{NH}_2$**

Q.10) The wavelength range for UV-visible region of electromagnetic spectrum is _____

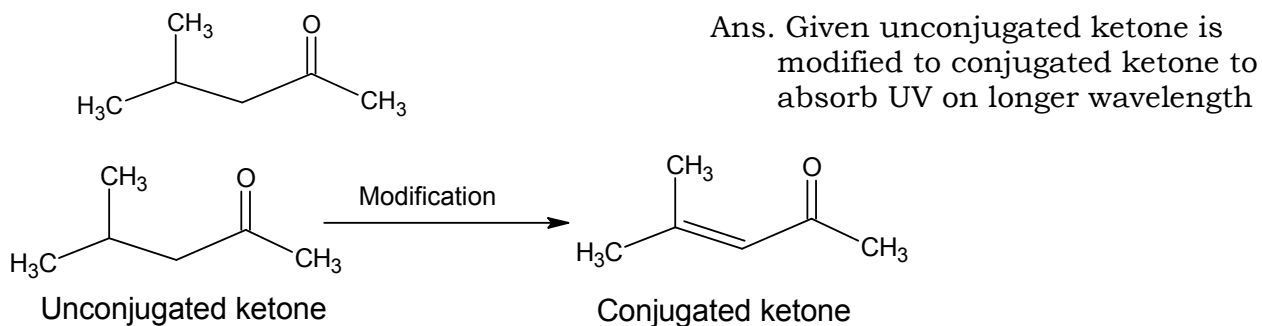
- a) 200-800nm **b) 200-800A⁰** c) 200-800cm d) 200-800 μm

Q. 11) Auxochrome contains the atoms having _____ 2012

- a) only σ electrons b) only π electrons
c) non-bonding electrons d) bonding electrons

Hint: Non-bonding electrons (i.e. lone pair on atoms like N, S, O & halogens)

Q. 12) What modification in the structure of the following compound will make it absorb in UV region? MSc. Oct.2012



Q. 13) Difference between HOMO and LUMO energy levels decreases due to _____

Ans. Due to effect of conjugation. MSc. Oct.2012

Q.14) _____ is used as a source in UV spectroscopy. MSc.March 2012

Ans. Deuterium or Hydrogen Lamp

Q. 15) What is the effect of H-bonding in ultra-violet absorption?

Ans. Due to H-bonding, UV absorptions shifts to **shorter** wavelength.

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IR spectroscopy

- Q.1) The electromagnetic radiation range between wavelength 400 to 750nm is called as _____ range. Oct.2015
a) **visible** b) infrared c) radio waves d) gamma
- Q.2) Due to absorption of IR radiation, _____ excitation occurs in the molecule. Dec.16 a) nuclear b) electronic **c) vibrational** d) All of these
- Q. 3) IR spectroscopy is used to determine _____ Oct.2015
a) extent of conjugation **b) functional group**
c) molecular weight d) nature of proton
- Q.4) IR-absorption occurs only when there is change in ____ April 2017
a) bond angle b) bond length
c) bond polarity (dipole moment) d) bond strength
- Q. 5) **Functional group region** of IR spectrum lies in the range of ____cm⁻¹.
a) 4000-650 b) 4000-1350 c) 400-750 d) 1350-650 **Dec.2016**
- Q. 6) **Finger print region** of IR spectrum lies in the range of ____cm⁻¹.
a) 4000-650 b) 4000-1350 c) 400-750 d) 1350-650 **Oct.15**
- Q. 7) The number of fundamental modes of vibrations for **linear molecule** are_____ April 2017 April 2016 a) 3N b) 3N-6 **c)3N-5** d) 5N-3
- Q. 8) The number of fundamental modes of vibrations for **non-linear** molecule are_____ a) 3N **b) 3N-6** c)3N-5 d) 5N-3
- Q. 9) The number of fundamental modes of vibrations for CO₂ molecule are_____ a) 3 **b) 4** c) 5 d)6
Hint: For linear CO₂, 3N-5= 3(3)-5=4 where N=no. of atoms
- Q.10) IR spectroscopy is useful in the determination of _____ 2012
a) conjugation **b) Functional group** c) molecular formula d) Molecular weight

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NMR Spectroscopy:

Q. 1) The NMR spectroscopy cannot be shown by _____ nuclei.

- a) ${}^1\text{H}^1$ b) ${}^7\text{N}^{15}$ c) ${}^6\text{C}^{12}$ d) ${}^6\text{C}^{13}$

Q. 2) The NMR phenomenon cannot be shown by _____ nuclei. 2013

- a) ${}^1\text{H}^1$ b) ${}^5\text{B}^{10}$ c) ${}^8\text{O}^{16}$ d) ${}^6\text{C}^{13}$

Hint: All nuclei having even atomic number and even mass number have I-value (spin value) equal to zero. So, they are non-magnetic e.g. ${}^6\text{C}^{12}$, ${}^8\text{O}^{16}$, ${}^2\text{He}^4$ etc.

Q.3) Nuclei with a odd atomic mass and an even or odd atomic number have__

- a) **zero spin** b) Integral spin c) Half integral spin d) None of these Nov. 2011

Q. 4) ___ is non-magnetic nuclei. Nov.2015 a) ${}^1\text{H}^1$ b) ${}^7\text{N}^{14}$ c) ${}^6\text{C}^{12}$ d) ${}^{15}\text{P}^{30}$

Q. 5) _____ is used as an internal reference standard in NMR spectroscopy. 2012

- a) **Tetramethylsilane** b) Calomel c) Aldehyde d) All of these

- a) **TMS** b) Benzene c) Acetone d) CCl_4 **April 2016**

Q. 6) Methyl proton peak will appear at highest δ -value for_____

- a) $\text{CH}_3\text{-CH}_3$ b) CH_3OH c) $\text{CH}_3\text{-F}$ d) $\text{CH}_3\text{-I}$ Nov. 2015

- a) $\text{CH}_3\text{-CH}_3$ b) CH_3Br c) $\text{CH}_3\text{-F}$ d) $\text{CH}_3\text{-I}$ April 2016

Q. 7) The delta value for methyl protons in _____ is maximum.2013

- a) CH_3Cl b) CH_3R c) $\text{CH}_3\text{-Br}$ d) $\text{CH}_3\text{-F}$

Q.8) Equivalent protons are a set of protons, _____ under uniform applied field is same. 2016

- a) Whose precessional frequency b) resonance simultaneously

- c) which gives a single NMR signal d) **all of these**

Q. 9) The protons having the **same precessional frequency** under uniform applied are called _____2009

- a) non-equivalent protons

- b) equivalent protons**

- c) shielding of protons

- d) deshielding of protons

Q.10) In NMR spectroscopy, the protons in identical electronic and magnetic environment are called _____ protons. 2011

- a) equivalent b) Non-equivalent c) semivalent d) Divalent

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- Q.11) In NMR spectrum of ethyl bromide, the number of signals at low resolution will be _____ 2009 a) 1 **b) 2** c) 3 d) 4
- Q. 12) _____ compound shows only one peak in PMR. April 2017
a) $\text{CH}_3\text{CH}_2\text{Br}$ **b) $\text{CH}_3\text{-O-CH}_3$** c) $\text{CH}_3\text{CH}_2\text{CH}_3$ d) $\text{CH}_3\text{CH}_2\text{-OH}$
- Q. 13) The number of set of protons in $\text{CH}_3\text{CH}_2\text{CHO}$ is _____ Dec.2016
a) 1 b) 2 **c) 3** d) 4

Mass spectroscopy

- Q. 1) Mass spectroscopy is used to determine _____ April 2016
a) Functional group **b) molecular weight**
c) conjugation d) nature of proton
- Q.2) The co-ordinates of mass spectrum are _____ April 2016 2017
a) wavelength & mass of ion
b) wavelength & absorbance
c) relative abundance & mass-charge ratio
d) frequency & mass-charge ratio
- Q. 3) Mass spectrum is also known as _____ 2012
a) Fragment graph b) Bar graph c) Graph d) None of these
- Q. 4) Mass spectrum is obtained by using _____ 2016
a) Radio frequency b) UV radiation c) IR radiation **d) Electron beam**
- Q.5) The deflection of ions in mass spectroscopy depends on _____
a) shape **b) mass/charge ratio** c) charge d) size Dec.2016
- Q. 6) Mass spectroscopy is a _____ 2011
a) Low pressure technique b) Low temperature technique
c) High pressure technique d) High temperature technique
- Q.7) In mass spectroscopy, **molecular ion peak** is used to determine ____ 2013
a) conjugation b) Functional group c) nature of proton **d) Molecular weight**
- Q.8) For a compound to be analysed in a mass spectrometer, it must be in the _____ state. A) solid b) liquid c) gaseous d) plasma
- Q.9) _____ cannot be detected in mass spectrometry.
a) Neutral radicals b) negative ions
c) Fragmentation molecules **d) All of these**

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Lect. No.	Unit-1) Introduction to Spectroscopy (3Lectures)
1	<ul style="list-style-type: none">➤ Introduction : Frequency, Amplitude, Energy, Wavelength, Wave number & their relation (For MCQ)➤ Numerical problems on Frequency, Energy, Wavelength and Wave number
2	<ul style="list-style-type: none">➤ Regions of Electromagnetic radiation (Electromagnetic Spectrum)➤ Interaction of radiation with matter- Absorption, Emission, Fluorescence and scattering
3	<ul style="list-style-type: none">➤ Types of spectroscopic methods (For MCQ)➤ Advantages of spectroscopic methods

Lect. No. 1) Introduction to Spectroscopy

Q. 1) Define the term spectroscopy. Give its any four advantages over chemical methods.

Ans. Spectroscopy is the **physical method used for analysis** in which study of the **interaction of matter with the electromagnetic radiation** takes place due to absorption, emission, fluorescence, scattering etc.

Advantages of spectroscopic method over chemical methods:

Compared to chemical methods,

- 1) Spectroscopic methods required **very less amount of samples** (in milligrams) for complete analysis
- 2) By almost all types of spectroscopic methods, **samples are recovered** at the end which is not possible in chemical methods.
- 3) Spectroscopic methods required **short time period** for complete analysis
- 4) It gives **more detailed structural information** about the molecule
- 5) These methods are useful for **detection of impurities**.
- 6) These methods give **more accurate result** in short time period.
- 7) All spectroscopic methods are clean.
- 8) In spectroscopic methods, a continuous analysis is possible and hence kinetics of a reaction can be studied.
- 9) Spectroscopic methods are also used to **predict completion of reaction**.

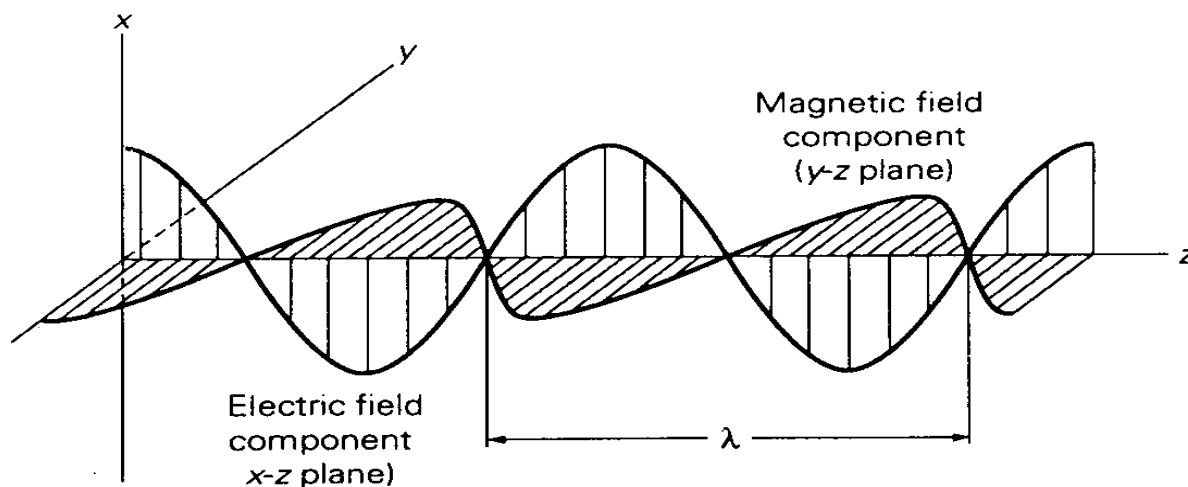
Disadvantages / Limitations / Drawbacks of Spectroscopic methods:

- 1) Instruments required for analysis are **very costly**.
- 2) **Trained / skilled persons** are required for operating instruments.
- 3) Experts are required for **interpretation of data regarding about structure** of the molecule.
- 4) The molecule may **undergo photochemical reactions** due to absorption of energy.
- 5) These methods are **extremely sensitive**

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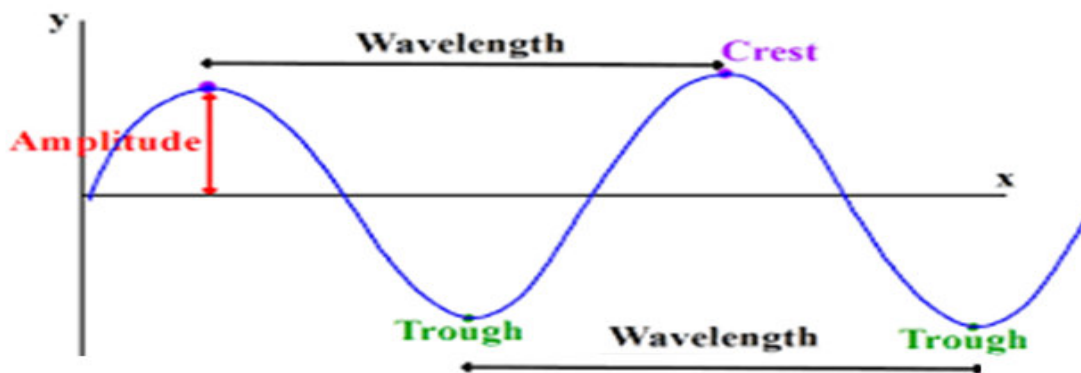
Introduction of Electromagnetic Radiation:

Electric and magnetic field components of plane polarized light



- Light travels in z-direction
- Electric and magnetic fields travel at 90° (i.e. perpendicular) to each other at speed of light in particular medium
- **Characterization of Radiation:**
 λ (wavelength), ν (frequency), E (energy) and $\bar{\nu}$ (wave number)

1) Wavelength: The wavelength of electromagnetic radiation is distance between identical points **on successive crests or troughs** as shown in fig.



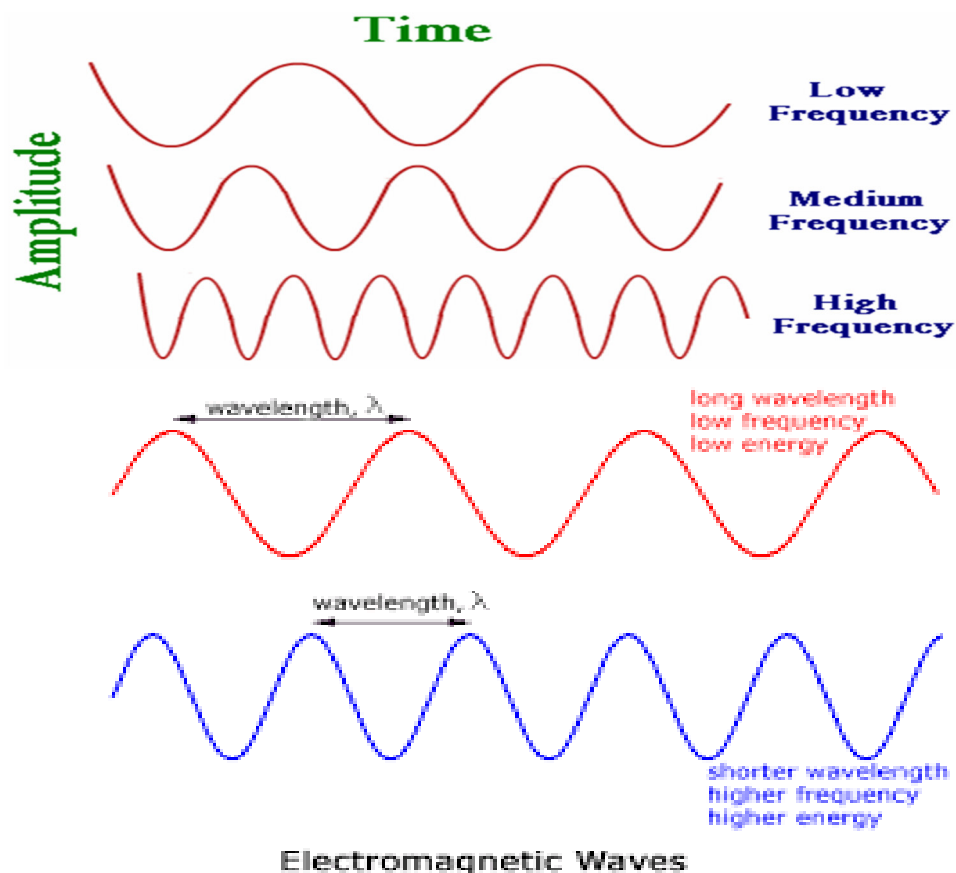
2) Amplitude: The **maximum displacement of wave** from X-axis is called as amplitude of radiation.

3) Frequency is the **number of complete cycles** or wavelengths passing through a point per second.

Or It is the ratio of velocity of radiation to the wavelength.

$$\nu = \frac{c}{\lambda} \quad \text{It is expressed in per second.} \quad \nu(\text{sec}^{-1}) = \frac{c(\text{cmsec}^{-1})}{\lambda(\text{cm})}$$

$$1 \text{ cps} = 1 \text{ Hz} \quad \text{and} \quad 1 \text{ MHz} = 10^6 \text{ cps} = 10^6 \text{ Hz}$$

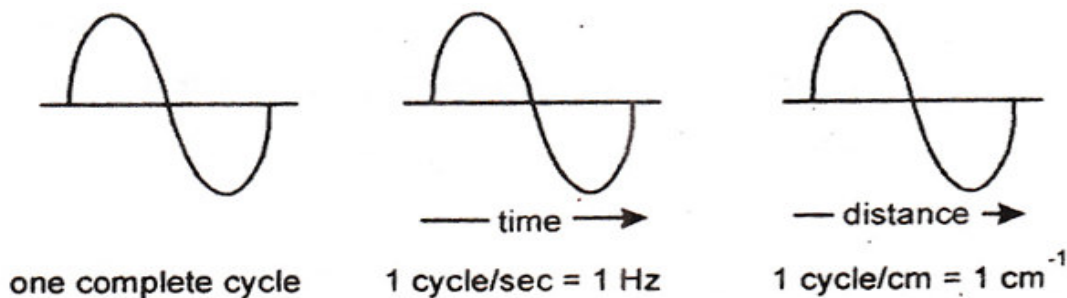


4) **Wave number** is the **reciprocal of the wavelength** (λ). It is expressed in per centimeter.

$$\text{Wave number (in cm}^{-1}\text{)} = 1 / \lambda \text{ (in cm)}$$

It is expressed in per centimeters.

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



5) **Energy** is directly proportional to frequency and wave number whereas it is inversely proportional to wavelength,

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad \text{Or} \quad \lambda = \frac{hc}{E}$$

Where, $h = 6.626 \times 10^{-27} \frac{\text{erg sec}}{\text{molecule}}$

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Q. State the relationship between nm, cm and A⁰ Oct.2013

Hint: $1\text{cm} = 10^8\text{A}^0 = 10^7\text{nm} = 10^4\mu = 10^7\text{m}\mu$

$$1\text{nm} = 10\text{A}^0 = 10^{-7}\text{cm}$$

$$1\text{A}^0 = 10^{-8}\text{cm} = 0.1\text{nm}$$

$$1\mu = 10^{-4}\text{cm} = 1000\text{nm} = 10,000\text{A}^0$$

Meaning

A⁰ = Angstrom

nm = Nanometer

μ = Micron

m μ = Milimicron

Relations:

For Wavelength (λ)	$1\text{A}^0 = 10^{-8}\text{cm}$	$1\text{nm} = 10^{-7}\text{cm}$	Largest unit - m
	Order of Unit: m > cm > μ > nm > A⁰		Smallest unit - A⁰
For Frequency (ν)	$1\text{cps} = 1\text{Hz}$	$1\text{kHz} = 10^3\text{Hz}$ $1\text{MHz} = 10^6\text{Hz}$	CPS = Hz < kHz < MHz
For Energy (E)	$1\text{cal} = 4.184\text{J}$ $1\text{cal} = 4.184 \times 10^7\text{erg}$	$1\text{J} = \frac{1}{4.184}\text{cal}$ $1\text{erg} = \frac{1}{4.184 \times 10^7}\text{cal}$	Largest unit - cal
	$1\text{J} = 10^7\text{erg}$	$1\text{erg} = \frac{1}{10^7}\text{J} = 10^{-7}\text{J}$	Smallest unit - erg
	Order of Unit: cal > J > erg		MCQ

Q.1) Calculate wave number and frequency of radiation having wavelength of 5μ .

Solution : Wavelength of radiation in cm

$$1\mu = 1,000\text{nm} = 10,000\text{A}^0 = 1 \times 10^{-4}\text{cm}$$

$$\text{So, } 5\mu = 5 \times 10^{-4}\text{cm}$$

Wavelength in terms of wave number ($\bar{\nu}$)

· We know,

$$\begin{aligned}\bar{\nu} &= \frac{1}{\lambda} = \frac{1}{5.0 \times 10^{-4}}\text{cm}^{-1} \\ &= 2,000\text{cm}^{-1}\end{aligned}$$

Wavelength in terms of frequency (ν).

$$\begin{aligned}\nu &= \frac{C}{\lambda} = \frac{3.0 \times 10^{10}\text{cm sec}^{-1}}{5.0 \times 10^{-4}\text{cm}} \\ &= 6.0 \times 10^{14}\text{Hz}\end{aligned}$$

Q. 2) Calculate velocity of radiation having 720nm wavelength and photons of energy $2.76 \times 10^{-19} \text{J}$

Solution : We know the energy of radiation is given by,

$$E = h\nu$$

Given Data:

$$\text{wavelength} = 720 \text{nm} = 720 \times 10^{-7} \text{cm}$$

$$\text{i.e. } E = \frac{hC}{\lambda}$$

$$\text{Energy (E)} = 2.76 \times 10^{-19} \text{J}$$

$$\text{So, } C = \frac{E\lambda}{h}$$

$$h = 6.623 \times 10^{-34} \text{ Js} = \text{Planks constant}$$

$$C = \frac{2.76 \times 10^{-19} \cancel{\text{J}} \times 720 \times 10^{-7} \text{cm}}{6.623 \times 10^{-34} \cancel{\text{J}} \text{s}} = \frac{2.76 \times 720 \times 10^{-7}}{6.623}$$

$$C = 300 \times 10^8 = 3.0 \times 10^{10} \text{cms}^{-1}$$

$$C = 3.0 \times 10^8 \text{ms}^{-1}$$

Q.3) Calculate the energy of photons of the radiation having wavelength of 450nm

Given Data:

$$\text{wavelength} = 450 \text{nm} = 450 \times 10^{-7} \text{cm}$$

$$C = 3.0 \times 10^{10} \text{cm}$$

$$h = 6.623 \times 10^{-34} \text{ Js}$$

As per Planks equation, energy of quanta is given by,

$$E = \frac{hC}{\lambda}$$

Substituting the values of h, C and λ ,

$$E = \frac{6.623 \times 10^{-34} \text{ J} \cancel{\text{s}} \times 3.0 \times 10^{10} \cancel{\text{cm}} \cancel{\text{s}^{-1}}}{450 \times 10^{-7} \cancel{\text{cm}}}$$

$$E = \frac{6.623 \times 3.0 \times 10^{17}}{450} = 0.4415 \times 10^{17}$$

$$E = 4.415 \times 10^{-19} \text{ J}$$

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Q.4) Sangli Aakashwani broadcasts on frequency of 1368kHz. Calculate wavelength of electromagnetic radiation emitted by transmitter. To what part of spectrum does it belongs?

Given Data:

wavelength = ?

$$C = 3.0 \times 10^{10} \text{ cm}$$

$$\nu \text{ (frequency)} = 1368 \text{ kHz} = 1368 \times 10^3 \text{ Hz} = 1368 \times 10^3 \text{ s}^{-1}$$

Solution : We know, $\lambda = \frac{C}{\nu}$

Substituting the values of C (velocity of light) and ν (frequency) of radiation.

$$\begin{aligned} \lambda &= \frac{3.00 \times 10^{10} \text{ cm s}^{-1}}{1368 \text{ kHz}} \\ &= \frac{3.0 \times 10^{10} \text{ cm s}^{-1}}{1368 \times 10^3 \text{ s}^{-1}} = \frac{3.0 \times 10^7}{1368} = 0.00219298 \times 10^7 \\ &= 21929.8 \text{ cm} = 219.3 \text{ m} \end{aligned}$$

This wavelength belongs to radio wave radiation.

Q.5) Calculate the energy in joules per quantum and joules per mole of photons of wavelength 400nm.

Given Data:

$$\lambda = \text{Wavelength of light} = 400 \text{ nm} = 400 \times 10^{-7} \text{ cm} \quad (\text{Since } 1 \text{ nm} = 10^{-7} \text{ cm})$$

$$c = \text{Velocity of light} = 3 \times 10^{10} \text{ cm/sec}$$

$$h = \text{Plank's constant} = 6.624 \times 10^{-27} \text{ erg.sec}$$

$$N = \text{Avogadro's number} = 6.023 \times 10^{23}$$

a) Energy in joules per quantum = $h \cdot \nu = \frac{h \cdot c}{\lambda} =$ _____
= _____ erg

b) Energy in joules per mole = $N \cdot h \cdot \nu = \frac{N \cdot h \cdot c}{\lambda} =$ _____
= _____ erg

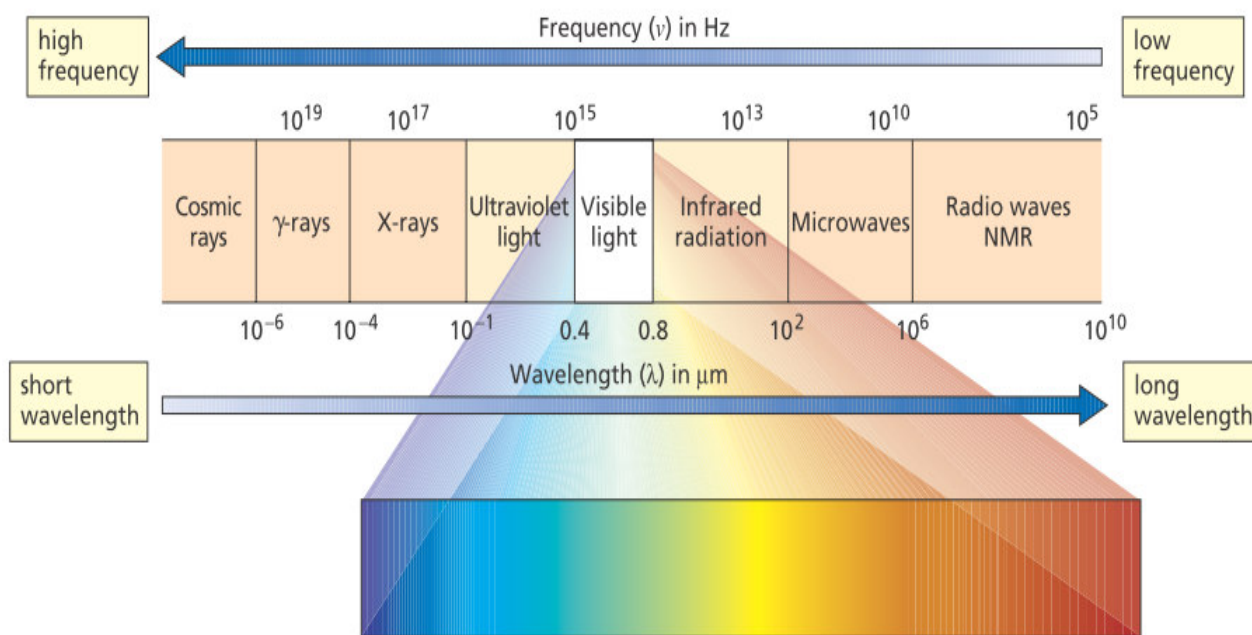
Q.6) Calculate energy of radiation with wavelength = 200nm. HW

Lect. No. 3) Regions of Electromagnetic radiation

3. Indicate the different regions of electromagnetic radiation (Electromagnetic Spectrum) or range.

➤ The whole range of electromagnetic radiation although has certain properties in common but the different portions are sufficiently different. So the different portions of electromagnetic radiation require different techniques for handling them. On this basis, the whole range of electromagnetic radiations has been divided into several regions depending on the wavelength as shown in the table below:

Regions	Cosmic rays	Gamma rays	X-rays	UV rays	Visible	Near IR	Far IR	Micro-wave	Radio-frequency
Wave length	10^{-12} cm	10^{-10} – 10^{-9} cm	10 nm	200 – 400 nm	400 – 800 nm	1 – 2.5 m	2.5 – 25 m	1 – 100 nm	1 cm – 15 m
Type of molecular spectrum	Mossbanur (Nuclear transitions)	Core orbitals (Electronics)	Electronic (valency orbitals)	Rotational and Vibrational	Rotational	Rotational	NMR (spin-orientation)		



MCQ

Q. The electromagnetic radiations having longest wavelength are_____

a) visible rays b) infrared rays c) **radio waves** d) gamma rays

April2016

Unit-1& 2) UV Spectroscopy By V.M. DESAI

- Q. The electromagnetic radiations having –
- highest frequency are _____
 - lowest frequency are _____
 - highest energy are _____
 - lowest energy are _____
 - longest wavelength are _____
 - lowest wavelength are _____

Q. The highest energy photons are found in the radiation of the type _____

Q. What is spectroscopy? How are spectroscopic techniques classified?

Ans. Spectroscopy is the **physical method used for analysis** in which study of the **interaction of matter with the electromagnetic radiation** takes place due to absorption, emission, fluorescence, scattering etc.

Classification of spectroscopic techniques:

On the basis of different regions of electromagnetic radiation interact with matter, following spectroscopic methods are classified as;

- Atomic absorption spectroscopy
- Atomic emission spectroscopy
- Molecular absorption spectroscopy
- Molecular emission spectroscopy

Types of Organic Spectroscopy:

- Ultraviolet Spectroscopy (UV)** – It requires Electronic Energy States
Use – Conjugated Molecules; Carbonyl Group, Nitro Group
- Infrared Spectroscopy (IR)** – It requires Vibrational Energy States
Use – Functional Groups; Compound Structure
- Mass Spectrometry (MS)** – It requires High Energy Electron Bombardment
Use – Molecular Weight, Presence of Nitrogen, Halogens
- Nuclear Magnetic Resonance (NMR)** – It requires Nuclear Spin States
Use – The number, type, and relative position of protons (Hydrogen nuclei) and Carbon-13 nuclei

**\ Don't limit your challenges, Challenge your limits. **

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Types of Spectroscopic	Radiation used	Nature of excitation
X -rays	Ionisation	Bond breaking or ionization .
UV- Visible spectroscopy	UV- Visible	Electronic, vibrational and rotational
IR- spectroscopy	IR	Vibrational accompanied by rotational
Microwave - spectroscopy	Microwaves	Rotational
NMR- spectroscopy	Radio waves	Nuclear

Molecular effects associated with different regions of the EM spectrum:

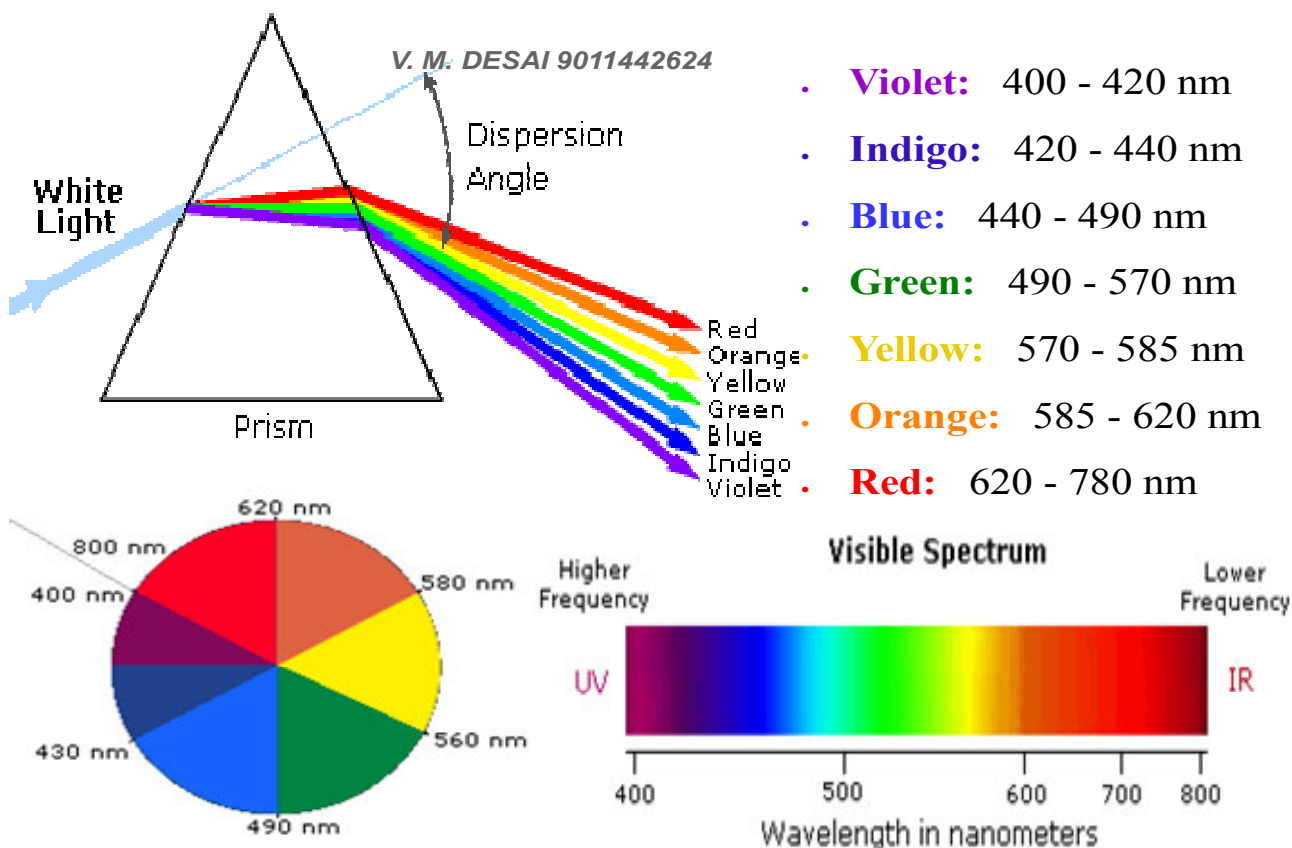
Wavelength (λ)		Energy/mole	Molecular effects
10^{-10} meter	gamma rays	10^6 kcal	
10^{-8} meter	X-rays	10^4 kcal	ionization
	vaccum UV	10^2 kcal	
	near UV		electronic transitions
10^{-6} meter	visible	10 kcal	
	infrared (IR)	1 kcal	molecular vibrations
10^{-2} meter	microwave	10^{-2} kcal	rotational motion
		10^{-4} kcal	
10^0 meter	radio	10^{-6} kcal	nuclear spin transitions
10^2 meter			

Energy \propto Frequency \propto Wave number & Energy $\propto 1/\lambda$

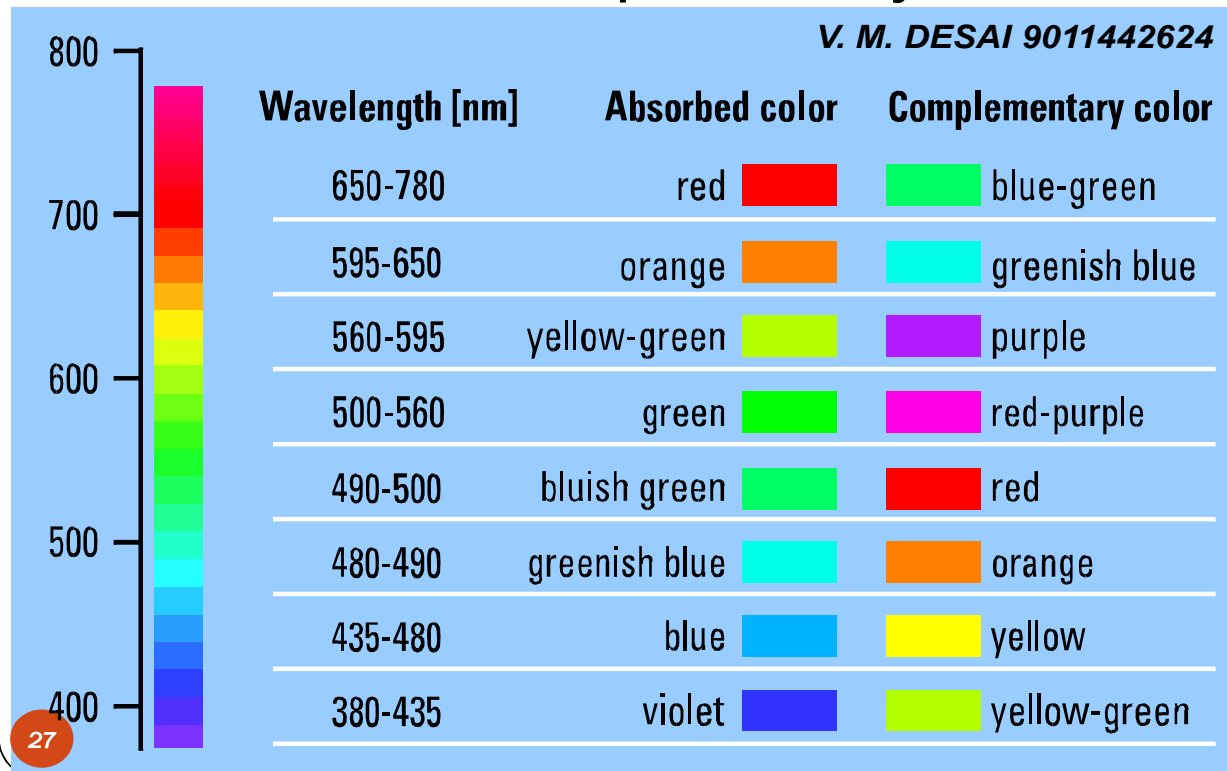
Highly Energetic radiation & shorter wavelength => Gamma rays

Least Energetic radiation & longer wavelength => Radio waves

Unit-1& 2) UV Spectroscopy By V.M. DESAI



Absorbance and Complementary Colors



Unit-2) Ultraviolet Spectroscopy (UV- Spectroscopy)

Q.1) Why UV-spectroscopy is called electronic spectroscopy? Mention various regions required for absorbing UV-visible radiations.

Ans. On the absorption of highly energetic UV and visible radiations, it **causes various electronic transitions** from lower to higher energy level. Thus, UV-spectroscopy is called '**Electronic spectroscopy**'.

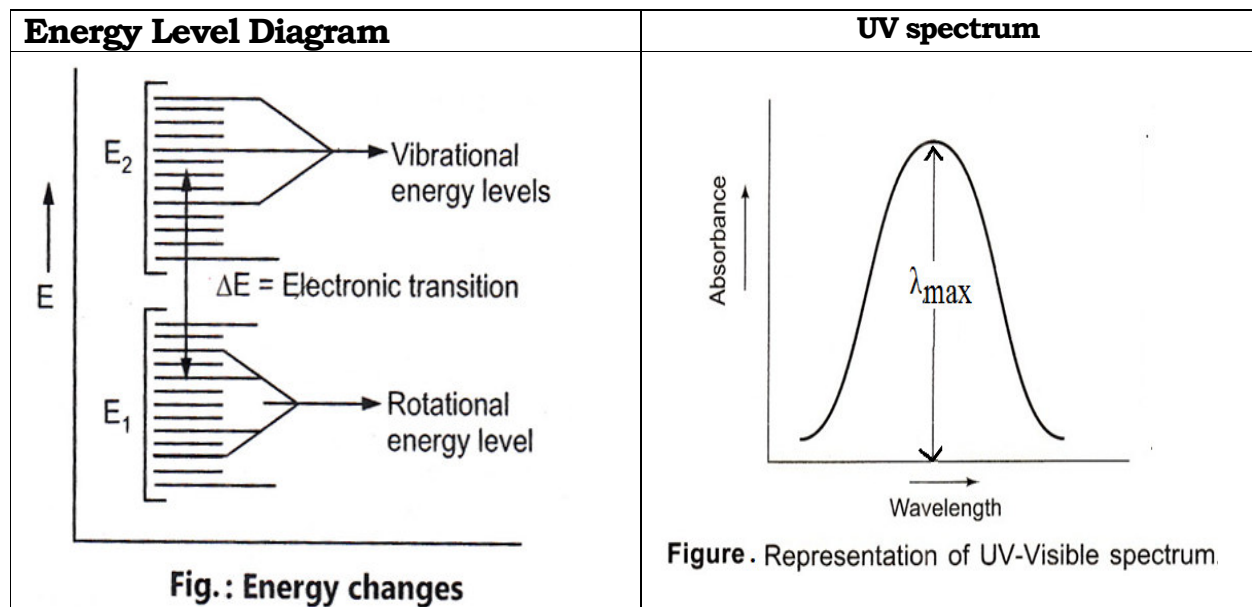
Region of UV –visible spectra: MCQ

	Type of spectra	Region (in λ)
1	Far UV or Vacuum UV	10 to 200nm
2	Near or Quartz UV	200 to 400nm
3	Visible	400 to 800nm

MCQ: Ultraviolet (UV) light is obtained by **deuterium discharge lamp** while visible range radiations are obtained from a **tungsten filament lamp**.

Q.2) Compared to the signals in other spectroscopic techniques, UV absorption bands are usually broad i.e. not sharp peaks.

Ans. The reason is that each electronic transition is accompanied by the changes in vibrational and rotational levels.



The total energy required for excitation of a molecule from ground state to an excited state is given by the equation,

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

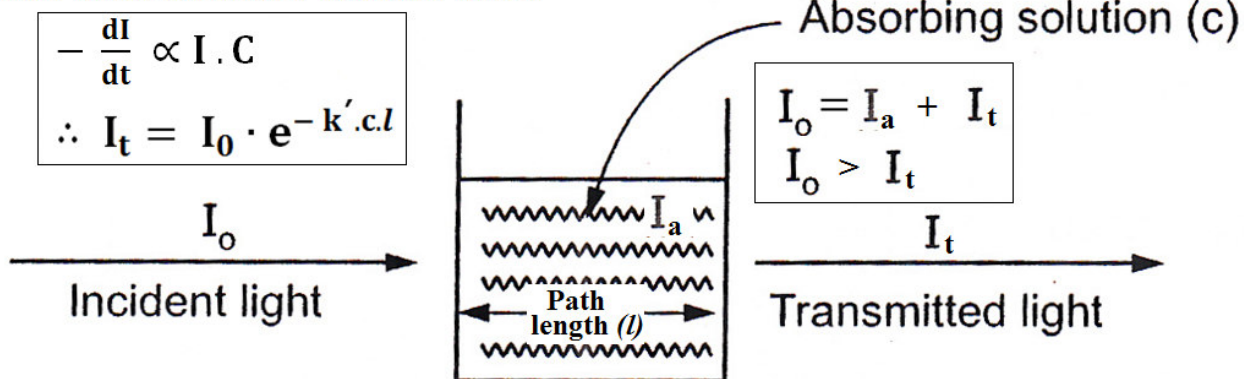
Thus, UV absorption bands are **usually broad i.e. not sharp peaks** as compared with other spectroscopic techniques.

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Q.8) Write short note 'Beer's Law Or Beer's-Lambert's Law' 5M MIMP

Or State Beer's Law Or Beer's-Lambert's Law and derive its equation. 5M

'Beer's Law Or Beer's-Lambert's Law'



1) **STATEMENT:** When a beam of monochromatic light is passed through a homogeneous solution of absorbing medium, then the **rate of decrease of intensity of incident light** with thickness (or path length) of medium is directly proportional **to the intensity of incident light as well as concentration of the solution.**

2) Mathematically, we can write,

$$-\frac{dI}{dt} \propto I \cdot c \Rightarrow -\frac{dI}{dt} = k' \cdot I \cdot c \Rightarrow \frac{dI}{I} = -k' \cdot c \cdot dt$$

Where, C = Concentration of solution in moles/dm³

k' = Proportionality constant called as '**Molar absorption coefficient**'

3) **Derivation:** According to Beer-Lambert's law (Beer's law),

$$-\frac{dI}{dt} \propto I \cdot c \Rightarrow -\frac{dI}{dt} = k' \cdot I \cdot c \Rightarrow \frac{dI}{I} = -k' \cdot c \cdot dt \quad \text{----- eq}^n(1)$$

By integrating equation (1), between the limits I_t (Intensity of transmitted light) to I_0 (Intensity of incident light) and path length or thickness $t=0$ to $t=l$

$$\int_{I_0}^{I_t} \frac{dI}{I} = -k'c \int_{t=0}^{t=l} dt \Rightarrow [\log_e I]_{I_0}^{I_t} = -k' \cdot c [t]_0^l$$

$$\log_e I_t - \log_e I_0 = -k' \cdot c [l - 0]$$

$$\log_e \left(\frac{I_t}{I_0}\right) = -k' \cdot c \cdot l \quad \text{-----eq}^n(2) \Rightarrow \frac{I_t}{I_0} = e^{-k' \cdot c \cdot l}$$

$$\therefore I_t = I_0 \cdot e^{-k' \cdot c \cdot l} \quad \text{-----eq}^n(3)$$

This is the equation for Beer-Lambert's Law.

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Statement: When a beam of monochromatic light is passed through absorbing solution, its intensity **decreases exponentially** with path length (thickness) as well as concentration of absorbing solution.

Now, from equation-2,

$$\log_e \left(\frac{I_t}{I_0} \right) = -k' \cdot c \cdot l \quad \text{-----eq}^n(2)$$

$$2.303 \log_{10} \left(\frac{I_t}{I_0} \right) = -k' \cdot c \cdot l \quad \text{----- (By changing } \log_e \text{ to } \log_{10} \text{)}$$

$$-2.303 \log_{10} \left(\frac{I_0}{I_t} \right) = -k' \cdot c \cdot l$$

$$\log_{10} \left(\frac{I_0}{I_t} \right) = \frac{k'}{2.303} c \cdot l$$

But Absorbance = $A = \log_{10} \left(\frac{I_0}{I_t} \right)$ and $\epsilon = \frac{k'}{2.303}$ = Molar extinction coefficient

$$\therefore A = \epsilon \cdot c \cdot l \quad \text{-----eq}^n(4)$$

Where, A = Absorbance or optical density (D)

When, c = concentration of absorbing solution = 1M and

l = path length or thickness of cuvette = 1cm

then, **A = ϵ** i.e. Molar extinction coefficient (ϵ) is defined as the absorbance when concentration of absorbing solution and path length are **unity**.

Since, for a given system ϵ and l are constant

$$\therefore A \propto c$$

Thus, absorbance is directly proportional to concentration of absorbing solution.

Deviations from Beer's law:

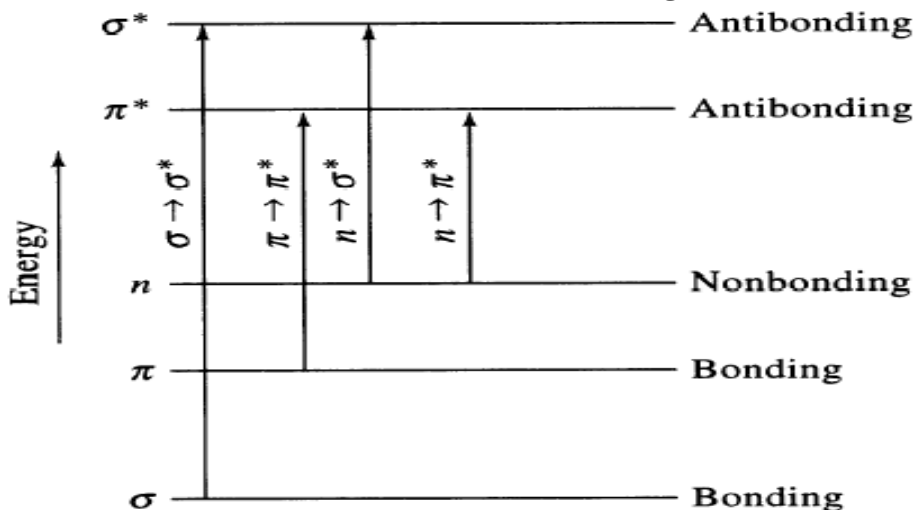
- 1) Deviations may occur due to **presence of impurities** that absorb at the absorption of wavelength.
- 2) Deviations may also occur if **monochromatic light is not used**.
- 3) It may occur if the solution species **undergo polymerization**.
- 4) Deviations are usually found when the **coloured solute dissociates or associates** in solution
- 5) Beer-Lambert law **cannot be applied to suspensions**.
- 6) The law does not **hold coloured solute forms complexes** the composition of which depends upon concentration.
- 7) When solutions of same coloured compounds are kept for long (certain period) time, their colour decomposes and its intensity decreases. Hence, deviations (discrepancies) are observed when readings are taken **after decomposition of colour**.

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Q. Why UV-spectroscopy is called electronic spectroscopy? Explain various types of electronic transitions produced by absorbing UV-visible radiations.

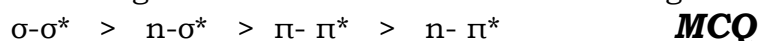
On the absorption of highly energetic UV and visible radiations, it **causes various electronic transitions** from lower to higher energy level. Thus, UV-spectroscopy is called '**Electronic spectroscopy**'.

All possible electronic transitions that occur in organic molecule are as shown below;



We know that $E \propto \frac{1}{\lambda}$,
i.e. smaller the energy (E) required for excitation of electron, larger is the wavelength (λ) of absorption.

Thus, relative energies for transition are in the following order;

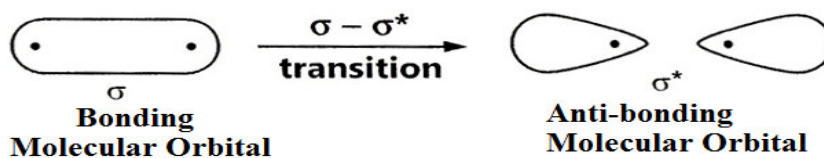


Types of electronic transitions:

- | | |
|---|--|
| a) $\sigma \rightarrow \sigma^*$ transition | c) $n \rightarrow \sigma^*$ transition |
| b) $\pi \rightarrow \pi^*$ transition | d) $n \rightarrow \pi^*$ transition |

a) $\sigma \rightarrow \sigma^*$ transition :

In this type of transition, the promotion of electron from **bonding σ -orbital to antibonding σ^* -orbital** takes place.

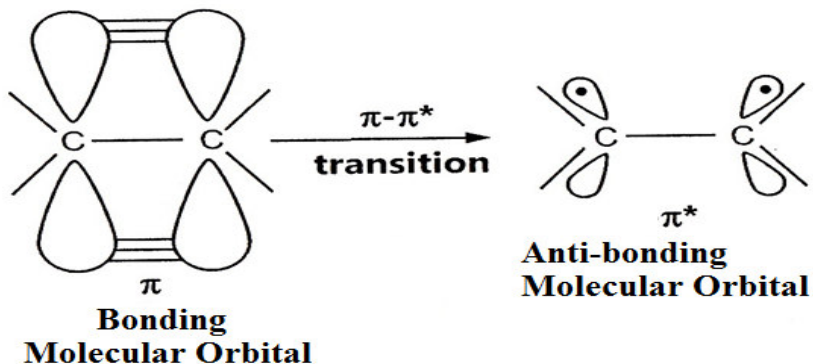


e.g. Saturated hydrocarbons like methane, ethane, n-hexane etc. undergo this type of transition.

As electrons from σ -bond are tightly held, **high energy is required** for such transition and absorption takes place **at very short wavelength** which is below the range of ordinary spectrophotometer and hence such absorption is not recorded in UV spectrum. Therefore **n-hexane can be used as solvent** to record UV spectra.

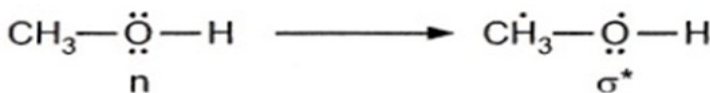
Unit-1& 2) UV Spectroscopy By V.M. DESAI

- b) $\pi \rightarrow \pi^*$ transition: In this type of transition, the promotion of electron from bonding π -orbital to antibonding π^* -orbital takes place.



Compounds having multiple bonds undergo $\pi \rightarrow \pi^*$ transition.
e.g. Alkenes, alkynes, carbonyl compounds, nitriles, and aromatic compounds undergo this type of transition.

- c) $n \rightarrow \sigma^*$ transition: In this type of transition, the promotion of electron from non-bonding (n) to higher energy antibonding σ^* -orbital takes place. Compounds containing non-bonding or unshared electrons (i.e. lone pair) present on hetero atoms (such as O, N, S and halogen) undergo $n \rightarrow \sigma^*$ transition. Examples : Alcohols, amines, alkyl halides, thiols etc. undergo this type of transition.



These transitions are **less energetic and hence occur at longer wavelength**. The ϵ -values for these transitions are very small and hence absorption is very weak. Thus, this transition has less importance for structure determination.

- d) $n \rightarrow \pi^*$ transition: In this type of transition, the promotion of electron from non-bonding (n) to higher energy antibonding π^* -orbital takes place. Compounds containing double bond involving hetero atoms ($>C=O$, $>C=S$, $-C \equiv N$, $-N=O$) undergo $n \rightarrow \pi^*$ transition.



The $n \rightarrow \pi^*$ transition requires **minimum energy and hence it shows absorption at longer wavelength**.

Energy Transition Examples

Increasing Energy	$n \rightarrow \pi^*$	in carbonyl compounds
	$n \rightarrow \sigma^*$	in oxygen, nitrogen, sulfur, and halogen compounds
	$\pi \rightarrow \pi^*$	in alkenes, alkynes, carbonyl and azo compounds
	$\sigma \rightarrow \pi^*$	in carbonyl compounds
	$\sigma \rightarrow \sigma^*$	in alkanes

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Q. Explain the following terms used in UV-spectroscopy:

a) Chromophore and b) Auxochrome

Or Explain Chromophore and Auxochrome with suitable examples.

a) **Chromophore:** It is an **unsaturated functional** group which is capable of **absorbing UV radiation and responsible for imparting colour** to the compound.

The compounds containing Chromophore are called as **Chromogens**.

Function of Chromophore:

- 1) It imparts colour to the compound.
- 2) It is capable of absorbing UV radiation

Examples of Chromophore: $>C=C<$ (alkene), $-C\equiv C-$ (alkyne), $>C=N-$, $-C\equiv N$ (cyanide or nitrile), Azo ($-N=N-$) group, nitro ($-NO_2$) and nitroso ($-N=O$) group, carbonyl ($>C=O$), thiocarbonyl ($>C=S$), quinonoid groups etc.

Generally, it contains **multiple bond** within its structure and undergoes **$n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition.**

b) **Auxochrome:** It is the **saturated functional** group which **does not absorb radiation** greater than 200nm but when it is attached to chromophore causes a **shift in absorption to longer wavelength and increases intensity of absorption peak**. Thus, Auxochromic group is known as **colour enhancing group**.

Or Auxochrome is a **saturated group** with non-bonded (i.e. lone pair) electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption.

Function of Auxochrome:

- 1) It intensify colour of Chromophore.
- 2) In dye, Auxochrome makes the chromogen by fixing it to the fabric either by salt formation or by association.

Examples of Auxochrome: $-OH$, $-SH$, $-OR$, $-NH_2$, $-NHR$, $-Cl$, $-Br$ etc. Generally, all Auxochrome groups are electron releasing or donating in nature. Also, Auxochrome contains the atoms like O, N, S & halogens having non-bonding electrons (i.e. it contains lone pair)

Remark: Types of Chromophores:

a) **Independent Chromophores:** When **single chromophore** is sufficient to impart colour to the compound.

In many cases, single chromophore like Azo (-N=N-) group, nitro (-NO₂) and nitroso (-N=O) group, carbonyl (>C=O), thiocarbonyl (>C=S), quinonoid groups etc. responsible for imparting colour to the compound.

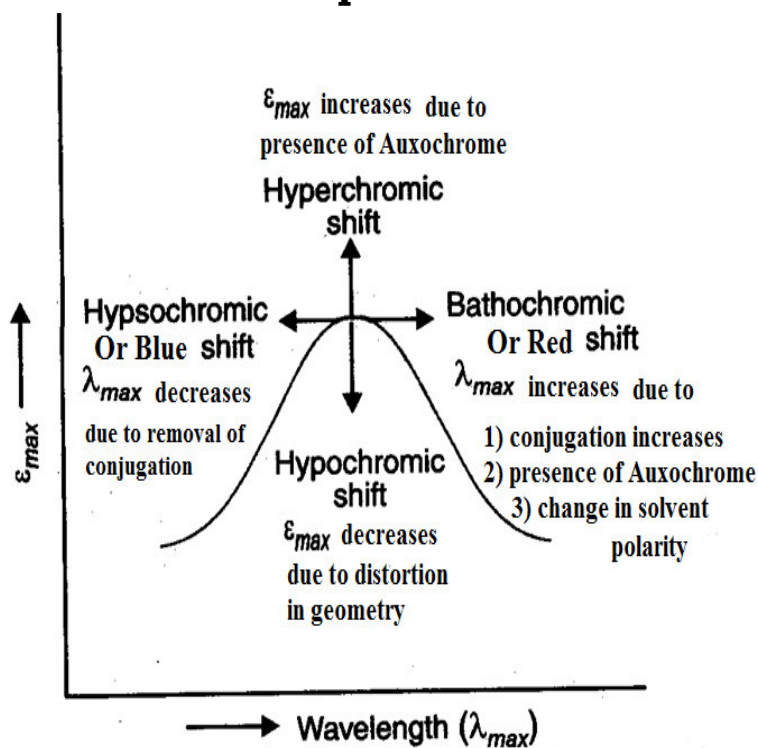
Generally, they show both **n → π*** and **π → π*** **electronic transitions**.

e.g. 1) Nitrobenzene is pale yellow coloured liquid.

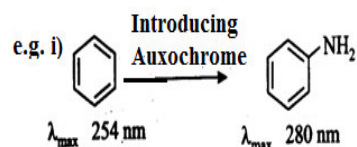
2) In azo dyes, azo (-N=N-) group is responsible for colour of dye.

b) **Dependent Chromophores:** In some cases, single chromophore like >C=C<, >C=O is **not sufficient** to impart colour. When **more than one chromophore** is required to impart colour where one chromophore is conjugated with another of the **same or a different** kind then the absorption is enhanced and a new absorption band appears at a higher wavelength. **e.g.** Acetone CH₃COCH₃ having one carbonyl group is colourless whereas diacetyl CH₃COCOCH₃ having two carbonyl groups is yellow.

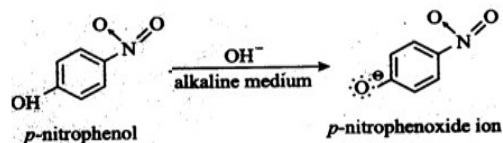
Shifts in UV Absorption band :



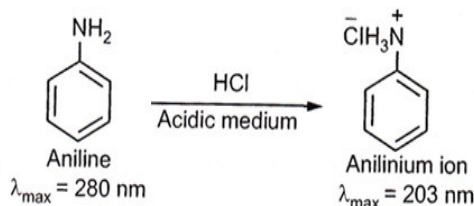
Examples of Bathochromic shift or Red shift



e.g. iii) When the surrounding medium is changed.



Examples of Hypso (Blue) shift:



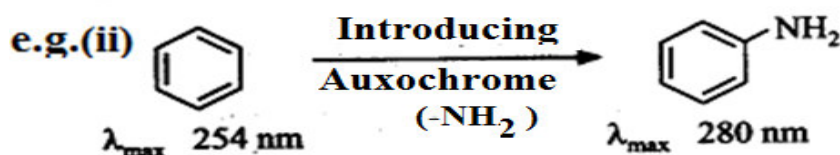
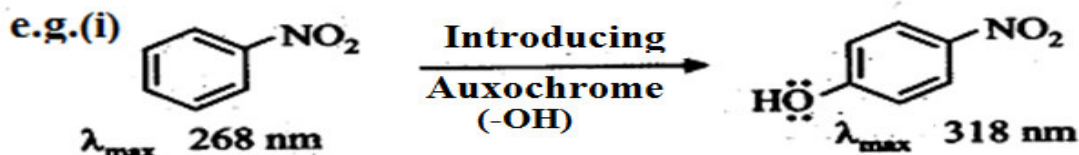
Q. Explain following terms. IMP

a) Bathochromic Effect or Red shift: The shift of absorption band to **longer wavelength** is called Bathochromic or red shift. It is observed due to-

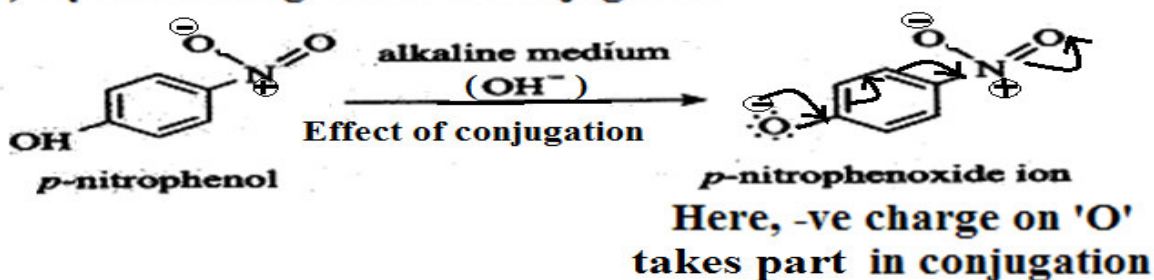
- i) introducing Auxochrome
- ii) changing medium i.e. changing (decreasing) solvent polarity
- iii) increasing conjugation

Examples:

(a) By introducing auxochrome to chromogen



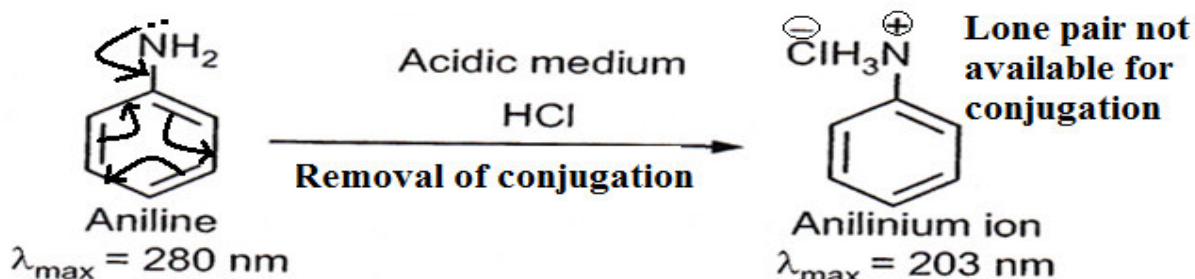
(b) By increasing effect of conjugation



2) Hypsochromic effect or Blue shift: The shift of absorption band to **shorter wavelength** is called **Hypsochromic effect or Blue shift**.

It is due to removal of conjugation or change in the polarity of solvent.

Example: Aniline shows hypsochromic shift upon addition of acid because anilinium ion has no lone pair of electrons on 'N' for conjugation i.e. there is removal of conjugation.



Unit-1& 2) UV Spectroscopy By V.M. DESAI

3) Hyperchromic shift: is effect due to which there is **increase in absorption intensity** (ϵ_{\max}). Generally, introduction of an Auxochrome causes hyperchromic shift.

4) Hypochromic Shift: is effect due to which there is **decrease in in absorption intensity** (ϵ_{\max}). The introduction of groups which distort the geometry of chromophore.

➤ Applications of UV spectroscopy:

Q. Explain how UV spectroscopy is used to determine –

i) Extent of conjugation Oct.2015 Dec.16 MIMP

ii) Study of Geometrical isomers Or MIMP

Distinguish between Cis and Trans isomer Oct.2015 Dec.16

iii) Detection of Chromophore

iv) Strength of Hydrogen Bond

v) Detection of Impurities

i) Extent of conjugation: IMP

(Distinction between conjugated and non-conjugated compounds):

As conjugation increases, λ_{\max} value also increases. In other words, non-conjugated diene has λ_{\max} less than that of conjugated diene. Thus, it can be distinguished between conjugated and non-conjugated compounds (structural analogues) by comparing its λ_{\max} value.



(non-conjugated diene)

$$\lambda_{\max} = 175\text{nm}$$

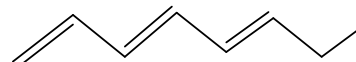
$$\pi \rightarrow \pi^* < 200\text{nm}$$



(conjugated diene)

$$\lambda_{\max} = 219\text{nm}$$

$$\pi \rightarrow \pi^* > 200\text{nm}$$



(extended conjugation)

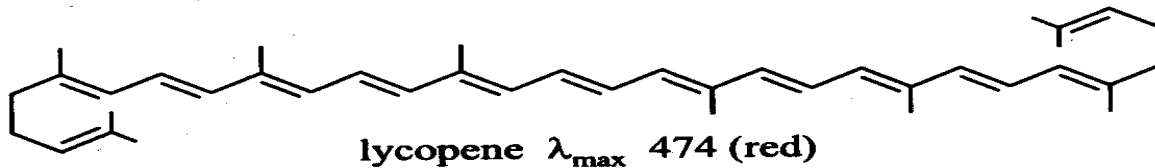
$$\lambda_{\max} = 269\text{nm}$$

Remark: 1) Generally, non-conjugated compounds have absorption due to $\pi \rightarrow \pi^*$ transition is less than 200nm whereas for conjugated compounds, it is greater than 200nm.

Unit-1& 2) UV Spectroscopy By V.M. DESAI

2) The extent of conjugation in polyenes $R-(CH=CH)_n-R$ can be estimated. If n increases i.e. conjugation increases λ_{max} increases.

If $n \geq 8$ then polyenes are coloured e.g. Lycopene with 11 $>C=C<$ in conjugation has $\lambda_{max} = 474\text{nm}$ and gives red colour to tomatoes.



ii) Study of Geometrical isomers / MIMP

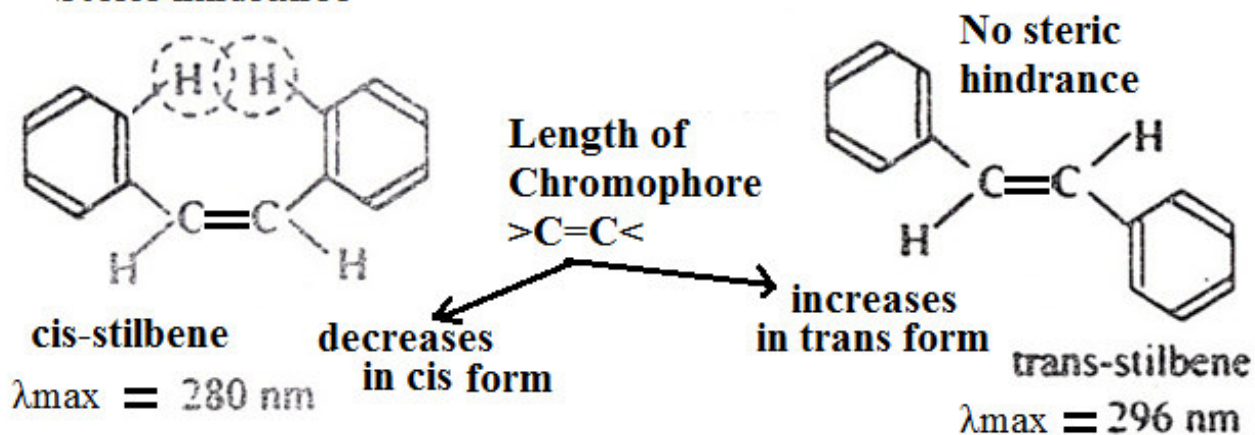
Distinguish between Cis and Trans isomer :

Compared to cis-isomer, trans isomer shows absorption at **higher λ_{max}** values with larger extinction coefficient. *MCQ*

Cis isomer absorbs at **lower (shorter) wavelength** than the trans isomer because-

- i) In cis isomer, there is a **steric hindrance** due to close proximity of two substituents which **disturbs planarity of π -system** by lowering resonance to some extent.
- ii) **The length of Chromophore decreases.** This situation demands pi to pi excitation **more energetic** and hence absorption towards a **shorter wavelength occurs.**

Steric hindrance



Trans isomer absorbs at **longer wavelength** than the cis isomer because-

- i) In trans isomer, the molecule is **planar and hence there is no steric hindrance.**
- ii) **The length of Chromophore increases.** This situation demands pi to pi excitation **less energetic** and hence absorption towards a **longer wavelength occurs.**

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Remark: Other examples given below;

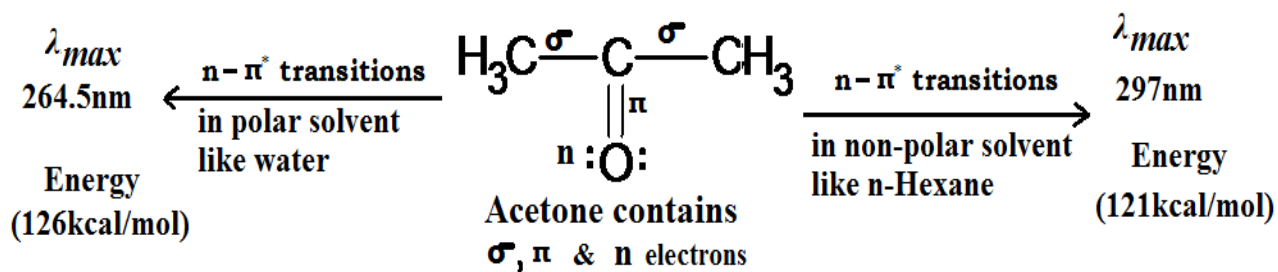
Compound	Cis isomer	Trans isomer
(a) Cinnamic acid ($C_6H_5CH=CH-COOH$)	λ_{max} 264 nm	λ_{max} 273 nm
(b) Azo benzene ($C_6H_5-N=N-C_6H_5$)	λ_{max} 285 nm	λ_{max} 319 nm

iii) Detection of Chromophore:

- A **strong absorption** ($\epsilon > 10,000$ and above 200nm) indicates presence of **conjugated system** of multiple bond due to $\pi \rightarrow \pi^*$ transitions.
- A **weak absorption** ($\epsilon = 10$ to 100 and 270-300nm) indicates presence of **isolated carbonyl group** (aldehyde or ketone) due to $n \rightarrow \pi^*$ transitions.

iv) **Strength of Hydrogen Bond:** The strength of Hydrogen bond can be calculated by measuring λ_{max} values of given compound in polar (water) and non polar (n-Hexane) solvents.

Explanation: Consider UV spectrum of acetone.



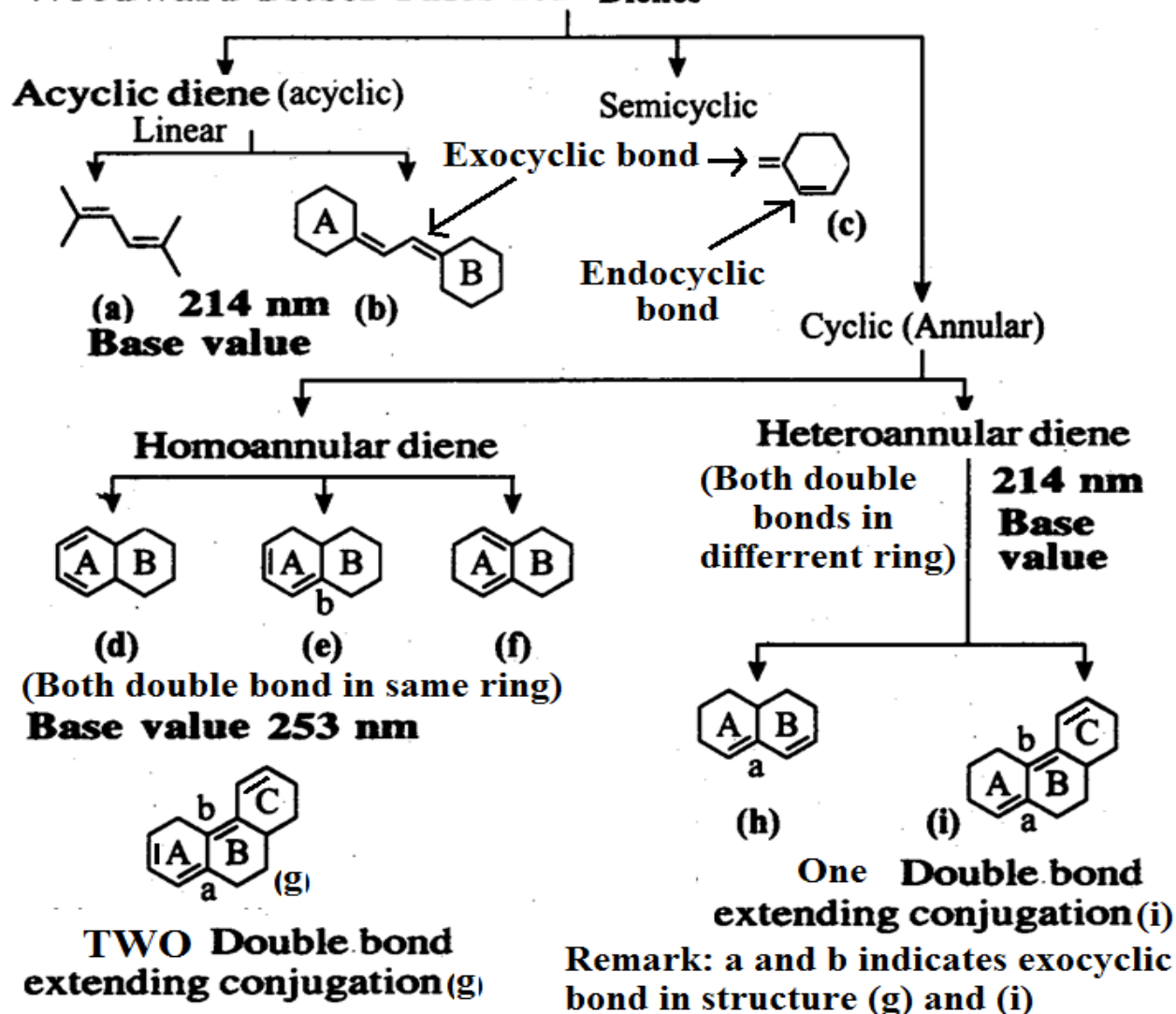
Water forms H-bonds with carbonyl carbon of acetone whereas in n-hexane, no such hydrogen bonding is observed. Thus, the difference in λ_{max} values in water and in n-hexane directly gives the strength of H-bond.

$$\begin{aligned}
 \text{Strength of H-bond} &= \left[\text{Amax value in polar solvent} \right] - \left[\text{Amax value in non-polar solvent} \right] \\
 &= (126 - 121) \text{ kcal/mol} \\
 &= 5 \text{ kcal/mol}
 \end{aligned}$$

Remark: Due to H-bonding, λ_{max} value decreases.

v) **Detection of Impurities:** Presence of impurities can be confirmed by the **appearance of additional peaks** in the spectra of the sample whenever it can be compared with standard material.

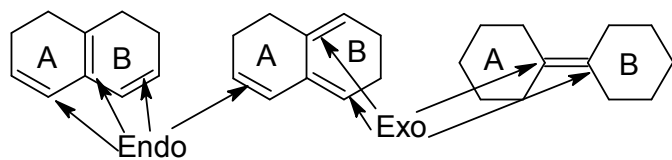
Woodward-Fieser rules for Dienes



Nature of substituent (Increments in value)

- R alkyl (including ring residues) +5
- OR alkoxy +6
- Cl, - Br +5
- O, COR acyloxy +0

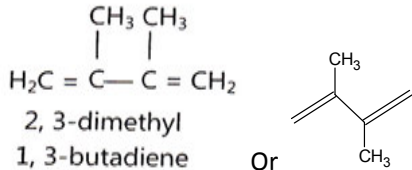
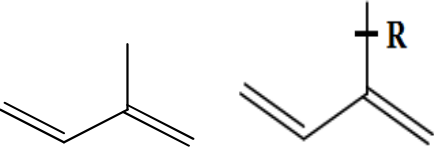
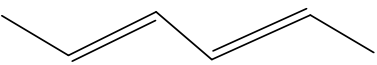
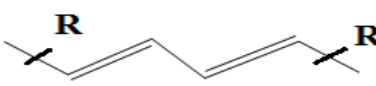
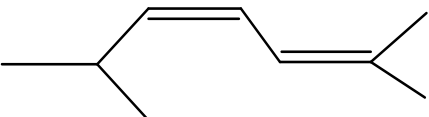
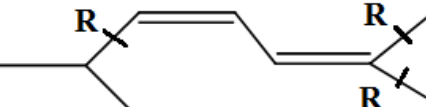
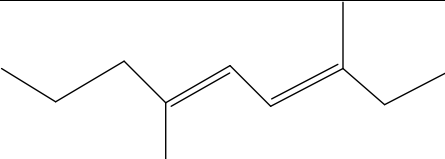
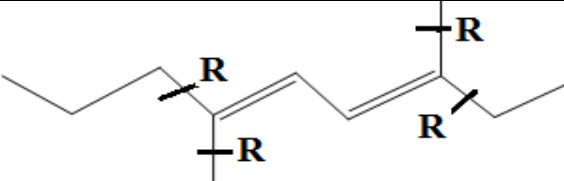
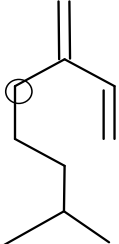
Examples of Exocyclic double bond:



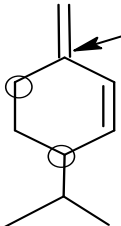
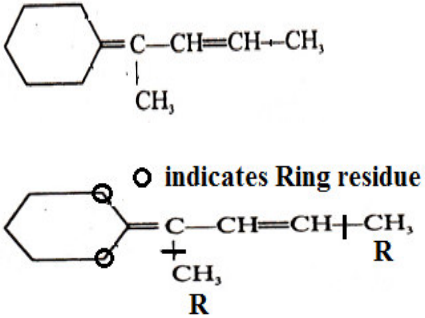
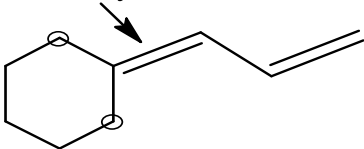
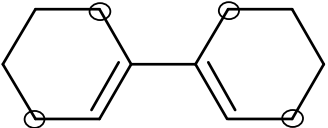
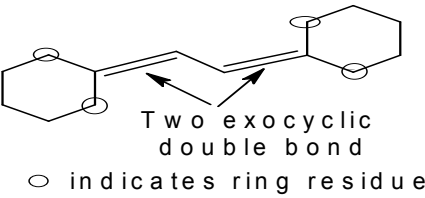
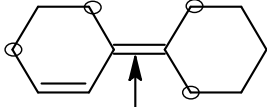
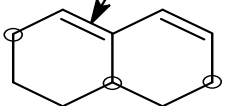
In third example, double bond is attached to both rings so, value of exocyclic bond is 10nm

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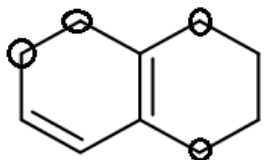
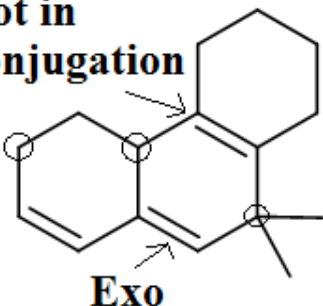
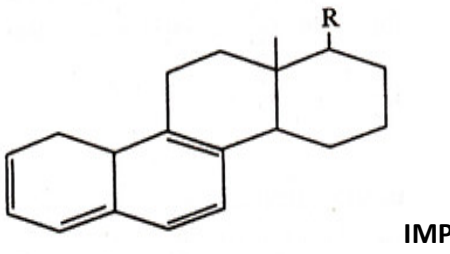
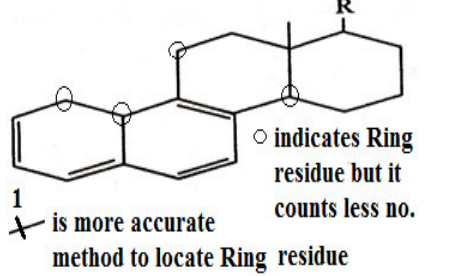
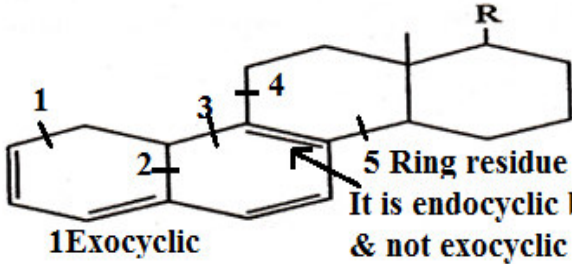
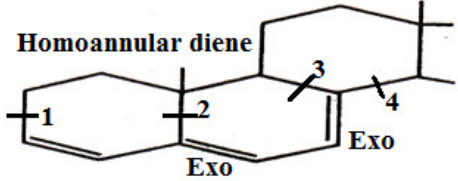
Q. 1) Using Woodward-Fieser rules, calculate λ_{\max} values for the following compounds

	Structure	Answer (Calculated λ_{\max})
1)	 <p>2, 3-dimethyl 1, 3-butadiene</p>	Basic value (acyclic diene) = 214nm 2-R(alkyl) substituent = (5x2) = +10nm Calculated λ_{\max} = 224nm
2)		Basic value (acyclic diene) = 214nm 1-R(alkyl) substituent = (5x1) = +5nm Calculated λ_{\max} = 219nm
3)		 <p>R = Alkyl substituent Basic value (acyclic diene) = 214nm 2-R(alkyl) substituent = (5x2) = +10nm Calculated λ_{\max} = 224nm</p>
4)		 <p>Basic value (acyclic diene) = 214nm 3-R(alkyl) substituent = (5x3) = +15nm Calculated λ_{\max} = 229nm</p>
5)		 <p>Basic value (acyclic diene) = 214nm 4-R(alkyl) substituent = (5x4) = +20nm Calculated λ_{\max} = 234nm</p>
6)	 <p>○ indicates one alkyl substituent</p>	Basic value (acyclic diene) = 214nm 1-R(alkyl) substituent = (5x1) = +5nm Calculated λ_{\max} = 219nm

Unit-1& 2) UV Spectroscopy By V.M. DESAI

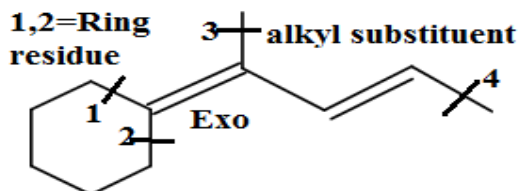
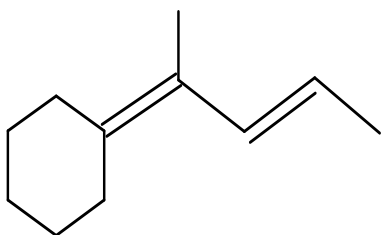
	Structure	Answer (Calculated λ_{\max})
7)	 <p>One exocyclic double bond</p>	Basic value (Semicyclic diene) = 214nm 2-R(alkyl) substituent = (5x2) = +10nm One exocyclic double bond = +5nm Calculated λ_{\max} = 229nm
8)	 <p>○ indicates Ring residue</p>	Basic value (acyclic diene) = 214nm 2-R(alkyl) substituent = (5x2) = +10nm 2 Ring residue = (5x2) = +10nm One exocyclic double bond = +5nm Calculated λ_{\max} = 239nm
9)	<p>1 Exocyclic double bond</p> 	Basic value (acyclic diene) = 214nm 2 Ring residue = (5x2) = +10nm One exocyclic double bond = +5nm Calculated λ_{\max} = 229nm
10)		Basic value (acyclic diene) = 214nm 4 Ring residue = (5x4) = +20nm Calculated λ_{\max} = 234nm
11)	 <p>○ indicates ring residue</p>	Basic value (acyclic diene) = 214nm 4 Ring residue = (5x4) = +20nm 2 exocyclic double bond = (5x2) = +10nm Calculated λ_{\max} = 244nm
12)	 <p>2 Exocyclic double bond</p>	Basic value (acyclic diene) = 214nm 4 Ring residue = (5x4) = +20nm 2 exocyclic double bond = (5x2) = +10nm Calculated λ_{\max} = 244nm
13)	<p>Exocyclic double bond</p> 	Basic value (Heteroannular diene) = 214nm 3 Ring residue = (5x3) = +15nm 1 exocyclic double bond = (5x1) = +5nm Calculated λ_{\max} = 234nm

Unit-1& 2) UV Spectroscopy By V.M. DESAI

	Structure	Answer (Calculated λ_{\max})										
14)	 <p>4 Ring residue</p> <p>Homoannular diene (Not heteroannular diene)</p>	<p>Basic value (Homoannular diene) = 253nm</p> <p>4Ring residue = $(5 \times 4) = +20\text{nm}$</p> <p>Calculated $\lambda_{\max} = \mathbf{273\text{nm}}$</p>										
15)	<p>Not in conjugation</p>  <p>Exo</p> <p>3 Ring residue</p>	<p>Not in conjugation</p> <p>Basic value (Heteroannular diene) = 214nm</p> <p>3Ring residue = $(5 \times 3) = +15\text{nm}$</p> <p>1 exocyclic double bond = $(5 \times 1) = +5\text{nm}$</p> <p>Calculated $\lambda_{\max} = \mathbf{234\text{nm}}$</p>										
16)	 <p>IMP</p>  <p>○ indicates Ring residue but it counts less no.</p> <p>✗ is more accurate method to locate Ring residue</p>	 <p>1 Exocyclic</p> <p>5 Ring residue It is endocyclic bond & not exocyclic</p> <table> <tr> <td>Basic value</td> <td>= 253 nm</td> </tr> <tr> <td>2 Double bonds extending conjugation</td> <td>= 60 nm</td> </tr> <tr> <td>5-Ring residues</td> <td>= 25 nm</td> </tr> <tr> <td>1-Exocyclic double bond 1×5</td> <td>= 5 nm</td> </tr> <tr> <td>Calculate value</td> <td>= 343 nm</td> </tr> </table>	Basic value	= 253 nm	2 Double bonds extending conjugation	= 60 nm	5-Ring residues	= 25 nm	1-Exocyclic double bond 1×5	= 5 nm	Calculate value	= 343 nm
Basic value	= 253 nm											
2 Double bonds extending conjugation	= 60 nm											
5-Ring residues	= 25 nm											
1-Exocyclic double bond 1×5	= 5 nm											
Calculate value	= 343 nm											
17)	<p>Homoannular diene</p>  <p>Exo</p>	<table> <tr> <td>Basic value</td> <td>= 253 n</td> </tr> <tr> <td>2-exocyclic double bonds (2×5)</td> <td>= 10nm</td> </tr> <tr> <td>1-Double bond extending conjugation</td> <td>= 30 nm</td> </tr> <tr> <td>4-Ring reside</td> <td>= 20 nm</td> </tr> <tr> <td>Calculated value</td> <td>= 313 n</td> </tr> </table>	Basic value	= 253 n	2-exocyclic double bonds (2×5)	= 10nm	1-Double bond extending conjugation	= 30 nm	4-Ring reside	= 20 nm	Calculated value	= 313 n
Basic value	= 253 n											
2-exocyclic double bonds (2×5)	= 10nm											
1-Double bond extending conjugation	= 30 nm											
4-Ring reside	= 20 nm											
Calculated value	= 313 n											

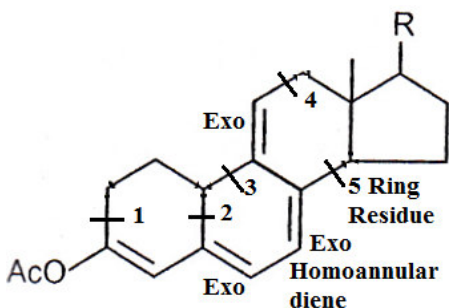
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18)



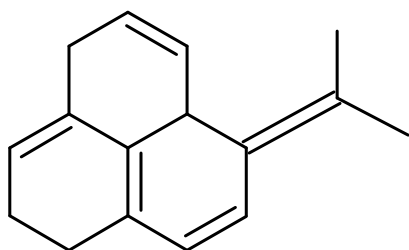
Basic value (for diene) = 214nm
 2Ring residue(1,2) = (5x2) = +10nm
 2 alkyl substituent (3,4) = (5x2) = +10nm
 1 exocyclic double bond = (5x1) = +5nm
 Calculated $\lambda_{max} = 239\text{nm}$

19)

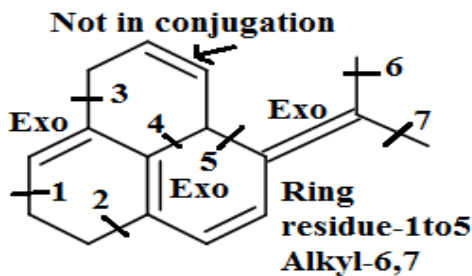


Basic value (Homoannular diene) = 253nm
 5Ring residue(1to5) = (5x5) = +25nm
 3 exocyclic double bond = (5x3) = +15nm
 2 double bonds extending conjugation = (30x2) = +60nm
 -OAc group = +0nm
 Calculated $\lambda_{max} = 353\text{nm}$

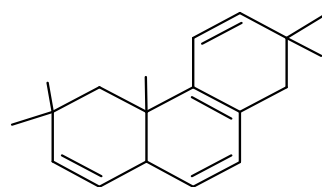
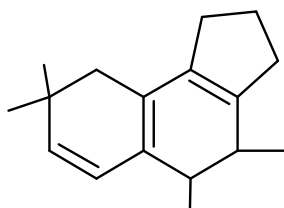
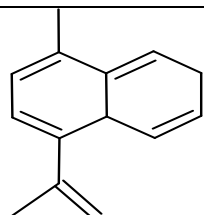
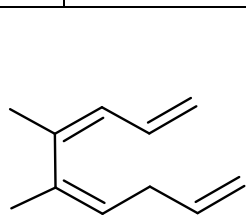
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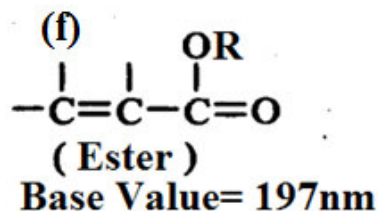
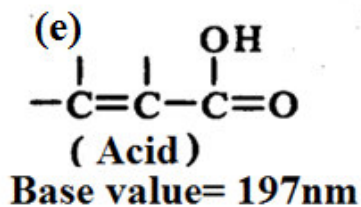
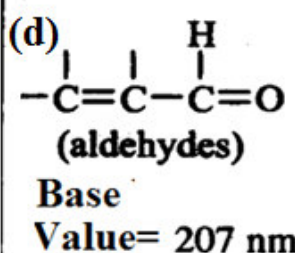
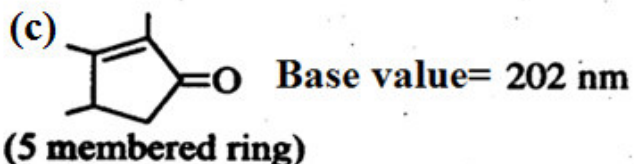
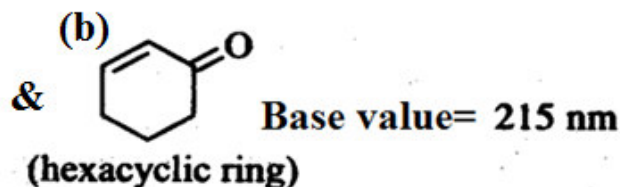
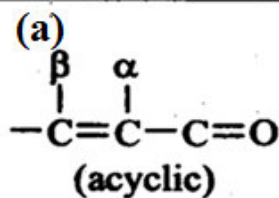
For more complicated structure, to locate ring residue / alkyl group, use dash surrounding double bond. This method is more accurate rather than marking circle.



Basic value (Homoannular diene) = 253nm
 5Ring residue(1to5) = (5x5) = +25nm
 2 Alkyl substituent = (5x2) = +10nm
 3 exocyclic double bond = (5x3) = +15nm
 2 double bonds extending conjugation = (30x2) = +60nm
 Calculated $\lambda_{max} = 353\text{nm}$



Woodward-Fieser rules for Enones = Ene ($>C=C<$) + One ($>C=O$)



Base Values, add these increments...

	α	β	γ	δ, ϵ
Extnd C=C	+30			
Add exocyclic C=C	+5			
Homoannular diene	+39			
-R alkyl	+10	+12	+18	+18
-OH Hydroxy	+35	+30		+50
-OCOCH ₃ Acyl	+6	+6	+6	+6
-OR Alkoxy i.e. ether	+35	+30	+17	+31
-NR ₂ Amines		+95		
-SR Thioether		+80		
Cl/Br	+15/+25	+12/+30		

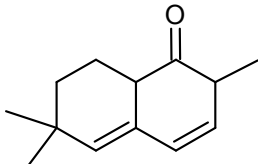
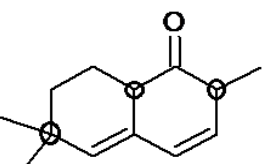
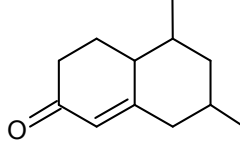
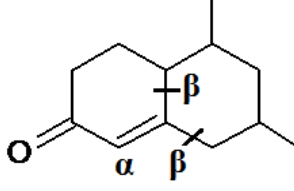
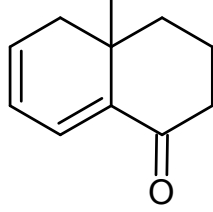
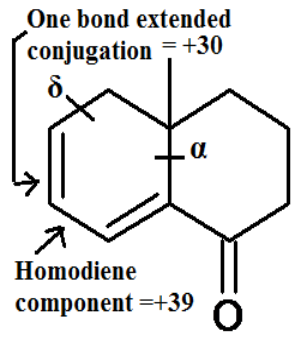
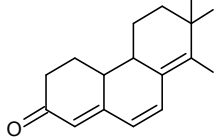
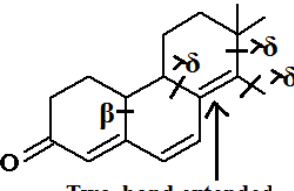
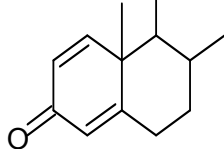
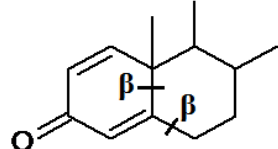
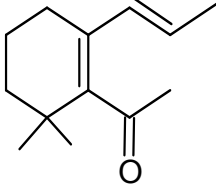
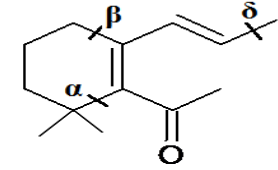
*“When you focus on problem, you will have more problems.
But when focus on possibility, you will have more opportunity.”*

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Q. 2) Using Woodward-Fieser rules, calculate λ_{\max} values for the following compounds

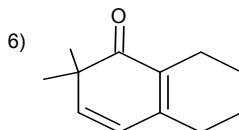
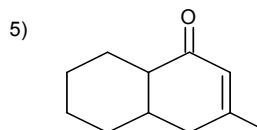
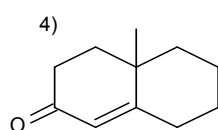
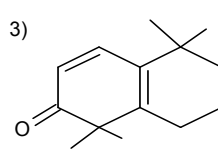
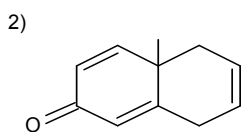
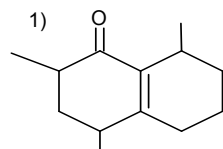
	Structure	Answer (Calculated λ_{\max})
1)		<p>Basic value (acyclic enone) = 215nm No α-substituent = + 0nm Two β- substituent = $(12 \times 2) = +24$nm Calculated $\lambda_{\max} = 239$ nm</p>
2)		<p>Basic value (acyclic enone) = 215nm One α-substituent = + 10nm One β- substituent = + 12nm Calculated $\lambda_{\max} = 237$ nm</p>
3)		<p>Base value (Hexacyclic enone) = 215 nm Two β- substituent $(2 \times 12) = +24$ nm Calculated λ_{\max} value = 239nm</p>
4)		<p>Basic value (enone system) = 215nm One α-substituent = + 10nm Two β- substituent = $(12 \times 2) = + 24$nm Calculated $\lambda_{\max} = 237$ nm</p>
5)		<p>Base value (Hexacyclic enone) = 215 nm One α-substituent = + 10nm One β- substituent = + 12nm Calculated λ_{\max} value = 237nm</p>
6)		<p>Base value (Pentacyclic enone) = 202 nm One α-Hydroxy substituent = + 35nm One β- substituent = + 12nm Calculated λ_{\max} value = 249nm</p>

Unit-1& 2) UV Spectroscopy By V.M. DESAI

	Structure	Answer (Calculated λ_{\max})
7)	 <p>IMP</p>	 <p>$>C=O$ not in conjugation It is Diene (not enone)</p> <p>Basic value (for diene) = 214nm 3 Ring residue = $(5 \times 3) = +15\text{nm}$ One exocyclic bond = +5nm Calculated $\lambda_{\max} = 237 \text{ nm}$</p>
8)		 <p>Basic value (for enone) = 215nm No α-substituent = +0nm Two β-substituent = $(12 \times 2) = +24\text{nm}$ Calculated $\lambda_{\max} = 239 \text{ nm}$</p>
9)	<p>IMP</p> 	 <p>One bond extended conjugation = +30 Homodiene component = +39</p> <p>Basic value (for enone) = 215nm One α-substituent = +10nm One δ-substituent = +18nm One exocyclic bond = +5nm Homodiene component = +39nm One double bond extended conjugation = +30nm Calculated $\lambda_{\max} = 317 \text{ nm}$</p>
10)		 <p>Two bond extended conjugation = +60</p> <p>Basic value (for enone) = 215nm One β-substituent = +12nm 3 substituent beyond $\delta = (18 \times 3) = 54\text{nm}$ Two exocyclic bond = $(5 \times 2) = +10\text{nm}$ Two double bond extended conjugation = $(30 \times 2) = +60\text{nm}$ Calculated $\lambda_{\max} = 351 \text{ nm}$</p>
11)		 <p>Basic value (for enone) = 215nm Two β-substituent = $(12 \times 2) = +24\text{nm}$ One exocyclic bond = +5nm Calculated $\lambda_{\max} = 244 \text{ nm}$</p>
12)		 <p>One bond extended conjugation = +30</p> <p>Basic value (enone system) = 215nm One α-substituent = +10nm One β-substituent = +12nm One δ-substituent = +18nm One double bond extended conjugation = +30nm Calculated $\lambda_{\max} = 285 \text{ nm}$</p>

Unit-1& 2) UV Spectroscopy By V.M. DESAI

Q.3) Following unsaturated ketones have λ_{\max} = 239, 244, 249, 254, 324, and 407nm. Assign λ_{\max} to these structures.



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- ✓ Digital Chemistry Magazine
- ✓ Information of Chemistry Software's and Android App
- ✓ SET/NET/GATE Study Materials & Question Papers
- ✓ Other Technical Supporting Links

Google Classroom Class Code is **kbtbu3**

V. M. DESAI Assistant Professor in Smt. KWC Sangli, M.Sc. (Org. Chem.), NET-LS (23rd All India Rank i.e. AIR June-2011), NET-JRF (85th AIR Dec-2010), 1st rank in Ph.D. Merit list, SUK 1st rank in M.Sc.(Org. Chem.) & B.Sc. Chemistry, 10th Rank in B.Sc. degree (including all subject) Shivaji University, 1st rank in SSC Kuditre center, Kolhapur, DRDO SET Written exam (B), Awarded as 'Best Teacher-2010' By DKTE Ichalkaranji, Ph.D. (Working) Mob. 9325941110

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ST-535

Total No. of Pages :4

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B.Sc. (Part - III) (Semester - V) Examination, December - 2016

CHEMISTRY

Organic Chemistry (Paper - XI)

Sub. Code : 65825

Day and Date : Friday, 02 - 12 - 2016

Total Marks : 40

Time : 12.00 noon to 2.00 p.m.

- Instructions :**
- 1) All questions are compulsory.
 - 2) Figures to the right indicates full marks.
 - 3) Spectroscopic chart supplied by the university is allowed.

Q1) Select the most correct alternative and rewrite the following sentences: [8]

- a) Functional group region of IR spectrum lies in the range of _____ cm^{-1}
- i) 4000-650
 - ii) 4000-1300
 - iii) 750-400
 - iv) 1300-909
- b) The energy of electromagnetic radiation is directly proportional to _____.
- i) Wavelength
 - ii) Intensity
 - iii) Frequency
 - iv) Velocity
- c) A shift in absorption towards longer wavelength is called as _____ shift.
- i) Bathochromic
 - ii) Hypsochromic
 - iii) Hyperchromic
 - iv) Hypochromic
- d) Due to absorption of IR radiation, _____ excitations occurs in the molecule.
- i) Nuclear
 - ii) Electronic
 - iii) Vibrational
 - iv) All of these
- e) The deflection of ions in mass spectroscopy depends on _____.
- i) Shape
 - ii) Mass/charge ratio
 - iii) Charge
 - iv) Size
- f) The number of sets of protons in $\text{CH}_3\text{CH}_2\text{CHO}$ is _____.
- i) One
 - ii) Two
 - iii) Three
 - iv) Four
- g) The highest energy electronic transition is _____.
- i) $n - \pi^*$
 - ii) $\pi - \pi^*$
 - iii) $n - \sigma^*$
 - iv) $\sigma - \sigma^*$

P.T.O.

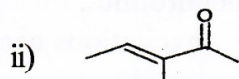
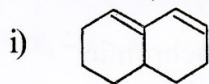
- h) The advantages of spectroscopic analysis include _____.
- i) Rapid
 - ii) Non - destructive
 - iii) Small sample requirement
 - iv) All of these

Q2) Attempt any two of the following: [20]

- a)
 - i) Explain how hydrogen bonding affects IR absorption in carboxylic acids.
 - ii) Explain applications of UV spectroscopy to determine
 - 1) Extent of conjugation
 - 2) Geometrical isomerism
- b)
 - i) Explain fundamental modes of vibrations in IR spectroscopy.
 - ii) What is TMS? Why it is used as reference compound in PMR spectroscopy.
- c)
 - i) Give applications of mass spectroscopy to determine the molecular weight of the compound.
 - ii) Write a note on spin - spin coupling.

Q3) Answer any three of the following: [12]

- a) Calculate λ max value for the following.



- b) Deduce the structure of the compound from following spectral data.

Molecular formula – C_4H_8O

IR : 1715cm^{-1}

PMR : δ 1.07 (triplet, 3H)

δ 1.12 (singlet, 3H)

δ 2.5 (quartet, 2H)

- c) Define the terms chromophore and auxochrome with examples.
- d) How will you distinguish following pairs by PMR spectroscopy?
 - i) CH_3OCH_3 and CH_3CH_2OH
 - ii) CH_3CHO and $HCHO$
- e) What is shielding and deshielding of protons? Explain with suitable examples.

Seat No.	
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B.Sc.(Part-III) (Semester-V) Examination, April-2016

CHEMISTRY

Organic Chemistry (Paper-XI)

Sub. Code : 65825

Day and Date : Monday, 04-04-2016

Total Marks : 40

Time : 12.00 noon to 2.00 p.m.

- Instructions :
- 1) All questions are compulsory.
 - 2) Figures to the right indicate full marks.
 - 3) Spectroscopic chart supplied by university is allowed.

Q1) Select the correct alternative and rewrite the following sentences: [8]

- a) The advantages of spectroscopic analysis includes _____.
- i) rapid
 - ii) non-destructive
 - iii) small sample required
 - iv) all of these
- b) The electromagnetic radiations having longest wavelength are _____.
- i) visible rays
 - ii) infrared rays
 - iii) radio waves
 - iv) gamma rays
- c) Methyl proton peak will appear at highest δ value for _____.
- i) CH_3I
 - ii) $\text{CH}_3 - \text{CH}_3$
 - iii) CH_3Br
 - iv) CH_3F
- d) _____ is used as internal reference standard in NMR spectroscopy.
- i) Benzene
 - ii) Carbon tetra chloride
 - iii) Acetone
 - iv) Tetra methyl silane
- e) Mass spectroscopy is used to determine _____.
- i) functional group
 - ii) molecular weight
 - iii) conjugation
 - iv) nature of proton
- f) The number of fundamental modes of vibrations for linear molecule are _____.
- i) $3N - 5$
 - ii) $3N - 6$
 - iii) $3 - 6N$
 - iv) $5N - 3$
- g) The co-ordinates of mass spectrum are _____.
- i) wavelength and mass of ion
 - ii) frequency and mass to charge ratio
 - iii) relative abundance and mass to charge ratio
 - iv) wavelength and absorbance

P.T.O.

Seat No.	
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B.Sc. (Part - III) (Semester - V) Examination, April - 2017

CHEMISTRY

Organic Chemistry (Paper - XI)

Sub. Code : 65825

Day and Date : Thursday, 20-04-2017

Total Marks : 40

Time : 3.00 p.m. to 5.00 p.m.

- Instructions :
- 1) All questions are compulsory.
 - 2) Figures to the right indicate full marks.
 - 3) Spectroscopic chart supplied by university is allowed.

Q1) Rewrite the sentences choosing correct alternatives given below: [8]

- a) The electromagnetic radiations having longest wavelength are _____.
- i) visible rays
 - ii) radiowaves
 - iii) infrared rays
 - iv) gamma rays
- b) _____ type of electronic transitions requires least energy.
- i) $\sigma \rightarrow \sigma^*$
 - ii) $\pi \rightarrow \pi^*$
 - iii) $n \rightarrow \sigma^*$
 - iv) $n \rightarrow \pi^*$
- c) The number of fundamental modes of vibrations for linear molecule are _____.
- i) $3N$
 - ii) $3N - 5$
 - iii) $3N - 6$
 - iv) $5N - 3$
- d) IR - absorption occurs only when there is change in _____.
- i) bond angle
 - ii) bond length
 - iii) bond polarity (dipole moment)
 - iv) bond strength
- e) The advantages of spectroscopic analysis includes _____.
- i) rapid
 - ii) small sample requirement
 - iii) non destructive
 - iv) all of these
- f) In bathochromic or red shift _____.
- i) λ_{\max} increases
 - ii) λ_{\max} decreases
 - iii) ϵ_{\max} increases
 - iv) ϵ_{\max} decreases

P.T.O.

- g) The formula of organic compound showing only one peak in PMR spectrum is _____.
- i) $\text{CH}_3 - \text{CH}_2 - \text{Br}$ ii) $\text{CH}_3 - \text{O} - \text{CH}_3$
 iii) $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ iv) $\text{CH}_3 - \text{CH}_2 - \text{OH}$
- h) The co-ordinates of mass spectrum are _____.
- i) Wavelength & mass of ion
 ii) Wavelength & absorbance
 iii) relative abundance & mass charge ratio
 iv) frequency & mass charge ratio

Q2) Attempt any two of the following: [20]

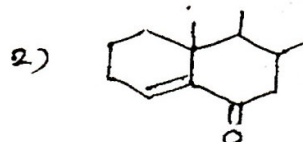
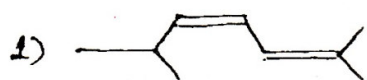
- a) i) Explain magnetic and non-magnetic nuclei with suitable examples.
 ii) Draw a neat and labelled schematic diagram of NMR - spectrometer.
- b) i) Explain the application of UV-visible spectroscopy to determine-
 1) geometrical isomers and
 2) extent of conjugation
 ii) Explain McLafferty rearrangement in carbonyl compound with suitable example.
- c) i) What are fundamental modes of vibrations involved in IR spectroscopy.
 ii) What is selection rule? Explain IR - active and inactive transitions with suitable examples.

Q3) Solve any three of the following: [12]

- a) Deduce the structure of the compound from the following spectral data.

Molecular formula	-	$\text{C}_4\text{H}_8\text{O}$
IR	-	1715 cm^{-1}
PMR	-	$\delta 1.2$ (singlet, 3H) $\delta 2.5$ (quartet, 2H) $\delta 1.07$ (triplet, 3H)

- b) How can you determine molecular weight by mass spectroscopy.
 c) Which compound is used as a reference in PMR - spectroscopy? Why?
 d) Calculate λ_{max} values for the following.



- e) State Hooks law. Give its mathematical expression.

Seat No.	
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B.Sc. (Part - III) (Semester - V) Examination, October - 2015

CHEMISTRY

Organic Chemistry (Paper - XI) (New)

Sub. Code : 65825

Day and Date : Thursday, 29 - 10 - 2015

Total Marks : 40

Time : 12.00 noon to 02.00 p.m.

- Instructions :**
- 1) All questions are compulsory.
 - 2) Figures to the right indicate full marks.
 - 3) Spectroscopic chart supplied by university is allowed.

Q1) Select the most correct alternative and rewrite the following sentences. [8]

- a) Finger print region of IR spectrum lies in the range of _____ cm^{-1}
- i) 4000 - 650
 - ii) 4000 - 1350
 - iii) 400 - 750
 - iv) 1350 - 650
- b) The energy (E) carried by photon is equal to _____ .
- i) $\frac{hc}{\lambda}$
 - ii) $h\nu$
 - iii) $h\bar{\nu}$
 - iv) both (i) & (ii)
- c) The advantages of spectroscopic analysis include _____ .
- i) rapid
 - ii) non - destructive
 - iii) small sample requirement
 - iv) All of these
- d) The electromagnetic radiation range between wave length 400 to 750 nm is called as _____ range.
- i) visible
 - ii) infrared
 - iii) radiowaves
 - iv) gamma
- e) A typical example of chromophore is _____
- i) $-\text{NH}_2$
 - ii) $-\text{OH}$
 - iii) $-\text{Cl}$
 - iv) $-\text{NO}_2$
- f) The highest energy electronic transition is _____ .
- i) $\pi \rightarrow \pi^*$
 - ii) $n \rightarrow \sigma^*$
 - iii) $\sigma \rightarrow \sigma^*$
 - iv) $n \rightarrow \pi^*$
- g) IR spectroscopy is used to determine _____
- i) extent of conjugation
 - ii) functional group
 - iii) molecular weight
 - iv) Nature of proton

h) The NMR spectroscopy cannot be shown by _____ nuclei.

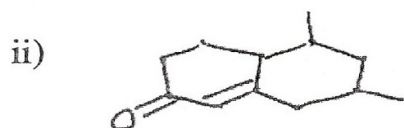
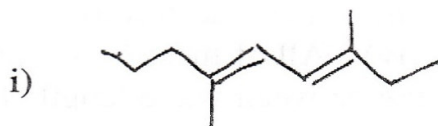
- i) $^1_1\text{H}^1$ ii) $^{13}_6\text{C}^{13}$
iii) $^{15}_7\text{N}^{15}$ iv) $^{12}_6\text{C}^{12}$

Q2) Attempt any TWO of the following [20]

- a) i) Explain how does the resonance effect causes change in IR absorption frequency of $\text{>C}=\text{O}$ (carbonyl) group.
ii) Explain equivalent and non-equivalent protons with suitable examples.
- b) i) Draw a neat and labelled schematic diagram of mass spectrometer.
ii) Explain how UV (ultra-violet) spectroscopy is used to determine
1) extent of conjugation and
2) geometrical isomers.
- c) i) What is chemical shift? Explain how inductive effect varies the chemical shift value.
ii) Explain McLafferty rearrangement in carbonyl compounds with suitable example.

Q3) Attempt any three of the following [12]

a) Calculate λ_{max} value for the following.



b) Deduce the structure of the compound from following spectral data

Molecular formula $\text{C}_7\text{H}_8\text{O}$

IR 3620 cm^{-1}

PMR δ 3.6 (S,1H)

δ 4.5 (S,2H)

δ 7.3 (S,5H)

c) Explain the fundamental modes of vibrations involved in IR spectroscopy.

d) How will you distinguish the following pairs by PMR spectroscopy?

- i) $\text{CH}_3 - \text{O} - \text{CH}_3$ and $\text{CH}_3 - \text{CH}_2 - \text{OH}$
 ii) $\text{C}_6\text{H}_5\text{Cl}$ and CH_3Cl
 e) What is TMS? Why it is used as reference compound in PMR spectroscopy.

SPECTROSCOPIC VALUES

a) Woodward and Fieser Rules for Diene and Triene

	λ max (nm)
Acyclic and heteroannular dienes 214 nm
Homoannular dienes 253 nm
Addition for each substituent -	
-R (alkyl, including part of carbocyclic ring) 5 nm
-OR (alkoxy) 6 nm
-Cl, -Br 5 nm
-OCOR (acyloxy) 0 nm
-CH = CH - additional conjugation 30 nm
If one double bond is exocyclic to one ring 5 nm
If exocyclic to two rings simultaneously 10 nm

b) Rules for α, β unsaturated Aldehydes and Ketones

Ketones : $-\overset{\beta}{\text{C}} = \overset{\alpha}{\text{C}} - \overset{\gamma}{\text{C}} = \text{O}$

acyclic or 6 - ring cyclic 215 nm
5 - ring cyclic 202 nm

Aldehydes :

$-\overset{\beta}{\text{C}} = \overset{\alpha}{\text{C}} - \text{CHO}$ 207 nm

Acids and esters :

$-\overset{\beta}{\text{C}} = \overset{\alpha}{\text{C}} - \text{COOH (R)}$ 197 nm

Extended Conjugation

$-\overset{\delta}{\text{C}} = \overset{\gamma}{\text{C}} - \overset{\beta}{\text{C}} = \overset{\alpha}{\text{C}} - \overset{\gamma}{\text{C}} = \text{O}$ etc.. add 30 nm

Homodiene component add 39 nm

Addition For (all figures in nm.)

	α	β	γ	δ
- R alkyl (including part of carbocyclic ring)	10	12	18	18
- OR (alkoxy)	35	30	17	31
- OH (Hydroxy)	35	30	30	50
- SR (Thioether)	-	80	-	-
- Cl (Chloro)	15	12	12	12
- Br (Bromo)	25	30	25	25
- OCOR (acyloxy)	6	6	6	6
- $\text{NH}_2, - \text{NHR}, - \text{NR}_2$ (amino)	-	95	-	-

- 1) If one double bond is exocyclic to one ring add 5 nm
 2) If exocyclic to two rings simultaneously add 10 nm

Chemical Shifts of Protons δ in ppm.

Proton	δ (ppm.)	Proton	δ (ppm.)
$\text{CH}_3 - \text{R}$	0.9	$-\text{C} - \text{CH}_2 - \text{C} -$	1.4
$\text{CH}_3 - \text{C} = \text{C}$	1.7	$-\text{C} - \text{CH}_2 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{OR}$	2.2
$\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{R}$	2.0	$-\text{C} - \text{CH}_2 - \text{C} = \text{C}$	2.3
$\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{R}$	2-2.7	$-\text{C} - \text{CH}_2 - \text{S} -$	2.5
$\text{CH}_3 - \text{S} -$	2.1	$-\text{C} - \text{CH}_2 - \text{N} -$	2.5
$\text{CH}_3 - \text{Ar}$	2.3	$-\text{C} - \text{CH}_2 - \text{Ar}$	2.7
$\text{CH}_3 - \underset{\text{I}}{\text{N}} - \text{R}$	2.3	$-\text{C} - \text{CH}_2 - \text{OR}$	3.4
$\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{Ar}$	2.6	$-\text{C} - \text{CH}_2 - \text{I}$	3.2
$\text{CH}_3 - \underset{\text{I}}{\text{N}} - \text{Ar}$	3.0	$-\text{C} - \text{CH}_2 - \text{Br}$	3.5
$\text{CH}_3 - \text{O} - \text{R}$	3.3	$-\text{C} - \text{CH}_2 - \text{Cl}$	3.6
$\text{CH}_3 - \text{O} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{R}$	3.7	$-\text{C} - \text{CH}_2 - \text{OH}$	3.6
$\text{CH}_3 - \text{O} - \text{Ar}$	3.8	$-\text{C} - \text{CH} - \text{C}$	1.5
$\text{Ar} - \text{H}$	7.3	$-\text{C} - \text{CH} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{R}$	2.5
$\text{R} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{H}$	9.0 - 10.0	$-\text{C} - \text{CH} - \text{N} -$	2.8
$\text{R} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{OH}$	10.5 - 12.0	$-\text{CH} = \text{Ar}$	3.0
$\text{R} - \text{OH}$	0.5 - 4.5	$-\text{C} - \text{CH} - \text{S} -$	3.2
$\text{Ar} - \text{OH}$	4.5	$-\text{C} - \text{CH} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{Ar}$	3.3
		$-\text{C} - \text{CH} - \text{O} - \text{R}$	3.7
		$-\text{C} - \text{CH} - \text{OH}$	3.9
		$-\text{CH} - \text{O} - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{R}$	4.8

BEST OF LUCK FOR YOUR BRIGHT FUTURE