Rayat Shikshan Sanstha's

Dr. Patangrao Kadam Mahavidyalaya, Ramanandnagar (Burli),

Department of Chemistry

B.Sc. Part-III; Organic Chemistry (Sem – V)

Question Bank

UNIT: I

Name of the Topic: Introduction to Spectroscopy

(A) Answer in one sentence (One mark for each question).

1. Define the spectroscopy?
2. What are the different types of Spectroscopy?
3. Define Absorption Spectroscopy?
4. Define the term: 1.Wavelength 2. Frequency
5. What are the different types of exciations?
6. What are the advantages of Spectroscopic methods ?
7. Define the term Fluorescence?
8. Define the term Scattering?
9. What are the different types of Scattering?
10. What is the relation between wavelength and frequency ?

(B) Choose the Correct Alternative for each of the following and rewrite the sentence:

1. The study of the responses of the molecule when it is exposed to certain kinds of radiations is called as …….
   (a) excitation (b) transition
   (c) spectroscopy (d) frequency
2. The distance between two successive crests (or troughs) is known as ……
   (a) wavelength (b) frequency
   (c) amplitude (d) energy
3. The reciprocal of wavelength is called as ……
   (a) frequency (b) wave number
   (c) wavelength (d) amplitude
4. The electromagnetic radiation is made up of discrete particles called ……
   (a) amplitude (b) frequency

(c) photons (d) wavelength

5. Frequency is measured in terms of ……
   (a) Hertz (b) centimeter
   (c) meter (d) millimicron
6. …… are used to undergo rotational excitations.
   (a) Microwaves (b) Radiowaves
   (c) Infrared radiations (d) Ultraviolet radiations
7. Wavelength is measured in terms of ……
   (a) Hertz (b) centimeter
   (c) cycles per second (d) per centimeter
8. The wavenumber of a transition is 2000 cm^{-1} ..... type of the electromagnetic spectrum does this come?
   (a) Microwave (b) Ultraviolet-visible
   (c) Radiowave (d) Infrared
9. The frequency of a transition is 5.4×10^{15} Hz. What is the corresponding wavelength?
   (a) 5.6×10^{-6} m (b) 560 nm
   (c) 5.6×10^{-8} m (d) 180 000 cm^{-1}
10. The wavelength of an absorption is 495 nm. In what part of the electromagnetic spectrum does this lie?
    (a) Radiowave (b) Ultraviolet-visible
    (c) Microwave (d) Infrared
11. The frequency of a transition is 3.1×10^{10} Hz. What is the energy of this transition?
    (a) 2.1×10^{-44} J (b) 2.0×10^{-23} J
    (c) 2.1×10^{-44} kJ (d) 2.0×10^{-23} kJ
12. A shift to lower wavenumber for an absorption in a spectrum corresponds to.....
    (a) a shift to lower wavelength. (b) a shift to lower frequency
    (c) a shift to higher energy (d) a loss of intensity
13. An absorption in an electronic spectrum is recorded at 17 000 cm^{-1}. What does this correspond to in nm?
    (a) 5900 nm (b) 59 nm (c) 59 000 nm (d) 590nm

[B] Short and Long Answer Type Questions:

1. Define the following terms:
   (a) Wavelength (b) Frequency
   (c) Wave number (d) Amplitude
   (e) Absorption spectroscopy
   (f) Emission spectroscopy.

(C) Long Answer Questions:

1. What is Electromagnetic Radiation? What are the different regions of electromagnetic radiations? Give their approximate range in terms of their wavelengths.
2. What are different kinds of excitations that are possible? Illustrate with molecular energy level diagram.
3. Discuss the interaction of radiation with molecules. What different kinds of excitations take place? How different types of radiations can be used to study these excitations?
4. Explain the terms: (a) Absorption, (b) Emission (c) Fluorescence, (d) Scattering.

(D) Short Answer Questions:

1. Give advantages of spectroscopic methods.
2. Types of spectroscopy
3. Electromagnetic spectrum

UNIT: II

Name of the Topic: UV Spectroscopy

[A] Objective Type Questions

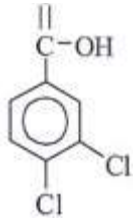
[I] Select the most correct alternative from among those given below.

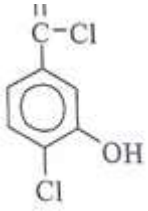
1. The wavelength range for UV-Visible region of electromagnetic spectrum is ……
   (a) 2000-8000 A^o (b) 200-800 A^o
   (c) 200-800 cm (d) 2000-8000 cm
2. Saturated hydrocarbons show …… type of transition.
   (a) π-π^* (b) σ-σ^*
   (c) n-σ^* (d) n-π^*
3. The shift of absorption band to longer wavelength is called as ……
   (a) bathochromic shift (b) hypsochromic shift
   (c) hyperchromic effect (d) hypochromic effect
4. The shift of absorption band to shorter wavelength is called as ……
   (a) bathochromic shift (b) hypsochromic shift
   (c) hyperchromic effect (d) hypochromic effect
5. A typical example of chromophore is ……
   (a) >C = O (b) −OH
   (c) $–NH_2$ (d) −Br
6. The molar absorption corresponding to wavelength maxima is called as ……
   (a) λ_{max} (b) γ_{max}
   (c) ε_{max} (d) ψ_{max}
7. A chromophore is an …… group
   (a) saturated (b) unsaturated

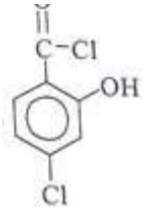
(c) paraffinic (d) single bonded

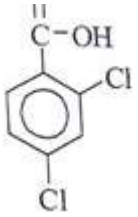
8. …… is an example of auxochrome.
   (a) $-NH_2$ (b) $>C = N-$
   (c) $>C = O$ (d) $>C = C<$
9. Absorption of UV radiations by an organic compound brings mainly about …… excitations
   (a) electronic (b) crotonic
   (c) rotational (d) vibrational
10. A plot of energy absorbed versus wavelength is called as ……
   (a) absorption spectrum (b) adsorption spectrum
   (c) desorption spectrum (d) deadsorption spectrum
11. α, β-unsaturated ketone is called as …… system.
   (a) diene (b) ene
   (c) enone (d) one
12. The $>C = C - C = C<$ group is called as …… system.
   (a) dienophile (b) diene
   (c) enone (d) one
13. The Nature of band obtained in U.V. spectrum is relatively ……
   (a) broad (b) sharp
   (c) intence (d) very sharp
14. The relative energies for transition are in …… order.
   (a) $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > n \rightarrow \pi^* > \pi \rightarrow \pi^*$
   (b) $\pi \rightarrow \pi^* > n \rightarrow \pi^* > n \rightarrow \sigma^* > \sigma \rightarrow \sigma^*$
   (c) $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$
   (d) $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$
15. …… type of transition takes place in $>C = O$ (ketone).
   (a) $\sigma \rightarrow \sigma^*$ (b) $n \rightarrow \sigma^*$
   (c) $n \rightarrow \pi^*$ (d) $\pi \rightarrow \pi^*$
16. An effect which leads to an increase in absorption intensity $\in_{max}$ is called as ……
   (a) hypsohromic shift (b) hyperchromic shift
   (c) bathochromic shift (d) hypochromic shift
17. When $>C = C<$ bond is in conjugation with a carbonyl group, such compounds are called as…
   (a) enones (b) dienes
   (c) enamines (d) dienophiles
18. Extensive correlations between U.V. spectra and the structures of organic compounds lead to simple empirical rules for the calculation of wavelength maxima is known as ……
   (a) Woodward Fieser rule (b) Fieser rule
   (c) Woodward rule (d) Fieser-Fieser rule

19. In diene …… type of transition takes place.
    (a) $\sigma \rightarrow \sigma^*$ (b) $n \rightarrow \sigma^*$
    (c) $n \rightarrow \pi^*$ (d) $\pi \rightarrow л^*$
20. When >C = C< bond is in conjugation with a carbonyl group, such compounds are called ……
    (a) dienes (b) enones
    (c) enes (d) enamines
21. Basic λ_{max} for an unsubstituted, conjugated, homoannular diene is ……
    (a) 215 nm (b) 207 nm
    (c) 312 nm (d) 253 nm
22. Which of the following wavelength ranges is associated with UV spectroscopy?
    (a) 0.8 - 500μm (b) 400 - 100nm
    (c) 380 - 750nm (d) 0.01 - 10n
23 . Which of the following compounds does not absorb light in the UV/visible spectrum?
    (a) Aspirin (b) Paracetamol
    (c) Chloral hydrate (d) Phenobarbitone
24. Which of the following comparison is correct for solvent shift on the n –>π* transition of acetone?
    (a)$H_20=CH_30H=C_2H_50H=CHC1_3=C_6H_{14}$ (b)$H_20>CH_30H>C_2H_50H>CHC1_3>C_6H_{14}$
    (c)$H_20<CH_30H<C_2H_50H<CHC1_3<C_6H_{14}$ (d) $H_20 > CH_30H < C_2H_50H < CHC1_3 < C_6H_{14}$
25. What is the correct order of λ_{max} for n–> π* transition for the following three compounds?
    (a) RCOOH > RCOOR' > $RCONH_2$ (b) RCOOH = RCOOR' = $RCONH_2$
    (c) RCOOH = RCOOR' < $RCONH_2$ (d) RCOOH = RCOOR' > $RCONH_2$
26. Which of the following structural formula that is consistent with the following observations: An acid, $C_7H_4O_2Cl_2$ shows a UV maximum of 242 nm?

(a) 

(b) 

(c) 

(d) 

[B] Long Answer Type Questions

1. Explain the significance of following electronic transitions. Illustrate with suitable examples.
    (a) $\sigma \rightarrow \sigma^*$ (b) $\pi \rightarrow \pi^*$
    (c) $n \rightarrow \pi^*$ (d) $n \rightarrow \sigma^*$

2. List all possible electronic transitions in the following compounds :

(a) CH_3Cl (b) H—C—H
‖
O

(c) Cyclohexyl chloride

(d) CH_4 (e) Cyclohexene

(f) $CH_3—CH_2—C \equiv N$ (g) $CH_3—C \equiv C—NH_2$

4. How will you differentiate the following pairs by U.V. spectroscopy ?

(a) 1, 3 butadiene and 1, 4 cyclohexadiene.

(b) Phenol and cyclohexanol.

(c) $H_2C = CH—CH = CH_2$ and $H_2C = CH_2$.

(d) 1, 3 pentadiene and 1, 4 pentadiene.

(e) Cyclohexa 1 : 3 diene and cyclohexa 1 : 4 diene.

(f) 1, 3, 5 hexatriene and 1, 3 hexadiene.

(g) Benzene and cyclohexane.

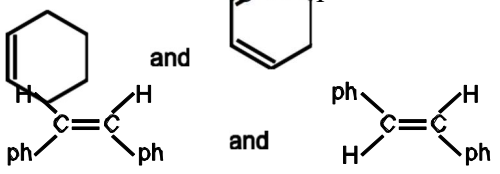
(h) Benzene and nitrobenzene.

(i) Nitrobenzene and p-nitrophenol.

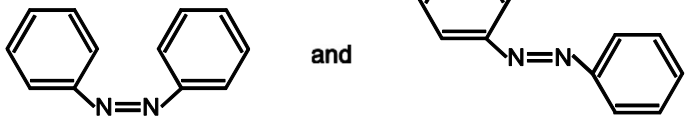
(j) Aniline and nitrobenzene.

(k) p-nitroaniline and m-nitroaniline.

5. Which of the following compounds have higher λ_{max} value ? Why ?

(a) 

(b) Cis stilbene Trans stilbene



(c) Cis azobenzene Trans azobenzene

(d) Cis -cinnamic acid and trans- cinnamic acid.

6. Explain the following:

(a) U.V. spectra are relatively broad as compared to IR spectra.

(b) Out of IR and U.V., which radiations have more energy ? Why ?

(c) Benzene shows absorption in U.V. region whereas hexane is transparent.

(d) Phenol shows bathochromic shift upon addition of alkali while aniline shows hypsochromic shift upon addition of acid.

(e) p-nitro dimethyl aniline gives a yellow solution in water which fades to colourless, when made acidic.

(f) p-nitroaniline shows pronounced red shift. Why ?

(g) Account for the following variations in λ_{max} values :

CH_3Cl = 173 nm, CH_3Br = 204 nm, CH_3I = 258 nm.

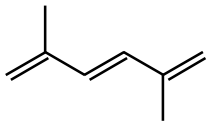
(h) Consider the following molecules and their λ_{max} values :

Ethylene = 170 nm; 1, 3 butadiene = 217 nm; 1, 3 cyclohexadiene = 256 nm; 1, 3, 5 hexatriene = 274 nm.

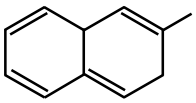
Draw the conclusion about the relationship between the structure and wavelength of absorption.

7. State and explain Beer-Lambert's law and give its limitations.
8. Explain the terms chromophore and auxochrome with suitable examples.
9. Explain the applications of UV spectroscopy.
10. How will you distinguish cis and trans geometrical isomers using UV spectroscopy.
11. Explain various types of electronic transitions in UV spectroscopy.
12. Explain the relation between the light absorbed and complementary colour in visible spectrum.
13. Calculate λ_{max} for the following compounds by using Woodword-Fieser rule.

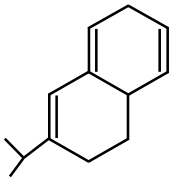
(a)



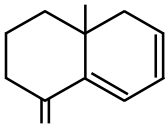
(b)



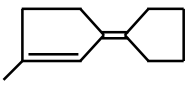
(c)



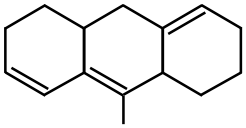
(d)



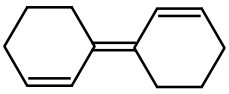
(e)



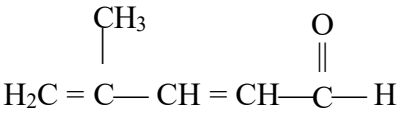
(f)



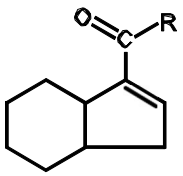
(g)

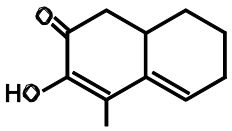


(h)

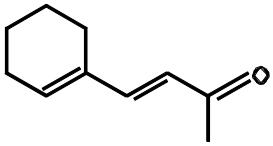


(i) (j)

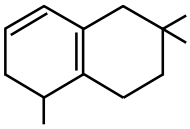




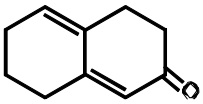
(k)



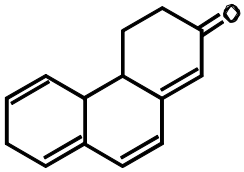
(*l*)



(m)



(n)



UNIT:III

Name of the Topic: IR Spectroscopy

[A] Objective Type Questions

[I] Select the most correct alternative from among those given below.

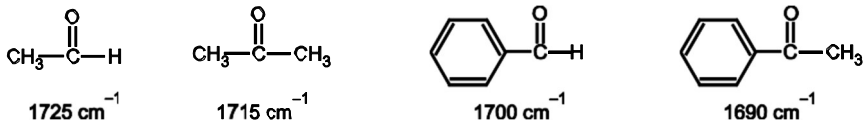
1. In electromagnetic spectrum, IR region lies in between ……
   (a) 12,500-4000 cm^{-1} (b) 4000-667 cm^{-1}
   (c) 667-50 cm^{-1} (d) 12,500-50cm^{-1}
2. The molecular vibrations can be detected in between the IR region ……
   (a) 1.5 μ to 15 μ (b) 2.5 μ to 15 μ
   (c) 3.5 μ to 15 μ (d) 4.5 μ to 15 μ
3. Ordinary IR (Middle region): lies in between ……
   (a) 4000-667 cm^{-1} (b) 12,500-4000 cm^{-1}
   (c) 4000-1600 cm^{-1} (d) 4000-556 cm^{-1}
4. Functional group region require ……
   (a) higher energy and lower frequency
   (b) higher energy and higher frequency
   (c) lower energy and higher frequency
   (d) lower energy and lower frequency

5. Aromatic region is due to …… vibration.
   (a) stretching (b) stretching and bending
   (c) bending (d) none of these
6. Aromatic region lies in between ……
   (a) 4000-667 cm^{-1} (b) 1300-909 cm^{-1}
   (c) 909-667 cm^{-1} (d) 4000-556 cm^{-1}
7. The absorbance of the sample at a particular frequency can be calculated as:
   (a) A = log I (b) A = log I_o
   (c) A = log T (d) A = log I/I_o
8. The finger print region is lies in between ……
   (a) 4000-667 cm^{-1} (b) 1300-909 cm^{-1}
   (c) 909-667 cm^{-1} (d) 4000-556 cm^{-1}
9. The fundamental modes of vibrations for non linear molecule are calculated by ……
   (a) 3N-6 (b) 3N-5
   (c) 3N-4 (d) 3N-8
10. The vibrational frequency of a bond increases when the bond strength ……
   (a) decreases (b) remain constant
   (c) increases (d) none of these
11. The number of fundamental modes of vibration of C_6H_6 are ……
   (a) 30 (b) 36
   (c) 34 (d) 35
12. The frequency(√) Hz of the vibrations is given by ……
   (a) $\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$ (b) $\nu = \frac{1}{2\pi c} f/\mu$
   (c) $\nu = m\sqrt{\frac{f}{\mu}}$ (d) $\nu = 1/\pi c$
13. The stretching frequency of alcohol shows broad band due to ……
   (a) C-H bonding (b) C-O bonding
   (c) O-O bonding (d) O-H bonding
14. The – C ≡ C – stretching frequency in IR spectrum appears at ……
   (a) 2200 cm^{-1} (b) 2500 cm^{-1}
   (c) 2700 cm^{-1} (d) 2800 cm^{-1}
15. In IR spectrum, the ≡ C – H stretching is observed at ……
   (a) 4000 cm^{-1} (b) 3500 cm^{-1}
   (c) 3300 cm^{-1} (d) 3600 cm^{-1}
16. The presence of an aldehyde group is confirmed by the occurrence of additional bands at ……
   (a) 2820 and 2720 cm^{-1} (b) 2920 and 2820 cm^{-1}
   (c) 3020 and 2920 cm^{-} (d) 3120 and 3020 cm^{-1}

17. The ether linkage C − O − C shows absorption at ……
    (a) 1450 cm^{-1} (b) 1250 cm^{-1}
    (c) 1650 cm^{-1} (d) 1550 cm^{-1}
18. The IR absorption bands due to –OH stretch in alcohol are ……
    (a) intense (b) broad
    (c) very weak (d) sharp
19. Hooks law is used in determination of ……
    (a) stretching frequency (b) bending frequency
    (c) functional group (d) molecular weight
20. IR spectroscopy is mainly used in determination of ……
    (a) molecular weight (b) diene
    (c) functional group (d) proton
21. Which compound would be expected to show intense IR absorption at 3300 cm^{-1} ?
    (a) butane (b) $CH_3CH_2C{=}CH$ (c) $CH_3C{=}CCH_3$ (d) but-1-ene
22. Which compound would be expected to show intense IR absorption at 2820,2710 and1705cm^{-1}?
    (a) $CH_3COCH_2CH_3$ B) $CH_2{=}CHCOCH_3$ C) $PhCOCH_3$ D) PhCHO
23. Which compound would be expected to show intense IR absorption at 2250 cm-1?
    (a) $(CH_3)_2CHCN$ (b) $CH_3CH_2CH_2CO_2H$ (c) $CH_3CH_2CH_2CONH_2$ d) $(CH_3)_2CHCH_2OH$
24. Ethyne (HC ≡ CH) does not show IR absorption in the region 2000-2500 cm-1 because.....
    (a) -C ≡ C- stretches occur at about 1640 cm^{-1}.
    (b) there is a change in the dipole moment when the -C ≡ C- bond in ethyne stretches.
    (c) there is no change in the dipole moment when the -C ≡ C- bond in ethyne stretches.
    (d) C-H stretches occur at lower energies
25. Which of the following most closely matches the -C ≡ C − stretching frequency?
    (a) 3000 (b) 3300 (c) 2200 (d) 1200

[B] Long Answer Type Questions:

1. Give the principle of I.R. spectroscopy and explain the different modes of vibration.
2. Explain the fundamental modes of vibrations.
3. State and explain Hook's law for assignment of stretching frequency.
4. What are the conditions required for exhibiting absorption of IR radiation ?
5. Explain how hydrogen bonding is detected by I.R. spectroscopy.
6. What are different types of vibrations ? How are fundamental modes of vibrations calculated for linear and non-linear molecules?
7. Calculate the fundamental modes of vibrations for the following molecules:
   (a) Carbon monoxide, (b) Ethane, (c) Nitrous oxide, (d) Methane, (e) Ammonia, (f) Benzene.
8. Explain the following carbonyl frequencies.



9. Derive the structure of the compound C_3H_5N which shows I.R. band at 2200 cm^{-1}. Explain your answer.
10. Derive the structures of two isomeric compound C_3H_8O based on the I.R. data given below. Explain your answer.
    (a) I.R. band at 3600 cm^{-1}.
    (b) No significant band above 1500 cm^{-1}.
11. An organic compound having molecular formula C_3H_6O shows I.R. band at 1620 cm^{-1} and 3300 cm^{-1}. Find out structural formula of the compound.
12. The two unsaturated esters having the same molecular formula $C_4H_6O_2$ give following I.R. data.
    (a) 1760, 1620, 990, 910 cm^{-1}.
    (b) 1710, 1620, 990, 910 cm^{-1}.
    Assign structures to (a) and (b) isomeric esters.
13. A compound $C_6H_{10}O$ shows the iodoform test. In I.R. it shows peak at 1690 cm^{-1} and in U.V. it absorbs at 240 nm. Suggest the structure of the compound.
14. A compound $C_6H_{10}O$ shows negative iodoform test. In I.R. it exhibits peaks at 2720 and 1700 cm^{-1}. In U.V. λ_{max} is 240 nm. Suggest the structure of the compound.
15. How will you distinguish the following pairs of compounds by I.R. spectroscopy ?
    (a) Phenol and cyclohexanol.
    (b) Methyl cyanide and acrylonitrile
    (c) Phenyl acetate and acetanilide.
    (d) Nitrobenzene and amino benzene.
    (e) Benzyl alcohol and benzoic acid.
    (f) Acetone and diethyl ether.
    (g) $phCOCH_2CH_3$ and $phCH_2COCH_3$.
    (h) Cyclohexanol and cyclohexanone.
    (i) Ethanol and dimethyl ether.
    (j) $CH_3 - C \equiv N$ and $CH_3 - \overset{\overset{O}{\|}}{C} - NH_2$.
    (k) Phenyl acetylene and diphenyl acetylene.
    (l) Chloroform and carbon tetrachloride.
16. Deduce a possible structure for the compound with the IR absorptions below. C3H3Br: 3300, 2900, 2100 cm^{-1}
17. Deduce a possible structure for the compound with the IR absorptions below. C3H5N: 2950, 2250 cm^{-1}

18. Deduce a possible structure for the compound with the IR absorptions below. C5H8O: 2950, 1750 cm^{-1}
19. Deduce a possible structure for the compound with the IR absorptions below. C4H8O: 2950, 2820, 2715, 1715 cm^{-1}
20. How could IR spectroscopy be used to distinguish between the following pair of compounds? $HOCH_2CH_2CHO$ and $CH_3CH_2CO_2H$
21. How could IR spectroscopy be used to distinguish between the following pair of compounds? $CH_3COCH{=}CHCH_2CH_3$ and $CH_3COCH_2CH_2CH{=}CH_2$
22. How could IR spectroscopy be used to distinguish between the following pair of compounds? $CH_3CH_2C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$
23. Which has a lower characteristic stretching frequency, the C=O bond or the C-O bond? Explain.
24. Rank the following bonds in order of increasing stretching frequency (cm-1) in IR spectroscopy: C-H, C=C, C-O, and C=O.

UNIT: IV

Name of the Topic: NMR Spectroscopy

1. The nuclear spin quantum number is the -------
   a. resultant spin of protons b. Average Spin of neutrons
   c. Total Spin of electrons d. Vector sum of spins of all the nucleons
2. The nuclei having---------- do not show nuclear magnetic resonance phenomenon.
   a. both atomic mass and atomic number even
   b. both atomic mass and atomic number odd
   c. atomic mass even and atomic number odd
   d. atomic massodd and atomic number even
3. The tiny magnets of protons are oriented --------- in absence of the applied magnetic field.
   a. along the field b. against the field
   c. randomly d. opposite to field
4. The energy of protons aligned against the magnetic field is--------
   a. zero b. More than zero
   c. less than zero d. lowest
5. When the radiofrequency radiations are absorbed by the nuclei they have their precessional frequency ---------- that of absorbed radiations.

a. equal to b. More than

c. less than d. Independent of

6. When the strength of applied magnetic field is kept constant, the frequency of radio waves is -------to study the resonance of exposed nuclei.

a. changed gradually b. Also kept constant

c. not required d. Absorbed

7. Upfield shift is due to absorption of higher frequency radiations show signals at ------ delta value.

a. lower b. greater

c. zero d. Irrespective of

8. Maximum delta value is observed in methyl protons in ---------among the following.

a. CH_3Br b. CH_3R

c. CH_3I d. CH_3Cl

9. Diamagnetic shielding leads to shift to a ------- delta value

a. lower b. greater

c. zero d. minimum

10. The chemical shift in aromatic protons is due to---------- deshielding phenomenon.

a. isotopic b. anisotropic

c. inductive effect d. electronegative

11. The---------value in the signals indicates the number of protons absorbing at that frequency.

a. integration b. Peak area ratio

c. chemical shift d. Multiplicity of the peaks

12. Due to more electronegative atom of silicon in TMS, the signal of methyl protons are----- - - - -.

a. highly deshielded b. Less deshielded

c. highly shielded d. At maximum delta value

13. Formaldehyde contains -------sets of equivalent protons.

a. 1 b. 2

c. 0 d. 3

14. The protons in acetone are ---------, therefore appear as single peak in PMR spectrum.

a. equivalent b. deshielded

c. PMR active d. Equal

15. The peak due to carboxylic proton in CH_3CH_2COOH appears at ---------- of the PMR spectrum

a. extreme right b. At the middle

c. at zero delta d. Extreme left

[B] Long answer type questions:

1. What are the magnetic and non magnetic nuclei ? which of the following nuclei show the phenomenon of nuclear magnetic resonance?

   i. $_1H^1$, $_3B^{10}$,$_6C^{12}$,$_6C^{13}$, $_8O^{16}$, $_{16}S^{31}$, $_{15}P^{30}$

2. What is nuclear magnetic resonance? Explain with the terms involved in NMR spectroscopy as : magnetic and nonmagnetic nuclei, chemical shift, shielding and deshielding,
3. Explain how the PMR spectroscopy is applied to identify the structure of given organic compound?
4. Describe the terms chemical shift w r t definition, calculation, factors affecting chemical shift and applications of chemical shift.
5. Explain the phenomenon of spin-spin coupling, rules of spin spin coupling .
6. What is coupling constant? Write the types of coupling and their applications .
7. What is the significance of TMS as reference compound in PMR spectroscopy?
8. What are equivalent and non-equivalent protons? explain with the examples of PMR spectra of ethanol and acetone.
9. Why the signals in PMR spectroscopy are split into multiplets? What are the rules governing this splitting and significance of the multiplicity of the peaks.
10. Explain the terms as precessional motion, gyromagnetic constant and the phenomenon of resonance in PMR spectroscopy.

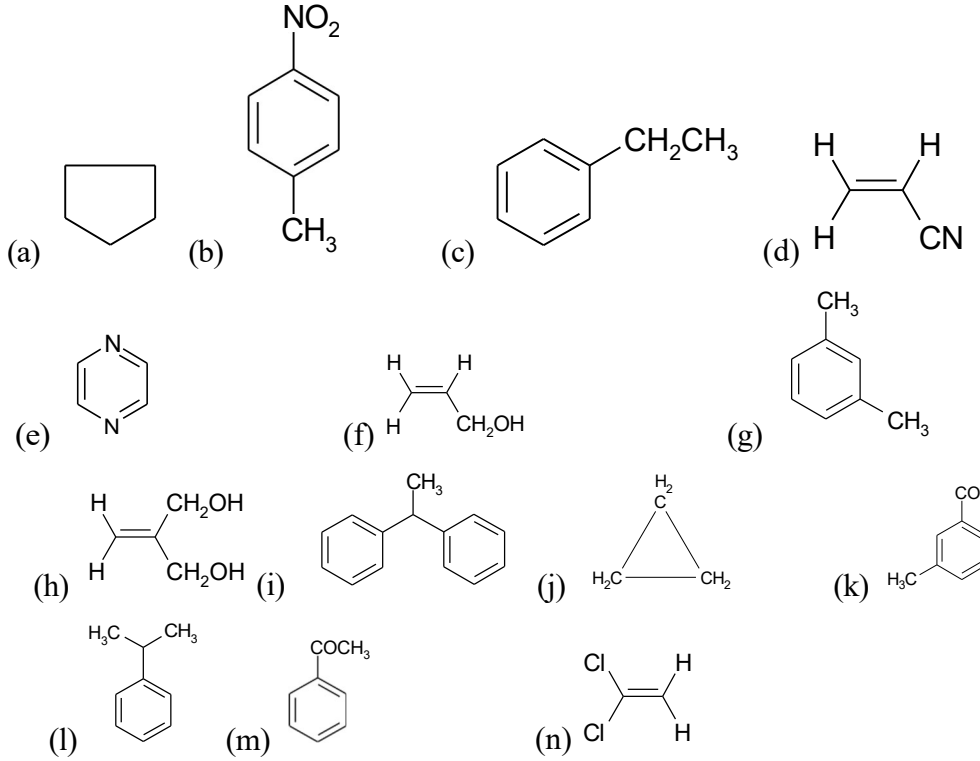
[C] Problems for practice:

Q.1. How many sets of equivalent protons are present in following compounds?

(a) C_6H_5OH (b) $CH_3CHBrCH_2CH_3$ (c) $CH_3CH_2NH_2$ (d) $(CH_3)_3CC_6H_5$ (e) $(CH_3)_2CHOH$ (f) HCHO (g)$(CH_3)_3N$ (h) $C_6H_5NH_2$ (i) CH_3-COO-CH_3 (j) CH_3-CO-CH_3 (k) $ClCH_2$-CH_2-

CH_2Cl (l) $Br_2CH\text{-}CH_{Br}\text{-}CH_2\text{-}CH_3$ (m) $CH_3\text{-}NH\text{-}CH_2CH_3$ (n)CH_3CHO

Q2.How many PMR signals are obtained under low resolution for the following compounds?



Q3. How many PMR signals are obtained for the following compounds at high resolution and what will be their multiplicity? OR

Q3. Applying the (N+1)rule , predict the splitting patterns of the signals shown by following compounds in PMR spectroscopy.

(a) C_6H_5OH (b) (c) $CH_3CH_2NH_2$ (d) $(CH_3)_3CC_6H_5$ (e) $(CH_3)_2CHOH$ (f) HCHO (g)$(CH_3)_3N$ (h) $C_6H_5NH_2$ (i) $CH_3\text{-}COO\text{-}CH_3$ (j) $CH_3\text{-}CO\text{-}CH_3$ (k) $ClCH_2\text{-}CH_2\text{-}CH_2Cl$ (l) $Br_2CH\text{-}CH_{Br}\text{-}CH_2\text{-}CH_3$ (m) $CH_3\text{-}NH\text{-}CH_2CH_3$ (n)CH_3CHO

Q.4. What is the peak area or integration ratio of the signals obtained in the following compounds?

(a)$ClCH_2\text{-}CH_2\text{-}CH_2Cl$(b) $CH_3CH_2CHBr_2$ (c) $C_6H_5CH_2C_6H_5$ (d) $CH_3COCH_2COCH_3$ (e) $CH_3CH_2CCl_3$ (f) $CH_3CHBrCH_2CH_3$ (g) $(CH_3)_3CHC_6H_5$ (h) CH_3CH_2COOH (i) C_6H_5OH (j) $(CH_3)_2CHOH$ (k) $CH_3\text{-}COO\text{-}CH_3$ (l) $CH_3\text{-}NH\text{-}CH_2CH_3$ (m) $CH_3CH_2CH_2OH$ (n) CH_3CHO

Q5. How will you distinguish the following from their PMR spectra?

(a) $CH_3COC_6H_6$ and $C_6H_5COC_6H_5$ (b) CH_3OCH_3 and CH_3CH_2OH

(c)CH_3CHO and HCHO (d) $CH_3CHBrCH_3$ and $CH_3CH_2CH_2Br$

(e) $ClCH_2CH_2Cl$ and CH_3CHCl_2 (f) $(CH_3)_2CHOH$ and $CH_3CH_2CH_2OH$

(g) C_6H_5Cl and CH_3Cl (h) $CH_3CH_2NH_2$ and CH_3NHCH_3

(i) $C_6H_5CH_2NH_2$ and $C_6H_5NHCH_3$

Q6. Predict the structure from the given PMR data.

(a) $C_{10}H_{13}Cl$: δ, ppm, 1.57(6H,s), 3.1(2H,s),7.3(5h,m)

(b) $C_3H_3Cl_5$: δ, ppm,4.52(1H,t),6.02(2H,d)

(c) $C_9H_{11}Br$: δ, ppm, 2.2(2H,quintet), 2.75 (2H,t)3.3.7(2H,t)7.35 (5H,m)

(d) $C_{10}H_{14}$: δ, ppm, 0.88 (9H,s); 7.28 (5H,s)

(e) C_3H_7Br: δ, ppm, 1.7(6H,d); 4.3(1H,septet)

(f) $C_3H_6Cl_2$: δ, ppm, 2.2 (2H,Quintet); 3.75 (4H,t)

(g) $C_4H_8O_2$: δ, ppm, 1.3, (3H, t) ; 2 (3H,s); 4.2 (2H,q)

(h) $C_4H_{10}O$: δ, ppm,1.28(9H,s); 1.35(1H,s)

(i) C_4H_9Cl: δ, ppm,1(6H,d);2 (1H,m); 3.35(2H,d)

Example 1: If the observed chemical shift of a proton is 200 Hz from TMS and instrument frequency is 60 MHz, what is the chemical shift in terms of δ? Express it also in τ value.

Example 2: Indicate the kinds of protons and number of PMR signals in the following compounds: (a) $CH_3CH_2CH_2Cl$, (b) $CH_3CHClCH_3$, (c) CH_3COCH_3

Example 3: Draw the structural formula of each of the following compounds and label all sets of equivalent protons. How many NMR signals do you expect from each of these compounds? (a) p-xylene, (b) Vinylchloride, (c) Cyclobutane, (d) Diethyl ether, (e) Two isomers of $C_2H_4Cl_2$.

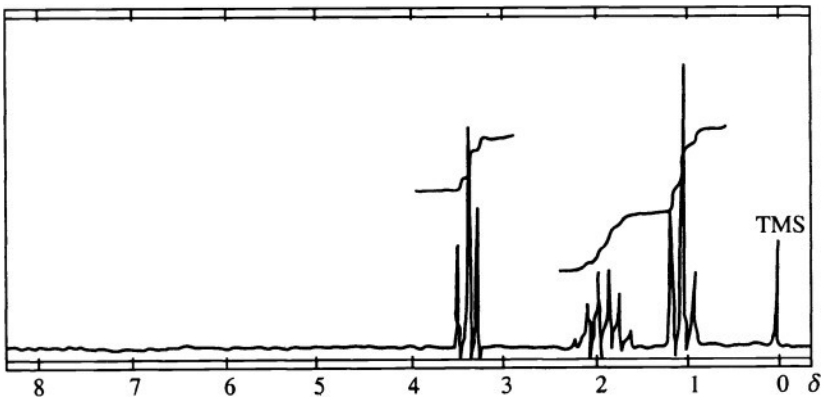
Example 4: Three isomeric dimethylcyclopropanes A, Band C give 2, 3 and 4 NMR signals, respectively. Draw the stereochemical formulae for A, Band C.

Example 5: Draw the structural formula of each of the following compounds, label the kinds of protons and indicate the expected number of NMR signals.

(a) Methylcyclopropane, (b) Mesitylene, (d) 2,3-Dichloropropanoic acid, (c) Ethyl succinate.

Example 6: In an organic compound, three kinds of protons appear at 60, 100 and 180 Hz when the spectrum is recorded at 60 MHz NMR spectrometer. What will be their relative positions (in Hz) when 90 MHz spectrometer is used?

Problem 7: An organic compound has molecular formula C_3H_7Br. Let's PMR spectrum of is shown in following figure. Deduce the structure of the compound.



Problem 8: The PMR spectrum of an organic compound C8H9Br shows a quartet at 5.5 8, a doublet at 2.0 8 and triplet at 7.4 8 in the intensity ratio 1 : 3 : 5, respectively. Deduce the structure of the compound.

Problem 9: Using PMR spectroscopy, how will you distinguish the following pairs?

(i) 1,2-dimethoxyethane and 1,1-dimethoxylethane

(ii) cis-1-chloropropene and trans-1-chloropropene

(iii) Acetone and methyl acetate.

Example 10: Predict the number of signals and their multiplicity in the PMR spectra of the following compounds:

(a) $ClCH_2CH_2Cl$ (b) $ClCH_2CHCl_2$ (c) $CH_3CH_2CH_2Br$

Example 11: Draw the structure of each of the following compounds which meets the given requirements in its PMR spectrum:

(i) $C_3H_3Cl_5$; one doublet and one triplet.

(ii) C_4H_{10}; one singlet, one doublet and one septet

(iii) C_4H_8; one singlet, one triplet and one quartet

(iv C_3H_7Cl; one doublet and one septet

(v) $C_4H_8Cl_2$, two triplets

Example 12: It should be noted that 8 is treated as a positive number. Shifts at higher field than TMS are rare. If such shifts are present, their 8 values are shown with a negative sign and r values increase numerically, e.g. 8-1.00 will be equal to r 11.00. Fig. 4.10 shows NMR scale at 60 MHz and 100 MHz.

Example 13: Protons of a compound exhibit a NMR signal at 8 2.5. What will be the value of chemical shift of these protons in Hz if the spectrum is recorded on a 60 MHz spectrometer?

UNIT: V

Name of the Topic: MASS SPECTROSCOPY

(A) Choose the Correct Alternative for each of the following and rewrite the sentence:

1. The Mass spectrometer is an analytical instrument in which ions, produced from a sample, are separated by electric or magnetic fields according to their----------

a. ratios of mass to charge
b. ratios of charge to atomic weight
c. mass of the proton
d. ratios of charge to mass.

2. In mass spectroscopy, the organic substance is bombarded with the beam of--------

a. electromagnetic radiations
b. infra red radiations
c. protons
d. electrons

3. The energy equal to the-------- of the molecule, results in the ionization of the molecule

a. molar mass
b. ionization potential
c. potential energy
d. size

4. The gaseous molecule on bombardment of electrons, emit an electron from the -------- energy molecular orbital

a. highest
b. moderate
c. zero
d. lowest

5. The gaseous molecule on bombardment of electrons, gives rise to an ion M^+ which is called ----------.

a. parent ion
b. molecular ion
c. radical cation
d. All a,b,c

6. The---------- cannot be detected in mass spectrometry.

a. neutral radicals
b. fragmentation molecules
c. negative ions
d. All a,b,c

7. A mass spectrum is a graph of ----------of the cations..

a. energy absorbed to strength of magnetic field
b. mass to intensity
c. atomic mass to energy absorbed
d. m/z ratio to the relative abundance

8. Because of natural abundance of ^{13}C and ^{2}H, there are small peaks at ------- than the parent peak

a. two units mass higher b. one unit mass higher

c. lower d. less intensity

9. For a compound to be analyzed in a mass spectrometer, it must be in the ---------- state

a. solid b. liquid

c. purest d. gaseous

10. Fragmentation of alkane often splits off simple alkyl groups results in the characteristic peaks at ------- due to loss of methyl group

a. (M^+ - 14) b. (M^+ +1)

c. (M^+ - 15) d. (M^+ + 15)

11. Branched alkanes tend to fragment forming the most stable ---------- --.

a. radicals b. carbocations

c. carbanions d. molecules

12. In mass spectra of straight chain alkanes there are peaks at ------ mass units apart from each other.

a. 14 b. 15

c. 2 d. 1

13. Allyl carbocation (m/z = 55) is an important fragment in the mass spectra of ----------

a. straight chain alkanes b. terminal alkenes

c. aromatic compounds d. aldehydes

14. Benzyl carbocation (m/z = 91) is an important fragment in the mass spectra of ----------

a. straight chain alkanes b. terminal alkenes

c. aromatic compounds d. aldehydes

16. α-Cleavage and dehydration are the common modes of fragmentations of ------- --.

a. phenols b. aldehydes

c. alcohols d. ketones

15. Favored modes of fragmentation involve--------- in phenols..

a. loss of a hydrogen atom to create an M – 1 peak

b. loss of carbon monoxide (CO) to produce a peak at M – 28

c. loss of a formyl radical (HCO•) to give a peak at M – 29

d. All a,b,c

16. Favored modes of fragmentation involve ---------in aldehydes..

a. loss of a hydrogen atom to create an M – 1 peak

b. loss of a formyl radical (HCO•) to give a peak at M – 29

c. loss of carbon monoxide (CO) to produce a peak at M – 28

d. both a & b,

17. Organic compounds having the γ carbon containing a hydrogen undergo the ---------- ---- commonly known as *McLafferty rearrangement* reaction

a. α-*H shift with* β-*cleavage*,

b. β-*H shift with* α-*cleavage*,

c. γ-*H shift with* α-*cleavage*,

d. γ-*H shift with* β-*cleavage*,

18. The Base Peak is the peak with the----------in the mass spectrum

a. lowest intensity

b. greatest intensity

c. greatest mass

d. greatest intensity and mass both

19. To find the m/z for the M peak of a compound, multiply the----------of each atom by the number of atoms of each in the formula

a. atomic weight,

b. isotopic mass,

c. atomic number

d. valency,

20. intensity of M+1 peak is used to calculate the---------- present in the molecule.

a. nature of the carbon atoms

b. number of the carbon atoms

c. number of the total atoms

d. number of the isotopic atoms

21. If M and M+2 peaks for any compound are of almost the same height, indicating that ---------- ------is present in the molecule

a. Chlorine, b. bromine,

c. Oxygen d. sulphur

22. If M+2 peak for any compound is 1/3 of the M peak, indicating that ---------- is present in the molecule

a. Chlorine, b. bromine,

c. Oxygen d. sulphur

23. Prsence of peak at m/z=127, indicates that---------- is present in the molecule

a. Chlorine, b. bromine,

c. iodine d. sulphur

24. Presence of more than 1 halogens and sulphur in a molecule can be known from the presence of - - - - - - - - - - - peaks.

a. M+1

b. M+2

c. M+3

d. M+4

25. The separation of ions in a mass spectrometer depends on ……

a. only on the charge on the ions.

b. only on the mass of the ions.

c. only on the velocity of the ions.

d. the mass and the charge of the ions.

26. What is the correct sequence for the processes occurring in a mass spectrometer?

a. vaporization, ionization, acceleration, deflection

b.vaporization, acceleration, ionization, deflection

c. ionization, vaporization, acceleration, deflection

d. ionization, vaporization, deflection, acceleration

27. The mass spectrum of $CH_3COOC_2H_5$ is not expected to show a major ion peak at which m/z ratio?

a. 88 b. 32 c. 29 d. 15

28. When injected into a mass spectrometer a compound gave a number of ion peaks. Two peaks one of which was the molecular ion, had m/z values of 58 and 43. Which of the molecular fragment below might have been lost from the original molecule?

a. CH_3 b. OH c. C_2H_5 d. CHO

29. Who discovered the mass spectrometer?

a. Francis Aston b. J. J Thomson

c. Ernest O. Lawrence d. Walter Kaufmann

30. In which state of matter mass spectroscopy is being performed?

a. solid b. liquid c. gaseous d. plasma

31. Which species of the following is used to bombard with the sample for which mass spectroscopy has been performed?

a. Alpha particles b. Neutrons c. Electrons d. Protons

32. Which type of ionic species are allowed to pass through the slit and reach the collecting plate?

a. Negative ions of all masses b. Positive ions of the specific mass

c. Negative ions of the specific mass d. Positive ions of all masses

33. Which of the following statement is false for mass spectroscopy?

a. Mass spectroscopy is used to identify unknown compounds within a sample, and to elucidate the structure and chemical properties of different molecules

b. Particle are characterized by their mass to charge ratios (m/z) and relative abundances

c. This technique basically studies the effect of ionizing energy on molecules

d. This technique can be used on all state of matter

34. Which of the following main component of mass spectroscopy deal with resolving the ions into their characteristics mass components according to their mass-to-charge ratio?

a. Ion Source b. Analyzer c. Detector System d. Analyzer tube

35. What are the main criteria on which mass spectrometer used for?

a. Composition in sample b. Relative mass of atoms

c. Concentration of elements in the sample d. Properties of sample

36. Bromine possesses two isotopes (79 Br and 81 Br) in an approximate 1 : 1 ratio. In the mass spectrum of Br_2, how many peaks will the parent ion contain?

a. 3 b. 4 c. 2 d. 1

37. The base peak in a mass spectrum is ……

a.the highest mass peak.

b. the peak corresponding to the parent ion.

c.the peak set to 100% relative intensity.

d. the lowest mass peak.

38. Triethylamine has the formula (CH_3CH_2) 3N. In the mass spectrum of triethylamine, the base peak is at m/z = 86. These data are consistent with ……

a. loss of an ethyl group (CH_2CH_3) from the parent molecule.

b.observation of the parent ion.

c. cleavage of a C – N bond in the parent molecule.

d. cleavage of a C – C bond in the parent molecule.

39. Which of the following formulae is consistent with a molecular ion of m/z 73 in a mass spectrometry experiment?

a. $C_3H_8N_2$ b. $C_4H_{11}N$ c. C_4H_{10} d. C_3H_5NO

40. The path of ions after deflection depends on ……

a. only the mass of the ion

b. only the charge on the ion

c. both the charge and the mass of the ion

d. neither the charge nor the mass of the ion

41. Which of the following is not a use for mass spectrometry?

a.Calculating the isotopic abundance in elements

b. Investigating the elemental composition of planets

c. Confirming the presence of O − H and C = O in organic compounds

d. Calculating the molecular mass of organic compounds

42. Which one of the following statements about the mass spectrum of CH_3Br is

correct?

a. The last two peaks are of equal size and occur at m/z values of 94 and 96

b. The last two peaks have abundances in the ratio 3 : 1 and occur at m/z values of 94 and 96

c. There is just one peak for the molecular ion with an m/z value of 95

d. There is just one peak for the molecular ion with an m/z value of 44

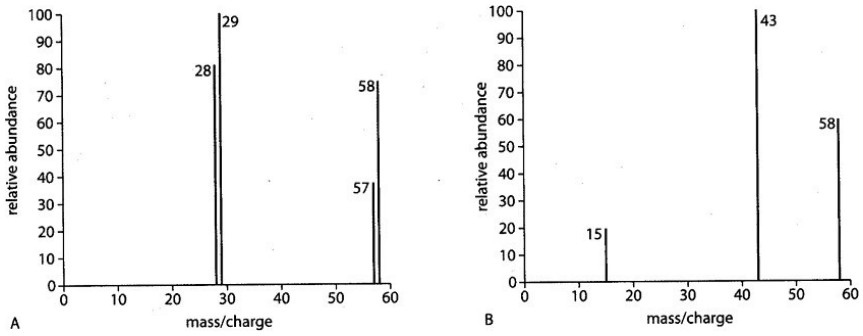
[B].**Long answer type questions:**

1. Describe principles of Mass spectrometry.
2. Write a brief note on instrumentation and working in mass spectrometry.
3. What are the different types of ions produced in mass spectrometry with suitable examples.
4. Explain Fragmentation patterns of-

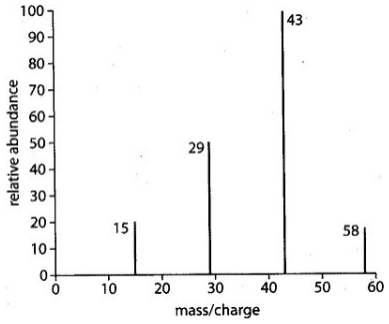
   a) Alkanes b) alkenes, c) aromatic hydrocarbons, d) alcohols, e)phenols, f) amines g) carbonyl compounds

5. Describe the McLafferty rearrangement with suitable examples.
6. Explain how to determine the molecular mass and formula from mass spectrum? .
7. Explain how will you determine the presence of chlorine, bromine and iodine in the molecule from mass spectrum?
8. How the number of carbon atoms and nitrogen atoms present in the molecule is determined from mass spectrum?
9. Describe different applications of mass spectrometry.
10. The mass spectra of two compounds are shown below. One is propanone (CH_3COCH_3) and the other is propanal (CH_3CH_2CHO). Identify the compound in each case and explain the similarities and differences between the two spectra.
11. Outline the mode of fragmentation during mass spectrometric study of the following compounds leading to the peak at indicated m/z: (i) I-butanol, at

m/z 56, (ii) I-hexanol, at m/z 56, (iii) cis-methyl crotonate, at m/z 68.



12. The simplified mass spectrum of a compound with empirical formula C_2H_5 is shown below. (a) Explain which ions give rise to the peaks shown. (b) Deduce the molecular structure of the compound.



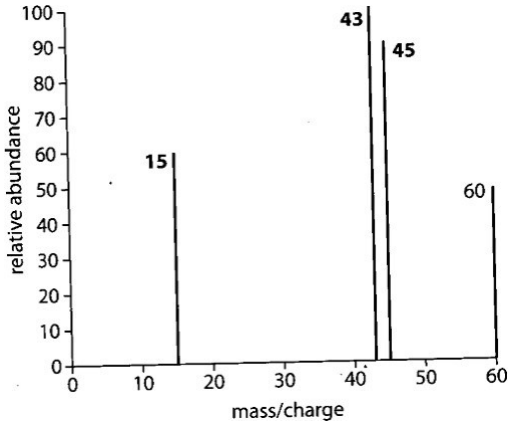
[C] How will you distinguish following compounds using MS?

Problem 1: [a] pentan-2-one and [b] pentan-3-one

Problem 2: (a) 3-methylcyclohexene and (b) 4-methyl-cyclohexene.

[D] Determination of molecular formula and possible structure of the compound.

Problem 1: A molecule with an empirical formula CH_2O has the simplified mass spectrum below. Deduce the molecular formula and possible structure of the compound.



Problem 2: In the mass spectrum of an unsaturated hydrocarbon, the molecular ion ~ peak has relative intensity 70.0, the M + 1 peak 4.7, and the base peak a relative intensity of 100. How many carbon atoms are there in the hydrocarbon per molecule.

[E] Problems based on fragmentataion:

Problem 1: Explain the formation ofprominent ion peaks at m/e 72, 71, 57 and 43 in the mass spectrum of 2-methylbutane. Indicate the ion responsible for the base peak.

Problem 2: The mass spectrum of 2-pentene exhibits prominent peaks at m/e 70, 55, 41, 39, 29 and 27. Explain the formation of the ions corresponding to these peaks.

Problem 3: Outline the mode of fragmentation during mass spectrometric study of the following compounds leading to the peaks at indicated m/z:

(a) Methylbutanoate, at m/e 74 and 59

(b) Benzyl methyl ether, at m/e 91 and 65

Problem 4: Rationalize the formation ofpeaks at m/z 122 (35%). 92 (65%), 91 (100%), 65 (15%), and metastable peaks at m/z 46.4 and 69.4 in the mass spectrum of 2-phenylethanol.

Problem 5: Outline the mode of fragmentation leading to the ions causing peaks at indicated m/e in the mass spectra of the compounds:

(a) Pentanoie acid, at m/z 60

(b) Phenetole, at m/z 94

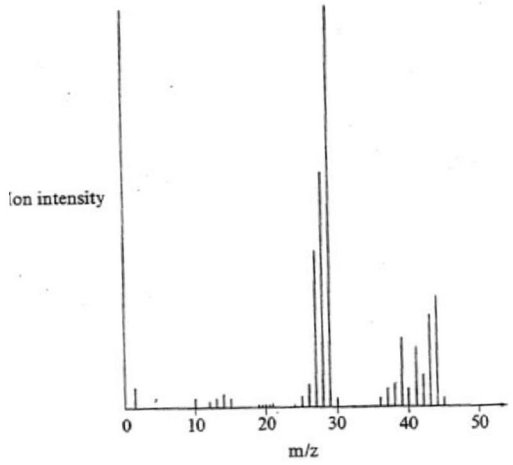
(c) Diethylamine, at m/z 30

(F) Define the following terms with example:

1. McLafferty rearrangement
2. Base peak
3. Parent ions
4. M + 1 and M + 2 peaks
5. Metastable peak
6. How is a molecular ion formed?
7. What information could be obtained from the mass/charge value of the molecular ion?
8. Why must the inside of the spectrometer be kept at a high vacuum?

(G) Short Answer Questions:

1. Give abrief account of McLafferty rearrangement.
2. Discuss nitrogen rule as applied to mass spectrometry.
3. What are the mostprobable species responsible for peaks at m/z 46, 45, 31, 29, 17 and 15 in the mass spectrum of ethanol?
4. The spectrum of propane is shown bellow:



(a) Why , there is a small peak at m/z 45?

(b) Why, there is no peak at higher m/z value?

(c) What is the formula of ion responsible for the peak of greatest intensity?

UNIT: VI

Combined Problems Based on UV, IR, NMR and Mass Spectral Data

1. Calculate the site of unsaturation of organic compound having the molecular formula $C_8H_{13}Br$
2. Calculate the site of unsaturation of organic compound having the molecular formula $C_8H_{11}N$.
3. Calculate the site of unsaturation of organic compound having the molecular formula C_3H_6O.
4. Deduce the structure of organic compound having Molecular formula: C_3H_6O
   I.R.: 2720, 1720 cm^{-1}
   PMR: 9.5 (t, 1H); 2.5 (quintet, 2H); 1.2 (t, 3H)
5. Deduce the structure of organic compound having Molecular formula:
   $C_4H_7BrO_2$.
   IR: 3300, 1725, 600 cm^{-1}
   PMR: 11.2 (s, 1H); 4.3 (t ,1H); 2.2 (quintet, 2H); 1.1 (t, 3H)

6. Deduce the structure of organic compound having Molecular formula: C_9H_{12}.
   IR: 3100, 1510, 1620 cm^{-1}
   NMR: 7.2 (s, 3H); 2.4 (s, 9H)

7. Deduce the structure of organic compound having Molecular formula: C_7H_8O
   IR: 3500, 3030, 1600, 1500, 1100 cm^{-1}.
   PMR: 7.2 (5H); 4.4 (s, 2H); 3.7 (s, 1H).

8. Deduce the structure of organic compound having Molecular formula: C_8H_7N
   IR: 2220, 1510, 1620 cm-1
   PMR: 7.2(d, 2H), 2.4(s, 3H); 7.5(d,2H)
9. Deduce the structure of organic compound having Molecular formula: $C_9H_{10}O$, UV: 265 nm
   IR: 1690, 1500, 1600, 700,750 cm^{-1}
   PMR: 7.2 (s, 5H); 2.5 (q, 2H); 1.1 (t, 3H)

(B) Derive structure of the compound using following spectral data:

1. Molecular weight: 58
   UV: No λ_{max} above 210 nm
   IR: 2941 – 2857 cm^{-1}; 1458 cm^{-1} (m)
   NMR: 4.75 δ (+, J = 7.1 Hz, 29.4 mm); 2.75 δ
   (quintet, J = 7.1 Hz, 14.6 mm)

2. Molecular formula: C_4H_8O
   UV : λ^{max} 274 nm, ε_{max} = 17
   IR : 2941-2857 cm^{-1} (m); 1715 cm^{-1} (m); 1460 cm^{-1} (m)
   NMR: 2.42 δ (q, J = 7.3 Hz, 12 mm); 2.12 (s, 17.6 mm);
   1.17 (t, J = 7.3 Hz, 18.2 mm)

3. Molecular formula: $C_4H_8O_3$
   UV: λ_{max} = 203 nm, ε = 40 (water)
   IR: 3125-2857 cm^{-1} (m); 2695 cm^{-1} (w); 1718 cm^{-1} (s), 1449 cm^{-1}.

NMR: 10.95 δ (s, 5.4 mm); 4.13 (s, 11.0 mm); 3.66 (q, J = 7.1 Hz, 10.6 mm), 1.27 (t, J = 7.1 Hz, 16.2 mm)

4. Molecular formula: C_3H_7ON
UV: λ_{max} = 219 nm, ε = 60 (water)
IR: 3413 cm^{-1} (m); 3236 cm^{-1} (m); 3030-2899 (m) cm^{-1}; 1667 cm^{-1}; 1634 cm^{-1}; 1460 cm^{-1}.
NMR: 6.5 δ (very broad singlet 13.0 mm); 2.25 δ (q, J = 7.5 Hz, 12.8 mm); 1.10 δ (t, J = 7.5 Hz, 19.7 mm).

5. Molecular formula: C_7H_8O
UV: λ_{max} = 25.5 nm, ε = 2.00 (water)
IR: 3401 cm^{-1} (s, b); 3077 cm^{-1} (w); 2899 (m) cm^{-1}; 1499 cm^{-1} (w, sh); 1456 cm^{-1} (m, sh).
NMR: 7.26 δ (s, 24.7 mm); 4.60 δ (s, 9.8 mm); 3.86 δ (s, 5.2 mm).

6. Molecular formula: C_9H_{12}
UV: 268 nm, ε = 480
IR: 3067-2907 (m) cm^{-1}; 1608 cm^{-1} (m. sh.); 1473 cm^{-1}
NMR: 6.8 (s, 10.4 mm); 2.26 δ (s, 31.0 mm).

7. Molecular formula: C_3H_7Cl
UV: 204 and 276 nm, ε = 4800 and 20
IR: 3030-2924 cm^{-1}; 1555 cm^{-1} (m); 1466 cm^{-1} (m)
NMR: 4.7 δ (septet, J = 6.7 Hz, 6.2 mm); 1.43 δ (d, J = 6.7 Hz, 37.8 mm).

8. Molecular formula: $C_5H_8O_3$
UV: λ_{max} = 270 mm, ε = 25 (water)
IR: 3125-2857 cm^{-1} (m); 2710 cm^{-1} (w); 2625 cm^{-1} (w); 1712 cm^{-1} (s); 1439 cm^{-1} (m)
NMR: δ, 10.98 (s, 5mm); 3.00-2.42 (m, 20.8); 2.12 (s, 14.8 mm).

9. Molecular formula: $C_{10}H_{12}O_2$
UV; 220 nm; ε = 1800
IR: 3077 cm^{-1} (w); 2976 cm^{-1} (w); 1745 cm^{-1} (s); 1608 cm^{-1} (m); 1497 cm^{-1} (m); 1456 cm^{-1} (m)
NMR: δ, 7.29 (s, 16.5 mm); 4.30 (t, J = 7.3 Hz, 6.2 mm); 3.00 (t, J = 7.3 Hz, 6.7 mm); 2.12 (s, 10.2 mm).

10. Molecular formula: C_4H_9NO
UV: λ_{max} = 220 mμ; ε_{max} = 63
IR: 3500 (m); 3402 (m); 2960 (w); 1682(s); 1610(s) cm^{-1}.
NMR: 9.0 τ (d, 23.2 squares); 7.9 τ (septet, 3.8 sqaures); 1.92 τ (s, 7.5, squares).

11. Molecular weight: 100

UV: λ_{max} = 274 mμ; ε_{max} = 2050

IR: 3031 (v); 2941 (w); 1725 (s); 1608, 1504 (w); 1060 (s) and 830 (s) cm^{-1}.

NMR: 7.65 τ (s, 3H); 6.18 τ (s, 3H); 2.15-2.8 τ (4H, unsymmetrical pattern).

12. Molecular weight: 108

UV: λ_{max} = 255 mμ; ε_{max} = 202

IR: 3402 (s, b); 3065 (w); 2288 (m); 1499 (w, sh) and 1455 (m) cm^{-1}.

NMR: 2.74 τ (s, 24.5 squares); 5.4 τ (s, 9.5 squares) and 6.10 τ (s, 4.8 squares).

13. Molecular weight: 130

IR: 3082-2860 (m); 1825 (s); 1755 (m); and 1455(m) cm^{-1}.

NMR: 8.7 τ (t, 7.3 squares, J = 7.1 cps); 7.8 τ (q, 4.9 squares, J = 7.1 cps)

14. Molecular weight: 130

UV: λ_{max} = 292 mμ; ε_{max} = 16

IR: 3042 (m); 2941 (w); 2862 (w); 1722 (s); 1605, 1575 (m) and 1462 (m) cm^{-1}.

NMR: 2.73 τ (m, 26.5 squares); 7.2 τ (d, 10.3 squares) and 0.22 τ (t, 5.2 squares).

15. Molecular weight: $C_9H_{10}O_2$

UV; 268 nm; 264 nm, 262 nm, 257 nm.

IR: 1745 cm^{-1} (s); 1225 cm^{-1} (br, s); 749 cm^{-1} (s);
697 cm^{-1} (m).

NMR: δ, 7.22 (s, 5H); 5.00 (s, 2H); 1.96 (s, 3H) .

16. Molecular formula: $C_2H_4Br_2$

UV: No λ_{max} above 210 nm.

IR: 3058 cm^{-1} (m); 1449 cm^{-1} (m).

NMR: δ, 5.89 (q, J = 6.0 Hz ,9.8 mm); 2.50 (d, J = 6.0, 30.3 mm).

17. Molecular formula: C_3H_7NO

UV: λ_{max} 238 mμ; ε_{max} = 10500.

IR: 3428 cm^{-1} (m); 2941-2857 cm^{-1} (w). 1681 cm^{-1} (s) and 1452 cm^{-1} (w).

NMR: 1.87 τ (s, 1H); 7.30 τ (s, 3H); 8.1 τ (s, 3H).

18. Molecular formula: $C_6H_5NO_3$

UV: λ_{max} = 280 mμ; ε_{max} = 6600.

IR: 3460 cm^{-1} (v, sh.); 3035 cm^{-1} (m). 1608 cm^{-1} (m), 1585 (m), 1510 (s), 1360 (s), 1320 (s) and 740 cm^{-1} (v, s). The band at 3460 cm^{-1} does not shift even on diluting the sample.

NMR: −2.0 τ (s, 1H); unsymmetrical pattern 2.61-2.75 τ (4H).

19. Molecular weight: 106
UV: 283 mμ; ε_{max} = 22
IR: 3000-2500 cm^{-1} (b); 1715 cm^{-1} (s); 1342 cm^{-1} (w).
NMR: 7.88 τ (s, 3H); 7.40 τ (t, 2H), 7.75 τ (t, 2H); −1.1 τ (s, 1H).

20. Molecular formula: C_4H_8
UV: λ_{max} transparent above 210 mμ
IR: 3031 cm^{-1} (m); 1676 cm^{-1} (m); 965 cm^{-1} (s).
NMR: 8.40 τ (d, 3H); 4.45 τ (q, 1H)

ΘΘΘ