

B.Sc. DEGREE EXAMINATION, APRIL 2015
BRANCH IV - CHEMISTRY
SIXTH SEMESTER

Reg. No

COURSE : MAJOR – CORE
PAPER : SPECTROSCOPY
TIME : 30 MINUTES

MAX. MARKS : 30

SECTION – A

TO BE ANSWERED ON THE QUESTION PAPER ITSELF.

ANSWER ALL THE QUESTIONS.

(30x1=30)

I Choose the correct answer:

(10x1=10)

- The lowest energy electronic transition in dimethyl ether molecule is _____.
a) $\sigma - \sigma^*$ b) $\pi - \pi^*$ c) $n - \pi^*$ d) $n - \sigma^*$
- The theoretical number of fundamental bands of benzene molecule is _____.
a) 12 b) 31 c) 30 d) 36
- Which of the following diatomic molecule do not absorb in the infrared region?
a) BrCl b) HCl c) O₂ d) all the above
- The characteristic stretching vibrations of carbonyl group in ketone is observed at ____ cm⁻¹.
a) 2230 b) 3400 c) 1710 d) 1280
- _____ line is observed when the frequency of the incident and scattered radiations are same.
a) stoke's b) antistoke's c) Rayleigh d) all the above
- The chemical shift value of acidic protons will be in the _____ range.
a) upfield b) downfield c) closer to TMS d) negative
- The number of nmr spectral signals observed for 2,2-dimethylpropane molecule is _____.
a) 3 b) 1 c) 5 d)
- The excited nucleus in NMR relaxes by _____ relaxation process.
a) spin-spin b) spin-lattice c) quadrupole d) all the above
- Which of the following cannot be used as a solvent in ¹H NMR spectral analysis?
a) CDCl₃ b) D₂O c) CCl₄ d) CH₃OH
- The intensity ratio observed in the mass spectrum of bromo derivatives of molecular ion and isotopic peaks is _____.
a) 1:1 b) 1:2 c) 1:3:1 d) both a and b

II Fill in the blanks: (10×1=5)

11. The λ_{\max} of $n \rightarrow \pi^*$ transition shows _____ shift in polar solvent.
12. Aromatic protons are _____ shielded than acetylenic protons.
13. Mass spectrum is a plot between _____ against m/z values.
14. The intensity ratio of triplet signal in nmr spectrum is _____.
15. Inter/intra molecular hydrogen bonding can be distinguished by _____ spectral technique.

III Match the following: (5×1=5)

- | | | |
|--------------------------------|---|------------------------|
| 16. Electronic transition | – | precessional frequency |
| 17. Vibrational spectroscopy | – | nitrogen rule |
| 18. Rotational spectroscopy | – | molar absorptivity |
| 19. Nuclear magnetic resonance | – | finger print region |
| 20. Mass | – | change in polarization |
| | – | electron spin |

IV Answer briefly in one or two lines: (5×1=5)

21. Arrange the following radiations in order of their increasing energy:
UV, X-ray, Microwaves, γ – rays
22. What are chromophores? Give an example.
23. What is ring rule? Give an example.
24. Why the symmetric stretching of CO_2 molecule is IR inactive and Raman active?
25. Why Raman spectral analysis needs strong radiation source?

26. State mutual exclusion principle.
27. Arrange the following methylene proton in their increasing order of chemical shift value.
 $\text{CH}_3\text{CH}_2\text{F}$, $\text{CH}_3\text{CH}_2\text{Cl}$, $\text{CH}_3\text{CH}_2\text{Br}$, $\text{CH}_3\text{CH}_2\text{I}$
28. Define coupling constant.
29. Predict the mass fragmentation pattern of ethanol molecule.
30. What are isotopic peaks?

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STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI 600 086
(For candidates admitted during the academic year 2011-12 & thereafter)

SUBJECT CODE: 11CH/MC/SP64

B.Sc. DEGREE EXAMINATION, APRIL 2015

BRANCH IV - CHEMISTRY

SIXTH SEMESTER

COURSE : MAJOR – CORE
PAPER : SPECTROSCOPY
TIME : 2 ½ HOURS

MAX. MARKS : 70

SECTION – B

ANSWER ANY FIVE QUESTIONS:

(5X6=30)

1. Explain Franck Condon principle with suitable diagram. (6)
2. a) Differentiate IR and RAMAN spectroscopy. (4)
b) Predict the possible vibrational frequency absorption values (in cm^{-1}) of $\text{C}_6\text{H}_5\text{OH}$ molecule. (2)
3. Describe the theory of Raman spectroscopy. (6)
4. What is the reference compound used in the NMR spectral analysis? Give its significances.
5. a) Acetylenic protons are more shielded than ethylenic protons. Explain.
b) What is spin-spin splitting? (4 +2)
6. a) How *cis* and *trans* olefin is distinguished by nmr spectral analysis. (3)
b) Predict the structure of the compound with molecular formula $\text{C}_8\text{H}_8\text{O}$ which gives the following pmr spectrum: δ (ppm) 7.28 (5 H, m); 2.8 (2 H, d); 9.78 (1 H, t). (3)
7. a) Describe the theory of mass spectrometry. (4)
b) State nitrogen rule. (2)

SECTION – C

ANSWER ANY TWO QUESTIONS:

2X20=40

8. a. Explain the types of absorption and intensity shifts in electronic spectroscopy. (5)
b. Calculate the λ_{max} value of for the following compounds. (5)
(i) $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ (ii) aniline
c. Discuss about the sampling technique in the IR spectral analysis? (5)
d. What are the various modes of molecular vibrations in IR spectral condition? (5)

9. a. An organic compound with molecular weight 72 absorbs at 274 nm, ϵ_{\max} 17.
In infrared, a strong absorption at 1710 cm^{-1} and medium absorption bands at $2941\text{-}2857\text{ cm}^{-1}$ and 1460 cm^{-1} . Predict the structure of the compound. (4)
- b. Predict the signal position and splitting of protons in the following molecules? (3+3)
(i) $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ (ii) $\text{CH}_3\text{OCH}_2\text{CH}_3$
- c. Explain the various factors which affect the chemical shift values. (5)
- d. Define the following: (i) coupling constant (ii) Pascal's triangle (3+2)
10. a. Explain the fragmentation pattern of 1° , 2° & 3° alcohols in the mass spectral analysis. (8)
- b. Mention the significances of isotopic peaks in mass spectral analysis. (4)
- c. Illustrate Mc Lafferty rearrangement with example. (3)
- d. A compound with molecular weight 120 gave the following spectral information:
i) UV : 268 nm ϵ_{\max} 480
ii) IR : $3067\text{-}2907\text{ (m)}$, 1608 (m) , and $1473\text{ cm}^{-1}\text{ (m)}$
iii) NMR : δ (ppm) 3.21 singlet (9 H), 7.74 singlet (3 H)
Find the structural formula of the compound. (5)

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