

B.Sc. DEGREE EXAMINATION, APRIL 2019
BRANCH IV - CHEMISTRY
SIXTH SEMESTER

COURSE : MAJOR – CORE
PAPER : SPECTROSCOPY
TIME : 3 HOURS

MAX. MARKS : 100

SECTION – A

ANSWER ALL THE QUESTIONS. (30x1=30)

I Choose the correct answer:

- According to Beer-Lambert Law, absorbance does not depend on _____.
 a) Extinction coefficient of the sample b) Colour of the solution
 c) Solution concentration d) Distance that the light has travelled through the sample.
- The wavelength of absorption is 495 nm. In what part of the electromagnetic spectrum does this lie?
 a) Microwave b) radiowave c) UV-Visible d) Infrared
- Which of the following statements is correct?
 a) Microwave radiation possesses more energy than infra radiation
 b) Infrared radiation has a shorter wavelength than visible light.
 c) UV radiation has a longer wavelength than infrared radiation
 d) Infrared radiation has a lower wavenumber than visible light.
- Match the molecular formula to the number of degrees of vibrational freedom. Which pair is *correct*?
 a) CO_2 ; 4 b) H_2S ;4 c) SO_2 ;3 d) CS_2 ; 3
- Which of the following transitions between rotational energy levels is *not* allowed?
 a) $J = 1 \leftarrow J = 3$ b) $J = 1 \leftarrow J = 2$ c) $J = 1 \rightarrow J = 0$ d) $J = 1 \leftarrow J = 0$
- Benzene exhibits _____ electronic transition.
 a) $\pi - \pi^*$ b) $n - \sigma^*$ c) $\sigma - \sigma^*$ d) $n - \pi^*$
- Which of the following statements is *incorrect*?
 a) Mass spectrometry provides direct structural data
 b) Mass spectrometry gives information about fragmentation patterns
 c) Parent ions are not always observed in the mass spectra of compounds
 d) Isotopic distribution patterns are observed in mass spectra.
- For which of the following molecules would you expect the infrared active fundamentals to be Raman inactive and vice versa?
 a) NO_2 b) fluorobenzene c) benzene d) fluoroethene
- In the proton NMR spectra recorded for *p*-xylene (1,4,-dimethylbenzene), the number of resonances observed are
 a) 1 b) 2 c) 3 d) 0
- The ^{13}C NMR spectrum of a compound A contains two signals and in the ^1H NMR spectrum there is a singlet. Which compound is consistent with these data?
 a) bromoethane b) dichloromethane c) acetone d) ethanol

II Fill in the blanks:

11. The decrease in polarity of the solvent will have _____ shift in the $n \rightarrow \pi^*$ transition.
12. The highest electronic energy transition of covalent molecule is _____.
13. In Raman spectrum, if λ is the wavelength of incident radiation, then the anti-stoke's lines will have wavelength equal to _____.
14. Water has _____ normal modes of vibrations.
15. In N_2O molecule, the bond sequence N-N-O or N-O-N is confirmed by _____ spectroscopy.
16. The number of spin states possible for 1H nucleus is _____.
17. In 1H NMR spectroscopy, the coupling of two hydrogen atoms on adjacent carbon atoms is called _____.
18. The number of different types of protons that are present in ethyl bromide is _____.
19. The peak set to 100% relative intensity in a mass spectrum is _____.
20. In the case of chloro compounds, M^+ and $[M^++2]$ peaks are formed with the intensity ratio of _____.

III State whether true or false:

21. ^{14}N has magnetic moment.
22. The unit of absorbance in Beer Lambert's law is cm^{-1} .
23. Glass cuvettes are used for holding samples in IR spectrometers.
24. A compound containing an even number of nitrogen atoms gives a molecular ion with an even mass number.
25. Radiowaves are ionizing radiations.

IV Answer briefly in one or two lines:

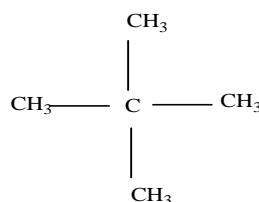
26. What is an isotope peak?
27. Define diamagnetic shielding.
28. Define Franck Condon principle.
29. Acetylenic proton absorbs at upfield compared to ethylenic proton, although the former is attached to a more electronegative carbon. Explain.
30. Which of the following molecule would show rotational spectra? Why? H_2 , HCl , CO .

SECTION – B**ANSWER ANY FIVE QUESTIONS:****(5X6=30)**

31. How will distinguish between 1^0 , 2^0 and 3^0 alcohols using mass spectrometry?
32. a) Differentiate between IR and Raman Spectroscopy.
b) Predict the number of NMR signals observed in the following compounds.

(i) (ii) CH_3COCH_3

(iii)

**(3+3)**

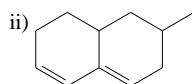
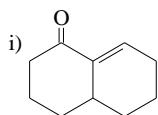
33. a) Arrange the following in their decreasing order of $\nu(\text{C}=\text{O})$ value and justify your answer. HCHO , CH_3CHO , CH_3COCH_3 (3)
 b) An organic compound with molecular formula $\text{C}_4\text{H}_8\text{O}$ gave the following IR spectral data: 1710 cm^{-1} , $2920\text{-}2850\text{ cm}^{-1}$, 1420 cm^{-1} . Predict the structure of the compound. (3)
34. a) Distinguish between 2-bromopentane and 3-bromopentane using NMR spectral data?
 b) A solution of a dye absorbs light of wavelength 480 nm , and for this absorption, the extinction coefficient is $18600\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. A sample of the dye of unknown concentration is placed in an optical cell of path length 1 cm and the absorbance reading is 0.18 . What is the concentration of the solution? (3+3)
35. Explain Retro – Diels Alder and mclafferty rearrangement with an example each. (3+3)
36. a) What are the reference compound used in NMR spectral analysis and mention their characteristics?
 b) Explain the effect of polar solvent on $n - \pi^*$ transition. (3+3)
37. Explain the mass spectral fragmentation pattern of the following compounds
 (i) n-butanol (ii) toluene (iii) CH_3CHO (3x2)

SECTION – C

ANSWER ANY TWO QUESTIONS:

2X20=40

38. a) Discuss the theory of Mass spectrometry (8)
 b) Calculate the moment of inertia, I , of the molecule $^1\text{H}^{35}\text{Cl}$. The masses of the two atoms are $m_{\text{H}} = 1.673 \times 10^{-27}\text{ kg}$ and $m_{\text{Cl}} = 5.807 \times 10^{-26}\text{ kg}$. The equilibrium bond length of the molecule is 1.275 \AA . (4)
 c) Calculate the absorption maxima for the following compounds. (4+4)



39. a) Explain the factors which affect chemical shift. (8)
 b) Define the following. (2+2+2)
 (i) Ring rule (ii) spin-spin splitting (iii) Pascal's triangle
 c) A compound with the molecular formula $\text{C}_8\text{H}_8\text{O}$ gives the following PMR spectral data: $\delta(\text{ppm})$: 9.78 (t, 1H) , 7.28 (m, 5H) , 2.8 (d, 2H) (6)

40. a) Using IR spectroscopy how would you distinguish between
- (i) Intra and Inter molecular hydrogen bonding (ii) Acetone and ethanol (3+3)
 - b) Draw the block Diagram of UV-Visible spectrophotometer (3)
 - c) Determine the structure of compound whose m/e values are $m/e = 74$ (molecular ion), 56, 43, and 31 (base peak). (6)
 - d) Discuss the sampling technique in IR spectroscopy. (5)

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