



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FOURTH SEMESTER – APRIL 2014

CH 4809 - APPLICATIONS OF SPECTROSCOPY

Date : 16/04/2014

Dept. No.

Max. : 100 Marks

Time : 09:00-12:00

Part-A

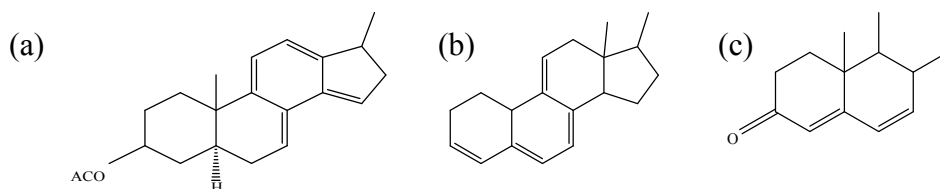
Answer *all* the questions. Each carries *two* marks.

1. In cyclic ketones $\gamma(\text{C}=\text{O})$ absorption increases as the size of the ring decreases. Why?
2. Define isobestic point. Give an example.
3. Why amines absorb at higher wavelength in the UV-Visible region than alcohols?
4. How is primary, secondary and tertiary alcohols differentiated by mass spectra?
5. What are the fragments obtained from benzene in mass spectroscopy?
6. Mention the spin system of *m*-xylene.
7. Vicinal coupling is minimum at 90° dihedral angle. Why?
8. What is hyperfine splitting? Give an example.
9. What is the significance of electric field gradient?
10. Define isomer shift.

Part-B

Answer any *eight* questions. Each carries *five* marks.

11. Discuss the IR absorption in phenol.
(i) 3330 cm^{-1} , (ii) 3040 cm^{-1} , (iii) $2000\text{-}1600\text{ cm}^{-1}$, (iv) $1580, 1495, 1470\text{ cm}^{-1}$, (v) 1360 cm^{-1} , (vi) 800 cm^{-1} .
12. An organic compound A with the molecular formula $\text{C}_3\text{H}_9\text{N}$ shows the following IR peaks (i) 3425 cm^{-1} , (ii) 3236 cm^{-1} , (iii) 3000 cm^{-1} , (iv) 1615 cm^{-1} . When compound A is treated with nitrous acid it forms a strong broad peak at 3400 cm^{-1} . Identify the compound A.
13. Calculate the λ_{max} for the following:



14. Draw and explain the Orgel energy level diagram of Mn^{2+} .
15. An organic compound with molecular weight 120 shows a prominent peak at 105 in its mass spectra. It also shows a positive test for iodoform test. Identify the structure of the compound and predict its mass spectral pattern.
16. Discuss the fragmentation pattern of pentanoic acid using mass spectroscopy.
17. Distinguish between enantiotopic and diastereotopic geminal protons with examples.
18. Discuss the EPR spectrum of high spin Mn(II) complex.
19. Explain the COSY of *m*-dinitrobenzene.
20. How is bond ionicity measured by NQR spectroscopy?
21. What is the effect of ionization on isomer shift in Mossbauer spectral technique?
22. Predict the number of lines in the ESR spectrum of the radicals $[\text{CF}_2\text{H}]^\bullet$ and $[\text{CF}_2\text{D}]^\bullet$

Part-C

Answer any *four* questions. Each carries *ten* marks.

23. An organic compound with the molecular mass 160 absorbs at $\lambda_{\max} = 210 \text{ nm}$, ($\epsilon_{\max} = 60$) in UV spectrum. It shows two strong IR bands at 1260 cm^{-1} and 1055 cm^{-1} . The other IR peaks are at 2940 cm^{-1} , 2855 cm^{-1} , 1742 cm^{-1} and 1460 cm^{-1} . In NMR, it shows a triplet (8.71τ , $J = 7.2 \text{ cps}$), quartet (5.84τ , $J = 7.2 \text{ cps}$), singlet (7.5τ). What is the structure of the compound? Predict its mass spectral pattern.
24. An organic compound with the molecular mass 72 gave the following spectral information
UV : $\lambda_{\max} = 273 \text{ nm}$, $\epsilon_{\max} = 17$
IR : 1715 cm^{-1} (s), 2941 cm^{-1} (s), 1460 cm^{-1} (m)
Mass : $m/e = 72, 43$ (100 % intensity), 29.
NMR : 7.42τ quartet, 7.88τ singlet and 8.93τ triplet
Predict the structure of the compound and explain the spectral data.
25. An organic compound with the molecular mass 116 gave the following spectral information.
UV : $\lambda_{\max} = 280 \text{ nm}$, $\epsilon_{\max} = 22$
IR : $3000 - 2500 \text{ cm}^{-1}$ (s, b), 1715 cm^{-1} (s), 1342 cm^{-1} (m)
Mass : 116, 73, 45, 43 (100 % intensity), 28.
NMR : 7.88τ (Singlet), 7.40τ (Triplet), 7.75τ (Triplet), -1.1τ (Singlet). Predict the structure of the compound and explain.
- 26a. Explain the aromatic coupling observed in phenol and benzoic acids.
b. What is vicinal coupling? Give an example. (6+4)
- 27a. Mention the importance of asymmetry parameter and quadrupole coupling constant in NQR spectroscopy.
b. Predict the number of NQR transitions possible for Cl_2 molecule in solid state. (7+3)
28. Explain the principle of Mossbauer spectroscopy and discuss the Mossbauer spectral features of $\text{K}_4[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_5(\text{NH}_3)]$ complexes.