 LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

**M.Sc.** DEGREE EXAMINATION - **CHEMISTRY**

FOURTH SEMESTER – APRIL 2012

# CH 4809 - APPLICATIONS OF SPECTROSCOPY

Date : 18-04-2012 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

**PART A**

Answer **all** the questions 10x2=20

1. State the fragmentation modes of benzene.
2. Mention the characteristic peaks of an acid anhydride in IR spectra.
3. What is transannular conjugation? Give an example.
4. Why a polar solvent usually shifts π→π\* transition to longer wavelength and

n→π\* transition to shorter wavelength?

1. Mention any two characteristic signals of primary alcohols in mass spectroscopy.
2. What is the significance of spectral editing?
3. Mention the conditions favorable for first-order coupling in NMR.
4. Compare the coupling constants in NMR and ESR spectra.
5. How does hydrogen bonding alter NQR frequencies?
6. What is the influence of energy of gamma ray on f – factor?

**PART B**

Answer **any eight** questions 8x5=40

1. Identify an acidic yellow compound which gave the following data:

i) UV: 280 nm, εmax = 6600

ii)IR : 3460 cm-1 (s), 3035 cm-1 (m), 1510 cm-1 (s), 1310 cm-1 (s), 740 cm-1 (s). The band at 3460 cm-1 does not shift even on diluting the sample.

iii) NMR : -2.1τ (singlet) 1H and unsymmetrical pattern 2.61-2.75 τ (4H).

1. Deduce the structure of the compound having the molecular formula C5H10O2 giving effervescence with sodium bicarbonate. It shows the following mass spectral patter at m/e values: 102, 73, 60 (100% intensity), 57, 45 and 29.
2. Suggest the structure of the liquid compound with the molecular formula C6H6O showing a violet colour with neutral FeCl3. The IR absorptions are at 3300 cm-1, 3040 cm-1, 1360 cm-1, 1220 cm-1 and 685 cm-1.
3. Calculate Λmax for the following compounds:



i) ii)



iii) iv)



v)

1. Identify the compound with molecular mass 120 which shows a UV peak at 268 nm (εmax = 480).In IR spectrum absorption bands are found at 3067-2907 cm-1 (m), 1608 cm-1 (m), and 1473 cm-1 (m). The NMR spectrum shows absorptions at 3.21τ (singlet) and 7.74τ (singlet).
2. Explain the IR absorption bands of aniline. The IR absorptions are at 3450 cm-1, 3026 cm-1, 1620, 1602, 1499 cm-1, 754, 696 cm-1, and 1306, 1257 cm-1.
3. Sketch the 13C NMR of 2–butanone under i) broad band decoupling of 1H and ii) coupling of 1H.
4. Highlight the coupling involved in the 1H NMR of 1 – nitro hexane.
5. What is hyper fine splitting? Discuss the hyper fine splitting exhibited by high spin Mn2+ complex.
6. How will you account for the trend, shown in the ionic character of the tetra chlorides of carbon group elements?
7. The compound NaAuCl4.2H2O shows four NQR lines. One of the lines shows positive temperature dependence – Explain.
8. Isomer shift measures principally the difference in valence s-orbital populations - Explain.

**PART C**

Answer **any four** questions 4x10 = 40

1. An organic compound with the molecular mass 108 is not acidic in nature, but can be easily oxidized to a crystalline compound. In UV, it absorbs at 255 nm (εmax =202). The IR spectrum shows absorptions at 3402 cm-1 (s,b), 3065 cm-1 (w), 2288 cm-1 (w), 1499 cm-1 (w), 1455 cm-1 (m). The signals in NMR are 2.74τ singlet, 5.4τ singlet and 6.10τ singlet. The mass spectral pattern shows m/e values at 108, 106, 105, 77, 51 and 39.
2. Explain the tetrahedral and octahedral complexes of Co2+ using Orgel energy diagram.
3. An organic compound with molecular mass 160 absorbs at 210 nm (εmax = 60) in the UV spectrum. In IR spectrum, absorption bands formed are at i) 2940-2855 cm-1 (m), ii) 1742 cm-1 (s), 1460 cm-1 (m), 1055 cm-1 (s), 1260 cm-1 (s). The following signals are formed in NMR spectrum i) 7.5 τ singlet, ii) 8.71 τ triplet, iii) 5.84 τ quartet. Deduce the structure of the compound and suggest its mass spectral pattern.
4. a) What is COSY? Explain with an example, the influence of a prochiral centre in COSY.

b) An enolic proton is downfield compared to an alcoholic proton – explain.

1. a) How will you account for the transitions, shown by the interaction of an electron with three equivalent protons?

b)35Cl NQR of hexachlorocyclopentadiene shows two lines in 2:1 intensity ratio. Arrive at the point group symmetry of the molecule.

1. a) Define: Isomer shift and Quadru pole splitting. How are they exhibited by high spin Fe2+ and Fe3+ complexes.

b) How many NQR transitions are possible for 51V nucleus.

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