

III Semester M.Sc. Examination, January 2018
(CBCS)
CHEMISTRY
303 – OC : Organic Spectroscopy

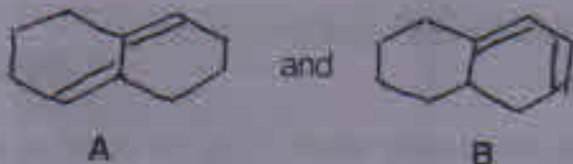
Time : 3 Hours

Max. Marks : 70

Instruction: Answer Question No. 1 and any five of the remaining questions.

1. Answer any ten of the following : (2×10=20)

a) How are the following pairs of structural isomers distinguished by uv-vis spectra ?

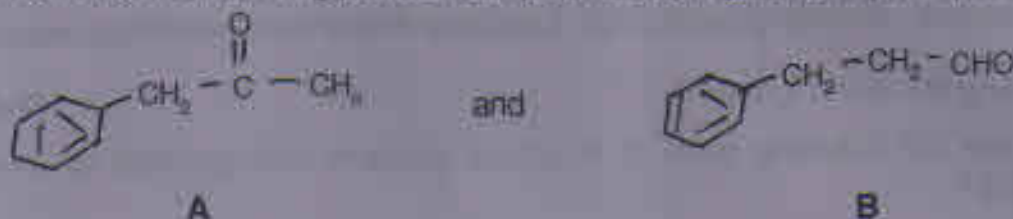


- b) What are Fermi resonance bands ? Give examples.
- c) Reason why nitro-compounds show two bands of equal intensity at 1550 and 1350 cm^{-1} .
- d) Differentiate spin-spin relaxation from spin-lattice relaxation process.
- e) Mention the most common internal standards used to record ^1H NMR spectra of
- i) aqueous and
 - ii) organic solutions.
- f) Write the Karplus equation and draw the Karplus curve. Give its importance.
- g) Sketch the GDNP spectrum of the methyl radical.
- h) Highlight the basic criterion for a molecule to exhibit NOE.
- i) Give the nuclear magnetic spin quantum numbers (I) for :
- i) ^2H ;
 - ii) ^{15}N ;
 - iii) ^{29}Si and
 - iv) ^{31}P
- j) What are metastable ions ? How are they recognized in a mass spectrum ?
- k) Draw the block diagram for a FAB-MS instrument.
- l) State and explain the nitrogen rule.



2. a) Outline the Woodward-Fieser rules to predict the λ_{max} of α, β -unsaturated carbonyl compounds.
- b) Citing examples, illustrate the usefulness of IR spectroscopy to distinguish :
- Inter-and intra-molecular H-bonding.
 - Keto-enol tautomerization. (5+5=10)

3. a) Write an account of solvent effects on the position of uv-bands of α, β -unsaturated carbonyl compounds.
- b) How are the following pairs of compounds distinguished by IR spectra ?



- c) Highlight the complementarity of IR-and Raman spectroscopies. (3+3+4=10)

4. a) Illustrate the criteria of a reference compound which may be used as an internal standard to record NMR spectra.
- b) State and explain the first order splitting rules of ^1H NMR.
- c) With the help of a diagram, indicate the anisotropic effects in aromatic hydrocarbons. (3+3+4=10)
5. a) Give any two methods to distinguish first and second-order ^1H NMR spectra.
- b) Citing suitable examples, distinguish chemically and magnetically-equivalent protons.
- c) How are the following compounds distinguished by ^1H NMR ?



6. a) Discuss any two methods for the simplification of complex ^1H NMR spectra.
- b) Ethyl benzene gave the following ^1H NMR data :
- δ : 7.27 (s, 5H), 2.71 (q, 2H) and 1.35 (t, 3H) ppm. Sketch the ^1H - ^1H cosy of ethyl benzene.
- c) Write a note on DEPT. (3+4+3=10)

7. a) Outline the quasi-equilibrium theory for fragmentation of organic molecules.
 b) How is the isotope abundance method useful in determining the molecular-ion peak?
 c) Deduce the structure of an organic compound from the following data and assign the values:

Mol. form. C_9H_8O

uv λ_{max} : 244, 292 nm.

IR: 2901, 2803, 1708, 1072 and 744 cm^{-1}

1H NMR: δ : 7.28(m, 4H) and 3.57(s, 4H) ppm.

^{13}C NMR: δ : 214.5, 137.8, 124.7 and 43.8 ppm.

MS m/e : 132(M^+), 104(base peak), 78, 77 and 28

(3+3+4=10)

8. a) Deduce the structure of an organic compound from the following data and assign the values:

Mol. form: $C_5H_{10}O_2$

uv: λ_{max} : 200 nm.

IR: 3052, 2980, 2876, 1722, 1652 and 1184 cm^{-1} .

1H NMR: δ : 7.25 – 6.36 (m, 1H, $J = 16.25$ Hz)

5.84 (m, 1H, $J = 16.25$ Hz)

3.82(q, 2H, $J = 7$ Hz)

1.82 – 1.49(d/d, 3H) and

1.11(t, 3H, $J = 7$ Hz) ppm.

^{13}C NMR: δ : 167.1, 144.3, 122.6, 60.9, 18.4 and 14.5 ppm.

MS $\frac{m}{e}$: 114(M^+), 99, 69(base peak) and 41.

- b) Write short notes on:

i) ^{19}F -NMR.

ii) HRMS and its usefulness.

(6+4=10)