61923

Reg. No.

III Semester M.Sc. Degree Examination, April/May - 2022

CHEMISTRY

Organic Spectroscopy

(CBCS Scheme 2019-2020)

Paper : CH - 303 IC/OC/PC

Time : 3 Hours **Maximum Marks : 70**

Instructions to Candidates:

1. Answer question No. **1** and any **five** of the remaining.
2. Figures to the right indicate marks.

1. Answer any **Ten** of the following. **(10×2=20)**

a. Sketch the MO diagram of benzene. Name and indicate the positions, of its UV bands.

b. Oultine the Nujol mull technique for recording IR spectra.

c. Carbonyl compounds are sensitive to changes of solvent in UV/IR spectra why?

d. Indicate why TMS is the internal standard of choice in ^{1}H NMR spectroscopy.

e. Assign pople's notation for the following spin systems :

i. CH_3CHO and

ii. 

f. How are first order ^{1}H NMR speactra differentiated from higher order ^{1}H NMR spectra?

g. State and explain Audier - Stevenson rule.

h. Deduce the expression for separation of ions in an ICR - MS instrument.

i. Illustrate NOE with suitable example.

j. How are the formation of free radical intermediates recognized by dynamic ^{1}H NMR spectroscopy?

k. Give the composition of a matrix. Highlight its importance in the MALDI technique for formation of molecular ions.

[P.T.O.

1. Assign the ^{13}CNMR chemical shift values for the methylene protons (A),(B) and (C).

$$R-\underset{(A)}{CH_2}-\overset{O}{\overset{\|}{C}}-O-\underset{(B)}{CH_2}-\underset{(C)}{CH_2}-R$$

i. δ : 68.9

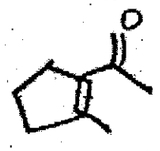
ii. δ : 26.4 and

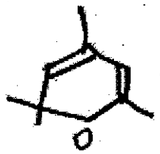
iii. δ : 22.7 ppm.

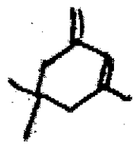
2. a. Outline the empirical rules to predict the λ_{max} of aromatic carbonyl compounds.

b. Illustrate the usefulness of IR spectroscopy to distinguish the isomers 2-hydroxybenzaldehyde from 4 - hydroxybenzaldehyde.

c. Predict the λ_{max} for the following.

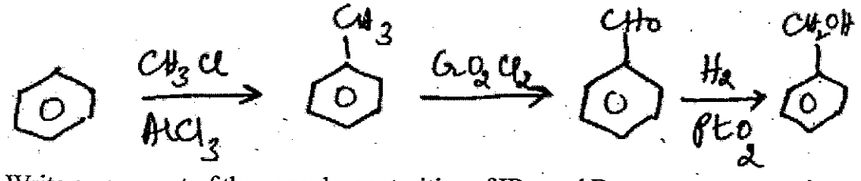
i. 

ii.  and

iii. 

(4+3+3=10)

3. a. Predict the prominent IR bands in the following sequence of transformations :



b. Write an account of the complementarities of IR - and Raman spectroscopies.

c. Expalin the phenomena of NMR on the basis of quantum mechanical theory.

(4+3+3=10)

4. a. Give an account of the principle and instrumentation of an 7T-NMR instrument.

b. Write the karplus equation. Sketch the karplus curve and indicate its importance.

c. Deduce the structure of an organic compound from the following data :

Mol. form : $C_6H_{12}O_2$.

^{1}H NMR: δ : 2.00 (s,2H), 0.84 (s, 9H), and 11.01 (s, 1H).

^{13}C NMR : δ : 179.4, 48.2, 29.8 and 28.2. **(4+3+3=10)**

5. a. Discuss any two methods for the simplification of complex NMR spectra.

b. With the help of a neat diagram, indicate the anisotropic effects prevalent in alkenes.

c. A compound has molecular formula $C_{10}H_{14}$ and gave the following data :

^{1}HNMR : δ : 7.01 (s, 1H) and 2.20 (s, 6H).

^{13}C NMR : δ : 133.0, 130.2 and 19.2

Deduce the structure of the molecule and assign the values. **(4+3+3=10)**

6. a. State and explain the first order splitting rules of ^{1}H NMR.

b. Citing suitable examples, illustrate the usefulness of DEPT.

c. Indicate the importance of nitrogen rule with suitable examples. **(4+3+3=10)**

7. a. Describe the quasi - equilibrium theory.

b. Write an account of the application of HRMS to determine the exact molecule formula of an organic compound.

c. Deduce the structure of an organic compound from the following data :

Mol. form : $C_{10}H_{12}O$

IR : 3019, 2987, 1718 and 1049 cm^{-1}

^{1}HNMR : δ : 7.30 to 7.19 (m, 5H),
2.85(t, 2H, J = 7Hz)
2.50 (t, 2H, J = 7 Hz) and
2.12 (s, 3H).

^{13}CNMR : δ : 207.2, 141.8, 128.6, 126.7, 124.3, 45.0, 29.3 and 27.8.

MS : 148 and 91 (base peak). **(3+3+4=10)**

8. a. A compound has molecular formula $C_9H_6O_6$ and gave the following data :

ATR - IR : 3500 - 2000, 1710 and 1259 cm^{-1}.

^{1}H NMR : δ : 13.01 (s) and 8.76 (s)

^{13}CNMR : δ : 165.9, 133.6, 132.0

MS : 210 (M^+) and 192 (base peak)

Deduce the structure of the compound and assign the values.

b. Write short notes on :

i. ^{19}F - NMR spectroscopy.

ii. INADEQUATE.

iii. ESI - MS. **(4+6=10)**