

III Semester M.Sc. Examination, December 2018
INDUSTRIAL CHEMISTRY
Spectroscopic Techniques

Time : 3 Hours

Max. Marks : 70

Note : Answer **any five** questions from Part – A and **any five** questions from Part – B.

PART – A**(5×2=10)**

1. a) How to distinguish between spherical, symmetric and asymmetric top molecules ?
- b) The rotational constant for H^{35}Cl is observed at 10.5909 cm^{-1} . What is the value of B for H^{37}Cl ?
- c) Reason out why symmetric stretching of CO_2 is IR inactive but Raman active.
- d) How you distinguish between $\text{CH}_3 - \text{O} - \text{CH}_3$ and $\text{CH}_3 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$ using IR spectroscopy ?
- e) What is the significance of blank solution in UV-V is spectroscopy ?
- f) Calculate the chemical shift value of whose frequency of a ^1H nucleus is 1250 Hz on 400 MHz spectrometer. What will its frequency in 60 MHz spectrometer ?
- g) Calculate number ^{13}C of signals for toluene and 2-chlorotoluene.
- h) How to distinguish the presence of chlorine and bromine in a molecule through mass spectrometry ?

PART – B

2. a) Derive an expression for the rotational energy levels of diatomic molecule based upon rigid-rotor model.
- b) Sketch the rotational spectrum for $^{12}\text{C } ^{16}\text{O}$ and $^{13}\text{C } ^{16}\text{O}$ molecules.

(6+6)

P.T.O.

3. a) "Rotational spectrum of OCS molecules enables to calculate bond lengths" Justify the statement.

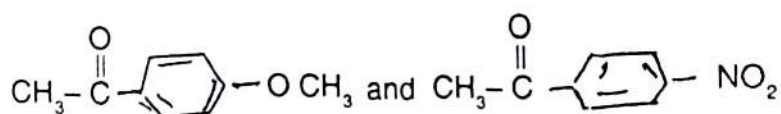
b) Derive an expression for the energy levels of anharmonic oscillation.

- c) Sketch vibration-rotation spectrum with an emphasis to PQR branches. (4+4+4)

4. a) Illustrate with examples how to distinguish between amides and esters using IR spectroscopy.

b) How intermolecular and intramolecular hydrogen bonding can be distinguished by IR spectroscopy ?

- c) How do you distinguish between using IR spectroscopy ?



(4+4+4)

5. a) Discuss different types of electronic transitions and how they affect λ_{max} .

b) Write a notes on :

i) Frank – Condon principle

ii) Wood word Fisher rule. (6+6)

6. a) Discuss about the relaxation processes of a nucleus revert back to α state.

b) Why TMS used as an internal standard in ^1H NMR experiments ?

c) How FTNMR technique offers itself as a advantage over CWNMR ? (4+4+4)

7. a) "In [18] annulene the peripheral protons appear δ 8.9 ppm where as inner protons at δ – 1.8 ppm" Justify the statement.

b) Predict the ^1H NMR spectrum of following compounds :

i) Acetaldehyde

ii) Acetamide

iii) Ethylacetate

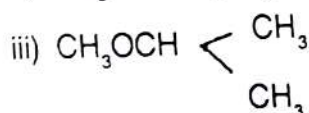
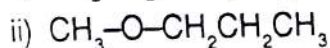
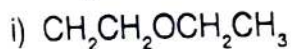
iv) Benzyl alcohol

c) Distinguish between AX and AMX spectral patterns with justifications. (4+4+4)

8. a) Discuss how vicinal protons coupling constants vary based on Karplus equation.

b) Explain the technique and use of spin decoupling.

c) Distinguish these compounds on the basis of ^{13}C NMR :



(4+4+4)

9. a) Illustrate with example how double irradiation technique helps in understanding NOE.

b) Explain with examples the fragmentation process in mass spectroscopy.

c) Write the feasible structures for these ions :

i) 1-Methyl cyclohexanone : m/z , 96, 81, 68, 67

ii) 4-Heptanone : m/z , 114, 86, 71, 58, 43, 41.

(4+4+4)

10. a) Discuss with examples McLafferty rearrangement.

b) The organic compound has following spectral data with mol formula $\text{C}_9\text{H}_{10}\text{O}_2$

IR $\nu_{\text{max}} = 1745 \text{ cm}^{-1}$ (S) 1225 cm^{-1} (br-S), 749 cm^{-1} (S), 697 cm^{-1} (s)

UV = λ_{max} at 268, 264, 262, 257 nm.

^1H NMR δ ppm : 1.96 (3H, s); 5.00 (2H, s) 7.22 (5H, s). Deduce the structure of the compound.

c) An organic compound containing C, H, N and halogen gave following spectral Data UV λ_{max} : 240 nm

IR $\nu_{\text{max}} = 3400, 3300, 3200$ (w), 2900, 1620, 1500, 1380, 880, 820 cm^{-1}

^1H NMR δ ppm : 7.20, (1H d, $J = 9\text{Hz}$), 6.50 (1 H, d, $J = 3.5 \text{ Hz}$), 6.30 (1 H, dd, $J = 9 \text{ \& } 3.5 \text{ Hz}$), 3.5 (2 H, s, D_2O exchangeable), 2.30 (3H, s).

Mass : m/z (RA) : 187 (90), 185 (90), 160 (20), 158 (10), 106 (100)

Deduce its structure.

(4+4+4)