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M.Sc.(Chemistry) (2018 Batch) (Sem.-1) SPECTROSCOPY - I

Subject Code: CHL404-18 Paper ID: [75116]

Time: 3 Hrs. Max. Marks: 70

INSTRUCTION TO CANDIDATES:

- SECTION-A is COMPULSORY consisting of TEN questions carrying TWO marks each.
- 2. SECTION-B contains EIGHT questions carrying FIVE marks each and students have to attempt any SIX questions.
- 3. SECTION-C will comprise of two compulsory questions with internal choice in both these questions. Each question carries TEN marks.

SECTION-A

Q1 Answer briefly: $(10\times2=20)$

- a) What do you understand by Frank-Condon principle?
- b) When p-nitrophenol is dissolved in water, the colour is yellow, but when NaOH is added, the colour deepens in intensity and moves to longer wavelength. Explain.
- c) Determine the index of hydrogen deficiency for C₂₁H₂₂N₂O₂.
- d) Primary alcohols have a strong peak at m/z = 31. What fragment is responsible for this peak?
- e) Write the McLafferty rearrangement in butyraldehyde along with m/z values.
- f) Write mass fragments in case of 2-Chloropropane at 80, 78, 65, 63, 43 (Base peak).
- g) λ_{max} for trans-stilbene is _____ than cis-stilbene. Explain.
- h) List three factors that influence the intensity of an IR absorption band.
- i) Which will occur at a higher frequency: the C-N stretch of an amine or the C-N stretch of an amide?
- j) Predict the appearance of proton-decoupled ¹³C NMR spectra for the following compounds.

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 $J_{CD} \cong 20 - 30 \text{ Hz (one bond)}$

SECTION-B

Q2-Q4 Give the mass fragmentation pattern along with m/z values for the following:

$$Q3$$
 \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc

$$Q4$$
 (5)

- Q5 Explain the ¹H NMR patterns and intensities of the isopropyl group in isopropyl iodide. (5)
- Q6 Explain proton decoupling in ¹³C NMR. (5)
- Q7 The hydrogen halides have the following stretching wavenumbers: 4148.3 cm⁻¹ (HF); 2988.9 cm⁻¹ (HCI); 2649.7 cm⁻¹ (HBr). Use Hooke's law to calculate the force constants for hydrogen-halogen bonds. (5)
- Q8-9 Calculate λ_{max} for the following in hexane (specify each assignment) :

Q8(a)
$$H_3COCO$$

Q8(b)

 C_9H_{19}
 C_9H_{19}
 C_9H_{19}

(5)

Q9(a)
$$H_3COCO$$

Q9(b) H_3C
 C_9H_{19}
 H_3C
 H_3C
 C_9H_{19}
 C_9H_{19

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SECTION-C

Q10 a) Give the structure(s) consistent with each of the following sets of NMR data: (10)

i) $C_{10}H_{14}$		ii) $C_{10}H_{12}$	
a doublet	δ 0.88, 6H	a multiplet	δ 0.65,2Η
b multiplet	δ 1.86,1Η	b multiplet	δ 0.81,2Η
c doublet	δ 2.45,2Η	c singlet	δ 1.37, 3H
d singlet	δ 7.12,5H	d singlet	δ 7.17, 5H
iii) C ₉ H ₁₀		iv) C ₁₀ H ₁₃ Cl	
a quintet	δ 2.04,2Η	a singlet	δ 1.57,6Η
b triplet	δ 2.91,4Η	b singlet	δ 3.07,2Η
c singlet	δ 7.17,4Η	c singlet	δ 7.27,5H

or

b) Discuss fragmentation pattern for amides, nitriles and carboxylic acids. (10)

Q11 a) Explain the principle of electronic spectroscopy. (10)

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b) How chemical ionization differs from electron impact phenomenon? How it helps in determining the accurate molecular ion peak? Explain. (10)

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