

**M. SC. CHEMISTRY**  
**SCLS, JAMIA HAMDARD**  
**SEMESTER II EXAMINATION -2019**  
**PAPER TITLE: APPLICATIONS OF SPECTROSCOPY**  
**TO STRUCTURAL ANALYSIS**  
**PAPER CODE: MCHCC-205**

**Time: 3hrs**

**Maximum marks: 75**

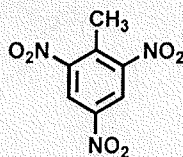
*(Write your roll no. at the top immediately after receipt of this question paper)*

**Attempt ALL the questions. All parts of a question must be attempted in continuation.**

**Q1. Answer briefly ANY TEN of the following:**

**1.5 x 10 = 15**

- i. Describe the working of photomultiplier tube.
- ii. The absorbance of a solution of Ferrous 1, 10-phenanthroline complex containing 1.00 microgram of iron (II) in 10 cm<sup>3</sup> of solution at 515 nm in 1.0 cm cuvette was found to be 0.0200. Calculate the molar absorptivity of the complex.
- iii. Discuss with suitable examples, the inductive, resonance and ring size effect in carbonyl stretching frequencies
- iv. What are the various UV/Vis radiation sources used in spectrophotometers?
- v. Propanoic acid was synthesized from propene. The <sup>1</sup>HNMR spectrum (recorded in CCl<sub>4</sub>) of the obtained product showed three peaks at δ11.7 (s), 2.3 (q) and 1.2 (t). Do these peaks confirm the formation of propanoic acid? If yes, assign the peaks to different protons. Also explain why does the peak at δ11.7 disappear on addition of D<sub>2</sub>O.
- vi. Which are the fragment peaks that would be present in the mass spectrum of n-heptane
- vii. Predict the chemical shifts of the peaks in <sup>1</sup>HNMR and <sup>13</sup>CNMR spectrum of



- viii. Why is the oxygen-hydrogen absorption of CH<sub>3</sub>OH such a broad band in the infrared?
- ix. How is nitrogen rule used to verify the presence of nitrogen in a molecule?
- x. Justify different chemical shift values for ethylenic, acetylenic and aromatic protons in <sup>1</sup>H NMR spectroscopy.
- xi. What are shift reagents?
- xii. What are metastable peaks? What is their importance?
- xiii. What is coupling constant? What does it indicate?

**Q2a. Attempt the following questions.**

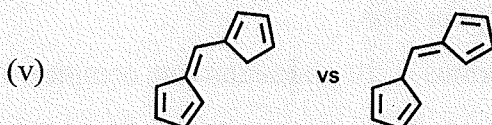
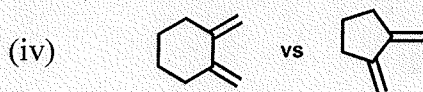
10 + 5 = 15

- A. Discuss the principle and applications of Fluorescence spectroscopy
- B. Which of the following compounds has absorbance at the longest wavelength in the UV/vis spectrum?  
Give reasons for your answer.

(i) Ethylene vs 1,3-Butadiene

(ii) Glucose vs  $\beta$ -carotene

(iii) Acetone vs 2-Butenone

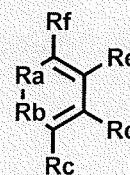
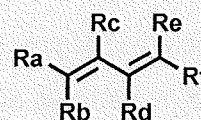
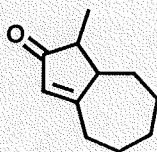
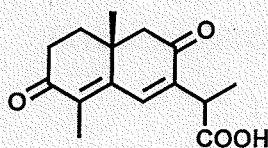
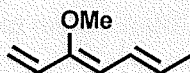
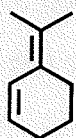


**OR**

**Q2b. Attempt the following questions.**

8 + 7 = 15

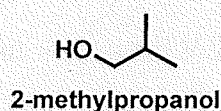
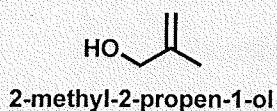
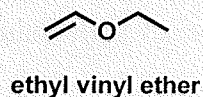
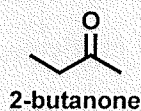
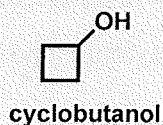
- A. Discuss the principle of UV –VIS spectroscopy? Outline the factors that may cause deviations from Beer and Lambert's law.
- B. Use Woodward-Fieser Rules to predict  $\lambda_{\max}$  of the following:



**Q3a. Attempt the following questions.**

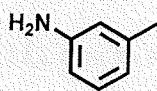
5 x 3 = 15

- A. Explain how we can differentiate amongst following five  $C_4H_8O$  isomers from their IR spectra.



B. A compound with the molecular formula  $C_8H_{18}$  shows given absorption bands;  $2925\text{ cm}^{-1}$  (st),  $1465\text{ cm}^{-1}$ ,  $1380\text{ cm}^{-1}$ ,  $720\text{ cm}^{-1}$ . Identify the structure of organic compound.

C. Give the important peaks associated with the IR spectra of the following compounds.



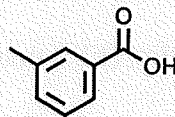
m-toluidine



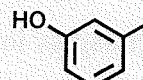
m-tolualdehyde



3-methylpyridine



m-toluic acid



m-cresol

OR

Q3b. Attempt the following questions.

7 + 8 = 15

A. Give a comparison of Raman and IR spectroscopy

B. How could you differentiate between the following on the basis of IR

- (i) and
- (ii) Acetic Anhydride and Acetic Acid
- (iii) 1-Butene and 1-butyne
- (iv) Propanal and Propanone

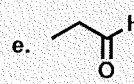
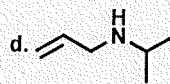
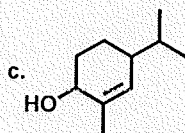
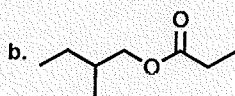
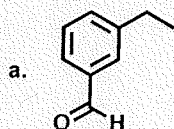
Q4a. Attempt the following questions.

5 + 10 = 15

A. Predict the splitting pattern expected for each kind of the proton in the  $^1\text{H}$ NMR spectrum of the following

- (i).  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$
- (ii).  $(\text{CH}_3)_3\text{COCH}_3$
- (iii). 3-hexanone
- (iv). Cyclobutanol
- (v). trimethylamine

B. For each of the following structures, indicate how many peaks would be found in the proton decoupled  $^{13}\text{C}$ NMR spectrum



OR

Q4b. Attempt the following questions.

7 + 8 = 15

A. What is the significance of the COSY and HMBC experiments? Illustrate giving examples?

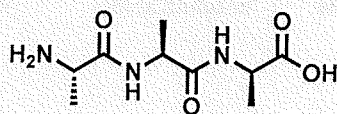
B. Draw structures for compounds that meet these descriptions:

- i.  $C_2H_6O$ ; one singlet
- ii.  $C_4H_8O_2$ ; one singlet, one triplet, and one quartet

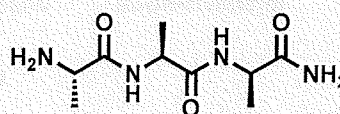
**Q5a. Attempt the following questions.**

**5 + 10 = 15**

- A. The electrospray ionization (ESI) mass spectrum of a peptide shows large peaks at  $m/z$  231 and  $m/z$  253.



Alanine tripeptide



Alanine tripeptide Amide

Which is the peptide the alanine tripeptide or the alanine tripeptide amide? Explain your answer, indicating clearly the compositions of the species that generate the observed peaks.

- B. Discuss Electron Impact, FAB and Electrospray ionization techniques for analysis of analytes by mass spectrometry?

**OR**

**Q5b. Attempt the following questions.**

**5 + 10 = 15**

- A. Discuss different fragmentation routes of ketones, aldehydes, esters and acids in mass spectrometry, giving suitable examples.
- B. What is mass-to-charge ratios ( $m/z$ ) for the three biggest peaks in the electron impact ionization (EI) mass spectrum associated with the intact, unfragmented molecular ion of m-dichlorobenzene.

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