

AS-422

M.Sc. (Chemistry) IV Semester (Reg./ATKT)

Examination June 2019

APPLICATION OF SPECTROSCOPY

Paper - I

Time Allowed : Three Hours] [Maximum Marks : 85

Section - A

Objective Type Questions

15 × 1 = 15

Q.1. Choose the correct option.

i) How many signals does the aldehyde $(CH_3)_3CCH_2CHO$ have in 1H NMR and ^{13}C NMR spectra?

- (a) Five 1H signals and six ^{13}C signals
- ~~(b) Three 1H signals and four ^{13}C signals~~
- (c) Five 1H signals and four ^{13}C signals
- (d) Three 1H signals and six ^{13}C signals

(2)

ii) Which of the following statements regarding NMR spectroscopy is wrong?

- (a) NMR signals towards the left of the spectral chart correspond to larger chemical shifts.
- (b) Chemical shifts are larger when the frequencies of the radiation which induces the nuclear transitions are higher.
- (c) Chemical shifts are larger when shielding effects are greater.
- (d) A hydrogen signal splits into $n + 1$ peaks by spin - spin coupling when the number of equivalent hydrogen atoms on adjacent atom(s) is n , and no other neighbouring atoms are involved.

iii) An IR active symmetric stretch limits?

- (a) 15
- ~~(b) 45~~
- (c) 10
- (d) 90

iv) Which statement corresponds to the case where the chemical shift difference between two coupling protons is less than 5-times the coupling constant?

- (a) An AB pattern is observed
- (b) A first-order spectrum is expected
- (c) An undistorted binomial splitting pattern is expected
- (d) AX pattern is observed

v) According to the Beer-Lambert Law, on which of the following does absorbance *not* depend?

- ~~(a) Extinction coefficient of the sample.~~
- (b) Colour of the solution.
- (c) Distance that the light has travelled through the sample.
- (d) Solution concentration.

vi) The dichromate ion absorbs light of wavelength close to 500 nm. Based on this information, what can you conclude?

- ~~(a) The dichromate ion absorbs in the ultraviolet region~~
- (b) Solutions of the dichromate ion are colourless
- (c) The dichromate ion absorbs outside the visible region
- (d) The dichromate ion absorbs within the visible region.

vii) On which factors the vibrational stretching frequency of diatomic molecule depend?

- (a) Force constant
- ~~(b) Atomic population~~
- ~~(c) Temperature~~
- (d) Magnetic field

(5)

viii) Which of the following bonds would show the strongest absorption in the IR?

- (a) Carbon-hydrogen
- ☒ (b) Oxygen-hydrogen
- (c) Nitrogen-hydrogen
- (d) Sulfur-hydrogen

ix) Why is the oxygen-hydrogen absorption of CH_3OH such a broad band in the infrared?

- (a) Rotational energy levels broaden the absorption
- (b) Hyperconjugation resonance broadens the absorption
- (c) Resonance broadens the absorption. Resonance broadens the absorption
- (d) Hydrogen bonding broadens the absorption

(6)

x) In mass spectrometer, the ion currents are measured using which of the following?

- (a) Scintillation counter
- ☒ (b) Ion counter
- (c) Electrometer tube
- ☒ (d) Electric fields

xi) Which of the following statements is not true about mass spectrometry?

- ☒ (a) Impurities of masses different from the one being analysed interferes with the result <http://www.onlinebu.com>
- (b) It has great sensitivity
- (c) It is suitable for data storage
- (d) It is suitable for library retrieval

xii) What are the main criteria on which mass spectrometer used for?

- (a) Composition in sample
- ☒ (b) Relative mass of atoms
- (c) Concentration of elements in the sample
- (d) Properties of sample

(7)

xiii) With accompanying 1,2 - rearrangement in wolff rearrangement, an α -diazocarbonyl compound is converted into a ketene by loss of which of the following compound?

- (a) Dioxygen
- ☒ (b) Dinitrogen
- (c) Disulphur
- (d) Ammonia

xiv) The sensitivity of a cryogenic probe on a 500 MHz spectrometer is close to that of a conventional probe on a spectrometer of

- (a) 600 MHz
- (b) 750 MHz
- (c) 900 MHz
- ☒ (d) 1,050 MHz

xv) Chemical shifts of protons have a frequency range of about

- (a) Megahertz
- (b) 250 MHz
- (c) Kilohertz
- ☒ (d) 10 Hz

(8)

Section - B

Short Answer Type Questions

5 × 5 = 25

Q.2. What is steric effect give advantages of its?

OR

Write comment on UV spectra?

Q.3. What is characteristic of vibrational frequencies of alkenes Show?

OR

Explain solvent effect on vibrational frequencies?

Q.4. How to define NMR of paramagnetic substances in solution?

OR

Explain pseudo contact shifts.

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Contd...

(9)

Q.5. What is coupling constants?

OR

Write about carbon - ^{13}C NMR spectroscopy.

Q.6. Give the theoretical principles of Mass spectroscopy explain FAB factors affecting fragmentation?

OR

What is meant by nitrogen rule? How is it used in the Mass spectroscopy?

Section - C

Long Answer Type Questions

$5 \times 9 = 45$

Q.7. Describe the various electronic transitions (185-800 nm) Beer-Lambert law.

OR

Describe selection rules & mechanism of breakdown of selection rules of electronic spectra of d^3 transition metal complexes.

(10)

Q.8. Describe why is there a peak at 3400 cm^{-1} in pyridine IR spectra, especially for anhydrous pyridine & carbonyl compounds?

OR

This question is going to give you three isomeric compounds and three IR spectra. What you have to do is to match each compound to its correct spectrum. You will find a list of useful infrared absorption data after the three spectra.

The three compounds you are concerned with are Propanoic acid: $\text{CH}_3\text{CH}_2\text{COOH}$, Methyl ethanoate: $\text{CH}_3\text{COOCH}_3$ hydroxypropanone: $\text{CH}_3\text{COCH}_2\text{OH}$

- Draw full structural formulae for the three compounds so that you can see exactly which bonds you need to think about.
- Decide which compound corresponds to each of the spectra below, explaining how you made your decisions.

(11)

Q.9. Describe application of biochemical systems in NMR. Spectroscopy.

OR

What you have to do is to match each compound to its correct spectrum by two dimension NMR spectroscopy?

Q.10. Describe the DEPT & HMBC techniques for carbon - ^{13}C NMR spectroscopy?

Q.11. Explain nitrogen rule. Why do I get fragment ions at higher m/z than that of the single charged precursor ion in an MS/MS experiment (product ion scan)?

OR

Describe the McLafferty rearrangement & high resolution mass.



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