

SEAT No. _____

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[73]

Sardar Patel University Examination, January-2021

M.Sc. (Inorganic Chemistry) Semester-III

Spectroscopy-I (PS03CINC21)

1st January 2021 (Friday)

Time: 10.00 am to 12.00 noon

Note: Numbers at the right show full marks.

Total Marks: 70

Q.1 [A]. Answer the followings:

[8]

- 1) When radiations with frequency _____ are absorbed, molecular rotation takes place in the substance.
(a) less than 100 cm^{-1} (b) less than 1000 cm^{-1}
(c) 100 cm^{-1} (d) 1000 cm^{-1}
- 2) Which of the following electronic transitions has lowest energy?
(a) $\sigma \rightarrow \sigma^*$ (b) $n \rightarrow \sigma^*$
(c) $\pi \rightarrow \pi^*$ (d) $n \rightarrow \pi^*$
- 3) The difference in energies (ΔE) of two spin states of a proton depends on _____.
(a) atomic mass (b) number of protons
(c) strength of magnetic field (d) number of protons and strength of magnetic field
- 4) A small peak at 7.26 ppm for CDCl_3 solvent in ^1H NMR is due to _____.
(a) deuterium of CDCl_3 , (b) proton of CHCl_3 impurity,
(c) moisture present in CDCl_3 (d) acidic impurities
- 5) For CH_3^\bullet , the number of lines in EPR spectrum is _____.
(a) one (b) two
(c) three (d) four
- 6) The value of g_e for a free electron is 2.0023. The value of g_e _____ in ionic crystals.
(a) is increased (b) is reduced
(c) remains unchanged (d) depends on free electrons availability
- 7) In Mass Spectrometry, electron removal will be easiest in which of the following molecules?
(a) C_2H_6 (b) C_2H_4
(c) $\text{C}_2\text{H}_5\text{-NH}_2$ (d) All of the above
- 8) In Chemical Ionization, which of the following gases leads to softest ionization of a molecule?
(a) CH_4 (b) NH_3
(c) H_2 (d) $i\text{-C}_4\text{H}_{10}$

Q.1 [B]. Answer the followings:

[16]

- 1) UV Spectroscopy is useful to measure conjugation in various molecules. State true or false.
- 2) An unsaturated group with non-bonding electrons, which when attached to a chromophore, alters the wavelength and intensity of absorption. State true or false.
- 3) The number of vibrational modes in CO_2 and SO_2 is different. State true or false.
- 4) On which factor, the intensity of the bands in IR Spectrum is dependent?
- 5) The aromatic protons are deshielded. State true or false.

- 6) Write the number of multiplets for ^{29}Si signal in proton coupled ^{29}Si NMR of tetramethylsilane.
- 7) Write the multiplicity for ^{13}C signal of CDCl_3 .
- 8) Write the number of lines in EPR spectrum of H_2^+ .
- 9) Write the number of EPR lines for $^{\bullet}\text{CH}_2\text{-OH}$ radical.
- 10) The solvents with high dielectric constant are suitable for EPR study. State true or false.
- 11) Write the number of lines in EPR spectrum of a molecule having an unpaired electron and four protons.
- 12) Write the ratio of line intensity in EPR spectrum of *para*-benzosemiquinone anion radical.
- 13) In Electrospray Ionization technique, what is the role of nebulizing gas?
- 14) In Magnetic Sector Mass Analyser, the resolution can be increased by subjecting the ions to _____.
- 15) Draw the structure of fragments of methyl 2-methyl benzoate molecule based on ortho effect reaction.
- 16) How many peaks will appear in the Mass spectrum of Cl_2 ?

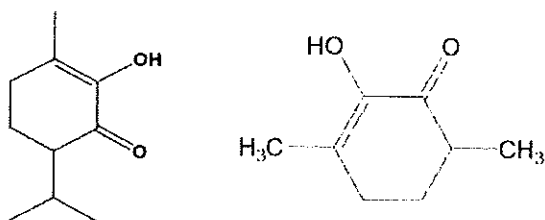
Q.2. Answer any SEVEN of the followings:

[14]

- 1) Explain. Chromophores and Auxochromes.
- 2) Calculate the frequency associated with -C=O vibration.
- 3) In the ^1H NMR, the protons of acetylene are shielded. Explain.
- 4) What are exchangeable protons? Give examples.
- 5) What is proton decoupled ^{13}C NMR spectrum? Explain with an example.
- 6) The magnetogyric ratio for ^1H (γ_{H}) and for ^{15}N (γ_{N}) are 26,753 and -2,712, respectively. Calculate the maximum NOE enhancement for ^{15}N .
- 7) Electron Zeeman splitting is higher than nuclear Zeeman splitting. Explain.
- 8) Give two Ionization methods with typical analytes, sample introduction, mass range and Ionization.
- 9) What is Mc-Lafferty Rearrangement? Explain with suitable example.

Q.3.[A] Calculate the λ_{max} values for following molecules.

[4]



[B] Explain the IR spectra of aldehyde, ketone and carboxylic acid.

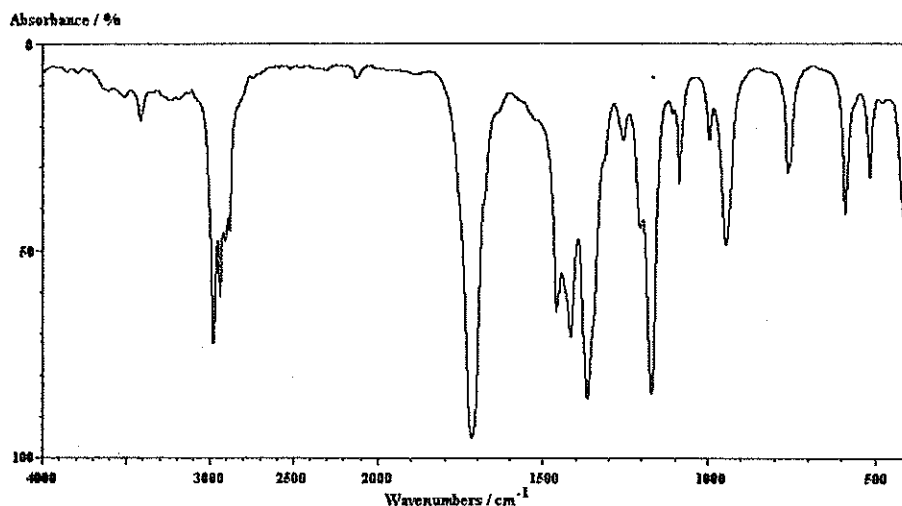
[4]

Or

[A] Explain various types of electronic transitions in UV spectroscopy in detail.

[4]

[B] Identify the molecule with molecular formula C_4H_8O whose IR spectrum is provided with proper justification. [4]



Q.4.[A] Discuss the vicinal and geminal Karplus correlations. [4]

[B] Calculate ^{13}C chemical shifts (δ ; ppm) for *n*-butane and *iso*-butane using the data (^{13}C shift parameters in hydrocarbons) given in the following table. [4]

^{13}C Atoms	Shift (ppm) (A)
α	9.1
β	9.4
γ	-2.5
δ	0.3
ϵ	0.1
$1^\circ(3^\circ)^a$	-1.1
$1^\circ(4^\circ)^a$	-3.4
$2^\circ(3^\circ)^a$	-2.5
$2^\circ(4^\circ)$	-7.2
$3^\circ(2^\circ)$	-3.7
$3^\circ(3^\circ)$	-9.5
$4^\circ(1^\circ)$	-1.5
$4^\circ(2^\circ)$	-8.4

Or

[A] What is Nuclear Overhauser Effect (NOE)? Explain with suitable examples. [4]

[B] Discuss DEPT (distortion enhancement by polarization transfer) spectroscopic technique with a suitable example. [4]

Q.5.[A] Discuss electron-nuclear hyperfine interaction giving example of 2,5-di-tert-semiquinone (2,5-DTBSQ) anion radical? [4]

[B] What is gyromagnetic ratio (g_e)? Discuss different factors which affect g_e . [4]

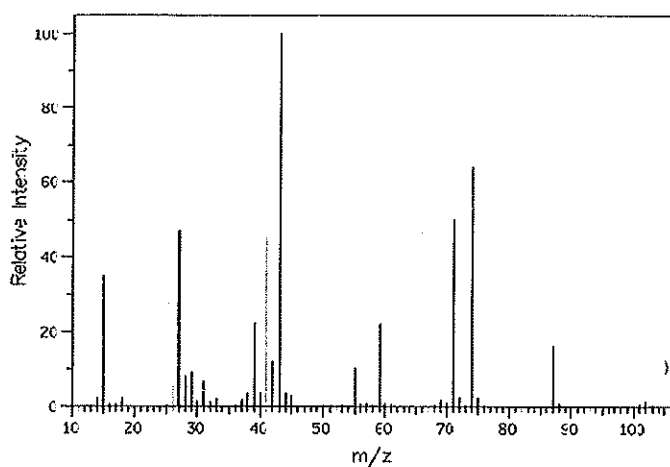
Or

[A] Explain super-hyperfine interaction in EPR spectra giving examples. [4]

[B] Discuss the application of EPR spectroscopy for characterization of free radical reaction intermediates giving example of reactions. [4]

Q.6.[A] Explain the Electrospray Ionization technique in Mass Spectrometry. [4]

[B] Following mass spectrum is of methyl butyrate. Assign all the peaks with suitable fragments and fragmentation pattern. [4]



Or

[A] Explain the Magnetic Sector Mass Analyzer in detail. [4]

[B] Describe the Chemical Ionization technique in Mass spectrometry. [4]

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