SEAT No._____ No. of printed pages : 03

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SARDAR PATEL UNIVERSITY

M. Sc. (Semester – III) (CBCS) Examination
Friday, 1st January 2021
10:00 a.m. to 12:00 noon
PS03CPHC21 : Molecular Spectroscopic Methods for Structure Determination

Total Marks : 70

Note : Figures to the right indicate full marks.

Q.1 (a) **Select the most appropriate answer from the alternatives given below to the each questions;** **[08]**

[i] Which of the following transition is symmetrically forbidden?

(a) singlet ground state to excited triplet state
(b) singlet ground state to excited singlet state
(c) singlet excited state to singlet ground state
(d) singlet excited state to excited triplet state

[ii] As per the selection rule for diatomic molecule, the value of frequency separation is;

(a) B (b) 2B
(c) 3B (d) 5B

[iii] Which pair of bending vibrations are in plane?

(a) Scissoring and Wagging (b) Wagging and Twisting
(c) Rocking and Scissoring (d) Rocking and Twisting

[iv] In an electromagnetic radiation, electric and magnetic field are ;

(a) mutually parallel (b) at an angle of 180°
(c) mutually perpendicular (d) at an angle of 0°

[v] How many ^{1}H-NMR signals are appears for *cis*-1,2 –dimethyl cyclopropane?

(a) 2 (b) 4
(c) 3 (d) 6

[vi] What are the multiplicity of signals obtained from CH_3-CH_2-OH in ^{1}H-NMR spectroscopy?

(a) singlet, triplet and quartet (b) three singlets
(c) two triplets and quartet (d) singlet, doublet and triplet

[vii] In case of polynuclear hydrocarbons, the base peak appears;

(a) as parent ion peak (b) at 91 due to tropylium ion
(c) at 77 due to phenyl cation (d) at 88 due to phenyl cation

[viii] McLafferty rearrangement ion peak in mass spectrum is usually the basic peak. This statement is not true for;

(a) 2-Octanone (b) Cyclohexane
(c) Methyl butyrate (d) Butyrophenone

[P. T. O.]

Q . 1 (b) Do as directed. [16]

(i) Match the following. (1 Marks × 5)

	Column I		Column II
(A)	X-rays	(a)	Molecular rotation
(B)	UV-visible	(b)	Nuclear spin transition
(C)	Infrared	(c)	Valence electron transition
(D)	Microwave	(d)	Inner-shell electron transition
(E)	Radiofrequency	(e)	Molecular Vibrations

(ii) Match the following. (1 Marks × 3)

	Nature of Proton		δ_{ppm}
(A)	Alkane (R-CH_3)	(a)	10.5 – 12.0
(B)	Aromatic (Ar-H)	(b)	0.9 – 1.0
(C)	Carboxylic acid (R-COOH)	(c)	6.0 - 9.0

(iii) Answer the following in TRUE/FALSE. (1 Marks × 4)

(a) The $\sigma \rightarrow \sigma^*$ electronic transition requires highest energy.

(b) If LASER is used as a source in Raman spectrophotometer than no filters are required.

(c) Particle are characterized by their charge to mass ratios (z/m) and relative abundances.

(d) A molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms.

(iv) For the following, fill in the blanks. (1 Marks × 4)

(a) Hydrogen bonding shift λ_{max} towards _____ wavelength.

(b) In IR spectroscopy, Gauche confirmation shows absorption band at _____ wavenumber than Staggered confirmation.

(c) NMR spectra are observed in _____ region.

(d) In ^{1}H-NMR, 1-propanol and 2-propanol give ____ and ___ signals respectively.

Q . 2 Answer the following in short. **(ANY SEVEN)** [14]

[a] Draw schematic diagram of double beam UV-visible spectrophotometer.

[b] Justify "Amines absorb at higher wavelength compared with alcohols".

[c] With the help of appropriate figure, explain Stokes and Anti-stokes lines in Raman spectra.

[d] Write down the equation for reduced mass, μ for diatomic molecules.

[e] The force constant of HF is listed at 880 $N.m^{-1}$. At what wavenumber is the fundamental $\upsilon = 0 \rightarrow \upsilon = 1$ vibrational absorption expected?

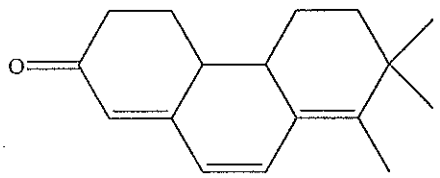
[f] With the help of suitable example, explain McLafferty rearrangement?

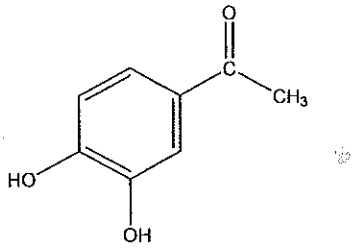
[g] What is the most characteristic feature of the mass spectra of compounds containing one bromine atom?

[h] What is double Resonance ?

[i] Explain spin-spin lattice.

Q.3 **[a]** Calculate λ_{max} for the following molecules. **[04]**





[b] With the help of appropriate figure explain different types of electronic transitions. **[04]**

OR

Q.3 Discuss any four applications of UV-visible spectroscopy in detail. **[08]**

Q.4 **[a]** Give difference between Raman and IR spectroscopy. **[04]**

[b] For polyatomic molecules, discuss how one can determine bond distance using Microwave spectroscopy. **[04]**

OR

Q.4 Discuss any four applications of IR spectroscopy in detail. **[08]**

Q.5 What is chemical shift? Describe briefly the factors affecting it. **[08]**

OR

Q.5 Write a detailed note on coupling constant (*J*) and various types of coupling. **[08]**

Q.6 Describe some importance features of the mass spectra of hydrocarbons. **[08]**

OR

Q.6 **[a]** Write a note on chemical ionization in mass spectroscopy. **[04]**

[b] Draw fragmentation pattern in *n*-nonane. **[04]**

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α, β UNSATURATED CARBONYL COMPOUNDS OR KETONES:

1. Base value:
   a) Acyclic α, β unsaturated ketones = 214 nm
   b) 6 membered cyclic α, β unsaturated ketones = 215 nm
   c) 5 membered cyclic α, β unsaturated ketones = 202 nm
   d) α, β unsaturated aldehydes = 210 nm
   e) α, β unsaturated carboxylic acids & esters = 195 nm
2. Alkyl substituent or Ring residue in α-position = 10 nm
3. Alkyl substituent or Ring residue in β-position = 12 nm
4. Alkyl substituent or Ring residue in γ-and higher positions = 18 nm
5. Double bond extending conjugation = 30 nm
6. Exocyclic double bonds = 5 nm
7. Homodiene compound = 39 nm
8. Polar groups: a) –OH in α-position = 35 nm, –OH in β-position = 30 nm
   –OH in δ-position = 50 nm
   b) –OAc in α, β, γ, δ-positions = 6 nm
   c) –OMe in α-position = 35 nm, –OMe in β-position = 30 nm,
   –OMe in γ-position = 17 nm, –OMe in δ-position = 31 nm,
   d) –Cl in α-position = 15 nm, Cl in β-position = 12 nm
   e) –Br in α-position = 25 nm, –Br in β-position = 30 nm
   f) $-NR_2$ in β-position = 95 nm

AROMATIC COMPOUNDS:

1) Base value: for a) ArCOR = 246 nm, b) ArCHO = 250 nm
   c) $ArCO_2H$ = 230 nm, d) $ArCO_2R$ = 230 nm
2) Alkyl group or ring residue in ortho and meta position = 3 nm
3) Alkyl group or ring residue in para position =10 nm
4) Polar groups: a) –OH, $-OCH_3$, –OAlkyl in o, m-position = 7 nm
   b) –OH, $-OCH_3$, –OAlkyl p position = 25 nm
   c) –O (oxonium) in o-position = 11 nm
   d) –O (oxonium) in m-position = 20 nm
   e) –O (oxonium) in p-position = 78 nm
   f) –Cl in o, m-position = 0 nm
   g) –Cl in p-position = 10 nm
   h) –Br in o, m-position = 2 nm
   i) –Br in p-position = 15 nm
   j) $-NH_2$ in o, m-position = 13 nm
   k) $-NH_2$ in p-position = 58 nm
   l) $-NHCOCH_3$ in o, m-position = 20 nm
   m) $-NHCOCH_3$ in p-position = 45 nm
   n) $-NHCH_3$ in p-position = 73 nm
   o) $-N(CH_3)_2$ in o, m-position = 20 nm
   p) $-N(CH_3)_2$ in p-position = 85 nm

CONJUGATED DIENE

i) Base value for homoannular diene = 253 nm
ii) Base value for heteroannular diene = 214 nm
iii) Alkyl substituent or Ring residue attached to the parent diene = 5 nm
iv) Double bond extending conjugation = 30 nm
v) Exocyclic double bonds = 5 nm
vi) Polar groups: a) -OAc = 0 nm,
b) -OAlkyl = 6 nm,
c) -Cl, -Br = 5 nm