Sc

[166] SEAT No.________ No. of printed pages : 04

SARDAR PATEL UNIVERSITY

M. Sc. (Semester – III) (CBCS) Examination
Tuesday, 23rd October 2018
2:00 p.m. to 5:00 p.m.

PS03CPHC21 : Molecular Spectroscopic Methods for Structure Determination

Total Marks : 70

Note : Figures to the right indicate full marks.

Q . 1 **Select the correct answer from the alternatives given below to the each questions;** **(08)**

[i] The energy required for various transitions follow the order;

(a) $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$
(b) $\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$
(c) $\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^* > n \rightarrow \sigma^*$
(d) $n \rightarrow \sigma^* > \sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

[ii] Which of the following spectroscopic technique works on the scattering phenomena?

(a) Infra-red (b) Raman
(c) Microwave (d) UV-visible

[iii] In IR spectroscopy, the pair of isomer which cannot be distinguished are;

(a) *cis-trans* isomers (b) functional isomers
(c) enantiomers (d) position isomers

[iv] Which of the following frequency range is known as finger print region in IR spectroscopy ?

(a) 400 – 1400 cm^{-1} (b) 1500 – 900 cm^{-1}
(c) 900 – 600 cm^{-1} (d) 600 – 250 cm^{-1}

[v] Which of the following statements in the context of ^{1}H NMR spectroscopy is true?

(a) Arene C-H chemical shift (δ) values are greater than simple alkenes C-H chemical shift values because of the aromatic ring current
(b) Arene C-H chemical shift (δ) values are smaller than simple alkenes C-H chemical shift values because of the aromatic ring current
(c) Arene C-H signals are always multiplets
(d) Arene C-H signals are always singlets

[vi] In the mass spectrum of trifluoroacetic acid, CF_3CO_2H, intense peaks are observed at $m/z = 69$ and 45 (base peak) in addition to other peaks. The peak at $m/z = 69$ is accompanied by a peak at $m/z = 70$ which is about 1.1% the intensity of the peak at $m/z = 69$. Which statement is inconsistent with these data?

(a) CF_3CO_2H fragments by sequential loss of F atoms

(b) $[HO_2C]^+$ is a fragment ion

(c) Fluorine is monotopic

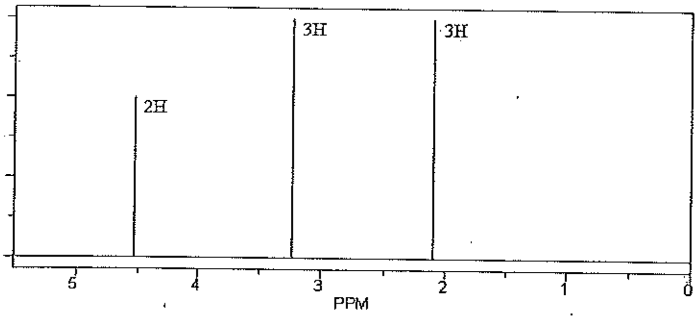
(d) C–C bond cleavage occurs

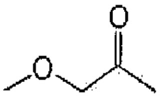
[P. T. O.]

[vii] A simulation of the isotopic pattern for the parent peak in the mass spectrum of acetonitrile (CH_3CN) gives peaks at $m/z = 41$, 42 and 43 with relative intensities 100.00 : 2.65 : 0.02. An experimental mass spectrum shows intense or relatively intense peaks at $m/z = 38$, 39, 40 and 41. What is the likely reason for the difference between the two sets of data?

(a) In the mass spectrometer, C–N bond cleavage occurs
(b) In the mass spectrometer, C–H bond cleavage occurs
(c) The simulation of an isotopic distribution pattern for a molecule is unreliable
(d) In the mass spectrometer, C–C bond cleavage occurs

[viii] An unknown compound **A** has the molecular formula $C_4H_8O_2$. Based on the following ^1H NMR spectrum, what is the structure of compound **A**?



(a)


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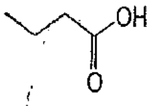

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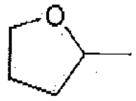

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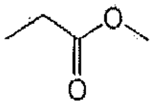
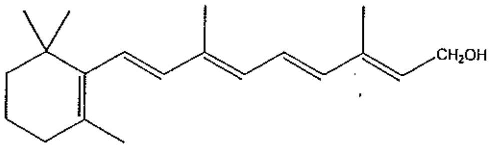


Q.2 Answer the following in short; **(ANY SEVEN)** **(14)**

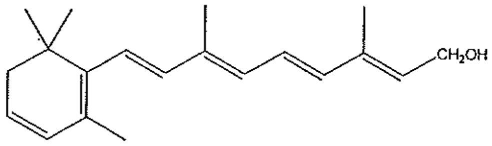
[a] Chloromethane has an absorption maximum at 172 nm and iodomethane shows a band at 258 nm. How can the trend of absorptions can be explained ?

[b] Explain bathochromic and hypsochromic shift in UV-spectroscopy.

[c] How can we distinguish following two compounds using UV-spectroscopy?



[A]



[B]

[d] Describe the various molecular vibrations in the IR technique. What is the major requirement for IR absorption ?

[e] What are Rayleigh, Stoke's and antistroke's lines?

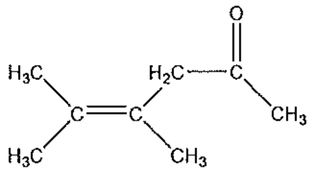
[f] Define: Larmor Frequency (ω); Saturation and Excess population in NMR.

[g] Why Modern instrumentation has been designed with increasingly higher operating frequencies in NMR?

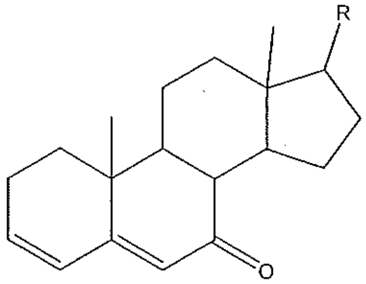
[h] How detection of ions being made in mass spectrometry?

[i] How do you classify general modes of fragmentation?

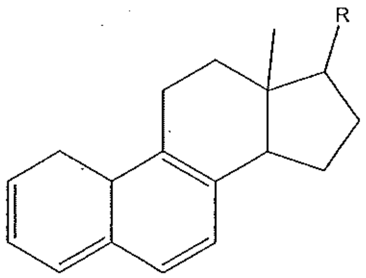
Q.3 **[a]** Calculate the absorption maximum of following compounds in the UV-spectrum. (06)



[A]



[B]



[C]

[b] Discuss applications of UV-spectroscopy with suitable examples. (06)

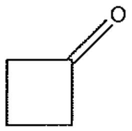
OR

[b] [i] Discuss the various types of electronic transitions occurs in UV-spectroscopy. (03)

[ii] "The wavelength as well as the molar extinction coefficient increases with the increase in conjugation in the compound" *Justify.* (03)

Q.4 **[a]** [i] How will you distinguish between the following pairs on the basis of IR spectra? (03)

[A]



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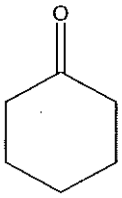
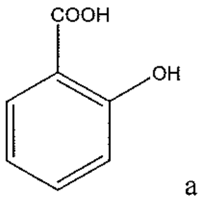


[B]



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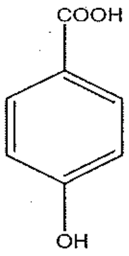

[ii] Give differences between IR and Raman spectroscopy. (03)

[b] [i] Using appropriate figure, discuss selection rule for microwave spectroscopy. (03)

[ii] Show that "*total number of vibrational degrees of freedom for linear molecule is 3n – 5*". (03)

OR

[b] [i] Discuss principle on which Raman spectroscopy is working ? (03)

[ii] Explain types of stretching and bending vibrations of molecule. (03)

[P. T. O.]

Q.5 **[a]** Describe in brief with suitable example chemical equivalence of the protons. **(06)**

[b] **[i]** Why peaks generated by a CW instrument have Ringing? Explain why Ringing is most noticeable when a peak is a sharp singlet in CW instrument. **(03)**

[ii] Describe in brief with suitable example Chemical Equivalence of the protons. **(03)**

OR

[b] Write a short note on Double resonance with suitable examples. **(06)**

Q.6 **[a]** Give detail on Fast Atom Bombardment (FAB) method for desorption Ionization Techniques for in volatile or Thermally Unstable Compounds. **(06)**

[b] **[i]** Exemplify following terms in relation to Mass Spectrum: **(03)**
[A] Base peak, **[B]** Molecular ion and parent ion, **[C]** Mass-to-Charge ration (*m/z*)

[ii] Illustrate following terms in relation to Mass Spectrum: **(03)**
[A] Doubly charged ions, **[B]** Metastable ions, **[C]** Isotopic clusters

OR

[b] Explain fragmentation of the molecular ion (M^+) by rearrangement reactions accompanied through McLafferty rearrangement. **(06)**

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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

Characteristic IR Absorption Frequencies

Bond		cm^{-1}
C-H	Alkanes	2850-2960
C-H	Alkenos	3020-3080
C-H	Arenes	3000-3100
C-O	Alcohols, ethers	1080-1300
C=O	Aldehydes, ketones...	1690-1760
O-H	Alcohols	3200-3600
	Acids	2500-3000
N-H	Amines	3300-3500

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

—X—