

PG Odd Semester (CBCS) Exam., December—2016

## CHEMISTRY

( 3rd Semester )

Course No. : CH-304 (C)

( Application of Spectroscopic Methods )

*Full Marks : 75**Pass Marks : 30**Time : 3 hours**The figures in the margin indicate full marks for the questions**Use separate answer books for Part—A and Part—B*

## PART—A

( Inorganic Chemistry )

( Mark : 30 )

Answer **one** question from each Unit

## UNIT—I

1. (a) How do you account the following trends in stretching frequencies of the carbonyl compounds?



Comment on the electrophilic behaviour of the coordinated Co. 4

- (b) Rationalise how nitro and nitrito complexes can be distinguished by IR spectroscopy. 4

- (c)  $\text{Fe}(\text{CN})_6 ]^3$  exhibits two sets of charge transfer absorptions in ultraviolet visible region. Explain. 2

2. (a) Describe different coordination modes of  $\text{SO}_4^{2-}$  distinguished by IR spectroscopy. 4

- (b) Arrange  $\text{Ni}(\text{CN})_4 ]^2$ ,  $\text{Pd}(\text{CN})_4 ]^2$  and  $\text{Pt}(\text{CN})_4 ]^2$  in terms of their increasing (CN) stretching frequency. Justify. 3

- (c) Explain the increase in ligand to metal charge transfer (LMCT) bands in the following series : 3



## UNIT—II

3. (a) Comment on the  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{19}\text{F}$ -NMR spectra of  $\text{HPF}_2$  (considering  $J_{\text{P-F}}$ ,  $J_{\text{P-H}}$ ,  $J_{\text{F-H}}$ ). 3

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- (b) Sketch the  $^1\text{H-NMR}$  spectrum of  $\text{Co}^{\text{III}}(\text{acac})_3$  and  $\text{Fe}^{\text{III}}(\text{acac})_3$ . Calculate the magnetic moment ( $\mu_{\text{eff}}$ ) of  $\text{Fe}^{\text{III}}(\text{acac})_3$ . (Given,  $g = 0.040$ ,  $\mu_B = 4.101 \text{ Hz}$  and  $h = 42.5 \text{ MHz}$ ) 3
- (c) What is meant by anisotropic ESR spectra? Mention three applications of ESR spectroscopy. 2+2=4
4. (a) Predict the number of ESR lines and their intensity ratio in  $\text{NH}_2$  ( $^{14}\text{N}, I = 1$ ). Sketch the ESR spectrum. 4
- (b) Why is  $\text{dppH}$  radical used as standard in ESR spectroscopy? 2
- (c) Explain why 'fac' isomer shows only one methyl signal whereas 'mer' isomer shows three methyl signals of equal intensity in  $[\text{Ru}(\text{2-(m-tolylazo)pyridine})_3]$ . 4

UNIT—III

5. (a) What is meant by isomer shift in Mössbauer spectroscopy? Explain the principle of isomer shift in Mössbauer spectroscopy. 1+3=4
- (b) What is meant by metastable ion? How are such transitions detected in mass spectroscopy? 3

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( Turn Over )

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- (c) Predict the probable structure of a compound with formula  $\text{Cl}_2\text{Mn}_2\text{C}_8\text{O}_8$  where the mass spectrum included prominent peaks at  $m/z$  404, 376, 348, 320, 292, 264, 236, 208, 180, 110 and 55 a.m.u. 3
6. (a) Mention different ionization modes in mass spectrometry. Discuss briefly any two of them. 4
- (b) Describe the electric quadrupole splitting in Mössbauer spectroscopy. Explain how this is helpful to identify the high- and low-spin Fe complexes. 3+3=6

PART—B

( Organic Chemistry )

( Marks : 45 )

Answer **one** question from each Unit

UNIT—I

( Marks : 12 )

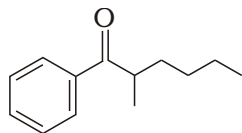
7. (a) Define and explain the following : 2+2=4
- (i) Nitrogen rule
- (ii) McLafferty rearrangement

J7/581

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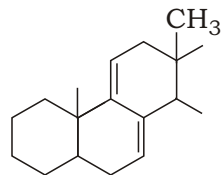
- (b) Predict two major fragmentation patterns for



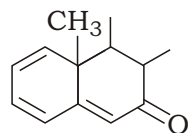
2

- (c) Explain EI and CI modes of mass spectrum. 2
- (d) Discuss the MS fragmentation of butanal and butanol. 2+2=4

8. (a) UV-spectrum of acetone in hexane shows two peaks of  $\lambda_{\max}$  279 nm,  $\epsilon_{\max}$  15 and  $\lambda_{\max}$  189 nm,  $\epsilon_{\max}$  900.
- (i) Identify the electronic transitions associated with each.
- (ii) Which one is more intense and why?
- (iii) What happens if H<sub>2</sub>O is used instead of hexane? 3
- (b) Using Woodward-Fieser rules, calculate the  $\lambda_{\max}$  for the following compounds : 1½×2=3



(A)



(B)

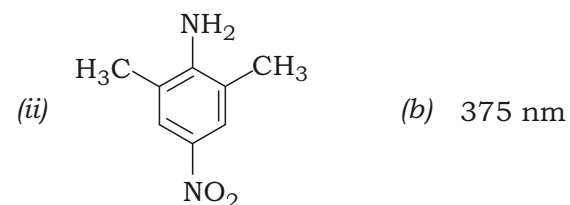
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- (c) Match the following compounds with correct UV-spectra ( $\lambda_{\max}$ ): 3

Compound  $\lambda_{\max}$



- (d) Why does butadiene exhibit a higher value of  $\lambda_{\max}$  for  $\pi \rightarrow \pi^*$  transition than that of ethylene? 2
- (e) Why does  $\beta$ -carotene absorb in visible range? 1

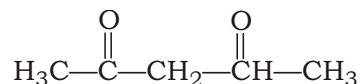
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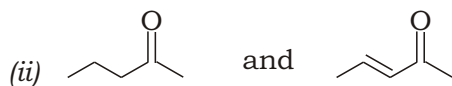
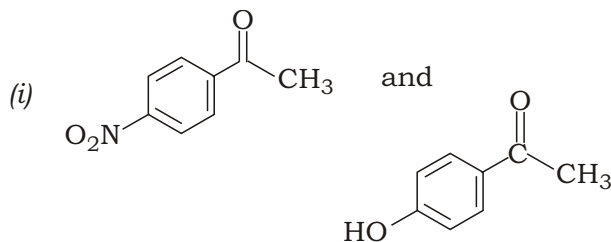
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UNIT—II  
( Marks : 11 )

9. (a) Why does the following compound exhibit broad band at around  $1630\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$ ? 2



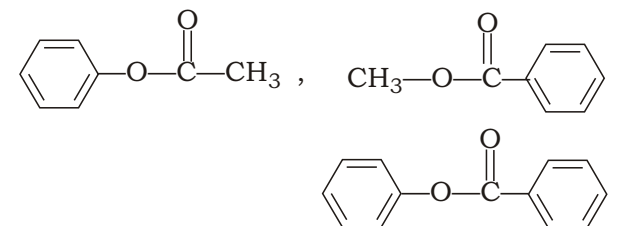
- (b) Discuss the effect of ring strain on exocyclic  $\text{C}=\text{C}$  stretching. 3
- (c) How can you distinguish the following compounds by IR spectroscopy? 2+2=4



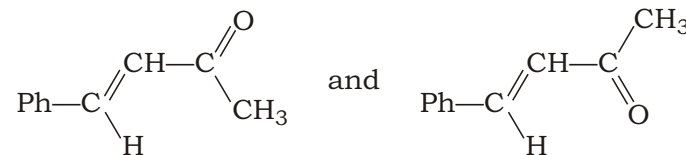
- (d) What are overtone and combination bands? 1+1=2

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10. (a) Arrange the following compounds in increasing order of  $\text{C}=\text{O}$  stretching frequency (with explanation) : 1+2=3



- (b) How can you distinguish the following geometrical isomers by IR spectroscopy? 2



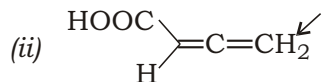
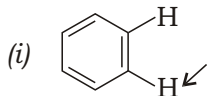
- (c) Why does the presence of conjugation decrease the  $\text{C}=\text{O}$  stretching frequency in a carbonyl compound? 3
- (d) Explain how intramolecular and intermolecular H-bonding can be distinguished by IR spectroscopy. 3

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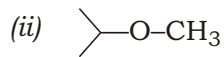
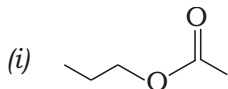
UNIT—III

( Marks : 11 )

11. (a) Characterize the indicated protons as homotopic, enantiotopic or diastereotopic : 1+1=2



- (b) Mention the splitting pattern and draw <sup>1</sup>H-NMR spectra (approx) for the following compounds : 2+2=4



- (c) Assign the structure of a compound C<sub>4</sub>H<sub>8</sub> having <sup>1</sup>H-NMR signal at 1.57 (A) and 5.55 (B) ppm, with J<sub>AB</sub> 6.5 Hz and J<sub>BB</sub> 15.0 Hz. Assign exact values to the protons in the structure. 3+1=4

- (d) What is Fourier transformation? 1

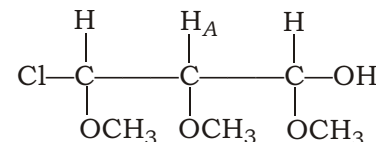
12. (a) The compounds A and B are isomers with molecular formula C<sub>6</sub>H<sub>10</sub>O<sub>2</sub>. Compound A exhibits <sup>1</sup>H-NMR resonance with 2.71 (s) and 2.19 (s); whereas

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compound B shows at 2.77 (q) and 1.09 (t). Predict the structures of A and B with exact mentioning of chemical shift values for both. 4

- (b) How the spin-spin coupling gets affected by the operating frequency of NMR spectrometer? 2

- (c) For the following compound, assign a spin system (including A) and depict the splitting pattern diagrammatically : 2



- (d) Write a short note on DEPT. 2

- (e) What is NOESY? 1

UNIT—IV

( Marks : 11 )

13. (a) An organic compound C<sub>3</sub>H<sub>6</sub>O shows +ve iodoform test and 2,4-DNP test but -ve Tollen's test. Its spectral data are

UV :  $\lambda_{\max}$  280 nm (Br),  $\lambda_{\max}$  15

IR : 1710 cm<sup>-1</sup>, 2918 cm<sup>-1</sup>, 2875 cm<sup>-1</sup>

<sup>13</sup>C-NMR : 33, 1, 206, 0

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For this compound—

- (i) predict the structure with explanation of all the observations;  
(ii) predict  $^1\text{H-NMR}$  spectra for it (approx).  $4+1=5$

- (b) An ester with molecular formula  $\text{C}_7\text{H}_{14}\text{O}_2$  has the following NMR data :

$^1\text{H-NMR}$  :

0.92 (*d*, 6*H*), 1.52 (*m*, 2*H*),  
1.69 (*m*, 1*H*), 2.04 (*s*, 3*H*), 4.09 (*t*, 2*H*)

$^{13}\text{C-NMR}$  :

21.0, 22.5, 25.1, 37.4, 63.1,  
171.2 ppm

Two inverted signal obtained in DEPT. Predict the structure of the compound and assign all the  $^1\text{H}$  and  $^{13}\text{C}$  values to it. 4

- (c) What are the full forms of HSQC and HMBC? What is the difference between these two techniques?  $1+1=2$

14. (a) Briefly describe various parameters for the generation of 2D-NMR data apart from sample preparation. What are the advantages of Fourier transformed FID?

$2+2=4$

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- (b) An organic compound has the molecular formula  $\text{C}_{12}\text{H}_8\text{Br}_2$ . Identify the compound using the following spectral data (with justification) :

UV vis :  $\text{max}$  264 nm,  $\text{max}$  45

Ir : at 1499  $\text{cm}^{-1}$  (*s*)

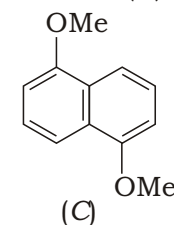
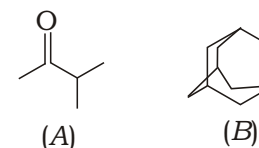
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) : 7.55 (*d*), 7.38 (*d*) ppm

$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) : 140.0, 130.3, 130.0,  
120.3 ppm

MS *m/z* 152 ( $M^\circ$ , 100), 76 (40)

4

- (c) How many signals would you expect in  $^{13}\text{C-NMR}$  of the following compounds?  $1 \times 3 = 3$



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