PG Odd Semester (CBCS) Exam., December—2018

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

PART—A

(*Marks* : 30)

Answer **one** question from each Unit

UNIT—I

1. *(a)* Discuss the different coordination modes of SO_4^{2} distinguished by IR spectroscopy. 4

(b) How do you account the following trends in CO stretching frequencies of the following carbonyl compounds?

$Ni(CO)_4$: $_{CO}$ 2046 cm ^{1}

$Co(CO)_4$: $_{CO}$ 1883 cm ^{1}

$Fe(CO)_4{}^{2}$: $_{CO}$ 1788 cm ^{1}

Account the electrophilic behaviour of coordinated CO from these results. 4

(c) Draw an Orgel diagram for d^1 octahedral system. Explain. 2

2. *(a)* How hydroxo- and aquo-complexes can be distinguished by IR spectroscopy? Explain. 4

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

(c) The ligand to metal charge transfer band (LMCT) increases from CoI_4 to $CoBr_4$ (CoI_4 $CoBr_4$). Explain. 2

UNIT—II

3. *(a)* Sketch ^{1}H-NMR spectrum of $Co^{III}(acac)_3$ and $Fe^{III}(acac)_3$. 2

(b) Describe the ^{1}H, ^{31}P and ^{19}F-NMR spectra of HPF_2 (considering J_{P-F} J_{P-H}, J_{P-H} J_{F-H}). 4

(c) Predict the number of ESR lines and their intensity ratio in CH_3 (^{13}C, I $\frac{1}{2}$). Sketch the ESR spectrum. 4

4. (a) ^{19}F-NMR spectrum of ClF_3 exhibits doublet and triplet with intensity ratio 2 : 1. Comment on the spectral feature and predict the structure of ClF_3. 4

(b) Why is dppH radical used as standard in ESR spectroscopy? 2

(c) Sketch the anisotropic ESR spectra in axial and rhombic symmetry. Explain. 1½+1½=3

(d) Mention at least two applications of ESR spectroscopy. 1

UNIT—III

5. (a) Write the principle of isomer shift in Mössbauer spectroscopy. 3

(b) Derive the splitting pattern for Fe, where the Mössbauer transition for ^{57}Fe is from I $\frac{1}{2}$ to I $\frac{3}{2}$ state in applied magnetic field. 3

(c) What are metastable ions? Predict the fragmentation pattern of $Ir_4(CO)_{12}$ and rationalize. 4

6. (a) What are the ionization modes used in mass spectrometry? Discuss these modes of ionization briefly. 6

(b) Describe the electrical quadruple splitting in Mössbauer spectroscopy. 4

PART—B

(*Marks* : 45)

Answer **one** question from each Unit

UNIT—IV

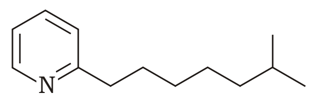
(*Marks* : 12)

7. (a) Define and explain the following : 2×2=4

(i) Nitrogen rule

(ii) McLafferty rearrangement

(b) The following compound exhibits an MS peak at m/z 93. Explain its fragmentation : 3



(c) Discuss the MS fragmentation of ethanol and butanol. 1½+1½=3

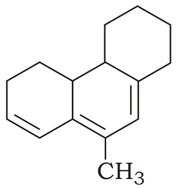
(d) A substance has the molecular formula C_4H_9N. Is there any likelihood that this material contains a triple bond? Explain. 2

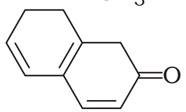
8. *(a)* Define the following and provide example for each : 2×2=4

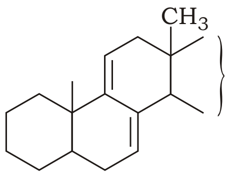
(i) Chromophore and Auxochrome

(ii) Red shift and Blue shift

(b) Use Woodward-Fieser rules to calculate the $_{max}$ of the following compounds : 2×3=6

(i) 

(ii) 

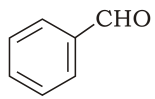
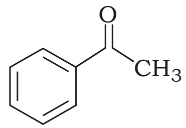
(iii) 

(c) Why biphenyl exhibits an intense absorption band at 252 nm (19000) but its 2,2-dimethyl derivative shows absorption at $_{max}$ 262 nm ($_{max}$ 270)? 2

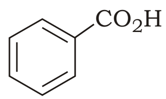
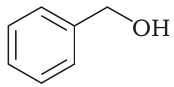
UNIT—V

(*Marks* : 11)

9. *(a)* Differentiate between the following pairs of compounds in IR spectroscopy : 1½×3=4½

(i)  and 

(ii) 1,2-diketone and 1,3-diketone

(iii)  and 

(b) Why does the presence of conjugation decrease the C=O stretching frequency in a carbonyl compound? 2½

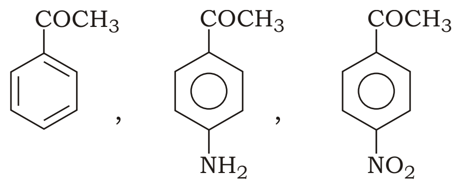
(c) Which of the following compounds has a vibration that is IR inactive? 2

H_2, O_2, Cl_2, CO_2, CO, ethane

(d) What do you mean by combination band and Fermi resonance? 2

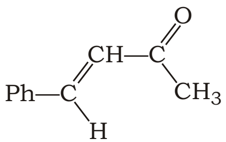
10. (a) Explain with example how intra-molecular and intermolecular H-bonding can be distinguished by IR spectroscopy. 3

(b) Arrange the following compounds in increasing order of C=O stretching frequency (with explanation) : 1+2=3



(c) Discuss the effect of ring strain on the carbonyl stretching frequency for cyclic ketones. 3

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



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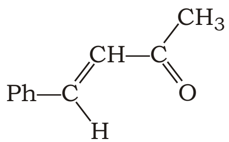
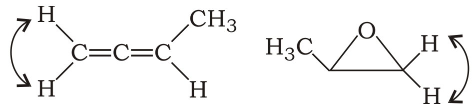


UNIT—VI

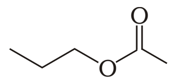
(*Marks* : 11)

11. (a) Assign topicity of the following (homotopic / enantiotopic / diastereotopic) and also comment if they are magnetically equivalent or non-equivalent : 1+1=2

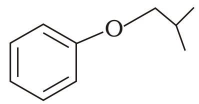


(b) Provide the splitting pattern and draw ^{1}H-NMR spectra (approx) for the following compounds : 2×2=4

(i)



(ii)

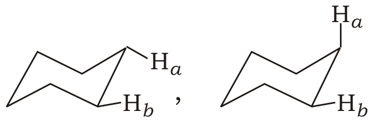


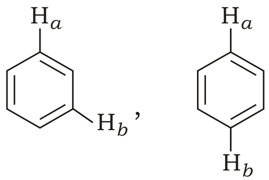
(c) Write a short note on DEPT. 2½

(d) How can the validity of a first-order NMR analysis be verified? Explain. 2½

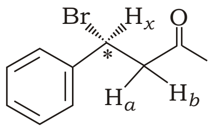
12. (a) A tri-substituted benzene possessing one —Br and two —OCH_3 substituents, exhibits three aromatic resonances at 6·40, 6·46 and 7·41 ppm. What is the structure of the compound? 2

(b) Assign *J* values for the set of given compounds : 1×2=2

(i) 

(ii) 

(c) Depict the splitting pattern for H_x, H_a and H_b signals for the compound *A*. Provide a brief justification for the observation : 1½+1½=3



(d) Explain NOE. How does NOE affect NMR spectra? 2+2=4

UNIT—VII

(*Marks* : 11)

13. *(a)* An organic compound with molecular formula C_4H_8O exhibited the following spectral data :

(i) MS : *m/z* 72, 57, 43, 29

(ii) IR : 2941–2857, 1715 cm ^{1}

(iii) ^{1}H-NMR : 2·48 (*q*, 2*H*), 2·12 (*s*, 3*H*), 6·07 (*t*, 3*H*) ppm

(iv) ^{13}C-NMR : 200, 39·5, 29·5, 8 ppm

Determine the structures with justification. 4

(b) How can COSY-45 can be distinguished from COSY-90? Mention the application for each. 3

(c) Compounds *A* and *B* having identical molecular formula C_4H_8O have the following :

^{13}C signals at 7·87, 29·43, 36·87, 209·28 ppm and 13·71, 15·69, 45·85 and 202·80 respectively

DEPT gave a single inverted peak for *A* and two inverted peaks for *B*. Predict the two structures of *A* and *B*. Assign peaks and identify the functional groups. 2+2=4

14. *(a)* What are cross-peaks in COSY? How can the confusion between closely peaked diagonal and cross-peaks be resolved through COSY? 2+3=5 *(b)* An organic compound has the molecular formula $C_{12}H_8Br_2$. Identify the compound using the spectroscopic data given : 4

UV-vis : $_{max}$ 264 nm ($\log_{10}$ 4·5)
IR : (KBr disc) at 1499 cm^{1} ( )
^{1}H-NMR ($CDCl_3$) : 7·55 (*d*), 7·38 (*d*) ppm
^{13}C-NMR ($CDCl_3$) : 140·0, 130·3, 130·0, 120·3 ppm
MS m/z : 152 (M , 100), 76 (40)

(c) What are the advantages of Fourier transformed FID? 2

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