PG Odd Semester (CBCS) Exam., December—2017

CHEMISTRY

(3rd Semester)

Course No. : CH–304

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

(Application of Spectroscopic Methods)

(*Marks* : 30)

Answer **one** question from each Unit

UNIT—I

1. *(a)* Rationalize how hydroxo- and aquo-complexes can be distinguished by IR spectroscopy. 4

(b) Arrange $V(CO)_6$, $Cr(CO)_6$ and $Mn(CO)_6$ in terms of their increasing $_{(CO)}$ stretching frequency. Justify. 3

(c) The ligands to metal charge transfer (LMCT) bands increases in the series CoI_4 $CoBr_4$ $CoCl_4$. Explain. 3

2. *(a)* Based on IR spectral feature, describe different coordination modes of SO_4^2 . 4

(b) Explain why $[Co(H_2O)_6]^2$ is pale pink whereas $[CoCl_4]^2$ is deep blue. Predict the possible allowed transition in each case. 3

(c) Arrange $Ni(CN)_4{}^2$, $Pd(CN)_4{}^2$ and $Pt(CN)_4{}^2$ in terms of their increasing $_{(CN)}$ stretching frequency. Comment. 3

UNIT—II

3. *(a)* Explain the ESR spectrum $\dot{H}$ and deduce the coupling constant (A) value. 4

(b) ^{19}F-NMR spectrum of ClF_3 exhibits a doublet and triplet with intensity ratio 2 : 1. Predict the structure of ClF_3. 3

(c) Comment on ^1H, ^{31}P and ^{19}F-NMR spectra of PHF_2. 3

4. *(a)* What is meant by anisotropic ESR spectra? Mention three applications of ESR spectroscopy. 2+2=4

(b) Why is dpp$\dot{H}$ used as internal standard in ESR spectroscopy? 2

(c) Explain why 'fai' isomer shows only one methyl signal whereas 'mer' isomer shows three methyl signals of equal intensity in [Rn(2-(*m*-tolylazo)pyridine)$_3$]. 4

UNIT—III

5. *(a)* Predict the probable structure of a compound with formula $Cl_2Mn_2C_8O_8$, where the mass spectrum included prominent peaks at $m/z = 404$, 376, 348, 320, 298, 264, 236, 208, 180, 110 and 55 amu. 4

(b) What is meant by metastable ion? How are such transitions detected in mass spectroscopy? 3

(c) Discuss the electric quadruple splitting in Mössbauer spectroscopy. 3

6. *(a)* Predict the probable fragmentation pattern of [Co(CO)$_3$(NO)]. 3

(b) Explain how Mössbauer spectroscopy is helpful to identify the high- and low-spin Fe complexes. 4

(c) Discuss briefly the principle of Mössbauer spectroscopy. 3

PART—B

(Organic Chemistry)

(*Marks* : 45)

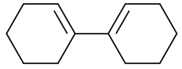
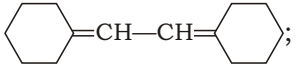
Answer **one** question from each Unit

UNIT—IV

(*Marks* : 11)

7. *(a)* Explain why—

(i) UV-vis is typically recorded as broad absorption maxima and not single, sharp lines;

(ii) $_{max}$ for  is lower than that of  ;

(iii) $_{max}$ values obtained for acetone occurs at 279 nm, in *n*-hexane, 270 nm in ethanol, and at 265 nm in water;

(iv) phenolate ion has $_{max}$ at 287 nm while phenol has $_{max}$ at 270 nm. 2×4=8

(b) Define the following and provide example for each : 1½×2=3

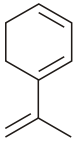
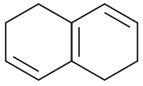
(i) Chromophore and auxochrome

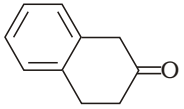
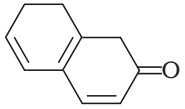
(ii) Red shift and blue shift

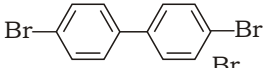
8. *(a)* A solution of 4-methyl-3-penten-2-one in ethanol shows an absorbance of 0·52 at 236 nm in a cell with a 1 cm path length. Its molar absorption in ethanol at that wavelength is 12600. What is the concentration of the compound? 2½

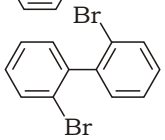
(b) Acetone shows two absorption bands at $_{max}$ 270 nm and 187 nm. Which of the two is a low intensity absorption band and why is it of low intensity? 2½

(c) How can the following be distinguished by UV-vis spectroscopy? 2×2=4

(i)  and 

(ii)  and 

(d)  has $_{max}$ 19000

whereas  has $_{max}$ 280.

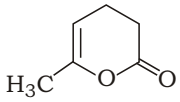
Provide a suitable reason. 2

UNIT—V

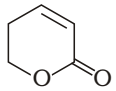
(*Marks* : 11)

9. *(a)* Discuss the effect of ring strain on the internal C=C stretching in cyclic alkenes. 3

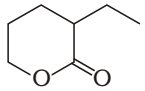
(b) Match the structures with the C=O stretching frequencies and justify your assignment : 1½+1½=3



(i)



(ii)



(iii)

C=O stretching frequencies : 1735 cm ^{1}, 1763 cm ^{1} and 1725 cm ^{1}.

(c) Explain why—

(i) an O—H stretch is more intense than an N—H stretch;

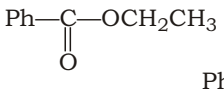
(ii) an O—H stretch of a carboxylic acid broader than the O—H stretch of an alcohol. 1½+1½=3

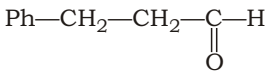
(d) Which of the following compounds has a vibration that is IR inactive? 2

H_2, CO_2, Cl_2, H_2O, CO, ethane

10. *(a)* How can the following compounds be distinguished through IR spectroscopy? 2×2=4

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

(ii)  and



(b) Explain why C=O stretching in carboxylic acid is lower than that of ester. Use an example to support your answer. 2½

(c) Substitution of an amino group on the para-position of acetophenone shifts C=O frequency from about 1685 cm ^{1} and 1652 cm ^{1}, whereas a nitro group attached to the para-position yields a C=O frequency of 1693 cm ^{1}. Explain the shift for each substituent from the 1685 cm ^{1} base value of acetophenone. 3

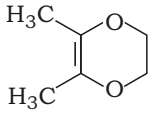
(d) Will phenol dissolved in Cs_2 or in ethanol show an O—H stretch at a higher frequency? Why? 1½

UNIT—VI

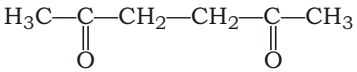
(*Marks* : 11)

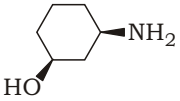
11. *(a)* How can the validity of a first-order NMR analysis be verified? Explain. 2

(b) How can the following set of compounds be distinguished by ^{1}H NMR? Assign chemical shift values, splitting patterns and their peak area ratios : 1½×3=4½

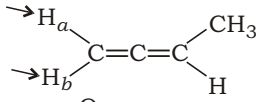
(i) 

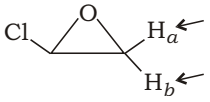
(ii) $H_3CO—CH_2C{\equiv}CCH_2OCH_3$

(iii) 

(c) The ^{1}H NMR spectra of the compound  was recorded at different temperatures. Explain the observed trends. 2½

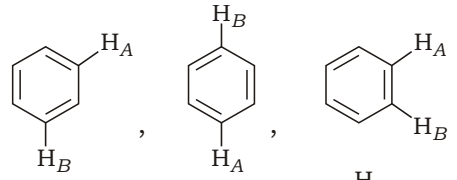
(d) Assign topicity for the given compounds : 2

(i) 

(ii) 

12. *(a)* Assign J values for the set of given compounds : 1½×2=3

(i)



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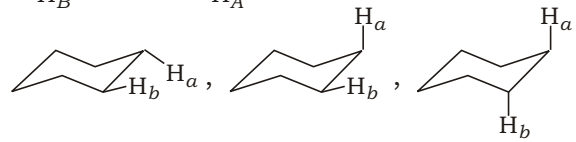
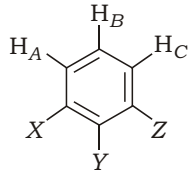


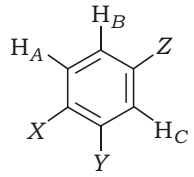
(b) Identify the structure and assign peaks, and J values for an organic compound C_4H_8O with NMR ($CDCl_3$, 400 MHz, 300 K) values at 1·01 (*t*), 1·56 (*m*), 2·47 (*m*), 2·73 (*m*), 2·88 (*m*) ppm, $3J_{HH}$ 2·7 Hz and $3J_{HH}$ 4·0 Hz. 3

(c) Provide splitting patterns for the following : 1½×2=3

(i)



(ii)



(d) Explain NOE and mention its application in brief. 2

UNIT—VII

(*Marks* : 12)

13. *(a)* A compound with molecular formula C_7H_8O exhibited m/z 108, 93, 78, 77, 65, 51. Derive the most probable structure. 2

(b) 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

(c) How is 2D NMR affected by FT-techniques? Draw the COSY spectra for $H_3C—CH_2—CH_2—\underset{\underset{O}{\|}}{C}—OCH_2—CH_3$ to depict the correlations expected. 2+3=5

(d) A substance has the molecular formula C_4H_9N. Is there any likelihood that this material contains a triple bond? Provide reasons. 1

14. *(a)* A compound with molecular formula $C_{12}H_{24}O_8$ gave a single peak at 3·66 ppm (for ^{1}H NMR) and 0·91 ppm (for ^{13}C). The ^{13}C peak was inverted under DEPT considerations. Predict the molecular structure and assign the values. 2½

(b) How can COSY-45 be distinguished from COSY-90? Mention the applications for each. 2½

(c) An organic compound with molecular formula $C_8H_{14}O_4$ exhibited the following spectral data :

(i) MS : m/z = 174, 129, 101

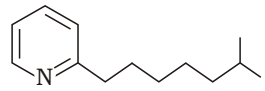
(ii) IR : 1736 cm ^{1}, 1095 cm ^{1}

(iii) ^{1}H NMR : 1·29 (*t*), 2·61 (*s*), 4·19 (*q*) ppm

(iv) ^{13}C NMR : 10·13, 20·89 (DEPT inverted), 60·01, 171·09 ppm

Determine the structure of the compound with justification for the data provided. 1×4=4

(d) The compound (*Z*) exhibits an MS peak at m/z 93. Explain the fragmentation patterns : 3



(*Z*)

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