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

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

(*Marks* : 30)

Answer **one** question from each Unit

UNIT—I

(*Marks* : 10)

1. *(a)* Rationalize the trends in CO stretching frequencies of the following sets of IR active compounds :

$Fe(CO)_4]^{2-}$ 1788 cm^{-1}

$Co(CO)_4]^{-}$ 1883 cm^{-1}

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

Comment on the electrophilic behaviour of coordinated CO to the metals. 5

(b) Distinguish between two ionization isomers of $[Co(NH_3)_5Cl]SO_4$ by IR spectroscopy. 5

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

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

(c) Explain why $[Co(H_2O)_6]^{2+}$ is pale pink (E_{max} 10 cm^2 mol^{-1}) whereas $[CoCl_4]^{2-}$ is deep blue (E_{max} 600 cm^2 mol^{-1}). Predict the possible allowed transition in each case. 3

UNIT—II

(*Marks* : 10)

3. *(a)* Comment on the ^1H-, ^{31}P- and ^{19}F-NMR spectra of HPF_2 (considering J_{P-F} J_{P-H}, J_{P-H} J_{F-H}). 3

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

(c) Explain the EPR spectrum of $\dot{H}$. Deduce the coupling constant (A) value. 4

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

(b) Furnish the EPR spectrum of $\dot{N}H_2$. (where I_N 1). 2

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

UNIT—III

(*Marks* : 10)

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 a.m.u. 4

(b) Discuss the electric quadruple splitting in Mössbauer spectroscopy. Explain how this is helpful to identify the high- and low-spin Fe complexes. 3+3=6

6. *(a)* What is meant by metastable ion? How are such transitions detected in mass spectroscopy? 1+2=3

(b) Mention different ionization modes in mass spectroscopy. Explain any one of them. 1+2=3

(c) The Mössbauer effect depends upon the recoilness of a -ray. How important is it to embed the emitter nucleus in a bulky, rigid, crystal lattice? Calculate the recoil energy of a free ^{57}Fe atom. (mc^2 5 10^{10} eV, E 14 4 keV) 4

PART—B

(*Marks* : 45)

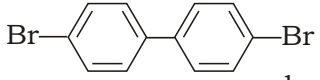
Answer **one** question from each Unit

UNIT—IV

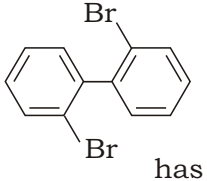
(*Marks* : 11)

7. *(a)* Explain why absorption of UV-vis is typically recorded as broad absorption maxima. 1½

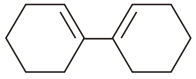
(b) Explain the following : 2+2+2½=6½

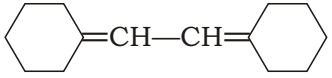
(i) 

has $_{max}$ > 19000

whereas, 

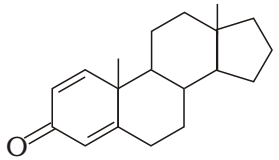
has $_{max}$ < 280

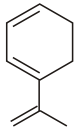
(ii) $_{max}$ for 

is lower than that of 

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

(c) Apply Woodward's rule to calculate $_{max}$ value for the following : 1½+1½=3

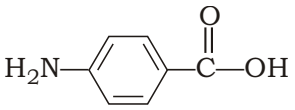
(i) 

(ii) 

8. *(a)* Benzene derivatives exhibit medium to strong absorption in UV-region. Explain why aniline and phenoxide ion have strong UV-absorptions. 1½+1½=3

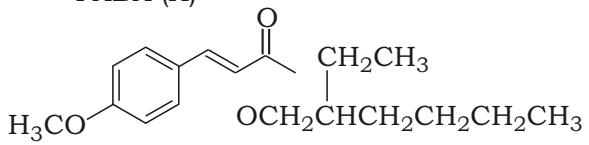
(b) Compound *X* (PABA) and compound *Y* (Giv Tan F) are both used as sunscreen. Compound *Y* protects the skin from both UV-B (290 nm–315 nm) and UV-A (315 nm–400 nm) whereas compound *X* only protects against UV-B. To protect against skin cancer both UV-A and UV-B protection is necessary. From the given structures of *X* and *Y*, comment on the

possible reason of the advantage of *Y* over *X*.



and

PABA (*X*)

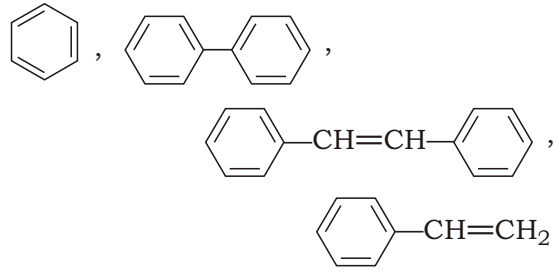


Giv Tan F (*Y*)

2½

(c) Rank the compounds in each group in order of decreasing $_{max}$: 1½+1½=3

(i)



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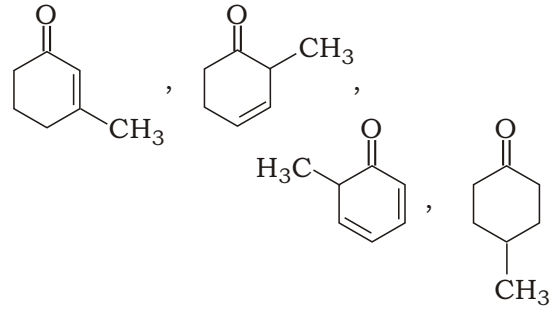


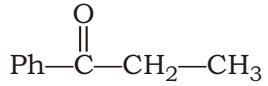
(d) A solution of 4-methyl-3-penten-2-one in ethanol shows an absorbance of 0·52 at 236 nm in a cell with a 1 cm light path. Its molar absorptivity in ethanol at that wavelength is 12600. What is the concentration of the compound? 2½

UNIT—V

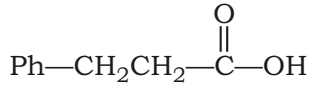
(*Marks* : 11)

9. *(a)* How can the following compounds be distinguished by IR spectroscopy? 4

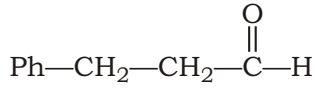
(i)



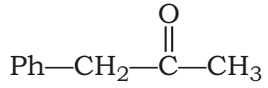
(ii)



(iii)



(iv)



(b) Discuss the effect of ring strain on the internal C═C stretching in cyclic alkenes. 3

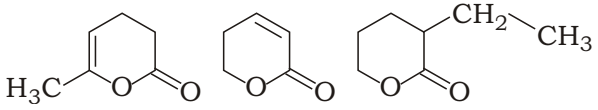
(c) Explain why C═O stretching in carboxylic acid is lower than that of ester. Provide the support of suitable examples. 2½

(d) Will phenol dissolved in CS_2 or in ethanol show an O—H stretch at a higher frequency? Why? 1½

10. *(a)* With suitable example, explain how can you distinguish between 1,2-diketone and 1,3-diketone by IR spectroscopy. 3

(b) Substitution of an amino group on the *para*-position of acetophenone shifts C═O frequency from about 1685 cm^{-1} to 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 substitutent from the 1685 cm^{-1} base value of acetophenone. 3

(c) Match the structures with the C═O stretching frequencies and justify your assignment :



C═O stretching frequencies 1735, 1763, 1725 cm^{-1}. 1½+1½=3

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

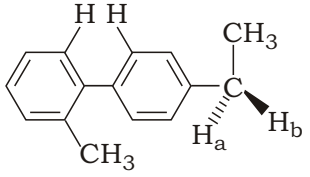
acetone, CO_2, CO, 1-butyne, 2-butyne, H_2, H_2O, Cl_2 and ethene

UNIT—VI

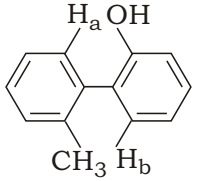
(*Marks* : 11)

11. *(a)* Assign topicity for the following H_a and H_b nuclei by identifying them as homotopic/enantiotopic/diastereotopic. Also comment if they are magnetically equivalent or non-equivalent : 1½+1½=3

(i)



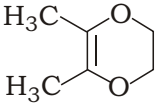
(ii)



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

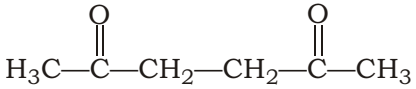
(c) How can the following set of compounds be distinguished by ^{1}H-NMR? Assign chemical shift values, splitting patterns and their peak area ratios. 3+1=4

(i)

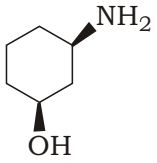


(ii) $H_3COCH_2C{\equiv}CCH_2OCH_3$

(iii)

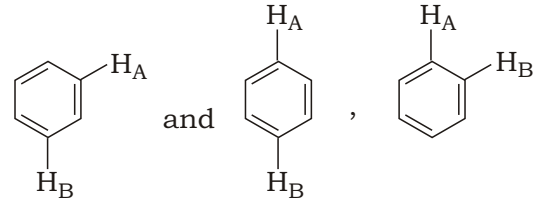


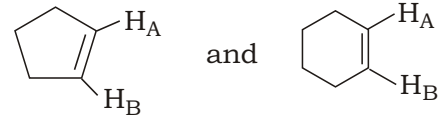
(d) The NMR spectra of the compound



was recorded at different temperatures. Explain the observed trend. 2

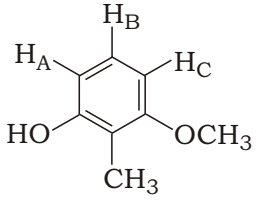
12. *(a)* Assign J values for the set of given compounds : 2½

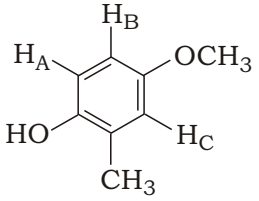
(i) 

(ii) 

Given : J_{HH} 10 Hz, 9 Hz, 2 Hz, 1·5 Hz, 6 Hz

(b) Provide splitting patterns for the following : 1½+1½=3

(i) 

(ii) 

(c) Explain why the ^{1}H-NMR of primary amides experience observable broadening of —NH peaks. 2

(d) Identify the structure, 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*). $3J_{HH}$ 2 7 Hz and $3J_{HH}$ 4 0 Hz. 2½

(e) Assign the -values of residual peaks obtained for $CDCl_3$ and explain. 1

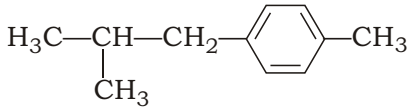
UNIT—VII

(*Marks* : 12)

13. *(a)* 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

(b) What is NOE? How can it be applied to 1D and 2D NMR techniques? 1+2=3

(c) How is 2D NMR affected by FT-techniques? Explain the COSY spectra of



by drawing a detailed spectra with expected peaks/signals. Explain the correlations. 1½+3½=5

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 70 91 ppm (for ^{13}C). The ^{13}C peak was inverted under DEPT considerations. Predict the molecular structure and assign values. 2½

(b) Explain how 2D NMR is different from 1D NMR in basic terms by highlighting the two extra functions involved. 2½

(c) How can COSY be distinguished from NOESY? Explain. 1½×2=3

(d) An organic compound with molecular formula $C_8H_{14}O_4$ exhibited the following spectral data : 1×4=4

(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.

★★★