2017/ODD/08/22/CHM–304/232

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

CHEMISTRY

(3rd Semester)

Course No. : CHMCC–304

(Application of Spectroscopic Methods)

Full Marks : 70

Pass Marks : 28

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

1. *(a)* Using IR spectroscopy, distinguish the linkage isomers of

$$AsPh_4[Co(DMG)_2(NCS)_2]$$ 3

(b) The $_{(NO)}$ values in $[Ru(bpy)_2(NO)X]^z$ are X Cl, z 2, $_{(NO)}$ 1927 cm ^{1}; X MeCN, z 3, $_{(NO)}$ 1970 cm ^{1}.

Explain and comment on the electrophilic behaviour of coordinated NO from these results. 4

(c) $[Fe(CN)_6]^3$ exhibits two sets of charge transfer absorptions in the visible and ultraviolet region but $[Fe(CN)_6]^4$ shows only one absorption in the ultraviolet region. Explain. 3

2. *(a)* Sulfato ligand can bind as chelated and bridging bidentate mode. How do IR spectroscopy distinguish these bonding features? 2+2=4

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

(c) The spectrum of $[CrF_6]^2$ has three spin-allowed transitions at 34 4, 22 7 and 14 9 KK respectively. Assign these bonds. 3

UNIT—II

3. *(a)* Tin(IV) fluoride forms two isomeric adducts of formula $SnF_4(base)_2$, with electron pair donors. How could you identify each isomer from its NMR spectra? 3

(b) Sketch the ^{1}H-NMR spectra of acetylacetone and explain. 3

(c) Predict the number of lines and explain their relative intensities in the ESR spectrum of $\dot{B}H_3$ (I_B 3/2). Sketch the spectrum. What is Kramer's doublet? 2+1+1=4

4. *(a)* When a solution of the complex *trans*-Pt(H)(CN)$(PEt_3)_2$ (*A*) was treated with HCl gas at – 90 °C, a new species (*B*) was formed which gave the ^{1}H and ^{31}P-NMR data shown below. On warming the solution, a gas was evolved and the spectra changed again (species *C*). What types of reactions are occurring? Use the data to identify the species present at the lower and higher temperature and derive their stereochemistry : 4

	T (°C)	(^{1}H) ppm	(^{31}P) ppm	(^{195}Pt) ppm	^{1}J(H-Pt) Hz	^{2}J(H-Pt) Hz	^{1}J(P-Pt) Hz
A	0	– 7·75	19·21	373·7	827	15·5	2500
B	– 90	– 12·31 – 18·40	8·25	265·4	706 1225	8·0 6·5	1677
C	0		16·41	373·3			2250

(b) Show the tetragonal distortion in hexacoordinated Cu(II) complexes and give expression for *g*-values. 2

(c) Illustrate the ESR spectra of penta coordinated [Co(1,3-diaminopropane)$_3$] $CuCl_5 \cdot 3H_2O$ complex in polycrystalline state at different temperatures. 4

UNIT—III

5. *(a)* In a $^{57}Fe^{*}$ Mössbauer experiment, it was found that the source had to be moved towards the sample at 2 2 mm s ^{1} in order to attain resonant absorption of the -ray. What is the shift (in MHz) between sample and source? 3

(b) The chemical shift of some tin compounds are as follows :

Sn^{4} , 0 mm s ^{1}

Sn (4-coordinate), 2·1 mm s ^{1}

Sn^{2} , 3·7 mm s ^{1}

Explain the observation. 3

(c) Write a short note on 'FAB' mass spectrometry. 4

6. *(a)* Discuss quadruple splitting in Mössbauer spectroscopy. 4

(b) A compound containing Mn, CO and C_5H_5 (Cp) shows in its IR spectrum a bond at 2000 cm ^{1}. Its mass spectrum shows peaks at $\dot{m}/z$ = 204, 176, 148, 120, 55 and metastable peaks at m^{*}/z = 155·8, 124·5, 97·2 and 25·2. Find the molar mass and suggest a probable fragmentation pathway. Predict the structure. 6

PART—B

(*Marks* : 40)

Answer **one** question from each Unit

UNIT—I

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

(b) An unknown hydrocarbon has a molecular ion peak at m/z 84 with a relative intensity of 31·3. The M ^{1} peak has a relative intensity of 2 06, and the M ^{2} peak has a relative intensity of 0·08. What is the molecular formula for this substance? 3

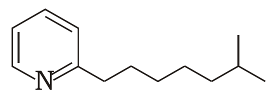
(c) A substance has the molecular formula C_4H_9N. Is there any likelihood that this material contains a triple bond? Explain. 2

(d) Explain why -carotene absorbs in the visible range and has an intense colour. 2

8. *(a)* Explain why absorption of UV-vis is typically recorded as broad absorption maxima and not single, sharp lines. 1½

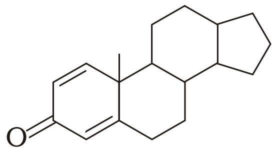
(b) The $_{max}$ values obtained for a ketone is 279 nm in *n*-hexane, 270 nm in ethanol and at 265 nm in water. Explain this change. 2

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



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

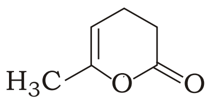
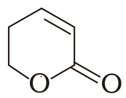
(e) Calculate the $_{max}$ for the following :

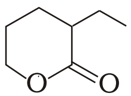


Predict the given compound is coloured or not. 1+½=1½

UNIT—II

9. *(a)* Match the structures with the C═O stretching frequencies and justify your assignment : 3

(i)  *(ii)* 

(iii) 

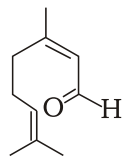
Given : C═O str. frequencies : 1735, 1763, 1725 cm ^{1}

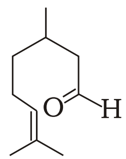
(b) Discuss the effect of ring strain on the internal C═O stretching in cyclic alkenes. 2

(c) Substitution of an amino group on the *para*-position of acetophenone shifts the C═O frequency from about 1685 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 for acetophenone. 3

(d) Why does acetic anhydride show two carbonyl stretching absorptions? 2

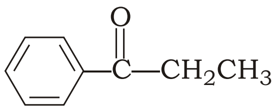
10. *(a)* Ants emit tiny amounts of alarm pheromones to warn other ants (of the same species) of the presence of an enemy, and two of their structures follow. Which compound has the infrared spectrum (as shown in Annexure)? 3

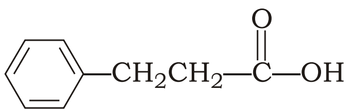

Citral

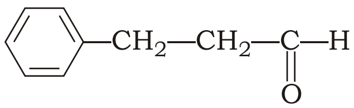

Citronella

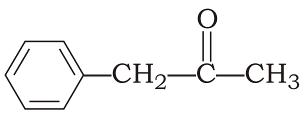
Justify your choice.

(b) How can you distinguish the following by IR? 2

(i) 

(ii) 

(iii) 

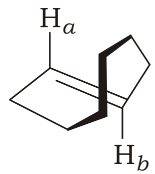
(iv) 

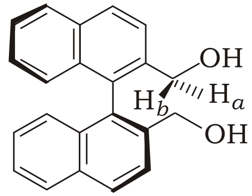
(c) Explain with suitable example, how C$=$O stretching in carboxylic acid is lower than that in ester. 2

(d) With suitable example, explain how 1,2-diketone and 1,3-diketone can be distinguished by IR spectroscopy. 3

UNIT—III

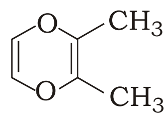
11. *(a)* Assign the topicity for the following (homotopic/enantiotopic/diastereotopic) and also comment if they are magnetically equivalent or non-equivalent. 1+1=2

(i) 

(ii) 

(b) Explain why the ^{1}H-NMR of primary amides experience observable broadening of —NH protons. 1½

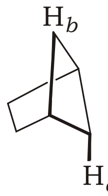
(c) How can the following compounds be distinguished by ^{1}H-NMR? Provide chemical shift, splitting patterns and peak area ratio for each : 1½×3=4½

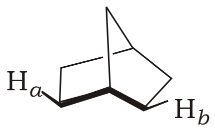
(i) 

(ii) $H_3COCH_2C\equiv CCH_2OCH_3$

(iii) $H_3C—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2—CH_2—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$

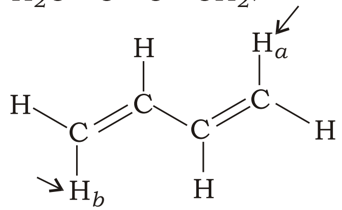
(d) Assign J values for the set of given compounds : 1+1=2

(i) 

and 

(ii) $H_3C—C\equiv C—CH_2—CH_3$,

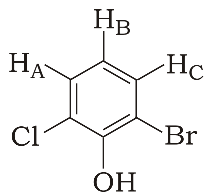
$H_2C=C=C=CH_2$,

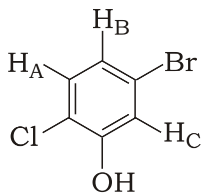


(Given :

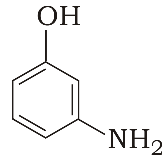
$4J_{HH}$ 7 Hz, $5J_{HH}$ 1 6 Hz,
$5J_{HH}$ 2 5 Hz, $4J_{HH}$ 1 5 Hz,
$5J_{HH}$ 7 Hz)

12. *(a)* Provide splitting patterns of the ^{1}H-NMR of the followng : 1½+1½=3

(i) 

(ii) 

(b) The ^{1}H-NMR spectra of the compound



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

(c) Identify the structure and assign peaks and J values for an organic compound C_4H_8O with *p*-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, $3J_{HH}$ 4 0 Hz. 2½

(d) How can the validity of a first-order NMR analysis be verified? Explain. 1½

(e) Can TMS be replaced as a standard? Explain. 1

UNIT—IV

13. *(a)* A compound with the molecular formula $C_{12}H_{24}O_8$ gives a single peak at 3 66 ppm (for ^{1}H-NMR) and a single ^{13}C (DEPT inverted) signal at 70 91 ppm. Predict the structure of the compound and assign values. 2

(b) What information do the cross peaks of COSY and NOESY offer? Explain. 2½

(c) Highlight the difference between COSY-45 and COSY-90 and mention their applications. 1½

(d) 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*) and 4 19 (*q*) ppm

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

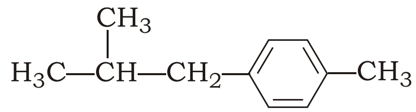
Determine the structure of the compound with justification of the data provided. 1×4=4

14. *(a)* Explain the dipolar relaxation pathway in NMR spectroscopy. How does such relaxation mechanism find application in 2D NMR? 2

(b) Two compounds *X* and *Y* 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, 202 80, respectively. DEPT gave a single-inverted peak for *X* and two inverted peaks for *Y*. Predict the two structures of *X* and *Y* and identify the functional groups. 2+2=4

(c) Why is 2D NMR dependent upon FT-techniques? Explain the COSY spectra of



through a detailed spectral representation of the expected peaks/signals expected for COSY and explain it. 1+3=4

★ ★ ★

ANNEXURE

For Question No. 10. *(a)*