

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

## 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

## ( Inorganic Chemistry )

( Marks : 30 )

Answer **one** question from each Unit

## UNIT—I

1. (a) Arrange  $V(CO)_6$ ,  $Cr(CO)_6$ ,  $Mn(CO)_6$  in terms of increasing carbonyl stretching frequency ( $\nu_{CO}$ ). Justify the order. 3
- (b) Based on IR spectral feature, state how O-bonded and N-bonded  $NO_2$  can be distinguished. 3

- (c)  $V(H_2O)_6^{3+}$  has readily observable absorption band at  $17800\text{ cm}^{-1}$  and  $25700\text{ cm}^{-1}$ . By using the appropriate Tanabe-Sugano diagram, account the most likely origin of the absorption bands. 4

2. (a) The  $\nu_3$  and  $\nu_4$  vibrations of the complexes are

	$[CrCl_6]^{3-}$	$[MnCl_6]^{3-}$	$[FeCl_6]^{3-}$
$\nu_3(\text{cm}^{-1})$	315	342	248
$\nu_4(\text{cm}^{-1})$	200	183	184

- Explain and comment on the changes of  $\nu_3$  and  $\nu_4$  values. 4

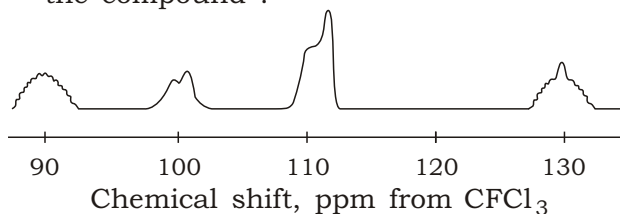
- (b) A titanium complex has a molecular formula  $TiCl_3 \cdot 6H_2O$ . The compound loses 13.61% of its weight at  $60^\circ\text{C}$ – $70^\circ\text{C}$ . The infrared spectrum of the compound exhibits bands at  $500\text{ cm}^{-1}$ ,  $336\text{ cm}^{-1}$ ,  $3520\text{ cm}^{-1}$ – $3000\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$ . Assign a suitable structure of the complex. 3
- (c) Account the change in energy of the MLCT bands of the following iso-electronic series : 3



( 3 )

UNIT—II

3. (a) Describe the expected  $^1\text{H}$ - and  $^{31}\text{P}$ -NMR spectrum of square planer  $[\text{PtH}(\text{PPh}_3)_3](\text{ClO}_4)$  complex. (Neglect  $J_{\text{Pt}-\text{H}}$  and  $J_{\text{Pt}-\text{P}}$ ) 3
- (b) Sketch  $^{19}\text{F}$ -NMR spectrum of  $\text{HP}(\text{O})\text{F}_2$ . (Considering  $^1J_{\text{P}-\text{F}}$  1110 Hz and  $^2J_{\text{F}-\text{H}}$  115 Hz) 2
- (c) How many EPR lines one can predict from the diphenylpicrylhydrazine radical ( $\text{dppH}$ )? Draw the EPR spectrum and explain the relative intensities of the lines in the spectrum. Why is  $\text{dppH}$  used as a standard in EPR studies?  $1+2^{1/2}+1^{1/2}=5$
4. (a)  $\text{CsF}$  and  $\text{SbF}_5$  react exothermally in  $\text{SO}_2$  solution to give a soluble product  $\text{CsSb}_2\text{F}_{11}$ . This product can be removed by evaporating. The  $^{19}\text{F}$ -NMR (94.077 MHz) spectrum of the solution is given below. Deduce the structure of the compound : 3



J7/840

( Turn Over )

( 4 )

- (b) Explain the splitting pattern of methine proton in  $[\text{Pt}(\text{acac})_2]$ . (Where  $\text{acac}$ =acetylacetonone,  $^{195}\text{Pt}$ ,  $I \frac{1}{2}$ , abundance 34%) 2
- (c) Show the application of EPR spectroscopy in determining the following :  $1^{1/2} \times 2 = 3$
- (i) Organic reaction mechanism
- (ii) Metal oxidation state
- (d) Predict the number of lines expected in EPR spectrum of *bis*(salicylaldiaminato) copper(II). Comment on their relative intensities. 2

UNIT—III

5. (a) A compound containing Mn, CO and Cl shows peaks at  $1950 \text{ cm}^{-1}$ – $2000 \text{ cm}^{-1}$  in IR spectrum. Mass spectral peaks were observed at  $\frac{m}{z}$  404, 376, 348, 320, 292, 264, 236, 208, 180, 110, 55. Metastable peaks were observed at 349.1, 322.1, 294.3, 211, 183.3, 155.8, 67.2, 27.5. Suggest the most probable fragmentation pathway and predict the molecular structure. 5

J7/840

( Continued )

( 5 )

- (b) Describe in brief the origin of isomer shift in Mössbauer spectroscopy.  $\text{Fe}^{2+}$  possesses a more positive isomer shift than  $\text{Fe}^{3+}$ . Explain. 3+2=5

6. (a) What causes formation of metastable ions? What are the characteristic features of peaks originating from such ions in mass spectroscopy? What role do they serve in deciphering mass fragmentations? 5
- (b) Give a brief account on the role of Mössbauer spectroscopy in various applications. 5

( 6 )

PART—B

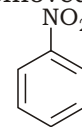
( Organic Chemistry )

( Marks : 40 )

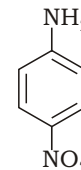
Answer **one** question from each Unit

UNIT—I

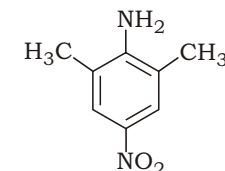
7. (a) The identity sticker of the container of the following three compounds got removed :



(A)



(B)



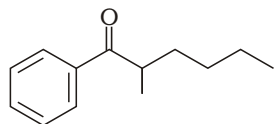
(C)

The UV-spectra of the compounds shows absorption at  $\lambda_{\text{max}}$  252 nm, 375 nm and 385 nm (not in order). Match the structure with appropriate UV-spectra with explanation. 3

- (b) Draw the Frontier orbital diagram to show the possible electronic transitions of  $\alpha,\beta$ -unsaturated carbonyl compounds. 2
- (c) Write the mathematical expression for metastable ion, indicating the terms involved. Explain the significance of metastable ion considering the MS of anisidine at  $m/z$  123, 108, 80, 94.8 and 59.2 1+2=3

( 7 )

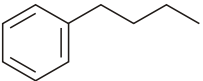
- (d) Predict two major fragmentation patterns for the following compound, and provide the supportive reasoning for your predictions : 2



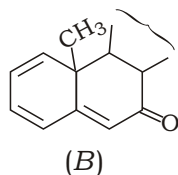
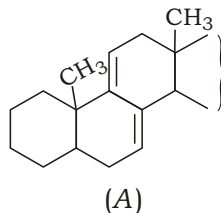
8. (a) A compound with molecular formula  $C_7H_8O$  exhibited  $m/z$  108, 93 (base peak), 78, 77, 65, 51 in MS pattern. Deduce the most probable structure of it. 2

- (b) Explain the appearance of the indicated peaks for the following compounds :  $1+2=3$

(i)  $CH_3(CH_2)_7NH_2$ ,  $m/z$  86

(ii)   $m/z$  92, 91

- (c) Using Woodward-Fieser rules, calculate the  $\lambda_{max}$  of the following compounds :  $1\frac{1}{2} \times 2 = 3$



J7/840

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( 8 )

- (d) THE UV-spectra of two isomers of cinnamic acid absorb at 272 nm and 268 nm. Identify the isomers with justification. 1

- (e) Identify the types of transition in each of the following compounds :  $\frac{1}{2} \times 2 = 1$

(i) Ethanol at 290 nm,  $\lambda_{max}$  17

(ii) Acetic anhydride at 227 nm,  $\lambda_{max}$  17

UNIT—II

9. (a) Substitution of an amino group at the *para*-position of acetophenone shifts the  $C=O$  frequency from  $1685\text{ cm}^{-1}$  to  $1652\text{ cm}^{-1}$ ; whereas a nitrogroup attached at that position yields the  $C=O$  frequency to appear at  $1693\text{ cm}^{-1}$ . Explain the shifts. 2

- (b) Why does a  $\beta$ -diketone appear as two broadbands at  $1640\text{ cm}^{-1}$ – $1580\text{ cm}^{-1}$  and at  $3100\text{ cm}^{-1}$ – $2700\text{ cm}^{-1}$ ? 2

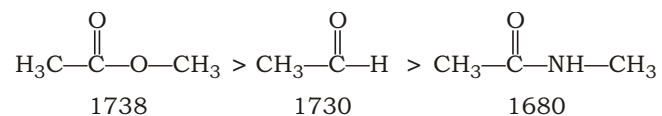
- (c) Discuss the effect of ring strain on the carbonyl stretching for cyclic ketones. 3

J7/840

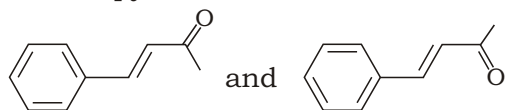
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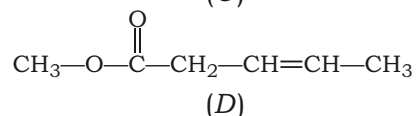
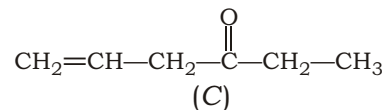
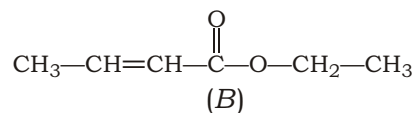
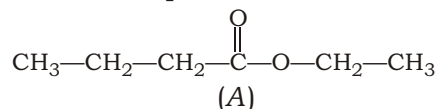
- (d) Why does the C=O frequency follow the following trend? 3



10. (a) How can the following geometric isomers be distinguished by IR spectroscopy? 2



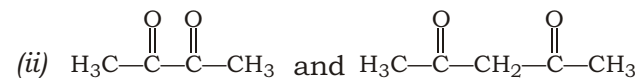
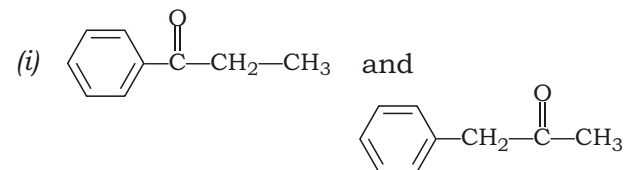
- (b) Which of the following structures best fits with the IR spectrum shown below?



Also explain the ground of rejection for other compounds (as shown in Annexure). 2+2=4

( 10 )

- (c) How can you distinguish the following compounds by IR spectroscopy? 1+2=3



- (d) What is overtone? 1

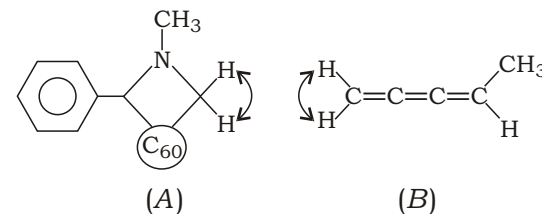
UNIT—III

11. (a) Explain the following : 2+1½=3½

(i) NMR time scale (with example)

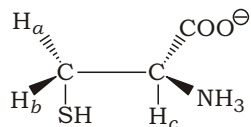
(ii) The —OH proton resonance is found at 5.80 ppm for phenol (in dil. CDCl<sub>3</sub>) and at 10.67 ppm for o-nitrophenol (in dil. CDCl<sub>3</sub>)

- (b) Determine the topicity of the groups or atoms indicated and comment on their magnetic equivalence : 1+1=2



( 11 )

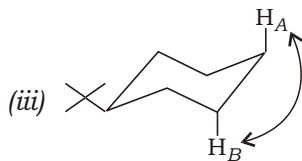
- (c) Predict the proton splitting pattern of  $H_a$ ,  $H_b$  and  $H_c$  in the following compound and explain briefly the effect of chirality : 3



- (d) A trisubstituted benzene possessing one bromine and two methoxy substituents exhibit three aromatic resonances at 6.40, 6.46 and 7.41. What is the substitution pattern? 1½

12. (a) Predict the following coupling constants :  $\frac{1}{2} + 1 + \frac{1}{2} = 2$

- (i) Nitrobenzene (2-3)  
(ii) Pyridine (2-3, 3-4)



- (b) How do the spectrometers operating at higher frequencies affect spin-spin coupling? 2

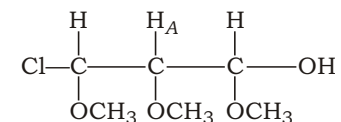
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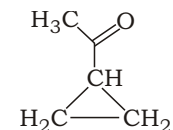
- (c) Compounds  $X$  and  $Y$  share the molecular formula  $C_6H_{10}O_2$ . Compound  $X$  has proton resonance,  $A$  2.71 (s),  $B$  2.19 (s) and compound  $Y$  has resonance  $A$  2.77 (q),  $B$  1.09 (t). Predict the structures of  $X$  and  $Y$ , assign exact chemical shift values and mention what type of isomers  $X$  and  $Y$  are. 2+2=4

- (d) For the given compound, assign a spin system (including  $A$ ) and depict the splitting pattern diagrammatically : 1+1=2



UNIT—IV

13. (a) Explain the  $^{13}C$ -NMR spectra of



with—

- (i)  $^1H$  off-resonance decoupled (SFORD);  
(ii) DEPT.

(First assign the chemical shift values)

1+1=2

J7/840

( Continued )

( 13 )

- (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  $cm^{-1}$ (s)

$^1H$ -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<sup>+</sup>, 100), 76 (40)

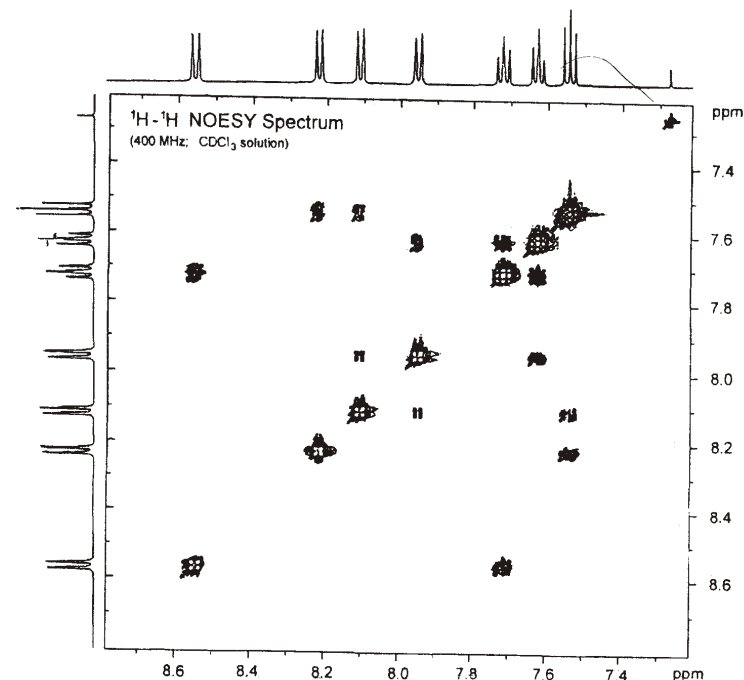
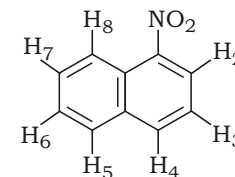
- (c) Briefly describe the various parameters for the generation of 2D-NMR data apart from preparation and detection (relevant to 1D-NMR). What are the advantages of Fourier transformed FID? 2+2=4

14. (a) Explain NOE and how it can be applied to 2D-NMR. Assign peaks (chemical shift values) to 1-nitronaphthalene.

( 14 )

From the attached  $^1H$  NOESY spectrum,  
 $^1H$ -NMR : 8.57, 8.21, 8.12, 7.95, 7.71,  
7.61 and 7.53 ppm.  $2\frac{1}{2}+3\frac{1}{2}=6$

$^1H$  NOESY spectrum of 1-nitronaphthalene  
(recorded in  $CDCl_3$  solution at 298 K at 400 MHz)



( 15 )

(b) A compound with molecular formula  $C_7H_{14}O_2$  upon hydrolysis produces an alcohol and an acid. It has the following NMR data :

$^1H$ -NMR (at 298 K, 600 MHz,  $CDCl_3$ ) :

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

$^{13}C$ -NMR :

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

DEPT provided two inverted signals. Predict the structure of the alcohol that is obtained through hydrolysis of the mentioned parent compound. Assign appropriate IR values,  $^1H$  and  $^{13}C$ -NMR resonances along with a mass spectral pattern for the alcohol.

4

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**ANNEXURE**

For Question No. 10. (b)

