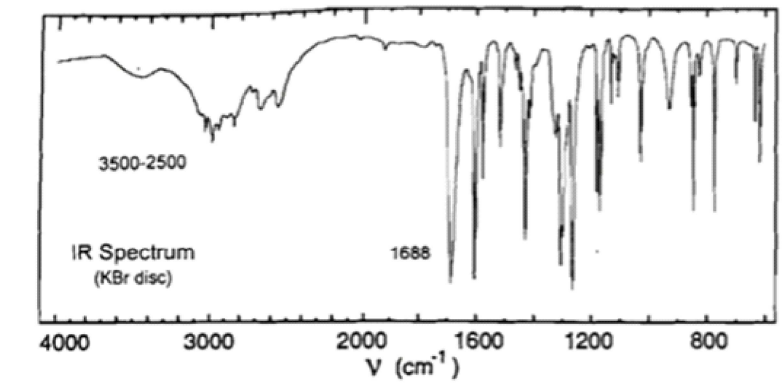

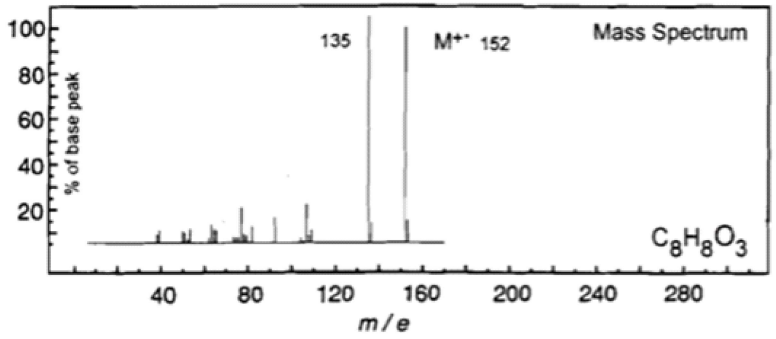

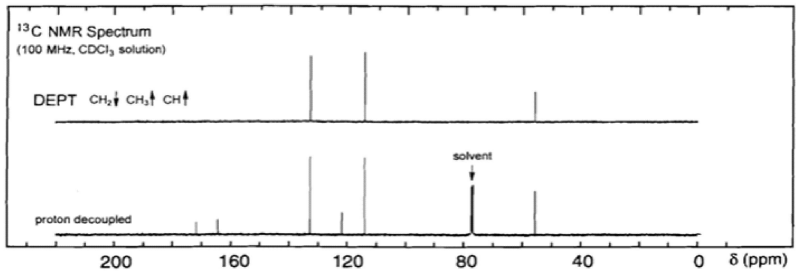

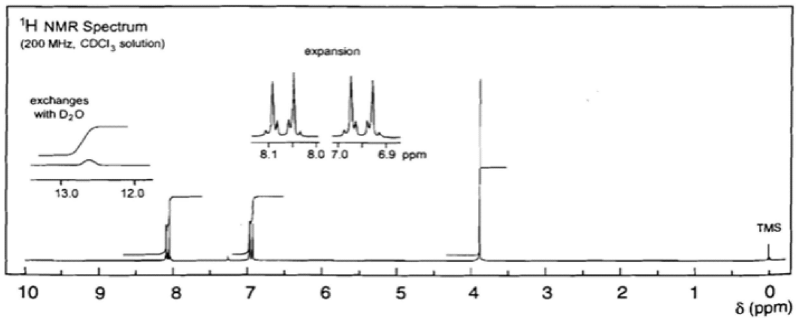

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PG (CBCS) ODD SEMESTER EXAMINATION, 2022

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

PART – A

(Marks: 30)

Answer **three** questions, selecting **one** from each unit.

UNIT - I

1. (a) Where do you expect the M-Cl and M-N stretching frequency in $[Co(NH_3)_4Cl_2]Cl$. How the cis- and trans- forms be distinguished? 3

(b) Explain, why $[Co(H_2O)_6]^{2+}$ is a pale pink (ε_{max}=10 $cm^2\,mol^{-1}$) whereas $[CoCl_4]^{2-}$ is deep blue (ε_{max} = 600 $cm^2\ mol^{-1}$). Predict the possible transition in each case. 4

(c) The ν(CO) of isoelectronic series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$ are 2090cm^{-1}, 2000cm^{-1} and 1860cm^{-1}, respectively. Why is this difference observed in the band positions. 3

2. (a) Comment on the nature of bonding of SO_4^{-2} in the following compounds:

$[Co(NH_3)_6]_2(SO_4)_3$ and $[Co(NH_3)_4SO_4]$ Br 4

(b) What is the number and nature of UV-visible bands expected of an octahedral Ni^{2+} complex? 3

(c) Explain how using IR features three possible linkage isomers of $AsPh_4[Co(DMG)_2(SCN)_2]$ can be distinguished. 3

(DMG= dimethylglyoxime)

UNIT - II

3. (a) Sketch the ^{1}H-NMR spectra of acetylacetone (acacH) in $CDCl_3$ and explain. 2

(b) The ^{19}F-NMR spectrum of SF_4 consists of two triplets of equal peak area. Suggest the structure of the compound with justification. 3

(c) Sketch and explain the isotropic ESR spectra of (i) $[Mn(CO)_5Cl]^+ I_{Mn}=5/2$ and (ii) $[Fe(CN)_6]^{3-}$. 3

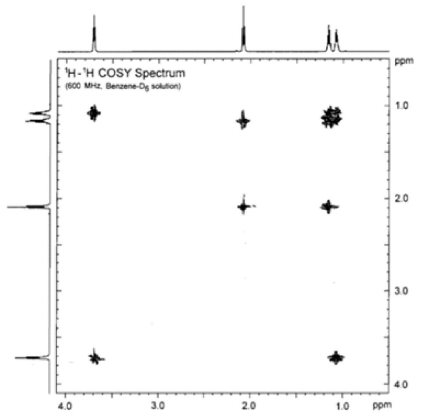
(d) Illustrate the anisotropic ESR spectrum of $Cu(acac)_2$. 2

4. (a) Describe the expected ^{13}C -NMR spectrum of DMSO-d_6. 2

(b) How many signals are expected in the ^{31}P- NMR spectrum of $[PF_4N(CH_3)_2]$ at room temperature and low temperature (173 K)? Explain. (Assume that N and H do not couple). 3

(c) Predict and sketch the ESR spectrum of (i) CH_2OH and (ii) naphthalene anion radical 2

(d) Give two examples showing applications of ESR spectroscopy in (i) spin traps and (ii) free radical reaction mechanism study. 3

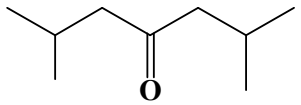


Provide the structure of the compound, assign resonance for each proton and ^{13}C and clearly show the correlations from the COSY. 2 + 1 + 1 = 4

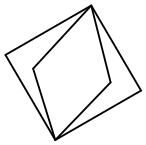
(c) Explain NOE with any example. How can the concept of NOE be used in 2D spectra? Explain two significant applications of NOE. 2 +1 +1 =4

8. (a) How many ^{13}C resonances will be obtained in ^{13}C NMR spectra for the compounds given below? Comment on their DEPT spectra. 1 x 2= 2

(1)



(2)



(b) How can the following be differentiated? Explain. 2 + 2 = 4

(i) 1D NMR and 2D NMR
(ii) COSY-90 and COSY-45

(c) From the given IR, Mass, proton-NMR and ^{13}C NMR spectra derive the structure of the molecule and characterise the IR, Mass, proton and ^{13}C of the structure. 2 + 2 = 4

(c) Which isomer of D_2O exchanged dimethyl phenol will have the following resonance for its proton signals? Identify compound E and assign peaks. 2
Isomer (E) with δ = 2.20 (s), 6.48 (s) and 6.55 (s) ppm.

(d) An α,β-unsaturated ketone ($C_{12}H_{15}O_2N$) has the following ^1H NMR signals at δ = 8.01(d, 1H, *J* = 12.3 Hz), 7.72 (d, 2H, *J* = 8.0 Hz), 6.80 (d, 2H, *J* = 8.0 Hz), 5.80 (d, 1H, *J* = 12.3 Hz), 3.82 (s, 3H), 3.11 (s, 6H) ppm. Identify the compound along with the correct geometric configuration with the help of the provided *J* values. 4

UNIT - IV

7. (a) For the compound $C_8H_{12}O_2N_2$ (*trans*-unsaturated amide) resonance signals are found at δ= 18.95, 123.02, 148.41, 172 ppm in its ^{13}C NMR spectrum recorded at 75 MHz. The proton coupled NMR spectrum of it showed the splitting as in the small bracket: δ = 18.95 (quartet), 123.02 (doublet), 148.41 (doublet), 172 (singlet). There was no inverted DEPT. Why this compound gave only four resonance signals in its ^{13}C NMR spectrum? Draw the structure of the molecule and assign each signal to carbons of the molecule. 2

(b) The ^1H and ^{13}C NMR spectra of compound (**X**) with molecular formula $C_5H_8O_2$ are given below recorded in C_6D_6 solution at 298K, at 600 MHz. The ^1H spectrum has signals at ? = 1.08 (m, 2H), 1.16 (m, 2H), 2.08 (t, 2H), and 3.71 (t, 2H) ppm. The ^{13}C spectrum has signals at 819.0, 22.2, 29.9, 68.8 and 170.0 ppm. The 2-dimensional $^1H\_^1H$ COSY spectrum is provided:

UNIT - III

5. (a) $Na_3[Fe(CN)_6]$ shows one singlet in the Mossbauer spectrum whereas substitution of one CN^- by a ligand L gives a doublet, explain. If L are arranged in increasing π-bond character, *viz*. L = NH_3, PPh_3, CN^-, CO, NO^+ how will the isomer shift value change? Explain the observation. 4

(b) A manganese(0) complex of cyclopentadienyl and carbonyl ligand show in its mass spectrum peaks at m/z values 204, 176,148,120, 55 and relatively less intense metastable peaks at m/z values 151.8, 124.5, 97.2, 25.2. Rationalise the fragmentation pattern, mark the metastable transition steps and suggest a plausible structure of the compound. 6

6. (a) Give the profile of the Mossbauer spectrum of $[Fe(CO)_5]$ and account for the observations on the basis of the structure of the above compound. 4

(b) Rationalize the Mossbauer isomer shift (δ): $SnCl_4$,0; $Sn(CH_3)_4$, 2.1 and $SnCl_2$, 3.7 mm s^{-1}. 2

(c) Explain citing a suitable example why ligands like CO, NO are lost from metal complexes in preference to ligands such as sulphide, halide, acac*etc*. during mass spectrometric fragmentation. 4

Part B: ORGANIC CHEMISTRY
(Total Mark = 40)

The figures in the margin indicate full marks for the questions

Answer **four** questions, taking **one** from each unit

UNIT - I

1. (a) Explain 2+2=4
(i) λ_{max} values obtained for acetone is at 279nm in hexane, at 270nm in ethanol and at 256nm in water. Explain

(ii) Benzene shows λ_{max}=256nm, ϵ_{max}=200 whereas aniline shows λ_{max}=280nm, ϵ_{max}=1430.

(b) What is ESI-Ms and MALDI mass spectroscopy? 3

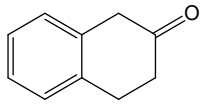
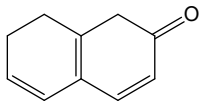
(c) Compound (A) $C_5H_{10}O$ is an alcohol. It shows prominent peak at m/e = 88(M+), 55, 42 (base peak), 31 and 29. Give the structure of the compound. 3

2. (a) Delineate the following terms in the light of spectroscopy 1+1=2

(i) Chromophore and auxochrome

(ii) Redshift and blue shift

(b) Calculate the λ_{max} for the following:

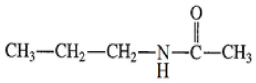
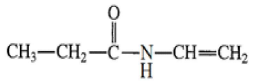
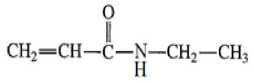
(i)  (ii)  2+2=4

(c) The mass spectrum of phenylpropyl ketone exhibits prominent peaks at *m/e* 148 (M+), 120, 106, 105 (base peak), 77 and 51. Explain the formation of the ions corresponding to these peaks. 2

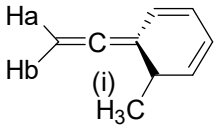
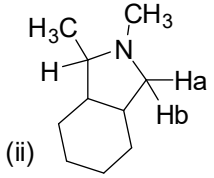
(d) Show the principal fragmentation that would be observed in mass spectra of *n*- propyl cyclohexane. 2

UNIT - II

3. (a) Which of the following amides will exhibit highest C=O stretching frequency? Explain 3

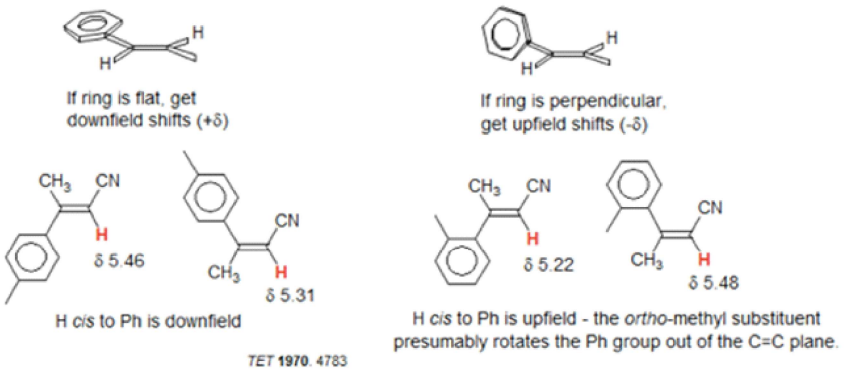
  

and chemical equivalence. How will the protons a and b split into for each example? $1\frac{1}{2}+1\frac{1}{2}=3$

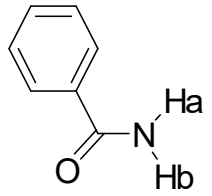
 

(d) Name the factors that influence spin-spin coupling. Can the presence of two or more compounds in a mixture be detected through spin-spin coupling? $\frac{1}{2}+\frac{1}{2}=1$

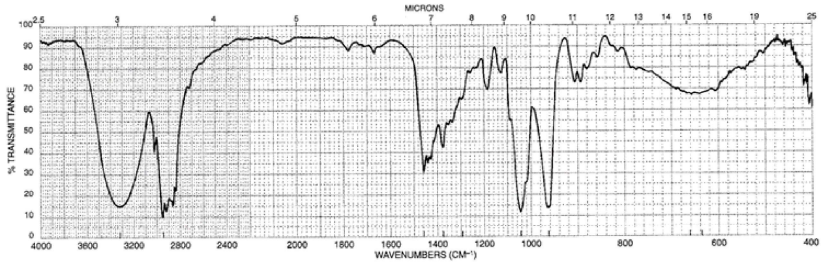
6. (a) Explain the trend of changes in the chemical shift for the two examples given below: 2



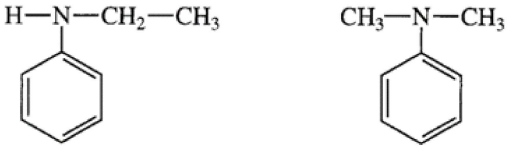
(b) Explain the phenomenon that causes the broadening of signals for the NH_2 signals for the given compound in its ^1H NMR spectra. 2



1½ x 2=3



(d) How can the following compounds be distinguished by IR spectroscopy, 2



A **B**

UNIT -III

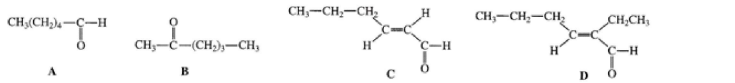
5. (a) Compound **A** ($C_7H_8O_3N_2$), when treated with $NaNO_2$ and HCl (at 0-5^oC) produces an intensely coloured salt **B**. The ^1H NMR signals obtained for Compound A are at $\delta = 7.75$ (dd, 1H, $J = 8.8$ & 2.4 Hz), 7.58 (d, 1H, $J = 2.4$ Hz), 6.70 (d, 1H, $J = 8.8$ Hz), 6.50 (s, 2H). From the data given for compound **A**, provide the structure of **B**. 4

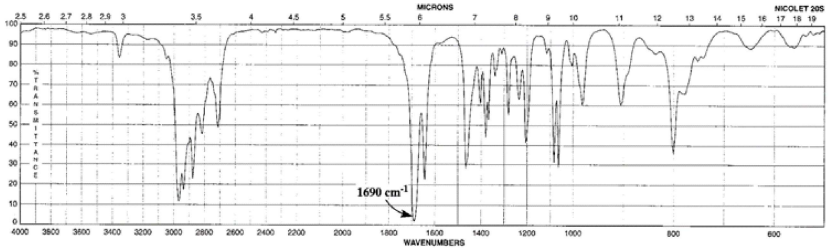
(b) The ^1H NMR of a compound **C** (without any labile proton) gave an additional signal at $\delta = 1.60$ ppm when dissolved in $CDCl_3$, and at $\delta = 3.31$ ppm when the spectrum was taken in DMSO-d_6. How will you account for these two extra signals? Explain. 2

(c) Identify the indicated H-atoms (a & b) as homotopic/ enantiotopic/diastereotopic and comment on their magnetic

(b) Explain how ring size effects endocyclic C=C in cycloalkenes? 3

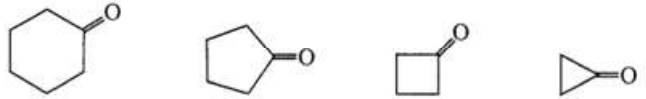
(c) Choose the structure which best fits the given IR spectrum. Provide justification to your selection. 3





(d) How C≡N can be distinguished from C≡C by IR Spectroscopy? 1

4. (a) An unlabelled bottle contains one of the following cyclic ketones,



A **B** **C** **D**

The IR spectrum of the compound exhibited a strong shark band at 1780 cm-1. Identify the compound with justification. 3

(b) How Inter- and intra-molecular H-bonding is differentiated by IR spectroscopy? 2

(c) How cis- and trans-1,2-disubstituted alkenes can be distinguished by IR spectroscopy? From the following IR spectrum of 3-haxene-1-ol, identify the geometric isomer: