DEPARTMENT OF CHEMISTRY
RANIRASHMONI GREEN UNIVERSITY
M.Sc. COURSE IN CHEMISTRY
SEMESTER III FINAL EXAMINATION: 2025

Course ID: CHEM–C31

Full Marks: 40 **Time: 2hrs**

Answer any <u>ONE</u> question from each UNIT in your own words with proper scientific justification.

Unit-1: IR and UV-Vis-NIR Spectral Study

Q1. (a) Explain why orthochloro benzoic acid shows two carbonyl stretching frequency.

(b) Distinguish isomers of the compound having formula $Mn(CO)_3Cl_3$ by IR spectroscopy.

(c) Compare and explain the λ_{max}(n to σ*) for the following compounds CH_3OH and CH_3Cl.

(d) Discuss the color intensity of the following complexes with proper reason:

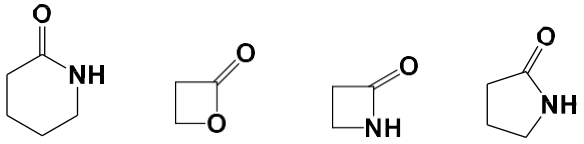
(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[MnCl_4]^{2-}$ **[2+2+2+2]**

Or

Q2. (a) Explain the C=O stretching frequency of the following complexes with suitable reason.

$[Ni(CO)_3PMe_3]$, $[Ni(CO)(PMe_3)_3]$, $[Ni(CO)_4]$, $[Ni(CO)_2(PMe_3)_2]$

(b) Arrange the following compounds in the decreasing order of C=O stretching frequency with suitable explanation



(c) Explain any two binding modes of nitrite ion by IR spectroscopy with suitable example.

(d) Discuss the significance of polar solvent for K and R band in UV spectroscopy.

[2+2+2+2]

Unit-2: NMR Spectral Study

Q3. (a) Discuss ring whizzing in ^1H NMR with suitable example.

(b) Explain why outer protons appear in upfield and inner protons appear in downfield for [16] annulene.

(c) Discuss the paramagnetic effect in ^1H-NMR of $Ni(MeNH_2)_2Cl_2$.

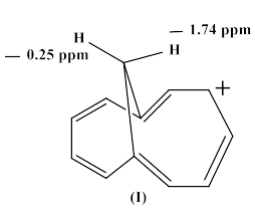
(d) Distinguish isomers of $Pt(PMe_3)_2ICl$ by ^{195}Pt NMR showing all reasonable coupling.

[2+2+1.5+2.5 = 8]

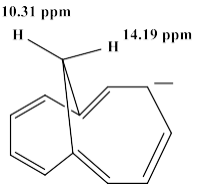
or

Q4. (a) Discuss fluxionality observed in DMF by ^{1}H-NMR.

(b) Discuss the chemical shift of the marked protons in NMR for following compounds (I and II).

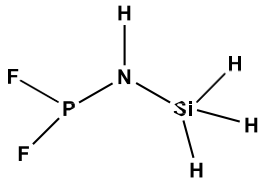


(I)



(II)

(c) Sketch the respective NMR (^{31}P) spectrum of the following compound showing all reasonable couplings.



(d) Explain the splitting pattern of the signals of ^{11}B, ^{10}B, ^{1}H NMR for diborane compound.

[2+2+1.5+2.5]

Unit-3: Mössbauer, Photoelectron and X-ray FluorescenceSpectral Study

Q5. (a) Draw the Mössbauer spectra of $[Fe(L)_2]I_2$ [L= 3,5-dimethyl-tris-pyrazolylborate] having temperature-dependent spin-transition behaviour of Fe(II) at 295K, 4.2K and 166K, respectively and explain the observation.

(b) Predict the variation of isomer shift in Sn^{4+} , Sn^{2+} and Sn (covalently bonded to four groups). Explain the cause of this variation.

(c) Show the quadruple splitting and hyperfine splitting pattern of $[Fe(CN)_5NO]^{4-}$.

[4+2+2=8]

Or

Q6. (a) Explain the basic principle of XRF spectroscopy

(b) What do you mean by K_α, K_β, L_α, L_β in XRF spectroscopy? Explain with pictorial diagram and arrange the according to their energy order.

(c) What are the basic difference between XPS and UPS? **[3+3+2=8]**

Unit-4: EPR and Auger Electron Spectral Study

Q7. (a) Explain the basic principle of Auger Electron Spectroscopy (AES) with an energy diagram.

(b) Explain how can you resolve the spectral overlaps between Auger lines and Photoelectron lines?

(c) Write two important applications of AES. **[4+3+1 = 8]**

Or

Q8. (a) Explain how many EPR lines can be observed in the complex $[Cu(H_2O)_6]^{2+}$; consider a Jahn-Teller tetragonal distortion in the complex and $I_{Cu} = 3/2$, $I_H = 1/2$, $I_O = 0$.

(b) Predict the number of Kramer's doublet of a system having 5 unpaired electrons and show them in an energy level diagram.

[5+3 = 8]

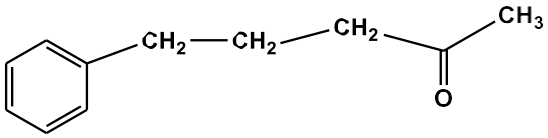
Unit-5: Mass and CD-ORD- MCD Spectral Study

Q9. (a) What is metastable ion peak? What would be the mass value (m/z) of metastable ion of toluene when bombarded with electrons and show also the different peaks obtained therefrom.

(b) Indicate the isotopic abundance of Cl^{35}, Cl^{37}, and Br^{79}, Br^{91} from mass spectral evidances also indicate the m/z value of different ion fragments of (i) 2-chloro propane (ii)1-bromo propane. [4+4 = 8]

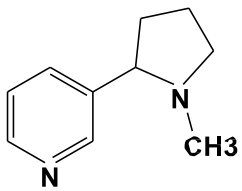
Or

Q10. (a) How McLafferty rearrangement is occurring in mass spectra studies of the following molecule. Indicate the different steps of the following molecule producing ion fragments (m/z).



Write the base peak.

(b) What is Nitrogen rule? Show the breaking pattern and different ion peaks (M/Z) of following nicotine in mass spectral studies.



[4+4 = 8]