PG Even Semester Examination, May 2025

CHEMISTRY

(4th Semester)

Course No.: CHM-651

(Applications of Spectroscopy Methods-II)

Full Marks: 70

Pass Marks: 28

Time: 3 hours

The figures in the right margin indicate full marks for the question.
Answer any five questions selecting one from each unit.

UNIT-I

1. (a) Rationalize how hydroxo- and aquo-complexes can be distinguished by IR spectroscopy. 3

(b) The compound of the type $[MCl_6]^{3-}$, where M= Cr, Mn and Fe. The í$_3$ and í$_4$ stretching frequencies of the compounds are

	Cr	Mn	Fe
ν_3 (cm^{-1})	315	342	248
ν_4 (cm^{-1})	200	183	184

Explain the variation of ν_3 band positions. 4

(c) What is the number and nature of UV-visible bands expected of an octahedral Ni^{2+} complex. 4

(d) Where would you expect the metal-halide stretching frequency in $[Ru(NH_3)_4Cl_2]Cl$? How the *cis*- and *trans*- form be distinguished? 3

2. (a) How do you distinguish three possible linkage isomers of $AsPh_4[Co(DMG)_2(NCS)_2]$ with the help of IR spectroscopy. 4

(b) Arrange $[SF_6]$, $[SiF_6]^{2-}$, $[AlF_6]^{3-}$ and $[PF_6]^{-}$ in terms of increasing í$_1$ and í$_3$ stretching frequency of M-F bond, (M = Al, S, Si and P) and rationalize your answer. 3

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

(d) Arrange $[Ag(CN)_4]^{3-}$, $[Ag(CN)_3]^{2-}$ and $[Ag(CN)_2]^{-}$ in terms of their increasing í$_{(CN)}$ stretching frequency . Justify 3

UNIT-II

3. (a) Calculate the hyperfine coupling constant of atomic hydrogen in an EPR spectrometer operating at 9.5 GHz. Two lines in the spectrometer appeared at 357.3 and 306.6 mT. The g value of an electron in atomic hydrogen is 2.0032.

Given : g = 2.0032; β= $9.273 \times 10^{-24} JT^{-1}$; h = $6.625 \times 10^{-34} Js$ 2

(b) A compound of copper consisting NH_2 and CN^- gives 20 number of ESR lines. Find out the formula and structure. Give reason. 2

formula, rationalise the probable fragmentation pathway and furnish the molecular structure. Indicate the metastable transitions. Explain the nature of metal-metal interaction. 9

(b) Why is it necessary to use at least 70 eV energy in mass spectroscopy? Explain how meta-stable ion peaks arise and are detected in a mass spectrum? 2+3=5

8. (a) A compound of vanadium (0) containing CO and Cp ligand showed in its mass spectra peaks at m/z = 228, 200, 172, 144, 116, 51 and some weak intensity peaks at m/z= 175.4, 148, 120.6, 93.5, 22. Work out the probable fragmentation pathway and suggest a molecular structure. Identify the metastable transition steps. Explain why CO ligands are lost in preference to Cp during the fragmentation. 9

(b) Write a brief note on 'MALDI-MS' as a powerful analytical technique. 5

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nucleus but an external magnetic field is applied? Draw the spectrum and explain. 4

8. (a) The isomer shift of some tin compounds are as follows.

Sn^{4+}, 0 mms^{-1}, Sn(4-covalent), 2.1 mms^{-1} and Sn^{2+}, 3.7 mm s^{-1}.

Explain the observation. 3

(b) Explain quadrupole splitting in Mossbauer spectroscopy. What information are obtained from the quadrupole splitting? 3+1=4

(c) Mossbauer spectrum of SnF_4 shows quadrupole splitting but $SnCl_4$ there is no quadrupole splitting. Why? 3

(d) Explain why high spin Fe(III) complexes have d value positive in the positive range (0.4 to 0.8 mm s^{-1}) where as low spin complexes have dvalue negative in negative side (-0.1 to -0.2 mm s^{-1}). 4

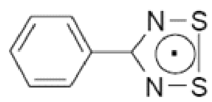
UNIT-V

7. (a) A mixed ligand manganese-carbonyl complex revealed on elemental analysis Mn (27.2%), C (23.8%), Cl (17.5%). The IR spectrum of the complex showed rather distinct peaks for carbonyl at 1950 cm^{-1} and 2050 cm^{-1}. Its mass spectrum showed signals at m/z = 404, 376, 348, 320, 292, 264, 236, 208, 180, 110, 55. Weak signals at non-integral m/z = 349.1, 322.1, 294.3, 211, 83.3, 155.3, 67.2, 27.5 were also observed. Find the molecular

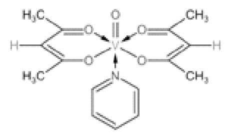
(c) Predict number of lines and elucidate their intensity ratio for H_3 radical. Deduce energy expression for hyperfine line splitting and show allowed transition. 4

(d) Furnish the Zeeman splitting in naphthalene diradical with electronic transition. 1.5

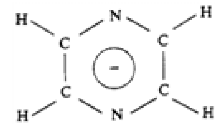
(e) Predict number of lines and their intensity ratio of following compounds. 4.5



(4-aryl-1,2, 3,5-dithiadiazole)
(a)



(VO(acac)$_2$(Py))
(b)



(Pyrazine anion radical)
(c)

4. (a) Find out number of ESR line (hypothetical) in NH_2 with AH=10G and AN=20G. 2

(b) Show zero field splitting in d^2 and d^5 transition metal ions. What is Kramer's degeneracy? 2+1=3

(c) Explain why $Ni(pz)_6(NO_3)_2$ single crystal does not show any ESR spectrum but Cu(II) doping in very low concentration gives EPR signal. Draw and elucidate the anisotropic Q-band ESR spectrum of Cu(II) doped $Ni(pz)_6(NO_3)_2$ single crystal. 1+3=4

(d) Illustrate ESR in studying reactive oxygen species (ROS) spin probe in biological system. 2

(e) Predict the number of lines and their intensity ratio of (consider superhyperfine coupling) 3

(i) H_2OH

(ii) $^{13}H_2$-F

(iii) $Co_3(CO)_9Rh$ (Co_3-Rh bond)

UNIT-III

5. (a) Draw and explain the ^{1}H-NMR spectra of acetylacetone in $CDCl_3$. Find out the keto -enol ratio where the integral area of CH peak of enol form is 1.00 and the CH_2 peak of keto form is 0.36. 2+1=3

(b) Sketch and explain the ^{19}F -NMR and ^{31}P -NMR spectra of HPF_2 where $J_{PF} > J_{FH}$ and $J_{PF} > J_{PH}$. 3

(c) How many $^{31}P\{^1H\}$-NMR signals will appear in *cis*-$[Pt(PEt_3)_2Cl_2]$, give explanation. 2

(d) Below -60 °C, the ^{1}H-NMR spectrum of $(Me_2C{=}C{=}CMe_2)Fe(CO)_4$ shows three peaks in the intensity ratio of 1:1:2 but at room temperature, a single, sharp and intense signal is observable. Explain. 3

(e) ^{19}F spectrum of $CsSb_2F_{11}$in SO_2 at -60 °C shows a low field multiplet, a doublet of doublets and a quintet. Based on this observation, predict the structure of the compound and explain. 3

6. (a) Draw the $^{13}C\{^1H\}$ and ^{13}C-NMR spectra of diethyl ether and explain. 3

(b) Draw and explain the ^{1}H-NMR spectra of $[Pt(acac)_2]$ where acac= acetylacetone, ^{195}Pt, I= ½, 34% abundance. 3

(c) Sketch the ^{19}F-NMR spectra of mer-$[RhCl_3F_3]$ isomer where $J_{Rh\text{-}F} > J_{FF}$ and ^{103}Rh (I= ½) and ^{19}F (I= ½) and explain. 3

(d) Briefly discuss the ^{31}P-nmr and ^{19}F-nmr spectra of compound PCl_2F_3. 3

(e) Predict the number and multiplicity of ^{31}P-nmr signals of $[Rh(PPh_3)_3Cl]$ (where ^{103}Rh , I= ½). 2

UNIT-IV

7. (a) Explain isomer shift in Mossbauer spectroscopy. How does it help to determine the valency of an element? 3+2=5

(b) In Mossbauer experiment, a source emitting at 14.4 KeV (3.48 ´ 1018 Hz) has to be moved towards absorber at 2.2 mm s^{-1} for resonance. Find out the shift in frequency between the source and absorber. 2

(c) Explain why the high spin complexes of Fe^{2+} always show a doublet and the low spin complexes of Fe^{2+} show a doublet only when the ligands are non-equivalent? 3

(d) ^{57}Fe has spin 3/2 and 1/2 in its excited and ground states, respectively. How many lines will the gamma ray spectrum split if there is no electric field gradient at the