11. Answer ***any five*** questions : $2\frac{1}{2} \times 5$

a) What do you mean by ORD ?

b) Discuss the nature of CD spectra of (–) Menthone is different solvents.

c) How can different isomers of tris(s-alaminato)cobalt(III) complex be isolated ?

d) Explain with one specific example, how the position of a functional group of a molecule be determined using CD.

e) What is LASER Raman spectroscopy ?

f) What are the advantages of Raman spectroscopy over Infrared spectroscopy ?

M. Sc. Chemistry Examination, 2017

(3rd Semester)

Analytical Chemistry Special

Paper - XII - A

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each group.

UNIT - A-3121-a

1. Explain why $J_{^{13}C-H}$ coupling constants of $-CH_2-$ moiety in $(C_6H_5)_2CH_2$ and $(CH_3)_2CH_2$ differ from their corresponding carbonium ions. 2

2. a) How could you identify all the possible isomers of the compound $SnF_4(base)_2$ from their NMR spectra ?

   b) Describe in detail the ^{19}F NMR spectrum of XeF_4. 3+2

3. Starting from Bloch equation derive the required relation between FID signal and T_1 that can be applied in determining longitudinal relaxation time (T_1). Describe in detail the Inversion Recovery (IR) method. 2+2

4. Comment on any one of the followings :

   a) ^{31}P NMR of P_4S_3.

   b) ^{19}F NMR of HPF_2. $1\frac{1}{2}$

UNIT - A-3121b

5. Why Mössbauer spectrum of ^{57}Fe often appear as doublet ? 1

6. Deduce the required relation between quadrupole coupling constant and radiofrequency applied to observe NQR spectrum of CH_3D molecule. 4

7. Describe how NQR spectroscopic technique can be applied to detect explosive or narcotic substances. 3

8. Complexes of composition FeX_2 $(pyridine)_2$ may be monomeric with four coordination or polymeric with six coordination in case of Fe. From the data given below for X = Cl and I, giving proper reason, deduce which one is polymeric.

Complex	IS/mms^{-1}	QS/mms^{-1}	
$FeCl_2(Py)_2$	1·21	1·25	
$FeI_2(py)_2$	0·86	1·33	3

9. What is meant by hyperfine coupling ? Give example. $1\frac{1}{2}$

UNIT - A - 3122

10. a) What makes a molecule Raman active ? Using classical theory, explain the occurrence of Stokes and anti-Stokes Raman scattering.

    b) The equilibrium vibration frequency of the iodine molecule (I_2) is 215 cm^{-1}, and the anharmonicity constant (x) is 0·003 ; what, at 300 K, is the intensity of the 'hot band' ($v = 1 \rightarrow v = 2$ transition) relative to that of the fundamental ($v = 0 \rightarrow v = 1$) ?

    c) How will you prove the occurrence of linkage isomerism in $[Ru(dmso)_6]^{2+}$ (dmso = dimethylsulfoxide) with the help of IR spectroscopy ?

    d) Taking υ_{CO} as a probe, how will you monitor the oxidative addition reaction in Vaska compound ?

    e) The symmetrical stretching mode of CO_2 is Infrared inactive but Raman active. Explain.

    f) Justify the infrared stretching frequencies observed for the following isoelectronic species :

    $[Mo(CO)_6]^+$: 2090 cm^{-1}

    $[Cr(CO)_6]$: 2000 cm^{-1}

    $[V(CO)_6]^-$: 1858 cm^{-1}

$3+2+2+2+1\frac{1}{2}+2$