

M. Sc. CHEMISTRY EXAMINATION, 2018

(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 unit.

UNIT - A - 3121a

1. a) How could you identify the possible isomers of $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}_3]$ from their ^{31}P NMR spectra ?
[^{103}Rh ; $I = \frac{1}{2}$] 3
- b) Draw the ^{19}F NMR spectrum you would expect to observe for TeF_4 and give proper explanation of your drawing. [^{125}Te , $I = \frac{1}{2}$] 2
- c) i) What is meant by nutation ?
ii) Explain why variation of waiting time between π and $\frac{\pi}{2}$ pulse is necessary for measurement of spin-lattice relaxation time.
iii) Write down the pulse sequence applied in Inversion Recovery method. 1+3+ $\frac{1}{2}$

[2]

- d) ^{19}F NMR spectrum of ethanolic solution of TiF_4 features only a singlet at 0°C , which on cooling to a temperature -30°C undergoes splitting into two triplets.

Elucidate the structure of the Ti complex formed at the above stated temperatures [For ^{48}Ti , $I = 0$] 3

[5]

4. a) How plane polarized light changes its behaviour in presence of chiral molecule ? Which spectroscopic technique(s) can be used to study the asymmetry in a molecule ? 3
- b) Diastereoisomers exhibit opposite CD spectra but they are not exact mirror image of each other. Justify this statement taking an example of inorganic metal complex. 2
- c) Discuss axial haloketone rule using one suitable xample. Why this rule is not applicable in case of fluorine. 3
- d) Discuss the wave theory for the mechanism of normal Raman scattering. 3
- e) How many $\nu_{\text{M-Cl}}$ bands are expected in the infrared spectrum for the *cis*- and *trans* isomers of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]$? $1\frac{1}{2}$

[4]

UNIT - A - 3122

Answer the following questions

3. a) Why are the Stokes lines in the vibrational Raman spectrum of a molecule being more intense than anti-Stokes lines? 2
- b) The selection rule for pure rotational spectrum of a diatomic molecule is $\Delta J = \pm 1$, while that of the rotational Raman spectrum is $\Delta J = \pm 2$. Suggest a reasonable explanation for the observation. $1 \frac{1}{2}$
- c) The symmetrical stretching mode of carbon dioxide is infrared inactive but Raman active, but reverse is true for its asymmetric stretching mode. Provide suitable explanation in favor of the experimental fact. 2
- d) Using IR data, how will you prove the occurrence of Jahn-Teller distortion in $[\text{Mn}(\text{dmsO})_6]^{3+}$ (dmsO = dimethylsulfoxide)? 2
- e) ν_{NO} stretching frequencies of $[\text{M}^{11}(\text{CN})_5\text{NO}]^{2-}$ (M = Fe, Ru, and Os) are respectively 1938, 1927, and 1905 cm^{-1} ... Rationalize the trend. 2
- f) The fundamental and first overtone transitions of $^{14}\text{N}^{16}\text{O}$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1} , respectively. Evaluate the equilibrium vibration frequency, the anharmonicity and the force constant of the molecule.

3

[3]

UNIT - A - 3121b

2. a) 'Electrical moment, not magnetic moment of nucleus is relevant in NQR spectroscopy' – Elaborate the statement. $2 \frac{1}{2}$
- b) 'State and explain the important results of EPR investigation of $[\text{Cu}(\text{O-phen})\text{Cl}_2]$ (O-phen = 1, 10 phenanthroline) in pure lattice and doped with $[\text{Zn}(\text{O-phen})\text{Cl}_2]$.' 3

OR

- It has been suggested that PCl_3O reacts with TeCl_4 to give a simple adduct $\text{PCl}_3\text{O} \cdot \text{TeCl}_4$, however, with AlCl_3 to give an ionic product $\text{PCl}_2\text{O}^+ \text{AlCl}_4^-$. How could you establish this by NQR spectroscopy? 3
- c) The cation $[\text{Co}\{\text{P}(\text{OMe})_3\}_5]^+$ is isoelectronic and isostructural with $\text{Fe}(\text{CO})_5$. Explain why it gives a three-line NQR spectrum. [^{59}Co ; $I = 7/2$] 3
- d) Derive the energy level diagram for ^{127}I in NQR spectrum of CH_3I and show how the quadrupole coupling constant (e^2Qq) of ^{127}I can be determined from NQR spectrum. [^{127}I ; $I = 5/2$; Natural abundance 100%] 2+2

[Turn over