

Roll No.

24/12/19(M)

Total Pages : 4

239303

December, 2019

M.Sc. (CHEMISTRY) - III SEMESTER

Analytical Techniques (CH-303A)

Time : 3 Hours]

[Max. Marks : 75

Instructions :

- 1. It is compulsory to answer all the questions (1.5 marks each) of Part-A in short.*
- 2. Answer any four questions from Part-B in detail.*
- 3. Different sub-parts of a question are to be attempted adjacent to each other.*

PART - A

1. (a) Define photo electric effect. (1.5)
(b) What is the significance of Koopman's theorem? (1.5)
(c) Define Zero field splitting. (1.5)
(d) How the values of 'g' vary in case of Frozen solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (aq.)? (1.5)
(e) What do you understand by term Berry psuedorotation? (1.5)

239303/80/111/473

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- (f) What is the reason for satellite peaks in case of NMR spectroscopy? (1.5)
- (g) How colorimetry differs from spectrophotometry? (1.5)
- (h) Draw the ^{19}F -NMR splitting stick diagram for BF_4^- -ion. ($I_{\text{B}}^{10} = 3$, $I_{\text{B}}^{11} = 3/2$, $I_{\text{F}}^{19} = 1/2$). (1.5)
- (i) How MB spectra varies with change in oxidation state for Sn(II) and Sn(IV) complexes? (1.5)
- (j) What do you understand by term mutual exclusion principle? (1.5)

PART - B

2. (a) Derive the fundamental modes of vibration for NH_3 molecule using group theoretical approach and assign the IR and Raman modes (character table is given at the end of the question paper). (10)
- (b) Discuss the application of Raman spectroscopy for the study of active sites of metalloproteins. (5)
3. (a) Discuss the principle of Hollow cathode lamp used in AAS. Explain in detail how a solution of alkali metal halide can be detected using this technique? (8)

(b) Give a detailed account of various interferences involved in different types of absorption spectroscopy. (7)

4. (a) How Double resonance techniques can be used to decouple the spectra in case of NMR spectroscopy and in reduction of hyperfine splitting in case of EPR spectroscopy? (10)

(b) Explain the usage of beta-diketone complexes of lanthanides in Inorganic NMR spectroscopy. (5)

5. (a) How does the isomer shift of a series of related compounds changes when electronegativity of ligands is varied? Is the trend same for all Mossbauer isotopes? (7)

(b) Discuss how the MB spectra of SnX_4 halides differ from each other where X is F, Cl, Br & I. (8)

6. (a) How ^{19}F NMR can be used to conclude that SF_4 has a C_{2v} point group? (5)

(b) Compare the fine splitting and Hyperfine splitting in case of $\text{CH}_3\cdot$ radical in ESR spectroscopy. Explain the cause of each type of splitting. (5)

(c) Explain the number of lines obtained in case of $\text{Ti}(\text{H}_2\text{O})_4(\text{NH}_3)_2]^{2+}$ according to Drago's rule in ESR spectroscopy. (5)

7. (a) Discuss the factors affecting the core chemical shift of an atom in XPS. How and why the XPS spectra shows shift in case of CH_4 , CO_2 and CF_4 ? (8)

(b) Explain the Jahn-Teller effect in copper (II) octahedral complexes is described in EPR spectroscopy. (7)

Character Table of C_{3v} point group.

C_{3v}	E	$2C_3$	$3\sigma_v$			
A_1	1	1	1	z	$x^2 + y^2, z^2$	$z^2, x(x^2 - 3y^2)$
A_2	1	1	-1	R_z		$y(3x^2 - y^2)$
E	2	-1	0	(x, y), (R_x, R_y)	$(x^2 - y^2, xy)(xz, yz)$	$(xz^2, yz^2), [xyz, z(x^2 - y^2)]$