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End Semester Examination of Semester–III, 2015
Subject : CHEMISTRY (PG)
Paper : CEM–301 (Inorg. Spl.) (Th)
Full Marks : 40
Time : 2 Hrs

The figures in the margin indicate the marks corresponding to the question

Candidates are requested to give their answers in their own word as far as practicable.

Illustrate the answers wherever necessary.

Attempt **one question** from each unit.

Unit–I

1. a) Work out the representations of vibrational modes of BF_3 (D_{3h}) molecules. Indicate IR and Raman activity of the vibrational modes. (Use D_{3h} character Table) 4

Given below the character table for D3h point group:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	–1	1	1	–1	R_x	
E'	2	–1	0	2	–1	0	(x,y) (T_x, T_y)	(x^2-y^2, xy)
A''_1	1	1	1	–1	–1	–1		
A''_2	1	1	–1	–1	–1	1	(Z, T_2)	
E"	2	–1	0	–2	1	0	(R_x, R_y)	(xz, yz)

b) Based on Group Theoretical principle derive Laporte selection rule for electronic transition between the states. 3

c) Using "Symmetry Based Selection Rules" for cyclisation reactions proposed by Wood ward and Hoffmann prove that 4n π-electron system of olefins undergo cyclic addition reaction in presence of light. 3

2. a) "A d^2 electronic configuration is placed in an octahedral environment". Work out splitting pattern and possible transitions in the weak field. 6

OR

First excitate states of the normal modes for trans-$[Co(en)_2cl_2]^+$ are $2A_1g$, B_1g, B_2g, Eg, $2A_2u$, B_1u, 3Eu. The single crystal polarised spectra of the complex show two different spectra–three transitions along (x, y)-polarisations while two transitions along z-polarisations. Explain the spectral features. 6

b) Using projection operations construct SALCS of $BF_3(D_{3h})$ and assign the hybridisation to central B atom. 4

Unit–II

3. a) Compute total VEC and assign the probable structure-category and geometry to (i) $Os_5C(Co)_{15}$ and (ii) $[Os_8(Co)_{22}]^{2-}$. 3

b) Write down the principle of NQR spectroscopy. What are its limitations? How does NQR spectroscopy propose the structure of the molecule? 4

c) Write happens when pyrazine is added to refluxing alcoholic solution of $Rucl_3$ followed by the addition of excess of ammonia? Comment on the structure, spectra and magnetic property of the complex. 3

4. a) Explain the metat metal bonding in $[Re_2Cl_8]^{2-}$. Give one experimental evidence in favour of your proposal. 4

b) An ammoniacal medium of $RuCl_3$ is exposed to air for a week with inter mitant addition of ammonia solution (for evaporations of ammonia). A red precipitate appears which shows very long wavelength (>1500 nm) high intense transition. Write the structure of the complex, explain high intense long wavelength transition. 3

c) If two peaks separated by 0.4 ppm on a spectrometer operating at 600 MHz. What is the resonance frequency difference? 1

d) What is the observed ^1H NMR spectrum for $K^+BH_4^-$ dissolved in D_2O? [^{11}B(80%), I = 3/2; ^{10}B(20%), I = 3]. 2

Unit–III

5. a) Explain: In PF_5 and PF_4Me all Fs are indistinguishable by ^{19}F NMR study but PF_3Me_2 shows different behaviour. 3

b) Temperature dependent ^1H NMR spectra of $(Ph_3As)_2Cl_2Ph(C_4H_7)$ shows signals at 3·74 and 4·24 ppm collapse at 60^0C while at 15^0C two signals are well defined. Comment on the structural features of the complex. 4

c) Using ^{31}P NMR spectra define the structures of H_3PO_3, H_3PO_2 and P_4S_3. 3

6. a) What do you mean by $^{13}C\{^1H\}$ symbolism? What is the technique involved in this process? How many difference spectral lines are obtained for a sigma bonded C_6H_5 ligand in $^{13}C\{^1H\}$ NMR spectrum? 3

b) Explain the ^1H NMR spectrum of $Sn(CH_3)_4$ [^{117}Sn(7.6%), I = ½; ^{119}Sn(8.6%), I = ½] 4

c) Explain the nature of adduct formation between AsF_3 and SO_3 using NMR spectra.] 3

Unit–IV

7. a) Give plots of (i) χ_M vs T and (ii) $1/\chi_M$ vs T for ferro, antiferro and ferromagnetic substances. 3+3

b) Define intensity of magetization, magnetic induction, magnetic permeability and magnetic susceptibility. 4

8. a) Explain why the equilibrium constant for addition of alkene to Vasca's compound are – (i) 1 for $CH_2=CH_2$, (ii) 1400 for (CN)CH=CH(CN) and (iii) 140000 for $(CN)_2C=C(CN)_2$? 4

b) What is mixed valence compound? Give an example. 2+1

c) Most quadruple bonded species are vividly coloured – why? 3