

CHEMISTRY 341 FINAL

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Answer all questions in the booklet(s) provided. A point group flow-chart, character tables, appropriate Tanabe-Sugano diagrams and a periodic table are supplied. Please write your name on each booklet used. You may use a calculator and a model kit to assist you. You have 3 hours.

[14] Question 1

The free atom beryllium (Be) has the ground-state electron configuration [He] $2s^2$. If one promotes an electron into the 2p orbital we obtain the excited-state configuration of [He] $2s^1 2p^1$.

- a) What is the ground-state term for Be? (2 marks):
- b) Using an M_L versus M_S table, determine all the microstates that correspond to the excited state configuration. (6 marks):
- c) Determine the excited-state terms from the microstates tabulated in b). (4 marks):
- d) Order your excited-state terms from lowest to highest energy. (2 marks)

[12] Question 2 (3 marks each)

- a) List all the allowed $d-d$ transitions you would expect to find in the electronic spectrum of an octahedral Ir(II) complex .
- b) The values of ϵ_{\max} for the most intense absorptions in the electronic spectra of $[\text{CoCl}_4]^{2-}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ differ by a factor of about 100. Comment on this and determine which complex would exhibit the larger value of ϵ_{\max} .
- c) In the electronic spectrum of a solution containing $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, the two lowest energy bands are observed at 17200 and 25600 cm^{-1} . No absorption for the ${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})$ transition is observed. Suggest a reason for this and assign the two observed absorptions.
- d) Why is the nephelauxetic parameter, β , significantly smaller for $[\text{CrI}_6]^{3-}$ than for $[\text{CrBr}_6]^{3-}$?

[10] Question 3

Use the supplied Tanabe-Sugano diagrams where necessary.

Label the following transitions as either: spin-forbidden, Laporte forbidden, Laporte allowed, ligand-to-metal charge transfer (LMCT) or metal-to-ligand charge transfer (MLCT). Choose the most *appropriate* label. There is only **one** label for each transition!

- i) $\text{CO}(\pi^*) \leftarrow \text{Fe}(3d\ t_{2g})$ _____
- ii) ${}^3E_u \leftarrow {}^3T_{1g}$ _____
- iii) ${}^4T_{1g} \leftarrow {}^2T_{2g}$ _____
- iv) ${}^4T_{1g} \leftarrow {}^4T_{2g}$ _____
- v) $\text{Au}(5d\ e_g^*) \leftarrow S^{2-}(\pi)$ _____

[10] Question 4

- a) Briefly discuss the principles involved in an electron paramagnetic resonance (EPR) experiment. (6 marks)
- b) Derive the splitting pattern (you do not need to fully draw it) and determine the number of lines in the EPR spectrum of $\text{Na}[\text{NbI}_5]$. (NOTE: for Nb, $I = 9/2$; for I, $I = 5/2$; and for Na, $I = 3/2$) (4 marks)

[12] Question 5 (4 marks each)

List all of the symmetry elements and determine the point group of:

- a) 1,2,4,5-tetrachlorobenzene b) $\Delta\text{-}[\text{Ru}(\text{en})_3]^{2+}$ c) IF_3

[9] Question 6 (3 marks each)

Determine the *symmetry label* for:

- a) the symmetric H-O-H stretching vibrational mode in H_2O
 b) the asymmetric H-O-H stretching vibrational mode in H_2O
 c) the asymmetric D-O-H stretching vibrational mode in DHO (partially deuterated water)

[14] Question 7

- What is the symmetry label of each SALC above under D_{3h} ? (Show how you determined it).
- What orbital or orbitals, if any, on the central atom is (are) of correct symmetry to combine with these SALC's?
- Which symmetry type(s) (of all symmetry types) in D_{3h} is (are) both IR active *and* Raman active.

[10] Question 8

An example of a linear 2-coordinate complex is $[\text{Ag}(\text{CN})_2]^-$.

- Draw and label (with the appropriate d orbital) the d-orbital splitting diagram for this complex and fill it with the appropriate number of electrons. (Remember that your z axis should correspond to your principal rotation axis!). (6 marks)
- Assuming $\text{V}(\text{CN})_2$ and $\text{Fe}(\text{CN})_2$ adopt the same structure and are low-spin, estimate their μ_{eff} . (4 marks)

[9] Question 9

- Draw the full structures of: (3 marks each)
 - cis, cis, cis* - diaquadiiododinitritopalladium(IV)
 - bis(ethylenediamine)chromium(III)- μ -chloro- μ -hydroxo-bis(ethylenediamine)cobalt(II) bromide
- Name the following: (3 marks)
 - $[\text{N}(\text{CH}_2\text{CH}_3)_4][\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (trans form)
(Note: $\text{C}_2\text{O}_4^{2-}$ = oxalate)