5.04 Principles of Inorganic Chemistry II
Fall 2008

100 points total

1. (**30 pts**) A Rydberg transition promotes an electron to an orbital of a principal quantum number greater than that of any occupied orbital of the ground state. Consider the nd(n+1)s Rydberg excited state of a d^2 ion. Construct the correlation diagram for the excited state in a D_{4h} crystal field. For determining the ligand field states from the free ion states, you may use the equations given in the lecture notes and reproduced here (but it is not necessarily the only way to deduce the ligand field states):

$$\chi(\alpha) = 2l + 1 \qquad \text{for } \alpha = 0$$

$$\chi(\alpha) = \frac{\sin\left(l + \tfrac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}} \qquad \text{for } \alpha \neq 0$$

2. (**30 pts**) Short answers.

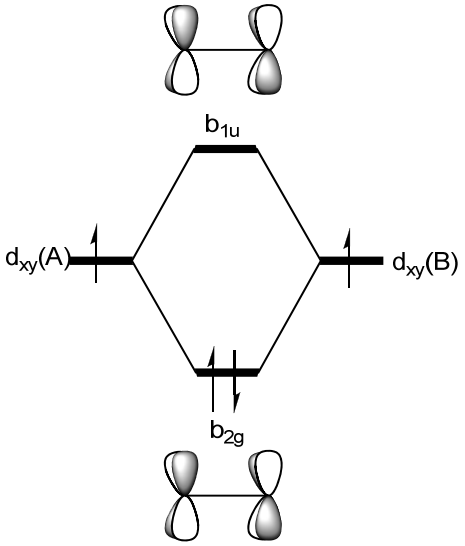
   a. (**5 pts**) Which ligand will be stronger field, $HC{\equiv}C^-$ or OH^-? Justify your choice.

   b. (**6 pts**) Is the ground state of $[CrCl_6]^{3-}$ subject to Jahn-Teller distortion? Explain why the $^4T_{2g}$ state (of $(t_{2g})^2(e_g)^1$ configuration) is subject to a Jahn-Teller distortion.

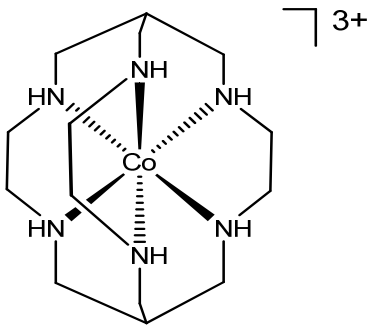
c. (**4 pts**) Under pressure, $10Dq$ of $[CrCl_6]^{3-}$ increases. Why?

d. (**5 pts**) In the lowest energy d-d excited state, $[Ni(CN)_4]^{2-}$ undergoes a $D_{4h} \rightarrow D_{2d}$ distortion. Explain.

e. (**10 pts**) List the four states that arise from two electrons residing in two d_{xy} orbitals in a D_{4h} ligand field. The MO diagram with molecular orbital symmetries is given below.



3. (**40 pts**) The $Co(sep)_3^{3+}$ is called a sephulcrate, first synthesized by Alan Sargeson at the Australian National University.



Two absorption bands arising from spin-allowed ligand field transitions are observed for this complex. Assign these transitions by using the $d^6(O_h)$ Tanabe-Sugano diagram. Predict the energies of the corresponding spin-forbidden triplet transitions.