Chemistry 734b 2008
Problem Set 6 Due: Tuesday April 15, 2008.

1.) a) If a deuteron is substituted for one of the protons in methane (CH_4, T_d point group) one obtains the C_{3v} molecule CH_3D. Show that the molecule has six fundamentals, three of species A_1 and three of species E, and that all theses fundamentals are both ir and R active.
b) The normal modes of CH_4 are $\Gamma_{vib} = A_1 \oplus E \oplus 2T_2$. Construct a correlation table between these states in T_d and those in C_{3v}. You should get the same answer as in part a).

2.) Derive all the Russell- Saunders terms ($^{2S+1}L_J$; including parity) for the following configurations.
a) (np n'p n"p), (n, n', n" are different principal quantum numbers)

b) (ns np nd nf)

3.) Derive the both Russell-Saunders ($^{2S+1}L_J$; including parity) and j-j coupling atomic terms for a (nd nf) configuration. In j-j coupling the states are simply labelled as J_{parity}. Spin multiplicities have no meaning as the spin orbit interactions couples them with the l's to make j's. The number of J states and their values should be the same regardless of the coupling scheme. Their energies however, could be very different.

4.) Consider the $Mo(CN)_8^{3-}$ and $Mo(CN)_8^{4-}$ ions which both have D_{2d} symmetry.
a) For both ions determine the charge on the Mo ion, and therefore, how many d-electrons are involved in electronic transitions; that is, find d^n for each molecule.
b) In D_{2d} symmetry the energy of the d-orbitals are ordered (in a crystal field sense) as: $E(d_{x2-y2}) < E(d_{z2}) < E(d_{yz}, d_{xz}) < E(d_{xy})$. Use the D_{2d} character table to establish the irreducible representations for each d-orbital.
c) For each ion establish the electronic configuration and possible symmetry allowed d ← d transitions. *(Keep in mind if necessary, all possible spin multiplicities).*
d) What normal mode symmetries are required to make the symmetry forbidden transitions vibronically allowed?