Chemistry 208—Spring 2009 **Problem Set 4**
Professor K. N. Raymond **Due 03/04/2008**

1) Indicate which species below (if either) will have a larger atomic scattering factor (*f*), and provide a short rationale for your choice.
   a) Ca^0 or Sr^0
   b) Fe^{2+} or Fe^{3+}
   c) Mg^{2+} or Na^+
   d) ^{12}C or ^{13}C

2) For each of the systematic absences listed below, indicate the symmetry element indicated. Provide proof that this element of lattice symmetry provides the indicated systematic absences (Massa **6.6.2** can provide a model if these directions are unclear).
   a) *h00*, $h = 2n$.
   b) *0k0*, $k = 4n$.
   c) *hk0*, $k = 2n$.
   d) *hkl*, $h + k = 2n$.

3) The X-ray diffraction intensities for MgO and NaF have *extremely* low intensities for all *hkl* ***except*** *h*, *k*, *l* all even. Explain. Which compound should have these faint spots be brighter, and why?

4) The compound $Ir[PPh_2Me]_4BF_4$ [Clark, Skelton & Waters (1975). *J. Organomet. Chem.* 85, 375-394] was reported to crystallize in the space group *C*2/*c* with the cell constants [a = 36.805, b = 22.93, c=21.676, β=121.41 ° , Z=12. It can alternatively described with the alternate cell choice of $R\bar{3}c$. The transformation matrix which accomplishes this is:

$$\begin{pmatrix} 0 & 1 & 0 \\ 1/2 & 1/2 & 1 \\ 1 & 0 & -1 \end{pmatrix}$$

   a) Write the equations which describe the new cell vectors in terms of the C2/c lattice vectors.
   b) Does the new space group ($R\bar{3}c$) have systematic absences which did not appear in the prior space group? Are there systematic absences from C2/c which disappear? Explain any discrepancies clearly.

5) The compound $U(C_8H_8)_2$ shows 2/m symmetry in its diffraction photographs and the systematic conditions: *h*0*l*, $h + l = 2n$; 0*k*0, $k = 2n$. The cell constants are a = 7.084, b = 8.715, c = 10.631 Å, and β = 98.75°. A density of 2.0 to 2.5 would be reasonable for a compound with this chemical formula.
   a) Calculate the volume and the number of molecules per unit cell.
   b) Identify the symmetry operations which are implied by the systematic absences.
   c) Name the space group based on your answer to (b). [Identify any other symmetry operations for the space group which do not appear in your answer to (a).]
   d) Is there any symmetry imposed on the molecule? If so, what does this imply about the structure, especially the relative orientations of the C_8H_8 rings?
   e) Calculate the closest uranium to uranium distance within the cell.
   f) All of the diffraction maxima which correspond to $h + k + l = 2n + 1$ are very weak, often to the point of not being observable. Explain.