Chemistry 851 ***Problem Set 4***

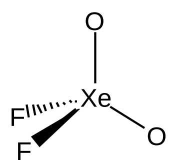
(1) Use VSEPR theory to predict the structures (and point group) and then identify and predict the number and symmetries of the normal modes of vibration for the following molecules. In each case, determine whether the modes are IR and/or Raman active.

(a) BF_4^- (b) ClNO

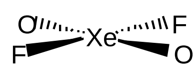
(c) XeO_3 (d) ClF_3

(e) SF_4

(2) Consider the molecule XeO_2F_2 in two possible geometries. Structure I has the F's and O's at the apices of a tetrahedron. Structure II consists of a trans-planar arrangement of the five atoms.



I



II

(a) Determine the symmetries for the normal modes for II.

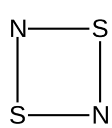
(b) Which modes from (a) are IR active? Which are Raman active?

(c) Assume that you know that tetrahedral CH_4 has normal modes of vibration of A_1, E, and $2T_2$ symmetry. The point group of geometry I is a subgroup of T_d. Determine the symmetries of the normal modes of vibration for I.

(d) Which modes from (c) are IR active? Which are Raman active?

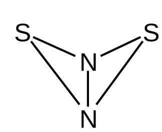
(e) A total of 7 modes are observed in the IR spectrum. Is I or II the correct structure for the molecule?

(3) Heating the cage molecule S_4N_4 leads to an interesting metallic polymer $(SN)_x$ which is highly conducting. An intermediate in this thermal reaction is S_2N_2. How would you attempt to determine the correct structure of S_2N_2 using IR and Raman data? The two structures that I wish you to consider are shown below.



A

square planar
all angles 90°
all distances equivalent



B

puckered butterfly structure
(N-N is the backbone, S atoms
are the wingtip atoms)

(4) Consider the D_{2h} molecule C_2H_4.

(a) Derive Γ_{vib} for the molecule and reduce it.

(b) Using appropriate internal coordinates, derive the irreducible representations that correspond to the stretching modes of the molecule.

(c) Use projection operators to express the stretching modes in terms of changes in internal coordinates.

(d) Use internal coordinates to derive the representations spanned by the in-plane bending modes. Are there any spurious representations?

(e) Use projection operators to express the in-plane bending modes in terms of changes in the internal coordinates. What constraints led to the spurious modes you found in part (d)?

(f) Repeat parts (d) and (e) for the out-of-plane modes.