Problem Set 16
on Applications of Symmetry to the Vibrations of Polyatomic Molecules

Of the 3N degrees of freedom of a molecule containing N atoms, 3 are translations of the center of mass, 2 (if linear molecule) or 3 (if non-linear) degrees of freedom correspond to rotations and the remaining 3N-6 (or 3N-5 for linear) degrees of freedom are vibrations. Since this is the case, one could find the symmetry of the vibrational degrees of freedom by starting with the 3N Cartesian displacement vectors x,y,z displacements at each nuclear position as the *basis for a reducible representation*. Out of these 3N, the translations will transform as X,Y, and Z. The rotations will transform as R_x, R_y, R_z. The 3N-6 remaining *irreducible representations* are then the *symmetry species* of the vibrational modes. Thus, it is possible to determine entirely from *point group symmetry* of a molecule what *symmetry species* its vibrations belong to. The nature of the coordinates which are involved in each of these vibrational modes can also be determined. This time, we need to use as *bases for the reducible representations* the internal displacement coordinates such as bond stretch such as r_i, bond angle deformation such as β_i and torsion angles ϕ. Find the *reducible representation* for which the Cartesian displacements form a basis, remove translations and rotations. Find the IR and Raman allowed vibrations. To find the nature of the normal modes, find symmetry coordinates (*symmetry adapted linear combinations* of bond stretches, angle deformations) by generating them with a *projection operator* for the desired *symmetry species*.

1. (a) By applying symmetry operations on Cartesian displacement vectors, determine the vibrational modes of thioformaldehyde $H_2C{=}S$, a planar molecule which is an analog of formaldehyde. For the sake of uniformity, put the z axis through C=S and make the yz plane the plane of the molecule.

   (b) What are the internal coordinates of thioformaldehyde. Find out which of the stretches and in-plane bond angle distortions contribute to each of the modes.

   (c) Which of these modes are IR allowed, which are Raman allowed?

2. Consider the ethylene molecule: Let R be the CH equilibrium bond length, and D the CC equilibrium bond length. Let the displacements from equilibrium be designated r_1, r_2, r_3, r_4, d, respectively, for the C-H_1, C-H_2, C-H_3, C-H_4 (numbered in a clockwise order around the center of the molecule), C-C, distances. Let β be the in-plane angle deformation from the equilibrium C-C-H angle, let γ be the out-of-molecular-plane angle, and let ϕ be the torsion angle.

Verify that the vibrational modes are:
three totally symmetric (A_{1g}) in-plane modes involving the CH and CC symmetric stretches
other in-plane modes : two B_{1g} , two B_{2g} , two B_{3g}
out-of-plane modes: B_{2g} A_u B_{1u}

The symmetry coordinates for A_{1g} modes can be written down easily *by use of projection operators*:

$$S_1 (A_{1g}) = (r_1 + r_2 + r_3 + r_4)/2$$
$$S_2 (A_{1g}) = d$$
$$S_3 (A_{1g}) = [RD/4]^{½} (\beta_1 + \beta_2 + \beta_3 + \beta_4)$$

By using projection operators, find the symmetry coordinates for all other modes.

3. Given the following formula types. In each case the letter X, Y, or Z represents an atom type.
XY_3 trigonal (such as BF_3)
XY_3 pyramidal (such as NH_3)
XY_3 T-shape (such as ClF_3)
X_2Y_2 trans planar
X_2Y_2 cis planar
XY_4 square planar
YXZ_3 (such as CHF_3)

Find the symmetry species of the vibrational modes. Assign them to infrared-allowed, Raman-allowed, active in both IR and Raman, and inactive.