Chemical Physics Cumulative Examination October 18, 2004

1. (20 points) The symmetry of a molecule can be described in terms of five types of symmetry elements. Define these five symmetry elements and their associated operators.

2. (8 points) What constitutes the point group of a molecule?

3. (12 points) Which point group do each of the following molecules belong to?

$$CH_2Cl_2 \ , CH_3Cl \ , C_2H_4(ethene) \ , SO_3 \ , C_6H_6(benzene) \ , CH_4$$

4. (12 points) What are the four criteria for a set of operators to form a group?

5. (8 points) Given the matrices

$$\hat{C}_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} , \hat{\sigma}_V = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} , \hat{\sigma}_V^{'} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} , \hat{\sigma}_V^{''} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

Show that

a. $\hat{\sigma}_V \hat{C}_3 = \hat{\sigma}_V^{''}$
b. $\hat{C}_3 \hat{\sigma}_V = \hat{\sigma}_V^{'}$
c. $\hat{\sigma}_V^{''} \hat{\sigma}_V^{'} = \hat{C}_3$
d. $\hat{C}_3 \hat{\sigma}_V^{''} = \hat{\sigma}_V$

6. (10 points) The water molecule belongs to the C_{2V} point group. Construct the multiplication table for C_{2V}.

7 (10 points) The molecular orbitals of a molecule have the symmetry of one of the irreducible representations of the molecular point group. What is the symmetry of each of the occupied molecular orbitals of the water molecule?

8 (10 points) Suppose the characters of a reducible representation of the C_{2V} point group are $\Gamma = 27, \ -1, \ 1, \ 5$. Determine how many times each irreducible representation of C_{2V} is contained in Γ.

9 (10 points) Using Group Theory, determine the symmetries of the normal modes of vibration of the water molecule.

Useful information

Character Table of the C_{2V} point group

C_{2V}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_V$	$\hat{\sigma}_V'$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

$$a_i = \frac{1}{h}\sum_{\hat{R}} \chi(\hat{R})\chi_i(\hat{R}) = \frac{1}{h}\sum_{classes} \eta(\hat{R})\chi(\hat{R})\chi_i(\hat{R})$$

$$\sum_{classes} \eta(\hat{R})\chi_j(\hat{R})\chi_i(\hat{R}) = \delta_{ij}$$

$$\sum_{j=1}^{N} d_j^2 = h$$

$$\chi(\hat{R}) = \sum_j a_j \chi_j(\hat{R})$$