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Chemistry 483 Exam 4 December 5, 2008

1. (50 points) define and/or characterize

a. The 5 symmetry elements

E, σ, $\hat{i}$, $\hat{S}$, $\hat{C}_N$

b. Degrees of freedom

We require $3N$ coordinates to specify the location & orientation of a molecule. We say that the molecule has $3N$ degrees of freedom.

c. Rotation reflection operator

$\hat{S}_N$; rotate through $\frac{2\pi}{N}$ degrees & reflect through the σ_h plane.

d. Normal coordinate

the set of coordinates that allow the potential energy for vibrational motion to be written as

$$\Delta V = \frac{1}{2} \sum_{j=1}^{N_V} f_j Q_j^2$$

e. Trace of a matrix

The sum of the diagonal elements

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f. Centrifugal distortion

When a diatomic molecule undergoes a transition from $v=0$ to $v=1$ its bond length increases & $\tilde{B}_1$ is $< \tilde{B}_0$. This effect is called centrifugal distortion.

g. Selection rule

constraints on the allowed changes of quantum numbers when absorbing or emitting a photon. For vibration $\Delta v = \pm 1$, for rotation $\Delta J = \pm 1$

h. Transition dipole

$$\mu_{if} = \int \psi_i \vec{\mu} \psi_f \, dV$$

i. Rotation matrix

relates the coordinates of a point in one coordinate system to those in a rotated coordinate system. For two dimensions $\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$

j. Basis for an irreducible representation

For 1 dim. A function ψ which is an eigenfunction of the symmetry group operator $\hat{R}\psi = \chi_i(R)\psi$

For irreducible representations of dimension 2 or higher the representation of the operator in this basis are the irreducible representation matrices.

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2. (25 points) The SO_2 molecule has C_{2v} symmetry. Suppose the molecule is in the yz plane with S at the origin and the two O atoms at $(0, \pm y_0, z_0)$. Use the p_x orbitals on S and the two O atoms as a basis and

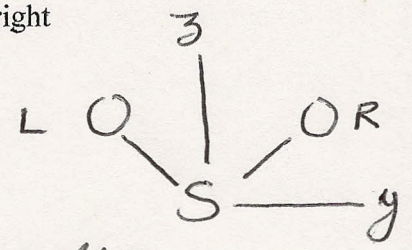
a. determine the representation matrices of C_{2v}.

b. what are the characters of this representation?

c. what irreducible representations are contained in this reducible representation?

d. if we denote the p_x orbitals on the O atoms as p_L and p_R for left and right respectively what irreducible representations does $p_L + p_R$ belong to?

e. what irreducible representation does the p_x orbital on S belong to.



a. First we need to order the basis

For example $\begin{pmatrix} x_L \\ x_R \\ x_S \end{pmatrix}$ x_L = Px on Left O

x_R = Px on right O

x_S = Px on S

Then $E = \begin{pmatrix} 1&0&0 \\ 0&1&0 \\ 0&0&1 \end{pmatrix}$; $C_2 = \begin{pmatrix} 0&-1&0 \\ -1&0&0 \\ 0&0&-1 \end{pmatrix}$; $\sigma_v = \begin{pmatrix} 0&1&0 \\ 1&0&0 \\ 0&0&1 \end{pmatrix}$; $\sigma_v' = \begin{pmatrix} -1&0&0 \\ 0&-1&0 \\ 0&0&-1 \end{pmatrix}$

b. $\chi =$ 3 −1 1 −3

Note; if we wrote basis as $\begin{pmatrix} x_L \\ x_S \\ x_R \end{pmatrix}$ we get

$E = \begin{pmatrix} 1&0&0 \\ 0&1&0 \\ 0&0&1 \end{pmatrix}$; $C_2 = \begin{pmatrix} 0&0&-1 \\ 0&-1&0 \\ -1&0&0 \end{pmatrix}$; $\sigma_v = \begin{pmatrix} 0&0&1 \\ 0&1&0 \\ 1&0&0 \end{pmatrix}$; $\sigma_v' = \begin{pmatrix} -1&0&0 \\ 0&-1&0 \\ 0&0&-1 \end{pmatrix}$

& $\chi =$ 3 −1 1 −3

So the order doesn't matter

c. $a_i = \frac{1}{4}\left(3 - \chi_i(C_2) + \chi_i(\sigma_v) - 3\chi_i(\sigma_v')\right)$

$a_{A_1} = \frac{1}{4}(3 - 1 + 1 - 3) = 0$ $a_{B_1} = \frac{1}{4}(3 + 1 + 1 + 3) = 2$

$a_{A_2} = \frac{1}{4}(3 - 1 - 1 + 3) = 1$ $a_{B_2} = 0$

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d. $\hat{E}(P_L + P_R) = +(P_L + P_R)$

$\hat{C}_2(P_L + P_R) = -(P_L + P_R)$

$\hat{\sigma}_v(P_L + P_R) = +(P_L + P_R)$

$\hat{\sigma}_v'(P_L + P_R) = -(P_L + P_R)$

$\Gamma = 1 \quad -1 \quad 1 \quad -1 \quad \therefore \boxed{B_1}$

e. as above $P_S \Rightarrow \boxed{B_1}$

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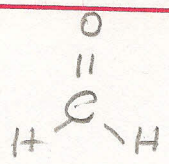
3. (25 points) Formaldehyde, H_2CO, has C_{2v} symmetry. How many normal modes of vibration does formaldehyde have? What are their symmetries? Which are IR active?

a. $3N-6 = 12-6 = 6$

b.



	E	$\hat{C}_2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
χ	12	-2	2	4

$$a_i = \frac{1}{4}\left(12 - 2\chi_i(C_2) + 2\chi_i(\sigma_v) + 4\chi_i(\sigma_v')\right)$$

$$a_{A_1} = \frac{1}{4}(12-2+2+4) = 4$$

$$a_{A_2} = \frac{1}{4}(12-2-2-4) = 1$$

$$a_{B_1} = \frac{1}{4}(12+2+2-4) = 3$$

$$a_{B_2} = \frac{1}{4}(12+2-2+4) = 4$$

From character table Translations are A_1, B_1, B_2

& Rotations are A_2, B_1, B_2

∴ remaining symmetries are vibrations

$$\boxed{3A_1,\ 1B_1,\ 2B_2}$$

They are all IR active.