Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
Second Semester 2016-2017
CHEM F244 Physical Chemistry - III
Mid-Semester Examination (Closed Book)

Time: 90 minutes **Date: 09.03.2017 (14.00 - 15.30 hrs.)** **Max. Marks: 75**

Instructions: Irrelevant writing for a question may lead to deduction of marks

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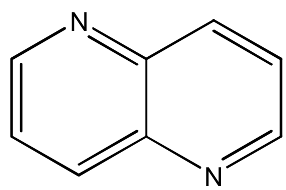
1 Answer the following questions which are based on the molecule as presented below:



(i) Determine all the symmetry operations possible for this molecule. **[2]**

(ii) What is the point group of the molecule? **[1]**

(iii) Using symmetry argument, comment on the dipole moment and optical activity of the molecule. **[1]**

(iv) Determine the number of classes present in the point group to which the above molecule belongs. What are the elements in individual classes? **[4]**

(v) What would be the dimension of the irreducible representations? **[2]**

(vi) Determine all the irreducible representations. **[2]**

(vii) Determine Mülliken symbol for each of the representation. **[2]**

(viii) Derive the irreducible representations for the coordinates x, y, and z. **[6]**

(ix) Determine the reducible representation considering all degrees of freedom. **[5]**

(x) Express rotational and vibrational motion of the molecule in terms of the irreducible representations of the point group. **[5]**

2 Consider OH_2 and cis-HYQ (Fig.1) molecules, those belong to C_{2v} point group.
{Character Table for C_{2v} point is provided in next page}

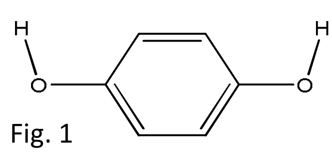


Fig. 1

Part A: For OH_2

The molecule is having three normal mode of vibrations: $\nu_1 = 3650$ cm^{-1}, $\nu_2 = 1595$ cm^{-1}, and $\nu_3 = 3756$ cm^{-1}. In general, we may represent any vibrational state using the quantum numbers (n_1, n_2, n_3) which are associated with the normal mode of vibrations, ν_1, ν_2, and ν_3, respectively. For example, a state represented by (p q r) means n_1 = p, n_2 = q, and n_3 = r. With this back ground information answer the following questions:

(i) Determine the value of zero point vibrational energy of OH_2. **[2]**

(ii) Determine the energy of (0 1 0) state. **[2]**

(iii) Determine the energy of the first overtone state. **[2]**

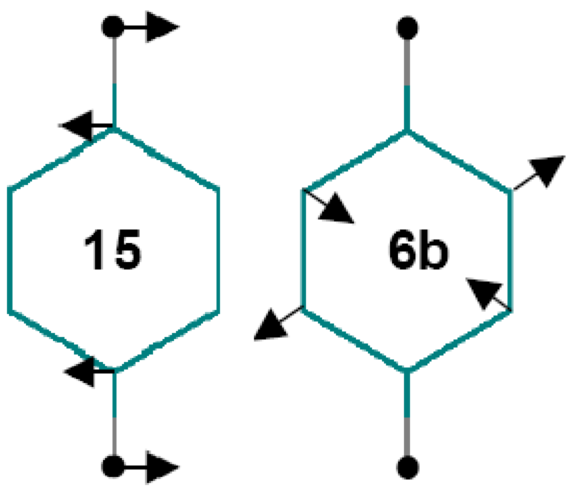
(iv) What would be energy of the first combination state? **[2]**

(v) What is the symmetry species of ν_1, ν_2, and ν_3 at v = 0 state? Explain your response. **[3]**

(vi) What would be the symmetry species of the two hydrogen atom 1s Atomic Orbitals of OH_2 molecule, if we consider a linear combination? **[3]**

(vii) **<u>Part B: For cis-HYQ</u>** **[16]**

Two vibrational modes, Mode-15 & Mode-6b, of cis-HYQ is described below:



Character Table for C_{2v} point group:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
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

Assume an experimental condition in which cis-HYQ molecules can be investigated under isolated condition. The experimental set-up is having two different types of spectrophotometers. The first one can record the pure vibrational spectrum in the ground electronic state and the second one is capable to record the vibrational transitions associated with electronic excitation.

Read the following two observations carefully:

(i) Mode 15 is observed both in pure vibrational spectrum and in S_0-S_1 electronic excitation spectrum.

(ii) Mode-6b is observed only in pure vibrational spectrum but is completely absent in S_0-S_1 electronic excitation spectrum.

Explain the above two observations with proper justifications.

3 (i) What would be the value of the following integral under C_{2v} symmetry, $\int x\,y\,z\,d\tau$. Justify your response. **[3]**

(ii) Derive the following expression for H_2 ground state using Molecular Orbital Theory. **[8]**

$$\rho_{MO} = \frac{1s_a^2 + 1s_b^2 + 2(1s_a\,1s_b)}{1 + S_{ab}}$$

(iii) Determine the value of ρ_{MO} at the mid point of the line joining the nuclei. **[4]**

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