**Birla Institute of Technology & Science, Pilani, Rajasthan 333 031**

**Second Semester 2019-2020**

**Course Number: CHEM F111 Course Title: General Chemistry**

**ASSIGNMENT 1 (Lecture No. 11 -16)**

**Q.1 (a)** (i) Write the ground state electronic configuration of He22+ molecule cation. (ii) Write the ground state wavefunction of the molecule (along with the spin parts). (iii) If the molecular orbitals are formed by linear combination of only the 1s orbitals of the two Helium ions, expand the spatial part of the ground state wavefunction in terms of the atomic orbitals and identify the terms corresponding to covalent and ionic interactions.

**(b)** Find the difference between the frequencies of first Strokes and anti-Stokes lines in rotational Raman spectrum of Li1H molecule if the average bond-length of the molecule in ground state is 1.68 Å and the mass of lithium is 6.94 amu.

**Q.2** **(a)** Consider a doubly excited state of H2 molecule corresponding to the electronic configuration, σu2. (i) Write the wavefunction of the molecule in this state and determine the bond order. (ii) If the molecular orbitals are formed by linear combination of only the 1s orbitals of the two Hydrogen atoms, expand the spatial part of the ground state wavefunction in terms of the atomic orbitals.

**(b)** Determine the frequency of the most intense line in the pure rotational spectrum of Li1H molecule if the average bond-length of the molecule in ground state is 1.68 Å and the mass of lithium is 6.94 a.m.u.

**Q.3** (a) If a normalized hybrid orbital is given by Фhybrid = csФ2s + cpФ2pz, then find the absolute values of the coefficients, cs and cp for the cases when, Фhybrid is (i) sp-hybridized (ii) sp2-hybridized (iii) sp3-hybridized.

(b) Find the number of normal modes of vibrations for each of the following and state how many of them are (I) IR active (II) Raman active:

(i) Acetylene (ii) Ethylene (iii) Toluene

**Q.4** (a) The sp2-hybrid orbitals of an atom are formed such that the density maxima of the hybrid orbitals lie on the XY-plane. The density maximum of the first orbitals lies along negative Y axis. Express the normalized hybrid orbitals in terms of the orthonormal pure orbitals.

**(b)** If Ф1 and Ф2 are normalized hybrid orbitals expressed in terms of orthonormal pure atomic orbitals, Ф2s , 2-1/2Ф2px and Ф2pz ; as:

Ф1 = N1( Ф2s + 21/2Ф2pz ) ; and Ф2 = N2( Ф2s + (3/2)1/2 Ф2px – 2-1/2Ф2pz ) ; find the normalization constants, N1 and N2 and check whether the hybrid orbitals are orthogonal with each other.

**Q.5 (a)** The first anti-Stokes line in the rotational Raman spectrum of H2 molecule occurs with wavenumber 364.99 cm-1 higher than the wavenumber of the incident radiation. Calculate the bond length (in picometer) of H2 molecule. (Given that the atomic mass of H-atom is 1.0079 amu)

**(b)** Which of the following compounds will show pure rotational spectra and rotational Raman spectra? (i) CH4 (ii) HCl (iii) H2

**Q.6 (a)** Particle on a sphere is a reasonable model for the description of the rotation of diatomic molecule. For a molecule 3H35Cl, a photon with a frequency 218.5 GHz brings about the transition from ground rotational energy level to the first excited rotational level. Given that the atomic masses of 2H, 3H and 35Cl are 2.015 amu, 3.016 amu and 35.45 amu, respectively. Consider that the bond length of 2H35Cl and 3H35Cl are same. (i) Determine the energy (in Joules) corresponding to the first rotational excited level of 2H35Cl. (ii) Will a photon of same frequency (218.5 GHz) result in the rotational excitation from ground level to first excited level in 2H35Cl? Explain in 1-2 sentences.

**(b)** Two normalized hybrid orbitals centred on C atom of H2C=CH2 are represented by:

and

**(i)** Calculate the values of A and B. Given that the atomic orbitals are orthonormal.

**(ii)** Do mention the plane, in which these orbitals exist.

**Q.7 (a)** From rotational spectrum of 1H35Cl, it has been observed that the level corresponding to J = 4 is the most populated level at 25°C. Based on this information, calculate separation between two adjacent Stokes or anti-Stokes lines in the rotational Raman spectrum of 1H35Cl and the internuclear distance in 1H35Cl.

**(b)** Arrange the following molecules in increasing order of the C=O stretching frequency in IR spectra. 

**Q.8 (a)** A wavefunction corresponding to one of the sp2 hybridized orbitals is . Determine the normalization constant of the wavefunction. Given that the atomic orbitals s, px and py are orthonormal.

**(b)** Determine number of normal modes of vibration for SO2 molecule and also comment on whether it will show rotational spectrum.

**(c)** Light of wavelength (λ) 2560 Å passes through a cell of path-length 1.0 mm containing a sample of 3.9 g of benzene in one litre of solution. The light intensity is reduced to 16% of its initial value. Calculate the molar absorption coefficient of the sample.

**Q.9 (a)** Write down the valence bond wavefunction ΨAB (in terms of Ψcov and Ψionic) for AB molecule assuming that the ionic character in A-B bond is 20 percent.

**(b)** The vibration-rotation spectrum of 12C16O has the center of the spectral bands at 2143.26 cm-1 and a set of closely spaced peaks on either side. The separation between two consecutive peaks on any side of the center is 3.828 cm-1. Based on these data and applying harmonic oscillator and rigid rotor approximations, calculate the following; (i) Zero-point vibrational energy (in cm-1) (ii) Force constant of CO bond (in Nm-1) (iii) Rotational constant for CO (in cm-1)

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