3 (Sem–5/CBCS) CHE HC 2

2021

(Held in 2022)

CHEMISTRY

(Honours)

Paper : CHE–HC–5026

(Physical Chemistry–V)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following as directed : 1×7=7

   (a) State which of the following radiations is associated with NMR spectroscopy : X-ray, γ-ray, radio waves, infrared.

   (b) Find the normal modes of vibrations in case of CH_4.

(c) The shift of an absorption maximum towards longer wavelength is known as

(i) Hyperchromic shift

(ii) Bathochromic shift

(iii) Hypochromic shift

(iv) Hypsochromic shift

(Choose the correct option)

(d) Write the expression for the Hamiltonian operator for a particle of mass m and potential energy V.

(e) Write the significance of ψ and ψ^2.

(f) State the Stark-Einstein law of Photochemical Equivalance.

(g) What is photosensitizer ? Give *one* example.

2. Answer the following questions : 2×4=8

(a) What is the lowest vibrational energy in terms of oscillation frequency for a diatomic molecule undergoing simple harmonic motion ? Give the expression. What does it imply ?

(b) A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to one-fourth of the initial value after passing through 10 *cm* length of the solution. Calculate the molar extinction coefficient of the substance.

(c) When a sample was irradiated by the 4358 *Å* line of mercury, a Raman line was observed at 4447 *Å*. Calculate the Raman shift in cm^{-1}.

(d) If two operators $\hat{A}$ and $\hat{B}$ commute then they have the same set of eigenfunctions. Justify it.

3. Anwer ***any three*** questions :

(a) Set up and solve the Schrödinger wave equation for a particle in one-dimensional box for wavelength and energy. 5

(b) Write how the molecular orbitals of a homonuclear diatomic molecule can be classified as σ and π. Which of these two is doubly degenerated and why ? What is the basis of classifying the MOs as g and u ? 2+2+1=5

(c) The pure rotational (microwave) spectrum of gaseous HCl consists of a series of equally spaced lines separated by 20.80 cm^{-1}. Calculate the

(i) moment of inertia and

(ii) internuclear distance of the molecule.

The atomic masses are :

$^1H = 1.673 \times 10^{-27} kg$; $^{35}Cl = 58.06 \times 10^{-27} kg$

3+2=5

(d) State Beer-Lambert law.

A substance when dissolved in water at 10^{-3} M concentration absorbs 10% of an incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90% of the same radiation ?

2+3=5

(e) Show that the Raman lines in the pure rotational Raman spectrum of a diatomic molecule appear at wave number

$$\bar{\nu} = \bar{\nu}_0 \pm 2B(2J+3)$$

where $\bar{\nu}_0$ is the wave number of the Rayleigh line. Draw the schematic diagram to show the Stokes lines and the Anti-Stokes lines. 4+1=5

4. Answer *(a)* **or** *(b)* ; *(c)* **or** *(d)* ; *(e)* **or** *(f)* :

(a) (i) With the help of Jablonski diagram, explain all the photophysical processes that an electronically excited molecule may undergo. Give *two* major differences between fluorescence and phosphorescence. 3+2=5

(ii) Write the mechanism of $H_2 - Cl_2$ photochemical reaction. Prove that the rate of formation of HCl is directly proportional to the intensity of the absorbed radiation.

2+3=5

Or

(b) (i) Use the LCAO method to form the MO wave function of H_2^+. Using this wave function, deduce the energy expressions for the bonding and the antibonding MOs.

1+4=5

(ii) Derive the expression for the energy of a particle in a two-dimensional box. 5

(c) (i) Discuss briefly the effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide. 5

(ii) Justify the quantization of energy and existence of zero-point energy for a particle confined in one-dimensional box. What will happen if the walls of the box are suddenly removed ? 4+1=5

Or

(d) (i) Considering the diatomic molecule to be a rigid rotator, deduce an expression in wavenumber unit for the energy required for rotational transition to take place. Explain how the spectrum will differ if the molecule is considered to be a non-rigid rotator. 3+2=5

(ii) Find the normal vibrational modes of CO_2. Out of these, how many are stretching and how many are bending vibrations ? Explain which vibrations are IR active and which are not. 1+1+3=5

(e) (i) What are the factors which determine intensities of spectral line ? Discuss. 5

(ii) Discuss Franck-Condon principle to explain intensities of vibrational transitions due to absorption or emission of a photon of appropriate energy. 5

Or

(f) (i) Discuss briefly the molecular orbital treatment of BeH_2 and H_2O molecules. 5

(ii) Calculate the rotational energy of CO molecule in the first excited state considering it to be rigid rotator, given that the bond length of CO is 113 *pm*. 5