Total number of printed pages–8

3 (Sem–5/CBCS) CHE HC 2

2023

CHEMISTRY

(Honours Core)

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 whether the following statement is True ***or*** False :

   For the particle in the box, the maximum probability density for every stationary state wave-function is at the midpoint of the box.

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(b) Show that *sin nx.* (*n* is an integer) is an eigenfunction of the operator $\frac{d^2}{dx^2}$ and find the eigenvalue.

(c) Derive the term symbol for the ground state configuration of *Na*.

(d) State which of the following are microwave active and why :

CO_2, *OCS*, *HF*, N_2

(e) The ionization energy of a molecule is 10 *eV*. Calculate the wavelength of the radiation that ionize the molecule. $(1eV = 1.602\times10^{-19} J)$

(f) What do you mean by inter system crossing ?

(g) What are photoinhibitors ?

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

(a) Show that the wave function for a particle in one-dimensional box of length *a*, where the potential energy is zero, is not an eigenfunction of the linear momentum operator in one dimension.

(b) The functions $\psi_1 = \left(\frac{1}{\pi}\right)^{1/2} \cos x$ and $\psi_2 = \left(\frac{1}{\pi}\right)^{1/2} \sin x$ are defined in the interval $x = 0$ to $x = 2\pi$. Examine if the functions are orthogonal to each other.

(c) Write how the population of states affects the intensity of spectral line.

(d) Microwave causes molecules to rotate more energetically. A molecule absorbs microwave photon of wavelength 20 cm. Calculate the energy difference between the two rotational levels in joule.

3. Answer ***any three*** questions :

(a) Show that the energy levels of a harmonic oscillator are evenly spaced and it has an energy greater than zero even in its lowest state. 5

(b) (i) Define complementary observable with *one* example. 1+1=2

(ii) Show that if two linear operators A and B have the same complete set of eigenfunctions, then $[\hat{A}, \hat{B}] = 0$. 3

(c) The first line in the pure rotational spectrum of $^{12}C\,^{16}O$ is observed at 3.8424 cm^{-1}. Calculate bond length considering the molecule as rigid rotator. Does the bond length of a real molecule change as rotational energy increases? If yes, how? 4+1=5

(d) (i) Discuss in brief what do you mean by hot bands: 2

(ii) Find the normal vibrational modes of CO_2. Explain which are IR active and which are not. 3

(e) Write the mechanism of the 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

4. Answer ***any three*** questions :

(a) (i) Write down the Hamiltonian operator for the hydrogen atom and show that the maximum radial probability density for the 1s state of H-atom occurs at a distance equal to Bohr radius. 2+3=5

(ii) Which of the following functions are eigenfunctions of d^2/dx^2 ?

(i) $\sin 2x$

(ii) $4\cos 3x$

(iii) $5x^2$

(iv) $\frac{1}{x}$

(v) $5e^{-3x}$

Determine the eigenvalue of each function. 5

(b) *(i)* Derive expression for the total energy of a particle in a three-dimensional box. Explain the concept of degeneracy. 4+2=6

(ii) Taking the example of H_2^+, explain how the potential energy diagram can be constructed. What information regarding characterization of a bond can be obtained from this diagram? 3+1=4

(c) *(i)* Considering the diatomic molecule to be a rigid rotator, deduce an expression in wave number 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) The force constant of CO is $1840 Nm^{-1}$. Calculate oscillation frequency and wave number in cm^{-1}. 3

(iii) Explain with examples the terms chromophore and auxochrome. 2

(d) *(i)* 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

(ii) Show diagrammatically the relative frequencies of following electronic transitions :

(i) $\sigma \rightarrow \sigma^*$

(ii) $\pi \rightarrow \pi^*$

(iii) $n \rightarrow \pi^*$

(iv) $n \rightarrow \sigma^*$

Discuss the effect of polarity of the solvent on the above transitions. 3+2=5

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

Contd.

(ii) *HCl* molecule has the fundamental frequency $2990 cm^{-1}$. The anharmonicity constant is 0·019. The depth of the potential well is $43000 cm^{-1}$. Calculate the dissociation energy is $kJ\,mol^{-1}$. 3

(iii) Write short note on : 2

Rule of Mutual Exclusion

(f) *(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) A substance was exposed to a radiation of wavelength 420*nm* for a definite period of time when an amount of 10·5*J* of energy was absorbed. During this time $1{\cdot}8 \times 10^{-5} mol$ of the substance was found to decompose. Calculate quantum efficiency. 3

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