2026

Chemistry (Core)

Paper Code : CH-CE-6334

Paper Name : Physical Chemistry - III

Time : 2 hours ***Full Marks : 50***

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

1. Answer the following questions as directed : 1×4=4

   a) Calculate the frequency and wave number of infrared lght of wavelength, $\lambda = 10\,\mu m$.

   b) Identify the microwave active molecules from the following :

   CO_2, OCS, HF, N_2

   c) What are the boundary conditions of wave function for a particle in 1D box ?

   d) What are photosensitizers ? Give one example.

2. Answer the following questions : 2×3=6

   a) Define normalized, orthogonal and orthonormal wave functions.

   b) What is normal vibration ? How many fundamental modes of vibration H_2O molecule possesses ? 1+1=2

   c) "Zero point energy for particle in 1D box is actually a consequence of the Heisenberg's uncertainity principle." Explain.

3. Answer the following questions ***(any two)*** : 5×2=10

   a) Discuss the important factors that may contribute to spectral line width and shape. 5

b) Define an operator in quantum mechanics. Show that if two operators $\hat{A}$ and $\hat{B}$ are Hermitian, then their product $(\hat{A}\hat{B})$ is also Hermitian if and only if $\hat{A}$ and $\hat{B}$ commute. 1+4=5

c) What is meant by quantum yield for photochemical reactions? Explain the factors responsible for low and high quantum yield. 2+3=5

d) Derive expression for the total energy of a particle in a two dimensional box. Explain the concept of degeneracy. 3+2=5

4. Answer the following questions ***(any three)*** : 10×3=30

a) i) Derive an expression for the radial distribution function. Draw the radial distribution function versus radial distance for a *3p* orbital. 4+1=5

ii) For a particle moving in a 3D box of length *a*, *b* and *c*, where potential energy is zero, find the energy expression and wave function. 5

b) i) Solve the time-independent Schrödinger equation for a particle confined in a one-dimensional box of length 'a' and hence obtain the allowed energy levels and normalized wave functions. 5

ii) Write the general expressions for the magnitude and *z*-component of angular momentum. Write what you mean by space quantisation of angular momentum. Discuss with diagram the orientations of angular momentum of magnitude $\sqrt{2}\ \hbar$ in presence of applied magnetic field in *z*-direction. 1+1+3=5

c) i) Classify molecules based on the relative values of their principal moments of inertia. 3

ii) Explain how isotopic substitution affects the rotational spectra of diatomic molecules, with reference to changes in moment of inertia and rotational constants. 4

iii) In the rotational spectrum of $^{12}C^{16}O$ absorption lines are observed at a constant separation of 3.84236 cm^{-1}. Determine the rotational constant and calculate the angular velocity in $J=1$ level. 3

d) i) Discuss the quantum mechanical theory of Raman spectroscopy. Illustrate schematically the Rayleigh, Stokes and anti-Stokes lines. 3+3=6

ii) Raman spectroscopy is complementary to Infrared Spectroscopy. Explain why ? 2

iii) What are hot bands ? Discuss in brief. 2

e) i) State the Franck-Condon principle. Using potential energy curves, explain how differences in equilibrium internuclear distances between ground and excited states influence the vibrational structure and intensity distribution of electronic spectra. 2+3=5

ii) Differentiate between fluorescence and phosphorescence. Using appropriate energy level diagrams, explain the underlying processes and briefly discuss their key characteristics. 2+3=5

f) i) Discuss the role of the solvent on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, giving suitable examples. 5

ii) Discuss the role of conjugation in *UV*-Visible spectra of a polyene system using free electron model. 5

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