

63/1 (SEM-5) CC12/CHMHC5126

2022

(Held in 2023)

CHEMISTRY

Paper : CHMHC5126

(Physical Chemistry—V)

Full Marks : 60

Pass Marks : 24

Time : 3 hours

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

1. Choose the correct answer : 1×5=5

(a) For the real atomic orbital with quantum numbers n , l , the total number of nodal surfaces is

(i) n

(ii) $n-1$

(iii) $n+l$

(iv) $n-l-1$

(2)

(b) The Hamiltonian for hydrogen molecular ion (H_2^+) is

$$(i) \hat{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2$$

$$(ii) \hat{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_A} + \frac{e^2}{r_B}$$

$$(iii) \hat{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B}$$

$$(iv) \hat{H} = -\frac{\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R}$$

(c) The total number of normal modes of vibration of a linear molecule consisting of N atoms is given by

$$(i) (3N-5)$$

$$(ii) (3N-6)$$

$$(iii) (3N-2)$$

$$(iv) (3N-7)$$

(d) The rotational spectrum of a rigid diatomic rotor consists of equally spaced lines with spacing is equal to

$$(i) 3B/2$$

$$(ii) 2B$$

$$(iii) B/2$$

$$(iv) B$$

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(Continued)

(3)

(e) Raman effect is

(i) inelastic scattering of light

(ii) elastic scattering of light

(iii) absorption of light

(iv) emission of light

2. Answer the following questions : 2×5=10

(a) What are eigenfunctions and eigenvalues? Explain with examples.

(b) Calculate the probability that a particle in a one-dimensional box of length, a is found to be between 0 and $a/2$.

(c) Consider a diatomic molecule to be rigid rotor. Write, in brief, how the presence of heavier isotope affects the rotational spectrum.

(d) What is degree of freedom? List the number of translational, rotational and vibrational degrees of freedom for H_2O molecule.

(e) Define photochemical reaction. Write the reaction involved in photosynthesis of carbohydrates in plants.

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(Turn Over)

3. Answer any five of the following questions :

5×5=25

- (a) Write the postulates of quantum mechanics.
- (b) Derive Schrödinger wave equation in the form $\hat{H}\psi = E\psi$.
- (c) Using the principle of LCAO for the wave function for H_2^+ ion, obtain the normalized wave functions for the BMO and ABMO.
- (d) What are the factors which determine intensities of spectral line? Discuss.
- (e) Write the quantum mechanical theory of Raman spectroscopy. Show schematically the Rayleigh lines, Stokes' lines and anti-Stokes lines. 4+1=5
- (f) Deduce the expression of Beer-Lambert law. What are the limitations of the law? 3+2=5
- (g) State and explain the term 'quantum yield'. How do you account for the fact that quantum yield of photochemical reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ is low while that of the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ is very large.

(Continued)

4. Answer any two of the following questions :

10×2=20

- (a) (i) Explain Heisenberg uncertainty principle. 2
- (ii) An electron has a speed of 300 ms^{-1} accurate up to 0.001%. What is the uncertainty in its velocity? Comment on the result. 2+1=3
- (iii) Solve the Schrödinger wave equation for a particle in an one-dimensional box and find the expression for the energy. Why is the value $n=0$ of the quantum number not permitted? 4+1=5
- (b) Write different types of molecular spectra. Explain each of them briefly. In what region of the electromagnetic spectrum are they obtained?
- (c) (i) Explain, why $(CH_3)_4Si$ is considered a good reference standard in NMR spectroscopy. 3
- (ii) What do you mean by chemical shift in NMR spectroscopy? Explain with example. 2

(Turn Over)

(6)

(iii) Show different photophysical processes using Jablonski diagram. Explain the differences between fluorescence and phosphorescence.

2+3=5
