

5. (a) The force constant of HF is 880 Nm^{-1} . At what wavenumber is the fundamental vibrational absorption expected?
- (b) Derive expression for Lambert-Beer's law. What are its limitations?
- (c) (i) Find $\hat{A}^2$ if $\hat{A} = x + d/dx$ operating on an arbitrary function $f(x)$.
 (ii) Find the value of commutator $(x, d/dx)$.
 (5,5,5)
6. (a) With the increase in vibrational quantum number the difference in energy levels remains constant whereas with the increase in rotational quantum number the difference in energy levels increases. Explain with the help of calculation.
- (b) Give the difference between atomic and molecular spectra. Elaborate different types of molecular spectra according to their respective frequency regions.
- (c) How many fundamental vibrational frequencies (i.e. fundamental vibrational degrees of freedom) are expected for the following molecules :
 (i) CO_2
 (ii) H_2O
 (iii) C_6H_6
 (iv) CHCl_3
 (v) O_2
 (5,5,5)

(2700)

[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 2918

L

Unique Paper Code : 2172513601

Name of the Paper : DSC: Quantum Chemistry & Spectroscopy

Name of the Course : B.Sc. (Prog.)

Semester : VI

Duration : 3 Hours

Maximum Marks : 90

Instructions for Candidates

- Write your Roll No. on the top immediately on receipt of this question paper.
- Attempt any **four** questions.

Physical ConstantsPlanck's Constant $6.626 \times 10^{-34} \text{ Js}$ Velocity of light $3 \times 10^8 \text{ ms}^{-1}$ Avogadro's Number 6.023×10^{23} Mass of electron $9.109 \times 10^{-31} \text{ kg}$

- (a) What do you understand by an eigen value equation? Show which of the following mathematical functions are eigen functions of d/dx operator. What are their eigen values.
 (i) $5e^{3x}$ (ii) $5 \cos 8x$

P.T.O.

(b) An electron is confined in a one-dimensional box of length 2 nm.

(i) What is the energy of the electron in $n = 4$ level? Plot the wavefunction and probability density curve for this level.

(ii) Calculate the energy absorbed when electron undergoes transition from E_5 to E_6 and E_6 to E_7 .

(c) What is the criterion for a molecule to be IR active? Based on this criterion, explain whether the following molecules are IR active or not and why?

(i) CS_2 (ii) HCl (iii) N_2 (iv) Br_2 ? (5,5,5)

2. (a) Define a Linear operator? Show that

$$(i) [\hat{A}, [\hat{B}, \hat{C}]] = \hat{A}[\hat{B}, \hat{C}] - [\hat{B}, \hat{C}]\hat{A}$$

$$(ii) [\hat{x}, \hat{p}_x] = -i\hbar$$

(b) The pure rotational spectrum of a molecule AB consists of a series of equally spaced lines separated by 40.64 cm^{-1} . Calculate the rotational constant, moment of inertia and internuclear distance of the molecule. The atomic masses are : $A = 1.673 \times 10^{-27} \text{ kg}$; $B = 58.06 \times 10^{-27} \text{ kg}$.

(c) Determine the expectation value of kinetic energy for particle in a one dimensional box. (5,5,5)

3. (a) Write short notes on **any two** of the following :

(i) Phosphorescence with diagram

(ii) Significance of ψ and ψ^2

(iii) Schrodinger wave equation for a Simple harmonic Oscillator with description of Kinetic Energy Operator & Potential Energy Operator.

(b) What are the assumptions of the free electron model or particle in a box model for polyenes. Apply this model to determine the energy for the first excited state of hexatriene molecule. Given that C-C single bond length is 135 pm & that of C=C double bond length is 154 pm. Radius of carbon atom at the end is 77 pm. (5+5=10,5)

4. (a) An electron is confined to a molecule of length 1nm. What is the probability of finding it in the region of the molecule lying between $x = 0$ and $x = 0.2 \text{ nm}$?

(b) What is auxochromes? Explain Bathochromic shift and Hypsochromic shift with examples.

(c) Calculate the transmittance, absorbance and absorption coefficient of a solution which absorbs 90% of a certain wavelength of light beam passed through a 1 cm cell containing 0.25 M solution.

(5,5,5)

P.T.O.