Name:

Enrolment No:

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES
End Semester Supplementary Examination, December 2023

Course: Advanced Physical Chemistry **Semester: I**
Program: M.Sc. Chemistry **Time : 03 hrs.**
Course Code: CHEM7016 **Max. Marks: 100**

Instructions:
1. Write your enrolment number on the top left of the question paper
2. Do not write anything else on the question paper except your enrolment number
3. Attempt all part of a question at one place only

SECTION A
(5Qx4M=20Marks)

S. No.		Marks	CO
Q 1	A particle in three dimensional cubic box with length "a" has energy of $17h^2/8ma^2$. What is the degeneracy of the state?	**4**	**CO1**
Q 2	Explain the origin of degeneracy in the cubic box.	**4**	**CO1**
Q 3	Find the value of commutator $[p_x, x]$, where p_x is the momentum and x is position.	**4**	**CO2**
Q 4	The absorbance of a dye solution at 500 nm is 1.2 when a quartz cuvette with path length of 1 cm is used. What is the transmittance of the dye solution?	**4**	**CO4**
Q 5	The energy 2nd vibrational state of 1D linear harmonic oscillator is 200 cm^{-1}. What is the zero-point energy?	**4**	**CO4**

SECTION B
(4Qx10M= 40 Marks)

Q 1	(a) Calculate the rotational energy of the J=2 state when rotational constant B = 500 cm^{-1}. What is the degeneracy of rotational state with J=1? (b) Explain 1st and 2nd postulates of quantum mechanics.	**5+5**	**CO3**
Q 2	(a) What are the gross and specific selection rule of pure rotational spectroscopy? (b) What are the characteristics of well behaved wavefunction?	**5+5**	**CO3**
Q 3	Find the eigen value of function $f = e^{-4ix}$ operated by an operator $\hat{A} = (\frac{d^2}{dx^2})$.	**10**	**CO3**

Q 4	(a) Find the expression of angular momentum operator along x, y and z directions. (b) What are the causes of spectral line broadening?	**5+5**	**CO3**
SECTION-C (2Qx20M=40 Marks)			
Q 1	**(i)** Using a suitable diagram show the origin fundamental, 1^{st} overtone, 2^{nd} overtone and hot bands in vibrational spectroscopy. **(ii)** (a) Write relation between rotational constant (B) and bond length (r). Explain all the terms involved. (b) The fundamental vibration frequency of $^{1}H^{35}Cl$ molecule is 5 X 10^{13} Hz. Calculate the force constant for this molecule. (Given: Plank constant = 6.626×10-34 Js). **OR** **(i)** Using thermodynamic square find all the Maxwell's relation. **(ii)** Derive the expression of wave function and energy of a particle in three-dimensional box.	**10+10**	**CO4**
Q 2	**(i)** Given that a particle is restricted to the region –a<x<a and has a wave function ψ proportional to $\mathbf{cos}\left(\frac{\pi x}{2a}\right)$, normalize the wave function. **(ii)** Using a suitable diagram show the origin of P, Q, R branch in a rotational-vibrational. Write the specific selection rules for P, Q and R branches.	**10+10**	**CO2**