Name: **Enrolment No:**	

UNIVERSITY OF PETROLEUM AND ENERGY STUDIES
End Semester Examination, December 2022

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
4. Internal choice is given for question number 1 of Section C only

SECTION A
(5Qx4M=20Marks)

S. No.		Marks	CO
Q 1	A particle in three dimensional cubic box with length "a" has energy of $14h^2/8ma^2$. What is the degeneracy of the state?	**4**	**CO1**
Q 2	Give the expression of wavefunction and energy of a particle in a cubic 3D box with length "a". Explain the origin of degeneracy in the cubic box.	**4**	**CO1**
Q 3	Find the value of commutator $[p_x, T_x]$, where p_x is the momentum and T_x is the kinetic energy in the x direction.	**4**	**CO2**
Q 4	The transmittance of a dye solution at 500 nm is 20% when a quartz cuvette with path length of 1 cm is used. What is the absorbance of the dye solution?	**4**	**CO4**
Q 5	The zero-point energy of 1D linear harmonic oscillator is 500 cm^{-1}. What is the energy of the 3rd vibrational state?	**4**	**CO4**

SECTION B
(4Qx10M= 40 Marks)

Q 1	(a) Calculate the rotational energy of the J=3 state when rotational constant B = 300 cm^{-1}. What is the degeneracy of rotational state with J=3? (b) Calculate the fundamental vibration frequency and the 1st excited state vibrational energy of $^1H^{35}Cl$ molecule. Given: force constant (k)= 200 Nm^{-1}, Plank constant = 6.626×10^{-34} Js).	**5+5**	**CO3**
Q 2	(a) What are the gross and specific selection rule of pure rotational, vibrational spectroscopy. (b) Explain the variational principal of quantum chemistry.	**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) Write the first order and second order perturbation energy corrections terms? Explain all the terms involved. (b) What are the causes of spectral line broadening?	**5+5**	**CO3**
SECTION-C (2Qx20M=40 Marks)			
Q 1	**(i)** (a) Using a suitable diagram show the origin fundamental, 1st overtone, 2nd overtone and hot bands in vibrational spectroscopy. (b) Write down the selection rules for P, Q and R branches in rovibrational spectroscopy. **(ii)** (a) Write relation between rotational constant (B) and bond length (r). Explain all the terms involved. (b) The fundamental vibration frequency of $^1H^{35}Cl$ molecule is 5 X 10^{13} Hz. Calculate the force constant for this molecule. (Given: Plank constant = 6.626×10-34 Js). **OR** **(i)** Derive all the Maxwell's relation using Euler's theorem. **(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)** Explain canonical, micro-canonical and grand-canonical ensembles with diagrams.	**10+10**	**CO2**