Name:

Enrolment No:

UPES

End Semester Examination, December 2024

Course: Physical Chemistry V **Semester: V**

Program: B.Sc. (H) Chemistry **Time : 03 hrs.**

Course Code: CHEM3015 **Max. Marks: 100**

Instructions:

- Do not write anything else on the question paper except your name and roll number.
- Use of scientific calculator is allowed.
- Attempt all the parts of a question at one place only. Internal choice is given in Q8 & Q10.
- CO1, CO2, & CO3 in the last column stand for course outcomes and are for official use only.

SECTION A
(5Qx4M=20Marks)

S. No.		Marks	CO
Q 1	How will the rotational spectra change when ^{12}C in $^{12}C^{16}O$ is replaced by ^{13}C?	**4**	**CO1**
Q 2	Homonuclear diatomic molecule H_2 is microwave inactive but is rotational Raman active. Why?	**4**	**CO1**
Q 3	What are the essential conditions for a molecule to show IR spectra? Which of the following will be IR active: O_2, CO_2, CO and SO_2.	**4**	**CO1**
Q 4	A particle of mass 'm' moves in a three dimensional box of sides a, b,c. If the potential is zero inside the box, give the expression for the energy eigen values and wavefunctions for a particle in a 3D box. What is the zero point energy of the system?	**4**	**CO2**
Q 5	Write the Hamiltonian operator for H-atom and rigid rotor. Explain each term.	**4**	**CO2**
	SECTION B **(4Qx10M= 40 Marks)**		
Q 6	For a one-electron homonuclear diatomic molecule the values of some relevant integrals are given below: $\int \varphi_A H \varphi_A d\tau = -3a.u.$, $\int \varphi_B H \varphi_B d\tau = -3a.u.$ $\int \varphi_A H \varphi_B d\tau = -1.5a.u.$, $\int \varphi_A \varphi_B d\tau = 0.5a.u.$ Where φ_A and φ_B are the normalized set of basis functions for an LCAO wavefunction. Find the energy of the binding and antibonding molecular orbitals.	**10**	**CO3**
Q 7	(a) Find the commutator of position and momentum operator and give its physical significance, giving the name of the principle it verifies.	**10**	**CO1**

	(b) What are the selection rules for observing IR spectra of an anharmonic oscillator? Derive the expressions for energy required for fundamental transition and first overtone.		
Q 8	Write a short note on: (i) Born-Oppenheimer approximation (ii) Variation principle. **OR** Calculate the fundamental vibration frequency and the 1st excited state vibrational energy of $^{1}H^{35}Cl$ molecule. Given: force constant (k)= 200 Nm^{-1}, Plank constant = 6.626×10^{-34} Js).	**10**	**CO2**
Q 9	(a) Prove that the eigenvalues of a Hermitian operator are real (b) The absorbance of 0.001M dye solution at 500 nm is 0.5 when a quartz cuvette with path length of 1 cm is used. What is the molar extinction coefficient of the dye solution?	**10**	**CO2**
SECTION-C (2Qx20M=40 Marks)			
Q 10	(a) What are normal modes of vibration? Draw the normal modes of vibration of CO_2 and H_2O. Also indicate which modes are IR active. **OR** Arrive at the following expression for H_2^+ $E_g = \frac{\alpha+\beta}{1+S}$ (where α is the coulomb integral, β is the exchange integral and S is the overlap integral) using LCAO-MO treatment. (b) (i) Discuss the causes of spectral broadening. (ii) What distinguishes homogeneous broadening from heterogeneous broadening, and which types of spectral lines are associated with each? **OR** (i) Show the general expression of radial and angular wave function of H-atom. (ii) Suppose the wave function of a one-dimensional system is $\psi = \cos(kx)\exp(4ikx)$ In an experiment measuring the momentum of the system, what are the expected outcomes?	**10+10**	**CO3**
Q 11	(a) Draw a neat diagram showing the origin of P, Q, R branch in a rotational-vibrational spectrum. What are the specific selection rules for P, Q and R branches? Why does the Q branch not appear in the spectra of all diatomic molecules? (b) The vibrational spectrum of HCl shows an intense fundamental transition band at 500 cm^{-1}. Given that the equilibrium frequency (ω_e) = 300 cm^{-1}. Calculate the anharmonicity constant for HCl molecule.	**10+10**	**CO3**