REV-01
BSC/05/10

2025/11

SET A

B.SC. CHEMISTRY [HONOURS]
SEVENTH SEMESTER
QUANTUM & MOLECULAR SPECTROSCOPY
BSC – 703

[USE OMR FOR OBJECTIVE PART]

Duration: 3 hrs. **Full Marks: 70**

(Objective)

Time: 30 min. **Marks: 20**

Choose the correct answer from the following: ***1×20=20***

1. The normalization condition of a wave function ψ ensures that
   a. ψ = 0 at infinity
   b. The total probability = 1
   c. ψ is real
   d. ψ is periodic

2. For a Hermitian operator $\hat{H}$, which of the following is true?
   a. Eigenvalues are complex
   b. Eigenvalues are always real
   c. Expectation value is imaginary
   d. Operator is non-linear

3. Orthogonal wavefunctions satisfy
   a. $\int \psi_1^* \psi_2 \, d\tau = 0$
   b. $\psi_1 = \psi_2$
   c. $\int \psi_1^* \psi_2 \, d\tau = 1$
   d. None

4. The eigenvalues of the angular momentum operator L^2 is
   a. $(l+1)\hbar^2$
   b. $\hbar^2$
   c. $m\hbar$
   d. $l\hbar$

5. Spontaneous emission occurs when
   a. Molecule absorbs radiation
   b. Excited state decays without external cause
   c. Stimulated by photon
   d. Collisions occur

6. The line width in spectroscopy arises from
   a. Instrumental error
   b. Natural lifetime
   c. Doppler effect
   d. All of the above

7. A linear molecule has
   a. Two equal moments of inertia
   b. All unequal moment of inertia
   c. One zero and two equal moments
   d. None of the above

8. Isotopic substitution affects rotational spectra because
   a. It changes the dipole moment
   b. It changes the moment of inertia
   c. It changes Planck's constant
   d. None of the above

9. The Stark effect arises due to
   a. Magnetic field
   b. Electric field
   c. Pressure
   d. Temperature

10. The probability of finding an electron at a node is
    a. Maximum
    b. Minimum
    c. Zero
    d. Constant

11. The angular momentum operator $\hat{L}_x$ is given by
    a. $\hat{L}_x = y\hat{p}_y - z\hat{p}_z$
    b. $\hat{L}_x = z\hat{p}_z - y\hat{p}_y$
    c. $\hat{L}_x = z\hat{p}_y - y\hat{p}_z$
    d. $\hat{L}_x = y\hat{p}_z - z\hat{p}_y$

12. Which of the following increases the translational energy (E_n) in the particle-in-a-box model?
    a. Increasing mass of the particle
    b. Decreasing Planck's constant
    c. Increasing the size of the box
    d. Decreasing the size of the box

13. What is the potential energy **V(x)** of a particle in a 1D infinite potential well (box) of length L?
    a. V(x) = constant everywhere
    b. V(x) = ∞ inside the box; V(x) = ∞ outside the box
    c. V(x) = 0 inside the box; V(x) = ∞ outside the box
    d. V(x) = 0 for all x

14. The zero point energy of a simple harmonic oscillator in 3D box
    a. $\frac{1}{2}h\nu$
    b. $h\nu$
    c. $\frac{3}{2}h\nu$
    d. $\frac{5}{2}h\nu$

15. The normalized ground-state wavefunction for a particle in a box (0 to l) is:
    a. $\psi = \sqrt{\frac{2}{l}}\sin\left(\frac{\pi x}{l}\right)$
    b. $\psi = \sin\left(\frac{\pi x}{l}\right)$
    c. $\psi = \sqrt{\frac{2}{l}}\cos\left(\frac{\pi x}{l}\right)$
    d. $\psi = \cos\left(\frac{\pi x}{l}\right)$

16. The fundamental frequency (ϑ_0) is related to reduced mass (μ) by which of the following relation
    a. $\vartheta_0 \propto \sqrt{\mu}$
    b. $\vartheta_0 \propto \mu$
    c. $\vartheta_0 \propto \mu^2$
    d. $\vartheta_0 \propto \frac{1}{\sqrt{\mu}}$

17. The first overtone corresponds to which transition?
    a. v = 0 → 1
    b. v = 1 → 2
    c. v = 0 → 2
    d. v = 0 → 3

18. The selection rule for vibrational transition in an anharmonic oscillator is:
    a. $\Delta v = 0$
    b. $\Delta v = \pm 1, \pm 2, \pm 3$
    c. $\Delta v = \pm 2, \pm 3$
    d. $\Delta v = \pm 1$

19. The number of vibrational modes in CO_2 is
    a. 3
    b. 5
    c. 4
    d. 6

20. In the R branch, the rotational quantum number J changes as:

a. $\Delta J = 0$ b. $\Delta J = -1$

c. $\Delta J = +1$ d. $\Delta J = -2$

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Descriptive

Time : 2 hrs. 30 min. **Marks : 50**

[Answer question no.1 & any four (4) from the rest]

1. a. Derive the expression for rotational energy levels of a diatomic molecule. **3+2+3 +2=10**

   b. State any two postulates of quantum mechanics.

   c. Calculate the force constant for HCl from the fact that fundamental vibration frequencies is $8.667 \times 10^{13}\ s^{-1}$ and reduced mass is 1.627×10^{-27} kg.

   d. Write the expression for the Hamiltonian operator for one and three dimensional single particle system.

2. a. Discuss the classification of molecules based on their moments of inertia. **4+2+2 +2=10**

   b. Define normalization and orthogonality of a wavefunction.

   c. Find the commutation value of **[d/dx, x]**

   d. The energy difference between the levels, J=10 to J=11 is 2200 cm^{-1}. Calculate the value of the rotational constant.

3. a. Compare linear, symmetric top, and asymmetric top molecules with examples. **3+2+2 +3=10**

   b. What is meant by isotopic effect in rotational spectra?

   c. Write the conditions for physically acceptable wave functions.

   d. Find if the operators of position & potential energy and kinetic energy & position commute or not.

4. a. State the condition for a molecule to show a pure rotational spectrum. **2+3+2 +3=10**

   b. Explain what is an wave function and the physical interpretation of it?

   c. Find which of the molecules are rotationally active and explain

why: ClF_3 and SF_4

d. Derive the Schrodinger's Wave Equation for a particle in a 2-D box of length '*l*'

5. a. Explain the Stark effect in detail. 3+2+3 +2=10

b. Write what you mean by Electronic, Translational, Vibrational and Rotational energy of a molecule.

c. An infra absorption band is observed at 3143 cm^{-1}. Convert this wave number into frequency in Hartz.

d. What do you mean by anharmonic oscillation? Explain using diagram.

6. a. A vibration has ω_e= 3000 cm^{-1} and anharmonicity constant x_e = 0.01. What is the first overtone in wavenumber (cm^{-1})? 3+4+2 +1=10

b. Draw and write different modes of vibration for the molecule CO_2. Identify Raman active and IR active vibration.

c. What do you mean by mutual exclusion principle?

d. What is the separation between two consecutive P lines in vibrational-rotational spectrum?

7. a. If e^{-2x^2} is an eigen function of the operator $(\frac{d^2}{dx^2} - 16x^2)$, what will be the corresponding eigen value? 3+3+2 +2=10

b. Obtain the normalized wave functions for a particle on a ring.

c. What is quantum mechanical tunneling?

d. What are the degeneracies of the 10^{th} and 11^{th} energy states of a simple harmonic oscillator in 3D box.

8. a. Consider an electron in a box of the size of the nucleus (10^{-14} m). Calculate the ground state energy. (Given mass of electron = 9.1 × 10^{-31} kg). 3+5+2 =10

b. Consider the operators, $\hat{a}_+ = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p}_x)$ and $\hat{a}_- = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p}_x)$, where $\hat{x}$ and $\hat{p}_x$ are the position and linear momentum operators, respectively. Find the commutator, $[\hat{a}_+, \hat{a}_-]$.

c. What is operator? What do you mean by eigen function and eigen value?

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