B.Sc. CHEMISTRY
FIFTH SEMESTER
PHYSICAL CHEMISTRY III
BSC - 502[SPECIAL REPEAT]
[USE OMR FOR OBJECTIVE PART]

SET A

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

Objective

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

Choose the correct answer from the following: ***1X20=20***

1. The Separation between any two adjacent stokes line of the Raman Spectra of $^{16}O_2$ molecule is
   a. 8B b. 4B
   c. 12B d. 20 B

2. The intensity of NMR Spectral line is proportional to
   a. N_0 b. N_0^2
   c. $\sqrt{N_0}$ d. N_0
   [N_0 is number of magnetic nuclei in the initial energy level]

3. Which of the following molecule exhibits rotational spectra
   a. H_2 b. O_2
   c. CO d. N_2

4. ESR Spectroscopy is obtained in
   a. Visible region b. Radio frequency region
   c. Ultra-violet region d. Micro-wave region

5. The equilibrium dissociation energy (D_e) is approximately equal to
   a. $\tilde{\omega}e/4\chi e$ b. $\tilde{\omega}e\ \chi e\ /4$
   c. $4\tilde{\omega}e/\chi e$ d. $3\tilde{\omega}e\chi e/4$

6. For a diatomic molecule AB, The energy for rotational transition from J=0 to J=1 is 4 cm-1. Then transition energy from J=3 to J=4 is
   a. 8 cm-1 b. 16 cm-1
   c. 20 cm-1 d. 4 cm-1

7. The selection rule for R and Q branches of rotational spectral lines are respectively
   a. ΔJ = Zero (0) and -1 b. ΔJ = +1 and -1
   c. ΔJ = +1 and zero (0) d. ΔJ = -1 and +1

8. The range of wave numbers in visible radiation is
   a. (1-100) cm^{-1} b. (25000-70000) cm^{-1}
   c. (500-4000) cm^{-1} d. (12500-25000) cm^{-1}

9. The radiative transition is
   a. Internal Conversion b. Intersystem crossing
   c. Vibrational relaxation d. Fluorescence

10. Beer-Lambert's law is applicable to _____ radiation only.
    a. Monochromatic
    b. Dichromatic
    c. Trichromatic
    d. Polychromatic

11. According to Born interpretation of wavefunction $\psi^* \psi$ is
    a. Probability
    b. Probability density
    c. Both a & b
    d. None of them

12. Which of the following phenomenon can't be explained by classical physics?
    a. Black body radiation
    b. Photoelectric effect
    c. Atomic spectra of hydrogen
    d. All of them

13. Which of the following motions doesn't have a zero point energy?
    a. Particle in a 3D box
    b. Simple harmonic oscillator
    c. Particle moving on a ring
    d. All of them

14. Which of the following is true with respect to energy of subshells in hydrogenic atoms?
    a. $1s < 2s < 2p < 3s < 3p < 4s < 3d$
    b. $1s < 2s = 2p < 3s = 3p = 3d < 4s$
    c. $1s < 2s < 2p < 3s < 3p < 3d < 4s$
    d. None of the above

15. The eigenfunctions of a one-dimensional simple harmonic oscillator are
    a. Spherical harmonics
    b. Bessel function
    c. Hermite polynomials
    d. Legendre polynomials

16. Which one of the following is true for angular momentum of a particle on a ring?
    a. It is a vector
    b. It is resultant of cross product of linear momentum and radius
    c. It is quantized
    d. All of the above

17. Reduced mass of HCl is
    a. Close to mass of H
    b. Close to mass of Cl
    c. Greater than mass of H & Cl
    d. Average of mass of H & Cl

18. Energy level are equally spaced in which of the following motions.
    a. Transnational
    b. Vibrational
    c. Rotational
    d. All of them

19. For a particle in a cubic box the second energy state is
    a. Less than the ground state energy
    b. Equal to the ground state energy
    c. Twice the ground state energy
    d. Thrice the ground state energy

20. Particle on a ring is solved by using
    a. Cyllindrical coordinate
    b. Polar coordinate
    c. Both a & b
    d. None of them

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Descriptive

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

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

1. a. Solve Schrodinger equation for particle on a sphere (3D rotation) using polar coordinates. **4+4+2 =10**
   b. Draw radial wavefunctions of 1s, 2s, 3s and 2p orbitals of hydrogen atom.
   c. Write the expression for Bohr radius. What is its value?

2. a. Mention the drawbacks of the harmonic oscillator model of the diatomic molecules. Write down the expression of vibrational term value of an anharmonic oscillator. Deduce the expression of the frequencies of fundamentals, 1st overtone, 2nd overtone and 1st hot band transitions. **7+3=10**

   b. Discuss the rotational Raman spectrum of $^{12}C^{16}O_2$ molecule and calculate the separation between the first stokes line and first anti-stokes lines.

3. a. Write down the unnormalized wavefunction of a particle in 1D box. Using this find the normalization constant of the wavefunction. **4+4+2 =10**

   b. Write down the two ways in which zero-point energy of a particle in 1D box can be explained.

   c. Write down properties of an well behaved wavefunction.

4. a. Define Chemical shift in NMR spectra. Mention the cause of chemical shift and state the scales used to measure it. Why TMS is used as a reference in NMR spectra? **6+4=10**

   b. State the cause of hyperline structure in ESR spectra. Write the expression of number hyperfine line , when the free electron interact with 'n' numbers of protons equally. How many hyperfines lines are found in the ESR spectrum of benzene radical ($\cdot C_6H_6$) ?

5. a. What are the laws of photochemistry? What do you mean by fluorescence quenching? **3+4+3 =10**

   b. Write notes on (i) Photosensitization (ii) Chemiluminescence

c. A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of radiation is reduced to one fourth of initial value after passing 10 cm length solution. Find molar absorption coefficient.

6. a. Suppose a hydrogen atom is adsorbed on the surface of a gold nanoparticle by a bond of force constant 855 N m−1. Calculate its zero-point vibrational energy. (MW of gold and hydrogen are 196.96657 and 1.0078 molecular units respectively). 4+4+2 =10

b. The 5th and 6th Hermite polynomials are given below. Using recursion relation find the 7th Hermite polynomial.

$H5(y) = 32y^5 - 160y^3 + 120y$

$H6(y) = 64y^6 - 480y^4 + 720y^2 - 120$

c. What is Virial theorem? How it is related to energies of simple harmonic motion?

7. a. Write the energy expression of a particle moving on a ring (2D rotation). What are the salient features of this expression. 4+3+3 =10

b. The particle-on-a-ring model is a crude but illustrative model of cyclic, conjugated molecular systems. Treat the π electrons in benzene as particles freely moving over a circular ring of carbon atoms and calculate the minimum energy required for the excitation of a π electron. The carbon-carbon bond length in benzene is 140 pm.

c. Prove that z-component of angular momentum for a particle on a ring model is quantized.

8. a. Write down the term value of a non rigid diatomic molecule. State the selection rule for rotational transitions and show that the separation of rotational spectral lines decreases with the increase of rotational quantum number. Discuss the effect of isotopic substitution of the diatomic molecule on rotational spectral lines. 7+3=10

b. Discuss how the intensity of the rotational spectrum of a diatomic molecule changes with the changes of rotational quantum number (J) and the moment of inertia.

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