REV-01
MSC/04/09

2023/08

SET A

M.Sc. CHEMISTRY
FIRST SEMESTER
QUANTUM CHEMISTRY & MOLECULAR SPECTROSCOPY I
MSC – 104 [SPECIAL REPEAT]

[USE OMR FOR OBJECTIVE PART]

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

[Objective]

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

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

1. The natural line width of the spectral line of wavelength λ due to the transition from the ground state to the excited state of life time ϒ is proportional to
   a. $\sqrt{\lambda}/\Upsilon$ b. λ/Υ^2
   c. λ^2/Υ d. λ/Υ

2. For a diatomic molecule AB, the energy for The rotational transition from J = 1 to J= 2 is 4 cm^{-1}.Then transition energy from J = 3 to J= 4 is
   a. 6 cm^{-1} b. 8 cm^{-1}
   c. 12 cm^{-1} d. 20 cm^{-1}

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

4. The vibrational frequency and anharmonicity constant of a molecule are respectively 300 cm^{-1} and 0.0025. The position of fundamental (in cm^{-1}) is
   a. 300.0 b. 298.5
   c. 301.5 d. 290.0

5. The symmetric top molecule among the following is
   a. CH_3Cl b. CH_4
   c. CCl_4 d. CH_2Cl_2

6. The centrifugal distortion constant (D) for a definite fundamental frequency in proportional to
   a. B b. B^2
   c. $1/B^2$ d. B^3

7. The frequency of first hot band is given by
   a. $\dot{\omega}_e (1- 1/2x_e)$ b. $\dot{\omega}_e (1-x_e)$
   c. $\dot{\omega}_e (1-4x_e)$ d. $\dot{\omega}_e (1-2x_e)$

8. The number of vibrational mode of CO_2 molecule common to both IR and Raman spectroscopy is
   a. Three b. Two
   c. One d. Zero

9. Doppler broadening of the wavelength λ from a source of atomic mass M at absolute temperature, T is proportional to
   a. $\sqrt{T}/M$ b. $\sqrt{M}/T$
   c. T/M d. M/T

10. If a molecule has three different notational constants, The molecule
   a. spherical top b. Asymmetric top
   c. Prolate symmetric top d. oblate symmetric top

11. For black body radiation if temperatures T1 > T2 > T3 then maximum wavelengths
   a. $\lambda 1max > \lambda 2max > \lambda 3max$ b. $\lambda 1max < \lambda 2max < \lambda 3max$
   c. $\lambda 1max > \lambda 2max < \lambda 3max$ d. $\lambda 1max = \lambda 2max = \lambda 3max$

12. Work function of a metal is analogous to
   a. Ionization energy b. Electron affinity
   c. Amplitude d. All of them

13. For a rotational motion moment of inertia (I) is equal to (m is mass of the body rotating around a center at a distance r)
   a. mr b. m/r
   c. mr^2 d. None of them

14. Which of the following is a linear operator?
   a. Square root b. Square
   c. Log d. Integration

15. The degeneracy of an excited state of a particle in 3-dimensional cubic box with energy 3 times it's ground state is
   a. 3 b. 2
   c. 1 d. 4

16. Average momentum of a particle in a box with side a is
   a. a^2 b. 0
   c. a/2 d. None of them

17. Which of the following function is an expectable wavefunction in the given interval?
   a. e^{-x} $(-\infty, \infty)$ b. $\sin^{-1} x$ $(-1, 1)$
   c. $e^{-|x|}$ $(-\infty, \infty)$ d. $(\sin x)/x$ $(0, \infty)$

18. Which of the following is correct expression for angular momentum
   a. lx = ypz - zpy b. ly = zpx - xpz
   c. lz = xpy - ypx d. All of them

19. Which of the following system doesn't have zero point energy?
   a. Particle in 1-D box b. Simple harmonic oscillator
   c. Particle in a ring d. All of them

20. The Hooke's law potential of an simple harmonic oscillator is
   a. A circle b. An ellipse
   c. A parabola d. A hyperbola

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Descriptive

Time : 2 hrs. 30 mins. Marks : 50

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

1. a. Write down the five postulates of Quantum mechanics. 5+5=10
   b. Using quantum theory calculate the frequencies of stokes and anti stokes Raman lines. Mention the draw backs of classical theory of Raman effect.

2. a. State the factors that decide the intensity of the spectral line. What conditions must be fulfill to show rotational spectrum of a molecule? Give the selection rule of rotational transition. 6+4=10
   b. Show diagrammatically the nature of variation of intensity with rotational quantum numbers of a diatomic molecule for (i) high and (ii) low rotational market constants.

3. a. Define term value. what is the advantage of using term value in spectroscopy ? write the team value of a rigid prolate symmetric top molecule. State the selection rule for notational transitions of it. Draw the energy level diagram to show the transitions. 7+3=10
   b. Calculate the bond length a diatomic molecule of reduced mass 1.627 x 1027 Kg if the average separation of the rotational spectral lines in 20.72 cm^{-1} (h= 6.626 X 10 J.s)

4. a. Calculate the frequencies of (i) fundamental (ii) 1^{st} overtone and (iii) hot band of an anharmonic oscillator. 4+4+2 =10
   b. State and explain with example of mutual exclusion principle. Define spectroscopic dissociation energy and express it interms vibrational term value.
   c. write down the potential used in anharmonic oscillation model of diatomic molecule. What are the drawbacks of harmonic oscillation model of diatomic molecule.

5. a. Show how commutator of position and momentum in x-axis can be used to verify uncertainty principle. 5+5=10
   b. What is a Harmitian operator? Show that eigen functions of a Harmitian operator are orthogonal.

6. a. Explain the rotational Raman spectra of $^{16}O_2$ molecule and the separations of Raman lines in terms of rotational Constant of the molecule. **5+5=10**

   b. When lithium is irradiate with light, the kinetic energy of the ejected electrons is 2.935×10^{-19} J for $\lambda = 300.0$ nm and 1.280×10^{-19} J for $\lambda = 400.0$ nm. Calculate the Planck constant, the threshold frequency and the work function of lithium from these data.

7. a. Graphically explain cylindrical coordinates. Using them find the wavefunction for a particle on a ring. **5+5=10**

   b. What is tunneling? Discuss it with respect to a particle in 1D box which has a potential wall of $V > E$ (energy of the particle). Write down the wavefunction of the particle inside the box, inside potential wall and outside the box.

8. a. The infrared spectrum of $^{75}Br^{19}F$ consists of an intense line at 380 cm^{-1}. Calculate the force constant of $^{75}Br^{19}F$. **3+4+3 =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. Write down the expression of energy for particle on a ring. Explain it's physical features.

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