M.Sc. CHEMISTRY
Second Semester
SPECTROSCOPY-I
(MSC – 201)

Duration: 3Hrs.

Full Marks: 70

Part-A (Objective) =20
Part-B (Descriptive) =50

(PART-B: Descriptive)

Duration: 2 hrs. 40 mins.

Marks: 50

Answer any *four* from *Question no.* 2 to 8
Question no. 1 is compulsory.

1. (i) Deduce the expressions for the Stokes and anti stokes Raman lines on the basis
   of Quantum theory. Explain the failure of classical theory and the success of
   Quantum theory over it. $(3+2=5)$

   (ii) The rotational spectral lines of HCl molecule is separated by a distance of
   $20.8cm^{-1}$. Calculate the bond length of the molecule. (5)

2. (i) Deduce the relation showing the variation of intensity with path length. Define
   optical density and how is it related with transmittance? $(3+1+1=5)$

   (ii) Write the rotational energy of a non rigid diatomic molecule. Mention the
   selection rule for transition. How the rotational energy and rotational spectra of
   non rigid diatomic molecule is different from rigid one? $(2+1+1+1=5)$

3. (i) State the factors on which intensity of the spectral line depends. Explain the
   effects of those factors. $(2+3=5)$

   (ii) Discuss how the intensity of rotational spectral lines changes with rotational
   Quantum number. Calculate the value of rotational quantum number (J) for
   maximum population. $(2+3=5)$

4. Why harmonic oscillator is not a true model of a vibrating diatomic molecule? How can you convert a harmonic oscillator to an anharmonic oscillator? Write down the energy of the anharmonic oscillator. Deduce the frequencies of fundamental, first overtone, second overtone and first hot band. Draw the potential energy versus displacement curve of an anharmonic oscillator. $(2+1+2+4+1=10)$

5. (i) Explain the symmetry properties of rotational energy levels of a diatomic molecule and the effect of nuclear spin on it. (5)

   (ii) Write down the rotational energy of a symmetric top molecule and deduce the frequency of transition stating the selection rule. $(2+2+1=5)$

6. (i) Define chemical shift and explain the origin of it taking CH_3OH as an example. $(1+4=5$

   (ii) Discuss the principle of proton NMR spectroscopy and deduce the condition of resonance. $(4+1=5$

7. (i) Calculate the frequencies of P, Q and R branches of rotational spectral lines in vibrational transitions. Mention the selection rules. $(3+2=5$

   (ii) Calculate the magnetic field for a 500 MHz proton NMR spectrometer. Given that $(\beta_N = 5.05 \times 10^{-27} J\ T^{-1}, g = 5.585$ and $h = 6.63 \times 10^{-34} J.S)$. (2)

   (iii) Discuss the rotational Raman spectra of $^{16}O_2$. (3)

8. (i) Explain what do you mean by spin-spin coupling? Discuss the high resolution NMR spectra of dry and pure ethanol. $(2+3=5$

   (ii) What are different types of relaxation in NMR spectroscopy? Explain. How relaxation is related with the breadth of NMR signal? $(2+2+1=5)$

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Duration: 20 minutes   Marks – 20

(PART A - Objective Type)

I. Choose the correct answer: 1×20=20

1. For the molecule CH_3CHO
   a) $I_a \neq I_b \neq I_c$ b) $I_a = I_b > I_c$
   c) $I_a = I_b < I_c$ d) $I_a = 0$

2. The spacing between rotational lines of HF molecule is $40 cm^{-1}$. The corresponding spacing of DF molecule is approximately
   a) $21 cm^{-1}$ b) $7.5 cm^{-1}$
   c) $10.5 cm^{-1}$ d) $30 cm^{-1}$

3. Distance between the first stokes and first anti stokes lines of rotational Raman spectra is
   a) 12B   b) 4B
   c) 8B   d) 20B

4. Pure rotational spectrum is exhibited by the molecule
   a) H Br   b) CH_4
   c) H_2 d) O_2

5. The nucleus which has spin $\frac{3}{2}$ is
   a) ^{35}Cl b) ^1H
   c) ^{15}N d) ^{14}N

6. Larmor frequency is given by
   a) $\frac{IBz}{2\pi\mu}$ b) $\frac{\mu Bz}{2\pi I}$
   c) $\frac{IBz}{2\pi\hbar}$ d) $\frac{\hbar Bz}{2\pi I}$

7. The nucleus which do not exhibit NMR spectra is
   a) ^{11}B b) ^{18}O
   c) ^{31}P d) ^{19}F

8. Pure rotational Raman spectrum is absent for the molecule
   a) C_2H_2 b) CH_4
   c) BF_3 d) SO_2

9. IR inactive molecule is
   a) CO   b) O_2
   c) H_2O d) NH_3

10. The molecule BF_3 is
    a) Prolate   b) Oblate
    c) Spherical top   d) Asymmetric top

11. The frequency range $7.5\times10^{14}Hz$--------$3.75\times10^{14}Hz$ belongs to the region of
    a) IR   b) Micro-wave
    c) Visible   d) Radio frequency

12. The degeneracy of rotational energy levels is
    a) $J(J+1)$ b) $J^2(J+1)^2$
    c) $(2J+1)$ d) $\sqrt{J(J+1)}$

13. The frequency of first hot band is
    a) $\overline{W}_e(i-2x_e)$ b) $2\overline{W}_e(1-3x_e)$
    c) $\overline{W}_e(1-4x_e)$ d) $2\overline{W}_e(1-2x_e)$

14. The distance between the 1st rotational spectral lines in P and R branch is
    a) 2B   b) 6B
    c) 4B   d) 8B

15. Non zero value of $\frac{d\alpha}{dr}$ of molecule are found in the spectroscopy of
    a) IR   b) NMR
    c) Raman   d) ESR

16. Radiations of wavelength range 200---400nm are obtained from
    a) Halogen lamp   b) Mercury arc
    c) Nernst filament   d) Deuterium lamp

17. At low pressure line width of rotational spectral lines are due to
    a) Heisenberg uncertainty relation   b) Collision broadening
    c) Life time broadening   d) Doppler effect

18. Successive lines are separated by 8 B in the Raman rotational spectrum of
    a) N_2 b) HCl
    c) CO   d) O_2

19. The selection rule for R and P branches of rotational spectral lines are respectively
    a) $\Delta J = 0, 1$ b) $\Delta J = -1, +1$
    c) $\Delta J = 1, 0$ d) $\Delta J = +1, -1$

20. The number of multiplet of - OH proton in pure and dry sample of ethanol in NMR spectra is
    a) One   b) Two
    c) Five   d) Three

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