

**M.Sc. CHEMISTRY
SECOND SEMESTER
SPECTROSCOPY-I
MSC-201**

(Use Separate Answer Scripts for Objective & Descriptive)

Duration : 3 hrs.

Full Marks : 70

(PART-A : Objective)

Time : 20 min.

Marks : 20

Choose the correct answer from the following:

1 × 20 = 20

6. a. Write down the rotational energy of a symmetric top molecule and deduce the frequency of transition. State the selection rule. 2+2+1
=5
- b. Explain the symmetry property of rotational energy levels of a diatomic molecule and the effect of nuclear spin on it. 5
7. a. Explain what do you mean by spin-spin coupling. Discuss the high resolution NMR spectra of dry and pure ethanol. What change in the spectrum will be observed if some acid is added to ethanol? 2+3+2
=7
- b. Calculate the magnetic field in a 300 MHz proton NMR spectrometer. Given that $(\beta_N = 5.05 \times 10^{-27} \text{ JT}^{-1})$, $g = 5.585$ and $h = 6.63 \times 10^{-34} \text{ JT}^{-1}$ 3
8. Write short notes on: 2 × 5 = 10
- a. Anisotropic polarizability.
- b. Doppler effect and its impact on spectral line.

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1. The nucleus which does not exhibit NMR spectra is
a. ^{18}O b. ^{11}B
c. ^{14}N d. ^{19}F
2. The frequency of first hot band is given by
a. $\tilde{\nu}_0(1-4x_e)$ b. $\tilde{\nu}_0(1-2x_e)$
c. $2\tilde{\nu}_0(1-2x_e)$ d. $2\tilde{\nu}_0(1-3x_e)$
3. The nucleus which has spin 3/2 is
a. ^{35}Cl b. ^{29}Si c. ^{14}N d. ^{15}N
4. Larmor frequency is given by
a. $\frac{Bz \mu}{2\pi I}$ b. $\frac{I Bz}{2\pi \hbar}$
c. $\frac{\hbar Bz}{2\pi I}$ d. $\frac{I Bz}{2\pi \mu}$
5. The intensity of NMR spectral line is proportional to
a. E_0^2 b. B_0
c. $\frac{1}{E_0^2}$ d. B_0^{-1} [B_0 =Magnetic field]
6. The separation of Stokes lines in the rotational Raman spectrum of O_2 molecule is
a. 4 B b. 8 B c. 6 B d. 10 B
7. Molecule which does not exhibit rotational Raman spectra is
a. SO_2 b. CH_4 c. BF_3 d. C_2H_2
8. The degeneracy of rotational energy level is
a. $J(J+1)$ b. $(2J+1)$
c. $J^2(J+1)^2$ d. $\sqrt{J(J+1)}$
9. If a molecule has three different rotational constants the molecule is a
a. Spherical top b. Asymmetric top
c. Prolate d. Oblate

10. IR inactive molecule is
 a. CO b. O₂ c. H₂O d. NH₃
11. For the molecule CH₃F
 a. I_A=I_B=I_C b. I_A≠I_B≠I_C c. I_B=I_C>I_A d. I_B=I_C<I_A
12. The first line of rotational Raman spectra of a diatomic molecule appear with a antistokes shift of 12cm⁻¹. The antistokes shift of the second line is
 a. 18cm⁻¹ b. 24cm⁻¹ c. 20cm⁻¹ d. 30cm⁻¹
13. The distance between the first rotational spectral line in P branch and that of R branch is
 a. 10B b. 6B c. 4B d. 8B
14. The intensity distribution of vibrational bands in electronic transitions of Iodine molecule (I₂) shows that
 a. r_e ≈ r_e' b. r_e > r_e' c. r_e >> r_e' d. r_e < r_e'
15. If B' < B'' the band head appear in
 a. P branch on the high wave number side of the band origin
 b. P branch on the low wave number side of the band origin
 c. R branch on the high wave number side of the band origin
 d. R branch on the low wave number side of the band origin
16. The width of the visible and ultraviolet spectra line is due to
 a. Natural broadening b. Doppler broadening
 c. Heisenberg Uncertainty Principle d. Collision broadening
17. Rotational constants of ¹⁴N₂ is 2 cm⁻¹. If the wave number of incident radiation in a Raman spectrometer is 20487 cm⁻¹. The wave number of first scattered stokes line (in cm⁻¹) of ¹⁴N₂ is
 a. 20479 b. 20495 c. 20499 d. 20475
18. The set of allowed electronic transitions among the following
 A. ⁴Σ → ²Π, B. ³Σ → ³Π, C. ¹Δ → ¹Δ, D. ²Π → ²Π, E. ³Σ → ³Δ
 a. A,B,E b. A,C,E c. C,D,E d. B,C,D
19. The wave number of rotational transition of diatomic molecule AB from J=0 to J=1 is 5 cm⁻¹. The wave number for the transition from J=3 to J=4 state would be
 a. 5 cm⁻¹ b. 10 cm⁻¹
 c. 15 cm⁻¹ d. 20 cm⁻¹
20. Neglecting the mass of hydrogen (1.0 amu) and deuterium (2.0 amu) with respect to Iodine (127 amu) the ratio of fundamental vibrational frequency of HI and DI is
 a. $\frac{1}{2}$ b. 2
 c. $\frac{1}{\sqrt{2}}$ d. $\sqrt{2}$

(PART-B : Descriptive)

Time : 2 hrs. 40 min.

Marks : 50

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

1. Draw the potential energy versus displacement curve of a diatomic molecule treating it as an anharmonic oscillator. What is the weakness of harmonic oscillator model of a diatomic molecule? Write down the potential used in anharmonic oscillator model of a diatomic molecule. Deduce the frequency of fundamental, first overtone, second overtone and first hot band starting from the energy of harmonic oscillator. 2+2+1+1=5
2. a. Write the rotational energy of a non rigid diatomic molecule. Show the difference of rotational energy and rotational spectrum of a non rigid molecule from the rigid one. State the selection rule for the transition. 2+1+1+1=5
 b. Rotational spectral lines of a diatomic molecule (HCl) is separated by a distance 20.8 cm⁻¹. Calculate the bond length of the molecule. 3
 c. Discuss the effect of isotope on the rotational spectra of the diatomic molecule. 2
3. a. Discuss the principle of proton NMR spectroscopy and deduce the condition of resonance. 4+1=5
 b. Define chemical shift and explain the origin of it taking CH₃OH as an example. 1+4=5
4. a. Calculate the frequencies of P, Q and R branches of rotational spectral lines in vibrational transition stating its selection rules. 5
 b. Discuss the rotational Raman spectra of ¹⁶O₂ molecule. 5
5. a. Calculate the frequencies of stokes and antistokes Raman line on the basis of quantum theory. Why the classical theory of Raman effect is not accepted as the true theory? 3+2=5
 b. Show that the intensity of NMR spectral line is dependent on the applied magnetic field. 5