LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

THIRD SEMESTER – NOVEMBER 2007

CH 3810 - MOLECULAR SPECTROSCOPY

AD 20

Date : 29/10/2007 Dept. No. Max. : 100 Marks

Time : 9:00 - 12:00

PART A

Answer ALL the questions. (10 x 2 = 20 Marks)

1. What is transition dipole moment? What is its importance in spectroscopy?
2. A certain molecular transition involved an energy change of 1700 cm^{-1}. If there are 100 molecules in the ground state, what will the approximate number of molecules (equilibrium population) found in the excited state at 25 ^{0}C??
3. What is an S/N ratio? How can it be enhanced?
4. Differentiate between a hot band and an overtone in the nature of their transitions.
5. What are the three important parts of a laser?
6. Write the McConnel equation and mention its application.
7. What are meta stable ions?
8. Illustrate W-Coupling with suitable example.
9. Write the structure of the hydrocarbon with molecular formula C_5H_{12} which has only a singlet in its ^{1}H NMR spectrum.
10. What is isomer shift?

PART – B

Answer ANY EIGHT questions (8 x 5 = 40 Marks)

11. Explain the factors affecting the intensity of spectral lines.
12. Given that the spacing of lines in the microwave spectrum of $^{35}Cl^{19}F$ is constant at 1.033 cm^{-1}. Calculate the rotational constant, B, and hence the moment of inertia and the bond length of the molecule. Find which transition gives rise to the most intense spectral line at room temperature (300K).
13. Sketch the energy transition processes to differentiate the origin of Stokes' lines, Anti-Stokes' lines and Rayleigh scattering with respect to their position in spectrum and the intensity of the spectral lines.
14. The Bond length of NO is 115.1 pm. Bond force constant is 1595 Nm^{-1}. Calculate (a) Zero-point energy and the energy of the fundamental vibration ν_0. (b) Calculate the rotational constant B. (c) Calculate the wave numbers of the lines P_1, P_2, R_0 and R_1
15. Draw Jablonski energy level diagram and explain the various absorption and emission processes.
16. With which type of spectroscopy would one observe the pure rotation spectrum of H_2? If the bond length of H_2 is 0.07417 nm, what would be the rotational constant and the spacing of the lines in the spectrum?
17. Write briefly on the chemical ionization method for the production of molecular ions in mass spectrometer.
18. Discuss the anisotropic effect on the chemical shifts in PMR spectroscopy with two examples.
19. Discuss the mechanism of spin-spin splitting in AX system.
20. Explain how the hydrogen bonding and solvent influence the chemical shifts in ^{1}H NMR spectroscopy.
21. Discuss the theory of NQR spectra.
22. Arrive at the hyperfine splitting pattern in the following species: (a) isopropyl radical (b) bis (salicylaldoxime) copper (II) ion.

PART – C

Answer ANY FOUR questions (4 x 10 = 40 Marks)

23. (a) Outline the causes for broadening of the spectral lines. (5)

(b) State and explain the Franck-Condon Principle. How are the intensity variations of electronic spectra explained by this principle?

24. a) Explain the origin of P, Q, R branches of the rotation-vibration spectra.

b) The fundamental and first overtone transitions of CO are centered at 2143.26 cm^{-1} and 4260.04 cm^{-1} respectively. Evaluate the equilibrium vibration frequency and the zero-point energy.

25. a) When a radiation of 304Å is used to obtain the PES of benzene, the ionization potential for the electron is 9.3 eV. Find the kinetic energy and velocity of the electrons. [1 eV = 1.602 x 10^{-19} J] (4)

b) What is population inversion? Prove that a population inversion cannot be achieved in a two level system while it is possible in a three level system. (6)

26. a) Describe the various parts of NMR spectrometer and explain their functions. (5)

b) What is meant by geminal coupling constant? Explain how the hybridization of carbon and the substituents affect the geminal coupling constant. (5)

27. a) What are lanthanide shift reagents? Mention their use in NMR spectra. (5)

(b) Explain proton exchange reactions with an example. (5)

28. (a) Explain the ^{13}C chemical shift values for the aromatic carbon atoms in the following molecules: (i) phenyl acetylene (ii) Ethyl benzene

Use the following substituent constant values: (5)

Substituent	z_1	z_2	z_3	z_4
C_2H_5-	15.7	- 0.6	- 0.1	- 2.8
HC≡C-	- 6.1	3.8	0.4	- 0.2

(b) An organic compound with molecular formula C_9H_{10} contains the following signals in its PMR spectrum. (5)

i) quintet, ∂ = 2.04 ppm, 2H

ii) triplet, ∂ = 2.91 ppm, 4H

iii) broad singlet, ∂ = 7.17 ppm, 4H

Assign a suitable structure to the compound which is consistent with the above data and explain.

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