LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

SECOND SEMESTER – **APRIL 2013**

CH 2821 - MOLECULAR SPECTROSCOPY

Date : 02/05/2013   Dept. No. [   ]   Max. : 100 Marks
Time : 9:00 - 12:00

Part A

Answer all questions   **(10 x 2 = 20)**

1. Rotational and centrifugal distortion constants of a diatomic molecule are 8.473 cm^{-1} and 3.7 x 10^{-4} cm^{-1} respectively. Estimate the vibrational frequency of the molecule.
2. How will you distinguish between Geometric isomers of ClCH=CHCl using IR spectroscopy?
3. Explain mutual exclusion rule with an example.
4. What is the nitrogen rule?
5. Calculate the value of g_n for ^{13}C nuclei if its resonance frequency is 10.7MHz at a field strength of 10 kilogauss.
6. Why is the electric quadrupole moment zero for Hydrogen atom?
7. How many signals are expected in the proton decoupled ^{13}C NMR spectrum of toluene?
8. The ESR spectrum of the radical AB_3° shows six lines. Predict the spin of the atom A.
9. What is isomer shift?
10. State Born – Oppenheimer approximation.

Part – B

Answer any EIGHT questions only   **(8 x 5 = 40)**

11. Explain the influence of rotation on parallel and perpendicular vibrations of symmetric top molecules
12. The fundamental band of DCl^{35} is centredat 2011 cm^{-1}. Assume that the internuclear distance is constant at 1.288 A, and calculate the wave numbers of the first two lines of each of the P- and R- branches of DCl^{35}.
13. How will you distinguish between the following pairs of organic compounds? Name the vibrations and appropriate positions of absorptions in each case. (i) $C_6H_5CH_2CH_2CH_3$ and $C_6H_5CH_2CH=CH_2$ (ii) $(CH_3)_3N$ and $CH_3CH_2CH_2NH_2$
14. The rotational Raman spectrum of HCl, the displacements from the exciting lines are represented by $\Delta v = \pm$ (62.4 + 41.6 J) cm^{-1}. Calculate the moment of inertia of the HCl molecule
15. Explain the isotopic effect in identifying the Bromine and Chlorine compounds.
16. Explain nuclear hyperfine splitting with an example.
17. Compare the proton NMR spectra of $^{31}PH_3$ and $^{14}NH_3$.
18. Assign a possible structure and the point group to HIO_3 molecule which shows a finite asymmetry parameter in Iodine quadrupole resonance.
19. State Franck-Condon principle and account for the intensity distribution in absorption bands.

20. A compound C_7H_8O produces the following signals in its ^1H NMR spectrum.
    Singlet $\delta=2.43$(1H); singlet $\delta=4.58$(2H); multiplet $\delta=7.28$(5H). Its IR spectrum consists of a broad peak in 3200-3500 cm^{-1} region. Identify the compound.
21. While the NMR frequency is expressed in MHz unit, EPR frequency is in GHz. – Account.
22. Discuss the application of NQR in the location of the principal axis in a molecule.

Part – C

Answer any FOUR questions only   **(4 x 10 = 40)**

23. a) The observed infrared absorption and Raman spectral lines of a molecule of the type XY_3 are given below. Deduce the structure of the molecule and assign observed funamentals. (4)

IR Frequencies (cm^{-1})	Raman Frequencies (cm^{-1})
482 ($\perp$)	482 weak depolarized
720 (‖)	-
-	888 strong polarized
1505($\perp$)	1497 weak depolarized

b) The fundamental and first overtone transition of CO arecentred at 2143.3 cm^{-1} and 4260.0 cm^{-1} respectively. Evaluate the equilibrium vibration frequency, the anhormonicity constant and force constant of the molecule. (6)

24. a) Explain the intensity of vibrational Raman lines. (4)

b) The three consecutive lines in the rotational spectrum of a diatomic molecule are observed at 84.544, 101.355 and 118.112 cm^{-1}. Assign these lines to their appropriate $J^{''}$ - J' transitions and deduce the values of B and D. Hence evaluate the approximate vibrational frequency of the molecule. (6)

25. a)What is a metastable peak? Explain it with an example. (3)

b) Predict the structure of an organic compound $C_{10}H_{12}O$ which exhibits m/e peaks at 15, 43, 57,91, 105 and 148 in its mass spectrum. (7)

26. a) Predict the multiplicity of each signal of isopentyl methyl ketone and discuss its correlation spectrum using 2D technique. (6)
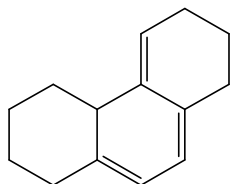
b) Explain virtual coupling with an example. (4)

27. a) Explain the effect of temperature on NQR frequencies in presence of and absence of hydrogen bonding with relevant examples. (6)

b) Calculate the chemical shift of a ^1H NMR signal which appears at 180Hz in a 60 MHz instrument. Find out the frequency at which the same signal would appear in a 100 MHz instrument. (4)

28. 28. a) Sketch the energy levels and discuss the Mossbauer transitions in $^{57}Fe^*$ nucleus from I = 1/2 to I = 3/2 level in presence of i) quadrupole splitting and ii) external magnetic field.(5)

b) Determine the maximum wave length of absorption of the following compounds.(5)

i)   ii)