LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

SECOND SEMESTER – APRIL 2017

16PCH2MC03/CH 2821 - MOLECULAR SPECTROSCOPY

Date: 24-04-2017 Dept. No. Max. : 100 Marks
Time: 01:00-04:00

Part-A

Answer ALL questions. **(10 x 2= 20)**

1. Which rotational state of CO would be the most populated at 300 K. The rotational constant of CO is 1.9212 cm^{-1}.
2. How will you differentiate nitro and nitrito metal complexes by IR spectroscopy?
3. What is hypsochromic effect? Mention an example.
4. The complex $[Cr(CO)_6]$ shows MLCT band and not LMCT band in electronic spectrum. Why?
5. State the even electron rule obeyed in mass spectrometry.
6. Mention the condition to observe virtual coupling.
7. Sketch the ^{31}P-NMR of H_3PO_2.
8. A free radical has a g-value of 2.2002. Calculate the field at which the resonance would occur in an ESR spectrometer operating at 9,300 MHz.
9. What is the significance of asymmetry parameter?
10. What are Kramer doublets?

Part-B

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

11. Explain the appearance of P and R branches in the spectrum of a diatomic vibrating rotor.
12. The rotational constant for $H^{35}Cl$ is 10.5909 cm^{-1}. Determine the rotational constant for $H^{37}Cl$.
13. An organic compound with molecular formula C_7H_8O gives the following spectral data:
    UV: λ_{max} – 255 nm (ε_{max} - 202)
    IR: ν_{max}(cm^{-1}) -3402 (s,br), 2888 (m), 1499 (w, sh), 1455 (m)
    NMR: δ 7.26 (5H, s), 4.6 (2H, s) and 3.9 (1H, s)
    Mass: m/z values – 108, 107, 77, 51
    Deduce the structure of the compound.
14. State Franck-Condon principle and show that if the ground and excited vibrational states have identical potential energy curves, the (0,0) transition is the most intense.
15. Write a detailed account on the various types of electronic transitions.
16. How will you distinguish the three isomeric butanols on the basis of mass spectrometry?
17. Explain diamagnetic anisotropy and vicinal coupling.

18. Distinguish between AB and AX types of spectrum with examples.
19. Calculate the g- value for the energy state $^4F_{9/2}$.
20. Distinguish between fine splitting and hyperfine splitting with suitable examples.
21. While chlorine molecule shows a finite quadrupole coupling constant, sodium chloride does not. – Justify.
22. How does hydrogen bonding affect the frequency of quadrupole transitions?

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

23a. Explain the various factors influencing vibrational frequencies in IR spectroscopy.

b. Discuss the pure rotational Raman spectrum of linear molecules. (5+5)

24a. The partial hydrogenation of a triene (A) gives three isomeric dienes. Show how the expected λ_{max} values could distinguish the isomers. The structure of A is

b. What are chromophores and auxochromes? (6+4)

25a. Explain the significance of retro-Diels-Alder fragmentation in mass spectral analysis with suitable examples.

b. Write the principle of fast atom bombardment ionisation technique and mention its advantages. (6+4)

26a. Explain the significance of diagonal and off diagonal spots in 2D NMR.

b. Calculate the ratio of ESR frequency of an electron to the NMR frequency of a proton in the same applied field. Given: $\beta_e = 9.27 \times 10^{-24}$ and $\beta_n = 5.05 \times 10^{-27}$. (6+4)

27a. The radical $AlH_3^{\bullet}$ shows 24 lines in its EPR. Calculate the spin of Al atom.

b. What are prolate and oblate nuclei. Give examples (5+5)

28a. Calculate the nuclear quadrupole energy levels for a nucleus with I = 2 as a function of e^2Qq. How many transitions are possible? Give the expressions for the frequencies of the transitions.

b. Distinguish between isotropic and anisotropic hyper fine interactions with examples. (6+4)

$$$$$$$$