LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECOND SEMESTER – NOVEMBER 2016

CH 2821 - MOLECULAR SPECTROSCOPY

Date: 17-11-2016 Dept. No. Max. : 100 Marks

Time: 09:00-12:00

Part-A

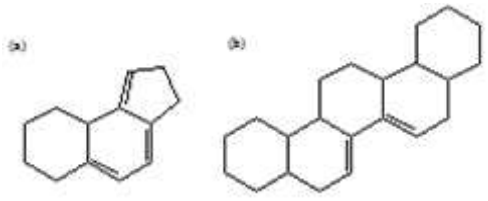
Answer ALL questions. **(10 × 2 = 20)**

1. State the reason for the exceptionally low carbonyl stretching frequency of 2,4,6-cycloheptatrienone in IR spectroscopy.
2. Why does the IR spectrum of benzoyl chloride show a band at 1770 cm^{-1} with a shoulder at 1740 cm^{-1}?
3. Calculate the concentration of camphor in hexane in a 10 cm cell with absorbance of 2.52 at 295 nm (ε = 14 cm^{-1} L mol^{-1}).
4. Azobenzene is a deep orange red while hydrazobenzene is colourless- Account.
5. How will you distinguish among three isomeric butanols on the basis of mass spectrometry?
6. Obtain the NMR frequency of proton in a magnetic field of strength 1.5 T. Given: g_e = 5.5.
7. Predict the number of signals possible in the proton decoupled ^{13}C NMR spectrum of toluene.
8. Mention the significance of asymmetric parameter.
9. Account for the doublet observed in the Mossbauer spectrum of $Fe(CO)_5$.
10. What is hyperfine splitting?

Part-B

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

11. The first line in the rotational spectrum of CO occurs at 3.8424 cm^{-1}. Calculate its rotational constant and bond length. The atomic mass of C is 12 g/mol and O is 15.99 g/mol.
12. Explain the IR spectrum of toluene, which shows absorptions at 3030, 2850-2960, 1600, 1580, 1460, and 730-770 cm^{-1}.
13. Explain the Stark effect of a linear molecule using rotational spectra.
14. Calculate λ_{max} for the following:



15. Predict the structure of the compound, which shows m/e peaks at 88, 70, 57, 43, 31 (much intense) and 29 in its mass spectra.
16. Determine the structure of the compound (molecular weight of $C_8H_{14}O_3$ is 158) which absorbs in the UV region at 225 nm. In IR spectrum, IR absorption bands are formed at 3077-2855 (m), 1825 (s), 1757 (m) and 1456 cm^{-1} (m). In NMR, two signals are observed at 7.30τ septet and 8.80 τ doublet.
17. How will you differentiate primary, secondary and tertiary amines using ^1H NMR?
18. What is coupling constant? How does it vary with dihedral angle?
19. Sketch the number of orientations and transitions possible for a low spin d^1 octahedral complex.
20. What is zero field splitting? Explain the causes of zero field splitting.
21. How is quadrapole resonance useful to determine the point group of a molecule?
22. Explain Franck-Condon principle to account for the intensity of electronic transitions.

Part-C

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

23 a. Using Mohr's curve explain the vibrational energy of a diatomic molecule. **(5)**

b. An organic compound with molecular weight 120 shows a prominent peak at 105 in its mass spectrum. It also shows a positive response towards iodoform test. Identify the structure of the compound and predict its mass spectral pattern. **(5)**

24 a. If the bond length of hydrogen is 0.07417 nm, calculate the position of the first three rotational Raman lines in the spectrum if the mass of hydrogen is 1.673×10^{-27} kg. **(5)**

b. How will you account for the origin of overtones and combination bands? **(5)**

25. An organic compound absorbs at λ_{max} = 210 nm, (ε_{max} = 60) in UV spectrum. In NMR, it shows a triplet (8.71 τ, J = 7.2 cps), quartet (5.84 τ, J = 7.2 cps) and singlet (7.5 τ). It shows IR absorptions at 2940 (m), 2855 (m), 1742 (s), 1460 (m), 1260 (s), and 1055 cm^{-1} (s). It shows a molecular ion peak at m/e = 60. Identify the structure of the compound and predict its mass spectral pattern.

26 a. Discuss the principle of HeteroCOSY with an example. **(6)**

b. Mention the importance of shift reagents in NMR. **(4)**

27 a. Explain hyperfine coupling with equivalent and non-equivalent protons. **(6)**

b. ^{35}Cl nucleus requires Zeemann effect to determine its quadrupole parameters- Expain. **(4)**

28 a. Explain the effect of octahedral geometry of $K_4[Fe(CN)_6]$ in its quadrupole resonance and Mossbauer transitions. **(6)**

b. Obtain the value of Lande-Splitting factor for the ground state term symbol $^1P_0$. **(4)**

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