LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

SECONDSEMESTER – APRIL 2018

17/16PCH2MC03/CH2821- MOLECULAR SPECTROSCOPY

Date: 21-04-2018 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

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

1. Find the vibrational wave number of HCl having a rotational constant of 10.593 cm^{-1} and centrifugal distortion constant of 5.3×10^{-4} cm^{-1}.
2. How will you distinguish $CH_3CH_2NH_2$ and $CH_3CH_2CONH_2$ using IR spectroscopy?
3. State Franck-Condon principle.
4. Why is the $\sigma \rightarrow \sigma^*$ transition observed only in vacuum UV region?
5. Predict the base peak in the mass spectrum of toluene.
6. Calculate the Larmor frequency of a ^{13}C nucleus in a magnetic field of 24.3 T, given that the gyromagnetic ratio is 6.73×10^7 T^{-1} s^{-1}.
7. Vicinal coupling constants in olefins is larger for *trans*coupling than for *cis* coupling - Why?
8. Write the McConnel equation and mention its application.
9. Determine the Doppler velocity of gamma ray emission whose line width is found to be 1.45×10^{-12}.
10. Justify how temperature dependence of NQR frequencies determines the hydrogen bonding strength of a compound.

Part-B

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

11. Discuss the factors influencing the intensity of spectral lines.
12. The vibrational Raman spectrum of $^{35}Cl_2$ shows a series of Stokes' lines separated by 0.9752 cm^{-1}. Find the bond length of Cl_2.
13. Explain P and R branches in the spectra of a diatomic vibrating rotor.
14. Discuss the different types of absorption bands seen in electronic spectrum of organic compounds.
15. Discuss MLCT and LMCT bands of transition metal complexes with suitable examples.

16a. Explain how linkage isomers can be studied with the help of IR spectroscopy?

b. What is a metastable ion peak? (3+2)

17. Explain the two kinds of relaxation process in ^1H NMR spectroscopy.
18. An acetylene proton signal is observed at downfield compared to an alkene proton. Why?

19. Arrive at the hyperfine splitting pattern of the following complexes:

(a) bis (salicyaldoxime) copper (II) ion (b) $[Ti(H_2O)_6]^{2+}$

20. An organic compound with the molecular weight 108 shows the following spectral data:

UV: λ_{max} 255 nm ε_{max} 202

IR: 3402 (s,b), 3065 (w), 2288 (m), 1499 (w,sh) and 1455 cm^{-1}(m)

NMR: 7.26 δ (singlet, 24.5 squares), 4.6 δ (singlet, 9.5 squares), 3.9 δ (singlet, 4.8 squares).

Arrive at the correct structure of the molecule.

21. Describe the importance of asymmetry parameter and quadrupole coupling constant in NQR spectroscopy.

22. Mössbauer spectra are recorded by mounting the sample nucleus in solid matrices-Justify.

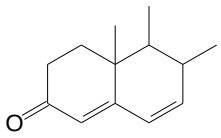
Part-C

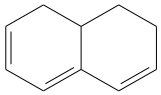
Answer any FOUR questions. **(4 x 10= 40)**

23a. Explain the influence of rotation on parallel and perpendicular vibrations of symmetric top molecules.

b. State and explain the rule of mutual exclusion principle. (6+4)

24a. Predictλ_{max} for the following compounds using Woodward-Fieser rule.

(i) 



(ii)

b. Distinguish between hypsochromic and bathochromic shifts with relevant examples. (6+4)

25a. The mass spectrum of an organic compound having molecular formula, $C_5H_{10}O$ shows peaks at m/z values 86, 85, 44 (base peak), 57,42 and 29. Predict the structure and confirm it by showing the various fragmentation patterns.

b. State the even electron rule followed in mass spectrometry. (7+3)

26a. ^1H NMR spectrum of an organic compound recorded on 400 MHz spectrometer shows a quartet with line position at 1859, 1853, 1847 and 1841 Hz. Calculate the chemical shift (δ,ppm) and coupling constant (J, Hz) of quartet peak.

b. Explain the significance of diagonal and off diagonal spots in 2D NMR spectrum of 3-bromobutane.

27a. Account for the importance of zero-field splitting in the EPR spectra of triplet naphthalene and V^{3+} ion.

b. What are lanthanide shift reagents? Mention their uses in NMR spectroscopy.

28a. Calculate the nuclear quadrupole energy levels and their corresponding NQR frequencies for a nucleus with I = 3 as a function of e^2Qq. How many transitions are possible?

b. Discuss the Mössbauer spectral features of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_5(NO)]$ complexes.

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