LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FOURTH SEMESTER – NOVEMBER 2016

CH 4809 – APPLICATIONS OF SPECTROSCOPY

Date: 10-11-2016   Dept. No.   Max. : 100 Marks
Time: 01:00-04:00

Part-A

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

1. Compare the electronic absorptions characteristics of biphenyl with 2,2$'$-dimethyl biphenyl and 2-methyl biphenyl.
2. What is isobestic point?
3. What are the types of in-plane bending present in IR spectroscopy?
4. Give an example for Retro-Diels Alder reaction.
5. What is the base peak of n-butyl benzene in mass spectrometry?
6. Mention the condition for virtual coupling in NMR.
7. Predict the ^{1}H-NMR spectrum of a compound containing enantiotopic hydrogen atoms.
8. What are isochronous protons? Give an example.
9. Mention the significance of asymmetry parameter.
10. Define isomer shift.

Part-B

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

11. Calculate λ_{max} for the following:
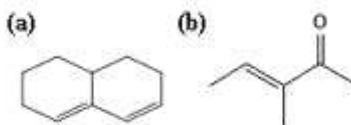
12. What is the effect of solvent in n $\rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions?
13. Explain the mass spectral pattern of methyl butanoate.
14. Distinguish between primary, secondary, tertiary amines and alcohols using mass spectra.
15. Explain the IR spectrum of cyclohexane that shows absorptions at 3030, 2940, 1433 and 720 cm^{-1}.
16. Rotational and centrifugal distortion constants of a molecule are 10.593 cm^{-1} and 5.3 x 10^{-4} cm^{-1} respectively. Estimate the vibrational frequency and force constant of the molecule.
17. Explain first and second order spectrum in NMR with relevant examples.
18. Discuss the splitting pattern in ^{1}H-NMR spectrum of methylamine and acetamide.
19. Define coupling constant. Explain its calculation with an example.
20. Explain nuclear hyperfine splitting exhibited by a high spin d^5 system.
21. How will you account for the difference in isomer shift shown by Sn^{2+} and Sn^{4+} compounds?
22. Sketch the energy levels and NQR transitions possible for I=5/2 and I=7/2 nuclei.

Part-C

23. a. How will you differentiate the types of hydrogen bonding using IR spectroscopy? (5)
    b. The Raman line associated with a vibrational mode which is both Raman and infrared active is found at 4600 Å when excited by light of wavelength 4358 Å. Calculate the wavelength of the corresponding infrared band. (5)

24. An organic compound absorbs at λ_{max} = 205 nm in its UV spectrum. IR absorption bands are formed at 3049-2924 cm^{-1}, 1445 cm^{-1} and 1735 cm^{-1}. It shows NMR signals at -1.93 τ (singlet), 5.88 τ (triplet), 8.33 τ (sextet) and 9.05 τ (triplet). It shows a molecular ion peak at m/e =88 and a base peak at 60. Suggest the structure of the compound and explain.

25. Explain the fragmentation pattern of pentanoic acid and acetophenone using mass spectroscopy.

26. a. Explain vicinal and aromatic coupling with examples. (5)
    b. Discuss hyperfine splitting observed in isotropic systems. (5)

27. a. Explain the principle of correlation spectroscopy with an example. (6)
    b. Sketch the energy levels and indicate the ERP transitions expected for $CF_3^{\bullet}$ radical. (4)

28. a. What is quadrupole coupling constant? Mention its importance. (6)
    b. Calculate the 'g' value for the ground state term symbol $^6S_{5/2}$. (4)

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