18P315 (Pages: 3) Name……..……

Reg. No……..……

THIRD SEMESTER M.Sc. DEGREE EXAMINATION, NOVEMBER 2019

(Regular/Supplementary/Improvement)

(CUCSS - PG)

(Chemistry)

CC15P CH3 C09 - MOLECULAR SPECTROSCOPY

(2015 Admission onwards)

Time: Three Hours Maximum: 36 Weightage

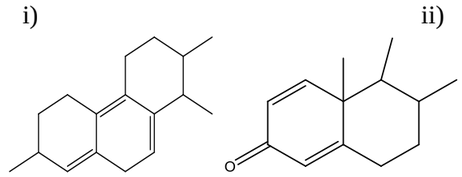
Part A

Answer ***all*** questions. Each question carries 1 weightage.

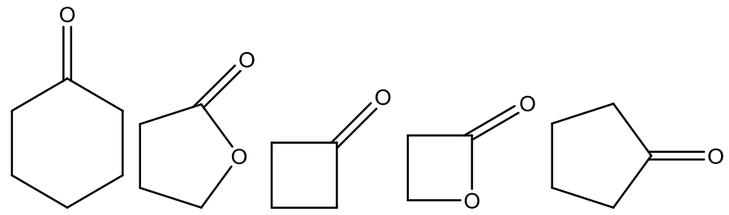
1. Explain the term Doppler Broadening.
2. Distinguish between Oblate and Prolate molecules. How many rotational constants are possible for each of them?
3. Distinguish between fundamental, overtone and hot bands.
4. Which of the following molecule(s) show rotational Raman spectrum? Justify your answer.

   i) CO_2 ii) CO iii) CH_4 iv) BCl_3
5. How many ESR hyperfine lines are observed for p-nitro benzoate dianion molecule? Explain.
6. In AX spectrum, four lines were observed at δ 5.8, 5.7, 1.1 and1.0 (measured from TMS with an instrument operating at 100 Hz). What is the coupling constant (in Hz) value between them?
7. Calculate the λ_{max} of the following compounds

   i) ii)

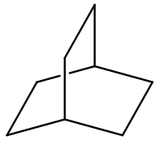


8. Arrange the following compounds in the increasing order of vibrational frequency.



9. Predict the number of proton NMR signals in N,N Dimethyl formamide. Explain.
10. Indicate the number of signals and their multiplicity in the off resonance ^{13}C NMR spectra of the following compounds

i) ii) p- Xylene



11. What are meta stable ion peaks? How they are formed?
12. Explain McLafferty rearrangement.

(12 x 1 = 12 Weightage)

Section B

Answer any ***eight*** questions. Each question carries 2weightage.

13. Define Stark effect. How it is useful for the calculation of Dipole moment of molecules?
14. Three Rotational lines in rotational spectrum of diatomic molecule are observed at 84544,101355, 118112cm^{-1}. Assign these line to their appropriate J"→J' transitions and Deduce the value of B and Distortion constant D.
15. Derive an expression for Jmax for the rigid rotor at which there is maximum population.
16. State and Explain with example mutual Exclusion principle.
17. Discuss Free Electron Molecular orbital theory for the electronic spectra of conjugated polyenes.
18. Briefly explain FT NMR? What are the advantages of FT NMR over conventional CW NMR?
19. Explain zero field spitting and Kramer Degeneracy.
20. Write short note on COSY.
21. How will you distinguish the following using IR spectroscopy?
    i) Ortho hydroxy benzaldehyde and para hydroxy benzaldehyde
    ii) Nitro alkane and alkyl nitrites
22. i) Explain with suitable example chemically, stereo chemically and magnetically equivalent Protons.
    ii) How NMR is useful for the distinguishing homotopic, enantiotopic an diastereotopic protons.
23. Explain how Octant rule and Axial haloketone rule are useful for the determination of conformation and configuration of 3-methyl cyclohexanone.
24. How will you distinguish 2-pentanone and 3-pentanone using mass spectroscopy?

(8 x 2 = 16 Weightage)

Section C

Answer any ***two*** questions. Each question carries 4 weightage.

25. Explain Mossbauer Effect. Explain the application of Mossbauer spectroscopy for the structural determination of iron complexes.
26. i) State Frank- Condon principle. Discuss its importance in understanding the intensity of electronic transitions.
    ii) Discuss the origin of P, Q, R lines in vibrational rotational spectrum of molecules.
27. Write short note on:
    i) Coupling constant and factors affecting coupling constants.
    ii) Karplus relationhips. iii) Nuclear Overhauser effect. iv) Shift reagents.
28. An organic compound with formula $C_6 H_{10} O_2$ gave the following spectral data. Deduce the Structure of compound an explain the spectral data.
    MS: prominent peak at m/e 146,87 and 43
    UV: No significant absorption bands above 210nm
    IR: Significant absorption band at 1760 an 2950cm^{-1}.
    PMR δ 1.5(3H,) 2.2(6H,s) an 6.8(1H,q)
    13C NMR (off resonance decoupled) one singlet δ 165, one doublet and two quartets.

(2 x 4 = 8 Weightage)

****