STELLA MARIS COLLEGE (AUTONOMOUS) CHENNAI-86
(For candidates admitted during the academic year 2019–2020 & thereafter)

M.Sc. DEGREE EXAMINATION, NOVEMBER 2023
BRANCH IV- CHEMISTRY
THIRD SEMESTER

COURSE : CORE
PAPER : MOLECULAR SPECTROSCOPY
SUBJECT CODE : 19CH/PC/MS34
TIME : 3 HOURS **MAX.MARKS :100**

SECTION – A **(20x1=20)**

Answer all the questions:
Choose the correct answer:

1. The order of different type of energies is
   a) $E_{el} >> E_{vib} >> E_{rot} >> E_{tr}$ b) $E_{el} >> E_{rot} >> E_{vib} >> E_{tr}$
   c) $E_{el} >> E_{vib} >> E_{tr} >> E_{rot}$ d) $E_{tr} >> E_{vib} >> E_{rot} >> E_{el}$

2. The region of electromagnetic spectrum for nuclear magnetic resonance is
   a) Microwave b) Radio frequency c) Infrared d) UV-rays

3. Which of the following is an application of molecular spectroscopy
   a) Structural investigation
   b) Basis of understanding of colors
   c) Study of energetically excited reaction products
   d) All of the above

4. The transition zone for Raman spectra is
   a) Between vibrational and rotational levels
   b) Between electronic levels
   c) Between magnetic levels of nuclei
   d) Between magnetic levels of unpaired electrons

5. Separation of ions in mass spectrometer take place on the basis of which of the following?
   a) Mass b) Charge c) Molecular weight d) Mass to charge ratio

Fill in the blanks:

6. If centre of gravity of the molecule changes during its motion, the molecule is said to possess ---------- energy.
7. The selection rule for pure rotational Raman spectra of diatomic molecule is ----------.
8. The standard used in NMR spectroscopy is ----------.
9. Increase in extent of conjugation shifts the absorption bands to --------- wavelength region.
10. Molecular term symbol for ground state O_2 molecule is ----------.

State whether True or False:

11. Sample recovery is possible after spectroscopic analysis because the sample is not chemically affected.
12. Alpha particles are used to bombard the sample for which mass spectroscopy has been performed
13. H_2 is infrared active.
14. Proton NMR spectra of C_6H_6 will have only one singlet.
15. Region between 600- 1400 cm^{-1} in IR spectra is Fingerprint region.

Answer in one or two sentences:

16. Which of the following HCl, CO, H_2 and O_2 will show rotational spectra.
17. Compare fundamental vibrations from hot bands.
18. State nitrogen rule in mass spectroscopy.
19. Mention any two factors affecting absorption spectra.
20. What is the significance of coupling constants in NMR spectroscopy.

SECTION – B (5 x 8 = 40)

Answer any FIVE questions:

21. What is Nuclear Overhauser Effect (NOE)? Explain with one example
22. State and explain Franck-Condon Principle.
23. Discuss the electronic transistions in σ, π and n molecular orbitals.
24. Discuss the Pure rotational and rotation-vibrational Raman Spectrum of a diatomic molecule.
25. The internuclear distance in HF molecule is 0.092 mm. Calculate moment of inertia of HF molecule. Atomic mass of H and F are 1.00 amu and 19.0 amu respectively.
26. What do you understand by line width of spectral line and intensities of spectral lines.
27. a) What is meant by chemical shift? Discuss on shielding and deshielding of protons.
    b) The compound having the molecular formula $C_{10}H_{14}$ gave the following PMR data 0.88δ (9H,s) and 7.28δ (5H,s). Assign the structure to the compound.

SECTION – C (2 x 20 = 40)

Answer any TWO questions:

28. a) Derive an expression for the rotational energy of a rigid diatomic molecule. Discuss the transistions between various rotational levels, spectrum and also discuss on the Intensities of the spectral lines. (8+4+3)
    b) The first line in the pure rotational spectrum of HCl appears at 20.7 cm^{-1}. Calculate the bond length of the molecule. Given atomic masses of H and Cl are 1.008 and 35.45 amu respectively. (5)

29. a) Discuss the principle and types of relaxation processes involved in NMR. (10)

b) An organic compound A (molecular formula $C_9H_{10}O_2$) exhibitis the following spectral data.

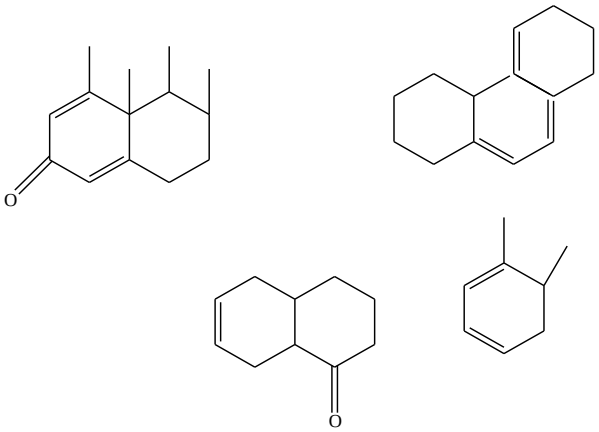
IR : 1745 cm^{-1} (s) 1225 cm^{-1} (br,s) 749 & 697 cm^{-1} (s).

UV : λ_{max} at 268, 264, 262, 257 mm

H^1 NMR : 1.96 δ (3H, s) ; 5 δ (2H, s) ; 7.22 δ (5H, s).

Deduce the structure of the compound. (10)

30. a) Apply Woodward-Hoffmann's rules to calculate λ_{max} for the following conjugated dienes and α, β – unsaturated ketones.



b) Write a note on McLafferty Rearrangement. and Retro Diels-Alder Cleavage.

c) The mass spectrum of the compound C_8H_8O gave peaks at m/z 120,105,77,55 & 43. Assign the structure of the compound showing the fragmentation pattern. (10+6+4)

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