**D2ACH2404** **(2 Pages)** **Name.....**
**Reg.No.....**

**SECOND SEMESTER M.Sc. DEGREE EXAMINATION, APRIL 2025**
**(Regular/Improvement/Supplementary)**
**CHEMISTRY**
**FCHE2C08: MOLECULAR SPECTROSCOPY**

**Time: 3 Hours** **Maximum Weightage: 30**

**Section A: Short answer questions. Answer any *eight* questions. Each carries 1 weightage.**

1. What is Stark effect? How does it influence rotational spectra?
2. Write the selection rules for rotational transitions in microwave spectroscopy.
3. Explain the mutual exclusion principle in Raman spectroscopy and its relevance in molecular symmetry analysis.
4. What is quadrupole broadening?
5. Give the role of Franck-Condon principle in determining the intensity of electronic transitions.
6. What is the Nuclear Overhauser Effect? How does it enhance NMR signal intensity?
7. Describe the Karplus relationship and its significance in predicting coupling constants in NMR spectra.
8. What is hyperfine interaction in ESR spectroscopy? How does it influence the spectral splitting of an unpaired electron?
9. Explain Kramers' theorem and its relevance in zero-field splitting in ESR spectroscopy.
10. Differentiate between enantiotopic, diastereotopic and homotopic protons in NMR spectroscopy. Provide examples for each.
11. What is the difference between off-resonance decoupling and noise decoupling in $^{13}C$ NMR?
12. Illustrating an example, explain McLafferty rearrangement.

**(8 × 1 = 8 weightage)**

**Section B: Short essay questions. Answer any *four* questions. Each carries 3 weightage.**

13. Compare the rotational spectra of symmetric, asymmetric, and spherical top molecules.
14. How is bond length determined using microwave spectral data? Illustrate with an example.
15. What is 2D NMR spectroscopy? Explain the working principles of COSY (Correlation Spectroscopy) and its application in structural determination.

**(P.T.O.)**

16. Discuss the empirical rules for calculating $\lambda_{max}$ of dienes, enones and benzene derivatives. Provide appropriate examples.
17. Explain spin-spin coupling and describe different types of coupling observed in $^{1}H$ NMR spectroscopy.
18. Describe the factors influencing $^{13}C$ chemical shifts in different molecular environments, including aliphatics, aromatics and carbonyl-containing compounds.
19. A compound with molecular formula $C_8H_8O_3$ exhibits $^{13}C$ NMR peaks at $\delta$ = 180, 160, 130, 120, 75, 55, and 20 ppm; assign these peaks to possible functional groups and propose a likely structure.

**(4 × 3 = 12 weightage)**

**Section C: Essay questions. Answer any *two* questions. Each carries 5 weightage.**

20. a) Explain the classical and quantum mechanical descriptions of the Raman Effect. How do they differ in their interpretation of Raman scattering?
    b) Explain the concept of dissociation and pre-dissociation in electronic spectroscopy.
21. Discuss the principles and applications of Mossbauer spectroscopy in the study of hyperfine interactions. How do isomer shifts, quadrupole splitting and magnetic interactions help in characterizing materials?
22. Explain in detail the principles of Optical Rotatory Dispersion and Circular Dichroism. How are these techniques used in the determination of conformation and configuration of *cis*- and *trans*-decalones and 3-methylcyclohexanone?
23. a) Explain the fragmentation pattern of alcohols, ethers and carbonyl compounds in mass spectrometry. How do the characteristic peaks help in identifying these functional groups?
    b) The mass spectrum of a compound shows a peak at m/z = 122 with an M+2 peak at 124 (relative intensity 32%). Identify the heteroatom present in the molecule and predict the possible molecular structure based on common fragmentation patterns.