D2ACH2304 **(3 Pages)** **Name.....**
Reg.No.....

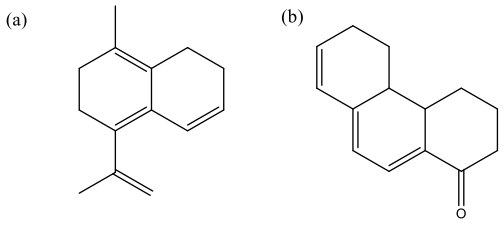
SECOND SEMESTER M.Sc. DEGREE EXAMINATION, APRIL 2024
(Regular/Improvement/Supplementary)

CHEMISTRY
FCHE2C08: MOLECULAR SPECTROSCOPY

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

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

1. Explain fundamental and overtone bands in IR spectroscopy.
2. State and explain Frank-Condon principle.
3. (*s*)-2-bromocyclohexanone can have two conformations. Explain which of these will display a strong Cotton effect.
4. Explain Stark effect.
5. Write a note on Karplus equation in the determination of vicinal coupling constant. Explain how it is useful in determining molecular geometry.
6. On the basis Wood-Fieser rules, calculate the λ_{max} of the following compounds.



7. Explain the term g-factor in ESR.
8. What is meta stable ion peak in mass spectra?
9. Discuss the application of NMR spectroscopy in identifying stereo isomers.
10. Explain INEPT in NMR spectroscopy?
11. Discuss the NMR spectra of fluxional molecules with illustrative examples.
12. Differentiate the positional isomers of xylene with the help of ^{1}H NMR spectroscopy.

(8 × 1 = 8 weightage)

(P.T.O.)

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

13. Discuss the factors affecting the width and intensity of the spectral lines.

14. Write a note on spin-spin coupling in NMR spectroscopy? Discuss the factors affecting coupling constants.

15. a) Explain DEPT technique in NMR spectroscopy. How is it useful in structure determination?

    b) What are shift reagents? How shift reagents are useful in simplification of NMR spectrum.

16. a) Derive the expression for the rotational energy of symmetric top molecule and explain the selection rules.

    b) Find the rotational quantum number corresponding to maximum intensity in the microwave spectrum of HCl. Rotational constant, B = 10.5 cm^{-1}.

17. a) Explain the electronic spectra of the conjugated molecules.

    b) Discuss first order and non-first order NMR spectra.

18. a) Discuss factors affecting the vibrational frequency.

    b) Explain the importance of isotope peaks in mass spectra in structure elucidation.

19. Explain octant rule. How is it useful in explaining the conformation of *cis*- and *trans*-decalones?

(4 × 3 = 12 weightage)

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

20. a) Discuss the theory and applications of Mossbauer spectroscopy by choosing different coordination complexes.

    b) Explain: (i) McConnell Relation; (ii) Kramer's theorem.

21. a) Explain quantum mechanical description of AX and AB NMR pattern. Also discuss the effect of relative magnitudes of spin-spin coupling and chemical shift on the AB type molecule.

    b) What is Nuclear Overhauser effect? Explain how is it useful in the structure elucidation of organic molecules.

22. a) Deduce the structure and stereochemistry of the compound from the following spectral data. Correlate spectral data to the obtained structure.

i) UVspectral data – 284, 308.

ii) IR- 1670 cm^{-1}, 2750 cm^{-1}.

iii) ^{1}H NMR δ (ppm): 6.63 (dd, *J* =16 Hz, 6.2 Hz, 1H), 7.33 – 7.53 (m, 5H), 7.74 (d, *J*-16 Hz, 1H), 9.68 (d, J = 8 Hz, 1H).

iv) ^{13}C NMR δ (ppm): 127.9, 128.6, 128.5, 128.9, 135.2, 152.6, 193.5.

v) Mass (m/z): 132, 131, 103.

b) Discuss the major peaks in EI mass spectra of:

i) 2-Hexanone; ii) Pentanoic acid.

23. a) Write a note on classical and quantum theory of Raman Effect.

b) Discuss P, Q, R branches of rotation vibration spectrum.

c) Illustrate how HMBC is useful in the structure elucidation of organic compounds.

(2 × 5 = 10 weightage)