LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

SECOND SEMESTER – **APRIL 2023**

PCH 2503 – MOLECULAR SPECTROSCOPY

Date: 02-05-2023 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

Part-A

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

1. Which of the following will have greater rotational constant, $I^{35}Cl$ or $I^{37}Cl$? Justify your answer.
2. State the rule of mutual exclusion principle and cite examples.
3. The complex, $[Cr(CO)_6]$ shows MLCT band and not LMCT band in electronic spectrum. Why?
4. Write Fieser-Kuhn rule applied for calculating absorption maximum in conjugated polyenes.
5. What is the most characteristic feature in the mass spectrum of the compounds containing one chlorine atom?
6. Distinguish between first and second order proton NMR spectra.
7. Predict the number of lines in ^{19}F and ^{1}H – NMR for the compound HF_2^-.
8. NaCl molecule does not show NQR transitions in spite of the nuclear spin value (I = 3/2) for chlorine atom Justify.
9. Define asymmetry parameter.
10. What is the significance of isomer shift?

Part-B

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

11. Using Morse's curve, explain the vibrational transitions in anharmonic oscillator and derive the expressions for $\Delta\varepsilon$ of fundamental band, first and second overtones.
12. The microwave spectrum of $H^{127}I$ consists of a series of equally spaced lines separated by 12.8 cm^{-1}. Calculate the moment of inertia and inter nuclear distance of $H^{127}I$.
13. Explain the Classical theory of Raman Effect.Mention its limitations.
14. Discuss the effect of polar solvents on the electronic transitions of carbonyl compounds.
15. Account for the intensity distribution in absorption bands based on Franck-Condon principle.
16. Illustrate double McLafferty rearrangement with an example.
17. What is virtual coupling? Mention the conditions required to observe virtual coupling.
18. Explain diamagnetic anisotropy with an example.
19. How is the EPR of a complex used to classify the symmetry of a complex into cubic or rhombohedral type?
20. Distinguish between isotropic and anisotropic hyperfine splitting with relevant examples.
21. Mention the importance of quadrupole coupling constant in NQR spectroscopy.
22. Explain the principle of Mossbauer spectroscopy with an example.

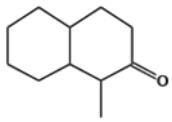
Part-C

Answer any FOUR questions. **(4 x 10 = 40)**

23a. Explain the appearance of P and R branches in the spectrum of a diatomic vibrating rotor. (6+4)

b. Discuss the various factors influencing vibrational frequencies in IR spectroscopy.

24a. Compound (A) has the formula $C_{11}H_{16}O$ and it is reduced to B, $C_{11}H_{18}O$ with hydrogen in presence of palladium. The ultraviolet spectrum of A showed strong absorption with λ_{max} at 255 nm and this absorption was absent in the ultraviolet spectrum of B. What is the structure of A? The structure of B is



b. Write a detailed account on the various types of bands observed in the electronic spectrum of organic compounds with examples. (6+4)

25a. Predict the structure of an organic compound with molecular formula $C_5H_{10}O$, which gives peaks having m/e values at 86, 71, 58 and 43 (100%) in its mass spectrum.

b. Explain fast atom bombardment technique for the generation of ions in the source of mass spectrometer. (5+5)

26. Discuss the principle of 2D NMR technique and explain the COSY and DEPT spectrum of Methyl cyclopropyl ketone.

27. Explain the following i) first derivative pattern of EPR lines.
ii) the EPR of high spin Mn^{2+} complex. (5+5)

28a. Mention the conditions to observe NQR transitions in a compound.

b. Discuss the Mossbauer spectral features of the complexes $K_4[Fe(CN)_6]$ and $K_4[Fe(CN)_5(NH_3)]$. (4+6)

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