



Date: 20-06-2022

Dept. No.

Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

Part – A

Answer ALL Questions.

(10 x 2 = 20)

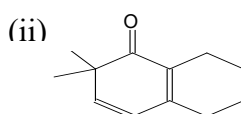
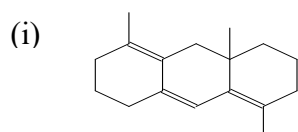
- Why do the thermochemical and spectroscopic dissociation energies of a molecule differ?
- Find the frequency (in cm^{-1}) for pure rotational line in the spectrum of NO molecule due to change in the quantum number from $J=2$ to $J=3$ level. (Moment of inertia of NO = $1.6427 \times 10^{-46} \text{ kg m}^2$)
- Sketch the different kinds of bending vibrations of polyatomic molecules.
- $[\text{Cr}(\text{Cl})(\text{NH}_3)_5]^{2+}$ shows LMCT band whereas $[\text{Fe}(\text{CO})_3(\text{bipy})]$ shows MLCT band-Justify.
- State even-electron rule followed in mass spectrometry.
- Calculate the magnetic field at which ^{13}C nucleus comes into resonance at 250 MHz (Given: $g = 1.405$ and $\beta_n = 5.05 \times 10^{-27} \text{ JT}^{-1}$).
- Predict the number of lines in ^{19}F and ^1H – NMR for the compound HF_2^- .
- Sketch the EPR spectrum of the radical $\bullet\text{CF}_2\text{H}$.
- A metal ion in a complex participates in hyperfine splitting and gives 6 lines. Predict its nuclear spin value.
- ^{35}Cl has $I = 3/2$ but still Cl atom and NaCl molecule do not show NQR transitions - Justify.

Part – B

Answer any EIGHT questions.

(8 x 5 = 40)

- Why do the spacing between the rotational lines in P and R branches for CO differ? Explain it with a suitable diagram.
- The successive rotational Raman lines are separated by 41.4 cm^{-1} in H^{35}Cl molecule. Obtain the moment of inertia and internuclear distance in H^{35}Cl .
- Write a detailed account on the various types of bands observed in the electronic spectrum of organic compounds with examples.
- Predict λ_{max} for the following compounds in cyclohexane as a solvent using Woodward-Fieser rule.



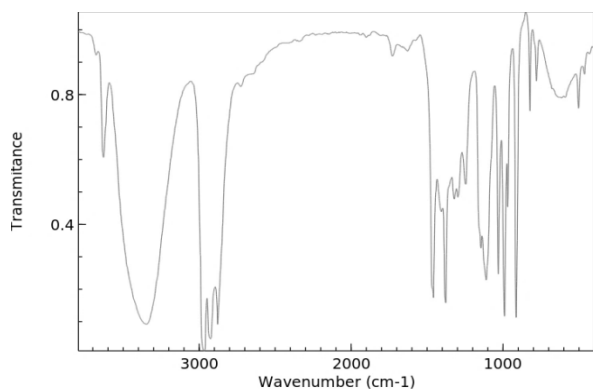
- Explain the classical theory of Raman effect.
- Explain double McLafferty rearrangement with an example.
- Define the term virtual coupling. Mention the conditions required to observe virtual coupling.
- What is DEPT spectrum? Draw the DEPT spectrum of Methyl cyclopropyl ketone.
- Account for the number of lines observed in the EPR spectrum of high spin octahedral complex of Mn^{2+} .
- Highlight the importance of 'g' values obtained from EPR spectrum to classify the symmetry of a complex into cubic or rhombohedral type?
- Compare the characteristics of Nuclear magnetic resonance with Nuclear quadrupole resonance.
- How will you account for the spectral lines observed in the Mössbauer spectra of low spin Fe^{2+} and Fe^{3+} complexes?

Part – C

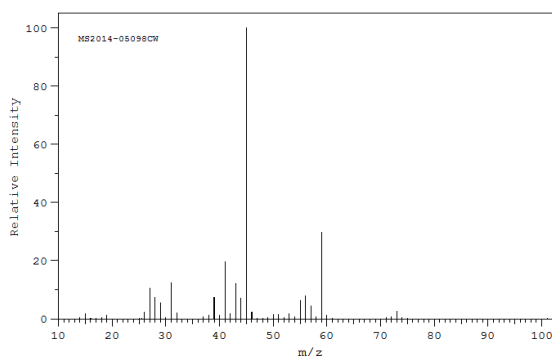
Answer any **FOUR** Questions.

(4 x 10 = 40)

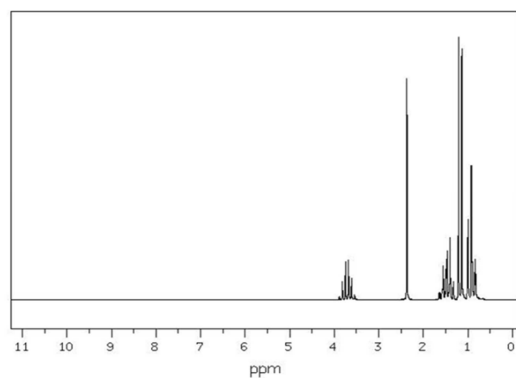
- 23 a. Discuss the influence of rotation on parallel and perpendicular vibrations of polyatomic linear molecules.
- b. The equilibrium vibrational frequency and anharmonicity constant for HI molecule are 2309.5cm^{-1} and 0.0172 respectively. Calculate the wave numbers of fundamental, first and second overtone transitions. (5+5)
24. An organic compound with the molecular formula $\text{C}_4\text{H}_{10}\text{O}$ shows the following spectral data in their FT-IR, ^1H NMR and Mass spectra. Deduce the molecular structure of the compound with the help of spectral data and justify your answer.
- IR: ν_{max} (cm^{-1}) - 3524 (*w*), 3353 (*broad*), and 1110 (*m*),
 ^1H NMR: δ (ppm)- 3.7 (1H, *hexet*), 2.4 (1H, *singlet*), 1.46 (2H, *quintet*), 1.2 (3H, *doublet*) and 0.93 (3H, *triplet*)
 Mass: m/z values – 74, 59 and 45



FT IR Spectrum



Mass Spectrum



^1H NMR Spectrum

- 25a. Write the influence of solvents on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of carbonyl compounds?
- b. Explain the electronic spectra of *cata* and *peri* condensed systems with examples. (6+4)
- 26a. Discuss the two dimensional correlation spectrum of 2-pentanone.
- b. What is Nuclear Overhauser Enhancement? Mention its importance. (5+5)
- 27a. Obtain the energies of NQR levels in non-axially symmetric electric field for a nucleus with $I = 3/2$ and account for the transitions.
- b. Mention the essential conditions to observe Mossbauer spectrum. (6+4)
28. What is zero field splitting? Explain with suitable examples the conditions to observe transitions in weak and strong zero field splitting.