

Roll No.

S.C.No.—701104

M. Sc. EXAMINATION, 2021

(First Semester)

CHEMISTRY

19CHE104

Spectroscopy-I

Time : 2 Hours

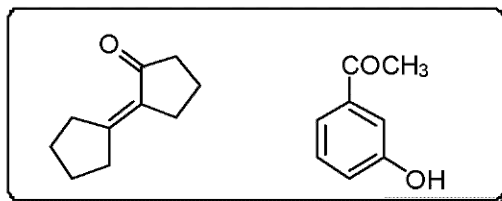
Maximum Marks : 80

Note : Attempt any *Four* questions. All questions carry equal marks. Use of scientific calculator is allowed.

1. (i) Using the given spectroscopic data, deduce the structure of an organic compound and assign all the spectral peaks.

(iv) If the fundamental vibrational frequency of $^{79}\text{Br}^{81}\text{Br}$ is observed at 323.2 cm^{-1} in its IR spectrum, then calculate the force constant of the bond.

4. (i) Calculate the value of absorption maxima for the following compounds using Woodward and Fieser rules ?



(ii) If the percentage transmittance of an aqueous solution of disodium fumarate at 250 nm and 25°C is 19.2% for a $5 \times 10^{-4}\text{ mol L}^{-1}$ solution in a 1 cm cell, then calculate the absorbance A and the molar absorption coefficient (ϵ).

(iii) Why does the transition of $\pi \rightarrow \pi^*$ require more energy than required for $n \rightarrow \pi^*$ transition ?

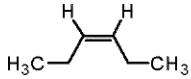
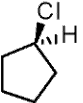
IR (cm^{-1}) :1735 (s), 1608 (w), 1060 (s)

^1H NMR (ppm): 2.35 (s, 3H); 3.82 (s, 3H); 7.20 (d, $J = 7.2$ Hz, 2H), 7.85 (d, $J = 7.2$ Hz, 2H).

^{13}C NMR (ppm): 21.3, 51.2, 127.0, 128.9, 129.8, 142.1, 165.9

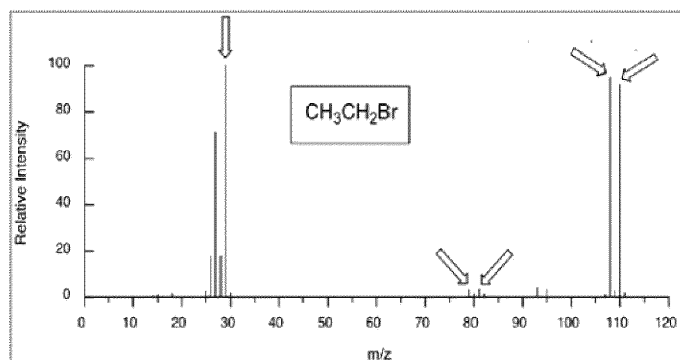
Mass spectrum (m/z): 150.07 (M^+ , 100), 119.

- (ii) Fill in the information's for each of the given compounds. (in the given format in your answer sheet).

Compounds	Number of signals (^1H -NMR)	Label the most de-shielded proton(s)	Number of signals in proton decoupled ^{13}C -NMR
(A) 			
(B) 			

2. (i) What are gross selection and specific selection rules for IR spectroscopy ?
- (ii) Using IR spectroscopy, how will you distinguish between Benzaldehyde and Benzoic acid ? Indicate prominent IR bands observed in the two compounds.
- (iii) In an IR spectrum, are stretching bands observed at lower or higher wavenumbers as compared to bending bands. Explain.
- (iv) The IR spectrum of propanol gives a broad band around 3340 cm^{-1} , while its IR spectrum when recorded in dilute solution of carbon tetrachloride gives a sharp peak at 3020 cm^{-1} . Explain.
3. (i) What is a finger print region in an IR spectrum ? Explain its significance.
- (ii) Arrange the acid derivatives [RCOOH , RCONH_2 , RCOOR] in the increasing order of observed $\text{C} = \text{O}$ stretching bands in them. Provide a proper justification.
- (iii) With a suitable example, explain the reason for observing overtones in an IR spectrum.

9. (i) The mass spectrum of 4-Nonanone [$C_9H_{18}O$] shows peaks at $m/z = 58, 71, 86, 99$. Justify their formation by drawing its fragmentation.
- (ii) Explain by giving relevant examples the Nitrogen rule.
- (iii) Justify the appearance of the peaks (indicated by arrows in the figure given below), which are observed by recording the ESI-MS of ethyl bromide.



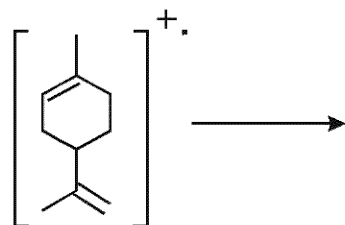
- (iv) Write short note on Fluorescence and phosphorescence.
5. (i) Draw and explain Jablonski diagram.
- (ii) If the absorbance of a solution containing an absorbing species for a particular length is 2.0, then calculate its transmittance ?
- (iii) Compounds **A**, **B** and **C** having same molecular formula C_5H_8 show the λ_{max} values of 176 nm, 211 nm and 215 nm respectively, in their UV spectra. Also, all the three compounds **A**, **B** and **C** upon hydrogenation yields *n*-pentane. Based on the above information, predict the structures of **A**, **B** and **C**.
6. (i) Explain the terms, shielding and deshielding zones with respect to the 1H NMR of Toluene.
- (ii) What are the factors that affect the Chemical shift (δ) of a peak and the coupling constant (J) for the observed multiplicity of a peak ?

(iii) Why tetramethyl silane is added in the NMR tube while recording the PMR of an organic compound ? Why deuterated solvents are used while recording the NMR of a compound ?

(iv) Calculate the Larmor frequency of a proton in a magnetic field of 1.0 T. [Given $\gamma_{\text{proton}} = 26.75 \times 10^7 \text{ T}^{-1} \text{ s}^{-1}$]

7. (i) The ESI-MS of ethylbenzene shows two prominent peaks at m/z 91 and 65. Explain by drawing suitable structures.

(ii) Predict the fragmentation pattern of the following compound in its ESI-MS :

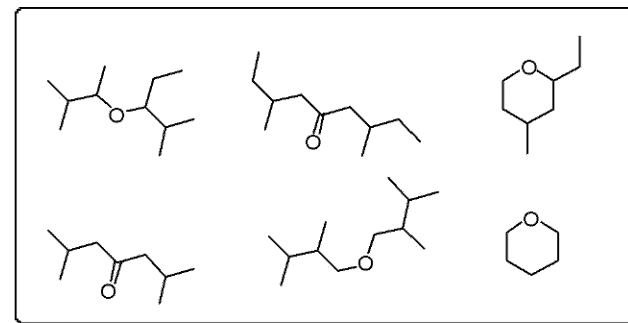


(iii) A cluster is observed for the molecular ion peak, when the mass spectrum of tetrabromomethane (CBr_4) was recorded. Explain in detail.

(iv) Explain briefly the different types of ionization methods employed in Mass-Spectrometry.

8. (i) What is NOE ? Explain with a suitable example.

(ii) Two organic compounds **X**, and **Y** shows 3 and 4 peaks respectively in their proton decoupled ^{13}C NMR spectra. Assign the structures of **X**, **Y** from the given pool of compounds.



(iii) Explain the difference between DEPT 135, and DEPT 90 by taking a suitable example.

(iv) What magnetic field strength is required for a fluorine magnetic resonance at 30.98 MHz. Given g factor for fluorine is 5.2567 and the nuclear magneton (μ_n) is $5.047 \times 10^{-27} \text{ J Tesla}^{-1}$.