Total No. of printed pages = 5

63/2 (SEM-2) CHM 204

2022

CHEMISTRY

(Theory Paper)

Paper Code : CHM 204

(Spectroscopy-II)

Full Marks – 80

Time – Three hours

The figures in the margin indicate full marks for the questions.

1. Answer any *three* of the following questions : 5×3=15

   (a) Determine the isotopic intensity ratio of the compounds : 5

   (i) 1-bromo-4-chlorobenzene

   (ii) Trimethyl silane (TMS).

   (b) Give a brief description about α-cleavage and inductive cleavage in molecular radical ion with suitable examples. 5

(c) Descirbe the fragmentation of toluene molecule and identify the species if the base peak and molecular ion peak are observed at m/z = 92 and m/z = 91, respectively. 5

(d) Compare the intensity of molecular ion peaks in the mass specturm of primary, secondary and tertiary alcohols. Explain. An alkane with molecular mass of 72 amu shows very weak molecular ion peak, if the base peak was observed at m/z = 57. What is the possible structure of the compound ? 2+3=5

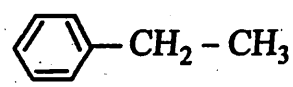
2. Answer any *three* of the following questions : 5×3=15

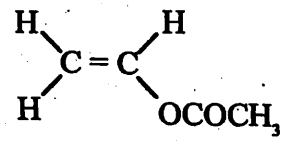
(a) Explain the importance of DEPT ^{13}C NMR technique. 5

(b) In the light of Karplus relationship, explain how the orientation of H-atoms affects the magnitude of coupling constant. 5

(c) What are shift reagents ? Name at least two of it and write their structures. Discuss the use of shift reagents in simplification of ^{1}H NMR spectra. 1+2+2=5

(d) What is spin-spin splitting ? Indicate the number of singals and the multiplicity of each signal in the NMR spectrum of each of the following compounds : 1+2+2=5

(i) 

(ii) 

3. Answer any *one* of the following questions : 5×1=5

(a) Explain basic principle of UV-VIS spectroscopy. Using Woodward's rule predict λ_{max} for the following compounds : β-carotene and 1, 1, 3-trimethyl butadiene.

(b) Explain the mechanism of CD and ORD.

4. Answer any *five* of the following questions : 5×5=25

(a) Determine the total number of vibrational modes, IR active modes and Raman active modes in NH_3 molecule.

(b) With the help of projection operation, show that the b_{2g} stretching vibration mode of $PtCl_4^{2-}$ cannot change the dipole moment of the compelx, hence IR incactive. Given that $v_s(a_{1g})$ of $PtCl_4^{2-}$ is $330cm^{-1}$, then $v_s(a_{1g})$ of PtI^{2-} is either 155 or $455cm^{-1}$.

(c) Write down the applications of the following types of CD according to their absorption of light –
Near UV CD, UV CD, UV-V is CD, Near IR CD and Vibrational CD.

(d) How coordination of different ligands changes spectral data of a metal complex ? Explain with suitable examples.

(e) Explain briefly about Job's method in metal-ligand equilibria.

(f) What are the basic differences between UPS and XPS ? Discuss briefly about ESCA. Taking the example of azide molecule discuss briefly about photoelection spectra.

5. Answer any *four* of the following questions : 5×4=20

(a) The ESR frequency of a free electron is 900 MHz. Calculate the magnetic field at which the ESR spectrometer is working. 5

(b) Explain the two important environmental interactions in the ESR spectrum of a free radical. 5

(c) Why does the Mossbauer spectral pattern of $[Fe(CN)_6]^{4-}$ and of $[Fe(CN)_6]^{3-}$ do not differ much ? 5

(d) Explain briefly the three Mossbauer parameters-isomer shift, quadruple splitting and hyperfine splitting. 2+2+1=5

(e) Explain why NMR spectroscopy is usually not considered to be a suitable technique to obtain structural information on paramagnetic transition metal compelxes. 5