2021

(held in 2022)

CHEMISTRY

(Theory Paper)

Paper Code: CHM-104

(Spectroscopy – I)

Full Marks - 80

Time – Three hours

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

- 1. Answer the following questions:
 - (a) State Frank-Condon principle and briefly explain the three typical situations of intensity distribution in absorption band.

2+3=5

- (b) Why we find broad bands in electronic spectra of metal complexes? 2
- (c) Discuss selection rules in d-d transitions with relaxation.

Turn over

(d) Write down the mechanism of Laser action.

O

Write down the mechanism of Phosphorescence. 5

- (e) How many charge transfer spectra are found in metal complexes? How can you identify charge transfer bands? Why the colour of KMnO₄ is purple? 2+2+1=5
- 2. Answer the following questions:
 - (a) Which one is microwave active?
 - (i) O_2

(ii) H,

(iii) Br₂

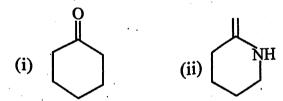
- (iv) HC1
- (b) Write the selection rule for Roto-vibrational spectra. 2
- (c) Mention few importance of rotational spectroscopy. 2
- (d) How rotational spectroscopy may be used to calculate temperature of a surface? 5
- (e) What kind of shifting of lines in the spectrum do you observe for a particular molecule centrifugal distortion and isotopic substitution? Explain with examples. 10

(2)

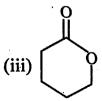
- 3. How do you calculate bond length in rotational spectroscopy? Does CO₂ show pure rotational spectrum? Explain briefly.

 1+1+3=5
- 4. Answer the following questions:
 - (a) Discuss the different mode of vibrations of IR spectroscopy. What is Hooke's law? Explain its significance in IR spectroscopy. 2+3=5
 - (b) Explain the effect of ring strain on carbonyl stretching frequency with examples. 5
 - (c) Why ketones absorb at a lower frequency than aldehydes? Arrange the following structures in order of their increasing C = O stretching frequency and explain why.

2+3=5



(3)



- (b) Explain the factors that affect the chemical shift in NMR spectrum.
- (c) What are chemically equivalent and non-equivalent protons? What are shielding and deshielding in NMR spectroscopy? Explain with examples. 2+3=5
- (d) For an octahedral copper complex that shows z-in tetrahedral distortion, $g_{\perp} > g_{\parallel}$. Explain briefly why. What will happen to the order of g values if the complex shows z-out tetragonal distortion? 2+3=5
- (e) How many g values do you expect for a complex in frozen state that shows an axial spectrum? Sketch the spectrum in both absorptive and first order derivative mode. Sketch both the absorptive and first order derivative mode of the ESR spectrum is recorded in solution state. 2+1+2=5

(4)

- 5. Answer any four of the following questions: 5×4=20
 - (a) Explain why benzene protons appear at a downfield compared to those of acetylene. At what range (δ value) the benzene protons can be expected to appear in ¹H NMR spectrum?

 1+4=5
 - (b) Explain the factors that affect the chemical shift in NMR spectrum.
 - (c) What are chemically equivalent and non-equivalent protons? What are shielding and deshielding in NMR spectroscopy? Explain with examples. 2+3=5
 - (d) For an octahedral copper complex that shows z-in tetrahedral distortion, $g_{\perp} > g_{\parallel}$. Explain briefly why. What will happen to the order of g values if the complex shows z-out tetragonal distortion? 2+3=5
 - (e) How many g values do you expect for a complex in frozen state that shows an axial spectrum? Sketch the spectrum in both absorptive and first order derivative mode. Sketch both the absorptive and first order derivative mode of the ESR spectrum is recorded in solution state. 2+1+2=5