POSTGRADUATE FOURTH SEMESTER EXAMINATION, 2022

CHEMISTRY

Course Code: CHEM 402E **Course ID: 41452**

Physical Chemistry Special

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer any *five* of the following questions: $5\times2 = 10$

a) Find the number of modes of vibration present in CO_2 molecule. Which of them are IR active?

b) Define spin-spin splitting in NMR spectra.

c) Write two advantages of UV-VIS spectroscopy.

d) How many lines are obtained in ESR spectra of napthyl radical? Explain.

e) What are the conditions for a molecule to be microwave active?

f) Why anthracene is fluorescent but phenanthrene is not?

g) $\Delta\bar{\nu}$ for H^1Cl^{35} is 20.3 cm^{-1}. Find out the bond length of H^1Cl^{35}.

2. Answer any *four* of the following questions: $4\times5 = 20$

a) What is the selection rule for the ESR transition? Draw the ESR spectra of methyl radical mentioning the assignment of the lines. 1+4 = 5

b) Explain the NMR spectra of ethanol under low and high resolution. 5

c) Explain the different modes of vibration of H_2O. 5

d) i) How would deuterium substitution affect the pure rotational spectrum of HCl?

ii) What is the frequency of the rotational line shown by a diatomic molecule, having the moment of inertia value 16.5×10^{-40} $g.cm^2$, the excited molecule being in the quantum state J=2? 2+3 = 5

e) i) Define chromophores.

ii) Explain why $\pi \rightarrow \pi*$ transition is generally more intense than $n \rightarrow \pi*$ transition?

iii) Aniline is 40 times more fluorescent than benzene and benzoic acid is not fluorescent - Explain. 1+2+2 = 5

f) i) Transitions generally start from the middle of v = 0 level of ground electronic state. - Explain.

ii) The symmetric stretching of CO_2 is IR inactive but Raman active. Explain.

iii) Define Stokes shift and anti-Stokes shift. 1+2+2 = 5

3. Answer any *one* of the following questions: 1× 10 = 10

a) i) Derive the quantum mechanical energy expression of vibrational spectra and show that there will be only a single frequency line in the vibrational spectra for all sorts of vibrational transitions.

ii) How many times does a molecule of H^1Cl^{35} rotate per second in the J=1 rotational level? Given B (H^1Cl^{35}) =10.6 cm^{-1}.

iii) Name a reference substance which is widely used for measurement of chemical shift in proton magnetic resonance study and why? 5+3+2 = 10

b) i) Derive the quantum mechanical energy expression for a rigid rotator and show that energy levels are not equispaced.

ii) What is hyperfine splitting?

iii) What is chemical shift in NMR spectroscopy?

iv) The position of the fundamental absorption of $C^{12}O^{16}$ molecule is at 2140 cm^{-1}. How many times will the molecule vibrate per second?

5+1+1+3 = 10