

2022

Chemistry

Paper : CH105

( Spectroscopy - I)

Full Marks : 60

Time : 3 hours

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

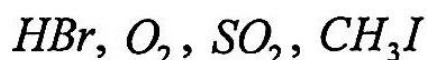
1. Answer *any five* of the following questions : 3×5=15

(a) How does electromagnetic radiation interact with matter? Explain the mechanism of interaction considering any one of the regions.

(b) Discuss the role of Fourier Transform in Spectroscopy.

(c) Explain how the Doppler effect causes line broadening.

(d) How many normal modes of vibration are possible for the following molecules



(e) Show that corresponding to the maximum population of the molecules in the rotational spectra.

(f) Which type of vibrational spectroscopy would one use to measure the vibrational frequency of the following bonds?

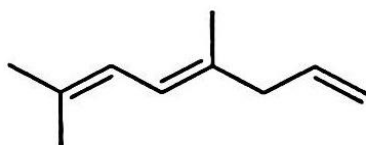
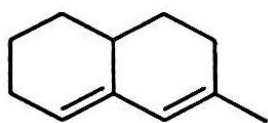
The stretching frequency of <sup>14</sup>N – <sup>15</sup>N

The C=O stretch in ethanal, CH<sub>3</sub>CHO

The C=C stretch in acetylene, C<sub>2</sub>H<sub>2</sub>

*Contd.*

- (g) Discuss the instrumentation used in UV-Vis spectroscopy.
- (h) Applying Woodward-Fieser rule, calculate the maximum wavelength ( $\lambda_{\text{max}}$ ) for the following compounds :



2. What is anisotropic polarizability? Discuss the Stokes and anti Stokes lines in rotational Raman spectra. 5

Or

Write the expression for Morse function of anharmonic oscillator model for a vibrating diatomic molecule. What will be the energy expression in terms of wave number for a given vibrational state for a diatomic molecule following harmonic oscillator model.

3. What different photophysical process are responsible for fluorescence Quenching? How can you distinguish between a static and dynamic quenching process? 5

or

Describe fluorescence, phosphorescence and delayed fluorescence phenomenon.

4. Answer *any seven* of the following questions : 5×7=35

- (a) What are spontaneous and stimulated emissions? Give one example for each of these emissions.
- (b) What are the units of Einstein co-efficient A and B? Can a three level system lead to population inversion at equilibrium?

- (c) Describe briefly two different sample preparation methods for IR measurement.
- (d) How does the Raman stretching frequency of  $O_2$  change when it binds with haemoglobin and hererythrin? Explain in details.
- (e) The fundamental vibrational frequency of  $H^{35}Cl$  is  $8.67 \times 10^{13} s^{-1}$ . Calculate the fundamental vibrational frequency of  $D^{35}Cl$  on the assumption that the force constants of the bonds are equal.
- (f) Why it is difficult to measure time domain spectrum directly with infrared radiations? How do you solve this problem to measure signal in Fourier transform IR measurement?
- (g) State how Born-Oppenheimer approximation can be used to explain the electronic spectra of diatomic molecules. Explain how intensities of the bands in vibrational-electronic spectrum can be explained in terms of Frank-Condon principle.
- (h) Using suitable example, explain why longer the conjugated system greater is the wavelength of absorption maxima. Draw the representative electronic absorption spectrum of lycopene and comment on the observed wavelength of maximum absorption.
- (i) Discuss with the help of suitable examples how change in pH and polarity of solvent can lead to significant changes in the electronic absorption spectra of chromophores.

## Appendix:

Parent values and increments for different substituents/groups.

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253 \text{ nm}$	$\lambda = 214 \text{ nm}$
Increment for :		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar grouping:		
-OCOCH <sub>3</sub>	0	0
-OR	6	6
-Cl, -Br	5	5
-NR <sub>2</sub>	60	60

