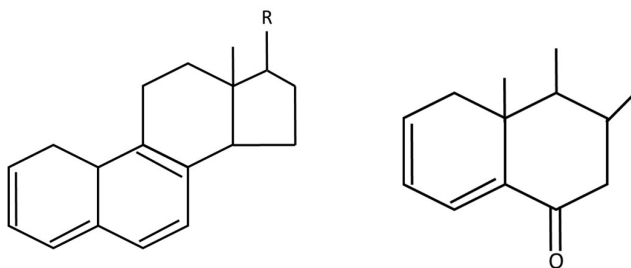


**Instructions to the students:**

1. There are **three questions** in all. Attempt all the questions in **separate answer sheet**.
2. Start answering each question on a fresh page. **Answer all parts of a question together**.
3. **In a derivation write all the in between steps. In case of missing steps, marks will be deducted.**
4. Write brief answers to the point with proper justifications.
5. Do not exchange your calculator.

Atomic number of Cu = 29, Fe = 26,  $h = 6.626 \times 10^{-34}$  J s, atomic mass of Cl = 35.459, H = 1.007, 1 amu =  $1.66054 \times 10^{-27}$  kg

1. (a) What is boxcar averaging? Explain how it helps to increase S/N ratio? (b) Distinguish between sensitivity and detection limit. (c) A 0.01 M solution compound transmits 20% of the radiation. Consider path length 1.5 cm. Calculate the molar extinction coefficient of the compound. (d) Do you expect any change in optical absorbance of Aniline in acidic solution? If yes, explain. (e) Calculate the  $\lambda_{\max}$  of the given compounds.



- (f) What is 'mirror image rule' in electronic spectroscopy? Explain your answer briefly.
- (g) What is the basic difference between dynamic quenching and static quenching? Suppose you have measured the fluorescence quenching of a solution of tryptophan in presence of quencher acrylamide, which obeys Stern-Volmer equation. Determine the Stern-Volmer Quenching constant using the following data.

[Acrylamide] (M)	0.032	0.065
F/F <sub>0</sub>	0.658	0.532

[3+2+2+2+3+3+5 = 20M]

2. (a) Using excitation radiation of wavelength  $4 \times 10^3 \text{ \AA}$ , the first Stokes line appears at a spacing of  $350 \text{ cm}^{-1}$  from Rayleigh line. Calculate the frequency of the first anti-Stokes line in wave number ( $\text{cm}^{-1}$ ). (b) How many vibrational modes are there in  $\text{H}_2\text{O}$ ? Explain which modes are Raman active with the help of polarizability ellipsoid. (c) Why do the anti-Stokes lines of carbon tetrachloride have the following order of intensity:  $218 > 314$

> 459 cm<sup>-1</sup>? (d) Calculate the zero-point vibrational energy (considering harmonic oscillator concept) of HCl given that the force constant of HCl is 516 Nm<sup>-1</sup>. (e) How do you distinguish between o-hydroxy benzoic acid and p-hydroxybenzoic acid using FTIR analysis? Explain. (f) An organic compound having molecular formula, C<sub>7</sub>H<sub>8</sub> burns with sooty flame. It shows the following absorption bands in its Infra-red spectrum: (i) 3030 cm<sup>-1</sup>, (iii) 2918, 2870 cm<sup>-1</sup>, (iv) 1600, 1580, 1460 cm<sup>-1</sup>, (v) 750 cm<sup>-1</sup>. Deduce the structure of the compound and assign the peaks. [2+3+3+3+3+3 = 17M]

3. (a) Indicate the significant possible fragmentations of ethyl propyl ether and pentanal and their m/z values. (b) How would you differentiate primary, secondary and tertiary amines (ethylamine, diethylamine and triethylamine) from mass spectrometry? (c) In Time of flight (TOF) mass analyser, derive the relationship of 'm/z' with time 't' and comment on the separation of different fragmented ions in the analyser. (d) How to separate K<sub>β</sub> line from K<sub>α</sub> in X-ray diffraction analysis of Cu target? If the wavelength of Cu K<sub>α</sub> is 1.542 Å, determine the Fe K<sub>α</sub> value. (e) A powder X-ray diffraction experiment using incident Cu radiation gives the following set of reflections expressed as 2θ: 38.40°; 44.50°; 64.85°; 77.90°; 81.85°; 98.40°; 111.20°. Determine the crystal structure and calculate the lattice constant, 'a'. (f) Find out the lattice spacing of (221) crystal plane of a tetragonal system (given lattice parameters are 0.407 nm and 0.625 nm).

[6+3+3+4+4+3 = 23M]

\*\*\*\*\*The END\*\*\*\*\*