Organic Chemistry Semester III

Total Hours:- 90 hrs.

(A) Applications of Spectroscopy: 34 hrs.

I. Ultraviolet and Visible Spectroscopy 3 hrs.

Various electronic transitions (185-800 nm), Beer-Lambert Law, effect of solvent on electronic transitions, ultraviolet bands for carbonyl compounds, unsaturated carbonyl compounds, dienes, conjugated polyenes. Fieser-Woodward rules for conjugated dienes and carbonyl compounds, ultraviolet spectra of aromatic and heterocyclic compounds. Steric effect in biphenyls.

II. Infrared Spectroscopy 5 hrs.

Instrumentation and sample handling. Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols and amines. Detailed study of vibrational frequencies of carbonyl compounds (ketones, aldehydes, esters, amides, acids, anhydrides, lactones, lactams and conjugated carbonyl compounds). Effect of hydrogen bonding and solvent effect on vibrational frequencies, overtones, combination bands and Fermi resonance. FTIR. IR of gaseous, solids and polymeric materials.

III. Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD) 3 hrs.

Definition, deduction of absolute configuration, octant rule for ketones.

IV. Nuclear Magnetic Resonance Spectroscopy 10 hrs.

General introduction and definition, chemical shift, spin-spin interaction, shielding mechanism, mechanism of measurement, chemical shift values and correlation for protons bonded to carbon (aliphatic, olefinic, aldehydic and aromatic) and other nuclei (alcohols, phenols, enols, carboxylic acids, amines, amides & mercapto), chemical exchange, effect of deuteration, complex spin-spin interaction between two, three, four and five nuclei (first order spectra), virtual coupling. Stereochemistry, hindered rotation, Karplus curve-variation of coupling constant with dihedral angle. Simplification of complex spectra-nuclear magnetic double resonance, contact shift reagents, solvent effects. Fourier transform technique, nuclear Overhauser effect (NOE).

V. Carbon-13 NMR Spectroscopy 5 hrs.

General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroaromatic and carbonyl carbon), coupling constants. **Two dimension NMR spectroscopy** – COSY, NOESY, DEPT, INEPT, APT and INADEQUATE techniques.

VI. Mass Spectrometry **8 hrs.**

Introduction, ion production – EI, CI, FD and FAB, factors affecting fragmentation, ion analysis, ion abundance. Mass spectral fragmentation of organic compounds, common functional groups, molecular ion peak, metastable peak, McLafferty rearrangement. Nitrogen rule. High resolution mass spectrometery. Examples of mass spectral fragmentation of organic compounds with respect to their structure determination.

(B) Photochemistry **14 hrs.**

(a) Photochemistry of Alkenes **6 hrs.**

Intramolecular reactions of the olefinic bond – geometrical isomerism, cyclisation reactions, rearrangement of 1, 4 - and 1, 5 – dienes.

(b) Photochemistry of Carbonyl Compounds **8 hrs.**

Intramolecular reactions of carbonyl compounds – saturated, cyclic and acyclic, β, γ-unsaturated and α,β-unsaturated compounds. Cyclohexadienones.

Intermolecular cyloaddition reactions – dimerisations and oxetane formation.

(C) Bioorganic Chemistry :

(i) Enzymes **21 hrs.**

Introduction and historical perspective, chemical and biological catalysis, remarkable properties of enzymes like catalytic power, specificity and regulation. Nomenclature and classification, extraction and purification. Fischer's lock and key and Koshland's induced fit hypothesis, concept and identification of active site by the use of inhibitors, affinity labeling and enzyme modification by site-directed mutagenesis. Enzyme kinetics, Michaelis-Menten and Lineweaver-Burk plots, reversible and irreversible inhibition.

Mechanism of Enzyme Action

Transition-state theory, orientation and steric effect, acid-base catalysis, covalent catalysis, strain or distortion. Examples of some typical enzyme mechanisms for chymotrypsin, ribonuclease, lysozyme and carboxypeptidase A.

Kinds of Reactions Catalysed by Enzymes

Nucleophilic displacement on a phosphorus atom, multiple displacement reactions and the coupling of ATP cleavage to endergonic processes. Transfer of sulphate, addition and elimination reactions, enolic intermediates in isomerization reactions, β-cleavage and condensation, some isomerization and rearrangement reactions. Enzyme catalyzed carboxylation and decarboxylation.

Co-Enzyme Chemistry

Cofactors as derived from vitamins, coenzymes, prosthetic groups, apoenzymes. Structure and biological functions of coenzyme A, thiamine pyrophosphate, pyridoxal phosphate, NAD^+, $NADP^+$, FMN, FAD, lipoic acid, vitamin B_{12}. Mechanisms of reactions catalyzed by the above cofactors.

Enzyme Models

Host-guest chemistry, chiral recognition and catalysis, molecular recognition, molecular asymmetry and prochirality. Biomimetic chemistry, crown ethers, cryptates. Cyclodextrins, cyclodextrin-based enzyme models, calixarenes, ionophores, micelles, synthetic enzymes or synzymes.

Biotechnological Applications of Enzymes

Large-scale production and purification of enzymes, techniques and methods of immobilization of enzymes, effect of immobilization on enzyme activity, application of immobilized enzymes, use of enzymes in food and drink industry-brewing and cheese-making, syrups from corn starch, enzymes as targets for drug design. Clinical uses of enzymes, enzyme therapy, enzymes and recombinant DNA technology.

(ii) Carbohydrate Chemistry : 21 hrs.

I. Structure, function, configuration & conformation of important derivatives of monosaccharides & glycosides; disaccharides (lactose, maltose and sucrose); Polysaccharides – structural polysaccharide (cellulose, chitin); storage polysaccharides (starch and glycogen).

II. Role of sugars in biological recognition.

III. Blood group determinants.

IV. Bioethanol from cellulose.