MC-06
APPLICATION OF SPECTROSCOPY, PHOTO CHEMISTRY AND SOLID STATE CHEMISTRY

Units	Topics
I	**Applications of Spectroscopy:**
	(a) **Infrared Spectroscopy** (Instrumentation and sample handling). Symmetry and shapes of AB2, AB3, AB3, AB4, and AB6, mode of bonding of ambidentate ligands, ethylenediamine and diketonato complexes, application of resonance Raman spectroscopy particularly for the study of active sites of metalloporteins. Characteristic vibrational frequencies of alkanes, alkenes, alkynes, aromatic compounds, alcohols, ethers, phenols and amines. (ketones. aldehydes, esters, amides, acides, 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 or gaseous, solids and polymeric materials.
	(b) **Ultraviolet and Visible Spectroscopy:** 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	**Applications of Spectroscopy**
	(a) **Nuclear Magnetic Resonance Spectroscopy:** 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 qromatic) 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). Resonance of other nuclei-F.P. The contact and pseudo contact shifts, factors affecting nuclear relaxation, some applications including biochemical systems, an overview of NMR of metal nuclides with emphasis on ^{195}Pt and ^{119}Sn NMR. General considerations, chemical shift (aliphatic, olefinic, alkyne, aromatic, heteroromatic and carbonyl carbon), coupling constants. Two dimensional NMR spectroscopy - COSY, NOESY, DEPT, INEPT, APT and INADEQUATE techniques.
	(b) **Electron Spin Resonance Spectroscopy:** Hyperfine coupling, spin polarization for atoms and transition metal ions, spin orbit coupling and significance of g-tensors, application to transition metal complexes (having one unpaired electron) including biological systems and to inorganic free radicals such as PH_4, F_2 and $[BH_3]$.
	(c) **Mass Spectrometry:** 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.

III **Applications of Spectroscopy**

(a) **Applications of Spectroscopy**

(i) **Mossbauer Spectroscopy:** Basic principles, spectral parameters and spectrum display. Application of the technique to the studies of (1) bounding and structures of Fe^{+2} and Fe^{+3} compounds including those of intermediate spin, (2) Sn^{+2} and Sn^{+4} compounds - nature of M-L bond, coordination number, structure and (3) detection of oxidation state and inequivalent MB atoms.

(ii) **Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD): Definition,** deduction of absolute configuration, octant rule or ketones.

(b) **Photo Chemistry**

(i) **Photochemical Reactions:** Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry.

(ii) **Determination of Reaction Mechanism:** Classification, rate constants and life times of reactive energy states determination of rate constants of reactions. Effect of light intensity on the rate of photochemical reactions. Types of photochemical reactions - photodissociation, gass-phase photolysis.

IV **Photochemistry**

(i) **Photochemistry of Alkenes: Intramolecular** reactions of the olefinic bond-geometrical isomerism, cyclisation reactions, rearrangement of 1, 4 - and 1, 5 - dienes.

(ii) **Photochemistry of Carbonyl Compounds:** Intramolecular reactions of carbonyl compounds - saturated, cyclic and acyclic, β, γ- unsaturated and α, β - unsaturated compounds. Cyclohexadienones. Intermolecular cyloaddition reactions - dimerisation and oxetane formation.

(iii) **Photochemistry of Aromatic Compounds: Isomerisations,** additions and substitution.

(iv) **Miscellaneous Photochemical Reactions:** Photo-Fries reactions of anilides. Photo-Fries rearrangement.

Barton reaction. Singlet molecular oxygen reactions. Photochemical formation of smog. Photodegradation of polymers. Photochemistry of vision.

V **Solid State Chemistry**

(i) **Solid State Reactions:** General principles, experimental procedures, co-pricipitation as a precursor to solid state reactions, kinetics of solid state reactions.

(ii) **Crystal Defects and Non-Stoichiometry:** Perfect and imperfect crystals, intrinsic and extrinsic defects - point defects, line and plane defects, vacancies-Schottky defects and Frenkel defects. Thermodynamics of Schottky and Frenkel defect formation, colour centers, non-stoichiometry and defects.

(iii) **Electronic Properties and Band Theory:** Metals, insulators and semiconductors, electronic structure of solids - band theory, band structure of metals, insulators and semiconductors. Intrinsic and extrinsic semiconductors, doping semiconductors, p-n junctions, super conductors.

(iv) **Organic Solids:** Electrically conducting solids, organic charge transfer complex, organic metals, new superconductors.

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