UNIVERSITY OF LUCKNOW
LUCKNOW
M.Sc. Chemistry Semester III (Core)
Inorganic Chemistry Syllabus
Paper III CH 301

Unit I

Applications of Spectroscopy

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 PH4, F2 and $[BH3]^{-}$.

Nuclear Magnetic Resonance Spectroscopy

Applications of multinuclear NMR with emphasis on ^{11}B, ^{19}F, ^{31}P, ^{125}Te, ^{119}Sn and ^{195}Pt NMR.

Mössbauer Spectroscopy

Basic Principles, spectral parameters and spectrum display. Application of the technique to the studies of (1) bonding and structures of Fe^{+2} and Fe^{+3} compounds including those of intermediate spin, (2) Sn^{+2} and Sn^{+4} compounds ï nature of M-L bond, coordination number, structure and (3) detection of oxidation state and in equivalent MB atoms.

Unit II

Bioinorganic Chemistry

Metal Ions in Biological Systems

(a) Essential and trace metals.

(b) Na^{+}/K^{+} Pump.

(c) Vitamin B12, methyl cobalamine, Biomethylation.

(d) Heme proteins and oxygen uptake, structure and function of hemoglobin, myoglobin, homocyanins and hemerythrin, model synthetic complexes of iron, cobalt and copper

Electron Transfer in Biology

Structure and function of metalloproteins in electron transport processes-cytochromes and ion sulphur proteins, synthetic models.

Nitrogenase

Biological nitrogen fixation, molybdenum nitrogenase, spectroscopic and other evidence, other nitrogenases model systems.

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Unit III

Environmental Chemistry

Inorganic Pollutants

1. Aquatic pollution: water quality parameters viz. dissolved oxygen, biochemical oxygen demand, heavy metals Cl-, SO4 2-, NO3-, PO4 3-contents.
2. Soil pollution (including agricultural, viz. pesticides, fertilizers, plastics and metals), Waste treatment.
3. Industrial pollution, viz. cement, sugar, distillery, drug, paper and pulp, thermal power plants, metallurgy.
4. Domestic pollution viz. sewage, detergents, oil pollutants and its management

Unit IV

Selected Topics

1. Chemistry of less familiar metals: Os, Ir, Ru, Rh, Pd
2. Platinium phosphine complexes
3. General method of preparation and important reactions (insertion reactions, metathetical reactions, Lewis acid-base reactions, reactions with protic compounds) of metal and metalloid amides.
4. Preparation of important radio isotopes ($_{1}H^{3}$, $_{6}C^{14}$, $_{11}Na^{22}$, $_{15}P^{32}$, $_{16}S^{35}$) and applications of coordination compounds of Tc^{99} as imaging agents in Nuclear Medicine
5. Principle, instrumentation and applications of TGA and DTA Ion exchange-preparation, mechanism, of exchange capacity of ion exchangers, Principle and applications of photometric and colorimetric techniques in inorganic analysis.

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Unit I

Applications of Spectroscopy:

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.

Infrared Spectroscopy

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.

Optical Rotatory Dispersion (ORD) and Circular Dichroism (CD)

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

Unit II

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 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).

Carbon-13 NMR Spectroscopy

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.

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Mass Spectrometry

Introduction, ion production ï El, Cl, 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.

Unit III

Photochemistry

Photochemistry of Alkenes

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

Photochemistry of Carbonyl Compounds

Intramolecular reactions of carbonyl compounds ï saturated, cyclic and acyclic, β, γ-unsaturated and α,β-unsaturated compounds. Cyclohexadienones. Intermolecular cyloaddition reactions ï dimerisations and oxetane formation.

Carbohydrate Chemistry :

i. Structure, function, configuration & conformation of important derivatives of monosaccharides & glycosides; disaccharides (lactose, maltose and sucrose); Polysaccharides ï structural polysaccharide (cellulose, chitin); storage polysaccharides (starch and glycogen).
ii. Role of sugars in biological recognition.
iii. Blood group determinants.
iv. Bioethanol from cellulose.

Unit IV

Bioorganic Chemistry :

Enzymes

Introduction and historical perspective, chemical and biological catalysis, remarkable properties of enzymes like catalytic power, specificity and regulation. Nomenclature and classification, extraction and purification. Fischerôs lock and key and Koshlandôs 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.

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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, □-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 B12. 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.

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Unit I

Solid State Reactions

General principles, experimental procedures, co-precipitation as a precursor to solid state reactions, kinetics of solid state reactions.

Crystal Defects and Non-Stoichiometry

Perfect and imperfect crystals, intrinsic and extrinsic defects ï 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.

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. Optical Properties ï Optical reflectance, photoconduction photoelectric effects.

Unit II

Magnetic Properties

Classification of materials: Quantum theory of paramagnetics-cooperative phenomena-magnetic domains, hysteresis.

Organic Solids

Electrically conducting solids, organic charge transfer complex, organic metals, new superconductors

Photochemical Reactions

Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy.

Energy States of Molecules

Phosphorescence and the triplet state, Delayed Fluorescence, Energy level diagrams, Intersystem crossing (Jablonski diagram), Franck ï Condon Principle, Physical properties of excited molecules, Light emission and chemical reaction from excited states, Radiationless deactivation of excited states,

Unit III

Determination of Reaction Mechanism

Classification, rate constants and life times of reactive energy states ï determination of rate constants of reactions. Effect of light intensity on the rate of photochemical reactions. Types of photochemical reactions ï photo-dissociation, gas-phase photolysis.

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Photochemical Process

Photoreductions, Photo oxidations, Electron transfer reactions, Photoconduction, Chemiluminiscence, Atom sensitized reactions, sensitization and quenching, Photosensitization, Stern ï Volmer equation. Photosynthesis, Photomorphogenesis and Photochemistry of vision.

Experimental Techniques

Spectrometry, Actinometry, Flash Photolysis and Laser Beam.

Biopolymers and their Molecular Weights

Evaluation of size, shape, molecular weight and extent of hydration of biopolymers by various experimental techniques. Sedimentation equilibrium, hydrodynamic methods, diffusion, sedimentation velocity, viscosity, electrophoresis and rotational motions.

Unit IV

Biological Cell and its Constituents

Biological cell, structure and functions of proteins, enzymes, DNA and RNA in living systems. Helix coil transition.

Statistical Mechanics in Biopolymers

Chain configuration of macromolecules, statistical distribution end to end dimensions, calculation of average dimensions for various chain structures. Polypeptide and protein structures, introduction to protein folding problem.

Biopolymer Interactions

Forces involved in biopolymer interactions. Electrostatic charges and molecular expansion, hydrophobic forces, dispersion force interactions. Multiple equilibria and various types of binding processes in biological systems.

Thermodynamics of Biopolymer Solutions

Thermodynamics of biopolymer solutions, osmotic pressure, membrane equilibrium muscular contraction and energy generation in mechanochemical system.

Cell Membrane and Transport of Ions

Structure and functions of cell membrane, ion transport through cell membrane, irreversible thermodynamic treatment of membrane transport. Nerve conduction.

Applications of Diffraction Methods in Biopolymers

Light scattering, low angle X-ray scattering, X-ray diffraction and photo correlation spectroscopy. ORD.