

Syllabus for the Entrance Examination for M.Sc. (Chemistry)

- I Inorganic Chemistry
- II Physical Chemistry
- III Organic Chemistry

Total Marks: 60

INORGANIC CHEMISTRY:

Atomic Structure: Idea of de-Broglie matter waves, Heisenberg uncertainty principle, atomic orbitals, quantum numbers, radial and angular, wave functions and probability distribution curves, shapes of s, p, d orbitals.

Periodic Properties:

General principles of periodic table: Aufbau and Pauli exclusion principles, Hund's multiplicity rule. Electronic configurations of the elements, effective nuclear charge, Slater's rules. Atomic and ionic radii, ionization energy, electron affinity and electronegativity – definition, methods of determination or evaluation, trends in periodic table (in s & p block elements).

Chemical Bonding:

Covalent Bond: Valence bond theory and its limitations, directional characteristics of covalent bond, various types of hybridization and shapes of simple inorganic molecules and ions (BeF_2 , BF_3 , CH_4 , PF_5 , SF_6 , IF_7 , SO_4^{2-} , ClO_4^-). Valence shell electron pair repulsion (VSEPR) theory to NH_3 , H_3O^+ , SF_4 , ClF_3 , ICl_2^- and H_2O . MO theory of heteronuclear (CO and NO) diatomic molecules, bond strength and bond energy, percentage ionic character from dipole moment and electronegativity difference.

Ionic Solids: Ionic structures [NaCl , CsCl , ZnS (Zinc Blende), CaF_2] radius ratio effect and coordination number, limitation of radius ratio rule, lattice defects, semiconductors, lattice energy (mathematical derivation excluded) and Born-Haber cycle, solvation energy and its relation with solubility of ionic solids, polarizing power and polarizability of ions, Fajan's rule.

Hydrogen Bonding & others forces: Definition, Types, effects of hydrogen bonding on properties of substances, application Brief discussion of various types of Vander Waals Forces.

Metallic Bond and Semiconductors: Brief introduction to metallic bond, band theory of metallic bond Semiconductors- Introduction, types and applications.

s-Block Elements: Comparative study of the elements including, diagonal relationships, salient features of hydrides (methods of preparation excluded), solvation and complexation tendencies including their function in biosystems.

p-Block Elements: Emphasis on comparative study of properties of p-block elements (including diagonal relationship and excluding methods of preparation).

Boron family (13^{th} gp): Diborane-properties and structure (as an example of electron – deficient compound and multicentre bonding).

Borazene: chemical properties and structure Trihalides of Boron – Trends in Lewis acid character structure of aluminium (III) chloride.

Carbon Family (14^{th} group): Catenation, p π - d π bonding (an idea), carbides, fluorocarbons, silicates structural aspects), silicons – general methods of preparations, properties and uses.

Nitrogen Family (15^{th} group): Oxides – structures of oxides of N,P. oxyacids – structure and relative acid strengths of oxyacids of Nitrogen and phosphorus. Structure of white, yellow and red phosphorus.

Oxygen Family (16^{th} group): Oxyacids of sulphur – structures and acidic strength H_2O_2 –structure, properties and uses.

Halogen Family (17^{th} group): Basic properties of halogen, interhalogens types properties, hydro and oxyacids of chlorine – structure and comparison of acid strength.

Chemistry of Noble Gases: Chemical properties of the noble gases with emphasis on their low chemical reactivity, chemistry of xenon, structure and bonding of fluorides, oxides & oxyfluorides of xenon.

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Chemistry of Transition Elements: *Chemistry of Elements of 1st transition series*, Definition of transition elements, position in the periodic table, General characteristics & properties of 1st transition elements, Structures & properties of some compounds of transition elements – TiO_2 , VOCl_2 , FeCl_3 , CuCl_2 and Ni(CO)_4 .

Chemistry of Elements of 2nd & 3rd transition series: General characteristics and properties of the 2nd and 3rd transition elements Comparison of properties of 3d elements with 4d & 5d elements with reference only to ionic radii, oxidation state, magnetic and Spectral properties and stereochemistry.

Coordination Compounds:

Werner's coordination theory, effective atomic number concept, chelates, nomenclature of coordination compounds, isomerism in coordination compounds, valence bond theory of transition metal complexes

Metal-ligand Bonding in Transition Metal Complexes: Limitations of valence bond theory, an elementary idea of crystal-field theory, crystal field splitting in octahedral, tetrahedral and square planar complexes, factors affecting the crystal-field parameters.

Thermodynamic and Kinetic Aspects of Metal Complex: A brief outline of thermodynamic stability of metal complexes and factors affecting the stability, substitution reactions of square planar complexes of Pt(II) .

Magnetic Properties of Transition Metal Complex: Types of magnetic behaviour, methods of determining magnetic susceptibility, spin-only formula, L-S coupling, correlation of μ_s and μ_{eff} values, orbital contribution to magnetic moments, application of magnetic moment data for 3d metal complexes.

Electron Spectra of Transition Metal Complexes: Types of electronic transitions, selection rules for d-d transitions, spectroscopic ground states, spectrochemical series.

Orgel-energy level diagram for d1 and d9 states, discussion of the electronic spectrum of $[\text{Ti(H}_2\text{O)}_6]^{3+}$ complex ion.

Chemistry of f – block elements :

Lanthanides: Electronic structure, oxidation states and ionic radii and lanthanide contraction, complex formation, occurrence and isolation, lanthanide compounds.

Actinides: General features and chemistry of actinides, chemistry of separation of Np, Pu and Am from U, comparison of properties of Lanthanides and Actinides and with transition elements.

Organometallic Chemistry: Definition, nomenclature and classification of organometallic compounds. Preparation, properties, and bonding of alkyls of Li, Al, Hg, and Sn a brief account of metal-ethylenic complexes, mononuclear carbonyls and the nature of bonding in metal carbonyls.

Silicones and Phosphazenes: Silicones and phosphazenes, their preparation, properties, structure and uses.

Acids and Bases, HSAB Concept :

Arrhenius, Bronsted – Lowry, Lux – Flood, Solvent system and Lewis concepts of acids & bases, relative strength of acids & bases, Concept of Hard and Soft Acids & Bases. Symbiosis, electronegativity and hardness and softness.

Non-aqueous Solvents : Physical properties of a solvent, types of solvents and their general characteristics, reactions in non-aqueous solvents with reference to liquid NH_3 and liquid SO_2 .

Theory of Qualitative and Quantitative Inorganic Analysis: Chemistry of analysis of various acidic radicals, Chemistry of identification of acid radicals in typical combinations, Chemistry of interference of acid radicals including their removal in the analysis of basic radicals. Chemistry of analysis of various groups of basic radicals, Theory of precipitation, co-precipitation, Post-precipitation, purification of precipitates.

Bioinorganic Chemistry: Essential and trace elements in biological processes, metalloporphyrins with special reference to haemoglobin and myoglobin. Biological role of alkali and alkaline earth metal ions with special reference to Ca^{2+} , Nitrogen fixation.

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II PHYSICAL CHEMISTRY:

Gaseous state: Maxwell's distribution of velocities and energies (derivation excluded) Calculation of root mean square velocity, average velocity and most probable velocity. Collision diameter, collision number, collision frequency and mean free path. Deviation of Real gases from ideal behaviour. Derivation of Vander Waal's Equation of State, its application in the calculation of Boyle's temperature (compression factor) Explanation of behaviour of real gases using Vander Waal's equation.

Critical Phenomenon: Critical temperature, Critical pressure, critical volume and their determination. PV isotherms of real gases, continuity of states, the isotherms of Vander Waal's equation, relationship between critical constants and Vander-Waals constants. Critical compressibility factor. The Law of corresponding states. Liquifaction of gases.

Liquid State : Structure of liquids. Properties of liquids – surface tension, viscosity vapour pressure and optical rotations and their determination.

Solid State: Classification of solids, Laws of crystallography – (i) Law of constancy of interfacial angles (ii) Law of rationality of indices (iii) Law of symmetry. Symmetry elements of crystals. Definition of unit cell & space lattice. Bravais lattices, crystal system. X ray diffraction by crystals. Bragg equation. Determination of crystal structure of NaCl. KCl. Liquid crystals: Difference between solids, liquids and liquid crystals, types of liquid crystals. Applications of liquid crystals.

Chemical Kinetics : Rate of reaction, rate equation, factors influencing the rate of a reaction – concentration, temperature, pressure, solvent, light, catalyst. Order of a reaction, integrated rate expression for zero order, first order, second and third order reaction. Half life period of a reaction. Methods of determination of order of reaction. Effect of temperature on the rate of reaction-Arrhenius equation.

Electrochemistry:

Electrolytic conduction, factors affecting electrolytic conduction, specific, conductance, molar conductance, equivalent conductance and relation among them, their variation with concentration. Arrhenius theory of ionization, Ostwald's Dilution Law. Debye-Huckel – Onsager's equation for strong electrolytes (elementary treatment only), Transport number, definition and determination by Hittorf's methods (numerical included). Kohlrausch's Law, calculation of molar ionic conductance and effect of viscosity, temperature & pressure on it. Application of Kohlrausch's Law in calculation of conductance of weak electrolytes at infinite dilution. Applications of conductivity measurements: determination of degree of dissociation, determination of K_a of acids, determination of solubility product of sparingly soluble salts, conductometric titrations. Definition of pH and pKa, Buffer solution, Buffer action, Henderson – Hazel equation, Buffer mechanism of buffer action.

Thermodynamics-I:

Definition of thermodynamic terms: system, surrounding etc. Types of systems, intensive and extensive properties. State, path functions and their differentials. Thermodynamic process. Concept of heat and work. Zeroth Law of thermodynamics, First law of thermodynamics: statement, definition of internal energy and enthalpy. Heat capacity, heat capacities at constant volume and pressure and their relationship. Joule's law – Joule – Thomson coefficient for ideal gas and real gas and inversion temperature.

Thermodynamics-II:

Calculation of w , q , dU & dH for the expansion of ideal gases under isothermal and adiabatic conditions for reversible process, Temperature dependence of enthalpy, Kirchhoff's equation. Bond energies and applications of bond energies.

Thermodynamics-III:

Second law of thermodynamics, need for the law, different statements of the law, Carnot's cycles and its efficiency, Carnot's theorem, Thermodynamics scale of temperature. Concept of entropy – entropy as a state function, entropy as a function of V & T , entropy as a function of P & T , entropy change in physical change, entropy as a criteria of spontaneity and equilibrium. Entropy change in ideal gases and mixing of gases.

Thermodynamics-IV:

Third law of thermodynamics: Nernst heat theorem, statement of concept of residual entropy, evaluation of absolute entropy from heat capacity data. Gibbs and Helmholtz functions; Gibbs function (G) and Helmholtz function (A) as thermodynamic quantities, A & G as criteria for thermodynamic equilibrium and spontaneity, their advantage over entropy change. Variation of G and A with P , V and T .

Chemical Equilibrium:

Equilibrium constant and free energy, concept of chemical potential, Thermodynamic derivation of law of chemical equilibrium. Temperature dependence of equilibrium constant; Van't Hoff reaction isochore, Van't Hoff reaction isotherm. Le-Chatelier's principle and its applications, Clapeyron equation, Clausius – Clapeyron equation and its

applications.

Distribution Law: Nernst distribution law – its thermodynamic derivation, Modification of distribution law when solute undergoes dissociation, association and chemical combination. Applications of distribution law: (i) Determination of degree of hydrolysis and hydrolysis constant of aniline hydrochloride. (ii) Determination of equilibrium constant of potassium triiodide complex and process of extraction.

Electrochemistry:

Electrolytic and Galvanic cells – reversible & irreversible cells, conventional representation of electrochemical cells. EMF of cell and its measurement, Weston standard cell, activity and activity coefficients. Calculation of thermodynamic quantities of cell reaction (ΔG , ΔH & K). Types of reversible electrodes – metal-metal ion gas electrode, metal-insoluble salt-anion and redox electrodes. Electrode reactions, Nernst equations, derivation of cell EMF and single electrode potential. Standard Hydrogen electrode, reference electrodes, standard electrodes potential, sign conventions, electrochemical series and its applications.

Concentration cells with and without transference, liquid junction potential, application of EMF measurement i.e. valency of ions, solubility product activity coefficient, potentiometric titration (acid-base and redox). Determination of pH using Hydrogen electrode, Quinhydrone electrode and glass electrode by potentiometric methods.

Quantum Mechanics:

Black-body radiation, Planck's radiation law, photoelectric effect, heat capacity of solids, Compton effect, wave function and its significance of Postulates of quantum mechanics, quantum mechanical operator, commutation relations, Hamiltonian operator, Hermitian operator, average value of square of Hermitian as a positive quantity, Role of operators in quantum mechanics, To show quantum mechanically that position and momentum cannot be predicated simultaneously, Determination of wave function & energy of a particle in one dimensional box, Pictorial representation and its significance.

Spectroscopy

Introduction & Rotational Spectrum:

Electromagnetic radiation, regions of spectrum, basic features of spectroscopy, statement of Born Oppenheimer approximation, Degrees of freedom. Diatomic molecules. Energy levels of rigid rotator (semi-classical principles), selection rules, spectral intensity distribution using population distribution (Maxwell-Boltzmann distribution), determination of bond length, qualitative description of non-rigid rotor, isotope effect.

Vibrational spectrum:

Infrared spectrum: Energy levels of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies, effects of anharmonic motion and isotopic effect on the spectra, idea of vibrational frequencies of different functional groups.

Raman Spectrum:

Concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules, Quantum theory of Raman spectra.

Electronic Spectrum:

Concept of potential energy curves for bonding and antibonding molecular orbitals, qualitative description of selection rules and Franck-Condon principle.

Qualitative description of sigma and pi and n molecular orbital (MO) their energy level and respective transitions.

Photochemistry:

Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry: Grotthuss-Draper law, Stark-Einstein law (law of photochemical equivalence) Jablonski diagram depicting various processes occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing), quantum yield, photosensitized reactions-energy transfer processes (simple examples).

Dilute Solutions and Colligative Properties:

Ideal and non-ideal solutions, methods of expressing concentrations of solutions, activity and activity coefficient. Dilute solution, Colligative properties, Raoult's law, relative lowering of vapour pressure, molecular weight determination, Osmosis law of osmotic pressure and its measurement, determination of molecular weight from osmotic pressure. Elevation of boiling point and depression of freezing point, Thermodynamic derivation of relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods for determining various colligative properties. Abnormal molar mass, degree of dissociation and association of solutes.

Phase Equilibrium:

Statement and meaning of the terms – phase component and degree of freedom, thermodynamic derivation of Gibbs phase rule, phase equilibria of one component system – Example – water and Sulphur systems. Phase equilibria of two component systems solid-liquid equilibria, simple eutectic Example Pb-Ag system, desilverisation of lead.

III ORGANIC CHEMISTRY

Fundamentals of organic chemistry & isomerism

Hybridization, Inductive, Electrometric, Resonance and hyperconjugative effects. Requirements of aromaticity, Huckel's rule and its significance. Strength of organic acids and bases: pK_a , origin of acidity, influence of solvent, simple aliphatic saturated and unsaturated acids, substituted aliphatic acid, phenols, aromatic carboxylic acids, pK_a and temperature, pK_b , aliphatic and aromatic bases, heterocyclic bases, acid base catalysis. Carbocations, Carbanions and Free radicals (Structure and stability) Carbenes, Benzyne and Nitrenes. Methods for determination of reaction mechanism.

Concept of stereo isomerism: elements of symmetry, molecular chirality, enantiomers and diastereomers, Inversion, retention and racemisation. Sequence rules. R,S-System of nomenclature. Geometrical isomers, E, Z-system of nomenclature. Optical isomerism, Conformations of n-butane, ethylene glycol and 1,2-dibromoethane, cyclohexane and its monosubstituted derivative, Axial and equatorial bonds. Baeyer's strain theory and its limitations. Ring strain in smaller rings with respect to cyclopropane ring.

Mechanism of Organic Reactions :

Curved arrow notation, drawing electron movements with arrows, half-headed and double-headed arrows, homolytic and heterolytic bond breaking. Types of reagents – electrophiles and nucleophiles. Types of organic reactions. Energy considerations. Reactive intermediates carbocations, carbanions, free radicals, carbenes, arynes and nitrenes (formation, structure & stability). Assigning formal charges on intermediates and other ionic species.

Alkanes and Cycloalkanes:

IUPAC nomenclature of branched and unbranched alkanes, the alkyl group, classification of carbon atoms in alkanes. Isomerism in alkanes, sources, methods of formation (with special reference to Wurtz reaction, Kolbe reaction, Corey-House reaction and decarboxylation of carboxylic acids), physical properties. Cycloalkanes nomenclature, synthesis of cycloalkanes and their derivatives – photochemical (2+2) cycloaddition reactions, dehalogenation of dihalides, pyrolysis of calcium or barium salts of dicarboxylic acids, Baeyer's strain theory and its limitations., theory of strainless rings.

Alkenes :

Nomenclature of alkenes, mechanisms of dehydration of alcohols and dehydrohalogenation of alkyl halides,. The Saytzeff rule, Hofmann elimination, physical properties and relative stabilities of alkenes. Chemical reactions of alkenes & mechanisms involved in hydrogenation, electrophilic and free radical additions, Markownikoff's rule, hydroboration-oxidation, oxymercuration-reduction, ozonolysis, hydration, hydroxylation and oxidation with $KMnO_4$.

Arenes and Aromaticity :

Nomenclature of benzene derivatives: Aromatic nucleus and side chain. Aromaticity: the Huckel rule, aromatic ions, annulenes up to 10 carbon atoms, aromatic, anti - aromatic and non - aromatic compounds. Aromatic electrophilic substitution & general pattern of the mechanism, mechanism of nitration, halogenation, sulphonation, and Friedel-Crafts reaction. Energy profile diagrams. Activating, deactivating substituents and orientation.

Dienes and Alkynes :

Nomenclature and classification of dienes: isolated, conjugated and cumulated dienes. Structure of butadiene, Chemical reactions :1,2 and 1,4 additions (Electrophilic & free radical mechanism), Diels-Alder reaction, Nomenclature, structure and bonding in alkynes. Methods of formation. Chemical reactions of alkynes, acidity of alkynes. Mechanism of electrophilic and nucleophilic addition reactions, hydroboration-oxidation of alkynes.

Alkyl and Aryl Halides :

Nomenclature and classes of alkyl halides, methods of formation, chemical reactions. Mechanisms and stereochemistry of nucleophilic substitution reactions of alkyl halides, SN_2 and SN_1 reactions with energy profile diagrams. Methods of formation and reactions of aryl halides, The elimination-addition mechanisms of nucleophilic aromatic substitution reactions. Relative reactivities of alkyl halides vs allyl, vinyl and aryl halides.

Alcohols :

Monohydric alcohols : nomenclature, methods of formation by reduction of aldehydes, ketones, carboxylic acids and

esters. Hydrogen bonding. Acidic nature. Reactions of alcohols. Dihydric alcohols — nomenclature, methods of formation, chemical reactions of vicinal glycols, oxidative cleavage [$\text{Pb}(\text{OAc})_4$ and HIO_4] and pinacol-pinacolone rearrangement.

Epoxides :

Synthesis of epoxides. Acid and base-catalyzed ring opening of epoxides, orientation of epoxide ring opening, reactions of Grignard and organolithium reagents with epoxides

Phenols :

Nomenclature, structure and bonding. Preparation of phenols, physical properties and acidic character. Comparative acidic strengths of alcohols and phenols, resonance stabilization of phenoxide ion. Reactions of phenols - electrophilic aromatic substitution, Mechanisms of Fries rearrangement, Claisen rearrangement, Reimer-Tiemann reaction, Kolbe's reaction and Schotten and Baumann reactions.

Carboxylic Acids & Acid Derivatives :

Nomenclature of Carboxylic acids, structure and bonding, physical properties, acidity of carboxylic acids, effects of substituents on acid strength. Preparation of carboxylic acids. Reactions of carboxylic acids. Hell-Volhard-Zelinsky reaction. Reduction of carboxylic acids. Mechanism of decarboxylation. Structure, nomenclature and preparation of acid chlorides, esters, amides and acid anhydrides. Relative stability of acyl derivatives. Physical properties, interconversion of acid derivatives by nucleophilic acyl substitution. Mechanisms of esterification and hydrolysis (acidic and basic).

Amines :

Structure and nomenclature of amines, physical properties. Separation of a mixture of primary, secondary and tertiary amines. Structural features affecting basicity of amines. Preparation of alkyl and aryl amines (reduction of nitro compounds, nitriles, reductive amination of aldehydic and ketonic compounds. Gabriel phthalimide reaction, Hofmann bromamide reaction. electrophilic aromatic substitution in aryl amines, reactions of amines with nitrous acid.

Aldehydes and Ketones :

Nomenclature and structure of the carbonyl group. Synthesis of aldehydes and ketones with particular reference to the synthesis of aldehydes from acid chlorides, advantage of oxidation of alcohols with chromium trioxide (Sarett reagent) pyridinium chlorochromate (PCC) and pyridinium dichromate. Physical properties. Comparison of reactivities of aldehydes and ketones. Mechanism of nucleophilic additions to carbonyl group with particular emphasis on benzoin, aldol, Perkin and Knoevenagel condensations. Condensation with ammonia and its derivatives, Wittig reaction, Mannich reaction. Oxidation of aldehydes, Baeyer-Villiger oxidation of ketones, Cannizzaro reaction. MPV, Clemmensen, Wolff-Kishner, LiAlH_4 and NaBH_4 reductions.

Carbohydrates :

Classification and nomenclature. Monosaccharides, mechanism of osazone formation, interconversion of glucose and fructose, chain lengthening and chain shortening of aldoses. Configuration of monosaccharides. Erythro and threo diastereomers. Conversion of glucose into mannose. Formation of glycosides, ethers and esters. Determination of ring size of glucose and fructose. Open chain and cyclic structure of D(+)-glucose & D(-) fructose. Mechanism of mutarotation. Structures of ribose and deoxyribose. An introduction to disaccharides (maltose, sucrose and lactose) and polysaccharides (starch and cellulose) without involving structure determination.

Heterocyclic Compounds :

Introduction: Molecular orbital picture and aromatic characteristics of pyrrole, furan, thiophene and pyridine. Methods of synthesis and chemical reactions with particular emphasis on the mechanism of electrophilic substitution. Mechanism of nucleophilic substitution reactions in pyridine derivatives. Comparison of basicity of pyridine, piperidine and pyrrole. Introduction to condensed five and six-membered heterocycles. Preparation and reactions of indole, quinoline and isoquinoline with special reference to Fischer indole synthesis, Skraup synthesis and Bischler-Napieralski synthesis. Mechanism of electrophilic substitution reactions of quinoline and isoquinoline.

Ultraviolet (UV) absorption spectroscopy :

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Absorption laws (Beer-Lambert law), molar absorptivity, presentation and analysis of UV spectra, types of electronic transitions, effect of conjugation. Concept of chromophore and auxochrome. Bathochromic, hypsochromic, hyperchromic and hypochromic shifts. UV spectra of conjugated enes and enones, Woodward-Fieser rules, calculation of λ_{max} of simple conjugated dienes and α, β -unsaturated ketones. Applications of UV Spectroscopy in structure elucidation of simple organic compounds.

Infrared (IR) absorption spectroscopy :

Molecular vibrations, Hooke's law, selection rules, intensity and position of IR bands, measurement of IR spectrum, fingerprint region, characteristic absorptions of various functional groups and interpretation of IR spectra of simple organic compounds. Applications of IR spectroscopy in structure elucidation of simple organic compounds.

NMR Spectroscopy :

Principle of nuclear magnetic resonance, the PMR spectrum, number of signals, peak areas, equivalent and nonequivalent protons positions of signals and chemical shift, shielding and deshielding of protons, proton counting, splitting of signals and coupling constants, magnetic equivalence of protons. Discussion of PMR spectra of the molecules: ethyl bromide, n-propyl bromide, isopropyl bromide, 1,1-dibromoethane, 1,1,2-tribromoethane, ethanol, acetaldehyde, ethyl acetate, toluene, benzaldehyde and acetophenone. Simple problems on PMR spectroscopy for structure determination of organic compounds.

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