

CORE COURSE XI - PHYSICAL METHODS IN CHEMISTRY – II

UNIT I

Electronic Spectroscopy

Microstates, terms and energy levels for $d^1 - d^9$ ions in cubic and square fields – Intensity of bands – group theoretical approach to selection rules – Effect of distortion and spin-orbit coupling on spectra – Evaluation of $10Dq$ and β for octahedral complexes of cobalt and nickel – applications to simple coordination compounds – charge transfer spectra – electronic spectra of $[\text{Ru}(\text{bipy})_3]^{2+}$.

Optical rotatory dispersion and circular dichroism and Magnetic circular dichroism – applications to metal complexes.

UNIT – II

Infrared and Raman Spectroscopy

Vibrations in simple molecules (H_2O , CO_2) and their symmetry notation for molecular vibrations – Group vibrations and the limitations- combined uses of IR and Raman Spectroscopy in the structural elucidation of simple molecules like N_2O , ClF_3 , NO_3^- , ClO_4^- – effect of coordination on ligand vibrations – uses of groups vibrations in the structural elucidation of metal complexes of urea, thiourea, cyanide, thiocyanate, nitrate, sulphate and dimethyl sulfoxide – Effect of isotopic substitution on the vibrational spectra of molecules – vibrational spectra of metal carbonyls with reference to the nature of bonding, geometry and number of C-O stretching vibrations (group theoretical treatment) – Applications of Raman Spectroscopy – Resonance Raman Spectroscopy. Mass Spectrometry: Principles and presentation of spectra – molecular fragmentation – ion reactions – Inorganic applications.

UNIT – III

NMR Spectroscopy

Examples for different spin systems – chemical shifts and coupling constants (spin-spin coupling) involving different nuclei (^1H , ^{19}F , ^{31}P , ^{13}C) interpretation and applications to inorganic compounds – Effect of quadrupolar nuclei (^2H , ^{10}B , ^{11}B) on the ^1H NMR spectra, Satellite spectra.

Systems with chemical exchange - evaluation of thermodynamic parameters in simple systems – study of fluxional behavior of molecules – an elementary treatment of second order spectra – examples – NMR of paramagnetic molecules – isotropic shifts contact and pseudo-contact interactions – Lanthanide shift reagents.

UNIT IV

EPR spectroscopy

Theory of EPR spectroscopy - Spin densities and McConnell relationship - Factors affecting the magnitude of g and A tensors in metal species - Zero-field splitting and Kramers degeneracy - Spectra of VO(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes - Applications of EPR to a few biological molecules containing Cu(II) and Fe(III) ions.

Magnetic properties:

Types of magnetism - Dia -para - ferro and antiferro magnetism. Magnetic properties of free ions - first order Zeeman effect - Second order Zeeman effect - states KT - states $<KT$. Determination of Magnetic moments and their applications to the elucidation of structures of inorganic compounds - temperature independent paramagnetism. Magnetic properties of lanthanides and actinides. Spin crossover in coordination compounds.

UNIT V

Mossbauer Spectroscopy

Isomer shifts - Magnetic interactions - Mossbauer emission spectroscopy - applications to iron and tin compounds.

NQR spectroscopy

Characteristics of quadrupolar nucleus - effects of field gradient and magnetic field upon quadrupolar energy levels - NQR transitions - applications of NQR spectroscopy.

REFERENCES:

1. R.S. Drago, Physical Methods in Inorganic Chemistry, 3rd Ed., Wiley Eastern Company .
2. R.S.Drago, Physical Methods in Chemistry, W.B. Saunders Company, Philadelphia, London.
3. F.A. Cotton and G.Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Wiley-Eastern Company, New Delhi 1990.
4. P.J. Wheatley, The Determination of Molecular Structure, .
5. Lewis and Wilkins, Modern Coordination Chemistry,.
6. E.A.V.Ebsworth, Structural Methods in Inorganic Chemistry, 3rd ed., ELBS, Great Britain, 1987.