Subject Code : P8CH7

CORE COURSE VII - PHYSICAL METHODS IN CHEMISTRY - I

UNIT I

Theoretical principles of Molecular Spectroscopy:

Interaction of electromagnetic radiation with molecular systems – Time evolution of the systems under radiation – Einstein transition probability for induced absorption and spontaneous and stimulated emission – Transition moment and Oscillator strength

Microwave spectroscopy – rotational spectra of diatomic molecules, rigid and nonrigid rotors, - Intensity of spectral lines, - Effects of isotopic substitution – Microwave spectra of polyatomic molecules – Linear and symmetric top molecules, Infrared spectra – diatomic molecules, simple harmonic and anharmonic oscillators, - diatomic vibrating rotator, rotation-vibration spectrum of carbon monoxide, - Interaction of rotation and vibration (breakdown of Born – Oppenheimer approximation) – Influence of the rotation on the spectrum of polyatomic molecules, linear and symmetric top molecules, parallel and perpendicular vibrations, Influence of nuclear spin.

Raman spectra – Rotational Raman spectra of linear and symmetric top molecules – Vibrational Raman spectra, Rotational fine structure. Electronic spectra of diatomic molecules, - Vibrational coarse structure – Intensity of vibrational lines in electronic spectra – Rotational fine structure – Fortrat digram.

UNIT II

Advanced Spectroscopy : NMR

^{1}H NMR Spectroscopy – Multiplicity – Coupling constant – First order and second order proton, Spin - spin splitting – Dependence of J on dihedral angle – Vicinal and geminal coupling constants – Karplus equation – long range coupling constants, Influence of stereochemical factors on chemical shift of protons. Simplification of complex spectra – Double resonance techniques, shifts reagents. Chemical spin decoupling of rapidly exchangable protons (OH, SH, COOCH, NH, NH_2), an elementary treatment of NOE phenomenon. ^{13}C NMR Spectroscopy – Basic theory of FT – NMR, Relaxation – Broad band decoupling. Off resonance decoupling and chemical shifts of common functional groups, DEPT spectra. Identification of small compounds based on NMR data. 2D Techniques: ^{1}H – ^{1}H COSY, ^{1}H – ^{13}C COSY – HMBC and NOESY.

UNIT III

Advanced Spectroscopy: UV –Vis, IR

UV-Visible Spectroscopy : Introduction - Instrumentation, Sampling techniques - Woodward–Fieser and Scott rules for conjucated dienes and polymers, ketones, aldehydes, ∝,β-unsaturated acids, esters, nitriles, and amides. Differentiation of geometrical isomers and positional isomers – Disubstituted benzene derivatives - Study of steric effect in aromaticity.

Infrared Spectroscopy : Introduction - Instrumentation, Sampling techniques, factors influencing group frequencies – Both internal and external – quantitative studies. Hydrogen bonding – (intermolecular and intramolecular).

UNIT IV

Electron spin resonance spectroscopy: Basic principles – comparison between esr and nmr spectra – hyperfine splitting – factors affecting the magnitude of g – values – calculation of unpaired electron density on an atom in a delocalized system – applications to organic free radicals.

Optical rotatory dispersion and circular dichroism : Introduction to theory and terminology – cotton effect – ORD curves – axial haloketone rule and its applications – octant rule – its applications – applications of ORD to determine absolute configuration of monocyclic ketones – comparision between ORD and CD – their inter relationships.

Mass Spectrometry

Instrumentation – Resolution, EI and CI methods – Base peak, isotopic peaks, metastable peak, parent peak, determination and use of molecular formula, recognition of molecular ion peak – FAB. Fragmentation – General rules – Pattern of fragmentation for various classes of compounds, McLafferty rearrangement, Importance of metastable peaks.

UNIT V

X-ray diffraction: X-ray diffraction by single crystal – Space groups – Systematic absences in X-ray data and identification of lattice types , glide planes and screw axes.X-ray intensities, structure factor and its relation to intensity and electron density , phase problem. Structure solution by Heavy atom method and direct method. Determination of absolute configuration of molecules. A brief account of Cambridge Structural Database (CSD) and Protein Data Bank (PDB).

Electron Diffraction by gases - Scattering intensity vs Scattering angle, wierl equation, measurement technique, elucidation of structure of simple gas phase molecules.

Neutron diffraction by crystals – magnetic scattering, measurement techniques. Elucidation of structure of magnetically ordered unit cell.

References:

1. C.N. Banwell, Fundamentals of molecular Spectroscopy, 3rd ed., TMH, New Delhi, 1983.
2. B.P. Straughan and S.Walker Spectroscopy Vol.3, Chapman Hall London, 1976.
3. G.M. Barrow, Introduction to Molecular Spectroscopy, McGraw Hill, New York, 1964.
4. P.K.Ghosh, Introduction to Photoelectron Spectroscopy, John Wiley New York, 1989.
5. P.M. Silverstein, F. X. Wester, Spectroscopic Identification of Organic Compounds, 6th ed., Wiley 1998.
6. W. Kemp, Organic Spectroscopy, 3rd Ed., MacMillon, 1994.
7. J.R. Dyer, Applications of Absorption Spectroscopy of Organic Compounds, Prentice Hall, 1965.
8. Y.R. Sharma , Elementary Organic Spectroscopy – Principles and Chemical applications, S.Chand,1992.
9. P.S.Kalsi, Spectroscopy of Organic Compounds.
10. Clegg,W., Crystal structure determination, Oxford University press , New York,1998.
12. Stout,G.H., Jensen , L.H. X-ray structure determination : A practical guide , John wiley & sons Publication: New York,1989
13. Glusker, J.P., Trueblood,K.N. Crystal structure analysis: A primer., Oxford university press, New York, 1972.

Webpages :

Cambridge Structural Database (CSD) -
http://www.ccdc.cam.ac.uk/products/csd/
Protein Data Bank (PDB) - http://www.rcsb.org/pdb/home/home.do