DISCIPLINE SPECIFIC CORE COURSE-18 (DSC-18): Photochemistry and Spectroscopy

CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Course title & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Photochemistry and Spectroscopy (DSC-18, Physical Chemistry VI)	**04**	**02**	**-**	**02**	**Class XII with Physics, Chemistry and Mathematics**	

Learning Objectives:

The Learning Objectives of this course are as follows:

- To make students understand the laws of photochemistry and their applications
- To understand the basis of molecular spectroscopy
- To study different types of spectroscopic techniques and their applications

Learning Outcomes:

By studying this course, students will be able to:

- Explain low and high quantum yield
- Explain photosensitized reactions
- Apply the concept of quantization to spectroscopy.
- Interpret various types of spectra and know about their application in structure elucidation

SYLLABUS OF DSC-18

Unit-1: Introduction to Molecular Spectroscopy and Photochemistry (Hours: 6)

Interaction of electromagnetic radiation with molecules and various types of spectra; Born Oppenheimer approximation.

Characteristics of electromagnetic radiation. Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitized reactions, quenching. Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence.

Unit-2: Rotational, Vibrational , Raman and Electronic Spectroscopy (Hours: 14)

Rotational spectroscopy: Selection rules, intensities of spectral lines, determination of bond lengths of diatomic molecules, isotopic substitution, classification of molecules based on moment of inertia, applications of rotation spectroscopy (e.g. microwave appliances)

Vibrational spectroscopy: Classical equation of vibration, computation of force constant, amplitude of diatomic molecular vibrations, anharmonicity, Morse potential, dissociation energies, fundamental frequencies, overtones, hot bands, degrees of freedom for polyatomic molecules, modes of vibration, concept of group frequencies.

Vibration-rotation spectroscopy: diatomic vibrating rotator, P, Q, R branches.

Raman spectroscopy: Qualitative treatment of Rotational Raman effect; effect of nuclear spin, Vibrational Raman spectra, Stokes and anti-Stokes lines; their intensity difference, rule of mutual exclusion.

Electronic spectroscopy

Franck-Condon principle, electronic transitions, singlet and triplet states, Jablonski diagrams, fluorescence and phosphorescence, dissociation and predissociation, calculation of electronic transitions of polyenes using free electron model.

Unit-3: NMR and ESR (Hours: 10)

Nuclear Magnetic Resonance (NMR) spectroscopy: Principles of NMR spectroscopy, Larmor precession, chemical shift and low-resolution spectra, different scales (δ and T), spin-spin coupling and high resolution spectra, interpretation of PMR spectra of simple organic molecules like methanol, ethanol and acetaldehyde.

Principles of ESR spectroscopy, hyperfine structures, ESR of simple radicals

Practical component

Practical: Credits: 02

(Laboratory periods: 15 classes of 4 hours each)

(A) Colorimetry :

1. Verify Lambert-Beer's law and determine the concentration of (i) $CuSO_4$ (ii) $KMnO_4$ (iii) $K_2Cr_2O_7$ in a solution of unknown concentration

2. Determine the concentrations of $KMnO_4$ and $K_2Cr_2O_7$in a mixture.
3. Study the kinetics of iodination of propanone in acidic medium.
4. Determine the amount of iron present in a sample using 1,10-phenathroline.
5. Determine the dissociation constant of an indicator (phenolphthalein).
6. Study the kinetics of interaction of crystal violet/ phenolphthalein with sodium hydroxide

(B) UV/Visible spectroscopy:

1. Study the 200-500 nm absorbance spectra of $KMnO_4$ and $K_2Cr_2O_7$ (in 0.1 M H_2SO_4) and determine the λ_{max} values. Calculate the energies of the two transitions in different units (J molecule^{-1}, kJ mol^{-1}, cm^{-1}, eV).
2. Study the pH-dependence of the UV-Vis spectrum (200-500 nm) of $K_2Cr_2O_7$.
3. Record the 200-350 nm UV spectra of the given compounds (acetone, acetaldehyde, 2- propanol, acetic acid) in water. Comment on the effect of structure on the UV spectra of organic compounds.

(C) Analysis of the given vibration-rotation spectrum of HCl(g)

Essential/recommended readings

Theory:

1. Banwell, C.N.; McCash, E.M. (2006), **Fundamentals of Molecular Spectroscopy**, Tata McGraw- Hill.
2. Kapoor, K.L. (2015), **A Textbook of Physical Chemistry**, McGraw Hill Education, Vol 4, 5th Edition, McGraw Hill Education.
3. Kakkar, R. (2015), **Atomic & Molecular Spectroscopy**, Cambridge University Press.

Suggested Readings:

1. Engel, T.; Reid, P. (2013), **Quantum Chemistry and Spectroscopy**, Pearson

Practical:

1. Khosla, B.D.; Garg, V.C.; Gulati, A. (2015), **Senior Practical Physical Chemistry**, R. Chand & Co, New Delhi.
2. Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. (2003), **Experiments in Physical Chemistry**, 8th Edition, McGraw-Hill, New York
3. Kapoor, K.L. (2019), **A Textbook of Physical Chemistry**, Vol.7, 1st Edition, McGraw Hill Education.

Note: Examination scheme and mode shall be as prescribed by the Examination Branch, University of Delhi, from time to time.