DISCIPLINE-SPECIFIC ELECTIVE COURSE - 18 (DSE-18)

Advanced Molecular Spectroscopy and Applications

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		
Advanced Molecular Spectroscopy and Applications (DSE-18)	**04**	**02**	**--**	**02**	—	**--**

Learning Objectives:

- Introduce the principles of molecular spectroscopy across electronic, vibrational, rotational, and nuclear domains.
- Apply quantum mechanical concepts such as the Born–Oppenheimer approximation, Heisenberg's Uncertainty Principle, and time-dependent perturbation theory to spectroscopic transitions.
- Use symmetry and operator-based formalisms to derive selection rules.
- Analyze UV-Vis, fluorescence, Raman, Mössbauer, and CD spectroscopy.
- Explore applications in structure elucidation, dynamics, and single-molecule detection.

Learning outcomes

By the end of the course, students will be able to:

- Understand the principles of electromagnetic radiation and molecular transitions.
- Interpret selection rules using quantum and symmetry considerations.
- Analyze vibrational fine structure and electronic transitions using the Franck–Condon principle.
- Describe the principles and applications of fluorescence, phosphorescence, and circular dichroism.
- Apply advanced tools such as Mössbauer spectroscopy, and single-molecule spectroscopy.

SYLLABUS OF DSE 18

Unit 1: Fundamentals & Quantum Background (Hours: 6)

Electromagnetic radiation and spectral regions. Born–Oppenheimer approximation and Uncertainty Principle. Time-dependent perturbation theory (TDPT) and transition moments. Einstein coefficients and derivation of Beer–Lambert law. Selection rules (qualitative) using symmetry and operator formalism.

Unit 2: Electronic Spectroscopy & Photophysical Processes in Molecules (14: Hours)

Electronic transitions in diatomic molecules (π–π*, n–π*, n–σ*, etc.). Selection rules (qualitative). Breakdown of selection rules. Franck–Condon principle and vibrational fine structure. P, Q, R branches in rovibrational spectra. Dissociation energies (e.g. iodine spectrum).

Polyatomic molecules: Chromophores and auxochromes: structure–property relationships. Solvent effects: polarity, hydrogen bonding and solvent shifts, vibronic coupling, Charge transfer (CT) transitions and their spectral features. Qualitative interpretation of UV-Vis spectra of polyatomic organics (e.g. ethene, formaldehyde, cis- and trans-butadiene) using symmetry principles.

Unit 3: Mössbauer Spectroscopy (Hours: 4)

Jablonski diagram, Fluorescence and phosphorescence: mechanisms and applications. Deactivation pathways, internal conversion, intersystem crossing. Mirror-image symmetry and polarization effects in emission spectroscopy.

Mössbauer spectroscopy: Isomer shifts, quadrupole and Zeeman splitting. Applications to oxidation state and bonding.

Unit 4: Advanced Applications (Hours: 6)

Fluorescence quenching (static/dynamic) and lifetime measurements. Single molecule spectroscopy and fluorescence correlation spectroscopy (FCS). Circular Dichroism (CD): principle and biological examples. Mirror-image symmetry and its breakdown. Selection rules and polarization effects.

Forward look: qualitative overview of emerging methods (e.g. AI-assisted spectra interpretation)-non-evaluative.

Practical Component

<u>Laboratory Exercises (Practical) (atleast 10)</u>:

1. Analyse UV-Vis absorption spectra of conjugated systems (e.g., β-carotene) and determine the HOMO-LUMO gap.
2. Use UV-Vis spectra of a pH-sensitive dye (e.g., phenolphthalein) to determine its pK_a.
3. Study the effect of structure on the UV spectra of organic compounds.
4. Study the spectra of mesityl oxide/benzophenone in different solvents and classify the observed transitions in terms of n→π* and π→π* transitions. Discuss the shift in transitions relative to those in acetone.
5. Find the stoichiometry of the charge transfer (CT) complex formed between thiocyanate ions and iron (III) by Job's method of continuous variation.
6. (a) Record the UV spectra of a weak acid (α-naphthol) at different pH and determine the dissociation constant in the ground state.

   (b) Record the fluorescence spectra of a weak acid (α-naphthol) at different pH and determine the dissociation constant in the excited state.

   Comment on the difference in the two values using MO theory.

Instruction Mode: Demonstration/Discussion of working principle/Hands-on with substantial literature analysis/Laboratory exercise

7. Record and compare IR spectra of alcohols in pure form and diluted in non-polar solvents to understand the effect of hydrogen bonding on O-H stretching frequency.
8. Create calibration curve and use it to determine the concentration of a fluorophore (quinine, riboflavin) in unknown samples.
9. Study UV-Vis spectra of d^0 transition metal complexes (e.g., Ti^{3+}) and assign electronic transitions using computational or experimental techniques.
10. Measure absorbance vs. time data to study the kinetics of fast photochemical reactions (using Time-Resolved Absorption Spectroscopy for Reaction Kinetics).
11. Resolve and assign vibrational fine structure in the UV-Vis spectrum of iodine vapour.
12. UV spectra comparison of substituted benzenes (π–π* vs n–π*)
13. Fluorescence quenching and lifetime (model system, Rhodamine or naphthol)
14. CD analysis of protein model (experimental or literature spectra)

15. Simulation and analysis of Franck–Condon transitions using potential energy diagrams for diatomic molecules.

16. Interpret Mössbauer isomer shift and quadrupole splitting data from literature spectra of iron complexes.

Recommended References and Text Books: (For Theory)

1. J. Michael Hollas, Modern Spectroscopy, 4th Ed.

2. Rita Kakkar, Atomic and Molecular Spectroscopy, Cambridge University Press
3. C. N. Banwell & E. M. McCash, Fundamentals of Molecular Spectroscopy
4. Satyanarayana, D. N., Handbook of Molecular Spectroscopy, I.K. International
5. P. Atkins & R. Friedman, Molecular Quantum Mechanics
6. Jeanne L. McHale, *Molecular Spectroscopy*
7. **J. Chem. Rev. 2021, 121, 9816–9872 –** *ML + Computational Chemistry*

Recommended References and Text Books: (For Practical's)

1. Rita Kakkar, Atomic and Molecular Spectroscopy, Cambridge University Press.
2. B. D. Khosla, V. C. Garg, A. Gulati, Senior Practical Physical Chemistry, R. Chand & Co., New Delhi.
3. Donald A. McQuarrie & John D. Simon, Physical Chemistry: A Molecular Approach.
4. J. Michael Hollas, Modern Spectroscopy.
5. Douglas A. Skoog, F. James Holler, Stanley R. Crouch, Principles of Instrumental Analysis.
6. Jeanne L. McHale, Molecular Spectroscopy.