DISCIPLINE SPECIFIC ELECTIVE COURSE – 17 (DSE-17): Molecular Spectroscopy and Structural Analysis

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		
Molecular Spectroscopy and Structural Analysis **(DSE-17)**	**04**	**02**	**--**	**02**	**Class 12th with Physics, Chemistry**	**--**

Course Objectives

The objectives of this course are as follows:

- To introduce the fundamental principles of spectroscopy, including the characterization of electromagnetic radiation and the Born-Oppenheimer approximation.
- To explore transition dipole moments and selection rules, with emphasis on symmetry ideas and time-dependent perturbation in spectroscopic processes.
- To analyze the principles and instrumentation of Raman spectroscopy and understand vibrational and rotational Raman spectra.
- To study the spectroscopic techniques for structural analysis i.e. AFM, SEM, and TEM.

Learning outcomes

By studying this course, the students will be able to:

- Understand the principles of electromagnetic radiation and fundamental spectroscopic concepts, including the Born-Oppenheimer approximation and time-dependent perturbation.
- Analyze Raman spectroscopy and deduce the structure of molecules using vibrational and rotational Raman spectra.
- Describe the Atomic spectra, the spin and orbital selection rules, spectra of complex atoms and basic principles of atomic photoelectron spectroscopy.
- Exhibit their understanding of theoretical basis of rotational, vibrational, raman and NMR spectroscopy.
- Have an insight into spectroscopic techniques for Structural Analysis i.e. SEM, TEM and AFM.

Unit 1: Basic Concepts of Spectroscopy and Atomic Spectra (8 Hours)

Spectroscopy and its importance in chemistry. Heisenberg Uncertainty Principal; Link between spectroscopy and quantum chemistry. Types of spectroscopy. Time dependent perturbation. Einstein coefficients. Integrated absorption coefficients. Transition dipole moments and general selection rules based on symmetry considerations.

Characterization of atomic states. Microstate and spin factoring methods. Hund's rules. Derivation of spin and orbital selection rules (based on recursion relations of Legendre polynomials. Spectra of complex atoms. Zeeman and Stark effects, Atomic photoelectron spectroscopy (Qualitative Discussion only).

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

Rotational spectroscopy Determination of bond lengths and atomic mass. Effect of isotopic substitution. Non-rigid rotator. Classification of polyatomic molecules. Energy levels and spectra of symmetric top molecules and asymmetric top molecules.

Normal coordinate analysis of homonuclear and heteronuclear diatomicmolecules. Anharmonic oscillator; Morse potential. Overtones and hot-bands. Dissociation energies from vibrational data. Vibration-rotation spectra, P, Q and R branches. Breakdown of the Born-Oppenheimer approximation. Nuclear spin effect. Symmetry of normal coordinates.

Stokes and anti-Stokes lines. Polarizability ellipsoids. Rotational and vibrational Raman spectroscopy. Selection rules. Rule of Mutual Exclusion. Polarization of Raman lines.

Unit 3: NMR spectroscopy: (5 Hours)

Larmor precession. Mechanisms of spin-spin and spin-lattice relaxations and quantitative treatment of relaxation. Quantum mechanical treatment of the AB system. Selection rules and relative intensities of lines.

Unit 4: **Microscopic Techniques for Structural Analysis (3 Hours)**

Elementary idea of Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), and Atomic Force Microscope (AFM) for structural analysis.

Practicals: Credits: 02
(Laboratory periods:15 classes of 4 hours each)

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

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

6. 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.
7. Perform IR and Raman spectroscopy on symmetrical molecules (e.g., CS_2, CO_2) and analyze the mutual exclusion principle.

8. Calculate the force constant (k) of diatomic molecules (e.g., HCl, N_2) from IR spectra.
9. Create a calibration curve and use it to determine the concentration of a fluorophore in unknown samples.
10. Simulate and analyze rotational spectra of rigid rotor molecules.
11. Measure absorbance vs. time data to study the kinetics of fast photochemical reactions (using Time-Resolved Absorption Spectroscopy for Reaction Kinetics).
12. Resolve and assign vibrational fine structure in the UV-Vis spectrum of iodine vapor.

Essential/recommended readings

Theory:

1. Hollas. J. M., *Modern Spectroscopy* 4th Ed., John Wiley & Sons (2004).
2. Satyanarayana, D. N., *Handbook of Molecular Spectroscopy: From radio waves to gamma rays*, I.K. International Publishing House, New Delhi (2015).
3. Kakkar, R., *Atomic & Molecular Spectroscopy,* Cambridge University Press (2015).
4. Brand, J. C. D. & Speakman, J. C. *Molecular Structure: The Physical Approach* 2nd Ed., Edward Arnold: London (1975).
5. Chang, R. *Basic Principles of Spectroscopy* McGraw-Hill, New York, N.Y. (1970).
6. Moore, W. J. *Physical Chemistry* 4th Ed. Prentice-Hall (1972).
7. Kapoor, K.L. (2015), A Textbook of Physical Chemistry, Vol 1, 1st Edition, Mc Graw Hill Education.

Practical:

1. B. D. Khosla, V. C. Garg, A. Gulati, Senior Practical Physical Chemistry, R. Chand & Co, New Delhi.
2. C. N. Banwell, E. M. McCash, Fundamentals of Molecular Spectroscopy.
3. A. Findlay, B.P. Levitt, J.A. Kitchener, Experimental Physical Chemistry.
4. Donald A. McQuarrie and John D. Simon, Physical Chemistry: A Molecular Approach.
5. J. Michael Hollas, Modern Spectroscopy.
6. Douglas A. Skoog, F. James Holler, Stanley R. Crouch, Principles of Instrumental Analysis.
7. Jeanne L. McHale, Molecular Spectroscopy.
8. Donald L. Pavia, Gary M. Lampman, George S. Kriz, Introduction to Spectroscopy.
9. Gurdeep R. Chatwal and Sham K. Anand, Spectroscopy: Atomic and Molecular.
10. Peter Atkins and Ronald Friedman, Molecular Quantum Mechanics.

Assessment Methods: All examination and assessments methods shall be in line with the University of Delhi guidelines issued from time to time.