

Spectroscopic Techniques

Spectroscopic Techniques – Quick Reference Notes

1. What Is Spectroscopy?

- **Definition:** Study of the interaction between electromagnetic radiation (light) and matter.
 - **Goal:** Obtain information about the composition, structure, dynamics, and environment of a sample.
 - **Key Concept:** Each molecule/atom has characteristic energy levels; transitions between them absorb or emit photons of specific wavelengths.
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2. Classification of Spectroscopic Methods

Domain	Technique	Typical Wavelength Range	Primary Information
Electronic	UV-Vis Absorption, Fluorescence, Phosphorescence	200 nm – 800 nm	Electronic transitions, conjugation, band gaps
Vibrational	Infrared (IR), Raman, FT-IR, Near-IR	2.5 μm – 25 μm (IR), 0.78 μm – 2 μm (NIR)	Bond types, functional groups, molecular symmetry
Rotational	Microwave, Millimeter-wave	0.3 mm – 10 mm	Gas-phase molecular geometry, bond lengths
Nuclear	Nuclear Magnetic Resonance (NMR)	Radiofrequency (10 MHz – 1 GHz)	Chemical environment of nuclei, connectivity
Mass-Based	Mass Spectrometry (MS) (often coupled with spectroscopy)	N/A (ion detection)	Molecular weight, fragmentation pattern, isotopic composition
Surface-Specific	X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES)	Soft X-ray (0.1–10 keV)	Elemental composition, oxidation states, surface chemistry
Time-Resolved	Pump-probe, Transient Absorption, Fluorescence Lifetime	Variable (depends on pump & probe)	Dynamics of excited states, reaction kinetics

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3. Core Principles

Phenomenon	Physical Basis	Observed Signal
Absorption	Photon energy matches a transition ? population moves to higher level	Decrease in transmitted intensity (Beer?Lambert law)
Emission	Excited species relax ? photon emitted	Fluorescence, phosphorescence, Raman scattering
Scattering	Incident photons interact with molecular polarizability	Raman shift (inelastic) or Rayleigh (elastic)
Resonance	Matching of photon energy with natural frequency of a system	Enhanced intensity (e.g., resonance Raman, ESR)
Relaxation	Non?radiative processes (vibrational cooling, intersystem crossing)	Affects line shape, quantum yield, lifetimes

4. Instrumentation Overview

4.1 Light Source

- **Continuum:** Deuterium (UV), Tungsten?halogen (Vis/NIR), Globar (IR).
- **Monochromatic:** Laser diodes, gas lasers, synchrotron radiation.

4.2 Monochromator / Spectrograph

- **Gratings** (diffraction) or **prisms** to disperse light.
- **Resolution** defined by slit width, groove density, detector pixel size.

4.3 Sample Interaction Region

- **Transmission cells** (quartz for UV?Vis, CaF? for IR).
- **ATR crystal** (IR) for surface?enhanced measurements.
- **Flow cells, cryostats, **pressure**