# Lecture 4 “Introduction to Molecular Spectroscopy Methods”

**Goal of the lecture:** To introduce the fundamental principles of molecular spectroscopy, explain how electromagnetic radiation interacts with matter, and describe the main types of spectroscopy used to study molecular structure, bonding, and dynamics.

**Brief lecture notes: Molecular spectroscopy** is the study of how molecules interact with electromagnetic radiation, such as light, to reveal information about their structure and composition. By analyzing how molecules absorb, emit, or reflect light, scientists can determine important molecular properties such as bond lengths, bond energies, and vibrational or rotational energy states. Each molecule produces a distinct interaction pattern with radiation, resulting in a unique spectral “fingerprint” that allows for its identification and characterization.

Molecular spectroscopy works through the interaction of molecules with electromagnetic radiation, causing transitions between specific, quantized energy levels. These energy levels can be **electronic**, **vibrational**, or **rotational**, depending on the type of radiation involved. When molecules absorb or emit energy, they produce a **spectrum**, which is a plot showing the intensity of absorption or emission as a function of wavelength or frequency. The resulting arrangement of peaks and valleys in the spectrum serves as a **molecular fingerprint**, enabling scientists to identify and study different substances precisely.

There are several major types of molecular spectroscopy, each focusing on different energy transitions. **Microwave spectroscopy** studies pure rotational transitions and provides information about the geometry and bond lengths of molecules. **Infrared spectroscopy** examines both vibrational and rotational transitions, allowing for the identification of functional groups and detailed molecular structure. **Ultraviolet-visible (UV-Vis) spectroscopy** investigates electronic transitions in molecules, especially in conjugated systems and transition metal complexes. **Raman spectroscopy** uses light scattering to study vibrational modes and provides complementary information to infrared spectroscopy. In addition, **Nuclear Magnetic Resonance (NMR)** and **Electron Spin Resonance (ESR)** spectroscopy are based on the magnetic properties of atomic nuclei and electrons, offering valuable insights into molecular environments and electronic structures.

Molecular spectroscopy has a wide range of applications. It is used for **qualitative analysis**, identifying unknown compounds through their unique spectral patterns, and **quantitative analysis**, determining the concentration of specific substances. Moreover, it allows for the measurement of **molecular properties**, including bond lengths, bond energies, and other structural parameters. Because of its sensitivity and specificity, spectroscopy remains one of the most powerful and versatile tools in modern chemistry, physics, biology, and materials science.

## 1. Nature of Electromagnetic Radiation

An electromagnetic wave consists of two oscillating fields — an **electric field** (shown in red) and a **magnetic field** (shown in blue) — that are perpendicular to each other and to the direction in which the wave travels. The **electric field** oscillates in one plane, while the **magnetic field** oscillates in a plane at a 90° angle to it. Both fields move together through space as the wave propagates.

The **wavelength (λ)** is the distance between two consecutive peaks (or troughs) of the wave. It determines the energy and type of electromagnetic radiation. According to the relationship

$$c = \lambda\nu$$

where c is the speed of light, λ is the wavelength, and ν is the frequency.

The **frequency** (ν) is the number of wave cycles that pass a given point per second and is measured in hertz (Hz). The **energy (E)** of each photon in the wave is related to its frequency by Planck’s equation:

$$E = h\nu$$

where h = is Planck's constant ($6.626 \times 10^{-34}$ J·s).

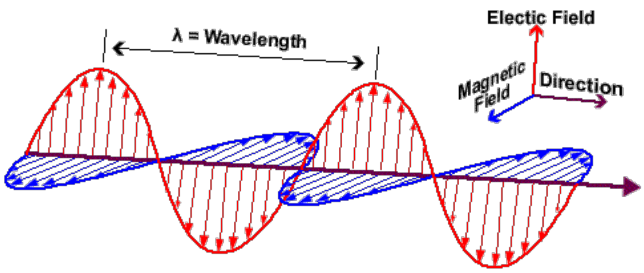


**Figure – 1. A diagram of an electromagnetic wave**

Radiation of different wavelengths interacts with matter in different ways, producing various types of spectra.

## 2. Types of Molecular Spectroscopy

Spectroscopic methods are classified according to the **region of the electromagnetic spectrum** and the **type of molecular transition** they cause.

### *2.1 Microwave Spectroscopy*

- Involves the absorption of low-energy microwaves.
- Causes **rotational transitions** in molecules.
- Provides information about **bond lengths** and **molecular geometry**.
- Example: Determining structure of HCl or CO molecules.

### *2.2 Infrared (IR) Spectroscopy*

- Involves absorption of infrared light.
- Causes **vibrational transitions** within molecules.
- Each chemical bond has a characteristic absorption frequency, making IR spectroscopy useful for identifying functional groups.
- Example: O–H stretching around 3400 $cm^{-1}$, C=O stretching near 1700 $cm^{-1}$.

### *2.3 Ultraviolet-Visible (UV-Vis) Spectroscopy*

- Involves electronic transitions between molecular orbitals.
- Used to study **electronic structure**, **conjugated systems**, and **transition metal complexes**.
- Absorption peaks correspond to transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$.
- Example: Absorption of benzene at 254 nm due to $\pi \rightarrow \pi^*$ transition.

### *2.4 Raman Spectroscopy*

- Based on **inelastic scattering** of monochromatic light (usually laser light).
- Provides information about **vibrational modes** similar to IR spectroscopy but follows different selection rules.
- Especially useful for studying **symmetric vibrations** and **aqueous samples**.

*2.5 Nuclear Magnetic Resonance (NMR) Spectroscopy*

- Involves the absorption of radiofrequency radiation by nuclei in a magnetic field.
- Provides detailed information about the **chemical environment of atoms**, **molecular connectivity**, and **dynamics**.
- Example: $^{1}H$ NMR and $^{13}C$ NMR are used to identify organic structures.

Advantages of Spectroscopic Methods

- **Non-destructive**: Samples can often be analyzed without damage.
- **High sensitivity**: Detects very small quantities of substances.
- **Specificity**: Each compound has a unique spectral pattern.
- **Versatility**: Applicable to gases, liquids, and solids.

**Table – 1. Regions of the electromagnetic spectrum and types of spectroscopy**

| **Spectral Region** | **Wavelength Range** | **Type of Transition** | **Spectroscopic Technique** |
|---|---|---|---|
| Microwave | 1 mm – 1 cm | Rotational | Rotational spectroscopy |
| Infrared | 2.5 – 50 μm | Vibrational | IR spectroscopy |
| Visible | 400 – 800 nm | Electronic | UV-Vis spectroscopy |
| Ultraviolet | 10 – 400 nm | Electronic | UV spectroscopy |
| X-ray | < 10 nm | Core electronic | X-ray spectroscopy |
| Radio | > 1 cm | Nuclear spin | NMR spectroscopy |

## Questions for self-control

1. What is the basic principle of spectroscopy?
2. What type of molecular transitions occur in microwave and IR spectroscopy?
3. Explain the difference between absorption and emission spectra.
4. How does UV-Vis spectroscopy differ from Raman spectroscopy?
5. What information can be obtained from NMR spectra?

## Literature:


1. Atkins, P., de Paula, J. *Atkins' Physical Chemistry*, 11th Edition, Oxford University Press, 2018.
2. Moran, M.J. *Fundamentals of Engineering Thermodynamics*, 9th Edition, Wiley, p.156.
3. House, J.E. *Fundamentals of Quantum Chemistry*, 2nd Edition, Academic Press, 2004.
4. Hammes-Schiffer, S. et al. *Physical Chemistry for the Biological Sciences*, University Science Books, 2009.
5. Zhdanov, V.P. *Elementary Physicochemical Processes on Solid Surfaces*, Springer, 1991.