1.3: Different types of Spectroscopy

There are many different types of spectroscopy, each tailored to a specific type of analysis, interaction of light with matter, and the information it provides. Here's a summary of some of the most common and widely used types of spectroscopy: Different types of spectroscopy focus on the absorption, emission, or scattering of light by molecules or atoms. Here's a summary of the three major types:

- **Absorption/Transmission Spectroscopy** measures light absorbed by the sample to identify and quantify substances.
- **Emission Spectroscopy** measures light emitted by excited atoms or molecules as they return to lower energy states.
- **Scattering Spectroscopy** measures the redirected light when it interacts with particles or molecules, providing information about molecular vibrations or particle size.

Each type of spectroscopy has its own advantages and applications, depending on the nature of the sample and the information required.

Absorption/Transmission Spectroscopies

Absorption spectroscopy involves the measurement of the amount of light absorbed by a sample as a function of its wavelength or frequency. When light passes through a substance, certain wavelengths of light are absorbed by the sample, causing transitions in the energy levels of atoms or molecules. The intensity of absorption is related to the concentration of the absorbing species in the sample.

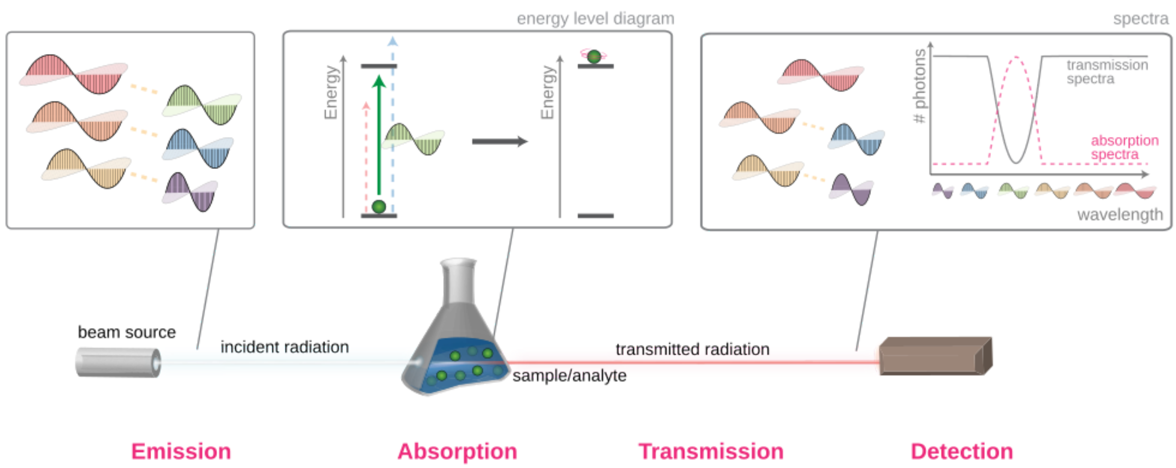


Figure 1.3.1: An overview of electromagnetic radiation absorption. This example discusses the general principle using visible light. A white beam source – emitting light of multiple wavelengths – is focused on a sample (the complementary color pairs are indicated by the yellow dotted lines). Upon striking the sample, photons that match the energy gap of the molecules present (green light in this example) are absorbed in order to excite the molecule. Other photons transmit unaffected and, if the radiation is in the visible region (400–700 nm), the sample color is the complementary color of the absorbed light. By comparing the attenuation of the transmitted light with the incident, an absorption spectrum can be obtained. (CC BY-SA 3.0; Jon Chui via Wikipedia)

The absorption of light at a given λ, can be used to measure concentration in solution. Electronic absorption spectra of solutes in liquid solution are generally broadened due to several factors including inhomogeneities in the local environment that do not average out – fluctuations that are too slow.

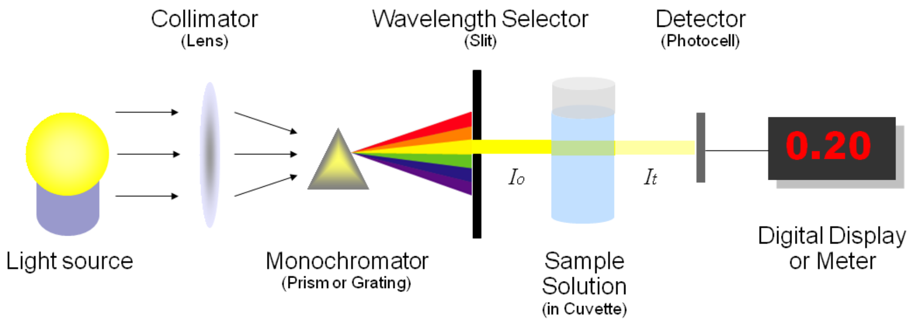


Figure 1.3.1: Basic structure of spectrophotometers (CC BY-4.0; Heesung Shim via LibreTexts)

Timescales

The characteristic timescale for the electronic transition is ~1 fs, while several fluctuations in the solvent are much slower ~ps. These local fluctuations of the solvent results in a “static inhomogeneity” of the absorption band. Thus rotational structure is not revealed and vibrational structure partially so (if at all) and are referred to as bands in the absorption.

The amount of photons that goes through the cuvette and into the detector is dependent on the length of the cuvette and the concentration of the sample. Once you know the intensity of light after it passes through the cuvette, you can relate it to **transmittance** (T) (Figure 1.3.2). Transmittance is the fraction of light that passes through the sample. This can be calculated using the equation:

$$\text{Transmittance}(T) = \frac{I_t}{I_o}$$

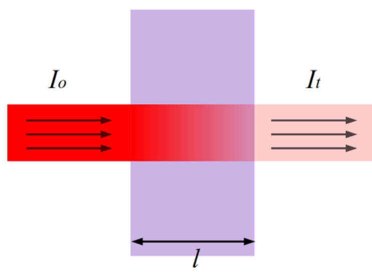


Figure 1.3.2: Transmittance (CC BY-4.0; Heesung Shim via LibreTexts)

Key Types of Absorption Spectroscopies

Ultraviolet-Visible (UV-Vis) Spectroscopy

- **Principle**: Measures the absorption of ultraviolet and visible light (200–800 nm) by a sample. Molecules absorb light at specific wavelengths corresponding to electronic transitions.
- **Applications**: Used to determine concentrations of organic compounds, metals, and transition metal complexes. It's also widely used in chemical and biochemical analysis.
- **Example**: Determining the concentration of a compound in solution by measuring the absorption of UV or visible light.

Infrared (IR) Spectroscopy

- **Principle**: Measures the absorption of infrared light (typically in the 4000–400 cm^{-1} range) by a sample, which causes molecular vibrations (stretching, bending, etc.).
- **Applications**: Identifies functional groups in organic molecules and characterizes chemical bonds. It’s commonly used in organic chemistry, environmental monitoring, and material science.
- **Example**: Identifying functional groups like -OH (hydroxyl), -NH (amine), and C=O (carbonyl) in organic compounds.

X-ray Absorption Spectroscopy (XAS)

- **Principle**: Measures the absorption of X-rays by a sample, which excites inner electrons, providing information about the local structure and electronic environment of specific elements.
- **Applications**: Used for the analysis of materials, especially in materials science, chemistry, and catalysis. It provides insights into coordination, oxidation state, and electronic structure.
- **Example**: Characterizing the local structure of metal ions in catalysts or materials.

Atomic Absorption Spectroscopy (AAS)

- **Principle**: Measures the absorption of light by free atoms in the gas phase, typically produced by a flame or graphite furnace. The absorption is characteristic of the element being analyzed.
- **Applications**: Commonly used to determine trace amounts of metals in samples, including environmental, pharmaceutical, and food analysis.
- **Example**: Measuring concentrations of metals such as lead, mercury, and calcium in water or soil samples.

Near-Infrared (NIR) Spectroscopy

- **Principle**: Measures the absorption of near-infrared light (1000–2500 nm), which interacts with overtones and combinations of molecular vibrations, especially in organic compounds.
- **Applications**: Used in agricultural, pharmaceutical, and food industries for non-destructive analysis, including moisture content, fat, and protein levels.
- **Example**: Determining moisture content in grains or pharmaceutical formulations.

✔ Example 1.3.1: UV-Visible Spectroscopy

Many transition metal ions, such as Cu^{2+} and Co^{2+}, form colorful solutions because the metal ion absorbs visible light. The transitions that give rise to this absorption are valence electrons in the metal ion's *d*-orbitals.

Figure 1.3.1: Transition Metal Rainbow (Copyright; tgent_007 via Reddit)

For a free metal ion, the five *d*-orbitals are of equal energy. In the presence of a complexing ligand or solvent molecule, however, the *d*-orbitals split into two or more groups that differ in energy. For example, in an octahedral complex of $\mathrm{Cu(H_2O)_6^{2+}}$ the six water molecules perturb the *d*-orbitals into the two groups shown in Figure 1.3.3 . The resulting $d \rightarrow d$ transitions for transition metal ions are relatively weak.

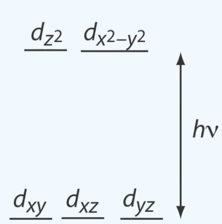


Figure 1.3.3 . Splitting of the *d*-orbitals in an octahedral field.

Emission Spectroscopies

Emission spectroscopy is based on the principle that atoms or molecules emit light (photons) when they transition from a higher energy state to a lower energy state. This emission occurs after the sample is excited by an external energy source (e.g., heat, light, or electrical energy). The emitted light is typically analyzed to determine the composition and concentration of the elements or compounds in the sample.

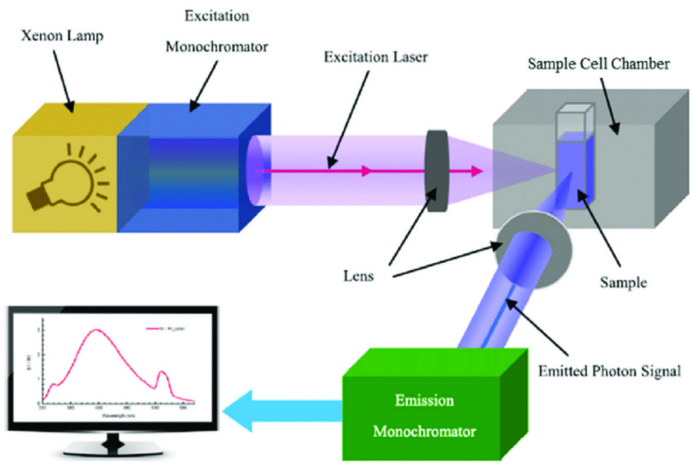


Figure 1.3.2: Schematic diagram of the arrangement of optical components in a typical fluorometer. (CC BY-SA 3.0 Unported; Changzheng Li and Yanan Yue via Wikipedia)

Key Types of Emission Spectroscopies

Fluorescence Spectroscopy

- **Principle**: Molecules absorb light (usually in the ultraviolet or visible range) and then emit light at a longer wavelength (lower energy) as they return to a lower energy state.
- **Applications**: Used for detecting and quantifying trace amounts of compounds, especially in biological, environmental, and chemical studies. It's highly sensitive and selective.
- **Example**: Detecting pollutants, biomarkers, or DNA sequences in medical diagnostics.

Atomic Emission Spectroscopy (AES)

- **Principle**: Atoms in a sample are excited (often by a flame, plasma, or electric arc) and then emit light at characteristic wavelengths as they relax to their ground state.
- **Applications**: Used to analyze the elemental composition of a sample, particularly in environmental, industrial, and pharmaceutical analysis.
- **Example**: Measuring the concentration of metals like sodium, potassium, and calcium in samples.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

- **Principle**: A sample is introduced into a plasma (a high-temperature ionized gas), which excites the atoms. The emitted light is analyzed to determine the sample's composition.
- **Applications**: Provides sensitive and multi-element analysis, commonly used in environmental testing, food safety, and materials analysis.
- **Example**: Detecting trace elements in water, soil, and food products.

Flame Emission Spectroscopy (FES)

- **Principle**: A sample is introduced into a flame, where it is atomized and excited. The emitted light is analyzed, which is characteristic of the elements in the sample.
- **Applications**: Primarily used for the determination of metal ions in aqueous solutions.
- **Example**: Testing for sodium or potassium levels in blood or urine.

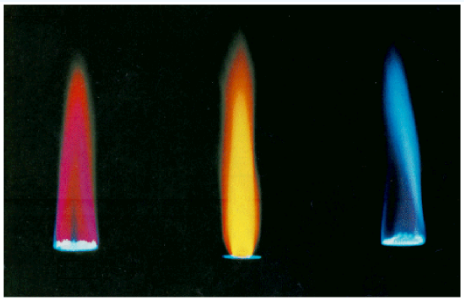
X-ray Emission Spectroscopy

- **Principle**: X-rays interact with a sample, causing inner shell electrons to be ejected. The atoms then release energy as X-ray fluorescence, which is measured.

- **Applications**: Used for elemental analysis, particularly in materials science and geology.
- **Example**: Identifying and quantifying elements in rocks, minerals, and metals.

Example 1.3.2: Flame Emission Spectroscopy (FES)

A common technique used for detecting metals in a sample by measuring the emitted light when a sample is heated in a flame. The emitted light has a characteristic wavelength corresponding to the energy difference between the excited and ground states of atoms or molecules.



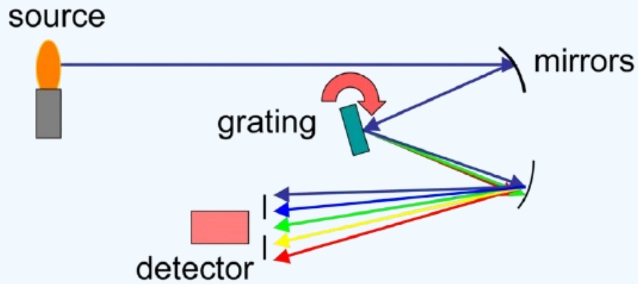


Figure 1.3.3: Many elements will still produce distinctive colors under such conditions, simple flame tests can be used to identify these elements. In fact, flame tests were used to identify elements long before the invention of modern techniques, such as emission spectroscopy. (left) flames from specific elements in a bunsen burner. (right) Schematic of a flame emission spectrometer. (CC BY-SA 3.0 Unported; Kkmurray via Wikipedia)

Scattering Spectroscopies

Scattering spectroscopy involves the scattering of light by molecules or particles in the sample. Unlike absorption, where light is absorbed by the sample, scattering occurs when light interacts with the sample and is redirected in different directions. The intensity and pattern of scattered light can provide information about the size, shape, and properties of particles, as well as the molecular structure of the sample.

Key Types of Scattering Spectroscopies

Raman Spectroscopy

- **Principle**: Measures the inelastic scattering of light (Raman scattering) when photons interact with molecular vibrations. The scattered light is shifted in frequency, providing information about molecular structure and bonding.
- **Applications**: Used to study molecular vibrations, chemical structure, and functional groups. It is widely used in material science, chemistry, and biological research.
- **Example**: Identifying chemical bonds, functional groups, and molecular structures in organic compounds.

Rayleigh Scattering

- **Principle**: Involves the elastic scattering of light by molecules or particles that are much smaller than the wavelength of the incident light. The scattered light has the same frequency as the incident light.
- **Applications**: Often used to study the size, shape, and concentration of small particles (e.g., in aerosols, colloids, and nanomaterials).
- **Example**: Determining particle size distribution in suspensions or colloidal systems.

Dynamic Light Scattering (DLS)

- **Principle**: A technique that measures fluctuations in the intensity of scattered light as particles move in a liquid. This can be used to determine the size and distribution of particles in solution.
- **Applications**: Primarily used for characterizing nanoparticles, colloids, and biomolecules in suspension.
- **Example**: Measuring the size of nanoparticles, proteins, or polymers in solution.

Neutron Scattering

- **Principle**: Uses neutrons instead of light to scatter off a sample. Neutron scattering provides information about atomic and molecular structures, especially for materials with lighter elements like hydrogen.

- **Applications**: Used in materials science, biology, and chemistry to study structures at the atomic and molecular level, including soft matter and complex materials.
- **Example**: Studying the structure of proteins, polymers, and crystalline materials.

Compton Scattering

- **Principle**: Involves the inelastic scattering of X-rays or gamma rays by electrons. The change in energy and direction of the scattered photons provides information about the electron density and the material's properties.
- **Applications**: Primarily used in physics and materials science to study the electronic structure and density of materials.
- **Example**: Investigating the electronic properties of metals and semiconductors.

Example 1.3.3: Raman Spectroscopy

In Raman scattering, most of the light is scattered at the same frequency (Rayleigh scattering), but a small portion of light is shifted to different frequencies (Stokes and Anti-Stokes scattering), providing insights into the sample's molecular vibrations. Measures the scattering of light when it interacts with vibrational modes of molecules. Raman spectroscopy provides information about molecular vibrations and can be used for structural analysis of compounds.

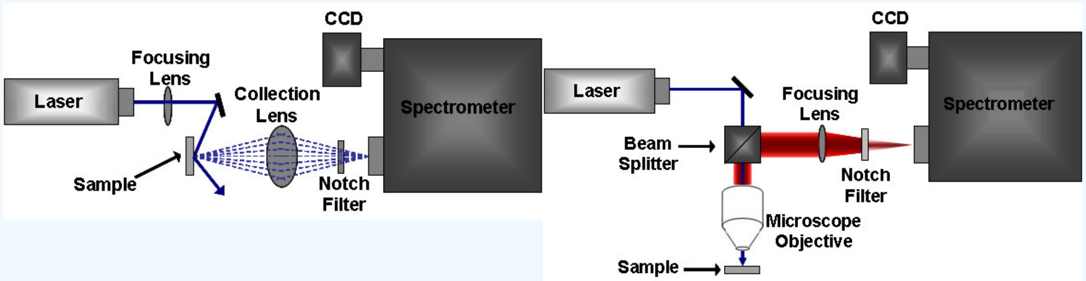


Figure 1.3.4: (left) Schematic of a macro-Raman spectrometer. (right) Schematic of a micro-Raman spectrometer where illumination and collection are performed through microscope objective. (CC BY 3.0; Pavan M. V. Raja & Andrew R. Barron via OpenStax CNX)
