# Chapter 3
# Various Spectroscopic Techniques

**Course Code: SSCP 4473**
**Course Name: Spectroscopy & Materials Analysis**

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# Essence of Spectroscopy

In spectroscopy, transitions between different energy levels within atoms and molecules are recorded and then used to give information on chemical structure as well as properties. Useful for various qualitative and quantitative analysis.

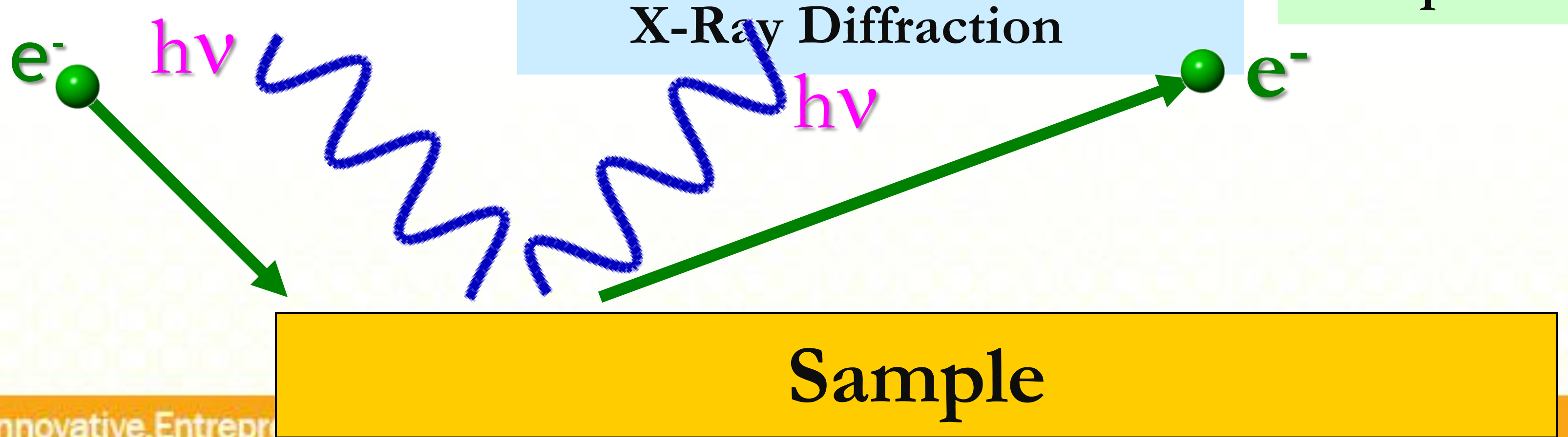
# Names: Based on Interaction Processes

## Probe: Photons

**Photons In**
- Infrared
- Visible
- Ultraviolet
- Radiofrequency
- X-Rays

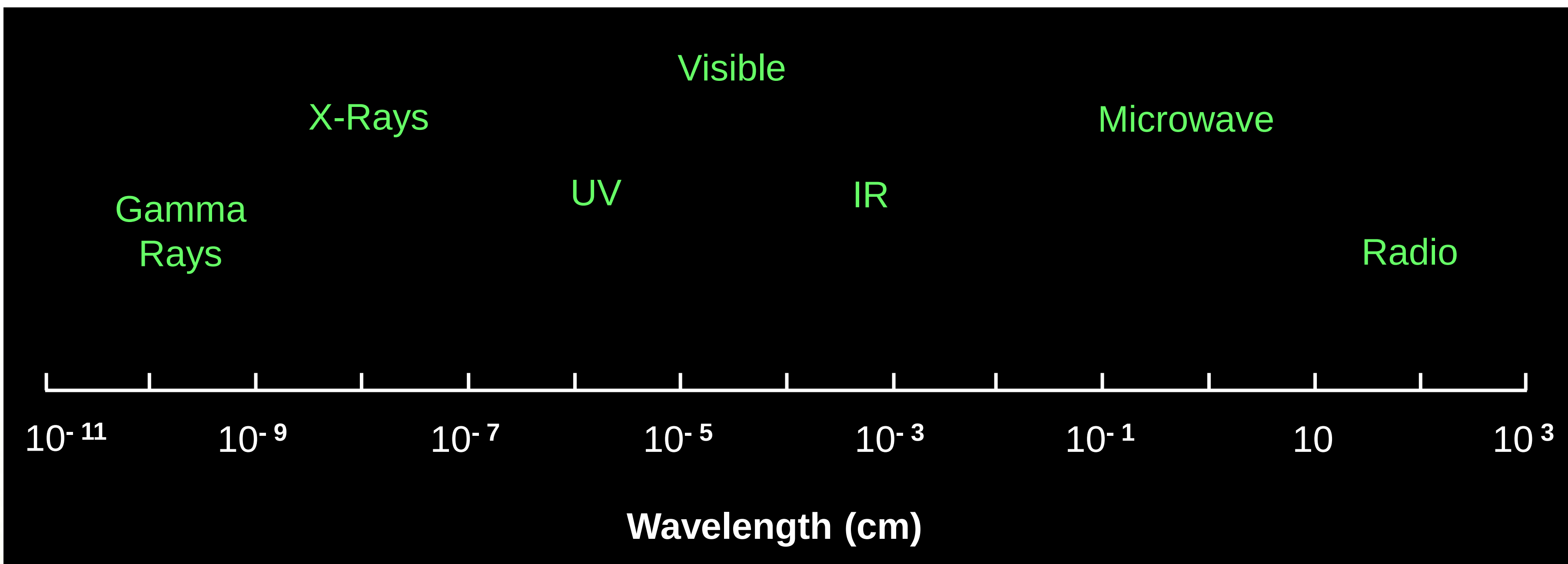
**Photons Out**
- Fourier Transform Infrared Spectroscopy
- Raman
- Visible
- Ultraviolet
- Radiofrequency
- X-Ray Fluorescence
- X-Ray Diffraction

**Electrons Out**
- XPS, X-ray Photoelectron Spectroscopy



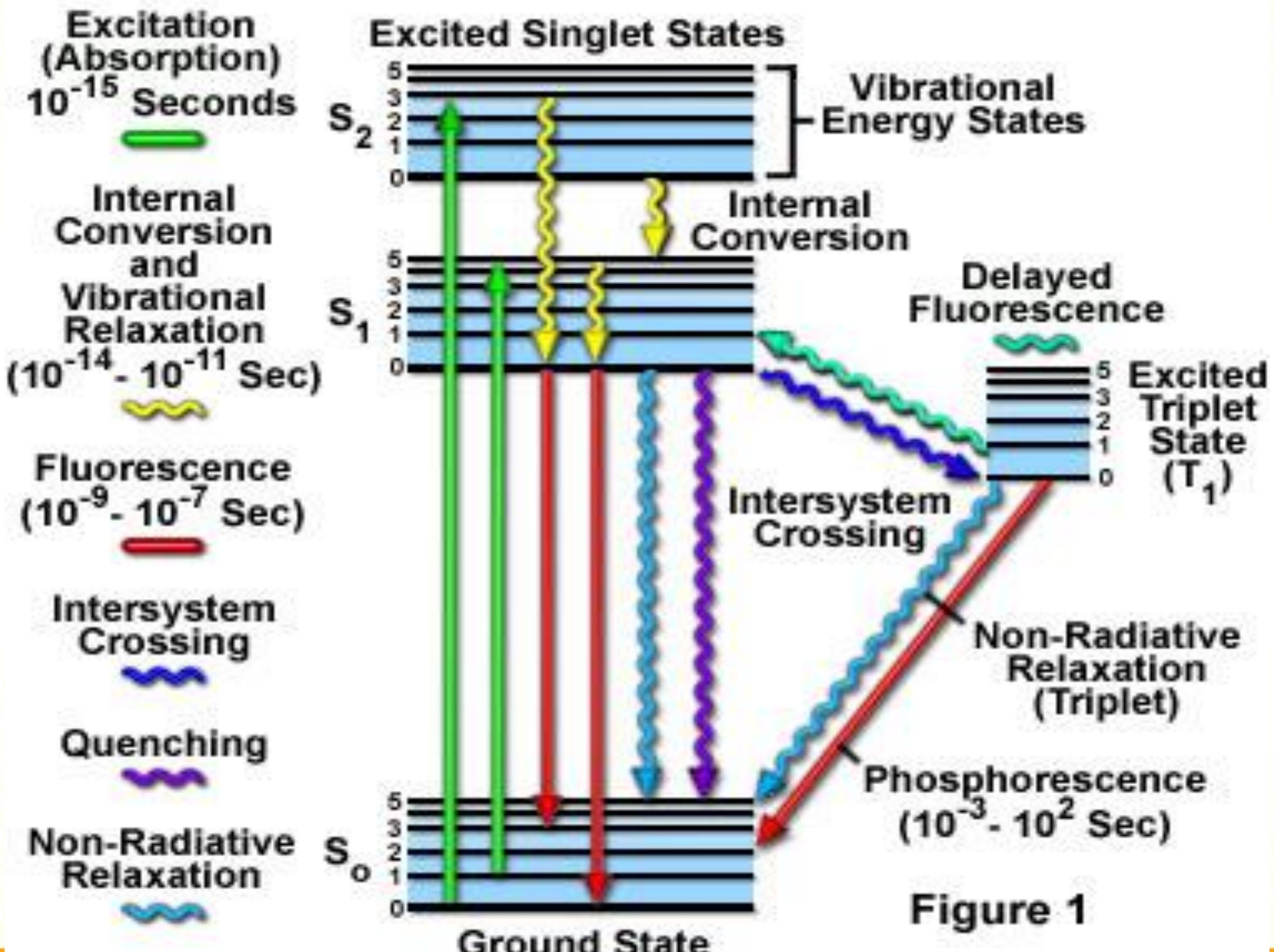
# EM Spectrum

- The range of energies that can be used for spectroscopy is very large and spans a large proportion of the electromagnetic spectrum.
- Electromagnetic radiation in different regions of spectrum can be used for qualitative and quantitative information
- Different types of chemical information
- The basic processes are absorption, emission and scattering



# Transitions: Length, Time, & Energy Scales

## Jablonski Energy Diagram



# Definitions

## Spectroscopy

The study of the interactions of electromagnetic radiation (radiant energy) and matter (molecules, atoms, or ions)

## Spectrometry

Quantitative measurement of the intensity of one or more wavelengths of radiant energy

## Spectrophotometry

The use of electromagnetic radiation to measure chemical concentrations (used for absorption measurements)

# Definitions

## Spectrophotometer

- Instrument used for absorption measurements

## Optical Spectrometer

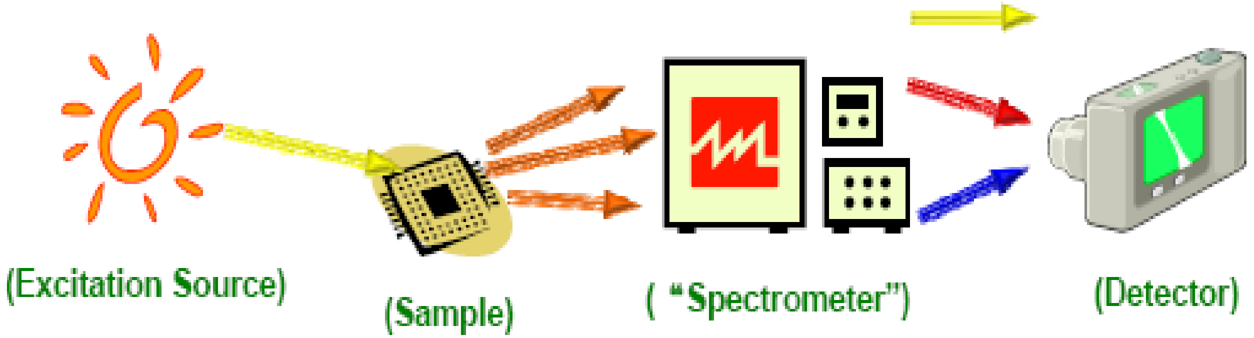
- Instrument that consists of prism or grating dispersion devise, slits, and a photoelectric detector

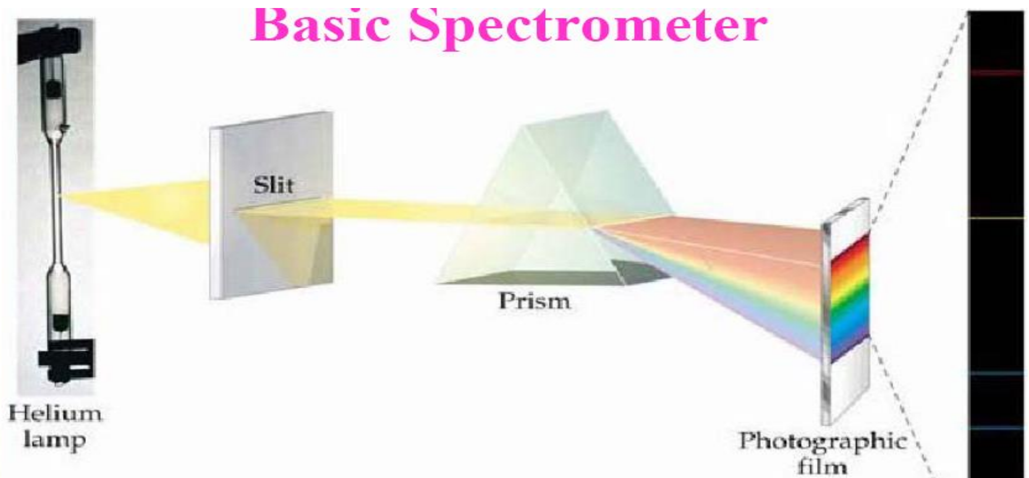
## Photometer

- Instrument that uses a filter for wavelength selection instead of a dispersion device

# What is Optical Spectroscopy?

## We need…




To have spectroscopy we need source, sample, wavelength (energy) analyser and detector

# Electromagnetic Radiation

- Light appears to behave as waves and also considered as stream of particles (the dual nature of light)

- Is sinusoidal in shape

- Light is quantized

Photons

- Particles of light

# Electromagnetic Radiation

$$\text{Energy of one photon}\,(E_{photon}) = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \text{wavenumber}\,(m^{-1})$$

h = Planck's constant (6.626 x $10^{-34}$ J-s)

$\nu$ = frequency of the radiation

$\lambda$ = wavelength of the radiation

E is proportional to v and inversely proportional to $\lambda$

# Interaction of EMR with Matter

- Takes place in many ways
- Takes place over a wide range of radiant energies
- Is not visible to the human eye
- Light is absorbed or emitted
- Follows well-ordered rules
- Can be measured with suitable instruments

# Spectroscopic Techniques & Structures They Probe

| | | |
|---|---|---|
| UV-Visible | UV-Vis region | bonding electrons |
| Atomic Absorption | UV-Vis region | atomic transitions (valence e-) |
| FT-IR | IR/Microwave | vibrations, rotations |
| Raman | IR/UV | vibrations |
| FT-NMR | Radio waves | nuclear spin states |
| X-Ray Spectroscopy | X-rays | inner electrons, elemental |
| X-ray Crystallography | X-rays | 3-D structure |

# Spectroscopic Techniques and Common Uses

| | | |
|---|---|---|
| UV-Vis | UV-Vis region | Quantitative analysis/Beer's Law |
| Atomic Absorption | UV-Vis region | Quantitative analysis Beer's Law |
| FT-IR | IR/Microwave | Functional Group Analysis |
| Raman | IR/UV | Functional Group Analysis/quant |
| FT-NMR | Radio waves | Structure determination |
| X-Ray Spectroscopy | X-rays | Elemental Analysis |
| X-ray Crystallography | X-rays | 3-D structure Analysis |

# Types of Spectroscopy

- ✓ Atomic absorption spectroscopy (AAS)
- ✓ Atomic emission spectroscopy (AES, OES)
- ✓ Atomic fluorescence spectroscopy (AFS)
- ✓ Electron spectroscopy
- ✓ Auger electron spectroscopy (AES)
- ✓ X-ray photoelectron spectroscopy (XPS)
- ✓ Vibrational spectroscopy
- ✓ Rotation-vibration spectroscopy
- ✓ Infrared (IR) absorption spectroscopy
- ✓ Raman spectroscopy
- ✓ Laser spectroscopy
- ✓ Doppler-limited spectroscopy
- ✓ Coherent anti-Stokes Raman spectroscopy (CARS)
- ✓ Cavity ring-down laser absorption spectroscopy (CRLAS)

# Types of Spectroscopy

- ✓ Intra-cavity absorption spectroscopy
- ✓ Resonance-ionization spectroscopy
- ✓ Molecular spectroscopy
- ✓ Near-infrared absorption spectroscopy (NIR)
- ✓ UV-Vis absorption spectroscopy (UV-Vis)
- ✓ Nuclear and electron resonance spectroscopy
- ✓ Electron paramagnetic resonance (EPR)
- ✓ Electron spin resonance (ESR)
- ✓ **Nuclear magnetic resonance (NMR) introduction**
- ✓ X-ray and gamma-ray spectroscopy
- ✓ Extended X-ray Absorption Fine Structure (EXAFS)
- ✓ X-ray fluorescence (XRF) spectroscopy
- ✓ Mossbauer spectroscopy
- ✓ Neutron activation analysis (NAA) spectroscopy

**Knowing their name is not important, what they do and how is significant!!**

# Interaction of EMR with Matter

Light striking a sample of matter may be

- Absorbed by the sample
- Transmitted through the sample
- Reflected off the surface of the sample
- Scattered by the sample

- Samples can also emit light after absorption (luminescence)

- Species (atoms, ions, or molecules) can exist in certain discrete states with specific energies

# Interaction of EMR with Matter

## Transmission

- Light passes through matter without interaction

## Absorption

- Matter absorbs light energy and moves to a higher energy state

## Emission

- Matter releases energy and moves to a lower energy state

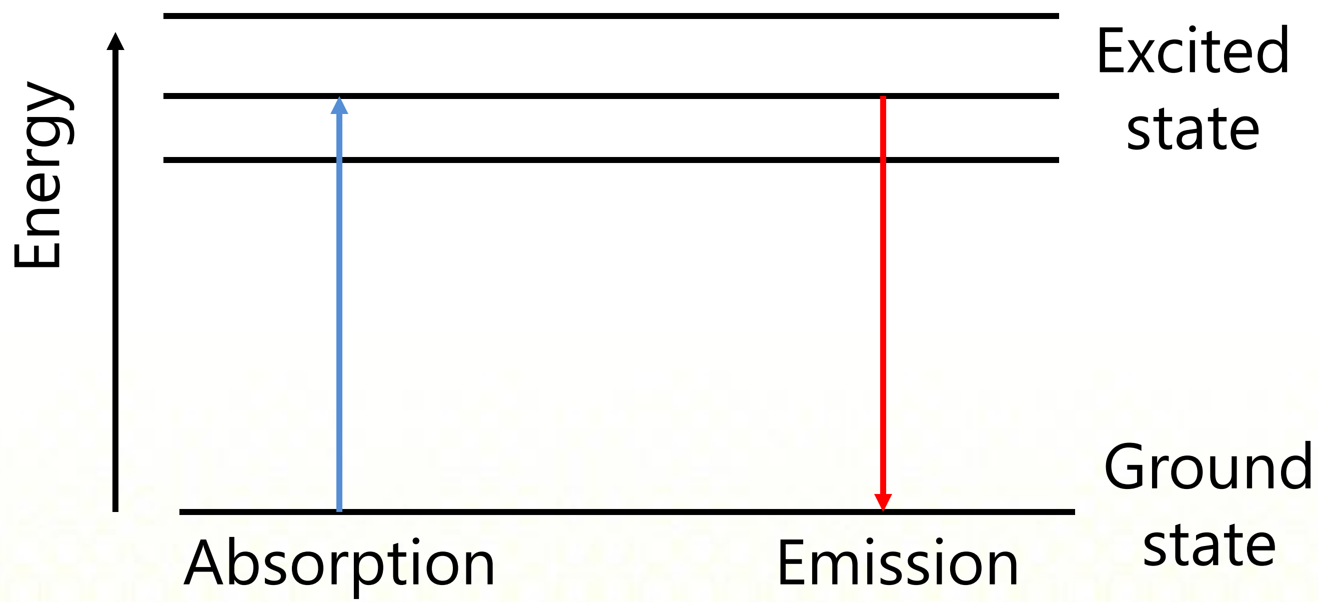
## Luminescence

- Emission following excitation of molecules or atoms by absorption of electromagnetic radiation

# Interaction of EMR with Matter

Ground State: The lowest energy state

Excited State: higher energy state (usually short-lived)



# Interaction of EMR with Matter

- Change in state requires the absorption or emission of energy

$$\text{Change in energy}\,(\Delta E) = h\nu = \frac{hc}{\lambda}$$

- Matter can only absorb specific wavelengths or frequencies

- These correspond to the exact differences in energy between the two states involved

Absorption: Energy of species increases (ΔE is positive)

Emission: Energy of species decreases (ΔE is negative)

## Absorption Spectrum

- A graph of intensity of light absorbed versus frequency or wavelength

- Emission spectrum is obtained when molecules emit energy by returning to the ground state after excitation

## Excitation may include

- Absorption of radiant energy
- Transfer of energy due to collisions between atoms or molecules
- Addition of thermal energy
- Addition of energy from electrical charges

- Wavelengths of absorption or emission are used for qualitative identification of elements in a sample

- The intensity of light absorbed or emitted at a given wavelength is used for the quantitative analysis

## Atomic Spectroscopy Methods

- Absorption spectroscopy
- Emission spectroscopy
- Fluorescence spectroscopy
- X-ray spectroscopy (makes use of core electrons)

- Energy states are quantized

## Rotational Transitions

- Molecules rotate in space and rotational energy is associated

- Absorption of the correct energy causes transition to a higher energy rotational state

- Molecules rotate faster in a higher energy rotational state

- Rotational spectra are usually complex

## Rotational Transitions

- Rotational energy of a molecule depends on shape, angular velocity, and weight distribution

- Shape and weight distribution change with bond angle

- Molecules with more than two atoms have many possible shapes

- Change in shape is therefore restricted to diatomic molecules

- Associated energies are in the radio and microwave regions

## Vibrational Transitions

- Atoms in a molecule can vibrate toward or away from each other at different angles to each other

- Each vibration has characteristic energy associated with it

- Vibrational energy is associated with absorption in the infrared (IR region)

Increase in rotational energy usually accompanies increase in vibrational energy

## Vibrational Transitions

- IR absorption corresponds to changes in both rotational and vibrational energies in molecules

- IR absorption spectroscopy is used to deduce the structure of molecules

- Used for both qualitative and quantitative analysis

## Electronic Transitions

- Molecular orbitals are formed when atomic orbitals combine to form molecules

- Absorption of the correct radiant energy causes an outer electron to move to an excited state

- Excited electron spontaneously returns to the ground state (relax) emitting UV or visible energy

- Excitation in molecules causes changes in the rotational and vibrational energies

## Electronic Transitions

- The total energy is the sum of all rotational, vibrational, and electronic energy changes

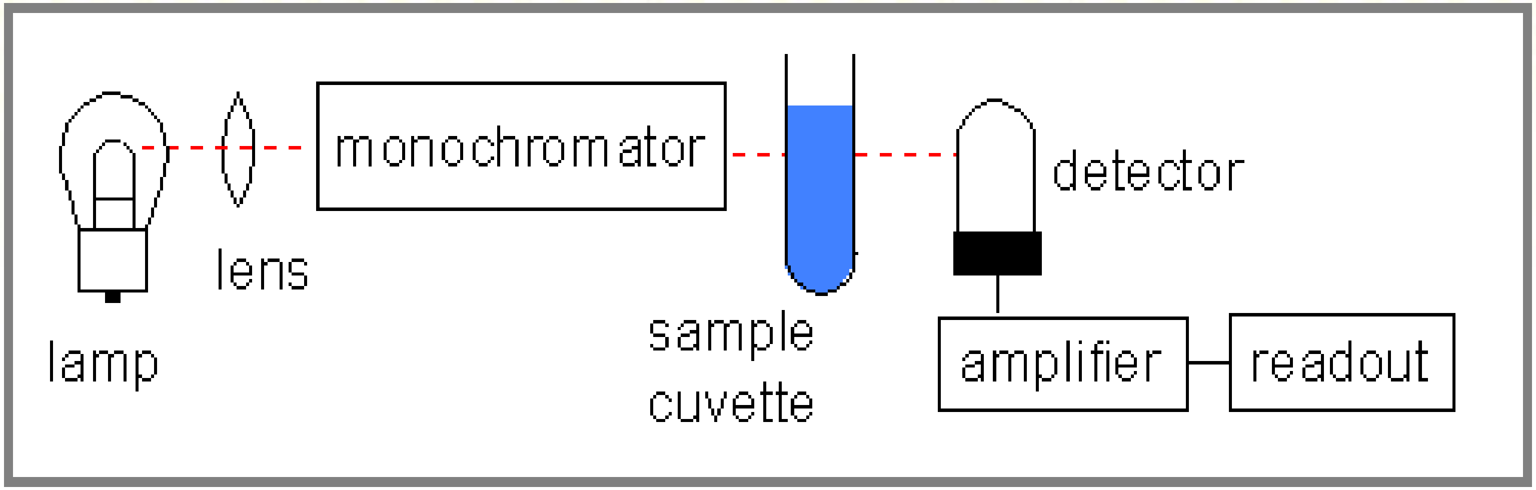
- Associated with wide range of wavelengths (called absorption band)

- UV-VIS absorption bands are simpler than IR spectra

## Molecular Spectroscopy Methods

- Molecular absorption spectroscopy
- Molecular emission spectroscopy
- Nuclear Magnetic Resonance (NMR)
- UV-VIS
- IR
- MS
- Molecular Fluorescence Spectroscopy

# General Optical Spectrometer




Light source - hot objects produce “black body radiation

- Wavelength separation
- Photodetectors

# Monochromator





- Entrance slit - provides narrow optical image
- Collimator - makes light hit dispersive element at same angle
- Dispersing element – directional
- Focusing element - image on slit
- Exit slit - isolates desired color to exit

# Filters – Inexpensive Alternative



- Adsorption type - glass with dyes to adsorb chosen colors
- Interference filters - multiple reflections between 2 parallel reflective surfaces - only certain wavelengths have positive interferences - temperature effects spacing between surfaces

# FTIR versus Raman: Information-wise

**FTIR Spectroscopy (arise from change in the dipole moment)**

- ✓ Lattice dynamics (phonons)
- ✓ Optical transitions (band structure)
- ✓ Absorption

**Raman Spectroscopy (arise from change in the polarizability)**

- ✓ Local structural information (symmetry, vacancies, dopants, etc.)
- ✓ Lattice dynamics (phonons)
- ✓ Electronic **excitations**, Magnetic excitations (energy, lifetime, symmetry)

**Why Raman ?**

- ✓ Non-destructive, contactless
- ✓ Informative
- ✓ Relatively painless
- ✓ Macro- to microscopic measurements possible
- ✓ Easy to implement external parameters (**T**, **B**, **P**, etc)
- ✓ No interference of water

# Purpose of NMR Spectroscopy

- ✓ Nuclear magnetic resonance (NMR) is a spectroscopy technique. It is based on the absorption of electromagnetic radiation in the radio-frequency region (4 to 900 MHz).
- ✓ Nuclei of atoms rather than outer electrons are involved in the absorption process.
- ✓ In order to cause nuclei to develop the energy states required for absorption to occur, it is necessary to place the analyte in an intense magnetic field.
- ✓ NMR spectroscopy is one of the most powerful tools for elucidating the structure of chemical species.

# UV/Vis Spectroscopy

✓ Chemical compounds are colored because they absorb visible light.

✓ In general, even organic compounds that are colorless will absorb UV light.

# Absorption laws

## Beer's Law

- I or T decreases exponentially with increasing path length

- A increases linearly with increasing path length

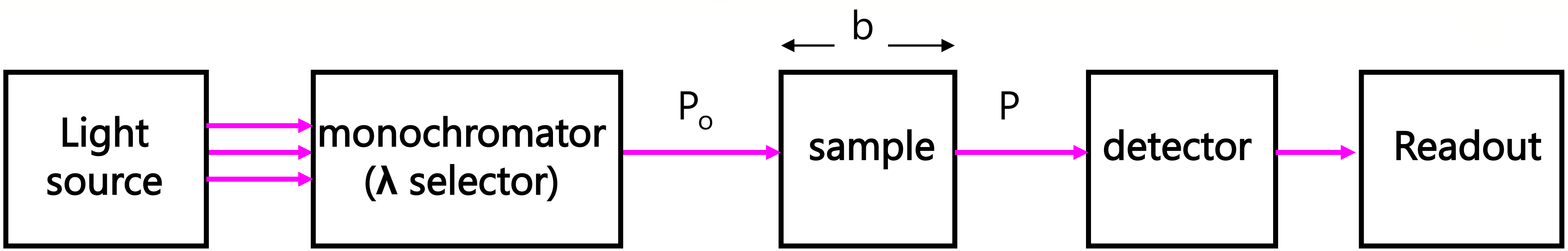
- A increases linearly with increasing concentration

- More intense color implies greater absorbance

- Basis of quantitative measurements (UV-VIS, IR, AAS etc.)

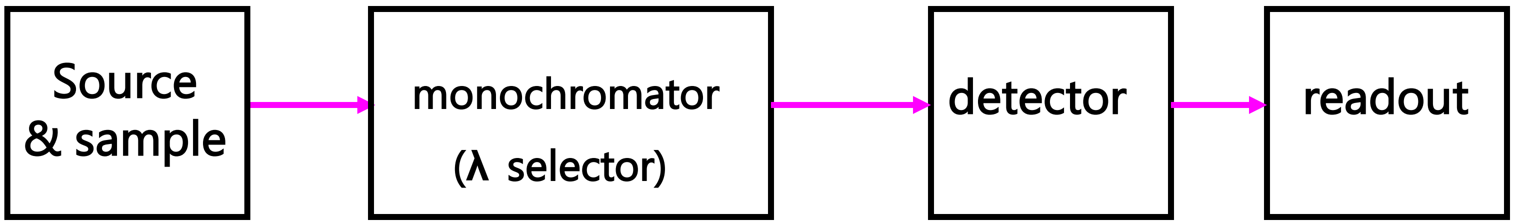
# Components of the Spectrometer

## Absorption (UV-Vis)



# Components of the Spectrometer

## Emission

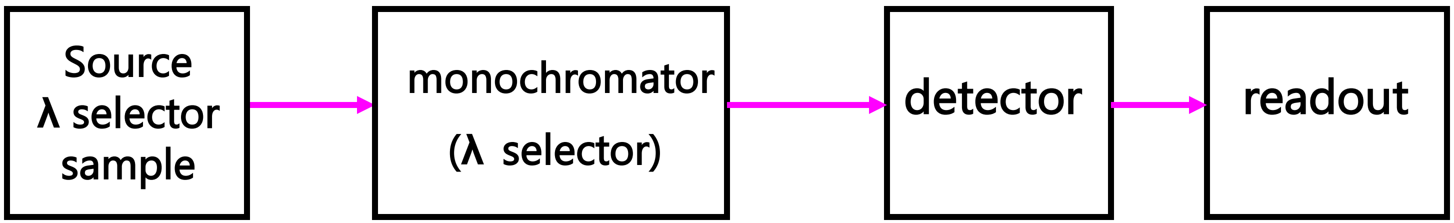



- Sample is an integral portion of the source

- Used to produce the EM radiation that will be measured

# Components of the Spectrometer

## Fluorescence



# Spectrophotometers

## Photodiode Array Spectrophotometers

- Records the entire spectrum (all wavelengths) at once

- Makes use of a polychromator

- The polychromator disperses light into component wavelengths

## Dispersive Spectrophotometers

- Records one wavelength at a time

- Makes use monochromator to select wavelength

# FT Spectrophotometers

- Have no slits and fewer optical elements

## Multiplex

-Instrument that uses mathematical methods to interpret and present spectrum without dispersion devices

- Wavelengths of interest are collected at a time without dispersion

- The wavelengths and their corresponding intensities overlap

- The overlapping information is sorted out in order to plot a spectrum

# FT Spectrophotometers

- Sorting out or deconvoluting the overlapping signals of varying wavelengths (or frequencies) is a mathematical procedure called Fourier Analysis

- Fourier Analysis expresses complex spectrum as a sum of sine and cosine waves varying with time

- Data acquired is Fourier Transformed into the spectrum curve

- The process is computerized and the instruments employing this approach are called FT spectrometers

# FT Spectrophotometers

## Advantages of FT Systems

- Produce better S/N ratios (throughput or Jacquinot advantage)

- Time for measurement is drastically reduced (all λs are measured simultaneously)

- Accurate and reproducible wavelength measurements

## Absorption

- Converts radiative energy into internal energy.

## Emission

- Converts internal energy into radiative energy.

## Scattering

- Radiative energy is first absorbed and then radiated.

✓ Photoluminescence implies both Fluorescence and Phosphorescence.
✓One broad peak may be superposition of two or several peaks: De-convolution is needed.
✓ Main peak may accompanied with kinks, shoulder or satellites.

Fluorescence – **ground state to *singlet* state and back.**

Phosphorescence – **ground state to *triplet* state and back.**

# Purpose of MW Spectroscopy

✓ It is mainly used to get information about gas molecules, such as

1. Accurate bond lengths and angles.
2. Electric dipole moments.
3. Centrifugal distortion constants.

✓ It can also be used to study relaxation times, dielectric constants, dipole moments in liquids and solutions, and potential energy barriers to rotation.

✓ Rotational spectroscopy is only really practical in the gas phase where the rotational motion is quantized. In solids or liquids the rotational motion is usually quenched due to collisions.

# Conclusion

- Know various interactions of EMW with Matter

- Understand different terminologies of spectroscopy

- Know the basic components of spectroscopic instruments

- Understand their functions

- Learn basic principle of each spectroscopy

# Questions ?

*Thank You*