Introduction

Spectroscopy is the study of the interaction between the electromagnetic radiation and the matter. Spectrophotometry is the measurement of these interactions i.e. the measurement of the intensity of light absorbed , emitted or scattered at a selected wavelength . The method depends on the light absorbing property of either the analyte or one of it's derivatives .

A plot of the interaction is referred to as a spectrum.

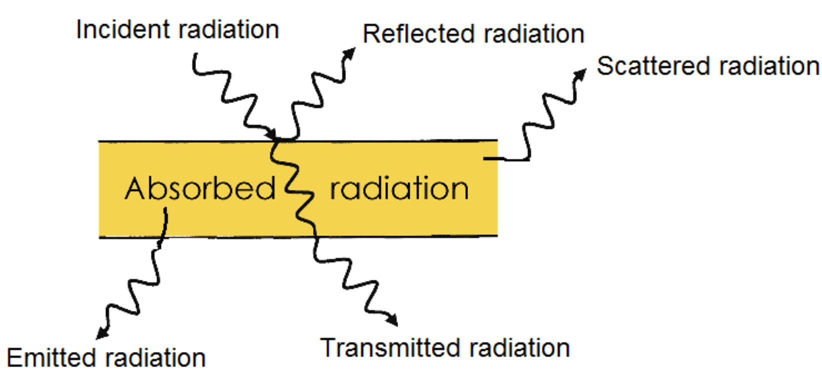
Classification of spectroscopic methods

Spectroscopy is a sufficiently broad field that many sub-disciplines exist, each with numerous implementations of specific spectroscopic techniques. The various implementations and techniques can be classified in several ways.

1- Nature of the interaction .
2- Type of EM radiation .
3- Type of material (matter).

1- Nature of the interaction

Types of spectroscopy can be distinguished by the nature of the interaction between the EM radiation and the material. When a beam of radiation of any kind penetrates matter, some of the radiation may be reflected , some may be absorbed completely, some of the absorbed may be emitted , some may be scattered and some may pass straight through without any interaction at all.



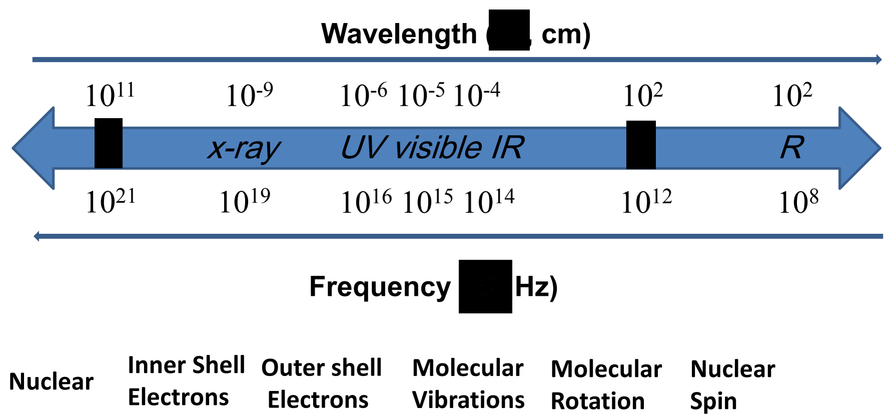
(a) Absorption : occurs when energy from the radiation source is absorbed by the material (atoms or molecules) . Absorption is often determined by measuring the fraction of energy transmitted through the material.

(b) Emission : indicates that EM radiation which is absorbed by the material (atoms or molecules) can be released . Emission can also be induced by other sources of energy such as flames or electricity .

(C) Scattering :

Raman scattering of light by molecules may be used to provide information on a sample's chemical composition and molecular structure. Also nephelometry and turbidimetry are applied for quantitative analysis as we shall see in this course .

THE ELECTROMAGNETIC SPECTRUM



Type of Radiation	Wavelength Range	Type of Transition
gamma-rays	<1 pm	nuclear
X-rays	1 nm-1 pm	inner electron
Ultraviolet	400 nm-1 nm	outer electron
Visible	750 nm-400 nm	outer electron
near-infrared	2.5 µm-750 nm	outer electron molecular vibrations
Infrared	25 µm-2.5 µm	molecular vibrations
Microwaves	1 mm-25 µm	molecular rotations, electron spin flips*
radio waves	>1 mm	nuclear spin flips*

2- Type of radiative energy

Types of spectroscopic methods of analysis are distinguished by the type of EM radiation involved in the interaction. These include:

Gamma-ray Spectroscopy
Gamma radiation is the energy source in this type of spectroscopy, which includes activation analysis and Mossbauer spectroscopy.

Infrared Spectroscopy
The infrared absorption spectrum of a substance is sometimes called its molecular fingerprint. Although frequently used to identify materials, infrared spectroscopy also may be used to quantify the number of absorbing molecules.

Laser Spectroscopy
Absorption spectroscopy, fluorescence spectroscopy and Raman spectroscopy, all commonly use laser light as an energy source. Laser spectroscopies provide information about the interaction of coherent light with matter. Laser spectroscopy generally has high resolution and sensitivity.

X-ray Spectroscopy
This technique involves excitation of inner electrons of atoms, which may be seen as x-ray absorption. An x-ray fluorescence emission spectrum may be produced when an electron falls from a higher energy state into the vacancy created by the absorbed energy.
The other methods include uv/vis spectrophotometry , microwave spect. And radio wave spect.

3- Type of matter

Spectroscopic studies are designed so that the radiant energy interacts with specific types of matter.

Atoms

Atomic spectroscopy was the first application of spectroscopy developed. Atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES) involve visible and ultraviolet light. These absorptions and emissions, often referred to as atomic spectral lines, are due to electronic transitions of outer shell electrons as they rise and fall from one electron orbit to another. Atoms also have distinct x-ray spectra that are attributable to the excitation of inner shell electrons to excited states.

Atoms of different elements have distinct spectra and therefore atomic spectroscopy allows for the identification and quantitation of a sample's elemental composition.

Modern implementations of atomic spectroscopy for studying visible and ultraviolet transitions include flame emission spectroscopy (**FAES**), inductively coupled plasma atomic emission spectroscopy (**ICP-AES**), and spark or arc emission spectroscopy. Techniques for studying x-ray spectra include X-ray fluorescence (**XRF**) and X-ray absorption (**XRA**) .

Molecules

The combination of atoms into molecules leads to the creation of unique types of energetic states and therefore unique spectra of the transitions between these states. Molecular spectra can be obtained due to electron spin states (electron paramagnetic resonance NMR), molecular rotations, molecular vibration and electronic transitions (**uv/vis molecular spectroscopy**). Rotations are collective motions of the atomic nuclei and typically lead to spectra in the microwave spectral regions; rotational spectroscopy and microwave spectroscopy are synonymous. Vibrations are relative motions of the atomic nuclei and are studied by both infrared and Raman spectroscopy. Electronic excitations are studied using visible and ultraviolet absorption and emission spectroscopy.

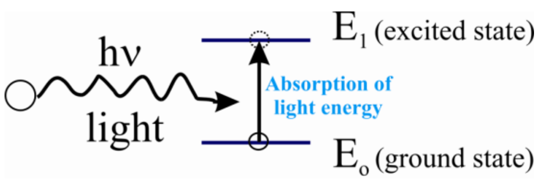
Nuclei

Nuclei also have distinct energy states that are widely separated and lead to gamma ray spectra. Distinct nuclear spin states can have their energy separated by a magnetic field, and this allows for NMR spectroscopy.

Absorption of Light

Ground and Excited State

under the normal conditions electrons exist in the ground state but when a chemical absorbs light, these electrons goes from a low energy state (ground state) to a higher energy state (excited state)

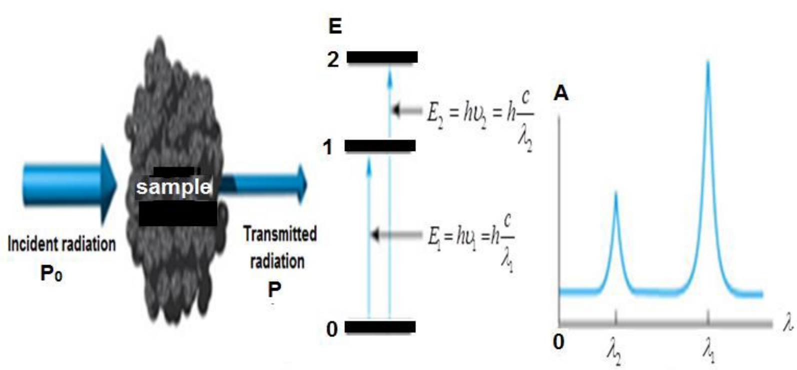


Energy required of photon to give this transition:

$$\Delta E = E1 - Eo$$

Only photons with energies exactly equal to the energy difference between the two electron states will be absorbed.

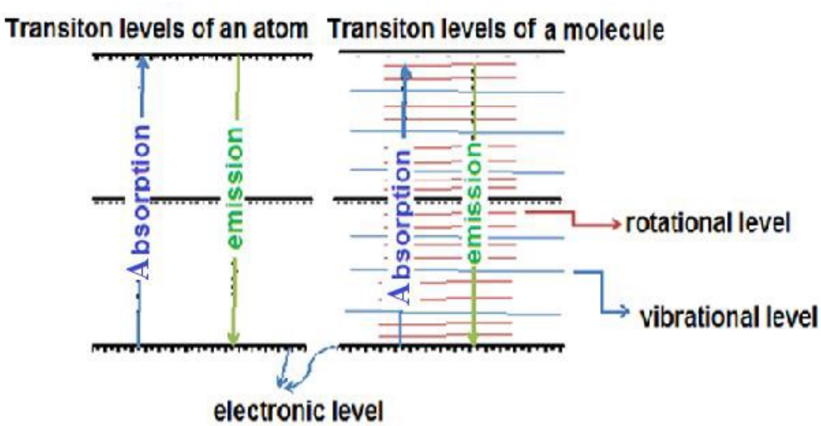
Since different chemicals have different electron shells which are filled, they will each absorb their own particular type of light because they all have different electron ground states and excited states



Atomic Absorption: The passage of polychromatic ultraviolet or visible radiation through a medium that consists of gaseous atoms results in the absorption of a few well-defined frequency. Such spectra is very simple due to the small number of possible states for the absorbing atoms (only electronic transitions). The atomic spectrum consists of few lines , therefore it is sometimes termed line spectrum .

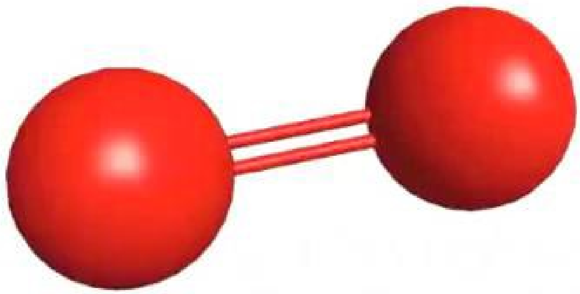
Molecular Absorption: Absorption spectra for polyatomic molecules are considerably more complex than atomic spectra because the number of energy states of molecules is generally enormous when compared with the number of energy states for isolated atoms. The energy E of a molecule is made up of three components,

$$E = E_{electronic} + E_{vibrational} + E_{rotational}$$

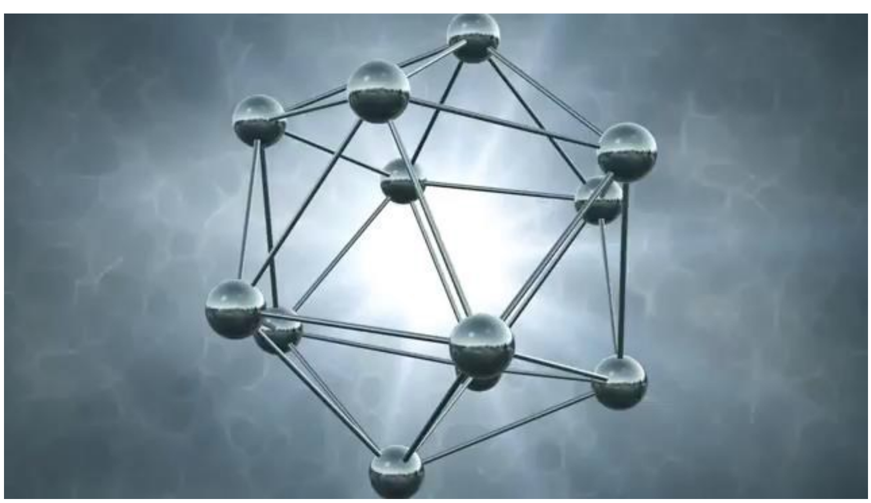


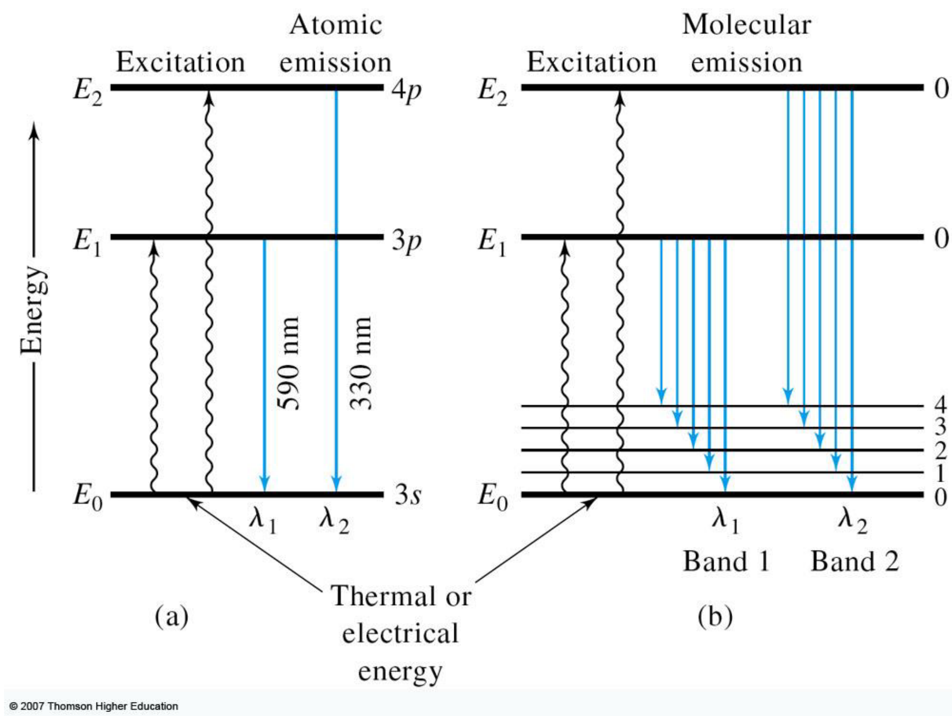
Atoms contain only electronic levels while molecules contain electronic lvels and every electronic level is divided into several vibrational levels and very vibrational level contains sevral rotational levels .

Vibrations of molecules



Rotations in a molecule




Excitation
Atomic emission
Excitation
Molecular emission
Energy
E_2
E_1
E_0
4p
3p
3s
590 nm
330 nm
λ_1
λ_2
Band 1
Band 2
Thermal or electrical energy
(a)
(b)
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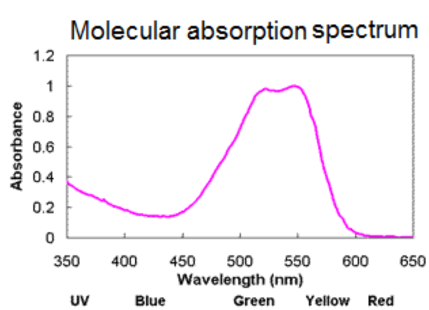
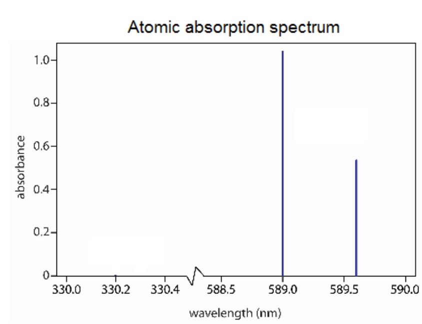

Molecular absorption spectrum
Absorbance
Wavelength (nm)
UV
Blue
Green
Yellow
Red


Atomic absorption spectrum
absorbance
wavelength (nm)

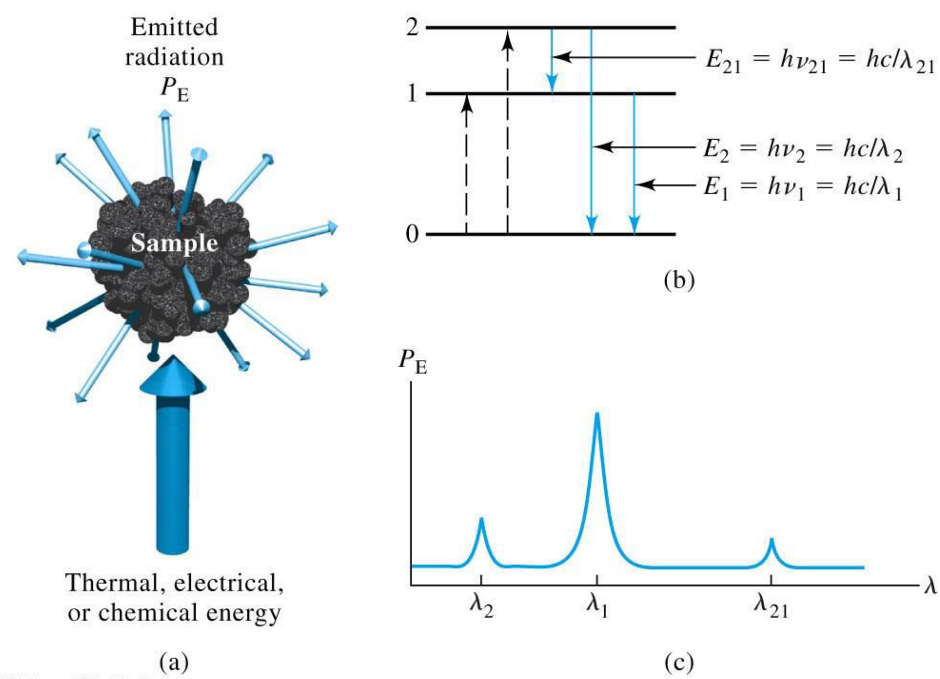
Emission of Radiation

Electromagnetic radiation is produced when excited particle (atoms or molecules) relax to lower energy levels by giving up their excess energy as photons. Radiation from an excited source is characterized by means of an emission spectrum.

$$\mathbf{X} \longrightarrow \mathbf{X^*} \longrightarrow \mathbf{X} + \text{[redacted]}$$

Excitation can be done by -

1. Bombardment with electrons
2. Electric excitation e.g. arc , spark, furnace or plasma.
3. Heat of a flame.
4. Beam of electromagnetic radiation.
5. a chemical reaction .

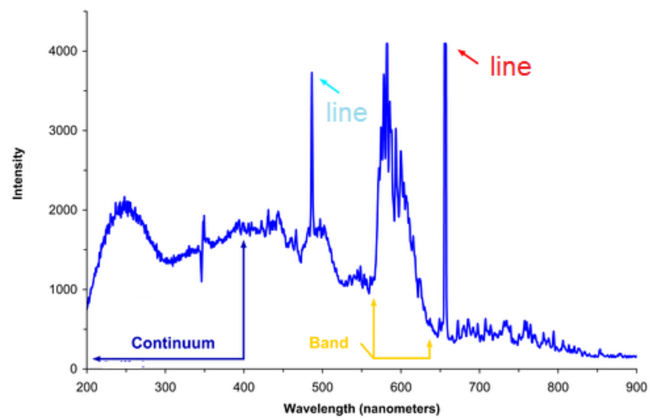


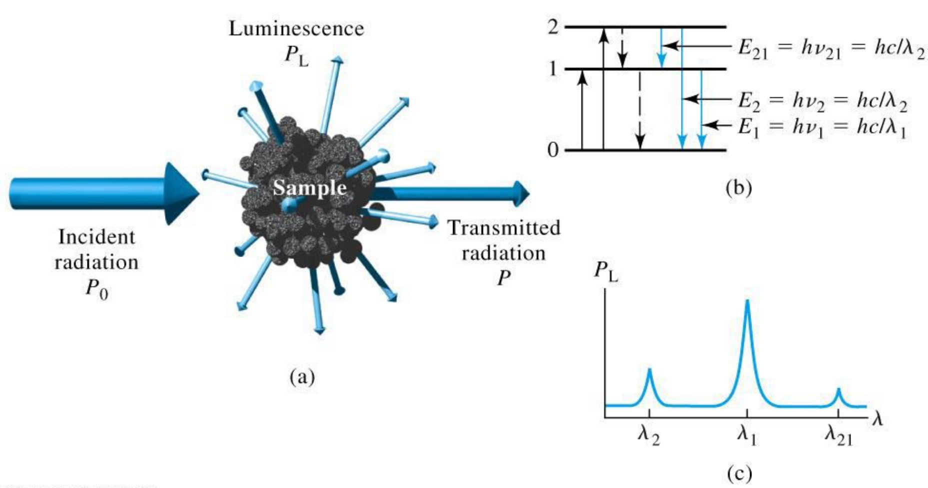
Three types of spectra:

1- Line Spectra

2- Band Spectra

3- Continuum Spectra





We can divide spectroscopy into two broad classes of techniques absorption and emission spectroscopy .

In **absorption spectroscopy** a photon is absorbed by an atom or molecule , which undergoes a transition from a lower-energy state to a higher energy , or excited state . The type of transition depends on the photon's energy. The electromagnetic spectrum (figures , slide 18 and 19) , for example, shows that absorbing a photon of visible light promotes one of the atom's or molecule's valence electrons to a higher-energy level. When a molecule absorbs infrared radiation, on the other hand, one of its chemical bonds experiences a change in vibrational energy.

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we called emission . This is the basis of **emission spectroscopy** . There are several ways as we mentioned earlier in which an atom or molecule may end up in an excited state . Molecular Emission following the absorption of radiation by molecules is called **photoluminescence** and that caused by a chemical reaction is called **chemiluminescence** .

The following two Tables provide a summary to the most common spectrometric methods of analysis and their applications .

Absorption Methods

Region of Electromagnetic Spectrum	Spectroscopic Techniques	Applications
y-ray	Y - ray spectroscopy	Quantitative and qualitative analysis of trace metals in the sample
X-ray	X-ray absorption spectroscopy	Quantitative and qualitative analysis of elements heaver than nitrogen
UV/Vis	UV/Vis spectroscopY	Quantitative analysis of trace elements and compounds in the sample
	atomic absorption spectroscopy	Quantitative analysis of trace metals in the sample
IR	Infrared spectroscopy	Identification and structural analysis of organic Compounds
	Raman spectroscopy	a fingerprint by which molecules can be identified
Radio wave	nuclear magnetic resonance spectroscopy (NMR)	Qualitative and structural analysis of organic compounds

Emission Methods

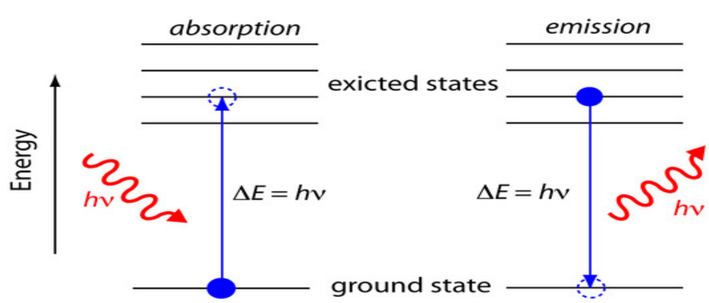
Type of Emission	Region of Electromagnetic Spectrum	Spectroscopic Techniques	Applications
emission (thermal and electrical excitation)	UV/Vis	atomic emission spectroscopy Inductively coupled plasms (icp) Arc - spark emission spectrometry	Quantitative analysis of trace metals in the sample
	X-ray	X-ray fluorescence	Quantitative and qualitative analysis of elements heaver than nitrogen
photoluminescence	UV/Vis	fluorescence spectroscopy phosphorescence spectroscopy	Quantitative and qualitative analysis of compounds
		atomic fluorescence spectroscopy	Quantitative analysis of trace metals
chemiluminescence	UV/Vis	chemiluminescence spectroscopy	Quantitative and qualitative analysis of elements and compounds

The following Table shows the relationship between the signal of the EM radiation and the concentration of the matter for most common spectrophotometric methods of analysis .

Major Classes of Spectrochemical Methods

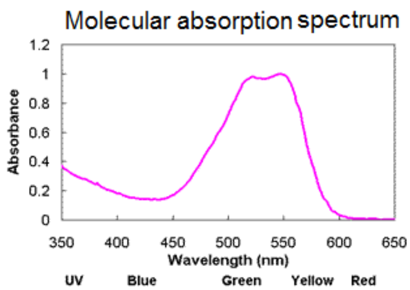
Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, P_e	$P_e = kc$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Scattering	Scattered, P_{sc}	$P_{sc} = kc$	Raman scattering, turbidimetry, and particle sizing
Absorption	Incident, P_0, and transmitted, P	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption

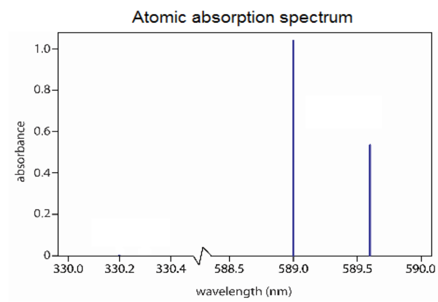
The absorption and emission of a photon by an atom or a molecule



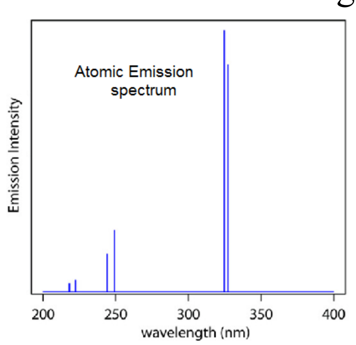
When a photon of energy hv strikes the atom or molecule, absorption may occur if the difference in energy, AE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hv, equals the difference in energy, AE, between the two states.

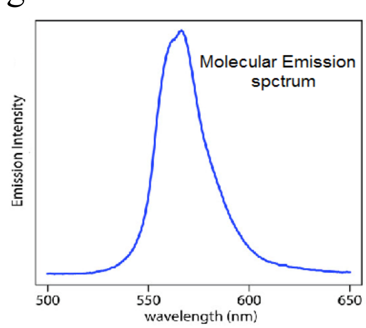
A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. The following Figures, shows typical atomic and molecular absorbance spectrum .





When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we called emission . A typical atomic and molecular **emission** spectrum are shown in the following Figures .





Why the molecular spectrum consists of bands while the atomic spectrum consists of lines ?