CHAPTER TEN

10. Introductions to Spectroscopy

10.1 Introduction

- Spectroscopy is a branch of science which studies the interaction of electromagnetic radiation with matter where the interaction of radiation with chemical species is measured to obtain characteristics quality and quantity of the species.
- Spectroscopic techniques can be divided in to two
  - **Atomic spectroscopy** (atomic absorption and atomic emission spectroscopy)
  - **Molecular spectroscopy** (Uv-Vis, IR, NMR, MS)

10.1.1 Electromagnetic Radiation

Electromagnetic radiation is a form of energy that is transmitted through space at enormous velocities. Electromagnetic radiation, or *light*, is described by the properties of both *waves* and *particles nature*.

- **Wave nature of light:** In dealing with phenomena such as reflection, refraction, interference, and diffraction, but electromagnetic radiation is conveniently modeled as waves.

An electromagnetic wave is characterized by several fundamental properties, including its frequency, velocity, amplitude, phase angle, polarization, and direction of propagation.

- *Frequency "ν"*: the number of oscillations of the field that occurs per second.
- *Wavelength*, "λ": the linear distance between successive maxima or minima of a wave. Mostly measured in nm = 10^{-9}m
- *Speed of light can be expressed as* $\boldsymbol{C = \nu\lambda}$ where "λ" is the wavelength; "ν" is the frequency, and "c" the speed of light in a medium.
- *wavenumber*, "$\tilde{\nu}$" another unit used to describe the wave properties of electromagnetic radiation which is the reciprocal of wavelength $\tilde{\nu} = 1/\lambda$
- **Particle Nature of light.** When matter absorbs electromagnetic radiation it undergoes a change in energy. The interaction between matter and electromagnetic radiation is easiest to understand if we assume that radiation consists of a beam of energetic particles called photons. When a *photon* is absorbed by a sample it is "destroyed," and its energy acquired by the sample. The energy of a photon, in joules, is related to its frequency, wavelength, and wavenumber.

$\boldsymbol{E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}}$, where "h" is Planck's constant = 6.63 x 10^{-34} J s.

> **Note.** $E \propto \tilde{\nu}$ and ν but E $\propto 1/\lambda$

Example 10-1. The energy difference between the 3p and the 3s orbitals in a sodium atom is 2.107 eV. Calculate the $\boldsymbol{\lambda}$ (in nm) that would be absorbed in exciting the 3s electron to the 3p state (l eV = 1.60 X 10^{-19} J).

Solution $\boldsymbol{\lambda = \frac{hc}{E} = \frac{6.63x10^{-34}J.S\ x\ 3x10^{8}m/s}{2.107eV\ x\ 1.6x10^{-19}J/eV} = 590nm}$

10.2 Electromagnetic radiation and its interactions with matter

The interactions of radiation and matter are the subject of spectroscopic studies. The most interesting types of interactions in spectroscopy are *absorption* and *emission* of radiation by molecular or atomic species of interest which involve transitions between different energy levels of the chemical species.

Absorption and emission.

- **Absorption:** When radiation passes through a transparent layer of a solid, liquid, or gas, certain frequencies may be selectively removed by the process of ***absorption.*** Here, electromagnetic energy is transferred to the atoms or molecules constituting the sample; as a result, these particles are promoted from a lower energy state to higher-energy states, or excited states (Figure 10.1). Note that at room temperature, most substances are in their lowest energy or ground state.
- **Emission:** 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 call emission (Figure 10.1).

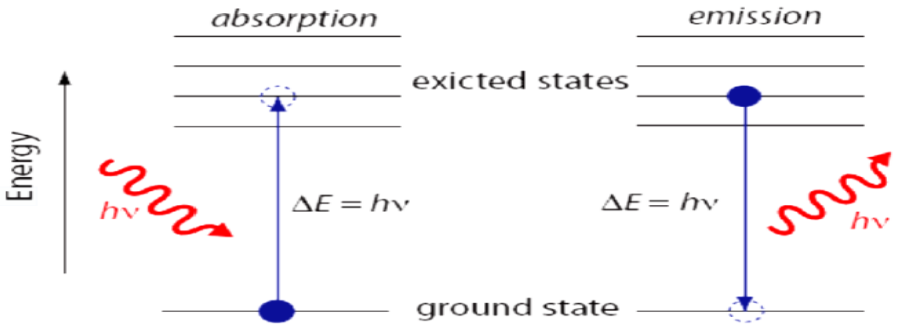


Figure 10.1 Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule.

Note. *When a photon of energy hν strikes the atom or molecule, absorption may occur only if the difference in energy, ΔE, 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. Here also the photon's energy, hν, equals the ΔE between the two states.*

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions. The *electromagnetic spectrum*-based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 10.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.

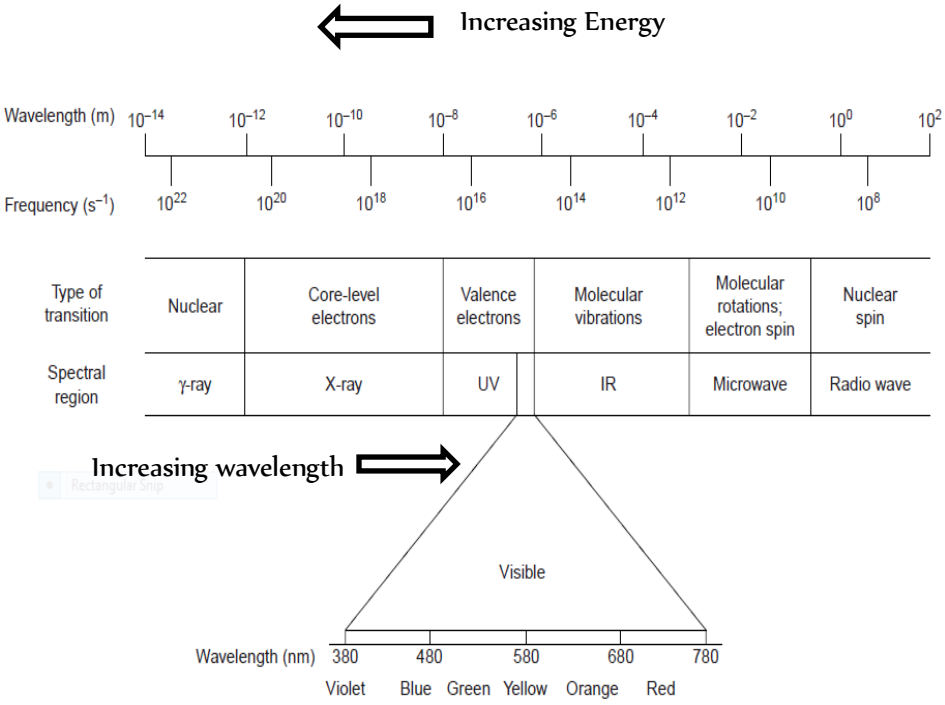


Figure 10.2 The electromagnetic spectrum showing the boundaries between different regions.

A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties.

That means

- ☞ X-ray photons excite inner-shell electrons;
- ☞ ultra-violet and visible-light photons excite outer-shell (valence) electrons;
- ☞ infrared photons are less energetic, and induce bond vibrations; and
- ☞ Microwaves are less energetic still, and induce molecular rotation.

10.3 Absorption Laws (Quantitative Analysis)

As light traverses a medium containing an absorbing analyte, decreases in intensity occur as the analyte becomes excited.

- ✍ For an analyte solution of a given concentration, the longer the length of the medium through which the light passes (path length of light), the more absorbers are in the path, and the greater the attenuation.
- ✍ Also, for a given path length of the light, the higher the concentration of absorbers, the stronger the attenuation.

✍ This attenuation of radiation is described quantitatively by two separate, but related terms: transmittance and absorbance. As shown in Figure 10.3 a, *transmittance* is the ratio of the source radiation's power exiting the sample, P_T, to that incident on the sample, P_0.

$$T = \frac{P_T}{P_O}$$

☞ Multiplying the transmittance by 100 gives the percent transmittance (%T), which varies between 100% (no absorption) and 0% (complete absorption). All methods of detection, whether the human eye or a modern photoelectric transducer, measure the transmittance of electromagnetic radiation.

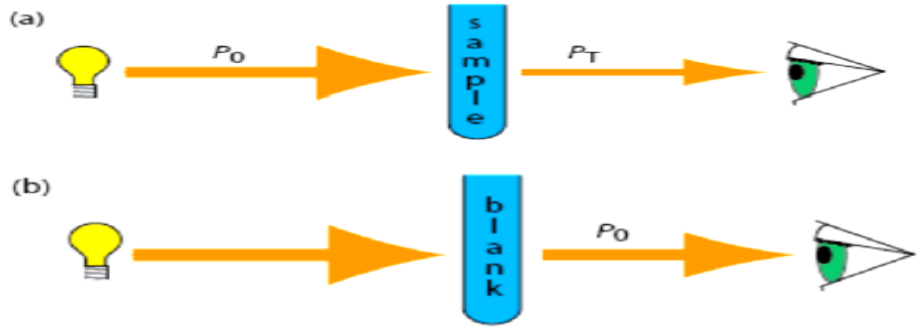


Figure 10.3 (a) Schematic diagram showing the attenuation of radiation passing through a sample; $P0$ is the radiant power from the source and PT is the radiant power transmitted by the sample. (b) Schematic diagram showing how we redefine $P0$ as the radiant power transmitted by the blank. Redefining $P0$ in this way corrects the transmittance in (a) for the loss of radiation due to scattering, reflection, or absorption by the sample's container and absorption by the sample's matrix.

✍ An alternative method for expressing the attenuation of electromagnetic radiation is absorbance, A, is defined as

$$\boldsymbol{A = -logT = -log\frac{P_T}{P_O} = log\frac{P_O}{P_T}}$$

Absorbance is the more common unit for expressing the attenuation of radiation. It is a linear function of the analyte's concentration.

Example 10.2 A sample has a percent transmittance of 50%. What is its absorbance?

Solution: A percent transmittance of 50.0% is the same as a transmittance of 0.500, and $A = -logT = -log0.5 = 0.301$

10.3.1 Absorbance and Concentration: Beer's Law

- The absorption law, also known as the *Beer-Lambert law* or just *Beer's law*, tells us quantitatively how the amount of attenuation depends on the concentration of the absorbing molecules and the path length over which absorption occurs.
- According to Beer's law, absorbance is directly proportional to the concentration of the absorbing species "c" and to the path length "b" of the absorbing medium, as expressed by following equation.

$$A \propto b \text{ and } c, \qquad hence, \qquad A = abc$$

- Here "a" is a proportionality constant called the absorptivity. Because absorbance is a unit less quantity, the absorptivity must have units that cancel the units of band c. If, for example, c has the units of gL^{-1} and b has the units of cm, absorptivity has the units of $L\ g^{-1}\ cm^{-1}$. If we express the concentration using molarity, then we replace "*a*" with the molar absorptivity "ε", which has units of $cm^{-1}\ M^{-1}$ or $L\ mol^{-1}\ cm^{-1}$.

$$A = \varepsilon bc$$

- Calibration curves based on Beer's law are common in quantitative analyses.

Example 10.3 A 5.00×10^{-4} M solution of an analyte is placed in a sample cell with a path length of 1.00 cm. When measured at a wavelength of 490 nm, the solution's absorbance is 0.338. What is the analyte's molar absorptivity at this wavelength?

Solution

Solving for ε and making appropriate substitutions gives

$$\varepsilon = \frac{A}{bc} = \frac{0.338}{1cm\ x\ 5x10^{-4}mol/L} = 676\ L\ mol^{-1}cm^{-1}$$

We can extend Beer's law to a sample containing several absorbing components. If there are no interactions between the components, the individual absorbance, *Ai*, are additive. That is the total absorbance for a multicomponent system at a single wavelength is the sum of the individual absorbance.

$$A_{total} = A_1 + A_2 + \cdots + A_n = \varepsilon_1 bc_1 + \varepsilon_2 bc_2 + \cdots + \varepsilon_n bc_n$$

Does Beer's Law applied for any electromagnetic radiation and at higher concentration?

Limitations to Beer's Law

Few exceptions are found for generalization of absorbance linearity with "b" and "c". These are

1. Instrumental deviation
   - Stray radiation (imperfection in λ selector)
   - Polychromatic radiation (applied only in monochromatic radiation)
2. Chemical deviation
   - Concentration deviation (applied only at low concentration)

10.4. Instruments for Optical Spectroscopy

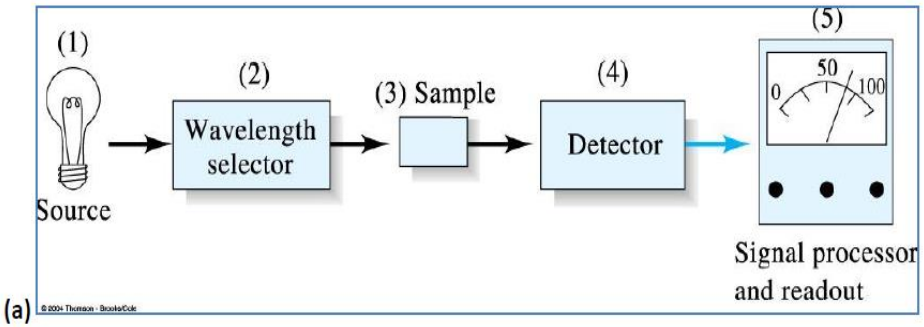
The basic components of instruments for absorption spectroscopy, as well as for emission and fluorescence spectroscopy; are remarkably alike in function and in general performance requirements whether the instruments are designed for ultraviolet, visible, or infrared radiation. Because of the similarities, such instruments are frequently referred to as ***optical instruments*** even though the eye is sensitive only to the visible region.

- Generally, most spectroscopic instruments are made up of ***five*** components while their configuration or arrangement may varies:

  - ***stable source of energy (radiation source)***
  - ***wavelength selector***
  - ***sample containers (may be one or more)***
  - ***radiation detector***
  - ***signal processing and readout device,***

- In absorption measurements (Figure 10.3a), source radiation of the selected wavelength is sent through the sample, and the transmitted radiation is measured by the detector/signal processing/readout unit.

- In emission spectroscopy (Figure 10.3b), the sample itself is the emitter and no external radiation source is needed. In these methods, the sample is usually fed into plasma or a flame, which provides enough thermal energy to cause the analyte to emit characteristic radiation. Here, a source of thermal energy, such as a flame or plasma, produces an analyte vapor that emits radiation isolated by the wavelength selector and converted to an electrical signal by the detector.



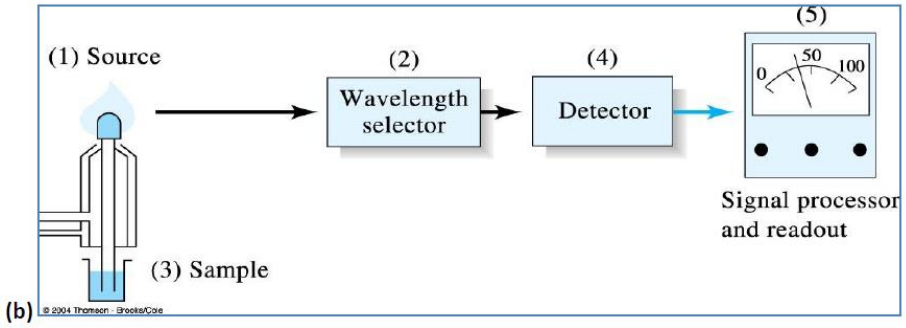


Figure 10.4 The arrangement of instruments components; **(a)** for absorption, **(b)** for emission spectroscopy

1. Sources of energy (radiation)

All forms of spectroscopy require a source of energy. In absorption spectroscopy this energy is supplied by photons. Emission spectroscopy uses thermal, radiant (photon), or chemical energy to promote the analyte to a less stable, higher energy state.

A source of electromagnetic radiation must provide an output that is both intense and stable in the desired region of the electromagnetic spectrum.

- Sources of electromagnetic radiation are classified as either continuum or line sources.

☞ A *continuum source* emits radiation over a wide range of wavelengths, with a relatively smooth variation in intensity as a function of wavelength.

☞ *Line sources*, on the other hand, emit radiation at a few selected, narrow wavelength ranges.

Table 10.1 Common Sources of Electromagnetic Radiation for Spectroscopy

Source	Wavelength Region	Useful for
H_2 and D_2 lamp	continuum source from 160–375 nm	UV molecular absorption
tungsten lamp	continuum source from 320–2500 nm	Vis molecular absorption
Xe arc lamp	continuum source from 250–600 nm	molecular fluorescence
Nernst glower	continuum source from 0.4–20 μm	IR molecular absorption
globar	continuum source from 1–40 μm	IR molecular absorption
nichrome wire	continuum source from 0.75–20 μm	IR molecular absorption
hollow cathode lamp	line source in UV/Vis	atomic absorption
Hg vapor lamp	line source in UV/Vis	molecular fluorescence
laser	line source in UV/Vis	atomic and molecular absorption, fluorescence and scattering

2. Wavelength selector

- We usually try to select a single wavelength where the analyte is the only absorbing species.
- Unfortunately, we cannot isolate a single wavelength of radiation from a continuum source. Instead, we use a wavelength selector which passes a narrow band of radiation.
- A wavelength selector passes a narrow band of radiation. Wavelength selector can be two types. ***Filter and monochromatic***.
- ***Filter***: The simplest method for isolating a narrow band of radiation. It can be absorption or interference *filter*.
  - Absorption filters work by selectively absorbing radiation from a narrow region of the electromagnetic spectrum.
  - Interference filters use constructive and destructive interference to isolate a narrow range of wavelengths.
- One limitation of an absorption or interference filter is that they do not allow for a continuous selection of wavelength. A further limitation is that filters are available for only selected nominal ranges of wavelengths.
- ***Monochromator:*** provides a continuous variation of wavelength.
- As monochromator converts a polychromatic source of radiation at the entrance slit to a *monochromatic* source of finite effective bandwidth at the exit slit.
  - **Interferometer:** a type of monochromator which allows sources or radiation of all λ to reach the detector. (All λ are measured simultaneously). It have two advantages
- **Jacquinot advantage**: results from the higher throughput of source radiation. Since an interferometer does not use slits and has fewer optical components from which radiation can be scattered and lost, the throughput of radiation reaching the detector is 80–200 times greater than that achieved with a normal monochromator.
- **Fellget advantage:** reflects a savings in the time needed to obtain a spectrum. Since all frequencies are monitored simultaneously, an entire spectrum can be recorded in approximately 1 s, as compared to 10–15 min with a scanning monochromator.

3. Sample containers

- Sample containers are required for all spectroscopic studies except emission spectroscopic studies.
- Sample containers, are usually called **sample *cells*** or ***cuvettes***, and must have windows that are transparent in the spectral region of interest.

- For example, quartz or fused silica is required for the UV region (wavelengths less than 350 nm) and may be used in the visible region and out to about 3000 nm (3 μm) in the IR region.
- Silicate glass is ordinarily used for the 375 to 2000-nm region because of its low cost compared with quartz. Plastic cells are also used in the visible region.

4. Detectors

In modern absorption and emission spectrometers, *radiation transducers* are invariably used to convert light intensity into electrical signals that can be subsequently amplified, manipulated, and finally converted into numbers proportional to the magnitude of light. Two general types of radiation transducers are employed; one responds to photons (photon transducers), and the other to heat (thermal transducers), several examples of which are listed in Table 10.4.

Table 10.2 Common Detectors for Absorption Spectroscopy

Type	Examples	Wavelength Range, nm
Photon Transducers	Phototubes	150-- 1000
	Photomultiplier tubes	150--1000
	Silicon photodiodes	350--1100
	Photoconductive cells	1000--50,000
Thermal Transducers	Thermocouples	600--20.000
	Bolometers	600--20.000
	Pneumatic cells	600--40.000
	Pyroelectric cells	1000--20.000

5. Signal Processor and readout device

- A transducer's electrical signal is sent to a signal processor where it is displayed in a form that is more convenient for the analyst. Examples of signal processors include analog or digital meters, recorders, and computers equipped with digital acquisition boards.
- A signal processor also is used to calibrate the detector's response, to amplify the transducer's signal, to remove noise by filtering, or to mathematically transform the signal.
- Finally, the processed signal displays on readout devices in a more convenient form for the analyst.

10.5 Atomic absorption and emission spectroscopy

Atomic spectroscopy is based upon the absorption or emission of electromagnetic radiation by *atomic particles*. Spectroscopic determination of atomic species can only be performed on a ***gaseous*** medium in which the individual atoms or elemental ions. This method is widely applied to a wide range of metals and nonmetals.

- The first step in all atomic spectroscopic procedures is ***atomization***, a process in which a sample is volatilized and decomposed to produce gas-phase atoms and ions.
- ***Atomization*** is a critical step in all atomic spectroscopy. Several methods are used to atomize samples for atomic spectroscopic studies. E.g. inductively coupled plasmas, flames, and electrothermal atomizers; Flames and electrothermal atomizers are widely used in atomic absorption spectrometry, while the inductively coupled plasma is employed in optical emission and in atomic mass spectrometry.

- **Atomic Absorption Spectroscopy (AAS):**

- Is a type of elemental analysis based on excitation of electron of atom.

> ❖ There are **two** fundaments proses during application of atomic absorption spectroscopy.
>
> - **Sample preparation and introduction**
> - **Sample atomization**
> - **In different atomic spectroscopy solid, liquid and gaseous samples are possible. But in AAS liquid samples or solution form samples are applied.**

- Many samples like solid, animal tissue, plant leaves, minerals etc. are not directly used as a sample, and rather they should be prepared as solution by extensive preliminary treatment.
- After the sample is prepared as a form of clear solution, it is introduced to the instrument for atomization process. In the atomization proses the sample is nebulized (conversion of samples to mist, i.e. small droplets of solution) by a flow of gaseous oxidant (e.g. air, O_2, N_2) mixed with gaseous fuel (e.g. natural gas, H_2, ethylene (C_2H_2)).

Instrumentation

- In the components of an *atomic absorption* or *flame absorption* apparatus, the flame can be considered to be a dilute gaseous solution of the atomized sample held in place by the aspirator-burner. Radiation from a suitable source is passed through the atomized sample and into the slit of a photometer or spectrophotometer.

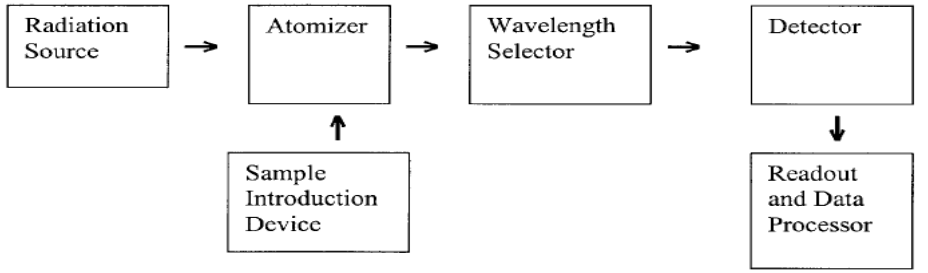


Figure 10.5 Block diagram of the components of an AAS.

- The light source (hollow cathode lamp or electrodeless discharge lamp) emits a spectrum specific to the element of which it is analyzed, which is focused through the sample cell into the monochromator. The anode and cathode are sealed in a glass cylinder normally filled with either neon or argon at low pressure. At the end of the glass cylinder is a window transparent to the emitted radiation.

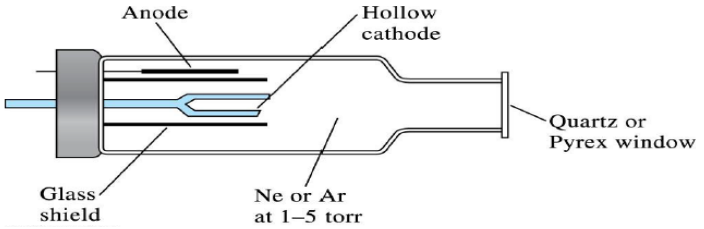


Figure 10.6 hollow cathode lamp

When an electrical potential is applied between the anode and cathode, some of the fill gas atoms are ionized. The positively charged fill gas ions accelerate through the electrical field to collide with the negatively charged cathode and dislodge individual metal atoms in a process called "sputtering". Sputtered metal atoms are then excited to an emission state through a kinetic energy transfer by impact with fill gas ions.

⌘ **Reactions in the hollow-cathode lamp**

- ☞ Ionization of filler gas: $Ar + e^- \rightarrow Ar^+ + 2e^-$
- ☞ sputtering of cathode atoms: $M(s) + Ar^+ \rightarrow M(g) + Ar$
- ☞ excitation of metal atoms: $M(g) + Ar^+ \rightarrow M^*(g) + Ar$
- ☞ light emission: $M^*(g) \rightarrow M(g) + h\nu$
- ☞ Where M* exited state of metal
- ☞ ***Each element has their own HCL.***

Application

AAS is an analytical technique used for the qualitative and quantitative determination of the elements present in different samples like food, water and wastewater sample, nanomaterial, biomaterials, forensics (blood sample), and industrial wastes.

1. **Qualitative analysis:** is based on color of flame test.

When alkali metals like calcium, strontium or barium salt is heated strongly in the Bunsen flame, a characteristic flame color is observed: e.g.

Na ⇨ yellow
Li ⇨ crimson
Ca ⇨ brick red
Sr ⇨ crimson
Ba ⇨ green

2. **Quantitative analysis**: it utilizes Beer's law. The procedure starts with preparation of series of standard solution over a concentration range of suitable for the sample being analyzed. I.e. the expected sample concentration should be within the range established by the standard.

☞ The standards and the sample are then aspirated into the flame and the absorbance read from the instrument and related with concentration of unknown sample using A= ac + b (where a and b are slop intercept of the calibration curve respectively, 'c' is concentration of unknown sample, and 'A' is absorbance of Unknown sample read from the instrument but 'a' and 'b' are determine using standard solution)

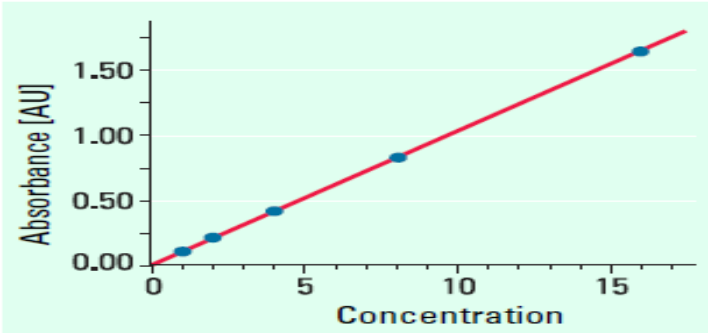


Figure 10.7 absorbance versus concentration calibration curve

In atomic emission spectroscopy (AES), in addition to liquid samples of metal, nonmetallic solids can be analyzed.

Comparison of AAS and AES

Activities	AAS	AES
Process measured	Absorption (light absorbed by unexcited atoms)	Emission (light emitted by exited atoms)
Use of flame	Atomization	Atomization and excitation
instrumentation	Uses light source	Do not use light source (independent of light source)
Beer's law	Applicable ($A \propto C$)	Not applicable ($I = KC$)
Data obtained	A Vs C	I Vs C

10.6. Ultraviolet and Visible (UV-Vis) Spectroscopy

- UV-Vis Spectrometry is based upon absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum resulting in changes in the electronic structure of ions and molecules. The wavelength of UV and visible light are substantially shorter than the wavelength of infrared radiation. The UV–Vis spectrum ranges from 200 to 700 nm. When a molecule or ion absorbs ultraviolet or visible radiation it undergoes a change in its valence electron transition.

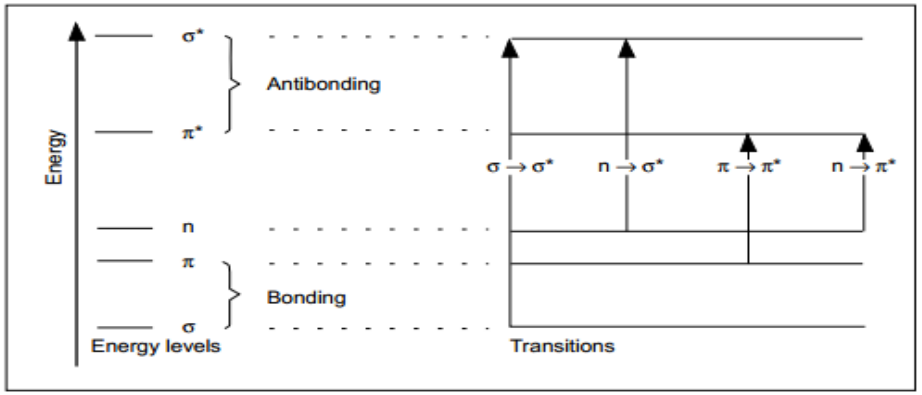


Figure 10.8 Relative energies of orbitals and possible transitions between them.

M + $h\nu \rightarrow M^*$ (when the molecule exposed to radiation hv, valance electron of the molecule is exited)

The wavelength of light absorbed is that having the energy required to move an electron from a lower energy level to a higher energy level. For example,

- $\sigma \rightarrow \sigma^*$ transitions: high-energy, accessible in vacuum UV (λmax < 150 nm). Not usually observed in molecular UV-Vis.
- $n \rightarrow \sigma^*$ transitions: non-bonding electrons (lone pairs), wavelength (λmax) in the 150-250 nm region.
- $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions: ***most common transitions*** observed in organic molecular UV-Vis, observed in compounds with lone pairs and multiple bonds with λmax = 200-600 nm.

- Of these transitions, the most important are the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, because they involve functional groups, or double/triple bonds that are characteristic of the analyte and wavelengths (Uv/vis) that are easily accessible.
- Absorption of Uv-Vis radiation in organic molecules is restricted to certain functional groups (known as chromophores which are unsaturated organic functional groups). Electrons involved in double and triple bonds of organic molecules are not as strongly held and are therefore more easily excited by Uv-Vis radiation. Uv-Vis radiation is not absorbed by saturated organic molecule. This is because Uv-Vis radiation is less energetic to excite electron from single bond.

Instrumentation

- Polychromatic light from the source is focused on the entrance slit of a monochromator, which selectively transmits a narrow band of light. This light then passes through the sample area to the detector.
- The absorbance of a sample is determined by measuring the intensity of light reaching the detector without the sample (the blank) and comparing it with the intensity of light reaching the detector after passing through the sample. As discussed above, most spectrophotometers contain two source lamps, a deuterium lamp and a tungsten lamp, and use either photomultiplier tubes or, more recently, photodiodes as detectors.

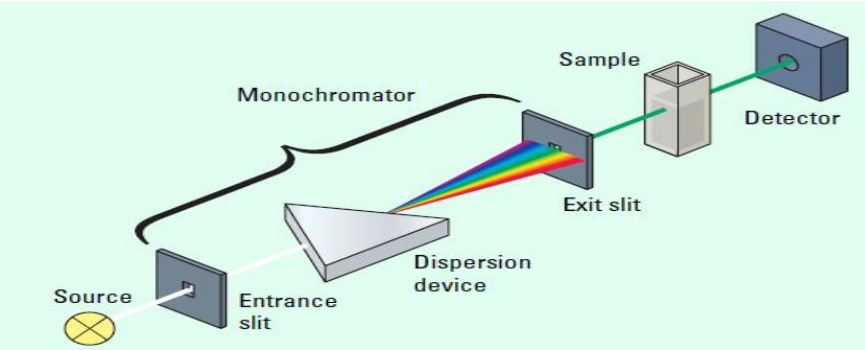


Figure 10.9 Schematic of a conventional spectrophotometer

Application

1. Qualitative analysis:

- Have limited application to ***identify the functional group*** or particular molecule as a result of absorption spectra.
- But in some extent it used to identify the unknown compound by comparing the absorption spectra with known compound spectra.
- E.g. a weak absorption band around 280-290nm indicates the presence of carbonyl ($—\overset{O}{\overset{\|}{C}}—$) group, absorption band around 257nm indicated existence of an aromatic ring.

2. Quantitative:

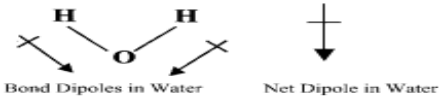
- It is widely used for quantitative analysis. Because of its
  - Widely applicability to both organic and inorganic compounds
  - Typically sensitive (i.e. 10^{-4} to 10^{-5} M) and up to 10^{-7} with some modification
  - High sensitivity
  - Good accuracy

The quantitative figure is determined as AAS using Beer's Law.

10.7 Infrared spectroscopy (IR) *basic principles*

- The energy associated with IR radiation is sufficient to cause molecules to rotate and to vibrate.
- There are two types of molecular vibrations or modes of vibration: stretching and bending.
  - In stretching vibration results in increasing or decreasing of bond length.
  - In bending vibration causes a change in bond angle. E.g. Twisting, Rocking, wagging, scissoring.
  - All molecules do not absorb IR radiation. i.e., the molecule must have a change in dipole moment during vibration in order to absorb IR radiation.
  - The dipole moment μ is the product of the charge (Q) and the distance between the charges (r). i.e. $\mu = Q \times r$
  - E.g. on vibration of the HF, HCl, CO, the dipole moment changes because the distance between the charges changes. It is IR active.

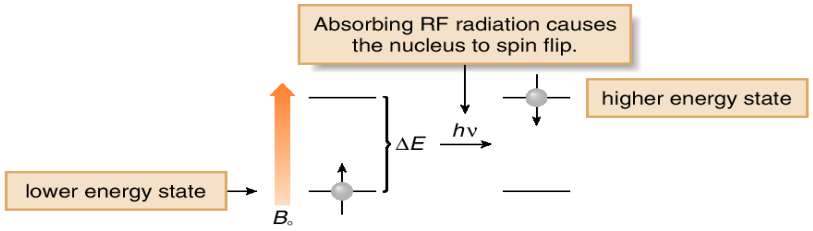
  - Symmetrical diatomic molecules do not absorb IR radiation and called as IR inactive. Example: H_2, N_2, O_2, Cl_2
  - Molecules like Carbon dioxide has two equal C=O bond dipoles but because the molecule is linear the bond dipoles cancel and the molecule has no net dipole moment. Hence do not absorb IR radiation.
- Water molecule has two equal H-O bond dipoles. The water molecule has a permanent net dipole moment. It is IR active.



10.8 Nuclear Magnetic Resonance Spectroscopy (NMRs)

- NMR spectroscopy is based on the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 900 MHz, which has long wavelengths, and low energy and frequency.
  - When low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements.
  - Nuclei of atoms rather than outer electrons are involved in the absorption process.
  - It is a powerful analytical technique used to elucidating (characterize) organic molecules by identifying carbon-hydrogen frameworks within molecules.
  - Two common types of NMR spectroscopy are used to characterize organic structure: ^{1}H NMR is used to determine the type and number of "H" atoms in a molecule; ^{13}C NMR is used to determine the type of carbon atoms in the molecule.

☞ When an external energy source ($h\nu$) that matches the energy difference (ΔE) between these two states is applied, energy is absorbed, causing the nucleus to "spin flip" from one orientation to another.



10.9 Mass Spectrometry

- Mass spectrometry (MS) is a technique for creating gas phase ions from the molecules or atoms in a sample, separating the ions according to their mass-to-charge ratio, m/z, and measuring the abundance of the ions formed.
  - Mass spectrometry is a technique used for measuring the molecular weight and determining the molecular formula of an organic compound.
  - In a mass spectrometer, a molecule is vaporized and ionized by bombardment with a beam of high-energy electrons.
  - ➢ Mass spectrometer performs the following essential functions.

☞ Firstly, it subjects molecules to bombardment by a stream of high-energy electrons, converting some of the molecules to ions, (***ion source***)

☞ Secondly, the mass Analyzer resolves (separates) the ions into their characteristics mass components according to their mass-to-charge ratio in a magnetic or electric field.

☞ Thirdly, the abundance of the resolved ions that have a particular mass-to-charge ratio are measure with a detector.

Finally, Process the signals from the detector that are transmitted to the computer and control the instrument using feedback