Spectroscopy

Contents

Course outline

Spectroscopy: *Quantization of energy, Basic elements of spectroscopy.*

Definition of spectroscopy

Spectroscopy can be defined as the study of interactions between the matter and electromagnetic radiation. [1]In spectrophotometric analysis a source of radiation is used that extends into the ultraviolet region of the spectrum. From this, definite wavelength of radiation are chosen possessing a bandwidth of less than 1 nm. This process necessitates the use of a more complicated and consequently more expensive instrument. The instrument employed for this purpose is a spectrophotometer, and as its name implies is really two instruments in one cabinet – a spectrometer and a photometer.

Figure 1. Principle of analysis with spectrochemical instrumentation

When an electromagnetic radiation falls on an objects, three phenomena are observed as follows

1. Some radiations are reflected by the object.

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[1] Vogel's text book of quantitative inorganic analysis

2. Some radiations are absorbed by the object.
3. Some radiations are transmitted through the objects.

In case of transparent objects most of the radiations are transmitted through the object.

Types of spectroscopy

Primarily, spectroscopy can be classified into two types

Atomic spectroscopy: The spectroscopy which is concerned with the interactions of electromagnetic radiations with atoms is called atomic spectroscopy. For example, atomic absorption spectroscopy for metal detection in a sample.
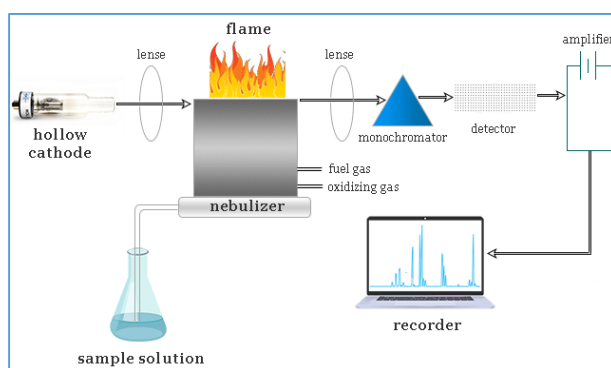

Figure 2: atomic absorption spectroscopy

Molecular spectroscopy: The spectroscopy which is concerned with the interactions of electromagnetic radiations with molecules of a substance is called molecular spectroscopy. For example, UV-Visible spectroscopy, Infra-red spectroscopy etc.
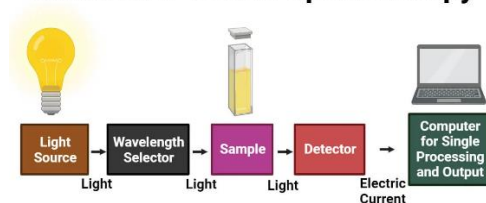

Figure 3: UV-Visible spectroscopy

In general all spectroscopic methods are classified into two types

Non-destructive methods: UV-Visible spectroscopy, IR spectroscopy, Nuclear magnetic resonance (NMR) spectroscopy etc.
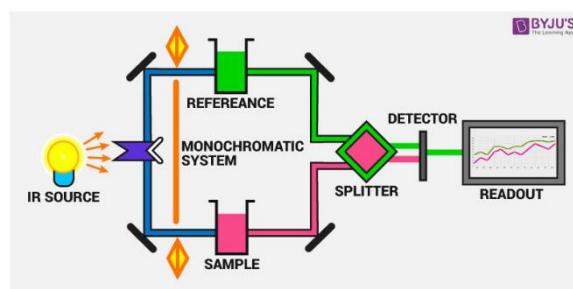
Figure 4: Infra-red spectroscopy

Destructive methods: Flame ionization spectroscopy (FES), atomic absorption spectroscopy (AAS), inductively coupled plasma – mass spectrometry (ICP-MS) etc.
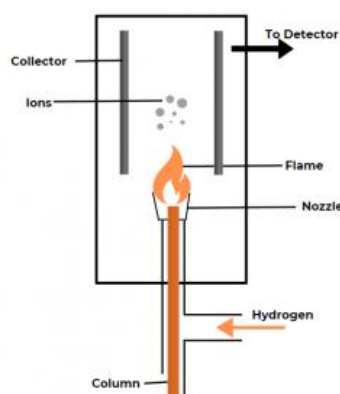

Figure 5: Flame ionization spectroscopy (FES)

Quantization of energy of an electromagnetic radiation

Energy is quantized in some systems, meaning that the system can have only certain energies and not a continuum of energies, unlike the classical case. This would be like having only certain speeds at which a car can travel because its kinetic energy can have only certain values. We also find that some forms of energy transfer take place with discrete lumps of energy. While most of us are familiar with the quantization of matter into lumps called atoms, molecules, and the like, we are less aware that energy, too, can be quantized. Some of the earliest clues about the necessity of quantum mechanics over classical physics came from the quantization of energy.

Electromagnetic radiation[2]

When an object moves up and down or vibrates continuously, energy, in the form of wave, is sent, or transmitted (or propagated) by the vibrating object to a distant place. The wave travels at right angle to the vibratory motion of the vibrating object and away from it. Wave produced by a vibrating object can be presented by a wavy curve. One such wavy curve is shown in Figure 6. The tops (maxima) of the wavy curve are called crest and the bottoms (minima) are called trough. When a stone is thrown

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[2] Modern inorganic chemistry, by RD Madan

in a pond of water, water molecules start to vibrate up and down and transmit their energy as waves on the water surface which are seen travelling towards the bank of the pond.
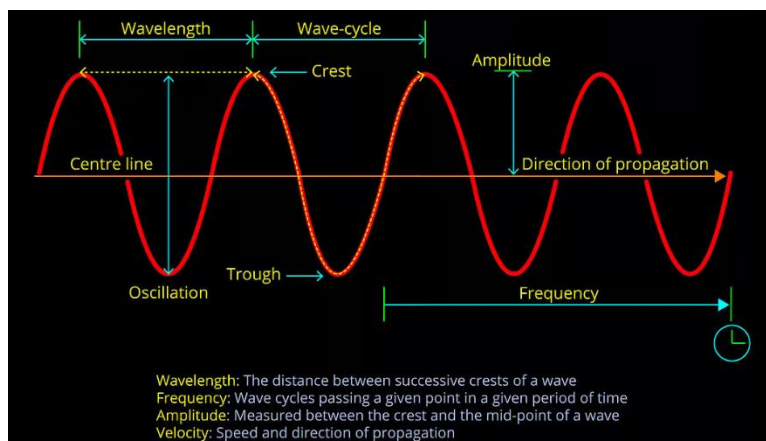

Figure 6: Features of electromagnetic waves (radiation)

In 1864 James Clark Maxwell showed that when an electric current is passed through a circuit (e.g., through a tungsten filament), it radiates energy in the form of waves. The energy radiated is called radiate energy and the waves produced are called electromagnetic waves or electromagnetic radiations. These waves are so called because similar sort of waves can also be obtained by moving a charged body as well as a magnet to and fro in a magnetic field. These waves do not require any medium for propagation or transmission; e.g., light and radio waves (which are electromagnetic waves) from the sun and stars reach the earth by travelling through non-material media i.e., through empty space. All these waves travel with the speed of light.

The radiations (or waves) emitted by the vibratory motion of an electron are also electromagnetic radiations. These radiations also travel with the speed of light.

Properties of waves – Waves parameters

Waves are characterized by the following properties or features:

1) Wavelength (λ)
2) Frequency (ν)
3) Speed or velocity (c)
4) Wave number

These properties are called wave parameters.

Wave length(λ): The wavelength of a wave is defined as the distance between two successive crests or two successive troughs of a wave (Figure 6). It is represented by lambda (λ) and is measured in terms of centimeter (cm) or miter or Angstrom or micrometer or nanometer units. These units are related as follows:

$$1cm = 0.01\ m = 10\text{Å} = 10^7 nm = 10^4 \mu m$$

Frequency (ν) and Velocity(c): Frequency is defined as the number of full waves or cycles which pass a given point on the wave in one second. It is represented by nu (ν) and is measured in terms of cycles

(or waves) per second (cps) or Hertz (Hz) units. A frequency of 100 Hz means 100 cycles (or waves) per second.

By the term cycle here, we mean a complete cycle of change. This involves the departure of a wave crest, the passing of a wave trough, and the arrival of the next crest. Frequency is also expressed in terms of reciprocal of second ($\frac{1}{s}$ or s^{-1}).

It has been found that a wave of higher frequency has shorter wavelength and vice-versa. Thus frequency of a wave is inversely proportional to its wavelength. i.e.,

$$v \infty \frac{1}{\lambda} \tag{1}$$

$$v = \frac{c}{\lambda} \tag{2}$$

Where, c is a constant which is called the velocity or speed of the wave. Velocity of a wave is defined as the distance travelled by the wave in one second. It is therefore, expressed in $cm.s^{-1}$ or $m.s^{-1}$. Its value has been found to be constant for all types of electromagnetic radiations. Its experimental value has been found to be equal to $3 \times 10^{10} cm.s^{-1}$ or $3 \times 10^8 m.s^{-1}$. As a matter of fact this value is the velocity of light in air. Thus this c is equal to the velocity of light ($3 \times 10^{10} cm.s^{-1}$ or $3 \times 10^8 m.s^{-1}$) for all types of electromagnetic radiations.

Equation (2) clearly shows that:

$$Velocity\ (c) = Wavelength\ (\lambda) \times Frequency\ (v)$$

$$c = \lambda \times v \tag{3}$$

Wave number ($\bar{v}$): in spectroscopy, frequency of light is generally expressed in terms of wavenumber ($\bar{v}$) which is defined as the number of wavelengths per meter and is equal to the frequency of wavelength. It is denoted by nu bar ($\bar{v}$). Thus:

$$Wave\ number\ (\bar{v}) = \frac{1}{\lambda} \tag{4}$$

The unit of wave number is the reciprocal of the unit of wavelength. Hence the unit of wave number is cm^{-1} or m^{-1}.

From equation (4)

$$Wave\ number\ (\bar{v}) = \frac{1}{\lambda} = \frac{1}{c/v} = \frac{v}{c} \tag{5}$$

$$Wave\ number\ (\bar{v}) = \frac{Frequncy\ (v)}{Velocity\ (c)} \tag{6}$$

Numerical problem-1: Calculate the wave number of the lines of frequencies $4 \times 10^{14}\ Hz$ and $4 \times 10^{16}\ Hz$. (Answer: $1.33 \times 10^6\ m^{-1}$ and $1.66 \times 10^8\ m^{-1}$ respectively)

Numerical problem-2: Calculate the wavelength of a wave of frequency $10^{11}\ Hz$ travelling with the speed of light ($3 \times 10^8 m.s^{-1}$). (Answer: $3 \times 10^{-3}\ m$)

Numerical problem-3: Calculate the frequency and wave number of a yellow light wavelength of 580 nm. (Answer: $5.172 \times 10^{14}\ Hz$ and $1.724 \times 10^6\ m^{-1}$ respectively)

Definition of Spectrum

A spectrum is an array of waves or particles which are spread out according to the increasing or decreasing order of some property such as wavelength or frequency or wave number.

Types of spectra

Depending on the nature of the source emitting the radiation, there are two types of spectra.

1. Emission spectra
   Emission spectra can be obtained from the substances which emit light on excitation. Their excitation can be done-as follows:
   a. By heating the liquid or solid substances in a flame at high temperature.
   b. By passing electric discharge through a gas at low pressure.
   c. By passing electric current through thin filament of a high melting point metal like Tungsten, when the filament becomes incandescent.
2. Absorption spectra

Emission spectra are further of two types:
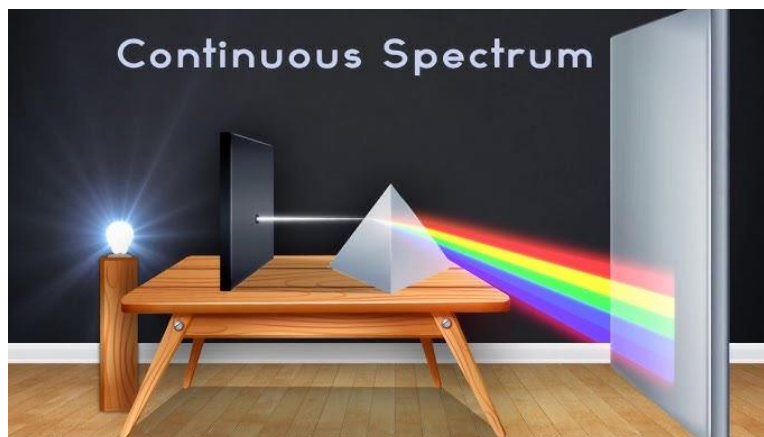
   i. Continuous spectra

Figure 7: Continuous spectrum
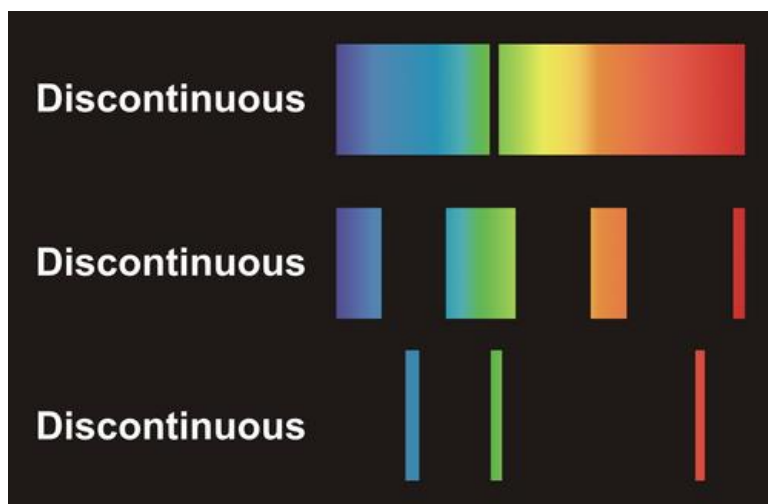
   ii. Discontinuous spectra

Figure 8: Discontinuous spectra

Discontinuous spectra may further be of two types.
   a. Band spectrum (molecular spectrum)
   b. Line spectra (atomic spectrum)

Principle of spectrophotometry[3]

When light (monochromatic or heterogeneous) falls upon a homogeneous medium, a portion of the incident light is reflected, a portion is absorbed within the medium, and a portion/remainder is transmitted through the medium. If the intensity of the incident light is expressed by I_o, that of the absorbed light by I_a, that of the transmitted light by I_t, and that of the reflected light by I_r, then:

$$I_0 = I_a + I_t + I_r \qquad (7)$$

For air-glass interfaces consequent upon the use of glass cells, it may be stated that about 4 percent of the incident light is reflected. I_r is usually eliminated by the use of a control, such as a comparison cell, hence:

$$I_0 = I_a + I_t \qquad (8)$$

Credit for investigating the change of absorption of light with the thickness of the medium is frequently given to Lambert, although he really extended concepts originally developed by Bouguer. Beer later applied similar experiments to solutions of different concentrations and published his results just prior to those of Bernard. The two separate laws governing absorption are usually known as Lambert's law and Beer's law. In the combined form they are referred to as Beer–Lambert Law.

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[3] Spectrophotometry is mainly

Lambert's Law

This law states that when a monochromatic light passes through a transparent medium, the rate of decrease in intensity of light with the thickness of the medium is proportional to the intensity of the light. This is equivalent stating that the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically, or that any layer of f=given thickness of the medium absorbs the same fraction of light incident upon it. We may express the law by the following differential equation:

$$-\frac{dI}{dl} \infty I$$

$$-\frac{dI}{dl} = kI \qquad (9)$$

Where I is the intensity of the incident light of wavelength λ, l is the thickness of the medium, and k is a proportionality constant. Integrating the equation (9) and putting $I = I_0 \ when \ l = 0$, we obtain:

$$\ln\frac{I_0}{I_t} = kl \qquad (10)$$

Or stated in other terms,

$$I_t = I_0 \cdot e^{-kl} \qquad (11)$$

Where, I_0 is the intensity of the incident light falling upon an absorbing medium of thickness l, I_t is the intensity of the transmitted light, and k is a constant for the wavelength of radiation and the absorbing medium used. By changing from natural to common logarithms we obtain:

$$I_t = I_0 \cdot 10^{-0.4343kl} = I_0 \cdot 10^{-Kl} \qquad (12)$$

Where, $K = k/2.303$ and is usually termed the **absorption coefficient**. The absorption coefficient is generally defined as the reciprocal of the thickness ($l \ cm$) required to reduce the light to $\frac{1}{10}$ of its intensity. This follows from equation (10), since:

$$\frac{I_t}{I_0} = 0.1 = 10^{-Kl} \ or \ Kl = 1 \ and \ K = \frac{1}{l}$$

The ratio I_t/I_0 is the fraction of the incident light transmitted by a thickness l of the n=medium and is termed the transmittance T. Its reciprocal I_0/I_t is the opacity, and the absorbance A of the medium (formerly called optical density D or extinction E) is given by:

$$A = \log\frac{I_0}{I_t} \qquad (13)$$

Thus, a medium with absorbance 1 for a given wavelength transmits 10 percent of the incident light at the wavelength in question.

Beer's law

We have so far considered the light absorption and the light transmission for monochromatic light as a function of the thickness of the absorbing layer only. In quantitative analysis, however, we are mainly concerned with solutions. Beer studied the effect of concentration of the colored constituent in the solution upon the light transmission or absorption. He found the same relation between transmission and concentration as Lambert had discovered between transmission and thickness of the layer, i.e., the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically. This may be written in the following form:

$$I_t = I_0 \cdot e^{-kc}$$
$$= I_0 \cdot 10^{-0.4343k'l} = I_0 \cdot 10^{-K'l}$$

(14)

Where c is the concentration of the substance in the solution, and k' and K' are constants. Combining equations (12) and (14), we obtain:

$$I_t = I_0 \cdot 10^{-acl}$$

(15)

$$Or, \qquad \log\frac{I_0}{I_t} = acl$$

(16)

This is the fundamental equation of colorimetry and spectrophotometry, and is often spoken of as the Beer–Lambert Law. The value of a will clearly depend upon the method of expression of the concentration. If c is expressed in mole/liter and l in cm then a is given the symbol ε and is called molar absorption coefficient or molar absorptivity (formerly molar extinction coefficient).

The specific absorption (or extinction) coefficient E_s (sometimes termed as absorbancy index) may be defined as the absorption per unit thickness (path length) and unit concentration.

It is apparent that there is a relationship between the absorbance A, the transmittance T, and the molar absorption coefficient, since:

$$A = \varepsilon cl = \log\frac{I_0}{I_t} = \log\frac{1}{T} = -\log T$$

(17)

Where T is the transmittance $T = \frac{I_t}{I_0}$.