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10.1 Introduction

Measurement based on light and other forms of electromagnetic radiation are widely used throughout analytical chemistry. The interaction of radiation and matter are the subject of the science called *spectroscopy*. Spectroscopic analytical methods are based on measuring the amount of radiation produced or absorbed by molecular or atomic species of interest.

We can classify spectroscopic methods according to the region of the electromagnetic spectrum involved in the measurement. The regions of the spectrum that have been used include γ -ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio-frequency (RF). Indeed, current usage extends the meaning of spectroscopy further to include techniques that do not even involve electromagnetic radiation, such as acoustic, mass, and electron spectroscopy.

10.2 Electromagnetic Radiation

Electromagnetic radiation, or light, is a form of energy whose behavior is described by the properties of both waves and particles. The optical properties of electromagnetic radiation, such as diffraction, are explained best by describing light as a wave. Many of the interactions between electromagnetic radiation and matter, such

as absorption and emission, however, are better described by treating light as a particle, or photon. Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

10.3 Wave Properties

In dealing with phenomena such as reflection, refraction, interference, and diffraction, electromagnetic radiation is conveniently modeled as wave consisting of perpendicularly oscillating electric and magnetic fields. The electric field for a single-frequency wave oscillates sinusoidally in space and time, as shown in Figure 10-1. The electric field is represented as a vector whose length is proportional to the field strength.



Figure 10-1 Radiation of Wavelength λ and Amplitude A. The arrows represent the electric vector of the radiation.

The *x*-axis in this plot is either time as the radiation passes a fixed point in space or distance at a fixed time. Note that the direction in which the field oscillates is perpendicular to the direction in which the radiation propagates.

10.4 Wave Characteristics

In Figure 10-1, the amplitude of the sine wave is shown, and the wavelength is defined. The time in seconds required for the passage of successive maxima or minima through a fixed point in space is called the *period*, p, of the radiation. The frequency, v, is the number of oscillations of the electric field vector per unit time and is equal to 1/p.

The frequency of a light wave, or any wave of electromagnetic radiation, is determined by the source that emits it and remains constant regardless of the medium traversed. In contrast, the velocity, v, of the wave front through a medium depends on both the medium and the frequency. The *wavelength*, λ , is the linear distance between successive maxima or minima of a wave, as shown in Figure 10-1. Multiplication

of the frequency (in waves per unit time) by the wavelength (in distance per wave) gives the velocity of the wave, in distance per unit time (cm s^{-1} or m s^{-1}), as shown in the equation:

$$v = v \lambda \dots 1$$

Table 10-1 gives the wavelength units for several spectral regions.

Region	Unit	Definition
X-ray	Angstrom, A ^o	10 ⁻¹⁰ m
Ultraviolet/visible	Nanometer, nm	10 ⁻⁹ m
Infrared	Micrometer, µm	10 ⁻⁶ m

 Table 10-1 Wavelength Units for Various Regions

10.5 The Speed of Light

In a vacuum, light travels at its maximum velocity. This velocity, which is given the special symbol c, is 2.99792×10^8 m s⁻¹. The velocity of light in air is only about 0.03% less than its velocity in a vacuum. Thus, for a vacuum or for air, Equation 1 conveniently gives the velocity of light.

$$c = v \lambda \dots 2$$

 $= 3.00 \times 10^8 \text{ m s}^{-1} = 3.00 \times 10^{10} \text{ cm}$

s⁻¹

In the medium containing matter, light travels, with a velocity less than c because of interaction between the electromagnetic field and electrons in the atoms or molecules of the medium. Since the frequency of the radiation is constant, the wavelength must decrease as the light passes from a vacuum to a medium containing matter.

The wavenumber \bar{v} is another way to describe electromagnetic radiation. It is defined as the number of waves per centimeter and is equal to $1/\lambda$. By definition, \bar{v} has the units of cm⁻¹.

10.6 Radiant Power and Intensity

The *radiant power* p in watts (W) is the energy of a beam that reaches a given area per unit time. The *intensity* is the radiant power-per-unit solid angle (Solid angle is the three dimensional spread at the vertex of a cone measured as the area intercepted by the cone on a unit sphere whose center is at the vertex). Both quantities are proportional to the square of the amplitude of the electric field. Although it is not strictly correct, radiation power and intensity are frequently used interchangeably.

10.7 The Particle Nature of Light: Photons

In many radiation/matter interactions, it is most useful to consider light as consisting of photons or quanta. We can relate the energy of a photon to its wavelength, frequency, and wavenumber by:

where *h* is Planck's constant (6.63×10^{-34} J s). Note that the wavenumber and frequency, in contrast to the wavelength, are directly proportional to the photon energy. Wavelength is inversely proportional to energy. The radiant power of a beam of radiation is directly proportional to the number of photon per second.

Example 1

Calculate the wavenumber of a beam of infrared radiation with a wavelength of $5.00 \,\mu$ m.

$$\bar{v} = \frac{1}{5.00 \ \mu m \times 10^{-4} \ cm/\mu m} = 2000 \ cm^{-1}$$

Example 2

Calculate the energy in joules of one photon of the radiation, if the wavenumber is 2000 cm⁻¹.

$$E = hc\bar{v}$$

= 6.63 × 10⁻³⁴ J.s × 3.00 × 10¹⁰ cm/s × 2000

cm⁻¹

 $= 3.98 \times 10^{-20} \text{ J}$

10.8 Interaction of Radiation and Matter

The most interesting types of interactions in spectroscopy involve transitions between different energy levels of chemical species. Other types of interactions, such as reflection, refraction, elastic scattering, interference, and diffraction, are often related to the bulk properties of materials rather than to energy levels of specific molecules or atoms. Although these bulk interactions are also of interest in spectroscopy, we limit our discussion here to those interactions that involve energy-level transitions. The specific types of interactions that we observe depend strongly on the energy of the radiation used and the mode of direction.

10.9 The Electromagnetic Spectrum

The electromagnetic spectrum covers an enormous range of energies (frequencies) and thus wavelengths (Table 10-2). Useful frequencies vary from >10¹⁹ Hz (γ -ray) to 10³ Hz (radio waves). An X-ray photon ($v \approx 3 \times 10^{18}$ Hz, $\lambda \approx 10^{-10}$ m), for example, is approximately 10,000 times as energy as a photon emitted by an ordinary light bulb ($v \approx 3 \times 10^{14}$ Hz, $\lambda \approx 10^{-6}$ m) and 10¹⁵ times as energetic as a radio-frequency photon ($v \approx 3 \times 10^{3}$ Hz, $\lambda \approx 10^{5}$ m).

The visible portion, to which our eyes respond, is only a minute portion of the entire spectrum. Such different types of radiation as gamma (γ) rays or radio waves differ from visible light in the energy (frequency) of their photons.

Region	Wavelength Range
UV	180-380 nm
Visible	380-780 nm
Near-IR	0.78-2.5 μm
Mid-IR	2.5-50 μm

Table 10-2 Regions of the UV, Visible, and IR Spectrum

Figure 10-2 shows the regions of the electromagnetic spectrum that are used for spectroscopic analysis. Also shown are the types of atomic and molecular transition that result from the interactions of the radiation with sample. Note that the low-energy radiation used in nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy causes subtle changes, such as changes in spin; the high-energy radiation used in γ -ray spectroscopy can produce much more dramatic effects, such as nuclear configuration changes.

Note that spectrochemical methods that use not only visible but also ultraviolet and infrared radiation are often called optical methods in spite of the fact that the human eye is sensitive to neither of the latter two types of radiation.

10.10 Spectroscopic Measurements

Spectroscopists use the interactions of radiation with matter to obtain information about a sample. Several of the chemical elements were discovered by spectroscopy. The sample is usually stimulated in some way by applying energy in the form of heat, electrical energy, light, particles or a chemical reaction. Prior to applying the stimulus, the analyte is predominantly in its lowest energy state, or *ground state*. The stimulus then causes some of the analyte species to undergo a transition to a higher energy or *excited state*. We acquire information about the analyte by measuring the electromagnetic radiation emitted as it returns to the ground state or by measuring the amount of electromagnetic radiation absorbed as a result of excitation.



Figure 10-2 The Regions of the Electromagnetic Spectrum. Interaction of an analyte with electromagnetic radiation can result in the types of changes shown.

Figure 10-3 illustrates the processes involved in emission and chemiluminescence spectroscopy. Here, the analyte is stimulated by heat or electrical energy or by a chemical reaction. *Emission spectroscopy* involves methods in which the stimulus is heated or electrical energy, while *chemiluminescence spectroscopy* refers to excitation of the analyte by a chemical reaction. In both cases, measurement of the radiant power emitted as the analyte returns to the ground state can give information about its identity and concentration. The results of such a measurement are often expressed graphically by a *spectrum*, which is a plot of the emitted radiation as a function of frequency or wavelength.



Figure 10-3 Emission or Chemiluminescence Processes. In (a), the sample is excited by the application of thermal, electrical, or chemical energy. These processes do not involve radiant energy and are hence called nonradiative processes. In the energy-level diagram (b), the dashed lines with upward pointing arrows symbolize these nonradiative excitation processes, while the solid lines with downward pointing arrows indicate that the analyte losses its energy by emission of a photon. In (c), the resulting spectrum is shown as a measurement of the radiant power emitted P_E as a function of wavelength, λ .

When the sample is stimulated by application of an external electromagnetic radiation source, several processes are possible. For example, the radiation can be scattered or reflected. What is important to us is that some of the incident radiation can be absorbed and thus promote some of the analyte species to an excited state, as shown in Figure 10-4.



Figure 10-4 Absorption Methods. In (a) radiation of incident radiant power P_0 can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power P. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b).The resulting absorption spectrum is shown in (c).

In *absorption spectroscopy*, we measure the amount of light absorbed as a function of wavelength. In *photoluminescence spectroscopy* (Figure 10-5), the emission of photon is measured after absorption. The most important forms of photoluminescence for analytical chemistry purposes are *fluorescence* and *phosphorescence spectroscopy*.



Figure 10-5 Photoluminescence Methods (Fluorescence and Phosphorescence). They result from absorption of electromagnetic radiation and then dissipation of the energy by emission of radiation (a). In (b), the absorption can cause excitation of the analyte to state 1 or state 2. Once excited, the excess energy can be lost by emission of a photon (luminescence, shown as solid line) or by nonradiative processes (dashed lines). The emission occurs over all angles, and the wavelengths emitted (c) correspond to energy differences between levels. The major distinction between fluorescence and phosphorescence is the time scale of emission, with fluorescence being prompt and phosphorescence being delayed.

10.11 The Absorption of Radiation

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. 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.

Figure 10-6 depicts the attenuation of a parallel beam of *monochromatic radiation* as it passes through an absorbing solution of thickness *b* centimeters and concentration *c* moles per liter. Because of interaction between the photons and absorbing particles, the radiant power of the beam decreases from P_o to *P*. The *transmittance T* of the solution is the fraction of incident radiation transmitted by the solution. Transmittance is often expressed as a percentage called the percent transmittance.

The *absorbance* A of a solution is related to the transmittance in a logarithmic manner as shown in Equation 5. Notice that as the absorbance of a solution increases, the transmittance decreases.



Figure 10-6 Attenuation of a Beam of Radiation by an Absorbing Solution. The larger arrow on the incident beam signifies a higher radiant power than is transmitted by the solution. The path length of the absorbing solution is b, and the concentration is c.

10.12 Measuring Transmittance and Absorbance

Ordinarily, transmittance and absorbance, as defined by equations 4 and 5, cannot be measured because the solution to be studied must be held in some sort of container (cell or cuvette). Reflection and scattering losses can occur at the cell walls. These losses can be substantial. For example, about 8.5% of the beam of yellow light is lost by reflection when it passes through a glass cell. Light can also be scattered in all directions from the surface of large molecules or particles (such as dust) in the solvent and this scattering can cause further attenuation of the beam as it passes through the solution.

The compensate for these effects, the power of the beam transmitted through a cell containing the analyte solution is compared with one that traverses either an identical cell containing only the solvent or a reagent blank. An experimental absorbance that closely approximates the true absorbance for the solution is thus obtained; that is:

$$A = \log - \approx \log \frac{P_0}{P} \frac{P_{\text{solvent}}}{P} \frac{P_{s$$

The term P_0 and P will henceforth refer to the power of a beam that has passed through cells containing the blank (solvent) and the analyte, respectively.

10.13 Beer's Law

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 Equation 7.

Here, *a* is a proportionality constant called the *absorptivity*. Because absorbance is a unitless quantity, the absorptivity must have units that cancel the units of *b* and *c*. If, for example, *c* has the units of g L⁻¹ and *b* has the units of cm, absorptivity has the units of L g⁻¹ cm⁻¹.

When we express the concentration in Equation 7 in moles per liter and *b* in centimeters, the proportionality constant is called the *molar absorptivity* and is given the special symbol, ε . Thus:

 $A = \varepsilon b c$

where ε has the units of L mol⁻¹ cm⁻¹.

10.14 Absorption Spectra

An absorption spectrum is a plot of absorbance versus wavelength. Absorbance could also be plotted against wavenumber or frequency. Most modern scanning spectrophotometers produce such an absorption spectrum directly.

10.15 Atomic Absorption

When a beam of polychromic ultraviolet or visible radiation passes medium containing gaseous atoms, only a few frequencies are attenuated by absorption. When recorded on a very high resolution spectrometer, the spectrum consists of a number of very narrow absorption lines.

10.16 Emission Spectra

Atoms, ions, and molecules can be excited to one or more higher energy levels by any of several processes, including bombardment with electron or other elementary particles; exposure to a high-temperature plasma, flame or electric arc; or exposure to a source of electromagnetic radiation. Radiation from a source is conveniently characterized by means of an emission spectrum, which usually takes the form of a plot of the relative power of the emitted radiation as a function of wavelength or frequency.