**Unit: 6.1**

**Introduction to Spectroscopy**

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* 1. **The Nature of Electromagnetic Radiation:**

Visible light is a complex phenomenon that is classically explained with a simple model based on propagating rays and wave fronts, a concept first proposed in the late 1600s by Dutch physicist Christiaan Huygens. Electromagnetic radiation, the larger family of wave-like phenomena to which visible light belongs (also known as **radiant energy**), is the primary vehicle transporting energy through the vast reaches of the universe. The mechanisms by which visible light is emitted or absorbed by substances, and how it predictably reacts under varying conditions as it travels through space and the atmosphere, form the basis of the existence of color in our universe.



The term **electromagnetic radiation**, coined by Sir James Clerk Maxwell, is derived from the characteristic electric and magnetic properties common to all forms of this wave-like energy, as manifested by the generation of both electrical and magnetic oscillating fields as the waves propagate through space. Visible light represents only a small portion of the entire spectrum of electromagnetic radiation (as categorized in Figure 1), which extends from high-frequency cosmic and gamma rays through X-rays, ultraviolet light, infrared radiation, and microwaves, down to very low frequency long-wavelength radio waves.

The link between light, electricity, and magnetism was not immediately obvious to early scientists who were experimenting with the fundamental properties of light and matter. Infrared light, which lies beyond the longer red wavelengths of visible light, was the first "invisible" form of electromagnetic radiation to be discovered. British scientist and astronomer William Herschel was investigating the association between heat and light with a thermometer and a prism when he found that the temperature was highest in the region just beyond the red portion of the visible light spectrum. Herschel suggested that there must be another type of light in this region that is not visible to the naked eye.

Ultraviolet radiation, at the other end of the visible spectrum, was discovered by Wilhelm Ritter, who was one of the first scientists to investigate the energy associated with visible light. By observing the rate at which various colors of light stimulate darkening of paper saturated with a solution of silver nitrate, Ritter discovered that another invisible form of light, beyond the blue end of the spectrum, yielded the fastest rates.

[**Electromagnetic Wave Propagation**](https://www.olympus-lifescience.com/microscope-resource/primer/java/electromagnetic/)**:**

Electricity and magnetism were first associated in 1820 when Danish physicist Hans Christian Oersted discovered that electrical current flowing through a wire could produce deflections of a compass needle. Later that same year, French scientist André-Marie Ampère demonstrated that two wires carrying electrical currents could be made to attract or repel each other, in a fashion similar to that of magnetic poles. During the next few decades, additional investigations following these leads produced an increasing amount of evidence that electricity and magnetism were very closely related to each other.

Finally, in 1865, Scottish scientist James Clerk Maxwell expanded his kinetic theory of gases to mathematically explain the links between electricity and magnetism. Maxwell speculated that the two phenomena were so closely bound that they often acted together as **electromagnetism**, and discovered that alternating current would produce waves composed of both entities that radiated out into space at the speed of light. From these observations, he concluded that visible light was a form of electromagnetic radiation.

An electromagnetic wave travels or **propagates** in a direction that is oriented at right angles to the vibrations of both the electric (**E**) and magnetic (**B**) oscillating field vectors, transporting energy from the radiation source to an undetermined final destination. The two oscillating energy fields are mutually perpendicular (Figure 2) and vibrate in phase following the mathematical form of a sine wave. Electric and magnetic field vectors are not only perpendicular to each other, but are also perpendicular to the direction of wave propagation. By convention, and to simplify illustrations, the vectors representing the electric and magnetic oscillating fields of electromagnetic waves are often omitted, although they are understood to still exist.



Whether taking the form of a signal transmitted to a radio from the broadcast station, heat radiating from a fireplace, the dentist's X-rays producing images of teeth, or the visible and ultraviolet light emanating from the sun, the various categories of electromagnetic radiation all share identical and fundamental wave-like properties. Every category of electromagnetic radiation, including visible light, oscillates in a periodic fashion with peaks and valleys (or troughs), and displays a characteristic **amplitude**, **wavelength**, and **frequency** that together define the direction, energy, and intensity of the radiation.

A standard measure of all electromagnetic radiation is the magnitude of the **wavelength** (in a vacuum), which is usually stated in units of nanometers (one-thousandth of a micrometer) for the visible light portion of the spectrum. The wavelength is defined as the distance between two successive peaks (or valleys) of the waveform (see Figure 2). The corresponding **frequency** of the radiated wave, which is the number of sinusoidal cycles (oscillations or complete wavelengths) that pass a given point per second, is proportional to the reciprocal of the wavelength. Thus, longer wavelengths correspond to lower frequency radiation and shorter wavelengths correspond to higher frequency radiation. Frequency is usually expressed in quantities of **hertz** (**Hz**) or cycles per second (**cps**).

The hertz was designated as a standard unit of electromagnetic radiation frequency in recognition of the work of German physicist Heinrich Hertz, who succeeded in generating and performing experiments with electromagnetic waves in 1887, eight years after the death of Maxwell. Hertz produced, detected, and even measured the wavelength (approximately one meter) of radiation that is now classified in the radiofrequency range. David Hughes, a London-born scientist who was a music professor in his early career, may have actually been the first investigator to succeed in the transmission of radio waves (in 1879), but after failing to convince the Royal Society, he decided not to publish his work, and it wasn't recognized until many years later.

[**Basic Electromagnetic Wave Properties**](https://www.olympus-lifescience.com/microscope-resource/primer/java/wavebasics/)**:**

Understood how the frequency, energy, and wavelength of an electromagnetic wave are related and how changing one automatically produces a corresponding change in the other two (and the color of visible light).

The different wavelengths and frequencies comprising the various forms of electromagnetic radiation are fundamentally similar in that they all travel at the same speed—about 186,000 miles per second (or approximately 300,000 kilometers per second), a velocity commonly known as the speed of light (and designated by the symbol **c**). Electromagnetic radiation (including visible light) travels 149 million kilometers (93 million miles) from the sun to Earth in about 8 minutes. In contrast, an automobile speeding at 100 kilometers per hour (60 miles per hour) would require 177 years to make the same one-way trip. In only one second, light can circumnavigate the Earth seven times.

The wavelength of light, and all other forms of electromagnetic radiation, is related to the frequency by a relatively simple equation:

ν = c/λ

where *c* is the speed of light (in meters per second), *ν* is the frequency of the light in hertz (Hz), and *λ* is the wavelength of the light measured in meters.

 From this relationship one can conclude that the wavelength of light is inversely proportional to frequency. An increase in frequency produces a proportional decrease in the wavelength of light, with a corresponding increase in the energy of photons that comprise the light. Upon entering a new medium (such as glass or water from air), the speed and wavelength of light is reduced, although the frequency remains unaltered.

Under normal circumstances, when traveling through a uniform medium, such as air or a vacuum, light propagates in straight lines until interaction with another medium or material induces a path change, through **refraction** (bending) or **reflection**. The intensity may be also reduced as a result of **absorption** by the medium. If the light waves pass through a narrow slit or aperture (hole), then they can be **diffracted** or dispersed (scattered) to form a characteristic diffraction pattern. In accordance with the well-known **inverse square law**, the intensity (or irradiance) of electromagnetic radiation is inversely proportional to the square of the distance traveled. Thus, after light has traveled twice a given distance, the intensity drops by a factor of four.



Visible light displays classical wave-like properties, but it also exhibits properties reminiscent of particles, which are manifested through entities that possess energy and momentum (but no mass), and are referred to as **photons**. The atom is the source of all forms of electromagnetic radiation, whether visible or invisible. Higher-energy forms of radiation, such as gamma waves and X-rays, are produced by events that occur to disrupt the nuclear stability of the atom. Radiation having lower energy, such as ultraviolet, visible, and infrared light, as well as radio and microwaves, originate from the electron clouds that surround the nucleus or the interaction of one atom with another. These forms of radiation occur due to fact that electrons moving in orbits around the nucleus of an atom are arranged in different energy levels within their probability distribution functions. Many of the electrons can absorb additional energy from external sources of electromagnetic radiation (Figure 3), which results in their promotion to an inherently unstable higher energy level.

Eventually, the "excited" electron loses the extra energy by emitting electromagnetic radiation of lower energy and, in doing so, falls back into its original and stable energy level. The energy of the emitted radiation equals the energy that was originally absorbed by the electron minus other small quantities of energy lost through a number of secondary processes.

Electromagnetic radiation energy levels can vary to a significant degree depending upon the energy of source electrons or nuclei. For example, radio waves possess significantly less energy than do microwaves, infrared rays, or visible light, and all of these waves contain far less energy than ultraviolet light, X-rays, and gamma waves. As a rule, higher electromagnetic radiation energies are associated with shorter wavelengths than similar forms of radiation having lower energy. The relationship between the energy of an electromagnetic wave and its frequency is expressed by the equation**:**

E = *h*ν = *h*c/λ

where *E* is the energy in kilojoules per mole, *h* is Planck's constant, and the other variables are defined as discussed previously. Based on this equation, the energy of an electromagnetic wave is directly proportional to its frequency and inversely proportional to the wavelength. Thus, as frequency increases (with a corresponding decrease in wavelength), the electromagnetic wave energy increases, and vice versa. Selected characteristics of the different types of electromagnetic radiation, as defined by their wavelength, frequency, and energy levels, will be reviewed individually in the following paragraphs.

Even though electromagnetic radiation is customarily described by the wavelength and frequency of the waveforms, other characteristic properties are important when considering how waves propagate through space. Presented in Figure 4 are various waveforms representing common states that are utilized to describe the degree of uniformity of electromagnetic radiation. Because visible light is the most commonly discussed form of radiation, the examples illustrated in Figure 4 are representative of wavelengths in this spectral region. For example, **monochromatic** light consists of waves all having the same wavelength and frequency, or macroscopically, the same color in visible light. In contrast, **polychromatic** visible light usually appears as **white** due to contributions from the mixture of all or most wavelengths in the spectrum ranging between 400 and 700 nanometers.



When light is **non-polarized** (Figure 4), the electric field vectors vibrate in all planes lying perpendicular to the direction of propagation. Light that has been reflected from a smooth surface at a critical angle, or passed through polarizing filters, assumes a **plane-polarized** orientation with all of the electric vectors vibrating in a single plane perpendicular to the direction of propagation. Light from the sun, and a majority of the common incandescent and fluorescent visible light sources, is non-polarized, while light seen through polarizing lenses of custom sunglasses is polarized in the vertical direction. In some instances, light can be elliptically or circularly polarized when it passes through materials that have more than one refractive index (**birefringent** or **doubly refracting** substances).

Most artificial and natural light sources emit **non-coherent** light that displays a variety of phase relationships among the wavelengths present in the spectrum (Figure 4). In this case, the peaks and valleys of the vibrational states in individual waves do not coincide in either space or time. **Coherent** light is composed of wavelengths that are in phase with each other, and behaves in a very different manner than non-coherent light with respect to the optical properties and interaction with matter. Wave fronts produced by coherent light have electric and magnetic vector vibrations that oscillate in phase, have low divergence angles, and are usually composed of monochromatic light or wavelengths that have a narrow distribution. Lasers are a common source of coherent light.

Light waves that have coaxial, relatively non-diverging paths as they travel through space are termed **collimated**. This organized form of light does not spread or converge to a significant degree over comparatively long distances. Collimated light forms a very tight beam, but does not necessarily have a narrow band of wavelengths (nor must it be monochromatic), a common phase relationship, or a defined state of polarization. Wave fronts of collimated light are planar and perpendicular to the axis of propagation. In contrast, **divergent** or non-collimated light spreads to varying degrees while traveling through space, and must be passed through a lens or aperture in order to be collimated or focused.

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