chapter**SIX**

An Introduction to Spectrometric Methods

This chapter treats in a general way the interactions of electromagnetic waves with atoms and molecules. After this introduction to spectrometric methods, the next six chapters describe spectrometric methods used by scientists for identifying and determining the elements present in various forms of matter. Chapters 13 through 21 then discuss the uses of spectrometry for structural determination of molecular species and describe how these methods are used for their quantitative determination.

Throughout this chapter, this logo indicates an opportunity for online self-study at **www.tinyurl.com/skoogpia7**, linking you to interactive tutorials, simulations, and exercises.

Spectrometric methods encompass a large group of analytical methods based on atomic and molecular spectroscopy. *Spectroscopy* is a general term for the science of the interactions of radiation with matter. Historically, the interactions of interest were between electromagnetic radiation and matter, but now spectroscopy has been broadened to include interactions between matter and other forms of energy. Examples include acoustic waves and beams of particles such as ions and electrons. *Spectrometry* and *spectrometric methods* refer to the measurement of the intensity of radiation with a photoelectric transducer or other type of electronic device.

The most widely used spectrometric methods are based on electromagnetic radiation, which is a type of energy that takes several forms, the most readily recognizable being light and radiant heat. Less obvious manifestations include gamma rays and X-rays as well as ultraviolet, microwave, and radiofrequency radiation.

6A GENERAL PROPERTIES OF ELECTROMAGNETIC RADIATION

Many of the properties of electromagnetic radiation are conveniently described by means of a classical sinusoidal wave model, which embodies such characteristics as wavelength, frequency, velocity, and amplitude. In contrast to other wave phenomena, such as sound, electromagnetic radiation requires no supporting medium for its transmission and thus passes readily through a vacuum.

The wave model fails to account for phenomena associated with the absorption and emission of radiant energy. To understand these processes, it is necessary to invoke a particle model in which electromagnetic radiation is viewed as a stream of discrete particles, or wave packets, of energy called *photons*. The energy of a photon is proportional to the frequency of the radiation. These dual views of radiation as particles and as waves are not mutually exclusive but are complementary. Indeed, the wave-particle duality applies to the behavior of streams of electrons, protons, and other elementary particles and is completely explained by quantum mechanics.

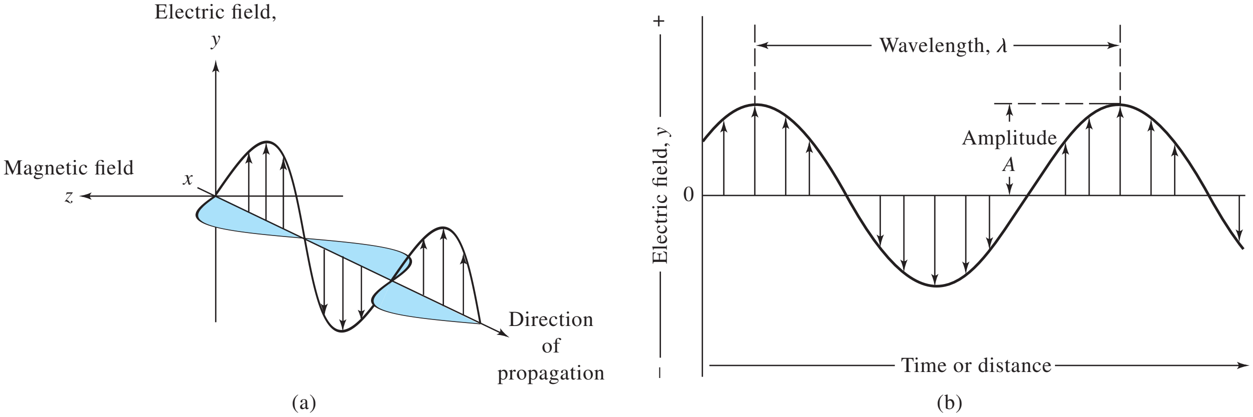


FIGURE 6-1 Wave nature of a beam of single-frequency electromagnetic radiation. In (a), a plane-polarized wave is shown propagating along the *x*-axis. The electric field oscillates in a plane perpendicular to the magnetic field. If the radiation were unpolarized, a component of the electric field would be seen in all planes. In (b), only the electric field oscillations are shown. The amplitude of the wave is the length of the electric field vector at the wave maximum, while the wavelength is the distance between successive maxima.

6B WAVE PROPERTIES OF ELECTROMAGNETIC RADIATION

For many purposes, electromagnetic radiation is conveniently represented as electric and magnetic fields that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation. Figure 6-1a is such a representation of a single ray of plane-polarized electromagnetic radiation. The term *plane polarized* implies that all oscillations of either the electric or the magnetic field lie in a single plane. Figure 6-1b is a two-dimensional representation of the electric component of the ray in Figure 6-1a. The electric field strength in Figure 6-1 is represented as a vector whose length is proportional to its magnitude (blue arrows). The abscissa of this plot is either time as the radiation passes a fixed point in space or distance traveled at a fixed point in time. Throughout this chapter and most of the remaining text, only the electric component of radiation will be considered because the electric field is responsible for most of the phenomena that are of interest to us, including transmission, reflection, refraction, and absorption. Note, however, that the magnetic component of electromagnetic radiation is responsible for absorption of radio-frequency waves in nuclear magnetic resonance (see Chapter 19).

6B-1 Wave Characteristics

In Figure 6-1b, the *amplitude A* of the sinusoidal wave is shown as the length of the electric vector at a maximum in the wave. 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* ν is the number of oscillations of the field that occur per second[1] and is equal to $1/p$.

The *wavelength* λ is the linear distance between any two equivalent points on successive waves (e.g., successive maxima or minima).[2] Multiplication of the frequency in cycles per second by the wavelength in meters per cycle gives the *velocity of propagation* v_i in meters per second:

$$v_i = \nu\lambda_i \tag{6-1}$$

It is important to realize that the frequency of a beam of radiation is determined by the source and *remains invariant*. In contrast, the velocity of radiation depends on the composition of the medium through which it passes. Thus, Equation 6-1 implies that the wavelength of radiation also depends on the medium. The subscript i in Equation 6-1 indicates these dependencies.

In a vacuum, the velocity of radiation is independent of wavelength and is at its maximum. This velocity, given the symbol c, is 2.99792×10^8 m/s. It is significant that the velocity of radiation in air differs only slightly from c (about 0.03% less). Thus, for either air or vacuum, Equation 6-1 can be written to three significant figures as

$$c = \nu\lambda = 3.00 \times 10^8\,\text{m/s} = 3.00 \times 10^{10}\,\text{cm/s} \tag{6-2}$$

In any medium containing matter, propagation of radiation is slowed by the interaction between the electromagnetic field of the radiation and the bound electrons in the matter. Since the radiant frequency is invariant and fixed by the source, the wavelength must decrease as radiation passes from a vacuum to another medium (Equation 6-2). This effect is illustrated in

---

[1] The common unit of frequency is the reciprocal second (s^{-1}), or *hertz* (Hz), which corresponds to one cycle per second.

[2] The units commonly used for describing wavelength differ considerably in the various spectral regions. For example, the angstrom unit, Å (10^{-10} m), is convenient for X-ray and short ultraviolet radiation; the nanometer, nm (10^{-9} m), is used with visible and ultraviolet radiation; the micrometer, µm (10^{-6} m), is useful for the infrared region. (The *micrometer* was called *micron* in the early literature; use of this term is discouraged.)

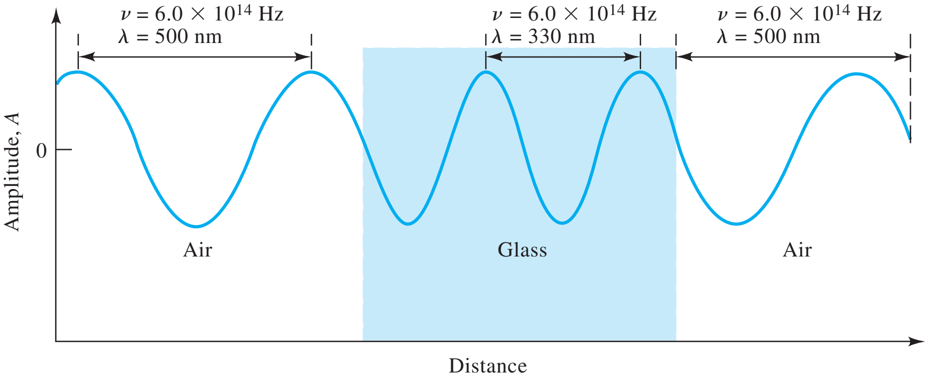


FIGURE 6-2 Change in wavelength as radiation passes from air into a dense glass and back to air. Note that the wavelength shortens by nearly 200 nm, or more than 30%, as it passes into glass; a reverse change occurs as the radiation again enters air.

Figure 6-2 for a monochromatic beam of visible radiation.[3] Note that the wavelength shortens nearly 200 nm, or more than 30%, as it passes into glass. The reverse change occurs as the radiation passes back into the air from the glass.

The *wavenumber* $\bar{\nu}$, which is defined as the reciprocal of the wavelength in centimeters, is yet another way of describing electromagnetic radiation. The unit for $\bar{\nu}$ is cm^{-1}. Wavenumber is widely used in infrared spectroscopy. The wavenumber is a useful unit because, in contrast to wavelength, it is directly proportional to the frequency, and thus the energy, of radiation. Thus, we can write

$$\bar{\nu} = k\nu \qquad (6\text{-}3)$$

where the proportionality constant k depends on the medium and is equal to the reciprocal of the velocity (Equation 6-1).

The *power* P of radiation is the energy of the beam that reaches a given area per second, whereas the *intensity* I is the power per unit solid angle. These quantities are related to the square of the amplitude A (see Figure 6-1). Although it is not strictly correct to do so, power and intensity are often used interchangeably.

6B-2 The Electromagnetic Spectrum

As shown in Figure 6-3, the electromagnetic spectrum encompasses an enormous range of wavelengths and frequencies (and thus energies). In fact, the range is so great that a logarithmic scale is required to represent it. Figure 6-3 also depicts qualitatively the major spectral regions. The divisions are based on the methods used to generate and detect the various kinds of radiation. Several overlaps are evident. Note that the portion of the spectrum visible to the human eye is tiny when compared with other spectral regions. Also note that spectrochemical methods using not only visible but also ultraviolet and infrared radiation are often called *optical methods* despite the human eye's inability to sense either of the latter two types of radiation. This somewhat ambiguous terminology arises from the many common features of instruments for the three spectral regions and the similarities in how we view the interactions of the three types of radiation with matter.

Table 6-1 lists the wavelength and frequency ranges for the regions of the spectrum that are important for analytical purposes and also gives the names of the various spectroscopic methods associated with each. The last column of the table lists the types of nuclear, atomic, or molecular quantum transitions that serve as the basis for the various spectroscopic techniques.

6B-3 Mathematical Description of a Wave

With time as a variable, the wave in Figure 6-1b can be described by the equation for a sine wave. That is,

$$y = A \sin(\omega t + \phi) \qquad (6\text{-}4)$$

where y is the magnitude of the *electric field* at time t, A is the amplitude or maximum value for y, and ϕ is the *phase angle*, a term defined in Section 2B-1, page 30. The angular velocity of the vector ω is related to the frequency of the radiation ν by the equation

$$\omega = 2\pi\nu$$

Substitution of this relationship into Equation 6-4 yields

$$y = A \sin(2\pi\nu t + \phi) \qquad (6\text{-}5)$$

6B-4 Superposition of Waves

The *principle of superposition* states that when two or more waves traverse the same space, a disturbance occurs that is the sum of the disturbances caused by the individual waves. This principle applies to electromagnetic waves, in which the disturbances involve an electric field, as well as to several other types of waves,

Exercise: Learn more about the **electromagnetic spectrum** at www.tinyurl.com/skoogpia7

---

[3] A *monochromatic* beam is a beam of radiation whose rays have identical wavelengths. A *polychromatic* beam is made up of rays of different wavelengths.

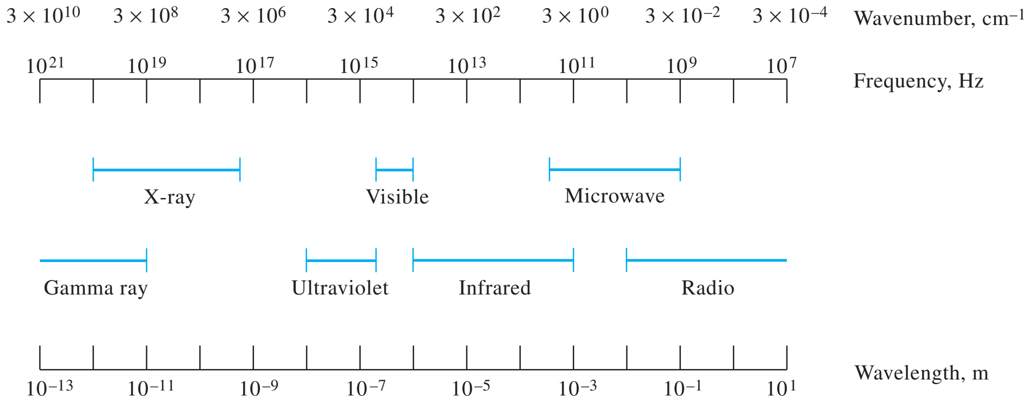


FIGURE 6-3 Regions of the electromagnetic spectrum.

TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type of Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, cm^{-1}	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	—	Nuclear
X-ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	—	Inner electron
Vacuum ultraviolet absorption	10–180 nm	1×10^6 to 5×10^4	Bonding electrons
Ultraviolet-visible absorption, emission, and fluorescence	180–780 nm	5×10^4 to 1.3×10^4	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 μm	1.3×10^4 to 3.3×10^1	Rotation/vibration of molecules
Microwave absorption	0.75–375 mm	13–0.03	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	1.7×10^{-2} to 1×10^3	Spin of nuclei in a magnetic field

*1 Å = 10^{-10} m = 10^{-8} cm
1 nm = 10^{-9} m = 10^{-7} cm
1 μm = 10^{-6} m = 10^{-4} cm

in which atoms or molecules are displaced. When n electromagnetic waves differing in frequency, amplitude, and phase angle pass some point in space simultaneously, the principle of superposition and Equation 6-5 permit us to write

$$y = A_1 \sin(2\pi\nu_1 t + \phi_1) + A_2 \sin(2\pi\nu_2 t + \phi_2) + \cdots + A_n \sin(2\pi\nu_n t + \phi_n) \qquad (6\text{-}6)$$

where y is the resultant field.

The black curve in Figure 6-4a shows the application of Equation 6-6 to two waves of identical frequency but somewhat different amplitude and phase angle. The resultant is a periodic function with the same frequency but larger amplitude than either of the component waves. Figure 6-4b differs from 6-4a in that the phase difference is greater; in this case, the resultant amplitude is smaller than the amplitudes of the component waves. A maximum amplitude occurs when the two waves are completely in phase—a situation that occurs whenever the phase difference between waves $(\phi_1 - \phi_2)$ is 0°, 360°, or an integer multiple of 360°. Under these circumstances, maximum *constructive interference* is said to occur. A maximum *destructive interference* occurs when $(\phi_1 - \phi_2)$ is equal to 180° or 180° plus an

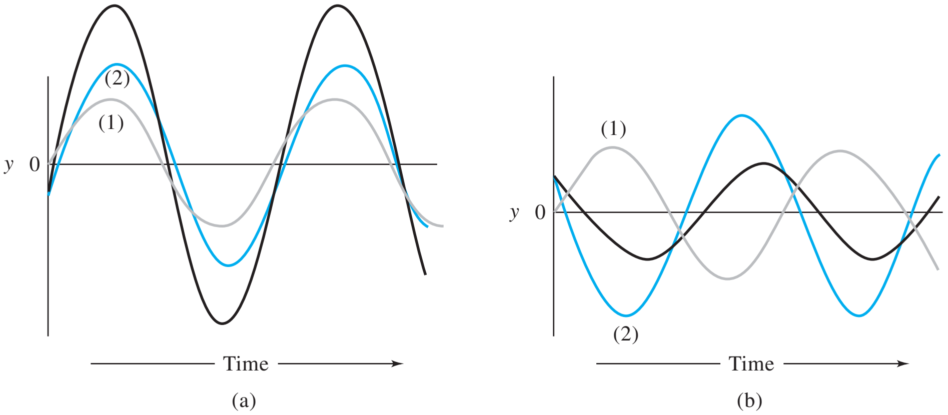


FIGURE 6-4 Superposition of sinusoidal wave: (a) $A_1 < A_2$, $(\phi_1 - \phi_2) = 20°$, $\nu_1 = \nu_2$; (b) $A_1 < A_2$, $(\phi_1 - \phi_2) = 200°$, $\nu_1 = \nu_2$. In each instance, the black curve results from the combination of the two other curves.

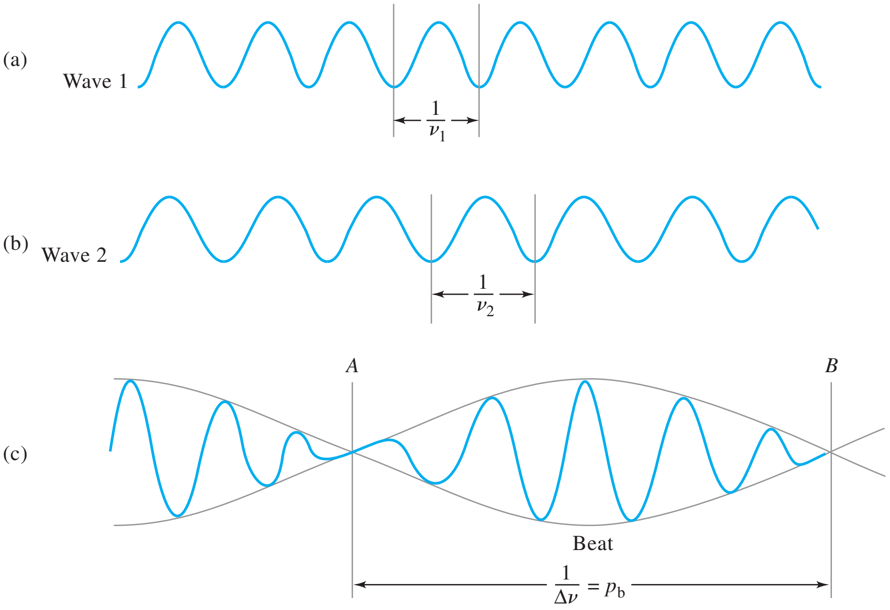


FIGURE 6-5 Superposition of two waves of different frequencies but identical amplitudes: (a) wave 1 with a period of $1/\nu_1$; (b) wave 2 with a period of $1/\nu_2$ $(\nu_2 = 1.25\nu_1)$; (c) combined wave pattern. Note that superposition of ν_1 and ν_2 produces a beat pattern with a period of $1/\Delta\nu$ where $\Delta\nu = |\nu_1 - \nu_2|$.

integer multiple of 360°. Interference plays an important role in many instrumental methods based on electromagnetic radiation.

Figure 6-5 depicts the superposition of two waves with identical amplitudes but different frequencies. The resulting wave is no longer sinusoidal but does exhibit a periodicity, or *beat*. Note that the period of the beat p_b is the reciprocal of the frequency difference $\Delta\nu$ between the two waves. That is,

$$p_b = \frac{1}{\Delta\nu} = \frac{1}{(\nu_2 - \nu_1)} \tag{6-7}$$

Simulation: Learn more about **superposition of waves** at www.tinyurl.com/skoogpia7

An important aspect of superposition is that a complex waveform can be broken down into simple components by a mathematical operation called the *Fourier transformation*. Jean Fourier, French mathematician (1768–1830), demonstrated that any periodic function, regardless of complexity, can be described by a sum of simple sine or cosine terms. For example, the square waveform widely encountered in electronics can be described by an equation with the form

$$y = A\left(\sin 2\pi\nu t + \frac{1}{3}\sin 6\pi\nu t + \frac{1}{5}\sin 10\pi\nu t + \cdots + \frac{1}{n}\sin 2n\pi\nu t\right) \tag{6-8}$$

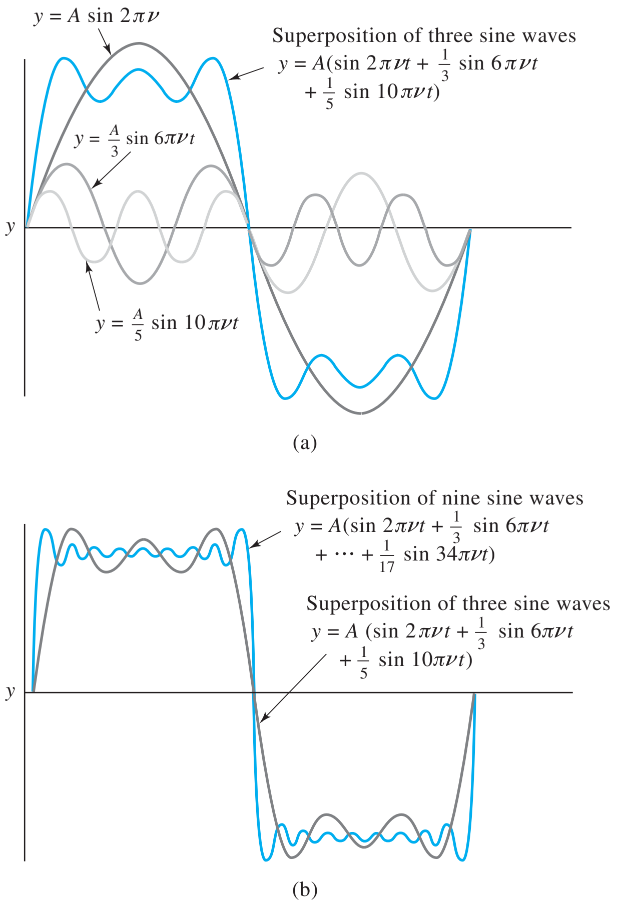


FIGURE 6-6 Superposition of sine waves to form a square wave: (a) combination of three sine waves; (b) combination of three, as in (a), and nine sine waves.

where n takes values of 3, 5, 7, 9, 11, 13, and so forth. A graphical representation of the summation process is shown in Figure 6-6. The blue curve in Figure 6-6a is the sum of three sine waves that differ in amplitude in the ratio of 5:3:1 and in frequency in the ratio of 1:3:5. Note that the resultant approximates the shape of a square wave after including only three terms in Equation 6-8. As shown by the blue curve in Figure 6-6b, the resultant more closely approaches a square wave when nine waves are incorporated.

Decomposing a complex waveform into its sine or cosine components is tedious and time consuming when done by hand. Efficient software, however, makes routine Fourier transformations practical. The application of this technique was mentioned in Section 5C-2 and will be considered in the discussion of several types of spectroscopy.

6B-5 Diffraction of Radiation

All types of electromagnetic radiation exhibit *diffraction*, a process in which a parallel beam of radiation is bent as it passes by a sharp barrier or through a narrow opening. Figure 6-7 illustrates the process. Diffraction is a wave property that can be observed not only for electromagnetic radiation but also for mechanical or acoustical waves. For example, diffraction is easily demonstrated in the laboratory by mechanically generating waves of constant frequency in a tank of water and observing the wave crests before and after they pass through a rectangular opening, or slit. When the slit is wide relative to the wavelength (Figure 6-7a), diffraction is slight and difficult to detect. On the other hand, when the wavelength and the slit opening are of the same order of magnitude, as in Figure 6-7b, diffraction becomes pronounced. Here, the slit behaves as a new source from which waves radiate in a series of nearly 180° arcs. The direction of the wave front appears to bend as a consequence of passing the two edges of the slit.

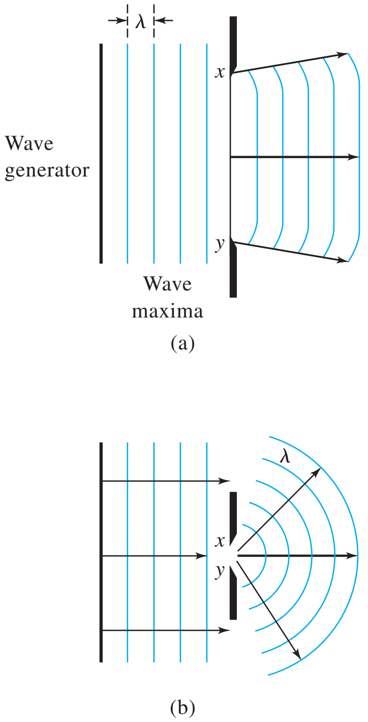
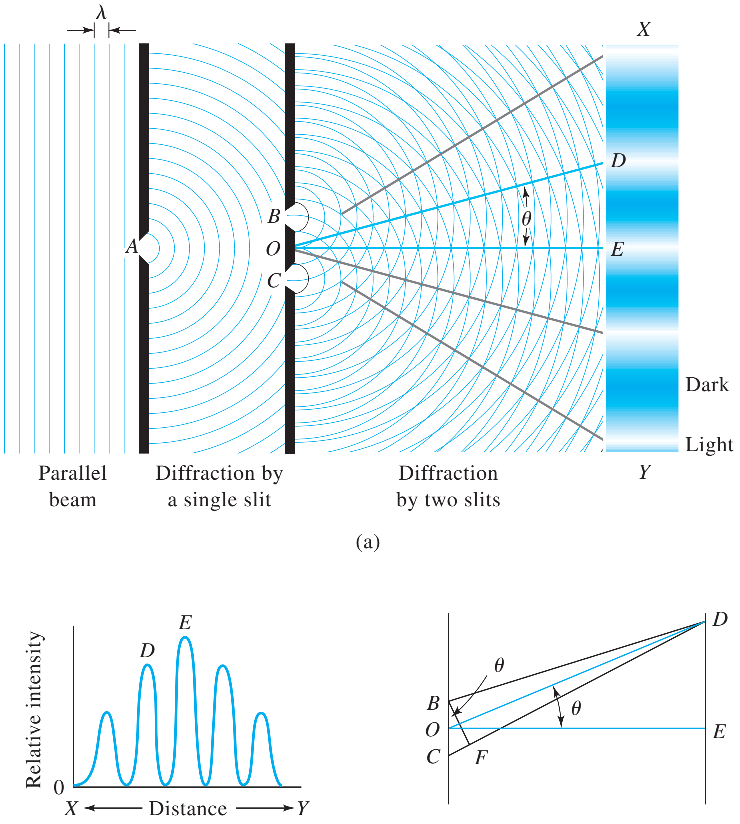


FIGURE 6-7 Propagation of waves through a slit: (a) $xy \gg \lambda$; (b) $xy = \lambda$.

Inferference phenomena cause diffraction. This relationship is most easily understood by considering an experiment, performed first by Thomas Young in 1800, in which the wave nature of light was demonstrated unambiguously. As shown in Figure 6-8a, a parallel beam of light is allowed to pass through a narrow slit A (or in Young's experiment, a pinhole) after which it is diffracted and illuminates more or less equally two closely spaced slits or pinholes B and C; the radiation emerging from these slits is then observed on the screen lying in a plane XY. If the radiation is monochromatic, a series of dark and light images perpendicular to the plane of the page is observed.

Figure 6-8b is a plot of the intensities of the bands as a function of distance along the length of the screen. If, as in this diagram, the slit widths approach the wavelength of radiation,



(a)

(b)

(c)

FIGURE 6-8 Diffraction of monochromatic radiation by slits.

the band intensities decrease only gradually with increasing distances from the central band. With wider slits, the decrease is much more pronounced.

In Figure 6-8a, the appearance of the central band *E*, which lies in the shadow of the opaque material separating the two slits, is readily explained by noting that the paths from *B* to *E* and *C* to *E* are identical. Thus, constructive interference of the diffracted rays from the two slits occurs, and an intense band is observed. With the aid of Figure 6-8c, the conditions for maximum constructive interference, which result in the other light bands, can be derived. In Figure 6-8c, the angle of diffraction θ is the angle formed by the lines *OE* (the normal) and *OD*, where *D* is the point of maximum intensity. The black lines *BD* and *CD* represent the light paths from the slits *B* and *C* to this point. Ordinarily, the distance $\overline{OE}$ is enormous compared to the distance between the slits $\overline{BC}$. As a consequence, the lines *BD*, *OD*, and *CD* are, for all practical purposes, parallel. Line *BF* is perpendicular to *CD* and forms the triangle *BCF*, which is, to a close approximation, similar to *DOE*; consequently, the angle *CBF* is equal to the angle of diffraction θ. We may then write

$$\overline{CF} = \overline{BC}\sin\theta$$

Because $\overline{BC}$ is so very small compared to $\overline{OE}$, $\overline{FD}$ closely approximates $\overline{BD}$, and the distance $\overline{CF}$ is a good measure of the difference in path lengths of beams $\overline{BD}$ and $\overline{CD}$. For the two beams to be in phase at *D*, it is necessary that $\overline{CF}$ corresponds to the wavelength of the radiation; that is,

$$\lambda = \overline{CF} = \overline{BC}\sin\theta$$

Reinforcement also occurs when the additional path length corresponds to 2λ, 3λ, and so forth. Thus, a more general expression for the light bands surrounding the central band is

$$\mathbf{n}\lambda = \overline{BC}\sin\theta \qquad (6\text{-}9)$$

where **n** is an integer called the *order* of interference.

The linear displacement $\overline{DE}$ of the diffracted beam along the plane of the screen is a function of the distance $\overline{OE}$ between the screen and the plane of the slits, as well as the spacing between the slits, and is given by

$$\overline{DE} = \overline{OD}\sin\theta$$

Substitution into Equation 6-9 gives

$$\mathbf{n}\lambda = \frac{\overline{BC}\,\overline{DE}}{\overline{OD}} = \frac{\overline{BC}\,\overline{DE}}{\overline{OE}} \qquad (6\text{-}10)$$

Equation 6-10 permits the calculation of the wavelength from the three measurable quantities.

Simulation: Learn more about **double-slit diffraction** at www.tinyurl.com/skoogpia7

EXAMPLE 6-1

Suppose that the screen in Figure 6-8 is 2.00 m from the plane of the slits and that the slit spacing is 0.300 mm. What is the wavelength of radiation if the fourth band is located 15.4 mm from the central band?

Solution

Substituting into Equation 6-10 gives

$$4\lambda = \frac{0.300 \text{ mm} \times 15.4 \text{ mm}}{2.00 \text{ m} \times 1000 \text{ mm/m}} = 0.00231 \text{ mm}$$

$$\lambda = 5.78 \times 10^{-4} \text{ mm} = 578 \text{ nm}$$

6B-6 Coherent Radiation

To produce a diffraction pattern such as that shown in Figure 6-8a, it is necessary that the electromagnetic waves that travel from slits *B* and *C* to any given point on the screen (such as *D* or *E*) have sharply defined phase differences that remain *entirely* constant with time; that is, the radiation from slits *B* and *C* must be *coherent*. The conditions for coherence are that (1) the two sources of radiation must have identical frequencies (or sets of frequencies) and (2) the phase relationships between the two beams must remain constant with time. The necessity for these requirements can be demonstrated by illuminating the two slits in Figure 6-8a with individual tungsten lamps. Under this circumstance, the well-defined light and dark patterns disappear and are replaced by a more or less uniform illumination of the screen. This behavior is a consequence of the *incoherent* character of filament sources (many other sources of electromagnetic radiation are incoherent as well).

With incoherent sources, light is emitted by individual atoms or molecules, and the resulting beam is the summation of countless individual events, each of which lasts on the order of 10^{-8} s. As a result, a beam of radiation from this type of source is not continuous but instead is composed of a series of *wave trains* that are a few meters in length at most. Because the processes that produce trains are random, the phase differences among the trains must also be variable. A wave train from slit *B* may arrive at a point on the screen in phase with a wave train from *C* so that constructive interference occurs; an instant later, the trains may be totally out of phase at the same point, and destructive interference occurs. Thus, the radiation at all points on the screen is governed by the random phase variations among the wave trains; uniform illumination, which represents an average for the trains, is the result.

There are sources that produce electromagnetic radiation in the form of trains with essentially infinite length and constant frequency. Examples include radio-frequency oscillators, microwave sources, and optical lasers. Various mechanical sources, such as a two-pronged vibrating tapper in a water-containing ripple tank, produce a mechanical analog of coherent radiation. When two coherent sources are substituted for slit *A* in the experiment shown in Figure 6-8a, a regular diffraction pattern is observed.

Diffraction patterns can be obtained from random sources, such as tungsten filaments, provided that an arrangement similar to that shown in Figure 6-8a is used. In this example, the very narrow slit *A* assures that the radiation reaching *B* and *C* emanates from the same small region of the source. Under this circumstance, the various wave trains that exit from slits *B* and *C* have a constant set of frequencies and phase relationships to one another and are thus coherent. If the slit at *A* is widened so that a larger part of the source is sampled, the diffraction pattern becomes less pronounced because the two beams are only partially coherent. If slit *A* is made sufficiently wide, the incoherence may become great enough to produce only a constant illumination across the screen.

6B-7 Transmission of Radiation

Experimental observations show that the rate radiation propagates through a transparent substance is less than its velocity in a vacuum and depends on the kinds and concentrations of atoms, ions, or molecules in the medium. It follows from these observations that the radiation must interact in some way with matter in its path. Because a frequency change is not observed, however, the interaction *cannot* involve a permanent energy transfer.

The *refractive index* of a medium is one measure of its interaction with radiation and is defined by

$$n_i = \frac{c}{v_i} \tag{6-11}$$

where n_i is the refractive index at a specified frequency i, v_i is the velocity of the radiation in the medium, and c is its velocity in a vacuum. The refractive index of most liquids lies between 1.3 and 1.8; it is 1.3 to 2.5 or higher for solids.[4]

The interaction involved in transmission can be ascribed to periodic *polarization* of the atomic and molecular species that make up the medium. Polarization in this context means the temporary deformation of the electron clouds associated with atoms or molecules that is brought about by the alternating electromagnetic field of the radiation. Provided that the radiation is not absorbed, the energy required for polarization is only momentarily retained (10^{-14} to 10^{-15} s) by the species and is reemitted without alteration as the substance returns to its original state. Since there is no net energy change in this process, the frequency of the emitted radiation is unchanged, but the rate of its propagation is slowed by the time that is required for retention and reemission to occur. Thus, transmission through a medium can be viewed as a stepwise process that involves polarized atoms, ions, or molecules as intermediates.

---

[4] For a more complete discussion of refractive index measurement, see T. M. Niemczyk, in *Physical Methods in Modern Clinical Analysis*, T. Kuwana, Ed., Vol. 2, pp. 337–400. New York: Academic, 1980.

Radiation from polarized particles should be emitted in all directions in a medium. If the particles are small, however, it can be shown that destructive interference prevents the propagation of significant amounts in any direction other than that of the original light path. On the other hand, if the medium contains large particles (such as polymer molecules or colloidal particles), this destructive interference is incomplete, and a portion of the beam is scattered in all directions as a consequence of the interaction step. Scattering is considered in Section 6B-10.

Since the velocity of radiation in matter is wavelength dependent and since c in Equation 6-11 is independent of wavelength, the refractive index of a substance must also change with wavelength. The variation in refractive index of a substance with wavelength or frequency is called its *dispersion*. The dispersion of a typical substance is shown in Figure 6-9. The intricacy of the curve indicates that the relationship is complex; generally, however, dispersion plots exhibit two types of regions. In the *normal dispersion* region, there is a gradual increase in refractive index with increasing frequency (or decreasing wavelength). Regions of *anomalous dispersion* are frequency ranges in which sharp changes in refractive index occur. Anomalous dispersion always occurs at frequencies that correspond to the natural harmonic frequency associated with some part of a molecule, atom, or ion of the substance. At such a frequency, permanent energy transfer from the radiation to the substance occurs and *absorption* of the beam is observed. Absorption is discussed in Section 6C-5.

Dispersion curves are important when choosing materials for the optical components of instruments. A substance that exhibits normal dispersion over the wavelength region of interest is most suitable for the manufacture of lenses, for which a high and relatively constant refractive index is desirable. Chromatic aberrations (formation of colored images) are minimized through the choice of such a material. In contrast, a substance with a refractive index that is not only large but also highly frequency dependent is selected for the fabrication of prisms. The applicable wavelength region for the prism thus approaches the anomalous dispersion region for the material from which it is fabricated.

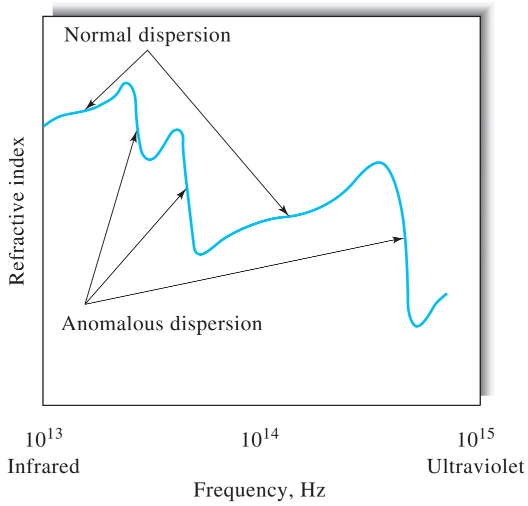


FIGURE 6-9 A typical dispersion curve.

6B-8 Refraction of Radiation

When radiation passes at an angle through the interface between two transparent media that have different densities, an abrupt change in direction, or *refraction*, of the beam is observed as a consequence of a difference in velocity of the radiation in the two media. When the beam passes from a less dense to a more dense environment, as in Figure 6-10, the bending is toward the normal to the interface. Bending away from the normal occurs when the beam passes from a more dense to a less dense medium.

The extent of refraction is given by Snell's law:

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{v_1}{v_2} \tag{6-12}$$

If M_1 in Figure 6-10 is a *vacuum*, v_1 is equal to c, and n_1 is unity (see Equation 6-11); with rearrangement, Equation 6-12 simplifies to

$$(n_2)_{\text{vac}} = \frac{(\sin \theta_1)_{\text{vac}}}{\sin \theta_2} \tag{6-13}$$

The refractive indexes of substance M_2 can then be computed from measurements of $(\theta_1)_{\text{vac}}$ and θ_2. For convenience, refractive indexes are usually measured and reported with air, rather than a vacuum, as the reference. The refractive index is then

$$(n_2)_{\text{air}} = \frac{(\sin \theta_1)_{\text{air}}}{\sin \theta_2} \tag{6-14}$$

Most compilations of refractive indexes provide data in terms of Equation 6-14. Such data are readily converted to

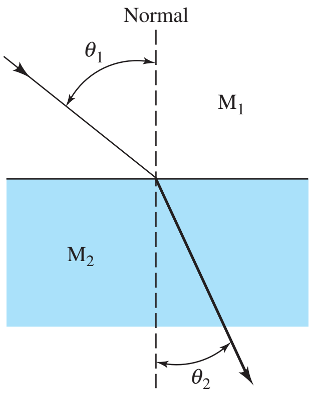


FIGURE 6-10 Refraction of light in passing from a less dense medium M_1 into a more dense medium M_2, where its velocity is lower.

refractive indexes with vacuum as a reference by multiplying by the refractive index of air relative to a vacuum. That is,

$$n_{\text{vac}} = 1.00027 n_{\text{air}}$$

This conversion is seldom necessary.

6B-9 Reflection of Radiation

When radiation crosses an interface between media that differ in refractive index, reflection always occurs. The fraction of reflected radiation becomes greater with increasing differences in refractive index. For a beam that enters an interface at right angles, the fraction reflected is given by

$$\frac{I_r}{I_0} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \qquad (6\text{-}15)$$

where I_0 is the intensity of the incident beam and I_r is the reflected intensity; n_1 and n_2 are the refractive indexes of the two media.

EXAMPLE 6-2

Calculate the percentage loss of intensity due to reflection of a perpendicular beam of yellow light as it passes through a glass cell that contains water. Assume that for yellow radiation the refractive index of glass is 1.50, of water is 1.33, and of air is 1.00.

Solution

The total reflective loss will be the sum of the losses occurring at each of the interfaces. For the first interface (air to glass), we can write

$$\frac{I_{r1}}{I_0} = \frac{(1.50 - 1.00)^2}{(1.50 + 1.00)^2} = 0.040$$

The beam intensity is reduced to $(I_0 - 0.040I_0) = 0.960I_0$. Reflection loss at the glass-to-water interface is then given by

$$\frac{I_{r2}}{0.960I_0} = \frac{(1.50 - 1.33)^2}{(1.50 + 1.33)^2} = 0.0036$$

$$I_{r2} = 0.0035I_0$$

The beam intensity is further reduced to $(0.960I_0 - 0.0035I_0) = 0.957I_0$. At the water-to-glass interface

$$\frac{I_{r3}}{0.957I_0} = \frac{(1.50 - 1.33)^2}{(1.50 + 1.33)^2} = 0.0036$$

$$I_{r3} = 0.0035I_0$$

and the beam intensity becomes $0.953I_0$. Finally, the reflection at the second glass-to-air interface will be

$$\frac{I_{r4}}{0.953I_0} = \frac{(1.50 - 1.00)^2}{(1.50 + 1.00)^2} = 0.0400$$

$$I_{r4} = 0.038I_0$$

The total reflection loss I_{rt} is

$$\begin{aligned} I_{rt} &= 0.040I_0 + 0.0035I_0 + 0.0035I_0 + 0.038I_0 \\ &= 0.085I_0 \end{aligned}$$

and

$$\frac{I_{rt}}{I_0} = 0.85 \quad \text{or} \quad 8.5\%$$

In later chapters we show that losses such as those shown in Example 6-2 are of considerable significance in various optical instruments.

Reflective losses at a polished glass or quartz surface increase only slightly as the angle of the incident beam increases up to about 60°. Beyond this angle, however, the percentage of radiation that is reflected increases rapidly and approaches 100% at 90°, or grazing incidence.

6B-10 Scattering of Radiation

As noted earlier, the transmission of radiation in matter can be pictured as a momentary retention of the radiant energy by atoms, ions, or molecules followed by reemission of the radiation in all directions as the particles return to their original state. With atomic or molecular particles that are small relative to the wavelength of the radiation, destructive interference removes most but not all of the reemitted radiation except the radiation that travels in the original direction of the beam; the path of the beam appears to be unaltered by the interaction. Careful observation, however, reveals that a very small fraction of the radiation is transmitted at all angles from the original path and that the intensity of this *scattered radiation* increases with particle size.

Rayleigh Scattering

Scattering by molecules or aggregates of molecules with dimensions significantly smaller than the wavelength of the radiation is called *Rayleigh scattering*. The intensity of the scattering is proportional to the inverse fourth power of the wavelength, the dimensions of the scattering particles, and the square of the polarizability of the particles. An everyday manifestation of Rayleigh scattering is the blue color of the sky, which results from greater scattering of the shorter wavelengths of the visible spectrum.

Scattering by Large Molecules

With large particles, scattering can be different in different directions (Mie scattering). Measurements of this type of scattered radiation are used to determine the size and shape of large molecules and colloidal particles (see Chapter 34).

Raman Scattering

The Raman scattering effect differs from ordinary scattering in that part of the scattered radiation suffers quantized frequency changes. These changes are the result of vibrational energy level transitions that occur in the molecules as a consequence of the polarization process. Raman spectroscopy is discussed in Chapter 18.

6B-11 Polarization of Radiation

Ordinary radiation consists of a bundle of electromagnetic waves in which the vibrations are equally distributed among a huge number of planes centered along the path of the beam. Viewed end on, a beam of monochromatic radiation, such as that shown in Figure 6-11a, can be visualized as an infinite set of electric vectors that fluctuate in length from zero to a maximum amplitude *A*. Figure 6-11b depicts an end-on view of these vectors at various times during the passage of one wave of monochromatic radiation through a fixed point in space.

Figure 6-12a shows a few of the vectors depicted in Figure 6-11b at the instant the wave is at its maximum. The vector in any one plane, say *XY* as depicted in Figure 6-12a, can be resolved into two mutually perpendicular components *AB* and *CD* as shown in Figure 6-12b. If the two components for all of the planes shown in Figure 6-12a are combined, the resultant has the appearance shown in Figure 6-12c. Removal of one of the two resultant planes of vibration in Figure 6-12c produces a beam that is *plane polarized*. The resultant electric vector of a plane-polarized beam then occupies a single plane. Figure 6-11c shows an end-on view of a beam of plane-polarized radiation after various time intervals.

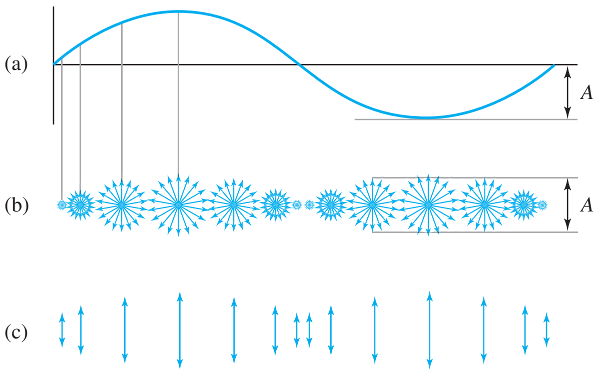


FIGURE 6-11 Unpolarized and plane-polarized radiation: (a) cross-sectional view of a beam of monochromatic radiation, (b) successive end-on view of the radiation in (a) if it is unpolarized, (c) successive end-on views of the radiation of (a) if it is plane polarized on the vertical axis.

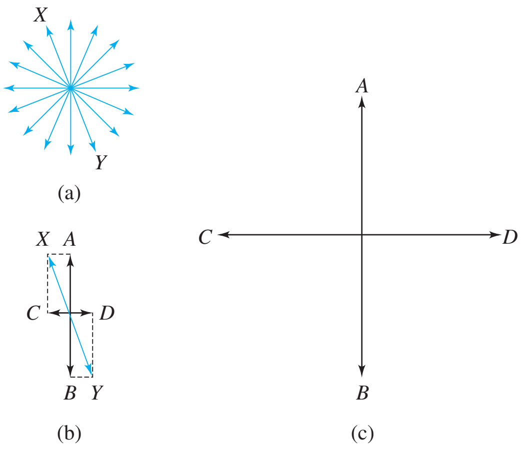


FIGURE 6-12 (a) A few of the electric vectors of a beam traveling perpendicular to the page. (b) The resolution of a vector in a plane *XY* into two mutually perpendicular components. (c) The resultant when all vectors are resolved (not to scale).

Plane-polarized electromagnetic radiation is produced by certain radiant energy sources. For example, the radio waves emanating from an antenna and the microwaves produced by a klystron tube are both plane polarized. Visible and ultraviolet radiation from relaxation of a single excited atom or molecule is also polarized, but the beam from such a source has no net polarization since it is made up of a multitude of individual wave trains produced by an enormous number of individual atomic or molecular events. The plane of polarization of these individual waves is random so that their individual polarizations cancel.

Polarized ultraviolet and visible radiation is produced by passage of radiation through media that selectively absorb, reflect, or refract radiation that vibrates in only one plane.

6C QUANTUM-MECHANICAL PROPERTIES OF RADIATION

When electromagnetic radiation is emitted or absorbed, a permanent transfer of energy from the emitting object or to the absorbing medium occurs. To describe these phenomena, it is necessary to treat electromagnetic radiation not as a collection of waves but rather as a stream of discrete particles called *photons* or *quanta*. The need for a particle model for radiation became apparent as a consequence of the discovery of the photoelectric effect in the late nineteenth century.

6C-1 The Photoelectric Effect

The first observation of the photoelectric effect was made in 1887 by Heinrich Hertz, who reported that a spark jumped more readily between two charged spheres when their surfaces were illuminated with light. Between the time of this observation and the theoretical explanation of the photoelectric effect by Einstein in 1905, several important studies of the photoelectric effect were performed with what is now known as a vacuum phototube. Einstein's explanation of the photoelectric effect was both simple and elegant but was far enough ahead of its time that it was not generally accepted until 1916, when Millikan's systematic studies confirmed the details of Einstein's theoretical conclusions.

Figure 6-13 is a schematic of a vacuum phototube circuit similar to the one used by Millikan to study the photoelectric effect. The surface of the large *photocathode* on the left is usually coated with an alkali metal or one of its compounds. When monochromatic radiation impinges on the photocathode, electrons are emitted from its surface with a range of kinetic energies. As long as the voltage *V* applied between the anode and the cathode is positive, the electrons are drawn from left to right through the phototube to produce a current *I* in the circuit. When the voltage across the phototube is adjusted so that the anode is slightly negative with respect to the cathode, the

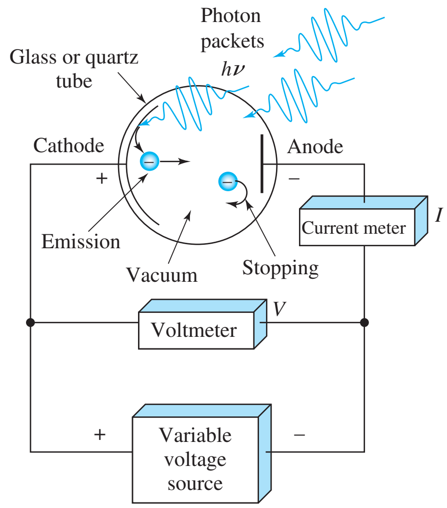


FIGURE 6-13 Apparatus for studying the photoelectric effect. Photons enter the phototube, strike the cathode, and eject electrons. The photoelectrons are attracted to the anode when it is positive with respect to the cathode. When the anode is negative as shown, the electrons are "stopped," and no current passes. The negative voltage between the anode and the cathode when the current is zero is the stopping potential.

photoelectrons are repelled by the anode, and the photocurrent decreases as expected. At this point in the experiment, however, some of the electrons have sufficient kinetic energy to overcome the negative potential applied to the anode, and a current is still observed.

This experiment may be repeated for phototubes with different materials coating the photocathode. In each experiment, the photocurrent is measured as a function of the applied voltage, and the voltage V_0 at which the photocurrent becomes precisely zero is noted. The negative voltage at which the photocurrent is zero is called the *stopping voltage*. It corresponds to the potential at which the most energetic electrons from the cathode are just repelled from the anode. If we multiply the stopping voltage by the charge on the electron, $e = 1.60 \times 10^{-19}$ coulombs, we have a measure of the kinetic energy in joules of the *most energetic* of the emitted electrons. When this experiment is repeated for various frequencies of monochromatic light, the following results are observed:

1. When light of constant frequency is focused on the anode at low applied negative potential, the photocurrent is directly proportional to the intensity of the incident radiation.
2. The magnitude of the stopping voltage depends on the frequency of the radiation impinging on the photocathode.
3. The stopping voltage depends on the chemical composition of the coating on the photocathode.
4. The stopping voltage is *independent of the intensity of the incident radiation*.

Tutorial: Learn more about **photoelectric effect** at www.tinyurl.com/skoogpia7

These observations suggest that electromagnetic radiation is a form of energy that releases electrons from metallic surfaces and imparts to these electrons sufficient kinetic energy to cause them to travel to a negatively charged electrode. Furthermore, the number of photoelectrons released is proportional to the intensity of the incident beam.

The results of these experiments are shown in the plots of Figure 6-14, in which the maximum kinetic energy, or stopping energy, $KE_m = eV_0$ of the photoelectrons is plotted against frequency for photocathode surfaces of magnesium, cesium, and copper. Other surfaces give plots with identical slopes, h, but different intercepts, ω. The plots shown in Figure 6-14 are described by the equation

$$KE_m = h\nu - \omega \tag{6-16}$$

In this equation, the slope h is Planck's constant, which is equal to 6.6254×10^{-34} joule second, and the intercept $-\omega$ is the *work function*, a constant that is characteristic of the surface material and represents the minimum energy binding electron in the metal. Approximately a decade before Millikan's work that led to Equation 6-16, Einstein had proposed the relationship between frequency ν of light and energy E as embodied by the now famous equation

$$E = h\nu \tag{6-17}$$

By substituting this equation into Equation 6-16 and rearranging, we obtain

$$E = h\nu = KE_m + \omega \tag{6-18}$$

This equation shows that the energy of an incoming photon is equal to the kinetic energy of the ejected photoelectron plus the energy required to eject the photoelectron from the surface being irradiated.

The photoelectric effect cannot be explained by a classical wave model but requires instead a quantum model, in which radiation is viewed as a stream of discrete bundles of energy, or photons as depicted in Figure 6-13. For example, calculations indicate that no single electron could acquire sufficient energy for ejection if the radiation striking the surface were uniformly distributed over the face of the electrode as it is in the wave model; nor could any electron accumulate enough energy rapidly enough to establish the nearly instantaneous currents that are observed. Thus, it is necessary to assume that the energy is not uniformly distributed over the beam front but rather is concentrated in packets, or bundles of energy.

Equation 6-18 can be recast in terms of wavelength by substitution of Equation 6-2. That is,

$$E = h\frac{c}{\lambda} = KE_m - \omega \tag{6-19}$$

Note that although photon energy is directly proportional to frequency, it is a reciprocal function of wavelength.

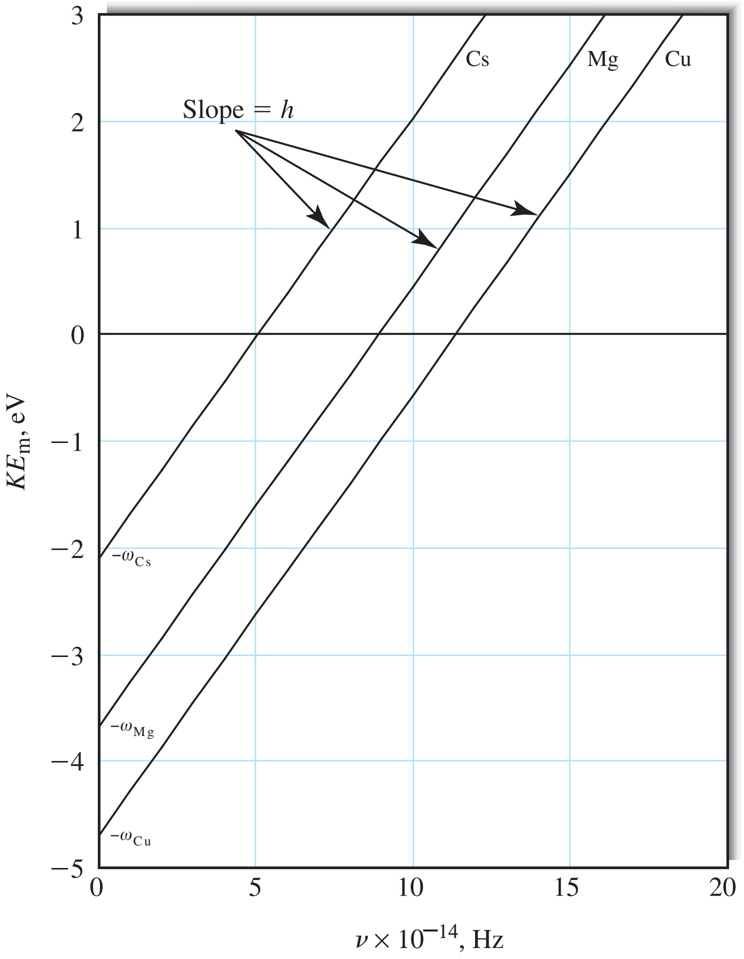


FIGURE 6-14 Maximum kinetic energy of photoelectrons emitted from three metal surfaces as a function of radiation frequency. The y-intercepts ($-\omega$) are the work functions for each metal. If incident photons do not have energies of at least $h\nu = \omega$, no photoelectrons are emitted from the photocathode.

EXAMPLE 6-3

Calculate the energy of (a) a 5.3-Å X-ray photon and (b) a 530-nm photon of visible radiation.

$$E = h\nu = \frac{hc}{\lambda}$$

Solution

(a) $$E = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s}) \times (3.00 \times 10^{8}\ \text{m/s})}{5.30\ \text{Å} \times (10^{-10}\ \text{m/Å})}$$

$$= 3.75 \times 10^{-16}\ \text{J}$$

The energy of radiation in the X-ray region is commonly expressed in electron volts, the energy acquired by an electron that has been accelerated through a potential of one volt. In the conversion table inside the front cover of this book, we see that 1 J = 6.24×10^{18} eV.

$$E = 3.75 \times 10^{-16}\ \text{J} \times (6.24 \times 10^{18}\ \text{eV/J})$$

$$= 2.34 \times 10^{3}\ \text{eV}$$

(b) $$E = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s}) \times (3.00 \times 10^{8}\ \text{m/s})}{530\ \text{nm} \times (10^{-9}\ \text{m/nm})}$$

$$= 3.75 \times 10^{-19}\ \text{J}$$

Energy of radiation in the visible region is often expressed in kJ/mol rather than kJ/photon to aid in the discussion of the relationships between the energy of absorbed photons and the energy of chemical bonds.

$$E = 3.75 \times 10^{-19}\ \frac{\text{J}}{\text{photon}}$$

$$\times \frac{(6.02 \times 10^{23}\ \text{photons})}{\text{mol}} \times 10^{-3}\ \frac{\text{kJ}}{\text{J}}$$

$$= 226\ \text{kJ/mol}$$

6C-2 Energy States of Chemical Species

The quantum theory was first proposed in 1900 by Max Planck, a German physicist, to explain the properties of radiation emitted by heated bodies. The theory was later extended to rationalize other types of emission and absorption processes. Two important postulates of quantum theory include the following:

1. Atoms, ions, and molecules can exist only in certain discrete states, characterized by definite amounts of energy. When a species changes its state, it absorbs or emits an amount of energy *exactly* equal to the energy difference between the states.
2. When atoms, ions, or molecules absorb or emit radiation in making the transition from one energy state to another, the frequency ν or the wavelength λ of the radiation is related to the energy difference between the states by the equation

$$E_1 - E_0 = h\nu = \frac{hc}{\lambda} \tag{6-20}$$

where E_1 is the energy of the higher state and E_0 the energy of the lower state. The terms c and h are the speed of light and the Planck constant, respectively.

For atoms or ions in the elemental state, the energy of any given state arises from the motion of electrons around the positively charged nucleus. Because of this, the various energy states are called *electronic states*. In addition to having electronic states, molecules also have quantized *vibrational states* that are associated with the energy of interatomic vibrations and quantized *rotational states* that arise from the rotation of molecules around their centers of mass.

The lowest energy state of an atom or molecule is its *ground state*. Higher energy states are termed *excited states*. At room temperature chemical species are primarily in their ground state.

6C-3 Interactions of Radiation and Matter

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 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 or scattered as a result of excitation.

Figure 6-15 illustrates the processes involved in emission and chemiluminescence spectroscopy. As shown in Figure 6-15a, the analyte is stimulated by heat or electrical energy or by a chemical reaction. *Emission spectroscopy* usually involves methods in which the stimulus is heat or electrical energy, and *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, as shown in Figure 6-15b, 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 (see Figure 6-15c).

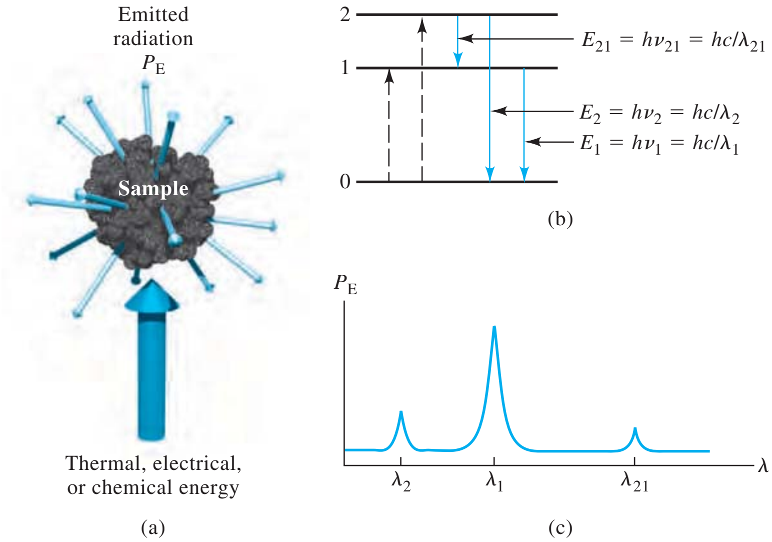


FIGURE 6-15 Emission or chemiluminescence processes. In (a), the sample is excited by the application of thermal, electrical, or chemical energy. These processes do not involve radiant energy and are hence called nonradiative processes. In the energy level diagram (b), the dashed black lines with upward-pointing arrows symbolize these nonradiative excitation processes, while the solid colored lines with downward-pointing arrows indicate that the analyte loses 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 reflected (Section 6B-9), scattered (Section 6B-10), or absorbed (Section 6C-5). When some of the incident radiation is absorbed, it promotes some of the analyte species to an excited state, as shown in Figure 6-16. In *absorption spectroscopy*, we measure the amount of light absorbed as a function of wavelength. This can give both qualitative and quantitative information about the sample. In *photoluminescence spectroscopy* (Figure 6-17), the emission of photons is measured after absorption. The most important forms of photoluminescence for analytical purposes are *fluorescence* and *phosphorescence spectroscopy*.

When radiation is scattered, the interaction of the incoming radiation with the sample may be elastic or inelastic. In elastic scattering, the wavelength of the scattered radiation is the same as that of the source radiation. The intensity of the elastically scattered radiation is used to make measurements in *nephelometry* and *turbidimetry*, and particle sizing. *Raman spectroscopy*, which is mentioned briefly in Section 6B-10 and is discussed in detail in Chapter 18, uses inelastic scattering to produce a vibrational spectrum of sample molecules, as illustrated in Figure 6-18. In this type of spectroscopic analysis, the intensity of the scattered radiation is recorded as a function of the frequency shift of the incident radiation. The intensity of Raman peaks is related to the concentration of the analyte.

Simulation: Learn more about the **interaction of radiation with matter** at www.tinyurl.com/skoogpia7

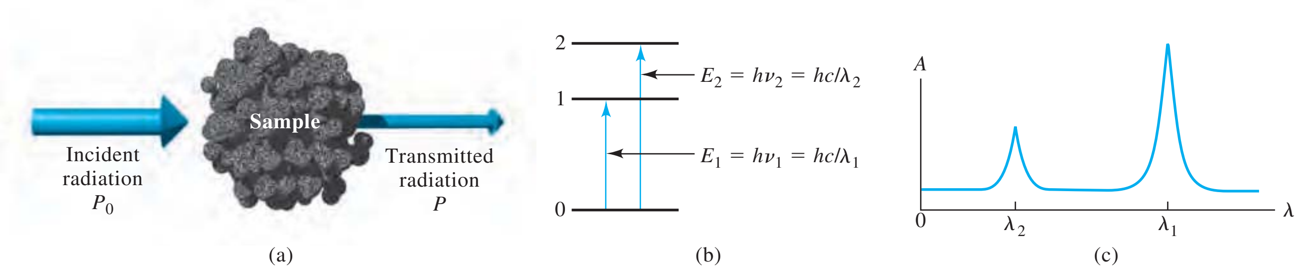


FIGURE 6-16 Absorption methods. Radiation of incident radiant power P_0 can be absorbed by the analyte, resulting in a transmitted beam of lower radiant power P. For absorption to occur, the energy of the incident beam must correspond to one of the energy differences shown in (b). The resulting absorption spectrum is shown in (c).

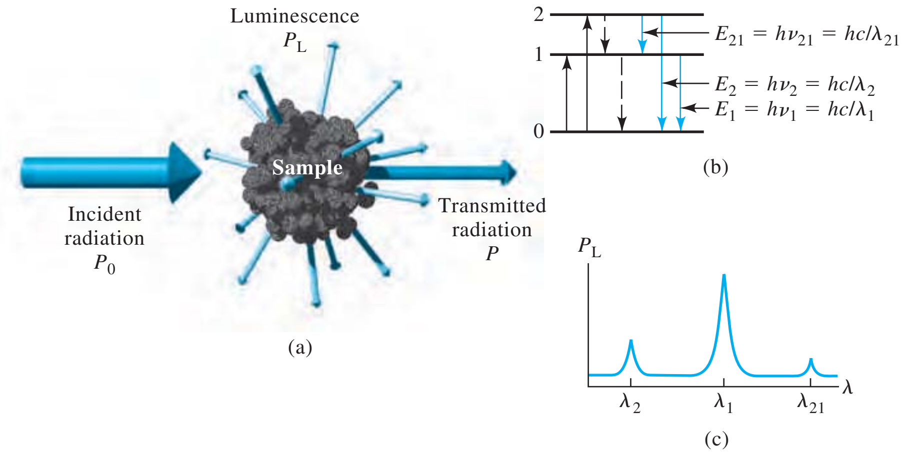


FIGURE 6-17 Photoluminescence methods (fluorescence and phosphorescence). Fluorescence and phosphorescence result from absorption of electromagnetic radiation and then dissipation of the energy emission of radiation (a). In (b), the absorption can cause excitation of the analyte to state 1 or state 2. 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.

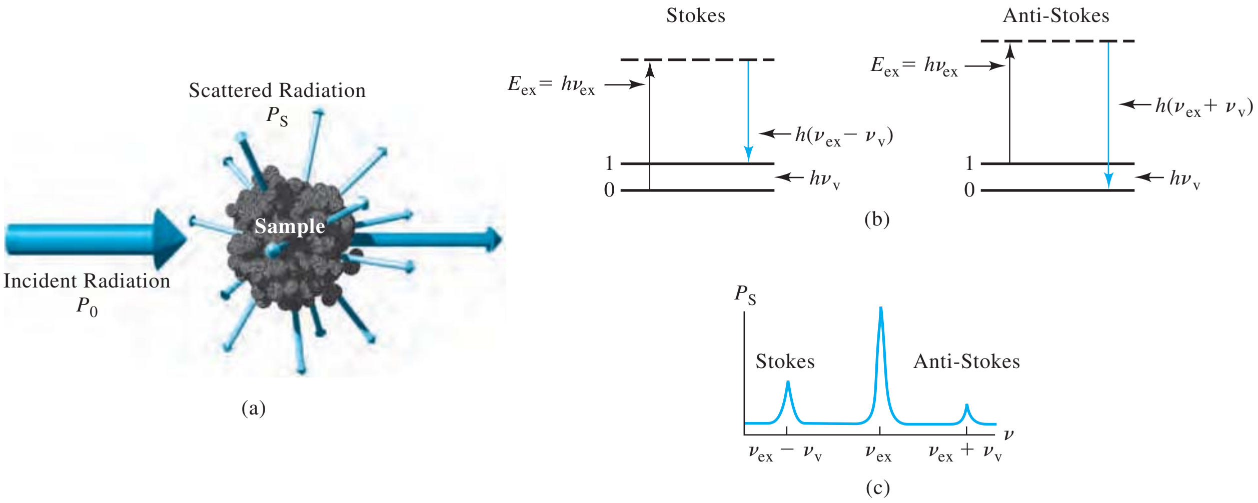


FIGURE 6-18 Inelastic scattering in Raman spectroscopy. (a) As incident radiation of frequency ν_{ex} impinges on the sample, molecules of the sample are excited from one of their ground vibrational states to a higher so-called *virtual state*, indicated by the dashed level in (b). When the molecule relaxes, it may return to the first vibrational state as indicated and emit a photon of energy $E = h(\nu_{ex} - \nu_v)$ where ν_v is the frequency of the vibrational transition. Alternatively, if the molecule is in the first excited vibrational state, it may absorb a quantum of the incident radiation, be excited to the virtual state, and relax back to the ground vibrational state. This process produces an emitted photon of energy $E = h(\nu_{ex} + \nu_v)$. In both cases, the emitted radiation differs in frequency from the incident radiation by the vibrational frequency of the molecule ν_v. (c) The spectrum resulting from the inelastically scattered radiation shows three peaks: one at $\nu_{ex} - \nu_v$ (Stokes), a second intense peak at ν_{ex} for radiation that is scattered without a frequency change, and a third (anti-Stokes) at $\nu_{ex} + \nu_v$. The intensities of the Stokes and anti-Stokes peaks give quantitative information, and the positions of the peaks give qualitative information about the sample molecule.

6C-4 Emission of Radiation

Electromagnetic radiation is produced when excited particles (atoms, ions, or molecules) relax to lower energy levels by giving up their excess energy as photons. Excitation can be brought about in several ways, including (1) bombardment with electrons or other elementary particles, which generally leads to the emission of X-radiation; (2) exposure to an electric current, an ac spark, or an intense heat source (flame, dc arc, or furnace), producing ultraviolet, visible, or infrared radiation; (3) irradiation with a beam of electromagnetic radiation, which produces fluorescence radiation; and (4) an exothermic chemical reaction that produces chemiluminescence.

Radiation from an excited 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. Figure 6-19 illustrates a typical emission spectrum, which was obtained by aspirating a brine solution into an oxyhydrogen flame. Three types of spectra appear in the figure: *lines*, *bands*, and a *continuum*. The line spectrum is made up of a series of sharp, well-defined peaks caused by excitation of individual atoms. The band spectrum consists of several groups of lines so closely spaced that they are not completely resolved. The source of the bands consists of small molecules or radicals. Finally, the continuum portion of the spectrum is responsible for the increase in the background that is evident above about 350 nm. The line and band spectra are superimposed on this continuum. The source of the continuum is described on page 137.

Figure 6-20 is an X-ray emission spectrum produced by bombarding a piece of molybdenum with an energetic stream of electrons. Note the line spectrum superimposed on the continuum. The source of the continuum in X-ray emission is described in Section 12A-1.

Line Spectra

Line spectra in the ultraviolet and visible regions are produced when the radiating species are individual atomic particles that are well separated in the gas phase. The individual particles in a gas behave independently of one another, and the spectrum consists of a series of sharp lines with widths on the order of 10^{-5} nm (10^{-4} Å). In Figure 6-19, lines for gas-phase sodium, potassium, and calcium are identified.

The energy-level diagram in Figure 6-21 shows the source of two of the lines in a typical emission spectrum of an element. The horizontal line labeled E_0 corresponds to the lowest, or ground-state, energy of the atom. The horizontal lines labeled E_1 and E_2 are two higher-energy electronic levels of the species. For example, the single outer electron in the ground state E_0 for a sodium atom is located in the 3*s* orbital. Energy level E_1 then represents the energy of the atom when this electron has been promoted to the 3*p* state by absorption of thermal, electrical, or radiant energy. The promotion is depicted by the shorter wavy arrow on the left in Figure 6-21a. After perhaps 10^{-8} s, the atom

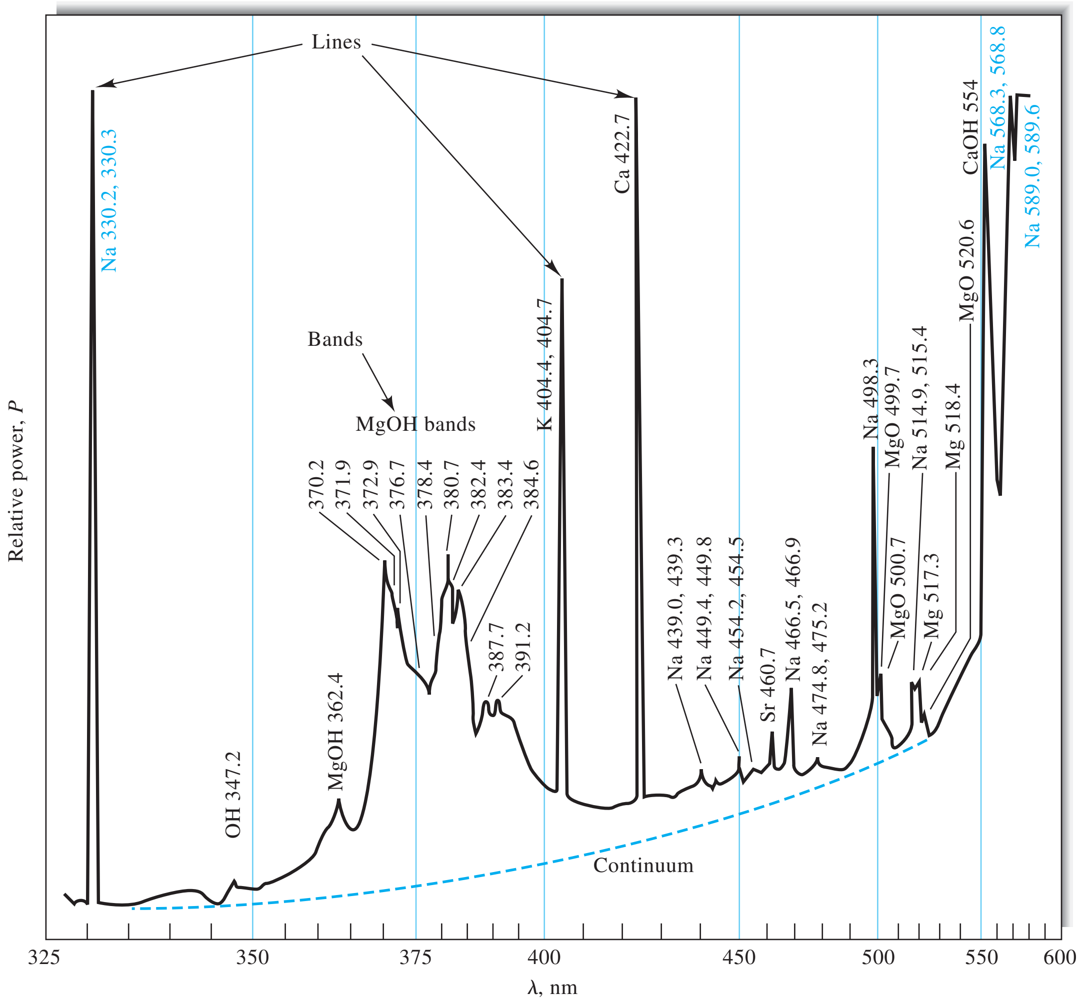


FIGURE 6-19 Emission spectrum of a brine sample obtained with an oxyhydrogen flame. The spectrum consists of the superimposed line, band, and continuum spectra of the constituents of the sample. The characteristic wavelengths of the species contributing to the spectrum are listed beside each feature. (R. Hermann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry,* 2nd ed., p. 484. New York: Interscience, 1979.)

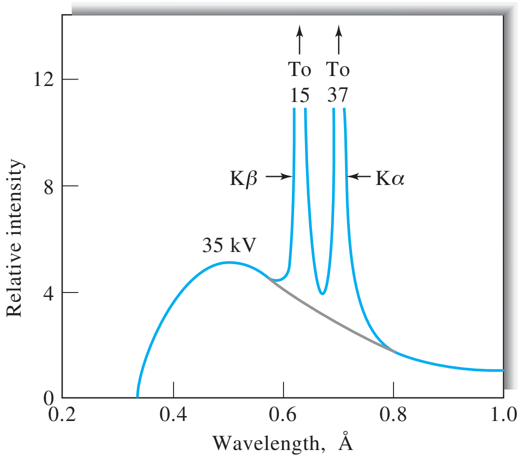


FIGURE 6-20 X-ray emission spectrum of molybdenum metal.

returns to the ground state, emitting a photon whose frequency and wavelength are given by Equation 6-20.

$$\nu_1 = (E_1 - E_0)/h$$

$$\lambda_1 = hc/(E_1 - E_0)$$

This emission process is illustrated by the shorter colored arrow on the right in Figure 6-21a. The line (actually lines) at about 590 nm is the result of the 3*p* to 3*s* transition.

For the sodium atom, E_2 in Figure 6-21 corresponds to the more energetic 4*p* state; the resulting emitted radiation λ_2 appears at a shorter wavelength or a higher frequency. The line at about 330 nm in Figure 6-19 results from this transition.

X-ray line spectra are also produced by electronic transitions. In this case, however, the electrons involved are those in the innermost orbitals. Thus, in contrast to ultraviolet and

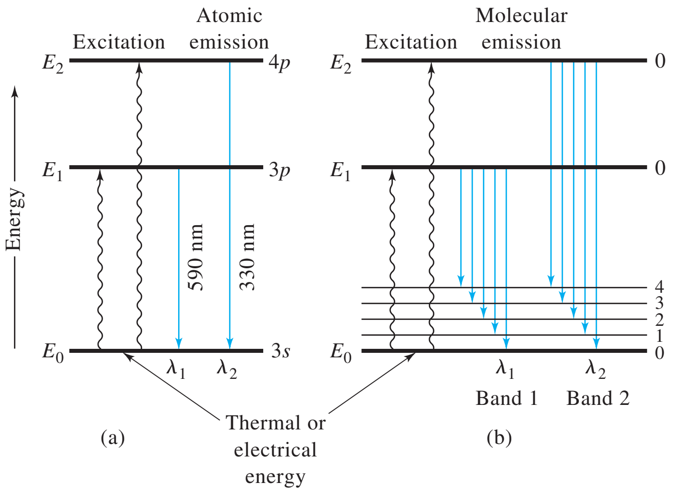


FIGURE 6-21 Energy-level diagrams for (a) a sodium atom showing the source of a line spectrum and (b) a simple molecule showing the source of a band spectrum.

visible emissions, the X-ray spectrum for an element is independent of its environment. For example, the emission spectrum for molybdenum is the same regardless of whether the sample being excited is molybdenum metal, solid molybdenum sulfide, gaseous molybdenum hexafluoride, or an aqueous solution of an anionic complex of the metal.

Band Spectra

Band spectra are often encountered in spectral sources when gaseous radicals or small molecules are present. For example, in Figure 6-19 bands for OH, MgOH, and MgO are labeled and consist of a series of closely spaced lines that are not fully resolved by the instrument used to obtain the spectrum. Bands arise from numerous quantized vibrational levels that are superimposed on the ground-state electronic energy level of a molecule.

Figure 6-21b is a partial energy-level diagram for a molecule that shows its ground state E_0 and two of its excited electronic states, E_1 and E_2. A few of the many vibrational levels associated with the ground state are also shown. Vibrational levels associated with the two excited states have been omitted because the lifetime of an excited vibrational state is brief compared with that of an electronically excited state (about 10^{-15} s versus 10^{-8} s). Because of this tremendous difference in lifetimes, an electron excited to one of the higher vibrational levels of an electronic state relaxes to the lowest vibrational level of that state before an electronic transition to the ground state can occur. Therefore, the radiation produced by the electrical or thermal excitation of polyatomic species nearly always results from a transition from the *lowest vibrational level of an excited electronic state* to any of the several vibrational levels of the ground state.

The mechanism by which a vibrationally excited species relaxes to the nearest electronic state involves a transfer of its excess energy to other atoms in the system through a series of collisions. As noted, this process takes place at an enormous speed. Relaxation from one electronic state to another can also occur by collisional transfer of energy, but the rate of this process is slow enough that relaxation by photon release is favored.

The energy-level diagram in Figure 6-21b illustrates the mechanism by which two radiation bands that consist of five closely spaced lines are emitted by a molecule excited by thermal or electrical energy. For a real molecule, the number of individual lines is much larger because in addition to the numerous vibrational states, a multitude of rotational states are superimposed on each. The differences in energy among the rotational levels is perhaps an order of magnitude smaller than that for vibrational states. Thus, a real molecular band would be made up of many more lines than we have shown in Figure 6-21b, and these lines would be much more closely spaced.

Continuum Spectra

As shown in Figure 6-22, truly continuum radiation is produced when solids are heated to incandescence. Thermal radiation of this kind, which is called *blackbody radiation*, is characteristic of the temperature of the emitting surface rather than the material composing that surface. Blackbody radiation is produced by the innumerable atomic and molecular oscillations excited in the condensed solid by the thermal energy. Note that the energy peaks in Figure 6-22 shift to shorter wavelengths with increasing temperature. It is clear that very high temperatures are needed to cause a thermally excited source to emit a substantial fraction of its energy as ultraviolet radiation.

As noted earlier, part of the continuum background radiation exhibited in the flame spectrum shown in Figure 6-19 is probably thermal emission from incandescent particles in the flame. Note that this background decreases rapidly as the ultraviolet region is approached.

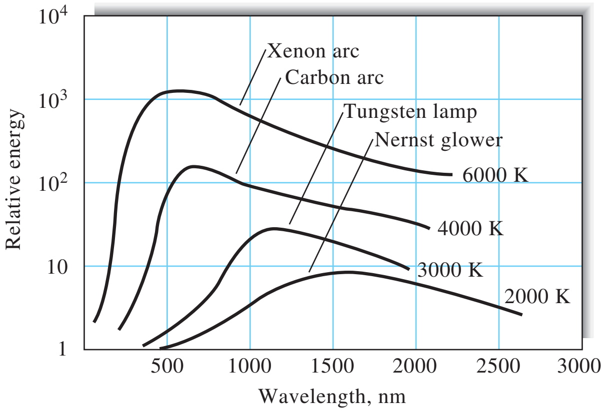


FIGURE 6-22 Blackbody radiation curves.

Heated solids are important sources of infrared, visible, and longer-wavelength ultraviolet radiation for analytical instruments.

6C-5 Absorption of Radiation

When radiation passes through a solid, liquid, or gaseous sample, certain frequencies may be selectively removed by *absorption*, a process in which electromagnetic energy is transferred to the atoms, ions, or molecules composing the sample. Absorption promotes these particles from their normal room temperature state, or ground state, to one or more higher-energy excited states.

According to quantum theory, atoms, molecules, and ions have only a limited number of discrete energy levels; for absorption of radiation to occur, the energy of the exciting photon must *exactly* match the energy difference between the ground state and one of the excited states of the absorbing species. Since these energy differences are unique for each species, a study of the frequencies of absorbed radiation can be used to characterize and identify the constituents of a sample. For this purpose, a plot of absorbance as a function of wavelength or frequency is experimentally determined (*absorbance*, a measure of the decrease in radiant power, is defined by Equation 6-32 in Section 6D-2). Typical absorption spectra are shown in Figure 6-23.

The four plots in Figure 6-23 reveal that absorption spectra vary widely in appearance; some are made up of numerous sharp peaks, while others consist of smooth continuous curves. In general, the nature of a spectrum is influenced by such variables as the complexity, the physical state, and the environment of the absorbing species. More fundamental, however, are the differences between absorption spectra for atoms and those for molecules.

Atomic Absorption

When polychromatic ultraviolet or visible radiation passes through a medium that consists of monoatomic particles, such as gaseous mercury or sodium, absorption can occur at a few well-defined frequencies (see Figure 6-23a). The relative simplicity of such spectra is due to the small number of possible energy states for the absorbing particles. Excitation can occur only by an electronic process in which one or more of the electrons of the atom are raised to a higher energy level. For example, sodium vapor exhibits two closely spaced, sharp absorption peaks in the yellow region of the visible spectrum (589.0 and 589.6 nm) as a result of excitation of the 3*s* electron to two 3*p* states that differ only slightly in energy. Several other narrow absorption lines, corresponding to other allowed electronic transitions, are also observed. For example, an ultraviolet peak at about 285 nm results from the excitation of the 3*s* electron in sodium to the excited 5*p* state, a process that requires significantly greater energy than does excitation to the 3*p* state (in fact, the peak at 285 nm is also a doublet; the energy difference between the two peaks is so small, however, that most instruments cannot resolve them).

Ultraviolet and visible radiation have enough energy to cause transitions of the outermost, or bonding, electrons only. X-ray frequencies, on the other hand, are several orders of magnitude more energetic (see Example 6-3) and are capable of interacting with electrons that are closest to the nuclei of atoms. Absorption peaks that correspond to electronic transitions of these innermost electrons are thus observed in the X-ray region.

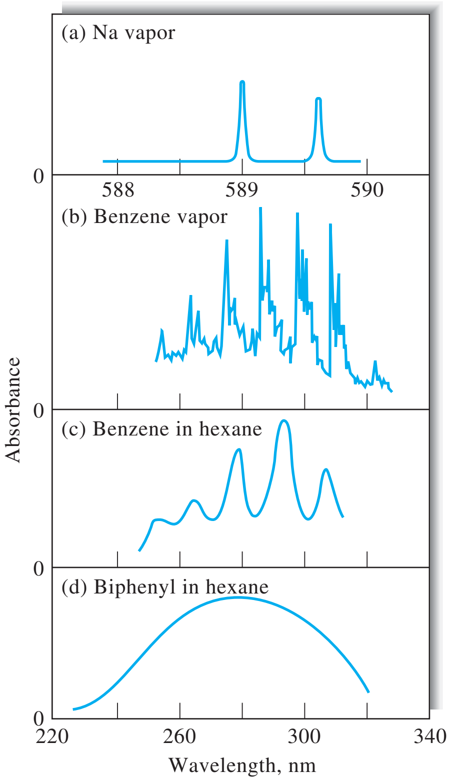


FIGURE 6-23 Some typical ultraviolet absorption spectra.

Molecular Absorption

Absorption spectra for polyatomic molecules, particularly in the condensed state, 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 associated with the bands of a molecule is made up of three components. That is,

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \tag{6-21}$$

where $E_{\text{electronic}}$ describes the electronic energy of the molecule that arises from the energy states of its several bonding electrons. The second term on the right refers to the total energy associated with the multitude of interatomic vibrations that are present in molecular species. Generally, a molecule has many more quantized vibrational energy levels than it does electronic levels. Finally, $E_{\text{rotational}}$ is the energy caused by various rotational motions within a molecule; again the number of rotational states is much larger than the number of vibrational states. Thus, for each electronic energy state of a molecule, there are normally several possible vibrational states. For each of these vibrational states, in turn, numerous rotational states are possible. As a result, the number of possible energy levels for a molecule is normally orders of magnitude greater than the number of possible energy levels for an isolated atom.

Figure 6-24 is a graphical representation of the energy levels associated with a few of the numerous electronic and vibrational states of a molecule. The heavy line labeled E_0 represents the electronic energy of the molecule in its ground state (its state of lowest electronic energy); the lines labeled E_1 and E_2 represent the energies of two excited electronic states. Several of the many vibrational energy levels ($e_0, e_1, \ldots, e_n$) are shown for each of these electronic states.

Figure 6-24 shows that the energy difference between the ground state and an electronically excited state is large relative to the energy differences between vibrational levels in a given electronic state (typically, the two differ by a factor of 10 to 100).

The arrows in Figure 6-24a depict some of the transitions that result from absorption of radiation. Visible radiation causes excitation of an electron from E_0 to any of the n vibrational levels associated with E_1 (only five of the n vibrational levels are shown in Figure 6-24). Potential absorption frequencies are then given by n equations, each with the form

$$\nu_i = \frac{1}{h}(E_1 + e_i' - E_0) \tag{6-22}$$

where $i = 1, 2, 3, \ldots, n$.

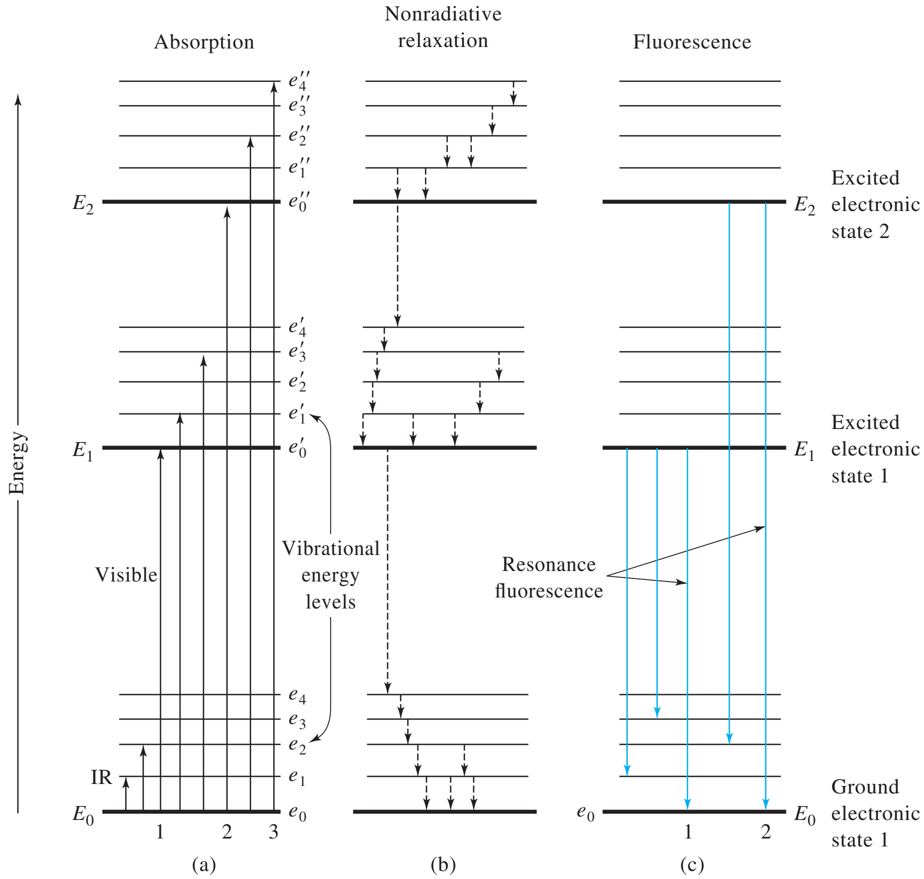


FIGURE 6-24 Partial energy-level diagrams for a fluorescent organic molecule.

Similarly, if the second electronic state has *m* vibrational levels (four of which are shown), potential absorption frequencies for ultraviolet radiation are given by *m* equations such as

$$\nu_i = \frac{1}{h}(E_2 + e_i'' - E_0) \tag{6-23}$$

where $i = 1, 2, 3, \ldots, m$.

Finally, as shown in Figure 6-24a, the less energetic near- and mid-infrared radiation can bring about transitions only among the *k* vibrational levels of the ground state. Here, *k* potential absorption frequencies are given by *k* equations, which may be formulated as

$$\nu_i = \frac{1}{h}(e_i - e_0) \tag{6-24}$$

where $i = 1, 2, 3, \ldots, k$.

Although they are not shown, several rotational energy levels are associated with each vibrational level in Figure 6-24. The energy difference between the rotational energy levels is small relative to the energy difference between vibrational levels. Transitions between a ground and an excited rotational state are brought about by radiation in the 0.01- to 1-cm-wavelength range, which includes microwave and longer-wavelength infrared radiation.

In contrast to atomic absorption spectra, which consist of a series of sharp, well-defined lines, molecular spectra in the ultraviolet and visible regions are ordinarily characterized by absorption regions that often encompass a substantial wavelength range (see Figure 6-23b, c). Molecular absorption also involves electronic transitions. As shown by Equations 6-23 and 6-24, however, several closely spaced absorption lines will be associated with each electronic transition, because of the existence of numerous vibrational states. Furthermore, as we have mentioned, many rotational energy levels are associated with each vibrational state. As a result, the spectrum for a molecule usually consists of a series of closely spaced absorption lines that constitute an *absorption band*, such as those shown for benzene vapor in Figure 6-23b. Unless a high-resolution instrument is used, the individual peaks may not be detected, and the spectra will appear as broad smooth peaks such as those shown in Figure 6-23c. Finally, in the condensed state, and in the presence of solvent molecules, the individual lines tend to broaden even further to give nearly *continuous spectra* such as that shown in Figure 6-23d. Solvent effects are considered in later chapters.

Pure vibrational absorption is observed in the infrared region, where the energy of radiation is insufficient to cause electronic transitions. Such spectra exhibit narrow, closely spaced absorption peaks that result from transitions among the various vibrational quantum levels (see the transition labeled IR at the bottom of Figure 6-24a). Variations in rotational levels may give rise to a series of peaks for each vibrational state; but in liquid and solid samples rotation is often hindered to such an extent that the effects of these small energy differences are not usually detected. Pure rotational spectra for gases can, however, be observed in the microwave region.

Absorption Induced by a Magnetic Field

When electrons of the nuclei of certain elements are subjected to a strong magnetic field, additional quantized energy levels can be observed as a consequence of the magnetic properties of these elementary particles. The differences in energy between the induced states are small, and transitions between the states are brought about only by absorption of long-wavelength (or low-frequency) radiation. With nuclei, radio waves ranging from 30 to 500 MHz ($\lambda = 1000$ to 60 cm) are generally involved; for electrons, microwaves with a frequency of about 9500 MHz ($\lambda = 3$ cm) are absorbed. Absorption by nuclei or by electrons in magnetic fields is studied by *nuclear magnetic resonance* (NMR) and *electron spin resonance* (ESR) techniques, respectively; NMR methods are considered in Chapter 19.

6C-6 Relaxation Processes

Ordinarily, the lifetime of an atom or molecule excited by absorption of radiation is brief because there are several *relaxation processes* that permit its return to the ground state.

Nonradiative Relaxation

As shown in Figure 6-24b, *nonradiative relaxation* involves the loss of energy in a series of small steps, the excitation energy being converted to kinetic energy by collision with other molecules. A minute increase in the temperature of the system results.

As shown by the blue lines in Figure 6-24c, relaxation can also occur by emission of fluorescence radiation. Still other relaxation processes are discussed in Chapters 15, 18, and 19.

Fluorescence and Phosphorescence Emission

Fluorescence and phosphorescence are analytically important emission processes in which species are excited by absorption of a beam of electromagnetic radiation; radiant emission then occurs as the excited species return to the ground state. Fluorescence occurs more rapidly than phosphorescence and is generally complete after about 10^{-5} s from the time of excitation. Phosphorescence emission takes place over periods longer than 10^{-5} s and may indeed continue for minutes or even hours after irradiation has ceased. Fluorescence and phosphorescence are most easily observed at a 90° angle to the excitation beam.

Resonance fluorescence describes the process in which the emitted radiation is identical in frequency to the exciting radiation. The lines labeled 1 and 2 in Figure 6-24c are examples of resonance fluorescence. Resonance fluorescence is most commonly produced by *atoms* in the gaseous state, which do not have vibrational energy states superimposed on electronic energy levels.

Nonresonance fluorescence is caused by irradiation of molecules in solution or in the gas phase. As shown in Figure 6-24a, absorption of radiation promotes the molecules into any of the several vibrational levels associated with the two excited electronic levels. The lifetimes of these excited vibrational states are, however, only on the order of 10^{-15} s, which is much smaller than the lifetimes of the excited electronic states (10^{-8} s). Therefore, on the average, vibrational relaxation occurs before electronic relaxation. As a result, the energy of the emitted radiation is smaller than that of the absorbed by an amount equal to the vibrational excitation energy. For example, for the absorption labeled 3 in Figure 6-24a, the absorbed energy is equal to $(E_2 - E_0 + e''_4 - e''_0)$, whereas the energy of the fluorescence radiation is again given by $(E_2 - E_0)$. Thus, the emitted radiation has a lower frequency, or longer wavelength, than the radiation that excited the fluorescence. This shift in wavelength to lower frequencies is sometimes called the *Stokes shift* as mentioned in connection with Raman scattering in Figure 6-18.

Phosphorescence occurs when an excited molecule relaxes to a metastable excited electronic state (called the *triplet state*), which has an average lifetime of greater than about 10^{-5} s. The nature of this type of excited state is discussed in Chapter 15.

6C-7 The Uncertainty Principle

The *uncertainty principle* was first proposed in 1927 by Werner Heisenberg, who postulated that nature places limits on the precision with which certain pairs of physical measurements can be made. The uncertainty principle, which has important and widespread implications in instrumental analysis, can be derived from the principle of superposition, which was discussed in Section 6B-4. Applications of this principle will be found in several later chapters that deal with spectroscopic methods.[5]

Let us suppose that we wish to determine the frequency ν_1 of a monochromatic beam of radiation by comparing it with the output of a standard clock, which is an oscillator that produces a light beam that has a precisely known frequency of ν_2. To detect and measure the difference between the known and unknown frequencies, $\Delta\nu = \nu_1 - \nu_2$, we allow the two beams to interfere as in Figure 6-5 and determine the time interval for a beat (*A* to *B* in Figure 6-5). The minimum time Δt required to make this measurement must be equal to or greater than the period of one beat, which as shown in Figure 6-5, is equal to $1/\Delta\nu$. Therefore, the minimum time for a measurement is given by

$$\Delta t \geq 1/\Delta\nu$$

or

$$\Delta t \Delta\nu \geq 1 \qquad (6\text{-}25)$$

Note that to determine $\Delta\nu$ with negligibly small uncertainty, a huge measurement time is required. If the observation extends over a very short period, the uncertainty will be large.

Let us multiply both sides of Equation 6-25 by Planck's constant to give

$$\Delta t \cdot (h\Delta\nu) = h$$

From Equation 6-17, we can see that

$$\Delta E = h\Delta\nu$$

and

$$\Delta t \cdot \Delta E = h \qquad (6\text{-}26)$$

Equation 6-26 is one of several ways of formulating the Heisenberg uncertainty principle. The meaning in words of this equation is as follows. If the energy E of a particle or system of particles—photons, electrons, neutrons, or protons, for example—is measured for an exactly known period of time Δt, then this energy is uncertain by at least $h/\Delta t$. Therefore, the energy of a particle can be known with zero uncertainty only if it is observed for an infinite period. For finite periods, the energy measurement can never be more precise than $h/\Delta t$. The practical consequences of this limitation are discussed in several of the chapters that follow.

6D QUANTITATIVE ASPECTS OF SPECTROCHEMICAL MEASUREMENTS

As shown in Table 6-2, there are four major classes of spectrochemical methods. All four require the measurement of *radiant power P*, which is the energy of a beam of radiation that reaches a given area per second. In modern instruments, radiant power is determined with a radiation detector that converts radiant energy into an electrical signal S. Generally S is a voltage or a current that ideally is directly proportional to radiant power. That is,

$$S = kP \qquad (6\text{-}27)$$

where k is a constant.

Many detectors exhibit a small, constant response, known as a *dark signal* or *dark response* (usually a current or voltage), in the absence of radiation. In those cases, the total signal is described by the relationship

$$S = kP + k_d \qquad (6\text{-}28)$$

where k_d is the dark response, which is generally small and constant at least for short periods of time. Spectrochemical instruments are usually equipped with a compensating circuit that reduces k_d to zero whenever measurements are made. With such instruments, Equation 6-27 then applies.

---

[5] A general essay on the uncertainty principle, including applications, is given by L. S. Bartell, *J. Chem. Ed.*, **1985**, *62*, 192, **DOI**: 10.1021/ed062p192.

TABLE 6-2 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

6D-1 Emission, Luminescence, and Scattering Methods

As shown in column 3 of Table 6-2, in emission, luminescence, and scattering methods, the power of the radiation emitted by an analyte after excitation is ordinarily directly proportional to the analyte concentration c ($P_e = kc$). Combining this equation with Equation 6-27 gives

$$S = k'c \tag{6-29}$$

where k' is a constant that can be evaluated by measuring S after excitation of one or more standards of known concentration.

6D-2 Absorption Methods

As shown in Table 6-2, quantitative absorption methods require two power measurements: one before a beam has passed through the medium that contains the analyte (P_0) and the other after passing through the medium (P). Two terms, which are widely used in absorption spectrometry and are related to the ratio of P_0 and P, are *transmittance* and *absorbance*.

Transmittance

Figure 6-25 shows a beam of parallel radiation before and after it has passed through a medium that has a thickness of b cm and a concentration c of an absorbing species. As a consequence of interactions between the photons and absorbing atoms or molecules, the power of the beam is reduced (attenuated) from P_0 to P. The *transmittance T* of the medium is then the fraction of incident radiation transmitted by the medium:

$$T = \frac{P}{P_0} \tag{6-30}$$

Transmittance is often expressed as a percentage or

$$\%T = \frac{P}{P_0} \times 100\% \tag{6-31}$$

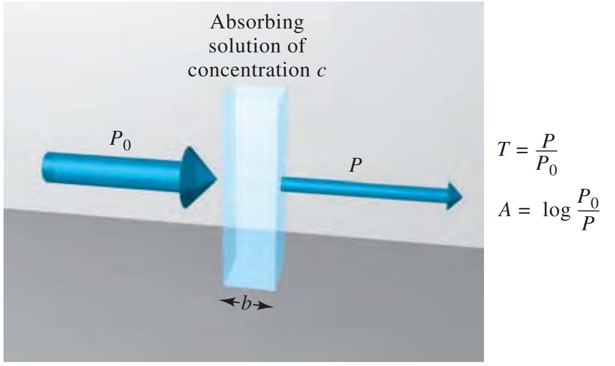


FIGURE 6-25 Attenuation of a beam of radiation by an absorbing solution. The larger arrow on the incident beam signifies a higher radiant power than is transmitted by the solution. The path length of the absorbing solution is b, and the concentration is c.

Absorbance

The absorbance A of a medium is defined by the equation

$$A = -\log_{10} T = \log \frac{P_0}{P} \tag{6-32}$$

Note that, in contrast to transmittance, the absorbance of a medium increases as attenuation of the beam becomes greater.

Beer's Law

For monochromatic radiation, absorbance is directly proportional to the path length b through the medium and the concentration c of the absorbing species. These relationships are given by

$$A = abc \tag{6-33}$$

where a is a proportionality constant called the *absorptivity*. The magnitude of a depends on the units used for b and c. For solutions of an absorbing species, b is often given in centimeters and c in grams per liter. Absorptivity then has units of L g^{-1} cm^{-1}.

When the concentration in Equation 6-33 is expressed in moles per liter and the cell length is in centimeters, the absorptivity is called the *molar absorptivity* and is given the special symbol ϵ. Thus, when b is in centimeters and c is in moles per liter,

$$A = \epsilon bc \tag{6-34}$$

where ϵ has the units L mol^{-1} cm^{-1}.

Tutorial: Learn more about **transmittance and absorbance** at www.tinyurl.com/skoogpia7

Tutorial: Learn more about **Beer's law** at www.tinyurl.com/skoogpia7

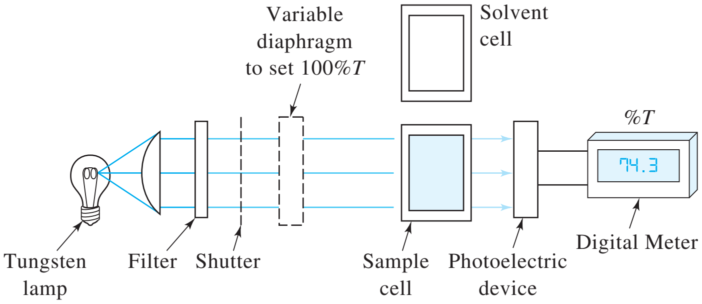


FIGURE 6-26 Single-beam photometer for absorption measurements in the visible region.

Equations 6-33 and 6-34 are expressions of *Beer's law*, which serves as the basis for quantitative analyses by both atomic and molecular absorption measurements. There are certain limitations to the applicability of Beer's law, and these are discussed in detail in Section 13B-2.

Measurement of Transmittance and Absorbance

Figure 6-26 is a schematic of a simple instrument called a *photometer*, which is used for measuring the transmittance and absorbance of aqueous solutions with a filtered beam of visible radiation. Here, the radiation from a tungsten bulb passes through a colored glass filter that restricts the radiation to a limited band of contiguous wavelengths. The beam then passes through a variable diaphragm that permits adjustment of the power of the radiation that reaches the transparent cell that contains the sample. A shutter can be imposed in front of the diaphragm that completely blocks the beam. With the shutter open, the radiation strikes a photoelectric transducer that converts the radiant energy of the beam to a signal (current or voltage) that can be measured with a digital meter as shown. The output of the meter S is described by Equation 6-28.

To make such an instrument direct reading in percent transmittance, two preliminary adjustments are made: the *0% T*, or *dark response adjustment*, and the *100% T adjustment*. The 0% T adjustment is made with the detector screened from the source by closing the mechanical shutter. Any small dark response in the detector is nulled electrically until the digital display reads zero.

The 100% T adjustment is made with the shutter open and with the solvent cell in the light path. Usually, the solvent is contained in a cell that is as nearly as possible identical to the cell that contains the sample. The 100% T adjustment with this instrument involves varying the power of the beam by means of the variable diaphragm; in some instruments, the same effect is realized by varying the radiant output of the source electrically. The radiant power that reaches the detector is then varied until the digital display reads exactly 100. Effectively, this procedure sets P_0 in Equation 6-31 at 100%. When the solvent is replaced by the cell that contains the sample, the scale then indicates the percent transmittance directly, as shown by the equation

$$\%T = \frac{P}{P_0} \times 100\% = \frac{P}{\cancel{100\%}} \times \cancel{100\%} = P$$

Many of today's photometers linearize the readout by conversion to a logarithmic function as discussed in Section 13D. For direct absorbance readout, the zero absorbance is set with the shutter open and the solvent in the sample cell. No measurement with the light blocked (corresponding to 0 %T) is needed. Hence, the dark response must be negligible or set to zero by other means.

QUESTIONS AND PROBLEMS

*Answers are provided at the end of the book for problems marked with an asterisk.

Problems with this icon are best solved using spreadsheets.

6-1 Define

- **(a)** coherent radiation
- **(b)** superposition principle
- **(c)** refractive index of a medium
- **(d)** normal dispersion of a substance

QUESTIONS AND PROBLEMS (continued)

- **(e)** anomalous dispersion
- **(f)** work function of a substance
- **(g)** photoelectric effect
- **(h)** ground state of a molecule
- **(i)** electronic excitation
- **(j)** fluorescence
- **(k)** phosphorescence
- **(l)** transmittance
- **(m)** absorptivity
- **(n)** absorbance
- **(o)** vibrational relaxation
- **(p)** Stokes shift

***6-2** Calculate the frequency in hertz, the energy in joules, and the energy in electron volts of an X-ray photon with a wavelength of 5.47 Å.

***6-3** Calculate the frequency in hertz, the wavelength in μm, and the energy in joules associated with the 2843 cm^{-1} vibrational absorption band of an aliphatic ketone.

***6-4** Calculate the wavelength and the energy in joules associated with an NMR signal at 250 MHz.

***6-5** Calculate the velocity, frequency, and wavelength of the sodium D line ($\lambda = 589\,\text{nm}$) as light from this source passes through a species whose refractive index, n_D, is 1.12.

***6-6** When the D line of sodium light impinges an air-diamond interface at an angle of incidence of 25.0°, the angle of refraction is 10.1°. What is n_D for diamond?

***6-7** What is the wavelength of a photon that has three times as much energy as that of a photon whose wavelength is 820 nm?

***6-8** The silver bromide bond energy is approximately 243 kJ/mol (AgBr is unusually sensitive to light and was widely used in photography). What is the longest wavelength of light that is capable of breaking the bond in silver bromide?

***6-9** Cesium is used extensively in photocells and in television cameras because it has the lowest ionization energy of all the stable elements.

- **(a)** What is the maximum kinetic energy of a photoelectron ejected from cesium by 520 nm light? Note that if the wavelength of the light used to irradiate the cesium surface becomes longer than 660 nm, no photoelectrons are emitted.
- **(b)** Use the rest mass of the electron to calculate the velocity of the photoelectron in (a).

***6-10** The Wien displacement law for blackbody radiators states that the product of temperature in kelvin and the wavelength of maximum emission is a constant k ($k = T \cdot \lambda_{\max}$). Calculate the wavelength of maximum emission for a Globar infrared source operated at 1900 K. Use the data in Figure 6-22 for the Nernst glower for the evaluation of the constant.

***6-11** Calculate the wavelength of

- **(a)** the sodium line at 589 nm in diamond, which has a refractive index of 2.419.
- **(b)** the output of a ruby laser at 694.3 when it is passing through a piece of acrylic sheet (Plexiglas®), which has a refractive index of 1.49.

*6-12 Calculate the reflection loss when a beam of radiant energy passes through an empty quartz cell assuming the refractive index of quartz is 1.55.

6-13 Explain why the wave model for radiation cannot account for the photoelectric effect.

*6-14 Convert the following absorbance values into percent transmittances:

(a) 0.173 **(b)** 0.799 **(c)** 1.145 **(d)** 0.056

*6-15 Convert the following percent transmittances into absorbances:

(a) 22.7 **(b)** 91.2 **(c)** 45.6 **(d)** 2.17

*6-16 Calculate the percent transmittance of solutions with half the absorbance of those in Problem 6-14.

*6-17 Calculate the absorbance of solutions with half the percent transmittance of those in Problem 6-15.

*6-18 A solution that was 3.59×10^{-3} M in X had a transmittance of 0.196 when measured in a 2.00-cm cell. What concentration of X would be required for the transmittance to be increased by a factor of 3 when a 1.00-cm cell was used?

*6-19 A compound had a molar absorptivity of 2.93×10^3 L cm^{-1} mol^{-1}. What concentration of the compound would be required to produce a solution that has a transmittance of 10.16% in a 2.00-cm cell?

Challenge Problem

6-20 One of the watershed events in the development of physics and chemistry was the appearance of Einstein's landmark paper explaining the photoelectric effect, establishing the corpuscular nature of light, and leading to the modern view of the wave-particle duality of the microscopic realm.

(a) Look up Millikan's paper on the photoelectric effect, and describe how he characterized Einstein's work.[6]

(b) In Section 6C-1 we described how measurements of the stopping voltage in a phototube as a function of frequency can be used to determine Planck's constant. Describe and discuss three experimental difficulties in the determination of the Planck constant by this method. You may find the paper by Keesing[7] useful in this discussion.

(c) Use the data in Table III of Millikan's paper to determine the stopping potential as a function of wavelength at 433.9, 404.7, 365.0, 312.5, and 253.5 nm.

(d) Enter these data into an Excel spreadsheet, and perform a least-squares analysis of the data to determine Planck's constant and its uncertainty. Compare your results to those of Millikan, and discuss any differences.

(e) One of the difficulties that you discovered in (b) and (c) is related to the determination of the stopping potential. Knudsen[8] has described a method based on the following normalized equations:[9]

$$\phi(\delta) = \frac{4\pi m k^2 T^2}{h^2}\left(e^{\delta} - \frac{e^{2\delta}}{2^2} + \frac{e^{3\delta}}{3^2} - \cdots\right) \quad (\delta \leq 0)$$

$$\phi(\delta) = \frac{4\pi m k^2 T^2}{h^2}\left[\frac{\pi^2}{6} + \frac{1}{2}\delta^2 - \left(e^{-\delta} - \frac{e^{-2\delta}}{2^2} + \frac{e^{-3\delta}}{3^2} - \cdots\right)\right] \quad (\delta \geq 0)$$

---

[6] R. A. Millikan, *Phys. Rev.*, **1918**, *7*, 355, **DOI**: 10.1103/PhysRev.7.355.

[7] R. G. Keesing, *Eur. J. Phys.*, **1981**, *2*, 139, **DOI**: 10.1088/0143-0807/2/3/003.

[8] A. W. Knudsen, *Am. J. Phys.*, **1983**, *51*, 725, **DOI**: 10.1119/1.13155.

[9] R. H. Fowler, *Phys. Rev.*, **1931**, *38*, 45, **DOI**: 10.1103/PhysRev.38.45.

QUESTIONS AND PROBLEMS (continued)

where $\phi(\delta)$ is normalized photocurrent and δ is the normalized retarding voltage in units of kT. Create a spreadsheet, and generate a plot of $\Phi(\delta) = \log \phi(\delta)$ versus δ for 56 values in the range $\delta = -5$ to $\delta = 50$. Also plot the following normalized data collected at 365.015 nm.

δ, kT	**$\log \phi(\delta)$**
33.24	0.17
33.87	0.33
34.72	0.53
35.46	0.79
36.20	0.99
36.93	1.20
37.67	1.39
38.41	1.58
40.43	1.97
42.34	2.27
44.25	2.47
46.16	2.64
47.97	2.77
49.99	2.89
51.90	3.01
53.82	3.10
55.63	3.19
57.65	3.25
59.56	3.33
61.48	3.38
63.29	3.44
65.31	3.51
67.23	3.54
69.04	3.60

Print two copies of the plot in full-page format, and overlay the two copies over a light source. Determine the stopping potential at 365.015 nm as described by Knudsen. Compare your result with his result in the table in (f).

(f) Perform a least-squares analysis of the data in the following table to determine Planck's constant. Compare these results to those of Millikan and your results from (c). Rationalize any differences in the results in terms of experimental differences and other fundamental considerations.

	Stopping Potential	
λ, nm	**kT**	**V**
435.834	56.7	1.473
404.656	48.1	1.249
365.015	35.4	0.919
334.148	23.4	0.608
313.170	14.0	0.364
296.728	5.8	0.151
289.36	1.3	0.034

(g) There is an element of circular reasoning in the Knudsen procedure. Describe and discuss critically the use of the curve-matching process to determine the stopping potential.

(h) Planck's constant is no longer determined by measurements on photocells. How is it determined?[10] What other fundamental constants depend on Planck's constant? What are the current values of these constants, and what are their uncertainties?

(i) Least-squares procedures can be used to adjust the values of the fundamental constants so that they are internally consistent.[11] Describe how this procedure might be accomplished. How does an improvement in the quality of the measurement of one constant such as Avogadro's number affect the values of the other constants?

(j) Over the past several decades, much effort has been expended in the determination of the values of the fundamental constants. Why is this effort important in analytical chemistry, or why is it not? What measurable quantities in analytical chemistry depend on the values of the fundamental constants? Why are these efforts important to science and to the world at large? Comment critically on the return on the investment of time and effort that has gone into the determination of the fundamental constants.

---

[10] E. R. Williams, R. L. Steiner, D. B. Newell, and P. T. Olsen, *Phys. Rev. Lett.*, **1998**, *81*, 2404, **DOI**: 10.1103/PhysRevLett.81.2404.

[11] J. W. M. DuMond and E. Richard Cohen, *Rev. Modern Phys.*, **1953**, *25*, 691, **DOI**: 10.1103/RevModPhys.25.691.