Chapter

6

An Introduction to Spectrometric Methods

Spectrometric methods are a large group of analytical methods that are based on atomic and molecular spectroscopy. Spectroscopy is a general term for the science that deals with the interactions of various types 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 radio-frequency radiation.

This chapter treats in a general way the interactions of electromagnetic waves with atomic and molecular species. After this introduction, the next five chapters describe the various types of spectrometric methods employed by chemists for the identification and determination of 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.

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 parameters 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* where energy is proportional to the frequency of the radiation. These dual views of radiation as particles and as waves are not mutually exclusive but, rather, complementary. Indeed, the wave-particle duality is found to apply to the behavior of streams of electrons, protons, and other elementary particles and is completely rationalized by wave mechanics.

6B WAVE PROPERTIES OF ELECTROMAGNETIC RADIATION

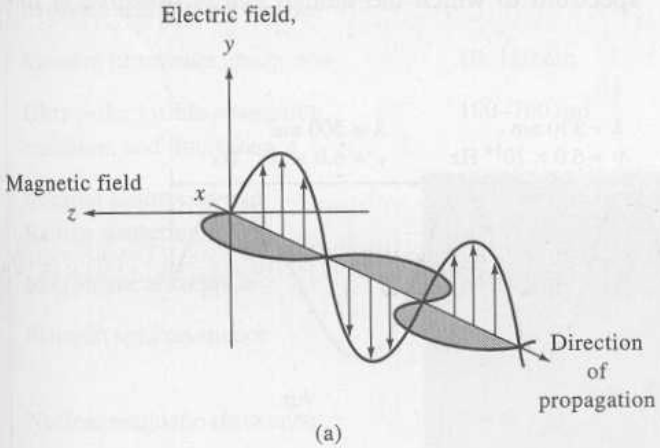
For many purposes, electromagnetic radiation is conveniently represented as electric and magnetic fields that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation. Figure 6-1a is such a representation of a single ray of plane-polarized electromagnetic radiation. The term *plane polarized* implies that all oscillations of either the electric or the magnetic fields lie within 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. The abscissa of this plot is either time as the radiation passes a fixed point in space or distance when time is held constant. 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.

6B-1 Wave Parameters

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 $1/p$. Another parameter of interest is the *wavelength,* λ, which 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 cy-

[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 employed with visible and ultraviolet radiation; the micrometer, mμ (10^{-6} m), is useful for the infrared region. (The *micrometer* was called the *micron* in the early literature; the use of this term is discouraged.)



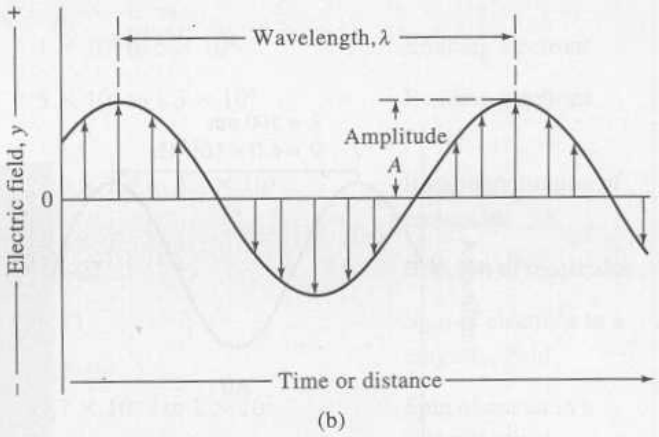


Figure 6-1 Representation of a beam of monochromatic, plane-polarized radiation: (a) electrical and magnetic fields at right angles to one another and direction of propagation, (b) two-dimensional representation of the electric vector.

cle 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 upon the composition of the medium through which it passes. Thus, Equation 6-1 implies that the wavelength of radiation is also dependent upon the medium. The subscript i in Equation 6-1 emphasizes these dependencies.

In a vacuum, the velocity of radiation is independent of wavelength and is at its maximum. This velocity, given the symbol c, has been determined to be 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 Figure 6-2 for a monochromatic beam of visible radiation.[3]

[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.

Note that the wavelength shortens nearly 200 nm, or more than 30%, as it passes into glass; a reverse change occurs as the radiation again enters air.

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 may write

$$\bar{\nu} = k\nu \tag{6-3}$$

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 synonymously.

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. Figure 6-3 also depicts qualitatively the major spectral regions. The divisions are based on the methods that are required to generate and detect the various kinds of radiation. Several overlaps are evident. Note that the visible portion of the spectrum to which the human eye is sensitive is tiny

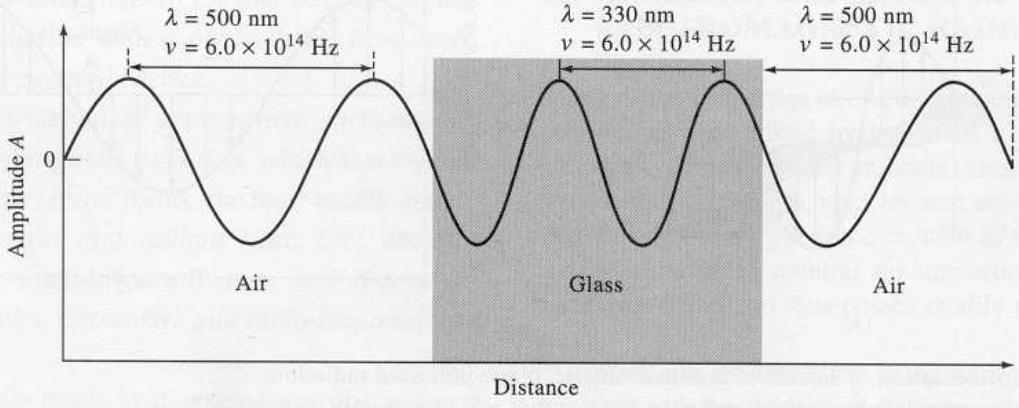


Figure 6-2 Effect of change of medium on a monochromatic beam of radiation.

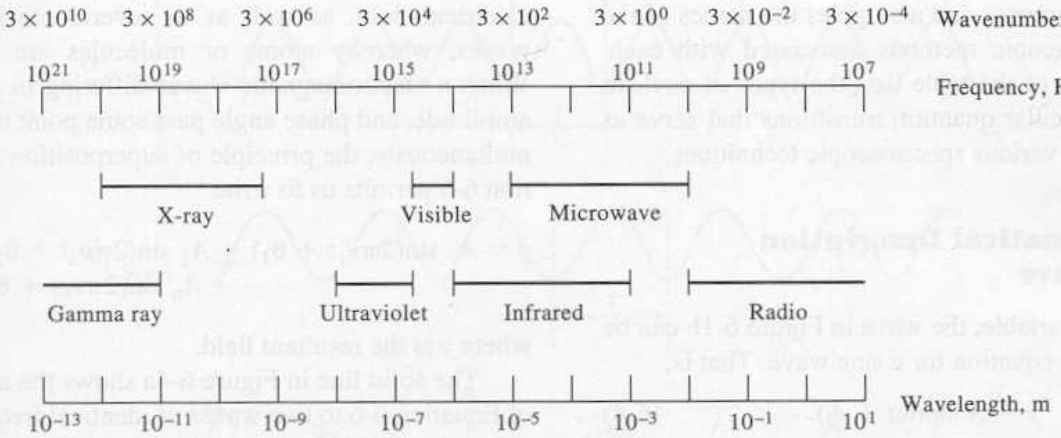


Figure 6-3 Regions of the electromagnetic spectrum.

when compared with other spectral regions. It should also be noted that spectrochemical methods that employ not only visible but also ultraviolet and infrared radiation are often called *optical methods* despite the fact that the human eye is sensitive to neither 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 the way in which 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

TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation

Type 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	0.75–3.75 mm	13–27	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} nm = 10^{-8} cm
1 nm = 10^{-9} m = 10^{-7} cm
1 μm = 10^{-6} m = 10^{-4} cm

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 *electric field*, A is the amplitude or maximum value for y, t is time, and ϕ is the *phase angle*, a term defined in Section 2B-1, page 28. 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, whereby the disturbances involve an electrical field, as well as to several other types of waves, whereby 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 permits us to write

$$y = A_1 \sin(2\pi\nu_1 t + \theta_1) + A_2 \sin(2\pi\nu_2 t + \theta_2) + \cdots + A_n \sin(2\pi\nu_n t + \theta_n) \qquad (6\text{-}6)$$

where y is the resultant field.

The solid line 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; here, the resultant amplitude is smaller than the amplitudes of the component waves. Clearly, a maximum amplitude occurs when the two waves are completely in phase—a situation that prevails whenever the phase difference between waves $(\phi_1 - \phi_2)$ is 0 deg, 360 deg, or an integer multiple of 360 deg. Under these circumstances, maximum *constructive interference* is said to occur. A maximum *destructive interference* occurs when $(\phi_1 - \phi_2)$ is equal to 180 deg or 180 deg plus an integer multiple of 360 deg. Interference plays an important role in many instrumental methods based on electromagnetic radiation.

Figure 6-5 depicts the superposition of two waves with the identical amplitudes but different frequencies.

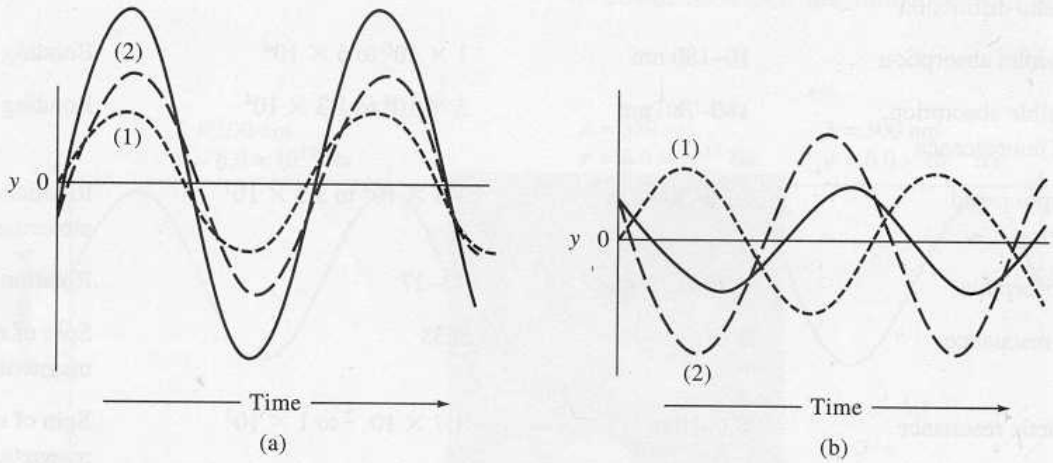


Figure 6-4 Superposition of sinusoidal wave: (a) $A_1 < A_2$, $(\phi_1 - \phi_2) = -20°$, $\nu_1 = \nu_2$; (b) $A_1 < A_2$, $(\phi_1 - \phi_2) = -200°$, $\nu_1 = \nu_2$. In each instance, the solid curve results from the combination of the two dashed curves.

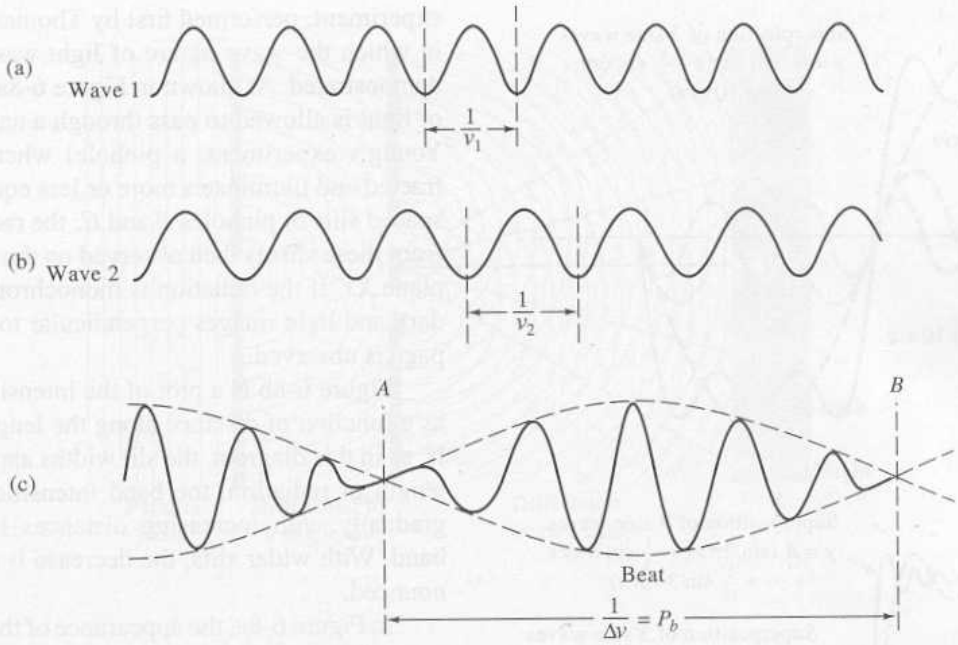


Figure 6-5 Superposition of two waves of different frequencies but identical amplitudes: (a) wave 1 with a period of $1/\nu_1$; (b) wave 2 with a period of $1/\nu_2$ ($\nu_2 = 1.25\ \nu_1$); (c) combined wave pattern. Note that superposition of ν_1 and ν_2 produces a beat pattern with a period of $1/\Delta\nu$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

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,

$$P_b = \frac{1}{\Delta\nu} = \frac{1}{(\nu_2 - \nu_1)} \qquad (6\text{-}7)$$

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, an early 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

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

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 solid 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 solid line 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 it practical to perform Fourier transformations on a routine basis on a computer. 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, which can be observed not only for electromagnetic radiation but also for mechanical or

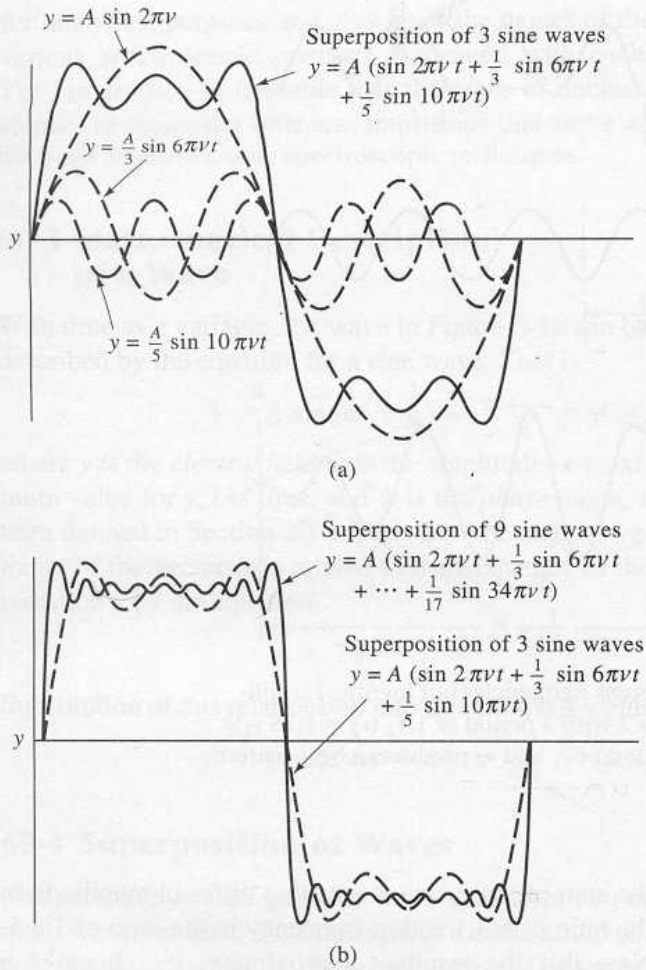


Figure 6-6 Superposition of sine waves to form a square wave: (a) combination of three sine waves; (b) combination of three, as in (a), and nine sine waves.

acoustical waves. For example, diffraction is readily 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-deg arcs. Thus, the direction of the wave front appears to bend as a consequence of passing the two edges of the slit.

Diffraction is a consequence of *interference*. 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 unambiguously demonstrated. 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) whereupon 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, 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

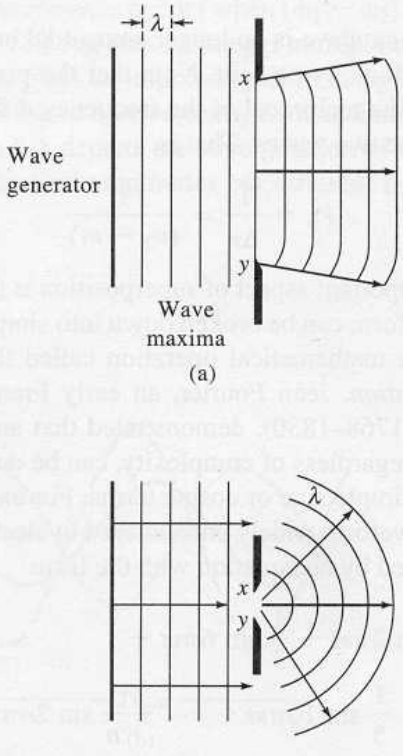


Figure 6-7 Propagation of waves through a slit: (a) $xy >> \lambda$; (b) $xy = \lambda$.

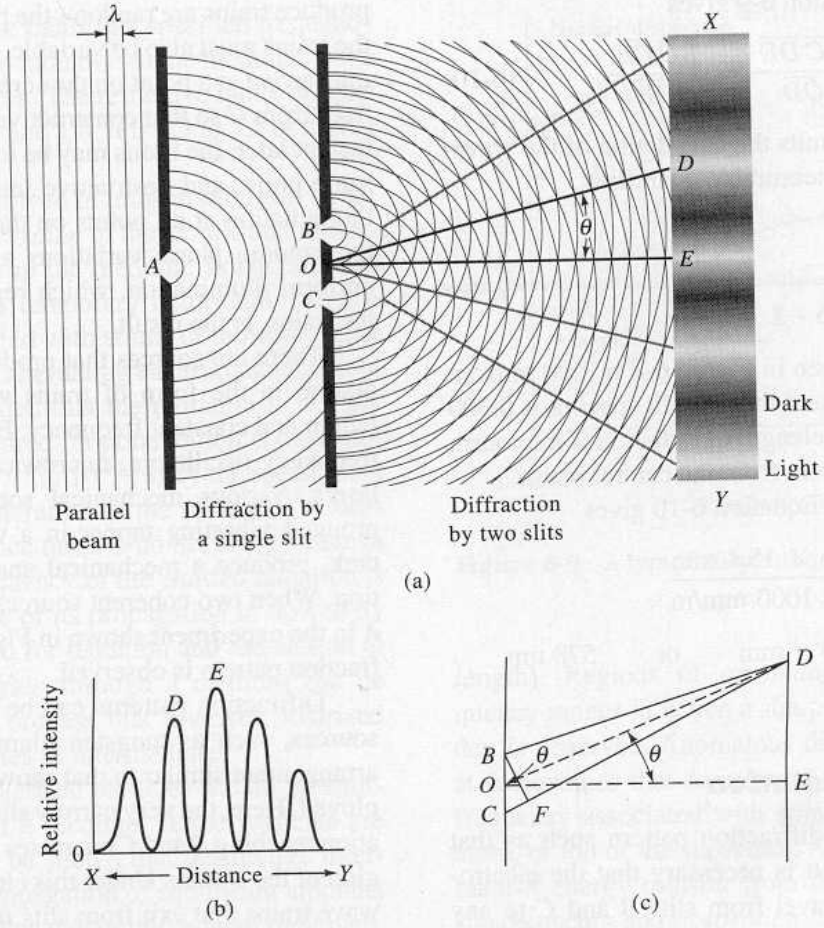


Figure 6-8 Diffraction of monochromatic radiation by slits.

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 from the normal, formed by the dotted line extending from a point *O*, halfway between the slits, to the point of maximum intensity *D*. The solid 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 *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 *BD* and *CD*. For the two beams to be in phase at *D*, it is necessary that $\overline{CF}$ correspond 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

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

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

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?

Substituting into Equation 6-10 gives

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

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

6B-6 Coherent Radiation

In order 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. Thus, 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 employed. Here, 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

It is observed experimentally that the rate at which radiation is propagated through a transparent substance is less than its velocity in a vacuum and depends upon 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 the matter. 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

$$\eta_i = \frac{c}{v_i} \qquad (6\text{-}11)$$

where η_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.

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 a later section of this chapter.

Since the velocity of radiation in matter is wavelength dependent and since c in Equation 6-11 is independent of this parameter, 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. Clearly, 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 a sharp change in refractive index is observed. Anomalous dispersion always occurs at frequencies that correspond to the natural harmonic frequency associated with some part of the 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 a later section.

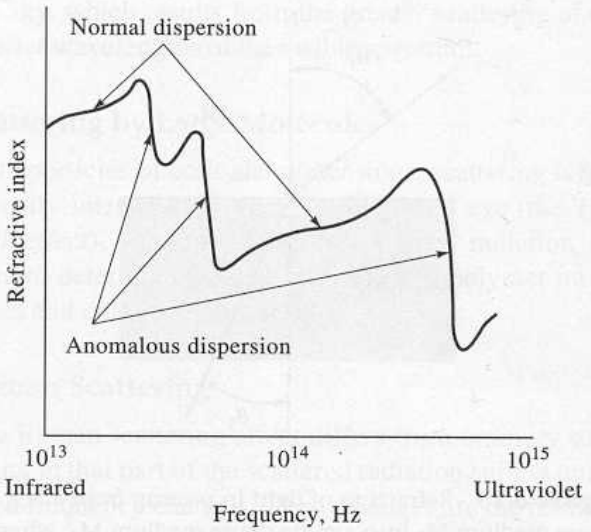


Figure 6-9 A typical dispersion curve.

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.

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 environ-

[4] For a more complete discussion of refractometry, see S. Z. Lewin and N. Bauer, in *Treatise on Analytical Chemistry,* I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 6, Chapter 70. New York: Interscience, 1965.

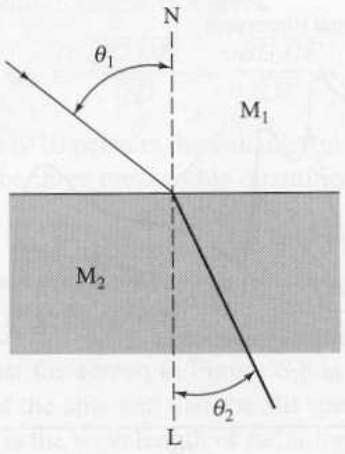


Figure 6-10 Refraction of light in passing from a less dense medium M_1 into a more dense medium M_2, where its velocity is lower.

ment, 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:

$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{\eta_2}{\eta_1} = \frac{v_1}{v_2} \qquad (6\text{-}12)$$

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

$$(\eta_2)_{vac} = \frac{(\sin \theta_1)_{vac}}{\sin \theta_2} \qquad (6\text{-}13)$$

The refractive indexes of substance M_2 can then be computed from measurements of $(\theta_1)_{vac}$ 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

$$(\eta_2)_{air} = \frac{(\sin \theta_1)_{air}}{\sin \theta_2} \qquad (6\text{-}14)$$

Most compilations of refractive indexes provide data in terms of Equation 6-14. Such data are readily converted to refractive indexes with vacuum as a reference by multiplying by the refractive index of air relative to a vacuum. That is,

$$\eta_{vac} = 1.00027\ \eta_{air}$$

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 radiation reflected becomes greater with increasing differences in refractive index. For a beam that enters an interface at right angles, the fraction reflected is given by

$$\frac{I_r}{I_0} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2} \qquad (6\text{-}15)$$

where I_0 is the intensity of the incident beam and I_r is the reflected intensity; η_1 and η_2 are the refractive indexes of the two media.

EXAMPLE 6-2

Calculate the percent 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.

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

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

$$I_{r2} = 0.0035\ I_0$$

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

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

$$I_{r3} = 0.0035\ I_0$$

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

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

$$I_{r4} = 0.038\ I_0$$

The total reflection loss I_{rt} is

$$I_{rt} = 0.040\ I_0 + 0.0035\ I_0 + 0.0035\ I_0 + 0.038\ I_0 = 0.085\ I_0$$

and

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

It will become evident in later chapters 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 deg. Beyond this figure, however, the percentage of radiation that is reflected increases rapidly and approaches 100% at 90 deg, 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 as a consequence of 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;* its intensity 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 the greater scattering of the shorter wavelengths of the visible spectrum.

Scattering by Large Molecules

With particles of colloidal dimensions, scattering is sufficiently intense to be seen by the naked eye (the *Tyndall effect*). Measurements of scattered radiation are used to determine the size and shape of polymer molecules and colloidal particles.

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 can be visualized as an infinite set of electrical 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.

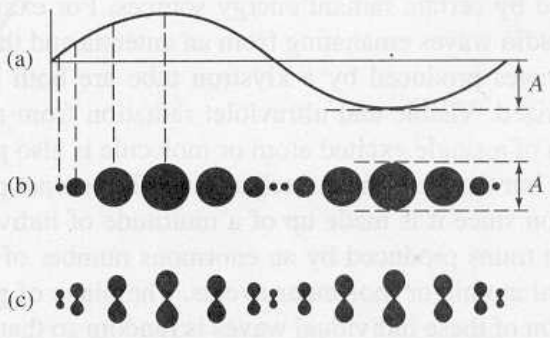


Figure 6-11 Unpolarized and plane-polarized radiation: (a) cross-sectional view of a beam of monochromatic radiation, (b) successive end-on view of the radiation in (a) if it is unpolarized, (c) successive end-on views of the radiation of (a) if it is plane polarized on the vertical axis.

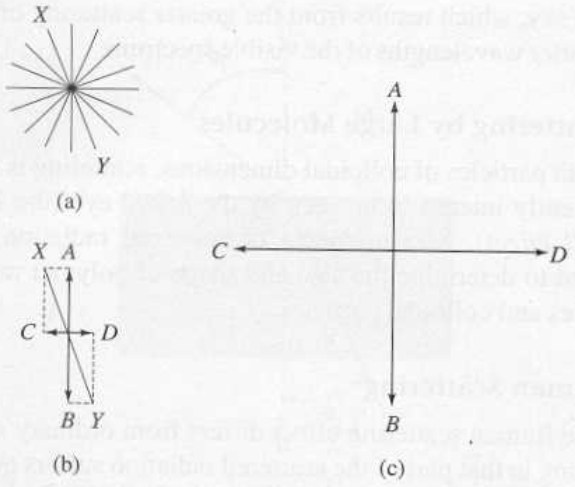


Figure 6-12 (a) A few of the electrical vectors of a beam traveling perpendicular to the page.
(b) The resolution of a vector in plane *XY* into two mutually perpendicular components.
(c) The resultant when all vectors are resolved (not to scale).

The vector in any one plane, say *XY* as depicted in Figure 6-11a, 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 in space. Figure 6-11c shows an end-on view of a beam of plane-polarized radiation after various time intervals.

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. In order 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 had confirmed Einstein's theoretical conclusions in every detail.

Figure 6-13 is a schematic of vacuum phototube circuit similar to the one used by Millikan to study the

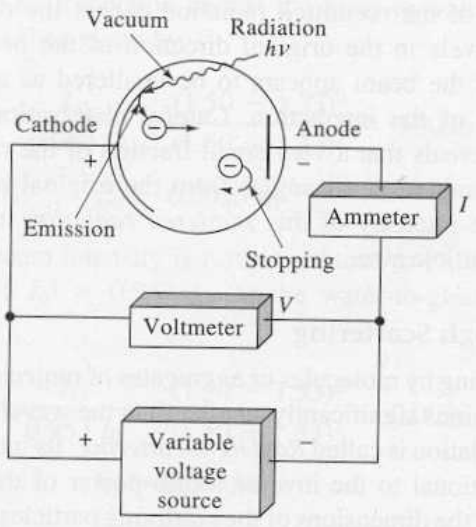


Figure 6-13 Apparatus for studying the photoelectric effect.

photoelectric effect. The surface of the large *photocathode* on the left usually is coated with an alkali metal or one of its compounds, but other metals may be used. 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 swept 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 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 coated on 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.*

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 eV_0, of the photoelectrons is plotted against frequency for photocathode surfaces of potassium, sodium, and copper. Other surfaces give plots with identical slopes, h, but different intercepts, ω.

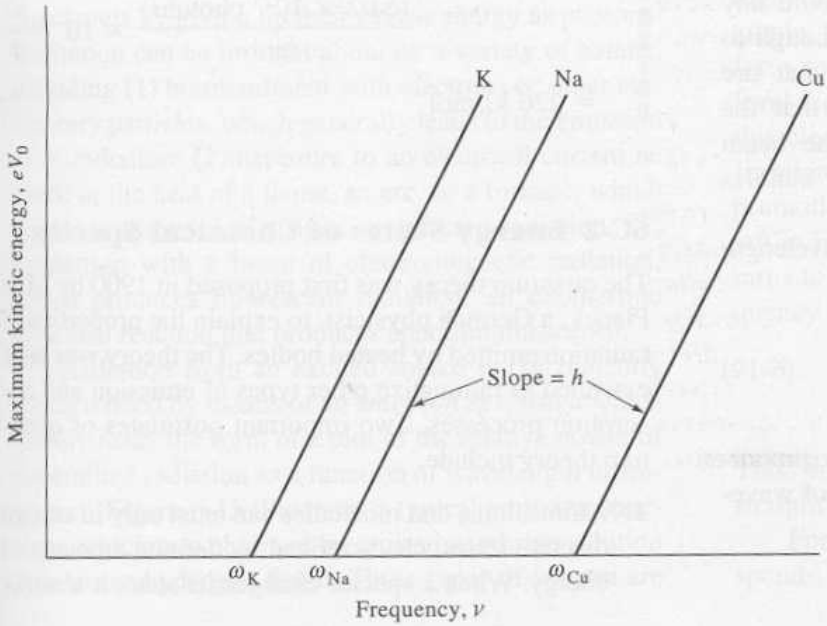


Figure 6-14 Maximum kinetic energy of photoelectrons emitted from three metal surfaces as a function of radiation frequency.

The plots shown in Figure 6-14 are described by the equation

$$eV_0 = h\nu + \omega \qquad (6\text{-}16)$$

In this equation, the slope h is the Planck constant, which is equal to 6.6254×10^{-34} joule second, and the intercept ω is the *work function,* a constant that is characteristic of the surface material. 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 his now famous equation

$$E = h\nu \qquad (6\text{-}17)$$

By substituting Einstein's equation into Equation 6-16 and rearranging, we obtain

$$E = h\nu = eV_0 - \omega \qquad (6\text{-}18)$$

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

The photoelectric effect cannot be explained by a wave model but requires instead a quantum model in which radiation is viewed as a stream of discrete bundles of energy, or photons. For example, calculations indicate that no single electron could acquire sufficient energy for ejection if the radiation striking the surface is 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,

$$E = h\frac{c}{\lambda} = eV_0 - \omega \qquad (6\text{-}19)$$

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

EXAMPLE 6-3

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

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

(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 $1\ \text{J} = 6.24 \times 10^{18}\ \text{eV}$.

$$E = 3.75 \times 10^{-16}\ \text{J} \times (6.24 \times 10^{18}\ \text{eV/J}) = 2.34 \times 10^{3}\ \text{eV}$$

(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:

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 a second, the frequency ν or the wavelength λ of the radiation is related to the energy difference between the states by the equation

$$E_1 - E_0 = h\nu = \frac{hc}{\lambda} \qquad (6\text{-}20)$$

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. As a consequence 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 gravity.

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

6C-3 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 by a variety of means, including (1) bombardment with electrons or other elementary particles, which generally leads to the emission of X-radiation; (2) exposure to an electrical current ac spark or the heat of a flame, an arc, or a furnace, which produces ultraviolet, visible, or infrared radiation; (3) irradiation with a beam of electromagnetic radiation, which produces fluorescent radiation; 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 6-15 illustrates a typical emission spectrum, which was obtained by aspirating a brine solution into an oxyhydrogen flame. Three types of spectra are evident 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 133.

Figure 6-16 is an X-ray emission spectrum produced by bombarding a piece of molybdenum with an energetic stream of electrons. Note that in Figure 6-16, there is also a line spectrum superimposed on a continuum. The source of the continuum 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 a 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 of about 10^{-4} Å. In Figure 6-15, lines for gas-phase sodium, potassium, strontium, and calcium are identified.

The energy-level diagram in Figure 6-17a 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 $3s$ orbital. Energy level E_1 then represents the energy of the atom when this electron has been promoted to the $3p$ state by absorption of thermal, electrical, or radiant energy. The promotion is depicted by the shorter wavy arrow on the left in Figure 6-17a. After perhaps 10^{-8} s, the atom 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 straight arrow on the right in Figure 6-17a.

For the sodium atom, E_2 in Figure 6-17 corresponds to the more energetic $4p$ state; the resulting

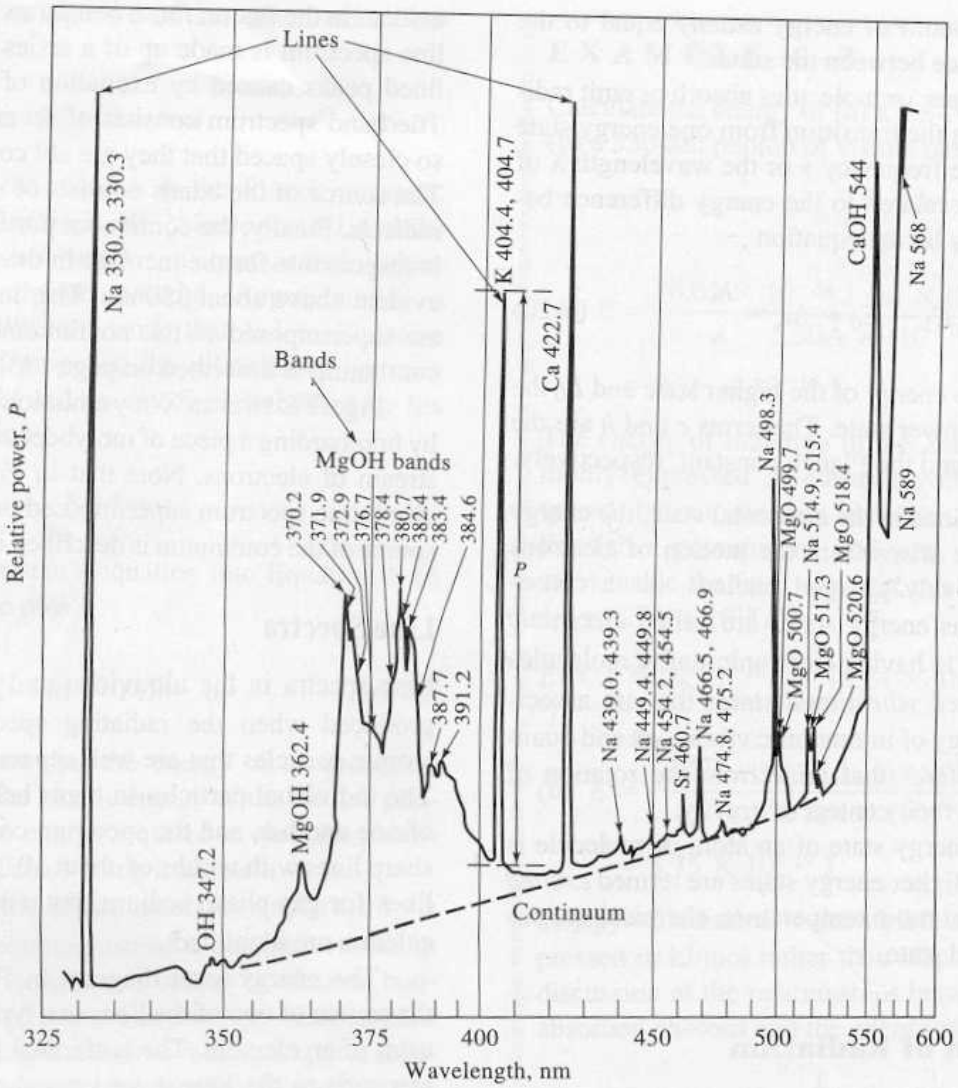


Figure 6-15 Emission spectrum of a brine obtained with an oxyhydrogen flame. *(F. Hermann and C. T. J. Alkemade,* Chemical Analysis by Flame Photometry, *2nd ed., p. 484. New York: Interscience, 1963. With permission.)*

emitting radiation λ_2 appears at a shorter wavelength or a higher frequency. The line at about 330 nm in Figure 6-15 results from this transition; the $3p$-to-$3s$ transition provides a line at about 590 nm.

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 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 6-15 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 6-17b is a partial energy-level diagram for a molecule that shows its ground state E_0 and two of its several excited electronic states, E_1 and E_2. A few of the

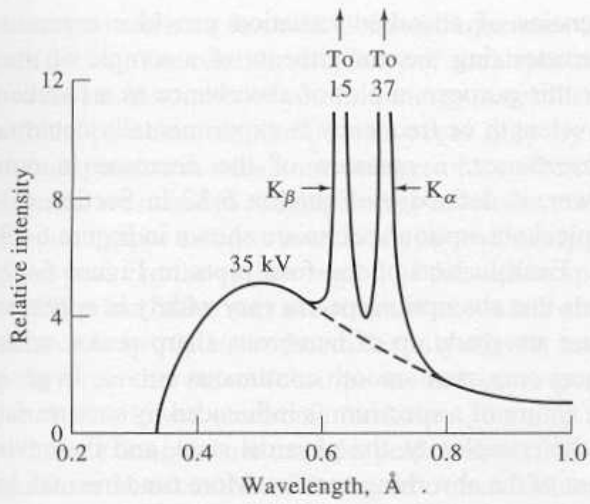


Figure 6-16 X-Ray emission spectrum of molybdenum metal.

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). A consequence of this tremendous difference in lifetimes is that when an electron is excited to one of the higher vibrational levels of an electronic state, relaxation to the lowest vibrational level of that state occurs 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 6-17b 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 would be 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 6-17b, and these lines would be much more closely spaced.

Continuum Spectra

As shown in Figure 6-18, 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

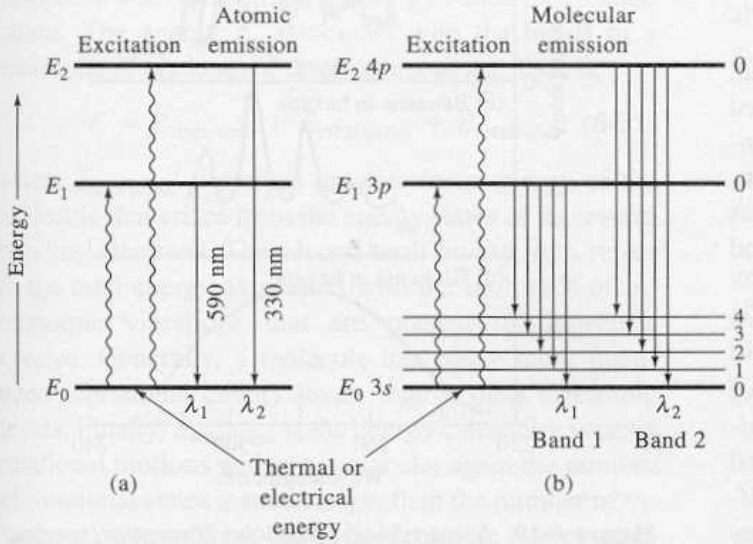


Figure 6-17 Energy-level diagrams for (a) a sodium atom showing the source of a line spectrum and (b) a simple molecule showing the source of a band spectrum.

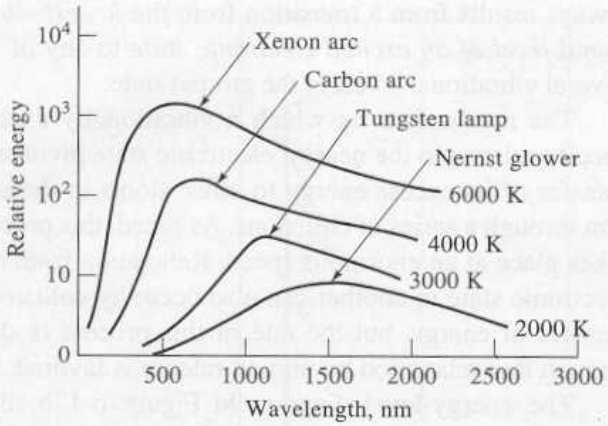


Figure 6-18 Blackbody radiation curves.

the emitting surface rather than the material of which that surface is composed. 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 6-18 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 6-15 is probably thermal emission from incandescent particles in the flame. Note that this background decreases rapidly as the ultraviolet region is approached.

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

6C-4 Absorption of Radiation

When radiation passes through a layer of solid, liquid, or gas, 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, or 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 provides a means of characterizing the constituents of a sample of matter. 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 6-19.

Examination of the four plots in Figure 6-19 reveals that absorption spectra vary widely in appearance; some are made up of numerous sharp peaks, whereas 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

The passage of polychromatic ultraviolet or visible radiation through a medium that consists of monoatomic particles, such as gaseous mercury or sodium, results in

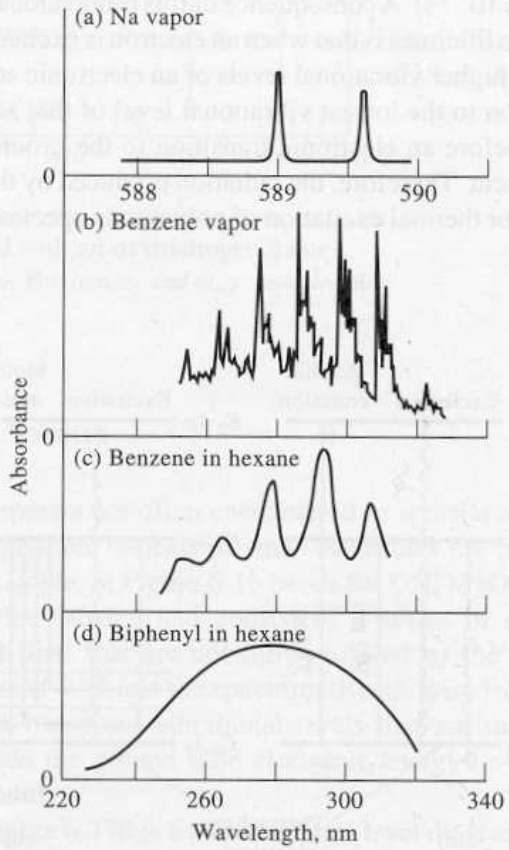


Figure 6-19 Some typical ultraviolet absorption spectra.

the absorption of but a few well-defined frequencies (see Figure 6-19a). 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 $3s$ electron to two $3p$ 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 $3s$ electron in sodium to the excited $5p$ state, a process that requires significantly greater energy than does excitation to the $3p$ 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 has sufficient 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.

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,

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} \quad (6\text{-}21)$$

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, several possible vibrational states normally exist; and for each of these vibrational states, in turn, numerous rotational states are possible. As a consequence, the number of possible energy levels for a molecule is normally orders of magnitude greater than the number of possible energy levels for an atomic particle.

Figure 6-20 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, $\cdots$, e_n) are shown for each of these electronic states.

As can be seen in Figure 6-20, 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 6-20a 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 6-20). Potential absorption frequencies are then given by n equations, each with the form

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

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

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

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

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

Finally, as shown in Figure 6-20a, the less energetic near- and mid-infrared radiation can only bring about transitions among the k vibrational levels of the ground state. Here, k potential absorption frequencies are given by k equations, which may be formulated as

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

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

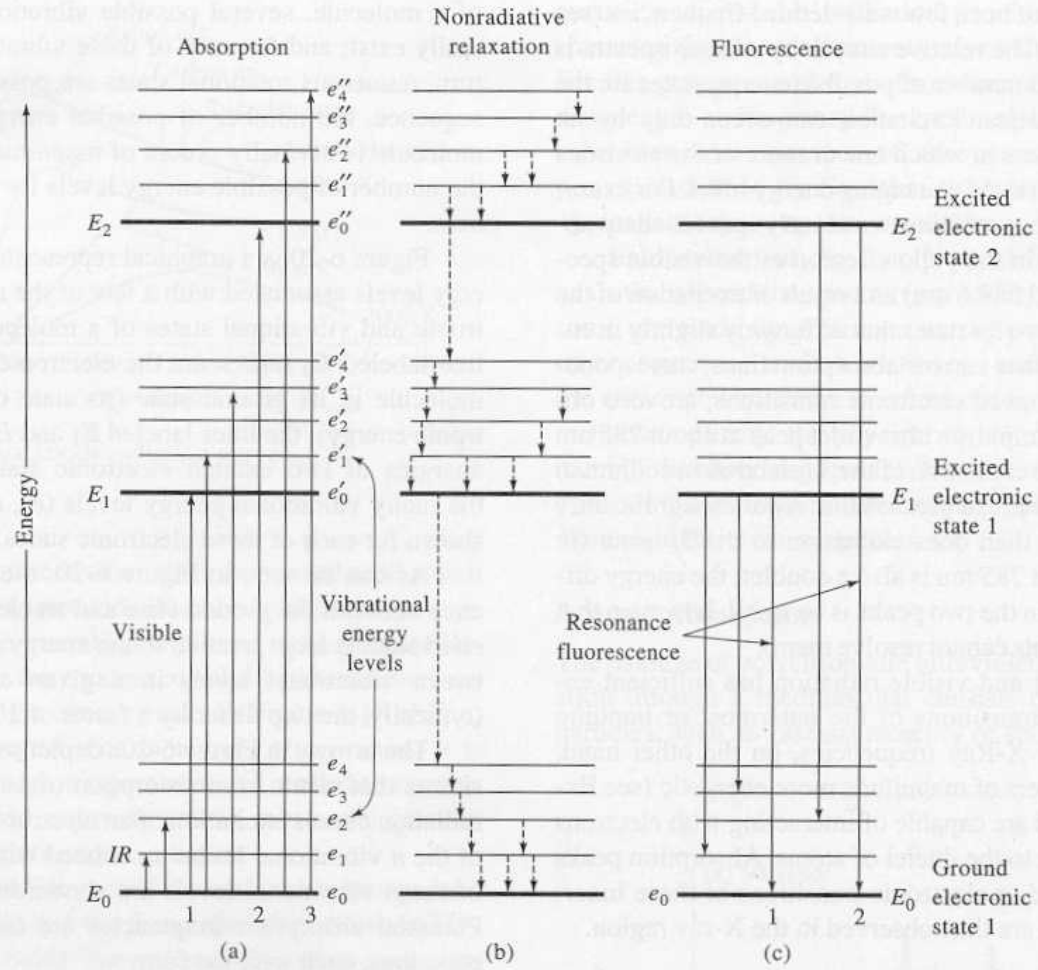


Figure 6-20 Partial energy-level diagrams for a fluorescent organic molecule.

Although they are not shown, several rotational energy levels are associated with each vibrational level in Figure 6-20. 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 is brought about by radiation in the 0.01- to 1-cm range, which includes microwave and longer 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 6-19b, 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, owing to the existence of numerous vibrational states. Furthermore, as we have mentioned, many rotational energy levels are associated with each vibrational state. As a consequence, the spectrum for a molecule ordinarily consists of a series of closely spaced absorption lines that constitute an *absorption band,* such as those shown for benzene vapor in Figure 6-19b. Unless a high-resolution instrument is employed, the individual peaks may not be detected, and the spectra will appear as broad smooth peaks such as those shown in Figure 6-19c. Finally, in the condensed state, and in the presence of solvent molecules, the individual lines tend to broaden even further to give *continuous spectra* such as that shown in Figure 6-19d. 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 6-20a). 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 ordinarily 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 (λ = 1000 to 60 cm) are generally involved; for electrons, microwaves with a frequency of about 9500 MHz (λ = 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; nuclear magnetic resonance methods are considered in Chapter 19.

6C-5 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 6-20b, *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 in Figure 6-20c, relaxation can also occur by emission of fluorescent radiation. Still other relaxation processes are discussed in Chapters 15, 18, and 19.

Fluorescence and Phosphorescence Relaxation

Fluorescence and phosphorescence are analytically important emission processes in which atoms or molecules 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-deg angle to the excitation beam.

Resonance fluorescence describes the process in which the emitted radiation is identical in frequency to the radiation employed for excitation. The lines labeled 1 and 2 in Figures 6-20a and 6-20c illustrate resonance fluorescence. Here, the species is excited to the energy states E_1 or E_2 by radiation that has an energy of $(E_1 - E_0)$ or $(E_2 - E_0)$. After a brief period, emission of radiation of identical energy occurs, as depicted in Figure 6-20c. Resonance fluorescence is most commonly produced by *atoms* in the gaseous state that do not have vibrational energy states superimposed on electronic energy levels.

Nonresonance fluorescence is brought about by irradiation of *molecules* in solution or in the gaseous state. As shown in Figure 6-20a, 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 consequence, 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 6-20a, the absorbed energy is equal to $(E_2 - E_0 + e''_4 - e''_0)$, whereas the energy of the fluorescent 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*. Both resonance and nonresonance radiation can accompany fluorescence of molecules, although the latter tends to predominate because of the much larger number of vibrationally excited states.

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-6 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, is readily 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 zero uncertainty, an infinite 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 the Planck constant to give

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

From Equation 6-17, it is apparent 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 will appear in several of the chapters that follow.

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

6D QUANTITATIVE ASPECTS OF SPECTROCHEMICAL MEASUREMENTS

As shown in Table 6-2, spectrochemical methods fall into four major categories. 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 current,* in the absence of radiation. In those cases, the response is described by the relationship

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

where k_d is the dark current, 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.

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 6-28 gives

$$S = k'c \qquad (6\text{-}29)$$

where k' is a constant that can be evaluated by exciting analyte radiation in one or more standards and by measuring S. An analogous relationship also applies for luminescence and scattering methods.

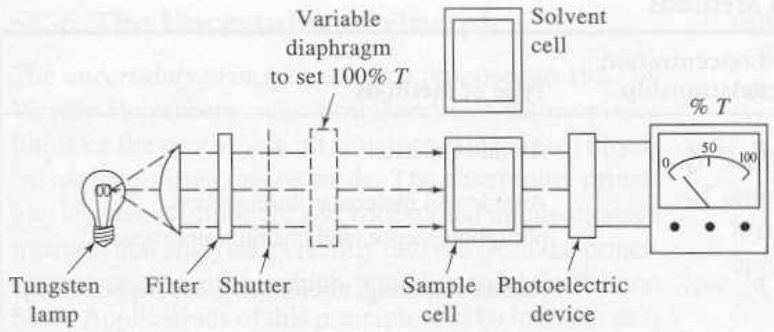


Figure 6-22 Single-beam photometer for absorption measurements in the visible region.

by both atomic and molecular absorption measurements. Certain limitations to the applicability of Beer's law are encountered, and these limitations will be discussed in detail in Section 13B.

Measurement of Transmittance and Absorbance

Figure 6-22 is a schematic of a simple instrument called a photometer 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 impinges on a photoelectric device that converts the radiant energy of the beam to a dc current that is detected and measured with a microammeter. The output of the meter S is described by Equation 6-28. Note that the meter has a linear scale that extends from 0 to 100.

In order to make such an instrument direct reading in percent transmittance, two preliminary adjustments are carried out, namely the *0% T,* or *dark current, 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 current in the detector is nulled electrically until the needle of the detector 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 meter 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

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

Obviously, an absorbance scale can also be scribed on the readout device. As shown in Figure 6-23, such a scale will be nonlinear unless the output is converted to a logarithmic function by suitable hardware or software.

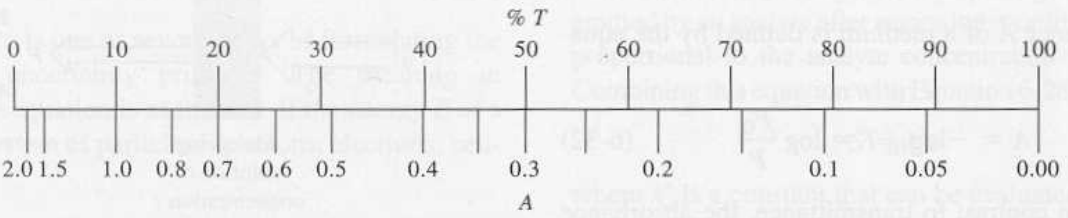


Figure 6-23 Readout for an inexpensive photometer.

6E QUESTIONS AND PROBLEMS

6-1 Define
(a) coherent radiation.
(b) dispersion of a transparent substance.
(c) anomalous dispersion.
(d) work function of a substance.
(e) photoelectric effect.
(f) ground state of a molecule.
(g) electronic excitation.
(h) blackbody radiation.
(i) fluorescence.
(j) phosphorescence.
(k) resonance fluorescence.
(l) photon.
(m) absorptivity.
(n) wavenumber.
(o) 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 2.70 Å.

6-3 Calculate the frequency in hertz, the wavenumber, the energy in joules, and the energy in kJ/mol associated with the 5.715 μm vibrational absorption band of an aliphatic ketone.

6-4 Calculate the wavelength and the energy in joules associated with an NMR signal at 220 MHz.

6-5 Calculate the velocity, frequency, and wavelength of the sodium D line ($\lambda = 589$ nm) as light from this source passes through a species whose refractive index, η_D, is 1.43.

6-6 When the D line of sodium light impinges an air/diamond interface at an angle of incidence of 30.0 deg, it is found that the angle of refraction is 11.9 deg. 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 500 nm?

6-8 The silver iodide bond energy is approximately 255 kJ/mol (AgI is one of the possible active components in photogray sunglasses). What is the longest wavelength of light that is capable of breaking the bond in silver iodide?

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 500 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 1400 K. Use the data in Figure 6-18 for the Nernst glower for the evaluation of the constant.

6-11 Calculate the wavelength of
(a) the sodium line at 589 nm in an aqueous solution that has a refractive index of 1.35.
(b) the output of a ruby laser at 694.3 when it is passing through a piece of quartz that has a refractive index of 1.55.

6-12 Calculate the reflection loss when a beam of radiant passes through an empty quartz cell assuming the refraction 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 data into percent transmittance:
(a) 0.375, (b) 1.325, (c) 0.012.

6-15 Convert the following percent transmittance data into absorbance:
(a) 33.6, (b) 92.1, (c) 1.75.

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 4.14×10^{-3} M in X had a transmittance of 0.126 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 2.17×10^3 L cm^{-1} mol^{-1}. What concentration of the compound would be required to produce a solution that has a transmittance of 8.42% in a 2.50-cm cell?