

## CHAPTER 4

# How Light and Sound Interact with Matter



## Read This Chapter to Learn About

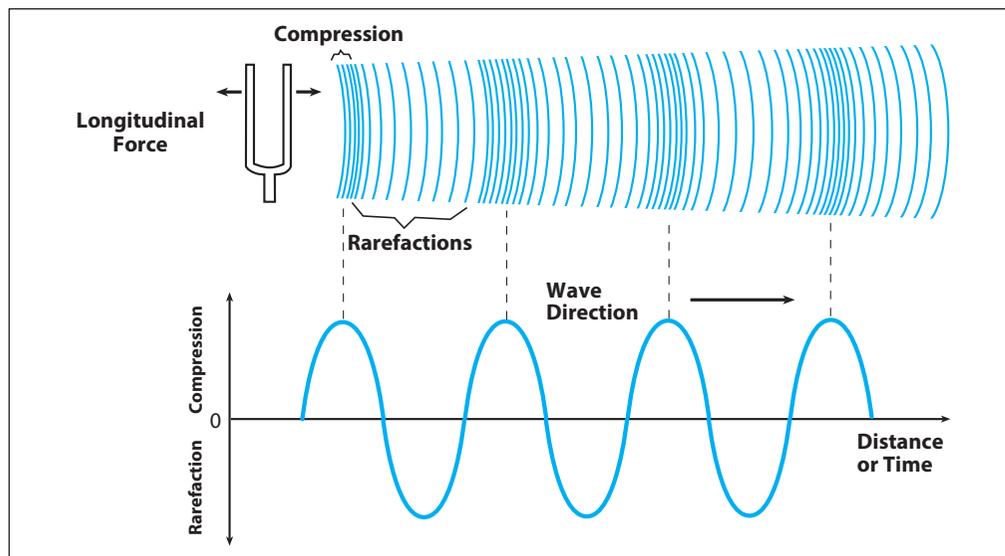
- > Sound
- > Light
- > Molecular Structure and Spectra
- > Geometrical Optics

## SOUND

Any sound that you hear—whether it be the whisper of a librarian, a lawnmower your neighbor is using, a car moving down the road, or a jet preparing for takeoff—begins with a vibration, a vibration that moves in space, or a wave. Sound is an example of **longitudinal waves**, or waves that are generated by a disturbance that moves parallel to the direction of motion of the wave. In this chapter, the characteristics and behavior of sound waves are discussed.

## Production of Sound

**Sound waves** are longitudinal waves that can propagate through all forms of matter—solids, liquids, and gases. Sound waves are generated by the motion of molecules or particles of a medium vibrating back and forth in a direction parallel to the direction of wave motion. As an object such as a tuning fork is struck, the vibration of the prong causes the air molecules to vibrate. As the air molecules vibrate, they alternate between being forced together (**compressions**) and then being separated at distances greater than the normal spacing (**rarefactions**). This example of a longitudinal wave is depicted in Figure 4-1.



**FIGURE 4-1** Longitudinal wave. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

## Relative Speed of Sound in Solids, Liquids, and Gases

The movement of sound requires molecules in a medium. The farther apart the molecules in the medium are spaced, the slower the speed of sound through the medium. Conversely, when molecules are tightly spaced, sound travels the fastest. Therefore, the speed of sound is the fastest in solids (where molecules are tightly spaced) and faster in liquids than in gases (where molecules are widely spaced).

The speed of sound through air is approximately 344 meters/second (m/s; 760 miles/hour). In contrast, the speed of sound in water is 1480 m/s.

## Sound Intensity

**Sound intensity** represents the rate of energy transported by a sound wave per unit area perpendicular to its direction of motion. The sound level  $\beta$ , expressed in units of decibels (dB), is defined in terms of sound intensity  $I$  as:

$$\beta = 10 \log \left( \frac{I}{I_0} \right)$$

where  $I_0$  is the threshold for human hearing [ $= 1 \times 10^{-12}$  watts per square meter ( $W/m^2$ )] and represents the intensity of the weakest sound detectable by the human ear. The following table lists representative values of sound intensity  $I$  and their corresponding sound level  $\beta$ .

**TABLE 4-1** Sound Intensity and Sound Level of Representative Sounds

Sound Intensity ( $\text{W}/\text{m}^2$ )	Sound Level (dB)	Representative Sounds
$1 \times 10^{-12}$	0	Threshold of hearing
$1 \times 10^{-10}$	20	Distant whisper
$1 \times 10^{-8}$	40	Normal outdoor sounds
$1 \times 10^{-6}$	60	Normal conversation
$1 \times 10^{-4}$	80	Busy traffic
$1 \times 10^{-2}$	100	Siren at 30 m
1	120	Loud indoor rock concert (threshold of pain)
$1 \times 10^2$	140	Jet airplane
$1 \times 10^4$	160	Bursting of eardrums

**EXAMPLE:** A particular sound level was measured at 75 dB. Determine its sound intensity.

**SOLUTION:** Using the expression for the sound level intensity, you have:

$$\beta = 10 \log \left( \frac{I}{I_0} \right)$$

$$75 \text{ dB} = 10 \log \left( \frac{I}{1 \times 10^{-12} \frac{\text{W}}{\text{m}^2}} \right)$$

Solving for  $I$  yields:

$$I = \left( 1 \times 10^{-12} \frac{\text{W}}{\text{m}^2} \right) \left( \log^{-1} \frac{75 \text{ dB}}{10} \right) = 3.16 \times 10^{-5} \frac{\text{W}}{\text{m}^2}$$

## Attenuation

**Attenuation**, also known as **damping**, is a gradual reduction in intensity of the sound wave and a subsequent loss of sound energy. Two primary factors behind attenuation include **scattering** and **absorption**. As it propagates from its source, the sound wave will reflect off of or pass around obstacles as it undergoes diffraction. Also, because sound is a form of energy, sound waves transfer a portion of their energy as they collide with and is absorbed by surrounding molecules in their path including air molecules.

## Doppler Effect

The **Doppler effect** refers to the shift in frequency of a transmitted sound that is caused by a change in distance between the source of the sound and the observer. Consider a source emitting a sound of frequency  $f_s$  detected by an observer as a frequency  $f_o$ . If the source is moving toward the observer, the observer perceives an increase in the sound frequency. If the source is moving away from the observer, the observer perceives a decrease in frequency. The altered frequency detected by the observer is known

as the **Doppler-shifted frequency**. These qualitative relationships can be expressed by:

$$f_o = f_s \left( \frac{v \pm v_o}{v \pm v_s} \right)$$

where  $v$  is the speed of sound in the given medium.

There are several specific cases of the Doppler effect:

- ▶ Moving sound source toward a fixed observer

$$f_o = f_s \left( \frac{v}{v - v_s} \right)$$

- ▶ Moving sound source away from a fixed observer

$$f_o = f_s \left( \frac{v}{v + v_s} \right)$$

- ▶ Fixed sound source with observer moving toward source

$$f_o = f_s \left( \frac{v + v_o}{v} \right)$$

- ▶ Fixed sound source with observer moving away from source

$$f_o = f_s \left( \frac{v - v_o}{v} \right)$$

**EXAMPLE:** A police car, in pursuit of a driver suspected of speeding, is traveling at 30 m/s when the siren is turned on, operating at a frequency of 1.2 kHz. Given that the speed of sound in air is 344 m/s, determine the frequency heard by a stationary or fixed witness as

1. the police car approaches the observer; and,
2. the police car passes the observer.

**SOLUTION:**

1. For the case of the moving source approaching a stationary observer, the Doppler-shifted frequency detected by the observer is given by:

$$f_o = f_s \left( \frac{v}{v - v_s} \right) = 1200 \text{ Hz} \left( \frac{344 \frac{\text{m}}{\text{s}}}{344 \frac{\text{m}}{\text{s}} - 30 \frac{\text{m}}{\text{s}}} \right) = 1315 \text{ Hz}$$

2. For the case of the moving source passing a stationary observer, the Doppler-shifted frequency detected by the observer is given by:

$$f_o = f_s \left( \frac{v}{v + v_s} \right) = 1200 \text{ Hz} \left( \frac{344 \frac{\text{m}}{\text{s}}}{344 \frac{\text{m}}{\text{s}} + 30 \frac{\text{m}}{\text{s}}} \right) = 1104 \text{ Hz}$$

## Pitch

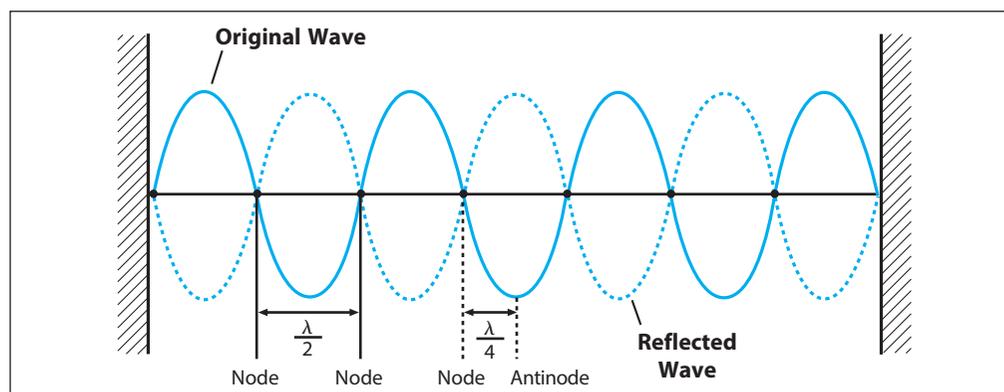
**Pitch** is often associated with the frequency of a sound wave. On a quantitative level, the pitch is given by the frequency of the sound wave. Pitch is also used to describe qualitatively how the frequency of the sound wave is perceived by an observer. The effect of pitch on an observer can be explained by the approach of an ambulance siren. As the ambulance approaches the observer, the observer notices an increasing pitch; as the ambulance passes the observer, the pitch of the siren decreases.

## Resonance in Strings and Pipes

Many objects, such as a tuning fork or plucked string, vibrate at a specific frequency. This frequency is referred to as the object's **natural frequency**. When a periodic, external force strikes the object with a frequency equal to the natural frequency of the object, the amplitude of the object's motion increases and hence energy is absorbed by the object, a condition referred to as **resonance**. Examples of resonance can be found in engineering in the analysis of structure failure in response to severe weather/natural disasters, in medicine with magnetic resonance imaging and lithotripsy of kidney stones, and in music with the tonal qualities of certain string and brass instruments.

## Standing Waves

Consider a wave generated on a stretched string with one side connected to a rigid surface. As the wave propagates toward the fixed end, it reflects, inverts, and continues back and forth across the string, causing the string to vibrate. In such instances, two waves (original and reflected waves) of equal frequencies and amplitudes are moving in opposite directions along the string, creating a **standing wave**, as shown in Figure 4-2.



**FIGURE 4-2** Standing wave. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

The points with no displacement from the horizontal axis are termed **nodes**, and the points that are maximally displaced from the horizontal axis—that is, points at the peaks and valleys of each wave—are termed **antinodes**. The distance between two adjacent displacement nodes is one-half wavelength and the distance from node to antinode is one-quarter wavelength. The frequency,  $f$ , of a standing wave is given by:

$$f = \frac{v}{\lambda}$$

where  $v$  is the velocity of the wave.

### FREQUENCIES IN A STRETCHED STRING

A stretched string of length  $L$  with both ends secured to a rigid surface possesses nodes at both ends. Because the distance between two adjacent nodes is  $\lambda/2$ , then  $\frac{\lambda}{2} = L$  or  $\lambda = 2L$ . Substituting this value into the expression for the frequency yields:

$$f = \frac{v}{\lambda} = \frac{v}{2L}$$

This is the lowest frequency that the string can accommodate and is termed the **fundamental frequency**, or first harmonic. **Harmonic frequencies**, second and greater, are integer multiples of the first harmonic and can be determined from the generalized relation

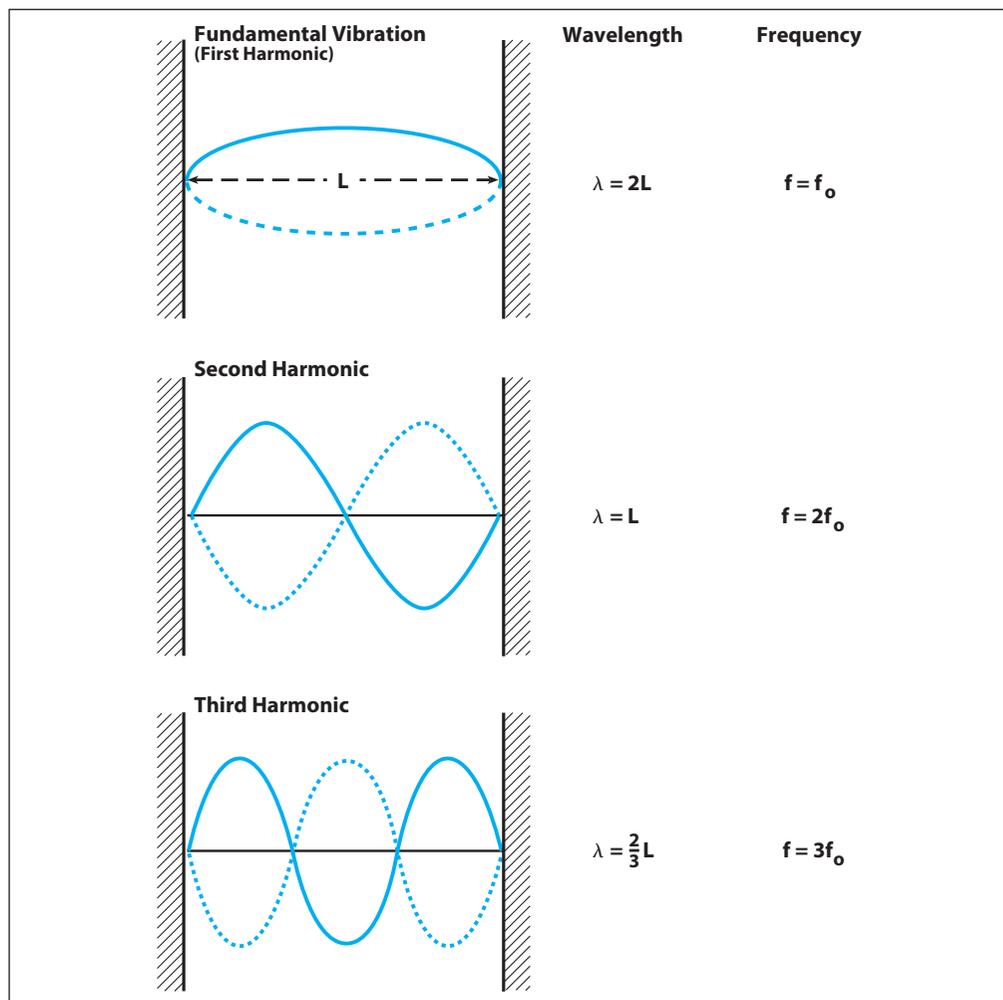
$$f = \frac{nv}{2L} \quad n = 1, 2, 3, \dots$$

The first, second, and third harmonics are illustrated in Figure 4-3.

### FREQUENCIES IN A PIPE

The frequencies in a pipe can be derived in a fashion similar to that for the stretched string. However, the pipe offers more conditions to consider, such as both ends open and one end open. A node can be found at the end of a closed pipe whereas an antinode is present toward the open end of the pipe. Given that the distance from node to node is  $\lambda/2$  and the distance from node to antinode is  $\lambda/4$ , the frequencies for a pipe of length  $L$  are as follows:

<b>Pipe with both ends open:</b>	$L = 2\frac{\lambda}{4} = \frac{\lambda}{2}$
Fundamental frequency:	$f_1 = \frac{v}{2L}$
Harmonics:	$f_n = \frac{nv}{2L} \quad (n = 1, 2, 3, \dots)$
<b>Pipe with one end open:</b>	$L = \frac{\lambda}{4}$
Fundamental frequency:	$f_1 = \frac{v}{4L}$
Harmonics:	$f_n = \frac{nv}{4L} \quad (n = 1, 3, 5, \dots)$



**FIGURE 4-3** First, second, and third harmonics of a standing wave in a stretched string. Source: From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

**EXAMPLE:** Determine the velocity of waves in an open pipe of 1.3 m length if the fundamental frequency is 225 Hz.

**SOLUTION:** For an open pipe, the fundamental frequency is given by:

$$f_1 = \frac{v}{2L}$$

Solving for  $v$  gives:

$$v = f_1 (2L) = (225 \text{ Hz}) (2) (1.3 \text{ m}) = 585 \frac{\text{m}}{\text{s}}$$

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## BEATS

**Beats** are produced during interference by sound waves at slightly different frequencies. The beat frequency  $f_{\text{beat}}$  is equal to the difference in the frequencies of the individual sound waves  $f_1$  and  $f_2$  or

$$f_{\text{beat}} = f_1 - f_2$$

**EXAMPLE:** Determine the number of beats per second that are heard when two tuning forks of frequencies 256 Hz and 264 Hz are struck simultaneously.

**SOLUTION:** The beat frequency or the difference between frequencies of the two tuning forks determines the number of beats per second, or

$$f_{\text{beat}} = f_1 - f_2 = 264 \text{ Hz} - 256 \text{ Hz} = 8 \text{ Hz}$$

## Ultrasound

**Ultrasound** refers to a region of sound frequencies that are above the range of frequencies that are audible to the human ear. The range of frequencies of human hearing is 20 Hz to 20 kHz (20,000 Hz). Ultrasound encompasses the range of frequencies from 20 kHz to 20 MHz (20,000,000 Hz). Ultrasound has a variety of applications in the medical and biological sciences including the assessment of fetal development and the diagnosis of cardiovascular and cerebrovascular disease, particularly in quantifying the presence and extent of atherosclerosis within the major vessels of the circulatory system.

## Shock Waves

**Shock waves** develop when the speed of an object becomes greater than the speed of sound. In this case, the wavefronts generated by the object surpass the position of the source, resulting in a cone-shaped formation of successive wavefronts referred to as a **Mach zone**. A shock wave occurs along the surface or edge of the cone, resulting in a drastic decrease in air pressure and a very large increase in sound wave amplitude.

## LIGHT

We are accustomed to thinking about light in terms of the output of a lamp or a fluorescent lightbulb illuminating a room. This type of light—visible light—represents only a very small subset of the physics definition of light waves, formally known as **electromagnetic waves**. Electromagnetic waves are an example of transverse waves, meaning that the direction of the disturbance is perpendicular to or at right angles to the direction of motion. This section introduces the concept of electromagnetic waves, defines them, and explains their characteristics and behavior as they interact with various surfaces or media, such as mirrors and lenses, to form images (geometrical optics).

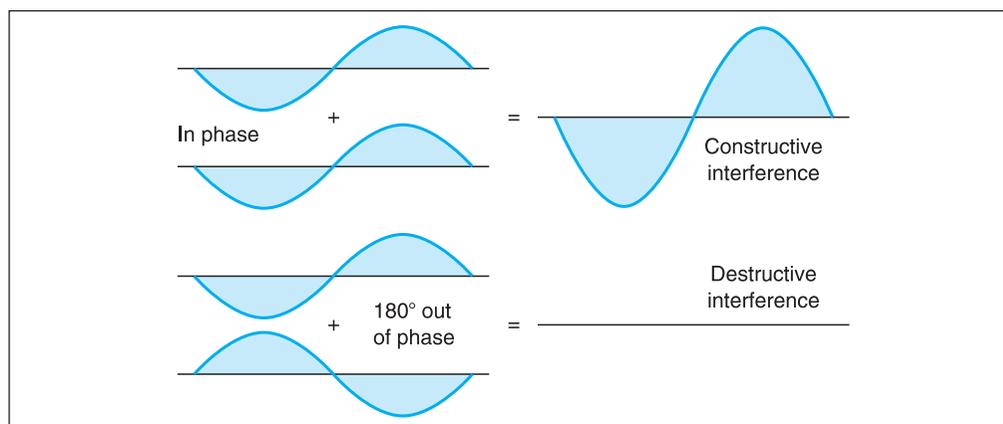


FIGURE 4-4 Wave interference.

## Interference

**Interference** refers to the superposition of two waves traveling within the same medium when they interact. When applied to light waves, interference occurs only when the waves have the same wavelength and a fixed phase difference (i.e., the difference in which the peaks of one wave lead or lag the peaks of the other wave remains constant with time). These types of waves are referred to as **coherent waves**. The **principle of superposition** states that the wave that results from the interaction between two or more waves is the algebraic sum or overlapping of the individual waves, also referred to as superposition. These resultant waves undergo interference, the type of which depends on the phase of the two interacting waves, as shown in Figure 4-4.

When coherent waves with the same amplitude are combined, **constructive interference** occurs when the two waves are in phase and **destructive interference** occurs when the two waves are out of phase (have a phase difference of  $180^\circ$ ).

Consider the experimental setup depicted in Figure 4-5, where two coherent light waves of wavelength  $\lambda$  impinge on two narrow slits separated by a distance  $d$ . The result is a fringe pattern of alternating bright and dark fringes where the bright fringes represent constructive interference and the dark fringes represent destructive interference. The position of the bright fringes (referred to as **maxima**) and the dark fringes (referred to as **minima**) can be determined from the relations:

$$\text{Bright fringes (maxima)} \quad d(\sin \theta) = m\lambda \quad m = 0, 1, 2, \dots$$

$$\text{Dark fringes (minima)} \quad d(\sin \theta) = \left(m + \frac{1}{2}\right)\lambda \quad m = 0, 1, 2, \dots$$

where  $d \sin \theta$  represents the **path difference**, or the difference between distances that the waves travel to reach the fringe position on the screen.

## Diffraction

**Diffraction** describes the ability of light waves to bend or spread through an aperture (opening) or around an obstacle. Consider a light wave with a wavelength  $\lambda$  that

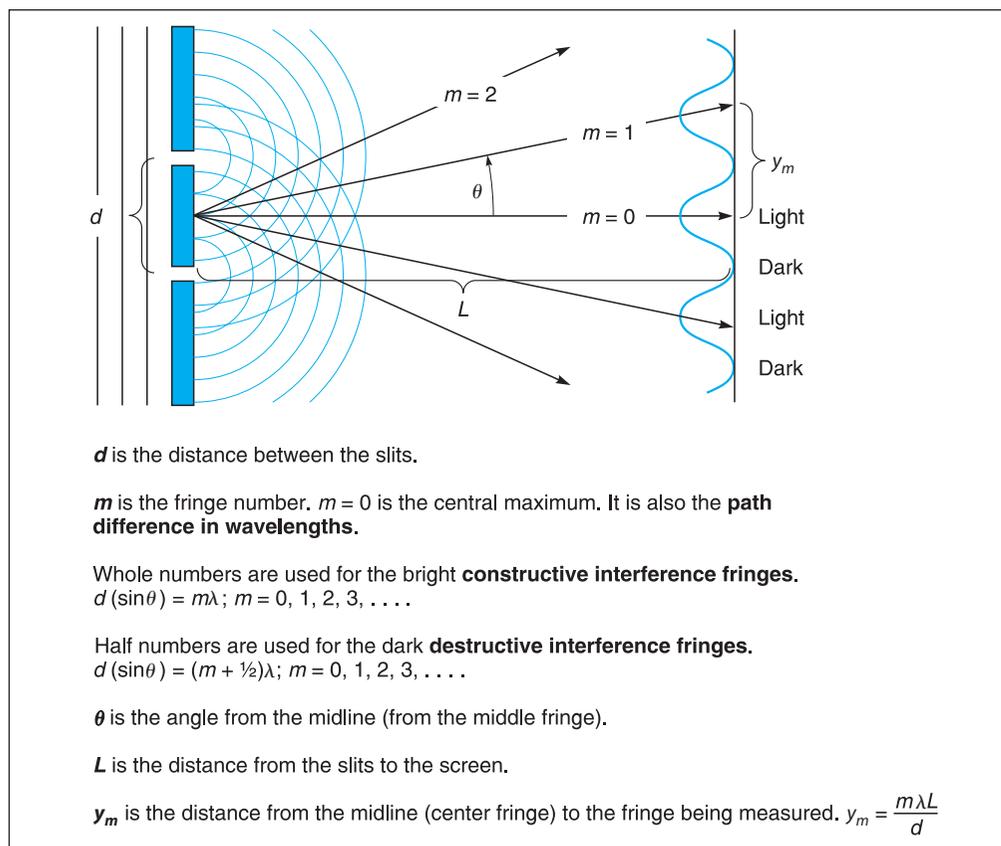


FIGURE 4-5 Experimental setup illustrating an interference pattern.

impinges on a narrow slit of width  $d$ . The light spreads out or diverges (a process known as **diffraction**) onto a viewing screen and results in a diffraction pattern consisting of alternating bright fringes and dark fringes. The position of the dark fringes observed at angles  $\theta$  with respect to the normal or perpendicular of the screen is:

$$n\lambda = d \sin \theta$$

where  $n = 1, 2, 3, \dots$  is the order number of the dark fringe with respect to the central fringe.

## Thin Films

The behavior of light as it passes through thin films is based primarily on reflection, refraction, and interference. As light strikes a thin film, the light ray will be partially reflected and partially refracted. The light ray that is refracted will also eventually reflect off of a subsequent film layer as it continues through the thin film. The objective of thin film interference is to determine the phase difference between the reflected first ray and the reflected refracted ray. If the light ray is reflected off of a layer with a higher

index of refraction, then the light ray will be  $180^\circ$  out of phase. If the light ray is reflected off of a layer with a lower index of refraction, then the light ray will be in phase.

Constructive interference will occur when the two reflected light rays are shifted by an integer plus  $\frac{1}{2}$  multiple of wavelengths. In this case, the path length difference of the light wave through the film can be determined from:

$$2nt = \left(m + \frac{1}{2}\right)\lambda \quad m = 0, 1, 2, \dots$$

where  $n$  is the index of refraction of the thin film,  $t$  is the thickness of the thin film, and  $\lambda$  is the wavelength of the light passing through the thin film.

Destructive interference will occur when the two reflected light rays are shifted by an integer multiple of wavelengths. In this case, the path length difference of the light wave through the film can be determined from:

$$2nt = m\lambda \quad m = 1, 2, 3, \dots$$

## X-Ray Diffraction and Bragg's Law

In x-ray-diffraction, x-rays are focused on a solid sample in the form of a crystal lattice. The structure of a crystal lattice is an array of atoms positioned an equal distance from each other. The intensity peaks obtained from x-ray diffraction occur as a direct result of (1) **law of reflection**: the angle of incidence of the x-ray is equal to its angle of scatter (as shown in Figure 4-6); and (2) the difference in pathlength occurs as an integer number of wavelengths, demonstrated in the following equation, known as **Bragg's law**, for the constructive interference of the x-rays:

$$n\lambda = 2d \sin \theta$$

where

$n$  = integer (= 1, 2, 3, ...)

$\lambda$  = wavelength of the incident x-rays (measured in angstroms)

$d$  = interatomic spacing distance (measured in angstroms)

$\theta$  = angle of incidence (measured in degrees)

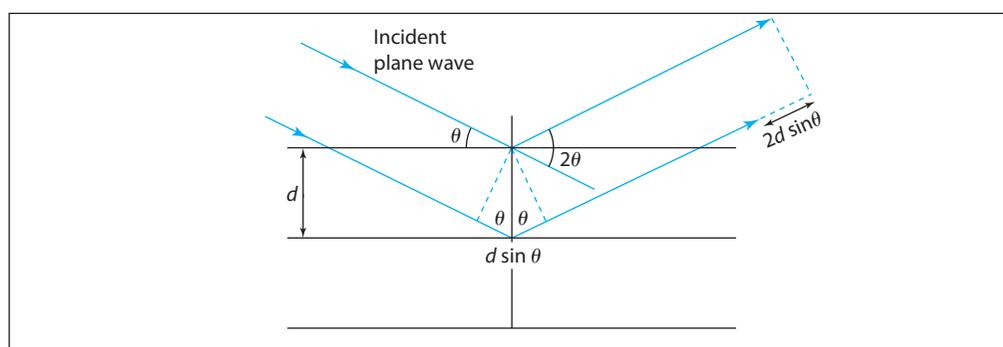


FIGURE 4-6 X-ray diffraction.

## Polarization of Light

The disturbance that generates electromagnetic (light) waves is coupled electric and magnetic fields that act in a direction perpendicular to the direction of wave motion. In typical light sources, the electric field vectors are oriented in random directions but still in a direction perpendicular to wave motion. (The same is true for magnetic field vectors, but for the purpose of this discussion on polarization, only the electric field vectors are significant.) A light wave with the electric field vectors oscillating in more than one plane is termed **unpolarized light**.

**Polarization** is a process by which the electric field vectors of the light waves are all aligned along the same direction; in other words, they are all parallel. Polarization can be accomplished in several ways, with a common one being filters constructed of special materials (such as those found in sunglasses) that are able to block an oscillating plane of electric field vectors that is not moving parallel to the direction of wave motion.

**Circular polarization** occurs when the two oscillating electromagnetic waves are equal in amplitude but possess a  $90^\circ$  phase difference, as shown in Figure 4-7.

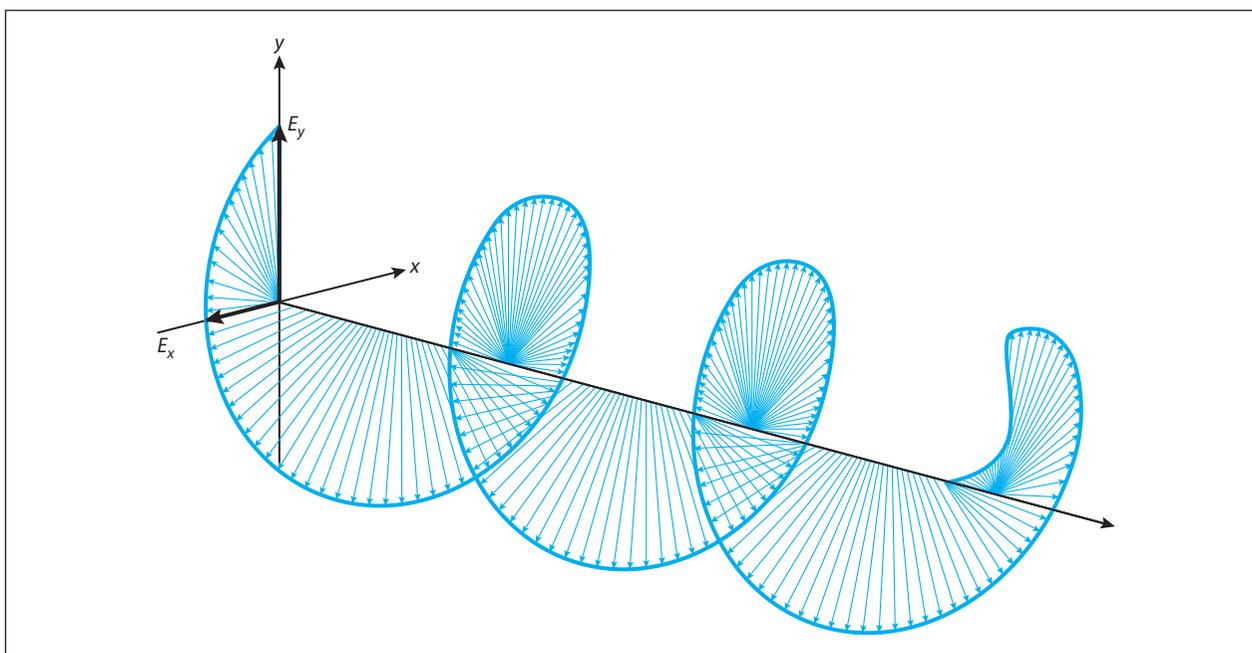


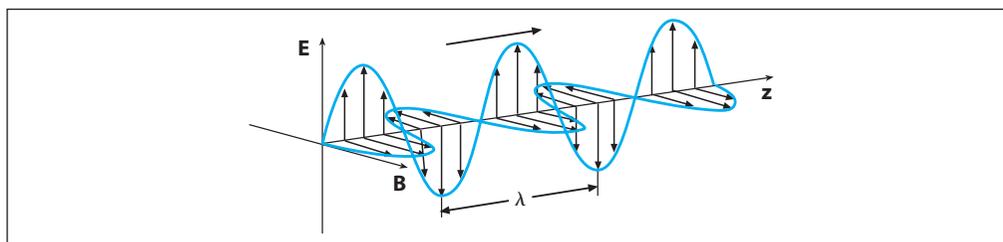
FIGURE 4-7 Circular polarization.

## Electromagnetic Radiation

Light is a form of energy that travels as waves in space. But as described in this context, light is much more than just the visible light that one sees emitted from a light-bulb. Visible light is a small part of the **electromagnetic spectrum**, a collection of waves that travel at the same speed [the speed of light in a vacuum, denoted by  $c = 3 \times 10^8$

meters/second (m/s)] but have different wavelengths. A **wavelength** of a wave is defined as the distance between two adjacent successive points of the wave.

**Electromagnetic waves** are transverse waves, meaning they occur as a result of a disturbance acting in a direction at right angles or perpendicular to the direction of wave motion. The disturbance that generates electromagnetic waves is coupled oscillating electric and magnetic fields, as shown in Figure 4-8.



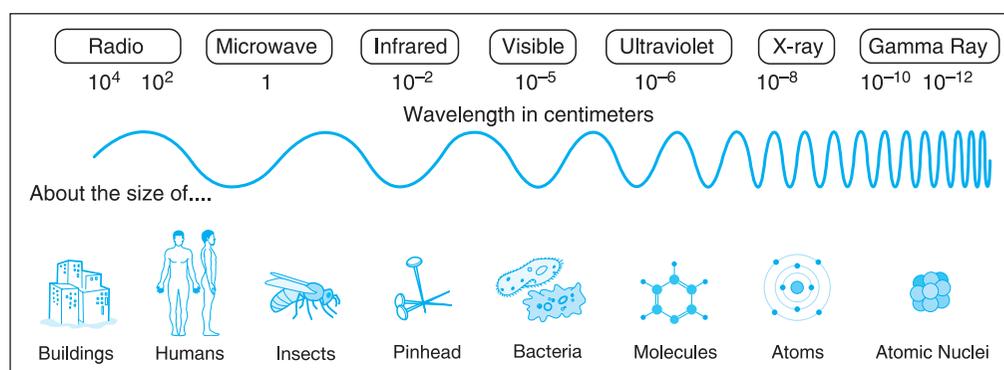
**FIGURE 4-8** Electromagnetic waves. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

## Electromagnetic Spectrum

The **electromagnetic spectrum** is a compilation of electromagnetic waves, arranged with the larger wavelengths (radio waves) to the left and the smaller wavelengths (gamma rays) to the right, as represented in Figure 4-9 and described in the following table.

**TABLE 4-2** Arrangement of Waves in the Electromagnetic Spectrum

Type of Electromagnetic Wave	Range of Frequencies (Hz)	Range of Wavelengths (m)
Radio waves	$< 3 \times 10^9$	$> 1 \times 10^{-1}$
Microwaves	$3 \times 10^9 - 3 \times 10^{11}$	$1 \times 10^{-3} - 1 \times 10^{-1}$
Infrared (IR) waves	$3 \times 10^{11} - 4 \times 10^{14}$	$7 \times 10^{-7} - 1 \times 10^{-3}$
Visible light	$4 \times 10^{14} - 7.5 \times 10^{14}$	$4 \times 10^{-7} - 7 \times 10^{-7}$
Ultraviolet (UV) light	$7.5 \times 10^{14} - 3 \times 10^{16}$	$1 \times 10^{-8} - 4 \times 10^{-7}$
X-rays	$3 \times 10^{16} - 3 \times 10^{19}$	$1 \times 10^{-11} - 1 \times 10^{-8}$
Gamma rays	$> 3 \times 10^{19}$	$< 1 \times 10^{-11}$



**FIGURE 4-9** Electromagnetic spectrum.

Notice as the waves move from radio waves to gamma rays, the frequencies become larger and the wavelengths become smaller. The wavelength is inversely related to the frequency by:

$$v = f\lambda$$

where  $v = c$ , the speed of light.

In addition, each region of the electromagnetic spectrum, represented by a particle or photon, exhibits an energy,  $E$ , given by:

$$E = hf = \frac{hc}{\lambda}$$

where  $h$  = Planck's constant ( $= 6.63 \times 10^{-34}$  J · s) and  $c$  = speed of light ( $= 3 \times 10^8$  m/s).

## Visible Spectrum

Of particular note is that **visible light**, that region of the electromagnetic spectrum that is visible to the human eye, is the smallest of all of the types of waves. Taken altogether, visible light is seen as white but can be separated into six colors (i.e., violet, blue, green, yellow, orange, and red), with each color defined by its characteristic wavelength. The wavelengths for visible light range from  $4.0 \times 10^{-7}$  m [400 nanometers (nm);  $1 \text{ nm} = 1 \times 10^{-9}$  m], which represents the color violet, to  $7.0 \times 10^{-7}$  m, which represents the color red.

**EXAMPLE:** Radio waves have a typical wavelength of  $10^2$  m. Determine their frequency.

**SOLUTION:**

$$f = \frac{c}{\lambda} = \frac{3 \times 10^8 \frac{\text{m}}{\text{s}}}{1 \times 10^2 \text{ m}} = 3 \times 10^6 \text{ Hz}$$

**EXAMPLE:** What is the speed of waves from radio station KQRS that broadcasts at a frequency of 710 kilohertz (kHz)?

**SOLUTION:** All electromagnetic waves, including radio waves, move with the same speed, the speed of light. Thus, the speed of these waves is  $3 \times 10^8$  m/s.

## MOLECULAR STRUCTURE AND SPECTRA

### Absorption Spectroscopy

Spectral properties are used to determine the structure of molecules and ions. Of special importance are ultraviolet (UV), infrared (IR), and nuclear magnetic resonance (NMR). The various types of molecular energy, such as electronic, vibrational, and nuclear spin, are quantized, or in other words, only certain energy states are

permitted. The molecule can be raised from its lower energy state (ground state) to a higher energy state (excited state) by the absorption of a photon (quantum of energy) of electromagnetic radiation of the permitted wavelength.

TABLE 4-3

Region of Electromagnetic Spectrum	Type of Excitation	Wavelength of Photon
Far ultraviolet	Electronic	100–200 nm
Near ultraviolet	Electronic	200–350 nm
Visible	Electronic	350–800 nm
Infrared	Molecular vibration	1–300 $\mu\text{m}$
Radio	Spin (electronic or nuclear)	1 m

## Infrared Spectroscopy

### BACKGROUND AND THEORY

Molecules have many degrees of freedom, and each electronic state (ground, first excited, second excited, etc.) has an array of energy levels corresponding to various vibrational and rotational states. Just like the electronic transitions, movement among vibrational energy levels is quantized and can be studied through spectrophotometric methods. These energy changes are, of course, much smaller; therefore, the electromagnetic radiation required for excitation is of correspondingly lower energy. For most vibrational excitations, absorption occurs in the infrared region of the spectrum.

Although governed by quantum considerations, many vibrational modes can be modeled using classical physics. For example, a stretching vibration between two nuclei can be characterized using **Hooke's law**, which predicts that the frequency of an absorbance is given by the relationship:

$$\bar{\nu} = 4.12 \sqrt{\frac{f}{\left(\frac{m_1 m_2}{m_1 + m_2}\right)}} \quad (1)$$

where  $\bar{\nu}$  is the frequency in wavenumbers (equal to  $1/\lambda$ ),  $m_1$  and  $m_2$  are the masses of the two nuclei in amu units, and  $f$  is the force constant, which can be roughly correlated to bond strength see the following table.

TABLE 4-4 Nominal Force Constant Values for Estimating IR Absorptions

Type of Bond	Nominal Force Constant ( $f$ ) (dynes/cm)
Single	$5 \times 10^5$
Double	$10 \times 10^5$
Triple	$15 \times 10^5$

Hooke's law provides a useful conceptual framework for predicting the position of various stretches in the IR spectrum. Essentially, there are two deciding terms: the **force constant** and the **reduced mass**, which is given by  $m_1 m_2 / (m_1 + m_2)$ . The former

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is fairly straightforward—for example, the higher the force constant (i.e., the stronger the bond), the higher the wavenumber of the absorbance. Therefore, the C=C bond is predicted to absorb at a higher wavenumber than the C—C bond, and the C≡C bond higher still. The reduced mass is a bit more subtle. Consider the C—C bond in relation to the C—H bond. The reduced mass for two carbon atoms would be  $144/24 = 6$ . In contrast, a carbon atom and hydrogen atom give a reduced mass of  $12/13 = 0.923$ . Since this term is in the denominator, the lower reduced mass translates into a higher wavenumber.

## EXTRACTING INFORMATION FROM IR SPECTRA

These two theoretic factors help understand the overview of IR absorptions given in Figure 4-10. The **IR spectrum** can be broken into four very broad (and fuzzy) categories. At very high frequencies ( $2500\text{--}4000\text{ cm}^{-1}$ ), you see what can be dubbed the X—H stretches, positioned at high energy by virtue of the very light hydrogen atom (reduced mass consideration). There are a few features here worth mentioning. First, the almost ubiquitous C—H stretches congregate around  $3000\text{ cm}^{-1}$ , but the exact positioning is diagnostic: aromatic C—H stretches tend to be just above  $3000\text{ cm}^{-1}$ , and aliphatic stretches tend to be just below that mark. The carbonyl C—H stretch also has a characteristic position, showing up at just less than  $2800\text{ cm}^{-1}$ . Another telltale feature in this region belongs to the O—H stretch, which tends to be very broad and dominating. Presence of such a band is a sure sign of an O—H group in your compound (or for the sloppy experimentalist, adventitious water in your IR sample!).

Next move to the region between  $1900$  and  $2500\text{ cm}^{-1}$ , which is home to the triple bond. This area is usually fairly empty, so that absorptions are easy to spot. The alkyne stretch is typically sharp but very weak, and sometimes absent altogether, particularly for symmetrically substituted triple bonds. Nitriles, however, tend to be more

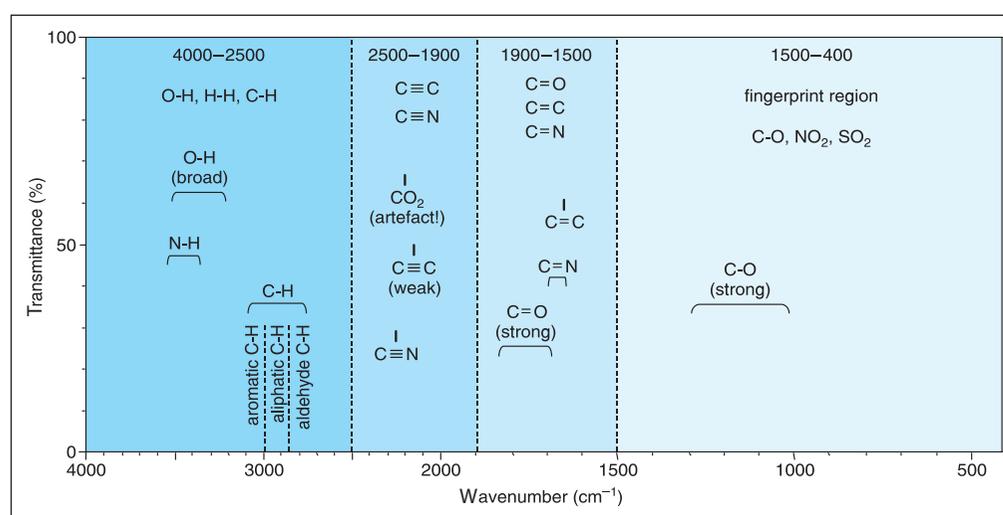


FIGURE 4-10 Overview of infrared absorbance ranges.

prominent, although they still tend toward the weak side. The only thing to watch out for here is that carbon dioxide also absorbs in this vicinity—because most instruments now take measurements in normal atmosphere and subtract out the background CO<sub>2</sub>, artifacts can arise from quirky subtraction errors.

The real estate between 1500 and 1900 cm<sup>-1</sup> houses many of the doubly bonded species, including alkene and carbonyl stretches. Alkenes give rise to a medium-intensity band just higher than 1600 cm<sup>-1</sup>, whereas the garden-variety carbonyl stretch for a ketone shows up as an intense absorption at about 1715 cm<sup>-1</sup>. Other carbonyl-containing functional groups wobble around this value: Esters absorb at slightly higher wavenumber (>1730 cm<sup>-1</sup>), whereas amides have a somewhat lower-frequency absorbance (<1700 cm<sup>-1</sup>). Often the carbonyl stretch, when present, is the predominant feature of the IR spectrum.

Finally, the portion of the spectrum bounded by 400 and 1500 cm<sup>-1</sup> is known as the **fingerprint region**. This area tends to be fairly busy, and in fact this preponderance of detail gives rise to its name, because each compound exhibits a characteristic pattern (or fingerprint) in the low-frequency end of the spectrum. Many of these bands are difficult to correlate to particular vibrational modes, but one particular absorption deserves mention. The C—O stretch gives rise to a medium but noticeable band around 1100 cm<sup>-1</sup>, which is diagnostic of ethers, esters, and alcohols.

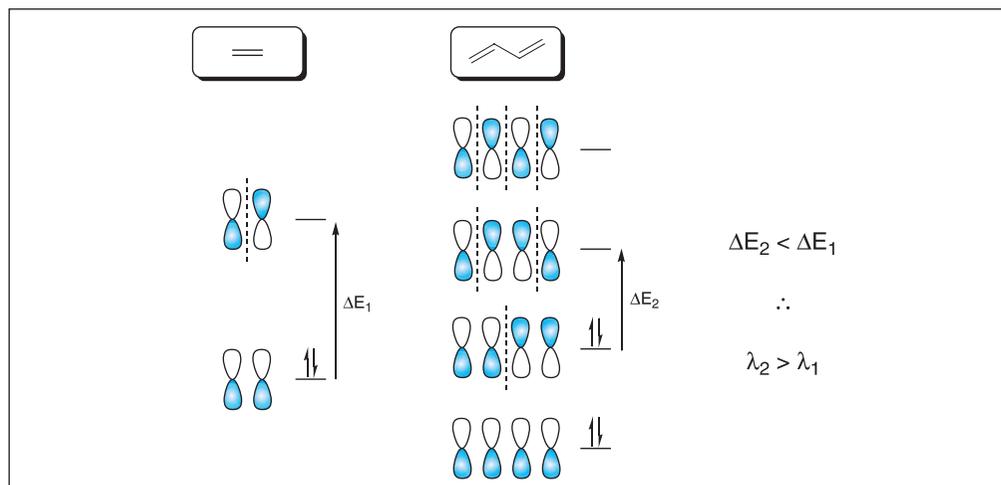
There is much more detail that can be extracted from an IR spectrum (e.g., substitution patterns on benzene rings and alkenes), and several other significant modes of vibrational transition (bending, ring breathing, etc.) that have not been treated here. However, by considering just the major stretching vibrations, you are able to obtain a very rich snapshot of the functional group landscape on a molecule. This information complements the other spectroscopic methods, and contributes to the ensemble of data necessary to fully characterize an organic compound.

## Ultraviolet-Visible Spectroscopy

### BACKGROUND AND THEORY

If a molecule exhibits multiple degrees of unsaturation, the question naturally becomes whether they manifest themselves as rings or double bonds—and if the latter, whether the  $\pi$  (pi) bonds are isolated or in conjugation. To address this dual question, turn to the first of three spectroscopic methods. Recall that  $\pi$  systems arise from the combination of adjacent  $p$  orbitals, and that the number of molecular orbitals is determined by the extent of the  $p$  orbital array. Furthermore, as the  $\pi$  system encompasses more orbitals, the energy spacing becomes more compact and the distance between the HOMO (highest energy occupied molecular orbital) and LUMO (lowest energy unoccupied molecular orbital) diminishes (Figure 4-11). With simple dienes, this distance is already close enough that absorption of light in the near-UV results in electronic excitation. As conjugation is extended, this absorption moves to longer wavelengths

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**FIGURE 4-11** The impact of extended  $\pi$  systems on absorbance.

(lower energy) and eventually creeps into the visible region. Therefore, these extended  $\pi$  systems are often called **chromophores**, as they are responsible for the color in many organic compounds. In any event, the wavelength of light absorbed is dependent on the degree of conjugation in the chromophore, and so this absorption can tell us much about the nature of the  $\pi$  system in an unsaturated molecule.

## INFORMATION FROM WAVELENGTH

It turns out that the  $\pi$  system is also remarkably sensitive to substituent patterns, a phenomenon that can be leveraged for extracting structural information. Through the examination of many experimentally derived values, sets of rules have been developed for predicting the wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) for various substrates as a function of structure, work carried out primarily by Woodward, Fieser, and Nielsen. A brief summary of these rules is presented in Figure 4-12. Although not immediately intuitive, they are straightforward to apply once the framework is understood, and they are very powerful predictive tools.

There are a couple of subtleties that tend to be pitfalls for the beginning spectroscopist. First, you must approach the calculation as an accountant, recognizing that you must be very mindful of what is already in the ledger, as well as those items that do not have an impact on the bottom line. Thus, when a double bond is added to the system to extend conjugation, the base value is increased by 30 nanometers (nm), and you have essentially a new chromophore. Also, for carbonyl-containing chromophores, the  $-\text{R}$  or  $-\text{OR}$  groups on the other side of the carbonyl group are already accounted for in the base absorbance value, so it is important not to double-count these substituents later on.

Two specialized terminologies also deserve mention. First, a **homoannular diene** refers to any two double bonds that are incorporated into the same ring. Therefore, 1,3-cyclohexadiene would be considered a homoannular diene, but cyclohex-2-enone would not, because only one double bond is incorporated into the ring itself. For every

instance of a homoannular component, add 39 nm to the base absorbance. Second, even though the etymology of an exocyclic double bond means “outside the ring,” it is best thought of as a double bond that terminates in a ring. Each time this occurs, add 5 nm to the base absorbance.

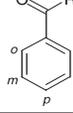
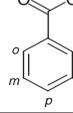
base chromophore	dienes	enones and enals				benzophenones, benzaldehydes, and benzoic acids				
										
base absorbance $\lambda_{\max}$ (nm)	214	202	215	245 208 (R=H)	246 250 (R=H)	230				
<b>modifications to the base absorbance</b>										
substituents	position	all	$\alpha$	$\beta$	$\gamma$	$\delta$	<i>o</i>	<i>m</i>	<i>p</i>	
	-R	5	10	12	18	18	3	3	10	
	-OR	6	35	30	17	31	7	7	25	
	-Br	5	25	30	25	25	2	2	15	
	-Cl	5	15	12	12	12	0	0	10	
	-NR <sub>2</sub>	60		95			20	20	85	
$\pi$ system architecture	double bond extending conjugation	+ 30 nm						not typically relevant		
	exocyclic character of a double bond	+ 5 nm								
	homoannular diene component	+ 39 nm								

FIGURE 4-12 Abbreviated rules for predicting  $\lambda_{\max}$  for UV-Vis absorptions.

To get some practice in applying these rules, consider the tricyclic enone shown in Figure 4-13. Choose the base absorption of 215 (six-membered-ring enone) and tack on three double bonds to extend the conjugation (30 nm each for 90 nm total). You have thus established the domain of the chromophore (shown in bold). It is often helpful to highlight the chromophore for accounting purposes, even by darkening it in with a pencil. Examination of the chromophore thus reveals that ring C houses one

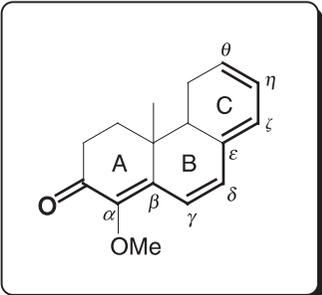
	Base chromophore (6-ring enone)	215
	3× double bond extensions	+ 90
	Homoannular diene (in ring C)	+ 39
	2× exocyclic double bonds	+ 10
	$\alpha$ -alkoxy substituent	+ 35
	$\beta$ -alkyl substituent	+ 12
	$\epsilon$ -alkyl substituent (same as $\gamma$ )	+ 18
	$\theta$ -alkyl substituent (same as $\gamma$ )	+ 18
	Predicted $\lambda_{\max}$	437

FIGURE 4-13 Example of the application of predictive UV-Vis rules.

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homoannular diene component, so add 39 nm to the ledger. Careful scrutiny also reveals two occurrences of exocyclic double bonds: both the  $\alpha,\beta$ , and the  $\varepsilon,\zeta$  olefins terminate in ring B. Add 5 nm for each occurrence.

The accounting of substituents is sometimes tricky, particularly for cyclic molecules. First, you must recognize that the substituent connected to the carbonyl group is already accounted for, so you do not double-count it. Start instead with the methoxy substituent in the  $\alpha$  position, which adds 35 nm to the chromophore. The rest of the substituents are dealt with in the same manner. To help sort out what are bona fide substituents, imagine the chromophore (bold portion) is a hallway you could walk through—how many doorways would you see, and in what positions? Thus, starting from the carbonyl, you would see a door to your right at the  $\alpha$  position, one on your left at the  $\beta$  position, another left door at  $\varepsilon$ , and finally a left door at  $\theta$ . For accounting purposes, it matters not that there are substituents attached to those substituents (it also is inconsequential whether the “doors” are on the right or left—it simply helps you visualize the virtual corridor).

### INFORMATION FROM INTENSITY

The intensity of the absorbance can also be diagnostic. For example, in the tricyclic enone shown previously we would expect to see at least two bands in the UV-Vis spectrum. The absorbance calculated in Figure 4-14 corresponds to the  $\pi \rightarrow \pi^*$  transition from the HOMO to the LUMO. However, the lone-pair electrons on oxygen can also undergo excitation. Because they are technically not connected to the extended  $\pi$  system, they are neither bonding nor antibonding; therefore, they are considered nonbonding ( $n$ ) electrons. The absorption is thus designated an  $n \rightarrow \pi^*$  transition. Because the energy gap is smaller, this absorption occurs at higher wavelengths than the  $\pi \rightarrow \pi^*$  transitions.

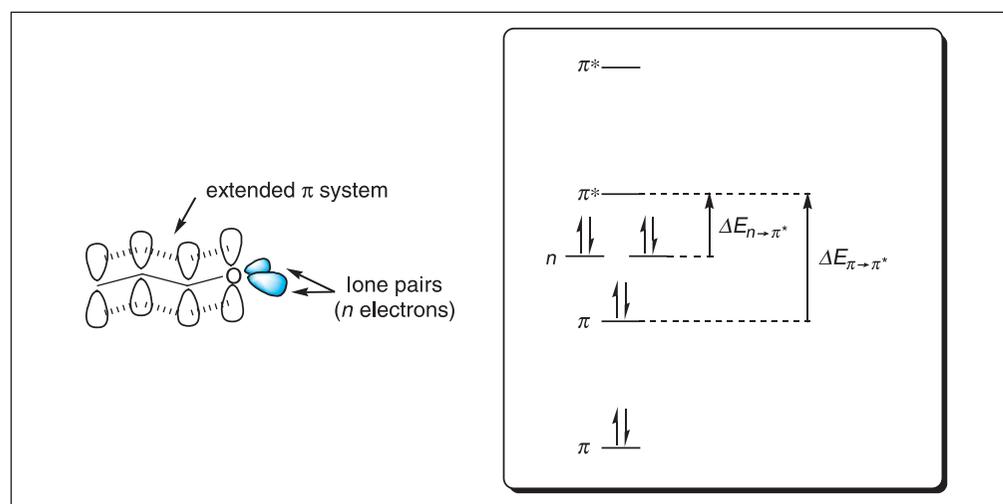


FIGURE 4-14 Two possible electronic transitions in enones.

The two types of excitation events differ not only in the maximum wavelength, but also in intensity. Because the lone pairs are essentially orthogonal to the extended  $\pi$  system, it would seem difficult to imagine how electrons could be promoted from one to the other. Indeed, these  $n \rightarrow \pi^*$  events are known as **symmetry forbidden electronic transitions**. Like so many other forbidden things, they still happen, but the quantum efficiency is much lower; therefore, the intensity of the absorption is considerably weaker than the  $\pi \rightarrow \pi^*$  absorption.

The intensity of a specific absorption is usually reported in terms of the molar extinction coefficient ( $\varepsilon$ ), which is given by the relationship:

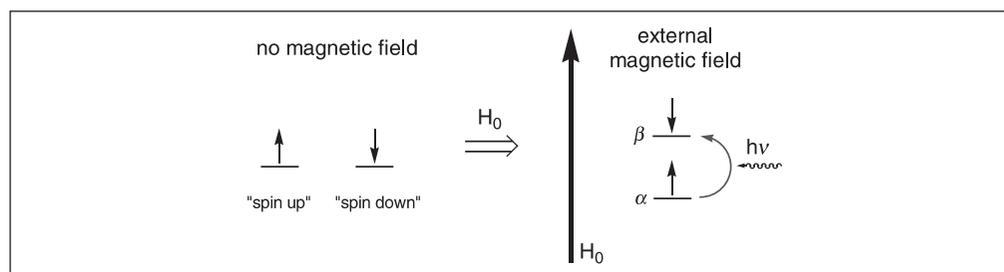
$$\varepsilon = \frac{A}{cl} \quad (2)$$

where  $A$  is the absorbance at the  $\lambda_{\max}$ ,  $c$  is the molar sample concentration, and  $l$  is the path length in centimeters (in most instruments, this is 1 cm). For allowed transitions, the molar extinction coefficients are on the order of  $10^3$  to  $10^6$ . Forbidden transitions are typically in the hundreds.

## Nuclear Magnetic Resonance Spectroscopy

### BACKGROUND AND THEORY

**Nuclear magnetic resonance (NMR)** represents the organic chemist's most powerful tool for structure elucidation. The principle of this spectroscopic method is based on the transition of nuclei between spin states, the so-called **spin flip**. Recall from general chemistry that a proton can have a quantum spin number of  $+1/2$  or  $-1/2$ ; these two states are also called "spin up" and "spin down." In the absence of a magnetic field, these spin states are of equivalent energy, or degenerate. However, when a strong magnetic field is applied, the energy states differentiate themselves (see Figure 4-15). Nuclei aligned with the magnetic field find a lower energy state (designated  $\alpha$ ), whereas those opposed to the field are at higher energy ( $\beta$ ).



**FIGURE 4-15** The splitting of degenerate nuclear spin states.

Analogous to electronic transitions in UV-Vis spectroscopy, nuclei in the lower energy state can be promoted to the next level by the absorption of electromagnetic radiation of the appropriate energy. In the case of spin flips, this absorption occurs

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in the radio frequency region—in other words, they are relatively low-energy transitions. In principle, this resonance can be observed with any nucleus of odd mass or odd atomic number. Examined here are two of the most indispensable methods,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR. However, methods for observing other nuclei have become widely available, including  $^{11}\text{B}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  (of obvious importance for biochemists).

Very high magnetic fields must be used for useful data, and much of the innovation in NMR hardware centered around magnet technology (e.g., superconducting magnets). For all our efforts, however, the nucleus never experiences the full, unadulterated magnetic strength of the external field ( $H_0$ ). This is because the electronic cloud surrounding the molecule shields the nuclei from the field. Instead, the  $\alpha$  and  $\beta$  levels are split by a somewhat attenuated magnetic field, called the effective magnetic field ( $H_{\text{eff}}$ ). Electron density, however, is a variable parameter. In a local environment in which the electron cloud has been impoverished (e.g., by the inductive effect of an electronegative atom), the nucleus is shielded less and thus experiences a stronger  $H_{\text{eff}}$  (see Figure 4-16). Consequently, the energy splitting is enhanced and the resonance occurs at correspondingly higher frequency. This phenomenon of higher-frequency absorbances in electron-poor regions is known as **deshielding**.

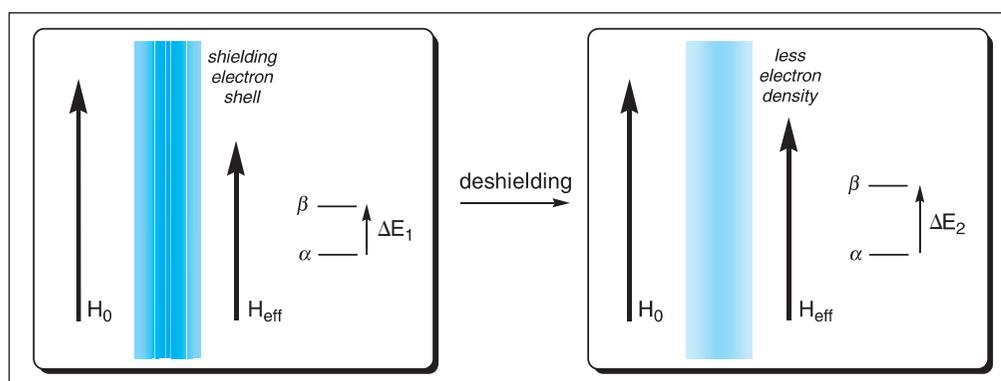


FIGURE 4-16 The shielding effect and deshielding.

Because the resonance frequency is field-dependent, no two spectrometers yield exactly the same resonance values. To alleviate this issue, spectroscopists historically have used an internal standard, against which all other signals are measured. The choice of **tetramethylsilane (TMS)** (see Figure 4-17) as an **NMR standard** was driven by a few practical considerations. First, it is thermally stable and liquid at room temperature; second, it has 12 protons that are identical, so the intensity of absorption is high; and finally, the protons in TMS are quite shielded (silicon is not particularly

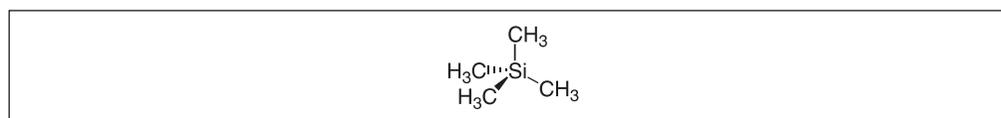


FIGURE 4-17 The NMR standard, tetramethylsilane (TMS).

electronegative), so almost all other proton resonances you observe occur at higher frequencies relative to TMS.

## PRINCIPLE OF CHEMICAL SHIFT

Instruments are characterized by the resonance frequency of TMS in the magnetic field of that instrument. For example, a 400-megahertz (MHz) NMR spectrometer incorporates a superconducting magnet in which TMS resonates at 400 MHz. Stronger magnets lead to higher values (e.g., 600 MHz, 900 MHz); in fact, magnets are so often specified by their TMS frequencies that we sometimes forget that the unit of MHz is a meaningless dimension for a magnetic field. That is, a 400-MHz NMR has a magnetic field strength of about 9.3 Tesla (T), yet for whatever reason, this parameter is almost never mentioned.

Nevertheless, you can use the TMS resonance to talk about the general landscape of the NMR spectrum. Figure 4-18 shows a typical measurement domain for a 400-MHz spectrometer, which is bounded on the right by the resonance frequency of TMS (400,000,000 Hz). The range through which most organic molecules absorb extends to about 400,004,000 Hz, or 4000 Hz relative to TMS. However, these values change as magnetic field strength is altered—an absorbance at 2000 Hz on a 400-MHz NMR would absorb at 1000 Hz on a 200-MHz NMR. To normalize these values, we instead report signals in terms of **parts per million (ppm)**, which is defined as:

$$\text{ppm} = \frac{\nu}{R} = \frac{\text{Hz}}{\text{MHz}} \quad (3)$$

where  $\nu$  is the signal frequency (in Hz) relative to TMS and  $R$  is the base resonance frequency of TMS (in MHz), a parameter known as **chemical shift**. Thus, on a 400-MHz

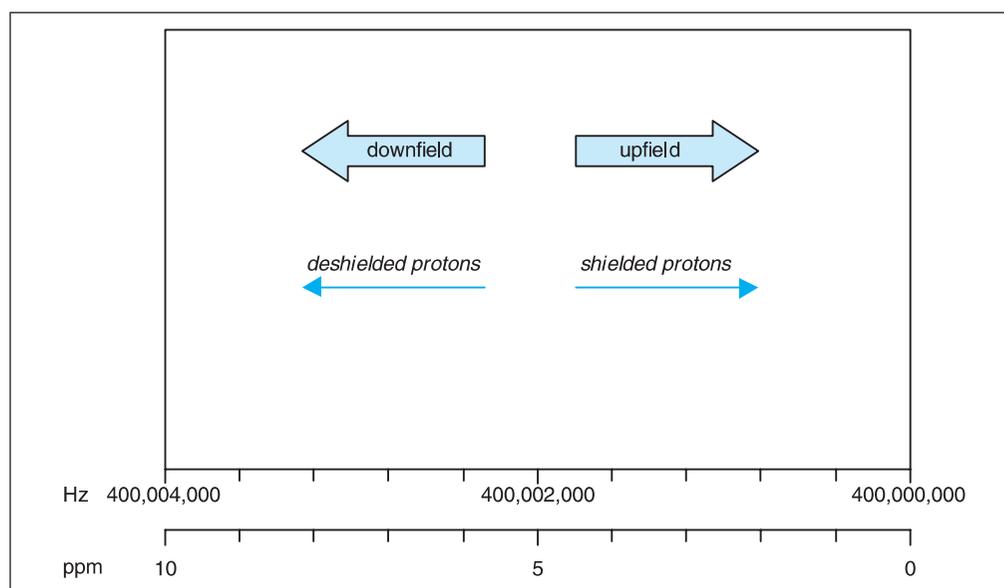


FIGURE 4-18 Important architectural features of the  $^1\text{H}$ -NMR spectrum.

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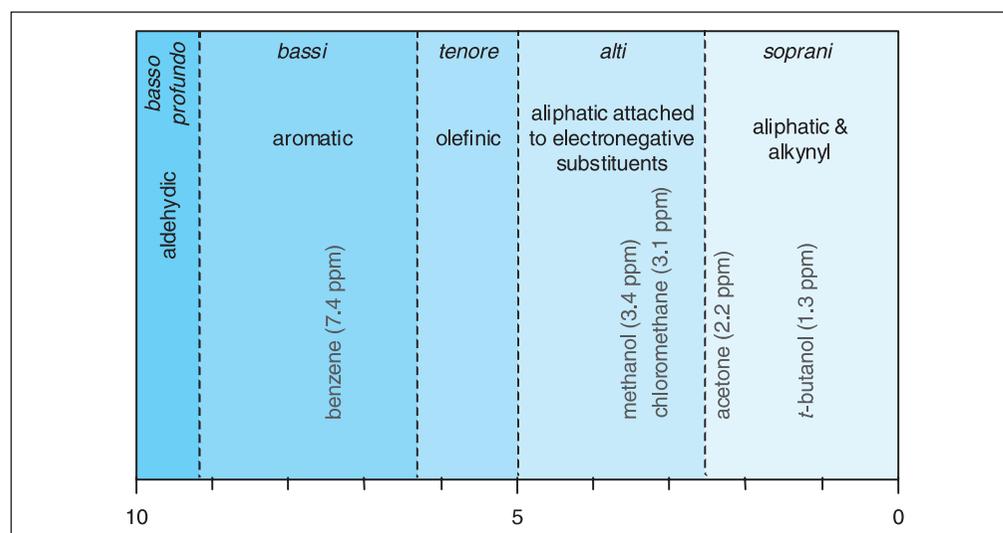
instrument a signal at 2000 Hz would be reported as having a chemical shift of 5 ppm (2000 Hz/400 MHz). This allows you to establish a universal scale for proton NMR ranging from 0 to about 10 ppm—although it is not terribly uncommon to find protons that absorb outside that range.

Working within this framework, it is important to understand certain features and terminology related to position in the NMR spectrum. First, the ppm scale obscures the fact that frequency increases to the left, so this must be borne in mind. Thus, as protons are deshielded, they are shifted to the left—spectroscopists have dubbed this a “downfield” shift (see Figure 4-18). Similarly, migrating to the right of the spectrum is said to be moving “upfield”. Phenomenologically, a downfield shift is evidence of deshielding, and this understanding helps us interpret NMR data.

### INFORMATION FROM CHEMICAL SHIFT

Using this idea, you can establish general regions in the NMR spectrum where various proton types tend to congregate (see Figure 4-19). For example, most purely aliphatic compounds (hexane, etc.) absorb far upfield in the vicinity of 1 ppm. The attachment of electron-withdrawing groups (e.g., carbonyls) tends to pull resonances downfield. Thus, the protons on acetone show up at around 2.2 ppm. In general, the region between 0 and 2.5 ppm can be thought of as home to protons attached to carbons attached to carbon (H—C—C). This is also where terminal alkyne protons absorb.

As electronegative elements are attached, however, resonances are shifted even farther downfield. Thus, the methyl protons on methanol resonate at about 3.4 ppm, and the protons on chloromethane appear at about 3.1 ppm. Multiple electronegative elements have an additive effect: compared to chloromethane, dichloromethane resonates at 5.35 ppm, and chloroform (trichloromethane) absorbs at 7.25 ppm. As a



**FIGURE 4-19** General regions of the  $^1\text{H}$ -NMR spectrum, with benchmarks.

rough guideline, the region between 2.5 and 5 ppm belongs to protons attached to carbons that are attached to an electronegative element (H—C—X).

Moving farther downfield, you encounter protons attached to  $sp^2$  carbons, starting with the **olefinic** (alkenyl) variety, which absorb in the region between about 5 and 6.5 ppm. Next come the **aromatic** protons, which range from about 6.5 to 9 ppm. As a benchmark, benzene—the prototypical aromatic compound—absorbs at 7.4 ppm. Just like their **aliphatic** cousins, the olefinic and aromatic protons are shifted downfield as electron-withdrawing groups are attached to the systems. Finally, signals in the region between about 9 and 10 ppm tend to be very diagnostic for **aldehydic** protons—that is, the protons connected directly to the carbonyl carbon.

Now a word of caution. These rough guidelines are just that—they do not represent strict demarcations. Rather, they paint the NMR spectrum in broad brush strokes, so that you can take away an immediate impression from the data to start our thought processes. Think of these regions as voices in a choir, whose ranges often cross each other. Just as tenors often sing the alto line in Early Music, so too can olefins exhibit resonances above 5 ppm.

## SPLITTING PATTERNS AND INTEGRATION

It would be enough of a gift if NMR told you only about a given proton's chemical environment—but you can gain much more information from the spectrum. One source of knowledge derives from a phenomenon known as **scalar (or spin-spin) coupling**, through which a proton is influenced by its nearest neighbors. Figure 4-20 explores this effect with the hypothetical situation of one proton ( $H_x$ ) being next door to a pair of protons ( $H_a$  and  $H_b$ ). The latter two protons are either spin up or spin down, and in fact you can imagine four permutations ( $2^2$ ) of two nuclei with two states to choose from. If both  $H_a$  and  $H_b$  are aligned with the external magnetic field, they will serve to enhance  $H_{\text{eff}}$ , thereby increasing the energy gap between the  $H_x\alpha$  and  $\beta$  states, which in turn leads to a higher frequency absorbance (a downfield shift). Conversely, the situation in which both  $H_a$  and  $H_b$  oppose the external magnetic field diminishes the  $H_{\text{eff}}$ , leading to an upfield shift. The two remaining permutations have one spin up and the other spin down, thereby canceling each other out. The result is a pattern known as a **triplet**, in which the three prongs of the signal are present in a 1:2:1 ratio.

Had there been only one neighboring proton, there would have been only two possibilities: The neighboring proton is either spin up or spin down. The resulting pattern would have been a **doublet**. By the same token, three neighboring protons would have eight permutations ( $2^3$ ), which could be all up, all down, two up and one down, or one up and two down. This would lead to a **quartet** pattern. To summarize the trends in these examples, one neighboring proton gives a doublet, two give a triplet, and three give a quartet. In other words, the pattern exhibited (or “multiplicity”) has one more prong than the number of neighboring protons. Patterns of this type are said to obey the “ **$n + 1$  rule**,” where  $n$  = the number of neighboring protons, and  $n + 1$  = the

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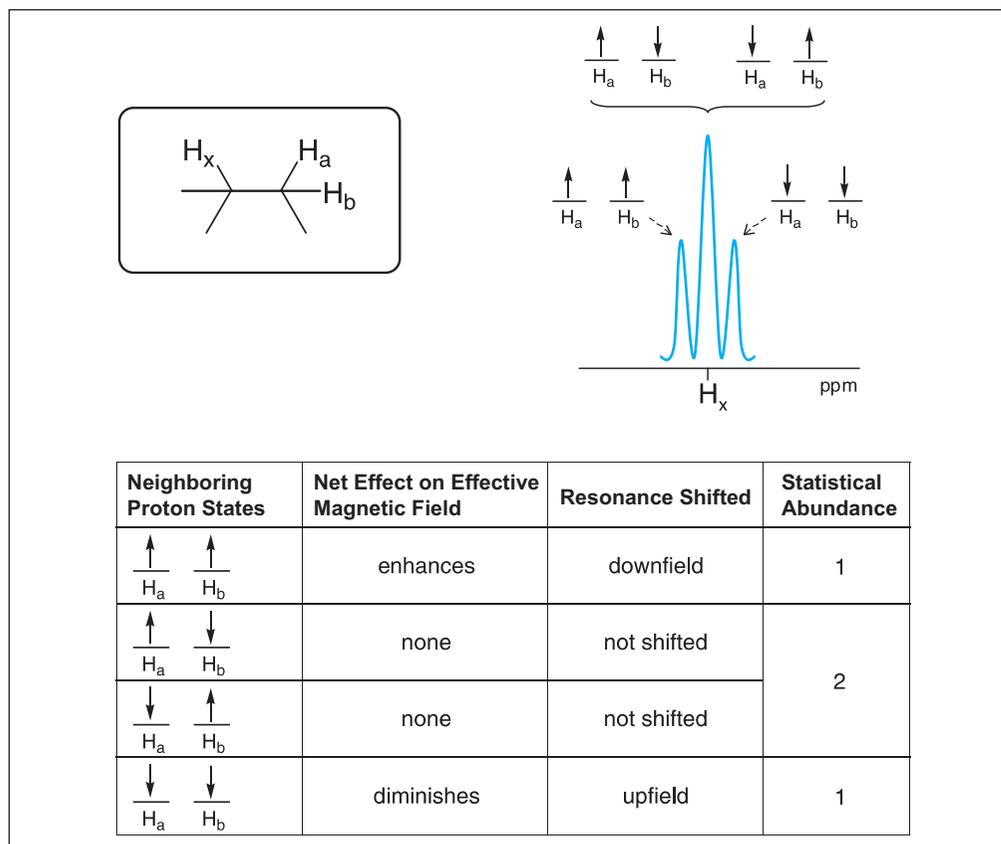
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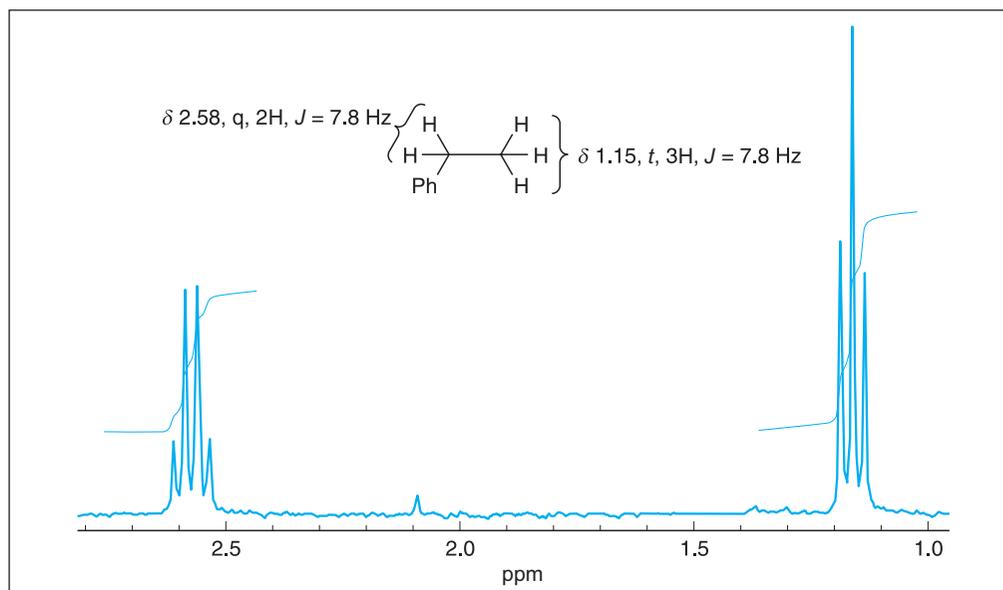
FIGURE 4-20 The origin of scalar splitting.

multiplicity of the signal. The most common splitting patterns and their abbreviations are summarized in the following table. It should be noted here that heteroatomic protons (N—H, O—H) are capricious beasts—in very dilute (and pure) solution, they behave much like any other proton, and obey the  $n + 1$  rule, although their chemical shift is hard to pin down. However, the usual state of affairs is to encounter O—H protons as very broad singlets that appear not to couple with adjacent protons. Chemical shift is typically highly variable.

TABLE 4-5 Some Common Splitting Patterns

Abbreviation	Pattern
<i>s</i>	Singlet
<i>d</i>	Doublet
<i>t</i>	Triplet
<i>q</i>	Quartet
quint	Quintet
<i>m</i>	Multiplet

So the chemical shift tells you about a proton's electronic environment, and splitting patterns tell you about the number of neighboring protons—but still the spectrum



**FIGURE 4-21** The ethyl moiety of ethylbenzene.

has further secrets to yield. It turns out that the area under each signal is proportional to the number of protons giving rise to that signal. Therefore, integrating the area under the curves allows you to establish a ratio for all chemically distinct protons in the NMR. As an illustration, Figure 4-21 presents a portion of the NMR spectrum of ethylbenzene corresponding to the ethyl moiety. There are two signals (at 1.15 ppm and 2.58 ppm), corresponding to the two sets of chemically distinct protons on the ethyl substituent (a methyl and methylene group, respectively). The downfield shift of the methylene group is an indication of its being closer to the slightly electron-withdrawing benzene ring. The splitting patterns tell us that the protons resonating at 1.15 (the triplet) are next to two other protons, and the protons at 2.58 (the quartet) are adjacent to three other protons. Furthermore, the integral traces reveal that the two sets of protons are present in a 3:2 ratio. Extract the integration data simply by taking a ruler and measuring the heights of the integral traces. The absolute values mean nothing by themselves, but taken together they establish a ratio of the various protons.

Within a given pattern, the spacing between the peaks is known as the coupling constant, or  $J$ -value, usually reported in Hz. Notice in Figure 4-21, the proper way to report NMR data is as follows (explanatory comments in parentheses):  $\delta$  (indicates the values are in ppm), 1.15 (the chemical shift),  $t$  [the multiplicity (here, a triplet)], 3H (the number of protons given by the integration),  $J = 7.8$  Hz (the measured coupling constant). This is a very inflexible format, and should always be used when reporting NMR data. A natural question, then, is how to extract the  $J$ -values from an NMR spectrum. Again, the ruler is your friend. By carefully measuring against the bottom scale, you can assign ppm values to each prong of the signal (see Figure 4-22). Applying Equation 4.3 (from page 107), if  $\text{ppm} = \text{Hz}/\text{MHz}$ , then  $\text{Hz} = (\text{ppm})(\text{MHz})$ . In other words, to convert ppm to Hz, simply multiply by the “field strength,” or more accurately, the native

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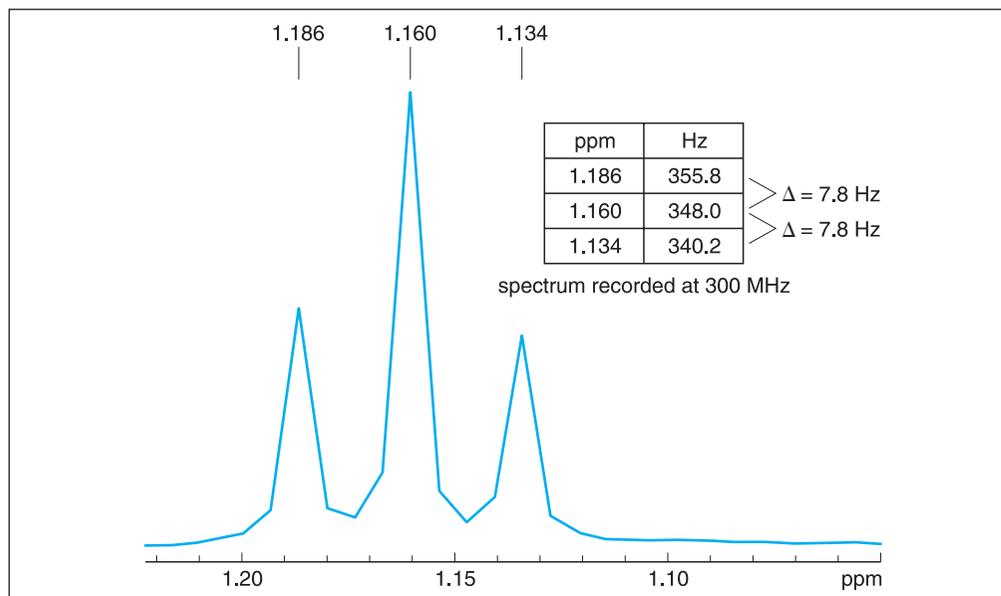
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FIGURE 4-22 Measuring  $J$ -values from a spectrum.

resonance of TMS. The spectrum in Figure 4-22 was obtained on a 300-MHz instrument, so the prong at 1.186 ppm corresponds to 355.8 Hz ( $1.186 \times 300$ ). Once the peaks are converted to units of Hz, the  $J$ -value is simply the distance between the peaks. It is worth noting at this point that chemical shifts are reported in ppm because their ppm values do not change with field strength; by the same token,  $J$ -values in Hz remain constant regardless of magnetic field, so this is how they are reported.

## INFORMATION FROM COUPLING CONSTANTS

As luck would have it, the magnitude of the coupling constant can also provide useful information about the structure of a molecule. It is important to understand here, that scalar coupling is not a through-space interaction, but a through-bond effect. In other words, the information about the neighboring nuclear spin states is actually communicated through the electronic network bonding the two sets of nuclei. Also bear in mind that this information must travel through three bonds (H—C, C—C, C—H). Consequently, the orientation relationship between the two C—H bonds is very important. In fact, an empirical relationship has been elucidated between the observed  $J$ -value and the dihedral angle ( $\phi$ ) set up between the two C—H bonds. Figure 4-23 shows this relationship in graphical format, which is known as the **Karplus curve**. The important outcomes are these: When the dihedral angle is at  $0^\circ$  (eclipsed) and  $180^\circ$  (antiperiplanar), the  $J$ -value is at a maximum (ca. 12 Hz), and at a  $90^\circ$  dihedral angle, the  $J$ -value is at a minimum (ca. 2 Hz). This makes sense, if one considers that when the two C—H bonds are orthogonal, communication between the  $\sigma$  bonds is practically nonexistent.

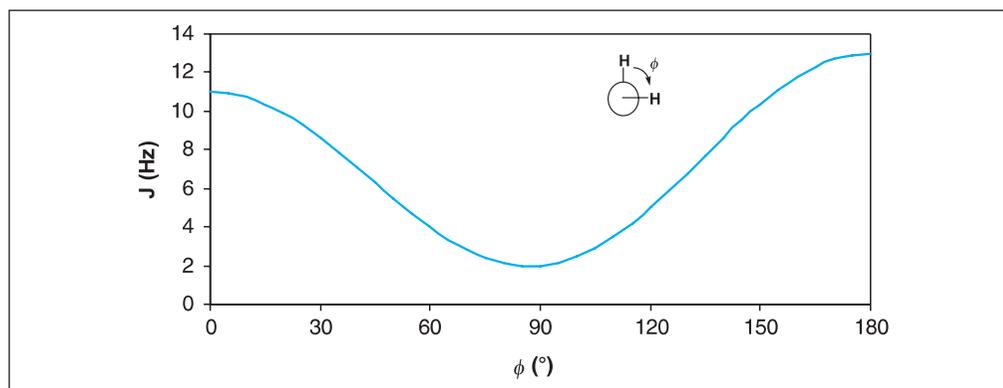


FIGURE 4-23 The Karplus curve.

The impact of the Karplus relationship can be seen in the ring-fusion hydrogens of *cis*- and *trans*-decalin systems (see Figure 4-24). In *cis*-decalin, the dihedral angle is locked at about  $60^\circ$  and the observed coupling constant is relatively low. By contrast, the same hydrogens in *trans*-decalin are antiperiplanar ( $\phi = 180^\circ$ ), and the observed *J*-value is quite large. The Karplus curve also explains the coupling constants in freely rotating systems, which exhibit a time-averaged value of about 7.5 Hz (our garden-variety *J*-value for most acyclic aliphatic protons).

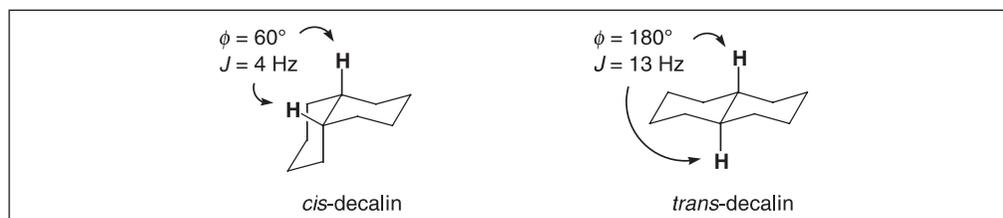


FIGURE 4-24 Impact of the Karplus relationship in constrained systems.

Generally speaking, protons connected to the same carbon (geminal protons) do not split each other—with one significant exception. Figure 4-25 shows three types of geminal protons: homeotopic, enantiotopic, and diastereotopic. To better understand the terminology, consider the imaginary products formed by replacing each of the two geminal protons with another atom, say a chlorine substituent. In the homeotopic example, the two “products” are identical (2-chloropropane); for the enantiotopic protons, two enantiomeric “products” are formed [*R*- and *S*-(1-chloroethyl)benzene]; and replacing  $H_a$  versus  $H_b$  in the cyclopropane derivative gives diastereomers (*cis*-dichloro vs. *trans*-dichloro).

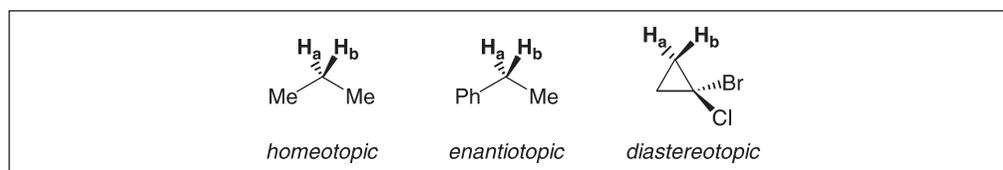


FIGURE 4-25 Three types of geminal protons.

**Homeotopic and enantiotopic geminal protons** do not split each other, because they are chemically equivalent. In other words, they are identical through a plane of symmetry (the plane of this page). However, **diastereotopic protons** are not chemically equivalent—in the example in Figure 4-25,  $H_a$  is in proximity to the chloro substituent, whereas  $H_b$  is close to the bromine. In short, they are in different worlds and therefore behave as individuals. Therefore, in these special cases, geminal protons do split each other, and the magnitude of the  $J$ -value is relatively large. Figure 4-26 lists this value, along with other representative coupling constants. This summary is useful for the interpretation of spectra.

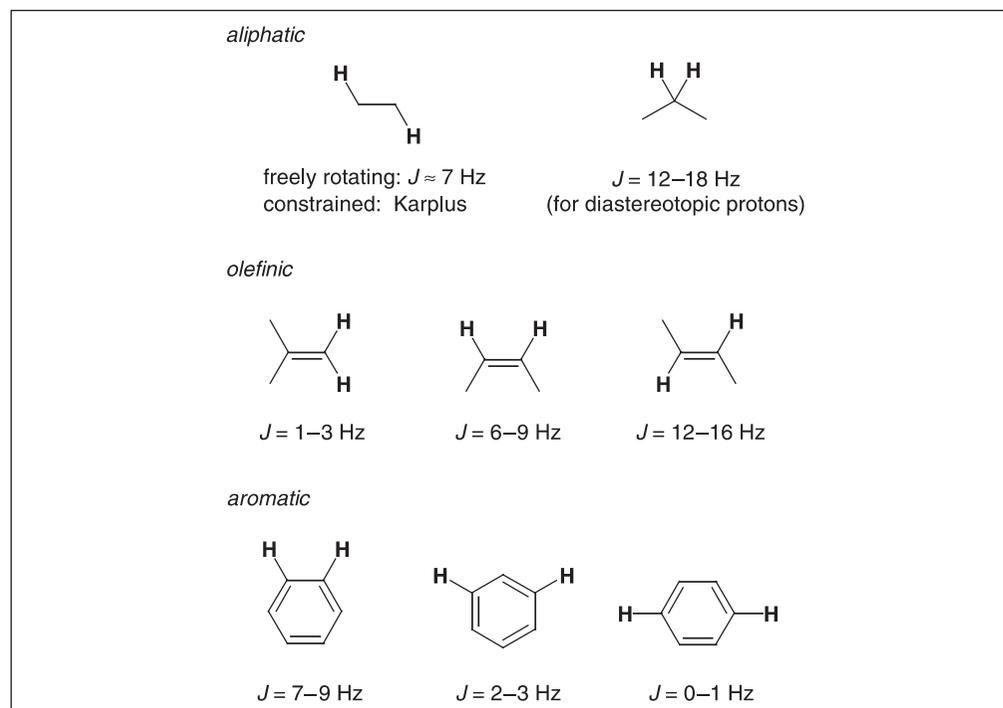


FIGURE 4-26 Some representative coupling constants.

Some interesting patterns arise when a proton is coupled to two different neighbors with divergent  $J$ -values. For example, terminal alkenes have three olefinic protons that are related with three different coupling constants (see Figure 4-26). The *trans*-olefinic coupling constant ( $J_{ac}$ ) is the largest, with typical values ranging from 12 to 16 Hz; the next largest is the *cis*-olefinic value ( $J_{ab}$ ), which is usually around 6–9 Hz; and finally the *gem*-olefinic coupling constant ( $J_{bc}$ ) is quite small—about 1–3 Hz.

With this information in hand, consider the excerpt of the NMR spectrum shown in Figure 4-27, which shows the resonances for  $H_c$  and  $H_b$ .  $H_a$  is split into a doublet by  $H_c$  (with a large  $J$ -value), and again into a doublet by  $H_b$  (with a small  $J$ -value). This pattern is known as a **doublet of doublets** (or colloquially, as a double doublet) and is designated with the abbreviation “dd.” Similarly,  $H_b$  is split into a doublet by  $H_a$  (with a medium  $J$ -value), and again into a doublet by  $H_c$  (with a small  $J$ -value), to give another

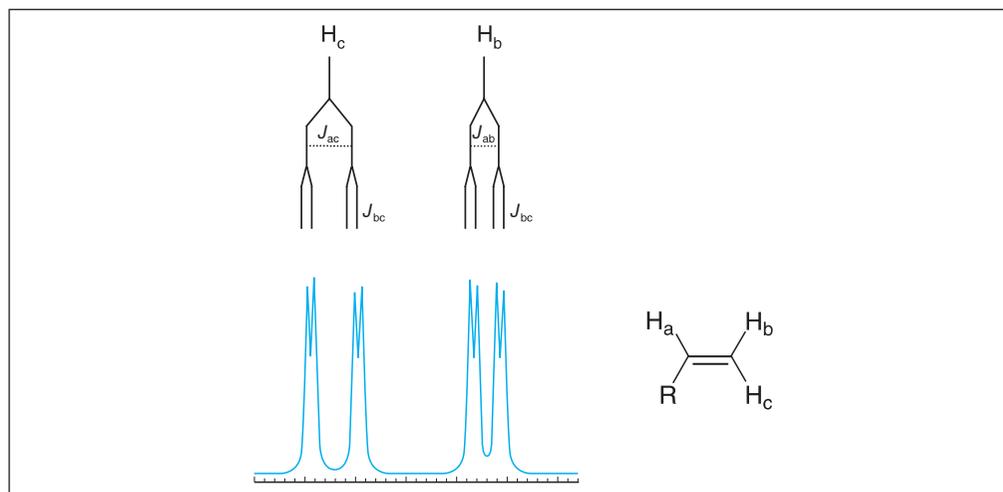


FIGURE 4-27 Multiple splitting patterns.

double doublet. The two double doublets are qualitatively different, and even casual visual inspection reveals that the downfield pattern is a combination of the large and small coupling constants, whereas the upfield pattern incorporates the medium and small coupling constants. This alone would allow you to make a fairly confident assignment of these peaks to  $H_c$  and  $H_b$ , respectively.

## GEOMETRICAL OPTICS

**Geometrical optics** is a branch of physics concerned with the propagation of light used to form images. In typical problems of geometrical optics, a light source is allowed to strike one of two basic types of optical components: mirrors and thin lenses.

**Mirrors** are optical components that reflect light rays from a light source to form an image. Two types of mirrors are **plane mirrors** and **spherical mirrors**. Spherical mirrors can be further subdivided into **concave** (curved inward) mirrors and **convex** (curved outward) mirrors.

**Thin lenses** are optical components that refract light rays from a light source to form an image. Thin lenses are generally curved and referred to as spherical thin lenses. Two general forms of spherical thin lenses are concave (curved inward) and convex (curved outward). These two components are discussed in greater detail later.

Terms describing parameters critical to problems in geometrical optics include the following:

- **Object distance**,  $o$ , is the distance between the object and the optical component.
- **Image distance**,  $i$ , is the distance between the image and the optical component.
- **Focal length**,  $f$ , is the distance between the image and the optical component observed when the source is imaged from an infinite distance. The point at which the incoming light rays converge to form the image is known as the **focal point**,  $F$ .

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- ▶ **Radius of curvature**,  $R$ , is the radius of a circle that most closely approximates the curvature of the spherical optical component. The point representing the center of this circle is termed the **center of curvature**,  $C$ .

Other terms that describe the image formed as a result of these optical components include the following:

- ▶ A **real image** is an image formed by the convergence of light rays and is characterized by a **positive image distance**,  $+i$ .
- ▶ A **virtual image** is an image formed by the divergence of light rays and is characterized by a **negative image distance**,  $-i$ .
- ▶ **Magnification**,  $m$ , of an optical component (thin lenses or mirror) is defined as:

$$m = -\frac{i}{o} = \frac{h_i}{h_o}$$

$$\text{Magnification} = -\frac{\text{image distance}}{\text{object distance}} = \frac{\text{image height}}{\text{object height}}$$

A **negative magnification value** indicates that the image is smaller than the object and is inverted, whereas a **positive magnification value** indicates that the image is larger than the object and is upright or erect.

In solving problems in geometrical optics, you are presented with an optical component and an object (light source) positioned a given distance from the component and asked to determine the image distance from the component where the image is formed and the type of image formed. This objective can be accomplished using two different techniques: an analytical technique and a graphical technique. The **analytical technique** consists of a mathematical relation between the image distance  $i$ , object distance  $o$ , focal length  $f$ , and radius of curvature  $R$ . The **graphical technique** involves ray tracing for the location of the image formed by the optical component. **Ray tracing** graphically follows the path of three principal light rays emitted from the object and interacting with the optical component.

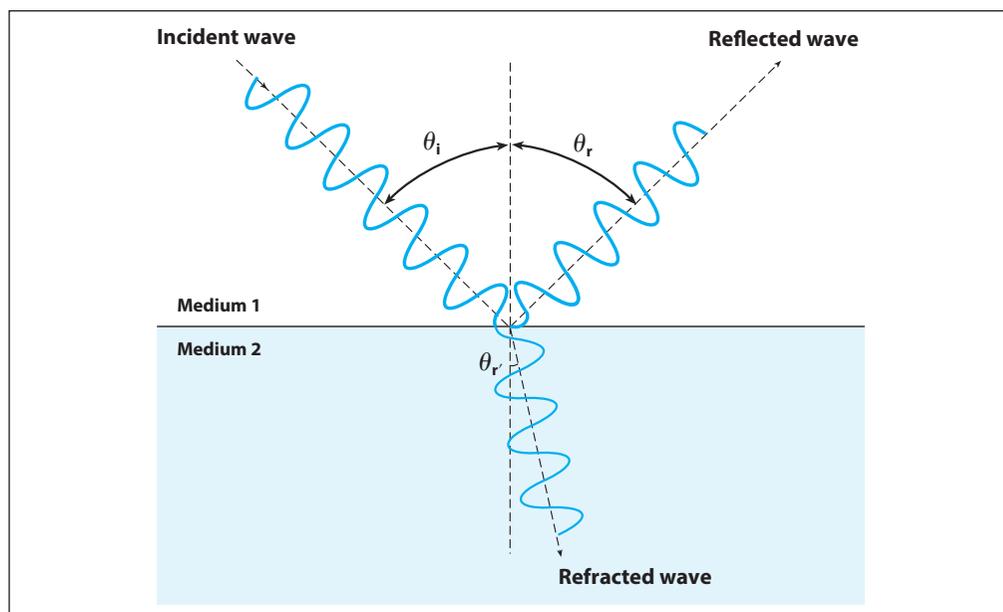
## Reflection and Refraction of Light

As light waves propagate through one medium and approach a second medium, they can interact with the boundary between the two media in primarily one of two separate ways: reflection and refraction. Consider a light ray that propagates through one medium and strikes the boundary at an incidence angle of  $\theta_i$  with the normal (axis perpendicular to the plane surface), as shown in Figure 4-28.

The light ray can reflect or bounce off the surface boundary at an angle of reflection  $\theta_r$ , also measured with respect to the normal, which is equal in magnitude to the angle of incidence. This is known as the **law of reflection**, represented by:

$$\theta_i = \theta_r$$

angle of incidence = angle of reflection



**FIGURE 4-28** A light wave propagating through one medium and striking a second medium. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

In addition to reflection, the light ray can bend or refract as it enters the second medium. The angle at which the light ray refracts,  $\theta_r'$ , is dependent on the ratio of the indices of refraction between the two media. The **index of refraction**  $n$  for a given material is defined as

$$n = \frac{\text{speed of light in vacuum}}{\text{speed of light in material}} = \frac{c}{v}$$

The index of refraction for common substances is as follows:

Air	$n = 1.00$	Ethyl alcohol	$n = 1.36$
Glass	$n = 1.52$	Polystyrene	$n = 1.55$
Water	$n = 1.33$	Sodium chloride	$n = 1.54$
Diamond	$n = 2.42$	Acetone	$n = 1.36$

The **angle of refraction**  $\theta_r'$  with respect to the normal is related to the incident angle by the **law of refraction**, also known as **Snell's law**:

$$n_1 \sin \theta_i = n_2 \sin \theta_r'$$

where  $n_1$  and  $n_2$  are the indices of refraction of the first medium and second medium, respectively.

**EXAMPLE:** A ray of light strikes the surface of a swimming pool at an angle of  $45^\circ$  from the normal. Determine the angle of refraction.

**SOLUTION:** From the law of refraction, the angle of incidence is equal to the angle of refraction. Thus,  $\theta_i = \theta_r' = 45^\circ$  from the normal.

**EXAMPLE:** A light ray in air ( $n = 1.00$ ) strikes the surface of a glass pane ( $n = 1.52$ ) at an angle of incidence of  $35^\circ$  from the normal. Determine the angle of refraction.

**SOLUTION:** From Snell's law:

$$n_1 \sin \theta_i = n_2 \sin \theta_r$$

$$1.00 \sin 35^\circ = 1.52 \sin \theta_r$$

$$\sin \theta_r = \frac{1.00 \sin 35^\circ}{1.52} = 0.377$$

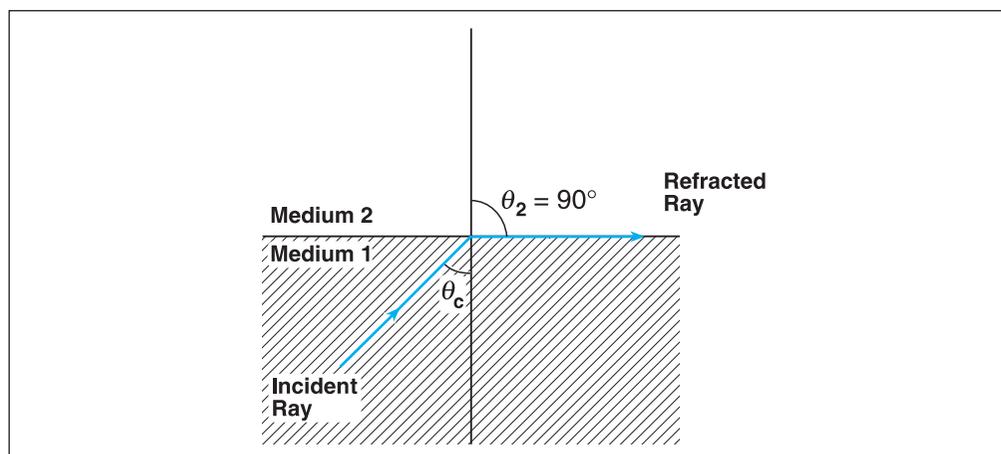
$$\theta_r = \sin^{-1} 0.377 = 22.1^\circ$$

## Total Internal Reflection

**Total internal reflection** is a phenomenon that occurs when light passes from a medium or material with a high index of refraction to a medium with a low index of refraction. For example, consider a light ray passing from glass ( $n = 1.52$ ) to air ( $n = 1.00$ ) at an angle of incidence  $\theta_i$ , as shown in Figure 4-29. In this case, the angle of refraction is greater than the angle of incidence. In fact, as one increases the angle of incidence, the light ray has an angle of refraction of  $90^\circ$  and is subsequently refracted along the interface between the two media. The angle of incidence that causes light to be refracted at  $90^\circ$  from the normal is called the **critical angle**  $\theta_c$ , given by:

$$\sin \theta_c = \frac{n_2}{n_1}$$

**EXAMPLE:** Assuming air as the external medium, determine the critical angle for total internal reflection for diamond ( $n = 2.42$ ).



**FIGURE 4-29** A light ray passing from glass to air, illustrating total internal reflection. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

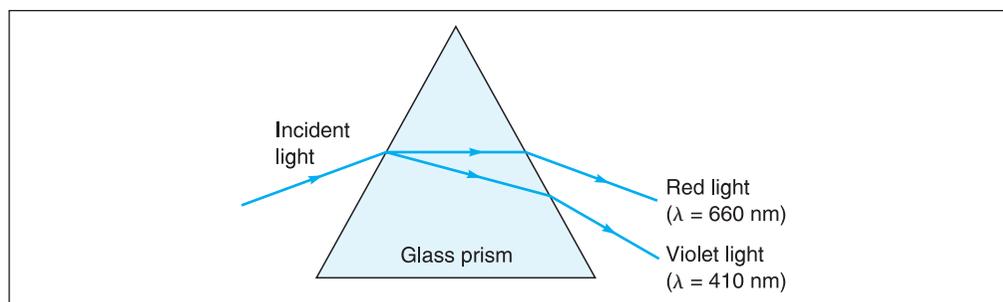
**SOLUTION:** Using the expression for the critical angle

$$\sin \theta_c = \frac{n_2}{n_1} = \frac{n_{\text{air}}}{n_{\text{diamond}}} = \frac{1.00}{2.42} = 0.413$$

$$\theta_c = \sin^{-1} 0.413 = 24.4^\circ$$

## Dispersion of Light

**Dispersion** is the separation of any traveling wave into separate frequency components. An example of dispersion is the separation of white light into its wavelength components and its corresponding elementary colors as it passes through a prism, as shown in Figure 4-30. As it passes through a prism, white light refracts at different angles with the smallest component wavelength (violet) being bent the farthest and the largest component wavelength (red) being bent the least.



**FIGURE 4-30** Separation of white light by dispersion.

## Mirrors

### PLANE MIRRORS

Light rays emanating from an object toward a plane mirror appear to converge at a point within the mirror, as shown in Figure 4-31. The image created by a plane mirror is always virtual and erect—that is, the image appears to be positioned the same distance from the mirror as the distance from the object to the mirror, but on the other side of the mirror.

### SPHERICAL MIRRORS

Spherical mirrors are mirrors that are curved and exist primarily in two forms, depending on their curvature. Concave mirrors are curved inward and convex mirrors are curved outward. The spherical mirrors are represented by their radius of curvature  $R$ , which is related to their focal length  $f$  by:

$$\text{Concave mirror} \quad R = +2f$$

$$\text{Convex mirror} \quad R = -2f$$

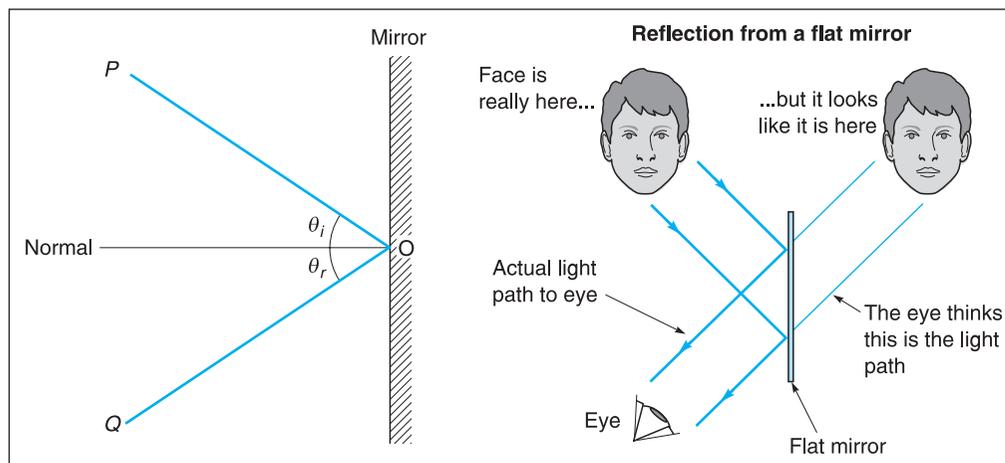


FIGURE 4-31 Image formation in a plane mirror.

In Figure 4-32a, parallel light rays emanating from an object toward a concave mirror reflect and ultimately converge at the real focal point  $F$ . Similarly, in Figure 4-32b, parallel light rays emanating from an object toward a convex mirror reflect and ultimately diverge, such that the reflected rays appear to converge at a virtual focal point  $F'$  behind the mirror.

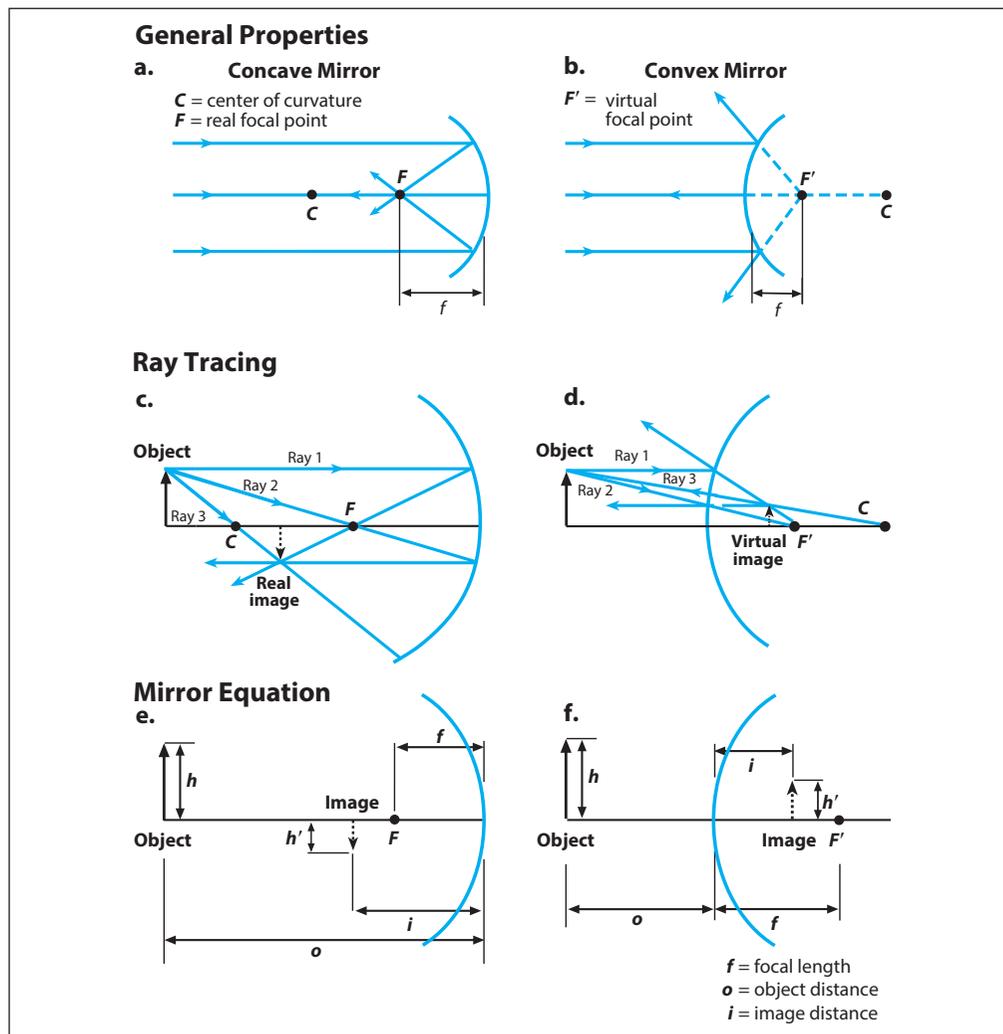
**Ray tracing** represents a graphical approach by which the image position and image size formed by a mirror can be determined. Ray tracing follows the path of three different principal light rays emanating from an object (typically represented by an arrow), interacting with the mirror, and either converging or diverging at the real or virtual focal point, depending on whether the lens is concave or convex, as shown in Figure 4-32c and d.

- One principal light ray (Ray 1) travels parallel to the optical axis of the mirror, reflects off the mirror, and passes through the real focal point  $F$  of a concave mirror or appears to originate from the virtual focal point  $F'$  of a convex mirror.
- One principal light ray (Ray 2) travels through the real focal point  $F$  and reflected in a direction parallel to the mirror axis.
- One principal light ray (Ray 3) travels along a radius of the mirror toward the center of curvature  $C$ , striking the mirror perpendicular to its surface. After reflection, the reflected ray travels back along its original path.

The **mirror equation** represents the analytical approach in the determination of the image type and location. The mirror equation relates the object distance  $o$ , the image distance  $i$ , the focal length  $f$ , and the radius of curvature,  $R$ , by:

$$\frac{1}{o} + \frac{1}{i} = \frac{1}{f} = \pm \frac{2}{R}$$

where  $o$ ,  $i$ ,  $f$ , and  $R$  are expressed in units of length. The mirror equation and associated parameters are displayed in Figure 4-32e and f.



**FIGURE 4-32** Spherical mirrors. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

**EXAMPLE:** The focal length of a concave mirror is 10 centimeters (cm). For an object placed 30 cm in front of the mirror, determine the following:

1. Image distance
2. Magnification

**SOLUTION:**

1. The image distance is related to the focal length by:

$$\frac{1}{o} + \frac{1}{i} = \frac{1}{f}$$

$$\frac{1}{30 \text{ cm}} + \frac{1}{i} = \frac{1}{10 \text{ cm}}$$

$$i = 15 \text{ cm}$$

2. The magnification is given by:

$$m = -\frac{i}{o} = -\frac{15 \text{ cm}}{30 \text{ cm}} = -0.5$$

Referring to the following table of sign conventions for spherical mirrors, the image is real, inverted, and located between the focal point and the center of curvature.

**TABLE 4-6** Sign Conventions for Spherical Mirrors

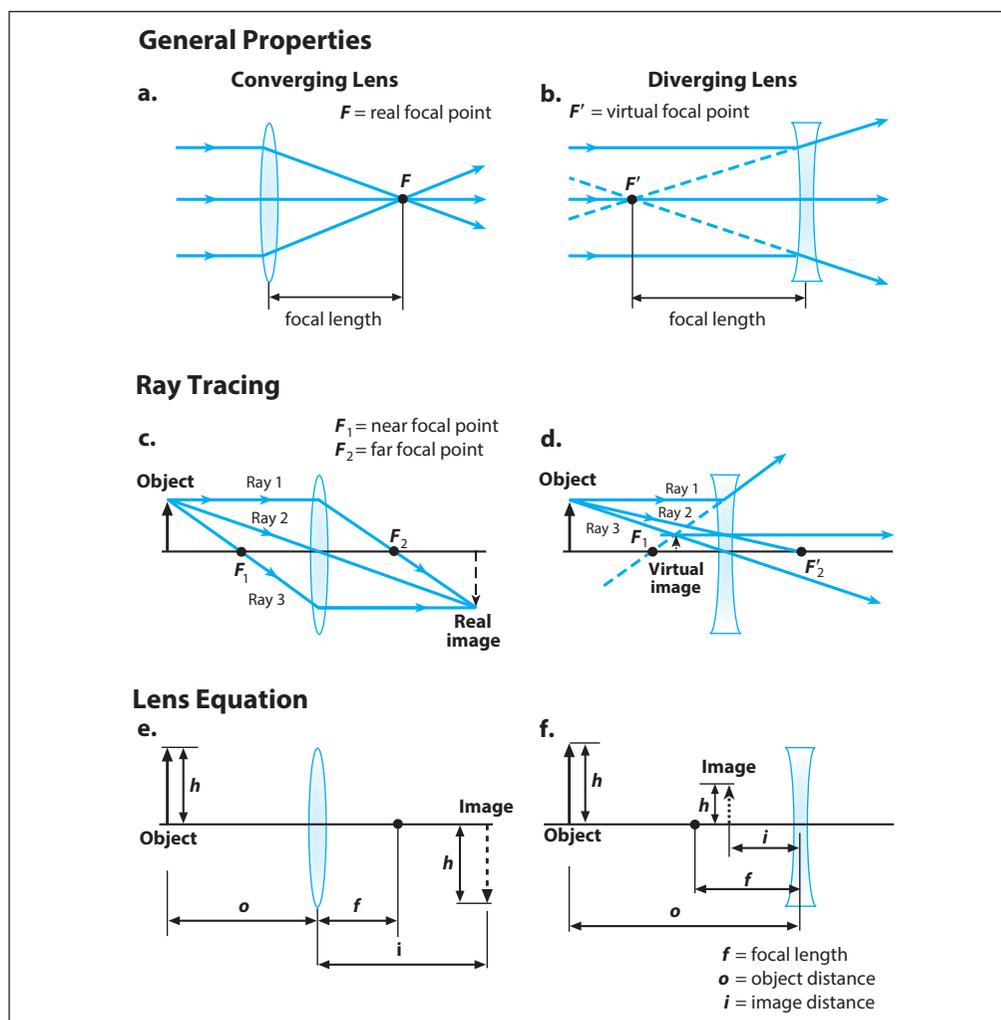
Parameter	Positive	Negative
Object distance, $o$	Real object	Virtual object
Image distance, $i$	Real image	Virtual image
Focal length, $f$	Concave mirror	Convex mirror
Radius of curvature, $R$	Concave mirror	Convex mirror
Magnification, $m$	Erect image	Inverted image

## Thin Lenses

Thin lenses, like mirrors, exist as convex or concave lenses. However, lenses form images by refracting light rays, as opposed to mirrors that form images by reflecting light rays. Thin lenses have two surfaces and are thus characterized by two radii of curvature  $R_1$  (side of lens closest to the object) and  $R_2$  (side of lens opposite to the object). A convex lens has a positive  $R_1$  and a negative  $R_2$ , whereas a concave lens has a negative  $R_1$  and a positive  $R_2$ . For a convex (also referred to as converging) lens, as shown in Figure 4-33a, all light rays emanating from an object refract through the lens and converge to generate an image at the real focal point  $F$  on the side of the lens opposing the object. For a concave (also referred to as diverging) lens, as shown in Figure 4-33b, all light rays emanating from an object refract through the lens and diverge to generate an image at the virtual focal point  $F'$  on the same side of the lens as the object.

Ray tracing can also be used to determine image position and image size formed by a thin lens. As in the case for mirrors, three particular principal rays of light are followed from the object and ultimately interacting with the lens, as shown in Figure 4-33c and d.

- One principal light ray (Ray 1) travels parallel to the optical axis of the lens, refracts through the lens, and passes through a second real focal point  $F_2$  for a convex lens or appears to originate from a second virtual focal point  $F'_2$  for a concave lens.
- One principal light ray (Ray 2) travels diagonally, directed toward and penetrating through the center of the lens without bending.
- One principal light ray (Ray 3) travels through the first real focal point  $F_1$  for a converging lens before it refracts and travels parallel to the optical axis. For a diverging lens, Ray 3 moves through the center of the lens in a straight line.



**FIGURE 4-33** Thin lenses. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

The **lens equation** relates the object distance  $o$ , image distance  $i$ , and the focal length  $f$  of a lens according to:

$$\frac{1}{f} = \frac{1}{i} + \frac{1}{o}$$

The lens equation and associated parameters are illustrated in Figure 4-33e and f.

Also of importance in creating the lens is the **lens maker's equation**, which can be expressed as:

$$\frac{1}{f} = (n - 1) \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$$

where  $f$  is the focal length,  $n$  is the index of refraction for the lens material,  $R_1$  is the radius of curvature of the lens closest to the object, and  $R_2$  is the radius of curvature of the lens farthest from the object.

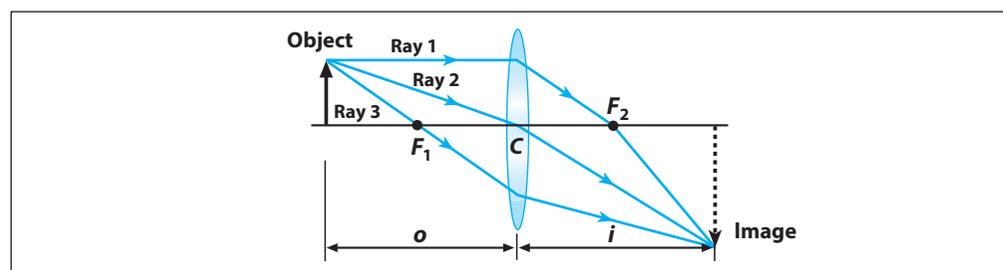
**TABLE 4-7** Sign Conventions for Spherical Lenses

Parameter	Positive	Negative
Object distance, $o$	Real object	Virtual object
Image distance, $i$	Real image	Virtual image
Focal length, $f$	Converging lens	Diverging lens
Magnification, $m$	Erect image	Inverted image

**EXAMPLE:** An object of height 5 cm is positioned 24 cm in front of a convex lens with a focal length of 15 cm. Determine the location and height of the produced image, using the following:

1. Ray tracing
2. The lens equation

**SOLUTION:** From Figure 4-34, three principal rays emanating from the object are followed through the convex lens, resulting in the formation of a real image.



**FIGURE 4-34** Three principal rays from an object through a convex lens. *Source:* From George Hademenos, *Schaum's Outline of Physics for Pre-Med, Biology, and Allied Health Students*, McGraw-Hill, 1998; reproduced with permission of The McGraw-Hill Companies.

- Ray 1 strikes the lens toward the top and refracts through it. Following refraction, Ray 1 passes through the principal focal point  $F_2$ .
- Ray 2 passes through the center of the convex lens and continues until it converges with Ray 1.
- Ray 3 strikes the lens toward the bottom and refracts through it. Following refraction, Ray 3 continues parallel to the optical axis until it converges with Rays 1 and 2.

The point where all three rays converge represents the size and location of the image. From the ray tracing in Figure 4-34, it can be concluded that the image is real, inverted, magnified, and located farther from the lens than the object.

The lens equation can be used to find the image distance:

$$\frac{1}{i} = \frac{1}{f} - \frac{1}{o} = \frac{1}{15 \text{ cm}} - \frac{1}{24 \text{ cm}} = 0.025 \frac{1}{\text{cm}}$$

so

$$i = \frac{1}{0.025 \frac{1}{\text{cm}}} = 40 \text{ cm}$$

A positive value of  $i$  indicates the image is real and on the side of the lens opposite the object.

The height of the object  $h_i$  can be determined from the magnification  $m$ :

$$m = -\frac{i}{o} = -\frac{40 \text{ cm}}{24 \text{ cm}} = -1.67$$

The magnification  $m$  is related to the image height by:

$$m = \frac{h_i}{h_o}$$

$$h_i = mh_o = (-1.67)(5 \text{ cm}) = -8.35 \text{ cm}$$

The negative value of  $h_i$  indicates that the image is inverted.

## Combinations of Lenses

In addition to single lenses, images can be formed from a combination of lenses. Many optical devices, including the compound microscope, use lens combinations to form images. In a system consisting of two lenses, an object is placed in front of the first lens, beyond its focal point ( $f_{\text{lens1}}$ ), as shown in Figure 4-35. The three rays emanate from the object and follow three paths through the lens, with all three rays converging on the opposite side of the lens to form the tip of the image.

When a second lens is placed next to the first lens, Ray 3 refracts upward from the second lens and passes through the focal point of the second lens ( $f_{\text{lens2}}$ ), labeled as 4 (lens 2). Yet a fourth individual ray, labeled 5 (lens 2), begins from the object and passes through the center of the second lens. The intersection of Rays 4 (lens 2) and 5 (lens 2) forms the point for the final image seen by the observer, as shown in Figure 4-36.

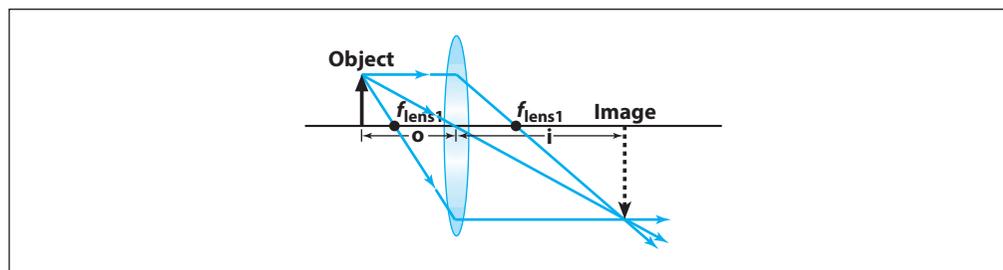


FIGURE 4-35 An object in front of first lens.

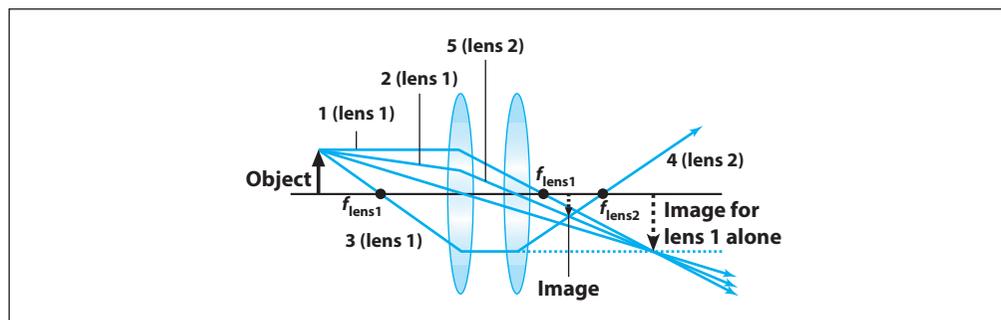


FIGURE 4-36 Combination of two lenses.

## Lens Aberrations

A ray diagram that describes the formation of an image with a lens involves three light rays that emanate from an object and refract through the lens at different points, with the rays converging on the opposite side at a point to form an image. This, however, is an ideal case and tends to differ in practice. The deviations from an ideal lens, referred to as **aberrations**, often result in a blurred image. There are two general types of lens aberrations: spherical aberrations and chromatic aberrations.

A **spherical aberration** is related to the geometrical structure of the lens. It occurs when the light rays passing through the lens do not refract as well at the edges of the lens compared to the rays moving through the center of the lens. As a result, the light rays passing through the lens do not converge onto a single point, causing slight blurring of an image. This effect can be addressed by polishing the lens and eventually removing the spherical contours of the lens.

A **chromatic aberration** has to do with the behavior of light. As it strikes the lens, light disperses or separates into its constituent wavelengths, much like it would do with a prism. The separation of the light according to wavelengths prevents the light rays from converging or focusing on a single point. This effect is addressed by using a combination of lenses.

## Optical Instruments

### COMPOUND MICROSCOPE

The **compound microscope**, shown in Figure 4-37, uses two lenses, an objective lens and an eyepiece lens, separated by an optical tube to produce a magnified image of an object. The object of interest is placed beyond the first focal point  $f_{o1}$  of the objective lens. The objective lens produces an intermediate image that is real, inverted, and magnified. This intermediate image serves as the object for the eyepiece lens, which further magnifies the intermediate image to form the final virtual image seen by the observer, as shown in Figure 4-37.

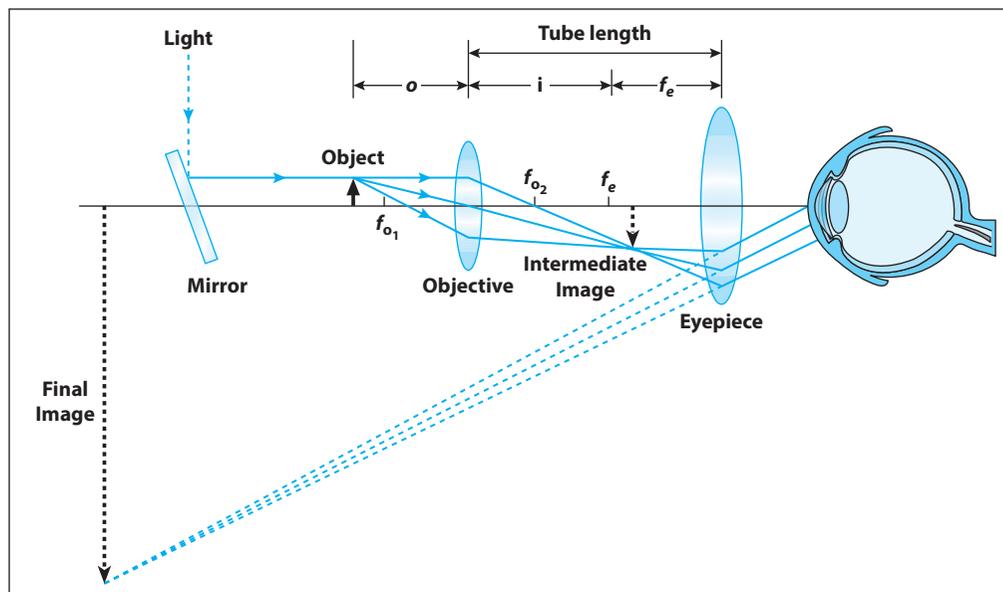


FIGURE 4-37 Compound microscope lenses.

## HUMAN EYE

The human eye is a remarkable visual instrument capable of visualizing objects from as far away as infinity to as close as to 20 cm in proximity into focus. The human eye can resolve particles of matter that are held approximately 0.1 mm apart. The ability to focus occurs as the result of **ciliary muscles** that control the curvature of the **cornea**.

Image formation in the human eye occurs on the **retina**, as shown in Figure 4-38, by refraction of light at three separate interfaces:

1. Surface of the cornea where light passes from air ( $n = 1.00$ ) into the cornea (filled with **aqueous humor**) ( $n = 1.33$ )

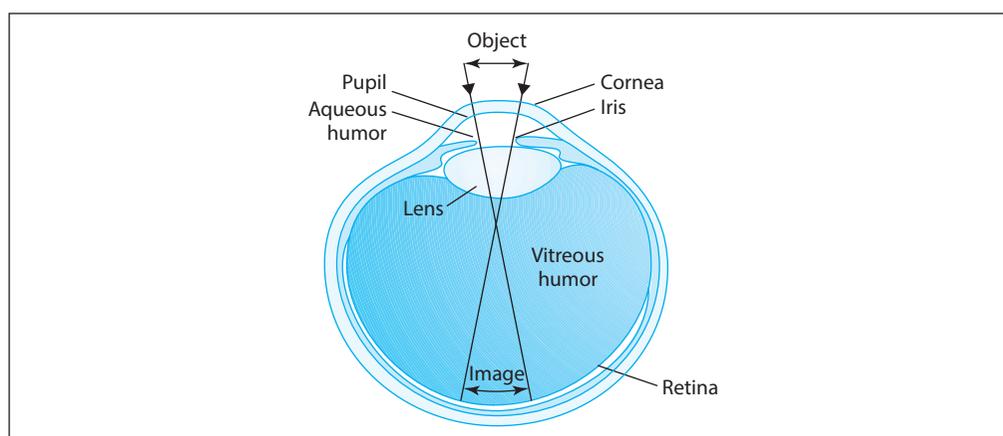


FIGURE 4-38 Image formation in the human eye.

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2. Anterior surface of the lens where light passes from the aqueous humor ( $n = 1.33$ ) into the lens ( $n = 1.41$ )
3. Posterior surface of the lens where light passes from the lens ( $n = 1.41$ ) through the **vitreous humor** ( $n = 1.33$ ) until it strikes the retina.

To find the eventual angle that light strikes the retina, **Snell's law of refraction** must be applied at each of the three interfaces, with each previous angle being the initial angle for the subsequent application. Assume, for example, that light strikes the cornea of the eye at an incidence angle of  $35^\circ$  to the normal. The angle at which the light rays strike the retina can be found by applying Snell's law at the first interface involving air and aqueous humor:

$$n_{\text{air}} \sin \theta_i = n_{\text{aq humor}} \sin \theta_r'$$

$$(1.00) \sin 35^\circ = (1.33) \sin \theta_r'$$

$$\sin \theta_r' = 25.5^\circ$$

This angle now becomes the angle of incidence for the light rays at the second interface. At the second interface involving aqueous humor and the lens:

$$n_{\text{aq humor}} \sin \theta_i = n_{\text{lens}} \sin \theta_r'$$

$$(1.33) \sin 25.5^\circ = (1.41) \sin \theta_r'$$

$$\sin \theta_r' = 23.9^\circ$$

This angle now becomes the angle of incidence for the light rays at the third interface. At the third interface involving the lens and vitreous humor:

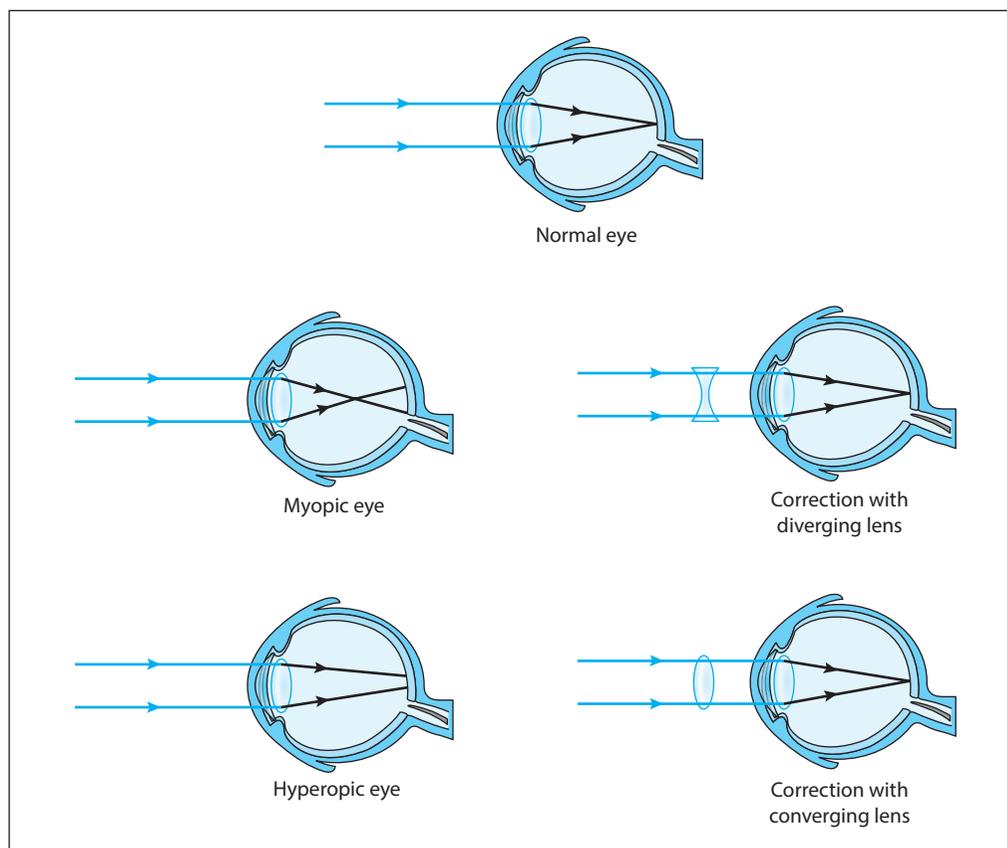
$$n_{\text{lens}} \sin \theta_i = n_{\text{vi humor}} \sin \theta_r'$$

$$(1.41) \sin 23.9^\circ = (1.33) \sin \theta_r'$$

$$\sin \theta_r' = 25.4^\circ$$

Common visual impairments of the eye include myopia (nearsightedness) and hyperopia (farsightedness), both of which can be readily corrected with the proper choice of eyeglass or contact lens. In **myopia**, focused vision is achieved for objects that are near, while vision becomes blurred for distant objects. The exact opposite is true in **hyperopia**, where distant objects can be seen clearly and close objects appear blurry. The nature of these impairments involves the point of convergence for parallel rays of light from the object. In the normal eye, parallel rays from an object enter through the lens and converge on the retina where the image is formed.

A myopic person can easily see close objects clearly, but vision becomes blurry for distant objects. The myopic eye focuses light in front of the retina due in part to a lens with too short a focal length. The shortened focal length occurs as a result of either an elongated eyeball or excessive curvature of the cornea. The objective in treating myopia is to reduce the converging power of the lens, which can be accomplished with the placement of a diverging (concave) lens in front of the eye.



**FIGURE 4-39** Common visual impairments and their related solutions.

A hyperopic person can easily see distant objects clearly, but vision becomes blurry for close objects. The hyperopic eye focuses light behind the retina due in part to inadequate curvature of the cornea or too flat a lens or too short an eyeball. The objective in treating hyperopia is to increase the converging power of the lens, which can be accomplished with the placement of a converging (convex) lens in front of the eye. These common visual impairments and their related solutions are illustrated in Figure 4-39.

