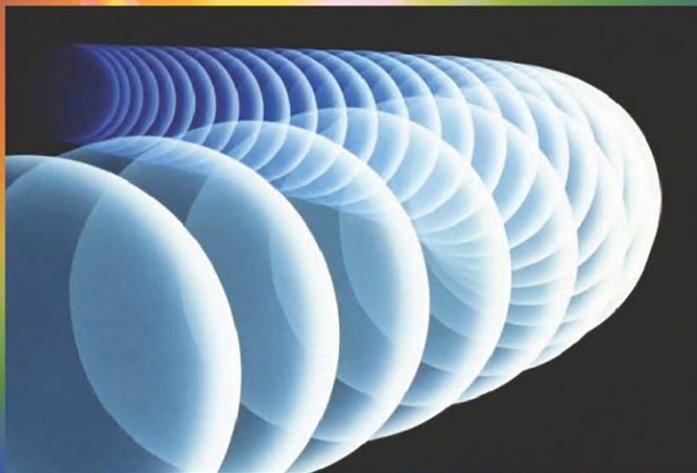Photonics-Enabled Technologies

Basics of Spectroscopy

OP-TEC

Optics and Photonics Series

Basics of Spectroscopy

Photonics-Enabled Technologies

OPTICS AND PHOTONICS SERIES

**STEP (Scientific and Technological Education
in Photonics), an NSF ATE Project**

OP-TEC

National Center for Optics and Photonics Education

PREFACE

This module is the first of three pertaining to the role of laser spectroscopy as a *photonics-enabled* technology. The combined series on photonics-enabled technologies (comprising both STEP and OP-TEC materials) consists of modules in the areas of manufacturing, biomedicine, forensic science and homeland security, environmental monitoring, and optoelectronics, as listed below. (This list will expand as the OP-TEC series grows. For the most up-to-date list of modules, visit http://www.op-tec.org.)

Manufacturing

Laser Welding and Surface Treatment

Laser Material Removal: Drilling, Cutting, and Marking

Lasers in Testing and Measurement: Alignment Profiling and Position Sensing

Lasers in Testing and Measurement: Interferometric Methods and Nondestructive Testing

Environmental Monitoring

Basics of Spectroscopy

Spectroscopy and Remote Sensing

Spectroscopy and Pollution Monitoring

Biomedicine

Lasers in Medicine and Surgery

Therapeutic Applications of Lasers

Diagnostic Applications of Lasers

Forensic Science and Homeland Security

Lasers in Forensic Science and Homeland Security

Infrared Systems for Homeland Security

Imaging System Performance for Homeland Security Applications

Optoelectronics

Photonics in Nanotechnology

The modules pertaining to each technology can be used collectively as a unit. Each module can also be used separately as a stand-alone item, as long as prerequisites have been met.

For students who may need assistance with or review of relevant mathematics concepts, a review and study guide entitled *Mathematics for Photonics Education* (available from CORD) is highly recommended.

The original manuscript of this module, *Basics of Spectroscopy,* was prepared by Leno Pedrotti (CORD). Formatting and artwork were provided by Mark Whitney and Kathy Kral (CORD).

CONTENTS

Basics of Spectroscopy

INTRODUCTION

This module is the first in a series of three modules that deal with *spectroscopy*. The three, taken in sequence, cover first the basic ideas of what spectroscopy is and what it does (*Basics of Spectroscopy*); second, the instruments used to form and measure spectra of various light sources (*Instruments of Spectroscopy*); and third, the applications of spectroscopy in diverse scientific and technical fields (*Applications of Spectroscopy*).

In this module you will learn how spectroscopy stands as an important science related to the identification of the emissions, absorptions, and structures of many substances. You will learn how the use of different parts of the electromagnetic spectrum enables one to probe the inner structures of atomic and molecular substances and provide one with "fingerprints" that can be used to identify these substances when they are present in complicated mixtures. Finally, we shall look (briefly) at the instruments used to provide spectra and the general applications of spectroscopy in today's technologies. We shall reserve for the two modules that follow a deeper treatment of measuring instruments and a survey of applications in spectroscopy.

PREREQUISITES

Several modules in Course 1, *Fundamentals of Light and Lasers,* form an ideal background for a study of this module. They are Module 1-1: *Nature and Properties of Light;* Module 1-3: *Light Sources and Laser Safety;* Module 1-4: *Basic Geometrical Optics;* and Module 1-5: *Basic Physical Optics.* In addition, a working understanding of algebra, geometry, and right-angle trigonometry will be helpful.

OBJECTIVES

When you have finished this module you will be able to:

- Define *spectroscopy, spectra,* and *spectrometer*.
- Outline the development of spectroscopy as a science.
- Distinguish between *emission* and *absorption* spectra.
- Distinguish between *line* and *band* spectra.

- Describe the *infrared* (IR), *ultraviolet* (UV), and *visible* regions of the electromagnetic spectrum.

- Describe how atoms and molecules *absorb, store,* and *emit* energy.

- Describe how electromagnetic energy is separated into different wavelengths by *prisms* and *gratings.*

- Describe how *prisms, diffraction gratings,* and *interferometers* are used in spectrometers to record emission and absorption spectra.

- List various sources of light that can be analyzed by spectroscopy.

- List at least six major areas in industry and technology that apply the science of spectroscopy to identify substances and control emissions.

SCENARIO

Jennifer works in a forensic laboratory in a large northeastern city. Her supervisor has asked her to analyze some synthetic fibers recently found in the car of a murder suspect. If the fibers match those taken from a torn article of clothing found on the murder victim, the suspect will be charged with the murder. According to an article in a local newspaper, the suspect's lawyers claim that the fibers taken from the suspect's car must have come from the car's carpeting. Using a stereomicroscope, Jennifer is able to confirm that the fibers—possibly polyester, nylon, or acrylic—are similar to those found at the crime scene. Next she uses infrared (IR) spectroscopy to confirm the suspected identity of the fibers. Jennifer places a single thread of each fiber sample—the sample from the crime scene, a sample cut from the car's carpeting for purposes of comparison, and the sample that may or not be traceable to the crime scene—into an analytical instrument that shines infrared light on it. Because different compounds absorb different wavelengths, the unique chemical structures of compounds within the fibers react to the light in distinctive ways. The spectroscopic instrument prints out a graph for each sample, enabling Jennifer to compare the graphs to one another and to graphs of known substances in reference books and online databases. Jennifer confirms that the fibers taken from the crime scene match the loose fibers taken from the suspect's car but not the fibers cut from the car's carpeting. Combined with other evidence, Jennifer's findings lead to the prosecution of the suspect.

Basic Concepts

Introduction

The science of *spectroscopy* grew out of studies of the interaction of electromagnetic energy with matter. When light shines on an object, for example, we know that part of the light is scattered (reflected) and part is absorbed. Of the initial part that is absorbed, some is later emitted as light of a different color or wavelength. Spectroscopy is that science which attempts to determine what specific energies and amounts of incident light are absorbed by specific substances, and what specific energies and amounts are later re-emitted. Optical instruments called *spectrometers* reveal in photographic or printed records—as a series of specific wavelengths or frequencies—the light energies absorbed and emitted. These records, in turn—referred to as *spectra*—provide us with important information pertaining to the atomic and molecular structure of the substances on which the electromagnetic energy is focused. These spectra provide us with "fingerprints" that are characteristic of—and therefore uniquely connected to—different elements and compounds.

A picture of such fingerprints—in this case emission line spectra—is shown in Figure 1-1 for the elements hydrogen, helium, and mercury vapor.
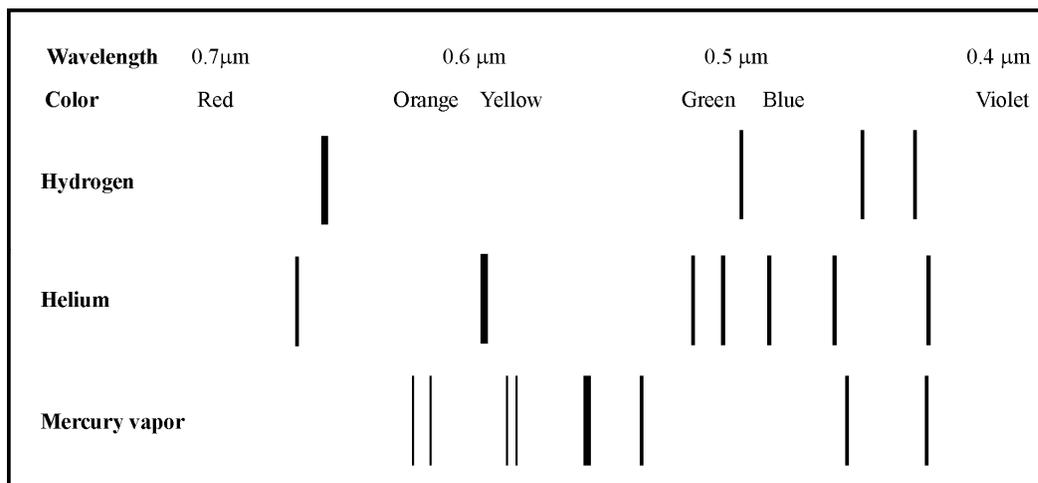
Figure 1-1 *Line spectra for three distinct elements* (Adapted from *Adventures in Physics,* Highsmith and Howard, 1972)

Notice that the array of narrow spectral lines (the spectrum) is different for each element and thus provides one with a unique, characteristic record or trace. The vertical lines in the various spectra shown in Figure 1-1 are actually the images of a narrow slit located in the optical instrument (spectrometer) shown in Figure 1-2. As can be seen, light from a source enters a narrow slit, is collimated by a lens, and falls on a prism. There it is separated (dispersed) into its constituent colors (wavelengths) and focused by a second lens onto a film plate to form the spectrum.

Figure 1-2 *The basic operation of a simple prism spectrometer. In other optical instruments for displaying or recording spectra, the prism is replaced by a diffraction grating or interferometer.* (Adapted from *Physical Science,* Robert Dixon, 1979)

A Brief History of Spectroscopy

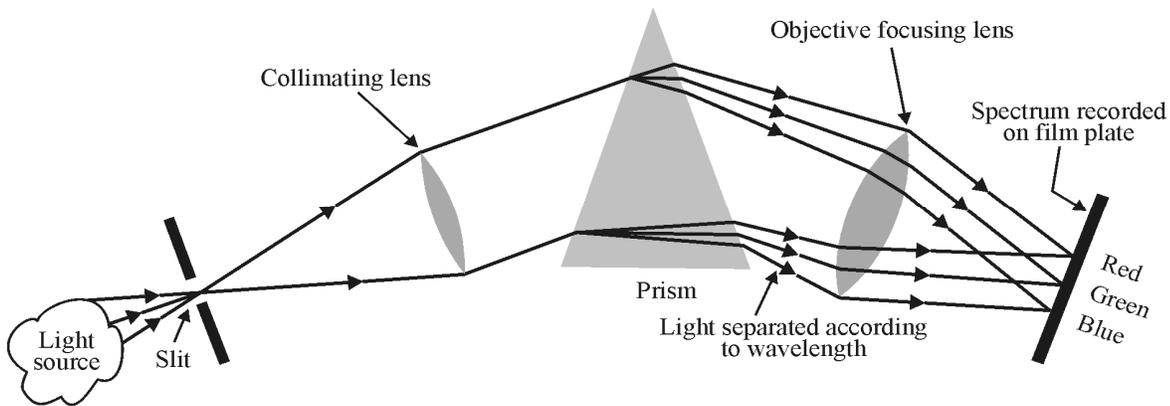Before we begin a review of electromagnetic spectra, photons, and the process of light absorption and emission in matter, let us outline briefly the development of spectroscopy as a science of detection in modern technologies.

In ancient times, Egyptians and Greeks thought about light and color and considered light to be mostly "something" that emanated from the eyes. The great minds of Ptolemy, Plato, and Aristotle failed to perceive of possible applications that might involve light as we know it. Following the Middle Ages (400–1350 AD) and the Renaissance period (1350–1700 AD), ancient, classical ways of thinking gave way to more creative, academic analyses and crude optical instruments began to appear. Scientists like Johann Kepler, Willebrord Snell, and Galileo Galilei used combinations of lenses in telescopes to see distant objects. And Sir Isaac Newton, in the latter half of the 17th century, showed how a prism "broke" white light passing through it into a rainbow of separate and distinct colors.

All through these years, the best scientific minds puzzled over the question "what is light?" The corpuscular or particle theory of light was championed by Isaac Newton and seemed securely entrenched in the mid-1700s. Later, the work of Christiaan Huygens, Thomas Young, and Augustin Fresnel lent considerable support to the wave theory of light. So the battle between "light as particle" and "light as wave" continued on into the 20th century with intellectual giants such as James Clerk Maxwell and Albert Einstein providing significant evidence for one or the other model.

In the midst of all the theoretical turbulence on the nature of light, the science of spectroscopy was nevertheless taking shape. In 1802 a physicist named W. H. Wolleston used a prism, lenses, and a narrow beam of light to produce an image of a *single wavelength* of the light. Following this work, with the help of a different light dispersing element—a diffraction grating—scientists produced similar *monochromatic* images of "split light."

The spectroscope as an instrument, like that sketched in Figure 1-2, became a practical laboratory instrument in the hands of German physicists such as Josef Fraunhofer, G. R. Kirchoff, and Robert Bunsen, during the first half of the 1800s. With Fraunhofer's study of solar

energy and the discovery of narrow dark lines in the solar spectrum, and with the ongoing analysis of light sources based on flames produced with Bunsen burners, there appeared bright lines as well as dark lines, and the science of spectroscopy was launched.

Scientists understood then that the dark and bright lines seen in absorption and emission were uniquely characteristic of the internal makeup of chemical elements. They assumed, correctly, that the energy in light could somehow excite the internal motions of atoms and molecules, extracting energy from the light at certain wavelengths, thereby giving rise to the narrow *absorption* lines. Similarly, heat or electrical energy could excite internal motions in matter which would then radiate away the absorbed energy as light, accounting for the bright or *emission* lines in the spectra. In every instance, the energy that was directed onto the target substance—to excite the internal motions of the electrons, atoms, and molecules—could be described as a well-known part of the electromagnetic spectrum.

Creating Electromagnetic (EM) Waves

All electromagnetic (EM) waves are created by accelerating electric charges. Thus the *frequency, wavelength,* and *energy* of EM waves all depend on charge acceleration and just how this acceleration changes with time. For example, for a charge moving with simple harmonic motion, the frequency f of the EM wave emitted by the accelerating charge is equal to the frequency f of the charge's motion. If the charge oscillates back and forth with a frequency of three times per second, it will emit a wave with a frequency of 3 cycles/sec, or 3 hertz.

To create light waves in the *visible* part of the electromagnetic spectrum—a wavelength range of 0.4 μm to 0.7 μm—an electric charge must accelerate at a rate high enough to generate waves of lengths around 0.5×10^{-6} meters. Now we know that for any wave,

$$v = f\lambda \tag{1-1}$$

where   v = wave speed in meters per second (m/s)
          f = frequency in cycles per second or hertz (Hz)
          λ = wavelength in meters (m)

Thus, for light in free space, where v = 3×10^8 m/s, and for the mid-visible region of light around 0.5×10^{-6} m, the frequency from Equation 1-1 would be

$$f = \frac{v}{\lambda} = \frac{3 \times 10^8 \, \text{ms}}{0.5 \times 10^{-6} \text{m}} = 6 \times 10^{14} \, \text{Hz}$$

a tremendously high value! Clearly, there are no ordinary "mechanical motions" of charged substances at our disposal that can attain such high frequencies. Only in regions inside atoms and molecules—where the electrons move very rapidly around the nucleus and where atoms vibrate and oscillate very rapidly in molecules—can such high frequencies of moving electric charges be realized. Figure 1-3a depicts the creation of a single wave by an oscillating charge, and Figure 1-3b shows how such charge made to oscillate along the arms of an antenna gives rise to EM waves moving outwardly in regions surrounding the antenna.
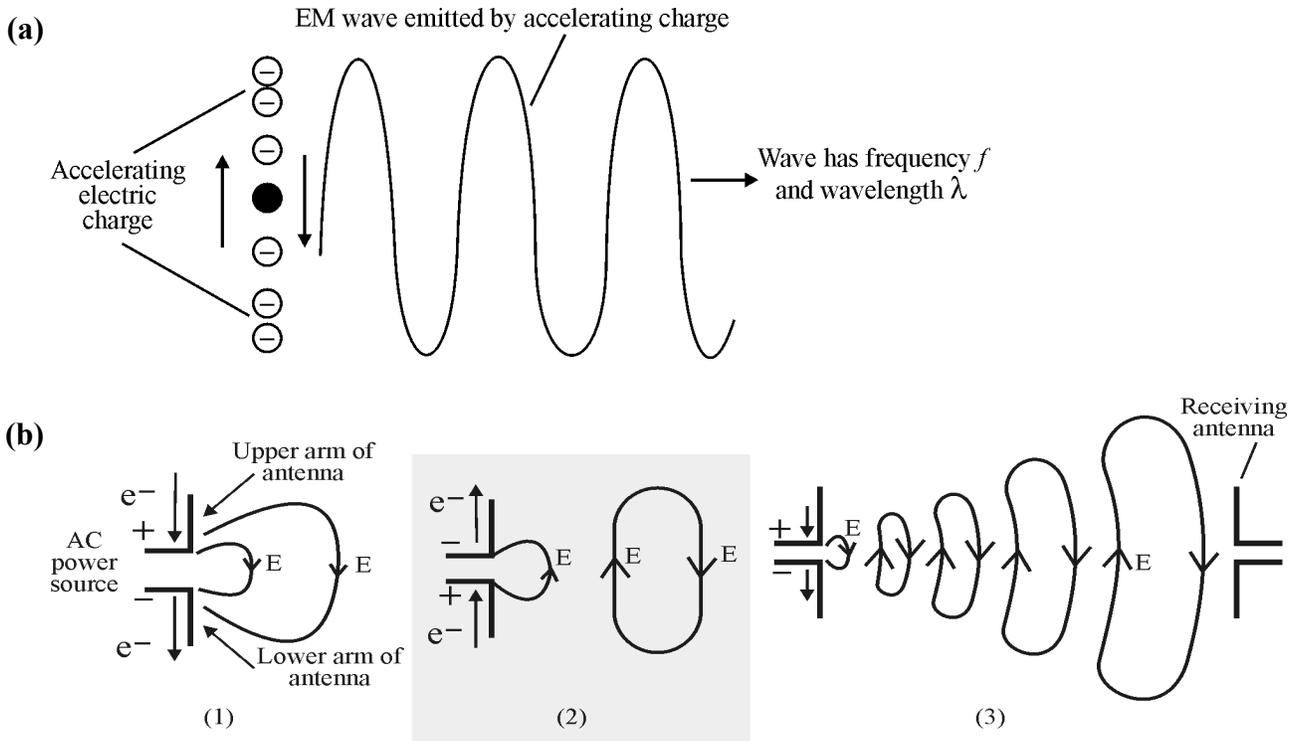
(a)

EM wave emitted by accelerating charge

Accelerating
electric
charge

Wave has frequency f
and wavelength λ

(b)

Upper arm of
antenna

e⁻

AC
power
source

E   E

e⁻

Lower arm of
antenna

e⁻

E   E   E

e⁻

Receiving
antenna

E

E

(1)   (2)   (3)

Figure 1-3 *(a) Accelerating charge e⁻ creates an EM wave of wavelength λ and frequency f as shown in (b). A wire antenna subjected to an AC voltage sends out an EM wave. In the propagating EM wave only the E-field is shown; the magnetic B-field not shown is perpendicular to the E-field. The developing EM field is shown in stages 1, 2, and 3, ultimately reaching a receiving antenna.*

The opposite terminals of an AC power supply, connected respectively to the upper and lower arms of the antenna, generate electrons e⁻ that accelerate up and down the two arms. In stage 1, the accelerating electrons are moving downward in both arms and create the outward-moving EM field with the E-field directed downward. As the applied AC voltage changes polarity, so does the direction of electron flow in the arms and so then the outward moving E-fields change directions, as shown in stage 2. As the electron flow in the arms of the antenna continues to change directions, the newly produced electric fields are created next to the antenna and the previous fields are forced further outward as shown in stage 3, where finally they may be detected by a similar receiving antenna.

The Electromagnetic Spectrum

As we have just seen, accelerating charges produce electromagnetic waves. There are many levels in the structure of matter where moving (accelerating) charges exist. Some of the more obvious are electrons in an atom, freely-moving electrons in conducting metals, vibrating atoms in molecules, and charged particles in a nucleus. Thus, two factors result in the many different types of electromagnetic waves we observe—the source of the charge motions and the accelerations inherent in the motions. The many different types of EM waves are categorized according to their origins and their frequency/wavelength values. A typical organization of the

electromagnetic spectrum is shown in Figure 1-4a with special emphases given to the location of the infrared, visible, and ultraviolet regions, Figures 1-4b, c.
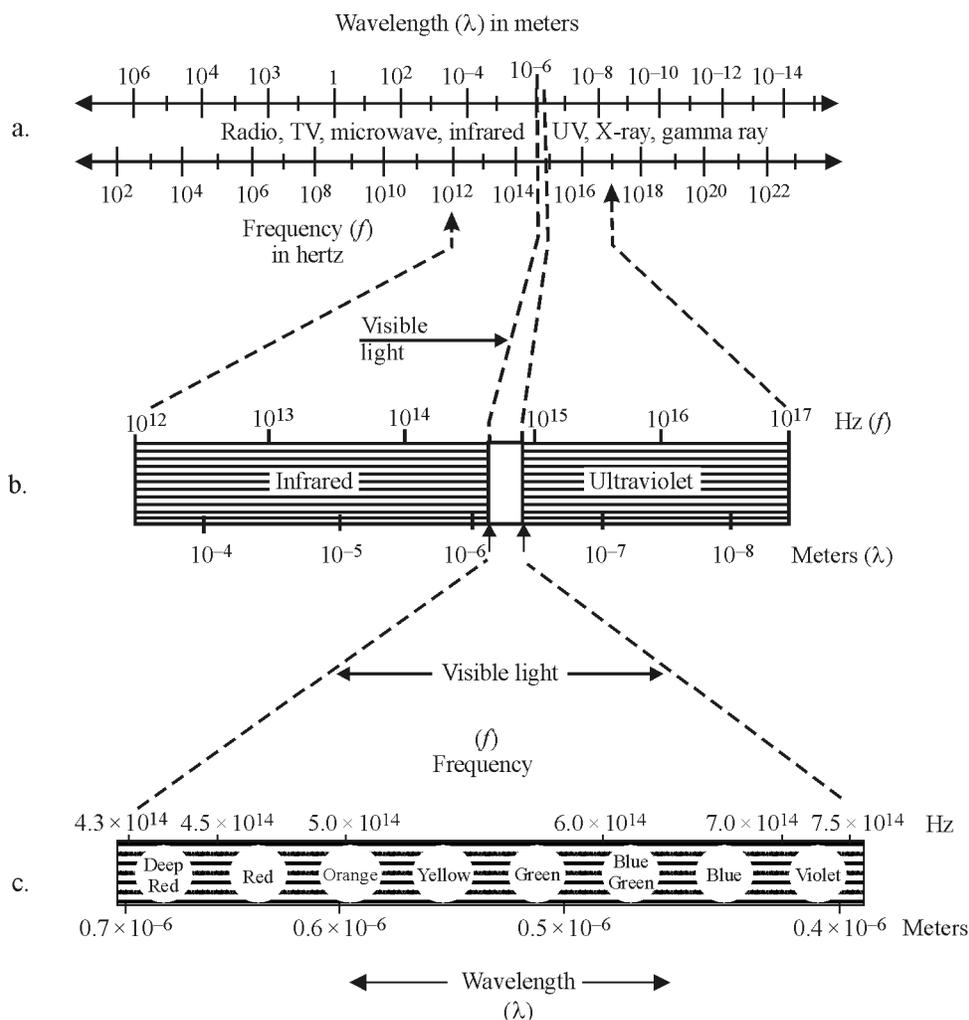

Figure 1-4 *The electromagnetic spectrum and its principal regions*

The span of wavelengths and frequencies shown in Figure 1-4a extends from 10^4 meters and 10^5 hertz in the *radio* region to 10^{-12} meters and 10^{20} hertz in the *gamma ray* region. The visible region, bracketed by the infrared and ultraviolet regions, extends from 0.7×10^{-6} m (4.3×10^{14} Hz) in the deep red down to 0.4×10^{-6} m (7.5×10^{14} Hz) in the violet.

Devices that produce or detect electromagnetic waves must be designed to operate at the frequency of the waves they emit or receive. For example, radio AM and FM transmitters and similar receivers operate at frequencies in the 10^3 to 10^7 Hz range and are designed to emit or respond to these frequencies. X-ray tubes and films are designed for use in the 10^{17} to 10^{19} Hz frequency range. Lasers generally produce laser light in the frequency and wavelength range indicated by Figure 1-4b, extending from the infrared to the ultraviolet.

Particle Properties of Electromagnetic Energy

In Figure 1-4 we have emphasized the wave properties of light. We treat light as a wave to describe its propagation from one point to another and to explain its behavior in interference, diffraction, and polarization phenomena. To describe its behavior in the process of reflection and refraction of light, or in the emission and absorption of light by atoms, we find it useful to treat light as a "particle"—a localized EM wave packet. We refer to this wave packet as a *photon*.

A photon is the smallest division of a light beam that retains the properties of the beam. The characteristics of a photon include its frequency, its wavelength, and its energy. A photon *should not* be visualized merely as a particle that has physical dimension or a specific location in space. More accurately, a photon is viewed as a "wave packet" that has a specific energy content.

The *energy* of a photon is directly proportional to the *frequency of light* in its wave packet and is given by Equation 1-2.

$$E \,=\, hf^{(1)} \tag{1-2}$$

where: E = Energy of photon in joules (J)
f = Frequency in hertz (Hz)
h = Planck's constant = 6.625×10^{-34} joule-seconds. (This famous constant was identified by the German physicist Max Planck in 1900, during his attempt to explain the spectral distribution of black-body radiation. His work introduced the concept of a "quantum of action," involving the constant h. The "quantum of action" led eventually to the idea of a photon.)

Alternatively, since $f = \dfrac{c}{\lambda}$ (Eq. 1-1), the energy E can be expressed in terms of the wavelength λ and speed c of the photon as in Equation 1-3.

$$E \,=\, \frac{hc}{\lambda} \tag{1-3}$$

where: E = Energy of photon in joules
c = Speed of light in vacuum in m/s
λ = Wavelength of light in meters
h = Planck's constant = 6.625×10^{-34} joule-seconds

Examples 1, 2, and 3 illustrate the use of these two equations.

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[1] Note that we are using the letter f to represent frequency, as we did in Equation 1-1. Be alert, however, since authors vary in their use of symbols and often the Greek letter ν (nu) is used to denote frequency.

Example 1

Calculation of the energy of a photon of given frequency

Given: The frequency of a photon of HeNe laser light is 4.74×10^{14} Hz.

Find: The energy of the photon

Solution:

$$E = hf \quad \text{(Eq. 1-2)}$$

$$E = (6.625 \times 10^{-34} \text{ J} \cdot \text{sec})(4.74 \times 10^{14}/\text{sec})$$

$$E = 3.14 \times 10^{-19} \text{ J}$$

Example 2

Calculation of the energy of a photon of a given wavelength

Given: The wavelength of a HeNe laser light is near 633 nm.

Find: The energy of the photon of this wavelength

Solution:

$$E = \frac{hc}{\lambda} \quad \text{(Eq. 1-3)}$$

$$E = \frac{(6.625 \times 10^{-34} \text{ J} \cdot \text{sec})(3 \times 10^{8} \text{ m/sec})}{6.33 \times 10^{-7} \text{ m}}$$

$$E = 3.14 \times 10^{-19} \text{ J} \quad \text{(Same as the photon energy calculated in Example 1 for a photon of frequency } 4.74 \times 10^{14} \text{ Hz)}$$

Example 3

**Calculation of wavelength and frequency
of a photon of given energy**

Given: A photon has an energy of 1.875×10^{-19} J.

Find: The frequency and the wavelength of the photon

Solution:

From Equation 1-2,

$$f = \frac{E}{h}$$

$$= \frac{(1.875 \times 10^{-19} \text{ J})}{(6.625 \times 10^{-34} \text{ J} \cdot \text{sec})}$$

$$f = 2.83 \times 10^{14}/\text{sec} = 283 \text{ THz}$$

Note: One terahertz (THz) equals (1×10^{12}) Hertz.

From Equation 1-3,

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

$$= \frac{(6.625 \times 10^{-34} \text{ J} \cdot \text{sec})(3 \times 10^{8} \text{ m/sec})}{(1.875 \times 10^{-19} \text{ J})}$$

$$\lambda = 1.06 \times 10^{-6} \text{ m} = 1.06 \text{ μm}$$

Energy Levels and Photons

The interaction of light with matter is best understood by treating light energy as if it were made up of photons—more like localized wave packets of energy rather than like the waves described by Thomas Young and Christiaan Huygens. The details of the interaction—including the absorption and emission of light—involve atoms, energy levels, and photons. Let us review briefly how Niels Bohr's model of the atom provides us with helpful insights to these interactions. All matter is made up of atoms. Recall that an atom is the smallest unit of matter that retains the characteristics of a chemical element. It consists of a positive nucleus surrounded by negative electrons arranged in distinct energy shells designated by the letters K through O, as shown in Figure 1-5. The notation K(2) indicates that the K-shell is complete when it has 2 electrons. Similarly, L(8) indicates that the L-shell is complete with 8 electrons and M(18) indicates that the M-shell is complete with 18, and so on. Different chemical elements correspond to atoms with various numbers of electrons in the available shells. For example, hydrogen has one electron in the K-shell, helium has two electrons in the K-shell, lithium has two in the K-shell and one in the L-shell, beryllium has two in the K-shell and two in the L-shell, and so on until all chemical elements are accounted for. The drawing of shells in Figure 1-5 depicts an element with 11 electrons—2 in the K-shell, 8 in the L-shell, and 1 (another electron called a *valence* electron) in the M-shell. The chemical element with 11 electrons would have to be sodium, a very active chemical element. It is "active" because its lone outer electron can absorb energy easily and combine with other elements that need an electron to fill a shell or a subshell. This figure also shows an
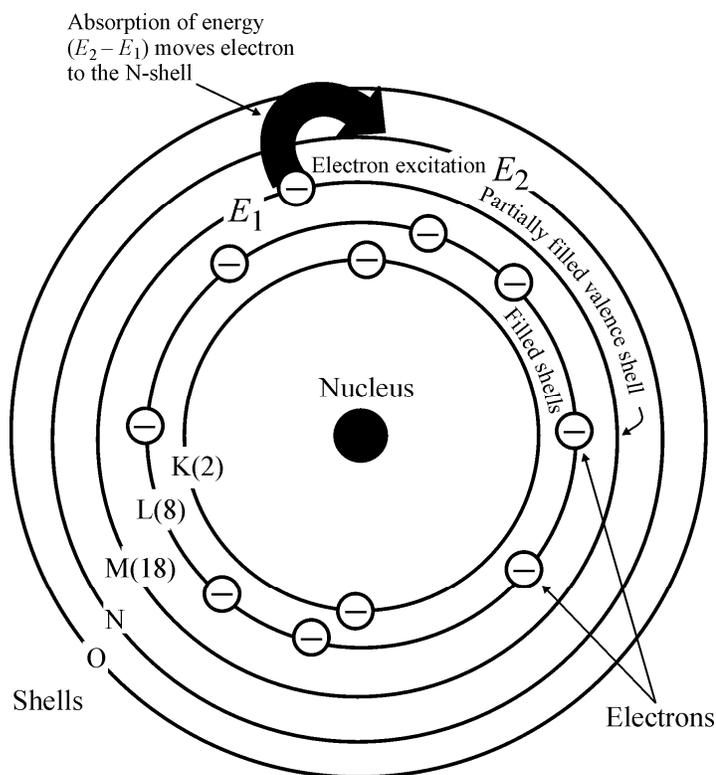

Figure 1-5 *Atomic model of energy shells according to Bohr*

absorption of energy ($E_2 - E_1$) which moves the valence electron from the M-shell to the N-shell.

We model the energy of an atom according to the different positions of its electrons. When all the electrons are in an unexcited, or ground, state, the atom is assumed to be in its lowest energy level. When the atom absorbs energy, electrons can be "excited" and moved into higher energy shells. As electrons move from one shell to another, unique amounts, or quanta, of energy are absorbed or emitted as we have noted earlier. A photon is such a quantum of energy.

An atomic energy-level diagram shows the unique electron energies available in a given atom. An energy-level diagram for hydrogen is shown in Figure 1-6a. Hydrogen has only one electron, and so it can exist in only one of the available energy levels shown at a time. The lowest level, E_1, is the *ground state*. Energy must be added to the atom for the electron to move to a higher level. Note that energy levels range from a negative value of –13.6 eV (electron volts) for the lowest energy level ($n = 1$) to a value of 0.0 eV for the very highest energy level ($n = \infty$)—when the electron breaks free from the atom. Next to the energy level diagram for hydrogen, we show (Figure 1-6b) the available energy shells and principal energy transition from higher energy levels down to the energy level marked $n = 2$ or E_2. There we see H_α for the 3-to-2 transition, H_β for the 4-to-2 transition, and H_γ for the 5-to-2 transition.
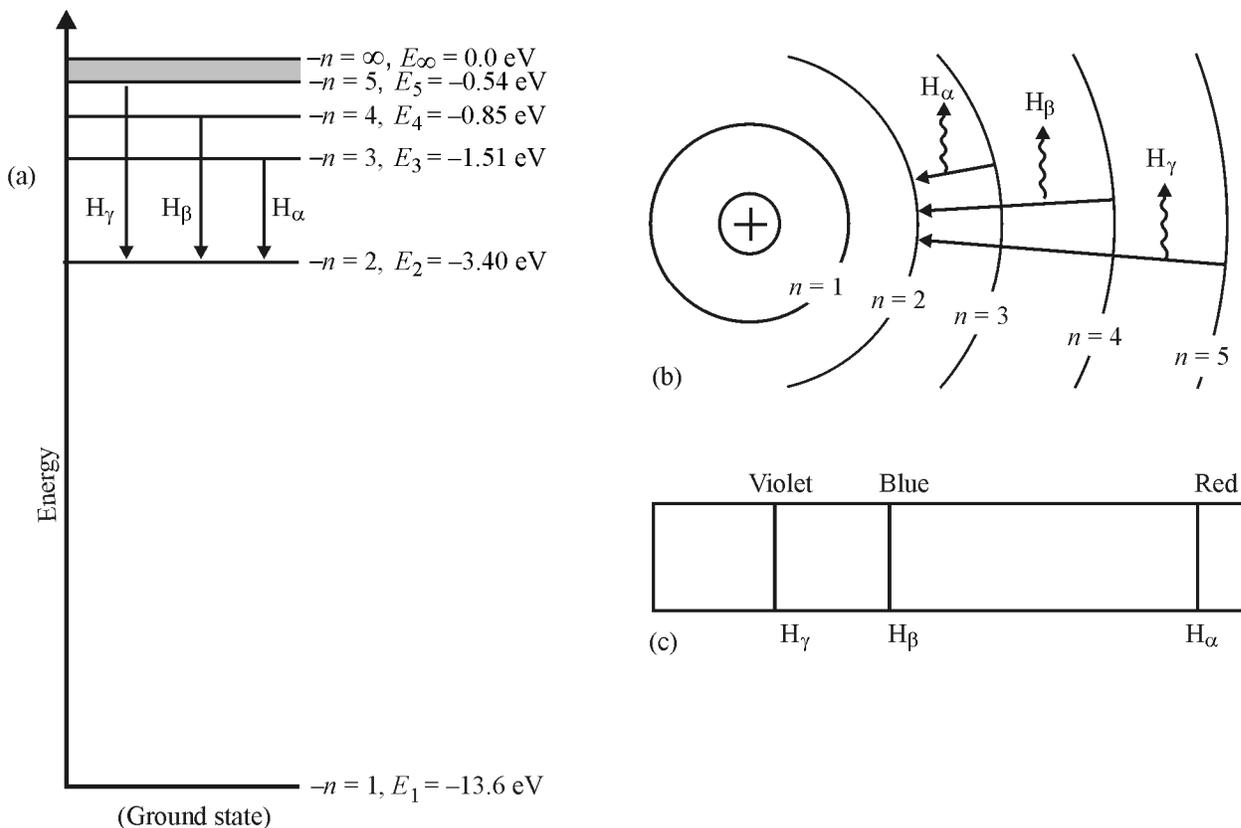

Figure 1-6 *Energy levels, shells, and line spectra for the hydrogen atom. In (a) transitions from levels n = 5, 4, 3 to n = 2 yield the energy emissions (spectral lines) H_γ, H_β, H_α respectively, as shown in (b), the energy shell view, and in (c), the line spectra view as seen on film—with colors shown in the visible EM region.*

Suppose a hydrogen atom is in an excited energy state that corresponds to the $n = 3$ level. The atom can make a transition to the $n = 2$ level by *emitting a photon*. The energy of the emitted photon equals the decrease in energy of the atom (in going from E_3 to E_2), as illustrated below.

$$E_{photon} = E_3 - E_2$$
$$= -1.51 \text{ eV} - (-3.4 \text{ eV})$$
$$= 1.89 \text{ eV}^{(2)}$$

(Be sure to pay close attention to negative signs for the energies.)

The atom can also *absorb photons*. This happens when the energy of a photon exactly matches the difference between two electron energy levels. For example, a hydrogen atom in the $n = 2$ state can absorb a photon whose energy is 1.89 eV. The electron in the atom will then move from energy level E_2 to energy level E_3.

Spectra of Light Sources

We see in Figure 1-6c the partial line spectra of a glowing hydrogen light source formed with a prism spectrometer. The sources of electromagnetic radiation are many. Usually sources are divided into two categories, *natural* and *man-made*. Examples of natural sources of radiation include the sun, observable stars, radio stars, lightning, and, in fact, any living body. Some of the man-made sources of radiation are incandescent and fluorescent lights, heaters, lasers, masers, radio and television antennas, radar, and X-ray tubes.

As we have already indicated, two types of spectra are especially important in spectroscopy: *emission* and *absorption* spectra. An emission spectrum is formed by light emitted from a source of radiation. An absorption spectrum is formed when light that passes through an optical medium is partially absorbed by the optical medium.

All materials with temperatures above absolute zero degrees Kelvin emit electromagnetic radiation. As we have noted, every atom and molecule has its own characteristic set of spectral lines. The specific wavelengths and energies produce a unique spectral trace that depends on the atomic and molecular structure of the material. The *line spectra* observed early in the scientific age led to a significant understanding of the structure of atoms and eventually to the development of modern quantum theory. This theory holds that light emitted by an atom or molecule has a discrete wavelength, corresponding to a specific energy level change within the atom or molecule, as indicated by Equation 1-3.

To observe *a line* or *band* spectrum, light is passed first through a slit, as shown earlier in Figure 1-2. The image of this slit is then refracted by a prism or diffracted by a grating and recorded on film or a spectrograph. The slit is imaged on the film at a different position and at a different intensity for each different wavelength of the light, thereby forming a "fingerprint" of that particular light.

A line spectrum generally shows sharp, well-defined images of the array of absorption or emission intensities versus wavelengths. For example, Figure 1-7a shows an absorption line spectrum for water vapor (H_2O) and carbon dioxide (CO_2) between wavenumbers of 1600 and 400 cm^{-1}. By contrast, the absorption spectrum of thioacetic acid (CH_3 CO SH) in Figure 1-7b

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[2] The unit of energy, eV, called an *electron-volt,* is equal to 1.6×10^{-19} joules. It is frequently used as a unit of energy for photons in the infrared, visible, and ultraviolet regions.

shows a band spectrum between wavenumbers of 3500 and 800 cm^{-1}, where we see clearly the enlarged widths of the absorption regions, that is, the bands.

(a)

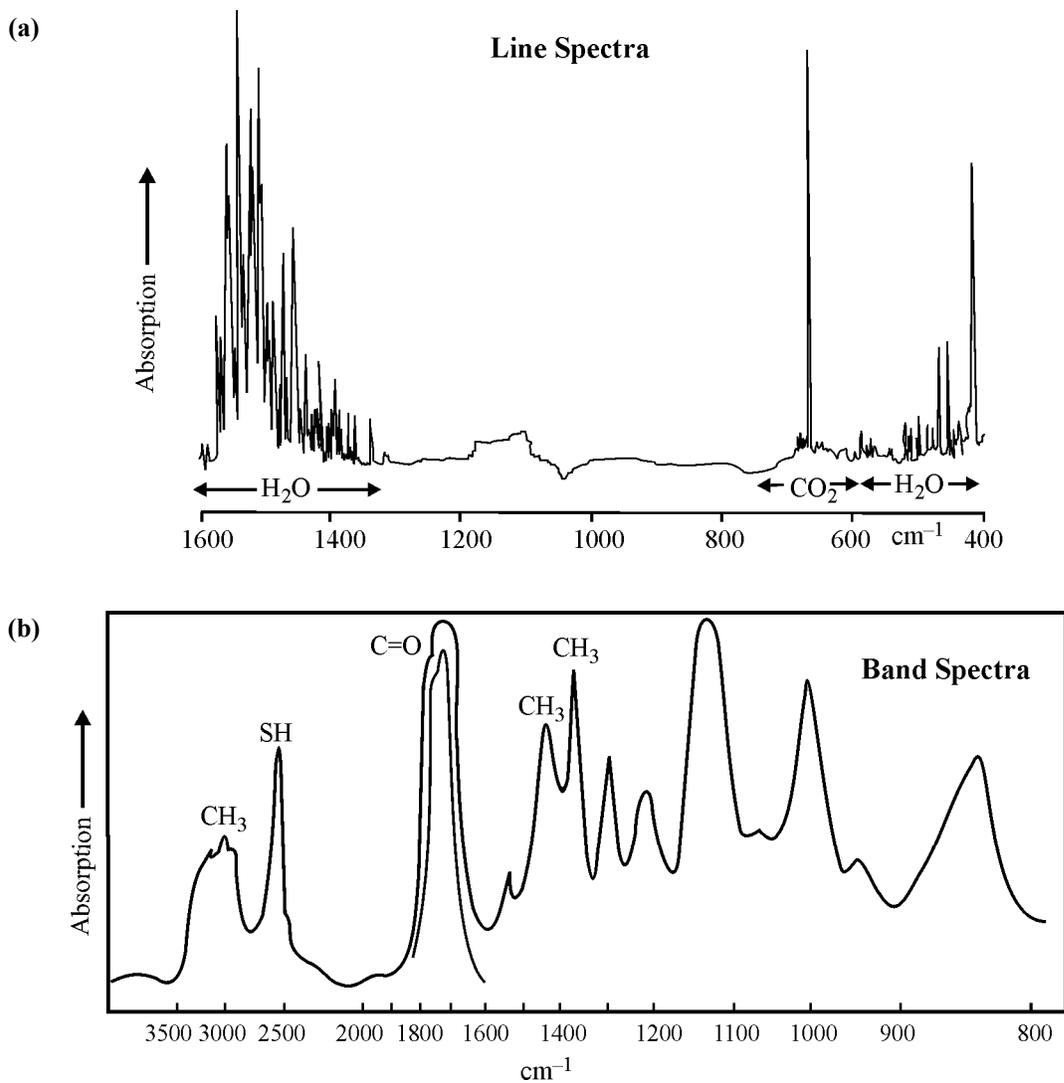**Line Spectra**

(b)

Band Spectra

Figure 1-7 *Contrasting line and band spectra: (a) absorption line spectrum for H_2O and CO_2 between 1600 and 400 cm^{-1}; (b) absorption band spectrum for thioacetic acid between 3500 and 800 cm^{-1}*

Regions of the Optical Spectrum

Regions of the electromagnetic spectrum that are of special interest in spectroscopy are identified in Table 1, in terms of both wavelengths and wavenumbers.

Table 1. EM Regions of Interest in Spectroscopy

	Wavelength Range	Wavenumber Range
Far ultraviolet	5 Å – 2,000 Å	2×10^7 cm^{-1} – 50,000 cm^{-1}
Ultraviolet	2,000 Å – 4,000 Å	50,000 cm^{-1} – 25,000 cm^{-1}
Visible	4,000 Å – 7,000 Å	25,000 cm^{-1} – 14,300 cm^{-1}
Near infrared	7,000 Å – 12,000 Å (1.2 µm)	14,300 cm^{-1} – 8,333 cm^{-1}
Infrared	1.2 µm – 40 µm	8,333 cm^{-1} – 250 cm^{-1}
Far infrared	40 µm – 1,000 µm	250 cm^{-1} – 10 cm^{-1}

The fundamental unit for describing *wavelength* is the *meter,* but it is awkwardly large for so tiny a length as that involved with light. Thus, other units of length have been introduced and used in spectroscopy. These include the *angstrom* (Å), the *micron* (µm), and the nanometer (nm). They are related as follows:

$$1 \text{ Å} = 10^{-10} \text{ meters} = 10^{-8} \text{ centimeters}$$
$$1 \text{ µm} = 10^{-6} \text{ meters}$$
$$1 \text{ nm} = 10^{-9} \text{ meters}$$

Thus, red light of wavelength $\lambda = 6500$ Å in the visible spectrum can also be described as $\lambda = 0.65$ µm or $\lambda = 650$ nm. The following conversions are often found to be useful.

Wavelength Conversion Table
1 Å = 0.0001 µm = 0.1 nm
1 µm = 10,000 Å = 1000 nm
1 nm = 10 Å = 0.001 µm

Example 4

Given: The sodium yellow doublet is very near 5890 Å.

Find: What is the corresponding wavelength in µm and nm?

Solution:

Using the conversions given in the table above,

$$5890 \text{ Å} \times 0.0001 \ \frac{\text{µm}}{\text{Å}} = 0.589 \text{ µm}$$

$$5890 \text{ Å} \times 0.1 \ \frac{\text{nm}}{\text{Å}} = 589 \text{ nm}$$

Example 5

Given: The visible region of the electromagnetic spectrum extends from 400 nm in the blue to 700 nm in the red.

Find: What is this range in angstroms and nanometers?

Solution:

Making use of the conversion table,

$$400 \text{ nm} \times \frac{10 \text{ Å}}{\text{nm}} = 4000 \text{ Å}$$

$$700 \text{ nm} \times \frac{10 \text{ Å}}{\text{nm}} = 7000 \text{ Å}$$

$$400 \text{ nm} \times 0.001 \frac{\mu\text{m}}{\text{nm}} = 0.4 \ \mu\text{m}$$

$$700 \text{ nm} \times 0.001 \frac{\mu\text{m}}{\text{nm}} = 0.7 \ \mu\text{m}$$

Thus the visible spectrum lies between 4000 and 7000 Å or between 0.4 and 0.7 μm.

Many spectroscopists prefer to use *wavenumbers* to identify spectral lines, principally because wavenumbers are proportional to the energy transitions involved. That is, the higher the wavenumber, the higher the energy of the transition giving rise to the spectral line in question.

The wavenumber ($\bar{v}$) is defined as the reciprocal of the wavelength (in cm) and is thus expressed in cm^{-1} as in Equation 1-4.

$$\bar{v}(\text{cm}^{-1}) \equiv \frac{1}{\lambda(\text{cm})} \tag{1-4}$$

To convert from wavenumber to frequency, one simply multiplies the wavenumber in cm^{-1} by the speed of light in cm/sec. Thus

$$f(\text{Hz}) = \bar{v}c = \frac{c(\text{cm/sec})}{\lambda(\text{cm})} \tag{1-5}$$

Example 6

Given: Table 1 indicates that the wavelength range for the far-infrared region is given as 40 μm to 1000 μm.

Find: (a) What is this range in angstroms and nanometers?
(b) What is this range in wavenumbers (cm^{-1})?

Solution:

(a) Making use of the conversion table,

    <u>In angstroms</u>

$$40 \ \mu m \times 10{,}000 \ \frac{\text{Å}}{\mu m} = 4 \times 10^5 \ \text{Å} = 400{,}000 \ \text{Å}$$

$$1000 \ \mu m \times \frac{10{,}000 \ \text{Å}}{\mu m} = 10 \times 10^6 \ \text{Å} = 10{,}000{,}000 \ \text{Å}$$

    <u>In nanometers</u>

$$40 \ \mu m \times 1000 \ \frac{\text{nm}}{\mu m} = 4 \times 10^4 \ \text{nm} = 40{,}000 \ \text{nm}$$

$$1000 \ \mu m \times 1000 \ \frac{\text{nm}}{\mu m} = 1 \times 10^6 \ \text{nm} = 1{,}000{,}000 \ \text{nm}$$

(b) Using Equation 1-4, we find the range in wavenumbers to be:

• at $40 \ \mu m = 40 \times 10^{-6} \ m = 40 \times 10^{-6} \times \dfrac{100 \ cm}{m} = 40 \times 10^{-4} \ cm$

$$\overline{v} = \frac{1}{\lambda (cm)} = \frac{1}{40 \times 10^{-4} \ cm} = \frac{10^4}{40} \ cm^{-1} = 250 \ cm^{-1}$$

• at $1000 \ \mu m = 10^{-3} \ m = 10^{-1} \ cm$

$$\overline{v} = \frac{1}{\lambda (cm)} = \frac{1}{10^{-1} \ cm} = 10 \ cm^{-1}$$

Another way of picturing the important regions of the optical spectrum in spectroscopy is given in Table 2. Here we see the spectral region described in terms of the energy transition that takes place within the material to produce spectral lines in that spectral region.

**Table 2. Types of Energy Transitions in Each Region
of the Electromagnetic Spectrum**

Region of Spectrum	Energy Transitions
X-rays	Breaking molecular bonds
Ultraviolet	Electronic rearrangements
Visible	Electronic rearrangements
Infrared	Vibrational motions of atoms in molecules
Microwave	Rotational motions of molecules
Radiofrequencies	Changes in nuclear spins Changes in electronic spins

Emission and Absorption Spectra

As we have already mentioned, emission spectra for a substance occurs when the substance receives energy from an external source, absorbs the energy to raise its atoms to higher energy levels, then emits characteristic energy amounts as the excited atoms return to their previous energy levels.

Absorption spectra are produced when white light, for example, is directed onto a particular substance and certain wavelengths in the spectrum of the white light are absorbed via internal energy excitations. This absorption leaves a dark line in the spectrum of the transmitted white light, at a wavelength characteristic of the energy levels in the substance which absorbed that part of the white light.

Emission spectra

Figure 1-8 shows an electrical discharge passing through a gas contained in a tube. This causes the gas to glow and emit light which is then analyzed by a prism spectrometer. Typical emission spectra for single-atom gases such as hydrogen, helium, sodium, and neon are shown in Figure 1-9. Figure 1-10 shows a trace of line intensity versus wavelength for helium. The intensity (height) of each line is a measure of how likely helium will undergo a transition at that particular wavelength.
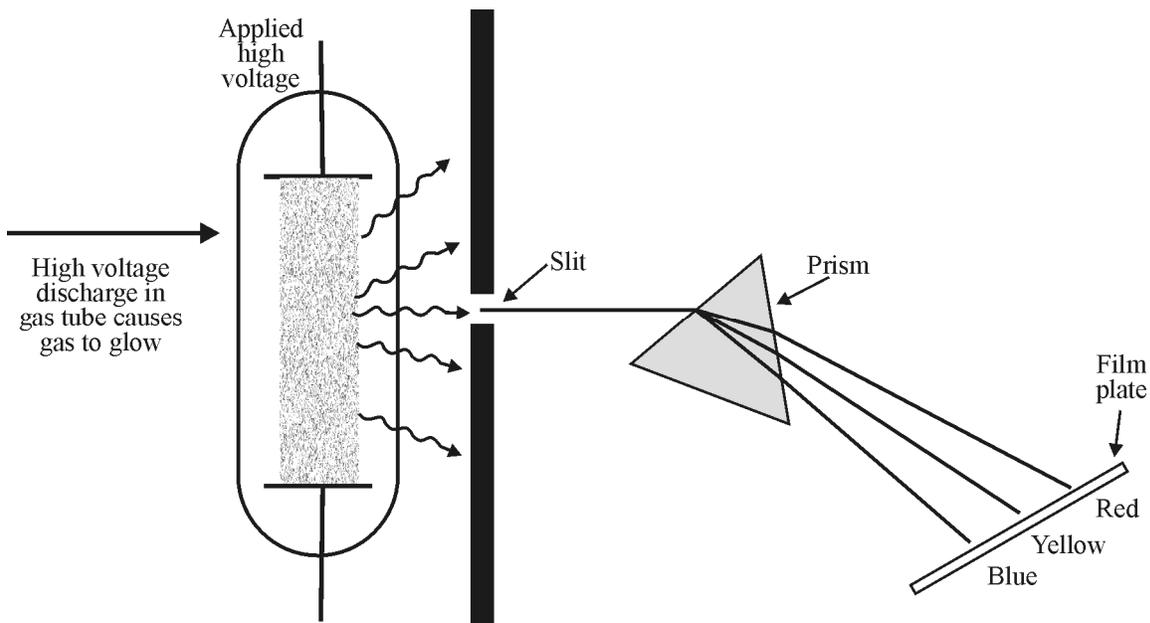

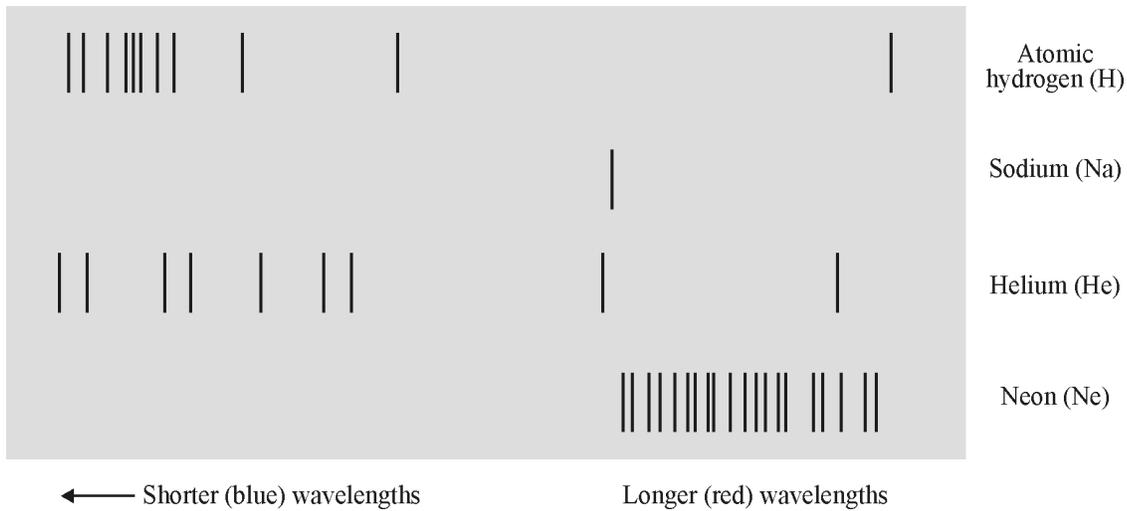**Figure 1-8** *Setup for producing line spectra of glowing gases*

Figure 1-9 *Emission line spectra for glowing gases of H, Na, He, and Ne*
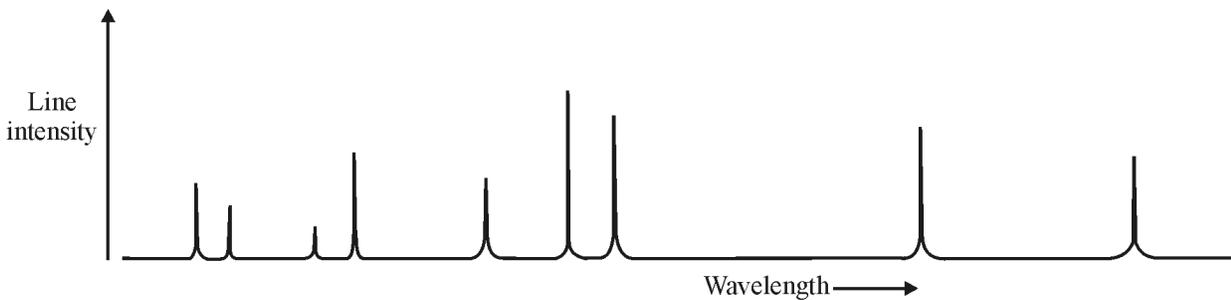

Figure 1-10 *Intensity versus wavelength for emission spectrum of neon*

Each of the lines in the neon emission spectrum of Figure 1-10 is produced by a single transition from one atomic energy level to another. The lines of higher intensity represent transitions occurring more often from energy states that have shorter atomic lifetimes. In any event, the spectrum of excited neon gas always gives rise to the unique set of spectral lines shown for neon in Figure 1-9. This particular set of spectral lines is the identifying "fingerprint" of neon.

Absorption spectra

As we have mentioned, absorption spectra give rise to dark lines showing up on a continuous or white light spectral background. For example, the complex absorption spectra of the sun (Figure 1-11), made by the Hale Observatory on Palomar Mountain, shows a multiplicity of dark lines, traceable to many different elements. Of the 92 elements that occur naturally on earth, over 70 have been identified in the solar spectrum. Thus one observes the presence of the elements calcium (Ca), iron (Fe), hydrogen (H), magnesium (Mg), sodium (Na), and argon (A) in the solar spectrum of Figure 1-11, over the visible region from 3900 to 6900 angstroms.

How are these dark lines formed? The continuous white-light radiation from the glowing sun passes through its atmosphere, which contains many gaseous elements like those shown in Figure 1-11. The characteristic energy levels belonging to each element provide appropriate energy-level differences to absorb (remove) particular wavelengths present in the continuous

white-light spectrum of the sun's glow. Figure 1-12 shows how the presence of hydrogen gas in the sun's atmosphere absorbs the wavelengths for H_α, H_β, and H_γ, thereby producing the dark lines for H_α, H_β, and H_γ in the solar spectrum. Similar reasoning accounts for the dark line spectra for all the elements present in the sun's atmosphere.
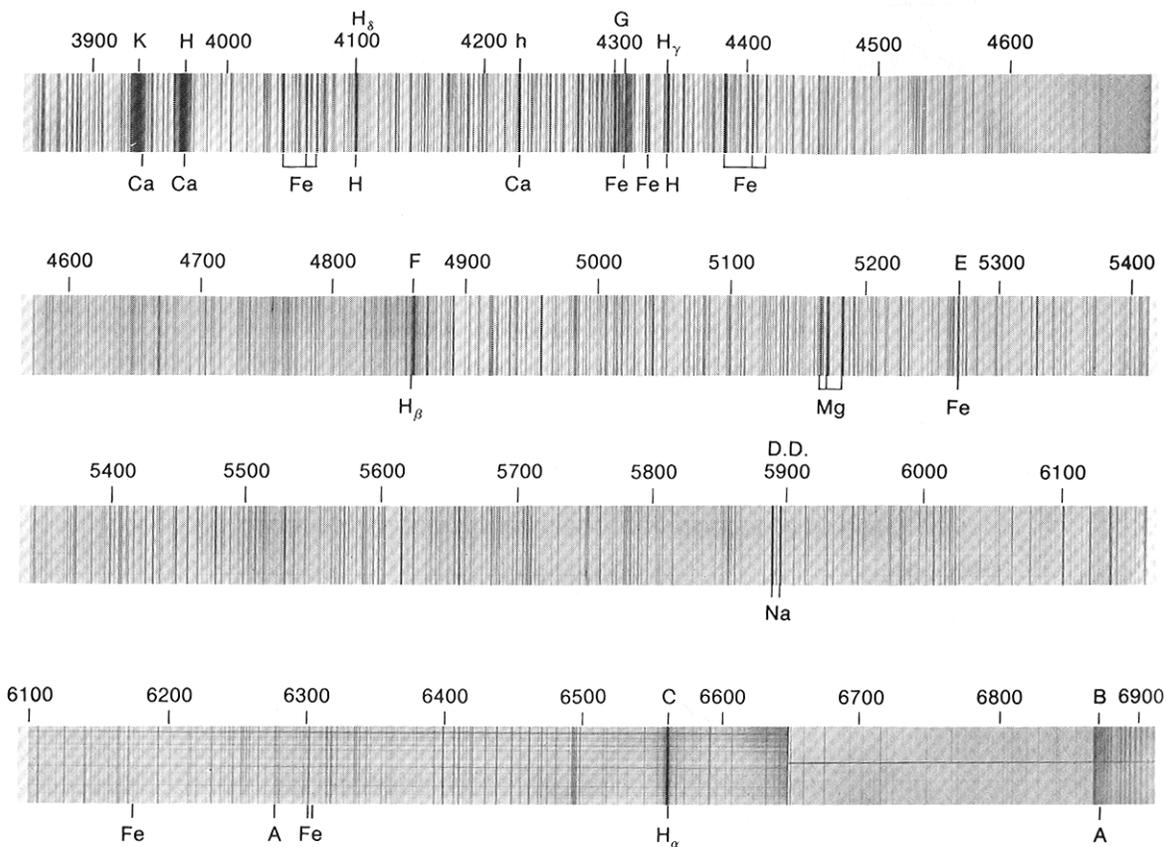

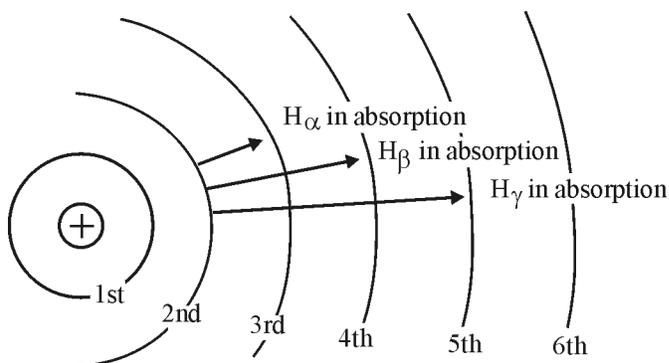**Figure 1-11** *Solar spectrum of the sun in the visible region (Hale Observatory)*

Figure 1-12 *The dark lines for H_α, H_β, and H_γ in the solar spectrum*

Fluorescence and Phosphorescence

Special materials are used to coat the interior walls of fluorescent light tubes and the dial faces of watches. These materials, when bombarded by photons of a given energy, cause the materials to glow and emit light in the visible regions. This emission is referred to as *fluorescence* and *phosphorescence,* each of which is important in spectroscopy.

Materials fluoresce when photons of ultraviolet light first excite the atoms in the material to a higher energy level. Following this initial excitation, the atoms return via smaller energy jumps to their original energy level. The smaller jumps give off photons of lower energy with wavelengths in the visible region of the spectrum. We observe such fluorescence when special paints and certain rocks are illuminated with UV light.

Objects such as the luminous dials on wrist watches glow in the dark and are said to be phosphorescent. Closely akin to fluorescence, phosphorescence differs only in the time the excited atoms in the material remain in the upper energy level before returning to their original energy level. In general, fluorescent materials cease fluorescing as soon as the incident radiation is removed, in times as short as 10 nanoseconds. By contrast, excited atoms in phosphorescent materials remain in upper energy levels for seconds or longer. In such *metastable* excited energy states, while some downward transitions will occur rather soon after excitation, others may not occur for many minutes, thereby enabling the phosphorescent material to continue glowing, long after the excitation light source has been removed.

Spectroscopic Instruments

The characteristics and operation of the instruments used in spectroscopy will be treated in detail in the module titled *Instruments in Spectroscopy* (Module SP-2). Here we content ourselves with a brief overview.

The three main instruments used in spectroscopy are a prism, a diffraction grating, and an interferometer. In physical size, they may vary in length from a foot or so on up to forty feet, depending on the precision required or the intended application. Each one has a particular use, which may include simply observing the spectrum, photographing the spectrum, or focusing in on a particular detail of the spectrum.

Prism spectrometer

Typically, prisms in spectrometers that are used to analyze the visible light region are made of glass. Rock salt, fluorite, and quartz are used in the optical components for viewing the ultraviolet regions of the spectrum. In the near-infrared region, lenses and prisms in the spectrometer are made generally of rock salt, fluorite, lithium fluorite, and potassium bromide. Prisms are not effective in the far-infrared or far-ultraviolet ends of the spectrum.

Diffraction grating

The diffraction grating, a device more versatile than a prism, is made usually of a mirror or transparent plate of glass on which are etched up to 180,000 closely spaced parallel lines. With a diffraction grating as the principal wavelength dispersing element, all parts of the spectrum—from the far-infrared to the far-ultraviolet—can be displayed and analyzed. As will be seen in Module SP-2, the many lines in a diffraction grating make the dispersion of light more accurate than that obtained with a prism.

Interferometer spectrometer

A spectrometer that uses an interferometer in the place of a prism or diffraction grating makes use of the principles of *interference* of light. An interferometer spectrometer provides the ultimate in wavelength resolution and precision of measurement of the spectrum provided.

Applications of Spectroscopy

Spectroscopy is a relatively ancient science, tracing its origins back to the 1600s. Its usefulness in an ever-increasing range of applications has continued to grow. Today, modern spectroscopy contributes to a fundamental understanding of the interaction of electromagnetic energy with matter in the following important fields:

Astronomy	Food packaging
Analytical organic chemistry	Toxicology
Remote sensing	Telecommunication
Agriculture and crop analysis	Acoustics and speech analysis
Terrestrial geography	National defense
Forensic science	

More will be said about these areas of spectroscopic applications in Module SP-3.

LABORATORY

In this laboratory you will perform several simple experiments involving light spectra. You will complete the following.

- Examine the *continuous* emission spectrum from an incandescent lamp with the eye and a bare grating, and with the eye and a handheld prism spectroscope.

- Examine emission spectra from light sources that provide examples of *line* and *band* spectra, and describe the major differences between the two. Do so with both a grating and a handheld spectroscope.

- Measure the spectral emission from an incandescent light source at several specific wavelengths with the help of a set of appropriate light filters and a suitable light detector.

- Plot the relative emitted power versus wavelength for the spectral emission from an incandescent lamp.

Equipment List

The following equipment is needed to complete this laboratory.

Incandescent lamp, single, long filament, clear glass bulb with socket

2 spectral glow lamps, with power supply, for line and band spectra (neon for line and carbon dioxide for band suggested)

Diffraction grating, transmission-type, plastic replica, 200–400 lines/mm

Handheld spectroscope (such as Edmond Optics T42-586)

Light meter with photometric detector (such as Edmond Optics #56-810 and #56-813 or United Detector Technology model 40A)

1 set of 7 broadband interference filters, of equal transmittance, 400–700 nanometers at 50-nanometer intervals (Optical Industries S.N. 03F1B015 or Edmond Optics Broadband Filter Kit T55-223/247)

Filter/holder support

Improvised light shield (large fruit-juice can, with 0.5-cm hole in side, at height of center of source lamp filament)

Some Helpful Comments

- **Practice safety!**
  Treat electrical power sources with proper caution and respect. When you make connections where high voltage is involved, use only one hand where possible. Don't look directly at ultraviolet sources, or permit excess exposure to the eyes. Use safety goggles where applicable.

- **Plan ahead.**
  When you set up the equipment, plan your layout for convenience and accuracy. Try to get the most accurate information your measuring devices can give. Work carefully. Record and identify all important information.

- **Control background lights.**
  Depending on the brightness of the light sources used and the distance from detector to source, room lighting may cause erroneously high readings of irradiance. You can check to see if this is a factor or not by moving the optical power meter over the measurement area, with the source turned off, while you watch the meter. If the meter indicator doesn't move off zero, you can ignore room light. If you see any deflection of the indicator, room light must be decreased or modified to eliminate it as a source of error.

Procedures

A. Examining a continuous spectrum

1. Set up the incandescent lamp and appropriate shield as shown in Figure L-1.
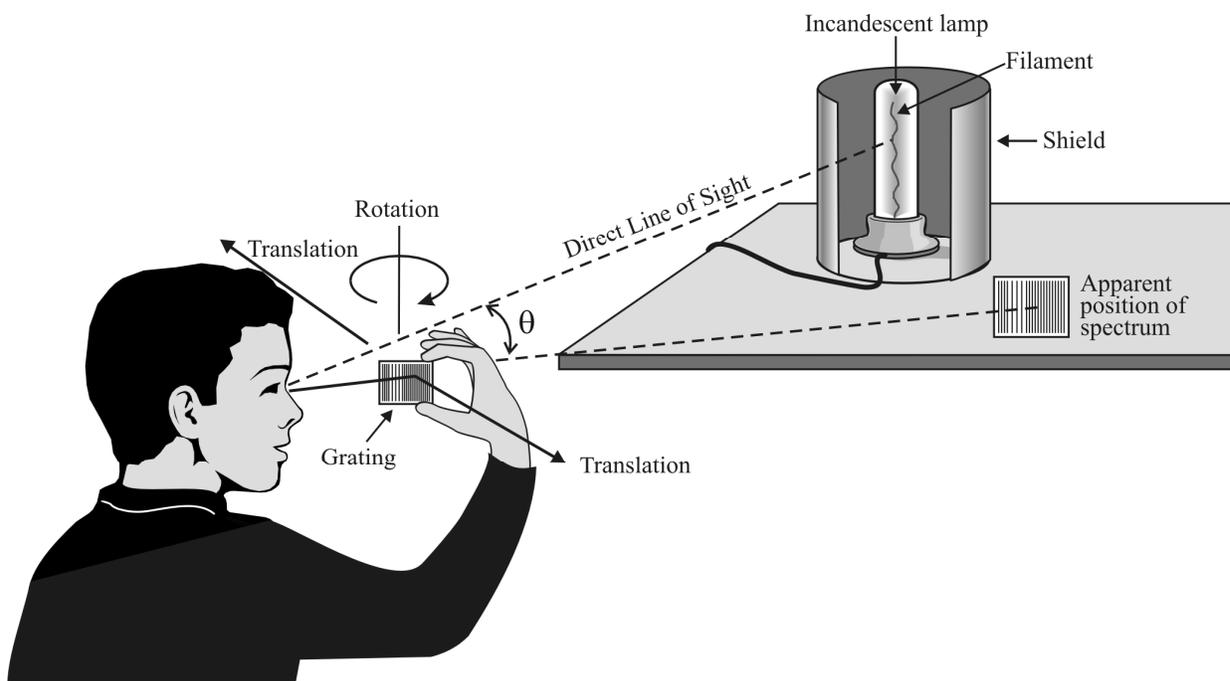

Figure L-1 *Experimental arrangement for observing a continuous spectrum*

2. Turn on the lamp and let it come to temperature equilibrium. Position the shield to reduce stray light. Hold a diffraction grating as shown in Figure L-1 with rulings parallel to the lamp filament. Try to hold the grating with its plane perpendicular to the line of sight.

3. Holding the grating at the same height, *translate* it a **short** distance to the right and left of the line of sight. At the correct position, you should see displayed a *continuous spectrum*. A slight *rotation* about the vertical axes of the grating one way or the other usually will peak the geometrical arrangement and brighten the spectrum in an optimum manner.

4. *Notes on grating details and location of spectra*

Depending on the number of lines (grooves) per millimeter of the grating you are using, the angular displacement θ of the "rainbow" spectrum you will see, measured from the direct line of sight (see Figure L-1), will vary. Below is a table that provides you with the displacement angle θ_{400} for the blue end (400-nanometer wavelength) and the displacement angle θ_{700} for the red end (700-nanometer wavelength) of the continuous white light spectrum. The table also provides the angular separation $\Delta\theta$ between the blue and red ends of the spectrum. This data is given for the gratings with rulings of 200, 300, and 400 lines/millimeter. (All data is for the *first order* grating diffraction.)

Grating Ruling	θ_{400}	θ_{700}	$\Delta\theta$
200 lines/mm	4.6°	8.0°	3.4°
300 lines/mm	6.9°	12.6°	5.7°
400 lines/mm	9.2°	16.3°	7.1°

As you can see, the more rulings per millimeter on the grating, the larger will be the angular displacement for the two ends of the observed spectrum.

B. Observing Spectra with a Handheld Spectroscope

The handheld spectroscope depicted below in Figure L-2 employs an Amici prism to separate light into its component wavelengths, and provides one with an easy-to-use spectroscopic instrument. It makes use of a precision lens and a 3-element Amici prism housed in a stainless steel tube enabling the user to focus on the target spectral image for increased clarity, providing a resolution of 2 nanometers (20 Å) over the visible wavelength range of 400 nm to 700 nm. One can use the adjustable entrance slit to regulate resolution and contrast. As the slit is narrowed, resolution increases but *throughput* and, hence, *contrast* decreases.
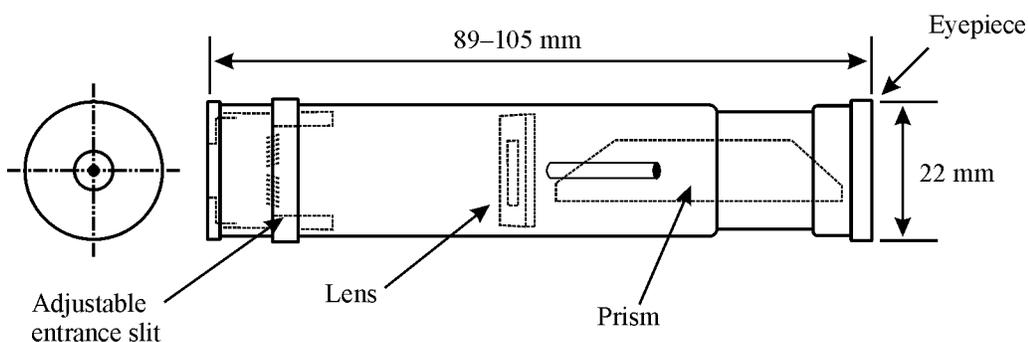

Figure L-2 *A handheld spectroscope*

1. Use the spectroscope to view the white light spectrum set up in Figure L-1 of Part A, replacing the grating with the handheld spectroscope.

2. Similarly, use the spectroscope to view the line and band spectra set up in Part C that follows.

3. Describe the difference in spectra produced with the grating and by the spectroscope, which uses a prism to separate the colors. Which gives the most angular separation between different colors? Which is most convenient to use?

C. Examining line and band spectra

1. Set up the power supply and a line spectral lamp, such as for neon. **Be sure the power is off while mounting the lamp in its holder!**

2. Turn on the lamp and position the shield as shown previously in Figure L-1. (If the lamp doesn't ignite after a short period of time, contact your instructor. Do not attempt any adjustment with the power on!)

3. Hold the diffraction grating as shown previously in Figure L-1, and locate the line spectrum characteristic of the line source. Rotate the grating to "peak" the line spectrum. Bring the grating to within a few inches of your eye to ensure that the entire line spectrum will be visible.

4. Examine the spectrum carefully and record a qualitative description. Include information on the spectral line spacing, spectral line width, and color (wavelength).

5. Repeat the step above for an appropriate spectral source, such as carbon dioxide, that produces a *band spectrum*.

6. Describe the major differences between the line and band spectra.

D. Measuring spectral emission

1. Arrange an optometer (with detectors), incandescent lamp, and filter holder as shown in Figure L-3. (Instead of the optometer, you may use a lightmeter with an appropriate detector, such as the Edmond Optics Light Meter #56-810/813. Follow the instructions provided with the Edmond Optics light meter.)
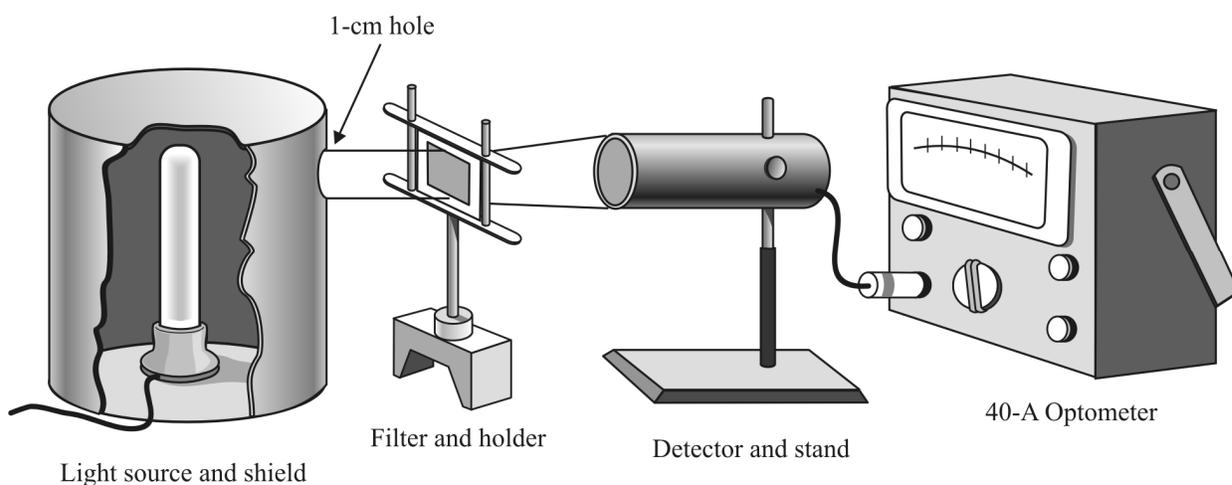

1-cm hole

Filter and holder

Detector and stand

40-A Optometer

Light source and shield

Figure L-3 *Measuring spectral emission*

2. Turn the 40A optometer function switch to the microwatt (μW) position. Turn the power scale knob to 10,000 and zero the meter.

3. Turn on the source lamp. Align it with the 1-cm hole in the shield, filter, and detector so that the brightest portion of light from the source passes through the central area of the filter and on to the sensitive surface of the detector. Reduce any unwanted stray light by shielding the detector and/or by reducing the ambient room light.

4. With the 700-nanometer filter in place, increase the meter sensitivity until the meter shows a fairly large reading. Either use the "C" function to obtain a full-scale meter reading, or reduce the separation of the source, filter, and detector to get a reading well over half scale.

5. Read and record the power on the data sheet given below.

6. Remove the 700-nm filter. Replace it with a 650-nm filter.

7. Repeat Steps 5 and 6 for the 650-nm filter.

8. Then repeat the procedure above for the five remaining filters in the set, ending with the 400-nm filter.

Suggested Data Table

Filter	Measured Power	Normalized or relative power*
700 nm		
650		
600		
550		
500		
450		
400		

*Normalized or relative power $= \dfrac{\text{Measured power}}{\text{Power of highest reading}}$

9. Based on the data in the Data Table, plot a graph of relative power at the seven filter settings versus the filter wavelength in nanometers.

10. To plot relative power, assign the highest power reading a value of 1.0 and plot it as 1.0 on the ordinate. Then divide each of the other six lower readings by the true power reading of the highest value. Plot the results on the ordinate versus the appropriate wavelength along the abscissa.

11. Connect the plotted points with a smooth curve. Your plot of the seven relative power points should appear similar to the one shown in Figure L-4.
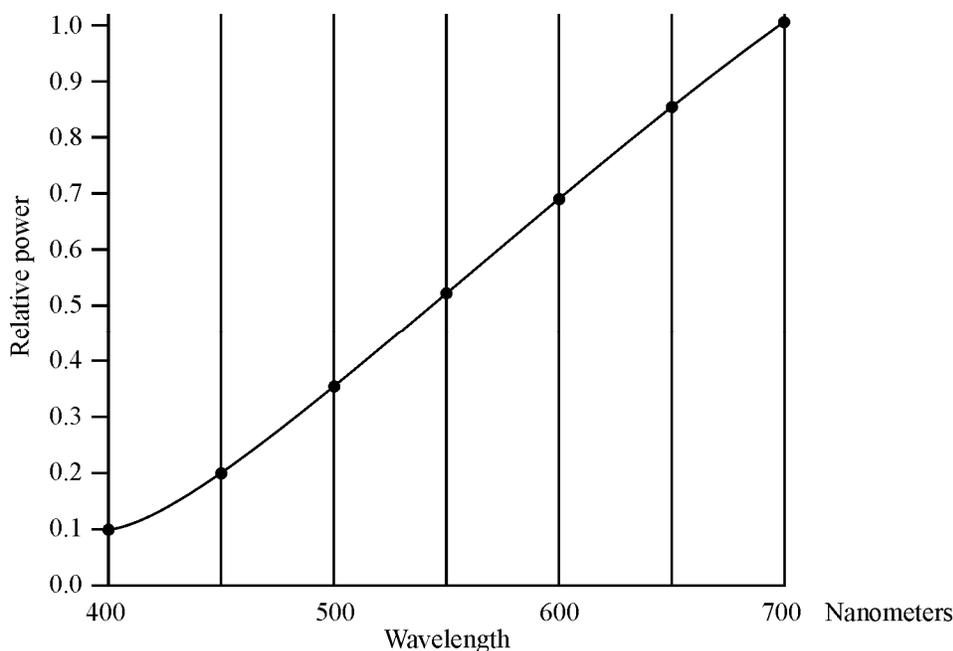
**Figure L-4** *A typical curve of relative power versus wavelength*

PROBLEM EXERCISES

1. The visible region of light extends from a wavelength of 0.4 μm to 0.7 μm. Assume a light speed $v = c = 3 \times 10^8$ m/s in free space.

    (a) What is the corresponding frequency region in hertz for the visible region?

    (b) For photons with $\lambda = 0.7$ μm and 0.4 μm, what is their energy in joules?

2. For Problem 1, determine the corresponding wavenumber $\bar{v}$ in cm^{-1} for the two photons, and the corresponding energy E, making use of the equation $E = hc\bar{v}$. How do these energies compare with those found in part (b) of Problem 1?

3. Figure 1-4 indicates that ultraviolet light has a mid-frequency around 10^{16} Hz.

    (a) Calculate the corresponding wavelength in meters, angstroms, nanometers, and micrometers. Use $v = c = 3 \times 10^8$ m/s.

    (b) What is the wavenumber (in cm^{-1}) and energy (in eV and joules) for such an ultraviolet photon?

4. In the emission spectrum of hydrogen, the H$_\gamma$ line is formed when the hydrogen atom moves from an energy state $n = 5$ of energy –0.54 eV to an energy state $n = 2$ of –3.40 eV.

    (a) What is the wavelength of this line in meters? In μm, angstroms, and nm?

    (b) What is the wavenumber $\bar{v}$ of the H$_\gamma$ line in cm^{-1}?

    (c) What is the frequency of this line in hertz?

Basics of Spectroscopy

5. Table 1 indicates that the wavenumber for the far-ultraviolet region of the electromagnetic spectrum extends from 2×10^{-7} cm^{-1} to 5×10^{4} cm^{-1}.

    (a) What is the corresponding frequency range in hertz?

    (b) What is this corresponding wavelength range in μm and nm?

    (c) Use the equations $E = hf$ and $E = hc\overline{v}$ to calculate the photon energies for the endpoints of this range, in both units of electron volts (eV) and joules.

6. Distinguish between line spectra and band spectra with general traces of spectral intensity versus wavelength or wavenumber.

7. How does absorption spectroscopy differ from emission spectroscopy?

8. The line spectra of three pure gases are shown at the right. The gases are mercury (Hg), helium (He), and cadmium (Cd).

Hg

He

Cd
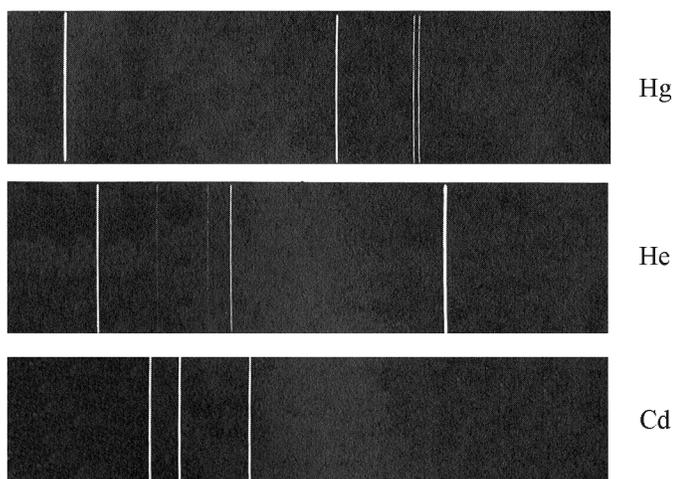
Each of the three spectra reproduced here represents mixtures of two of the three gases—Hg, He, and Cd. Determine by a comparison of lines which elements are involved in spectra A, B, and C.

Spectrum A

Spectrum B

Spectrum C
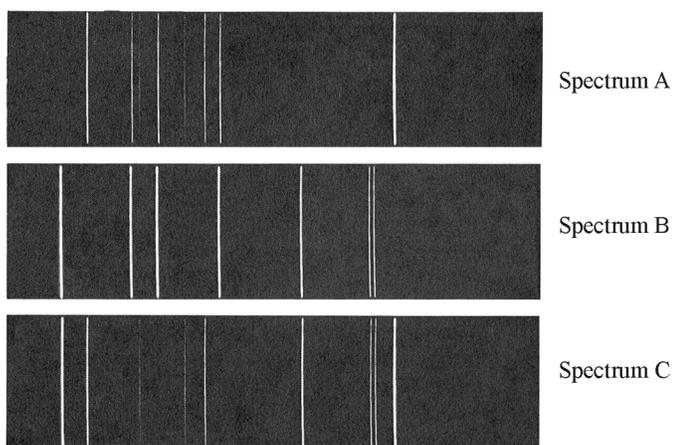
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