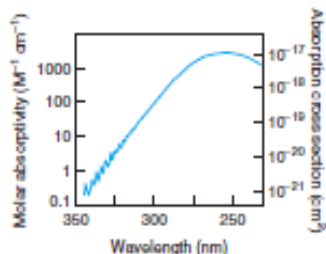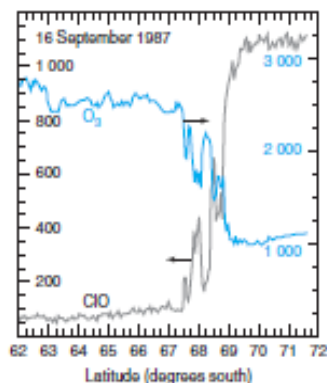# 17 | Fundamentals of Spectrophotometry

THE OZONE HOLE[1]

Spectrum of ozone, showing maximum absorption of ultraviolet radiation at a wavelength near 260 nm. At this wavelength, a layer of ozone is more opaque than a layer of gold of the same mass. [Adapted from R. P. Wayne, *Chemistry of Atmospheres* (Oxford: Clarendon Press, 1991).]

Spectroscopically measured concentrations of O_3 and ClO (measured in ppb = nL/L) in the stratosphere near the South Pole in 1987. The loss of O_3 at latitudes where ClO has a high concentration is consistent with the known chemistry of catalytic destruction of O_3 by halogen radicals. [From J. G. Anderson, W. H. Brune, and M. H. Proffitt, *J. Geophys. Res.* 1989, *94D*, 11465.]
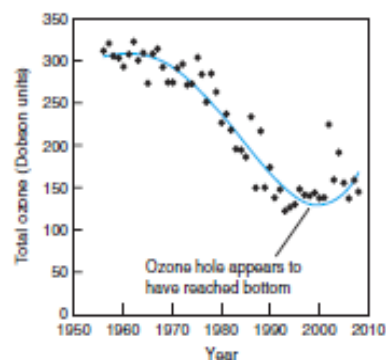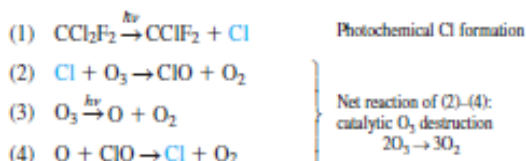

Mean atmospheric O_3 at Halley in Antarctica in October. *Dobson units* are defined in Problem 17-14. [From J. D. Shanklin, British Antarctic Survey, http://www.antarctica.ac.uk/met/jds/ozone/.]

Ozone, formed at altitudes of 20 to 40 km by the action of solar ultraviolet radiation ($h\nu$) on O_2, absorbs ultraviolet radiation that causes sunburn and skin cancer.

$$O_2 \xrightarrow{h\nu} 2O \qquad\qquad O + O_2 \rightarrow \underset{\text{Ozone}}{O_3}$$

In 1985, the British Antarctic Survey reported that the total ozone in the Antarctic stratosphere had decreased by 50% in early spring, relative to levels observed in the preceding 20 years. Ground, airborne, and satellite observations have since shown that this "ozone hole" occurs only in early spring (Figure 1-1) and continued to deepen until the year 2000.

An explanation begins with chlorofluorocarbons such as Freon-12 (CCl_2F_2), formerly used in refrigerators and air conditioners. These long-lived compounds, which are not found in nature,[2] diffuse to the stratosphere, where they catalyze ozone decomposition.

(1) $\quad CCl_2F_2 \xrightarrow{h\nu} CClF_2 + Cl \qquad$ Photochemical Cl formation

(2) $\quad Cl + O_3 \rightarrow ClO + O_2$

(3) $\quad O_3 \xrightarrow{h\nu} O + O_2$

(4) $\quad O + ClO \rightarrow Cl + O_2$

Net reaction of (2)–(4): catalytic O_3 destruction $2O_3 \rightarrow 3O_2$

Cl produced in step 4 reacts again in step 2, so a single Cl atom can destroy $>10^5$ molecules of O_3. The chain is terminated when Cl or ClO reacts with hydrocarbons or NO_2 to form HCl or $ClONO_2$.

Stratospheric clouds[3] formed during the Antarctic winter catalyze the reaction of HCl with $ClONO_2$ to form Cl_2, which is split by sunlight into Cl atoms to initiate O_3 destruction:

$$HCl + ClONO_2 \xrightarrow[\text{polar clouds}]{\text{surface of}} Cl_2 + HNO_3 \qquad\qquad Cl_2 \xrightarrow{h\nu} 2Cl$$
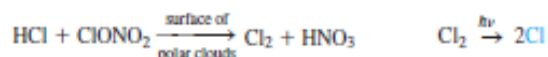
Polar stratospheric clouds require winter cold to form. Only when the sun is rising in September and October, and clouds are still present, are conditions right for O_3 destruction.

To protect life from ultraviolet radiation, international treaties now ban or phase out chlorofluorocarbons, and there is an effort to find safe substitutes.

Spectrophotometry is any technique that uses light to measure chemical concentrations. A procedure based on absorption of visible light is called *colorimetry*. The most-cited article in the journal *Analytical Chemistry* from 1945 to 1999 describes a colorimetric method by which biochemists measure sugars.[4] Chapter 17 is intended to give a stand-alone overview of spectrophotometry sufficient for introductory purposes. Chapter 18 goes further into applications, and Chapter 19 discusses instrumentation.

Following the discovery of the Antarctic ozone "hole" in 1985, atmospheric chemist Susan Solomon led the first expedition in 1986 specifically intended to make chemical measurements of the Antarctic atmosphere by using balloons and ground-based spectroscopy. The expedition discovered that ozone depletion occurred after polar sunrise and that the concentration of chemically active chlorine in the stratosphere was ~100 times greater than had been predicted from gas-phase chemistry. Solomon's group identified chlorine as the culprit in ozone destruction and polar stratospheric clouds as the catalytic surface for the release of so much chlorine.

17-1 Properties of Light

It is convenient to describe light in terms of both particles and waves. Light waves consist of perpendicular, oscillating electric and magnetic fields. For simplicity, a *plane-polarized* wave is shown in Figure 17-1. In this figure, the electric field is in the xy plane, and the magnetic field is in the xz plane. **Wavelength, λ,** is the crest-to-crest distance between waves. **Frequency, ν,** is the number of complete oscillations that the wave makes each second. The unit of frequency is 1/second. One oscillation per second is called one **hertz** (Hz). A frequency of 10^6 s^{-1} is therefore said to be 10^6 Hz, or 1 *megahertz* (MHz).

The relation between frequency and wavelength is

Relation between frequency and wavelength:　　$\nu\lambda = c$ 　　　　(17-1)

where c is the speed of light (2.998×10^8 m/s in vacuum). In a medium other than vacuum, the speed of light is c/n, where n is the **refractive index** of that medium. For visible wavelengths in most substances, $n > 1$, so visible light travels more slowly through matter than through vacuum. When light moves between media with different refractive indexes, the frequency remains constant but the wavelength changes.

With regard to energy, it is more convenient to think of light as particles called **photons.** Each photon carries the energy, E, which is given by

Relation between energy and frequency:　　$E = h\nu$ 　　　　(17-2)

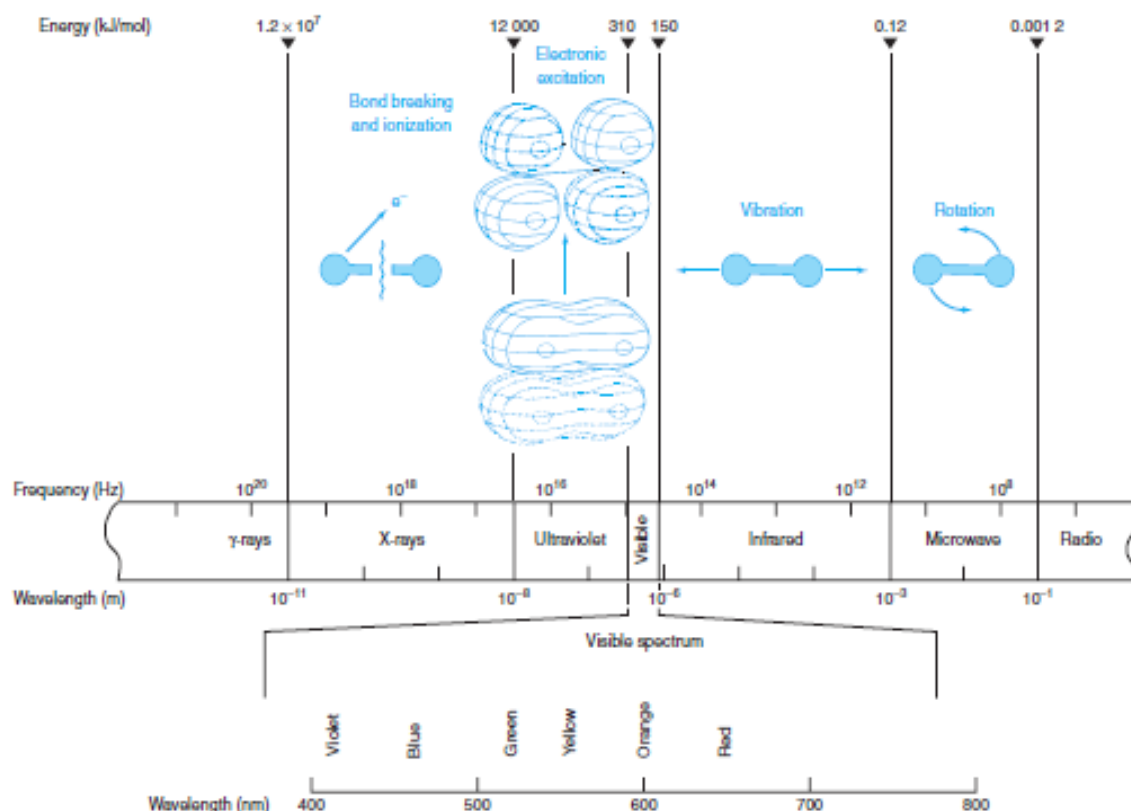where h is *Planck's constant* ($= 6.626 \times 10^{-34}$ J·s).

Equation 17-2 states that energy is proportional to frequency. Combining Equations 17-1 and 17-2, we can write

$$E = \frac{hc}{\lambda} = hc\bar{\nu}$$　　　　(17-3)

where $\bar{\nu}(=1/\lambda)$ is called **wavenumber.** Energy is inversely proportional to wavelength and directly proportional to wavenumber. Red light, with a longer wavelength than blue light, is less energetic than blue light. The most common unit of wavenumber in the literature is cm^{-1}, read "reciprocal centimeters" or "wavenumbers."
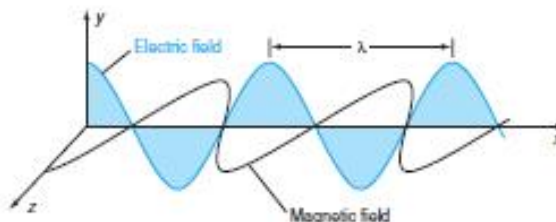
FIGURE 17-1 Plane-polarized electromagnetic radiation of wavelength λ, propagating along the x-axis. The electric field of plane-polarized light is confined to a single plane. Ordinary, unpolarized light has electric field components in all planes.

Energy (kJ/mol) 1.2×10^7 12 000 310 150 0.12 0.001 2

Electronic excitation

Bond breaking and ionization

Vibration

Rotation

Frequency (Hz) 10^{20} 10^{18} 10^{16} 10^{14} 10^{12} 10^8

γ-rays X-rays Ultraviolet Visible Infrared Microwave Radio

Wavelength (m) 10^{-11} 10^{-8} 10^{-6} 10^{-3} 10^{-1}

Visible spectrum

Violet Blue Green Yellow Orange Red

Wavelength (nm) 400 500 600 700 800

FIGURE 17-2 Electromagnetic spectrum, showing representative molecular processes that occur when light in each region is absorbed. The visible spectrum spans the wavelength range 380–780 nanometers (1 nm = 10^{-9} m).

The names of regions of the **electromagnetic spectrum** in Figure 17-2 are historical. There are no abrupt changes in characteristics as we go from one region to the next, such as visible to infrared. Visible light—the kind of electromagnetic radiation we see—represents only a small fraction of the electromagnetic spectrum.

17-2 Absorption of Light

When a molecule absorbs a photon, the energy of the molecule increases. We say that the molecule is promoted to an **excited state** (Figure 17-3). If a molecule emits a photon, the energy of the molecule is lowered. The lowest energy state of a molecule is called the **ground state.** Figure 17-2 indicates that microwave radiation stimulates rotation of molecules when it is absorbed. Infrared radiation stimulates vibrations. Visible and ultraviolet radiation promote electrons to higher energy orbitals. X-rays and short-wavelength ultraviolet radiation break chemical bonds and ionize molecules. Medical X-rays damage the human body, so your exposure should be minimized.
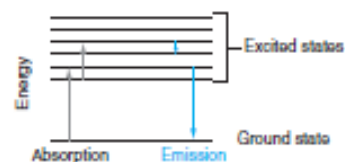
FIGURE 17-3 Absorption of light increases the energy of a molecule. Emission of light decreases its energy.

EXAMPLE Photon Energies

By how many kilojoules per mole is the energy of O_2 increased when it absorbs ultraviolet radiation with a wavelength of 147 nm? How much is the energy of CO_2 increased when it absorbs infrared radiation with a wavenumber of 2 300 cm^{-1}?

Solution For the ultraviolet radiation, the energy increase is

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

$$= (6.626 \times 10^{-34} \text{ J} \cdot s)\left[\frac{(2.998 \times 10^8 \text{ m/s})}{(147 \text{ nm})(10^{-9} \text{ m/nm})}\right] = 1.35 \times 10^{-18} \text{ J/molecule}$$

$$(1.35 \times 10^{-18} \text{ J/molecule})(6.022 \times 10^{23} \text{ molecules/mol}) = 814 \text{ kJ/mol}$$

This is enough energy to break the O=O bond in oxygen. For CO_2, the energy increase is

$$\Delta E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu} \qquad \left(\text{recall that } \bar{\nu} = \frac{1}{\lambda}\right)$$

$$= (6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(2.998 \times 10^{8}\ \text{m/s})(2\ 300\ \text{cm}^{-1})(100\ \text{cm/m})$$

$$= 4.6 \times 10^{-20}\ \text{J/molecule} = 28\ \text{kJ/mol}$$

Infrared absorption increases the amplitude of the vibrations of the CO_2 bonds.

Test Yourself What is the wavelength, wavenumber, and name of radiation with an energy of 100 kJ/mol? (*Answer:* 1.20 μm, $8.36 \times 10^{3}\ \text{cm}^{-1}$, infrared)

When light is absorbed by a sample, the *irradiance* of the beam of light is decreased. **Irradiance**, P, is the energy per second per unit area of the light beam. A rudimentary spectrophotometric experiment is illustrated in Figure 17-4. Light is passed through a **monochromator** (a prism, a grating, or even a filter) to select one wavelength (Color Plate 12). Light with a very narrow range of wavelength is said to be **monochromatic** ("one color.") The monochromatic light, with irradiance P_0, strikes a sample of length b. The irradiance of the beam emerging from the other side of the sample is P. Some of the light may be absorbed by the sample, so $P \le P_0$.
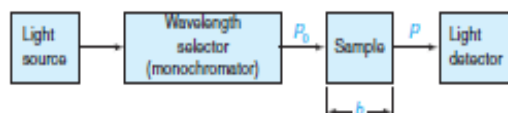
FIGURE 17-4 Schematic diagram of a single-beam spectrophotometric experiment. P_0, irradiance of beam entering sample; P, irradiance of beam emerging from sample; b, length of path through sample.

Transmittance, T, is defined as the fraction of the original light that passes through the sample.

Transmittance: $$T = \frac{P}{P_0} \qquad (17\text{-}4)$$

Therefore, T has the range 0 to 1. The *percent transmittance* is simply $100T$ and ranges between 0 and 100%. **Absorbance** is defined as

Absorbance: $$A = \log\left(\frac{P_0}{P}\right) = -\log T \qquad (17\text{-}5)$$

When no light is absorbed, $P = P_0$ and $A = 0$. If 90% of the light is absorbed, 10% is transmitted and $P = P_0/10$. This ratio gives $A = 1$. If only 1% of the light is transmitted, $A = 2$. Absorbance is sometimes called *optical density*.

Absorbance is so important because it is directly proportional to the concentration, c, of the light-absorbing species in the sample (Color Plate 13).

Beer's law: $$A = \varepsilon bc \qquad (17\text{-}6)$$

Equation 17-6, which is the heart of spectrophotometry as applied to analytical chemistry, is called the *Beer-Lambert law,*[6] or simply **Beer's law.** Absorbance is dimensionless, but some people write "absorbance units" after absorbance. The concentration of the sample, c, is usually given in units of moles per liter (M). The pathlength, b, is commonly expressed in centimeters. The quantity ε (epsilon) is called the **molar absorptivity** (or *extinction coefficient* in the older literature) and has the units $\text{M}^{-1}\ \text{cm}^{-1}$ to make the product εbc dimensionless. Molar absorptivity is the characteristic of a substance that tells how much light is absorbed at a particular wavelength.

EXAMPLE Absorbance, Transmittance, and Beer's Law

Find the absorbance and transmittance of a 0.002 40 M solution of a substance with a molar absorptivity of 313 $\text{M}^{-1}\ \text{cm}^{-1}$ in a cell with a 2.00-cm pathlength.