14.1: Vocabulary

Electromagnetic radiation—light—is a form of energy whose behavior is described by the properties of both waves and particles. Some properties of electromagnetic radiation, such as its refraction when it passes from one medium to another are explained best by describing light as a wave. Other properties, such as absorption and emission, are better described by treating light as a particle. The exact nature of electromagnetic radiation remains unclear, as it has since the development of quantum mechanics in the first quarter of the 20th century.[1] Nevertheless, the dual models of wave and particle behavior provide a useful description for electromagnetic radiation.

Electromagnetic radiation consists of oscillating electric and magnetic fields that propagate through space along a linear path and with a constant velocity. In a vacuum electromagnetic radiation travels at the speed of light, c, which is 2.997×10^8 m/s. When electromagnetic radiation moves through a medium other than a vacuum its velocity, v, is less than the speed of light in a vacuum. The difference between v and c is sufficiently small (<0.1%) that the speed of light to three significant figures, 3.00×10^8 m/s, is accurate enough for most purposes.

The oscillations in the electric and magnetic fields are perpendicular to each other, and to the direction of the wave's propagation. Figure 14.1.1 shows an example of plane-polarized electromagnetic radiation, consisting of a single oscillating electric field and a single oscillating magnetic field.
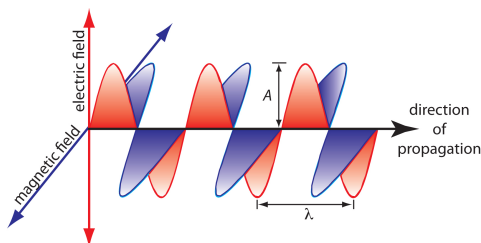

Figure 14.1.1: Plane-polarized electromagnetic radiation showing the oscillating electric field in red and the oscillating magnetic field in blue. The radiation's amplitude, A, and its wavelength, λ, are shown. Normally, electromagnetic radiation is unpolarized, with oscillating electric and magnetic fields present in all possible planes perpendicular to the direction of propagation.

An electromagnetic wave is characterized by several fundamental properties, including its velocity, amplitude, frequency, phase angle, polarization, and direction of propagation.[2] For example, the amplitude of the oscillating electric field at any point along the propagating wave is

$$A_t = A_e \sin(2\pi\nu t + \phi) \tag{14.1.1}$$

where A_t is the magnitude of the electric field at time t, A_e is the electric field's maximum **amplitude**, ν is the wave's **frequency**—the number of oscillations in the electric field per unit time—and ϕ is a **phase angle**, which accounts for the fact that A_t need not have a value of zero at $t = 0$. The identical equation for the magnetic field is

$$A_t = A_m \sin(2\pi\nu t + \phi) \tag{14.1.2}$$

where A_m is the magnetic field's maximum amplitude.

Units

Other properties also are useful for characterizing the wave behavior of electromagnetic radiation. The **wavelength**, λ, is defined as the distance between successive maxima (Figure 14.1.1). For ultraviolet and visible electromagnetic radiation the wavelength is usually expressed in nanometers (1 nm = 10^{-9} m), and for infrared radiation it is given in microns (1 μm = 10^{-6} m). The relationship between wavelength and frequency is

$$\lambda = \frac{c}{\nu} \tag{14.1.3}$$

Another unit useful unit is the **wavenumber**, $\tilde{\nu}$, which is the reciprocal of wavelength

$$\tilde{\nu} = \frac{1}{\lambda} \tag{14.1.4}$$

Wavenumbers are frequently used to characterize infrared radiation, with the units given in cm^{-1}.

✔ **Example 14.1.1**

In 1817, Josef Fraunhofer studied the spectrum of solar radiation, observing a continuous spectrum with numerous dark lines. Fraunhofer labeled the most prominent of the dark lines with letters. In 1859, Gustav Kirchhoff showed that the D line in the sun's spectrum was due to the absorption of solar radiation by sodium atoms. The wavelength of the sodium D line is 589 nm. What are the frequency and the wavenumber for this line?

Solution

The frequency and wavenumber of the sodium D line are

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{589 \times 10^{-9} \text{ m}} = 5.09 \times 10^{14} \text{ s}^{-1} \tag{14.1.5}$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{589 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 1.70 \times 10^4 \text{ cm}^{-1} \tag{14.1.6}$$

❓ **Exercise 14.1.1**

Another historically important series of spectral lines is the Balmer series of emission lines form hydrogen. One of the lines has a wavelength of 656.3 nm. What are the frequency and the wavenumber for this line?

Click here to review your answer to this exercise.

Regions of the Spectrum

The frequency and wavelength of electromagnetic radiation vary over many orders of magnitude. For convenience, we divide electromagnetic radiation into different regions—the **electromagnetic spectrum**—based on the type of atomic or molecular transition that gives rise to the absorption or emission of photons (Figure 14.1.2). The boundaries between the regions of the electromagnetic spectrum are not rigid, and overlap between spectral regions is possible.
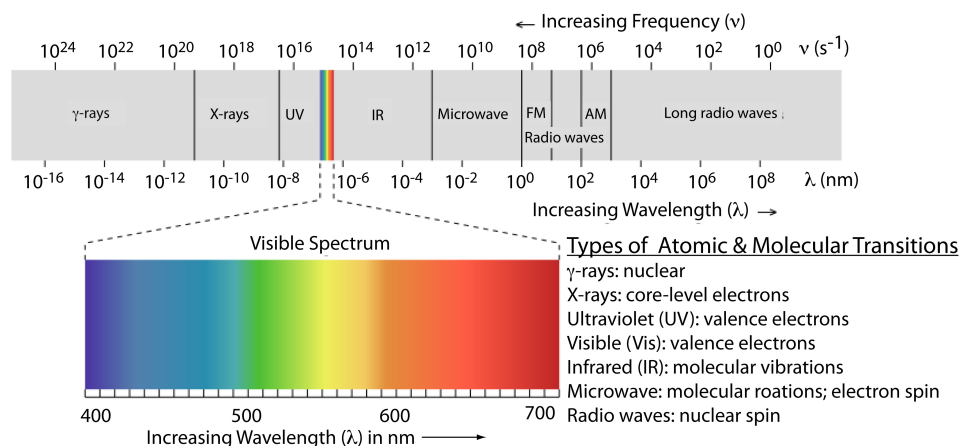

Figure 14.1.2: The electromagnetic spectrum showing the boundaries between different regions and the type of atomic or molecular transition responsible for the change in energy. The colored inset shows the visible spectrum. Source: modified from Zedh (www.commons.Wikipedia.org).

Above, we defined several characteristic properties of electromagnetic radiation, including its energy, velocity, amplitude, frequency, phase angle, polarization, and direction of propagation. A spectroscopic measurement is possible only if the photon's interaction with the sample leads to a change in one or more of these characteristic properties. We can divide spectroscopy into two broad classes of techniques. In one class of techniques there is a transfer of energy between the photon and the sample. Table 14.1.1 provides a list of several representative examples.

Table 14.1.1: Examples of Spectroscopic Techniques Involving an Exchange of Energy Between a Photon and the Sample

Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea

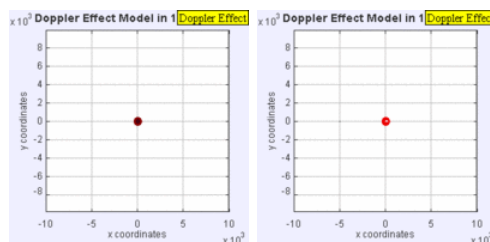| Type of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Techniquea
absorption	γ-ray	Mossbauer spectroscopy
	X-ray	X-ray absorption spectroscopy
	UV/Vis	*UV/Vis spectroscopy atomic absorption spectroscopy*
	IR	*infrared spectroscopy* raman spectroscopy
	Microwave	microwave spectroscopy
	Radio wave	electron spin resonance spectroscopy nuclear magnetic resonance spectroscopy
emission (thermal excitation)	UV/Vis	*atomic emission spectroscopy*
photoluminescence	X-ray	X-ray fluorescence
	UV/Vis	*fluorescence spectroscopy phosphorescence spectroscopy* atomic fluorescence spectroscopy
chemiluminescence	UV/Vis	chemiluminescence spectroscopy

Line Widths

A spectral line extends over a range of frequencies, not a single frequency (i.e., it has a nonzero linewidth). There are multiple reasons for this broadening and shifts and only two are discussed below.

- **Lifetime Broadening.** This mechanism ordinates directly from the Heisenberg Principle, which the lifetime of an excited state (due to the spontaneous radiative decay) with the uncertainty of its energy Δt. Since the system is changing in time, it is impossible to estimate the energies of wavefunctions exactly (ΔE.

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

(14.1.7)

Hence, systems with excited-states that have short lifetimes will have a large energy uncertainty and a broad emission. This broadening effect results in an broadened profile. As expected, the lifetime broadening can be experimentally if the decay rates can be artificially suppressed or enhanced.

- **Doppler Broadening**. This mechanism is intrinsic to atoms in a gas which are emitting radiation will have a distribution of velocities. Each photon emitted will be "red"- or "blue"-shifted by the Doppler effect depending on the velocity of the atom relative to the observer. The Doppler effect is the change in frequency of a wave (or other periodic event) for an observer moving relative to its source. It is commonly heard when a vehicle sounding a siren or horn approaches, passes, and recedes from an observer. Compared to the emitted frequency, the received frequency is higher during the approach, identical at the instant of passing by, and lower during the recession.
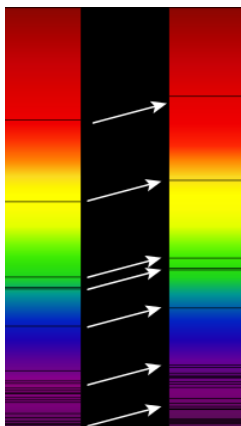

Doppler Broadening example with sound, but applies to light too. (left): Stationary sound source produces sound waves at a constant frequency υ, and the wave-fronts propagate symmetrically away from the source at a constant speed c (assuming speed of sound, c = 330 m/s), which is the speed of sound in the medium. The distance between wave-fronts is the wavelength. All observers

will hear the same frequency, which will be equal to the actual frequency of the source where $u = u - o$ (right): The same sound source is radiating sound waves at a constant frequency in the same medium. However, now the sound source is moving with a speed so the center of each new wavefront is now slightly displaced to the right. As a result, the wave-fronts begin to bunch up on the right side (in front of) and spread further apart on the left side (behind) of the source. An observer in front of the source will hear a higher frequency. Images used with permission from Wikipedia (credit Lookang).

If the speeds are small compared to the speed of the wave, the relationship between observed frequency u_o and emitted frequency u is approximately

$$u = \left(1 + \frac{\Delta v}{c}\right) v_0 \tag{14.1.8}$$

The Doppler effect also applies for spectroscopy. For example, the higher the temperature of the gas, the wider the distribution of velocities in the gas (via the Maxwell-Bolztmann Distribution). Since the spectral line is a combination of all of the emitted radiation, the higher the temperature of the gas, the broader the spectral line emitted from that gas. If the average velocity of a gas is non-zero, then a Doppler shift will be observed that is correlated with the amplitude of this average velocity.

Redshift of spectral lines in the optical spectrum of a supercluster of distant galaxies (right), as compared to that of the Sun (left) since the sun is not moving with respect to Earth (or weakly) and the galaxy is moving away. from Wikipedia (Credit Georg Wiora).

Doppler broadening is one of the explanations for the broadening of spectral lines, and as such gives an indication for the temperature of observed material. Other causes of velocity distributions may exist, though, for example due to turbulent motion. Doppler broadening can also be used to determine the velocity distribution of a gas given its absorption spectrum. In particular, this has been used to determine the velocity distribution of interstellar gas clouds.

> ✔ **Example 14.1.2**
>
> Find the uncertainty of simultaneously measuring the frequency and wavelength of an emission from an excited molecule, if the wavelength is 430 nm and the excited state lifetime is 0.50 nanoseconds.
>
> **Soluton**
>
> 1. Use Heisenberg's uncertainty principle and the relationship between energy and frequency to find the uncertainty of frequency.
>
> $$\Delta E \Delta t \geq \frac{h}{4\pi}$$
>
> $$\Delta E = h \Delta u$$
>
> $$h \Delta u \Delta t \geq \frac{h}{4\pi}$$
>
> $$\Delta u \geq \frac{1}{4\pi \Delta t}$$
>
> The maximum value for Δt is the lifetime of the excited state.

$$\Delta u \geq \frac{1}{4\pi 0.50 ns \times \dfrac{s}{10^9 \ ns}}$$

$$\Delta u \geq 1.6 \times 10^8 \ s^{-1}$$

2. Use the uncertainty of frequency and the relationship between frequency and wavelength to find the uncertainty of the wavelength.

$$\lambda = \frac{c}{u}$$

$$|\Delta\lambda| = \frac{c}{u^2}|\Delta u|$$

$$|\Delta\lambda| = \frac{\lambda^2|\Delta u|}{c}$$

$$|\Delta\lambda| = \frac{(430 \ nm)^2 \times 1.6 \times 10^8 \ s^{-1}}{2.998 \times 10^8 \ m/s} \times \frac{m}{10^9 \ nm}$$

$$|\Delta\lambda| = 2.3 \times 10^{-7} \ nm$$

Absorption and Emission

In absorption spectroscopy a photon is absorbed by an atom or molecule, which undergoes a transition from a lower-energy state to a higher-energy, or excited state (Figure 14.1.3). The type of transition depends on the photon's energy. The electromagnetic spectrum in Figure 14.1.2, for example, shows that absorbing a photon of visible light promotes one of the atom's or molecule's valence electrons to a higher-energy level. When an molecule absorbs infrared radiation, on the other hand, one of its chemical bonds experiences a change in vibrational energy.
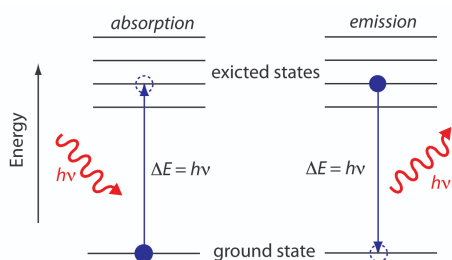

Figure 14.1.3: Simplified energy diagram showing the absorption and emission of a photon by an atom or a molecule. When a photon of energy hv strikes the atom or molecule, absorption may occur if the difference in energy, ΔE, between the ground state and the excited state is equal to the photon's energy. An atom or molecule in an excited state may emit a photon and return to the ground state. The photon's energy, hv, equals the difference in energy, ΔE, between the two states.

When it absorbs electromagnetic radiation the number of photons passing through a sample decreases. The measurement of this decrease in photons, which we call **absorbance**, is a useful analytical signal. Note that the each of the energy levels in Figure 14.1.3 has a well-defined value because they are quantized. Absorption occurs only when the photon's energy, hv, matches the difference in energy, ΔE, between two energy levels. A plot of absorbance as a function of the photon's energy is called an **absorbance spectrum**. Figure 14.1.4, for example, shows the absorbance spectrum of cranberry juice.
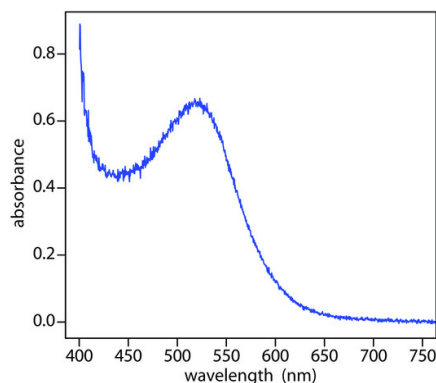
Figure 14.1.3). As a result, the juice appears red.

When an atom or molecule in an excited state returns to a lower energy state, the excess energy often is released as a photon, a process we call **emission** (Figure 14.1.4). There are several ways in which an atom or molecule may end up in an excited state, including thermal energy, absorption of a photon, or by a chemical reaction. Emission following the absorption of a photon is also called **photoluminescence**, and that following a chemical reaction is called **chemiluminescence**. A typical emission spectrum is shown in Figure 14.1.6.
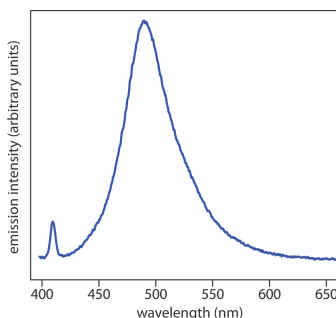

Figure 14.1.5: Photoluminescence spectrum of the dye coumarin 343, which is incorporated in a reverse micelle suspended in cyclohexanol. The dye's absorbance spectrum (not shown) has a broad peak around 400 nm. The sharp peak at 409 nm is from the laser source used to excite coumarin 343. The broad band centered at approximately 500 nm is the dye's emission band. Because the dye absorbs blue light, a solution of coumarin 343 appears yellow in the absence of photoluminescence. Its photoluminescent emission is blue-green. Source: data from Bridget Gourley, Department of Chemistry & Biochemistry, DePauw University).

Selection Rules

The transition probability is defined as the probability of particular spectroscopic transition to take place. When an atom or molecule absorbs a photon, the probability of an atom or molecule to transit from one energy level to another depends on two things: the nature of initial and final state wavefunctions and how strongly photons interact with an wavefunction. Transition strengths are used to describe transition probability. Selection rules are utilized to determine whether a transition is allowed or not. Electronic dipole transitions are by far the most important for the topics covered in this module.

In an atom or molecule, an electromagnetic wave (for example, visible light) can induce an oscillating electric or magnetic moment. If the frequency of the induced electric or magnetic moment is the same as the energy difference between one wavefunction ψ_1 and another wavefunction ψ_2, the interaction between an atom or molecule and the electromagnetic field is resonant (which means these two have the same frequency). Typically, the amplitude of this (electric or magnetic) moment is called the transition moment. In quantum mechanics, the transition probability of one molecule from one wavefunction ψ_1 to another wavefunction ψ_2 is given by $|\vec{M}_{21}|^2$, and $\vec{M}_{21}$ is called the **transition dipole moment**, or transition moment, from ψ_1 to ψ_2. $\vec{M}_{21}$ can be written as

$$\vec{M}_{21} = \int \psi_2 \vec{\mu} \psi_1 d\tau \tag{14.1.9}$$

where ψ_1 and ψ_2 are two different wavefunctions in one molecule, and $\vec{M}_{21}$ is the **electric dipole moment operator**. If we have a system with n atoms and each has charge q_n, and the dipole moment operator is can be written as

$$\vec{\mu} = \sum_n q_n \vec{r}_n \tag{14.1.10}$$

the $\vec{r}_n$ is the position vector operator for the ith charge. The nature of ψ_1 and ψ_1 change (e..g, the quantum numbers associated with each wavefunction) $\vec{M}_{21}$. Large values of $\vec{M}_{21}$ signify transitions with strong probabilities and small $\vec{M}_{21}$ values represent weak probabilities. A zero probability for a transition is a forbidden transition.

For electronic wavefucntion (either atoms or molecules), the two primary selection rules governing transitions between electronic energy wavefunctions are:

1. $\Delta S = 0$ (The Spin Rule)
2. $\Delta l = \pm 1$ (The Orbital Rule (or Laporte rule))

The spin multiplicity can be calculated from the quantum number S of the total spin or from the number of unpaired electrons (like when determining paramagnetic properties of molecules). The spin-multiplicity is $(2S+1)$, where

$$S = \sum_{\text{spin quantum \#}} s \tag{14.1.11}$$

The Spin Rule says that allowed transitions must involve the promotion of electrons **without** a change in their spin. The Orbital Rule says that transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden. The orbital rule can be used to construct Grotrian diagrams, which show the allowed electronic transitions between the energy levels of atoms (Figure 14.1.6) by taking into account the specific selection rules related to the system (e..g, the Orbital or Spin Rules).
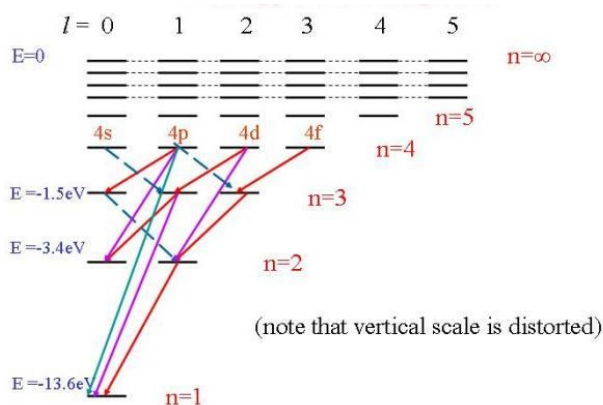

Figure 14.1.6: A Grotrian diagram of the hydrogen atom. Only transitions between adjacent columns are allowed, as per the selection rule $\Delta l = \pm 1$. from Tufts OCW (CC SA-BY; Gary Goldstein).

> Transitions not permitted by selection rules are said forbidden, which means that theoretically they must not occur. However, in practice they may occur, but very low probabilities (see 14.1.3 below).

The Beers-Lambert Law

The Beer-Lambert law relates the attenuation of light to the properties of the material through which the light is traveling. This page takes a brief look at the Beer-Lambert Law and explains the use of the terms absorbance and molar absorptivity relating to UV-visible absorption spectrometry. For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as I_o - that's I for Intensity.
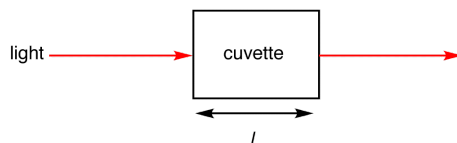

Figure 14.1.6: Light absorbed by sample in a cuvetter

The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol, I. If I is less than I_o, then the sample has absorbed some of the light (neglecting reflection of light off the cuvetter surface). A simple bit of math is then done in the computer to convert this into something called the absorbance of the sample - given the symbol, A.

> **📌 Note**
>
> The absorbance of a transition depends on two external assumptions.
>
> 1. The absorbance is directly proportional to the concentration (c) of the solution of the the sample used in the experiment.
> 2. The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption one relates the absorbance to concentration and can be expressed as

$$A \propto c \tag{14.1.12}$$

The absorbance (A) is defined via the incident intensity I_o and transmitted intensity I by

$$A = \log_{10}\left(\frac{I_o}{I}\right) \tag{14.1.13}$$

Assumption two can be expressed as

$$A \propto l \tag{14.1.14}$$

Combining Equations 14.1.12 and 14.1.14:

$$A \propto cl \tag{14.1.15}$$

This proportionality can be converted into an equality by including a proportionality constant.

$$A = \epsilon cl \tag{14.1.16}$$

This formula is the common form of the *Beer-Lambert Law*, although it can be also written in terms of intensities:

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon lc \tag{14.1.17}$$

The constant ϵ is called molar absorptivity or molar extinction coefficient and is a measure of the probability of the electronic transition. On most of the diagrams you will come across, the absorbance ranges from 0 to 1, but it can go higher than that. An absorbance of 0 at some wavelength means that no light of that particular wavelength has been absorbed. The intensities of the sample and reference beam are both the same, so the ratio I_o/I is 1. $\log_{10}$ of 1 is zero.

> **✔ Example 14.1.3**
>
> In a sample with an absorbance of 1 at a specific wavelength, what is the relative amount of light that was absorbed by the sample?
>
> **Solution**
>
> This question does not need Beer-Lambert Law (Equation 14.1.16) to solve, but only the definition of absorbance (Equation 14.1.13)
>
> $$A = \log_{10}\left(\frac{I_o}{I}\right)$$
>
> The relative loss of intensity is
>
> $$\frac{I - I_o}{I_o} = 1 - \frac{I}{I_o}$$
>
> Equation 14.1.13 can be rearranged using the properties of logarithms to solved for the relative loss of intensity:
>
> $$10^A = \frac{I_o}{I}$$

$$10^{-A} = \frac{I}{I_o}$$

$$1 - 10^{-A} = 1 - \frac{I}{I_o}$$

Substituting in $A = 1$

$$1 - \frac{I}{I_o} = 1 - 10^{-1} = 1 - \frac{1}{10} = 0.9$$

Hence 90% of the light at that wavelength has been absorbed and that the transmitted intensity is 10% of the incident intensity

To confirm, substituting these values into Equation 14.1.13 to get the absorbance back:

$$\frac{I_o}{I} = \frac{100}{10} = 10$$

and

$$\log_{10} 10 = 1$$

You will find that various different symbols are given for some of the terms in the equation - particularly for the concentration and the solution length.

The Greek letter epsilon in these equations is called the molar absorptivity - or sometimes the molar absorption coefficient. The larger the molar absorptivity, the more probable the electronic transition. In uv spectroscopy, the concentration of the sample solution is measured in $molL^{-1}$ and the length of the light path in cm. Thus, given that absorbance is unitless, the units of molar absorptivity are L mol^{-1} cm^{-1}. However, since the units of molar absorptivity is always the above, it is customarily reported without units.

✔ Example 14.1.4

Guanosine has a maximum absorbance of 275 nm. $\epsilon_{275} = 8400 M^{-1} cm^{-1}$ and the path length is 1 cm. Using a spectrophotometer, you find the that $A_{275} = 0.70$. What is the concentration of guanosine?

Solution

To solve this problem, you must use Beer's Law.

$$A = \epsilon l c$$

$$0.70 = (8400 \text{ M}^{-1} \text{ cm}^{-1})(1 \text{ cm})(c)$$

Next, divide both side by [(8400 M^{-1} cm^{-1})(1 cm)]

$$c = 8.33 \times 10^{-5} \text{ mol/L}$$

✔ Example 14.1.5

There is a substance in a solution (4 g/liter). The length of cuvette is 2 cm and only 50% of the certain light beam is transmitted. What is the extinction coefficient?

Solution

Using Beer-Lambert Law, we can compute the absorption coefficient. Thus,

$$-\log\left(\frac{I_t}{I_o}\right) = -\log(\frac{0.5}{1.0}) = A = 8\epsilon$$

Then we obtain that

$$\epsilon = 0.0376$$

✔ **Example 14.1.6**

In Example 3 above, what is the molar absorption coefficient if the molecular weight is 100?

Solution

It can simply obtained by multiplying the absorption coefficient by the molecular weight. Thus,

$$\epsilon = 0.0376 \text{ x } 100 = 3.76 \text{ L·mol}^{-1}\text{·cm}^{-1}$$

The proportion of the light absorbed will depend on how many molecules it interacts with. Suppose you have got a strongly colored organic dye. If it is in a reasonably concentrated solution, it will have a very high absorbance because there are lots of molecules to interact with the light. However, in an incredibly dilute solution, it may be very difficult to see that it is colored at all. The absorbance is going to be very low. Suppose then that you wanted to compare this dye with a different compound. Unless you took care to make allowance for the concentration, you couldn't make any sensible comparisons about which one absorbed the most light.

✔ **Example 14.1.7**

In Example 14.1.3 above, how much is the beam of light is transmitted when 8 g/liter ?

Solution

Since we know ϵ, we can calculate the transmission using Beer-Lambert Law. Thus,

$$log(1) - log(I_t) = 0 - log(I_t) \quad = 0.0376 \text{ x } 8 \text{ x } 2 = 0.6016$$

$$log(I_t) = \text{-}0.6016$$

Therefore, I_t = 0.2503 = 25%

✔ **Example 14.1.7**

The absorption coefficient of a glycogen-iodine complex is 0.20 at light of 450 nm. What is the concentration when the transmission is 40 % in a cuvette of 2 cm?

Solution

It can also be solved using Beer-Lambert Law. Therefore,

$$-\log(I_t) = -\log_{10}(0.4) = 0.20 \times c \times 2$$

Then c = 0.9948

The Beer-Lambert law Equation 14.1.16 can be rearranged to obtain an expression for ϵ (the molar absorptivity):

$$\epsilon = \frac{A}{lc} \tag{14.1.18}$$

Remember that the absorbance of a solution will vary as the concentration or the size of the container varies. Molar absorptivity compensates for this by dividing by both the concentration and the length of the solution that the light passes through. Essentially, it works out a value for what the absorbance would be under a standard set of conditions - the light traveling 1 cm through a solution of 1 mol dm-3. That means that you can then make comparisons between one compound and another without having to worry about the concentration or solution length.

Values for molar absorptivity can vary hugely. For example, ethanal has two absorption peaks in its UV-visible spectrum - both in the ultra-violet. One of these corresponds to an electron being promoted from a lone pair on the oxygen into a pi anti-bonding orbital; the other from a π bonding orbital into a π anti-bonding orbital. Table 14.1.2 gives values for the molar absorptivity of a solution of ethanal in hexane. Notice that there are no units given for absorptivity. That's quite common since it assumes the length is in cm and the concentration is mol dm^{-3}, the units are mol^{-1} dm^3 cm^{-1}.

Table 14.1.2:

electron jump	wavelength of maximum absorption (nm)	molar absorptivity
lone pair to π anti-bonding orbital	290	15
π bonding to π anti-bonding orbital	180	10,000

The ethanal obviously absorbs much more strongly at 180 nm than it does at 290 nm. (Although, in fact, the 180 nm absorption peak is outside the range of most spectrometers.) You may come across diagrams of absorption spectra plotting absorptivity on the vertical axis rather than absorbance. However, if you look at the figures above and the scales that are going to be involved, you are not really going to be able to spot the absorption at 290 nm. It will be a tiny little peak compared to the one at 180 nm. To get around this, you may also come across diagrams in which the vertical axis is plotted as $\log_{10}$(molar absorptivity). If you take the logs of the two numbers in the table, 15 becomes 1.18, while 10,000 becomes 4. That makes it possible to plot both values easily, but produces strangely squashed-looking spectra!

Table 14.1.3: Expected intensities of electronic transitions

Transition type	Typical values of ε /$m^2 mol^{-1}$
Spin forbidden and Laporte forbidden	0.1
Spin allowed and Laporte forbidden	1 - 10
Spin allowed and Laporte allowed e.g. charge transfer bands	1,000 - 10^6

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