Some Comments on Spectroscopy

The color of objects has always fascinated human beings. The discovery that sunlight can be broken up (dispersed) into a spectrum (light of a range of colors—often described as Red-Orange-Yellow-Green-Blue-Violet) opened up opportunities for both the qualitative and quantitative investigation of color. The further discovery that visible light is only a small part of a much broader range of electromagnetic radiation expanded these opportunities to regions to which the human eye does not respond (e.g., ultraviolet light, infrared light, microwave “light,” etc.).

The Properties of Light

Spectroscopy is the study of the interaction between matter and electromagnetic radiation. To understand what types of interactions can occur requires knowing the basic properties of electromagnetic radiation. For a long time, light has been characterized in two apparently inconsistent ways. On one hand, it has been thought of as consisting of “particles” (now called photons) which travel along a path. This model has been able to explain many of the properties of light. Some phenomena that light exhibits are difficult to describe with a particle model. These are better understood if light is thought of as a “wave.” Modern physics tells us that these two models are, in fact, not inconsistent. Indeed, the objects that one usually thinks of as particles, such as electrons, also have wave-like properties. It is entirely appropriate to mix the language of waves and particles. Indeed, the word radiation generally applies to a range of phenomena that includes visible light, X-rays, gamma rays, as well as beta particles and alpha particles.

The word electromagnetic is used to distinguish radiation in which the particles are photons (which effectively have no mass) from radiation consisting of beams of particles that have well-characterized masses (such as the electrons and helium nuclei in beta and alpha “rays”). The “electro” and “magnetic” in the word electromagnetic come from the observation that the waves associated with a photon as it travels through space have both electric and magnetic characteristics. These are the basis for the
interaction between electromagnetic radiation and matter. We use the word light to include any form of electromagnetic radiation—visible, ultraviolet, infrared, microwave, X-rays, gamma rays, etc.

What characteristics describe light? Light has a **fixed speed** (a subtle, and important concept). The speed of light in a vacuum is a universal constant usually designated by the letter “c” with an approximate value of $3.00 \times 10^8$ m/sec. The speed can be thought of as applying to both the particle of light (photon) and the associated waves. The waves have a **wavelength** ($\lambda$) and **frequency** ($\nu$) as illustrated in Figure 5-1.*

$$v = 2.0 \times 10^9 \text{ sec}^{-1}$$

**Figure 5-1.**

These can be thought of as characterizing the “color” of the light. The wavelength, frequency and speed are related by $\lambda \nu = c$. In addition, there is **energy** associated with light. The warmth of the sun is powerful evidence of this energy. It is convenient (but not necessary) to think of the energy as transported by light particles. This energy is dependent on the frequency of the wave associated with the photon and is given by $E = h\nu$ where $h$ is another universal constant, Planck’s constant, with an approximate value of $6.63 \times 10^{-34}$ Joule-sec. Note the interchangeability of wave and particle descriptions of light in this paragraph.

**The Interaction of Light with Matter**

What kinds of things can happen when light encounters a sample of matter? We consider three important phenomena: reflection, absorption, and transmission (we ignore refraction and scattering for the moment). These are illustrated in Figure 5-2. What determines the extent to which each of these occurs? Consider a mirror, a sheet of black paper and a window pane. These appear to be objects that each display only one of the three phenomena. The mirror reflects essentially all of the light that

*Another characterization commonly used in the infrared region is the wavenumber—the reciprocal of the wavelength. It measures the number of cycles in a given length of the wave—the spatial frequency.
impinges on it. It neither absorbs, nor transmits any visible light. The black paper reflects none of the visible light and transmits none—it **absorbs** all of the visible light that reaches it. The window pane appears to permit all of the visible light to be **transmitted** through it. It absorbs none and reflects none. Our observations have, however, been limited to what these objects do with respect to the light that our eyes can detect—visible light. The window pane, for example, actually transmits only light near the visible region. It absorbs most of the infrared and ultraviolet light that reach it. Depending on the reflecting material on the mirror, it may indeed transmit light at wavelengths other than those characterizing visible light—for example, X-rays may be transmitted very effectively. Similarly, the black paper may reflect or transmit a considerable amount of light in other than the visible region.

![Reflection, absorption and transmission of light](image)

**Figure 5-2.**

Reflection, absorption and transmission of light are highly dependent on the wavelengths of the light in question. A blue glass pane clearly transmits blue light. What about the other colors that constitute “white” light? These are presumably absorbed or reflected. A piece of blue paper exposed to white light must reflect blue light in order to appear blue. What does it do with the other colors in the white light?

On what else do these interactions depend? Against a white background, a large sample of water appears slightly blue when viewed from directly above. If the water is still, a reflection may be visible. When viewed along the surface instead (as one would view a lake from the shore), the water at a considerable distance from the viewer seems to reflect all of the light. Copper sulfate forms crystals with a distinctive blue color. If those crystals are ground to a fine powder, the blue color fades to what appears almost to be white. The interactions between light and matter depend on the state of the matter as well as the wavelength. They can depend even on the relative position of the light source and the observer.

**The Microscopic Basis for Absorption of Light**

What property of **light** determines whether or not it can be absorbed by a sample of matter? The answer depends in part on the relationship between the wavelength or frequency of a photon and its associated energy. A given photon has a discrete (quantized) amount of energy which is proportional to its frequency ($E = hv$). It normally must transfer all of its energy to a sample, or none of it. Partial transfer is not permitted. Like the photon, the energies that can be absorbed by a sample of matter are also discrete (i.e., quantized. The reverse of absorption, e.g., the emission of light by excited atoms, occurs at discrete frequencies or wavelengths.). One fundamental
condition for the absorption of a photon of a given energy is that the sample of matter must have energy levels whose separation (ΔE) match the photon energy (hν). When that occurs (i.e., ΔE = hν), conservation of energy suggests that the sample of matter is “excited” to a new state of energy higher than the original by an amount equal to the energy of the photon.

What types of energy levels are characteristic of matter? The atoms or molecules that make up a sample of matter are capable of several types of motion. Atoms or molecules can move with respect to one another in a crystal, or with respect to the walls of a container (e.g., for a gas or liquid). Molecules are made up of atoms and these can move with respect to one another (e.g., such as in vibrations) or with respect to their orientation in space (e.g., rotate). The motions of electrons in atoms and molecules are also subject to discrete energy levels such as are described by atomic or molecular orbitals. Each of these motions gives rise to sets of energy levels that represent states of different energies with discrete spacings. If the spacing between a pair of energy levels (ΔE) matches the energy of a photon of frequency v (and therefore of energy hν) that photon can, in principle, be absorbed. The sample that has absorbed the photon will be in a higher energy state which normally corresponds to a higher temperature at the macroscopic level.

In addition to the requirement of matched energy level spacing, the photon must also be able to “see” (i.e., interact with) the matter sample. Here we rely on the electric or magnetic waves associated with the photon for a mode of interaction. If molecular or atomic motions are associated with changes in electric or magnetic properties, the photon can “see” the motion and a mechanism for its absorption exists.

What are the energy level spacings characteristic of the several types of motions of electrons, atoms and molecules? Table 5-1 provides a summary.

**Table 5-1.**

<table>
<thead>
<tr>
<th>TYPE OF MOTION</th>
<th>ENERGY LEVEL SPACING (J)</th>
<th>TYPICAL PHOTON FREQUENCY (E/H) (HZ)</th>
<th>TYPICAL PHOTON WAVELENGTH (C/N) (M)</th>
<th>NAME OF ELECTROMAGNETIC RADIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Translation</td>
<td>10^{-27}</td>
<td>10^6</td>
<td>10^2</td>
<td>Radio</td>
</tr>
<tr>
<td>Rotation</td>
<td>10^{-23}</td>
<td>10^{10}</td>
<td>10^{-2}</td>
<td>Microwave</td>
</tr>
<tr>
<td>Vibration</td>
<td>10^{-21}</td>
<td>10^{12}</td>
<td>10^{-4}</td>
<td>Infrared</td>
</tr>
<tr>
<td>Outer Electron</td>
<td>10^{-18}</td>
<td>10^{15}</td>
<td>10^{-7}</td>
<td>Visible Ultraviolet</td>
</tr>
<tr>
<td>Inner Electron</td>
<td>10^{-15}</td>
<td>10^{18}</td>
<td>10^{-10}</td>
<td>X-Ray</td>
</tr>
</tbody>
</table>
Absorption Spectroscopy

How is the absorption of “light” measured experimentally? A typical arrangement is shown in Figure 5-3, below.

**Figure 5-3.**

In general, the components of a spectrometer are:

- a source of light
- an element to select a particular wavelength of light (monochromator)
- sample container
- detector to measure the intensity of light transmitted through the sample
- electronic circuits to translate the detector output into numbers

The source of light may be an electric arc, (visible and ultraviolet region), incandescent bulb (visible region), a heated object (infrared region), an electron tube or solid state device (microwave), an X-ray tube (X-ray region), tunable lasers, etc. Monochromators (*mono* = one, *chroma* = color) may be prisms or diffraction gratings accompanied by a slit or maybe more complex devices.** Sample containers must accommodate both the state of the sample (gas, liquid, solid) and the wavelength region of interest (they should absorb as little of the light as possible to prevent interference with the sample). Detectors range from photoelectric devices to a variety of solid state devices depending on the wavelength range. The electronic circuits can involve sophisticated computations based on the detector signal.

To eliminate variations in the source, sample container and detector, it is common to measure the absorption or transmission of a sample relative to a configuration in which everything except the investigated sample is present—i.e., relative to a **blank**.

What does the detector normally measure? Most detectors are constructed to respond to the **intensity***** of the light that reaches them. By the intensity of light of a given wavelength, we mean the amount of energy per unit area in a given unit of time that the light would deposit on a perfectly absorbing surface perpendicular

**Newer spectroscopic techniques have made the monochromator superfluous in some spectrometric instruments such as the Fourier transform Infrared spectrophotometer (FTIR).

***What we are calling *intensity* is actually called *irradiance* by physicists.
to the light path. This can be viewed as the number of photons that impinge on a unit area of the surface per unit time. The electronic circuits are usually constructed to produce an output that is directly proportional to the intensity—i.e., if twice as many photons of identical energy per unit area and time reach the detector, its output should be twice as large.

If we call the intensity of the transmitted light at a given wavelength through a blank, \( I_0 \), and the intensity at the same wavelength through a sample, \( I_t \), it is convenient to define a quantity called the **percent transmittance**, \( \%T \), of the sample at that wavelength as:

\[
\%T = 100 \times \frac{I_t}{I_0}
\]

Note that \( \%T \) does not have any associated physical units. It is a pure number. Any details dealing with the detector and the electronic circuits that process its output have disappeared in this final measurement. Also, we assume that any reduction in the transmitted intensity is due to **absorption** by the sample—i.e., we assume that reflection (or scattering) by the sample plays no role. Note further that the \( \%T \) will always lie between 0 and 100—the former corresponding to complete absorption and the latter to complete transmittance.

The following example illustrates the above principles.

**EXAMPLE 1**

Potassium permanganate dissolves in water to give an intensely colored violet solution. We wish to measure the absorption of light of wavelength 599 nm due to potassium permanganate by an aqueous solution that is 0.01 M in potassium permanganate and 0.10 M in sulfuric acid. The steps are as follows:

1. Adjust the source and monochromator so that light impinging on the cell is at 599 nm
2. Fill a cell with 0.10 M aqueous sulfuric acid (a blank)
3. Measure the intensity of the transmitted light—suppose it is 80.0 in arbitrary units
4. Replace the sulfuric acid in the cell with an equal volume of the desired potassium permanganate solution in 0.10 M sulfuric acid
5. Measure the intensity of the transmitted light—suppose it is 60.0 in the same arbitrary units

The percent transmittance of the 0.01 M potassium permanganate at 599 nm is \( 100 \times 60.0 / 80.0 = 75.0 \) Note that the difference in transmittance must be due **only** to the presence of the potassium permanganate. As above, we assume that the light that was not transmitted was absorbed.
A Spectrum

Suppose we repeat the measurement in the example above at a large number of different wavelengths, being careful in each case to measure the transmittance of the sample relative to the blank. What can we expect?

Since the sample is presumed to be able to absorb light only at discrete wavelengths characteristic of the sample’s energy levels, we might expect the transmittance to vary considerably over a sufficiently large range of wavelengths (photon energies). That is indeed the case. A graph of the transmittance as a function of wavelength is called a spectrum (plural: spectra), specifically a transmittance spectrum. The spectrum of a typical-colored substance is shown in Figure 5-4. The discrete “line” spectra characteristic of the emission spectra of excited atoms have become rather broad absorptions due to all of the different types of motions that are possible for complex molecules in concentrated samples.

![Figure 5-4: Absorbance](image)

Absorbance

We have been considering absorption spectra, and yet all of our measurements thus far have dealt with transmittance. How can we display our observations in a form that reflects our interest in the absorption of light? The answer lies in the observation that the transmittance of many substances shows significant regions where it is basically 0—i.e., the light appears to be completely absorbed over considerable ranges of wavelength. Transmittances near 100% are relatively uninteresting (i.e., they represent no absorption by the sample). On a scale of 0–100%, transmittances of 0.01% and 0.0000001% will be essentially indistinguishable, and yet, it is precisely these distinctions which may contain valuable information. When the range of a variable becomes large (e.g., the range is over many powers of 10) it is convenient to define a related variable that bears a logarithmic relationship to the original variable. An example of such a practice is pH, which is defined so as to be able to compare solutions with \([H^+]\) that vary over a wide range—e.g., 1.0 M \([H^+]\) with its pH of 0 and 1.0 M \([OH^-]\) with \([H^+] = 1 \times 10^{-14}\) and a pH of 14.
It is convenient to define the quantity **absorbance**, $A$ as follows:

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

Note that, being related to the ratio of two similar quantities, absorbance again carries no units—i.e., it is dimensionless. Given the definition of percent transmittance shown earlier, it is easy to show that

$$A = 2.0000 - \log (\%T)$$

Note that when $\%T = 100$ (the sample absorbs none of the light), the absorbance is appropriately 0. When $\%T$ is small, the absorbance is large—e.g., when $\%T = 0.100\%$ (one-tenth of a percent of the light is transmitted), the absorbance is 3.00. As defined, absorbance is able to distinguish extents of absorption when absorption is large, which is the range of interest for absorption spectroscopy.

**The Beer-Lambert Law**

Our focus has so far been primarily on the light. What characteristics of the sample will affect transmittance and absorbance? We have already mentioned the variation in transmittance (and therefore absorbance) with wavelength which gives rise to **spectra** (the plural of spectrum). On what other properties of the sample will the interaction with light depend? It should not be surprising that the total amount of an absorbing sample will affect the amount of light transmitted through the sample.

**EXAMPLE 2**

Suppose that the cell in the earlier example (Example 1) is 1.00 cm long. Assume the light coming out of the sample has an intensity 75% of that which impinged on it. If we put a second 1.00 cm long sample behind the first, the incident light on that sample will be only 75% of that seen by the original sample. We might expect that the light transmitted through the second sample will again be reduced to 75% of the incident light. Therefore, the percent of the original incident light which leaves the second sample is $75\% \times 75\% = 56\%$. (See Figure 5-3.) The corresponding absorbances will be:

$$A_1 = 2.00 - \log (75) = 2.00 - 1.875 = 0.125, \text{ and}$$

$$A_2 = 2.00 - \log (75 \times 0.75) = 2.00 - 1.750 = 0.250$$

i.e., the total absorbance by a 2.00 cm long sample will be twice that of a 1.00 cm sample.

Instead of placing a second cell after the first, consider doubling the concentration of potassium permanganate. We now have twice the number of absorbing species in the light beam. Should we again expect the absorbance to double?
The answer to this question was determined by Beer (in 1865) who found that for dilute solutions of many substances, the answer is yes. The result was an empirical law, now called the Beer-Lambert law. The law expresses the relation between absorbance \( \text{A} \), cell length \( \text{b} \) and concentration \( \text{c} \) of the absorbing species as:

\[
\text{A} = \varepsilon \text{c} \text{b}
\]

i.e., **absorbance is directly proportional to the cell length and concentration.**

When cell lengths are measured in cm and concentrations are measured in moles/L, the proportionality constant, \( \varepsilon \), is called the **molar absorptivity**. For substances that follow Beer’s law closely, the molar absorptivity at a specific wavelength is a constant for the substance in a specified environment—i.e., it is independent of the instrument in which the absorbance is measured. Beer’s law is equally applicable to gases and to many solids. It is also applicable to all wavelength ranges.

The consequence is that quantitative **concentration measurements** can be made by measurements of absorbance if a substance is known to follow Beer’s law. When substances do not follow Beer’s law, it is usually an indication that the nature of the chemical species change when concentration changes (e.g., through forming complexes or dimers, etc.). Indeed, deviations from Beer’s law are commonly used as evidence of such chemical changes.

Having defined absorbance, the most common way of displaying absorption spectra is by plotting absorbance, \( A \), vs. wavelength, rather than percent transmittance, %T. Figure 5-5 shows the absorbance corresponding to the transmittance shown in Figure 5-4.

![Figure 5-5](image-url)
Using Spectra for Quantitative Analysis

Beer’s law provides the basis for quantitative determinations of the concentrations of species that absorb electromagnetic energy in various frequency ranges. Since absorbance is proportional to concentration, we can relate quantitative measures of absorbance to concentrations if we know the proportionality constant. The proportionality constant consists of two parts—the molar absorptivity, $\varepsilon$, which is characteristic of the substance that absorbs the electromagnetic energy, and the second, the path length, which is a characteristic of the container (cell) that holds the absorbing substance. The molar absorptivity of any substance varies with wavelength. Figure 5-5 is typical of that variation. What frequency, or wavelength, shall we use? It is reasonable to expect that the larger the absorptivity (i.e., the larger the proportionality constant between absorbance and concentration), the more sensitive our measurement will be to variations in concentration.

The appropriate range of wavelengths is fixed first by the type of instrument we will use. It may, for example, be a visible spectrophotometer, or one capable of measuring ultraviolet absorption, or an instrument that measures infrared radiation.

Once we establish a wavelength range, the wavelength with the maximum absorptivity of a given substance in that range is called the analytical wavelength for the substance. We can determine that wavelength by taking a spectrum of the substance and finding a list of such wavelengths in a reliable reference.

Since cell construction varies considerably depending on the type of instrument, the safest way to determine the slope of Beer’s Law, is to determine the proportionality constant at the analytical wavelength by preparing a series of solutions of accurately known concentration of the substance under study. If Beer’s law applies, plotting the absorbance of these solutions as a function of concentration will provide a straight line graph whose slope is the desired proportionality constant. The resultant graph is called a Beer’s law plot. It assumes that the measured absorbance at each concentration is due to the desired substance and only the desired substance.
A sample of a Beer’s law plot is shown in Figure 5-6, below.

![Beer’s law plot](image)

**Figure 5-6.**

Note that the slope of the graph permits the conversion of absorbance values to concentrations and vice versa.

**Using Spectra for Qualitative Analysis**

A second general principle about absorption spectra is that they are **additive**, i.e., the spectrum of a mixture of substance A and substance B should show absorptions in all the regions characteristic of the two pure substances. Assuming that the substances do not undergo any chemical reactions, the relative intensities of the absorptions of each substance should be related to the relative amounts of each of the two substances in the mixture.

If each substance that could be in a mixture absorbs radiation in a unique region, examinations of each relevant region can be used to determine which substances are present in the mixture. The limits of detectability will depend on the intensity of the absorption (i.e., on its molar absorptivity).

**Infrared Spectroscopy and Molecular Structure**

We have noted earlier that energies characteristic of photons in the infrared region of the electromagnetic spectrum are associated with vibrations of molecules. The frequencies of vibration of atoms in molecules depend primarily on the masses of the atoms and the strength of the bonds between them. The maximum number of different frequencies with which a non-linear polyatomic molecule with N atoms can vibrate is given by $3N - 6$. This means that molecules with many atoms can, in principle, absorb many different frequencies of infrared radiation. It is found empirically
that the characteristic frequencies of certain groups of atoms that occur in many different molecules are, to a large extent, the same, independent of the molecule in which the group is found. This makes absorption in the infrared region particularly useful in identifying molecular structure. We will make use of this feature in some of the laboratory exercises. Table 5-2 summarizes the typical absorptions due to certain molecular fragments. The units used are the reciprocal of the wavelength, cm$^{-1}$. This quantity is proportional to frequency.

Table 5-2.

| IMPORTANT IR ABSORPTIONS (cm$^{-1}$) IN THE RANGE 1000 cm$^{-1}$–4000 cm$^{-1}$ |
|-------------------------------------------------|------------------|
| C — C (alkane)                                  | 1200             |
| C = C (aromatic)                                | 1600 & 1450–1500 (strong) |
| C = C (alkene)                                  | 1640–1680        |
| C ≡ C (alkyne)                                  | 2180             |
| C — Cl (organic chloride)                      | 600–830 (strong) |
| C — H (alkane)                                  | 2850–2960 (med–strong) |
| C — H (alkene)                                  | 3000–3100 (med–strong) |
| C — H (aromatic)                                | 3030–3050 (med)  |
| C ≡ N (nitriles)                                | 2210–2260        |
| C — O (alcohols)                                | 1050–1150        |
| C = O (acids, esters, aldehydes)                | 1680–1750 (strong) |
| C = O (amide)                                   | 1630–1690 (strong) |
| N — H (amines)                                  | 3300–3500        |
| O — H (acid)                                    | 2500–3100 (broad, strong) |
| O — H (phenol)                                  | 3200 (broad, strong) |
| O — H (alcohol)                                 | 3400–3650 (broad, strong) |

Figure 5-7 gives an example of the infrared absorption spectrum of the complex molecule carbon tetrachloride, CCl$_4$, with five (5) atoms and therefore, a maximum of 3 x 5 – 6 = 9 distinct absorptions. Note the number of detectable absorptions in the region displayed is different from 9. On the one hand, the actual wavelengths at which a complex molecule absorbs may include sums and differences of the 9 basic vibrations producing more than that predicted number. On the other hand, some of the vibrations may not give rise to absorption because the motion does not provide for an interaction with electromagnetic radiation. Note in particular the intense absorption at ~ 750 cm$^{-1}$. This is consistent with the C-Cl absorption frequency listed in Table 5-2.
The spectrum is displayed as %Transmittance vs reciprocal wavelength. This is a common practice for spectra in the infrared region.

![Figure 5-7: Carbon Tetrachloride spectrum.](image)

**Summary**

Absorption Spectroscopy is the study of the absorption of electromagnetic radiation (light) by matter. That absorption depends on:

- energy of the light,
- energy levels of the matter sample, and
- electric and magnetic properties of the matter sample.

The wavelength and frequency of light are related by $\lambda \nu = c$. They are related to the energy of light by $E = h\nu$.

The different types of motions of atoms and molecules and the nuclei and electrons in a sample of matter determine the ranges of wavelengths of light that it can absorb.

The absorbance of a sample is related to percent transmittance by $A = 2 - \log(\%T)$ and to its concentration by Beer’s law, $A = \epsilon c b$.

In the absence of chemical reactions, the spectrum of a mixture is the sum of the spectra of its components.