# CHAPTER 1

# Preliminaries
## A Review of Optical Physics

### 1.1 Introduction

The concentration of metal species in analytical laboratories has frequently been measured by observing an atom's interaction with electromagnetic radiation (e.g. light.) Since atomic species produce a unique line spectrum, the observation of these transitions can be used to both identify a particular metal (spectroscopy) and its concentration (spectrometry). While these terms are sometimes used interchangeably in common speech, spectroscopy is the *study of the interaction* of radiation with matter and the term spectrometry is applied to *the measurement of concentrations* of a compound (analyte). Before spectroscopic techniques or instruments are presented in the following chapters, it is important to review a general understanding of the ways electromagnetic radiation interacts with sample molecules.

An atom's interaction with electromagnetic radiation is critical in detecting its presence and concentration. It is necessary to manipulate the signal radiation to measure small concentrations of analyte. This is performed by placing optical components, for example a mirror or prism, in the path of the radiation to alter the property or path of the radiation. These devices will be discussed in the second half of this chapter, given their importance to various types of atomic absorbance spectroscopy (AAS) and inductively coupled plasma – atomic emission spectroscopy (ICP-AES). Once a general understanding of their function has been illustrated, the following chapters will illustrate how these components are utilized in series to achieve different purposes.

Before this discussion is initiated, it is necessary to become familiar with abbreviations that are commonly used in analytical laboratories. Given the length of many instrument's names, it has become common practice to abbreviate them. Liquid chromatography (LC) and nuclear magnetic resonance (NMR) are likely two of these acronyms that students should be familiar with from organic chemistry. The following table contains the common acronyms of instruments and techniques that are used to measure metal concentrations.

Table 1.1 Common Types of Spectrometric Analyses and Their Acronyms

| **Acronym** | **Technique/Instrument** |
|---|---|
| AAS | Atomic Absorption Spectrometry |
| AES | Atomic Emission Spectrometry |
| OES | Optical Emission Spectrometry |
| FAAS | Flame Atomic Absorption Spectrometry |
| FAES | Flame Atomic Emission Spectrometry |
| ICP | Inductively Coupled Plasma |
| ICP-AES or OES | Inductively Coupled Plasma-Atomic Emission Spectrometry (Optical Emission Spectroscopy) |
| ICP-MS | Inductively Coupled Plasma-Mass Spectrometry |

## 1.2 The Interaction of Electromagnetic Radiation with Sample Molecules

Various types of interactions (both absorption and emission spectrometry) are utilized to measure the concentration of metal analytes. Despite these different techniques, they both rely upon the excitation of valence electrons. This is caused by the absorption of energy from a collision or energy from a photon.

The absorption of a photon by a chemical species occurs when electromagnetic energy is transferred to the chemical species. In all cases these transitions are wavelength specific, meaning that the energy of the photon must very closely match the energy of the electronic transition. For a given molecular species the energy is the sum of the electronic, vibrational, and rotational energies. However, an atomic species cannot undergo vibrational or rotational excitations since there are no chemical bonds, thus only electronic energy levels are shown in the figure below. After a transition occurs, a number of relaxations can be measured for a wide variety of analytical purposes. For the purposes of this text, only electronic transitions are discussed in determining the presence and concentration of a metal analyte. Figure 1-1 below summaries the possible ways an energy excitation could occur in an atomic (or molecular) species. Recall that the difference in two adjacent energy levels is not constant but is instead a function of the type of transition. For example, moving up an electronic energy level requires more energy than moving up a single vibration or rotational level. If a photon is not absorbed by a chemical species, it is transmitted through a sample and is left unaltered by the sample media.

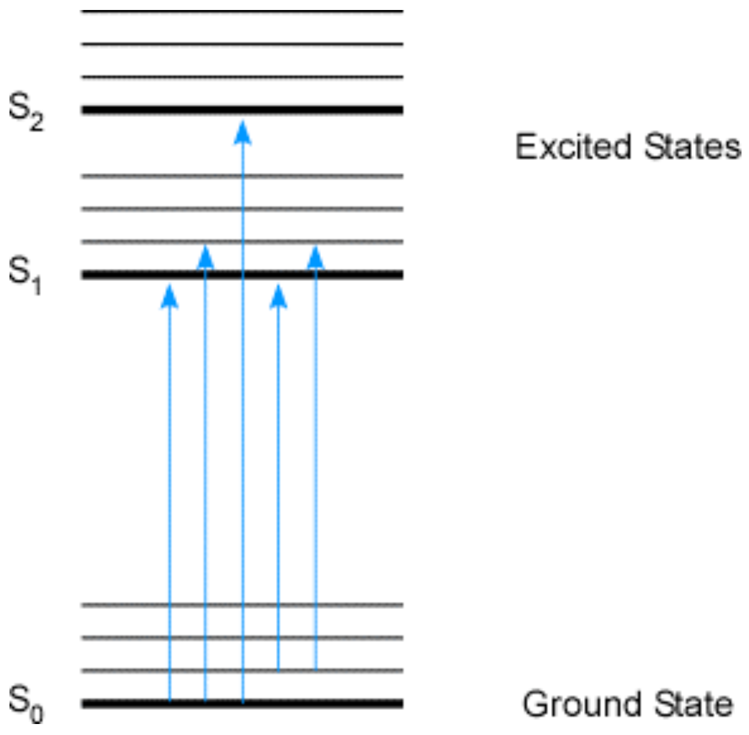

Figure 1-1. A Jablonski Diagram Showing Electronic Energy Transfer Levels for Singlet States in Atomic Species. (S represents the electronic energy level of a singlet electron; the smaller lines above each electronic energy lines represent possible rotational levels)

The energy of electromagnetic radiation utilized in the analytical technique must match the energy of the transition of interest. It is important to recall the energy/frequency/wavelength associated with different types of radiation described in Figure 1-2. Table 1.2 summarizes the usual energy transitions that result from each type of radiation. The analytical techniques discussed in this text usually only utilize UV or visible radiation, since these photons have sufficient energy to excite valence electrons in atomic species.

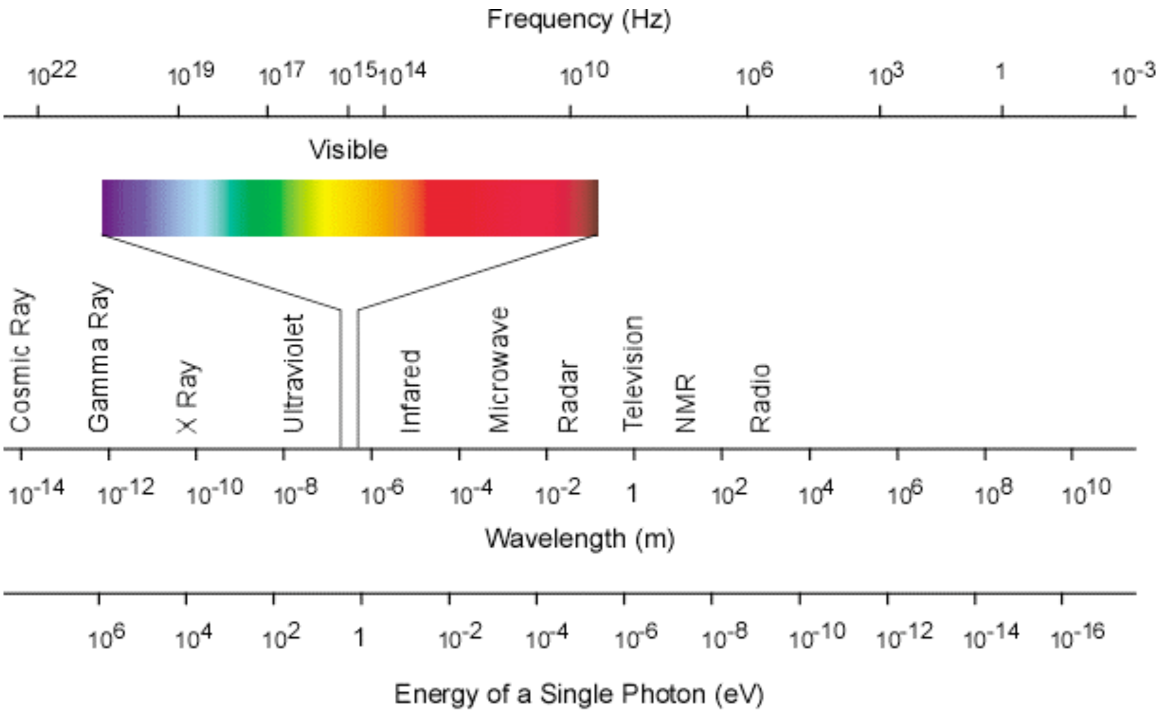

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Figure 1-2 The Electromagnetic Spectrum.

Table 1.2 Typical Atomic and Molecular Energy Transitions Associated with Each Type of Photon and Photon Wavelength.

| | | |
|---|---|---|
| x-rays | Angstroms to 0.1 nm | Can promote or remove inner (core) electrons |
| Vacuum UV | 10-190 nm | Can break molecular bonds. Results in the removal or promotion of electrons to excited states |
| UV | 190-300 nm | Can break molecular bonds. Results in the removal or promotion of electrons to excited states |
| Visible | 350 to 800 nm | Results in the removal or promotion of electrons to excited states |
| IR | 0.8-300 μm | Increases the amplitude of vibrations |
| Microwaves | ~1-4 mm | Increases the rate of molecular rotation |

The other factor that determines the wavelength of a given absorption is the type of atomic species. For example, Figure 1-3 shows the possible electronic transitions of a 3s electron of atomic sodium. The most likely transitions are indicated by the thicker yellow lines at 589.0 and 589.6 nm. These spectral lines are utilized for analytical measurements and are so intense that they can be observed by the human eye. Yellow light is emitted when sodium-containing compounds are placed in a common flame. These sodium atoms are excited by the flame and subsequently relax by releasing a photon which is then observed by our eye. These types of electronic transitions and energy relations should be familiar to the reader from basic first-year general chemistry principles where fundamental equations such as

$$c = \lambda\ \upsilon, \text{ and}$$
$$E = \upsilon\ h$$

were used in combination with Bohr's equation (for hydrogen)

$$E = -Rhc\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where E is energy, c is the speed of light in a vacuum, $\lambda$ is a photon's wavelength, $\upsilon$ is a photon's frequency, h is Planck's constant, R is Rydberg's constant, $n_i$ is the initial electronic energy level, and $n_f$ is the final electronic energy level. Thus, electronic transitions such as $n_1$ to $n_2$, can be related to energy, frequency, and wavelength by the equations given above.

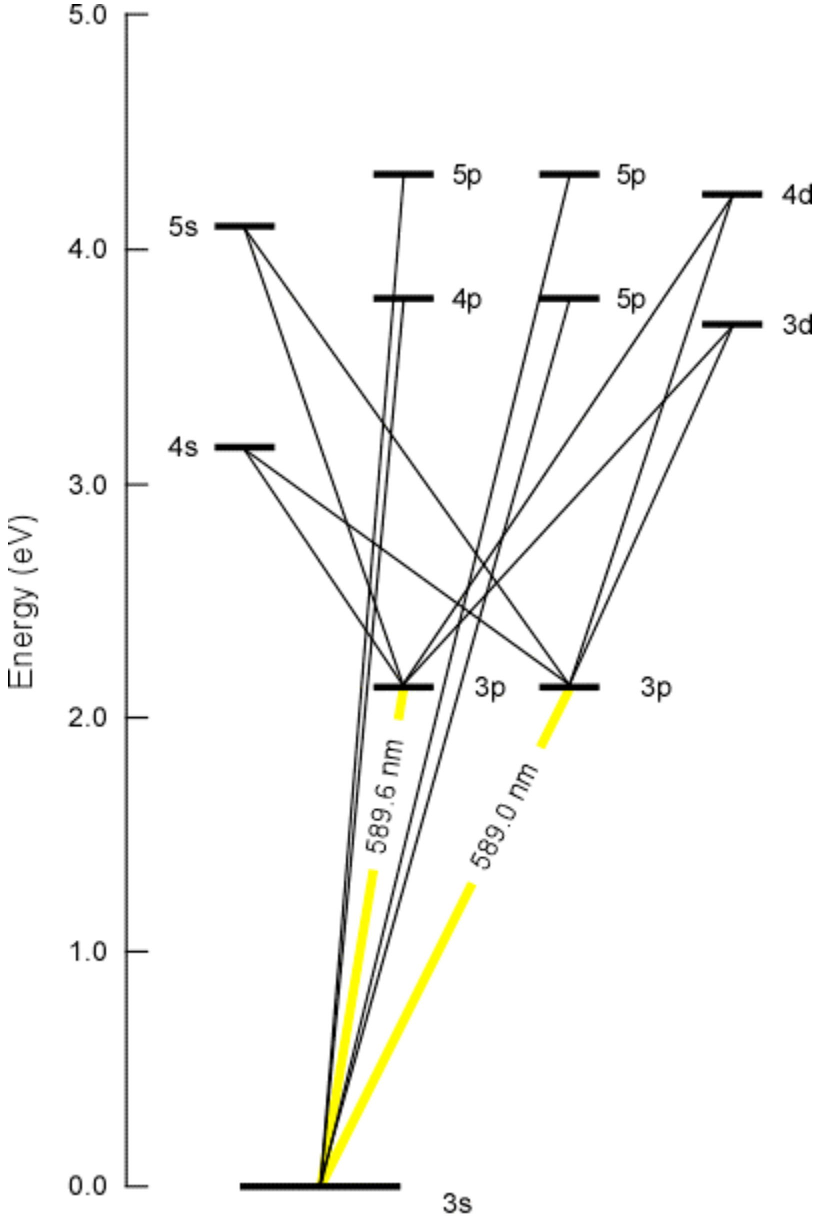


Figure 1-3. Possible Electronic Transitions for a 3s Electron in a Sodium Atom. (Note the two different 3p energy levels, one with a higher energy for j=3/2 and a lower energy with j=1/2).

The possible transitions shown in Figure 1-3 are specific to a particular element and such a diagram can be constructed for every metal. When energy (or a photon) corresponding to a specific transition is absorbed, the electronic state is changed (i.e. from 3s to 3p). Some metals have only a few likely electronic transitions while others will have more. Usually, the most prominent wavelength produced by this transition is used in instrumental absorption and emission measurements. Atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) are only concerned with the absorption of a photon by a ground state atomic species, and the emission of photon from a singlet electronic level.

This absorption of a photon is one potential way that FAAS will produce signal data. Sometimes, the absorbance of a sample is converted to transmission by the following equation:

$$\text{Absorbance} = -\log(\text{Transmission})$$

$$\text{Transmission} = \frac{I}{I_0}$$

where I is the intensity of light passing through a sample and $I_o$ is the intensity of light passing through a blank sample (reference sample cell).

In addition to absorption and transmission of photons, scattering of UV/visible radiation is another common interaction of electromagnetic radiation with matter. The scattering of radiation by large molecules or small particles can be a very useful phenomenon, and is the basis for other analytical techniques such as Raman spectroscopy or photocoupled spectroscopy, respectively. However, for the instruments discussed here, photon scattering is a detriment to analytical measurements since it reduces the intensity of radiation that interacts with a sample. Scattering is caused when the electric field of a photon interacts nonresonantly with the energy level structure of an atom or molecule. Scattering is a problem when stray photons occasionally reach the detector creating a false analyte signal. In optical spectrometry, scattered light is prevented from reaching the detector by non-reflective black surfaces inside the instrument, and by enclosing the detector in a separate compartment.

### 1.2.1 Correlating Absorbance to Concentration

For the majority of metal analysis performed by AAS, the absorbance A of a beam of photons is measured by a detector. In order for this signal to be useful, this physical process must be correlated to the concentration of the analyte of interest. This can be accomplished by Beer's law

$$A = \varepsilon\ b\ C$$

where $\varepsilon$ is the molar extinction coefficient (a measure of the absorbance of a particular chemical or chromophore), b is the cell path length (usually 1.0 cm), and C is the molar concentration of the analyte. Beer's law, as shown above, is the result of some mathematical simplifications that are only applicable over absorbance ranges from 0.000 (100 percent transmission) to approximately 2 (1 percent transmission). This limitation is usually enforced by sample preparation techniques that concentrate or dilute the sample to values within the acceptable range. Also note that Beer's law only governs absorption. Emission measurements are not limited from 0.0 to 2.0 "absorbance" units. In emission spectrometry the intensity of the emitted light is typically measured in units of counts per time.

The difficult task of measuring low concentrations of an analyte requires the reduction of instrumental noise to a minimum level (Section 2.2.10). Ideally, instruments would only measure the exact wavelength that the given analyte absorbs. However, the light that reaches the detector is not always spectrally pure due to various imperfections in instrumental components and due to interactions with instrument components. The slit width of the monochromator (a common instrument component used to select for a specific wavelength of electromagnetic radiation) limiting the bandwidth must be wide enough to allow enough radiation in to produce a sufficient signal (over the noise), but be narrow enough to provide sufficient wavelength resolution. If the entrance slit is too wide, other wavelengths can create background noise in the signal, creating a non-linearity in the calibration. These two conflicting needs are balanced by selecting a proper exit slit width in the monochromator.

### 1.2.2 Relaxation Processes:

The absorption of a photon by an atom or molecule results in the creation of an excited energy state. Given that this atom or molecule would prefer to exist in the ground state, the energy that was absorbed is quickly dissipated by various pathways of relaxation, or (rarely) by breaking a bond. While the instruments that are described in this Etextbook produce atomic species from molecular ones with a variety of heat sources, they do not use electromagnetic radiation for atomization (the creation of gaseous). Instead they produce atomic species from organic or inorganic molecules in a flame or plasma. Nonradiative relaxation, emissions, fluorescence, and phosphorescence are all types of relaxations that occur without breaking a bond. For purposes of clarity, it should be noted that while some of these relaxations are not analytically useful for the techniques described here, they are of importance in other spectroscopic techniques. Some of these are only relevant to molecular spectrometry, while others are relevant to both atomic and molecular spectrometry. For completeness, all three will be described in this text.

Nonradiative relaxations are not completely understood, but occur through the transfer of very small amounts of energy through molecular or atomic collisions. These result in the generation or transfer of heat energy, but do not cause the emission of a UV or visible photon. Emission of a photon that has the same amount of energy as the absorbed photon is also a very common form of relaxation.

Fluorescence is a relatively rare form of relaxation in polyatomic compounds. Fluorescence occurs when an analyte is excited to a higher energy state by the absorption of a photon. The molecule then undergoes a vibrational relaxation (again, in polyatomic compounds) to a lower vibrational state within the same electronic state. Fluorescence emission occurs when the electron falls from one excited electronic state back to the ground electronic state (a singlet to singlet transition). This type of transition occurs since most vibrational transitions occur faster ($10^{-15}$ to $10^{-12}$ seconds) than electronic transitions (around $10^{-8}$ seconds). Since the vibrational relaxation emits energy in the form of heat, the energy of the fluorescence emission is lower (and consequentially the wavelength is longer) than the absorbed energy. This is illustrated in Figure 1-4. Measurements of fluorescence usually yield detection limits that are from one to three orders of magnitude more sensitive than typical absorption or emission detection limits. The lower detection limits are due to lower background noise, since the exciting radiation is not detected in the analytical measurement.

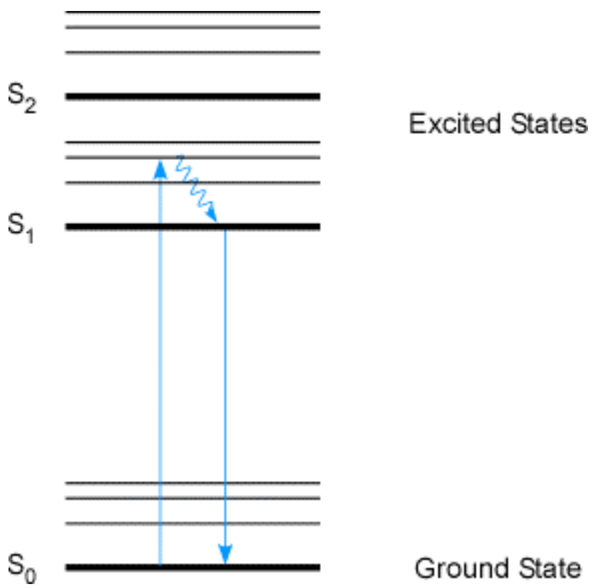


Figure 1-4. A Jablonski Diagram Illustrating Fluorescence Decay in a Molecular Species. (Bold lines are electronic transition states while lighter shaded lines represent vibrational transitions)

Phosphorescence occurs when a radiationless vibrational transition occurs between two different spin states (for example from a singlet ($S_1$) to a triplet ($T_1$) excited state). After this spin forbidden transition, another spin forbidden transition from the excited state to the singlet state must occur (from a triplet to singlet state in Figure 1-5). Phosphorescence transitions are easy to distinguish from fluorescence since they occur much more slowly; fluorescence occurs over time scales of $10^{-5}$ seconds while phosphorescence occurs over time scales of minutes to hours since spin forbidden transitions have a low probability of occurring (a low transition rate).

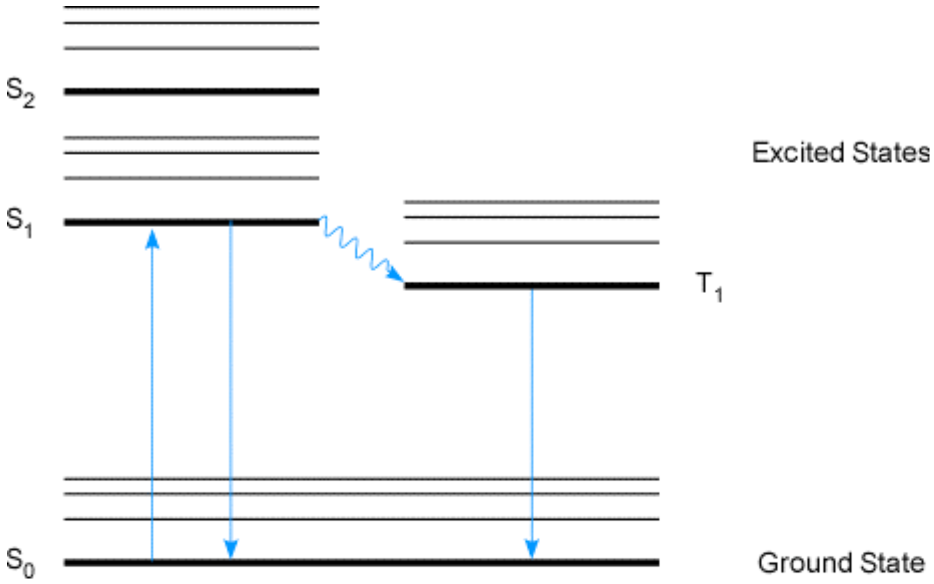


Figure 1-5. A Jablonski Diagram Illustrating Phosphorescence Decay in a Molecular Species.

In molecular spectroscopy fluorescence and phosphorescence instruments, the incident (source) radiation never reaches the detector. Instead the detector aperture is orthogonal (90 degrees off set) to the source lamp's path in order to reduce background noise from the incident source light. Source light is focused through a sample and generally passes straight through, with the exception of scattered radiation. Fluorescence and phosphorescence are emitted from the sample at all angles, so orientation of the detector at 90 degrees minimizes the source light scattered to the detector. A very useful technique is possible with phosphorescence, since emission can still be detected after the source lamp is turned off. It is possible to place a shutter between the excited sample and the detector. The shutter is opened after the source lamp is turned off and phosphorescence is occurring. This allows the detector to measure only phosphorescence. Phosphorescence has no use in atomic spectrometry, but can be used for the analysis of metals in polyatomic states, such as those occurring for uranium oxide species.

For quantification of fluorescence (F) and phosphorescence (P) of polyatomic species, Beer's law is slightly modified to

$$F \text{ or } P = I\,\Phi\,\varepsilon\,b\,C$$

where I is the intensity of radiation passing through the sample, $\Phi$ is the yield of fluorescence or phosphorescence (or how much of the source radiation is converted to fluorescence or phosphorescence), $\varepsilon$ is molar extinction coefficient, b is the cell path width, and C is the molar concentration.

Other forms of fluorescence are possible, but they involve molecular vibrational relaxations that are not relevant to atomic species. One common type of florescence is referred to as "resonance fluorescence". This occurs when an electron in the ground state is excited to a higher energy state by a photon whose energy is nearly resonant with the transition energy. This is followed by the emission of a photon of the same energy as the electron relaxes (basically a normal absorption/emission process; this is the same type of emission that was discussed earlier). Emission of a photon from resonance fluorescence almost always occurs in absorbance spectroscopy, but is usually not relevant because the fluorescence intensity is relatively weak in comparison to the intensity of the light source. Two other types of florescence occur that cause the emitted photon to have less energy than the absorbed photon. ”Direct line fluorescence” is when an electron is excited to an upper energy level ($S_3$) and emits a photon to go to a lower energy level ($S_2$) that is not the ground state. "Stepwise line fluorescence" occurs when an electron is excited to a higher energy state ($S_3$), and relaxes to $S_2$ by some form of nonradiative relaxation, followed by a photon emission to return to the ground state.

## 1.3 The Interaction of Electromagnetic Radiation with Surfaces

In addition to the interactions between electromagnetic radiation and samples, the analyst must also be concerned with interactions between electromagnetic radiation and the components of the instrument. Most of these interactions are a result of the instrument design and help ensure proper function. At the most basic level these components also act like the sample molecules; they can potentially absorb electromagnetic radiation. The absorptive properties of black surfaces are utilized to absorb scattered light to prevent it from generating noise. However, some of these interactions will act in a detrimental way to interfere with the proper operation of the instrument. The absorption of light by any component in the path of the radiation would detrimentally affect the accuracy of the measurement.

1.3.1 Reflection: Mirrors are used to direct the beam of electromagnetic radiation in specific directions. Curved mirrors can be used to ensure that the beam is focused on the components of the instruments such as monochromator slits and the detector. In addition to mirror reflections, reflection also occurs any time electromagnetic radiation passes from a medium with one index of refraction into a medium with a different index of refraction. The amount of reflection tends to increase as the difference in refractive indexes between two adjacent media increases. The refractive index is defined as

$$\eta_i = \frac{c}{c_i}$$

where c is the speed of light in a vacuum and $c_i$ is the speed of light in a specific medium; thus, refractive index values in normal materials are always greater than or equal to 1.00. The refractive index will be important in the following sections on reflection and dispersion.

For dielectric (non-conducting) materials, as the difference in refractive indexes between two media increases, more reflection occurs. For a beam of light entering an interface at a right angle, the fraction of radiation reflected is calculated by

$$\frac{I_r}{I_o} = \frac{(\eta_2 - \eta_1)^2}{(\eta_2 + \eta_1)^2}$$

where $I_r$ is the reflected intensity, $I_o$ is the intensity of the incoming beam, and $\eta_1$ and $\eta_2$ are the refractive indexes of the two media. The mathematical formula for metal surfaces is more complicated but the basic principle of reflection is the same.

Reflective surfaces are also present in grating systems. Common mirrors create a phenomenon that is referred to as “ordinary reflection” where an object is seen as it reflects off a mirror (Figure 1-6). Grating systems utilize higher-order diffraction arising from wave interference that will be discussed in more detail in (Section 1.3.2). Ordinary reflection can be thought of effectively as zero-order diffraction.

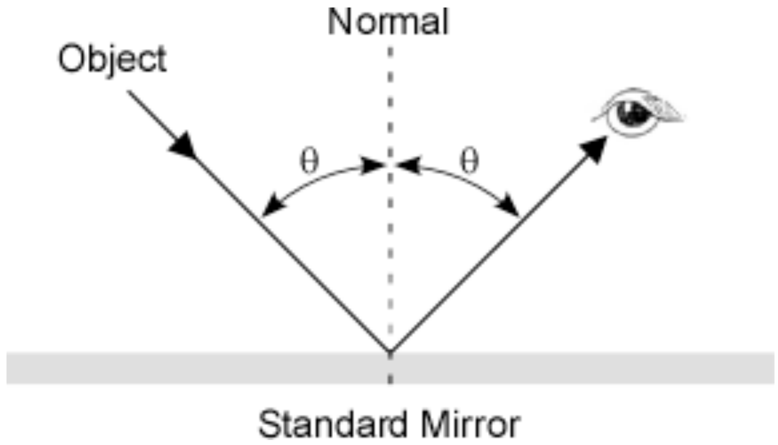
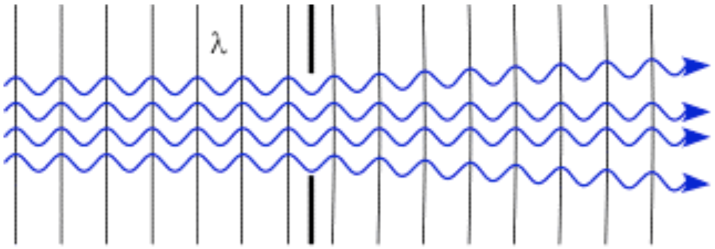


Figure 1-6 Ordinary Reflection (zero-order diffraction).

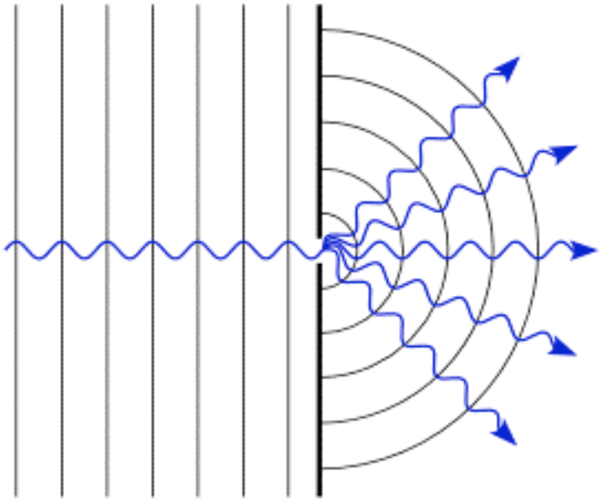
Reflection can also be a detriment to optimal instrumental function at the surfaces of sample containers and lenses. As the radiant light passes through the glass, the difference in refractive index of glass and air can cause reflection, which subsequently lowers the amount of incident radiation reaching the sample. Changes in the refractive indexes between these media can be overcome with the use of sample blanks and dual beam instruments (a reference light beam and a sample beam). The problem is more serious with reflective surfaces in the instrument. The composition of reflective surfaces and coatings are selected to minimize reflective losses. Reflection can decrease the source intensity since some of the light is lost. In these cases, reflection decreases sensitivity and detection limits, due to a loss of radiant intensity of the wavelength of interest.

1.3.2 Diffraction: Diffraction is a process in which a collimated beam of radiation spreads out as it passes (1) though a narrow opening or (2) by a sharp barrier. An interesting distraction effect was observed in a laboratory setting by Thomas Young in 1801 when he performed the two-slit experiment (discussed below). Because diffraction depends on the wavelength of light, it can be used to separate polychromatic light (white light) into its constituent optical frequencies; in the case of white light, this would result in a rainbow of colors. The manipulation of diffraction forms the basis of selecting a narrow range of wavelengths of light in a monochromator.

In order to more easily understand how diffraction can be used to disperse wavelengths, picture the passage of radiation through a narrow barrier. Figure 1-7 illustrates such a barrier. As the slit width narrows waves of radiation spread out more strongly. The Heisenberg Uncertainty Principle indicates that as the uncertainty in the position of a photon decreases (in a direction transverse to its propagation direction), the uncertainty in its transverse momentum must increase; this uncertainty in transverse momentum is what causes the light to spread out. When the slit is sufficiently wide, the diffraction is small because there is still great uncertainty in position (Figure 1-7a). As the slit becomes more narrow (Figure 1-7b), the uncertainty in position becomes smaller which results in greater diffraction.



Slit Width >> λ



Slit Width ≈ λ

Figure 1-7. Variation in Slit Width Openings.

Diffraction is intimately related to the constructive and destructive interference of waves. Start by considering monochromatic electromagnetic radiation passing through two slits (Figure 1-8). The monochromatic light is passing through one narrow slit before being passed through two more slits. As radiation is passes through the second slits, diffraction occurs at both slits creating two beams that spread out and overlap. Constructive and deconstructive interference between these beams can be observed on a flat plate (a detector in this case). Regions on the detector in which the path length difference between these two waves is an integer multiple of the wavelengths constructively interfere and produce a large intensity. Positions on the detection plate that correspond to odd integer multiples of half a wavelength create deconstructive interference, with no resulting intensity. Overall the intensity distribution on the detector varies sinusoidally, with high intensity corresponding to constructive interference, and zero intensity corresponding to destructive interference. Each of these situations is illustrated in Figure 1-8.

If the two slits are replaced by many narrow, equally spaced slits (i.e. a diffraction grating) the regions of constructive interference become very narrow. Instead of a sinusoidal variation in intensity, a series of narrow bright bands appears on the detector.

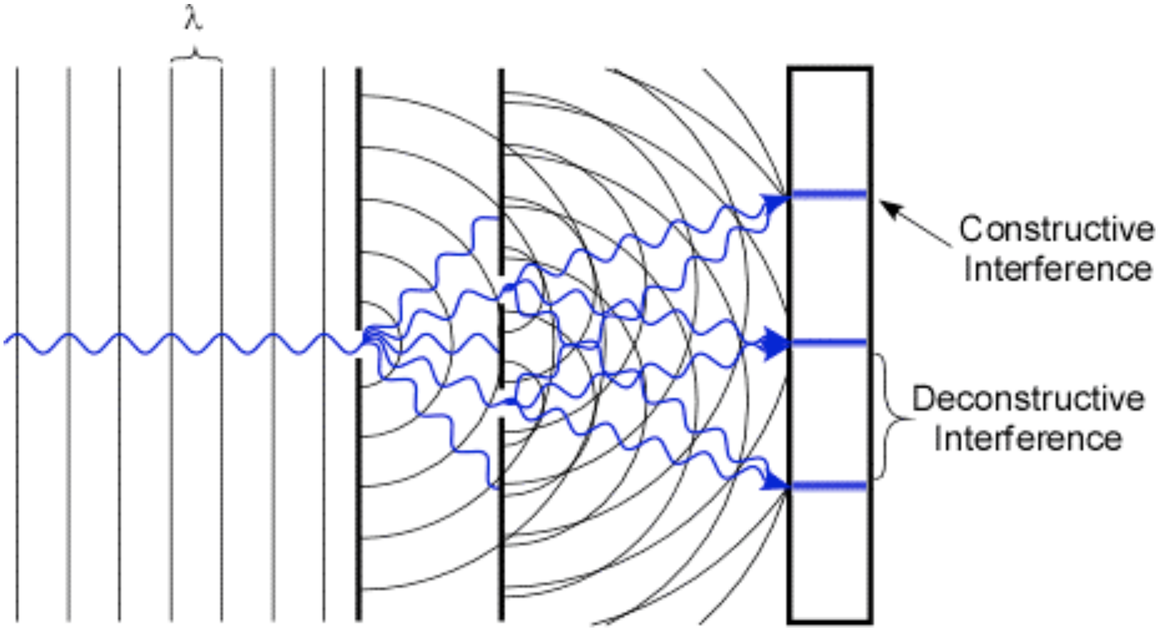
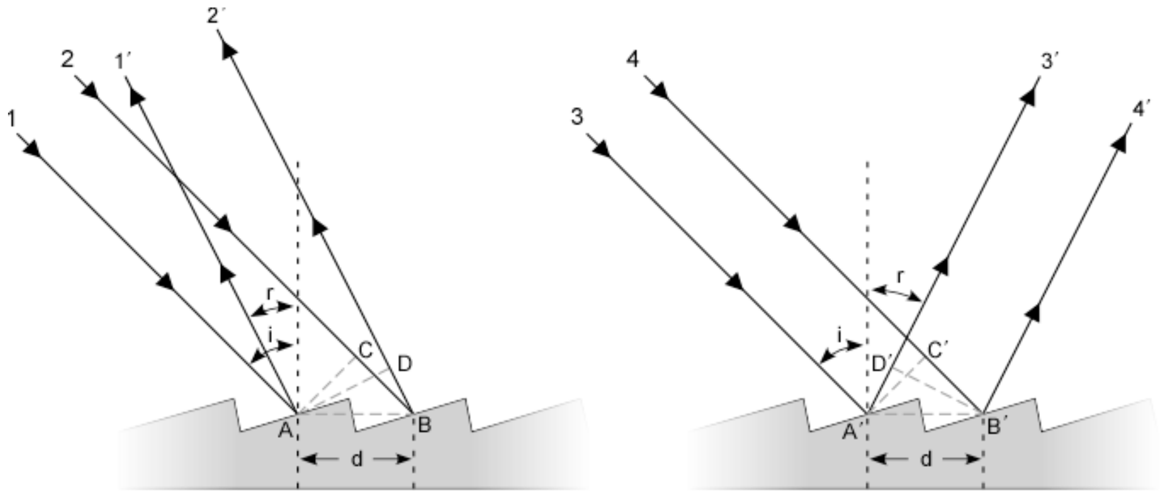


Figure 1-8. An Idealized Illustration of the Two-Slit Experiment Illustrating the Constructive and Deconstructive Nature of Electromagnetic Radiation. Distinct bands are show here for illustrative purposes only; the bands are actually broader areas of light (constructive interference) that gray to areas with no light (deconstructive interference). The blue lines above correspond to the alignment of maximum constructive interference.

The above discussion was for monochromatic radiation. If the concepts in Figure 1-8 are extended one step further and polychromatic light is used, the different colors of radiation are separated. All of the different wavelengths will constructively interfere in the center of the detector. However, since each color has a specific wavelength, the locations of the other interference maxima depend on the wavelength. As a result, two “rainbow” spectra of light will be centered around the top and bottom constructive interference lines shown in Figure 1-8.

While the diffractive properties of multiple transmissive slits could be utilized in analytical instruments, this would result in the creation of very narrow, but long instruments. As a result, mirrors that also create diffraction are utilized to make instruments more compact. They do this by bending light at a sharp angle, as observed below in the case of reflection grating monochromators. The principle is the same as a transmission grating; each of the sawtooth shaped steps in Figure 1-9 (referred to as a blazed surface) acts as a “slit”. Waves are diffracted off of each of these slits, and wavelength dependent constructive and destructive interference creates a rainbow spectrum in reflection. Monochromatic light is used for illustration purposes here to lessen the complexity of the figure. However the principles discussed below for a single wavelength apply to a mixture of wavelengths.



$n\lambda = d(\sin(i) + \sin(r))$ $n\lambda = d(\sin(i) - \sin(r))$

Figure 1-9 Diffraction Resulting from a Echellette (Conventional) Grating.

Typically radiant waves constructively interfere in two directions (+1 and -1) depending on the incident angle of incoming radiation and the grating spacing d. These two directions are analogous to the upper and lower constructive interference bands in Figure 1-8. There is one more complication that has been added to Figure 1-9, in Figure 1-8 incident radiation was perpendicular to the slits (parallel to the grating normal), whereas in Figure 1-9 incident radiation makes an angle i with respect to the grating normal (the dashed vertical line in Figure 1-9). Radiation will be diffracted to the left and to the right of the grating normal; these will be mathematically characterized below separately for two types of grating surfaces. The left-of-normal diffraction will be discussed first (the left-hand figure). The lower right-hand diagonal lines 1 and 2 are incoming monochromatic radiation and the upper right-hand diagonal lines 1’ and 2’ are the diffracted monochromatic radiation.

The basis of the following derivation is that in order for constructive interference to occur the path length differences between waves from adjacent slits must be an integer number of wavelengths. Before beginning the derivation it is first necessary to define the problem and parameters. The line “d” is the distance between corresponding points on each grating line (a grating surface contains numerous blazed parallel lines of reflective material, in this case points A and B). Line segments AC and AD are the distances at 90-degree angles from the point of diffraction to the diffracted wave on the next grating surface (parallel ray). The maximum constructive interference will occur at the diffracted angle "r" where the path length difference between rays 1 and 2 is an integer number of wavelengths. As shown in Figure 1-9, ray 2 travels a greater distance than ray 1 and the difference in the paths is equal to the addition of line segment distances CB and BD. Again, in order for constructive interference to occur, the path difference (CB + BD) must be equal to the wavelength times an integer (n, not to be confused with the index of refraction), thus

$$n \lambda = (\overline{CB} + \overline{BD})$$

The integer n is referred to as the diffraction order and λ is the wavelength of interest. Observe that the angle of CAB is equal to angle "i" and the angle DAB is equal to "r". From basic trigonometry principles, we obtain

$$\overline{CB} = d \sin(i)$$

and

$$\overline{BD} = d \sin(r)$$

where d is the distance between points A and B on two adjacent blazed surfaces. By substituting these two-line segment equations into the previous equation, we obtain the governing equation correlating the angle of reflection to wavelength

$$n \lambda = d(\sin(i) + \sin(r)) .$$

This is called the grating equation.

A similar diffraction pattern can occur in the opposite direction (to the right in Figure 1-9). As drawn in this figure, the low blazing angles will result in a higher intensity of reflected light to the right as compared to the light reflected in the left-hand side of Figure 1-9; this occurs due to the ordinary angle of reflection off of each surface being equal to the diffraction angle, and the intensity is maximized. In this case, illustrated in the right-hand side of Figure 1-9, rays 3 and 4 entering from the left are reflected at the surface angles i plus r. Using line segments A', B', C', and D' a similar mathematic derivation can be made for the constructive interference shown by lines 3' and 4' as was made earlier for the left-hand side of Figure 1-9. This can also be derived by noting that the integer n, can have plus or minus values of 1.

$$\begin{aligned}
&d \sin i = \overline{CB} \\
&d \sin r = \overline{AD}, \\
&n\,\lambda = (\overline{CB} - \overline{AD}), \text{ thus} \\
&n\,\lambda = d(\sin(i) - \sin(r))
\end{aligned}$$

Thus, constructive interference can occur at a negative and a positive angle, relative to the normal plane, and is indicated by a plus and minus sign in the governing equation, respectively.

$$n\,\lambda = d(\sin(i) \pm \sin(r))$$

A positive sign results when the incident and diffracted beams are on the same side of the grating normal line (the vertical line in the middle of each grating), with the converse for a negative sign. It should be noted again that the angle of diffraction is highly dependent on the angle of the incoming incident radiation and the wavelength of radiation. This will be important when different types of grating monochromators are discussed in Chapter 2.

The diffraction pattern illustrated in Figure 1-9 for monochromatic light is the same concept as that illustrated for the two-slit experiment described in Figure 1-8. Both the slit and each individual blaze behave as point sources of light. Both systems cause constructive interference when radiation from each blaze or slit travels the same distance or a distance that is an integer multiple of the wavelength (nλ). When polychromatic light is reflected by a grated surface as shown in Figure 1-10, a "rainbow" dispersal of wavelengths would occur on the surface of the detector. Subsequently, each wavelength of the rainbows is collimated with a collimating mirrors (or lens) and focused onto a sample container or instrumental component, such as the entrance slit to a detector.

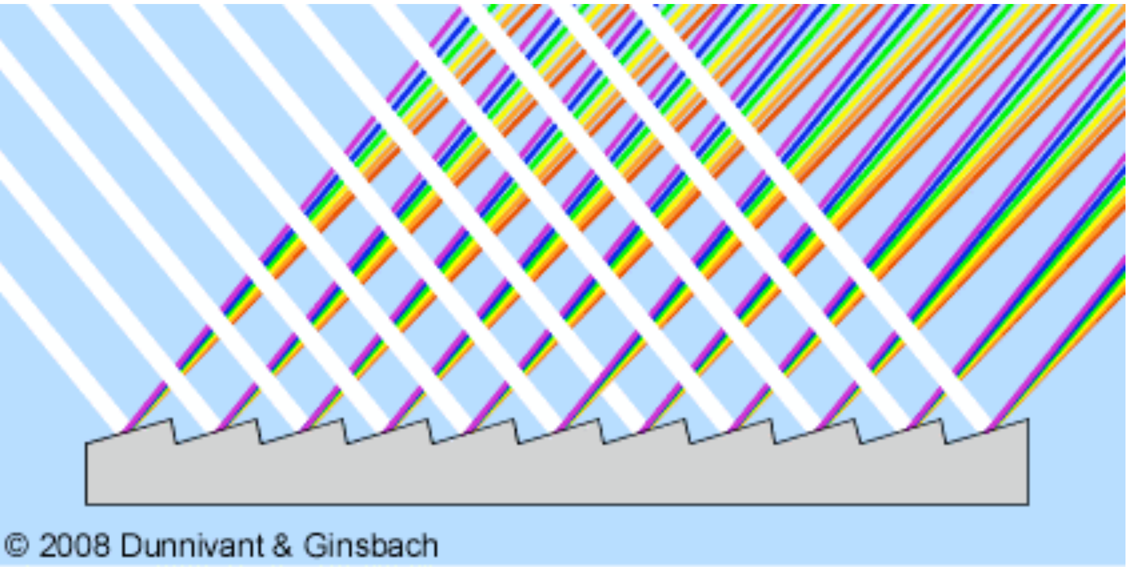


Figure 1-10. Separation of White Light by a Grating Monochromator.

Further analysis of the governing equations given above indicates that several wavelength solutions exist for each diffraction angle r, depending on the integer n, referred to as the order of diffraction. The first wavelength, referred to as first-order diffraction is (n=1), is always the longer wavelength (i.e. 400 nm), with second-order diffraction being half the wavelength (i.e. 200 nm), and so on. Fortunately for our purposes of obtaining as pure radiation as possible (with respect to wavelength) usually more than 90% of the incident intensity is first-order diffraction. When second-order and third-order diffraction is a problem these wavelengths can be removed with a secondary filter or second monochromator (as presented in Chapters 2 and 3). In some cases, such as in the presence of high concentrations of analyte, second- and third-order diffraction is used for quantification since the corresponding wavelength is less intense and will not damage the detector.

For an Echellette grating, high dispersion (separation of wavelengths, which is desired) is obtained by making the groove width d as small as possible (having a high number of grooves or blazes) and by making the focal length large (the focal length is the distance between the monochromator or the focusing lens and the exit slit). However, achieving high dispersion is difficult since a large focal length results in a reduction in light intensity and dense gratings are relatively expensive to produce. Improvements in resolution result if the blaze angle is made steeper (called an Echelle-style grating), and a correspondingly large value for the diffraction order (n~100) is used. In the typical Echelle grating configuration the angles r and i (in Figure 1-9) are now approximately equal, and r or i is represented by $\beta$. For this situation, the governing equation reduces to

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

The Echelle grating achieves higher dispersion while maintaining high diffraction intensity by making the angle $\beta$ and the order of diffraction (n) large (i.e. by increasing the blaze angle and diffraction order). Echelle gratings have fewer blazings (grooves) than Echellette gratings. Again, while the previous normal grating resulted in first, second, and third order diffraction (n=1,2,3), n values for an Echelle are much larger (75th to over 100th ). For example, as shown in Table 1.3, a diffraction order of 1 for a normal grating correlates to n=75 for an Echelle grating. This higher order of diffraction is selected for by increasing the blaze angle to maximize the reflection of radiation at the 75th order of diffraction. This results in superior resolution of spectral lines over conventional grating systems. For example in a conventional grating the emission lines of Zn (at 202.55 nm) and Mg (at 202.58) overlap and cannot be resolved. In the Echelle grating, considerable baseline resolution is achieved for these two spectral lines.

Table 1.3. Comparisons of Figure of Merit for Echellette and Echelle Grating Monochromators.

| **Feature** | **Echellette (Conventional) Grating** | **Echelle Grating** |
|---|---|---|
| Focal length (m) | 0.5 | 0.5 |
| Groove density (grooves/mm) | 1200 | 79 |
| Angle of diffraction | $10^{o}$ 22’ | $63^{o}$ 26’ |
| Width of grating (mm) | 52 | 128 |
| Order of 300 nm | 1st | 75th |
| Resolution at 300 nm | 62 400 | 763 000 |
| Linear dispersion at 300 nm (mm/nm) | 0.61 | 6.65 |
| Reciprocal linear dispersion at 300 nm (nm/mm) | 1.6 | 0.15 |
| f-number | f/9.8 | f/8.8 |

Source: Keliher and Wohlers, Anal. Chem., 1976, 48, 333A

Echelle grating monochromators can produce highly pure spectral separations of radiation; these will be used in applications in the next two chapters where a combination of dispersive devices (prisms, Echelle, and Echellette gratings) are used to separate wavelengths of light. The use of an Echelle grating will allow more powerful imaging and detectors to be used in emission spectrometry where spectral overlap can be a problem. The wavelength separations in combined gratings systems are nearly as pure as the emitted radiation from a hollow cathode lamp, which will minimize most spectral interferences from the flame emissions or from the absorption and emission of other elements in the sample. Grating monochromators are the heart of modern absorption (AAS) and emission (AES) instruments.

1.3.3 Dispersion: Dispersion has been alluded to several times in the previous discussions, but a more formal description will be provided here. First, dispersion is the separation of polychromatic radiation by a material that alters the velocity of a wave based upon its frequency. Dispersion can be both an important tool as well as a nuisance. For example, some mirrors are coated with polymers to protect them from corrosive environments. If this coating disperses different wavelengths of light, it can deteriorate the integrity of the light by acting like a prism (and separate wavelengths even further).

The positive aspects of dispersion occur in prisms, where separation of wavelengths of light is desirable. When a change in refractive index occurs at an interface between substances in the path of a beam of radiation the net affect is a bending of the light. This bending results from the fact that the waves travel at different speeds in the two substances. Because the amount of bending depends on the speed, and different wavelengths have different speeds, different wavelengths of radiation (light) bend at different angles at the interface. The net result is a separation of wavelengths.

Devices that separate light, such as monochromators and prisms are "rated" by their ability to separate wavelengths, with a number of parameters to quantify their resolution. If the equation, derived above, that describes the constructive interference of radiation

$$n \lambda = d(\sin i \pm \sin r)$$

is differentiated while holding i constant, the angular dispersion of a grating can be obtained

$$\frac{\Delta r}{\Delta \lambda} = \frac{n}{d \cos r}$$

This equation relates the angle of diffraction to the wavelength, referred to as angular dispersion. This can be taken one step further by relating the angular dispersion to linear dispersion (D), a measure of the quality of the monochromator, by

$$D = \frac{\Delta y}{\Delta \lambda} = \frac{F\,\Delta r}{\Delta \lambda}$$

where F is the focal length of the monochromator (the distance between the monochromator grating to the exit slit). In this equation, the analyst is concerned with the variation of wavelength as a function of the distance along the line AB in the monochromator figure (Figure 1-8). A more useful measure of dispersion (and the quality of the monochromator) is the reciprocal linear dispersion ($D^{-1}$) that is commonly used by the manufactory industry

$$D^{-1} = \frac{\Delta \lambda}{\Delta y} = \frac{1}{F}\,\frac{\Delta \lambda}{\Delta r}$$

where $D^{-1}$ typically has values expressed in nm/mm or Angstroms/mm, and small numbers represent superior instruments.

Furthermore, substitution of the angular dispersion equation into the above equation yields the reciprocal linear dispersion, another figure of merit, for a grating monochromator

$$D^{-1} = \frac{\Delta \lambda}{\Delta y} = \frac{d \cos r}{n\,F}$$

From this equation it is evident that angular dispersion increases as the distance, d, between the parallel grating lines decreases (as the number of grating lines per millimeter increases). Typical numbers of parallel grating lines in monochromators range from tens to hundreds of lines per millimeter for IR wavelengths, to several thousands for UV/visible wavelengths.

Finally, the resolving ability (where R is the resolution) of a monochromator refers to its power to separate adjacent wavelengths, represented mathematically by

$$R = \frac{\lambda}{\Delta \lambda}$$

Values of R for UV-visible monochromators of interest here range from 1000 to 10 000. It can also be shown that R is related to the total number of illuminated grating lines by

$$R = \frac{\lambda}{\Delta \lambda} = nN$$

where n is the diffraction order, and N is the number of grating lines illuminated by the radiation of interest. The number of illuminated lines is usually determined by the width of the entrance slit to the monochromator, and the “f” number (f#) of the monochromator.

Decades ago, an analyst could request that a monochromator in an instrument be made to specific specifications based on reciprocal dispersion. However, today the above discussion of figures of merit is only of educational interest, as only a limited number of instrument variations are commercially available due to the more economical mass production of a few instrument designs. In essence, technicians purchase what is available and the price of the instrument is correlated to its dispersion and resolution. As a note, there are manufacturers that will custom make a monochromator with specific blaze density and blaze angle, but these are relatively costly.

1.3.4 Refraction: Refraction goes "hand in hand" with dispersion. Dispersion of radiation in prisms is the result of refraction. The amount of refraction is described by Snell's law

$$\frac{\sin\theta_2}{\sin\theta_1} = \frac{\eta_1}{\eta_2} = \frac{\text{velocity 1}}{\text{velocity 2}}$$

where $\theta$ is the angle of refraction relative to the normal plane, $\eta$ is the refractive index, and subscripts 1 and 2 are the two media. The effect of refraction on light moving through two materials is illustrated in Figure 1-11.

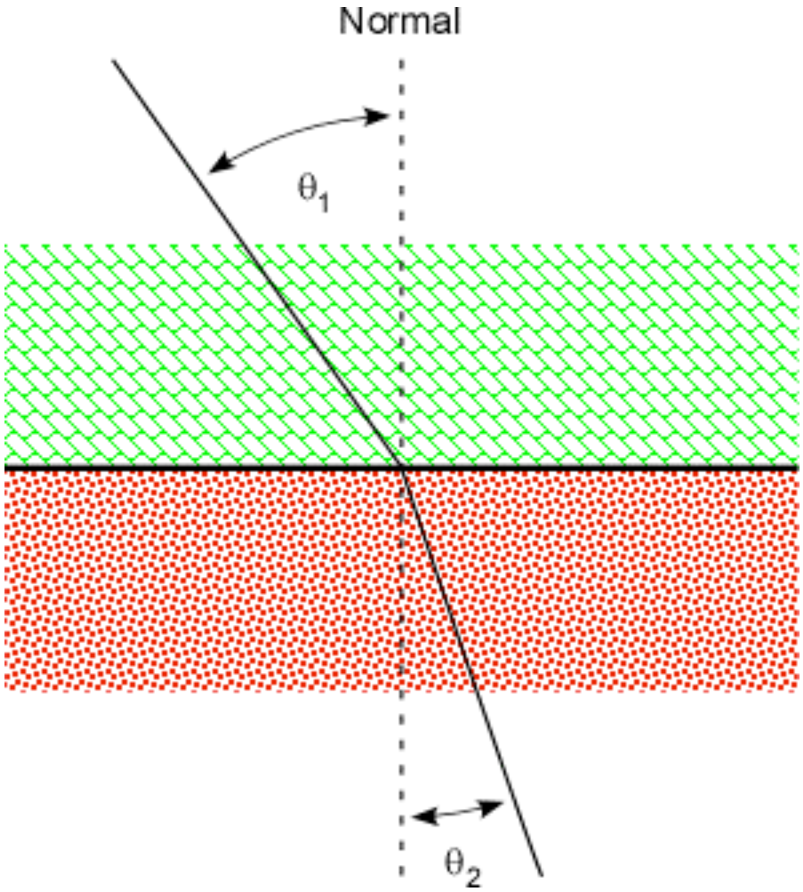


Figure 1-11. Illustration of the refraction of light passing through two media, one is less optically dense (the green-shaded region) and one more optically dense (the red-shaded region).

As mentioned in the previous sections (specifically Section 1.3.6), refraction is the basis of the separation (dispersion) of light in prisms while diffraction is responsible for dispersion in grating monochromators.

## 1.4 Summary

This chapter focused on the physics of light and how these principles can be used to separate components of UV and visible light into specific wavelengths. While this has mostly been a review of college physics, it was necessary to review these concepts in regard to components of analytical instruments. In the following chapters, the optical physics and components presented in this chapter will be combined to construct instruments capable of measuring the absorbance or emission of gaseous atomic species with visible and UV radiation. These concepts will also be further extended to explain how a variety of additional instrumental components work. Chapter 2 will focus on flame atomic absorption and emission techniques, while Chapter 3 will focus on inductively coupled plasma combined with atomic emission spectrometry. Finally, Chapter 4 will extend atomic spectrometry to include mass spectrometry, the current standard in the analysis of metals in atmospheric, aqueous, soils, and biological tissues.

## 1.5 Questions:

What is the difference between spectrometry and spectroscopy?

What does each of the acronyms stand for?
AAS
ICP
AES
OES
FAAS
FAES
MS

Draw a Jablonski Diagram Showing Electronic Energy Transfer Levels.

Name all of the types of electromagnetic radiation starting with the longest wavelength to the shortest wavelength. Correlate the frequency and energy levels with wavelength.

Name the color of the visible wavelengths.

What are the general wavelengths of each type of electromagnetic radiation.

What types of atomic and molecular energy transitions are associated with each type of electromagnetic radiation (Table 1.2)?

Show the mathematical relationships between the wavelength of an absorbed or emitted photon and the energy transitions (n values) of a valence electron.

How is absorbance related to transmission?

How is absorbance related to analyte concentration (Beer's law)?

Explain how fluorescence occurs with a Jablonski diagram and in words.

Explain how phosphorescence occurs with a Jablonski diagram and in words.

How do fluorescence and phosphorescence differ in transition time scales?

How does the quantification of fluorescence and phosphorescence differ from basic absorbance measurements?

Name and explain all of the possible interactions between electromagnetic radiation and material surfaces, including reflection, diffraction (both types), dispersion, and refraction.

Dispersion can occur by diffraction and refraction. Explain how each occurs.

What is the refractive index of a substance?

What is the major difference between Echellette and Echelle gratings?

How are linear dispersion, reciprocal linear dispersion, and resolution used to judge the quality of a monochromator?