EXPERIMENT 6
INTRODUCTION TO SPECTROSCOPY

INTRODUCTION

Much of what we know about the structures of atoms and molecules has been learned through experiments in which photons (electromagnetic radiation—visible light, microwaves, ultraviolet or infrared radiation, radio waves, etc.) are emitted or absorbed by the atoms or molecules. The energy of a photon is related to its frequency, ν, and wavelength, λ, according to

$$E_{photon} = h\nu = h\frac{c}{\lambda} \qquad (6\text{-}1)$$

where h is Planck's constant, and c is the speed of light. The energy of an emitted or absorbed photon corresponds to the *change* in energy the atom or molecule experiences.

$$E_{photon} = \Delta E = E_{final} - E_{initial} \qquad (6\text{-}2)$$

Whether photons are absorbed or emitted is correlated with the type of energy *change* the atom or molecule is undergoing. Thus, for example, a molecule can be raised to an excited electronic state by absorbing a visible or ultraviolet photon. A molecule already in an excited electronic state can return to the unexcited, or ground state by emitting a visible or ultraviolet photon. The energies of photons in this portion of the electromagnetic spectrum correspond to the differences between the ground and excited electronic states. For changes in vibrational or rotational energy, infrared and microwave photons respectively, have energies corresponding to the differences between states. Careful analysis of the details of the radiation absorbed or emitted as a function of wavelength (the absorption or emission *spectrum*), coupled with the formulation of physical models to interpret and explain them, has provided a wealth of detailed information about atoms and molecules.

In addition to the structural information that can be gained, studies involving the absorption and emission of electromagnetic radiation have proven to be extremely useful in other practical ways. For example, even without knowing why particular wavelengths are absorbed or emitted, we can often use the observed spectra to identify the substances responsible. This is particularly true in the infrared region for organic molecules, where many vibrational spectra have been recorded and cataloged and can often serve as "fingerprints" to identify what is present. In a similar way, the specific wavelengths of visible and ultraviolet radiation emitted by atoms and ions in a flame or in an electrical discharge can provide an unambiguous means of identification. In fact, a number of elements were first discovered in this way, when previously unknown emissions were observed. Spectroscopic measurements are now routinely employed in the analysis of chemical samples.

While measurement of the *wavelengths* emitted or absorbed can provide a convenient means for *qualitative* analysis of samples (i.e., *what* is present), measurement of *how much* light is emitted or absorbed can be used for *quantitative* analysis (i.e., *how much* of a substance is present). Carrying out such measurements is sometimes referred to as *spectrometry*, from "spectrum measure" rather than *spectroscopy*. Although quantitative experiments can be performed using various regions of the electromagnetic spectrum, one of the most useful is the visible portion, sometimes in combination with the ultraviolet region. In this experiment we will be working with visible electromagnetic radiation, ordinary light.

In order to study the emission and absorption of visible light, we will make use of an instrument known as a spectrometer. A simplified drawing of the main components of our spectrometer is shown in FIGURE 6-1. A spectrometer is an instrument that accomplishes two main tasks. First, it disperses, or spreads out, the light entering it into all of the wavelengths or colors present. This can be done with either a prism or a diffraction grating. Our spectrometer uses a grating. Second, it provides a signal proportional to the intensity of the light of each wavelength. It does this by directing the dispersed light onto a detector, which provides the electrical signal. In our spectrometer the detector consists of an array of 2048 tiny diodes arranged in a straight line and positioned so that the dispersed light is spread from one end of the array to the other. Therefore we actually have 2048 tiny, individual detectors, and each one has light of a slightly different wavelength, or color, falling on it.

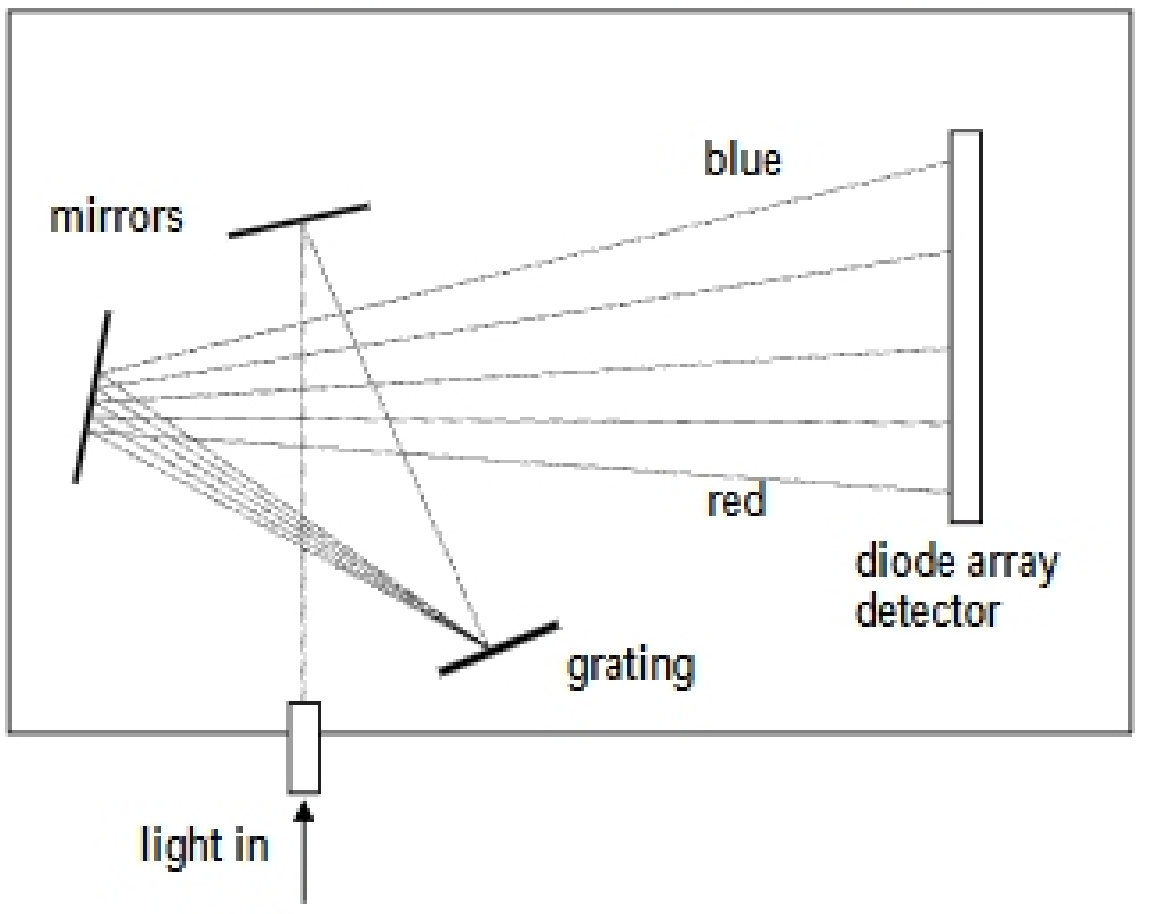

Figure 6-1. Simplified Spectrometer Diagram

Whatever type of experiment we are carrying out, the signal from the spectrometer is always just a set of values, one from each of the tiny diodes, indicating the intensity of the light reaching them. (In actual practice we reduce the amount of data to be handled by averaging the signals from the diodes in adjacent pairs, thereby obtaining 1024 values from the original 2048.)

The diodes are more sensitive to red light than blue light, so signals in the blue end of the spectrum will be somewhat reduced compared with the red end. However, the signal for any wavelength is proportional to the intensity of the light of that wavelength. Thus, for example, no matter what the color, the signal will double if the intensity of the light of that color is doubled.

When we use the spectrometer to measure an emission spectrum, we simply direct the light emitted by the sample (gas in a discharge tube, flame, etc.) into the spectrometer. The set of values we get from the spectrometer can then be examined to see what wavelengths of light were emitted. We will only do qualitative emission experiments, where only the wavelengths, and not the intensities, of the emitted light are important, so the variation of detector sensitivity with wavelength will not affect its usefulness.

When we use the spectrometer to measure an absorption spectrum, the situation is quite different. We use a lamp to supply light of all wavelengths throughout the visible region and use the spectrometer to determine the extent to which light of each wavelength is absorbed. The physical arrangement is shown in FIGURE 6-2. The sample is contained in a *cuvet*, a small container with clear windows. $I_{0,\lambda}$ is the intensity of the light incident on the sample as a function of wavelength, λ. The wavelength variation of $I_{0,\lambda}$ is determined by the characteristics of the lamp. We use a tungsten-halogen lamp, for which the intensity goes through a maximum in the visible region. I_λ is the intensity of the light remaining *after* passing through the sample. At wavelengths where the sample does not absorb, I_λ is equal to $I_{0,\lambda}$. Where the sample does absorb, I_λ is less than $I_{0,\lambda}$. We measure I_λ as shown in FIGURE

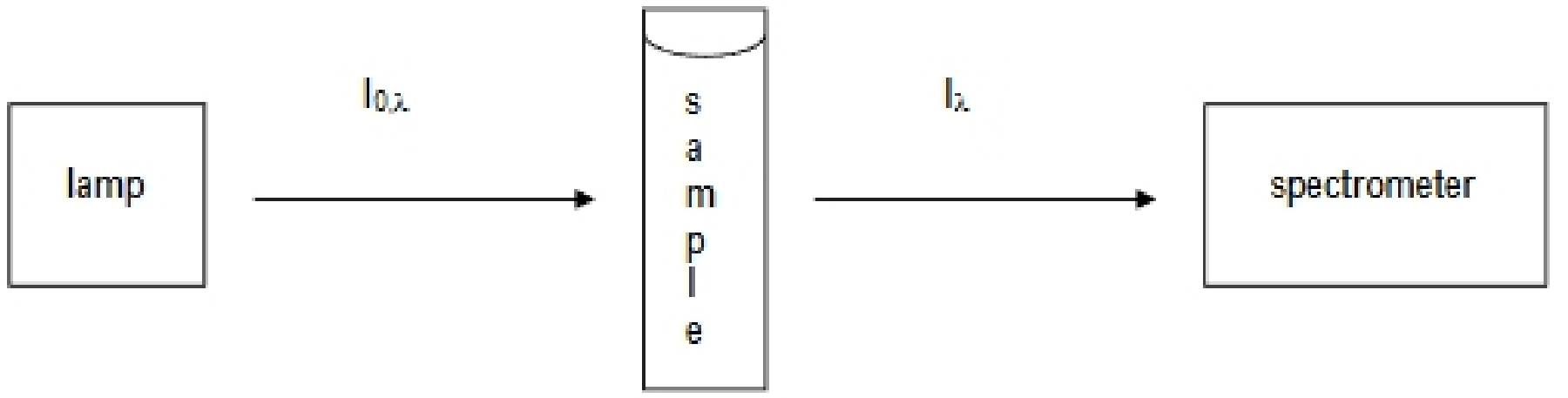

Figure 6-2. Measurement of light absorption as a function of wavelength.

6-2. To measure $I_{0,\lambda}$, we replace the sample cuvet with a reference cuvet, which is identical to the sample in every way except that it does not contain the absorbing molecules. It is important to measure $I_{0,\lambda}$ this way, since some light could be lost by reflections or by absorption in the walls of the cuvet or by the solvent. Using a reference cuvet provides the best measurement of the decrease in light intensity due only to absorption *by the absorbing molecules in the sample*.

The most important routine use of absorption measurements is for the determination of the concentration of absorbing molecules. This requires knowledge of the quantitative relationships between the light intensities and the concentration. This has been worked out experimentally, as summarized briefly in the following. The percent transmittance, $\%T_\lambda$, is defined to be

$$\%T_\lambda = \frac{I_\lambda}{I_{0,\lambda}} \times 100\% \qquad (6\text{-}3)$$

The value of $\%T_\lambda$ has been found to depend on three things. First, the nature of the absorbing molecules determines what particular wavelengths of light will be absorbed. Second, the longer the path the light travels through the sample, the greater the fraction of light absorbed (as found by J. H. Lambert). Third, the greater the concentration of absorbing molecules, the greater the fraction of light absorbed (as found by A. Beer). These three factors combine quantitatively in the following manner (Lambert-Beer Law, or, sometimes just Beer's Law),

$$A_\lambda = \varepsilon_\lambda \cdot b \cdot C \qquad (6\text{-}4)$$

where ε_λ is the molar absorptivity, characteristic of the absorbing molecules, b is the path length of the light through the sample, measured in cm, C is the molar concentration of the absorbing species, and A_λ is called the absorbance. A plot of A_λ vs. λ is called the absorption spectrum.

Since, as **Equation 6-4** shows, the absorbance is directly proportional to the concentration of absorbing molecules, it is the quantity we use to determine the concentration. Unfortunately, absorbance itself cannot be measured directly. It can be calculated, however, from the observed light intensities, as shown in **Equation 6-5**.

$$A = \log_{10}\left(\frac{I_{0\lambda}}{I_\lambda}\right) = \log_{10}\left(\frac{100\%}{\%T_\lambda}\right) \qquad (6\text{-}5)$$

As **Equation 6-5** shows, the absorbance could be calculated from the percent transmittance, but it is simpler just to calculate it from the light intensities directly. We use the two sets of values, $I_{0,\lambda}$ and I_λ, to calculate A_λ point by point, for all of the elements in the diode array. Since only ratios of intensities are used in the calculations, the