

Experiments

EXPERIMENT 9

Introduction to Electronic Spectroscopy

9.1. Safety

Emission lamps are hot. **Do not touch the bulb with your hand or with the fiber optic probe.** Do not touch the sockets of the emission lamp, since these lamps operate at high voltage (2000 V) and high current. The dyes that are used in this laboratory are approved food coloring dyes and, therefore, are not toxic. However, the color is intense and will stain skin and clothing. Be careful when handling these dyes.

9.2. Introduction

Electromagnetic radiation, or light, can be characterized by the frequency (or wavelength) of the radiation. The frequency ν and wavelength λ are related through the speed of light c , or

$$c = 2.998 \times 10^8 \text{ m/s} = \lambda \times \nu . \quad (9.1)$$

(We should note here that the units of frequency are s^{-1} , or Hertz (Hz), and that the units of wavelength are meters.) The electromagnetic spectrum, which is shown in Fig. 9.1, illustrates the broad frequency range of electromagnetic radiation. The interaction of electromagnetic radiation with matter is called spectroscopy, with the type of spectroscopy being defined by the wavelength of the electromagnetic radiation. For example, infrared (IR) spectroscopy studies the interaction of matter with electromagnetic radiation having a wavelength between 1 μm (near IR) and 1 mm (far IR). In this experiment, you will use emission spectroscopy to investigate atomic systems and absorption spectroscopy to investigate molecular systems.

9.3. Atomic spectroscopy

One of the fundamental principles of quantum mechanics (or the study of systems with dimensions close to the atomic scale) is that the energy of a quantum mechanical system is discrete. This principle is referred to as the quantization of energy. Energy quantization implies that electrons within an atom (or molecule) occupy orbitals. For atomic systems in the simplest approximation, each electron possesses four quantum numbers:

- the principal quantum number n , which varies from 1 to ∞ ;
- the azimuthal quantum number ℓ , which varies from 0 to $n - 1$;
- the magnetic quantum number m_ℓ , which varies from 0 to $\pm\ell$; and
- the spin projection quantum number m_s which, for electrons, is $\pm 1/2$.

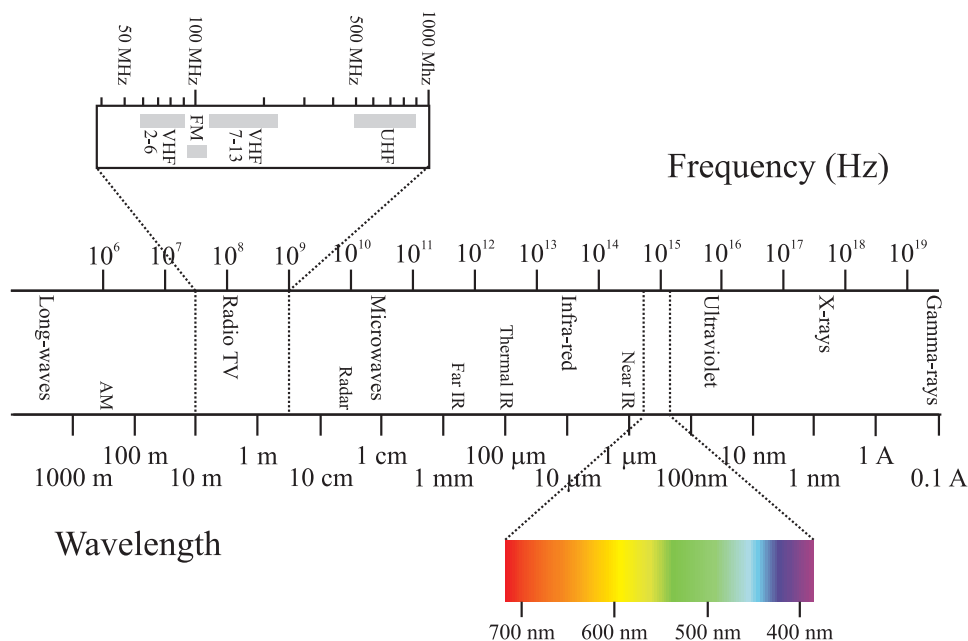


Fig. 9.1: The electromagnetic spectrum.

Table 9.1: Name and wavenumber (cm^{-1}) of various helium energy levels.

Name	Wavenumber (cm^{-1})
$1s2s\ ^3S$	159856.0
$1s2s\ ^1S$	166277.4
$1s2p\ ^3P$	169086.8
$1s2p\ ^1P$	171134.9
$1s3s\ ^3S$	183236.8
$1s3s\ ^1S$	184864.8
$1s3p\ ^3S$	185564.6
$1s3d\ ^3D$	186101.5
$1s3d\ ^1D$	186105.0
$1s3p\ ^1P$	186209.4

The quantum numbers specify the orbitals that the electron occupies and **no** electron can have the same set of four quantum numbers. The principal quantum number n gives the shell for the electron, with the valence electrons always being those with highest n . Each row in the periodic table indicates the principal quantum number of elements in that row. The energies of the orbitals increase as n increases, as does the average distance of the electron from the nucleus. The azimuthal quantum number ℓ divides each shell into sub-shells. The sub-shells were given letter designations based upon spectroscopic characteristics, with $\ell = 0$ being designated s , $\ell = 1$ being designated p , $\ell = 2$ being designated d , and $\ell = 3$ being designated f . Higher ℓ states can exist in atoms that have been excited using electromagnetic radiation. However, $\ell = 3$ is the largest ℓ value for filled sub-shells (i.e., sub-shells containing electrons) in a non-excited (or ground state) atom. Because of energy quantization, atoms (and molecules) only absorb or emit electromagnetic radiation at discrete wavelengths.

Absorption spectroscopy measures the amount of light at a given energy absorbed by the atom (or molecule) relative to the total intensity of the light. When the energy is at an appropriate wavelength to cause an electron to change orbitals, then the intensity of transmitted light at this wavelength will decrease. This orbital excitation is called an *electronic transition*. Emission spectroscopy uses high voltage (or other means) to excite atoms (or molecules) into excited electronic states. These states then decay towards the ground state electron configuration. In decaying, light is emitted at energies characterized by the difference in energy between the excited state energy and the ground state energy. The energy of an electronic state in atomic hydrogen is related to the principal quantum number n by

$$E_n = -\frac{E_1}{n^2}, \quad (9.2)$$

where E_1 is a constant. Thus, the difference ΔE in energy levels in atomic hydrogen is given by

$$\Delta E = E_{n_f} - E_{n_i} = -E_1 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right), \quad (9.3)$$

where E_{n_i} and E_{n_f} are the energies of the initial and final electronic states, respectively and n_i and n_f are the principle quantum numbers of the initial and final states, respectively. If an electronic transition occurs because light was absorbed, then $E_{n_i} < E_{n_f}$ and, therefore, $\Delta E > 0$. On the other hand, if an electronic transition occurs because light is emitted, $\Delta E < 0$ because $E_{n_i} > E_{n_f}$. Planck's law states that the wavelength λ of an absorbed (or emitted) photon is related to the energy through Planck's constant h , or

$$\frac{hc}{\lambda} = |\Delta E|. \quad (9.4)$$

Substituting eq. (9.3) into eq. (9.4) and rearranging yields the Rydberg equation, or

$$\frac{1}{\lambda} = \left| R_y \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \right|, \quad (9.5)$$

where $R_y = 109,737.32 \text{ cm}^{-1}$ is the Rydberg constant. [The Rydberg constant R_y is related to the proportionality constant E_1 through $R_y = E_1/(hc)$.] As more electrons are added to the system, eq. (9.5) can still hold if n is redefined.

Fig. 9.2a shows an example emission spectrum from an argon arc lamp, while Fig. 9.2b gives the energy transitions that lead to each emission line in Fig. 9.2a. You will be asked to determine the energy transitions for emission lines in helium. In this experiment, you will measure emission spectra of hydrogen and helium. For hydrogen, the final state n_f is 2 and you will use eq. (9.5) to determine the initial states. For helium, the energy and name of the possible initial and final states are given in Table 9.1 and you will use these values to determine ΔE and to identify each observed transition.

9.3.1. Setup of spectrophotometer

- (1) Plug in the LabQuest unit and turn it on using the small silver button in the upper left hand corner. The unit will take several minutes to start.
- (2) Once the unit has started, plug in the SpectroVis Spectrophotometer into the USB port on the top of the LabQuest unit.
- (3) The mode given in the right hand side of the screen should read **Full Spectrum**. If not, use the stylus to touch the mode and change the mode to Full Spectrum.
- (4) Return to the Data Collection screen by touching mode to adjust the wavelength range to read 400 - 750 nm. Thus, the data collection screen should contain the following values:

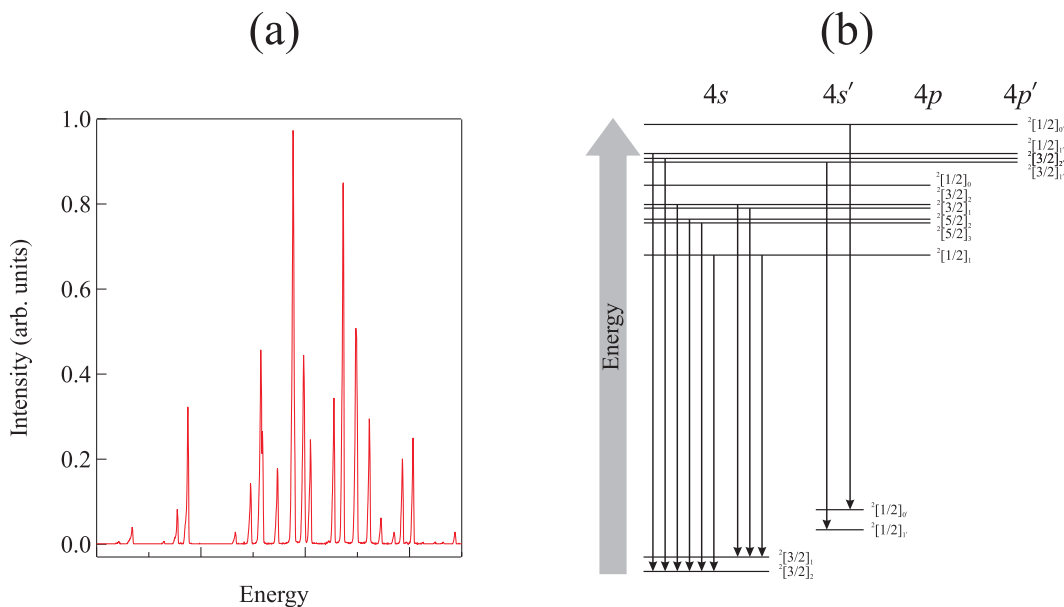


Fig. 9.2: (a) The emission intensity plotted as a function of energy for an argon emission lamp. (b) A schematic of selected energy transitions that lead to some of the intense emission lines in (a). The shorter the arrow, the lower the energy.

- Mode: Full Spectrum
 - Sample Time: 15 ms
 - Wavelength smoothing: 0
 - Samples to Average: 3
 - Wavelength Range: 400 - 750 nm
- (5) Once complete select **OK** with the stylus.
 - (6) Now touch the red area in the center of the screen (or select **Sensors** in the top menu). In the drop down menu, select **Change Units** and then select **Intensity**. This sets the spectrophotometer to display the intensity of light hitting the detector.
 - (7) Touch the red area in the center of the screen and select **Calibrate**. Press the **Skip Warmup** button and then the **Disable Calibration** box. Then hit **OK**.
 - (8) Insert the fiber optic probe with the arrow pointed towards the arrow on the top of the spectrophotometer. This will align the output of the fiber optic with the input of the detector.
 - (9) In the upper menu, press the graph icon. The unit is now ready to collect data.

Before Laboratory Questions – Experiment A

These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.

- (1) What is the purpose of Experiment A?
- (2) What is your hypothesis? Answer in if/then statements.
- (3) What materials are required for this experiment? Are any chemicals needed? If so, what are they? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
- (4) Create a table to record the emission wavelength, emission energy and intensity for the hydrogen emission lines.
- (5) Create a table to record the emission wavelength, emission energy and intensity for the helium emission lines.

9.3.2. Experiment 9A. Emission from atoms

Hold the fiber optic end facing the hydrogen lamp. Press the right arrow button to begin data collection. Move the fiber optic around until a set of peaks appears with high intensity. You should observe two peaks. Then hit the right arrow again to stop data acquisition. Show the results to your instructor for approval before continuing. Tap the stylus on the top of the peak to determine the wavelength and intensity of each peak. If you cannot see a peak, you can zoom in by drawing a box around the peak of interest and then selecting **Graph** and **Zoom In**. To return to the original screen, select **Graph** and **Autoscale Once**. Write the wavelength and intensity of all observed peaks. Then move the fiber optic to the helium lamp and press the right arrow. A screen will appear asking if you want to discard, cancel or store the previous results. Select **Discard**. Again, move the fiber optic around until a suitable set of peaks appears and then hit the right arrow again to stop data acquisition. Record the wavelength and intensity of all observed peaks.

After Laboratory Questions – Experiment A

These questions should be used to help you write your notebook and should be answered in some form after the laboratory.

- (1) What is the difference between emission and absorption?
- (2) Convert all of the wavelengths to wavenumbers (i.e., units of cm^{-1}) for use in the Rydberg equation.
- (3) Using the data for hydrogen emission and assuming that the final state is $n = 2$, what are the principal quantum numbers for the initial state of the two experimentally observed transitions?
- (4) Two other transitions which you probably did not observe occur at wavelengths of 410.2 nm and 434.2 nm. If the final state is again $n = 2$, what are the principal quantum numbers for the initial states of these two transitions in hydrogen?
- (5) The data in Table 9.1 gives some of the helium energy levels with units of wavenumber. Light will be emitted when an electron moves from a higher energy level to a lower energy level. The energy of the emitted photon will be equal to the energy difference between the higher energy level and the lower energy level. This photon energy can then be converted to wavelength. Using the data obtained for helium emission, what are the experimentally observed transitions? (Write the transitions as *Name of initial state* \rightarrow *Name of final state*.)

9.4. Molecular spectroscopy

The interaction of electromagnetic radiation with molecular systems can cause an increase in molecular rotation, an increase in molecular vibration, or the transition of an electron from one molecular orbital to another. The difference ΔE in energy between the initial and final states for molecular rotation is smaller than that for molecular vibrations, which is smaller in turn than that for electronic transitions. Rotations and vibrations, which frequently cannot be observed as individual peaks, cause electronic transitions to appear as broad peaks. Visible light tends to excite valence electrons to various low lying electronic excited states. The colors that we observe in food and in clothing are caused by the absorption of light by large molecules, commonly known as dyes. For instance, the blue that we observe in blue jeans is caused by the absorption of red and yellow light. Thus, the only light that is transmitted toward our eyes is blue.

In absorption spectroscopy, the spectroscopist can either measure the transmittance or the absorbance of a sample. The **transmittance** T is defined as the ratio of the intensity I of light after it passes through the sample in comparison to the intensity I_0 of light before striking the sample, for any fixed wavelength λ , or

$$T = \frac{I}{I_0} . \quad (9.6)$$

The transmittance is more commonly reported as percent transmittance $\%T$ with

$$\%T = \frac{I}{I_0} \times 100 . \quad (9.7)$$

However, when a photon is absorbed $I < I_0$ and, therefore, the amount of light striking the detector decreases. Thus, one observes a reduction in the $\%T$ for each electronic transition. Reductions in values are more difficult to fit theoretically using nonlinear least squares analysis (because of the square root), which leads to the development of a new scale called **absorbance** A . Absorbance is defined as

$$A \equiv -\log\left(\frac{I}{I_0}\right) = 2 - \log(\%T) . \quad (9.8)$$

Experimentally, we observe the following:

- Two pieces of colored glass with the same concentration of dye and the same thickness will have the same absorbance.
- Two pieces of colored glass with different thicknesses, but the same concentration of dye, will have different absorbances. The thicker piece of glass will have a larger absorbance.
- Two pieces of colored glass with the same thickness, but different dye concentrations, will have different absorbances. The more concentrated solution will have the larger absorbance.

These empirical observations are summarized by the Beer-Lambert Law, or

$$A = a b c , \quad (9.9)$$

where a is a constant that depends upon the dye molecule (known as the molar absorptivity constant), b is the thickness of the sample being studied (known as the optical path length), and c is the molar concentration of the solution. As the molar concentration increases, systems tend to deviate from the Beer-Lambert law and, therefore, eq. (9.9) can only be applied to dilute solutions. In this experiment, you will use absorption spectroscopy to study the effect of concentration on the absorption of light.

9.4.1. Setup of spectrophotometer for absorbance

- (1) Plug in the LabQuest unit and turn it on using the small silver button in the upper left hand corner. The unit will take several minutes to start.
- (2) Once the unit has started, plug in the SpectroVis Spectrophotometer into the USB port on the top of the LabQuest unit.
- (3) The mode given in the right hand side of the screen should read **Full Spectrum**. If not, use the stylus to touch the mode and change the mode to Full Spectrum.
- (4) Return to the Data Collection screen by touching mode to adjust the wavelength range to read 400 - 750 nm. Thus, the data collection screen should contain the following values:
 - Mode: Full Spectrum
 - Sample Time: 15 ms
 - Wavelength smoothing: 0
 - Samples to Average: 3
 - Wavelength Range: 400 - 750 nm
- (5) Once complete select **OK** with the stylus.
- (6) Now touch the red area in the center of the screen (or select **Sensors** in the top menu). In the drop down menu, select **Change Units** and then select **Absorbance**. This sets the spectrophotometer to display the A .
- (7) Touch the red area in the center of the screen and select **Calibrate**. Let the lamp warm up for 60 s. Then insert an empty cuvette and select calibration. Once the calibration is finished, hit **OK**.
- (8) In the upper menu, press the graph icon. The unit is now ready to collect data.

Before Laboratory Questions – Experiment B

These questions should be used to help you write your notebook and should be answered in some form before you go to the laboratory.

- (1) What is the purpose of Experiment B?
- (2) What is your hypothesis? Answer in if/then statements.
- (3) What materials are required for this experiment? Are any chemicals needed? If so, what are they? Which materials must be obtained from the stockroom, which must be obtained from the instructor, and which are in your laboratory drawer?
- (4) Create a place to record the name of the dye and the initial concentration of the dye.
- (5) Create a table to record the volume of the dye, the total volume of the solution, the wavelength λ_{max} at the maximum absorbance A_{max} , A_{max} , and the concentration of the diluted dye.

9.4.2. Experiment 9B. Absorption data

- (1) Obtain from your instructor the name of the dye that you will investigate. The molecular structure and molecular weight for each of the possible dyes is given in Fig. 9.3.
- (2) Obtain two burettes from the stockroom. Clean both burettes. Then place approximately 25 mL of the assigned dye in one burette and distilled water in the second burette.
- (3) Using the burette with the dye, carefully fill a plastic cuvette 3/4 full. This should use approximately 4 mL of dye.
- (4) Place the cuvette into the spectrophotometer with the two clear sides facing the light and the arrow on the top of the instrument.

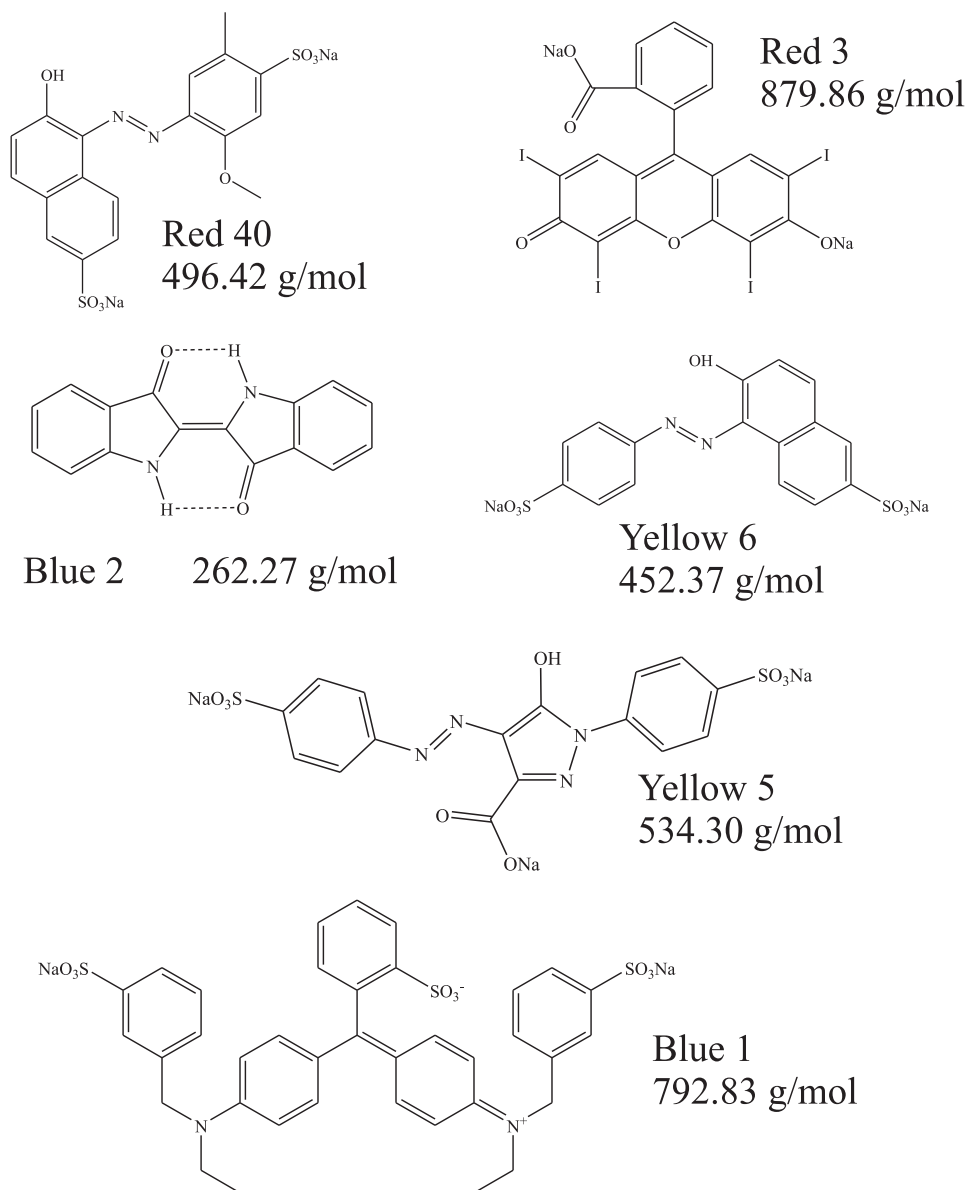


Fig. 9.3: The structure and molecular weight of the six USDA approved food coloring dyes used in this laboratory.

- (5) Touch the right arrow button on the LabQuest device to start data collection. Once a spectrum appears, touch the right arrow button again to stop the data collection. The LabQuest software will automatically select the peak and show both the wavelength and absorbance. Record both values, remove the cuvette and return to your laboratory bench.
- (6) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 0.5 mL of dye and 3.5 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.

- (7) Obtain the absorbance and wavelength for this solution. If you are asked whether to discard, save or cancel when starting data acquisition, always discard the previous data.
- (8) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 1.0 mL of dye and 3.0 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.
- (9) Obtain the absorbance and wavelength for this solution. If you are asked whether to discard, save or cancel when starting data acquisition, always discard the previous data.
- (10) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 1.5 mL of dye and 2.5 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.
- (11) Obtain the absorbance and wavelength for this solution. If you are asked whether to discard, save or cancel when starting data acquisition, always discard the previous data.
- (12) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 2.0 mL of dye and 2.0 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.
- (13) Obtain the absorbance and wavelength for this solution. If you are asked whether to discard, save or cancel when starting data acquisition, always discard the previous data.
- (14) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 2.5 mL of dye and 1.5 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.
- (15) Obtain the absorbance and wavelength for this solution. If you are asked whether to discard, save or cancel when starting data acquisition, always discard the previous data.
- (16) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 3.0 mL of dye and 1.0 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.
- (17) Obtain the absorbance and wavelength for this solution. If you are asked whether to discard, save or cancel when starting data acquisition, always discard the previous data.
- (18) Empty the cuvette into a waste beaker and rinse the cuvette with distilled water two to three times. Then place approximately 3.5 mL of dye and 0.5 mL of water into the cuvette. Place the top on the cuvette and mix the solution by inverting several times.

After Laboratory Questions – Experiment B

These questions should be used to help you write your notebook and should be answered in some form after completion of the laboratory.

- (1) What is the concentration of the dye after each dilution? Be sure to show all work in your notebook.
- (2) What is the % transmittance for each of the dye solutions investigated?
- (3) Generate the Beer's Law graph using the data obtained for your system and include it in your notebook.
- (4) Use the Beer's law graph to determine the molar absorptivity coefficient a . Be sure to use the correct units for this coefficient.
- (5) For the unknown sample, what is the concentration of your dye that is present in the sample?
- (6) If you were given a 25.0 mL volumetric flask, a burette containing 25.00 mL of your dye, and a bottle of distilled water, how would you create a dye solution that had a concentration that was half of the original concentration of your dye? What would the absorbance of this solution be?

9.5. Resetting spectrophotometer

If the LabQuest device locks-up, the device can be reset by your instructor. Please go to your instructor if the system is not responding.

9.6. Practice problems

The problems below are excellent practice problems for the laboratory quiz and the laboratory practical. Since these problems will not be graded, the answers are given in Appendix I.

- (1) What is the wavelength, frequency and energy emitted or absorbed when the following electronic transitions occur in hydrogen? Be sure to indicate whether the process is absorption or emission.
 - (a) from $n = 4$ to $n = 2$ state
 - (b) from $n = 2$ to $n = 6$ state
 - (c) from $n = 6$ to $n = 9$ state
 - (d) from an orbit of radius 2.12 Å to one of radius 8.46 Å. (Note: The radius of an orbit is equal to an^2 , where a is a constant.)
 - (e) from an orbit of radius 4.76 Å to one of radius 0.529 Å.
 - (f) an electron combines with the H^+ ion ending in a $n = 3$ final state
 - (g) Do any of the above transitions emitted or absorb visible light?
- (2) How much energy is required to ionize the hydrogen atom? Put the answer in units of kJ/mol. If the experimentally determined value is 1310 kJ/mol, what is the percent error of your calculation?
- (3) The visible emission lines observed by Balmer all involved $n_f = 2$. Calculate the wavelength, wavenumber (cm^{-1}), energy (J/mol) and frequency of each of the first three lines in the Balmer series. Determine the region of the electromagnetic spectrum in which each of these lines is observed.
- (4) The Lyman series of emission lines of the hydrogen atom are those for which $n_f = 1$. Calculate the wavelength, wavenumber (cm^{-1}), energy (J/mol) and frequency of each of the first three lines in the Lyman series. Determine the region of the electromagnetic spectrum in which each of these lines is observed.

- (5) The Paschen series of emission lines of the hydrogen atom are those for which $n_f = 3$. Calculate the wavelength, wavenumber (cm^{-1}), energy (J/mol) and frequency of each of the first three lines in the Paschen series. Determine the region of the electromagnetic spectrum in which each of these lines is observed.
- (6) For $n = 4$, what are the possible values of ℓ ?
- (7) For $\ell = 3$, what are the possible values of m_ℓ ?
- (8) If m_ℓ is 1, what are the possible values of ℓ ?
- (9) Certain elements emit light of a specific wavelength when they are burned. Chemist can use such characteristic emission wavelengths λ_{em} to identify the elemental composition of a sample. Some of these characteristic wavelengths are given below.

Element	λ_{em} (nm)	Element	λ_{em} (nm)
Ag	328.1	Fe	372.0
Au	267.6	K	404.7
Ba	455.4	Mg	285.2
Ca	422.7	Na	589.6
Cu	324.8	Ni	341.5

Answer the following questions.

- (a) Which elements emit radiation in the visible part of the spectrum?
- (b) Which element emits photons of highest energy? Of lowest energy?
- (c) When burned, a sample of an unknown substance is found to emit light of frequency 6.59×10^{14} Hz. Which of these elements is probably in the sample?
- (d) An unknown mixture emitted light of wavelengths 455.1 nm, 285.7 nm, and 324.6 nm. What elements were in the mixture?
- (10) Express the following absorbances in terms of percent transmittance.
- (a) 0.038
- (b) 0.399
- (c) 0.435
- (d) 0.692
- (11) Convert the following transmittance data to absorbances.
- (a) 68.7%
- (b) 23.8%
- (c) 0.492%
- (d) 5.38%
- (12) A solution containing 5.24 mg/100 mL of a dye with a molar mass of 335 g/mol has a transmittance of 55.20% in a 1.50 cm cell at 425 nm. Answer the following.
- (a) Calculate the molar absorptivity a [in units of $\text{L}/(\text{mol cm})$] of this dye at 425 nm.
- (b) If 1.00 mL of this solution was added to 4.00 mL of water, what absorbance would be observed in a cell with a 2.00 cm pathlength?
- (c) If we wanted to make 10.00 mL of a solution with an absorbance of 0.15 in a 1.50 cm cell, how much of the original dye solution would need to be mixed with how much water?
- (13) A solution containing the complex formed between Bi(III) and thiourea has a molar absorptivity of 9.32×10^3 $\text{L}/(\text{mol cm})$ at 470 nm. Answer the following questions.
- (a) What is the absorbance of a 3.79×10^{-5} M solution of the complex at 470 nm in a 1.00 cm cell?
- (b) What is the percent transmittance of the solution described in (a)?

- (c) What is the molar concentration of the complex in a solution that has an absorbance of 3.79×10^{-5} M when measured at 470 nm in a 2.50 cm cell?
- (14) The absorbances of solutions containing chromate ion in 0.05 M potassium hydroxide were measured in a 1.0 cm cell at 375 nm. The following results were obtained.

$[\text{K}_2\text{CrO}_4]$ (g/L)	A at 375 nm
0.0050	0.123
0.0100	0.247
0.0200	0.494
0.0300	0.742
0.0400	0.991

Find the absorptivity of the chromate ion in units of L/(g cm) and the molar absorptivity of the chromate ion in units of L/(mol cm).

- (15) The concentration of a compound X is to be determined by UV-visible spectrophotometry. The following standard data was obtained.

$[\text{X}]$ (ppm)	A at 500 nm
0.50	0.24
1.5	0.36
2.5	0.44
3.5	0.59
4.5	0.70

A solution of unknown X concentration had an absorbance of $A = 0.50$. Construct a Beer's law plot and determine the slope and intercept (along with error) for the regression line. Determine the concentration by hand from the Beer's law plot and by using the regression line. Discuss the differences between the two values obtained.