

ATOMIC SPECTROSCOPY

LABORATORY OBJECTIVES AND ASSESSMENTS

1. Understand relationships between energy levels and spectroscopy.
 - a. Sketch emission, absorption, and ionization processes on an energy diagram.
 - b. Calculate E_n of Bohr orbits, and ΔE associated with a given n-to-n transition.
 - c. Determine the n-to-n transition given a measured λ .
 - d. Calculate λ of light emitted or absorbed for a given n-to-n transition.
 - e. Describe common characteristics of lines in the Balmer, Paschen and Lyman emission series.
 - f. Explain differences between bright-line and dark-line spectra.
2. Be familiar with the use of spectroscopic methods to record bright-line spectra.
 - a. Demonstrate appropriate precautions in the use of high-voltage gas cells.
 - b. Read wavelengths from a spectroscope and convert to other units.
 - c. Describe the relative advantages and disadvantages of a spectroscope and a spectrophotometer.
3. Develop calculator, hand-graphing, and spreadsheet skills.
 - a. Demonstrate proper entry of formulas using scientific notation, with optimal (i.e., least) use of parentheses.
 - b. Demonstrate appropriate use of calculator functions (e.g., variable memory).
 - c. Describe and demonstrate circumstances under which "\$" referencing is appropriate.
 - d. Format cells in various formats (decimal, scientific notation, etc.).

INTRODUCTION

Gaseous atoms and molecules that are excited by light or electrical energy tend to emit light at discrete wavelengths rather than as the continuous blackbody radiation spectrum that is observed with solid metals. When the light emitted by an excited gas is passed through a narrow slit and separated by wavelength using a prism or diffraction grating it produces a series of bright lines referred to as an **emission spectrum**. (A device for obtaining such a spectrum is called a spectroscope.) If a blackbody light source (for example, an incandescent light bulb) is analyzed with a spectroscope one observes a rainbow of colors across the spectrum, with no discrete lines. However, if the light from the blackbody source is first passed through a sample of a gas and then analyzed, one observes a series of discrete dark lines at the same wavelengths as the lines in the emission spectrum for that gas. This type of spectrum is called an **absorption spectrum**.

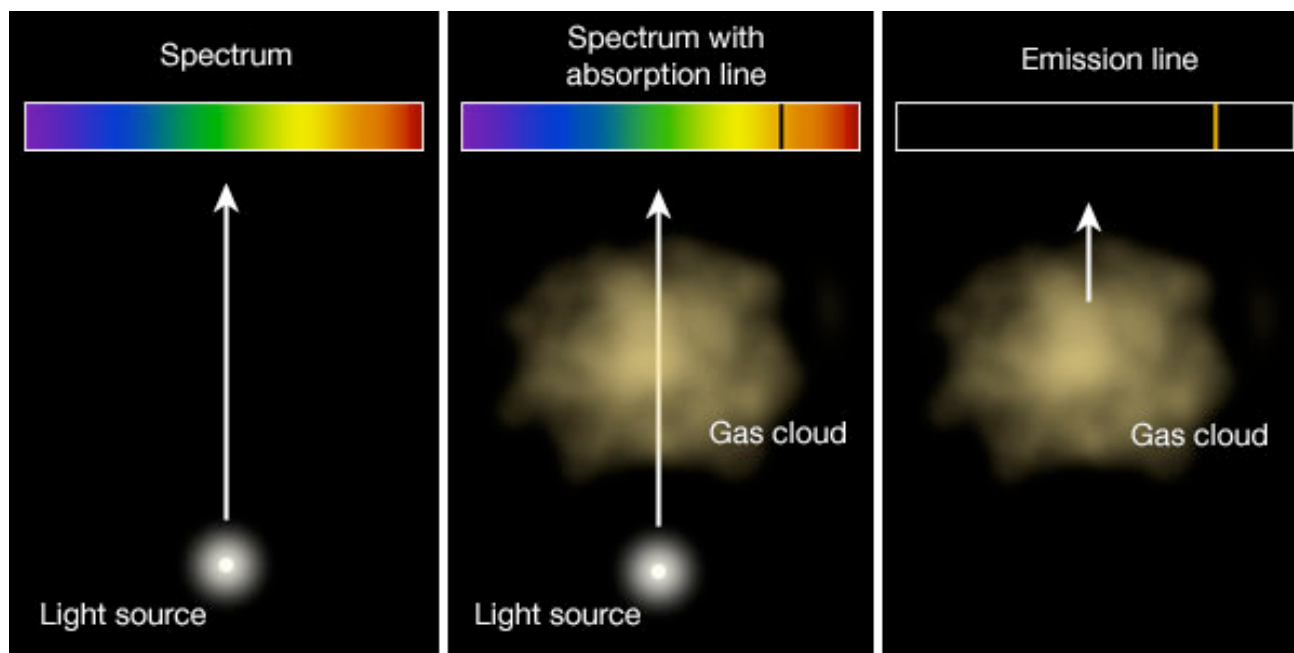


Figure 1. Examples of a continuous spectrum, an absorption spectrum and an emission spectrum. (From <http://www.astro.psu.edu/astrofest/kirchoffslaws.jpg>)

Each type of atom or molecule has its own unique spectrum. By looking at the spectrum of an unknown substance it is often possible to determine its identity. This is a powerful tool for astronomers since it allows them to identify the types of atoms and molecules in distant regions of our universe. The element helium was, in fact, first detected through the unusual dark spectral lines it produced in the sun's spectrum. Subsequently, helium was found on earth, and the match in spectral lines was regarded as definitive evidence that this was the same species.

In 1913 Neils Bohr presented a theory to account for the discrete lines observed in the spectrum of hydrogen. He suggested that an electron in a hydrogen atom can only possess certain discrete energies, associated with shells or *energy levels* numbered in integers from $n = 1$ through $n = \text{infinity } (\infty)$. He called these allowed energy levels **stationary states** of the atom. According to his model, the energy of the electron comes in discrete amounts or is **quantized**. One example of a quantized object is a bar of chocolate. You could buy a whole bar, but not half a bar of chocolate. Likewise, the mass of chocolate is in fixed increment amounts. If the mass of a single, uneaten bar is 5 grams, then you could buy 10 grams, 15 grams, 20 grams, etc. of chocolate, but never 2.5 grams.

Bohr used a planetary picture to visualize the stationary states in an atom. He viewed the stationary states as **orbits** of *quantized energy*, in which electrons move about the nucleus much the same way the planets move about the sun. Although Bohr's picture of electron *orbits* turned out to be incorrect, the idea that the energy of an electron in an atom is quantized is an essential component of our modern theory of the atom.

ATOMIC ABSORPTION AND EMISSION

Bohr's great insight was in showing that each line in a spectrum corresponded to the electron moving from one quantized energy level or stationary state, to another. When a hydrogen atom *absorbs* energy in the form of light, heat, electricity, etc., the electron is excited to a *higher* energy level. Conversely, when the atom *emits* energy

usually in the form of electromagnetic radiation, the electron moves to a *lower* energy level (See Figure 2 below.)

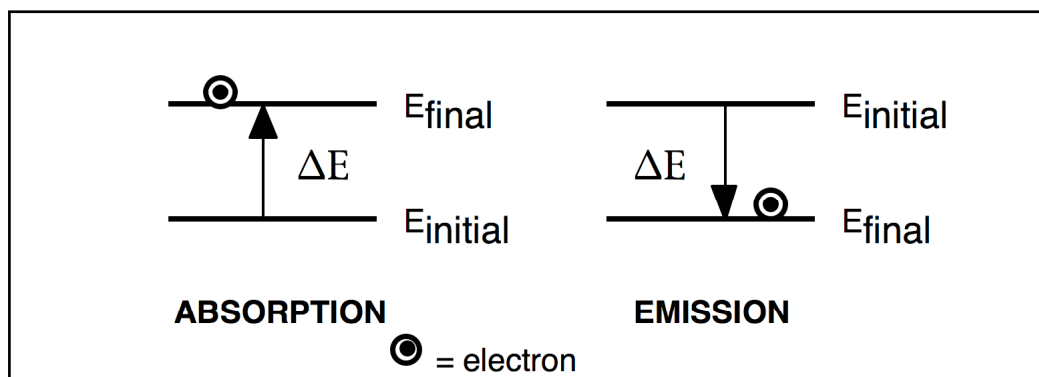


Figure 2. A representation of absorption and emission in the hydrogen atom.

Figure 3 shows two of the lowest energy stationary states in a sodium atom. These energy levels have energies of -8.25×10^{-19} J and -4.87×10^{-19} J, *below* the energy of the ionized atom ($E_{\text{ionization}}$) which is arbitrarily assigned the value of zero. The ionized atom is the reference point or “zero” of the energy scale, and thus both lower energy levels in Figure 3 have negative values. The stationary state with the most stable, lowest energy arrangement of electrons is called the **ground state** (E_{ground}). Each higher energy level is an **excited state** (E_{excited}). After a sodium atom is excited to E_{excited} by a flame or electric charge, the atom will *emit* energy and make a transition back to a more stable energy level as indicated by the 1st arrow in Figure 3. In some cases the energy emitted by an atom is in the form of visible light. In the case of sodium, the brightest line in the spectrum is the yellow color you associate with certain street lamps.

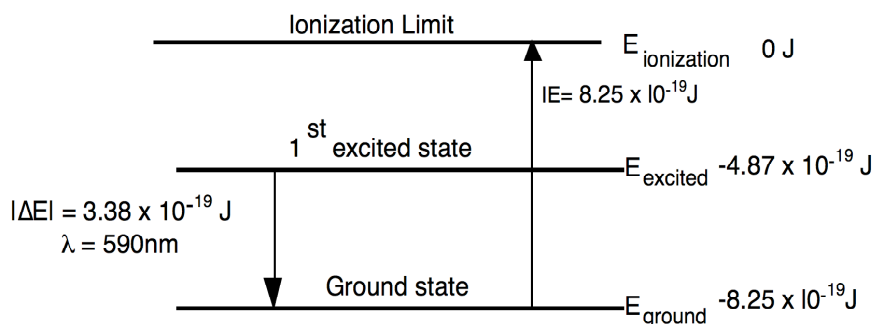


Figure 3. Select energy levels of the sodium atom.

The absolute value of the energy difference between the two levels, $|E| = |E_{\text{final}} - E_{\text{initial}}|$, then corresponds to the photon frequency that is observed:

$$|E| = hv = \frac{hc}{\lambda} \quad (1)$$

We can plot these discrete wavelengths or frequencies in a line spectrum. We often refer to the spectral lines as **spectral transitions**. Using the observed spectral

transition wavelengths, Bohr found that the energies of the levels in the hydrogen atom were given by:

$$E_n = \frac{(-2.178 \times 10^{-18}\text{J}) Z^2}{n^2} \quad (2)$$

In this equation, n represents the energy level, numbered from $n = 1$ to $n = \infty$, Z is the atomic number, and energy is in Joules.

EXPERIMENTAL PROCEDURE

WORK WITH A PARTNER

In this activity you will

- Part I. Calculate the hydrogen energy levels, using Equation (2) and complete Table 1. With the calculated energies prepare an **accurately scaled energy level diagram**.
- Part II. a) Calculate the ΔE s for each transition in Table 2 by taking the differences.
b) Using Planck's equation (Eq. 1) calculate the wavelengths for each transition. These results will be compared to theoretical values resulting from calculations based on equations developed by Bohr.
- Part III. Measure wavelengths of some of the observed lines in the hydrogen atomic spectrum with a spectroscope to add to Table 3. Complete Table 3 by matching the calculated λ s in Table 2 to the observed λ s listed in Table 3.
Draw arrows to represent the transitions in Table 3 on the **accurately scaled energy level diagram** from Part I.

PART I: CALCULATING ENERGY LEVELS OF HYDROGEN - BOHR THEORY

Table 1. Hydrogen Energy Levels

n level	Energy (J)
1	
2	
3	
4	
5	
6	
∞	0

- Given the expression for E_n in equation (2) above, with $Z = 1$, it is possible to calculate the energy of each energy level of hydrogen, starting with $n = 1$.
 - In your notebook reproduce **Table 1**, using a half page in portrait orientation. Calculate the energies of the 6 lowest energy levels, and enter these values in Table 1 in your notebook.

- b. On one full page in portrait orientation, in your lab notebook using a straight-edge, create an **accurately scaled energy level diagram**. Along the left edge, the y-axis, is the Energy scale with 0 Joules at the top and the line representing the 1st energy level near the bottom. Plot each of the energy levels scaled appropriately along the y-axis and drawing a horizontal line. Beside the line, write the corresponding energy (in attoJoules, aJ) and n value. Also draw a line ($n_{\text{ionization}}$) representing the ionization limit with $E = 0$. (For example, see Figure 3.)

PART II: ASSIGNING SPECTRAL LINES OF HYDROGEN

Table 2. Calculated Spectral Wavelengths

	$n_i = 6$	$n_i = 5$	$n_i = 4$	$n_i = 3$	$n_i = 2$
	$ \Delta E $ (J), λ (nm)	$ \Delta E $ (J), λ (nm)	$ \Delta E $ (J), λ (nm)	$ \Delta E $ (J), λ (nm)	$ \Delta E $ (J), λ (nm)
$n_f = 1$	2.119×10^{-18} 93.98				
$n_f = 2$					
$n_f = 3$					
$n_f = 4$					
$n_f = 5$					
$n_f = 6$					

- In your notebook reproduce **Table 2**, using one full page in landscape orientation. The lines in the hydrogen spectrum all arise from transitions made by the electron from one energy level to another. The wavelengths of these transitions are calculated by taking the absolute value of the energy difference, $\Delta E = E_{\text{final}} - E_{\text{initial}}$, between any two levels, E_n .
 - Calculate ΔE in Joules, for the transitions that can arise from any two of the levels of hydrogen as indicated in Table 2. Enter these values in Table 2 in your notebook. For emission, n_{final} is the lower energy level and n_{initial} is the higher level.

Q.1. For absorption, is n_{final} higher or lower than n_{initial} ?

- Then, determine the wavelength in nanometers ($1\text{m} = 10^9 \text{nm}$) using equation (1) and solving for λ . Enter these values in Table 2 in the same cell as the respective transition.
- Indicate the value of the IE and the ionization process in hydrogen on your energy level diagram by drawing an arrow between the appropriate levels. *Hint: The zero of energy for hydrogen is set in the same way as in Figure 3 for sodium.*

Q.2. What is the ionization energy (IE) of hydrogen? Express your answer in J and in kJ.

PART III: MEASURING THE SPECTRUM OF HYDROGEN

Table 3. Hydrogen Spectral Line Assignments

Wavelength (nm)	Assignment
	$n_{\text{initial}} \rightarrow n_{\text{final}}$
97.25	4 \rightarrow 1
102.57	...
...	...

1. In your notebook reproduce an expanded **Table 3**, using at least a half page in portrait orientation. Record the following wavelengths (nm) in Table 3; 97.25, 102.57, 121.56, 954.60, 1004.94, 1093.81, 1281.81, 1875.10, 4050.0. These lines are not in the visible region, so you will be unable to see them. In addition, leave several spaces in your table for the visible lines of hydrogen that you will observe using the spectroscope.

When you look at a hydrogen emission lamp through a spectroscope, the light is spread out into its individual wavelength components by a diffraction grating.

Q.3. Indicate the region (IR, UV, etc.) of the electromagnetic spectrum corresponding to each wavelength.

2. Use the spectroscope to measure the visible wavelengths of the spectral lines of the hydrogen spectrum between 380 nm to 660 nm. Record your data in **Table 3**. Sketch the line spectrum in your lab notebook. See Figure 4 for an example.

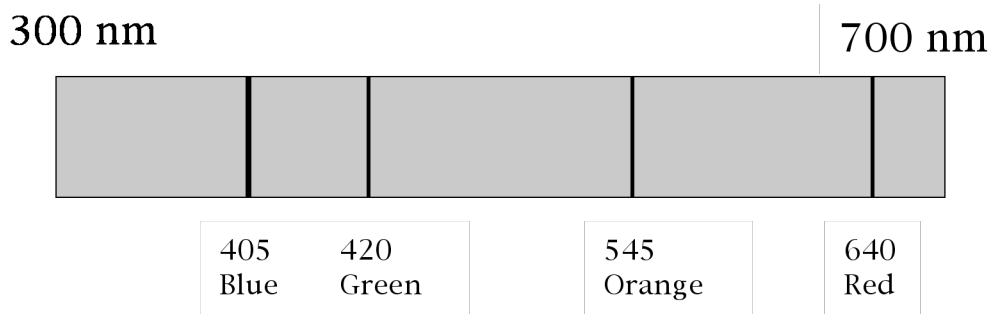


Figure 4. Example of a sketch of observed line spectrum.

3. Compare the wavelengths you calculated in **Table 2** with the ones you measured and recorded in **Table 3**. Your *calculated* wavelengths should match several of the *observed* transition wavelengths in Table 3. Complete Table 3 by writing the upper and lower energy levels (n_{initial} and n_{final}), involved in each transition.
4. On the **energy level diagram** you began in **Part I Section 1b**, draw a vertical arrow in the direction E_{initial} to E_{final} between pairs of energy levels associated with each transition in Table 3. Label each transition with its corresponding **wavelength**.

The **Balmer series** in the hydrogen spectrum consists of a series of lines in the visible region from 300 nm to 700 nm.

Q.4. From your entries in Table 3, what common characteristic do the Balmer lines in an **emission** spectrum have?

Q.5. In a Balmer **absorption** spectrum?

Q.6. What would be the longest possible wavelength for a line in the Balmer series? Explain your reasoning.

PART IV: SPECTRA OF ADDITIONAL ELEMENTS

1. **Helium** - View the line spectrum of helium (He). Record the wavelengths of the lines you observe. Sketch the line spectrum in your lab notebook.
2. **Mercury** - View the line spectrum of mercury (Hg). Record the wavelengths of the lines you observe. Sketch the line spectrum in your lab notebook.
3. Examine the spectra of hydrogen from Part III), helium, and mercury. Helium (He) has two electrons, while mercury (Hg) has 80 electrons. Compare the spectrum of H with one electron to He and Hg with many electrons.

Q.7. Describe some significant qualitative and quantitative differences between these spectra.

4. **Fluorescent Light** - View the spectrum of a fluorescent light. Record the wavelengths of the lines you observe. Sketch the line spectrum in your lab notebook.

Q.8. From the observed spectrum identify an element present in the fluorescent lights?

PART V: USING VIS-NIR SPECTROPHOTOMETER

In a hood area in the laboratory an Ocean Optics USB3000 Spectrophotometer will be setup with a fiber-optic extension connected to the detector with a hydrogen discharge tube as the light source. The spectrophotometer is controlled by a computer using LoggerPro software.

1. Using the "EXAMINE" tool from the ANALYZE menu record the wavelengths of the lines you observe in your notebook.

Q.9. Describe some significant qualitative and quantitative differences between the spectroscopy results and the spectrophotometer results for hydrogen.

PART VI: USING SPREADSHEET FOR PREPARING TABLES

The primary objective of this part of this experiment is to demonstrate a valuable function spreadsheets can serve in chemistry and encourage their use for both problem solving and preparing tables for your laboratory reports.

With a new worksheet on the monitor of your computer using Microsoft Excel or a similar spreadsheet program, produce copies of **Table 2. Calculated Spectral Wavelengths** from this lab, *Exp.5 – Atomic Spectroscopy, page 5*. Make one table for calculating $|\Delta E|$ and a second table for calculating λ . Set up a list of constants, i.e., c (speed of light), h (Planck's constant), etc. for those needed in the calculations to use as cell references. Use **calculated fields** for the entries in the cells of the table. Use the "Fill" commands and others to complete the columns or rows. Format the spreadsheet column and row headings and lines according to the "Guidelines for Making Tables including a Table of Reagents" as shown in the following sample.

When it is completed and **SAVED** as an Excel compatible file, (please use **.xls** not **.xlsx**) e-mail an electronic copy of Table 2 as a properly formatted Excel™ spreadsheet as an attachment to your CA, before next weeks' lab.

	A	B	C	D	E	F
1	2.178E-18					
2	ni = -->	6	5	4	3	2
3	nf =	\Delta E (J)	\Delta E (J)	\Delta E (J)	\Delta E (J)	\Delta E (J)
4	1	2.12E-18				
5	2					
6	3					
7	4					
8	5					
9						
10						
11						
12						
13						
14						

=ABS((\$A\$1/(\$A4)^2)-(\$A\$1/(B\$2)^2))

Figure 5. Sample of spreadsheet for $|\Delta E|$ from Table 2, Exp. 5 showing an example of the formula entry for the cell B4. An additional spreadsheet is needed for the wavelengths (λ) that are in the respective cells of Table 2.

WHAT TO DO

BRING to lab

- From **Exp. 4–Hess’s Law** – Hand-in all of your notebook “copy” pages associated with the following (STAPLED);
 - a) Prelab assignment including purpose and Table of Reagents. (This may have been collected in lab.)
 - b) Tables for data, results for the calibration and the reactions for Hess’s Law.
 - c) A table (Table 6) summarizing your results for the test of Hess’s Law including the literature values.
 - d) Write the reactions (11), (12) and (13) showing the Hess’s law summation with ΔH s as in example equations on page 3.
 - e) A complete set of sample calculations showing all work.
 - f) Answers to all questions compiled on separate page of experiment.
 - g) Turn in all additional copy pages of observations, etc., stapled.
- Print a copy of this experiment, read it and bring it to your laboratory class.
- Bring your Lab Notebook with the PreLab assignment completed. **You will not be allowed to do the experiment without the prelab assignment completed.**
- **Bring a flash drive for obtaining a copy data files and documents generated in the laboratory.**
- **Bring your Gilbert textbook and a calculator to lab.**

PreLab Assignment –

1. Set up your lab notebook appropriately for this experiment including a title bar and a purpose.
2. Prepare pages in your notebook with tables to record data and calculations. Reproduce Tables 1, 2, and 3 into your laboratory notebook (Table 1 must be a half-page in portrait page orientation, Table 2 must be one full page, landscape orientation, in your notebook and Table 3 must be at least a half-page in portrait orientation). Leave one full page blank after Table 2 for your **energy-level diagram** in portrait orientation.

DURING LAB

Write observations and record data directly into the lab notebook. Show at least one sample calculation for each calculated parameter **in the notebook**. Also include, in your laboratory notebook, a page for answers to the questions and a page of sketches of the line spectra.

TO BE TURNED IN AT THE NEXT LABORATORY SESSION:

Hand in all the “copy” pages that contain your observations, calculations, completed tables, answers to questions, sketches, and the figure of the energy diagram.

E-mail to your CA Table 2, Exp. 5 from Part VI as properly formatted Excel™ (please use **.xls** not **.xlsx**) spreadsheet, as an attachment, **BEFORE** your next lab period. Give your spreadsheet file a name using the following format:

Lastname_Exp#_E1.xls

(Your last name underscore experiment number underscore exercise (or part) number dot xls)

Note: Use this naming format for all files saved on Chemistry Lab Computers.

Points are assessed as follows

Prelab	____/10
Data Tables	____/25
Organization	____/ 5
Format	____/10
Overall	____/10
Energy Diagram	____/15
Sample Calcs	____/10
Questions	____/18
Spectra Data	____/10
Spreadsheet	____/12
TOTAL	____/100