Lab 2: Spectroscopy of Atoms and Ions

Laboratory Goals
In this week’s laboratory you will:

$\times$ use spectroscopy to determine the identity of unknown cations in a solution
$\times$ demonstrate your understanding of atomic structure by constructing an energy-level diagram from your experimental observations

Introduction
One of the most amazing and telling properties of the elements is the fact that their gas-phase atoms will only emit or absorb certain wavelengths of light. The observation by Joseph Fraunhofer in 1814 of dark lines in the solar spectrum (the light of the sun dispersed into its component wavelengths, each with its own color) began the science of spectroscopy. Fraunhofer observed over 700 of these dark lines. (Actually each line was just the image of the slit Fraunhofer used to define a beam of sunlight prior to passing it through a prism; narrower lines resulted when the slit width was reduced.) No explanation for these lines was available, but in 1861 Robert Bunsen and Gustav Kirchhoff discovered that laboratory flames from a natural gas burner (now known as a Bunsen burner) produced characteristic bright lines from various metal salts, and that some of these lines had exactly the same wavelengths as Fraunhofer’s dark lines. Eventually, through many interesting twists and turns, chemists came to know that each element, as a gas-phase atom, has its own characteristic line spectrum. An atom’s spectrum results from its electrons making transitions between energy levels (in the case of emission the electrons start at one energy level and move to a lower level while in absorption the electrons move to a higher energy level), and therefore is not only a unique reflection of its chemical identity, allowing chemists to analyze unknown samples and mixtures, but provides an important clue about its inner workings. We will examine these phenomena and the exercises given below using your own data will help you understand the latter connection.

Metal ions in aqueous solution also have unique spectra, which are easiest to measure by absorption, where white light (i.e., light containing all the wavelengths in the visible region of the electromagnetic spectrum) is passed through the solution and the ions absorb or remove certain wavelengths. This is analogous to Fraunhofer’s dark lines except that in solution, due to the perturbing effect of the solvent molecules, a continuous range or band of wavelengths is absorbed.

Prelab Assignment
Your prelab for this experiment will be to go to the tutorial on the “Quantum Atom” at:

http://www.colorado.edu/physics/2000/TOC.html

Go through the tutorial in the following order:
1. Electromagnetic Waves and Particles (Just under the major heading “Science Trek”)
2. The Electric Force
3. Electric Force Fields
4. Vibrating Charges and Electromagnetic Waves
5. Quantum Atom
6. Bohr’s Atom (within this tutorial click on the “Extra for Advanced Students” for “Wiggling Charges Revisited”)
7. Energy Levels (within this tutorial click on the link “Schrödinger Atom” and within “Schrödinger Atom” click on “Two-Slit Experiment”)
8. Atomic Spectra

Note that clicking on “next” at the bottom of the page will take you to the next tutorial for 1-4 and for 5-8 (you only need to click on the Quantum Atom on the Vibrating Charges and Electromagnetic Waves page.). This portion of the prelab assignment will be done on the honor system. Please spend at least 15 minutes looking at this stuff. Realize that the more time that you spend the better you will be able to understand this lab, the concept of quantization, the material in lecture and generally how the atom works. You will discuss these concepts for a few minutes in small groups before starting the lab. No pre-written procedure is required.

Please also begin your lab book by putting in a title, page number as well as a brief purpose section (why are you doing this lab? What are you trying to figure out? What instruments/technique do you expect to be using to collect your data?) This portion of the prelab will be required for all labs.

The Experiment

In today’s experiment you will use small, hand-held spectrosopes and more powerful electronic spectrometers to observe and record the wavelengths of light emitted by discharge tubes of the pure gases H (present in the discharge tube before the power is on as H₂), He, Ne, and Ar, and Bunsen-burner flames containing the chloride salts of Li, Na, Mg, Ca, Sr, Ba, Fe and an unknown mixture. In addition you will observe the absorption of light by copper(II) (Cu²⁺), cobalt(II) (Co²⁺), and permanganate (MnO₄⁻) ions in aqueous solution.

The illustration on the next page shows the spectroscope you will use. Its main component is a transmission grating, which bends light of different wavelengths through different angles. Light enters through a small slit opposite the grating, strikes the grating, gets dispersed into a spectrum of wavelengths, and can be viewed against a wavelength scale to an accuracy of ±5.0 nm.
You will work in pairs, as this eases the task of recording the wavelengths and maintaining the flames of the chloride salts. However, you should observe every tube, flame, and solution to get a feel for the differences in the spectra and the difficulties in obtaining accurate data. The Ocean Optics spectrometer will demonstrate the more modern method of obtaining accurate data, but lacks some of the fun of the data collection and in actually SEEING the diffracted light.

Included with procedures A-D are a few questions for you to think about as you perform that part of the experiment. These questions will be the basis for your lab report.

You may do Parts B, C, and D in any order. Stations will be set up for each part. You may return to any section later, time permitting, if you were not satisfied with the results of your first effort.

**Procedure**

**A. Calibration of the spectroscope**

In order to ensure that the data that you collect from the spectroscope is accurate, we need to carefully compare your data to a known set of values. This can be done by comparing the lines read from the spectroscope with those either previously determined from another source. In this case you will use the lines collected by the Ocean Optics spectrometer for the fluorescent lights in the lab. Look at the fluorescent lights in the lab and determine the position of the lines that are observed. Then use the Ocean Optics spectrometer to “look” at the lights as well. Try to determine how your lines match with those on the Ocean Optics. Is there some mathematical way to correct your lines to more accurately reflect those measured with the spectrometer? [Keep in mind that the Ocean Optics can be far more sensitive, so you will likely only be able to observe and differentiate the most intense peaks.]
**Exploratory Questions:** As a quick side activity, you can use the spectroscope to look at a light source that gives off a wide range of light (incandescent light bulb or the sun). What is the highest wavelength of light you can see? What is the lowest? How does this compare to other people in your lab? What do you think would be the case for someone who is colorblind?

B. Gas discharge spectra

As you may have seen previously, when a high voltage is applied to a gas at low pressure, the gas “breaks down” and becomes an electrical conductor. This is accompanied by a “glow” produced mainly by emission from excited atoms, and even today is the major means by which spectra of gases are obtained (it is also part of how fluorescent lights work).

At different times during the lab session, hydrogen, helium, argon, and neon discharge tubes will be installed in a high voltage supply and mount. To observe the spectrum, sit on a stool with your spectroscope quite close (<10 cm away) to the bright capillary in the center of the tube. Read off the wavelengths and colors of each line to your partner, and then let him/her do the same. On your data sheet record the element, overall appearance of the discharge (color, brightness), observed wavelengths and their colors and brightness (bright, “average”, faint).

Argon displays a large number of lines over a small range of wavelengths in part of its spectrum; to save time, record only the limiting wavelengths and number of lines in this dense region of the spectrum.

**Exploratory Questions**

1. Which gas had the most complicated emission spectrum? Which had the simplest?
2. Is there a trend, and if so does it correlate to any physical property or placement in the periodic table? Briefly explain your thinking.

C. Flame spectra

At least two stations will be set up for each of the salts LiCl, NaCl, CaCl₂, SrCl₂, and BaCl₂ plus one for each unknown A and B. One partner must observe the spectrum while the other prepares the flame and records colors and wavelengths. Both partners should view the spectrum. The stations will be equipped with a burner, a spatula, and aqueous solution of the salt.

To produce a flame from the solution, dip a spatula (or inoculating ring) into the solution and place spatula (inoculating ring) into the flame. Repeat as necessary to get all the lines.
As in part B, the spectrum is observed most easily by positioning yourself, on a chair or stool, as close to the flame as possible (being careful not to melt the plastic spectroscope!). The spectrum will flicker with the flame, and your partner may have to make several flames before you are able to record all the spectral lines.

The partner creating the flame must also record the salt, the overall color and brightness of the flame, and the wavelengths, colors, and brightness of the observed spectral lines on the data sheet. You should alternate roles with your partner for the different salts.

The unknowns A and B will contain two or more salts, excluding NaCl since sodium is a common contaminant, drawn from the five samples. Choose one of these to observe, and report your findings. You may do both unknowns if you wish for extra credit.

**Exploratory Questions**

1. How do you know the emission spectrum you observed comes only from the metal ion–what about the anion? Propose an experiment by which you could prove that the emission spectrum does indeed come only from the metal ion (feel free to carry this out if you have time).

2. Do the flame spectra uphold your hypothesis from question 2 (above)? What evidence makes you say this?

**D. Solution Absorption Spectra**

Here you will measure “dark” portions of a continuous spectrum. There will be solutions of CuSO₄, CoCl₂, and KMnO₄ set on an overhead projector, which will serve as a light source. Both partners can easily perform the measurements independently. Adjust your spectroscope for good viewing of the light from the projector bulb, then slide the beaker over the bulb and note the change in the spectrum. Record the identity, color, and concentration of the solution and the color or colors and range of wavelengths absorbed on your data sheet. This tends to work the best if the beaker is near the edge of the illuminated portion of the projector.

**Exploratory Questions**

1. What is “white”? What is “black”?

2. Consider the colors of the CuSO₄, CoCl₂, and KMnO₄ solutions–before you record the absorption spectrum, what colors do you predict will be absorbed? What colors actually are absorbed? Is there a relationship between the colors observed and the colors transmitted?

**Report**

Your report will be written with your partner. This will be a “bare bones” report
containing thoughtful answers to **all** the questions above as well as the identification of the metal ions in the unknown solution you selected. The answers should rely use your data as much as possible to support your explanation. This will be similar to what you would normally include in your results and discussion sections. You should also include all data sheets with original and corrected wavelengths. There is no need to include any procedure in the lab report. Include the following exercises in your report as well:

**Part B: (Gas discharge spectra)**

**B1.** The lines you observed in the hydrogen spectrum were some of the strongest evidence for an atom with quantized energy levels. In this exercise you will construct an energy level diagram for the hydrogen atom using your observed spectral lines. Follow these directions in making your energy level diagram:

a) You should have seen (at least) three lines in the hydrogen discharge that arise from the so-called Balmer series of the hydrogen atom. In 1885 Rydberg showed that the wavelengths of these lines could be represented by the formula

\[
\frac{1}{\lambda} = R \left( \frac{1}{4} - \frac{1}{n^2} \right), \quad n = 3, 4, 5, \ldots
\]

where \( n \) indexes the wavelengths from longest to shortest. This is known as the Rydberg Equation. Assuming that your longest recorded wavelength corresponds to \( n=3 \) and using the value 109,737.32 cm\(^{-1}\) for the constant \( R \) (called the Rydberg constant), match up your wavelengths with an integer \( n \).

b) Calculate the energy corresponding to each wavelength using the relation \( E = \frac{hc}{\lambda} \).

c) Finally, create an energy level diagram similar to Figure 7.10 in your book. Use units of J, and you need only label the energy levels as \( n=2 \), \( n=3 \), etc. although the spacing should accurately reflect the energy difference between levels. Draw in the transitions the electron made between energy levels that correspond to each Balmer spectral line you observed.

**Explanatory Notes**

As described in the introduction, the accepted explanation for the line spectra of atoms is that the energy of an atom can have only certain values (levels) with nothing “in between” i.e., atomic energies are **quantized**. Line spectra in emission result from “transitions” of the electrons of an atom from a higher to a lower energy level (orbital), with the energy lost by the
atom appearing as a newly created photon of light. This model explains why Fraunhofer’s dark lines, which are due to absorption of the sun’s light by elemental vapors in the sun’s atmosphere, occur at exactly the same wavelengths as emission from those elements. Since an atom’s energy levels are fixed, the amounts of energy it can gain from white light are exactly the same as those it can lose when excited in a discharge or flame.

You may have noticed the difficulty of seeing lines at the violet (short-wavelength, 400 nm) end of the spectrum. This is not due to an intrinsic lack of intensity, but to your eye’s low sensitivity to short wavelengths. The spectrum of every element extends into the ultraviolet (\( \lambda < 400 \) nm) to a certain limiting wavelength, and then abruptly terminates. This cutoff wavelength corresponds to the ionization energy of that atom. For example, this wavelength is 92.1 nm for the hydrogen atom, corresponding to its ionization energy, 13.6 eV. The Ocean Optics UV/Vis instruments allow you to observe these higher energy lines effectively. All elements also show a myriad of weak lines in the infrared (\( \lambda > 700 \) nm) region. Ultraviolet and infrared spectroscopy require special light detectors or “eyes”, but combining these with the visible spectrum gives us a complete picture of an atom’s energy level structure. We (chemists and atomic physicists) then match the energy levels with the atom’s orbitals to interpret the spectrum. The result is a diagram (called a Grotrian diagram–see the following page) of labeled energy levels and transition wavelengths like the one on the next page for the lithium atom.

Chemicals
Saturated solutions of LiCl, NaCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, FeCl₃ unknowns.
1 M solutions of CuSO₄, CoCl₂
0.01 M solution of KMnO₄

Chemical Disposal
All solutions may be rinsed down the drain with lots of water.

Equipment
H, He, Ne, and Ar, gas discharge tubes with power supplies, Nichrome wire loops, spectrometers.

References
Fig. 24. Energy Level Diagram of the Li Atom [after Grottrian (8)]. The wave lengths of the spectral lines are written on the connecting lines representing the transitions. Doublet structure (see Chapter II) is not included. Some unobserved levels are indicated by dotted lines. The true principal quantum numbers for the $S$ terms are one greater than the empirical running numbers given (see p. 61); for the remaining terms, they are the same.